UNIVERSITY OF NAIROBI

ASSESSMENT OF THE CONCENTRATIONS AND DISTRIBUTION OF SELECTED POLYBROMINATED DIPHENYL ETHERS IN NAIROBI RIVER DRAINAGE BASIN AND THEIR PHOTOCATALYTIC DEGRADATION PATHWAYS

BY

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(I80/51442/2017)

A thesis submitted to the Faculty of Science and Technology in Fulfillment of the Requirements for Award of the Degree of Doctor of Philosophy in Chemistry of the University of Nairobi

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DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for award of a degree in any University. 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

This thesis is dedicated to my understanding and caring wife Edina, my sons Emmanuel and Ethan Osoro, my parents Mr. Osoro (the late) and Mrs. Rose Nyambeki, my father and mother in-law Mr. and Mrs. Okindo, my brothers: Ladisilus, Fredrick and Walter, my sister Gesare, my nephews: Brian, Hillary, Ramadhan, Cleophas and Osoro, my nieces: Pacificah and Jasmine and friends for their moral and financial support.

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ABSTRACT

Polybrominated diphenyl ethers are linked to adverse health effects that include thyroid hormone disruption, neuro-developmental deficit, abnormal pregnancy, and potential carcinogens. This study was aimed at assessing the levels and spatial distribution of selected polybrominated diphenyl ethers in water, sediments, soil and air of Nairobi River basin. The study also investigated the photo-catalytic degradation of BDEs 28, 85 and 183. Water, sediments, soil and air samples were collected, extracted, cleaned and analysed for brominated diphenyl ethers using gas chromatography coupled with mass spectrometer. Nitrogen doped titanium oxide catalyst was prepared by sol-gel method, characterized and its photo catalytic activity tested using methylene blue and methylene red. The mean concentration of PBDEs in water ranged from ≤0.001 to 72.89±6.15 ng/L, river sediments ranged between 134.70±3.07 to 24,386.13±207.22 ng/kg, soil ranged between 16.46±1.99 to 30,561.35±145.57 ng/kg and air samples ranged from ≤0.001 to 152.72±3.19 pg/m^3. Nitrogen was successfully doped into titanium oxide matrix and caused visible light response. The synthesized nitrogen doped titanium oxide degraded both methylene blue and methyl red. The photo-catalyst degraded methylene blue up to 96.7% at pH 7.0. Nitrogen doped titanium oxide nanoparticles synthesized and characterized degraded BDEs 28, 85 and 183 through stepwise debromination. The debromination efficiency by nitrogen doped titanium oxide was about 96.70%, 70.54% and 67.57% for BDEs 28, 85 and 183 respectively in 120 minutes. The calculated degradation half-life of BDEs 28, 85 and 183 were 70.01, 65.39 and 20.81 minutes respectively. The data shows anthropogenic contamination of Nairobi River by polybrominated diphenyl ethers, suggesting a potential risk to aquatic organisms that inhabit the river. The use of the water for irrigating vegetables and watering livestock also poses a potential health risk due to contamination across the food chain. This study is the first of its kind to assess the levels of polybrominated diphenyl ethers in Nairobi River basin and the photo catalytic degradation of polybrominated diphenyl ethers in tropical environment. The information obtained from this study forms a baseline data on the levels of polybrominated diphenyl ethers in Kenya and methods to enhance removal of polybrominated diphenyl ethers from the environment. The information will also be used by policy formulators to make decisions concerning the use of polybrominated diphenyl ethers.

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LIST OF ABBREVIATIONS

$^{13}C_{12}$-PBDEs	Mass-labelled polybrominated diphenyl ethers
ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
A_S	Surface area of the sampler
ATSDR	Agency for Toxic Substances and Disease Registry
BDE 100	2,2′,4,4′,6-pentabromodiphenyl ether
BDE-153	2,2′,4,4′,5,5′-hexabromodiphenyl ether
BDE-154	2,2′,4,4′,5,6′-hexabromodiphenyl ether
BDE-183	2,2′,3,4,4′,5′,6-heptabromodiphenyl ether
BDE-28	2,4,4’-tribromodiphenyl ether
BDE-47	2,2',4,4'-tetrabromodiphenyl ether
BDE-66	2,3',4,4'-tetrabromodiphenyl ether
BDE-85	2,2′,3,4,4′-pentabromodiphenyl ether
BDE-99	2,2′,4,4′,5-pentabromodiphenyl ether
BDL	Below detection limit
BFR	Brominated flame retardant
C-PBDE	Commercial Polybrominated Diphenyl Ether
C_S	Concentration of analyte in air
DCM	Dichloromethane
Deca- BDE	Decabromodiphenyl Ether
deca-BDE	decabromodiphenyl ethers
EDCs	Endocrine disrupting compounds
EEE	Electronic and electronic equipment
EI^+	Electron impact Ionization

E-waste	Electronic waste
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GMP	Global monitoring plan
HCB	Hexachlorobenzene
HIPS	High impact polystyrene
Kd	Partition coefficients
K_O	Mass transfer coefficient
K_{OA}	Octanol-air partition coefficient
Kow	Partition coefficients
K_{SA}	The sampler/ air partition coefficient
LOD	Limit of detection
log K_{OW}	Octanol-water partition coefficient
NEMA	National Environment Management Authority
Octa BDE	Octa brominated Diphenyl Ether
PAS	Passive air sampling
PBDEs	Polybrominated diphenyl ethers
PBT	Polyethylene polybutylene terephthalate
PCB	Polychlorinated biphenyls
PCG	Polymer-Coated Glass
penta BDE	Penta brominated Diphenyl Ether
PFOs	perfluorooctane sulfonate
POPs	Persistent organic pollutants
PUF	Polyurethane Foam

SD	Standard deviation
SEM	Scanning Electron Microscopy
SIM	Selected ion monitoring (SIM)
SPMD	Semi permeable membrane devices
SPSS	Statistical Package for the Social Science
TPH	Total Petroleum Hydrocarbons
TSH	Thyroid-stimulating hormone
UNEP	United Nation Environmental Program
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
V_S	Volume of sampler
WEEE	Waste electrical and electronic equipment
WHO	World Health Organization
XRD	X-ray diffraction
α-HCH	*alpha* hexachlorocyclohexane
β-HCH	*beta* hexachlorocyclohexane
γ-HCH	*gamma* hexachlorocyclohexane

UNITS OF MEASUREMENTS

µg	Microgram
µL	Microlitre
µS	Micro Siemen
g	Grams
Kg	Kilograms
L	Litre
m	Meter
mg	Milligram
mL	Millilitre
ng	Nanogram
nm	Nanometre
pg	Picogram
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion

CHAPTER ONE

INTRODUCTION

1.1 Background Information

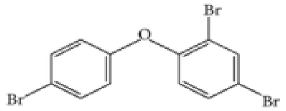
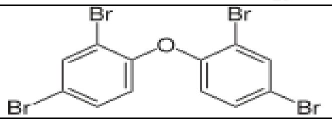
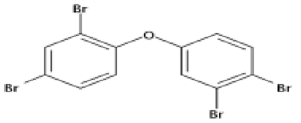
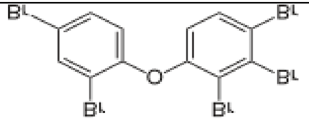
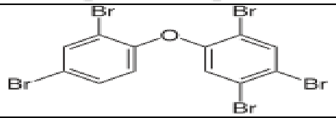
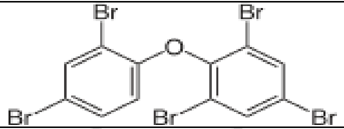
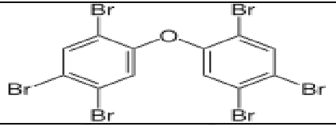
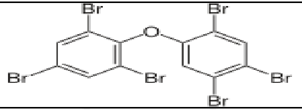
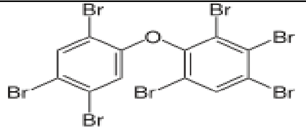
The international chemical industry has grown dramatically since the 1970s leading to the manufacture of a variety of goods that have enhanced the quality of people's life. The chemical products consist of beauty products, pesticides, drugs, fertilizers, petrochemicals, flame retardants, short chain chlorinated naphthalene and polychlorinated biphenyls (Cribb, 2021; Pure Earth, 2016). The international chemical industry's manufacture capacity nearly doubled between 2000 and 2017, from about 1.2 to 2.3 billion tonnes. This development in chemical manufacturing has created new opportunities for employment, trade and economic progress globally (UNEP, 2019).

The negative effect of industrial development is the accumulation and biomagnification of pollutants in the environment causing adverse effects to human health and the environment. These chemicals are universal and have been detected on the top of mountains, in the deepest oceans, from pole to pole and in the most remote, uninhabited areas, in soil, water, air, and in the human food chain (Gruber, 2018; Diaz and Rosenberg, 2008; Laffoley and Baxter, 2019). Hence the sustainable development goal of clean water free from contaminants cannot be achieved. Accordingly, a variety of global economic and regulatory instruments have been instituted to assist in management of chemical production, transport, import and export, use and disposal.

The protection of the environment is of great significance for healthy living. However, due to increasing industrial development and globalism, many nations are facing severe environmental contamination complications like air, soil, sediment and water contamination (Priti and Mandal, 2019). A number of the environmental contamination are initiated by Persistent Organic Pollutants (POPs), which are described as "chemical elements that remain in the environment for long, biomagnify through the food chain, and pose a risk of causing a variety of adverse health effects to humans and the environment (UNEP, 2013; European Commission, 2006). POPs listed in the annex of the Stockholm convention include: polybrominated diphenyl ethers (PBDEs), pesticides, aldrin, dioxins, furans and polychlorinated biphenyls (UNEP, 2009). PBDEs have been branded the "next generation of POPs" (Blake, 2005) or emerging chemical contaminants (Schecter *et al.,* 2005), and are alleged to be the cause of numerous harmful health effects on the environment and human (UNEP, 2013).

Polybrominated diphenyl ethers are a group of brominated flame retardants (BFRs) chemical additives that are applied for a long time in common household and commercial goods such as fabrics, electronics and electrical goods, building materials and chairs (Stubbings and Harrad 2014; Shaw *et al.,* 2010; Frouin *et al.,* 2013). PBDEs are mainly used to interrupt ignition of home goods and in case of a fire it forms a blanket after melting hence minimizing the speed at which fire's spreading (ATSDR, 2015). PBDEs consist of double halogenated aromatic rings surrounded by up to ten bromine atoms. Classification of PBDEs is based on the position and the number of bromine atoms on the aromatic rings (UNEP/FAO, 2019). PBDEs consists of 209 possible configurations of $C_{12}H_{(10-x)}Br_xO$: Where $x = 1, 2, \ldots, 10 = m + n$ which are called congeners (ranging from mono- to deca-bromodiphenyl ethers) (UNEP/FAO, 2019). Table 4.1 shows names, chemical structure, acronym, and molecular formula of polybrominated diphenyl ethers investigated in this study.

Table 1.1: Names, Chemical Structure, Acronym, and Molecular Formula of Polybrominated Diphenyl Ethers investigated in this Study

Name of PBDE	Chemical Structure	Acronym	Molecular formula
2,4,4'-tribromodiphenyl ether		BDE28	$C_{12}H_7Br_3O$
2,2′,4,4′-tetra-bromodiphenyl ether		BDE47	$C_{12}H_6Br_4O$
2,3',4,4'-tetrabromodiphenyl ether		BDE66	$C_{12}H_6Br_4O$
2,2′,3,4,4′-penta-bromodiphenyl ether		BDE85	$C_{12}H_5Br_5O$
2,2′,4,4′,5-penta-bromodiphenyl ether		BDE99	$C_{12}H_5Br_5O$
2,2′,4,4′,6-penta-bromodiphenyl ether		BDE100	$C_{12}H_5Br_5O$
2,2′,4,4′,5,5′-hexa-bromodiphenyl ether		BDE153	$C_{12}H_4Br_6O$
2,2′,4,4′,5,6′-hexa-bromodiphenyl ether		BDE154	$C_{12}H_4Br_6O$
2,2′,3,4,4′,5′,6-hepta-bromodiphenyl ether		BDE183	$C_{12}H_3Br_7O$

There are three main commercial PBDE formulations namely penta-bromodiphenyl ethers (Penta-BDE), octa-bromodiphenyl ethers (Octa-BDE) and deca-bromodiphenyl ethers (Deca-BDE). The latter accounts for 83% of the overall PBDE manufactured globally (BSEF, 2012; Besis and Samara, 2012). In America, the penta-BDE formulation is sold with the trade names of DE-62, DE-60F, DE-61 and DE-71, the octa-BDE formulation is distributed under the trade name of DE-79 while the deca-BDE formulation is sold with the trade names of Saytex 102E and DE 83R (BSEF, 2012). The penta-BDE formulation is mainly applied in mattresses and soft plastics, whereas the octa- and deca-BDE mixtures are mainly used in the hard plastics of construction materials and molded casings (Vonderheide *et al.,* 2008).

PBDEs are not covalently bonded to the polymer matrices. Hence, they leak out of the polymer matrix during manufacturing, use or disposal and become airborne thus extensively spread in the environment (Law, 2010). PBDEs are highly non-degradable hence they can be transported far from the source and biomagnify in animal and human being tissues when consumed (Law *et al.,* 2014; Harrad *et al.,* 2010).

Kenya is experiencing information and communication technology growth as it moves towards becoming part of the developing global information society. Hence, the quantity of electrical and electronic equipment has increased. According to Perez-Bilis *et al.,* (2015) the quantity of waste electrical and electronic equipment (WEEE) continues to grow in the world more so in developing countries due to increased manufacture and usage of electronic and electronic equipment (EEE) (Perez-Bilis *et al.,* 2015). In East Africa alone 6,000 kg of liquid crystal display and cathode ray tubes are sorted out every day while 30,000 kg of other electronics and electronic equipment are collected for disposal every year (GoK, 2014). In Kenya most of the disposed electronics and electronic apparatus and plastic waste are handled by informal sector that lacks experience on how to handle the waste hence the process of recycling increases the chances of releasing toxic chemicals more so PBDEs to the environment (GoK, 2014).

In order for Kenya to manage electronic and electronic equipment waste effectively, The National Environment Management Authority (NEMA) released electronic and electronic equipment waste guidelines in 2010 to provide ways on how to handle the various types of electronic and electronic equipment waste including transportation, sorting, treatment, recycling, re-use and disposal (GoK, 2014).

1.2 Persistent Organic Pollutants-Polybrominated Diphenyl Ethers Listed in the Stockholm Convention

In 2001 the world governments converged and formed the Stockholm Convention, whose consent was to guard the environment and human health from the negative impact of Persistent Organic Pollutants (POPs) by minimizing or eradicating their release to the environment (Stockholm convention, 2008). Kenya is a signatory to the Stockholm Convention on POPs, which it approved on 24th September, 2004. There are 28 chemicals listed as POPs under the Stockholm Convention (UNEP, 2019).

In 2004 the primary twelve POPs that were registered in annexes to the Stockholm convention on POPs were: polychlorinated biphenyls (PCB), toxaphene, aldrin, mirex, furans, chlordane, hexachlorobenzene, dieldrin, endrin, heptachlor, dichloro diphenyl trichloroethane (DDT) and dioxins (UNEP, 2011). The convention also defined criteria for including new chemicals basing on their persistence, bioaccumulation, likely for long-range transport and adverse health effects (UNEP, 2013). Consequently, the conference of parties to the convention approved in June, 2017 to include sixteen new POPs to the convention's annexes. The sixteen new POPs include: lindane, hexabromocyclododecane, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, hexachlorobutadiene, chlordecone, hexa-bromobiphenyl, 2,2',4,4',5,5'-Hexabromodiphenyl ether, perfluorooctane sulfonyl fluoride, 2,2',3,4,4',5',6-Heptabromodiphenyl ether, pentachlorobenzene, pentachlorophenol and its salts and esters, perfluorooctane sulfonic acid its salts, polychlorinated naphthalenes, technical endosulfan and its associated isomers, tetrabromodiphenyl ether, pentabromodiphenyl ether and decabromodiphenyl ether (UNEP, 2017). Commercial deca-BDE can debrominate to lower congeners of either octa- or penta-BDE representing a key source POP-PBDEs (UNEP, 2010).

The listed PBDEs in Annex A of the convention are tetra-, penta-, hexa-, hepta- and deca-BDE and are usually referred as POP-PBDEs. The use and production of all the POPs listed in Annex A should stop immediately by the party states and focus to the exclusions endorsed by the treaty. The nona-BDE and octa-BDEs which are common in commercial mixture of PBDEs are not included in the Annex as POPs since they do not meet all POP conditions. These extremely brominated PBDEs, can debrominate to lower congeners of either penta-BDE representing a key source of POP-PBDEs (UNEP, 2010).

POPs-PBDEs are extremely persistent in the environment hence they stay long before they are degraded, bio-accumulative and are likely to undergo long-range atmospheric transport in the environment. These compounds have been identified in human and biota around the world. There is proof of harmful effects in human and wildlife (Shaw *et al.*, 2010).

According to research conducted by European Chemicals Agency (ECHA) on deca-BDE in accordance with Annex XIII of the registration, evaluation, authorization and restriction of chemicals (REACH), deca-BDE is deliberated to be a polybutylene terephthalate substance in agreement with Annex XIII of the REACH Regulation, and is classified as a substance of serious concern (ECHA, 2012). The commercial deca-BDE has been suggested for addition in Annex of the Stockholm Convention (UNEP, 2013). POPs Review Committee (POPRC) at its tenth meeting in October, 2014 confirmed that BDE 209 was likely to lead to substantial human health and environmental effects hence worldwide action against its use was necessary. Henceforth due to the risk profile of the BDE 209 was accepted into Annex of the convention (POPRC, 2014).

1.3 Production of Commercial Polybrominated Diphenyl Ethers Mixture

Commercial penta-BDE production was mainly done in European Union (EU), China, United States of America and Israel (UNEP, 2010). It’s alleged that the manufacture of POPs-PBDEs in China, European Union and United States started in 1990 with the European Union stopping production in 1997 while China and the United States terminated the production in 2004 (UNEP, 2010). Commercial octa-BDE production was done in Israel, United Kingdom, United States of America, Netherlands, Japan and France. Manufacturing ended in 2004 in the

European Union and America and there is no data showing that it is being manufactured in developing nations (BSEF, 2012).

The POPs Review Committee (POPRC) projected that the overall manufacture of all PBDE from 1970 to 2005 ranged from 1300 million to 1500 million kilograms (UNEP, 2010). The overall quantities of commercial deca-, octa- and peta-BDE that was produced worldwide were projected to be about 1100 million, 100 million and 100 million kilograms respectively (UNEP, 2010). The production of commercial deca-BDE continues while the manufacture of commercial octa-BDE and commercial penta-BDE was terminated in 2004. Table 1.2 shows estimated total production of PBDE commercial mixtures from 1970 to 2005.

Table 1. 2: Estimated Total Production of Polybrominated Diphenyl Ethers Commercial Mixtures, 1970-2005

Commercial Mixture	**Tonnes**
commercial penta-BDE	91,000 to 105,000
commercial octa-BDE	102,700 to 118,500
commercial deca-BDE	1,100,000 to 1,250,000

(Source; UNEP, 2010)

1.4 Former Uses of Polybrominated Diphenyl Ethers

PBDEs were used in various sectors of the economy as follows: organobromine industry, construction material industry, textiles and carpeting industry, furniture production, automobile industry, recycling industry, electrical and electronics manufacturing (UNEP, 2007).

1.4.1 Former Uses of Commercial Penta-Brominated Diphenyl Ether

Approximately 95% of commercial penta-BDEs have been used in the production of polyurethane forms. These polyurethane forms were used in locomotive and fabric applications (UNEP, 2007). Other uses which accounted for 5% are in cable sheets, insulation foam, printed circuit boards, fabrics, drilling oils, conveyer belts and paint (UNEP, 2010). Studies have estimated that 85,000 tonnes and 15,000 tonnes of commercial penta-BDE were sold in America and Europe respectively. The study further reported that there was no reliable data available to indicate that there was usage of commercial penta-BDE in Asia (Alcock *et al.*, 2003). Generally, it's estimated that the supply of commercial penta-BDE use is 60% in home fittings, 36% in vehicles and 4% in other articles (UNEP, 2010).

Countries like United Kingdom and Unites States of America who have strict flammability standards to warrant application of BDEs on their manufactured goods, the amount of commercial penta-BDE in polyurethane foam is about 3-5% for fabric, pillows, beddings, and carpet padding (ENVIRON, 2003; UNEP, 2010). Lower amounts of 0.5-1% of commercial penta-BDE have been used in the manufacture of locomotives (Ludeka, 2011).

1.4.2 Former Uses of Commercial Octa- Brominated Diphenyl Ethers

Approximately 95% of commercial octa-BDE distributed in the European Union was formerly used in acrylonitrile-butadiene-styrene polymers (UNEP, 2019). The acrylonitrile-butadiene-styrene was applied in casings for cathode ray tube covers, copying equipment and printers (UNEP, 2019). Other minor uses were in polyamide polymers, high impact polystyrene, unsaturated polyesters, adhesives and coatings, polybutylene terephthalate, low density polyethylene and polycarbonate (UNEP, 2019). Some of the polymers were applied in manufacture of locomotive industry, while high percentage of the polymers were applied in electronics (UNEP, 2010). Concentrations in the key applications were between 12% and 18% (UNEP, 2019). Since the recycling of commercial octa-BDE in new plastic goods (secondary pollution), the overall amount of impacted plastics is expected to be significantly more than the reported data (UNEP, 2010).

1.5 Risk Associated with Persistent Organic Pollutants-Polybrominated Diphenyl Ethers

In some regions, present exposure to POP-PBDEs are already at concentrations where serious health effects are being reported in epidemiological research (Herbstman *et al.*, 2010). The technical evaluation of the effects of reprocessing commercial penta-bromodiphenyl ether and octa-bromodiphenyl ether for the persistent organic pollutants review committee decided that the following groups are considered to be at high risk, if exposed to POP-PBDEs as a consequence of being involved in recycling activities (UNEP, 2010): employees in informal waste electronic and electronic equipment activities (Steubing *et al.,* 2010), people residing in regions of undeveloped nations where traditional methods are used to handle waste electronic and electronic equipment (Wong *et al.,* 2007), workers involved in production, reusing and connecting foam products (Stapleton *et al.,* 2008), breast feeding children particularly in nations where body burdens are already high and women of reproductive age and those who are expectant, and subsequent neurobehavioral effects on the unborn child (Herbstman *et al.,* 2010).

Persistent organic pollutants review committee also resolved that the development of polybrominated dibenzo-p-dioxins or polybrominated dibenzofurans through the lifespan of PBDEs poses relevant dangers that need to be considered in the assessments of risks associated with PBDEs (Shaw *et al.,* 2010; UNEP, 2010). Polybrominated dibenzo-p-dioxins are present in PBDEs as impurities and can be produced as a result of thermal, chemical or photochemical processes involving PBDEs (Pliszczyńska and Maszewski, 2014). Polybrominated dibenzo-p-dioxins or polybrominated dibenzofurans are formed from PBDEs by chemical reaction through photochemical degradation and from flame-retarded plastic goods under warm air pressure (Marek *et al.,* 2015).

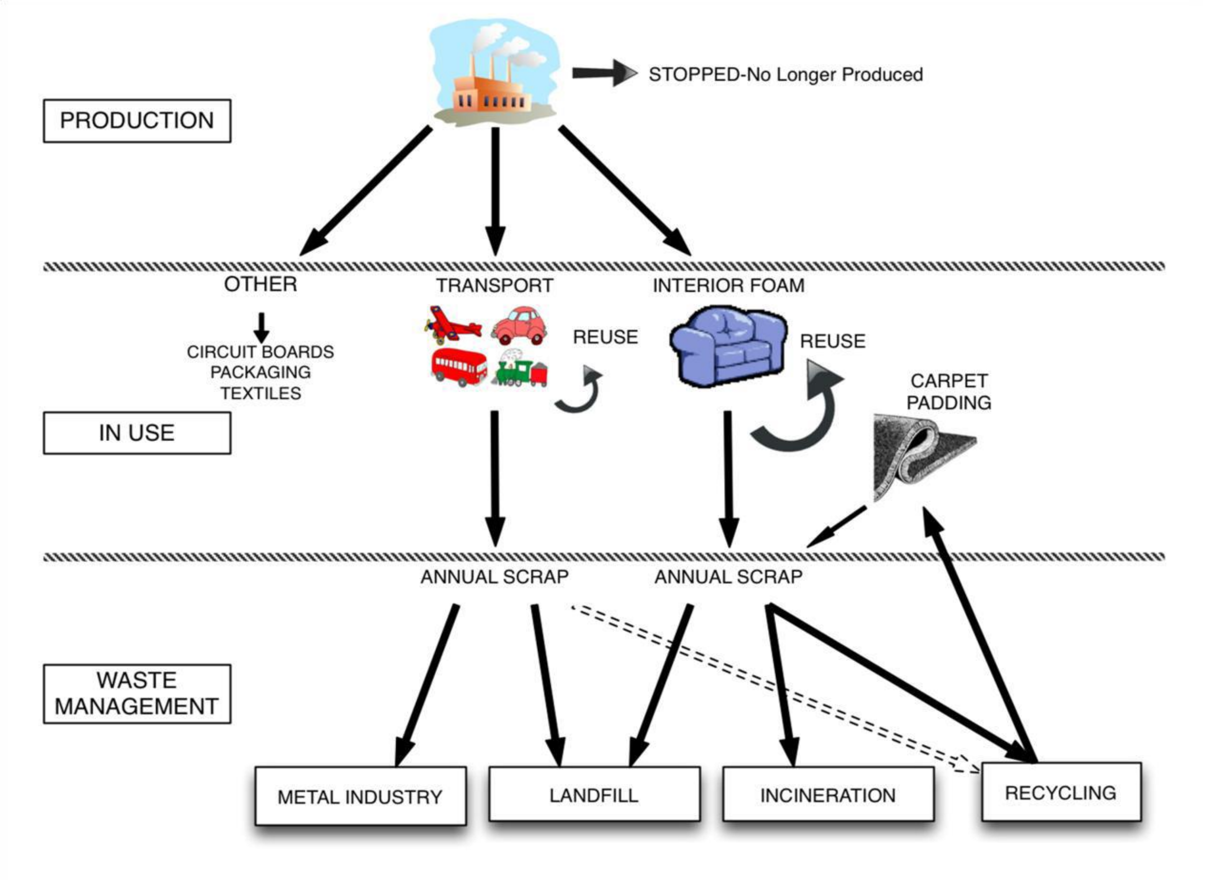
1.6 Persistent Organic Pollutants-Polybrominated Diphenyl Ethers in Waste Flow

Manufacture of commercial penta-BDE and commercial octa-BDE stopped in 2004 since they are toxic and bioaccumulate in both human and the environment, however commercial deca-BDE manufacture and usage continue (Jinhui *et al.,* 2017). The main problem for POP-BDEs removal is in the identification of predominant reservoir, goods having POP-PBDEs and the disposal of wastes containing POP-PBDEs. Bulk of products containing POP-BDEs are in the international recycling movement and will continue to be used in consumer products (Jinhui *et al.,* 2017).

The conference of parties for the Stockholm Convention allowed the recycling of products and wastes having POP-PBDEs under certain conditions. The technical review suggestions on recycling of POP-BDE highlighted that it was clearly not sensible to risk increased exposure when serious health effects from POP-BDEs were being measured in epidemiological studies in some regions (UNEP, 2010). Therefore, the recycling of materials containing POP-PBDEs into uses where further exposure could not be effectively controlled needed to be controlled (UNEP, 2010), and at the end of their lifetimes, the articles become waste with the potential of causing additional releases (Hale *et al.,* 2006). Therefore, some residual reservoir of PBDEs should be eradicated or can be exposed to advanced environmental management.

1.6.1 Commercial Penta-Polybrominated Diphenyl Ethers in Recycle, Reuse and Waste Flow

Commercial penta-BDE is mostly used on polyurethane foam applied in cars, buses, trains, airplanes and furniture like sofas, chairs and pillows with limited use in mattresses (UNEP, 2010). Other applications of commercial penta-BDE include insulation in building, fridges, treated rubber, fabrics and epoxy resins (UNEP, 2010). The main application and reusing flows of goods having commercial penta-BDE are shown in Figure 1.1.



(Adapted from UNEP, 2010)

Figure 1. 1: Schematic Diagram of the Life Cycle of Commercial Penta-BDE

1.6.1.1 Transport

The lifetime for vehicles in developed nations is 10 to 12 years, while buses and trains might have a longer life expectancy. A considerable number of second-hand vehicles have been and are still being imported by developing countries from developed nations for reuse; the automobiles are usually used for a long time before they finally break down and thereafter the spare parts are also reused further. Cars, buses and maybe trains that were manufactured in 1970 to 2004 contain commercial penta-BDE are still in operation likely in developing nations. These vehicles will need to be identified with respect to reuse and recycling when they reach end of their lifespan. Therefore, the transport sector needs specific best available techniques or best environmental practices deliberations for more management and control of commercial penta-BDE containing goods.

1.6.1.2 Furniture and Mattresses

The use of flame retardants (commercial penta-BDE) in furniture and mattresses depends on the flammability standards of a country (Shaw *et al.,* 2010). Due to flammability standards for furniture in the United States and United Kingdom in particular, furniture in North America and the United Kingdom are often flame retarded (Shaw *et al.,* 2010). Therefore, older furniture and mattresses in these countries may contain flame retardants (Shaw *et al.,* 2010).

The lifetime of furniture in developed nations is about 10 years (ESWI, 2011). Hence, it is likely that a substantial portion of furniture that have commercial penta-BDE in developed countries has been dumped or burned with a small portion recycled like in carpets (ESWI, 2011). The number of furniture exported to developing counties from developed countries for reuse or recycling has not been assessed and is considered as a likely source of commercial penta-BDE in developing nations (ESWI, 2011). Commercial penta-BDE was similarly used in rigid polyurethane foam in construction, but this is considered a insignificant application (ESWI, 2011). Additional reprocessing works for rigid polyurethane foam are unknown (ESWI, 2011).

1.6.1.3 Textiles and Rubber

Commercial penta-BDE has been used in small amounts for the treatment of fabrics for uses including back-coating, for curtains and for functional textiles (UNEP, 2009). Though the magnitude of reusing of clothes having commercial penta-BDE is uncertain, it can sensibly be presumed to be minor for composite goods like those used in vehicle (UNEP, 2009). There might be a limited restricted reusing of further commercial penta-BDE having textiles nevertheless it is probable that only fairly insignificant amounts of POP-PBDEs having fabrics are in use as commercial penta-BDE ended approximately ten years ago (Burçin *et al.,* 2020). Commercial penta-BDE was applied in foam rubber for conveyor belts and other minor uses (Burçin *et al.,* 2020).

1.6.1.4 Printed Circuit Boards

Commercial penta-BDE was previously used in printed wiring boards but this use has been phased out (Yu *et al.,* 2008). Printed wiring boards are a part of waste electronic and electrical equipment that are usually exported to developing nations, where the metals are improved by primitive means in the formal sector, or through simple smelters (Yu *et al.,* 2008). This can be the source of certain POP-PBDEs pollution (Yu *et al.,* 2008).

1.6.1.5 Recycling of Polyurethane Foam to New Articles

Polyurethane foams frequently used in vehicle and home appliances like furniture and beddings at the end of their lifespan are partially reprocessed into new goods by procedures like mat rebound and sanding (Ludeka, 2011). Large scale reprocessing of polyurethane foams into carpet padding is presently practiced in Canada and the United States (Ludeka, 2011). Polyurethane foams scrap is used in the manufacture of cushions, pet sheet, insulation and luxurious toys (UNEP, 2010).

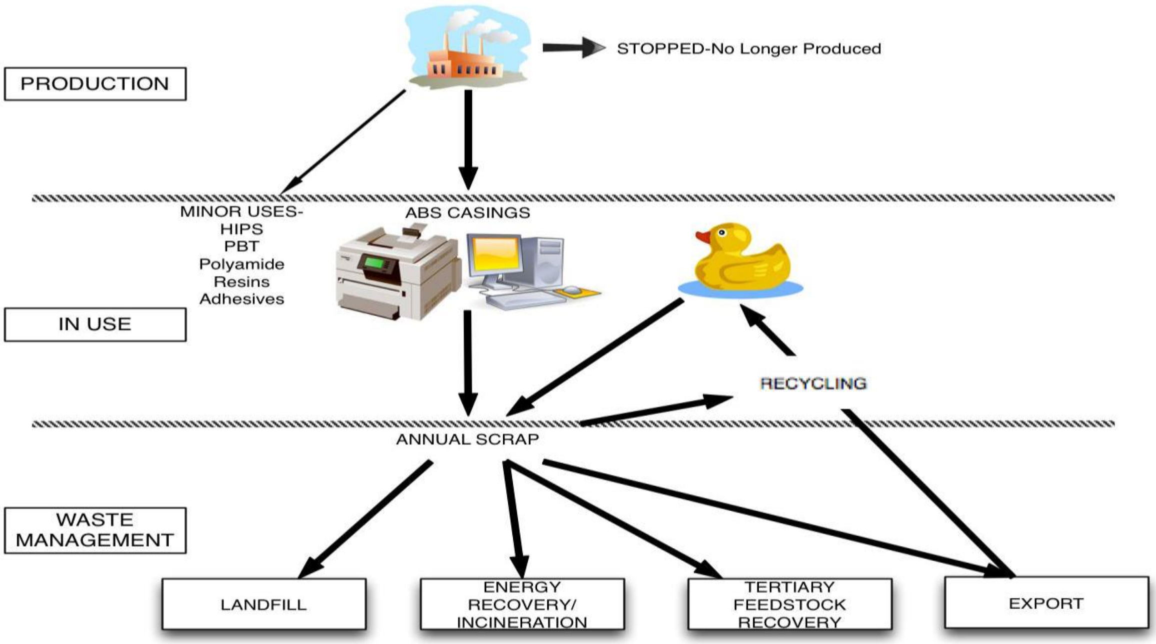
1.6.2 Commercial Octa- Polybrominated Diphenyl Ethers in Reuse, Recycle and Waste Flow

Production of commercial octa-BDE ended in 2004 in many countries (UNEP, 2010). The main commercial octa-BDE content is found in acrylonitrile-butadiene-styrene and high impact polystyrene polymers used in electrical and electronic equipment and waste electrical and electronic equipment (UNEP, 2010).

Majority of electrical and electronic equipment manufactured before 2005 contained commercial octa-BDE (UNEP, 2010). Most developing countries were and, in some cases, still are importing large amounts of old electrical and electronic equipment and waste electrical and electronic equipment from developed countries (like Japan, United Kingdom, United States, Europe and Hungary) for reuse or recycling (UNEP, 2010). Old recycling skills for waste electrical and electronic equipment have caused huge polluted zones in developing nations and exposure of people working in the recycling plants and the overall inhabitants to POP-BDEs is possible (Wong *et al.,* 2007; UNEP, 2010).

Majority of plastic wastes are mechanically recycled in developing countries (UNEP, 2010). However, when plastics are polluted with POPs and other harmful ingredients specific care should be taken on how the waste is recycled. The recycling of waste electrical and electronic equipment has resulted in plastics containing commercial octa-BDE (Chen *et al.,* 2010). A fraction of plastic from waste electrical and electronic equipment is shipped to countries like India and China where they are recycled into new articles (Chen *et al.,* 2010).

Plastics containing commercial octa-BDE and other brominated flame retardants additives have been recycled in the manufacture of articles for which no flame retardancy is required including children’s toys, household goods and video tapes (Hirai and Sakai, 2007). This is evident that the flow of plastics containing POP-PBDEs and other flame retardants for recycling are not well controlled and that plastics containing POP-PBDEs are being mixed with non-flame-retarded polymers for the production of items with sensitive end uses (Hirai and Sakai, 2007). Therefore, in some cases, the use of recycled plastic may be significantly more hazardous than the original use (Chen *et al.,* 2010). Figure 1.2 shows schematic diagram of the life cycle of commercial octa-BDE and potential for emissions



(adapted from Alcock *et al.*, 2003)

Figure 1. 2: Schematic Diagram of the Life Cycle of Commercial Octa-BDE and Potential for Emissions

1.7 Statement of the Problem

The future of Nairobi River hangs in the balance between economic exploitation and ecosystem restoration. Not only does the river act as a source of living to the riparian populations but also as a repository of wastes from municipal and industrial activities within Nairobi City County. The Nairobi river is one of the most contaminated rivers in Kenya (UNEP, 2009), as it receives a conglomerate of wastes including; industrial waste released directly from factories at Nairobi's industrial area and light industries in Kariobangi (UNEP, 2009), the garbage that includes unsorted waste of electronics and electrical goods from Dandora dumping site, insufficiently treated sewages from Ruai sewage treatment plant (UNEP, 2009), pesticides from urban agricultural activities (Nduda *et al.*, 2018), oil and grease, heavy metals, total petroleum hydrocarbons, polychlorinated biphenyl and other wastes from municipal and industrial activities (Budambula and Mwachiro, 2005; Masese, 2010). There are few studies on environmental contamination by PBDEs in Kenya (Makokha *et al.*, 2018; Hongwei *et al.*, 2016). Existing studies have focused on soil contamination from suburban and rural areas of Kenya excepting the City of Nairobi where the contamination is expected to be high; in addition, information on water and sediment contamination in Kenya is unavailable.

The presence of different congeners of PBDEs in the environment has raised key concerns in many countries more so developing countries (Taheran *et al.*, 2017). The general resistance to degradation and the potential toxicity of PBDEs also triggered substantial investigations on the development of efficient methods and techniques to properly treat this type of compound. Because PBDEs are difficult to oxidatively degrade, most of their decontamination methods are based on reductive debromination. For these reasons, it is urgent to develop effective remediation technologies to achieve the deep debromination of the PBDEs. From the overview of several options available for removal of PBDEs from different matrices, all treatment techniques appear to have drawbacks in terms of costs, applicability on large scale, environmental considerations and treatment efficiency. It is imperative that a combination of cost effective, environmentally friendly treatment processes, be used to safely destroy or eliminate PBDEs from the environment.

Information on the distribution of PBDEs in Kenya and Photo-catalytic degradation experiments of PBDE in tropical climate are not available in literature. Therefore, the current study, investigated the levels and spatial distribution of selected polybrominated diphenyl ethers in water, river sediment, soil and air of the Nairobi River basin. Information from this study is important in policy formulation to mitigate POP-PBDE pollution in Kenya. Nitrogen-doped TiO_2 for photocatalytic degrading of BDE 183, 85 and 28 under UV light. The effect of loading amount, optimum pH and debromination mechanisms and pathways were carefully investigated and discussed.

1.8 Hypothesis

Nairobi River basin area has elevated levels of PBDEs which can be removed or destroyed by photo catalytic degradation.

1.9 Objectives

1.9.1 Main Objective

Assessment of selected polybrominated diphenyl ethers in Nairobi River basin area and evaluation of the photocatalytic degradation of BDE 28, 85 and 183.

1.9.2 Specific objectives

i. To determine the concentration of selected polybrominated diphenyl ether residues in water, sediment and soil of Nairobi River basin

ii. To determine the concentration of selected polybrominated diphenyl ether residues in air from Nairobi and Mount Kenya regions.

iii. To synthesize N-TiO_2 photocatalyst.

iv. To determine the optimum conditions for N-TiO_2 photocatalytic degradation of BDE 28, 85 and 183.

1.10 Justification of the Study

Nairobi River traverses Nairobi County, which is the major national industrial hub. The river and its tributaries serve as a sink for industrial and domestic wastes (Budambula and Mwachiro, 2005). This is coupled with the numerous problems in waste management including electronic and electrical waste which are major sources of PBDEs. Despite the heavy load of effluent discharged into the river, it is widely used as a source of drinking and irrigation water downstream (Budambula and Mwachiro, 2005). This exposes human being at a potential risk to PBDE and other toxic compounds. Hence, it’s necessary for a comprehensive assessment of PBDE to be carried out in Nairobi River.

In Kenya most of the disposed electronics and electronic equipment and plastic waste are handled by informal sector that lacks experience on how to handle the waste hence the process of recycling increases the chances of releasing toxic chemicals more so PBDEs to the environment. Nairobi’s largest dumping site is in Dandora, where open burning of waste is the most common way of disposal and sorting of the waste is also done by informal sector. Monitoring of PBDEs in urban air environment is of specific significance since the air is exposed to all kinds of contaminants. 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 PBDEs.

The photo catalytic degradation of some selected PBDE by TiO_2 doped with nitrogen (N-TiO_2) /UV rays’ processes is selective and achieves varying degrees of degradation of PBDE in different matrixes. It is therefore imperative that integrating several environmentally sustainable degradation methods, simultaneously or sequentially, is required for enhanced destruction of a wide range of PBDEs. The potential of N-TiO_2 and solar energy which is abundant in the tropics as a renewable source of UV radiation for PBDE degradation was explored.

CHAPTER TWO

LITERATURE REVIEW

2.1 Polybrominated Diphenyl Ethers (PBDEs)

Polybrominated diphenyl ethers are organobromine chemical substances with up to ten bromine atoms usually attached to a biphenyl structure (ATSDR, 2015). The quantity and position of bromine atom attached to the biphenyl ring determines the congener and in total there are 209 congeners of PBDEs (ATSDR, 2015). PBDEs have been used for ages as brominated fire retardants chemical additives in electrical and electronic products, fabrics, building materials and furnishings (Stubbing *et al.,* 2014; Shaw *et al.,* 2010). PBDEs release bromine radicals at high temperatures that decrease the speed of burning and spreading of fire (Hahladakis *et al.,* 2018). They are loosely attached to the polymer matrix hence a part of these chemicals might leak out from the polymer during use, disposal, manufacture and reuse processes (Hahladakis *et al.,* 2018). The general chemical structure of PBDE is shown in Figure 2.1.

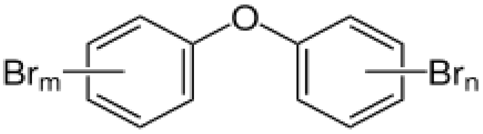


Figure 2. 1: General Chemical Structure of Polybrominated Diphenyl Ethers

The family of PBDEs consists of 209 possible congeners (PBDE = $C_{12}H_{(10-x)}Br_xO$ (x = 1, 2, ..., 10 = m + n)).

2.2 Sources of Polybrominated Diphenyl Ethers

PBDEs are supplementary materials in polymer production, but are not chemically bonded to the synthetic compound, hence they can easily leak to the surrounding atmosphere (a process known as blooming) (Hahladakis *et al.,* 2018). PBDEs can be released into the environment through vaporization or dust formation when using products that have PBDEs (Xu *et al.*, 2019), emissions through production of PBDEs or PBDE having products, discarding of wastes containing PBDEs (O'Driscoll *et al.*, 2016), using treated wastewater for agriculture (Goel *et al.*, 2006) and reprocessing of goods having flame retardants (USEPA, 2006; Sepulveda *et al.*, 2009; Destaillats *et al.*, 2008;). Debromination of deca-BDE is a possible source for PBDEs with few bromine in the environment (La Guardia *et al.*, 2006).

The existence of PBDEs in the global environment was first detected in samples of fish caught in Swedish waters in 1981 (Andersson and Blomqvist, 1981). PBDEs manufacture internationally is projected to be 67,000 tons per annum (Hale *et al.*, 2002) with market demand for all PBDEs estimated at 58 % in Asia, 26 % in America and 14 % in Europe (Kalantzi *et al.*, 2004). PBDEs decrease the spread of fire in a selection of goods hence their presence in the atmosphere in several parts of the environment is expected.

Huwe and coworkers (2008) suggested that people can get into contact with PBDEs through intake of contaminated food or dust and breathing contaminated air. PBDEs are bioaccumulative in fat and have been found in aquatic animals like fish (Hale *et al.*, 2002), harbor seals (She *et al.*, 2002), herring gull eggs (Norstrom *et al.*, 2002) and beluga whales (Lebeuf *et al.*, 2001). PBDEs enter the food web through fatty foods like fish. Studies have shown bioaccumulation of PBDEs in marine animals hence people are commonly exposed to PBDEs through consuming marine animals (Frederiksen *et al.*, 2009 and Luo *et al.*, 2007). Total PBDE distribution in human milk have been found to be high in persons who consume a lot of sea foods (Ohta *et al.*, 2002).

Infants are at risk as they can be exposed to PBDEs through placental transport and mother's milk (Lee *et al.*, 2013). Breast feeding is a major PBDE introduction pathway to children (Darnerud *et al.*, 2011; Carrizo *et al.*, 2007 and Jones-Otazo *et al.*, 2005). People can be exposed to PBDEs through indoor dust at home and in the workplace mainly because of high amount of PBDEs in home appliances, people working in electronic production and recycling site, plastic production and recycling area being at high risk. Leakage from dumping sites and through atmospheric deposition are the key sources of PBDEs in rivers, lakes and oceans. PBDEs remain in the environment for decades and hence accumulate in animal tissues (Sjodin *et al.*, 2001; Meironyte *et al.*, 2001).

Various researchers have established that PBDE congeners are present in the environment virtually in all the matrices and in disturbing levels. Consequently, they are nearly constantly present in native and marine creatures, since the current methods of wastewater and solid waste management does not eliminate the contaminant well to a non-poisonous level and this leads to increasing the concentration of the pollutant (Wu *et al.*, 2009). Discharging wastes contaminated with PBDEs into the environment instigate these pollutants into marine or earthbound food web, hence leads in their bioaccumulation and biomagnification in the animal muscles. Studies conducted in China have shown substantial augmented levels of 2,2′,4,4′-tetra-bromodiphenyl ether in polluted lake food chain (Wu *et al.*, 2009).

2.3 Physicochemical Properties of Polybrominated Diphenyl Ethers

Polybrominated diphenyl ethers are solid at room temperature, non-flammable, and do not present a physiochemical danger. Polybrominated diphenyl ethers are highly water insoluble contaminants with low osmotic pressures and high octanol-water partition coefficient (log K_{OW}) (USEPA, 2010). The octanol-water partition coefficient increases with the increase in the number of bromine atoms while water solubility and vapour pressure decrease with increasing number of bromine atom (Kierkegaard, 2007; Teclechiel, 2008). Consequently, with decreasing number of bromine atom there is increased propensity for PBDEs to be dissolving in water or partition to the vapour phase rather than to be adsorbed to air particles, soil and sediment (Kierkegaard, 2007). Physicochemical properties differ significantly between the various congeners of PBDE (Table 2.1), hence results in related variances in their toxicological effects, ecological fate, habits, spreading and exposure pathways (Kierkegaard, 2007; Hui-Ying *et al.*, 2007). These physicochemical properties as well govern in what way PBDEs released from their causes will be moved, dispersed, debrominated and finally collected in numerous ecological compartments as well as human being (USEPA, 2010). Table 2.1 shows physicochemical properties of selected PBDE congeners.

Table 2. 1: Physicochemical Properties of Selected Polybrominated Diphenyl Ethers Congeners investigated in this Study

Name of PBDE	Acronym	Molar Mass	Melting Point (^{o}C)	Water Solubility (mol/m^{3})	Henrey's law Costant	Log K_{ow}
2,4,4'-tri-bromodiphenyl ether	BDE 28	407.1	64-64.5	$1.72\text{x}10^{-4}$	5.1	5.98
2,2′,4,4′-tetra-bromodiphenyl ether	BDE 47	485.82	83.5-84.5	$3.09\text{x}10^{-5}$	1.5	6.55
2,3',4,4'-tetra-bromodiphenyl ether	BDE 66	485.82	104–108	$3.71\text{x}10^{-5}$	0.5	6.73
2,2′,3,4,4′-penta-bromodiphenyl ether	BDE 85	564.75	119-121	$1.06\text{x}10^{\cdot 5}$	0.11	7.03
2,2′,4,4′,5-penta-bromodiphenyl ether	BDE 99	564.75	90.5-94.5	$1.66\text{x}10^{-5}$	0.23	7.13
2,2′,4,4′,6-penta-bromodiphenyl ether	BDE 100	564.75	100–101	$7.08\text{x}10^{-5}$	0.069	6.89
2,2′,4,4′,5,5′-hexa-bromodiphenyl ether	BDE 153	643.62	160–163	$1.35\text{x}10^{-6}$	0.067	7.62
2,2′,4,4′,5,6′-hexa-bromodiphenyl ether	BDE 154	643.62	131-132	$1.35\text{x}10^{-6}$	0.24	7.39
2,2′,3,4,4′,5′,6-hepta-bromodiphenyl ether	BDE 183	722.4	131–132	$1.35\text{x}10^{-6}$	0.24	7.7

(Source; Danish EPA, 2016)

2.4 Environmental Fate, Behaviour and Distribution of Polybrominated Diphenyl Ethers

Polybrominated diphenyl ethers are of ecological and human wellbeing threat as a result of their persistence in the environment, high hydrophobicity, hence high log K_{ow} and toxicity to wildlife and humans (Kierkegaard, 2007). PBDEs have shown regional movement (Jones-Otazo *et al.,* 2005) and long-range environmental movement abilities hence they have been found to exist in remote places like the Arctic and Antarctica oceans (Li *et al.,* 2008), in the air and frost at the highest peak of mountains in different parts of the world (Pozo *et al.,* 2015) and in living creatures dwelling these regions.

Polybrominated diphenyl ethers transport in the environment takes place through numerous multifaceted processes like hopping (Gou *et al.,* 2016) and fractionation (Shen *et al.,* 2006). These mechanisms are influenced by wind and temperature patterns. PBDEs are insoluble in water, have low vapour pressures, high log K_{ow} values and persist in the environment hence they attach to the organic layer of particulate matter, mainly in sediments and soils, with merely minor quantities separating into air and water (Hale *et al.,* 2006; Environment Canada, 2004). Therefore, sediment and soil acts as store for PBDE releases (La Guardia *et al.,* 2006).

Polybrominated diphenyl ethers with lower bromine atoms are more bioconcentrated and stay longer in the environment than PBDE with more bromine atoms (de Wit, 2002). Research has shown bioconcentration of PBDEs in wildlife including dolphins and whales in oceans and seas even nearby the Arctic Ocean and Brazilian coast (Alava *et al.,* 2016; Salvadó *et al.,* 2016; Lavandier *et al.,* 2016). The less brominated PBDE congeners are of urgent concern because they have been gotten in mother's milk, serum and other biota and have a tendency to persist in the atmosphere, while more brominated PBDE congeners like BDE 209 have a habit of strongly binding to particles in sediment and soil which is their environmental sink (Hale *et al.,* 2006; de Boer *et al.,* 2003; La Guardia *et al.,* 2006; de Wit, 2002; Palm *et al.,* 2002).

Vaporization from water bodies and wet soils provides a major ecological pathway for tetra- to penta-BDEs, however the PBDEs with higher number of bromine atoms have low Henry's Law constants hence this provides a minor environmental fate process (Rauert, 2014). In the environment, PBDEs with few numbers of bromine atom like tetra- to penta- BDEs mostly befall in the particulate and gaseous phases whereas those with higher number of bromine atom such as BDE 209 experience atmospheric transport solitary in the particulate phase (O'Driscoll *et al.,* 2016). The likelihood for long range atmospheric transport is high for PBDEs congeners with less bromine atoms, whereas for PBDEs congeners with higher number of bromine atoms the possibility is directed by the movement of space of air particles (Law *et al.,* 2014; Wania and Dugani, 2003).

Photo degradation has provided an important pathway via which PBDE congeners can be degraded whereas biodegradation is not a major pathway for PBDE degradation (Rahman *et al.,* 2001). There is an understanding of polybrominated dibenzofurans (PBDFs) and photolytic removal of bromine atoms from deca-BDEs congener to penta- via nona-BDEs congeners (Olsman *et al.,* 2002) and to hepta- through nona-BDEs once it is diffused in solvent like toluene and exposed to non-natural ultraviolet rays for two forty minutes (Hagberg *et al.,* 2006). BDE 209 also can photolytically degrade into lower brominated PBDEs congeners if diffused in some solvents or if exists in non-natural and ordinary sand, soil and sediment (Eriksson *et al.,* 2004; Soderstrom *et al.,* 2004) Furthermore, degradation of PBDEs happens in thermal stress settings in the same way they are available during manufacture or reusing procedures resulting to the formation of polybrominated dibenzofurans and dibenzodioxins (Ebert and Bahadir, 2003; Weber and Kuch, 2003).

2.5 Health Effects of Polybrominated Diphenyl Ethers

The toxicology of deca-BDE (BDE 209) is the most understood, however in overall, PBDEs are associated to cancer, thyroid hormone disruption, developmental neurotoxicity, immune dysfunction, liver dysfunction and pancreas dysfunction (Muhammad *et al.,* 2003). Polybrominated diphenyl ethers have low severe toxicity, with an acute oral toxicity being more than 5000 ppb. When exposed to PBDEs in high amounts, the reproductive organs, renal system, liver, and thyroid gland are the main organs that are affected (Khalil *et al.,* 2016; Allen *et al.,* 2016, Gross, 2016; Wang *et al.,* 2016). Mostly, various PBDE congeners demonstrate similar toxicological properties where lower brominated BDE have higher effects than higher brominated congeners (Costa *et al.,* 2008).

Hardell and co-workers proposed 2,2',4,4' tetra-brominated diphenyl ether to be carcinogenic in human, because it was linked to fatty tissue concentration with increased non-Hodgkin malignancy in a number of cancer victims (Hardell *et al.,* 1998). A new study linked octa- and nona-BDEs congeners to acute lymphoblastic leukemia (Ward *et al.,* 2014). Earlier research proposed the rise in people exposed to PBDE congeners as a likely cause for the rise of thyroid cancer (Zhang *et al.,* 2008). Similarly, PBDEs exposure for long-term to mice has been shown to alter cell roles that give to metabolic cancer vulnerabilities (Dunnick *et al.,* 2012). Up to date, there is no strong proof that PBDEs can cause cancer. Henceforth, neither U.S. Department of Health and Human Services (DHHS) nor the International Agency for Research on Cancer (IARC) have categorized PBDEs has possible cancer agent.

There is a higher exposure and associated possible continuing poisoning of personnel employed in transport sector. In this sense there are contentious sentiments. For instance, a study by Harrad and coworkers showed that deca-BDE was significantly higher in cabin dust and at the equivalent period, that levels in the back seats were lower than in the front seats (Harrad and Abdallah, 2011). It's stated that the average day-to-day intake of PBDEs during traveling had maximum level of 2.91 ng /day with median of 0.22 ng/day and contributed 29% of the total day-to-day contact to PBDEs through breathing and that old vehicles contributed lower concentrations than the new units (Mandalakis *et al.,* 2008). A study conducted by Olukunle and coworkers revealed that deca-BDE was the main congener in all the dust specimens from vehicles.

One of the present highest worries for possible toxic effects of PBDEs relates to their disruption of the nervous system in children (Costa *et al.,* 2008; Zhang *et al.,* 2016; Hoffman *et al.,* 2016). This worry is owing to baby and kids giving the maximum PBDEs concentration per kilo associated to intake through interior dirt and mother's milk (Costa and Giordano, 2007; Guo *et al.,* 2016). Furthermore, earlier research showed immune suppressive effects (He *et al.,* 2009;), deoxyribonucleic acid damage (Tagliaferri *et al.,* 2010) cell deaths (He *et al.,* 2008), reactive oxygen species manufacture (He *et al.,* 2008) and chromosomal abnormalities in human cell cultures with PBDE (He *et al.,* 2008).

Hydroxylated Polybrominated Diphenyl Ethers (OHPBDEs) are typically produced through metabolic alteration of phylogenesis of PBDEs. Furthermore, formation of OHPBDEs occur naturally in the aquatic environment (by prokaryotes or algae) (Malmberg *et al.,* 2005). Since there is basic resemblances of hydroxyl-PBDE congeners with the hormones T2, T3 and T4, some PBDEs can modify the natural action of these hormones (Muhammad *et al.,* 2003). A study has confirmed that PBDEs congeners with small number of bromine atom can interrupt the thyroid causing malfunction and hormonal imbalance within a short period of exposure. For example, rats that were exposed to penta-BDE congeners developed hyperplasia as a result of reduced thyroid levels and this decreased the quantity of T4 in rats (Fowles *et al.,* 1994). Likewise, deca-BDE triggered thyroid hyperplasia and tumours in rats with contact time of three months (Muhammad *et al.,* 2003).

Workers involved in commercial PBDEs manufacturing for instance BDE 209 developed clinical hypothyroidism (Bahn *et al.,* 1980). A study by Meerts and co-workers demonstrated that PBDEs are estrogen disruptors as revealed by eleven PBDEs with substantial estrogen disrupting potential (Meerts *et al.,* 2001). BDE-51, 75 and 100, showed high properties for estrogen interruption (Meerts *et al.,* 2001). At higher levels, certain hydroxy-PBDEs exhibited extra forceful persuading effects than estradiol leading to 50% induction that varied from 2.5 to 7.3 µM (Meerts *et al.,* 2001).

2.6 Polybrominated Diphenyl Ethers Studies Conducted in the World

2.6.1 Polybrominated Diphenyl Ethers Residues in Water

A number of studies conducted in the world have reported varying concentrations of PBDEs in water. Olutona and co-workers assessed the levels of polybrominated diphenyl ethers in Asunle stream water, a connecting stream of the Obafemi Awolowo University dumpsite, Ile-Ife, Nigeria. The average concentration of PBDE ranged from 30 to 450 ng/L. Seasonal variation of the PBDE congeners revealed that higher concentrations were found in the rainfall period. When comparing the concentration of PBDE documented with other studies, they were fairly lower than the concentrations reported in literature from other industrialized countries (Olutana *et al.,* 2017).

Daso and co-workers studied the distribution of PBDEs in Diep River water, Cape Town, South Africa. Average levels of the summation of PBDEs were 4,290, 4,830 and 2,600 ug/L for the downstream, discharge location and upstream sampling positions, correspondingly. The predominant congener was 2,2',4,4'-tetrabromodiphenyl ether contributing between 19 and 26 % to the overall PBDEs across the sample collection locations (Daso *et al.,* 2013).

A study conducted in Chaohu Lake, a typical shallow fresh water lake in China by Liu and co-workers reported polybrominated diphenyl ethers in the ranges of 110–4,480 ng/mL, 60–5,410 ng/kg and 20–1,500 ng/kg dry mass in water, sediment, and biota samples, respectively. The mean levels revealed extensive disparities in the study location, though the congener profiles in all the water, sediment, and biota samples were frequently considered by only a number of congeners (BDE 47, 99 and 209). The temporal investigation showed increasing tendency of PBDEs from east to west of Chaohu Lake, dependable with local development degree (Liu *et al.,* 2018).

North, (2004) investigated Polybrominated diphenyl ethers in water, surface sediment, and pelecypod samples that were collected from the San Francisco creek. The mean concentration of PBDE in water was between 3 to 513 ug/ L, Lower South Bay region which receives about 26 % of the Estuary's wastewater processing facility effluent recorded the highest mean levels (North, 2004).

2.6.2 Polybrominated Diphenyl Ethers Residues Levels in Sediment

Studies have revealed existence of PBDE deposits in sediments from the Vaal River, South Africa. Chokwe and co-workers reported presence of residue BDE 209, 99, and 153 with concentrations range from 9.4 to 56, 4 to 32, and 1 to 10.6 ng/g, respectively. They further reported the concentrations of deca-bromodiphenyl ethane (DBDPE) in the range of 64,000 to

359,000 pg/g dry whereas the mean levels of polybrominated biphenyls was between 3300 to 7100 pg/g dry weight. The ratios of Alternative halogenated flame retardants to PBDE witnessed in the research were 0.76, 1.17, and 7.3 for 2-ethyl-1-hexyl-2,3,4,5-tetrabromobenzoate and bis-(2-ethylhexyl)-tetrabromophthalate (EH-TBB & BEH-TEBP)/penta-BDE; 1,2-bis-(2,4,6-tribromophenoxy) ethane (BTBPE)/octa-BDE; and DBDPE/BDE 209, correspondingly. The finding shows the predominance of some alternative halogenated flame retardants compared to PBDEs in the river (Chokwe *et al.*, 2019).

Analysis of the Kuils and Diep rivers sediment samples in South Africa revealed the presence of PBDE with the average concentrations of the summation of PBDE varied in the range of 0.001 to 0.025 ug/g in the Diep River. The concentrations were comparatively greater in the Kuils River. 2,2',4,4',5,5'-Hexabromobiphenyl recorded average concentrations of BDL to 390 ng/g. Likewise, 2,2',4,4',5,5'-Hexabromobiphenyl recorded average concentrations of BDL to 1 ng/g in the Kuils River. All the PBDE congeners, excluding BDE 209 showed robust positive association with the total organic carbon. While sewage released from neighboring sewage purification facility was acknowledged as main source of PBDEs, other prominent sources, together with grey water intrusion can result to the pollution of the upstream of both rivers (Daso *et al.*, 2016).

La Guardia and co-workers reported high amounts of PBDEs in inland and beach sediments in the Thekwini urban metropolis, South Africa, the mean concentrations competing with those in the severely impacted Pearl River Delta, China. They suggested that the PBDEs likely entered the South African environment through production of PBDE-containing goods, throughout the use of goods (particularly after discarding and due to reusing of goods), and from nonpoint sources like atmospheric effect and municipal overspill. The summation of the average concentration of PBDE was between 0.114 to 47.10 ng/kg. Deca-bromodiphenyl ether had the highest detected frequencies of 93 % in samples with mean concentration of 3208 ng/g, followed by 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) at 91% with average concentration of 0.545 ug/g. PBDEs in Durban Bay is as a result of municipal overflow and tidal hydrology, and sediments within showed total mean concentration of PBDE ranging from 1,850 to 25,400 ng/g with median concentration of 3,240 ng/g (La Guardia *et al.*, 2013).

Adewuyi and Adeleye reported PBDEs in sediment of Lagos Lagoon, Nigeria. The sum levels of PBDEs in sediment samples was between 110 to 23,330 ug/kg. At the four sampling points, 2,4,4'-tribromodiphenyl ether, 2,2′,4,4′,5,5′-hexa-bromodiphenyl ether, 2,2′,4,4′,5,6′-hexa-bromodiphenyl ether and 2,3,3',4,4',5,5',6-Octabromodiphenyl ether were identified in all sediment samples at mean levels of 220 to 23,330 ug/kg. The summation of tri- to hepta-BDEs was 61.32 %, whereas 2,3,3',4,4',5,5',6-Octabromodiphenyl ether was 38.68 % of the sum of PBDEs in the sediment samples. Brominated congeners 2,2′,4,4′-tetra-bromodiphenyl ether, 2,2′,4,4′,5,5′-hexa-bromodiphenyl ether and 2,2′,4,4′,5,6′-hexa-bromodiphenyl ether were the most frequent with a detection frequency of 18.31, 12.06 and 34.75 %, respectively. The study concluded that deca-BDE technical combination was the main contaminant sources with a small percentage of penta-BDE combination in Lagos Lagoon sediment samples (Adewuyi and Adeleye, 2013). Dirbaba *et al.*, (2018) observed low mean concentration of PBDEs in sediments in the range of 3,710 to 18,950 ng/kg dry weight with a total mean concentration of 7,330 ng/kg dry weight. 2,4,4'-tribromodiphenyl ether recorded a fairly wide range of mean values of 610 to 12,510 ng/kg among the analyzed PBDE congeners (Dirbaba *et al.*, 2018).

2.6.3 Polybrominated Diphenyl Ethers Residues Levels in Soil

A study conducted in Kenya has revealed varying concentrations of pollution by PBDE residues. Sun and co-workers analyzed soil from Limuru, Juja, Suswa and Mai Mahiu in Kenya, Eastern Africa and found PBDEs concentrations between 190 to 35,640 ug/kg dry weight. The major PBDE congeners were 2,4,4'-tribromodiphenyl ether, 2,2′,4,4′-tetra-bromodiphenyl ether and 2,2′,4,4′,5-pentabromodiphenyl ether, varying amongst different sample collection locations (Sun *et al.*, 2016).

Ohajimwa and co-workers determined the concentration of PBDEs in soil and dust at electronic waste recycling sites in three cities in Nigeria namely: Ibadan, Aba, and Lagos. The summation of the mean values was between 17 to 149,771 pg/kg. The major congeners among all the congeners analysed was 3,3',4,4',5,'5',6,6'-decabromodiphenyl ether in all the sampling sites and samples, with average concentrations between 1 to 147,091 pg/kg. The dust from electronic restoration workshop in Ibadan recorded the highest total PBDE concentration. The profusion of the PBDE congeners (bearing in mind the median of all the samples) in all the sampling sites were in this order: BDE 209 > BDE 207 > BDE 206 > BDE 183 > BDE 208, BDE 99 > BDE 153 > BDE 47 > BDE 190 > BDE 154 > BDE 100 >BDE 28 > BDE 138. There were major variances in the concentration of PBDEs congeners among each of the e-waste reprocessing locations and the matching control location. The concentration of PBDEs at the electronic waste reprocessing location surpassed the concentration at the control sites by a factor of 100 s to 1000 s. PBDE congeners were recorded in all sampling locations, signifying that PBDEs were extensive contaminants in this study location (Ohajinwa *et al.,* 2019).

A research conducted by Francisco and co-workers aimed at assessing the concentration of polybrominated diphenyl ethers (PBDEs) in soils from the city of San Luis Potosi in Mexico from different zones of the city. The average summation of PBDEs obtained in the research locations were 25,000 ± 39.5 ng/kg in the brick furnace manufacturing region; 34,500 ± 36.0 ng/kg in the city region; 8,00 0± 7.10 ng/kg in the manufacturing region and 16,6000 ± 15.3 ng/kg in the farming region (Francisco *et al.,* 2016).

2.6.4 Polybrominated Diphenyl Ethers Residues Levels in Biota

The existence of PBDE in biota was first reported in 1981 in samples collected along the Visken River in Sweden (Andersson and Blomkvist, 1981). From that time, studies of biological existence have been carried out internationally and in remote environments like the Arctic.

PBDE has been determined in over 50 classes at various trophic concentrations in Asia, the Arctic, America and Europe with 2,2′,4,4′-tetra-bromodiphenyl ether, 2,2′,4,4′,5-penta-bromodiphenyl ether and 3,3',4,4',5,'5',6,6'-decabromodiphenyl ether being the dominant congeners (de Wit *et al.,* 2006). Currently, studies have been done in aquatic ecology and the PBDE concentrations are mostly higher in sea creatures, while the earthly food web are likely to biomagnify more of the higher brominated PBDE congeners (Voorspoels *et al.,* 2007; Christensen *et al.,* 2005; Jaspers *et al.,* 2006).

A study conducted by Boon and co-workers showed various trophic concentrations fluctuating from protozoan to sea animals. They revealed the maximum noticeable upsurge in lipid-normalized concentration of the PBDE congeners studied (an order of magnitude) in samples ranging from fish to sea creatures (Boon *et al.,* 2002). Another study by Fuglei *et al.* (2007) on predator of an earthly food chain confirmed higher tissue pollutant concentration due to bioaccumulation in the food pyramid (Fuglei *et al.,* 2007). Biomagnification of approximately 38 ng/kg (lipid-normalized) PBDE congeners by ground worms in cultivated soils covered with manure mud shows the likelihood of substantial bioaccumulation in supplementary earthly food chains (Sellström *et al.,* 2005).

A research conducted by Tomy and co-workers on the salmonid food and sport fishes' biochemical pathway of PBDEs, revealed that PBDEs with high number of bromine atoms were the main congeners. Debromination was similarly noted as the main pathway in aerobic soil microorganisms (Vonderheide *et al.,* 2006).

Polybrominated diphenyl ethers have been detected in human serum with North America and Europe recording the highest concentration (McDonald, 2002). A research in a Chinese electronic equipment waste dismantling employee on work-related contact with PBDEs showed high levels of PBDE in the serum of the employees with BDE 209 recording the highest levels of 3.43 µg/Kg (Weiyue *et al.,* 2007). Li and coworkers (2008) conducted a study on the effects of PBDEs on enzymatic activities of hepatic and thyroid hormone in the growth of young male rat. The result showed reduced serum T3 count levels on contact with PBDE (Li *et al.*, 2008). Another study conducted on mothers' milk from Sweden from 1972 to 1997 to evaluate the concentration of PBDEs revealed an increase in concentration of PBDE from 70 to 4020 ng/Kg in period of 2 decades (Meironyte *et al.*, 1999). Another study on people's milk from Sweden showed average PBDE concentration of 3400 ng/Kg (Viberg *et al.*, 2002).

Mazdai and co-workers measured the level of PBDEs in the United States of America in foetus and mother blood and how they are related. The result showed a high relationship between mother and fetal blood samples (Mazdai *et al.*, 2002). Another study was conducted in sediment and fish samples from the River Vero in Spain, where high concentrations of PBDEs was recorded in samples from down the stream. The levels of PBDEs recorded were 0.012 ng/Kg and 0.707 ng/Kg in sediment and fish respectively while PBDEs where not detected upstream (Ethel *et al.*, 2007).

Degradation of PBDEs (BDE- 183, 153, 100, 99, 47 and 28) under UV light was carried out in a solvent. The result showed that different PBDEs congeners degraded rapidly with BDE 183 having the shortest half-life of 15 minutes, further it was concluded that the UV-degradation decreased with the decrease number of bromines in the structure (Lei *et al.*, 2008).

2.7 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 2.1

Where

V_S is the capacity of passive air sampler

C_S is the level of analyte in air

K_O is the general weight transmission 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 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 polyurethane foam (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 kilometers 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 minimize 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) (UNEP, 2015).

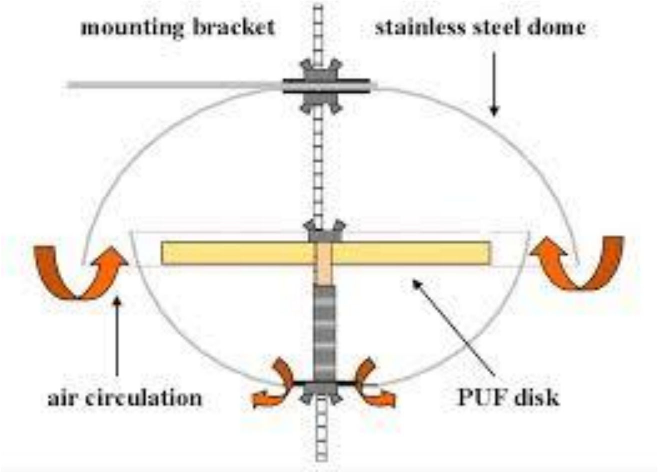


Figure 2. 2: Schematic Diagram of the Passive Air Sampling Device

Polyurethane foam (PUF) passive air samplers (PAS) are ordinary and extremely suitable technique of sampling persistent organic pollutants (POP) levels in ambient air. They were effectively useful as an instrument for POPs measurements on the worldwide and local levels. For example, under the global monitoring plan 2008-2012 (UNEP, 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 periods (months) enable discovery of a widespread variety of chemicals in large scale air sampling operations (Jaward *et al.*, 2005).

2.8 Advanced Oxidation Process

Advanced Oxidation Process (AOP) is a procedure that yields hydroxyl ions which are non-selective and highly reactive chemical substance that can destroy poisonous organic substance (Mota *et al.,* 2008). The OH^- radical has high oxidation ability and react with majority of the organic chemicals giving product of CO_2, H_2O and salt or change them to non-toxic chemicals (Pera-Titus *et al.*, 2004; Bolton *et al.*, 2001). Bossmann and coworkers (1998), explained the reaction pathways of a OH^- ion onto organic chemical as: the electrophilic reaction of a OH^- to organic chemical by a π -bond as a result of organic radicals released, the reaction of saturated aliphatic compound with hydroxyl radical by hydrogen abstraction and formation of an organic substrate by electron transmission with decrease of the hydroxyl radical into a hydroxyl anion (Bossmann *et al.*, 1998).

Chemical species like carbonate and bicarbonate ions influence the reaction of hydroxyl radical with on organic substrates (Andreozzi *et al.*, 1999).

$HO\cdot + HCO_3^{\,-} \rightarrow CO_3^{\,\cdot -} + H_2O$ ………..……. Equation 2.2

$HO\cdot + CO_3^{\,2-} \rightarrow CO_3\cdot^{-} + HO^-$………………. Equation 2.3

2.8.1 Fenton Systems

Henry John Horstman discovered the Fenton's reagent in the year 1894 which comprises of hydrogen peroxide and Fe^{3+} ions. Fenton systems is a process that involve oxidation of Fe (II) to Fe (III) by use of H_2O_2, which then attacks the peroxide to regenerate the original radical species as shown in scheme 2.1.

Scheme 2. 1: Generation of Radicals in Fenton System

$H_2O_2 + Fe^{2+} \longrightarrow OH^- + Fe^{3+} + {}^{\bullet}OH$ ………..…..…. Equation 2.4

$HO_2^{\bullet} + Fe^{3+} \longleftrightarrow H^+ + O_2 + Fe^{2+}$ ……….…..…….. Equation 2.5

$HO_2^{\bullet} + Fe^{2+} \longrightarrow Fe^{3+} + HO_2-$ …………….………. Equation 2.6

$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^-$ …………………..…. Equation 2.7

In this regard, Fenton reagent is simply a Fe^{3+}/ H_2O_2 (Fenton like reagent), implying that Fe (II) can be replaced by Fe^{3+}.

The use of Fenton system in wastewater treatment has been increasing because it is effective for hydroxyl radical generation and Fe^{3+} is highly plentiful and not poisonous, while H_2O_2 can be handled easily and is ecological friendly. However, the procedure involves equimolar consumption of each of Fe^{2+} and H_2O_2, demanding a high concentration of Fe^{2+} (Munter, 2001). Another major limitation of the Fenton reaction is it is favored by acidic medium near pH 3, limiting its application in near neutral and alkaline aquatic environments. The formation of insoluble hydrous oxyhydroxides ($Fe_2O_3.nH_2O$) further inhibits regeneration of the Fe (III)/ Fe (II) process, making the reagent ineffective in removing organic pollutants from wastewater (Kundu, 2010).

2.8.2 Photocatalytic Oxidation (UV/TiO_2)

Photo-catalysis is a process where a solid semiconductor is photo-excited as a result of absorbing electromagnetic energy, mostly in the near ultra-violent light range of the spectrum. Photons with enough energy may excite suitable semiconductor to yield group of valence holes (h^+) and group of conduction electrons (e^-). The h^+ and e^- are capable of initiating the process of oxidation and reduction. The commonly used semi-conductor is TiO_2 due to it being biologically and chemically inactive, cheap, and does not undergo chemical- and UV-corrosion (Karpova, 2007).

The electron-hole pairs initiate photo catalysis semiconductor after band gap excitation. When a photo catalyst is excited by UV- energy superior than band-gap energy, the e^- are mostly excited to a group of conduction, leaving h^+ in the valence band:

$TiO_2 + h\upsilon \longrightarrow TiO_2 (e^- + h^+)$ .... Equation 2.8

Subsequent reactions generate the required. OH radicals (Karpova, 2007):

$e^- + O_2 \longrightarrow O_2^{\cdot}-$ .... Equation 2.9

$O_2^{\cdot -} + H^+ \longrightarrow O_2H$ .... Equation 2.10

$2O_2H^{\cdot} \longrightarrow O_2 + O_2H_2$ .... Equation 2.11

$O_2H_2 + e^- \longrightarrow OH^- + HO$ .... Equation 2.12

The holes are extremely positive potential, and are able to oxidize all chemicals, even water:

$h^+ + H_2O \longrightarrow {}^{\cdot}OH + H^+$ .... Equation 2.13

TiO_2 exist in two most commonly crystal forms; anatase or rutile. TiO_2 anatase with 3.2 eV energy band gap can be triggered by around 387.5 nm.

In theory, all kinds of toxic chemicals are degradable by photocatalytic oxidation (PCO). However, the efficiency of PCO, like other AOPs, is chemical specific and no generalizations can be made about optimum conditions of operation for all waste waters. Moreover, high production of hydroxyl radicals may not necessarily be favourable as they may recombine (Karpova, 2007). Optimization of conditions for PCO; namely: pH, initial contaminant concentration, and catalyst application mode and amount, is necessary to effectively remove pollutants from water. PCO rate is generally directly proportional to contaminants concentration, though initial maximum rates are followed by decrease, due to UV screening and/or deactivation of the catalyst. Other factors affecting PCO effectiveness are irradiation density, whereby the rate of oxidation is directly proportional to light intensity; and reactor design. Due to the complex effect of each of the factors a generalization of its effect on PCO is not possible; requiring experimentation for each particular case (Munter, 2001).

The catalyst may be finely divided powder suspended in water, or restrained on water surface (Coleman *et al.*, 2005). The efficiency of suspended batch reactor operation depends on light strength, the catalyst quantum efficiency and contaminants characters like adsorption. Fixed bed reactors may be more convenient, but the smaller surface area limits its practical application. Commercial UV lamps with an output ranging between 254-380 nm have been used in various studies, indicating potential for use of solar UV.

Nakashima and co-workers, (2002) investigated degradation of 17-estradiol (E2) employing TiO_2 using fluorescent lamps. Two systems, one with a restrained catalytic agent scheme, and another with a revolving restrained absorbent catalytic chemical agent, were used. Adsorption onto the immobilized catalyst, rather than photolysis, was found to achieve 98 % and 90 % degradation of E2 in the respective systems. Coleman and co-workers, (2000) studied PCO of E2 using TiO_2 immobilized on Ti-6Al-4V alloy. 98 % degradation of E2 was achieved within 3.5 h, with optimum pH 12.

Due to extensive band-gap of TiO_2 which prevents the utilization of visible light, new or modified semi-conductor photo catalysts have been developed whose absorbances are in the UV range, this includes doping of semi-conductor with metal or non-metal element doping (Asahi *et al.,* 2001). It has been recommended that doping of TiO_2 with anion has increases the energy band gap (Sakthive *et al*., 2003). Five methods exist for the preparation of N-TiO_2 photo catalyst namely; sol-gel, sputtering, ion embedding, chemical gas deposition, oxidation of Ti-N, and decomposition of organic precursors (Sathish *et al.*, 2004).

Sol-gel method was chosen in this study for the synthesis of N-TiO_2 because it's one of the multipurpose process to prepare nanosized materials. The method is good for the preparation of titanium oxide photocatalyst (Devi *et al.*, 2014). The key benefit of the sol-gel technique is its outstanding control over the characteristics like grain size, compositional, porosity, homogeneity and particle morphology of the produce through a multitude of features that are available in all four main preparation stages: development of a gel, aging, dehydrating and heat management. The combination of an active metal or non-metal in the sol stage during the gelation process lets the metal to have a straight contact with support, hence the material has superior catalytic properties (Avasarala *et al.*, 2016).

2.9 Scanning Electron Microscopy (SEM)

SEM employs an intensive ray of high-energy electrons to yield an assortment of signals on a sample (Pareek and Pareek, 2013). The electron-specimen interaction produces signals that give information about the material including chemical texture, composition, crystalline structure and orientation of sample (Pareek and Pareek, 2013). Mostly information is collected within a designated area of the sample and a two- dimensional picture is created (Shariff, 2015). SEM can scan samples with thickness from 1 cm to 5 microns in thickness (Pareek and Pareek, 2013).

Point locations on the sample is analysed by SEM which is very essential in semi qualitatively or quantitatively investigating crystalline arrangement, chemical structure using energy dispersive spectroscopy (EDS) and crystal alignments using electron backscatter diffraction (EBSD) (Pareek and Pareek, 2013).

2.9.1 Fundamental Principles of Scanning Electron Microscopy (SEM)

Fast moving electrons in a SEM transport main quantity of kinetic energy, and this energy is degenerate as a diversity of signals are released by sample- electron interaction (Pareek and Pareek, 2013). These signals include bent backscattered electrons and mostly give the crystal organization and mineral position, secondary electrons which yield SEM imageries, backscattered electrons, photons used for characteristic X-rays for elemental inspection and continuum X-rays, visible light and heat (Pareek and Pareek, 2013).

Secondary electrons and backscattered electrons mostly used for sample imaging. The morphology and structure of samples is shown by secondary electrons while backscattered electrons are used in indicating differences in arrangement in samples with many phases. Crash of incident electrons and electrons in discrete orbitals of atoms in the sample produce X-ray (Saravanam and Rani, 2012). SEM analysis is non-destructive (Saravanam and Rani, 2012).

2.10 Gas Chromatograph-Mass Spectrometry

Gas Chromatography – Mass Spectrometry (GC-MS) is the leading technique that has been used for decades to analyse environmental samples.

2.10.1 Principle of Gas Chromatograph-Mass Spectrometry

The GC-MS has two main components the GC where the chemical mixtures are separated and the MS components where identification of the chemical is done. GC-MS is mostly used for analyzing environmental samples because it is accurate. The main working principle of GC is that a mixture will separate into different components on higher temperatures (Maštovká and Lehotay, 2004). Volatiles are carried by the carrier gas through the stationary phase. The instrument purity gas is introduced to GC machine at first. The carrier gas comes in through the injection pot just at the liner and moves in to the stationary phase with the sample and finally into the detector. The injector is maintained at high temperatures (423-523 K) this is to change the liquid sample to gaseous form. The volatile sample is carried to the stationary phase by the carrier gas (Karasek and Clement, 2008).

In the column the sample interacts with the stationary phase. The sample is carried through the stationary phase of the column whose particles don’t move; hence there is separation between the stationary and mobile phases (Steve *et al.*, 2005). All molecules that are associated to a particular chemical are carried through the stationary phase almost at the same speed and they are seen like a band of particles. The velocity at which the particles move on the stationary phase is determined by factors like; the chemical component of the stationary phase, structure of sample and the oven temperature (Steve *et al.*, 2005).

The operating temperatures of the oven and dimension of the stationary phase influence the extent of the compound or analyte. Retention time is the duration a particle takes from the time of injection until it comes to the detector. The retention time usually is given to specific analyte peak (McCready *et al*., 2000).

Depending on the interaction of the sample with the stationary phase in the column it leaves the column and enters the detector. The identification of a sample in GC-MS is usually by the use of retention time and pure sample (standard). The pure standard is analyzed using the GC-MS and its retention time is compared with the sample. If the retention time of the sample and standard match then the sample has the analyte of the standard (Fetzer, 2000). Identity of analyte is confirmed by mass spectral data.

2.10.2 Components of Gas Chromatograph/Mass Spectrometry

Figure 2.3 shows the main components of a GC-MS. Mainly GC-MS can be separated into two key components; first the Gas Chromatograph (GC) where separation occurs and a detector (mass spectrometer or Mass Selective Detector) where identification of the solutes occurs. The other components of the GC include injection port, carrier gas, oven and column. Most of the GC has automated injection.

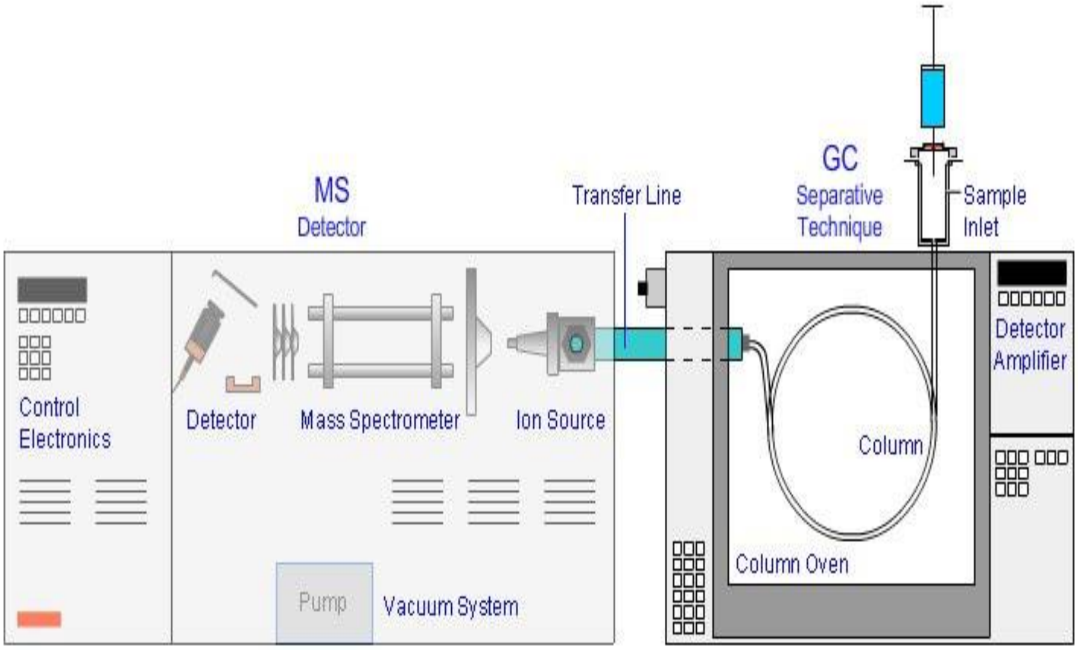


Figure 2. 3: Diagram showing Components of GC –MS Instrument

The carrier gas which sometimes is called mobile phase in GC is a crucial, but limiting, aspect in separation. The mobile phase is the means to transport components of a sample through the stationary phase. Selection of carrier gas is determined by aspects like the kind of solutes to be analysed and the cost (Clescerl *et al.*, 2007). The commonly used carrier gas is helium because it is inert to most compounds.

When the sample is injected, mostly 1µL of sample is injected into the GC through the injection port with the temperature maintained at 300 °C so that all the samples injected are vaporized. The Common injection mode systems are split, pulsed split, splitless and pulsed splitless (Clescerl *et al.*, 2007).

The column is enclosed in the oven and the fan. The oven provides heat to the column to transport the molecules through the column while the fan is used to cool the column. The oven temperature is from 313 to 593 K. The stationary phase is mainly a thin pipe with a superior polymer covering on the inside. Analytes are separated according to their volatility and are transported through the stationary phase by the carrier gas. Molecules that are very volatile move through the column faster than molecules that are less volatile (Fetzer, 2000).

Mass spectrometry instrument contains three major components. These include detector, ion source and filter. The molecules from the column first pass through the ion source whose main function is to supply electrons to the molecules, and splint them into small particles and turn into positively charged ions (h^+). This is essential as the atoms must be positively charged to move through the filter (Fetzer, 2000).

The filter is sometimes named as an analyzer; its chief purpose is to resolve the ions into their characteristics mass components according to their mass-to-charge ratio (Steve *et al.,* 2005).

Finally, the ions pass through the detector and its main function is to tally the quantity of ions with a particular weight. This data is transferred to the output which usually is a computer and a spectrum is drawn (Steve *et al.*, 2005). The computer components perform various functions like: control the instrument, acquire and manipulate data and compare spectra to spectra. The molecule elutes heaters the hot detector, an electronic motion is produced depending on created contact of the analyte and the detector. We have different software used to record the motions produced by the detector and a chromatogram is produced (Karasek and Clement, 2008).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Design

The aim of this research was to assess the concentration of selected PBDEs in Nairobi River basin area and evaluate the photocatalytic degradation of BDE 28, 85 and 183. The first component involved collection and analysis of Nairobi River basin water, sediment and soil samples to assess the concentration of PBDEs. The second component involved collection and analysis of Nairobi County region and Mount Kenya air samples to assess the concentration of PBDEs. The third component involved laboratory experiment in which nitrogen dopped titanium oxide photocatalyst prepared by sol-gel method was used to study the photocatalytic degradation of BDE 28, 85 and 183.

3.2 Study Area

Nairobi County is among the 47 counties in Kenya. It is the capital city of Kenya. It is located South of the equator approximately between 36^{o} 45"E to 37^{o} 05’E and 1^{o} 10’’S; to 1^{o}30’’S at a mean altitude of 1,700 m above sea level. Commercial and administrative activities are concentrated at the central business district while most of the industrial activities are located to the South East (UON/UNEP, 2005).

Nairobi has a subtropical climate and has four major seasons: the dry and warm season (January to March), heavy rain season (April to the June), the dry and cool season (July to September) and the short rainy season (October to December) (GoK, 2018). Temperatures generally vary from 11 ^{o}C in the June /July season to about 29 ^{o}C from December to March (GoK, 2018).

The source of Nairobi River is Ondiri swamp, from Ondiri swamp the river flows through Dagoreti, Lavington, Museum Hill, Kamukunji and Ngomongo. The Ngong River that runs through the industrial area joins it at Njiru. The river passes past Ruai where treated sewer is released to the river. After which the river runs through Kangundo and Kilimambogo area. The river discharges its water to Athi River and finally the Sabaki River which releases its water into the Indian Ocean. Nine sampling sites were chosen to represent the river catchment from upstream, midstream and downstream as shown in Figure 3.1 and Table 3.1.

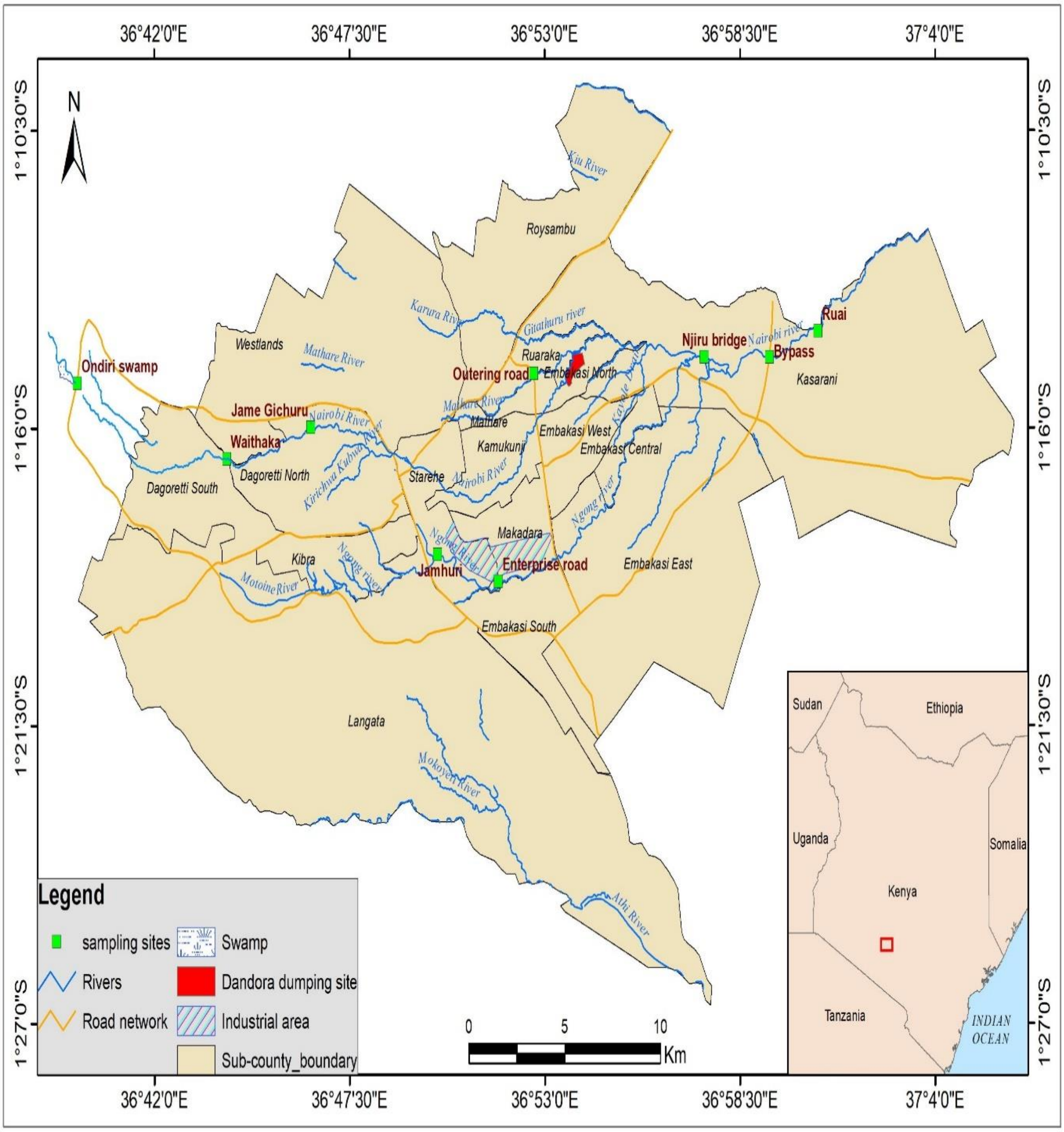


Figure 3. 1: Map of the Study Area showing the Nine Sampling Sites along Nairobi River Basin

Table 3.1: Description of Sampling Sites along Nairobi River Basin

Local Name	Coordination	Altitudes (m)	Human activities Captured
Upstream			
Ondiri	01º15’10’’S 036º39’48’’E	1970	Farming, human settlement
Waithaka	01º 16’34’’S 036º 44’03’’E	1791	Farming, human settlement
Jamhuri	01º18’22’’S 036º49’58’’E	1761	Farming, human settlement
Midstream			
James Gichuru road	01º 18’36’’S 036 49’42’’E	1647	Farming, human settlement
Enterprise Road	01º 18’22’’S 036º 49’35’’E	1648	Garage, burning of used tires, industries
Outering Road	01º 18’22’’S 036º 53’21’’E	1620	Garage, Farming, industries, human settlement
Downstream			
Njiru	01º 14’44’’S 036º 59’19’’E	1522	Farming, Open burning of Waste, human settlement
By Pass	01º 14’ 35’’S 036º 56’27’’E	1541	Farming
Ruai	01º 14’ 35’’S 036º 56’27’’E	1565	Farming, sewerage treatment plant

The PBDE in air study covered three sites in Nairobi on the basis of potential anthropogenic sources of PBDEs. Nairobi City County government main dumpsite in Dandora and Industrial area site represented potential hot spots for PBDEs and Kabete was chosen as an urban agricultural background site because of the agricultural activity around the area. Remote high hilly, mountain areas are known as important ‘‘early warning’’ locations with regard to global and medium-range transport, as well as for distribution processes for semi volatile persistent organic pollutants (Roland, 2005), hence this research was extended to Mt. Kenya as a representation of a high elevation zone which also acted as a control site (Figure 3.2). Air sampling was done four times, over three-month periods (January – March; April – June; July – September; and October – December, 2018). January – March, 2018 represented the warm dry season; April - June was to represented the heavy rain season; July - September, 2018 represented the cool dry season, while October - December, 2018 represented the short rain season to capture the effects of various seasons and human activities on the concentration of PBDEs in air.

The passive air samplers were installed at the four sites; Industrial area, Dandora, Kabete and Mt. Kenya and replaced after every 90 days (three months). Figure 3. 2 shows the map of the study area showing the four air sampling locations namely; Dandora, Industrial Area, Kabete and Mount Kenya.

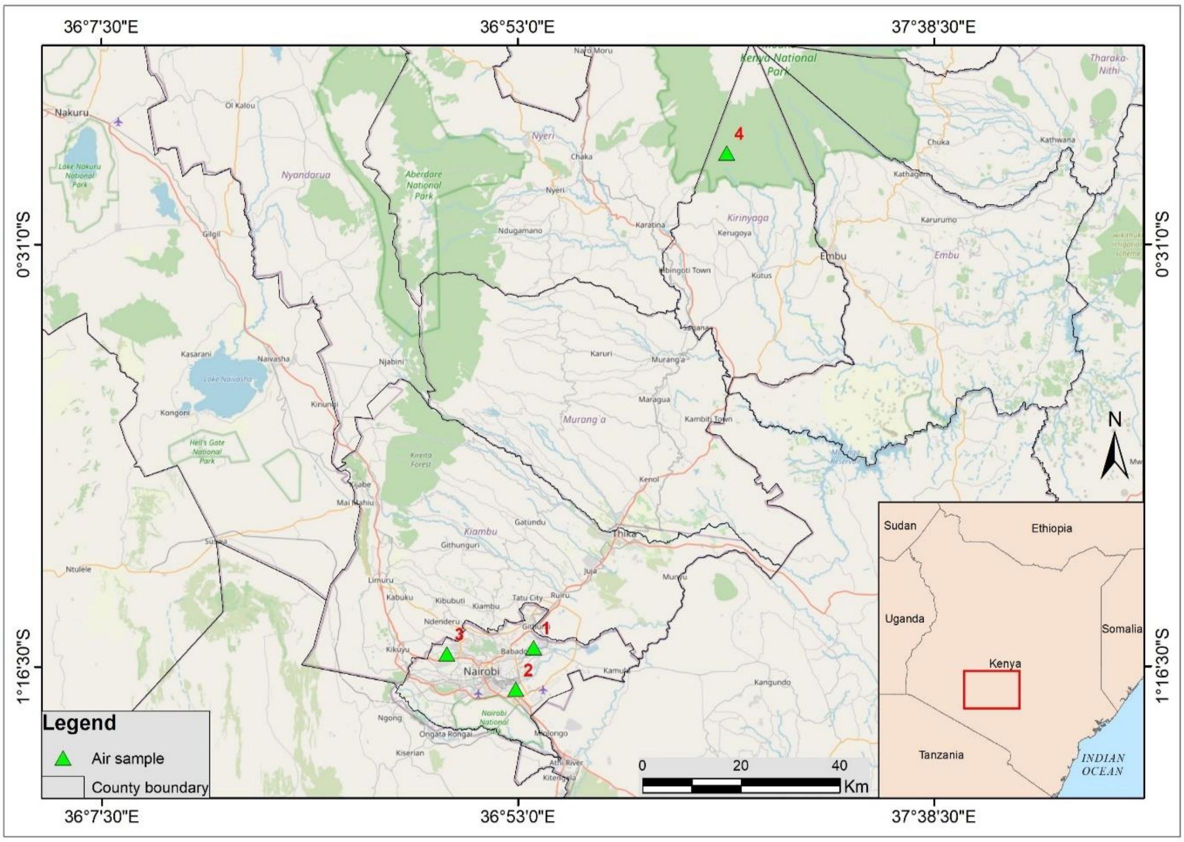


Figure 3. 2: Map of the study area showing the Four Air sampling sites i.e., 1-Dandora, 2-Industrial Area, 3-Kabete and 4-Mount Kenya.

Table 3.2: Description of Air Sampling Sites

Local Name	**Coordination**	**Altitudes (m)**	**Main Human activities**
Dandora	036^{0}53’17” E 01^{0} 15’ 05 S	1625	Waste management
Industrial area	036^{0}52’30” E 01^{0}18’24” S	1623	Manufacturing
Kabete	036^{o}44’33” E 01^{o} 14 58” S	1841	Residential, Farming
Mt. Kenya	037^{0}17’84’E 00^{0} 03’ 75’’S	3599	No activities

3.3 Chemicals and Reagents

Analytical grade silica gel (0.063–0.2 mesh), acetone, hexane, sodium hydroxide, sulphuric acid, anhydrous sodium sulphate and dichloromethane were purchased from Sigma-Aldrich, USA, through the local agent Kobian Kenya LTD. HPLC grade isooctane, analytical grade titanium (iv) isopropoxide (sigma Aldrich), ammonium (sigma Aldrich), isopropanol (sigma Aldrich) and methylene blue were purchased from Sigma-Aldrich, USA, through the local agent Kobian Kenya LTD. White sport nitrogen gas (99.9999 %) and helium gas(99.9999 %) were purchased from BOC Kenya limited. High purity ^{13}C labelled 3,3',4,4'-tetra-bromodiphenyl Ether standard and high purity pure individual BDE 28, 85 and 183 standards used in photodegradation experiments were procured from Sigma-Aldrich, USA, through the local agent Kobian Kenya LTD. High purity PBDE standard mixture was provided by Research Centre for Toxic Compounds in the Environment (RECETOX), Czech Republic and had been procured from Sigma-Aldrich, USA. Water used to make solutions and wash glassware was distilled at the Department of Chemistry, University of Nairobi.

3.4 Instruments and Apparatus

Soxhlet set up comprising of heating mantles, Soxhlet extractors and condensers was used in the extraction of sediment, air and soil samples. Water samples were extracted using 2.0 L glass separatory funnel. Glass column of length 150 mm and internal diameter of 20 mm was used in cleaning the samples, while the samples were concentrated using rotary evaporator. Oakton meter model PC2700 was used to measure electrical conductivity, pH and total dissolved solids of the samples. All masses were measured by analytical Shimadzu AUW220D weighing balance. The extracted samples were stored in a lab-line blast resistant fridge and deep freezer was used for storing of PUFs, soil and sediment samples before extraction.

Perkin Elmer Lambda 25 UV-Vis spectrophotometer with 1 cm matching quartz cuvette cells was used for the absorbance measurements for the determination of absorbance for the photodegradation of methylene blue and methyl Red. Stirrer and magnetic stirrer bar, marble furnace was used during the preparation of photocatalyst. Scanning electron microscope (ZEISS ULTRA PLUS FEG SEM-Microscopes) and X-ray diffraction (XRD) (Bruker D2 PHASER) were used in characterization of the photocatalyst. 65Watts tungsten halogen lamp was used during photodegradation experiment. Agilent technologies gas chromatograph (Agilent 6890N, Palo Alto, USA) coupled to mass spectrometry (Agilent 5973, USA) was used for analysis of PBDEs. Fluorine tin oxide glass substrate, screen printing mesh (63T, silk screen printing services LTD, USA) and hot plate were used for determination of the photocatalyst band gap. Glassware used in this research comprised; auto sampler vial (1.5 mL), conical flasks (25, 100, 250 and 1000 mL), Pasteur pipettes, desiccators, glass vials (10 ml and 30 mL), measuring cylinders (20, 100, 500 and 1000 mL), Beakers, and syringes for sample injection (10, 25, 50, 100 µL).

3.5 Sampling

3.5.1 Water Sampling

Water was collected by grab method into pre-washed 2500 mL amber glass bottles, covered with Teflon screw caps and transported to the pesticide analytical laboratory at the Department of Chemistry, University of Nairobi in Colman cooler box containing ice cubes for extraction and analysis. The samples were kept in a fridge at 4 °C for maximum period of 72 hour prior to extraction (USEPA, 2010).

3.5.2 Sediment Sampling

Sediment samples were collected from the same sites as water samples. They were sampled using a pre-cleaned stainless-steel shovel. Three composite samples were mixed on clean piece of aluminum foil and a 500 g representative sample picked, wrapped in another clean piece of aluminum foil, labeled, and then placed into a self-sealing bag. They were then packed in a cooler box and transported to the laboratory where they were stored in a deep freezer at -20 °C prior to analysis (USEPA, 2010).

3.5.3 Soil Sampling

Soil samples were collected from places and farms closer to the river where water and sediments were collected. Soil samples were dug using a pre-cleaned hoe and scooped using stainless steel shovel down to the depth of 15-30 cm from five different locations within the site. Five composite samples were mixed on clean piece of aluminum foil and a 500 g representative sample picked and wrapped in another clean piece of aluminum foil, labeled, then placed into a self-sealing polythene bag. They were then packed in a cooler box, transported to the laboratory and stored in a deep freezer at -20 °C prior to analysis (USEPA, 2010).

3.5.4 Passive Air Sampling

Passive air samplers consisting of polyurethane foam disks housed in protective stainless-steel chambers were employed in this study. Passive samplers were deployed over three-month periods (January – March, 2018; April - June, 2018; July - September, 2018 and October - December, 2018). Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All PUFs were pre-cleaned (using a measuring cylinder two liters of ultrapure water was measured, transferred into a beaker and PUF introduced into the beaker. The beaker was placed in an ultrasonic bath for 15 minutes. The process was repeated twice, each time with fresh ultrapure water. The foam was drained, placed in a Soxhlet set up and extracted with acetone followed by toluene for 24 hours. The excess solvent was removed manually from the polyurethane foam then transferred to desiccator to completely dry). The PUFs were wrapped in two layers of aluminum 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, labeled and placed in self-sealing polythene bags then stored in polyurethane cool box containing dry ice. In the laboratory samples were kept in a freezer at -20 ^{o}C awaiting extraction. PBDEs residue analysis was done within 7 days (UNEP, 2010).

3.6 Extraction

3.6.1 Water Extraction

Water was extracted by liquid-liquid partitioning using methylene chloride. Two liters of water was transferred into a 2000 mL separatory funnel and spiked with ^{13}C labeled 3,3',4,4'-tetrabromodiphenyl ether extraction standard. Sixty milliliters of dichloromethane were added to the water, shaken vigorously while freeing pressure and allowed to settle to increase separation into two layers. The lower organic phase was collected into a pre-cleaned 250 mL conical flask and the extraction procedure was repeated twice with 60 mL dichloromethane. The collective extracts were dried using anhydrous sodium sulphate, after which 2 mL of isooctane was added as a keeper and the extracts reduced to 2 mL using a rotary evaporator. The concentrated extracts were quantitatively transferred into 15 mL vials using Pasteur pipettes and stored in a refrigerator at 4 ^{o}C prior to clean-up (USEPA, 2010).

3.6.2 Soil and Sediment Extraction

Sediment and soil samples were removed from deep freezer and given time to defrost before extraction. Twenty grams of the sample was measured in triplicates and dried with activated anhydrous Na_2SO_4 for twelve hours. The dried samples were transferred to the Soxhlet thimble then spiked with ^{13}C labelled BDE 77 extraction standard and were extracted for 18 hours using 0.2 L of dichloromethane. 2 mL of isooctane was added as keeper then the solvent was reduced to about 3 mL using rotary evaporator. The reduced extracts were then transferred into vials and kept in a fridge at 4 ^{o}C a waiting clean-up process (USEPA, 2010).

3.6.3 Air Polyurethane Foam Extraction

The polyurethane foam (PUF) sorbents initially stored in the freezer at -20 °C were removed and allowed to attain room temperature. The polyurethane foams were placed in the Soxhlet extractor and were extracted for 18 hours using 0.2 L of dichloromethane. 2 mL of isooctane was added as keeper then reduced to about 3 mL using rotary evaporator. The reduced extracts were then put in vials and kept in a fridge at 4 ^{o}C a waiting clean-up process (UNEP, 2010).

3.7 Clean up

Sample extracts were cleaned by passing through a chromatographic glass column loaded with 1cm anhydrous sodium sulphate at the bottom, followed by 1000 mg activated silica, 4 g basic silica (3:1 silica gel: 1Molar sodium hydroxide, weight/weight), 1000 mg activated silica, 8 g acidic silica (1:1 silica gel: H_2SO_4, weight/weight), 2 g activated silica and on top 1 cm anhydrous sodium sulphate. Preconditioning of the column was done using 50 mL of hexane. The extracts were quantitatively loaded and eluted with 50 mL of hexane. One milliliter of isooctane was added as keeper then reduced using a rotary evaporator to 1 mL. The reduced samples were quantitatively transferred into auto sampler vials and further reduced to 0.5 mL under a gentle flow of white spot nitrogen (99.999 %). Finally, the samples were ready for GC-MS analysis (USEPA, 2010).

3.8 Gas Chromatography Mass Spectrometry Analysis and Quantification of the Sample Extracts

The samples were analysed for nine PBDE congeners (BDE 28, 47, 66, 85, 99, 100, 153, 154 and 183) using gas chromatography (Agilent 6890N, Palo Alto, USA) coupled to mass spectrometry (Agilent 5973, USA) equipped with a thermo scientific trace GOLD GC column (TG 5SILMS 30 m X 0.25 mm X 0.25 µm). The mass spectrometer was operated in selected ion monitoring (SIM) mode with the electron impact (EI+) ionization method in the resolution of >5000. The injection temperature was 280 ^{o}C and the detector temperature was 320 ^{o}C. Helium (99.9999 %) was used as the carrier gas at a flow rate of 1 mL min^{-1}. GC oven temperature program was 90 ^{o}C (1 minute hold), then 40 ^{o}C min^{-1} to 180 ^{o}C, followed by 10 ^{o}C min^{-1} to 260 ^{o}C (2 minutes hold), and 25 ^{o}C min^{-1} to 320 ^{o}C (8 minutes hold). Split less injection mode was used and injection volume of 1 µL for all samples including the PBDE calibration standards, control samples and sample extracts (USEPA, 2010).

Identification of the targeted PBDE analytes was accomplished by comparing the retention time and mass spectra of analytes in samples to those of reference standards run following the same conditions. Confirmation of the compounds was carried out using the NIST mass spectral library, version 2.0 (Standard reference data program of the US National Institute of Standards and Technology). A specific PBDE was identified based on matching retention time to that of the reference standard (within a deviation of ±0.05 min) and the NIST library spectra (USEPA, 2010.

3.9 Physico-Chemical Parameters Determination

3.9.1 Determination of pH of Samples

The pH of water sample was measured using Oakton meter model CP2700. Calibration of the meter was done using buffers of pH 10.0, 7.0, and 4.0 prior to use.

The pH of sediment was determined by measuring 10,000 mg of the sediment and addition of 0.025 L of purified water in a ratio of 2:5 (sediment: water). The mixture was shaken in orbital shaker for 30 minutes before the electrode was plunged into the suspension to determine the pH (Avery and Bascomb, 1982).

The pH of soil was determined by measuring 10,000 mg of the soil sample and addition of 0.025 L of purified water in a ratio of 2:5 (soil: water). The mixture was shaken in orbital shaker for 30 minutes before the electrode was plunged into the suspension to determine the pH (Avery and Bascomb, 1982).

3.9.2 Total Suspended Solids, Total Dissolved Solids and Electrical Conductivity Determination

Water samples were shaken thoroughly to homogenize and 100 mL filtered through dried pre weighed Whatman filter paper No.1. The deposit retained on the filter was dried overnight in an oven at 105 ^{o}C for constant weight. Total Suspended Solids (TSS) was considered as the mass of the deposit per capacity of the sample filtered and the result was expressed in mg/L

$$\text{TSS (mg/L)} = \frac{(A\text{-}B) \text{ X } 1000}{\text{Sample volume (mL)}} \qquad \text{……………………………Equation 3.1}$$

Where:

A = weight of filter paper + dried residue (mg) and

B = weight of filter paper (mg)

Total Dissolved Solids (TDS) and electrical conductivity were measured using Oakton meter model CP2700, in the field. The instrument was calibrated before use.

3.9.4: Soil and Sediment Moisture Content Determination

The moisture in soils and sediment was measured by drying 5 g of the samples in a watch glass that had been pre-cleaned and pre-weighed in the oven at 105 °C for 24 hours. The moisture content was determined by getting the difference in mass among dry and wet sample (Avery and Bascomb, 1982).

The percentage of moisture in the samples were calculated using equation 3.2.

$$\% \text{ moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample}) \times 100}{\text{Weight of wet sample.}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Assessment of the moisture content of the soil samples was required because the PBDEs degrades fast under moist environments.

3.9.5 Soil Characterization

This was done to get the baseline information of the soil in question. Physical chemical analysis such as pH, moisture retention was done while chemical parameter included total organic carbon was done at Kenya Agriculture Research and Livestock Research Organization (KARLO) in Nairobi using the method described by Avery and co-worker (Avery and Bascomb, 1982)

3.10 Photo Catalytic Degradation Experiment

3.10.1 Synthesis of the Photocatalyst

N-doped TiO_2 was prepared by sol-gel method (Dubey *et al.*, 2019). Titanium (IV) isopropoxide (97 %, Sigma Aldrich) as a titania precursor, 25 % ammonia solution and isopropanol in the ratio of 2:1:10 was measured and the combination placed in a conical flask. This was then stirred at 250 rotations per minute for 1 hour at room temperature and pressure. At first there was quick hydrolysis and condensation reaction producing development of a colloid. The subsequent white gel was oven dried at 120 ^{o}C for 1 hour to remove excess NH_3 and other by-products of hydrolysis. The dried solid was calcined at 673 ^{o}C for 12 hours. Calcination was carried out in porcelain crucibles. Pure TiO_2 was prepare without NH_3 solution.

3.10.2 Determination of TiO_2 and N-TiO_2 Band Gap by Screen Printing Technique

Varying ratios of the two powders were mixed with 2 mL of 2-propanol (IPA: isopropyl alcohol, Scharlan Chamia) and 2 mL of deionized water. Thin TiO_2 and N-TiO_2 composite layers were coated on glass substrate using screen printing mesh (63T, silk screen printing services LTD, USA). The films were then dried in air at ambient temperature for 10 minutes, transferred to a hot plate at 120 ^oC for five minutes and allowed to cool to room temperature before sintering stepwise at 500 ^oC for one hour in a furnace.

To relate the optical features of the deposited TiO_2 and N-TiO_2 photocatalyst compact layers, both the optical transmittance (T) and absorption (A) were determined in the wavelength range 300 -1100 nm (UV-VIS range) on a computerized scanning double beam spectrophotometer (Perkin Elmer Lambda 25). Using the experimentally gotten optical transmittance data in SCOUT 4.06 software, optical constants like refractive index n_f and extinction coefficient k and thickness of the samples were determined. Drude and OJL dielectric function models were utilized to get finest fitting results for the optical spectra of metal oxide structure. The optical band gap of the films, the absorption coefficient α obtained from the simulated data in SCOUT software was plotted in Tauc plot, where the direct band gap was determined by extrapolating the linear section of the curve to zero. The Tauc method is based on the assumption that the energy-dependent absorption coefficient α can be expressed by the following equation 3.3 (Liu *et al.*, 2016).

$(\alpha h\nu)^{1/\gamma} = B(h\nu - E_g)$ ………………………………………………………. Equation 3.3

where

h is the Planck constant,

ν is the photon’s frequency,

E_g is the band gap energy, and

B is a constant.

The γ factor depends on the nature of the electron transition and is equal to 1/2 or 2 for the direct and indirect transition band gaps.

3.10.3 Morphological and Structural Characterization of Photocatalyst

Scanning electron microscope (SEM) (ZEISS ULTRA PLUS FEG SEM-Microscopes) was used to study the surface morphologies of the deposited thin films. The films were characterized without any further treatment before the scanning was performed. Micrograph images were taken at a constant acceleration potential of 15 kV (Soe *et al.*, 2019).

X-ray diffraction (XRD) was performed to identify the crystal structure and the preferred orientation growth of the thin films. This was carried out using Bruker D2 PHASER diffractometer with $CuK_{\alpha.}$ X-ray radiation (λ =1.5418 nm) with unique LYNXEYE XE-T detector. The accelerating voltage of 35 kV and emission current of 30 mA, 2θ scanning range of 2.00° – 80.00° with a step time of 2° min^{-1} (Soe *et al.*, 2019).

3.10.4 Methylene Blue Degradation

Stock solution of methylene blue was made using distilled water. It was also diluted as necessary.

3.10.4.1 Effect of Catalyst Weight on Methylene Blue Degradation

Methylene blue (MB) was used as the perfect organic contaminant to assess the photocatalytic activity of the N-doped TiO_2. (ISO, 2010) Using a measuring cylinder 0.04 L of MB was measured and transferred into different vials, 0, 100, 200, 400, 600, 800 and 100 mg of the catalyst was loaded to the vials and stimulated in triplicate. Prior to illumination, the suspensions were mixed using magnetic stirrer for 60 minutes in the dark to confirm that the mixture got adsorption stability.

These were then exposed to UV for two hours. 0.1M sodium hydroxide was used to adjust the pH. The photocatalyst was separated from the solution by centrifugation and the absorbance of the residual fluid was determined using UV-visible spectroscopy at an absorbance of 616.8 nm.

3.10.4.2 Effect of Time on Methylene Blue (MB) Degradation

This was carried out in bright light for 120 minutes, between 11.00 am and 1.00 pm. 40 mL of aqueous dye solution (0.03 gL^{-1}, pH 7) and 0.40 g of the catalyst was exposed to sunlight for two hours. The pH was adjusted with 0.10 M sodium hydroxide solution. Before illumination, the suspension was magnetically stirred for 120 minutes in the dark to ensure the mixture had reached adsorption equilibrium. During the photoreaction process, 6 ml of the solution was removed after every 20 minutes, the photocatalyst separated from the solution by centrifugation and the absorbance of the remaining clear liquid tested by UV-visible spectroscopy at absorbance of 613.8 nm.

The MB degradation was calculated as follows:

MB degradation % = (A0-A)/Ao x100 …………………………. …………. Equation 3.4

Where,

A0 is the initial absorption of MB and

A is the absorption of MB at sampling time.

3.10.4.3 Effect of Varied pH on Methylene Blue Degradation

Using analytical balance 0.10 g of photocatalyst was measured and added to the solution in different concentrations from 10 mg/L to 50 mg/L. Initial pH was adjusted by adding HCl and NaOH (0.05 M). pH was varied from value of 2 up to 12. Solutions were then placed under UV lamp for particular time interval and the percentage removal determined. The highest percentage was selected for the investigation of photocatalysis. The tests were all carried out in triplicate.

3.10.5 Methyl Red Degradation

Weight of the photo catalyst, exposure time and initial dye concentration were explored to determine the optimum working conditions of the photocatalyst for methyl red degradation. 20 ppm Methyl Red solution and varying amounts of 0.025, 0.05, 0.10, 0.20, 0.40, 0.60 and 0.80 g of photocatalyst. This was used to establish the optimum amount of the photo-catalyst. The illumination time was 120 minutes, and aliquots of the samples were taken at 20 minute intervals and absorbances measured at 413 nm to determine change of concentration with time. The % degradation of methyl red was determined according to the equation 3.5.

% degradation of methyl red =([Ro-Rt]/[Ro]) *100 …………………………… Equation 3.5

Where,

Ro is the initial methyl red concentration and

R_t the concentration after time, t, in minutes.

Degradation percent versus the time for all the variables was plotted for data analysis.

3.10.6 N-TiO$_2$ Photo Degradation of Polybrominated Diphenyl Ethers

Photo catalytic degradation was conducted using procedure designed by Zhang et al., 2016, with some amendments to fit tropical solar radiations. The experiment was performed in cylindrical quartz reactor. UV-lamp with solar radiation corresponding to tropical solar radiation was positioned horizontally over the reactor. 100 mL of PBDEs mixture solution was added into the reactor mixed with N-TiO$_2$ photo catalyst while magnetically stirring and then the process was irradiated with the UV lamp.

To investigate if PBDEs degraded in the absence of UV, blank experiment without UV irradiation was conducted. Blank experiment without photo catalyst was also performed to determine the ability of photo degradation of PBDEs without photo catalyst. The pH was adjusted with NaOH or HCl. 10 mL of Samples were collected for analysis after every 15 minutes for a period of 2 hours intervals.

The collected samples were immediately extracted using the method described in 3.6.1 and 1 ml of isooctane added then concentrated to around 1ml and qualitatively transferred to amber auto sampler vials. Analysis was done using gas chromatography (Agilent 6890N, Palo Alto, USA) coupled to mass spectrometry (Agilent 5973, USA) equipped with a thermo scientific traceGOLD GC column (TG 5SILMS 30 m X 0.25 mm X 0.25 µm).

The rate of PBDEs degradation was determined using the Langmuir-Hinshelwood kinetic model for reaction rate dependence on initial reactant concentration (Kar *et al.*, 2013).

r = dC/dt = kKC/(1+KC) ---------------------------------------Equation 3.6

When the initial concentration Co is <<<1, the denominator in equation 1 above can be ignored as 1, and the equation can be simplified to an apparent first-order equation:

dC/dt=kKC--- Equation 3.4

dC/C=kKdt--- Equation 3.8

$$dC/dt = -Kt - - - - - - - - - - - - - - - - - - - \text{ Equation 3.9}$$

Integrating equation 3 and taking boundary conditions of C = Co at t = 0, gives

Ln(Co/Ct)= kKt=k_{abs}--- Equation 3.10

Or

Ct= Coe^{-kt} -- Equation 3.11

Which is the first order rate equation, also written as:

$$\ln C_t = \ln(C_0) - K_{obs}Xt - - - - - - - - - - - - - \text{ Equation 3.12}$$

Where; C_t= PBDEs concentration at time, t

K_{obs}= first order rate constant

t= time in minutes

C_o= the original BDE 28, 85 and 183 concentration

r = rate of degradation

Consider the half-life of the reaction where the remaining concentration of the PBDE is half the original amount; $C_t= C_o/2$ and substituting in Equation 3.12 above gives:

$Ln(C_o/2C_o=-Kt_{1/2}$--------------------------------------- Equation 3.13

$Ln\ 0.5=-Kt_{1/2}$ --- Equation 3.14

$-0.693/K =t_{1/2}$ --- Equation 3.15

Hence the degradation half- life of BDE 28, 85 and 183 was determined according to the equation 3.15.

3.11 Quality Assurance and Quality Control

Amber glass bottles were used for sampling and storage of water samples to prevent photo degradation of PBDEs. The GC-MS instrument was regularly injected with solvent blank (isooctane) and procedural blanks to check potential ghost peaks and contamination. Analysis of air samples was done in duplicate while water, sediment and soil samples were done in triplicate to verify the presence of the analytes in the samples. Sample blanks, spiked standards were included in the sample extraction and cleanup to verify the method performance. The use of internal standard (^{13}C BDE 77) was applied to check the recoveries. Multilevel Calibration curves were used for quantification of analytes.

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. These were stored and treated in similar manner as air samples to serve as field and laboratory blanks for air. They were extracted and analyzed in the similar manner as the samples, and the levels in field blanks never exceeded 5% of the amounts noticed in samples for POPs demonstrating negligible pollution through transport, storing and analysis therefore no blank correction was necessary (Harner *et al*., 2006).

Compound recoveries were carried out by spiking distilled water, anhydrous sodium sulphate and pre-extracted unexposed PUF with 100 µL of 1 ppm standard mixture consisting of nine different PBDE congeners to validate method performance. The recoveries for individual PBDE congeners were as follows; BDE 28 98 %, BDE 47 102 %, BDE 66 105 %, BDE 99 101 %, BDE 100 97 %, BDE 85 89 %, BDE 154 104 %, BDE 153 103 % and BDE 183 102 %. The limit of detection was determined as three times the noise divided by the response of the compound in the lowest calibration point multiplied by the concentration of analytes at that point. All PBDE found with concentrations below the detection limit was stated as below detection limit (BDL). The LOQ (limit of quantification) was calculated in the same way, using ten times the noise level. Dark experiment was performed to act as control for photocatalytic degradation experiment.

3.12 Statistical Analysis of Data

Microsoft Excel 2010 was used to Process the data. Statistical Package for the Social Science (SPSS) version 20 for window evaluation was employed for analysis of the data. One-way ANOVA was used to determine significant differences between mean values, while the Pearson Correlation (two-tailed) was employed to approximate the amount of association among the PBDE compounds.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Qualitative Characteristics

Reference standards of PBDE were used in numerous stages in the analysis. Working PBDE reference standard mixtures between 0.1 to 500 ug/L were prepared individually for each standard and measurement was based on calculation from calibration curves for each standard. The calibration curve of each of the PBDE standard was a straight line and is best line of fit drawn from the plot of the response factor, particularly, instrument response (peak area) against standard (analyte) concentration ratio. All calibration curves had a correlation factor (R^2) exceeding 0.9 demonstrating a good association between instrument response ratio and analyte values. The calibration graphs are attached in Appendix 6. The standard (analytes) mean were calculated by interpolation from the graphs using the calculation of the graph that is $Y= mX+c$.

Where; Y= Instrument response (peak area)

X=-Standard mean value,

m=Slope, and

C= Constant

Base ions were selected as quantitative ions, whereas the extra ions selected as confirmatory ions (Table 4.1). Quantification of the target PBDE analytes were based on peak areas by means of external multilevel calibration graphs by drawing peak areas versus concentrations of individual PBDE analyte. Correlation coefficients (r^2) greater than 0.99 were considered adequate for linearity. Table 4.1 shows accuracy, retention time, monitoring ions, linearity, limit of quantification, and limit of detection of PBDE congeners investigated in this study.

Table 4.1: Accuracy, Retention Time, Monitoring Ions, Linearity, Limit of Quantification and Limit of Detection of Polybrominated Diphenyl Ether Congeners investigated in this Study

PBDE Analytes	Retention Time	Linearity (R2)	LOD (pg)	LOQ (pg)	Quantitative ion (m/z)	Quantifier ion (m/z)
BDE28	9.475	0.998	1.1	3.6	405	245.90,407.80, 417.90 and 419.90
BDE47	11.590	0.997	1.1	3.3	485.70	483.70, 495.70, 497.70 and 345.90
BDE66	12.670	0.990	1.3	4.3	485.70	483.70, 495.70, 497.70 and 345.90
BDE100	13.714	0.996	1.3	4.2	405.90	563.60, 565.60, 575.60 and 577.60
BDE99	14.548	0.998	1.4	4.3	405.90	563.60, 565.60, 575.60 and 577.60
BDE85	17.041	0.994	0.9	2.9	405.90	563.60, 565.60, 575.60 and 577.60
BDE154	18.313	0.992	1.0	3.0	483.80	641.50, 643.50, 653.60 and 655.50
BDE153	19.279	0.998	1.4	4.6	483.80	641.50, 643.50, 653.60 and 655.50
BDE183	20.130	0.997	1.2	3.9	561.70	721.40, 733.40, 735.40 and 723.40

LOD- limit of detection, LOQ- limit of quantification

4.2 Chromatograms

Standard calibration curves for the selected PBDEs was obtained for the individual PBDE’s retention time (for identification) and peak area (for quantification) and the process was reproduced for the combined standard mixtures curves. Chromatograms for the standards are attached in Appendix 3 and PBDE structures obtained from the NIST library version 2.0 are attached in Appendix 4.

The chromatograms for field samples extract are attached in Appendix 5. The unidentified peaks indicate compounds that were present in the samples but not in the standard mixture. The chromatogram was obtained from a plot of instrument detector response (peak area) versus the analyte retention time (minutes). The horizontal axis shows the retention time of each analyte and is expected to coincide with that of the reference standard peak for a particular analyte for the peak to be identified.

4.3 Limit of Detection

Limit of detection (LOD) of analyte is lowest concentration of the analytes that the analytical process can reliably detect, but not necessarily quantitated as an exact value. It may be described as the concentration which gives a signal (Y) on the instrument which is different from the blank or background signal. It is calculated as the analyte concentration giving a signal equal to the blank signal Y_B plus two standard deviations of the blank, S_B (Miller and Miller, 1993). The relationship is expressed as $Y - Y_B = 3S_B$. The LOD of each of the PBDE congener was calculated based on the lowest concentration of the calibration standards injected and the corresponding noise signals using the relationship adapted from the equation below:

$$LOD = \frac{3 \times Noise\ peak\ area \times concentration\ of\ standard\ injected (ng)}{Analyte\ response\ in\ the\ lowest\ calibration\ point}$$

LOD for PBDEs was between 0.9 pg/L for BDE 85 to 1.2 pg/L for BDE 153. Any other values detected below the recorded ones were considered as noise and hence reported as below detection limit (BDL). Table 4.1 shows the Limit of Detection (LOD) of various PBDE congeners.

4.4 Polybrominated Diphenyl Ethers Recovery Levels

The mean percentage recoveries of the nine PBDEs was between 89± 4.21 % for BDE 28 to 105± 3.33 % for BDE 66. Table 4.2 shows percentage recoveries of the PBDEs in water, soil, sediment and air samples. The PBDEs residue levels detected in samples were not corrected since all recovery values were within the acceptable range of 70 - 120 % (Hill, 2000).

Table 4. 2: Average Percentage Recovery Tests Results for Selected Polybrominated Diphenyl Ethers

PBDEs	Water Recovery (%±S.D)	Soil Recovery (%±S.D)	Sediment Recovery (%±S.D)	Air Recovery (%±S.D
BDE28	98.14±8.31	96.25±10.56	96.36±14.20	99.21±7.87
BDE47	102.86±4.06	99.26±5.23	102.84±6.09	100.99±22.32
BDE66	105.06±9.58	104.83±3.33	96.71±11.24	99.22±6.87
BDE85	89.35± 5.12	92.08±4.56	89.96± 11.32	96.33± 7.14
BDE99	97.89±3.41	97.81±8.63	101.92±2.23	94.08±6.35
BDE100	101.54±6.95	103.01±4.21	98.71±16.95	92.46±12.35
BDE153	103.58±4.95	104.23±6.86	99.05±22.36	101.21±10.34
BDE154	104.31±2.84	98.35±2.45	102.41±9.63	96.81±2.84
BDE183	102.23±7.13	99.07±3.17	97.23±8.56	99.21±6.56

Mean± S.D

4.5 Polybrominated Diphenyl Ethers Residue Levels in Water

The nine PBDE congeners selected for analysis have been classified as “PBDEs of primary interest” by the USEPA Method 1614 and are frequently found in lake and river water (USEPA, 2010; North, 2004). The mean concentrations of PBDE congeners (i.e., BDE 28, 47, 66, 85, 99, 100, 153, 154 and 183) in water ranged between ≤0.009 to 72.89±6.15 ng/L with those of BDE 47 and 99 ranging between 1.23± 0.46 to 72.89± 6.15 ng/L and 0.11±0.00 to 43.67±1.47 ng/L, respectively. The most frequently detected PBDEs are BDEs 47, 99, 100, 153, and 154 with a detection frequency of 100 %. The result in this study was comparable to similar studies by Guan and co-workers in Pearl River, China which had mean concentration of 0.34 – 68 ng/L (Guan *et al.,* 2007) but the concentration was lower than the levels reported by Olutona and Co-workers in Asunle Stream, Ile-Ife, Nigeria which had a mean concentration of 0.03 to 0.45 ng/mL (Olutona *et al.,* 2017) and Diep River, Cape Town, South Africa which had a concentration of 0.84 to 12,000 ng/mL (Daso *et al.,* 2013). The mean concentration of PBDE congeners for upstream, midstream and downstream locations in Nairobi River ranged from ≤0.009to 43.67±1.47, ≤0.009 to 40.46±1.08 and ≤0.009 to 72.89±6.15 ng/L, respectively. Table 4.3 summarizes the range and mean concentration of PBDEs in Nairobi River water. Upstream sites are; Ondiri, Waithaka and Jamhuri. Midstream sites are; James Gichuru, Outering road and Enterprise road. Downstream sites are; Njiru, Bypass and Ruai.

Table 4. 3: Range, Detection Frequency and Mean Concentration of Polybrominated Diphenyl Ethers in Nairobi River Water over the Entire Period (ng/L)

Site/ PBDE		BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	Range	1.37-4.14	3.44-11.12	0.02-0.49	≤0.009-2.69	0.11-11.78	0.89-12.26	0.81-4.53	0.07-0.49	≤0.009-4.09
	Mean± SD	2.62±1.17	6.54±3.71	0.36±0.22	1.25±0.44	4.34±1.72	8.47±2.11	1.87 ±1.7	0.31±0.18	1.31±0.99
Jamhuri	Range	3.76-16.1	3.78-10.12	0.11-4.8	BDL-7.25	1.83-43.67	1.31-11.42	1.94-3.22	0.12-2.72	0.14-10.34
	Mean± SD	8.46±2.15	6.88±2.96	2.23±1.17	4.54±1.69	16.04±6.72	5.33±1.73	3.74 ±0.6	1.19±0.28	5.06±0.36
Waithaka	Range	2.95-13.54	2.99-8.26	≤0.009-0.37	≤0.009-3.55	0.16-4.08	2.29-17.49	0.93-4.31	0.07-0.85	0.81-3.28
	Mean± SD	6.41±0.94	6.32±2.36	0.15± 0.18	2.06± 1.60	2.58±0.64	3.64±0.68	2.01 ±0.2	0.44±0.12	2.11±1.17
James Gichuru Road	Range	≤0.009-12.18	1.43-37.2	0.39-5.42	BDL-9.41	0.65-11.37	1.64-8.30	1.00-1.96	0.06-0.98	0.95-12.23
	Mean± SD	6.41±1.24	11.90± 1.94	1.98±0.75	4.81±3.03	4.39±1.29	3.32±0.03	1.44 ±0.4	0.56±0.37	4.28±0.73
Enterprise Road	Range	5.17-10.5	4.14-22.1	≤0.009-0.71	≤0.009-10.57	1.23-19.11	0.22-11.35	1.50-8.07	0.05-5.76	0.13-8.84
	Mean± SD	7.59±1.31	12.26± 0.4	0.18±0.00	4.78±3.66	8.49±3.60	3.56±0.81	3.64 ±0.8	1.87±0.46	3.85±2.24
Outering Road	Range	4.48-14.96	6.63-40.46	0.33-7.32	≤0.009-10.02	0.18-12.71	1.97-6.21	0.69-4.89	0.09-2.39	0.30-2.60
	Mean± SD	9.67±1.56	18.79± 4.62	8.58±1.99	2.84±0.52	5.06±3.01	3.16±0.15	2.34 ±0.7	1.34±0.96	1.67±0.67
By-Pass	Range	3.01-6.98	4.14-15.05	0.28-7.3	4.55-5.87	2.66-34.09	2.83-10.59	1.73-5.49	0.05-2.42	0.96-5.50
	Mean± SD	4.97±1.85	8.68±0.53	3.36±1.25	5.15±0.58	14.51± 5.39	5.17±1.24	3.21 ±0.6	0.89±0.27	5.75±2.93
Njiru	Range	2.75-8.93	3.99-72.89	0.18-0.46	4.51-9.91	3.01-43.22	2.1-20.86	2.82-4.04	0.12-1.48	0.55-3.59
	Mean± SD	5.56±2.75	22.61± 33.55	0.31±0.13	6.48±2.41	18.58± 7.07	13.36± 2.77	3.24 ±0.9	0.69±0.29	2.21±0.97
Ruai	Range	2.41-20.79	22.61± 1.84	0.14-3.62	2.32-7.59	10.79-28.41	4.09+ 18.74	1.21-10.2	0.14-3.17	1.71-11.75
	Mean± SD	9.70±4.08	14.37± 2.39	1.49±1.65	5.53±2.51	15.44± 8.65	9.68±2.23	4.03 ±1.2	1.32±0.31	4.95±1.22
Frequency	%	97	100	86	83	100	100	100	100	94

Upstream sites are; Ondiri, Waithaka and Jamhuri. Midstream sites are; James Gichuru, Outering road and Enterprise road. Downstream sites are; Njiru, Bypass and Ruai

4.5.1 Polybrominated Diphenyl Ethers Residue in Water during the Cooler Dry Season

The mean concentration of PBDEs in water during the cooler dry season ranged between BDL to 72.89±6.15 ng/L. The most abundant PBDE congeners were BDE 47, 99 and 100. BDE 47 recorded the highest mean concentration (72.89±6.15 ng/L) at Njiru sampling site. Calculated PBDE concentrations in water during the cool dry season are provided in Table 4.4.

Table 4. 4: Concentration of Polybrominated Diphenyl Ethers in Water samples collected During Cool Dry season (ng/L)

Site/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	2.82± 0.69	11.12± 0.75	0.49± 0.00	≤0.001	11.78± 0.14	12.26± 1.07	1.22± 0.04	0.07± 0.00	4.09± 0.36
Waithaka	2.95± 0.48	6.36± 0.02	0.22± 0.00	≤0.001	3.21± 0.07	3.06± 0.06	0.93± 0.00	0.07± 0.00	3.28± 0.09
James Gichuru	≤0.001	37.2± 1.83	5.42± 0.06	≤0.001	0.65± 0.00	1.69± 0.08	1.32± 0.03	0.06± 0.00	12.23± 1.07
Jamhuri	3.76± 0.09	10.12± 0.74	4.85± 0.01	≤0.001	43.67± 1.47	4.18± 0.05	2.93± 0.04	0.15± 0.00	10.34± 1.22
Outering	4.48± 1.08	40.46± 1.08	7.32± 0.24	≤0.001	5.9± 0.33	2.25± 0.03	2.21± 0.02	0.09± 0.00	2.42± 0.07
Enterprise Rd	7.71± 0.39	4.71± 0.39	≤0.001	≤0.001	5.2± 0.17	0.88± 0.00	3.07± 0.04	0.05± 0.00	1.83± 0.05
Bypass	6.04± 0.46	1.23± 0.46	2.03± 0.07	4.55± 0.18	34.09± 0.04	2.49± 0.09	2.97± 0.00	0.01± 0.00	5.81± 0.34
Njiru	3.99± 0.65	72.89± 6.15	0.23± 0.00	5.11± 0.31	43.22± 0.82	20.86± 1.54	3.96± 0.08	0.12± 0.00	2.99± 0.00
Ruai	2.41± 0.94	55.37± 2.94	0.78± 0.00	7.59± 0.98	10.79± 0.97	7.81± 0.36	10.26± 0.25	0.14± 0.01	11.75± 0.97

BDL= below detection limits n=3, mean ± standard deviation

4.5.1.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling Sites during the Cool Dry Season

2,2′,4,4′-tetra-bromodiphenyl ether (BDE 47) recorded the highest mean concentration of 72.89±6.15 ng/L from Njiru sampling site. The concentration of BDE 47 detected in the water samples was higher than the set maximum limits (24 ng/L) by the Government of Canada (Environment Canada, 2013). The highest mean concentration of BDE 28 was recorded at Enterprise road sampling site (7.71±0.39 ng/L) while it was below detection limit (0.001 ng) at James Gichuru (≤0.001 ng). BDE 66 was below detection limit (0.001 ng) at Enterprise road sampling site and the highest mean concentration (7.32±0.24 ng/L) was recorded at Outering road. BDE 85 was detected at Njiru, Bypass and Ruai sampling sites while it was below detection limit (0.001 ng) in Ondiri, Jamhuri, James Gichuru, Waithaka, Enterprise road and

Outering road sampling location. BDE 99, 100, 153, 154 and 183 were present in all the water samples with the maximum levels detected in water samples from Jamhuri (43.67±1.47 ng/L), Njiru (20.86±1.54 ng/L), Ruai (10.26±0.25 ng/L), Ruai (0.14±0.01 ng/L) and James Gichuru (12.23±1.07 ng/L) respectively while the lowest concentration was recorded in water from James Gichuru (0.65±0.00 ng/L), enterprise road (0.88±0.00 ng/L), Waithaka (0.93±0.00 ng/L), Bypass (0.01±0.00 ng/L) and Enterprise Road (1.83±0.05 ng/L), respectively. The mean concentration of polybrominated diphenyl ethers in water per site during the cool dry season is attached in appendix 8A.

4.5.2 Polybrominated Diphenyl Ethers Residue Levels in Water during the Short Rain Season

During the short rain season the level of PBDEs in water was between BDL (0.001 ng) to 15.05±0.31 ng/L. Table 4.5 shows the concentration of PBDEs in water during the short rain season. BDE 47 recorded the highest mean concentration of 15.05±0.31 ng/L at Bypass sampling site.

Table 4. 5: Concentration of Polybrominated Diphenyl Ethers in Water Samples during Short Rain Season (ng/L)

Site /PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	2.13± 0.18	3.44± 0.54	0.80± 0.00	2.06± 0.14	0.11± 0.00	0.89± 0.00	0.81± 0.00	0.49± 0.00	0.14± 0.00
Waithaka	4.47± 0.07	2.99± 0.19	≤0.001	3.55± 0.25	0.16± 0.00	2.29± 0.13	1.41± 0.01	0.85± 0.00	1.19± 0.02
James Gichuru	5.85± 0.79	1.43± 0.04	1.72± 0.04	3.41± 0.33	2.39± 0.01	1.64± 0.08	1.48± 0.09	0.98± 0.00	0.95± 0.00
Jamhuri	28.06± 1.19	3.78± 0.87	3.19± 0.28	4.12± 0.59	1.83± 0.00	1.31± 0.05	1.94± 0.04	1.8± 0.04	4.63± 0.17
Outering	6.47± 1.03	6.63± 0.26	4.5± 0.81	0.30± 0.00	0.18± 0.00	2.22± 0.39	0.69± 0.00	1.23± 0.00	1.35 ±0.05
Enterprise Road	5.17± 0.23	4.14± 0.16	≤0.001	4.53± 0.23	1.23± 0.05	0.22± 0.01	1.5± 0.02	0.75± 0.00	4.58± 0.39
Bypass	3.85± 0.69	15.05± 0.31	7.3± 0.71	4.77± 0.02	13.44± 0.32	10.59± 0.23	5.49± 0.35	0.74± 0.00	10.74± 1.06
Njiiru	6.58± 0.67	5.87± 0.13	0.35± 0.00	6.38± 0.89	10.96± 0.79	5.7± 0.15	2.82± 0.19	1.48± 0.06	3.59± 0.25
Ruai	5.17± 0.61	7.33± 0.88	3.62± 0.31	2.32± 0.00	11.67± 1.44	8.08± 0.66	1.23± 0.02	0.74 ±0.00	2.31± 0.08

4.5.2.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in Different Sampling Sites during the Short Rain Season

Brominated diphenyl ether 28 was present in all the samples with the highest mean level detected in water sampled at Jamhuri (28.06±1.19 ng/L), while Ondiri (2.13±0.18 ng/L) sampling site recorded the lowest concentration. The highest concentration of BDE 47 was recorded at Bypass sampling site (15.05±0.31 ng/L) while James Gichuru (1.43±0.04 ng/L) recorded the lowest concentration. BDE 66 was not detected (≤0.001 ng) in Waithaka and Enterprise road sampling sites, highest concentration was recorded at Bypass sampling site (7.30±0.71 ng/L). BDE 85 was detected in all the water samples with the highest concentration detected in water from Njiru (6.38±0.89 ng/L), while the lowest concentration was recorded in water from Outering road (0.3±0.00 ng/L). The highest concentration of BDE 99 was recorded at Bypass sampling site (13.44±0.32 ng/L) while the lowest concentration was recorded at Ondiri (0.11±0.00 ng/L). BDE 100 was present in all the water samples with the highest mean concentration detected in samples from Bypass (10.59±0.23 ng/L), while the lowest concentration was recorded in samples from Enterprise road (0.22±0.01 ng/L). BDE 153, 154 and 183 were present in all of the water samples with the highest concentration detected in water from Bypass (5.49±0.35 ng/L), Jamhuri (1.8±0.04 ng/L) and Bypass (10.74±1.06 ng/L) respectively while the lowest concentration was recorded in water from Outering road (0.69±0.00 ng/L), Ondiri (0.49±0.00 ng/L) and Ondiri (0.14±0.00 ng/L) respectively. The mean concentration of polybrominated diphenyl ethers in water per site during the short rain season is attached in appendix 8B.

4.5.3 Polybrominated Diphenyl Ethers Residue Level in Water during the Hot Dry Season

Table 4.6 shows the mean concentration of PBDE congeners during the hot dry season. The mean concentration of PBDE congeners in water samples in the hot dry season ranged between BDL to 28.41±3.63 ng/L. BDE 99 recorded the highest concentration (28.41±3.63 ng/L) at Ruai sampling location.

Table 4.6: Concentration of Polybrominated Diphenyl Ethers in Water Samples Collected during Hot Dry season (ng/L)

Site/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	4.14± 0.34	3.61± 0.02	0.02± 0.00	8.23± 0.49	1.92± 0.07	8.73± 0.31	4.53± 0.31	0.30± 0.00	≤0.001
Waithaka	13.54± 1.09	8.26± 0.82	0.37± 0.00	14.08± 0.68	4.08± 0.46	17.49± 1.55	4.31± 0.25	0.17± 0.00	0.81± 0.00
James Gichuru	12.18± 0.41	5.31± 0.06	0.39± 0.00	9.41± 0.32	3.18± 0.17	8.30± 0.16	1.96± 0.41	0.59± 0.00	2.41± 0.06
Jamhuri	16.1± 1.23	5.07± 0.93	0.11± 0.00	7.25± 0.48	14.46± 1.02	11.42± 0.74	6.87± 0.67	0.12± 0.00	0.14± 0.00
Outering	14.96± 1.15	15.81± 0.58	0.33± 0.00	1.04± 0.00	1.46± 0.00	1.97± 0.09	1.57± 0.94	1.66± 0.00	0.33± 0.00
Enterprise Road	10.5± 0.96	22.1± 1.13	0.71± 0.00	14.04± 0.26	19.11± 0.87	11.35± 0.94	1.95± 0.05	0.94± 0.00	0.13± 0.00
Bypass	6.98± 0.94	14.31± 0.24	0.28± 0.00	5.81± 0.03	2.66± 0.01	4.78± 0.06	1.73± 0.18	0.36± 0.00	0.96± 0.00
Njiru	8.93± 0.44	3.99± 0.14	0.46± 0.00	9.91± 0.11	17.11± 1.14	24.78± 2.49	4.04± 0.62	0.12± 0.00	0.55± 0.00
Ruai	20.79± 2.51	11.92± 1.07	0.14± 0.00	4.73± 0.05	28.41± 3.63	4.09± 0.67	1.21± 0.00	1.24± 0.04	1.71± 0.00

BDL= below detection limits n=6, mean ± standard deviation. n=3

4.5.3.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in Different Sampling Sites during the Hot Dry Season

Brominated diphenyl ether 28 recorded concentration values ranging from 4.14±0.34 ng/L to 20.79±2.51 ng/L. The highest mean concentration was recorded at Ruai sampling site and the lowest concentration was recorded at Ondiri sampling site. Brominated diphenyl ether 47 was present in all the samples with Enterprise road (22.1±1.13 ng/L) recording the highest concentration while Ondiri (3.61±0.02 ng/L) recorded the lowest mean concentration. The highest concentration of brominated diphenyl ether 66 was recorded at Enterprise road sampling site (0.71±0.00 ng/L) while Ondiri (0.02±0.00 ng/L) the recorded the lowest mean concentration. Brominated diphenyl ether 99 was present in all the water samples with the lowest average concentration recorded at Ondiri sampling site (1.92±0.07 ng/L) and the highest concentration was recorded at Ruai sampling site (28.41±3.63 ng/L). BDE 100 was present in all the water samples with Njiru (24.78±2.49 ng/L) recording the highest concentration, while the lowest mean concentration was recorded in water from Ruai (4.09±0.67 ng/L).

The highest concentration of BDE 85 was recorded at Waithaka sampling site (14.08±0.68 ng/L) while the lowest concentration was recorded at Outering (1.04±0.00 ng/L). The highest concentration of brominated diphenyl ether 153 was recorded at Jamhuri sampling site (6.87±0.67 ng/L) while Ruai (1.21±0.00 ng/L) recorded the lowest concentration. Brominated diphenyl ether 154 was present in all the water samples with the highest mean concentration detected in samples from Outering (1.66±0.00 ng/L), while the lowest mean levels was recorded in water from Jamhuri (0.12±0.00 ng/L). Brominated diphenyl ether 183 was BDL (≤0.0012 ng) at Ondiri sampling site while the highest mean concentration was recorded in water from James Gichuru sampling site (2.41±0.06 ng/L). The mean concentration of polybrominated diphenyl ethers in water per site during the hot dry season is attached in appendix 8C.

4.5.4 Polybrominated Diphenyl Ethers Residue Levels in Water during the Heavy Rain Season

During the heavy rain (March, 2018) season the concentration of PBDEs in water was between BDL to 27.44±1.68 ng/L. Table 4.7 shows the concentration of PBDEs in water during the heavy rain (March, 2018) season. It is again noted that BDE 47 congener recorded the highest mean concentration (27.44±1.68 ng/L) at Ruai sampling site.

Table 4.7: Concentration of Polybrominated Diphenyl Ethers in Water Samples Collected during Heavy Rainfall Season (ng/L)

Site / PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	1.37± 0.04	8.00± 0.73	0.19± 0.00	2.69± 0.49	3.55± 0.12	8.47± 0.49	0.91 ± 0.00	0.41 ± 0.00	≤0.001
Waithaka	4.68± 0.17	7.71± 0.54	≤0.001	1.64± 0.05	2.85± 0.01	3.64± 0.07	1.38 ± 0.00	0.68 ± 0.00	3.17± 0.07
James Gichuru	7.61± 0.65	33.6± 1.77	0.42± 0.00	6.41± 0.25	1.37± 0.32	1.65± 0.01	1.01 ± 0.00	0.62 ± 0.00	1.54± 0.00
Jamhuri	5.91± 0.05	8.56± 0.21	0.79± 0.00	6.8± 0.14	4.19± 0.09	4.43± 0.23	3.22 ± 0.02	2.72 ± 0.51	5.14± 0.78
Outering	12.74 ± 0.31	12.24± 0.61	22.18 ± 1.58	10.02 ± 0.36	12.71 ± 0.57	6.21± 0.91	4.89 ± 0.13	2.39 ± 0.03	2.60± 0.21
Enterprise Road	6.99± 0.77	18.1± 0.91	≤0.001	10.57 ± 0.27	8.42± 0.98	1.85± 0.45	8.07 ± 0.91	5.76 ± 0.87	8.84± 0.79
Bypass	3.01± 0.41	4.14± 0.94	3.81± 0.24	5.47± 0.77	7.85± 0.24	2.83± 0.08	2.68 ± 0.00	2.42 ± 0.02	5.50± 0.44
Njiru	2.75± 0.01	7.67± 0.02	0.18± 0.00	4.51± 0.73	3.01± 0.00	2.1± 0.00	2.17 ± 0.06	1.06 ± 0.01	1.69± 0.03
Ruai	10.44 ± 0.53	27.44± 1.68	1.45± 0.08	7.48± 1.84	10.9± 0.66	18.74 ± 1.06	3.42 ± 0.21	3.17 ± 0.62	4.06± 0.04

BDL= below detection limits, mean ± standard deviation, n=3

4.5.4.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling Sites During the Heavy Rain Season

Brominated diphenyl ether 28 was present in all water samples with the highest mean concentration detected in samples from Outering road (12.74±0.31 ng/L), while the lowest concentration was recorded in samples from Ondiri sampling site (1.37±0.04 ng/L). The highest concentration of brominated diphenyl ether 47 was recorded at Ruai sampling site (27.44±1.68 ng/L) while the lowest mean concentration was recorded at James Gichuru (3.66±0.32 ng/L). Brominated diphenyl ether 66 was BDL (≤0.001 ng) in Waithaka and Enterprise road sampling site while the highest mean concentration was recorded at Outering road sampling site (22.18±1.58 ng/L). Brominated diphenyl ether 85 was present in all water samples with the highest concentration detected in samples from Outering road (10.02±0.36 ng/L), while the lowest concentration was detected in samples from Waithaka (1.64±0.05 ng/L).

The highest concentration of Brominated diphenyl ether 99 was recorded at Outering sampling site (12.71±0.57 ng/L) while the lowest concentration was recorded at James Gichuru (1.37±0.32 ng/L). Brominated diphenyl ether 100 was present in every water samples with the highest mean concentration detected in water from Ruai (18.74±1.06 ng/L), while the lowest concentration was detected in samples from James Gichuru (1.65±0.01 ng/L). Brominated diphenyl ether 153 was present in every water samples with the highest mean concentration detected in samples from Enterprise road (8.07±0.91 ng/L), while the minimum mean concentration was recorded in water from Ondiri (0.91±0.00 ng/L). Brominated diphenyl ether 154 and 183 recorded the highest concentration in water from Enterprise road (5.76±0.87 ng/L and 8.84±0.79 ng/L) respectively while the lowest concentration was recorded in water samples from Ondiri (0.91±0.00 and ≤0.001 ng/L) respectively. The mean concentration of PBDEs in water per site during the heavy rain season is attached in appendix 8D.

4.5.5 Spatial and Seasonal Variation of Polybrominated Diphenyl Ethers Level in Nairobi River Water

Nairobi River was divided into three sections, namely, the upstream, midstream, and downstream locations. Upstream sites were; Ondiri, Waithaka and Jamhuri; midstream sites were; James Gichuru, Outering road and Enterprise road and downstream sites are; Njiru, Bypass and Ruai. The mean concentration of the ∑9PBDEs for the upstream, midstream, and downstream locations in Nairobi River ranged from BDL to 43.67±1.47, BDL to 40.46±1.08, and BDL to 72.89±6.15 ng/L, respectively. The observed trend of contamination of PBDEs downstream of the river profile can be attributed to human activities around the river since the river is located in residential areas at the upstream and industrial areas in the midstream and downstream of the river. The results show that the use of consumer goods containing PBDEs formulations in Kenya is higher despite the effort made by the international community to stop the manufacture and use of PBDEs by 2013 (Sutton *et al.*, 2019). This shows that the Kenyan government needs to regulate and eradicated the use of PBDEs products due to the increasing fear of the health effect posed by PBDEs.

The mean concentrations of PBDEs at the nine sampling sites along Nairobi river basin were assessed to measure their variation designs. The data gotten for the nine sampling sites during the four seasons is shown in Table 4.8. The result showed that the PBDE congeners were portable and can be moved over a long distance over period. Additionally, the nine PBDEs investigated were detected in all sampling location in the river at different levels.

Njiru site situated downstream of the river recorded the highest concentration of PBDEs among the nine locations which was attributed to leaking of the PBDEs from open burning of wastes including plastics at Dandora dumpsite and discharge of industrial wastewater from light industries at Kariobangi.

Generally, from the source of the river, the mean concentration of these contaminants increased downstream. The sampling sites; Ruai, By-pass, Njiru, Outering road and Enterprise road had relatively higher concentration of PBDEs that is associated with their close proximity to Dandora municipal dumpsite where unsorted wastes are dumped including plastics, domestic and industrial wastes hence leaching of the contaminants into the receiving river is highly probable. Dismantling and burning of electronic wastes are considered key sources of PBDEs in Kenya (GoK, 2014). It is projected that 7,350 tons of electronic wastes were produced in Kenya annually generating 143.19 tons of PBDEs into the environment (GoK, 2014). The upstream section of Nairobi River had relatively low concentration of PBDEs that is as a result of atmospheric deposition from open burning of solid debris. Hence suggests that atmospheric deposition is a possible route of movement of particulate pollutants to Nairobi River's ecosystem (Streets *et al.*, 2006).

Table 4. 8: Mean Levels (ng/L) of the Spatial Allocation of Polybrominated Diphenyl Ethers in the Nairobi River Water Samples during the Four Seasons

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	2.61± 1.02	6.54± 0.12	0.37± 0.21	1.24± 1.05	4.34± 1.15	7.58± 0.18	1.87± 0.07	0.32± 0.05	1.31± 0.00
Waithak	6.41± 0.94	6.32± 0.97	0.19± 0.11	2.06± 0.33	2.57± 0.25	6.62± 2.11	2.01± 0.02	0.44± 0.12	2.11± 0.07
James Gichuru	6.41± 1.24	11.9± 1.97	1.98± 0.02	4.81± 2.12	4.39± 0.55	3.32± 0.01	1.44± 0.24	0.56± 0.02	4.28± 0.61
Jamhuri	8.45± 1.25	6.88± 2.46	2.23± 1.17	4.54± 0.33	16.03± 1.66	5.34± 0.17	3.74± 2.16	1.19± 0.02	5.06± 0.36
Outering Road	9.66± 1.40	18.78± 3.22	8.58± 1.99	2.84± 0.52	5.06± 0.91	3.16± 0.15	2.34± 0.45	1.34± 0.30	1.66± 0.12
Enterprise Road	7.59± 1.30	12.26± 4.94	0.17± 0.00	4.78± 0.34	8.49± 2.27	3.57± 0.68	3.65± 0.31	1.87± 0.13	3.85± 1.19
Bypass	4.97± 1.61	8.68± 0.52	3.35± 1.25	5.15± 0.51	14.51± 3.66	5.17± 0.24	3.22± 0.20	0.89 ±0.26	5.76± 0.22
Njiru	5.56± 2.39	22.61± 1.84	0.31± 0.11	6.47± 0.89	18.57 ±5.62	13.36± 2.54	3.25± 0.45	0.69± 0.29	2.21± 0.42
Ruai	9.70±1.95	14.37±2.39	1.49±0.47	5.53±0.08	15.44±0.48	9.68±0.19	4.03±0.01	1.32±0.42	4.96±0.42

Figure 4.1 shows the seasonal variation in the concentration of PBDE congeners in water samples from Nairobi River. The concentration (ng/L) of these congeners for cool dry, short rain, hot dry and heavy rain seasons are as follows: BDE 28 (34.16, 47.75, 108.12 and 55.52); BDE 47 (194.88, 50.66 , 90.38 and 97.51); BDE 66 (21.34, 21.48, 2.81 and 29.02); BDE 85 (17.25, 31.44, 45.50 and 55.59); BDE 99 (158.51, 41.97, 92.39 and 64.85); BDE 100 (55.48, 32.94, 92.91 and 49.92); BDE 153 (28.87, 17.37, 28.17 and 27.74); BDE 154 (0.8, 9.06, 5.5 and 19.23) and BDE 183 (54.74, 30.48, 7.01 and 32.54), respectively. The concentrations of BDE 47 and 99 congeners presented substantial variances in the cool dry period in the river water but the concentration observed for BDE 47 in the cool dry period was more distinct. The high concentration of BDE 47 and 99 in the cool dry period maybe attributed to the high technical formulation of BDE 47 and 99 compounds available in the waste at Dandora dumping site. Additionally, the less flora cover of the Nairobi River could allow the penetration of sunshine thus enhancing the removal of bromine atoms from PBDE congeners to different levels (Streets *et al.*, 2006). Polybrominated diphenyl ether congeners could leak from the

dumpsite due to heavy precipitation and consequent release of runoff into the river leading to the high levels of PBDE congeners observed in the cool dry season after the heavy rain season.

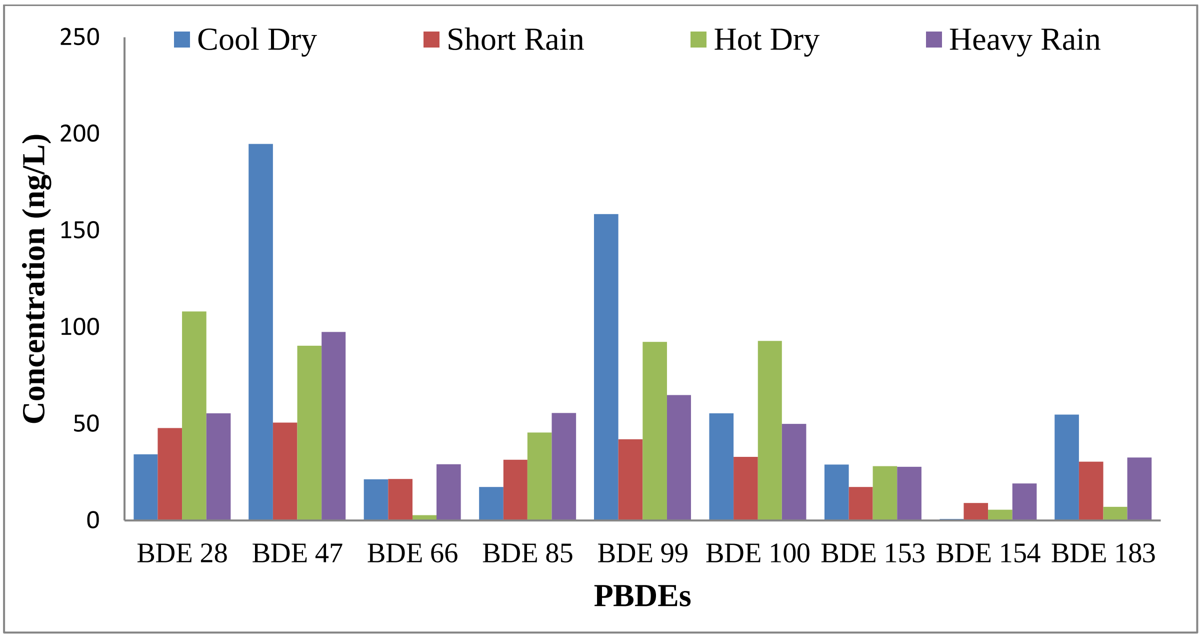


Figure 4.1: Seasonal Variation in the Levels of Polybrominated Diphenyl Ether Compounds in Nairobi River Water Samples

Detection frequencies of PBDE congeners in water were as follows; BDE 28 97 %, BDE 47 100 %, BDE 66 86 %, BDE 85 83 %, BDE 99 100 %, BDE 100 100 %, BDE 153 100 %, BDE 154 100 % and BDE 183 94 %. High frequency of all the PBDEs analysed in this study suggests extensive contamination of Nairobi River water by PBDEs. Penta-BDE congeners recorded high concentrations in water which can be attributed to deposits from dumping of polyurethane foams into the river. The octa-PBDE formulation is mostly used in plastics. They are deposited into the soil when plastic materials are burned and are eventually washed by runoffs. Kenya does not manufacture PBDEs, it imports products containing PBDEs but comprehensive information about their composition is not known (GoK, 2014). It is presumed that these products have low levels of BDE 153 which is in agreement with a study done by Hongwei and co-workers who found low levels of BDE 153 in Kenyan soil (Hongwei *et al.*, 2016). Furthermore, Liu and co-workers stated that BDE 47 and 99 were the major PBDEs in Chaohu Lake in China (Liu *et al.*, 2018).

The levels of PBDEs in the current research were compared to Environment Canada set limit for surface water, which are 46 ng/L for BDE 28, 24 ng/L for BDE 47, 24 ng/L for BDE 66, 0.2 ng/L for BDE 85, 4 ng/L for BDE 99, 0.2 ng/L for BDE 100, 120 ng/L for BDE 153, 120 ng/L for BDE 154 and 17 ng/L for BDE 183 (Environment Canada, 2013). The mean concentrations recorded for BDE 47, 85, 99 and 100 far exceeded the guideline levels provided by Environment Canada signifying the shocking nature of Nairobi River's water contamination state.

Lower molecular weight PBDE congeners are very toxic and hence more bio accumulative, when consumed they accumulate in human fatty tissues (breast milk, adipose tissues and serum) (Roze *et al.*, 2009). Therefore, their occurrence especially the high amount of BDE 47, 85, 99 and 100 could have had a substantial contribution to the increased cases of cancer and other forms of diseases in Kenya (Macharia *et al.*, 2019), since these BDE are known cancer agents (Lilientha *et al.*, 2006).

4.5.6 Comparison of Polybrominated Diphenyl Ether Levels in Nairobi River Water Samples with Levels in various Countries of the World

A comparison of different research done around the globe is challenging because of variations in the PBDE contaminants analysed. The mean concentration of nine PBDEs analysed in this study which ranged between BDL to 72.89±6.15 ng/L (Table 4.3) was lower than those observed in Asunle Stream, Ile-Ife (0.45 ng/ml) in Nigeria (Olutona *et al.*, 2017), Chaohu Lake (4,480 ng/L) in China (Liu *et al.*, 2018) and wastewater treatment plant (29,023 ng/ml) in California (North, 2004) but they were comparable to levels measured in water from Pearl River, China which had mean concentration of 0.344–68 ng/L (Guan *et al.*, 2007). The concentration of PBDEs in Nairobi River were higher than those reported in water from Mendoza River (1.9 ng/L) Argetina States (Lana *et al.*, 2010), Diep/Kuils Rivers (4.83 ng/L) in South Africa (Daso *et al.*, 2013) and Lake Shihwa (11.0 ng/L) in Korea (Moon *et al.*, 2012).

A comparison of the concentration of PBDEs in the current study with similar studies around the world is summarized in Table 4.9.

Table 4.9: Comparison of Polybrominated Diphenyl Ethers Levels in Nairobi River Water Samples with other Studies around the World

Location	**ΣPBDEs (ng/L)**	**Reference**
Mendoza River, Argentine	Nd-1.9 [a]	Lana *et al.*, 2010
Lake Shihwa, Korea	0.16 -11.0[b]	Moon *et al.*, 2012
Pearl River, China	0.344 – 68[c]	Guan *et al.*, 2007
Asunle Stream, Ile-Ife, Nigeria	30 – 450[d]	Olutona *et al.*, 2017
Chaohu Lake, China	110 - 4,480 [e]	Liu *et al.*, 2018
Diep/Kuils Rivers, South Africa	2.6 – 4.830[f]	Daso *et al.*, 2013
Nairobi River	BDL-72.89	Data for current study

Nd, Not Detected

BDL, Below detection limit

[a] *PBDE analysed are BDE 47, 99, 100 and 153*

[b] *total concentration of BDE 17, 28, 47,49, 66, 71, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191,196, 197, 206, 207 and 209*

[c] *sum of BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 206, 207, 208, and 209*

[d] *sum of BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 206, 207, 208, and 209*

[e] *Total concentrations BDE28, 47, 99, 100, 153, 154, 183, and 209*

[f] *mean concentrations of the sum of BDE 28, 47, 100, 99, 154, 153, 183 and 209.*

In this study: mean concentration BDE 28, 47, 66, 85, 99, 100, 153, 154, 183

4.6 Polybrominated Diphenyl Ethers Residue Level in Nairobi River Sediment

Sediments were chosen as matrices of concern for analysis because they function as sink for majority of hydrophobic organic contaminants, they strongly attach to the particulate matter due to its good octanol-water partition coefficient (K_{ow}) (Floehr *et al.,* 2013). Analysis of sediment samples from nine sites along Nairobi River showed presence of PBDEs residues at varying concentrations. The mean concentration of the $\sum_9$PBDEs in sediment ranged from 134.70±3.07 to 24,386.13±207.22 ng/Kg (Table 4.10). PBDE concentration measured in the current research were higher compared to those observed by Olutona and Co-workers for Asunle Stream, Ile-Ife, Nigeria, where the average concentration of the $\sum_6$PBDEs sediment samples was between 0.83 to 10.45 ng/g (Olutana *et al.,* 2016). But, mean concentrations in the current research were lower than those observed in sediment samples collected from Pearl river in China whose concentration ranged from 150,110 to 230,130 µg/kg (Zheng *et al.,* 2004), coastal zones of Korea whose concentration ranged from 180,560 to 260,380 µg/kg (Moon *et al.,* 2002), those from Portugal whose concentrations ranged from 185,500 to 277,200 µg/kg (Lacorte *et al.,* 2003), Osaka Bay of Japan whose concentrations ranged from 8,800 to 13,520 µg/kg (Ohta *et al.,* 2002) and those from America whose concentrations ranged from BDL to 2,120 ug/kg (Oros *et al.,* 2005). The mean concentrations of PBDEs in this study were below Environment Canada's safe limit (Environment Canada, 2013).

Table 4. 10: Range and Mean Concentration of Polybrominated Diphenyl Ethers Residue Level in Nairobi River Sediment over the entire Period (ng/Kg, dry weight)

Site/ PBDE		BDE 28	BDE47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	Range	216.27-1321.44	1051.23-6521.00	191.55-718.43	134.70-538.22	1021.53-3059.17	478.48-1232.15	233.48-1645.22	352.63-2813	653.87-864.27
	Mean ±SD	860.79±213.19	3871.46±121.43	515.70±113.45	296.96±130.26	12505.76±584.23	824.56±58.55	701.65±39.78	1078.65±140.66	727.04±23.76
Jamhuri	Range	791.75-1688.62	1116.73-8733.92	464.78-1785.67	582.51-1758.99	876.89-5742.18	758.45-1687.27	681.06-3913.25	987.72-3699.28	478.38-1536.18
	Mean ±SD	1232.09±268.35	5035.78±821.24	1097.08±234.53	911.04±40.41	3437.43±612.54	1236.87±286.55	1775.11±102.62	2182.61±172.45	940.22±73.59
Waithaka	Range	524.36-1532.4	1517.75-6980.11	141.67-1294.00	364.68-924.20	1087.44-5196.00	330.64-711.51	371.64-1725.64	738.19-1247.23	761.89-2315.00
	Mean ±SD	1018.78±344.39	4041.02±589.52	662.49±398.12	661.61±6.60	13050.73±299.31	445.54±129.99	893.67±84.61	1161.93±275.61	1187.58±65.61
James Gichuru Road	Range	515.67-1165.42	1792.16-8912.09	281.76-1826.03	361.00-1224.11	1839.76-10785.00	1526.29-1843.1	586.70-2226.21	816.91-2526.00	271.54-1981.99
	Mean ±SD	1214.30±326.64	5684.26±2442.36	879.58±281.76	805.44±76.16	4960.32±221.42	1771.86±176.31	1135.62±95.47	1269.08±28.75	939.26±2.11
Enterprise Road	Range	1683.65-2382.6	10772.95-12332.5	681.91-2556.37	1168.27-2867.6	4843.61-10082.93	681.91-2556.37	1257.7-3687.57	1564.46-5736.1	1156.76-2167.1
	Mean ±SD	1978.01±302.93	11608.75±751.06	1801.85±113.54	1738.36±234.98	8260.61±777.21	1622.63±810.01	2332.64±93.46	2314.03±41.14	1715.84±229.56
Outering Road	Range	1262.81-1886.7	6692.03-10483.16	682.69-2476.83	1119.56-1716.2	7716.94-11914.72	967.00-1362.15	1172.3-3916.30	1700.31-3916.3	1054.80-3279.9
	Mean ±SD	1982.75±319.34	9593.26±1188.43	1709.68±397.94	1400.51±154.96	10051.19±801.87	12737.07±215.6	1991.31±41.95	2533.43±132.48	1828.03±82.07
By-Pass	Range	1954.36-3816.8	8968.24-14117.73	1669.87-3226.2	952.41-2554.23	5731.03-12856.34	1262.23-3491.3	1841.9-4213.69	1328.61-3851.7	1384.45-2616.3
	Mean ±SD	2515.14±162.59	10656.23±642.10	2260.27±308.41	1687.33±387.76	9468.08±1028.02	1900.57±158.61	3324.55±318.18	2420.17±379.51	2016.93±302.21
Njiru	Range	1345.30-3362.4	8955.9-24386.1	1768.59-3971.4	1296.74-2719.5	6961.86-11245.21	1731.89-2832.0	1861.5-5497.66	2816.99-4752.2	1520.14-3116.9
	Mean ±SD	2475.48±491.63	13686.91±1102.02	2635.09±604.61	1884.55±607.69	9380.82±917.00	2107.50±337.44	3224.94±309.14	3665.49±208.06	2029.70±201.45
Ruai	Range	1731.88-3095.2	6874.90-10556.99	1119.79-3331.6	1015.74-2554.3	8445.89-10668.32	1334.52-2786.1	1519.8-3648.79	2154.19-3914.2	1199.74-3007.7
	Mean ±SD	2309.06±277.74	9248.14±677.06	2372.47±510.97	1726.40±206.33	9651.81±857.98	12089.14±445.7	2635.29±454.39	2780.32±61.61	2509.26±63.32
Detection Frequency	%	100	100	100	100	100	100	100	100	100

BDL= below detection limits n=6, mean ± standard deviation, n=3

4.6.1 Polybrominated Diphenyl Ethers Residue in Nairobi River Sediment during the Cooler Dry Season

Polybrominated diphenyl ethers residue levels detected in Nairobi River sediment during the cooler dry season ranged from 134.70±3.07 to 24,386.13±207.22 ng/Kg, the highest detected was BDE 47 at Njiru sampling site. The PBDEs in Nairobi River sediment from the nine sampling sites during the cooler dry season is presented in Table 4.11.

Table 4.11: Concentration of Polybrominated Diphenyl Ethers in Nairobi River Sediment Samples Collected during Cooler Dry Season (ng/kg, dry weight) Dry Weight

SITE/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	964.32 ±20.37	6,521.0 ±10.38	498.67 ±45.9	134.70 ±3.07	3,059.17 ±5.12	1,026.32 ±45.9	1,645.22 ±54.87	2,813.00 ±13.9	695.81 ±25.1
Waithaka	1,532.4 ±1.76	6,980.1 ±16.27	1,294.21 ±11.03	924.20 ±38.14	5,196.91 ±77.91	498.71 ±18.9	1,725.64 ±41.82	1,637.26 ±55.7	2,315.89 ±36.18
James Gichuru	1,165.42 ±47	8,912.1 ±109.4	1,826.03 ±10.40	361.37 ±18.4	10,785.34 ±46.10	1,550.67 ±6.16	2,226.21 ±36.89	2,526.45 ±2.92	1,229.61 ±31.15
Jamhuri	1,688.62 ±26.72	2,278.2 ±63.6	1,785.67 ±28.91	658.74 ±23.29	5,742.18 ±1.24	1,114.37 ±61.87	3,913.25 ±77.18	3,699.28 ±51.21	582.45 ±42.38
Outering	1,886.70 ±83.01	10,483.2 ±26.83	2,476.83 ±22.1	1,412.4 ±37.71	10,853.5 ±56.21	967 ±71.3	3,081.38 ±29.25	3,916.31 ±29.25	1,054.88 ±27.46
Enterprise Rd	1,894.26 ±151.31	12,332.5 ±125.3	2,496.15 ±56.41	1,168.2 ±223.2	10,082.9 ±384.16	681.91 ±41.3	3,687.57 ±26.17	5,736.16 ±58.74	1,776.51 ±39.31
Bypass	2,024.85 ±24.27	8,968.24 ±89.29	2,275.19 ±42.16	952.41 ±16.6	12,856.3 ±105.18	1,296.32 ±29.69	4,213.69 ±48.13	3,851.75 ±5.31	2,916.34 ±36.21
Njiru	3,362.41 ±21.55	24,386.1 ±207.22	3,971.45 ±21.46	1,296.7 ±66.21	9,622.54 ±118.24	1,616.21 ±74.65	5,497.66 ±76.66	3,693.51 ±94.21	1,520.14 ±122.24
Ruai	2,256.2 ±25.40	10,288.1 ±72.5	3,331.61 ±27.16	1,015.7 ±25.14	9,073.54 ±124.63	1,894.57 ±125.86	3,648.79 ±24.96	3,914.23 ±105.21	2,948.32 ±94.36

BDL= below detection limits n=6, mean ± standard deviation, n=3

4.6.1.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in Different Sampling Sites during the Cooler Dry Season

Brominated diphenyl ether 28 was present in all sediment samples with the highest mean concentration detected in sediment from Jamhuri (3,362.41±21.55 ng/Kg), while the lowest concentration was detected in sediment from Ondiri (964.32±20.3 ng/Kg). The highest concentration of brominated diphenyl ether 47 was recorded at Njiru sampling site (24,386.1±207.22 ng/Kg) while the lowest concentration was recorded at James Gichuru (2,278.15±63.6 ng/Kg). Brominated diphenyl ether 66 was detected in all the sediment samples with the lowest concentration recorded at Ondiri (498±45.9 ng/Kg) while the highest concentration was recorded at Njiru sampling site (3,971.45±21.46 ng/Kg). Brominated diphenyl ether 85 was present in every sediment samples with the highest mean concentration detected in sediment from Outering Road (1,412.4±37.71 ng/Kg), while the lowest concentration was detected in sediment from Ondiri (134.7±3.07 ng/Kg).

The highest concentration of brominated diphenyl ether 99 was recorded at Bypass sampling site (12,856.34±105.18 ng/kg) while the lowest concentration was recorded at Ondiri (3,059.17±5.12 ng/kg). Brominated diphenyl ether 100 was recorded in every sediment samples with the highest concentration detected at Ruai (1,894.57±125.86 ng/kg), while the lowest concentration was recorded at Waithaka (498±45.9 ng/Kg). BDE 153, 154 and 185 were recorded in all the sediment samples with the highest concentration detected in sediment from Njiru (5,497.66±76.66 ng/Kg), Enterprise road (5,736.16±58.74 ng/Kg) and Bypass (2,948.32±94.36 ng/Kg) respectively while the lowest concentration was recorded in sediment from Ondiri (1,645.22±54.87 ng/Kg), Waithaka (1,637±55.7 ng/Kg) and Ondiri (695.8±25.1 ng/Kg) respectively. The mean concentration of PBDEs in sediment per site during the cooler dry season is attached in appendix 8E.

4.6.2 Polybrominated Diphenyl Ethers Residue in Nairobi River Sediment during the Short Rain Season

During the short rainfall period the concentration of PBDEs in sediment ranged from 141.67±4.33 ng/Kg to 12,146.19±73.34 ng/Kg. Table 4.12 shows the concentration of PBDEs in sediment during the short rainfall season. It was observed that BDE 47 (12,146.19±73.34 ng/Kg) recorded the highest concentration detected at Enterprise road sampling site.

Table 4.12: Concentration of Polybrominated Diphenyl Ethers in Sediment Samples during Short Rainfall Season (ng/Kg, dry weight)

Site /PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	1321.44 ±181.25	6,349.2 ±80.17	654.81 ±26.85	538.22 ±30.97	4,094.5 ±11.26	1,232.1 ±32.17	638.14 ±37.22	516.33 ±43.87	653.87 ±37.69
Waithaka	1,174.58 ±12.21	6,146.4 ±270.6	642.47 ±23.33	914.86 ±84.89	4,772.7 ±45.29	711.51 ±9.12	798.53 ±62.76	738.19 ±74.1	787.32 ±39.16
James Gichuru	2,394.29 ±62.25	7,796.9 ±83.56	612.64 ±17.89	1,116.4 ±43.81	3,764.8 ±19.73	1,526.2 ±28.97	586.70 ±68.72	816.91 ±30.52	271.54 ±51.66
Jamhuri	1,231.73 ±83.16	8,733.9 ±67.51	464.78 ±20.62	643.96 ±39.43	2,254.7 ±89.66	1,687.2 ±76.93	681.06 ±71.16	1,231.6 ±29.73	1,163.8 ±43.69
Outering	3,331.87 ±60.93	9,412.3 ±52.19	682.69 ±70.88	1,716.2 ±27.89	11,914.7 ±161.21	1,037.1 ±86.91	1,231.6 ±29.98	2,629.4 ±18.65	1,170.8 ±99.91
Enterprise Road	2,382.68 ±52.05	12,146.1 ±73.34	1,029.1 ±51.69	1,294.2 ±93.67	8,554.1 ±224.2	2,232.4 ±41.99	2,126.5 ±73.91	332.83 ±74.26	1,156.7 ±29.35
Bypass	3,816.81 ±49.02	9,324.1 ±67.22	1,669.8 ±89.44	1,656.1 ±16.36	8,915.5 ±52.16	3,491.3 ±68.23	3,396.3 ±69.33	2,634.9 ±44.57	1,974.8 ±154.1
Njiru	2,812.66 ±122.41	10,258.7 ±1.27	1,917.8 ±24.14	1,629.3 ±2.66	9,693.6 ±71.20	2,249.8 ±33.55	3,241.8 ±31.58	3,399.2 ±27.09	1,584.8 ±17.24
Ruai	3,095.23 ±38.56	9,272.5 ±12.12	1,842.4 ±19.68	1,813.6 ±41.21	8,445.8 ±128.91	2,341.3 ±61.27	2,366.3 ±61.17	2,154.2 ±38.16	1,199.7 ±97.28

BDL= below detection limits, mean ± standard deviation, n=3

4.6.2.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling Sites during the Short Rain Season

Brominated diphenyl ether 28 was present in every sediment samples with the highest mean concentration detected in sediment from Bypass sampling site (3,816.81±49.02 ng/Kg), while the lowest concentration was detected in sediment from Waithaka (1,174.58±12.21 ng/Kg). The highest concentration of brominated diphenyl ether 47 was recorded at Enterprise road sampling site (12,146.19±73.34 ng/Kg) while the lowest concentration was recorded at Waithaka (6,146.40±270.65 ng/Kg). Brominated diphenyl ether 66 was present in every sediment samples with the highest mean concentration detected at Njiru (1,917.88±24.14 ng/Kg) while the lowest concentration was recorded at Jamhuri (464.78±20.62 ng/Kg). BDE 100 was not detected in sediment samples from Jamhuri with the highest concentration detected in sediment from Ruai (3,491.34±68.23 ng/Kg).

Brominated diphenyl ether 85 was present in every sediment samples with the highest mean concentration detected in samples from Ruai (1,813.65±41.21 ng/Kg), while the lowest concentration was recorded in samples from Ondiri (538.22±30.97 ng/Kg). The highest concentration of brominated diphenyl ether 99 was recorded at Outering road sampling site (11,914.72±161.21 ng/Kg) while the lowest concentration was recorded at Jamhuri (2,254.73±89.66 ng/Kg). Brominated diphenyl ether 153, 154 and 183 was present in every sediment samples with the highest mean concentration detected in sediment from Bypass sampling sites (3,396.31±69.33 ng/Kg), Njiru (3,399.26±27.09 ng/Kg) and Bypass (1,974.82±154.09 ng/kg) while the lowest mean concentration was detected in sediment from James Gichuru (586.70±68.72 ng/kg), Ondiri (516.33±43.87 ng/Kg) and James Gichuru (271.54±51.66 ng/kg). The mean concentration of PBDEs in sediment per site during the short rain season is attached in appendix 8F.

4.6.3 Polybrominated Diphenyl Ethers Residue Levels in Nairobi River Sediment during the Hot Dry Season

The concentration of PBDEs during the hot dry season in Nairobi River sediment ranged from 141.67±4.33 ng/Kg to 14,117.73±181.52 ng/Kg. Table 4.13 shows the concentration of PBDEs in Nairobi river sediment during the hot dry season. 2,2′,4,4′-tetra-bromodiphenyl ether congener recorded the highest concentration at Bypass sampling site.

Table 4.13: Concentration of Polybrominated Diphenyl Ethers in Nairobi River Sediment Samples Collected during Hot Dry Season (ng/Kg, dry weight)

Site/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	216.27 ±14.11	1,564.3 ±39.22	191.55 ±39.82	366.7 ±41.11	1,021.5 ±79.21	561.29 ±51.20	289.7 ±18.8	352.6 ±17.2	694.21 ±61.88
Waithaka	524.36 ±44.19	1,519.8 ±14.80	141.67 ±4.33	442.6 ±14.62	1,146.7 ±28.45	242.01 ±6.28	371.6 ±28.3	1,025. ±23.1	761.89 ±71.34
James Gichuru	515.67 ±10.39	4,235.9 ±31.02	797.89 ±44.35	520.2 ±126.8	3,451.6 ±24.33	2,167.3 ±120.2	1,007. ±96.07	865.9 ±191.7	274.51 ±24.26
Jamuhuri	1,216. ±24.16	8,014.3 ±251.5	1,453.9 ±114.3	1,758.9 ±123.5	4,875.9 ±230.5	758.45 ±13.88	1,679.9 ±107.3	987.7 ±45.8	478.38 ±86.74
Outering	1,265.8 ±21.64	11,785.4 ±211.71	1,687.91 ±198.80	1,353.8 ±121.3	9,719.5 ±345.2	1,382.02 ±144.05	1,644.9 ±168.6	1,700.3 ±154.9	3,279.9 ±86.25
Enterprise Road	1,831.4 ±29.31	10,772.9 ±299.29	1,189.7 ±24.18	1,623.2 ±85.74	9,561.7 ±260.6	1,019.7 ±51.49	1,257.7 ±66.78	1,622.6 ±32.11	2,167.1 ±258.57
Bypass	1,954.3 ±41.24	14,117.7 ±181.52	1,869.8 ±261.56	1,586.5 ±223.5	10,369.3 ±124.16	1,262.2 ±154.67	1,841.9 ±264.7	1,865.3 ±24.47	1,384.4 ±23.46
Njiru	1,345.3 ±161.97	8,955.9 ±16.56	1,768.5 ±91.50	1,892.5 ±141.3	11,245.2 ±127.23	1,731.8 ±36.00	1,861.5 ±66.52	2,816.9 ±15.12	1,896.8 ±18.69
Ruai	1,731.8 ±71.79	6,874.9 ±60.23	1,119.7 ±91.24	1,521.8 ±54.01	10,419.4 ±46.40	2,786.1 ±12.98	1,519.8 ±88.94	2,241. ±14.76	2,881.2 ±251.1

BDL= below detection limits, mean ± standard deviation, n=3

4.6.3.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling Sites during the Hot Dry Season

Brominated diphenyl ether 28 recorded concentration values ranging from 216.27±14.11 ng/Kg to 1,954.36±41.24 ng/kg, the highest concentration was recorded at Bypass sampling site while Ondiri sampling sites recorded the lowest concentration. Brominated diphenyl ether 47 was present in every sediment samples with the highest mean concentration detected in samples from Bypass (14,117.73±181.52 ng/kg), while the lowest mean concentration was detected in sediment from Waithaka (1,519.83±14.80 ng/kg). The highest concentration of BDE 66 was recorded at Bypass sampling site (1,869.82±261.56 ng/kg) while the lowest concentration was recorded at Waithaka (141.67±4.33 ng/Kg). The highest concentration of BDE 85 was recorded at Njiru sampling site (1,892.57±141.37 ng/kg) while the lowest concentration was recorded at Ondiri (366.72±41.11 ng/kg). Brominated diphenyl ether 99 was present in every sediment samples with the highest concentration detected in sediment from

Njiru (11,245.21±127.23 ng/kg), while the lowest mean concentration was detected in samples from Ondiri (1,021.53±79.21 ng/kg).

Brominated diphenyl ether 100 was present in every sediment samples with the highest mean concentration detected in samples from Waithaka (242.01±6.28 ng/kg) and the highest concentration was recorded at Ruai sampling site (2,786.13±12.98 ng/kg). Brominated diphenyl ether 153 was present in every sediment samples with the highest mean concentration detected in sediments from Njiru (1,861.51±66.52 ng/kg), while the lowest mean concentration was recorded in samples from Ondiri (289.74±18.87 ng/kg). Brominated diphenyl ether 154 was was present in every sediment samples with the highest mean concentration detected in sediments from Njiru (2,816.99±15.12 ng/kg), while the lowest mean concentration was recorded in sediment from Ondiri (352.63±17.24 ng/kg). Brominated diphenyl ether 183 recorded the highest concentration in sediment from Outering road (3,279.93±86.25 ng/kg) while the lowest mean concentration was recorded in sediment from James Gichuru (274.51±24.26 ng/kg). The mean concentration of polybrominated diphenyl ethers in sediment per site during the hot dry season is attached in appendix 8G.

4.6.4 Polybrominated Diphenyl Ethers Residue in Nairobi River Sediment during the Heavy Rain Season

The concentration of PBDEs in sediment ranged from 148.09±11.28 ng/Kg to 11,183.32±316.48 ng/Kg during the heavy rain season. Table 4.14 shows the concentration of polybrominated diphenyl ethers in sediment during the heavy rain season. Brominated diphenyl ether 47 congener recorded the highest concentration at Enterprise road sampling site.

Table 4.14: Concentration of Polybrominated Diphenyl Ethers Residue Levels in Nairobi River Sediment Collected during Heavy Rainfall Season (ng/Kg, dry weight)

Site / PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	941.12 ±82.62	1051.23 ±62.68	718.43 ±53.38	148.09 ±11.28	1847.7 ±75.31	478.48 ±15.03	233.48 ±22.47	632.62 ±47.01	864.27 ±42.19
Waithaka	843.78 ±18.64	1,517.7 ±112.66	571.81 ±81.37	364.68 ±9.00	1,087.4 ±147.89	330.64 ±29.14	678.87 ±26.26	1247.2 ±16.31	886.09 ±13.98
James Gichuru	781.79 ±60.20	1,792.16 ±111.74	281.76 ±21.09	1,224.1 ±60.22	1,839.7 ±111.21	1,843.14 ±164.02	721.71 ±51.09	867.49 ±9.68	1,981.99 ±48.74
Jamuhuri	791.75 ±142.38	1,116.7 ±81.93	683.88 ±18.34	582.51 ±6.42	876.89 ±48.24	1,387.38 ±36.07	826.19 ±26.39	2,812.6 ±92.39	1,536.18 ±51.87
Outering Road	1,446.6 ±82.67	6,692.03 ±275.01	1,991.2 ±124.25	1,119.5 ±47.42	7,716.9 ±68.30	1,362.15 ±91.84	1,172.34 ±65.28	1,887.6 ±116.59	1,806.52 ±26.24
Enterprise Road	1,683.6 ±45.47	11,183.3 ±316.48	2,492.43 ±122.17	2,867.6 ±41.60	4,843.6 ±42.33	2,556.37 ±135.27	2,258.73 ±42.34	1,564.4 ±89.51	1,762.92 ±21.54
Bypass	2,264.5 ±123.38	10,214.7 ±34.78	3,226.22 ±162.70	2,554.2 ±106.81	5,731.3 ±45.41	1,552.41 ±84.48	3,846.29 ±27.68	1,328.6 ±36.19	1,792.09 ±61.67
Njiru	2,381.5 ±31.65	11,146.9 ±25.65	2,882.43 ±161.75	2,719.5 ±26.62	6,961.8 ±62.47	2,832.03 ±121.01	2,298.71 ±100.29	4,752.2 ±57.61	3,116.96 ±84.52
Ruai	2,152.9 ±187.88	10,556.9 ±241.39	3,196.07 ±158.16	2,554.3 ±51.55	10,668.3 ±254.31	1,334.52 ±22.69	3,006.18 ±172.83	2,811.5 ±31.62	3,007.78 ±80.44

BDL= below detection limits, mean ± standard deviation, n=3

4.6.4.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling Sites during the Heavy Rain Season

Brominated diphenyl ether was present in every sediment samples with the lowest mean concentration detected at James Gichuru (781.79±60.20 ng/Kg) and the highest concentration reported in sediment samples at Njiru sampling site (2,381.52±31.65 ng/kg). The highest concentration of brominated diphenyl ether 47 was reported in sediment collected from Enterprise road sampling site (11,183.32±316.48 ng/kg) while the lowest concentration was recorded at Ondiri (1,051.23±62.68 ng/Kg). Brominated diphenyl ether 66 was detected in all sediment samples with the lowest concentration recorded at James Gichuru (281.76±21.09 ng/Kg) and the maximum level reported in sediment from Bypass sampling site (3,226.22±162.70 ng/kg). The highest concentration of BDE 85 was recorded at Njiru sampling site (2,719.52±26.62 ng/kg) while the lowest concentration was recorded at Ondiri (148.09±11.28 ng/kg). Brominated diphenyl ether 99 was reported in every sediment samples with the highest concentration detected in samples from Njiru (10,668.32±254.31 ng/kg), while the lowest mean concentration was documented in sediment from Jamhuri (876.89±48.24 ng/kg).

Brominated diphenyl ether 100 was detected in all sediment samples with the lowest concentration recorded at Waithaka (330.64±29.14 ng/kg) and highest concentration recorded at Njiru sampling site (2,832.03±121.01 ng/kg). Brominated diphenyl ether 153 was detected in all sediment samples with the highest concentration detected in sediment samples from Bypass (3,846.29±27.68 ng/kg), while the lowest concentration was recorded in samples from Ondiri (233.48±22.47 ng/kg). Brominated diphenyl ether 154 was detected in all the sediment samples with the highest concentration detected in sediment from Njiru (4,752.2±57.61 ng/kg), while the lowest concentration was recorded in sediment from Ondiri (632.62±47.01 ng/kg). Brominated diphenyl ether 183 recorded the highest concentration in sediment from Njiru (3,116.96±84.52 ng/kg) while the lowest concentration was recorded in sediment from Ondiri (864.27±42.19 ng/kg). The mean concentration of PBDEs in sediment per site during the heavy rain season is attached in appendix 8H.

4.6.5 Spatial and Seasonal Variation of Polybrominated Diphenyl Ethers Residue Level in Nairobi River Sediment

The mean concentrations of PBDEs in sediment at the nine sampling sites along Nairobi river basin were assessed to measure their variation designs. The result showed that the PBDE congeners were ubiquitous and were spread over a long distance over the period. Additionally, the nine PBDEs investigated were recorded in every sampling location in the river at different concentration.

Njiru site situated downstream of the river recorded the highest concentration of PBDEs among the nine locations which was attributed to leaking of the PBDEs from open burning of wastes including plastics at Dandora dumpsite and discharge of industrial wastewater from light industries at Kariobangi.

Generally, from the source of the river, the mean concentration of these contaminants increased downstream. The sampling sites; Ruai, By-pass, Njiru, Outering road and Enterprise road had relatively higher concentration of PBDEs that is associated with their close proximity to Dandora municipal dumpsite where unsorted wastes are dumped including plastics, domestic and industrial wastes hence leaching of the contaminants into the receiving river is highly probable. The upstream section of Nairobi River had relatively low concentration of PBDEs as a result of atmospheric deposition from open burning of solid wastes. Hence suggesting that atmospheric deposition is a route of movement of particulate pollutants to Nairobi River's ecosystem (Streets *et al.*, 2006). Also, these could be attributed to the varying distances of the sampling locations to the source of contaminants.

Table 4.15: Mean Levels (ng/Kg, dry weight) of the Spatial Allocation of Polybrominated Diphenyl Ethers in Nairobi River Sediment during the Four Seasons

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	860.78± 16.40	3871.46 ±121.43	515.69 ±44.98	296.93 ±9.46	2505.75 ±465.27	824.56 ±58.55	701.65 ±39.78	1078.65 ±82.22	727.03 ±23.76
Waithaka	1018.78 ±225.86	4041.02 ±1.47	662.48 ±49.96	661.60 ±6.60	3050.73 ±41.95	445.54 ±62.67	893.67 ±84.62	1161.93 ±156.93	1187.57 ±17.98
James Gichuru	1214.29 ±188.17	5684.26 ±788.56	879.58 ±130.99	805.44 ±76.16	4960.31 ±221.41	1771.87 ±17.23	1135.62 ±95.47	1269.08 ±7.85	939.26 ±2.10
Jamhuri	1232.09 ±10.93	5035.77 ±508.83	1097.08 ±154.92	911.04 ±10.42	3437.42 ±612.54	1236.86 ±212.05	1775.11 ±102.62	2182.80 ±172.44	940.22 ±158.14
Outering	1982.74 ±127.84	9593.26 ±757.15	1709.68 ±214.52	2900.51 ±165.68	10051.1 ±801.87	1187.07 ±49.58	1991.31 ±41.95	2533.43 ±132.47	1828.02 ±82.06
Enterprise Road	1948.01 ±108.12	11608.7 ±131.76	1801.85 ±113.54	1738.35 ±89.10	8260.60 ±368.52	1622.63 ±229.03	2332.65 ±93.46	2314.03 ±41.14	1715.83 ±9.61
Bypass	2515.13 ±162.59	10656.2 ±251.67	4760.27 ±141.38	1687.32 ±49.21	9468.07 ±1028.2	1900.57 ±24.11	3324.55 ±318.18	2420.17 ±379.51	2016.92 ±129.21
Njiru	2475.47 ±73.03	13686.9 ±921.23	2635.08 ±105.56	1884.55 ±186.11	9380.81 ±50.28	2107.49 ±81.79	3224.94 ±309.15	3665.49 ±208.06	2029.70 ±45.74
Ruai	2309.05 ±571.07	9248.14 ±190.12	2534.60 ±52.39	1726.40 ±206.33	9651.81 ±175.94	2089.14 ±314.51	2635.29 ±454.39	2780.32 ±61.61	2509.26 ±63.32

Figure 4.2 shows the seasonal difference in the concentration of PBDE congeners in sediment samples from Nairobi River. The mean concentration (ng/kg) of these congeners for the cooler dry, short rain, hot dry, heavy rain seasons are as follows: BDE 28 (16775.18, 21561.29, 10601.35 and 13287.66); BDE 47 (91149.51, 79440.51, 67841.373 and 55271.90); BDE 66

(19954.93, 9516.69, 10220.91 and 16044.32); BDE 85 (7924.16, 11323.09, 11066.72 and 14134.71); BDE 99 (77271.25, 62410.76, 61811.29 and 41573.61); BDE 100 (10645.37, 16509.36, 11911.14 and 13677.12); BDE 153 (30474.33, 15067.16, 11475.13 and 15042.5); BDE 154 (31787.23, 14453.72, 13478.16 and 17904.42); BDE 183 (15038.36, 9963.61, 13818.61 and 16754.80). The sums of nine PBDE congeners in sediment were higher during the cooler dry season just after the heavy rain this can be attributed to seasonal differential influx of industrial wastes into the river due to the surface runoff during the heavy rain season (Umulor *et al.*, 2018).

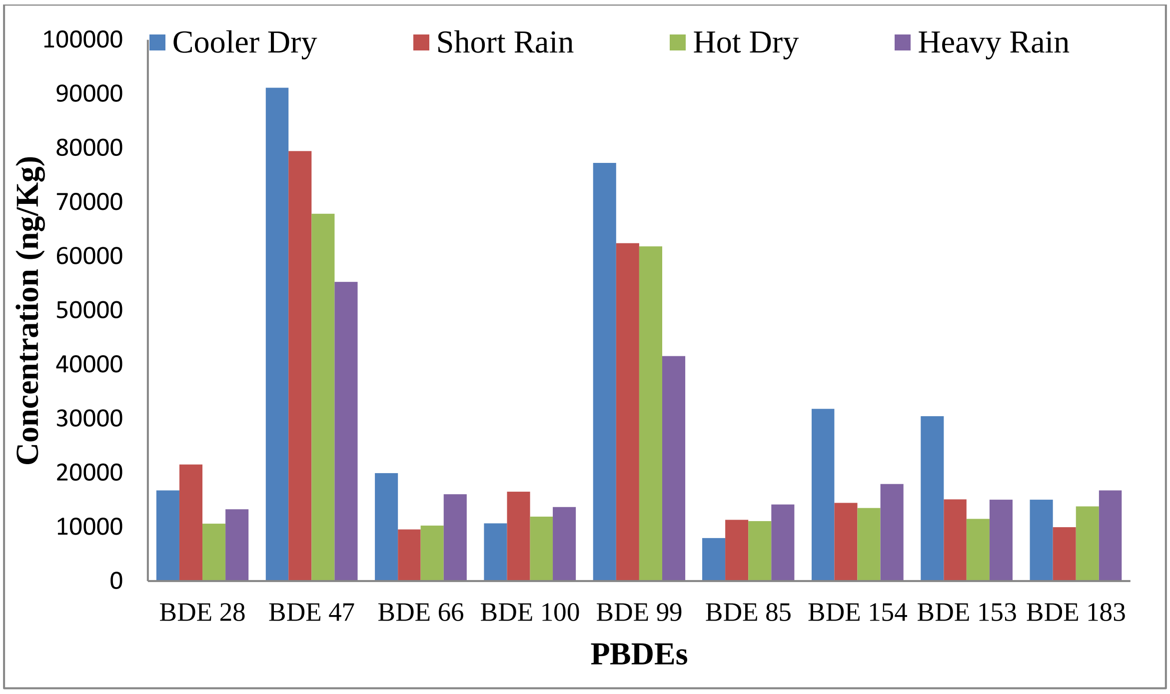


Figure 4. 2: Seasonal Variation of Polybrominated Diphenyl Ethers Residue Levels in Nairobi River Sediment

The PBDEs in Nairobi river sediment samples is likely to come from a combination of point and non-point sources. Manufacturing and reprocessing works including disassembling electrical goods, chains and cables, lubricants stores and chemical factories were probably accountable for increased levels of PBDEs in Nairobi River sediment. Higher detection frequencies of 100 % for all the PBDE congeners in sediment in this study suggest a widespread distribution of the contaminants in Nairobi River basin. The high concentration of penta-BDE formulation in the river sediment can be attributed to inappropriate dumping of polyurethane foam products. The octa-PBDE formulation is mostly used in plastics which when burned release PBDEs into the environment.

All the nine PBDE congeners studied were usually well-known since they are the main congeners in the penta-BDE technical combination (Darnerud, 2003). 2,2′,4,4′-tetra-bromodiphenyl ether is usually used in the manufacture of fittings and fabrics (Botaro and Torres, 2007). The penta-BDE mixture, which includes BDE 47, 85 99, 100, 153 and 154, is usually used in fittings, while the octa and deca-BDEs technical combinations are applied in the production of several kinds of polymers, particularly those applied in TVs, laptops and computer chains (Botaro and Torres, 2007). 2,2′,4,4′-tetra-bromodiphenyl ether predominant congener in the sediment samples, followed by BDE 99. According to literature BDE 47 and 99 are the PBDE congeners that are most commonly reported in ecological samples and living fluids (Mariussen, 2005).

4.6.6 Comparison of Polybrominated Diphenyl Ethers Residue Levels in the Nairobi River Sediment with Levels in Other Countries

The polybrominated diphenyl ethers concentration obtained was compared with the concentrations reported worldwide in order to better analyse the data gotten in the current study, as portrayed in Table 4.16. The mean concentration of nine PBDEs analyzed in this study ranged between 134.70±3.07 to 24,386.13±207.22 ng/Kg was lower than those observed in the Fuhe River in China, Baiyangdian Lake in China, the Chaohu Lake in China, and Olkhon lake in Russia. The mean concentration of PBDEs in Nairobi River sediment were higher than those reported in sediment from Lake Shihwa in Korea and Jiaojian River in China, hence the Nairobi River was moderately contaminated with PBDEs.

Table 4.16: Comparison of Polybrominated Diphenyl Ethers Levels in Nairobi River Sediment Samples with Other Studies Around the World

Country	Aquatic System	ΣPBDEs (ng/g)	Reference
Brazil	Saibro Lagoon	nd –5.4	Ferrar *et al.,* 2019
Brazil	Paranoá Lake	2.5–8.1	Annunciação *et al.,* 2017
Chile	Copncepción Bay	0.02–21	Pozo *et al.,* 2015
China	Baiyangdian Lake	0.05–5.03	Hu *et al.,* 2010
China	Fuhe River	0.13–6.39	Hu *et al.,* 2010
China	Shanghai rivers	0.44–12.0	Wang *et al.,* 2015
China	Jiaojiang River	8.93–45	Yang *et al.,* 2015
South Korea	Shihwa Lake	1.13–18,700	Moon *et al.,* 2012
Canada	Nigara River	1.10–148	Samara *et al.,* 2006
USA	White Lake	0.39–2.4	Bradley *et al.,* 2011
USA	Muskegon Lake	0.98–3.9	Bradley *et al.,* 2011
Italy	Maggiore Lake	0.02–27.1	Mariani *et al.,* 2008
Russia	Olkhon Island	0.164–0.670	Ok *et al.,* 2013
Kenya	Nairobi River	0.134 – 24.39	This study

4.7 Polybrominated Diphenyl Ethers Residue Level in Nairobi River Basin Soil

The analysis of soil samples from nine sites along Nairobi River basin showed presence of PBDEs residues at varying concentrations. The $\sum_9$PBDEs in soil recorded concentration range between 16.46±1.99 to 30,561.35±145.57 ng/Kg. Polybrominated diphenyl ether levels analysed in this research were comparable to those stated by Sun and Co-workers in soils collected from Kenya, Eastern Africa (Sun *et al.,* 2016). However, the levels of PBDEs in the present research were higher than those reported in soil from Pearl River delta in China (Zou *et al.,* 2007), Indus River Basin, Pakistan (Ali *et al.,* 2015), European countries like United Kingdom and Norway (Hassanin *et al.,* 2004). The results of the PBDEs concentration in this research were lower than that in Izmir, Turkey (Cetin *et al.,* 2007). Table 4.17 shows the range and mean concentration of PBDEs residues in soil from the Nairobi river basin.

Table 4.17: Range and Mean Concentration of PBDE Residues in Nairobi River Basin Soil over the entire Period (ng/Kg, dry weight)

Site/ PBDE		BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	Range	368.1-1522.6	963.52-6171.2	81.94-865.21	32.51-9364.5	528.23-5229.5	137.82-1641.9	21.01-1221.0	134.39-1834.1	91.20-1295.3
	Mean± SD	831.39 ±73.51	3250.34±28.45	431.01 ±51.34	2669.4 ±149.7	2383.6 ±278.8	774.52 ±167.7	444.05 ±140.2	794.67 ±85.77	631.81 ±59.24
Jamhuri	Range	719.21-2241.7	1,031.76-10413.08	155.06-825.68	181.26-1581.2	542.26-5896.3	258.96-1488.3	140.19-1949.8	99.69-2399.7	82.76-812.61
	Mean± SD	1423.09±7.26	5727.22±385.98	475.26 ±169.3	879.18 ±119.5	2986.8 ±299.9	747.18 ±76.62	943.43 ±87.43	1182.3 ±100.1	411.56 ±30.96
Waithaka	Range	287.16-1312.0	929.25-7837.92	51.07-695.78	242.55-1246.37	794.96-4194.96	191.26-1981.72	57.31-1757.6	178.52-1378.2	145.73-1425.8
	Mean± SD	815.29 ±126.9	4202.87±638.76	329.82 ±45.65	729.79 ±95.05	2397.08±27.7	1025.12±10.1	909.51 ±134.2	765.50 ±220.5	770.05 ±78.14
James Gichuru	Range	333.59-1945.9	1562.89-8291.76	91.53-974.22	369.85-1364.82	785.16-5485.16	423.10-1502.09	167.44-1267.5	226.66-1601.2	167.49-1967.3
	Mean± SD	1074.26±99.0	4446.99±333.14	478.78 ±94.13	830.04 ±70.30	2465.3 ±155.8	858.05 ±71.56	683.03 ±85.93	979.28 ±52.63	868.61 ±73.58
Enterprise Road	Range	346.79-1034.6	586.35-15338.59	394.21-1096.3	191.34-1618.68	426.98-12812.06	193.76-4194.3	72.20-3754.1	233.22-2136.9	27.51-2078.9
	Mean± SD	727.22 ±49.46	7733.41±282.04	733.45 ±98.72	902.86 ±298.5	5718.96±60.4	1966.29±91.1	1561.1 ±127.7	1157.88±92.4	998.29 ±51.24
Outering Road	Range	719.2-2241.1	527.13-18457	361.57-968.41	210.16-1432.1	516.24-11513.89	367.22-3647.4	16.46-2716.4	36.57-2366.8	91.08-1451.2
	Mean± SD	559.41 ±43.76	8482.04±42.99	694.61 ±168.5	831.75 ±185.4	5573.8 ±128.2	1717.07±4.87	1201.57±99.2	1085.8 ±183.5	720.49 ±65.22
By-Pass	Range	273.16-2563.3	932.55-19763.14	174.33-1274.7	76.1-1522.3	797.51-12877.41	298.57-4292.13	31.35-3213.3	496.11-2519.7	273.35-2072.9
	Mean± SD	1386.11±134.15	10180.62 ±689.15	662.95 ±34.76	771.06 ±41.71	5707.49±56.5	1986.84±84.9	1560.8 ±209.2	1421.3 ±261.6	1073.84±30.2
Njiru	Range	267.03-3621.5	556.96-30561.35	167.47-1186.3	96.07-2496	486.24-19686.24	364.65-3614.6	155.91-3424.1	313.97-3913.9	161.56-1061.2
	Mean± SD	1858.2 ±287.2	14589.29 ±755.67	699.95 ±134.2	1325.92±91.9	8669.1 ±233.7	1709.05±54.8	1746.7 ±119.7	2004.7 ±115.9	626.86 ±62.23
Ruai	Range	478.30-3378.9	883.35-28183.78	126.66-1342.6	197.24-1917.96	733.52-17734.19	294.46-2594.4	141.-4141.	254.32-2514.0	88.89-2288.4
	Mean± SD	1762.5 ±382.2	12786.21 ±960.12	735.68 ±269.4	1046.6 ±31.11	9355.3 ±233.6	1359.17±8.54	2086.79±5.05	1365.6 ±207.7	1123.00±98.5

BDL= below detection limits, mean ± standard deviation, n=3

4.7.1 Polybrominated Diphenyl Ethers Residue in Nairobi River Basin Soil during the Cooler Dry Season

Polybrominated diphenyl Ethers residue levels detected in soil during the cooler dry season ranged between 812.61±87.23 to 30,561.35±145.57 ng/Kg, BDE 47 recorded the highest mean concentration at Njiru sampling site. Table 4.18 shows the mean concentration of PBDEs residue levels in soil samples collected during cooler dry season.

Table 4.18: Concentration of Polybrominated Diphenyl Ethers Residue Levels in Soil during Cooler Dry season (ng/kg, dry weight)

Site/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	1,522.64 ±44.36	6,171.2 ±82.51	865.21 ±28.20	1,036.47 ±86.03	5,229.55 ±78.37	1,641.91 ±87.39	1,221.01 ±89.99	1,834.15 ±36.92	1,295.38 ±32.26
Waithaka	1,312.06 ±69.10	7837.92 ±108.91	695.78 ±53.27	1,246.37 ±72.47	4,194.96 ±60.26	1,981.72 ±24.23	1,757.63 ±63.41	1,378.23 ±80.23	1,425.88 ±62.86
James Gichuru	1,945.99 ±19.31	8,291.76 ±304.59	974.22 ±29.26	1,364.82 ±21.57	5,785.16 ±68.05	1,502.09 ±36.55	1,267.59 ±40.71	1,526.85 ±45.84	1,967.34 ±19.45
Jamuhuri	2,241.71 ±32.28	10,413.1 ±281.54	825.68 ±21.39	1,581.26 ±58.10	4,542.26 ±73.21	1,488.31 ±17.82	1,949.86 ±46.48	2,399.78 ±72.92	812.61 ±87.23
Outering Road	916.22 ±70.82	18,457.2 ±23.11	968.41 ±20.13	1,212.19 ±83.75	11,513.89 ±134.98	3,647.45 ±25.70	2,716.44 ±23.08	2,366.83 ±39.99	1,451.27 ±34.24
Enterprise Road	1,034.66 ±20.40	15,338.5 ±38.60	1,096.3 ±53.51	1,618.68 ±27.49	1,2812.06 ±321.95	4,194.36 ±47.40	3,754.19 ±34.97	2,136.93 ±38.20	2,078.96 ±30.34
Bypass	2,563.31 ±20.90	19,763.1 ±82.45	1,274.7 ±17.78	1,522.31 ±69.45	12,877.41 ±98.102	4,292.13 ±122.61	3,213.33 ±81.98	2,519.76 ±77.94	2,072.92 ±40.67
Njiru	3,621.55 ±79.71	30,561.3 ±145.57	1,186.3 ±47.91	2,496.62 ±170.76	19,686.24 ±238.51	3,614.60 ±24.73	3,424.15 ±71.66	3,913.97 ±89.84	1,061.22 ±76.46
Ruai	3,378.96 ±108.78	28,183.7 ±96.12	1,342.6 ±48.33	1,917.96 ±75.62	17,734.19 ±70.19	2,594.46 ±64.37	4,141.96 ±215.89	2,514.07 ±82.29	2,288.46 ±77.58

BDL= below detection limits, mean ± standard deviation, n=3

4.7.1.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in Different Sampling Sites During the Cooler Dry Season

Brominated diphenyl ether 28 was present in every soil samples with the highest mean concentration detected in samples from Njiru (3,621.55±79.71 ng/Kg), while the lowest mean concentration was detected in soil from Outering road (916.22±70.82 ng/Kg). The highest concentration of brominated diphenyl ether 47 was recorded at Njiru sampling site (30,561.35±145.57 ng/Kg) while the lowest concentration was recorded at Ondiri (6,171.23±82.51 ng/Kg). Brominated diphenyl ether 66 was present in every soil samples with the lowest mean concentration level detected in samples from Jamhuri (825.68±21.39 ng/Kg) while the highest concentration was recorded at Ruai sampling site (1,342.69±48.33 ng/Kg). Brominated diphenyl ether 85 was present in every soil samples with the highest mean concentration detected in samples from Njiru (2,496.62±170.76 ng/Kg), while the lowest mean concentration was recorded in soil samples from Ondiri (1,036.47±86.03 ng/Kg). Highest mean concentration of Brominated diphenyl ether 99 was reported in soil samples from Njiru sampling site (19,686.24±238.51 ng/kg) while the lowest mean concentration was recorded in soil samples from Waithaka (4,194.96±60.26 ng/kg). Brominated diphenyl ether 100 was present in every soil samples with the lowest mean concentration detected in samples from Bypass sampling site (4,292.13±122.61 ng/kg), while the lowest mean concentration was recorded in soil samples from Jamhuri (1,488.31±17.82 ng/Kg). Brominated diphenyl ether 153, 154 and 185 were present in every soil samples with the highest mean concentration detected in samples from Ruai (4,141.96±215.89 ng/Kg), Njiru (3,913.97±89.84 ng/Kg) and Ruai (2,288.46±77.58 ng/Kg) respectively while the lowest mean concentration was recorded in soil samples from Ondiri (1,221.01±89.99 ng/Kg), Waithaka (1,378.23±80.23 ng/Kg) and Njiru (1,061.22±76.46 ng/Kg), respectively. The mean concentration of PBDEs in soil per site during the cooler dry season is attached in appendix 8I.

4.7.2 Polybrominated Diphenyl Ethers Residue Levels in Nairobi River Basin Soil during the Short Rain Season

The mean concentration of PBDEs in soil during the short rainfall season ranged from 81.43±4.30 to 2,241.17±41.35 ng/Kg. Table 4.19 shows the concentration of PBDEs in Nairobi River basin soil during the short rainfall season. 2,2′,4,4′-tetra-bromodiphenyl ether recorded the highest mean concentration at Ruai sampling site.

Table 4.19: Concentration of Polybrominated Diphenyl Ethers Residue Levels in Nairobi River Basin Soil during Short Rainfall Season (ng/Kg, dry weight)

Site /PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	472.13 ±15.90	1,003.76 ±60.62	154.55 ±3.85	244.33 ±5.53	922.58 ±28.65	374.99 ±6.29	167.92 ±7.67	255.69 ±3.17	174.98 ±8.18
Waithaka	287.16 ±16.93	1,109.73 ±25.49	115.63 ±11.51	376.98 ±25.49	834.18 ±62.75	205.62 ±19.60	255.26 ±29.46	438.98 ±8.62	256.24 ±30.29
James Gichuru	333.59 ±14.31	1,562.89 ±86.48	224.66 ±17.28	469.27 ±14.96	1,005.59 ±94.50	423.10 ±11.51	288.97 ±11.72	562.32 ±30.29	271.56 ±8.14
Jamhuri	729.48 ±68.62	1,596.80 ±72.18	334.12 ±25.04	341.99 ±10.85	966.45 ±19.08	367.32 ±7.82	263.84 ±12.66	241.37 ±9.06	126.55 ±26.05
Outering Road	344.26 ±37.05	587.93 ±12.35	631.89 ±56.09	472.48 ±9.19	697.57 ±26.75	374.11 ±12.66	156.79 ±10.95	295.44 ±32.18	183.32 ±5.51
Enterprise Road	562.71 ±25.27	985.21 ±34.19	486.44 ±43.05	191.34 ±13.21	426.98 ±33.06	322.69 ±8.40	254.85 ±12.47	255.13 ±17.76	99.98 ±6.97
Bypass	334.36 ±16.68	1238.26 ±19.29	223.49 ±8.44	76.13 ±8.27	797.51 ±42.91	418.67 ±27.74	81.43 ±4.30	496.11 ±11.19	316.15 ±9.13
Njiru	267.03 ±11.08	1,625.64 ±47.28	359.27 ±6.81	344.39 ±11.80	816.79 ±49.13	442.18 ±53.39	155.91 ±9.09	477.88 ±62.93	311.44 ±9.81
Ruai	354.31 ±39.60	2,241.17 ±41.35	546.18 ±15.47	197.24 ±9.72	1,063.13 ±79.96	306.55 ±26.98	148.28 ±8.12	548.16 ±38.24	228.21 ±16.29

BDL= below detection limits n=3, mean ± standard deviation

4.7.2.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling sites during the Short Rain Season

Brominate diphenyl ether 28 was present in every soil samples with the highest mean concentration detected in samples from Jamhuri (729.48±68.62 ng/Kg), while the lowest mean concentration was reported in samples from Njiru (267.03±11.08 ng/Kg). Brominated diphenyl ether 47 was present in every soil samples with the highest mean concentration detected in samples from Ruai sampling site (2,241.17±41.35 ng/Kg) while the lowest mean concentration was reported in soil samples from Outering road sampling site (587.93±12.35 ng/Kg). Brominated diphenyl ether 66 was detected in all the soil samples with the highest mean concentration recorded at Ruai sampling site (546.18±15.47 ng/Kg) while the lowest mean concentration was recorded at Waithaka sampling site (115.63±11.51 ng/Kg). The highest mean concentration of Brominated diphenyl ether 85 was recorded at Outering road (472.48±9.19 ng/Kg), while the lowest mean concentration was recorded at Bypass sampling sites (76.13±8.27 ng/Kg). Brominated diphenyl ether 99 was detected in all soil samples with the highest concentration recorded at Ruai sampling site (1,063.13±79.96 ng/Kg) and the lowest mean concentration was recorded at Enterprise road sampling site (426.98±33.06 ng/Kg). Brominated diphenyl ether 100 was present in every soil samples with the highest mean concentration detected in samples from Njiru (442.18±53.39 ng/Kg), while the lowest mean concentration was reported in soil from Waithaka (205.62±19.60 ng/kg). The highest mean concentration of Brominated diphenyl ether 153 was reported at James Gichuru (288.97±11.72 ng/Kg), while the lowest mean concentration was recorded at Bypass sampling sites (81.43±4.30 ng/Kg). The highest concentration of Brominated diphenyl ether 154 was recorded at James Gichuru (562.32±30.29 ng/Kg), while it the lowest mean concentration was recorded at Jamhuri sampling sites (241.37±9.06 ng/Kg). Brominated diphenyl ether 183 was present in every soil samples with the highest mean concentration detected in samples from Bypass sampling site (316.15±9.13 ng/Kg) and the lowest concentration was recorded at Enterprise road sampling site (99.98±6.97 ng/Kg). The mean concentration of PBDEs in soil per site during the short rain season is attached in appendix 8J.

4.7.3 Polybrominated Diphenyl Ethers Residue Levels in Soil during Hot Dry Season

The concentration of PBDEs in soil during the hot dry season ranged from 366.27±15.47 ng/Kg to 25,613.21±134.01 ng/Kg. Table 4.20 shows the concentration of PBDEs in soil during the hot dry season. Brominated diphenyl ether 47 congener recorded the highest concentration at Njiru sampling site.

Table 4.20: Concentration of Polybrominated Diphenyl Ethers Residue Levels in Soil Samples Collected during Hot Dry season (ng/Kg, dry weight)

Site/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	962.64 ±51.32	4,862.8 ±216.2	622.34 ±44.18	9,364.5 ±258.3	2854.37 ±104.32	943.36 ±67.15	366.27 ±15.47	954.44 ±38.96	965.67 ±55.21
Waithaka	1,132.5 ±29.87	6934.57 ±66.25	455.41 ±74.69	1,053.2 ±35.41	3,764.21 ±36.90	1,721.8 ±20.54	1,567.8 ±55.40	1,066.2 ±85.43	1,252.3 ±61.73
James Gichuru	1,543.8 ±67.43	6,841.53 ±68.58	624.71 ±45.39	1,116.2 ±15.50	2,285.54 ±75.83	982.70 ±81.89	1,008.1 ±15.81	1,601.2 ±95.59	1,067.3 ±44.85
Jamhuri	2,001.9 ±89.16	9,867.2 ±69.33	586.19 ±33.75	1,412.2 ±50.05	5,896.34 ±78.41	874.11 ±16.08	1,419.8 ±95.54	1,988.6 ±84.56	624.33 ±14.33
Outering	854.33 ±43.52	14,355.8 ±70.20	816.57 ±87.62	1,432.1 ±65.15	9,567.62 ±47.82	2,479.4 ±85.76	1,916.5 ±26.11	1,644.7 ±77.85	1,156.2 ±32.83
Enterprise Road	964.71 ±61.47	14,023.5 ±73.97	956.77 ±71.01	1,187.8 ±72.76	9,124.33 ±73.36	3,154.3 ±63.72	2,161.2 ±90.72	2,006.2 ±39.10	1,786.7 ±72.58
Bypass	2,373.5 ±89.95	18,788.5 ±74.38	979.24 ±24.10	1,463.3 ±62.64	8,277.59 ±16.64	2,936.7 ±36.09	2,917.3 ±190.25	2,149.7 ±149.4	1,632.9 ±96.79
Njiru	3,215.6 ±94.56	25,613.2 ±134.01	1,084.6 ±95.64	2,366.6 ±81.28	13,687.1 ±54.97	2,414.7 ±75.36	3,081.7 ±45.29	3,313.2 ±99.04	973.22 ±22.12
Ruai	2,838.4 ±83.34	19,836.5 ±91.99	927.19 ±70.01	1,873.9 ±52.31	17,889.2 ±14.51	2,241.2 ±57.92	3,915.9 ±94.45	2,145.8 ±87.41	1,886.4 ±54.46

BDL= below detection limits, mean ± standard deviation, n=3

4.7.3.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling Sites during the Hot Dry Season

Brominated diphenyl ether 28 recorded mean concentration values ranging from 854.33±43.52 ng/Kg to 3,215.64±94.56 ng/kg the highest mean concentration was recorded at Njiru sampling site while Outering road sampling sites recorded the lowest concentration. Brominated diphenyl ether 47 was present in every soil samples with the highest mean level detected in samples from Njiru (25,613.21±134.01 ng/kg), while the lowest mean concentration was detected in soil from Ondiri (4,862.85±216.02 ng/kg). The highest concentration of brominated diphenyl ether 66 congener was recorded at Njiru sampling site (1,084.66±95.64 ng/kg) while the lowest concentration was recorded at Waithaka (455.41±74.69 ng/Kg). The highest concentration of brominated diphenyl ether 85 was recorded at Njiru sampling site (2,366.61±81.28 ng/kg) while the lowest concentration was recorded at Ondiri (364.51±8.36 ng/kg). BDE 99 was present in every soil samples with the highest mean concentration detected in samples from Ruai (17,889.26±14.51 ng/kg), while the lowest concentration was recorded in samples from James Gichuru (2,285.54±75.83 ng/kg). Brominated diphenyl ether 100 was present in every soil samples with the highest mean concentration detected in samples from Jamhuri (874.11±16.08 ng/kg) and the lowest mean concentration reported in soil from Enterprises road sampling site (3,154.38±63.72 ng/kg). Brominated diphenyl ether 153 was present in every soil samples with the highest mean concentration detected in samples from Ruai (3,915.96±94.45 ng/kg), while the lowest mean concentration was reported in samples from Ondiri (366.27±15.47 ng/kg). Brominated diphenyl ether 154 was present in every soil samples with the highest mean concentration detected in samples from Njiru (3,313.27±99.04 ng/kg), while the lowest mean concentration was detected in samples from Ondiri (954.44±38.96 ng/kg). Brominated diphenyl ether 183 recorded the highest concentration in soil samples from Ruai (1,886.46±54.46 ng/kg) while the lowest mean concentration was recorded in soil from Ondiri (624.33±14.33 ng/kg). The mean concentration of PBDEs in soil per site during the hot dry season is attached in appendix 8K.

4.7.4 Polybrominated Diphenyl Ethers Residue Levels in Nairobi River Basin Soil during the Heavy Rain Season

The concentration of PBDEs in Nairobi River basin soil during the heavy rain season ranged from 21.01±2.45 ng/Kg to 1,091.76±61.59 ng/Kg. Table 4.21 shows the concentration of PBDEs during heavy rain season. Brominated diphenyl ether 47 congener recorded the highest concentration at James Gichuru sampling site.

Table 4.21: Concentration of Polybrominated Diphenyl Ethers Residue Levels in Soil Samples Collected during Heavy Rain Season (ng/Kg, dry weight)

Site/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	368.17 ±16.25	963.52 ±55.35	81.94 ±16.45	32.51 ±1.55	528.23 ±31.66	137.82 ±6.96	21.01 ±2.45	134.39 ±7.12	91.23 ±4.83
Waithaka	529.44 ±67.86	929.25 ±41.22	51.07 ±4.31	242.55 ±14.82	794.96 ±25.47	191.26 ±5.20	57.31 ±3.70	178.52 ±18.29	145.73 ±6.64
James Gichuru	473.63 ±14.48	1091.76 ±61.59	91.53 ±7.12	369.85 ±6.78	785.16 ±48.32	524.37 ±35.22	167.44 ±15.74	226.66 ±6.41	167.49 ±7.88
Jamhuri	719.21 ±22.91	1,031.76 ±37.06	155.01 ±16.64	181.23 ±8.09	542.26 ±34.48	258.94 ±18.27	140.19 ±15.32	99.79 ±7.91	82.75 ±9.72
Outering Road	122.84 ±4.87	527.13 ±36.08	361.57 ±5.11	210.16 ±7.68	516.24 ±17.65	367.22 ±19.38	16.46 ±1.99	36.57 ±3.75	91.08 ±5.35
Enterprise Road	346.79 ±12.71	586.35 ±42.14	394.21 ±19.53	613.62 ±18.71	512.46 ±22.95	193.76 ±12.18	74.24 ±4.59	233.22 ±7.28	27.51 ±1.96
Bypass	273.16 ±10.31	932.55 ±48.12	174.33 ±9.17	22.51 ±1.15	877.46 ±38.76	298.57 ±19.27	31.35 ±4.30	519.76 ±69.21	273.35 ±11.25
Njiru	328.91 ±23.98	556.96 ±48.50	169.47 ±14.52	96.07 ±9.87	486.24 ±43.80	364.65 ±15.99	325.22 ±13.93	313.97 ±6.72	161.56 ±10.63
Ruai	478.66 ±8.94	883.35 ±38.74	126.51 ±7.42	197.24 ±11.21	733.52 ±43.16	294.46 ±10.41	141.06 ±7.296	254.32 ±18.53	88.89 ±4.32

BDL= below detection limits n=3, mean ± standard deviation

4.7.4.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in Different Sampling Sites during the Heavy Rain Season

Brominated diphenyl ether 28 was detection in all the soil samples with the lowest concentration recorded at Njiru (328.91±23.98 ng/Kg) and the highest mean concentration was detected in samples from Jamhuri (719.21±22.91 ng/kg). The highest mean concentration of brominated diphenyl ether 47 was reported in samples collected from James Gichuru sampling site (1,091.76±61.59 ng/kg) while the lowest mean concentration was recorded in soil samples from Outering (527.13±36.08 ng/Kg). Brominated diphenyl ether 66 was present in every soil samples with the lowest mean concentration detected in samples at Waithaka (51.07±4.31 ng/Kg) and the highest concentration was recorded in soil samples from Enterprise road sampling site (394.21±19.53 ng/kg). The highest mean concentration of brominated diphenyl ether 85 was recorded at Enterprise road sampling site (613.62±18.71 ng/kg) while the lowest mean concentration was recorded at Ondiri (32.51±1.55 ng/kg). Brominated diphenyl ether 99 was detected in all the soil samples with the highest concentration detected in soil samples from Bypass (877.46±38.76 ng/kg), while the lowest mean concentration was recorded in soil samples from Njiru (486.24±43.80 ng/kg). Brominated diphenyl ether 100 was present in every soil samples with the lowest mean concentration detected in samples from Ondiri (137.82±6.96 ng/kg) and the highest mean concentration reported in soil samples from James Gichuru sampling site (524.37±35.22 ng/kg). Brominated diphenyl ether 153 was present in every soil samples with the highest mean concentration detected in samples from Njiru (325.22±13.93 ng/kg), while the lowest mean concentration was detected in samples from Ondiri (21.01±2.45 ng/kg). Brominated diphenyl ether 154 was detected in all the soil samples with the highest mean concentration detected in soil samples from Bypass (519.76±69.21 ng/kg), while the lowest concentration was recorded in soil samples from Outering (36.57±3.75 ng/kg). Brominated diphenyl ether 183 recorded the highest mean concentration in soil samples from Bypass (273.35±11.25 ng/kg) while the lowest mean concentration was recorded in soil samples from Jamhuri (82.75±9.72 ng/kg). The mean concentration of PBDEs in soil per site during the heavy rain season is attached in appendix 8L.

4.7.5 Spatial and Seasonal Variation of Polybrominated Diphenyl Ethers Levels in Nairobi River Basin Soil

The mean concentrations of PBDEs in soil at the nine sampling sites at Nairobi river basin were assessed to measure their variation designs. The data gotten for the nine sampling sites is shown in Table 4.22. The result showed that the PBDE congeners were portable and can be moved over a long distance over period. Additionally, the nine PBDEs investigated were present in every sampling site at different amounts. Njiru sampling site recorded the highest concentration of PBDEs among the nine locations which was attributed to leaking of the PBDEs from open burning of wastes including plastics at Dandora dumpsite and discharge of industrial wastewater from light industries at Kariobangi.

Table 4.22: Mean Levels (ng/Kg, dry weight) of the Spatial Allocation of Polybrominated Diphenyl Ethers in Nairobi River Basin Soil Samples

Site/ PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Ondiri	831.39 ±73.51	3250.34 ±28.45	431.01 ±51.34	2669.4 ±84.98	2383.68 ±278.84	774.52 ±167.71	444.05 ±140.25	794.67 ±85.77	631.81 ±59.24
Waithaka	815.29 ±126.9	4202.87 ±127.61	329.82 ±45.65	729.79 ±95.05	2397.08 ±27.73	1025.12 ±10.54	909.51 ±134.20	765.50 ±184.17	770.05 ±78.14
James Gichuru	1074.26 ±99.02	4446.99 ±333.13	478.78 ±94.13	830.04 ±70.30	2465.36 ±155.86	858.05 ±71.55	683.03 ±85.93	979.28 ±52.63	868.61 ±73.58
Jamhuri	1423.09 ±7.26	5727.22 ±385.98	475.26 ±178.2	879.18 ±113.6	2986.83 ±299.94	747.18 ±76.62	943.43 ±87.43	1182.36 ±100.18	411.56 ±30.96
Outering	559.41 ±43.76	8482.04 ±42.99	694.61 ±107.3	831.75 ±185.4	5573.83 ±128.21	1717.07 ±4.87	1201.57 ±99.22	1085.89 ±183.04	720.49 ±65.22
Enterprise Road	727.22 ±49.46	7733.41 ±282.03	733.45 ±98.72	902.86 ±204.5	5718.96 ±60.44	1966.29 ±91.16	1561.12 ±127.73	1157.88 ±15.49	998.29 ±51.24
Bypass	1386.11 ±43.27	10180.62 ±216.16	662.95 ±34.76	771.06 ±37.93	5707.49 ±56.53	1986.84 ±84.92	1560.86 ±35.41	1421.34 ±16.72	1073.84 ±30.26
Njiru	1858.28 ±43.75	14589.29 ±755.67	699.95 ±71.93	1325.9 ±91.93	8669.12 ±233.73	1709.05 ±54.82	1746.76 ±119.72	2004.77 ±115.90	626.86 ±62.22
Ruai	1762.51 ±87.67	12786.21 ±960.12	735.68 ±293.8	1046.6 ±0.92	9355.03 ±109.65	1359.17 ±8.54	2086.79 ±5.04	1365.60 ±207.73	1123.00 ±98.51

BDL= below detection limits n=3, mean ± standard deviation

Figure 4.3 shows the seasonal variation in the concentration of PBDEs in soil samples from Nairobi River basin. The mean concentration (ng/kg) of the congeners for the cooler dry, short rain, hot dry, heavy rain seasons are as follows: BDE 28 (18537.10, 3685.03, 3640.45 and 3640.45); BDE 47 (145018.07, 11951.39, 121123.83 and 7502.63); BDE 66 (9229.54, 3076.23, 7053.08 and 1605.84); BDE 85 (13996.68, 2714.12, 12270.14 and 1965.77); BDE 99 (94375.72, 7530.78, 73346.43 and 5776.53); BDE 100 (24957.03, 3235.23, 17748.67 and 2631.01); BDE 153 (23446.16, 1773.17, 18354.88 and 974.24); BDE 154 (20590.57 , 3571.02, 16870.45 and 1997.10) and BDE 183 (14454.04, 1968.42, 11345.29 and 1129.57) respectively.

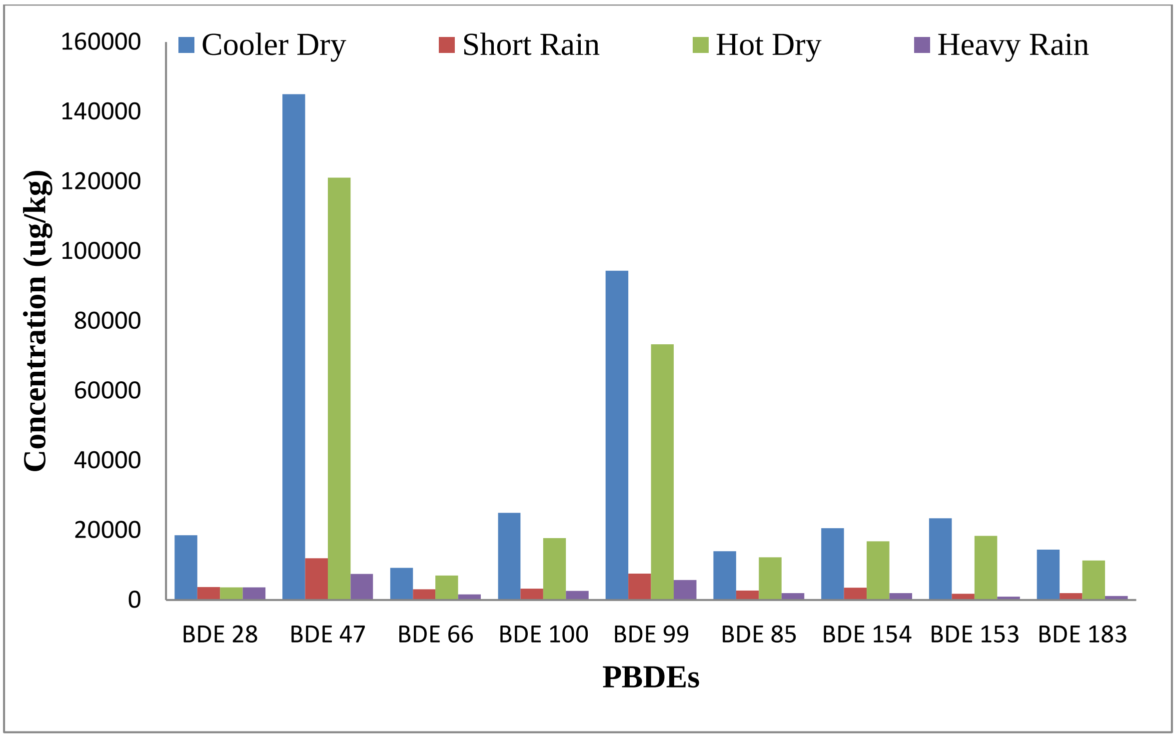


Figure 4. 3: Seasonal Variation of Polybrominated Diphenyl Ethers Residue Levels in Nairobi River Basin Soil

4.7.6 Comparison of Polybrominated Diphenyl Ethers Levels in Nairobi River Basin Soil Samples with other Studies around the World

The mean concentration of $\sum_9$PBDEs in soil ranged between 16.46±1.99 to 30,561.35±145.57 ng/Kg (Table 4.23). The PBDEs present at this site seemed to arise from the transportation of contaminants from other places, for example, through aerosol condensation and deposition (Ali *et al.*, 2015; Cetin *et al.*, 2007). PBDE concentration analysed in the current research were comparable to those detected by Sun and Co-workers in soils from Limuru, Juja, Mai mahiu and Mt. Suswa in Kenya whose concentration was between 190 to 35,640 ng/ kg (Sun *et al.*, 2016). However, the concentration of PBDEs in the current study were more than those in Pearl River delta soil in China (Zou *et al.*, 2007), the Indus River Basin, Pakistan (Ali *et al.*, 2015), European countries like United Kingdom and Norway (Hassanin *et al.*, 2004). The results of the PBDEs concentration in this study were lower than that in Izmir, Turkey (Cetin *et al.*, 2007).

Table 4. 23: Comparison of Polybrominated Diphenyl Ethers Levels in Nairobi River Soil Samples with other Studies around the World

Country	Location	ΣPBDEs (ng/g)	Reference
Kenya	Limuru, Suswa, Mahimahi and Juja	0.19 -35.64	Sun *et al.,* 2016
China	Pearl River Delta	0.13 - 3.81	Zou *et al.,* 2007
Pakistan	Indus River Basin	0.047 - 2.377	Ali *et al.,* 2015
UK and Norway	UK and Norway	0.065 – 12.00	Hassanin *et al.,* 2004
Turkey	Izmir	0.504 – 2,840	Cetin and Odabasi, 2007
Kenya	Nairobi River basin	0.016- 30.561	This study

4.8 Polybrominated Diphenyl Ethers Residues Levels in Air

Analysis of field, laboratory and solvent blank samples showed no peaks for the analytes of interest, hence excluding possibilities of cross contamination from the field, glassware and solvents used. The sampling sites covered Industrial area of Nairobi City to track contamination from industries, Dandora which is Nairobi's largest dumping site to track PBDEs that can leak from the wastes, Kabete is sub-urban and was chosen to track contamination from other parts and traffic of the city and mount Kenya was considered as the remote part of the country to track contamination due to long range transport of PBDEs.

The rate of sampling for passive PUF disk has been reported to be averagely 4 m^3/day (Pernilla *et al.,* 2020) hence deployment of the sampler for three months provided an equal air volume of about 360 m^3, which is adequate for the analysis of most persistent organic pollutants (UNEP, 2015).

Nine target PBDE congeners, BDE 28, 47 66, 85, 99, 100, 153, 154 and 183 were analysed in all 48 air samples collected from four sampling sites. The nine PBDEs analysed in air samples reported mean concentrations between BDL to 152.72±3.19 pg/m^3 with those of BDE 47 and 99 being 1.94±0.03 to 152.72±3.19 pg/m^3 and 1.32±0.06 to 66.83±1.19 pg/m^3, respectively (Table 4.24). In the environment of Nairobi and Mount Kenya the abundant PBDEs were BDEs

47 and 99 with 100% detection frequency. The high proportion of 2,2′,4,4′-tetra-bromodiphenyl ether and 2,2′,4,4′,5-penta- bromodiphenyl ether in air samples has been reported in a number of other research, for instance, in the Northern Lake Victoria region, Entebe, East Africa (Arinaitwe *et al.,* 2014), Guiyu (electric waste reprocessing location), Hong Kong and Guangzhou regions in South China (*Deng et al.,* 2007), iron and steel making plants in South Korea (Choi *et al.,* 2008) and ambient air of Azerbaijan (Aliyeva *et al.,* 2017).

The mean concentration of the PBDE congeners for the industrial (Dandora and Industrial area), residential (Kabete) and rural (Mount Kenya) locations ranged from 1.33±0.03 to 152.72±3.19 pg/m^3, BDL to 22.84±0.04 pg/m^3 and BDL to 4.56±0.39 pg/m^3, respectively.

Table 4.24: Range and Mean Concentration of Polybrominated Diphenyl Ethers Residues Levels in Air over the Entire Study Period (pg/m^3)

Site/ PBDE		BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Kabete	Range	3.24-24.67	3.88-15.48	≤1.3-2.60	≤0.9-2.07	7.28-22.84	≤1.3-4.86	1.65-2.26	≤1.4-3.56	≤1.2-3.45
	Mean ±SD	12.39 ±9.67	11.97 ± 5.46	1.30± 1.50	2.07± 0.86	11.65± 7.51	1.48± 2.31	1.99± 0.31	1.24± 1.68	1.94± 1.44
Dandora	Range	4.58-9.17	79.24-152.72	6.54-40.19	1.20-4.48	26.07-66.83	3.00-15.48	5.02-10.29	2.36-7.06	4.64-8.57
	Mean ±SD	5.85± 2.22	106.63 ± 33.5	15.54 ±16.4	3.58± 2.66	45.18± 16.72	10.12± 6.32	7.72± 2.25	4.40± 2.65	6.39± 1.94
Industrial Area	Range	3.11-7.85	26.98-69.34	3.39-39.96	1.33-3.24	14.38-51.93	3.29-24.71	3.78-12.94	1.67-7.94	4.91-9.56
	Mean ±SD	5.17± 2.19	40.65± 22.24	14.04 ±17.4	2.31± 0.87	23.9± 16.67	10.15± 9.82	6.93± 4.09	4.46± 2.88	6.92± 1.98
Mt. Kenya	Range	≤1.1-2.48	1.52-4.56	≤1.3-1.99	≤0.9-1.30	1.32-2.33	≤1.3-2.55	≤1.0-1.24	≤1.4-1.21	≤1.2-1.22
	Mean ±SD	1.29± 1.02	2.85± 1.38	0.99± 1.15	0.58± 0.68	1.78± 0.48	1.05± 1.27	0.91± 0.66	0.30± 0.61	0.87± 0.58
Detection Frequency	%	94	100	75	75	100	75	94	69	94

BDL= below detection limits, mean ± standard deviation, n=3

The result in this study was comparable to similar studies by Hu and co-workers in Beijing, China which recorded average concentration of 210 pg/m^3 using an active high-volume air sampler (Hu *et al.,* 2011) but the concentration was higher than the levels reported by Arinaitwe and Co-workers in Northern Lake Victoria region, East Africa which had a mean concentration of 9.84 pg/m^3 (Arinaitwe *et al.*, 2014). Table 4.24 shows range and mean concentration of polybrominated diphenyl ethers residues levels in air over the entire study period.

4.8.1 Polybrominated Diphenyl Ethers Residue Levels in Air during the Hot Dry Season

The sample collection period of deployment for hot dry season was 91 days, which began early January, 2018, and ended in early April, 2018. Table 4.25 presents the mean concentration of PBDEs in air samples collected from four sampling sites in the hot dry season. The mean concentration ranged between BDL to 152.72±11.49 pg/m^3. Brominated diphenyl ether 47 recorded the highest mean concentration from Dandora sampling site.

Table 4.25: Mean Concentration of Polybrominated Diphenyl Ethers PBDEs Residues in Air during Hot Dry Season (pg/m^3)

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Kabete	6.76±0.29	15.48±0.49	2.66±0.01	4.86 ±0.06	22.84 ±0.04	1.36±0.00	3.56±0.16	2.26±0.04	3.45±0.52
Dandora	2.04±0.08	152.72 ±11.49	40.19 ±3.62	15.41 ±1.94	66.83 ±1.19	1.48±0.64	6.29±0.43	10.29 ±0.55	8.57±0.24
Industrial Area	7.85±0.92	69.34 ±0.72	41.96 ±3.51	24.71 ±0.53	51.93 ±4.68	3.24±0.25	7.94±0.06	12.94±1.35	9.56±1.44
Mt. Kenya	2.48±0.05	4.56 ±0.39	1.99±0.00	2.55±0.01	2.33±0.11	1.34±0.01	1.21±0.07	1.87±0.05	1.22±0.013

BDL= below detection limits, mean ± standard deviation, n=3

4.8.1.1 Comparison of Polybrominated Diphenyl Ethers Residue Levels in different Sampling Sites during the Hot Dry Season

The highest concentration of brominated diphenyl ether 28 was detected in air samples from Industrial area site (7.85±0.92 pg/m^3), while the lowest concentration was recorded in air from Dandora (2.04±0.08 pg/m^3). 2,2′,4,4′-tetra-bromodiphenyl ether was also reported in air samples with the highest concentration recorded at Dandora sampling location (152.72±11.49 pg/m^3) and the lowest concentration was detected at Mount Kenya sampling site (4.56±0.39 pg/m^3). The highest concentration of brominated diphenyl ether 66 was recorded at Industrial area sampling site (41.96±3.51 pg/m^3) while the lowest concentration was recorded at Mount Kenya (1.99±0.00 pg/m^3). The highest concentration of brominated diphenyl ether 85 was recorded at Industrial area sampling site (24.71±0.53 pg/m^3) while the lowest concentration was recorded at Mt. Kenya (2.55±0.01 pg/m^3).

Brominated diphenyl ether 99 was present in every air sample with the highest concentration detected in samples from Dandora (66.83±1.19 pg/m^3), while the lowest concentration was reported in samples from Mount Kenya (2.33±0.11 pg/m^3). Brominated diphenyl ether 100 was reported in every air sample with the lowest concentration detected at Mount Kenya (1.34±0.01 pg/m^3) and the highest concentration recorded at Industrial area sampling site (3.24±0.25 pg/m^3).

Brominated diphenyl ether 153 was reported in every air samples with the highest mean concentration detected in air from industrial area (7.94±0.06 pg/m^3), while the lowest mean concentration was reported in samples from Mount Kenya (1.21±0.07 pg/m^3). Brominated diphenyl ether 154 was reported in every air samples with the highest mean concentration detected in air from Industrial area (12.94±1.35 pg/m^3), while the lowest concentration was recorded in air from Mount Kenya (1.87±0.05 pg/m^3). The highest mean concentration of brominated diphenyl ether 183 was reported in air samples from Industrial area (9.56±1.44 pg/m^3) while the lowest concentration was recorded in air from Mount Kenya (1.22±0.013 pg/m^3). The mean concentration of polybrominated diphenyl ethers in air per site during the hot dry season is attached in appendix 8M.

4.8.2 Polybrominated Diphenyl Ethers Residue Levels in Air during the Heavy Rain Season

Heavy rain season sampling time span averaged 92 days of deployment. This period's deployment started in the time of collection of hot dry season samples; hence, it began early April, 2018, and ended early July, 2018. The mean concentration of PBDEs in air samples in the heavy rain season was between BDL to 84.50±3.19 pg/m^3. Table 4.26 shows the mean concentration of polybrominated diphenyl ethers in air during the heavy rainfall season. BDE 47 congener recorded the highest mean concentration detected at Dandora sampling site.

Table 4.26: Mean Concentration of Polybrominated Diphenyl Ethers Residues in Air during Heavy Rain Season (pg/m^3)

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 154	BDE 153	BDE 183
Kabete	2.35±0.30	3.88±0.09	≤1.13	≤0.9	9.21±0.11	≤1.1	1.39±0.01	2.24±0.02	≤1.2
Dandora	5.04±0.46	84.50±3.19	6.57±0.05	1.39±0.21	42.88±3.34	3.00±0.13	2.36±0.26	5.02±0.07	7.46±0.87
Industrial Area	3.11±0.06	26.98±3.86	4.63±0.19	1.33±0.03	36.76±2.19	5.79±0.06	1.67±0.01	3.78±0.16	6.06±0.42
Mt. Kenya	1.23±0.16	1.94±0.03	≤1.13	≤0.9	1.45±0.07	≤1.1	≤1.2	1.51±0.05	≤1.2

BDL= below detection limits, mean ± standard deviation, n=3

4.8.2.1 Comparison of Polybrominated Diphenyl Ether Residue Levels in different Sampling Sites during the Heavy Rain Season

The highest mean concentration of BDE 28 in air samples was recorded in air samples from Dandora (5.04±0.46 pg/m^3) and the lowest concentration was detected at Mount Kenya sampling site (1.23±0.16 pg/m3). Brominated diphenyl ether 47 was recorded in all air samples with the highest mean concentration recorded at Dandora sampling site (84.50±3.19pg/m^3) and the lowest concentration was detected at Mount Kenya sampling site (1.94±0.03 pg/m^3). The highest concentration of brominated diphenyl ether 66 was recorded at Dandora sampling site (6.57±0.05 pg/m^3) while it was below detection limit (≤1.13 pg) at Mount Kenya. The highest concentration of BDE 85 was recorded at Dandora sampling site (1.39±0.21 pg/m^3) while it was below detection limit (≤0.9 pg) at Mount Kenya and Kabete sampling sites.

Brominated diphenyl ether 99 was reported in every air samples with the highest mean concentration detected in air from Dandora (42.88±3.34 pg/m^3), while the lowest mean concentration was reported in air from Mount Kenya (1.45±0.07 pg/m^3). Brominated diphenyl ether 100 was below detection limit at Kabete and Mount Kenya with highest mean concentration recorded at Industrial area sampling site (5.79±0.06 pg/m^3). Brominated diphenyl ether 153 was reported in every air samples with the highest mean concentration detected in air from Dandora sampling site (5.02±0.07 pg/m^3), while the lowest concentration was recorded in samples from Mount Kenya (1.51±0.05 pg/m^3).

Brominated diphenyl ether 154 was below detected limit (≤1.0 pg) at Mount Kenya while the highest concentration was recorded in air from Dandora (2.36±0.26 pg/m^3). Brominated diphenyl ether 183 was below detection limit (≤1.2 pg) at Kabete and Mount Kenya sampling sites while the highest concentration was recorded in air from Dandora (7.46±0.87 pg/m^3). The mean concentration of polybrominated diphenyl ether in air per site during the heavy rain season is attached in appendix 8N.

4.8.3 Polybrominated Diphenyl Ether Residue Levels in Air during the Cooler Dry Season

The sample collection period of deployment for cooler dry season was 93 days, started early July, 2018, and ended in early October, 2018. During the cooler dry season, the mean concentration of PBDEs in air was between BDL to 79.24±8.59 pg/m^3. Table 4.27 shows the concentration of Polybrominated Diphenyl Ether in air during cooler dry season. BDE 47 congener recorded the highest mean concentration detected at Dandora sampling site.

Table 4.27: Mean Concentration of Polybrominated Diphenyl Ether Residues in Air during Cooler Dry Season (pg/m^3)

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Kabete	2.27±0.12	13.57±0.67	≤1.13	≤0.9	7.29±2.89	≤1.1	1.65±0.01	≤1.2	2.18±0.01
Dandora	4.58±0.43	79.24±4.59	6.79±2.02	15.48±1.05	26.07±1.73	1.22±0.01	8.59±0.40	7.06±0.08	4.88±0.23
Industrial Area	6.04±0.10	19.71±0.64	3.39±0.43	3.29±0.15	14.38±0.43	1.87±0.12	5.69±0.33	5.67±0.88	4.91±0.58
Mt. Kenya	≤1.1	1.52±0.01	≤1.13	≤0.9	1.32±0.06	≤1.1	1.24±0.09	≤1.2	1.07±0.02

BDL= below detection limits, mean ± standard deviation, n=3

4.8.3.1 Comparison of PBDE Residue Levels in different Sampling Sites during the Cooler Dry Season

Dandora site recorded the highest mean concentration of BDE 28 while it was below detected limit at Mount Kenya sampling sites. Brominated diphenyl ether 47 was reported in all air samples with the highest mean level recorded at Dandora sampling site (79.24±4.59 pg/m^3) and the lowest concentration was detected at Mount Kenya sampling site (1.52±0.01 pg/m^3). The highest concentration of brominated diphenyl ether 66 was recorded at Dandora sampling site (6.79±2.02 pg/m^3) while it was below detection limit at Mount Kenya and Kabete sampling sites. The highest concentration of brominated diphenyl ether 85 was recorded at Dandora sampling site (15.48±1.05 pg/m^3) while it was below detection limit at Mount Kenya and Kabete sampling sites.

Brominated diphenyl ether 99 was reported in all air samples with the highest mean concentration detected in air from Dandora (26.07±1.73 pg/m^3), while lowest mean concentration was reported in air from Mount Kenya (1.32±0.06 pg/m^3). Brominated diphenyl ether 100 was below detected limit at Kabete and Mount Kenya with highest mean concentration recorded at Industrial area sampling site (1.87±0.02 pg/m^3). Brominated diphenyl ether 153 was recorded in every air samples with the highest mean level detected in air from Dandora sampling site (8.59±0.40 pg/m^3), while the lowest concentration was recorded in samples from Mount Kenya (1.24±0.09 pg/m^3). BDE 154 was below detection limit at Mount Kenya and Kabete sampling sites while the highest concentration was recorded in air from Dandora (7.06±0.08 pg/m^3). BDE 183 reported in all air samples with the highest mean concentration reported in air samples from Industrial area (4.91±0.58 pg/m^3) and the lowest mean concentration was recorded in air from Mount Kenya (1.07±0.02 pg/m^3). The mean concentration of PBDEs in air per site during the cooler dry season is attached in appendix 8O.

4.8.4 Polybrominated Diphenyl Ether Residue Levels in Air during the Short Rain Season

The sample collection period of deployment for short rain season was 92 days, that began early October, 2018, and ended in early January, 2019. The concentration of PBDEs in air during the short rain season ranged from BDL to 110.08±3.63 pg/m^3. Table 4.28 shows the concentration of Polybrominated Diphenyl Ether in air during the short rain season.

Table 4.28: Mean Concentration of Polybrominated Diphenyl Ether Residues in Air during Short Rain Season (pg/m^3)

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Kabete	2.75± 0.33	14.96± 0.41	≤1.13	2.07± 0.08	7.28± 0.53	1.07± 0.02	1.84± 0.03	≤1.2	2.14± 0.02
Dandora	4.64± 0.74	110.08 ±3.63	8.64± 0.14	3.58± 0.09	44.95± 4.95	6.57± 0.58	6.75± 0.45	1.89± 0.62	4.64± 0.20
Industrial Area	3.67± 0.51	46.57± 0.58	8.16± 0.15	2.80± 0.22	44.96± 0.14	6.80± 0.21	5.31± 0.18	2.57± 0.29	7.13± 0.61
Mt. Kenya	1.44± 0.04	3.36± 0.01	≤1.13	1.3±0.03	2.05± 0.08	1.65± 0.05	≤1.2	≤1.2	1.17± 0.12

4.8.4.1 Comparison of Polybrominated Diphenyl Ether Residue Levels in Different Sampling Sites During Short Rain Season

The lowest mean concentration of BDE 28 was recorded at Mount Kenya sampling site (1.44±0.04 pg/m^3) while the highest mean concentration was recorded in air samples from Dandora (4.64±0.74 pg/m^3). The highest mean level of brominated diphenyl ether 47 was recorded at Dandora sampling site (110.08±3.63 pg/m^3) and the lowest concentration was detected at Mount Kenya sampling site (3.36±0.01 pg/m^3). The highest concentration of brominated diphenyl ether 66 was recorded at Dandora sampling site (8.64±0.14 pg/m^3) while it was below detection limit (≤1.3 pg) at Mount Kenya and Kabete sampling sites. The highest concentration of brominated diphenyl ether 85 was recorded at Dandora sampling site (3.58±0.09 pg/m^3) while the lowest concentration was recorded at Mount Kenya (1.30±0.03 pg/m^3).

Brominated diphenyl ether 99 was present in every air samples with the highest mean level detected in samples from Industrial area (44.96±0.14 pg/m^3) while the lowest concentration was recorded in samples from Mount Kenya (2.05±0.08 pg/m^3). Brominated diphenyl ether 100 was present in every air samples with highest mean level recorded at Industrial area sampling site (6.80±0.21 pg/m^3) while the lowest concentration was recorded in samples from Kabete (1.07±0.02 pg/m^3). Brominated diphenyl ether 153 was below detected limit (≤1.4 pg) at Mount Kenya with the highest concentration detected in air from Dandora sampling site (6.75±0.45 pg/m^3).

Brominated diphenyl ether 154 was below detected limit (≤1.0) at Mount Kenya and Kabete while the highest concentration was recorded in air from industrial area (2.57±0.29 pg/m^3). Brominated diphenyl ether 183 was present in all air samples with highest concentration recorded at Industrial area sampling site (7.13±0.61 pg/m^3) while the lowest concentration was recorded in samples from Mount Kenya (1.17±0.12 pg/m^3). The mean concentration of polybrominated diphenyl ether in air per site during the short rain season is attached in appendix 8P.

4.8.5 Spatial and Seasonal Variation of Polybrominated Diphenyl Ether Levels in Air

Passive air sampling apparatus mostly made of polyurethane form (PUF) offer analysis within a specified time; hence, PUFs are not able to differentiate among instants of extreme highs or lows (Gevao *et al.*, 2010). They are suitable for obtaining a mean within a short period, like season. Statistical analysis of the data was done to test for seasonal variation in air concentrations within the research period. Air was sampled in four seasons covering the hot dry, heavy rain, cooler dry and shot rain season.

Dandora was the most polluted of the three municipal locations in this research, which was attributed to leaching from industrial and domestic waste which include electrical and electronic and other articles (carpets, firefighting foams, aviation hydraulic fluids, shoes, textiles, etc.) and due to ignorance and lack of appropriate technical infrastructures in Nairobi city’s largest dumping site. Open burning of electronic waste having PBDEs has shown to contribute to PBDEs pollution (Leung *et al.,* 2006). Secondly, it may be from the activities of nearby light industries like metal degreasing and construction material production that are situated in Kariobangi. Industrial area was also contaminated and the pollution can be attributed to leaching from end-of-life vehicles (cars, buses, minibuses, trucks) from the vehicle body parts recycling plants and other industrial activities in the area. Mount Kenya site had generally low levels of PBDEs which can be attributed to long range transport. Table 4. 29 shows mean levels of the spatial allocation of polybrominated diphenyl ether in air samples.

Table 4. 29: Mean Levels (pg/m^3) of the Spatial Allocation of Polybrominated Diphenyl Ether in Air Samples during the Four Seasons

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Kabete	3.53± 2.16	11.97± 5.45	1.30± 1.30	0.85± 0.89	9.91± 8.94	1.48± 1.99	2.00± 0.30	1.24± 1.46	1.94± 1.43
Dandora	5.86± 2.21	106.64 ±33.66	15.51± 14.25	2.66± 1.48	35.72± 26.38	10.12± 5.48	7.72± 2.25	4.40± 2.29	6.38± 1.94
Industria Area	5.17± 2.19	40.65± 22.23	14.04± 15.06	2.31± 0.75	28.76± 23.31	10.15± 8.50	6.93± 4.09	4.46± 2.50	6.92± 1.98
Mt. Kenya	1.29± 1.02	2.85± 1.39	1.00± 0.99	0.58± 0.59	1.80± 0.47	1.05± 1.09	0.91± 0.66	0.30± 0.52	0.87± 0.58

The sampling period covered the hot dry, heavy rain, cool dry and short rain periods witnessed in Nairobi and Mount Kenya. Hot dry season recorded the highest mean concentration of PBDEs in air. This is attributed to the high environmental temperature (27 °C) in the sampling time (January-March), causing increased degrees of volatilization of PBDEs. Elevated temperatures are likely to increase atmospheric concentration of persistent organic pollutants due to elevated volatilization from polluted surfaces (TerSchure *et al.,* 2004). Figure 4.4 shows the seasonal variation of the Polybrominated Diphenyl Ether in air across the sampling sites.

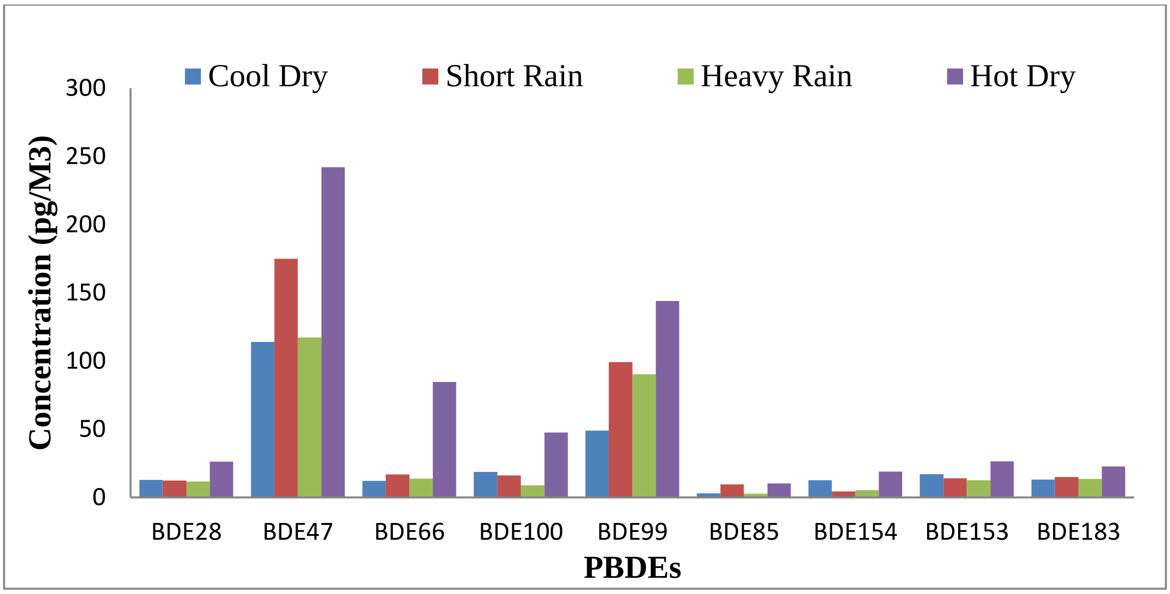


Figure 4. 4: Mean Concentration of Polybrominated Diphenyl Ether in Air across the Sampling Sites

Detection frequencies of PBDE congeners in air were high for most compounds with BDE 28 recording 94 %, BDE 47; 100 %, BDE 66; 75 %, BDE 99; 100 %, BDE 85; 75 %, BDE 100; 75 %, BDE 153; 94 %, BDE 154; 69 % and BDE 183; 94 %. High detection frequencies of BDE 28, 47, 66, 85, 99, 100, 153, 154 and 183 suggest a widespread distribution of the contaminants in the study areas. The high concentrations of penta-BDE formulation in the air can be attributed to inappropriate dumping of polyurethane foam products. The octa-PBDE formulation is mostly used in plastics which when burned release PBDEs into the environment.

The percentage composition of total PBDE congeners in air are as follows; BDE 28 4 %, BDE 47 43 %, BDE 66 8 %, BDE 85 2 %, BDE 99 25 %, BDE 100 6 %, BDE 153 4 %, BDE 154 2 % and BDE 183 4 %.

Among the commercial mixture based on the penta-PBDEs is 2,2′,4,4′,5 penta-bromo diphenyl ether is the main congener (approximately 44 – 58 %) followed by 2,2′,4,4′ tetra-bromo diphenyl ether being the major secondary constituent (approximately 24 – 42 %). High concentration of 2,2′,4,4′-tetra-bromodiphenyl ether and 2,2′,4,4′,5-penta- bromo diphenyl ether are indeed reported in air samples, their ratio is reversed (BDE 47: BDE 99 approximately

2:1) compared to the original mixtures (Wei *et al.,* 2016). This is because of the chemical stabilities and differences in vapour pressure of BDE 47 and 99 (Wei *et al.,* 2016). 2,2′,4,4′-tetra-bromodiphenyl ether is the most abundant congeners in human tissues (Leonetti *et al.,* 2016). The current research shows that PBDEs with few numbers of bromine atom like BDE 47 and 99 were the predominant congeners in air. This is in agreement with the penta-PBDE combination (Vonderheide *et al.,* 2008; La Guardia *et al.,* 2006;) likewise it's in agreement with results from other findings (La Guardia *et al.,* 2006).

It seems that seasonal differences in overall air concentrations of PBDEs in Nairobi and Mount Kenya regions were as a result of burning incident, identified point source of PBDEs (Vonderheide *et al.,* 2008), at the dumping site of Dandora. Results, like these, are in agreement with the results of other research relating burning procedures (Wyrzykowska-Ceradini *et al.,* 2011). Furthermore, the nearness to human inhabitant's centers has revealed to have a bigger consequence on the amount of PBDEs in the environment (Shen *et al.,* 2006). High amounts of PBDEs at industrial area sampling sites could be attributed to the nearness to the road (Choi *et al.,* 2009) and industrial activities (Farrar *et al.,* 2004; Martin *et al.,* 2004).

The spatial spreading pattern seen is strongly connected to the closeness to human inhabitants and anthropogenic events, that is similar to other patterns witnessed worldwide (Shen *et al.,* 2006). Polybrominated diphenyl ether are new and emerging pollutants of concern (Richardson, 2008). PBDEs was first detected in 1970s since then the amount of PBDEs in the environmental have gradually increased (Watanabe and Sakai, 2003) and, of great concern is the rising fear on the dangers to people' health as well as to flora and fauna and whole environment. The occurrence of PBDEs is progressively detected in larger amount in remote and virgin ecosystem, which shows that PBDEs have turn out to be a worldwide fear and is not just a problem to developed countries.

Polybrominated diphenyl ether behaves in different ways in the air subject to the number of bromine atoms. The highly brominated PBDEs have a habit to travel to other environmental partitions and, hence, congener like BDE 209 is not voluntarily found in the environment. BDE 209 was not determined in the current research though, imagined to be a major cause of environmental concentration than PBDEs with less bromine atom detected in the environment (Vonderheide *et al.,* 2008; La Guardia *et al.,* 2006). BDE 209 is currently in use in many developed countries and, although not produced in Kenya, BDE 209 containing products might be imported into the country.

Polybrominated diphenyl ether congeners with 4 to 6 bromine atoms like BDE 47, BDE 66, BDE 85 and BDE 99, mainly contribute to the penta- technical mixture. Because of the physiochemical properties, these congeners are highly vulnerable to long-range atmospheric transport (LRAT), biomagnifications and bioaccumulation, (Harley *et al.,* 2010). The high concentration of these PBDEs congeners and all the other PBDEs congeners studied in remote areas like Mount Kenya in the air suggests that long-range atmospheric transport (Goosey, 2006; Palm *et al.,* 2012), use of penta-BDE added products (Miglioranza *et al.,* 2013), and burning events (Farrar *et al.,* 2004; Wyrzykowska-Ceradini *et al.,* 2011) are likely taking place in this region.

4.9 Correlations

Statistical package for social scientist was used to compute the Pearson's correlation coefficients that has a mathematical number (r) varying from -1.000 to +1.000. These number signify the linear association among double statistics sets (Situma, 2010). Positive values show direct association in variables whereas negative values show opposite difference association. The strength of the linear association of the variables is measured by the arithmetical value of r, hence nil values shows no association among the data sets, ≤0.5 shows weak association, whereas those beyond ≥0.5 shows strong association. The meaning of the associations is shown by the p value. Associations are important if $p<0.005$ and are not important if $p>0.005$ (APA, 2001).

4.9.1 Correlation of Polybrominated Diphenyl Ether Residue Levels Across matrices

The association coefficient values (p) of PBDEs in water were moderately positive with those in sediment (0.644) and negligible negative with those in soil (-0.015), while the sediment was moderately positively correlated with the soil as illustrated in Table 4.30. A positive association is as a result of desorption to overlying water by sediments when they have been reorganized at high amounts or adsorption on sediments organic carbon as PBDEs are hydrophobic. Likewise, as PBDEs have high attraction to organic matter, they can be released from the soil to sediment by leaching and surface runoff at high concentration or evaporation due to high volatility.

Table 4.30: Correlation of levels of $\sum_9$PBDEs in Water, Sediment and Soil Samples

		Water	Soil	Sediment
Water	Pearson Correlation	1	-.015	.644
	Sig. (2-tailed)		.970	.061
	N	9	9	9
Soil	Pearson Correlation	-.015	1	.574
	Sig. (2-tailed)	.970		.106
	N	9	9	9
Sediment	Pearson Correlation	.644	.574	1
	Sig. (2-tailed)	.061	.106	
	N	9	9	9

4.9.2 Correlation of Polybrominated Diphenyl Ether Residue Levels Across the Sampling Seasons per Matrix

There was a direct relationship between the concentration of PBDEs in air across the sampling season as indicated by positive Pearson correlation value of 0.469, 0.876 and 0.728. Hot dry season was moderately positively correlated to short rain season while it was strongly positively correlated to heavy rain and cool dry season. Table 4.31 illustrates the correlation of polybrominated diphenyl ether across the sampling seasons in air.

Table 4.31: Correlation of Levels of $\sum_9$PBDEs in Air Across the Sampling Seasons

		Hot Dry	Short Rain	Heavy rain	Cool Dry
Hot Dry	Pearson Correlation	1	.469	.876	.728
	Sig. (2-tailed)		.531	.124	.272
	N	4	4	4	4
Short Rain	Pearson Correlation	.469	1	.837	.943
	Sig. (2-tailed)	.531		.163	.057
	N	4	4	4	4
Heavy rain	Pearson Correlation	.876	.837	1	.967*
	Sig. (2-tailed)	.124	.163		.033
	N	4	4	4	4
Cool Dry	Pearson Correlation	.728	.943	.967*	1
	Sig. (2-tailed)	.272	.057	.033	
	N	4	4	4	4
*. Correlation is significant at the 0.05 level (2-tailed).					

There was a direct relationship of the concentration of PBDEs in water across the sampling season as indicated by positive Pearson correlation value of 0.579, 0.742 and 0.839. Hot dry season was moderately positively correlated to short rain season while it was strongly positively correlated to heavy rain and cool dry season. Table 4.32 illustrates the correlation of PBDEs across the sampling seasons in water.

Table 4. 32: Correlation of Levels of $\sum_9$PBDEs in Water Across the Sampling Seasons

		Hot Dry	Short Rain	Heavy rain	Cool Dry
Hot Dry	Pearson Correlation	1	.579	.742	.839
	Sig. (2-tailed)		.463	.145	.291
	N	4	4	4	4
Short Rain	Pearson Correlation	.579	1	.812	.865
	Sig. (2-tailed)	.463		.171	.042
	N	4	4	4	4
Heavy rain	Pearson Correlation	.742	.761	1	.932*
	Sig. (2-tailed)	.145	.143		.031
	N	4	4	4	4
Cool Dry	Pearson Correlation	.839	.865	.932*	1
	Sig. (2-tailed)	.291	.042	.031	
	N	4	4	4	4
*. Correlation is significant at the 0.05 level (2-tailed).					

Polybrominated diphenyl ether in soil had weak positive correlation in cooler dry season with the short rain and hot dry season (0.238 and 0.189) respectively but they were weak negatively corelated during the heavy rain season (-0.279). During the heavy rain season the PBDEs deposited in the soil are washed away into the water bodies. Table 4.33 shows the correlation of levels of $\sum_9$PBDEs in soil across the sampling seasons.

Table 4.33: Correlation of Levels of $\sum_9$PBDEs in Soil Across the Sampling Seasons

		Cool Dry	Short Rain	Hot Dry	Heavy Rain
Cool Dry	Pearson Correlation	1	.238	.189	-.279
	Sig. (2-tailed)		.537	.626	.468
	N	9	9	9	9
Short Rain	Pearson Correlation	.238	1	.521	-.080
	Sig. (2-tailed)	.537		.151	.838
	N	9	9	9	9
Hot Dry	Pearson Correlation	.189	.521	1	-.269
	Sig. (2-tailed)	.626	.151		.483
	N	9	9	9	9
Heavy Rain	Pearson Correlation	-.279	-.080	-.269	1
	Sig. (2-tailed)	.468	.838	.483	
	N	9	9	9	9

There was a direct relationship of the concentration of PBDEs in sediment across the sampling season as indicated by positive Pearson correlation value 0.433, 0.823 and 0.569. Cool dry season was moderately positively correlated to short rain season while it was strongly positively correlated to heavy rain and hot dry season. Table 4.34 illustrates the correlation of polybrominated diphenyl ether across the sampling seasons in sediment.

Table 4.34: Correlation of Levels of ∑₉PBDEs in Sediment across the Sampling Seasons

		Cool Dry	Short Rain	Hot Dry	Heavy Rain
Cool Dry	Pearson Correlation	1	.433	.823**	.569
	Sig. (2-tailed)		.245	.006	.110
	N	9	9	9	9
Short Rain	Pearson Correlation	.433	1	.478	.625
	Sig. (2-tailed)	.245		.193	.072
	N	9	9	9	9
Hot Dry	Pearson Correlation	.823**	.478	1	.712*
	Sig. (2-tailed)	.006	.193		.031
	N	9	9	9	9
Heavy Rain	Pearson Correlation	.569	.625	.712*	1
	Sig. (2-tailed)	.110	.072	.031	
	N	9	9	9	9
**. Correlation is significant at the 0.01 level (2-tailed).					
*. Correlation is significant at the 0.05 level (2-tailed).					

4.9.3 Correlation of Polybrominated Diphenyl Ether with Selected Physical-chemical Properties per Matrix

During the cooler dry season there was a negative association among PBDEs in water with pH as shown by the negative Pearson's correlation values. There was a moderate positive association of TSS, TDS and electrical conductivity with r values of 0.555, 0.517 and 0.503 respectively. PBDEs have a tendency to attach to the water organic matter therefore the direct association of PBDEs with TSS.

During the short rain season there was a negative association among water PBDEs with those of pH as shown by the negative Pearson's association (r) values. A moderate positive association was revealed by TSS, TDS and electrical conductivity with Pearson's correlation values of 0.648, 0.379 and 0.367. During the hot dry season there was a negative correlation between PBDEs in water with those of pH as indicated by the negative Pearson's correlation values. A direct moderate relationship was shown by TSS, TDS and electrical conductivity with r value of 0.406, 0.454 and 0.444. During the heavy rain season there a direct relationship was shown by pH, TSS, TDS and electrical conductivity with r values of 0.276, 0.548, 0.96

and 0.119 This might be as a result of the hydrophobic actions of majority of PBDEs therefore not expected to be affected by pH and Electrical conductivity. Association of concentration of PBDEs in water with physico-chemical parameters is attached in appendix 7 A, B and C.

4.10 Physical-Chemical Parameters Values for Nairobi River Water

4.10.1 pH of River Water Samples

The measurement of pH is based on the fact that few molecules of water separate to produce hydroxyl and protons ions. The comparative quantity of the proton ions equated to hydroxyl ions controls the acidity or the basicity (USEPA, 1997). The pH of Nairobi river water samples varied between 6.50±0.33 to 8.46±0.14 as shown in Table 4.35.

Table 4.35: pH of Water Samples from Nairobi River

Site/Season	Cooler Dry	Short Rain	Hot Dry	Heavy Rain
Ondiri	7.32±0.52	7.74±0.09	7.60±0.75	7.34±0.26
Waithaka	8.46±0.14	8.41±0.66	8.14±0.45	8.22±0.96
James GIchuru	7.42±01.01	7.49±0.21	7.96±0.36	7.47±0.54
Jamhuri	8.26±0.12	8.47±0.99	7.7±0.5	7.99±0.87
Outering Road	6.50±0.33	6.72±0.18	6.61±0.96	6.98±0.32
Enterprise Road	6.56±0.52	6.92±0.09	6.69±0.75	6.88±0.26
Bypass	7.57±0.14	7.49±0.66	7.40±0.45	7.37±0.96
NJiiru	7.67±01.01	7.69±0.21	7.83±0.36	7.47±0.54
Ruai	6.96±0.12	6.71±0.99	6.67±0.5	6.99±0.87

The highest pH value was recorded at Waithaka in the cooler dry season whereas the lowest was reported at outering sampling site during the cooler dry season. The river is affected by high rate of release of effluents from the growing population in the town. The water pH values recorded were within the WHO suggested standard for natural water bodies which is 6.5 to 8.5 for drinking water in all the sampling points (WHO, 2004).

4.10.2 Total Suspended Solids in Nairobi River Water

Total Suspended Solids values ranged from a minimum of 84.5 ±3.5 mg/L at James Gichuru sampling point to a high of 342±11.31mg/L at Njiru sampling point. Total suspended solids include organic and mineral atoms that are elated in the water column and cannot pass through a filter of 2 uL. The average values are shown in Table 4.36.

Table 4. 36: Total Suspended Solids in Water Samples from River Nairobi (mg/L±sd)

Site/Season	Cooler Dry	Short Rain	Hot Dry	Heavy Rain
Ondiri	110±18.66	113±11.22	104±1.1	97±2.36
Waithaka	124±7.07	190±5.6	71± 9.8	266.67±2.3
James Gichuru	108±11.31	132.5±6.3	84.5 ±3.5	116±4.2
Jamhuri	98±7.07	42± 9.8	140.5±4.9	153.5±2.1
Outering	305±4.9	264±3.5	334±7.07	192±2.8
Enterprise Road	251±5.6	224± 3.5	214±8.5	232±9.8
Bypass	278±7.07	150±5.6	219± 9.8	117±2.3
Njiru	342±11.31	235±6.3	284±3.5	307±4.2
Ruai	240±7.07	122±9.8	148±4.9	253±2.1

4.10.3 Total Dissolved Solids and Electrical Conductivity in Nairobi River Water

Total dissolved solids values in water samples ranged between 152.8±6.6 mg/L to 596.5±2.6 mg/L while those of conductivity ranged from 312.7±6.8 µS/cm to1,206.1±48.5 µS/cm. Tables 4.37 and 4.38 shows the total dissolved solid and electrical conductivity, respectively.

Table 4.37: Total Dissolved Solids in Nairobi River Water samples (mg/L)

Site/Season	Cooler Dry	Short Rain	Hot Dry	Heavy Rain
Ondiri	310 .1±6.2	263.6±7.2	165±8.0	201.8±10.4
Waithaka	361.2±2.8	355.7±4.1	214.7±9.7	266.0±3.7
James Gichuru	169.1±11.2	223.7± 2.2	159.2±4.2	157.7±0.83
Jamhuri	162.3±2.1	152.8±6.6	161.3±6.5	163.0±1.3
Outering	462.8±2.4	414.4±1.1	339.5±4.7	474.6±2.9
Enterprise Road	529.4 ±3.1	596.5±2.6	465.5±6.7	568.8±2.9
Bypass	525.6±6.3	527.2±4.7	518.7±7.7	516.0±4.7
Njiru	569.4±1.4	543.7± 7.1	529.2±4.2	517.7±0.83
Ruai	562.3±2.1	552.8±6.6	561.3±6.5	563.0±1.3

Table 4.38: Electrical Conductivity in Nairobi River Water Samples

Site/Season	Cooler Dry (µS)	Short Rain (µS)	Hot Dry (µS)	Heavy Rain (µS)
Ondiri	622 .3±30.8	531.0±7.8	333.5±9.2	405.8±11.1
Waithaka	724.2±8.1	715.1±4.8	431.7±10.4	512±3.1
James Gichuru	336.8±1.7	457.1± 3.8	325±16.7	316.7±4.12
Jamhuri	345.7±7.2	312.7±6.8	325.1±7.6	328.4±4.8
Outering	915.4±8.7	832.7±11.9	684.25±18.2	933.6±2.2
Enterprise Road	1060.7 ±22.9	1206.1±48.5	966.2±11.8	1036.87±28.0
Bypass	1052.17±68.7	1047.2±86.8	1041.2±7.8	1033.5±55.0
Njiru	1150.1±16.8	1087.1± 26.3	1060.7±18.2	1034.1±86.3
Ruai	1025.1±33.6	1106.3±55.4	1112.3±84.9	1165.1±15.2

Total Dissolved Solids is a measure of the total amount of all inorganic and organic ingredients enclosed in a water in molecular, ionized or micro-granular (colloidal sol) suspended form. Normally, the solids need be sufficiently small to endure filtration through a filter the size of 2 µM. The electrical conductivity of water is directly associated to the number of dissolved solids in water. Ions from dissolved solids in water guide the capability of that water to conduct electrical current. The electrical conductivity value was twice the total dissolved solids value. The levels were above the recognized EPA drinking water quality guideline of 500 ppm and 900 µS/cm in some sites for total dissolved solids and electrical conductivity, correspondingly.

The main cause of total dissolved solids in water are farming and residential runoff, leakage of soil pollution and point source water contamination releases from manufacturing or sewage management activities. The main chemical components are phosphates ions, sodium ions, potassium ions, nitrates, chlorides ions and calcium ions which originate from nutrient overflow. Furthermore, the exotic and detrimental compounds of total dissolved solids are pesticides and polychlorinated biphenyls that originate from surface overflow (Water Research Commission, 2004).

4.11 Physical-Chemical Properties of Soil

Table 4.39 shows the physico-chemical properties of soil. Njiru soil samples recorded the highest pH value of 8.66, while Waithaka soil samples recorded the highest conductivity value of 3.87±0.09. The percentage total nitrogen in soils ranged between 0.10±0.0- 1.51±0.01%, the highest percentage total nitrogen (1.51%) was recorded at Outering road followed by Enterprise road sampling site (1.13±0.04%), then Bypass (0.96±0.00%). The % organic carbon ranged between 0.18±0.0- 1.94±0.00%, highest % organic carbon (1.94± 0.00 %) was recorded at Njiru followed by Waithaka (1.88±0.03%) and Outering road (1.78± 0.06%). The concentration of total organic carbon was low ranging between 0.18±0.0 to 1.94±0.00%, resulting the soil to have low capability to hold organic matter therefore high contamination in the course of substantial soil overflow. Phosphorous concentration ranged between 20.39 ± 1.5 and 55.0±3.97mg/kg. The highest concentration of phosphorous (55.0±3.97 mg/kg) was recorded at Enterprise road followed by Bypass (45.0±4.77 mg/kg), while Ondiri recorded the lowest concentration (20.39±1.55 mg/kg).

The metal levels in soil were relatively adequate, whereby copper ranged between 1.18±0.06 to 1.75±0.50 mg/kg, Potassium ranged between 86.2±0.63 to 154.3±0.09 mg/Kg, calcium levels ranged between 28.43±0.00 to 352.1±0.99 mg/Kg while magnesium concentration ranged between 27.8±0.0 to 343.4±1.06 ppm. The concentration of manganese in soil was between 22.8±0.00 to 52.96±0.54 mg/Kg, iron ranged between 256 ±17.7 to 635±44.85 mg/kg, Zinc ranged between 3.07± 0.00 to 3.91±0.00 mg/kg and Sodium concentration ranged between 50.93±0.0 to103.90±0.00 mg/Kg.

Table 4. 39: Physical-Chemical Properties of Soil

Parameters/ Sites	Ondiri	Waithaka	James Gichur	Jamhuri	Outering	Enterprise	By Pass	Njiru	Ruai
pH	7.85± 0.3	7.82± 0.00	8.51± 0.2	8.22± 0.09	8.45± 0.62	8.26± 0.00	8.34± 0.88	8.66± 0.03	8.41± 0.08
Total nitrogen%	0.14± 0.00	0.26± 0.04	0.10± 0.00	1.22± 0.06	1.51± 0.01	1.13± 0.04	0.96± 0.00	0.63± 0.01	0.62± 0.09
Total organic C%	1.62± 0.06	1.88± 0.03	1.63± 0.00	1.32± 0.01	1.78± 0.06	0.18± 0.00	1.34± 0.09	1.94± 0.00	1.06± 0.00
Phosphorus ppm	20.39± 1.55	33.20± 3.27	20.45± 1.96	33.62± 2.66	33.71± 1.54	55.0± 3.97	45.0± 4.77	45.02 ±2.22	45.1± 1.98
Potassium (ppm)	131.4± 0.01	128.3± 0.1	129.6± 0.00	142.5± 0.69	129.3± 0.33	90.3± 0.96	154.± 0.09	113.± 0.85	86.2± 0.63
Calcium (ppm)	308.2± 1.21	352.1± 0.99	28.43± 0.00	28.44± 0.08	309.6± 2.14	102.3± 0.65	300.2 ±0.2	250.5 3±0.9	252.6 ±1.1
Magnesium (ppm)	300.8± 0.32	343.4± 0.06	27.8± 0.08	28.8± 0.74	301.4± 0.00	100.± 0.85	292.± 0.05	244.± 0.06	241.± 0.00
Manganese (ppm)	52.96± 0.54	49.84± 0.42	52.94± 0.06	41.54± 0.08	32.21± 0.00	22.8± 0.00	28.6± 0.08	33.2± 0.06	32.2± 0.00
Copper (ppm)	1.75± 0.05	1.41±0 0.03	1.05± 0.00	1.31± 0.00	1.44± 0.09	1.96± 0.01	1.78± 0.04	1.67± 0.01	1.18± 0.06
Iron (ppm)	601± 25.6	485± 39.7	523± 48.1	500± 15.2	400± 12.44	352± 38.66	356± 17.76	635± 44.85	631± 39.16
Zinc (ppm)	3.63± 0.03	3.91± 0.00	3.29± 0.63	3.41± 0.01	3.51± 0.00	3.41± 0.06	3.47± 0.09	3.07± 0.00	3.44± 0.06
Sodium (ppm)	102.1± 0.00	57.07± 0.00	59.10± 0.01	103.9± 0.00	77.44± 0.06	50.9± 0.00	55.3± 0.06	65.2± 0.00	68.2± 0.09
Elect.Cond. µS/cm	3.25± 0.00	3.87± 0.09	3.19± 0.04	3.46± 0.08	3.00± 0.00	2.87± 0.07	3.11± 0.05	1.64± 0.04	1.61± 0.08

4.12 Physico-Chemical Parameter of Sediment

Table 4.4 shows the physico-chemical properties of sediment samples. Jamhuri sediment samples recorded the highest pH value of 6.61, while James Gichuru sediment samples recorded the highest conductivity value of 3.26± 0.05. The percentage total nitrogen in sediment ranged between 0.14±0.0 to 1.06±0.00 %, the highest % total nitrogen (1.06 %) was recorded at Ruai followed by 1.02±0.00 Njiru sampling site (1.02±0.00 %), then Waithaka (0.96±0.00 %). The % total organic carbon ranged between 0.28±0.0 to 0.96±0.01 %, highest % organic carbon (0.96±0.01 %) was recorded at Jamhuri followed by Ondiri (0.87±0.01 %) and Ruai (0.69± 0.01 %). The carbon levels ranged between 0.28±0.0 to 0.96±0.01 %. Phosphorous concentration ranged between 20.2 ± 0.6 to 57.9± 1.96 mg/kg. The highest concentration of phosphorous (57.9± 1.96 mg/kg) was recorded at Njiru followed by Ruai (52.1±2.1 mg/kg), while James Gichuru recorded the lowest concentration (28.2±3.5 mg/kg).

The metal levels in sediment samples were relatively adequate, whereby copper ranged between 9.06±0.09 to 10.75±0.05 mg/kg, Potassium ranged between 16.4±0.00 to 78.96±0.04 mg/Kg, calcium levels ranged between 124.21±0.0 to 219.99±0.68 mg/Kg, magnesium ranged between 43.18±0.0 to 68.41±0.05 mg/Kg. Manganese ranged between 21.09±0.0 to 4.01±0.05 mg/Kg, iron ranged between 306 ±14.5 to 409±36.9 mg/kg, Zinc ranged between 6.25± 0.00 to 8.23±0.54 mg/kg and Sodium between 18.45±0.0 1 to 49.23±0.03 mg/Kg.

Table 4. 40: Physico-Chemical Properties of Nairobi River Sediment

Parameters	Ondiri	Waithaka	James Gichuru	Jamhuri	Outering	Enterprise Rd	By Pass	Njiru	Ruai
pH	6.56± 0.1	5.89± 0.0	5.86± 0.2	6.61± 0.0	6.32± 0.1	5.96± 0.2	5.87± 0.6	6.21± 0.0	6.19± 0.01
Total nitrogen%	0.45±0.00	0.96± 0.00	0.14± 0.00	0.29± 0.00	0.81± 0.00	0.14± 0.00	0.57± 0.00	1.02± 0.0	1.06± 0.00
Total organic C%	0.87±0.01	0.51± 0.00	0.28± 0.00	0.96± 0.01	0.66± 0.00	0.45± 0.00	0.35± 0.00	0.69± 0.01	0.69±003
Phosphorus (ppm)	45.0±2.8	42.36± 6.1	28.2± 3.5	34.81± 4.1	44.5± 3.7	20.2± 0.6	28.32± 1.9	57.9± 1.96	52.1± 2.1
Potassium (ppm)	20.52± 0.00	28.72± 0.01	16.4± 0.00	20.51± 0.00	22.55± 0.03	66.66± 0.06	68.67± 0.01	57.4± 0.07	78.96± 0.04
Calcium (ppm)	201.48 ±1.02	171.57 ± 0.63	124.21± 0.00	171.58 ± 0.01	171.56 ± 0.9	192.62 ± 0.00	171.56 ± 0.1	202.14±1.6	219.99 ±0.68
Magnesium (ppm)	59.6 ±0.04	43.18± 0.01	45.26± 0.00	54.73± 0.05	54.73± 0.09	54.71± 0.04	54.72± 0.00	68.41 ±0.00	60.00± 0.01
Manganese (ppm)	40.01± 0.05	31.56± 0.06	22.13± 0.01	30.51± 0.00	34.71± 0.00	28.43± 0.68	39.96± 0.07	27.35 ±0.33	21.09± 0.01
Copper ppm	9.77±0.84	9.71± 0.13	10.75±0.05	10.24± 0.99	9.96± 0.07	9.18± 0.22	9.06± 0.09	9.81± 0.25	9.22±0.56
Iron ppm	402±22.3	326± 31.8	356± 33.4	306± 14.5	393± 36.8	389± 24.1	409± 36.9	345± 29.6	356±13.4
Zinc ppm	7.7± 0.33	7.7± 0.06	8.23± 0.54	7.6± 0.01	7.4± 0.55	6.25± 0.63	7.84± 0.92	7.8± 0.87	7.91± 0.14
Sodium (ppm)	37.93± 0.00	25.64± 0.01	36.90± 0.00	49.23± 0.03	26.66± 0.02	18.45± 0.01	38.96± 0.00	38.9± 0.05	36.92± 0.0
Elect..Cond. µS/cm	2.36±0.32	1.23± 0.06	3.26± 0.05	2.65± 0.00	1.84± 0.09	2.65± 0.04	1.56± 0.01	1.86± 0.01	1.22± 0.00

4.13 Photodegradation of Polybrominated Diphenyl Ethers

4.13.1 Characterisation of Photocatalyst

4.13.1.1 Determination of Pure TiO_2 and N-TiO_2 Band Gaps

The band gap energy (Eg) of TiO_2 and N-TiO_2 was determined by plotting $\pi h\nu$ against $h\nu$ based on Tauc equation (equation 3.3). Band gap was calculated by extrapolation of the target to the linear part of $\pi h\nu$ against $h\nu$ curve where the intercept to $h\nu$ gives the band gap. The extrapolation, in the plots of $\pi h\nu$ versus photon energy $h\nu$, of the linear portion of the modified spectra to zero absorption determines the band gap energies of the photocatalysts. The values of band gap energies developed shows that effectively the doping of TiO_2 with nitrogen produced a decrease of band gap as expected. The determined band gap for N-TiO_2 and pure TiO_2 are 3.19 eV and 3.25 eV while the λ (nm) values are 383 and 390 respectively.

4.13.1.2 Scanning Electron Microscope Analysis of N-TiO_2 and Pure TiO_2

The results of Scanning Electron Microscope (SEM) shows that the photocatalyst contain irregular agglomerated nanoparticles. The pictures show that the dimension and morphology of the particles were not altered on addition of nitrogen into the pure TiO_2 by introducing the Ammonia Solution. The Morphology of the TiO_2 particles was not changed on N-doping owing to the similar atomic dimensions of N_2 and O_2 (Palaez *et al.*, 2012). Figure 4.5 and 4.6 show the SEM micrographs for pure titanium oxide and nitrogen dopped titanium oxide, correspondingly.

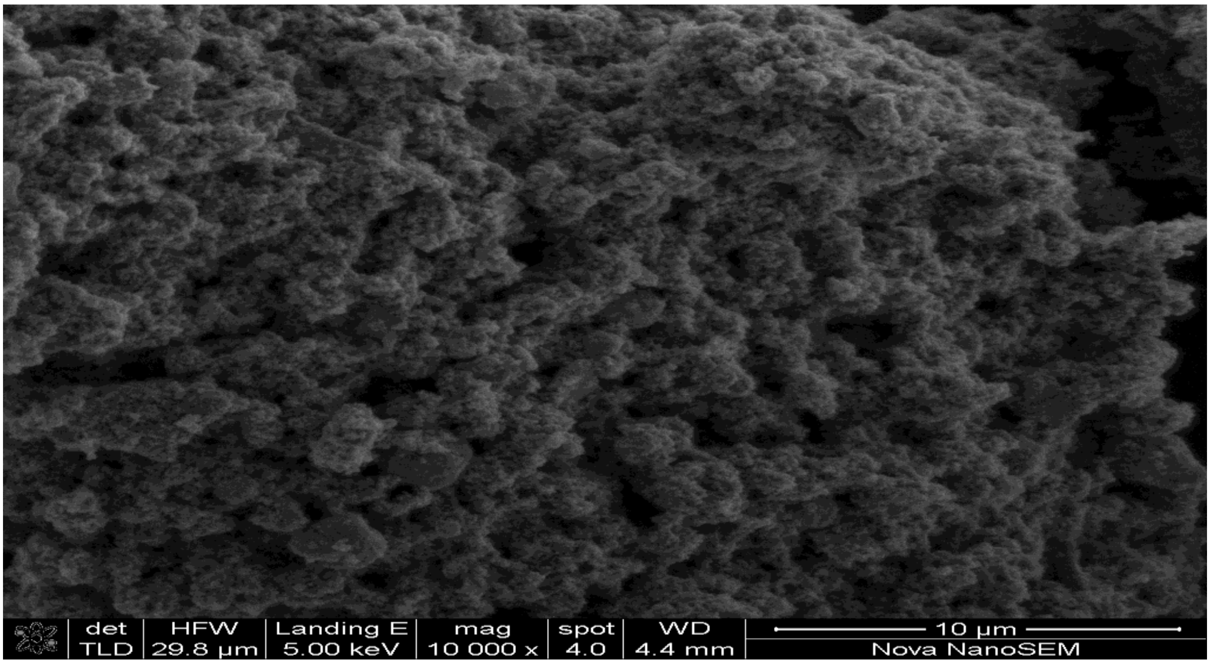


Figure 4. 5: Scanning Electron Microscope micrographs for TiO_2 Photocatlyst

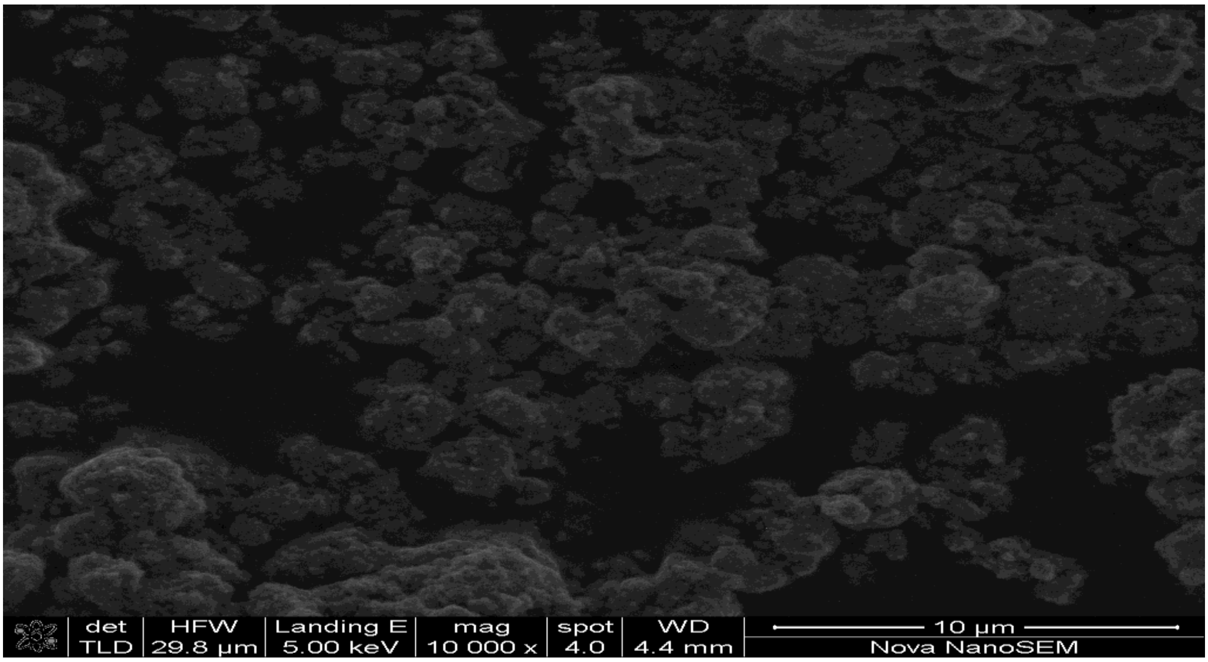


Figure 4. 6: Scanning Electron Microscope Micrographs for N-doped TiO_2 Photocatlyst

4.13.1.3 X-ray Diffraction Analysis

The phase configuration and the crystal size of pure TiO_2 and N-TiO_2 were assessed by X-ray diffraction (XRD) analysis. Figure 4.7, shows 2θ values of diffraction peaks detected in XRD spectra of pure TiO_2 at 25.5, 27.5, 36.12, 41.2, 44.1 48.1, 54.3, 54.4, 55.1, 62.8, 68.90 and 70.36. These peaks were allocated to reflections from (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes, which usually corresponds to anatase phase (Veluru *et al.,* 2011). Hence anatase is the main phase and this is advantageous as anatase is described to be more photo catalytically active than rutile (Ocwelwang and Tichagwa, 2014). Figure 4.8, 2θ values of diffraction peaks detected in XRD spectra of N-TiO_2 at peak 25.4° confirms the anatase structure of titanium oxide (Ba-Abbad *et al.*, 2012). Robust diffraction peaks at 25° and 48° demonstrating TiO_2 in the anatase phase (Thamaphat *et al.,* 2008). The 2θ peaks at 25.27° and 48.01° approves its anatase structure. The intensity of XRD peaks of the N-TiO_2 shows that the prepared photocatalyst is crystalline and broad diffraction peaks show small size crystallite. The nitrogen doping causes stabilization of anatase this is clear as the doped photocatalyst does not show any recrystallisation peak, and this is in agreement with XRD analyses. Figure 4. 7 presents XRD Pattern for pure TiO_2 and figure 4. 8 presents XRD Pattern for N-doped TiO_2.

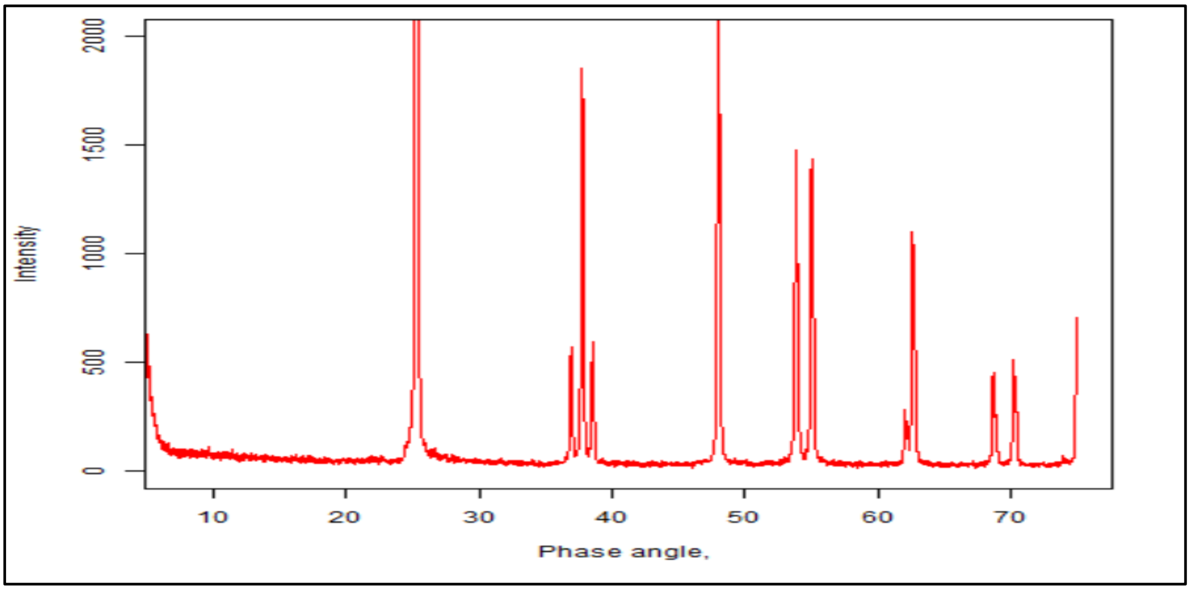


Figure 4. 7: X-ray Diffraction pattern of Pure TiO_2

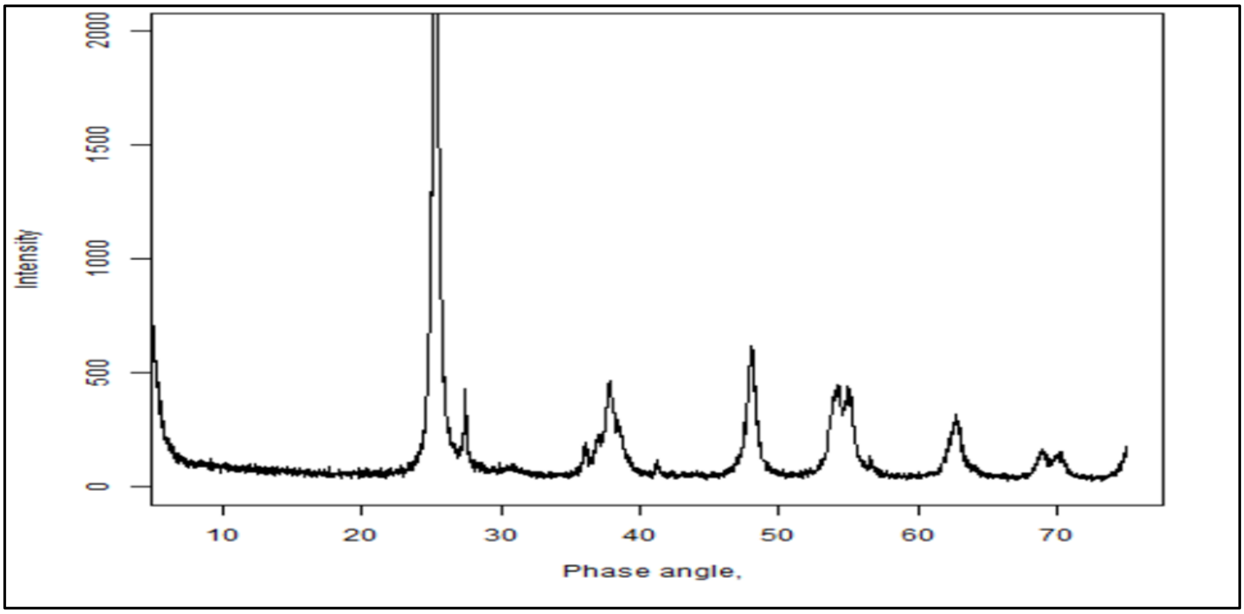


Figure 4. 8: X-ray Diffraction Pattern for N-doped TiO_2

Using the XRD data, the photocatalyst particle size can be determined by the Debye-Scherrer's method specified by the equation (Bokuniaeva and Vorokh, 2019):

$D = K\lambda / (B\cos\theta)$ --------------------------Equation 4.1

Where, B at 2θ is the Full Width at Half Maxima (FWHM) of the base peak (I/II=100) in radians calculated as 0.007652.

K is the Scherer constant = 0.89

λ is the wavelength of the Cu-ka Xx-rays used = 0.15406 nm

D is the crystal size (diameter) in nm

θ is the angle in degrees, 12.750 (2θ=25.500) for the base peak from Figure 4.24, cosθ = 0.9753 Substituting these figures into the Debye-Scherrer equation yielded a crystal size of 18.372 nm. Using the XRD data, synthesized pure TiO_2 particle size was determined by the Debye-Scherrer's method given by the equation given by equation 4.1 above, and substituting all the parameter the Pure TiO_2 crystal size is 25.48 nm showing that doping of nitrogen inhibited the development of TiO_2 crystallites.

Using information in table 4.41, it shows that the crystal sizes of pure TiO_2 is greater than the N-dopped TiO_2, showing that doping of nitrogen successfully prevents the development of TiO_2 crystal. Once nitrogen ion is located in a substitutional place of TiO_2, the electron density of the doped TiO_2 a little decline, and when declining of the feed molar ratio of N:Ti, the electron density of nitrogen doped TiO_2 sample comparatively rises. Table 4.41 shows the characteristic parameters of the photocatalyst.

Table 4.41: Characteristic Parameters of The Photocatalyst

	Crystal Size (nm)	Band Gap (eV)	λ (nm)
Pure TiO_2	25.48	3.25	390
N-TiO_2	18.32	3.19	383

4.13.2 Methylene Blue Degradation

Methylene blue (MB) degradation was used in current research to assess the photocatalytic activity of the prepared photocatalyst. Degradation of methylene blue as the organic dye model molecule in aqueous medium is used for the test of a new photocatalytic activity according to international organization standards (ISO, 2010). Methylene blue absorbs little light between 320 and 520 nm and shows insignificant degradation without the catalyst.

The effects of degradation of methylene blue in dark settings exhibited a reduction in the amount of methylene blue in 60 minutes of the experiment, then afterward amounts of MB was unaffected after 120 minutes. The data shows that the adsorption equilibrium of MB in presence of catalyst was gotten within 60 minutes. Discoloration of dye in the presence of titania films is in agreement with described photocatalytic properties of TiO_2. Figure 4.9 shows the methylene blue degradation rates.

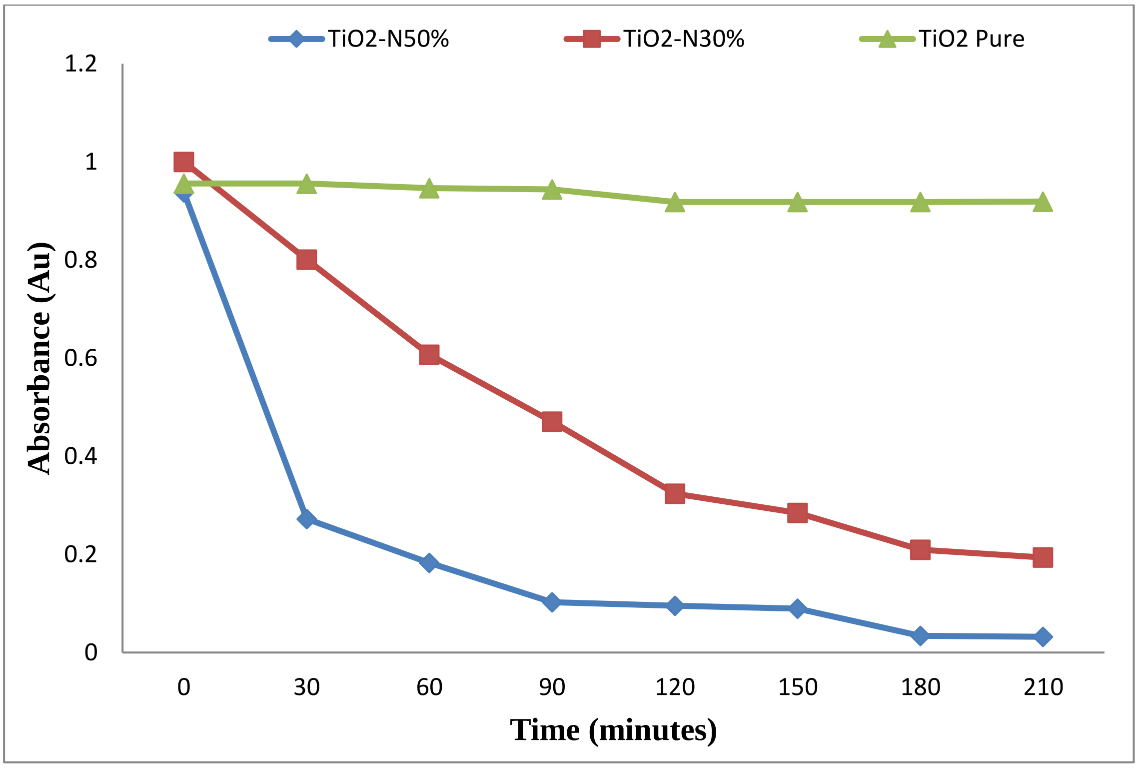


Figure 4. 9: Methylene Blue Degradation Rates

4.13.2.1 Effect of pH on Degradation of Methylene Blue

The efficiency of photocatalytic process is affected by the pH solution. The influence of pH on MB degradation was studied and the result shows that the rate of photo-degradation of methylene blue increased from 22.2 to 96.9 % as the acidity of the reaction combination decreases from 2 to 7, while, as the alkalinity of the solution increases from 7 to 11 the rate of photo-degradation decreased from 96.9 to 77.6 %. Figure 4.10 shows the result of pH on the degradation of methylene blue.

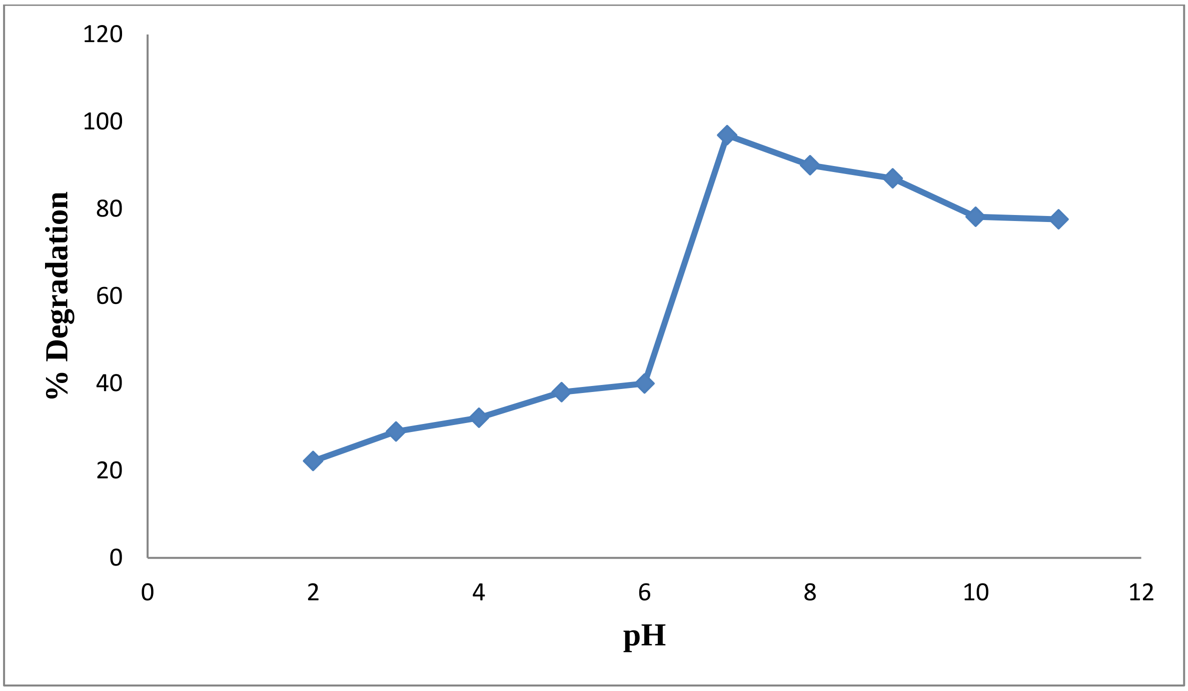


Figure 4. 10: Effect of pH on Methylene Blue Degradation Rate

pH 7 recorded the highest rate of methylene blue photo-degradation (96.9 %). Thus, pH 7 was chosen as the best pH situation for MB photo-degradation tests (Figure 4.10). At the alkaline pH range the rate of photo-degradation started to reduce. This is as a result of the development of CO_3^{2-} ions making good foragers of OH^- ions, hence decreasing the degradation speed (Mbugua *et al.*, 2014; Akbar and Onar, 2003). At acidic pH values, the hydroxyl ions are quickly foraged that they do not have the chance of combining with the MB ions (Madhu *et al.*, 2009; Mbugua *et al.*, 2014).

4.13.2.2 Effect of Loading N-TiO_2 Catalyst on Degradation of Methylene Blue

Figure 4.11 displays result of various loading of the photocatalyst on the methylene blue degradation process. Range between 0.05 to 1g and pH at 7.0 were used to investigate the optimum loading of the catalyst. The higher photodegradation efficiency was obtained with increasing amount of catalyst up to 0.6 g, and then the efficiency remained constant. As the amount of the catalyst increased the solution mixture become more turbid leading to low light penetration hence decreased surface area by agglomeration of the catalyst (Behnajady, 2008).

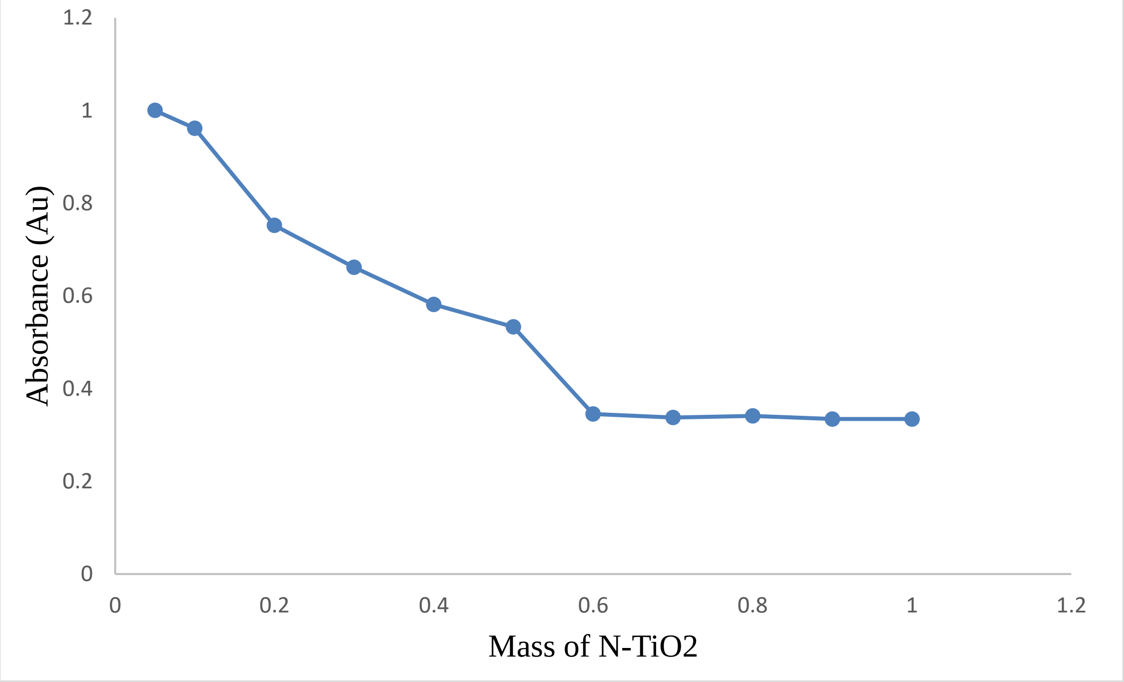


Figure 4. 11: Graph of Absorbance of Methylene Blue against Catalyst Loading

The optimal quantity of N-TiO_2 photocatalyst on degradation of methylene blue was 600 mg in 100 mL of the solution (Figure 4.11). The N-TiO_2 shows best adsorption ability since it has huge surface area that allows the distribution of the methylene blue particles easily into the photocatalyst molecules (Moellmann *et al.*, 2002). But, numerous sets of hole-electrons formed by radiation are rapidly consumed hence causing reduction in the photocatalytic degradation of methylene blue particles (Moellmann *et al.*, 2002).

4.13.3 Degradation of Methyl Red

4.13.3.1 Degradation of Methylene Red Using Varying Amounts of the Photocatalyst

The photodegradation of methylene red using different concentrations of the photocatalyst exhibited that cumulative the amount of the photocatalyst increased the rate of degradation of methylene red in the solution up to 0.70 g in 100 mL of the solution (Figure 4.12). The highest percentage photo-degradation achieved was 95.1% achieved at the loading of 0.70 g of the photocatalyst, beyond which photodegradation reduced greatly. The resultant reduction in photo-degradation of methyl red after 0.70 g loading of the photocatalyst might be attributed to accumulation of catalyst atoms that reduced the catalyst surface area available for photon absorption (Tang and Chen, 2004). In addition, increasing the amount of photocatalyst increased turbidity of the solution that inhibits light penetration into the photoreactor, hence reducing photocatalytic degradation (Saquib and Muneer, 2003). Figure 4.12 shows the percentage degradation of methyl red with varying N-TiO2 catalyst loading.

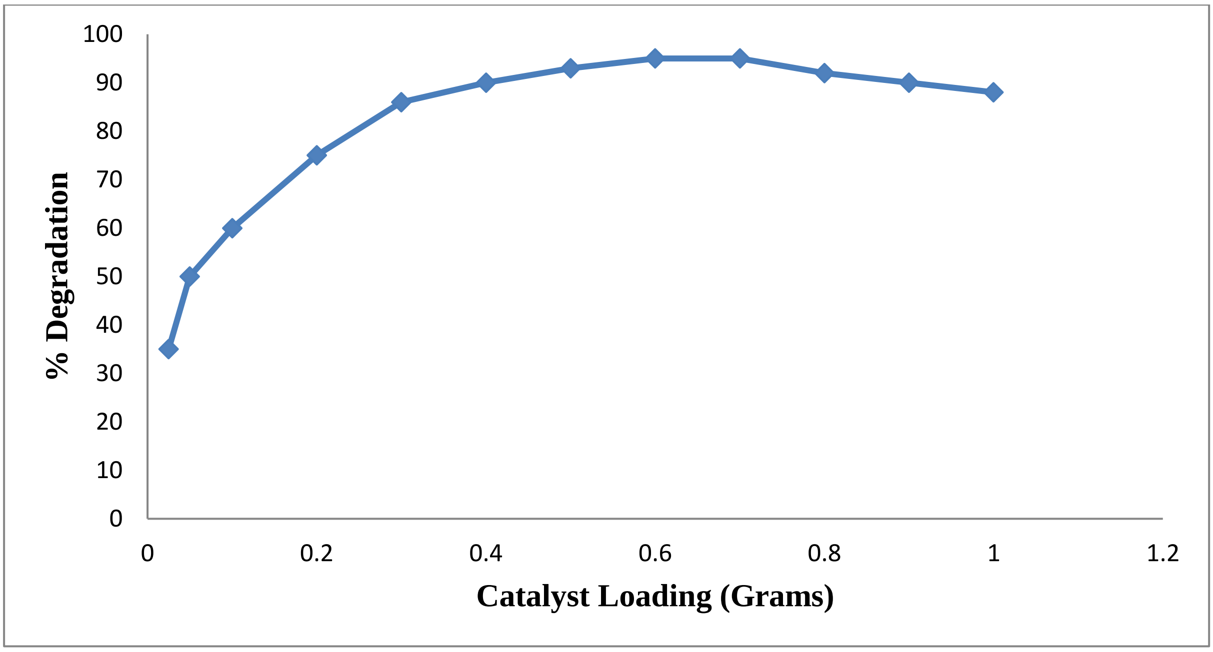


Figure 4. 12: Percentage Degradation of Methyl Red with Varying N-TiO$_2$ Catalyst Loading

4.13.3.2 Degradation of Methylene Red under Varying Irradiation time

It was established that the percentage photo-degradation increased with increasing irradiation time (Figure 4.29). Irradiation of up to 180 minutes resulted in 97 % reduction in the amount of the dye in the solution with photo-catalyst loading of 0.7 g/L. Figure 4.13 shows the percentage degradation methyl red with given time.

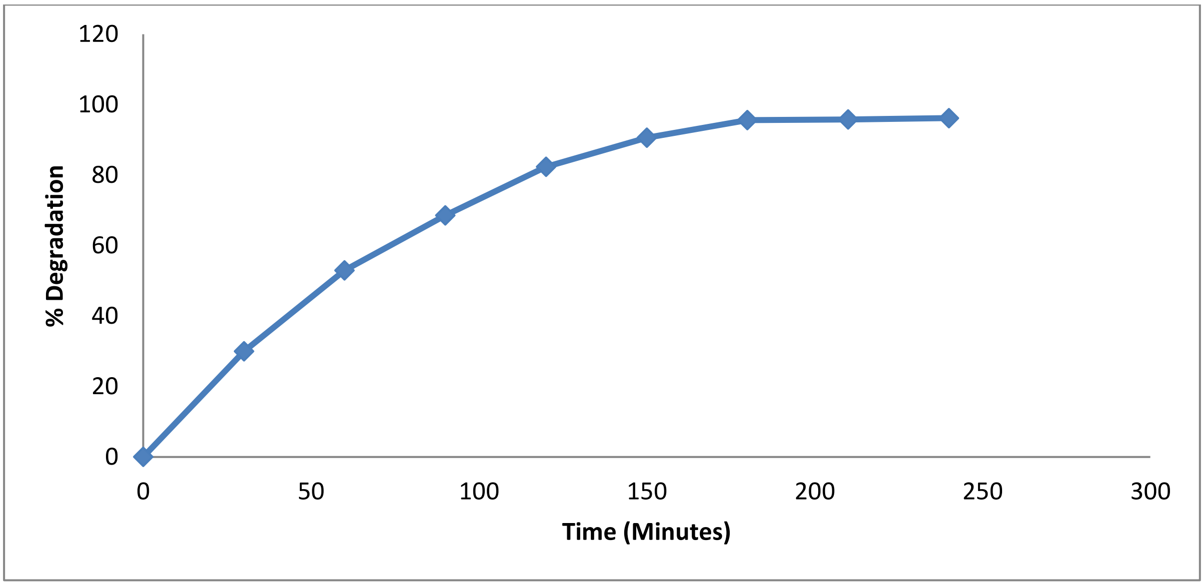


Figure 4. 13: Percentage Degradation Methyl Red with given Time

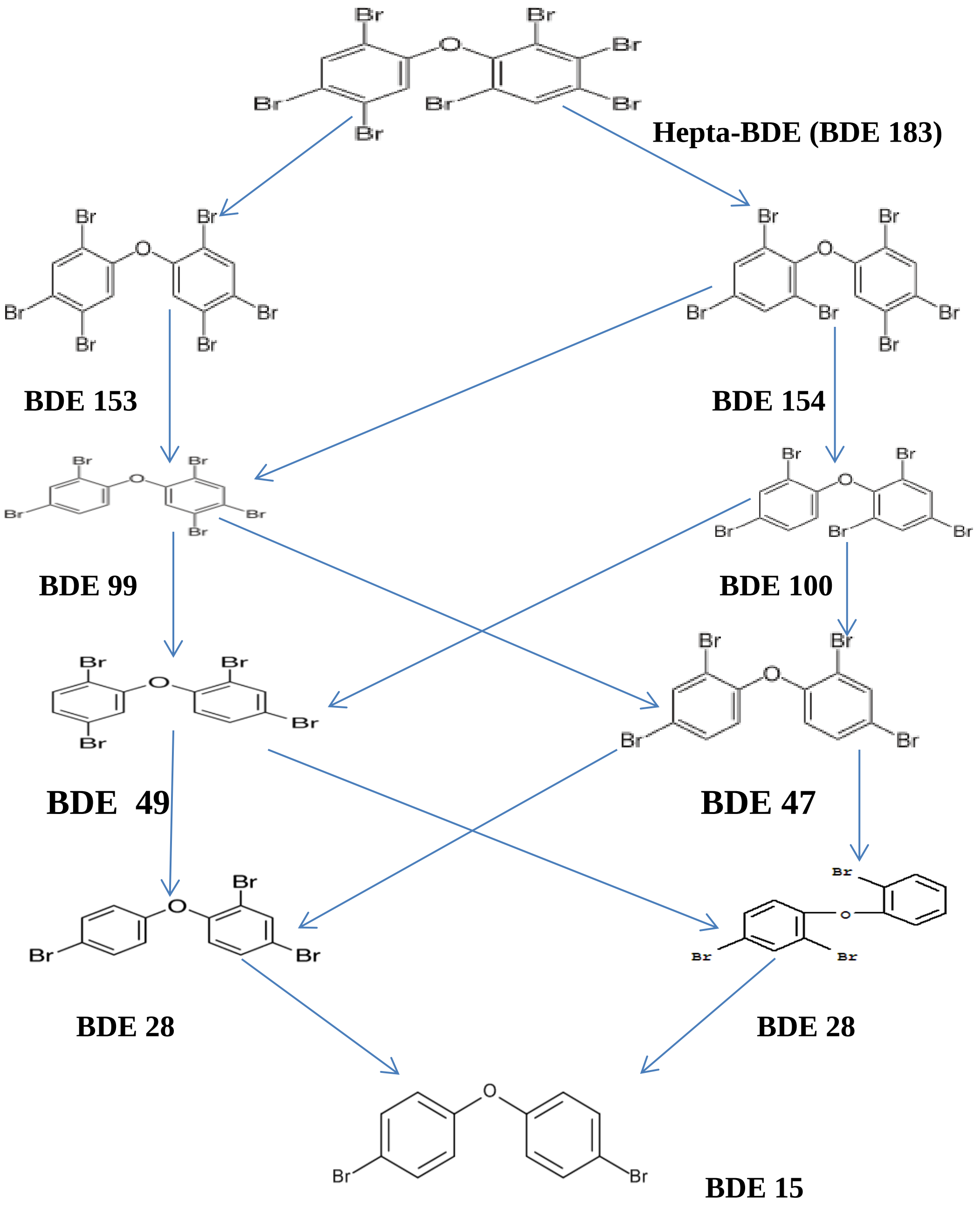
4.14 Photocatalytic Activity Performance of N-dopped TiO_2 Photocatalyst in Polybrominated Diphenyl Ethers Degradation

The dark experiments (absence of UV and without N-TiO_2) and the reaction system containing pure TiO_2 showed no disappearance of BDE 28, 85 and 183, indicating pure TiO_2 is ineffective to photocatalytic degrade BDE 28, 85 and 183. This result is different with the result of earlier research using deca-bromodiphenyl ether (Sun *et al.*, 2009). This is because brominated diphenyl ether 28, 85 and 183 have higher energy of lowest unoccupied molecular orbital than BDE 209, and therefore is less susceptible to electrons (Wei *et al.*, 2013; Zhuang *et al.*, 2010).

The degradation of brominated diphenyl ether 183, 85 and 28 was conducted in the presence of N- TiO_2 under UV irradiation and analysis was performed using gas chromatography- mass spectrometer. The retention times and mass spectra were related to reference standards available at the National Institute of Standards and Technology (NIST). Due to the lack of certain standards, other congeners were identified only within structural isomer groups if their mass spectra contained distinctive characteristics of these structural isomers. The studies were done using 0.6 g of N-TiO_2.

4.14.1 Degradation of 2,2′,3,4,4′,5′,6-hepta-bromodiphenyl Ether (BDE 183)

Degradation of 2,2′,3,4,4′,5′,6-hepta-bromodiphenyl ether using N-TiO_2 in the presence of UV light was achieved within 120 minutes of irradiation. The initial stage in the degradation of BDE-183 is removal of a single bromine atom, forming two hexa-BDEs, namely; BDE 153, and 154 this was achieved after 30 minutes of degradation (scheme 4.1). After 60 minutes of irradiation two penta-BDEs were seen which were identified as BDE 99 and 100. At irradiation time of 75 minutes three tetra-BDE peaks were seen and the PBDEs were identified as BDE 47, 49 and 66. As the reaction continued, tri-BDEs which were identified as BDE 17 and 28 at irradiation time of 90 minutes. At irradiation time of 105 minutes the di-BDE was seen which was identified as BDE 15. The chromatogram at 105 and 120 minutes irradiation time were the same. After 120 minutes of degradation a minor peak of BDE 183 was seen while peaks of hexa-BDE were dominant and all the other PBDEs identified were present. Scheme 4.1 summarizes the observed degradation pathway for BDE 183



Scheme 4. 1: Proposed Mechanistic Degradation Pathway of BDE 183 by N dopped-TiO$_2$ Nano-particles under UV Radiation

The average initial concentration of BDE 183 was 5.2±0.03 mg/L (0 minutes) and the final residue was 0.17±0.00 mg/L at 120 minutes (Table 4.42). Table 4.42 shows the removal efficiency of BDE 183.

Table 4. 42: Removal Efficiency of BDE 183

Time (minutes)	Concentration (mg/L)
0	5.2±0.03
15	5.01±0.25
30	2.86±0.01
45	2.01±0.00
60	1.09±0.06
75	0.56±0.00
90	0.21±0.00
105	0.19±0.00
120	0.17±0.00

The trend of dissipation (Figure 4.14) was gotten by drawing calculated concentration of BDE 183 against time in minutes using Table 4.42.

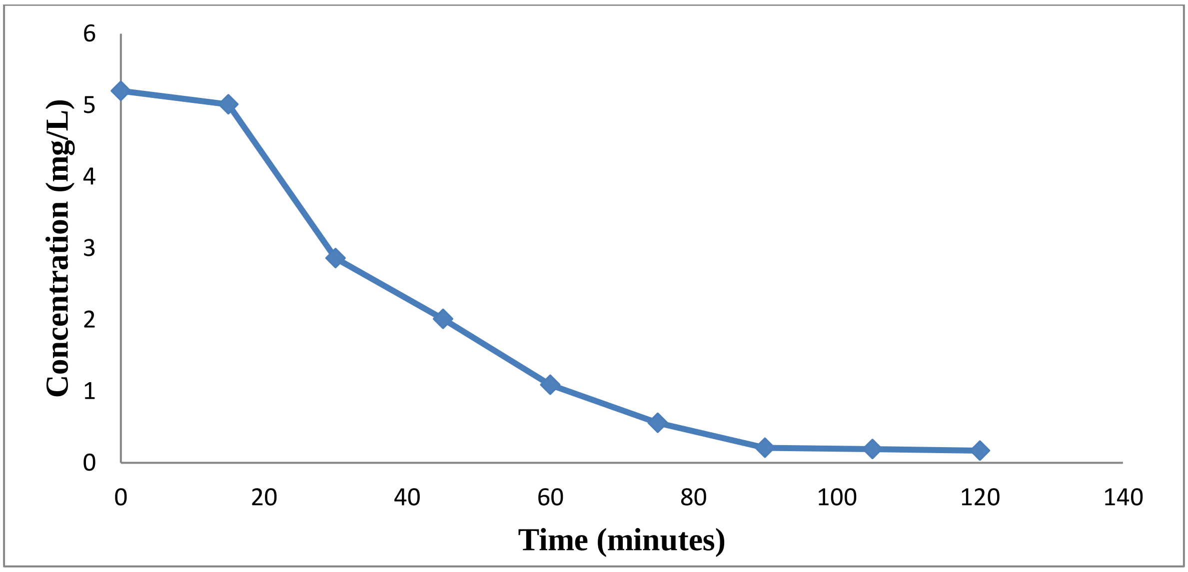


Figure 4. 14: Trends of BDE 183 Dissipation Rate

After 15 minutes of irradiation 3.6 % of BDE 183 had degraded, after 30 minutes 45.0 % of BDE 183 had degraded while by 120 minutes after the irradiation of BDE 183, 96.73 % had degraded. The results exhibited that there was fast degeneracy of BDE 183 for the first 75 minutes that the typical two-phase dissipation pattern display the primary rapidly dissipation rate shadowed by lower frequency commencing after 75 minutes.

The photocatalytic degradation of BDE 183 on the surface of catalyst could be fitted to the Langmuir Hinshelwood kinetic model. The photocatalytic degradation of BDE 183 over N-TiO_2 could be simplified to first-order kinetic equation -0.693/K =$t_{1/2}$.

A straight line is obtained when a plot of natural logarithm of concentration versus time is made. Upon linear regression, the gradient of the line matches the first order rate constant, K_{obs}. Using the first order kinetic equation, a graph of ln of PBDE residue concentration (mg/L) versus time t (minutes) was made. Figures 4.15 show the regression curve of BDE 183.

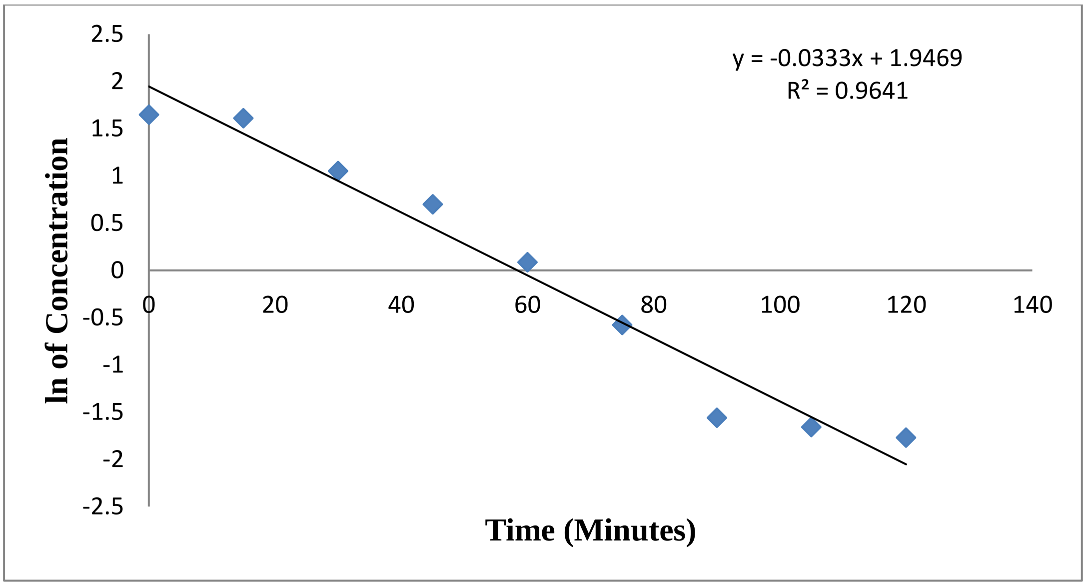
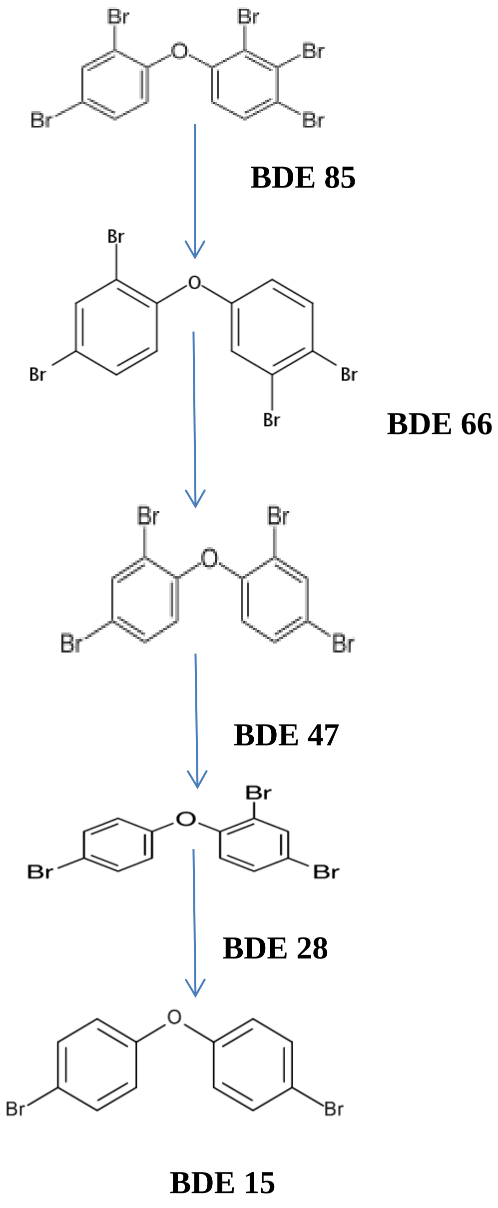


Figure 4. 15: Regression Curve for Disappearance of BDE 183

Equation 3.14 (Ln 0.5=-Kt1/2) is in the form of y = mx + C. A graph of ln (C_t) against time (t) provides a straight line, the gradient of which upon linear regression gives the first order rate constant $K_{obs.}$ Hence, the K_{obs} are the experimental degradation rate constant. The values gotten by this study were similar as that of the exponential regression study. Centered on first order kinetic, a graph of ln concentration of residues against time t (minutes), Figure 4.15 presented a regression equation, y = -0.0333x-1.9469. A slope of -0.0333 was gotten (corresponding to the constant K_{obs}). In this research the degradation of BDE 183 follows Langmuir-Hinshelwood kinetic equation and using equation 3.15 ($-0.693/K = t_{1/2}$), the half-life of BDE 183 was 20.81 minutes by the Langmuir-Hinshelwood kinetic model.

4.14.2 Degradation of 2,2′,3,4,4′-penta- bromodiphenyl ether (BDE 85)

The degradation of BDE 85 with N-dopped TiO_2 was effective within 120 minutes (scheme 4.2). The initial stage in the degradation of BDE 85 is removal of a single bromine atom, forming tetra -BDEs, namely; BDE 66 was achieved after 30 minutes of degradation. After 45 minutes of irradiation two tetra-BDEs were seen which were identified as BDE 66 and BDE 47. At irradiation time of 75 minutes one tri-BDE peak was seen and the PBDE was identified as BDE 28. Finally, at irradiation time of 90 minutes di-BDE was introduced which was identified as BDE 15. After 120 minutes of degradation a small peak of BDE 85 was seen while all the other PBDEs identified were present Scheme 4.2 shows the observed degradation pathway for BDE 85.



Scheme 4. 2: Proposed Mechanistic Degradation Pathway of BDE 85 by N Dopped-TiO_2 Nano-Particles under UV Radiation

The average initial concentration of BDE 85 was 5.67±0.05 mg/L (0 minutes) and the final residue was 1.67±0.00 mg/L at 120 minutes. Table 4.43 shows the removal efficiency of BDE 85.

Table 4.43: Removal Efficiency of BDE 85

Time (minutes)	Concentration (mg/L)
0	5.67±0.05
15	5.52±0.00
30	4.94±0.1
45	4.09±0.09
60	3.84±0.02
75	3.33±0.00
90	2.26±0.00
105	1.98±0.00
120	1.67±0.00

The trend of dissipation (Figure 4.16) was gotten by plotting concentration of BDE 85 against time in minutes.

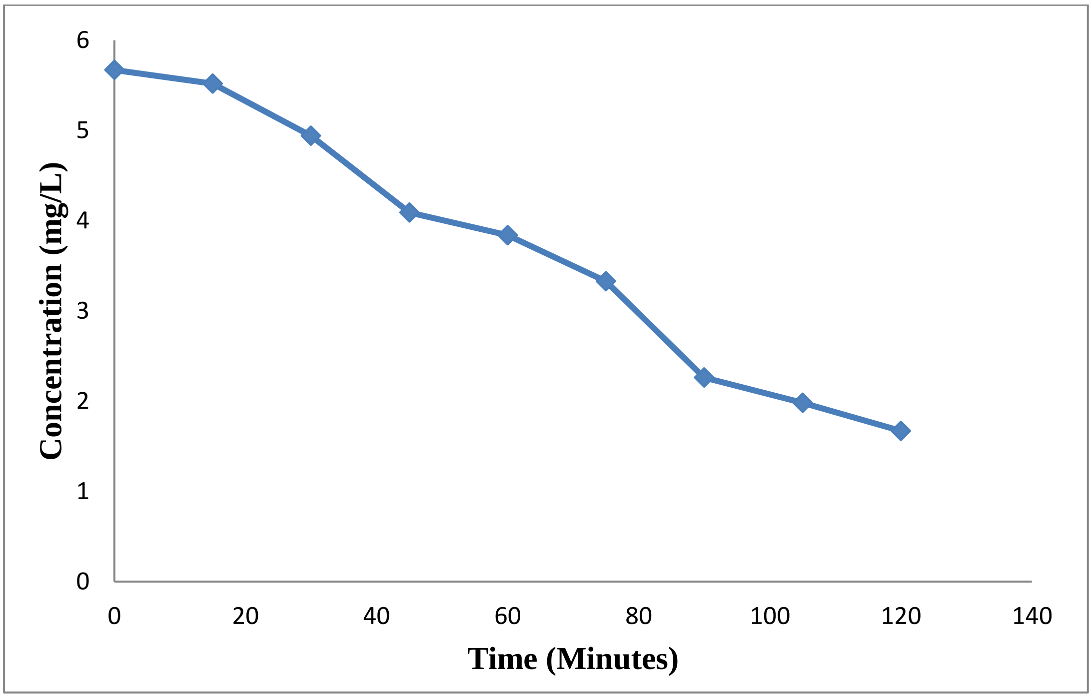


Figure 4. 16: Trends of BDE 85 Dissipation

After 15 minutes of irradiation 2.6 % of BDE 85 had degraded, after 30 minutes 12.87 % of BDE 85 had degraded while by 120 minutes after the irradiation of BDE 85, 70.54 % had degraded. The information was fitted into the Langmuir-Hinshelwood kinetic model for reaction rate dependence on primary reactant amount (Kar *et al.*, 2013). The regression graph for the degradation of BDE 85 is shown in Figure 4.17.

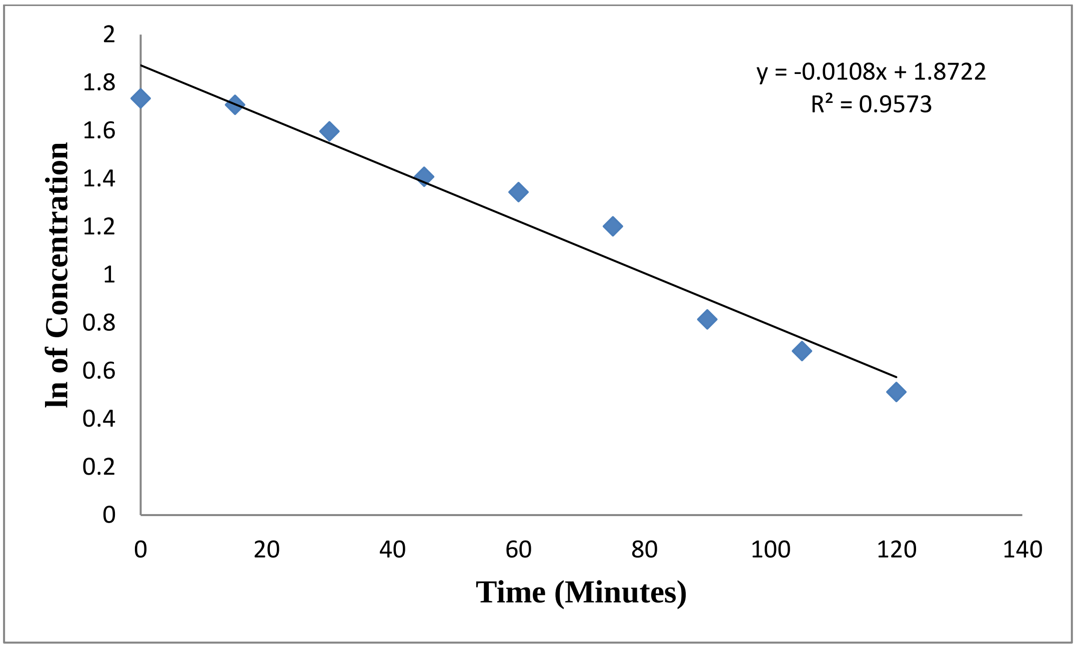
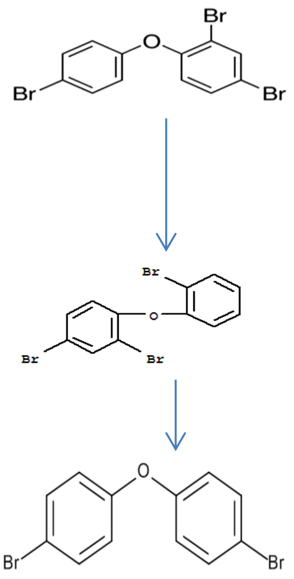


Figure 4. 17: Regression curve for disappearance of BDE 183

Using equation 3.15, Y =- 0.0108X+1.8722 for BDE 85 from the regression curve (Figure 4.17). A slope of -0.0108 was gotten (corresponding to the constant K_{obs}). In the current research the degradation of BDE 85 follows Langmuir-Hinshelwood kinetic equation and applying equation 3.15, the half-life of BDE 85 was 65.39 minutes by the Langmuir-Hinshelwood kinetic model.

4.14.3 Degradation of 2,4,4'-tribromodiphenyl ether (BDE 28)

The degradation of BDE 28 was slow compared to BDE 85 and 183. After the first 30 minutes there was no degradation observed but at 45 minutes there was degradation observed in which one bromine atom was removed, forming di-BDEs, namely; BDE 15. After 120 minutes of degradation a small peak of BDE 28 was seen while peaks of di-BDE were dominant and all the other PBDEs identified were present. Scheme 4.3 shows the observed degradation pathway for BDE 28.



BDE 28

BDE 17

BDE 15

Scheme 4. 3: Proposed Mechanistic Degradation Pathway of BDE 28 by N Dopped-TiO_2 Nano-Particles under UV Radiation

The average initial concentration of BDE 28 was 5.89±0.14 mg/L (0 minutes) and final residue was 1.91±0.02 mg/L at 120 minutes. Table 4.44 shows the removal efficiency of BDE 28.

Table 4.44: Removal Efficiency of BDE 28

Time (minutes)	Concentration (mg/L)
0	5.89±0.14
15	5.85±0.09
30	5.86±0.02
45	4.91±0.00
60	4.34±0.01
75	3.69±0.00
90	2.91±0.00
105	2.37±0.00
120	1.91±0.02

The trend of dissipation (Figure 4.18) was gotten by drawing concentration of BDE 28 against time in minutes.

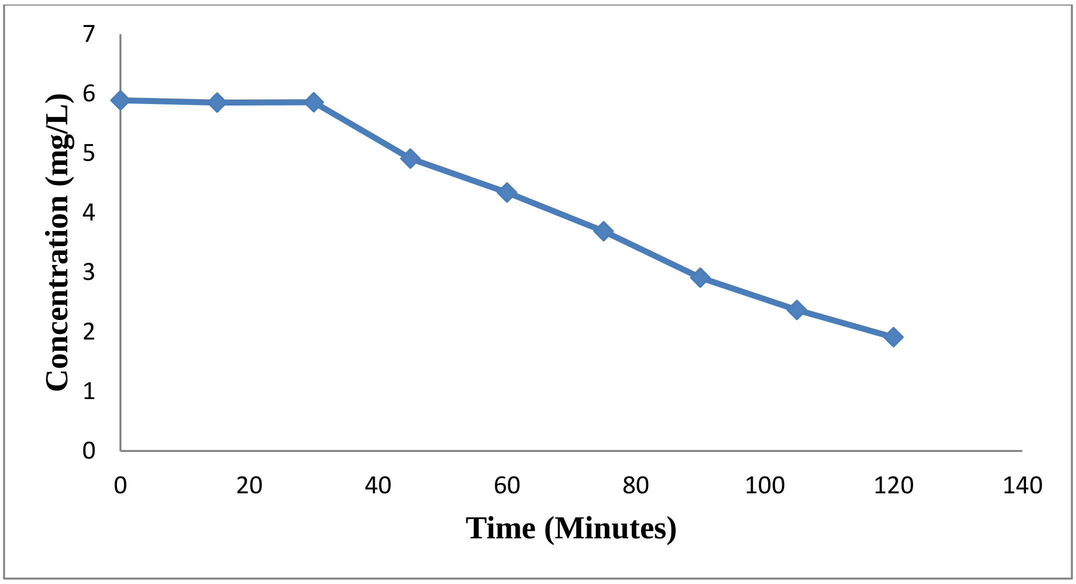


Figure 4. 18: Trends of BDE 28 Dissipation

After 15 minutes of irradiation 0.67 % of BDE 28 had degraded, after 30 minutes 0.58 % of BDE 28 had degraded while by 120 minutes after the irradiation of BDE 28, 67.57% had degraded. The data was fitted into the Langmuir-Hinshelwood kinetic model for reaction rate dependence on initial reactant concentration (Kar *et al.*, 2013). The regression curve for the degradation of BDE 28 is shown in Figure 4.19.

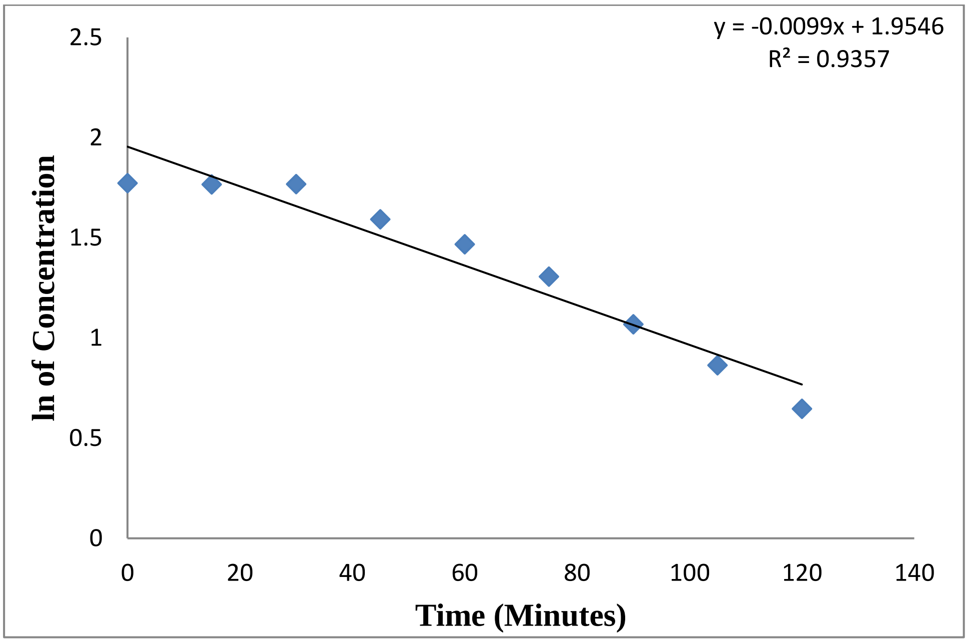


Figure 4. 19: Regression Curve for Disappearance of BDE 28

From the regression curve (Figure 4.19) and using Equation 3.14, Y = -0.0099X+1.9546 for BDE 28. A gradient of -0.0099 was obtained (which is equivalent to the constant K_{obs}). In this study the degradation of BDE 28 follows Langmuir-Hinshelwood kinetic equation and using Equation 3.15, the half-life of BDE 28 was 70.01 minutes by the Langmuir-Hinshelwood kinetic model.

4.14.4 Summary of Degradation Result of Brominated Diphenyl Ether 28, 85 and 183

In the current search, the photocatalytic degradation of BDE 28, 85 and 183 in the presence of N-TiO_2 catalyst followed the first-order reaction kinetics model. The value of ln (concentration) against irradiation time (minutes) showed straight lines, the gradients of which upon linear regression expressed the apparent first order rate constants K_{obs}. The r^2 values of linearity for BDE 28, 85 and 183 are 0.93, 0.95 and 0.96 respectively. The apparent first-order rate constants for BDE 28, 85 and 183 are -0.0099, -0.0108 and -0.0333. The half-life ($t_{1/2}$) for BDE 28, 85 and 183 are 70.01, 65.39 and 20.81 minutes respectively. In this study BDE 183 had the lowest half-life. Table 4.45 shows the summary of UV-induced photocatalytic degradation kinetic parameters of BDE 28, 85 and 183 in the presence of N-TiO_2.

Table 4.45 Summary of UV-Induced Photocatalytic Degradation Kinetic Parameters of BDE 28, 85 And 183 in the presence of N-TiO_2

	K_{obs}	R^2	$t_{1/2}$ (minutes)
BDE 28	0.0099	0.93	70.01
BDE 85	0.0108	0.95	65.39
BDE 183	0.0333	0.96	20.81

Based on the results, the rate of degradation of PBDEs by N-dopped TiO_2 in the presence of UV light is dependent on the number of bromine atom. Hence, PBDEs with high number of bromine atom degrade more rapidly than PBDEs with fewer number of bromine atom. This observation can be explained based on the absorbance characteristics of PBDEs in which the highly brominated diphenyl ethers can easily absorb at longer wave lengths. The current opinion was in agreement with earlier research conducted where they settled that the PBDEs with high number of bromine atom like BDE 209, 206 and 203 degraded more rapidly than three hepta BDEs (BDE 190, 181 and 183) investigated (Eriksson *et al.*, 2004). Another study by Nashaida and co-workers observed that hexa-BDE (BDE 154 and 153) degraded faster than penta-BDE (BDE 100) and tetra-BDE (BDE 47) (Nashaida *et al.,* 2016). Also, it might be stated that there is a big degradation rate variance among the full brominated PBDE ring and the unsubstituted brominated PBDE ring (Niu *et al.,* 2006).

The rate of photodegradation of PBDEs is also influenced by the energy of the highest occupied molecular orbital (HOMO energy), which influences the electron donor capability. The lower the donor ability, the particular photodegradation ability turn out to be lower as well. A research by Niu and coworkers found that increasing the number of occupied molecular orbital energy gives rise to advanced reactivity (Niu *et al.,* 2006). Highest occupied molecular orbital energies decrease with declining quantity of bromine substituent. Therefore, decreasing the quantity of bromine particles led to the decrease of photodegradation frequency of PBDEs. BDE 28 recorded the slowest degradation rate of the PBDE congeners investigated in the current study which is in agreement with other studies conducted (Niu *et al.,* 2006).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

PBDEs residues were detected at varying concentrations in water, sediment and soil samples from Nairobi River basin and air samples from Nairobi and Mount Kenya regions.

The mean concentration of PBDEs in water samples ranged between ≤0.009 to 72.89±6.15 ng/L. The dominant PBDEs in water were BDE 47, 85, 99, 100 and 183.

The mean concentration of PBDEs in sediment samples ranged between 134.70±3.07 to 24,386.13±207.22 ng/Kg. The dominant PBDEs in sediment were BDE 28, 47, 66, 85, 99, 100 153, 154 and 183.

The mean concentration of PBDEs in soil samples ranged between 16.46±1.99 to 30,561.35±145.57 ng/Kg. The dominant PBDEs in soil were BDE 28, 47, 66, 85, 99, 100 153, 154 and 183.

The PBDEs screened in air samples had concentrations range from ≤ 0.9 to 152.72±3.19 pgm^{-3}. The dominant PBDEs in air were BDE 47 and 99.

Nitrogen was successfully doped into TiO_2 matrix and its photocatalytic activity studied for the degradation of methylene blue under visible light.

Nitrogen doped TiO_2 nanoparticles was synthesized and effectively degraded BDE 28, 85 and 183 through stepwise debromination.

The degradation half-life for BDE 28, 85 and 183 were 70.01, 65.39 and 20.81 minutes respectively.

5.2 Recommendations

5.2.1 Policy Recommendations

- Levels of PBDEs in water from Nairobi River that should be of concern to human health were detected in this study. The community should be educated on the adverse ecological and human health effects of PBDEs.
- Regular monitoring of PBDEs and others chemical pollutants in water, air, soil and sediments to determine impact on human health and environment.
- Dandora recorded high mean concentration of PBDEs in air, showing that PBDEs are the products of waste disposal, hence the government should take steps to ensure that waste dumping and sorting is done in the right way.
- The government through the National Environment management Authority to enact the electronic and electric equipment waste management act to enable Kenya manage efficiently disposal of waste.
- There should be a follow up on the products used in Kenya to guarantee that the PBDEs are not unlawfully recycled.

5.2.2 Research Recommendations

There is increasing information related to the ecological existence, destiny and behaviour of PBDEs and human contact to PBDEs. Nevertheless, relevant study gaps still exist and further research is vital to:

- Need to delineate the sources of PBDEs into air, water, soil and sediment to assist in developing measures to prevent pollution.
- Extend research to investigate the levels of contamination in fish and other forms of food stuff to assess exposure risks to human health.
- Study environmental persistence of PBDEs in Kenyan soils and its long-term effect on presence of these compounds.

- Determine the effectiveness of the N-Doped TiO_2 in degrading other chemical pollutants in the environment.
- Further research should be carried out to investigate the concentration of other emerging brominated frame retardants like BTBPE in environment, especially e-waste dismantling plants.
- Advanced study is needed to investigate on non-dietary (like particulate matter ingestion, air breathing and related soil and dust dermal interaction) and dietary contact to PBDEs.

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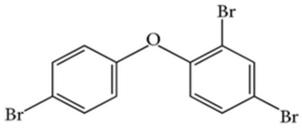
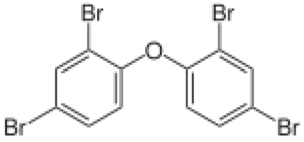
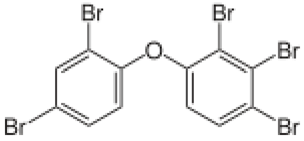
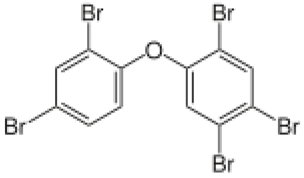
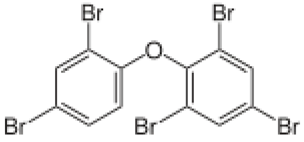
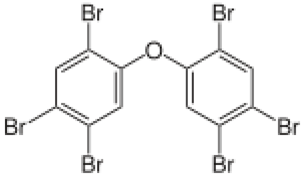
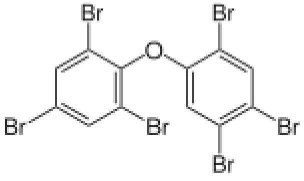
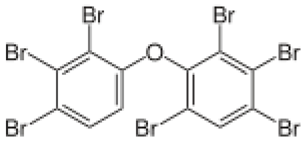
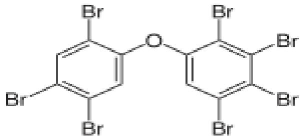
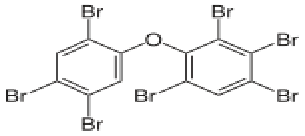
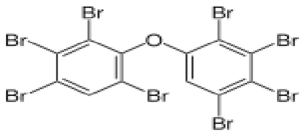
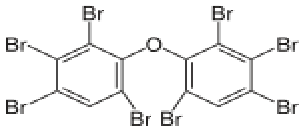
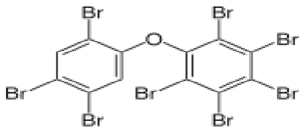
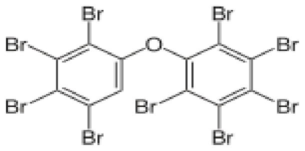
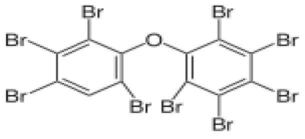
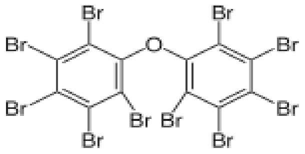
APPENDICES

Appendix 1: Common PBDE Structures

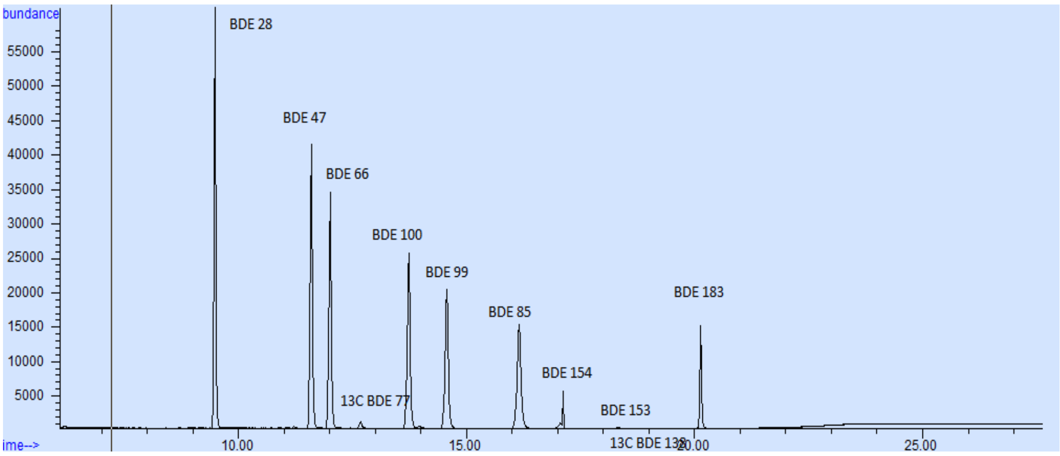
Structure	Congener	Name
	BDE-28	2,4,4'-tribromodiphenyl ether
	BDE-47	2,2′,4,4′-tetra- bromodiphenyl ether
	BDE-85	2,2′,3,4,4′-penta- bromodiphenyl ether
	BDE-99	2,2′,4,4′,5-penta- bromodiphenyl ether
	BDE-100	2,2′,4,4′,6-penta-bromodiphenyl ether
	BDE-153	2,2′,4,4′,5,5′-hexa-bromodiphenyl ether
	BDE-154	2,2′,4,4′,5,6′-hexa-bromodiphenyl ether

	BDE-171	2,2′,3,3′,4,4′,6-hepta-bromodiphenyl ether
	BDE-180	2,2′,3,4,4′,5,5′-hepta- bromodiphenyl ether
	BDE-183	2,2′,3,4,4′,5′,6-hepta-bromodiphenyl ether
	BDE-196	2,2′,3,3′,4,4′,5,6′-octa-bromodiphenyl ether
	BDE-197	2,2′,3,3′,4,4′,6,6′-octa-bromodiphenyl ether
	BDE-203	2,2′,3,4,4′,5,5′,6-octa-bromodiphenyl ether
	BDE-206	2,2′,3,3′,4,4′,5,5′,6-nona-bromodiphenyl ether
	BDE-207	2,2′,3,3′,4,4′,5,6,6′-nona-bromodiphenyl ether
	BDE-209	Deca-bromodiphenyl ether

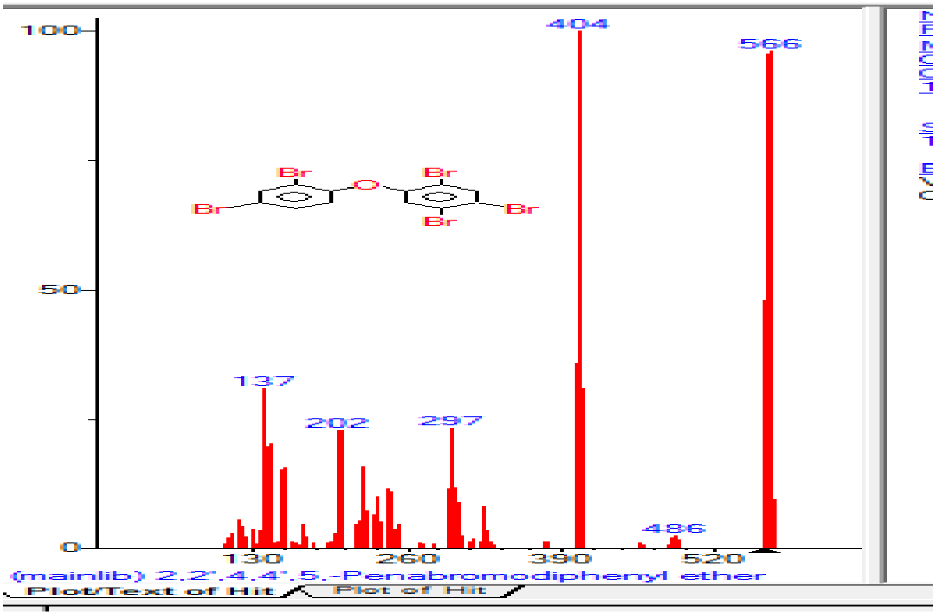
Appendix 2: PBDE Congener Numbers and Chemical Composition of the Commonly Studied Congeners (US EPA, 2010).

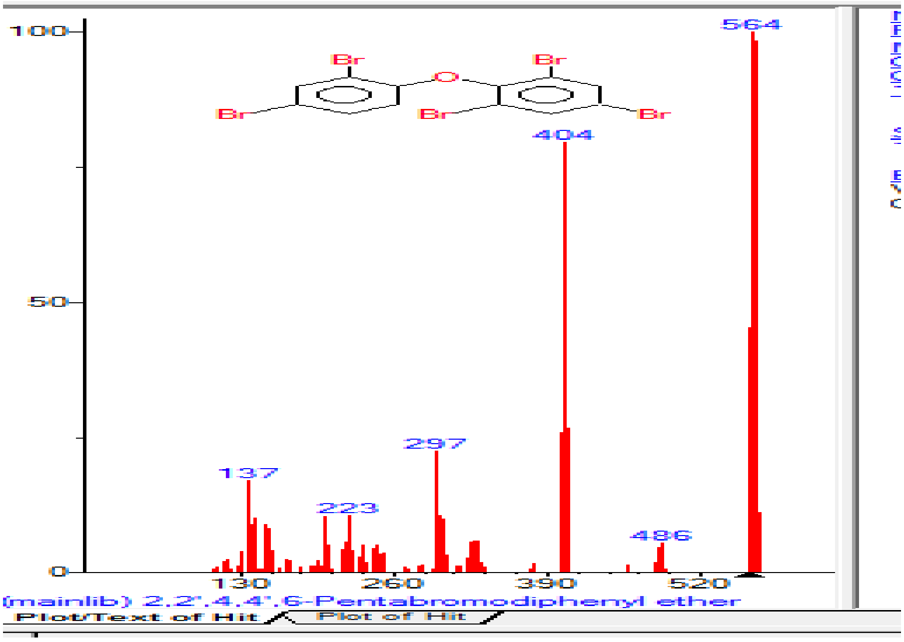
Homologs of PBDEs	IUPAC Number	Chemical Formula
Mono-BDE	BDE-3	4-BDE
Di-BDE	BDE-7	2,4-BDE
Di-BDE	BDE-15	4,4’-BDE
Tri-BDE	BDE-17	2,2’,4-BDE
Tri-BDE	BDE-28	2,4,4’-BDE
Tetra-BDE	BDE-47	2,2’,4,4’-BDE
Tetra-BDE	BDE-66	2,3’,4,4’-BDE
Tetra-BDE	BDE-49	2,2’,4,5’-BDE
Tetra-BDE	BDE-71	2,3’,4’,6-BDE
Penta-BDE	BDE-85	2,2’,3,4,4’-BDE
Penta-BDE	BDE-99	2,2’,4,4’,5-BDE
Penta-BDE	BDE-100	2,2’,4,4’,6-BDE
Penta-BDE	BDE-119	2,3’,4,4’6-BDE
Penta-BDE	BDE-126	3,3’,4,4’,5-BDE
Penta-BDE	BDE-138	2,2’,3,4,4’,5’-BDE
Hexa-BDE	BDE-153	2,2’,4,4’,5,5’-BDE
Hexa-BDE	BDE-154	2,2’,4,4’,5,6’-BDE
Hexa-BDE	BDE-156	2,3,3’,4,4’,5 -BDE
Hepta-BDE	BDE-183	2,2’,3,4,4’,5’,6-BDE
Hepta-BDE	BDE-184	2,2',3,4,4’,6,6’-BDE
Hepta-BDE	BDE-191	2,3,3’,4,4’,5’,6-BDE
Octa-BDE	BDE-196	2,2’,3,3’,4,4’,5’,6-BDE
Octa-BDE	BDE-197	2,2’,3,3’,4,4’,6,6’-BDE
Nona-BDE	BDE-206	2,2’,3,3’,4,4’,5,5’,6-BDE
Nona-BDE	BDE-207	2,2’,3,3’,4,4’,5,6,6’-BDE
Deca-BDE	BDE-209	2,2’,3,3’,4,4’,5,5’,6,6’-BDE

Appendix 3: PBDE Standard Mixture Chromatogram

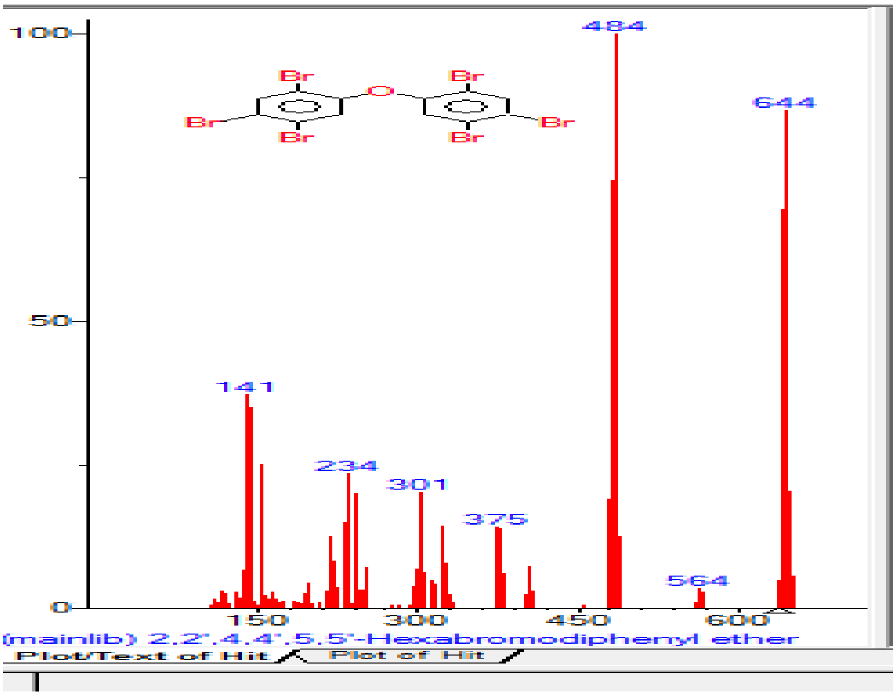


Appendix 4: NIST Library Search for PBDE

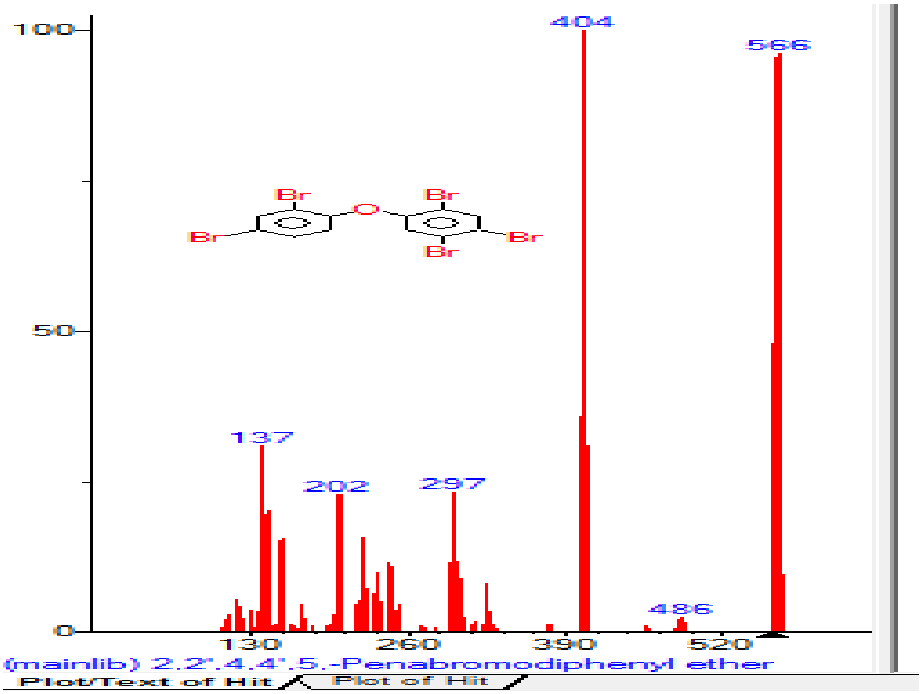


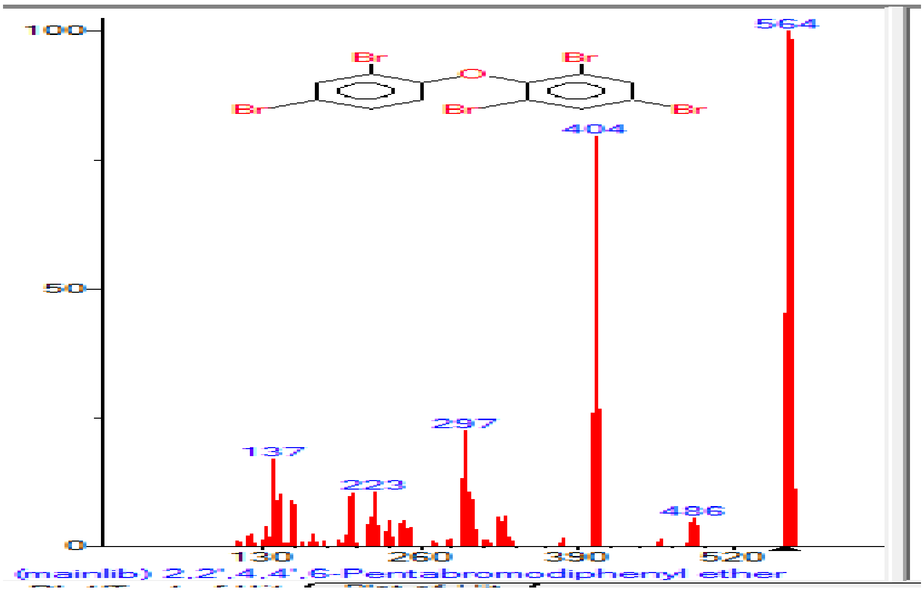


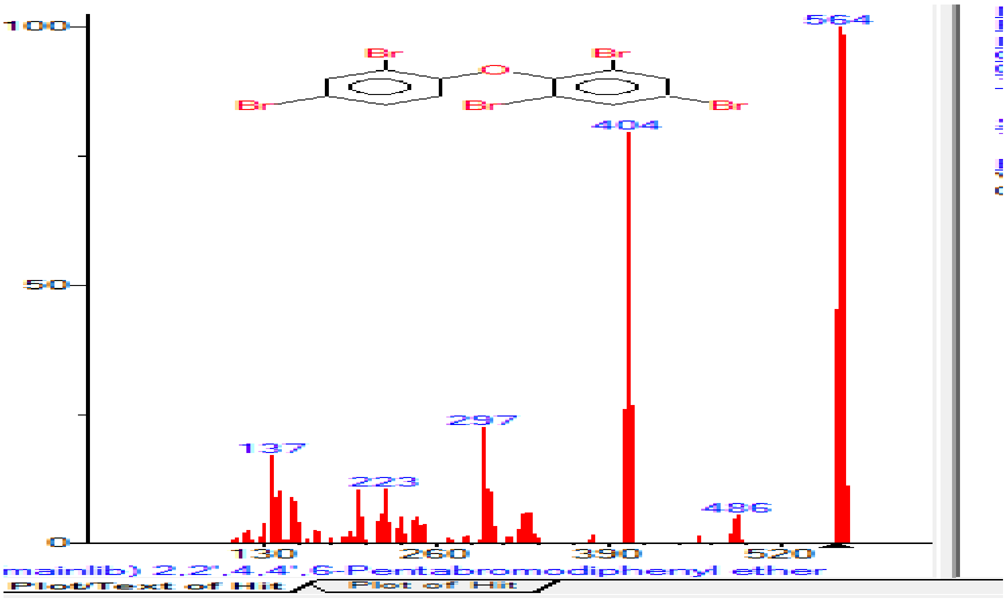
(mainlib) 2,2',4,4',6-Pentabromodiphenyl ether



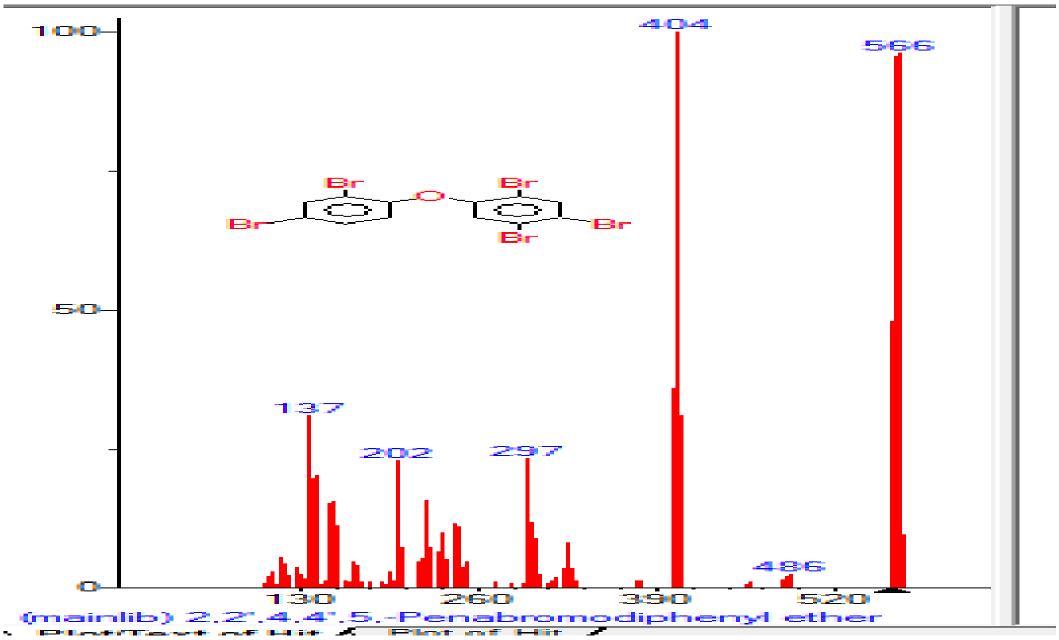
(mainlib) 2,2',4,4',5,5'-Hexabromodiphenyl ether


100
50
0
404
566
137
202
297
486
Br
O
Br
Br
Br
Br
130
260
390
520
(mainlib) 2.2'.4.4'.5.-Penabromodiphenyl ether
Plot/Text of Hit
Plot of Hit

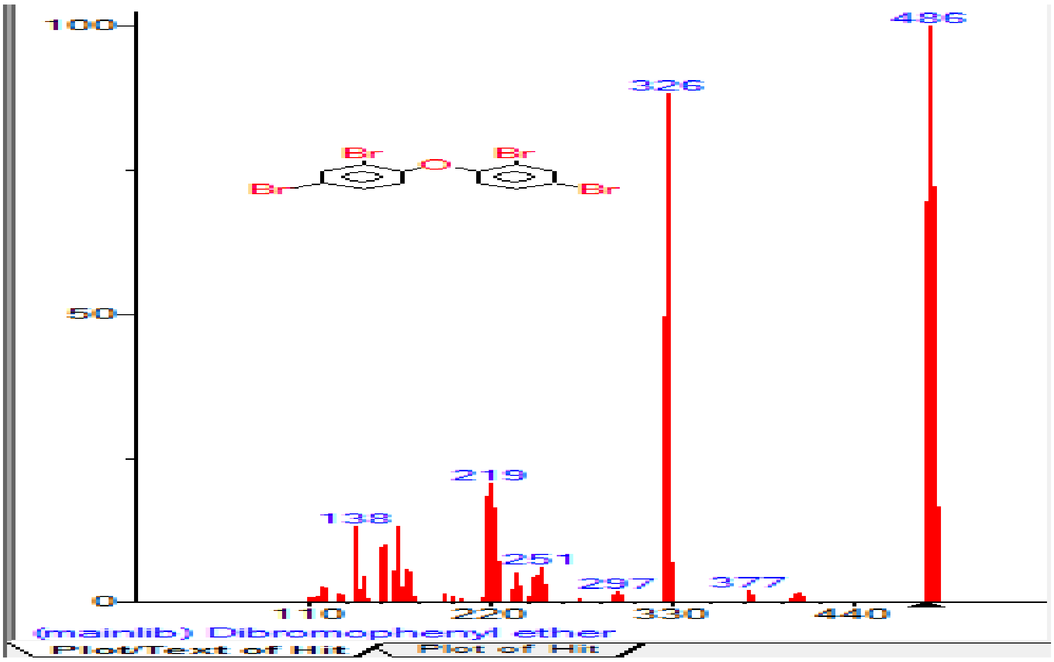

100
50
0
564
404
137
223
297
486
Br
O
Br
Br
Br
Br
130
260
390
520
(mainlib) 2.2'.4.4'.6-Pentabromodiphenyl ether



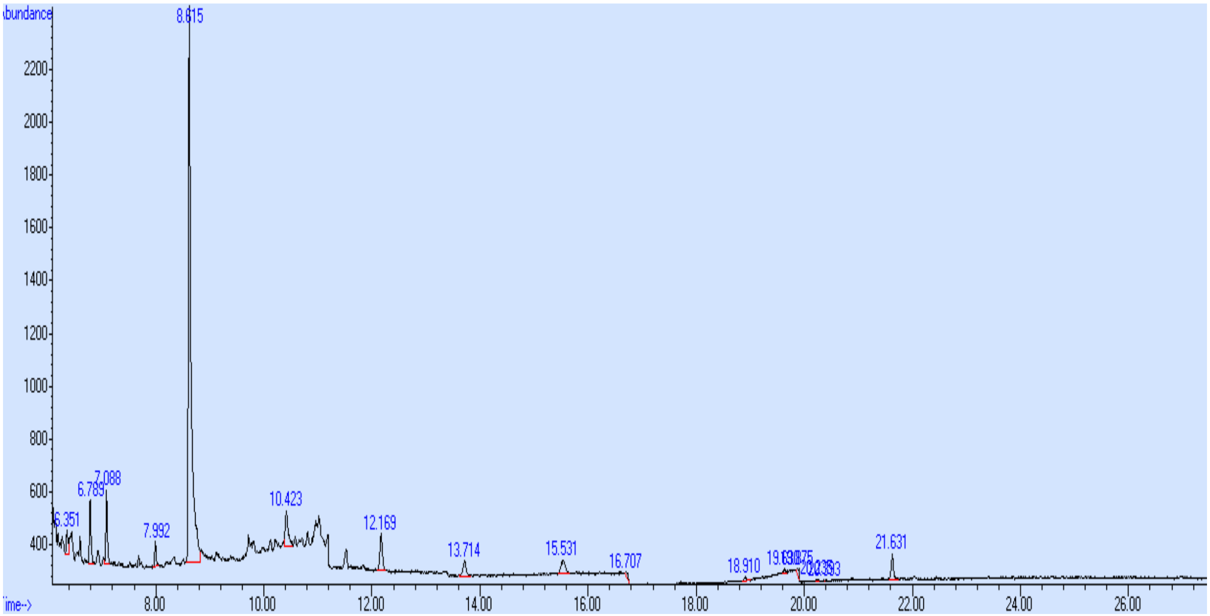
mainlib) 2,2',4,4',6-Pentabromodiphenyl ether

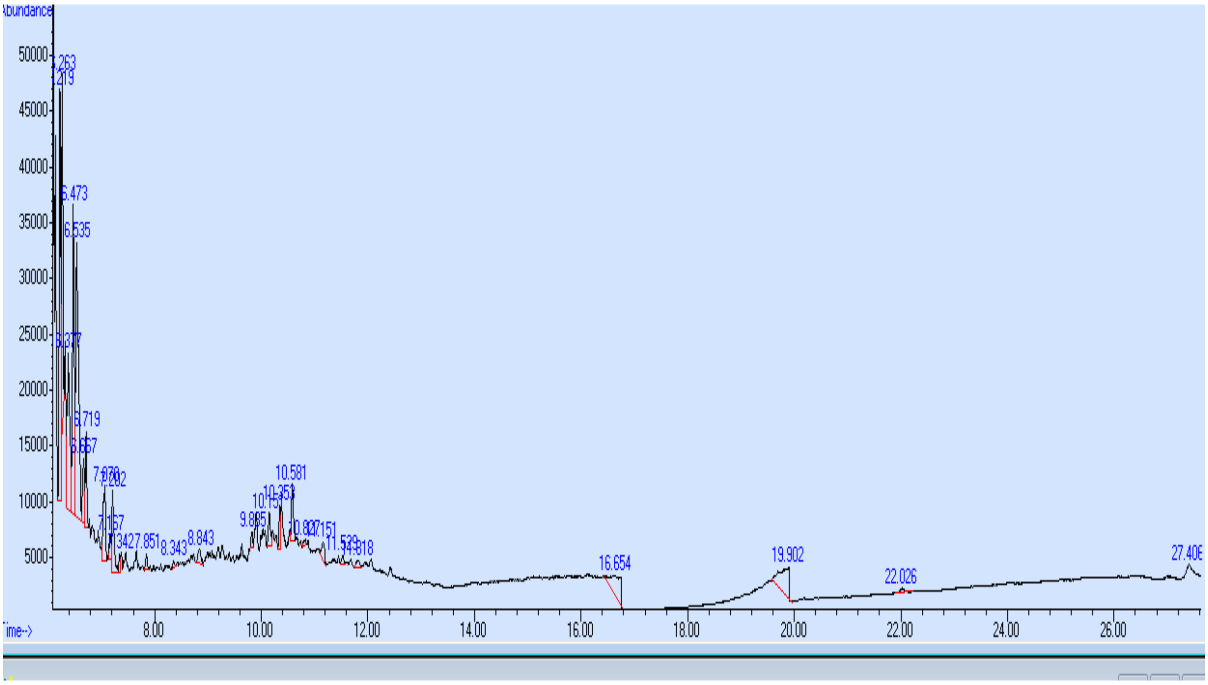


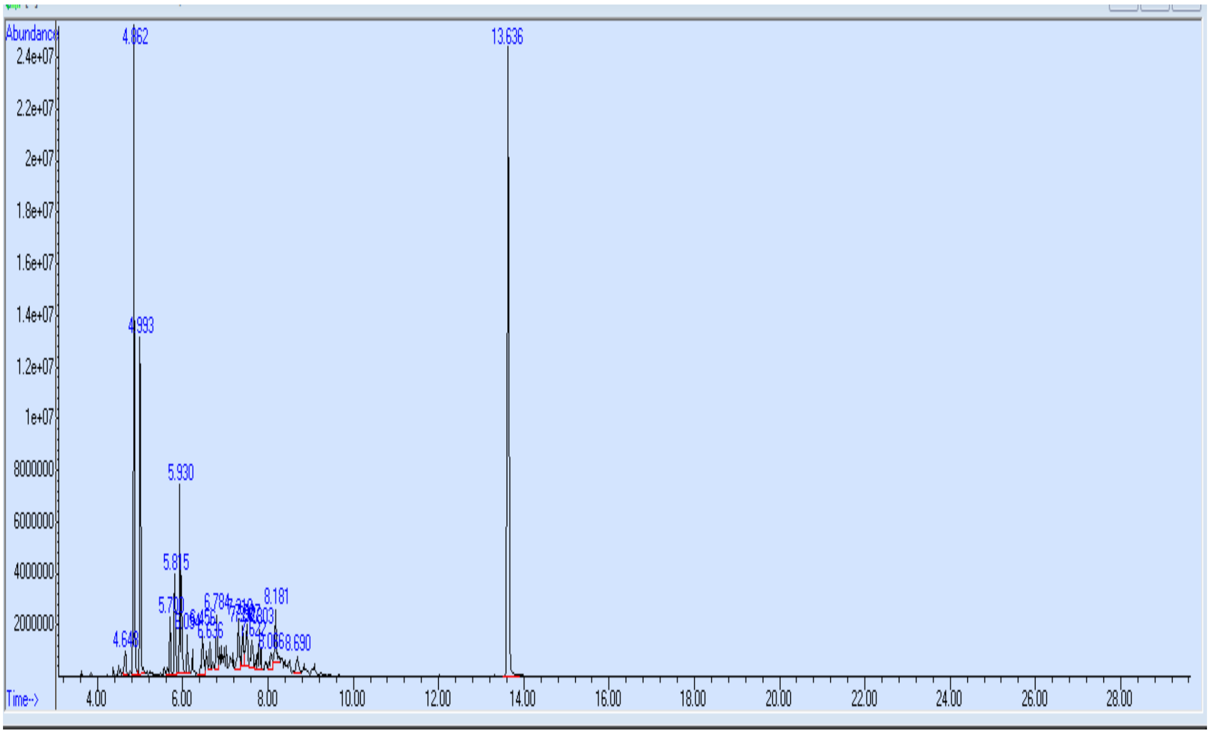
(mainlib) 2,2',4,4',5,-Penabromodiphenyl ether

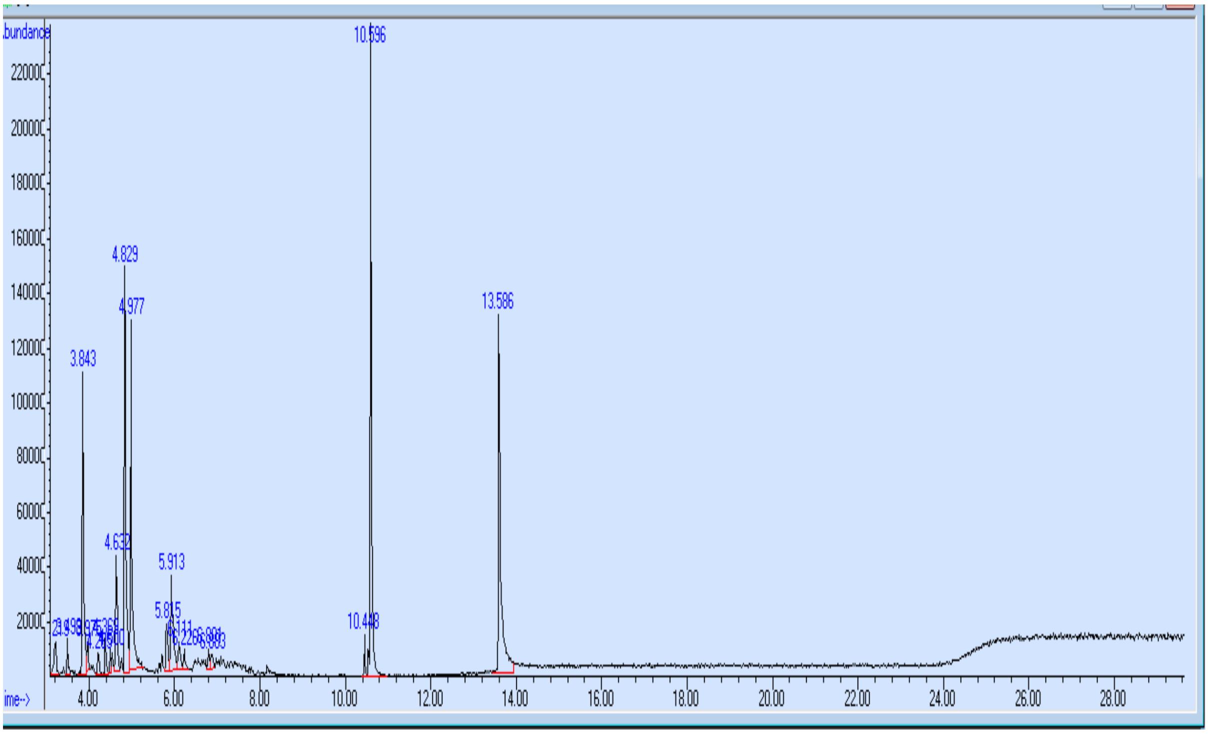


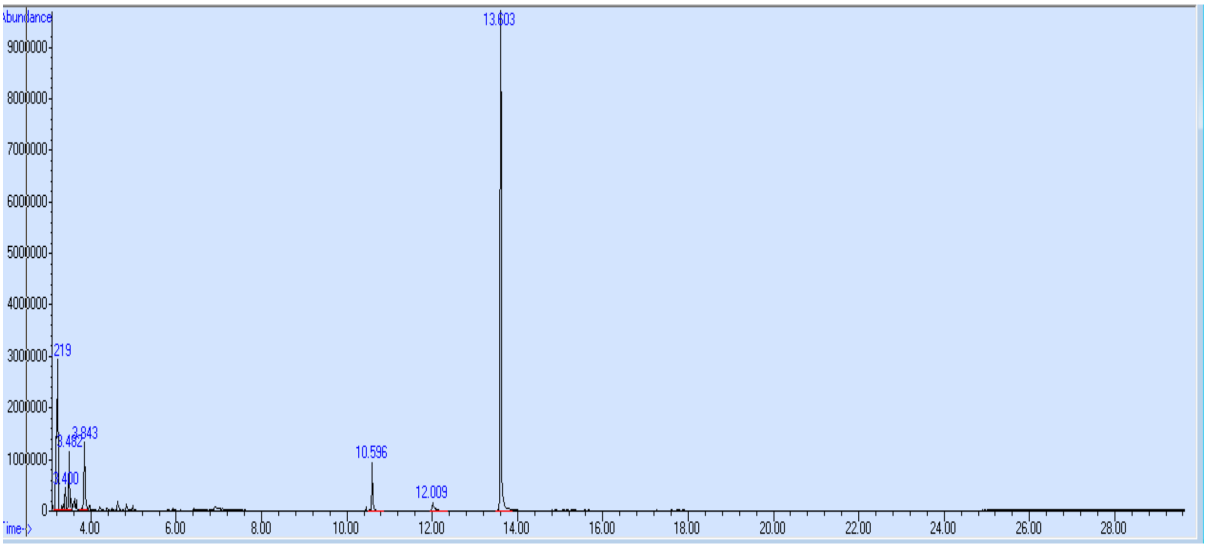
Appendix 4: Chromatogram of Sample

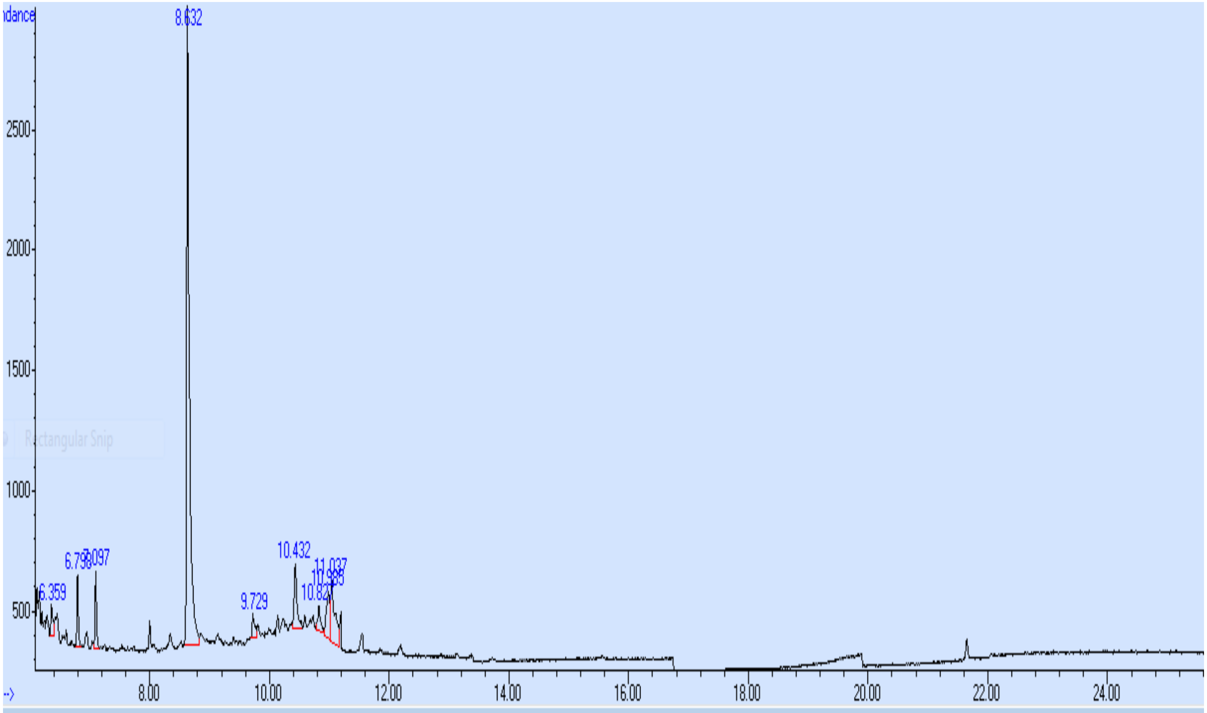

Abundance
2200
2000
1800
1600
1400
1200
1000
800
600
400
8.615
6.351
6.789
7.088
7.992
10.423
12.169
13.714
15.531
16.707
18.910
21.631
Time-->
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00


Abundance
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
6.473
6.535
6.719
7.202
7.167
7.851
8.343
8.843
10.581
10.353
16.654
19.902
22.026
27.406
Time-->
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00


Abundance
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
4.862
13.636
4.993
5.930
5.815
5.700
6.784
8.181
6.636
4.648
8.690


Abundance
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
10.596
13.586
4.829
4.977
3.843
4.632
5.913
5.815
10.448


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
219
3.482
3.843
3.400
10.596
12.009
13.603
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00

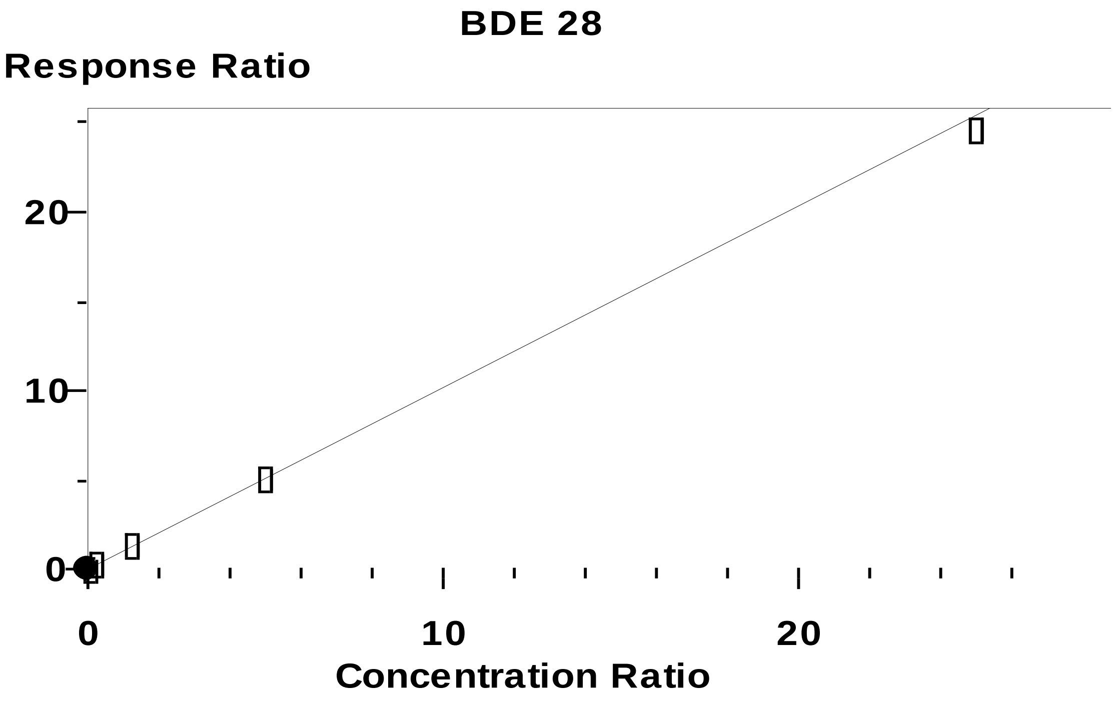

ndance
8.632
2500
2000
1500
1000
500
6.359
6.796
7.097
9.729
10.432
10.827
10.983
11.037
-->
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00

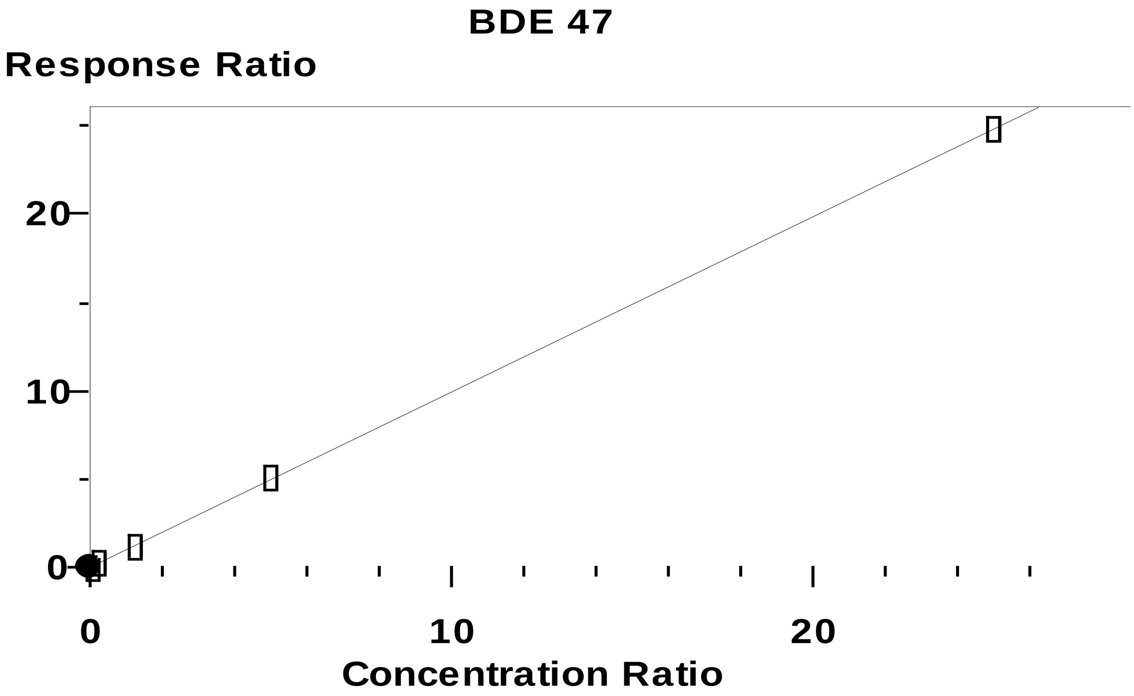
Appendix 5: Federal Environmental Quality Guidelines for Polybrominated Diphenyl Ethers (PBDEs)

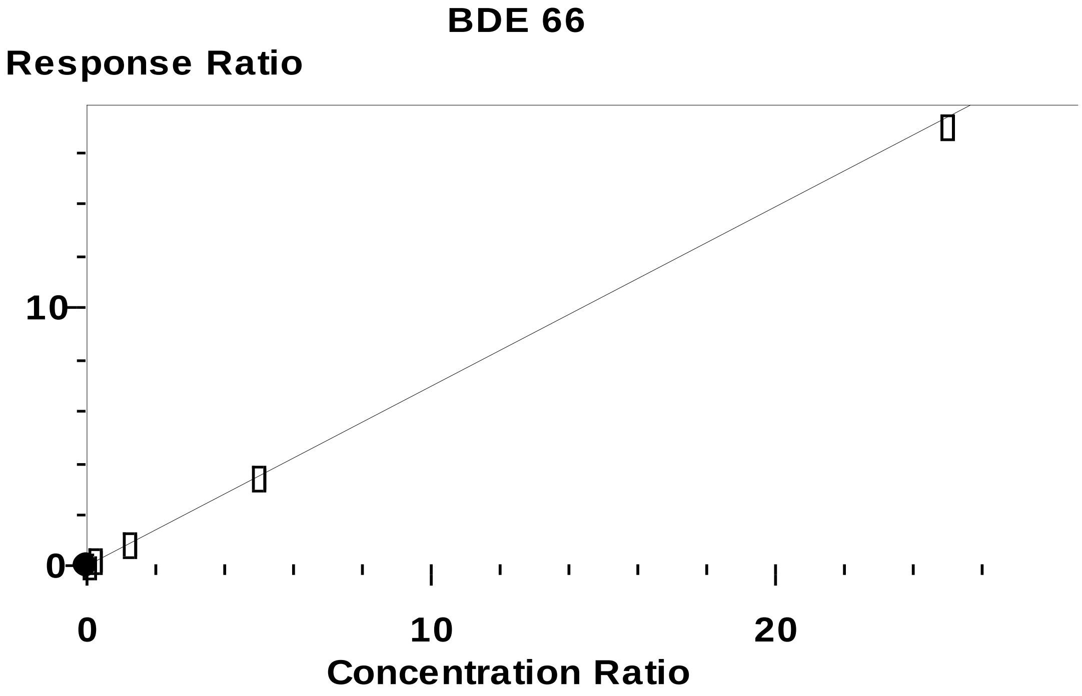
Homologue	Congener	Water (ng/L)	Fish Tissue (ng/g)	Sediment (ng/g)	Wildlife Diet (ng/g food source)	Bird Eggs (ng/g)
triBDE	total	46	120	44	–	–
tetraBDE	total	24	88	39	44	–
pentaBDE	total	0.2	1	0.4	3 (mammal) 13 (birds)	29
pentaBDE	BDE-99	4	1	0.4	3	–
pentaBDE	BDE-100	0.2	1	0.4	–	–
hexaBDE	total	120	420	440	4	–
heptaBDE	total	17	–	–	64	–
octaBDE	total	17	–	5600	63	–
nonaBDE	total	–	–	–	78	–
decaBDE	total	–	–	19	9	–

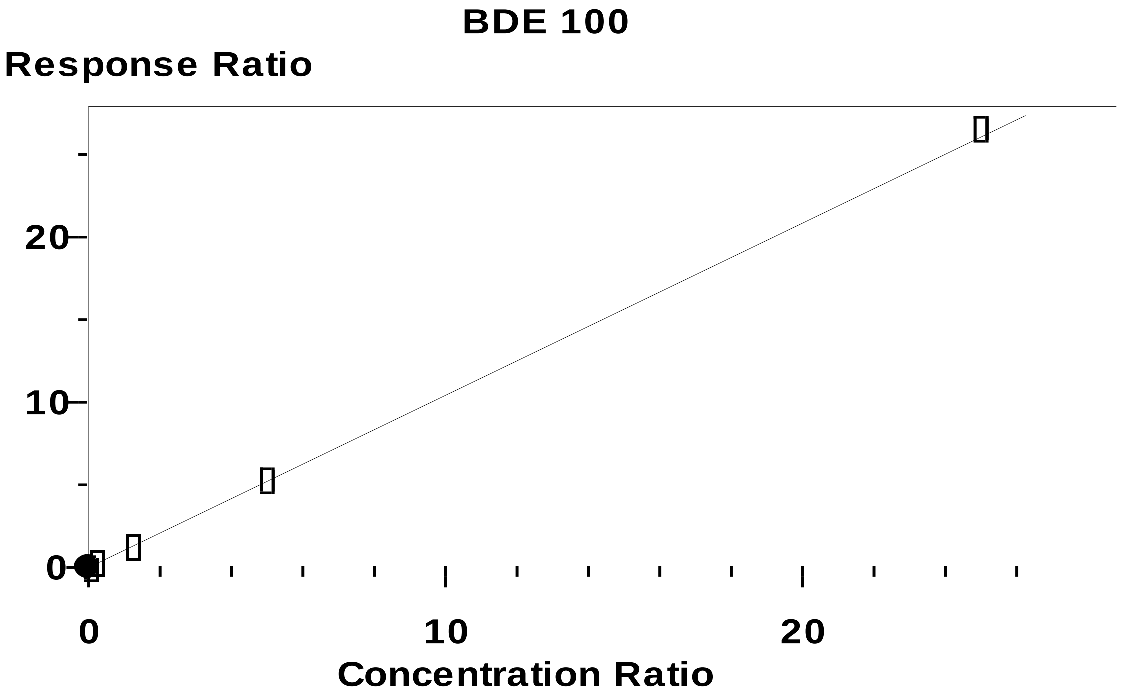
A

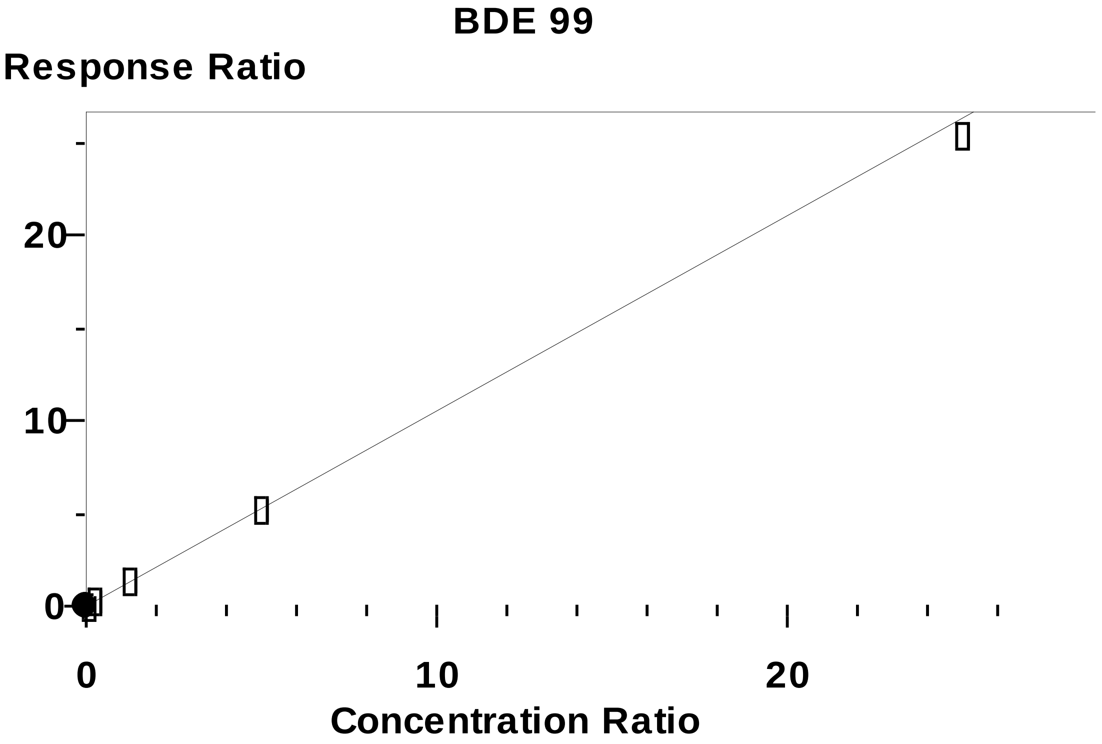
Appendix 6: Calibration Curves



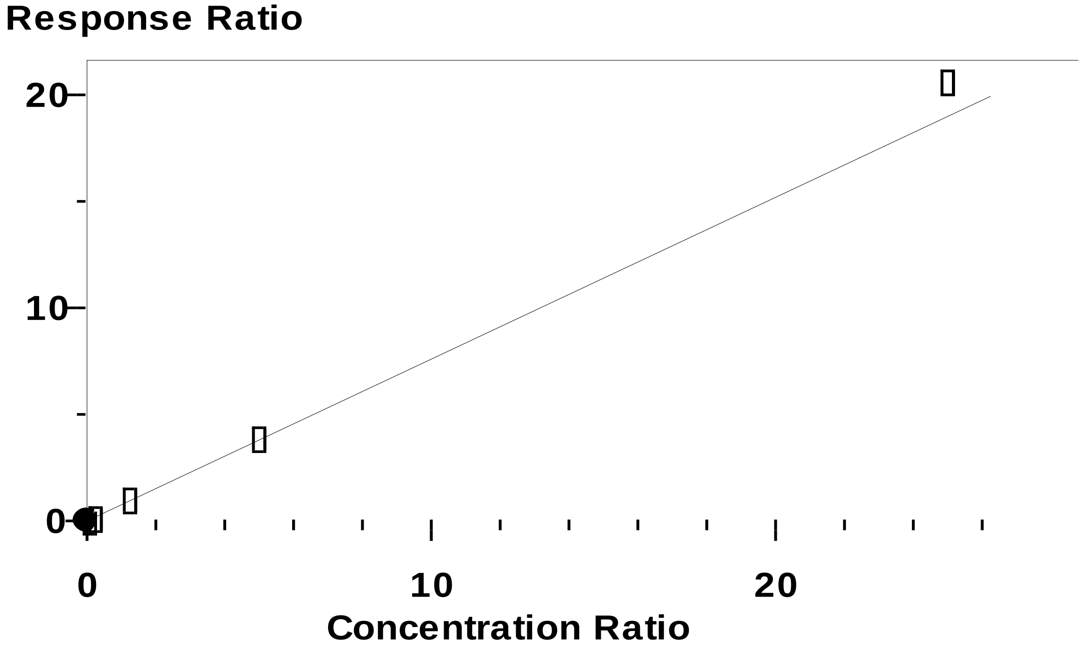

BDE 47
Response Ratio
0
10
20
0
10
20
Concentration Ratio


BDE 66
Response Ratio
0
10
0
10
20
Concentration Ratio

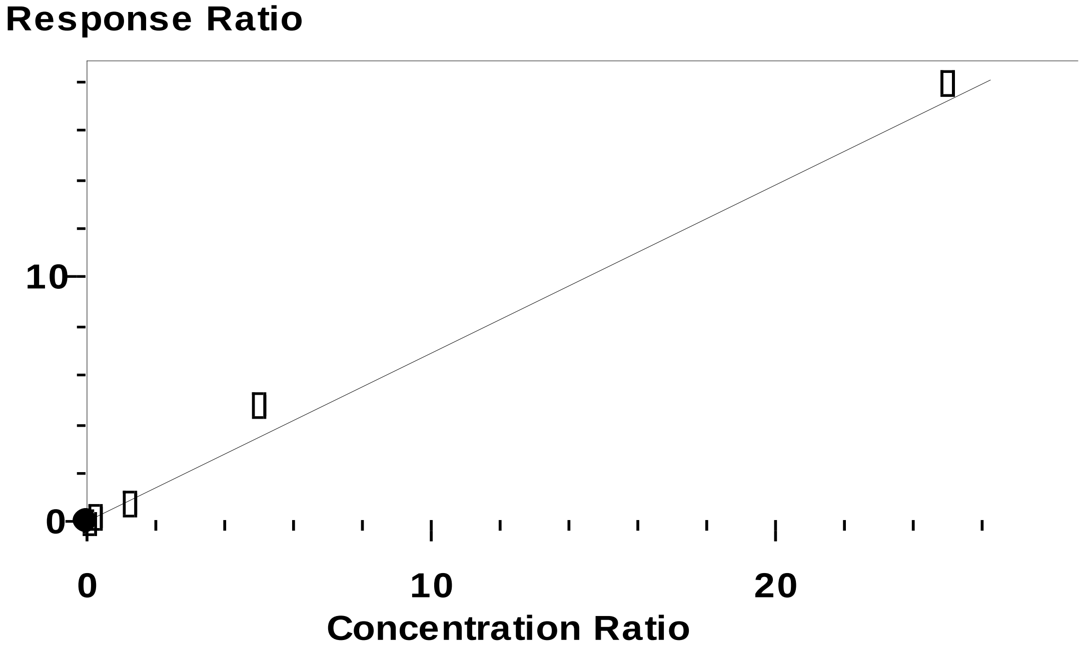

BDE 100
Response Ratio
20
10
0
0
10
20
Concentration Ratio


BDE 99
Response Ratio
20
10
0
0
10
20
Concentration Ratio

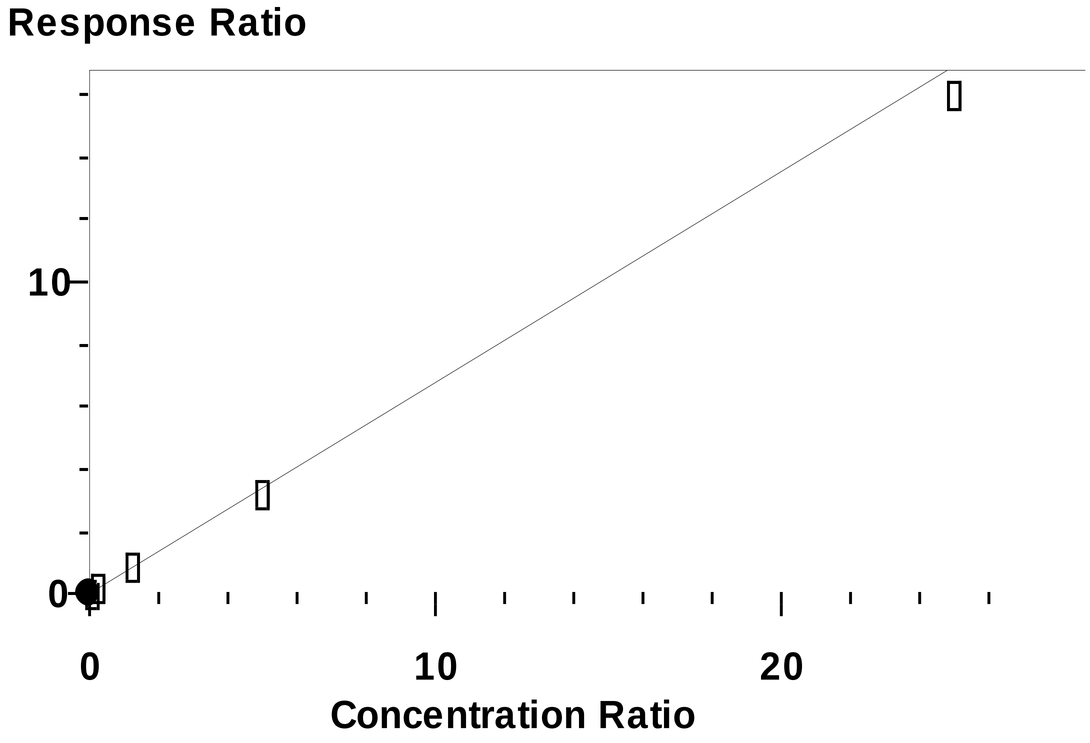
BDE 85



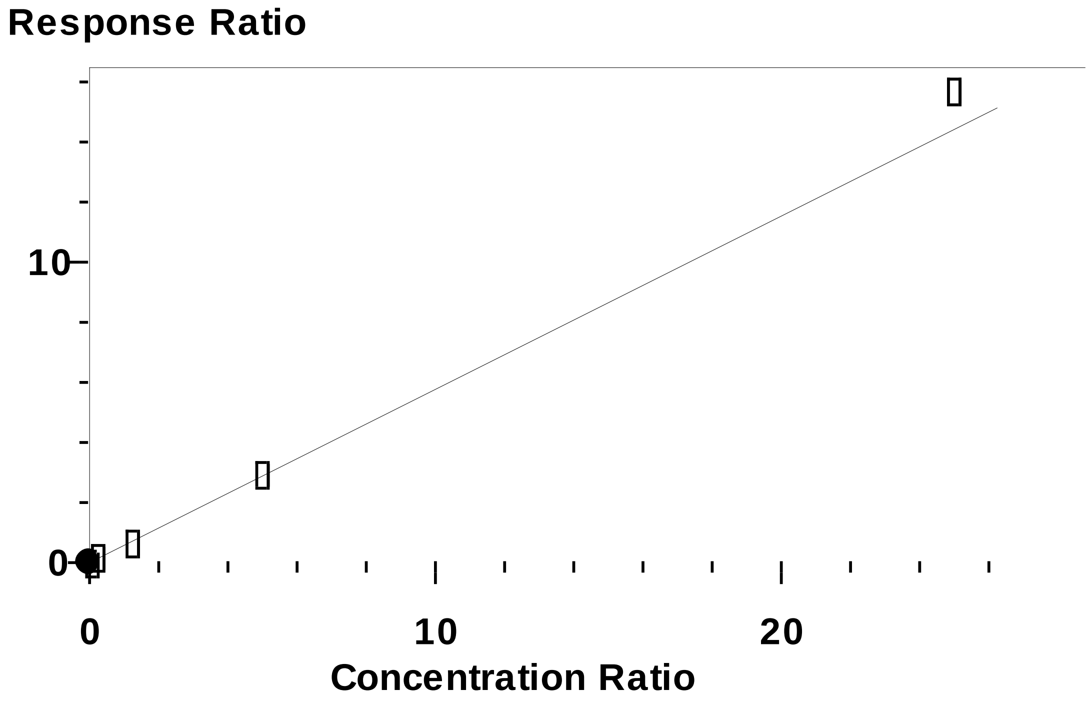
BDE 154



BDE 153



BDE 183



Appendix 7

Appendix 7A: Correlation of PBDEs with Physio-chemical Parameter in Water during Cool Dry Season

Correlations

		pH Cooler Dry Season	TSS Cooler Dry Season	TDS Cooler Dry Season	eC Cooler Dry Season	PBDEs Cool Dry Season
pH Cool Dry Season	Pearson Correlation	1	-.491	-.523	-.472	-.121
	Sig. (2-tailed)		.180	.149	.200	.756
	N	9	9	9	9	9
TSS Cooler Dry Season	Pearson Correlation	-.491	1	.879**	.895**	.555
	Sig. (2-tailed)	.180		.002	.001	.121
	N	9	9	9	9	9
TDS Cooler Dry Season	Pearson Correlation	-.523	.879**	1	.995**	.517
	Sig. (2-tailed)	.149	.002		.000	.154
	N	9	9	9	9	9
eC Cooler Dry Season	Pearson Correlation	-.472	.895**	.995**	1	.503
	Sig. (2-tailed)	.200	.001	.000		.168
	N	9	9	9	9	9
PBDEs Cooler Dry Season	Pearson Correlation	-.121	.555	.517	.503	1
	Sig. (2-tailed)	.756	.121	.154	.168	
	N	9	9	9	9	9

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 7B: Correlation of PBDEs with physiochemiacal parameter in water during Short Rain Season

Correlations

		pH Short Rain Season	TSS Short Rain Season	TDS Short Rain Season	eC Short Rain Season	PBDEs Short Rain Season
pH Short Rain Season	Pearson Correlation	1	-.597	-.613	-.618	-.318
	Sig. (2-tailed)		.090	.079	.076	.405
	N	9	9	9	9	9
TSS Short Rain Season	Pearson Correlation	-.597	1	.839**	.835**	.648
	Sig. (2-tailed)	.090		.005	.005	.059
	N	9	9	9	9	9
TDS Short Rain Season	Pearson Correlation	-.613	.839**	1	1.000**	.379
	Sig. (2-tailed)	.079	.005		.000	.314
	N	9	9	9	9	9
eC Short Rain Season	Pearson Correlation	-.618	.835**	1.000**	1	.367
	Sig. (2-tailed)	.076	.005	.000		.331
	N	9	9	9	9	9
PBDEs Short Rain Season	Pearson Correlation	-.318	.648	.379	.367	1
	Sig. (2-tailed)	.405	.059	.314	.331	
	N	9	9	9	9	9

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 7C: Correlation of PBDEs with Physio-Chemical Parameter in Water during Hot Dry Season

Correlations						
		pH Hot Dry Season	TSS Hot Dry Season	TDS Hot Dry Season	eC Hot Dry Season	PBDEs Hot Dry Season
pH Hot Dry Season	Pearson Correlation	1	-.550	-.544	-.551	-.194
	Sig. (2-tailed)		.125	.130	.124	.617
	N	9	9	9	9	9
TSS Hot Dry Season	Pearson Correlation	-.550	1	.592	.597	.406
	Sig. (2-tailed)	.125		.093	.090	.279
	N	9	9	9	9	9
TDS Hot Dry Season	Pearson Correlation	-.544	.592	1	.999**	.454
	Sig. (2-tailed)	.130	.093		.000	.219
	N	9	9	9	9	9
eC Hot Dry Season	Pearson Correlation	-.551	.597	.999**	1	.444
	Sig. (2-tailed)	.124	.090	.000		.231
	N	9	9	9	9	9
PBDE Hot Dry Season	Pearson Correlation	-.194	.406	.454	.444	1
	Sig. (2-tailed)	.617	.279	.219	.231	
	N	9	9	9	9	9

**. Correlation is significant at the 0.01 level (2-tailed).

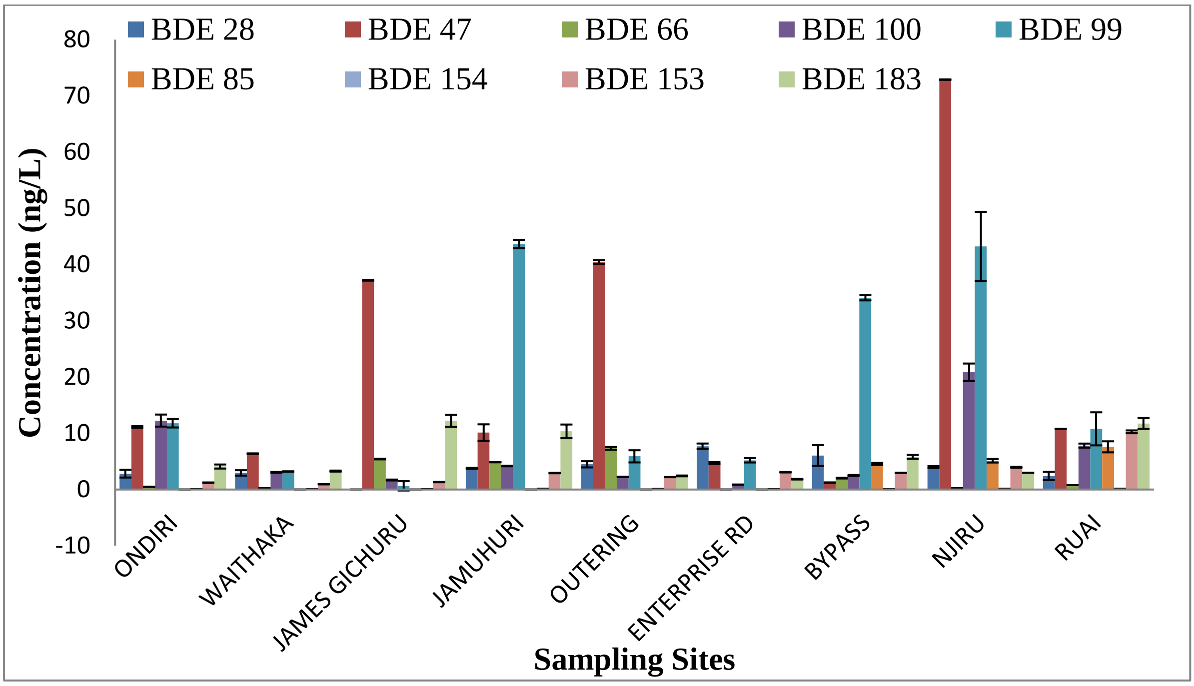
Appendix 7D: Correlation of PBDEs with Physio-Chemical Parameter in Water during Heavy Rain Season

Correlations						
		pH Heavy Rain Season	TSS Heavy Rain Season	TDS Heavy Rain Season	eC Heavy Rain Season	PBDEs Heavy Rain Season
pH Heavy Rain Season	Pearson Correlation	1	-.032	-.623	-.598	.276
	Sig. (2-tailed)		.934	.073	.089	.472
	N	9	9	9	9	9
TSS Heavy Rain Season	Pearson Correlation	-.032	1	.536	.529	.548
	Sig. (2-tailed)	.934		.137	.143	.127
	N	9	9	9	9	9
TDS Heavy Rain Season	Pearson Correlation	-.623	.536	1	.995**	.096
	Sig. (2-tailed)	.073	.137		.000	.806
	N	9	9	9	9	9
eC Heavy Rain Season	Pearson Correlation	-.598	.529	.995**	1	.119
	Sig. (2-tailed)	.089	.143	.000		.761
	N	9	9	9	9	9
PBDEs Heavy Rain Season	Pearson Correlation	.276	.548	.096	.119	1
	Sig. (2-tailed)	.472	.127	.806	.761	
	N	9	9	9	9	9

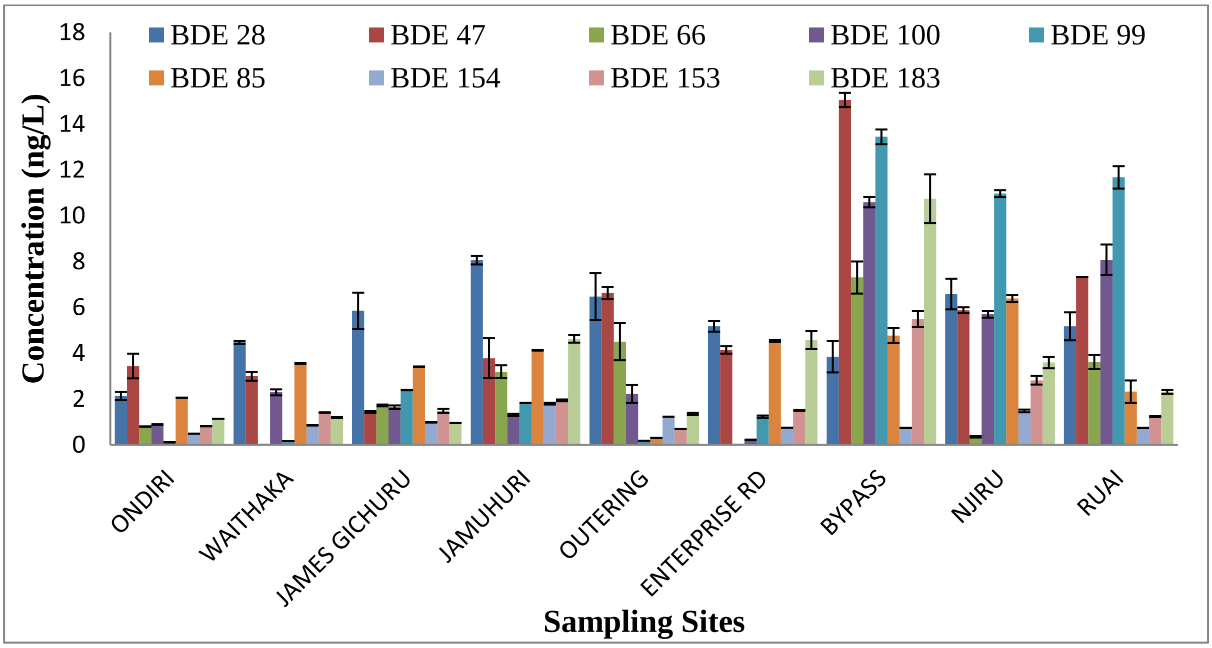
**. Correlation is significant at the 0.01 level (2-tailed).

Appendix 8

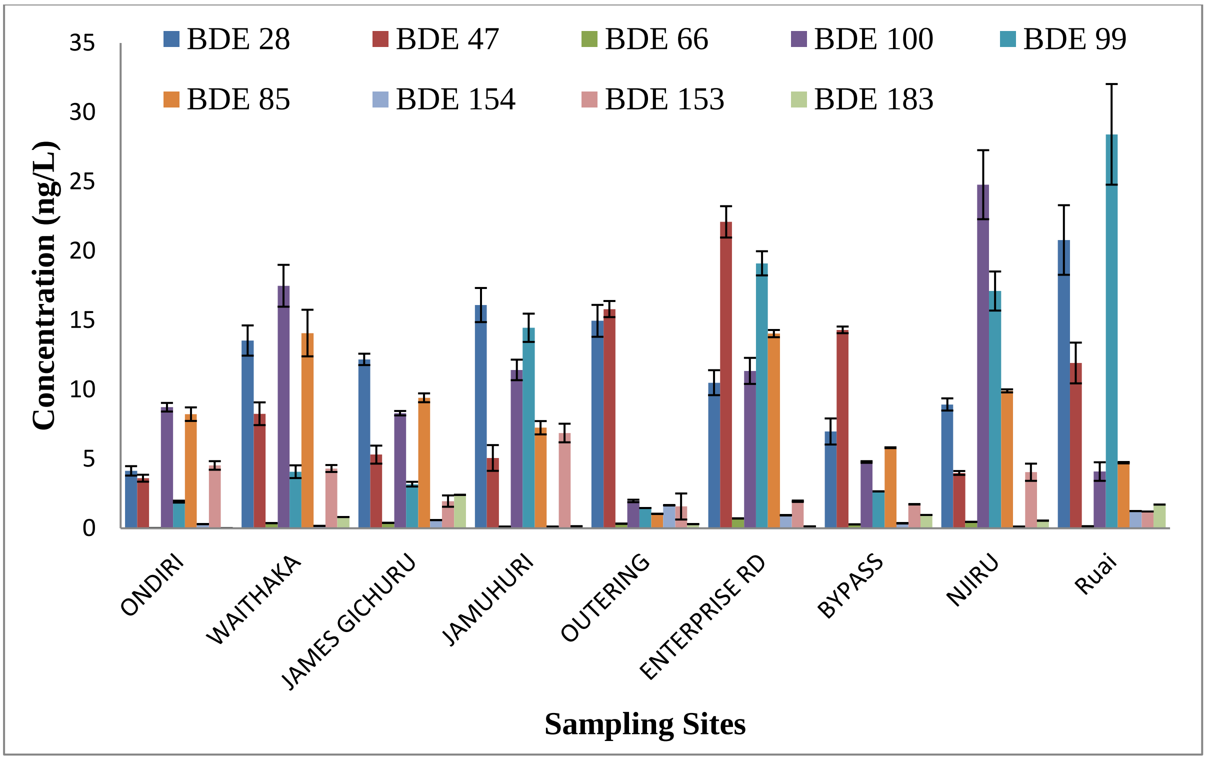
Appendix 8A: Mean Concentration of Polybrominated Diphenyl Ethers in Water per Site during the Cool Dry Season



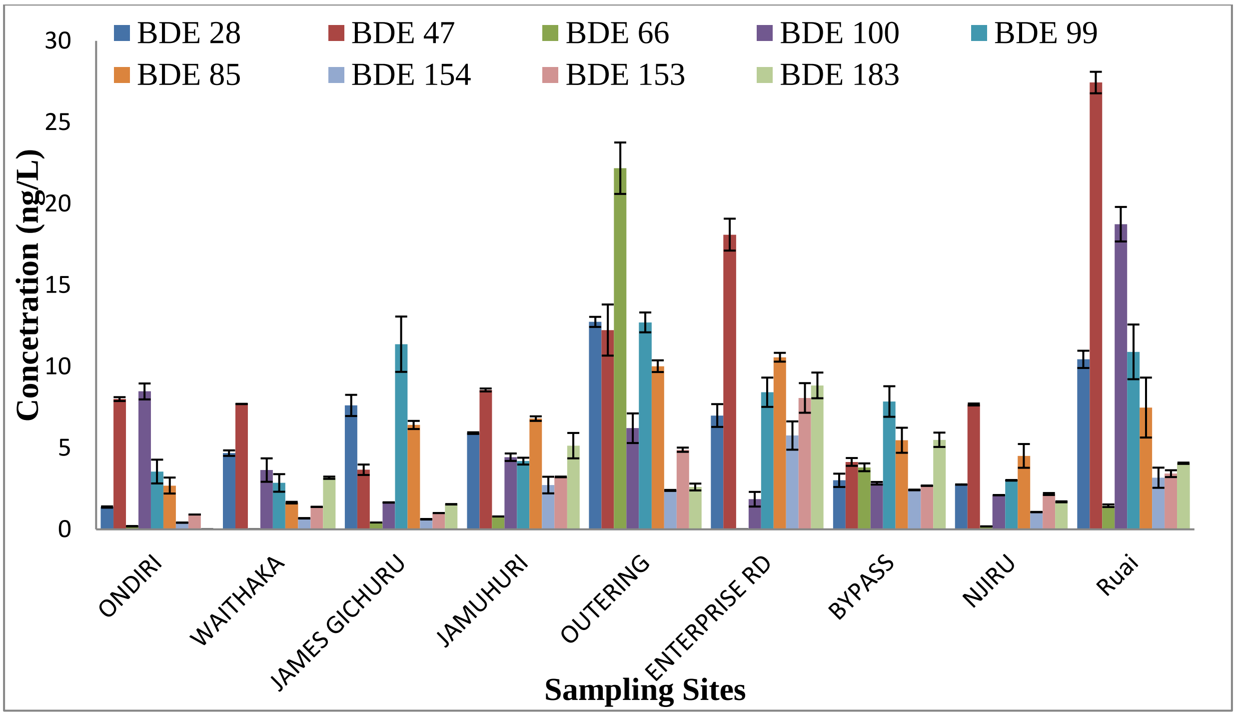
Appendix 8B: Mean Concentration of Polybrominated Diphenyl Ethers in Water per Site during Short Rain Season



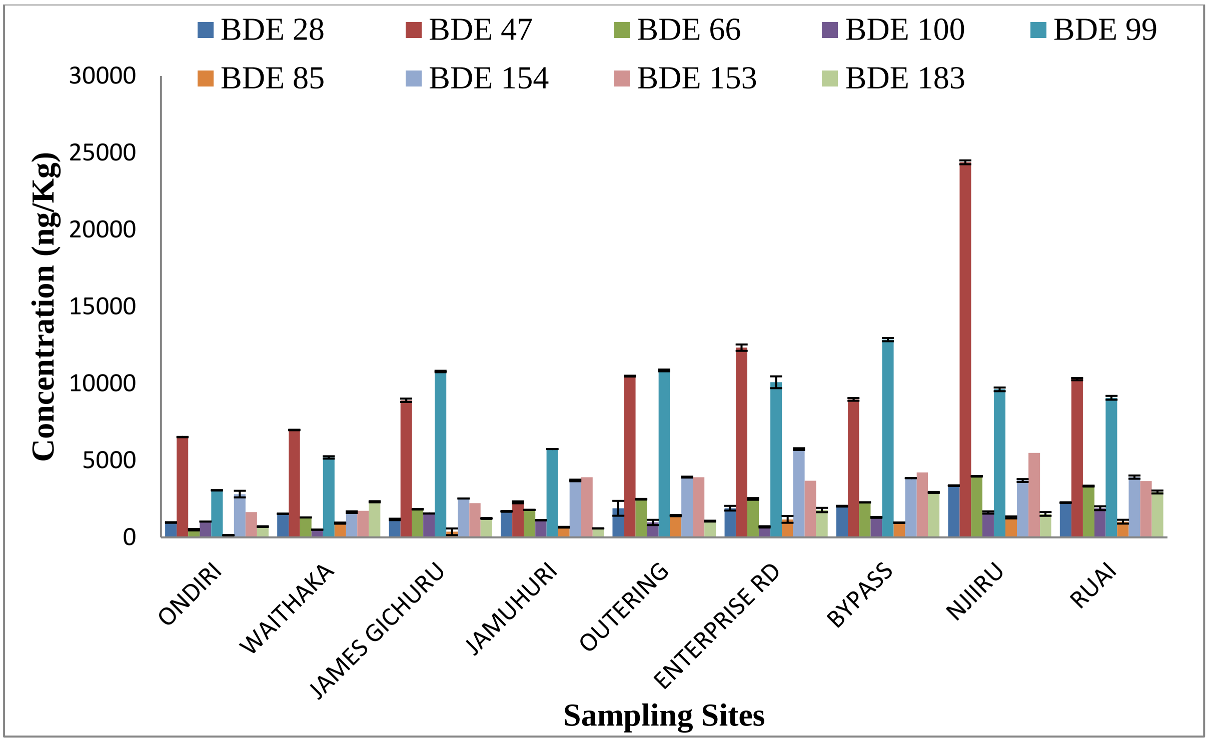
Appendix 8C: Mean Concentration of Polybrominated Diphenyl Ethers in Water per Site during Hot Dry Season



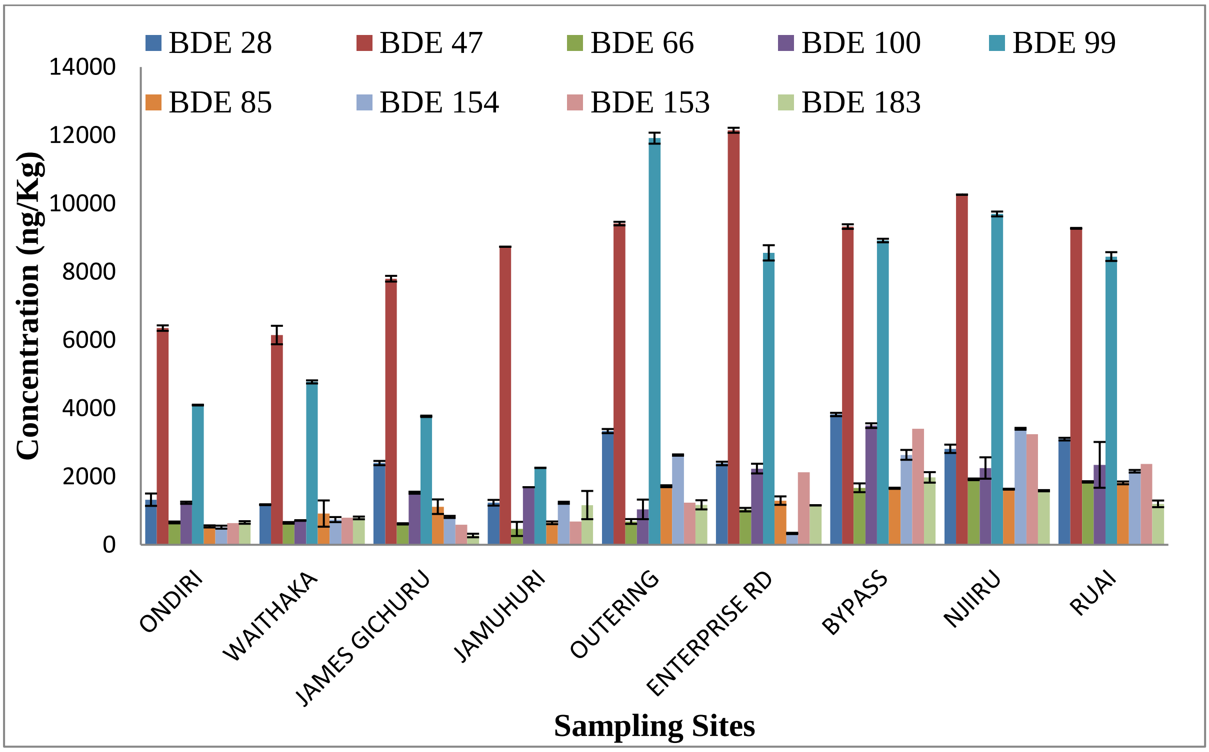
Appendix 8D: Mean Concentration of Polybrominated Diphenyl Ethers in Water per Site during the Heavy Rain Season



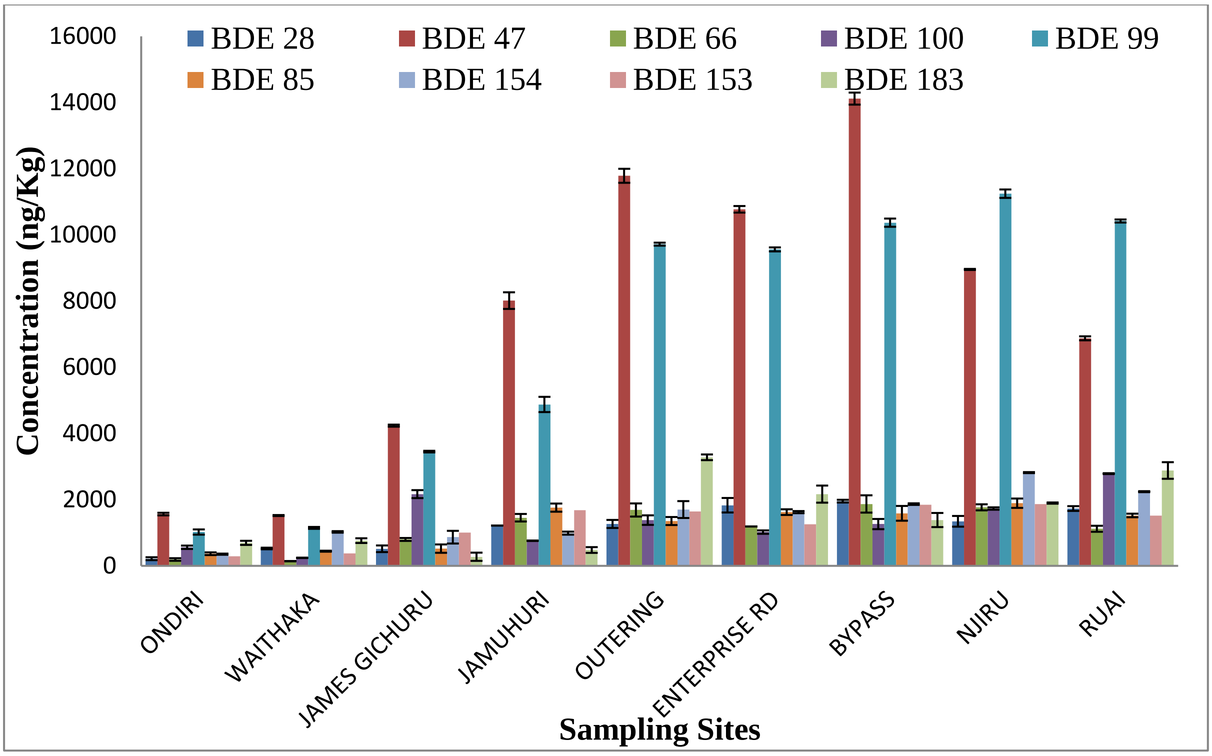
Appendix 8E: Mean Concentration of Polybrominated Diphenyl Ethers in Nairobi River Sediment per Site during the Cool Dry Season



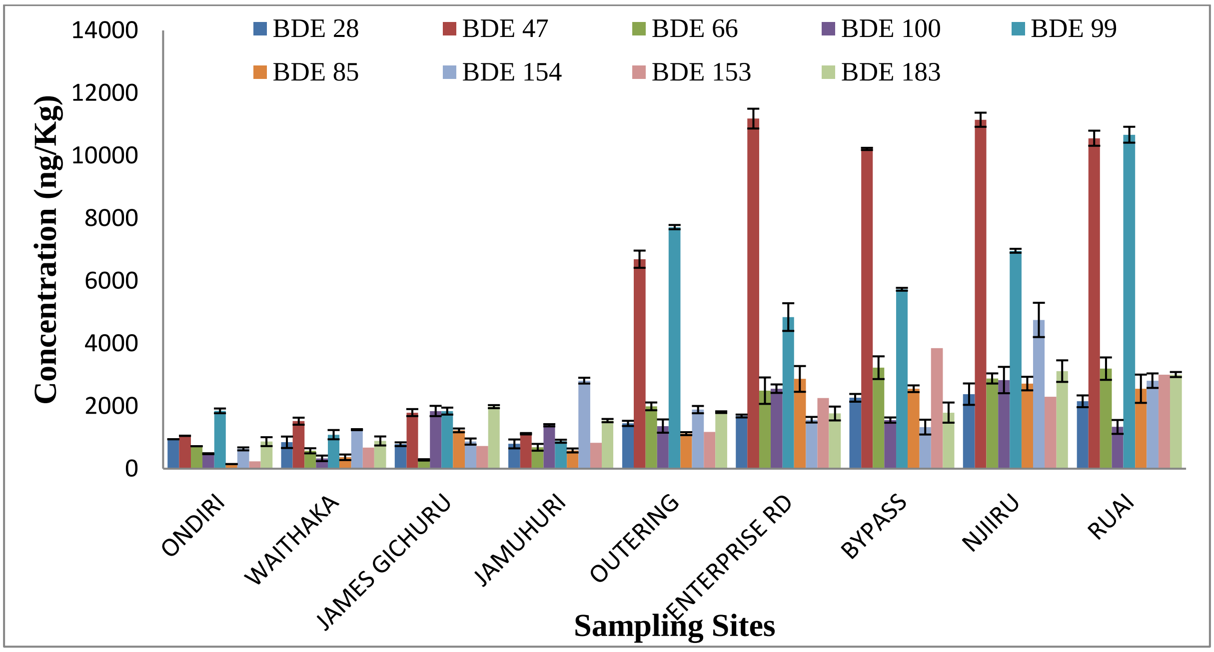
Appendix 8F: Mean Concentration of Polybrominated Diphenyl Ethers in Sediment per Site during the Short Rain Season



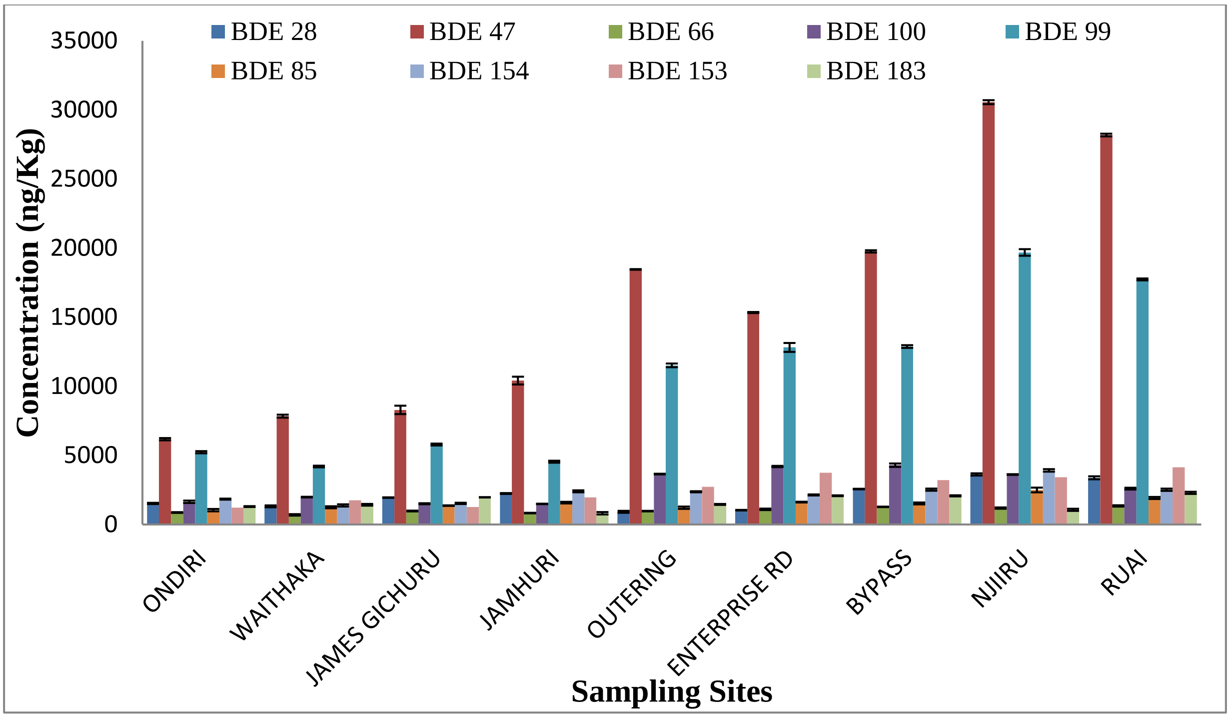
Appendix 8G: Mean Concentration of Polybrominated Diphenyl Ethers Residue Levels in Sediment per site during the Hot Dry Season



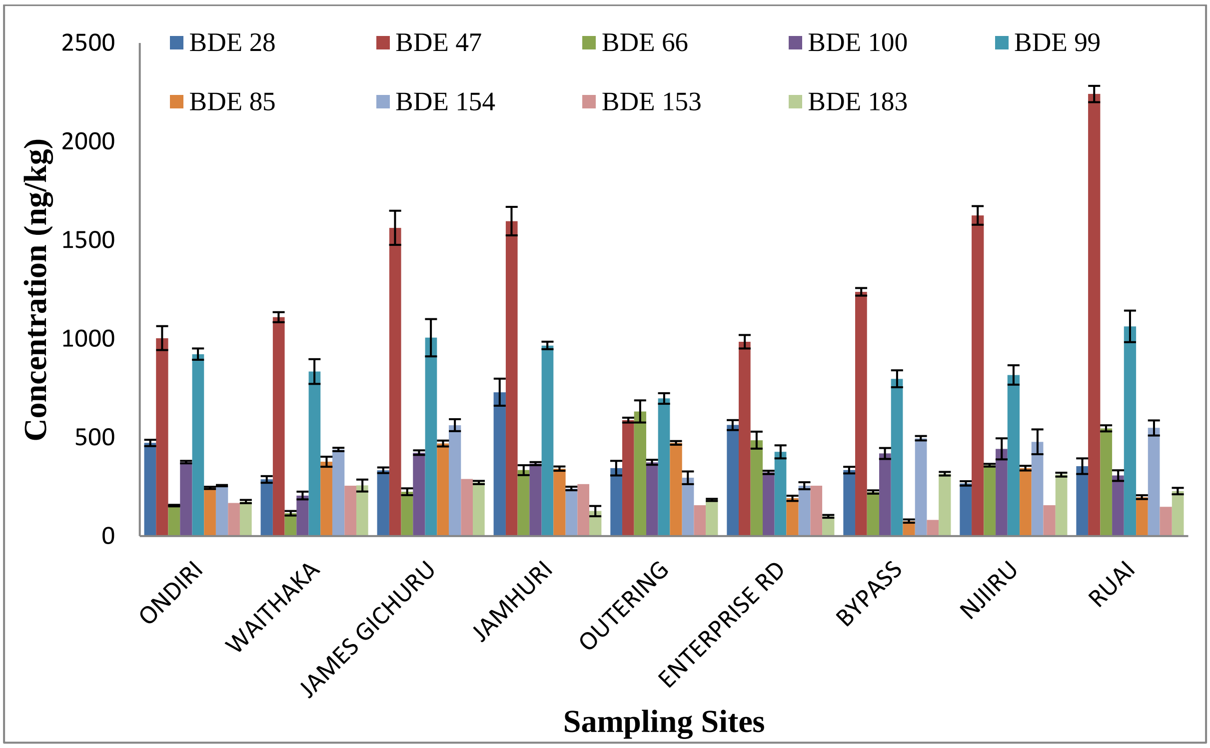
Appendix 8H: Mean Concentration of Polybrominated Diphenyl Ethers in Sediment per Site during Heavy Rain Season



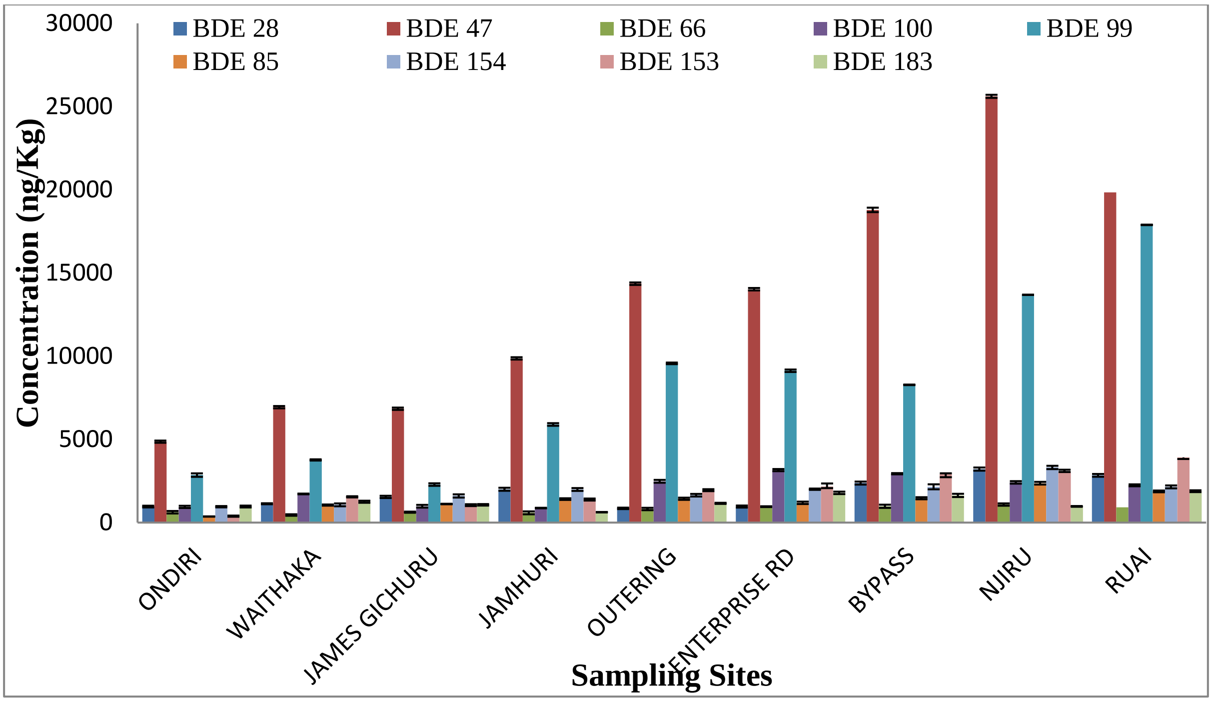
Appendix 8I: Mean Concentration of P Polybrominated Diphenyl Ethers BDEs in Nairobi River Basin Soil per Site during Cooler Dry Season



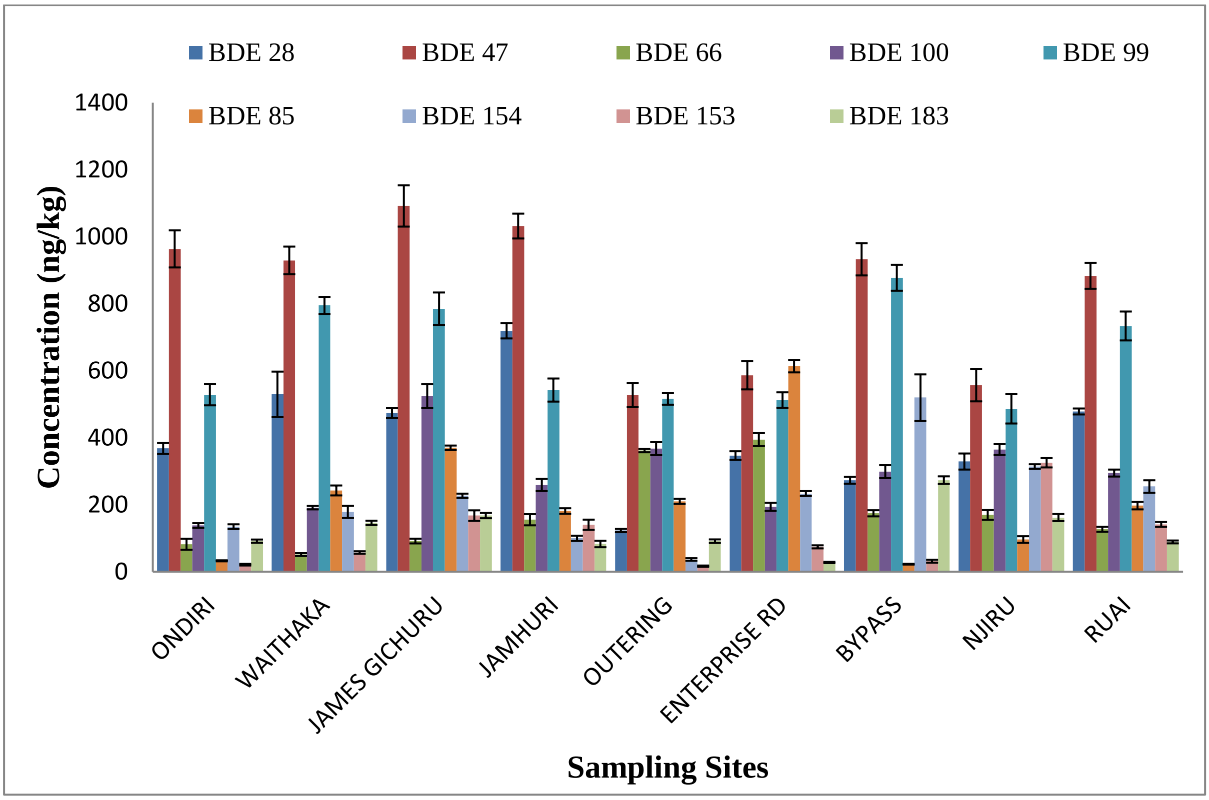
Appendix 8J: Mean Concentration of Polybrominated Diphenyl Ethers Residue Levels in Soil per Site during the Short Rain Season



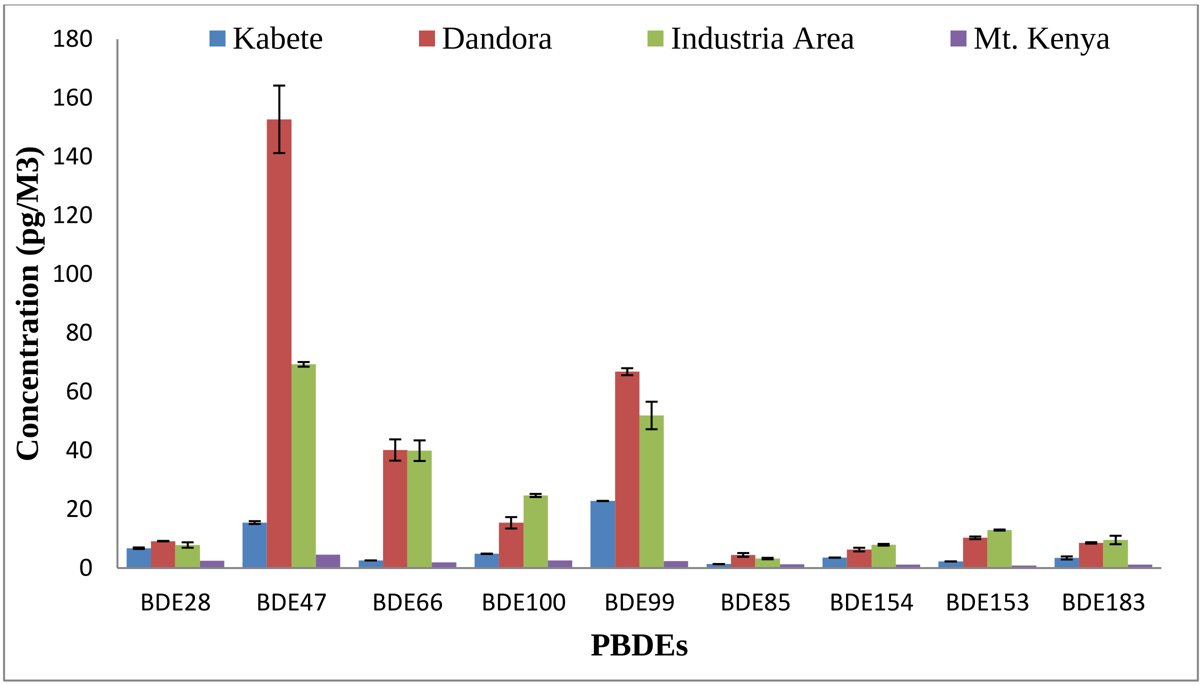
Appendix 8K: Mean Concentration of Polybrominated Diphenyl Ethers Residue Levels in Soil per Site during the Hot Dry Season



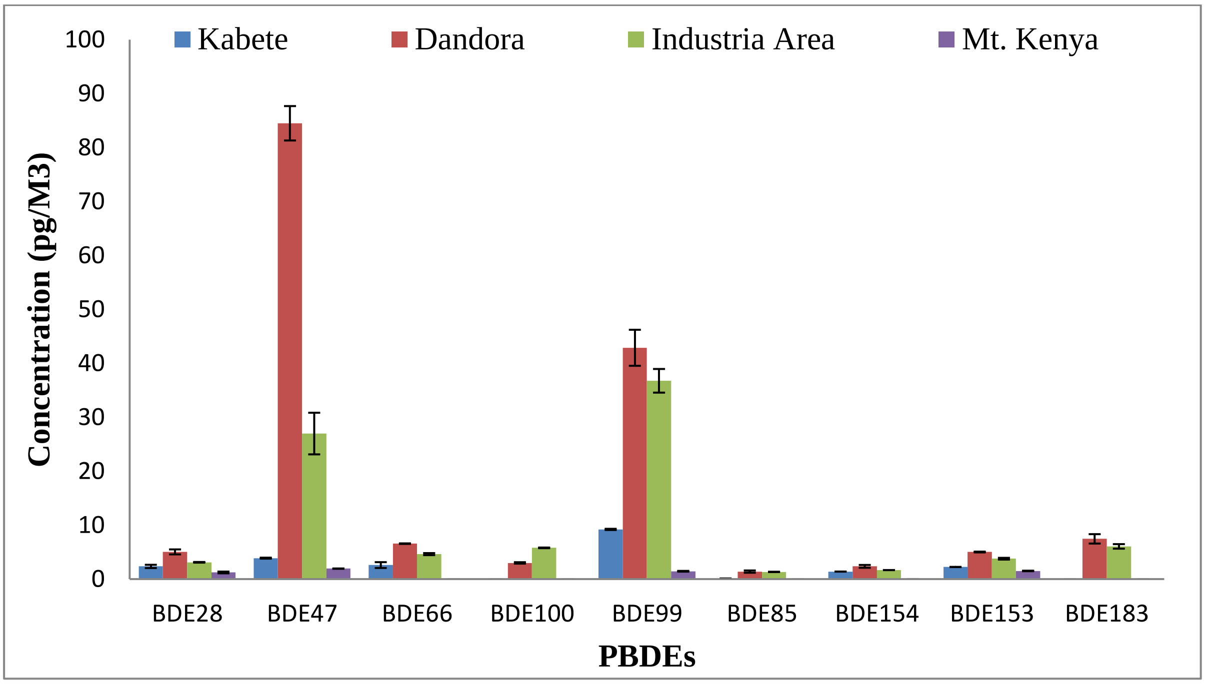
Appendix 8L: Mean Concentration of Polybrominated Diphenyl Ethers in Soil per Site during the Heavy Rain Season



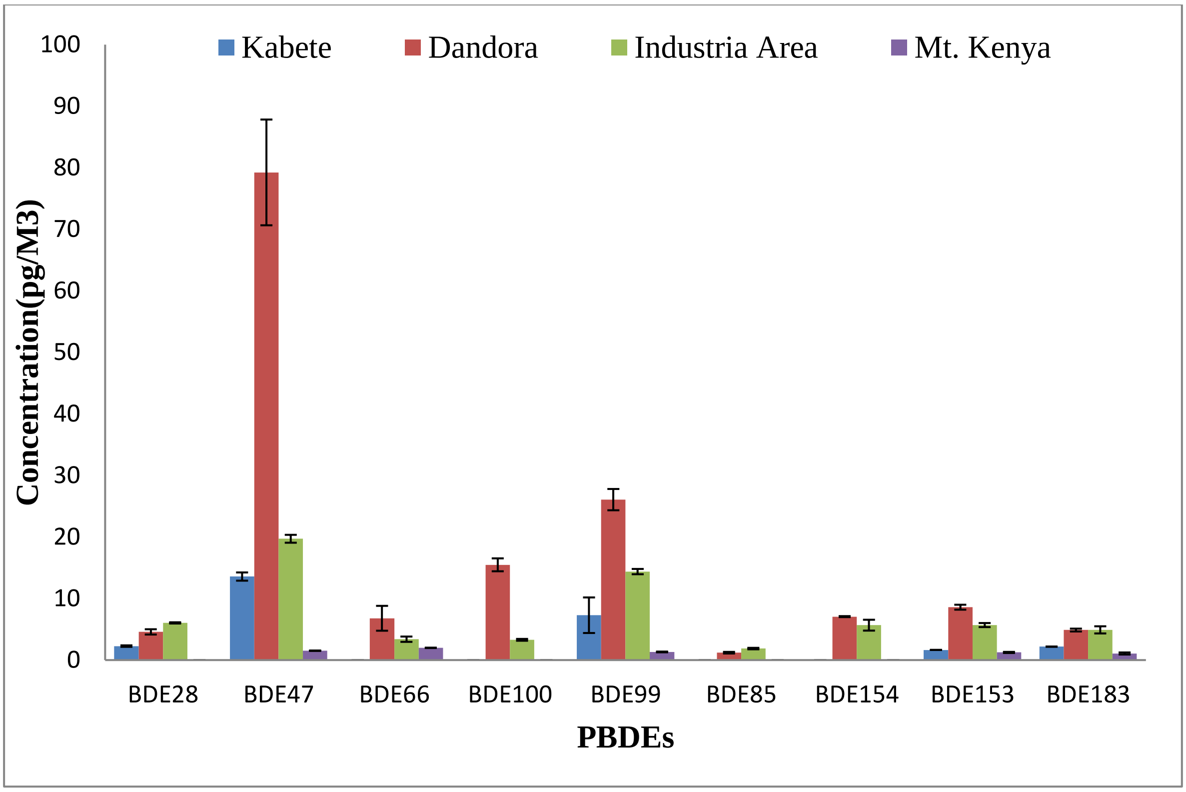
Appendix 8K: Mean Concentration of Polybrominated Diphenyl Ethers Residue in Air per Site during the Hot Dry Season



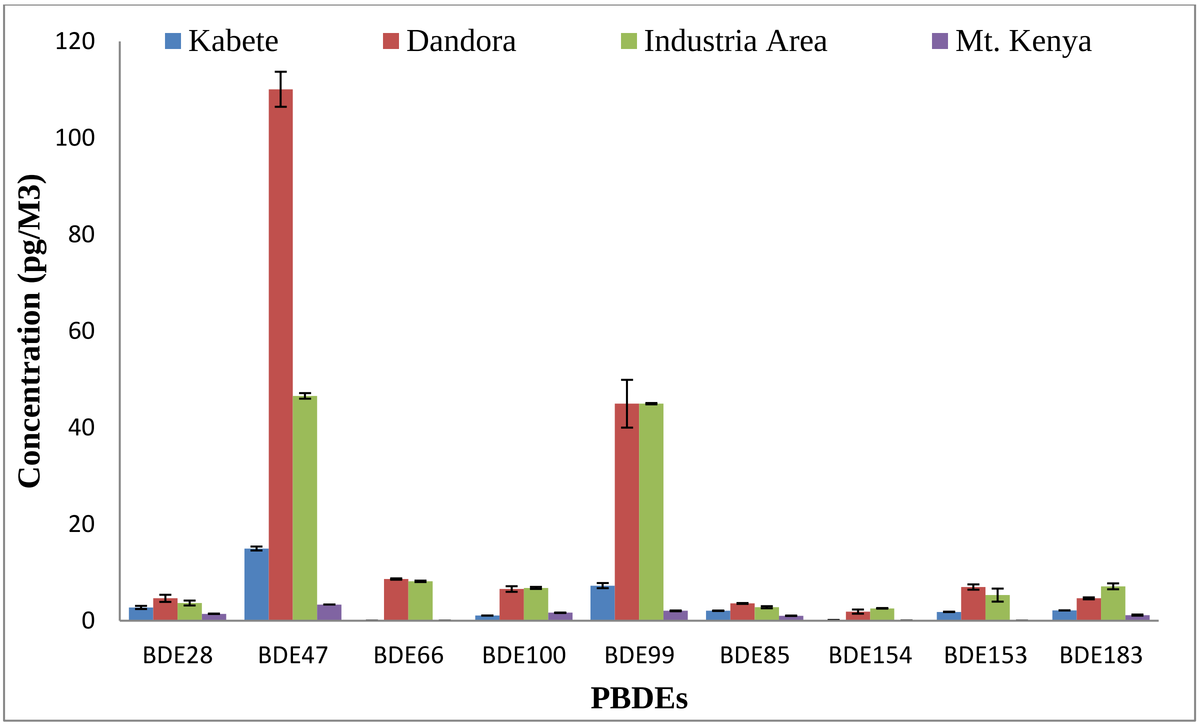
Appendix 8M: Mean Concentration of Polybrominated Diphenyl Ether Residue in Air per Site during the Heavy Rain Season



Appendix 8N: Mean Concentration of Polybrominated Diphenyl Ether Residue in Air per Site during the Cooler Dry Season



Appendix 8O: Mean Concentration of Polybrominated Diphenyl Ether Residues in Air per Site during the Short Rain Season



PUBLICATIONS FROM THESE WORKS

Enock M. Osoro, Shem O. Wandiga, Vincent O. Madadi, Deborah A. Abong'o (2021) Occurrence and Distribution of Polybrominated Diphenyl Ethers in Sediments from Nairobi River Basin, Kenya, East Africa. *International Journal of Scientific Research in Science, Engineering and Technology (IJSRSET*), 8 (1):274 - 286.

Enock M. Osoro, Shem O. Wandiga, Vincent O. Madadi, Deborah A. Abong'o (2021) Occurrence and Distribution of Polybrominated Diphenyl Ethers in Water from Nairobi River Basin, Kenya, East Africa. *Africa Journal of Physical Sciences*, 6, 1-14.

Enock M. Osoro, Shem O. Wandiga, Vincent O. Madadi, Deborah A. Abong'o (2021) Polybrominated Diphenyl Ethers Pollution in Urban and Rural Settings' Ambient Air in Kenya: An Insight into Concentration Levels, Compositional Profile and Seasonal Variation. *Africa Journal of Physical Sciences*. 6, 88-100.