ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN AIR AND SOIL FROM SELECTED SITES IN NAIROBI

BY:

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DECLARATION

This thesis is my original work. It has not and will not be submitted for examination in any other University.
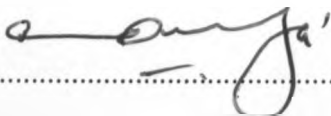
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DEDICATION

To my beloved children Daisy and Newton

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

ANOVA   Analysis of Variance

APA   American Psychological Association

ATSDR   Agency for Toxic Substances and Diseases Registry

B(a)P   Benzo(a)pyrene

BBC   British Broadcasting Corporation

BD   Below Detection Limit

CBS   Central Bureau of Statistics

CCME   Canadian Council of Ministers of Environment

CPCB   Central Pollution Control Board, India

DNA   Deoxyribonucleic acid

EMCA   Environmental Management and Coordination Act

EC   European Commission

GAPS   Global Atmospheric Passive Sampling

GC   Gas Chromatograph

GC/FID   Gas Chromatograph with Flame Ionization Detector

GC/MS   Gas Chromatograph with Mass Spectrometer Detector

GMP   Global Monitoring Plan

IARC   International Agency for Research on Cancer

ICCS   International Centre for Chemical Studies

LOD   Limit of Detection

MENR   Ministry of Environment and Mineral Resources

MONET-Africa   Monitoring Network for Africa

OECD   Organization for Economic Cooperation and Development

PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzo furans
POPs	Persistent Organic Pollutants
PTFE	Polytetrafluoroethylene
PUF	Polyurethane Foam
RECETOX	Research Centre for Environmental Chemistry and Ecotoxicology
SPSS	Statistical Programme for Social Scientists
TPB	Triphenyl Benzene
UNEP	United Nations Environment Programme
UNESCO	United Nations Educational, Scientific and Cultural Organization
UoN	University of Nairobi
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
WHO	World Health Organization

Abstract

This study was undertaken to investigate the occurrence, spatial distribution and temporal and seasonal variations of sixteen Polycyclic Aromatic Hydrocarbons (PAHs) in Industrial Area, Dandora Municipal dumpsite and Kabete sites on a monthly basis from February to July 2008. The sixteen PAHs have been identified by various Regional and International Agencies as priority compounds due to their toxicity, potential for human exposure and adverse effects on human health and the environment.

Identification and quantification of the PAHs in air and soils was done using a Varian CP 3800 gas chromatograph equipped with a flame ionisation detector. Confirmatory analysis was conducted using Gas Chromatography equipped with a mass spectrometer (HP 6890-HP 5972).

Compound detection limits ranged between 0.0165 ng/ filter for acenaphthene and 0.117 ng/filter for anthracene. Levels of PAHs in air were lower at the Kabete site than in Dandora and Industrial Area. The concentrations of individual PAHs in air ranged from below detection level to 3939.66 ±10.28 ng/filter. The sum of the concentrations of the compounds ($\sum$16 PAHs) ranged from 1704.05 ±191.16 ng/filter to 1881.81 ±202.86 ng/filter in Kabete; 6470.27 ±724.42 ng/filter to 8726.93 ±716.53 ng/filter in Dandora; and between 5853.69 ±631.28 ng/filter and 7822.87 ±851.89 ng/filter in Industrial Area. Individual PAHs in soils ranged between below detection level to 526.66 ±18.62 ng/g. The sum of the concentration of the 8 PAHs ($\sum$8 PAHs) ranges (ng/g) were 17.30 ±1.19 to 62.21 ±0.97 in Kabete, 141.44 ±1.03 to 726.60 ±4.51 in Dandora; and 63.37 ±1.29 to

138.68 ±1.93 in Industrial Area. Medium weight PAHs, especially phenanthrene were more abundant than the low molecular weight compounds.

There was a general increase in the monthly levels of PAHs in air at the Dandora and Kabete sites. On the contrary, there was a general decrease in the mean levels of PAHs in air from industrial area. Levels of PAHs in soils increased slightly in Dandora but declined slightly in Kabete. There was stronger seasonal dependence in levels of PAHs in air than in soils. Higher levels were observed during the cool season than the dry and wet seasons in Kabete and Dandora. A reverse trend was observed at the Industrial Area site.

The Pearson's correlation coefficients as determined for the PAHs present between air and soil were positive at all the sites. The strongest and most significant inter-matrix correlation was observed in Kabete (r=0.821) followed by Dandora (r=0.503) while that for Industrial Area was weak (r=0.166). Correlation coefficients for temporal and seasonal variations of PAHs were positive except in relation to Kabete soil (r=0.039) and Industrial Area air (r=0.792).

CHAPTER ONE

INTRODUCTION

The environment and its closely interdependent biotic and abiotic components have over the years been thought to consist of infinite resources and self regenerating processes that have been of little concern to the past generations. However, humans have started to realise that their activities are impacting negatively on the local and global environment: depleting its resources, destabilizing ecosystems and polluting the earth.

Environmental degradation contributes to over 60% of the global health burden [CPCB, 2003; UNEP/WHO, 1996]. This awareness has raised concerns on the sustainable management of the environment in order to minimize the negative impacts of human activities. A great deal of attention has been drawn to pollutants mainly heavy metals, sulphur oxides, carbon oxides and nitrogen oxides. Most of these pollutants are found in large quantities sufficient for obvious adverse effects on humans and the environment [ATSDR, 1995].

In the last few decades, concern has turned to a number of pollutants, which though found in relatively small concentrations, have the potential to adversely affect human health and the environment through long-term exposure. Among these are persistent, bio-accumulative contaminants usually composed of persistent organic pollutants (POPs) and the closely related toxic organic contaminants including polycyclic aromatic hydrocarbons [ATSDR, 1995; CPCB, 2003; EC, 2006].

Polycyclic Aromatic Hydrocarbons (PAHs) are organic compounds with at least two fused aromatic or other cyclic rings constituted by carbon and hydrogen only; the simplest member

of which is naphthalene. They are found in complex mixtures mainly as by-products of combustion in natural and anthropogenic activities. The main concerns associated with PAHs are that some of them are probably or potentially carcinogenic, mutagenic and/or genotoxic [ATSDR, 1995; Butler, 1979; UNESCO-ICCS, 1996].

Although PAHs are not yet officially recognized as POPs, they have been proposed as candidates for inclusion in the Stockholm Convention which aims at eradication of POPs. The World Health Organization (WHO) has added PAHs into the list of the priority pollutants in both air and water. The United States Environmental Protection Agency (USEPA) has identified sixteen priority PAHs based on the potential of human exposure to these PAHs and their adverse health effects. Other agencies including United Nations Environment Programme (UNEP), United Nations Economic Cooperation for Europe (UNECE) and the Organization for Economic Cooperation and Development (OECD) have similarly adopted the USEPA priority PAHs for monitoring [ATSDR, 1995; EU, 2006; UNEP/WHO, 1996]. However, PAHs are not included in the list of priority air pollutants in Kenya in the draft of air quality regulations [EMCA, 2008].

Benzo(a)pyrene, a five ringed polycyclic aromatic hydrocarbon, is the most characterised of the 16 priority PAHs. The other fifteen are naphthalene(two ringed); acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene which are three ringed; fluoranthene, pyrene, benzo(a)anthracene and chrysene which are four ringed; benzo(b)fluoranthene, benzo(k)fluoranthene and dibenzo(a,h)anthracene which are five ringed, indeno(1,2,3,-c,d)pyrene and benzo(g,h,i)perylene which have six aromatic rings. The structures of the PAHs are given in Appendix I.

Some of these pollutants, especially lighter PAHs are known to be abundant in the urban atmosphere and may react with other pollutants such as nitrous oxides and ozone to form more toxic secondary pollutants [ATSDR, 1995; Sitaras and Siskos, 2007]. These substances move from major point sources in cities to remote sites through atmospheric transport and particle deposition, thus posing risks to human populations far away from contaminant sources [ATSDR, 1995]. They may also exert significant effects on the global radiative budgets, hence their identification and quantification in different environmental matrices is an important analytical problem [Gatari *et al.,* 2006].

PAHs are formed mainly as a result of incomplete combustion of organic matter from both natural and anthropogenic activities. They are mainly directly released to the atmosphere, from where they redistribute between the gaseous and particulate phases. They are then subsequently transported and deposited in other environmental matrices such as soil, water and vegetation through wet and dry deposition. In air, soil and water, PAHs are mostly adsorbed to particulate matter, on which they are transported and can be degraded slowly [ATSDR, 1995].

Urban areas being the geographic focus of resource consumption and human activities have potential for higher environmental pollution than the rural areas [Wong *et al.,* 2004]. This is mainly due to increased dependence on fossil fuels for domestic use, industry and transport. The use of inefficient and poorly maintained combustion systems further aggravates the situation. Rapidly rising populations in cities also put an increasing demand for manufactured products and municipal waste disposal facilities. The pace of technological advancement in most African cities is way below the capacity to cope with the increase in wastes and emissions generated from human activities and lifestyles. Lack of proper regulatory

frameworks makes sustainable environmental management a big challenge to these cities [UNEP/WHO, 1996].

The trends in concentrations of PAHs in urban areas have been related to vehicular traffic patterns, human settlement and industrial activities. Concentrations of PAHs in urban soils up to ten times as great as those found in sub-urban areas; and up to 30 times as great as those in rural sites have been reported. Levels of PAHs in soil have been found to range from 61 ng/g at a rural site to 3922 ng/g at an urban site [Wong *et al.*, 2004]. Similar trends have been reported in ambient air on a rural urban transient [Garban *et al.*, 2002; Impey *et al.*, 2000].

Nairobi is the capital city of Kenya and is also the commercial and industrial city. Due to urbanisation, industrialisation and rapid population growth, Nairobi faces challenges in waste disposal, vehicular congestion and emission control. There are no regulations on PAHs in Kenya and data on the status of this class of organic contaminants in Nairobi is limited. This study was therefore carried out to identify and quantify priority PAHs in air and soils at three sites in Nairobi.

CHAPTER TWO

LITERATURE REVIEW

2.0 Background

Polycyclic aromatic hydrocarbons (also called Polynuclear Aromatic Hydrocarbons or Polyaromatic Hydrocarbons) are a large group of organic compounds with two or more (up to seven) fused aromatic rings which are produced as by-products of incomplete combustion processes [ATSDR, 1995]. Besides PAHs, there are a number of other heterocyclic aromatic compounds such as dioxins, furans, carbazole and acridine co-produced during combustion. There are also substituted derivatives including chloro-, nitro-, oxy-, hydroxyl- and hydroxynitro-PAHs formed when PAHs undergo chemical reactions with other pollutants in the environment [ATSDR, 1995; Holton *et al.*, 1984; Sitaras and Siskos, 2007].

The physical and chemical properties of PAHs are governed by the size (number of carbon atoms) and shape (ring linkage pattern) of the individual molecule. Pure PAHs usually occur as colourless, white or pale yellow-green solids at room temperature and have relatively high melting and boiling points as shown in Table 2.1 [ATSDR, 1995].

Table 2.1 Some Physical Properties of Selected PAHs found in the Environment

Compound	No. of rings	Molecular Weight	MP (^{o}C)	BP (^{o}C)
Naphthalene	2	128	80	218
Acenaphthene	3	154	96	278
Anthracene	3	178	216	340
Fluorene	3	166	116	295
Phenanthrene	3	178	100	340
Fluoranthene	4	202	110	384
Benzo(a)anthracene	4	228	150	400
Benzo(a)pyrene	5	252	102	179
Benzo(k)fluoranthene	5	252	217	480
Benzo(ghi)perylene	6	276	273	550

Source: ATSDR, 1995

PAHs generally have low vapour pressures and low water solubility which tend to decrease with increase in molecular weight as shown in Appendix II [CCME, 2008].

2.1 Sources of PAHs in the Environment

PAHs are some of the most widespread organic pollutants in the environment formed by incomplete combustion of organic materials. Anthropogenic sources account for a greater proportion of PAHs than the natural ones. Natural sources of PAHs include forest fires and volcanoes [ATSDR, 1995]. Biogenic sources such as plants, phytoplankton, algae and micro-organisms are minor sources [CCME, 2008; Morillo *et al.*, 2007]. Phenanthrene, for example occurs in plants which may synthesise it biologically, but this source only accounts for background levels [Wilcke *et al.*, 2005].

Anthropogenic sources include wood and fossil fuel combustion, industrial processes such as aluminium production, petroleum refining, fossil fuel power generation, paper milling, coal gasification, coke ovens and iron and steel foundry incineration. Automobile exhaust emissions are also the major sources of PAHs especially in urban areas characterised by heavy traffic flows [Impey et al. 2000; Wong et al., 2004]. Tobacco smoke is a significant source of PAHs, especially in indoor air although wood burning is noted as the single largest source of PAHs in homes [Holton et al., 1984]. PAHs can also be found in coal tar, bitumen and crude oil, creosote and roofing tar [ATSDR, 1995; CPCB, 2003].

Only a few PAHs such as naphthalene, anthracene, phenanthrene, fluorene and pyrene are produced for commercial use. Naphthalene, for example, is used in making dyes, explosives, plastics, lubricants and moth repellents. Due to its inherent high vapour pressure, it may be released directly into the environment. Anthracene is used in making dyes, insecticides and preservatives. Other PAHs are manufactured for research or are used in medicines, cosmetics and pesticides [ATSDR, 1995; CPCB, 2003; Zuydan, 2007].

Due to a great number of chemical events which may take place in the combustion process with different materials, and the complex phenomena involved, PAHs are released as a complex mixture of compounds [Butler, 1979]. The emissions are largely to the atmosphere [Holton et al., 1984]. They then re-circulate into other environmental media such as surface water, sediment, soil, food and lipid tissues of both aquatic and terrestrial organisms [Berko, 2002]. Contamination of PAHs in soils is mainly as a result of dry and wet deposition of atmospheric PAHs, oil spills, dumping of contaminated wastes and burning of organic matter on surface soils.

2.2 Indicators and Source Markers of PAHs in the Environment

There is a complex mixture of PAHs in most environmental samples; the composition of which may depend on the source(s) of input, and possible environmental transformations. The signature or compositional pattern of PAHs can be used to distinguish between combustion-based (pyrogenic) versus petrogenic inputs, or more recently, plant-derived PAHs. The PAH composition in contaminated environmental samples is also useful in delineating between different anthropogenic sources, especially in urbanized, industrialized areas [CCME, 2008].

Benzo(a)pyrene is the most characterised of these compounds and is used as indicator polycyclic aromatic hydrocarbon. Other PAHs such as Benzo(b)fluoranthene, benzo(k)fluorene and indeno(1,2,3,c,d)pyrene have also been identified as emission inventory indicators [UNECE, 1998]. The relative amounts of PAH emissions depends on the fuel used and the thermal process involved [Bruno *et al.*, 2000]. Berko [2002] reported that two and three ring PAHs were responsible for 98, 76, 92, 73 and 80 percent of the total concentration of the measured 20 PAHs from coke ovens, diesel engines, highway tunnels, petrol engines and wood combustion samples, respectively. In the same study, the six ring PAHs such as indeno (1, 2, 3-c, d) pyrene and benzo (g,h,i)pyrene were mostly below detection limit.

Chrysene and benzo (k) fluoranthene are source markers for coal combustion while benzo (g,h,i)pyrene, coronene and phenanthrene are markers for motor vehicle emissions. Phenanthrene, fluoranthene and pyrene are associated with road salt particles, which appear to adsorb volatile PAH emissions from motor vehicles, while, pyrene, fluoranthene and phenanthrene are markers of incineration. Oil combustion is associated with high loadings of the more volatile PAHs (fluorene, fluoranthene and pyrene), along with moderate loadings of

higher molecular mass compounds (benzo(b)fluoranthene and indeno(1,2,3-c,d) pyrene). On the other hand, benzo(a) pyrene and fluoranthene are reported as markers of wood combustion [Berno, 2002].

There is similarity and overlap between profiles from different source categories. These categorizations therefore, serve only as a rule of thumb about what the predominant PAHs are likely to be. Most environmental PAH mixtures include trace quantities of the vast majority of the sixteen priority PAHs [CCME, 2008].

2.3 Mechanism of Formation of PAHs

There seems to be no clear mechanism for PAH formation in the literature but according to Frenklach [2002], the optimum temperature range for PAH formation is 660-740° C and the combustion temperature determines the specific PAHs formed. PAHs form under conditions of incomplete combustion especially in extremely fuel rich regions of flames where hydrocarbon polymerisation reactions are more likely to occur than complete oxidation reactions.

Hydrocarbons with low molecular weights may act as precursors for PAH formation through pyrosynthesis. This may be explained as formation of free radicals by means of scissioned carbon-hydrogen and carbon-carbon bonds. The radicals then undergo dehydrogenation and combine chemically to form aromatic ring structures that are contributory to the PAH formation [Connell, 2005]. The molecules are resistant to thermal degradation and also unsaturated molecules are particularly susceptible to addition reactions in PAH formation. Once formed, PAHs might undergo further pyrolytic reactions to form new PAH compounds [Frenklach, 2002].

2.4 Fate of PAHs in Air and Soil

Once released into the environment, PAHs partition into air, water, soils, sediments and other media. Physical forms of PAHs determine their transport, behaviour, degradation and their subsequent fate in the environment [ATSDR, 1995; Berno, 2002; CCME, 2008]. In the atmosphere, PAHs are partitioned between the vapour and solid phases. Two ringed PAHs such as naphthalene exist exclusively in the vapour phase. Those with three to four rings occur as either gases or particles in air; while five or more ringed PAHs tend to be solids, which are adsorbed onto particulate matter in the atmosphere [ATSDR, 1995].

PAHs are removed from the atmosphere by transformation, especially photochemical and thermal reactions involving hydroxyl radicals, oxygen, ozone and oxides of nitrogen and sulphur, and by wet and dry deposition [ATSDR, 1995; CCME, 2008]. Sub-micron particles in air have a higher surface area and may contain higher organic carbon allowing more adsorption of PAHs [Sheu *et al.*, 1997]. Soils, especially those with high organic fractions are the main primary sinks of PAHs in the environment

PAHs are removed from soils principally by volatilization and microbial activity. Photolysis accounts for their minor transformation in soil. The extent of removal of PAHs varies; depending on several factors such as temperature, soil type, pH, oxygen content, presence of other contaminants and previous contamination. The microbial population of the soil and the properties of the PAH present are also important factors [CCME, 2008; CPCB, 2003]. Contaminated soils release light weight, volatile PAHs especially acenaphthene, fluorene and phenanthrene, which act as atmospheric sources of PAHs [Cousins and Jones, 1998; Wicke *et al.*, 2005]. PAHs with three or more rings bind tightly to soils and sediments rich in organic carbon, from where they are difficult to dissipate [Guerin, 1998; Morrillo *et al.*, 2007].

Microbial degradation is mainly applicable to lighter PAHs, while that of the compounds with four or more rings is slower, making them more persistent in soils [Morrilo *et al.*, 2007].

2.5 Human Exposure to PAHs

PAHs are found everywhere in the environment: in soil, dust, air, water, food and some household products. The most dominant routes of exposure are by active and passive inhalation of the compounds in tobacco smoke and contaminated air, and ingestion of the compounds in foodstuffs. Higher than background levels of PAHs are found in foods that are roasted, grilled or smoked [ATSDR, 1995; FAO/WHO, 2004]. Other modes of exposure include drinking contaminated water or through skin contact with soot, tars or contaminated soils. Nursing infants of mothers living near hazardous waste sites may also get exposed through their mother's milk [ATSDR, 1995].

Intake of PAHs from contaminated soil may occur via ingestion, inhalation or dermal exposure to contaminated soil or dust and from inhalation of PAH vapours. Tilling of dry soil can result in ingestion of small but significant amounts of PAHs [ATSDR, 1995; Butler 1979]. Young children are prone to behaviour that may increase their potential for exposure, such as by crawling on bare dirty surfaces, eating soil, and more hand-to-mouth activities [ATSDR, 1995].

2.6 Some Adverse Health Effects Associated with PAHs

PAHs have been associated with adverse effects on human health since they were first linked with skin cancers among young British chimney sweepers as early as 1775 and German coal tar workers in the late 1800s [Butler, 1979; Heitkamp, 1988]. The International Agency for Research on Cancer (IARC) has classified PAHs as being carcinogenic or potential carcinogens. Table 2.2 shows this classification of the PAHs of interest [CCME, 2008].

Table 2.2: IARC Classification of Carcinogenicity of PAHs of Interest

IARC Group 1(carcinogenic to humans)	IARC Group 2 (probably carcinogenic to humans)	IARC Group 3 (possibly carcinogenic to humans)	IARC Group 4 (Not classifiable due to limited data)
Coal tars	Benzo(a)pyrene	Benzo(b)fluoranthene	Anthracene
Coal pitches	Benzo(a)anthracene	Benzo(k)fluoranthene	Benzo(ghi)perylene
Coke production	Dibenz(ah) anthracene	Indeno(1,2,3,cd)pyrene	Chrysene
Shale oils		Naphthalene	Fluoranthene
Soot			Fluorene
Tobacco smoke			Phenanthrene
			Pyrene

Source: CCME, 2008

The chemical carcinogenicity of PAHs is initiated by transformation of bio-available PAHs into active metabolites that can finally bind to deoxyribonucleic acid (DNA) to form covalent adducts potentially leading to mutations [CCME, 2008; Sram *et al.*, 2005]. There are a large number of biochemical mechanisms that are capable of repairing this initial mutation and thereby arresting carcinogenesis at the initiation stage. However genotoxicity, as the major part of initiation can be further potentiated by other non-carcinogenic PAHs that increase the rate of bio-activation and/or decrease the rate of detoxification and elimination from the body of reactive intermediate metabolites [CCME, 2008].

Epidemiological studies indicate that prolonged exposure to particulate air pollution enriched with PAHs is associated with increased risk of cardiovascular disease and cancer in general populations as well as affecting pregnancy outcomes. Embryo toxicity *in vivo* and *in vitro* studies as well as chromosome aberrations have also been reported [Sram *et al.*, 2005].

PAHs have also been found to cause morphological, physiological, and developmental abnormalities in test animals; increase allergic immune responses in humans at low levels; and act synergistically with other air toxicants such as ozone in causing adverse health effects [ATSDR, 1995; IARC, 1983; UNESCO-ICCS, 1996]. Mixtures of PAHs are known to cause skin effects in animals and humans such as irritation and inflammation [Friedmann, 2005]. Anthracene, benzo(a)pyrene and naphthalene are direct skin irritants while anthracene and benzo(a)pyrene are reported to be skin sensitizers [UNESCO-ICCS, 1996].

A summary of some toxicological data for selected PAHs found in the environment is given in Table 2.3.

Table 2.3: Toxicity of some PAHs found in the Environment

Substance	Toxicity,LD_{50} (mg/kg; rats)[1]	Chronic effects[1]	Carcinogenicity[2]
Acenaphthylene	1700(intra-periconeal)	tumorigen,mutagen	data no reported
Anthracene	430 (intra-peritoneal)	mutagen, irritant	data no reported
Benzo(a)anthracene	200 (intravenous)	tumorigen,mutagen	moderate
Benzo(a)pyrene	50 (subcutaneous)	tumorigen, mutagen, irritant,teratogen	extreme
Benzo(b)fluoranthene	Data not Reported	tumorigen,mutagen	high
Benzo(k)fluoranthrene	Data not Reported	tumorigen, mutagen	data no reported

Sources: 1.UNESCO-ICCS, 1996; 2. Butler, 1979

Other health effects from chronic exposure to PAHs may include cataracts, kidney, and liver damage and jaundice whereas repeated contact with skin may induce dermatitis and skin inflammation. Naphthalene can cause breakdown of red blood cells if inhaled or ingested in large amounts and lead to anaemia. The acute effects due to inhalation or ingestion are

headaches, dizziness and vomiting. In worst cases, death resulting after kidney failure can occur [Rodriguez, 2004].

2.7 Guidelines for PAHs in the Environment

Continuous monitoring of levels of PAHs and related risk assessment of guidelines on the threshold limit values for PAHs are limited. The OECD countries; France, Japan, Germany, Netherlands, Sweden and Switzerland have prescribed emission standards of PAHs with benzo(a)pyrene as an indicator species. WHO and the Netherlands have prescribed ambient Air Quality Guidelines (AQG) as outlined in Table 2.4 below [CPCB, 2003].

Table 2.4: Ambient Air Quality Standard for the PAHs

Compound	Limit Value	Guide Value	Measuring Period
Netherlands PAH	5 ng/m^3	0.5 ng/m^3	Years as ng benzo(a)pyrene/m^3
WHO-AQG PAH	None	1.0 ng/m^3	Years as ng benzo(a)pyrene/m^3

Although the limits are not legally binding, it is common consensus that PAHs require maximum emission reduction or 'zero levels'. For instance, there is no known cancer threshold for benzo(a)pyrene and no safe level can be recommended for this PAH due to its carcinogenicity. The European Union has proposed ambient limits for PAH indicator parameter Benzo(a)pyrene at 6.0 ng/m^3 [CPCB, 2003].

The major limitation is that complete removal of PAHs from the environment is impossible, and therefore they can only be controlled. This requires standards to be set on the basis of the dose-response carcinogenesis bioassays that can be extrapolated to man. On the basis of such

evaluation, the former Union of Soviet Social Republics (USSR) Ministry of Health proposed the maximum allowable concentration (MAC) of Benzo (a) pyrene at $0.1 ng/m^3$ in ambient air and 15 ng $/m^3$ for industrial working zones. MAC for other PAHs is yet to be set up [CPCB, 2003].

The USEPA has offered an upper bound lifetime cancer risk estimate of 62 per 100,000 exposed people per μg benzene soluble coke-oven emission per cubic metre of ambient air. The public health concern is that PAHs are spread over large urban population. The guideline values for benzo(a)pyrene corresponding to an excess lifetime cancer risk of 1 per 100,000 exposed people was estimated at 0.7mg/L in Guideline for drinking water quality.

WHO (1984) guidelines for drinking water have given PAH standard for water for the concentration of six representative PAHs: fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3 cd)pyrene not to collectively exceed 0.2 μg/litre. The limit for benzo(a)pyrene is 0.01 μg/L. The European Commision drinking water guideline (98/83/EC) also gives special attention to Benzo(a)pyrene and has set a threshold limit of 10 ng/L for this single compound [CPCB, 2003].

The Danish criteria for the level of $\sum16$ PAHs in soil quality for human and ecological health are 1.5 mg/kg and 1.0 mg/kg, respectively. Limit levels for benzo(a)pyrene and dibenz(a,h)anthracene are 0.1 mg/kg for both human health and ecological risk. The Netherlands has set maximum permissible limits (MPC) for PAHs in water, soil and sediment as shown in Table 2.5 [CCME, 2008].

Table 2.5: Netherlands Maximum Permissible Concentrations of PAHs

PAHs	MPC-WATER (µg/l)	MPC-SOIL (mg/kg)	MPC-SEDIMENT (mg/kg)
Naphthalene	1.2	0.14	0.14
Anthracene	0.07	0.12	0.12
Phenanthrene	0.3	0.51	0.51
Fluoranthene	0.3	2.6	2.6
Benz[a]anthracene	0.01	0.25	0.36
Chrysene	0.34	10.7	10.7
Benzo[a]pyrene	0.05	0.26	2.7
Benzo[g,h,i]perylene	0.033	7.5	7.5
Benzo[k]fluoranthene	0.04	2.4	2.4

(Source: CCME, 2008)

2.8 Levels of PAHs detected in Urban Areas

The concentration of human activities in urban areas and cities implies higher levels of PAHs in urban environments than in rural ones. The highest concentrations of PAHs in soils occur in urban areas near point sources and in soils with high organic matter [Morrilo *et al.*, 2007; Zuydam, 2007]. In a study by Wong *et al.* [2004] carried out from Downtown Toronto to approximately 8 km away from the city, the concentration of PAHs in soils decreased along the urban-rural profile. Total concentrations (ng/g) at the urban sites of High Park and Riverdale were 3922 and 1750, respectively and were approximately ten times greater than those at the sub-urban locations of New York (662 ng/g), Downsview (320 ng/g), Aurora, (212 ng/g) and Richmond (82) ng/g. The rural background level of PAHs at Borden was 61 ng/g.

Similar trends were observed in ambient air on a rural urban transient. Impey *et al.* [2000] reported concentrations of fluorene and indeno(1,2,3,cd)pyrene at rural sites ranging from 9.4 pg/m^3 to 111.9 pg/m^3 at rural sites and 11.2 pg/m^3 to 520.6 pg/m^3 at urban sites. In a study in France, the highest concentrations of PAHs (pg/m^3) were detected in the traffic tunnel:

fluorene, 1448; fluoranthene, 3284.2; pyrene 4738.2; benzo(a)pyrene 17001.1; indeno(1,2,3,c,d) pyrene 2341.1; and dibenzo(ah) anthracene 376.7 [Garban *et al.*, 2002].

Data for environmental concentration of PAHs in Kenya is limited. Some research on PAH levels in Nairobi has been done on aerosols [Gatari *et al.*, 2006] and air particulate matter [Muthini *et al.*, 2006]. Mwakwari [1999] reported the presence (without quantification) of naphthalene, fluorene, phenanthrene and chrysene in air and soil.

Gatari *et al.* [2006] targeted PAHs with sampler cut off aerodynamic diameter of 30-50 μm over the city of Nairobi at 25 m above the ground. The average concentrations of PAHs ranged between 0.1 and 8.1 ng/m^3 and are comparable with those in other major cities in the world [Berno, 2002; Impey *et al.*, 2000]. The most abundant PAHs were chrysene, benzo(a)anthracene, benzo(k)fluoaranthene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3,-c,d)pyrene, benzo(g,h,i)perylene and coronene; implying low air quality during the measurement period.

Median PAH concentrations in three zones studied by Muthini *et al.* [2002] were highest in the area with high traffic volume (201 ng/m^3), followed by residential area (141 ng/m^3), and lowest in industrial area (128 ng/m^3) in Nairobi. Of the 26 PAHs reported, pyrene was the most abundant PAH, with concentrations ranging between 0.53 ng/m^3 and 42.2 ng /m^3. The findings suggested higher loadings of PAHs nearer the ground surface than levels in aerosol in another study in the city by Gatari *et al.* [2006].

2.9 Principle of Passive Air Sampling

The most widely used methods for sampling gas and vapour contaminants in air consist of either drawing a known volume of air through a suitable adsorbent material or porous

polymer. However, both sampling techniques require "active" pumping of the air stream through the sample device and hence restricted for use only where a power source is available. In recent years, a simpler and more cost-effective alternative to the conventional pumped sampling systems have been developed in the form of what is referred to as "passive" samplers [Berko, 2002; Brown *et al.,* 1984; Klanova *et al.,* 2008; Kohoulek *et al.,* 2006].

Passive sampling devices do not require pumps since they rely on gaseous diffusion or permeation gradients towards a surface [Brown *et al.,* 1984]. Passive air samplers have low sensitivity to accidental short–term changes in the concentration of pollutants and provide information on the long term contamination of air [Kohoulek *et al.,* 2006]. These samplers therefore offer a simple method of measuring time-weighted average concentration of airborne gases and vapours for integrated sampling measurements. Air streams move freely around a filter membrane or other medium which captures pollutants during the period of passive sampling [Klanova *et al.,* 2008].

In order to obtain reasonable quantities of PAHs (and POPs) for analysis, sampling is done over a twenty eight day period [Klanova *et al.,* 2008; Kohoulek *et al.,* 2006]. The estimated average passive sampling rate of air using polyurethane foam plugs is 3.57 m^3/day. Thus, during the four weeks of passive sampling, about 100 m^3 of air is obtained, equivalent to the volume of air sampled actively for one day. Therefore, a conversion factor of 0.01 is applied to the concentration of analytes per filter to obtain the amount of analyte(s) per cubic metre.

The adsorbent used for sampling of airborne PAHs determines which phase; particulate or gaseous, is trapped. Efficiency of collection of PAHs is dictated by their physical state: whether it exists entirely in solid phase or partly in vapour phase. PAHs associated with

particles are usually collected on filters such as fibre glass, quartz fibres or polytetrafluoroethylene (PTFE) or PTFE coated fibre, from where they are vaporised. Due to good mechanical strength and low cost, fibre glass is the popular choice for airborne particulate matter samples [Berko, 2002]. Vapour phase PAHs can also be trapped by a back up solid adsorbent on the filter.

Vapour phase PAHs are normally trapped onto plugs of polyurethane foam (PUF). Other adsorbents that have been successfully used to trap PAHs include Amberlite XAD-2 (a styrene –divinylbenzene polymer resin), Porapak PS and Tenax GC. PUF, unlike the alternative adsorbents also effectively traps other organic contaminants in air such as pesticides, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo furans (PCDFs). In addition, PUF cartridges are easier to handle in the field and demonstrate superior flow characteristics during sampling [Berko, 2002].

2.10 Statement of the Problem

Nairobi is a fast growing city with increasing levels of industrialisation and urbanisation. The domestic, commercial and industrial activities in Nairobi lead to release of solid wastes, effluents and emissions to the atmosphere, water and soils. Combustion processes in particular, emit PAHs to the environment, posing a health hazard to humans and the environment. The city does not have air and soil quality regulations in place and also has low capacity for environmental monitoring [UNEP/WHO, 1996]. The Environmental Management and Coordination Act (EMCA) air quality draft regulations for Kenya does not include PAHs as priority pollutants for Kenya [EMCA, 2008].

Data on PAHs and other organic pollutants in air from Nairobi is limited. The scarcity of data on PAHs in air may be attributed to the elaborate sampling and analytical protocols for these

compounds. The traditional active air sampling equipments that require electricity are out of reach for most developing African countries such as Kenya. There is therefore a need to adopt a more affordable method for air sampling.

The passive air sampling technique was employed as a suitable alternative for use in monitoring of PAHs and other POPs with a view of adapting it for regular air quality monitoring. Analysis of PAHs in soils was carried out as a complementary survey to that of air quality since soil are significant primary sinks of atmospheric PAHs.

The work reported in this thesis contributes to the wider Pilot study for the development of the Monitoring Network in Africa (MONET-Africa) for the Global Atmospheric Passive Sampling (GAPS) Network of the Global Monitoring Plan (GMP) of POPs under the Stockholm Convention. Kenya is one of the fifteen African countries which participated in the survey on persistent organic pollutants (POPs) including pesticides and PCBs. PAHs, though not formally classified as POPs, have been identified as candidates for monitoring owing to their harmful effects on human health and the environment; and their potential for long range transport.

Studies on these contaminants in soil in Kenya are also limited. The study addresses part of the information gap on baseline data for PAHs' in air and soil. The thesis provides the background information and rationale for the development of air and soil quality guidelines for the protection of the environment and human health from potential carcinogenic and other PAHs. The baseline data will be useful for developing and updating the National Inventory on PAHs and other POPs in Kenya. This is vital in evaluating the risk of exposure of humans and other life forms to PAHs and is hoped to inform policy formulation for mitigation purposes.

2.11 Objectives of the Study

Overall objective

To assess the pollution status of Nairobi City with respect to PAHs and provide baseline data on the level of concentration of PAHs in ambient air and soils with a view to inform policy makers to put in place a regular environmental monitoring programme for PAHs.

Specific Objectives

1. To determine the nature, levels and spatial distributions of PAHs in air and soil in Nairobi.

2. To investigate the temporal and seasonal variations of the concentration of PAHs in ambient air and soils at selected sites in Nairobi.

3. To establish the correlation between concentrations of PAHs in ambient air and soils.

CHAPTER THREE

EXPERIMENTAL SECTION

3.1 Description of Study Area

Nairobi, the capital city of Kenya is a rapidly growing city with a population of over 3 million people [CBS, 2009]. The City is located South of the equator approximately between $36^{\circ} 45"E$ to$37^{\circ} 05"E$ and $1^{\circ} 10"S$; to $1^{\circ}30''S$ at a mean altitude of 1700 m above sea level. It covers an area of about 700 km^2 and is the administrative, commercial, and industrial centre of Kenya. Commercial and administrative activities are concentrated at the central business district while most of the industrial activities are located to the South East.

Nairobi has a subtropical climate and has four major seasons: the warm dry season (from December to mid March), the long rainy season (from end of March to the end of May), the cool and dry season (June to October) and the short rainy season (October to November). Temperatures generally vary from $11^{\circ}C$ in the June /July season to about $29^{\circ}C$ from December to March [BBC, 2009]. The prevailing winds are mainly North Easterly, with speeds generally fluctuating between 2.50 and 7.50 m/s [Gatari and Boman, 2003; Wafula, 1999].

The study covered three sites in Nairobi on the basis of the potential effects of anthropogenic activities. A municipal dumpsite in Dandora, and Industrial Area were selected as the urban hot spots in addition to Kabete as the urban background site. The map of the study area is given in Figure 2.1.
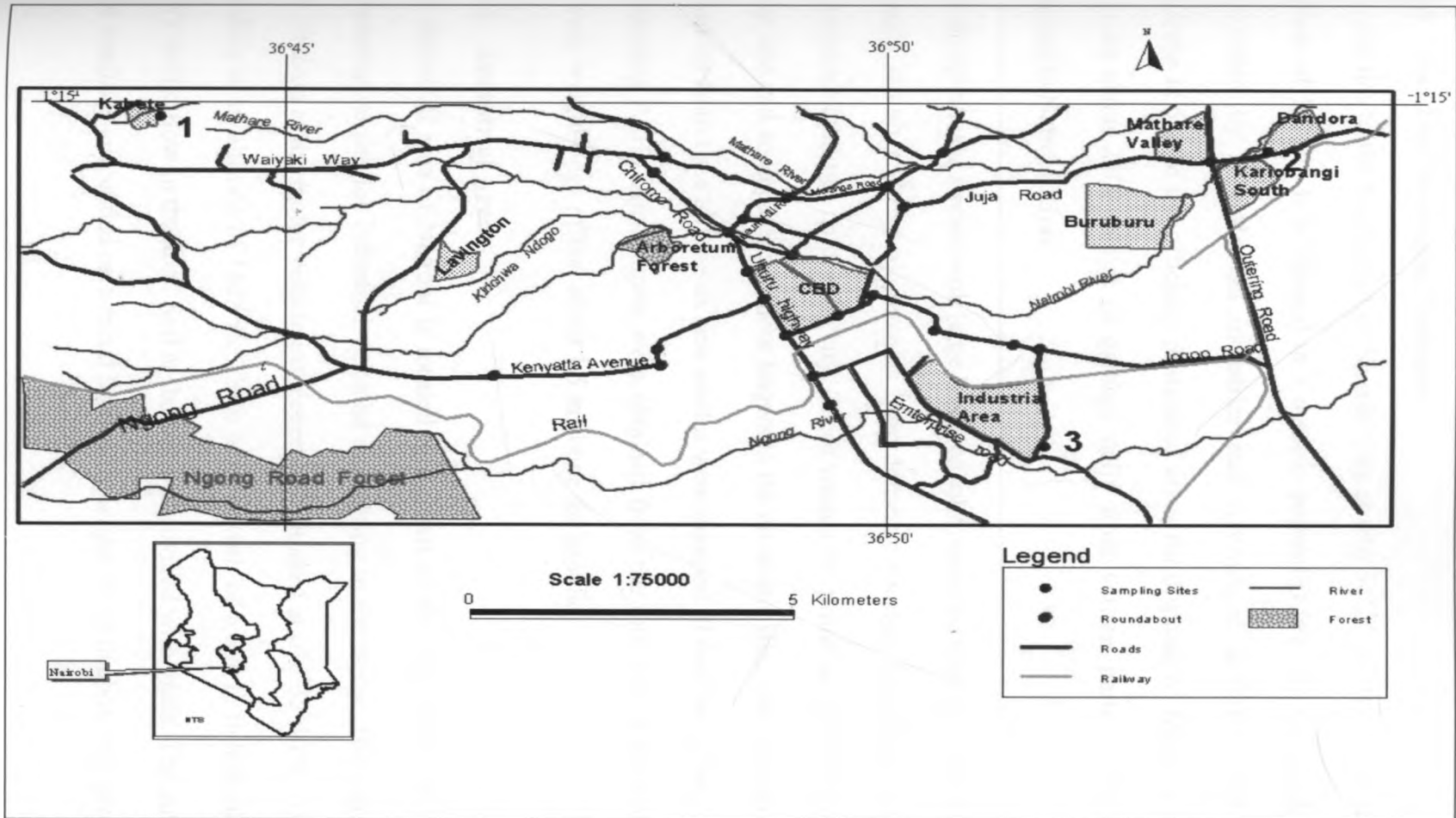
Source: Survey of Kenya

Figure 2.1: Map of the Study Area

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3.1.1 Dandora Municipal Dumpsite

The site lies to the South East of Nairobi City at $036^0 54'22"E$, $01^0 14'35"S$ and at an altitude of 1625m. It is situated in a densely populated low income residential area surrounded by several light industries and commercial activities. The Dandora dumpsite is one of the officially designated areas for disposal of waste in the city. It receives about 2000 tonnes of garbage daily from various parts of the city. It is adjacent to Nairobi River.

The dumpsite was strewn with large heaps of solid waste consisting of unsorted paper, plastics, metals and organic remains from domestic sources, industries, medical and commercial facilities across the city. These wastes are prone to spontaneous burning at the site and an unpleasant odour lingers in the air at this site. Soil was bare and was mixed up from time to time as new wastes were dumped. It was the urban hotspot for monitoring PAHs. Air samples were obtained from the roof top of the Nairobi City Council weighbridge office, about 1.5 m above the ground.

3.1.2 Industrial Area

The industrial area of Nairobi is located to the east of the city centre. This was the representative site for industrial–oriented monitoring in the study. The sampling site was situated at the motor vehicle inspection unit situated at $036°52'30"E$, $01°18'24"S$ standing at an altitude of 1623 m. There is a network of roads in industrial area and heavy traffic flow in the area. Soil at the site was covered with grass. The air samplers were similarly suspended on a metal frame at a height of 1.2 m above the ground.

3.1.3 Kabete

The Kabete Campus of the University of Nairobi has low human settlement with no industrial activities. Though there is minimum traffic at the site, it is situated about 2 km away from a major highway and serves as the urban background site in the study. Soil at the site was covered with grass. Soil and air samples were obtained from the premises of the Kabete Meteorological station situated at 036° 44' 33" E, 01°14 58" S and standing at 1841 m above sea level.

3.2 Air Sampler Description

Passive air samplers consisted of two stainless steel bowls with diameters of 30 cm and 24 cm respectively positioned on a common axis, which also fixed the filter in position. All other parts of the sampler (hooks, pads, nuts and tubes) were made from stainless steel. Figure 2.2 shows the schematic diagram of the air sampling devices used in the study.
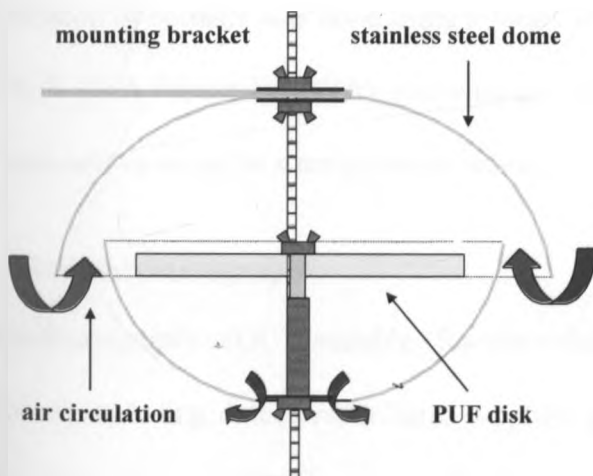
Figure 2.2: Schematic Diagram of the Passive Air Sampling Device

Filters made of white, non-coloured polyurethane foam (PUF) with density of 0.030 kg/m^3 (type N3038; producer Gumotex Breclac, Czech Republic) were used as an adsorbent for passive sampling of PAHs. The filters were circular in shape with thicknesses measuring 15 mm and a diameter of 150 mm, with a 15 mm stainless steel insert to fit on the central axis of the sampler.

3.3 Instrumentation and Laboratory Devices

3.3.1 Soxhlet extractor

Extraction of PAHs from soil and PUF adsorbents was carried out in a Soxhlet extractor using appropriate solvents according to established USEPA methods. The soxhlet apparatus consisted of a 500 ml round bottomed flask, a condenser and extractor tube seated in a temperature controlled heating mantle (Electrothermal Unimantle, UM0250/IT).

3.3.2 Rotary evaporator

Concentration of extracts was done using a rotary evaporator (Labconco,) loaded with water bath (IKA-Wasserbad WA) and vacuum pump (Welch 1399, DuaSeal). The water bath was operated at a temperature between 35 and 40 °C.

3.3.3 Gas Chromatographs

Gas chromatographs (GC) suitable for on-column injections and all required accessories, including detectors, column supplies, gases, syringes and auto-samplers were used for the quantification of the PAHs. Analysis of PAHs was done using a Varian gas chromatograph fitted with a flame ionisation detector (GC/FID) with fused silicon capillary column (30 m x 0.25 mm I.D. SE-54) using helium as the carrier gas and nitrogen as make up gas. A gas chromatograph fitted with a mass spectrometer

(GC/MS, HP 6890-HP 5972) with a fused silica column DB-5MS at the Research Centre for Environmental Chemistry and Toxicology (RECETOX) laboratory in Czech Republic was used for confirmatory analysis.

3.4 Reagents and Chemicals

High performance liquid chromatography (HPLC) grade hexane (Pancreac Quimac, SA), acetone (Sigma-Aldrich) and dichloromethane (amylene stabilized, Fisher Chemicals) were used for extraction of air samples. Triple distilled general purpose grade hexane and dichloromethane were used for extraction of soil samples.

Analytical grade granular sodium sulphate (Riedel-de Haen, Germany) was used as the drying agent. Alumina (analytical grade, neutral activity, 70-230 mesh, ASTM) was used as the adsorbent for cleanup of sample extracts. HPLC grade Triphenyl benzene in isooctane (Dr. Ehrenstorfer GmbH, Augsburg, Germany) was used as the recovery standard while benzylbenzoate was used as the syringe normalisation standard.

3.5 Methodology

Air and soil samples under the samplers were collected on a monthly basis between February and August 2008 from the three selected sites. The first air sampling campaign was launched in February while soil sampling was started in March to coincide with the end of the first air sampling. This captured three main seasons of the end of dry and sunny season in February, long rains between March and May and the cool dry season in June to August. The short rains which were due in October to December fell outside this study.

Soil and air samples were extracted by Soxhlet extraction. Sample extracts were then concentrated by rotary evaporation, cleaned and concentrated to the desired volume with a slow stream of ultra-pure nitrogen. Each sample was spiked with a known amount of internal standard followed by GC/FID analysis. Confirmatory analyses were done by GC/MS at the RECETOX Laboratory.

The PAHs analysed were assigned numerical numbers 1-16 as follows: naphththalene (PAH1), acenaphthylene (PAH2), acenaphthene (PAH3), fluorene (PAH4), phenanthrene (PAH5), anthracene (PAH6), fluoranthene (PAH7), pyrene (PAH8), benzo(a)anthracene (PAH9), chrysene(PAH), benzo(k)fluoranthene (PAH11), benzo(k)fluoranthene (PAH12), benzo(a)pyrene (PAH13), dibenzo(ghi)perylene (PAH14), indeno(1,2,3,cd) pyrene (PAH15) and dibenzo(ah) anthracene (PAH16).

3.5.1 Sampling and Treatment of Air samples

3.5.1.1 Air Sampling Procedure

Samples of air were collected in duplicates using passive samplers fitted with foam (PUF) plugs. The samplers consisted of two stainless steel bowls of diameters 30 cm and 24 cm positioned on the same axis so as to also support the polyurethane foam plugs. The bowls were pre-cleaned by rinsing with absolute ethanol prior to assembling the passive samplers as described by Kohoutek et al. [2006].

The samplers were then hooked freely onto support stands so as to hang vertically, with the larger bowl up. Sampling at the Kabete and Industrial area sites were placed at a height of 1.2 metres above the ground. At the Dandora site the samplers were hung on top of a building resting at 3.5m above the ground for security reasons. The samplers were left at the sites for a period of 4 weeks. At the end of each sampling

period, the PUF plugs were removed from the samplers and wrapped in double layers of aluminium foil and placed on top of ice in a cooling box at 4 °C and transported to the Laboratory for storage in a freezer at -20 °C.

3.5.1.2 Preparation of Reagents

Anhydrous sodium sulphate was baked out in an oven at 400 °C for 16 hours in a shallow tray to remove all moisture and cooled to room temperature in a vacuum dessicator before use. Alumina for clean- up was baked out in an oven at 450 °C for 16 hours to remove impurities. It was then allowed to cool to room temperature and deactivated by adding 8 ml distilled water to 92 g alumina (8 % deactivation). The deactivated alumina was then conditioned for 12 hours before use.

A certified 16 USEPA PAHs mixture standard stock solution of 10 µg/ml (Dr. Ehrenstorfer GmbH; Augsburg, Germany) was used for preparing multi-level calibration curves for identification and quantification of PAHs. Calibration standards of concentrations between 0.0301 and 6.304 µg/ml were prepared by reconstitution in isooctane.

3.5.1.3 Extraction of Air Samples

The PUF sorbents initially stored in the freezer were removed and allowed to attain room temperature for 6 hours. The foam plugs were then placed in the extraction thimbles and were spiked with 100 µg/ml triphenyl benzene recovery standard. The samples were extracted in a sohxlet extractor using 135 ml hexane/acetone 3:1 (v/v) mixture followed by dichloromethane in a sohxlet extractor for 16-18 hours for each

solvent. Sample extracts were concentrated in a rotary evaporator to about 5ml before clean-up.

3.5.1.4 Cleanup of Air Samples

A glass column (with frit) was packed with a layer of 1cm of baked out sodium sulphate, followed by 15 g of deactivated alumina and another 1cm layer of baked-out sodium sulphate. The sides of the column were gently tapped during packing to ensure it was packed homogeneously. The column was conditioned with 15ml of hexane and the sample eluted using 100 ml of hexane followed by 100 ml dichloromethane.

The eluate was then concentrated to about 2 ml using a rotary evaporator, transferred into a glass vial and further reduced to about 0.5 ml under a gentle stream of nitrogen at room temperature. 100 µl of benzyl benzoate syringe standard was added before GC/FID analysis.

3.5.1.5 Treatment of Air Samples for Confirmatory Tests

Samples at the RECETOX laboratory were extracted with 100 ml dichloromethane in a Buchi systemB-811 automatic extractor. One laboratory blank (unused polyurethane foam plug) and one reference material were analysed with each set of ten samples. Surrogate recovery standards d8-naphthalene, d10-phenanthrene and d12-perylene were spiked on each filter prior to extraction. Triphenyl benzene (terphenyl) in isooctane was used as the internal standard for PAHs.

The volume of each air sample extract was reduced to 1ml under a gentle stream of nitrogen at ambient temperature. Fractionation was done on a silica gel column prior

to analysis. The eluate was concentrated to 1 ml under a gentle stream of nitrogen prior to analysis using a gas chromatograph fitted with a mass spectrometer (GC/MS).

3.5.2 Sampling and Treatment of Soil samples

3.5.2.1 Soil Sampling and Preparation Procedure

At each site, random composite soil samples of 10 cores were taken from 0 to 10 cm depth (root layer) with a stainless steel shovel over an area of about 16 m^2. Roots, leaves and stones were removed from each sample. The samples were then put in aluminium foil, mixed thoroughly and sub-sampled by serial quarterly method to obtain a representative bulk of about 300 g. The soil samples were then packed in two layers of aluminium foil, placed in zip lock plastic bags and placed in a cooling box at 4 °C and transported to the laboratory for storage in a freezer and maintained at -20 °C awaiting analysis.

3.5.2.2 Determination of Soil Moisture Content

The aliquot of about 5 g of each soil sample was placed in a pre-weighed crucible and dried overnight at 105 °C. The samples were allowed to cool in the oven and then weighed. The percentage mass of water lost was calculated to obtain moisture content for each sample and the sample discarded. The values obtained were used to calculate the dry weights of the soils.

3.5.2.3 Drying and Extraction of Soil Samples

Granular anhydrous sodium sulphate (approximately 3g Na$_2$SO$_4$ per 1 g soil sample) was used as the drying agent.10 g of each soil sample was blended with 30 g anhydrous sodium sulphate in 250 ml beaker, covered and left to dry for 4-6 hours. Dried soil samples were transferred into the Soxhlet thimbles and 100 µl of 100 ppm

triphenyl benzene in isooctane recovery standard solution added. Soxhlet extraction was carried out using hexane/acetone (3:1; v/v mixture) followed by triple distilled dichloromethane. 135 ml of each of the solvent regimens was put in a 500 ml round bottomed flask and extraction with each solvent carried out for 16-18 hours.

2 ml of isooctane was added to each extract as a keeper and the extracts concentrated to about 3 ml using the rotary evaporator. Concentrated samples were then transferred to amber vials, rinsing the flasks three times with 1 ml of hexane/acetone (3:1, v/v mixture). The sample extracts were further reduced to 1ml by evaporation at room temperature under a gentle stream of nitrogen.

3.5.2.4 Clean-up of Soil Samples

Soil sample extracts were cleaned using hexane/acetone mixture followed by dichloromethane in the same manner as described for air samples in section 3.5.1.4.

3.5.3 Analytical Method

3.5.3.1 Analysis of PAHs in Soil and air Samples

Quantitative analysis was conducted using external calibration with multilevel calibration curves obtained from the 10 µg/ml of 16 USEPA mixture standard stock solutions. Peak areas were normalised using 100 µg/ml benzyl benzoate as syringe standard which was added to each sample just before injection into the GC.

Analysis of PAHs in air and soil was conducted employing fused silicon capillary column (30 m x 0.25 mm I.D. SE-54). Varian gas chromatograph (GC) was used with helium as the carrier gas at a flow rate of 20 cm^3/s. White spot nitrogen was used as the make-up gas. The initial column temperature was 100 °C and increased at 4 °C/

minute to 280 °C with hold time of 15 minutes. 1 µl aliquot of the extract was injected into a GC using the flush technique and the sample analysed in a splitless mode. Confirmatory analysis was done at RECETOX laboratory using GC/MS (HP 6890-HP 5972) supplied with a fused silica column DB-5MS.

3.5.3.2 Quantification of GC Chromatograms and Evaluation of Results

Star GC Workstation software was used for evaluation of the chromatograms and calculation of the concentrations in the samples. Quantification of individual PAHs in the samples was done using multilevel calibration curves of each analyte in a standard mixture of the 16 USEPA PAHs. In every analysis the peak sizes of surrogate internal standard and syringe standard were quantified and used for quality control. Reagent blanks, matrix spikes and replicate samples were subjected to exactly the same analytical procedures as those used for actual samples.

3.5.4 Quality Assurance and Quality Control

Anhydrous sodium sulphate was used as the soil matrix blank. 10 g of the blank was extracted and treated in the same way as the samples to test the effect of the solvents on the analytical method. Polyurethane foam plugs pre-extracted using dichloromethane were wrapped in aluminium foil and carried to the field during each sampling trip. These were stored and treated in the same way as air samples to serve as field and laboratory blanks for air.

Soil samples were sub-sampled and analysed in triplicate while air samples were sampled and analysed in duplicate. Method recoveries were determined for all samples by spiking with triphenyl benzene as surrogate standards prior to extraction. Benzyl benzoate was used as syringe standard for normalisation of GC responses.

Confirmatory analysis for PAHs in air was done using GC/MS at the RECETOX laboratory and results were comparable with those at the University of Nairobi laboratory.

3.5.5 Statistical Analysis

Statistical analysis was done using the statistical package for social scientists (SPSS). Comparison of means was done using t-tests and analysis of variance (ANOVA). Bivariate correlations were done using Pearson's correlation coefficients. Statistical data is reported using the American Psychological Association (APA) format [APA, 2001].

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Calibration Curves and Chromatograms

Multi-level calibration curves were used to quantify PAHs in soil and air. A sample chromatogram of the calibration reference standards used for quantification of PAHs is given in Figure 4.1. The horizontal axis shows the retention time of each analyte which increases with the relative molecular weight of the PAHs while the vertical axis shows the detector response.
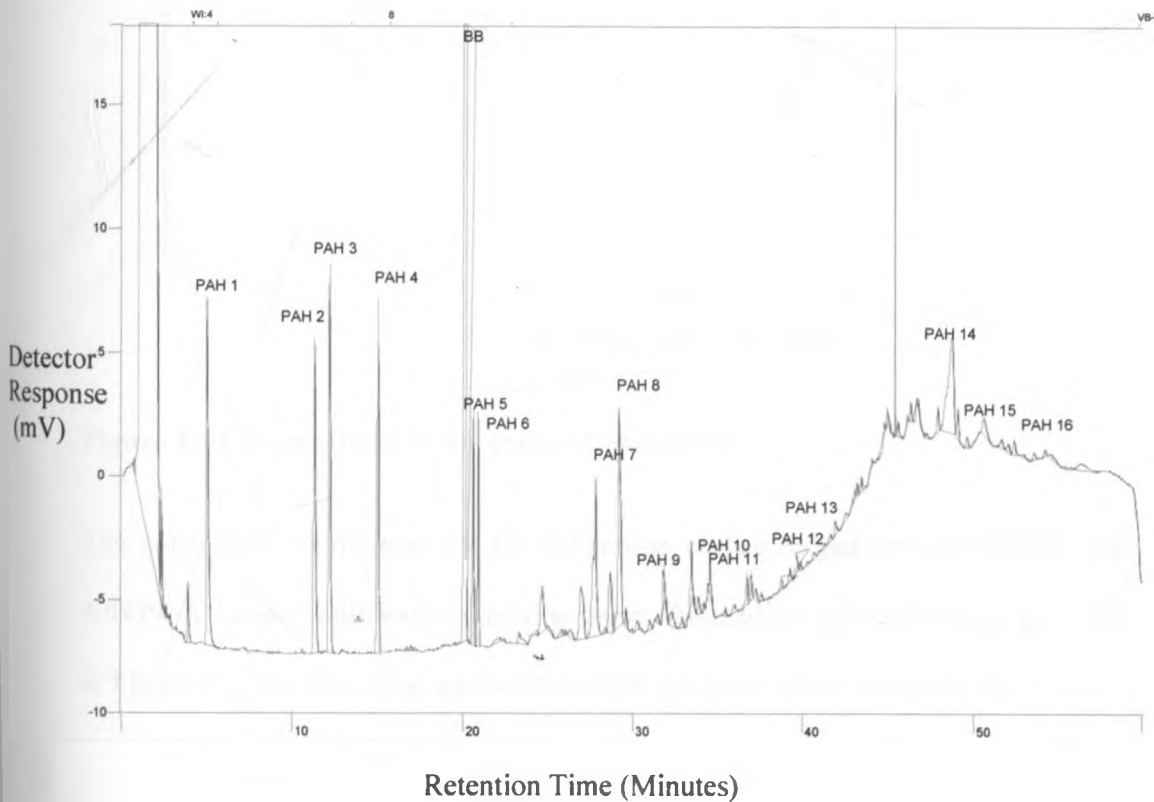
Figure 4.1 Sample Chromatogram for Reference Standards

Figure 4.2 below shows the chromatogram of the internal standards only. The first peak at retention time of about 20 minutes is for benzyl benzoate which was used as the peak normalisation standard while the second one at retention time of about 46 minutes is for the triphenyl benzene, the recovery standard.
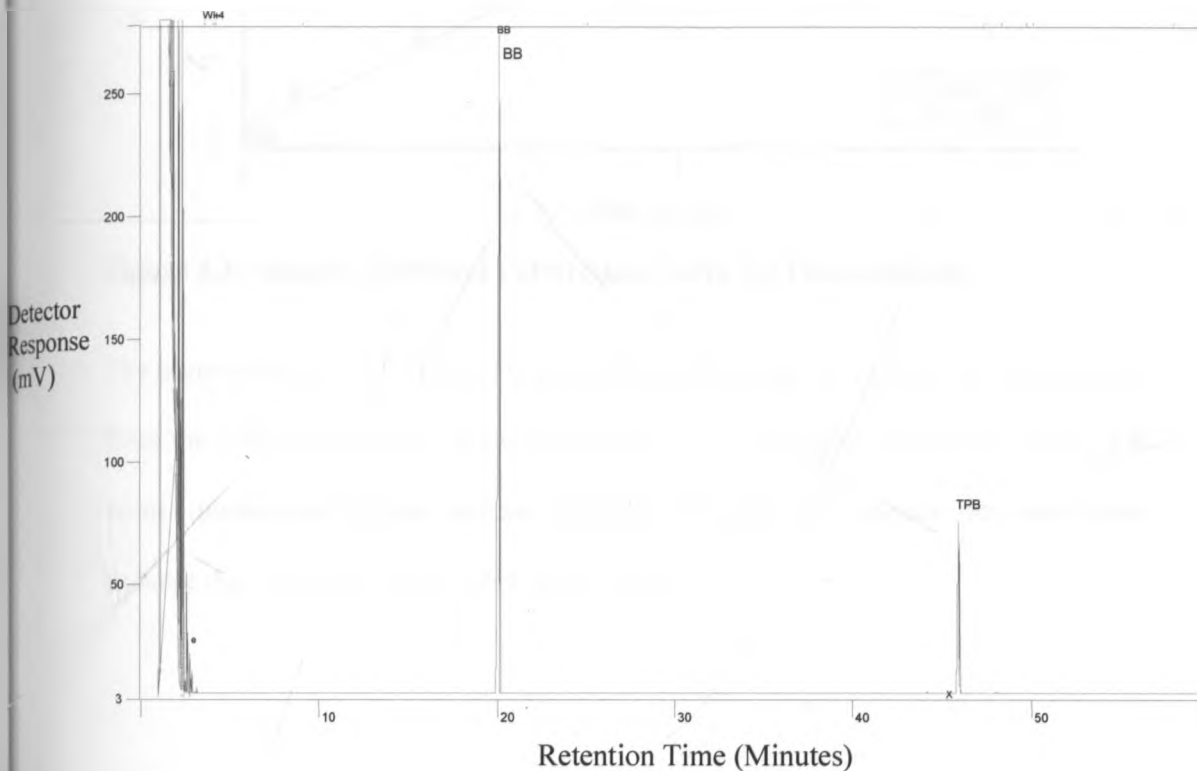
Figure 4.2 Chromatograms for Internal Standards

The correlation coefficients for the calibration curves ranged between 0.9805 and 0.9979. A sample multilevel calibration curve obtained for phenanthrene is provided in Figure 4.3. The rest of the calibration curves are given under Appendix III.
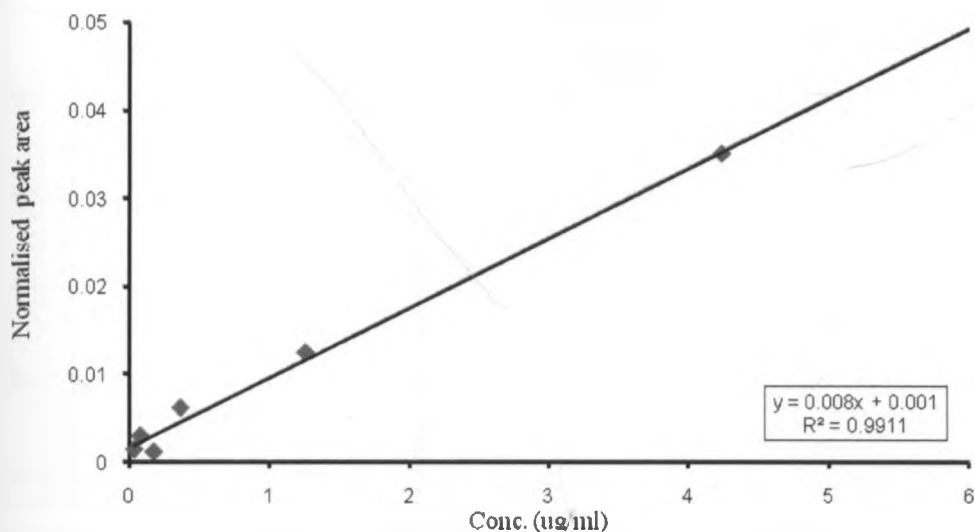
Figure 4.3: Sample Multilevel Calibration Curve for Phenanthrene

The concentrations of PAHs in air and soil samples were determined by interpolation from the calibration curves. A chromatogram of a soil sample is given in Figure 4.4. Some unidentified peaks indicate presence of other compounds not determined because they were out of the scope of this study.
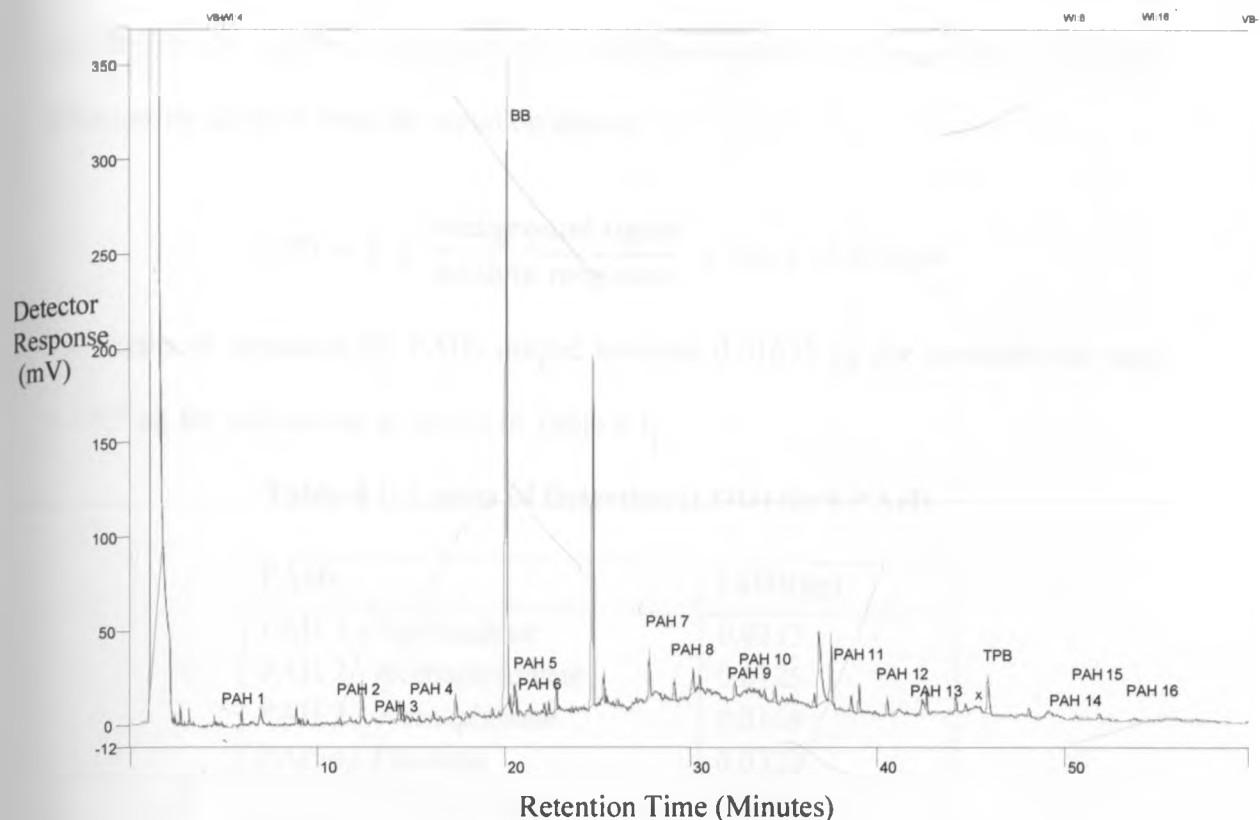
Figure 4.4 Chromatogram of PAHs in a Soil Sample

4.2 Compound Detection Limits

The limit of detection (LOD) of a compound is the lowest concentration of the analyte

that the analytical process can reliably detect. It may be described as the concentration

which gives an instrument signal (y) significantly different from the blank or

background signal. Thus it is calculated as the analyte concentration giving signal

equal to the blank signal y_B plus three standard deviations of the blank, s_B [Miller &

Miller, 1993]. The relationship is generally expressed as:

$y - y_B = 3 s_B$

The LOD of each of the PAHs was calculated based on the lowest concentration of the calibration standards injected and the corresponding noise signals using the relationship adapted from the equation above:

$$LOD = 3 \times \frac{Background\ signal}{Analyte\ response} \times Mass\ of\ analyte$$

The limits of detection for PAHs ranged between 0.01675 ng for acenaphthene and 0.1107 ng for anthracene as shown in Table 4.1.

Table 4.1: Limits of Detection (LOD) for 8 PAHs

PAHs	LOD(ng)
PAH 1 - Naphthalene	0.0213
PAH 2 - Acenaphthylene	0.0125
PAH 3 - Acenaphthene	0.0168
PAH 4 - Fluorene	0.0322
PAH 5 - Phenanthrene	0.0001
PAH 6 - Anthracene	0.1104
PAH 7 - Fluoranthene	0.0411
PAH 8 - Pyrene	0.0260

Any values obtained below these were considered as noise and hence reported as below detection (bd).

4.3 Levels of PAHs Detected in Air

Sixteen polycyclic aromatic hydrocarbons were designated numbers 1 to 16 which are used alternately with their common names in the discussion herein. Analysis was done for PAH 1 to PAH 8 at the local laboratory and confirmatory tests were carried out at the RECETOX laboratory, which also quantified the concentrations of PAHs 9-16. Levels of the PAHs in air are reported in ng/filter. Since concentrations of PAHs sampled on a filter are time dependent, the values reported are the weighted

concentrations of the PAHs on a twenty eight day scale. This provides information on time integrated values which are approximately equivalent to 100 m^3 of air obtained during one day of active sampling [Kohoulek *et al.*, 2008].

The major challenge experienced in the course of this work was the low sensitivity of the GC to calibration standards for PAHs 9 to 16. This made the quantification of the high molecular weight PAHs at the University of Nairobi laboratory from the 10 µg/ml stock untenable. The levels of PAHs 1 to 8 reported in air are the average values for the replicate samples, while those for higher PAHs are calculated from RECETOX data. Levels of the 8 PAHs in soils reported here are averages from the triplicate samples analysed at the University of Nairobi laboratory.

4.3.1 Spatial Distribution of PAHs in Air

PAHs were detected in air samples from all sites. Tables 4.2, 4.3 and 4.4 show the levels of PAHs detected in air at the Kabete, Dandora and Industrial Area sites respectively.

Table 4.2: Levels of PAHs Detected in Air at the Kabete Site (ng/filter ±sd), N=2

PAHs		February	March	April	May	June	July	Average
PAH 1	Naphthalene	235.68±5.33	171.04±12.79	123.14±6.51	312.19±2.09	225.21±23.70	83.02±1.39	191.71±83.08
PAH 2	Acenaphthylene	19.96±0.45	21.12±1.58	16.87±0.89	12.71±0.08	23.00±0.25	9.22±0.15	17.14±5.30
PAH 3	Acenaphthene	18.06±0.41	17.95±1.34	19.40±1.03	23.60±0.16	31.36±0.35	19.29±0.32	21.61±5.20
PAH 4	Fluorene	171.06±3.87	161.54±12.08	175.44±9.28	167.89±1.13	247.75±2.80	163.52±2.73	181.20±32.98
PAH 5	Phenanthrene	765.95±17.34	670.72±5,26	790.32±41.80	694.26±4.65	985.79±11.12	710.28±11.86	769.55±115.02
PAH 6	Anthracene	31.36±0.71	29.56±2.21	39.64±2.11	37.21±0.25	47.04±0.53	34.38±0.57	36.53±6.33
PAH 7	Fluoranthene	326.96±7.38	266.48±2.09	313.77±16.59	301.30±2.02	429.65±4.85	338.79±5.66	329.32±55.03
PAH 8	Pyrene	240.43±5.44	215.39±16.10	247.13±13.07	238.68±1.60	342.88±3.87	270.02±4.51	259.09±44.65
PAH 9	Benzo(a)anthracene*	16.41	10.0	16.63	13.55	19.70	22.06	16.39±4.29
PAH 10	Chrysene*	30.90	23.0	29.75	33.42	46.67	39.88	33.94±8.29
PAH 11	Benzo(b)fluoranthene*	8.69	6.0	9.63	6.32	12.44	6.79	8.31±2.47
PAH 12	Benzo(k)fluoranthene*	4.83	4.0	4.38	5.42	8.30	5.09	5.33±1.53
PAH 13	Benzo (a)pyrene*	2.91	2.0	2.63	1.81	5.19	1.70	2.70±1.30
PAH 14	Benzo(ghi)perylene*	2.90	2.0	1.75	0.00	2.07	0.00	1.45±1.19
PAH 15	Indeno(1,2,3cd)pyrene*	bd	bd	Bd	bd	bd	bd	bd
PAH 16	Dibenz(ah)anthracene*	6.76	3.00	1.75	1.81	3.11	bd	2.74±2.27
Σ16 PAHs		1881.81 ±202.86	1603.80 ±175.92	1792.21 ±205.40	1850.15 ±190.60	2430.17 ±261.21	1704.05 ±191.16	1877.03 ±203.44

*N=1

Table 4.3: Levels of PAHs Detected in Air at the Dandora Site (ng/filter ±sd), N=2

PAHs	February	March	April	May	June	July	Average
Naphthalene	163.16±1.38	145.69±3.80	177.49±12.19	191.24±7.31	318.09±22.49	208.13±5.12	200.63±61.48
Acenaphthylene	66.22±0.55	60.1±1.57	84.61±5.81	59.41±2.27	117.14±8.28	45.58±1.12	72.18±25.41
Acenaphthene	75.82±0.64	75.39±1.97	58.86±4.04	90.98±3.48	72.38±5.12	55.04±1.36	71.41±13.00
Fluorene	575.87±4.87	737.60±19.24	696.18±47.81	671.19±25.67	737.14±52.23	643.30±15.84	676.88±61.73
Phenanthrene	3060.74±25.88	3939.66±10.28	3159.94±21.70	2961.38±113.27	3343.80±23.65	3411.73±8.40	3312.88±350.25
Anthracene	229.39±1.94	365.75±9.54	275.90±18.95	252.51±9.66	241.90±17.11	288.97±7.11	275.74±49.21
Fluoranthene	1135.42	1620.89±42.28	1349.14±9.27	1269.03±4.86	1467.62±10.38	1706.30±42.01	1424.73±216.00
Pyrene	934.83±7.90	1455.85±37.97	1293.04±88.80	1281.10±4.90	1360.00±96.17	1592.77±39.21	1319.60±221.39
Benzo(a)anthracene*	¿ 74.34	100.0	85.75	97.55	95.0	111.13	93.96±12.63
Chrysene*	92.69	133.0	116.38	125.55	137.0	157.50	127.02±21.72
Benzo(b)fluoranthene*	24.14	37.0	25.38	32.52	38.0	37.63	32.44±6.28
Benzo(k)fluoranthene*	10.62	14.0	13.13	21.68	23.0	22.75	17.53±5.55
Benzo (a)pyrene*	10.62	15.0	11.38	17.16	21.0	4.38	13.26±5.79
Benzo(ghi)perylene*	7.72	13.0	8.75	17.16	18.0	21.00	14.27±5.34
Indeno(1,2,3cd)pyrene*	0.00	0.0	0.00	0.90	2.0	1.75	0.78±0.92
Dibenz(ah)anthracene*	8.69	14.0	10.50	20.77	24.0	21.00	16.49±6.29
∑16 PAHs	6470.27 ±851.89	8726.93 ±716.53	7366.41 ±784.66	7110.13 ±631.28	8016.08 ±651.60	8328.95 ±653.67	7669.79 ±838.58

*N=1

Table 4.4: Levels of PAHs Detected in Air at the Industrial Area Site (ng/filter ±sd), N=2

PAHs	February	March	April	May	June	July	Average
Naphthalene	233.44±35.2	188.69±6.63	162.83±2.59	164.77±5.84	326.78±6.77	229.10±4.74	217.60±56.17
Acenaphthylene	68.09±10.27	53.33±1.87	58.410.93	49.34±1.75	87.28±1.81	54.17±1.12	61.77±12.82
Acenaphthene	52.96±7.99	64.61±2.27	69.91±1.11	41.41±1.47	70.03±1.45	59.5±01.23	59.73±10.12
Fluorene	456.28±7.61	495.31±17.41	534.51±8.50	385.94±13.69	528.74±10.95	493.72±10.22	482.42±50.24
Phenanthrene	2902.16±7.93	2465.27±8.86	2720.35±43.28	2086.5±27.99	2419.42±50.95	2378.94±49.23	2495.44±25.93
Anthracene	257.22±38.79	278.93±9.80	300.88±4.79	219.40±7.78	197.90±4.10	199.80±4.13	242.36±39.37
Fluoranthene	1747.93±29.16	1444.91±50.78	1558.41±24.79	1273.23±45.15	1197.53±24.79	1211.22±25.06	1405.54±200.28
Pyrene	1715.69±28.62	1491.05±5.29	1608.85±25.59	1259.14±44.65	1134.61±23.49	1203.23±24.90	1402.09±216.23
Benzo(a)anthracene*	115.86	104.0	115.04	112.00	98.0	83.13	104.679±11.52
Chrysene*	164.14	133.0	146.90	147.23	135.0	119.00	140.889±14.10
Benzo(b)fluoranthene*	40.55	43.0	47.79	34.32	34.0	25.38	37.519±7.24
Benzo(k)fluoranthene*	17.38	16.0	17.70	21.68	19.0	17.50	18.219±1.78
Benzo (a)pyrene*	16.41	17.0	19.47	19.87	18.0	12.25	17.179±2.52
Benzo(ghi)perylene*	15.45	15.0	16.81	18.06	13.0	11.38	14.959±2.24
Indeno(1,2,3cd)pyrene*	bd	bd	bd	bd	2.0	1.75	0.639±0.89
Dibenz(ah)anthracene*	19.31	18.0	19.47	20.77	19.0	13.13	18.289±2.44
∑ 16 PAHs	7822.87 ±851.89	6828.09 ±716.53	7397.34 ±784.66	5853.69 ±631.28	6300.28 ±651.60	6113.18± 653.67	6719.249 ±704.94

*N=1

The sum of the concentrations of 16 PAHs (Σ 16 PAHs) were generally lowest at the Kabete site and highest at the Dandora site as shown in Table 4.5.

Table 4.5 Monthly Levels of PAHs Detected in Air (ng/filter ±sd), N=2

Sites	February	March	April	May	June	July
Kabete	1881.81 ± 202.86	1603.80 ±175.92	1792.21 ±205.40	1850.15 ±190.60	2430.17 ±261.21	1704.05 ±191.16
Dandora	6470.27 ±851.89	8726.93 ±716.53	7366.41 ±784.66	7110.13 ±631.28	8016.08 ±651.60	8328.95 ±653.67
Industrial Area	7822.87 ±724.42	6828.09 ±793.53	7397.34 ±615.57	5853.69 ±661.43	6300.28 ±663.51	6113.18 ±653.67

In Kabete, the levels of Σ16 PAHs ranged between 1603.80 ±175.92 and 2430.17 ±261.21 ng /filter with a monthly average concentration of 1877.03±289.30 ng/filter. In Dandora concentrations ranged between 6470.27 ±851.89 and 8726.93 ±716.53 ng /filter with a monthly mean concentration of 7669.79 ±838.58 ng /filter. Those in Industrial area ranged between 5953.69 ±661.43 and 7822.87 ±724.42 ng/filter and averaged 6719.25 ±704.94 ng/filter per month.

The minimum and maximum values (ranges) obtained for each PAH obtained in air at each site are given in Appendix IV. The relative concentrations of 16 PAHs in the areas studied in Nairobi in addition to two other sites studied in the GAPS survey are illustrated in Appendix V [Klanova et al., 2008].

A one way analysis of variance (ANOVA) test [$F_{(2, 15)}$ =125.589, p<0.01] showed that there was a significant difference in spatial variations of PAHs in air at the three

sites (Appendix VI). The average levels of PAHs in air from Kabete were significantly lower than that from the two other sites. However, levels of PAHs in Dandora were in the same range of magnitude as those from Industrial Area.

The high levels of PAHs in Dandora are attributed to burning of wastes at the dumpsite. Other contributions are petrol stations and vehicular emission from nearby roads. Sources of PAHs in Industrial Area are mainly from fuel combustion in industries and motor vehicle emissions. Though levels of $\sum$ 16 PAHs were lower at Kabete than the other sites, non-point sources are responsible for the higher than rural background concentrations at a rural site on Mount Kenya where levels of $\sum$ 16 PAHs below 200 ng/filter were reported [Klanova *et al.*, 2008]. Emissions from anthropogenic sources such as transportation, biomass burning in residential area and informal industries from the city are possible sources of PAHs at the Kabete site.

Figure 4.5 shows the average monthly levels of the 16 PAHs detected at the three sampling sites.
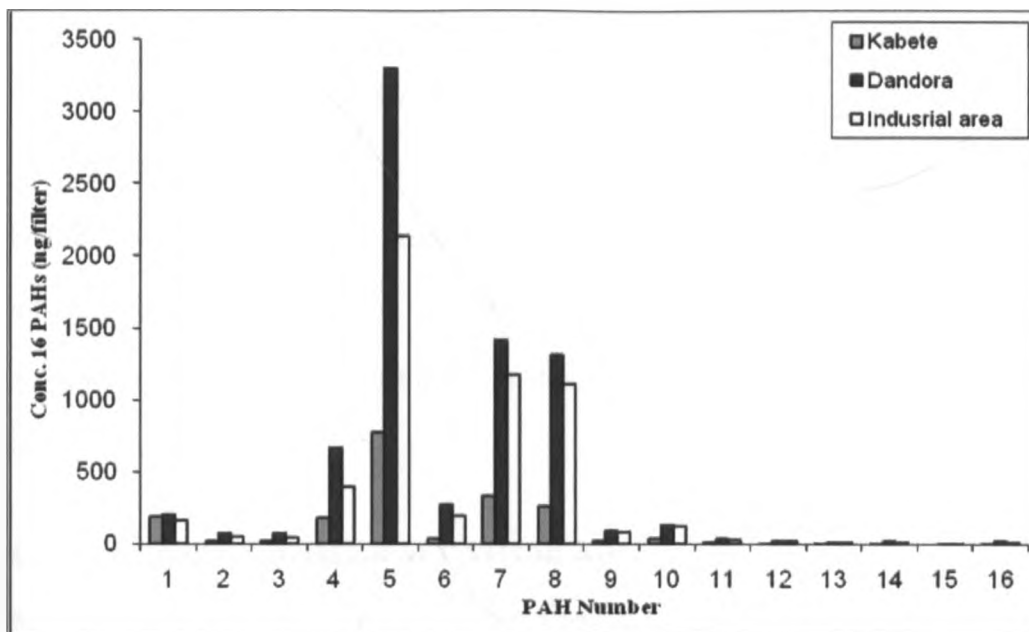
Figure 4.5 Average Monthly Concentrations of PAHs in Air

Phenanthrene (PAH 5) was the most abundant compound in air with average monthly levels 769.66 ±115.02 ng/filter, 3312.88 ±350.25 ng/filter and 2495.44 ±25.93 ng /filter at the Kabete, Industrial Area and Dandora sites, respectively. There were also high levels of fluoranthene (PAH 7), pyrene (PAH 8) and fluorene (PAH 4). Lower average concentrations of the higher molecular weight PAHs 10 to 16 were detected ranging between below detection and 37.52 ±7.24 ng /filter.

The compositional pattern of the PAHs with high levels of phenanthrene, fluoranthene and pyrene in air at the study sites show that there are both petrogenic and pyrogenic sources of PAHs in Nairobi. Phenanthrene predominated because it is released from multiple sources, both petrogenic and pyrolytic. High levels of the compound at the Dandora site are attributed to burning of wastes and vehicular emission from the nearby roads, while those in Industrial Area sites are attributed to emissions from vehicles, incineration and coal combustion.

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Fluoranthene and pyrene account for petrogenic sources from both petrol and diesel motor vehicle engines in Dandora and Industrial Area. Owing to their thermodynamic stability, phenanthrene and pyrene stay in air over long periods of time [Berko, 2002]. Fluorene and naphthalene are from diverse sources and their levels were above the rural background of 200ng/filter. Lower signatures of higher molecular weight PAHs may be as a result of the sampling material which is optimised for the lower molecular weight PAHs.

4.3.2 Temporal Variation of PAHs in Air

At the beginning of the study in February the highest levels of $\Sigma16$ PAHs (7822.87 ± 724.42 ng/filter) were detected at the Industrial Area site but in later months as from May, the highest concentrations (97710.13 ± 631.28 ng/filter) were detected at the Dandora site. The trends in the monthly levels of $\Sigma16$ PAHs are shown in Figure 4.6.
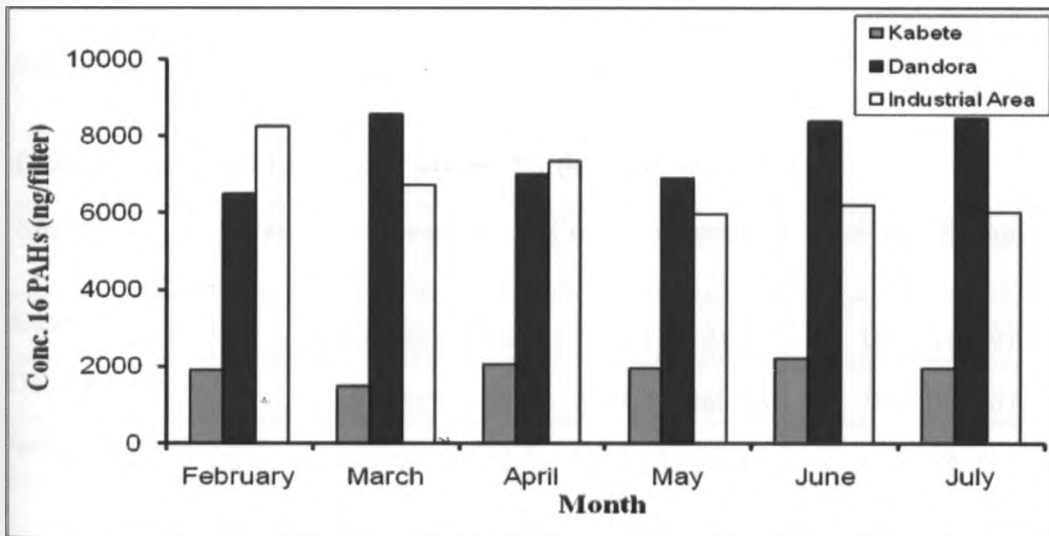

Figure 4.6 Temporal Variation in Level of PAHs in Air

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Using one sample t-tests to compare the monthly levels of Σ 16 PAHs with February levels as test levels at each site, it was observed that mean difference (md) in levels of Σ 16 PAHs in air samples from Dandora (md =1199.80 ng/filter; t(5)=3.504, p=0.017) and industrial area (md=-1103.63 ng/filter; t(5)=-3.501, p=0.017) were significant while that of Kabete (md=2.97 ng/filter, t(5)= 0.025, p=0.981) was not. This implies that overall; there was slight increase in level of PAHs in Kabete, a significant increase in the levels of PAHs in Dandora and a marked decrease in levels of PAHs in industrial air from one month to the next across the sampling period. This is in agreement with the correlations discussed later in section 4.5. Seasonality may have played a role in the observed temporal trends.

4.3.3 Seasonal variation of PAHs in Air

The main seasons captured during the study were the warm dry season (February), the cool, wet season (March to May) and the cool dry season in (June and July). The concentrations of Σ16 PAHs in Kabete were fairly constant while those in Dandora and Industrial Area varied across the seasons as shown in Table 4.6.

Table 4.6: Seasonal Levels of PAHs in Air (ng/filter ±sd), N=2

| Site	Warm- Dry Season	Cool-Wet Season	Cool- Dry Season
Kabete	1808.43±202.86	1689.11±121.23	1980.61±497.91
Dandora	6241.45±851.89	7424.31±860.63	7804.95±207.71
Industrial Area	7433.76±724.42	6325.33±780.63	5895.98±132.30

At the Kabete site, the average concentrations of Σ16 PAHs decreased slightly from 1808.43 ±202.86 ng/ filter in the warm dry season to 1689.11 ±121.23ng /filter during

the rainy season and then increased to 1980.61 ±497.91 ng/filter in the cool dry season. Higher levels of PAHs during colder seasons are due to increased residence time of the pollutants as a result of poorer dispersion of air than during warm seasons. High temperatures also favour volatilisation of compounds However, wet deposition accounts for wash out of the compounds from the atmosphere, hence detection of relatively lower levels of PAHs in the cool-wet season that the dry ones.

There was an increase in levels of PAHs across the seasons from 6241.45 ±851.89 ng/filter in the warm-dry season, to 7424.31 ±860.63 ng/filter in the cool-wet season and then to the highest levels of 7804.95 ±07.71 ng/filter in the cool-dry season at the Dandora site. Seasonal impacts on dispersion of PAHs similar to those at the Kabete site were evident.

In contrast to this trend, the levels of PAHs at the Industrial Area site decreased from 7433.76 ±724.42 ng/filter in the warm-dry season to 6325.33 ±780.63 ng/filter in the cool-wet season, and then decreased slightly to 5895.98 ±132.30 ng/filter during the cool-dry season. Gradual decline in the concentration of PAHs at the Industrial area site could be attributed to a shift in patterns of vehicular traffic flow at the motor vehicle inspection unit, which was one of the localised sources of the contaminants.

The seasonal variations in levels PAHs are further illustrated in Figure 4.7.
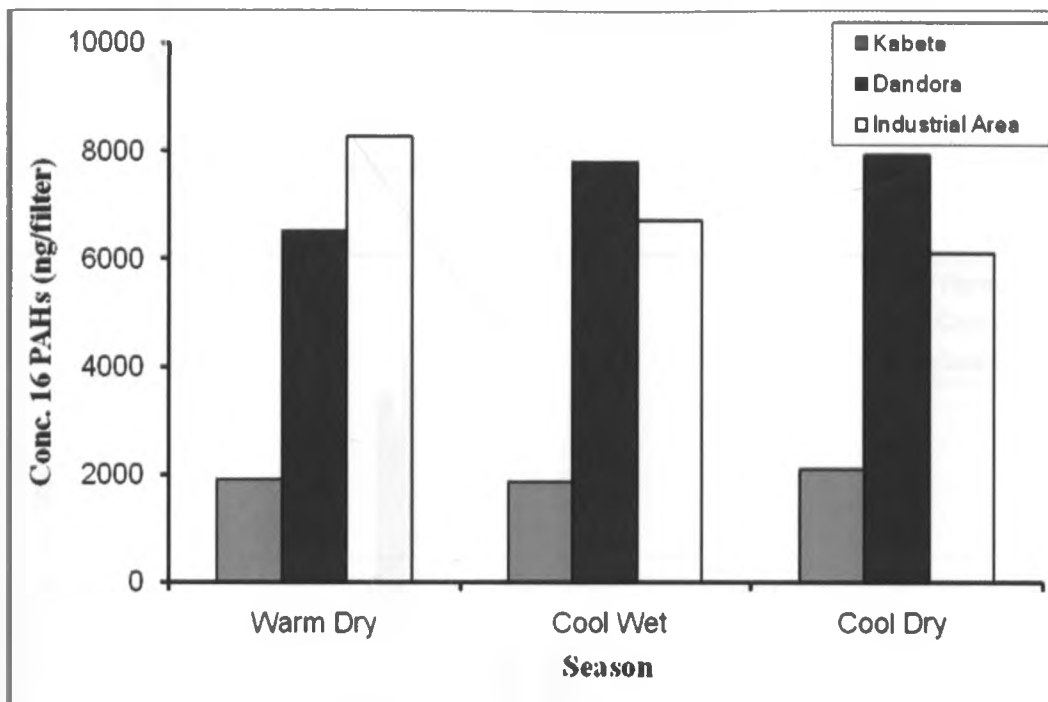
Figure 4.7 Seasonal Variations of PAHs in Air

One–way ANOVA indicted that there was a significant impact of seasonal variations on the mean levels of PAHs in air [F (8, 90) = 43.523, p<0.01].The statistics indicate a general increase in the levels of PAHs from the warm season to the cool seasons. This was expected because dispersion of substances tends to be higher during hot seasons, leading to lower concentrations of point source contaminants. Conversely, the poorer dispersion during cool seasons leads to higher concentrations of pollutants at the source. Contrary observations may imply the impact of other factors such as wind direction and speed. Since data for the warm-dry season was limited, multi-component analysis of PAHs for each site could not be processed by SPSS.

On the basis of individual PAHs, the most abundant PAHs at all sites were fluorene (PAH 4), phenanthrene (PAH 5,) fluoranthene (PAH 7) and pyrene (PAH 8). Seasonal trends in individual PAHs at the Kabete site are given in Figure 4.8.
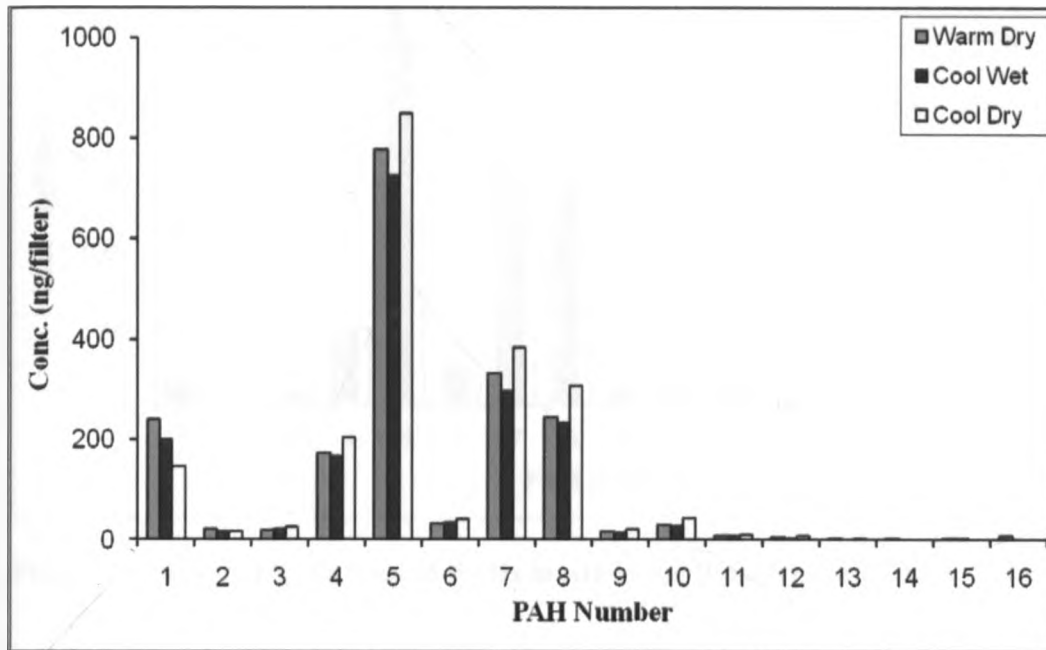
Figure 4.8 Seasonal Variations of PAHs in Air at the Kabete Site

The levels of PAHs 4, 5, 7 and 8 were lowest in the wet season and highest during the cool-dry season at the Kabete site. Levels of naphthalene (PAH 1) which were also in appreciable concentrations at this site were lowest during the cool- dry season and highest in the warm-dry season.

At the Industrial Area site, the levels of the phenanthrene (PAH 5), fluoranthene (PAH 7) and pyrene (PAH 8) were highest during the warm dry season and lowest in the cool dry season. The highest concentration of fluorene (PAH 4) was detected during the cool-dry season while the lowest was found in the warm-dry season. The

seasonal trends in the levels of PAHs at the industrial area site are shown in Figure 4.9.
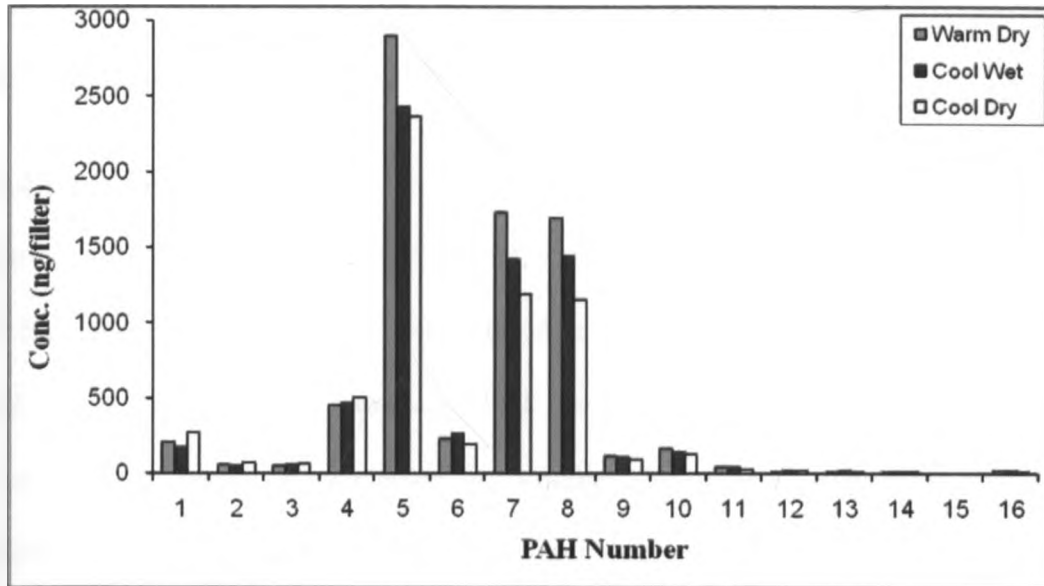

Figure 4.9 Seasonal Variations of PAHs in Air at the Industrial Area Site

Figure 4.10 shows the seasonal trends in levels of all PAHs detected at the Dandora site.
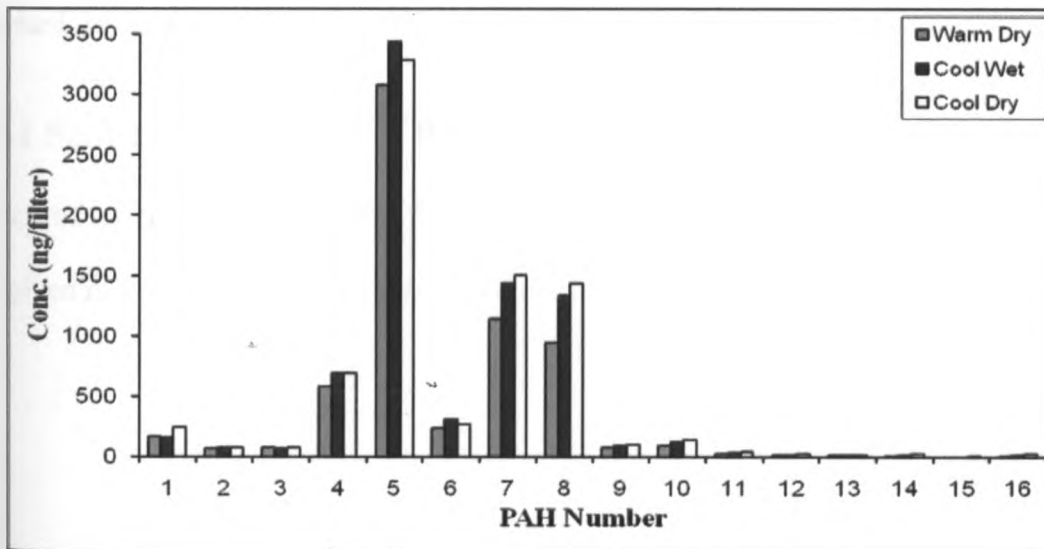

Figure 4.10 Seasonal Variations of PAHs in Air at the Dandora Site

At the Dandora site, the levels of PAHs 4 (fluorene), 5 (phenanthrene), 7 (fluoranthene) and 8 (pyrene) were generally lowest in warm dry season and highest in the cool dry season. This can be accounted for by the more pronounced diffusion and dispersion of the PAHs during the warm season than the cool ones.

4.3.4 Recovery Tests

Recovery of native analytes measured for the reference materials ranged between 72-102 %. Laboratory blanks were below the detection limits for selected compounds. Field blanks consisting of pre-extracted PUF discs taken to each sampling site did not exceed 3% of quantities detected in samples for PAHs, indicating minimal contamination during transportation, storage and analysis.

4.4 Levels of PAHs detected in Soils

Data reported for soils is that of the first 8 PAHs analysed in the University of Nairobi laboratory based on dry weight of triplicate samples expressed as arithmetic mean ± standard deviation.

4.4.1 Spatial Distribution of PAHs in Soils

Levels of individual PAHs in soil from the Kabete, Dandora and Industrial Area sites are given in Tables 4.7, 4.8 and 4.9, respectively.

Table 4.7 Levels of PAHs Detected in Soil from the Kabete Site (ng/g ±sd), N=3

PAHs		February	March	April	May	June	July
PAH 1	Naphthalene	bd	bd	3.14±0.99	10.18±0.01	6.95±0.99	bd
PAH 2	Acenaphthylene	bd	bd	bd	bd	2.33±0.09	0.5±0.04
PAH 3	Acenaphthene	bd	bd	bd	bd	bd	bd
PAH 4	Fluorene	bd	bd	bd	bd	bd	bd
PAH 5	Phenanthrene	bd	bd	bd	bd	bd	0.93±0.02
PAH 6	Anthracene	bd	bd	bd	bd	bd	bd
PAH 7	Fluoranthene	33.10±1.63	23.83±0.69	18.64±0.03	30.46±8.26	37.61±0.08	4.28±0.29
PAH 8	Pyrene	7.24±0.49	8.27±1.61	16.62±3.45	11.27±0.43	15.31±2.81	11.60±1.76
$\sum$8PAHs (ng/g)		40.34±0.84	32.10±0.46	38.40±1.53	51.91±1.27	62.21±0.97	17.30±1.19

Key: bd=below detection limit

Table 4.8 Levels of PAHs Detected in Soil from the Dandora Site (ng/g ±sd), N=3

PAHs		February	March	April	May	June	July
PAH 1	Naphthalene	8.37 ±1.23	bd	3.69±0.00	2.59±0.09	bd	11.96±1.52
PAH 2	Acenaphthylene	bd	bd	1.98±0.00	bd	bd	bd
PAH 3	Acenaphthene	bd	0.12±0.00	bd	bd	bd	bd
PAH 4	Fluorene	bd	6.05±0.11	bd	4.475±0.32	6.25±0.00	146.39±7.52
PAH 5	Phenanthrene	14.94±2.76	73.41±4.71	65.75±0.10	69.84±1.633	73.96±2.83	526.66±18.62
PAH 6	Anthracene	137.35±5.86	162.61±18.70	68.13±1.57	26.04±1.72	9.59±0.82	6.51±0.10
PAH 7	Fluoranthene	18.59±0.11	23.62±0.17	22.41±1.37	21.51±1.21	40.23±2.90	27.32±2.44
PAH 8	Pyrene	25.00±0.17	15.66±1.33	13.84±0.17	16.98±3.39	81.94±9.53	7.75±2.9
$\sum$ 8 PAHs (ng/g)		204.25±1.26	281.37±3.56	175.79±2.46	141.43±1.03	212.98±2.10	726.60±4.51

Key: bd=below detection limit

Table 4.9: Levels of PAHs Detected in Soil from the Industrial Area Site (ng/g ±sd), N=3

PAHs		February	March	April	May	June	July
PAH 1	Naphthalene	9.65±1.56	7.08±0.11	4.84±0.6	5.53±0.01	bd	9.45±1.50
PAH 2	Acenaphthylene	36.97±1.03	4.76±0.23	39.38±0.23	bd	bd	18.82±0.98
PAH 3	Acenaphthene	bd	bd	bd	bd	bd	1.51±0.31
PAH 4	Fluorene	bd	bd	bd	bd	bd	bd
PAH 5	Phenanthrene	17.47±0.87	12.75±0.4	19.75±1.03	12.80±1.05	13.11±1.06	13.95±0.01
PAH 6	Anthracene	25.37±1.30	2.86±0.1	20.33±3.01	30.67±1.49	16.06±3.44	41.56±1.15
PAH 7	Fluoranthene	24.10±0.09	16.78±3.01	29.79±1.40	35.49±4.27	45.27±0.01	31.18±7.90
PAH 8	Pyrene	19.25±5.65	19.15±1.33	10.20±3.11	25.26±0.14	25.43±1.44	22.26±3.52
∑8 PAHs(ng/g)		132.81±1.30	63.37±1.29	124.29±1.16	109.74±4.33	99.87±0.74	138.68±1.93

Key: bd=below detection limit

Just like in air, levels of PAHs in soil were generally lowest in Kabete compared with Dandora and Industrial Area. Table 4.10 shows the sum of the levels of 8 PAHs (Σ 8 PAHs) detected in the soils. Minimum and maximum levels of each of the PAHs detected in soil at each site are given in Appendix VII.

**Table 4.10 Monthly Levels of PAHs Detected in Soil (ng/g ±sd), N=3**

Site	February	March	April	May	June	July
Kabete	40.34 ±0.84	32.10 ±0.46	38.40±1.52	51.91±1.28	62.21±0.97	17.32 ±1.19
Dandora	204.25±1.26	281.38±3.56	175.79±2.46	141.44±1.03	211.98±2.10	726.60±4.51
Industrial Area	132.81±1.30	63.37 ±1.29	124.29±1.16	109.74±4.33	99.87±0.74	138.67±1.93

In Kabete the levels of Σ 8 PAHs ranged between 32.10 ±0.46 ng/g and 117.32 ±1.28 ng/g with average monthly concentrations of 40.37 ±15.59 ng/g. In Dandora the concentrations ranged between 141.44 ±1.03 ng/g and 726.59 ±4.53 ng/g, with mean monthly concentration of 290.24 ±218.75 ng/g. Soil from Industrial Area had Σ 8 PAHs levels ranging between 63.37 ±1.29 ng/g and 138.67±1.93 ng/g with average monthly concentrations of 111.46 ±27.60 ng/g. The relative concentrations of Σ 16 PAHs in some soil samples at sites studied in Nairobi in addition to two other sites studied in the GAPS survey are illustrated in Appendix VIII [Klanova et al., 2008].

One-way ANOVA statistics [$F_{(2, 15)} = 6.107$, p=0.011] showed that spatial variations of Σ 8 PAHs were significant. Mean concentrations of Σ 8 PAHs in soil from Dandora were higher than those in soil from Kabete, but in the same range of magnitude as those

in the soil from Industrial Area. Levels of $\sum 8$ PAHs in soils from Industrial Area and Kabete were also comparable as shown in Appendix IX.

On average, phenanthrene (PAH 5) was the most abundant of the 8 PAHs while acenaphthene (PAH 3) was the least abundant. There were higher levels of the 4-5 ringed PAHs than the lighter 2-3 ringed ones in the soils as show in Figure 4.11.
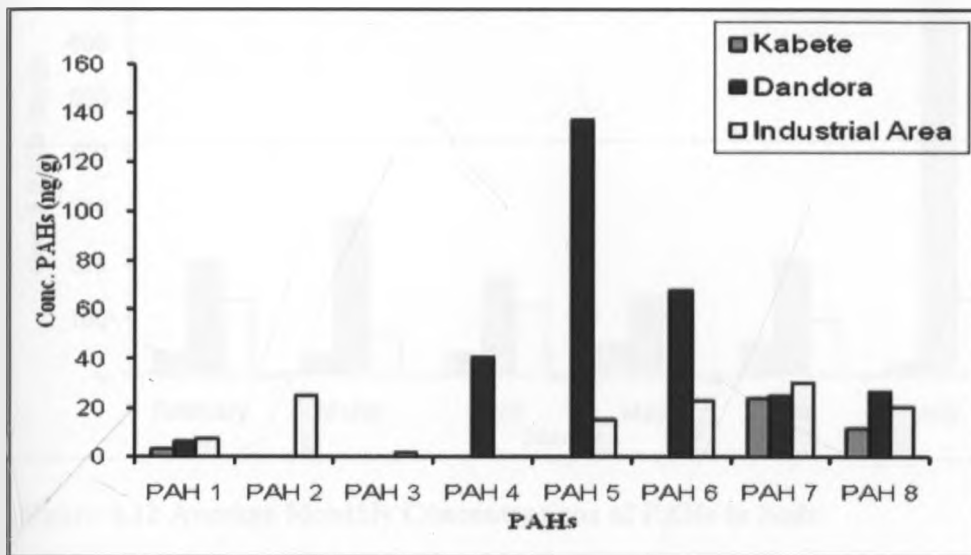
Figure 4.11 Average Monthly Concentrations of PAHs in Soils

This may be as a result of loss of low molecular weight PAHs from soils due to their high volatility. The less volatile, high molecular weight PAHs tend to bind more tightly to soils [Morillo *et al.*, 2007]. Moreover, since phenanthrene (PAH5), fluoranthene (PAH 7) and pyrene (PAH 8) were found in relatively high quantities in air, similar levels in soils were likely due to adsorption of the compounds on soils. Acenaphthene which was not detected in air was also below detection limit in soil at all sites.

4.4.2 Temporal Variation of PAHs in Soil

There were more marked variations in levels of the $\Sigma 8$ PAHs in soils at Dandora than at the Industrial Area and Kabete sites. The trends in the monthly levels of $\Sigma 8$ PAHs in soils at each site are shown in Figure 4.12.
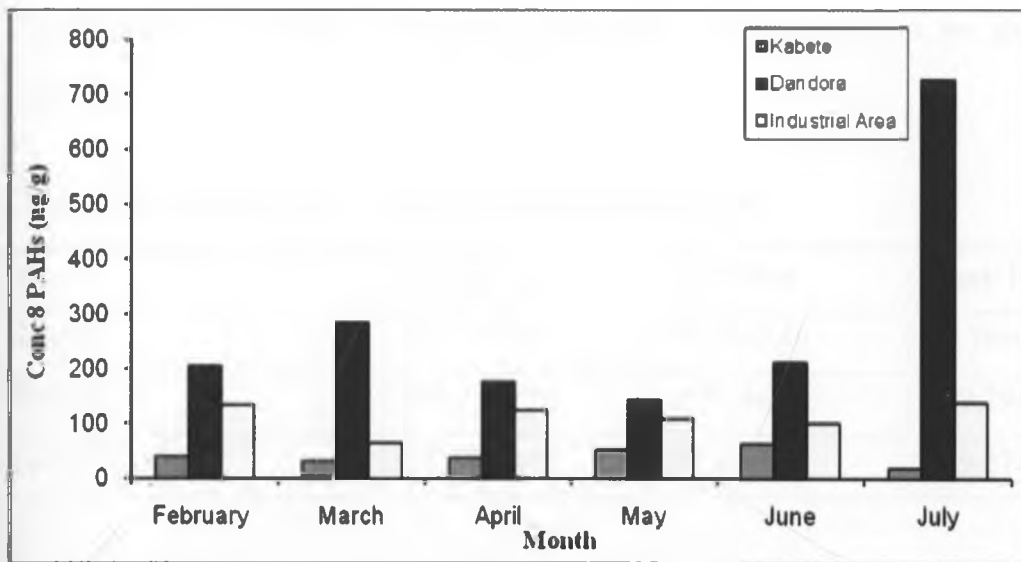

Figure 4.12 Average Monthly Concentrations of PAHs in Soils

It is evident from Figure 4.12 that Levels of PAHs were highest in Dandora and lowest in Kabete over the study period. On average there was a decline in the levels of $\Sigma 8$ PAHs in Industrial Area soil while those in Dandora and Kabete increased. Similar trends were observed in air (Figure 4.6).

A one-sample t-test used to assess temporal trends in the levels of $\Sigma 8$ PAHs in soils, compared with levels detected in February showed that there were no significant variations in the levels of $\Sigma 8$ PAHs from the test values, except in soils from the Dandora site where a remarkable increase was observed in July. Mean differences were as follows: 0.037 ng/g [t (5) = 0.006, p= 0.996] in Kabete; 85.99 ng/g [t (5) = 85.99, p= 0.380] in

Dandora; and -21.35 ng/g [t (5) = -1.894, p= 0.117] in Industrial Area. This indicates that

changes in the levels of PAHs in the soils are minimal on a small time scale.

4.4.3 Seasonal variation of PAHs in Soil

Like in air, the levels of $\sum 8$ PAHs in the soil were fairly constant at the Kabete site. The

concentrations of $\sum 8$ PAHs at the three sites studied across the seasons are given in

Table 4.11.

Table 4.11 Seasonal Levels of PAHs in Soil (ng/g ±sd), N=3

| Site	Warm-Dry	Cool-Wet	Cool- Dry
Kabete	40.34±0.84	40.81±0.46	39.76±0.97
Dandora	204.25±1.26	199.54±2.35	469.29±3.07
Industrial Area	132.81±1.30	99.14±1.31	119.27±0.74

Levels of PAHs in Kabete soils were within 40.00 ±0.90 ng/g indicating minimal

seasonal impacts. In the soils from Dandora, the concentration of $\sum 8$ PAHs was higher

in the cool dry season than in the wet and warm dry seasons as expected. This shows that

there was more volatilisation and loss of PAHs from the soil under warm conditions than

during cooler ones. Levels of PAHs in wet soils were lowest in soils from Dandora and

Industrial Area, probably due to partitioning and leaching of some of the PAHs into the

aqueous medium under wet conditions.

The seasonal variation in levels of $\sum 8$ PAHs in soils from Industrial area were on the

contrary, lowest in the cool-dry season. A similar trend was observed in the levels of $\sum 8$

PAHs in air at this site. The variation in local inputs of PAHs from the industries and

motor vehicles may account for this observation. However, more data on the warm-dry

season could have shed more light on this seasonal anomaly for a more plausible explanation

The seasonal variations in levels of $\sum 8$ PAHs in the soils are illustrated in Figure 4.13.
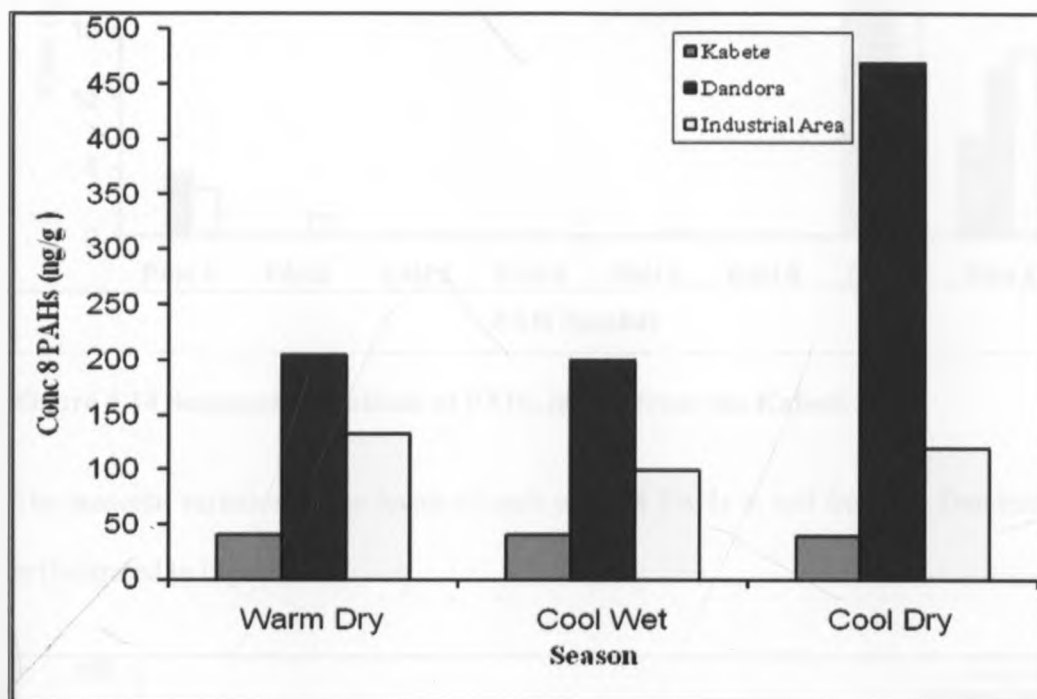
Figure 4.13: Seasonal Variation in Concentrations of PAHs in Soils

Figures 4.14, 4.15 and 4.16 show the seasonal variation of levels of individual PAHs in soils from the three study sites. In Kabete soil, the most abundant PAHs were fluoranthene (PAH 7) and pyrene (PAH 8) across the seasons as shown in Figure 4.14. Other PAHs of notable levels were naphthalene (PAH 1) and acenaphthylene (PAH 2), with the latter evident only during the cool dry season.
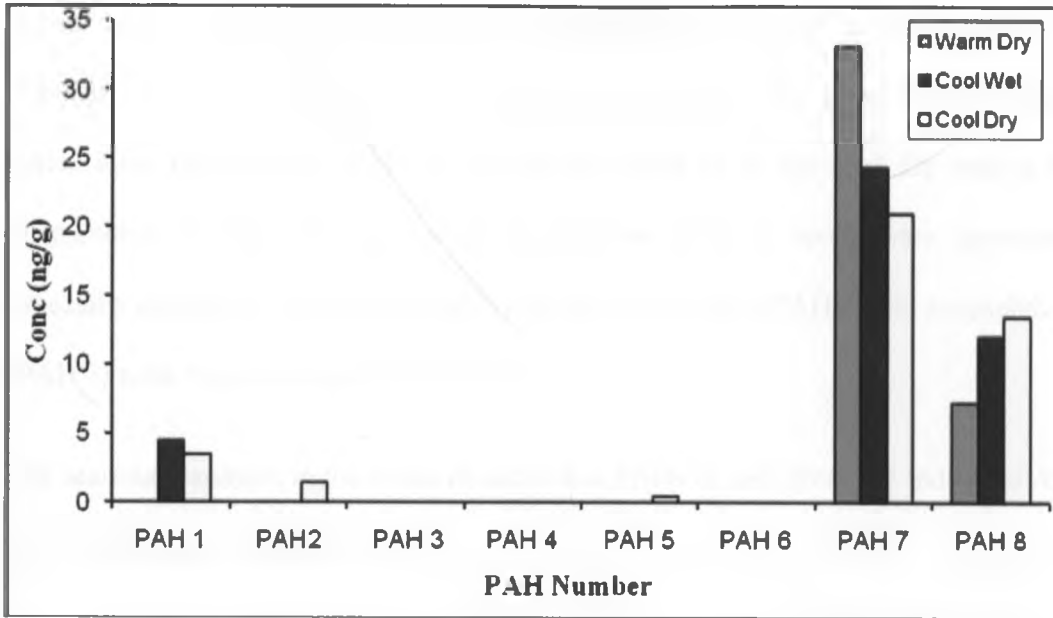
Figure 4.14 Seasonal Variations of PAHs in Soil from the Kabete Site

The seasonal variation in the levels of each of the 8 PAHs in soil from the Dandora site is illustrated in Figure 4.15.
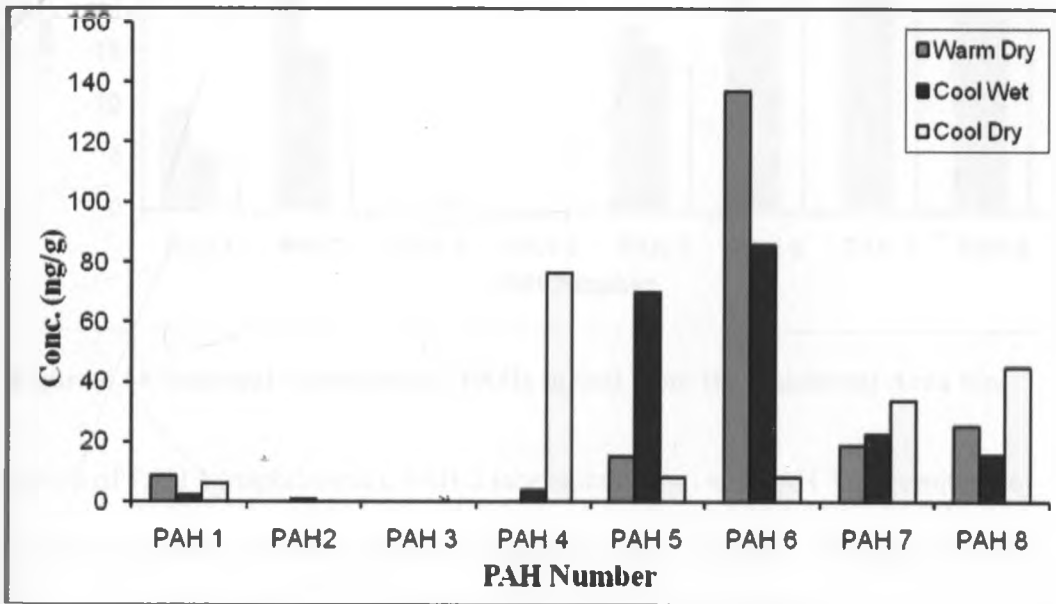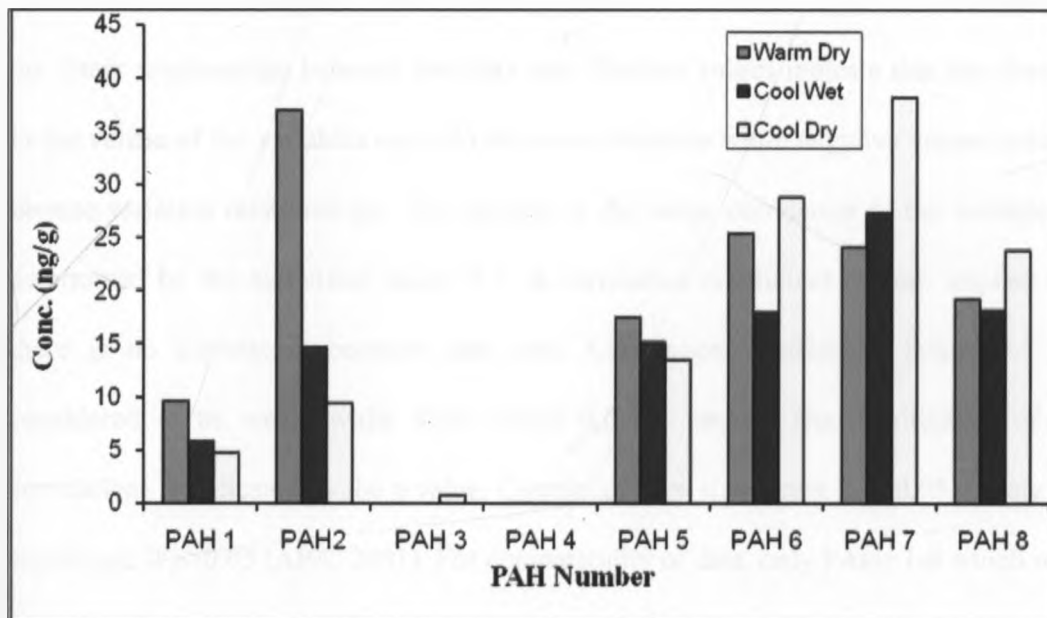

Figure 4.15 Seasonal Variations of PAHs in Soil from the Dandora Site

In soil from the Dandora site, anthracene (PAH 6) was predominant in the warm dry and wet seasons, while fluorene (PAH 4) dominated in the cool dry season. Other notable PAHs were fluoranthene (PAH 7) and pyrene (PAH 8) in the cool dry season and phenanthrene in the cool wet season. Naphthalene (PAH 1) levels were appreciable especially during the warm dry season; while acenaphthylene (PAH 2) and acenaphthene (PAH 3) were below detection limit levels.

The seasonal variation in the levels of individual PAHs in soils from the Industrial Area site is illustrated in Figure 4.16.

Figure 4.16 Seasonal Variations of PAHs in Soil from the Industrial Area Site

Levels of PAH 1 (naphthalene), PAH 2 (acenaphthylene) and PAH 5 (phenanthrene) decreased gradually from the warm dry season to the cool season. The highest levels of anthracene (PAH 6), fluoranthene (PAH 7) and pyrene (PAH 8) were detected during the cool dry season.

These trends show that lower molecular weight PAHs were more sensitive to seasonal changes than the high molecular weight compounds. The seasonal variations of PAHs in soil from the Industrial Area site require further investigation to determine the other possible external factors that would affect their levels such as industrial and motor vehicle emissions, as well as the impacts of biological communities on the levels of individual PAHs in soil at this site.

4.5 Correlations of Levels of PAHs in Air and Soil

Correlation was done using Pearson's Correlation coefficient from SPSS. Correlation coefficients have numerical values (r) ranging from -1.000 to +1.000 which represents the linear relationships between two data sets. Positive values indicate that the changes in the values of the variables occur in the same direction while negative values indicate inverse variation relationships. The strength of the linear correlation of the variables is determined by the numerical value of r. A correlation coefficient of zero implies that there is no correlation between data sets. Correlation coefficients below 0.5 are considered to be weak, while those above 0.5 are strong. The significance of the correlations is indicated by the p value. Correlations are significant if $p < 0.05$ and are not significant if $p > 0.05$ (APA, 2001). For comparability of data, only PAHs 1-8 which were quantified in both matrices for the entire study period were considered.

The first set of correlations, discussed in Section 4.5.1 was done to establish possible relationship between the variation in the levels of $\sum 8$ PAHs in air and that in soils at each site on a monthly basis followed by seasonal comparisons. Correlations were also done to determine the possibility of a relationship between the levels of $\sum 8$ PAHs in air as well as soils as a function of time; both temporal and seasonal. This was done by

assigning numerical values to the six months and three seasons covered by the study. Correlations between the levels of PAHs on a monthly time scale are discussed in Section 4.5.2 while those on a seasonal scale are discussed in section 4.5.3.

4.5.1 Correlation of Inter-matrix Levels of PAHs

The correlations between the monthly levels of $\sum 8$ PAHs in air versus those in soils were positive at each site, although that at the industrial area site was weak (Appendix X). The Pearson's Correlation Coefficients of the temporal levels of $\sum 8$ PAHs in soils and air (N=6) were 0.821, 0.503 and 0.166 at Kabete, Dandora and Industrial Area, respectively. This indicates that the changes in levels of $\sum 8$ PAHs in air versus $\sum 8$ PAHs in soils were varying in the same direction: as one increases or decreases in air the same change occurs in the soils. However, only correlation between the Kabete soil/Kabete air pair was significant (p< 0.05) at 95 % confidence level. The stronger inter-matrix correlations at the Kabete and Dandora sites indicate more balanced exchanges of PAHs between the air and soil than in Industrial Area.

On the seasonal basis, the correlations between the levels of $\sum 8$ PAHs in air versus those in soils (N=3) were -0.999, 0.677 and 0.614 at the Kabete, Dandora and Industrial Area sites, respectively (Appendix XI). All the three r values show a strong relationship between the levels of $\sum 8$ PAHs in air and those in soils at the three sites. However, while levels of the PAHs were varying in a similar way at the Dandora and Industrial Area sites, a reverse trend was observed in Kabete. It is also notable that the inter-matrix correlation at the Kabete site was significant (p<0.05).

4.5.2 Correlation of Temporal Levels of PAHs in Air and Soil

Pearson's Correlation coefficients for spatial and temporal levels of $\sum$ 8 PAHs in air and soils are shown in Appendix X. For air samples from Kabete and Dandora, there were weak positive correlation of 0.291 and 0.402, respectively; while correlations between monthly values and levels of $\sum$ 8 PAHs in air from Industrial area was -0.792. This implies that while the levels of $\sum$ 8 PAHs in air decreased to a great extent with time from February to July in Industrial Area, there was an overall slight increase in the levels of the $\sum$ 8 PAHs at the Kabete and Dandora sites over the same period of time.

For soils, there was a greater increase in levels of $\sum$ 8 PAHs in Dandora (r=0.579) than Industrial Area (r=0.241) while in Kabete (r= -0.039) there was a very small decrease with time. Correlation coefficients with the rest of the samples were positive though weak. All p values were greater than 0.05: the temporal variations in the levels of $\sum$ 8 PAHs in air and soils at the three sites were not significant.

4.5.3 Correlation of Seasonal Levels of PAHs in Air and Soil

Pearson's Correlation coefficients for seasonal levels of $\sum$ 8 PAHs are given in Appendix XI. There were strong, positive correlations between the seasonal progression and the levels of PAHs in air from Kabete (r=0.587) and Dandora (r=0.959). The air samples from the Kabete and Dandora sites thus had highest levels of PAHs during the cool season when wind speeds of relatively denser air masses during cold weather are lower than under hot conditions. However, negative correlation of seasonal variation with levels of $\sum$ 8 PAHs in air from Industrial Area shows that point sources of the PAHs may have reduced during the cool season. Another possible influence could have been the changes in wind direction.

In Dandora, the r value of 0.959 shows that the level of $\sum 8$ PAHs increased greatly as the season changed from warm-dry to cool-dry. This can be accounted for by reduced volatilisation of PAHs from soils, coupled with longer residence time of PAHs in the atmosphere during cool seasons. Negative correlation coefficients between seasonal variations and levels of $\sum 8$ PAHs in soils from Kabete (r=-0.551) and Industrial Area (-0.400) show that there was a decline in the levels of $\sum 8$ PAHs in soils from the two sites. However, since the correlations were not significant (p>0.05), these decline in the levels of PAHs in the soils may have been influenced by other factors besides seasonal variability such as microbial activity in the soils [CCME, 2008].

4.7 Comparison of Levels of PAHs in Air and Soils from Nairobi with Other Cities

The monthly average levels of $\sum 16$ PAHs in air from industrial area (6760.15 ±897.19 ng/filter) and Dandora (7649.11 ±927.56 ng/filter) were higher than those detected in urban and industrial areas of most cities in Africa studied in 2008. Levels of $\sum 16$ PAHs in Kabete (1943.91 ±241.03 ng/filter) were within the same range of magnitude as some urban sites but generally lower than those in some major cities in Africa. Average concentrations of $\sum 16$ PAHs in air from Industrial Area and Dandora in Nairobi were higher than those reported in Khartoum (4230.67 ±699.53 ng /filter), Tunis (1604.17 ±484.79 ng/filter, Sheda in Nigeria (3667.83 ±1769.06 ng/filter), Lusaka (1628.33 ±513.84 ng/filter) and the industrial Vander Park of South Africa (5147.86 ±1360.82 ng/filter). However, the levels of the $\sum 16$ PAHs were much higher at an urban sampling site in Dakar (13872.80 ±2904.16 ng/filter) than those at the Kenyan urban sites [Klanova *et al.*, 2008].

A comparison between the average levels of $\sum 8$ PAHs in soils from Kabete (40.38 ng/g), Dandora (290.24 ng/g) and Industrial Area (111.46 ng/g) with those from other cities in Africa indicates that soils in Nairobi had higher levels than those in sites from Dakar (58.9 $\pm$ 8.5 ng/g), Vandenderbijl Park (47.1 $\pm$6.5 ng/g), Khartoum (17.2 $\pm$1.9 ng/g), Tunis (14.9 $\pm$1.8) and Lusaka (46.8 $\pm$7.9 ng/g) [Klanova et al., 2008].

Levels of PAHs in air from the three study sites in Nairobi were however, below those detected in areas with high traffic flow, but higher than those detected in other urban sites of Europe [Garban et al.,2002; Impey et al., 2000]. This can be accounted for by more stringent emission regulations in resulting in more efficient combustion systems in European countries than in Kenya. Levels of higher molecular weight PAHs in soil not quantified in this study are expected to have elevated levels of PAHs beyond those reported in some urban areas in Canada and New York [Berko, 2002; Wong et al., 2004]. This is due to the fact that higher molecular weight PAHs are less susceptible to environmental degradation and volatilisation. Moreover, they tend to bind more tightly to soils than the lower molecular PAHs [Morillo et al., 2007].

4.8 Implications to Human Health and the Environment

Using the estimated average sampling rate of air at 3.57 m^3/day and a sample volume of 100 m^3 of air during the four weeks of passive sampling of air, the average levels of $\sum$ 16 PAHs at the Kabete, Dandora and Industrial Area sites were 18.77 $\pm$2.89 ng/m^3, 76.70 $\pm$8.3 ng/$m^3$and 67.19 $\pm$7.05 ng/m^3, respectively. The levels of indicator species benzo(a) pyrene were 0.03 $\pm$0.00 ng/m^3 in Kabete, 0.13 $\pm$0.06 ng/m^3 in Dandora and 0.17 $\pm$0.03 ng/m^3 in Industrial Area. These levels of benzo (a) pyrene were well below the WHO and USSR guideline value of 1ng/m^3 and the Netherlands guideline value of 0.5 ng/m^3.

However, the levels as determined using passive samplers are more suited for gas phase analytes than the particle bound PAHs. Therefore, the levels could have been underestimated and consequently underscore the actual health risks. Moreover, the levels of $\sum$ 16 PAHs were high and hence the need for environmental and ecological risk assessment of the mixture of compounds. The level of most PAHs detected in the soils from Nairobi was below the Canadian and Danish soil guidelines of PAHs in soils. However, the level of phenanthrene in soil from the Dandora site in the month of July exceeded the Danish guidelines [CCME, 2008]. Wash-out and leaching of PAHs from the soil at the dumpsite is a source of pollutants to the already contaminated Nairobi River; with far reaching implications to the aquatic ecosystem downstream (UNEP/UoN, 2009). Chronic exposure of urban populations to PAHs may lead to increased risk of cancer and other adverse effects associated with PAHs [ATSDR, 1995; IARC, 1983]. Since toxicological data for most PAHs is limited, emissions of the compounds should be reduced in order to protect humans and the ecosystem from possible risk.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The levels of PAHs in air and soil at three sites in Nairobi were assessed. There were generally lower levels of PAHs in air and soil from the Kabete site than those from Dandora and Industrial Area. This suggests more significant anthropogenic input of PAHs in Dandora and Industrial Area than the Kabete environment. The results indicate a progressive decline in air quality in Nairobi, more so at the Dandora dumpsite. Consequently, more people may be at risk of adverse health effects of contaminated air in the densely populated Dandora residential area. The effects of the anthropogenic activities of the city were evident at the Kabete site, with levels of PAHs above those detected at a remote rural site on Mt. Kenya. The study showed that Nairobi had higher levels of PAHs than most of the cities in Africa whose concentrations have been reported [Klanova et al., 2008].

Higher levels of medium weight PAHs: pyrene, phenanthrene, fluoranthene, anthracene and pyrene, were detected in air and soils at all the three sites. However, phenanthrene was the most abundant compound in air and soil especially at the Dandora site. In Industrial Area, phenanthrene was predominant in air, closely followed by anthracene and fluoranthene. Two- and three- ring PAHs (PAH 2 to PAH 7) accounted for the greatest percentage loading in air and soil. This shows that there was a mixture of PAHs from diverse sources during the study period. Very low levels of PAHs of higher

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molecular masses (PAHs 10-16) were detected in air, with six ringed indeno (1,2,3,c,d) pyrene below detection at all the sites studied. This was probably due to the passive sampling technique employed in this study.

Identification of emission indicators of individual PAHs is complicated by the fact that the compounds are released as complex mixtures. However, from the observations made at the sites, it is evident that burning of wastes at the Dandora site accounts for the loadings of phenanthrene, fluoranthene and pyrene. Sources of PAHs at the Industrial Area site are motor vehicle emissions and oil combustion from the industries. Lower levels in air and soils from Kabete can be accounted for by circulation and mixing of PAHs in the air since there were no known local inputs.

Passive air sampling using polyurethane foam is more suitable for adsorption of the lower molecular mass PAHs than the higher ones and may lead to an underestimation of the latter. This is evident from comparison of results of this study with that by Gatari *et al.* [2006] which reported that the most abundant species in air particulates from Nairobi (diameters 30-50 µm) were chrysene, benzo(a) antharacene, benzo (k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d) and benzo(ghi)perylene. However; the results of this study are consistent with those in Australian cities in which polyurethane foam was used for air sampling [Berko, 2002]. Data on levels of PAHs in soils in Nairobi was not found in the literature.

5.2 Recommendations

More sustainable solid waste management strategies are needed to minimise disposal and uncontrolled burning of municipal wastes in the city. Some of the wastes, especially plastics should be recycled or reused instead of being burned at the dump site. Organic

wastes should be digested to generate biogas. More efficient combustion systems and use of cleaner fuels in industries and motor vehicles will also ease the burden of PAHs in air and soils in the city. The emission source markers and sporadic correlations of PAHs in air and soil in Nairobi and its environs need further investigation.

Continuous monitoring of levels of PAHs and other toxic by-products of combustion such as volatile organic compounds (VOCs), PCDDs and PCDFs in Nairobi and other major towns in Kenya is needed to further investigate trends in their levels. Contamination of air and soil by PAHs and POPs needs to be prioritised under EMCA for human and ecological protection. Risk assessment studies are needed to establish the risk posed to humans and other life forms by the levels of PAHs in air and soil, as well as in water in Nairobi. Dandora and industrial area, where high levels of PAHs were detected, are of particular concern.

Soils were less sensitive to seasonal dependencies in the levels of PAHs and so can be used in preliminary studies to scan the status of PAHs at different localities. They have an added advantage of simpler and more affordable sampling procedures than air.

The use of polyurethane foam plugs for sampling of PAHs may underestimate the higher molecular weight PAHs 10-16. Further studies employing filters that sample both vapour phase and particulate bound PAHs are needed. Passive sampling complemented by active sampling at pollutant hotspots is required to calibrate the two methods for long term air quality monitoring. There is also need to build capacity in local laboratories to handle compressive environmental quality assessment studies.

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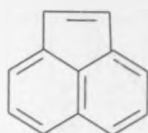
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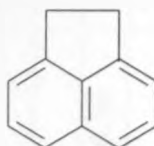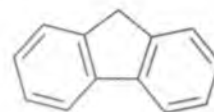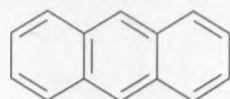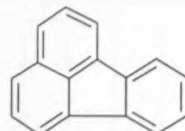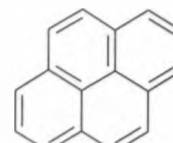
APPENDIX

APPENDIX I
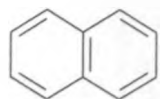
naphthalene

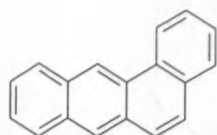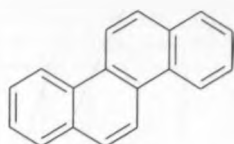acenaphthylene

acenaphtene

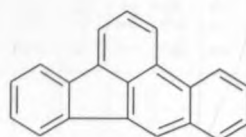fluorene

Phenanthrene

anthracene
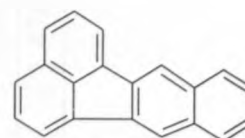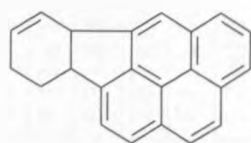
Fluoranthene

Pyrene

Benzo[a]anthracene

chrysene

benzo(b)fluoranthene

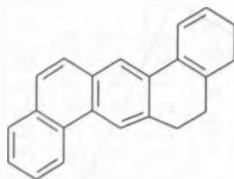benzo(k)fluoranthene

benzo(a)pyrene

indeno(1,2,3-c,d) pyrene

dibenzo(a.h)anthracene

benzo[ghi]perylene

Structures of the 16 PAHs Studied

Some Physico-Chemical Properties of 16 PAHs Studied

PAHs	Molecular Weight	Aqueous Solubility mg/L	Vapour Pressure mmHg	Henry Law (atm m^3/mol)	Log Kow	LogKoC
Naphthalene	128	31.7	8.5×10^{-2}	4.83×10^{-4}	3.36	2.7-3.0
Acenaphthene	154	3.9	2.5 x 10-3	1.55×10^{-4}	3.92	3.3-3.6
Acenaphthylene	152	16.1	9.12 x 10-4	1.13×10^{-5}	3.9-4.1	3.75
Fluorene	166	1.9	6.33-8.42x10-3	6.34×10^{-5}	4.18	3.45-3.95
Anthracene	178	0.043	2.67×10^{-6}	1.93-6.5x10-5	4.45-4.55	4.2-4.4
Phenanthrene	178	1.15	1.12×10^{-4}	2.33x10-3	4.46-4.55	3.4-4.3
Fluoranthene	202	0.26	1.23×10^{-8}	1.30-1.6x10-5	4.95	4.62
Pyrene	202	1.35	2.45-4.59 x 10^{-6}	1.10x10-5	4.88-5.18	4.6-5.1
Benzo(a)anthracene	228	9.4×10^{-3}	3.05-1.05 x 10^{-7}	3.35x10-6	5.7	5.3
Chrysene	228	$2-6.3\times10^{-3}$	6.3 x 10-9	9.46x10-5	5.7	5.1
Benzo(b) fluoranthene	252	1.5×10^{-3}	5.0 x 10-7	1.1x10-4	6.2	5.2
Benzo(k)fluoranthene	252	8.0×10^{-4}	2.0 x 10-9	8.29x10-7	6.2	4.3
Benzo(a)pyrene	252	1.6×10^{-3}	5.49 x 10-9	1.13x10-6	5.97-6.58	6.0-6.7
Benzo(ghi)perylene	272	2.6×10^{-5}	1.0 x 10-10	1.41x10-7	6.7	5.61
Indeno(1,2,3,cd) perylene	272	2.2x10-5	1.0 x 10-10	1.60x10-6	6.6	6.2
Dibenzo(ah) anthracene	278	2.49×10^{-3}	1.0 x 10-10	1.47x10-7	6.5-6.69	5.8-6.3

Source: CCME (2008)

APPENDIX III

Multilevel Calibration Curves

$$y = 0.0172x + 0.005$$
$$R^2 = 0.9805$$
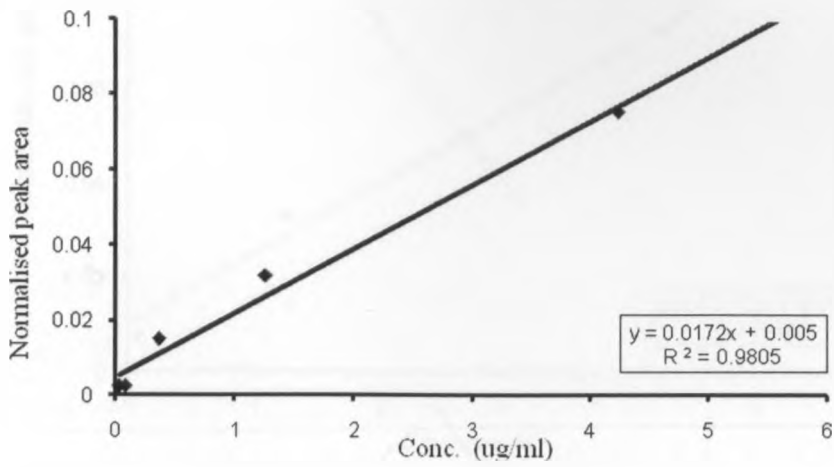
Calibration Curve for Naphthalene

$$y = 0.0144x + 0.0064$$
$$R^2 = 0.9840$$
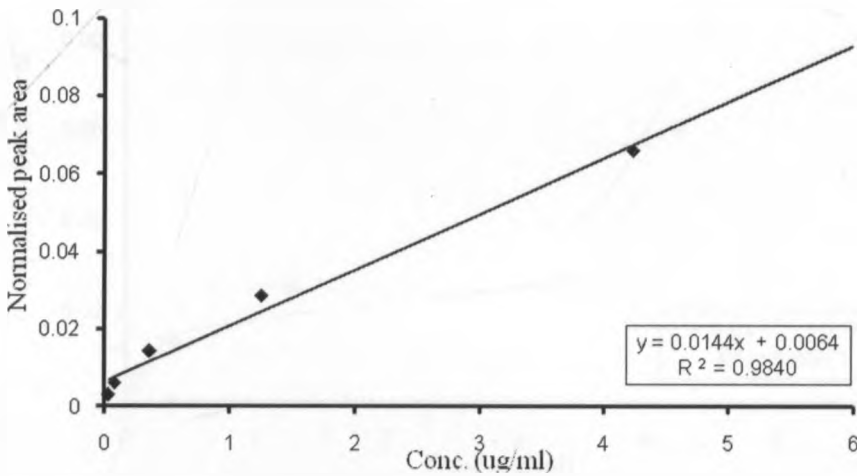
Calibration Curve for Acenaphthylene
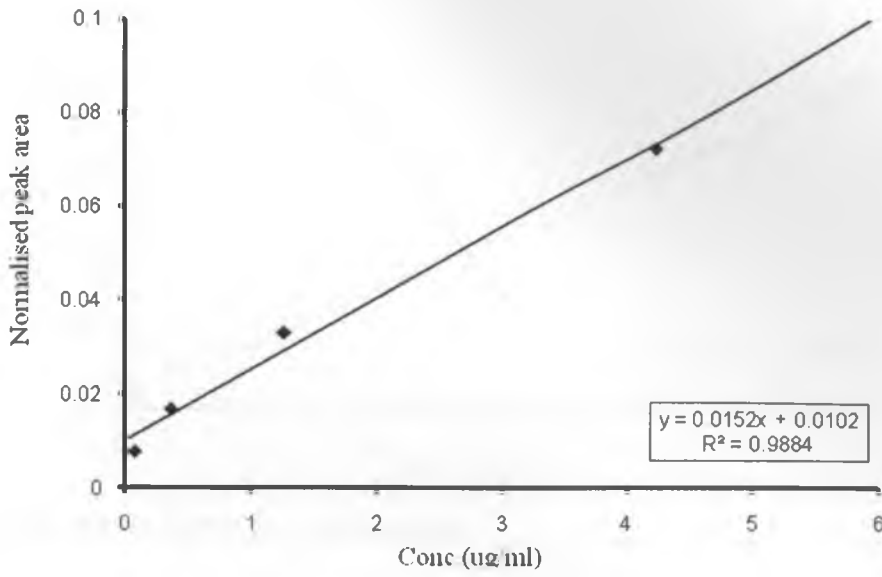
Figure: Calibration Curve for Acenaphthene
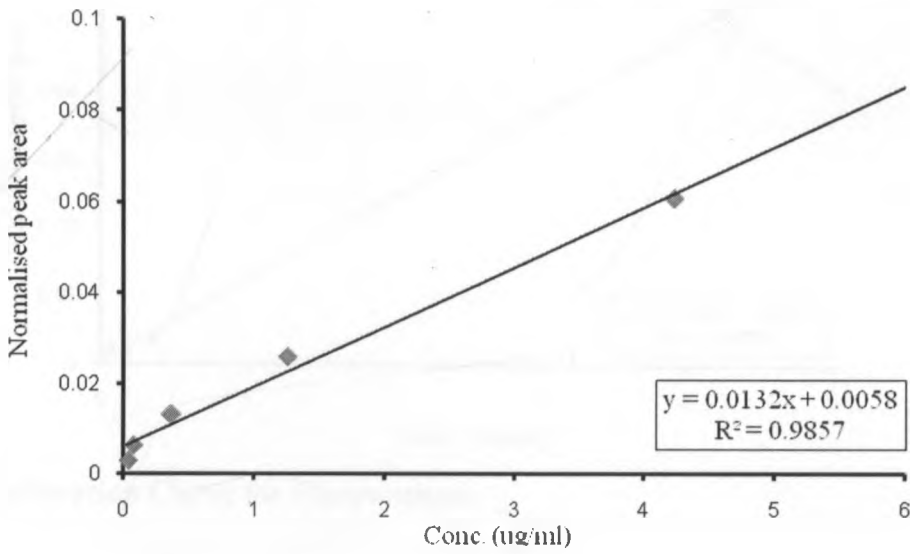
Calibration Curve for Fluorene

Calibration Curve for Anthracene

Calibration Curve for Fluoranthene

y = 0.0168x - 0.0023
R^2 = 0.9963
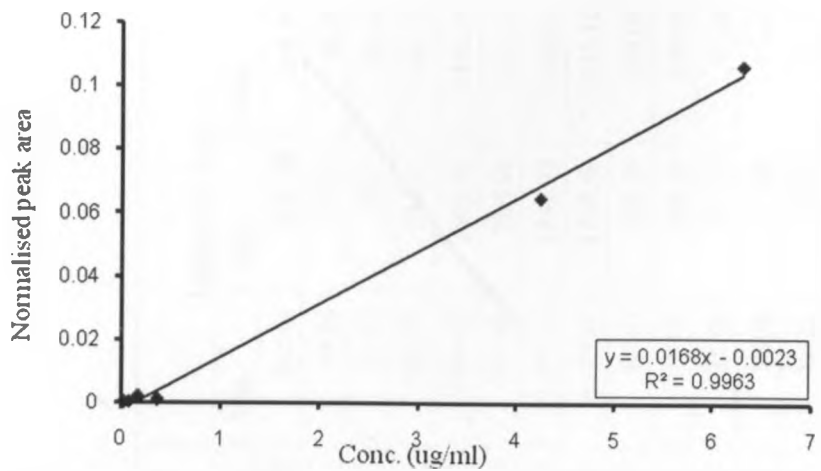
Calibration Curve for Pyrene

Ranges and Median Levels of PAHs Detected in air (ng/filter)

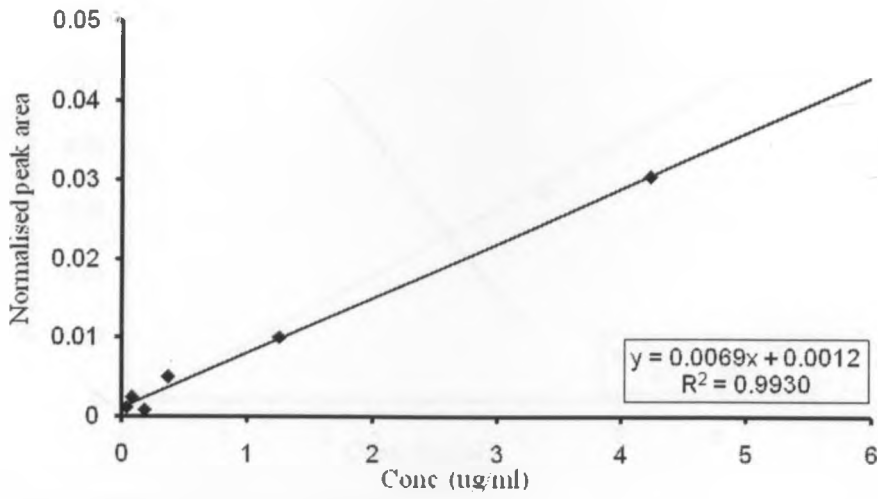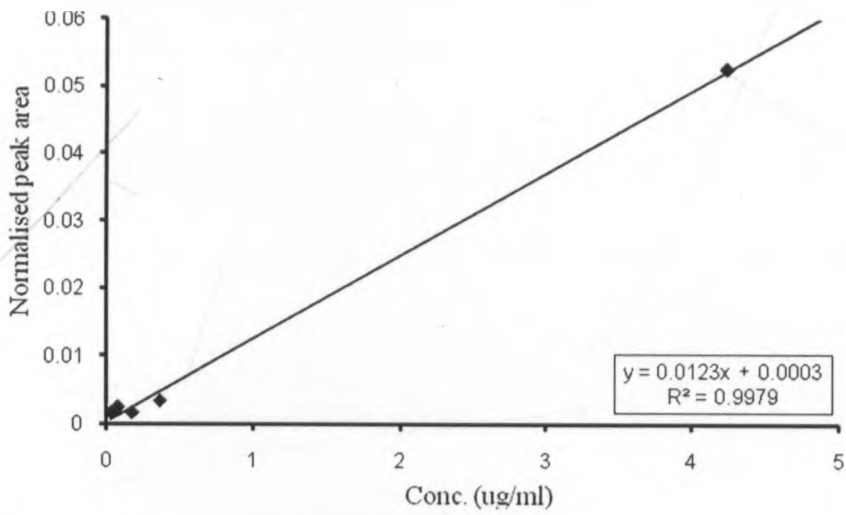| PAHs		Kabete			Dandora			Industrial Area		
PAHs		Min.	Max.	Med.	Min.	Ma.	Med.	Min.	Max.	Med.
PAH 1	Naphthalene	83.02	312.19	198.12	145.69	318.09	184.37	162.83	326.78	208.90
PAH 2	Acenaphthylene	9.22	23.00	18.41	45.58	117.14	63.17	49.34	87.28	56.29
PAH 3	Acenaphthene	17.95	31.36	19.34	55.04	90.98	73.89	41.41	70.03	62.05
PAH 4	Fluorene	161.54	247.75	169.47	575.87	737.60	683.68	385.94	534.51	494.52
PAH 5	Phenanthrene	670.72	985.79	738.11	2961.38	3939.66	3251.87	2086.52	2902.16	2442.34
PAH 6	Anthracene	29.56	47.04	35.80	229.39	365.75	264.20	197.90	300.88	238.31
PAH 7	Fluoranthene	266.48	429.65	319.86	1135.42	1706.30	1408.38	1197.53	1747.93	1359.07
PAH 8	Pyrene	215.39	342.88	243.78	934.83	1592.77	1326.52	1134.61	1715.69	1375.10
PAH 9	Benzo(a)anthracene	10.0	22.06	16.52	74.34	111.13	96.27	83.13	115.86	108.00
PAH 10	Chrysene	23.0	46.67	32.16	92.69	157.5	129.27	119.00	164.14	140.95
PAH 11	Benzo(b)fluoranthene	6.0	12.44	7.74	24.14	38.0	34.76	25.38	47.79	37.44
PAH 12	Benzo(k)fluoranthene	4.0	8.30	4.96	10.62	23.0	17.84	16.00	21.68	17.60
PAH 13	Benzo (a)pyrene	1.70	5.19	2.31	4.38	21.0	13.19	12.25	19.87	17.50
PAH 14	Benzo(ghi)perylene	bd	2.90	1.88	7.72	21.0	15.08	11.38	18.06	15.22
PAH 15	Indeno(1,2,3cd)pyrene	bd	bd	bd	Bd	2.0	0.45	bd	2.00	bd
PAH 16	Dibenz(ah)anthracene	bd	6.76	2.40	8.69	24.00	17.39	13.13	20.77	19.16
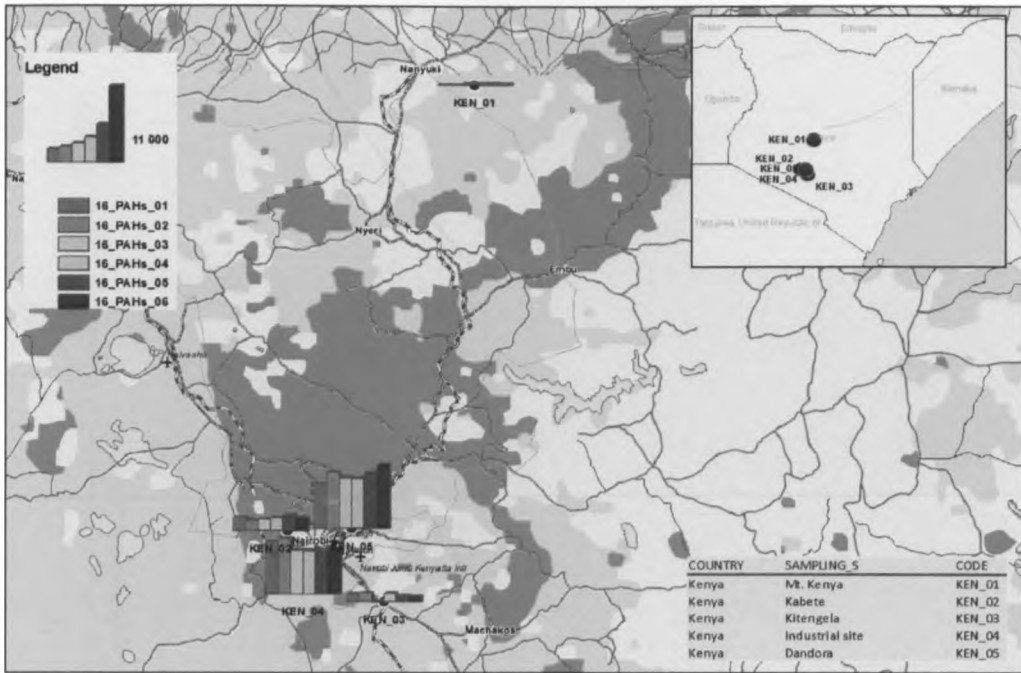
Levels of PAHs in Air in Kenya (ng/filter)

APPENDIX VI

ANOVA Table for Spatial Distribution of PAHs in Air

(I) matrix by site	(J) matrix by site	Mean Difference (I-J)	Std .Error	Sig.	95% Confidence Interval Lower Bound	Upper Bound
Kabete Air	Dandora Air	-5792.7633*	392.0380	.000	-6811.0745	-4774.4522
	Industrial Air	-4842.2100*	392.0380	.000	-5860.5211	-3823.8989
Dandora Air	Kabete Air	5792.7633*	392.0380	.000	4774.4522	6811.0745
	Industrial Air	950.5533	392.0380	.069	-67.7578	1968.8645
Industrial Air	Kabete Air	4842.2100*	392.0380	.000	3823.8989	5860.5211
	Dandora Air	-950.5533	392.0380	.069	-1968.8645	67.7578

* The mean difference is significant at the 0.05 level, (Tukey HSD)

Ranges and Median Levels of PAHs in Soil (ng/g)

PAHs		Kabete			Dandora			Industrial Area		
		Min	Max	Med	Min	Max	med	Min	Max	Med
PAH 1	Naphthalene	bd	10.1813	6.95	bd	11.96195452	6.03	bd	9.648338	7.08
PAH 2	Acenaphthylene	bd	bd	1.42	bd	1.98	1.98	bd	39.38	27.90
PAH 3	Acenaphthene	bd	1.47	0.00	bd	bd	0.02	bd	1.47	1.47
PAH 4	Fluorene	bd	0.00	0.00	bd	146.39	6.15	bd	bd	bd
PAH 5	Phenanthrene	bd	bd	0.93	14.94	526.66	71.63	12.75	19.75	13.53
PAH 6	Anthracene	bd	bd	0.00	6.51	162.61	47.08	16.06	41.56	22.85
PAH 7	Fluoranthene	4.28	37.61	27.14	18.59	40.23	23.01	0.00	0.00	30.48
PAH 8	Pyrene	7.24	16.62	11.44	7.75	81.94	16.32	19.25	25.43	20.75
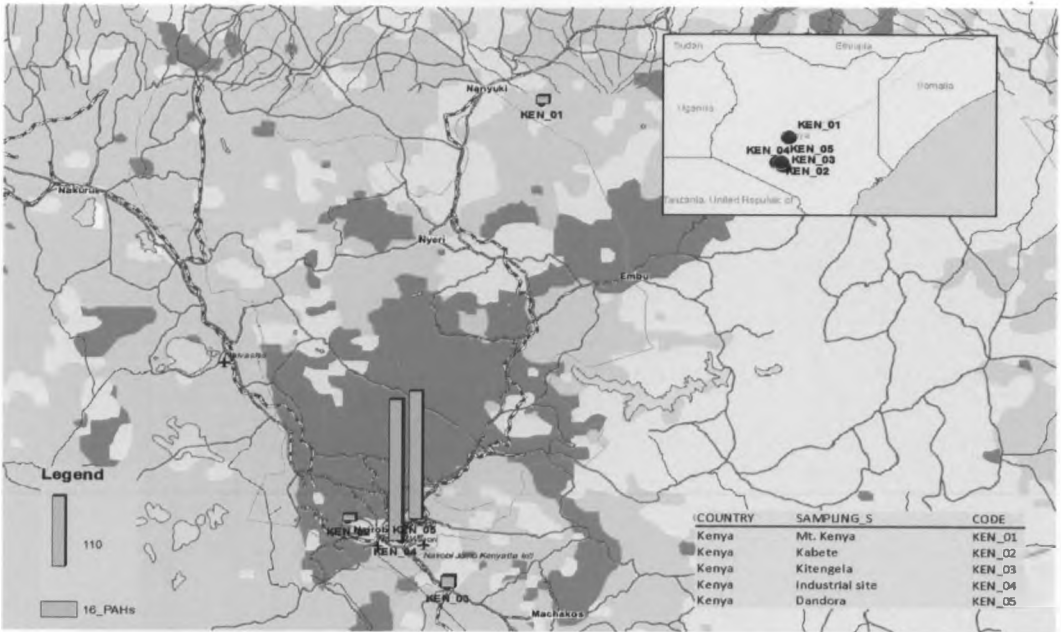
Levels of PAHs in Soil in Kenya (ng/g)

ANOVA Table Spatial Distribution of PAHs in Soil

(I) matrix by site	(J) matrix by site	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval		
					Lower Bound	Upper Bound	
Kabete Soil	Dandora Soil	-249.8633*	73.6770	.011	-441.2380	-58.4887	
	Industrial soil	-71.0833	73.6770	.609	-262.4580	120.2913	
Dandora Soil	Kabete Soil	249.8633*	73.6770	.011	58.4887	441.2380	
	Industrial soil	178.7800	73.6770	.069	-12.5946	370.1546	
Industrial soil	Kabete Soil	71.0833	73.6770	.609	-120.2913	262.4580	
	Dandora Soil	-178.7800	73.6770	.069	-370.1546	12.5946	

* The mean difference is significant at the 0.05 level, (Tukey HSD)

Correlations Coefficients for Spatial and Temporal Distribution of $\sum$ 8PAHs in Air and Soils

		Month	Kabete Soil	Kabete Air	Dandora Soil	Dandora Air	Industrial Soil	Industrial Air	
Month	Pearson Correlation	1.000	-.039	.291	.579	.402	.241	-.792	
	Sig. (2-tailed)	.	.942	.576	.229	.429	.646	.060	
	N	6	6	6	6	6	6	6	
Kabete Soil	Pearson Correlation	-.039	1.000	.821*	-.774	-.353	-.246	-.153	
	Sig. (2-tailed)	.942		.	.045	.071	.493	.639	.772	
	N	6	6	6	6	6	6	6	
Kabete Air	Pearson Correlation	.291	.821*	1.000	-.348	-.165	.006	-.174	
	Sig. (2-tailed)	.576	.045	.	.499	.755	.990	.741	
	N	6	6	6	6	6	6	6	
Dandora Soil	Pearson Correlation	.579	-.774	-.348	1.000	.503	.337	-.290	
	Sig. (2-tailed)	.229	.071	.499	.	.309	.514	.578	
	N	6	6	6	6	6	6	6	
Dandora Air	Pearson Correlation	.402	-.353	-.165	.503	1.000	-.578	-.390	
	Sig. (2-tailed)	.429	.493	.755	.309	.	.229	.445	
	N	6	6	6	6	6	6	6	
Industrial Soil	Pearson Correlation	.241	-.246	.006	.337	-.578	1.000	.166	
	Sig. (2-tailed)	.646	.639	.990	.514	.229	.	.754	
	N	6	6	6	6	6	6	6	
Industrial Air	Pearson Correlation	-.792	-.153	-.174	-.290	-.390	.166	1.000	
	Sig. (2-tailed)	.060	.772	.741	.578	.445	.754	.	
	N	6	6	6	6	6	6	6	

* Correlation is significant at the 0.05 level (2-tailed). Month Value Labels: 1=February, 2=March; 3=April, 4=May, 5=June, 6=July

Correlation Coefficients for Seasonal Variation of $\sum$ 8PAHs in Air and Soils

		SEASON	Kabete Air	Kabete soil	Dandora Air	Dandora soil	Industrial Air	Industrial Soil	
SEASON	Pearson Correlation	1.000	.587	-.551	.959	.858	-.969	-.400	
	Sig. (2-tailed)		.600	.628	.183	.343	.159	.738	
	N	3	3	3	3	3	3	3	
Kabete Air	Pearson Correlation	.587	1.000	-.999*	.333	.919	-.369	.507	
	Sig. (2-tailed)	.600		.028	.784	.257	.759	.661	
	N	3	3	3	3	3	3	3	
Kabete soil	Pearson Correlation	-.551	-.999	1.000	-.292	-.901	.328	-.544	
	Sig. (2-tailed)	.628	.028		.812	.285	.787	.633	
	N	3	3	3	3	3	3	3	
Dandora Air	Pearson Correlation	.959	.333	-.292	1.000	.677	-.999*	-.644	
	Sig. (2-tailed)	.183	.784	.812		.526	.024	.555	
	N	3	3	3	3	3	3	3	
Dandora soil	Pearson Correlation	.858	.919	-.901	.677	1.000	-.705	.127	
	Sig. (2-tailed)	.343	.257	.285	.526		.502	.919	
	N	3	3	3	3	3	3	3	
Industrial Air	Pearson Correlation	-.969	-.369	.328	-.999	-.705	1.000	.614	
	Sig. (2-tailed)	.159	.759	.787	.024	.502		.579	
	N	3	3	3	3	3	3	3	
Industrial Soil	Pearson Correlation	-.400	.507	-.544	-.644	.127	.614	1.000	
	Sig. (2-tailed)	.738	.661	.633	.555	.919	.579		
	N	3	3	3	3	3	3	3	

* Correlation is significant at the 0.05 level (2-tailed), Seasonal Value Labels: 1=Warm Dry, 2= Wet, 3=Cool Dry