DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) RESULTING FROM WOOD STORAGE AND WOOD TREATMENT FACILITIES FOR ELECTRICITY TRANSMISSION IN SWAZILAND

by

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DECLARATION

I, Constance van Zuydam, hereby declare that Determination of Polycyclic Aromatic Hydrocarbons (PAHs) resulting from wood storage and wood treatment facilities for electricity transmission in Swaziland is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references. The thesis has not been submitted or will not be submitted to a university or any institution for the award of a degree.

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Signed (Supervisor) ______________________ Date __________________

ABSTRACT

A study was conducted in two sites: one at an electricity storage facility belonging to the Swaziland Electricity Board (SEB) and the other at a facility that belongs to its treated pole supplier, the Thonkwane wood creosote treatment plant. The drainage system of these sites leads to surface waters in rivers. This is a cause of concern since creosote contains polycyclic aromatic hydrocarbons (PAHs), which are listed as priority pollutants by the US Environmental Protection Agency. They have toxic, mutagenic and carcinogenic effects and as a result they pose a threat to human life and the environment. No previous studies have been done on PAHs in Swaziland. The main objective of this study was to determine the impact of the SEB storage facility and the creosote treatment plant by investigating the extent of PAHs in surrounding environments (soil, sediments and surface waters).

Preliminary studies were undertaken on the storage facility and the creosote treatment plant. No PAHs were detected from the pole storage facility; therefore the creosote wood treatment facility was selected as the ideal site at which to conduct the research. Soil samples were collected from depths 15 cm and 60 cm at points around the creosote plant, including effluent discharge points. The samples were extracted by solid-phase micro extraction (SPME) and analysed by GC/MS. The GC/MS, incorporating a solid phase micro extraction step, provided detection limits ranging from 0.12 μg/g to 20.08 μg/g. The pollution patterns in the study site were assessed using cluster analysis and principal component analysis.

Most of the 16 US EPA-listed priority pollutants were detected from the creosote wood treatment facility. PAHs such as anthracene, fluorene, naphthalene and fluoranthene were dominant in all the sampling sites. The compounds occurred in very high concentrations (0.64, 0.46, 0.27 and 0.26 mg/kg respectively). These compounds are found in pure creosote as determined in the sample taken from the Thonkwane creosote tank site. The highest concentration of PAHs was observed in the soil samples taken next to the road site.

The concentrations of the identified PAHs were above the acceptable minimal level allowed in soil by the US EPA and Swaziland Environment Authority (SEA). The levels of the PAHs are also above the recommended US EPA limit in soil, which is 0.1 mg/kg. The results indicated that significant soil pollution was taking place in some of the sampling sites.

The top layer (0 – 15 cm) contained many PAHs at high levels whilst the 60 cm layer had a lower number of PAHs which were also in low concentrations. This provided an indication that there is no downward movement of PAHs from the surface layer to underground layers. The potential exists for contamination of surface waters when there is runoff from the project area. This is a cause of concern, since both the creosote treatment plant and areas outside the facility are contaminated. Therefore, the site has to be cleaned up, preferably by using a phytoremediation technique.

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May the Almighty bless you all.

ABBREVIATIONS AND ACRONYMS

CSIR	Council for Scientific and Industrial Research
EPA	Environmental Protection Agency
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
IARC	International Agency for Research on Cancer
ISO	International Standard Organisation
MFO	Mixed function oxidises
PCA	Principal Component Analysis
PAH	Polyaromatic hydrocarbons or (polycyclic aromatic hydrocarbons)
PCB	Polychlorinated biphenyl
PIDS	Photo-Ionisation Detectors
SAPP	Southern African Power Pool
SEA	Swaziland Environment Authority
SEB	Swaziland Electricity Board
SFE	Supercritical Fluid Extraction
SPME	Solid phase Micro Extraction
STEM	Short-Term Energy Market
WHO	World Health Organisation

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CHAPTER 1

BACKGROUND

1.1 Introduction

Electricity is the vital ingredient for modernisation and economic development in the world today. However, the production and transmission of electricity comes at a cost, namely the various factors that have an impact on the environment. These factors are of particular relevance to this study.

The Swaziland Electricity Board (SEB) is a parastatal under the Ministry of Natural Resources and Energy. It is the sole supplier of electricity in Swaziland and its main customers are the agricultural, manufacturing and residential sectors. It contributes about 30% to Swaziland's Gross Domestic Product (GDP). In 2006 the revenue from this industry was E394 206 million (Emalangeni) and 855 MG/h units were sold (SEB, 2006).

The mission of this company is to supply cheap, reliable and adequate electricity to its customers. To achieve this mission SEB has engaged in various projects such as the 400 kVA line from South Africa to Maputo, 132 kV Integration project and the rural electrification project funded by the Republic of China (SEB, 2004). The ongoing implementation of these projects has increased the customer base by 11.32%. The distribution network has been increased by 6 183 km.

All the above projects are aimed at improving the quality of supply of electricity and ensuring security of supply in Swaziland. The projects are also aimed at expanding the SEB network so that 36% of the residents in the country are connected to the electricity supply grid. The Swaziland Electricity Board is also involved in ongoing projects such as system reinforcement and maintenance of infrastructure. These projects ensure that electricity is supplied efficiently and adequately at all times (SEB, 2003).

The three main operations that take place within the SEB are the generation, transmission and distribution of electricity throughout Swaziland. Electricity generation is done in three hydropower stations, namely Maguduza, Ezulwini and Edwaleni. The electricity generated in these power stations accounts for about 20% of local demand and the rest is imported from ESKOM (Republic of South Africa), Mozambique or the Southern African Power Pool (SAPP) through the Short Term Energy Market (STEM). The second main operation of SEB is transmission. This involves the transmission of power at high voltage to substations within close proximity of the users. The third operation is distribution, which entails the distribution of low-voltage power to the different final users of power. The distribution to customers is handled by 10 depots, namely Pigg’s Peak, Matsapha, Malkerns, Manzini, Hluti, Nhlangano, Siteki, Mhlume, Big Bend and Stonehenge (see Fig 1.1).

Figure 1.1 Location of power stations and transmission and distribution lines in Swaziland (Source: SEB Drawing Office)

In the Environmental Policy of the SEB the company commits itself to

> *Protect the environment by adhering to all existing laws and regulations on the environment, and creating environmental awareness amongst its employees, contractors, suppliers and customers.*

The policy principles state that the SEB will employ processes and technologies that seek to prevent and/or minimise negative environmental interactions on SEB's resources and infrastructure. It will also disseminate a sound environmental culture and practices amongst its employees, contractors, suppliers and customers, and implement systems such as ISO 14001. In implementing ISO 14001 one of the requirements is pollution prevention. One of the impacts that the SEB has on the environment is polycyclic aromatic hydrocarbons (PAH) pollution resulting from the treatment of transmission and distribution poles with creosote in order to extend the lifespan of the poles.

The Swaziland Electricity Board obtains transmission and distribution poles from a company called Swazi Timber and Planks (Pty) Ltd, also known as Thonkwane. Once these poles are purchased from Swazi Timber and Planks (Pty) Ltd they are transported to the SEB Central Stores in Matsapha where they are stored before being used in electricity distribution and transmission projects across Swaziland.

1.2 Problem statement

Electricity transmission and distribution facilities are known to create a number of environmental impacts. The main impacts result from poles and transformers that are used in transmission and distribution. These contain chemical substances that pollute the environment. One of these substances, creosote, is applied to poles that will be used as transmission and distribution poles in order to increase their lifespan. Creosote is the primary concern of this study. Creosote is made up of hundreds of different organic constituents of which many are known to be highly toxic to the environment. Usually creosote is constituted of around 85% polycyclic aromatic hydrocarbons (PAHs) and between 5 and 15% monocyclic aromatic hydrocarbons, phenolic compounds, and N-, S-, and O-heterocyclics (Mueller, Chapman & Pritchard, 1997; Bestari, Robinson & Steel*,* 1998). PAHs are a group of hazardous organic substances detrimental to public health due to their carcinogenic properties and bioaccumulation. Thus they are a concern to the environment (April, Sims, Sims & Matthews, 1990).

The U.S. Environmental Protection Agency (US EPA) lists 16 PAHs as priority pollutants (Mihelcic & Luthy, 1988). These chemical properties have led to legislative restrictions on their release in the environment. PAH pollutants are present in the air, water, and soil and have been a world-wide concern for a considerable period of time. The determination of the concentration of PAH-contaminated sites is therefore of critical concern. Thus the primary interest of the study lies in the determination of the PAH levels in the soil and surface waters surrounding the Matsapha Central Stores of the SEB as well as the Swazi Timber and Planks (Pty) Ltd creosote treatment plant in Thonkwane.

1.3 Justification for the study

The literature review process revealed that no study has been done in Swaziland to investigate the impact of electricity transmission and distribution facilities on soils and water. Most studies undertaken in the Southern African regions have not focused on Swaziland specifically. These studies focused on the impact of transmission lines on the environmental health aspects and general ecology. This study adds a new dimension to previous investigations, as it focuses on the likely impact of the operations in the transmission and distribution of electricity (i.e. the storage facility) on soils and water. The main focus of this study will be on PAHs derived from a storage facility for electricity transmission poles as well as from the wood treatment plant.

There has been a growing concern within SEB about environment and pollution. This has put pressure on the industry to control the environmental impact of its activities. The Swaziland Electricity Board is striving towards the implementation and accreditation of ISO 14001. The company needs to have a sound environmental management system, both to demonstrate their responsibility to society and to meet the applicable legislative requirements for environmental control. ISO 14001 has proven to be a useful tool to evolve from maintaining regulatory compliance to a position of improved productivity and enhanced competitive advantage. The ISO 14001 Environmental Management System standard requires an organisation to establish an environmental policy and objectives for the prevention of pollution, commitment to legal compliance and continual improvement. The industry standard provided guidelines that aim to integrate the need for environmental protection and prevention of pollution with socioeconomic needs.

When implementing ISO 14001, the first step is to identify the impacts and aspects associated with the organisation. When doing that one has to take into account the inputs and outputs of the organisation. In addition, one of the ISO 14001 requirements is pollution prevention from processes, resources, and so forth. Therefore it was necessary for study to be undertaken to ensure that both the SEB and its suppliers comply with environmental regulations, which is a prerequisite for the SEB to attain ISO 14001 accreditation.

Thonkwane, the supplier of creosote-treated wooden poles, would also have to adhere to ISO 14001 standards. According to Neilson (1998), the creosote used in the treatment of wood contains PAHs that are considered priority pollutants. These are a large group of compounds consisting of molecules containing two or more fused benzene rings. PAHs, also known as polyarenes, are widespread environmental contaminants of anthropogenic or natural origin. Owing to their ubiquitous distribution, PAHs are frequently detected in soils and sediments and are thus of ongoing interest in the field of analytical chemistry.

According to Edlund (2001), PAHs are regarded as priority pollutants. They exhibit properties such as persistence, bioaccumulation, mutagenicity, carcinogenicity, toxicity and potential for long-range environmental transportation to a certain extent. Low-molecular-weight PAHs (containing less than four benzene rings) are acutely toxic, some having effects on the reproduction and mortality rates of aquatic animals, and most high-molecular-weight PAHs (containing four or more benzene rings) are mutagenic and carcinogenic (Boonchan, Britz & Stanley, 2000).

Edlund (2001) further states that due to the low vapour pressure, some PAHs are present at ambient temperatures in air, both as gases and associated with particles. However, most PAH compounds are predominantly found in the particulate phase under ambient conditions, attached to dust or fine particles, especially particles with high carbon content, such as coal and soot. The extent of the association of PAH compounds with particulate matter varies with individual compounds, the nature of the particles (e.g. size, surface area, chemical properties etc) and, most importantly, with temperature. The heavier PAHs, such as benzo(a)pyrene, are almost totally adsorbed onto particles, and the lighter, such as phenanthrene, are found most exclusively in the gas phase. The semi-volatile property of PAHs makes them highly mobile throughout the environment via deposition and re-volatilisation between air, soil and water bodies. Therefore, a proportion of PAHs released into the atmosphere is deposited in the oceans and/or undergoes long-range transport making it both a local and a global environmental problem.

Due to their hydrophobic nature, most PAHs in aquatic and terrestrial ecosystems bind to particulates in soil and sediments, rendering them less available for biological uptake, and they also bioaccumulate in food chains (Boonchan *et al*., 2000). The bioaccumulating properties of PAHs result in a magnification of the substances in the trophic levels of food webs. The longer the food chain, the more is accumulated at the top, leaving top-predators especially sensitive. These properties lead to increased concern for the toxic effects that they can exert, even at extremely low levels in the ambient environment. Effects include cancers, birth defects, disruption of the immune system, nervous system damages, which disrupt the hormone systems of humans and wildlife and cause subtle undesirable effects in infants.

A number of countries have legislation to regulate persistent organic pollutants (POPs). The domestic regulatory arrangements in many countries could not adequately control POPs due to their transboundary nature. This therefore became a concern for many nations. As a global instrument for POPs regulation, the Stockholm Convention on Persistent Organic Pollutants (POPs) was signed in May 2001 by 127 countries. This treaty seeks to globally eliminate or strongly restrict the production and use of intentionally produced POPs and the continuing minimisation and, where feasible, the elimination of unintentionally produced POPs. Currently, 12 substances are regulated by the convention, and the work on finding new candidate chemicals to the convention has started. One group of substances in focus is polycyclic aromatic hydrocarbons (PAHs). Thus since Swaziland is party to this convention, it is necessary to conduct a study to provide baseline data estimating the amount of PAHs released by the impregnated wood source. This data will be used to determine if the treated wooden poles pose a threat to the environment.

Other conventions interrelated to the Stockholm Convention are the Basel Convention and the Rotterdam Convention. The Basel Convention strictly regulates the trans-boundary movements of hazardous wastes and provides obligations to its parties to ensure that such wastes are managed and disposed of in an environmentally sound manner, whilst the Rotterdam Convention enables the world to monitor and control very dangerous substances (UNEP, 2002). Since Swaziland is a signatory of all three conventions, it has to adhere to the requirements of the three conventions. The PAHs of concern in this study are listed as hazardous substances in the conventions; therefore this study would also be an indication of whether the country is in conformance with these conventions.

1.4 Study area

This study was conducted in two study areas, Matsapha CSO and the Thonkwane wood treatment plant. Figure1.2 indicates the general orientation of the study sites in Swaziland.

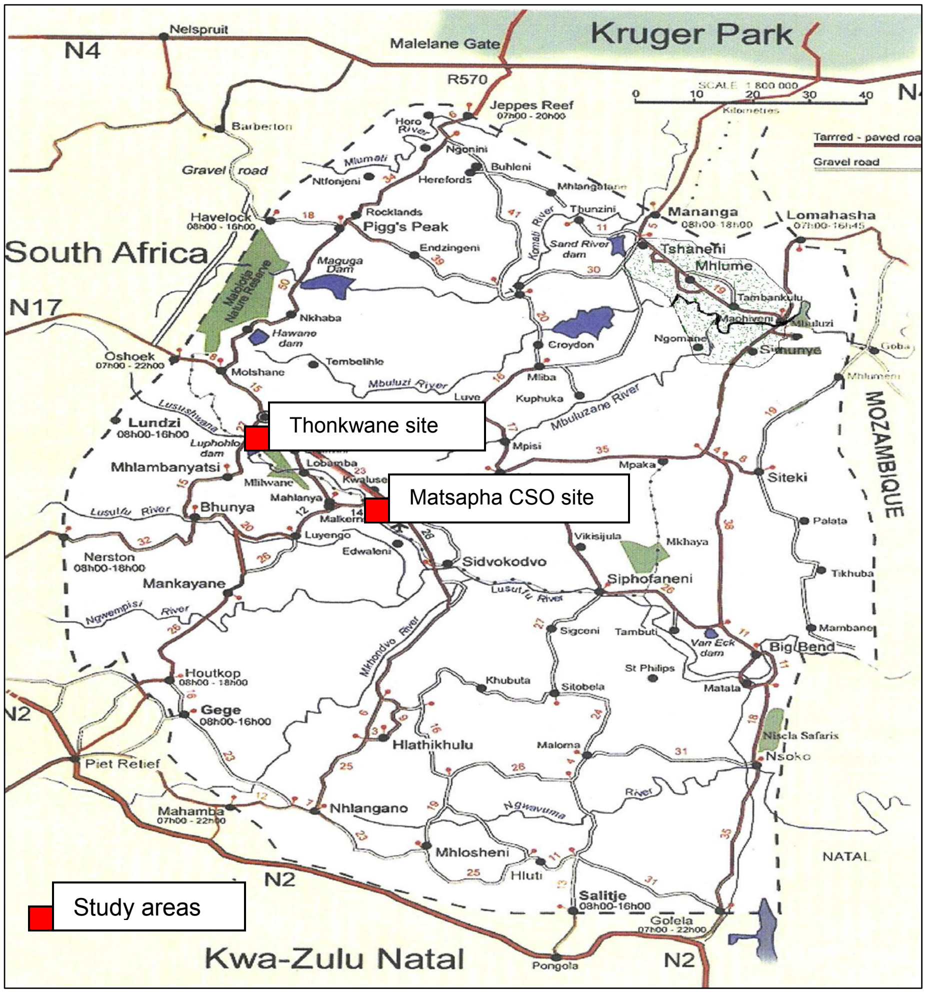
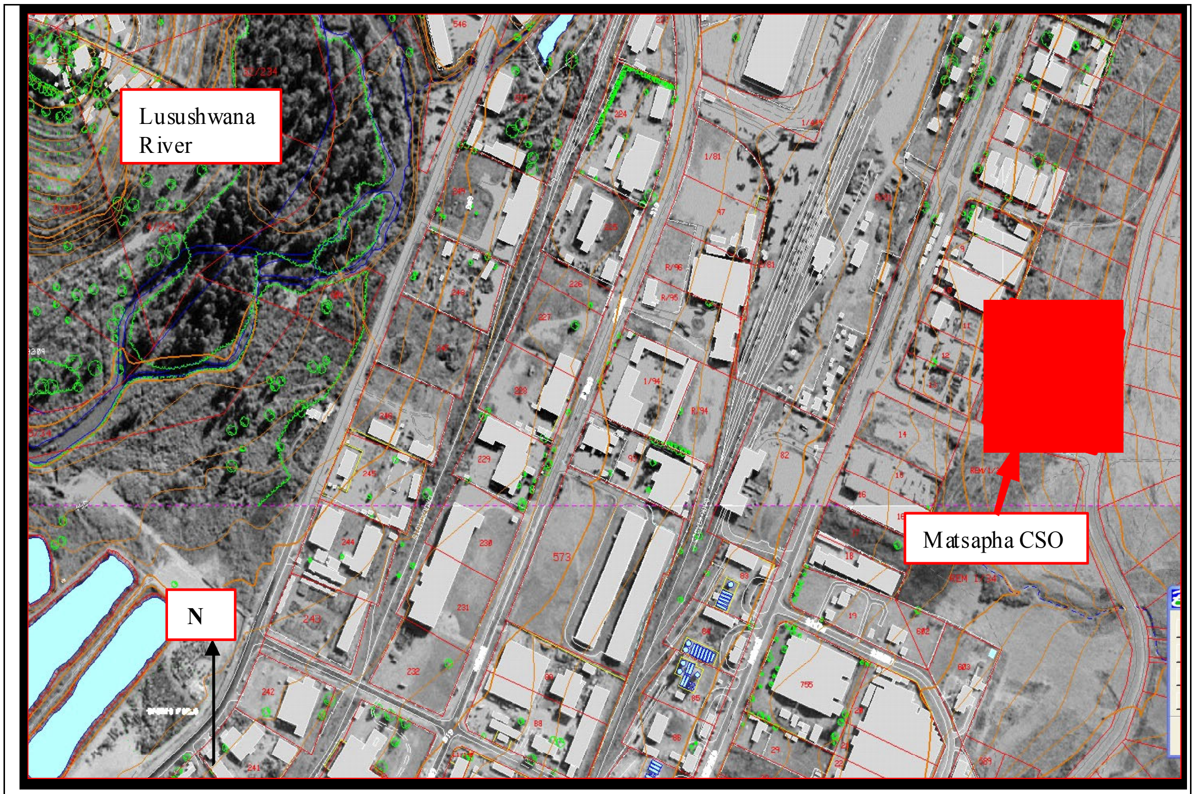


Figure 1.2 Study areas: Matsapha CSO (wood storage facility) and Thonkwane. (wood treatment facility)

1.4.1 Study area 1, Matsapha Central Stores (wood storage facility)

The Matsapha Central Stores office or CSO is situated in the Matsapha industrial site (Figure 1.3). This storage area has been in use since 1998. The stores consist of three platforms where materials are stored. Platform one is a bare soil area used for the storage of creosote treated poles. Approximately 20 000 to 30 000 poles are stored here at any one time throughout the year. This platform has an unlined drain at its lowest section, which drains to a concrete v-drain along an access road. The second platform is used for the storage of transformers, conductors, insulators and other construction material. The third platform consists of offices, general stores and a wash bay. The three platforms discharge their runoff into the concrete drain bordering the study site. This drain finally discharges into the Lusushwana River.



Scale: 1: 7500

Figure 1.3 Wood storage site in Matsapha CSO

The Lusushwana River runs below the Matsapha industrial site (see Plate 1). All effluent from the various industries is carried in the drains and discharged into the river, which is a primary water supply for some downstream communities at Edwaleni and Nhlambeni. These communities use the water for all their domestic activities such as cooking, washing and bathing. The river has been in the headlines as result of unprecedented pollution exacerbated in the river by industries, which is the only water source for downstream communities. In March 2003, some residents and concerned citizens protested against the development of a pulp and chipping plant in the same industrial area citing that they suffered from ’chronic cholera’ due to the highly toxic substances already contaminating the river. In addition, concerned citizens have been calling on the government to declare the river and its surrounding environments a ’national disaster’. They requested the government to allocate funds for its rehabilitation. In the latest incident, the Swaziland Environmental Authority (SEA) investigated complaints by residents downstream. They alleged that the growing Matsapha Industrial Estate was making the Lusushwana River ‘poisonous’, and that the consumption of this ‘poison’ was causing various ailments.

Plate 1 Photos taken in Matsapha CSO and Lusushwana River

a) Treated wood pole storage area in Matsapha Central Stores

b) Leaking transformer oil drums c) Used transformer storage site

1.4.2 Study area 2, Thonkwane (wood treatment facility)

The second study area was Swazi Timber and Planks (Pty) Ltd, which is located in the Highveld of Swaziland, approximately 8 km from Mbabane city. This site is also known as Thonkwane (Figure 1.4 and Plate 2). The treatment plant is situated on a flat area, which is surrounded by gentle slopes that are planted with plantations. On the western side of the treatment plant various species of weeds are now occurring as a result of a fire that devastated the pine plantation two years ago. The treatment plant consists of a pretreatment plant, a treatment plant, an effluent storage site and an effluent disposal area. The final effluent is discharged into a waterway that drains down slope.

Scale 1: 7500

Figure 1.4 Creosote wood treatment facility in Thonkwane

Since effluent from the Matsapha Central Stores and Thonkwane is discharged into drains that lead directly into surface waters, it is critical that this discharge as well as surrounding soils must be monitored for PAH contamination.

Plate 2 Creosote wood treatment facility at Thonkwane

a) Creosote storage tank b) Rail with untreated wood

c) Creosote cylinder d) Steamer

e) Effluent ponds and trench f) Effluent ponds

g) Effluent from trench and discharge point

h) Effluent tank discharge point

i) Effluent movement down slope from pine logs to the road

1.5 Hypotheses

The hypotheses of this study are the following:

1.5.1 Hypothesis 1

H1 The pole storage site in Matsapha CSO is contaminating soils and surrounding surface waters with PAHs.

1.5.2 Hypothesis 2

H2 The wood creosote treatment plant in Thonkwane (Swazi Timber Sales) is contaminating soils and surrounding surface waters with PAHs.

1.6 Aims and objectives

The following aims and objectives have been formulated in an attempt to answer both Hypothesis1 and Hypothesis 2 as stated above.

1.6.1 Aims of the study

The main aim of this study was to determine the impact of the SEB storage facility as well as the creosote treatment plant by investigating the extent of PAH in surrounding environments (soil, sediments and surface waters).

1.6.2 Objectives of the study

The main objectives of the study were the following:

1 To determine PAH levels in soils and water at the Matsapha Central Stores and Thonkwane.
2 To determine leachability and distribution of PAHs in Matsapha Central Stores and Thonkwane.
3 To compare levels with standards to determine compliance with US EPA and the Swaziland Environment Authority (SEA).

1.7 Chapter outline

The outline below provides an indication of the different chapters in this study and assists the reader in understanding the flow of the investigation procedure that was followed and the main sections that are dealt with in each chapter.

The thesis consists of five chapters. Chapter 1 provides the background and the purpose of this investigation. It briefly explores the issues of polycyclic aromatic hydrocarbons. The study areas as well as the hypothesis, aims and objectives of the study are discussed.

The next chapter, Chapter 2, explores the literature relevant to the study. It describes the characteristics of PAHs, the sources of PAH and the uses of PAH.

The chapter also explores the relevant chemical and environmental properties of PAHs as well as the main risks and human exposure to PAHs. It also provides international and national standards with regard to PAHs. Finally it discusses trends in PAH research as well as the shortcomings of the research.

Chapter 3 describes the methodology and experimental procedures used in the study. It also describes the sampling procedure and the data-collection procedure.

The following chapter, Chapter 4, presents an analysis of the data collected, and provides illustrations and the discussion of the results. It also compares the results with international and national standards.

Finally, Chapter 5 seeks to answer the research problem, and to accept or reject the hypotheses. It suggests possible solutions and provides conclusions to the study.

Literature on these issues is reviewed in the next chapter, Chapter 2, which lays the theoretical foundations for the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discusses the arguments and findings of a number of researchers with regard to PAHs in creosote, with special attention to the issues raised in the study. Issues that will be addressed in this chapter include the history, use of creosote, properties as well as health and environmental effects of creosote and creosote derived PAHs. It also examines the various methods used by other researchers worldwide to determine PAHs in soil samples.

2.2 Theoretical studies

2.2.1 Identity and properties of creosote

Many sites worldwide have been polluted by creosote as a result of wood-preserving activities. Past practices of applying creosote and coal tar preservatives to wood, such as the use of unlined pits and trenches, have contaminated the surface and groundwater at thousands of sites. According to Choudhary, Citra, McDonald and Riviera (2002), creosote is a complex mixture of different chemicals such as polycylic aromatic hydrocarbons (PAHs) (Table 2.1), phenols, and metals. The American Wood Preservation Association (AWPA) describes creosote (CAS Registry Number 8001-58-9) as:

> *[A] distillate of coal-tar produced by high temperature carbonization of bituminous coal; it consists principally of liquid and solid aromatic hydrocarbons and contains appreciable quantities of tar acids and tar*

bases; it is heavier than water, and has a continuous boiling range of approximately 275°C, beginning at about 175 °C (AWPA, 1977).

According to U.S. EPA (1987) and Zapff-Gilje, Gary and Rankin (2001), there are five major classes of compounds in creosote. The first one is aromatic hydrocarbons including PAHs, alkylated PAHs, benzene, toluene, and xylene (PAHs constitute up to 90% of creosote). The other class is phenolics (1 to 3% of creosote). The third class of compounds is Nitrogen-containing heterocycles (1 to 3% of creosote), whilst the fourth class is sulphur-containing heterocycles (1 to 3% of creosote); and finally the oxygen-containing heterocycles (5 to 7.5% of creosote).

Table 2.1 Polycyclic Aromatic Hydrocarbon (PAH) constituents in creosote Source: Mueller, Cerniglia & Pritchard, 1996

PAH CONSTITUENTS	PERCENTAGE BY WEIGHT
Naphthalene	13
Anthracene	13
2-Methylnaphthalene	13
Phenanthrene	13
Biphenyl	8
Fluorene	8
1- Methylnaphthalene	8
2, 3 Dimethylnaphthalene	4
2, 3 Dimethylnaphthalene	4
2, 6 Dimethylnaphthalene	4
Acenaphthylene	4
Fluoranthene	4
Chrysene	2
Pyrene	2
Antrhaquinone	1
2 – Methylantracene	1
2,3 Benzo Florene	1
Benzo (a)pyrene	1
Total PAHs in creosote	100

2.2.2 Properties of creosote

The general characteristics common to the polycyclic aromatic hydrocarbons are high melting and boiling points, low vapour pressure, and very low solubility in water, as can be observed in Table 2.2 (IARC, 1983). The physical properties of creosote that largely determine its behaviour in subsurface include its specific gravity (which is near that of water), its high viscosity and low interfacial tension.

Table 2.2 Chemical characteristics of PAHs

Source: ATSDR, 1993

PAH	Chemical formula	Molecular weight	Water solubility	Melting point °C	Boiling point °C	Log K_{OW}	Log K_{OC}
Naphthalene	$C_{10}H_{12}$	128	3.169	81	218	3.37	2.97
Acenaphthylene	$C_{12}H_8$	152	3.93			4.07	1.40
Acenaphthene	$C_{10}H_{12}$	154.21	3.93			3.98	3.68
Fluorene	$C_{13}H_{10}$	166.2	1.68-1.98			4.18	3.86
Phenanthrene	$C_{14}H_{10}$	178.2	1-1.6	100	340	4.45	4.15
Anthracene	$C_{14}H_{10}$	178.2	0.0446	218	342	4.45	4.15
Fluoranthene	$C_{16}H_{10}$	202.26	0.206	107	384	4.90	4.58
Pyrene	$C_{16}H_{10}$	202.3	0.129-0.165	147	404	4.88	4.58
Chrysene	$C_{18}H_{12}$	228.3	0.0015-0.0022			5.61	5.30
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.3	0.0012			6.04	5.74

Creosote is denser than water. For some wood preservation uses, creosote is mixed 1:1 with fuel oil. In these uses, the density will be less than pure creosote, but will still be heavier than water (Hoffman & Hrudey, 1990). The vast majority of the components of creosote have low aqueous solubility. This limits the degree to which these components can dissolve in water, which causes them to be available to the environmental microbial community (Reid, Stokes & Jones, 2004). In line with this statement, Romanowski, Funcke, Grossmann, Konig & Balfanza, (1983) state that creosote is insoluble in water although the components have a wide range of solubilities, from the readily soluble tar acids and bases (i.e. phenols, cresols, acridines) to the insoluble six-ring PAHs. Creosote is soluble in many organic solvents, including oil and diesel fuel (U.S. EPA, 1987; Bos, Hulshof, Theuws & Henderson, 1983). It is an effective preservative, almost insoluble in water and therefore resistant to leaching. Other attributes are that it is normally not corrosive to metals, it protects timber against splitting and weathering and it has a high electrical resistance.

Creosote is a non-aqueous liquid that will slowly sink when placed in water. However, floating and sinking phases have been reported. Viscosity will vary widely, depending on creosote composition and temperature, but it is typically much higher than that of water. The viscosity reduces the velocity at which creosote can migrate through soil. Creosote migration through a porous medium is determined to a much greater extent by the interfacial tension between creosote and soil pore water or groundwater. This implies that creosote may travel further and leave behind much lower residual concentrations in the soil than would be expected for a comparable petroleum oil (Zapff-Gilje *et al*., 2001).

According to Miller, Wasik, Huang, Shiu and MacKay (1985), the vapour pressure (Pv) of creosote is variable because of the number of compounds involved. It is difficult to characterise. Vapour pressures range from 2.0 x 10^{-10} Pascals (Pa) for ibenzo[b]chrysene to 11.6 Pa for naphthalene. The tendency for PAHs to prefer either biota or water in aquatic systems is given by the Octanol-Water Partition Coefficient (Ko_w). The range of log (K_{OW}) values for PAHs is from 3.29 to 7.19. Other components of creosote have widely varying log K_{OW} values, from 0.65 for pyridine to 3.95 for biphenyl. The range of log K_{OC} values for PAHs is from 2.97 to 6.74.

2.2.3 Uses of creosote

Ikarishi, Kaniwa and Tsuchiya (2005) and Edlund (2001) state that creosote is used as a wood preservative in poles used in railway sleepers, telecommunication and electricity transmission. The poles can also be used in the foundations of houses, as fences, as stakes for agricultural and fruit production, and for the manufacture of garden furniture and outdoor recreational facilities in parks. The wood is durable because the chemicals in the preservative are toxic to decay fungi and insects. However, these chemicals that are beneficial in protecting the wood are also potentially toxic to aquatic organisms. This has caused some concern that chemicals might leach out of the wood and accumulate in the environment to harmful levels (Brooks, 2000). In Swaziland, Swaziland Treated Poles uses creosote for the preservation of electricity poles. The extent of the usage has necessitated this study.

2.2.4 Creosote treatment process of wood

According to Holoubek, Kocan, Holoubková, Hilscherová, Kohoulek, Falandysz and Roots (2000), the methods used for creosote preservation of timber are spraying, dipping or vacuum high-pressuring. The simplest production process involves dipping the timber into an open vessel containing creosote oil for approximately three minutes. Once the timber is taken out of the vessel, the excess creosote drips off and the timber is dried. All types of wood can be dip-treated. The pressure-treatment process is done in closed reactors. In principle, the process consists of three process steps: a pre-vacuum step, an impregnating step when warm creosote oil is pressured into the timber, and a final vacuum step when the remaining creosote is sucked from the timber. Through these methods 20 – 25 litres of creosote oil per cubic meter wood is pressed into the timber. Following the treatment the timber is dried before use, allowing the solvent and volatile compounds to evaporate into the atmosphere.

Bestari *et al*. (1998) state that there is concern over the use of creosote because a wide range of its constituents is released to the environment over a long term. Kohler, Kunniger, Guger and Crockett (2000) state that PAHs constitute 40% of the total mass of creosote. These PAHs have been listed as priority pollutants by US EPA (1995).

2.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Since PAHs constitute a larger portion of creosote, they were used in the study as an indicator for creosote contamination. This study concentrated only on compounds that fall in the category of polycyclic aromatic hydrocarbons. Sometimes the term ‘polynuclear’ is used in the literature instead of ‘polycyclic’ to describe these compounds. The properties, formation, sources and fate, health effects and ecological impacts of PAHs will be described in the next section.

2.3.1 Sources and pathways of PAHs

Polycyclic aromatic hydrocarbons (PAHs), also known as polyarenes, are widespread environmental contaminants of anthropogenic or natural origin usually occurring in mixtures. Anthropogenic PAH sources include fuel oil or gasoline spills, natural seeps, combustion of fossil fuels (coal, oil, natural gas) and wood, as well as creosote releases. The main source of PAHs is to be found in the incomplete combustion of coal, oil and petrol, as well as in wood-preservation sites or processes involving the petrochemical industries (Lundstedt *et al*., 2003).

They occur naturally in the environment, during such processes as thermal geological reactions and natural fires. PAHs also occur naturally in peat, lignite, coal and crude oil. Forest fires and volcanoes are biogenic PAH sources (Neilson, 1998). Human activities are significant sources in the environment, since PAHs are formed in all processes involving incomplete combustion (insufficient oxygen supply) of organic compounds. Hazards associated with these compounds derive from their persistence, their hydrophobic character, their bioaccumulation and their carcinogenic properties of several individual polyarenes. Owing to their ubiquitous distribution, PAHs are frequently detected in soils and sediments and are thus of ongoing interest to analytical chemistry.

PAHs are one of the typical persistent organic compounds (POPs) featured in regional and global cycling. PAHs are emitted mainly into the atmosphere, adsorbed to particles, and may then be transported over long distances where they can be detected. PAHs are thus ubiquitous environmental pollutants that are generally found in elevated levels near emission sources (Bergknut, Kitti, Lundstedt, Tysklind & Haglund, 2003). Because of their low vapour pressures, compounds with five or more aromatic rings exist mainly adsorbed to airborne particulate matter, such as fly ash and soot. Those with four or fewer rings will occur both in the vapour phase and adsorbed to particles. PAHs reach the hydrosphere and pedosphere mainly through dry and wet deposition and road runoff but additionally from industrial wastes containing PAHs and leaching from creosote-impregnated wood. PAHs are adsorbed strongly to the organic fraction of sediments and soils (see Figure 2.1). Therefore it can be concluded that sediments and soils are usually considered as the main sinks for PAHs in the environment and PAHs with four or more aromatic rings are persistent in the environment.

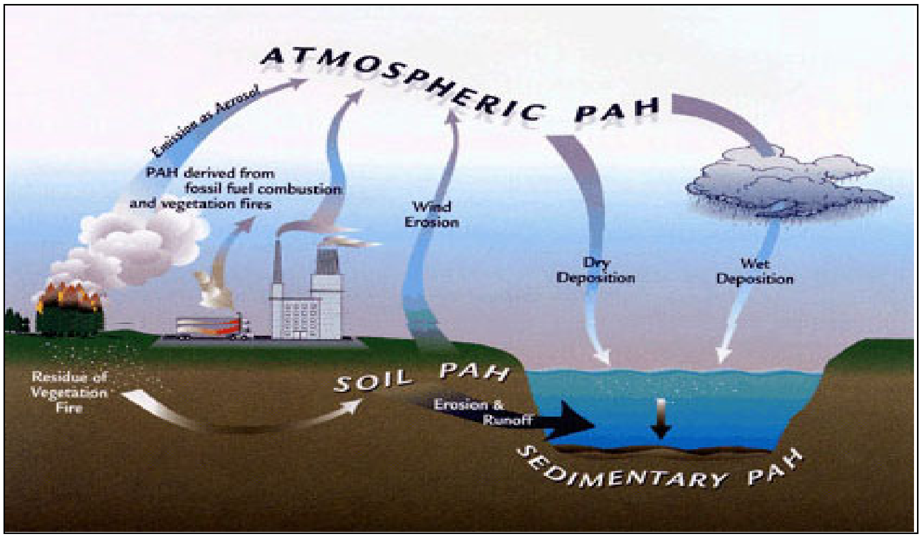


Figure 2.1 Pathways of PAHs in the environment
Source: OSPAR commission, 2001

2.3.2 Formation of PAHs

PAH is the commonly used name for numerous benzene rings connected to one unit. The benzene rings can be fused in a linear, angular, or clustered arrangement, as shown in Figure 2.2 (Bergknut, 2006; Lundstedt, Haglund & Orberg, 2003).

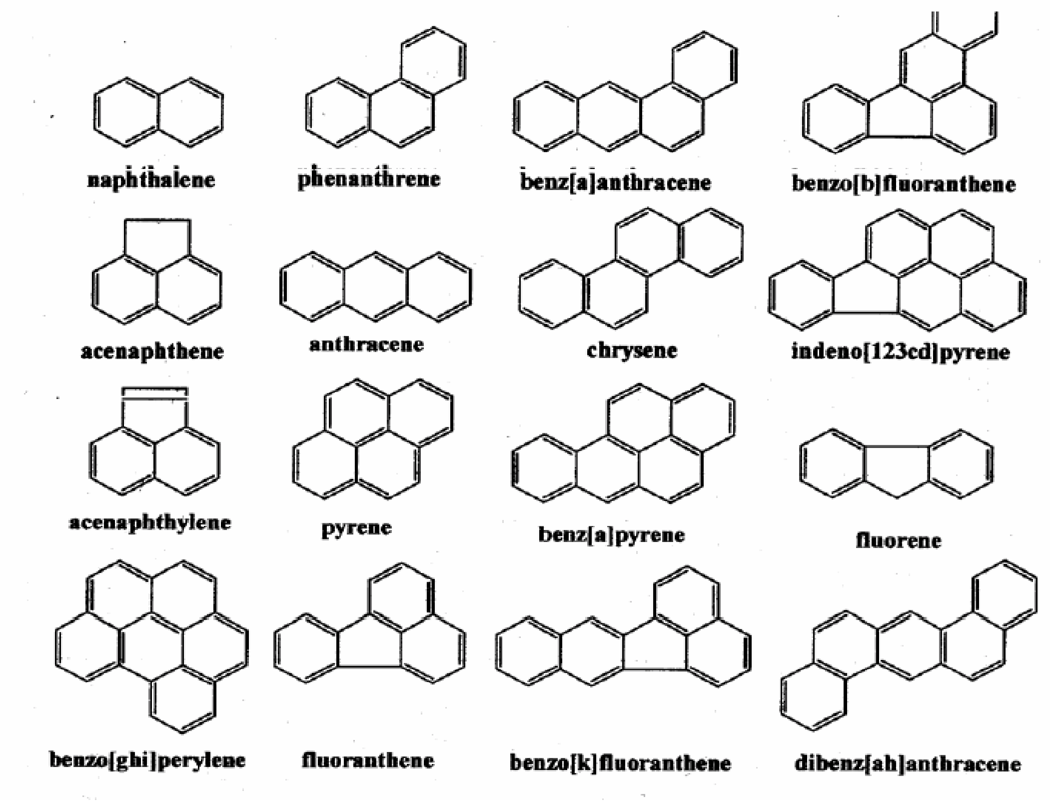


Figure 2.2 The chemical structure of common PAHs
Source: Sims and Overcash, 1983

One or more hydrogen atoms in a PAH molecule can be substituted for one or more methyl or ethyl groups. PAHs are formed during organic combustion processes without sufficient amounts of oxygen present (pyrolysis). The formation of PAHs can occur in different ways: when parts of the fuel's polycyclic hydrocarbon backbone does not completely decompose or through high temperature processes of smaller alkanes clustering together to form aromatic compounds. Therefore, PAHs are formed during almost all forms of combustion, at different ratios depending on the temperature. PAHs have been thoroughly studied because of their toxicity, persistency and environmental prevalence (Blumer, 2003). However, these studies have been limited to 16 PAHs, designated as priority pollutants by the United States Environmental Protection Agency (US EPA).

2.3.3 Properties and environmental fate of PAHs

According to Holoubek *et al*. (2000), the fate of PAHs is of great environmental concern due to their toxic, mutagenic and carcinogenic properties. It depends on several factors such as atmospheric photolysis, sorption, water and lipid solubility, chemical oxidation, volatisation, and microbial degradation. Zapfft-Gilje *et al*. (2001) state that PAHs are a diverse group of organic compounds composed of hydrogen and carbon atoms arranged in two or more fused benzene rings. They are grouped into two categories based on their molecular structure: Low molecular weight (LMW) compounds with fewer than four rings and high molecular weight (HMW) with four or more rings. About 75% of PAHs fall in the LMW category.

According to Lundstedt *et al*. (2003), the PAHs containing three or less benzene rings LMW have a higher vapour pressure and can normally be found in the gas phase. This implies that they are semi-volatile and exist in the atmosphere partly as vapours, which are highly susceptible to atmospheric degradation processes. Thus they are to be considered a regional pollutant. The semi-volatile property of PAHs makes them highly mobile throughout the environment via deposition and re-volatilisation between air, soil and water bodies.

PAHs with five or more rings are less volatile and condense on soot particles formed during the combustion. Lundstedt *et al*. (2003) who also mention this aspect, argue that the high molecular weight HMW PAHs, on the other hand, are primarily associated with particles in the atmosphere and water, and are therefore less available for degradation. These are adsorbed to particles. Condensation on particles makes it less probable that the PAHs will oxidise in the atmosphere. This enhances their transportation over long distances in the atmosphere and therefore causes them to be ubiquitous in the environment. The extent of the association of PAH compounds with particulate matter varies with individual compounds, the nature of the particles (e.g. size, surface area, chemical properties, etc.) and, most importantly, with temperature. The heavier PAHs, such as benzo(a)pyrene, are almost totally adsorbed onto particles, and the lighter ones, such as phenanthrene, are found most exclusively in the gas phase (OSPAR Commission, 2001).

PAHs are generally insoluble in water but can be readily solubilised in organic acids. This implies that in an aqueous environment they are found adsorbed on particulates and solubilised in any oily contaminant that may be present in water, sediment and soil. In line with this statement, Lundstedt *et al*. (2003) state that PAHs are generally lipophilic compounds that show a high affinity for organic matter. This statement is supported by Quantin, Joner and Portal (2005) and Yuan, Chang, Yen and Chang (2001) who state that PAHs have high boiling points, are very lipophilic and are hard to dissolve in water. Due to their hydrophobicity and their recalcitrance, both increasing with increasing molecular weight, PAHs can accumulate in sediments in high concentrations.

The low molecular weight (LMW) PAHs are more water soluble and volatile than the higher molecular weight (HMW) compounds. Thus three-ring PAHs tend to be more soluble in water than the five ring-compounds (RECETOX TOCOEN and Associates, 2004). The solubility of PAHs in water is inversely proportional to the number of rings they contain. Thus, LMW PAHs are much more water soluble and volatile than their high molecular weight (HMW) relatives, while the HMW PAHs show higher hydrophobicity than the LMW compounds (Mackay, Shiu & Ma, 1992). The difference in hydrophobicity is also reflected by the octanol-water-partitioning coefficient. These physico-chemical properties largely determine the environmental behaviour of PAHs and indicate that transfer and turnover will be more rapid for LMW PAHs than for the heavier PAHs (Lundstedt *et al*., 2003).

2.3.4 PAHs from a creosote treatment facility

Mueller *et al.* (1997) states that numerous wood-impregnation sites are highly contaminated with PAHs, and that PAHs consist of approximately 85% of the components in creosote. The other components in creosote are N-, S-, and O-heteocyclics (5%) and phenolic compounds (10%). When released into the environment, creosote does not readily dissolve in groundwater, but persists largely as a separate non-aqueous-phase liquid (NAPL) in the subsurface. PAH emission from the creosote-treating installations is mainly due to leakage from vessels and reactors, and evaporation and drip-off from treated timber. The potentially negative impact of creosote is not restricted to the treatment process, as PAHs and other substances are also emitted during the use phase and during the final disposal. These risks are not necessarily of the same intensity as those relating to the production plant, but the quantities of treated timber that will be in service in coming years mean that the issue of widespread low-level contamination and ultimate disposal is of great significance (UNEP,1994).

2.3.5 PAHs in soil

PAHs in the subsurface are strongly sorbed to the organic matter. This makes them relatively unavailable for degradation processes (Wild & Jones, 1995). PAHs can therefore remain in the soil for many centuries, posing a long-term threat to the environment. The adsorption of the PAHs in different soil matrices results from their low vapour pressure. Mastral and Callen (2000), indicate that the hydrophobicity of PAHs is reflected by their low water solubility and the matrix nature. Also, their hydrophobic and lipophilic properties result in a high tendency for bioaccumulation and persistence in the environment, a reason for high eco-toxicological concern (Schwarzenbach, Gschwend & Imboden , 2003).

Alexander (1995), Bossert and Bartha (1986), Lundstedt (2003), Sims and Overcash (1983) and Wild and Jones (1995), argue that LMW PAHs are partly lost through degradation processes, volatilisation and leaching. The effect of sorption generally increases as the number of benzene rings in the PAH-molecule increases since this implies higher lipophilicity. Furthermore, it has been shown that the degradability and extractability of organic compounds in soil decrease with the time they have been in contact with the soil: a phenomenon referred to as ‘aging’ or ‘weathering’. Aging is mainly a result of slow diffusion into the soil organic matter, but other mechanisms involved include the formation of bound residues and physical entrapment within soil micropores (Alexander, 1995). On the one hand, the processes of sorption and aging limit the degradability of the contaminants. On the other, these processes reduce the toxicity of the soil contaminants by lowering the fraction available for uptake by living organisms.

2.3.6 Chemical characteristics of monitored PAHs

Two PAHs, such as naphthalene and benzo(b)fluoranthene, can possess very different chemical properties and behave quite differently in air/water/soil systems. Naphthalene is the most soluble of the monitored PAHs. Naphthalene also has the highest vapour pressure of the 10 PAHs and a characteristic mothball smell. Naphthalene does not adhere strongly to soils or sediments and can pass through sandy soils with relative ease and readily contaminate groundwater supplies (ATSDR, 1993). Conversely, benzo(b)fluoranthene has the lowest solubility of the monitored PAHs. Benzo(b)fluoranthene is a non-volatile PAH that adheres very strongly to soil and organic matter. Contrasting the chemically-related parameters of an LMW and HMW PAH demonstrates the difficulty associated with the remediation of complex mixtures of PAHs, such as creosote.

PAHs are semi-volatile, and consequently present in both the gas and particulate phases of air (Gundel, Lee, Mahanama, Stevens & Daisey, 1995). These ubiquitous compounds have attracted much attention since quite large numbers of them are carcinogenic. Benzo[a]pyrene (B[a]P) was the first chemical to be proven a carcinogen (IARC, 1983; Van Leeuwen & Hermens, 1995). Its effect was shown to be due to mixed function oxidises (MFO) activation. B[a]P is initially transformed to an epoxide that can either be activated or deactivated. Deactivation normally involves diol formation or conjugation to form glutathione conjugates, which are easily excreted in the bile or urine. However, in some cases the initial activation leads to a series of events that finally results in DNA adduct formation. Such defects may lead to cancer.

2.3.7 Toxicological effects

According to Delistray (1997), a wide range of ecotoxicological effects in diverse suite of biota including micro organisms, terrestrial plants, aquatic biota, amphibians, reptiles and terrestrial mammals have been reported. Effects have been documented on survival, growth, metabolism, and tumour formation, i.e. acute toxicity, developmental and reproductive toxicity, cytotoxicity, genotoxicity and carcinogenity. Pickering (1999) states that the primary focus of toxicological research on PAHs has been on genotoxicity and carcinogenicity. In these studies, several PAHs have been shown to damage DNA and to cause mutations, which in some cases may result in cancer. However, for the unsubstituted PAHs it is not the original compound that reacts with DNA. The PAHs require metabolic activation and conversion to display their genotoxic and carcinogenic properties. This happens as the PAHs are metabolised in higher organisms.

Pickering (1999) further argues that PAHs do not accumulate in the same manner as some other lipophilic organic compounds such as PCBs. Instead, they are converted to more water-soluble forms, which facilitates their subsequent excretion from the organism. Unfortunately, this may also lead to the formation of reactive intermediates that may react with DNA to form adducts, preventing the gene involved from functioning normally. The DNA damage may be repaired, but if the repair fails, i.e. if there is irreparable genetic damage, a mutation will have occurred. Mutations may affect many different functions of a cell, but above all they may induce cancer.

PAHs have been shown to induce a number of toxic effects. Several PAHs have been shown to cause death in rodents after short-term exposure to high doses. On the other hand, no deaths have been reported from short-term occupational exposure in humans (Mueller *et al*., 1997). Since the environmental levels are generally much lower than the occupational exposure, it is extremely unlikely that short-term exposures to PAHs would lead to death. On the other hand, eye irritation, photophobia and skin toxicity such as dermatitis and keratosis have been demonstrated in workers occupationally exposed to PAHs.

Adverse respiratory effects, including acute and subacute inflammation and fibrosis, have been demonstrated experimentally. With benzo [a] pyrene severe and long-lasting hyperplasia and metaplasia were observed. These effects manifest themselves as precancerous lesions and are consistent with the general assertion that one of the main targets of PAH toxicity is the respiratory tract.

2.3.8 Human exposure and risks of PAHs

Human exposure to PAHs occurs primarily through the smoking of tobacco, inhalation of polluted air and ingestion of food and water contaminated by combustion effluents. The main sources of human exposure are emissions from the combustion of coal, diesel, petrol, kerosene, wood, biomass and synthetic chemicals such as plastics. Pollution of indoor air by PAHs is mainly due to tobacco smoking, residential heating and PAHs from outdoor ambient air. The level of individual PAHs in air tends to be higher in winter than in summer. The predominant source in winter is residential heating and in summer motor traffic. Average concentrations of 1-30 ng/m^3 of individual PAHs were detected in the ambient air of various urban areas. In large cities with heavy motor traffic and extensive use of biomass fuels, such as Calcutta, levels of up to 200 ng/m^3 of individual PAHs were found. Near industrial sources, the average concentration of individual PAHs ranged from 1 to 10 ng/m^3. The background values of PAHs are at least one or two orders of magnitude lower than those near sources like motor vehicle traffic or industries. For example, the levels in rural areas at 1 100 m ranged from 0.004 to 0.03 ng/m^3 (International Programme on Chemical Safety, 1998).

2.4 International standards

According to WHO (1998) standards, the maximum PAH level allowed in the wood-preserving industry is 0.05 mg/l. The Environmental Protection Agency has stipulated (1995) that a lower limit of application of 0,01 mg/kg (expressed as dry matter) can be ensured for each individual PAH in any type of soil.

2.5 Soil remediation techniques

The term ‘soil remediation’ refers to actions designed to eliminate or minimise the risk associated with contaminated soil. This goal may be achieved in several different ways and the selected method depends on factors such as the contaminants present, the site conditions and the cost. The (US DOD, 1994) refers to remediation as removing, degrading or transforming contaminants to harmless substances. Additionally, it includes methods that reduce mobility and migration of the contaminants, preventing them from spreading to uncontaminated areas. The toxicity of the contaminants remains unaltered, but the risk they pose to the environment is reduced.

According to Rabbabah and Matsuzawa (2002), there are various remediation techniques that can be used for the degradation of PAH-contaminated matrices. However, these are dependent on various factors such as duration required for treatment, type of environmental matrix, cost, site sensitivity and climate, PAH molecular weight and concentration as well as the end use of the site. Remediation of the contaminated sites can take place without removing the soil in situ or by removing the soil where the excavated soil is treated somewhere else.

The ultimate goal of any degradation process is complete mineralisation of the organic contaminants, resulting in carbon dioxide, water and other inorganic compounds. However, Lundstedt (2003) states that during biological and chemical degradation processes, partial transformation may lead to the formation of other organic compounds. This may cause problems if the transformation products are also hazardous and persistent. In the worst case it could lead to increased toxicity, even if the original contaminants have been degraded. This potential problem is seldom considered during remedial monitoring programmes, in which only the original contaminants are usually analysed.

The most common method is still to excavate the contaminated soil and transport it to a landfill that is considered to be safe from an environmental point of view. However, for organic contaminants this is not the preferred solution. Instead, an environmentally sustainable policy should ideally be based on methods that permanently destroy the contaminants, i.e. destruction methods. The most effective and reliable method to destroy organic contaminants in soil is incineration. However, this method is expensive, it makes the soil sterile and depletes it of all organic matter. Hence, other methods have been developed. Biological and chemical remediation methods utilise micro organisms and reactive chemicals to accomplish the degradation. These methods also have the potential to degrade a wide variety of soil contaminants, but they usually need careful optimisation.

Although there is a very wide range of remediation methods available to tackle contamination, three broad approaches can be distinguished:

- Engineering approaches – these are primarily the traditional methods of excavation and disposal to landfill, or the use of appropriate containment systems
- Process-based techniques that include physical, biological, chemical, stabilisation/ solidification, and thermal processes
- Hydraulic measures and natural attenuation.

2.5.1 Engineering approaches

Landfill involves the three stages of soil excavation, transport, and burial at the landfill site. Contaminants in the soil are not necessarily removed, stabilised or destroyed on site and are ultimately transferred to another site. Landfills are designed to ensure that contaminants are either isolated from the environment or subjected to attenuation processes so that they no longer cause harm to the environment. Containment measures are those which are designed to prevent or limit the migration of contaminants that may be either left in place or confined to a specific storage area, to the wider environment. Approaches include hydraulic measures, capping, and the use of break layers and low permeability barriers.

Most remediation practices of underground contamination rely on excavating the soil and treating it in separate areas or treatment facilities. These treatments include, for example, thermal treatment and land filling. Incineration is a very effective treatment method, but it is costly and after burning, the soil has lost most of its nutritional value and structure. Land filling does remove the contaminants but only relocates the problem (Lageman, Clarke & Pool, 2005).

2.5.2 Process-based techniques

Physical processes used in soil treatment are used to remove contaminants from the soil matrix, concentrating them in process residues that require further treatment or safe disposal. Contaminants in the concentrated fractions may subsequently be destroyed, recovered by some other process (e.g. chemical or thermal), or they may be disposed of at a landfill. The process-based techniques include the following: bioremediation, phytoremediation, electrokinetic remediation stabilisation, and chemical processes. These processes are discussed below.

2.5.2.1 Bioremediation

The bioremediation technique involves the breakdown of organic contaminants by microbial processes. Biological processes of soil treatment depend on the natural physiological processes of micro organisms, such as bacteria and fungi, to transform, destroy, fix or mobilise contaminants. In bioremediation, the microbes or microbial communities capable of degrading the contaminants need to be present. Furthermore, the groundwater should contain the nutrients to support this degradation so that they can support the reactions. When bioremediation is enhanced, these nutrients (typically nitrogen and phosphorus source), air (oxygen source) or any additional carbon source (easily degradable organic compound) are added into the ground through wells. The additional carbon source can facilitate destruction of the contaminants through co-metabolic reactions. Because the vast majority of the components have low solubilities in water and hence have limited bioavailability, the remediation technique of enhanced biodegradation is often not suitable for creosote-contaminated soils. However, it should be noted that many creosote-contaminated sites are not intensively being remediated. This means that bioremediation is one of the processes that result in the slow decontamination of these sites. This is often termed ‘natural attenuation’, and because of the costs associated with other more proactive techniques, it is often employed.

2.5.2.2 Phytoremediation

Cunningham, Anderson, Schwab and Hsu (1996) and McCutcheon and Schnoor (2003) define phytoremediation as the in situ use of plants and their associated micro organisms to degrade, contain or render harmless contaminants in soil or groundwater or any other contaminated media. It can use higher plants to degrade contaminants, to fix them in the ground, to accumulate them in a harvestable biomass, or to release them to the atmosphere through transpiration. Phytoremediation has been used to treat sites contaminated with a variety of contaminants including heavy metals, solvents, PAHs, PCBs, hydrocarbons, radionuclides, explosives, and pesticides Studies have confirmed that certain plant species can take up chlorinated solvents from the groundwater in the root zone (Chappel, 1997; Schnoor, 1997). Once plant takes up the solvent, it can store the chemical in its body via covalent bonding with plant lignin (Schnoor, 1997). The plant may metabolise the chemical to other compounds. Research has also indicated that the growth of plant roots can stimulate degradation of TCE by micro organisms in the root zone via reductive dechlorination (Chappell, 1997). The plants exude substances through their roots that can stimulate the growth of microbes required to carry out these reactions. However, this is a time-consuming technique and it is in the early stages of development.

The main advantages of phytoremediation is that it is a low-cost technique because it is solar driven and eliminates the need for excavation and ex situ treatment (see Appendix 1). This type of treatment does not generate secondary waste. The limitations of the technique are that it is applicable above the water table and in very shallow groundwater, and it is a very time-consuming technique. Phytoremediation for the treatment of dissolved chlorinated solvents is in a very early stage of development.

2.5.2.3 Electrokinetic remediation

Electrokinetic remediation has traditionally been used to remove metals and organic compounds from soils, sludges, and sediments. According to McIntyre and Lewis (1997), this method has been a subject of research and is now in an advanced stage. It is used in contaminated soils on a large scale. Electrokinetic remediation methods use electrodes with a low-level direct current electric field (usually <10 V/cm or mA/cm2) installed into the contaminated soil. The current mobilises and transports charged chemicals in the soil’s liquid phase towards the electrodes. Negatively charged anions and organic compounds will move to the anode, whereas positively charged chemicals, such as metals, will move towards the cathode.

2.5.3 Chemical processes

Chemical processes in soil treatment systems are used to destroy, fix or neutralise hazardous compounds. Many processes in other categories may use chemical processes for the treatment of effluents and gaseous emissions.

2.5.3.1 Stabilisation/solidification

Stabilisation/solidification processes involve solidifying contaminated materials, converting contaminants into less mobile chemical forms and/or binding them within an insoluble matrix presenting a minimal surface area to leaching agents. It is when the process results in chemical fixation of contaminating substances that the term ‘stabilisation’ can be applied. Thermal processes use heat to remove or destroy contaminants by incineration, gasification, desorption, volatilisation, pyrolysis or some combination or these.

2.5.3.2 Hydraulic measures and natural attenuation

Hydraulic measures entail the control of the groundwater regime so that a contamination source or contaminated groundwater is separated, isolated, treated or contained. Natural attenuation is the effective reduction of contaminant toxicity, mobility or volume by natural processes.

In this study phytoremediation will be recommended as a means for the remediation of the PAHs-contaminated soil. The literature has indicated that it is an effective method for the cleanup of polycyclic hydrocarbons from contaminated soils. Successful trials have involved a variety of plants such as legumes and grass. See Appendix 2 for a list of plants and micro organisms that can be used for rehabilitating contaminated areas.

In fact, legumes have been found to grow naturally in contaminated sites. Plants and micro organisms participate both indirectly and directly in the remediation of the contaminated soils through three main mechanisms, namely degradation, containment and transfer of contaminants from the soil to the atmosphere (Cunningham *et al*., 1996).

Plants and micro organisms accomplish degradation either independently or through joint interaction, such as in the rhizosphere effect. Plants supply root exudes (sugars, alcohols and acids) for microbial use, realising root-associated enzymes that degrade contaminants in the soil and altering the soil to promote phytoremediation (Cunningham *et al*., 1996; Sims & Overcash, 1983).

The literature regarding containment and transfer of contaminants focuses on the direct role of plants. According to April *et al*. (1990), plants prevent the spread of petroleum hydrocarbons in soil by taking them from the soil and absorb them onto their roots or keeping them near their root zone via water uptake. Plants are also capable of transferring volatile petroleum hydrocarbons, for instance naphthalene, from the soil to the atmosphere via transpiration. Although this mechanism removes the contaminants from the soil, it simply moves them into the atmosphere, which can serve as an alternative source of exposure. Thus health risks associated with the contaminant may still arise.

Research has, however, suggested that certain petroleum hydrocarbons are easier to phytoremediate than others. The one- to three-ring PAHs are easier to remediate than the four- to five-ring PAHS.

2.6 Methods survey

According to Lundstedt *et al*. (2003), the procedure for the analysis of PAHs in soils follows the following steps: pretreatment, extraction, clean-up and instrumental analysis.

2.6.1 Sample pretreatment

Sample pretreatment is performed to increase the homogeneity of the soil and to increase the extractability of the analytes in the soil. It includes sieving, air-drying and grinding. According to Wischmann, Steinhart, Hupe & Montreson (1996), soil is acidified in some studies prior to extraction to improve the extractability of acidic transformation products. Samples are air-dried to facilitate grinding and to increase contact between soil and the organic solvent for extraction. However, drying at elevated temperature needs to be avoided since it may result in losses of volatile analytes such as naphthalene. After drying, the samples are ground to further increase the homogeneity of the sample and to increase the extractability of the analytes by increasing the exposed surface area in the soil.

2.6.2 Extraction

Extraction is performed to release contaminants from the solid matrix and to transfer them quantitatively to another medium, which is usually an organic solvent. The PAH samples are collected, after being extracted with appropriate solvents, and the solvent volume reduced prior to instrumental analysis. Methods used for the extraction of contaminants from analytes include Soxhlet, ultrasonic extraction, supercritical fluid extraction pressurised liquid extraction (PLE), and microwave-assisted extraction (MAE), a solid-fluid fluidising series extraction procedure, and recently solid-phase micro-extraction (SPME).

According to Guerin (1999), PAHs are traditionally extracted from various matrices by Soxhlet extraction. The Soxhlet method is a very efficient method for extracting PAHs and it is the preferred procedure in the US EPA method TO-13/A and the ISO standard method 12884 for PAH determination. It is the oldest and mostly widely used approach for conventional extraction of solid samples. The main advantage of Soxhlet extraction is that the sample phase is always in contact with fresh solvent and due to moderate extraction conditions, compounds are not decomposed. In a comparative study of the Soxhlet extraction and sonication method carried out by Guerin (1999) it was observed that the Soxhlet extraction method recovered 95% of the PAHs. However, the Soxhlet extraction method requires extremely long extraction times, which is a disadvantage. It also involves the use of environmentally hazardous solvents. In recent years, the classic Soxhlet extraction of PAHs from solid matrices such as soils and sediments has been replaced by faster, less solvent-consuming and often-automated techniques, which include one or more extraction cycles.

Portugal, Disdier, Arfi, Pastor and Pauli (1999) also point out that the Soxhlet extraction method requires extremely long extraction times (8 hours) and involves the use of environmentally hazardous solvents, imposes a high cost of analysis. However in most recent years, instrumental techniques have been developed which save both time and the solvent. Representative examples of these new extraction techniques are ultrasonic extraction supercritical fluid extraction pressurised liquid extraction (PLE), and microwave-assisted extraction (MAE), and recently, a solid-fluid fluidising series extraction procedure, which provides for a relative simple and cost-effective alternative.

Lee, Zou, Ho and Chan (2001) state that ultrasonic extraction has been used instead of Soxhlet extraction. It uses water as agitation energy and total recovery can be reached within a short time (45 – 50min.). It also extracts non-polar compounds in a short time. However, it has certain limitations.

According to Manoli and Samara (1999), conventional techniques such as liquid-liquid extraction (LLE) or solid phase extraction (SPE) have been used for the determination of PAHs in liquid samples matrices. Compared to SPE, LLE is time-consuming and requires more solvents. Thus LLE has been replaced by SPE, using a variety of sorbents.

Supercritical fluid extraction (SFE) is being used as a rapid alternative to conventional solvent extraction from polyurethane foam absorbents (Hawthorne, Galy, Schmidt & Miller, 1995). It has been in the market for 20 years and was amongst the first instrumental techniques. According to Portugal *et al.*, (1999), SFE reduces extraction time (less than 90 min.) and optimises recovery. The high diffusivity and low density/viscosity of supercritical fluids allows them to penetrate a sample matrix rapidly and to effect a more rapid extraction of the PAHs. Supercritical carbon dioxide has been used for the extraction of PAHs in urban dust samples (Langenfeld, Hawthorne & Miller 1996; Janda, Bartle & Clifford, 1993) and diesel exhaust particulates. Extraction time is about 90 minutes and little waste is produced. The use of a 10% methanol modifier increases PAH recoveries considerably. This method is environmentally friendly.

Supercritical fluid extraction (SFE) was initially introduced as a complement to, or even substitute for, conventional extraction techniques like Soxhlet and liquid-liquid extraction (LLE). The use of SFE and other recently introduced extraction techniques has been described by several authors (Janda *et al.*, 1993; Hawthorne *et al.*, 1995; Neilson, 1998), and some of its limitations have been discussed in a critical review by Smith (1999). SFE is more rapid and selective than the conventional techniques, and was therefore used to extract Swedish adipose tissue samples. It was concluded that SFE is a very good choice for samples where the analyte-matrix interactions are minor.

The other method is microwave-assisted extraction (MAE), where the solvent and sample are subjected to radiation. Unlike SFE, where samples are extracted sequentially, MAE allows up to 14 samples to be extracted simultaneously. The major limitation of this method is that the solvent has to be physically removed from the sample matrix upon completion of extraction before analysis (Janda *et al*., 1993, Hawthorne *et al*., 1995; Neilson, 1998).

SPE and solid-phase disk extraction (SPDE) are other extraction methods that have gained popularity for the environmental analysis of organic contaminants and it has an important role to play in the modern analytical laboratory since it is both an extraction and a clean-up technique. Other advantages are that it minimises sample handling and gives high concentration factors, tunable selectivity (choice of adsorbent), and increased precision. SPE has a number of advantages, which have made it famous and has allowed it to compete with procedures such as liquid-liquid extraction. These advantages include a reduction in the total organic solvent used in the extraction. SPE also provides cleaner extracts with minimum amounts of contaminants and impurities and the recoveries are normally high and reproducible with no emulsions (Bergknut, 2006).

According to Dean and Xiong (2000), another extraction method that is used is pressurised fluid extraction (PFE), which has been available in the market as accelerated solvent extraction (ASE) since 1995. An organic solvent is used together with heat and pressure to extract analyte from the matrix. It is automated and can extract 24 samples in 12 minutes. However, it has its limitations. ASE was evaluated as a possible rapid, low-solvent replacement for Soxhlet and bath sonication/shaking extraction in established soil-screening methods. ASE recoveries were equivalent or superior to bath sonication/shaking, with ASE giving approximately double the total PAHs content for matrices containing small stones and/or coal. ASE would be a suitable replacement for existing extraction methods; however, more work is required to reduce background interference. In a study by Wilke, Sung and Jung (2002), three extraction methods Soxhlet, ultrasonic and shaking, were also compared. Recovery rates were determined in two soils. The study showed that the number of aromatic rings, rather than extraction procedures, significantly influenced the recovery rates of individual samples. The extraction efficiency decreased in the following order: shaking, ultrasonic and Soxhlet.

More recently, one technique that is being used increasingly in the isolation and extraction of environmental contaminants is solid phase microextraction (SPME). SPME is a solvent-free extraction technique that has been used by various researchers for a variety of environmental applications. It has been used principally for the study of PAHs in water samples of different origins (Langenfeld *et al*., 1996; Doong, Chang & Sun, 2000a) and in soils (Liu, Hopke, Han, Yi, Holsen, Cybart, Kozlowski & Milligan, 2003; Doong *et al*., 2000b; Seduikiene, Vickackaite & Kazlauskas, 2000), sediments Cam, Gagni, Meldolesi & Galletti, 2000) and air particulate matter. The technique used in many cases is direct immersion of the fibre in the samples, but it can also be applied to the headspace (Djozan & Assadi, 1999; Doong *et al*., 2000b; Waidyanatha, Zheng & Rappaport, 2003), so that liquid and solid samples can be analysed. The main advantage of this method is its simplicity: besides the SPME only a standard GCMS instrument is required. It is based on sorption (partitioning of the analytes present in the sample) into a layer of stationary phase coated on to a syringe-like device.

The SPME method is suitable to determine substances directly without pretreatment of samples, and especially when analysing and screening volatile substances in complex matrices such as soil samples (Górecki, Boyd-Boland, Zhang & Pawliszyn, 1995). It has other advantages over other water-extraction techniques such as solid phase extraction or liquid-liquid extraction. It is fast and does not require any organic solvents, which is clearly of environmental benefit. Many of the more traditional extraction techniques involve multi-step procedures that always present the risk of analyte loss, while SPME achieves contaminant extraction and concentration in a single step, thus reducing this risk. The technique is also relatively inexpensive with a single fibre being capable of performing between 50 and 100 extractions. In 2001, Erikson, Dalhammar and Borg-Karlson conducted a study whereby solid-phase micro-extraction was used to screen and determine volatile and non-polar substances in a PAH-contaminated site in Stockholm Sweden. When compared to liquid extraction, the detection limits can be increased by using larger samples (gives a higher total mass of each compound in the samples) but still using the same fibre.

Aqueous samples can be studied directly by immersing the fibres in the solution, while particulate as well as aqueous samples can be extracted by exposing fibres to the headspace above the samples. Finally, the technique can be used for in situ extraction of environmental samples, hence minimising the disturbance of sample matrices. In a study by King, Readman & Zhou, (2004), the method showed good linearity up to 10 microgram per litre. The reproducibility of the measurements expressed as relative standard deviation (RSD) was generally less than 20%. Due to the advantages and performance of the SPME, this method was selected for use in this study.

2.6.3 Clean-up

Clean-up is performed to co-extract compounds that could interfere during subsequent analysis and separate different classes of analytes prior to analysis. The clean-up of samples can be performed by adsorption chromatography using open-column chromatography, solid-extraction phase (SPE) or high performance liquid chromatography (Zdrahal, Karasek, Lojkova, Buckova, Vecera & Vejrosta, 2000; Bodzek, Janoszka, Dobosz, Warzecha & Bodzek, 1997). The high performance liquid chromatography (HPLC) techniques have the greatest resolution and reprocibility and may be coupled to a wide range of detectors for analyte detection. However, the other instruments are simpler to use, less costly and have higher sample capacity than HPLC and are therefore used in environmental analysis (Hale & Anerio, 1997).

2.6.4 Instrumental analysis

Instrumental analysis is performed to separate, identify and quantify the individual analytes in the sample. Instrumental methods for the analysis of PAHs in environmental samples vary depending on the sample type and purpose of the analysis. Mayer, Vaes, Wijnker, Legierse, Kraaij, Tolls and Hermens (2004) found that the choice of which method to use for analysis depends on the advantages and disadvantages of each, based on their sensitivity and specificity.

According to US EPA (1995), other methods such as photo-ionisation detectors (PIDS) can be used to screen for PAHs in soil samples. The PIDS use an ultraviolet lamp to ionise organic vapours. They are sensitive to aromatic hydrocarbons. They have various limitations, such as that they are affected by humidity and electric currents. According to Lundstedt *et al*., (2003), PAHs can be analysed by flame ionisation detection, or by HPLC with UV or florescence detection. Bestari *et al*. (1998) point out that HPLC is sensitive to PAHs, but that identification of individual PAHs by comparison to retention time is less accurate with GC. Thus, for a more thorough characterisation of the contaminants present in soil, higher resolution and sensitivity are needed. GC fulfils these requirements and facilitates the identification and quantification of a large number of compounds in soil.

According to Fernandez, Vilanova and Grimalt (1999), GC has become more popular due to its high selectivity, good precision and resolution. Recently, the mass spectrophotometer has become more important for the analysis of environmental samples. According to Marcè and Borrull (2000), GCMS is a good technique, which requires the use of surrogate standards to quantify and clean up both solid and liquid samples after extraction. It allows for the detection of small quantities of PAHs in groundwater and air. According to Ikarishi *et al*., Kaniwa and Tsuchiya (2005), PAHs are recovered at high yield 97 – 133% using gas chromatography. GC/MS is one of the most powerful techniques available for environmental analysis. Every compound has a specific mass spectrum.

Compounds are identified by comparing the spectra with mass spectral databases. For the purposes of this study, GC/MS coupled with solid phase micro extraction have been selected as the best instrument for the analysis and extraction of PAHs in the soil and water samples from the creosote treatment plant and storage facility. This has been based on the properties and advantages of GC/MS and SPME over other techniques.

The next chapter (Chapter 3) gives a detailed explanation of the preferred methodology from the literature, which was used to accomplish the objectives of the study.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter presents the methodology and experimental procedures used in the study. It also describes the sampling procedure as well as the data-collection procedure. The experimental research method was used in this study and a qualitative approach was used for the collection of data. Soil and water samples were collected for polycyclic aromatic hydrocarbon analysis. The methodology for the determination of polycyclic aromatic hydrocarbons (PAHs) in environmental samples involved a preliminary survey to identify sampling sites. This was followed by a three-step procedure: sampling, extraction by solid phase micro extraction (SPME) and analysis by gas chromatography (GC/MS). The steps are described in the next sections.

3.2 Preliminary survey

In order to identify the study sites and assess the content of PAHs, a preliminary survey was done. The photo ionisation technique was used to select the study site between Matsapha Central Stores (creosote wood storage facility) and the Thonkwane creosote treatment plant. Soil and water samples were placed in an airtight container (Consol bottle), leaving one half to one third empty. The container was shaken and left to sit for 20 minutes to partition into the headspace (the air space above the sample). The PAHs were measured using the photo ionisation detector. Since no PAHs were detected in the Matsapha site, the Thonkwane creosote treatment plant was selected as the study site.

3.3 Sampling

Two sites were used for the collection of soil samples: the Matsapha Central Stores pole storage sites and the Thonkwane creosote wood treatment plant. At least 1 kg of soil was collected from each site.

3.3.1 Matsapha site

The study involved the collection of soil samples from the storage site, and water samples from the drain and the Lusushwana River. Sediment was also collected from the river and the effluent drains discharging into the river. A raft and a 10cm hard ground steel auger were used for sampling with polyethylene bags.

The soil samples were collected from Platform 1 of the study sites and nine sampling points were identified where treated wooden poles are stored. Two control points were selected out of the pole storage site. In Platform 2 of the study site, two soil samples were collected below transformers and from a drain discharging effluent from Platform 1. Other soil samples were collected in a drain below the Matsapha Central Stores storage site.

The soil samples were collected at depths of 15 cm and 60 cm. Three samples were collected at each sampling point 3 m apart to get a composite sample.

Water and sediment samples were collected in the drains where the storage site discharges effluent and at a point where the effluent is discharged into the river. One sample was collected upstream to act as control point and one downstream of the industrial site. Three other water and sediment samples were taken at 1900 m intervals. One was taken below sewer ponds and one above the SEB reservoir. These samples were discarded after the preliminary survey.

3.3.2 Thonkwane creosote wood treatment plant

The creosote wood treatment facility was selected as the study site for this project. The samples in the site were collected in the following areas (see Figure 3.1 and Plate 3):

A. Next to the effluent pond.
B. Next to a trench below that drains effluent to the veld
C. On a sloppy site where the effluent drains from a tank
D. In a donga with pine trees where effluent drains
E. Above a road that acts as a buffer or blocker of effluent
F. Control point.

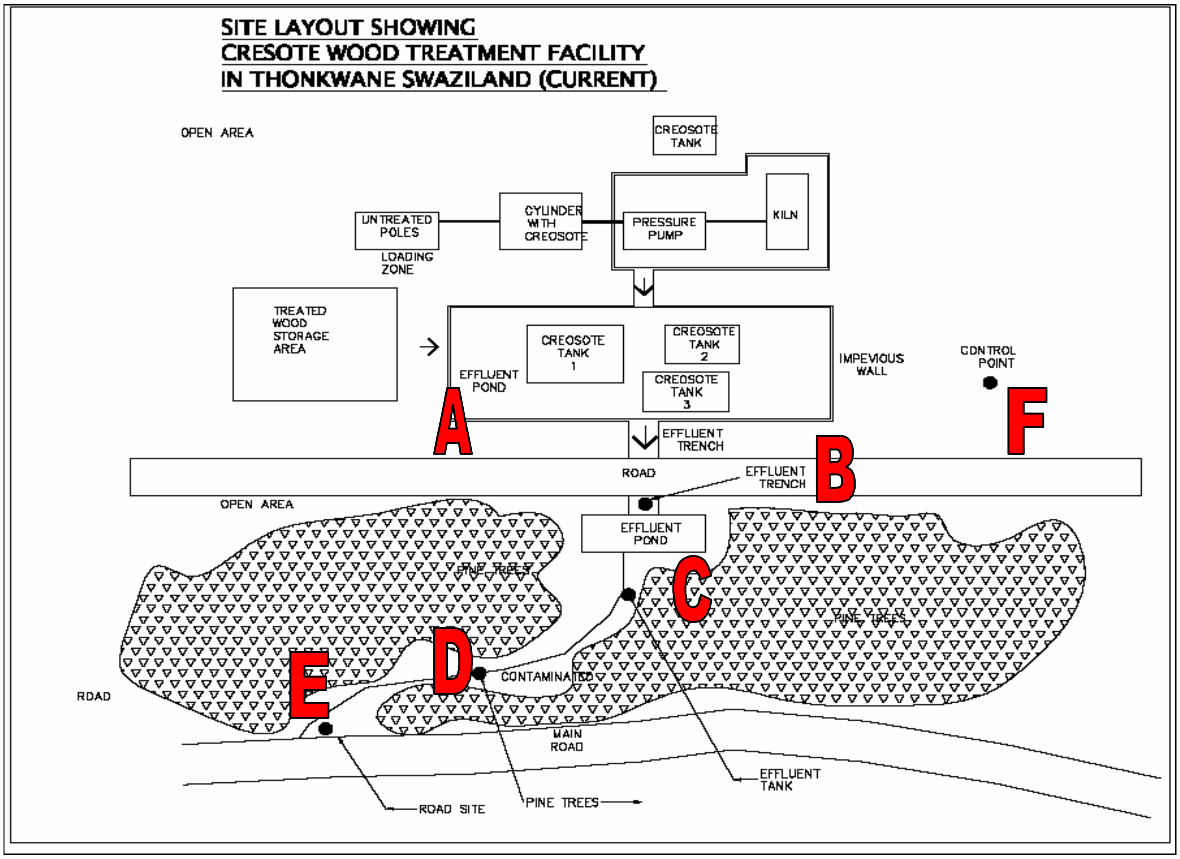


Figure 3.1 Sampling points at the Thonkwane wood treatment facility

Plate 3: Photos showing sampling sites at Thonkwane

a) Sampling point next to creosote tank

b) Sampling point below cylinder

c) Sampling point below effluent pond

d) Sampling point at effluent trench

e) Sampling point below effluent tank

f) Sampling point below pine logs and the road.

Three samples were taken in each site at intervals of 1 m and a homogenised composite sample was obtained from these. The soil samples were taken at depths 15 cm and 60 cm.

The soil samples were collected and collected in clean wide-necked Consol bottles and plastic bags. They were stored in coolers for transport to the Protechnik Laboratory in Pretoria.

3.4 Laboratory

Due to financial and time constrains EPA methods for PAH extraction from soil samples was not used. Thus this study used the Protechnik Laboratory, which adopted the NIOSH 5515 method (see Appendix 3). This method uses extraction by SPME and analysis by gas chromatography (GC/MS). The methods are described below.

3.4.1 Sample extraction using SPME

The SPME device and polydimethylsiloxane fibres (100 μm film thickness) were purchased from Supelco. Fibres were conditioned in the injection port of a gas chromatography (GC) instrument for one hour before use according to the manufacturer's instructions. Blank desorptions of the fibre were carried out to ensure that no contamination would be present both before and during use.

A total of 19 priority PAHs, including the seven B2-PAHs (probable human carcinogens) US EPA (1995), were measured in the soil samples. The 19 target PAHs included: naphthalene, 2-ethylnaphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene, fluorene, dibenzofuran, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, and dibenzo[ah]anthracene. The reference standard used was supplied by Chem Service at concentration 2000 µg/ml in CH2Cl2. The solvent was benzene at ratio (50:50), Lot 340-97A.

A soil sample of 10 g was accurately weighed into a crimp cap vial. The vial was sealed and placed on a hot plate (60 ºC). The SPME apparatus was inserted into the vial via the septa and the fibre exposed to the headspace above the soil sample for 30 minutes. The fibre was then retracted and the SPME assembly removed from the vial and placed in the inlet of an Agilent GC/MS system where the fibre was again exposed and the adsorbed components desorbed onto the GC column (Stack, Fitzgerald, O'Connell, & James, 2000).

3.5 Analyses

The sample extracts and standard solutions were analysed by a 70 eV electron impact (EI) GC – MS. An Agilent 5973 Mass Selective Detector coupled to an Agilent 6890 Network GC system was used for the analyses. Data acquisition and processing were performed with a ChemStation data system. The GC column (J+W Scientific, Folsom, CA, USA) was a DB-5MS fused silica capillary (30 m, 0.25 mm ID, 0.25 µm film thickness). Helium was used as the GC carrier gas. The carrier gas helium was maintained at a constant pressure of 60KPa. The injector port temperature was set to 250 ºC. Fibre desorption took place in split less mode with the splitter activated after seven minutes to purge the fibres of any residual compounds so as to eliminate the risk of carryover of compounds between extractions. Following injection, the GC column was held at 40 ºC for two minutes and was temperature programmed to 280 ºC at 10 ºC/minute and held at 280 ºC for 25 minutes. Peaks monitored were the molecular ion peaks and associated characteristic fragment ion peaks. Identification of the target analytes was based on GC retention times relative to a reference standard and the relative abundance of the monitored ions. Quantification was performed by comparing the response of the integrated ion current of the target ions to those of the reference standard using average response factors of the target analytes generated from standard.

In conclusion, the methodology section of the study covered aspects on how the data required in the study was collected. The sources of primary data were identified, and the qualitative techniques and approaches of collecting the data were discussed in terms of how the researcher used them in the field. The methodology was crucial to the study in the sense that it led to a logical extraction of data required in the study, in a manner appropriate for the nature of the study. The methodology, therefore, resulted in the collection of mostly qualitative data, as the nature of the study is qualitative. The data collected is presented and analysed in the next chapter (Chapter 4). Discussion and conclusions are provided in Chapter 5.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents and analyses the results obtained from the samples taken from Matsapha CSO and Thonkwane wood treatment facility. The results of calibration and standards are presented. PAHs were not detected in the Matsapha site and thus no results are presented for this site.

4.2 Calibration and chromatograms

The soil samples were analysed using Solid phase Micro extraction and Gas Chromatography. The compounds analysed in the soil samples from the study area includes the following, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo(a)pyrene, indeno(1.2.3-cd)pyrene, 1.2:5.6-dibenzanthracene and 1.12-benzoperylene. These compounds are listed as the 16 priority pollutants by EPA.

Calibration curves were prepared for each of the PAH compounds for concentration ranges between 0.05 ppm to 20 ppm. An example of a calibration curve is presented in Figure 4.1 where the peak area is plotted against standard concentration.

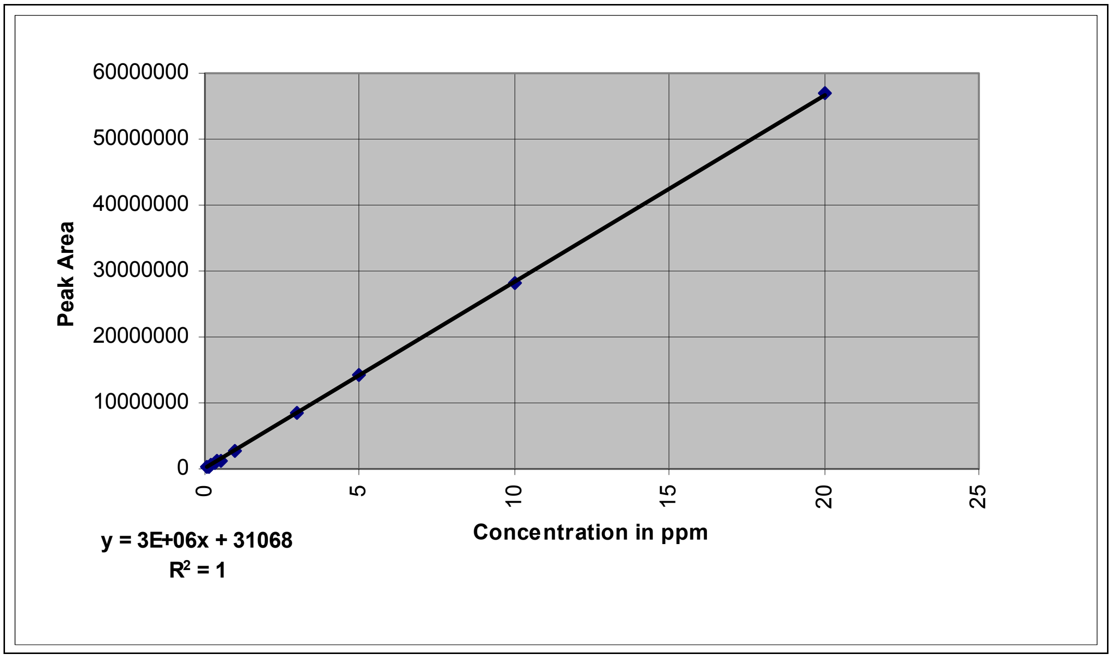


Figure 4.1 An example of a calibration curve prepared for naphthalene

Linear calibration graphs were obtained for all sample concentration ranges that were determined. The correlation coefficient ranged from 0.7931 to 1 where the average correlation coefficient is 0.921. The curves were used to determine each PAH compound found in the samples.

The chromatogram indicated in Figure 4.2 shows a 10 ppm standard used for the calibration of the GC/MS. Figure 4.3 shows a chromatogram with results from sample H1. It indicates that PAHs were detected in the sample at various retention times (refer to Table 4.1).

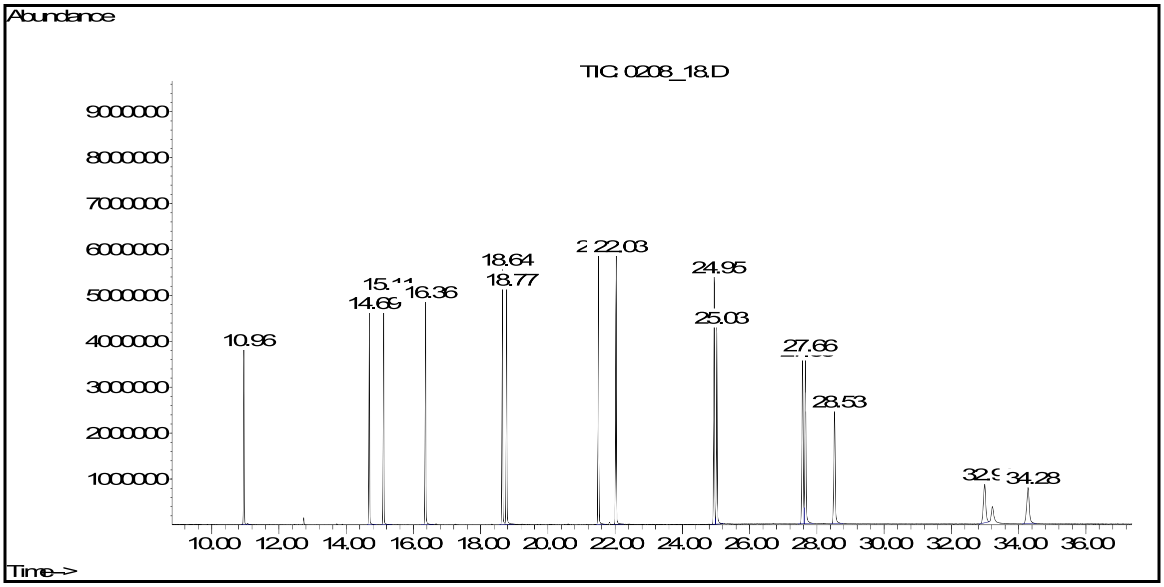


Figure 4.2 Chromatogram for reference standard with 10 ppm

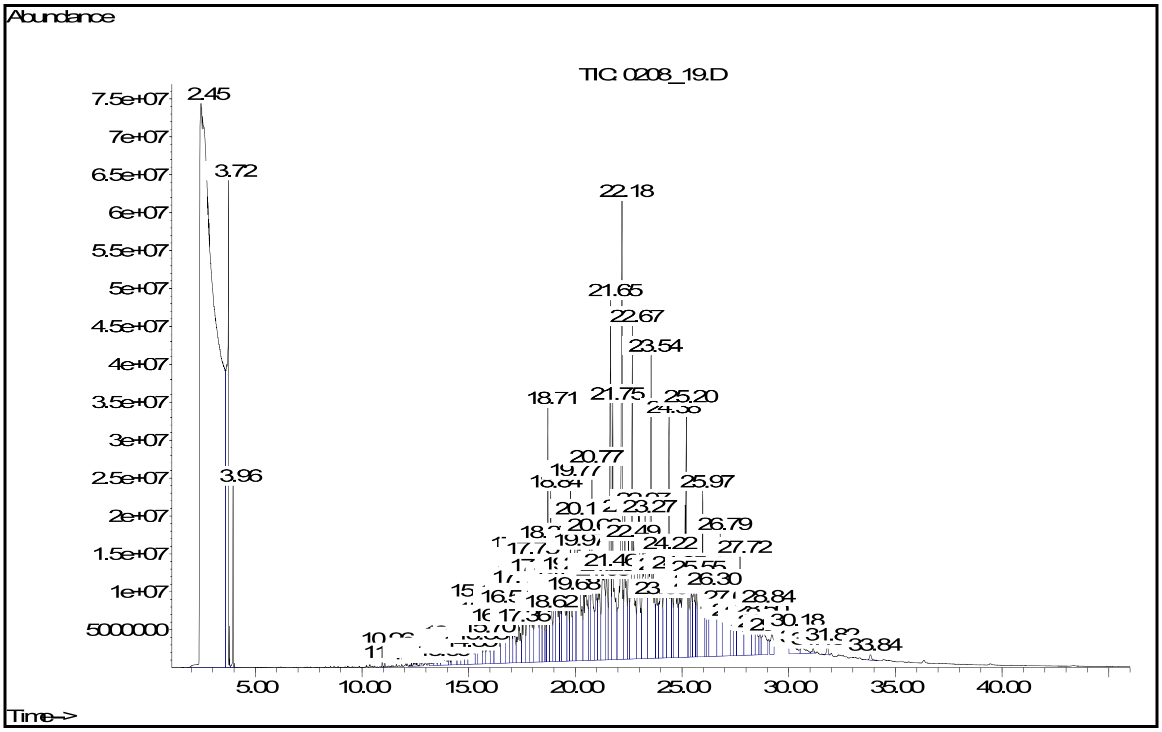


Figure 4.3 Chromatogram showing concentration of various PAHs in sample H1

Table 4.1 Retention times of various PAHs

COMPOUND	Retention Time	COMPOUND	Retention Time
Naphthalene	10.96	Benzo[a]anthracene	24.95
Acenaphthylene	14.69	Chrysene	25.03
Acenaphthene	15.11	Benzo[b]fluoranthene	27.58
Fluorene	16.36	Benzo[k]fluoranthene	27.66
Phenanthrene	18.65	Benzo(a)pyrene	28.53
Anthracene	18.77	Indeno(1.2.3-cd)pyrene	34.28
Fluoranthene	21.51	1.2:5.6-Dibenzanthracene	32.99
Pyrene	22.03	1.12-Benzoperylene	33.22

4.2.1 Method detection limit

The term ‘detection limit’ refers to the smallest amount that can be detected above the noise procedure and within a stated confidence limit. Table 4.2 shows the detection limits for the PAHs in the study. The method detection in this study ranged from 0.12 μg/g to 20.08 μg/g. Any samples with values less than the detection limit were recorded as below detection limit.

Table 4.2 Detection limits for 16 PAHs

COMPOUND	LOD µg/g	COMPOUND	LOD µg/g
Naphthalene	0.18	Benzo(a)anthracene	20.08
Acenaphthylene	1.52	Chrysene	1.16
Acenaphthene	0.12	Benzo(b) fluoranthene	0.94
Fluorene	0.14	Benzo(k) fluoranthene	0.90
Phenanthrene	0.22	Benzo(a)pyrene	7.12
Anthracene	0.20	Indeno1,2,3-cd)pyrene	2.52
Fluoranthene	0.30	1,2,5,6-Dibenzoanthracene	2.56
Pyrene	0.30	1.12 benzoperylene	2.87

LOD - Limit of detection

4.2.2 Instrument performance

The performance of a GC/MS is obtained from the number of theoretical plates usually 4 0000 theoretical plate and the height of the theoretical plates and this is achieved by using the Van Deemter equation.

According to Van Deemter, Zuiderweg and Klinkenberg (1956), this equation in chromatography relates the variance per unit length of a separation column to the linear mobile phase velocity by considering physical, kinetic, and thermodynamic properties of a separation. The variance per unit length of the column is taken as the ratio of the column length to the column efficiency in theoretical plates. The Van Deemter equation is a hyperbolic function that predicts that there is an optimum velocity at which there will be the minimum variance per unit column length and, thence, a maximum efficiency.

The number of theoretical plates is given as:

$$N = L/H$$

Where : N - No. of theoretical plates or plate count
L - Length of the column (which we have from instrument settings)
H - Plate height.

The column used in the GC/MS had 128 400 theoretical plates. This is far above the recommended number of theoretical plates, which is 40 000. The height of the theoretical plate was calculated to be 0.023 and is also close to the ideal figure of 0.

4.3 Sample concentrations

This section outlines and discusses the sample concentrations obtained from the preliminary survey where the study site was selected and the results obtained from the soil samples taken in the study site.

4.3.1 Preliminary survey results

PAHs were analysed in two sites, namely Matsapha CSO (wood storage facility) and Thonkwane (creosote wood treatment facility). Neither the photo ionisation detector nor the laboratory analysis identified any PAHs in the Matsapha CSO site soils. Similarly, none were identified in the sediments and water samples from the Lusushwana River. Therefore no further investigations were made in the Matsapha CSO site. PAHs were detected in the Thonkwane wood creosote sites and thus this site was further analysed for PAH contamination.

The results obtained from the Thonkwane site are shown in Table 4.2 and Figure 4.4. The PAHs were detected in three randomly selected sites, namely pure creosote (creosote), contaminated soil below creosote tank (tank site) and a waste disposal site at the Thonkwane creosote wood treatment facility. These were naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. The concentration of the detected PAHs ranged from 0.0001 mg/kg to 0.0793 mg/kg. The dominant PAH compound in the three sites were acenaphthene, fluorene, phenanthrene and fluoranthene. This can be attributed to the fact that the above compounds are the predominant PAHs in creosote. Highest PAH levels were recorded for naphthalene. This can be attributed to the fact that when the percentage by weight of PAHs in creosote is compared, naphthalene is found to be amongst the highest.

Table 4.3 PAH concentration in creosote plant (soil)

SAMPLING SITES			
	Concentrations in mg/kg		
Compound	**Waste site**	**Tank site**	**Creosote**
Naphthalene	0.0166	B/D	0.0793
Acenaphthene	0.0350	0.001	0.0069
Fluorene	0.0039	0.0033	0.0060
Phenanthrene	0.0035	0.0025	0.0046
Anthracene	0.0037	B/D	0.0046
Fluoranthene	0.0002	0.0001	0.0004
Pyrene	0.0001	B/D	0.0002

B/D below detection limit

It can be seen from Figure 4.4 that the sample (pure creosote) contained most of the PAH compounds and that these were also in high concentrations. The compounds detected in the creosote are generally those found in creosote.

The waste site had many PAHs at high levels when compared to the tank site. This can be attributed to soil type and the organic matter present in the study sites. The creosote tank site (tank site) is made up of clay soil without organic matter whilst the waste site has loamy soils with organic matter. According to Manahan (2000), soil type determines the mobility of PAHs. The levels of acenaphthalene and naphthalene from the three sampling sites were more than the recommended EPA limit, which is 0.01 mg/kg.

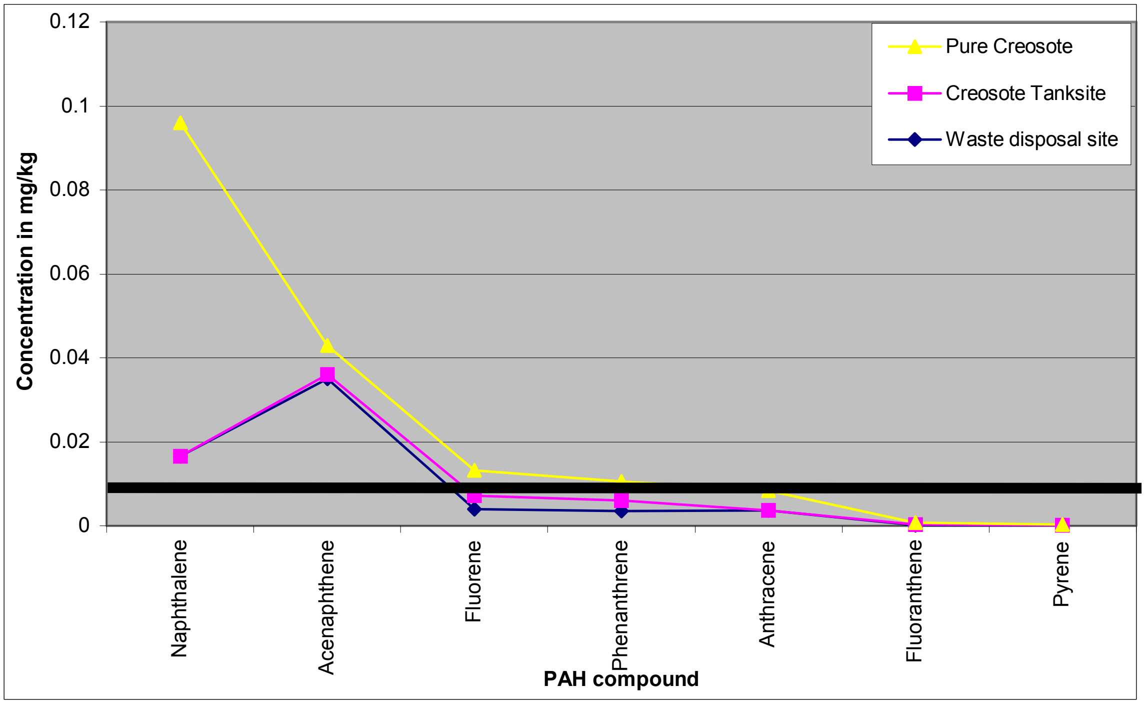


Figure 4.4 PAH levels from various sampling sites at Thonkwane

4.3.2 Further investigation of PAHs at the Thonkwane creosote wood treatment facility

The results of the distribution of PAHs in the study area (Thonkwane creosote wood treatment facility) are presented in Table 4.4. A broad spectrum of the PAHs listed in the EPA priority pollutants list were detected from the soil samples even though some were at very low levels. The PAH concentration ranged from 0.01 to 0.29 mg/kg. No PAHs were detected in the control point.

There are some compounds which were not picked up in some of the sampling sites. For instance benzo[b]fluoranthene was picked up in only three sampling sites out of 11 sites.

Table 4.4 Concentration of PAHs from various sampling points (in mg/kg)

	EFFLUENT PONDS (A)		TRENCH (B)		EFFLUENT TANKS (C)		PINE LOGS (D)		ROAD (E)		CONTROL (F)	
COMPOUND	H0	H1	H2	H3	H4	H5	H6	H7	H8	H9	C1	C2
Naphthalene	0.05	0.01	n/d	n/d	0.07	n/d	n/d	n/d	0.14	n/d	n/d	n/d
Acenaphthene	0.01	0.02	0.01	n/d	0.06	0.02	0.04	n/d	n/d	n/d	n/d	n/d
Fluorene	0.03	0.01	0.04	n/d	0.01	0.06	0.01	0.01	0.29	n/d	n/d	n/d
Phenanthrene	0.03	n/d	0.06	n/d	n/d	0.05	0.01	0.01	0.02	n/d	0.02	n/d
Anthracene	0.01	n/d	0.06	n/d	0.20	0.02	0.20	0.01	0.03	n/d	0.03	n/d
Fluoranthene	0.01	0.03	0.05	n/d	0.06	0.02	0.01	0.01	0.03	n/d	0.04	n/d
Pyrene	0.01	0.01	0.06	n/d	n/d	0.02	n/d	0.01	0.01	n/d	0.02	n/d
Benzo[a]anthracene	n/d	n/d	0.01	n/d	n/d	n/d	0.02	n/d	0.01	n/d	0.01	n/d
Chrysene	n/d	n/d	0.01	n/d	0.01	0.01	0.02	n/d	0.11	n/d	n/d	n/d
Benzo[b]fluoranthene	n/d	n/d	0.01	n/d	0.01	n/d	n/d	n/d	n/d	n/d	0.01	n/d

- Units in mg/kg
- n/d= not detectable

H0	15 cm below effluent pond	H6	15 cm above pine logs
H1	60 cm below effluent pond	H7	60 cm above pine logs
H2	15 cm next to trench	H8	15 cm on the road
H3	60 cm next to trench	H9	60 cm on the road
H4	15 cm below effluent tank	c1	15 cm control
H5	60 cm below effluent tank	c2	60 cm control

The dominance of fluorene, anthracene, fluoranthene, phenanthrene and pyrene in almost all the samples is noted. There is an indication that the creosote treatment facility has some sites that are contaminated which have PAH levels of more than 0.01 mg/kg. The levels of PAHs detected in most of the sample areas were observed to be higher than the control point. This is an indication that the plant is adding contaminants to the surroundings where the effluent is discharged.

The trench, effluent tank, pine logs and road are contaminated with various PAHs. The road seems to be more contaminated than all the other sampling sites.

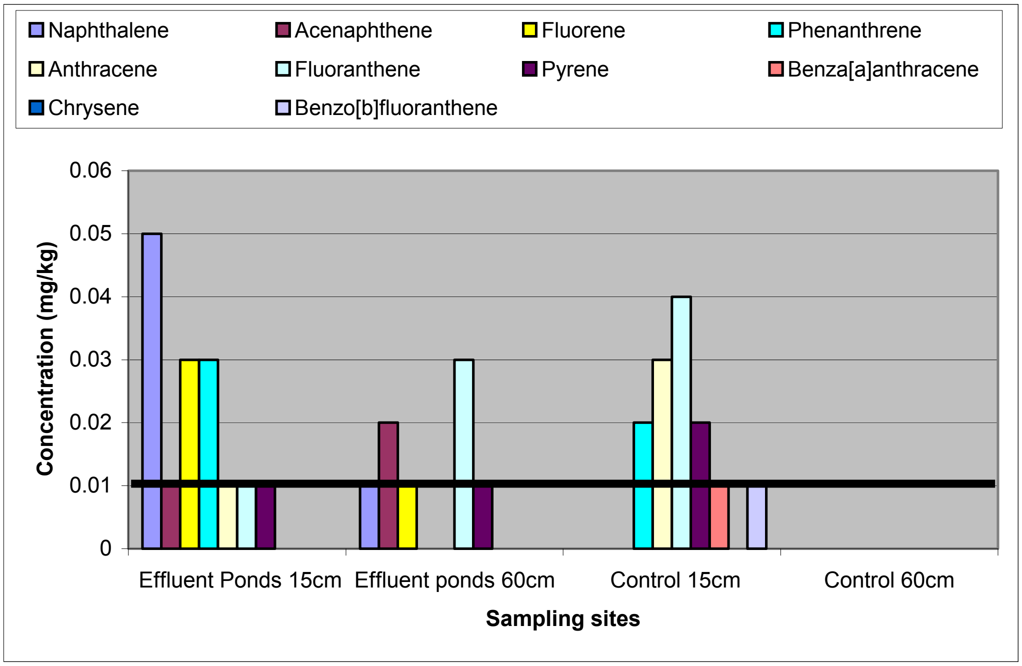


Figure 4.5 Graphical representation of PAHs next to effluent ponds (A)

Figure 4.5 presents the concentration of PAHs next to the effluent pond (A). The concentration of the two- to three-ring PAHs, naphthalene, fluorene, phenanthrene and anthracene is high in this site. The PAH compounds were also detected in the sample containing creosote from the preliminary survey. This is an indication that the effluent pond overfills and contaminates its surroundings with PAHs. The levels of the PAHs are above the recommended limit, as shown by the bold line. This is an indication that the site has been contaminated by PAHs and has to be cleaned up.

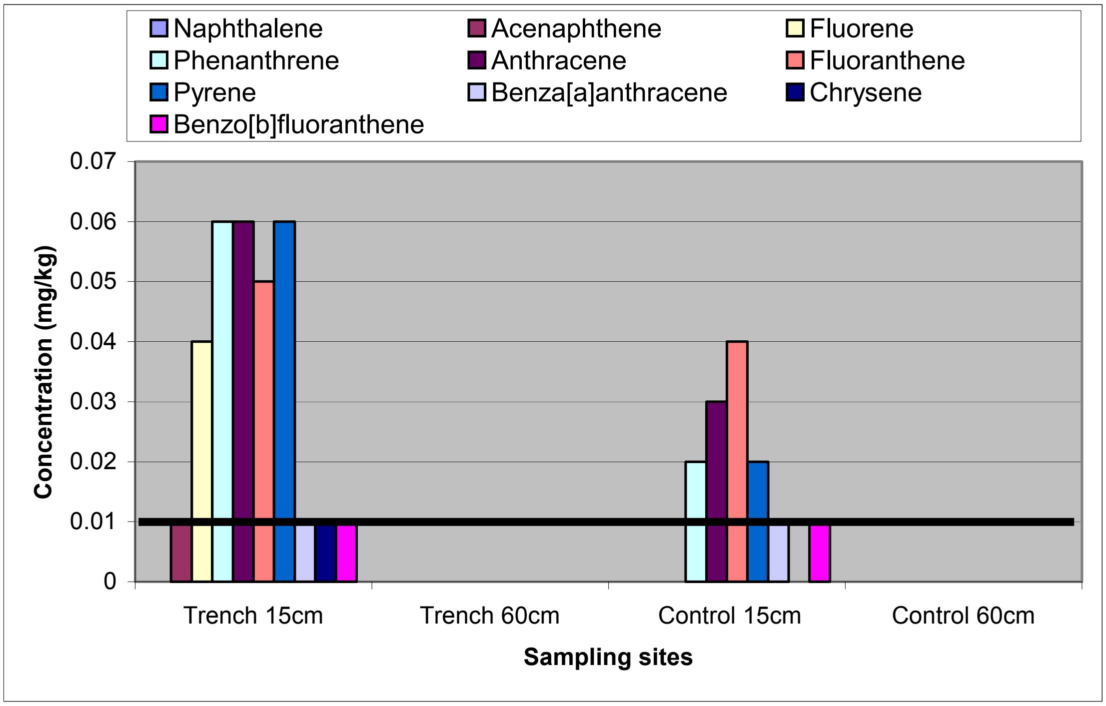


Figure 4.6. Graphical representation of PAHs detected below effluent trench (B)

PAHs were not detected at 60 cm depths. Most of the PAHs, which are dominant in creosote, were recorded at the 15 cm depth. The high levels of PAHs in the 15 cm layer can be attributed to the grass vegetation found in this layer. This is in agreement with the literature, which states that PAHs tend to bind with organic matter (Lundstedt, 2003).

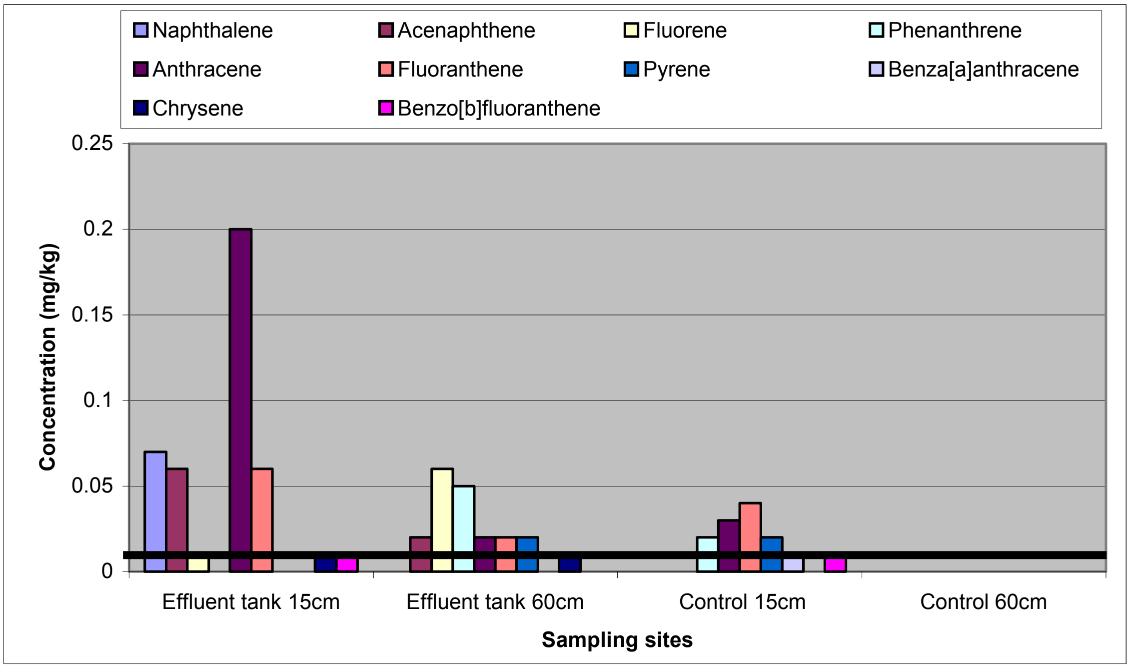


Figure 4.7 Graphical representation of PAHs detected below the effluent tank (C)

Figure 4.7 indicates that the PAH concentrations were higher in the top layer (15 cm) than the 60 cm layer. For instance, high levels of anthracene, acenaphthalene, fluorene and benzo[b]fluoranthene and fluoranthene were found. The bold line shows that some the PAHs, for instance fluorene, anthracene and naphthalene, are above the recommended US EPA limit. This implies that this site has been contaminated by PAHs. The pattern that some of the PAHs found in the 60 cm layer shows that some PAHs, for instance pyrene, are not found in the top 15 cm layer. This is an indication that the PAHs in the 60 cm layer originated from a different source. According to Wilke (2000), the source can be either anthropogenic or of biopedogenic origin or can be a result of both.

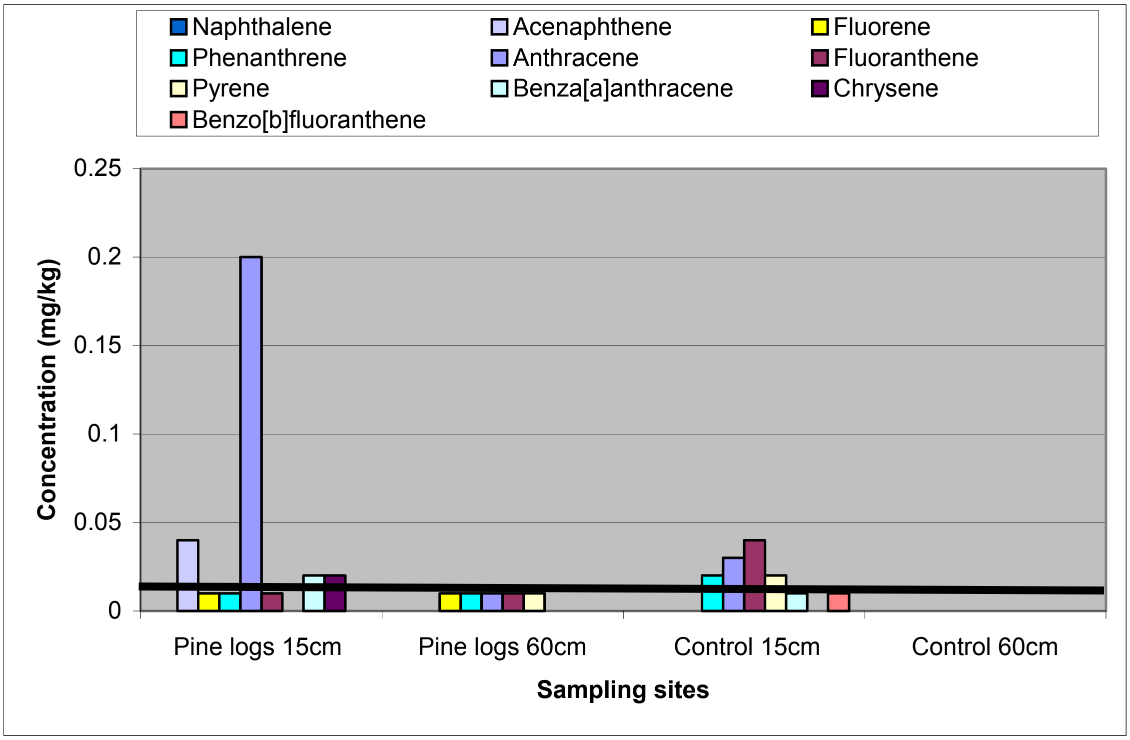


Figure 4.8 Graphical representation of PAHs detected on the pine logs (D)

Figure 4.8 shows that no PAHs were recorded in the control point. High levels of PAHs were observed in the 15 cm layer when compared to the 60 cm layer. The PAH levels of were quite low when compared to the other sites. This can be explained by the fact that the physical chemical properties of the PAHs, such as the octanol / water partitioning coefficient (Kow) and solubility suggest that these compounds are not easy to biodegrade in the environment. Generally, PAH compounds have very high Kow values within the family of organic compounds, indicating that they prefer to adsorb themselves onto biota (plant and animal fatty tissues) as opposed to the soil matrix. They also have correspondingly high bioaccumulation factors (BCF), which indicate the tendency of a compound to bioaccumulate and become part of the food chain.

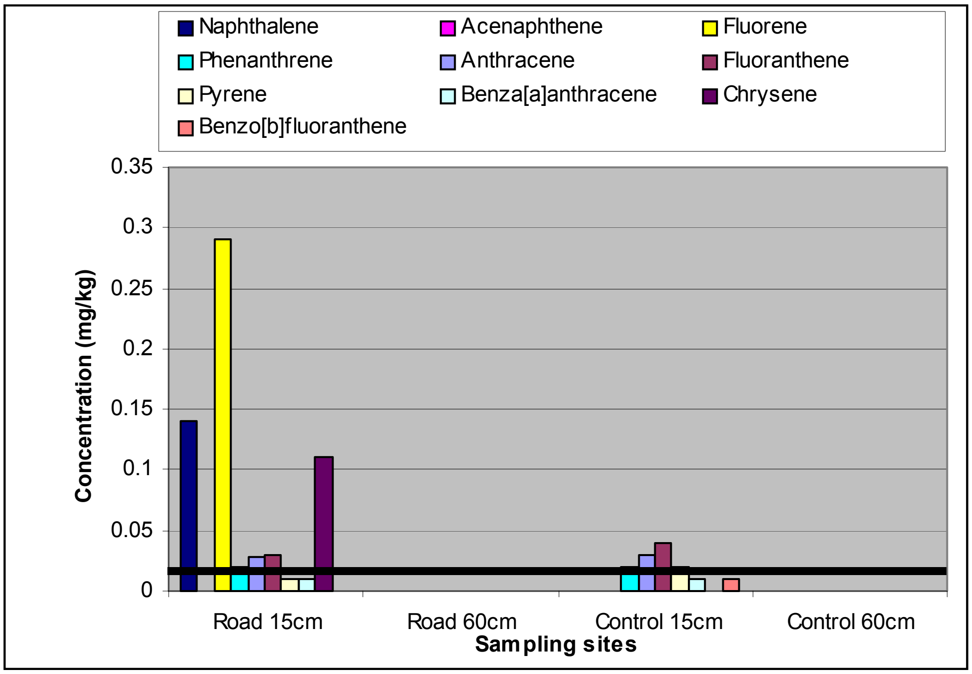


Figure 4.9 Graphical representation of PAHs at the road (E)

Figure 4.9 indicates that the road sample recorded high levels of fluorene (0.29 mg/kg) followed by naphthalene (0.14 mg/kg) and chrysene (0.11 mg/kg). These are PAHs that are prevalent in creosote. The only PAH that was not picked up in the 15 cm layer was acenaphthene. It can be noted that the PAH levels on the roadside were higher in the upper layer (15 cm) than the lower 60 cm layer of soil. The results are in line with a study by Wilcke, Krauss, Safrronov, Fokin and Kaupenjohann (2005), who observed that significant concentrations of PAHs are deposited and accumulate in surface soils. The effluent, as well as other factors such as the vehicles using the road, is likely to influence the PAH levels in the road. The results are in line with a study by Adamczewska, Siepak and Gramskwa (2000) who observed that the PAH content next to roads is high and the surface layer is more contaminated. The results of the study are a cause for concern since the PAHs are likely to get to the food chain and contaminate all trophic levels with PAHs.

According to Manahan (2000), soil type is also an important factor determining the mobility of organic pollutants, such as PAH compounds. The type of soil found at the roadside, where there were high concentrations, was found to be loamy and thus rich in organic matter. This would explain why the PAH compounds preferred to be transported from their source to that point where they then formed strong complexes with the organic matter. The formation of these complexes limits the mobility of these compounds in the environment. This is opposed to the soil type found at the processing plant, which was mostly clay and so lacked the capacity of having enough organic matter on which pollutants would adsorp.

The spatial distribution of the PAH compounds revealed that the concentrations of some of compounds were higher at a distance away from the point of discharge, where one would expect very high concentrations. For instance, the concentrations at the sites found at the trench, an outlet from the plant which discharges the creosote onto the environment, had lower levels than at the roadside a few metres downward from the trench. Although one would expect higher levels at the trench due to the constant input from the plant, this is not the case. This can also be attributed to the low water solubility constants of PAH compounds in aqueous media, meaning that they are lipophilic. This, therefore, suggests that these compounds do not dissolve in water but become suspended in the aqueous solution downslope, so that higher levels are found away from the processing plant at the road site.

4.3.3 Depth

Figure 4.10 shows that the control point had concentrations of PAHs below detection limits. The trench at this depth had more types of PAHs (10) followed by the road with eight types. The dominant PAHs from the various sampling sites at 15 cm depth were fluorene, phenanthrene, anthracene and fluoranthene. According to Wilke (2000) and Muller (1989), these are predominant compounds found in contaminated soil subsurface horizon. The road site recorded the highest PAH level for fluorene (0.29 mg/kg) and naphthalene (0.14 mg/kg). The highest level for anthracene (0.20 mg/kg) was recorded in the pine logs and effluent tanks.

The results in Figure 4.10 generally show that the 15 cm layer contained more PAHs in high levels when compared to the 60 cm layer. The PAHs in the control site (road 60 cm and trench 60 cm) were below detection limit. The variation in the PAH concentrations and type can be explained by the differences in the site conditions such as organic matter content, soil type and structure and leachability of soil as well as the physicochemical properties of PAHs.

The results are in line with a study by Wilcke *et al.,* (2005), who observed that significant concentrations of PAHs are deposited and accumulate in surface soils. This is also explained by Wild and Jones (1995), who state that the top 15 cm of soil acts as a major repository, containing about 94% of all PAHs in the environment. The influence of organic matter can be explained by Adamczewska *et al.* (2000), who observed that in soils with more organic matter, the PAH concentration is higher than those with less organic matter.

The observed results can be also largely be attributed to the physicochemical properties of PAHs. PAHs are liphopholic and hydrophobic, showing a high affinity for organic matter (Lundstedt, 2003). The octanol / water partitioning coefficient (Kow) and solubility of PAHs also suggest that these compounds are not easy to biodegrade in the environment. These have very high Kow values within the family of organic compounds, indicating that they prefer to adsorb themselves onto biota (plant and animal fatty tissues) as opposed to the soil matrix. They also have correspondingly high bioaccumulation factors (BCF), which indicate the tendency of a compound to bioaccumulate and become part of the food chain. This then means that the PAH compounds, in as much as they do not biodegrade easily, become incorporated into the fatty tissues of biota. In this case they are likely to be found in high concentrations on the upper soil with vegetation. This reduces the overall load of the pollutants in the lower soil, which explains why the concentrations are lower than expected.

On another note the leaching process of individual PAHs and their persistence against microbial decomposition can influence the distribution pattern in the soil profile (Wilke, 2000).

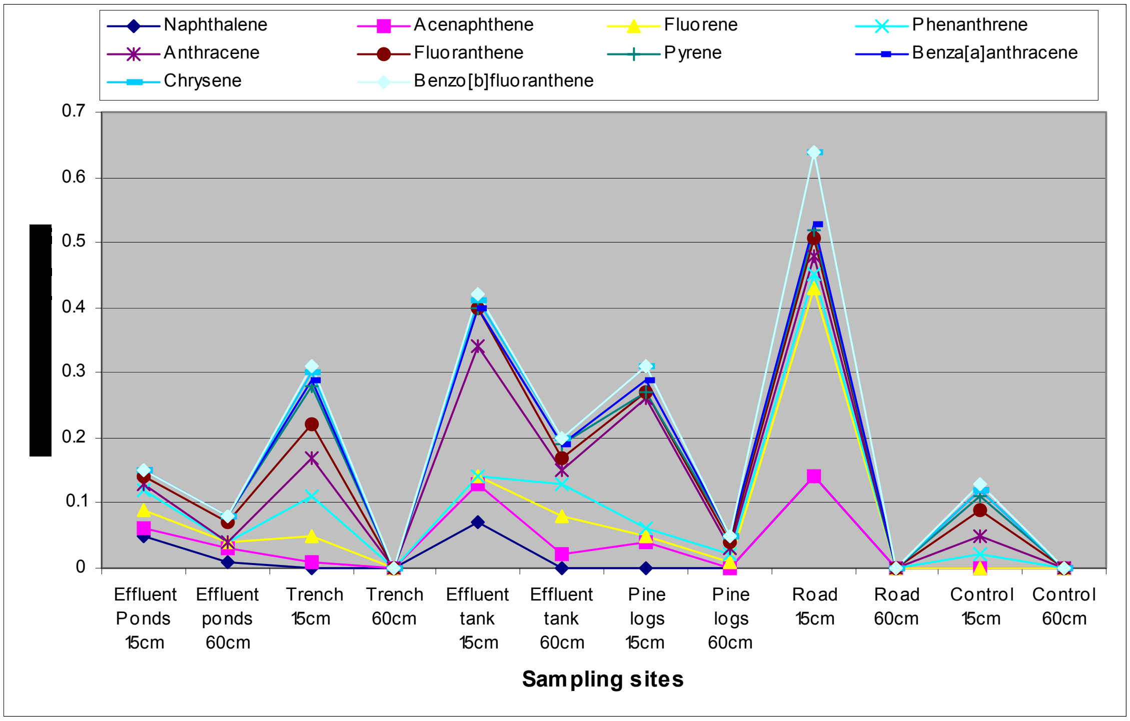


Figure 4.10 Graphical representation of PAHs in 15 cm and 60 cm layers

4.4 Chemometric data analyses

The raw data from the analysis containing the relative concentrations of the PAH compounds was treated for any variations, correlations and the spatial distribution of the variables. Chemometrical data analysis deals with the manipulation of the multivariate data set so that any hidden trends in the data are magnified and explained. This was done using a software-based approach, the knowledge of the sites and the chemistries of the pollutants under investigation. The software Statistica 6.1 was used to aid in the analysis of the data.

It is important to know if there are any correlations between the variables in the data set throughout the study area. A correlation matrix was constructed to assess the linear dependence of the variables, and the results are shown in Table 4.5.

Table 4.5 Variable to variable linear dependence correlation matrix

	Naph	Acen	Fluore	Phen	Anthr	Fluora	Pyren	Benz[a]a	Chrys	Benz[b]f
Naph	1.00	0.14	0.83	-0.02	0.90	0.34	-0.14	0.09	0.83	-0.06
Acen		1.00	-0.18	-0.08	0.29	0.50	-0.16	0.17	-0.07	0.41
Fluore			1.00	0.25	0.78	0.18	0.11	0.26	0.97	0.03
Phen				1.00	0.04	0.34	0.85	0.24	0.12	0.63
Anthr					1.00	0.58	0.01	0.22	0.82	0.14
Fluora						1.00	0.52	0.21	0.19	0.43
Pyren							1.00	0.25	0.01	0.44
Benz[a]a								1.00	0.41	-0.14
Chrys									1.00	-0.06
Benz[b]f										1.00

The correlation matrix above shows that, throughout the study area, there is a strong positive correlation between the compound naphthalene with fluorene, anthracene and chrysene. The data was further treated to observe PAH pollutant compounds, which have similar pollution signatures with respect to the study area. This was done by projecting the data onto tree diagrams (dendograms) which then group the data depending on the type of similarities in their pollution signatures. The results of this analysis are shown in Figure 4.11.

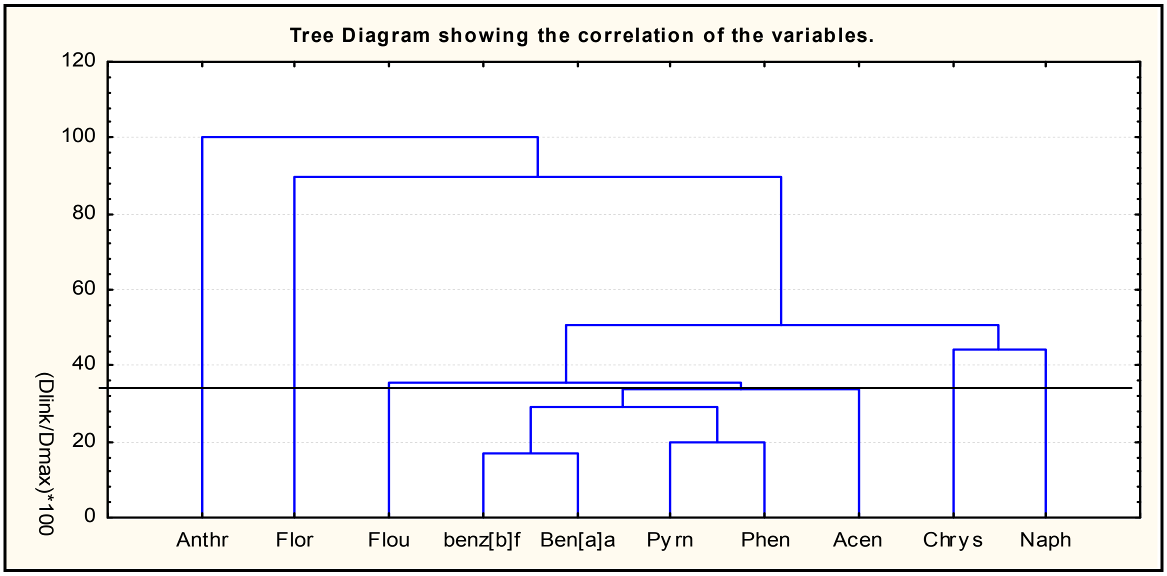


Figure 4.11 A variable tree diagram for the study area

Figure 4.11 above identifies three distinct pollutant clusters, at the 40 % linkage distance, with respect to their pollutant signature and behaviours in the environment. The tendency of the pollutants to cluster together is a function of many factors. This includes the fact that they probably have a similar source, or that their physical chemical properties are similar or that their degradation patterns and / or mobility indices are similar in the environment. It is evident from this figure that the compounds chrysene and naphthalene form an independent cluster and that the compounds, fluoranthene, benzo[b]fluoranthene, benzo[a]anthracene, pyrene, phenanthrene, and acenaphthalene form a larger and separate cluster. The last cluster is that involving fluorene and anthracene.

The cluster from this analysis was confirmed using principal component analysis (PCA). In PCA, the variables are projected onto a few principal components (PCs), which are selected such that the first PC explains much of the variance or correlation in the data as far as possible and the second is by definition orthogonal to the first and explains as much variance or correlation as possible, not yet explained by the first, and so on. The data was first projected onto the PC1, PC2 plane and the necessary variations were noted. The results of this analysis are shown in Figure 4.12.

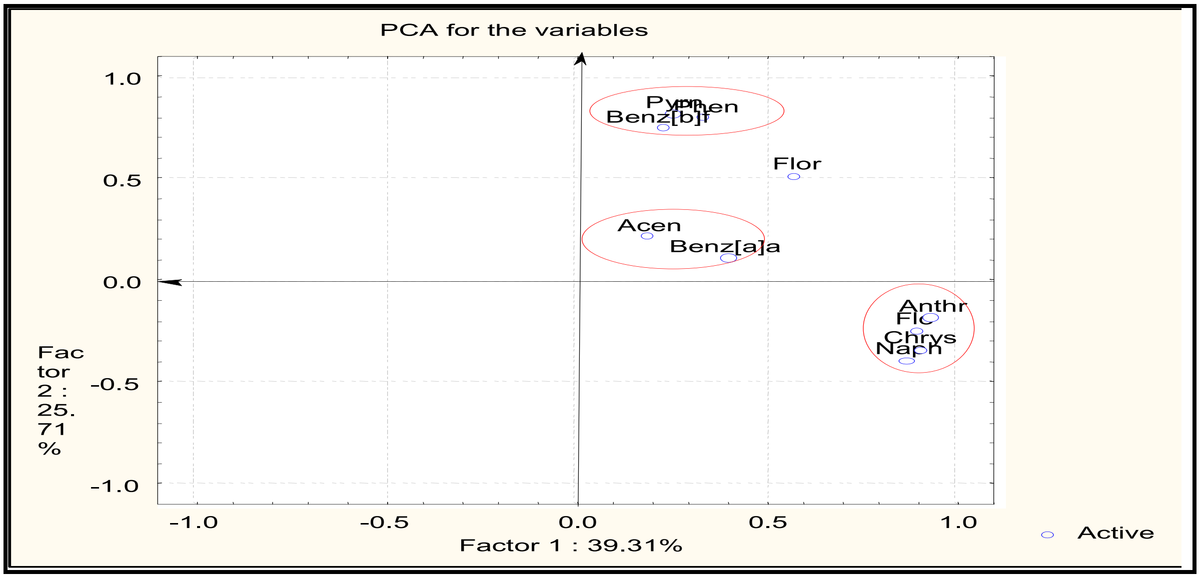


Figure 4.12 PCA plot projecting the variables along the PC1, PC2 plane

The results from Figure 4.12 confirm the results from Figure 4.11 in that three clusters of pollutant groups are identified. This then confirms the notion that the variables contained in those clusters have similar properties or pollution signatures and they will then become the subject of much discussion.

It is also worth noting from Figure 4.12 that the PAH compounds acenaphthalene and benzo[a]anthracene form a separate cluster from the others. This confirms an earlier representation using cluster analysis in Figure 4.11. These approaches are in agreement that these two pollutants have some common pollution signatures, which make them behave in a characteristic manner. The variables in the cluster involving the compounds naphthalene, fluorene, anthracene and chrysene are also in line with the results from the tree diagrams in Figure 4.11.

According to the principles of PCA, clusters furthest from the origin imply that the variables contained herein contribute a larger proportion to the observed variances in the data set. This means that the compounds naphthalene, fluorene, anthracene and chrysene are the major contributors to the variance, as well as the group containing pyrene, phenanthrene and benzo[b]fluoranthene.

However, the proximity of the cluster containing the compounds acenaphthalene and benzo[a]anthracene to the origin causes them to have low contributions to the observed pollution trends in the study. This, according to the premises of the PCA, necessitates that the analysis be projected along the PC1 and PC3 plane to observe if there are any changes in the projection of the variables. The analysis was carried out and the results are projected in Figure 4.13.

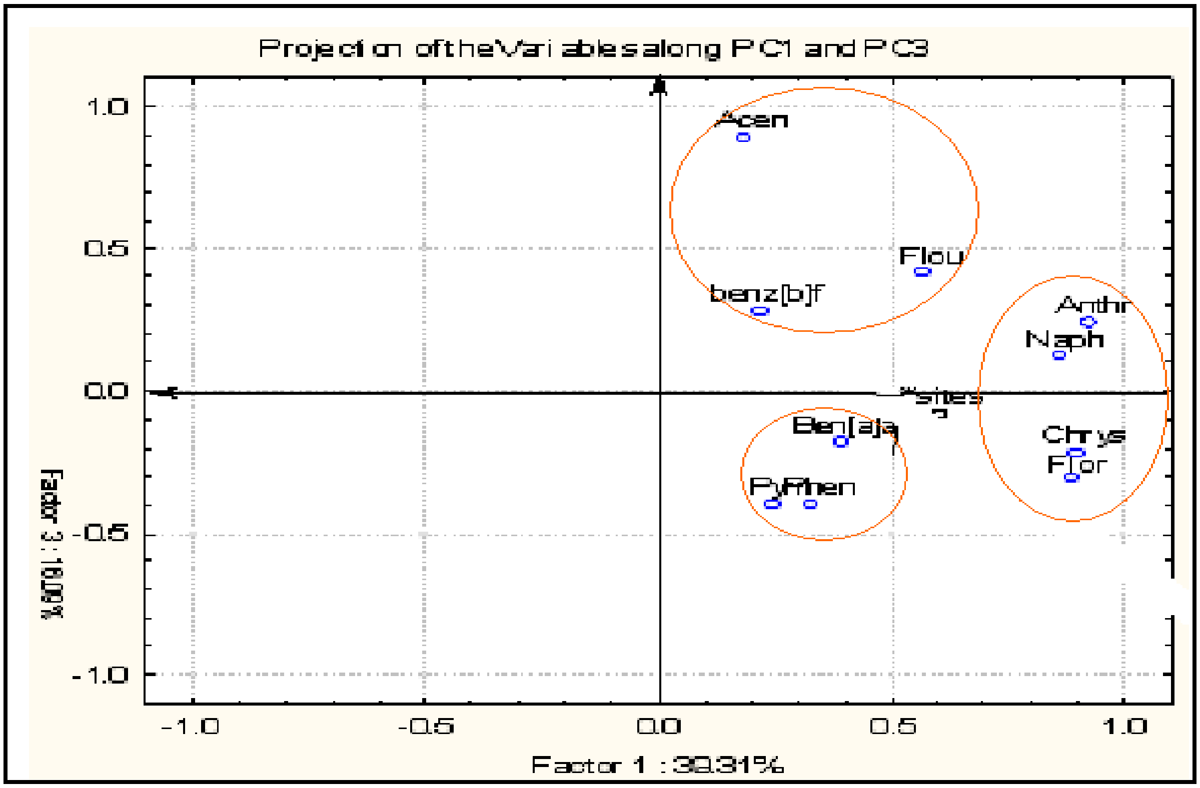


Figure 4.13 PCA plot projecting the variables along the PC1, PC3 plane

It is evident from the projections in Figure 4.13 above that the cluster in question containing the variables acenaphthalene and benzo[a]anthracene aligns itself differently along the PC1, PC3 plane. The compound acenaphthalene clearly shows that it has a strong correlation along the PC3 plane and very weak along the PC1 plane. This then explains that this variable was masked when the data was projected along the PC1, PC2 plane, as shown in Figure 4.12. However, the compound benzo[a]anthracene prefers to align itself with the vicinity of the origin, meaning that even along the PC1, PC3 plane, it does not have any significant contribution to the overall variance in the analysis.

In summary, the PCA was able to identify four separate clusters, onto which the variables prefer to align themselves. There are three clusters within the PC1, PC2 plane and one within the PC1, PC3 plane. The variables are discussed based on this grouping system.

Principal component analysis was further employed to determine the distribution of the variables in space. The sites were also inputted into the software to ascertain their preferred clustering, as a function of the variables. The results of this analysis are shown in Figure 4.14.

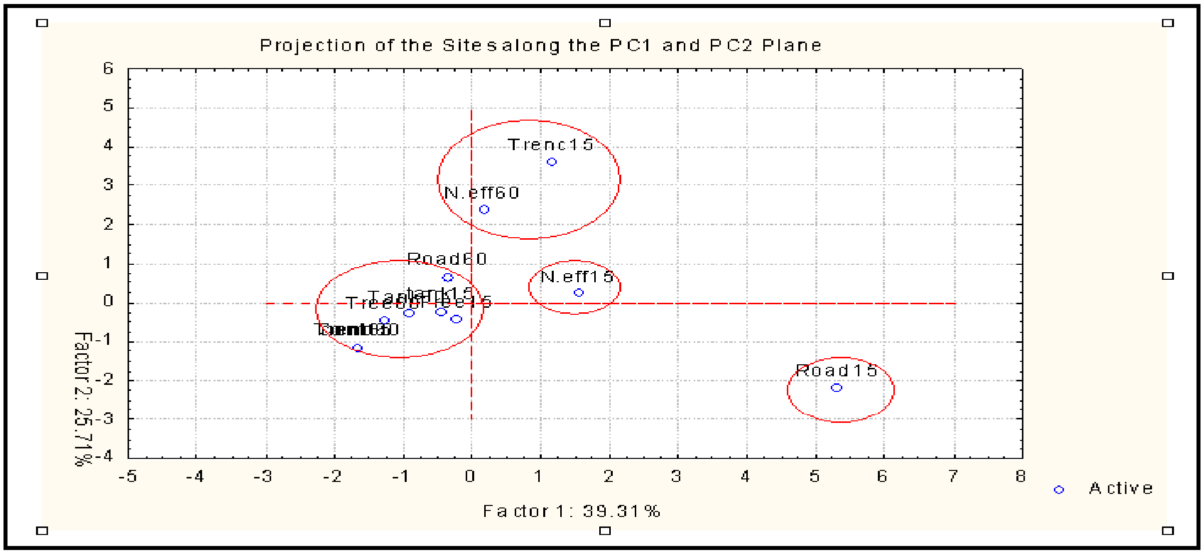


Figure 4.14 PCA plot projecting the sites along the PC1, PC2 plane

Figure 4.14 shows the alignment of the sites along the PC1, PC2 plane. This preferred orientation of the sites depends, to a large extent, on the types of the dominant pollutant compounds contained in each site, with respect to the PCA output. This then suggests that in order for one to be able to explain these observations there is need for a comparative approach. The spatial distribution is explained side to side with the PCA variable plots, as shown in Figures 4.14 and 4.12.

From these plots it can be observed that the cluster which contains the compounds pyrene, benzo[b]fluorene and phenanthrene contribute significantly along the PC1 plane, in the variable PCA plot. Interestingly, a closer look at the spatial distribution of the sites in Figure 4.14 reveals that the preferred trends depicted by the sites is as a result of the overall pollution signatures of the compounds. This, therefore, means that the sites, trench 15 cm and effluent tank 60 cm, are enriched with the compounds pyrene, benzo[b]fluorene and phenanthrene. In the same vein, the compounds naphthalene, fluorene, anthracene and chrysene have particular pollution signatures which influence the site, road 15 cm, to have a strong correlation with respect to both the PC1 and PC2 planes.

The compounds which are located within the vicinity of the origin (acenaphthalene and benzo[a]anthracene) as shown in Figure 4.12, influence the orientation of many sites in the study area. These are the sites, road 60 cm, pine logs 15 cm, pine logs 60 cm, effluent tank 15 cm, effluent tank 60 cm and trench 60 cm. However, due to their proximity to the origin, there is a need to project them in the PC1, PC3 plane so as to observe any hidden trends. The results are shown in Figure 4.15.

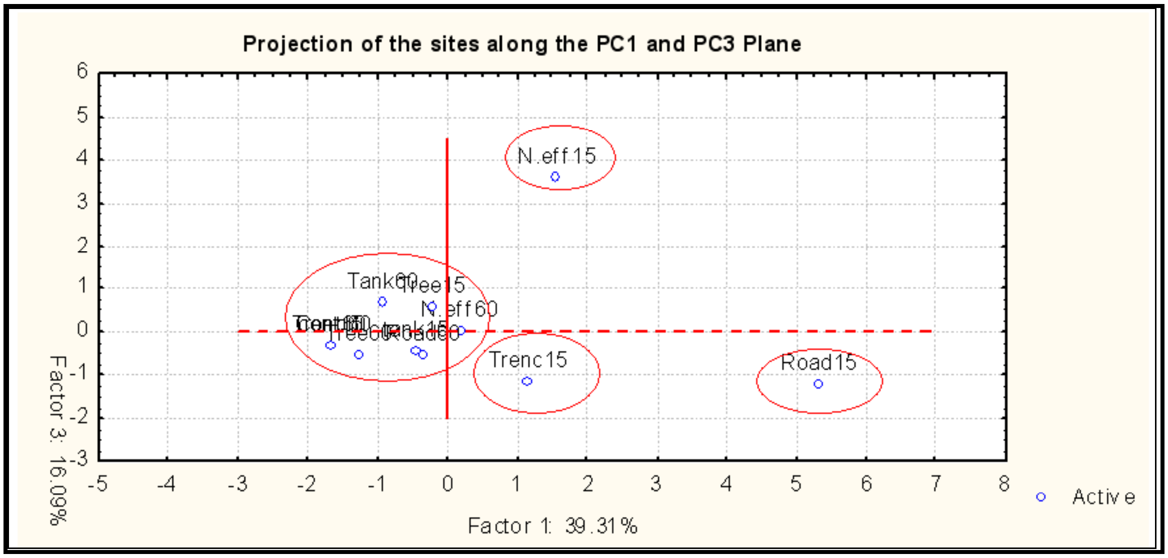


Figure 4.15 PCA plot projecting the sites along the PC1, PC3 plane

The results shown in Figure 4.15 above suggest that even when the data is projected in this dimension there is still minimum contribution of this whole group to the observed variances and trends. This then leads one to conclude that their behaviour is as a result of the signatures of the compound benzo[a]anthracene, which also failed to contribute much to the variance (see Figure 4.13 above). In summary, the PCA clusters resulting from the projection of the sites indicate that there are only three groupings that the compounds prefer to align themselves onto, with respect to the sites. This would imply that the fourth group identified with the variables does not contribute much to the observed trends, and so will not form part of the next discussions.

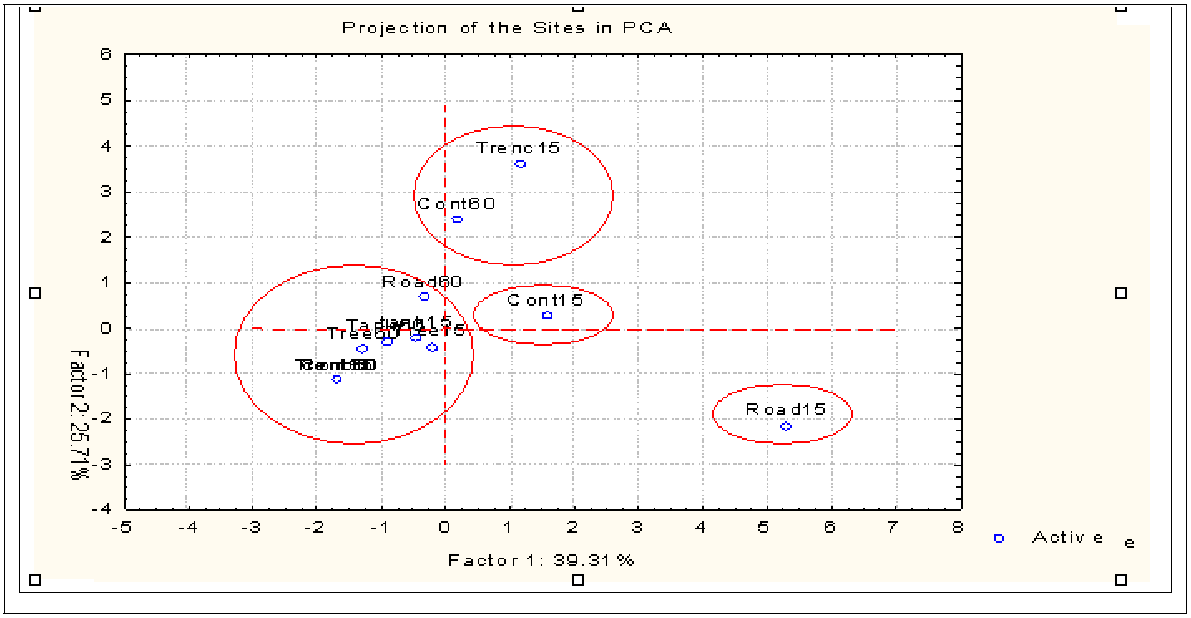


Figure 4.16 PCA plot projecting the sites along the PC1, PC3 plane

Figure 4.16 shows the spatial distribution of the pollutants throughout the study area, with respect to depth variations. This figure confirms some of the findings from Figure 4.12, in terms of the clusters observed. For instance, the site road 15 cm has a predominance of the PAH compounds as depicted in Figure 4.12. They are naphthalene, anthracene, fluorene and chrysene. This explains the preferred cluster, as they share the same source in terms of pollution signatures at this site. The position of this site in the PC1 plane also suggests a strong contribution of this site and the compounds to the overall observed pollution trend. The other sites, trench15 cm and control 60 cm, also share some similarities in terms of their correlations. Figure 4.16 explains that the observed relationship between these sites (though not so strong) is due to the contribution of the PAH compounds as shown in the cluster in Figure 4.12 above. The last cluster at the origin of the PCA plane is also explained in terms of the cluster that is around the origin, which shows that the site, trench 15 cm, pine logs 15 cm and effluent tanks, have made a minimal contribution to pollution in the study area.

In conclusion it must be stated that the project site has been contaminated with PAHs. Even though these are not in very high concentrations, for the company to comply with EPA, SEA and the ISO requirements for its major client for the treated poles (SEB), the site has to be rehabilitated. Phytoremediation is the mitigation measure recommended for clean-up of the contaminated area.

CHAPTER 5

CONCLUSION

5.1 Introduction

The objectives of the study were to determine the presence of Polycyclic Aromatic Hydrocarbons (PAHs) in soils and water samples in the Matsapha Central Stores Office (CSO) wood storage facility and the Thonkwane creosote wood treatment facility, to determine leachability and to compare the results with SEA and US EPA standards. This chapter answers the research problem, accepts or rejects the hypothesis, and concludes the findings on the extent of PAH pollution in the creosote wood storage facility in Matsapha CSO and the creosote wood treatment facility in Thonkwane, Swaziland. It also presents mitigation measures and recommendations for future work.

5.2 Total PAHs and pollutant profile

The study investigates the extent of PAH pollution in surrounding environments (soil, sediments and surface waters), SEB's wood storage facility in Matsapha Central Stores Office and a creosote wood treatment facility in Thonkwane. The results from the Matsapha Central Stores indicated that no PAHs were picked up from the soils and surface waters where the study area drains, whilst the results from the wood treatment facility in Thonkwane indicated that the soils in the project area were contaminated by PAHs and these were concentrated in the upper 0 – 15 cm soil layer. The PAH levels in the creosote facility were also observed to be above the recommended US EPA and SEA limit in soils except for fluoranthene and benzo[a]anthracene.

Therefore, based on the results of the study it can be concluded that the hypothesis that the pole storage site in Matsapha CSO is contaminating soils and surrounding surface waters with PAHs is rejected. However, the second hypothesis that the wood creosote treatment plant in Thonkwane (Swazi Timber Sales) is contaminating soils and surrounding surface waters with PAH is accepted.

The results from the creosote wood treatment facility in Thonkwane indicated that the study site was contaminated with a wide range of PAHs. The PAHs and the detected average concentrations are as follows: naphthalene (0.023 m/kg), acenaphthene, (0.013 mg/kg) fluorene (0.038 mg/kg), phenanthrene (0.017 mg/kg), anthracene (0.054 mg/kg), fluoranthene (0.022 mg/kg), pyrene (0.012 mg/kg), benzo[a]anthracene (0.004 mg/kg), chrysene (0.013 mg/kg) and benzo[b] fluoranthene (0.003 mg/kg). The concentrations of the identified PAHs were beyond the acceptable minimal level, which is 0.01 mg/kg as recommended by US EPA and SEA. This is an indication that the site is contaminated with the various PAHs mentioned above. This can only be attributed to the effluent from the creosote wood treatment plant.

The results from the creosote wood treatment facility in Thonkwane also showed that PAHs such as anthracene, fluorene, naphthalene and fluoranthene were dominant in all the sampling sites. The compounds occurred in very high concentrations (0.64 mg/kg, 0.46 mg/kg, 0.27 mg/kg and 0.26 mg/kg). These compounds are those found in pure creosote as determined in the sample taken from the site. The soil samples taken from the road site had the highest PAHs concentration when compared to all the sites. The high levels of the various PAHs in the road can be attributed to the effluent as well as to the traffic that uses the road.

The concentrations of the monitored PAHs generally increased downslope of the creosote wood treatment works. There were high concentrations of PAHs in the road, which is at low altitude when compared with the samples taken next to the effluent ponds, which are on a higher altitude. For instance, the concentration of naphthalene was 0.05 mg/kg next to the effluent ponds and 0.14 mg/kg on the road. One would have expected the concentration of PAHs to decrease as one moves away from the creosote plant.

5.3 Regulations

The Matsapha CSO site did not record any PAHs, thus it can be concluded that the levels were below the recommended US EPA and SEA limit. However, the levels of most of the PAHs recorded in the Thonkwane site were above the recommended US EPA limit in soil, which is 0.1 mg/kg. The results indicate that significant soil pollution takes place in all the study sites. The top layer (0 – 15 cm) generally contained many PAHs, and at levels above the recommended US EPA and SEA limit. The concentration of PAHs in the 60 cm layer ranged from 0.01 mg/kg to 0.06 mg/kg. These levels are also above the recommended levels of PAHs in soil.

5.4 Depth/leachability of PAHs

The understanding that PAHs have a tendency to bind strongly with organic matter has been found to be true in this study. There was a general decrease of the PAH concentrations with depth in the various soil samples. According to Lundstedt (2003) PAHs have a tendency to bind with organic matter. This has ecotoxicological implications to burrowers such as earthworms and grazers such as livestock and caterpillars, since their habitat as well as their food is in this layer of soil. These organisms are exposed to the toxic effects of the PAHs, which bind with their tissues and hence are introduced to the food chain. The PAH levels at the Thonkwane site tend to be higher in the 15 cm layer than in the lower 60 cm layer. This is a serious problem to livestock that graze in the study site as well as to burrowers such as earthworms that feed at this trophic level. This is in agreement with the literature, which states that PAHs tend to bind with organic matter. There is, however, low mobility between the 15 and 60 cm layers as a result of the fact that lower concentrations are found in the 60 cm layer when compared to the 15 cm layer.

It was observed that the trench, effluent tank, pine logs and road were contaminated with various PAHs. The trench was noted to be more contaminated than all the other sampling sites. It is worth noting that the highest PAH concentrations were found away from the effluent pond. It was expected that the PAHs would be concentrated next to the effluent pond and at the discharge point after the effluent tank. The soil type, the amount of organic matter present in the site, and other sources are important components responsible for the concentration and mobility of the PAHs in the study site.

The use of chemometrical approaches to the results obtained from the study site made it easier to draw conclusions on the potential sources of PAHs. The PCA was able to identify four groups of clusters, onto which the variables preferred to align themselves. The cluster with compounds naphthalene, fluorene, anthracene and chrysene, and the cluster with phenanthrene and benzo[b]fluoranthene are the major contributors to the variance. Acenaphthene and benzo[a]anthracene have low contributions to the observed pollution trends.

The PCA was further used to determine the distribution of variables in space. The sites next to the trench 15 cm and next to the effluent pond 60 cm had high PC values along the PC2 plane due to the presence of acenaphthalene. The second cluster has a single site, which is next to the effluent ponds at 15 cm. This site is enriched with benzo[b]fluorene and fluorene. The third cluster has one site, and the road has 15, which has a strong correlation to the PC1 and PC2 planes. The compounds naphthalene, fluorene, anthracene, and chrysene have particular pollution signatures, which influence the road 15 cm. The sites which are located within the vicinity of the origin such as the road 60 cm, tank 60 cm, trench 60 cm, pine logs 15 cm and pine logs 60 cm have hidden compounds influencing them which could not be picked up in the analyses. However, when the data are further analysed it was observed that the fourth group identified with the variables still have low contributions to the pollution trends in the study.

The study was able to achieve its intended objectives, which were firstly to determine PAH levels in soils and water at the Matsapha Central Stores and Thonkwane, and secondly to determine leachability and distribution of PAHs in SEB sites and Thonkwane. PAHs were only detected in the creosote treatment plant in Thonkwane. Thus the study on the Matsapha storage site and river was not pursued. The PAH levels were also compared with standards to determine compliance with US EPA and the Swaziland Environment Authority (SEA).

There are no known studies undertaken in Swaziland on PAHs. Therefore the data from this study will be used as baseline data for PAH studies in Swaziland. It will also assist the Swaziland Environment Authority who are currently conducting an inventory of persistent organic pollutants in the country as a requirement by the Stockholm Convention, which Swaziland is party to. It will also enable SEA to know the pollution status of the project site for any monitoring initiatives according to the Environmental Management Act (2002).

5.5 Recommendations and mitigation

5.5.1 Mitigation measures for health and safety in the study areas

In order to minimise the potential and existing environmental pollution impacts, the Thonkwane creosote treatment plant and the SEB are advised to adhere to occupational health and safety rules and regulations and implement best environmental practices.

The urgent issue which has to be addressed on the safety aspect of the mitigation measure would be to supply the workers in the creosote plant and pole storage facility with the right protective clothing such as gloves, respirators, overalls and boots. The employees, suppliers, contractors and clients must also be made aware of the dangers of creosote and how they must manage the products in a safe and environmentally sound manner.

5.5.2 The best environmental practices

5.5.2.1 Thonkwane

The best environmental practices will include waste minimisation and stormwater management. Wastewater volumes must be minimised by eliminating leaks, spills and drips, and by segregating stormwater runoff and improving general maintenance. Furthermore, oil separators, which can be purchased from Drizit, can be installed and used to clean up water from the effluent ponds. Following the removal of the oil the remaining water in the pond can be evaporated. The principle behind the evaporation of wastewater is to dispose the water fraction whilst leaving the organic constituents for subsequent recycling or disposal. The facility should also install basins and drip trays to capture all creosote from drippings to be reused.

The cylinder and treated wood storage facility should be covered to prevent rain from collecting on the pads (see Figure 5.1). Stormwater must also be diverted away from the contaminated areas. The reduction and diversion of water flows also allow for the more reliable and consistent operation of the wastewater treatment system (Morgan & Burdell, 1978).

5.5.2.2 Matsapha CSO (wood storage facility)

A concrete slab must be constructed and the treated wood must be stored on this area. Drains must be constructed around the pole storage facility and these must drain into an oil separator before the effluent is discharge into the Matsapha drainage system. The water must be continually monitored to check if the effluent is within the water quality guidelines.

Finally, awareness must be increased amongst workers on best management practices, waste reduction techniques and the environmental impacts of the processes, products and waste.

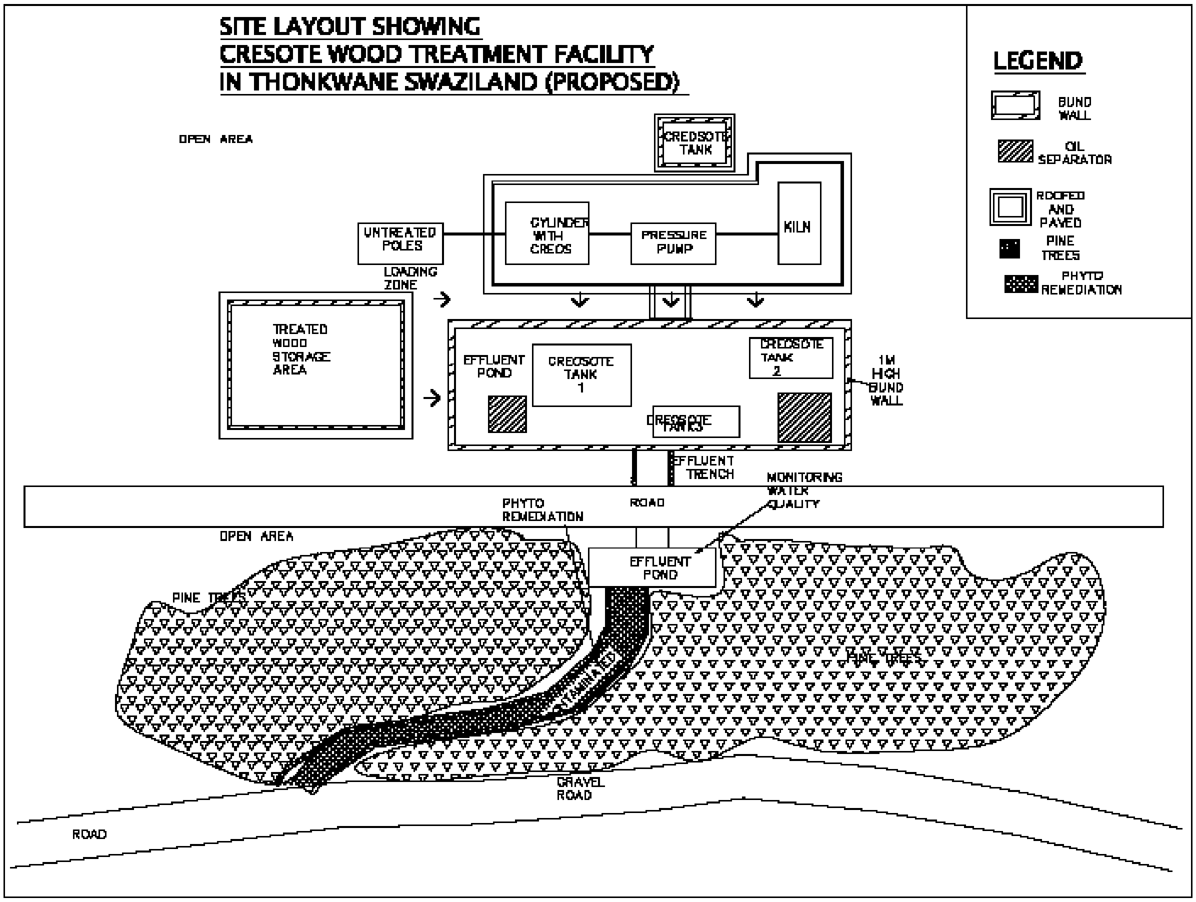


Figure 5.1 Recommended mitigation measures in the Thonkwane creosote wood treatment facility

5.5.3 Mitigation for contaminated soil

The remediation of soils contaminated with organic chemicals can be achieved by using various techniques such as phytoremediation, bioremediation, engineering and natural attenuation. Due to the limitations of bioremediation, engineering and natural attenuation, the phytoremediation technique has been selected as the most suitable technology for the remediation of the contaminated sites in the creosote treatment facility in Thonkwane. The other remediation techniques are expensive and produce secondary waste.

According to Molobela (2005), Madsen (2003) and Cunningham *et al*. (1996), phytoremediation is quicker than natural attenuation and conversely slower but less expensive than most of the engineering techniques and traditional bioremediation methods. It is solar-driven and does not generate secondary waste. Phytoremediation does not require intensive engineering techniques or excavations and thus limits environmental disturbance. The public and government regulators also favour phytoremediation since it involves exploiting the natural ability of the environment to restore itself. The technique is also considered to be more aesthetically pleasing than the other techniques. It is a self-sustaining technology since the soil is reusable after treatment.

To date studies of plant species for the remediation of petrochemical contaminated soils showed that various grasses and leguminous plants were suitable for phytoremediation. However, Kuiper, Lagendijk, Bloembergs and Lugtenburg (2004) state that grasses have proved to be the most efficient plants in phytoremediation. This is due to the fact that grasses have a highly developed branch root system that harbours a large number of bacteria which are useful in cleaning up contaminated environments. According to Mehmannavaz, Prasher and Ahmad (2002), the roots provide ideal attachment sites for microbes and a supply of exudates consisting of complex carbohydrates. Therefore it is recommended that grasses such as *Cyperus esclentus, Panicum maximum* and *Elucine coracana* be planted on the contaminated site. The contaminated area must be irrigated at least twice a week until the plants have become established.

5.6 Conclusion and recommendations

In order to determine PAHs resulting from the pole storage area Matsapha CSO and the creosote wood treatment facility at Thonkwane, soil and water samples were collected for the purposes of this study. A preliminary survey was undertaken on both sites and no PAHs were detected from the Matsapha CSO site. No further investigations were made on this site. PAHs were detected in the Thonkwane site and thus the site was further analysed for PAHs contamination.

Soil samples were taken at depths of 15 cm and 60 cm at strategic points within the project area to determine PAH distribution and leachability. The results were compared with the US EPA and SEA limit in soil, which is 0.1mg/kg. The results showed that the 15 cm layer had high PAH levels. In most of the samples these were above the SEA and US EPA limit, which is 0.1mg/kg. No leaching of PAH compounds was observed to be taking place in the project area. The results confirmed findings by other researchers that PAHs accumulate in the surface layer and do not leach.

Based on the above it is suggested that further investigations be undertaken in future to broaden the scope of the study. This study was not extensive since it focused on soil samples and water samples in the Matsapha Central Stores and soil samples only at depths of 15 cm and 60 cm in the creosote wood treatment plant in Thonkwane. For future work it is recommended that more soil samples are taken to depths up to 1 m. A future study should further analyse water samples in the streams below the creosote treatment plant in Thonkwane.

It is clear from the results that the study site has PAH levels that are above the recommended levels determined by national and international laws. Therefore it is necessary that a clean-up by phytoremediation, as well as a monitoring programme be implemented to minimise the impacts of these toxic elements on the environment. However, it is recommended that future work be undertaken to explore the best option for remediating the site.

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APPENDICES

Appendix 1

Comparison of phytoremediation to alternative remediation methods, natural attenuation, engineering and bioremediation (Frick, Farrel & Germida, 1999)

Characteristics	Phytoremediation	Natural attenuation	Engineering	Bioremediation
1. Ex situ or in situ	In situ	In situ	Ex situ or in situ	Ex situ or in situ
2.General description	Use microbes and plants to degrade, contain or transfer contaminants	Use microbes and plants to degrade, contain or transfer contaminants.	Ex situ excavations, land filling, incineration In situ = soil vapour extraction, chemical or thermal treatment, solidification, pump and treat, vacuum extraction and sparging	Use microbes and plants. to Degrade, contain or transfer contaminants. Ex situ involves excavations coupled with solid-phase slurry phase treatment.
3. Human intervention	Yes. Agronomic , tillage,, tillage and fertilizer, inoculation and planting	No	Yes, extensive	Yes, extensive. Provide proper temperature, oxygen, and nutrients to optimise microbial activity.
4. Direct benefits	In situ: solar driven, well suited to large areas of surface contamination, good aesthetics, favourable public perception, plants as indicators of contamination. Plants degrade a variety of contaminants. Plants transfer oxygen to rhizosphere. Plants help contain contaminants. Relatively easy to apply	In situ No disturbance	Dependable, leaves clean site, has definite starting and end points, especially faster than other remediation methods. , Proven to be effective. Vacuum extraction not limited by depth to groundwater.	Limited disturbance with in situ, proven to be effective.
5. Indirect benefits	Improves soil quality., Prevents soil erosion. Plants eliminate secondary air and waterborne wastes such as greenhouse gases.	Hardy plants can help other less hardy plants to grow on contaminated areas once established plants prevent erosion and		

	Trees can reduce noise from industrial sites. Hardy plants can help other less hardy plats to grow on contaminated areas.	help eliminate secondary air and waterborne wastes.		
6. Limitations	Contamination must typically be shallow. Plants may not grow if contamination is high. Slower than ex situ methods. Contaminants may not be bioavailable. Environmental conditions have to be right. Leaching or vitalisation may occur before phytoremediation.	Slower than any other remediation method, therefore longer period of higher risks to human and ecosystem health. Plants, microbes, or environmental conditions most beneficial to remediation may not be naturally present.	Highly disruptive, especially excavation. Landfill only transfers contaminants to a second site. Disposal issues of fly ash exist with incineration. Pump and treat does not treat soils directly and is very slow.	Highly disruptive with ex situ excavations. In situ requires extensive collection systems, treatment longer engineering but not as long as attenuation. May not work if contaminant is toxic to microbes. Requires intensive monitoring
7. Cost	\$17 to \$3US/m^3 each year ; cropping system = \$0.02-\$1.00US/m^3	No operational costs. May have costs associated with monitoring.	Generally \$10 to over \$1,00/ m^3, \$10-100US/ m^3 for volatile or water-soluble contaminants in situ. \$200-700US/ m^3 for special land filling, incineration or secured landfill costs of \$260-1064 per m^3	\$50 to \$133 for in situ, \$133 to \$400/ m^3 for ex situ

Appendix 2

Genera of hydrocarbon-degrading micro organisms isolated from soil (Cerniglia, 1992; Bossert & Bartha,1986; Frick *et al*., 1999).

Bacteria	Hydrocarbon	Fungi	Hydrocarbon
Acidovorax	Phenanthrene and Anthracene	Cunninghamella	Benzo [a] pyrene
Alcaligenes	Phenanthrene, Fluoranthene and Fluorene	Fusarium	Benzene, Naphthalene, Phenanthrene and (n-alkanes (C_{10} to C_{40})
Arthrobacter	Benzene, Naphthalene and Phenanthrene and (n-alkanes (C_{10} to C_{40})	Penicillium	Benzene, Naphthalene and Phenanthrene and (n-alkanes (C_{10} to C_{40})
Mycobacterium	2-methylnaphthalene, Phenanthrene , Pyrene and benzo [a] pyrene		
Pesuedomonas	Phenanthrene , Benzo[a]pyrene, Fluoranthene		
Spingomonas	Phenanthrene , Fluoranthene and Anthracene		
Rhodococcus	Benzene and benzo[a]pyrene		
Other bacteria			
Achromabacter	Norcadia	Acremonium	Monilla
Acinetobacter	Proteus	Aspergillus	Mortierella
Micrococcus	Sarcina	Aureobasidium	Paecilomyces
Spirillum	Serratia	Beaveria	Phoma
Brevibacterium	Streptomyces	Botrytis	Rhodotorula
Vibrio	Erwinia	Candida	Saccharomyces
Flavobacterium	Cytophaga	Chrsosporium	Scolecobasidium
Corynebacterium		Cladosporium	Sporobolomyces

Appendix 3

Plants with a potential to tolerate petroleum hydrocarbons (Frick *et al.*, 1999)

Plant and Scientific Name	
Crested wheat grass (Agropyron desertorum)	Cattails (Typha latifolia)
Oat (Avena sativa)	Field pea (Pisium arvense)
Water sedge (Carex aquatilis)	Three square bulrush (Scirpus pungens)
Rock sedge (Carex rupestris)	White clover (Trifolim repens)
Tall cotton grass (Eriophorum angustifolium)	Reed grass (Phragmites australis)
Sunflower (Helianthus annus)	Round sedge (Carex rotundata)
Birdsfoot trefoil (Lotus cornilatus)	Barley (Hordeum vulgare)
Maize (Zea mays L)	
Wheat (Trichum aestivum)	
Faba bean (Vicia faba)	
Jack pine (Pinus banksiana)	
Soy bean (Glycine max)	
Carrot (Doucus carota)	

Appendix 4

Polyaromatic hydrocarbons

Method	EVALUATION: PARTIAL		ISSUE : 15 AUGUST 1994
COMPOUNDS	Acenaphthene Acenaphthylene Anthracene Benzo [a] anthracene Benzo [b] fluoranthene Benzo [k] fluoranthene	Benzo[ghi]perylene Benzo[a]pyrene Benzo[e]pyrene Chrysene Dibenz[a,h]anthracene Fluoranthene	Fluorene Indeno[1,2,3-cd]pyrene Naphthalene Phenanthrene Pyrene
Sampling		Measurement	
Sampler :	Filter and sorbent (2-µm, 37mm PTFE+ washed XAD-2 100mg/50mg)	Method:	Gas Chromatography capillary column FID
Flow rate :	2L//min	Analyte:	Compounds above
Vol. - Min: Max:	200L 1000L	Extraction:	5ml organic solvent appropriate to sample matrix
Shipment:	Transfer filters to culture tubes , wrap sorbent and culture tubes in A1 foil ship at 0 °C	Injection volume:	4µL; 10:1 split
Sample stability:	Unknown protect from heat and uv radiation	Column:	30m×0.32-mmID fused capillary 1-µm DB 5
Field Blanks:	2 to 10 field per set	Temperature injector: 200 °C Dejector: 250 °C Programme: 130 to 290 °C at 4 °C/min	
Media Blanks:	6 to 10	Gases – carrier : Helium at 1 mL/min Makeup: He at 20 mL/min	
Area Samples:	8 Replicates on preweighed filters for solvent selection	LOD: ca. 0.3 to 0.5 µg per sample Calibration: external standards in toluene	

Accuracy		
Range studied accuracy , bias and overall precision (not measured		

Applicability: The working range for B[a]P is to 150 $\mu g/m^3$ for 400-L air sample . Specific sample sets may require modification in filter extraction solvent, choice of measurement method and conditions.

Interferences: Any compound which elutes at the same GC retention time may interfere. Heat ozone, nitrogen or UV light may cause degradation.

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Appendix 5

Principal Component Analysis (PCA)

Principal component analysis is an analytical tool for simplifying data by reducing multidimensional data sets to lower dimensions for analysis. It is a component of multivariate analysis in statistics. According to Gardner (2001), the main interest of PCA lies in assessing the variables as a set of interrelationships (correlations) between them and the information these relationships contain jointly about the samples on which measurement has taken place. PCA can help understand the interrelationship between variables, help determine the dimensionality of data set and finally help derive a low dimensional representation of data (Miller & Miller, 2000).

Miller and Miller (2000) further states that variables are projected onto a few principal components (PCs). The first PC explains variation in the data and the second one is orthogonal and explains variation not explained by the first one. According to Shine, Ika and Ford*,* (1995), subsequent PCs are calculated to each other and retain increasingly smaller variances. The projection of a variable on a PC is called the score of that variable. When the scores of the variables, for example, PC1 and PC2, are plotted against each other this is referred to as a score plot. Therefore, objects that plot out next to each other have similar variables. Mathematically the weighted sum of the original variable is called a PC and the weights are called loadings. Therefore, when an object has a high score for a certain PC then that variable has high values for those variables that have high loadings for the PC.

The PCA is preferred above other multivariate statistical approaches because it gives a better indication of the similarities of variable patterns than comparison between individual variables. It also allows for the examination of relationships between and among variables, through the variable loading plot. Finally, the location of variables in the loading plot indicates their effect on the placement of the samples on the PC plot.