ASSESSMENT OF NEW PERSISTENT ORGANIC POLLUTANTS-PESTICIDES IN AIR AND SOIL SAMPLES FROM SITES IN NAIROBI AND MOUNT KENYA

BY

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(I56/68771/2011)

A thesis submitted for Examination in partial fulfilment of the requirements for Award of the Degree of Master of Science in Environmental Chemistry of the University of Nairobi

2015

DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other people's work, or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements..

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DEDICATION

I dedicate this work to my beloved children; Jeanne, Jael, Jerry and Josh.

ACKNOWLEDGEMENTS

My sincere gratitude goes to my supervisors Prof. Shem. O. Wandiga and Dr. Deborah A. Abong'o for their intellectual input in this work. Their guidance and mentorship is highly appreciated.

I am indebted to Dr. Vincent Madadi for his valuable comments that helped me shape my ideas. His selfless commitment in training me during sampling, sample preparation and analysis is highly appreciated. I am grateful to him for the supply of solvents used in this work.

I acknowledge my employer, The Teachers' Service Commission for granting me study leave with pay. This went along way in ensuring that I met my financial obligations while studying. I appreciate the valuable assistance I received from the research students in the Pesticides Research Laboratory at the University of Nairobi. I am particularly grateful to Jane Macharia and Enock Osoro for their assistance in solvent preparation for extraction.

I am very grateful to my family for their patience and support while I spent long hours working. Jeanne, Jael, Jerry and Josh, you were a great source of inspiration and motivation. I thank my husband, James, for encouraging me to study and for his financial and moral support. I am thankful for the encouragement and prayers I received from my mother, Esnas. I thank God for this far He has brought me. His grace was sufficient during the study period.

ABSTRACT

Persistent organic pollutants (POPs) are compounds of great concern because of the adverse effects they have on humans, wildlife and the environment. They are toxic and have a tendency to accumulate in the food chains. They are also capable of persisting in the environment for a long time, migrating in air, water, soil and sediments. The result is wide spread distribution of POPs in the atmosphere.

This study was undertaken to determine the spatial distribution, temporal and seasonal variations of the new persistent organic pollutants-organochlorine pesticides in air and soil in Nairobi and Mt. Kenya areas. Four out of the ten new Persistent Organic pollutants (new POPs) and some of their isomers and metabolites were analysed in air and soil samples from Industrial area, Dandora dumpsite, Kabete and Mt. Kenya. Air samples, collected using passive samplers and soil samples collected using Auger samplers were sampled on quarterly basis between July 2012 and April 2013.

The identification and quantification of the new POPs- pesticides was done using a gas chromatographic system (Agilent 6890N) in combination with an auto sampler (Agilent 7683 Series injector), and an electron capture detector (Agilent µECD). The new POPs that were detected include; α-HCH, β-HCH, γ-HCH (lindane), α- endosulfan, β-endosulfan and Endosulfan sulfate.

The residue levels of the new POPs were lower at the Mt. Kenya and Kabete sites than at the Dandora and Industrial area sites. The sum of the concentrations of the aerial new POPs (∑new POP) ranged between 3.4643 ng/M^3 and 14.3746 ng/M^3 at the Dandora site; 4.1236 ng/M^3 and 5.6328 ng/M^3 at the Kabete site; 7.5279 ng/M^3 and 11.4572 ng/M^3 at the Industrial area site; and 0.6874 ng/M^3 and 1.3336 ng/M^3 at the Mt. Kenya site. The levels of the new POPs in air increased while the levels of the new POPs in soil decreased during the warm-dry season signifying the effect of volatilization from soil when temperatures are high. The sum of the concentrations of the new POPs in soil ranged between 10.93ng/kg and 230.48 ng/kg at the Dandora site; 17.06 ng/kg and 29.05 ng/kg at Kabete site; 19.65 ng/kg and 78.41ng/kg at Industrial area; and 1.71 ng/kg and15.02 ng/kg at the Mt. Kenya site. The concentrations of the new POPs in soil declined during the warm-dry season at all the four sites. At the Dandora site, the concentrations declined from 230.48 ng/kg to10.93 ng/kg; from 29.05 ng/kg to28.77 ng/kg at the Kabete site; from 78.41 ng/kg to 52.18 ng/kg at the Industrial area; and 15.02 ng/kg to5.76 ng/kg at the Mt. Kenya site. The average residue levels of the new POPs analysed in air at the four sites revealed that the one with the highest average level was β-HCH (7.6434 ng/M^3) while α-HCH had the lowest residue level in air of the new POPs of 0.0358 ng/M^3.

The residue levels of the new POPs in air and soil were generally high at the Dandora and Industrial area sites. This indicates that industrial activities such as Tetra-Pac, general plastics, Phillips industries waste and stock piles are the main sources of the new POPs in Nairobi. The high concentration level poses a health risk to residents of Dandora and Industrial area workers. The levels of the new POPs were higher in air than in soil at the four sites during all the three sampling sessions. At the Kabete site, the average levels of the new POPs in air were 4.8504 ng/$M^3$and 24.96 ng/kg in soil. This trend was repeated at the other sites; 8.8684 ng/M^3 in air and 97.70 ng/kg in soil at the Dandora site; 1.0583ng/M^3 in air and 7.49 ng/kg in soil at the Mt. Kenya site; 9.0152 ng/$M^3$and 50.08 ng/kg at the Industrial area site.

The Pearson's correlation coefficients as determined for the seasonal levels of the new POPs present in air were positive at all the sites and were negative at some sites for soil. The inter-matrix correlation was very weak at the Kabete site (p=0.043)

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ABBREVIATION AND SYMBOLS

AFSDR	Agency for Toxic Substances and Disease Registry
AMAP	Arctic Monitoring and Assessment Programme
APHRC	African Population and Health Research Centre
DHHS	Department of Health and Human Services Centres for Disease Control and Prevention
EHP	Environmental Health Perspective
EJF	Environmental Justice Foundation
EPA	Environmental Protection Agency
GC	Gas Chromatography
GMNPDV	Guidance Material on New POPs Draft Version
GMP	Global Monitoring Plan
HCB	Hexachlorobenzene
HPLC	High Performance Liquid Chromatography
IARC	International Agency for Research on Cancer
KNIP	Kenya National Implementation Plan
MONET	Monitoring Network
NARAP	North American Regional Action Plan

PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzo furans
PFOS	Perfluorooctane sulfonate
POPRC	Persistent Organic Pollutants Review Committee
POPs	Persistent Organic Pollutants
PUF	Polyurethane Foam
SC	Stockholm Convention
SPSS	Statistical Programme for Social Scientists
SVOCs	Semi-Volatile Organic Compounds
UN	United Nations
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
α	alpha
β	beta
γ	gamma
g	gram

Kg	kilogram
m	metre
mg	milligram
ng	nanogram
pg	Picogram

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CHAPTER ONE

INTRODUCTION

1.1 General Background

Persistent organic pollutants (POPs) are a group of semi-lipophilic chemicals, including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polychlorinated dibenzo-p-dioxins (dioxin) and polybrominated diphenyl ethers PBDE (Duk-Hee *et al*, 2012). Persistent organic pollutants (POPs) are globally distributed and found in environmental media like sediment, air, soil and biota (Van Leewen *et al.*, 2013). They are toxic compounds of anthropogenic origin that resist degradation in environmental compartments and may undergo long-range transport Dvorska *et al.*, 2009.

In 2002, a global treaty, the Stockholm Convention (SC) on Persistent Organic Pollutants, was adopted by the world's governments to protect human health and the environment from POPs in line with the aims of the Stockholm convention to protect humans and the environment from hazardous and persistent chemicals by reducing or eliminating their production and introduction to the environment (Stockholm Convention, 2001).

In 2004 the first twelve POPs to be listed in annexes to the Stockholm convention on POPs were; aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, polychlorinated biphenyls (PCB), DDT, dioxins and furans (Harner *et al.*, 2005). The convention also defined criteria for including new chemicals basing on their persistence, bioaccumulation, and potential for long- range transport and adverse effects (AMAP, 2002). Accordingly, the conference of parties to the convention agreed in May 2009 to add nine new POPs to the convention's annexes. The nine new POPs include; pentabromodiphenylether (PentaBDE), octabromodiphenylether (Octa-BDE), perfluorooctane sulfonate (PFOs), pentachlorobenzene, and chlordecone, hexabromobiphenyl, lindane (*gamma* hexachlorocyclohexane, γ-HCH) *alpha* hexachlorocyclohexane (α-HCH) and *beta* hexachlorocyclohexane (β-HCH). At its fifth meeting held in May 2011, the Conference of Parties adopted an amendment to annex A to the Stockholm convention to list technical Endosulfan and its related isomers (Stockholm convention, 2008).

The new POPs are categorised as; pesticides: chlordecone, endosulfan, *alpha* hexachlorocyclohexane(α-HCH), beta hexachlorocyclohexane (β-HCH), lindane (γ-HCH), pentachlorobenzene; Industrial chemicals: hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, pentachlorobenzene, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether and penta bromodiphenylether; By-products: *alpha*-hexachlorocyclohexane, *beta*-hexachlorocyclohexane and pentachlorobenzene(Stockholm convention, 2008).

Kenya is a Contracting Party to the Stockholm Convention on Persistent Organic Pollutants (POPs), which she ratified on 24th September, 2004. Article seven 1 of the Convention states that, each Party shall develop, and endeavour to develop a plan for the implementation of its obligations under the Convention (KNIP, 2007). The inclusion of the ten new POPs to the Stockholm Convention brings the need for Kenya to conduct an evaluation on the current status of each of the new POPs at the national level, in order to update the National Implementation Plan (NIP) (GMNPDV, 2009). Under the Stockholm convention, signatory countries must conduct source inventories, identify ongoing sources, and provide environmental monitoring evidence that ambient levels of POPs are declining (Stockholm convention, 2001). There is limited data available on the status of Nairobi as far as levels of these compounds in ambient air are concerned.

This study was undertaken in Nairobi, the capital city of Kenya which is also an industrial city and Mt. Kenya which is a remote site near Nairobi to provide evidence for long range transport of the new POPs. Due to urbanisation, industrialisation and rapid population growth, Kenya requires data on the current state of pollution with regard to the new POPs. This study provides baseline spatial data on the distribution of the new persistent organic pollutants (POPs) in air in Nairobi and Mt. Kenya. The present study is on five new POPs-pesticides; endosulfan and its metabolites, *alpha*-hexachlorocyclohexane (α-HCH), *beta*-hexachlorocyclohexane (β-HCH), and lindane (γ-HCH). Chlordecone was not analysed because it was not available in the organochlorine pesticides, OCP-17 mix standard used for quantitative analysis in this work.

Passive air samplers (PAS) were used in this study because they have been confirmed to have very good capability to reflect temporal and spatial fluctuations in concentrations of POPs in ambient air (Jana *et al.*, 2005). Having undergone considerable technological development in the past 15 years, passive air sampling is both simple and economical. This sampling method relies on a sorbent with an appropriate capacity for POPs, such as polyurethane foam (PUF). Sampling was done using PUF passive sampler on quarterly basis because, for a PUF-disk sampler, a 3-month sampling period uses approximately 270–360 m^3 of air volume, which may be sufficient for the detection of POPs. POPs do not change significantly during storage but dehydrochlorinations of α and β-HCH may occur (Weiguang *et al.*, 2013).

1.2 Statement of the Problem

Nairobi is a fast growing city with increasing levels of industrialisation and urbanisation. The domestic, commercial and industrial activities in Nairobi lead to release of solid wastes, effluents and emissions to the atmosphere, water and soils. Many of the new POPs included in the Stockholm Convention may not be produced or registered for use in this country. However, Kenyan citizens and habitats could still be at risk from new POPs that have persisted in the environment, from unintentionally produced POPs that are being released from industrial activities in Kenya, and from POPs that are released elsewhere and then transported here (by wind or water).

Being party to the Stockholm Convention, Kenya is required to update her National Implementation Plan (NIP) and implement the obligations of the Convention. There is need therefore to provide comprehensive quality data on the levels of the new POPs in ambient air, soil, water, sediments and biota. Although a number of regional and global monitoring programs have been established to report on the levels of POPs in the environment, there is scarce data on the levels of the new POPs.

This study was undertaken to provide data on the residue levels of the new POPs in ambient air and soil between July 2012 and April 2013 in an effort to update the Kenya national implementation plan and advice the policy makers accordingly.

1.3 Objective of the Study

The overall objective of this study is to÷

To assess the pollution status of the city of Nairobi with regard to selected new Persistent Organic Pollutants-Pesticides.

The specific objectives of this study were;

i. To determine the levels and spatial distribution of selected new POPs; Endosulfan, and its isomers and metabolite, Lindane (γ-HCH), *alpha* hexachlorocyclohexane (α-HCH) and *beta* hexachlorocyclohexane (β-HCH) in air and soil in designated sites in Nairobi.

ii. To assess the temporal and seasonal variations of levels of the selected new POPs-pesticides in ambient air and soil in selected sites in Nairobi.

iii. To establish the correlation between the levels of the selected new POPs in ambient air and soil.

CHAPTER TWO

2.0 LITERATURE REVIEW

Persistent organic pollutants (POPs) are a range of organic chemicals that enter the environment as a result of human activities. They are persistent in the environment and become widely distributed via long range transport through air and water. They have a high tendency to partition between air, water and organic phase which permits the relatively easy movement from phase to phase e.g. the cycling between the earth's atmosphere and surface by deposition and evaporation (Wania *et al.*, 1999) as shown in Figure 2.1.

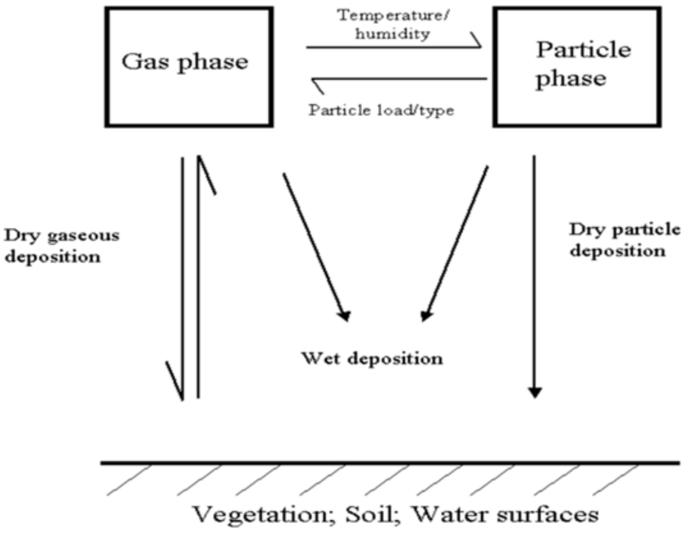


Figure 2.1: Diagram illustrating interaction of POPs with their environment

The Stockholm convention's 2001 list of POPs consisted of 12 chlorinated compounds (The dirty dozen). The Convention also defined criteria for including new chemicals basing on their persistence, bioaccumulation, potential for long-range transport and adverse effects (AMAP, 2002). In 2004, the first 12 POPs to be listed in annexes to the Stockholm Convention on Persistent Organic Pollutants were aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, polychlorinated biphenyls (PCB), DDT, dioxins and furans.(Harner *et al.*, 2005). In 2009, nine new compounds were added to the Stockholm convention, including brominated and fluorinated compounds (Andrea't *et-al.*, 2013). The list of the new POPs in the Stockholm convention is as shown in Table; 2.1.

Table 2.1: The list of the 10 new POPs listed in the Stockholm convention

Chemical	**Annex**	**Acceptable purpose or specific exemption**	**Availability of alternatives**
Alpha-hexachlorocyclohexane	A	None	No alternatives. It is a by-product
Beta-hexachlorocyclohexane	A	None	No alternatives. It is a by-product
Chlordecone	A	None	Yes
Hexabromobiphenyl	A	None	Yes, for some uses
Hexabromodiphenyl ether	A	Use of recycled articles containing the chemical	Yes, for some uses
Lindane	A	Pharmaceutical use	Yes
Tetrabromodiphenyl ether	A	Use of recycled articles containing the chemical	Yes, for some uses
and pentabromodiphenyl ether			
Pentachlorobenzene	A & C	None	No. It is no longer used
Perfluorooctane sulfonic acid (PFOS) its salts and perfluorooctane sulfonyl fluoride (PFOS-F)	B	Production for specific uses and uses for acceptable purposes	Yes, for some uses

2.1Properties of Persistent Organic Pollutants

There are many thousands of POP chemicals, often coming from certain families of chemicals (Jones *et al.*, 1999). POP substances often have three characteristics in common; one or more cyclical ring structures of either aromatic or aliphatic nature, a lack of polar functional groups, and a variable amount of halogen substitutions, usually chlorine . This diverse group of pollutants are classified as: poly aromatic hydrocarbons (PAH), PCDD/Fs which refer to chlorinated tricyclic hydrocarbons. PCDD/Fs include 210 possible congeners, combined in 14 homologue groups with different chlorination level. Physical-chemical properties of these congeners are different, leading to differences in their environmental behaviour. The toxic properties of PCDD/F are fairly well-known and characterised. The most toxic forms of PCDD/Fs are the 2, 3, 7, 8-PCDD/Fs (IARC, 1998).

The third family is of PCBs which are referred to as class of organochlorine aromatic compounds, which have been used in many countries for a long period of time. There are 209 possible PCB congeners with different physical chemical properties and toxicity depending on the number and position of chlorine atoms on the biphenyl molecule. According to International Agency of Research on Cancer (IARC), PCBs belong to a group of probable carcinogens for man. PCBs can also affect the human reproductive system and exhibit embryo toxic effect. A number of PCB congeners with coplanar configuration possess toxicological properties similar to that of the PCDD/Fs. γ-HCH is one of eight possible isomers of 1,2,3,4,5,6-hexachlorocyclohexane (HCH), thus belonging to the group of organochlorine compounds(IARC, 1998).

2.2 The Ten New Pops

One characteristic of the majority of these chemicals is that they, or precursors, have been at one time, high production volume chemicals i.e. N454 t/y in USA or N1000 t/y globally. Another is that they have molecular structures which convey sufficient stability and physical–chemical properties for transport to remote areas (Derek *et al.*, 2009). Previous assessments of POPs have emphasized that POPs have semi-volatile characteristics and relatively high Henry's law constants which give rise to global fractionation and multi-hopping (Derek *et al.*, 2009). The structures of the 10 new POPs are given in Appendix I

2.2.1. Endosulfan

Endosulfan is a broad-spectrum insecticide consisting of α- and β-isomers (Appendix II). It has been widely used leading to environmental accumulation of its residues including those of its metabolite endosulfan sulfate which are persistent and toxic to the environment. It inhibits RNA and protein content in brain, liver and skeletal muscle of fresh water catfish, *C. batrachus* (Tripathi and Verma, 2004).

It is the most currently used pesticide in the arctic environment (Derek *et al.*, 2009). It is applied to crops using air-blast or ground boom sprayers thus allowing for chance of drift and long- range atmospheric transport. In soils, α- and β-endosulfan degrade via microbial biotransformation to endosulfan sulfate (major metabolite) and other products i.e. diol, ether, α-hydroxy ether and lactone forms. Whereas α-endosulfan disappears within 60 days in soil and 7 days in river water, β-endosulfan and endosulfan sulfate may not disappear for two years. During winter, degradation is effectively halted [Harris, *et-al.*, 2000].

2.2.2. Chlordecone

Chlordecone is a tan to white crystalline odourless solid. Synonyms include Kepone, decachlorooctahydro-1, 3, 4-metheno-2H-cyclobuta [cd]-pentalen-2-one, and GC-1189. Chlordecone is also a contaminant in mirex formulations and is a degradation product of mirex. Chlordecone was primarily used as an insecticide. Specific applications have included control of the banana root borer, application on non-fruit-bearing citrus trees to control rust mites, control of wireworms in tobacco fields, control of apple scab and powdery mildew, control of the grass mole cricket, and control of slugs, snails, and fire ants. Chlordecone is resistant to degradation in the environment. It is not expected to react with hydroxyl radicals in the atmosphere or to hydrolyze or photolyze. Chlordecone is likely to be removed from air by deposition of particles. Studies have shown that microorganisms degrade chlordecone slowly. Chlordecone is expected to adsorb to soil and to stick to suspended solids and sediments in water. Small amounts of chlordecone will evaporate from soil or water surfaces. It has a high potential for bioaccumulation in fish and other aquatic organisms (EPA, 2009).

2.2.3. Beta Hexachlorocyclohexane (β-HCH)

Beta-HCH is more soluble in water compared to other organochlorine pesticides. Its chemical structure seems to confer the greatest physical and metabolic stability (e.g. β-HCH has a lower vapour pressure and a higher melting point than the alpha-isomer). The physico-chemical properties (Table 2.2) of beta-HCH allow for "cold condensation", an enrichment of the substance in cold climates compared to concentrations near sources, on altitudinal and latitudinal scales. The physico-chemical properties allow the dispersal of the substance from its sources to the arctic by long range transport via ocean currents (POPRC, 2007).

Beta-HCH is the most recalcitrant isomer. It is persistent in soil especially under low temperatures. It is mainly associated with particles and has a low leaching potential (UNEP, 2003). This property of β-HCH allows the dispersal of the substance from its sources to the arctic.

Table 2.2: Selected physico-chemical properties of beta-HCH

Melting Point (°C)	314-315 1
Boiling Point (°C)	60 at 0.5 mmHg 1
Density (g cm^{-3} at 19 °C)	1.891
Water solubility (mg/l at 20 °C)	0.22
Vapour pressure (mmHg at 20 °C)	$3.6x10^{-72}$
Henry´s law constant (atm m^{3} mol^{-1})	$6.9x10^{-72}$
Log K_{ow}	3.78 1
Log K_{oa} (0°C)	10.4 3

Note: Log K_{ow}; Octanol-water partition coefficient; Log $K_{oa:}$ Octanol-air partition coefficient

Monitoring data shows the distribution of β-HCH in all environmental media. For example concentrations of 40-225 mg/kg were found in top soil around a chemical plant in Albania. Mean levels of 0.02 mg/kg were reported for soils from the Pearl River delta in China. Russian soil near the Lena River contained 0.001-0.017 mg/kg (UNEP, 2003). According to (Li *et al.*, 2006), elevated levels of β-HCH were detected in air in higher mountains (Mt. Everest region) of 11.2 pg/m^3 compared to up to 1 pg/m^3 in the arctic. Seasonal changes in beta-HCH concentrations in Japan (mean 23 pg/m^3) in 2000 were probably caused by re-emissions from a terrestrial source (Muraya *et al.*, 2003).

2.2.4. Alpha Hexachlorocyclohexane (α-HCH)

The intentional use as an insecticide was phased out long ago but it is still produced as a by-product of lindane. Releases occur from stockpiles and contaminated sites. It is highly persistent in colder regions and may bioaccumulate and biomagnify in biota and arctic food webs. Alpha-HCH is subject to long range transport. It is potentially carcinogenic to humans and has adverse effects on human health and wildlife in contaminated regions (EHP, 2008).

2.2.5. Lindane (gamma Hexachlorocyclohexane, γ-HCH)

It is an organochlorine chemical variant of hexachlorocyclohexane that has been used both as an agricultural insecticide and as a pharmaceutical treatment for lice and scabies (NARAP, 2005). Although its production and agricultural use was banned under the Stockholm Convention in 2009, it still remains the primary cause of environmental contamination (EPA, 2006). This is due to the specific exemptions to that ban which allows it to be used as a second-line pharmaceutical treatment for lice and scabies (Eliane, 2009). For every ton of lindane manufactured, about 9 tons of toxic waste is produced (EHP, 2008). It persists in the environment, it is transported by natural processes like global distillation and it can bioaccumulate in food chains though it is rapidly eliminated when exposure is discontinued (POPRC, 2007).

2.2.6 Pentachlorobenzene

1, 2, 3, 4, 5-Pentachlorobenzene (PeCB) has the molecular formula C_6HCl_5 which is a chlorinated aromatic hydrocarbon. There are no current large scale uses but it can be produced as a by-product of the manufacture of carbon tetrachloride and benzene (Robert and Bailey, 2007). Most of the releases from the environment are as a result of backyard trash burning and municipal waste incineration (Robert and Bailey, 2007). It was also used as the intermediate in the manufacture of pesticides like fungicide pentachloronitobenzene and as a fire retardant (EPA, 2006).

2.2.7 Perfluorooctane Sulfonate (PFOS)

According to the Stockholm convention, 2008, PFOS is a manmade fluorosurfactant and global pollutant. It can form from the degradation of precursors in addition to industrial production. The C_8F_{17} subunit of PFOS is hydrophobic and lipophilic like other fluorocarbons, while the sulfonic acid/ sulfonate group adds polarity. It is a stable compound in industrial application and in the environment because of the effect of aggregate carbon-fluorine bonds. PFOS is a fluorosurfactant that lowers the surface tension of water. The straight chain isomer (n-PFOS) is the most dominant in commercial mixtures and environmental samples. There are 89 linear and branched congeners of perfluorooctane sulfonate with different physical, chemical and toxicological properties (Rayne *et-al.*, 2009).

Perfluorooctane sulfonic acid (PFOS) and its salts do not follow the “classical” pattern of partitioning into fatty tissues, but instead bind preferentially to proteins in the plasma and are hydrophilic (GMP, 2015).The most important emission sources of PFOS are metal plating and fire-fighting foams (Betts,2008]. Recently, high serum levels of PFOS were found to be associated with increased risk of chronic kidney disease in the general United States population (Shankar, *et al.,* 2011). According to a study in animals, PFOS cause cancer, physical development delays, endocrine disruption and neonatal mortality (Betts, 2007). PFOS levels in pregnant women have been associated with preeclampsia (Stein *et al.*, 2009). It has also been associated with altered thyroid hormone values (Dallaire *et-al.*, 2009) and increased risk of high cholesterol (Steenland, *et al.*, 2009).

2.2.8 Hexabromobiphenyl

Hexabromobiphenyl is one of the chemicals in the class of poly brominated biphenyls PBBs. They are used in plastics used in products such as home electrical appliances, textiles, plastic foams, and laptop cabinets', to make them difficult to burn. The mechanism of toxicity is oxidative stress by aryl hydrocarbon receptor activation. It has great potential for bioaccumulation and biomagnification. Due to its physical and chemical properties and based on findings in environmental samples, it is assumed that hexabromobiphenyl can be transported long distances in air. It is a possible human carcinogen and a substance of endocrine disrupting activity (Curran *et al.*, 2006).

2.2.9 Pentabromodiphenyl ether

It is also known as pentabromodiphenyl oxide. It is a brominated flame retardant which belongs to the group of polybrominated diphenyl ethers (PBDEs). Commercial pentaBDE is a mixture of different PBDE congeners, with BDE-47 (2,2',4,4'-tetrabromodiphenyl ether) and BDE-99 (2,2',4,4',5-pentabromodiphenyl ether) as the most abundant (POPRC, 2007).

The term pentaBDE alone refers to isomers of pentabromodiphenyl ether (PBDE congener's numbers 82-127) (ATSDR, 2004). It is released by emissions from manufacture of pentaBDE-containing products such as flexible polyurethane foam, printed circuit boards and from the products themselves (POPRC, 2007). Elevated concentrations can be found in air, water, soil, food, sediment, sludge and dust (Hale *et al.*, 2006). It may enter the body by ingestion or inhalation and stored in body fat and may stay in the body for years. PBDE 47 (a tetra BDE) and PBDE 99 (a pentaBDE) have biomagnification factors in terrestrial carnivores and humans (ATSDR, 2004). There are no proven health effects in humans; however, based on animal experiments, pentaBDE may have effects on the liver, thyroid and neurobehavioral development (ATSDR, 2004).

2.2.10 Octabromodiphenyl ether

Octabromodiphenyl ether (octaBDE, octa-BDE) is a brominated flame retardant which belongs to the group of polybrominated diphenyl ethers (PBDEs). The most common congeners in commercial octaBDE are those of heptabromodiphenyl ether and octaBDE (POPRC, 2007). The term octaBDE alone refers to isomers of octabromodiphenyl ether (PBDE congener numbers 194-205).

OctaBDE is used in conjunction with antimony trioxide as a flame retardant in the housing of electrical and electronic equipment, mainly in the plastic acrylonitrile butadiene styrene, but also in high impact polystyrene, polybutylene terephthalate and polyamides (EU, 2003).

In the environment, photolysis, anaerobic degradation and metabolism in biota can cause debromination of octaBDE, which produces PBDEs with fewer bromine atoms which may have higher toxicity and bioaccumulation potential (POPRC, 2007). It may enter the body by ingestion or inhalation (ATSDR, 2004).

2.3 Health Effects of the New POPs

Air pollution is an issue of great public health concern. Due to the new POPs' widespread distribution, ability to bioaccumulate in fatty tissues, carcinogenicity, mutagenicity and endocrine disruption potentials, they remain the centre of attention. Persistent Organic Pollutant compounds can adversely influence immune and respiratory system development (Mireia *et al.*, 2013). Organic pollutants present in ambient air have been associated with several adverse effects on respiratory, cardiovascular, immune, and reproductive systems (Anita *et al.*, 2014).

The U.S. Department of Health and Human Services (DHHS, 2005) has determined that chlordecone may reasonably be anticipated to be a carcinogen. There are no studies available on whether chlordecone is carcinogenic to humans. However, studies in mice and rats have shown that ingesting chlordecone can cause liver, adrenal gland and kidney tumours.

Increased plasma concentrations of PCBs, Organochlorine pesticides, and OCDD were associated with an increased risk of developing or progression of stroke in the elderly. Taken together with previous experimental and epidemiological studies, POPs may play a fundamental role in the development of stroke (Duk-Hee *et al.*, 2012).

2.4 Sources of POPs in the Environment

Although some natural sources of organochlorines are known to exist, most POPs originate almost entirely from anthropogenic sources associated largely with the manufacture, use and disposition of certain organic chemicals. They are released by application and post application volatilization (Jana *et al.*, 2005). OCPs (organochlorinated pesticides) are emitted from primary and, being semivolatile, also from secondary sources (re-volatilisation). Soils have a huge retention capacity and they may act as re-emission sources to the atmosphere. Volatilisation from contaminated water, freshwater and shelf seas is another important source for their presence in the European atmosphere. In addition, hot-spot areas can also serve as source areas in case of not being sufficiently protected (Dvorska *et al.*, 2008).

Halogenated and particularly chlorinated organic compounds have become entrenched in contemporary society, being utilized by the chemical industry in the production of a broad array of products ranging from polyvinyl chloride (millions of tonnes per year) to solvents (several hundreds of thousands of tonnes) to pesticides (tens of thousands of tonnes) and speciality chemicals and pharmaceuticals (thousands of tonnes down to kilogram quantities). In addition, both anthropogenic and non-anthropogenic sources also lead to production of undesirable by-products and emissions often characterized by their persistence and resistance to breakdown. Persistent Organic Pollutants (POPs) are persistent in the environment, and become widely distributed via long range transport through air and water (Andrea't *et-al.*, 2013).

Large stockpiles of α-HCH and β-HCH are present in the environment although their use was phased out years ago because they are unintentionally produced as by-products of lindane production (Stockholm convention, 2008).

Climate, air-surface exchange or atmospheric transport, influence the spatial and temporal variability of atmospheric POPs concentration. This necessitates frequent measurements of air concentrations in different locations (Jana, *et al.*, 2005).

2.5 Characteristics of the New POPs

2.5.1 Persistence

POPs are persistent in the environment, having long half-lives in soils, sediments, air or biota. A POP could have a half-life of years or decades in soil/sediment and several days in the atmosphere. POPs are typically `water-hating' and `fat-loving' chemicals, i.e. hydrophobic and lipophilic (Jones *and Voogt*, 1999). In aquatic systems and soils they partition strongly to solids, notably organic matter, avoiding the aqueous phase. They also partition into lipids in organisms rather than entering the aqueous milieu of cells and become stored in fatty tissue. This confers persistence on the chemical in biota since metabolism is slow (Jones *and Voogt*, 1999).

Endosulfan degrades relatively quickly in water (half life = 2-22 days) but persists longer in soil (half life = 60-800 days), and its major degradation product, endosulfan sulphate, is not only more persistent but is equally toxic (POPRC, 2007).

2.5.2 Bioaccumulation and Bioconcentration

The combination of resistance to metabolism and lipophilicity means that POPs will accumulate in food chains (Jones *et al.*, 1999). Most pesticides are drained into water bodies where fish encounter with them and develop various metabolic abnormalities. They accumulate in fish and affect human health through ecological cycling and biological magnification (Tripathi and Verma, 2004). In mammals, commercial endosulfan is transformed into more hydro-soluble metabolites, endosulfan sulfate, followed by ether and diol metabolites which bioaccumulate in adipose tissue depending on their lipophilicity (Cerrillo, *et-al.*, 2004). Endosulfan bioaccumulates in humans and other animals particularly in the liver, kidney and fatty tissues (POPRC, 2007).

Estimates of the bioconcentration factor (BCF) of endosulfan vary by almost four orders of magnitude ranging from 1.97 to 11583 depending on the lipid content and the metabolic ability of the organism tested. Endosulfan sulfate metabolite is included in the calculation of BCF since it is as toxic as the parent compound (Harris *et-al.*, 2000).

2.5.3 Long-range transport

Persistent organic pollutants (POPs) are toxic compounds of anthropogenic origin that resist degradation in environmental compartments and may undergo long-range atmospheric transport (Dvorska *et al.*, 2008). The combination of stability and propensity to form a gas under appropriate environmental conditions means that POPs are subject to long-range atmospheric transport (Jones *et al.*, 1999). According to (Dvorska *et-al.*, 2008), the source loadings distributions, the geographical positions of their weighted mean centres (COGs) and the allocation of source loadings to countries enabled locating potential source areas for some POPs and decadal trends over the period 1997–2006. Major emissions of α-HCH in Poland, γ-HCH in France, had significantly decreased by 2004–2006 (Dvorska *et-al.*, 2008). POPs move around the globe, evaporating in warm places, riding the wind and dust particles, settling to earth in cool spots and then vaporizing and moving on again hence they drift toward the poles and mountain areas (UNEP, 2005).

2.6 Fate of the New POPs in the Environment

The role of the atmosphere in supplying POPs to terrestrial and aquatic food chains, and in their global recycling is of key importance. This may follow emissions from obvious and strong point sources or from diffusive primary and secondary sources (e.g. 'old' pesticides emitted from soils). This has focussed international regulation on reducing emissions to air and risk assessment/modelling efforts on their ambient distribution (Klecka *et al.*, 2000). They enter the atmosphere from a number of industrial sources such as power stations, heating stations, incinerating plants as well as from household furnaces, transport, use of agricultural sprays, evaporation from water surfaces, soil, or from the landfills. Other sources include wastes which can be found in many areas and stemming from different activities, e.g. the use of obsolete oil, the repairing and maintenance of equipment, demolition of building, evaporation, cement manufacture, animal carcass incinerator, coal combustion, lixiviation of dumps and recycling operations, incineration-municipal, hazardous, medical waste, sewage sludge, industry-chlor-alkali plants, aluminium secondary plants, organochlorine pesticide plant and landfills-hazardous waste/plastic waste, fly ash storage, and organochlorine pesticide storage (Wenzl *et al.*, 2006).

In recent years perfluorinated alkylated substances (PFAS) have appeared as a new class of global pollutants. Besides being an industrially important group of compounds, PFAS are regarded as highly toxic and extraordinarily persistent chemicals that pervasively contaminate human blood and wildlife throughout the world. Dietary intake seems to be the main source of exposure of the general population to PFOS and PFOA (Fromme *et al.*, 2007). In

Germany, recently 12.2 g/L of PFOS and 5.3 g/L (median values) of PFOA were found in non-occupationally exposed volunteers (14 - 16 years of age) living in the southern part of Bavaria, Germany (Fromme *et al.*, 2007).

According to a research on the levels of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA) in the fish from Lake Victoria where two fish species namely *Lates niloticus* (Nile perch) and *Oreochromis niloticus* (Nile tilapia) were obtained and analysed for PFOS and PFOA in muscles the mean concentrations of PFOS obtained from all sampling locations in both fish analysed was between 1.23 to 11.75 ng/g. Higher concentrations of PFOS than PFOA in muscles and liver, with liver samples containing several orders of magnitude higher than in muscles in samples analysed was observed (Orata et al., 2008).

If the POP is mobile (e.g., in the soil environment), subsequent rainfall may transport the POP so that eventually it may directly enter the drinking water supply. If the POP is immobile in the soil environment, the POP is potentially amenable to both chemical and, perhaps more significantly, microbial attack. This can result in the creation of other, often more polar, organic chemicals, some of which may be more toxic than the parent compounds (Dean *and Scott*, 2004).

Soils have a huge retention capacity and they may act as re-emission sources to the atmosphere. Volatilisation from contaminated water, fresh water and shelf seas is another important source of POPs-pesticides in the European atmosphere. Hot-spot areas also serve as source areas in case of not being sufficiently protected. Not only decreasing use and/or banning of POPs, but also meteorological and flood-induced remobilisation of POPs stored in soils and sediments may influence POPs levels (Dvorska *et al.*, 2009).

High concentrations of β-HCH could be associated with the fact that, in the environment, α-HCH and γ-HCH can be converted to β-HCH, and β-HCH is more stable than the other HCH isomers. Therefore, the higher residue ratio of β-HCH is evident in the historical HCHs residues in the sediment core. According to a research on historical contamination and ecological risk of organochlorine pesticides in sediment core in north eastern Chinese river, β- HCH was overall predominant which accounted for 47 percent and 51 percent in surface sediment and sediment core, which implied that HCHs contaminations might have originated from a relatively long-time source and accumulation (Luo *et al.*, 2013).

The transport of POPs depends on temperature; in a process known as the 'grasshopper effect'. They move around the globe, evaporating in warm places, riding the wind and dust particles, settling to earth in cool spots and then vaporizing and moving on again. This results in general drift of these compounds toward the poles and mountain areas (UNEP, 2005).

2.7 Human Exposure to New POPs

Human exposure to new POPs begins in the uterus, since most new POPs cross the placental barrier (Mireia *et al*, 2012). After birth, newborns are exposed to POPs through breastfeeding, diet or by direct contact with materials containing these compounds (Aliyu *et al.*, 2010).

Endosulfan is acutely toxic and is readily absorbed by the stomach and lungs, and through the skin (EJF, 2009).It is the most frequent contaminant found in food, soil or water in Europe. It was the most frequent pesticide detected in surface waters in Almeria, Spain. Humans can be exposed to endosulfan through their occupational activity, environment or food which is the most common exposure route among the general population (Cerrillo *et-al.*, 2004).

Human exposure to beta-HCH results mostly from ingestion of contaminated plants, animals and animal products. High exposure is expected in contaminated areas of extensive use, former production, disposal sites and stockpiles. Inhalation of ambient air and consumption of drinking water are further sources of exposure, although to a minor extent. Intake through indoor air may be considerable for people living in houses treated for pest control purposes (POPRC, 2007).The available data for humans and animals indicate that chlordecone is well absorbed following oral exposure. Once absorbed, it is widely distributed and eventually concentrates in the liver. Chlordecone was also detected in the blood of Hopewell community residents living near a pesticide plant with concentrations ranging from 0.005 to 0.0325 ppm. Potential exposure routes for community residents included inhalation of chlordecone associated with fine particulate matter and ingestion of contaminated soil and drinking water (EPA, 2009).

It is the uptake of new POPs from the soil environment that is of concern. In this context, the uptake of new POPs to humans is most likely via the growing of food crops on contaminated soil which are subsequently consumed. POPs can enter the food chain to humans via animals eaten as part of the diet. In this situation, POPs can enter animals via the pasture on which they are reared or via their diet. In addition, it is known that some humans eat soil directly either unintentionally (e.g., unwashed vegetables) or deliberately (geophagia) (Dean *and Scott*, 2004).

2.8 Some Adverse Health Effects Associated with POPs

Diverse studies have pointed environmental pollutants, including persistent organic Pollutants (POPs), as important factors that can impact susceptibility to infections and the development of allergy and asthma during the first years of life. Current epidemiological evidence suggests that early-life exposure to POPs can adversely influence immune and respiratory systems development (Mireia *et al.*, 2012).Organochlorine pesticides (OCPs) have some important features of difficult biological decomposition, high lipid solubility and moderate chronic and acute toxicities (Luo *et al.*, 2013).

Persistent Organic Pollutants (POPs) are a range of organic chemicals which become widely distributed via long range transport through air and water. Due to their stability and lipophilic properties, POPs are stored in fat tissues and bio-accumulate in the food chain. Exposure to POPs has been associated with a range of toxic effects in wildlife (Tanabe, 2002) and humans (Li, *et al*., 2006) and it has been recognised for several decades that concerted action is needed to reduce environmental levels of POPs (Andrea 't *et al.*, 2013).

Heterogeneity between studies in exposure and outcome assessment and the small number of studies for any given exposure–outcome relationship currently make comparisons difficult and meta-analyses impossible (Mireia *et al.*, 2012). Background exposure to persistent organic pollutants (POPs), lipophilic xenobiotics that accumulate mainly in adipose tissue, has recently emerged as a new risk factor for cardiovascular diseases. This prospective study was performed to evaluate if plasma concentrations of selected POPs predict incident stroke among the elderly (Duk-Hee *et al.*, 2012).

Endosulfan may cause mutagenic effects in humans if exposure is high enough (EJF, 2009). Endosulfan causes impaired development in amphibians, reduced cortisol secretions and metabolism in fish (Tripathi *and Verma*, 2004), impaired development of the genital tract in birds and reduced sperm production in mammals (Stockholm convention, 2008). Lindane affects the nervous system, liver and kidney of humans; it may also be a carcinogen (AFSDR, 2005). It is not clear whether lindane is an endocrine disruptor (WHO, 2004).

2.9 Toxicity of the New POPs Pesticides

Lindane is a neurotoxin that disrupts the neurotransmitter function by interacting with the receptor channel complex at the picrotoxin binding site (ATSDR, 2005). Endosulfan has been shown to be genotoxic to human cells under experimental conditions (EJF, 2002). It has been reported to produce neurotoxicity effects as a result of overstimulation of the central nervous system (Stockholm Convention, 2008).

The National Institute for Occupational Safety and Health (USA) recommended that endosulfan be recognised as a group I pesticide because it poses a significant risk of adverse acute health effects at low concentrations, are carcinogenic, teratogenic, neurotoxic or cause reproductive effects (Cerrillo *et al.*, 2004). It interferes with reproduction in newts at concentrations as low as 5µg/g (Park *et al.*, 2001). Endosulfan acts on the central nervous system by binding at the picrotoxin site in the g-aminobutyric acid (GABA) chloride ionophore. It impairs the inhibitory actions of this complex resulting in chloride influx into the nerve, hyper excitation results which when prolonged may lead to respiratory failure. External symptoms include depressed activity a few hours after exposure followed by hyper excitability, tremors and convulsions (Harris *et al.*, 2000).

The concentration range for lethal acute effects of β-HCH is 150 mg/kg to >16000 in mice and 600mg/kg to >8000 mg/kg in rats (POPRC, 2007). Beta-HCH has been shown to increase foetal deaths within 5 days of birth at a dose of 20 mg/kg/day given to rat dams (USEPA, 2006).

2.10 New POPs Levels in Ambient Air and Guidelines in Kenya

Data from the annual sampling campaign between 2008 and 2012 revealed that the concentration of various POPs ranged from 0.0036 pg.m^3 of PBDE 28 in 2012 to 146 pg.m^3

of alpha-endosulfan in 2009. The concentration of POP pesticides was in the range of 0.058 pg.m^3 (trans-nonachlor in 2009) and 146.44 pg.m^3(alpha-endosulfan in 2009). The level of alpha-endosulfan increased from 1.97 pg.m^3 to 146.44 pg.m^3 in 2009 and then decreased to 9.88 pg.m^3 at the end of the sampling campaign in 2012 in Kenya (GMP, 2015).

Pesticide safety is classified by the World Health Organisation (WHO,2004) according to the results of LD_{50} tests, which document the amount of a chemical required to kill 50% of a population of laboratory rats (EJF, 2009).Unfortunately there no available guidelines on the levels of the new POPs in air in Kenya.

2.11 Principle of Passive Air Sampling

The fundamental principle of passive air sampling (PAS) is that chemicals from ambient air accumulate in sampling medium via gaseous diffusion. The uptake of a chemical from the ambient air to a PAS medium is based on the effective concentration gradient between the air and the sampler described by the following equation:

$V_S \; d\,C_S / d\,t = K_o A_S (C_A - C_S / K_{SA})$……………………………………..Equation I

Where

V_S is the volume of sampler

C_S is the concentration of analyte in air

K_O is the overall mass transfer coefficient

A_S is the surface area of the sampler

K_{SA} is the sampler/ air partition coefficient which can be determined from K_{OA}.

K_{OA} is the Octanol-air partition coefficient

The uptake and elimination rates of chemicals by the passive sampler are related to A_S, V_S and K_{OA}. For compounds of high K_{OA} ($>10^7$) and low atmospheric concentration, the mass transfer of the chemical from ambient air to the sampling medium is controlled by the air-side mass transfer rate (i.e. $K_O = K_A$) and thus is primarily a function of the air supply rate to the chamber. Wind speed affects the magnitude of PAS sampling rates and a combination of wind speed and direction affect the proportion of different air masses sampled by the PAS (Lisa *et al.*, 2011).

Very good capability of passive air samplers to reflect temporal and spatial fluctuation in concentrations of persistent organic pollutants in the ambient air has been confirmed. They have high sensitivity which makes them suitable for the monitoring of local sources. They sample the variety of POPs at a similar rate of a few m^3 of air per day (Jana *et al*, 2005). Deployments at several locations simultaneously enable spatial mapping and source identification (Harner *et al.*, 2004). They are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring spatial, seasonal and temporal variations. They are not sensitive to short-term fluctuations in concentrations hence passive air samplers are suitable for measurement of long-term, average concentrations of contaminants. This makes them suitable for the monitoring of pollutants from sources with rather stable releases, such as long-range transport. Volumetric concentrations of the POPs can be derived by dividing the amount of chemical collected on the PUF disk by the product of the deployment period and an average PUF disk sampling rate of 4 m^3/day. Depuration compounds DCs could be added to the PUF disk prior to deployment to assess site-to-site differences in sampling rates (Harner *et al.*, 2006).

They have a high retention capacity for semi-volatile organic compounds (Chakra *et al*, 2009). For the PUF-disk samplers; a three month sampling period uses approximately 270-

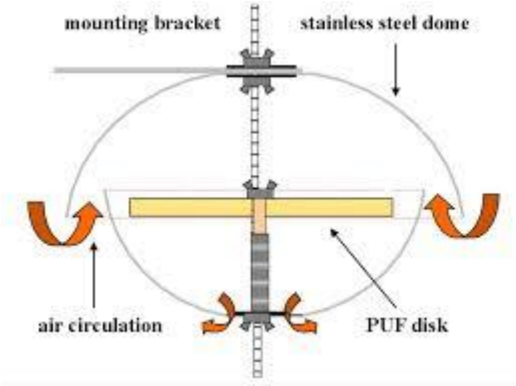
360 m^3 of air volume which may be sufficient for the detection of POPs. Research also shows that most POPs do not change significantly during storage but dehydrochlorinations of α and β-HCH may occur (Weiguang *et-al.*, 2013).

The dependence of sampling rates on the physical- chemical properties of POPs, the effects of environmental variables such as wind speed and temperature on sampling rates, and uncertainty about the proportion of particle-bound POPs sampled by PUF-PAS is still under investigation. Despite the shortcomings of PAS, their obvious utility outweighs their disadvantages (Lisa *et al.*, 2011). Several passive air sampler types have been recently developed and applied to air monitoring of POPs. These include semi permeable membrane devices (SPMDs), polyurethane foam (PUF) disks, samplers employing XAD-resin, and Polymer-Coated Glass (POGs) (Harner, *et al.*, 2005).

Passive air samplers using PUF filters are suitable to study vapor-phase air concentrations of some types of POPs, particularly more volatile compounds from the group of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorinated pesticides. Passive samplers can be used for point source evaluation in the scale of several square kilometres or even less from the local plants to diffusive emissions from transportations or household incinerators as well as for evaluation of diffusive emissions from secondary sources (Jana *et al.*, 2005).

Most types of passive samplers collect mainly volatile compounds, thus omitting a portion of pollutants that are less volatile, and are associated with particulate matter (Shoeib and Harner, 2002). Moreover, the volume of sampled air cannot be measured precisely so it is difficult to normalize concentrations of pollutants on volumetric basis (Harner *et al.*, 2004). However, the advantages make this approach convenient for long-term monitoring (Jana *et al.*, 2005) even at localities without expert technical support, such as Africa, where active sampling would be more difficult (Anita *et al.*, 2014). PAS are small, easy to assemble, cheap to produce and deploy, and can be used by an untrained operator (Chakra *et al.*, 2009).

The outdoor PUF-based passive air sampler mainly consists of the chamber (made of two stainless steel bowls) to protect the PUF disk from light and rain, and to minimise the effect of wind speed on the uptake of chemical on the PUF disk. The disk is placed in the middle of the chamber and is supported by metal rods on metal clamps (Chakra *et al.*, 2009) as shown in Figure 2.2 The polyurethane foam disks have 15 cm diameter, 1.5 cm thickness and a density of 0.030 g cm^{-3}, type N 3038; Gumotex Breclav, Czech Republic).



Source; MonAirNet project

Figure 2.2: Schematic diagram of the passive air sampling device

Polyurethane foam (PUF) passive air samplers (PAS) are a common and highly useful method of sampling persistent organic pollutants (POP) concentrations in air. They were successfully applied as a tool for POPs monitoring on the global and regional levels e.g. under the global monitoring plan 2008-2012 (GMP, 2015). PAS were used in this study because they are small, relatively inexpensive, simple to deploy and do not require electricity (Harner *et al.*, 2005). The mass of chemical accumulated over time can be converted to an estimated air concentration. Deployment times- months enable detection of a wide range of compounds in large scale ambient sampling campaigns (Jaward *et al.*, 2004)and (Jaward *et al.*, 2005).

CHAPTER THREE

MATERIALS AND METHODS

3.1 The Study Area

Nairobi, the capital city of Kenya is located at the south-eastern end of Kenya’s agricultural heartland, at approximately **1° 9’S, 1° 28’S** and **36° 4’E, 37° 10’E**. It occupies an area of about 696 km^2 and the altitude varies between 1,600 and 1,850 metres above sea level (Mitullah, 2003). The western part of Nairobi is on high ground (approximately 1700–1800 m) with rugged topography, the eastern side is generally low (approximately 1600 m) and flat (Saggerson *et al.*, 1991). It is the administrative, commercial and industrial city of Kenya. Commercial and administrative activities are concentrated at the commercial business centre while most of the industrial activities are located to the south East. According to a report by the Japanese International cooperation Agency, Nairobi is the most industrialized urban centre in Kenya and in East Africa in general (JICA, 2004). A total of 338 industries have registered with the Directorate of Occupational Health and Safety (DOHS) (JICA, 2004). Out of these, 123 are located in the industrial area, 53 in the central business district (CBD), 28 along Mombasa road and the rest dispersed in other parts of the city (JICA, 2004).

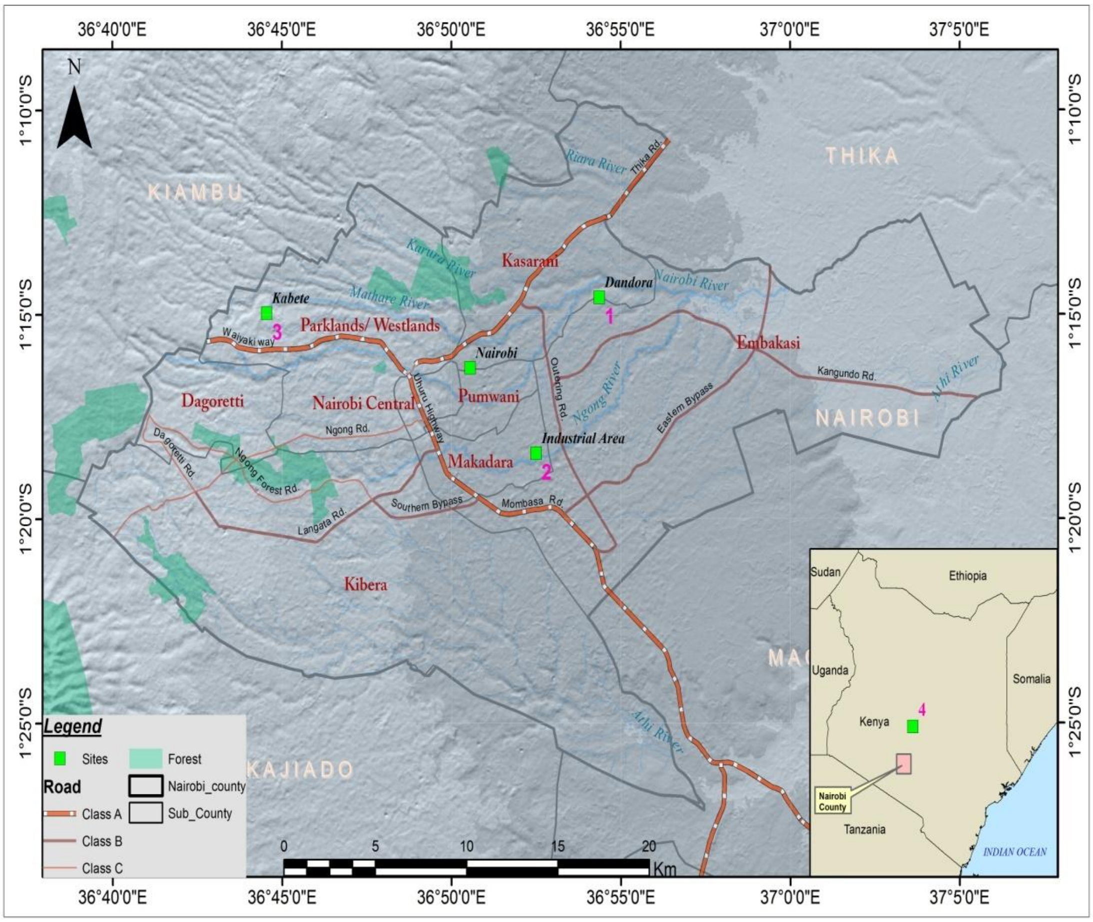


Figure 3.1 Map of the study area

3.2 Population, Climate and Economic Activities in the Study Area

The population of Nairobi is estimated to be about 3.4 million inhabitants (APHRC, 2014). Rapid population growth of about 4.6 per year has led to high congestion. The city has a population density of 3080 persons per square kilometre compared to 50 persons per sq. km countrywide (Omwenga, 2011).

Nairobi has a subtropical climate with four major seasons: the warm dry season (December – February) the long rainy season (March - May), the cool and dry season (June-October) and the short rainy season (October - November). Temperatures generally vary from 12^0C during the cold season to 29^0C during the warm and dry season from December -March. These seasons have changed in the recent past. During the sampling period, the months of July to October were predominantly cool and dry, November to January months were predominantly warm and dry while the months of February to April were generally wet.

Key physical features include the Nairobi, Ngong and Mathare rivers and the indigenous Karura forest in northern Nairobi. The Ngong hills stand towards the west, Mount Kenya towards the north and Mount Kilimanjaro towards the south-east. Nairobi is adjacent to the Rift Valley hence minor earthquakes and tremors occasionally occur (UNEP, 2005).

Air pollution in Nairobi is mainly as a result of anthropogenic activities. The main sources of atmospheric pollution are vehicles, industries, emissions from the use of charcoal and firewood for energy, and other municipal sources such as the open dumping of waste. Air pollution adversely affects human health, properties and the environment. Compared to other urban centres in Kenya, Nairobi has the greatest concentration of industrial and vehicle air pollutant sources (Mulaku and Kairui, 2001).

3.3 Sampling Sites and Plan

This study covered three sites in Nairobi on the basis of potential anthropogenic sources of POPs. The county council dumpsite in Dandora and Industrial area served as the hot spots and Kabete as an urban agricultural background site. Remote mountainous, alpine regions are identified as important ‘‘early warning’’ sites with respect to global and medium-range transport, as well as for distribution processes for semi volatile POPs (Roland, 2005), therefore this study was extended to Mt. Kenya as a representation of a high altitude area near Nairobi (Figure 3.1). Air sampling was done three times, in July to October 2012 which were predominantly cool and dry months to represent the cool dry season, October to January 2013 to represent the warm and dry season and January 2013-April 2013 which were wet months to represent the long rain season to capture the effects of different seasons and human activities on the levels of POPs in air. Soil samples were collected in October, January and April. The four sampling sites (Figure 3.1) were selected in the study area based on the levels of human interference (low vs. high human impact) and air pollution.

The passive air samplers were deployed at the four sites; Dandora, Industrial area, Kabete and Mt. Kenya and replaced after every 90 days (three months) and soil samples were also collected from the sampling sites described in Sections 3.3.1,3.3.2, 3.3.3 and 3.3.4.

3.3.1 Dandora Municipal Dumpsite Sampling Site

Dandora dumpsite is located south-east of Nairobi city at 036^{0}53’17”E, 01^0 15’ 05S and at an altitude of 1625 m. It is situated in a densely populated low income residential area. Nairobi has one official disposal site (County government-owned and operated) situated in Dandora, Eastland, about 7.5 km from the city centre, where about 30 per cent of the wastes collected are dumped (AfDB, 2002). Dandora dumpsite is adjacent to the Nairobi River. It was selected as a primary point source of POPs (Figure 3.1). During the three sampling sessions, the dumpsite was strewn with large heaps of solid waste consisting of unsorted paper, plastics, metals and organic remains. Studies have shown that 68 per cent of waste is from domestic sources, 14 per cent industrial, 8 per cent roads, 2 per cent hospitals, 1 per cent markets and 7 per cent from other sources (NEMA, 2003). There was open air burning of the waste and the situation was aggravated by the fact that waste was not sorted at source, so hazardous waste such as that from clinics was mixed together with manufacturing and biodegradable waste. An unpleasant odour lingered in the air at the site. The soil was bare and was mixed up from time to time as new waste was dumped. This is a hot spot for monitoring new POPs. The passive air samplers were placed at the roof top of the county government weighbridge office, about 2.5 m above the ground.

Table 3.1: Description of Sampling Sites

Site	Local Name	GIS		Altitude (m)	Human activities around the sampling sites
1	Dandora dumpsite	036^{0}53’ 17”E	01^{0} 15’ 05S	1625	The dumpsite strewn with large heaps of solid waste consisting of unsorted paper, plastics, metals and organic remains, open air burning of the waste. The samplers were deployed at a height of 2.5 m above the ground
2	Industrial area	036^{0}52’ 30”E	01^{0}18’24”S	1623	The sampling site was at the vehicle inspection unit. It was surrounded by industries. The air samplers were deployed on a metal frame at a height of 1.5 m above the ground.
3	Kabete	036^{o} 44’ 33”E	01^{o} 14 58” S	1841	The site has low human settlement with no industrial activities. There were agricultural activities around the site. Soil was covered with grass. The samplers were deployed on a metal frame at a height of 1.5 m above the ground.
4	Mt. Kenya	037^{0} 17’84’’ E	00^{0} 03’ 75’’S	5199	The highest mountain in Kenya. Lies in the North-East of Nairobi. Its climate, flora and fauna vary with altitude. The samplers were deployed on a metal frame at a height of 1.5 m above the ground. The samplers were installed at an altitude of 4500m

3.3.2 Industrial Area Sampling Site

The Nairobi’s industrial area is located east of the city centre. This served as the representative site for monitoring industrial sources of the new POPs in the study (Figure 3.1). The sampling site was situated at the motor vehicle inspection unit situated at **036^{0}52’30”E, 01^{0}18’24”S** standing at an altitude of 1623 m. The soils at the site were covered with grass. The air samples were collected through the suspension of the air samplers on a metal frame at a height of 1.5 m above the ground.

3.3.3 Kabete Sampling Site

Kabete campus of the University of Nairobi is on the western side of the city of Nairobi (Figure 3.1). It has a low human settlement with no industrial activities. It is situated about 2 km away from a major highway and serves as the urban background site in the study. There were agricultural activities around the site. The soil at the site was covered with grass. Soil and air samples were obtained from the premises of the Kabete Meteorological station situated at **036^o 44’ 33” E, 01^o 14 58” S** (Table 3.1) and standing at 1841 m above sea level.

3.3.4 Mount Kenya Sampling Site

Mt. Kenya was considered as a remote area in this study (Figure 3.2). It is located east of the great rift valley about 175 km north-east of Nairobi with its flanks across the equator. It is situated at **037^0 17’84’’E, 00^0 03’ 75’’S**. Vegetation varies with altitude and rainfall (Table 3.1). Continuous vegetation stops at about 4500 m although isolated vascular plants have been found at over 5000 m. As the climate warms, the vegetation is expected to shift higher up the mountain. The samplers were installed at an altitude of about 4500m. They were suspended on metal frames at a height of 1.5m above the ground.

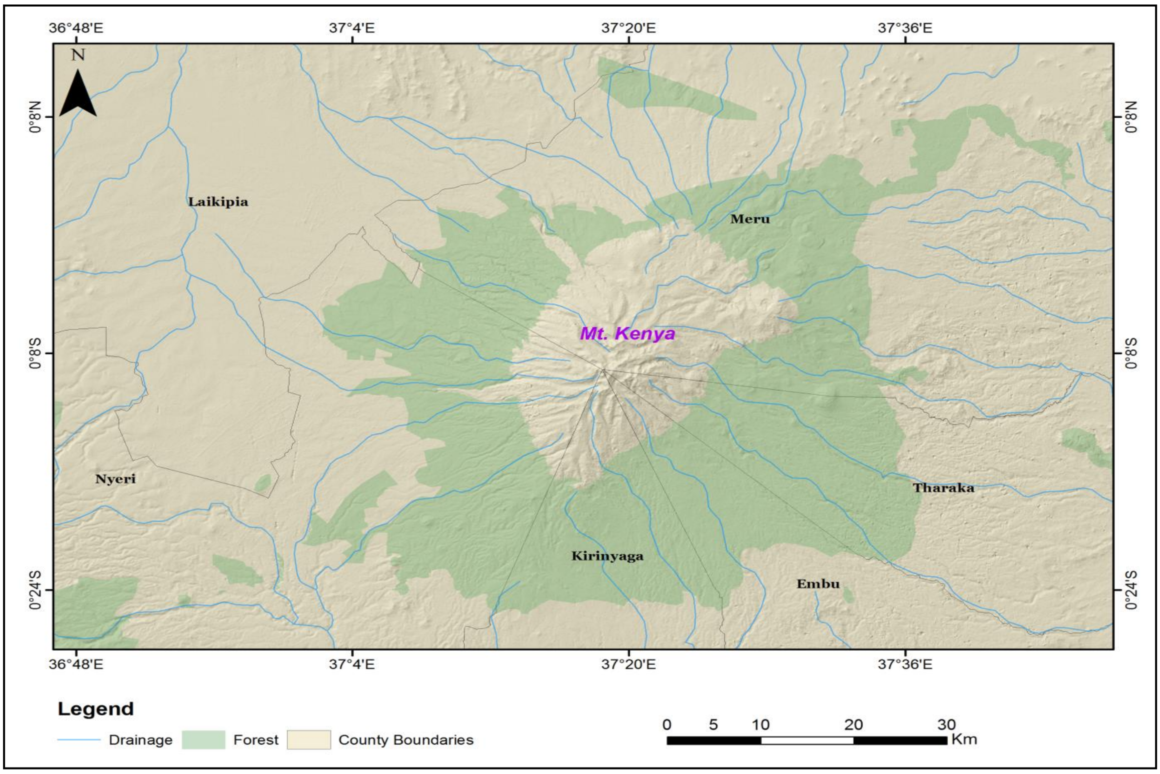


Figure 3.2: Map of the Mount Kenya Region

3.4 Sample Collection

3.4.1 Passive Air Sampling

Passive air samplers consisting of polyurethane foam disks (15 cm diameter, 1.5 cm thick, density of 0.030 g cm^{-3}, type N 3038; Gumotex Breclav, Czech Republic) housed in protective stainless steel chambers were employed in this study. Passive samplers were deployed over three-month periods (July -October 2012, October 2012- January 2013, January 2013- April - 2013). Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All filters were prewashed, cleaned (8 hours extraction in acetone and 8 hours in dichloromethane), wrapped in two layers of aluminium foil, placed into zip-lock polyethylene bags and kept in a freezer prior to deployment. Exposed filters were wrapped in two layers of sterile aluminium foil, labelled and placed in self-sealing polythene bags and stored in polyurethane cool-boxes containing dry ice. In the laboratory samples were kept in a freezer at ≤ -19 ° C to await extraction. Pesticide residue levels analysis was done within 7 days.

3.4.2 Soil Sampling

Due to the interaction of the new POPs with their environment as illustrated in Figure 2.1, soil samples were collected from under the air samplers within an area of 16 m^2. Grass or vegetation from the soil surface was removed and soil dug up to about 10 cm of relatively homogenous soil in vertical direction. 200 g of soil from four different points in one sampling site of the 16 m^2 were dug. These were then put on aluminium foil mixed to form a composite sample from which 500 g were taken to the laboratory for analysis. A cleaned stainless shovel was used. Roots, leaves and stones were removed from each sample. The soil samples were then packed in two layers of aluminium foil, placed in zip-lock plastic bags and placed in cooling boxes at 4 ° C and transported to the laboratory for storage in a freezer at -18 °C awaiting extraction.

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

3.5 Materials and Chemicals

The chemicals used were of analytical grade and were obtained from international suppliers, including Fisher Scientific (USA) and Aldrich Chemicals. Organochlorine pesticides reference standards were obtained from LoIc (Warsaw: Puder, Poland). All the general purpose solvents (acetone, dichloromethane and hexane), used were triply distilled before use. All other solvents i.e. diethyl ether and HPLC grade hexane were not distilled as these were bought at 99% purity. HPLC grade isooctane was used as a keeper during concentration of the extracts after extraction, clean-up and fractionation while HPLC grade hexane was used for rinsing. Anhydrous sodium sulphate (drying agent), was activated at 200 ˚C before use. The activated anhydrous sodium sulphate was then cooled in a dessicator. Analytical grade neutral aluminium oxide for sample cleanup was prepared by baking in a Memmert UM 400 oven at 200 ^{0}C overnight and cooled in a dessicator. Alumina was used as the adsorbent for cleanup of sample extracts. Activated aluminium oxide was deactivated by treating with 8% (w/w) distilled water and allowed to stay overnight before use. Analytical grade neutral silica was prepared by baking it in a Memmert UM 400 oven at 200 ^{0}C overnight and cooled in a dessicator. The activated silica was deactivated by treating with 1.5% (w/w) distilled water and allowed to stay overnight before use. It was then mixed to obtain a homogenised powder which was allowed to stay for 12 hours to condition before use. HPLC grade hexane and diethylether were used in fractionating air samples while triple distilled hexane and HPLC grade diethylether were used in fractionating soil samples. Activated copper was used for sulphur removal from soil samples. Labconco rotary evaporator loaded with water bath (IKA-Wasserbad WA) and a vacuum pump (Welch 1399, Duaseal) was used for concentration of the sample extracts. The detergents were bought from the supermarkets. Glassware and crucibles were soaked in detergent water for at least two hours, washed with tap water, rinsed with distilled water and finally with triply distilled acetone. The apparatus were then dried in a Gallenkamp oven for 4-5 hours at 105˚C before use.

3.6 Extraction and Clean-up of Air Samples

3.6.1 Air Samples Extraction

The PUF sorbents initially stored in the freezer at -19 ˚C were removed and allowed to attain room temperature for 6 hours. The polyurethane foams were placed in the extraction thimbles and spiked with 100 µg/ml isodrine standard. 200 ml of dichloromethane (DCM) was transferred to a round bottomed flask and boiling chips added for smooth boiling. The samples were extracted in a soxhlet extractor for 16-18 hours (overnight).

1 ml of isooctane was added as a keeper and the extract concentrated on a rotary evaporator to 3 ml. The extract was then transferred to a clean tube and the flask rinsed 3 times with 1 ml hexane. The extract was then concentrated under a gentle stream of nitrogen to 1 ml.

3.6.2 Clean Up of Air Samples

The concentrated sample extract was cleaned by using 15 g deactivated neutral alumina column and eluting with 165 ml of HPLC grade hexane. A 25 cm long glass column (with frit) with sintered glass bottom was packed with 1 cm anhydrous sodium sulphate, followed by 15 g deactivated alumina then topped with 1 cm anhydrous sodium sulphate while gently tapping the sides to ensure that the alumina settled uniformly in the column. The column was conditioned with 20 ml HPLC hexane and discarded. The sample was gently transferred on top of the anhydrous sodium sulphate and allowed to elute through the stationary phase. The sample vial was rinsed 3 times with 1ml portions of HPLC hexane and transferred into the column. The sample was then eluted further with 165 ml of HPLC hexane and collected in a 500 ml round bottomed flask. 1ml of isooctane was added to the cleaned sample and concentrated using rotary evaporator to 2 ml then transferred into a glass vial and further reduced to about 0.5 ml under a gentle stream of nitrogen at room temperature.

3.7 Extraction and Clean Up of Soil Samples

3.7.1 Soil Sample Extraction

10 g of each sample was thoroughly mixed with desiccant (30 g, anhydrous sodium sulphate activated at 200 ^{o} C) to dry the samples and then ground to powder in a mortar. The samples

were covered with aluminium foil and allowed to stay overnight to dry further before extraction. The samples were transferred into the Soxhlet thimbles and spiked with 100 µl of isodrine as an internal standard. 175 ml hexane: acetone (3:1v/v) extracting mixture was transferred into 250 ml round bottomed flasks and placed onto the heating mantle. Three boiling chips were added to the flasks to ensure smooth boiling. The sample was placed into the Soxhlet extractor and fitted onto a round bottomed flask containing the extracting mixture. A Soxhlet condenser was fitted on top of the extractor and extraction done for 16 hours. After extraction, 2ml of isooctane was added to the extract as a keeper before evaporating to 1ml using a rotary evaporator. The extract was transferred into a 20 ml glass vial and the round bottom flask rinsed 3 times with 1ml portions of HPLC grade hexane. The rinses were combined with the sample in the glass tube before concentrating to 1ml under a gentle stream of nitrogen and taken for sample clean-up.

3.7.2 Clean Up of Soil Samples

The concentrated sample extracts were cleaned by eluting with165 ml of HPLC hexane on a deactivated neutral alumina column. A 25 cm long glass column (with frit) with sintered glass bottom was packed with 1cm anhydrous sodium sulphate, followed by 15 g deactivated alumina then topped with 1cm anhydrous sodium sulphate while gently tapping the sides to ensure that the alumina settles uniformly in the column. The column was conditioned with 20 ml HPLC hexane and discarded. The sample was gently transferred on top of the anhydrous sodium sulphate and allowed to elute through the stationary phase. The sample vial was rinsed 3 times with 1ml portions of HPLC hexane and transferred onto the column. The sample was then eluted further with 165 ml of HPLC hexane and collected in a 500 ml round bottom flask. 1ml of isooctane was added to the cleaned sample and concentrated using the rotary evaporator.

3.7.3 Sulphur Removal from Soil Samples

The soil samples obtained may have contained sulphur hence cleanup was required. Activated copper was used for sulphur removal from soil samples. This was done by adding activated copper metal powder to the extract before fractionation whereby the sulphur would be oxidised when copper is added to the extract. The copper was activated by adding 10 ml of 10% HCL to 1 g of copper powder and shaken for a few minutes. The mixture was then centrifuged for 1 minute at 300 rpm, to separate the powder from the liquid. The liquid was discarded and an amount of methanol added to the copper. This mixture was shaken and centrifuged again and the process repeated. The copper was dried with a gentle stream of nitrogen. The dry copper was kept under some hexane before use because the copper would have been oxidised very rapidly.

3.7.4 Soil Characterisation

Soil characterisation was done at the National Agricultural Laboratory (NAL) based at Kenya Agricultural Research Institute (KARI), in Nairobi using the method of Avery and Bascomb, (1982), to ascertain the properties of the soil from the four sampling sites.

3. 8 Fractionation of Air and Soil Samples

Air and soil samples were fractionated because different types of halogenated POPs are often required to be separated into different analytical groups to reduce co-elution problems in chromatography (Weiguang *et al.*, 2013). Fractionation was done by eluting the samples through a silica column. The fractionating column was packed with 1 cm anhydrous sodium sulphate followed by 1.8 g deactivated silica and topped with 1cm layer of anhydrous sodium sulphate. The column was conditioned with 4 ml of isooctane before sample elution. The cleaned sample extract was transferred into the column using a pasture pipette. The glass vial was rinsed three times with 1 ml HPLC grade hexane and transferred onto the column. The fractionation was effected by eluting PCBs with 11 ml HPLC grade hexane in the first fraction and organochlorine pesticides in the second fraction using 10 ml mixture of hexane/ diethyl ether in the ratio of 85:15. Both fractions were analysed by gas chromatography.

3.9 Preparation of the Calibration Curve

The calibration of the gas chromatography (GC) instrument was done using a stock solution of 17 organochlorine pesticides (OCP) standards which include: *alpha* HCH, *beta* HCH, *gamma* HCH, heptachlor, aldrin, heptachlor epoxide, endosulfan, ppDDE, dieldrin, endrin, endosulfan II, ppDDD, endrin aldehyde, ppDDT, endosulfan sulfate and methoxychlor. Eight level calibration series were prepared from the 10 µg/ml of 17 OCP mixture standard stock solutions and appropriate volume transferred directly into autosampler vials. Multilevel calibration curves were developed and used to calculate the concentrations of analytes in the samples using internal calibration method. Measurement of standards and samples was done by taking appropriate volumes and confirming by weighing the exact masses using analytical balance.

3.10 GC Analysis and Quantification of the Samples Extract

Analysis of the persistent organic pollutants-pesticides in air and soil was carried out with a gas chromatograph (Agilent 6890N) in combination with an auto sampler (Agilent 7683 Series injector), and an electron capture detector (Agilent µECD). The Injector and detector temperatures for the Agilent 6890N were maintained at 250 ºC and 300 ºC, respectively. Helium gas was used as the carrier gas and nitrogen as make-up gas with a constant flow rate of 2 ml/min. The injection volume was 1µl with a pulsed splitless injection mode. The following injection temperature program was applied: 90 ºC (3 min), 90 ºC to 200 ºC (at 30 ºC / min and hold time of 15 min), 200 ºC to 275 ºC (at 30 ºC /min and hold time of 5min). The column was a high performance capillary column, (length of 30 m, internal diameter of

0.25 mm and film thickness of 0.25 μm). Data processing was done using Chemstation software.

3.11 Integration and Quantification of GC Chromatograms

Chemstation software was used for evaluation of the chromatograms and calculation of the concentrations in the samples. The calibration curves were constructed for all compounds using Chemstation. The system linearity was checked for each compound before consideration of the calibration curve. Quantification of individual POPs in the sample was done using individual calibration curves of each analytes in a standard mixture of 17 0rganochlorine pesticides (OCPs). Reagent blanks and replicate samples were subjected to exactly the same analytical procedures as those used for actual samples. Isodrine was used as an internal standard to check the recoveries.

3.12 Quality Assurance and Quality Control

Analysis of air samples was done in duplicate while soil samples were done in triplicate to verify the presence of the analytes in the samples. Sample blanks, spiked samples were included in the sample extraction, cleanup and fractionation to verify the method performance. The use of internal standard (isodrine) was applied to check the recoveries.

Blank Polyurethane foam plugs pre-extracted using dichloromethane were wrapped in aluminium foil then carried in zip-lock polyethylene bags to the field during each sampling trip. This were stored and treated in the same way as air samples to serve as field and laboratory blanks for air. They were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 5% of the quantities detected in samples for POPs indicating minimal contamination during transport, storage and analysis therefore no blank correction was necessary (Harner *et al*., 2006).

3.13 Statistical Data Analysis

Statistical analyses were performed using Excel and SPSS. Correlation analysis was done to establish seasonal variations. Results obtained were presented by use of text, graphs and statistical tables.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 RESULTS

4.1 Multi Level Calibration Curves

Quantification was based on calculations from calibration curves in the concentration range of 0.005 ppm to 1ppm for all the organochlorine pesticides analysed. The calibration curve of the standard was a straight line for all the seventeen compounds and the best line of fit drawn from plotting the relative response factor, that is, ratio of instrument response (peak area), against the analytes concentration. All analytes lines gave a correlation factor (R^2) above 0.9980 indicating a high correlation between instrument response ratio and analytes concentration. The multi-level calibration curves were used to quantify the new POPs in air and soil samples. The calibration curves for the new POPs that were analysed in this study are given in the Appendix III.

The correlation coefficients for the calibration curves ranged between 0.989- 0.9996 as shown in the Table 4.1

Table 4.1: The correlation coefficients for calibration curves

New POP	Correlation coefficient for calibration curve
Alpha HCH	0.9994
Beta HCH	0.9983
Gamma HCH	0.9990
Endosulfan	0.9996
Endosulfan II	0.9986
Endosulfan sulfate	0.9890

4.2 Chromatograms of the New POPs in Air and Soil Samples

Some sample chromatograms of soil and air samples are given in Appendix IV. The concentrations of the new POPs in air and soil were determined by interpolation from the calibration curves using Chemstation software.

4. 3 Distribution of the New POPs Residue Levels in Air Samples

Analysis was done for four out of the ten new POPs; *alpha*-hexachlorocyclohexane (α-HCH), *beta*-hexachlorocyclohexane (β-HCH), lindane (γ-HCH), endosulfan, its isomers and metabolite. Chlordecone, perfluorooctane sulfonate and the chlorinated aromatic hydrocarbon were not analysed due to the lack of their reference standard at the pesticide analytical laboratory at the University of Nairobi. Recoveries were higher than 70% for all samples respectively. Recovery factors were not applied to any of the data (Hill, 2000***).*** The levels of the new POPs reported in this work are the average values of the replicate samples.

Tables 4.2, 4.3, 4.4 and 4.5 show the new POPs residue levels detected in air at Kabete, Dandora, Industrial area and Mount Kenya sites, respectively. The levels of the Old POPs and other pesticides analysed in this work are given in Tables 4.12, 4.13, 4.14 and 4.15

4.3.1 Temporal Distribution of the New POPs Residue Levels in Air

4.3.1.1Temporal Distribution of the New POPs Residue Levels in Air at Kabete

In Kabete sampling site, the levels of ∑ new POPs ranged between 4.1236 and 5.6328 ng/M^3 (Table 4.2) with a quarterly average concentration of 4.8504 ng/M^3. All the new POPs analyzed were detected at almost all the sites with *beta* hexachlorocyclohexane (β-HCH) giving the highest residue level of 3.6068±0.2755 ng/M^3 during the July-October sampling session.

Table 4.2: New POPs residue levels in air at Kabete (ng/M^3), N=2

Pesticide/Season	**July/October**	**October/January**	**January/April**	**Average**
α-HCH	0.036±0.004	0.4665± 0.002	0.0210± 0.003	0.1744
β-HCH	3.6068±0.2755	3.0024±0.216	2.6536± 0.003	3.0876
γ-HCH	0.2887± 0.025	0.3599±0.028	0.7249± 0.051	0.4579
α-Endosulfan	0.0441± 0.003	0.4161± 0.007	0.5499± 0.016	0.3367
β-Endosulfan	0.0449± 0.007	0.1201± 0.002	0.0606± 0.0003	0.0752
Endosulfan sulfate	0.1033±0.022	1.2678 ±0.055	0.7847±0.016	0.7186
∑ OCP	4.1236±0.337	5.6328± 0.309.	4.7947±0.165	4.8504

[a]**N=2,** mean ± standard deviation

The residue levels of the other organochlorine pesticides analysed in the Kabete site samples are given in Table 4.12 below.

4.3.1.2 Temporal Distribution of the New POPs Residue Levels in Air at Dandora Site

At the Dandora sampling site, the New POPs residue levels ranged between 3.464±0.260 ng/M³ and 14.374±0.423 ng/M³ with an average of 8.868 ng/M³ for each of the three, 90 day sampling sessions. β-HCH had the highest residue level of 11.508 ±0.016 ng/M³ during the long rain season (January-April sampling session) this was followed by α-Endosulfan with residue levels of 1.303±0.025 ng/M³ in the same period **(**Table 4.3).

Table 4.3: New POPs residue levels in air at Dandora site (ng/M³), N=2

Pesticide/Season	**July/October**	**October/January**	**January/April**	**Average**
α-HCH	0.0784±0.003	0.025±0.017	0.0156±0.003	0.0397
β-HCH	2.1827±0.168	7.09662±0.332	11.5083±0.016	6.9291
γ-HCH	0.104±0.011	1.0969±0.012	0.2976±0.010	0.4996
α-Endosulfan	0.3581±0.038	0.0511±0.005	1.3030±0.025	0.5707
β-Endosulfan	0.0606±0.000	0.077±0.002	0.0997±0.010	0.0791
Endosulfan sulfate	0.6803±0.040	0.4203±0.056	1.1502±0.133	0.7503
∑ OCP	3.4643±0.260	8.7667±0.423	14.3743±0.197	8.8684

^{a}**N=2,** mean ± standard deviation

The levels of α-HCH (0.0397 ng/M³) were the lowest on average while the highest was β-HCH at an average of 6.929 ng/M³. The levels of the other organochlorine pesticides analysed in this study are given in Table 4.13 of Section 4.3.5.

4.3.1.3 Temporal Distribution of the New POPs Residue Levels in Air at the Industrial Area Site

The total mean New POPs residue levels in Industrial area ranged between 7.528 ng/M³ and 11.457 ng/M³ with an average of 9.015 ng/M³ per sampling session. The highest levels were of β-HCH at 9.376±0.429 ng/M³, during the October-January sampling period representing the warm and dry season, this was followed by endosulfan sulfate at 0.829±0.027 ng/M³ during the same sampling period (Table 4.4).

Table 4.4: New POPs residue levels air at the Industrial area site (ng/ M³), N=2

Pesticide/Season	**July/October**	**October/January**	**January/April**	**Average**
α-HCH	0.0651±0.007	0.0130±0.001	0.029±0.002	0.0358
β-HCH	5.7351±0.575	9.3757±0.404	7.8194±0.057	7.6434
γ-HCH	0.0212±0.003	0.4588±0.009	0.0275±0.005	0.1691
α-Endosulfan	0.6954±0.040	0.6954±0.059	0.0341±0.019	0.475
β-Endosulfan	0.0775±0.012	0.0849±0.012	0.1504±0.012	0.1043
Endosulfan sulfate	0.9336±0.0.057	0.8292±0.027	BDL	0.8814
∑ OCP	7.5279±0.693	11.4572±0.512	8.0606±0.094	9.0152

[a]**N=2,** mean ± standard deviation, BDL = below detection limits

On average, the levels of α-HCH were the lowest (0.036 ng/M³) while the levels of β-HCH were the highest at 7.643 ng/M³. The levels of the other Organochlorine Pesticides analysed during this sampling session are given in Table 4.14.

4.3.1.4 Temporal Distribution of the New POPs Residue Levels in Air at the Mt. Kenya Site

Mt. Kenya recorded the lowest concentrations generally with a range of between 0.687 ng/M^3 and 1.334 ng/M^3. β-HCH had the highest levels of 0.649 ng/M^3 during the cool dry reason (July-October); this was followed by endosulfan sulfate at 0.219 ng/M^3 during the same season (Table 4.5). The lowest level recorded was of α-HCH at 0.013 ng/M^3 during the sampling period between January and April.

Table 4.5: New POPs residue levels in air at the Mt. Kenya site (ng/ M^3), N=2

Pesticides/Sites	**July/October**	**October/January**	**January/April**	**Average**
α-HCH	0.0430±0.007	0.0278±0.0001	0.0132±0.002	0.028
β-HCH	0.6492±0.055	0.0603±0.012	0.5888±0.060	0.4328
γ-HCH	0.1646±0.001	0.3069±0.012	0.1579±0.0336	0.2098
α-Endosulfan	0.0509±0.006	0.1869±0.013	0.1869±0.005	0.1415
β-Endosulfan	0.0271±0.004	0.0185±0.009	0.2623±0.029	0.1026
Endosulfan sulfate	0.2191±0.045	0.0870±0.009	0.1246±0.025	0.1436
∑ OCP	1.1539	0.6874	1.3336	1.0583

[a]**N=2,** mean ± standard deviation

The average concentrations for Mt. Kenya were 1.058 ng/M^3 the 90 day sampling session Table 4.14 shows the levels of other Organochlorine Pesticides analysed at the Mt. Kenya site. The sum of the New POPs (∑ new POP) were on averagely highest at the Dandora dumpsite during the rainy season and lowest at the Mt. Kenya site during the three seasons.

The concentrations of α-endosulfan were generally higher than those of β-endosulfan at the Mt. Kenya site. This is because α-endosulfan persists in the environment for a longer period

(800 days) than β-endosulfan (60 days) (POPRC, 2007). The concentrations of β-endosulfan were lower than those of endosulfan sulfate except during the third sampling session where degradation was hindered by the low temperatures (Harris *et al*, 2000). This could also be attributed to the fact that the β-endosulfan isomer may have degraded in the environment to the more stable endosulfan sulfate, hence increasing the concentrations of endosulfan sulfate in the environment (Harris *et al*, 2000).

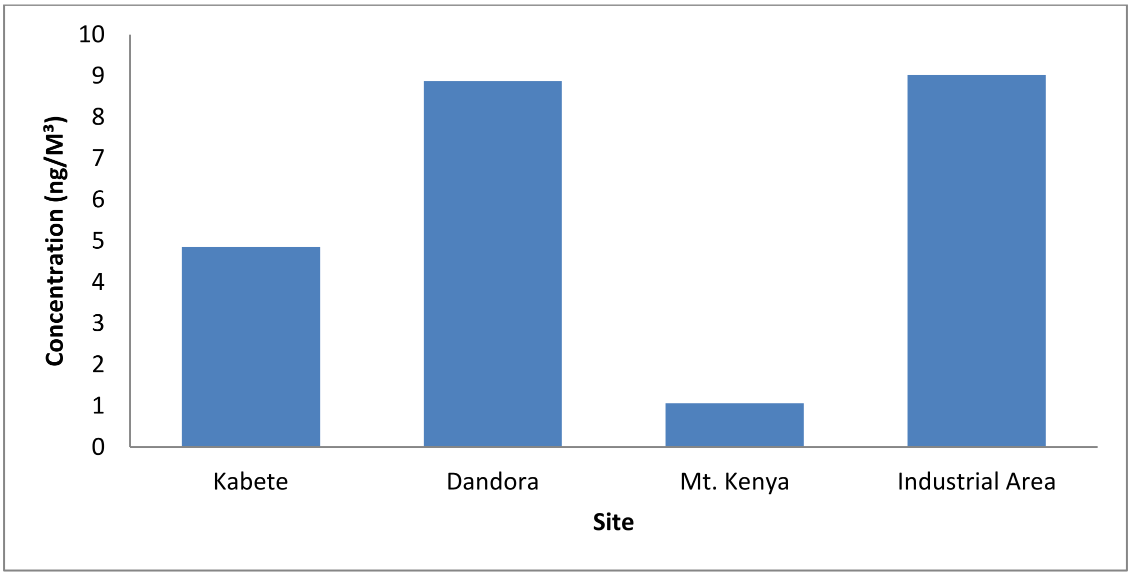
4.3.1.5 Average Temporal Distribution of the New POPs

The distributions of the new persistent organic pollutants in air is discussed for only six compounds among the seventeen organochlorine pesticides (OCP) compounds analysed in this study. Only four are classified among the new POPs. They were detected in all air samples from all sites except endosulfan sulfate at Industrial area whose levels were below the detection limits during the January-April sampling period. Those discussed in this work include; *alpha*-hexachlorocyclohexane, *beta*-hexachlorocyclohexane, lindane (gamma-hexachlorocyclohexane) and endosulfan metabolite; endosulfan sulfate and isomers; α-endosulfan and β-endosulfan. Chlordecone was not analysed because it was not available in the organochlorine pesticides, OCP-17 mix standard used for quantitative analysis in this work.

Table 4.6 shows the average levels of ∑ new POPs, isomers and metabolites residue levels in air samples from all the four sampling sites for all the seasons. This is also shown in Figure 4.1. The average levels of ∑new POPs in air from Mt. Kenya were significantly lower (1.058 ng/M^3) than those from the Kabete, Dandora and Industrial area sampling sites. However the average levels of ∑new POPs in Dandora (8.868 ng/M^3) and industrial area (9.015 ng/M^3) sites are very high (Table 4.6). This is an indicator that Dandora and industrial area are the point sources of the new POPs in Nairobi because of the municipal waste dumpsite and the industrial activities, respectively. Pesticide residue levels detected at the agricultural area of Kabete (4.850 ng/M³) is responsibly higher than those detected at the remote site of Mt. Kenya site (1.058 ng/M³).

Table 4.6: Average levels of the new POPs at the four sampling sites

Site	**Average levels of ∑ new POPs**
Kabete	4.8504
Dandora	8.8684
Mt. Kenya	1.0583
Industrial Area	9.0152



Key: Average levels of all new POPs analysed during the three sampling sessions

Figure 4.1: The average new POPs residue levels in air at the four sampling sites

4.3.2 The Spatial Distribution of POPs Residue Levels in Air

4.3.2.1 The Spatial Distribution of POPs Residue Levels in Air during the First Sampling Session (July-October)

Beta-hexachlorocyclohexane (β-HCH) dominated the composition of the new POPs in the four sampling sites and was followed by endosulfan sulfate and α-endosulfan as shown in Table 4.7 and Figure 4.2. The levels of β-HCH were highest at the Industrial area (5.735±0.575 ng/M^3) and Kabete (3.607±0.276 ng/M^3) sites while endosulfan sulfate and α-endosulfan were high at Industrial area and Dandora sites. The levels of ∑new POPs were highest at the Industrial area site (7.528 ng/M^3) and lowest at the Mt. Kenya site (1.154 ng/M^3), see table 4.7. This may indicate production or use of these compounds in industries in the industrial area site

Table 4.7: The spatial distribution of the New POPs residue levels in air between July and October (cool-dry season) (ng/M^3), N=2

Pesticides/Sites	**Kabete**	**Dandora**	**Mount Kenya**	**Industrial Area**
α-HCH	0.036±0.004	0.078±0.003	0.043±0.00	0.065±0.007
β-HCH	3.607±0.27	2.183±0.168	0.649±0.05	5.735±0.575
γ-HCH	0.289±0.024	0.104±0.011	0.165±0.001	0.021±0.002
α-Endosulfan	0.044±0.038	0.358±0.037	0.051±0.005	0.695±0.039
β-Endosulfan	0.0449±0.007	0.061±0.00	0.027±0.004	0.077±0.010
Endosulfan sulfate	0.103±0.03	0.68±0.039	0.219±0.045	0.934±0.058
∑ OCP	4.124	3.464	1.154	7.528

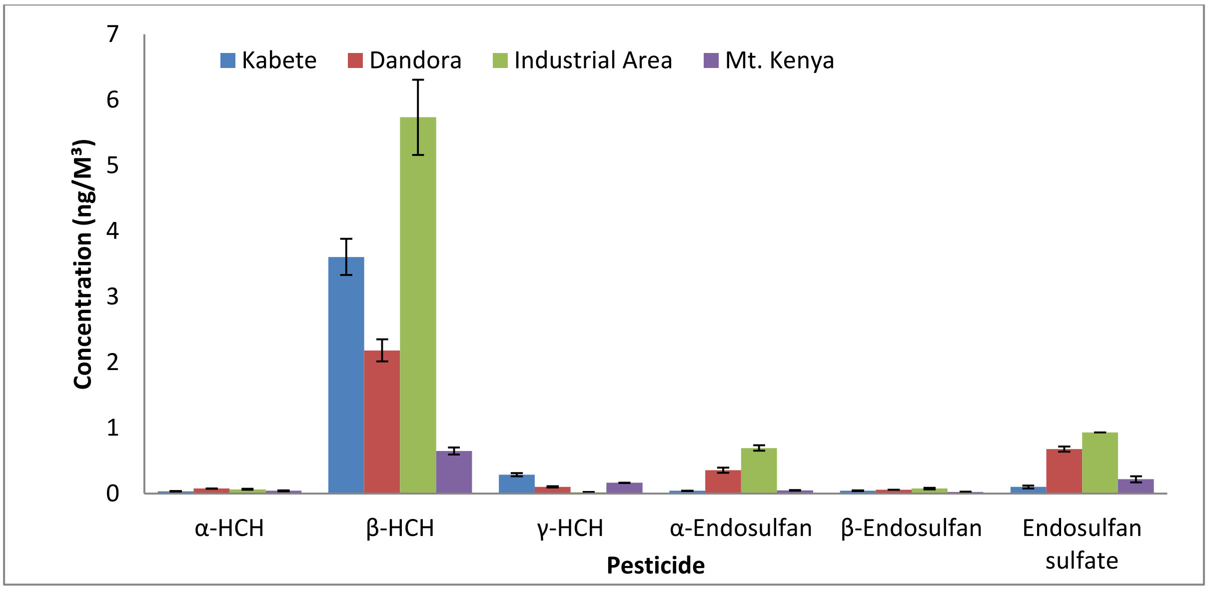


Figure 4.2: The spatial distribution of the new POPs residue levels in air in July-October sampling period in ng/M³

4.3.2.2 The Spatial Distribution of New POPs Residue Levels in Air during the Second Sampling Session (October-January)

The average new POPs residue levels were high in air during the warm-dry season (October-January) are indicated in Table 4.8. These values are also presented in Figure 4.3. β-HCH) was in high levels at three sites and was followed by endosulfan sulfate and γ- HCH (lindane). The levels of β-HCH were highest at the Industrial area (9.376±0.404 ng/M³); Dandora (7.097±0.332 ng/M³); and Kabete (3.002±0.216 ng/M³) sites while endosulfan sulfate and γ- HCH were high at Kabete and Dandora sites respectively (Figure 4.3). The Mt. Kenya site recorded the lowest levels of β-HCH, γ-HCH, β-endosulfan and endosulfan sulfate. During this sampling session, Industrial area recorded the highest level of ∑ new POPs of 11.457±0.512 ng/M³ followed by Dandora (8.767±0.423 ng/M³) then Kabete (5.633±0.309 ng/M³) and lastly Mt. Kenya with the sum of all the new POPs during that session at 0.687±0.055 ng/M³. This shows that Industrial area and Dandora are point sources of this POPs.

Table 4.8: The spatial distribution of new POPs residue levels in air between October and January (warm-dry season) (ng/M³), N=2

Pesticides/Sites	**Kabete**	**Dandora**	**Industrial Area**	**Mt. Kenya**
α-HCH	0.4665± 0.002	0.025±0.017	0.0130±0.001	0.0278±0.0001
β-HCH	3.0024±0.216	7.09662±0.332	9.3757±0.404	0.0603±0.012
γ-HCH	0.3599±0.028	1.0969±0.012	0.4588±0.009	0.3069±0.012
α-Endosulfan	0.4161± 0.007	0.0511±0.005	0.6954±0.059	0.1869±0.013
β-Endosulfan	0.1201± 0.002	0.077±0.002	0.0849±0.012	0.0185±0.009
Endosulfan sulfate	1.2678 ±0.055	0.4203±0.056	0.8292±0.027	0.0870±0.009
∑ OCP	5.6328± 0.309.	8.7667±0.423	11.4572±0.512	0.6874±0.055

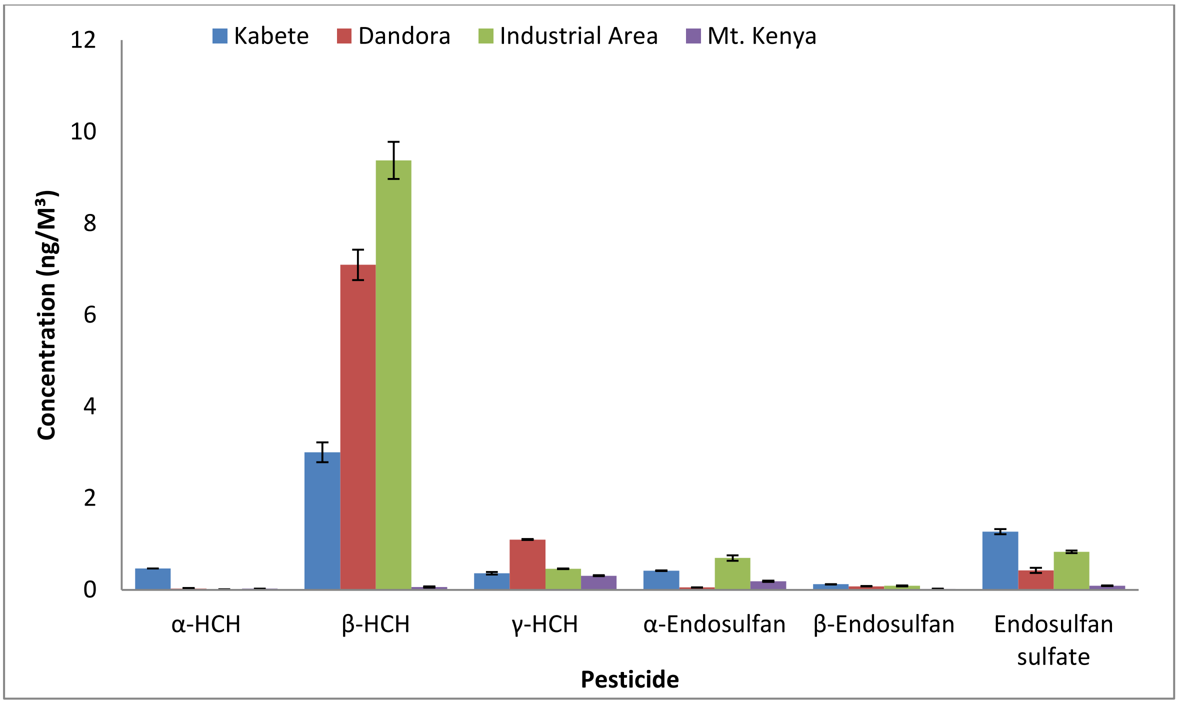


Figure 4.3: The spatial distribution of the new POPs residue levels in air in October-January sampling period in ng/M³

4.3.2.3 The Spatial Distribution of the New Pops Residue Levels in Air During the Third Sampling Session (January- April)

The average new POPs residue levels in air during the third sampling session (January-April 2015) are indicated in Table 4.9. These values are also presented in Figure 4.4.

During the third sampling session which represented the wet season (January-April), Dandora had highest ∑ new POPs residue levels (14.374±0.197 ng/M³) followed by Industrial area (8.061±0.094 ng/M³), Kabete (4.795±0.165 ng/M³) and Mt. Kenya (1.334±0.154 ng/M³) sites (Table4.9).

Table 4.9: The spatial distribution of the New POPs residue levels in air between January and April (ng/M³), N=2

Pesticides/Sites	**Kabete**	**Dandora**	**Industrial Area**	**Mt. Kenya**
α-HCH	0.0210± 0.003	0.0156±0.003	0.029±0.002	0.0132±0.002
β-HCH	2.6536± 0.003	11.5083±0.016	7.8194±0.057	0.5888±0.060
γ-HCH	0.7249± 0.051	0.2976±0.010	0.0275±0.005	0.1579±0.0336
α-Endosulfan	0.5499± 0.016	1.3030±0.025	0.0341±0.019	0.1869±0.005
β-Endosulfan	0.0606± 0.0003	0.0997±0.010	0.1504±0.012	0.2623±0.029
Endosulfan sulfate	0.7847±0.016	1.1502±0.133	BDL	0.1246±0.025
∑ **OCP**	4.7947±0.165	14.3743±0.197	8.0606±0.094	1.3336±0.154

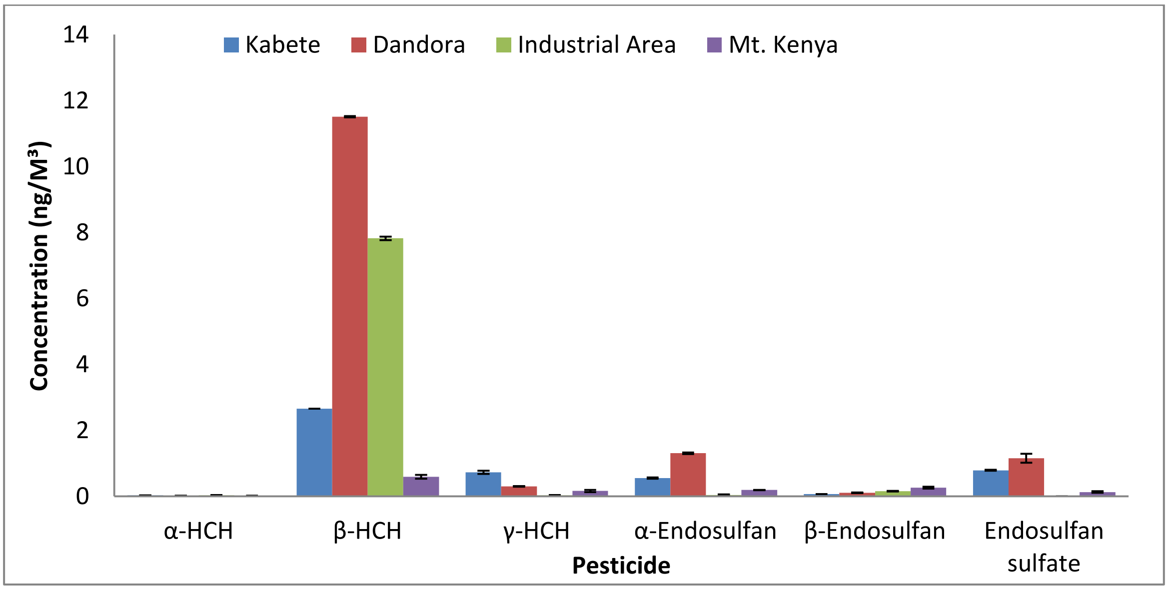


Figure 4.4: The average new POPs residue levels in air in January-April sampling period

4.3.2.4: Average Spatial Variation of the New POPs at the Four Sampling Sites

The highest mean of *alpha*-hexachlorocyclohexane was detected at the kabete site (0.174 ng/M³) while the lowest levels were detected at the Mt. Kenya site (0.028 ng/M³). The high levels at Kabete could be attributed to application and post application volatilization due to the agricultural activities at the site (Jana *et al.*, 2005).

Table 4.10: Average levels of the new POPs in air at the four sampling sites in ng/M³

Pesticides/Sites	**Kabete**	**Dandora**	**Industrial Area**	**Mt. Kenya**
α-HCH	0.1744	0.0397	0.0358	0.028
β-HCH	3.0876	6.9291	7.6434	0.4328
γ-HCH	0.4579	0.4996	0.1691	0.2098
α-Endosulfan	0.3367	0.5707	0.475	0.1415
β-Endosulfan	0.0752	0.0791	0.1043	0.1026
Endosulfan sulfate	0.7186	0.7503	0.8814	0.1436

The concentrations of *beta*-hexachlorocyclohexane (β-HCH) were the highest among all the new POPs analysed in study. They ranged between 7.643 ng/M³ at the Industrial area site and 0.433 ng/M³ at the Mt. Kenya site. The high levels of β-HCH mostly result from extensive use, former production, disposal sites and stockpiles (POPRC, 2007). The chemical structure of β-HCH also confers the greatest physical and metabolic stability hence its high concentrations at the Dandora, Industrial area and Kabete sites (POPRC, 2007). *Alpha* and *beta* hexachlorocyclohexane are also unintentionally produced as by-products of lindane production (Stockholm Convention, 2008). Lindane (γ- HCH) was detected at all the four sampling sites. Its production and agricultural use are the main causes of environmental contamination (EPA, 2006). It is still in use as a second-line pharmaceutical treatment for lice and scabies (Eliane, 2009). Since it relatively persists in the environment and is transported long distances by global distillation, it was detected at all the sites though in low levels ranging from 0.497 ng/M^3 at the Dandora site and 0.169 ng/M^3 at the Industrial area site (POPRC, 2007).

Endosulfan is degraded in the environment and metabolised in living beings (Derek et al. 2009). The endosulfan isomers; α-endosulfan, β-endosulfan and the metabolite; endosulfan sulfate were detected in all the sites in relatively low concentrations. The concentrations for α-endosulfan ranged between 0.142 ng/M^3 at the Mt. Kenya site and 0.571 ng/M^3 at the Dandora site. The average concentrations of β-endosulfan ranged between 0.075 ng/M^3 at the Kabete site and 0.104 ng/M^3 at the Industrial area site. Those for the metabolite endosulfan sulfate ranged between 0.144 ng/M^3 at the Mt. Kenya site and 0.750ng/M^3 at the Dandora site. The low concentrations of endosulfan suggest that the four sites may not be point sources of this POP. Since it is applied to crops using air-blast or ground boom sprayers, it may have drifted or long-range transported from other point sources (Derek et al., 2009).

Endosulfan-I (α-endosulfan) and endosulfan-II (β-endosulfan) persist in the environment for 800 and 60 days respectively (POPRC, 2007). There is a continuous degradation of isomer β-endosulfan to the metabolite in soil and sediment (Harris *et al.,* 2000). This explains the very low concentrations of β-endosulfan in all the sites compared to the concentrations of α-endosulfan and endosulfan sulfate. The relatively high concentration of β-endosulfan at the Mt. Kenya site could be attributed to the halting of the degradation of the same during winter (Harris *et al*, 2000) considering the cool climatic conditions at the Mt. Kenya sampling site. The average spatial distribution of the new POPs pesticides is shown in Figure 4.5.

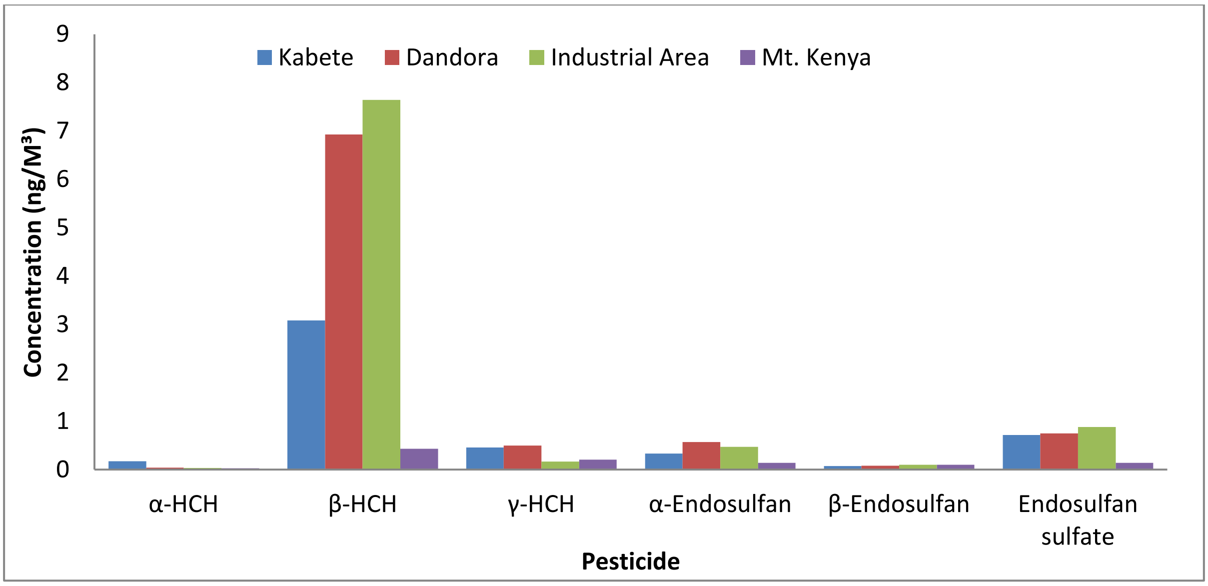


Figure 4.5: Spatial variation of the average levels of individual new POP in air at the four sites

4.3.3 Seasonal Variation of the New POPs in Air

The main seasons captured during the study were the cool/dry season (July to October), warm and dry (October to January) and wet season (January to April) to represent the short rain, warm-dry and long rain seasons, respectively. The levels of ∑ new POPs in Kabete and Mt. Kenya were fairly constant while in Industrial area and Dandora they varied across the seasons as shown in the Table 4.11. This is attributed to the fact that Industrial area and Dandora could be point sources of the new POPs. The seasonal variations in levels of the new POPs in air are further illustrated by the Figure 4.6.

Table 4.11: Seasonal variation of the new POPs in air in ng/M³, N=2

Site/Season	Cool/Dry	Warm/Dry	Wet	Average
Kabete	4.1236	5.6328	4.7947	4.8504
Dandora	3.4643	8.7667	14.3743	8.8684
Industrial Area	7.5279	11.4572	8.0606	9.0152
Mt. Kenya	1.1539	0.6874	1.3336	1.0583

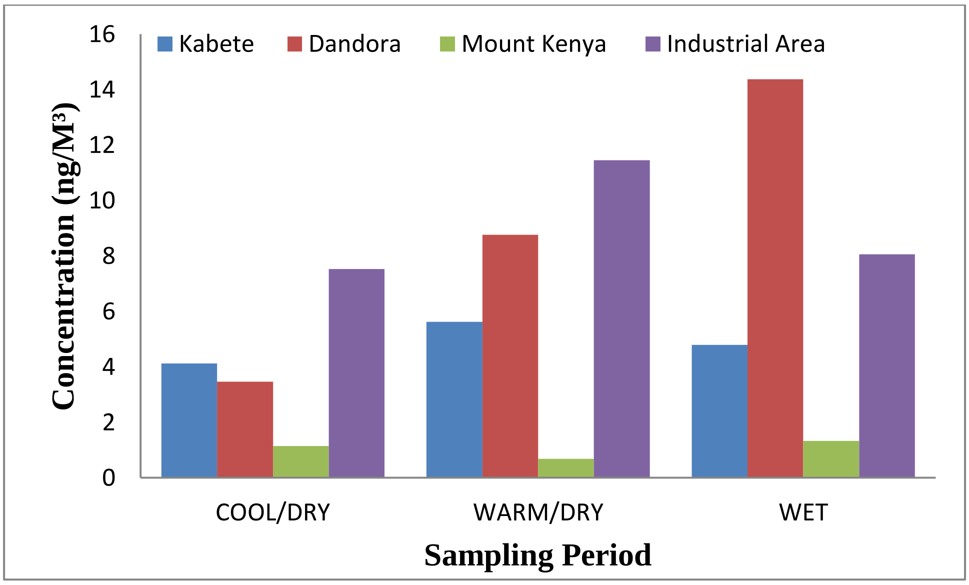


Figure 4.6: Seasonal Variation of the New POPs in Air

The average levels of ∑new POPs at the Kabete and industrial area sites were high during the warm- dry seasons. This is due to high temperatures favouring volatilisation of compounds from soil (Jana *et al.*, 2005). The seasonal variations of the levels of POPs in air at the Kabete site and Industrial area sites were similar. There was an increase in levels of new POPs from 4.124ng/M³ in the cool season to 5.633 ng/M³ in the completely warm-dry season, and then decreased slightly to 4.795 ng/M³ during the wet season at the Kabete site. This trend was replicated at the industrial area site. The relatively low levels recorded during the wet season could be as a result of wet deposition which accounts for wash out of the compounds from the atmosphere (Cerrillo *et al*., 2004).

The trend was different at the Dandora and Mt. Kenya sites. At the Dandora site, the levels of new POPs increased from 3.464ng/M³ in the cool season to 8.767ng/M³ in the warm-dry season. The highest levels of the compounds at the Dandora site were recorded during the wet season at 14.374 ng/M³. This could be attributed to change in the quantities and components of the waste dumped at the site which is one of the localised sources of the contaminants, wind speeds and increased volatilisation of compounds from the dumped waste favoured by high temperatures (Lisa *et al*., 2011).

The average levels remained relatively low at the Mt. Kenya site during the sampling seasons. The highest levels of the new POPs recorded at the Mt. Kenya site was 1.334 ng/M³ while the lowest was 0.687 ng/M³ during the warm-dry season. The climatic conditions at the Mt. Kenya site were different from the climatic conditions at the other sites. It was cold during the three sampling seasons. Lack of anthropogenic activities at the Mt. Kenya site can also explain the low levels of POPs in ambient air.

It was expected that the concentrations of these compounds should be high at point sources during the cold seasons because of poorer dispersion during cool seasons which leads to higher concentrations of pollutants at the source (Derek *et al.*, 2009). This trend was not witnessed instead the levels of the new POPs probably increased during the warm-dry season due to volatilisation of these compounds from contaminated soil because soils have a huge retention capacity and may act as re-emission sources to the atmosphere (Dvorska, *et al.*, 2008). Contrary observations made imply the impact of other factors such as wind direction and speed (Lisa *et al*., 2011).

The most abundant new POP at all the four sites was *beta*-Hexachlorocyclohexane. High levels of β-HCH mostly result from extensive use, former production, disposal sites and stockpiles. The chemical structure of β-HCH confers the greatest physical and metabolic stability (POPRC, 2007) hence the high concentrations at the Dandora, Kabete and Industrial area sites. The high levels could also be associated with the fact that, in the environment, α-HCH and γ-HCH can be converted to β-HCH (Luo *et al.*, 2013).

4.3.3.1 Seasonal Variations of the Levels of the New POPs in Air at the Four Sampling Sites

Figures, 4.7, 4.8, 4.9 and 4.10 show the levels of the new POPs at the four sampling sites during the three seasons. The levels of β-HCH increased during the warm and dry season at the Dandora and Industrial area sites due to volatilisation or dumping or industrial activities but decreased at the Kabete and Mt. Kenya sites. This could be because the two sites are not hot-spots and the β-HCH in the soil may not have volatilised during the warm season because β-HCH is more soluble and it partitions more strongly in water and soil (Li *et al.*, 2005).

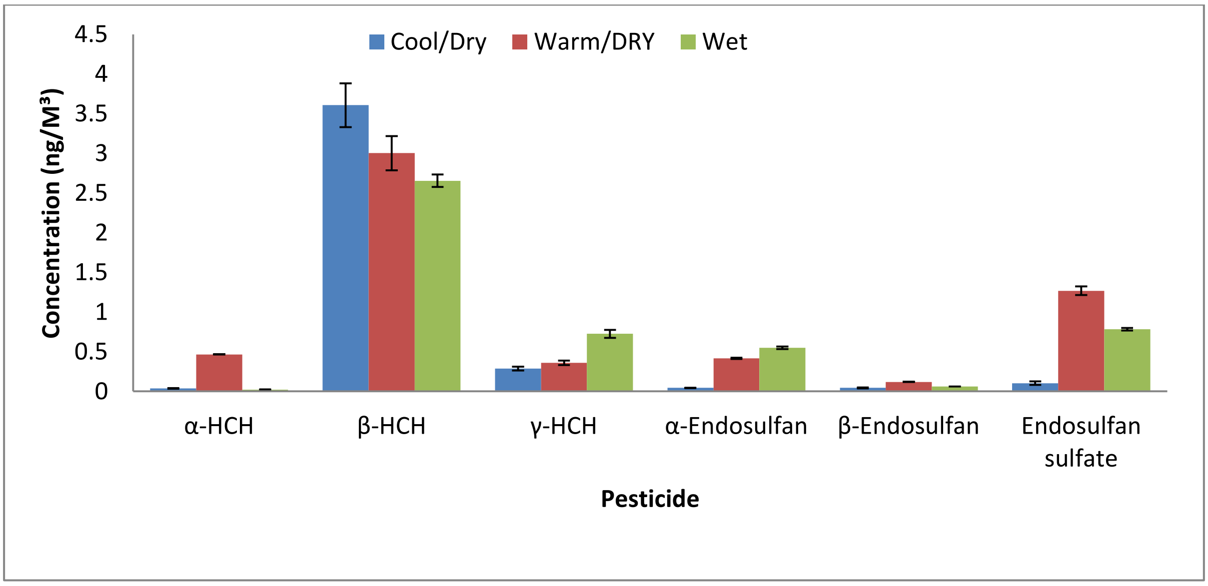


Figure 4.7: Seasonal variation of the new POPs in air at the Kabete site

The levels of α-endosulfan were highest during the wet season and lowest during the warm dry season. This could be accounted for by the more pronounced diffusion and dispersion of the new POPs during the warm season than the cool season (Derek *et al.*, 2009). The concentrations of α-HCH and β-endosulfan remained generally low and almost constant during the three seasons. This could be linked to their degradation in the environment to form more stable organic compounds (Derek *et al*., 2009).

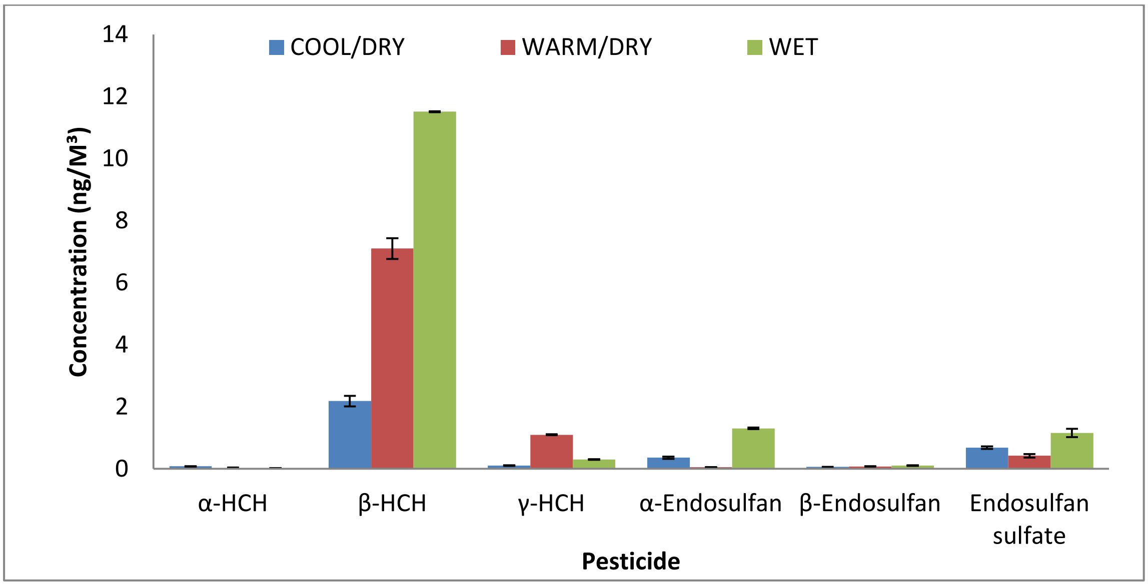


Figure 4.8: Seasonal variations of the new POPs in air at Dandora site

The levels of the new POPs were high during the warm-dry season and low during the wet season at the Industrial area site as shown in Figure 4.9

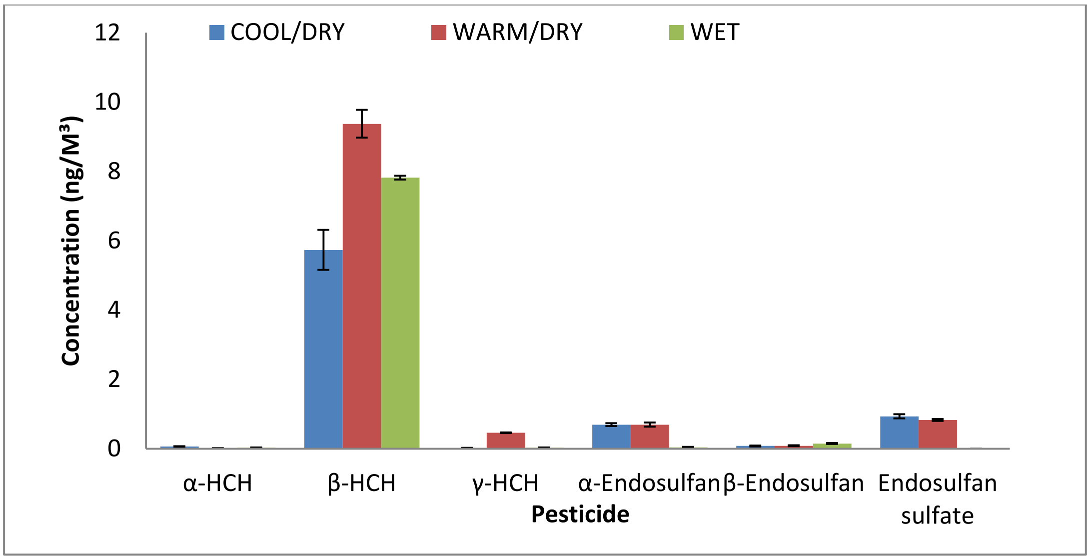


Figure 4.9: Seasonal variations of the new POPs at the industrial area site.

At the industrial area site, the levels of β-HCH, γ-HCH, α-endosulfan and endosulfan sulfate were high during the warm and dry season. The highest concentration of α-HCH was detected during the cool season. The levels of β-endosulfan, which were in low levels at this site, remained almost constant during the three seasons.

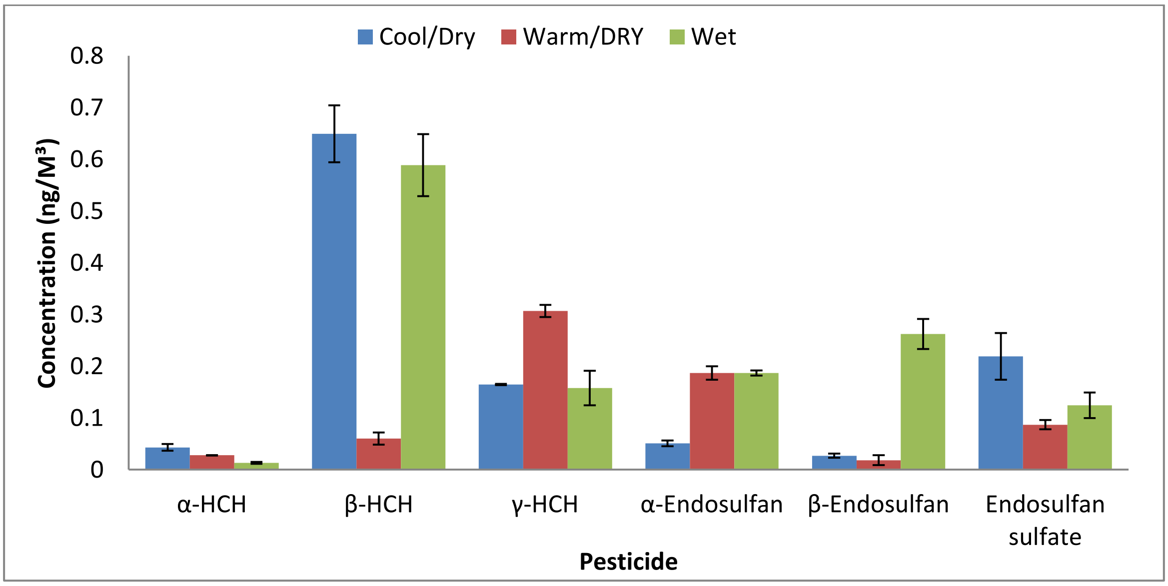


Figure4.10: Seasonal variations of the new POPs in air at the Mt. Kenya site

The four new POPs, isomers and metabolite of endosulfan were detected at the Mt. Kenya site where there are no anthropogenic sources associated with the manufacture, use and deposition of the organic compounds. This implies that the reasonably high concentrations of the new POPs could be as a result of long range transport from other point sources. During winter, degradation of β-endosulfan is effectively halted (Harris *et al.*, 2000). This explains the relatively high concentrations of the β-endosulfan at the Mt. Kenya site during the wet session (January -April) which was relatively cold and wet.

4.3.4 Recovery Tests

Recovery of the analyte measured for the reference materials ranged between 72-102%. Laboratory blanks were below detection limits for selected compounds. Laboratory blanks were pre-extracted PUF discs preserved in the laboratory which were extracted alongside the exposed PUF filters. Field blanks consisting of pre-extracted PUF discs taken to the sampling sites did not exceed 3% of quantities detected in samples for the new POPs, indicating minimal contamination during transportation, storage and analysis.

4.3.5: Temporal Distribution of the other Organochlorine Pesticides and Old POPs in Air

Other persistent organic pollutants and organochlorine pesticides analysed in this work include; δ-HCH, Heptachlor, Aldrin, Heptachlor epoxide, pp-DDE, Dieldrin, Endrin, pp-DDD, Endrin Aldehyde, pp-DDT and Methoxychlor. In 2004, all this compounds and their metabolites except δ-HCH were listed in annexes to the Stockholm convention on Persistent Organic Pollutants. Though their production and use were banned, they still contaminate the environment. These compounds and their metabolites are referred to as the Old POPs in this work. The levels of this old POPs and organochlorine pesticides analysed in this work are listed in tables 4.12, 4.13, 4.14 and 4.15.

4.3.5.1: Temporal Distribution of the other Organochlorine Pesticides and Old POPs in air at the Kabete site in ng/M³

The levels of pp-DDE were the highest at 0.780 ng/M³ whiles the levels of endrin aldehyde were the lowest at 0.026 ng/M³ on average at the Kabete site (Table 4.12).

Table 4.12: Temporal distribution of the Old POPs and other pesticide residue levels air at Kabete site (ng/M³)

Pesticides/Sampling period	July/October	October/January	January/April	Average
δ-HCH	0.036±0.011	0.075±0.019	0.027±0.014	0.046
Heptachlor	0.117±0.023	0.139±0.022	0.227±0.026	0.161
Aldrin	0.079±0.004	0.102±0.007	0.244±0.008	0.142
Heptachlor epoxide	0.175±0.009	0.074±0.004	0.044±0.003	0.098
pp-DDE	0.043±0.011	1.404±0.083	0.893±0.014	0.780
Dieldrin	0.184±0.009	0.137±0.011	0.143±0.004	0.155
Endrin	0.024±0.000	0.101±0.019	0.113±0.001	0.079
pp-DDD	0.161±0.008	0.119±0.008	0.099±0.007	0.126
Endrin Aldehyde	0.021±0.000	0.021±0.000	0.036±0.000	0.026
pp-DDT	0.372±0.025	0.221±0.013	0.429±0.048	0.341
Methoxychlor	0.064±0.002	0.087±0.008	0.203±0.088	0.118

[a]**N=2,** mean ± standard deviation

4.3.5.2: Temporal Distribution of the other Organochlorine Pesticides and Old POPs in Air at the Dandora site in ng/M³

At the Dandora site, high levels of pp-DDE (2.042 ng/M³) were recorded while endrin recorded the lowest levels of 0.043 ng/M³ as shown in Table 4.13.

Table 4.13: Temporal Distribution of the Old POPs and Organochlorine Pesticide Residue Levels in Air at Dandora Site (ng/M³)

Pesticides/Sampling period	July/October	October/January	January/April	Average
δ-HCH	0.056±0.013	0.187±0.018	0.827±0.040	0.356
Heptachlor	0.159±0.007	0.115±0.015	0.330±0.010	0.201
Aldrin	0.112±0.003	0.202±0.006	0.744±0.049	0.353
Heptachlor epoxide	0.036±0.003	0.428±0.018	0.190±0.017	0.218
pp-DDE	0.493±0.054	0.036±0.012	5.599±0.177	2.042
Dieldrin	0.084±0.001	0.097±0.021	0.284±0.032	0.155
Endrin	0.048±0.003	0.052±0.004	0.028±0.008	0.043
pp-DDD	0.110±0.014	0.130±0.016	0.132±0.009	0.124
Endrin Aldehyde	0.040±0.005	0.061±0.006	0.407±0.004	0.170
pp-DDT	0.324±0.007	0.419±0.054	0.349±0.045	0.364
Methoxychlor	0.068±0.023	0.152±0.012	0.624±0.075	0.281

[a]**N=2,** mean ± standard deviation

4.3.5.3: Temporal Distribution of the other Organochlorine Pesticides and Old POPs in Air at the Industrial Area site in ng/M³

The average levels of individual organochlorine pesticides ranged between 0.550 ng/M³ for heptachlor epoxide and 0.073 ng/M³ for δ-HCH. High levels of pp-DDE (1.434 ng/M³) were recorded during the July/ October sampling session (Table 4.14)

Table 4.14: Temporal Distribution of the Old POPs Residue Levels in Air at the Industrial Area Site (ng/M³)

Pesticides/Sampling period	July/October	October/January	January/April	Average
δ-HCH	0.054±0.012	0.067±0.011	0.099±0.003	0.073
Heptachlor	0.103±0.002	0.147±0.010	0.108±0.012	0.120
Aldrin	0.157±0.024	0.146±0.020	0.396±0.046	0.233
Heptachlor epoxide	0.221±0.003	0.554±0.033	0.876±0.052	0.550
pp-DDE	1.434±0.058	0.010±0.006	0.013±0.003	0.486
Dieldrin	0.095±0.007	0.115±0.009	0.053±0.010	0.088
Endrin	0.048±0.005	0.066±0.018	0.184±0.008	0.099
pp-DDD	0.143±0.012	0.188±0.024	0.063±0.010	0.131
Endrin Aldehyde	0.137±0.026	0.244±0.027	0.244±0.024	0.209
pp-DDT	0.701±0.048	0.206±0.010	0.148±0.009	0.352
Methoxychlor	0.083±0.003	0.075±0.010	0.816±0.020	0.325

[a]**N=2,** mean ± standard deviation

4.3.5.4: Temporal Distribution of the Old POPs Residue Levels in Air at the Mount Kenya Site (ng/M³)

The levels of these organochlorine pesticides and Old POPs were generally low at the Mt. Kenya site compared to the other sites. The highest levels at this site were of pp-DDT at 0.364ng/M³ while the lowest levels were for endrin at 0.035 ng/M³ (Table 4.15).

Table 4.15: Temporal Distribution of the Old POPs Residue Levels[a] in Air at the Mt. Kenya Site (ng/M³)

Pesticides/Sampling period	July/October	October/January	January/April	Average
δ-HCH	0.035±0.003	0.068±0.008	0.056±0.003	0.053
Heptachlor	0.028±0.000	0.085±0.002	0.085±0.002	0.066
Aldrin	0.031±0.002	0.240±0.006	0.205±0.066	0.159
Heptachlor epoxide	0.024±0.002	0.110±0.010	0.027±0.011	0.053
pp-DDE	0.607±0.016	0.069±0.006	0.090±0.025	0.255
Dieldrin	0.076±0.006	0.076±0.006	0.112±0.014	0.088
Endrin	0.031±0.001	0.041±0.006	0.032±0.005	0.035
pp-DDD	0.116±0.008	0.022±0.005	0.084±0.029	0.074
Endrin Aldehyde	0.031±0.006	0.058±0.024	0.136±0.014	0.075
pp-DDT	0.158±0.040	0.180±0.009	0.755±0.102	0.364
Methoxychlor	0.058±0.003	0.112±0.008	0.109±0.026	0.093

4.4 Levels of New Pops in Soil

4.4.1 Physico-chemical Characteristics of Soil from the Four Sites

The Table 4.16 below shows the composition of soil properties from the four sampling sites.

Table 4.16: Physico-chemical parameters of soil from the four sites

Physico-chemical parameter	Industrial area	Kabete	Dandora	Mt. Kenya
soil pH	8.08	7.23	8.62	6.14
Electrical conductivity $mScm^{-1}$	0.43	0.28	0.56	0.27
% Total organic carbon	1.15	1.1	0.96	1.77
% Sand	22	14	54	54
% Silt	28	24	22	40
% Clay	50	62	24	6
Soil texture	Clay	Clay	sandy/Clay Loam	Sandy Loam
cations exchange capacity mean	31.4	26.2	26.6	25.4
% Calcium mean	35.8	32.8	70.8	2.57
% Magnesium mean	1.22	3.25	3.18	0.17
% Potassium mean m	1.22	2.29	4.75	0.76
% Sodium mean	0.5	0.7	3.99	0.35
% Sum mean	38.74	38.95	82.72	3.85
%Base	100+	100+	100+	15
ESP	1.6	2.7	15	1.4

ESP; Exchangeable Sodium Percentage

The soil pH ranged between 6.14 and 8.62 with the highest and lowest values measured at the Dandora and Mt. Kenya sites, respectively. The percentage organic carbon was highest in Mt. Kenya soil (1.77%) and lowest in the Dandora soil (0.96%). Dandora and Mt. Kenya soils were 54% sandy, industrial area soil was 22% sandy while the Kabete soil was 14% sandy. The amount of silt in the soil was highest in the Mt. Kenya soil at 40% and lowest in the Dandora soil (22%). This is due to the presence of natural vegetation cover at the Mt Kenya site and the lack of it at the Dandora site.

Clay content was highest in the Kabete soils (62%) followed by Industrial area (50%), Dandora (24%) and lowest in soils from the Mt. Kenya site (6%). Analysis of the texture of the soil revealed high levels of sand in most of the sites, followed by clay and silt. The high composition of sand implies low levels of organic matter hence low ability to retain organic contaminants such as pesticides as is the case for the Mt Kenya site (Cerrillo *et al*., 2004)

4.4.2: Temporal Distribution of the New POPs in Soil

The distribution of the residue levels of the new POPs in soil from the four sampling sites in the three sampling months are given in Tables 4.17, 4.18, 4.19 and 4.20. The residue levels of the old POPs and other pesticides analysed in soil in this work are given in Tables 4.24, 4.25, 4.26 and 4.27. The concentrations of these compounds in soil were based on dry weights of the soil

4.4.2.1: Temporal Distribution of the New POPs in Soil at Kabete

At the Kabete site, the highest residue levels of the new POPs were recorded in the month of October (29.05 ng/kg) which was relatively cool. The lowest levels were recorded in April (17.06 ng/kg) which was a wet month (Table 4.17). The levels of the Old POPs in soil from the Kabete sit are recorded in Table 4.24.

Table 4.17: Temporal distribution of new POPs residue levels[a] in soil at Kabete (ng/kg)

New POP	**October** **short rain**	**January** **Warm-dry**	**April** **long rain**
α-HCH	0.57 ±0.15	0.80± 0.03	0.42 ±0.09
β-HCH	2.70 ± 0.77	6.09± 0.18	1.93 ±0.44
γ-HCH	0.51 ±0.03	9.74± 0.03	9.89 ±2.51
α-Endosulfan	19.83 ± 0.01	1.98± 0.77	0.41± 0.00
β-Endosulfan	5.44 ± 0.42	6.23± 0.41	1.89± 0.00
Endosulfan sulfate	BDL	3.93± 0.56	2.52 ±0.07
∑ New POP	29.05	28.77	17.06

[a] n=3, mean ± standard deviation

In the soil from the Kabete site, α-endosulfan was predominant in the cool-dry month of October while γ-HCH dominated in January and April. During the warm-dry month of January, β-HCH, γ-HCH, β-endosulfan and endosulfan sulfate levels were appreciable.

4.4.2.2: Temporal Distribution of the New POPs in Soil at Dandora Site

The residue levels of the new POPs in soil at the Dandora site were high in October (230.48 ng/kg) (Table 4.18) which was a cool month hence huge retention of the POPs in soil (Dvorska, *et al.*, 2008). The lowest residue levels were recorded in January at 10.934 ng/kg. This could be attributed to increased volatilisation of the new POPs from soil to air favoured by high temperatures which were recorded in January (Jana, *et al*., 2005). The levels of the old POPs in soil from Dandora site are in Table 4.25.

Table 4.18: Temporal distribution of the New POPs residue levels[a] in soil at Dandora (ng/kg)

New POP	October Cool month	January Warm-dry	April Wet month
α-HCH	0.83 ±0.054	1.10 ±0.02	2.14 ±0.42
β-HCH	131.21 ± 14.41	2.92± 0.19	26.88± 8.89
γ-HCH	25.80 ± 4.09	0.15 ±0.01	1.79 ±0.05
α-Endosulfan	57.21 ± 2.19	0.65 ±0.00	3.51± 0.77
β-Endosulfan	3.06 ±0.36	3.75 ±0.16	4.44 ±0.19
Endosulfan sulfate	12.38 ± 0.09	2.36 ±0.377	12.92 ±2.39
∑ OCP	230.48	10.93	51.68

[a]n=3, mean ± standard deviation

The levels of ∑ new POPs in the Dandora soil was higher during the cool dry month than in the wet and warm-dry months as expected. This shows that more volatilization and loss of POPs from the soil happened under the warm dry conditions than during the cooler ones. Levels of new POPs in soils were lowest in wet soils from Kabete, Industrial area and Mt. Kenya, probably due to partitioning and leaching of some of the new POPs into aqueous media under wet conditions (Situma, 2010). For organochlorine pesticides, when moisture content of soil is high and evaporation is high, then volatilisation is encouraged.

4.4.2.3: Temporal Distribution of the New POPs in Soil at Industrial Area Site

The residue levels of the new POPs in soil at the Industrial area site ranged between 19.65 ng/kg and 78.41 ng/kg (Table 4.19). At the Industrial area site, the highest residue levels were recorded in October which was a cool month hence reduced volatilisation (Jana *et al.*, 2005).

The lowest levels were recorded in April. The low levels in April could be because the POPs were washed away into rivers by surface run-off and leaching (UNEP, 2003). The levels of the Old POPs in soil from the industrial area site are given in Table 4.26.

Table 4.19: Temporal distribution of the New POPs residue levels[a] in soil from the Industrial area site (ng/kg)

New POP	October	January	April
α-HCH	1.34 ± 0.04	0.81± 0.10	0.72 ±0.06
β-HCH	5.70 ± 0.31	2.52 ±0.75	3.28± 0.64
γ-HCH	0.40 ± 0.03	2.25 ±0.23	0.61± 0.02
α-Endosulfan	8.68 ± 0.11	5.89± 0.03	4.07 ±1.35
β-Endosulfan	22.12± 1.08	38.36 ±5.39	1.79 ±0.04
Endosulfan sulfate	40.17 ± 9.62	2.36 ±0.38	9.19 ±0.91
∑ OCP	78.41	52.18	19.65

[a] n=3, mean ± standard deviation

The levels of endosulfan sulfate were highest during the cool-dry month of October and lowest during the warm dry month of January as expected due to high volatilisation during the warm-dry season. The concentrations of α-HCH were the lowest followed by γ-HCH (Lindane). Since there use was banned, these low concentrations could point to reduced contamination of the environment with these compounds.

4.4.2.4: Temporal Distribution of the New POPs in Soil at the Mt. Kenya Site

In the Mt. Kenya soil, the residue levels of the new POPs ranged between 1.71ng/kg and 15.02 ng/kg (Table 4.20). Just like in air, levels of the new POPs were generally lowest in the

Mt. Kenya soil compared to Dandora, Industrial area and Kabete in all the three sampling months. This is because Mt. Kenya is not a point source of the new POPs. The soil from Mt Kenya was 54% sandy (Table 4.16) hence low ability to retain persistent organic pollutants such as the ones analysed in this study (Cerrillo *et al.*, 2004). The Old POPs residue levels are given in Table 4.27. Although soil concentrations correlate positively with organic matter content of the soil, Mt. Kenya, despite high organic matter content of 1.77%, recorded low levels because the contamination of this site is basically from long-range transport of the contaminants.

Table 4.20: Temporal distribution of the New POPs residue levels[a] in soil from the Mt. Kenya site (ng/kg)

New POP	October	January	April
α-HCH	0.87 ± 0.01	0.42± 0.1	0.38± 0.06
β-HCH	0.5 ±0.01	0.34 ±0.33	0.22 ±0.00
γ-HCH	0.16 ±0.05	0.49 ±0.06	0.13± 0.02
α-Endosulfan	0.67 ± 0.07	0.29± 0.00	0.51± 0.25
β-Endosulfan	1.93 ±0.69	2.72± 0.00	0.26± 0.00
Endosulfan sulfate	10.90 ±4.38	1.51 ±0.06	0.21 ±0.01
∑ OCP	15.02	5.76	1.71

[a]n=3, mean ± standard deviation

The levels of endosulfan sulfate at the Mt. Kenya site were the highest during the cool month of October (10.90±4.38ng/kg). This could be attributed to the fact that both α-endosulfan and β-endosulfan degrade primarily via microbial biotransformation to endosulfan sulfate raising its concentration at this remote site (Harris *et al.,* 2000). The isomers and metabolites of endosulfan are also persistent and undergo long-range transport. Although the concentrations of the new POPs were generally low at this remote site (Figure 4.11), this data suggests potential contribution of long-range transport to POPs contamination at this site, since there are on point sources there.

4.4.2.5: Average Temporal Distribution of the New POPs in Soil

The trends in monthly levels of ∑ new POPs in soils at each site are as shown in figure 4.11 below.

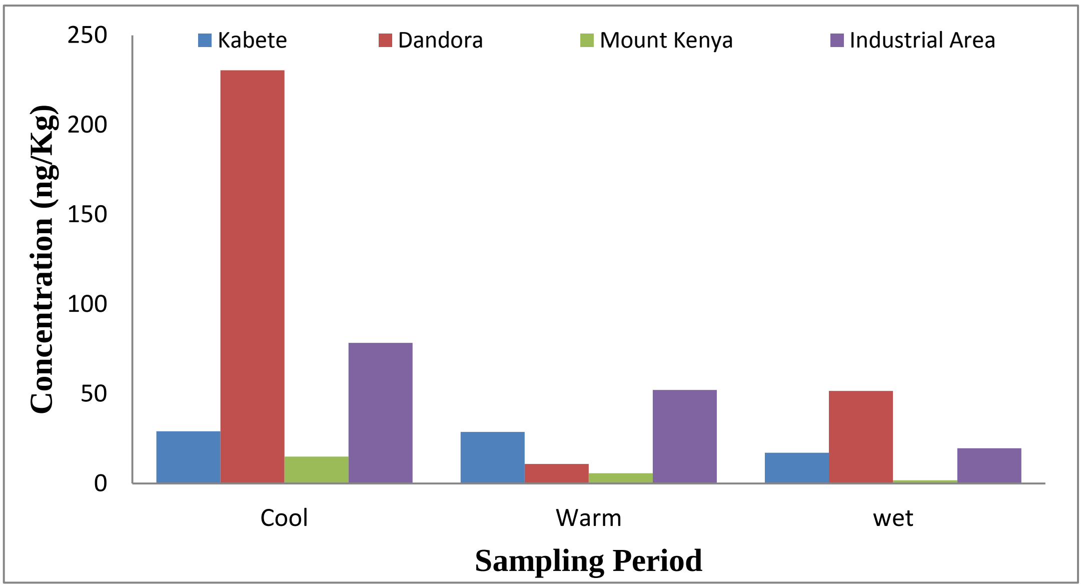


Figure 4.11: The average temporal variation of the new POPs in soil

There was a decline in the levels of ∑new POPs in industrial area, Kabete and Mt. Kenya soil from October to January with the levels in Dandora decreasing significantly in January. This is attributed to increased volatilisation of POPs from the soil to air in January as a result of the high temperatures (Jana *et al.*, 2005). The levels of the new POPs were generally low in the April (wet month) samples despite the wet-deposition due to the fact that a number of pesticides are drained into water bodies by surface run-off (Cerrillo *et-al.*, 2004) or through volatilization especially during the day.

4.4.3 Spatial Variation of the New POPs in Soil

Tables 4.21, 4.22 and 4.22 and Figures; 4.12, 4.13 and 4.14 below summarise the distribution of the new POPs-pesticides in soil from Kabete, Dandora, Industrial area and Mt. Kenya sites during the three sampling months.

In October, the highest residue levels were recorded at the Dandora site (230.48ng/kg) while the lowest residue levels were recorded at the Mt. Kenya soil (15.02 ng/kg) (Table 4.21) (Figure 4.12).

Table 4.21: Spatial distribution of the New POPs residue levels[a] soil in October (ng/kg)

New POP/site	**Kabete**	**Dandora**	**Mount Kenya**	**Industrial Area**
α-HCH	0.57 ±0.15	0.83 ±0.054	0.87 ± 0.01	1.34 ± 0.04
β-HCH	2.70 ± 0.77	131.21 ± 14.41	0.5 ±0.01	5.70 ± 0.31
γ-HCH	0.51 ±0.03	25.80 ± 4.09	0.16 ±0.05	0.40 ± 0.03
α-Endosulfan	19.82 ± 0.01	57.21 ± 2.19	0.67 ± 0.07	8.68 ± 0.11
β-Endosulfan	5.44 ± 0.42	3.06 ±0.36	1.93 ±0.69	22.12 ± 1.08
Endosulfan sulfate	BDL	12.38 ± 0.09	10.90 ±4.38	40.17 ± 9.62
∑ **new POPs**	29.05	230.48	15.02	78.41

[a]**n=3,** mean ± standard deviation, BDL- Below detection limit

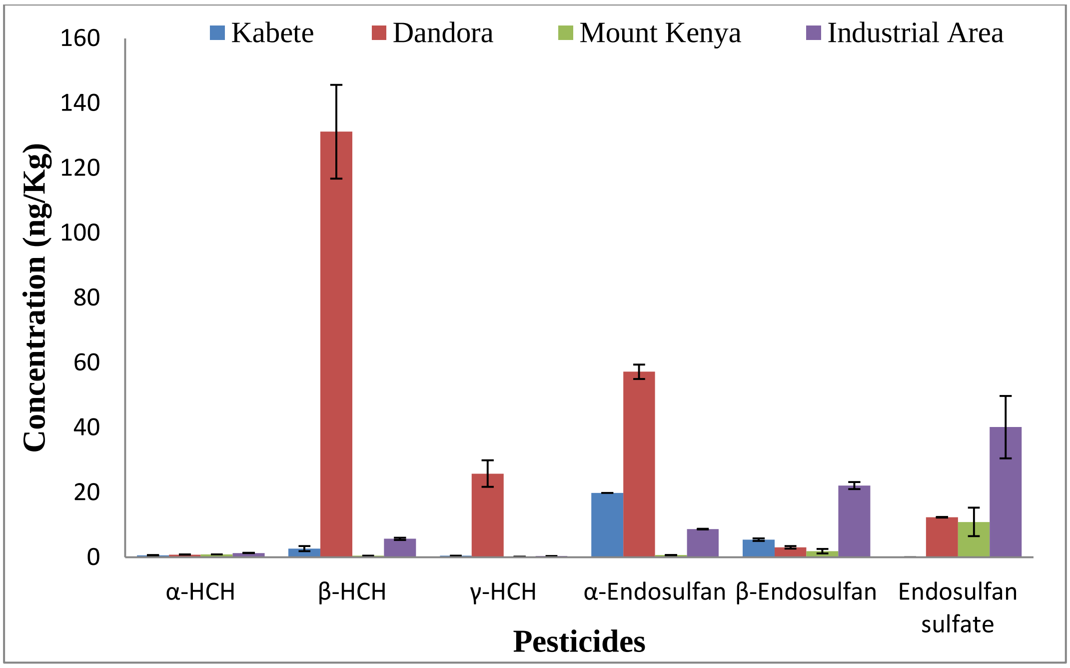


Figure 4.12: Spatial distribution of the New POPs residue levels[a] soil in October

In January, the highest levels of ∑ new POPs were recorded at the Industrial area site (52.18 ng/kg) while Mt. Kenya recorded the lowest levels of 5.76 ng/kg (Table 4.22) (Figure 4.13).

Table 4.22: Spatial distribution of the New POPs residue levels[a] soil in January (ng/kg)

New POP/ site	**Kabete**	**Dandora**	**Mount Kenya**	**Industrial Area**
α-HCH	0.80± 0.03	1.10 ±0.02	0.42± 0.1	0.81± 0.10
β-HCH	6.09± 0.18	2.92± 0.19	0.34 ±0.33	2.52 ±0.75
γ-HCH	9.74± 0.03	0.15 ±0.01	0.49 ±0.06	2.25 ±0.23
α-Endosulfan	1.98± 0.77	0.65 ±0.00	0.29± 0.00	5.89± 0.03
β-Endosulfan	6.23± 0.41	3.75 ±0.16	2.72± 0.00	38.36 ±5.39
Endosulfan sulfate	3.93± 0.56	2.36 ±0.377	1.51 ±0.06	2.36 ±0.38
∑ new POPs	28.77	10.93	5.76	52.18

[a]**n=3,** mean ± standard deviation

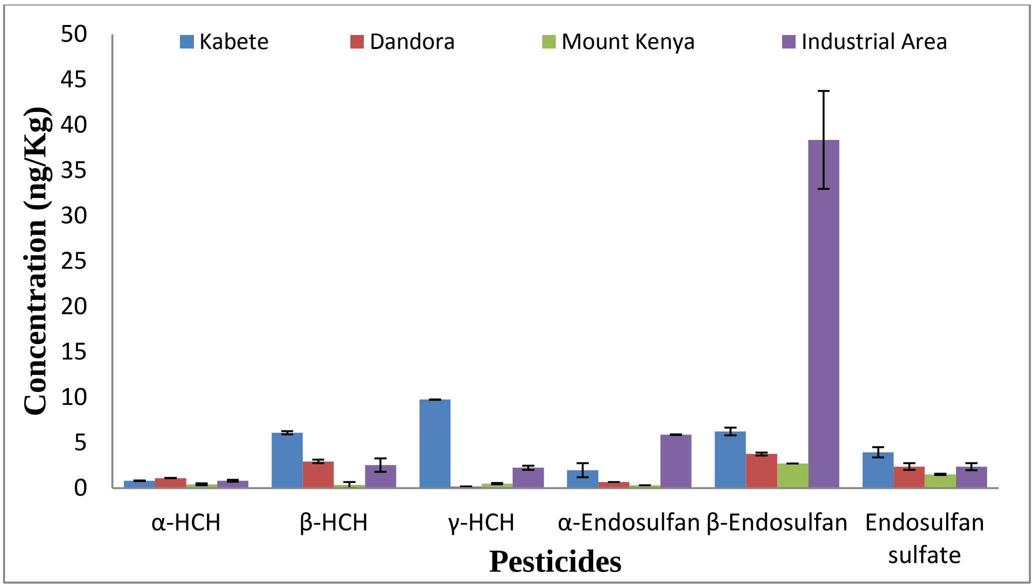


Figure 4.13: Spatial distribution of the New POPs residue levels[a] soil in January

The residue levels ranged between 51.68 ng/kg in soil from Dandora site and 1.71 ng/kg in soil from Mt. Kenya site (Table 4.23) (Figure 4.14).

Table 4.23: Spatial distribution of the New POPs residue levels[a] in soil in April (ng/kg)

New POP/site	**Kabete**	**Dandora**	**Mount Kenya**	**Industrial Area**
α-HCH	0.42 ±0.09	2.14 ±0.42	0.38± 0.06	0.72 ±0.06
β-HCH	1.93 ±0.44	26.88± 8.89	0.22 ±0.00	3.28± 0.64
γ-HCH	9.89 ±2.51	1.79 ±0.05	0.13± 0.02	0.61± 0.02
α-Endosulfan	0.41± 0.00	3.51± 0.77	0.51± 0.25	4.07 ±1.35
β-Endosulfan	1.89± 0.00	4.44 ±0.19	0.26± 0.00	1.79 ±0.04
Endosulfan sulfate	2.52 ±0.07	12.92 ±2.39	0.21 ±0.01	9.19 ±0.91
∑ new POPs	17.06	51.68	1.71	19.65

[a]**n=3,** mean ± standard deviation

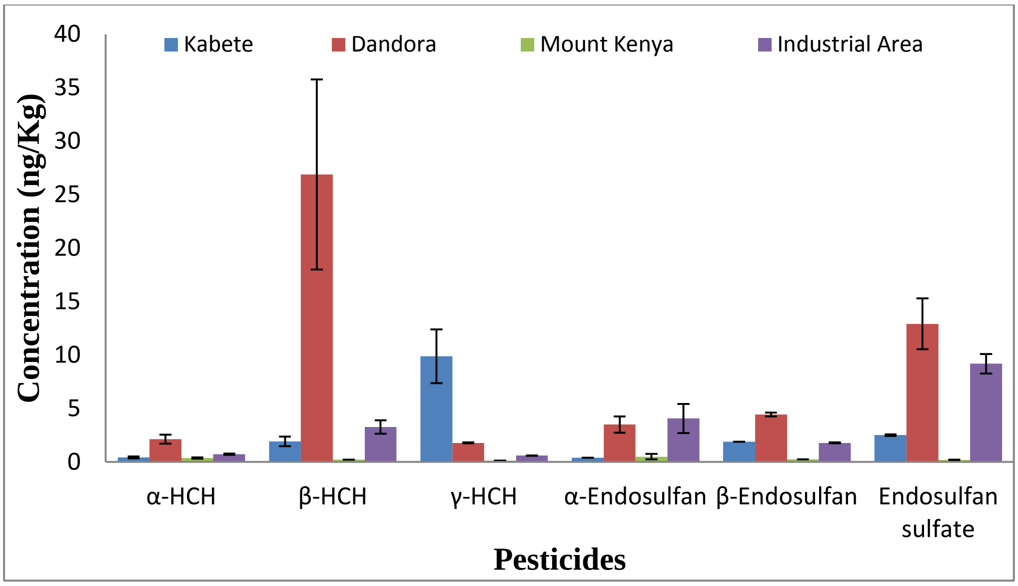


Figure 4.14: Spatial distribution of the New POPs residue levels[a] in soil in April

There were more significant variations in the levels of the∑ new POPs in soils at the Dandora and Industrial area sites than at Mt. Kenya and Kabete sites.

On average, β-HCH was the most abundant of the new POPs analysed because of its stability in the environment while α-HCH was the least abundant. The use of *alpha* hexachlorocyclohexane as an insecticide was phased out many years ago but it is still produced as a by-product of lindane (EPH, 2008). There were relatively higher concentrations of endosulfan isomers and metabolite in the soils compared with HCHs because β-endosulfan and endosulfan sulfate persist in soil for over two years (Harris *et al.*, 2000). POPs may not change significantly during chemical storage but dehydrochlorinations of α and β-HCH may occur (Weiguang *et al.*, 2013) resulting in low levels in soil. The levels of the new POPs were high in the Dandora and Industrial area soils over the sampling period than in the Kabete and Mt. Kenya soils. This is attributed to their release into the environment by the industrial activities and dumping of contaminated wastes at the two sites, respectively. On average, the concentrations of β-endosulfan and endosulfan sulfate were higher than the concentrations of α-endosulfan. This is explained by the persistence of β-endosulfan and endosulfan sulfate in soil for over two years while α-endosulfan disappears within 60 days in soil and 7 days in river water (Harris *et al.*, 2000).

The residue levels of endosulfan isomers and metabolites at the Mt. Kenya are higher than those of HCHs confirming drift and long range-transport of this POP to the site. The average residue levels of all the POPs detected in soil in all the sites in the three months are illustrated in Figure 4.15 below

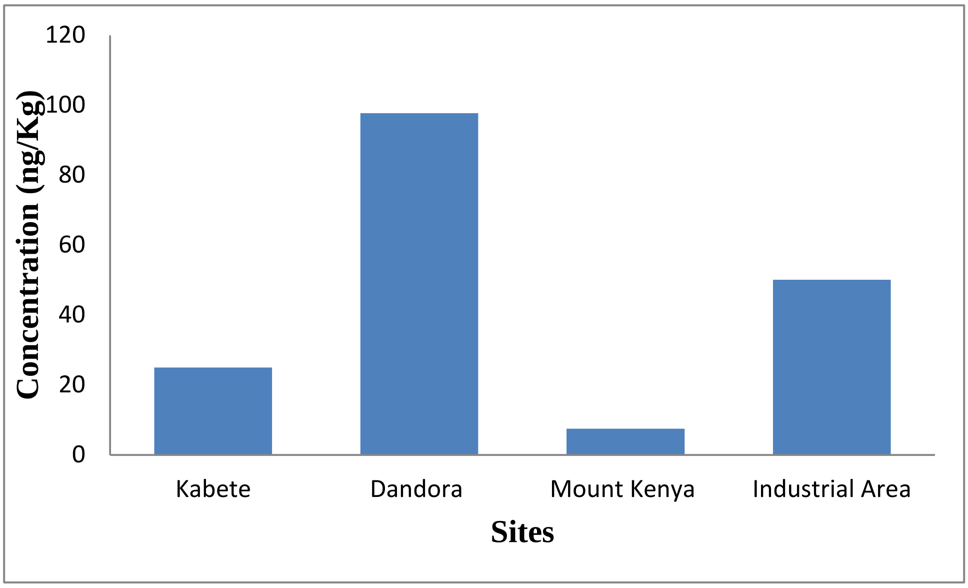


Figure 4.15: The average new POPs residue levels in soil at the four sites

Dandora site had the highest levels of New POPs followed by industrial area site as shown in Figure 4.15. This is attributed to the high adsorption of the analytes on soil due to dumping of contaminated domestic and industrial wastes at the dumpsite and releases from industrial activities (Jones *et al.*, 1999). Mt. Kenya site had the lowest levels of new POPs.

4.4.4 Seasonal Variations of the New POPs in Soil

Soil was sampled in October, January and April so it is not possible to talk about seasonal variation because soil was sampled only once a month in the three sampling months which coincided with the end of each air sampling period. The levels of new POPs in soil remained fairly constant at the Kabete site during the three sampling periods. The residue levels were lower during the warm month of January than during the cool month of October. This confirms the effect of volatilisation during the warm month.

The seasonal variations in levels of POPs in the soils are illustrated in Figure 4.16 and Figure 4.17.

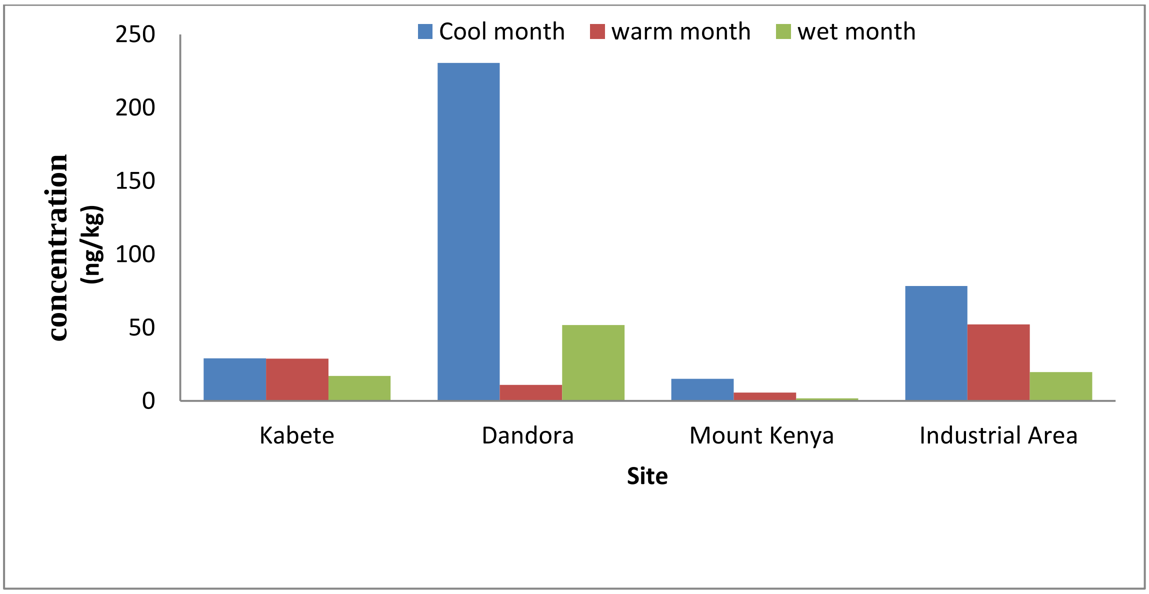


Figure 4.16: Seasonal Variation of the new POPs pesticides in soil

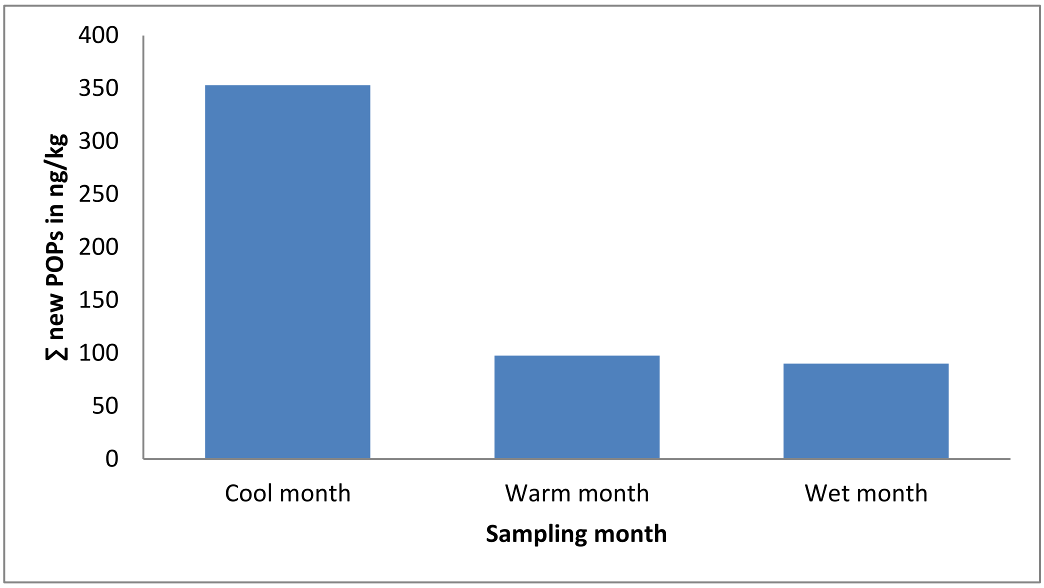


Figure 4.17: Seasonal distribution of ∑ new POPs residue levels in soil

4.4.5: The Old POPs and other Organochlorine pesticides analysed in soil in ng/Kg

The residue levels of the old POPs and other organochlorine pesticides analysed in this work are listed in tables 4.24, 4.25, 4.26 and 4.27 below.

Table 4.24: Levels of organochlorine pesticides and Old POPs in soil at Dandora site (ng/kg)

Pesticides/Month	**October**	**January**	**April**	Average
δ-HCH	4.408 ± 0.17	1.891 ±0.00	2.475±1.06	2.92
Heptachlor	14.34 ±2.02	12.35± 1.77	2.207±0.18	9.63
Aldrin	2.65 ± 0.65	1.277 ±0.13	2.799±0.05	2.24
Heptachlor epoxide	4.945 ±0.01	4.953 ±0.00	12.328±1.54	7.41
pp-DDE	2.305 ± 0.99	0.809 ±0.04	13.000±0.09	5.37
Dieldrin	2.601 ± 0.73	2.243 ±0.54	2.296± 0.43	2.38
Endrin	3.643 ±0.28	2.905 ±0.51	1.643 ±0.15	2.73

pp-DDD	2.379 ±0.37	0.842 ±0.03	7.317 ±2.21	3.51
Endrin Aldehyde	1.931 ± 0.01	0.842± 0.03	2.301 ±0.67	1.69
pp-DDT	4.81 ±0.12	10.377 ±0.40	8.464± 0.41	7.88
Methoxychlor	19.940 ± 4.2	10.461 ±4.90	47.975±13.35	26.13
∑ OLD POPS	63.952	48.95	102.805	71.90

[a]**N=3,** mean ± standard deviation

Table 4.25: Levels of organochlorine pesticides and old POPs in soil at Kabete site (ng/kg)

Pesticides/Month	**October**	**January**	**April**	Average
δ-HCH	2.52 ±0.77	2.72 ±0.54	0.87 ±0.01	2.04
Heptachlor	5.33 ±0.21	4.98 ±1.05	2.26 ±0.05	4.19
Aldrin	0.74 ± 0.00	2.10± 0.43	1.65± 0.61	1.49
Heptachlor epoxide	1.44 ±0.15	2.43 ±0.05	0.83 ±0.07	1.57
pp-DDE	6.66 ±0.13	5.84± 0.20	8.20 ±2.7	6.90
Dieldrin	0.88 ±0.11	2.08 ±0.70	1.17 ±0.61	1.38
Endrin	1.88 ±0.19	2.40 ±0.96	BDL	1.43
pp-DDD	2.26 ± 0.13	5.278± 0.09	2.35 ±0.09	3.30
Endrin Aldehyde	1.56 ±0.36	1.28 ±0.3	BDL	0.95
pp-DDT	3.18 ±1.84	10.49 ±1.97	13.03±1.19	8.90
Methoxychlor	4.92 ±0.67	2.94 ±0.96	2.11 ±1.08	3.32
∑OLD POP	31.35	42.54	32.47	35.45

[a]**N=3,** mean ± standard deviation

Table 4.26: Old POPs and organochlorine residue levels in soil at the industrial area site (ng/kg)

Pesticides/month	**October**	**January**	**April**	Average
δ-HCH	1.33 ±0.3	2.25± 0.23	2.25 ±0.23	1.94
Heptachlor	5.57 ±1.54	2.28 ±0.28	5.39 ±0.35	4.41
Aldrin	2.98 ±1.12	3.04± 0.00	2.42± 0.21	2.81
Heptachlor epoxide	2.36 ±0.17	3.06± 0.14	2.64 ±0.22	2.69
pp-DDE	15.99 ±1.83	15.99 ±1.83	10.13± 3.85	14.03
Dieldrin	3.57 ± 0.23	4.71 ±0.18	4.71 ±0.19	4.33
Endrin	3.11 ±0.75	3.22 ±0.42	1.33 ±0.12	2.55
pp-DDD	6.10 ±2.39	18.78± 4.09	26.65± 3.98	17.17
Endrin Aldehyde	10.70 ± 0.20	3.42 ±0.51	1.84± 0.18	5.32
pp-DDT	6.20 ± 3.63	4.45± 0.00	4.61 ±0.78	5.09
Methoxychlor	7.61 ±0.56	21.58± 3.87	1.86 ±0.39	10.35
∑ OLD POPS	65.52	82.77	63.83	

[a]**N=3,** mean ± standard deviation

Table 4.27: Old POPs and organochlorine residue levels[a] in soil at the Mt. Kenya area site (ng/kg)

Pesticides/Month	**October**	**January**	**April**	Average
δ-HCH	1.89 ±0.00	0.03± 0.00	2.79 ±0.43	1.57
Heptachlor	3.16 ±0.79	1.81± 0.05	0.02 ± 0.00	1.66
Aldrin	1.57 ± 0.09	0.34± 0.00	0.70 ±0.00	0.87
Heptachlor epoxide	1.34 ± 0.07	BDL	0.58± 0.00	0.64
pp-DDE	1.456 ± 0.36	0.76 ±0.01	0.81± 0.06	1.01
Dieldrin	1.74 ± 0.15	0.87 ±0.07	0.85 ±0.00	1.15
Endrin	1.70 ±0.09	1.16 ±0.56	0.80± 0.03	1.22
pp-DDD	2.35 ± 0.09	0.85 ±0.08	1.70 ±0.27	1.63
Endrin Aldehyde	2.39 ±1.30	BDL	0.83 ±0.05	1.07
pp-DDT	4.17 ±0.62	BDL	4.15 ±0.07	2.77
Methoxychlor	1.51 ± 0.27	0.41± 0.00	0.26 ±0.00	0.73
∑ OLD POPS	23.25	6.23	13.49	

[a]**N=3,** mean ± standard deviation

4.5 Correlations of Levels of New POPs in Air and Soil

Correlation was done using Pearson's correlation coefficient from SPSS. Correlation coefficients have numerical values (r) ranging from -1.000 to +1.000 which represents the linear relationships between two data sets (Situma, 2010). Positive values indicate that the changes in the variables occur in the same direction while negative values indicate inverse variation relationship. The strength of the linear correlation of the variables is determined by the numerical value of r. A correlation coefficient of zero implies that there is no correlation between the data sets. Correlation coefficients below 0.5 are considered to be weak, while those above 0.5 are strong. The significance of the correlations is indicated by the p value. Correlations are significant if $p<0.005$ and are not significant if $p >0.005$ (APA, 2001).

Correlations were done to establish possible relationship between the variations in the levels of ∑ new POPs in air and that in soils at each site for each sampling period. Correlations were done to determine the possibility of a relationship between the levels of ∑ new POPs in air and soil as a function of time, both temporal and seasonal. Three seasons were covered by the study.

4.5.1 Correlation of the ∑new Pops in air

Table 4.28: Correlation of the ∑new Pops in Air

		July/October. Air	October/ January Air	January/ April Air
July/October. Air	Pearson Correlation	1	.894	.356
	Sig. (2-tailed)		.106	.644
	N	4	4	4
October/ January Air	Pearson Correlation	.894	1	.737
	Sig. (2-tailed)	.106		.263
	N	4	4	4
January/ April Air	Pearson Correlation	.356	.737	1
	Sig. (2-tailed)	.644	.263	
	N	4	4	4

The correlation coefficient values (p values) were positive at all the sites. This indicates direct variation relationships.

4.5.2 Correlation of new POPs levels in soil

Table 4.29: Correlation of new POPs levels in soil

		October Soil	January Soil	April Soil
October Soil	Pearson Correlation	1	-.174	.970*
	Sig. (2-tailed)		.826	.030
	N	4	4	4
January Soil	Pearson Correlation	-.174	1	-.082
	Sig. (2-tailed)	.826		.918
	N	4	4	4
April Soil	Pearson Correlation	.970*	-.082	1
	Sig. (2-tailed)	.030	.918	
	N	4	4	4
*. Correlation is significant at the 0.05 level (2-tailed).				

The correlation coefficient values (p values) were positive at all the sites. This indicates direct variation relationships. There is a stronger correlation (p = 0.970) for soil samples in April and October. April soil samples also showed a stronger correlation (p = 0.918) to the January.

4.5.3: Correlation of Levels of New POPs in Air and Soil

Table 4.30: Correlation of levels of new POPs in air and soil

		Kabete Air	Dandora Air	Mt. Kenya Air	Industrial Area Air	Kabete Soil	Dandora Soil	Mount Kenya Soil	Industrial Area Soil
Kabete Air	Pearson Correlation	1	.429	-.744	.945	.043	-.916	-.631	-.387
	Sig. (2-tailed)		.718	.466	.213	.972	.262	.566	.747
	N	3	3	3	3	3	3	3	3
Dandora Air	Pearson Correlation	.429	1	.285	.109	-.884	-.755	-.972	-.999*
	Sig. (2-tailed)	.718		.816	.931	.310	.455	.152	.029
	N	3	3	3	3	3	3	3	3
Mt. Kenya Air	Pearson Correlation	-.744	.285	1	-.922	-.700	.413	-.050	-.328
	Sig. (2-tailed)	.466	.816		.253	.506	.729	.968	.787
	N	3	3	3	3	3	3	3	3
Industrial Area Air	Pearson Correlation	.945	.109	-.922	1	.369	-.734	-.341	-.063
	Sig. (2-tailed)	.213	.931	.253		.759	.475	.779	.960
	N	3	3	3	3	3	3	3	3
Kabete Soil	Pearson Correlation	.043	-.884	-.700	.369	1	.360	.748	.904
	Sig. (2-tailed)	.972	.310	.506	.759		.765	.462	.281
	N	3	3	3	3	3	3	3	3
Dandora Soil	Pearson Correlation	-.916	-.755	.413	-.734	.360	1	.889	.724
	Sig. (2-tailed)	.262	.455	.729	.475	.765		.303	.484
	N	3	3	3	3	3	3	3	3
Mount Kenya	Pearson Correlation	-.631	-.972	-.050	-.341	.748	.889	1	.960
	Sig. (2-tailed)	.566	.152	.968	.779	.462	.303		.181
	N	3	3	3	3	3	3	3	3

Soil									
Industrial Area Soil	Pearson Correlation	-.387	-.999*	-.328	-.063	.904	.724	.960	1
	Sig. (2-tailed)	.747	.029	.787	.960	.281	.484	.181	
	N	3	3	3	3	3	3	3	3
*. Correlation is significant at the 0.05 level (2-tailed). Labels: 1=1st sampling; 2=2nd sampling; 3=3rd sampling									

The correlation coefficient values were negative at all the sites except Kabete site with p=0.043. Kabete is an agricultural site hence the application of fertilizers could be contributing to the positive correlation. This indicates inverse variation relationships. When the levels of POPs are increasing in air, they are decreasing in soil at the site. This confirms the effect of climate on temporal levels of POPs in air and soil. The correlation between air and soil at the Dandora soil was -755 indicating that as the concentrations in air were increasing , the concentration of the POPs in soil were decreasing. This is attributed to the interaction of POPs with the environment. These compounds volatilize from the soil during warm seasons and are deposited from air during wet seasons. Negative correlations between air and soil were also obtained from Industrial area and Mount Kenya sites.

4.5.4 Correlation of Seasonal levels of New POPs in Air and Soil

Table 4.31: Correlation of seasonal levels of new pops in air and soil

		Air cool-dry to warm dry	Air warm and dry	Air warm-dry to wet	Soil cool-dry to warm dry	Soil warm and dry	Soil warm-dry to wet
Air cool-dry to warm dry	Pearson Correlation	1	.894	.356	.116	.958*	.198
	Sig. (2-tailed)		.106	.644	.884	.042	.802
	N	4	4	4	4	4	4
Air warm and dry	Pearson Correlation	.894	1	.737	.548	.728	.610
	Sig. (2-tailed)	.106		.263	.452	.272	.390
	N	4	4	4	4	4	4
Air warm-dry to wet	Pearson Correlation	.356	.737	1	.964*	.075	.979*
	Sig. (2-tailed)	.644	.263		.036	.925	.021
	N	4	4	4	4	4	4
Soil cool-dry to warm dry	Pearson Correlation	.116	.548	.964*	1	-.174	.970*
	Sig. (2-tailed)	.884	.452	.036		.826	.030
	N	4	4	4	4	4	4
Soil warm and dry	Pearson Correlation	.958*	.728	.075	-.174	1	-.082
	Sig. (2-tailed)	.042	.272	.925	.826		.918
	N	4	4	4	4	4	4
Soil warm-dry to	Pearson Correlation	.198	.610	.979*	.970*	-.082	1

wet	Sig. (2-tailed)	.802	.390	.021	.030	.918	
	N	4	4	4	4	4	4
*. Correlation is significant at the 0.05 level (2-tailed).1=Kabete; 2=Dandora; 3=Mt. Kenya; 4=Industrial Area							

4.6 Comparison of Levels of New POPs in Ambient Air from Nairobi and Other Cities

Data is available for the original POPs but minimal data is available for the new POPs in ambient air and soil for the sampling sites. According to the global monitoring plan report, 2015, both new and old Pops were detected in Nairobi and Mt Kenya sites over the sampling period (2008-2012). The concentration of the various POPs ranged from 0.0036 pg/m^3 to 146.44 pg/ m^3 (*alpha*-endosulfan in 2009). The concentration of POP pesticides was in the range of 0.058 pg/m^3 and 146.44 pg/m^3. The level of *alpha*-endosulfan increased from 1.97 pg/m^3 to 146.44 pg.m^3 in 2009 and then decreased to 9.88 pg/m^3 at the end of the sampling campaign in 2012. Likewise, *gamma*-HCH increased from 4.80 pg/m^{3}in 2008 to 33.04 pg/m^{3}in 2009 and then decreased to 5.83 pg/ m^3 at the end of the sampling period in 2012. *Alpha* and *beta*- HCHs' concentrations in ambient air decreased from 2010 to 2012 while the *gamma*-HCH showed an irregular trend over the sampling period, with a decrease in 2011 and an increase in 2012. Levels of many pesticides tended to decrease from 2010 to 2011.

The contamination of ambient air at Mt. Kenya site was the lowest making this site the least polluted in the African region (GMP, 2015). This trend was also replicated in this work in the 2012- 2013 sampling period for Nairobi sites and the Mt. Kenya site. Almost all the new POPs discussed in this thesis were found at the Mt. Kenya site in low levels indicating a pollution that originated from atmospheric current as a component of the long range transport of POPs to this remote site.

The distribution of HCHs in ambient air for the region for the period 2010-2012 showed that HCHs were widely detected at all the sites in the region. The highest levels of *alpha*, *beta* and *gamma* HCHs were measured at Darkar Ngoye (Senegal), Khartoum, Abetefi, Sheda, Brazaville, Reduit and Asela (GMP, 2015).

4.7 Implications to Human Health and the Environment

The presence of these new POPs in the air and soil signals a threat to human health and environment due to deleterious effects associated with the new POPs that negatively impact on reproductive health, immunity and general well being. These chemicals pose a health risk to the Kenyan population and environment hence there is need to strengthen the Nairobi County's capacity for management of the county's waste, Industrial waste, medical waste and industrial gaseous emissions and particulate. There were very low levels of the new POPs pesticides in soil suggesting potential contaminations that need to be managed through the national implementation plan activities. Although the levels were relatively low, the findings raise environmental and health concerns as these chemicals have long persistence, bioaccumulate in the body and cause toxicity to humans.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

The study documents new POPs residue levels in air and soil in Nairobi and Mt. Kenya areas for the 2012-2013 sampling period. The results reveal that β-HCH was the most abundant of the new POPs analysed in air and soil while α-HCH was the least abundant. Most new POPs residue levels detected in the sampling area were high in Dandora > Industrial area >Kabete> Mt. Kenya. Since most new POPs residue levels were detected in Dandora and Industrial areas in ambient air during short rain and the dry seasons, it implies that in Nairobi area these pesticides are in high active releases from the waste and industrial activities during the period between July and December. .

Data on the spatial distribution revealed that Dandora site had the highest residue levels of the new POPs in air and soil while the Mt. Kenya site had the lowest residue levels of the new POPs. The residue levels of the new POPs in air increased during the warm and dry months of October-January and decreased during the wet months. The high residue levels in air were attributed to the effect of volatilisation of these compounds from soil during the warm season. On the other hand the residue levels in soil decreased during the warm and wet months and increased during the cool months, a trend attributed to high volatilization and surface wash-off during the warm and wet months respectively. The trends observed in this work attribute environmental pollution to poor waste management practices and industrial activities.

5.2 RECOMMENDATIONS

The high prevalence of the new POPs pesticides such as α-HCH, β-HCH, γ-HCH, α-Endosulfan, β-Endosulfan and endosulfan sulfate in ambient air reinforces the need to strengthen POPs management and control activities to reduce releases of these chemicals into the environment. Although these chemicals have been banned or restricted in Kenya, the management of contaminated sites and soil and treatment of obsolete stocks remain top priority activity hence there is need to strengthen the Nairobi County's capacity for management of the county's waste at the Dandora dumpsite, Industrial waste and medical waste. Adoption of alternatives to the new POPs pesticides should be encouraged. Further, targeted research activities on POPs pesticides alternatives should be encouraged to reduce overreliance on pesticide POPs and adequately contribute to minimising POPs releases. Endosulfan is still in use in farming in Kenya.

There is need for collection of additional new POPs data for air and soil to allow evaluation of temporal trends. The presence of new POPs at the Mt. Kenya site indicate long range transport although more information on local climatology and meteorology is needed to correctly analyse the relationship between the variability of the atmospheric POPs. The initial analysis of back trajectories conducted under the Global Monitoring Plan revealed that the transport of POPs in the region is highly dynamic and influenced by climatological factors (UNEP, 2010).

The PFOS and PBDEs levels in ambient air and soil were not analysed due to lack of capacity in terms of equipment at the university of Nairobi pesticides laboratory. There is need for research on this class of POPs in ambient air in Nairobi, Kenya. Continued research on levels of POPs in air and soil is important so as to update the database on POP levels and enable trend analysis for both interpretation of temporal change. More new POPs should be included in future monitoring programmes to ensure continuity in data production. This study indicates that the main sources of POPs are industrial chemical waste, industrial emissions and waste management; therefore I recommend a confirmatory study in similar industrial cities for example Kisumu, Mombasa, Thika as well as Eldoret because of agrochemical use, be undertaken by NEMA.

REFERENCES

African Development Bank-AFDB, (2002). *Study on Solid Waste Management Options for Africa, Project Report Final Draft Version*. Sustainable Development and Poverty Reduction Unit, Abidjan

Agency for Toxic Substances and Disease Registry (ATSDR), (2005). *Toxicologic profile for alpha, beta, gamma and delta-hexachlorocyclohenxane.* U.S. Department of Health and Human Services, August 2005.

Agency for Toxic Substances and Disease Registry (ATSDR), (2004). *Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers*; Department of Health and Human Services, Public Health Service; Atlanta, GA, U.S.,.

Aliyu, M.H., Alio, A.P., Salihu, H.M., (2010). *To breastfeed or not to breastfeed: a review of the impact of lactational exposure to polychlorinated biphenyls (PCBs) on infants*. J Environmental Health; 73:8-14.

AMAP, (2002). Persistent Organic Pollutants-Old and New; Arctic Monitoring and Assessment Programme (AMAP) October 2002.

Andrea't, M., Jonathan, C., Phil, B., Collin, B., Stuart, H., Allan H., Smith, P., Jeroen, D., (2013). *Current Concentrations, Temporal Trends and Determinants of Persistent Organic Pollutants in Breast Milk of New Zealand Women*. Science of the Total Environment; 458-460, 399-407.

Anita, E., Klára, H., Jana, K., John, P., Jiří, N., (2014). *Effect-based assessment of passive air samples from four countries in Eastern Europe*. Environ Monit Assess DOI 10; 1007/s10661-014-3667-z

APHRC, (2014). Population and health dynamics in Nairobi's informal settlements; Report of the Nairobi Cross-Sectional Slums Survey (NCSS) 2012

Avery B.W; Bascomb C.L., (1982): Soil Survey Laboratory Methods Harpenden, UK

Betts, K. S., (2007). *"Perfluoroalkyl acids: what is the evidence telling us?"* Environ. Health Perspect, 115 (5). A250-6.

Betts, K. S., (2008). *"Not immune to PFOS effects?"* Environment Health Perspective; 116 (7): A290.

Cerrillo, I., Granada, A., Espinosa, M., Olmos, B., Jimec nez, M., Cano, A., Olea-Serrano, M., (2004*). Endosulfan and its metabolites in fertile women placenta, cord blood and human milk.* Environmental Research 98; 233-239.

Chakra, C., Jonathan, L., Kyoung-Sim, K., Tom, H., Kevin, C., (2009). *Further studies on the uptake of POPs by polyurethane foam disk passive air samplers*. Atmospheric environment 43; 3843-3849

Curran, C. P., Miller, K. A., Dalton, T. P., Vorhees, C. V., Miller, M. L., Shertzer, H. G., Nebert, D. W., (2006). *"Genetic Differences in Lethality of New-born Mice Treated in Utero with Coplanar versus Non-Coplanar Hexabromobiphenyl".* Toxicological Sciences 89 (2): 454–464.

Dallaire, R., Dewailly, E., Pereg, D., Dery, S., Ayotte, P., (2009). *"Thyroid function and plasma concentrations of polyhalogenated compound in Inuit adults".* Environ Health Perspective, 117 (9): 1380–6.

Dean, J., Scott, W.C., (2004). *Recent developments in assessing the bioavailability of persistent organic pollutants in the environment.* Trends in Analytical Chemistry. 23; No. 9.

Department of Health and Human Services, DHHS, (2005). *National Centre for Environmental Health, Third National Report on Human Exposure to Environmental Chemicals*. Centres for Disease Control and Prevention; NECH Pub. 05- 0570, Atlanta.

Derek, C., Cynthia, A., (2010). *Pollution in the circumpolar arctic: overview, conclusions and recommendations*. Science of the total environment 408; 3044-3051

Derek, C.G., Muir, Cynthia, A., Wit. (2009).*Trends of legacy and new persistent organic pollutants in the circumpolar arctic*: *Overview, conclusions, and recommendations*. Science of the Total Environment 408 (2010) 3044–3051

Duk-Hee, L., Monica Lind P., David, R., Jacobs, J., Samira, S., Bert, B., Lars, L., (2012). *Background exposure to persistent organic pollutants predicts stroke in the elderly*. Environment International. 47; 115–120

Dvorska’, A., Lammel, G., Holoubek, I., (2008). *Recent trends of persistent organic pollutants in air in central Europe- Air monitoring in combination with air mass trajectory statistics as a tool to study the effectivity of regional chemical policy*. Atmospheric Environment 43 (2009); 1280-1287.

Elaine, E., (2009) "UN: *Treaty expanded by 9 more dangerous chemicals*". Associated Press 2009-05-09

EJF (2009). End of the road for endosulfan. *Pushing For a Global Ban on a Deadly Pesticide*. Environmental Justice Foundation, London, UK, Second version. ISBN NO; 1-904523-18-8.

Environmental Protection Agency-EPA, (2002). *Persistent Organic Pollutants, A Global Issue a Global response*. Office of international affairs (2610R), EPA-160-F-02-00

Environmental Protection Agency (EPA), (2006). *Assessment of lindane and other hexachlorocyclohexane isomers.* U.S

Environmental Protection Agency (EPA), (2009). Toxicological Review of Chlordecone (Kepone). In support of Summary Information on the Integrated Risk Information System (IRIS). EPA/635/R-07/004F.

European Union (EU), (2003). *Directive 2003/11/Ec of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether)*, Official Journal of the European Union 15.2.

Fromme, H., Midasch, O., Twardella, D., Angerer, J., Boehmer, S., Liebl, B., (2007). *Occurrence of perfluorinated substances in an adult German population in southern Bavaria.* Int Arch Occup. Environ. Health 80(4): 313-319.

Global Monitoring Plan-GMP., (2015). *Global monitoring plan for persistent organic pollutants under the Stockholm convention article 16 on effectiveness Evaluation*. Second regional monitoring draft report Africa region.

Guidance Material on New POPs Draft Version-GMNPDV, (2009) Hale, R.C., Guardia, M.J., Harvey, E., Gaylor, M.O., Mainor, T.M., (2006). *Brominated flame retardant concentrations and trends in abiotic media*. Chemosphere. 64(2):181

Harner, T., Karla, P., Todd, G., Anne-Marie, M., Hayley, H., Jill, C., Andrew, P., (2005). *Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers*; Environmental Pollution 144: 445-452

Harner, T., Shoeib, M., Diamond, M., Stern, G., Rosenberg, B. (2004), *Using passive air samplers to assess urban and rural trends for persistent organic pollutants, Polychlorinated biphenyls and organochlorine pesticides*, Environmental Science and Technology 38: 4474-4483.

Harner,T., Bartkow, M.,Holoubek, I.,Klanova,J., Wania,J.,Gioia, R., Moekel,C., Sweetman, A., Jones, K., (2005*). Passive Air Sampling for Persistent Organic Pollutants; Introductory Remarks to the Special Issue.* Environmental Pollution 144(2006) 361-364

Harner, T., Shoeib, M., Diamond, M., Ikonomou, M., Stern, G., 2006. Passive sampler derived air concentrations of PBDEs along an urban-rural transect: spatial and temporal trends. Chemosphere 64, 262e267

Harner, T., Karla, P., Todd, G., Anne-Marie, M., Hayley, H., Jill, C., Andrew, P., (2006). *Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers*. Environmental Pollution 144; 445-452.

Harris, M., Van den Heuvel, M., Rouse, J., Martin, P.A., Struger, J., Bishop, C.a., Takacs, P., (2000). *Pesticides in Ontario; a critical Assessment of Potential Toxicity of Agricultural products to wildlife with consideration for Endocrine Disruption*.

Volume 1: Technical Report series No. 340; Canadian wildlife service, Ontario Region.

Hill, A., (2000). Quality control procedures for pesticide residue guidelines for residue monitoring in the European Union, Second Edition, Document No SANCO/ 3103/2000, European Commission.

International Agency for Research on Cancer (IARC), (1998). *Summaries & Evaluations: Hexachlorocyclohexanes (Group 2B)*. Updated March 2, 1998.

Jana, K., Jirı, K., Lenka, H., Petra, U., Ivan, H., (2006). *Passive air sampler as a tool for long term air pollution monitoring; part 1.performance assessment for seasonal and spartiol variation.* Environmental pollution 144: 393-405.

Japanese International Cooperation Agency-(JICA), (2004). *Study on Master Plan for Urban Transport in the Nairobi Metropolitan Area in the Republic of Kenya*. Ministry of Roads and Public Works, Ministry of Local Government/, Nairobi.

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C., (2004). *Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe.* Environmental Science and Technology 38; 34-41.

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C., (2005). *Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalene's across Europe.* Environmental Toxicology and Chemistry 23; 1355-1364

Jones, K.C., Voogt, P., (1999); *Persistent Organic Pollutants Pops, State Of Science,* Environmental Pollution 100; 209-221.

KNIP, (2007), National Implementation Plan on Persistent Organic Pollutants. Nairobi, Kenya.

Klecka, G., Boethling, B., Franklin, J., Graham, G., Grady, L., Howard, P., Kannan, K., Larson, R., Mackay, D., Muir, D., van de Meent, K, (2000). *Evaluation of Persistence and Long-range Transport of Organic Chemicals in the Environment*. (Special Publication Series). SETAC, Pensacola, FL, USA.

Li, YF., Macdonald, RW, (2005); Sources and pathways of selected Organochlorine pesticides to the Arctic and the effect to pathway divergence on HCH trends in biota: a review, The science of the Total Environment 342:87-106

Li, J., Zhu, T., Wang, F., Qiu, X.H., Lin, W.L., (2006). *Observation of organochlorine pesticides in the air of the Mount Everest region*. Ecotoxicol Environ Saf, 63: 33-41

Lisa, M., Matthew, R., Paul, A. H., Mirriam, L.D., (2011). *Evaluation of passive air sampler calibrations; Selection of sampling rates and implications for the measurement of persistent organic pollutants in air*. Atmospheric Environment 45: 1867-1875

Luo Wang, HongliangJia, XianjieLiu, YeqingSun, MengYang, WenjunHong, HongQi, Yi-FanLi, (2013). *Historical contamination and ecological risk of organochlorine pesticides in sediment core in north eastern Chinese river*. Ecotoxicology and Environmental Safety 93: 112–120

Mireia, G., Eva M., Jordi, S., Martine, V., (2013). *Effect of persistent organic pollutants on the developing respiratory and immune system. A systematic review*. Environment international; 52: 51-65.

Mitullah, W., (2003). *Understanding Slums: Case Studies for the Global Report on Human Settlements 2003: The Case of Nairobi, Kenya*, UN-habitat, Nairobi

Mulaku, G.C., Kairui, L.W., (2001). *Mapping and analysis of air pollution in Nairobi, Kenya, International Conference on Spatial Information for Sustainable Development*, Nairobi, Kenya 2- 5 October 2001

Muraya, H., Takase, Y., Mitobe, H., Mukai, H., Ohzeki, T., Shimizu, K., Kitayama, Y., (2003). *Seasonal change of persistent organic pollutant concentrations in air at Niigata area, Japan*. Chemosphere 52(4): 683-940

National Environment Management Authority-NEMA, (2003). *State of the Environment Report for Kenya, Nairobi.* Environmental Monitoring 4: 371-376

North American Regional Action Plan-NARAP, (2005). *The North American regional action plan on lindane and other hexachlorocyclohexane (HCH) isomers*. Commission for environmental cooperation.

Omwenga, M. (2011). Intergraded Transport System for Liveable City Environment; A case study of Nairobi, Kenya; 47th ISOCARP Congress.

Orata, F., Quinete, N., Maes, A., Werres, F., Wilken, R., (2008). *Perfluorooctanoic acid and perfluorooctane sulfonate in Nile perch and tilapia from gulf of lake Victoria*. African Journal of Pure and Applied Chemistry. Vol 2 (8): 075-079.

Park, D., Hempleman, S. C., Propper.C.R. (2001). *Endosulfan exposure disrupts pheromonal systems in the Red-spotted Newt; a mechanism for subtle effects of environmental chemicals*. Environmental Health Perspective 109: 669-673.

Persistent Organic Pollutant Review Committee-POPRC, (2003).

Persistent Organic Pollutants Review Committee (POPRC) of the Stockholm Convention, (2007*). Ad hoc working group on C-Octabromodiphenyl ether under the Draft risk profile: commercial octabromodiphenyl ether*. United Nations Environment Programme.

(POPRC, 2007). Persistent Organic Pollutants Review Committee (POPRC), (2007). *Draft risk profile for beta-Hexachlorocyclohexane*, Stockholm convention on persistent organic pollutants

(POPRC, 2007). Persistent Organic Pollutants Review Committee-POPRC, (2007*). Ad hoc working group on C-Octabromodiphenyl ether. Draft risk profile: commercial octabromodiphenyl ether*. Stockholm convention. United Nations Environment Programme.

Rayne, S., Forest, K., Friesen, K. J., (2009). *Estimated congener specific gas phase atmospheric behaviour and fractionation of perfluoroalkyl compounds: Rates of reaction with atmospheric oxidants, air-water partitioning, and wet/dry deposition lifetimes*. Journal of Environmental Science and Health, Part A: Toxic / Hazardous Substances and Environmental Engineering; 44 (10): 936–954.

Robert, E., Bailey., (2007). *Pentachlorobenzene-Sources, environmental fate and risk characterization.* Pentachlorobenzene fact sheet. U.S. Environmental Protection Agency – EuroChlor.

Roland, K., (2005). *Persistent Organic Pollutants (Pops) As Environmental Risk Factors in Remote High-Altitude Ecosystems.* Ecotoxicological and Environmental Safety. 63; 100-107, Saggerson, E.P., (1991). *Geology of the Nairobi Area.* Degree Sheet 51, NE QUARTER, Mines and Geology Department, English Press, Nairobi, Kenya.

Shankar, A., Jie, X., Alan, D., (2011*). Perfluoroalkyl Chemicals and Chronic Kidney Disease in US Adults*. American Journal of Epidemiology; 174 (8): 893–900.

Shoeib, M., Harner, T., (2002). *Characterization and comparison of three passive air samplers for persistent organic pollutants*. Environmental Science and Technology **36** (19): 4142–4151.

Situma, D., (2010*). Assessment of Polycyclic Aromatic Hydrocarbons in Air and Soil from Selected Sites in Nairobi*. Msc Thesis. Department of Chemistry, University of Nairobi.

Steenland, K., Tinker, S., Frisbee, S., Ducatman, A., Vaccarino, V., (2009). *Association of perfluorooctanoic acid and perfluorooctane sulfonate with serum lipids among adults living near a chemical plant.* Am. J. Epidemiol. 170 (10): 1268–78.

Stein, C. R., Savitz, D. A., Dougan, M., (2009). *Serum levels of perfluorooctanoic acid and perfluorooctane sulfonate and pregnancy outcome*. Am. J. Epidemiol. 170 (7): 837–46.

Stockholm Convention, (2001). New York and Geneva.

Stockholm Convention, SC, (2008). *End of the road for Endosulfan*. Geneva

Tanabe, S., (2002): *Contamination and toxic effects of persistent endocrine disrupters in marine mammals and birds*. *Marine pollution bulletin* 45: 69 – 77

Tripathi, G., Verma, P., (2004). *Endosulfan-mediated biochemical changes in the fresh water fish Clarias batrachus.* Department of zoology, J. N. V. University, Jodhpur-342001, India. Biomedical and environmental sciences. 17**:** 47-56.

United Nations Environment Programme-UNEP, (2003). *Regionally based assessment of persistent toxic substances, Global Report*. UNEP Chemicals; Chatelaine, Switzerland.

United Nations Environment Programme-UNEP, (2005), *Ridding the world of POPs; A guide to the Stockholm convention on persistent organic pollutants*.

United Nations Environmental Programme-UNEP, (2010), *Chemical POPs Training Project Report,* Practical Training Course in Nairobi, Kenya (October 18-22, 2010. The Department of Chemistry, University of Nairobi.

United States Environmental Protection Agency-USEPA, (2006). *Assessment of lindane and other hexachlorocyclohexane isomers*.

Van Leewen S.P.J., Van Bavel, B., De Boer, J., (2013). *First world wide UNEP interlaboratory study on persistent organic pollutants, with data on polychlorinated biphenyls and organochlorine pesticides.* Trends in Analytical chemistry, 46: (110-117)

Wania, Mackay, D., (1999). *The evolution of mass balance models of persistent organic pollutant fate in the environment*. Environmental pollution 100: 223-240

Weiguang, X., Wang, X., Cai, Z., (2013). *Analytical chemistry of persistent organic pollutants identified in the Stockholm convention, a review*. Analytical Chimica Acta; 790: 1-13

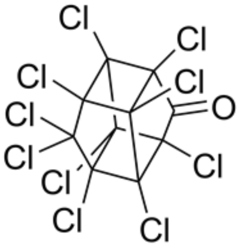
Weiguang, X., Xian, W., Zongwei, C., (2013). *Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention*; A review. Analytica Chimica Acta 790: 1– 13

Wenzl, T., Simon, R., Kleiner, J., Auklam, E., (2006). *Trends Analytical Chemistry*. 25; 716.

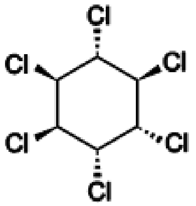
WHO, (2004), World Health Organization Lindane in Drinking Water: Background Document for Development of World Health Organisation Guidelines for Drinking-Water Quality.

APPENDIX

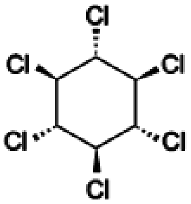
Appendix I; Structures of the ten new POPs



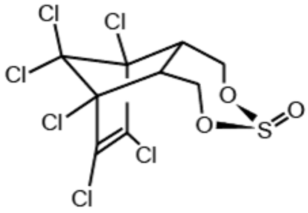
Chlordecone



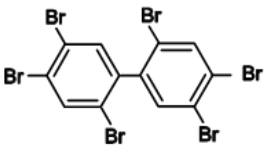
α-HCH



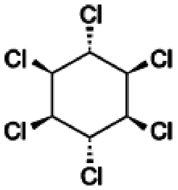
β –HCH



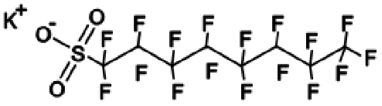
Endosulfan



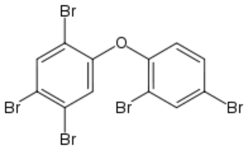
Hexabromobiphenyl



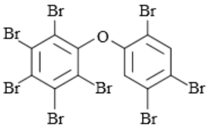
Lindane (γ-HCH)



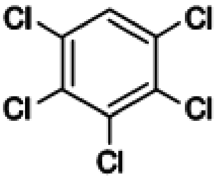
Perfluorooctane sulfonate (PFOs)



Pentabromodiphenyl ether

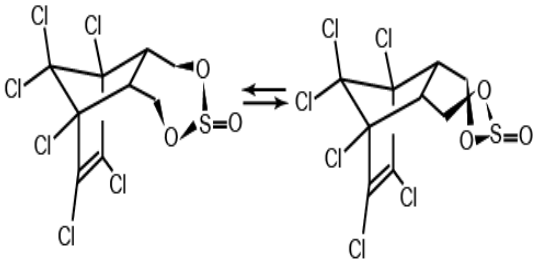


Octabromodiphenyl ether (octa-BDE)

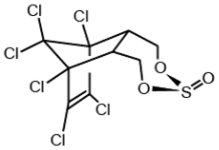


Pentachlorobenzene

Appendix II; Structures of the α- and β- isomers of endosulfan

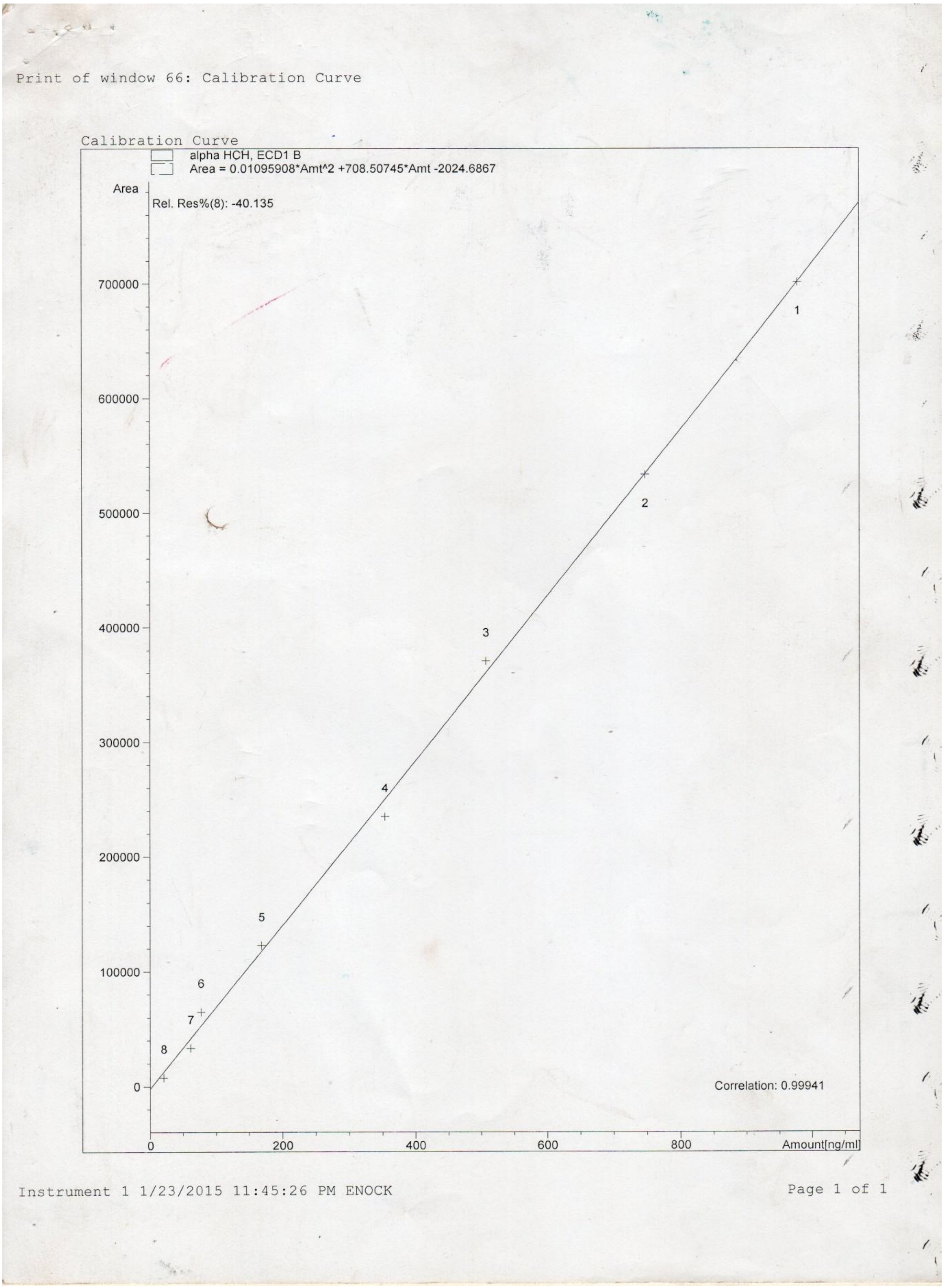


α-endosulfan



β-endosulfan

Appendix III; Calibration curves for the new POPs



Print of window 66: Calibration Curve

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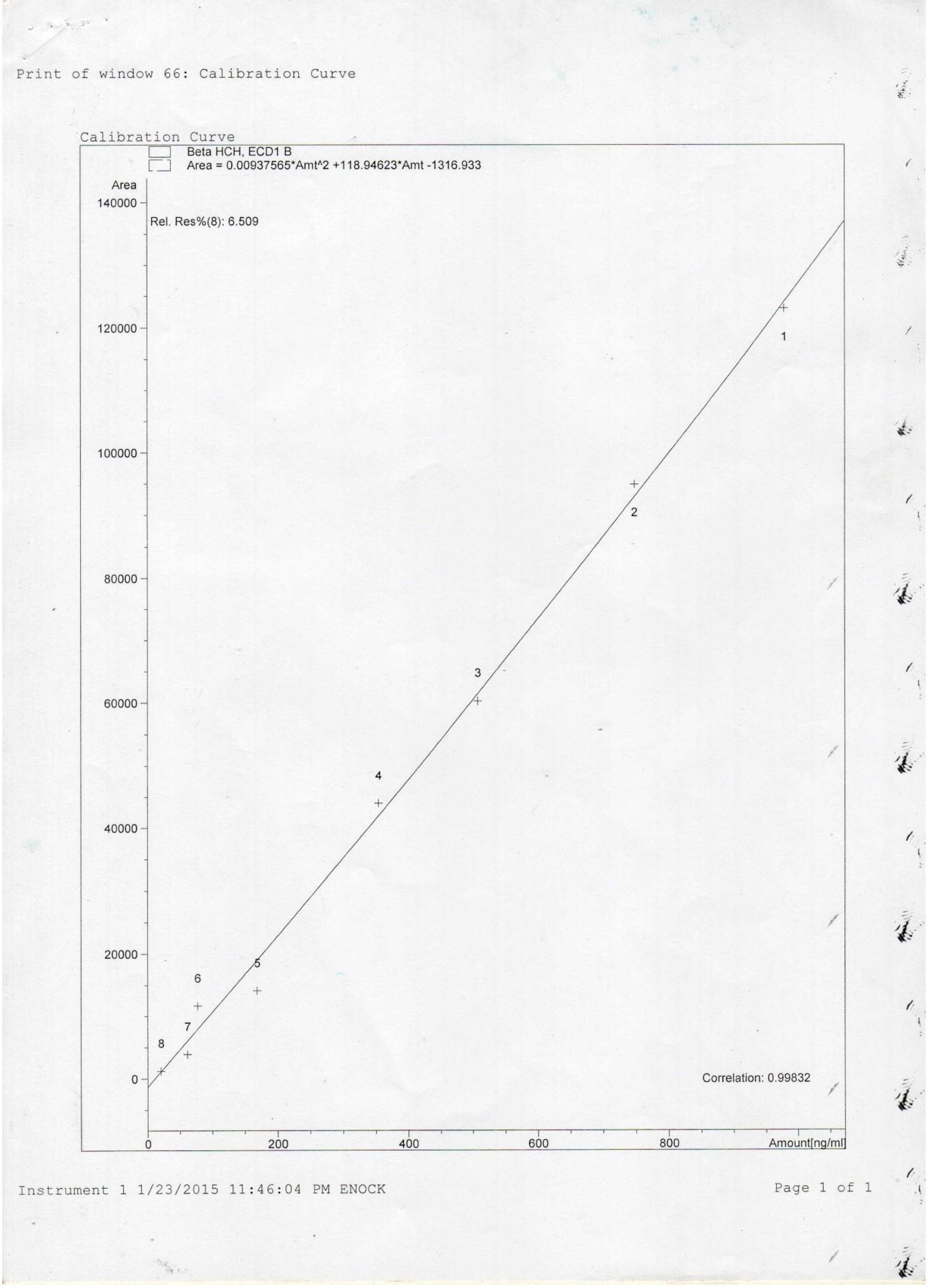

Print of window 66: Calibration Curve

Calibration Curve

Beta HCH, ECD1 B

Area = 0.00937565*Amt^2 +118.94623*Amt -1316.933

Rel. Res%(8): 6.509

Correlation: 0.99832

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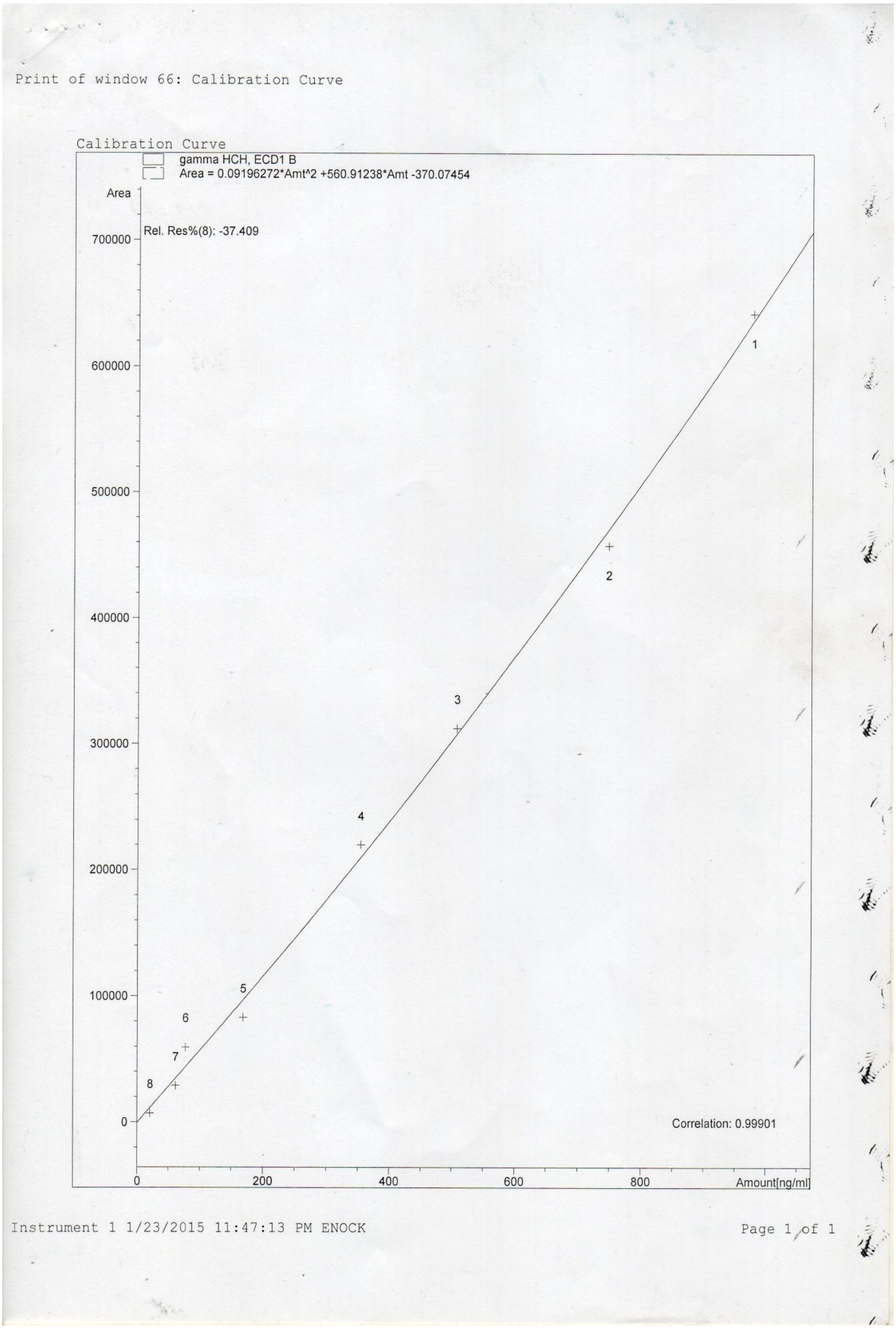

Print of window 66: Calibration Curve

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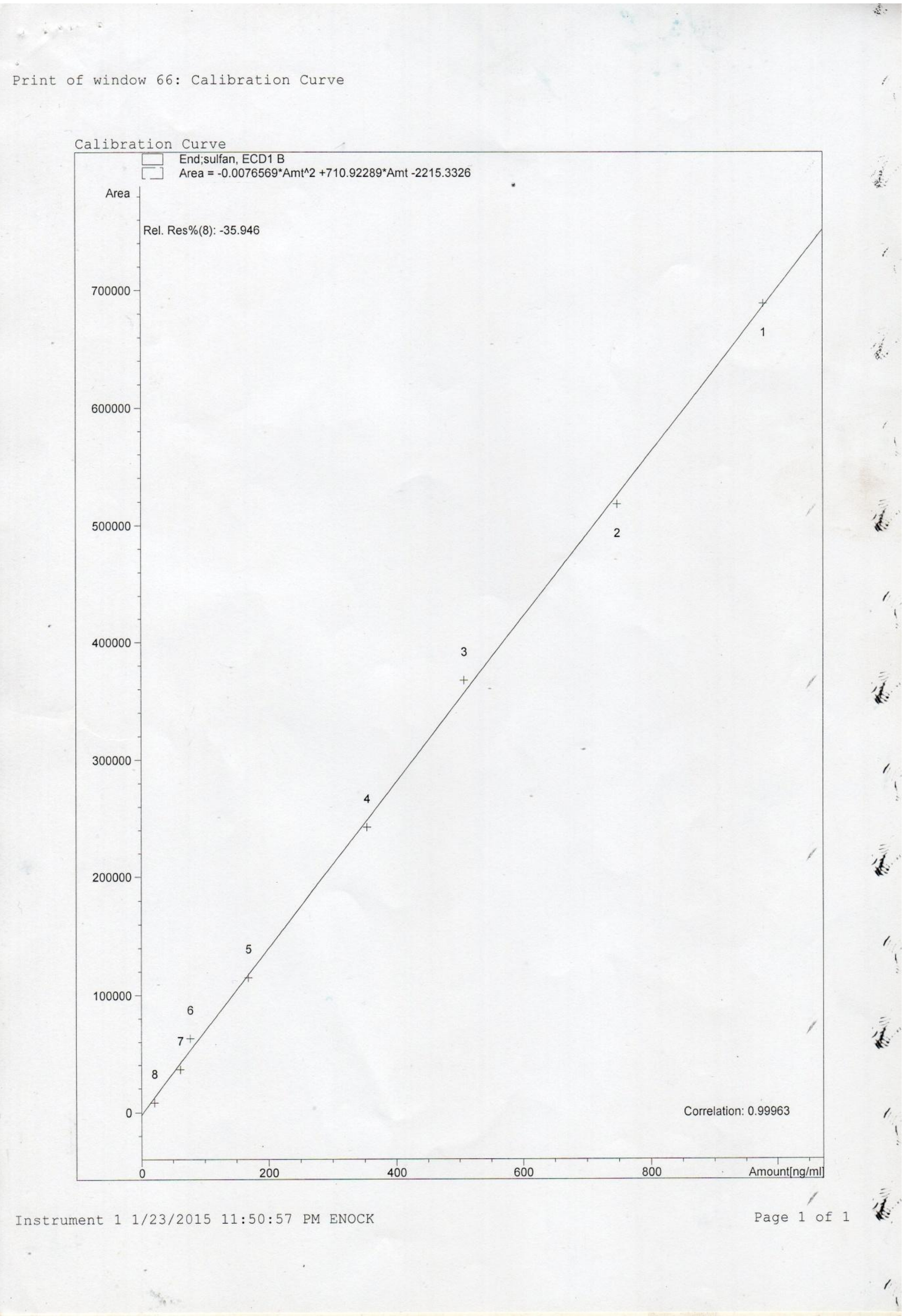

Print of window 66: Calibration Curve

Calibration Curve

End;sulfan, ECD1 B

Area = -0.0076569*Amt^2 +710.92289*Amt -2215.3326

Rel. Res%(8): -35.946

Correlation: 0.99963

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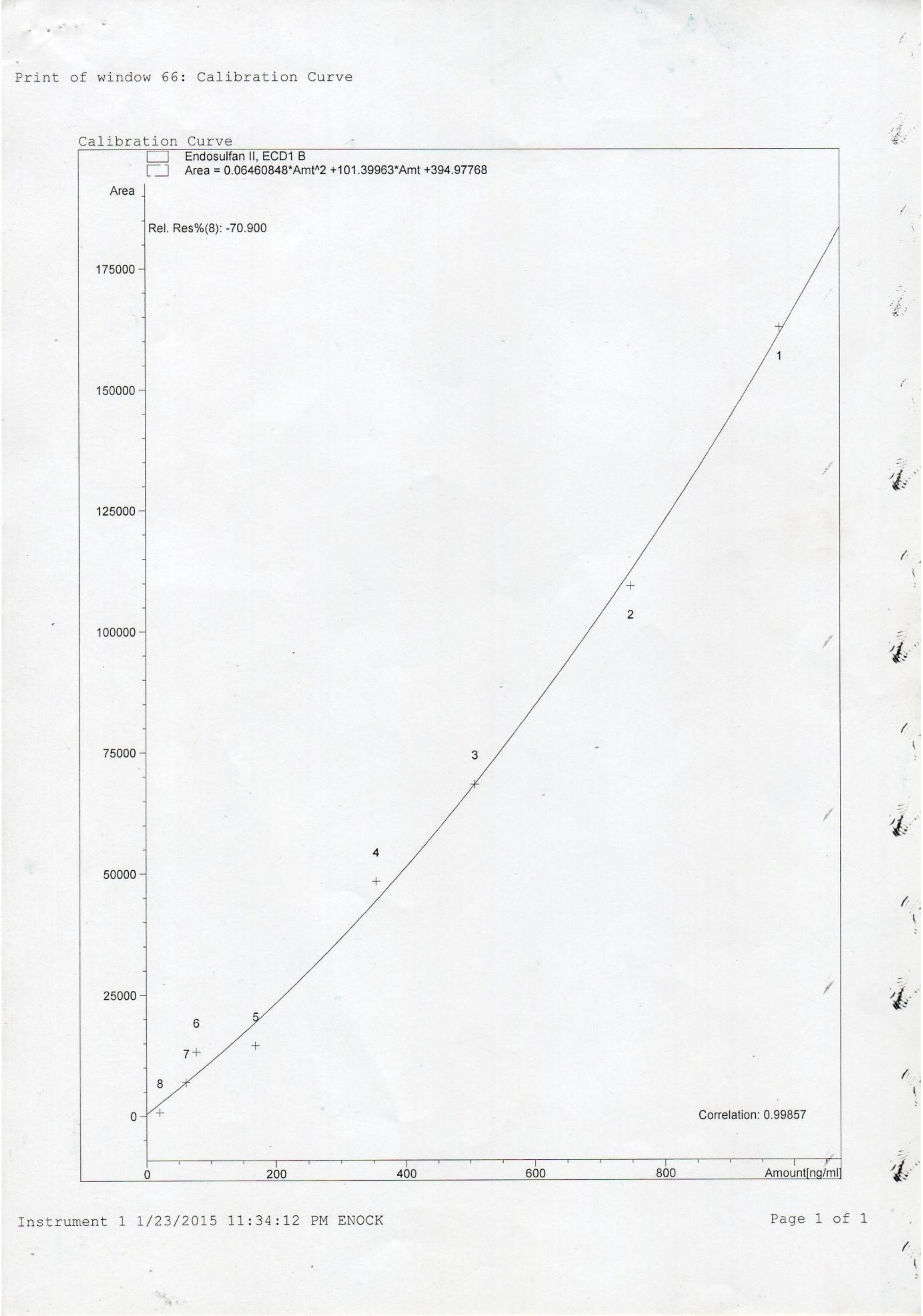

Print of window 66: Calibration Curve

Calibration Curve

Endosulfan II, ECD1 B

Area = 0.06460848*Amt^2 +101.39963*Amt +394.97768

Rel. Res%(8): -70.900

Correlation: 0.99857

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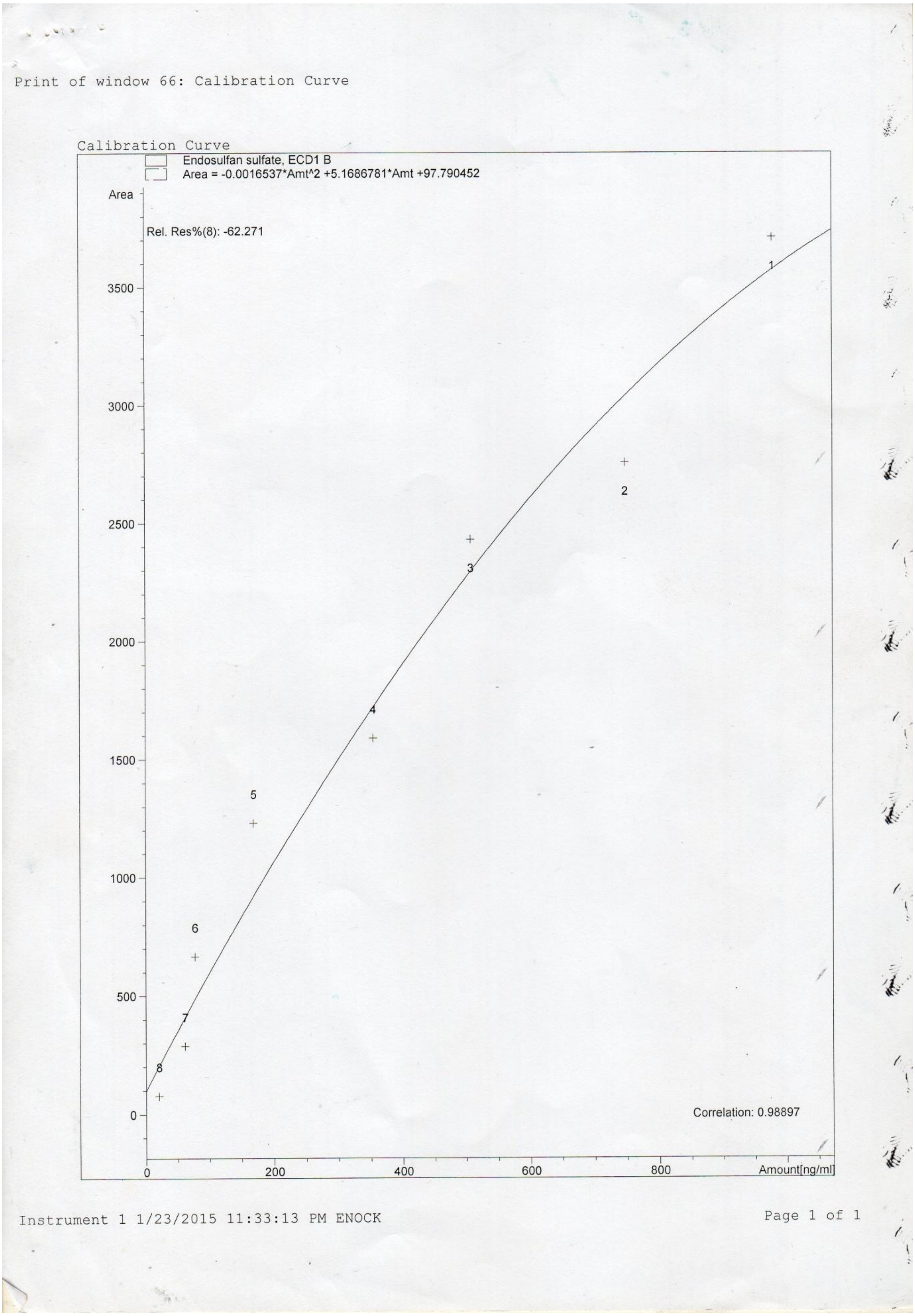

Print of window 66: Calibration Curve

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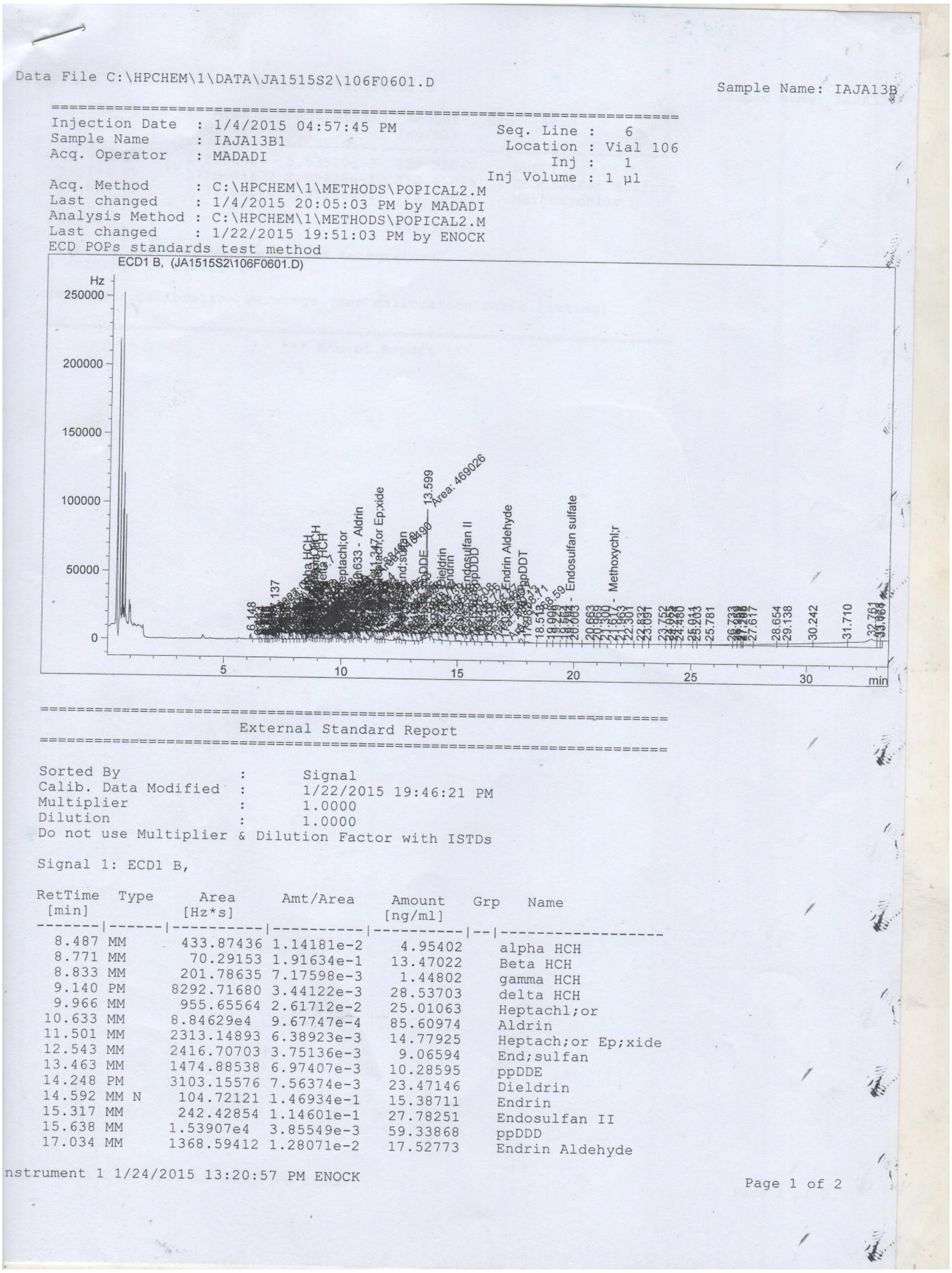
Appendix IV; Some chromatograms for air and soil analysis

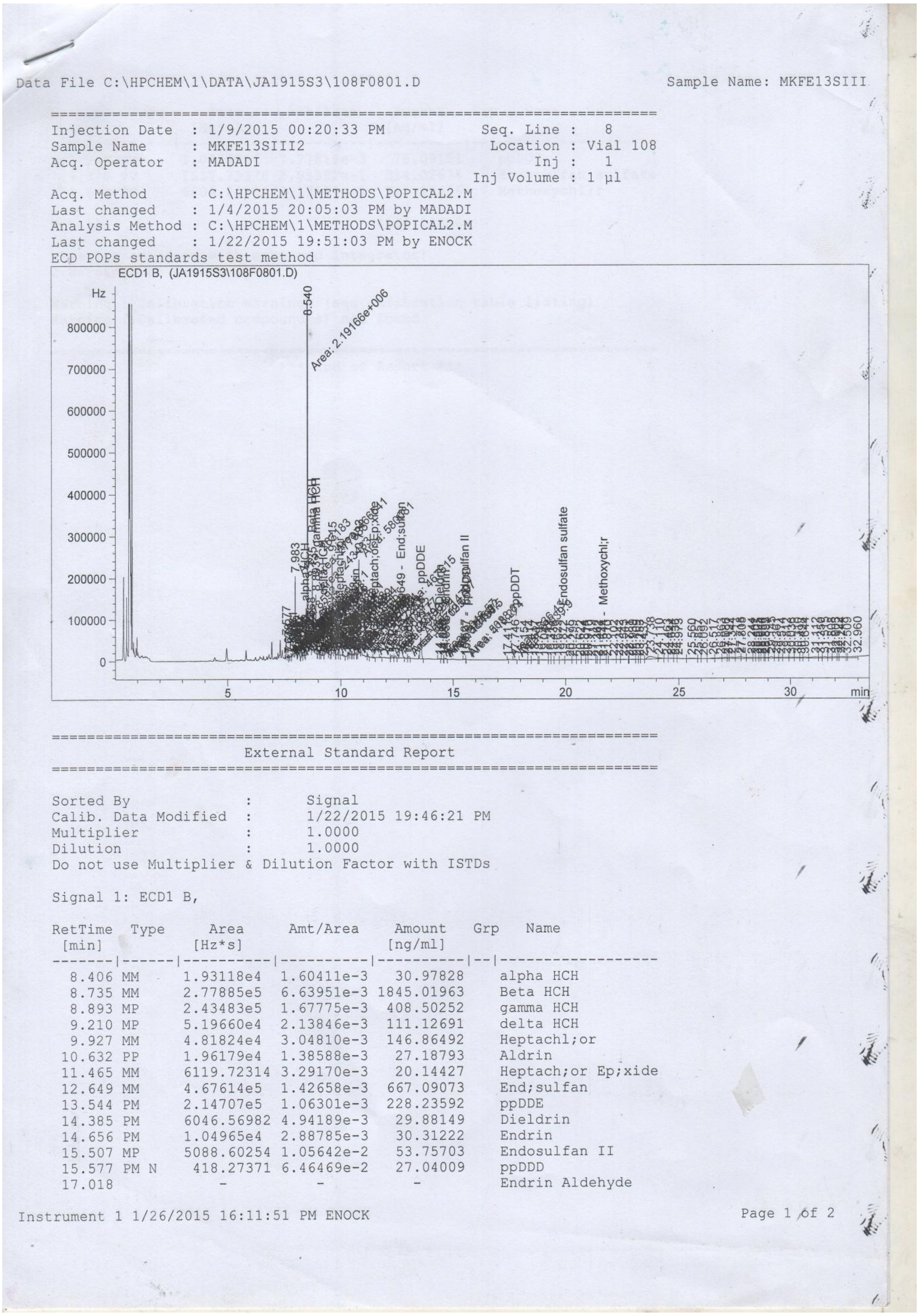
A chromatogram for an Industrial area air sample



```
Data File C:\HPCHEM\1\DATA\JA1515S2\106F0601.D                          Sample Name: IAJA13B

    ====================================================================
    Injection Date  : 1/4/2015 04:57:45 PM            Seq. Line :   6
    Sample Name     : IAJA13B1                         Location : Vial 106
    Acq. Operator   : MADADI                                Inj :   1
                                                     Inj Volume : 1 µl
    Acq. Method     : C:\HPCHEM\1\METHODS\POPICAL2.M
    Last changed    : 1/4/2015 20:05:03 PM by MADADI
    Analysis Method : C:\HPCHEM\1\METHODS\POPICAL2.M
    Last changed    : 1/22/2015 19:51:03 PM by ENOCK
    ECD POPs standards test method
```

```
   ====================================================================
                         External Standard Report
   ====================================================================

   Sorted By             :      Signal
   Calib. Data Modified  :      1/22/2015 19:46:21 PM
   Multiplier            :      1.0000
   Dilution              :      1.0000
   Do not use Multiplier & Dilution Factor with ISTDs

   Signal 1: ECD1 B,

   RetTime  Type     Area      Amt/Area     Amount    Grp   Name
    [min]          [Hz*s]                   [ng/ml]
   -------|------|----------|----------|----------|--|------------------
     8.487 MM     433.87436 1.14181e-2    4.95402     alpha HCH
     8.771 MM      70.29153 1.91634e-1   13.47022     Beta HCH
     8.833 MM     201.78635 7.17598e-3    1.44802     gamma HCH
     9.140 PM    8292.71680 3.44122e-3   28.53703     delta HCH
     9.966 MM     955.65564 2.61712e-2   25.01063     Heptachl;or
    10.633 MM    8.84629e4  9.67747e-4   85.60974     Aldrin
    11.501 MM    2313.14893 6.38923e-3   14.77925     Heptach;or Ep;xide
    12.543 MM    2416.70703 3.75136e-3    9.06594     End;sulfan
    13.463 MM    1474.88538 6.97407e-3   10.28595     ppDDE
    14.248 PM    3103.15576 7.56374e-3   23.47146     Dieldrin
    14.592 MM N   104.72121 1.46934e-1   15.38711     Endrin
    15.317 MM     242.42854 1.14601e-1   27.78251     Endosulfan II
    15.638 MM    1.53907e4  3.85549e-3   59.33868     ppDDD
    17.034 MM    1368.59412 1.28071e-2   17.52773     Endrin Aldehyde

nstrument 1 1/24/2015 13:20:57 PM ENOCK                             Page 1 of 2
```

A chromatogram for a soil sample from Mt. Kenya



```
Data File C:\HPCHEM\1\DATA\JA1915S3\108F0801.D                     Sample Name: MKFE13SIII

    =================================================================
    Injection Date  : 1/9/2015 00:20:33 PM         Seq. Line :   8
    Sample Name     : MKFE13SIII2                   Location : Vial 108
    Acq. Operator   : MADADI                             Inj :   1
                                                  Inj Volume : 1 µl
    Acq. Method     : C:\HPCHEM\1\METHODS\POPICAL2.M
    Last changed    : 1/4/2015 20:05:03 PM by MADADI
    Analysis Method : C:\HPCHEM\1\METHODS\POPICAL2.M
    Last changed    : 1/22/2015 19:51:03 PM by ENOCK
    ECD POPs standards test method

    =================================================================
                         External Standard Report
    =================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      1/22/2015 19:46:21 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: ECD1 B,

    RetTime  Type    Area      Amt/Area    Amount   Grp   Name
     [min]          [Hz*s]                [ng/ml]
    -------|------|----------|----------|----------|--|------------------
      8.406 MM     1.93118e4  1.60411e-3   30.97828     alpha HCH
      8.735 MM     2.77885e5  6.63951e-3 1845.01963     Beta HCH
      8.893 MP     2.43483e5  1.67775e-3  408.50252     gamma HCH
      9.210 MP     5.19660e4  2.13846e-3  111.12691     delta HCH
      9.927 MM     4.81824e4  3.04810e-3  146.86492     Heptachl;or
     10.632 PP     1.96179e4  1.38588e-3   27.18793     Aldrin
     11.465 MM     6119.72314 3.29170e-3   20.14427     Heptach;or Ep;xide
     12.649 MM     4.67614e5  1.42658e-3  667.09073     End;sulfan
     13.544 PM     2.14707e5  1.06301e-3  228.23592     ppDDE
     14.385 PM     6046.56982 4.94189e-3   29.88149     Dieldrin
     14.656 PM     1.04965e4  2.88785e-3   30.31222     Endrin
     15.507 MP     5088.60254 1.05642e-2   53.75703     Endosulfan II
     15.577 PM N    418.27371 6.46469e-2   27.04009     ppDDD
     17.018            -          -          -          Endrin Aldehyde

Instrument 1 1/26/2015 16:11:51 PM ENOCK                        Page 1 of 2
```