



UNIVERSITY OF NAIROBI

**ASSESSMENT OF THE LEVELS OF BISPHENOL A AND DI-BUTYL
PHTHALATES IN WATER, SOIL, SEDIMENT AND WEEDS ALONG THE
COASTAL BEACHES OF KENYA.**

By

Emily Wanjiru Karanja

I56/8515/2017

**A thesis submitted in partial fulfilment of the Requirements for the award of the Degree
of Master of Science in Environmental Chemistry of the University of Nairobi**

2022

DECLARATION

I declare that this research thesis is solely my original work. It has not been submitted to any other university for the purpose of research or any other purposes. In instances where reference to other scholars' work has been used, clear acknowledgment as well referencing has been done following the guidelines set by the University of Nairobi.

Signature...  .

Date...4/12/2022

Emily Wanjiru Karanja

(I56/8515/2017)

Department of Chemistry,

University of Nairobi.

This thesis is submitted with our approval as university supervisors.

Signature...  .

Date...5/12/2022

Dr. Vincent O. Madadi

Department of Chemistry,

University of Nairobi.

Signature...  .

Date...4/12/2022

Dr. John M. Wanjohi

Department of Chemistry,

University of Nairobi.

Signature ...  .

Date... 4/12/2022

Dr. Deborah A. Abong'o

Department of Chemistry,

University of Nairobi.

DEDICATION

This research work is dedicated to my dear loving husband Simon Njoroge, my loving son Brevyn Braxton Mwangi and my caring parents Mr. & Mrs. Karanja Gacii and Serah Wanjiru.

ACKNOWLEDGEMENTS

Above all I thank God the Almighty for granting me the gift of life, wisdom, knowledge and grace to pursue my research project.

It is with sincere gratitude that I appreciate my supervisors; Dr. Vincent O. Madadi, Dr. Deborah A. Abong'o and Dr. John M. Wanjohi for their great patience, guidance, dedication, support, inspiration and for their persistent encouragement throughout the course of this study.

I am indebted to Dr. Enock Osoro for his support in the laboratory as he taught me how to operate the various laboratory equipment which culminated to obtaining accurate and precise results. I also thank Tom Mbewa, Simon Gikonyo, Eng. Petronilla Ogut, Eng F. Gitau, Eng. Peter kiarie and Eng. Isaac Mungamangi for their support.

I acknowledge the University of Nairobi for granting me the scholarship without which I would not have been able to undertake my studies.

Many thanks to the academic and technical staff of the Department of Chemistry, University of Nairobi, for their co-operation, encouragement and support during the course of this research work.

ABSTRACT

Plastic materials have a wide range of uses in the society today. However, large scale application of plastic materials has resulted into accumulation of wastes with potential toxic effect to human health and the environment. Plastic materials may contain a variety of toxic chemicals such as phthalates, heavy metals, BPA, brominated flame retardants, nonylphenol, polychlorinated biphenyl ethers among others. These compounds are known to induce ill health effects such as immune system suppression, tetragenic disorders, fetal developmental defects and cancer. The goal of this research was to determine the levels of Bisphenol A and Di-butyl phthalate in water, soil, sediments and sea weeds along the Kenyan coastal Beaches of Pirate, Mombasa, Kilifi, Malindi and Sabaki estuary. Sampling was done quarterly between the months of October 2018 and January 2019, covering the short rain and the dry season respectively. DBP and BPA analytes extraction from water samples was achieved by liquid-liquid extraction while from soil, sediment and sea weeds was by soxhlet extraction method using DCM solvent. Sample clean-up was conducted using chromatographic columns filled with silica gel while analysis of BPA and DBP was done using Agilent 6890 coupled to 5973 Mass Selective Detector. Electrical conductivity was lowest in Sabaki River water samples, followed by Sabaki Beach compared to other coastal Beaches while Ph was relatively similar for all the sites. DBP concentrations in water were $< 1.29 \pm 0.13$ ng/mL, soil ($< 39.75 \pm 0.91$ ng/g), sediments ($< 3.04 \pm 0.38$ ng/g) and sea weeds ($< 1.49 \pm 0.25$ ng/g). BPA levels were $< 2.74 \pm 0.57$ ng/mL (water), $< 3.39 \pm 0.14$ ng/g (soil), 0.10 ± 0.03 - 3.76 ± 0.17 ng/g (sediments) and $< 11.66 \pm 0.94$ ng/g (sea weeds). Pirate and Mombasa Beaches registered the highest levels of BPA and DBP in water samples, while the wet season had higher levels of pollution than the dry season. BPA levels in soil were higher than in water, sediments and sea weed samples during dry season as compared to the wet season. Concentrations of DBP and BPA residue levels in soil from Mombasa sites were higher in the dry season as compared to the wet season. According to the results, plastic pollution along Kenya's Beaches may be a factor in the occurrence of DBP and BPA in water, soil, sediments and sea weeds. Therefore, there is need for prudent management of plastic wastes and regular monitoring of pollution load along the coastal Beaches to protect human health and wildlife from toxic effects of ingredients from plastic wastes.

Key words: *Kenyan Coastal Beaches, Plastic pollution, BPA and DBP in water, soil, sediments and sea weeds.*

TABLE OF CONTENTS

DECLARATION	II
DEDICATION	III
ACKNOWLEDGEMENTS	IV
ABSTRACT	V
LIST OF TABLES	X
LIST OF FIGURES	XI
LIST OF ABBREVIATIONS	XII
UNITS OF MEASUREMENTS	XIII
CHAPTER ONE	1
1.0 INTRODUCTION	1
1.1 BACKGROUND INFORMATION	1
1.2 APPLICATION OF PLASTIC MATERIALS	2
1.3 PLASTIC POLLUTION	3
1.4 HEALTH AND ENVIRONMENTAL EFFECTS OF PLASTIC WASTES	4
1.5 STATEMENT OF THE PROBLEM.....	7
1.6 OBJECTIVES.....	7
1.6.1 <i>Main objective</i>	7
1.6.2 <i>Specific objectives</i>	7
1.7 JUSTIFICATION OF THE STUDY.....	8
CHAPTER TWO	9
2.0 LITERATURE REVIEW	9
2.1 EFFECT OF PLASTIC POLLUTION ON ENVIRONMENT	9
2.2 SIGNIFICANT PATHWAYS BY WHICH PLASTIC DEBRIS CAN AFFECT WILDLIFE	10
2.2.1 <i>Entanglement</i>	10
2.2.2 <i>Ingestion</i>	10
2.2.3 <i>Interaction</i>	11
2.3 THE EFFECTS OF WATER PH, ELECTRICAL CONDUCTIVITY (EC) AND TEMPERATURE ON ECOSYSTEM.....	11
2.3.1 <i>Effects of temperature on DBP</i>	12
2.3.2 <i>Effects of temperature on BPA</i>	13
2.3.3 <i>Soil and sediment characterization</i>	13
2.4 BISPHENOL A	14
2.4.1 <i>Uses of Bisphenol A</i>	15

2.4.2 Global production of Bisphenol A.....	15
2.4.3 Sources of Bisphenol A	16
2.4.4 Health effects of Bisphenol A	18
2.4.5 Studies of BPA conducted globally	19
2.5 PHTHALATES	21
2.5.1 Uses of Di-butyl phthalate.....	21
2.5.2 Plasticizers' mode of action.....	22
2.5.3 Global production of phthalates	22
2.5.4 Di-butyl phthalate	22
2.5.5 Uses of Di-butyl phthalate.....	23
2.5.6 Health effects of DBP	23
2.5.7 Sources of Di-butyl phthalates	24
2.5.8 Routes of exposure to DBP	25
2.5.9 Di-butyl phthalates studies conducted globally	25
2.6 POSSIBLE SOLUTION TO PLASTIC POLLUTION.....	26
2.7 RECYCLING PLASTICS	26
2.8 GAS CHROMATOGRAPH-MASS SPECTROMETRY AND ITS WORKING PRINCIPLE	27
2.9 COMPONENTS OF GAS CHROMATOGRAPH-MASS SPECTROMETRY	29
CHAPTER THREE.....	31
3.0 MATERIALS AND METHODS	31
3.1 STUDY DESIGN	31
3.2 CHEMICALS AND REAGENTS USED	33
3.3 INSTRUMENTS AND APPARATUS USED.....	34
3.4 SAMPLING	35
3.4.1 Sampling plan.....	35
3.4.2 Monitoring plastic litter at the shoreline of the six sampling sites	35
3.4.3 Collection of sediment samples.....	35
3.4.4 Collection of soil samples	36
3.4.5 Collection of sea weed samples.....	36
3.5 PHYSICAL-CHEMICAL PARAMETER DETERMINATION	36
3.5.1 Determination of electrical conductivity of the water samples and pH of water, soil and sediment samples	36
3.5.2 Water temperature measurement.....	37
3.5.3 Determination of organic content of soil and sediment samples.....	37
3.6 PREPARATION OF REAGENTS.....	38
3.7 EXTRACTION.....	39
3.7.1 DBP/BPA extraction from water samples.....	39

3.7.2 Extraction of DBP/BPA from soil, sediment and sea weed samples	39
3.7.3 Samples cleanup and fractionation	40
3.8 QUALITY ASSURANCE AND QUALITY CONTROL	40
3.9 QUALITATIVE CHARACTERISTICS	41
3.10 CHROMATOGRAMS	41
3.10.1 BPA and Di-butyl phthalate recovery levels	41
3.11 LIMITS OF DETECTION AND QUANTIFICATION OF BPA AND DBP	42
3.12 DATA ANALYSIS AND INTERPRETATION	42
CHAPTER FOUR	43
4.0 RESULTS AND DISCUSSION	43
4.1 WATER PHYSICAL-CHEMICAL PARAMETERS	43
4.1.1 The pH, EC and temperature in dry and wet seasons from the selected coastal Beaches	43
4.2 SOIL AND SEDIMENT PHYSICAL-CHEMICAL PARAMETERS	45
4.2.1 The pH, % organic content of soil, sediment and quantity of plastic litter in dry and wet seasons from the selected coastal Beaches	45
4.3 CALIBRATION CURVES FOR BPA AND DBP STANDARDS	47
4.3.1 Calibration curve for BPA standard	47
4.3.2 Calibration curve for DBP standard	48
4.4 LIMITS OF DETECTION AND QUANTIFICATION OF BPA AND DBP	49
4.5 MEAN PERCENTAGE RECOVERIES TESTS FOR BPA AND DBP IN WATER, SOIL, SEDIMENT AND SEA WEED SAMPLES	49
4.6 THE DBP LEVELS IN THE COASTAL BEACHES	50
4.6.1 The DBP levels in water, soil, sediment and sea weed samples in wet and dry season	50
4.6.1 DBP levels in water samples collected in wet and dry seasons	51
4.6.2 DBP levels in soil samples in wet and dry seasons	52
4.6.3 DBP levels in sediment samples in wet and dry seasons	53
4.6.4 DBP levels in sea weed samples in wet and dry season	54
4.7 THE BPA RESIDUE LEVELS IN WATER, SOIL, SEDIMENT AND SEA WEED SAMPLES FROM KENYAN COASTAL BEACHES	55
4.7.1 The BPA residue levels in water samples in wet and dry season	55
4.7.2 BPA residue levels in soil samples in wet and dry season	57
4.7.3 The BPA residue levels in sediments samples in wet and dry season	58
4.7.4 BPA residue levels in sea weed samples in wet and dry season	59
4.8 SEASONAL VARIATION EFFECTS ON DBP AND BPA RESIDUE LEVELS IN SOIL, SEDIMENTS AND SEA WEED SAMPLES IN WET AND DRY SEASON	60
4.8.1 The effects of seasonal variation on DBP residue levels in Soil, Sediments and Sea weed samples in wet and dry season	60
4.8.2 The effects of seasonal variations on BPA residue levels in soil, sediments and sea weed samples in wet and dry season	62

4.9 CORRELATION COEFFICIENCY OF DBP RESIDUE LEVELS IN WATER, SOIL, SEDIMENT AND SEA WEED SAMPLES	64
4.9.1 Correlation coefficient of DBP residue levels in water and sea weed samples in wet and dry season	66
4.9.2 Correlation coefficient of DBP residue levels in water and soil samples during dry and wet season	66
4.9.3 Correlation coefficient of DBP residue levels in water and sediment samples during dry and wet season	67
4.9.4 Correlation coefficient of DBP residue levels in soil and sediment samples in dry and wet season	67
4.9.5 Correlation coefficient of DBP residue levels in sediments and sea weed samples in dry and wet season	68
4.10 CORRELATION COEFFICIENCY OF BPA RESIDUE LEVELS IN WATER, SOIL, SEDIMENT AND SEA WEED SAMPLES	68
4.10.1 Correlation coefficient of BPA residue levels in water and sea weed samples in wet and dry season	68
4.10.2 Correlation coefficient of BPA residue levels in water and soil samples during dry and wet season	69
4.10.3 Correlation coefficient of BPA residue levels in water and sediments samples during the dry and wet seasons	69
4.10.4 Correlation coefficient of BPA residue levels in soil and sediments samples during dry and wet season	69
4.10.5 Correlation coefficient of BPA residue levels in sediments and sea weed samples during dry and wet season	69
4.11 CORRELATIONS COEFFICIENCY OF PLASTIC WEIGHT, NUMBER OF PLASTICS AND % SOIL ORGANIC CARBON IN WET AND DRY SEASON	71
4.12 CORRELATIONS COEFFICIENCY OF PLASTIC WEIGHT, NUMBER OF PLASTICS AND % SEDIMENT ORGANIC CARBON IN WET AND DRY SEASON	72
4.13 DISCUSSION OF RESULTS	73
CHAPTER FIVE	75
5.0 CONCLUSION AND RECOMMENDATIONS	75
5.1 CONCLUSION	75
5.2 RECOMMENDATIONS	76
5.2.1 Policy recommendations	76
5.2.2 Research recommendations	76
REFERENCES	77

LIST OF TABLES

Table 3.1 The altitude, coordination and human activities near the sampling sites.	336
Table 4.1 Water Physical-chemical parameters recorded during wet and dry season from the selected coastal beaches.	448
Table 4.2 Physical-chemical parameters of soil and sediment samples in wet and dry seasons	50
Table 4.3 Concentrations and peak area for BPA standard	52
Table 4.4 Concentrations and Peak area for DBP standard	54
Table 4.5 The limit of detection and Quantification of BPA and DBP	55
Table 4.6 Mean percentage recovery tests for BPA and DBP in Water, Soil, Sediment and Weeds samples.....	55
Table 4.7 DBP levels in water, soil, sediment and weeds samples in wet and dry seasons ...	57
Table 4.8 BPA residue levels in water, soil, sediment and weeds samples in wet and dry season.	62
Table 4.9 Correlations coefficient of DBP residue levels in water, soil, sediment and weeds samples in the wet and dry season.	71
Table 4.10 Correlations coefficient of BPA residue levels in water, soil, sediment and weeds samples in wet and dry season.	75
Table 4.11 Correlations coefficient of plastic weight, number of plastics and % soil organic carbon in wet and dry season.	717
Table 4.12 Correlations coefficient of plastic weight, number of plastics and % sediment organic carbon in wet and dry season.	728

LIST OF FIGURES

Figure 2.1 Chemical structure of Bisphenol A	14
Figure 2.2 Synthesis of Bisphenol A from acetone and phenol.....	15
Figure 2.3 Reaction of Bisphenol A and phosgene to form polycarbonate	16
Figure 2.4 General structure of phthalate.....	22
Figure 3.1 Map of Kenyan Coastal beaches showing sampling sites	32
Figure 4.1 The Calibration curve for BPA standard.....	53
Figure 4.2 Calibration curve for DBP standard.	49
Figure 4.3 DBP levels in water samples in the wet and dry season.....	52
Figure 4.4 DBP residue levels in soil samples in the wet and dry seasons.....	53
Figure 4.5 DBP residue levels in sediment samples in wet and dry season	60
Figure 4.6 DPB levels in weed samples in wet and dry season.....	61
Figure 4.7 BPA residue levels in water samples in wet and dry season	63
Figure 4.8 BPA residue levels in Soil samples in wet and dry season	64
Figure 4.9 The BPA residue levels in Sediment samples in wet and dry season	65
Figure 4.10 The BPA residue levels in weed samples in wet and dry season	66
Figure 4.11 The variation of DBP residue levels in soil, sediment and weeds samples in the season.....	67
Figure 4.12 The variation of DBP residue levels in soil, sediment and weeds samples in dry season.....	68
Figure 4.13 Variation of BPA residue levels in soil, sediment and weed samples in wet season.....	69
Figure 4.14 Variation of BPA residue levels in soil, sediment and weeds samples in dry season.....	70

LIST OF ABBREVIATIONS

BPA	Bisphenol A
CDCP	Centers for Disease Control and Prevention
DBP	Di-Butyl Phthalate
ECA	European Chemicals Agency
EDC	Endocrine-Disrupting Chemical
FDA	Food and Drug Administration
GC-MS	Gas Chromatography-Mass Spectrometry
ISWM	Integrated Solid Waste Management
LMW	Lower Molecular Weight
PAEs	Phthalate Esters
PVC	Polyvinyl Chloride
UN	United Nations

UNITS OF MEASUREMENTS

g	Grams
Kg	Kilograms
μg	Microgram
nm	Nanometre
mL	Millilitre
L	Litre
μL	Microlitre
μS	Micro Siemens
ppm	Parts per millions
ppb	Parts per billion
ηg	Nanogram

CHAPTER ONE

1. INTRODUCTION

1.1 Background information

The International Council of Chemical Associations (ICCA) report estimated the contribution of chemical industry to the global economy amounted to be 5.7 trillion USD to gross domestic product (GDP) in 2019 (Li *et al.*, 2021). In addition, the chemicals industry also supported 120 million jobs in the same year (Kircher, 2019). Chemical products are widely used in energy, transport, information & communication technologies (ICT), construction sectors among others (Pethrick *et al.*, 2013).

Diverse groups of chemicals products include; plastics, fertilizers, pesticides, paints, coatings, soaps, detergents, pharmaceuticals, personal care products and petrochemical (Sauders, 2012). These products are known to have a broad influence on the everyday life. For instance, products like automobile polymers are required to be stronger, lighter, as well as readily recyclable (Yang *et al.*, 2012). Since polymers are lighter, stronger, and have the ability to save fuel in addition to generally improving safety and performance, they are used extensively in the aerospace sector. Manufacture of improved polymers permit the safe delivery of diverse types of foods stuff across the globe. As noted by Song *et al.* (2015), packaging materials that are recyclable as well as degradable are key in reversing the unwanted build-up of various solid waste within industrialized societies. Regardless of the significance of plastic packaging materials' inability to degrade, there is a need for new goods that are competitive in the market. (Garretti and Taisch, 2012). Plastics are among the major groups of chemical based products that have captured the world attention.

Globally, the production of plastics has risen immensely (North and Halden, 2013). The United Nations Environmental Program (UNEP) predicts a rise in production of plastics to 619 Million tons by the year 2030 (UN Environment, 2016). Currently, rapid growth in population, urbanization and industrialization contribute to large scale production of plastic wastes in marine and terrestrial environment (Andrady and Neal, 2009).

1.2 Application of plastic materials

Plastics are macromolecules formed through the process of polymerization and can be shaped through the application of a reasonable amount of heat and pressure or alternative forms of forces (Sukanto *et al.*, 2021). They consist of substances such as carbon, hydrogen, oxygen, nitrogen, chlorine, and sometimes sulfur (Kumar *et al.*, 2011). There are two classes of plastics namely; thermoplastics and thermosetting plastics (Sukanto *et al.*, 2021).

Plastics that can be shaped into desired shapes under heat plus pressure and solidify on cooling are called thermoplastics Sukanto *et al.* (2021) and examples include polyethylene, polystyrene, and polyvinylchloride. Thermosetting materials are those that heat cannot be used to soften or remold into other shapes and include compounds like phenol-formaldehyde as well as Urea-formaldehyde (Sukanto *et al.*, 2021). Thermoplastics and thermosetting materials form 80% and 20% of total plastics used, respectively (Sukanto *et al.*, 2021). In the environment, thermoplastics are not readily biodegradable resulting in plastic litters persisting for long in the environment (Teuten *et al.*, 2009).

Plastic materials are widely preferred because they are cheap, light weight, easily made, strong, adaptable, economical and requires minimal energy to yield than different materials like glass or metal (Andrady and Neal, 2009). Plastics can be processed to acquire various characteristics in terms of durability, resistance, corrosion, and thermal & electrical conductivity (North and Halden, 2013). Global concern about plastic is motivated by the adverse impact of these materials on the environment and human health.

The benefits accrued from plastics contributed to the production bloom of various plastic products in the 21st century (North and Halden, 2013). Disposable syringes, intravenous bags, sterile packaging for medical equipment, joint replacements, and tissue engineering are just a few examples of the wide range of plastics applications in the field of health. Non medical applications include in transport, building, agriculture, information technology, packaging materials for water, food, drink and other goods (Andrady and Neal, 2009).

Tanks used in water supply systems and other forms of storage are frequently made of plastic. They are also frequently used in cars and airplanes to substitute metals (Fan and Njuguna, 2016).

Plastic materials are widely applied in protective clothing as well as safety equipment such as fireproof, helmets, and air bags that ensure people are protected from injury (Andrady and Neal, 2009).

Additionally, a lot of plastic is utilized to make prosthetics, throw away syringes, tubing and blood bags (Andrady and Neal, 2009; Muncke, 2009). Wide application of plastics in production of disposable plastic items such as latex gloves, intravenous bags, dialysis tubes has been linked to their inexpensive nature, safety of patients and time saving by overall elimination of sterilization process (Muncke, 2009).

1.3 Plastic pollution

The accumulation of plastic materials within the environment is referred to as plastic pollution and it causes adverse effects on wildlife and human health (Thompson *et al.*, 2009). Plastic wastes are among the greatest sources of global marine pollution (Rebolledo *et al.*, 2013). When microplastics wash down the drain, they pollute the environment by spreading far across the ocean (Alimba and Faggio, 2019). Diverse sources of microplastics include runoffs from agriculture, aquaculture, cruise ships, dumping in the oceans, storm water, industries such as shipping and fishing, runoffs from urban centers, as well as general waste management (Thompson *et al.*, 2009).

Plastic pollution occurs in diverse forms which include littering, marine debris, plastic particles and plastic netting (Bråte *et al.*, 2017). Debris can be explained as waste originating from man activities that are released into the waterways, sea, ocean or lake (Rebolledo *et al.*, 2013). The debris forms of plastics wastes that pollute environment are classified into three: micro-, meso-, and macro debris (Thompson *et al.*, 2009). According to Claessens *et al.* (2011), plastic debris undergoes fragmentation at various environmental levels such as sea resulting in the formation of microscopic particles of plastics that are referred to as ‘microplastics’. The buoyant, as well as persistent properties of the microplastics, enables them to disperse widely across the marine environment through hydrodynamic and ocean current processes.

1.4 Health and environmental effects of plastic wastes

Despite the clear usefulness of plastic materials, some ingredients used in the manufacture of the materials are non-biodegradable, and toxic to human health and environment (Reddy *et al.*, 2014; North and Halden, 2013). The world is currently grappling with management of large amounts of wastes in the environment since only a small portion is recycled (Andrady and Neal, 2009).

Plastic materials pose twofold challenges in terms of production and disposal (Thompson *et al.*, 2009). The growth witnessed in plastic production and consumption globally pose environmental and health threats especially to developing countries, that often lack adequate plastic management facilities, leading to dispose of such materials in the open environment (Teuten *et al.*, 2009). In addition, to the negative impact that plastic production and disposal have on the environment, there are also several health threats connected to the use of this material (Thompson *et al.*, 2009). In most instances, plastics are used in a mixture with other products like resins used as additives for enhancing performance, but eventually contribute to environmental pollution (Teuten *et al.*, 2009). This happens when plastics release compounds used in the manufacture of plastic materials (Siddique *et al.*, 2008). Environmental pollution through the leaching of chemicals from plastic materials into food, beverages, air, soil in addition to water has currently emerged as an area of concern (Siddique *et al.*, 2008). The greatest health concern relating to the usage of plastic is the chemical migration that can occur amid plastic packaging and its content, allowing these toxic additives to leak and contaminate the packaged products (Muncke, 2009). The leached compounds include BPA and polybrominated diphenyl ether (Hahladakis *et al.*, 2018). The use of plasticizers as an additive renders the material flexible, fire resistant and UV stable to prevent degradation when exposed to sunlight (Hahladakis *et al.*, 2018). Phthalate plasticizers such as 1,2-benzenedioic acid or phthalic acid are used to enhance plasticity of industrial polymers (Meeker *et al.*, 2009) for industrial and commercial products. Phthalic esters are key in production of flexible vinyl plastics that are employed as chemical additives in gel capsules, cosmetics and self-care products (Hahladakis *et al.*, 2018). Phthalates are also widely found in various medical devices, automobile materials, materials used in floors of buildings, computer materials, perfumes and cosmetics (Meeker *et al.*, 2009).

The production of epoxy resins, as well as polycarbonate plastics products uses BPA as the main chemical agent. The chemical agent is equally used in the production of the water bottle, as coating for various dental sealants, in food or beverage containers, as well as linings cans used for food packaging (Mikołajewska *et al.*, 2015). Diverse effects on health like obesity and heart disease have been linked to exposure to BPA (Muncke, 2009). In general, higher health effects concerns have been raised in infants and young children exposed to BPA. This has been associated with their undeveloped body systems to remove toxins from their bodies (Vanderberg *et al.*, 2007). Barraza (2013) asserts the overall need of developing regulatory actions to protect the general public health as well as vulnerable individuals such as fetuses, infants, as well as children from the listed negative outcomes of exposure to BPA.

DBP is a significant chemical additive in special paints as well as in adhesives (Meeker *et al.*, 2009). DBP is known to be a teratogenic compound to various aquatic organisms (Howdeshell *et al.*, 2007). The toxic properties of DBP are due to its high rate of bioaccumulation that ranges between 100 and 3000 mg/L in diverse organisms raises more concern (Xu *et al.*, 2008). DBP is a stable compound within natural environment and its half-life time was appraised to be around twenty years (Du *et al.*, 2015). Studies of biodegradation of DBP within fresh waters, marine waters, sediments, wastewaters as well as sludge reported reduced degradation rate ranging from a few days to months (Du *et al.*, 2015). As a result, DBP is discharged into the natural habitat in the course of production process as well as through disposal causing leaching from the disposed plastic (Janjua *et al.*, 2007). While these plasticizing agents impact beneficial properties, leaching of phthalates out of products occurs easily and thus contaminating the external environment. This is since they aren't chemically bound to the plastic matrix or different chemical formulations (Heudorf *et al.*, 2007).

The epoxy resins, polycarbonate plastics production and brominated flame retardants use Bisphenol A as one of the key compounds (Andrady and Neal, 2009). BPA functions as a monomer rather than an additive in the manufacture of polycarbonate plastics that are in most cases good for food as well as beverage contacts and other products (Tsai, 2006). Furthermore, BPA has wide use in manufacturing transparent and hard polycarbonate plastics as well as strong epoxy coatings including adhesives. They can be found in the linings of food cans, medical equipment, compact discs, and packing bottles (Tsai, 2006). The principal human exposure to

BPA is by mouth through ingestion of plastic packed foods, such as plastic bottles and the lining of epoxy in metal cans of food and beverages (Le *et al.*, 2008).

Many additives like BPA and phthalates are well-known to be toxic (Vandenberg *et al.*, 2007). Once the additives are released into the atmosphere, they have the general potential for long-range transport, thus eventually entering the food chain (Fu and Kawamura, 2010). Their repeated exposure to the environment has been proved to pose health threats to humans (Kabir *et al.*, 2015). The European Food Safety Authority (2018) established a Tolerable Daily Intake or “TDI” for BPA of 4 micrograms per kg/day and a Specific Migration Limit or “SML” of 0.05 mg of BPA per kg of food (Almeida *et al.*, 2018). BPA compounds have all been detected in humans and their effect on humans is established as disruption of the endocrine system (Kabir *et al.*, 2015). Endocrine disruptors are compounds that are known to mimic or antagonize the activities of normal estrogens (Muncke, 2009). The compounds can alter the hormonal system that is involved in several biological metabolisms thus producing huge health-related complications (Kabir *et al.*, 2015). The health problems include early puberty in the females, reduced sperm levels of males, alteration of reproductive functions, and obesity (Kabir *et al.*, 2015). Moreover, health issues like alteration on gender behaviors, and increased risks of acquiring cancers of different types such as breast, ovarian, testicular, and prostate cancers (Thompson *et al.*, 2009). In women, BPA mimics the hormone estrogen (Almeida *et al.*, 2018). Children and women who are at the productive age are most vulnerable to the hormone-disrupting nature of BPA as explained by Vandenberg *et al.* (2007). The hormone disruption of these compounds is not limited to humans only but to animals also (Rochman *et al.*, 2013). The animals affected by this hormonal disruption live within terrestrial, aquatic, and marine habitats (Canesi and Fabbri, 2015). Once these chemicals enter the body through food packaging materials or any other kind of plastic objects, they can interfere with the production of hormones in the body (Gall and Thompson, 2015). Because of the diverse ecological and human health associated with chemical pollution, countries are required to embrace sound management of chemical substances. This can be done via Strategic Approach to International Chemicals Management (SAICM) as well as various activities under Sustainable Development Goals (SDG) 12 for sustainable production and consumption (Hub, 2019).

1.5 Statement of the problem

Plastic pollution has become a global environmental challenge due to the associated release of hazardous compounds into the environment (Kabir *et al.*, 2015; Thompson *et al.*, 2009). The extensive use of plastics that are disposable in delivering products that are used once like bottled water, wrappers, and disposable cups has led to environmental pollution due to the leftover of plastics. Measurable levels of BPA, as well as phthalate, have been recorded in the urine (North and Halden, 2013). Disposal of plastic wastes is a major cause for environmental concern, with its potential to release chemical contaminants that are carcinogenic to humans, causing birth defects, suppression of the immune system, and endocrine disruption (Kabir *et al.*, 2015). Likewise, whenever plastic materials are dumped into marine environments, several species of organisms are harmed due to entanglement and ingestion of plastic litter (Nelms *et al.*, 2016). Consequently, this study seeks to determine concentrations of BPA and DBP in soil, sediment, sea weeds and water along coastal beaches of Kenya to minimize plastic pollution in our environment.

1.6 Objectives

1.6.1 Main objective

To determine the impact of plastic pollution on the levels of BPA and DBP along the coastal Beaches of Kenya.

1.6.2 Specific objectives

1. To determine levels of selected water physical-chemical parameters, pH, EC and temperature, in the wet and dry seasons from the selected coastal Beaches.
2. To determine the residue levels of DBP in the water, soil, sediment and weeds in wet and dry seasons from the selected coastal Beaches of Pirate, Mombasa, Kilifi, Malindi, Sabaki, Sabaki River mouth and Sabaki River.
3. To determine the BPA residue levels in water, soil, sediment and sea weeds in wet and dry seasons from the selected coastal Beaches.

4. To determine the effects of seasonal changes on the levels of DBP and BPA in water, soil, sediments and sea weed samples from coastal Beaches.

1.7 Justification of the study

Poor management of plastic wastes lead to unwanted exposure to endocrine-disrupting chemicals such as Bisphenol A as well as Di-butyl phthalate to humans and the environment (Aurah, 2013). As such, related concerns regarding health effects of BPA has made several producers substitute BPA with alternatives like bisphenol S (BPS) as well as diphenyl sulfone. Nonetheless, health issues regarding the substitutes has equally been brought up (Hahladakis *et al.*, 2018). Major toxic pollutants are contained within plastic materials thus giving it the potential ability to pollute the air, water, and land that in the long run affects the food chain (Teuten *et al.*, 2009). Toxic chemicals such as Phthalates and BPA leaching out of plastics are very harmful to both human health and wildlife since they are used in food and beverages packaging (Meeker *et al.*, 2009).

Both BPA and DBP can harm human health by changing the endocrine functions as well as other biological mechanisms (Kabir *et al.*, 2015) hence continuous evaluation of toxicity levels is very vital. Since plastic materials are rich in these DBP and BPA chemicals, there is a need to know how much of these chemicals are emanating from plastics into the water, soil, sediment and sea weeds.

United Nations member SDGs adapted in 2015 recognize ending poverty with strategies that improve human health, boost economic growth whereas addressing climate change besides aiming to preserve our oceans together with our environment at large. In addition to Vision 2030, the African Agenda 2063 recognizes that inclusive growth and sustainable development are essential to protecting the environment, including the marine and terrestrial resources from plastic wastes (Kauzya, 2020).

The data acquired from this research gives indicative information on the levels of BPA and DBP in our Kenyan marine environs and this will educate industries and the public to prioritize sound environmental management in plastic production, disposal, recycling, and ensuring clean production for waste minimization. It will also guide the Policy makers to set regular environmental monitoring programs, mitigating strategies of minimizing the contaminants and come up with workable adaptation strategies and appropriate policies for sustainability.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Effect of plastic pollution on environment

The major concerns of governments around the world regarding plastic materials are focused on accumulation of plastic wastes in the environment which causes adverse effects on wildlife and humans (Reddy *et al.*, 2014). Diverse types of chemicals are in plastic materials depends on the type of plastic (Hahladakis *et al.*, 2018). Some of the chemicals used in the production of plastic materials can be absorbed by a human being through the skin (Tsai, 2006). Exposure to plastic additives such as BPA together with Di-butyl phthalates may alter endocrine activity, disrupt reproductive system and fetal development through several biological mechanisms (Meeker *et al.*, 2009). In addition, large marine animals have been found to suffer severe consequences as a result of contamination from plastic products. (Muncke, 2009), disrupting the food chain for humans (Reddy *et al.*, 2014). Plastic materials that enter the oceans as waste may leach Bisphenol A and other toxic compounds into the waters (Rebolledo *et al.*, 2013).

Application of plastic materials has enabled innovation in several other industrial sectors through development of new materials and products (Andrady and Neal, 2009). This is due to the versatility, lightweight, flexibility, high tensile strength, and moisture resistance of plastic materials as well as low costs associated with plastics. Whenever the plastics have been used, the materials can be easily repaired or reused (Hopewell *et al.*, 2009). However, in the long run, they form waste which is considered a new resource and needs to be placed in the general life cycle of plastics again. On the contrary, large quantities of plastic materials such as disposable cups and packaging materials, and other plastic products are produced for one-time use (Hopewell *et al.*, 2009). These are thrown away permanently through out the year leading to large scale accumulation of environmental and health hazards.

2.2 Significant routes via which plastic waste can harm wildlife

The three main ways that wildlife may be harmed by plastic litter are entanglement, ingestion and interaction.

2.2.1 Entanglement

Entanglement involves entrapping, encircling of animals living within marine environments by plastic debris (Gall and Thompson, 2015). 344 cases of entanglement of marine animals were reported in 2016 (Nelms *et al.*, 2016) including the turtles in the marine environs, seal species, whales and seabirds species. Furthermore, 89 fish species, as well as 92 species of invertebrates, have also been reported in cases of entanglement (Gall and Thompson, 2015). Plastic ropes and netting, as well as abandoned finishing gears constitute the majority of entanglement cases. Entanglement by other plastic types such as packaging plastics have also been reported (Meeker *et al.*, 2009).

2.2.2 Ingestion

Ingestion of plastic materials has been reported to occur directly through intentional or unintentional uptake of plastic materials (Rochman *et al.*, 2013). It can also occur indirectly by ingestion of various species that contain plastic materials. Research has shown that indirect ingestion has been reported for at least 233 marine species (Rochman *et al.*, 2013). Plastic debris is known to litter aquatic habitats universally, most of what is defined as microscopic (< 1 mm) and a wide variety of species consume it (Thompson *et al.*, 2009).

Risks that are associated with such small fragments are known to leach from product itself besides being sorbed to it from chemical pollutants from the neighborhood (Rochman *et al.*, 2013). However, hazards that are linked to the plastic compound mixture including concentrated contaminants are generally unidentified.

Fish fed on virgin polyethylene fragments in studies showed evidence of stress, however the levels were lower than for fish fed on marine polyethylene fragments (Nelms *et al.*, 2016). The result provides data that can be used as guides with regard to the bio-accumulation of chemicals

and associated health problems from fish ingesting plastics. Moreover, future evaluations ought to assess the general complex mixture of the plastic materials coupled with related chemical contaminants (Rochman *et al.*, 2013). Effects of ingestion of plastic materials have several impacts on the health of all organisms that include: obstruction or perforation of the gut, causing ulcerative lesions, or rupture of the gastric duct thus leading to death thereafter (Nelms *et al.*, 2016). Biochemical responses to the ingestion of plastic materials have also been observed in laboratory where oxidative stress, metabolic disruptions, the lowered enzymatic activity and cellular necrosis were reported (Rochman *et al.*, 2013).

2.2.3 Interaction

The contact with plastic debris excluding entanglement is defined as interaction in view of the pathway of plastics to the environment (Law, 2017). This includes collisions, obstructions, abrasions, as well as plastic use as substrates and may result in multiple scenarios which can have an impact on organisms (Gall and Thompson, 2015). Abrasion has been linked to the use of fishing gears damaging the coral reef ecosystems upon impact (Reddy *et al.*, 2014). Plastics can interfere with ecosystem structures through the substrate and plastic interaction. This can further have an impact on light penetration, availability of organic matter and exchange of oxygen in the ecosystem (Gall and Thompson, 2015).

2.3 The effects of water pH, electrical conductivity (EC) and temperature on ecosystem

In general, physical-chemical indicators offer information on various issues that impact the ecosystem. For instance, specific factors that affect dissolved oxygen include organic waste and some types of toxicants (Patil *et al.*, 2012). Several parameters such as pH, EC and temperature analysis are important and each of their obtained values should be compared with the set standard guidelines by the World Health Organization (WHO, 2006), United States Environmental Protection Agency (USEPA, 2006) and the Government of Kenya (GoK, 2006) to determine whether the water quality meets the safe limits.

The base ten negative logarithm of the hydrogen ion concentration is used to express the pH (Talling, 2010). It indicates the strength of a solution that is acidic or basic. Water's pH level

indicates how acidic or basic it is. In water, pH is used as a significant measurement in the general determination of water quality. As reported by Marion *et al.* (2011), the pH of any given water body does affect the life of an organism that lives in the said water. For instance, a change in pH within a stream can thus indicate a general increase in pollution or some other diverse environmental factors.

To be more specific, acidic water has more hydrogen ions (H^+), whereas basic water contains more hydroxyl (OH^-) ions (Sörensen, 2013). The pH of any given solution varies from 0 to 14. A pH of 7 indicates neutrality; anything below or above that level indicates acidity or basicity, respectively (Song *et al.*, 2018). While usual rainfall water has a pH of about 5.6, which is somewhat acidic due to ambient carbon dioxide gas, pure water is known to have a neutral pH of 7.0 at 25 °C (Nafae *et al.*, 2019). The pH range of safe drinking water for residential use and the requirements of living things is between 6.5 and 8.5 (Islam *et al.*, 2017). Pollution can adjust the water pH hence harm plants and animals living in water (Bhateria and Jain, 2016). Aquatic plants and animals in large numbers have adapted to living in water with a specific pH and may suffer from a small pH adjustment. (Flynn *et al.*, 2012). Low pH levels affect the ability of organisms to incorporate calcium carbonate (Nafae *et al.*, 2019).

According to Omer (2019), the ability of a solution to carry an electric current by its ions is known as the electric conductivity (EC) of water. Any given solution's electric conductivity rises as its ion concentration does and vice versa. Drinking water has a conductivity of 0 to 1,500 uS/cm, while normal sea water has a conductivity of around 50,000 uS/cm (Omer, 2019). Temperature influences diverse properties such as palatability, viscosity, solubility, odors as well as chemical reactions. Subsequently, processes such as sedimentation, chlorination and biological oxygen demand (BOD) are reliant on temperature (Omer, 2019).

2.3.1 Effects of temperature on DBP

Leaching of phthalates out of products occurs easily and thus contaminating the external environment. This is because they aren't bound chemically to the plastic matrix or different chemical formulations (Heudorf *et al.*, 2007). Certainly, environmental pollution through the

leaching of chemicals from plastic materials into food, beverages, air, soil in addition to water has currently emerged as an area of concern.

2.3.2 Effects of temperature on BPA

According to Le *et al.* (2008), the rate of BPA migration increased by exposure to boiling water having a temperature of 100 °C. The leaching rate of BPA from plastic materials is increased by heating, elevated pH and washing repeatedly (Shrinithiviahshini *et al.*, 2014). Due to plastics use in kitchens and storage facilities for food or beverages, toxic compounds like BPA leaching that result from plastics are extremely detrimental to both human health and wildlife (Meeker *et al.*, 2009).

2.3.3 Soil and sediment characterization

Soil and sediments characterization is essential to classify and determine physical-chemical properties of soil and sediments. According to Jin *et al.* (2015), different soils and sediments have different pH, organic matter, micro and macro-nutrients.

Any plant or animal remains that are returned to the soil and undergo the decomposition process are considered organic matter, a natural source from which plants obtain nutrients (Brevik, 2010). All organic material contains carbon (C), but it also contains other elements such as nitrogen (N), phosphorous (P), sulphur (S), potassium (K), magnesium (Mg), calcium (Ca), and other micronutrients like zinc (Zn) and copper (Cu). The physical-chemical characteristics of soil and its general health are impacted by soil organic matter, which is a byproduct of on-site biological decomposition (Jin *et al.*, 2015). Organic matter in soil and sediment is influenced by moisture, temperature, the physical and chemical composition of the soil and sediment, as well as water leaching.

According to Jin *et al.* (2015), sorption of BPA and DBP to soil and sediments is highly dependent on organic matter concentrations. BPA has a pKa of 10.29 which results in increased sorption at a reduced pH values and greater solubility or desorption at pH values nearer to pKa. Low pH and high organic matter content with the presence of plastic wastes creates a favorable environment for BPA release in to the soil.

Soil degradation presents a major challenge on human wellbeing and the environment worldwide. A considerable deterioration in soil quality has occurred globally due to negative changes in soil physical, chemical and biological features and pollution by inorganic and organic pollutants. Some physical-chemical indicators of a change in soil quality include organic matter, nutrient availability/retention capacity and pH (Zotica *et al.*, 2020). According to Wu *et al.* (2018), increment of organic matter may increase adsorption of DBP/BPA in soils and thus influence its bio-accumulation and transformation in soils. Presence of microplastics changes the physical properties of soils like water-holding capacity, soil bulk density as well as soil fertility (Zhang *et al.*, 2020).

2.4 Bisphenol A

Chemically, BPA is an organic artificial substance having a chemical formulae of $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$ as shown by Figure 2.1 below (Krishnan *et al.*, 2019) . BPA is further classified under bisphenols and derivatives of di-phenylmethane that have two hydroxyphenyl groups as substituents (Testai *et al.*, 2016). The compound is a solid which is colorless and soluble in solvents that are organic such as ethanol and alkalis according to Almeida *et al.* (2018), while solubility in water is 120-300 mg/L at 25°C (Corrales *et al.*, 2015). The condensed molecular formulae of BPA is $\text{C}_{15}\text{H}_{16}\text{O}_2$ and its IUPAC name is 4,4'-(propane-2,2- diyl) diphenol. BPA has a molar mass of 228.287 g/mol and melting point of 153 °C (Corrales *et al.*, 2015).

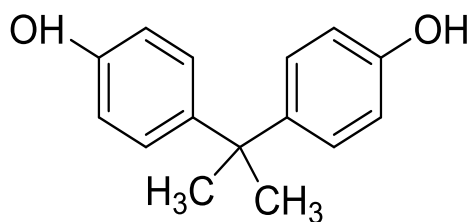


Figure 2.1: Chemical structure of Bisphenol A

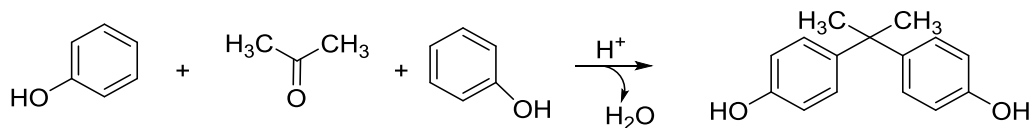
2.4.1 Uses of Bisphenol A

BPA as a chemical agent has various uses. It's utilized in the overall manufacturing of epoxy resins together with polycarbonate plastic products. Moreover, BPA is used to manufacture water bottles, dental sealants, food or beverage container coatings as well as lining for canned foods (Le *et al.*, 2008). According to Almeida *et al.* (2018), BPA is a chemical compound that mimics the action of the human hormone estrogen and it leaches from polycarbonate plastics. It is used in most cases as a monomer in manufacturing polycarbonate plastics majorly due to its known environmental estrogen nature (Kabir *et al.*, 2015). Likewise, it is used as a part of linings in majority of food and beverage cans as well as dental fillings (Vandenberg *et al.*, 2007). BPA further functions as an additive in many extensively utilized produce of plastics consumed worldwide (Geens *et al.*, 2011).

2.4.2 Global production of Bisphenol A

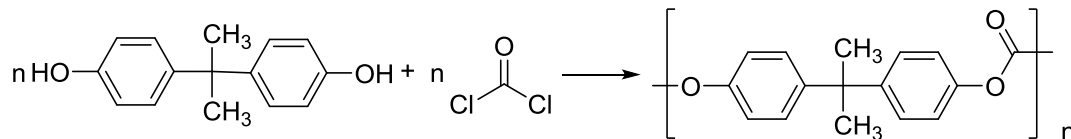
Globally, BPA is among chemicals that are produced in large volumes (Birnbaum *et al.*, 2012). In 2003, the mass production capacity of BPA was 2,214,000 metric tons which are greater than 6.4 billion representing between six and ten percent demand annually (Birnbaum *et al.*, 2012).

BPA is a chemical compound that is synthesized by condensing acetone and two equals of phenol, catalyzing the chemical reaction with a strong acid (Figure 2.2), for example, sulfonated polystyrene resin or hydrochloric acid (Geens *et al.*, 2011). In Industrial processes, excessive phenol is used in overall manufacture thus ensuring complete condensation; the product mixture of Bisphenol A and phosgene (COCl_2) may also be used to prepare polycarbonate (Figure 2.3) as starting material (Hammad, 2015).



(Shimizu *et al.*, 2010)

Figure 2.2: Synthesis of Bisphenol A from acetone and phenol



(Hidaka *et al.*, 2009)

Figure 2.3: Reaction of Bisphenol A and phosgene to form polycarbonate

Widespread exposure to BPA among humans has been due to its ester bonds in its polymer structure having the ability to hydrolyze thus causing leaching (Tsai, 2006). Hydrolysis of the ester bonds that links the BPA molecules in polycarbonates as well as in resins is accelerated by heat and contacts of either acidic or basic compounds (Nugroho *et al.*, 2019). This is evident when cans are repeatedly washed with acidic solutions and heated in order to sterilize them, the hydrolysis of the ester bond in polycarbonate is accelerated. Consequently, the rate of BPA molecules leaching has been reported (Vandenberg *et al.*, 2007). The major sinks for BPA are river and lakes as has been seen in many other chemicals (Canesi and Fabbri, 2015). This accounts for the high quantity of estrogenic activities that arise from leaching from landfills into various immediate ecosystems (Birnbaum *et al.*, 2012).

2.4.3 Sources of Bisphenol A

The BPA products come from both pre- and post-consumer sources. Pre-consumers include the direct release of BPA from plastics containing these compounds and shipping BPA. On the other hand, Post-consumer leaching is from wastes resulting from ocean dumping, municipal waste disposal, poorly managed landfills and inadequate waste material recycling techniques (Birnbaum *et al.*, 2012). The point sources of BPA within the environment are sewage effluents and leaches from the landfill (Vandenberg *et al.*, 2007). On the other hand, non- point sources include fragmentation of epoxy resins and debris of polycarbonate plastic products that are washed through runoffs creating huge challenges (Vandenberg *et al.*, 2007). The leaching of BPA molecules can occur in the event polycarbonate plastic products are exposed to heat (Nugroho *et al.*, 2019). Despite the ability of BPA to degrade easily in an environment rich in microbes, the presence of fragments as polycarbonates guarantee the creation of a non-point

source of leaching (Le *et al.*, 2008). This ensures the slow leaching of synthetic polymers that make the majority of debris that are anthropogenic within watersheds as well as in marine environments (Erni-Cassola *et al.*, 2019).

According to Tsai (2006), consuming contaminated foods and beverages that have come into touch with epoxy resins or polycarbonate plastics is the main way that humans get exposed to BPA. A study by Le *et al.* (2008) analyzing the amount of BPA that migrated into high-quality, new and used polycarbonate bottles of stored water at various temperatures and throughout varied periods of bottle-to-water contact discovered that BPA migration increased with sample temperature. The content of BPA was higher in instances of longer contact time (Le *et al.*, 2008) and BPA migrated from the polycarbonate bottles at the rates of between 0.20 to 0.79 ng on an hourly basis, and was independent of bottle used at room temperature (Le *et al.*, 2008). The rate of BPA migration increased to 55 fold by exposure to boiling water having a temperature of 100 °C (Le *et al.*, 2008).

The entirety of human exposure to BPA is incompletely defined even though people living in industrialized areas get exposed on daily basis (Geens *et al.*, 2011). However, assessment of exposure to BPA through bottles made of polycarbonates as well as cans of both food and beverages made of epoxy resins has been made (Geens *et al.*, 2011). Nevertheless, the exposures lack sufficient explanations through dietary pathways (Geens *et al.*, 2011).

BPA is used in containers made of plastic as well as epoxy-based linings of canned food containers (Almeida *et al.*, 2018). However, as reported by Vandenberg *et al.* (2007), because of the hazardous effects on the human being, the compound-BPA, is no longer used in baby bottles. Humans are primarily exposed to BPA through food contamination arising from polycarbonate bottles as well as cans that are coated with epoxy resins (Le *et al.*, 2008). The compound is still used in several containers moreso in epoxy-based lining canned foods thus giving protection from pathogens (Le *et al.*, 2008). Nonetheless, the compound may find its way into food since it is in direct contact with food thus into the human body (Mustieles *et al.*, 2015). Conversely, a discrepancy exists between assessments on exposure to human-based on bio-monitoring data and that based on food or drink concentrations (Hays and Aylward, 2009).

Several studies reviewed have as well shown significance of non-food sources (Thompson *et al.*, 2009). Besides the polymerization use of BPA in polycarbonates and epoxy manufacture, BPA can also be used as an additive that can easily be released (North and Halden, 2013). Scientific evidence has been provided by several studies showing BPA sources from dermal sealant absorption (Vandenberg *et al.*, 2007). For example, from BPA thermal receipt papers (Liao and Kannan, 2011). The application of BPA as a polymer necessitates further investigations to determine quantities of BPA present including factors that affect its release as well as a possible epidermic or non-dermic exposures arising from the listed sources (Bach *et al.*, 2013). The sources of BPA compounds in our environs have not all been established necessitating further studies to identify the unexpected sources.

BPA is released during the manufacture of polycarbonates or epoxy resins and from several other products as well as their disposals within the landfills following their use (Vandenberg *et al.*, 2007). In the process of manufacturing, traces of BPA are continuously released directly into the receiving water bodies in addition to the atmosphere via various discharges from the facilities of production (Erni-Cassola *et al.*, 2019). The release of BPA could also occur indirectly in the process of handling the compound when being used in the manufacture of different commercial products (Geens *et al.*, 2011).

2.4.4 Health effects of Bisphenol A

BPA is commonly known as an endocrine-disrupting chemical (EDC) (Kabir *et al.*, 2015). Obesity and heart disease are only a couple of the numerous, diverse adverse health outcomes linked to BPA exposure (Tsai, 2006). Due to their underdeveloped biological systems for removing poisons from their bodies, infants and young children are subject to extensive long-term effects of BPA exposure. (Barraza, 2013). BPA has shown clear roles in the pathogenesis of several disorders related to the endocrine system (Careghini *et al.*, 2015). These disorders include infertility for both males and females, tumors reliant on hormones, and other diseases associated with a metabolism like polycystic ovary syndrome (Vandenberg *et al.*, 2007). Studies on epidemiology show that exposure to endocrine-disrupting chemicals (EDCs) that are produced in large volumes such as BPA and DBP are ubiquitous (Fu and Kawamura, 2010). BPA exposure links towards the development of allergy, asthma as well as dysfunctions have

been studied in various forms namely Vitro, Vivo, and cohort studies of humans (Robinson and Miller, 2015).

BPA molecules are known to bind themselves to the cell membrane of estrogen receptors (Kabir *et al.*, 2015). When in high levels of concentration within humans, BPA interacts with the thyroid receptor via simulating the androgen receptor (Geens *et al.*, 2009). BPA has been linked to numerous health issues through studies of both humans and animals. The health issues include infertility, gaining of weight, changes in behavior, early start of puberty, prostate as well as mammary gland cancers, diabetes, and effects related to cardiovascular problems (Birnbaum *et al.*, 2012).

2.4.5 Studies of BPA conducted globally

Various studies conducted in the world have shown varying levels of contamination by BPA residues. According to Kabir *et al.* (2015), there is extensive exposure to BPA in the United States. The study examined urine samples through the Centers for Disease Control and Prevention (CDC) and discovered 95% of the analysed samples had measurable BPA levels. The values had a mean of 1.3 ppb and varied from 0.4 ppb at the 10th percentile to 8 ppb at the 95th percentile. The levels reported in this study are consistent with those found in other countries (Kabir *et al.*, 2015).

Research done by Somm *et al.* (2009) on prenatal exposure of BPA on mice showed the diverse effects on offsprings of mice. These included; enhanced puberty, increase in body weight, alteration on the mammary gland, alteration on female genital tracts, alteration on structure as well as the function of the ventral prostate in male mice as outlined by Somm *et al.* (2009).

Concentrations of unconjugated parent BPA molecule have also been reported in human tissues and blood to vary from 0.1 to 10 ppb in urine (Vandenberg *et al.*, 2007). Additionally, research has revealed indications of BPA metabolism. The studies reviewed suggest that a significant amount of BPA exposure to humans is continuous and through various sources. Studies have reported the relationship that exists between BPA levels in blood and body fat in women. Low amounts of BPA exposure have impacted several aspects of development and sexual health (Vandenberg *et al.*, 2007). Additionally, such exposure affects levels of the hormone in the

blood, functions of the reproductive organs, fertility as well as immune functions (Robinson and Miller, 2015). The effect is further extended to enzyme activity, the structure of the brain, the chemistry of the brain, and general human behavior (Kabir *et al.*, 2015).

Another study was conducted by the Food and Drug Administration (FDA) on BPA in the year 2010 as part of their mandate in exercising regulatory authority for consumer and medical products that contain BPA (Barraza, 2013). The study supported earlier observations on BPA's effects on the brain, behavior, and prostate gland of fetuses, newborns and children (FDA, 2012). Furthermore, FDA found significant ambiguities in the research findings concerning BPA as well as implications on the health of humans (FDA, 2012). The need for further research in addressing these uncertainties was asserted by this study. For interim intervention, FDA outlined the need for reducing human exposures to BPA through the use of reasonable steps, especially among infants (Barraza, 2013). The European Chemicals Agency recommended after many completed studies that BPA ought to be placed among substances of high concern to health due to its endocrine disruption property (Kabir *et al.*, 2015).

Use of BPA in products meant for babies especially bottles was banned in the year 2012 by Food and Drug Administration (FDA) of the United States (Nugroho *et al.*, 2019). Research conducted in 2015 established that there are areas of concern on risk factors for endocrine-disrupting substances plus BPA compounds in our environs (Kabir *et al.*, 2015). The report further asserted that such substance ought to be assessed continually and be regulated tightly. The Environmental Protection Agency of the United States in the year 2010 reported more than one million pounds of BPA residues were emitted into the environment every year (Birnbaum *et al.*, 2012). The study underscored that pre-consumer leaching mechanisms and post-consumer leaching mechanisms are the two ways that BPA can be introduced into the environment. Post-consumer BPA waste is known to occur as a result of the release of effluents from municipal wastewater treatment facilities (Hahladakis *et al.*, 2018). The wastes can further arise from pipes of irrigation used in agriculture, trash of plastics born from oceans, indirect leaching from paper and plastics among others (Erni-Cassola *et al.*, 2019).

The present regulations on BPA have been found not to reach far enough. As such, extra aggressive regulatory actions are required for the general protection of public health as well as

individuals that are considered vulnerable like fetuses, infants, as well as children (Barraza, 2013).

2.5 Phthalates

Phthalate plasticizers consist of phthalate ester. In principle, they are defined as phthalate with a given ester group as outlined by Meeker *et al.* (2009). Phthalates (Figure 2.4) are di-esters of phthalic acid (1, 2-benzene dicarboxylic acid) (Guo *et al.*, 2015).

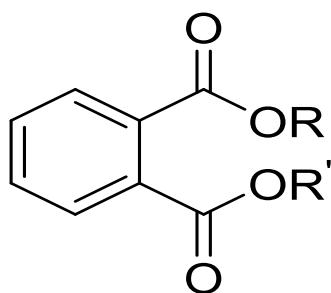


Figure 2.4: General structure of phthalate (Hahladakis *et al.*, 2018)

2.5.1 Uses of Di-butyl phthalate

DBP are chemicals that are used broadly in industrial productions such as plastics, personal care products and solvents (Meeker *et al.*, 2009). DBP is a colorless and odorless liquid produced by reacting phthalic anhydride with the suitable alcohol. In production of plastics, they are utilized as plasticizers, commonly known as softeners through addition to polyvinyl chloride (PVC) products when making them (Arbneshi *et al.*, 2021). Di-alkyl phthalate is broadly applied as plasticizer in diverse resins, particularly PVC resins. In addition, DBP is a crucial add-on in special paints and adhesives (Meeker *et al.*, 2009). Likewise, they are added to personal care products to enable the fragrances to last longer (Meeker *et al.*, 2009).

DBP appears to be a more typical non-associated liquid (Kumar *et al.*, 2017). It is generally applied as additives to make-ups and skin care products (Guo *et al.*, 2015) due to its oily texture that makes skin feel soft and their capability to provide flexibility to thin films like in mascara and nail polish (Guo *et al.*, 2015).

2.5.2 Plasticizers' mode of action

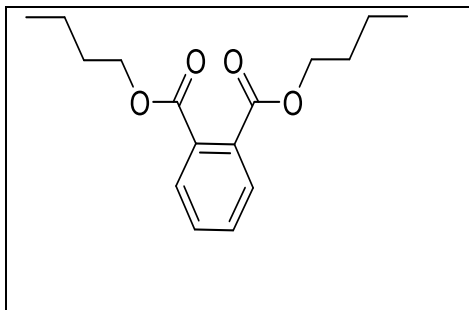
Plasticizers are defined as polymer additives that play the role of increasing the flexibility, elongation as well as easing processing of products. In general, by reducing the cohesive intermolecular forces along the polymer chains, plasticizers increase the freedom of motion proportionate to each chain and decrease the stiffness of the polymer (Erni-Cassola *et al.*, 2019). Plasticizers are known to be inert organic substances with high vapor pressures and boiling temperatures. Among compounds, esters are frequently employed due to their positive physical interactions with polymers that have high molecular weight thus forming homogenous physical units (Carragher and Seymour, 2012). In the present times, di-2-Ethylhexyl phthalate (DEHP) and DBP are the two common types that are used especially in PVC-related products in several medical delivery systems as well as in making children toys (Arbneshi *et al.*, 2021).

2.5.3 Global production of phthalates

Phthalates make up 90 percent of the plasticizer market (Yglesias, 2014). This has been a major source of phthalates exposure for the last 50 years resulting in the general exposure of the world population (Rajkumar *et al.*, 2017). The majority of individuals are exposed to plasticized plastics because of their ubiquity (Rodgers *et al.*, 2014). According to USEPA (2006), the production of phthalates is in high volumes yearly amounting to over 470 million pounds.

2.5.4 Di-butyl phthalate

DBP has a lower molecular weight of 278 g/mol according to Zhang *et al.* (2021), thus reasonably soluble in water (Figure 2.5). It is known to be a colorless odorless liquid that is not generally found in nature (Roy *et al.*, 2017). Precisely, the chemical compound is mostly added to hard plastics with the general purpose of making them soft. DBP molecular weight is rapidly converted to Mono-butyl phthalate (MBP) in rat and human (Huang *et al.*, 2018). The mono-ester metabolite is believed to be a more toxic chemical (Lu *et al.*, 2016).



(Zhang *et al.*, 2021)

Figure 2.5: Chemical structure of DBP

2.5.5 Uses of Di-butyl phthalate

The major uses of DBP as PAEs is its wide use in the production process of plastics together with cosmetics (Zhou *et al.*, 2011). The compound is commonly used as an additive in cosmetics as well as in skin care products due to its oily texture. The texture softens and gives them the ability to add flexibility to thin films like mascara in addition to nail polish (Janjua *et al.*, 2007). What is more, Di-alkyl phthalates are equally used in a wide manner amongst plasticizers within diverse resins especially PVC. DBP is equally significant add-on in cases of special paints as well as adhesives (Ravikumar *et al.*, 2012). It is mostly used in plastic products containing nitrocellulose, polyvinyl acetate or polyvinyl (Stipek and Daoust, 2012). These plastics are used to make most of our everyday products like paints, glue, hair spray, nail polish, skin emollient; fingernail elongators and hair spray (Du *et al.*, 2015).

2.5.6 Health effects of DBP

Functional effects of phthalates on health are different from BPA. Phthalates functions as anti-androgens while BPA as estrogens (Fénichel *et al.*, 2019). DBP are known as ubiquitous contaminants within soil thus largely influence general health of various organisms (Li *et al.*, 2016). Currently, the consequences of di-butyl phthalate exposure to human health are very significant (Thompson *et al.*, 2009). According to Swan (2008), the toxicity of DBP to humans is centered on reproductive and respiratory systems typically asthma and allergies (Robinson and Miller, 2015). However, the agents can also be involved in carcinogenesis as well as autism spectrum disorders in humans (Fénichel *et al.*, 2019).

The exposure of DBP to humans has also been found to link to several human health and development problems such as the early start of puberty, interference with both male and female reproductive tract development (Ahmad *et al.*, 2014). Furthermore, the exposure causes problems such as tampering with the normal functioning of hormonal system, defects in reproduction including genitals, low testosterone levels and low sperm count issues in adolescents (Swan, 2008).

In animals, DBP adversely affects the male reproductive system (Zhu *et al.*, 2009). Once exposed, the DBP are quickly metabolized and then excreted within the urine and faeces (Zhu *et al.*, 2009). Another key health effect of DBP is the ability to function as an endocrine disruptor although in a weak manner and androgen blocking (Erkekoglu and Kocer-Gumusel, 2016). Once absorbed in the body, DBP may mimic or block the female hormones or they can function to suppress those hormones that are linked with male sexual development (Meeker *et al.*, 2009).

2.5.7 Sources of Di-butyl phthalates

Phthalic acid esters (PAEs), which are important organic compounds, have been utilized in several plastic polymers due to their ability to increase the plasticity of the said materials (Wang *et al.*, 2021). The US Environmental Protection Agency (USEPA, 1991) and the China National Environmental Monitoring Center have already categorized PAEs as prime environmental contaminants (Wang *et al.*, 2016). DBP is a key compound utilized in the process of production of plastics as well as cosmetics. The compound is known to a ubiquitous environmental contaminant because of its occurrence in air, water as well as soil globally (Janjua *et al.*, 2007).

DBP is released into any given natural environment during the process of its manufacture, use, disposal as well as leaching from various plastic materials (Hahladakis *et al.*, 2018). DBP are released to the environment easily because it does not persist for long in its parent materials. Moreover, the compound is known to undergo rapid biodegradation, photo degradation as well as anaerobic degradation (Net *et al.*, 2015). There are multiples sources of DBP that are being released into the environment. The sources include releases from industries, disposals resulting from manufacturing processes, processing as well as industrial waste, municipal solid wastes,

utilization of sewage sludge on land and DBP release from products that contain them (Somashekar *et al.*, 2015).

2.5.8 Routes of exposure to DBP

The potential pathways for exposure of plastic waste pollution in the environment are through ingestion, inhalation among animals and humans, skin absorption since DBP are broadly utilized in most personal care and consumer products (Weiss *et al.*, 2018). After exposure, DBP undergo rapid metabolism and are excreted in urine and feces (Krais *et al.*, 2018).

2.5.9 Di-butyl phthalates studies conducted globally

Eight phthalates are presently under the U.S. Environmental Protection Agency's (EPA's) management plan. These comprise of; Di-butyl phthalate, di-isobutyl phthalate (DIBP), butyl benzyl phthalate (BBP), di-n-pentyl phthalate (DnPP), di (2-Ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP), grounded on the lethality of phthalates, their ubiquity in the environment, frequent use, and human exposure (USEPA, 2012). Through numerous research, different amounts of DBP residue contamination in persons around the world have been reported (Cao, 2010). Studies of Di-butyl phthalate biodegradation in freshwaters, marine waters, sediments, wastewaters as well as sludge has been conducted. One such study found a low rate of degradation that might last anywhere from a few days to a few months in some circumstances (Du *et al.*, 2015). From a study done by Chen *et al.* (2008) that examined urinary phthalate metabolites, it was observed that the general public appears to be exposed to higher quantities of DBP compared to other forms of phthalates. It has equally been established from research that, in animals like rabbits, low quantities of DBP interfere with spermatogenesis and can lead to damages in the reproductive system, especially during the intrauterine period. This is true in cases of frogs, where reduced testosterone levels in fetal testes are a similarly reported consequence of utero exposure to DBP (Ji *et al.*, 2014). A study conducted in Mexico investigating the relationship between exposures of Di-butyl phthalate and preterm births (Meeker *et al.*, 2009) where comparisons were done in the third trimester experimenting on urinary Di-butyl phthalate metabolite concentrations (Meeker *et al.*, 2009). The results showed that DBP exposure was relevant among thirty women who delivered

preterm (Less than thirty-seven weeks of pregnancy) with thirty controls (37 and more weeks of pregnancy) (Meeker *et al.*, 2009). The study further found out that DBP can be associated with premature birth (Meeker *et al.*, 2009).

DBP have been found as significant environmental factors in the development of pathogenesis of asthma from a study conducted in Taiwan (Tsai *et al.*, 2012). Several epidemiological studies have shown that there is a relationship that exist between phthalate exposure and asthma in consideration of the last decade (Tsai *et al.*, 2012). However, experimental studies have shown adjuvant inflammatory responses relating to inflammatory cells that are known to have phthalate exposure (Tsai *et al.*, 2012).

2.6 Possible solution to plastic pollution

This study shall propose a possible solution that can be used to address plastic pollution geared by the need to ensure plastics are useful even at the end of their first life thus establishing sustainable options for managing such plastic waste (Hopewell *et al.*, 2009). The proposed solutions would thus include; encouraging recycling of plastic wastes, use of energy recovery methods as complementary options for manufacturing, and ensuring deposits of recoverable plastic wastes are restricted in landfills. Plasticizers as well as other additives leach from landfills relative to the extent of diverse conditions like pH as well as organic contents (Thompson *et al.*, 2009). Nonetheless, there are efficient treatment approaches that have been established in some countries relative to such contaminants (Teuten *et al.*, 2009). In reducing the quantities of plastic materials and particularly the plastic packaging materials, the 3R's waste management approach has been employed namely; reduce, reuse, as well as recycle (Satsangi, 2020). Opportunities exist of reducing the usage of such raw materials by reusing them especially in the transportation of goods on particular industrial crates as well as domestic ones (Thompson *et al.*, 2009).

2.7 Recycling plastics

There are several advantages of recycling plastics due to their non-biodegradability since without recycling they will pose high risks to both people and the environment. Consequently, recycling plastics would ensure environmental problems are reduced and thus provide sustainable raw

materials to the industries that manufacture plastic products (Hopewell *et al.*, 2009). Moreover, recycling of plastics ensures problems of the landfill are reduced thus minimizing the quantities of plastics that are being taken in already diminishing sites of the landfill (Moh and Manaf, 2014). The process of recycling plastics makes use of less energy compared to the production of plastics from original raw materials. The saved energy could be diverted into other energy requirements of the country thus saving the economy (Ayodele *et al.*, 2018).

In the normal production of plastics, raw materials are costly as well as the process taking much time compared to the recycling process (Gu *et al.*, 2017). Recycling plastic wastes can be economically viable if it produces resources that can be used in the production of other products. In the long run, the recycling of plastics will help in improving the country's economy while boosting the general standards of living of the people. This has been applied in various developed countries because of the establishment of commercial-level resource recoveries targeting plastic wastes (Kerdlap *et al.*, 2019).

2.8 Gas chromatograph-mass spectrometry and its working principle

Gas chromatographic-mass spectrometric analysis is one of the precise and reproducible methods for environmental analysis (GC-MS). GC-MS machine uses the (Gas Chromatograph) GC component to separate chemical mixtures and identify the components at the molecular level using the MS component. The method is considered one of the most accurate tools that are used to analyze samples from the environment. The working principles of GC is on separation of substances into individual components through heat (Maurer, 2013). The solutes in a solution as well as volatile compounds in a gas are put in a mobile phase and passed over a selected adsorbent material commonly referred to as the stationary phase.

The initial step in analyzing samples using GC is to provide high-purity gas as necessary. The carrier gas is then introduced into the injector via the column and enters the detector. The sample is then introduced into the injector which is prior heated to 150-250 °C. This causes the samples which are volatile or solute to vaporize. The vaporized samples are then carried to a capillary column of the GC via the carrier gas while maintaining the oven in a temperature-controlled manner as explained by Asfaw *et al.* (2019).

The solute molecules distribute themselves between the stationary and mobile phases upon introduction into the column. Those molecules in the mobile phase are transported down along the column while molecules in the stationary phase become temporarily immobile. In process of molecules moving down the column, a collision occurs and they reenter the stationary phase. Likewise, part of the solutes in the stationary phase leave and enter the mobile phase (Asfaw *et al.*, 2019). The process occurs repeatedly as molecules are transported and introduced into the column. The molecules traveling through the column travel as sample band that is traveling in the same rate and appearing as band molecules.

The rate of movement of each sample molecule within sample bands depends upon the structure of compounds as well as the chemical structure of the stationary phase coupled with the temperature of the column (Maurer, 2013). The operating condition of the column and its dimensions affects the width of the column. Moreover, the retention time of molecules is affected by hydrogen bonding and polarity between the analytes and stationary phase. The retention time is the length of time it takes a solute to move through a column. This is assigned mostly to the corresponding peak of solute. It measures the amount of time that a solute has spent in the column. Principally, it estimates the time the solute molecule spends embedded in the stationary phase and the time it takes traveling along with the mobile phase. Given compounds will have the same retention time in the event operating conditions of the column and the column itself are kept constant (Maurer, 2013). The peak size of molecules and retention times are crucial in determining the quantity and for qualitative identification of analytes, respectively.

In elution stage of solutes, as they enter the heating detector, an electrical signal is generated and sent depending on the solute interaction with the detector. Signal range is registered on a given information system software such as Agilent's ChemStation. A chromatogram is produced by plotting the signal against time. The peak area shows the concentration of compound within the sample. As the chemical concentration in the sample rises, the peak enlarges. However, a compound's retention duration alone cannot be used to determine its identity. According to Hermabessiere *et al.* (2018) retention times and peak areas of known authentic and pure samples must be determined first through analysis to aid in the identification of related compounds. The

results are used in comparing unknown compounds to check whether retention times are similar thus determining identities and quantities through retention times and peak sizes.

Ideal chromatograms are expected to have closely spaced peaks that do not overlap also known as co-elution. Co-elution does not allow one to measure peak sizes easily. Additionally, it does not allow easy identification of peaks that have the same retention times. Once the substances are separated, they flow into the MS. MS uses the mass of the analyte molecules to identify the compounds. The MS uses a library of compounds that have different spectra masses to identify the compounds (Stein, 2012).

2.9 Components of gas chromatograph-mass spectrometry

There are two major components of GC-MS namely; the Gas Chromatograph (GC) and a detector. The detector has a mass spectrometer which is also known as Mass Selective Detector (MSD). In Figure 2.6 below is a GC-MS component which is composed of carrier gas, injection port, oven, and column. The carrier gas or mobile phase in Gas Chromatography is an indispensable part of the machine. However, it is a limiting factor in separations. The means used to move constituents along the column is carrier gas. The choice of carrier gas used is highly restricted (McNair *et al.*, 2019). An injection of 1 μL of the solvent containing the sample molecules mixture is done through the injection port. The sample is further carried through an inert gas such as helium.

The injection port is thereafter heated to approximately 300 $^{\circ}\text{C}$ thus converting the sample into a gaseous form. The inlet systems are categorized into two types: Split and splitless injectors (Stashenko and Martínez, 2014). GC has a specialized oven-like structure in the outer part. The column is always heated to allow movement of molecules from a typical temperature between 40 $^{\circ}\text{C}$ and 320 $^{\circ}\text{C}$. This column is well placed inside the oven. It is a thin tube that is made of a specialized coating of polymer on the inside. The column aids in the traveling of chemical molecules due to their different volatility.

The molecules with low volatility travel faster in the column (Rahman *et al.*, 2015). Mass spectrometry on the other hand contains three main components namely; the ion source, filter,

and detector. The ion source helps in the production of gaseous ions from samples being analyzed. Once through with GC, chemical pulses proceeds to Mass spectrometry. The samples of molecules are then bombarded with electrons, which causes them to fragment and become positively charged particles. This allows the particles to pass through the filter (Stashenko and Martínez, 2014). The filter is also called the analyzer that is used in resolving ions thus characterizing then according to mass components that is mass to charge ratio. The ions are filtered via the movement through the electromagnetic field based on their mass. The filter continually scans the variety of masses as they flow from the ion source (Vinaixa *et al.*, 2016). The detector then sums up the number of ions having a specific mass. The information collected is then transmitted to a computer hence developing mass spectrum. The mass spectrum can be defined as a chart showing the total number of ions with different masses that have traveled through the analyzer (Vinaixa *et al.*, 2016).

Lastly, the GC-MS must be connected to a computer. The computer is significant in controlling the instrument, acquiring, and manipulating as well as compare all the spectra. The data obtained throughout the analysis is stored on the software installed in the computers (Stashenko and Martínez, 2014) Analysis of BPA and DBP in water, soil, sediment and sea weeds was carried out with a gas chromatography (Agilent 6890N) connected to an autosampler (Agilent 7683 Series injector) and an MS detector.

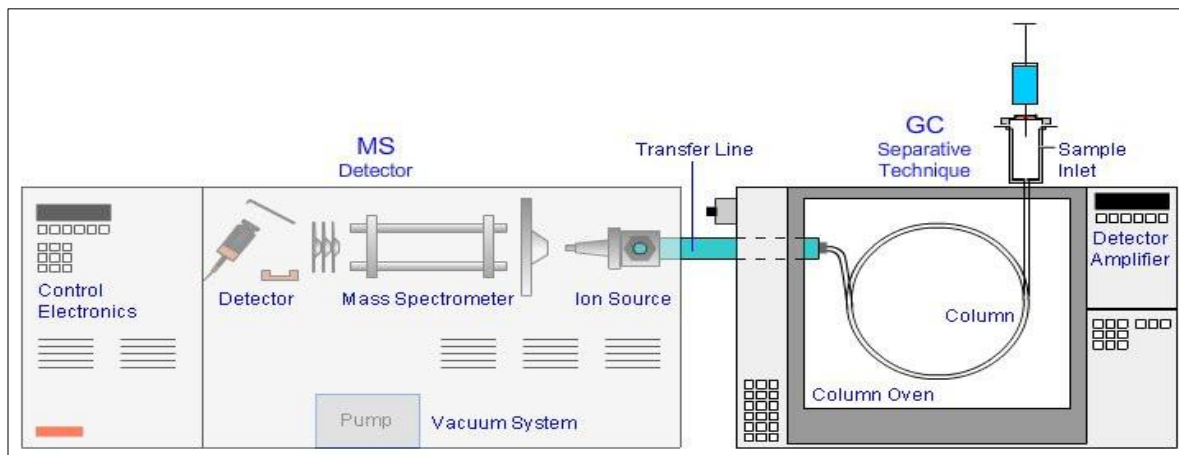


Figure 2.6: Component of GC-M

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study design

The study was conducted on the coastal Beaches of Kenya; Pirate, Mombasa, Kilifi, Malindi, Sabaki, Sabaki river mouth and Sabaki River sites in the wet and dry seasons, respectively, in October 2018 and January 2019. These sites are from Mombasa County and Kilifi County in Kenya. Malindi is the largest center in Kilifi County (12,610 km²) and it is located in the northeast of Mombasa City, with a population of 119,859 people, while the Kilifi as a County has got a population of 1,453,787 people. Mombasa is the country's oldest, and 2nd largest city (294.7 km²), with a population of 3,528,940 people (Kenya National Bureau of Statistics, 2019). Mombasa is highly industrialized compared to Malindi and Kilifi, leading to higher environmental impact. Mombasa is known to be one of the warmest regions in Kenya, with the average daily temperatures of 31 °C. In Kilifi County's coastline region, the yearly mean temperature ranges from 21 to 30 °C. At the coastal belt, annual average rainfall varies from 1,300 mm in the hinterland to 300 mm. Mombasa experiences a tropical wet and dry climate where rainfall amount basically depends on the season.

Seven sampling sites; Pirate Beach, Mombasa Beach, Kilifi Beach, Malindi Beach, Sabaki Beach, Sabaki River mouth (Table 3.1) were chosen along the Kenya coastal beaches and the Sabaki River (Figure 3.1). A summary of the GPS locations of the sampling locations are given in Table 3.1.

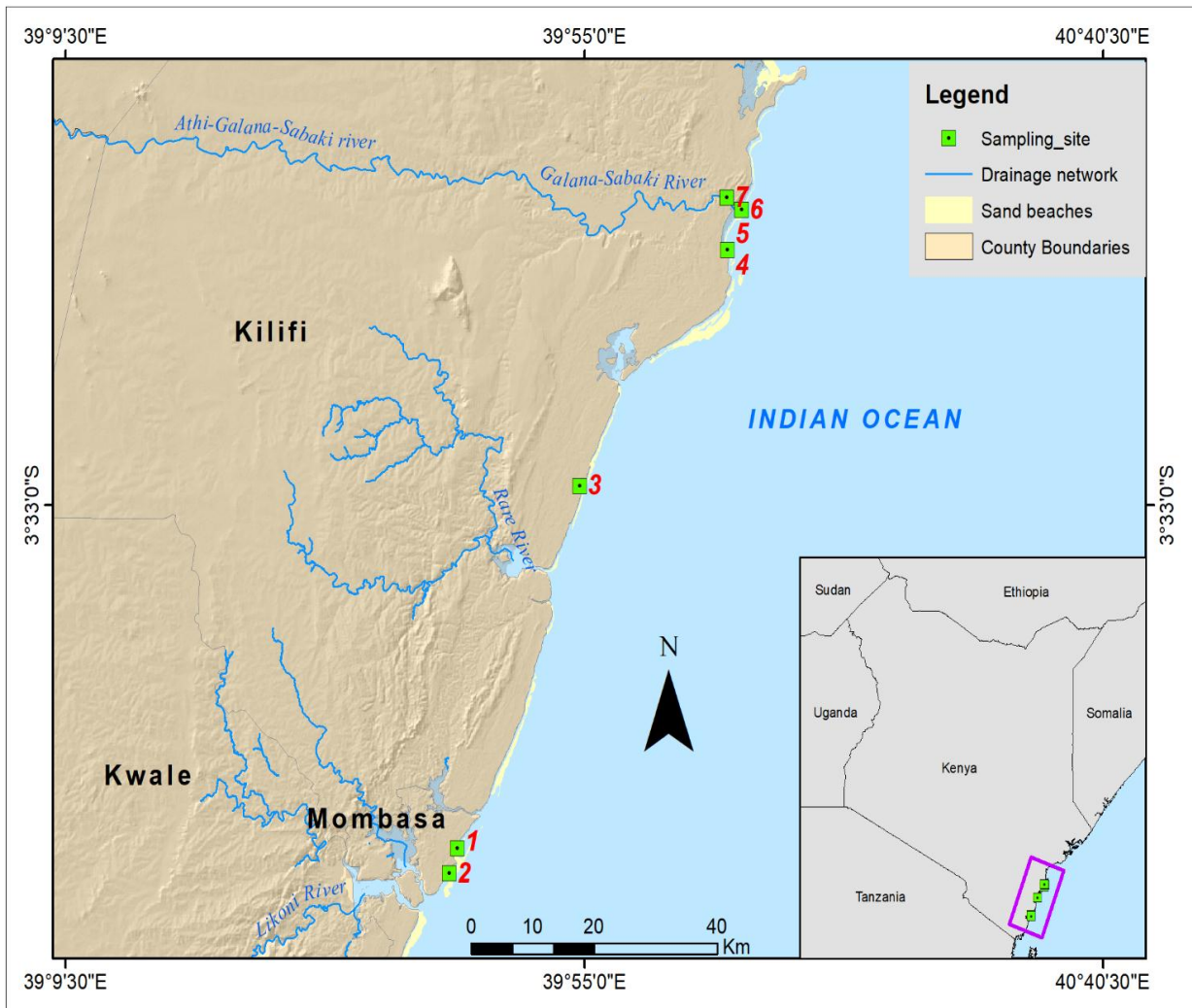


Figure 3.1: Map of Kenyan coastal Beaches showing sampling locations

Table 3.1: The altitude, coordination and human activities near the sampling sites

Site number	Local name	Altitude (m)	GIS Position	Human activities at the sampling sites
1	Pirate Beach	50	S2°44'8.3256" E 40°13'8.2272"	Recreational activities, tourism, playing games, Hotel industries, boat riding
2	Mombasa Beach	17	S2°44'8.3256" E40°13'8.2272"	Recreational activities, tourism, playing games, Hotel industries
3	Kilifi Beach	15	S3°31'29.802" E39°54'37.224"	Recreational activities, tourism sandy beaches and beach sporting activities
4	Malindi Beach	7	S3°12'56.808" E40°7'34.4604"	Recreational activities, tourism, playing water sports, Hotel industries
5	Sabaki Beach	200	S3°9'57.934" E39°8'44.194"	Recreational activities, tourism sandy beaches and beach sporting activities
6	Sabaki River mouth	5	S3°9'47.3292" E40°8'50.046"	Recreational activities, tourism sandy beaches and beach sporting activities
7	Sabaki River	5	S3°8'50.892" E40°7'30.7164"	Recreational activities, Fishing, herding, farming, wildlife, tourism

3.2 Chemicals and reagents used

General Purpose Grade n-hexane, dichloromethane, acetone and HPLC grade iso-octane were purchased from SCIELAB LTD, Nairobi. Before use, triple distillation was performed on the general-purpose grade solvents. Analytical grade Aluminum oxide, anhydrous sodium sulphate, sodium chloride, Dipotassium hydrogen phosphate, hydrochloric acid, sodium hydroxide and silica gel were purchased from SCIELAB LTD, Nairobi. High purity nitrogen gas (99.999%) purchased from Gas labs LTD, Nairobi was used for concentrating the extracted samples. High purity helium gas (99.999%) N6 and white spot nitrogen were purchased from BOC Kenya LTD. Distilled water used for solution preparations as well as rinsing glassware was provided by the Department of Chemistry, University of Nairobi. Di-butyl Phthalate (purity >99%) and Bisphenol A (purity >99%) were supplied from Sigma Aldrich, U.S.A.

3.3 Instruments and apparatus used

Analytical balance type A-160 from Fisher (SHIMADZU model ATX224) was used for all weight measurements. Gallenkamp oven model OV 160 was used for drying of glassware. Temperature, pH, TDS and electrical conductivity of samples were measured using; Scientific HANNA instruments model HI 9812-5 portable pH /EC/TDS/ °C. Samples were preserved in a refrigerator and a deep freezer in the laboratory. Stuart scientific mini orbital shaker SO5 was used to agitate the samples.

Beakers, glass vials (10 and 30 mL), auto-sampler vials 1.5 mL, conical flasks (25, 100, 250 and 1000) mL, Pasteur pipettes, desiccators, measuring cylinders and syringes for sample injection (10, 25, 50, 100) µL were among the glasswares utilized in this study.

Agilent Series Gas chromatograph Hewlett Packard GC HP6890 equipped with a mass spectrophotometer detector MSD 5973 inert and 7683 series injector was used for identification and quantification of the DBP and BPA.

In this study, the Agilent 6890N's injector and detector temperatures were set at 250 °C and 300 °C, respectively. Helium served as the carrier gas, and the inlet temperature was set at 250 °C. The injection mode was split less while 1 mL per minute was the column flow rate. The initial oven temperature was 80 °C, which was held for 2 minutes before being raised to 120 °C at a rate of 8 °C/minute in under 5 minutes. This temperature was held for 12 minutes then ramped up at 275 °C at an increased rate of 8 °C/minute. The column was a high-performance capillary column with a film thickness of 0.25 µm, an internal diameter of 0.25 mm and a length of 30 m. Data of this experiment was processed using Chem-station software.

Extraction of DBP and BPA from sediment, sea weed and soil samples were done using a Soxhlet extractor while 2.0 L glass separatory funnel was used for DBP and BPA extraction from water. For the cleanup process, a glass column with a 2 cm internal diameter and a 20 cm length was used. Sample extracts were concentrated using a rotary evaporator from LABCONCO, and the solvents were distilled using a fractional distiller.

3.4 Sampling

3.4.1 Sampling plan

Sampling was done two times in October (2018) and January (2019). Samples collected in October captured the short rain season, while the samples collected in January represented the dry season. Using the grab method, water samples were obtained in 2.5 L amber glass bottles. These amber bottles were pre-cleaned with clean, soapy water before being rinsed with distilled water and oven dried at 105 °C. 100 g of activated sodium chloride was added to each sample for preservation. This was followed by sealing of the bottles with activated aluminum foils, corking and labeling appropriately. Finally, the samples were then transported in cooler boxes packed with dry ice to laboratory. Once in laboratory, the samples were kept in a freezer at a temperature of 4 °C prior extraction.

3.4.2 Monitoring plastic litter at the shoreline of the six sampling sites

Shoreline which is the interface between land and sea is important compartment for monitoring because it's where marine plastic litter is present in large quantities and closer to land-based sources. Plastic litter items which included drinking water bottles, disposable caps, soft drink bottles, bottle tops, straws, plastic papers, plastic plates, shoes, cigarette lighters among others were collected from three points each measuring 20 m by 20 m at the shoreline where water samples were collected. All plastic litter items were counted, weighed and recorded.

3.4.3 Collection of sediment samples

Sediment samples were scooped under water by use of a previously cleaned stainless steel scoop from three points at the sampling sites where water samples were collected from and put on activated aluminum foil. The compound samples scooped were homogenized extensively using the stainless steel scoop onto a clean piece of aluminum foil. Thereafter, the 500 g representative sample of the compound collected were enclosed in an activated aluminum foil, labeled clearly then placed in zip-lock bags made of polyethylene, stored in an ice box, carried to the laboratory and preserved in a freezer at -18 °C awaiting extraction.

3.4.4 Collection of soil samples

Soil samples were scooped at the points adjacent to the same sites where water and sediment samples were picked up. Soil samples were scooped 15 cm from the surface by use a previously cleaned stainless steel scoop from three points and put on clean activated aluminum foil. The compound samples were scooped then homogenized extensively using the scoop on a clean aluminum foil. Then 500 g of the representative sample of the compound sample was enclosed in aluminum foil, labeled clearly, placed in zip-lock bags made of polyethylene, stored in an ice box, carried to the laboratory and preserved in a freezer at -18 °C awaiting extraction.

3.4.5 Collection of sea weed samples

Whole plant of sea weed samples were collected at the shoreline from the same sites where water and sediment samples were sampled. Sea weed samples were collected using a previously cleaned stainless steel scoop out of three points and put on the aluminum foil. The compound samples collected was quartered to obtain a 500 g of the representative sample, wrapped in a clean aluminum foil, labeled clearly, placed in zip-lock bags made of polyethylene, stored in an ice box, carried to the laboratory and preserved in a freezer at -18 °C awaiting extraction.

3.5 Physical-chemical parameter determination

3.5.1 Determination of electrical conductivity of the water samples and pH of water, soil and sediment samples

Utilizing Scientific Hanna apparatus model HI 9812-5 portable pH / EC / TDS / oC, which was calibrated using buffers of pH 10.0, 7.0, and 4.0 before use, the pH of water samples was determined. Meter reading was taken after thoroughly rinsing the electrode with distilled water followed by immersion of the rinsed electrode in the water sample with the tip of the electrode in water sample for a minute before a reading was recorded. By weighing 10 g of the sediment sample and adding 25 mL of distilled water to create a 2:5 suspension of sediment and water, the pH of the sediments was calculated. The combination was then shaken for five minutes in an

orbital shaker, allowed to settle for thirty minutes and the pH was measured by immersing the electrode into the suspension. Same procedure was followed for soil's pH.

Electrical conductivity was measured using Scientific HANNA instruments model HI 9812-5 portable pH /EC/TDS/ °C which was calibrated before and electrode rinsed with distilled water before every use.

3.5.2 Water temperature measurement

Water temperature measurement was measured in degree Celsius using HANNA portable meter model HI 9812-5 pH /EC/ °C. Measurements were carried out directly by dipping the probe in the water sample and temperature recorded.

3.5.3 Determination of organic content of soil and sediment samples

The moisture, ash, and organic matter of organic soils and sediments were measured using the standard test technique ASTM D2974 in order to account for the presence of water in the soil and to measure solely organic matter. The ash content and organic material of organic soils was determined by igniting the oven-dried specimen as obtained from the water content determination in a furnace at 440 ± 40 °C. Sample quartering was done to obtain a representative sample of about 300 g of soil and representative sample was reduced to obtain the test specimen by quartering. 50.00 ± 10 grams of test specimen was weighed and immediately placed in separate tightly-sealed.

Mass of a container, M_c , fitted with a lid or a heavy-duty aluminum foil cover was recorded to the nearest 0.01. The soil test specimen obtained was placed in the container, crushed with a spatula to a thickness not exceeding 30 mm. The moist mass of the soil test specimen plus container fitted with lid/cover, M_{cms} was recorded to the nearest 0.01. Then the container was placed in the oven and dried uncovered for a minimum of 16 hrs at 110 ± 5 °C. It was removed from the oven, covered tightly, and allowed the test specimen to cool in a desiccator to room temperature. The mass of the oven-dried test soil specimen plus container with lid/cover, $M_{c ds}$ was recorded, to the nearest 0.01 keeping exposure to the room atmosphere to a minimum.

The lid/cover was removed and placed the container with the test specimen in a furnace while gradually bringing the temperature in the furnace to 440±40 °C. The specimen was considered fully ashed once this temperature was attained and the container was left within for at least one hour, then it was taken out of the furnace, the container's lid or cover was carefully replaced, and placed in a desiccator. It was allowed to come to room temperature and the mass of the container with lid/cover plus the ashed specimen, M_{cas} , was recorded to the nearest 0.01.

Water content, w , as a percentage of oven-dried mass was calculated using Equation (3.1) below:

$$w = \frac{M_w}{M_s} \times 100 = \frac{M_{cms}}{M_{cds}} - \frac{M_c}{M_c} \times 100 \dots\dots\dots \text{Equation (3.1)}$$

Where, w = water content, nearest 1 %, M_w = mass of water ($M_w = M_{cms}-M_{cds}$), nearest 0.01 grams, M_s = mass of oven-dried specimen ($M_s = M_{cds}-M_c$), nearest 0.01 grams, M_{cms} = mass of container with lid plus moist specimen, nearest 0.01 grams, M_{cds} = mass of container with lid plus oven-dried specimen, nearest 0.01 grams, M_c = mass of container plus lid, nearest 0.01 grams.

The ash content was calculated using Equation (3.2) below:

$$A_c = \frac{M_a}{M_s} \times 100 = \frac{M_{cas}}{M_{cds}} - \frac{M_c}{M_c} \times 100 \dots\dots\dots \text{Equation (3.2)}$$

Where, A_c = ash content, nearest 0.1 %, M_a = mass of ash ($M_a = M_{cas} - M_c$), nearest 0.01 grams, and M_{cas} = mass of container with lid plus ashed specimen, nearest 0.01 grams. The organic material was calculated using Equation (3.3) below:

$$O_m = 100 - A_c \dots\dots\dots \text{Equation (3.3)}$$

Where, O_m = organic material, nearest 0.1 % and the same procedure was followed for sediment samples.

3.6 Preparation of reagents

1kg of anhydrous sodium sulphate (Na_2SO_4) was activated for 16 hours at 200 °C in a Gallenkamp oven to eliminate all the impurities. Solvents used were fractionally distilled before they were applied in the sample preparation. Buffer solution was made by adding 29.6 mL 0.2 M HCl to 50 mL of 0.2 M dipotassium hydrogen phosphate.

Preparation of 50 mL of 0.2 M K_2HPO_4 was done by weighing 1.7418 g of K_2HPO_4 into a 50 mL volumetric flask, 0.2 N HCl in 500 mL was prepared by measuring 8.3 mL HCL into 500 mL volumetric flask, 0.1 N HCl in 500 mL was done by measuring 4.2 mL HCL into 500 mL volumetric flask, while the preparation of 0.1 N NaOH in 500 mL was done by weighing 2 grams NaOH into 500 mL volumetric flask and all were then topped up to the mark with distilled water.

3.7 Extraction

3.7.1 DBP/BPA extraction from water samples

DBP and BPA analytes extraction from water samples was achieved by liquid-liquid extraction method. 2.0 L of water sample was transferred into 3.0 L beaker and the pH of the water samples taken and recorded. 50 mL of 0.2 M dipotassium hydrogen phosphate buffer was added to the water samples and by putting in few drops of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions, pH was set to 7. Then the neutral solution was transferred to 2.0 L separating funnel and treated with 100 g of sodium chloride to salt out the analyte from the aqueous phase to the organic phase. Shaking thoroughly and adding in 60 mL dichloromethane followed. Further, the mixture was shaken gently at the same venting to release pressure then let to stand for 30 minutes to increase separation of the bi-layers. The bottom part of the bi-layers was then separated into a clean, dried 250 mL conical flask and extraction procedure was replicated, each time using 60 mL dichloromethane. 2 to 10 grams of anhydrous Na_2SO_4 were added to the extracted organic layer to dry. 2 mL of isooctane was added as a keeper and concentrated using rotary evaporator to 2 mL. The concentrated extracts were transferred into 4 mL vials and preserved in a refrigerator at 4 °C awaiting cleanup.

3.7.2 Extraction of DBP/BPA from soil, sediment and sea weed samples

The soil samples were thawed for about 6 hours and mixed thoroughly by grinding in a mortar and pestle prior to weighing. 20 g triplicate samples were weighed, mixed with anhydrous sodium sulphate and ground to a fine powder. The mixture was covered up with aluminum foil and kept all night to dry. The samples were Soxhlet extracted with 200 mL of dichloromethane

in 250 mL round bottomed flask for 16 hours in a Soxhlet extractor. 2 mL of iso-octane was then added as a keeper and concentrated to 2 mL using rotary evaporator. The concentrated extracts was then transferred into vials and preserved in a refrigerator at 4 °C awaiting cleanup process. Same extraction procedure was employed for both sediment and sea weed samples.

3.7.3 Samples cleanup and fractionation

Cleanup of water, soil, sediments and sea weed samples extracts were conducted using chromatographic columns filled with silica gel. Chromatographic columns 25 cm × 1.5 cm diameter were each packed with 1cm Na₂SO₄ (previously activated overnight at 200 °C) as the bottom layer, 10 g of silica gel (previously activated overnight at 200 °C) followed by 1 cm of the baked anhydrous Na₂SO₄ at the top. The column was conditioned with 20 mL hexane and eluent discarded. Each sample extracts was quantitatively introduced to the column and eluted with 180 mL of n-hexane. Each sample extract was then transferred into a clean 250 mL round bottomed flask and treated with 2 mL of isooctane as a keeper solvent before rotary evaporation to 1 mL. Finally each extract was quantitatively transferred separately into a clean 1.5 mL auto-sampler vial and reconcentrated to 0.5 mL by use of gentle stream of white spot nitrogen.

3.8 Quality assurance and quality control

Quality control and quality assurance involved matrix spiking for determination of recoveries, analysis of blanks and control samples. Distilled water sample was spiked with target analytes and extracted to determine extraction efficiency and method recoveries. Field and trip blanks containing distilled water and anhydrous Na₂SO₄ were integrated in the sampling plan to assist in tracking transport and storage contamination. All samples were analysed in triplicate to verify present analytes in the samples. Sample blanks and spiked samples were included in the sample extraction and clean-up to verify method performance. Calibration of the instrument was done using reference standards. A multi-level calibration curves were used to determine the concentration of the analytes.

3.9 Qualitative characteristics

Reference standards of Di-butyl phthalate and BPA were used in development of calibration curves and spike recoveries. Working reference standard solutions ranging from 0.05 ppm to 100 ppm were prepared individually for each standard. Each working reference standard was from the standard stock solution as in Equation (3.4) below.

$$1000 \text{ ppm} \times V_2 = 100\text{ppm} \times 10 \text{ cm}^3 \dots\dots\dots \text{Equation (3.4)}$$

$$V_2 = 1\text{cm}^3$$

The standard curve of each calibration was a straight line correlation coefficient (R^2) of above 0.99, which indicated good linearity. The concentration of analytes in the samples were obtained using the regression.

3.10 Chromatograms

The chromatograms obtained from instrument were used to determine the analytes retention time and peak areas. Standard calibration curves for BPA and DBP analysed were obtained for retention time, identification and peak area for quantification. The retention time for BPA was 11.285 minutes while that for DBP was 8.321 minutes.

3.10.1 BPA and Di-butyl phthalate recovery levels

Percentage recovery which is the amount of original substance retained after the completion of the reaction was calculated using Equation (3.5) below. The recovery of the spiked analyte was carried out to check the efficiency of the method.

$$\% \text{ recovery} = \frac{\text{amount of substance recovered on purification}}{\text{Amount of substance originally taken}} \times 100 \dots\dots\dots \text{Equation (3.5)}$$

Percentage recovery tests for BPA and DBP in water, soil, sediment and weeds samples were done by spiking with BPA and DBP standard solution for % recoveries.

3.11 Limits of detection and quantification of BPA and DBP

Limit of Detection (LOD) of any given compound is defined as the lowest analyte concentration that an analytical procedure can dependably detect although not necessarily quantified as an exact value. It's the concentration that displays a peak (y) on the equipment which is separate from the 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 . The relationship is expressed as $Y - Y_B = 3S_B$. The LOD of each (DBP and BPA) was computed on the basis of the minimum concentration of the calibration standards introduced along with the correspondent noise signals using the relationship adapted from Equation (3.6) below.

$$\text{LOD} = \frac{3 \times \text{Noise peak area} \times \text{concentration of standard injected } (\eta\text{g})}{\text{Analyte response in the lowest calibration point}} \dots\dots\dots \text{Equation (3.6)}$$

LOQ of a machine does not only refer to the least quantity of analyte that analytical equipment can constantly and reliably detect and measure but also addresses the point at which some predefined objectives for imprecision and bias are attained. LOQ was calculated using Equation (3.7) shown below.

$$\text{LOQ} = (\text{LOD} \times 3) \dots\dots\dots \text{Equation (3.7)}$$

3.12 Data analysis and interpretation

The quantitative data was processed and analyzed by Microsoft Excel and other computer statistical packages while the Pearson correlations between the levels of DBP, BPA and residue levels in water, soil, sediment and weed samples during dry and wet seasons were obtained using Statistical Package for Social Sciences (SPSS 22). The data was analyzed with linear regression method and external calibration curves. Results obtained were illustrated by the use of text, graphs and statistical tables.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Water physical-chemical parameters

4.1.1 The pH, EC and temperature in dry and wet seasons from the selected coastal Beaches

pH, conductivity and temperature values of the samples were measured during the wet as well as dry seasons and results were recorded in Table 4.1. The pH values within the seven sites varied between 7.62 ± 0.01 and 8.66 ± 0.05 during wet season while that in dry season varied between 7.64 ± 0.01 and 8.67 ± 0.05 as shown in Table 4.1. The Kilifi Beach recorded the highest pH value both in wet and dry seasons with 8.66 ± 0.05 and 8.67 ± 0.05 , respectively. pH increases with increase in salinity until the water reaches calcium carbonate saturation. Ocean usually has a high alkalinity value as a result of carbonate content hence have a greater ability to buffer free hydrogen ions. Sabaki River recorded the lowest pH value in both wet and dry seasons with 7.62 ± 0.01 and 7.64 ± 0.01 respectively. Sabaki River is the main transporter of sediment to the study area. Anthropogenic activities causes pH fluctuations related to pollution through agricultural run-off, industrial run-off among others. This could be the reason for Sabaki river having lower pH than Kilifi Beach. Kilifi Beach which is a cosmopolitan town has got many industrial activities in close proximity to Kilifi Beach compared to Sabaki River leading to an impact on pH levels of Kilifi Beach. The Sabaki River's pH levels were within the range suggested by the WHO for natural water bodies, which is between 6 and 8.5 for drinking water intended for household use and between 8 and 9 for estuary and marine water (WHO, 2006).

The electrical conductivity values for the Sabaki River which is used for domestic purposes during wet and dry seasons ($1,460 \pm 4.95$ and $1,650 \pm 4.24$) $\mu\text{S}/\text{cm}$ respectively, were above the established EPA drinking water quality standards of $900 \mu\text{S}/\text{cm}$. This could be due to changes during high tides which leads to mixing of the river water and the ocean water which is saline. Electrical conductivity of water is directly related to the concentration of dissolved solids in

water. Ions from dissolved solids in water influences the ability of that water to conduct electric current.

Table 4.1: Water physical-chemical parameters recorded during wet and dry season from the selected coastal Beaches.

Site	Local name	pH		Conductivity ($\mu\text{S/cm}$)		Temperature ($^{\circ}\text{C}$)	
		Wet	Dry	wet	Dry	wet	dry
1	Pirate Beach	7.92 \pm 0.12	7.91 \pm 0.01	11,520 \pm 3.53	17,450 \pm 5.66	22 \pm 0.10	23 \pm 0.15
2	Mombasa Beach	7.91 \pm 0.01	7.96 \pm 0.03	11,400 \pm 6.36	16,850 \pm 6.36	22 \pm 0.12	24 \pm 0.17
3	Kilifi Beach	8.66 \pm 0.05	8.67 \pm 0.05	11,880 \pm 5.66	19,050 \pm 2.83	22 \pm 0.15	23 \pm 0.10
4	Malindi Beach	8.24 \pm 0.03	8.25 \pm 0.07	11,100 \pm 6.36	15,750 \pm 3.53	22 \pm 0.10	23 \pm 0.12
5	Sabaki Beach	8.06 \pm 0.08	8.36 \pm 0.08	9,360 \pm 5.66	16,450 \pm 4.24	22 \pm 0.12	23 \pm 0.15
6	Sabaki River	7.93 \pm 0.03	7.96 \pm 0.05	5,960 \pm 4.95	6,990 \pm 4.24	22 \pm 0.10	23 \pm 0.10
7	Sabaki River	7.62 \pm 0.01	7.64 \pm 0.01	1,460 \pm 4.95	1,650 \pm 4.24	22 \pm 0.17	24 \pm 0.17
	WHO recommendation	(6-8.5) drinking water (8-9) seawater	(6-8.5) drinking water (8-9) seawater	<1,000 (drinking water) (5,000-51,500) seawater	<1000 (drinking water) (5,000-51,500) seawater	≥ 2 above the max ambient temp.	≥ 2 above the max ambient temp.
	KEBS recommendation	(6.5–8.5) drinking water	(6.5–8.5) drinking water	Not specified (drinking water)	Not specified (drinking water)	≥ 2 above the max ambient temp	≥ 2 above the max ambient temp
	US EPA recommendation	(6-8.5) drinking water (8-9) seawater	(6-8.5) drinking water (8-9) seawater	<900 drinking water $\geq 5,000$	<900 drinking water $\geq 5,000$	≥ 2 above the max ambient temp.	≥ 2 above the max ambient temp.

Source: World Health Organisation (WHO, 2006), Kenya Bureau of Standards (2010) and US Environmental Protection Agency (USEPA 2006).

The electrical conductivity values for the rest of the sites during the wet and dry seasons were within the recommended WHO of between 5,000-51,500 $\mu\text{S}/\text{cm}$. It was ranging from 5,960 - 11,880 \pm 5.66 and 6,990-19,050 \pm 2.83 $\mu\text{S}/\text{cm}$ during the wet and dry season respectively. Electrical conductivity is dependent on water salinity/TDS. Changes in water level as well as flow can also contribute to change in conductivity through their impact on salinity. The electrical conductivity values during the dry season were higher than during the wet season. This could be due to low water flow and low water level during the dry season leading to high electrical conductivity.

For the wet and dry seasons, respectively, the temperature of the water samples ranged between 22 \pm 0.10 $^{\circ}\text{C}$ and 23 to 24 \pm 0.17 $^{\circ}\text{C}$. This was within WHO recommended value of increase not more than 2 $^{\circ}\text{C}$ above the maximum ambient temperature.

4.2 Soil and sediment physical-chemical parameters

4.2.1 The pH, % organic content of soil, sediment and quantity of plastic litter in dry and wet seasons from the selected coastal Beaches

pH and percentage organic content values of the soil and sediment samples were measured during the wet as well as dry seasons as shown in Table 4.2. The quantity of plastic litter items at the shoreline of the six sampling sites was also done as shown in the same table.

The pH values for soil samples within the sites varied between 7.52 \pm 0.01 and 9.68 \pm 1.02 during wet season, 7.53 \pm 1.20 and 9.69 \pm 1.01 during dry season while that of sediment samples varied between 7.54 \pm 0.01 and 9.91 \pm 0.03 during wet season, 7.54 \pm 1.01 and 9.91 \pm 1.23 during dry season as shown in Table 4.1. Pirate beach and Mombasa Beach recorded the lowest pH value both in soil and sediment samples the during wet as well as in the dry season. Pirate Beach recorded the highest % organic content of 74.02 in soil samples and 69.65 in sediment samples followed by Mombasa Beach with 70.41 in soil and 69.66 in sediment samples.

Table 4.2: Physical-chemical parameters of soil and sediment samples in wet and dry seasons

SOIL SAMPLES								
Site	Local name	pH		% organic content	Average no. of plastics litter items of the		Average weight (kg) of plastics of the three points	
		Wet	Dry		Wet	Dry	Wet	Dry
1	Pirate Beach	7.52±0.01	7.54±0.41	74.02	180	87	3.22	1.03
2	Mombasa Beach	7.52±0.21	7.53±1.20	70.41	170	20	2.97	0.72
3	Kilifi Beach	9.44±0.11	9.48±0.41	26.55	56	14	1.18	0.73
4	Malindi Beach	8.56±1.56	8.56±2.56	41.98	36	12	1.60	0.69
5	Sabaki Beach.	9.68±1.02	9.69±1.01	31.02	15	16	0.42	0.30
6	Sabaki River Mouth	9.64±1.36	9.66±1.06	28.73	20	19	0.92	1.08
7	Sabaki River	9.60±0.02	9.61±1.66	26.71	-	-	-	-
SEDIMENT SAMPLES								
1	Pirate Beach	7.66±0.56	7.67±0.16	69.65	180	87	3.22	1.03
2	Mombasa Beach	7.54±0.01	7.54±1.01	69.66	170	20	2.97	0.72
3	Kilifi Beach	9.42±1.18	9.45±1.18	30.55	56	14	1.18	0.73
4	Malindi Beach	8.33±0.13	8.36±0.01	54.90	36	12	1.60	0.69
5	Sabaki Beach	9.76±1.42	9.77±1.22	29.63	15	16	0.42	0.30
6	Sabaki River Mouth	9.91±0.03	9.91±1.23	34.34	20	19	0.92	1.08
7	Sabaki River	8.86±0.48	8.87±0.08	51.54	-	-	-	-

4.3 Calibration curves for BPA and DBP standards

Individual reference standards of DBP and BPA were used in development of calibration curve. Identification of the analytes was achieved by comparing their individual retention times with those of the respective standards while quantification was based on external multi-level calibration curve of standards ensuring high, middle and lower bound limits were catered for. Concentrated samples were diluted to fit in the calibration window.

4.3.1 Calibration curve for BPA standard

A plot of BPA concentrations against peak area of the standards was obtained (Table 4.3) The corresponding equation for the linear regression in the form $y=mx+c$ and Correlation coefficients, R^2 were drawn from the graph (Figure 4.1).

Table 4.3: Concentrations and peak area for BPA standard

Concentration (ng/mL)	Peak area
0.01	10
0.05	229
0.1	1,041
0.5	5,076
1	19,004
2	46,127
7	129,085
10	183,380

Calibration curve of BPA standard was a straight line with a correlation coefficient R^2 of 0.997 indicating good linearity. The straight line equation for BPA was $y = 18430x + 398.18$.

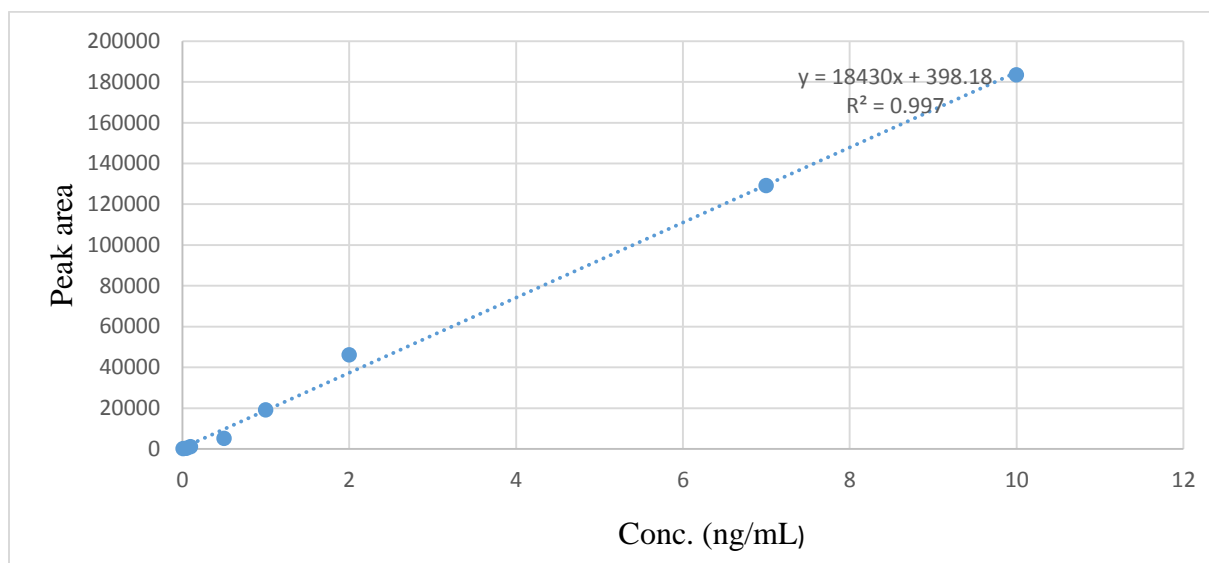


Figure 4.1: The calibration curve for BPA standard

4.3.2 Calibration curve for DBP standard

A plot of BPA concentrations against peak area of the standards was obtained (Table 4.4) The corresponding equation for the linear regression in the form $y=mx+c$ and Correlation coefficients, R^2 were drawn from the graph (Figure 4.2).

Table 4.4: Concentrations and peak area for DBP standard

Concentration (ng/mL)	Peak area
0.05	10
0.01	35
0.5	137
1	275
2.5	1,867
5	1,673
7.5	2,160
10	3,246
50	14,035
100	27,470

Calibration curve of DBP standard was a straight line with a correlation coefficient R^2 of 0.998 indicating good linearity. The straight line equation for DBP $y=272.89x+272.63$.

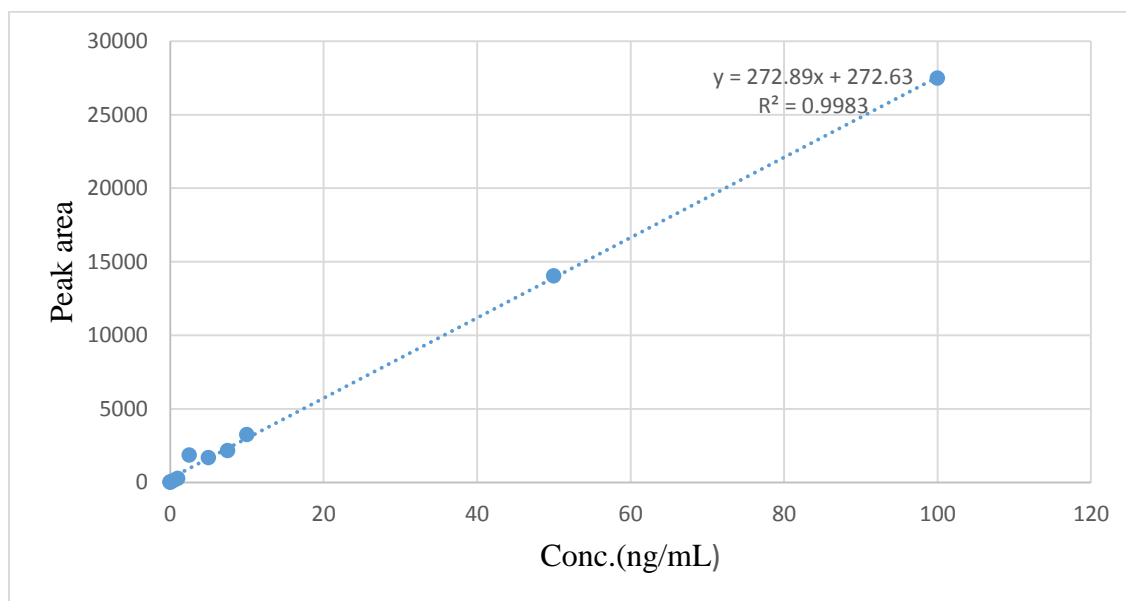


Figure 4.2: Calibration curve for DBP standard

4.4 Limits of detection and quantification of BPA and DBP

Limits of detection (LOD) for Bisphenol A and Di-butyl Phthalate and limits of quantifications (LOQ) are shown in Table 4.5. BPA's limit of detection (LOD) and limit of quantification (LOQ) were 0.002 ng/mL and 0.005 ng/mL, respectively, while DBP's were 0.5 ng/mL and 1.0 ng/mL.

Table 4.5: The limit of detection and quantification of BPA and DBP

Analyte	LOD (ng/mL)	LOQ (ng/mL)
BPA	0.002	0.005
DBP	0.5	1.0

4.5 Mean percentage recoveries tests for BPA and DBP in water, soil, sediment and sea weed samples

Mean percentage recovery result for BPA and DBP in water, soil, sediment and sea weed samples are shown in Table 4.6. The mean percentage recovery for BPA in water, soil, sediment and sea weed samples ranged between 96.66±5.23% to 99.56±3.89% while that of DBP ranged between 92.76±9.65% to 101.33±3.44%.

Table 4.6: Mean percentage recovery tests for BPA and DBP in water, soil, sediment and sea weed samples

Analyte	water (ng/mL)	soil (ng/g, DW)	sediment (ng/g, DW)	sea weed (ng/g, DW)
BPA	96.70±7.55	99.56±3.89	96.66±5.23	90.98±6.22
DBP	101.33±3.44	94.88±7.06	93.54±4.33	92.76±9.65

Where DW is the weight of the dry mass. The BPA and DBP levels detected were within the acceptable range of 70-120 %, therefore no correction was done (Socas-Rodríguez *et al.* , 2017).

4.6 The DBP levels in the coastal Beaches

4.6.1 The DBP levels in water, soil, sediment and sea weed samples in wet and dry season

DBP levels in water, soil, sediment and sea weeds samples in wet and dry season from all sites are shown in Table 4.7. During wet season, only Pirate and Mombasa Beaches recorded measurable levels of DBP in water, soil, sediment and sea weeds. Only soil samples from Pirate and Mombasa Beaches recorded measurable amount of DBP residue level of 39.75±0.91 ng/g and 18.53±0.29 ng/g, respectively. The other sites had levels below 0.5 ng/mL in water, sediment and sea weed samples.

Table 4.7: DBP levels in water, soil, sediment and sea weed samples in wet and dry seasons

Wet season					
Site	local name	water (ng/mL)	soil (ng/g)	sediments (ng/g)	sea weed (ng/g)
1	Pirate Beach	1.29±0.13	7.56±0.63	3.04±0.38	1.49±0.25
2	Mombasa Beach	0.79±0.22	4.25±0.89	2.18±0.49	0.53±0.39
3	Kilifi Beach	< 0.5	< 0.5	< 0.5	< 0.5
4	Malindi Beach	< 0.5	< 0.5	<0.5	< 0.5
5	Sabaki Beach	< 0.5	< 0.5	< 0.5	< 0.5
6	Sabaki River mouth	< 0.5	< 0.5	< 0.5	< 0.5
7	Sabaki River	< 0.5	< 0.5	< 0.5	< 0.5
Dry season					
1	Pirate Beach	< 0.5	39.75±0.91	< 0.5	< 0.5
2	Mombasa Beach	< 0.5	18.53±0.29	< 0.5	< 0.5
3	Kilifi Beach	< 0.5	< 0.5	< 0.5	< 0.5
4	Malindi Beach	< 0.5	< 0.5	< 0.5	< 0.5
5	Sabaki Beach	< 0.5	< 0.5	< 0.5	< 0.5
6	Sabaki River mouth	< 0.5	< 0.5	< 0.5	< 0.5
7	Sabaki River	< 0.5	< 0.5	< 0.5	< 0.5

4.6.1 DBP levels in water samples collected in wet and dry seasons

DBP levels in water samples collected in wet and dry season is shown in Figure 4.3. DBP levels at Pirates beach recorded a concentration of 1.29±0.13 ng/mL in wet and < 0.5 ng/mL in dry seasons (Table 4.7). Mombasa site recorded 0.79±0.22 ng/mL in wet and < 0.5 ng/mL in dry season while the other sites had < 0.5 ng/mL of DBP (Figure 4.3). Mombasa city has larger population, leading business centres and a home to Kilindini Harbour. Due to many industrial activities in Mombasa compared to other sites. This could be the reason why Pirate and Mombasa Beaches recorded higher levels of DBP in water samples during the wet season from wastewater and industrial run-off.

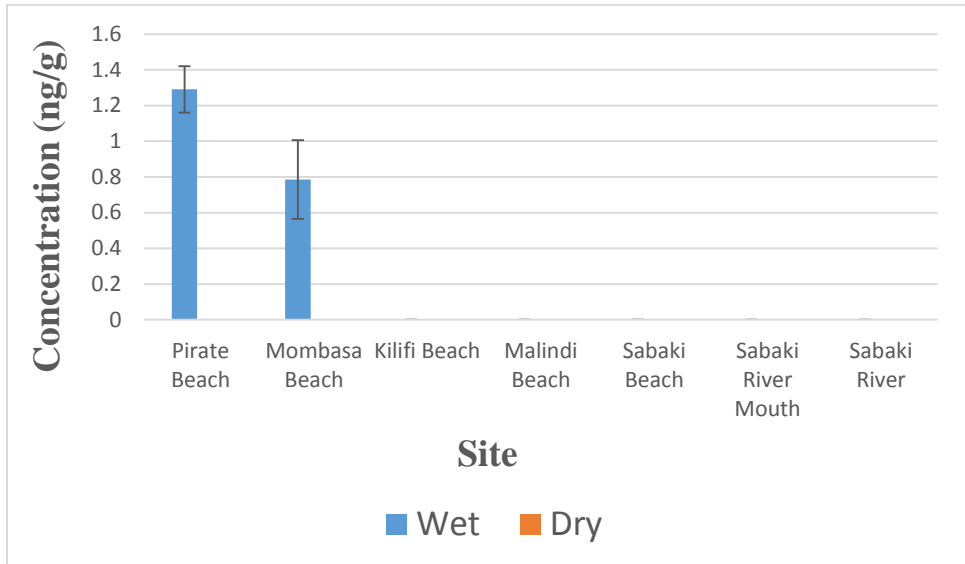


Figure 4.3: DBP levels in water samples in the wet and dry season

4.6.2 DBP levels in soil samples in wet and dry seasons

The DBP residue levels in soil samples collected within the wet and dry season is shown in Figure 4.4. Pirate and Mombasa Beaches had measurable levels of DBP in soil samples while Kilifi, Malindi, Sabaki Beaches, Sabaki River mouth and Sabaki River sites had low levels less of 0.5 ng/g in wet and dry seasons. Soil samples had the highest levels in Pirate Beach of 7.56 ± 0.63 ng/g and 39.75 ± 0.91 ng/g this was followed by Mombasa Beach with 4.25 ± 0.89 ng/g and 18.53 ± 0.29 ng/g (Table 4.7) in wet and dry seasons, respectively.

Seasonal variation is likely to have an impact on DBP leaching. In the wet season, water leaching through the soil will transport DBP down the soil profile and into the groundwater while during the dry season DBP will remain in the soil since there is no transportation down the soil profile. Increase in temperature, increased the concentration of DBP in the soil. This was attributed to DBP becoming less bound to the plastic waste materials on the soil hence leaching to the soil at elevated temperatures (Li and Tang, 2013). Mombasa county being highly populated and highly industrial, this could be the reason why Pirate and Mombasa Beaches recorded some levels of DBP.

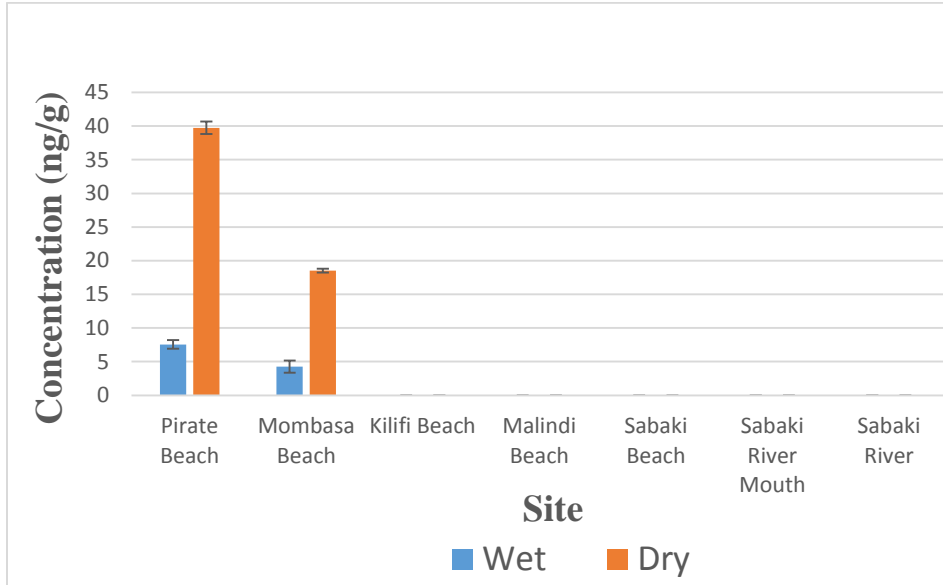


Figure 4.4: DBP residue levels in soil samples in the wet and dry seasons

4.6.3 DBP levels in sediment samples in wet and dry seasons

The DBP residue levels in sediment samples in wet and dry seasons is presented in Figure 4.5. The DBP residue levels in sediments from Pirate beach was 3.04 ± 1.38 ng/g and Mombasa Beach had 2.18 ± 0.49 ng/g in wet and levels below 0.5 ng/g in dry season, respectively (Table 4.7). The other sampling sites had probably levels of less than 0.5 ng/g in wet and dry season (Figure 4. 5). In comparison to other sites where DBP levels were less than 0.5 ng/g, the cause for the levels found at Pirate and Mombasa Beach may be related to the transportation and deposition of contaminated soil from anthropogenic activities in Mombasa in water-borne sediment.

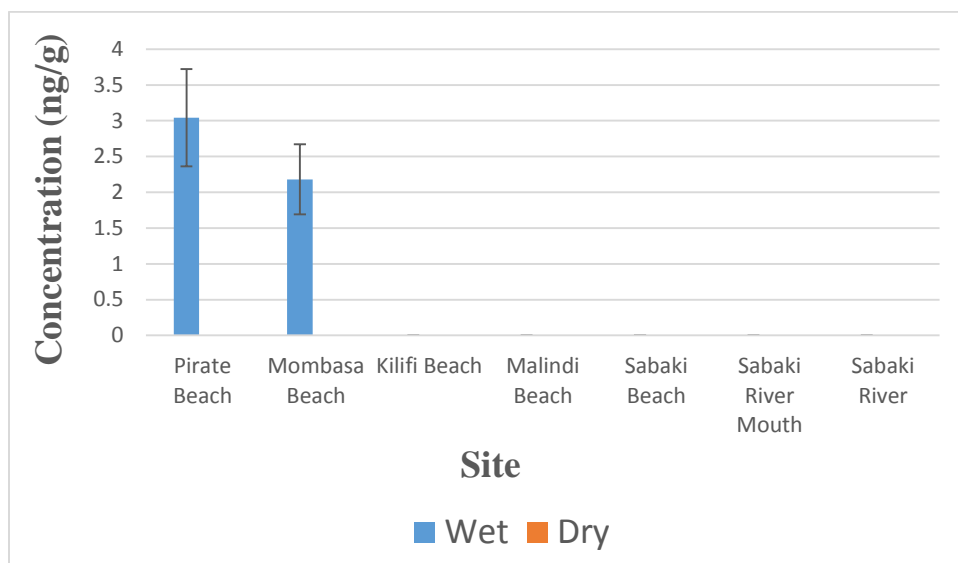


Figure 4.5: DBP residue levels in sediment samples in wet and dry season

4.6.4 DBP levels in sea weed samples in wet and dry season

DPB levels in weed samples collected in wet and dry season is shown in Figure 4.6. DBP residue levels in weed samples from Pirate was 1.49 ± 0.25 ng/g and Mombasa had 0.53 ± 0.39 ng/g in wet season but had below detection limits levels of less than 0.5 ng/g in dry season, respectively (Table 4.7). The other sampling sites had levels of less than 0.5 ng/g in wet and dry season (Figure 4. 6). Due to many industrial activities around Mombasa and Pirate Beaches as compared to the other sites, this could be the reason why Pirate and Mombasa beaches each recorded some amount of DBP in weed samples during the wet season from wastewater run-off/ industrial run-off which ends up being absorbed by the weeds.

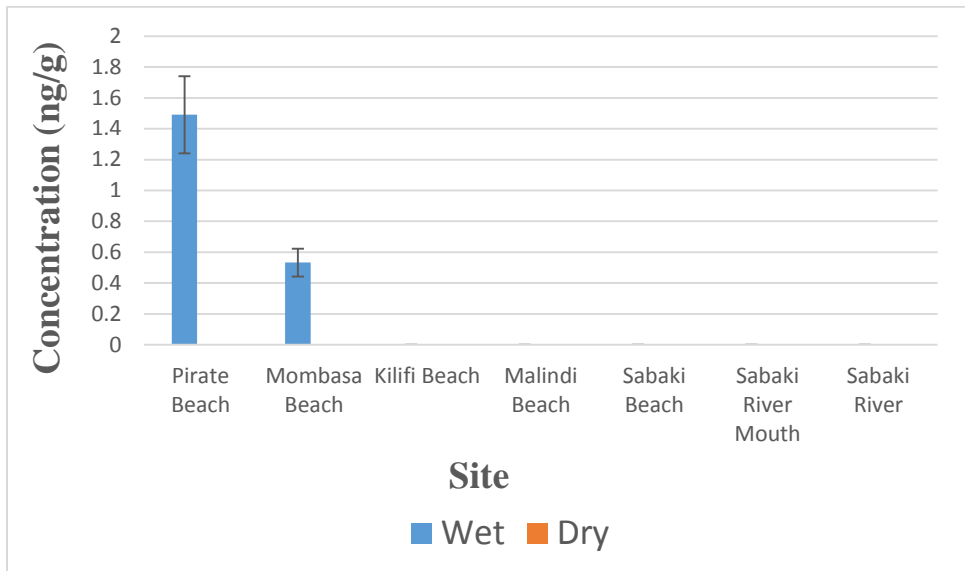


Figure 4.6: DPB levels in sea weed samples in wet and dry season

4.7 The BPA residue levels in water, soil, sediment and sea weed samples from Kenyan coastal Beaches

4.7.1 The BPA residue levels in water samples in wet and dry season

Residue levels of BPA in water, soil, sediment and sea weed samples in wet and dry season from the sampling sites are shown in Table 4.8. During wet and dry seasons, Mombasa Beach had the maximum level of BPA in water samples at 2.74 ± 0.57 ng/mL and 0.43 ± 0.01 ng/mL, respectively. Pirate Beach followed with 2.24 ± 0.01 ng/mL and below 0.002 ng/mL during wet and dry seasons, respectively. Sabaki beach recorded the lowest DBP residue levels of 0.57 ± 0.11 ng/mL in water during the wet season (Table 4.8).

Table 4.8: BPA residue levels in water, soil, sediment and sea weed samples in wet and dry season

Wet season					
	Site	water (ng/mL)	soil (ng/g)	sediments (ng/g)	sea weeds (ng/g)
1	Pirate Beach	2.24±0.01	< 0.002	1.46±1.29	5.91±0.92
2	Mombasa Beach	2.74±0.57	1.55±0.28	2.31±0.58	11.66±0.94
3	Kilifi Beach	0.61±0.25	3.39±0.14	1.99±1.08	0.51±0.27
4	Malindi Beach	0.87±0.72	1.66±0.67	3.76±0.17	2.91±0.05
5	Sabaki Beach	0.57±0.11	< 0.002	3.53±0.42	< 0.002
6	Sabaki River mouth	1.19±0.19	< 0.002	0.60±0.25	< 0.002
7	Sabaki River	0.60±0.25	3.26±0.30	1.86±0.38	< 0.002
Dry season					
1	Pirate Beach	< 0.002	1.34±1.04	0.16±0.05	2.70±0.03
2	Mombasa Beach	0.43±0.01	2.71±0.45	1.36±0.41	0.28±0.24
3	Kilifi Beach	0.002±0.10	< 0.002	1.29±0.12	0.42±0.11
4	Malindi Beach	< 0.002	2.87±0.62	0.41±0.11	0.40±0.00
5	Sabaki Beach	0.06±0.01	< 0.002	0.52±0.31	< 0.002
6	Sabaki River Mouth	0.22±0.02	< 0.002	0.10±0.03	< 0.002
7	Sabaki River	0.04±0.01	3.24±1.05	0.50±0.13	< 0.002

The BPA residue levels in water samples in wet and dry season is shown in Figure 4.7. Pirate and Malindi beaches had BPA levels less than 0.002 ng/mL in dry season. Due to many industrial activities and agricultural activities in Mombasa as compared to the other sites, this could be the reason why Pirate and Mombasa Beaches recorded measurable BPA levels of (2.24±0.01 and 2.74±0.57) ng/mL respectively, from water samples during the wet season from wastewater and industrial run-off. Levels of BPA were considerably smaller in the dry season may be because of less agricultural activities taking place.

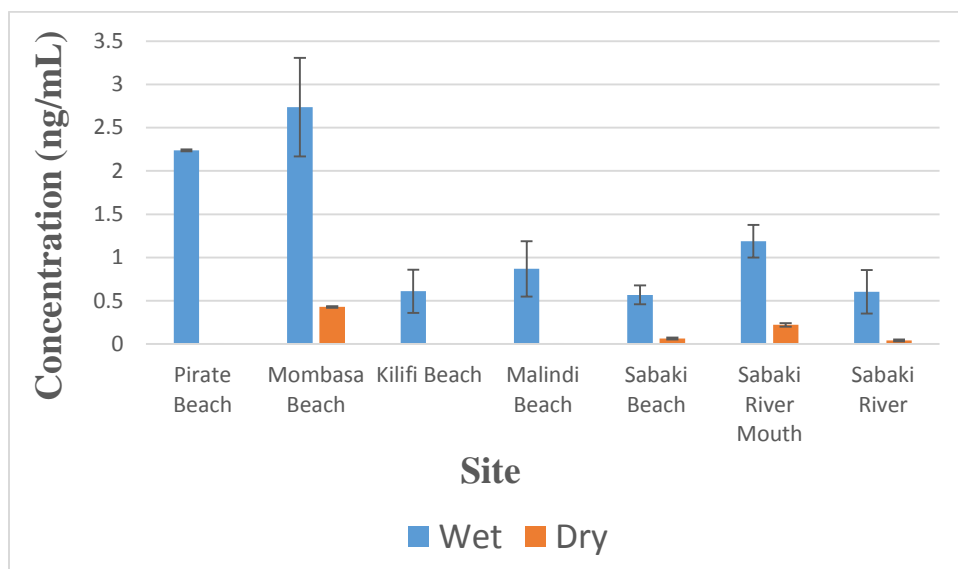


Figure 4.7: BPA residue levels in water samples in wet and dry season

4.7.2 BPA residue levels in soil samples in wet and dry season

Soil samples registered utmost levels of BPA in Kilifi Beach at 3.39 ± 0.04 ng/g followed by Sabaki River at 3.24 ± 1.05 ng/g while Pirate Beach had levels below detection limit in wet season (Table 4.8). In dry season, Sabaki River was leading having 3.24 ± 1.05 ng/g, Malindi beach with 2.87 ± 0.62 then Mombasa having 2.71 ± 0.45 ng/g. Higher temperature in Mombasa Beach during the dry season could have been the cause of increased levels of BPA in soil samples due to the BPA becoming less bound to the plastic waste materials on the soil hence leaching to the soil at elevated temperature.

Kilifi and Sabaki Beaches had BPA levels less than 0.002 ng/g in soil samples in dry season yet a relatively high amount (similar to Sabaki River) were obtained in wet season (Figure 4.8). Despite the high rate of leaching during the rainy season, there are several human activities during this time, which may have resulted in additional unanticipated BPA sources entering the soil during this time.

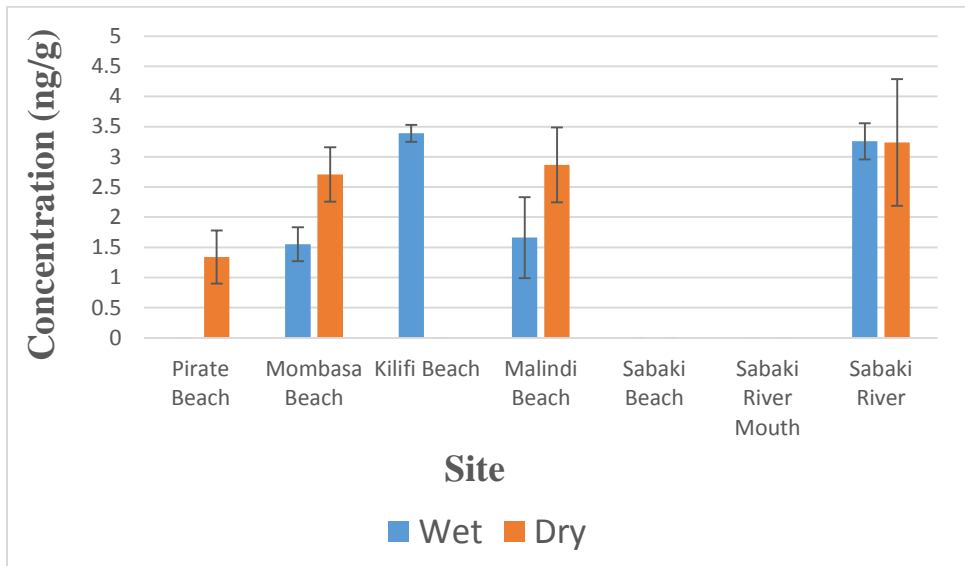


Figure 4.8: BPA residue levels in soil samples in wet and dry season

4.7.3 The BPA residue levels in sediments samples in wet and dry season

BPA residue levels in sediment samples in wet and dry season is presented in Figure 4.9. Wet season recorded higher levels than the dry period in sediment samples. Malindi beach had the highest level of 3.76 ± 0.17 ng/g then Sabaki beach with 3.53 ± 0.42 ng/g. In the dry season, Mombasa and Kilifi Beaches reported the maximum BPA concentrations at $1.360.41$ ng/g and $1.290.12$ ng/g, respectively (Table 4.8). All the sampling sites had detectable BPA residue levels in wet and dry seasons (Figure 4.9) which may have been caused by the increasing manufacturing of BPA items due to the growing population and demand for these products in these sampling areas. Improper waste management of these plastics increased the BPA levels in the environment.

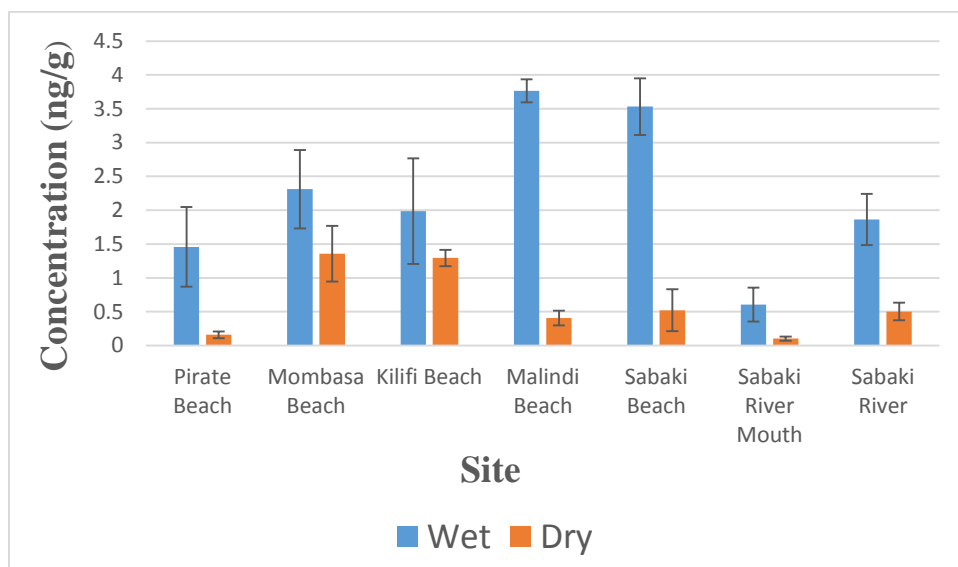


Figure 4.9: The BPA residue levels in sediment samples in wet and dry season

4.7.4 BPA residue levels in sea weed samples in wet and dry season

BPA residue levels in sea weed samples in wet and dry season is displayed in Figure 4.10. The amounts of BPA residues were identified in varying quantities with not many sites registering below detection limit levels. The sea weed samples had the highest levels in the wet season in Mombasa Beach at 11.66 ± 0.94 ng/g followed by Pirate Beach 5.91 ± 0.92 ng/g while the BPA concentrations were below detection limits of 0.002 ng/g at Sabaki Beach. Due to many industrial activities around Mombasa and Pirate Beaches as compared to the other sites, this could be the reason why Pirate and Mombasa Beaches recorded some levels of BPA in sea weed samples during the wet season from wastewater run-off which ends up being absorbed by the sea weeds.

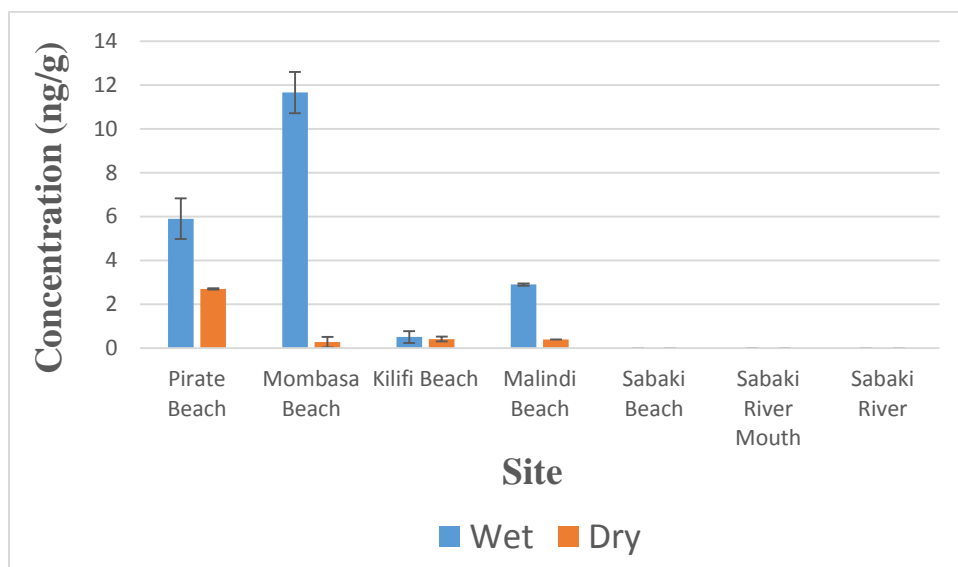


Figure 4.10: The BPA residue levels in sea weed samples in wet and dry season

4.8 Seasonal variation effects on DBP and BPA residue levels in soil, sediments and sea weed samples in wet and dry season

4.8.1 The effects of seasonal variation on DBP residue levels in Soil, Sediments and Sea weed samples in wet and dry season

Seasonal variation effects on DBP residue levels in soil, sediment and sea weed samples in wet season is shown in Figure 4.11. Pirates and Mombasa Beaches had DBP residue levels detected while the rest had below detection limits of 0.5 ng/g for DBP. Pirate Beach had higher DBP residue levels in soil, sediment and sea weed samples in the order than Mombasa Beach during the wet season (Figure 4.11).

Considering the obtained result, it is clear that the residue levels of DBP were greater during the wet season as compared to the dry season except for soil samples. In essence, the rate of leaching of DBP was higher in wet season. This was in general agreement with the overall expectation of residue levels of DBP during the wet season. It could have been attributed to the higher flow of water in the overall wet season. Nonetheless, general effect of the residue levels will be dependent on ecosystem effects that go beyond the leaching process. Precisely, the levels are

affected by the concentration of the compound in water as well. Even though the leaching rate may be elevated in wet season, the resultant absolute concentrations in the receiving waters could be less in the stated wet season in comparison to the dry season because of higher rates of dilution. This made the soil during the wet season record higher concentrations despite the leaching the high flow of rainwater and run-offs to the recipient water lead to water dilution lowering the concentration of DBP in water. This was followed by DBP residue levels in sediment samples in wet season which could be as a result of this soil being transported and deposited in water in form of sediment.

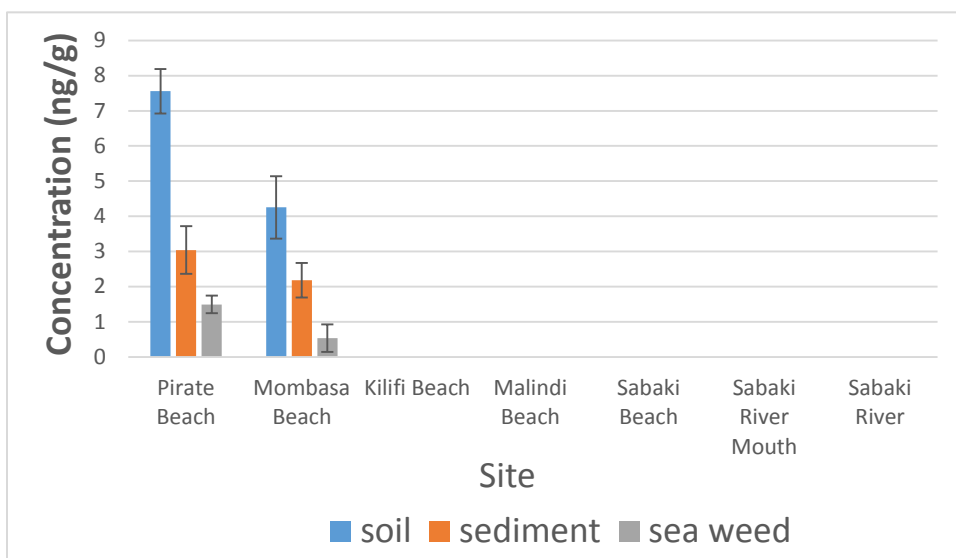


Figure 4.11: The variation of DBP residue levels in soil, sediment and sea weed samples in the wet season.

DBP residue levels in soil, sediment and weeds samples in dry season is shown in Figure 4.12. Pirates and Mombasa Beaches had DBP residue levels detected in soil samples while the other sites had < 0.5 ng/g in dry season (Figure 4.12). Pirate Beach had more DBP residue levels in soil samples compared to Mombasa Beach. Leaching of DBP residue was higher during wet season than in dry. This is due to the higher flow of water during the wet season. Therefore, the DBP residue level was retained in soil during the dry season since there was no water to do leaching to underground water or to transport to surface water through run-off. The other sites

registered below detection limit levels of DBP which could be due to less agricultural activities during the dry season.

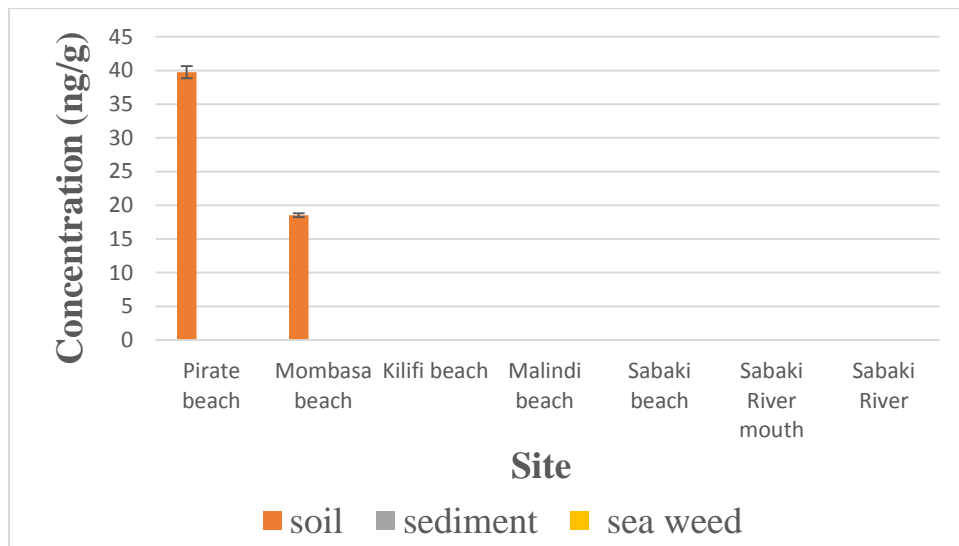


Figure 4.12: The variation of DBP residue levels in soil, sediment and sea weed samples in dry season

4.8.2 The effects of seasonal variations on BPA residue levels in soil, sediments and sea weed samples in wet and dry season

BPA residue levels in soil, sediment and sea weed samples in wet season is shown in Figure 4.13. During the wet season, sea weed samples from Mombasa Beach had the highest BPA residue levels of 11.66 ± 0.94 ng/g, then Pirate Beach at 5.91 ± 0.92 ng/g. Pirate Beach, Sabaki Beach and Sabaki River mouth had BPA level of less than 0.002 ng/mL in soil while Sabaki Beach and Sabaki River mouth only had BPA residue levels in sediments samples in wet season (Figure 4.13). During the wet season, there is more waste water run-off which transport the contaminated soil depositing it in water bodies in form of sediment which ends up being absorbed by sea weeds owing to its high concentration of BPA residue level.

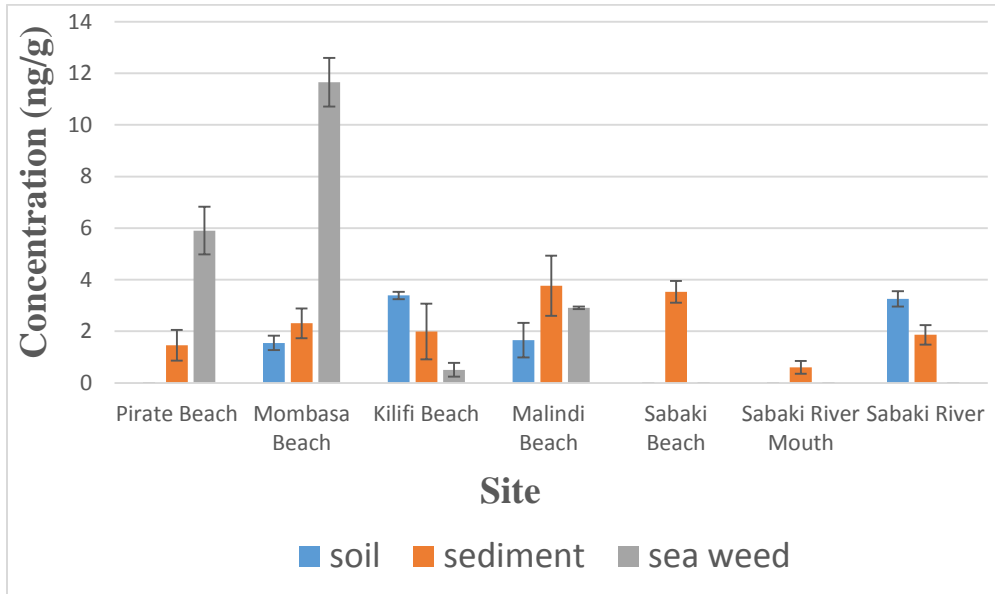


Figure 4.13: Variation of BPA residue levels in soil, sediment and sea weed samples in wet season

BPA residue levels in soil, sediment and sea weed samples in dry season is shown in Figure 4.14. During the dry season, soil samples had high BPA residue levels in Sabaki River, Malindi, Mombasa and Pirate Beaches at 3.24 ± 1.05 ng/g, 2.87 ± 0.62 ng/g, 2.71 ± 0.45 ng/g and 1.34 ± 1.04 ng/g, sequentially while Sabaki beach and Sabaki River mouth only had BPA sediments (Figure 4.14). Leaching is lower during dry seasons, which could have led to higher BPA residue concentration in soil samples in most sites during the dry season.

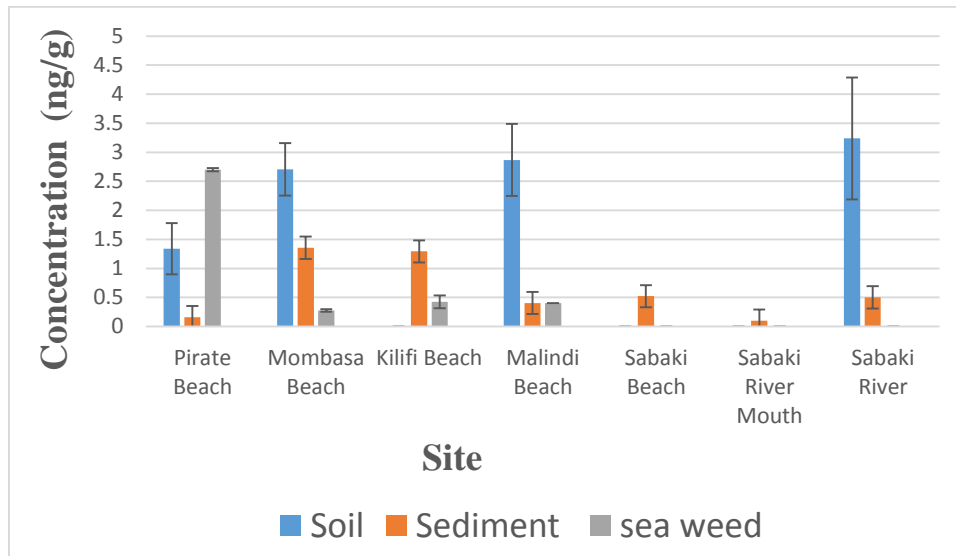


Figure 4.14: Variation of BPA residue levels in soil, sediment and sea weed samples in the dry season

4.9 Correlation coefficient of DBP residue levels in water, soil, sediment and sea weed samples

Correlations coefficients were obtained using Pearson's Correlations from SPSS tool (SPSS 22) to establish relationships between DBP/BPA residue levels in water, soil, sediment and sea weed samples in wet and dry seasons from the selected seven sites from the coastal beaches. Bivariate coefficient were established using the Pearson product-moments correlation coefficient R , a dimensionless index whose value is in the range $-1.0 \leq R \leq 1.0$, which is a linear relationship between two sets of data was used. The linear correlation strength of the variables is determined by numerical value of correlation coefficients in that, a correlation coefficient of 0 (zero) means that there is no relationship between the considered set of data while when a numerical value less than 0.5 is recorded, the relationship between the set is considered weak while when it is greater than 0.5 is considered strong and significant whether positive or negative (Hazra and Gogtay, 2016). The positive values imply a direct proportionality of variables while the negative values indicate existence of inverse variation relationships (Hazra and Gogtay, 2016). The correlation coefficient for concentration of DBP residue levels in water, soil, sediment and sea weed samples in dry and wet season are shown in Table 4.9.

Table 4.9: Correlations coefficient of DBP residue levels in water, soil, sediment and sea weed samples in the wet and dry season

		water wet	water dry	sea weed wet	sea weed dry	sediment wet	sediment dry	soil wet	soil dry
water wet	Pearson Correlation	1	.839 [*]	.970 ^{**}	.837	.996 ^{**}	.961 ^{**}	.999 ^{**}	.992 ^{**}
	Sig. (2-tailed)		.018	.006	.077	.000	.001	.000	.000
	N	7	7	5	5	7	7	6	6
water dry	Pearson Correlation	.839 [*]	1	.646	.999 ^{**}	.883 ^{**}	.656	.805	.749
	Sig. (2-tailed)	.018		.239	.000	.008	.109	.053	.087
	N	7	7	5	5	7	7	6	6
sea weed wet	Pearson Correlation	.970 ^{**}	.646	1	.679	.943 [*]	.999 ^{**}	.980 ^{**}	.994 ^{**}
	Sig. (2-tailed)	.006	.239		.207	.016	.000	.003	.001
	N	5	5	5	5	5	5	5	5
sea weed dry	Pearson Correlation	.837	.999 ^{**}	.679	1	.885 [*]	.641	.813	.755
	Sig. (2-tailed)	.077	.000	.207		.046	.244	.094	.140
	N	5	5	5	5	5	5	5	5
sediment wet	Pearson Correlation	.996 ^{**}	.883 ^{**}	.943 [*]	.885 [*]	1	.933 ^{**}	.991 ^{**}	.976 ^{**}
	Sig. (2-tailed)	.000	.008	.016	.046		.002	.000	.001
	N	7	7	5	5	7	7	6	6
sediment dry	Pearson Correlation	.961 ^{**}	.656	.999 ^{**}	.641	.933 ^{**}	1	.970 ^{**}	.988 ^{**}
	Sig. (2-tailed)	.001	.109	.000	.244	.002		.001	.000
	N	7	7	5	5	7	7	6	6
soil wet	Pearson	.999 ^{**}	.805	.980 ^{**}	.813	.991 ^{**}	.970 ^{**}	1	.996 ^{**}

	Correlation								
	Sig. (2-tailed)	.000	.053	.003	.094	.000	.001		.000
	N	6	6	5	5	6	6	6	6
soil dry	Pearson	.992**	.749	.994**	.755	.976**	.988**	.996**	1
	Correlation								
	Sig. (2-tailed)	.000	.087	.001	.140	.001	.000	.000	
	N	6	6	5	5	6	6	6	6
*. Correlation is significant at the 0.05 level (2-tailed).									
**. Correlation is significant at the 0.01 level (2-tailed).									

4.9.1 Correlation coefficient of DBP residue levels in water and sea weed samples in wet and dry season

Results in Table 4.9 indicates the Pearson's correlations coefficient of DBP concentration levels in water and weeds samples during wet and dry season. The most significant correlation coefficient of 0.999 and 0.970 were obtained between DBP residue levels in water and weeds samples in dry and wet seasons at five sampling sites respectively, the correlation was significant at 0.01 level, showing a strong relationship between the DBP residue levels in water and sea weed samples. DBP residue levels in water and sea weed samples in dry and wet seasons may lead to high health effects to humans and aquatic animals (Hahladakis *et al.*, 2018).

4.9.2 Correlation coefficient of DBP residue levels in water and soil samples during dry and wet season

Table 4.9 indicates the Pearson's correlations coefficient of DBP concentration levels in water and soil samples during the wet and dry seasons. There was no significant correlation coefficient of DBP residue levels in water and soil samples recorded in dry season. A significant correlation coefficient of 0.999 was obtained between DBP residue levels in water and soil samples in the wet season at six sampling sites, the correlations was significant at 0.01 levels, showing a strong relationship between the DBP residue levels in water and soil samples. DBP

residue levels in soil and water samples in both seasons may have high health effects in human, animals and environment (Lü *et al.*, 2018).

4.9.3 Correlation coefficient of DBP residue levels in water and sediment samples during dry and wet season

Table 4.9 indicates the Pearson's correlations coefficient of DBP concentration levels in water and sediments samples during wet and dry season. There was no significant correlation coefficient of DBP residue levels in water and sediment samples recorded in dry season. A correlation coefficient 0.996 was the most significant obtained between DBP residue levels in water and sediment samples wet seasons at all the seven sampling sites, the correlation was significant at 0.01 level. This shows that there was a strong relationship between the DBP residue levels in water and sediments samples during the wet season. DBP residue levels in water and sediments samples mostly in wet season may have high health effects in human and aquatic animals (Hahladakis *et al.*, 2018).

4.9.4 Correlation coefficient of DBP residue levels in soil and sediment samples in dry and wet season

Table 4.9 indicates the Pearson's correlations coefficient of DBP concentration levels in soil and sediments samples during wet and dry season. The most significant correlation coefficient of 0.988 and 0.991 were obtained between DBP residue levels in soil and sediment samples in dry and wet season at six sampling sites, respectively. The correlations in both seasons were significant at 0.01 level. This shows that there was a strong correlation relationship between the DBP residue levels in soil and sediments samples in the dry and wet season, this may be as a result of soil being transported and deposited in water in form of sediment. The DBP residue levels in soil and sediment samples in wet and dry season may have high health effects in human, organisms living in soil and aquatic animals (Hahladakis *et al.*, 2018).

4.9.5 Correlation coefficient of DBP residue levels in sediments and sea weed samples in dry and wet season

Table 4.9 indicates the Pearson's correlations coefficient of DBP concentration levels from sediment to sea weed samples during the wet and dry seasons. There was no significant correlation coefficient of DBP residue levels in sediment and sea weed samples recorded in dry season. The most significant correlation coefficient of 0.943 was obtained between DBP residue levels in sediment and sea weed samples in wet seasons at five sampling sites. The correlations in the wet was significant at 0.05 level. This shows that there was a strong and significant correlation relationship between DBP residue levels in sediment and sea weed samples in wet season which may be as a result of sea weed samples absorbing the DBP residue levels from the sediment. DBP residue levels in sediment and sea weed samples in wet season may have high health effects in aquatic animals and environment (Hahladakis *et al.*, 2018).

4.10 Correlation coefficient of BPA residue levels in water, soil, sediment and sea weed samples

Correlation coefficient of BPA residue levels in water, soil, sediment and sea weed samples in dry and wet season are shown in Table 4.10.

4.10.1 Correlation coefficient of BPA residue levels in water and sea weed samples in wet and dry season

Results in Table 4.10 indicates the Pearson's correlations coefficient of BPA residue levels in water and sea weed samples during wet and dry season. The most significant correlation coefficient of 0.957 was obtained between BPA residue levels in water and sea weed samples in wet season at five sampling sites while no significant correlation coefficient in dry season was recorded. This shows that there was a strong Correlation and significant relationship between BPA residue levels in water and sea weed samples at the 0.05 level. The BPA residue levels in water and sea weed samples in wet season may have high health effects in human, animals and aquatic environment (Nzediegwu *et al.*, 2019).

4.10.2 Correlation coefficient of BPA residue levels in water and soil samples during dry and wet season

Results in Table 4.10 indicates the Pearson's correlations coefficient of BPA residue levels in water and soil samples during wet and dry season. There was no significant correlation coefficient of BPA residue levels in water and soil samples recorded in both the dry and the wet seasons. BPA residue levels in water and soil samples in wet season varied inversely (Corrales *et al.*, 2015).

4.10.3 Correlation coefficient of BPA residue levels in water and sediments samples during the dry and wet seasons

No significant correlation coefficient of BPA residue levels was obtained in the wet and dry seasons at seven sampling sites. BPA residue levels in water and sediment samples in wet season varied inversely while it had a direct proportionality in the dry season. (Nzediegwu *et al.*, 2019).

4.10.4 Correlation coefficient of BPA residue levels in soil and sediments samples during dry and wet season

There was no significant correlation coefficient of BPA residue levels in soil and sediment samples in both seasons. BPA residue levels in soil and sediment samples varied inversely in dry and wet season, where dry season recorded -0.267 and wet -0.149 correlation coefficient, respectively.

4.10.5 Correlation coefficient of BPA residue levels in sediments and sea weed samples during dry and wet season

There was no significant correlation coefficient between BPA residue levels in sediment and sea weed samples during dry and wet seasons, which recorded -0.373 and 0.225 respectively. BPA residue levels in sediment and sea weed samples in dry season, varied inversely.

Table 4.10: Correlations coefficient of BPA residue levels in water, soil, sediment and sea weed samples in wet and dry season.

		water wet	water dry	sea weed wet	sea weed dry	sediment wet	sediment dry	soil wet	soil dry
water wet	Pearson Correlation	1	.639	.957*	.466	-.133	.267	-.574	.128
	Sig. (2-tailed)		.123	.011	.429	.777	.563	.233	.810
	N	7	7	5	5	7	7	6	6
water dry	Pearson Correlation	.639	1	.820	-.314	-.079	.515	-.231	.121
	Sig. (2-tailed)	.123		.089	.607	.866	.237	.660	.820
	N	7	7	5	5	7	7	6	6
sea weed wet	Pearson Correlation	.957*	.820	1	.219	.225	.397	-.625	.202
	Sig. (2-tailed)	.011	.089		.723	.716	.508	.259	.744
	N	5	5	5	5	5	5	5	5
sea weed dry	Pearson Correlation	.466	-.314	.219	1	-.150	-.373	-.809	-.374
	Sig. (2-tailed)	.429	.607	.723		.810	.536	.097	.535
	N	5	5	5	5	5	5	5	5
sediment wet	Pearson Correlation	-.133	-.079	.225	-.150	1	.199	-.149	.088
	Sig. (2-tailed)	.777	.866	.716	.810		.668	.778	.868
	N	7	7	5	5	7	7	6	6
sediment dry	Pearson Correlation	.267	.515	.397	-.373	.199	1	.297	-.267
	Sig. (2-tailed)	.563	.237	.508	.536	.668		.568	.608
	N	7	7	5	5	7	7	6	6
soil wet	Pearson Correlation	-.574	-.231	-.625	-.809	-.149	.297	1	.261
	Sig. (2-tailed)	.233	.660	.259	.097	.778	.568		.618
	N	6	6	5	5	6	6	6	6
soil dry	Pearson Correlation	.128	.121	.202	-.374	.088	-.267	.261	1
	Sig. (2-tailed)	.810	.820	.744	.535	.868	.608	.618	
	N	6	6	5	5	6	6	6	6

*. Correlation is significant at the 0.05 level (2-tailed).

4.11 Correlations coefficient of plastic weight, number of plastics and % soil organic carbon in wet and dry season

Results in Table 4.11 indicates the Pearson's correlations coefficient of plastic weight, number of plastics and % soil organic carbon in wet and dry seasons. The most significant correlation coefficient of 0.952 was obtained between number of plastics and % soil organic carbon in dry season while that between plastic weight and soil organic carbon was 0.945 in wet season at $p = 0.01$ level, showing a strong relationship between the plastic weight and the % soil organic carbon.

Table 4.11: Correlations coefficient of plastic weight, number of plastics and % soil organic carbon in wet and dry season.

		wet season plastic weight	dry season plastic weight	% soil organic carbon	wet season number of plastic	dry Season number of plastic
wet season plastic weight	Pearson Correlation	1	.649	.945**	.725	.962**
	Sig. (2-tailed)		.115	.001	.065	.001
	N	6	6	6	6	6
dry season plastic weight	Pearson Correlation	.649	1	.434	.588	.515
	Sig. (2-tailed)	.115		.330	.165	.237
	N	6	6	6	6	6
% soil organic carbon	Pearson Correlation	.945**	.434	1	.723	.952**
	Sig. (2-tailed)	.001	.330		.066	.001
	N	6	6	7	6	6
wet season number of plastic	Pearson Correlation	.725	.588	.723	1	.734
	Sig. (2-tailed)	.065	.165	.066		.060

	N	6	6	6	6	6
dry season number of plastic	Pearson Correlation	.962**	.515	.952**	.734	1
	Sig. (2-tailed)	.001	.237	.001	.060	
	N	6	6	6	6	6

*. Correlation is significant at the 0.05 level (2-tailed).

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

4.12 Correlations coefficient of plastic weight, number of plastics and % sediment organic carbon in wet and dry season

Table 4.12: Correlations coefficient of plastic weight, number of plastics and % sediment organic carbon in wet and dry season

		% sediment organic carbon	Number of plastic in dry season	Number of plastic in wet season	Weight of plastic in wet season	Weight of plastic in dry season
% sediment organic carbon	Pearson Correlation	1	.809*	.611	.889**	.425
	Sig. (2-tailed)		.028	.145	.007	.401
	N	7	7	7	7	6
Number of plastic in dry season	Pearson Correlation	.809*	1	.734	.962**	.738
	Sig. (2-tailed)	.028		.060	.001	.094
	N	7	7	7	7	6
Number of plastic in wet season	Pearson Correlation	.611	.734	1	.725	.569
	Sig. (2-tailed)	.145	.060		.065	.239
	N	7	7	7	7	6

Weight of plastic in wet season	Pearson Correlation	.889**	.962**	.725	1	.758
	Sig. (2-tailed)	.007	.001	.065		.081
	N	7	7	7	7	6
Weight of plastic in dry season	Pearson Correlation	.425	.738	.569	.758	1
	Sig. (2-tailed)	.401	.094	.239	.081	
	N	6	6	6	6	6

*. Correlation is significant at the 0.05 level (2-tailed).

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

Results in Table 4.12 indicates the Pearson's coefficient of plastic weight, number of plastics and % sediment organic carbon in wet and dry. The most significant correlation coefficient of 0.889 was obtained between weight of plastics and % sediment organic carbon in wet season at 0.01 level, showing a strong relationship between the weight of plastics and % sediment organic carbon while that between number of plastics and % sediment organic carbon was 0.809 in dry season at 0.05 level, showing a strong relationship between the number of plastics and the % sediment organic carbon.

4.13 Discussion of results

All other sites except Pirate and Mombasa Beaches recorded DBP levels below the detection limit in soil samples during the wet season. Mombasa being a highly populated County than the rest could have attributed to this exceptional measurable amounts of DBP in soil samples in the wet season due to its industrialization and high number of people along these two Beaches. Bench mark values for BPA according to WHO, (2017) is 0.1 µg/L (100 ng/g) to determine if the surface water source is impacted by treated sewage effluent known to contain BPA, which is an oestrogenic EDCs while the TDI is 4 µg/kg of body weight.

BPA was more frequently detected than DBP possibly owing to distinct origination of these compounds in the seven sampling sites. Variations observed were accredited by the contrast in

the environmental factors, physical-chemical properties of the pollutants, site location as well seasonal changes during sampling.

Odera (2019) study to determine BPA in thermal papers, in selected soil samples reported higher concentrations of BPA residues (1.548×10^8 ng/g) from Dandora dumpsite in Nairobi, than those detected in this research study. Chen *et al.* (2019) recorded a higher residue levels of DBP (3.47×10^4 ng/g) in a research done on the sources, distribution and environmental risk assessment of DBP in sediment of a typical Yangtze River Delta City, China.

In a multi-residue determination of 47 organic compounds in water, soil, sediment and fish in Turia River in Spain, Carmona *et al.* (2017) recorded 0.041 ng/mL BPA residue levels in water, which was comparable to concentrations measured during the dry season in the current study.

This study gives information on the levels of DBP as well as BPA in the soil, water, sediments and sea weeds in different seasons.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Conductivity was lowest in Sabaki River water samples, followed by Sabaki Beach compared to other coastal Beaches, while pH was relatively similar for all the sites.

The study detected measurable levels of DBP in the water, soil, sediment and sea weeds from the selected Kenyan coastal beaches which showed that our coastal beaches are polluted by this pollutant. The maximum levels were measured in samples from Pirate and Mombasa Beaches. All the sites except Pirate and Mombasa Beaches recorded DBP residue levels less than 0.5 ng/mL in soil, water, sediment and weeds samples during the wet season. In the dry season, only soil samples from pirate and Mombasa recorded measurable amounts of DBP of (39.75 ± 0.91 and 18.53 ± 0.29) ng/g respectively, while the rest of the sites recorded residue levels less than 0.5 ng/mL. This could be due to no surface run-off during the dry season and all the pollutants are retained in the soil.

Higher levels of BPA were recorded in soil compared to water, sediments and sea weed samples during the dry season for most of the sampling sites. The results suggest accumulation of BPA in soil during dry season compared to wet season. BPA was more frequently detected than DBP may be due to different sources of these two compounds, environmental factors and physical chemical properties of the two contaminants.

Levels of DBP and BPA in the soil were higher during the dry season compared to wet season in Mombasa. This could have been attributed to DBP and BPA compounds becoming less bound to the plastic waste materials on the soil hence leaching to the soil at elevated temperature. The seasonal variation is likely to have an impact on DBP and BPA leaching. In the wet season, leaching will transport DBP and BPA down the soil profile and into the groundwater while

during the dry season these pollutants will remain in the soil since there is no transportation down the soil profile.

5.2 Recommendations

5.2.1 Policy recommendations

1. Existence of BPA and DBP in water, soil, sediment and sea weeds from the selected Kenyan coastal Beaches suggest environmental pollution by these hazardous chemicals. This raises concern due to the negative health effects to human and wildlife. Regular awareness creation should be done to educate industries and general public on the adverse environmental and human health impacts of these microplastics, to stop rampant disposal of plastic wastes disposal and embrace environmental sound management of plastic wastes.
2. Policy makers should put in place a regular environmental monitoring program, mitigating strategies of minimizing the pollutants as well as coming up with workable adaptation strategies and appropriate policies for sustainability of our marine ecosystem.
3. Steps should be taken to educate the informal sector who are engaged in handling plastics waste to promote recycling of plastics and industries to ensure clean production for waste minimization. In addition, pollution from manufacturing facilities needs to be reduced.

5.2.2 Research recommendations

1. Further research should be carried out to determine the point and non-point sources of this BPA and DBP since several areas of uncertainty remains in risk assessment of these toxic compounds.
2. Effluent from industries and waste dumpsites around the coastal beaches should be tested to determine the levels of BPA and DBP.
3. Further research should be carried out on BPA and DBP in air during the dry and wet season to determine environmental deposition and emissions.

REFERENCES

- Ahmad, R., Gautam, A. K., Verma, Y., Sedha, S., & Kumar, S. (2014). Effects of in utero di-butyl phthalate and butyl benzyl phthalate exposure on offspring development and male reproduction of rat. *Environmental Science and Pollution Research*, **21**(4), 3156–3165.
- Alimba, C. G., & Faggio, C. (2019). Microplastics in the marine environment: current trends in environmental pollution and mechanisms of toxicological profile. *Environmental toxicology and pharmacology*, **68**, 61-74.
- Almeida, S., Raposo, A., Almeida-González, M., & Carrascosa, C. (2018). Bisphenol A: Food exposure and impact on human health. *Comprehensive Reviews in Food Science and Food Safety*, **17**(6), 1503-1517.
- Andrady, A. L., & Neal, M. A. (2009). Applications and societal benefits of plastics. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, **364**(1526), 1977–1984.
- Arbneshi, T., Mustafa, B., Berisha, L., & Hajdari, A. (2021). The concentration of phthalates in toys and children's care items in Kosovo. *Journal of Environmental Science and Health, Part A*, **56**(14), 1496-1502.
- Asfaw, A. A., Aspromonte, J., Wolfs, K., Schepdael, A. V., & Adams, E. (2019). Overview of sample introduction techniques prior to GC for the analysis of volatiles in solid materials. *Journal of Separation Science*, **42**(1), 214–225.
- Aurah, C. M. (2013). Assessment of Extent to Which Plastic Bag Waste Management Methods Used in Nairobi City Promote Sustainability. *American Journal of Environmental Protection*, **1**(4), 96–101.
- Ayodele, T. R., Alao, M. A., & Ogunjuyigbe, A. S. O. (2018). Recyclable resources from

- municipal solid waste: Assessment of its energy, economic and environmental benefits in Nigeria. *Resources, Conservation and Recycling*, **134**, 165–173.
- Bach, C., Dauchy, X., Severin, I., Munoz, J.-F., Etienne, S., & Chagnon, M.-C. (2013). Effect of temperature on the release of intentionally and non-intentionally added substances from polyethylene terephthalate (PET) bottles into water: Chemical analysis and potential toxicity. *Food Chemistry*, **139**(1–4), 672–680.
- Barraza, L. (2013). A New Approach for Regulating Bisphenol A for the Protection of the Public's Health. *The Journal of Law, Medicine & Ethics*, **41**(s1), 9–12.
- Bhateria, R., & Jain, D. (2016). Water quality assessment of lake water: a review. *Sustainable Water Resources Management*, **2**(2), 161-173.
- Birnbaum, L. S., Bucher, J. R., Collman, G. W., Zeldin, D. C., Johnson, A. F., Schug, T. T., & Heindel, J. J. (2012). Consortium-Based Science: The NIEHS's Multipronged, Collaborative Approach to Assessing the Health Effects of Bisphenol A. *Environmental Health Perspectives*, **120**(12), 1640–1644.
- Bråte, I. L. N., Huwer, B., Thomas, K. V., Eidsvoll, D. P., Halsband, C., Almroth, B. C., & Lusher, A. (2017). *Micro-and macro-plastics in marine species from Nordic waters*. Nordic Council of Ministers.
- Braun, J. M., Sathyanarayana, S., & Hauser, R. (2013). Phthalate exposure and children's health: *Current Opinion in Pediatrics*, **25**(2), 247–254.
- Brevik, E. C. (2010). Soil health and productivity. *Soils, plant growth and crop production*, **1**, 106.
- Canesi, L., & Fabbri, E. (2015). Environmental Effects of BPA: Focus on Aquatic Species. *Dose-Response*, **13**(3), 155932581559830.

- Cao, X.-L. (2010). Phthalate Esters in Foods: Sources, Occurrence, and Analytical Methods. *Comprehensive Reviews in Food Science and Food Safety*, **9**(1), 21–43.
- Careghini, A., Mastorgio, A. F., Saponaro, S., & Sezenna, E. (2015). Bisphenol A, nonylphenols, benzophenones, and benzotriazoles in soils, groundwater, surface water, sediments, and food: a review. *Environmental Science and Pollution Research*, **22**(8), 5711-5741.
- Law, K. L. (2017). Plastics in the Marine Environment. *Annual Review of Marine Science*, **9**(1), 205–229.
- Carmona, E., Andreu, V., & Picó, Y. (2017). Multi-residue determination of 47 organic compounds in water, soil, sediment and fish—Turia River as case study. *Journal of pharmaceutical and biomedical analysis*, **146**, 117-125.
- Carraher Jr, C. E., & Seymour, R. B. (2012). Structure—Property Relationships in Polymers. *Springer Science & Business Media*.
- Chen, H., Mao, W., Shen, Y., Feng, W., Mao, G., Zhao, T., ... & Wu, X. (2019). Distribution, source, and environmental risk assessment of phthalate esters (PAEs) in water, suspended particulate matter, and sediment of a typical Yangtze River Delta City, China. *Environmental Science and Pollution Research*, **26**(24), 24609-24619.
- Chen, J. A., Liu, H., Qiu, Z., & Shu, W. (2008). Analysis of di-n-butyl phthalate and other organic pollutants in Chongqing women undergoing parturition. *Environmental pollution*, **156**(3), 849-853.
- Claessens, M., Meester, S. D., Landuyt, L. V., Clerck, K. D., & Janssen, C. R. (2011). Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Marine Pollution Bulletin*, **62**(10), 2199–2204.

- Corrales, J., Kristofco, L. A., Steele, W. B., Yates, B. S., Breed, C. S., Williams, E. S., & Brooks, B. W. (2015). Global assessment of bisphenol A in the environment: review and analysis of its occurrence and bioaccumulation. *Dose-response*, **13**(3), 1559325815598308.
- Du, L., Li, G., Liu, M., Li, Y., Yin, S., Zhao, J., & Zhang, X. (2015). Evaluation of DNA damage and antioxidant system induced by di-n-butyl phthalates exposure in earthworms (*Eisenia fetida*). *Ecotoxicology and Environmental Safety*, **115**, 75–82.
- Erkekoglu, P., & Kocer-Gumusel, B. (2016). Environmental effects of endocrine-disrupting chemicals: a special focus on phthalates and bisphenol A. *Environmental Health Risk-Hazardous Factors to Living Species*. London: IntechOpen, 155-90.
- Erni-Cassola, G., Zadjelovic, V., Gibson, M. I., & Christie-Oleza, J. A. (2019). Distribution of plastic polymer types in the marine environment; A meta-analysis. *Journal of Hazardous Materials*, **369**, 691–698.
- Fan, J., & Njuguna, J. (2016). An introduction to lightweight composite materials and their use in transport structures. In *Lightweight Composite Structures in Transport* (pp. 3–34).
- Fénichel, P., Chevalier, N., Lahlou, N., Coquillard, P., Wagner-Mahler, K., Pugeat, M., ... & Brucker-Davis, F. (2019). Endocrine disrupting chemicals interfere with Leydig cell hormone pathways during testicular descent in idiopathic cryptorchidism. *Frontiers in Endocrinology*, **9**, 786.
- Flynn, K. J., Blackford, J. C., Baird, M. E., Raven, J. A., Clark, D. R., Beardall, J., ... & Wheeler, G. L. (2012). Changes in pH at the exterior surface of plankton with ocean acidification. *Nature climate change*, **2**(7), 510-513.
- Fu, P., & Kawamura, K. (2010). Ubiquity of bisphenol A in the atmosphere. *Environmental*

- Pollution*, **158**(10), 3138–3143.
- Gall, S. C., & Thompson, R. C. (2015). The impact of debris on marine life. *Marine Pollution Bulletin*, **92**(1), 170–179.
- Garetti, M., & Taisch, M. (2012). Sustainable manufacturing: Trends and research challenges. *Production Planning & Control*, **23**(2–3), 83–104.
- Geens, T., Goeyens, L., & Covaci, A. (2011). Are potential sources for human exposure to bisphenol-A overlooked?. *International journal of hygiene and environmental health*, **214**(5), 339-347.
- Geens, T., Roosens, L., Neels, H., & Covaci, A. (2009). Assessment of human exposure to Bisphenol-A, Triclosan and Tetrabromobisphenol-A through indoor dust intake in Belgium. *Chemosphere*, **76**(6), 755–760.
- Giulivo, M., de Alda, M. L., Capri, E., & Barceló, D. (2016). Human exposure to endocrine disrupting compounds: Their role in reproductive systems, metabolic syndrome and breast cancer. A review. *Environmental research*, **151**, 251-264.
- Government of Kenya (GoK 2006) "environmental management and co-ordination (water quality) regulations, (NEMA 2006). <http://WWW.nema.go.ke>
- Gu, F., Guo, J., Zhang, W., Summers, P. A., & Hall, P. (2017). From waste plastics to industrial raw materials: A life cycle assessment of mechanical plastic recycling practice based on a real-world case study. *Science of the total environment*, **601**, 1192-1207.
- Guo, Y., Yang, Y., Gao, Y., Wang, X., & Zhou, B. (2015). The impact of long term exposure to phthalic acid esters on reproduction in Chinese rare minnow (*Gobiocypris rarus*). *Environmental Pollution*, **203**, 130–136.
- Hahladakis, J. N., Velis, C. A., Weber, R., Iacovidou, E., & Purnell, P. (2018). An overview of

- chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *Journal of Hazardous Materials*, **344**, 179–199.
- Hammad, A. Y., Awad, F. M., & Abdelgadir, W. S. A. (2015). Determination amount of bisphenol A in drugs and water drinking container in Khartoum State, Sudan. *International Journal of Nutrition and Food Sciences*, **4**, 609.
- Hays, S. M., & Aylward, L. L. (2009). Using Biomonitoring Equivalents to interpret human biomonitoring data in a public health risk context. *Journal of Applied Toxicology*, **29**(4), 275–288.
- Hermabessiere, L., Himber, C., Boricaud, B., Kazour, M., Amara, R., Cassone, A.-L., Laurentie, M., Paul-Pont, I., Soudant, P., Dehaut, A., & Duflos, G. (2018). Optimization, performance, and application of a pyrolysis-GC/MS method for the identification of microplastics. *Analytical and Bioanalytical Chemistry*, **410**(25), 6663–6676.
- Heudorf, U., Mersch-Sundermann, V., & Angerer, J. (2007). Phthalates: Toxicology and exposure. *International Journal of Hygiene and Environmental Health*, **210**(5), 623–634.
- Hidaka, K., Iwakawa, Y., Maoka, T., Tanimoto, F., & Oku, A. (2009). Viable chemical recycling of poly(carbonate) as a phosgene equivalent illustrated by the coproduction of bisphenol A and carbohydrate carbonates. *Journal of Material Cycles and Waste Management*, **11**(1), 6–10.
- Hopewell, J., Dvorak, R., & Kosior, E. (2009). Plastics recycling: Challenges and opportunities. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, **364**(1526), 2115–2126.
- Howdeshell, K. L., Furr, J., Lambright, C. R., Rider, C. V., Wilson, V. S., & Gray, L. E. (2007).

- Cumulative Effects of Dibutyl Phthalate and Diethylhexyl Phthalate on Male Rat Reproductive Tract Development: Altered Fetal Steroid Hormones and Genes. *Toxicological Sciences*, **99**(1), 190–202.
- Huang, Y. H., Huang, X. J., Chen, X. H., Cai, Q. Y., Chen, S., Mo, C. H., ... & Wong, M. H. (2018). Biodegradation of di-butyl phthalate (DBP) by a novel endophytic bacterium *Bacillus subtilis* and its bioaugmentation for removing DBP from vegetation slurry. *Journal of Environmental Management*, **224**, 1-9.
- Hub, I. S. K. (2019, 11march). ICCA Report Highlights Chemical Industry's Contribution to Global Economy News SDG Knowledge Hub IISD.
<https://sdg.iisd.org:443/news/icca-report-highlights-chemical-industrys-contribution-to-global-economy/>
- Islam, M. S., Akbar, A., Akhtar, A., Kibria, M. M., & Bhuyan, M. S. (2017). Water quality assessment along with pollution sources of the Halda River. *Journal of the Asiatic Society of Bangladesh, Science*, **43**(1), 61-70.
- Janjua, N. R., Mortensen, G. K., Andersson, A.-M., Kongshoj, B., & Wulf, H. C. (2007). Systemic Uptake of Diethyl Phthalate, Dibutyl Phthalate, and Butyl Paraben Following Whole-Body Topical Application and Reproductive and Thyroid Hormone Levels in Humans. *Environmental Science & Technology*, **41**(15), 5564–5570.
- Jin, J., Sun, K., Wang, Z., Han, L., Pan, Z., Wu, F., ... & Xing, B. (2015). Characterization and phthalate esters sorption of organic matter fractions isolated from soils and sediments. *Environmental pollution*, **206**, 24-31.

- Ji, Y., Wang, F., Zhang, L., Shan, C., Bai, Z., Sun, Z., Liu, L., & Shen, B. (2014). A comprehensive assessment of human exposure to phthalates from environmental media and food in Tianjin, China. *Journal of Hazardous Materials*, **279**, 133–140.
- Kabir, E. R., Rahman, M. S., & Rahman, I. (2015). A review on endocrine disruptors and their possible impacts on human health. *Environmental Toxicology and Pharmacology*, **40**(1), 241–258.
- Karkosh, H. N., Al-Tameemi, N. H. A., Al-Najar, H. A., & Nafae, T. M. (2019). Assessment of the Environmental Impact of Acid Rains on the Human Health and the Environment in Baghdad City. *Iraqi Journal of Science and Technology*, **10**(1).
- Kauzya, J. M. (2020). *African Local Government and Cities in the Implementation of the 2030 Agenda to Achieve Sustainable Development Goals*. In *Reflections on African Cities in Transition* (pp. 119-146). Springer, Cham.
- Kenya National Bureau of Statistics-KNBS (2019). Kenya Population and House Census: **Vol. 1 Population by County and Sub-county**. pp. 17, 19, 20, 22, 31, 40. ISBN 9789966102096
- Kerdlap, P., Low, J. S. C., & Ramakrishna, S. (2019). Zero waste manufacturing: A framework and review of technology, research, and implementation barriers for enabling a circular economy transition in Singapore. *Resources, Conservation and Recycling*, **151**, 104438.
- Kircher, M. (2019). Bioeconomy: Markets, implications, and investment opportunities. *Economies*, **7**(3), 73.
- Krais, A., Andersen, C., Eriksson, A., Johnsson, E., Nielsen, J., Pagels, J., Gudmundsson, A., Lindh, C., & Wierzbicka, A. (2018). Excretion of Urinary Metabolites of the Phthalate Esters DEP and DEHP in 16 Volunteers after Inhalation and Dermal Exposure. *International Journal of Environmental Research and Public Health*, **15**(11), 2514.

- Krishnan, S., Karim, A. V., Singh, S. P., & Shrivastav, A. (2019). Measurement, Analysis, and Remediation of Bisphenol-A from Environmental. *Measurement, Analysis and Remediation of Environmental Pollutants*, **423**.
- Kumar, S., Panda, A. K., & Singh, R. K. (2011). A review on tertiary recycling of high-density polyethylene to fuel. *Resources, Conservation and Recycling*, **55**(11), 893–910.
- Kumar, V., Sharma, N., & Maitra, S. S. (2017). Comparative study on the degradation of dibutyl phthalate by two newly isolated *Pseudomonas* sp. V21b and *Comamonas* sp. 51F. *Biotechnology Reports*, **15**, 1–10.
- Lambert, S., Sinclair, C., & Boxall, A. (2014). Occurrence, degradation, and effect of polymer-based materials in the environment. *Reviews of Environmental Contamination and Toxicology*, **Vol. 227**, 1-53.
- Le, H. H., Carlson, E. M., Chua, J. P., & Belcher, S. M. (2008). Bisphenol A is released from polycarbonate drinking bottles and mimics the neurotoxic actions of estrogen in developing cerebellar neurons. *Toxicology Letters*, **176**(2), 149–156.
- Liao, C., & Kannan, K. (2011). Widespread Occurrence of Bisphenol A in Paper and Paper Products: Implications for Human Exposure. *Environmental Science & Technology*, **45**(21), 9372–9379.
- Li, C., Chen, J., Wang, J., Han, P., Luan, Y., Ma, X., & Lu, A. (2016). Phthalate esters in soil, plastic film, and vegetable from greenhouse vegetable production bases in Beijing, China: Concentrations, sources, and risk assessment. *Science of The Total Environment*, **568**, 1037–1043.

- Li, C., & Tang, K. H. D. (2022). Effects of pH and Temperature on the Leaching of Di (2-Ethylhexyl) Phthalate and Di-n-butyl Phthalate from Microplastics in Simulated Marine Environment. *Biointerface Research in Applied Chemistry*, **13**.
- Li, W. T., Gao, S. B., Zhang, J. Q., & Guo, S. X. (2021). Training Method and Device of Chemical Industry Chinese Language Model Based on Knowledge Distillation. *Scientific Programming*, 2021.
- Lü, H., Mo, C. H., Zhao, H. M., Xiang, L., Katsoyiannis, A., Li, Y. W., ... & Wong, M. H. (2018). Soil contamination and sources of phthalates and its health risk in China: a review. *Environmental research*, **164**, 417-429.
- Lu, H., Zhang, C., Hu, Y., Qin, H., Gu, A., Li, Y., Zhang, L., Li, Z., & Wang, Y. (2016). MiRNA-200c mediates mono-butyl phthalate-disrupted steroidogenesis by targeting vimentin in Leydig tumor cells and murine adrenocortical tumor cells. *Toxicology Letters*, **241**, 95–102.
- Marion, G. M., Millero, F. J., Camões, M. F., Spitzer, P., Feistel, R., & Chen, C.-T. A. (2011). PH of seawater. *Marine Chemistry*, **126**(1), 89–96.
- Maurer, H. H. (2013). Stéphane Bouchonnet: Introduction to GC-MS coupling. *Analytical and Bioanalytical Chemistry*, **405**(26), 8385-8386.
- McNair, H. M., Miller, J. M., & Snow, N. H. (2019). *Basic Gas Chromatography*. John Wiley & Sons.
- Meeker, J. D., Hu, H., Cantonwine, D. E., Lamadrid-Figueroa, H., Calafat, A. M., Ettinger, A. S., ... & Téllez-Rojo, M. M. (2009). Urinary phthalate metabolites in relation to preterm birth in Mexico City. *Environmental Health Perspectives*, **117**(10), 1587-1592.

- Meeker, J. D., Sathyanarayana, S., & Swan, S. H. (2009). Phthalates and other additives in plastics: Human exposure and associated health outcomes. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, **364** (1526), 2097–2113.
- Mikołajewska, K., Stragierowicz, J., & Gromadzińska, J. (2015). Bisphenol A—Application, sources of exposure and potential risks in infants, children and pregnant women. *International Journal of Occupational Medicine and Environmental Health*, **28**(2).
- Moh, Y. C., & Abd Manaf, L. (2014). Overview of household solid waste recycling policy status and challenges in Malaysia. *Resources, Conservation and Recycling*, **82**, 50–61.
- Muncke, J. (2009). Exposure to endocrine disrupting compounds via the food chain: Is packaging a relevant source? *Science of The Total Environment*, **407**(16), 4549–4559.
- Mustieles, V., Pérez-Lobato, R., Olea, N., & Fernández, M. F. (2015). Bisphenol A: Human exposure and neurobehavior. *NeuroToxicology*, **49**, 174–184.
- Nelms, S. E., Duncan, E. M., Broderick, A. C., Galloway, T. S., Godfrey, M. H., Hamann, M., Lindeque, P. K., & Godley, B. J. (2016). Plastic and marine turtles: A review and call for research. *ICES Journal of Marine Science*, **73**(2), 165–181.
- Net, S., Sempere, R., Delmont, A., Paluselli, A., & Ouddane, B. (2015). Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. *Environmental Science & Technology*, **49**(7), 4019-4035.
- North, E. J., & Halden, R. U. (2013). Plastics and Environmental Health: The Road Ahead. *Reviews on Environmental Health*, **28**(1), 1–8.
- Nugroho, B., Pramudya, Y., & Widodo, W. (2019). The Content Analysis of Bisphenol A (BPA) on Water in Plastic Glass with Varying Temperatures and Contact Times using UV-VIS Spectrophotometer. *Indonesian Review of Physics*, **1**(2), 27–32.

- Nzediegwu, C. (2019). *The role of biochar in enhancing safe use of untreated wastewater in agriculture*. McGill University (Canada).
- Nzisa, J., (2019). Kaizen Principle Of Constant Improvement: Could This Reengineer The Competitiveness Of Kenya's Manufacturing Sector?
<http://ir.kabarak.ac.ke/handle/123456789/1>.
- Odera, P. A. (2019). Determination of Bisphenol A (BPA) in Thermal Papers, Selected Soil Samples and the Effect of Temperature and Humidity on Its Concentration (Doctoral dissertation, University of Nairobi).
- Omer, N. H. (2019). Water quality parameters. *Water quality-science, assessments and policy*, **18**, 1-34.
- Patil, P. N., Sawant, D. V., & Deshmukh, R. N. (2012). Physico-chemical parameters for testing of water-a review. *International Journal of Environmental Sciences*, **3**(3), 1194.
- Pethrick, R. A., Pearce, E. M., & Zaikov, G. E. (2013). Polymer products and chemical processes: Techniques, analysis, and applications. In *Polymer Products and Chemical Processes: Techniques, Analysis, and Applications* (pp. 1-293).
- Rahman, M. M., Abd El-Aty, A. M., Choi, J. H., Shin, H. C., Shin, S. C., & Shim, J. H. (2015). Basic overview on gas chromatography columns. *Analytical separation science*, 823-834.
- Rajkumar, A. P., Horsdal, H. T., Wimberley, T., Cohen, D., Mors, O., Børghlum, A. D., & Gasse, C. (2017). Endogenous and antipsychotic-related risks for diabetes mellitus in young people with schizophrenia: a Danish population-based cohort study. *American Journal of Psychiatry*, **174**(7), 686-694.
- Ravikumar, H. R., Rao, S. S., & Karigar, C. S. (2012). Biodegradation of paints: a current status. *Indian Journal of Science and Technology*, **5**(1), 1977-1987.

- Rebolledo, E. L. B., Van Franeker, J. A., Jansen, O. E., & Brasseur, S. M. (2013). Plastic ingestion by harbour seals (*Phoca vitulina*) in The Netherlands. *Marine pollution bulletin*, **67**(1-2), 200-202.
- Reddy, M. S., Reddy, P. S., Subbaiah, G. V., & Subbaiah, H. V. (2014). Effect of plastic pollution on environment. *J Chem Pharm Sci*, **14**, 28-29.
- Robinson, L., & Miller, R. (2015). The Impact of Bisphenol A and Phthalates on Allergy, Asthma, and Immune Function: A Review of Latest Findings. *Current Environmental Health Reports*, **2**(4), 379–387.
- Rochman, C. M., Hoh, E., Kurobe, T., & Teh, S. J. (2013). Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Scientific reports*, **3**(1), 1-7.
- Rodgers, K. M., Rudel, R. A., & Just, A. C. (2014). Phthalates in food packaging, consumer products, and indoor environments. In *Toxicants in food packaging and household plastics* (pp. 31-59). Springer, London.
- Roy, D. N., Goswami, R., & Pal, A. (2017). The insect repellents: A silent environmental chemical toxicant to the health. *Environmental Toxicology and Pharmacology*, **50**, 91–102.
- Saunders, K. J. (2012). *Organic polymer chemistry: an introduction to the organic chemistry of adhesives, fibres, paints, plastics and rubbers*. Springer Science & Business Media.
- Shimizu, K., Kontani, S., Yamada, S., Takahashi, G., Nishiyama, T., & Satsuma, A. (2010). Design of active centers for bisphenol-A synthesis by organic–inorganic dual modification of heteropolyacid. *Applied Catalysis A: General*, **380**(1-2), 33-39.

- Shrinithiviahshini, N. D., Mahamuni, D., & Praveen, N. (2014). Bisphenol A migration study in baby feeding bottles of selected brands available in the Indian market. *Current science*, 1081-1084.
- Siddique, R., Khatib, J., & Kaur, I. (2008). Use of recycled plastic in concrete: A review. *Waste Management*, **28**(10), 1835–1852.
- Socas-Rodríguez, B., González-Sálamo, J., Herrera-Herrera, A. V., Hernández-Borges, J., & Rodríguez-Delgado, M. Á. (2017). Recent advances and developments in the QuEChERS method. *Comprehensive Analytical Chemistry*, **76**, 319-374.
- Somashekar, K. M., Mahima, M. R., & Manjunath, K. C. (2015). Contamination of water sources in Mysore city by pesticide residues and plasticizer—A cause of health concern. *Aquatic Procedia*, **4**, 1181-1188.
- Somm, E., Schwitzgebel, V. M., Toulotte, A., Cederroth, C. R., Combescure, C., Nef, S., Aubert, M. L., & Hüppi, P. S. (2009). Perinatal Exposure to Bisphenol A Alters Early Adipogenesis in the Rat. *Environmental Health Perspectives*, **117**(10), 1549–1555.
- Song, Q., Li, J., & Zeng, X. (2015). Minimizing the increasing solid waste through zero waste strategy. *Journal of Cleaner Production*, **104**, 199–210.
- Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., ... & McElroy, M. B. (2018). Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models. *Atmospheric Chemistry and Physics*, **18**(10), 7423-7438.
- Sørensen, S. P. L. (2013). Enzyme studies II. The measurement and meaning of hydrogen ion concentration in enzymatic processes. In *A Source Book in Chemistry, 1900-1950* (pp. 16-19).

- Stashenko, E., & Martínez, J. R. (2014). Gas chromatography-mass spectrometry. *Advances in gas chromatography*, 1-38.
- Stein, S. (2012). Mass spectral reference libraries: an ever-expanding resource for chemical identification.
- Stipek, J., & Daoust, H. (2012). *Additives for plastics (Vol. 5)*. Springer Science & Business Media.
- Sukanto, H., Raharjo, W. W., Ariawan, D., Triyono, J., & Kaavesina, M. (2021). Epoxy Resins Thermosetting for Mechanical Engineering. *Open Engineering*, **11**(1), 797-814.
- Swan, S. H. (2008). Environmental phthalate exposure in relation to reproductive outcomes and other health endpoints in humans. *Environmental Research*, **108**(2), 177–184.
- Talling, J. F. (2010). pH, the CO₂ system and freshwater science. *Freshwater Reviews*, **3**(2), 133-146.
- Testai, E., Hartemann, P., Rodríguez-Farre, E., Rastogi, S. C., Bustos, J., Gundert-Remy, U., Hensten, A., Kopperud, H. M., Olea, N., Piersma, A., De Jong, W., Epstein, M., Emri, I., Hartemann, P., Hoet, P., Leitgeb, N., Martínez Martínez, L., Proykova, A., Rizzo, L., ... Vermeire, T. (2016). The safety of the use of bisphenol A in medical devices. *Regulatory Toxicology and Pharmacology*, **79**, 106–107.
- Teuten, E. L., Saquing, J. M., Knappe, D. R., Barlaz, M. A., Jonsson, S., Björn, A., ... & Takada, H. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical transactions of the royal society B: biological sciences*, **364**(1526), 2027-2045.
- Thompson, R. C., Moore, C. J., vom Saal, F. S., & Swan, S. H. (2009). Plastics, the environment

- and human health: Current consensus and future trends. *Philosophical Transactions of the Royal Society B: Biological Sciences*, **364**(1526), 2153–2166.
- Tsai, M.-J., Kuo, P.-L., & Ko, Y.-C. (2012). The association between phthalate exposure and asthma. *The Kaohsiung Journal of Medical Sciences*, **28**(7), S28–S36.
- Tsai, W.-T. (2006). Human Health Risk on Environmental Exposure to Bisphenol-A: A Review. *Journal of Environmental Science and Health, Part C*, **24**(2), 225–255.
- U.S. Environmental Protection Agency - USEPA. (2012) Phthalates Action Plan: Providing Access to Information on PBT chemicals
<http://www.epa.gov/pbt/>
- US Environmental Protection Agency -USEPA (2006) "TRI Explorer: Providing Access to EPA's Toxics Release Inventory Data." *Toxicol.* **18**(2):241-264.
<http://WWW.epa.gov/triexplorer/>.
- Vandenberg, L. N., Hauser, R., Marcus, M., Olea, N., & Welshons, W. V. (2007). Human exposure to bisphenol A (BPA). *Reproductive Toxicology*, **24**(2), 139–177.
- Vinaixa, M., Schymanski, E. L., Neumann, S., Navarro, M., Salek, R. M., & Yanes, O. (2016). Mass spectral databases for LC/MS-and GC/MS-based metabolomics: State of the field and future prospects. *TrAC Trends in Analytical Chemistry*, **78**, 23-35.
- Wang, X., Xu, M., Yang, A., Wang, Y., Hou, S., Zheng, N., ... & Dong, D. (2021). Health risks of population exposure to phthalic acid esters through the use of plastic containers for takeaway food in China. *Science of The Total Environment*, **785**, 147347.
- Wang, Z., Liu, S., Xu, W., Hu, Y., Hu, Y., & Zhang, Y. (2016). The microbiome and functions of black soils are altered by dibutyl phthalate contamination. *Applied Soil Ecology*, **99**, 51-61.

- Weiss, J. M., Gustafsson, Å., Gerde, P., Bergman, Å., Lindh, C. H., & Kraus, A. M. (2018). Daily intake of phthalates, MEHP, and DINCH by ingestion and inhalation. *Chemosphere*, **208**, 40-49.
- World Health Organization (2006). Guidelines for Drinking Water Quality; Incorporating First Addendum, third ed., **Vol. 1**.
<https://apps.who.int/iris/handle/10665/43428>
- Wójtowicz, A. K., Szychowski, K. A., Wnuk, A., & Kajta, M. (2017). Dibutyl phthalate (DBP)-induced apoptosis and neurotoxicity are mediated via the aryl hydrocarbon receptor (AhR) but not by estrogen receptor alpha (ER α), estrogen receptor beta (ER β), or peroxisome proliferator-activated receptor gamma (PPAR γ) in mouse cortical neurons. *Neurotoxicity research*, **31**(1), 77-89.
- Wu, W., Sheng, H., Gu, C., Song, Y., Willbold, S., Qiao, Y., ... & Wang, F. (2018). Extraneous dissolved organic matter enhanced adsorption of dibutyl phthalate in soils: insights from kinetics and isotherms. *Science of the Total Environment*, **631**, 1495-1503
- Xu, G., Li, F., & Wang, Q. (2008). Occurrence and degradation characteristics of dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in typical agricultural soils of China. *Science of The Total Environment*, **393**(2-3), 333-340.
- Yang, Y., Boom, R., Irion, B., van Heerden, D.-J., Kuiper, P., & de Wit, H. (2012). Recycling of composite materials. *Chemical Engineering and Processing: Process Intensification*, **51**, 53-68.
- Yglesias, C. (2014). *The Innovative Use of Materials in Architecture and Landscape Architecture: History, Theory and Performance*. McFarland.
- Zhang, B., Yang, X., Chen, L., Chao, J., Teng, J., & Wang, Q. (2020). Microplastics in soils: a

- review of possible sources, analytical methods and ecological impacts. *Journal of Chemical Technology & Biotechnology*, **95**(8), 2052-2068.
- Zhang, Y. J., Guo, J. L., Xue, J. C., Bai, C. L., & Guo, Y. (2021). Phthalate metabolites: Characterization, toxicities, global distribution, and exposure assessment. *Environmental Pollution*, **291**, 118106.
- Zhou, D., Wang, H., & Zhang, J. (2011). *Di-n-butyl* phthalate (DBP) exposure induces oxidative stress in epididymis of adult rats. *Toxicology and Industrial Health*, **27**(1), 65–71.
- Zhu, Y. J., Jiang, J. T., Ma, L., Zhang, J., Hong, Y., Liao, K., ... & Liu, G. H. (2009). Molecular and toxicologic research in newborn hypospadiac male rats following in utero exposure to di-n-butyl phthalate (DBP). *Toxicology*, **260**(1-3), 120-125.
- Zotica, T. A., Chirila, S. D., Balan, C., & Volf, I. (2020). Physical and chemical characterization and floristic peculiarities of a soil affected by anthropic activities. *Environmental Engineering and Management Journal*, **19**(2), 219-227.