MONITORING AND CANCER RISK ASSESSMENT OF SELECTED PERSISTENT ORGANIC POLLUTANTS IN NAIROBI CITY, KENYA

BY

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DECLARATION

I certify that this thesis has not been previously presented for a degree award in Maseno University or any other university. The work is my original work and all the sources of information have been supported by relevant references.

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DEDICATION

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ABSTRACT

In Kenya, cancer is the third cause of death, after infectious and cardiovascular diseases. However, the causes of these high cancer burdens are not fully documented. Analysis of human milk from Nairobi City revealed possible human exposure to bioavailable persistent organic pollutants (POPs), which are known carcinogens. However, the levels, distribution, spatial variations and sources of these bioavailable POPs in the city are not known. The Stockholm Convention on POPs banned the use of eight organochlorine pesticides (OCPs), while USEPA monitors 16 priority polycyclic aromatic hydrocarbons (PAHs) in the environment, due to their carcinogenic risks. However, the cancer risks posed by environmental OCPs and PAHs to the residents of Nairobi City have never been assessed. Use of passive sampling and active sampling in monitoring of environmental OCPs and PAHs was evaluated. Levels of bioavailable OCPs and PAHs were monitored in air and selected surface waters in Dandora, Kibera, City Square, Industrial Area and Ngong Forest using semipermeable membrane devices (SPMDs) in a split-plot design replicated three times. SPMDs were exposed for 28 days, extracted by dialysis and analytes fractionated by solid phase extraction. The OCPs were analysed by GC-ECD while PAHs were analysed by GC-FID, and confirmed by GC/MS. Analysis of variance was done, and the data used to determine the distribution, spatial variation, sources, and cancer risks posed in Nairobi City. Active sampling gave lower ($p \leq 0.05$) pollutants' levels than passive sampling; indicating possible underestimation of their actual environmental levels in previous studies. Adoption of passive sampling in monitoring of environmental PAHs and OCPs is therefore recommended. Levels of gas-phase OCPs were $0.018\ \text{ng m}^{-3} - 1.277\text{ng m}^{-3}$, while dissolved OCPs were $< \text{LOD} - 1297.667\ \text{ng m}^{-3}$ in the order:Industrial area $> Dandora > Kibera > City\ Square > Ngong' Forest$. Levels of gas-phase and dissolved PAHs were $0.104\ \text{ng m}^{-3} - 1.773\ \text{ng m}^{-3}$and $< LOD - 1144.000\ ng\ \text{m}^{-3}$, respectively, in the order: City Square $> Industrial\ Area > Dandora > Kibera > Ngong'$Forest. The results suggested mixed sources of PAHs. Fugacity ratios revealed that Nairobi River contributed ($p \leq 0.05$) to atmospheric PAHs and OCPs in Nairobi City. The OCPs inhalation incremental lifetime cancer risks (ILCR) values were $2.3745\ \text{x}10^{-13} - 1.6845\ \text{x}\ 10^{-11}$ (adult) and$5.5404\ \text{x}\ 10^{-13} - 3.9306\ \text{x}\ 10^{-11}$ (child), while the PAHs inhalation ILCR were $2.3573\ \text{x}\ 10^{-11} - 1.5920\ \text{x}\ 10^{-08}$(adult), and $5.5003\ \text{x}\ 10^{-11} - 3.7147\ \text{x}\ 10^{-08}$(child). The ILCR for both OCPs and PAHs in Nairobi City were below the acceptable risk levels, indicating that neitheratmospheric PAHs norOCPs in Nairobi City posed significant cancer risks to the residents.

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LIST OF ABBREVIATIONS

ASTDR	Agency for Toxic Substances and Disease Registry
BaP_{eq}	Equivalent concentration of Benzo (a) pyrene
BCFs	Bioconcentration factors
CSF	Cancer slope factor
CV	Coefficients of variation
Cw_{SPMD}	SPMD-based aqueous concentrations
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EMDL	Estimated method detection limit
f_A	Fugacity in air
f_W	Fugacity in water
GC-MS	Gas chromatography-mass spectrornetry
GLOBOCAN	Global Cancer Observatory.
H_C	Henry's law constant
HCH	Hexachlorocyclohexane
HOC	Hydrophobic organic chemicals
HPLC	High performance liquid chromatography
IARC	International Agency for Research on Cancer
IDL	Instrument detection limit
ILCR	Incremental Lifetime Cancer Risks
K_{AW}	Air-water partition

k_e	Performance reference compound release rate
Koc	Soil/sediment adsorption coefficients / organic carbon partition coefficient
K_{OW}	Octanol-water partition coefficient
K_{PW}	SPMD-water partition coefficient
LADD	Lifetime Average Daily Dose
LBNL	Lawrence Berkeley National Laboratory
LDPE	porous low-density polyethylene
LOD	Limit of detection
LSD	Least significant difference
MDL	Method detection limit
MOH	Ministry of Health
MRL	Minimal risk levels
NIP	National Implementation Program
OCPs	Organochlorine pesticides
OECD	Organization for Economic Co-operation and Development
PAHs	Polycyclic aromatic hydrocarbons
PBCR	population-based cancer registries
PCBs	Polychlorinated biphenyls
PCN	polychlorinated naphthalenes
POPs	Persistent organic pollutants
ppm	Parts per million
PRC	Performance reference compound
PRC SPMDs	Performance reference compound semipermeable membrane devices

PUF	Polyurethane foam
PUF - PAS	Polyurethane foam –based passive air sampler
RRF	Relative response factor
S.E.D	Standard errors of differences of means
SIM	Selected ion monitoring
SPMDs	Semipermeable membrane devises
TEQ	Toxicity Equivalency
TWA	Time-weighted average
UNECE	United Nations Economic Commission for Europe
UNEP/UNDP	United Nations Environmental Programme / United Nations Development Programme
UNEP-GEF	United Nations Environmental Programme – Global Environment Fund
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
WHO	World Health Organisation
WHO-TEF	World Health Organization Toxic Equivalent Factor
WWTP	Waste water treatment plant

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CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

In Kenya, cancer has been ranked third as a cause of death after infectious diseases and cardiovascular diseases and is estimated to account for about 7% of total national mortality every year (MOH, 2011; 2020). By the year 2011, it was estimated that the risk of getting cancer before the age of 75 years in Kenya is estimated at 14% while the risk of dying of cancer is estimated at 12% (MOH, 2011). However, the possible causes of these cancers have not been determined. National estimates of cancer incidences and mortality are predominantly based on data from population-based cancer registries (PBCR) (Parkin et al., 2014). In Kenya, the Nairobi Cancer Registry covers the population of Nairobi County, and thus documents cancer cases among the residents of Nairobi City. Data from the Nairobi Cancer Registry shows that the age standardized cancer incidence rates, per year, for the 5 year period (2004–2008), among men were 161 per 100,000 and 231 per 100,000 among women (Korir et alet al., 2015) in Nairobi City. The percentage of the cases with morphological verification of diagnosis (overall 85.7% in males, 87.0% in females) was higher than in the other registries of sub-Saharan Africa (Korir et al., 2015). However, the reasons for the high burden of cancers in Nairobi City are not fully understood. Though there has been overwhelming public concern over the possible contribution of environmental pollution in Nairobi City to increasing number of cancer cases, the possible cancer risks posed by various environmental contaminants in the city have never been evaluated.

Analysis of human milk samples from breastfeeding mothers in Nairobi City, Kenya, revealed presence of high levels of DDTs, dieldrin, furans, dioxins and PCBs in the milk (UNEP-GEF Project, 2012). This indicated human exposure to bioavailable persistent organic pollutants

(POPs) in Nairobi City. POPs are a class of pollutants that are not easily degraded in the environment (Field & Sierra-Alvarez, 2008). These pollutants include organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dioxins. POPs are highly lipophilic, undergo bio-accumulation and even though they occur in trace amounts in the environment, they pose significant toxic hazards (Krahn et al., 2007; Mos et al., 2004; Ross, 2006; Ross & Birnbaum, 2003; Van Oostdam et al., 2005; Weisglas-Kuperus et al., 2004). Most POPs are known carcinogens (UNECE, 1998a). However, the environmental pollution status of Nairobi City, with reference to POPs, is not fully documented.

Organochlorine pesticides (OCPs) are a broad class of synthetic substances which are used for pest control (Regan et al., 2012). OCPs have long persistence in the environment and are associated with damaging and/or suppressing the human immune system (Ritter et al., 1995). OCPs are also listed as possible human carcinogens, especially with regard to hormonal cancers, such as breast cancer. As a result, The Stockholm Convention on POPs banned the use of a number of POPs, most of which were OCPs (Bouwman, 2004). However, despite the ban, OCPs are still found in the environment in significant levels (Afful et al., 2010). Further, from the National Inventory of POPs, Kenya is still grappling with the management of stockpiles of obsolete pesticides and other persistent chemicals, some of which were banned under the Stockholm Convention (UNEP-GEF Project, 2012). This indicates poor enforcement of the environmental protection laws in Kenya. Some of the obsolete pesticides could be finding their way into the environment, causing high levelshuman exposure to these environmental pollutants. However, the levels, distribution, sources and the health risks posed by bioavailable environmental OCPs in Kenya have never been evaluated.

Polycyclic aromatic hydrocarbons (PAHs) refer to a large class of organic compounds with two or more fused aromatic rings (Lee et al., 1976). Most PAHs have been classified as carcinogenic, teratogenic, as well as mutagenic, besides other potential toxic effects (Schramm et al., 2001; Zhu et al., 2013). About 500 PAHs have been characterized in air (WHO, 1998; Bostrom et al., 2002), as well as in aquatic and terrestrial environments; many of which are classified as carcinogenic (IARC, 1983, 1984a, 1984b, 1985, 2010). The sources of these environmental POPs included petrogenic sources (IARC, 1985, 1989, 1984a) and industrial sources (IARC, 1984b), as well as pyrogenic sources (Boleij et al., 1989; Lisouza et al., 2011). Among these PAHs is benzo(a)pyrene which was upgraded to a Group 1 known human carcinogen in the latest reassessment of carcinogenic potential of PAHs(IARC, 2010). As a result, there is considerable concern about the relationship between exposure to PAHs in the ambient air, as well as in other environmental sectors, and their potential contribution to human cancer incidence.

The United States Environmental Protection Agency (USEPA) monitors 16 priority PAHs in air, and in aquatic and terrestrial ecosystems due to these health concerns (IARC, 1983). These PAHs include naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, Benzo(a)Pyrene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)-perylene, and dibenz(a,h)anthracene (IARC, 1983). In Kenya, recent studies indicate potential human exposure to high concentrations of PAHs originating from indoor biomass combustion (Lisouza et al., 2011, 2013; Boleij et al., 1989), roasted meat and fish (Onyango et al., 2012), fresh fish (Orony et al 2016) and in waste waters and sediment from car washing points at the Kisumu City Bay of Winam Gulf, Lake Victoria-Kenya (Kwach et al., 2009). However, the levels, distribution, sources and the health risks posed by bioavailable environmental PAHs in Kenya, and specifically in Nairobi City, have

never been evaluated. The most notable sources of POPs in urban areas include anthropogenic activities such as waste incineration (Tuppurainen et al., 1998; Xu et al., 2009; Liu et al., 2013), industrial chemical processes, and motor vehicle emissions as a result of incomplete combustion of organic carbon, obsolete electronic waste, poor disposal of textiles, and agriculture (Moon et al., 2012; Antunes et al., 2012). Most of these processes take place in Kenyan urban areas, especially in Nairobi City, which hosts more than 40% of the industries in Kenya; majority of them located in the industrial area. The city is also home to more than 4.5 million people. This high population, in turn, leads to heavy traffic on the roads as people travel within the city, as well as into and out of the city. However, the distribution, spatial variations and possible sources of the various POP congeners in outdoor air and surface waters in the city, with reference to bioavailable POPs, are not known.

International regulations have been focusing on reducing emission of POPs into the environment (UNECE, 1998a, 1998b), risk assessment and modeling efforts on the ambient distribution of POPs (Klecka et al., 2000). In Kenya, the National Implementation Plan for POPs recommended the need to expand air monitoring assessment to capture high gradient sites (UNEP-GEF Project, 2012). This would track the impact of remediation and mitigation measures taken at national regulatory levels to reduce POPs in environment. Stewart and Wild, (2014), on the other hand, stressed the need for adequate legislation to encourage healthier behaviour, and to protect people from workplace hazards and environmental pollutants. However, such regulations should be based on valid data that show the real risks posed by the POPs; that is, the proportion of the POPs in the environment that are bioavailable to humans. The UNEP-GEF Project (2012) recommended that a more holistic sampling of POPs should be adopted to capture their actual environmental concentrations. The report further observed that this will require high investment

in active air sampling designed for POPs sampling. A major limitation of the high-volume samplers (active sampling) is that the data collected gives information about the total concentrations of the POPs (both free and adsorbed phase POPs), but do not provide any information on what fraction of the POPs is bioavailable (Huckins et al., 1990; Alvarez et al., 2004). Further, data from active sampling is not time-integrated and hence it is not representative of the actual environmental levels of the contaminants (Alvarez et al., 2004; Alvarez, 2010). Such data may, therefore, not provide valuable information in the assessment of the risks posed by POPs in Kenya. It is not documented if integration of graded filters in active sampling during environmental monitoring of POPs would be effective in isolating of the bioavailable fraction of the POPs from the various environment media.

Passive sampling for POPs give time-integrated data that is representative of the actual environmental levels of the contaminants, provides information about the bioavailability of the sampled compounds and is more reproducible (Söderström et al., 2005; Vrana et al., 2007). According to Esteve-Turrillas, (2008), the contaminant uptake by passive samplers is affected by environmental factors such as temperature, wind speed, turbulence, flow rate and biofouling (Esteve-Turrillas, 2008). Semipermeable membrane devises (SPMDs) have been used in both the temperate and sub-tropical regions in environmental monitoring of POPs (Esteve-Turrillas, 2008; Söderström et al., 2005; Vrana et al., 2006, 2007; Huckins et al., 1990; Lebo et al., 1992). For instance SPMDs have been extensively used in monitoring POPs in the Yangtze Three Gorges Reservoir, China, (Wang et al., 2009; Schramm et al., 2012) which is situated in a region classified as having a subtropical climate. According to the Köppen-Geiger climate classification, Nairobi City is also classified as having subtropical highland climate (Pidwirny, 2006; Beck et al., 2018). Though, polyurethane foam has been used in passive sampling of POPs

in Kenya (UNEP-GEF Project, 2012), no procedure was put in place to separate the free-phase POPs from those adsorbed on particulate matter. The data, therefore, provided no information on the levels of the bioavailable fraction of the sampled POPs. Since SPMDs have never been used in monitoring environmental POPs in Kenya, the levels, distribution and possible sources of the bioavailable POPs in Nairobi City is not documented.

Each POP congener established to be toxic, has an assigned World Health Organization Toxic Equivalent Factor (WHO-TEF), which is used for the computation of the Toxicity Equivalency (TEQ) of the congener (Van den Berg et al., 2006). These TEQs are used as a scale in risk assessment studies for POPs to calculate their probability of causing cancer and other life threatening diseases for humans and/or animals. However, the TEQs are only computed using the levels of the pollutant in food, water or air, which is bioavailable to humans and/or animals. Since the sampling methods used in the previous studies for POPs in Kenya (Lisouza et al., 2011, 2013; Boleij et al., 1989; Onyango et al., 2012; Kwach et al., 2009; UNEP-GEF Project, 2012) did not provide any information on the bioavailable fractions of the sampled POPs, such data could not be used in risk assessment studies. Consequently, the cancer risks posed by environmental POPs, probably emitted into the air and surface waters in Nairobi City, have not been evaluated.

1.2 Statement of the Problem

In Kenya, cancer is ranked third as a cause of death after infectious diseases and cardiovascular diseases. Data from Nairobi Cancer Registry show that the cancer incidence rates in Nairobi City are higher than those in other registries of sub-Saharan Africa. However, the causes of this high cancer burden in the country are not known. Though there has been overwhelming public concern over the possible contribution of environmental pollution in Nairobi City to increasing

number of cancer cases, the possible cancer risks posed by various environmental contaminants in the city have never been evaluated. Analysis of human milk samples from breastfeeding mothers in Nairobi City revealed human exposure to bioavailable POPs; which are known carcinogens. This raises need for legislation to protect people from exposure to high levels of workplace and environmental pollutants. But such regulations must be based on valid data that show the real risks posed by the environmental POPs. A critical part of any analytical procedure for environmental monitoring is sampling; data from active sampling provides no information on the bioavailability of the sampled contaminants. However, use of SPMDs in passive sampling of environmental POPs mitigates these weaknesses. Integration of graded filters into active sampling will enable sampling of only bioavailable POPs. However it is not known how the data will compare to that collected using SPMDs in passive sampling.

The Stockholm Convention on POPs (2001) banned the manufacture and/or use of organochlorine pesticides (OCPs), while the USEPA monitors 16 priority polycyclic aromatic hydrocarbons (PAHs) in the environment, due to their potential carcinogenic risks to humans. The OCPs and PAHs, on the contrary, are still reported in the Kenyan environment, including Nairobi City and surrounding areas. However, the identities, levels, distribution, spatial variations and possible sources of the bioavailable fraction of these environmental contaminants in outdoor air and surface waters in the city are not known. Further, the possible cancer risks posed by environmental OCPs and PAHs to the residents of the city have never been evaluated.

1.3 Objectives

1.3.1Main Objective

To determine the OCPs and PAHs pollution status of outdoor air and surface waters, in Nairobi City, Kenya using passive sampling and to evaluate the cancer risks they pose to the residents of the city.

1.3.2 Specific Objectives

(i) To comparatively evaluate the use of active sampling integrated with graded filters and passive sampling using SPMDs in monitoring of gas-phase and dissolved OCPs and PAHs in air and surface waters

(ii) To determine the distribution, spatial variation and possible sources of bioavailable OCPs in air and selected surface waters at various sites in Nairobi City, Kenya using passive sampling.

(iii) To determine the distribution, spatial variation and possible sources of bioavailable PAHs in air and selected surface waters in various sites in Nairobi City, Kenya using passive sampling.

(iv) To assess the cancer risks posed by these OCPs and PAHs in Nairobi City, Kenya.

1.4 Null hypothesis (H_0)

(i) There is no significant difference between the amount of POPs collected by active sampling integrated with graded filters and those collected by SPMDs.

(ii) There are no quantifiable levels of gas-phase and dissolved OCPs in air and surface waters in Nairobi City, Kenya, and hence there are no significant differences ($p \leq 0.05$) in the levels of OCPs in various sites and environmental media in the city.

(iii) There are no quantifiable levels of gas-phase and dissolved PAHs in air and surface waters in Nairobi City, Kenya, and hence there are no significant differences ($p \leq 0.05$) in the levels of PAHs in various sites and environmental media in the city.

(iv) OCPs and PAHs do not pose any cancer risks to the residents of Nairobi City, Kenya.

If the null hypothesis is not realized, then the alternative hypothesis (H_1) will be adopted.

1.5 Justification

In Kenya, cancer is ranked third as a cause of death; it accounts for about 7% of total national annual mortality. However, until the causes of the cancer cases are identified, it will be difficult to develop effective management strategies to curb the high cancer related mortality in Kenya.

CHAPTER TWO

LITERATURE REVIEW

2.1 Toxicity and Sources of Persistent Organic Pollutants

Persistent organic pollutants (POPs) are substances that undergo long-range transport in the atmosphere (Li et al., 2007), accumulate in fatty tissue of living organisms (Cok et al., 2007; Bordajandi et al., 2008) and are not readily broken down in the environment (Field & Sierra-Alvarez, 2008). As a result, POPs form a class of environmental contaminants described as ubiquitous. These substances include organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dioxins.

Prolonged exposure to POPs or their mixtures has been linked to adverse health effects involving immune system, reproductive, developmental, and neurological dysfunction as well as carcinogenic effects in high trophic level wildlife and humans (Krahn et al., 2007; Mos et al., 2004; Ross, 2006; Ross & Birnbaum, 2003; Van Oostdam et al., 2005; Weisglas-Kuperus et al., 2004). Some of the compounds have also been associated with endocrine disrupting properties; studies show that some POPs have the capacity of altering natural hormone-signaling pathways such as thyroid hormones (Brouwer et al., 1998; Cheek et al., 1999; Lans et al., 1993), estrogens and androgens (Bonefeld-Jorgensen et al., 2001). A number of POPs have carcinogenic, hepatotoxic, reproductive, and immunotoxic effects (Safe, 1994; Schecter et al., 2006; Schmidt, 1999). Studies have reported possible human exposure to high levels of environmental POPs in Kenya (Boleij et al., 1989; Kwach et al., 2009; Lisouza et al., 2011; UNEP-GEF Project, 2012; Omwoma et al., 2015; Sun et al., 2016; Aucha et al., 2017). Data show that, in Kenya, cancer-related death accounts for about 7% of total national mortality every year (MOH, 2011; 2020).

However, the health risks, especially the incremental lifetime cancer risk (ILCR) posed by human exposure to environmental POPs in Kenya have never been evaluated.

2.1.1 Toxicity and Sources of Organochlorine Pesticides

Organochlorine pesticides (OCPs) are a broad class of a variety of synthetic substances which are used for pest control (Regan et al., 2012). The characteristic feature in the structure of organochlorines (OCs) is the presence of carbon-chlorine bond or bonds (Stimman et al., 1985). The most notable compound among OCPs is dichlorodiphenyltrichloroethane (DDT) (Figure 1.1). Other examples of OCPs include gamma-hexachlorocyclohexane (γ-HCH), which is commonly known as lindane, dieldrin, among others. The chlorine-carbon bonds in organochlorines are very strong, which means that they do not break down easily. As a result, OCPs have high persistence in the environment; this led to the ban of most of them both as agrochemicals to control pests and as formulations of other pesticide products such as mosquito coils (Bouwman, 2004).

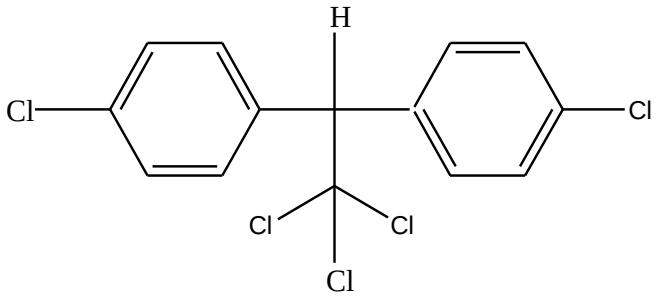


Figure 1.1: Structure of DDT

The Stockholm Convention on Persistent Organic Pollutants (2001) focused on reducing and/or eliminating the manufacture and use of 12 POPs, eight of which are organochlorine pesticides: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, and toxaphene (Stockholm Convention, 2008). Aldrin readily converts to dieldrin in plants and animals (Ritter et al., 1995). Besides their agricultural uses, aldrin, chlordane, dieldrin and heptachlor are also used to protect

wooden structures from termites. DDT is still used in many countries to control mosquitoes which are responsible for spreading malaria (WHO, 2007).

Acute exposure to aldrin caused death in waterfowl, shorebirds, fish and humans (Ritter et al., 1995) while dieldrin is suspected to negatively affect the immune response in humans (Ritter et al., 1995). On the other hand, chlordane is suspected of damaging the human immune system and is listed as a possible human carcinogen (Ritter et al., 1995). Similarly, DDT and its metabolite DDE are listed as possible human carcinogens, particularly as regards hormonal cancers, such as breast cancer (Ritter et al., 1995; Brouwer et al., 1998). Endrin is suspected of suppressing the human immune system. Heptachlor, mirex and toxaphene are listed as a possible human carcinogen (Ritter et al., 1995; Brouwer et al., 1998). Studies (Afful et al., 2010; Sun et al., 2016; Aucha et al., 2017) show that OCPs are still found in the environment, including in Nairobi City and its surrounding areas, in significant levels. However, information on the potential sources and distribution of the OCPs in the ambient air in Nairobi City, Kenya and the potential health risks they pose has never been documented.

From the National Inventory of POPs, Kenya grapples with the management of Stockpiles of obsolete pesticides and other persistent chemicals, some of which have been banned under the Stockholm Convention (UNEP-GEF Project, 2012). According to the inventory there were over 15,000 tons of obsolete pesticides in Kenya, distributed countrywide (UNEP-GEF Project, 2012), majority of which were in Nairobi City. This indicated poor enforcement of the environmental protection laws in Kenya. It is probable that some of the obsolete pesticides could be finding their way into the environment. This is likely to result in human exposure to high levels of these pollutants in the environment. However, the levels, distribution and human health

risks posed by the pollutants, particularly in Nairobi City, and Kenya in general, have never been evaluated.

2.1.2 Toxicity and Sources of Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) refer to a large class of organic compounds with two or more fused aromatic rings (Lee et al., 1976). They are sometimes referred to as polycyclic organic matter, polynuclear organic matter or polynuclear aromatic compounds, (Minnesota Pollution Control Agency, 1998). PAHs are resistant to biodegradation and can bioaccumulate in the environment through the food chain (Lenndorf & Schwark, 2004). Inhalation is one of the main means of human exposure to PAHs because of their ubiquitous presence in the atmosphere, especially in urban areas. However, most studies in Kenya considered only PAHs found in the particle phase (Boleij et al., 1989; Lisouza et al., 2011, 2013), soils and sediments (Kwach et al., 2009), while omitting the contribution of the gas-phase PAHs to the risk. Information on the potential sources and distribution of PAHs in the ambient air in Nairobi City of Kenya and the potential health risks they pose is not documented.

Exposure to polycyclic aromatic hydrocarbons (PAHs) has been associated with induction of a number of biological responses, including immunotoxicity (Head & Lawrence, 2009; Kerkvliet, 2009). PAHs reduce bone marrow and thymus cellularity, to impair B- and T-lymphocyte proliferation, and to alter the differentiation and function of B- and T-lymphocyte (Head & Lawrence, 2009; Kerkvliet, 2009). The alterations in immune system function result in a decrease in pathogen and tumor immunity (Head and Lawrence, 2009; Kerkvliet, 2009) and skewing of immune responses toward pathologic autoimmunity (Funatake et al., 2005; Quintana et al., 2008; Veldhoen et al., 2008). Most PAHs have been classified carcinogenic, teratogenic, as well as mutagenic, besides other potential toxic effects (Schramm et al., 2001; Zhu et al.,

2013). In Kenya, cancer has been and continues to pose major health challenges across the entire population, and is reported to contribute to a significant proportion of deaths nationwide (MOH, 2020). Studies have reported exposure to PAHs through consumption of fish (Onyango et al., 2012; Orony et al., 2016) and through environmental exposure (Lisouza et al., 2011, 2013; Boleij et al., 1989; Kwach et al., 2009). However, the health risks posed by environmental PAHs in Kenya have never been evaluated.

The most significant source of PAHs in the environment is the combustion of fossil fuels, mainly crude oils, bituminous deposits and petroleum products (Nikolaou et al., 2009; Miller &Olejnik, 2001),automobile engine exhausts (Lalah & Kaigwara, 2005) , usually referred to as petrogenic sources. Another major source of environmental PAHs is the incomplete combustion of organic matter (Webster et al., 2000). These include incineration of agricultural, industrial and municipal wastes, from power stations and motor vehicles, (Pufulete et al., 2004; Tsapakis et al., 2003; Nikolaou et al., 2009), domestic biomass burning (Lisouza et al., 2011, 2013), among others. These are usually referred to as pyrolytic or pyrogenic sources. Many of these processes take place in Kenyan urban areas, especially in Nairobi City which hosts more than 40% of all the industries in Kenya. However, the levels and distribution of bioavailable fraction of these PAHs emitted into the receiving environment are not known.

Sources of PAHs in surface waters include municipal and industrial effluent, atmospheric depositions of airborne particulates and precipitation, and aquatic pathways such as road run off, sewage spillage and oil spills (Boehm et al., 2007). Once present in the surface waters, the lower molecular weight PAHs are usually depleted through volatilisation, microbial oxidation and sedimentation (Boehm et al., 2007). Volatilisation is sometimes a major transport process for

lower molecular weight PAHs (Lee, 1975). For instance, studies reported that up to 50% of the naphthalene contained in marine oil spill was lost depending on various environmental parameters including water temperature and wind speed through volatilization (Southworth, 1979; Lee, 1975). This volatilization increases the amount of PAHs in the atmosphere, which increases human exposure to gas-phase PAHs. The spatial distribution of various PAHs in Kenyan urban areas, especially Nairobi City, is not documented.

In Kenya, no major natural sources of PAHs have been identified since forest fires are rare and there are no coal deposits that have been opened up. Thus, the most probable major PAHs sources in the country are the anthropogenic sources. Estimates reveal that motor vehicles are a major source of atmospheric PAHs emission (Van Metre et al., 2000) in urban environment. Domestic heating in general and residential wood combustion, in particular, could be another major source of PAHs to both urban and rural outdoor air (Menichini, 1992; Lisouza et al., 2011, 2013). Nairobi City hosts more than 40% of the industries in Kenya, and is home to more than 4.5 million people. This results in heavy traffic on the roads as people travel within the city, as well as in to and out of the city. Thus in Kenyan urban areas, PAH emissions are likely to result from industries due to burning of fuels such as gas, oil and diesel; as well as from motor vehicle emissions. Although a number of studies have reported presence of PAHs in Kenyan environment (Boleij et al., 1989; Kwach et al., 2009; Lisouza et al., 2011, 2013; Onyango et al., 2012), data on the environmental levels of PAHs in Kenya, especially in the urban environments, remains scanty. Further, the possible spatial variation in the levels of PAHs in outdoor air and surface waters has not been documented.

PAHs exhibit different distribution patterns according to their pollution sources (Yunker et al., 2002; Budzinski et al., 1997). As a result, isomer ratios are often used as diagnostic signatures

for source apportionment, on the assumption that the paired isomers get diluted to a similar extent during transport, and therefore maintaining constant ratios along the paths from sources to receptors (Yunker et al., 2002; Katsoyiannis et al., 2011). For instance, an anthracene/(anthracene + phenenthrene)) ratio of 0.1 is often applied to distinguish between petrogenic (<0.1) and pyrogenic (>0.1) sources (Yunker et al., 2002; Katsoyiannis et al., 2011; Shen et al., 2013). Similarly, a ratio of fluoranthene/(fluoranthene + pyrene) <0.5 indicate petrogenic sources, while a ratio > 0.5 indicate emissions from coal and biomass burning (Yunker et al., 2002; Katsoyiannis et al., 2011; Shen et al., 2013). An indeno(1,2,3-cd)pyrene/(indeno(1,2,3-cd)pyrene + benzo(ghi)perylene) ratio of 0.5 is usually recommended as a criterion separating coal (>0.5) and biomass (<0.5) burning (Yunker et al., 2002; Katsoyiannis et al., 2011). A benzo (a)pyrene/(benzo(a)pyrene + benzo(ghi)perylene) ratio is used to distinguish traffic sources (>0.38) from non-traffic contributions (<0.38) (Yunker et al., 2002; Katsoyiannis et al., 2011; Birks et al., 2017). Similarly, a benzo (a) anthracene/(benzo (a) anthracene + chrysene) ratios >0.35 have been reported to indicate combustion sources, those between 0.20 and 0.35 indicate either petrogenic or pyrogenic sources, while ratios <0.20 indicate petrogenic sources (Yunker et al., 2002; Shen et al., 2013; Stogiannidis & Lane, 2015). Similarly, benzo (a)anthracene/(benzo(a)anthracene + chrysene) ratio <0.2 has been reported to indicate petrogenic sources while a ratio >0.35 indicates combustion sources (Yunker et al., 2002; Shen et al., 2013; Stogiannidis & Lane, 2015). Shen et al., (2013) suggested that for the specific purpose of distinguishing certain sources, combinations of more than one ratio can be used to provide a multidimensional basis for diagnoses of sources. The source apportionment of environmental PAHs in Kenya is not documented.

2.2 Physical Properties of Persistent Organic Pollutants

The environmental transport, distribution, spatial variation, accumulation and fate of persistent organic pollutants (POPs) in the environment are predominantly governed by the physical properties of the individual pollutants. To elucidate the environmental dynamics of POPs, information on a number of equilibrium parameters characteristic to each of the pollutants is necessary (Mackay & Shiu, 1981). These parameters include; water solubility, vapor pressure, air-water partition coefficients or Henry's law constants, octanol/water partition coefficient, adsorption coefficient and bioconcentration factor. Mackay and Paterson (1981) described the environmental behavior of a chemical on thermodynamic basis using the fugacity approach (Equation 1). Fugacity (f) can be regarded as the ''escaping tendency'' of a chemical substance from one phase to the other.

$$f = x\gamma f_r \qquad (Equation\ 1)$$

Where; x = mole fraction of contaminant in water phase

γ = the activity coefficient of the contaminant expressed in Raoult's law convention (This characterizes the degree of ideality between water and the contaminant)

f_r = reference fugacity (P_a) which is the fugacity exerted by a solute/ contaminant when pure and in liquid state at the system temperature

Fugacity has units of pressure and can be related to concentration. According to Mackay and Shiu (1981), at environmental pressure of 1 atmosphere, fugacity can be taken to be equal to the vapour pressure of the liquid. For gaseous contaminants, f_r and γ in form of Henry's law constant (H_M), are expressed as a ratio of partial pressure p (Pa) to mole fraction (Equation 2).

$$p \approx f = x\gamma f_r = xH_M \qquad (Equation\ 2)$$

But the mole fraction (x) is related to concentration (C) of the pollutant in the water phase expressed in mol m^{-3} (Equation 3).

$$p = H_C C \qquad (Equation\ 3)$$

Where H_C is Henry's law constant expressed in Pa $m^3 mol^{-1}$

The fugacity ratios provide important information in understanding the spatial distribution of pollutants under the specific environmental conditions. However, information on the fugacities of various POPs under the environmental conditions in Nairobi City is not documented. As a result, possible contribution of contaminated surface waters to atmospheric POPs is not known.

The octanol-water partition coefficient (K_{OW}) is the equilibrium ratio of concentration of a dissolved chemical between octanol and water at a specified temperature (OECD, 1995). K_{OW} therefore represents the membrane lipid-water barrier because the behavior of POPs in n-octanol closely resembles that in lipids of living organisms. Further, K_{OW} is related to water solubility (S), soil/sediment adsorption coefficients (K_{OC}), and bioconcentration factors (BCFs) for aquatic life (Environment Canada, 2008; USEPA, 2011; Meeker et al., 2009). K_{OW} is thus used as an indicator of the bioconcentration and bioaccumulation (Geyer et al., 2000). To determine if a given contaminant undergoes either bioconcentration or bioaccumulation in biota, information on the levels of the bioavailable fraction of the contaminant in the environment is vital. However data obtained from conventional methods for sampling of POPs do not provide any information on the bioavailability of the sampled contaminants.

POPs have generally low Henry's law constant values. Henry's Law constant is an index of partitioning for a compound between the atmospheric and the aqueous phase (Mackay et al., 1982). The air-water partitioning for a hydrophobic contaminant is expressed as the ratio between the concentrations of the contaminant in air (C_A) to the concentration of the contaminant in the water phase (C_W), in mol m^{-3}. From the ideal gas law, C_A is equivalent to the number

moles, n, and hence; $C_A = P/RT$. This implies that; $K_{AW} = H_C/RT$. But since the value of RT range between 22000 and 22500 Pa m^3 mol^{-1} at environmental conditions; the implication of this is that a hydrophobic contaminant with H_C values in this range, will partition in equal concentrations between the air and water. The possible portioning of dissolved pollutants released into surface waters into the atmosphere has never been evaluated.

The relative volatility (α) of a hydrophobic contaminant is useful in estimating whether or not the concentration of the contaminant in water will increase or decrease when the water in which it is dissolved is exposed to the atmosphere (Mackay & Shiu, 1981). For a hydrophobic contaminant whose mole fraction in the liquid phase is x and that in vapour phase is y; $\alpha = y(1-x)/x(1-y)$. When its concentrations in water and air are very low, x and y are very low compared to unity. Thus α may be expressed as Equation 4.

$$\alpha = \frac{y}{x} = \frac{H_M}{P_T} = \frac{H_C}{P_T V_W} \quad \textit{Equation 4}$$

Where P_T is the total pressure of the vapour phase while $1/V_W$ is the concentration of pure water. Though there is no evidence that the waters of Nairobi River and its tributaries are directly used for domestic and/or recreational activities, possible surface water – air partitioning of pollutants that get into the river through industrial discharge and surface run-off could be contributing significantly to human exposure to increased levels of atmospheric POPs. This has never been investigated.

The sampling rate of the various substances on SPMDs depends on their physical–chemical properties. These include the octanol–water coefficient (K_{OW}) of the compound. Other environmental variables which affect the contaminant uptake include temperature, turbulence, flow rate and biofouling (Esteve-Turrillas et al., 2008). Information on the physical and chemical

properties of persistent organic pollutants is essential to understanding and modeling the environmental transport and transformation of the organic compounds. Most of the pollutants in Nairobi River and its tributaries result from discharge of industrial effluents into the river and surface run-off. The possible partitioning of these pollutants into the atmosphere has never been evaluated.

2.2.1 Physical Properties of PAHs

The physical properties influence the interphasial and spatial distribution of PAHs in the environment. Table 2.1 shows the physical properties of some polycyclic aromatic hydrocarbons.

Table 2.1: Some of the physical properties of the sixteen USEPA priority PAHs

PAH	Formula	Molecular Mass	Melting Point (°C)	Boiling point (°C)	Vapour pressure (Pa; 25°C)	Henry's Constant ($Atmm^3mol^{-1}$)*	Log K_{ow}
Naphthalene	$C_{10}H_8$	128.2	81	217.9	1.04×10^{1}	4.24×10^{-4}	3.45
Acenaphthylene	$C_{12}H_8$	152.2	92-93	Nf	8.9×10^{-1}	8.29×10^{-5}	4.08
Acenaphthene	$C_{12}H_{10}$	154.2	95	279	2.9×10^{-1}	1.20×10^{-4}	4.22
Fluorene	$C_{13}H_{10}$	166.2	115-116	295	9.0×10^{-2}	7.77×10^{-5}	4.38
Anthracene	$C_{14}H_{10}$	178.2	216.4	342	8.0×10^{-4}	3.91×10^{-5}	4.54
Phenanthrene	$C_{14}H_{10}$	178.2	100.5	340	1.6×10^{-2}	3.20×10^{-5}	4.46
Fluoranthene	$C_{16}H_{10}$	202.3	108.8	375	1.2×10^{-3}	1.02×10^{-5}	5.20
Pyrene	$C_{16}H_{10}$	202.3	150.4	393	6.0×10^{-4}	9.04×10^{-6}	5.30
Benzo(a)anthracene	$C_{18}H_{12}$	228.3	160.7	400	2.8×10^{-5}	5.73×10^{-6}	5.91
Chrysene	$C_{18}H_{12}$	228.3	253.8	448	8.4×10^{-5}	9.46×10^{-5}	5.61
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.3	168.3	481	6.7×10^{-5}	1.11×10^{-4}	5.78
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.3	215.7	480	1.3×10^{-8}	1.58×10^{-7}	6.20
Benzo(a)pyrene	$C_{20}H_{12}$	252.3	178.1	496	7.3×10^{-7}	4.54×10^{-7}	6.35
Benzo(ghi)perylene	$C_{22}H_{12}$	276.3	278	550	2.60×10^{-4}	3.30×10^{-7}	6.63
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.3	163.6	536	1.3×10^{-8}	1.60×10^{-6}	6.75
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278.4	266.6	524	1.3×10^{-8}	1.47×10^{-8}	6.51

Source: Adopted from Lisouza et al., (2013); * Compiled from IARC (2007)

PAHs have very low solubility in water, especially those with high molecular weights. In general, PAHs have high melting and boiling points hence all PAHs are solids at room

temperature. The PAHs have low vapour pressures which decreases with increasing molecular mass (IARC, 1983). These affect the adsorption of individual PAH on to particulate matter in the atmosphere and retention on the particulate matter (Thrane & Mikalsen, 1981). The vapour pressure of PAHs, however, increases markedly with rise in ambient temperature (Murray et al., 1974), which affects the distribution coefficients, between gaseous and particulate phases (Lane, 1989). In the environment, PAHs exist mostly in the vapour and particulate phases. Due to high temperatures in the tropical environments, the PAHs adsorbed onto particles are likely to vaporise (Yamasaki et al., 1982), increasing their atmospheric levels in vapour phase. To evaluate the phase partitioning, distribution and spatial variation of environmental PAHs, it is necessary to understand their physical properties.

2.2.2 Physical Properties of OCPs

The most important properties for understanding the behavior of the halogenated POPs in the environment are; water solubility, vapor pressure, octanol/water partition coefficient (K_{OW}), and organic carbon partition coefficient (K_{OC}). Some of the important physical properties of OCPs are summarized in Table 2.2.

Table 2.2: Some of the physical properties of some OCPs

Organochlorine Pesticide	Molecular Mass	Melting point (°C)	Solubility (At 25°C)	Vapour pressure (Pa at 25°C)	Henry's constant (Atm m^3mol^{-1})	Log K_{ow}
Aldrin	364.90	104	$2.0x10^{-1}$	7.5×10^{-5}	$4.9x10^{-5}$	6.5
Chlordane	409.78	165	5.6×10^{-2}	1.0×10^{-6}	4.8×10^{-5}	6.29
Dieldrin	380.92	176	1.40×10^{2}	1.78×10^{-7}	5.8×10^{-5}	4.60
Endrin	380.92	200	2.60×10^{2}	7.0×10^{-7}	5.0×10^{-7}	4.63
Gamma-HCH	290.83	159-160	7.3	$4.5x10^{-5}$	$3.5x10^{-6}$	3.78
Heptachlor	373.32	96	1.8×10^{-1}	3.0×10^{-4}	2.3×10^{-3}	5.91
p,p'-DDE	318.03	89	$1.2x10^{-1}$	$6.0x10^{-6}$	$2.1x10^{-5}$	6.0
p,p'-DDT	349.49	108.5	5.0	nf	1.29×10^{-5}	5.47
p,p'-DDD	320.25	109-110	9.0×10^{-2}	1.35×10^{-6}	4.0×10^{-6}	6.02

nf = not found in literature

The Henry's law constant, (H_C), for the pure water is the ratio between the vapour pressures of pure water and the mole ratio of pure water. Halogenated POPs have very low vapour pressures compared to water (Table 2.2), hence when released into surface waters, they will tend to remain in the water phase as waters vaporizes into the atmosphere. Determining the fugacities of OCPs under the environmental conditions of Nairobi City will provide valuable information in understanding the environmental distribution and spatial variations in the environmental levels of these OCPs in Nairobi City.

2.3 Human Exposure

Human exposure to POPs is mainly through inhalation of contaminated air, water used for drinking and cooking, dermal absorption and food intake (CCME, 2002; Drabova, 2011; Lisouza et al., 2011; Boleij et al., 1989; Onyango et al., 2012). The Agency for Toxic Substances and Disease Registry (ATSDR) has formulated the minimal risk levels (MRLs) to estimate the maximum daily human exposure to a hazardous pollutant that will not yield adverse non-cancer health effects (ATSDR, 2005). The MRLs define various exposure durations: These include acute exposure (1-14 days), intermediate exposure (15-364 days) and chronic exposure (365 days and longer). They also detail whether the exposure route is oral or inhalation. Inhalation MRLs are expressed in parts per million (ppm) for gases and volatiles, or milligrams per cubic meter (mg m^{-3}) for particles. On the other hand, the oral MRLs are expressed as daily human doses in milligrams per kilogram per day (mg $kg^{-1}day^{-1}$) (ATSDR, 2005). Several activities associated with emission of various POPs to the environment take place in Nairobi City of Kenya daily; however, the extent to which the city residents are exposed to health risks from these emissions has never been evaluated.

2.4 Global Cancer Burden

Statistics on trends in cancer incidence and mortality worldwide reveal that the global cancer burden is growing at an alarming pace (Stewart & Wild, 2014). For instance, from the year 2008 to 2012, the global burden of cancer increased to an estimated 14 million new cases per year (Stewart & Wild, 2014). This figure is expected to rise to 22 million annually within the next two decades. Over the same period, cancer deaths have been predicted to rise from an estimated 8.2 million annually to 13 million per year (Stewart & Wild, 2014). Globally, in 2012 the most common cancers diagnosed were those of the lung (1.8 million cases, 13.0% of the total), breast (1.7 million, 11.9%), and large bowel (1.4 million, 9.7%), (Stewart and Wild, 2014). The most common causes of cancer death were cancers of the lung (1.6 million, 19.4% of the total), liver (0.8 million, 9.1%), and stomach (0.7 million, 8.8%), (Stewart & Wild, 2014). According to GLOBOCAN, (2012), 14.1 million new cancer cases were diagnosed in 2012, 8.2 million cancer deaths recorded and 32.6 million people were living with cancer (within 5 years of diagnosis) in 2012 worldwide. About 57% (8 million) of the new cancer cases, 65% (5.3 million) of the cancer deaths and 48% (15.6 million) of the 5-year prevalent cancer cases occurred in the less developed regions (Table 2.3), including Kenya.

The overall age standardized cancer incidence rate was almost 25% higher in men than in women, with rates of 205 and 165 per 100,000 people respectively. Male incidence rates varied almost five-fold across the different regions of the world, with rates ranging from 79 per 100,000 in Western Africa to 365 per 100,000 in Australia/New Zealand. On the other hand, from the data collected (Table 2.3), there was less variation in female incidence rates across the five sampling regions (almost three-fold) with rates ranging from 103 per 100,000 in South-Central Asia to 295 per 100,000 in Northern America. In terms of mortality, there was less regional

variability than for incidence, the rates being 15% higher in less developed regions than in the more developed regions in men, and 8% higher in women. In men, the rates were highest in Central and Eastern Europe (173 per 100,000) and lowest in Western Africa (69). In contrast, the highest rates in women were in Melanesia (119) and Eastern Africa (111), and the lowest in Central America (72) and South-Central Asia (65), (GLOBOCAN, 2012).

Table 2.3: Estimated Incidence, Mortality and Prevalence of all cancers (excluding non-melanoma skin cancer) worldwide in 2012

Estimated numbers (thousands)	Men			Women			Both sexes		
	Cases	Death	5-Year Prev.	Cases	Death	5-Year Prev.	Cases	Death	5-Year Prev.
World	7410	4653	15296	6658	3548	17159	14068	8202	32455
More developed regions	3227	1592	8550	2827	1287	8274	6054	2878	16823
Less developed regions	4184	3062	6747	3831	2261	8885	8014	5323	15632
WHO Africa region (AFRO)	265	205	468	381	250	895	645	456	1363
WHO Americas region (PAHO)	1454	677	3843	1429	618	4115	2882	1295	7958
WHO East Mediterranean region (EMRO)	263	191	461	293	176	733	555	367	1194
WHO Europe region (EURO)	1970	1081	4791	1744	852	4910	3715	1933	9701
WHO South-East Asia region (SEARO)	816	616	1237	908	555	2041	1724	1171	3278
WHO Western Pacific region (WPRO)	2642	1882	4493	1902	1096	4464	4543	2978	8956
IARC membership (24 countries)	3689	1900	9193	3349	1570	9402	7038	3470	18595
United States of America	825	324	2402	779	293	2373	1604	617	4775
China	1823	1429	2496	1243	776	2549	3065	2206	5045
India	477	357	665	537	326	1126	1015	683	1790
European Union (EU-28)	1430	716	3693	1206	561	3464	2635	1276	7157

Source: Compiled from GLOBOCAN (2012)

Kenya was ranked among the top 50 countries with the highest cancer rate in women worldwide, with a score of 196.6 women per 100,000 being diagnosed with cancer in the year 2012 (Ferlay et al., 2014). Besides Kenya, the only other African countries in the top 50 ranking for cancer in women were Zimbabwe (209.1 women per 100,000) and Mauritius (193.9 women per 100,000).

Globally, the highest cancer rate for men and women together was found in Denmark with 338 people per 100,000 being diagnosed in 2012. In men only, the highest cancer rate was found in France with 385 men per 100,000 being diagnosed in the same year (Ferlay et al., 2014). Kenya was not ranked among the top 50 countries in the cancer rate for men. Kenya has so far moved to impose high taxes in cigarettes in the country and compelled cigarette manufacturers to display cancer warnings on cigarette packaging. However, in Kenya cigarette smoking is more prevalent in men than in women. This data indicates that, besides smoking, other sources of these carcinogenic contaminants in the country are not known.

National estimates of cancer incidences and mortality are predominantly based on data from population-based cancer registries (PBCR), most of which cover relatively limited subnational populations (Parkin et al., 2014). In Kenya, the Nairobi Cancer Registry covers the population of Nairobi County, and thus documents all cancer cases among the residents of Nairobi. A resident was defined as anyone who had continuously lived/worked in Nairobi for a period of at least six months and excluded persons who visited the city for purposes of accessing treatment (Korir et al., 2015). From the data obtained, the age standardized incidence rates (Doll et al., 1966), per year, for the 5 year period (2004–2008), among men were 161 per 100,000 and 231 per 100,000 among women (Korir et al., 2015). Of all the cancer cases in men, 15% were prostate cancer, 8.6% cancer of the oesophagus, 7.6% cancer of the large bowel, 6.2% stomach cancer, 5.2% cancer of the oral cavity and 4.6% liver cancer. In women, 23% of all the cases were breast cancer, 21.1% cervical cancer, 4.9% cancer of oesophagus, 4.8% large bowel, 3.8% stomach and 3.4% ovarian cancer (Korir et al., 2015). The percentage of cases with morphological verification of diagnosis (overall 85.7% in males, 87.0% in females) was higher than in the other registries of sub-Saharan Africa (Korir et al., 2015). The reasons for the high burden of cancers

in Nairobi City are not fully understood. Though tobacco and alcohol are clear risk factors in South Africa (Pacella-Norman et al., 2002), they do not explain the high rates in Nairobi compared with other regions. The prevalence of daily tobacco use in Kenya is 20% among males, and <1% among females (WHO, 2013). Although prevalence (in men) appears quite high, the intensity of smoking (number of cigarettes per day) is low; smoking Kenyan consumers retain their habit of purchasing sticks of cigarettes as opposed to full packets (Eriksen et al., 2012). The annual cigarette consumption in Kenya is 144 cigarettes per person. This consumption rate is very low compared with 1028 per person in USA, 1104 per person in Egypt and 2786 per person in Russia (WHO, 2013). While the incidence of cancer of the nasopharynx is not very high in Nairobi, the rates were greater than those observed elsewhere in sub-Saharan Africa (Korir et al., 2015).Breast cancer is the leading cancer among women in Nairobi, with an incidence of 51.7 per 100,000; that is the highest so far recorded in an African cancer registry (Korir et al., 2015). The possible causes of these cancer cases in Nairobi have not been investigated. POPs are known carcinogens (UNECE, 1998a). The possible contribution of environmental POPs to these cancer cases has never been evaluated.

2.5 Environmental Sampling Methods for POPs

2.5.1 Active Sampling

The active sampling technique involves collection of discrete amounts of sample for extraction (Keith, 1991; Lane et al., 2003; Alvarez et al., 2012). However, the results obtained by this method may not be representative of the actual environmental levels of the contaminant and level of exposure risk posed by the contaminant, due to local distinct contaminant concentrations in the environment and questionable bioavailability of extracted contaminants. For instance, Burgess et al., (2015), observed that the exposure of aquatic organisms to hydrophobic organic

chemicals (HOCs) like PAHs and chlorinated pesticides, among others, in water was most strongly correlated to their freely dissolved concentrations. This is due to the fact that uptake of these contaminants from environmental sorptive phases, like colloids or suspended particles, is often limited (Burgess et al., 2015). From the surveyed literature, data on the levels of bioavailable POPs in the tropical environments, such as Kenya, is not documented. Active sampling can however be modified to integrate in graded filters to eliminate particulate matter from the sampled medium before extraction. This would help resolve the questions relating to the bioavailability of the sampled contaminants (Huckins et al., 1990; Alvarez et al., 2004). However, the efficiency of the method in estimating the environmental levels of the contaminants is not known. One major weakness of active sampling is the challenge of possible underestimation or overestimation of the levels of a contaminant in an environmental medium due to choice of the sampling time. For instance, variation in weather conditions, such storms and/or times of discharge of the contaminant from a point source into the receiving environmental medium, may result in huge variations in the reported environmental levels of the contaminant in active sampling, as illustrated in Figure 2.1.

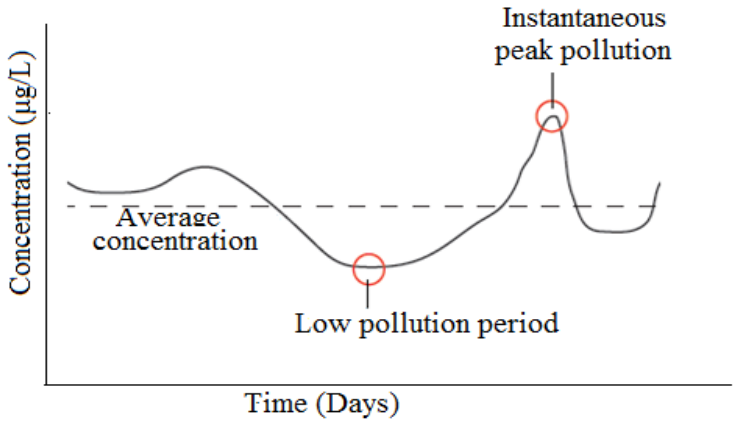


Figure 2.1: An illustration of possible variation in local pollutant levels in the environment with time

There is therefore need for a sampling method which gives time-integrated data that provides information on the average pollutant concentration in the sampling environment, over a period of time. Such data will mitigate possible underestimation or overestimation of the levels of a contaminant in an environmental medium

2.5.2 Use of Biota

The concentration of POPs in various plants and organisms has been used in the past as indicators of POPs pollution in various environments. For instance, mussels (*Perna viridis*) have been used in monitoring the aquatic levels of OCPs (Regan et al., 2012) as well as PAHs and petroleum hydrocarbons (Richardson et al., 2003), in coastal waters. Though the mussels were reliable biota monitors for marine waters; it was noted that finding reliable biota monitors for the catchment studies was extremely challenging, when ecosystem-specific sampling variabilities were put into focus (Regan et al., 2012). These variabilities included mobility of organisms, the size, species, sex and trophic level, as well as the age of the organism.

Similarly, plant samples such as tree barks (Simonich & Hites, 1995), lichen and pine needles (Hellström et al., 2004; Ockenden et al., 1998; Kylin & Sjodin, 2003; Tremolada et al., 1996) have been used in several studies to monitor atmospheric concentrations of organic pollutants on a large scale. In these studies, the basic assumption was that the spatial pollution distribution of the pollutant in the plants and the atmosphere were closely related. However, one major limitation in using plant tissues is that the concentration capacity and sampling rate of plant tissues vary with the plant species and age, location and season (Söderström et al., 2005). The consequence is that plant data are subject to several uncertainties and this complicates the interpretation of such data, which limits the potential of plants as monitoring tools. There is therefore need for a sampling method or tool that provides us with information about the

bioavailability of the sampled POPs, while mitigating the weakness of using biota as monitoring tools.

2.5.3 Passive Sampling

Passive sampling broadly refers to any sampling technique based on free flow of molecules of the analyte from the sampled medium to a receiving phase in a sampling device (Hazrati &Harrad, 2007), due to the difference between the chemical potentials of the analyte in the two media (Vrana et al., 2005). The analytes get trapped or retained in a suitable medium within the receiving phase (Vrana et al., 2006). The net flow of the analyte molecules from the sampled medium to the receiving medium continues until equilibrium is established, or until the sampling period is stopped. This receiving phase may be in form of a solvent, chemical reagent or a porous adsorbent (Vrana et al., 2007). Passive samplers include filter papers, polyurethane foam (PUF), as well as semipermeable membrane devices (SPMDs).

The development of environmental passive samplers began in the 1930s but it was until the 1970s that these devices could be mathematically characterized (Hazrati & Harrad, 2007). Passive samplers which could be used to measure volatile organic compounds in water were first developed in 1987 (Soedergren, 1987). These were made of a dialysis membrane containing hexane and were used to simulate the uptake of pollutants by aquatic organisms. Huckins et al (1990) described the use of a semipermeable membrane device (SPMD), filled with a synthetic lipid triolein. These devices were used to sample the aquatic environment for volatile organic compounds (VOCs). Since then, passive sampling devices have been widely used for monitoring both organic and inorganic contaminants (Vrana et al., 2005). Passive sampling devices have been widely used for sampling and analysis of several environmentally persistent pollutants: these include PCBs, OCs, PAHs, PCBs and dioxins (Aguilar-Martínez et al., 2009; Kot-Wasik et

al., 2007; Levy et al., 2009). Passive sampling has also been used in the study of inorganic substances and heavy metals (Zhang et al., 2007; Tonello et al., 2007).

Passive samplers present a number of advantages over conventional active air samplers especially when determining the atmospheric distribution of organic pollutants at multiple sites on a wider scale: Passive air samplers are not powered by electricity and do not require maintenance (Söderström et al., 2005). The fact that passive samplers can be exposed for a long period of time in the medium being sampled, presents the analyst with a more convenient way of determining time-weighted average (TWA) environmental concentrations of the pollutants (Figure 2). Another major advantage of passive samplers is that their variability at different locations is low, and their sampling period can be controlled. Passive samplers, therefore, present a reliable and convenient way of monitoring environmental pollution, despite their additional costs and the need to be deployed. However, SPMDs have never been used in environmental monitoring of POPs in Kenya.

2.5.3.1 Polyurethane Foam-based Passive Air Samplers

Polyurethane foam-based passive air sampler (PUF-PAS) is one of the most widely used passive air samplers. A polyurethane foam (PUF) disk is mounted between two dome-shaped disks made of stainless steel (Figure 2.2). The steel disks are used to protect the sampler from precipitation and UV radiation from sunlight, and to control air-flow within the sampling chamber (Qu et al., 2018; Joward et al., 2004). PUF-PAS have been used in the assessment of spatial distribution of a range of POPs, including OCPs and PAHs (Harner et al., 2004; Pozo et al., 2009; Qu et al., 2018). PUF-PAS are simple to use, easy to operate, less expensive and do not depend on electric power (Qu et al., 2018). In Kenya, PUF-PAS were used in monitoring the distribution of OCPs in Nairobi City and Mt. Kenya Region (Aucha et al., 2017).

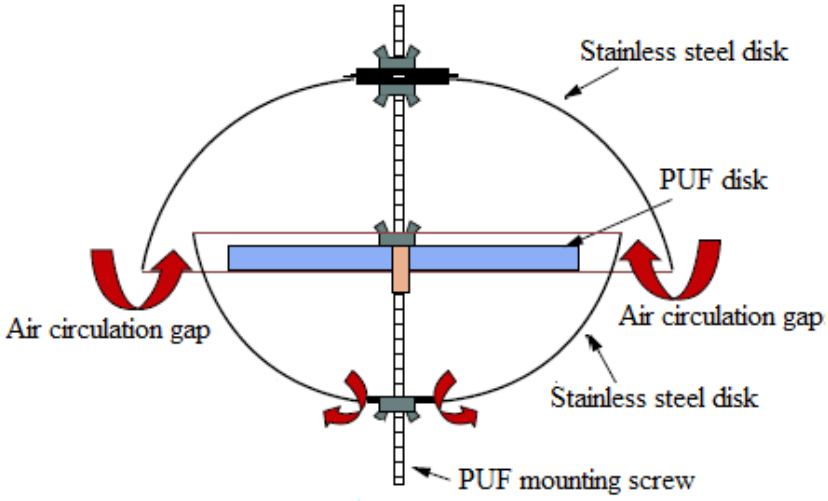


Figure 2.2: An illustration showing the deployment kit for PUF-PAS.

Studies have reported that particle-associated compounds get trapped by the PUF-PAS (Bohlin et al., 2010; Chaemfa et al., 2009). However, there is no agreement on the size of atmospheric particles that get trapped by the PUF. While Chaemfa et al., (2009) reported that particles of diameters up to 1 mm consistently got trapped by PUF, another study reported that particles with diameters up to 2 mm were sampled (Bohlin et al., 2010). Approximately 10% of ambient particles, regardless of particulate size, have been reported to get trapped by PUF (Kla´nova´ et al., 2008). This complicated the estimation of air concentration of gas-phase POPs using PUF-PAS (Qu et al., 2018). Since PUF-PAS sample both the gas-phase and particle-bound POPs from the air, such data do not provide any information on the bioavailability of the sampled POPs, and cannot be used in assessment of human health risk posed by the sampled POPs. This challenge could be overcome by passing the air through graded filters to remove the particulate matter, before it is passed through the PUF samplers. However, there is the possibility of the filters getting clogged with particulate matter before the end of the passive sampling period. This change could, in turn, be overcome by reducing the sampling period and introducing a suction pump into the set-up, as in active sampling. However, it is not known how these modifications

will affect the reported levels of the sampled POPs. One way of determining this is to compare the data obtained to that collected using semipermeable membrane devices (SPMDs) as passive samplers.

2.5.3.2 Semipermeable Membrane Devices

Semipermeable membrane devices (SPMDs) consist of an additive free lay-flat tube, made of low-density polyethylene (LDPE), with pore diameter approximately 10 Å (Huckins et al., 1990). The membrane is filled with a relative non-polar liquid with large molecules and has constant porosity all over. The most widely used filling material is a synthetic triolein (1, 2, 3-tri-[cis-9-octadecenoyl]-glycerol) (Kočí et al., 2003), as illustrated in Figure 2.3. Triolein was chosen as the standard for use in SPMDs because it is the major storage lipid found in most organisms and has high molecular weight resulting in extremely low LDPE membrane permeability, even during dialysis (Huckins et al., 2006). The membrane is permeable for small environmental pollutant molecules but not for triolein. Because triolein is highly lipophilic, the pollutants cannot penetrate back to the environment. A typical SPMD is about 90cm long, 2-2.5 cm wide with a LDPE membrane of thickness about 75-90 μm loaded with 0.5-1 ml of triolein in a thin layer (Huckins et al., 1990). SPMDs are used for sampling neutral organic chemicals that have a K_{ow} value greater than 3, which include; polycyclic aromatic hydrocarbons (PAHs) and chlorinated pesticides (Alvarez, 2010).

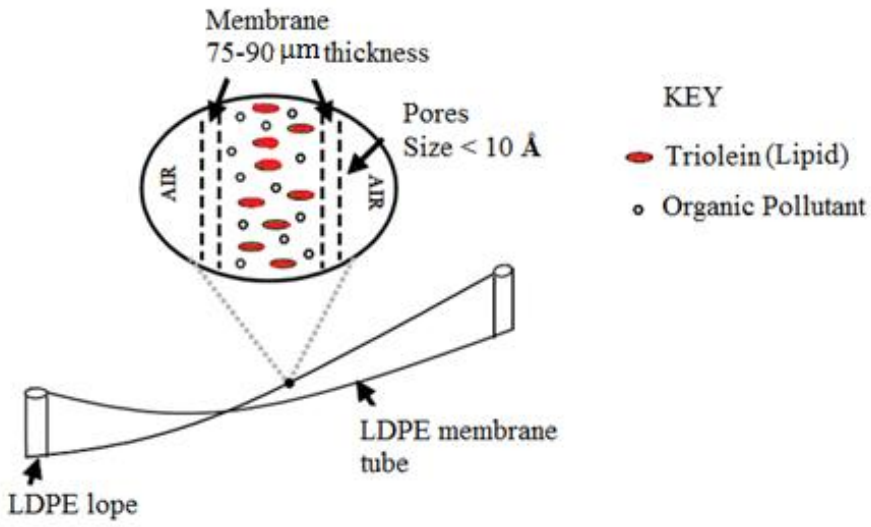


Figure 2.3: Schematic representation of a lay flat thin-walled tube of non-porous low-density polyethylene (LDPE) filled with triolein

In the SPMD, sampling is achieved by either physical absorption of the analyte in the membrane tube, or by diffusion of the analyte through the membrane tube, resulting in absorption of the analyte(s) in the triolein (Soderstrom & Bergqvist, 2004). Since passive sampling methods give time-averaged concentrations, the risk of underestimation or overestimation of total pollutant mass flows due to accidental sampling is reduced (Soderstrom & Bergqvist, 2004; Esteve-Turrillas et al., 2008). In addition, since the passive samplers exclusively sample the bioavailable fraction of the pollutant in the environment (Soderstrom & Bergqvist, 2004), results from passive samplers are used as a good estimate of human exposure to the pollutant in the environment.

SPMDs are used in passive sampling of pollutants for screening and identification of sources of a variety of non-polar and moderately polar organic contaminants from water and air environments. Use of SPMDs has been associated with the following advantages, over other sampling methods (Esteve-Turrillas et al., 2008): SPMDs can be deployed for extended time periods to integrate long-term data (Figure 2.4); only bioavailable compounds are sampled; they are easy to use; SPMDs are more reproducible than live biota samplers, which helps the

researcher to avoid drawbacks related to migration, mortality, metabolism or selective depuration of contaminants. The use of SPMDs also provides selective analyte isolation and especially pre-concentration (Esteve-Turrillas et al., 2008).As a result, the selectivity and sensitivity of pollutant determination method can be greatly improved.

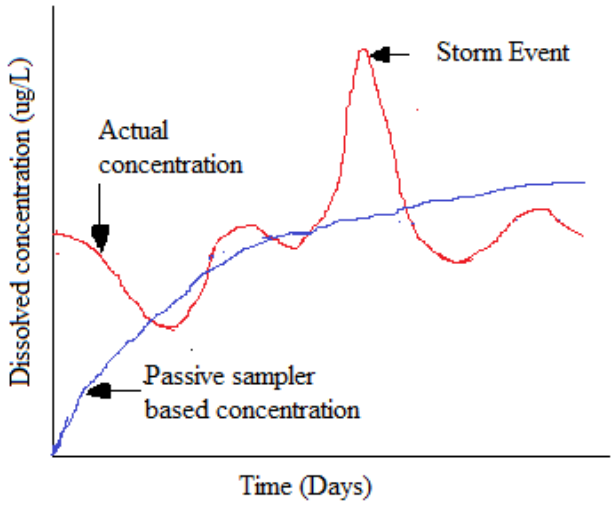


Figure 2.4: Conceptual representation of the concentration of a hydrophobic contaminant in receiving waters and in a deployed SPMD over a sampling period

SPMDs accumulate organic pollutants through diffusion (Dixon-Anderson & Lohmann, 2018). Since they rely on diffusion, SPMDs inherently select only gaseous hydrophobic contaminants in air and dissolved hydrophobic contaminants in water (Adams et al., 2007; Lohmann et al., 2011; 2012). On the other hand, most active sampling techniques do not discriminate between gas-phase/aqueous-phase pollutants from those in the particulate-phase. Further, the ability of SPMDs to quantify both aqueous and atmospheric concentrations at the sampling sites provides the analyst with insight into the transport processes that dictate the environmental movement of the pollutant and the quantification of the air water fluxes (Khairy et al., 2014; Mcdonough et al., 2014). Since the absorption of compounds through SPMDs mimics that through cell membranes, SPMDs can be used to assess the bioconcentration factor in aquatic animals; adsorption of

organic pollutants present in water to particles such as sediments makes the adsorbed compounds less available to aquatic animals (Robertson & Hansen, 2001). Thus, SPMDs can be used as indicators of the bioavailability of hydrophobic contaminants in the environment.

SPMDs have been used in a number of studies: Lohmann et al., (2001) and Meijer et al (2003) used SPMDs in spatial surveys of atmospheric gas phase concentrations of organic pollutants, while Jaward et al., (2004) used SPMDs as passive samplers to simultaneously monitor the atmospheric distribution of PAHs, polychlorinated naphthalenes (PCNs), polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), and organochlorine pesticides across Europe in a defined time period. The ability of SPMDs to simultaneously sample multiple POPs saves the researcher the time and cost of carrying out multiple sampling and extractions, as noted by Jaward et al., (2004).

2.5.3.2.1 Factors that Influence Uptake of Compounds in SPMDs

The uptake of POPs by SPMDs is influenced by several site-specific environmental factors. Table 2.4 shows the average temperatures by continents between 1980 and 2018.

Table 2.4: Average temperatures by continents 1980 to 2018

Region	1980-89	1990-99	2000-09	2010-18
Europe	7.5 °C	8.1 °C	8.6 °C	8.6 °C
Asia	15.7 °C	16.3 °C	16.5 °C	16.6 °C
North America	11.0 °C	11.4 °C	11.7 °C	12.2 °C
Africa	21.1 °C	21.2 °C	21.5 °C	21.9 °C
Australia	14.2 °C	14.0 °C	14.4 °C	14.9 °C
Oceania	23.4 °C	23.7 °C	23.9 °C	23.9 °C

Source: German Weather Service (2019).

The data indicate that the average temperatures in the tropical environments of Africa were much higher than those in the all the other parts of the world, except in Oceania. From the literature surveyed (Alvarez 2010; Karacik et al., 2013; Zhu et al., 2013; Tian et al., 2009; Wu et al., 2001;

Schramn et al., 2001), all the studies using SPMDs as samplers were carried out in temperate regions and sub-tropical climatic zones, mainly in Europe, Asia and North America, where climatic data vary greatly from those in the tropics. The quantity of target compounds sampled by SPMDs depends on the sampling rate (R_S) of the SPMD. The sampling rate of SPMDs is affected by a number of site-specific factors. These include:

a) Physicochemical properties of the compound sampled.
b) Wind speeds/turbulence: Söderström and Bergqvist (2004) reported that high wind speeds/turbulences affected the amounts sequestered by the SPMDs.
c) Particulate matter: it possible for the contaminants bound to particles or aerosols to be trapped on the membrane surfaces and thereby influence the amount sequestered by the SPMD (Lohmann et al., 2001; Bartkow et al., 2004).
d) Temperature: Studies (Huckins et al., 1999; Booij et al., 2003), reported that the ambient temperature can have an effect on the sampling rate of SPMDs. Increase in temperature can increase the gas phase partitioning of PAHs and nitro- PAHs that occur both in the gas and particle phases (Huckins et al., 1999; Booij et al., 2003). Consequently, the amounts taken up by the SPMDs could vary with temperature in complex ways since PAH-emission and source parameters are also likely to change with ambient temperature (Huckins et al., 1999)
e) Sunlight: Degradation of UV-sensitive compounds such as PAHs and nitro-PAHs are also likely to occur in the SPMDs (Orazio et al., 2002), if the SPMDs are exposed to sunlight.

Kenya is in the tropics where both the temporal and geographical variations over time in temperature, UV-radiation and wind turbulence can be high. Ockenden et al., (2001) and Soderstrom and Bergqvist (2004) demonstrated that the wind speed can be reduced by protecting the SPMDs with metal devices. The monthly averages of climatic data for Nairobi City from the

year 1981 to 2011 are presented in Table 2.5. From the data, it evident that in the tropical environments, the weather parameters, such as temperature, can vary significantly during the course of a day and between days. Such significant variations in weather parameters are likely to influence the sampling rate of SPMDs, as reported by Huckins et al., (1999) and Booij et al., (2003). For instance, when it is wet, the amount of particulates in the atmosphere is likely to be lower due to deposition resulting from association with rain drops, than during the dry weather conditions. These factors are likely to result in variation between the amount of POPs sampled by active and passive sampling, as reported by Lohmann et al., (2001) and Bartkow et al., (2004).

Table 2.5: Monthly Averages of Climate data for Nairobi from 1981-2011.

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Average high Temp. (°C)	25.5	26.7	26.8	25.0	23.5	22.5	22.0	22.7	25.0	25.7	24.0	24.5	24.5
Average low Temp. (°C)	10.5	10.9	12.1	13.4	12.1	10.0	9.2	9.1	9.7	11.3	12.7	11.7	11.1
Average precipitation (mm)	58.3	49.8	92.2	242.3	189.5	38.6	17.6	24.0	31.2	60.8	149.6	107.6	1,061.5
Average precipitation days (≥ 1.0 mm)	4	4	8	15	13	5	3	4	4	7	14	9	90
Mean monthly sunshine hours	288.3	266.0	266.6	204.0	189.1	159.0	130.2	127.1	180.0	226.3	198.0	257.3	2,491.9
Mean daily sunshine hours	9.3	9.5	8.6	6.8	6.1	5.3	4.2	4.1	6.0	7.3	6.6	8.3	6.8

Source: German Weather Service (2019)

Though Nairobi City experiences generally higher average temperatures than those in Europe and North America (Table 2.4 and Table 2.5), the average temperatures were in the same range as those in parts of Asia where SPMDs have also been widely used as passive samplers. Such regions include the Yangtze Three Gorges Reservoir, China, (Wang et al., 2009; Schramm et al.,

2012) which is situated in a region classified as having a subtropical climate. According to the Köppen-Geiger climate classification, Nairobi City is also classified as having subtropical highland climate (Pidwirny, 2006; Beck et al., 2018).

The performance reference compound (PRC) approach is used in SPMDs to account for these site-specific variations in environmental factors (Huckins et al., 1999). A PRC is a compound with moderate to high fugacity that is added to the sampler during fabrication. During the exposure period, a percentage of each PRC is lost to the surrounding water or air (Huckins et al., 1999; Booij et al., 2003). The amount of PRC loss during the field deployment period of the sampler is used in computing the site-specific sampling rates of targeted analytes (Huckins et al., 2002; Alvarez 2010). In order, to accurately determine the PRC loss, the PRC used must not naturally occur in the environment (Huckins et al., 2002; Alvarez et al.,, 2012). For this reason, either, deuterated or ^{13}C-labeled versions of the target compounds are usually used as PRCs. However, in cases where the same SPMD is used to simultaneous sample multiple classes of chemicals, it is not necessary to have a PRC for each class of chemicals (Huckins et al., 2006). The rate of PRC loss depends on the log K_{ow} of the compound used as the PRC: the higher the log $K_{ow}$of the compound used as the PRC the lower the rate of PRC loss (Huckins et al., 2006). Consequently, choice of a PRC with a log K_{ow} greater than 5.5 to 6 is usually avoided, because the amount of the PRC lost during exposure will be very low except at high temperatures or if the deployment days are prolonged (Alvarez, 2010). Determination of the amount of PRC lost provides an exposure adjustment factor which is used to adjust laboratory-derived sampling rates to site-specific conditions.

2.5.3.2.2 Extraction of Pollutants from SPMDs

2.5.3.2.2.1 Dialysis

In this procedure, hexane is used as solvent in the extraction of the analytes from the SPMD matrix. However other solvents can be used, depending on the target analyte (Alvarez et al., 2008, 2012). The main advantages of dialysis are that, the method is easy to use; no special instrumentation required; there are few triolein co-extractions. However, the main disadvantages of dialysis procedures are long extraction times and excessive solvent consumption that increase the cost of analysis (Huckins et al., 2002). Given that the instrumentation required in the other extraction methods are generally expensive and most often beyond the reach of the researcher, especially in developing countries such as Kenya, dialysis presents the researcher in such conditions with an alternative method of obtaining valid and reliable data on POPs.

2.5.3.2.2.2 Accelerated Solvent Extraction

This procedure was first suggested by Wenzel et al., (2004), as an alternative to dialysis, for the extraction of POPs from SPMDs. The technique, also referred to as pressurized fluid extraction or pressurized liquid extraction or "rapid dialysis procedure", employs an accelerated solvent device to extract POPs from SPMDs. The solvent system in the technique is an organic solvent or a combination of solvents at high pressure and temperature. These conditions provide increased solubility, better desorption and enhanced diffusion of POPs from the matrix during the extraction. The advantages of this technique are that, the extraction time can be reduced considerably and solvent consumption is low. The main drawbacks in this technique are that, it cannot be used for unstable analytes; an internal mesh is required; and there is high matrix co-extraction (Esteve-Turrillas et al., 2008). This requires elaborate clean-up procedures which will compromise sample quality.

2.5.3.2.2.3 Microwave-assisted Extraction

This technique allows rapid extraction of analytes from solid matrices by employing microwave energy as a source of heat. The partitioning of analytes from the sample matrix to the solvent used for extraction depends on the temperature and the nature of the solvent (Alvarez, 2010). Microwave radiation provides a fast and selective heating of polar compounds, leading to a very short extraction time. However, the maximum temperature resisted by SPMDs, depends on the solvent employed (Esteve-Turrillas et al., 2008). As a consequence, treatments with high temperatures particular solvents dissolve and collapse the polyethylene membrane, which make compound determination impossible due to the high amount of plastic residues co=extracted.

2.5.3.2.2.4 Ultrasonic Extraction

In this technique the sample is immersed in a suitable solvent in a vessel, and placed in an ultrasound water bath. The extraction efficiency depends on the polarity of the solvent used, the homogeneity of the matrix, and the sonication time. The sampler is cut lengthwise using sharp object and then extracted three times with 100mL hexane for 20 min each (Esteve-Turrillas et al., 2008). This dissolves the whole amount of triolein in the SPMD, and hence an elaborate clean-up procedure is required to remove the co-extracted compounds. Besides being time demanding, the elaborate clean-up in likely to compromise sample quality.

2.5.3.2.2.5 Head-space Direct Determination

Headspace analysisinvolves examination of the vapours derived from a sample by warming in a pressurized partially filled and sealed container. After equilibration under controlled conditions, the proportions of volatile sample components in the vapours of the headspaceare representative of those in the bulk sample. The system consists of a thermostatically heated compartment in which batches of samples are equilibrated, and small volumes of the headspace vapours

introduced into the carrier gas stream for injection into the chromatograph (Fifield & Kealey, 2000). The technique is particularly useful for samples that are mixtures of volatile and non-volatile components such as residual monomers in polymers. Sensitivity is improved by combining headspace analysis with thermal desorption whereby the sample vapours are first passed through an adsorption tube to pre-concentrate them prior to analysis (Fifield & Kealey, 2000). This technique is applied in the analysis of volatile organic compounds, including POPs, in both environmental samples as well as in food samples. In head-space technique, the oven temperature and extraction time are the main parameters that affect the extraction (Tian et al., 2009; Zhu et al., 2013). The advantages presented by head-space technique include, the absence of sample handling; the reduction of interferences; and the possibilities of a full automation of the method (Alvarez, 2010; Zhu et al., 2013; Wang et al., 2009). For, instance, a total processing time of 20 min for each sample allows a sample throughput of 72 samples per day. This makes head-space technique the fastest methodology developed for the determination of volatile compounds retained in SPMDs (Alvarez, 2010; Zhu et al., 2013; Vrana et al., 2005). The greatest advantage of head-space direct determination is the estimation of a chemical's site-specific $R_S$and its concentration in the atmosphere or surface waters is automatically and accurately determined by the instrument (Alvarez, 2010; Schramm et al., 2012; Vrana et al., 2005; Wang et al., 2009). However, the equipment required for this procedure is extremely expensive and are not available in Kenya.

2.6 Health Risk Assessment

These POPs are classified either as "dioxin-like" and "non-dioxin-like", depending on their mode of toxicity. The mechanism of action of dioxin-like compounds involves a cytosolic protein referred to as the aryl hydrocarbon receptor (AhR) (Arisawa et al., 2005; Ross & Birnbaum, 2003). The AhR and its translocator protein (ARNT) have remained conserved

throughout evolution and are common across fish, birds and mammals (CCME, 2002; Simms, 2000). Dioxin-like compounds strongly bind on to AhR which promotes the formation of the AhR nuclear translocator (ARNT). The ARNT moves into the nucleus where it binds specific DNA sequences and alters the induction of specific enzymes, many of which are responsible for detoxification of the xenobiotic compound itself (Arisawa et al., 2005; Simms, 2000). The most toxic dioxin compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), which was a contaminant in the chemical herbicide Agent Orange utilized in the Vietnam War. According to the Toxic Equivalency Factor (TEF) approach developed by the World health Organization (WHO), 2,3,7,8-TCDD has been assigned a TEF equal to 1.0 (Van den Berg et al., 1998). Basing on the toxicity of 2,3,7,8-TCDD, the relative toxicity of each of the other dioxin-like compounds was quantified by assigning them a TEF value (Van den Berg et al., 1998).

Many PAHs have been reported to exert their toxic effects by binding to and activating the AhR (Fernandez-Salguero et al 1996). Consequently, the AhR activates transcription of multiple genes, such as those responsible for metabolism of PAHs [e.g., cytochrome P450 (CYP) genes], and suppresses the transcription of others (e.g., immunoglobulin) (Denison et al 2002; Sulentic et al 1998). Benzo (a) pyrene (BaP) is the most well studied PAH and is generally considered the most toxic and carcinogenic PAH, and has been reported to be a cancer-inducing substance for which toxicological data serve as quantitative benchmarks for the rest of the PAHs (Guo et al., 2003; USEPA, 2011; Ha et al., 2016). One method to calculate risk assessment is the use of toxic equivalence factors (BaP-TEFs) and hence BaP has been assigned a TEF of 1 (Guo et al., 2003; Nisbert & LaGoy, 1992; Knafla et al., 2006; USEPA, 2011; Ha et al., 2016). BaP-TEFs allow the toxicity of a mixture of PAHs to be expressed as a single number representing the equivalent concentration of the most toxic or carcinogenic congener. The BaP-TEF represents a ratio of the

toxicity of a PAH congener to that of B(a)P. The use of BaP-TEFs allows the concentration of PAHs other than BaP to be converted to equipotent concentrations of BaP (toxic equivalent) (Guo et al., 2003; Nisbert & LaGoy, 1992; Knafla et al., 2006; USEPA, 2011; Ha et al., 2016).

The incremental lifetime cancer risk (ILCR) is the probability of developing cancer as the result of exposure to a specific carcinogen. ILCR indicates an incremental increase in cancer cases in the exposed population over what would occur in the absence of exposure (Bleam, 2012). Thus the lifetime cancer risk is the probability of developing cancer, based on the number of cancer cases in the population, regardless of age. Carcinogen toxicity is quantified by the cancer slope factor (SF) in ($mg_{toxicant}^{-1}$ x $kg_{toxicant}$ x day) of each pollutant (Bleam, 2012). Cancer Risk is hence determined as the product of the pollutant dose and its toxicity as shown in Equation 5.

$$\text{ILCR} = \text{Lifetime Daily Dose (LDD)} \times \text{SF} \qquad Equation\ 5$$

An ILCR value $\leq 10^{-6}$ represents very low risk, $10^{-6} \leq$ value $\leq 10^{-4}$ low risk, $10^{-4} \leq$ value $\leq 10^{-3}$ moderate, $10^{-3} \leq$ value $\leq 10^{-1}$ high and value $\geq 10^{-1}$ very high cancer risk (Yahaya, 2017; Ge et al., 2013; Sruthi et al., 2016; Qu et al., 2015).

CHAPTER THREE

METHODOLOGY

3.1 Study Area

This study was conducted in selected sites in Nairobi City, Kenya and a control site in Ngong' Forest. Nairobi City lies between latitudes 1.1654°S and 1.4469°S, and longitudes 36.6497°E and 37.1057°E. The city occupies an area of 696 square kilometers (Figure 3.1).

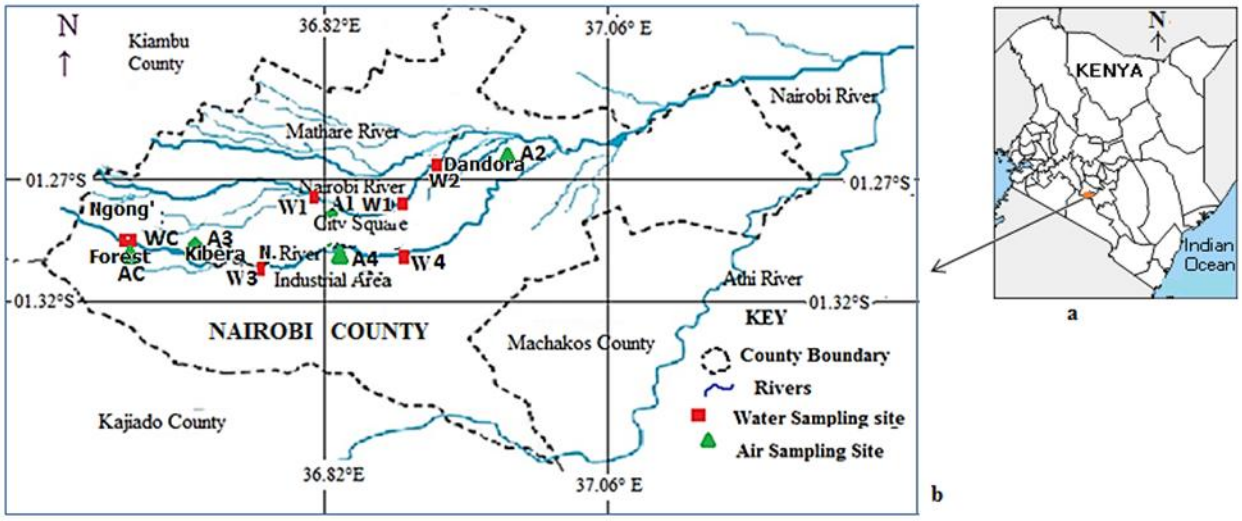


Figure 3.1: Map showing the sampling Area

The probable sources of POPs in Nairobi City are industrial activities and emissions from traffic, as well as waste management and disposal practices. In view of these, Nairobi City was broadly divided into five sections: (i) the central business district (also known as the City Centre), where the probable sources of POPs are emissions from vehicles. (ii) The Industrial Area, where the greatest proportion of the all the industries in Nairobi City are located. (iii) Dandora; the sources of POPs in these regions are likely to be waste incineration and disposal (iv) Residential areas: Such as Kibera where the sources of POPs are domestic activities which include pest control practices and biomass burning. (v) The Ngong' Forest, an indigenous forest on the extreme western part of the Nairobi City, where hardly any anthropogenic activity associated with emission of POPs takes place. The forest was considered to be pristine. Based on the

predominant wind directions in Nairobi City, Ngong' Forest was chosen as a control site to determine if long transport significantly contributed to the amount of environmental POPs in the city.

Nairobi River and its tributaries, with sources in the Ngong' Forest, traverse the city. For the purpose of study, the most important sections of the river were those which pass through the Central Business District and Ngong' River, its tributary, which passes through the Industrial Area.

3.2 Study Design

3.2.1 Methods Comparison Study

Prior to the main study, a comparison study was set up at sampling sites A_4 and W_4 in the Industrial Area sampling sub-region (Figure 6). The purpose of this was to compare the data collected by active sampling integrated with graded filters with that collected using triolein filled SPMDs samplers for POPs in the Kenyan environment. The main factor was the sampling method: active sampling versus passive sampling. The comparison study was laid out in a completely randomized block design replicated four times. To minimize the variations resulting from source distribution, the span of the sampling area was reduced to establish a near-homogenous sampling block. Since the daily patterns of the various industries and distribution of the industrial activities that may result in environmental pollution was not predictable, this was considered as a probable source of variation during sampling. To mitigate these variations, the weekly sampling days were staggered: During first week, sampling was done on the Monday; during the second week sampling was done on the Wednesday and in the third week sampling was done on the Friday; the sampling during the fourth week was carried out on the Tuesday. To mitigate the uncertainty resulting from possible variations in the times of release of effluents

during the day, two sets of samples were collected on each sampling day; the first set of samples was collected between 9.00 am and 12.00 noon, and another set collected between 2.00 pm and 5.00 pm.

3.2.2 Main Study

The main study was laid out in a 2 x 5 factorial split-plot design with environmental media the main plot, while the site was the subplot. In split-plot design the procedure for randomization in both the main plot and the subplot followed the procedures of completely randomized block design (Gomez & Gomez, 1983). The purpose of the experiments was to determine the distribution and spatial variations of free-phase organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in air and surface waters in Nairobi City. The main factor was the environmental medium: air and surface water. The sub-factor was the site; there were four sampling sites for each media. Sampling from each medium at every site was replicated 3 times. Samples were collected for monitoring of PAHs and OCPs.

3.3 Materials and Methods

3.3.1 Materials

Standard length 92 cm performance reference compound semipermeable membrane devices (PRC SPMDs) made of low-density polyethylene (LDPE), and filled 99.9% pure grade triolein, were acquired from Sampling and Testing Department, E&H Services Inc., in Prague, Czech Republic along with 5-SPMD carrier deployment canisters made of stainless steel. Stevenson screens, made of untreated wood, 1-1.5 m above the ground, used in air sampling, were fabricated at a carpentry workshop (Embakasi, off Outering Road, Nairobi City, Kenya). Analytical grade solvents and reagents were acquired from Sigma-Aldrich (St. Louis, Missouri,

USA), while standards and certified reference materials were acquired from Industrial Analytical (PTY) Ltd, (Part of LGC Standards), (Vorna Valley, 1686, Republic of South Africa).

3.3.2 Sampling

3.3.2.1 Sampling Sites

The experiments for air sampling were set in protected sites in Nairobi City, to avoid interference from the population and at sampling sites along Nairobi River and its tributaries. The sampling sites for air were:

(i) City Square: The August 7 Memorial Park (1.2913°S, 36.8413°E), Moi Avenue Nairobi Primary School (1.2802°S, 36.8201°E) and St. Peter Clavers Primary School (1.2856°S, 36.8311°E)

(ii) Dandora: Dandora Primary School (1.2593°S, 36.8903°E); James Gichuru Primary School (-1.2458, 36.9054); Bishop Robert Mdzomba Academy (1.252805°S, 36.8969°E)

(iii) Kibera: Mashimoni Squatters Primary School – Kibera (1.3123°S, 36.7907°E), Kibera Church of God Primary School (1.3109°S, 36.7950°E) and MOC Primary School - Silanga, off Sheikh Mahmoud Road (1.3158°S, 36.7944°E).

(iv) Industrial Area: Mareba Health Centre, (1.3105°S, 36.3624°E); Nairobi City Water and Sewerage Company (1.3095°S, 36.8525°E); Nairobi East SDA Church (1.3010°S, 36.8809°E).

(v) Ngong' Forest: Rowallan National Scouts Camp, (1.31104°S, 36.7688°E), Kenya Scouts Association Headquarters (1.3125°S, 36.7697°E), Off Southern Bypass, after Buffalo Park Restaurant (1.3173°S, 36.7708°E).

The sampling sites for surface waters were:

(i) City Square on Nairobi River: Chiromo (1.2711°S, 36.8072°E);John Michuki Memorial Park (1.2765°S, 36.8320°E); Ngara bridge (1.2812°S, 36.8320°E) and Gikomba foot bridge (1.2862°S, 36.8375°E) along the river

(ii) Dandora on Nairobi River: Korogocho/Dandora Foot Bridge (1.2542°S, 36.8895°E); Next to Mercy Seat of God Church (1.2462°S, 36.8953°E); and Dandora Phase 1, just before joining Mathare River (-1.2427°S, 36.9000°E)

(iii) Kibera on Nairobi River: off Ngong Forest Road at (1.3174°S, 36.7809°E); off Ngong Forest Road at (1.3169°S, 36.7915°E); and just before Nairobi Dam at (1.3192°S, 36.7946°E).

(iv) Industrial Area on Ngong River: Belle View (1.2969°S, 36.8238°E); Enterprise Road Bridge (1.3157°S, 36.8615°E); near Bridge International Academies – Lunga Lunga (1.3115°S, 36.8763°E) and Donholm Outer Ring Road Bridge (1.3063°S, 36.8882°E).

(v) Ngong' Forest on Nairobi River: off Southern Bypass, near Buffalo Park Restaurant at (1.3173°S, 36.7808°E); off Ngong Forest Road at (1.3166°S, 36.7734°E); and off Ngong Forest Road, just before Kibera at (1.3166°S, 36.7738°E).

3.3.2.2 Sampling during the Methods Comparison Study

Prior to the main study, data from air and water samples were collected from two of the selected sites (sites A_4 and W_4 respectively (Figure 6)), weekly using active sampling. Passive sampling experiments were set up concurrently over the same period.

The SPMDs, which were used in passive sampling, were deployed in air and surface waters for 28 days, according to the procedure used by other studies (Alvarez, 2010; Karacik et al., 2013; Zhu et al., 2013; Tian et al., 2009; Wu et al., 2001; Schramn et al., 2001). During this same

period, air samples were collected from the study area using a low volume air sampler, fitted with a stainless steel sampling tube, standing at a height of 1.5 m above the ground level. The sampling tube was tightly fitted with 0.45 μm glass-fiber air filters. The air sucked through the sampling tube was passed through a polyurethane foam (PUF) sorbent filter (UNEP-GEF Project, 2012), with the aid of the sampler pump at the rate of 10 L min^{-1}. This was regulated by adjusting the sampling rate gauge on the sampler. Sampling was done for 15 minutes at each sampling unit. After each sampling, the PUF was removed and sealed in pre-extracted aluminum foil and transported to the laboratory in a dry-ice cooler box for extraction.

Water samples were also collected from Ngong River, a tributary of Nairobi River, weekly as described above, in pre-cleaned I L brown bottles which were immediately sealed after sampling and wrapped in pre-cleaned aluminum foil. The sample bottles were then transported to the laboratory for extraction. Selected physical-chemical parameters were determined at the sampling site.

3.3.2.3 Sampling during the Main Study

Sampling of surface waters were based on the methods used in previous studies (Alvarez, 2010; Karacik et al., 2013; Zhu et al., 2013; Tian et al., 2009; Wu et al., 2001; Schramn et al., 2001). The SPMDs were placed in metal cages suspended in water at the selected sampling sites on Nairobi River and its tributaries (Plate 1), over four continuous weeks. Each cage contained three sets of SPMDs for simultaneous sampling of OCPs and PAHs. During deployment, the metal cages were secured at the sampling sites to a fixed point using galvanized steel cables.

Plate 1: Photographs showing the deployment of SPMDs on surface waters

Sampling for air monitoring was based on the methods used in previous environmental monitoring studies (Soderstrom & Bergqvist, 2004; Zhu et al., 2013; Li et al., 1999). The SPMDs described above were placed in Stevenson screens, made of untreated wood, 1.5m above the ground (Plate 2).

Plate 2: Photographs showing the deployment of SPMDs for air sampling

The samplers were deployed in selected institutional compounds where they were safe, in the selected sites in Nairobi City and a control site at a location along Ngong' Forest, which was considered to be pristine. The SPMDs were exposed for 4 weeks continuously in three replicates. The daily weather parameters in Nairobi City were obtained from the Meteorological Department of Kenya at the Imara Daima weather station, throughout the sampling period. These parameters included: Precipitation, temperature, humidity and wind speed.

3.3.3 Quality Control during Sampling

The quality control measures during sampling from water bodies included the use of field blanks, laboratory blanks, and use of performance reference compounds (PRCs):

(i) The field blanks were prepared according to the method described by Alvarez (2010). The field blanks were stored in airtight metal-can containers and transported to the sampling sites in cooler boxes lined with cooled ice packs. During the deployment and retrieval the lids to the metal cans containing the field blanks were opened to allow exposure to the surrounding air. The lids were then replaced immediately the deployment was completed. This was also done during retrieval of the samplers from the sampling sites to the laboratory. The field blanks were extracted, cleaned and analysed alongside the deployed samplers. The data obtained from the blanks was used to correct the determined amount of sampled analytes for possible contamination during transportation of the samplers to and from the sampling sites, during the deployment and retrieval periods, and from storage, processing and analysis.

(ii) Preparation of the laboratory blanks were also based on the method described by Alvarez (2010). A set of unexposed SPMDs were extracted, cleaned and analysed alongside the field samplers. The data obtained from the laboratory blanks were used to correct the

amount of analysed determined from the samplers for possible contamination during processing and analysis of the samples.

(iii) ^{13}C - labeled compounds,$^{13}C_{12}$ CB – 52 and $^{13}C_{12}$ CB – 153, and a deuterated compound, D_{14}-*m*-terpheny, were used as performance reference compounds (PRCs), were loaded into the SPMD samplers during fabrication. The PRC loss was used to compute the site-specific SPMD sampling rate.

3.3.4 Extraction, Purification and Concentration

3.3.4.1 Extraction of Samples from Active Sampling

The PUF samplers were extracted in soxhlet apparatus according to the USEPA method TO-13A (US EPA, 1999), using 300 mL of a solvent mixture of diethyl ether : n-hexane (1:9, v:v), at 40℃ for 7 hours to achieve a minimum of 24 fill-empty cycles. The PAHs and OCPs were extracted alongside other persistent organic pollutants (POPs), as mixtures from the same PUF sampler. Hence a fractionation procedure was necessary (Ozcan et al., 2008). The volume of the extract was reduced to 2 mL in a rotary evaporator prior to the clean-up and fractionation procedure.

The water samples from active sampling were filtered through 0.45μm glass-fiber filters to remove particulate matter and subsequently through a 0.2μm cellulose acetate filter to remove colloidal particles. The filtered water samples were extracted by adsorption chromatography using reverse-phase (bonded silica) SPE sorbents (C_{18} – SPE cartridges) according to USEPA method TO-13A (USEPA, 1999), modified accordingto the method used by Ma et al., (2010), . The cartridges were mounted onto a solid-phase extraction vacuum Manifold (Supelco, USA) and conditioned before extraction of the water samples. A 10 mL n-hexane portion was added onto the cartridge, allowed to elute, and followed with 10 mL of methanol to remove air and

polar impurity, which was also allowed to elute. This was followed with 10 mL of distilled water which was allowed to elute before loading the sample. The sample was extracted at a flow rate of 5.0 mL min^{-1}, and the cartridge kept onto the vacuum for 30 min to remove residual water. The cartridge was then eluted by 15 mL diethyl ether : n-hexane (1:9, v:v) at the flow rate of 1 mL min^{-1}, the eluate collected into a clean test tube containing about 1g of pure-grade anhydrous sodium sulphate. The sample was then reduced to about 2 mL in a rotary evaporator prior to clean-up and fractionation.

3.3.4.2 Extraction of SPMD samples from Passive Sampling

The SPMDs used as field samplers, field blanks, and laboratory blanks were extracted and cleaned according to the methods in literature (Alvarez, 2010; Alvarez et al., 2004, 2008; Huckins et al., 2006; Petty et al., 2000). Each SPMD was removed from the metal cage and immediately cleaned using a soft brush to remove any particulate matter and any bio-film on its surface. The sampler was then immediately submerged in dilute nitric acid to remove salts that could be on the surface. The cleaned SPMD was then placed in a glass conical flask containing a 300 mL of hexane to cover the SPMD and the conical flask covered with a pre-cleaned aluminum foil. The flasks were the placed on an orbital shaker for 24 hours, at a low rate. After this first dialysis period, the extract was decanted into a pre-cleaned conical flask covered in aluminum foil, and a second portion of the hexane added to the flask containing the SPMD. This second dialysis period was performed for 12 hours. The n-hexane extracts from both dialysis periods were combined and the SPMD discarded.

3.3.4.3 Sample Clean-up and Concentration

Though extracts from SPMDs are generally considered to be “cleaner” than many other environmental matrices (Alvarez, 2010), the extracts may contain traces of co-extracted triolein.

In addition, fractionation of the POPs in the sample was necessary to minimize interferences. All the n-hexane extracts were concentrated to about 2 mL in a rotary evaporator at a temperature of 35°C, prior to the cleanup and fractionation procedures.

The OCPs fraction was obtained by adsorption fractionation according to USEPA Method 3630C: Each sample was quantitatively transferred to preconditioned silica gel (100 – 200 μm mesh) cartridges, containing 0.5 g anhydrous Na_2SO_4 and eluted with 5 mL n-hexane at approximately 2 mL min^{-1}. An additional 5 mL of n-hexane was added to the cartridge, allowed to soak for 1 minute, and allowed to elute. The eluates were collected in a vial as Fraction 1. The cartridge valve was then closed, the collection vial replaced and 5 mL of diethyl ether/hexane (50/50, v/v) added to the cartridge. The solvent was then allowed to elute and the eluate collected as Fraction 2; this fraction was analyzed for OCPs after concentration. The cartridge was preserved for recovery of PAHs. The fraction was then reduced to about 2 mL in a rotary evaporator at 35^0C and stored in amber coloured vials wrapped in aluminum foil at -4^0C.

The PAHs fraction was also obtained by adsorption fractionation according to USEPA Method 3630C: The silica gel cartridges preserved from the OCPs recovery procedure were eluted using 5 mL of dichloromethane/cyclohexane (2:3 v/v) at a rate of 2 mL min^{-1} and collected as Fraction 3: this fraction was analyzed for PAHs after concentration. The fraction was reduced to about 2 mL in a rotary evaporator at 35^0C and stored in amber coloured vials wrapped in aluminum foil at -4^0C.

3.3.5 Preparation of Standards and Samples for GC Analysis

The samples were prepared for GC-analysis according to the USEPA method 8100/8015 (USEPA 1997a). Prior to GC-analysis, the cleaned OCPs and PAHs samples were each evaporated to dryness under a stream of analytical grade nitrogen (99.99%) and the OCPs

reconstituted in 1 mL analytical grade n-hexane, while the PAHs were reconstituted in 1 mL analytical grade toluene.

Each 1 mL reconstituted OCPs sample was spiked with 1 µL of octachloronaphthalene as the internal standard, while each of the 1 mL reconstituted PAHs sample was spiked with 1µL of the dodecane, which was used as the internal standard. Calibration standards of concentration levels; were prepared from the authentic standards, in 1 mL toluene and also spiked with 1 µL of dodecane and stored in amber coloured glass vials with teflon-lined screw caps, wrapped in aluminium foil and kept at 4 ^{0}C.

3.3.6 Analysis of the Samples

The OCPs samples were analysed according to the method used by Wang et al., (2009), using an Agilent Technologies 7890A gas chromatograph instrument equipped with an electron capture detector (GC-ECD) and a Model 5975 mass spectrometer (MS). The instrument was run using an electron-ionization ion source (EI) in the selected ion monitoring (SIM) mode (Agilent Technologies, Santa Clara, CA, USA). Analyte separation was achieved using a capillary column HP-5MS, 30 m long, 0.25 mm internal diameter and a film thickness of 0.25 μm. A volume of 1 μL was injected and the GC was run in splitless injection mode with a total flow rate of 1.2 mL min^{-1}, linear velocity of 39.6 cm/sec, and a pressure of 8.8271 psi using helium as the carrier gas. The temperatures of the inlet and detector were 270 ^{0}C and 300 ^{0}C, respectively. The oven temperature programme was: 35 ^{0}C for 5 min, to 280 ^{0}C at 10^{0}C min^{-1}, held for 5.5 min, and finally to 285 ^{0}C at 50 ^{0}C min^{-1} and held for 19.9 min. The total run time for each sample was approximately 55 min. The ion source temperatures were set to 300 ^{0}C. The data were acquired and processed with Mass Hunter software (Agilent Technologies).

The analysis of the PAHs samples was done according to the US EPA method 8270C (US EPA 1997b), using Agilent Technologies 7890A gas chromatograph equipped with with a flame ionisation detector (GC-FID) and a Model 5975 mass spectrometer system. Analyte separation was achieved using a HP-5MS, (5% methyl silox), (30 m × 250 µm × 0.25 µm) column. The injector was set in the splitless mode with a total flow rate of 10.2 mL min^{-1}, septum purge flow rate of 3 mL min^{-1} and a pressure of 8.8271 psi using heliumas the carrier gas. The oven equilibration time was 1 min. The oven temperature was held at 35 ^{o}C for 5 min, and then increased to 280 ^{o}C at the rate of 10 ^{o}C min^{-1} and held there for 10.5 min. Finally the temperature was increased to 285^{o}C at the rate of 50 ^{o}C min^{-1} and held there for 9.9 min. The injector temperature was set at 250 ^{o}C. Only 1 µL of sample was injected for analysis. The data were processed with Mass Hunter software (Agilent Technologies).

3.4 Characterization and Quantification of the Analytes

3.4.1 Characterization of the Analytes

The analytes were characterized using the method used by Lalah and Kaigwara (2005) as modified by Lisouza et al., (2011). Identification was done by comparing the peak retention times on the sample chromatograms with the chromatograms of the authentic standards and confirmed by mass spectrometry.

3.4.2 Determination of Relative Response Factors (RRF)

The relative response factors of the analytes were determined according to the US EPA method 8100/8015 (US EPA 1997a). The peak area responses of the identified analytes were tabulated against their concentration and that of the internal standard; n-dodecane for PAHs and octachloronaphthalene for OCPs. The relative response factors (RRF) for each of the analytes calculated using the equation 6:

$$RRF = \frac{A_S \text{ x } C_{IS}}{A_{IS} \text{ x } C_S} \qquad (Equation\ 6)$$

Where, A_S is the peak area for the target analyte measured; A_{IS} is the peak area for the internal standard; C_{IS} is the concentration of the internal standard; C_S is the concentration of the target analyte.

3.4.3 Quantification of analytes in the SPMDs (M_S)

The amount M_S (ng) of the analytes in the extracts from the field samples and blanks was determined from peak areas using the internal standard method, according to the US EPA method 8100/8015 (US EPA 1997a). Equation 7 was used in the calculations:

$$\text{Amount, } M_S, (ng) = \frac{A_S \text{ x } W_{IS} \text{ x } W_S \text{ x } D}{A_{IS} \text{ x } RRF \text{ x } W_i} \text{x } 1000 \qquad (Equation\ 7)$$

Where, A_S is the peak area for the analyte in the sample; A_{IS} is the peak area for the internal standard in the sample; W_{IS} is the amount (ng) of internal standard added to the sample; W_i is the volume (µL) of sample injected into the GC; W_S is the final volume (µL) of extract per SPMD; D is the dilution factor; since no dilution was made on the sample prior to analysis, D = 1, dimensionless.

To track possible losses during the extraction, clean-up and concentration procedures, 10 µL portions of standard reference compounds containing a known amount, M_0 (ng), of the analyte were spiked into blank SPMDs, in triplicates, and stored for three days the same way as the samplers. The spiked blanks were processed through the same extraction, clean-up and concentration procedures as the samples. The extracts were also analysed using the same procedure as the samples. The amount, M_R (ng) of the each analyte recovered was determined using the internal standard method, after correction for blank concentration. The results were used to determine the extraction efficiency (EE %) of each of the analytes using Equation 8

$$\text{EE}\ (\%) = \frac{\text{M}_\text{R}}{\text{M}_0}\ \text{x}\ 100 \qquad (Equation\ 8)$$

Where: M_R = Total amount (ng) of analyte recovered after extraction and clean-up

M_0 = Amount (ng) spiked into the blank SPMD

The total amount M_S (ng) determined from the field samples were corrected for both blank and extraction efficiency, to get the amount of analyte concentrated by the SPMD, M_{SPMD} (ng), using Equation 9

$$\text{M}_{\text{SPMD}} = \frac{\text{M}_\text{S} - \text{M}_{\text{Blank}}}{\text{EE}\ (\%)} \qquad (Equation\ 9)$$

Where: M_S = Total amount (ng) of analyte determined from field samples

M_{Blank} = Amount (ng) determined from the field and laboratory blanks

M_{SPMD} = Amount (ng) of analyte concentrated by the SPMD

3.4.4 Calculation of sampling rate (R_S) and Concentrations for SPMDs

Models have been used in the estimation of a chemical's site specific $R_S$and its concentration in the atmosphere (C_A) or surface waters (Cw*),* when using SPMDs samplers. These models are based on the log $K_{OW}$of the compound, the PRC's release rate constant (K_e) and SPMD-water partition coefficient (K_{PW}). The PRC release rate (K_e)was determined by comparing the amount of PRC initially added to the SPMD (N_o) and the amount remaining (N_t) time t days (Equation 10) (Huckins et al., 1999; Wang et al., 2009; Booij et al., 2006). This was determined by analyzing a set of SPMDs, deployed in the same sampling cages as those used in the study for the same duration, by head-space direct determination, using a head-space gas chromatograph instrument coupled with tandem mass spectrometry (Headspace GC/MS/MS).

$$K_e = \frac{[\ln(\frac{N_t}{N_0})]}{t} \qquad (Equation\ 10)$$

Then, $Log\ K_{pw}$ is determined from a regression model of the PRC's Log K_{ow}using Equation 11which is empirically derived.

$$LogK_{PW} = a_0 + 2.321logK_{OW} - 0.1618(logK_{OW})^2 \qquad (Equation\ 11)$$

Where, a_0 is the intercept determined to be -2.61 for OCs, PAHs and PCBs (Wang et al., 2009). The sampling rate for PRCs is then calculated as shown in Equation 12;where *V*s is the volume of the SPMD (in L or mL) (Huckins et al., 1999; Wang et al., 2009; Booij et al., 2006).

$$R_S = V_S K_{PW} K_e \qquad (Equation\ 12)$$

The sampling rate for a passive sampler can be interpreted, in this study, as the volume of water or air cleared of analyte per unit of time by the passive sampling device.

The time-weighted average concentration of an analyte in the gas phase or water phase was then calculated, using a non-linear kinetic uptake model (Huckins et al., 1999), Equation 13,

$$C_{W(SPMD)} = \frac{M_S(t)}{R_S t} \qquad (Equation\ 13)$$

Where *M*sis the amount of an analyte accumulated in the sampler after exposure for time, t.

The sampling rates of the kinetic passive samplers are not affected by the concentration of the analyte in the environment (Booij et al., 2006). This means that they can be used in environmental media of variable concentrations of analytes and still sequester contaminants from point source discharges and seasonal changes. They can also be used to quantify ultra-trace level contaminants over extended time periods. For most samplers operating in the kinetic mode, although the sampling rate (*R*s) is not affected by the concentration present in the gas phase or water phase (C_W), it is affected by water flow and water turbulence as well as bio-fouling and temperature (Booij et al., 2006)

In cases where sampling was in the non-linear kinetic uptake mode, the SPMD-based concentrations (Cw_{SPMD}) in the air or surface waters were calculated using a non-linear kinetic uptake model as described by Huckins et al (1999), Equation 14.

$$Cw_{\text{SPMD}} = \frac{M_S}{K_{PW} V_s [1 - \exp(-k_e t)} \qquad (Equation\ 14)$$

3.5 Statistical Analysis of Data

Analysis of variance of the data, for a two factor split-plot design was done using GenStat programme and subsequently used to separate means for site, and means for environmental media. Thereafter, pair-wise comparison of means using t-test was used to determine if there exist significant differences between the means at $p \leq 0.05$.

3.6 Air-Water Fugacity Ratios

The concentrations from SPMD samplers give the levels of dissolved and gas-phase POPs in water or air, respectively. Concurrent air and water concentrations of individual contaminants were used to evaluate the equilibrium state of individual POPs in the air water interphases (Odabasi et al., 2008). The gaseous exchange was determined using the fugacity approach (Mackay, 1979). The fugacity in air (f_A) was calculated using the ideal gas law, equation 15 (Environment Canada, 2008; Bidleman & McConnell, 1995; Wania et al., 1998).

$$f_A = \left(\frac{n}{V}\right) RT = C_A RT \qquad (Equation\ 15)$$

Similarly, the fugacity in water (f_W) was calculated using Equation 16, which is a form of Equations 2 and 3 written to indicate fugacity in surface waters (Environment Canada, 2008; Bidleman & McConnell, 1995; Wania et al., 1998).

$$f_W = C_W H \qquad (Equation\ 16)$$

Where, C_A and C_W were the concentrations of the contaminant exclusively in gas-phase and dissolved-phase respectively (Devi et al., 2011; Odabasi et al., 2008), in mol m^{-3}; while f_A and f_W were in atmospheres; H is Henry's law constant for the organic contaminant in m^{-3} atm K^{-1} mol (Table 1 and Table 2); R is the ideal gas constant (8.2057 x 10^{-5} m^{-3} atm K^{-1} mol^{-3}) and T was the average temperature during the sampling period in Kelvin (Devi et al., 2011; Odabasi et al., 2008).

The ratio between the fugacities in air and surface waters were then calculated using Equation 17 (Environment Canada, 2008; Wania et al., 1998; Mackay, 1979)

$$\frac{f_W}{f_A} = \frac{C_W H}{C_A RT} \qquad (Equation\ 17)$$

Where; H/RT represents a compound-specific temperature-corrected Henry's law value (Tidwell et al., 2015; Odabasi et al., 2008).

The following fugacity decision rules (Equation 18) were adopted for the net gas exchange direction (Devi et al., 2011; Odabasi et al., 2008; Environment Canada, 2008; Wania et al., 1998; Mackay, 1979):

$$\begin{aligned} f_W/f_A &> 1 \quad Net\ volatilization \\ f_W/f_A &= 1 \quad Equilibrium\ (no\ net\ exchange) \\ f_W/f_A &< 1 \quad Net\ deposition \end{aligned} \qquad (Equation\ 18)$$

Gaseous exchange in the air-water interface is dictated both deposition and volatilization processes which occur simultaneously. The process which predominates determines the net exchange (Meire et al., 2016). The net exchange provided vital information concerning the possible sources of the contaminant in a given environmental location (Meire et al., 2016).

3.7 Risk Assessment

The toxicity equivalency (TEQ) of the congener was calculated by multiplying the concentration of the bioavailable fraction of each congener with its TEF value (Van den Berg et al., 2006). The total toxicity of a sample was then determined by multiplying the concentrations of the bioavailable fractions of the individual target contaminants by their respective TEFs.

Human exposure to OCPs occurs mainly through three pathways: inhalation, dermal contact and consumption (Toan, 2015). The carcinogenic human health impact of OCPs in Nairobi City was evaluated by determining the Incremental Lifetime Cancer Risks (ILCR) from inhalation of the atmospheric free-phase OCPs using Equation 19 (Sruthi et al., 2016).

$$\mathrm{ILCR_{Inhalation}} = \frac{\mathrm{C_{Air}\ x\ CSF\ x\ InhR\ x\ ET\ x\ EF\ x\ ED\ x\ IUR}}{\mathrm{BW\ x\ AT}} \qquad (Equation\ 19)$$

Where:

C_{Air} = Concentration of the OCPs in air (mg m^{-3}),

CSF = Inhalation cancer slope factor of OCP (kg day^{-1} mg^{-1})

= 0.007 mg kg^{-1} $days^{-}$ (USEPA, 1991)

InhR = inhalation rate (m^3 h^{-1}) = 0.6 m^3 h^{-1} for standing adult males and 0.48 m^3 h^{-1} for standing adult females, and 0.27 (USEPA, 1997c)

= An average of 0.54 m^3 h^{-1} for both standing males and females (Jin et al., 2018)

ET = Daily exposure duration (h day^{-1}): For this study, the times spent outdoors in the sampling sites were taken to be from 8.00 am – 6.00 pm = 10 h day^{-1}

EF = Exposure frequency (days yr^{-1}) = 365 days yr^{-1}.

ED = Lifetime exposure duration (yr): In this study this was taken as 30 years as adopted from USEPA (1989)

IUR = Inhalation unit risk (0.057 mg m^3),

BW = Body weight (kg); In this study an average body weight of 70 kg and 15 kg for an adult and child, respectively, were used, as adopted from USEPA (1989).

AT = Averaging time (d) = Lifetime Average Daily Dose (LADD) = 365 days/year x 70 years for a carcinogenic contaminant (USEPA, 1989)

This study considered the average hours spent outdoors for an average resident of Nairobi to be between 8.00 am and 6.00 pm, which gave daily exposure duration to outdoor inhalable OCPs in the air of 10 hours. During the computations, the concentrations of OCPs were converted to mg m^{-3}. The concentrations of carcinogenic PAHs were converted to equivalent concentration of BaP (BaP_{eq}) using their toxicity equivalency factor (TEF) (USEPA, 1993; Hu et al., 2007; Yang et al., 2017; Jin et al., 2018) using equation 20 (USEPA, 1989; Jin et al., 2018).

$$BaP_{eq} = \sum C_i \text{ x } TEF_i \qquad (Equation\ 20)$$

Where: $C_i$and $TEF_i$are the concentrations (ng m^{-3}) and TEF corresponding to species *i*.

The BaP_{eq} values (ng m^{-3}) calculated (Equation 20) were converted into mg m^{-3} before being used in assessing the cancer risks posed by human exposure to PAHs through inhalation, in various regions of Nairobi City of Kenya. The USEPA model (Equation 21) was employed to assess the incremental lifetime cancer risk (ILCR) of adults due to exposure to PAHs in the city (USEPA, 1989).

$$ILCR = \frac{CSF \text{ x } BaP_{eq} \text{ x } IR \text{ x } ET \text{ x } EF \text{ x } ED}{BW \text{ x } AT} \qquad (Equation\ 21)$$

Where:

CSF = Inhalation cancer slope factor of BaP (kg day^{-1} mg^{-1})

= 3.1 mg^{-1}kg day (USEPA, 1991)

BaP_{eq} = concentration (mg m^{-3}) calculated in Equation 20.

IR = inhalation rate (m^3 h^{-1}) = 0.6 m^3 h^{-1} for standing adult males and 0.48 m^3 h^{-1} for standing adult females, and 0.27 m^3 h^{-1} for children (USEPA, 1997c)

= An average of 0.54 m^3 h^{-1} for both standing males and females (Jin et al., 2018)

ET = Daily exposure duration (h day^{-1}): For this study, the times spent outdoors in the sampling sites were taken to be from 8.00 am – 6.00 pm = 10 h day^{-1}

EF = Exposure frequency (days yr^{-1}) = 365 days yr^{-1}.

ED = Lifetime exposure duration (yr): In this study this was taken as 30 years as adopted from USEPA (1989)

BW = Body weight (kg); In this study an average body weight of 70 kg and 15 kg for an adult and child, respectively, were used, as adopted from USEPA (1989).

AT = Averaging time (d) = Lifetime Average Daily Dose (LADD) = 365 days/year x 70 years for a carcinogenic contaminant (USEPA, 1989).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Weather Data in Nairobi city during the Sampling Period

The accumulated monthly precipitation in Nairobi City between May – December 2017 is presented in Table 4.1.

Table 4.1: Accumulated monthly precipitation and number of monthly precipitation days of Nairobi during the sampling period

Month in 2017	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec
Accumulated precipitation (mm)	51.2	2.0	32.0	12.6	15.0	113.0	140.4	7.2
Precipitation days ($\geq$ 0.1 mm)	9	1	2	3	2	7	18	3

Source: Meteorological Department of Kenya (2017).

The accumulated monthly precipitation ranged between 2.0 mm over a single day in June and 140.4 mm over 18 days in November 2017. Nairobi City experiences two rainy seasons: From March to May (long rains) and October to December (short rains), (Meteorological Department of Kenya, 2017). During these seasons the rains come late in the evenings in form of showers, hence do not affect the sunshine hours to a large extent. The amount of precipitation closely relates to humidity, which affects the distribution of POPs between environmental media and hence the rate of sampling of POPs by SPMDs. Table 4.2 shows the daily and weekly averages of temperature, humidity and wind speed in Nairobi City during the sampling periods between 16th May 2017 and 11th June 2017 for the comparison study, and between 16th October and 3rd December 2017 during the main study.

Table 4.2: Weekly means of Nairobi weather data during the sampling periods.

Week	May15 –May 21	May 22 –May28	May 29 – Jun 4	Jun 5-Jun11	Oct 16– Oct 22	Oct 23– Oct 29	Oct 30– Nov 5	Nov 6 – Nov 12	Nov 13– Nov 19	Nov 20– Nov 26	Nov 27 –Dec 3
Average max. Temp (°C)	24.9±0.9	26.6±1.6	25.0±1.4	25.3±0.5	26.1±2.4	24.6±1.0	23.1±1.8	22.3±2.0	22.7±0.8	24.0±0.9	24.3±1.4
Daily mean Temp (°C)	20.3±0.5	20.7±1.0	21.1±1.3	20.6±0.6	21.9±2.7	21.2±1.0	19.4±0.7	19.5±0.7	19.6±0.4	20.3±0.8	20.2±0.5
Average min. Temp (°C)	15.4±0.8	14.9±1.8	17.2±2.0	16.0±1.5	17.7±2.3	17.9±2.3	15.7±0.8	16.7±1.0	16.4±0.5	16.7±0.8	16.1±1.2
Average max. Humidity (%)	89.3±4.5	87.6±4.5	80.4±16.0	77.4±5.3	73.3±11.4	78.4±14.0	83.4±11.1	90.6±4.0	80.0±7.7	88.3±8.5	82.1±10.0
Daily mean Humidity (%)	71.8±3.2	67.2±4.9	70.3±11.0	63.4±2.7	63.1±10.3	67.1±9.2	73.6±11.6	79.0±4.5	69.9±8.9	70.6±6.1	64.9±3.8
Average min. Humidity (%)	54.3±6.7	46.9±9.0	60.2±8.4	49.4±3.7	53.0±11.5	55.7±6.6	63.7±13.4	67.4±9.2	59.9±10.3	53.1±5.5	47.6±5.2
Mean daily wind speed (Km/hr)	11.3±1.1	10.9±1.6	12.0±3.7	10.5±2.4	10.2±2.7	14.1±4.7	11.6±4.1	12.9±3.4	18.7±3.0	14.8±3.5	16.0±2.1

SOURCE: Meteorological Department of Kenya (2017).

The weekly average maximum temperatures ranged between 22.3 ± 2.0 - 26.6 ± 1.6^{0}C, while the weekly average minimum temperatures ranged between 14.9 ± 1.8 - 17.7 ± 2.3 ^{0}C. This translated to daily mean temperature range of 19.4 ± 0.7 - 21.9 ± 2.7 ^{0}C. Similarly, the weekly average maximum humidity ranged between 73.3 ± 11.4 % - 90.6 ± 4.0 %, the while the weekly average minimum humidity ranged between 46.9 ± 9.0 % - 67.4 ± 9.2 %. This gave the daily humidity means in the range of 63.1 ± 10.3 % -79.0 ± 4.5 %. This type of climate in Nairobi is classified as a subtropical highland climate according to the Köppen-Geiger climate classification system (Pidwirny, 2006). SPMDs have been successfully used in monitoring the environmental levels of POPs in Melbourne Australia (Prest et al., 1995) which is classified as having the same climate as Nairobi City. Climatic conditions in Nairobi were not therefore an impediment to the use of SPMDs. POPs have generally low Henry's law constant (H_C) values (Table 2.2). These low Hc values imply that when these compounds are released in to the surface waters, as in the case of contaminated waste waters effluent from industrial processes or surface

run-off during storms, the compounds will tend to remain more in the surface water phase than partition into the air. This results in increase in human exposure to the POPs in the surface waters, if the waters are used for cooking, drinking and other domestic uses, as well as swimming. However, the surface waters in Nairobi are not used for any of these purposes, since the city has a fairly good treated water supply system.

Conversely, when relative volatility is factored in, a different scenario is likely to emerge regarding the low H_C values, depending on the weather conditions: During the dry season, the air is generally dry and hence the behaviour of the contaminant will obey Henry's law; substances with H_C value less than the H_C value for water will concentrate more in the water phase, as water volatilizes faster into the air than the substance (Huckins et al., 2006). This is because air does not affect the fugacities of the contaminants. On the other hand, during the wet season, as was the case in Nairobi City during most of the sampling period, the percentage humidity in air increases (Table 2.5). This increase in the amount of water vapour in the atmosphere hinders evaporation of the surface water into the atmosphere (Huckins et al., 2006). However this does not affect the evaporation of the pollutant. The resulting scenario is that under humid conditions, substances such as POPs, which have very low vapour pressures in comparison to water, can still exhibit high relative volatility, relative to water, because of their high hydrophobic character. The implication here is that, if industrial effluent or/and surface run-off containing POPs gets into a river or any other surface water body, the POPs pose risk to the population, even though the water is not used for drinking or cooking.

The average wind directions in Nairobi City during the sampling period are given in Table 8. The mean daily wind speeds were generally high, ranging between 10.2±2.7Km/hr and 18.7±3.0 Km/hr. Such high wind speeds are likely to carry the POPs released from point sources in one

section of the city to many other regions of the city within a short time interval. This in turn increases the probable risk of human exposure to POPs in Nairobi City. The observation agreed with that of Söderström and Bergqvist (2004) who reported that high wind speeds/turbulences affected the amounts of POPs sequestered by the SPMDs.

Table 4.3: Wind direction in Nairobi City between May 2017 and December 2017

Wind Direction	N	NE	E	SE	S	SW	W	NW
Percentage hours (%)	14	28	22	14	14	5	2	1

Source: Meteorological Department of Kenya (2017).

The predominant wind directions in Nairobi City were NE > E > N, SE, and S. The wind direction determines the locations of the areas, with non-points sources of the contaminants, which are contaminated via diffuse sources such as atmospheric transport and deposition (Grimalt et al., 2004). Ngong' Forest is situated to the West of Nairobi City (Figure 3.1); given the predominant wind directions in the city during the sampling period, it is not probable that the contaminants from the other regions of the city were carried to Ngong' Forest though atmospheric transport and deposition. This makes Ngong' Forest relatively pristine, when compared to the other parts of the city, regarding POPs contamination.

4.2 Physical – chemical Parameters of the Waters of Nairobi River during Active Sampling

Some physical-chemical parameters of the surface waters determined during the preliminary study are shown in Table 4.4. These include the flow rate of the river at the sampling point, the temperature, turbidity, pH and dissolved oxygen of the sampled waters.

Table 4.4: Physical – chemical parameters of the waters at on Nairobi River at the sampling points during active sampling

Sampling Week	May 15 – May 21	May 22 – May 28	May 29 – June 4	June 5- June 11
Flow Rate (m/s)	0.51±0.02	0.50±0.01	0.50±0.01	0.49±00
Temperature (^{0}C)	20.3±0.3	20.6±0.80	21.1±0.9	20.7±0.50
Turbidity (NTU)	77.34± 7.32	85.83±4.79	81.23±3.43	75.71±2.57
pH	6.87±0.00	6.68±0.02	6.63±0.01	6.88±0.01
DO (mg/L)	5.81±0.04	5.72±0.03	4.99±0.01	6.15±0.05

In diverse aquatic systems SPMD sampling rates vary as much as ten-fold due to differences in water velocity/turbulence at the membrane surface, about four fold due to differences in environmental exposure temperatures (i.e., for a range of 2 to 30℃) and 3 to 4 fold (compounds with log K_{OW}> 6.0) for membrane biofouling (Huckins et al., 2002). Even when SPMDs are exposed inside a protective deployment cages, the differences in water velocity among sites have the great effect on sampling rate (Huckins et al., 2002). However, measurements of linear flow rates and other parameters, as those reported in Table 9, provide only a rough indicator of changes in sampling rates (Huckins et al., 2002). To determine the actual sampling rate, performance reference compounds (PRCs) were used during passive sampling (Huckins et al., 2005). PRCs are sensitive to the environmental conditions such as; flow-turbulence, temperature and biofouling, as well as photolysis of chemical classes such as POPs (Huckins et al., 2005).

4.3 Evaluation of Modified Active Sampling and Passive Sampling as Alternative Methods for Monitoring Persistent Organic Pollutants in Kenya

The data obtained using triolein-filled SPMD samplers for air and surface waters were compared to the results obtained using active sampling integrated with graded filters. These results were used to evaluate the feasibility of using modified active sampling as a complementary method to triolein-filled SPMDs for monitoring the environmental levels and distribution of organochlorine

pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in Nairobi City, and Kenya, in general.

The identification of the analytes following GC-MS analyses of the POPs were determined using retention times of authentic standards and confirmed by GC-MS analysis (Appendices 1 and 2), as discussed in the main study, in the subsequent sections (section 4.4). This was done so to avoid repetition in the presentation of results.

4.3.1 Evaluation of Modified Active Sampling and Passive Sampling as Alternative Methods for Monitoring OCPs in Kenya

Nine OCPs were detected and quantified during the evaluation study. These included; aldrin, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT , chlordane, endrin, heptachlor and γ-HCH. Table 4.5 gives the detection frequencies, the means of levels, the coefficients of variation percentages (CV %) and the standard errors of differences of means (S.E.D) of OCPs obtained from active sampling and passive sampling of surface waters and air in Nairobi City of Kenya.

Table 4.5: Levels of OCPs obtained from the air (ng m^{-3}) and surface waters (ng L^{-1}) using both active and passive sampling

OCP	Environ. Medium	Sampling method		Mean	CV (%)	LSD (p≤0.05)	S.E.D	% Freq. (n = 8)
		Active	Passive					
Aldrin	Air	0.064±0.015	0.102±0.001	0.083± 0.027	11.4	0.021	0.007	100.0
	S. Waters	0.096±0.012	0.141±0.001	0.119± 0.032	6.9	0.018	0.006	100.0
p,p'-	Air	0.080±0.007	0.163±0.007	0.122± 0.058	35.0	NS	0.030	87.5
DDT	S. Waters	0.144± 0.059	0.234±0.003	0.189± 0.064	22.5	NS	0.030	100.0
p,p'-	Air	0.021±0.047	0.092±0.004	0.056± 0.051	50.2	0.064	0.020	62.5
DDD	S. Waters	0.021±0.041	0.127±0.005	0.074± 0.075	30.5	0.059	0.019	62.5
p,p'-	Air	0.000	0.099±0.006	0.050± 0.070	8.4	0.009	0.003	50.0
DDE	S. Waters	0.111±0.013	0.158±0.019	0.134± 0.033	5.4	0.017	0.005	100.0
Chlordane	Air	0.021 ± 0.043	0.089 ± 0.005	0.055± 0.048	58.7	0.024	0.011	62.5
	S. Waters	0.000	0.091 ± 0.005	0.045± 0.064	42.9	0.035	0.015	25.0
Dieldrin	Air	0.103 ± 0.010	0.115 ± 0.003	0.109± 0.008	3.5	0.009	0.003	100.0
	S. Waters	0.074± 0.010	0.158 ± 0.004	0.116± 0.059	8.6	0.023	0.007	100.0
Endrin	Air	0.112 ± 0.020	0.166 ±0.006	0.139± 0.038	12.3	0.038	0.012	100.0
	S. Waters	0.054± 0.064	0.192 ± 0.013	0.123± 0.097	40.1	0.111	0.035	75.0
Heptachlo	Air	0.206 ± 0.015	0.225 ± 0.008	0.215± 0.013	8.2	0.040	0.012	100.0
	S. Waters	0.023 ± 0.046	0.114 ± 0.001	0.068± 0.064	46.6	0.072	0.023	75.0
HCHs	Air	0.135 ± 0.023	0.189 ± 0.004	0.162± 0.038	7.0	NS	0.008	100.0
	S. Waters	0.087 ± 0.062	0.16± 0.006	0.111± 0.034	41.3	NS	0.033	87.5

NS = not significant; Freq = frequency; S.E.D = standard error of differences of means

Aldrin was detected in all the water and air samples with relatively high atmospheric concentrations of 0.064±0.015 ng m^{-3} and 0.102±0.001 ng m^{-3} from active and passive sampling respectively. These values were within the range of those reported in the air in Alexandria, Egypt (>LOD – 0.147 ng m^{-3}) (Khairy & Lohmann, 2013). The levels of aldrin in both air and surface

water samples collected by passive sampling were higher ($p \leq 0.05$) than those collected active sampling. This trend was also observed in both the atmospheric and dissolved phase levels of *p,p'*-DDD, *p,p'*-DDE, chlordane, dieldrin, endrin and heptachlor, as well as the atmospheric levels of γ-HCH. However, though the atmospheric and dissolved phase levels of *p,p'*-DDT collected by active sampling were lower than those collected by passive sampling, they were not different ($p \leq 0.05$). This was also observed in the levels of dissolved phase γ-HCH sampled by the two methods.

Though *p,p'*-DDE was detected and quantified from all the samples collected by passive sampling of air and surface waters, they were below detection limit in the air samples collected by active sampling. In the surface waters, the levels of *p,p'*-DDE were lower ($p \leq 0.05$) than those collected by passive sampling. Similarly, while chlordane was detected and quantified in all the samples by passive sampling from both the air and surface waters, it was below detection limit in the water samples collected active sampling. Additionally, though the level of chlordane quantified from one of the samples collected by active sampling was within the range of those collected by passive sampling, it was below detection limit in the rest of the samples. Further, a number of the OCPs were below detection limit in all the replicates collected by active sampling; in the air samples, *p,p'*-DDD was found in only one of the replicate samples, chlordane in one, while *p,p'*-DDT was found in three replicates. In the water samples collected by the active method, *p,p'*-DDD was detected in one replicate; heptachlor in one; and γ-HCH in three replicates.

These observations from the evaluation study were, in part, attributed to possible uncertainties related to probable unscheduled and/or accidental contaminant release into the environment.

These probably resulted in variances relating to choice of the sampling time and days during the sampling weeks, in active sampling. According to previous studies (Alvarez et al., 2004; Alvarez, 2010), active sampling is not time integrated and hence, the data collected may not be representative of the actual environmental levels of the contaminants. One of the advantages of using SPMDs, over active sampling, is that SPMDs can be deployed for extended time periods to integrate long-term (Esteve-Turrillas et al., 2008). Since passive sampling methods give time-averaged concentrations, (Soderstrom & Bergqvist, 2004) the risk of underestimation or overestimation of total pollutant mass flows due to accidental sampling is reduced.

The coefficient of variation percentages (CV (%)) across all the analytes monitored in the all the samples ranged between 3.5 % (dieldrin) to 58.7% (chlordane). The fairly high CV (%) values in a number of the analytes were indications of non-homogeneity in the variance of the experimental errors (Gomez & Gomez, 1983; Hopkins, 2000; Osborne, 2002), in the collected data. The high CV (%) values further indicated that the data variances were significantly different (Gomez & Gomez, 1983; Hopkins, 2000; Osborne, 2002; Lisouza, 2011). This non-homogeneity was attributed to the difference and poor replication caused by non-uniformity over time in the sampling methods. Similarly, the standard errors of differences of means (S.E.D) values for *p,p'*-DDT, *p,p'*-DDD, chlordane, Endrin, heptachlor and γ-HCH were high, especially when considered as a percentage of the differences between the means. This indicated high variation in the levels of the sampled analytes with sampling time.

The span of the sampling area was reduced to minimize the variations resulting from probable source distribution, to establish a near-homogenous sampling block. To make the data collected more representative, the replications were increased and the sampling days randomized. The

results of this study were in agreement withGouin et al., (2005) who reported that use of passive and active sampling could provide a complementary approach for monitoring the spatial and temporal trends of persistent organic pollutants. However, Gouin et al., (2005) did not make provision in their experimental procedure to separate the free-phase pollutants from those in adsorbed phase during active sampling; this resulted in comparison of data that were different in nature. The introduction of graded filters into the design resolved the questions regarding the bioavailability of the sampled contaminants in active sampling, raised in previous studies (Huckins et al., 1990; Alvarez et al., 2004). Use of graded filters to remove particulate matter and colloidal particles presented the possibility of loss of some of the dissolved, and probably gas-phase, OCPs through adsorption onto the filtered particles and/or onto the filters (Carlson & Thomson, 2000). Since these probable variances were likely to be matrix-dependent, the effect of these on individual samples could not be conclusively evaluated.

4.3.2 Evaluation of modified active sampling and passive sampling as alternative methods for monitoring PAHs in Kenya

Table 4.6 gives the detection frequencies, the means, the coefficients of variation percentages (CV%) and the standard errors of differences of means (S.E.D) of the PAHs obtained from active sampling and passive sampling of surface waters and air in Nairobi City of Kenya. Twelve of the sixteen USEPA priority PAHs were detected and quantified during the evaluation study. These were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene and dibenzo(a,h)anthracene. However, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-c,d)anthracene and benzo(ghi)perylene were not detected in any of the collected samples.

Table 4.6: Levels of PAHs obtained from the air (ng m^{-3}) and surface waters (ng L^{-1}) using both active and passive sampling

PAH	Environ. medium	Sampling method		Mean	CV %	LSD ($p \leq 0.05$)	S.E.D	Freq. % (n = 8)
		Active	Passive					
Naphthalene	Air	0.124± 0.006	0.169± 0.001	0.146± 0.032	3.1	0.010	0.003	100.0
	S. Waters	0.115± 0.005	0.131± 0.001	0.123± 0.011	2.4	0.007	0.002	100.0
Acenaphthylene	Air	0.104± 0.005	0.154±0.001	0.129± 0.036	2.9	0.008	0.003	100.0
	S. Waters	0.126± 0.007	0.140± 0.001	0.133± 0.010	3.6	0.011	0.003	100.0
Acenaphthene	Air	0.127 ±0.007	0.185± 0.003	0.156± 0.041	3.7	0.013	0.004	100.0
	S. Waters	0.131± 0.005	0.150± 0.001	0.140± 0.013	2.3	0.007	0.002	100.0
Fluorene	Air	0.028± 0.032	0.089± 0.003	0.058± 0.043	35.7	0.047	0.015	75.0
	S. Waters	0.085± 0.007	0.099± 0.001	0.092± 0.010	4.5	0.009	0.003	100.0
Phenanthrene	Air	0.027± 0.031	0.087± 0.001	0.057± 0.043	38.1	0.049	0.015	75.0
	S. Waters	0.079± 0.007	0.097± 0.003	0.077± 0.003	9.1	0.017	0.003	100.0
Anthracene	Air	0.082± 0.004	0.122± 0.002	0.102± 0.028	4.1	0.009	0.003	100.0
	S. Waters	0.097± 0.005	0.118± 0.001	0.107± 0.015	3.2	0.008	0.002	100.0
Fluoranthene	Air	0.067± 0.004	0.098± 0.003	0.082± 0.022	4.9	0.009	0.003	100.0
	S. Waters	0.059± 0.004	0.088± 0.001	0.073± 0.021	4.1	0.007	0.002	100.0
Pyrene	Air	0.073± 0.002	0.113± 0.001	0.093± 0.028	1.4	0.003	0.001	100.0
	S. Waters	0.073± 0.004	0.107± 0.001	0.090± 0.024	3.7	0.008	0.002	100.0
Benzo(a)anthra	Air	0.052± 0.003	0.083± 0.002	0.068± 0.022	4.9	0.008	0.002	100.0
cene	S. Waters	0.055± 0.003	0.076± 0.001	0.066± 0.015	2.8	0.004	0.001	100.0
Chrysene	Air	0.026± 0.030	0.078± 0.001	0.052± 0.037	39.8	0.047	0.015	75.0
	S. Waters	0.050± 0.004	0.065± 0.001	0.057± 0.010	4.4	0.006	0.002	100.0
Benzo(a)pyrene	Air	0.093± 0.003	0.142± 0.002	0.117± 0.035	1.6	0.004	0.001	100.0
	S. Waters	0.086± 0.005	0.095± 0.001	0.090± 0.006	3.8	0.008	0.002	100.0
Dibenzo(a,h)	Air	0.050± 0.004	0.068± 0.003	0.059± 0.013	3.2	0.004	0.001	100.0
anthracene	S. Waters	0.043± 0.002	0.049± 0.001	0.046± 0.004	5.0	0.005	0.002	100.0

LSD = Least significant difference; Freq = Frequency

Benzo(a)pyrene, which is classified as both carcinogenic and mutagenic, and commonly used as a biomarker of PAH pollution was detected in all the air samples from both active sampling and passive sampling . Similarly, benzo (a) pyrene was found in all the surface water samples collected by active sampling as well as those collected by passive sampling. Analysis of the results showed that the levels of benzo(a) pyrene obtained by passive sampling, from both the environmental media, were higher ($p \leq 0.05$) than those collected by active sampling. This trend was observed in the levels of naphthalene, acenaphthylene, acenaphthene, anthracene,

fluoranthene, pyrene, benzo(a)anthracene, benzo(a)pyrene and dibenzo(a,h)anthracene in the air and surface waters collected by the two sampling methods. However, whereas fluorene, phenanthrene and chrysene were present in all the air and surface water samples collected passively, they were not detected in two of the air samples collected by active sampling. These results were in agreement with both Alvarez et al., (2004) and Alvarez, (2010) that since active sampling was not time integrated, the data collected might not be representative of the actual environmental levels of the contaminants. Since SPMDs can be deployed for extended time periods to integrate long-term data, SPMDs give time-averaged concentrations (Esteve-Turrillas et al., (2008), which reduces the risk of underestimation or overestimation of total pollutant mass flows due to accidental sampling (Soderstrom & Bergqvist, 2004). The design adopted, which involved modification of active sampling to include graded filters resolved questions regarding the bioavailability the sampled PAHs. These results indicated that, in the absence of passive samplers, it was possible to use active sampling, as modified, to generate data that provide insight into the levels of bioavailable PAHs in the environment.

The coefficient of variation percentages (CV %) across all the PAHs quantified ranged between 1.4% (pyrene in the air) to 9.1% (phenanthrene in the surface waters); except fluorene (35.7%), chrysene (39.8 %) and phenanthrene (35.5 %) which were not detected in half of the air samples collected by active sampling. These low CV % values were an indication of the homogeneity in the variance of the experimental errors (Gomez & Gomez, 1983; Hopkins, 2000; Osborne, 2002). These results showed that the study design adopted, in which the span of the sampling area was reduced, created a homogeneous sampling block in terms of PAH pollution. The low CV (%) values further indicated that the data variances were not significantly different (Gomez & Gomez, 1983; Hopkins, 2000; Osborne, 2002), hence means could be compared. In addition,

replication and randomization, as adopted in the study design, successfully mitigated any probable variations that were not attributable to the treatments. Thus any significant variations in the levels of the sampled PAHs could be attributed to the treatments; difference in the sampling method.

The standard errors of differences of means (S.E.D) values for all the sampled PAHs, except fluorene, phenanthrene in air and chrysene in air, were low especially when considered as a percentage of the differences between the means. These results show that if the two sets of data were collected repeatedly many times, the variability between the means from passive and active sampling will be low. The analysis of results showed that, besides the results providing data on the bioavailability of the sampled PAHs, the results were reproducible. SPMDs mimic the contaminant uptake process in aquatic organisms and hence could be used to quantify bioavailable fractions of pollutants in the water phase, as well as in the air (Lebo et al., 1992; Axelman et al., 1999). Verweij et al., (2004) used SPMDs and fish to simultaneously measure the bioavailable fraction of OCPs and PAHs in the water phase at several freshwater sites in and around the city of Amsterdam.

In the study, SPMDs gave more realistic estimates of the aqueous contaminant concentration than fish data. However, though use of biota in environmental sampling of POPs also provides information on the bioavailability of the contaminants, the data from biota is not reproducible (Söderström et al., 2005). From the results of this study, modification of active sampling to include graded filters resolved questions regarding the bioavailability of the sampled PAHs, indicating the data obtained was reproducible. The results gave low CV % indicating that the variances in the experimental errors in the data collected by both active sampling and SPMDs

samplers were homogeneous. It was concluded that, in the absence of SPMDs, integration of graded filters in active sampling could provide an insight into levels of bioavailable PAHs in the environment.

4.3.3 Conclusions from the evaluation study

Modification of active sampling to include graded filters resolved questions regarding the bioavailability of both the sampled OCPs and PAHs. However, the data still presented the possibility of underestimation of the bioavailable POPs. Further the results showed that the data on OCPs and PAHs was reproducible.

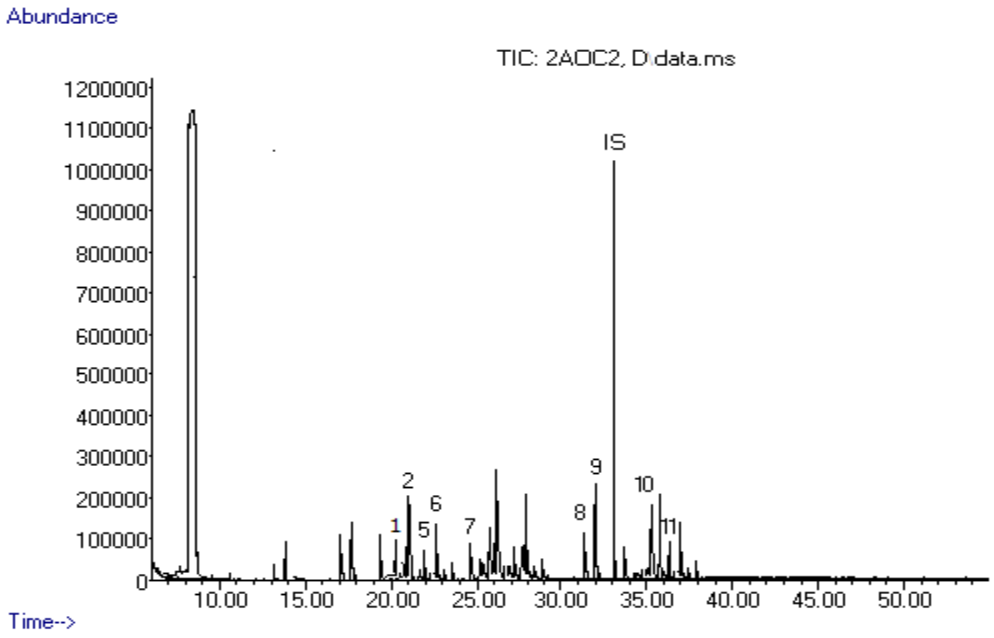
4.4 Sources and distribution of free-phase OCPs and PAHs in air and surface waters in Nairobi City, Kenya

The gas-phase and dissolved OCPs, and PAHs, in the air and surface waters, respectively, were monitored, using triolein-filled SPMDs and quantification based on a kinetic uptake model. Nine OCPs and thirteen PAHs were detected using SPMDs at various sampling sites in the Nairobi City. The levels and distribution of the OCPs and PAHs are presented in this section

4.4.1 The Levels, Distribution and Possible Sources of the Bioavailable OCPs in air and Surface Waters in the Nairobi City, Kenya

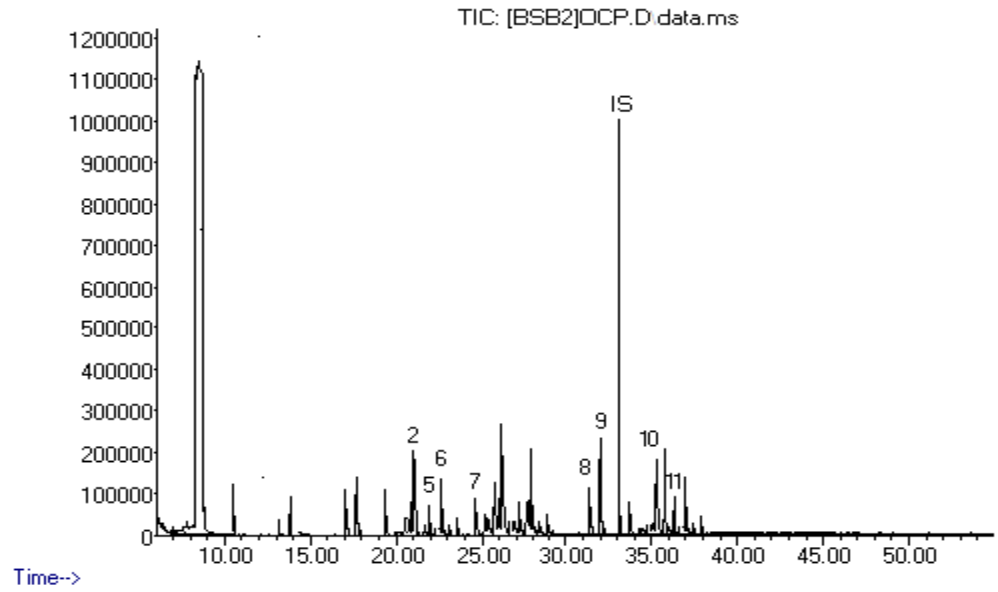
4.4.1.1 Identity of the Sampled OCPs

Eleven OCPs were identified in the air and surface water samples, collected from the various sampling sites in Nairobi City by passive sampling using retention times of authentic standards and confirmed by mass spectra analysis using GC-MS instrument (Appendix 2). These were; aldrin, *p,p'*-DDE, *p,p'*-DDD, and *p,p*'-DDT , chlordane, dieldrin, endrin, heptachlor, α – HCH, δ- HCH and Lindane (γ-HCH). Figure (4.1 and 4.2) shows chromatograms obtained from GC analysis of air and water samples, respectively.



KEY: 1=α – HCH; 2 = γ - HCH; 3 = δ - HCH; 4 = Chlordane; 5 = Endrin; 6 = Heptachlor; 7 = Aldrin; 8 = p,p'- DDE; 9 = Dieldrin; 10 = p,p'-DDD; 11 = p,p'- DDT; IS = Octachloronaphthalene

Figure 4.1: GC- chromatogram of one of the air sample.



KEY: 1= α – HCH; 2 = γ - HCH; 3 = δ - HCH; 4 = Chlordane; 5 = Endrin; 6 = Heptachlor; 7 = Aldrin; 8 = *p,p'*- DDE; 9 = Dieldrin; 10 = *p,p'*-DDD; 11 = *p,p'*- DDT; IS = Octachloronaphthalene

Figure 4.2: GC chromatogram of one of the surface waters sample.

Table 4.7 shows the retention times of the OCPs in, the sampling site at which they were sampled and the percentage of the samples from the site in which the OCP was detectable.

Table 4.7: Retention times of OCPs in GC-MS analyses

OCP	Retention Time	Sampling site where detected	% Samples detected (n = 30)
α - HCH	20.482	Dandora, Kibera, Industrial Area	23.33
γ- HCH	20.930	Dandora, Kibera, Industrial Area, Ngong' Forest	80.00
δ- HCH	21.168	Dandora, Kibera, Industrial Area	16.67
Chlordane	21.410	Dandora, Kibera, Industrial Area	16.67
Endrin	21.904	Dandora, Kibera, Industrial Area, City Square	70.00
Heptachlor	22.590	Dandora, Kibera, Industrial Area	60.00
Aldrin	24.695	Dandora, Kibera, Industrial Area	60.00
p,p'-DDE	31.751	Dandora, Kibera, Industrial Area, City Square	66.67
Dieldrin	31.950	Dandora, Kibera, Industrial Area, City Square, Ngong' Forest	80.00
p,p'-DDD	34.539	Dandora, Kibera, Industrial Area	63.33
p,p'-DDT	35.736	Dandora, Kibera, Industrial Area	56.67

γ- HCH and dieldrin had the highest prevalence across all the sampling sites, including Ngong' Forest, with each being detected in 80.00 % of the samples collected. Chlordane, endrin, heptachlor, aldrin, *p,p'*- DDE, *p,p'*- DDD, and *p,p'*- DDT were detected in >56.00 % of the samples, but not in any of the samples collected from Ngong' Forest. α – HCH, δ- HCH and chlordane were, however, detected in <25.00 % of the collected samples. These results indicated that there was appreciable human exposure to both gas-phase and dissolved OCPs in Nairobi City of Kenya.

Although a previous study (Aucha et al., 2017) reported presence of the endosulfan isomers (α-endosulfan and β-endosulfan) and, endosulfan sulfate, in Dandora, Industrial Area and Kabete sites of Nairobi City, in low concentrations, these OCPs were not detected in any of the sites in this study. Aucha et al., (2017) used polyurethane foam (PUF) disks as passive samplers, which sampled both particulate-phase and gas-phase OCPs. However, such data could not be used to

evaluate the human health risks posed by OCPs. In the current study, only the gas-phase OCPs were sampled. The findings of this study are, therefore, useful in evaluation of the level of human exposure to bioavailable OCPs within Nairobi City, and hence in the assessment of human health risks posed by OCPs pollution in the city. Such information may, in part, shed light on the possible causes of the many cancer cases in Nairobi City, and Kenya at large.

4.4.1.2 Sampling Rates of OCPs in the SPMDs

Table 4.8 shows the PRC-based sampling rates of the OCPs identified and quantified in the air and surface waters. The data obtained showed that the concentration of the analytes in the SPMDs did not attain the equilibrium levels.

Table 4.8: Sampling rates of OCPs in surface waters $R_{s\,(Water)}$ and air $R_{s\,(Air)}$

OCP	$R_{s\,(Water)}(L\,day^{-1})$	$R_{s\,(Air)}\,(m^3\,day^{-1})$
Aldrin	0.156	0.236
p, p'-DDT	0.145	0.219
p, p'-DDD	0.152	0.230
p, p'-DDE	0.152	0.230
Chlordane	0.155	0.234
Dieldrin	0.129	0.194
Endrin	0.129	0.195
Heptachlor	0.151	0.228
γ - HCH	0.107	0.161
Means	0.142 ± 0.017	0.214 ± 0.025

The sampling rates obtained were used together with the concentrations of the analytes in the SPMDs to determine the concentration of each of the OCPs in air and surface water using Equation 12.

4.4.1.3 Method detection limits (MDL) for OCPs

The method detection limit (MDL) for each of the OCPs was defined as the mean of the concentration of the analyte in the blanks plus three standard deviations (Ozcan et al., 2008). The blank samples analyzed in the same manner as the real samples. In almost all the blanks no peaks of the target compounds were found. Thus, MDLs for each of the OCPs were estimated

from the instrument detection limits (IDLs) set at a signal-to-noise ratio (S/N) of three (Ozcan et al., 2008) using the compounds sampling rate (equation 12). Table 4.9 gives the IDLs and the estimated method detection limits (EMDLs) of the sampled OCPs.

Table 4.9: Method detection limits for OCPs

OCP	IDL ($ng\ L^{-1}$)	Estimated method detection limits (EMDLs)	
		Air ($pg\ m^{-3}$)	Water ($pg\ L^{-1}$)
Aldrin	0.090	13.56	20.46
p, p'-DDT	0.086	14.07	21.21
p, p'-DDD	0.086	13.42	20.23
p, p'-DDE	0.090	13.93	21.01
Chlordane	0.086	13.20	19.91
Dieldrin	0.090	16.48	24.85
Endrin	0.096	17.56	26.49
Heptachlor	0.086	13.52	20.39
γ - HCH	0.077	17.03	25.68

Limit of quantification (LOD) for the sampled OCPs was determined as three times the MDL.

4.4.1.4 Variation in the Levels of the Gas-phase and Dissolved OCPs in Nairobi City, Kenya

Table 4.10 shows the levels, distribution and fugacity ratios of bioavailable OCPs in the air in Nairobi City, and the waters of Nairobi River and its tributary, Ngong' River, traversing through the city, at the Dandora, Kibera, City Square, Industrial Area and Ngong' Forest sampling sites. The concentrations of dissolved OCPs were reported in $ng\ m^{-3}$ to enable the calculations of fugacity ratios of individual OCPs (Tidwell et al., 2015).

Table 4.10: Variation in the levels of the bioavailable fraction of OCPs in air (ng m^{-3}) and surface waters (ng m^{-3}) in the Nairobi City of Kenya

Organochlorine Pesticide	Environmental medium	Site					Mean (Environ. medium)
		Dandora	Kibera	City Square	Industrial Area	Ngong' Forest	
Aldrin	Air	0.108	0.138	bdl	0.180	bdl	0.085
	Surface Waters	159.333	95.333	bdl	212.000	bdl	93.333
	Mean (Site)	79.721	47.736	bdl	106.090	bdl	
	CV (%)			22.26			32.7
	LSD (p≤0.05)			19.857			12.443
	Interaction			12.350			
p, p'- DDT	Air	0.090	0.124	bdl	0.038	bdl	0.051
	Surface Waters	111.333	152.000	bdl	99.333	bdl	72.533
	Mean (Site)	55.712	76.062	bdl	49.686	bdl	
	CV (%)			29.1			39.4
	LSD (p≤0.05)			19.865			11.647
	Interaction			11.910			
p, p'- DDD	Air	0.097	0.197	0.027	0.088	bdl	0.082
	Surface Waters	210.333	183.000	29.000	150.333	bdl	114.533
	Mean (Site)	105.215	91.598	14.514	75.211	bdl	
	CV (%)			23.6			31.8
	LSD (p≤0.05)			25.485			14.835
	Interaction			15.550			
p, p'- DDE	Air	0.226	0.147	0.028	0.094	bdl	0.099
	Surface Waters	264.333	162.667	32.333	232.000	bdl	138.267
	Mean (Site)	132.280	81.407	16.181	116.047	bdl	
	CV (%)			22.1			34.8
	LSD (p≤0.05)			28.824			19.591
	Interactions			18.81			
Chlordane	Air	bdl	0.027	bdl	0.062	bdl	0.0180
	Surface Waters	66.333	bdl	bdl	bdl	bdl	13.267
	Mean (Site)	33.167	0.014	bdl	0.031	bdl	
	CV (%)			197.2			278.9
	LSD (p≤0.05)			24.658			15.073
	Interactions			15.120			
Dieldrin	Air	0.175	0.226	0.044	0.203	0.018	0.133
	Surface Waters	111.333	239.667	64.333	247.667	bdl	132.600
	Mean (Site)	55.754	119.947	32.189	123.935	0.009	
	CV (%)			11.6			17.0
	LSD (p≤0.05)			14.553			9.184
	Interactions			9.090			
Endrin	Air	0.125	0.120	0.092	0.116	bdl	0.091
	Surface Waters	99.000	70.000	bdl	80.333	bdl	49.867
	Mean (Site)	49.562	35.060	0.046	40.225	bdl	
	CV (%)			20.6			28.3
	LSD (p≤0.05)			9.691			5.761
	Interactions			5.854			
Heptachlor	Air	0.239	0.135	bdl	0.179	bdl	0.111
	Surface Waters	138.333	81.333	bdl	120.333	bdl	68.000

Organochlorine Pesticide	Environmental medium	Site					Mean (Environ. medium)
		Dandora	Kibera	City Square	Industrial Area	Ngong' Forest	
	Mean (Site)	69.286	40.734	bdl	60.256	bdl	
	CV (%)			23.3			35.2
	LSD (p≤0.05)			14.914			9.756
	Interactions			9.510			
γ - HCH	Air	0.128	0.093	0.116	0.206	bdl	0.108
	Surface Waters	115.000	246.667	107.333	200.333	bdl	133.867
	Mean (Site)	57.564	123.380	53.725	100.269	bdl	
	CV (%)			15.4			25.1
	LSD (p≤0.05)			19.391			13.683
	Interactions			12.950			
Total OCPs	Air	1.277	1.260	0.306	1.234	0.018	0.819
	Surface Waters	1297.667	1230.667	233.000	1391.000	bdl	830.467
	Mean (Site)	649.472	615.964	116.653	696.117	0.009	
	CV (%)			10.9			16.4
	LSD (p≤0.05)			85.455			55.513
	Interactions			54.270			

bdl = Below limit of detection

The levels of total gas-phase OCPs were in the order: Dandora > Industrial Area > Kibera > City Square > Ngong Forest. On the other hand, the levels of total dissolved phase OCPs in surface waters were in the order Industrial Area > Dandora > Kibera > City Square > Ngong Forest. The means for site concentrations of total OCPs in Industrial Area, Dandora and Kibera were not different (p≤0.05). However, each of the three means was different (p≤0.05) from those of City Square. This trend in the levels of OCPs was in agreement with Aucha et al., (2017) that Industrial area and Dandora in Nairobi City recorded the highest level of total OCPs in air in comparison to the other regions of the city. Globally, although a ban or restrictions on the use of most OCPs by the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention, 2008), has been in place for more than a decade, presence of these OCPs is still reported various environmental matrices.

In Kenya, DDT was banned for agricultural use in 1986, but the other OCPs remained in use till 2004 when a ban or restrictions were imposed against its use (Kenya NIP, 2007). However, some

OCPs were still in use for public health purposes by 2007 (Kenya NIP, 2007). Since OCPs persist in the environment, it is possible that OCPs from previous as well current use, if any, could still be available in the environment. This suggestion was supported by the findings of previous studies which reported presence of OCPs in soils, air and human milk samples in Kenya (Aucha et al., 2017; Sun et al., 2016; UNEP-GEF Project, 2012). Similarly across the world OCPs have been detected in air, dust, soil, sediment, surface waters and biota samples by several studies (Ssebugere et al., 2010; Ge et al., 2013; Qiao et al., 2010; Whitehead et al., 2015; Zhang et al., 2007; Odabasi et al., 2008: Jiang et al., 2009; Wang et al., 2012). The sources of these OCPs were attributed to anthropogenic activities coupled with environmental transport into surface waters and the atmosphere through industrial discharge, surface runoff from non-point sources, volatilization, atmospheric deposition, among others (Feng et al., 2011), which led to cross-contamination (Yang et al., 2013). The results of this study indicated that Industrial Area, Kibera and Dandora were possible point sources of bioavailable OCPs in Nairobi City of Kenya. However, the levels of OCPs obtained from Ngong' Forest were lower ($p \leq 0.05$) than those of the rest of the sampling sites. These results showed that Ngong' Forest could be described as pristine ($p \leq 0.05$) with reference to gas-phase or dissolved OCPs pollution when compared to the other parts of the city.

Aldrin was not detected in the City Square and Ngong Forest, however its concentration trend across the other three sampling sites was in the order: Industrial Area > Dandora > Kibera. Though the levels of aldrin in Industrial Area and Dandora were not significantly different ($p > 0.05$), the levels of aldrin in Industrial Area were higher ($p \leq 0.05$) than the rest of the sampling sites. These results indicated that Industrial Area and Dandora could be possible major sources of bioavailable aldrin in Nairobi City, with Kibera as the minor point source. Dandora

had the highest levels of p,p'-DDD, p,p'-DDE, chlordane, endrin and heptachlor in the order; Dandora > Industrial Area > Kibera > City Square, except for p,p'-DDD where the levels in City Square were higher than those in Kibera. However, none of the five OCPs was detected in both surface waters and air in Ngong Forest. From the results obtained at the Ngong' Forest sites and the predominant wind-direction in the city during the sampling period (Table 4.2), the OCPs were not transported into Nairobi City from outside (Figure 4.1). Consequently, there was no significant contamination of the city by any of the four pollutants from non-point sources, outside the city, through either inflow of contaminated surface water or atmospheric transport. The result further strengthened the possibility of existence of point sources of these contaminants within Nairobi City. This observation was in agreement with Grimalt et al., (2004) who suggested that environmental contamination with persistent organochlorine pesticides could be related to presence of point sources within the environment under investigation.

The Ngong Forest sampling sites were selected to provide information on the possible contamination of air and surface waters in Nairobi City with OCPs from point sources out of the city through atmospheric transport and down-stream flow. From the predominant hourly wind direction in Nairobi City (Table 4.2) coupled with the position of the Ngong Forest sampling sites, relative to the rest of the sampling sites (Figure 6), the results of the current study indicated that the contribution of environmental transport, to the levels of total bioavailable OCPs in the city, from external sources was not significant ($p \leq 0.05$). The findings pointed to the possibility of presence of point sources for OCPs pollution in air and surface waters within the city. To evaluate the strength of this suggestion, the current study determined the fugacity ratios of individual OCPs at the various sampling sites to elucidate the possible sources of these OCPs in the city.

4.4.1.5 Spatial Distribution and Sources of Bioavailable OCPs in Nairobi City, Kenya

The water-air fugacity ratios were calculated from concentrations of dissolved phase and gas-phase OCPs using their compound-specific temperature-corrected Henry's law value (Tidwell et al., 2015; Odabasi et al., 2008), corrected to 292.8 K (Equation 16) (Appendix 4). The water-air fugacity ratios obtained were used to assess the equilibrium state of individual OCP between that of air and surface waters (Equation 17). Table 16 shows the water-air fugacity ratio for all the OCPs quantified in the current study.

Table 4.11: Water-air fugacity ratio for the OCPs quantified

OCP	Water – air fugacity ratio (f_W/f_A)				
	Dandora	**Kibera**	**City Square**	**Industrial Area**	**Ngong' Forest**
Aldrin	2.511	1.176	nd	2.005	nd
p, p'- DDT	0.664	0.658	nd	1.404	nd
p, p'- DDD	0.361	0.155	0.179	0.290	nd
p, p'- DDE	1.022	0.967	1.009	2.157	nd
Chlordane	nd	nd	nd	nd	nd
Dieldrin	1.536	2.560	3.530	2.945	nd
Endrin	0.016	0.012	nd	0.014	nd
Heptachlor	0.554	0.577	nd	0.644	nd
γ - HCH	0.131	0.386	0.135	0.142	nd

nd = could not be determined

The fugacity ratio (f_W/f_A) for aldrin in each of the three sites was greater than 1, which showed net volatilization (Equation 6) of the OCP from surface waters into the atmosphere (Devi et al., 2011; Odabasi et al., 2008; Environment Canada, 2008; Wania et al., 1998; Mackay 1979). *p,p'*-DDE and dieldrin had $f_W/f_A > 1$ in Industrial Area and Dandora. Similarly $f_W/f_A > 1$ were determined for *p,p'*-DDT in Industrial Area, Dieldrin in the City Square and Kibera. This indicated strong contribution of contaminated surface waters to the levels gas-phase OCPs. *p,p'*-DDE had $f_W/f_A \approx 1$ in Kibera and City Square which indicated existence of equilibrium state between gas-phase and dissolved DDE in the two sites.

While the fugacity ratios of chlordane could not be determined due to non-detection of the analyte in some of the environmental matrices, endrin, heptachlor, *p,p'*-DDD and γ - HCH gave $f_W/f_A < 1$ in Dandora, Kibera and Industrial Area; indicating net contribution of gas-phase pollutants to the dissolved levels of the four pollutants in surface waters. The fugacity ratio of *p,p'*-DDT in Kibera and Dandora indicated net deposition of gas-phase *p,p'*-DDT into surface waters.. In the City Square the fugacity ratios of *p,p'*-DDD and γ – HCH showed net deposition of the two OCPs into the surface waters. The sources of these high levels of gas-phase OCPs in the atmosphere were attributed to volatilization of the OCPs from contaminated soils and surfaces into the atmosphere. This was in agreement with other recent studies which suggested that soils could be a re-emission source of OCPs and subsequently postulated a secondary distribution pattern for some OCPs based on volatilization of the OCPs from contaminated soils during warm seasons (Qu et al., 2019; Qu et al., 2016; Qu et al., 2017, Tao et al., 2008; Wang et al., 2011).Current use and/or re-volatilization of previously applied compounds from contaminated soils have been reported to play an important role in the atmospheric deposition of semi-volatile organic pollutants in tropical and subtropical mountain regions (Daly et al., 2007; Estellano et al., 2008). Nairobi is classified as having subtropical highland climate according to the Köppen-Geiger climate classification (Pidwirny, 2006). Further, Bailey, (2001) reported continued volatilization of HCB from contaminated soils, while Meire et al., (2016) noted that the microbiologic oxidation of the technical-grade endosulfan in soils, and its further re-emission to air was regarded as the main source endosulfan to the atmosphere in the mountain sites of Brazil. In Kenya, Sun et al., (2016) reported high levels of OCPs in soils samples collected from the areas neighbouring Nairobi City. The relatively higher levels of OCPs contamination could have arisen from historical and current applications of pesticides in tea plantations (Sun et al.,

2016). This study observed that this probable volatilization of these OCPs from contaminated soils and surfaces into the atmosphere raises the levels of gas-phase OCPs increase human exposure to bioavailable OCPs.

The greatest proportion of the all the industries in Nairobi City, and in Kenya, are situated in the Industrial Area of the city. The most likely source of the high levels of some OCPs in the surface waters and air in this region are the discharges and effluents from these industries. Similarly, the main sources of OCPs in Dandora are likely to be waste incineration, effluents and volatilization from the large dumpsite situated in the region. This suggestion is reinforced by the reported air-water fugacity ratios. These results show industrial effluents and run-off from the Dandora dumpsite in to the surface waters are major sources of atmospheric OCPs in the city. The results were in agreement with Feng et al., (2011) who reported that OCPs can be transported into rivers through run-off from non-point sources and industrial discharges. Kibera is the largest urban slum in Africa and in characterized by temporal housing and poor drainage. The fight to control termites, which destroy the wood used for construction, and mosquitoes, which breed on the stagnant waters necessitates use of pesticides. This makes Kibera a probable point source for some OCPs. This study could not identify any anthropogenic activities associated with emission of OCPs at the Ngong' Forest and City Square sampling sites.

In summary, from the air-water fugacity ratios of individual OCPs Industrial Area, Dandora and Kibera were major sources of gas-phase OCPs in the City. This is likely to pose health risks to the residence of Nairobi City. Moreover, though the waters of Nairobi River and its tributaries are not directly used for cooking, drinking or fishing, the contaminants released into these surface waters pose risks to the residents through volatilization.

4.4.1.6 Assessment of the Cancer Risks Posed by OCPs in Nairobi City, Kenya

Table 4.12 gives the incremental lifetime cancer risks (ILCR) values for both adults and children residing in various regions of Nairobi City of Kenya resulting from inhalation of outdoor atmospheric gas-phase OCPs.

Table 4.12: OCPs inhalation ILCR values for adults and children in various sites in Nairobi City

Sampling Site	Total OCP ($ng\ m^{-3}$)	Total OCP ($mg\text{-}m^{-3}$)	ILCR (Adult)	ILCR (Child)
Dandora	1.2770	1.2770×10^{-06}	1.6845×10^{-11}	3.9306×10^{-11}
Kibera	1.2600	1.2600×10^{-06}	1.6621×10^{-11}	3.8783×10^{-11}
City Square	0.3060	3.0600×10^{-07}	4.0366×10^{-12}	9.4187×10^{-12}
Industrial Area	1.2340	1.2340×10^{-06}	1.6278×10^{-11}	3.7983×10^{-11}
Ngong' Forest	0.0180	1.8000×10^{-08}	2.3745×10^{-13}	5.5404×10^{-13}

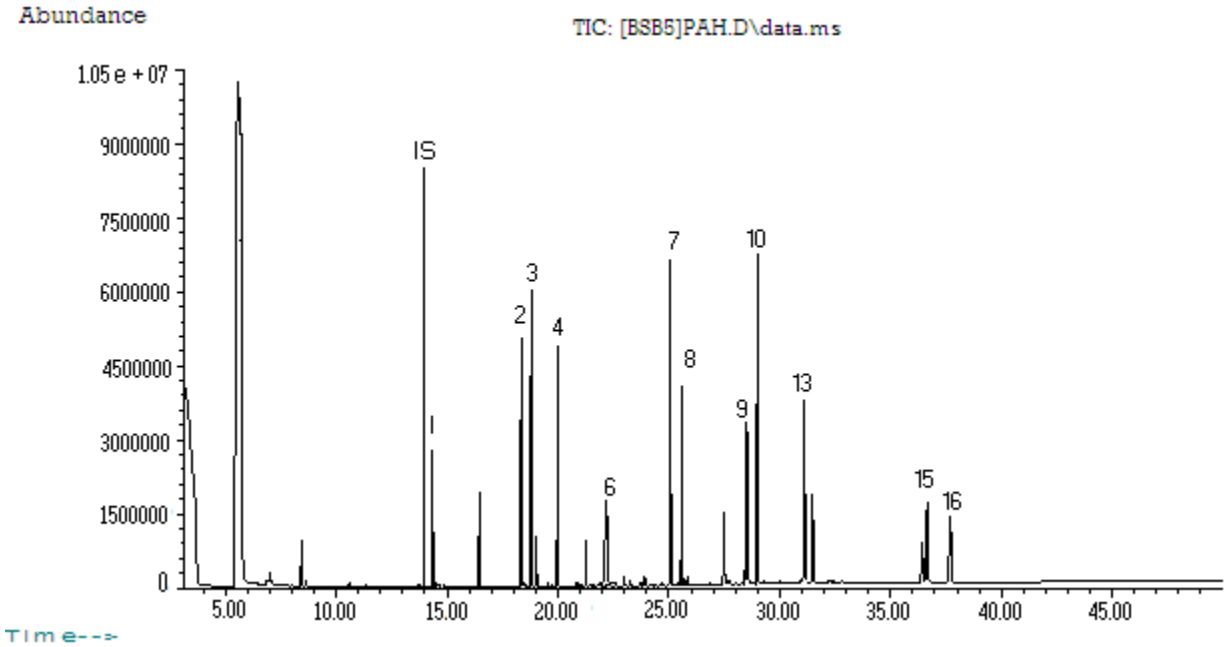
The lifetime cancer risks of the residence of Nairobi City resulting from outdoor inhalation of gas-phase OCPs in the atmosphere were in the order Dandora > Kibera > Industrial Area > City Square > Ngong Forest. However, the cancer risks in Dandora, Kibera and Industrial Area, for both adults and children were not significantly different, falling within a narrow range of 1.6278×10^{-11} - 1.6845×10^{-11} for an adult and 3.7983×10^{-11} - 3.9306×10^{-11} for a child. This meant that the residents in these three sub-regions were subjected to approximately the same levels of lifetime cancer risks from inhalation of OCPs. Conversely, the lifetime cancers risks in the three sites were about two and three magnitudes higher than those in the City Square and Ngong' Forest respectively.

The inhalation exposure risks in all the five sampling sites were lower than the acceptable risk range (10^{-6} - 10^{-4}) set by the USEPA (1990). It is concluded that exposure to environmental OCPs in Nairobi City via inhalation of outdoor air did not pose lifetime cancer risks to the residents of the city.

4.4.2 The Levels, Distribution and Possible Sources of the Bioavailable PAHs in Air and Surface Waters in the Nairobi City, Kenya

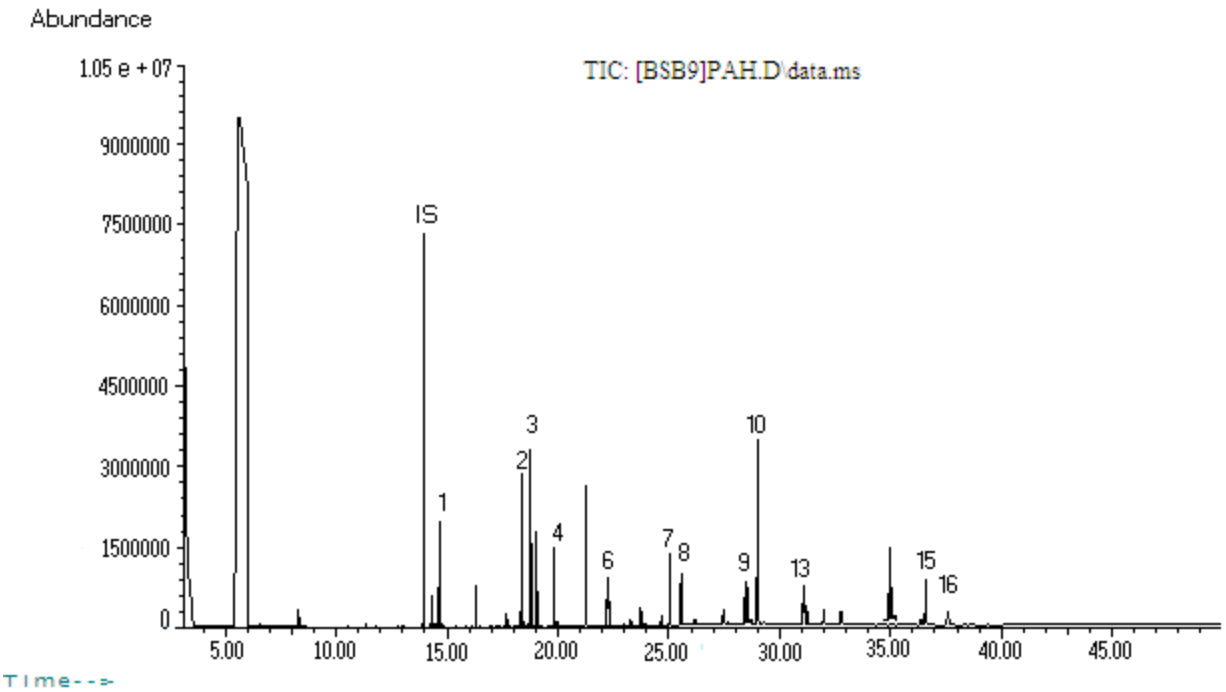
4.4.2.1 Identity of the Sampled PAHs

Fourteen out of the target 16 USEPA priority PAHs were identified in the air and surface waters samples collected using passive samplers in Nairobi City. The identification was achieved by comparing retention times of authentic standards with those of the samples (Figure 4.3 and Figure 4.4) and confirmed by mass spectra analysis using GC-MS instrument.



Key: IS = internal standard (dodecane); 1= Naphthalene; 2 = acenaphthylene; 3 = acenaphthene; 4 = fluorine; 5 = anthracene, 6 = phenanthrene; 7 = fluoranthene; 8 = pyrene; 9 = benzo(a)anthracene; 10 = chrysene; 11 = benzo(b)fluoranthene; 12 = benzo(k)fluoranthene; 13 = benzo(a)pyrene; 14 = indeno(1,2,3-c,d) anthracene; 15 = dibenzo(a,h)anthracene; 16 = benzo(ghi)perylene

Figure 4.3: Some of the GC chromatograms of SPMD samples from surface waters



Key: IS = internal standard (dodecane); 1= Naphthalene; 2 = acenaphthylene; 3 = acenaphthene; 4 = fluorine; 5 = anthracene, 6 = phenanthrene; 7 = fluoranthene; 8 = pyrene; 9 = benzo(a)anthracene; 10 = chrysene; 11 = benzo(b) fluoranthene; 12 = benzo(k)fluoranthene; 13 = benzo(a)pyrene; 14 = indeno(1,2,3-c,d) anthracene; 15 = dibenzo(a,h)anthracene; 16 = benzo(ghi)perylene

Figure 4.4: Some of the GC chromatograms of SPMD samples from air

Naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzo(ghi)perylene, benzo(a)anthracene, chrysene benzo(b)fluoranthene, benzo(a)pyrene and dibenzo(a,h)anthracene were detected from various sampling sites collected by passive sampling using triolein-filled SPMDs samplers (Table 4.13).

Table 4.13: Retention times of PAHs in GC analyses

PAH	Retention Time	Sampling sites	% Frequency
Naphthalene	14.450	Dandora, Kibera, Industrial Area, City Square, Ngong' Forest	86.67
Acenaphthylene	18.650	Dandora, Kibera, Industrial Area, City Square, Ngong' Forest	86.67
Acenaphthene	18.742	Dandora, Kibera, Industrial Area, City Square	83.33
Fluorene	19.974	Dandora, Kibera, Industrial Area, City Square	76.67
Anthracene	22.210	Dandora, Kibera, Industrial Area, City Square	80.00
Phenanthrene	22.214	Dandora, Kibera, Industrial Area, City Square	80.00
Fluoranthene	25.036	Dandora, Kibera, Industrial Area, City Square	80.00
Pyrene	25.551	Dandora, Kibera, Industrial Area, City Square	83.33
Benzo(a)anthracene	28.463	Dandora, Kibera, Industrial Area, City Square	30.00
Chrysene	29.000	Dandora, Kibera, Industrial Area, City Square	76.67
Benzo(b)fluoranthene	31.110	Dandora, City Square	13.33
Benzo(k)fluoranthene	-	ND	0.00
Benzo(a)pyrene	31.128	Dandora, Kibera, Industrial Area, City Square, Ngong' Forest	83.33
Indeno(1,2,3-c,d) anthracene	-	ND	0.00
Dibenzo(a,h)anthracene	36.660	Dandora, Kibera, Industrial Area, City Square	60.00
Benzo(ghi)perylene	27.520	Dandora, Kibera, Industrial Area, City Square	53.33

ND = not detected

Kibera, the largest slum dwelling in Africa, is home to more than 300,000 people who predominantly depend on biomass fuels for cooking and space warming under poorly ventilated conditions. All the 14 PAHs characterized in this study, except benzo(b)fluoranthene, had presence in Kibera. This was attributed to possible use of biomass fuel for cooking and space warming by the residents. This suggestion was agreement with Lisouza et al., (2011) who reported presence of high levels of PAHs in soot generated from burning biomass fuels indoors in the poorly ventilated rural households of Kenya. Similarly, all the fourteen PAH characterized were detected in Dandora where the most predominant anthropogenic activity was municipal waste disposal and incineration, and in Industrial area which is home to more than 40% of all the industries in Kenya. Other studies have also reported presence of PAHs in surface waters: In

Brazil, da Costa Lima et al., (2015) reported presence of PAHs in Piracicaba River and Doce River within the municipality of Ipatinga, Minas Gerais, in southeastern Brazil, where the main economic activity is industry. Presence of all the sixteen USEPA priority PAHs were also reported in surface waters of Eleme and Okrika Creeks in Nigeria (Nwineewii & Abiye, 2015). In Kenya, recent studies reported presence of thirteen of the 16 USEPA priority PAHs in the surface waters of Ngong River (Erick et al., (2016), and in the water and sediment of Kisumu City Bay of Winam Gulf, Lake Victoria (Kwach et al., 2009). These results indicate that contaminated surface waters could be sources of bioavailable PAHs in urban environments. From the literature surveyed, data on the atmospheric levels of PAHs in Nairobi City, in particular, and in Kenya, in general, is not documented. This study reports presence of gas-phase PAHs in air, in Nairobi City of Kenya. These results showed that the residents of Nairobi City are exposed to bioavailable PAHs through inhalation.

4.4.2.2 Sampling Rates of PAHs in the SPMDs

Table 4.14 shows the PRC-based sampling rates of the PAHs identified and quantified in the air and surface waters.

Table 4.14: Sampling rates of PAHs in surface waters $R_{s\,(Water)}$ and air $R_{s\,(Air)}$

PAH	$R_{s\,(Water)}(L\,day^{-1})$	$R_{s\,(Air)}\ (m^3\,day^{-1})$
Naphthalene	0.096	0.145
Acenaphthylene	0.116	0.174
Acenaphthene	0.119	0.180
Fluorene	0.123	0.186
Anthracene	0.127	0.192
Phenanthrene	0.125	0.189
Fluoranthene	0.141	0.213
Pyrene	0.143	0.215
Benzo(a)anthracene	0.151	0.228
Chrysene	0.147	0.222
Benzo(b)fluoranthene	NS	NS
Benzo(k)fluoranthene	NS	NS
Benzo(a)pyrene	0.155	0.234
Indeno(1,2,3-c,d)anthracene	NS	NS
Dibenzo(a,h)anthracene	0.156	0.236
Benzo(ghi)perylene	0.157	0.237
Means	0.135±0.019	0.204±0.029

NS = not sampled

The sampling rates obtained were used together with the concentrations of the analytes in the SPMDs to determine the concentration of each of the PAHs in air and surface water using Equation 12.

4.4.2.3 Method Detection Limits (MDL) for PAHs

The mean of the concentration of each PAH in the blanks plus three standard deviations was taken as the method detection limit (MDL) the analyte (Ozcan et al., 2008). In almost all the blanks analysed, no peaks of the target PAHs were found. Consequently, MDLs for each of the PAHs were estimated from the instrument detection limits (IDLs) set at a signal-to-noise ratio (S/N) of three (Ozcan et al., 2008) using the individual compounds sampling rate (equation 13). Table 4.15 gives the IDLs and the estimated method detection limits (EMDLs) of the sampled PAHs.

Table 4.15: Method detection limits for PAHs

PAH	IDL ($ng\ L^{-1}$)	Estimated method detection limits (MDL)	
		Air ($pg\ m^{-3}$)	Water ($pg\ L^{-1}$)
Naphthalene	0.070	17.31	26.11
Acenaphthylene	0.077	15.74	23.74
Acenaphthene	0.083	16.51	24.90
Fluorene	0.090	17.18	25.92
Anthracene	0.080	14.87	22.43
Phenanthrene	0.086	16.31	24.60
Fluoranthene	0.080	13.44	20.26
Pyrene	0.080	13.27	20.02
Benzo(a)anthracene	0.083	13.02	19.64
Chrysene	0.090	14.38	21.69
Benzo(b)fluoranthene	0.083	13.16	19.84
Benzo(k)fluoranthene	0.086	13.27	20.01
Benzo(a)pyrene	0.083	12.68	19.12
Indeno(1,2,3-c,d)anthracene	0.080	12.02	18.12
Dibenzo(a,h)anthracene	0.080	12.11	18.26
Benzo(ghi)perylene	0.083	12.54	18.91

The limit of quantification (LOD) of the sampled PAHs was determined as three times the MDL.

4.4.2.4 Variation in the Levels of the Gas-phase and Dissolved PAHs in Nairobi City, Kenya

The concentrations of dissolved PAHs were reported in $ng\ m^{-3}$ to enable the calculations of fugacity ratios of individual PAHs (Tidwell et al., 2015). Table 4.16 shows the levels and distribution of bioavailable PAHs in the air and the surface waters of Nairobi City of Kenya.

Table 4.16: Variation in the levels of the bioavailable fraction of PAHs in air (ng m^{-3}) and surface waters (ng m^{-3}) in the Nairobi City of Kenya

PAH	Environmental medium	Sampling Site					Mean (Environmental medium)
		Dandora	Kibera	City square	Industrial Area	Ngong' Forest	
Naphthalene	Air	0.124	0.134	0.241	0.159	0.029	0.137
	Surface Waters	91.667	51.667	103.000	124.000	bdl	74.067
	Mean (Site)	45.895	25.900	51.621	62.079	0.015	
	CV (%)	4.1					5.3
	LSD (p≤0.05)	2.850					1.599
	Interactions	1.670					
Acenaphthylene	Air	0.102	0.106	0.189	0.146	0.014	0.111
	Surface Waters	82.000	51.333	88.333	151.333	bdl	74.600
	Mean (Site)	41.051	25.720	44.261	75.740	0.007	
	CV (%)	4.8					7.3
	LSD (p≤0.05)	3.402					2.211
	Interactions	2.161					
Acenaphthene	Air	0.103	0.114	0.158	0.140	0.032	0.109
	Surface Waters	61.667	33.667	73.667	144.333	bdl	62.667
	Mean (Site)	30.885	16.890	36.912	72.237	0.016	
	CV (%)	22.0					30.6
	LSD (p≤0.05)	12.977					7.816
	Interactions	7.896					
Fluorene	Air	0.098	0.084	0.163	0.088	bdl	0.087
	Surf-.ace Waters	66.000	29.333	76.333	89.667	bdl	52.267
	Mean (Site)	33.049	14.709	38.248	44.877	bdl	
	CV (%)	22.9					31.9
	LSD (p≤0.05)	11.270					6.783
	Interactions	6.854					
Phenanthrene	Air	0.072	0.071	0.108	0.083	bdl	0.067
	Surface Waters	51.000	42.333	50.000	88.667	bdl	46.400
	Mean (Site)	25.536	21.202	25.054	44.375	bdl	
	CV (%)	5.6					7.8
	LSD (p≤0.05)	2.450					1.469
	Interactions	1.487					
Anthracene	Air	0.090	0.076	0.137	0.119	bdl	0.084
	Surface Waters	53.333	46.333	63.667	104.000	bdl	53.467
	Mean (Site)	26.712	23.205	31.902	52.059	bdl	
	CV (%)	5.8					7.5
	LSD (p≤0.05)	2.940					1.629
	Interactions	1.712					
Fluoranthene	Air	0.051	0.078	0.129	0.089	bdl	0.069
	Surface Waters	48.000	51.667	60.333	92.000	bdl	50.400
	Mean (Site)	24.023	25.872	30.231	46.044	bdl	
	CV (%)	6.5					8.7
	LSD (p≤0.05)	3.070					1.793
	Interactions	1.837					
Pyrene	Air	0.106	0.083	0.206	0.115	0.015	0.105
	Surface Waters	61.333	45.667	96.333	92.667	bdl	59.200
	Mean (Site)	30.720	22.875	48.270	46.391	0.008	
	CV (%)	4.4					6.4
	LSD (p≤0.05)	2.430					1.548
	Interactions	1.526					
Benzo(a)	Air	0.061	bdl	0.016	0.062	bdl	0.058

PAH	Environmental medium	Sampling Site					Mean (Environmental medium)
		Dandora	Kibera	City square	Industrial Area	Ngong' Forest	
anthracene	Surface Waters	bdl	bdl	bdl	58.000	bdl	11.600
	Mean (Site)	0.030	bdl	0.008	29.031	bdl	
	CV (%)	193.2					273.3
	LSD (p≤0.05)	21.153					12.926
	Interactions	12.970					
Chrysene	Air	0.103	0.066	0.095	0.083	bdl	0.069
	Surface Waters	48.000	43.333	47.333	60.667	bdl	39.867
	Mean (Site)	24.052	21.700	23.714	30.375	bdl	
	CV (%)	59.2					83.5
	LSD (p≤0.05)	22.253					13.571
	Interaction	13.63					
Benzo(a) pyrene	Air	0.065	0.052	0.100	0.067	bdl	0.068
	Surface Waters	14.000	bdl	46.333	bdl	bdl	12.067
	Mean (Site)	7.032	0.029	23.217	0.034	bdl	
	CV (%)	5.4					7.4
	LSD (p≤0.05)	2.751					1.647
	Interactions	6.341					
Dibenzo(a,h) anthracene	Air	0.052	0.056	0.049	0.066	bdl	0.045
	Surface Waters	31.667	28.667	bdl	32.667	bdl	18.600
	Mean (Site)	15.859	14.362	0.025	16.367	bdl	
	CV (%)	113.7					158.3
	LSD (p≤0.05)	19.965					12.010
	Interactions	12.14					
Benzo (ghi) perylene	Air	0.092	0.089	0.122	0.139	0.014	0.091
	Surface Waters	60.333	49.000	56.667	106.333	bdl	54.467
	Mean (Site)	30.213	24.545	28.394	53.236	0.007	
	CV (%)	91.6					126.9
	LSD (p≤0.05)	10.456					6.261
	Interactions	1.669					
Total PAH	Air	1.125	1.015	1.773	1.354	0.104	1.074
	Surface Waters	668.333	473.000	762.667	1144.000	bdl	609.667
	Mean (Site)	334.752	237.008	382.197	572.844	0.052	
	CV (%)	7.0					9.3
	LSD (p≤0.05)	40.172					23.170
	Interactions	23.88					

The total PAHs in Nairobi City ranged from 0.104 ng m^{-3} of air in Ngong Forest to 1.773 ng m^{-3} of air in the City Square in the order City Square > Industrial Area > Dandora > Kibera > Ngong' Forest. The lower molecular weight PAHs (MW≤ 128.2) accounted for the highest proportion of the total gas-phase PAHs in all the sampling sites: City Square (87.37%), Industrial Area (84.05%), Dandora (79.94%), Kibera (82.86%), and Ngong' Forest (100.00%). In surface water the total PAHs ranged from non-detection in the Ngong Forest to 1144.000 ng m^{-3} in the

Industrial Area, in the order: Industrial Area > City Square > Dandora > Kibera > Ngong Forest. The lower molecular weight PAHs (MW≤ 128.2) accounted for the highest proportion of the total dissolved PAHs in all the sampling sites: Industrial Area (91.84%), City Square (87.63%), Dandora (86.00%) and Kibera (84.78%).

The levels of naphthalene, acenaphthylene, acenaphthene and fluoranthene in the air were in the order: City Square > Industrial Area > Kibera > Dandora > Ngong' Forest. Whereas the means for site of the levels of naphthalene, acenaphthene and fluoranthene were significantly different ($p \leq 0.05$) across all the sampling sites, the means of acenaphthylene in Dandora were not significantly different from those in the City Square. The levels of fluorene, phenanthrene, anthracene, pyrene, benzo (ghi) perylene, chrysene and benzo (a) pyrene were in the order: Industrial Area > City Square > Dandora > Kibera > Ngong' Forest. While the levels of pyrene, anthracene and benzo (ghi) perylene were significantly different ($p \leq 0.05$) across all the sampling sites, those of phenanthrene in the City Square and in Dandora, and those of chrysene across all the sampling sites, except the Ngong' Forest, were not different. The levels of fluorene in the City Square, Dandora and Industrial Area were not significantly different ($p \leq 0.05$). Benzo (a) pyrene, which is used as a biomarker of PAH pollution, was detected and quantified across all the sampling sites, except in Ngong' Forest. The levels of benzo (a) pyrene in the City Square were significantly higher ($p \leq 0.05$) than those in all the other sampling sites.

While benzo (a) anthracene was detected in the Industrial Area, City Square and Dandora in the order: Industrial Area > City Square > Dandora, it was not detected in Kibera and Ngong' Forest. The levels of benzo (a) anthracene in the Industrial Area were higher ($p \leq 0.05$) than those in all the other sampling sites. The levels of dibenzo (a, h) anthracene in the air in City Square was significantly lower ($p \leq 0.05$) than those in the Industrial Area, Dandora and Kibera. The levels of

the PAHs in Ngong' Forest ranged from non-detection to 0.032 ng m^{-3}(acenaphthylene) in the air. The levels were significantly lower ($p \leq 0.05$) than those in the other sampling regions. The results indicated that Ngong' Forest was significantly pristine with regard to PAHs pollution than the other regions of the city.

4.4.2.5 Source Apportionment of the Sampled PAHs in Nairobi City, Kenya

The classification of the sources of the sampled environmental PAHs in Nairobi City was based on the criteria used in previous of studies: Studies have reported that, benzo (a) anthracene / (benzo (a) anthracene + chrysene) ratios >0.35 indicated combustion sources, those between 0.20 and 0.35 indicated either petrogenic or pyrogenic sources, while ratios <0.20 indicate petrogenic sources (Yunker et al., 2002; Shen et al., 2013; Stogiannidis &Lane, 2015). Other studies have reported that an anthracene / (anthracene + phenanthrene) ratio < 0.1 indicated petrogenic sources while a ratio >0.1 was attributed to pyrogenic sources (Yunker et al., 2002; Katsoyiannis et al., 2011; Shen et al., 2013). Other studies have reported that a benzo (a) pyrene / (benzo (a) pyrene + benzo (ghi) perylene) ratio could be used to distinguish between traffic sources (>0.38) and non-traffic contributions (<0.38) to environmental PAHs (Katsoyiannis et al., 2011; Birks et al., 2017). Table 4.17 gives the results of three ratios determined for each of the sampling sites: Benzo (a) anthracene / (benzo (a) anthracene + chrysene), anthracene / (anthracene + phenanthrene) and benzo (a) pyrene / (benzo (a) pyrene + benzo (ghi) perylene).

Table 4.17: Source characterization of the sampled PAHs from isomer ratios

Sampling Region	Environmental Media	ANT/(ANT + PHE) (**< 0.1**)	BaA/(BaA + CHR) (**0.2 – 0.35**)	BaP/(BaP + BghiP) (**< 0.38**)
Dandora	Air	0.5556 (Pyrogenic)	0.3910 (Pyrogenic)	0.4171 (Traffic)
	Surface Waters	0.5112 (Pyrogenic)	0	0.6032 (Traffic)
Kibera	Air	0.3932 (Pyrogenic)	0.3196 (pyrogenic/petrogenic)	0.3729 (Non-traffic)
	Surface Waters	0.3835 (pyrogenic)	0	1.0000 (Traffic)
City Square	Air	0.5592 (Pyrogenic)	0.1345 - Petrogenic	0.5470 (Traffic)
	Surface Waters	0.5601 (Pyrogenic)	0	0.5125 (Traffic)
Industrial Area	Air	0.5891 (Pyrogenic)	0.4276 Pyrogenic	0.6674 (Traffic)
	Surface Waters	0.5398 (Pyrogenic)	0.4888 Pyrogenic	1.0000 (Traffic)
Ngong' Forest	Air	ND	ND	1.000 (Traffic)
	Surface Waters	ND	ND	ND

ANT/(ANT+PHE) - anthracene/(anthracene + phenanthrene); BaA/(BaA + CHR) - Benzo (a) anthracene / (benzo(a)anthracene + chrysene); BaP/(BaP + BghiP) - benzo(a)pyrene / (benzo(a)pyrene + benzo(ghi)perylene); ND – Not detected

From the benzo (a) anthracene / (benzo (a) anthracene + chrysene) ratios, the sources of PAHs in Dandora and Industrial Area were classified as predominantly pyrogenic, while the sources of PAHs in the City Square were predominantly classified as petrogenic. However, the sources of PAHs in Kibera were classified as both pyrogenic and petrogenic. Since dissolved benzo (a) anthracene was not detected in the surface waters in Dandora, Kibera, and City square, the sources of the PAHs in these waters could not be classified using this ratio. However, the sources of the PAHs in the surface waters in Industrial Area were classified as pyrogenic.

Based on the anthracene/(anthracene + phenanthrene), the sources of PAHs in air and surface waters in Dandora, Kibera, City Square and in the Industrial Area were classified as being predominantly pyrogenic. In contradiction, based on the benzo (a) pyrene / (benzo (a) pyrene + benzo (ghi) perylene) ratio, the sources of PAHs in all the sites were classified as traffic sources, except in the air in Kibera which was classified as non-traffic and surface waters in Ngong' Forest where both benzo (a) pyrene and benzo (ghi) perylene were below detection limit. These results show that the sources of free-phase PAHs in Nairobi City may not strictly follow one pattern; the classifications revealed mixed sources of the PAHs in the various sampling sites which included both petrogenic and pyrogenic sources. This was reinforced by the observation that anthracene, which is used as a marker for biomass burning and diesel exhaust (Chuesaard et al., 2014; Feilberg et al., 2001) was found in all the sampling sites, except in Ngong forest. City Square and Industrial Area had the highest levels of anthracene. These results were consistent with previous studies that reported mixed sources of environmental PAHs in the industrial Northern African coastal city of Bizerte in Tunisia (Barhoumi et al., 2018) and in the coastal region off Macao, China (Mai et al., 2003). In contaminated areas the main sources of environmental reported to be combustion and petroleum sources which give specific PAHs isomer ratios (Yunker et al., 2002), At lower concentrations of environmental PAHs, multiple sources at times make interpretations based on a single ratio misleading (Yunker et al., 2002). Consequently, it was concluded that strict source apportionment for the sampled environmental PAHs at each of the sampling sites in Nairobi City was not possible.

The most predominant anthropogenic activity associated with PAH emission in Dandora was massive waste incineration at the Dandora Dumpsite. Volatilization of the PAHs from the contaminated dumpsite soils during dredging, and vehicular emissions resulting from public

transport and heavy diesel trucks transporting the waste to the dumpsite also contributed to the environmental PAHs load in Dandora. . The most predominant anthropogenic activity in the City Square associated with PAHs emissions were vehicular emissions. Other sources of PAHs in the City Square were burning of old car tyres, and burning of biomass waste from wood workshops. Leakage of sewage into surface waters and surface run-off during storms were also sources of PAHs in the in the City Square. Though use of biomass fuels was the most predominant activity associated with PAHs emission in Kibera, vehicular emissions from both public and private transport, leakage of sewage into surface waters and waste incineration in open air were other sources of PAHs in the area. In the Industrial Area, effluents and emissions from the Industries, as well as emissions from heavy diesel engine trucks used to transport raw materials into and finished products out of the industries were the most predominant activities associated with PAHs emission into the environment. Vehicular emissions from public transport, oil spillage, wood workshops, and small-scale waste incineration, also contributed to the environmental PAHs levels in the Industrial Area.

The surface waters of Nairobi River and its tributary, Ngong' River gets progressively heavily coloured as they pass through Kibera, Industrial Area, City Square and Dandora due to discharge of sewage and industrial effluents directly flow into the river waters, and surface run-off during storms. The discharge of industrial effluents and leakage of sewage into the waters of Nairobi River and its tributaries could be major sources of PAHs in the surface waters in Nairobi City. Surface runoffs during storms could also be playing an important role in altering the levels of these PAHs in the surface waters of Nairobi City: This suggestion was in agreement with Qi et al., (2013) who reported extremely high levels of dissolved total 16 priority USEPA PAHs, in the range of 193 - 1790 ng/L were reported in the surface waters of Wenyu River in Beijing, China.

The results were attributed to discharge of effluents from wastewater treatment plants (WWTP) and wastewater from open sewers that directly into the river system (Qi et al., 2013). The study also reported the levels of total 16 priority USEPA PAHs in the WWTP effluents in the range 245 - 404 ng/L and 431 - 2860 ng/L in the wastewater from the small sewers, even though the flow from each sewer was small (Qi et al., 2013). The conclusion was also in agreement with McCarthy, (2003) and LBNL, (2004), who reported that urban runoff, a common non-point source, accounted for an estimated 36% of the total PAH input into Rhode Island's Narragansett Bay in USA. Similarly, storm water analysis in coastal Massachusetts in USA revealed that fluoranthene, phenanthrene, pyrene and chrysene were the most pervasive PAHs (McCarthy, 2003).

4.4.2.6 Spatial Variations in the Levels PAHs in Nairobi City, Kenya

The water-air fugacity ratios were calculated from concentrations of dissolved phase and gas-phase PAHs using their compound-specific temperature-corrected Henry's law value (Tidwell et al., 2015; Odabasi et al., 2008), corrected to 292.8 K (Equation 16) (Appendix 5). The water-air fugacity ratios obtained were used to assess the equilibrium state of individual PAHs between that air and surface waters (Equation 17). Table 23 shows the water-air fugacity ratio for all the PAHs quantified.

The fugacity ratio (f_W/f_A) of naphthalene, acenaphthylene, acenaphthene, fluorene, and chrysene were >1 in all the sampling sites, except in Ngong' Forest where it could not be determined due to non-detection. While benzo (a) pyrene gave $f_W/f_A > 1$ in Dandora and City Square, its fugacity ratios in Industrial Area and Kibera could not be determined due to non-detection of the pollutant in the surface waters at the two sites.

Table 4.18: Water-air fugacity ratio (f_W/f_A) for the quantified PAHs

PAH	Water – air fugacity ratio (f_W/f_A)				
	Dandora	Kibera	City square	Industrial Area	Ngong' Forest
Naphthalene	13.046	6.804	7.542	13.763	nd
Acenaphthylene	2.774	1.671	1.613	3.576	nd
Acenaphthene	2.990	1.475	2.329	5.149	nd
Fluorene	2.178	1.129	1.515	3.295	nd
Phenanthrene	0.943	0.794	0.617	1.423	nd
Anthracene	1.206	1.062	0.959	2.039	nd
Fluoranthene	0.400	0.281	0.199	0.439	nd
Pyrene	0.218	0.207	0.176	0.303	nd
Benzo(a)anthracene	nd	nd	nd	0.223	nd
Chrysene	1.835	2.585	1.962	2.878	nd
Benzo(a)pyrene	6.311	nd	13.576	nd	nd
Dibenzo(a,h)anthracene	0.0004	0.0003	nd	0.0003	nd
Benzo (ghi) perylene	0.012	0.010	0.009	0.015	nd

nd = could not be determined

These results were similar to those reported in previous studies (Devi et al., 2011; Odabasi et al., 2008; Environment Canada, 2008; Wania et al., 1998; Mackay 1979). These results indicated net volatilization (Equation 6) of the PAHs from the surface waters into the atmosphere at the sites. The observations showed that the contaminated waters of Nairobi River and its tributaries contribute to the levels of gas-phase PAHs in Nairobi City.

The f_W/f_A values of fluoranthene, pyrene, benzo (ghi) fluoranthene and benzo (a,h) anthracene were <1in all the sampling sites, except the Ngong' Forest sites. This indicated net deposition of the PAHs from the atmosphere into surface waters (Devi et al., 2011; Odabasi et al., 2008; Environment Canada, 2008; Wania et al., 1998; Mackay 1979). Also, benzo (a) anthracene which was only detected in Industrial Area gave $f_W/f_A < 1$which indicated net deposition of the pollutant into the surface waters in the sampling site. However, while the fugacity ratio of phenanthrene was <1 in Dandora, Kibera and City Square, indicative of net deposition from the atmosphere into the surface waters, the ratio in the Industrial Area was >1 which showed net

volatilisation of the pollutant from the surface waters into the atmosphere. These results indicated that volatilization of dissolved PAHs and deposition of atmospheric PAHs into the surface waters played an important role in the spatial distribution of PAHs in Nairobi City. Consequently, it was concluded that contaminated surface waters, even if they were not used directly for domestic and recreational purposes, contributed to human exposure to bioavailable PAHs through inhalation.

4.4.2.7 Assessment of the Cancer Risks posed by PAHs in Nairobi City, Kenya

There is no evidence on the direct use of the surface waters of Nairobi River and its tributaries by the residents of Nairobi City for drinking, cooking, and other domestic uses, as well as use of the waters for recreational activities such as swimming. The inhalation of gas-phase PAHs may therefore be considered as the only human exposure route to the sampled PAHs. Consequently, the assessment of cancer risks posed by PAHs in Nairobi City was based inhalation of atmospheric PAHs. The PAHs with concentrations below the detection limits, in the air, were assigned a concentration of zero. The concentration were converted into Benzo (a) pyrene toxicity equivalent (TEQ) values using their specific toxic equivalent factors (TEF). The determined TEQs were referred to as BaP_{eq} concentration (Zero) values. Table 4.19 gives the calculated BaP_{eq} concentrations (ng m^{-3}) of gas-phase PAHs in Nairobi City of Kenya.

Table 4.19: BaP_{eq} concentrations (ng m^{-3}) of the sampled PAHs in Nairobi City

PAH	TEF	BaP_{eq} concentrations (ng m^{-3})				
		Dandora	Kibera	City Square	Industrial Area	Ngong' Forest
Naphthalene	0.001	1.24×10^{-4}	1.34×10^{-4}	2.41×10^{-4}	1.59×10^{-4}	2.90×10^{-5}
Acenaphthylene	0.001	1.02×10^{-4}	1.06×10^{-4}	1.89×10^{-4}	1.46×10^{-4}	1.40×10^{-5}
Acenaphthene	0.001	1.03×10^{-4}	1.14×10^{-4}	1.58×10^{-4}	1.40×10^{-4}	3.20×10^{-5}
Fluorene	0.001	9.80 x 10-^{5}	8.40×10^{-5}	1.63×10^{-4}	8.80×10^{-5}	0.00
Anthracene	0.01	9.00×10^{-4}	7.60×10^{-4}	1.37×10^{-3}	1.19×10^{-3}	0.00
Phenanthrene	0.001	7.20×10^{-5}	7.10×10^{-5}	1.08×10^{-4}	8.30×10^{-5}	0.00
Fluoranthene	0.001	5.10×10^{-5}	7.80×10^{-5}	1.29×10^{-4}	8.90×10^{-5}	0.00
Pyrene	0.001	1.06×10^{-4}	8.30×10^{-5}	2.06×10^{-4}	1.15×10^{-4}	1.50×10^{-5}
Benzo(a)anthracene	0.1	6.10×10^{-3}	0.00	1.60×10^{-3}	6.20×10^{-3}	0.00
Chrysene	0.01	1.03×10^{-3}	6.60×10^{-4}	9.50×10^{-4}	8.30×10^{-4}	0.00
Benzo(b)fluoranthene	0.1	0.00	0.00	0.00	0.00	0.00
Benzo(k)fluoranthene	0.1	0.00	0.00	0.00	0.00	0.00
Benzo(a)pyrene	1.0	6.50×10^{-2}	5.20×10^{-2}	1.00×10^{-1}	6.70×10^{-2}	0.00
Indeno(1,2,3-cd)pyrene	0.1	0.00	0.00	0.00	0.00	0.00
Dibenzo(a,h)anthracene	1.0	5.20×10^{-2}	5.60×10^{-2}	4.90×10^{-2}	6.60×10^{-2}	0.00
Benzo(ghi)perylene	0.01	9.20×10^{-4}	8.90×10^{-4}	1.22×10^{-3}	1.39×10^{-3}	1.40×10^{-4}
$\sum$ **BaP_{eq} Conc (Zero)**		**0.12661**	**0.11098**	**0.15533**	**0.14343**	**0.00023**

Human exposures to OCPs occur mainly through three pathways: inhalation, dermal contact and consumption (Toan, 2015). The cancer risks posed by human exposure to environmental PAHs were based on inhalation. The incremental lifetime cancer risk (ILCR) of both adults and children due to exposure to PAHs in the city were calculated using the USEPA model (Equation 21) (USEPA, 1989). Table 4.20 gives the incremental lifetime cancer risks (ILCR) posed by atmospheric PAHs to adults and children due to outdoor inhalation of gas-phase PAHs in Nairobi City of Kenya

Table 4.20: PAHs inhalation ILCR values for adults and children at various sites in Nairobi City

Sampling Site	$\sum BaP_{eq}$ Conc. (ng m^{-3})	$\sum BaP_{eq}$ Conc. (mg m^{-3})	ILCR (Adult)	ILCR (Child)
Dandora	0.12661	1.2661×10^{-07}	1.2976×10^{-08}	3.0277×10^{-08}
Kibera	0.11098	1.1098×10^{-07}	1.1374×10^{-08}	2.6540×10^{-08}
City Square	0.15533	1.5533×10^{-07}	1.5920×10^{-08}	3.7147×10^{-08}
Industrial Area	0.14343	1.4343×10^{-07}	1.4700×10^{-08}	3.4300×10^{-08}
Ngong' Forest	0.00023	2.3000×10^{-10}	2.3573×10^{-11}	5.5003×10^{-11}

The lifetime cancer risks of the residence of Nairobi City resulting from outdoor inhalation of atmospheric gas-phase PAHs ranged from 2.3573 x 10^{-11}in Ngong' Forest to 1.5920 x 10^{-08}in the City Square for adults. For a child, the ILCR values ranged from 5.5003 x 10^{-11} in Ngong Forest to 3.7147 x 10^{-08} in the City Square. The risk values determined were in the order City Square > Industrial Area > Dandora > Kibera > Ngong Forest. However, the cancer risks in City Square, Industrial Area, Dandora and Kibera, for both adults and children fell within a narrow range of 1.1374 x 10^{-08} - 1.5920 x $10^{-08}$for an adult and 2.6540 x 10^{-08} - 3.7147 x 10^{-08} for a child. This indicated that the residents in these three sub-regions were subjected to approximately the same levels of lifetime cancer risks from inhalation of outdoor atmospheric PAHs. Conversely, the lifetime cancers risks in the four sites were about three magnitudes higher than those in Ngong' Forest. The outdoor PAHs inhalation exposure risks in all the five sampling sites were lower than the acceptable risk range (10^{-6} - 10^{-4}) set by the USEPA (1990). This study concluded that exposure to outdoor atmospheric gas-phase PAHs in Nairobi City via inhalation of outdoor air did not pose significant lifetime cancer risks to the residents of the city.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

1) Modification of active sampling, to include graded filters, yielded data on the levels of bioavailable OCPs and PAHs in air in surface waters in Nairobi City. The pollutants' levels from active sampling were lower ($p \leq 0.05$) than levels from passive sampling; indicating possible underestimation of their actual environmental levels in active sampling. However, the data on PAHs and OCPs collected using the two sampling methods were reproducible.

2) The levels of total gas-phase OCPs in Nairobi City ranged between 0.018ng m^{-3}- 1.277 ng m^{-3} in the order: Dandora > Industrial Area > Kibera > City Square > Ngong Forest. While the total dissolved phase OCPs in Nairobi River ranged from non-detection - 1297.667 ng m^{-3} in the order: Industrial Area > Dandora > Kibera > City Square > Ngong Forest. Industrial Area, Dandora and Kibera were the major sources of gas-phase OCPs in the Nairobi City. Though the waters of Nairobi River and its tributaries are not directly used for cooking, drinking or fishing, the contaminants released into the river contributed to atmospheric OCPs pollution in the city through volatilization.

3) The total PAHs in Nairobi City ranged between 0.104 ng m^{-3} - 1.773 ng m^{-3} in air in the order: City Square > Industrial Area > Dandora > Kibera > Ngong Forest, while in surface waters, the total dissolved PAHs ranged from non-detection - 1144.000 ng m^{-3} in the order: Industrial Area > City Square > Dandora > Kibera > Ngong Forest. City Square, Industrial Area, Dandora, and Kibera were the main sources of PAHs in Nairobi City. However, the results revealed mixed emission sources of the PAHs in the city, which included both petrogenic and pyrogenic sources. Though the waters of Nairobi River and its tributaries are not directly

used by the residents for cooking, drinking or fishing, the contaminants released into the river contributed to atmospheric PAHs pollution in the city through volatilization.

4) The incremental lifetime cancer risk (ILCR) values of Nairobi City resulting from outdoor inhalation of either gas-phase OCPs or gas-phase PAHs in the atmosphere in all the five sampling sites were below the acceptable risk range (10^{-6} - 10^{-4}) set by the USEPA.

5.2 Conclusions

1) Modification of active sampling to include graded filters resolved uncertainty regarding the bioavailability of the sampled OCPs and PAHs. However, the pollutants' levels from active sampling were lower ($p \leq 0.05$) than levels from passive sampling; indicating possible underestimation of their actual environmental levels in active sampling.

2) Industrial Area, Dandora and Kibera are point sources of environmental bioavailable OCPs in Nairobi City. The results show that waste management, disposal of industrial effluents and domestic activities are major sources of OCPs in air and surface waters in Nairobi City, Kenya

3) City Square, Industrial Area, Dandora, and Kibera are point sources of environmental bioavailable PAHs in Nairobi City. The results show that waste management, disposal of industrial effluents, traffic emissions and domestic activities are major sources of OCPs and PAHs in air and surface waters in Nairobi City, Kenya.

4) Exposure to atmospheric OCPs and PAHs in Nairobi City via inhalation of outdoor air did not solely pose significant lifetime cancer risks to the residents. However, this study could not rule out possible contribution of the environmental bioavailable OCPs and PAHs to the cancers through synergetic effects.

5.3 Recommendations

1) Passive sampling should be adopted in environmental monitoring of persistent organic pollutants in Kenya. However, in the absence of SPMDs, integration of graded filters in active sampling could provide an insight into the environmental levels of bioavailable POPs.
2) The Pest Control Products Board (PCPB), in conjunction with the National Environmental Management Authority (NEMA), should intensify market monitoring programmes to ensure that none of the OCPs banned under the Stockholm Convention is used as formulation for the pesticides currently in the Kenyan market.
3) Environmental friendly waste management methods, industrial effluents disposal and domestic activities ought to be adopted in Nairobi City to minimize pollution of air and surface waters with POPs. Release of industrial effluents and untreated sewage into the waters of Nairobi River and its tributaries should be stopped. Road network in Nairobi City should be improved to reduce environmental pollution resulting from traffic jams.
4) There is need for legislation focusing on reducing emission and/or release of POPs into the environment to protect people from the pollutants in Nairobi City, followed by regular monitoring and risk assessment of the environmental and workplace bioavailable POPs in the city. This would track the impact of remediation and mitigation measures taken by both the National government and Nairobi County government to reduce POPs in the city.

5.4 Suggestions for Future Studies

1) Potential loss of the sampled OCPs and PAHs using active sampling integrated with graded filters due to adsorption of the analytes on the filters should be investigated.
2) The cancer risks posed by other classes of persistent organic pollutants, such as polychlorinated biphenyls and dioxins, to the residents of Nairobi City should be determined.

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APPENDICES

Appendix 1: Gas Chromatograph Instrument Parameters For PAH Analysis

INSTRUMENT CONTROL PARAMETERS: Icipe MSD2

C:\MassHunter\GCMS\1\methods\DCM-HP5-MS Prog-35-280 temp-55min.M
Tue Jul 31 12:02:40 2018

Control Information

Sample Inlet : GC
Injection Source: GC ALS
Injection Location: Front
Mass Spectrometer: Enabled

No Sample Prep method has been assigned to this method.

GC

Oven	
Equilibration Time	0 min
Max Temperature	290 °C
Slow Fan	Disabled
Oven Program	On
Oven Program	35 °C for 5 min
Oven#1	then 10 °C/min to 280 °C for 5.5 min
Oven#2	then 50 °C/min to 285 °C for 19.9 min
Run Time	55 min
Cryo	Off

ALS

Front Injector	
Syringe Size	10 µL
Syringe	A Syringe has not been selected.
Injection Volume	1 µL
Solvent A Washes (PreInj)	3
Solvent A Washes (PostInj)	3
Solvent A Volume	8 µL
Solvent B Washes (PreInj)	3
Solvent B Washes (PostInj)	3
Solvent B Volume	8 µL
Sample Washes	0
Sample Wash Volume	8 µL
Sample Pumps	4
Dwell Time (PreInj)	0 min
Dwell Time (PostInj)	0 min
Solvent Wash Draw Speed	300 µL/min

Solvent Wash Dispense Speed 3000 µL/min
Sample Wash Draw Speed 300 µL/min
Sample Wash Dispense Speed 3000 µL/min
Injection Dispense Speed 6000 µL/min
Viscosity Delay 0 sec
Sample Depth Disabled
Injection Type Standard
L1 Airgap 0.2 µL
Sample Overlap
Mode Sample overlap is not enabled
ALS Errors Pause for user interaction

Front SS Inlet He
Mode Splitless
Heater On 270 °C
Pressure On 8.8271 psi
Total Flow On 7.2 mL/min
Septum Purge Flow On 3 mL/min
Gas Saver Off
Purge Flow to Split Vent 3 mL/min at 0.8 min

Thermal Aux 2 (MSD Transfer Line)
Heater On 270 °C

Column
Column #1
Agilent 19091S-433UI: 001
HP-5ms Ultra Inert
0 °C—325 °C (350 °C): 30 m x 250 µm x 0.25 µm
Column lock Unlocked
In Front SS Inlet He
Out MSD
(Initial) 35 °C
Pressure 8.8271 psi
Flow 1.2 mL/min
Average Velocity 39.621 cm/sec
Holdup Time 1.262 min
Flow Program On
Flow Program 1.2 mL/min for 0 min
Run Time 55 min

Signals
Signal #1: Test Plot
Description Test Plot
Details
Save Off

Data Rate 50 Hz
Signal #2: Test Plot
Description Test Plot
Details
Save Off
Data Rate 50 Hz

Signal #3: Test Plot
Description Test Plot
Details
Save Off
Data Rate 50 Hz

Signal #4: Test Plot
Description Test Plot
Details
Save Off
Data Rate 50 Hz
MS Information
-- -----------

General Information
------- -----------
Acquisistion Mode : Scan
Solvent Delay (minutes) : 6.00
Tune file : C:\gcms\MSexe\ATUNE.U
EM Setting mode Gain : 1.000000

Normal or Fast Scanning : Normal Scanning
Trace Ion Detection : Off
Run Time (if MS only) : 10 minutes

[Scan Parameters]
Start Time : 6.00
Low Mass : 38.00
High Mass : 550.00
Threshold : 150
A/D Samples : 4

[MSZones]
MS Source : 230 ^{0}C maximum 250 ^{0}C
MS Quad : 150 ^{0}C maximum 200 ^{0}C

Timed Events
----- ------
Number Events= 0

END OF MS ACQUISTION PARAMETERS

TUNE PARAMETERS for SN: US1326M203

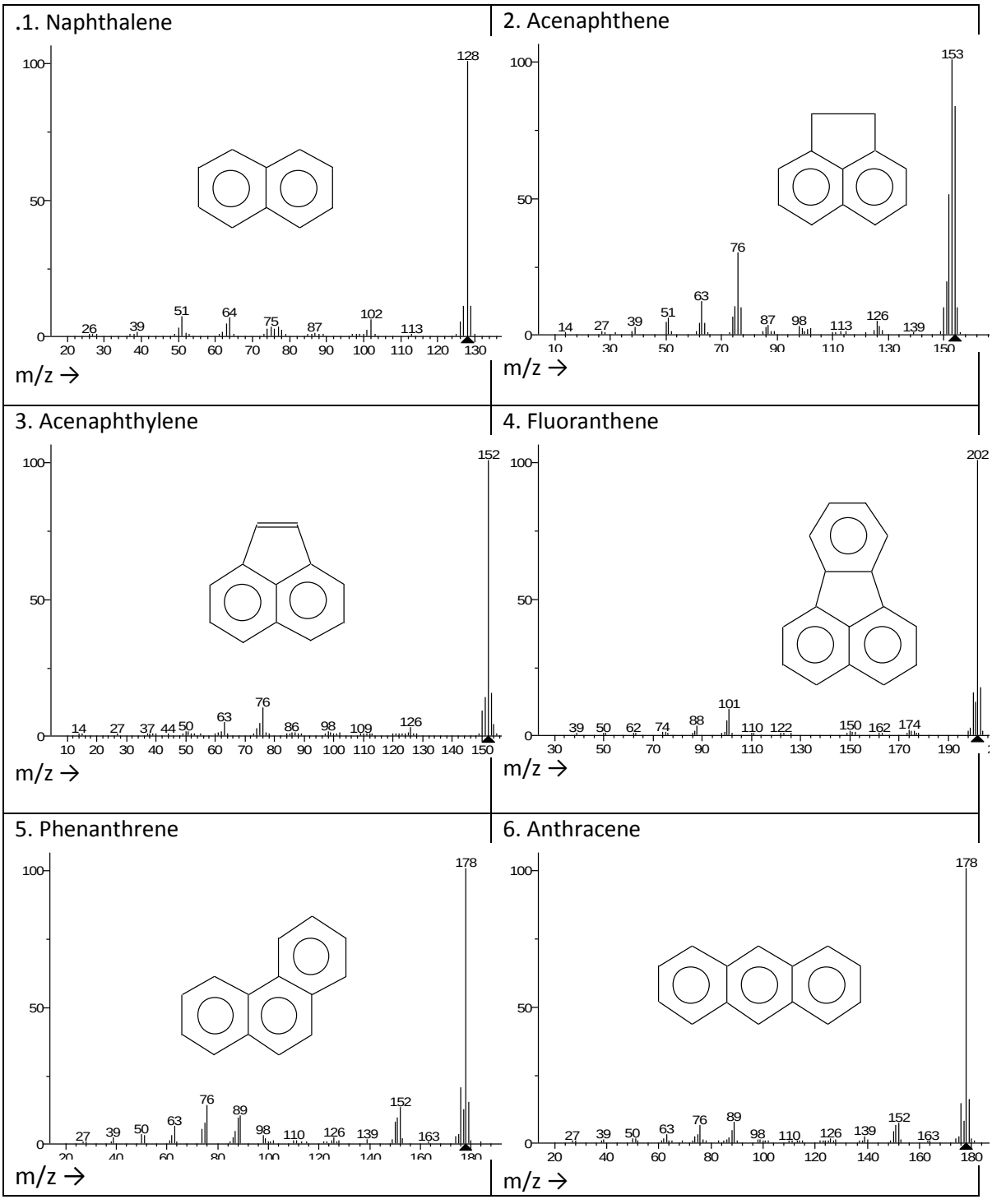
Trace Ion Detection is OFF.

EMISSION : 34.593
ENERGY : 70.007
REPELLER : 34.899
IONFOCUS : 90.301
ENTRANCE_LE : 15.136
EMVOLTS : 1747.116
Actual EMV : 1435.1
GAIN FACTOR : 1.00
AMUGAIN : 487.000
AMUOFFSET : 123.313
FILAMENT : 1.000
DCPOLARITY : 0.000
ENTLENSOFFS : 14.605
MASSGAIN : -1045.000
MASSOFFSET : -34.000

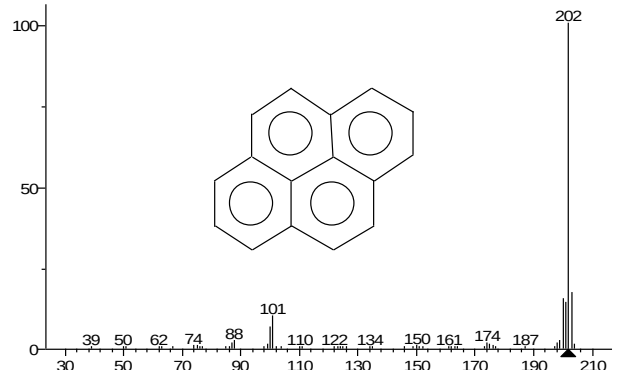
END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

Appendix 2: Mass spectra for PAHs identified in the samples

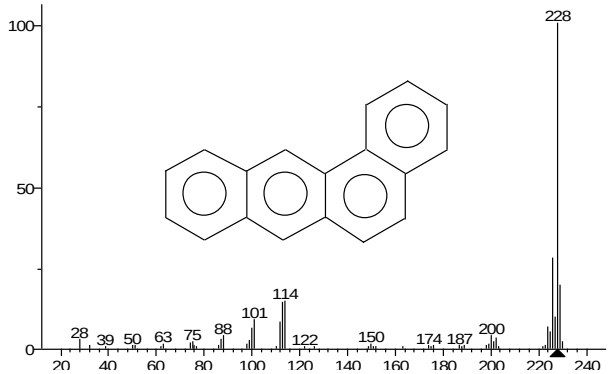


7. Pyrene



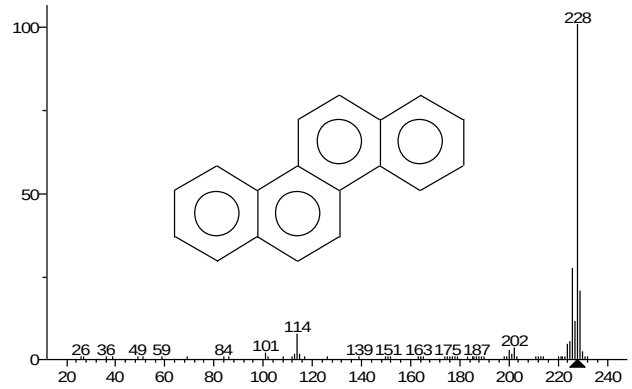
m/z →

8. Benzo(a)anthracene



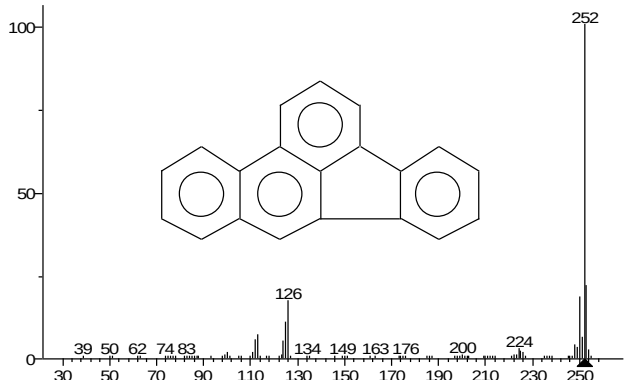
m/z →

9. Chrysene



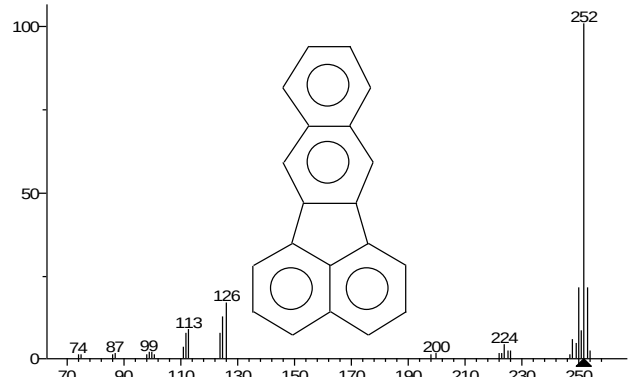
m/z →

10. Benzo(b)fluoranthene



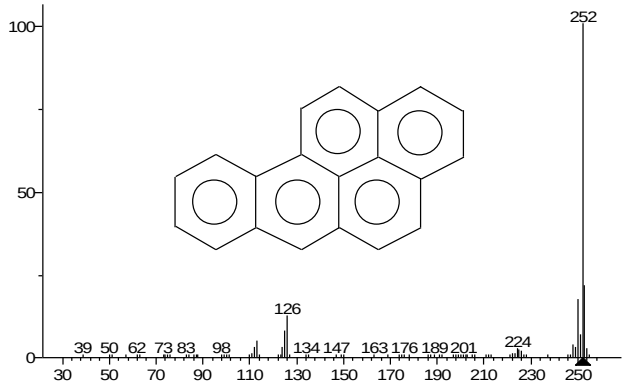
m/z →

11. Benzo(k)fluoranthene



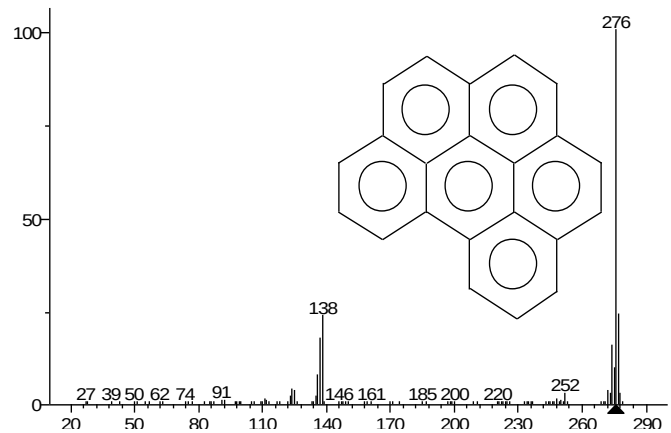
m/z →

12. Benzo(a)pyrene



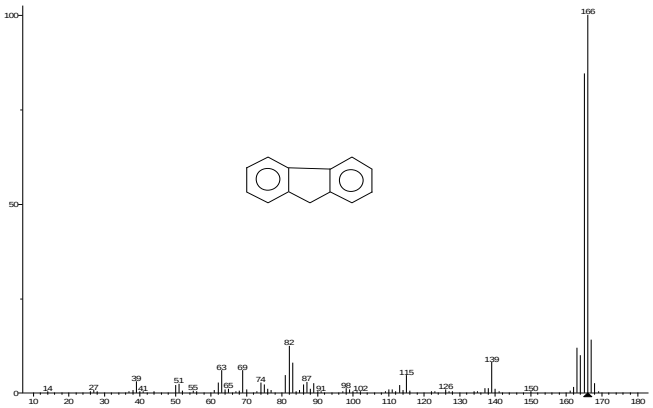
m/z →

14. Benzo(g,h,i)perylene



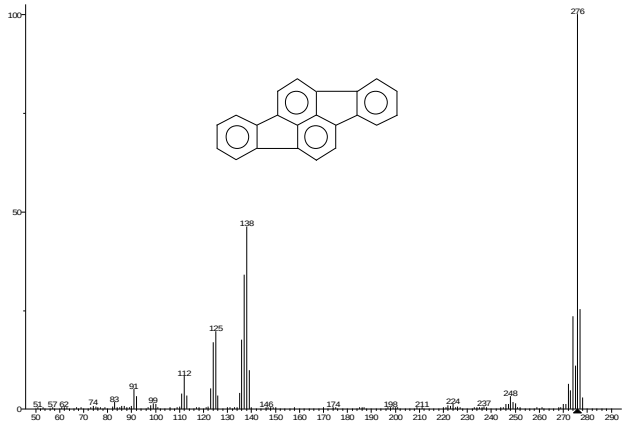
m/z →

15. Fluorene



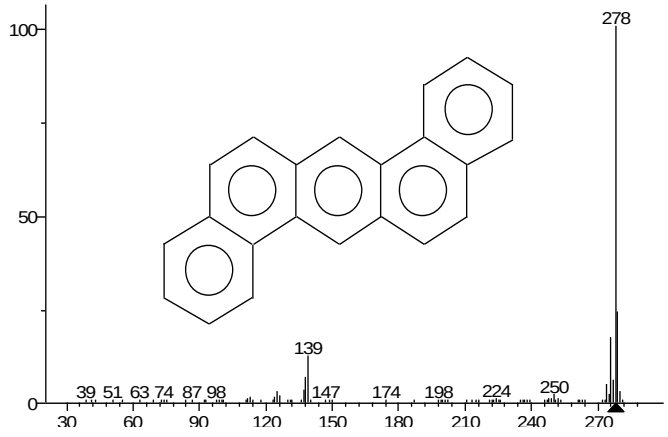
m/z →

16. Indeno[1,2,3-cd]fluoranthene



m/z →

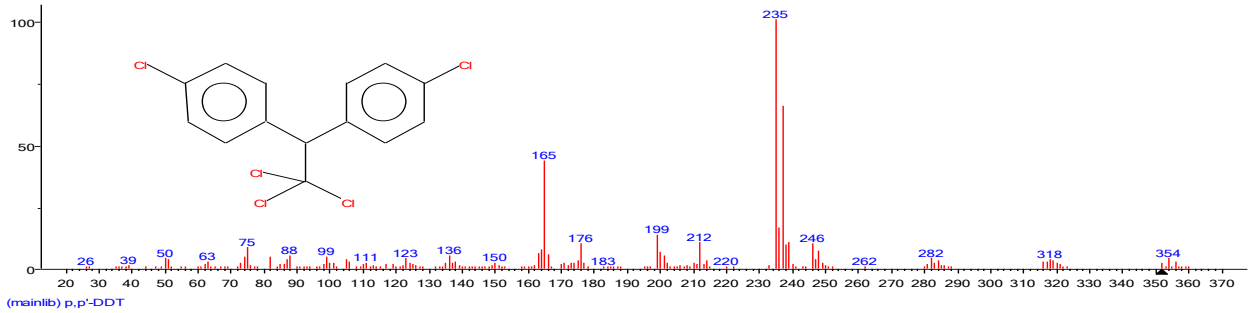
13. Didenzo(a,h)anthracene



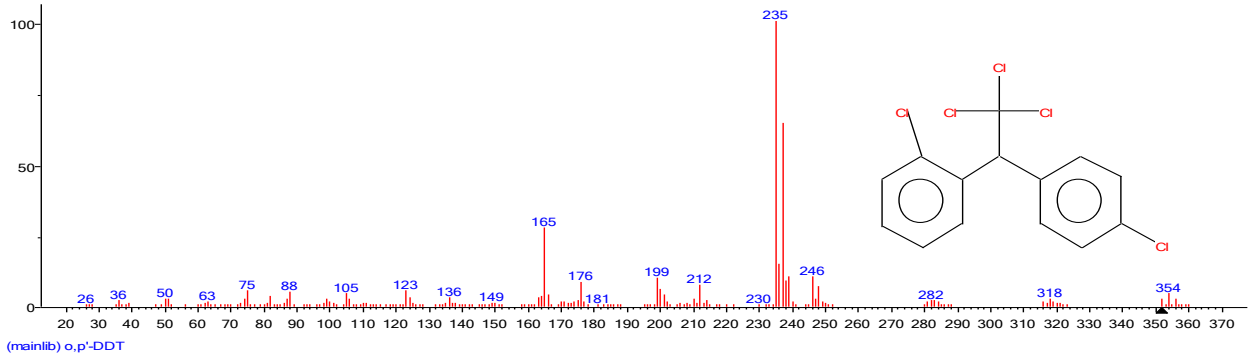
m/z →

Appendix 3: Mass spectra of some of the sampled OCPs

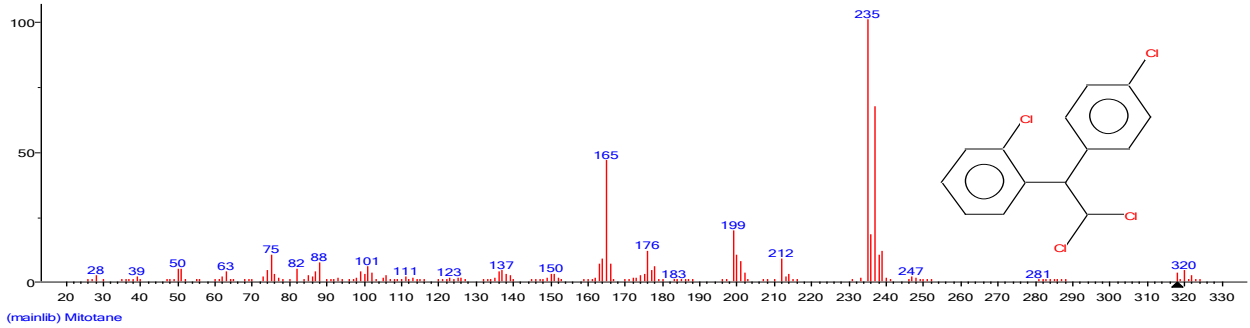
1. p.p'-DDT



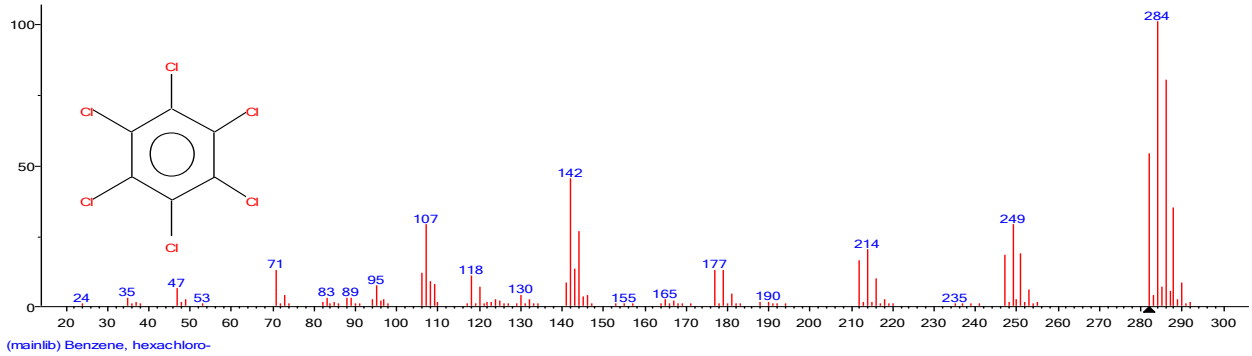
2. o,p'-DDT



3. o, p'-DDD



4. HCB



Appendix 4: Fugacity ratio calculations for sampled OCPs

OCP	Site	Cw ng/m3	Cw mol/m3	fw = CwH	CA ng/m3	CA mol/m3	R	T	fA = CA(RT)	fw/fA
Aldrin	Dandora	159.333	0.4366484	0.0017859	0.108	0.000295971	8.21E-05	292.8	7.1111E-06	251.1416
	Kibera	95.333	0.26125788	0.0010685	0.138	0.000378186	8.21E-05	292.8	9.0864E-06	117.5982
	City Square	0	0	0	0	0	8.21E-05	292.8	0	
	Industrial Area	212.000	0.58098109	0.0023762	0.18	0.000493286	8.21E-05	292.8	1.18518E-05	200.4933
	Ngong Forest	0	0	0	0	0	8.21E-05	292.8	0	
Alachlor	Dandora	22.333			0.089					
	Kibera	0			0.052					
	City Square	0			0					
	Industrial Area	48.667			0.067					
	Ngong Forest	0			0					
DDT	Dandora	111.333	0.318558471	4.1094E-06	0.09	0.000257518	8.21E-05	292.8	6.1872E-06	0.664178
	Kibera	152	0.434919454	5.61046E-06	0.124	0.000354803	8.21E-05	292.8	8.52459E-06	0.65815
	City Square	0	0	0	0	0	8.21E-05	292.8	0	
	Industrial Area	99.333	0.284222725	3.66647E-06	0.038	0.00010873	8.21E-05	292.8	2.61238E-06	1.403502
	Ngong Forest	0	0	0	0					
DDD	Dandora	210.333	0.656777518	2.62711E-06	0.097	0.000302888	8.21E-05	292.8	7.27728E-06	0.361001
	Kibera	183	0.571428571	2.28571E-06	0.197	0.000615144	8.21E-05	292.8	1.47796E-05	0.154653
	City Square	29	0.090554254	3.62217E-07	0.027	8.43091E-05	8.21E-05	292.8	2.02564E-06	0.178816
	Industrial Area	153.333	0.478791569	1.91517E-06	0.088	0.000274785	8.21E-05	292.8	6.60207E-06	0.290086
	Ngong Forest	0	0	0	0	0				
DDE	Dandora	264.333	0.831157438	1.74543E-05	0.226	0.000710625	8.21E-05	292.8	1.70737E-05	1.022293
	Kibera	162.667	0.511483193	1.07411E-05	0.147	0.000462221	8.21E-05	292.8	1.11054E-05	0.967196
	City Square	32.333	0.101666509	2.135E-06	0.028	8.8042E-05	8.21E-05	292.8	2.11532E-06	1.009301
	Industrial Area	232	0.729490929	1.53193E-05	0.094	0.00029557	8.21E-05	292.8	7.10144E-06	2.157211
	Ngong Forest	0	0	0	0	0	8.21E-05	292.8	0	
Chlordane	Dandora	66.333	0.161874664	7.76998E-06	0	0	8.21E-05	292.8	0	
	Kibera	0	0	0	0.027	6.5889E-05	8.21E-05	292.8	1.58307E-06	0
	City Square	0	0	0	0	0	8.21E-05	292.8	0	
	Industrial Area	0	0	0	0.062	0.000151301	8.21E-05	292.8	3.63519E-06	0
	Ngong Forest	0	0	0	0	0	8.21E-05	292.8	0	
Dieldrin	Dandora	111.333	0.292273968	1.69519E-05	0.175	0.000459414	8.21E-05	292.8	1.1038E-05	1.535773
	Kibera	239.667	0.629179355	3.64924E-05	0.226	0.0005933	8.21E-05	292.8	1.42548E-05	2.560007
	City Square	64.333	0.168888481	9.79553E-06	0.044	0.00011551	8.21E-05	292.8	2.77527E-06	3.529575
	Industrial Area	247.667	0.65018114	3.77105E-05	0.203	0.00053292	8.21E-05	292.8	1.28041E-05	2.945191
	Ngong Forest	0	0	0	0.018	4.7254E-05	8.21E-05	292.8	1.13534E-06	0
Endrin	Dandora	99	0.259897091	1.29949E-07	0.125	0.000328153	8.21E-05	292.8	7.8843E-06	0.016482

	Kibera	70	0.18376562	9.18828E-08	0.12	0.000315027	8.21E-05	292.8	7.56892E-06	0.012139
	City Square	0	0	0	0.092	0.000241521	8.21E-05	292.8	5.80284E-06	0
	Industrial Area	80.333	0.210892051	1.05446E-07	0.116	0.000304526	8.21E-05	292.8	7.31663E-06	0.014412
	Ngong Forest	0	0	0	0	0	8.21E-05	292.8	0	
Heptachlor	Dandora	138.333	0.370548055	0.000852261	0.239	0.000640201	8.21E-05	292.8	1.53817E-05	55.40756
	Kibera	81.333	0.217864031	0.000501087	0.135	0.00036162	8.21E-05	292.8	8.68839E-06	57.67321
	City Square	0	0	0	0	0	8.21E-05	292.8	0	
	Industrial Area	120.333	0.322332048	0.000741364	0.179	0.000479481	8.21E-05	292.8	1.15202E-05	64.3536
	Ngong Forest	0	0	0	0	0	8.21E-05	292.8	0	
Gamma-HCH	Dandora	115	0.395420005	1.38397E-06	0.128	0.00044012	8.21E-05	292.8	1.05744E-05	0.130879
	Kibera	246.667	0.848148403	2.96852E-06	0.093	0.000319774	8.21E-05	292.8	7.68299E-06	0.386375
	City Square	107.333	0.369057525	1.2917E-06	0.116	0.000398858	8.21E-05	292.8	9.58309E-06	0.13479
	Industrial Area	200.333	0.688831964	2.41091E-06	0.206	0.000708318	8.21E-05	292.8	1.70182E-05	0.141666
	Ngong Forest	0	0	0	0	0	8.21E-05	292.8	0	

Appendix 5: Fugacity ratio calculations for sampled PAHs

PAH	Site	Cw ng/m3	Cw mol/m3	fw = CwH	CA ng/m3	CA mol/m3	R	T	fA = CA(RT)	fw/fA
Naphthalene	Dandora	91.667	0.715031201	0.000303173	0.124	0.000967239	0.000082057	292.8	2.32392E-05	13.0458
	Kibera	51.667	0.403018721	0.00017088	0.134	0.001045242	0.000082057	292.8	2.51133E-05	6.8044
	City Square	103.000	0.803432137	0.000340655	0.241	0.001879875	0.000082057	292.8	4.51664E-05	7.5422
	Industrial Area	124.000	0.96723869	0.000410109	0.159	0.00124025	0.000082057	292.8	2.97986E-05	13.7627
	Ngong Forest	0	0	0	0.029	0.000226209	0.000082057	292.8	5.43496E-06	0.0000
Acenaphthylene	Dandora	82.000	0.538764783	4.46636E-05	0.102	0.000670171	0.000082057	292.8	1.61017E-05	2.7738
	Kibera	51.333	0.337273325	2.796E-05	0.106	0.000696452	0.000082057	292.8	1.67332E-05	1.6709
	City Square	88.333	0.580374507	4.8113E-05	0.189	0.001241787	0.000082057	292.8	2.98355E-05	1.6126
	Industrial Area	151.333	0.994303548	8.24278E-05	0.146	0.000959264	0.000082057	292.8	2.30476E-05	3.5764
	Ngong Forest	0	0	0	0.014	9.19842E-05	0.000082057	292.8	2.21004E-06	0.0000
Acenaphthene	Dandora	61.667	0.399915694	4.79899E-05	0.103	0.000667964	0.000082057	292.8	1.60487E-05	2.9903
	Kibera	33.667	0.218333333	0.0000262	0.114	0.0007393	0.000082057	292.8	1.77626E-05	1.4750
	City Square	73.667	0.477736706	5.73284E-05	0.158	0.001024643	0.000082057	292.8	2.46184E-05	2.3287
	Industrial Area	144.333	0.936011673	0.000112321	0.14	0.000907912	0.000082057	292.8	2.18138E-05	5.1491
	Ngong Forest	0	0	0	0.032	0.000207523	0.000082057	292.8	4.986E-06	0.0000
Fluorene	Dandora	66.000	0.397111913	3.08556E-05	0.098	0.000589651	0.000082057	292.8	1.41671E-05	2.1780
	Kibera	29.333	0.176492178	1.37134E-05	0.084	0.000505415	0.000082057	292.8	1.21433E-05	1.1293
	City Square	76.333	0.459283995	3.56864E-05	0.163	0.000980746	0.000082057	292.8	2.35637E-05	1.5145
	Industrial Area	89.667	0.539512635	4.19201E-05	0.088	0.000529483	0.000082057	292.8	1.27215E-05	3.2952
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	
Phenanthrene	Dandora	51.000	0.286195286	9.15825E-06	0.072	0.00040404	0.000082057	292.8	9.70759E-06	0.9434
	Kibera	42.333	0.237558923	7.60189E-06	0.071	0.000398429	0.000082057	292.8	9.57276E-06	0.7941
	City Square	50.000	0.280583614	8.97868E-06	0.108	0.000606061	0.000082057	292.8	1.45614E-05	0.6166
	Industrial Area	88.667	0.497570146	1.59222E-05	0.083	0.000465769	0.000082057	292.8	1.11907E-05	1.4228
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	
Anthracene	Dandora	53.333	0.299287318	1.17021E-05	0.09	0.00040404	0.000082057	292.8	9.70759E-06	1.2055
	Kibera	46.333	0.260005612	1.01662E-05	0.076	0.000398429	0.000082057	292.8	9.57276E-06	1.0620
	City Square	63.667	0.357278339	1.39696E-05	0.137	0.000606061	0.000082057	292.8	1.45614E-05	0.9594
	Industrial Area	104.000	0.583613917	2.28193E-05	0.119	0.000465769	0.000082057	292.8	1.11907E-05	2.0391
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	
Fluoranthene	Dandora	48.000	0.237271379	2.42017E-06	0.051	0.000252101	0.000082057	292.8	6.05705E-06	0.3996
	Kibera	51.667	0.255397924	2.60506E-06	0.078	0.000385566	0.000082057	292.8	9.26372E-06	0.2812
	City Square	60.333	0.298235294	0.000003042	0.129	0.000637667	0.000082057	292.8	1.53208E-05	0.1986
	Industrial Area	92.000	0.454770143	4.63866E-06	0.089	0.000439941	0.000082057	292.8	1.05701E-05	0.4388
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	
Pyrene	Dandora	61.333	0.303178448	2.74073E-06	0.106	0.000523974	0.000082057	292.8	1.25892E-05	0.2177

	Kibera	45.667	0.225739001	2.04068E-06	0.083	0.000410282	0.000082057	292.8	9.85755E-06	0.2070
	City Square	96.333	0.476188828	4.30475E-06	0.206	0.00101829	0.000082057	292.8	2.44657E-05	0.1760
	Industrial Area	92.667	0.458067227	4.14093E-06	0.115	0.000568463	0.000082057	292.8	1.3658E-05	0.3032
	Ngong Forest	0	0	0	0.015	7.41473E-05	0.000082057	292.8	1.78148E-06	0.0000
Benzo (ghi) perylene	Dandora	14.000	0.061864781	4.35528E-05	0.065	0.000287229	0.000082057	292.8	6.90106E-06	6.3110
	Kibera	0	0	0	0.058	0.000256297	0.000082057	292.8	6.15786E-06	0.0000
	City Square	46.333	0.204741494	0.000144138	0.1	0.000441891	0.000082057	292.8	1.0617E-05	13.5761
	Industrial Area	0	0	0	0.067	0.000296067	0.000082057	292.8	7.1134E-06	0.0000
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	
Benzo(a)anthracene	Dandora	0	0	0	0.016	7.00832E-05	0.000082057	292.8	1.68384E-06	0.0000
	Kibera	0	0	0	0	0	0.000082057	292.8	0	
	City Square	0	0	0	0.061	0.000267192	0.000082057	292.8	6.41964E-06	0.0000
	Industrial Area	58.000	0.254051686	1.45572E-06	0.062	0.000271572	0.000082057	292.8	6.52488E-06	0.2231
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	
Chrysene	Dandora	47.333	0.207328077	1.96132E-05	0.095	0.000416119	0.000082057	292.8	9.9978E-06	1.9618
	Kibera	43.333	0.189807271	1.79558E-05	0.066	0.000289093	0.000082057	292.8	6.94584E-06	2.5851
	City Square	48.000	0.210249671	1.98896E-05	0.103	0.000451161	0.000082057	292.8	1.08397E-05	1.8349
	Industrial Area	60.667	0.265733684	2.51384E-05	0.083	0.000363557	0.000082057	292.8	8.73492E-06	2.8779
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	
Benzo(a)pyrene	Dandora	60.333	0.239131986	1.08566E-07	0.092	0.000364645	0.000082057	292.8	8.76107E-06	0.0124
	Kibera	49.000	0.194213238	8.81728E-08	0.089	0.000352755	0.000082057	292.8	8.47539E-06	0.0104
	City Square	56.667	0.224601665	1.01969E-07	0.122	0.000483551	0.000082057	292.8	1.16179E-05	0.0088
	Industrial Area	106.333	0.421454618	1.9134E-07	0.139	0.000550931	0.000082057	292.8	1.32368E-05	0.0145
	Ngong Forest	0	0	0	0.014	5.54895E-05	0.000082057	292.8	1.33321E-06	0.0000
Dibenzo(a,h) anthracene	Dandora	31.667	0.113746408	1.67207E-09	0.052	0.000186782	0.000082057	292.8	4.48767E-06	0.0004
	Kibera	28.667	0.102970546	1.51367E-09	0.056	0.000201149	0.000082057	292.8	4.83287E-06	0.0003
	City Square	0	0	0	0.049	0.000176006	0.000082057	292.8	4.22877E-06	0.0000
	Industrial Area	32.667	0.117338362	1.72487E-09	0.066	0.000237069	0.000082057	292.8	5.69589E-06	0.0003
	Ngong Forest	0	0	0	0	0	0.000082057	292.8	0	