

THE OCCURRENCE OF BROMINATED FLAME RETARDANTS
(POLYBROMINATED DIPHENYL ETHERS AND
POLYBROMINATED BIPHENYL) IN THE CAPE TOWN
ENVIRONMENT

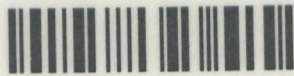
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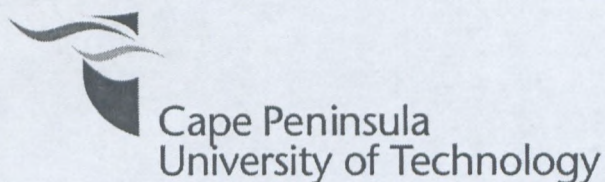
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**THE OCCURRENCE OF BROMINATED FLAME RETARDANTS (POLYBROMINATED
DIPHENYL ETHERS AND POLYBROMINATED BIPHENYL) IN THE CAPE TOWN
ENVIRONMENT**

by

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Thesis submitted in fulfilment of the requirements for the degree

Doctor of Technology: (Environmental Health)

in the Faculty of Applied Sciences

at the Cape Peninsula University of Technology

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Cape Town

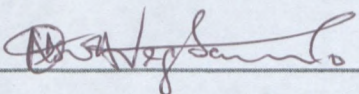
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DECLARATION

I, **Adegbenro Peter Daso**, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.



Signed

23rd April, 2012.

Date

ABSTRACT

This study was aimed to provide baseline information about the environmental levels of selected PBDEs (BDE 28, 47, 100, 99, 154, 153, 183 & 209) and BB 153 in different matrices, including wastewater treatment plants' effluent, sludge, landfill leachate, river water and bottom sediment samples from different locations within the City of Cape Town. The monitoring of these contaminants was carried out bi-monthly over an extended period of 12 months beginning from April 2010 to March 2011. In this study, a total of 63, 168, 312, 93 and 108 samples for leachate, wastewater treatment plant (WWTP) sludge, effluent, river water and bottom sediment, respectively were collected from three landfill sites, four WWTPs and two rivers within the City of Cape Town.

The aqueous matrices were extracted using a liquid-liquid extraction technique. The extraction of both sediment and sludge samples were performed using mechanical shaking and soxhlet extraction techniques, respectively. Extract obtained were further purified using multi-layer silica gel column chromatographic technique. The routine analysis of these target compounds was carried out using a gas chromatograph equipped with an electron capture detector (GC- μ ECD). However, the structural elucidation of these compounds was performed with a gas chromatography-time of flight-mass spectrometry (GC-TOF-MS) instrument.

The results obtained from this study showed that the average concentrations of the eight PBDE congeners ranged from 0.28 – 2240 ng/l, 7.36 – 1520 ng/l, 4.41 – 104,000 ng/g for raw leachate, WWTP influent and sewage sludge, respectively. In the rivers investigated, these levels ranged from 0.84 – 12,100 ng/l, 0.71 – 18,500 ng/l, 0.06 – 2.47 ng/g and 0.22 – 9.95 ng/g for the Diep river water, Kuils river water, Diep bottom sediment and Kuils bottom sediment samples, respectively. The levels obtained for BB 153 were generally low compared to those of PBDEs and these ranged from ND – 415 ng/l, 0.91 – 1700 ng/l, ND – 159 ng/g, ND – 843 ng/l, ND – 281 ng/l, ND – 0.39 ng/g and ND – 1.21 ng/g for raw leachate, WWTP influent, sewage sludge, Diep river water, Kuils river water, Diep bottom sediment and Kuils bottom sediment samples, respectively. The major congeners of the technical formulation of PBDEs, including BDE 47, 99, 153, 183 and 209 were dominant congeners found in most of the samples analysed.

The multivariate principal component analysis (PCA) performed on these data showed that most of these contaminants had similar source into the rivers investigated. Statistical analysis (ANOVA) further revealed that there were significant differences ($p < 0.05$) in the levels of these compounds from one treatment plant to the other and from one sampling regime to the other. All the congeners in bottom sediment were strongly correlated with the total organic carbon (TOC) except BDE 209 which had a significant negative correlation with the TOC.

The seasonal variability of these contaminants in different matrices investigated indicated that higher levels were generally found during the spring season at the landfill sites. The patterns assumed in the WWTPs were quite different with higher levels being found in the influent during the summer and spring seasons. A similar trend was observed for river water and bottom sediment samples except that higher levels of contaminants were found in water samples of the rivers during the winter season. The presence of higher levels of these target compounds downstream of the rivers investigated suggests that WWTP discharges are important sources of these contaminants into the Cape Town environment.

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The financial assistance of the National Research Foundation towards this research is acknowledged. Opinions expressed in this thesis and the conclusions arrived at, are those of the author, and are not necessarily to be attributed to the National Research Foundation.

DEDICATION

I dedicate this work to the ETERNAL, INVISIBLE, THE ONLY WISE GOD, MY REDEEMER and SAVIOUR – the one who out of his abundant love and mercy has lifted up my head beyond my comprehension.

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GLOSSARY

ABS	acrylonitrile-butadiene-styrene
ANOVA	analysis of variance
APCI	atmospheric pressure chemical ionisation
BB 153	2,2',4,4',5,5'-hexabromobiphenyl
BDE 28	2,4,4'-tribromodiphenyl ether
BDE 47	2,2',4,4'-tetrabromodiphenyl ether
BDE 77	3,3',4,4'-tetrabromodiphenyl ether
BDE 99	2,2',4,4',5-pentabromodiphenyl ether
BDE 100	2,2',4,4',6-pentabromodiphenyl ether
BDE 153	2,2',4,4',5,5'-hexabromodiphenyl ether
BDE 154	2,2',4,4',5,6'-hexabromodiphenyl ether
BDE 183	2,2',3,4,4',5',6-heptabromodiphenyl ether
BDE 209	2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether
BFR	brominated flame retardants
BOD	biochemical oxygen demand
CCT	City of Cape Town
CI	chemical ionization
DAF	dissolved air flotation
DED	daily exposure dose
DMR	Duncan Multiple Range test
dw	dry weight
EC	electrical conductivity
ECD	electron capture detector
EDCs	endocrine disrupting compounds
EDI	estimated daily intake
EI	electron ionization
FID	flame ionization detector
FOG	fats, oil and grease
FR	flame retardant
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
GPC	gel permeation chromatography
HBCD	hexabromocyclododecane
HIPS	high impact polystyrene

HRT	hydraulic retention time
IUPAC	International Union of Pure and Applied Chemistry
K_h	Henry's law constant
K_{oc}	octanol-organic carbon partition co-efficient
K_{ow}	octanol-water partition co-efficient
LC	liquid chromatography
LD ₅₀	lethal dose for 50% of subjects
LLE	liquid-liquid extraction
LRAT	long-range atmospheric transport
LTP	leachate treatment plant
lw	lipid weight
MAE	microwave-assisted extraction
MBR	membrane bioreactor
MPCA	Minnesota Pollution Control Agency
MSPD	matrix solid-phase dispersion
m/z	mass to charge ratio
NCI	negative chemical ionization
NHANES	National Health and Nutrition Examination Survey
NTU	nephelometric turbidity unit
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PCA	principal component analysis
PCBs	polychlorinated biphenyls
PCNB	pentachloronitrobenzene
PK	pharmacokinetic (model)
PLE	pressurized liquid extraction
POPs	persistent organic pollutants
PTV	programmable temperature vapourisation
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical substances
RSD	relative standard deviation
S/N	signal to noise ratio
SPE	solid-phase extraction
SPME	solid-phase microextraction
SRT	solid retention time
SVHC	substance of very high concern

T3	triiodothyronine
T4	tetraiodothyronine
TBBPA	tetrabromobisphenol A
TDS	total dissolved solids
TOC	total organic carbon
TOF	time-of-flight
TSS	total suspended solids
TR- α 1	thyroid receptor proteins
TTR	transthyretin
UDP	uridine diphosphate
USE	ultrasonic extraction
v/v	volume to volume ratio
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
VOCs	volatile organic compounds
WWTP	wastewater treatment plant
WHO	World Health Organisation
ww	wet weight

CHAPTER ONE

BACKGROUND

1.1 Introduction

Fire is a major cause of property damage, loss and even death throughout the history of mankind. To circumvent this phenomenal losses as a result of fire accidents, man introduced a group of chemicals known as 'flame retardants' to reduce the likelihood of ignition and burning in a wide range of textiles, plastics, building materials and electronic equipment used in commerce and residential homes (Alaee and Wenning, 2002). The use of flame retardants dates back to the ancient Egyptian periods, more than 2000 years ago, when papers and wood were soaked and dried so as to render them fireproof. Certain ammonium salts were also found to be effective for the protection of precious textiles in the early nineteenth century, a practice that continues today.

With the rapid replacement of traditional building materials like wood and metal with plastics; the previously used inorganic salts could no longer be applied because they considerably reduce the materials thermal stability (Vonderheide *et al.*, 2008). The development of halogen-based organic flame retardants was a major advancement as they could be incorporated into plastic substances. This scientific advancement has resulted in the production and use of several flame retardants broadly classified into three major groups, namely brominated flame retardants (BFRs), phosphorus-based flame retardants and inorganic flame retardants (usually magnesium and aluminium hydroxides) (Minnesota Pollution Control Agency (MPCA), 2008). Amongst these groups of chemicals, the halogenated organics and organophosphorus flame retardants are of great concern to public health due to their environmental persistence and toxicity.

The halogenated organic flame retardants are generally classified as either chlorinated or brominated flame retardants. The brominated flame retardants (Fig 1.1) are extensively used due to their thermal stability, high bromine content and relatively low cost (Darnerud *et al.*, 2001). Depending on their mode of incorporation into the polymeric materials, two groups of BFRs exist, namely: reactive and additive BFRs. Reactive BFRs are those that are covalently bonded to the polymers, e.g. tetrabromobisphenol A and its derivatives. Additive BFRs which include polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are not covalently bonded to the polymeric materials. As a result, they are more likely to diffuse out of the treated polymer during their lifetime (de Wit, 2002). This possibility has been confirmed with increased levels of these chemicals reported in various components of the environment, thus, making their investigation in this present study very essential.

Brominated flame retardants have been detected in various environmental components including: sewage sludge (Clarke *et al.*, 2008; Gevao *et al.*, 2008); sediment (Eljarrat *et al.*, 2004; Binelli *et al.*, 2007); indoor dust (Gevao *et al.*, 2006a; Abdallah *et al.*, 2008) wildlife (Xiang *et al.*, 2007; Polder *et al.*, 2008; Johansson *et al.*, 2009) as well as in human breast milk (Akutsu *et al.*, 2003; Kazda *et al.*, 2004; Fangstrom *et al.*, 2008; Sudaryanto *et al.*, 2008). The widespread presence of these emerging contaminants in the environment is largely due to their ever-increasing global demand. For instance, the global demand for BFRs in 2001 exceeded 200,000 metric tons; a somewhat higher quantity was recorded in 2003. The summary of global BFR demand in 2001 and 2003 is presented in Table 1.1.

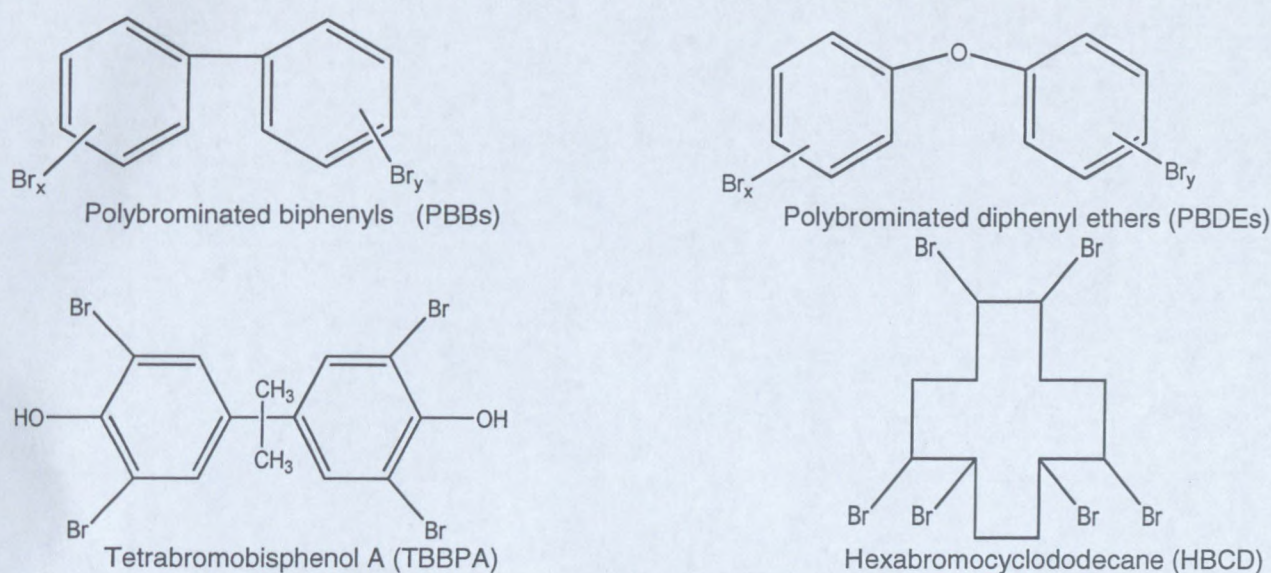


Figure 1.1: Chemical structures of brominated flame retardants

Besides the rapidly increasing environmental levels of BFRs, there have been intense global concerns about their persistence, toxicity, bioaccumulative potential as well as their ability to undergo long-range environmental transport (WHO, 1994; 1997; UNEP, 2009). The presence of these contaminants in living organisms, particularly in humans is undesirable because they are known to cause thyroid hormone imbalances, neurobehavioural effects, reproductive dysfunctions and even cancer in exposed subjects (WHO, 1994, 1997). Several risk assessment studies to assess the potential risks to humans by these chemicals have been conducted in most developed countries. These have resulted into restrictive use and production, and even ban of some of these chemicals in these countries. Unfortunately, many developing countries, including South Africa are yet to recognise the health impacts arising from the use of these chemicals.

Table 1.1: BFR volume estimates in 2001 and 2003 in metric tons

Flame Retardant	Americas 2001	Europe 2001	Asia 2001	Rest of the world 2001	Total 2001	Total 2003
TBBPA	18 000	11 600	89 400	600	119 700	145 113
HBCD	2 800	9 500	3 900	500	16 700	21 951
DecaBDE	24 500	7 600	23 000	1 050	56 100	56 481
OctaBDE	1 500	610	1 500	180	3 790	---
PentaBDE	7 100	150	150	100	7 500	---

--- - no data given; Source: Minnesota Pollution Control Agency, 2008.

The review of current literature on brominated flame retardants revealed that there is insufficient information on the production estimate, use, as well as environmental levels of these chemicals in Africa.

1.2 Global production and usage of PBDEs

In the last few decades, the global production and usage of PBDEs had significantly increased until certain restrictions were enforced on their usage in recent times. PBDEs are commercially marketed in three different technical formulations, namely penta, octa and deca-formulations (La Guardia *et al.*, 2006). These formulations are produced under a variety of trade names (e.g. DE-71, Bromkal 70-5DE; DE-79, Bromkal 79; Great Lakes DE-60F, Saytex 115, Bromkal 82-E) since the early 1970s (de Boer and Cofino, 2002; Talsness, 2008). These technical formulations are produced as mixtures with varying compositions of different PBDE congeners. The percentage compositions of PBDE congeners for the three technical mixtures are presented in Table 1.2.

Table 1.2: The percentage composition of polybrominated diphenyl ether (PBDE) congeners in technical formulations (WHO, 1994)

Technical products	PBDE congeners (%)							
	Tri	Tetra	Penta	Hexa	Hepta	Oct	Nona	Deca
Penta-BDE	0-1	24-38	50-62	4-8				
Octa-BDE				11-12	44-45	31-35	10-11	0-1
Deca-BDE							0.3-3	97-98

The global demand for BFRs has dramatically increased from 25,000 tonnes in 1975 to 200,000 tonnes in 2000 (Arias, 2001). Bromine is a principal ingredient in the production of a variety of products, including flame retardants, pesticides, gasoline additives, drilling fluids and biocides. With the increasing demand for BFRs, the global production of bromine has consequently increased from 296,000 tonnes in 1975 to 520,000 tonnes in 2000 (Arias, 2001).

As indicated in Table 1.3, the total world production of bromine for each country did not follow the same trend. While the amount of bromine produced in the USA and Israel increased steadily, its production in the EU countries decreased by about fifty per cent. According to the World Health Organisation (WHO, 1994), 600,000 tonnes of flame retardants were used globally in 1992, of which 40,000 tonnes were

PBDEs. Of the three technical formulations, deca-BDE was the most widely used accounting for 75% of the total PBDE used. The octa and penta-formulations accounted for 15 and 10% of the total PBDE used, respectively.

Table 1.3: A comparison of annual global bromine production in tonnes

Countries	1975	1990	1995	2000
United States	189 000	177 000	218 000	229 000
Israel	18 500	135 000	160 000	185 000
China	N/A	<1000	33 000	45 000
European Union	63 800	46 000	32 000	32 000
Japan	11 800	15 000	15 000	20 000
Former USSR	13 000	60 000	6 000	6 000
India	N/A	<1 000	1 500	1 500

Source: Arias, 2001; N/A – not available.

With the ban of penta and octa-formulations, the global demand for deca-BDE continues to grow significantly. In 2003, the global market demand of BFRs was estimated at 223,483 metric tonnes, of which 56,418 metric tonnes constituted of deca-BDE and 145,113 metric tonnes constituted of TBBPA (Bromine Science and Environmental Forum, 2009a). The United States is the largest producers of PBDEs. In 1999, for instance, the global market demand was 60,000 tonnes for the deca-BDE, of which 40% was produced in the United States while 12.5% was produced in Europe (Arias, 2001). Similarly, the amount of octa and penta-formulations produced in the US representing 1,370 and 8,290 tonnes, respectively, were significantly larger than those produced in Europe where only 450 and 210 tonnes of octa and penta-formulations were produced, respectively.

The deca-BDE mixture is the most widely used PBDE technical formulation in the production of many plastics, especially high impact polystyrenes (HIPS). It is also used for the treatment of textiles used for soft furnishing, automobile fabrics, television and circuit boards, and camping tents (WHO, 1994; Wenning, 2002). Octa-BDE is an important PBDE technical formulation used to coat or mixed with acrylonitrile-butadiene-styrene (ABS), a material used in the production of computer and other office equipment (WHO, 1994). Penta-BDE, on the other hand, is used mainly as additive to polyurethane foams for upholstery and furnishings, mostly in concentrations of up to 30%. It also finds extensive use in epoxy resins, phenol resins, unsaturated polyesters and some textiles (WHO, 1994).

Certain plastics such as polyvinylchloride (PVC) do not require the addition of flame retardants due to their inherent fire-resistant properties. In many industrial applications, today, fire safety is still an important criterion for the selection of a suitable plastic for any given application. Hence, the addition of BFRs to plastics might continue to be a preferred option considering the numerous advantages this practice offers. These include better product performance, amenability to recycling, excellent appearance, strength and stability (Odusanya, 2008). A list of annual production of major polymers together with the

BFRs commonly used to enhance their fire resistance is given in Table 1.4. Going by these figures, the total tonnage of BFR-laden waste plastics, which eventually ends up in different dumpsites across the world, could pose a serious threat to both public health and the environment, in general.

Table 1.4: Global annual production of polymers in 2000 and their BFR content (Arias, 2001)

Polymer	BFR content (%)	Type of BFR	Annual production (10 ³ TPA)
Polystyrene foam	0.8 – 4	HBCD	600
High impact polystyrene	11 – 15	d-PBDE, Br Ps	350
Epoxy resin	19 – 33	TBBPA	300
Polyamides	13 – 16	d-PBDE, Br Ps	200
Polyolefin	5 – 8	d-PBDE, DBS	200
Polyurethanes	10 – 18	p-PBDE, Br Polyols	150
Polyterephthalate	8 – 11	Br Ps, der-TBBPA	150
Unsaturated polyesters	13 – 28	TBBPA	150
Polycarbonate	4 – 6	Br Ps, der-TBBPA	100
Styrene copolymers	12 -15	o-PBDE, Br Ps	50

HBCD – hexabromocyclododecane; PBDE – polybrominated diphenyl ether (d: deca, o: octa, and p: penta formulations); TBBPA – tetrabromobisphenol A (der: derivative); Br Ps – brominated polystyrene; DBS – propylene dibromo styrene; Br Polyols – esters of TBBPA; TPA – tonnes per annum (metric)

1.1.3 Choice of target analytes

A list of commonly investigated PBDE congeners to be monitored in different environmental matrices in this study is presented in Table 1.5. The choice of these congeners was based on their toxicity and their relatively high percentage composition in the technical PBDE formulations. Secondly, the selected congeners were those predominantly reported in various environmental matrices, thus, allowing for comparison of the outcome of this study with similar studies around the world. In the same vein, BB 153 was included in the list of target compounds because it is the main congener of the widely used hexabromobiphenyl technical formulation. This formulation was extensively used as flame retardant until it was unintentionally mixed with livestock feed in Michigan in 1973, an incidence that led to its eventual ban in the USA in 1974 (WHO, 1994). Commercial productions of other technical formulations were also phased out in 2000 in the Europe (Alaee *et al.*, 2003). The assessment of BB 153 in different matrices, as it is the case in this study, will further indicate the degree of persistence of these categories of organic contaminants in the environment.

Table 1.5: Chemical information of target compounds (polybrominated diphenyl ethers and polybrominated biphenyl) investigated

Serial No.	BDE Number	IUPAC Name	CAS Number
1	BDE 28	2,4,4'-Tribromodiphenyl ether	41318-75-6 (Unlabelled)
2	BDE 47	2,2',4,4'-Tetrabromodiphenyl ether	5436-43-1 (Unlabelled)
3	BDE 99	2,2',4,4',5-Pentabromodiphenyl ether	60348-60-9 (Unlabelled)
4	BDE 100	2,2',4,4',6-Pentabromodiphenyl ether	189084-64-8 (Unlabelled)
5	BDE 153	2,2',4,4',5,5'-Hexabromodiphenyl ether	68631-49-2 (Unlabelled)
6	BDE 154	2,2',4,4',5,6'-Hexabromodiphenyl ether	207122-15-4 (Unlabelled)
7	BDE 183	2,2',3,4,4',5',6-Heptabromodiphenyl ether	207122-16-5 (Unlabelled)
8	BDE 209	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether	1163-19-5 (Unlabelled)
9	BB 153	2,2',4,4',5,5'-Hexabromobiphenyl	59080-40-9 (Unlabelled)

1.4 Research problem

The global production and use of computers, television sets, automobiles, mobile phones, furniture as well as electrical and electronic equipment (EEE) have greatly increased in the past few decades. The frequent introduction of newer design of these products ultimately makes the older products become obsolete thus resulting in high volume of wastes from their use. Today, one of the greatest challenges of most countries is achieving sustainable management of these electronic wastes. This is largely due to their high toxicity and extremely high volume being generated annually. Surprisingly, brominated flame retardants constitute a significant proportion of these wastes.

Nnorom and Osibanjo (2008a) reported that over 60,000 tonnes of second-hand electrical and electronic equipment (EEE) are imported annually into Nigeria, which may contain as much as 18,000 tonnes of BFR-laden plastics. By implication, about 30% of the total tonnage of most obsolete or “fairly-used” electrical and electronic equipment being shipped annually to developing countries may constitute these contaminants. The authors concluded that, in most cases, an estimated percentage of seventy-five or more of these imported devices are short-lived or completely unusable. Once, these products have outlived their lifespan, they are often discarded into landfill sites. Generally, these wastes are often disposed together with municipal wastes (which are mostly rich in organic matter) into these landfill sites. Although this scenario is not the case in South Africa, reconnaissance visits to some of the landfill sites revealed that products other than e-wastes such as old furniture, plastics, amongst others, probably containing these contaminants are also disposed together with other municipal wastes in these sites.

Since the mode of incorporation of some BFRs such as PBDEs and PBBs into the polymeric materials is additive, several chemical and biological processes taking place in these landfill sites may enhance their leaching from these waste materials. Kim *et al.* (2006) reported that the leaching potentials of some PBDEs were remarkably enhanced in the presence of dissolved humic matter when compared to distilled water. The prolonged build up of these emerging contaminants in landfill leachates constitute a serious threat to public health. This is because these contaminants may migrate into the groundwater and surface water bodies via the underlying soil, thus predisposing people who depend on these water sources for their livelihood to these endocrine disrupting chemicals.

In addition, the poor management of these wastes may result in the production of more highly toxic chemicals like ‘dioxin and furan’, particularly when they are burnt under uncontrolled conditions. Furthermore, the vast amount of sewage sludge generated from both municipal and industrial wastewater treatment plants, which are either incinerated, landfilled or used as agricultural compost are important sources of these contaminants in the environment. In most countries, a significant proportion of this sludge is usually applied to agricultural lands. Although, sludge conditioning of agricultural lands helps to

improve soil fertility, it has also significantly encouraged the redistribution of BFRs in the environment contributing to their widespread presence and elevated levels in freshwater and marine ecosystems.

Besides dietary exposure via consumption of contaminated meat, fish and dairy products, plant uptake of these contaminants from sludge-conditioned agricultural lands may pose additional exposure route to humans. The presence of these contaminants in humans is undesirable as they may cause disruption of thyroid hormone homeostasis, neurobehavioral effects, reproductive dysfunctions and even cancer (WHO 1994; 1997). Unfortunately, the health impacts of these contaminants have not been fully recognised by most developing countries, including South Africa. It is therefore envisaged that the results from this study will not only provide baseline information about these contaminants but also provide additional policy and decision-making tools for relevant government's agencies.

1.5 Research questions

- i. Are the present methods of determination of polybrominated diphenyl ethers and polybrominated biphenyls suitable for investigating them in the various sample matrices to be monitored in this study?
- ii. What are the possible sources of these pollutants into the Cape Town environment?
- iii. To what extent has the Cape Town environment been polluted with polybrominated diphenyl ethers and polybrominated biphenyl?
- iv. Are there seasonal variations in the levels of these brominated flame retardants in the Cape Town environment?

1.6 Objectives of the research

1.6.1 Broad objective

The main objective of this research is to investigate the occurrence of commonly occurring polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) and to determine their concentrations in different environmental samples.

1.6.2 Specific objectives

- i. To evaluate the suitability of some present methods of determination of polybrominated diphenyl ethers and polybrominated biphenyl in various sample matrices and to improve on them where necessary.

- ii. To validate the experimental methods to be used for the analysis through appropriate optimization procedures.
- iii. To determine the concentrations of PBDEs and PBB in effluents and sewage sludge samples from selected wastewater treatment plants; leachate samples from selected landfill sites; river water and bottom sediment samples from selected rivers in the City of Cape Town.
- iv. To identify the dominant congeners of these brominated flame retardants in all analysed samples.
- v. To identify possible point sources of brominated flame retardants in the Cape Town environment.
- vi. To evaluate the distribution patterns of selected PBDEs and BB 153 in different matrices collected from different parts of the City of Cape Town.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview

This chapter gives an overview of general information on polybrominated diphenyl ethers (PBDEs) as well as polybrominated biphenyls (PBBs) and their physicochemical properties. It provides insights into how these properties could possibly influence their environmental fate and transport within various components of the environment. The various sources of these contaminants and how they contribute to environmental contamination were discussed. Different routes and pathways of human exposure to PBDEs and some important characteristics they exhibit, which qualifies them as emerging persistent organic pollutants, were mentioned. Analytical approaches and techniques employed for their investigation in different environmental matrices were extensively reviewed. Lastly, the development of legislative framework in different regions and internationally aimed at controlling the production and use of these chemicals were also mentioned.

2.2 Flame retardants

Flame retardants (FRs) are chemicals which are incorporated into materials during or after they are manufactured, so as to inhibit or even suppress the combustion or ignition process (Darnerud *et al.*, 2001). Flame retardants have also been defined as materials that inhibit or resist the propagation of fire (Bromine Science and Environmental Forum, 2009b). These chemicals are generally incorporated into various consumer products including textiles, plastics, electronics, furniture, carpets, cushioning foams for automobile interiors and other products used at homes and offices. They primarily serve to protect them against ignition and to prevent fire-related damage (Segev *et al.*, 2009).

The application of FRs to products in itself does not guard against incidences of fire outbreaks. However, it does ensure that the rate of fire growth is slowed down and helps to hinder the spread of fire, thus, providing valuable time for escape at the commencement of fire accidents. No doubt, the use of these chemicals had saved thousands of lives and several billion dollars worth of properties were rescued with these chemicals. Some of the benefits associated with these chemicals have led to their widespread usage globally. Presently, there are more than 175 chemicals being classified as flame retardants. These include inorganic, halogenated organic (which could either be chlorinated or brominated), organophosphorus and nitrogen-based flame retardants which account for 50%, 25%, 20% and >5% of the annual production, respectively (WHO, 1997). Although, all the categories of FRs are of environmental relevance, the focus of this study is on some class of brominated flame retardants, which are generally found at an increasingly high level in different environmental components.

2.2.1 Brominated flame retardants

Brominated flame retardants (BFRs) are high volume industrial chemicals usually incorporated into a wide range of textiles and polymers used in several consumer products. These chemicals are extensively used in plastic housings of electronic appliances, printed circuit boards of computers, as well as in upholstery and construction materials (WHO, 1994). BFRs, which are important group of halogenated organic flame retardants, are often classified into two different classes, namely reactive or additive.

Reactive BFRs are covalently bonded to the polymers, e.g. Tetrabromobisphenol A (TBBPA) and its derivatives. Additive BFRs, which include polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), are not covalently bonded to the polymeric materials, hence, they are more likely to diffuse out of the treated polymer during their lifetime (de Wit, 2002).

2.2.1.1 Tetrabromobisphenol A

Tetrabromobisphenol A (TBBPA) is a reactive brominated flame retardant with the highest volume of 210,000 tonnes amongst the BFRs currently used in the world today. It is produced via bromination of bisphenol A in an organic solvent. TBBPA finds extensive use in the production of epoxy and polycarbonate resins where it serves as reactive intermediate. Epoxy resins are mainly used in the manufacturing of printed circuit boards that contain approximately 20% bromine (Alaee *et al.*, 2003). Other uses of TBBPA involve its transformation into derivatives such as dimethyl TBBPA which is mainly used as additive BFR in acrylonitrile-butadiene-styrene (ABS) resin and high impact polystyrene. Other derivatives such as Bis (2-hydroxyethylether) TBBPA find extensive use as flame retardants for paper and textile adhesives and coatings (Alaee *et al.*, 2003). Although TBBPA is covalently bound to the polymer, its presence in different environmental matrices suggests that it could be an important environmental contaminant.

TBBPA has been detected in soil, sediment, sewage and landfill samples in quantifiable amounts (Morris *et al.*, 2004; Sanchez-Brunete *et al.*, 2009; Zhang *et al.*, 2009). The accumulation of this chemical in living organisms as observed in aquatic biota calls for concerns (Morris *et al.*, 2004). A major concern about this chemical is its structural similarity with the thyroxine hormone (T_4). Meerts *et al.* (2000) demonstrated in in-vitro T_4 -TTR assay that TBBPA has stronger affinity for binding with the thyroid hormone transport protein transthyretin (TTR) than the natural ligand T_4 . This implies that TBBPA can interfere with the transport of thyroxine hormone and retinol to the brain, which is the major function of TTR. TBBPA has been classified in the EU as an R50/53 substance for the environment, which categorises it as a toxic substance to aquatic organisms and may cause long-term adverse effects in the aquatic environment (Dawson and Landry, 2006). In the updated EU risk assessment reports recently published, it was

concluded based on established scientific findings that TBBPA is not an “endocrine disruptor” and does not have a significant potential for bioaccumulation (Bromine Science and Environmental Forum, 2011). Hence, there is no regulation restricting its production and use in the world.

2.2.1.2 Hexabromocyclododecane (HBCD)

HBCD is a brominated aliphatic cyclic hydrocarbon used as additive flame retardants in thermal insulation for building materials, upholstery textiles and electronics (Covaci *et al.*, 2006). It is extensively used in articles made of polystyrene and in textile backcoating. It is also used in foams and expanded polystyrene with end products, including upholstered furniture, interior textiles, automobile interior textiles, car cushions and insulation blocks in trucks and caravans. HBCD is equally used in building materials such as house walls, cellars, roofs and parking decks, against frost heaving in roads and railway embankments and packaging materials (de Wit, 2002). The technical HBCD is a mixture of three diastereoisomers: α -, β -, γ -HBCD (Heeb *et al.*, 2008). These three diastereoisomers are chiral and exist as pairs of enantiomers in the technical HBCD resulting in six stereoisomers (+/-) α -, (+/-) β -, and (+/-) γ -HBCD. Studies from thermal rearrangement indicate that α -HBCD is the most thermodynamically stable isomer of the three (Smith *et al.*, 2005).

With the recent restrictions on the use of penta- and octa-BDE technical formulations, especially in Europe, the demand for HBCD has increased significantly, as it can serve as a viable alternative for PBDEs in some applications. Like PBDEs, HBCD can enter the environment via different pathways such as emission during production of BFRs or the manufacture of flame-retarded products, by leaching from consumer products or following disposal (Covaci *et al.*, 2006). The occurrence of HBCD has been reported in biological as well as environmental samples worldwide (Covaci *et al.*, 2006; Law *et al.*, 2006; Johnson-Restrepo *et al.*, 2008). Increasing levels of HBCD in living organisms has led to its inclusion in the candidate list for authorisation under the REACH programme by European Union. Hence, HBCD has been identified as a substance of very high concern (SVHC) by the Swedish authorities. Although, the risk assessment for HBCD identified no health risk to consumers, it however has the potential to persist in the environment, bioaccumulate and exhibit certain degree of toxicity.

2.2.1.3 Polybrominated biphenyls (PBBs)

PBBs were the earliest BFRs introduced as flame retards in the early 1970's. The commercial production of PBBs involves bromination of biphenyl, a process involving a much more specific reaction and that produces a small number of product mixtures than chlorination (de Wit, 2002). Three commercial PBB products were manufactured (i.e. hexabromobiphenyl, octabromobiphenyl and decabromobiphenyl).

Hexabromobiphenyl was the most widely used. In 1973, commercial flame retardants formulations (Firemaster BP-6® and FF-1®) containing PBBs were accidentally mixed into feed for dairy cattle, livestock and poultry in the state of Michigan, US (Alaee *et al.*, 2003). The feed was widely used leading to widespread PBB contamination of milk, meat and eggs and poisoning in animals. Many people were exposed to PBBs from food. Extensive studies conducted revealed that the toxicology of PBBs in poisoned animals and exposed humans was essentially the same as those seen for PCBs (de Wit, 2002). This incidence led to the ban of hexabromobiphenyl technical formulation in the USA in 1974 (WHO, 1994). Nevertheless, the production of octa- and deca-PBB technical formulations continued until 1979.

In Europe, the production of highly brominated PBBs continued in Germany until 1985, and in France, the deca-PBB formulation was in production until 2000 (Hardy, 1999). Prior to its termination, hexabromobiphenyl formulation was used as a flame retardant mainly in thermoplastics for constructing business machine housings and in industrial (e.g. motor housing), and electrical (e.g. radio and TV parts) products. Smaller amounts were used as fire retardants in coating and lacquers, and in polyurethane foam for auto upholstery. Due to their high degree of persistence, bioaccumulation and toxicity, PBBs were considered as persistent organic pollutants. Hence, hexabromobiphenyl formulation was listed in Annex A of the Stockholm Convention on Persistent Organic Pollutants during its fourth Conference of the Parties meeting in May, 2009 making it a bonafide member of the “dirty twelve” class (UNEP, 2009).

2.2.2 Polybrominated diphenyl ethers (PBDEs)

PBDEs are additive brominated flame retardants with the second highest production volume amongst the BFRs in the world market today. PBDEs are produced by bromination of diphenyl ether in the presence of Friedel-Craft catalyst (i.e. AlCl_3) in a solvent such as dibromomethane (Alaee *et al.*, 2003). Theoretically, 209 possible congeners of PBDEs could be produced by the replacement of any of the 10 hydrogen atoms on the diphenyl molecule with bromine. PBDEs are structurally similar to the widely studied PCBs. Hence, the numbering of the congeners is analogous to the IUPAC nomenclature and systematic numbering system for PCBs (Ballschmiter and Zell, 1980). In this numbering system, the total numbers of bromine substituent as well as their relative positions on the diphenyl group were specified. The PBDE congeners are divided into ten groups depending on the number of bromine atoms, classified as mono- to decabromodiphenyl ethers. The technical PBDE products are penta-, octa- and decabromodiphenyl ether products (specifically identified as pentaBDE, octaBDE and decaBDE). Each product is made up of a limited number of congeners and is named after the dominant congener (Darnerud, 2003).

The uncertainties in possible health risks associated with the increasing usage and rising levels of PBDE in the environment as well as human subjects has been under intense scrutiny, especially in Europe, in the

last two decades. Sweden and Germany were the first two countries to support the voluntary ban of pentaBDE production. In the EU, the official ban of this formulation eventually came into effect in 2004. This restriction was also enforced for both penta- and octaBDE formulations in the USA in 2005 (McKenzie, 2009). As at today, only decaBDE formulation is being produced and it is ranked second, next to TBBPA, in terms of global production volume. Following the ban on both penta- and octaBDE formulations, it is envisaged that the release of these chemicals from discarded or in-service products may continue for several decades (Chen *et al.*, 2008). To be able to predict the behaviours of PBDEs in different environmental matrices, it is essential that their physicochemical properties are fully understood.

2.2.2.1 Physicochemical properties of PBDEs

The general chemical formula of PBDEs is $C_{12}H_{(10-x)}Br_{(x)}O$, where $x = 1, 2, \dots, 10$ and the sum of H and Br atoms will always be equal to 10. The different technical formulations of PBDEs possess varying physical properties. For instance, pentaBDE formulation is a viscous liquid, which contain 70% bromine by weight with varying congener composition (see: Table 1.2). OctaBDE and decaBDE formulations are white powder containing 79 and 83% bromine by weight, respectively (Alaee *et al.*, 2003). PBDEs are very lipophilic, with low water solubility. They have high log octanol-water partition coefficient values ranging from 3.7 (tetraBDEs) to 11 (BDE 209). The log K_{OW} values may give an indication of the possible degree of accumulation of these chemicals. The higher the value is, the more the tendency of the compound to accumulate in fatty tissues or oily components of living organisms.

PBDEs, like most persistent organic chemicals, are hydrophobic and as such, tend to bind strongly to suspended organic materials. This ability of organics to bind with suspended solids plays a vital role in the removal of organic contaminants treated by wastewater treatment plants. PBDEs have low vapour pressures. The more substituted the PBDE congener is, the heavier the molecule becomes and consequently the less volatile the molecule is. Hence, the highly brominated congeners are less volatile than the lower brominated congeners. This could also explain why air stripping techniques commonly used in some WWTPs enhance the removal of lower brominated congeners than the highly brominated congeners (Seriki *et al.*, 2008). Table 2.1 gives detailed physicochemical properties of some technical formulations of PBDEs as well as PBBs.

Table 2.1: Physicochemical properties of some PBDEs and PBBs technical formulations

	TetraBDE^a	PentaBDE^a	OctaBDE^a	DecaBDE^a	HexaBB^b
Chemical formula	C ₁₂ H ₆ OBr ₄	C ₁₂ H ₅ OBr ₅	C ₁₂ H ₂ OBr ₈	C ₁₂ OBr ₁₀	C ₁₂ H ₄ Br ₆
Molecular mass	485.8	564.8	801.5	959.2	627.4
Vapour pressure (Pa)	2.7 – 3.3 x 10 ⁻⁴ (20°C)	2.9 – 7.3 x 10 ⁻⁵ (20°C)	1.2 – 2.7 x 10 ⁻⁷ (20°C)	< 1 x 10 ⁻⁴ (25°C)	7 x 10 ⁻⁶ (25°C)
Melting point (°C)	79 – 82 (BDE47)	92 (BDE99) 97 - 98 (BDE100)	~200	290 – 306	72
Boiling point (°C)	-	> 300°C	-	(decomposition)	-
Water solubility (µg/L)	-	0.0009 (20°C)	-	20 – 30	0.06 (deionised)
Log K _{ow}	5.9 – 6.2	6.5 – 7.0	8.4 – 8.9	10	< 7 (calculated)

^a adapted from Darnerud *et al.*, 2001; b, extracted from WHO, 1994.

2.2.3 Sources of polybrominated diphenyl ethers in the environment

The pathways through which most BFRs get released into the environment are associated with their technical products. Hence, the environmental occurrence of these contaminants may, therefore, result from several activities associated with the production, use and eventual disposal of these products. On this basis, the various means of BFR release into the environment can be classified into two, namely: point (localised) and non-point sources. Discharges from manufacturing industries, wastewater treatment plants as well as leachates from landfill sites are important point sources of these contaminants. On the other hand, non-point sources, which include atmospheric deposition of emitted BFRs, indiscriminate disposal of electronic wastes and other BFR-treated waste products, redistribution of BFRs in sewage-conditioned agricultural soils and others, are often not localised. Therefore, the extent and magnitude of impacts associated with these sources are usually great and difficult to control. Once released, BFRs may be transported and redistributed in the environment (Eljarrat *et al.*, 2008).

During manufacturing activities and recycling of BFR-treated waste materials, significant amounts of BFRs may be released into the environment. This could occur through either spillage or volatilisation into the surrounding air. This has often constituted a major exposure route to industrial workers, particularly those working in disassembly or recycling plants. Recent studies have shown that high contaminant levels are detected in tissues of workers who are occupationally exposed to these chemicals (Bradman *et al.*, 2007; Zhao *et al.*, 2008; 2009a). Similarly, dust in indoor environments, including homes and workplaces may be significantly laden with these contaminants. Usually, these BFR-laden dust particles are derived from hot electrical and electronic appliances as well as from carpets and furniture. Since these contaminants are mostly bound to airborne dust particles, they may be transported beyond the point of generation (Gevao *et al.*, 2006a; Abdallah *et al.*, 2008).

Furthermore, the contribution of sewage sludge and effluents derived from wastewater treatment plants to environmental BFRs burden is highly significant. Usually, the BFRs originate from wastewater, and like

most hydrophobic organic pollutants, they tend to bind strongly with organic matter (Clarke *et al.*, 2008). During the treatment process, a significant amount of BFRs is removed from the waste stream, resulting in reduced levels of contaminants in the effluent discharged into receiving water bodies. Although, the contaminant levels are greatly reduced in the effluents, the enormous volume of effluents frequently discharged makes wastewater treatment plants (WWTPs) important sources of these contaminants.

In addition, sludge being generated by these WWTPs is often disposed of by several methods that may result in further contamination of the environment. These include incineration, land filling and agricultural land application. For instance, incineration of sludge containing these contaminants may lead to the formation of highly toxic chemical substances. Polybrominated dibenzo-p-dioxin and polybrominated dibenzofurans are important combustion products formed during incineration. Their formation is particularly enhanced when the process operating conditions are not well-controlled (Soderstrom and Marklund, 2002; Ebert and Bahadir, 2003). Debromination of higher brominated flame retardants, particularly BDE 209 may also occur under this condition, leading to PBDEs with lower degrees of bromination which are known to be more bioavailable and bioaccumulable (de Wit, 2002).

Land-conditioning by sewage sludge could contribute to increased levels of organic pollutants in soils. Eljarrat *et al.* (2008) observed that sewage-sludge amendment of agricultural soils significantly contributed to increased BDE 209 soil burdens. The influence of precipitation and runoff on land-applied sludge may particularly encourage BFRs redistribution within the environment. Hence, locations with high precipitation may experience a more highly dispersed distribution of these contaminants. Precipitation may therefore be playing a major role in the re-distribution of these contaminants especially in the remote areas.

Another important disposal option for sewage sludge is land filling. Most landfill sites are usually designed to accommodate municipal and non-hazardous industrial wastes. In most developing countries, however, the practice of incorporating electronic wastes (e-wastes) into household wastes handled by these treatment facilities cannot be completely ruled out. Hence, the chemical reactions between the organic matter present in sludge buried in these treatment facilities and BFR-treated products may encourage the leaching of these contaminants into the environment (Osako *et al.*, 2004; Odusanya *et al.*, 2009). Choi *et al.* (2009) confirmed this assumption in their studies where they found that dissolved humic matter in leachate remarkably enhanced PBDE leachability. The released contaminants may, therefore, migrate into the groundwater and surface water, thus, predisposing people to harmful health effects of these chemicals.

Globally, the contribution of leachates from landfill sites to the overall environmental burden is highly significant. This is due to the fact that most consumer products treated with BFRs eventually end up in these facilities. This scenario is worse in developing countries where little or no attention is paid to the proper sorting and treatment of wastes before disposal into landfill sites. Nnorom and Osibanjo (2008b) estimated that about 60,000 tonnes of second-hand electrical and electronic equipment (EEE) imported annually in Nigeria may contain as much as 18,000 tonnes of plastic which may possibly contain BFRs. Unfortunately, a greater percentage (up to 75 %) of these imported devices are unusable and are mostly discarded into dumpsite or even burnt openly before any form of reuse takes place (Nnorom and Osibanjo, 2008a). These sources of brominated flame retardants are typically responsible for the increased levels of these contaminants in various environmental compartments, including humans.

2.2.4 PBDEs in the environment

Like most legacy POPs, PBDEs are almost ubiquitous in nature. Since the discovery of their presence in Viskan River in Sweden in the early 1980's, PBDEs levels have continued to increase rapidly in the environment. There is increasing scientific evidence confirming their presence in the world's remotest regions, particularly in the Arctic and the Antarctica (de Wit *et al.*, 2006; Hale *et al.*, 2008) thus, confirming their widespread distribution globally. This, of course, could be due to human intrusions, long-range atmospheric transport of volatile congeners as well as through biota migration. Presently, PBDEs have been detected in several environmental matrices, particularly in soils, sediment, sewage sludge, air particulates, river water and other aqueous samples.

2.2.4.1 PBDEs in sediment

Monitoring the levels of environmental pollutants in sediment samples has provided useful information about the extent of pollution in aquatic environment. Due to the hydrophobic nature of most organic pollutants, particularly the BFRs, there is high tendency for them to bind to suspended particles in the water column where they are further transferred to the bottom sediment (Gevao *et al.*, 2006b). The continuous accumulation of sediment layers in water bodies over time could be explored to assess the long-term pollution status of such water bodies. In this case, the use of special sampling devices such as corers and augers, which are capable of stratifying the collected sediment samples into different layers, is necessary.

The analysis of PBDEs concentrations in sediment samples collected from freshwater as well as marine water systems has been extensively carried out globally (Yun *et al.*, 2008; Ramu *et al.*, 2010; Vane *et al.*, 2010; Pan *et al.*, 2011; Zhao *et al.*, 2011). Binelli *et al.* (2007) investigated the PBDE burden on sediment

cores collected from different sampling sites in Subardan wetland in northeastern part of Bay of Bengal, India. The overall concentration of the 12 PBDE congeners found in different sediment layers ranged from 0.08 to 29.03 ng/g. The results obtained showed that there was non-uniformity in the temporal trend observed in PBDEs levels. This was attributed to the hydrological characteristics of the wetland and non-homologous inputs from point sources such as untreated municipal and local industrial wastewater, and electronic wastes from dumpsites.

In another study conducted on the Korean coast, the total PBDEs concentrations including BDE 209 found in surface sediment ranged from 0.45 to 494 ng/g dry weight. The diverse industrial activities and intense ship traffic in this region were identified as the possible sources of PBDEs in the coastal sediment (Moon *et al.*, 2007). The assessment of PBDEs levels in both surface sediment and sediment cores collected from the lower reach of Dongjiang River depicted an interesting scenario. In the study, the sum concentration of tri- to heptaBDE representing the technical pentaBDE and octaBDE formulations ranged from 0.7 to 7.7 ng/g dry weight while the sum of congeners (BDE 206, 207, 208 and 209) representing the decaBDE formulation ranged from 30 to 5,700 ng/g dry weight (Zhang *et al.*, 2009). Although, the authors presumed that the observed levels of the decaBDE formulation were decreasing due to the increasing demand for other alternatives, it did reflect the heavy consumption pattern of decaBDE formulation in the region.

In most of the studies conducted, the predominance of BDE 209 congener was often observed; although, certain lower brominated congeners (such as BDE 47 and 99) also predominate in sediment samples in some cases. The dominance of any congener, therefore, might indicate the dependence on certain technical formulations as depicted by the dominant congeners in sediment from such regions. A declining trend in the levels of PBDEs in sediment samples of rivers, estuaries and oceans across Europe is expected with time. This is due to the recent restrictions on the use of penta- and octaBDE technical formulations in this region. Generally, the levels of PBDEs found in sediment samples in Europe, Asia and other regions of the world are comparatively lower than those reported in most North American studies (de Wit, 2002; Binelli *et al.*, 2007; Yun *et al.*, 2008). This trend is a reflection of the consumption rate of these chemicals in these regions.

2.2.4.2 PBDEs in aqueous samples

Until recently, data from literatures on PBDEs levels in aqueous matrices were generally scarce. It is assumed that the hydrophobic characteristics of these contaminants could have been responsible for this lack of data in the time past. Before the environmental fate and transport processes of the contaminants were fully understood, scientists generally believed that their physicochemical properties might not favour

their partitioning in the aqueous media. As such, they were often discouraged from assessing their levels in aqueous environmental matrices.

Today, PBDEs have been determined in several aqueous samples, including coastal water, river water, WWTP effluents, landfill leachate, storm water amongst others (Oliaei *et al.*, 2002; Osako *et al.*, 2004; Song *et al.*, 2006; Odusanya *et al.*, 2009). PBDEs, like most organic pollutants, do bind to suspended materials in aqueous matrices. Hence, suspended materials play essential roles in influencing their ultimate fate, transport and distribution in these matrices. More so, suspended materials could influence the extent of their biogeochemical transformation and re-distribution in the aquatic environment.

2.2.4.3 Soil and atmospheric burdens of PBDEs

The atmosphere is an important reservoir of diverse pollutants, especially semi-volatile organics (SOCs). As a class of SOCs, PBDEs may be released into the atmosphere through several activities related to their handling, recycling and ultimate disposal (Wang *et al.*, 2009). The open burning of plastics containing BFRs, for instance, could release considerable amount of PBDEs into the atmosphere (de Wit, 2002). Since these chemicals vary considerably in their physicochemical properties, certain congeners of PBDEs when released may undergo long-range atmospheric transport (LRAT). Usually, the impacts of this phenomenon are huge and cut across geographical boundaries of local sources. Apart from contributing to the widespread occurrence of these contaminants, it also facilitates their mass transfer to regions far away from emission sources (Dickhut *et al.*, 2005). Hence, the need to regulate persistent organic pollutants that have the potential to undergo LRAT cannot be over-emphasised.

Recent studies which confirmed the presence of PBDEs in remote regions of the Arctic and the Antarctica further indicated the ubiquity of PBDEs in the environment (Borghesi *et al.*, 2008; Hale *et al.*, 2008; Sørmo *et al.*, 2009; Yogui and Sericano, 2009; Möller *et al.*, 2011). Continuous release of these contaminants through open burning, emission during manufacturing and recycling activities could significantly contribute to soil PBDEs burden. Upon release into the atmosphere, several processes could facilitate their removal from the gaseous media. Raff and Hites (2007) highlighted a number of these processes, which include wet and dry deposition, gaseous adsorption, photolytic degradation and reactions with hydroxyl radicals. Besides the possible emission from industrial and e-waste recycling activities to surrounding soils, atmospheric deposition represents an important pathway of soil contamination in locations far from emission sources.

PBDEs in soils usually congregate in the uppermost layer (Yang *et al.*, 2010). The mobility of these contaminants in the environment, therefore, would depend on their degree of volatility, water solubility

and the extent of adsorption onto solid samples (Watanabe and Sakai, 2003). Several factors, including soil texture, composition, hydro-geological processes as well as interactions with soil microorganisms could significantly influence the fate and transport of PBDEs in soil. Therefore, an assessment of the vertical profile of these contaminants in soil where all these inter-related processes are believed to be taking place is essential to understand their overall fate in soil. Yang *et al.* (2010) speculated that the determination of relatively high levels of BDE 209 at soil depth 15 – 20 cm might be due to possible transport of suspended particles and dissolved organic matter in soil eluted by rainwater. Their findings further indicated the significant roles that certain soil organic matter components play in the distribution of PBDEs in soil. PBDEs are highly persistent organic chemicals and could accumulate in soils receiving high dose of PBDEs-laden materials (Sellström *et al.*, 2005; Eljarrat *et al.*, 2008). Increasing level of PBDEs in soil makes these contaminants readily available to soil microorganisms, thus, presenting an additional exposure pathway into the terrestrial food web.

2.2.4.4 PBDEs in sewage sludge

The monitoring of pollutants in sewage sludge to assess the extent of chemical pollution of the environment has been widely explored. Sewage sludge is an important sink for persistent organic pollutants, its analysis for these pollutants has been providing useful and valuable information about chemical pollution, and the risk associated with the re-use of sewage sludge as biosolids for land application (Clarke *et al.*, 2008). The release of BFRs, especially PBDEs into wastewater may occur during their synthesis, during incorporation into polymers or related finished products, during their use and disposal or recycling of these products, by cycling in the environment or a combination of any of these processes (Clarke *et al.*, 2008).

The concentration of pollutants in wastewater is generally influenced by factors such as the lifestyle of the inhabitants in the area, the population and socio-economic status of the inhabitants in the area, the type of businesses, factories and offices located in the catchment area connected to the wastewater treatment plant (Gevao *et al.*, 2008). WWTPs are designed to effectively remove pollutants from the aqueous waste streams. It is therefore necessary that the various mechanisms of pollutant removal such as sorption, hydrolysis, photolysis, photo-oxidation, volatilization, electrochemical-oxidation, amongst others are fully understood. Four of these mechanisms are particularly relevant to pollutant removal by WWTPs; these include sorption, biodegradation, volatilization and air stripping.

Sorption is an important physical process, which occurs when hydrophobic contaminants bind to suspended solids in aqueous medium. This tendency to adsorb to sewage sludge is often related to the octanol-water partitioning co-efficient (K_{OW}) of the compound. While K_{OW} simulates the uptake of a

pollutant by lipids, and thus relates to its bioaccumulation, K_{OC} (octanol-organic carbon partition coefficient) indicates the capacity of a compound to adsorb to organic particles (Seriki *et al.*, 2008). This also represents the potential of the compound to bind strongly to organic matter. The fraction that is bound to particulate matter is not directly available, under equilibrium conditions, for mass transfer across the water-air interface (Byrns, 2001). Hence, this mechanism essentially contributes to the removal of PBDEs from wastewater during treatment processes. More than 90% removal of certain congener of PBDEs has been reported in a typical WWTP (Ricklund *et al.*, 2009). According to Rogers (1996), the significance of volatilization losses of specific organic compounds during wastewater treatment can be evaluated using the following empirically defined categories based on Henry's Law constant (K_h) and K_{OW} .

- $K_h > 10^{-4}$ and $K_h/K_{OW} > 10^{-9}$ -----High volatilization potential
- $K_h < 10^{-4}$ and $K_h/K_{OW} < 10^{-9}$ -----Low volatilization potential

In WWTPs, biodegradation of organic contaminants occurs under both aerobic and anaerobic conditions. However, the complete mineralization of these contaminants rarely occurs, hence the term 'biotransformation' gives a better definition of the processes that take place in treatment plants (Byrns, 2001). Biotransformation therefore refers to the potential changes in the composition and molecular structure of chemical pollutants caused by living organisms, precisely microorganisms.

Air forced into wastewater during the activated sludge treatment process facilitates the removal of volatile organic compounds (VOCs). During this process, known as air stripping, volatile organic pollutants are removed from wastewater and transferred into the air. The percentage of compounds removed through stripping, thus depend on the airflow rate in the aeration basin and on the type of aeration equipment employed (Seriki *et al.*, 2008). Figure 2.1 summarises the important mechanisms essential for pollutant removal during wastewater treatment.

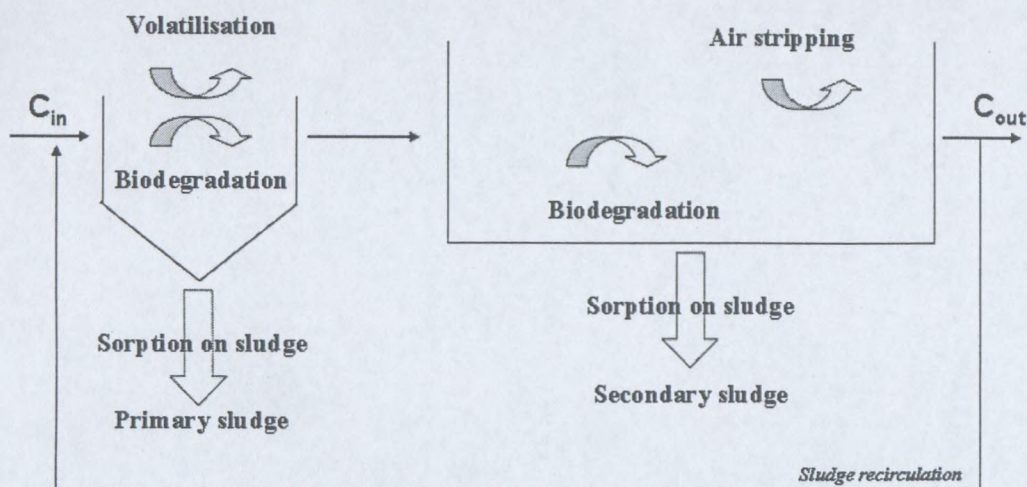


Figure 2.1: Major pollutant removal pathways in conventional activated sludge WWTP

(adapted from Seriki *et al.*, 2008)

2.3 Possible routes of PBDE exposure to humans

Human body burden of PBDEs could result from either one or a combination of the following identified exposure pathways: dietary intake, inhalation and ingestion of airborne particulates and dust, and dermal absorption. Since PBDEs, like other organic pollutants, are lipophilic, the tendency for them to accumulate in the fat-rich regions of human bodies is relatively high. It is, therefore, necessary to evaluate the possible pathways through which these contaminants may enter the human system.

2.3.1 Dietary intake

A human diet with high lipid content especially from food items such as fish, meat, chicken, vegetable oil, dairy products to mention but few, are important sources of BFRs to humans. A number of studies have found PBDEs in various foodstuffs across the world. However, the relative contribution of human diet to the overall body burden has been evaluated recently (Meng *et al.*, 2007; Domingo *et al.*, 2008; Spliethoff *et al.*, 2008; Staskal *et al.*, 2008; Fraser *et al.*, 2009; Roosens *et al.*, 2009). Fraser *et al.* (2009) found that the intake of contaminated poultry and meat contributes significantly to PBDE body burden in the United States. In this study, serum Σ PBDEs were 23% lower in vegetarians than in omnivores. An increase of 19% among heavy poultry consumers compared with light consumers (48.3 versus 40.6 ng/g lipid weight), and 18% higher among heavy red meat consumers compared with light consumers (47.0 versus 39.8 ng/g lipid weight) was observed.

In a recent review publication, the relative contribution of human diet to overall PBDE body burden was found to follow this order: fish > meat > dairy $\geq$ vegetables (Frederiksen *et al.*, 2009). Similarly, PBDE levels in different foodstuffs in Catalonia (Spain) were evaluated. The observed levels follow this pattern: fish and shellfish > oils and fats > bakery products > eggs > dairy products > meat and meat products > tubers > cereals > pulses > vegetables > fruits. The Σ PBDEs (tetra- to octa-BDEs) in these foodstuffs were 563.9, 359.3, 98.8, 94.8, 67.1, 49.9, 46.9, 37.3, 30.0, 23.9, and 19.0 ng/Kg fresh weight, respectively (Domingo *et al.*, 2008). Other studies have also reported relatively high concentration of BFRs, especially PBDEs in fish than in other classes of food (Kiviranta *et al.*, 2004; Gomara *et al.*, 2006; Voorspoels *et al.*, 2007). These evaluations suggest that fish consumption may significantly contribute to BFR body burden in humans.

Meng *et al.* (2007) examined human exposure to PBDE associated with fish consumption and inhalation in China. In this study, PBDE daily intake via fish consumption, inhalation, as well as human milk for different age groups was estimated. The median intake of Σ_7 PBDEs (sum of 7 congeners) via human milk was 48.2 ng/day for nursing infants (0–1 year old) with a range of 23.4 – 99.1 ng/day. The median intake of Σ_{11} PBDEs (sum of 11 congeners) via fish consumption was 1.7 – 12.9 ng/day with a range of 0.59 – 56.3 ng/g, for other age groups. The median estimated daily intake (EDI) for exposure via inhalation was between 2.7–9.2 ng/day, ranging from 0.72 to 108 ng/day for all age groups. Fish, being the major contributor to PBDE dietary intake, was found to contribute much less than exposure via inhalation.

In a survey of PBDE intake through consumption of edible marine species, an estimated 20.8 ng/day was found for all fish species investigated. Of this, tuna contributed the most having 5.7 ng/day, followed by salmon (3.6 ng/day). The lowest PBDE intakes were found in clam and swordfish with 0.02 and 0.06 ng/day, respectively (Domingo *et al.*, 2006). In the USA, findings from dietary studies aimed at identifying possible contributions of fish consumption to PBDE body burdens have not been consistent. Some have shown that consumption of fish, in particular sport-fish does not contribute strongly to PBDE exposure (Anderson *et al.*, 2008). Others have indicated that fish consumption can contribute measurably to PBDE body burden (Spliethoff *et al.*, 2008; Staskal *et al.*, 2008). Generally, the relative contribution of fish consumption to PBDE dietary intake in the US is less than those of European and Asian countries. While fish consumption contributes significantly to body burden in the Europe, poultry and meat consumption constitute major exposure pathway to humans in the USA.

Wu *et al.* (2007) evaluated possible correlations between human exposure and PBDE body burden in various exposure media (house dust and dietary intake) and levels in human breast milk. A statistically significant positive association between PBDE concentrations in human breast milk and house dust ($r =$

0.76, $p = 0.003$, not including BDE-209) was found. Similar positive association was also found between PBDE concentration in breast milk and some dietary habits, particularly the consumption of dairy products and meat. The association with fish though positive was not significant. Since this observation was not consistent with results obtained from Europe and Japan, the authors suggested that the lesser importance of fish in the typical American diet might be responsible for the observed difference.

Gomara *et al.* (2006) observed in their survey of PBDEs in Spanish commercial foodstuff the highest concentration of PBDEs in fish samples (median of 189 pg/g, range of 24 – 880 pg/g fresh weight). A similar study in Finland also found fish to contribute the most to the PBDE intake (Kiviranta *et al.*, 2004). In general, PBDE dietary intake via fish consumption may become highly significant in geographical locations where more fish are being consumed.

Exposure via other food sources, such as meat, chicken, dairy product as well as vegetables, are also very essential to evaluating human exposure to PBDE through diet. For instance, in North America where fish consumption is less important in their typical diet, meat and fats become the main contributors to the total dietary exposure. This trend was observed by Schecter and co-workers (2006) who found that meat consumption especially poultry and processed meat contributed 60 – 70% of the total PBDE exposure through diet for Americans while only 10 – 20% was obtained for fish (Schecter *et al.*, 2006). In another study where PBDE contamination in poultry and possible human exposure via consumption of poultry in an e-waste recycling plant were evaluated, Luo *et al.* (2009) observed alarming PBDE levels. PBDE concentrations in both muscle and liver of chickens (5.7 to 4381 and from 1.5 to 7897 ng/g lw, respectively) were much higher compared to those found in duck (2.4 to 51 and from 1.9 to 134 ng/g lw). The difference observed in these birds was attributed to their different living habitat and feeding habits. The intake of PBDE through the consumption of poultry could be highly significant especially in countries where poultry consumption is relatively high.

Plant uptake of BFRs, especially PBDEs, will have serious implications for human exposure through edible plant consumption. Since these contaminants exhibit low solubility in water, it is expected that their uptake by plants will be less significant. However, studies have shown that PBDEs are present in plants especially in some edible vegetables, fruits, tubers, pulses and cereals (Ohta *et al.*, 2002; Bocio *et al.*, 2003; Zhao *et al.*, 2009b). Although, the pathway through which these contaminants migrate into plants is still not clearly understood; it could be inferred that atmospheric deposition or uptake via the root system are likely possibilities. Ohta *et al.* (2002) observed the highest concentration (134 pg/g fresh weight) of PBDE in spinach amongst the three kinds of edible plants (spinach, carrot and potato) they investigated. This level was significantly higher than those obtained in the same study for pork, beef and chicken with 63.6, 16.2 and 6.25 pg/g fresh weight, respectively. The authors speculated that the uptake of PBDE from

0.76, $p = 0.003$, not including BDE-209) was found. Similar positive association was also found between PBDE concentration in breast milk and some dietary habits, particularly the consumption of dairy products and meat. The association with fish though positive was not significant. Since this observation was not consistent with results obtained from Europe and Japan, the authors suggested that the lesser importance of fish in the typical American diet might be responsible for the observed difference.

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the surrounding air by leafy vegetables like spinach, especially in the vicinity of possible local sources, may be responsible for the trend observed. This study, therefore, affirms the importance of taking into consideration the contribution from edible plants when estimating the total dietary exposure index for BFRs.

The use of dietary intake data to estimate human body burden of BFRs has been explored. Lorber (2008) employed a simple pharmacokinetic (PK) model to convert various dietary intake data obtained for Americans in order to predict BFR body burden arising from different exposure pathways. This was done by comparing the predicted body burden with representative profiles of PBDEs in blood and milk. He found the adult intake dose of total PBDEs to be 7.7 ng/Kg body weight/day, and children's estimated intakes were higher at 49.3 ng/Kg body weight/day for ages 1 – 5, 14.4 ng/Kg/day for 6 – 11, and 9.1 ng/Kg/day for 12 – 19. The predicted adult body burden of total PBDEs of 33.8 ng/Kg lipid weight, compared to the representative measurements in blood and milk at 64.0 and 93.7 ng/g lipid weight, respectively was found. The apparent under-prediction in total concentration was attributed to an under-prediction of a key congener, BDE-47. Similar studies have reported calculated intake of PBDEs of 81.9 – 97.3 ng/day in Spain and 44 ng/day in Finland (Bocio *et al.*, 2003; Kiviranta *et al.*, 2004).

2.3.2 Exposure via dust

Besides dietary exposure to PBDEs through food consumption, exposure via inhalation and ingestion of contaminated dust have been reported to substantially contribute to the overall PBDEs levels in humans (Jones-Otazo *et al.*, 2005; Stapleton *et al.*, 2005; Allen *et al.*, 2007). This exposure pathway has also been implicated as a major contributor to higher PBDE levels among children between the ages of 2 – 5 years (Toms *et al.*, 2009). This observation is expected since children within this age group usually engage in activities that may increase their vulnerability to these contaminants. These activities include: hand-mouthing, eating dust-laden food items, spending more time playing on the floor, amongst others, which can significantly contribute to higher contaminant levels in their body system. In addition to this, the increasing levels of BFRs especially PBDEs found in human milk could be responsible for the trend observed among children who must have previously been breast-fed. The authors suggested that the observed trend might be due to lower tendency by these children to eliminate these contaminants from their system.

Human exposure to BFRs via inhalation and ingestion of dust is not limited to young children; it is a phenomenon that cuts across all age groups. Recent studies have shown that every category of people may be exposed to these contaminants via dust and airborne particulates especially within microenvironments such as cars, trains, aeroplanes, amongst others (Mandalakis *et al.*, 2008; Lagalante *et al.*, 2009).

However, the degree of exposure will be highly dependent on duration as well as the prevailing environmental conditions within these microenvironments.

Several studies have been conducted to monitor BFR levels in both indoor and outdoor environments. While most outdoor studies monitor contaminant levels in air particulates and dust around recycling plants and waste disposal facilities (Julander *et al.*, 2005; Mandalakis *et al.*, 2009), indoor studies are mostly designed to identify sources of these contaminants in dust and air particulates with a view to establish a possible association between observable effects and BFR levels in human tissues (Karlsson *et al.*, 2007; Meeker *et al.*, 2009; Toms *et al.*, 2009; Zhao *et al.*, 2009a).

Indoor environments, including living rooms, workplaces, cars, amongst others are believed to be important sources of contaminant exposure to humans since more than 80% of the day is spent indoors. Household and commercial products, which are reservoirs of these contaminants in our homes, offices, schools, cars, amongst others have made the indoor investigation of these contaminants feasible. Consequently, reported indoor studies monitoring BFR levels in house dust have increased significantly in recent times (Jones-Otazo *et al.*, 2005; Stapleton *et al.*, 2005; Allen *et al.*, 2007; Tan *et al.*, 2007; Sjodin *et al.*, 2008; Meeker *et al.*, 2009; Takigami *et al.*, 2009a; 2009b).

The process through which the above contaminants is released from the treated product and subsequently migrate into dust particle is still not clearly understood. Takigami *et al.* (2008) suggested that the higher BFR levels observed in their study must have been transferred from TV components into dust. In this study, TV set components (parts of housing front cabinets, rear cabinets and circuit boards) as well as dust samples collected from inside TV sets were analysed for PBDEs, TBBPA, HBCD and PBDD/Fs. The respective Σ PBDE and Σ PBDF concentrations in dust samples were 67 – 500 $\mu\text{g/g}$ (mean 300 $\mu\text{g/g}$) and 180 – 650 ng/g (mean, 410 ng/g), while 48,000 $\mu\text{g/g}$, 19,000 $\mu\text{g/g}$ and 9,600 ng/g as mean values were reported for PBDEs, TBBPA and PBDFs, respectively, in the TV components. The highest BFR levels were found in the rear cabinet and the comparison of congener patterns of BFRs in the dust identified the components as the source of these BFRs.

PBDEs in both dust and human diet in some studies showed that exposure to PBDEs via dust could be particularly significant. Lorber (2008) noted that this comparison will be misleading since most European studies on dietary intake for PBDEs do not include BDE 209, a major congener found in most dust samples analysed. Secondly, the upper limit of the daily dust intake value used for the estimation of PBDE intake for adults in most studies was assumed for people who are exposed to high loads of dust. Therefore, the use of intake estimates to compare the relative contribution of both dust and human diet to the overall BFR body burden is still very limiting and thus require further investigation.

2.3.3 Exposure via human milk

Human breast milk, like other environmental matrices, acts as a storehouse of persistent organic pollutants (POPs), including BFRs. The presence of contaminants in human milk reflects the environmental conditions to which a person was exposed in the past. Since young children are the most vulnerable to harmful contaminants reaching the human systems from this pathway, the need for effective monitoring of organic pollutants especially brominated flame retardants in human milk samples has been emphasised (Hooper and McDonald, 2000).

Breastfeeding, though, offers great advantages of improved healthy conditions to young infants, has been a major route of harmful chemicals to these children. Carrizo and Grimalt (2007) observed higher levels of PBDE in the sera of 4 year old children fed with maternal milk than those being fed with formula. The observed increases of average body burden of total PBDEs between birth and the first 4 years of growth were 65 and 10 ng for breastfed and infant formula fed children, respectively. Concerns over the increasing levels of brominated flame retardants in various human tissues (blood serum, adipose tissue, hair, milk, amongst others) have been expressed (WHO, 1994). This has led to intense efforts targeted at evaluating BFRs levels in human milk samples worldwide.

Schecter *et al.* (2003) analysed 13 congeners of PBDEs in 47 human milk samples collected from 24 donors from Austin, Texas and 23 donors from Dallas, Texas, USA between August and December, 2002. The mean total BDE (including BDE 209) was found to be 73.9 ng/g lipid weight (median = 34; range: 6.2 to 419 ng/g lipid weight). While major congeners of both penta- and octa-BDE technical formulations were detected in nearly all the samples, BDE 209 was only detected in approximately 15 % of the samples investigated. An assessment of potential sources and pathways of human exposure to PBDE was recently conducted for different age groups in the United States (Johnson-Restrepo and Kannan, 2009). The total daily exposure dose (DED) was found highest for breastfed infants (< 1 year) (86.4 ng/kg body weight/day), contributed primarily from the consumption of breast milk. The average DED of PBDE for toddlers (1 – 5 years), children (6 – 11 years), teenagers (12 -19 years) and adults (> 20 years) were 13.3, 5.3, 3.5 and 2.9 ng/Kg body weight/day, respectively. While breast milk was identified as the main source of PBDE to the infants, ingestion and dermal absorption of house dust were implicated as the major pathways of PBDE exposure to other age groups.

Akutsu *et al.* (2003) conducted a time-trend study of PBDEs in Japanese mother's milk from 1973 to 2000. Pooled milk samples collected from donors living in Osaka were analysed for 16 PBDE congeners. These PBDEs were also measured in 13 individual samples collected from donors living in Kanagawa and Okayama. The total concentration of all PBDEs (excluding BDE 209) in the pooled samples were found to

increase between 1973 and 1988 while those observed for the individual samples were found to be low (0.56 – 3.97 ng/g lipid weight). In a pilot study where a total of 103 breast milk samples obtained from mothers living in Olomouc region, Czech Republic, were analysed for 10 PBDEs in 2003, BDE 47 was found to be the most dominant congener with concentration ranging from 0.2 to 2 ng/g lipid weight (Kazda *et al.*, 2004). Bi *et al.* (2006) measured levels of seven PBDE congeners in 27 breast milk samples collected from donors in South China. The concentrations of the total PBDEs (excluding BDE 209) ranged from 1.5 to 17 ng/g lipid weight. BDE 47 and 153 were the dominant congeners in this study accounting for 60 % of the total PBDEs.

Pooled breast milk samples totalling 157 collected in 2002 and 2003 in 12 regions of Australia were analysed for 18 PBDE congeners. The mean Σ PBDE concentration was found to be 11.1 ng/g lipid weight (range, 6.1 – 18.7 ng/g lipid weight). The data from this study shows that there is no regional difference in PBDE levels measured (Toms *et al.*, 2007). Sudaryanto *et al.* (2008) investigated the geographical distribution of PBDEs in milk samples collected from Indonesian mothers. A total of 30 samples were monitored for 12 congeners of PBDEs including BDE 209. The total concentration of Σ PBDE ranged from 0.49 to 13 ng/g lipid weight. Breast milk samples collected from primiparous women in Tianjin, China in 2006 were analysed for PBDEs. The median total PBDE concentration was 2.5 ng/g lipid weight, ranging from 1.7 to 4.5 ng/g lipid weight. This study also established a significant positive relationship between mother's PBDE concentration and the time she used electronic appliance (h/day), thus implicating electronics as potential source of PBDEs to people (Zhu *et al.*, 2009).

In a related study, a total of 33 human milk samples collected in 2004 from primipara and multipara mothers residing in Payatas (Philippines) near a waste dump site and Malate (Philippines) as a reference site were analysed for eight organohalogen compounds, including PBDEs and HBCDs. The overall mean concentrations obtained for PBDE (7.5 ng/g lipid weight) were higher than those reported in most Asian studies. The mean concentrations obtained for HBCD was 0.86 ng/g lipid weight (Malarvannan *et al.*, 2009). Raab *et al.* (2008) investigated PBDE (19 congeners) together with other potentially harmful persistent pollutants levels in mother's milk from Bavaria, Germany. A total of eighty-five breast milk samples collected between May 2005 and August 2005 were analysed for these contaminants. The sum PBDE (5 congeners) ranged between 0.57 and 6.54 ng/g lipid weight. Twelve PBDE congeners were found below the limit of detection, BDE 153 and BDE 47 were the most predominant congeners accounting for about 66% of the total PBDE. The background levels of PBDE monitored were found to be significantly lower than those reported in other European countries.

Recent studies are now focussing on identifying possible relationship between PBDE levels in human milk and different exposure factors. Thomsen *et al.* (2010) conducted a large scale study in line with this objective in Norway. In this study, a total of 393 breast milk samples were analysed for PBDE and HBCD. The median concentrations of the sum of the seven most prominent PBDEs (BDE 28, 47, 99, 100, 153, 154 and 183), BDE 209 and HBCD were 2.1, 0.32 and 0.86 ng/g lipid, respectively. Of all the exposure factors investigated, maternal age, parity, education, having a cohabitant employed as electrician, and ventilation were factors that significantly show some degrees of association with some of the BFRs. Statistical analysis revealed that these factors only explained a small amount of the variability ($R^2 = 0.04 - 0.16$). Interestingly, the dietary intake of mothers investigated did not influence the breast milk PBDE and HBCD levels.

Wang *et al.* (2008) examined the levels of PBDE in breast milk samples ($n = 20$) of Taiwanese mothers consuming different varieties of seafood. The authors were attempting to establish possible influence of dietary habits as well as certain demographic factors on PBDE levels in participants' breast milk. The study revealed that women who ate more fish and meat did not show significantly higher PBDE levels than those who ate less. Surprisingly, a significant difference in PBDE levels was demonstrated between the higher (2.15 ng/g lipid) and lower (3.98 ng/g lipid) shellfish consuming subjects ($p = 0.002$) after an adjustment for the confounders. These studies further affirmed that sources other than diet might be responsible for the variability observed in breast milk BFR concentrations.

Generally, the levels of BFRs, especially PBDEs, reported in North America were higher than those reported elsewhere. These levels have doubled every 4 – 6 years (Hites, 2004). More so, the lower brominated PBDE congeners such as BDE 47 were found to be the most dominant congener in most of the studies. The implication of this to young children is the tendency for them to accumulate more of these lower brominated PBDE congeners which are found to be more toxic than the highly brominated ones (Darnerud *et al.*, 2001).

2.3.4 Occupational exposure to BFRs

Most of the studies conducted to evaluate human exposure to BFRs have focused mainly on those working at recycling plants, e-waste disassembly sites and waste treatment facilities (Julander *et al.*, 2005; Lee *et al.*, 2007; Zhao *et al.*, 2008; Zhao *et al.*, 2009a). Secondly, it is generally believed that highly brominated PBDE congeners (especially BDE 209) are less bioaccumulative. This is due to their large molecular size and high octanol-water partition coefficient (Hites, 2004). Zhao *et al.* (2010) have demonstrated that high brominated PBDEs as well as low brominated PBDE congeners are bioavailable in humans.

Julander *et al.* (2005) investigated the distribution of BFRs in different dust fractions in air from an electronics recycling facility. The dust fractions (inhalable, total and respirable) were dominated by BDE 209 with concentrations ranging from 157.6 – 208.6, 13.9 – 16.7 and 2.8 – 3.3 ngm⁻³, respectively. Lee *et al.* (2007) found the mean PBDE (19.24 ng/g lipid) in blood samples of incinerator workers were slightly higher than those obtained for residents (15.22 ng/g lipid) and controls (17.74 ng/g lipid). Similarly, Thuresson *et al.* (2005) observed increased PBDE levels in serum of workers manufacturing or handling flame-retarded rubber relative to a referent group, abattoir workers with no occupational exposure to PBDE. The median concentration of BDE 209 among rubber workers was 37 pmol/g lipid weight (35 ng/g l.w). The median found among the referents was 2.5 (range 0.92 – 9.7) pmol/g l.w (median 2.4 ng/g l.w). The results confirm bioavailability of BDE 209 in humans and also indicate a potential for *in vivo* formation of lower BDEs in workers investigated.

Similarly, higher levels of BFRs were found in hair samples of people living around an e-waste disassembly site than those observed in hair of people from the control sites. The highest levels of PBBs (57.77 ng/g dw) and PBDEs (29.64 ng/g dw) were two times more than those observed in hair for both PBBs and PBDEs from the control site (Zhao *et al.*, 2008). While exposure to BFRs via dust and airborne particulates as well as dietary intake could be important pathways through which these contaminants enter the system of these workers; the possibility of dermal absorption could not be ruled out. Several animal studies have demonstrated this possibility particularly with studies involving PBDEs (WHO, 1994).

Stapleton *et al.* (2008) observed higher PBDE serum levels in foam recyclers and carpet installers relative to that of the general US population. Total PBDE levels were found to be significantly higher ($p = 0.05$) in the individuals recycling foam and installing carpet ($n = 15$) relative to the control group ($n = 5$). Median Σ PBDE levels in the foam recyclers, carpet layers and control group were 160, 178 and 19 ng/g lipid, respectively. BDE 47, 99 100 and 153 contributed 90 % of the Σ PBDE concentration in serum. There was no apparent difference in congener patterns among the different groups. Concentrations measured in occupationally exposed people in this study were an order of magnitude higher than those measured in the recently published National Health and Nutrition Examination Survey (NHANES) data.

There is limited information in the literature regarding dermal absorption studies aimed at evaluating human exposure to these contaminants. Those reported are often limited to laboratory animals (WHO, 1994). However, the detection of PBDEs in clothes dryer lint in some German and American homes could possibly increase the exposure pathways to occupationally exposed people, particularly professional laundry workers and housekeepers (Schechter *et al.*, 2009). In general, the degree to which people are exposed to these contaminants depends on the safety regulations being implemented in different workplaces across the globe. Also, improvement in the workplace environment can considerably reduce

the magnitude of exposure (Thuresson *et al.*, 2006). However, periodic evaluation of existing safety regulations and proper enforcement of these regulations must be implemented across the board to ensure that human exposure to these harmful contaminants is abated.

2.4 Toxicology

Despite the growing concerns over the increasing levels of PBDEs in the environment, only limited data is available about the toxicity of these chemicals. Generally, most of the toxicological studies conducted were performed using the commercial formulations of PBDEs. Presently, there is still insufficient information about the congener specific effects of PBDEs (Naert, 2007; Odusanya, 2008).

2.4.1 Acute toxicity and subacute/subchronic toxicity

Laboratory studies on test animals showed that the acute toxicity of commercial PBDEs is generally low. Lethal doses (LD₅₀) administered orally, dermally or by inhalation were generally high and ranged between 0.5 and 28 g/Kg body weight. Oral administration studies revealed that pentaBDE formulation was more toxic than octa- and decaBDE formulations. Subacute or subchronic oral toxicity studies in rats showed that toxic effects were more pronounced with penta- and octaBDE formulations than with decaBDE. Specific targets of these effects are the kidney, liver and thyroid gland. These are evidenced by the enlargement of these organs with or without some degenerative changes (WHO, 1997; Darnerud *et al.*, 2001).

2.4.2 Endocrine disruption

Endocrine disruptors are exogenous substances that interfere with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for development, behaviour, fertility and maintenance of homeostasis (Kavlock *et al.*, 1996). These categories of substances are sometimes referred to as hormonally active agents, endocrine disrupting chemicals or endocrine disrupting compounds (EDCs). Considering some of the physicochemical as well as toxicological properties of PBDEs as outlined in several studies, they fit well as emerging EDCs.

Structurally, PBDEs are closely related to the thyroid hormones, 3, 3', 5 – triiodothyronine (T3) and 3, 3', 5, 5' – tetraiodothyronine (T4). Thyroid hormones, like metabolites of PBDEs, are hydroxylated, halogenated-diphenylethers (Fig. 2.2). Methoxylated metabolites of PBDEs have also been found, however, data on their toxicity are still scarce (McDonald, 2002). On the other hand, hydroxylated metabolites are known to demonstrate high tendency to bind strongly to the thyroid hormone transport

protein (i.e., transthyretin) (Meerts *et al.*, 2000) and their common receptors – TR- α 1 and TR- β (Marsh *et al.*, 1998). Their ability to mimic important thyroid hormones has led to several health effects, including endocrine disruption, reproductive and developmental defects, impaired learning and memory functions, amongst others.

All the commercial formulations of PBDE affect the thyroid hormone homeostasis to a certain extent. Although the effects exerted by the penta-BDE were most pronounced in the exposed subjects, others showed less critical effects on the thyroid hormone system. Several studies have investigated these effects employing different test animals. In one of such studies, the effects of penta-BDE and its pure tetra- and penta- congeners (the latter at doses of 10 – 18 mg/Kg body wt./day for 2 weeks) produced effects on serum thyroxine levels in rats and mice (WHO, 1994; Zhou *et al.*, 2001; Hallgren and Darnerud, 2002). Similarly, the effects of penta-BDE on the thyroid system of rodents were investigated. Observed defects following oral administration of 18 mg/Kg for 14 days include decreased T4 in rats and mice. In addition, hyperplasia was observed in rodents exposed via diet for 90 days (10 mg/Kg) and decreased T4 among mice exposed for 8 days after a single oral administration of 0.8 mg/Kg (Fowles *et al.*, 1994).

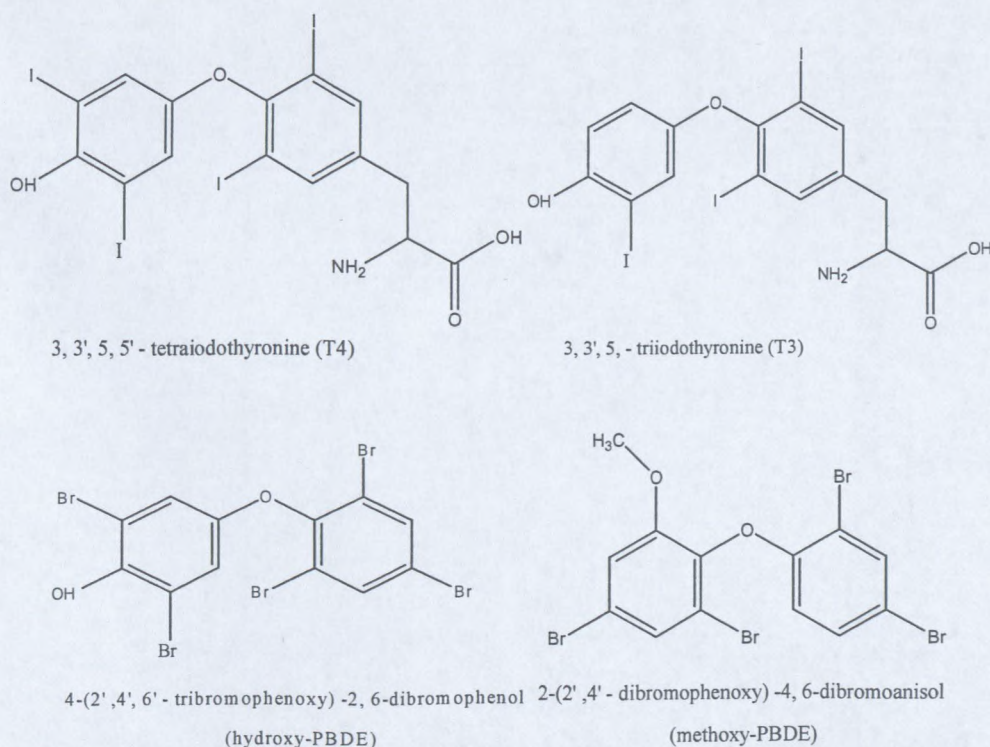


Figure 2.2: Structural similarities of the thyroxine hormones and PBDEs metabolites

Majority of the studies conducted so far employed commercial formulations of PBDEs; congener-specific toxicity data especially for the highly brominated congeners are still scanty. Hallgren and Darnerud (1998)

showed that 2, 2', 4, 4' – tetra-BDE which is a major congener commonly found in most human and animal tissue samples, reduced the thyroid hormone levels among female rats following oral administration of 18 mg/Kg for 14 days. At relatively low doses (from 0.6 to 0.8 mg/Kg body wt.), the BDE 99 congener was found to cause impaired habituation and impaired learning and memory functions in mice pups after oral administration at day 10 after *partus* (Eriksson *et al.*, 2001).

Generally, the mechanism of thyroid hormone disruption by PBDEs is yet to be fully characterised. However, there are at least two important mechanisms, which may probably explain how these chemicals exert their toxic effects on target organs of the exposed subjects. First, PBDEs are capable of enhancing the activity of liver enzymes of different families, including cytochrome P450 1A1 induction (i.e., Ah-receptor- or dioxin-like induction) or cytochrome P450 2B induction (i.e., Phenobarbital-like induction) (von Meyerinck *et al.*, 1990; Fowles *et al.*, 1994; Zhou *et al.*, 2001; Brown *et al.*, 2004). The induction of liver UDP-glucuronosyltransferases by technical formulations of penta- and octa-BDEs is believed to increase the rate of T4 conjugation and excretion, thus, resulting in the mechanism associated with 2, 3, 7, 8 – tetrachlorodibenzodioxin (TCDD)-induced thyroid effects.

Second, PBDEs may alter the thyroid system through hormone mimicry (McDonald, 2002). Meerts *et al.* (2002) demonstrated that 14 of the 17 PBDE congeners investigated were metabolised *in vitro* by liver enzymes (which are inducers of the CYP1A1 or CYP2B1 enzyme families) to metabolites that competed with the thyroid transport protein, transthyretin. Marsh *et al.* (1998) equally demonstrated the binding of synthesised hydroxylated PBDE to thyroid receptor proteins TR- α 1 and TR- β . Örn and Klasson-Wehler (1998) reported the formation of five different hydroxylated tetra-BDE metabolites after the administration of 2, 2', 4, 4'- tetra-BDE to mice. Arising from these findings, it is apparent that the ability of hydroxyl-PBDEs to mimic thyroid hormones and bind to the transport protein, transthyretin, is a potentially important mechanism for the delivery of PBDEs to the foetus, as has been suggested for hydroxy-PCBs (Brouwer *et al.*, 1998).

Transthyretin plays essential role in transporting T4 from the mother to the foetus as well as delivering T4 across the blood-brain barrier (reviewed in Brouwer *et al.*, 1998). Consequently, the strong affinities of hydroxyl-PCBs and hydroxy-PBDEs for transthyretin may result in facilitated delivery of these metabolites to the foetal brain compartment where they may concentrate to high levels (Brouwer *et al.*, 1998). Although it is not clear whether this medium is operative for the PBDEs (McDonald, 2002), by considering the metabolic products and the ultimate fate of these chemicals in exposed subjects, it is certain that foetus, infants and pregnant mothers are the most vulnerable population. Hence, measures should be taken to reduce human exposure to these chemicals via food intake and uptake through dermal

assimilation. This is necessary to avoid the deleterious health effects associated with exposure to PBDEs especially during the developmental stages of the young ones.

2.4.3 Neurobehavioral effects

Exposure of mice as newborns to 1.4 – 21.1 $\mu\text{mol/Kg}$ body weight clearly indicates that PBDE can cause learning and motor deficits that worsen with age (Eriksson and Fredriksson, 1998; Eriksson *et al.*, 2001; Eriksson *et al.*, 2002; Viberg *et al.*, 2003; Eriksson *et al.*, 2006; Viberg *et al.*, 2006). Eriksson *et al.* (1998) observed reduced learning and memory loss in treated mice exposed to 0.8 or 12 mg/Kg of 2, 2', 4, 4', 5 – penta-BDE. This research group further extended the scope of the study by exposing mice to a single dose of 2, 2', 4, 4', 5 – penta-BDE (8 mg/Kg body weight) on postnatal days 3, 10 or 19 (Eriksson *et al.*, 1999; Viberg *et al.*, 2000). Measurable changes in spontaneous behaviour and in behaviour following a dose of nicotine indicating a clear deficit of brain development was observed. It was therefore suggested that the cholinergic system was likely to be affected, an effect similar to those observed for PCB studies.

The mechanisms through which these chemicals perform these processes are yet to be fully understood. However, McDonald (2002) has suggested three possible mechanisms by which PBDEs, like non-coplanar PCBs, can adversely affect brain development. These include: (1) thyroid hormone disruption, (2) disruption of second messenger communications, and (3) alteration of neurotransmitter systems.

Thyroid hormones are essential for brain development in both foetal and neonatal periods (de Escobar *et al.*, 2000). Studies have shown that relatively small defects in the thyroid hormone system can negatively affect the intelligence and psychomotor skills of children (Haddow *et al.*, 1999, Pop *et al.*, 1999). Since the mother is the only source of thyroid hormones for the foetus during the early stages of life, pregnant women, foetus as well as infants should be viewed as sensitive populations for exposure to PBDEs.

The observed malfunctioning effects on the cholinergic system on exposure to PBDEs were typical examples of neurotoxicity of these chemicals on the neurotransmitter systems. In fact, animal studies have shown that neonatal exposure to PBDEs could reduce the density of nicotinic and muscarinic receptors in the hippocampus at adult age (Viberg *et al.*, 2003; Viberg *et al.*, 2004; Viberg *et al.*, 2005).

Exposure to PBDEs may also result in the malfunctioning of the intracellular second messenger systems, e.g. Ca^{2+} homeostasis in neuronal cells, inositol phosphates and protein kinase C, which play a vital role in neuronal growth and normal cellular physiology (Kodavanti and Ward, 2005). PBDEs have also been shown to release arachidonic acid in cerebellar granule cells via activation of the phospholipase A2 pathway, which is associated with learning and memory processes (Kodavanti and Deri-Yellin, 2002).

2.4.4 Carcinogenicity

Besides the thyroid hormone disruption caused by PBDEs, their potential to induce cancer in test animals is also of great concern. In chronic toxicity tests (103 weeks) with rats and mice, the incidence of tumour was observed after test animals were exposed to deca-BDE via the diet. Hepatic and pancreatic adenomas and carcinomas were observed, but only at very high doses (1200 mg/Kg body weight day⁻¹ and above) (as reviewed by Hooper and McDonald, 2000). Other relevant evidence include the observations of lower molecular weight PBDE congeners inducing genetic recombination in mammalian cells (Helleday *et al.*, 1999) and the formation of macromolecular adducts in various tissues in both rats and mice exposed to 2, 2', 4, 4'-tetra-BDE (Örn and Klasson-Wehler, 1998).

In general, a concrete evidence of tumour induction has only been established for deca-BDE; carcinogenicity tests for other congeners or congener groups have not been undertaken. It was only speculated that the marginal increases in the liver and thyroid tumours associated with deca-BDE would likely be more pronounced in carcinogenicity studies using tetra-, penta- or octa-BDEs (reviewed in McDonald, 2002).

2.5 Legislation

Since the accidental mixture of chemicals suspected to be hexabromobiphenyl with animal feeds in Michigan (USA) in the early 70's, there has been several attempts to regulate the use of flame retardants and other potentially harmful chemicals. In 1976, the European Union issued a directive (Directive 76/769/EEC) to establish limitations on the marketing and use of harmful substances and their preparations amongst member states. With the broader scope of application of these chemicals and their substitutes, this directive has been amended several times to accommodate other potentially harmful chemicals. In one of such amendments, the use of penta-BDE and octa-BDE was restricted in all applications for the EU market with effect from August 15, 2004 (Directive 2003/11/EC).

Similarly, the directive on 'the restriction of certain hazardous substances in electrical and electronic equipment (RoHS)' was proposed to phase out the use of some substances including penta-BDE and octa-BDE, which were considered to be hazardous in electrical and electronic equipment beginning from July 1, 2006. In this directive, deca-BDE was exempted. This was to allow for the comprehensive evaluation of its environmental and human health risk assessment (Commission Directive 2005/717/EC). Due to the contradicting reports emanating from different studies, deca-BDE still remains the only unregulated PBDE formulation in most parts of the world today. Although certain States in the USA, including California, Hawaii, Illinois, Maine, Maryland, Michigan, New York, Oregon and Rhode Island have banned the use of this formulation in mattresses effective from January 1, 2008. Its use in other products such as

upholstered furniture, television or computers has also been prohibited with effect from January 1, 2011 in Washington (Washington State Legislature, 2007).

Generally, there are no federal laws in the USA that prohibits the use of PBDE formulations in various consumer products. However, only certain States (as mentioned above) have regulated the use of these chemicals in various products. In China, the RoHS legislation limits the use of both penta-BDE and octa-BDE in electrical and electronic products (Kirschner, 2007). Similarly, PBDEs were amongst the chemicals added to the List of Toxic Substances in Schedule 1 of the Canadian Environmental Protection Act of 1999. Consequently, the manufacture of PBDEs and the use of tetra-BDE, penta-BDE and hexa-BDE is prohibited in Canada (Environment Canada, 2011).

Presently, there are no regulations on the use of PBDEs in most parts of Africa. In South Africa, the existing environmental laws do not regulate the production as well as usage of these chemicals in consumer products. In 2009, the United Nations' Environment Programme (UNEP) took a decisive stand by including the major congeners of penta-BDE and octa-BDE as well as hexabromobiphenyl (BB 153) into the Annex A list of persistent organic pollutants in their fourth Conference of Party meeting in Geneva, Switzerland (UNEP, 2009). The ratification of this regulation by member states will ensure that most countries will eventually integrate it into their national laws where it can be domesticated.

2.6 Overview of current analytical techniques for PBDE analysis

This section will provide a brief review of analytical methods and techniques commonly utilised for the determination of PBDEs in various environmental samples. A detailed review on the recent analytical approaches can be found in Covaci *et al.* (2009). Over the years, rapid advances and progresses have been made in the development of appropriate analytical protocols for the analysis of PBDEs. An ideal analytical protocol for PBDE analysis would ensure that analytes of interest are quantitatively isolated from the sample matrix and are removed from other interfering components that might interfere with their determination. Therefore, a good analytical method for the determination of PBDEs will consider the following: sample extraction, extract clean-up, fractionation and instrumental analysis.

2.6.1 Sample extraction

This is the process involving the isolation or release of analyte from sample matrix with optimum yield and selectivity using appropriate solvent(s) in such a way that few potential interfering species as possible are carried into the analytical separation stage. The solvents employed may be organic liquids, supercritical fluids, pressurized, or superheated liquids (Fidalgo-Used *et al.*, 2007). A number of

extraction techniques are commonly used depending on the type of sample matrix in question and these include: soxhlet extraction, sonication-assisted extraction, supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE), matrix solid-phase dispersion (MSPD), solid phase extraction (SPE), liquid-liquid extraction (LLE) and solid-phase micro-extraction (SPME).

The efficiencies of extraction of these techniques depend on several factors. These include the choice of extraction medium (solvents), duration of extraction, temperature of extraction medium, pressure in extraction chamber and the ability of the solvent to penetrate the matrix, all of which must be adequately optimized in order to exhaustively extract the analyte from the sample matrix (van Leeuwen and de Boer, 2008). For solid samples, the absence of water makes the sample matrix more accessible to organic solvents. That is why some sample pre-treatment measures such as evaporation, grinding with anhydrous sodium sulphate or freeze-drying are required. Other pre-treatment measures may specifically be required for aqueous samples.

2.6.1.1 Soxhlet extraction

Although soxhlet extraction method requires longer extraction time and relatively large volume of solvent; it is still widely used today due to its simplicity, applicability under routine conditions and amenability to different solid matrices and possibility of multiple samples extraction at the same time (van Leeuwen and de Boer, 2008). In this liquid-solid extraction technique, the dried sample is continuously extracted by non-polar solvent or a mixture of non-polar and polar solvents. With hot Soxhlet extraction, the solvent vapour is distilled into an extraction chamber, which is heated below the boiling of the solvent. In this way, the sample maintains a continuously contact with hot, but not boiling solvent, thus resulting in a reduction of the extraction time (Naert, 2007).

2.6.1.2 Supercritical fluid extraction (SFE)

In this technique, carbon dioxide (CO₂) is mostly utilised as the extraction medium. For this purpose, CO₂ is brought above its critical pressure (73 atm.) and critical temperature (31.1°C), thus resulting in the formation of supercritical CO₂. This diffuses through solid sample like a gas and dissolves matrix components like a liquid. PBDEs dissolve easily in supercritical CO₂ and are extracted together with lipids (Hartonen *et al.*, 1997). Extracts containing PBDEs as well as other co-extractants are sometimes collected or trapped into a collection device, e.g. a vessel containing a small volume of suitable organic solvent or a column filled with adsorbing materials (Focant *et al.*, 2004; Turner *et al.*, 2002). Fat-retaining adsorbents (e.g. florisil, silica or basic alumina) are sometimes added directly into the extraction cell to obtain a fat-free extract (Jaremo *et al.*, 2000).

2.6.1.3 Accelerated solvent extraction (ASE)

This technique, sometimes referred to as pressurised liquid extraction (PLE) finds a wide application in PBDE analysis. In contrast to SFE, the technique employs an organic solvent or a combination of solvents to effect sample extraction at elevated pressures and temperatures. By subjecting the extraction cell to high pressure, it is possible to keep the organic solvent as a liquid at relatively high extraction temperatures. This speeds up the extraction process, thus considerably reducing the extraction time required. A major advantage of this technique over the traditional soxhlet extraction technique is the shorter extraction time and the use of relatively small volume of extraction solvent. In addition, the simultaneous extraction and clean-up is also possible with this technique (Abrha and Raghavan, 2000; Covaci *et al.*, 2003; Focant *et al.*, 2004).

2.6.1.4 Liquid-liquid extraction (LLE)

PBDEs are seldom analysed in aqueous matrices, probably due to their hydrophobic characteristics. LLE is a common and widely used technique for the determination of persistent organic pollutants in water samples (USEPA, 2007). Presently, most of the studies conducted on PBDEs in aqueous matrices so far have employed LLE technique (Osako *et al.*, 2004; Odusanya *et al.*, 2009). This perhaps is due to the ease of isolation of compounds of interest from the aqueous matrix without any form of threat of thermal decomposition or chemical interaction. More so, the possibility of selective separation of compounds with similar relative volatilities or adsorption isotherms associated with this technique is particularly advantageous. Although the technique uses a high volume of solvent and sample, is laborious and time-consuming, Santos and Galceran (2002) established that this method is simple, more reliable and inexpensive than other liquid extraction techniques.

2.6.1.5 Other extraction techniques

Depending on the nature and type of sample to be analysed, other extraction techniques could be applied. These include matrix solid-phase dispersion (MSPD), ultrasonic extraction (USE), microwave-assisted extraction (MAE), solid phase extraction (SPE) amongst others. In MSPD, simultaneous extraction and clean-up procedures can be carried out. In this case, the sample is dispersed with an appropriate adsorbent, e.g. florisil. The mixture is then packed into a column and PBDEs are eluted with organic solvents, e.g. dichloromethane:hexane (1:1) (Covaci *et al.*, 2002; Valsamaki *et al.*, 2006). In USE, like the traditional mechanical shaking methods, the sample is immersed in a vessel with an appropriate organic solvent and placed into an ultrasonic bath (Bayen *et al.*, 2004; Li *et al.*, 2006). USE is a fast technique, has a high sample throughput, and often requires no sophisticated laboratory materials.

With MAE, extraction of compounds of interest is effected by subjecting the solvent and sample to high-energy radiation either in a sealed or open vessel. A major disadvantage of both USE and MAE is that an additional off-line clean-up procedure is required. SPE technique allows for rapid extraction of aqueous samples. This generally involves initial pre-conditioning of SPE-cartridges with appropriate solvent or solvent combination. Although this technique is faster than the conventional LLE method, the optimisation of the operating parameters of the SPE system is essential to obtain a good recovery and reproducibility of target compounds.

2.6.2 *Extract clean-up*

Prior to chromatographic analysis, the elimination of co-extracted substances (lipids, elemental sulphur and other interfering substances) must be accomplished. Elemental sulphur which is often present in abiotic samples (sediment, soil and sewage sludge) has been mostly removed by simple treatment of sample extract with activated copper powder (Wang *et al.*, 2005; Gevao *et al.*, 2006b; Binelli *et al.*, 2007; Eljarrat *et al.*, 2007) or by the use of gel permeation chromatography (GPC) (de Boer *et al.*, 2001). Lipid removal is often accomplished by two different methods – destructive and non-destructive methods.

2.6.2.1 *Destructive method of lipid removal*

Treatment of sample extract with sulphuric acid to remove organic matter is the most commonly used destructive method in brominated flame retardant analysis (Covaci *et al.*, 2007). This is because BFRs have been found to be very resistant to acid treatment. However, this treatment often requires series of sequential liquid-liquid extraction and centrifugation steps. The dispersion of sulphuric acid onto the surface of activated silica gel to form a sorbent which can easily be loaded into a column has been widely explored (Wang *et al.*, 2005; Moon *et al.*, 2007). Saponification is another alternative but has not found wide use in BFRs analysis (van Leeuwen and de Boer, 2008).

2.6.2.2 *Non-destructive method of lipid removal*

The general method for non-destructive lipid removal involves the use of gel permeation chromatography and adsorption chromatography on selected sorbents. Gel permeation chromatography (GPC) is mainly carried out on polystyrenedivinyl benzene columns with dichloromethane as eluent (de Boer *et al.*, 2001). Further clean-up process is often required with the use of GPC either by another serially connected GPC column or by adsorption chromatography for complete removal of fat or isolation of BFRs from other organohalogenated compounds (Covaci *et al.*, 2007). The use of silica gel, alumina and florisil with

varying degree of activation in adsorption chromatography is another viable alternative for lipid removal. Silica gel is most often used in combination with alumina due to its limited capacity for retention of lipids. Gevao *et al.* (2006b) employed a liquid–solid chromatographic column (i.d. 9 mm) for further purification of extract that has been previously cleaned on silicic acid/alumina column. This consists of 2 g of silica gel (Merck, 60-230 mesh), 1 g of alumina (BDH, neutral alumina) all baked at 450°C loaded as slurry in hexane and capped with 0.2 g of anhydrous sodium sulphate.

Extracts of sediment and bivalves from Korean coastal waters were cleaned by passage through a multilayer silica gel column. The column was packed with anhydrous Na₂SO₄ (4 g), 10%(w/w) AgNO₃-silica gel (3 g), silica (0.6 g), 22% (w/w) H₂SO₄-silica gel (3 g), 44%(w/w) H₂SO₄-silica gel (4 g), silica (0.6 g) and 2%(w/w) KOH-silica (2 g). Target compounds were eluted with successive eluants of 120 ml of hexane and 100 ml of 10% methylene chloride (Dioxin analysis grade, Wako Pure Chemicals) in hexane (Moon *et al.*, 2007). In some instances, a further isolation of the target analyte from other organohalogenated compounds present in the extract is necessary to avoid interferences during final analysis.

2.6.3 Fractionation of cleaned sample extract

The polarity of various organohalogenated pollutants plays a vital role in their isolation from each other. PBDEs due to their higher polarity than other organohalogenated pollutants typically present in the extract (e.g. PCBs, PCDDs or PCDFs) can be isolated in a separate fraction using classical sorbents such as silica gel, alumina and Florisil (Covaci *et al.*, 2007). Xian *et al.* (2008) successfully isolated HBCD from PBDEs by passing concentrated GPC fraction containing organohalogens through 4 g of activated silica gel. The first fraction eluted with 80 ml 5% dichloromethane in hexane for clean-up contained PBDEs while the second fraction eluted with 100 ml 25% dichloromethane in hexane contained HBCDs.

Ueno *et al.* (2006) also used 8g of activated silica gel in an open column to fractionate GPC fraction containing HBCD and other organohalogens. The first fraction eluted with hexane contained some organohalogens, while the second fraction eluted with 50% dichloromethane in hexane contained HBCD. Alumina and florisil show less selectivity for PBDEs than silica gel and using similar solvents as extractants, some planar PCBs were found to elute together with PBDEs in the second fraction (Covaci *et al.*, 2007). Deactivated silica gel has been successfully applied for the quantitative isolation of PBDEs from HBCD diastereoisomers and TBBPA. In this case, iso-octane was used for the elution of PBDEs while a more polar solvent, that is, 15% diethylether:iso-octane (v/v) was required to elute HBCD and TBBPA. Once, the clean fraction of the analyte of interest is obtained and suitable recovery standards are added, then the sample will be ready for the final determination using either GC or LC techniques.

2.7 Gas chromatography (GC)

Both GC and LC techniques have been widely explored for the qualitative and quantitative assessment of brominated flame retardants in a variety of complex sample matrices. Today, gas chromatographic methods remain the most common techniques for PBDE determination. PBDEs are volatilised at relatively high injector temperature; hence, their separations are easily effected using an appropriate gas chromatographic technique. Irrespective of its type, a GC instrument would consist of a system to control the flow of the carrier gas, an inlet system, a column and at least a suitable detector. A schematic diagram of a typical GC is shown in Figure 2.3. The principle of operation of GC is generally based on the concentration equilibrium of the components of interest, between two immiscible phases. That is, their ability to partition or distribute between the moving gas phase and the stationary liquid phase (Rouessac and Rouessac, 2007).

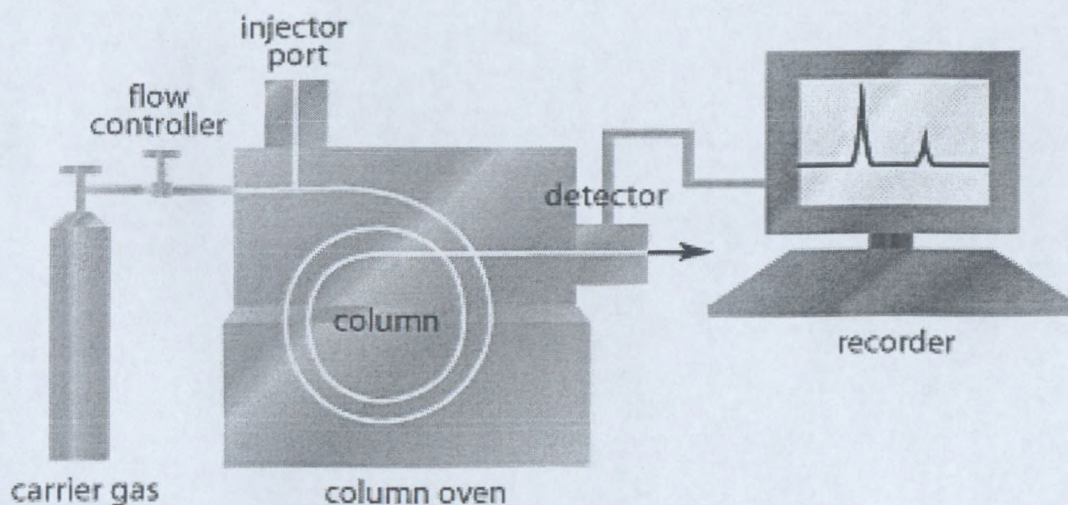


Figure 2.3: A schematic diagram of a modern gas chromatograph showing its basic components (adapted from Naert, 2007).

2.7.1 Injection techniques

A number of sample injection techniques are commonly employed in the analysis of PBDEs. These include splitless injection, programmable temperature vaporisation (PTV) injection, on-column injection amongst others. Each of these techniques has some specific advantages over the other. For instance, with splitless injection, a relatively small volume of sample ($1 - 2 \mu\text{l}$) is often injected. During injection, the split flow is stopped and is allowed to continue after the sample has been transferred to the column. This measure is taken to ensure that solvent 'leftovers' from the liner are completely purged (Tipler, 1993). In

splitless injection, the injection unit is usually maintained at high temperature between 250 and 300°C. At these elevated temperatures, the analysis of certain PBDE congeners especially the thermally labile BDE 209 becomes problematic. This congener degrades rapidly on exposure to high temperatures, hence, its analysis employing this injection technique would require a thorough optimization. It is used when sensitivity is most important (McMahon, 2007).

In contrast to splitless injection, the initial temperature is generally low in PTV technique, which is later increased rapidly after solvent evaporation has taken place. This technique allows for the concentration of component of interest in the liner through multiple injections of relatively large volume of samples. Since the temperature of the injection unit is initially maintained around the boiling point of the solvent, solvent evaporation from this unit via the split valve will result in the build-up of the component of interest in the liner. Usually the split valve is open during injection and the column oven is maintained below the PTV to prevent the transfer of target compounds into the column. As soon as the split valve is closed, the temperature of the liner is rapidly increased. As the components originally suspended in the solvent becomes vaporised, they are swept from the liner onto the column and thus will not be subjected to a temperature higher than necessary. With this technique, large volume multiple injections can also be made (Hübschmann, 2001; Bailey, 2005; Stapleton, 2006).

In cool on-column injection, sample extract is injected directly onto the column. This technique causes less degradation and discrimination. However it is required that the extract be clean to prevent possible damage of the GC column caused by deposition of involatile materials. The use of a retention gap is recommended when larger volumes (10 – 250 µl) need to be injected. It can also serve as a guard column to protect the analytical column from these involatile residues (Hübschmann, 2001; Bailey, 2005; Stapleton, 2006).

2.7.2 GC capillary columns for PBDE analysis

The choice of an appropriate capillary column is essential in the process of developing a suitable analytical protocol for PBDE analysis. Since there are 209 possible PBDE congeners where only a few of these are normally found in environmental samples, their complete separation on a single column could sometimes be problematic. This is due to the imminent co-elution amongst congeners within a homologue as well as with other similar halogenated compounds. As it is the case in this study, PBDEs are analysed simultaneously with hexabromobiphenyl (BB 153) which necessitated for a separate analysis for the highly brominated PBDE congener.

Generally, the separation of PBDEs are achieved on non-polar capillary columns such as 100% dimethyl polysiloxane (e.g. DB-1 MS) and 5% diphenyl – 95% dimethyl polysiloxane (e.g. DB-5 MS) with length ranging from 25 to 60 m (Covaci *et al.*, 2006). Separation of lower brominated PBDEs favours the use of longer chromatographic column (>30 m) with non-polar stationary phase. The analysis of higher brominated PBDEs particularly BDE-209 usually requires the use of shorter columns (10-15 m). Due to the degradation problems associated with this congener at elevated temperatures, there is need to shorten its residence time in the column (Covaci *et al.*, 2007).

Bjorklund *et al.* (2004) described how different column types could significantly influence the determination of PBDEs. Columns with similar stationary phases from two manufacturers were evaluated: DB-1 and DB-5 MS from J & W Scientific and HP-1 and HP-5 MS from Agilent Technologies. Although there was no significant difference in yield for low molecular weight PBDEs observed in these columns; a significant difference between the brands was observed for higher brominated PBDEs. In HP-1 column the degradation increased with the degree of bromination; nona-BDE and BDE-209 were virtually not visible on the chromatogram produced. Similar result was also obtained for the 5% phenyl-methylpolysiloxane columns DB-5 MS and HP-5 MS. Three columns with different stationary phase polarity were also investigated; DB-1 with 100% dimethylpolysiloxane, DB-5 MS with (5% phenyl-methylpolysiloxane) and DB-35 with (35% phenylmethylpolysiloxane). DB-1 and DB-5 MS showed similar properties while the DB-35 demonstrated an increasing degradation of high molecular weight BDE congeners starting with heptaBDE to BDE-209. Reduced yield of BDE-209 to around 20% on the DB-35 column compared to DB-1 and DB-5 MS columns was also noticed.

The effect of stationary phase thickness on chromatographic separation of PBDEs was also investigated using two 15 m long DB-5 MS columns with different stationary phase thickness, 0.1 and 0.25 μm . The retention time of BDE-209 was 23.3 and 25.6 min., respectively. Starting from BDE-153 onwards, the yield of PBDEs was significantly lower on 0.25 μm stationary phase film. For hepta- to nona-BDE, the relative area decreased to around 70%, while that of BDE-209 was as low as 40%. Similarly, the difference in discrimination of high molecular weight BDE congeners was investigated by using columns (DB-5 MS, 0.25 mm i.d.) of three lengths 30, 15 and 5 m. The effect of degradation was strongest for BDE-209 but still significant down to hepta-BDE on 30 m column length demonstrating the importance of designing GC systems in such a way that the shortest possible residence time is obtained for the highly brominated PBDEs.

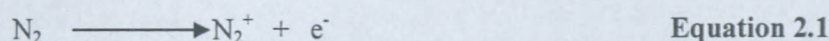
When compared with PCBs and PBDEs, the number of PBB congeners generally found in environmental samples is small. Therefore, a single-capillary column with non-polar stationary phase offers sufficient

resolution. However, BDE 154 usually co-elutes in most gas chromatographic columns with BB 153. The use of sufficiently long GC column is required to ensure complete separation of BDE154 and BB153. In addition, the use of heart-cut and multidimensional gas chromatography may resolve the problem of co-elution amongst PBDE congeners (Korytar *et al.*, 2005; Bucheli and Brandli, 2006). Since the use of shorter GC column favours the determination of higher brominated PBDEs, the simultaneous analysis of PBDEs and PBB could best be performed in two separate GC measurements under different operating conditions.

2.7.3 Electron capture detection (ECD)

Besides the flame ionization detector (FID), the ECD represents one of most commonly used detectors in gas chromatographic analysis. It is a highly selective and sensitivity detector for halogenated compounds. ECD has been widely employed for the analysis of environmental samples containing chlorinated pesticides, herbicides and other halogenated industrial chemicals. The innermost unit of the detector is usually lined with a radioactive β -emitter held in a sealed foil and is maintained as small as necessary (Fowlis, 1998). Either nickel (^{63}Ni) or hydrogen (^3H) could be used as the radioactive source. The inlet tube and cylindrical body are employed as electrode cells and are properly insulated from one another.

The carrier gas entering the detector unit is ionised by the β -radiation leading to the formation of free-electrons. Since hydrogen and helium gasses are commonly employed in most GC systems as carrier gases, a high molecular weight make up gas (e.g. N_2 and CH_4) is required for effective operation of the ECD. The free electrons, before they re-combine with the nitrogen cations to form neutral nitrogen molecules, rapidly move to the anode under the impact of the potential gradient (Fowlis, 1998), hence, an ion current is produced. A common mechanism of ionisation of nitrogen gas is represented in equation 2.1.



In the presence of an electronegative species, these electrons may be captured before reaching the anode, resulting in decrease in the total ion current, which is shown in the displayed chromatogram. A schematic diagram of a typical ECD is shown in Figure 2.4.

The GC-ECD technique has been widely used for the analysis of PCBs in various environmental samples (Falandysz *et al.*, 2001; Yuan *et al.*, 2001). Its application for the analysis of PBDEs was equally explored due to its high sensitivity and excellent resolution especially at very low concentration range (Sellström *et al.*, 1998; Sjodin *et al.*, 1999; Troitzch, 1999). In addition, the ease of operation and its cheap cost of maintenance generally favour its widespread usage in environmental analysis of halogenated organic

compounds. Consequently, this technique is very suitable for carrying out routine analysis, especially when a proper choice of capillary column is made and the confirmation is done with in GC-MS technique, (de Boer *et al.*, 2001; Sellström *et al*, 2001).

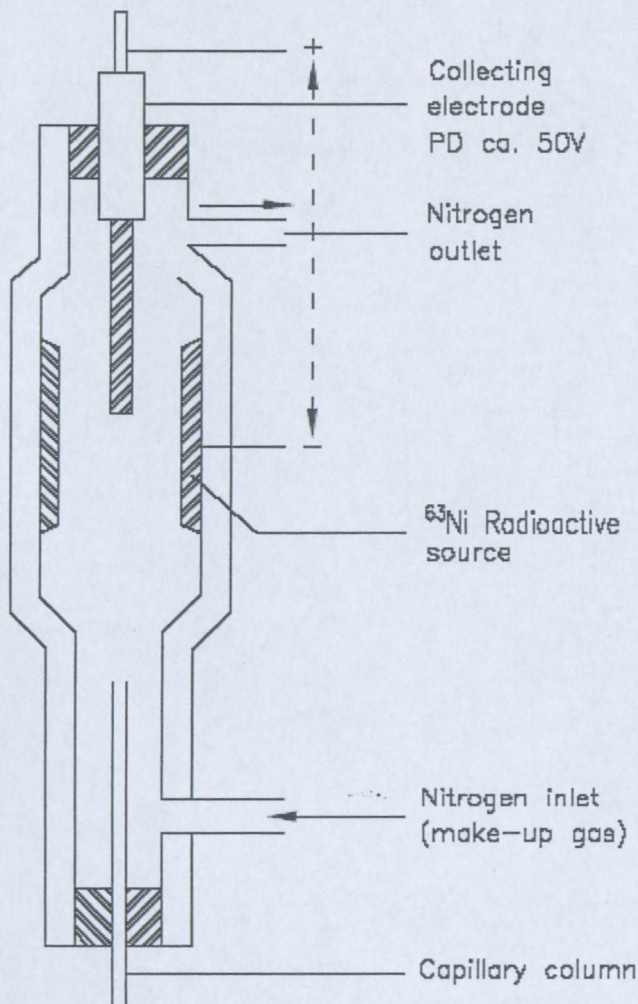


Figure 2.4: A schematic diagram of a typical electron capture detector (ECD)

2.7.4 Detection by mass spectrometry

The coupling of gas chromatograph with mass spectrometers has resulted into a number of applications widely used to analyse environmental contaminants. This technique is gaining widespread popularity in the analysis emerging contaminants, including PBDEs. According to Alaei *et al.* (2001), the HRMS analytical method offers additional advantages of performing congener specific analysis and also provides the most selective and sensitive method for PBDE determination. The technique is highly sophisticated

and very expensive; hence, its use requires trained personnel and frequent maintenance for routine analysis.

Electron impact (EI) and chemical ionization (CI) are the two ionization methods commonly used in GC-MS analysis. Of these two, EI is more often used where it produces both molecular and fragment ions. The stream of gaseous analyte molecules are bombarded by energetic electrons at 70 electron volts. The transfer of energy to the neutral molecule leads to the ejection of one of its own electrons as depicted in equation 2.2. This process results in the generation of a molecular radical ion (M^+).



The dissipation of excess energy possessed by the molecular ion could further lead to the fragmentation of its chemical bonds, thus generating more ionized fragments. These fragments are particularly useful as they often provide information needed for the structural elucidation of unknown compounds (de Hoffman and Stroobant, 2001; Covaci *et al.*, 2003).

In contrast to EI, a chemical reagent gas is used in CI. Typical reagent gases commonly used include methane, ammonia amongst others. The ratio of sample molecules to that of the reagent gas molecules present in the ion source is very small. Hence, the reagent gas molecules are preferentially ionized and the resulting ions collide with other reagent gas molecules, creating ionization plasma which contains product ions and low energy electrons (Naert, 2007). Both positive and negative chemical ionization processes can be take place. In positive chemical ionization (PCI), proton is transferred from the ionized reagent gas to sample d molecules. This type of reagent is typical of sample molecules that have a higher proton affinity than the reagent gas. In negative chemical ionization (NCI), the low-energy electrons present in the plasma react with electrophilic molecules (e.g. PBDEs or PBBs) to form negative molecular ions.

The MS spectra obtained for PBDE analysis were usually dominated by the mass fragment (Br^-) (m/z 79 and 81) and the molecular cluster was not observed or constituted only a minor peak. Since only ion due to bromine can be monitored, this constitutes a major setback for this technique as it results in poor selectivity. While EI-MS offers better selectivity, the analytical determination where improved sensitivity is desired, the use of NCI-MS technique is best suited. Eljarrat *et al.* (2002) investigated the NCI-MS spectra of 40 PBDE congeners and concluded that NCI (SIM mode) gives 15 times higher responses for PBDEs than EI (SIM mode). The ions produced in the ion source need to be separated according to their masses. For this purpose, different MS systems are equipped with different mass analysers, which employ electric and/or magnetic field to affect the paths or velocities of charged particles in some ways.

The time-of-flight mass analyzer uses an electric field to accelerate ions through the same potential. It then measures the time taken by each ion to get to the detector. In this case, particles having the same charge will possess identical kinetic energies and their velocities will only depend on their masses. Consequently, lighter ions will reach the detector first (Wollnik, 1993). Both quadrupole and ion trap mass analyzers are somewhat similar in their mode of operation. These mass analyzers use oscillating electrical fields to selectively stabilise or destabilise the paths of ions passing through a radio frequency (RF) quadrupole field created between four parallel rods. The quadrupole mass analyzers (linear or triple) are designed to pass the untrapped ions whereas the ion trap mass analyzers (linear or three-dimensional quadrupole ion trap) are configured to collect and pass the trapped ions. However, the triple quadrupole differs from the linear quadrupole in configuration. This has three consecutive quadrupoles arranged in series to incoming ions. The first quadrupole functions as a mass filter. The second quadrupole acts as a collision cell where selected ions are broken into fragments. Fragments that result from this process are further filtered by the third quadrupole or are allowed to pass through to the detector yielding an MS/MS fragmentation pattern.

In most MS systems, electron multiplier is commonly used as the detector, which records either the charge induced or the current produced when an ion passes by or hits a surface. Because the number of ions leaving the mass analyzer in a given instance is quite small, considerable amplification becomes necessary to obtain a readable signal. As a result, modern commercial instruments are now equipped with microchannel plate detectors (Dubois *et al.*, 1999). Each of these GC-MS instruments has specific advantages over the others. For instance, the single quadrupole instruments rely on selected ion monitoring (SIM) to enhance its sensitivity (Alder *et al.*, 2006), while the triple-quadrupole instruments can be operated in tandem MS mode with selected reaction monitoring (SRM) to enhance its specificity. Ion-trap instruments have high sensitivities for full-scan analysis of endocrine active substances and can also be used for tandem mass spectrometry. While the excellent scan rate of time-of-flight (TOF) instruments allows for rapid analysis of environmental contaminants (Dalluge *et al.*, 2002; Beens and Brinkman, 2005).

In the recent past, the analysis of brominated flame retardants, especially PBDEs has been extensively carried out using both GC-ECD and GC-MS techniques. Nowadays, the use of GC-MS techniques is the preferred method of analysis of these emerging contaminants. This is because these techniques provide structural information in addition to their quantitative capabilities, which further boost their widespread applicability, especially in the environmental analysis of complex matrices. Consequently, the use of non-specific analytical techniques such as GC-ECD for the analysis of these contaminants must be done in conjunction with a suitable mass spectrometric technique. An overview of different chromatographic techniques commonly employed for PBDEs as well as PBBs is presented in Table 2.2.

Table 2.2: Analytical techniques commonly employed for emerging brominated flame retardants in environmental and biological samples

Target compounds	Matrices	Extraction methods	Method of detection	References
PBDEs	soil	soxhlet extraction	GC-NCI-MS	Yang <i>et al.</i> , 2008
PBDEs, PBBs	soil, sediment	soxhlet extraction	HRGC-HRMS, GC-ECD	Yun <i>et al.</i> , 2008
PBDEs, TBBPA, DBDPE	sediment	soxhlet extraction	GC-ECNI-MS, GC-EI-MS	Zhang <i>et al.</i> , 2009
PBDEs	sediment, bivalves	soxhlet extraction, LLE	HRGC-EI-HRMS	Moon <i>et al.</i> , 2007
PBDEs, TBBPA	water, sediment	SPE, sonication	GC-NCI-MS	Labadie <i>et al.</i> , 2010
PBDEs	sewage sludge, soil	soxhlet extraction	GC-ECNI-MS	Eljarrat <i>et al.</i> , 2008
PBDEs	sewage sludge	soxhlet extraction	GC-SIM(EI+)-LRMS	Knoth <i>et al.</i> , 2007
PBDEs	sewage sludge	ASE	GC-EI-MS	Clarke <i>et al.</i> , 2008
PBDEs	landfill leachate	LLE	GC-ECD, GC-MS	Odusanya, 2008
PBDEs, TBBPA	landfill leachate	LLE, SE for residue	HRGC-HRMS	Osako <i>et al.</i> , 2004
PBDEs	house dust	soxhlet extraction	GC-MS	Meeker <i>et al.</i> , 2009
PBDEs	dust	PLE	LC/NI-APPI/MS/MS	Lagalante <i>et al.</i> , 2009
PBDEs	indoor air, dust	ASE	HRGC-HRMS	Toms <i>et al.</i> , 2009b
PBDEs	human milk	ns	HRGC-HRMS	Toms <i>et al.</i> , 2009b
PBDEs, HBCD	human milk	LLE	GC-MS	Thomsen <i>et al.</i> , 2010
PBDEs	human blood, milk	LLE	GC-MS	Bi <i>et al.</i> , 2006

ASE – accelerated solvent extraction; DBDPE – decabromodiphenylethane; LLE – liquid-liquid extraction; PLE – pressurized liquid extraction; ns – not specified.

A new trend in the analysis of these contaminants involves the use of liquid chromatography-mass spectrometry. Although these techniques have been extensively employed for the analysis of hydroxylated and methoxylated metabolites of PBDEs, their application to PBDEs is becoming popular day by day (Mascolo *et al.*, 2010; Zhou *et al.*, 2010; Guerra *et al.*, 2011). With this new trend, the thermal decomposition of certain PBDEs, especially the highly brominated congeners during GC analysis would be overcome because liquid chromatographic analyses are usually carried out at relatively low temperatures. Therefore, the application of LC-MS techniques for the analysis of PBDEs would prevent possible losses during their analysis.

A major setback with the use of these techniques has been their relatively poor detection limits, especially when compared with the GC techniques. However, with the careful selection of the ionization source and appropriate optimization of important parameters of the LC-MS instruments, these techniques could compare favourably with the GC techniques in terms of sensitivity, reproducibility and repeatability.

Abdallah *et al.* (2009) investigated the levels of 14 tetra- to decaBDE congeners in house dust samples using LC-APPI-MS/MS technique. The results obtained were compared with those of GC-EI-MS and GC-NCI-MS techniques. In this study, the GC-EI-MS was used for the tetra- to hexaBDEs, while the analysis of hepta- to decaBDE was done using the GC-NCI-MS technique.

The statistical analyses performed on these results showed no significant difference between the results obtained from the two compared methods. For most of the congeners, the linear correlation for the two sets of results nearly approached 1, thus indicating an excellent agreement between the results obtained from both techniques. Unfortunately, the high cost of the LC-MS/MS instruments has resulted in limited availability of these instruments in most laboratories today. Hence, the need for alternative analytical methodologies for the analysis of these contaminants is essential.

In this study, the choice of GC-ECD for the routine analysis of the target compound was done because of several reasons. First, the technique is suitable for routine analysis because of its robustness, ease and low cost of maintenance and high stability. It is also highly selective and possesses excellent sensitivity, especially to halogen-containing compounds. Hence, the GC-ECD technique was employed for the routine analysis of all the target compounds investigated in this study. Although the use of GC-MS for the structural elucidation of these contaminants was proposed, the persistent breakdown of the instrument at the preliminary stage of this study led to the eventual use of the GC-TOF-MS instrument. This technique was therefore employed for the structural confirmation of investigated PBDE congeners and BB 153 in different environmental matrices monitored in this study.

CHAPTER THREE MATERIALS AND METHODS

3.1 Materials, chemical reagents and standards

The selection of materials used for the investigation of target analytes was carefully considered. For instance, the choice of amber glass bottles for sample collection, the use of glassware instead of plastic and high purity solvents were necessary measures required for the development of a reliable analytical protocol for PBDE analysis. With this in mind, care was taken in selecting appropriate materials required for the analytical protocols employed in this study.

3.1.1 *Cleaning of glassware and apparatus*

All glassware were thoroughly washed with liquid detergents and rinsed properly with tap water. These were soaked in dilute nitric acid solution overnight. They were then rinsed properly with de-ionised water and allowed to drain completely. The glassware were finally rinsed with pure acetone and dried in the oven at 105°C overnight before use.

3.1.2 *Analytical reagents and their purification*

All the organic solvents used in this analysis, namely: n-hexane, dichloromethane, acetone and isooctane were of pro-analysis grade from Merck (Germany) and were double distilled before use. Silica gel (60 - 100) mesh supplied by Sigma-Aldrich was used for column chromatography. Granular sodium sulphate (anhydrous) from Radchem (Pty) South Africa was preheated by drying in the oven at 240°C overnight before use. Copper powder used for the removal of sulphur in the solid matrices was supplied by Sigma-Aldrich.

Unlabelled individual PBDE standards (50 µg/ml), mixed PBDE standard (Method 1614 (EO-5278) standards) produced by Cambridge Isotope Laboratories (CIL) MA, USA and BB 153 (produced by Chizon, Norway) were supplied locally by Industrial Analytical (Pty) South Africa. Pentachloronitrobenzene (PCNB) and BDE 77 used as surrogate standards were supplied by Industrial Analytical (Pty) South Africa and Sigma-Aldrich.

3.2 Description of the study area

Amongst the cities in South Africa, the City of Cape Town has the largest land area of about 2,455 square kilometres. The city has an estimated population of 3.5 million in 2007, thus having a comparatively lower

population density of 1,425 inhabitants per square kilometre. Cape Town is a multicultural city and the heart of tourism in Africa. The city is home to all South Africans and people from other parts of the world. The Western Cape Province where the city is situated has one of the highest levels of biodiversity of any equivalent area in the world. Consequently, it is home to more than 16 different vegetation types, of which several are indigenous to the region, and occur nowhere else in the world (CCT, 2006a).

The Mediterranean climate of the city might particularly contribute to the huge diversity of plant and animal species in this region. The climate is characterised with mild, wet winters and dry and warm summers. During the winter period, which usually begins in June to end of August, large cold fronts come across from the Atlantic Ocean with heavy precipitation and strong north-westerly winds. The average minimum and maximum temperatures during the winter are 7°C and 17.5°C, respectively. The summer begins in December and ends in February. During this period, frequent winds from the south-east caused by high-pressure system blows away pollution and clean the air. The city is host to the point of convergence of two important coastal water bodies (the Atlantic and the Indian oceans). It is also a host to numerous inland water bodies through which treated effluents from wastewater treatment facilities are being discharged (Brown and Magoba, 2009). The sampling locations where different environmental samples are collected are shown in Figure 3.1.

3.3 Description of the study sites

In this study, samples were collected from three main categories of sampling sites, namely: WWTPs, rivers and landfill sites within the City of Cape Town. A brief description of these sites is therefore essential to understand the possible influence of activities taking place around these sites on the outcome of this study.

3.3.1 The river systems

Two freshwater rivers were investigated in this study, namely: the Diep and Kuils Rivers. The Diep River has its source from the Perdeberg and Riebeeck-Kasteel Mountains around Malmesbury which is outside the borders of Cape Town. The river flows south-easterly direction for approximately 65 kilometres before forming an extensive vlei popularly known as the Rietvlei. The vlei which is renowned for its recreational potentials is located on the Table Bay coastline, which is a few metres away from the sea, between Milnerton and Table View. The river drains into the sea via the Milnerton lagoon.

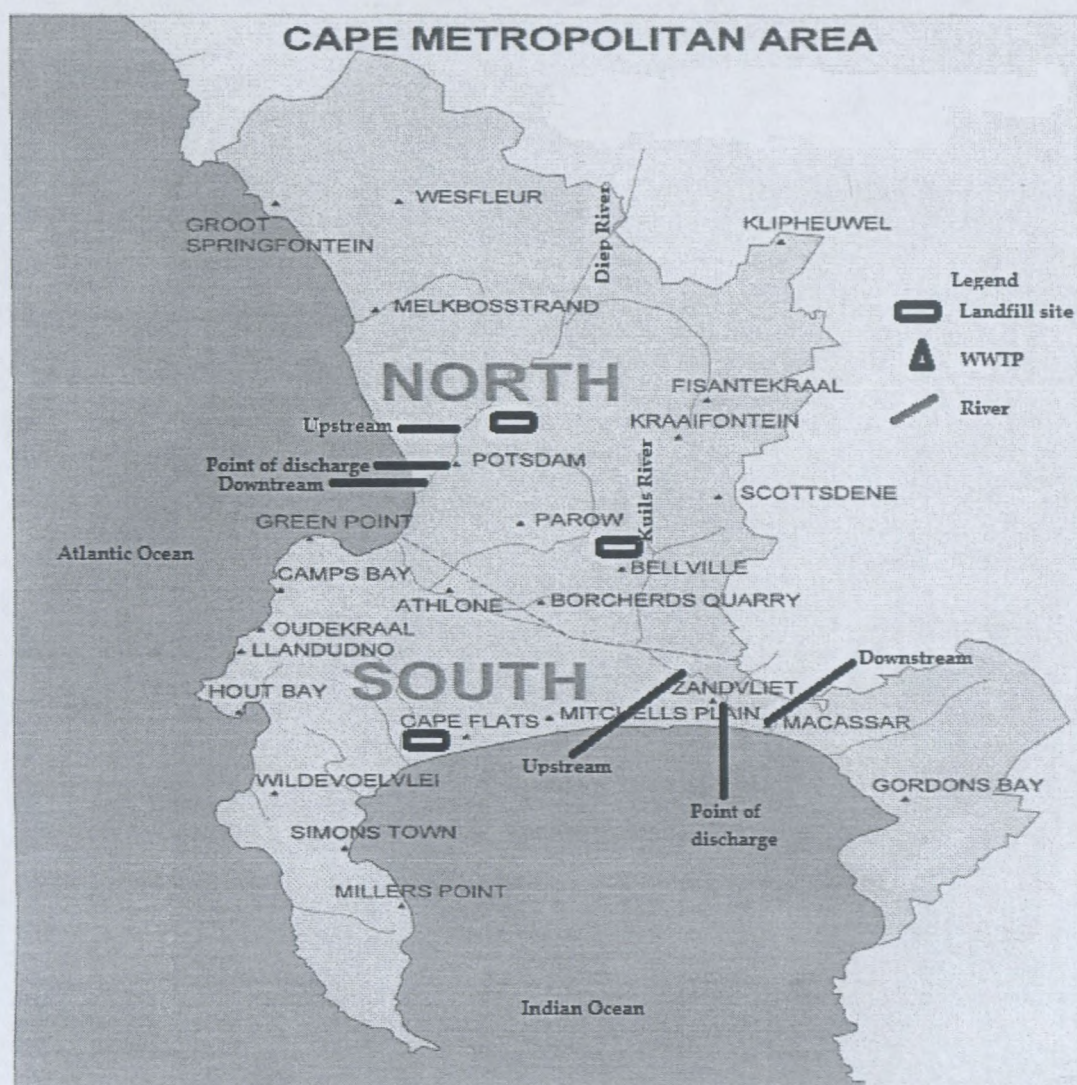


Figure 3.1: Map of the Cape Metropolis showing the WWTPs in the City of Cape Town and other sampling sites monitored

The Diep River was so-called because it was extremely deep. In fact, it was believed that it could allow grain barges or sailing boats to sail up as far as Viessershok which is over 10 kilometres upstream of the mouth (Brown and Magoba, 2009). Several tributaries join the Diep River on its way to the sea. These include the Klein River, the Groen River and the Mosselbank River which drains the Durbanville and Kraaifontein areas. The major activities along the catchment of the Diep River include large-scale crop and pastoral farming where WWTP derived compost materials are used as soil conditioners. This river is also bound in this area to the Viessershok landfill site as well as an informal settlement just before it drains through the Potsdam WWTP area. The selected sampling points on the river were about 150 – 200 metres away on both sides (i.e., the upstream and downstream sampling points) of the point of discharge of treated effluent into the river.

The Kuils River, on the other hand, was historically seasonal, draining a vast area of sand dunes, and recharging the Cape Flats Aquifer before ever reaching the sea. The river drains through a large expanse of land and never reached the sea, but emptied into a system of pools, or “kuils”, which are now occupied by the Khayelitsha Township (Brown and Magoba, 2009). The river which has its source from the low hills near the present town of Durbanville has witnessed a tremendous change along its catchment over the years. Presently, the extensive townships of Mfuleni, Kleinvelei, Blue Downs and Delft were built on relatively high ground along the catchment. Several informal settlements have also sprung up along the floodplain of the river. The development of new industrial areas as well as the rapid urban housing development in towns such as Bellville, Brackenfell and Kuilsriver has led to the construction of new and larger wastewater treatment works. These WWTPs, including the Old & New Bellville and Zandvliet WWTPs discharge their treated effluent into the Kuils River at different points along the riverbank.

The progressive spread of urban areas along the catchment of the river in the last sixty years is notable. As a result of these developments, however, there is lack of capacity to drain the floodwater especially during high precipitation. Hence, there was regular overflow of the riverbank especially at Kuilsriver and at several other points downstream. The perennial link of the Kuils River with the Eerste River further downstream has also resulted in periodic flooding of the Macassar-Zandvliet farming area. The perturbation caused on the riparian wetlands while measures were made to control flooding along the riverbank has further reduced the flood retention capacity and the health of the river system (Brown and Magoba, 2009).

The major tributaries (Kleinvelei Canal and Bottelary River) which drain into the Kuils River convey treated effluents which are sometimes rich in plant nutrients and other organic contaminants. This has consequently led to the infestation of the river with alien vegetation such as water hyacinth and some indigenous plants such as bulrush (*Typha capensis*) to flourish. The treated effluent from the Bellville WWTPs is discharged into the Kuils River via an underground pipeline which is connected to the river some few distances away from the plant. As a result, more convenient sampling points were carefully selected around the Zandvliet WWTP point of discharge into the river. The upstream and downstream points were about 100 and 200 metres away from the point of discharge, respectively.

3.3.2 The choice of WWTPs investigated

A total of twenty-two operational WWTPs are constructed for effective wastewater treatment within the City of Cape Town. Of these, only five WWTPs, namely: Cape Flats, (Old & New) Bellville, Potsdam and

Zandvliet were investigated in this study. The increasing coverage area of most WWTPs as a result of the rapid urban housing development in recent years has led to the expansion of the treatment capacities of some of these plants. In most cases, the expansion is done by constructing new treatment plants. Both Bellville and Potsdam WWTPs fall into this category of treatment plants which have both old and new plants situated in the same location. However, samples were only collected at the new Potsdam plant while both old and new Bellville plants were monitored throughout the study period.

Many factors were considered for the choice of WWTPs investigated in this study. These include: the capacity of each plant, the population equivalents covered by each plant, the types of influents being processed by each plant, the location and the potential of treated effluent and sludge re-use from each treatment plant. The information showing some of these criteria is presented in Table 3.1. The WWTPs monitored in this study covered a wide range of treatment capacity from small, medium to large. The selected plants also covered the urban, semi-urban and rural areas of the city. All the plants receive both industrial and domestic effluents. However, there are some that receive mostly domestic effluents, especially those (e.g. Zandvliet WWTP) sited in the semi-urban areas of the city. While the Cape Flats WWTP discharges its treated effluent into the adjacent Indian Ocean, the other three plants discharge their treated effluent directly into adjacent rivers.

Table 3.1: Characteristics of the WWTPs investigated in this study

WWTPs	Treatment process used	Design capacity (Mt/d)	Population equivalents
Cape Flats	Activated sludge + primary sedimentation + maturation ponds	200	1,645,000
Potsdam	Primary sedimentation + activated sludge + maturation pond	47	385,000
Zandvliet	Extended aeration activated sludge (Bio-reactor)	59	338,000
Bellville Old	Activated sludge + primary sedimentation	9	592,000
Bellville New	Extended aeration activated sludge	46	

Source: City of Cape Town’s Department of Water and Wastewater Management (*personal communication*)

In this case, both Bellville and Zandvliet discharge into the Kuils River while the Potsdam WWTP discharges into the Diep River. Treated sludge from these plants are being re-used as compost in agricultural soils. Similarly, the treated effluent from all the plants except Zandvliet WWTP are increasingly used for agricultural and landscape irrigation in different parts of the city. Lastly, the selected WWTPs were strategically located within the city. Two of which are located in the southern suburb and the other three are located in the northern suburb of the city.

3.3.3 Landfill sites

All the three operational landfill sites within the City of Cape Town were investigated for PBDEs levels in their leachate samples. The general description of the landfill sites is presented in Table 3.2.

Table 3.2: Detailed description of investigated landfill sites (CCT's Department of Solid Wastes, *personal communication*)

Name of landfill	Age (years)	Size (Ha)	Permit Status	Annual tonnage†	Waste types received
Bellville	51	60	Yes	545 000	G, H, I
Coastal Park	41	75	Yes	383 000	G, H, I
Vissershok	41	117	Yes	608 000	G, H, I, S, LMHZ

G – General waste; H – Household waste; I – Industrial waste; S – Special waste; LMHZ – Low – Medium Hazardous waste; † Based on 2011 figures

Of these three landfill site, only the Vissershok site is equipped with leachate treatment plant (LTP). The leachate generated from other sites is usually pumped from the ponds or reservoirs where the leachate is contained into a nearby WWTP for treatment. For instance, the leachate from the Bellville landfill site, which is sited adjacent to the Bellville WWTP is usually pumped from the reservoir where it is contained into the WWTP. Similarly, the Coastal Park landfill site is situated in close proximity to the Cape Flats WWTP and the leachate generated from this site is pumped for treatment at the Cape Flats WWTP.

As indicated in the table, all the landfill sites have been licensed to operate as solid waste treatment facilities by the South African Department of Environmental Affairs. However, the approval stipulates in strong terms the conditions required for the operations of landfill sites which include the location of the site, permissible wastes, site specification, monitoring exercise and other criteria required to operate the landfill site in a manner that will prevent the creation of nuisance conditions or health hazards (DEA, 2011). All the landfill sites receive considerable quantities of waste materials that would probably contain these contaminants. Notable amongst these wastes are the old furniture with polyurethane foams and plastic materials previously used in housing compartment of some electronic products. These are generally landfilled together with other waste types without any form of pre-treatment prior to their disposal at these sites.

3.4 Optimisation of GC parameters

The development of a good analytical procedure for the analysis of organic contaminants requires appropriate optimisation of the various components of the entire analytical process. In this study, several parameters on the GC-ECD and GC-MS employed were optimised. Some sample preparation steps (including, sample extraction and extract clean-up techniques) were also optimised. The following GC parameters were optimised during the method development, namely: GC injector temperature, oven temperature programming, column flow rate and detector temperature.

3.4.1 *Injector temperature*

One of the basic prerequisites for the analysis of organic compounds using GC techniques is that the compound must be volatile or semi-volatile in nature. However, due to the high molecular weight of certain organic compounds, which considerably reduces their volatilities, the GC injector temperature needs to be appropriately optimised. This is necessary to ensure that these compounds remain volatilised after sample injection so that the chromatographic separation of analytes could be effected. Furthermore, extremely high injector temperature could be a disadvantage to some thermally labile compounds. BDE 209 belongs to this category of compounds, which makes its analysis problematic. At high injector and oven temperatures, BDE 209 degrades rapidly showing numerous peaks during analysis. To overcome this challenge, efforts must be targeted at obtaining an appropriate temperature where its degradation will be minimal. The optimum injector temperature employed for tri-heptaBDEs as well as BDE 209 is presented in Table 3.3.

3.4.2 *Oven temperature ramping*

The oven where the capillary column is situated is the heart of the gas chromatograph. Essentially, the chromatographic separation of analytes takes place within this unit. Therefore, the oven temperature ramping is a crucial step to obtaining a good resolution of all the target analytes. Of particular relevance is the simultaneous determination of co-eluting BDE 154 and BB 153 investigated in this study. Ordinarily, the peaks of the co-eluting species overlap even with the use of a long capillary column of moderate polarity (30 m DB-5 MS) but with appropriate optimisation of the oven temperature, the complete resolution of these congeners was made possible.

3.4.3 *Column flow rate*

The choice of carrier gas employed for GC analysis is important. The use of high purity helium gas (99.999%) employed was preferred because it exhibits a flat baseline. More so, it has been found to improve the separation of low boiling compounds.

Since there is a relationship between the average velocities of the carrier gas, its flow rate and the oven temperature, different carrier gas flow rates were tested to achieve better peak resolution and a relatively fast analysis time. The carrier gas flow rate of 1.5 mL/min was achieved under the optimum GC conditions.

Table 3.3: GC operating parameters optimized for PBDE and BB 153 analyses

Parameters	Operating conditions	
	tri-heptaBDEs	BDE 209
Injection volume (μl)	1, 2 and 5	1, 2 and 5
Injection mode	Splitless	Splitless
Injection temperature ($^{\circ}\text{C}$)	250, 270 and 280	250 , 270 and 280
Column flow rate (mL/min)	1, 1.2, 1.5 , 1.8 and 2.0	1.8, 2.0, 2.5 and 3.0
Column	HP 5MS (30 m, 0.25 mm ID, 0.25 μm film thickness) DB 5 MS (60 m, 0.25 mm ID, 0.10 μm film thickness)	DB 5 MS (6 m, 0.25 mm ID, 0.10 μm film thickness) DB 5 MS (15 m, 0.25 mm ID, 0.10 μm film thickness)
Oven ramping	100 $^{\circ}\text{C}$ ramped at 10 $^{\circ}\text{C/min}$ to 225 $^{\circ}\text{C}$ (5 min.), ramped at 3 $^{\circ}\text{C/min}$ to 300 $^{\circ}\text{C}$ (10 min.). 90 $^{\circ}\text{C}$ (2 min.), ramped at 4 $^{\circ}\text{C/min}$ to 150 $^{\circ}\text{C}$ (5 min.), ramped at 10 $^{\circ}\text{C/min}$ to 220 $^{\circ}\text{C}$ (2 min.), ramped at 5 $^{\circ}\text{C/min}$ to 320 $^{\circ}\text{C}$ (2 min.). 100$^{\circ}\text{C}$ (2 min.) ramped at 20$^{\circ}\text{C/min}$ to 220$^{\circ}\text{C}$, ramped at 4$^{\circ}\text{C/min}$ to 300$^{\circ}\text{C}$ (7 min.).	150 $^{\circ}\text{C}$ ramped at 40 $^{\circ}\text{C/min}$ to 225 $^{\circ}\text{C}$ (5 min.), ramped at 25 $^{\circ}\text{C/min}$ to 310 $^{\circ}\text{C}$ (10 min.). 100$^{\circ}\text{C}$ held for 1 min, ramped at 50$^{\circ}\text{C/min}$ to 150$^{\circ}\text{C}$, ramped at 12.5$^{\circ}\text{C/min}$ 310$^{\circ}\text{C}$. 110 $^{\circ}\text{C}$ ramped at 20 $^{\circ}\text{C/min}$ to 200 $^{\circ}\text{C}$ (5 min.), ramped at 12 $^{\circ}\text{C/min}$ to 300 $^{\circ}\text{C}$ (10 min.).
Detector temperature ($^{\circ}\text{C}$)	250, 270, 280 and 300	250, 270, 280 and 300
Make-up gas (N_2) flow rate (mL/min)	30 , 45 and 60	30, 45 and 60

Optimum operating condition in **bold**

3.4.4 Detector temperature

Generally, it is recommended that detector temperature be higher than the injector temperature during GC analysis. This measure is necessary to avoid re-condensation of the gaseous stream of analytes from the capillary column. The limit to which this could be done is crucial to ensuring a good response of the detector to the target analytes. Since the responses of most GC detectors is temperature dependent, to obtain the appropriate detector temperature is an important task in the analysis of PBDEs. In this study, the detector temperature ranging from 250 to 300 $^{\circ}\text{C}$ were tested and the optimum temperature was 280 $^{\circ}\text{C}$. Other parameters, which were not optimised but equally important for PBDE analysis include: sample injection volume, injection mode (splitless, split or purge split), detector make-up gas flow rate, amongst others.

3.5 Method development for PBDEs and BB 153 analysis in aqueous (landfill leachate, WWTP effluents and river water) samples

The various activities involved in the ultimate assessment of all target analytes in different aqueous samples investigated in this study were discussed in this section.

3.5.1 *Sample collection and preservation*

All the aqueous samples were collected bi-monthly between April 2010 and March 2011. River water samples were collected from the upstream, point of discharge and downstream sampling points of two WWTP-effluent receiving rivers, namely: Diep and Kuils Rivers within the City of Cape Town. Samples (n=6) were also collected from the Black River for method validation purposes. Effluent samples from four WWTPs were collected at different stages of the wastewater purification process, namely: inlet section (raw water); primary settling tank (primary effluent); secondary settling tank (secondary effluent) and disinfection unit (final effluent).

Of the three functional landfill sites within the city, only one has a leachate treatment facility on-site. Leachate from others is usually pumped from the pond or reservoir into a nearby WWTP for treatments. As the case may be, raw and treated leachate samples were collected from the three landfill sites during the study period. All samples were collected in triplicate into thoroughly cleaned 1 l amber glass bottles with amber glass caps throughout the sampling regime. The samples were kept cool *en-route* the laboratory in an ice container. Samples were immediately refrigerated on arrival at the laboratory at 4°C until analysis.

3.5.2 *Sample extraction*

This sub-section outlines the various activities involved in the isolation of the target compounds from the complex matrices in which they are found. In this study, the evaluation of different extraction techniques commonly applied to aqueous samples was investigated. These include: separatory funnel extraction (SFE), magnetic stirring extraction (MSE) and solid-phase extraction (SPE) techniques. For this purpose, ultra-pure MilliQ water (RiOs8™, France) were spiked with standard mixture of all target compounds to be investigated. These were extracted using all the techniques to be evaluated. The procedures employed for each of the techniques were discussed below.

3.5.2.1 *Separatory funnel extraction technique*

About 800 ml of MilliQ water was measured into a thoroughly cleaned 1 l capacity separatory funnel. The water was thereafter spiked with 1 ml of standard solution containing all the target compounds. The set up was allowed to equilibrate for exactly 60 minutes before extraction. Analytes extraction was carried out by shaking the spiked water with 40 ml of dichloromethane for 2 minutes with periodic venting during the extraction. Phase separation of the two layers that results was allowed to take place for about 10 to 15 minutes. The lower organic layer was thereafter collected over anhydrous sodium sulphate into a 250 ml capacity round bottom flask. The extraction of aqueous layer was repeated twice using 40 ml of

dichloromethane in each occasion. The separatory funnel was rinsed twice with 20 mL and 10 mL of dichloromethane in succession after the aqueous layer had been discarded. The extract obtained was concentrated using a rotary evaporator at 45°C to about 1 mL.

3.5.2.2 *Magnetic stirring extraction technique*

Similarly, 800 mL of MilliQ water was measured into a thoroughly cleaned 2 L capacity beaker. The water was spiked and allowed to equilibrate as previously described for the separatory funnel technique. In contrast to the SFE technique, however, the analytes were extracted once using a total of 120 mL dichloromethane with moderately rigorous stirring for 30 minutes by employing a magnetic stirrer (FMH Electronics, South Africa). The phase separation of both aqueous and organic layers was allowed to take place for about 30 minutes. The clear supernatant was thereafter decanted and the bottom layer was transferred into a clean 500 mL capacity separatory funnel for further phase separation. The lower organic layer was then collected over anhydrous sodium sulphate into a pre-cleaned 250 mL capacity round bottom flask. The beaker and separatory funnel used were rinsed with 20 mL and 10 mL of dichloromethane in succession. The extract obtained was thereafter concentrated to about 1 mL using a rotary evaporator.

3.5.2.3 *Solid-phase extraction technique*

This technique began with the initial conditioning of the C-18 cartridges employed. This was done by passing 5 mL of n-hexane, 5 mL of dichloromethane, 5 mL of methanol and 5 mL of MilliQ water in succession through the cartridge at low pressure (1.5 inHg) employing a Visiprep manifold (Sigma-Aldrich). To investigate the influence of pH of aqueous matrices on the recovery of target analytes using SPE cartridges, two different set ups including those with pH adjustment and the other without pH adjustment were investigated. First, the set up with pH adjustment had its pH adjusted to between 2.05 and 2.12 using conc. H₂SO₄ (98% purity), while the other set up maintained its pH between 7.28 and 7.69. These set ups were allowed to equilibrate for 60 minutes after each had been spiked with 1 mL of standard solution containing all the target compounds. Each of the spiked MilliQ water was then extracted by passing it through the pre-conditioned cartridge at a pressure of 10 inHg.

Upon completion of the extraction, the cartridges were vacuum dried for an additional 45 minutes. The analytes were thereafter eluted with 6 mL n-hexane:dichloromethane (1:2) at a pressure of 1.0 inHg with an average flow of 2 drops per 10 seconds. The eluate was subsequently spiked with 300 µL of iso-octane and concentrated under a gentle stream of nitrogen gas to a suitable volume. The extract was then quantitatively transferred into amber samples for instrumental analysis.

3.5.3 Extract clean up procedure

Extracts obtained from both separatory funnel and magnetic stirring techniques were subjected to further purification treatment. The extracts were cleaned on a Pasteur pipette containing different forms of silica gel. The Pasteur pipette packing was done by first clogging its tip with a clean glass wool. This was followed by the addition of 0.1 g activated silica gel; 0.2 g basic silica gel; 0.1 g activated silica gel; 0.4 g 44% acidic silica gel; 0.1 g activated silica gel; 1.0 g anhydrous sodium sulphate) in this sequence from the bottom. The packed column was thereafter conditioned with 5 mL of n-hexane. The extract was carefully and quantitatively transferred into the pre-conditioned column and eluted with 10 mL of n-hexane. The eluate was further concentrated using a rotary evaporator to about 1 mL. The concentrated cleaned extract was then spiked with about 300 µL of iso-octane before the final concentration was done under a gentle stream of nitrogen gas. The prepared samples were stored in amber sample vials and kept in the refrigerator until the final instrumental analysis.

3.6 Method development for PBDEs and BB 153 analysis in solid (bottom river sediment and sewage sludge) samples

The detailed analytical procedures employed for the investigation of PBDEs and BB 153 in bottom sediment of rivers as well as sewage sludge samples were discussed in this section.

3.6.1 Sample collection and preservation

Bottom sediment samples were collected bi-monthly at the same time with freshwater samples from the Diep and Kuils Rivers between April 2010 and March 2011. The samples were collected from the upstream, point of discharge and downstream sampling points of WWTP-effluent receiving rivers. The samples were collected using a stainless steel scoop (often attached to a long wooden stick) into a wide-mouth amber glass bottles.

Sewage sludge samples from five WWTPs were collected from the primary, secondary and de-watered units of each plant. The samples were collected into 1 L wide-mouth amber glass bottles. Because the process design of each plant differs in many respects from one another, the types and number of samples collected from different plants also differ. Of the five WWTPs monitored, three have the conventional activated sludge system, while others have modern membrane bio-reactor (MBR) system. Since the MBR system does not have a primary settling unit, only the de-watered sludge was monitored throughout the study period in the plant. All the samples collected were iced immediately in an ice container and kept in the refrigerator on arrival at the laboratory.

3.6.2 *Sample preparation*

The bottom sediment samples were spread on an aluminium foil previously cleaned with pure acetone. The samples were then dried at 50°C in a vacuum oven. The dried samples were then ground and sieved with 500-micron stainless steel sieve. Samples were stored in a properly labelled 250 mL amber glass bottles and kept in the refrigerator until further analysis was required. Similarly, the different sewage sludge samples (primary, secondary and de-watered) as well as treated (digested and DAF) sludges were oven-dried at 50°C. The dried samples were then ground and sieved with 500-micron stainless steel sieve. The samples were stored in a clean 250 mL capacity amber glass bottles kept in the refrigerator until further analysis was required.

3.6.2.1 *Sample extraction technique for sediment samples*

The efficiency of the mechanical shaking technique employed for the extraction of sediment samples was tested. This was done by first evaluating the extraction efficiencies of three extraction solvent systems, namely: (n-hexane: acetone (1:1,v/v), n-hexane:acetone (2:1,v/v) and n-hexane:dichloromethane (2:1,v/v). For this purpose, 10 g of the pre-extracted sediment samples ($n = 3$) were spiked with a known mixture of all target analytes. Prior to extraction, about 2 g of copper powder was added to all samples to remove any traces of sulphur which can interfere with analytes determination. The spiked samples were thereafter extracted with 120 mL of the extraction solvent combinations.

The influence of extraction time on the overall efficiency of the extraction technique was equally investigated. In this case, four extraction times, namely: 3, 6, 12 and 16 h were evaluated. The solvent combination as well as the extraction time that gave the best recovery of all the target analytes was applied to the analysis of the real field samples. All the field samples were similarly processed as previously described. Although a known amount of surrogate standards (Pentachloronitrobenzene, PCNB and BDE 77) were generally added to the samples prior to the commencement of the extraction. This was done to assess the analytical recoveries of the target analytes in the real samples. Upon completion of the extraction, samples were filtered into a thoroughly cleaned 250 mL round-bottom flask. The filtrate was thereafter concentrated using a rotary evaporator to about 1 mL. The extract obtained was subjected to the purification procedures discussed in section 3.5.3.

3.6.2.2 *Sample extraction technique for sewage sludge samples*

About 5 – 10 g of the dried sewage sludge sample was weighed into a clean glass thimble (Porosity No.4) for Soxhlet extraction. Samples were spiked with known amount of the surrogate standards (Pentachloronitrobenzene and BDE 77) employed to monitor the analytical recovery of the target analytes.

Each of the samples was thereafter extracted with 300 mL of n-hexane:acetone (3:1, v/v) for 16 h. Prior to extraction, however, about 2 g of copper powder was added to each sample to remove traces of elemental sulphur that could possibly interfere with the analytes' determination.

3.6.3 Extract clean-up technique

Several approaches have previously been adopted for the purification of sample extracts containing PBDEs. These include the use of gel permeation chromatography (GPC) and multi-layer silica gel column chromatography (Knoth *et al.*, 2007; Kupper *et al.*, 2008; Yun *et al.*, 2008). In this study, the use of the conventional multi-layer silica column chromatography was employed for the purification sewage sludge extracts. This was done in accordance with the USEPA Draft Method 1614 for the analysis of PBDEs in wastewater and bio-solids, although with some modifications. The extracts obtained were concentrated to about 2 mL using a rotary evaporator. Depending on the degree of viscosity of the extracts obtained, 2 – 3 drops of conc. H_2SO_4 were generally added and gently swirled to allow for proper mixing. These set ups were allowed to stand for about 30 min. before the purification of the extracts on the silica gel column. The glass column was packed from the bottom with 1 g activated silica gel, 4 g of basic silica gel (30% NaOH, w/w), 1 g activated silica gel, 8 g acidic silica gel (44% H_2SO_4 , w/w), 2 g activated silica gel and 4 g anhydrous sodium sulphate.

The packed column was pre-conditioned with 50 mL of doubly-distilled n-hexane to remove trapped air and background contaminants within the column. The n-hexane layer over the uppermost layer in the column was maintained at 2 mm to prevent further infiltration of air into the column. The concentrated extract was then quantitatively transferred into the column and eluted with 125 mL of n-hexane. The eluate was concentrated to about 1 mL using a rotary evaporator. Further concentration of extract was done upon the addition of 300 μL of isooctane under a gentle stream of nitrogen to a suitable volume. The prepared samples were then kept in the refrigerator until the final instrumental analysis.

3.7 Instrumental analyses

In this study, two important and versatile instrumental techniques were employed for the analysis of all the target compounds. First, the routine analysis of all the analytes was done using a GC- μECD (Agilent 6890) while the structural confirmation of these analytes was done using a GC-TOF-MS technique. The GC- μECD was equipped with an Agilent 7890B auto sampler. The chromatographic separation of tri-heptaBDEs as well as BB 153 was performed using a DB-5 MS column (60 m length, 0.25 mm i.d. and 0.1 μm film thickness). Helium gas was employed as the carrier gas with a flow rate of 1.5 mL/min using a

constant flow mode. High purity nitrogen gas was used as a make-up gas for the detector at a flow rate of 30 mL/min. The injector and detector temperatures were set at 280°C and 300°C, respectively.

The oven temperature was programmed as follows: 100°C held for 2 min, ramped at 20°C/min to 220°C; it was further ramped at 4°C/min to 300°C and held for 7 min. A 1 µL of standard and experimental samples was injected using a splitless injection mode. Quantification was based on peak areas of target compounds using external calibration technique. Five to six calibration levels containing 1, 5, 10, 25, 50 and 100 ng/mL for all target compounds except BDE-183 which had a calibration level of 5, 10, 25, 50 and 100 ng/mL. Identification of analyte was done by comparing the retention times with those of reference standards. Similarly, the analysis of BDE 209 was done by employing the GC-µECD technique but with a relatively shorter column (DB-5 MS: 15 m long, 0.25 mm i.d. and 0.1 µm film thickness). The optimum conditions used for its analysis are shown in Table 3.3. An external calibration technique with a single calibration level of 2000 ng/mL was used for its quantification.

The structural elucidation of the investigated compounds was carried out using GC-TOF-MS technique. This analysis was performed at the Central Analytical Facility Unit of the University of Stellenbosch, Cape Town, South Africa. The specification of the equipment as well as the operating conditions employed for the analysis is presented in Table 3.4.

Table 3.4: Specification and the operating conditions of the GC-TOF-MS employed

Parameters	Specification/operating condition
Instrument	Waters GCT equipped with CTC CombiPAL autosampler
Column	HP-5 MS (30 m, 0.25 mm ID, 0.25 µm film thickness)
Injector temperature	280°C
Column flow rate	1 mL/min
Injection volume	2 µL
Injection mode	Splitless
Purge flow	50 mL/min
Purge time	1 min.
Carrier gas	Helium
MS mode	EI ⁺
Source temperature	180°C
Electron energy	70 eV
Re-entrant temperature	150°C
Oven temperature programming	110°C (2 min.), ramped at 25°C/min to 210°C (5 min.), ramped at 20°C/min to 300°C (5 min.), ramped at 50°C/min to 320°C (5 min.).

3.8 Total organic carbon determination

The total organic carbon content of sediment samples were determined by weight loss on ignition method described by Dean (1974). Prior to the gravimetric determination, the sediment samples were dried at 105°C overnight to ensure that there is complete removal of moisture. After obtaining a constant weight of the crucibles, about 5 g of sediment sample was weighed and ignited at 440°C for 4 h. The set up was

allowed to cool and later transferred into a dessicator. The final weight of the ignited sediment was then determined to estimate the total organic carbon content of each sample.

3.9 Quality control and quality assurance

Most of the glass wares employed in this study were amber glass bottles, while those that were not, were shielded with aluminium foil. For instrument performance, regular injection of solvent blanks and standard solutions of target compounds was done before and during instrumental analyses. The sensitivity of the ECD detector was equally assessed through regular injection of a calibration standard (100 ng/mL) before the commencement of real sample analysis. The performance of the methods employed was evaluated by recovery experiments. In this case, a laboratory reference matrix was employed. In most cases, the analysis of surrogate standards was done to monitor the analytical recoveries of compounds of interest. Similarly, the periodic analysis of solvent blanks and procedural blanks were carried out to identify possible sources of sample contamination during analysis. The method detection limit (MDL) was estimated for each compound in different matrices through repeat analysis ($n = 7$) of low spiked samples. MDL is defined as three times the standard deviation of these replicates. All data were processed with Microsoft Excel software (2007 version). For statistical purposes, target compounds whose levels were below the detection limits were assigned zero. Duncan Multiple Range test was done using Statistical Analysis Software SAS version 9 for Windows (2002) developed by SAS Inc. USA. ANOVA and PCA analyses were performed with SPSS 19.

3.10 Calculations

The concentrations of all the target compounds presented in this study were obtained by taking into consideration the following inputs, namely: the sample size analysed, the analyte concentration obtained after injection and the final volume of extract analysed. Depending on the sample type, the final concentration of each analyte was reported as either nanogram per gram (ng/g) or nanogram per litre (ng/L).

For the solid samples, the formula given below was applied for the estimation of the target compounds.

$$\text{Conc. of analyte (ng/g)} = \frac{\text{conc. of analyte (ng/mL)} \times \text{total volume of extract (mL)}}{\text{mass of sample (g)}} \quad \text{Equation 3.1}$$

Similarly, the analytes' concentrations in the aqueous samples were obtained using the equation given below.

$$\text{Conc. of analyte (ng/}\ell\text{)} = \frac{\text{conc. of analyte (ng/mL)} \times \text{total volume of extract (mL)}}{\text{volume of sample (}\ell\text{)}} \quad \text{Equation 3.2}$$

The estimation of percent organic carbon content of each sediment sample determined with the equation given below:

$$\text{Total organic carbon (TOC) (\%)} = \frac{X - Y}{X} \times \frac{100}{1} \quad \text{Equation 3.3}$$

where: X = initial weight of crucible and sediment before ignition (g)

Y = final weight of crucible and sediment after ignition (g).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Method development for the analysis of aqueous and solid samples

The analytical procedures outlined in the draft USEPA Method 1614 for the analysis of PBDEs in wastewater and biosolid was used as a guide in the development of an appropriate technique employed in this study. However, there were certain aspects of these procedures which were partially or completely modified during the method development processes. The detailed modifications carried out as well as the evaluation of the performance of the developed method are discussed in this section.

4.1.1 Optimisation of the extraction and clean up techniques

The appropriateness of three different extraction techniques for the aqueous samples was evaluated. These include separatory funnel, magnetic stirring and solid-phase extraction techniques. To assess the extraction efficiencies of these techniques, spiked MilliQ water samples were extracted by each technique to be investigated. Although there are other sophisticated techniques (Llorca-Porcel *et al.*, 2006; Fontana *et al.*, 2009), which could have been employed for the extraction process, the choice of the extraction techniques evaluated was based on the need to ensure the feasibility of this study.

Most of the techniques selected for evaluation have either been employed for the assessment of PBDEs or other similar contaminants such as PCBs, organochlorine pesticides, phenols amongst others in aqueous matrices (Pauwels *et al.*, 1999; Covaci and Schepens, 2001). The results indicating the extraction efficiency of each of these techniques are presented in Table 4.1. Based on these findings, it was apparent that the separatory funnel technique had the best extraction efficiency for most of the congeners investigated. Although a good recovery of these congeners was also achieved with the magnetic stirring technique, the majority of the congeners were efficiently isolated with the separatory funnel technique. Both techniques employ dispersion of fine droplets generated by the agitation of the aqueous samples present in the extraction chamber. The isolation of the compounds of interest is therefore achieved with the continuous contact maintained between the aqueous and organic droplets within the chamber.

In contrast, the solid-phase technique effects the extraction of these compounds through adsorption mechanism. Essentially, the technique explores the differential affinities of components present in the aqueous matrix to effect the isolation or purification of the desired compounds (Rouessac and Rouessac, 2007). Besides the numerous advantages this technique offers, which include ease of automation, higher recoveries of polar compounds and cleaner extracts, certain problems are still associated with the use of this technique. These include incomplete removal of interferences, low recovery of analytes and high degree of variability (in terms of relative standard deviation (RSD)).

The recoveries of PBDEs as well as BB 153 employing this technique were generally low. A slight improvement in the extraction efficiency was observed when the pH of the aqueous medium was adjusted as shown in Figure 4.1. It therefore implies that the recovery of these contaminants could be enhanced by simply acidifying the aqueous medium containing them if SPE technique is to be employed for their extraction. Another aspect where certain modifications were carried out during the method development was in the clean up procedure. While the conventional silica gel column chromatography was used for the purification of the sewage sludge extracts, a modified clean up technique was employed for the extracts of bottom sediment and aqueous samples investigated in this study.

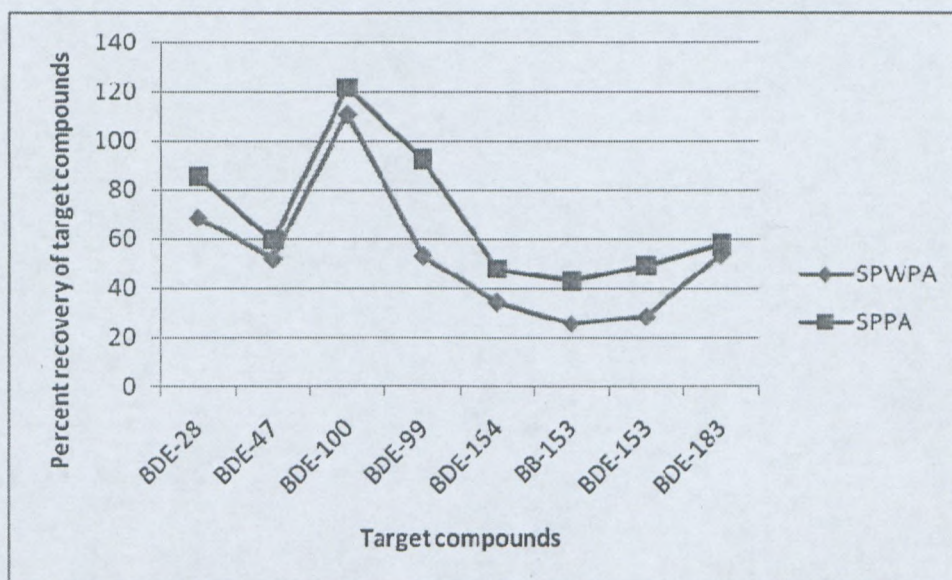


Figure 4.1: Influence of pH adjustment on the recovery of target compounds

(SPWPA – solid phase extraction without pH adjustment; SPPA –solid phase extraction with pH adjustment)

Considering the number of samples to be analysed, methods which will ensure minimal usage of both eluting solvent and adsorbent materials are highly essential. Consequently, the use of Pasteur pipette packed with different forms of silica gel for “clean-up” ensured that this objective was achieved. The methods adopted to achieve this objective involved the use of equivalent ratios of different forms of the adsorbent used in established conventional methods. In this case, the draft USEPA Method 1614 was employed.

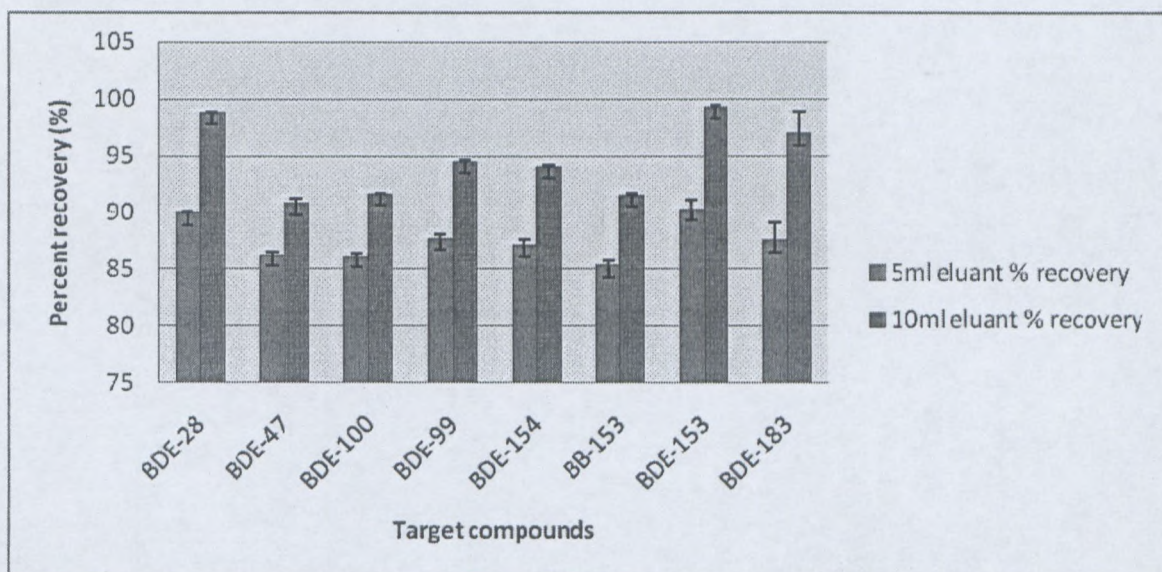


Figure 4.2: Percent recovery of target compounds using different eluting volumes on modified clean up technique

Furthermore, the use of different volumes of eluting solvent evaluated in this study was guided by information obtained from previous knowledge retrieved from the literature (USEPA, 2007; Gevaio *et al.*, 2008; Yun *et al.*, 2008).

An attempt was made to compare the efficiency of the modified Pasteur pipette technique with the conventional glass column method. During the preliminary studies, both techniques were optimised using varying volumes of the eluting solvent. This measure was undertaken to establish the optimum volume of the eluting solvent required for both techniques. The outcomes of these investigations are presented in Table 4.2 and Figure 4.2. Figure 4.2 shows the recovery of target analytes using the modified technique. With this technique, a yield greater than 85% was achieved with the use of 5 ml of the eluting solvent. Recoveries comparable to those obtained with 125 ml of the eluting solvent in the conventional glass column technique were achieved when 10 ml of the eluting solvent was used. With these modification measures, the conservation of up to 92% of the eluting solvent and 88.1% of the sorbent was achieved relative to the conventional glass column chromatographic technique investigated in this study. Although the modified technique proved to offer improved separation of analytes, fast and cost-effective; its major setback was decreased efficiency with the age of the sorbent materials employed. Consequently, the use of freshly prepared sorbents must be employed in order to obtain acceptable results.

Table 4.1: Percent recoveries of target compounds obtained from different extraction techniques

Target compounds	Spiked concentration (ng/ml)	SFM			MSM			SPWPA			SPPA		
		Concentration recovered (ng/ml)	% Recovery	Concentration recovered (ng/ml)	% Recovery	Concentration recovered (ng/ml)	% Recovery	Concentration recovered (ng/ml)	% Recovery	Concentration recovered (ng/ml)	% Recovery		
BDE 28	10	7.94±0.13 ^a	79.40	8.14±0.19 ^a	81.40	6.89±0.43	68.90	8.58±0.21	85.80				
BDE 47	10	8.93±0.35	89.30	8.41±0.22	84.10	5.23±1.77	52.30	5.97±1.62	59.70				
BDE 100	10	7.36±0.93	73.60	6.47±1.05	64.70	11.1±2.19	111	16.2±0.55	162				
BDE 99	10	8.41±0.27	84.10	7.24±0.42	72.50	5.35±2.26	53.50	9.30±5.37	93.00				
BDE 154	10	7.80±0.40	78.00	7.21±0.51	72.10	3.45±0.15	34.50	4.79±0.12	47.90				
BB 153	10	7.16±0.53	71.60	6.50±0.43	65.00	2.57±0.21	25.70	4.32±0.30	43.20				
BDE 153	10	8.18±0.51	81.80	7.29±0.71	72.90	2.86±0.56	28.60	4.93±1.31	49.30				
BDE 183	10	7.81±2.38	78.10	7.78±1.22	77.80	5.40±0.98	54.00	5.78±1.48	57.80				

^a – values represent mean (±standard deviation) of six replicates and three replicates for SPWPA and SPPA; SFM – separatory funnel extraction method; MSM – magnetic stirring extraction method; SPWPA – solid phase extraction without pH adjustment; SPPA – solid phase extraction with pH adjustment.

Table 4.2: Mean percent recovery of target compounds with the conventional glass column clean up technique.

Target compounds	Percent recovery (%)				
	Volume of eluting solvent				
	25 ml	50 ml	75 ml	100 ml	125 ml
BDE 28	-	7.11	92.90	95.20	95.90
BDE 47	-	12.40	94.00	95.70	97.10
BDE 100	-	66.00	94.60	97.40	98.50
BDE 99	-	47.90	96.30	99.30	101
BDE 154	-	70.10	93.70	100	101
BB 153	-	82.80	100	100	104
BDE 153	-	68.80	97.10	103	104
BDE 183	-	71.70	93.20	95.90	98.80
BDE 209	NA	NA	NA	NA	NA

NA – not analysed.

4.1.2 Optimisation of extraction techniques for the solid samples

The procedures required for the isolation of target compounds from solid matrices is critical to their successful determination. In this study, the bottom sediment and sewage sludge samples were extracted with mechanical shaking and soxhlet extraction techniques, respectively. In the literature, the application of soxhlet apparatus for the extraction of PBDEs and other similar contaminants abounds. However, the use of mechanical shaking technique for the extraction of PBDEs is hardly reported. This, of course, could be due to its relatively longer extraction time relative to newer techniques such as SFE, MAE, and ASE amongst others, commonly employed nowadays.

As previously mentioned, the need to ensure the feasibility of this study so as to be able to fill the wide knowledge gap in PBDEs levels in Sub-Sahara Africa is the driving force behind this study. Consequently, the analysis of these contaminants in sewage sludge samples was done in accordance with established protocols reported in the literature (Gevao *et al.*, 2008). There were certain modifications which were made during the method development processes. These include the use of 5 – 10 g of dried sludge sample rather than the 15 – 20 g wet weight that was used. More so, the use of BDE 35 and 181 to monitor the analytical recoveries of target compounds was replaced with pentachloronitrobenzene (PCNB) and BDE 77. The selected surrogate standards were employed because they were not commonly found in different environmental samples investigated in this study.

For the mechanical shaking technique, some parameters were specifically optimised. These include the extraction time and solvent combination employed. The choice of 10 g of sediment sample employed in this method was based on the recommendation contained in the draft USEPA Method 1614 for the analysis of PBDEs in environmental samples (USEPA, 2007). Solvent combinations commonly employed for PBDE analysis were tested. In this study, the extraction efficiencies of n-hexane:acetone (1:1), n-

hexane:dichloromethane (2:1) and n-hexane:acetone (2:1) were evaluated. The use of similar volume ratios (2:1) for the last two combinations was deliberate. This was done to allow for comparative evaluation of n-hexane:dichloromethane (2:1) and n-hexane:acetone (2:1).

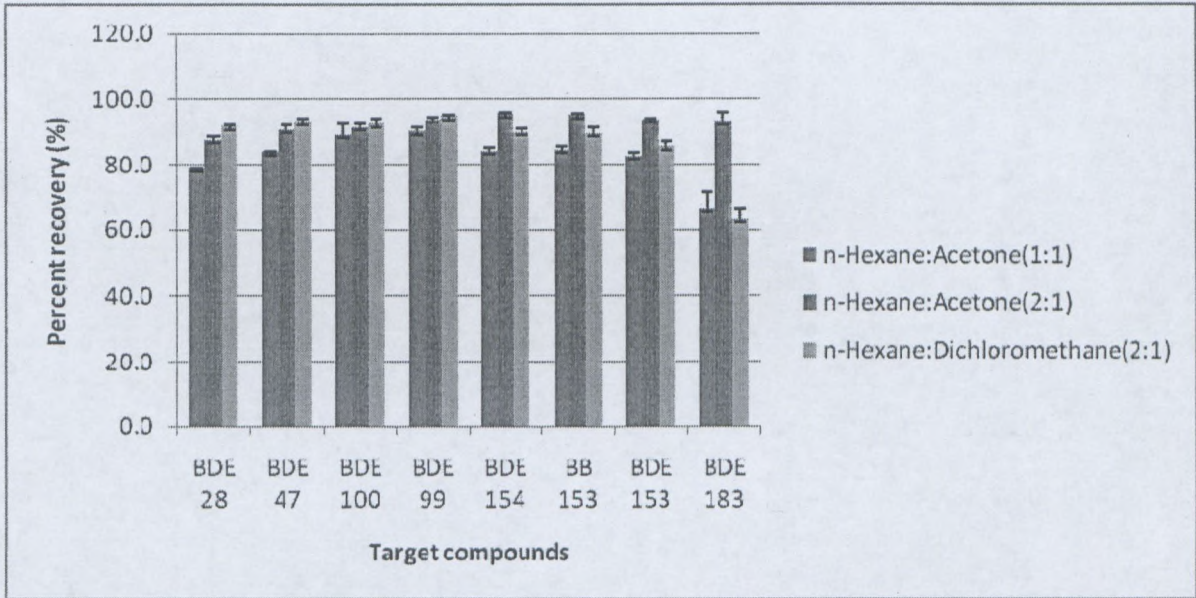


Figure 4.3: Mean percent recovery of target compounds using different extraction solvent combinations (error bars correspond to standard deviation of three replicates)

As shown in Figure 4.3, the former gave good recoveries of the lower brominated congeners, while the latter had a relatively better recovery of all the target compounds, particularly for the highly brominated congeners. Furthermore, the influence of the extraction time on the overall efficiency of the proposed method was also investigated. In this case, four different extraction times (3, 6, 12 and 16 h) were evaluated.

The percent recoveries of target compounds in the spiked sediment samples at different extraction times are shown in Table 4.3. No statistically significant difference ($p > 0.05$) was observed when the extraction time was increased beyond 12 h. Hence, the extraction time was considered as the optimum for the proposed method. A reduction in the overall recovery of BDE 28 was, however, observed when the spiked samples were extracted for 16 h. This is probably due to its relatively lower molecular weight which could have possibly enhanced its volatilisation. In general, possible losses of analytes could result through volatilisation especially during the concentration steps, adhesion of analytes onto the inner surface of glass container, thermal degradation in GC injector and/or incomplete recovery of analytes during extract clean up steps (de Wit, 2002).

Table 4.3: Mean recoveries of target compounds in spiked sediment samples at different extraction times

Target compounds	Amount spiked (ng)	Extraction time							
		3 h		6 h		12 h		16 h	
		Amount recovered (ng)	Percent recovered (%)	Amount recovered (ng)	Percent recovered (%)	Amount recovered (ng)	Percent recovered (%)	Amount recovered (ng)	Percent recovered (%)
BDE 28	5.09	4.21	82.90	4.89	96.20	5.07	100	4.59	90.30
BDE 47	3.72	3.07	82.60	3.89	105	4.27	115	3.78	102
BDE 100	3.60	3.16	87.90	3.89	108	4.36	121	4.40	122
BDE 99	2.61	2.47	94.80	2.59	99.10	3.06	117	3.39	130
BDE 154	3.01	2.31	76.60	2.76	91.60	3.55	118	3.81	126
BB 153	2.05	1.66	81.20	1.92	93.60	2.49	122	2.51	122
BDE 153	2.55	2.03	79.40	2.38	93.30	2.73	107	2.58	101
BDE 183	2.03	1.99	98.30	2.18	108	2.29	113	2.43	120

values reported represent mean of duplicate analyses

4.2. GC optimisation

In this study, several GC conditions were optimised. These include injection volume, injector and detector temperatures, oven temperature and carrier and make-up gases' flow rates, amongst others. The optimum conditions obtained for these parameters for GC-ECD technique are shown in Table 3.3 (Chapter 3). These conditions gave a good resolution of all the target compounds investigated. A typical chromatogram obtained for the PBDE mixtures as well as BB 153 for the GC-ECD technique is shown in Figure 4.4. Due to its ease of operation and maintenance, robustness and high sensitivity to halogen-containing compounds, the GC-ECD technique was employed for the routine analysis. The quantification of all the compounds of interest was carried out using this technique.

Similar parameters in the GC-TOF-MS instrument, which was only used for qualitative purpose, were also optimized. The optimum conditions employed are shown in Table 3.4 (Chapter 3), while typical chromatograms of target compounds and surrogate standards in a representative final effluent and mixed standards are shown in Figure 4.5. The GC-TOF-MS, which was operated in EI mode, provided structural information from the characteristic base and fragment ions of the target compounds. Both the pre-determined target ions as well as the retention times of these compounds were used to obtain the qualitative information needed. Typical extracted ion spectra for BDE 47 obtained from the technique are shown in Figure 4.6., while the target and confirmatory ions monitored for each compound are presented in Table 4.4.

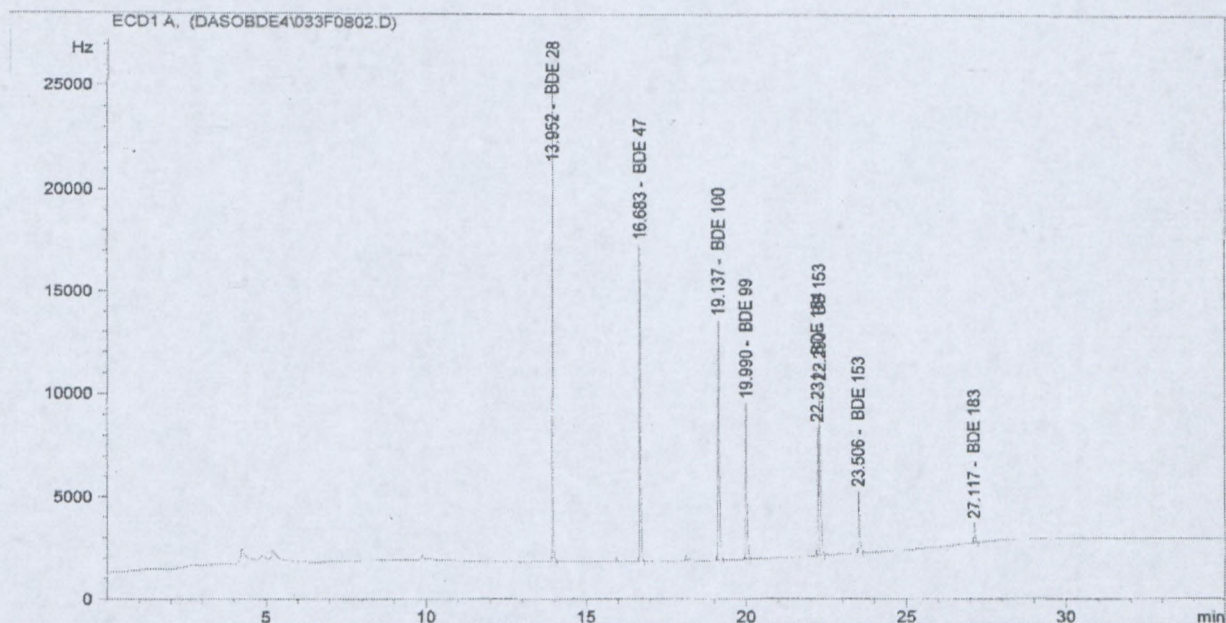


Figure 4.4: A chromatogram of PBDE congeners and BB 153 (100 ng/ml) without the surrogate standards

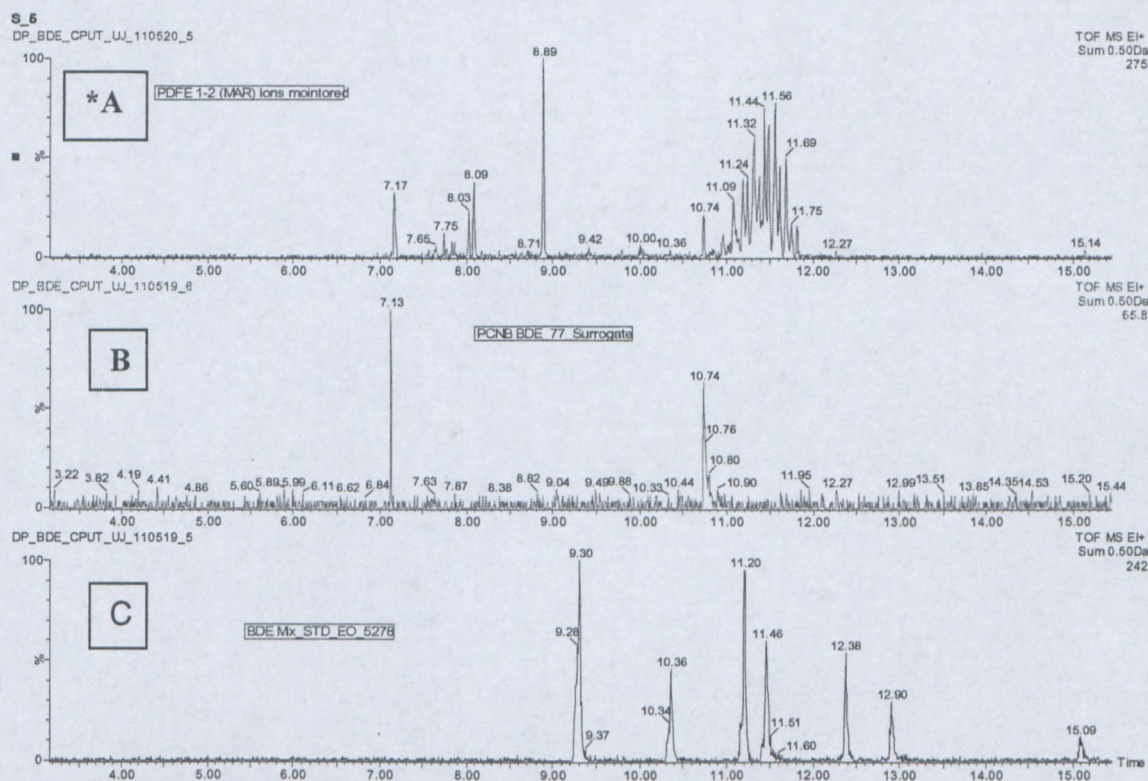


Figure 4.5: GC-TOF-MS chromatograms of [A] a representative Potsdam final effluent, [B] surrogate standards (PCNB and BDE 77) and [C] PBDE mixed standards (EO 5278)

*A – represents extracted GC-TOF-MS chromatogram

Table 4.4: Target ions of selected PBDE congeners, BB 153 and surrogate standards monitored with the GC-TOF-MS

Target compounds	Retention time (min.)	Target ions (m/z)
PCNB (surrogate standard 1)	7.13	294 , 264, 248, 236, 213, 176
BDE 28	9.30	405 , 327, 247
BDE 47	10.36	485 , 325, 263
BDE 77 (surrogate standard 2)	10.74	485 , 405, 325, 246
BDE 100	11.20	563, 405 , 296
BDE 99	11.46	563, 483, 405
BDE 154	12.38	643 , 483, 565
BB 153	12.38	627 , 546, 467, 307
BDE 153	12.90	643 , 563, 483
BDE 183	15.09	721 , 643, 561

bold numbers – represent confirmatory ions for each target compound

A common problem with the simultaneous determination of PBDEs with other similar contaminants is the imminent co-elution amongst the congeners. This problem was encountered in this study as both BDE 154 and BB 153 co-eluted giving rise to a single peak. This scenario makes the quantification of these congeners extremely difficult, hence, there is need to resolve the co-eluting peaks. Two different GC column types having different lengths (30 and 60 m) were tested. With several optimisation measures, the peaks could not be resolved using the 30 m column. However, the optimisation of the GC conditions made the resolution of these peaks possible on the 60 m column. The chromatogram showing the resolved peaks under the optimum conditions is presented in Figure 4.7.

The extensive investigation on seven different GC columns by Korytar and co-workers (2005) had led to the development of a database which made the choice of an appropriate GC column less critical. The outcome of their study does not only allow for a proper selection of GC columns but ensures that the prediction of elution order of PBDE congeners on these columns can easily be made. A major contribution of this study was the possibility of overcoming co-elution problems associated with the principal PBDE congeners with the proper selection of GC columns (Korytar *et al.*, 2005). Similarly, the influence of injection techniques and GC capillary column systems was investigated. Bjorklund *et al.* (2004) concluded that both the injection technique as well as the type of capillary column employed in PBDE analysis would determine to a large extent their yield from the chromatographic system and the precision of the determination. Several other methods have been used to overcome the problems of co-elution amongst PBDE congeners. These include the use of multidimensional GC x GC systems and high resolution mass spectrometry (Clarke *et al.*, 2008; 2010; Gevao *et al.*, 2008).

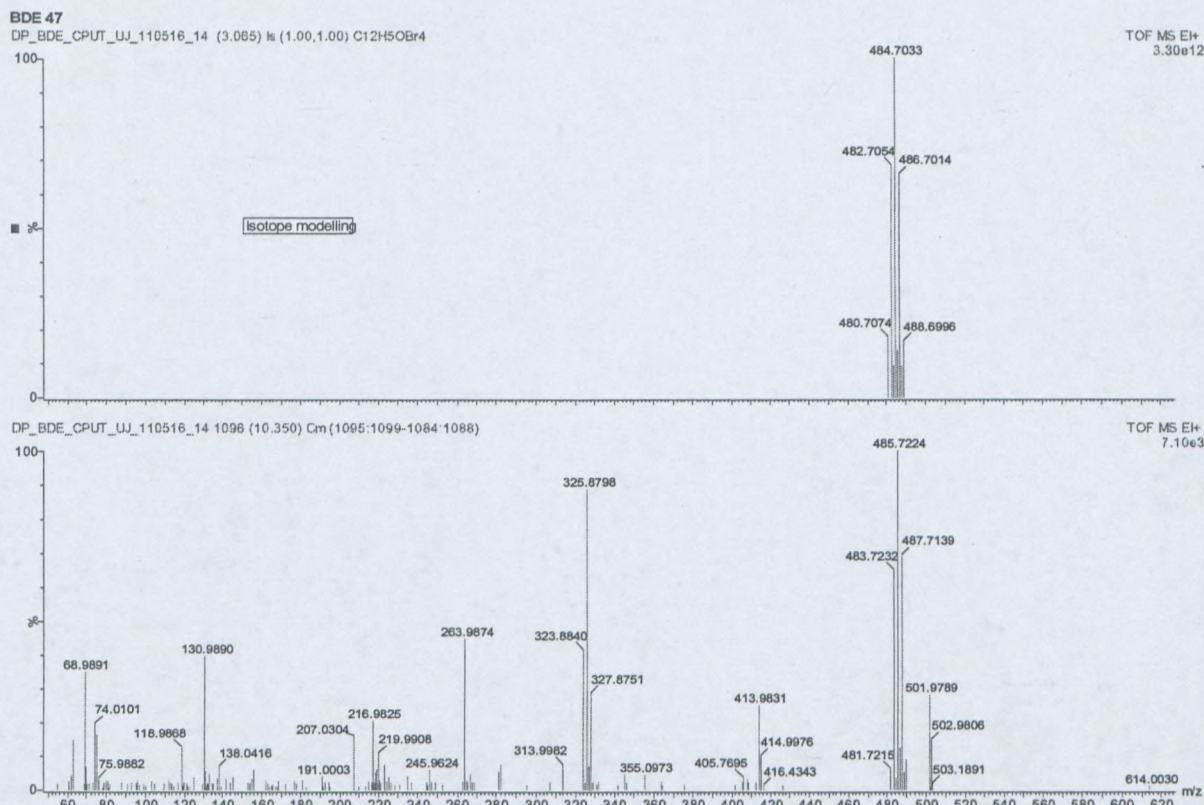


Figure 4.6: Mass spectra showing the extracted confirmatory and target ions for BDE 47

Recent approaches involve the use of liquid chromatographic techniques for the analysis of PBDEs. Zhou *et al.* (2010) successfully developed a novel LC-APCI-MS/MS technique for the analysis of several halogenated flame retardants, including PBDEs. With this measure, certain analytical challenges associated with the use of GC were overcome. Notable amongst these are incomplete volatilisation of target compounds, the need for derivatization of non-volatile species and limited applicability of the GC technique.

The analysis of BDE 209 is generally problematic. Besides the thermal as well as photo-degradation problems associated with this congener, its analysis requires having a certain level of expertise in GC analysis. In this study, several challenges were faced during its determination in various matrices investigated. The chief amongst these was the instability of the reference standard sourced from the local supplier. Since the congener was known to degrade at relatively high injector and oven temperatures, it was difficult to timely recognise this problem. The problem was, however, identified when a new reference standard from the same supplier was used. Due to some of these challenges, it was difficult to incorporate this congener with the other congeners during the preliminary studies. Therefore, the determination of BDE 209 would require a separate analysis to be carried out.

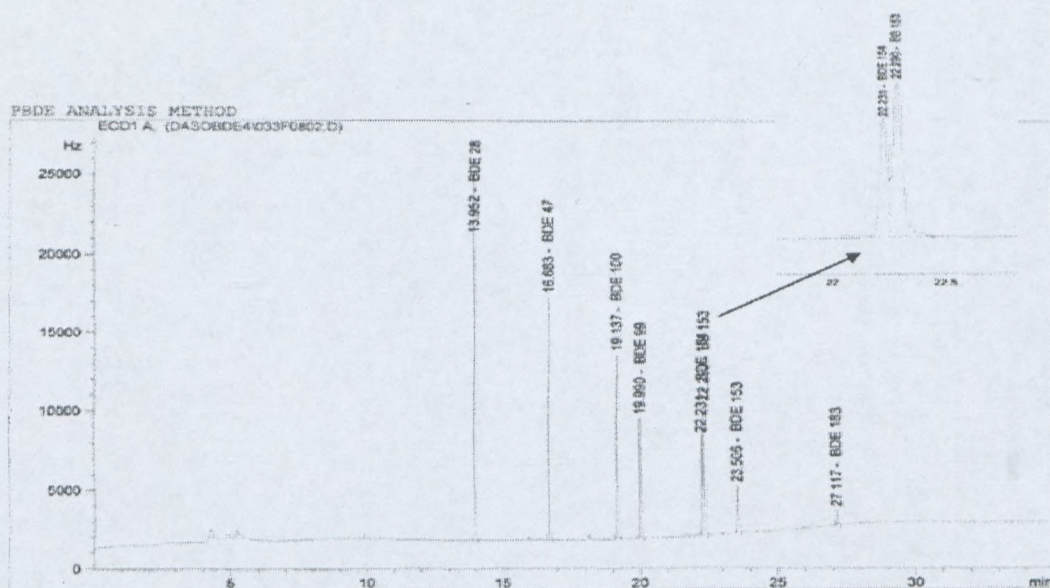


Figure 4.7: A chromatogram showing the resolution of co-eluting BDE 154 and BB 153

4.3 Method performance and evaluation

It is essential that analytical methods developed for the assessment of environmental pollutants are validated. This step does not only ascertain the presence of these contaminants but also guarantees the reliability of the results obtained. For this purpose, certain tests such as linearity, repeatability, sensitivities and recovery studies were performed to establish the suitability of the proposed method.

4.3.1 Retention times of the target compounds

The elution pattern of organic contaminants during GC analysis differs greatly depending on the degree of polarity of the stationary phase of the capillary column employed. In this study, capillary columns with non-polar stationary phase (5% dimethyl-95% phenyl polysiloxane, DB 5-MS) of varying lengths were employed. The choice of the length depends on the type of compounds to be analysed. The shorter column (15 m) was used for the analysis of BDE 209, while a longer column (60 m) was used for the analysis of other compounds. These compounds were eluted based on their molecular sizes where compounds with lower molecular weight eluted first and the heavier molecules thereafter. The order of elution of these compounds is indicated in a typical chromatogram shown in Figure 4.4.

In this study, the same GC instrument but with different capillary column types was employed for all the target compounds. However, due to the requirement for a separate analysis for BDE 209, the installed column was changed severally for this purpose. In doing this, it is recommended that 5 – 10 cm of the both sides of the column be cut off whenever the column is being changed to avoid the possible clogging of the column which might have occurred during storage. Hence, the reason for the slight drift in the retention times of the target compounds investigated as might be noted in the chromatograms of the real samples. However, appropriate measures, including re-calibration of the capillary column and the calibration plots to avoid imminent problems of peak identification and quantification was regularly carried out.

4.3.2 *Linearity, precision and accuracy*

The linear response of detector in any analytical equipment to varying concentrations of the target analytes must be evaluated. In this study, external calibration plot was employed for the quantification of target analytes in the environmental samples investigated. Hence, the need to establish the linear range of the detector used is essential. The linear range employed for the tri-hexaBDEs as well as BB 153 was 1 – 100 ng/mL while BDE 183 had a linear range of 5 – 100 ng/mL. In these cases, the correlation co-efficient (R^2) was greater than 0.999 indicating an excellent response of the detector to the target compounds. However, due to the instability problems encountered with BDE 209, a single calibration plot (2000 ng/mL) was employed for its quantification. Since it was commonly found in environmental samples at much higher concentrations than other congeners, a higher calibration range was used to accommodate the expected concentrations in the various samples investigated.

The precision of the method was assessed through repeatability tests which were performed using 8 - 26 ng/mL concentrations of all the target compounds which was injected consecutively seven times on different days. The relative standard deviations (RSD) of these measurements were thereafter estimated. The results obtained are shown in Table 4.5. Similarly, the accuracy of the method was assessed through recovery studies. Since there was no certified reference materials for most of the matrices investigated, matrix spike experiments were employed. In this case, a known amount of different environmental matrices to be investigated was spiked with a known volume of the mixed standard solution containing all the target compounds. After equilibration, the spiked samples were taken through the entire analytical procedures for each of the sample types previously discussed in Chapter 3. The amount of the analytes recovered was determined and the percent recovery was estimated.

Table 4.5: Linearity and precision evaluation of the developed method

Target compounds	Linearity (R ²)	Repeatability tests		
		Concentration (ng/ml)	Mean±standard deviation	Relative Standard Deviation (RSD)
BDE 28	0.99998	14.00	14.10±0.20	1.42
BDE 47	0.99997	15.40	15.60±0.21	1.35
BDE 100	0.99998	15.50	15.60±0.22	1.41
BDE 99	0.99986	17.20	17.60±0.17	0.97
BDE 154	0.99995	12.20	12.30±0.18	1.46
BB 153	0.99991	26.10	26.30±0.21	0.80
BDE 153	0.99961	14.90	15.80±0.28	1.77
BDE 183	0.99928	8.12	8.17±0.11	1.35
BDE 209	1.00000	25.00	24.80±0.45	1.81

The results of the recovery studies performed for different sample types monitored in this study are shown in Table 4.7. The percent recoveries for these sample types ranged from 105 to 184, 95.5 to 157, 106 to 131, 50.1 to 136 and 68.7 to 97.3 for sewage sludge, WWTP primary effluent, riverwater, treated leachate and MilliQ water samples, respectively.

4.3.3 Recovery of surrogate standards and spiked standards

Both PCNB and BDE 77 were employed as surrogate standards to assess the analytical recoveries of the target compounds in different matrices investigated. Unfortunately, due to the late delivery of these standards, some samples were already analysed before their delivery. The outcomes of the preliminary recovery studies conducted for all the target compounds were used as a guide when the surrogate standards were not available. Hence, a separate calibration plot was prepared for the quantitation of the surrogate standards. The chromatogram showing the target compounds as well as the surrogate standards is indicated in Figure 4.8. The average percent recoveries of the target compounds and the surrogate standards are presented in Table 4.6.

Table 4.6: Percent recoveries of target compounds and surrogate standards in different matrices investigated

Target compounds	Sludge	Sediment	Riverwater	Treated leachate	Primary effluent	MilliQ water
PCNB (SS1)	97.20±0.12	86.70±1.48	103±0.45	72.30±0.87	96.20±1.21	98.80±0.34
BDE 28	107±0.04	110±12.90	129±1.52	65.60±0.17	140±1.63	94.50±1.51
BDE 47	135±0.11	96.10±7.01	131±1.34	73.60±0.34	121±0.43	97.30±1.97
BDE 77 (SS2)	74.90±0.82	71.70±1.64	98.90±1.11	58.40±1.91	75.20±0.53	87.90±1.03
BDE 100	166±0.11	94.10±4.38	122±1.02	57.30±0.22	122±0.82	83.80±0.35
BDE 99	184±0.26	97.40±6.42	115±1.22	54.00±0.20	112±1.17	85.60±4.70
BDE 154	118±0.04	98.60±5.80	108±1.06	55.10±1.28	95.50±3.23	68.70±0.81
BB 153	132±0.03	103±7.07	106±1.05	54.00±0.20	112±1.65	69.10±0.05
BDE 153	135±0.03	96.60±4.93	121±0.80	136±8.25	157±9.58	80.30±5.11
BDE 183	105±0.22	84.40±6.71	107±0.48	50.10±3.29	104±2.03	78.70±6.54

SS1 – surrogate standard 1; SS2 – surrogate standard 2.

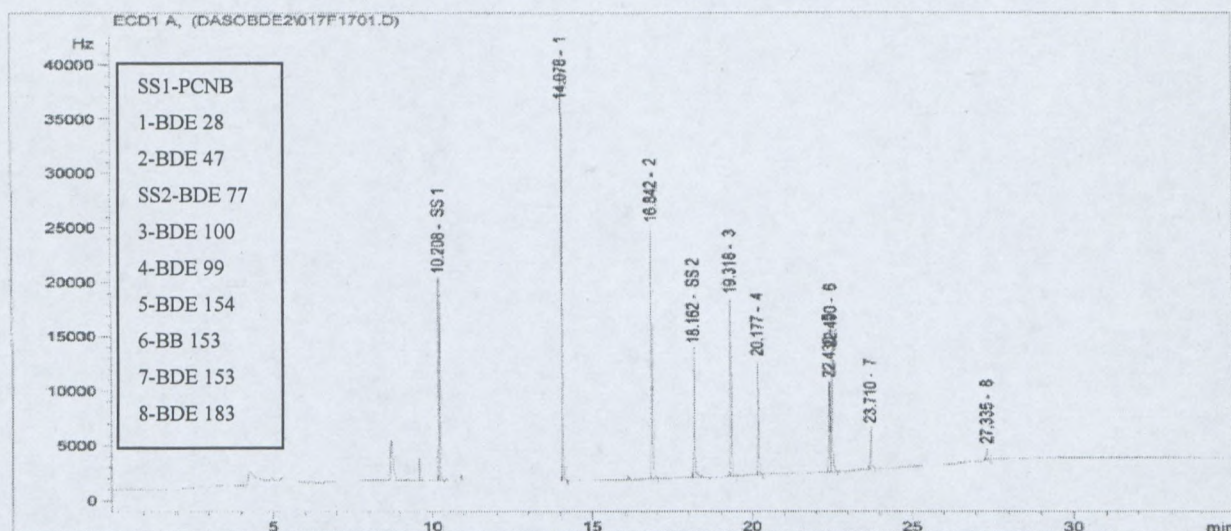


Figure 4.8: A chromatogram showing the target compounds as well as the surrogate standards (100 ng/ml)

4.3.4 Method detection limit (MDL) and instrument detection limit (IDL)

The method detection limit indicates the sensitivity of a given analytical method to test compounds. It is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analytes concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analytes (Wisconsin's Department of Natural Resources, 1996). Similarly, the instrument detection limit refers to the minimum concentration of analytes, which an analytical instrument can detect that can be distinguished from the background noise. Several approaches have been put forward for the estimation of MDL. These include the signal to noise (S/N) ratio, the use of blanks and derivation from calibration plots.

In this study, the method proposed by the United States' Wisconsin Department of National Resources Laboratory Certification Program was used. This method involves the use of low-spike samples with a minimum of seven replicates for the estimation of the MDL. MDL values are statistically determined where the standard deviation of the replicate analysis is multiplied by the t-value obtained from the degree of freedom of the number of samples analysed. Essentially, MDL values are both analytes and matrix specific. The results obtained for different sample types investigated are shown in Table 4.7.

Table 4.7: MDL values for different matrices investigated

Target compounds	IDL (ng/l)	Sludge (ng/g)	Sediment (ng/g)	Riverwater (ng/l)	Treated leachate (ng/l)	Primary effluent (ng/l)
BDE 28	1.00	0.04	0.08	0.67	0.30	0.94
BDE 47	1.00	0.11	0.06	0.89	0.42	0.43
BDE 100	1.00	0.11	0.03	1.02	0.83	0.61
BDE 99	1.00	0.26	0.07	0.33	0.81	0.83
BDE 154	1.00	0.04	0.05	0.81	0.60	0.96
BB 153	1.00	0.03	0.09	1.54	1.45	1.52
BDE 153	1.00	0.03	0.08	0.16	0.81	0.61
BDE 183	2.50	0.22	0.13	0.25	1.52	0.35
BDE 209	5.00	0.25	NA	NA	NA□	NA

□NA – not analysed; IDL – instrument detection limit.

4.4 Environmental levels of target compounds investigated

The assessment of the various environmental components for selected PBDE congeners as well as BB 153 was conducted. This section attempts to present and discuss the findings of this study with respect to the observed trends in different sample types investigated, congener profiling of the contaminants and seasonal variability observed in their levels.

4.4.1 PBDE occurrence in landfill leachate

The results obtained for the analysis of selected PBDEs and BB 153 in leachate samples collected from the three landfill sites are presented in Table 4.8. The overall mean concentrations of the total PBDEs, including BDE 209 ranged between 5.65 – 2240, 0.28 – 20.5 and 1.66 – 1170 ng/l for Bellville, Coastal Park and Vissershok landfill sites, respectively. The mean concentrations of BB 153, which were generally low in most of the samples analysed, were 70.4, 7.14 and 8.16 ng/l for Bellville, Coastal Park and Vissershok sites, respectively.

The observed trend in PBDE levels in these landfill sites is not surprising. The City of Cape Town is the second largest city in South Africa with its current waste generation growing at 7% per annum. According to the 2002 – 2003 figures, about 2.3 million tonnes of waste were generated by residents, visitors and businesses, which transported to various landfill sites in Cape Town (CCT, 2011). Today, only three of the six landfill sites in the city are operational and these are filling up faster than expected.

Of the three operational landfill sites, only the Vissershok site is designated to handle hazardous waste materials. Others mainly receive residential and non-hazardous industrial waste materials.

The time required for these waste materials to degrade depends largely on the type of waste, the moisture content within the landfill and other variables (CCT, 2011). Amongst these variables, the frequency of precipitation, temperature as well as the age of the landfill site could significantly influence the quality

and quantity of leachate produced from a particular site. The combination of these factors plays a critical role in the pattern of results observed in this study.

In this study, the highest concentration of total PBDE was found during the September sampling regime at the Bellville landfill site. All the congeners except BDE 28 and 209 had relatively high concentrations during this period than was observed in other sampling periods. Since this period coincides with the late winter and early spring season, it is assumed that the high frequency of rain witnessed during the winter season could have triggered the rapid release of these contaminants from the disposed materials. A similar trend was also observed for most of the congeners at the Vissershok site during the same sampling period. In this case, both BDE 154 and BB 153 were not detected in the samples analysed. Although relatively high concentrations of most of the congeners were found at the Vissershok site, the overall trend of the results obtained for the Coastal Park site was similar to those observed at the Vissershok site. This suggests that the possible sources of these contaminants might be similar in both sites.

A common source of these contaminants is the disposal of WWTP derived sludge, which are often land filled in these sites. Sewage sludge is an important sink of organic pollutants, including PBDEs (De la Torre *et al.*, 2011). During wastewater treatment, a considerable amount of these contaminants tends to accumulate in settled sludge, which could disperse if disposed in dumpsites or when applied to agricultural soils. In addition, leachate from both sites drain into properly lined ponds, which were constructed in accordance with the DWAF guidelines for waste disposal by landfill (DWAF, 1998), whereas leachate from the Bellville site drains into an underground concrete reservoir where it is pumped for treatment at a nearby WWTP. The observed differences in PBDE levels in these landfill sites could possibly be due to the method employed for leachate collection at different sites. It is possible that organic matter present in bottom sediment of leachate ponds at both Vissershok and Coastal Park could influence the availability of these contaminants. PBDEs, like most organic pollutants, could bind strongly with suspended organic matter present in aqueous matrices (Gorgy *et al.*, 2010).

Table 4.8: Mean (±standard deviation) concentrations (ng/l) of selected PBDE congeners and BB 153 in landfill leachate samples

Sampling Location	Sampling period	Target compounds										$\sum_{i=1}^n \text{PBDEs}$
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209	$\sum_{i=1}^n \text{PBDEs}$	
Belville (S33°56'05", E18°38'24")	May, '10	ND	8.91±0.24	0.47±0.23	1.38±0.24	0.29±0.51	ND	0.74±1.28	NID	2400±1150	1.68 (35.40)	302 (7240)
	Jul, '10	0.57±0.24	0.42±0.01	0.69±0.07	1.40±0.25	0.43±0.01	0.69±0.05	2.03±0.14	2.73±0.63	6380±85.20	1.18 (24.80)	799 (19200)
	Sept, '10	ND	2990±314	1180±199	2160±560	713±65.60	415±13.60	5020±134	5890±1410	0.47±0.29	2560 (53900)	2240 (53900)
	Nov, '10	0.14±0.12	0.27±0.07	0.12±0.02	33.70±4.52	0.51±0.39	0.80±0.95	1.71±1.30	4.20±3.40	4.60±0.28	5.80 (122)	5.65 (136)
	Jan '11	26.60±1.66	19.40±1.23	20.90±3.48	16.10±0.98	7.86±1.05	2.27±0.78	5.46±1.78	14.90±8.17	2.76±2.44	15.90 (334)	14.20 (342)
	Mar, '11	26.00±2.11	9.57±2.96	5.87±1.10	6.34±1.36	3.02±0.33	2.94±1.17	5.73±4.30	3.97±2.87	6.22±0.98	8.65 (182)	8.35 (200)
	April, '10	7.93±2.07	22.90±15.80	2.01±0.60	9.69±5.80	10.60±10.80	7.67±6.95	11.30±1.48	21.50±8.64	ND	12.30 (258)	10.80 (258)
	June, '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
Coastal Park (S34°05'05", E18°30'16")	Aug, '10	0.25±0.05	0.29±0.08	0.73±0.14	0.38±0.04	0.36±0.03	0.26±0.03	0.78±0.12	NID	74.60±26.50	0.40 (8.38)	9.67 (232)
	Oct, '10	ND	27.90±1.85	26.50±18.00	64.30±32.00	28.80±16.40	25.90±15.50	6.76±2.25	7.50±6.45	2.28±0.35	23.10 (485)	20.50 (492)
	Dec '10	0.07±0.04	0.05±0.02	0.06±0.01	0.10±0.02	ND	ND	ND	ND	1.97±0.26	0.04 (0.87)	0.28 (6.77)
	Feb, '11	16.90±2.12	74.00±5.95	34.60±3.76	25.70±1.51	3.43±0.57	1.89±0.34	6.94±0.39	1.85±0.16	0.49±0.08	23.40 (490)	20.50 (492)
	May, '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
	Jul, '10	19.10±11.10	12.00±5.10	7.11±2.19	34.40±21.10	10.50±3.90	2.68±0.94	49.20±13.50	29.50±5.36	5350±1980	23.10 (486)	690 (16500)
	Sept, '10	ND	289±7.91	4.22±2.36	952±487	ND	ND	7990±2180	125±5.36	0.37±0.32	134 (28100)	1170 (28100)
	Nov, '10	0.23±0.19	103±30.00	35.80±9.75	113±11.10	79.00±4.70	28.10±5.02	78.90±19.30	123±13.30	1.74±0.18	76.20 (1600)	66.90 (1600)
Vissershok (Raw) (S33°56'49", E18°32'16")	Jan '11	42.40±5.14	89.70±15.30	29.90±7.94	45.2±10.8	17.10±3.03	9.59±3.43	11.00±4.53	14.50±10.10	4.16±2.30	35.70 (749)	31.70 (761)
	Mar, '11	2.49±0.27	1.51±0.13	1.19±0.08	1.52±0.19	0.56±0.17	0.45±0.27	1.43±0.48	2.56±0.30	2.00±0.64	1.61 (33.80)	1.66 (39.80)
	May, '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
	Jul, '10	0.43±0.21	1.42±0.48	2.28±2.45	4.68±1.73	2.57±1.29	3.94±2.08	7.34±1.37	3.03±2.76	2400±815	3.11 (65.20)	303 (7270)
	Sept, '10	ND	35.00±0.76	7.23±0.23	4.77±0.87	ND	0.08±0.14	1.07±0.56	7.93±4.86	ND	8.00 (168)	7.00 (168)
	Nov, '10	1.17±1.80	201±50.30	111±24.80	191±11.60	138±11.90	90.40±5.88	62.10±11.50	7.36±3.20	1.81±0.06	102 (2130)	89.10 (2140)
	Jan '11	40.30±4.37	54.30±2.66	27.30±3.74	30.30±14.40	7.18±3.51	7.91±3.57	5.54±1.04	23.10±6.71	3.28±3.14	26.90 (564)	23.90 (574)
	Mar, '11	60.0±4.67	55.00±1.88	11.50±1.78	6.66±2.48	1.37±1.11	0.53±0.30	6.14±0.82	2.35±0.61	1.08±0.91	20.40 (429)	18.00 (432)

ND – not detected; NA – not analysed; values in parentheses represent sum of PBDE congeners; a and b – represent the mean values of the sum (Σ) of 7 (excluding BDE 209) and 8 PBDE congeners, respectively.

With time, the PBDE-laden suspended particles could settle out of the aqueous medium thereby influencing the availability of these contaminants in the aqueous phase of the leachate.

The data obtained from this study were subjected to statistical analyses. The ANOVA analysis showed that all the congeners vary significantly ($p < 0.05$) from one landfill site to the other throughout the study period. This clearly indicated the non-uniformity in the release of these contaminants from these landfill sites. This, of course, could be due to the varying degree of waste composition and quantities being treated in these sites from time to time. Considering the estimated population of about 4 million people in the city and their highly stratified social status, possible variations in waste composition from different homes as well as industries is expected.

Similarly, it was also observed that statistically significant differences ($p < 0.05$) in the levels of all congeners exist in these landfill sites from one sampling period to the other. The observed trend was peculiar to all the landfill sites investigated in this study. This observation, however, is not surprising, since these samples were collected at different periods representing different seasons of the year. The imminent fluctuations in the weather conditions at different seasons of the year could remarkably influence both the characteristics and quality of leachate produced from each landfill site (Visvanathan *et al.*, 2003; Trankler *et al.*, 2005). These also depend on the type of cover material employed, the quantity of waste materials received as well as the degree of waste compaction at each landfill site (Trankler *et al.*, 2005; Odusanya *et al.*, 2009).

The data were also subjected to Duncan Multiple Range test. This was done to establish possible differences in the mean values of target compounds in each landfill site. The statistical analysis showed that nearly all the congeners except BDE 100, 183, 209 and BB 153 had significant differences in all the landfill sites investigated. While the mean values of these congeners (BDE 100, 183 and BB 153) were not statistically different at both the Vissershok and Coastal Park landfill sites, BDE 209 had similar mean values at both Bellville and Vissershok sites. This pattern might be reflection of the similar waste types received by these landfill sites. Generally, the highest mean concentrations of all the congeners except BDE 209 was found during the August/September sampling regime. As previously mentioned, this period coincides with the early spring season, hence, the observed trend might be due to the high precipitation witnessed during the winter season. With respect to monthly variations in all the landfill sites, all the congeners, except BDE 28 showed almost similar trend in their mean concentrations from one sampling period to the other.

The PBDE congener profile of leachate sample analysed revealed that all the technical formulations were fully represented. However, there were distinct differences in the composition of these congeners from one site to the other. This might be due to differences in the composition of wastes received by these landfill sites. More so, there were several tonnes of waste materials, which might contain considerable amounts of these chemicals but were not regarded as e-waste. As such, these were often treated together with other municipal wastes. Typical examples include cushion foam, mattresses, toys, furniture, carpets, plastics, amongst others, which are regularly land filled in all the landfill sites investigated.

Of the three landfill sites investigated in this study, only the Vissershok site was equipped with leachate treatment facility. An attempt was, however, made to evaluate the efficiency of the leachate treatment plant (LTP) with respect to PBDE removal. In this case, both raw and treated leachate were simultaneously analysed for these contaminants.

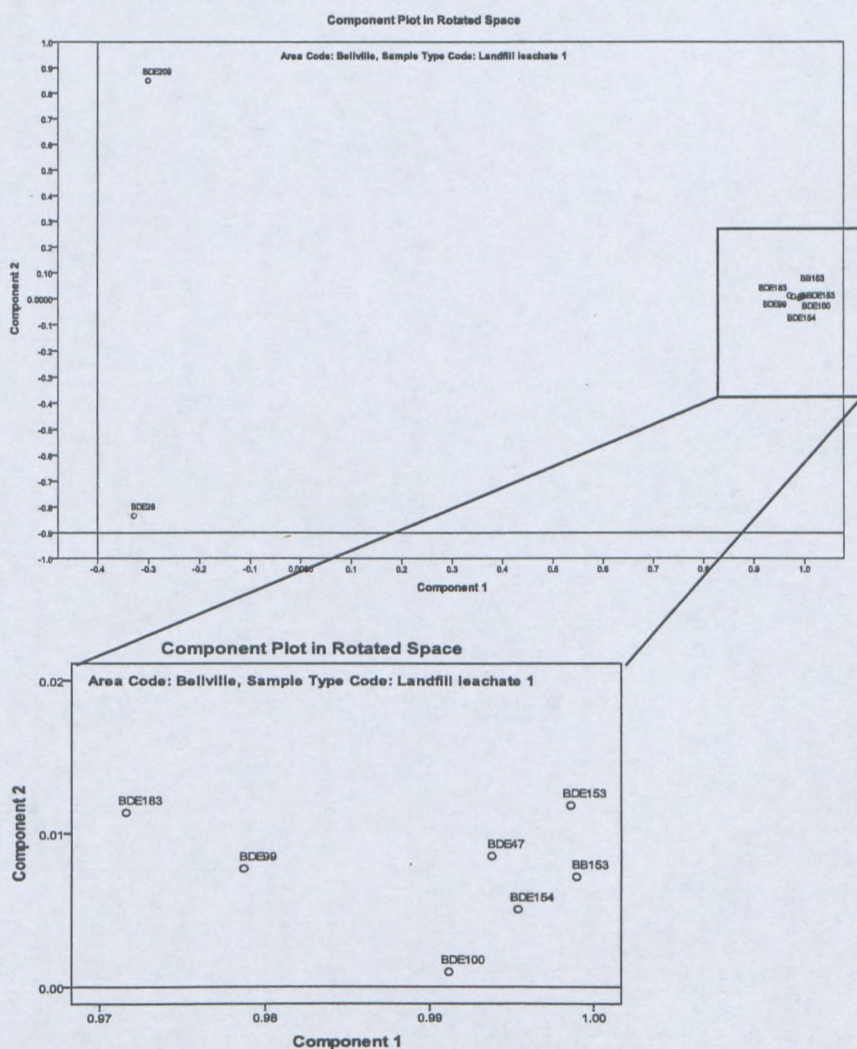


Figure 4.9: PCA component plot for leachate collected from the Bellville landfill site

Although the total mean concentrations of PBDEs were higher in treated leachate than in the raw leachate in certain months, the observed trend was not unlikely, especially when grab samples of extremely heterogenous aqueous samples were collected for analysis. The percent removal of PBDEs in the LTP ranged from 24.6% (January) to 99.4% (September).

To predict and identify the possible sources of these contaminants, the results obtained in this study were subjected to multivariate analysis. The principal component analysis (PCA) was done to establish if the contaminants were actually originating from the same source. The analysis revealed that there were varied sources of these contaminants in the leachate samples. The component plot for the Bellville site indicated that congeners of penta- and octa-BDE technical formulations were emanating from the same source as shown in Figure 4.9. Only BDE 28 and 209 did not form cluster with these congener groups. The total variance for these two components was, however explained by 94.2% where components 1 and 2 had 78.4 and 15.8%, respectively.

4.4.1.1 PBDE technical formulations representatives in leachate samples

All the major congeners of PBDE technical formulations were well represented in most of the leachate samples analysed in this study. The degree of their dominance varied from one landfill site to the other. For the purpose of this classification, BDE 47, 100, 99, 154 and 153 were regarded as representatives of the penta-BDE formulation, while BDE 183 and 209 represented octa- and deca-BDE technical formulations, respectively. The overall trend of results obtained in this study clearly indicated the dominance of the deca-BDE formulation in all the landfill sites investigated (Fig. 4.10 & 4.11). Presently, there is no data regarding the production volume and use of these chemicals in South Africa. It is only assumed that products containing these chemicals might have been imported into the country (Odusanya *et al.*, 2009). Hence, the trend observed in these landfill sites could be a reflection of the consumption pattern of these chemicals or products containing them within Cape Town.

Surprisingly, the average levels of pentaBDE formulation representatives at both Bellville and Vissershok landfill sites were comparable to one another. This might suggest the possible similarities in the sources of these contaminants in both sites. It is also possible that the disposed products from which these contaminants are leached exhibit similar leaching behaviour, since they are most likely to be subjected to the same environmental conditions. The relatively high levels of the pentaBDEs in these leachate samples call for concern. These congeners possess certain physicochemical properties, which enhances their ease of volatilization. Consequently, in regions where there are no specific sources of these chemicals into the

environment, emissions of these congeners from dumpsites and landfill sites could represent an important PBDE burden (Weinberg *et al.*, 2011). The contributions from these sites could be very significant in tropical regions especially during the dry or hot season.

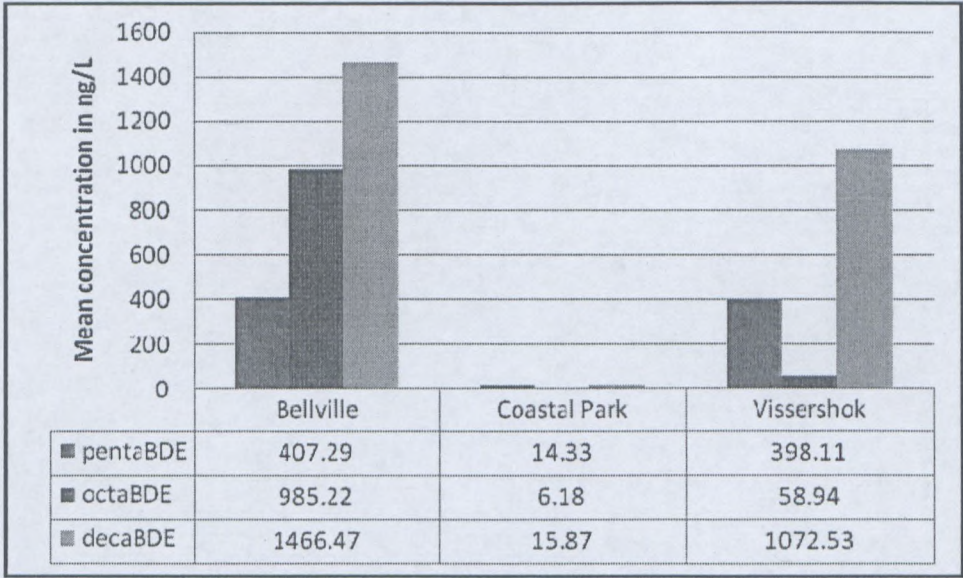


Figure 4.10: Mean concentrations of representatives of PBDE technical formulations in raw leachates from different landfill sites

St-Amand *et al.* (2008) observed higher levels of gaseous PBDEs during the summer season, thus suggesting that increased volatilization of lower brominated congeners could contribute to atmospheric PBDE burden.

More so, various types of e-wastes, auto shredder and sewage sludge are important repositories of these contaminants. The series of activities involved in the recycling of previously treated products and other e-waste materials might result in increased release of PBDEs into the environment (Petreas and Oros, 2009; Tsydenova and Bengtsson, 2011). The Bellville site, for instance, reprocesses builders’ rubble through crushing and grinding for other construction purposes. During these activities, enormous amounts of dust are generated on which these contaminants might have been bound. The prevailing windy and stormy weather conditions especially during the spring season (SAWS, 2011, *personal communication*) could enhance their transport and re-distribution to other regions far away from the point of generation.

The relatively low overall mean concentrations of the lower brominated congeners in the landfill sites investigated as shown in Fig. 4.11, could be a reflection of possible losses of these congeners through volatilisation into the atmosphere. Considering the high temperature commonly observed in this region especially during summer (SAWS, 2011, *personal communication*), PBDE losses via volatilization could

be highly significant. Several activities taking place on landfill sites during waste disposal and compaction could ultimately enhance the rate at which these contaminants are lost. Weinberg *et al.* (2011) investigated possible contribution of landfills to atmospheric burdens of certain organic contaminants, including PBDEs. The outcomes of the study suggest that landfill sites might be an important source of PBDE and other volatile organic contaminants into the atmosphere. The study further affirms that active landfill sites are more significant sources than the closed landfill sites.

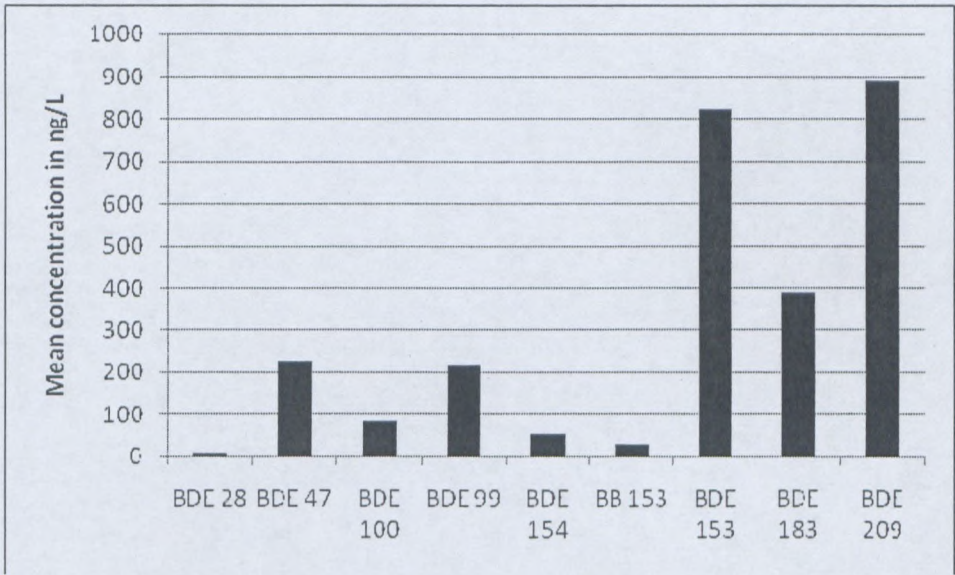


Figure 4.11: Overall mean concentrations of target compounds found in all the landfill sites

Treated leachate at the Vissershok site was generally used to wet the unpaved road networks within the landfill site. Due to the possible incomplete removal of PBDEs from the leachate during treatment, considerable amounts of these contaminants could still migrate into the environment during this process. The spraying of this treated leachate during ground wetting does not only release these contaminants into the atmosphere but also contribute to their build up in the affected soil. In periods of high precipitation, these are often washed off via run-off into the nearby water bodies, thus resulting in their continued distribution within the environment.

A comparison of the outcome of this study with other related studies is presented in Table 4.9. This showed that the levels obtained in this study were generally higher than those obtained in Osako, Japan and Pretoria, South Africa but were comparable to those found in Minnesota, USA. The non-inclusion of BDE 209, which is the dominant congener in this study, could be responsible for the observed differences. Again, the difference in the sampling year in these studies could possibly account for the trend observed. The deca-BDE technical formulation is still the only commercial PBDE formulation whose production and use have not been globally restricted.

Table 4.9: Comparison of PBDE levels (ng/l) in landfill leachate with other studies around the world

Location	Number of landfill site investigated	Highest PBDEs	Congeners monitored	Reference
Minnesota, USA	5	>7000	47, 99, 100, 153, 154, 207, 208	Oliaei <i>et al.</i> , 2002.
Osaka, Japan	7	4.00 ^a	47, 99, 100	Osako <i>et al.</i> , 2004.
Pretoria, South Africa	5	9.79 ^a	28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183	Odusanya <i>et al.</i> , 2009
Cape Town, South Africa	3	2,240	28, 47, 99, 100, 153, 154, 183, 209	This study.

^a – mean concentrations of total PBDEs investigated.

4.4.2 Occurrence of target compounds in WWTP samples

The levels and temporal distribution of selected PBDE congeners as well as BB 153 were assessed. The evaluation was specifically carried out to monitor the fate of these contaminants in various WWTPs investigated. In this assessment, both effluent and sewage sludge samples were collected at different stages of the wastewater purification for analysis.

4.4.2.1 Levels and distribution of PBDEs and BB153 in sewage sludge samples

The concentrations of selected PBDE congeners as well as BB 153 monitored in different sewage sludge types collected from Potsdam, Cape Flats, (Old and New) Bellville and Zandvliet WWTPs are presented in Tables 4.10, 4.11, 4.12 and 4.13, respectively. The overall mean concentrations of the eight commonly investigated PBDE congeners in these samples were in the range of 1.02 – 814, 1.16 – 487, 0.18 – 4330 and 13.1 – 652 ng/g for Potsdam, Cape Flat, (Old and New) Bellville and Zandvliet WWTPs, respectively. Similarly, the overall mean concentrations of BB 153 ranged from ND – 159, ND – 7.80, ND – 4.75 and ND – 7.32 ng/g for Potsdam, Cape Flats, (Old and New) Bellville and Zandvliet WWTPs, respectively. Generally, the results obtained in this study showed a somewhat consistent trend, except for certain months where extremely high levels of these contaminants were observed. Interestingly, the major congeners of both octa- and deca-BDE technical formulations were those contributing the most to these elevated levels. In Potsdam WWTP, for instance, the total mean concentration of PBDEs was highest in the secondary and de-watered sludge during the September sampling regime. A similar trend was also observed in other WWTPs during the July, August and September sampling regimes.

The reasons for the upsurge in the PBDEs levels in these samples are unknown. A possible explanation could result from some of our observations during the sampling exercise. It was observed in some of the WWTPs, especially at the Potsdam WWTP, that untreated industrial effluents were off-loaded from heavy-duty tankers. These effluents were mixed with the wastewater to be treated at the inlet section of

the plant. Some of these industries might have been sited at locations that were not probably connected to the urban sewer system, thus would require the transportation of effluents generated from their processes to the nearby WWTP for treatment. Depending on the origin of these effluents, a significant amount of these contaminants could be contributed through this practice.

Secondly, there were several construction and rehabilitation works taking place in some of the WWTP during these periods. The rehabilitation of the sludge digestion units at the Cape Flats WWTP was notable. It is therefore likely that certain materials containing these contaminants could be released from these activities during these periods. Lastly, the reprocessing of demolition materials at the landfill site adjacent the Bellville WWTP might contribute significantly to the observed levels. Indoor environments, which are known to contain high levels of these contaminants, could play a vital role. While crushing the demolished building materials, considerable amounts of air-borne dust particles are generated on which the contaminants might be bound. The prevailing stormy and windy weather conditions could therefore accelerate their rapid deposition and subsequent transfer into the treatment plants (SAWS, 2011, *personal communication*).

In these plants, especially in the open sedimentation tanks deposited particles which are mostly suspended in the aqueous media could greatly influence the ultimate fate and distribution of PBDEs in the WWTP. Of all the twenty-two WWTPs sited in different sub-regions within the borders of the City of Cape Town, the WWTPs investigated in this study had the largest treatment capacities in each sub-region. These were generally equipped with facilities to receive and treat industrial effluents. Although different sludge types were analysed, the contaminants were found to concentrate mostly in the secondary sludge.

In most of these WWTPs, the preferential accumulation of PBDE congeners, especially BDE 209 in primary sludge relative to those found in secondary sludge was notable at the Old Bellville plant. As shown in Figure 4.12, six out of the nine congeners investigated had higher levels in secondary sludge than in the primary sludge. This further suggests that sorption of PBDEs to finely suspended particles might be playing an important role in their removal from the wastewater stream. This is consistent with observations earlier reported in the literature (Song *et al.*, 2006; Knoth *et al.*, 2007).

Table 4.10: Mean (±standard deviation) concentrations (ng/g) of selected PBDE congeners and BB 153 in sewage sludge samples collected from the Potsdam WWTP

Sample type	Sampling period	Target compounds										$\sum_{\text{PBDEs}}$	$\sum_{\text{SPBDEs}}$
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
Primary sludge	May, '10	0.91±0.77	3.82±0.17	2.10±0.27	1.13±0.27	0.04±0.07	0.22±0.38	2.02±0.70	2.95±0.37	ND		38.90 (1.85)	38.90 (1.62)
	Jul, '10	2.20±1.19	6.51±4.35	9.10±3.05	2.22±1.04	3.86±3.19	3.73±0.37	11.10±0.98	74.90±4.29	450±13.20		329 (15.70)	1680 (69.90)
	Sept, '10	2.93±1.44	13.57±2.58	7.19±0.36	4.69±0.07	3.40±0.31	ND	43.0±2.86	8.53±3.30	0.49±0.04		250 (11.9)	251 (10.50)
	Nov, '10	0.36±0.16	3.60±0.32	1.51±0.36	1.12±0.06	0.71±0.20	ND	3.91±0.34	1.51±0.34	0.28±0.10		38.20 (1.82)	39.00 (1.63)
	Jan '11	0.91±0.15	1.50±0.03	0.18±0.09	1.91±0.15	0.27±0.05	0.12±0.05	2.23±0.51	0.52±0.23	0.78±0.20		22.50 (1.07)	24.80 (1.03)
Secondary sludge	Mar, '11	3.00±0.31	2.35±0.09	0.75±0.47	0.50±0.55	1.05±0.20	0.27±0.07	2.45±0.30	0.55±0.28	3.69±2.57		32.00 (1.52)	43.00 (1.79)
	May, '10	27.60±2.61	31.80±2.03	12.8±0.70	7.30±2.22	1.11±0.08	0.74±0.06	1.70±0.21	2.80±1.39	1930±1700		255 (12.20)	6030 (251)
	Jul, '10	2.11±0.07	1.03±0.03	0.48±0.04	1.54±0.05	0.80±0.37	0.33±0.15	1.40±0.81	2.22±0.73	ND		28.70 (1.37)	28.70 (1.20)
	Sept, '10	0.07±0.11	843±66.50	122±57.00	422±55.10	154±90.00	159±38.90	1470±428	3490±912	10.10±1.25		19500 (928)	19500 (814)
	Nov, '10	1.49±0.27	1.75±0.20	0.56±0.10	0.97±0.73	0.39±0.10	0.37±0.05	1.13±0.41	0.74±0.22	1.13±0.32		21.10 (1.00)	24.50 (1.02)
De-watered sludge	Jan '11	0.44±0.44	2.67±0.06	0.30±0.17	1.13±0.11	1.15±1.01	0.41±0.15	2.12±0.32	0.96±0.26	0.79±0.29		26.30 (1.25)	28.70 (1.19)
	Mar, '11	0.72±0.25	1.12±0.11	0.65±0.51	1.89±0.46	0.25±0.08	0.15±0.04	1.39±1.03	0.78±0.15	17.90±3.27		20.40 (0.97)	74.10 (3.09)
	May, '10	7.80±0.08	3.75±0.08	0.89±0.04	4.26±0.06	0.05±0.01	0.32±0.07	1.24±0.28	1.35±0.21	437±85.80		58.00 (2.76)	1370 (57.10)
	Jul, '10	1.68±0.53	1.33±0.43	2.43±1.59	1.39±0.88	0.23±0.02	0.14±0.01	1.15±0.13	3.59±2.44	69.60±31.20		35.40 (1.69)	244 (10.20)
	Sept, '10	ND	586±60.10	50.80±39.0	231±61.20	66.8±44.1	157±197	798±306	2290±916	11.90±1.64		12100 (574)	12100 (504)
	Nov, '10	1.93±0.36	38.30±7.59	7.97±2.81	1.21±0.004	2.59±0.87	0.05±0.01	28.00±1.88	13.10±2.82	0.47±0.04		279 (13.30)	280 (11.70)
	Jan '11	0.63±0.12	2.09±0.63	0.37±0.10	7.65±0.75	1.10±0.98	0.51±0.12	4.10±0.87	4.52±3.75	10.70±6.66		61.40 (2.92)	93.40 (3.89)
	Mar, '11	0.49±0.04	1.03±0.02	0.19±0.02	0.93±0.004	0.26±0.19	0.12±0.05	1.83±0.99	1.04±0.60	4.77±1.85		17.30 (0.82)	31.60 (1.32)

values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent mean values of PBDE congeners; $\sum_{\text{PBDEs}}$ denotes sum of tri-heptaBDEs investigated; $\sum_{\text{PBDEs}}$ denotes sum of all PBDE congeners, including BDE 209

Table 4.11: Mean (±standard deviation) concentrations (ng/g) of selected PBDE congeners and BB 153 in WWTP samples collected from the Cape Flats Plant

Sampling Location	Sampling period	Target compounds														ΣPBDEs	ΣPBDEs
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209	ΣPBDEs	ΣPBDEs					
Primary sludge	Apr. '10	16.30±10.90	607±71.60	34.80±8.11	37.50±12.80	6.90±1.53	4.04±0.98	22.80±9.27	150±32.40	613±290	2610 (124)	4450 (185)					
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA							
	Aug. '10	3.81±2.19	12.60±0.25	44.90±1.27	11.50±5.52	12.10±9.14	2.10±2.10	3.84±2.34	6.43±0.85	30.50±12.20	286 (13.60)	377 (15.70)					
	Oct. '10	2.44±0.49	4.14±0.05	0.15±0.04	3.68±0.38	0.70±0.47	0.21±0.01	0.75±0.04	1.33±0.29	88.90±21.20	39.6 (1.88)	306 (12.80)					
	Dec. '10	0.83±0.06	3.56±0.55	0.68±0.16	1.51±0.55	0.64±0.68	0.45±0.55	0.87±0.10	ND	2.79±0.57	24.30 (1.15)	32.60 (1.36)					
	Feb. '11	6.31±3.16	10.70±0.92	2.18±1.16	15.90±2.08	1.18±0.48	0.25±0.43	42.60±4.92	5.90±3.19	1.62±0.22	254 (12.10)	259 (10.8)					
Secondary sludge	Apr. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-					
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-					
	Aug. '10	0.67±0.07	3.53±0.24	7.79±0.42	2.49±0.22	1.50±0.16	1.45±0.57	1.98±0.27	1.86±0.25	4360±1140	63.80 (2.66)	13100 (487)					
	Oct. '10	1.10±0.45	0.97±0.37	0.57±0.37	25.84±0.96	1.79±1.44	0.13±0.03	0.38±0.05	0.88±0.28	10.30±1.70	94.90 (3.95)	126 (4.66)					
	Dec. '10	ND	0.09±0.01	ND	ND	ND	ND	ND	ND	10.40±9.63	0.27 (0.01)	31.40 (1.16)					
	Feb. '11	2.01±1.11	3.41±0.31	1.11±0.05	3.35±0.50	0.73±0.04	ND	1.99±1.73	3.86±1.49	66.30±33.30	49.3 (2.06)	248 (9.19)					
DAF sludge	Apr. '10	10.00±2.89	4.89±0.24	2.01±0.35	1.83±1.54	2.08±0.14	0.65±0.13	9.80±1.93	4.85±1.71	2580±643	106 (5.07)	7840 (327)					
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA							
	Aug. '10	2.41±1.67	9.30±3.33	8.90±4.41	11.90±0.80	14.50±4.49	7.80±4.00	91.90±28.00	742±248	164±86.30	2640 (126)	3140 (131)					
	Oct. '10	0.43±0.36	7.96±1.56	2.45±0.28	1.53±0.16	1.48±0.26	ND	21.90±2.44	8.17±1.21	3.28±1.08	132 (6.27)	141 (5.89)					
	Dec. '10	2.56±2.49	4.94±1.14	1.79±0.37	1.22±0.10	0.99±0.25	0.21±0.15	7.44±0.46	2.85±1.70	15.90±0.49	65.40 (3.11)	113 (4.71)					
	Feb. '11	1.83±0.27	5.60±0.22	1.58±0.10	5.50±0.22	0.41±0.03	0.86±0.11	3.56±0.73	2.82±0.13	162±39.50	63.90 (3.04)	550 (22.90)					
Digested sludge	Apr. '10	10.90±5.71	4.61±2.29	3.63±4.49	7.63±0.89	1.61±0.83	0.23±0.10	13.70±5.97	5.54±1.02	56.70±34.00	143 (6.80)	313 (13.00)					
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-					
	Aug. '10	0.49±0.23	2.49±0.24	10.60±2.28	2.42±0.30	1.20±0.86	0.59±0.45	1.83±0.43	2.75±1.27	13.20±12.30	65.40 (3.11)	105 (4.38)					
	Oct. '10	0.94±0.68	2.34±1.71	4.87±1.06	1.29±0.10	ND	ND	42.30±2.26	11.6±1.93	8.50±0.21	190 (9.05)	216 (8.98)					
	Dec. '10	2.06±0.70	9.43±4.68	3.48±0.69	2.43±1.02	1.97±1.08	1.05±0.17	15.00±5.28	1.93±0.70	13.70±0.81	109 (5.18)	150 (6.25)					
	Feb. '11	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-					

values reported are mean and standard deviation of triplicate analyses; NA – not analysed; ND – not detected; values in parentheses represent mean values of PBDE congeners; $\sum_{i=1}^{10} \text{PBDEs}$ denotes sum of tri-heptaPBDEs investigated; $\sum_{i=1}^{10} \text{PBDEs}$ denotes sum of all PBDE congeners, including BDE 209

Table 4.12: Mean ($\pm$ standard deviation) concentrations (ng/g) of selected PBDE congeners and BB 153 in sewage sludge samples collected from the (Old & New) Bellville

Sample type	Sampling Period	Target compounds										
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209	$\sum_{7PBDEs}$	$\sum_{8PBDEs}$
Primary	May, '10	NA	NA	NA	NA	NA	NA	NA	NA	NA		

WWTP

sludge	Jul. '10	10.30±1.45	42.10±1.35	6.29±0.74	6.06±0.18	2.12±1.08	1.05±0.56	5.28±0.41	14.60±1.24	6300±2500	260(12.40)	19200 (798)
	Sept. '10	57.60±15.00	27.90±2.25	74.90±28.00	39.90±26.70	17.40±15.70	4.75±7.80	27.82±8.19	19.20±8.75	34400±7440	794 (37.80)	104,000 (4330)
	Nov. '10	0.29±0.01	19.20±1.92	10.00±8.20	79.30±26.00	4.70±3.24	1.37±0.96	6.27±5.23	35.80±28.20	ND	467 (22.20)	467 (19.50)
	Jan '11	0.31±0.10	1.03±0.31	0.38±0.08	0.88±0.005	ND	ND	0.33±0.33	0.67±0.64	4.44±0.40	10.80 (0.51)	24.10 (1.01)
	Mar. '11	1.78±0.11	2.23±1.02	1.95±1.20	2.85±1.63	0.77±0.67	ND	3.17±2.96	ND	7.27±1.79	38.30 (1.82)	60.10 (2.50)
	May. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
Secondary sludge (old)	Jul. '10	1.63±2.53	5.41±1.88	7.27±1.25	4.75±0.83	5.08±3.88	1.19±0.66	7.58±1.16	22.80±12.00	791±185	163 (7.78)	2540 (106)
	Sept. '10	32.40±19.40	69.90±0.56	10.00±1.06	4.37±0.03	0.85±0.33	0.36±0.11	1.26±0.65	1.20±0.41	ND	360 (17.10)	360 (15.00)
	Nov. '10	2.41±1.19	19.40±4.45	2.77±0.06	4.80±0.61	0.24±0.21	0.12±0.13	1.91±0.73	0.87±0.19	1.49±0.43	97.2 (4.63)	102 (4.24)
	Jan '11	3.32±0.32	11.70±0.29	2.52±0.19	7.41±0.67	1.51±1.03	1.13±0.30	3.20±2.26	4.64±0.58	3.08±1.15	103 (4.90)	112 (4.67)
	Mar. '11	1.58±0.10	9.90±0.22	1.72±0.07	4.29±0.06	0.81±0.21	0.32±0.14	1.00±0.16	1.88±0.43	1.80±0.40	63.5 (3.02)	68.90 (2.87)
	May. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
Secondary sludge (New)	Jul. '10	14.50±3.72	19.90±0.45	2.56±0.21	5.22±0.69	1.20±0.61	0.42±0.17	2.65±0.57	1.51±0.87	1820±889	142 (6.78)	5600 (234)
	Sept. '10	32.40±33.20	1150±706	42.50±30.80	89.20±72.90	34.20±18.30	1.75±3.03	16.80±15.40	76.90±92.60	505±120	4320 (206)	5840 (243)
	Nov. '10	0.06±0.03	0.07±0.02	0.03±0.01	0.06±0.01	0.04±0.01	ND	0.09±0.01	0.19±0.01	0.92±0.33	1.65 (0.08)	4.41 (0.18)
	Jan '11	0.89±0.49	2.51±1.19	2.84±0.15	4.07±0.49	1.93±1.30	0.96±0.80	4.16±1.75	2.31±2.05	4.12±2.59	56.10 (2.67)	68.50 (2.85)
	Mar. '11	0.71±0.37	3.65±0.33	0.31±0.09	0.81±0.15	0.69±0.25	0.47±0.12	2.55±0.33	0.64±0.05	1.37±0.72	28.0 (1.33)	32.10 (1.34)
	May. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
De-watered sludge	Jul. '10	1.45±1.95	61.80±1.40	6.47±0.29	5.91±1.25	7.25±1.21	0.89±0.63	1.37±0.57	13.20±2.52	321±277	292 (13.90)	1250 (52.30)
	Sept. '10	6.73±1.87	77.80±9.41	9.07±0.56	1.27±0.25	4.15±0.07	0.30±0.07	4.14±1.77	4.07±2.78	747±465	322 (15.30)	2560 (107)
	Nov. '10	6.62±2.78	12.80±9.43	0.52±0.60	0.62±0.86	0.61±0.52	0.44±0.41	7.58±1.84	1.46±0.31	0.23±0.07	90.70(4.32)	91.40 (3.81)
	Jan '11	3.89±4.52	17.10±2.44	7.03±0.82	7.88±1.69	6.64±1.79	0.66±0.77	38.50±3.48	4.72±2.30	1.69±0.60	257 (12.20)	262 (10.90)
	Mar. '11	1.51±0.32	2.92±0.65	0.23±0.16	0.41±0.11	0.82±0.40	0.30±0.21	4.06±1.00	1.91±1.34	2.11±0.98	35.60 (1.70)	41.90 (1.75)

values reported are mean and standard deviation of triplicate analyses; NA – not analysed; ND – not detected; values in parentheses represent mean values of PBDE congeners; $\sum_{7PBDEs}$ denotes sum of tri-heptaBDEs investigated; $\sum_{8PBDEs}$ denotes sum of all PBDE congeners, including BDE 209

Table 4.13: Mean (±standard deviation) concentrations (ng/g) of selected PBDE congeners and BB 153 in de-watered sludge samples collected from the Zandvliet WWTP

Sample type	Sampling period	Target compounds										Σ _{7PBDEs}	Σ _{8PBDEs}
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
De-watered sludge	Apr. '10	ND	40.50±23.00	7.55±2.26	5.32±1.46	3.20±2.78	7.32±2.57	7.67±1.94	26.70± 3.60	297±267		273 (13.00)	1160 (48.40)
	Jun. '10	2.76±0.30	1.03±0.29	2.81±0.25	2.29±0.04	1.71±0.71	ND	2.25±0.19	22.10±2.77	ND		105 (4.99)	105 (4.37)
	Aug. '10	ND	125±1.88	6.04±1.57	9.24±3.22	4.24±0.75	1.41±1.41	3.52±0.36	37.80±0.15	105±36.00		558 (26.60)	871 (36.30)
	Oct. '10	1.29±1.09	1.53±1.04	0.96±0.23	2.00±1.74	1.49±0.33	ND	7.35±0.71	2.08±1.82	2.44±0.26		50.10 (2.39)	57.40 (2.39)
	Dec. '10	0.22±0.16	3.20±0.31	0.68± 0.20	1.44±0.85	0.33±0.28	ND	7.21±0.66	0.85±0.73	2.82±0.57		41.80 (1.99)	50.20 (2.09)
	Feb. '11	4.64±1.59	13.8±1.13	7.98±0.11	2.06±0.98	0.71±0.73	0.11±0.19	7.88±0.89	3.78±1.47	1.59±0.34		122 (5.83)	127 (5.30)

values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent mean values of PBDE congeners; Σ_{7PBDEs} denotes sum of tri-heptaBDEs investigated; Σ_{8PBDEs} denotes sum of all PBDE congeners, including BDE 209

PBDEs are known to bind with finely suspended particles whose ultimate settling takes place in the secondary sedimentation tanks. Most organic contaminants do not degrade completely during these treatment processes, hence they tend to accumulate in the sludge.

The statistical analysis (ANOVA) performed on these data showed that the levels of all the PBDE congeners varied significantly ($p < 0.05$) from plant to plant. Similarly, statistically significant variations ($p < 0.05$) in contaminant concentrations from one sampling regime to the other were also observed. The observed trends could be attributed to diverse sources of these contaminants into the wastewater stream being treated by the WWTPs. Gevaio *et al.* (2008) observed a similar trend in their study and attributed the inconsistent variations in PBDE levels to possible changes in the lifestyles of people connected to the WWTPs. Furthermore, the observed variations in PBDEs levels in different plants could be due to the irregular fluxes of suspended solids reaching each plant from time to time.

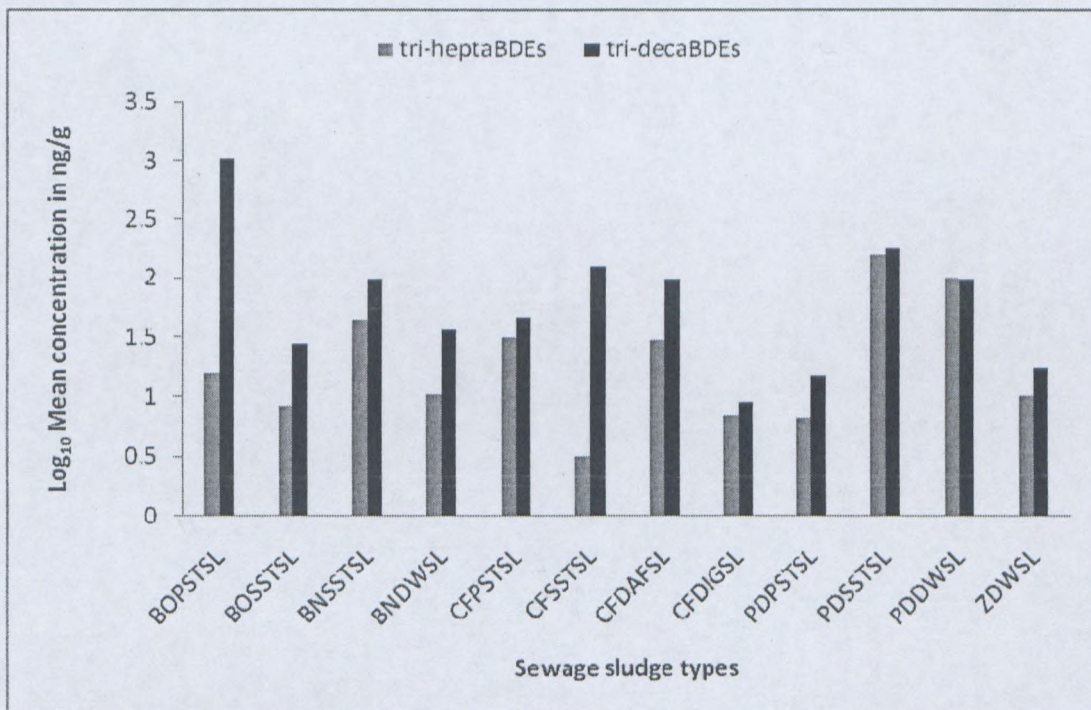


Figure 4.12: A graphical representation of mean concentrations of the sum of tri-heptaBDEs and tri-decaBDEs in the entire study period

(BOPSTSL – Old Bellville primary sludge; BOSSTSL – Old Bellville secondary sludge; BNSSTSL – New Bellville secondary sludge; BNDWSL – New Bellville de-watered sludge; CFPSTSL – Cape Flats primary sludge; CFSSTSL – Cape Flats secondary sludge; CFDAFSL – Cape Flats dissolved air flotation sludge; CFDIGSL – Cape Flats digested sludge; PDPSTSL – Potsdam primary sludge; PDSSTSL – Potsdam secondary sludge; PDDWSL – Potsdam de-watered sludge; ZDWSL – Zandvliet de-watered sludge)

The data obtained in this study were further subjected to the Duncan Multiple Range (DMR) test. This was done to establish possible variations in the levels of these contaminants by comparing their mean values in different samples, sampling months and treatment plants. The analysis revealed that the mean

values of most contaminants did not vary significantly in each sample types investigated. Only BDE 99, 153, 183 and 209 showed significant differences ($p < 0.05$) in these matrices. While the mean values of BDE 153, 183 and 209 found in primary sludge were statistically different from those obtained in other sample types, BDE 99 exhibited a difference in the secondary sludge. It is possible that these congeners could have additional source inputs into the wastewater system. The possibility of debromination of highly brominated congeners to produce daughter congeners cannot be ruled out. Although studies have shown that some of these congeners are resistant to biodegradation (Riget *et al.*, 2006; Shin *et al.*, 2010); evidences of both photo degradation and microbial transformation of highly brominated congeners have been widely reported (Stapleton and Dodder, 2008; Deng *et al.*, 2011).

The levels of most of the contaminants investigated were highest during the August/September sampling regimes. These periods coincide with the late winter and early spring seasons of the year. Possible changes in the lifestyle of residents connected to these WWTPs during the cold winter season could contribute to the levels observed. During these periods, residents stay longer at homes or offices due to the cold weather condition and as such would normally increase the operating hours of most products especially electronic and electrical appliances that contain a significant amount of these chemicals. Consequently, increased leaching of these chemicals is expected when products' operating hours are further extended.

Changes in land-use pattern covered by the WWTP could also be an important factor. During the study period, many developmental activities ranging from construction and rehabilitation of social parks, residential homes and other social amenities were on top gear in preparation for the global sport fiesta recently hosted in the country. These new developments further increased the coverage areas of the WWTP, hence, it could possibly influence the efficiency of the plant at removing certain organic contaminants. The Cape Flats area where both the Cape Flats and Zandvliet WWTPs are located is known for hosting the largest informal settlements in the entire Western Cape Province (CCT, 2006b). The numbers of these settlements have continued to increase since its first count in 1993. These have grown from 50 to over 200 in 2005, where an estimated 13% of the city population resides (CCT, 2006b). The shacks in most of these informal settlements are generally characterised by old furniture and other products such as electronics, which are believed to contain brominated flame retardants (BFRs). In addition, both industrial and domestic wastewaters from the informal settlement are channelled to the WWTP, which could probably explain the increased PBDE levels observed in this study.

4.4.2.2 Levels and distribution of PBDEs and BB 153 in WWTP effluent samples

The results obtained from the analysis of selected PBDEs and BB 153 in different effluent types collected from the Potsdam, Cape Flats, Old Bellville, New Bellville and Zandvliet WWTPs are presented in Tables

4.14, 4.15, 4.16, 4.17 and 4.18, respectively. The overall mean concentrations of the eight PBDE congeners monitored in this study were generally the highest in the raw water samples in nearly all the WWTPs investigated. These values ranged between 13.8 – 1520, 7.36 – 660, 8.32 – 579, 40.4 – 356, and 48.8 – 401 ng/ℓ for Potsdam, Old Bellville, New Bellville, Cape Flats and Zandvliet WWTPs, respectively. Similarly, the overall mean concentrations of BB 153 were highest in the raw water samples. These ranged from 0.91 – 1700, 1.91 – 700, 1.69 – 1190, 3.89 – 127 and 0.98 – 15.8 ng/ℓ for Potsdam, Old Bellville, New Bellville, Cape Flats and Zandvliet WWTPs, respectively.

The effluents reaching each of these WWTPs are derived from various sources, including residential and commercial homes, agricultural and industrial sectors. Although each of the plants receives varying percentages of these effluents, their overall efficiency at removing the target contaminants is limited to the successful implementation of the in-house best environmental practices adopted for effective wastewater management in each plant. In addition, the treatment efficiency of each plant will also depend on the design capacity and treatment process designed for each plant. Hence, the combined effects of these factors might be responsible for the high variation in the levels of target contaminants investigated.

Generally, there was a reduction in contaminants' levels at different sampling points along the process flow within each plant investigated. Surprisingly, there were cases where higher contaminants' levels were found in cleaner effluents than in the raw water samples. One might speculate that these observations actually indicated the poor performance in terms of PBDE removal of the plants concerned. In actual fact, this assumption might completely be misleading as there were occasions during the sample collection when highly contaminated industrial effluents were off-loaded from heavy-duty tankers directly into the wastestream. This was done in such a way that the raw water sampling point was by-passed, thus resulting into a scenario where relatively high contaminants' load were observed in other compartments where samples were collected for analysis. In this way, higher levels of contaminants might be found in primary, secondary or even final effluents than those found in the raw water. Excessive loading of treatment plants leads to the over-stretching of their treatment capacities which consequently results in shorter residence time of the aqueous wastestream. The resultant effects are excessive accumulation of contaminants and poor effluent quality evidenced by highly variable levels of contaminants within the plant concerned.

Table 4.14: Mean (±standard deviation) concentrations (ng/l) of selected PBDE congeners and BB 153 in effluent samples collected from the Potsdam WWTP

Sample type	Sampling period	Target compounds										Σ _{PBDEs}	Σ _{PPBDEs}
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
Raw water	May, '10	28.10±46.20	18.10±25.50	0.95±0.72	3.16±4.11	0.78±1.09	0.91±0.81	10.70±18.50	28.10±48.70	321±413	12.80 (269)	51.30 (1230)	
	Jul, '10	16.20±15.90	111±42.20	22.50±16.30	31.10±6.24	7.05±5.75	3.65±1.89	35.70±3.07	103±6.49	289±174	46.60 (978)	76.80 (1840)	
	Sept, '10	26.20±2.50	12.10±2.27	11.80±0.63	16.60±0.45	5.46±1.51	2.18±0.67	30.30±14.60	206±38.40	639±30.00	44.10 (927)	119 (2850)	
	Nov, '10	ND	605±102	673±155	2060±221	2350±520	1700±336	3530±285	2940±1310	12.30±0.00	1740 (36400)	1520 (36500)	
	Jan '11	16.10±5.21	1040±58.70	152±15.90	61.60±9.01	64.0±11.30	27.70±9.73	31.70±0.87	27.70±6.38	3.53±0.71	199 (4189)	175 (4200)	
	Mar, '11	2.51±0.49	20.50±0.25	6.73±2.96	8.22±7.97	3.06±0.63	2.58±1.41	11.70±14.20	4.42±3.18	53.00±16.20	8.15 (171)	13.80 (330)	
Primary effluent	May, '10	3.20±3.52	8.50±11.80	2.66±3.02	9.66±12.90	2.01±3.13	1.94±2.54	14.40±23.30	31.00±47.30	222±317	10.20 (214)	36.70 (880)	
	Jul, '10	59.20±6.36	70.80±20.60	4.67±1.86	7.16±4.86	2.19±1.49	0.57±0.34	21.00±1.67	47.30±22.00	112±194	30.30 (637)	40.50 (973)	
	Sept, '10	5.24±1.91	11.30±3.61	6.18±6.02	9.28±7.28	0.95±0.42	1.24±1.08	8.52±3.83	78.20±36.50	141±43.70	17.10 (359)	32.60 (782)	
	Nov, '10	0.71±0.44	354±72.30	303±79.20	230±56.30	460±99.60	343±62.50	385±59.30	608±34.90	4.36±0.65	334 (7020)	293 (7040)	
	Jan '11	16.90±2.24	15.90±1.20	29.80±6.91	49.60±2.63	17.20±1.39	4.74±0.83	22.10±0.68	26.40±6.06	3.85±0.26	25.40 (534)	22.70 (545)	
	Mar, '11	583±91.70	876±10.90	30.20±6.54	69.80±28.5	24.20±1.32	16.70±0.88	38.30±31.50	109±86.30	12.65±6.56	247 (5190)	218 (5230)	
Secondary effluent	May, '10	44.40±7.02	29.90±5.57	16.80±13.40	9.06±3.33	13.70±1.00	4.43±3.66	26.40±14.70	35.90±40.70	ND	25.20 (528)	22.00 (528)	
	Jul, '10	97.10±12.10	65.80±51.10	6.06±1.27	27.60±30.10	42.40±49.30	28.70±28.60	14.60±6.19	57.60±18.70	ND	44.50 (934)	38.90 (934)	
	Sept, '10	ND	2430±805	138±8.53	194±9.17	68.10±26.70	68.70±45.60	146±45.70	121±78.70	4.41±1.38	442 (9290)	388 (9300)	
	Nov, '10	ND	0.15±0.26	ND	ND	ND	ND	ND	9.02±4.21	5.27±0.05	1.31 (27.50)	1.81 (43.30)	
	Jan '11	3.39±0.34	10.30±1.94	9.10±0.20	7.32±2.27	7.50±0.93	4.00±3.06	2.87±2.68	ND	4.04±0.76	5.79 (122)	5.57 (134)	
	Mar, '11	3.74±0.43	3.08±1.24	5.73±1.95	4.76±1.26	4.44±2.12	0.73±1.27	2.18±2.96	3.40±1.56	33.3±14.80	3.90 (82.00)	7.58 (182)	
Final effluent	May, '10	26.30±1.18	16.80±8.53	5.10±4.43	7.95±0.09	1.37±0.47	ND	ND	ND	ND	8.21 (172)	7.19 (172)	
	Jul, '10	85.70±2.69	152±9.65	27.40±2.06	19.20±11.10	24.70±2.18	14.30±1.85	6.14±0.85	105±3.83	ND	60.00 (1260)	52.50 (1260)	
	Sept, '10	ND	25.70±7.74	4.96±4.30	44.10±22.50	75.80±42.30	39.10±23.10	89.80±8.71	354±4.29	1.89±0.64	84.90 (1780)	74.50 (1790)	
	Nov, '10	ND	1920±142	ND	ND	ND	ND	ND	2.23±1.96	4.65±0.44	275 (5770)	241 (5790)	
	Jan '11	2.07±0.20	6.48±2.19	2.29±0.68	2.48±0.72	6.45±0.41	1.19±0.23	1.70±1.49	ND	3.87±1.06	3.07 (64.40)	3.17 (76.00)	
	Mar, '11	0.99±0.06	3.83±0.37	1.52±0.19	7.97±2.36	1.18±0.12	0.67±0.39	2.08±0.58	2.11±1.05	3.83±1.35	2.81 (59.10)	2.94 (70.50)	

values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent the sum of PBDE congeners; ΣPBDEs denotes sum of tri-heptaBDEs investigated; ΣPBDEs denotes sum of all PBDE congeners, including BDE 209

Sample type	Sampling period	Target compounds										$\sum_{7PBDEs}$	$\sum_{8PBDEs}$
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
Raw water	Apr. '10	4.44±3.22	7.88±0.88	7.42±3.36	11.80±2.14	5.38±3.86	13.60±3.47	51.10±9.73	19.90±7.96	215±16.00	15.40 (323)	40.40 (970)	
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-	
	Aug. '10	47.10±5.64	285±34.80	52.40±5.70	218±39.40	68.00±6.29	47.40±2.67	138±17.40	53.70±10.90	1.56±0.49	123 (2590)	108 (2590)	
	Oct. '10	ND	464±118	26.30±18.8	1700±130	209±19.80	127±15.40	436±36.20	7.66±3.33	3.51±0.33	406 (8530)	356 (8540)	

Table 4.15: Mean (±standard deviation) concentrations (ng/l) of selected PBDE congeners and BB 153 in effluent samples collected from the Cape Flats WWTP

Primary effluent	Dec. '10	0.72±0.28	468±52.70	16.00±8.32	20.00±11.6	14.50±5.48	3.89±1.41	386±21.90	34.10±8.33	4.38±1.42	134 (2820)	118 (2830)
	Feb. '11	414±22.40	561±18.90	67.20±9.85	440±39.10	60.60±17.30	24.60±5.52	773±689	284±60.70	2.94±1.37	371 (7800)	325 (7810)
	Apr. '10	3.98±2.01	10.90±1.73	5.44±0.71	14.50±3.09	10.10±3.27	8.01±6.29	45.70±40.90	29.90±2.04	160±69.20	17.20 (362)	34.60 (830)
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
	Aug. '10	110±76.90	41.20±18.30	175±116	308±174	184±127	41.80±20.00	166±70.40	54.80±9.83	ND	148 (3120)	130 (3120)
	Oct. '10	ND	503±16.20	16.80±2.48	1490±46.00	1.94±0.11	0.79±0.34	5.76±3.35	3.83±3.19	4.28±0.40	288 (6050)	253 (6070)
	Dec. '10	495±21.30	36.40±10.70	19.90±1.13	11.40±3.37	81.50±11.50	25.20±7.24	23.50±9.28	16.00±0.81	6.11±2.00	97.70 (2050)	86.20 (2070)
	Feb. '11	345±18.70	467±15.7	56.00±8.21	367±32.60	50.50±14.40	20.50±4.60	644±574	236±50.6	2.67±1.25	310 (6500)	271 (6510)
	Apr. '10	2.77±1.82	1.06±0.13	2.98±2.83	1.80±1.56	3.48±4.51	1.41±1.22	7.82±5.92	6.64±1.46	ND	3.79 (79.60)	3.32 (79.60)
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
Secondary effluent	Aug. '10	92.60±18.40	118±41.50	30.00±3.59	144±9.82	122±79.3	62.60±19.40	80.20±20.50	18.50±3.67	ND	86.40 (1810)	75.60 (1810)
	Oct. '10	ND	288000±197	199±8.68	106±90.50	83.50±68.60	51.80±44.70	12.10±11.80	18.50±8.40	3.93±0.14	41100 (864000)	36000 (864000)
	Dec. '10	2.58±0.22	14.80±0.64	4.72±0.07	10.20±0.44	0.29±0.11	0.23±0.14	3.41±0.18	3.51±0.72	0.13±0.23	5.66 (119)	4.97 (119)
	Feb. '11	366±6.84	3.85±1.58	9.08±0.11	25.90±1.99	19.20±7.49	6.95±1.76	10.10±2.60	1.46±0.40	6.53±4.86	62.20 (1310)	55.20 (1330)
	Apr. '10	1.82±0.50	1.47±0.53	1.90±0.67	2.54±2.28	3.35±0.12	ND	13.70±0.52	1.24±2.14	ND	3.72 (78.20)	3.26 (78.20)
	Jun. '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-
	Aug. '10	0.99±0.48	1.66±0.79	1.31±0.75	0.72±0.24	1.17±0.37	0.46±0.28	2.69±0.42	3.03±1.84	ND	1.65 (34.70)	1.45 (34.70)
	Oct. '10	ND	1660±643	1.70±2.13	0.29±0.25	ND	ND	0.31±0.53	9.27±5.18	3.57±0.22	239 (5010)	209 (5020)
	Dec. '10	105±55.60	6.86±1.06	10.50±3.90	23.0±4.38	7.36±3.56	17.60±7.66	66.20±8.18	38.00±4.61	4.48±0.21	36.80 (772)	32.70 (785)
	Feb. '11	5.39±0.37	1.55±0.58	2.47±1.40	4.44±0.50	9.41±0.82	7.12±0.68	43.50±3.74	2.41±0.45	1.84±0.27	9.88 (207)	8.87 (213)
values reported are mean and standard deviation of triplicate analyses; NA – not analysed; ND – not detected; values in parentheses represent the sum of PBDE congeners; $\sum_{PBDEs}$ denotes sum of tri-heptaBDEs investigated; $\sum_{arades}$ denotes sum of all PBDE congeners, including BDE 209												

Sample type	Sampling period	Target compounds										$\sum_{\text{PBDEs}}$	$\sum_{\text{SPBDEs}}$
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
Raw water	May. '10	28.30±5.69	109±14.00	10.80±4.83	16.10±0.84	5.34±0.68	3.17±0.48	112±29.40	254±60.10	411±315	76.40 (1600)	118 (2840)	
	Jul. '10	0.24±0.08	465±2.43	36.5±20.90	29.40±7.12	17.80±3.79	22.50±15.30	36.20±5.43	69.00±14.20	292±27.10	93.50 (1962)	118 (2840)	
	Sept. '10	8.76±7.07	38.60±2.38	5.86±0.83	13.50±3.32	11.40±8.55	17.70±12.00	1.70±0.87	15.70±1.18	2670±1250	13.60 (286)	346 (8290)	

Table 4.16: Mean (±standard deviation) concentrations (ng/f) of selected PBDE congeners and BB 153 in effluent samples collected from the Old Bellville WWTP

	Nov. '10	ND	1160±186	449±135	1020±145	738±87.80	670±83.70	1640±84.10	272±58.10	7.25±1.15	754 (15800)	660 (15900)	
Sample type	Jan '11	129±55.60	301±50.10	144±32.80	204±19.40	57.30±39.70	28.90±28.60	310±101	370±249	27.10±15.90	216 (4540)	193 (4620)	
	Sampling period	Target compounds											
	May '10	261±246.49	21.20±15.53	1.52±0.45	5.12±0.97	5.12±0.97	4.04±1.80	1.91±2.05	5.19±1.85	2.11±0.25	8.04 (169)	7.36 (177)	
											2.73±0.20	2.73±0.20	
	Jul. '10	712±89.08	1010±30.70	70.7±52.30	49.00±3.59	49.00±3.59	10.00±1.00	1630±106	48.28±2.98	2.80±0.30	63.90 (1380)	98.30 (21880)	
	Sept. '10	33.80±1.33	521±2.28	45.50±1.36	21.60±1.35	8.60±2.47	61.3±1.68	27.40±1.73	13.9±1.00	7.69±0.85	4.10±0.94	96.5 (21880)	
	Nov. '10	0.37±0.65	445±2.54	388±118	984±78.80	374±88.50	11.90±1.28	2130±22.40	270±21.30	9.93±1.78	487 (19380)	473 (13880)	
	Jan '11	813±82.60	132±73.90	125±39.10	108±14.40	52.70±7.07	34.40±8.18	158±117	174±8.44	71.10±11.90	223 (4690)	204 (4900)	
Secondary effluent	Mar. '11	30.00±1.52	25.30±0.34	4.31±2.01	4.06±1.19	4.31±5.71	3.44±1.17	1.60±0.79	1.66±0.16	11.20±7.71	10.20 (214)	10.30 (247)	
	May. '10	12.10±11.50	10.40±4.72	13.20±8.72	6.96±2.22	4.45±4.00	6.01±2.61	3.62±1.77	6.09±5.86	20.90±36.20	8.13 (171)	9.73 (233)	
	Jul. '10	7.48±1.56	1.16±0.37	1.53±0.98	1.94±0.06	1.38±0.80	0.51±0.03	5.87±2.94	45.70±13.00	ND	9.29 (195)	8.13 (195)	
	Sept. '10	0.35±0.06	0.66±0.02	0.73±0.40	0.57±0.18	0.34±0.16	0.77±0.30	0.52±0.02	1.74±1.27	2630±330	0.70 (14.80)	329 (7910)	
	Nov. '10	3.62±3.17	12000±1150	172±38.10	75.50±10.90	620±46.50	225±32.50	607±91.60	52.6±17.10	13.60±0.98	17400 (364000)	15200 (364000)	
	Jan '11	18.70±5.36	3.30±1.11	7.62±0.60	20.20±1.96	25.30±3.06	20.00±2.13	8.34±1.26	1.75±0.74	55.10±9.63	12.20 (257)	17.60 (422)	
Final effluent	Mar. '11	13.60±3.35	21.50±2.09	8.95±3.04	7.07±0.41	5.31±1.19	6.47±0.30	1.82±1.60	3.37±1.49	1.31±1.00	8.81 (185)	7.87 (189)	
	May. '10	11.80±1.21	16.60±3.84	12.10±4.78	6.29±0.52	6.27±5.43	12.10±8.31	20.50±14.20	49.30±40.50	ND	17.50 (368)	15.40 (368)	
	Jul. '10	1.33±0.35	2.63±1.71	3.61±2.74	3.91±3.26	2.26±1.96	0.75±1.16	4.61±3.02	10.80±8.78	ND	4.16 (87.40)	3.64 (87.40)	
	Sept. '10	1.19±0.02	0.32±0.03	0.24±0.08	0.44±0.13	0.28±0.10	0.33±0.13	0.66±0.14	1.49±0.45	ND	0.66 (13.80)	0.58 (13.80)	
	Nov. '10	0.10±0.09	0.21±0.10	3.87±6.26	1.81±1.99	0.30±0.24	0.28±0.18	0.80±0.57	7.24±8.84	9.81±0.96	2.05 (43.00)	3.02 (72.40)	
	Jan '11	30.90±2.34	1.54±0.94	8.10±0.41	26.50±1.57	22.49±3.06	10.20±7.42	6.26±0.51	1.64±0.18	3.95±0.74	13.90 (292)	12.70 (304)	
	Mar. '11	2.98±0.10	11.50±2.33	2.20±0.25	4.34±0.28	5.81±0.46	5.24±0.35	1.07±0.07	2.06±0.14	ND	4.28 (90.00)	3.75 (90.00)	

values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent the sum of PBDE congeners; $\sum_{PBDEs}$ denotes sum of tri-heptaPBDEs investigated; $\sum_{PBDEs}$ denotes sum of all PBDE congeners, including BDE 209

Table 4.17: Mean (±standard deviation) concentrations (ng/l) of selected PBDE congeners and BB 153 in effluent samples collected from the New Bellville WWTP

	Jan '11	170±143	1220±876	101±14.50	274±145	72.80±53.00	27.50±20.50	663±335	561±436	83.30±1.83	437 (9180)	393 (9430)
Secondary effluent	Mar. '11	15.30±0.31	8.50±0.70	1.92±0.06	8.02±0.65	2.10±2.63	1.69±2.14	1.92±1.77	2.99±1.30	25.80±4.16	5.82 (122)	8.32 (200)
	May '10	23.90±0.67	18.20±6.52	34.30±17.2	13.60±8.60	ND	18.50±13.90	37.0±32.10	66.20±57.30	ND	27.60 (579)	24.10 (579)
	Jul. '10	7.04±0.87	2.16±0.60	1.88±0.10	0.38±0.02	1.05±0.22	0.77±0.28	24.10±0.35	16.00±2.71	ND	6.68 (140)	5.84 (140)
	Sept. '10	0.29±0.01	0.23±0.02	0.25±0.05	0.37±0.05	ND	0.14±0.12	0.60±0.05	1.21±1.05	ND	0.42 (8.85)	0.37 (8.85)
	Nov. '10	0.45±0.77	53000±8360	115±61.70	134±48.80	139±43.20	169±10.70	305±19.80	547±81.40	8.72±0.35	7750 (163000)	6790 (163000)
Final effluent	Jan '11	13.90±1.36	6.88±1.22	9.45±3.34	11.40±3.02	7.14±2.00	7.18±2.07	5.19±1.04	2.72±0.49	7.97±6.22	8.10 (170)	8.08 (194)
	Mar. '11	7.04±0.87	3.87±0.21	3.24±0.25	5.70±0.45	11.10±0.43	3.89±0.60	5.93±1.60	13.10±1.43	2.69±1.09	7.14 (150)	6.58 (158)
	May '10	24.20±9.70	19.40±4.01	9.31±5.18	5.29±1.74	ND	2.64±2.68	6.30±4.18	16.40±11.30	ND	11.60 (243)	10.10 (243)
	Jul. '10	59.60±6.80	40.40±5.01	11.80±11.60	45.20±25.90	81.10±32.70	41.60±1.45	24.20±16.20	227±6.29	ND	69.80 (1470)	61.10 (1470)
	Sept. '10	0.09±0.03	127±9.31	0.17±0.08	0.51±0.35	0.50±0.07	0.35±0.03	2.50±0.08	12.50±4.57	1.97±0.26	20.50 (430)	18.20 (436)
values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent the sum of PBDE congeners; $\sum_{7PBDEs}$ denotes sum of tri-heptaBDEs investigated; $\sum_{8PBDEs}$ denotes sum of all PBDE congeners, including BDE 209	Nov. '10	ND	52800±4480	200±8.45	104±7.87	195±26.90	149±13.30	369±37.10	734±193	5.56±0.73	7780 (163000)	6800 (163000)
	Jan '11	15.80±0.96	5.44±2.36	4.98±2.66	9.94±0.96	16.10±3.05	12.60±1.76	5.66±2.63	10.40±3.40	2.37±0.74	9.76 (205)	8.84 (212)
	Mar. '11	12.90±3.97	7.00±1.54	4.19±0.10	10.60±1.07	17.30±0.52	5.63±0.34	8.02±4.62	9.48±6.21	2.50±1.27	9.93 (208)	9.00 (216)

Sample type	Sampling period	Target compounds										$\sum_{7PBDEs}$	$\sum_{8PBDEs}$
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
Raw water	Apr. '10	5.49 ±4.75	1.54±1.35	1.57±1.39	6.08±4.17	1.19±0.37	0.98±1.02	7.19±6.80	37.60±32.60	2240±248	8.66 (182)	287 (6890)	
	Jun. '10	12.60±2.98	12.40±6.13	6.50±4.63	7.76±3.26	0.75±1.30	1.50±1.32	24.80±9.67	62.30±16.90	2340±1850	18.20 (381)	309 (7410)	
	Aug. '10	7.76±7.77	321±8.28	10.80±6.55	18.70±3.93	15.90±1.67	13.20±2.57	31.70±44.10	18.20±6.25	405±126	60.60 (1270)	104 (2490)	
	Oct. '10	ND	531±30.10	4.17±2.74	2620±209	7.77±4.52	5.26±4.05	38.5±20.80	6.37±2.40	4.92±0.96	459 (9630)	401 (9640)	
	Dec. '10	85.70±16.50	209±30.50	23.80±4.11	33.90±6.27	3.97±0.11	3.27±2.12	2.33±1.58	19.00±4.38	12.80±3.09	54.0 (1130)	48.80 (1170)	
	Feb. '11	1850±380	506±14.60	35.30±5.09	67.10±9.80	22.10±4.60	15.80±2.59	45.7±20.00	130±41.80	11.60±5.43	379 (7960)	333 (7990)	
Secondary effluent	Apr. '10	7.74±0.01	17.90±10.10	13.00±6.31	12.90±4.58	0.70±1.21	4.64±1.61	13.30±3.97	ND	220± 240	9.36 (197)	35.70 (857)	
	Jun. '10	88.10±78.30	10.60±8.10	13.00±9.42	14.20±9.06	11.40±7.34	0.96±1.67	22.80±12.10	30.00±16.80	1770±583	27.10 (570)	245 (5880)	

Table 4.18: Mean (±standard deviation) concentrations (ng/l) of selected PBDE congeners and BB 153 in effluent samples collected from the Zandvliet WWTP

Final effluent	Aug. '10	1.06±0.21	8.01±0.22	0.67±0.08	2.17±0.46	ND	ND	3.89±0.69	4.04±0.85	ND	2.83 (59.5)	2.48 (59.5)
	Oct. '10	ND	2220±365	0.41±0.07	0.44±0.06	ND	ND	0.57±0.49	4.01±1.35	0.42±0.73	317 (6660)	278 (6670)
	Dec. '10	281±5.65	15.70±11.30	4.12±3.07	9.19±0.65	4.02±0.65	0.78±0.84	1.28±0.59	1.37±0.47	12.80±2.10	45.30 (950)	41.20 (989)
	Feb. '11	7.62±2.94	17.80±2.79	14.40±11.60	18.40±14.10	11.90±4.18	8.19±7.36	10.10±2.27	10.50±9.19	8.12±0.32	12.90 (272)	12.30 (296)
	Apr. '10	52.40±10.10	18.50±0.60	6.22±1.96	9.48±4.71	5.41±6.42	2.81±3.73	15.00±11.40	27.70±13.80	9770±5030	19.20 (404)	1240 (29700)
	Jun. '10	15.40±5.00	11.50±5.75	6.02±1.59	2.52±2.96	0.43±0.75	0.43±0.42	16.20±0.46	32.90±43.30	2260±1150	12.10 (255)	293 (7040)
	Aug. '10	5.09±0.39	16.50±0.14	2.48±0.56	22.70±3.37	12.90±1.65	13.70±5.57	8.19±3.39	29.70±0.44	ND	13.90 (293)	12.20 (293)
	Oct. '10	0.08±0.01	924±379	0.21±0.14	0.35±0.12	0.14±0.05	0.15±0.07	0.41±0.15	4.54±5.34	ND	133 (2790)	116 (2790)
	Dec. '10	517±34.90	3.46±1.88	5.87±2.82	31.30±4.74	6.38±2.13	1.22±1.35	2.39±1.87	1.13±0.22	5.29±0.58	81.10 (1700)	71.60 (1720)
	Feb. '11	5.78±0.96	18.10±2.33	17.00±4.65	68.00±3.22	7.38±0.42	11.40±0.79	5.97±2.49	6.23±6.58	2.77±0.33	18.30 (385)	16.40 (393)

values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent the sum of PBDE congeners; $\sum_{PBDEs}$ denotes sum of tri-heptaBDEs investigated; $\sum_{PBDEs}$ denotes sum of all PBDE congeners, including BDE 209

The ANOVA analysis which these results were subjected to clearly showed a statistically significant difference ($p < 0.001$) in contaminants' load in different effluent types at all the WWTPs investigated. Similarly, there was a significant difference ($p < 0.001$) in all the contaminants' levels from one sampling regime to the other. The analysis further revealed that the observed variations were common to all the WWTPs investigated in this study. The observed variation in concentrations amongst PBDE congeners within a plant and between plants were generally within 2 to 50-fold except in a few extreme cases. A similar trend has been reported for PBDEs (Vogelsang *et al.*, 2006) and other organic micropollutants in WWTP influents (Manoli and Samara, 1999; European Commission, 2003). In this case, large temporal variations (at least 10-fold) were said to be expected within the same plant and between plants.

Several factors could be responsible for the trend observed in this study. First, the influence of suspended solids on the fate and distribution of these contaminants in the aqueous wastestream cannot be ruled out. It is widely accepted that suspended solids have strong affinities for organic contaminants, including PBDEs. The potential of any WWTP to effectively remove PBDEs from the wastestream depends on its ability to significantly remove suspended solids from the aqueous matrix. Therefore, operational measures aimed at reducing the quantity of suspended solids escaping from the treatment plant would ultimately result in minor contamination of the receiving waterbodies via treated effluent discharges.

Besides the manipulation of the hydraulic retention times (HRTs) as well as the solids residence times (SRTs) of the clarifiers, another important approach to resolve excessive solid losses is to channel treated effluent into maturation ponds. This measure will ensure a drastic reduction in the quantity of suspended solids often laden with organic contaminants reaching the receiving waterbodies. Unfortunately, some of the WWTPs investigated do not have efficient maturation ponds and those that do have are grossly overloaded. For instance, the residence time of the treated effluent in the maturation pond at the Potsdam WWTP was too short to allow for effective settling of the suspended solids.

In this study, an attempt was made to assess the overall efficiency of each of the WWTPs investigated with respect to PBDE removal. As a result, certain assumptions were made. Since grab samples were collected from these plants within an estimated time of one hour during each sampling regime, it was assumed that the use of the average total PBDEs values over the entire study period would be more appropriate for the evaluation. This decision was also arrived at due to the possible re-suspension of certain PBDE congeners into the aqueous phase during the re-circulation of excess sludge within the plant, especially in the activated sludge systems. The possible contribution of the degradation products of the highly brominated congeners to the levels of the lower congeners in the WWTP was also taken into consideration. In lieu of these aforementioned points, it was concluded that the estimation of the

percentage removal for each PBDE congener might be misleading. Hence, the approach adopted in this study was to use the overall mean values of the total PBDEs in raw water and final effluent samples for the estimation of the removal efficiency at different sampling regime in each plant.

Using this approach, the PBDE removal efficiency for these plants ranged from 31.6 – 98.2%, 41.3 – 98.7%, 49.0 – 99.8%, 79.8 – 97.8% and 5.18 – 95.1% for Potsdam, Cape Flats, Old Bellville, New Bellville, and Zandvliet WWTPs, respectively. These findings were comparable to those reported for BDE 47 and 99 where their removal efficiencies ranged from 44 to 99% in typical chemical and biological wastewater treatment plants (Vogelsang *et al.*, 2006). Although in the present study, some anomalies were observed. These involved higher overall mean values in the final effluent than in the raw water. Both New Bellville and Zandvliet plants were affected in this regard. This observation might be a reflection of additional local sources of contaminants via atmospheric deposition. More so, the poor performance of some WWTPs as a result of rising sludge or hydraulic overload, which results in considerable amounts of finely suspended solids being transferred into the final effluent in these treatment plants, could be responsible for the observed anomalies. The detailed representation of the estimation of the PBDEs removal efficiency of each plant is presented in Figure 4.13.

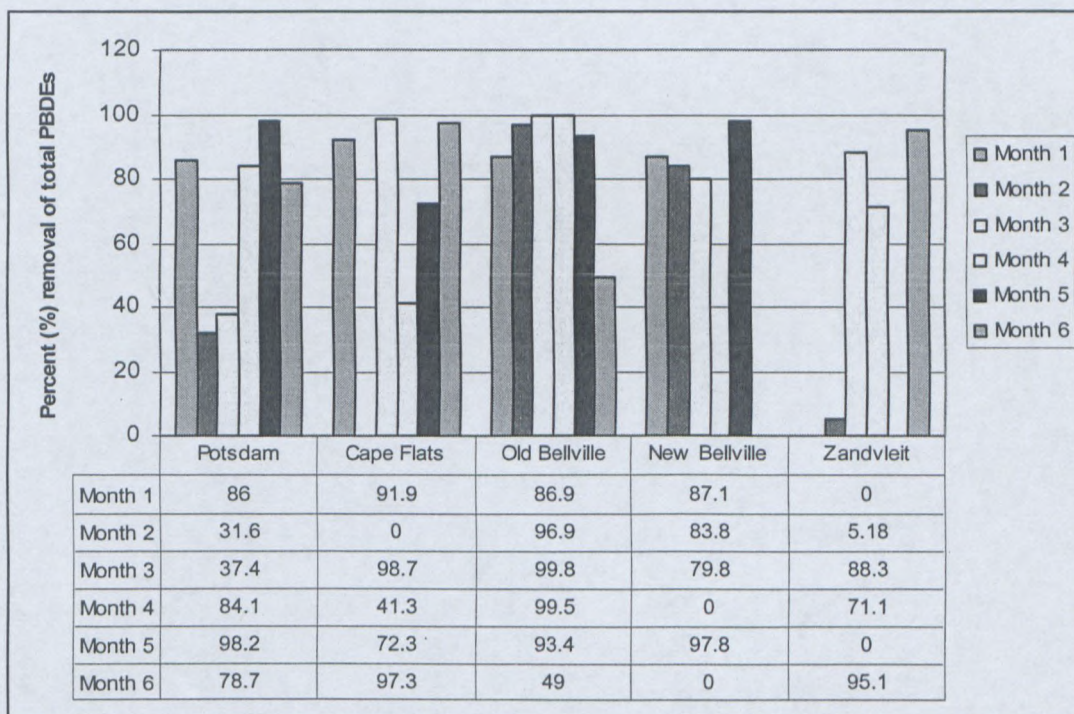


Figure 4.13: Percent removal of the total PBDEs from the wastewater at different WWTPs

4.4.3 Levels and distribution of PBDEs and BB 153 in river systems

A critical assessment of certain matrices can clearly indicate the pollution status of any given freshwater system. For river systems, both river water and bottom sediment are important sinks of different contaminants in the freshwater systems and their assessment for these contaminants can reveal the extent to which these systems have been polluted (Cheung *et al.*, 2003; Guo *et al.*, 2007). In this study, the assessment of the levels of selected PBDEs as well as BB 153 in both river water and bottom sediment was conducted with a view to determine the degree of contamination of the rivers investigated.

4.4.3.1 Levels and distribution of PBDEs and BB 153 in river water samples

The results obtained from the analysis of river water samples collected from both the Diep and Kuils Rivers are presented in Tables 4.19 and 4.20, respectively. The overall mean concentrations of the total PBDEs in the Diep River ranged from 0.84 to 10,900, 4.99 to 12,000 and 2.89 to 569 ng/l for the upstream, point of discharge and downstream sampling locations, respectively. Similarly, the overall mean concentrations of BB 153 in the Diep River for the entire study period were 104, 283 and 117 ng/l for the upstream, point of discharge and downstream sampling locations, respectively. These levels were relatively higher than those found at similar sampling locations in the Kuils River. The overall mean concentrations of the total PBDEs ranged from 0.71 to 18,500, 22.5 to 176 and 23.6 to 403 ng/l for the upstream, point of discharge and downstream sampling locations, respectively. The overall mean concentrations of BB 153 were also relatively lower in the Kuils River compared to those found in the Diep River. The concentrations obtained were 49.2, 70.4 and 58.6 ng/l for the upstream, point of discharge and downstream sampling locations, respectively.

With the exception of the extreme cases observed during the October and November sampling regimes in both rivers, the trends of the results obtained were consistent. However, the presence of the target compounds at the upstream regions of both rivers suggests that there are other possible sources of these contaminants into the rivers investigated apart from the discharge of treated effluent. This ascertainment does not undermine the possible contribution of WWTP discharges to PBDE contamination of the receiving waterbodies. In fact, it was clearly shown that most of the congeners investigated had relatively high concentrations at the point of discharge than at the upstream sampling location. The levels of most of these contaminants did not change considerably further downstream in both rivers.

Table 4.19: Mean (±standard deviation) concentrations (ng/l) of selected PBDE congeners and BB 153 in water samples collected from the Diep River

Sampling location	Sampling period	Target compounds										Σ7PBDEs	Σ8PBDEs
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
Upstream	May, '10	1.87±1.09	16.7±9.84	6.29±5.30	3.89±1.40	1.70±0.47	ND	ND	ND	ND	4.35 (91.40)	3.81 (91.40)	
	Jul, '10	1.30±0.13	3.39±0.08	0.31±0.27	1.36±0.21	0.35±0.61	ND	ND	ND	ND	0.96 (20.10)	0.84 (20.10)	
	Sept, '10	ND	2170±34.00	ND	ND	ND	ND	0.64±0.08	4.01±0.50	2.84±1.61	311 (6540)	273 (6550)	
	Nov, '10	0.13±0.04	83900±4250	562±58.30	481±33.80	528±81.40	622±25.70	1530±105	443±459	6.86±1.40	12500 (262000)	10900 (262000)	
	Jan '11	0.45±0.26	2.61±2.41	0.34±0.08	0.88±0.11	0.27±0.26	0.19±0.16	0.86±0.21	3.89±1.48	2.56±0.69	1.33 (27.90)	1.48 (35.60)	
	Mar, '11	2.28±0.26	5.18±2.17	7.68±0.22	4.73±0.48	5.13±0.08	0.65±0.18	6.33±1.55	5.30±2.50	4.37±1.05	5.23 (110)	5.12 (123)	
Point of discharge	May, '10	19.90±0.68	11.6±0.28	1.94±0.27	8.01±0.48	6.40±1.24	4.82±0.36	1.86±1.69	1.55±0.89	ND	7.32 (154)	6.40 (154)	
	Jul, '10	25.70±0.52	13.70±3.00	3.42±1.04	14.50±3.68	7.10±0.18	6.14±0.27	1.95±1.25	2.29±1.18	ND	9.80 (206)	8.58 (206)	
	Sept, '10	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	-	
	Nov, '10	0.36±0.38	93100±4220	533±54.10	484±48.30	694±100	843±267	1380±167	956±134	4.44±1.09	13900 (291000)	12100 (291000)	
	Jan '11	27.50±3.06	0.93±0.35	8.36±1.30	4.49±1.01	23.40±2.46	7.58±4.54	1.95±1.56	6.47±2.22	0.95±0.61	10.40 (219)	9.25 (222)	
	Mar, '11	2.12±0.32	3.54±0.11	1.75±0.24	4.76±0.41	4.44±3.69	0.85±0.84	1.54±0.87	3.15±0.79	18.60±7.83	3.04 (63.90)	4.99 (120)	
Downstream	May, '10	12.80±1.97	18.10±5.75	11.90±0.06	16.60±2.56	2.69±1.34	ND	13.50±4.30	98.20±54.90	0.85±0.05	24.80 (521)	21.80 (524)	
	Jul, '10	1.06±0.06	4.46±0.21	0.61±0.23	1.40±0.11	1.11±0.10	0.52±0.04	2.58±0.06	ND	549±122	1.60 (33.70)	70.10 (1680)	
	Sept, '10	0.03±0.04	17.70±29.50	9.95±17.2	53.00±91.90	3.09±5.36	2.48±4.30	4.73±8.19	14.10±24.40	8.41±0.44	14.70 (308)	13.90 (333)	
	Nov, '10	0.11±0.03	984±380	464±41.00	437±71.60	583±60.70	694±55.10	1320±89.80	755±231	3.33±0.23	649 (13600)	569 (13600)	
	Jan '11	9.55±1.49	5.68±0.14	4.87±0.69	4.94±0.35	8.32±1.26	4.33±0.60	2.39±1.71	2.20±0.37	ND	5.42 (114)	4.74 (114)	
	Mar, '11	2.62±0.33	4.54±0.71	3.29±0.75	5.49±0.08	3.24±0.34	0.24±0.05	0.85±0.10	1.67±0.39	1.43±0.70	3.10 (65.10)	2.89 (69.40)	

values reported are mean and standard deviation of triplicate analyses; NA – not analysed; ND – not detected; values in parentheses represent the sum of PBDE congeners; Σ7PBDEs denotes sum of tri-heptaBDEs investigated; Σ8PBDEs denotes sum of all PBDE congeners, including BDE 209

Table 4.20: Mean (±standard deviation) concentrations (ng/t) of selected PBDE congeners and BB 153 in water samples collected from the Kuils River

Sampling location	Sampling period	Target compounds										$\sum_{7PBDEs}$	$\sum_{8PBDEs}$
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209			
Upstream	April, '10	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	-	-	
	June, '10	3.83±1.78	10.50±2.61	8.06±5.86	6.71±1.36	0.19±0.23	0.35±0.21	0.27±0.46	4.50±4.44	1330±877	4.86 (102)	170 (4090)	
	Aug, '10	0.79±0.04	2.38±0.30	2.36±0.32	9.42±3.10	16.50±1.48	20.80±1.73	7.17±0.84	21.40±4.12	14.30±24.80	8.58 (180)	9.30 (223)	
	Oct, '10	0.17±0.02	147000±194	88.20±13.40	2.83±1.98	132±19.50	213±30.60	640±96.9	30.10±9.76	ND	21200 (445000)	18500 (445000)	
	Dec '10	1.04±0.15	0.16±0.04	0.27±0.15	0.26±0.002	ND	ND	ND	ND	3.92±0.41	0.25 (5.18)	0.71 (16.9)	
	Feb, '11	9.44±2.78	31.30±16.50	12.90±3.53	38.20±9.25	15.50±7.20	12.10±6.50	4.04±2.45	8.05±1.53	576±195	17.10 (358)	87.00 (2090)	
Point of discharge	April, '10	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	-	-	
	June, '10	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	-	-	
	Aug, '10	280±5.81	231±15.80	14.90±1.72	23.90±1.27	24.80±2.99	35.00±1.29	6.33±1.18	15.60±0.43	ND	85.10 (1790)	74.50 (1790)	
	Oct, '10	0.29±0.04	212±48.30	69.8±16.9	159±31.00	259±40.70	232±30.50	191±37.70	516±85.30	ND	201 (4220)	176 (4220)	
	Dec '10	287±41.20	4.33±2.41	1.12±0.52	5.56±1.64	1.57±1.17	1.01±0.71	1.64±1.87	4.74±4.03	10.00±9.19	43.60 (917)	39.40 (947)	
	Feb, '11	5.92±1.25	56.40±1.22	12.60±3.63	76.20±4.89	9.82±0.89	13.70±0.87	13.90±11.10	4.10±1.53	1.00±0.38	25.60 (537)	22.50 (540)	
Downstream	April, '10	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	-	-	
	June, '10	10.70±1.39	6.16±2.57	2.43±0.27	3.26±0.32	1.80±0.13	ND	4.42±0.28	3.03±0.56	2310±552	4.54 (95.40)	292 (7020)	
	Aug, '10	0.64±0.13	4.70±0.22	1.00±0.06	0.72±0.05	ND	ND	ND	0.36±0.62	1310±123	1.06 (22.20)	165 (3970)	
	Oct, '10	0.14±0.01	2260±1040	79.00±3.43	127±12.30	272±13.50	281±9.58	149±5.52	341±68.00	ND	460 (9670)	403 (9670)	
	Dec '10	163±16.90	4.47±0.70	2.93±0.16	8.58±0.54	2.22±0.25	0.60±0.39	0.58±0.35	1.44±0.82	5.25±2.11	26.20 (550)	23.60 (566)	
	Feb, '11	55.60±2.49	27.60±8.51	19.10±2.69	66.30±0.70	21.00±1.29	11.10±0.96	20.30±6.07	5.33±1.85	117±74.60	30.70 (646)	41.50 (996)	

values reported are mean and standard deviation of triplicate analyses. NA – not analysed; ND – not detected; values in parentheses represent the sum of PBDE congeners; $\sum_{7PBDEs}$ denotes sum of tri-heptaBDEs investigated; $\sum_{8PBDEs}$ denotes sum of all PBDE congeners, including BDE 209

This scenario, especially with the unusually high levels observed in both rivers during the October and November sampling regimes, calls for immediate concern. Since these observations cut across all the sampling locations, it is difficult to predict the possible sources of these contaminants into the investigated rivers. It might be reasonable to speculate that the several activities taking place at the upstream of these rivers could be responsible for the observed trend. Both rivers have a somewhat similar activities taking place along their catchment areas as well as their drainage basins. Besides the large scale farming in these locations, two out of the three operational landfill sites in the City of Cape Town are also housed within these locations.

The October/November periods coincide with the onset of the summer season when an increase in the temperature of the underlying soil is expected. During this period, it is also expected that there will be increased biodegradation of waste materials disposed into the landfill sites. The enhanced leaching of PBDEs from previously treated products in the presence of dissolved humic substances has been reported (Choi *et al.*, 2009). Incidentally, the LTP at the Vissershok landfill site which is situated further upstream of the Diep River was undergoing rehabilitation during this period. Usually the treated leachate from this site is often sprayed on unpaved roads to reduce dust generation as a result of vehicular movement within the site. This practice might contribute to the re-distribution of PBDEs into the adjacent river especially during heavy rainfall.

The drainage basins of the rivers covered in this study were within the remote and semi-urban areas of the city. The continuous usage of compost derived from the WWTP sludge to improve soil productivity in these farms could contribute to PBDE contamination of the rivers. During heavy rainfall, contaminants released from the land-applied sludge could be washed off and transported into the river via the run-off. Eljarrat *et al.* (2008) affirms the significant role this practice could play in the re-distribution of PBDEs released from land-applied sludge in the environment. Furthermore, the greywater inputs from the informal settlements adjacent to these rivers might be an important factor for consideration. Greywater are known to contain and transport considerable amount of organic pollutants, including PBDEs (Donner *et al.*, 2010). Due to the proximity of these settlements to these rivers, especially the Kuils River, a significant amount of organic contaminants could be released into the river via run-off and seepages.

With the increasing usage of treated effluent, especially for agricultural irrigation (Adewunmi *et al.*, 2010), there is need for conscious steps to be taken to evaluate the possible impacts of this practice on the public health. One of the implications of increasing PBDE levels, especially in the aquatic ecosystem, is the possible accumulation and magnification of these contaminants in living organisms. Recently, evidences are emerging that plants can take up and accumulate these contaminants in their tissues and

these have been well documented in the literature (Kiviranta *et al.*, 2004; Gomara *et al.*, 2006; Meng *et al.*, 2007; Voorspoels *et al.*, 2007; Huang *et al.*, 2011). It is therefore imperative to ensure that appropriate measures are put in place to checkmate further release of these contaminants into the environment so as to forestall the irreversible consequences of human exposure to these harmful chemicals.

4.4.3.2 Levels and distribution of PBDE congeners and BB 153 in bottom sediment

The results obtained from the analysis of bottom sediment for selected PBDE congeners and BB 153 are presented in Tables 4.21 and 4.22 for the Diep and Kuils Rivers, respectively. The overall mean concentrations of the total PBDEs ranged from 0.06 – 2.47, 0.07 – 0.58 and 0.10 – 0.78 ng/g for the upstream, point of discharge and downstream sampling locations of the Diep River, respectively. These values were relatively higher in the Kuils River samples where the range of the overall mean concentrations were 0.22 – 1.52, 2.36 – 9.95 and 0.31 – 5.38 ng/g for the upstream, point of discharge and downstream sampling locations, respectively. The mean concentrations of BB 153, which were generally low and these ranged from ND – 0.33, ND – 0.22 and 0.04 – 0.39 ng/g for the upstream, point of discharge and downstream sampling locations of the Diep River, respectively. Observed levels of BB 153 in the Kuils River were also higher than those obtained at similar sampling locations in the Diep River. These values ranged from ND – 0.18, ND – 1.01 and ND – 1.21 ng/g for the upstream, point of discharge and downstream sampling points, respectively.

Unlike the river water samples, the trend of the results obtained for bottom sediment in both rivers were consistent throughout the study period. The pattern exhibited by these results demonstrated the suitability of bottom sediment as a better indicator of pollutants, especially when the temporal assessment of their impacts on the aquatic environment is most desired. To further investigate the behaviours of the target compounds in the rivers investigated, the results obtained were subjected to statistical analysis. The ANOVA analysis showed that only BDE 28 and 47 had significant difference ($p < 0.001$) in both riverwater and bottom sediment samples analysed. These congeners also exhibited this trend at all the sampling locations and during the sampling regimes in both rivers, others did not. However, the analysis further revealed that there were no statistical differences ($p > 0.001$) in the levels of BDE 100, 99, 154, 153, 183 and BB 153 in both sample types collected from all the sampling locations. This suggests that these congeners might have similar sources into both rivers.

Table 4.21: Mean (±standard deviation) concentrations (ng/g) of selected PBDE congeners and BB 153 in sediment samples collected from the Diep River

Sampling location	Sampling period	Target compounds										Σ _{7PBDEs}	Σ _{8PBDEs}	TOC (%)
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209				
Upstream	May. '10	0.18±0.03	0.22±0.02	0.17±0.04	0.17±0.02	0.27±0.05	0.13±0.03	0.18±0.03	0.13±0.02	NID	0.19 (3.91)	0.16 (3.91)	2.13±0.13	
	Jul. '10	0.48±0.17	1.95±0.25	1.91±0.11	1.47±0.97	1.48±0.24	0.33±0.12	5.17±0.16	7.30±1.11	NID	2.82 (59.30)	2.47 (59.30)	5.41±0.16	
	Sept. '10	0.04±0.03	0.15±0.14	0.09±0.02	0.33±0.21	0.55±0.48	0.09±0.05	0.14±0.05	0.19±0.01	1.26±0.20	0.21 (4.48)	0.34 (8.24)	0.83±0.36	
	Nov. '10	0.05±0.003	0.03±0.01	0.09±0.04	0.01±0.02	0.06±0.06	NID	0.07±0.03	NID	0.13±0.03	0.04 (0.94)	0.06 (1.33)	1.60±0.13	
	Jan '11	0.11±0.04	1.95±0.20	1.83±0.15	0.44±0.08	0.52±0.17	0.15±0.16	0.49±0.12	0.83±0.06	0.79±0.39	0.88 (18.5)	0.87 (20.90)	1.58±0.15	
Point of discharge	Mar. '11	0.05±0.01	0.12±0.03	0.14±0.05	0.10±0.06	0.07±0.04	0.04±0.01	0.10±0.03	0.13±0.01	1.01±0.37	0.10 (2.14)	0.22 (5.17)	0.84±0.01	
	May. '10	0.11±0.02	0.13±0.01	0.11±0.02	0.10±0.01	0.16±0.03	0.08±0.02	0.11±0.02	0.08±0.01	0.15±0.08	0.11 (2.40)	0.12 (2.84)	2.78±0.31	
	Jul. '10	0.09±0.03	1.06±0.11	0.30±0.18	0.28±0.06	0.15±0.02	0.22±0.03	0.63±0.11	0.76±0.05	1.36±0.06	0.47 (9.79)	0.58 (13.90)	1.23±0.02	
	Sept. '10	0.04±0.02	0.06±0.03	0.08±0.03	0.16±0.10	0.11±0.03	0.04±0.01	0.20±0.07	0.06±0.05	0.26±0.02	0.10 (2.11)	0.12 (2.87)	0.72±0.02	
	Nov. '10	0.04±0.02	0.07±0.02	0.13±0.07	0.02±0.02	0.05±0.01	NID	0.07±0.13	0.03±0.06	0.11±0.04	0.06 (1.29)	0.07 (1.62)	0.84±0.03	
	Jan '11	0.11±0.001	0.87±0.01	0.29±0.03	0.23±0.01	0.21±0.06	0.13±0.05	0.57±0.20	0.67±0.17	0.88±0.53	0.42 (8.82)	0.48 (11.50)	0.64±0.03	
	Mar. '11	0.17±0.03	1.15±0.04	0.22±0.05	0.38±0.10	0.15±0.04	0.10±0.01	0.38±0.23	0.76±0.16	0.50±0.27	0.46 (9.62)	0.46 (11.1)	1.20±0.01	
Downstream	May. '10	0.54±0.06	0.66±0.01	0.53±0.08	0.51±0.04	0.82±0.09	0.39±0.07	0.55±0.13	0.38±0.07	1.25±0.01	0.57 (12.00)	0.66 (15.70)	0.57±0.01	
	Jul. '10	0.07±0.01	0.76±0.02	0.31±0.19	0.27±0.02	0.11±0.04	0.27±0.09	0.27±0.03	0.65±0.07	1.01±0.11	0.35 (7.31)	0.43 (10.40)	0.77±0.01	
	Sept. '10	0.08±0.01	0.18±0.02	0.07±0.01	0.14±0.01	0.05±0.01	0.06±0.02	0.11±0.02	0.22±0.01	1.79±0.35	0.12 (2.52)	0.33 (7.88)	1.12±0.03	
	Nov. '10	0.06±0.01	0.05±0.01	0.10±0.06	0.04±0.01	0.07±0.02	0.04±0.08	0.10±0.07	0.29±0.22	1.00±0.04	0.10 (2.13)	0.10 (2.43)	0.32±0.02	
	Jan '11	0.07±0.01	0.61±0.02	0.44±0.02	0.33±0.09	0.13±0.04	0.11±0.04	0.35±0.03	0.24±0.12	1.15±0.41	0.31 (6.50)	0.41 (9.94)	0.51±0.10	
	Mar. '11	0.42±0.15	0.70±0.05	1.00±0.13	1.54±0.12	0.69±0.02	0.28±0.08	0.33±0.11	0.72±0.37	0.86±0.26	0.77 (16.20)	0.78 (18.70)	0.44±0.01	

values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent the sum of PBDE congeners; Σ_{7PBDEs} denotes sum of tri-heptaBDEs investigated; Σ_{8PBDEs} denotes sum of all PBDE congeners, including BDE 209

Sampling location	Sampling period	Target compounds										$\sum_{7PBDES}$	$\sum_{8PBDES}$	TOC (%)
		BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BB 153	BDE 153	BDE 183	BDE 209				
Upstream	April, '10	0.04±0.02	0.23±0.05	0.14±0.003	0.15±0.03	0.20±0.08	0.09±0.02	0.20±0.07	0.19±0.19	1.19±0.73	0.15 (3.72)	0.29 (7.02)	1.77±0.04	
	June, '10	ND	10.00±0.26	ND	ND	1.97±0.07	ND	ND	0.15±0.25	0.07±0.01	1.51 (36.30)	1.52 (36.50)	1.80±0.02	
	Aug, '10	ND	7.57±0.20	ND	ND	ND	ND	ND	0.22±0.17	ND	1.11 (23.30)	0.97 (23.30)	1.88±0.02	
	Oct, '10	ND	10.14±0.98	0.12±0.20	ND	ND	ND	0.04±0.01	0.23±0.08	ND	1.32 (31.60)	1.32 (31.60)	1.78±0.02	
	Dec '10	0.05±0.02	0.20±0.01	0.16±0.10	0.27±0.10	0.28±0.13	0.12±0.06	0.34±0.08	0.22±0.15	0.25±0.05	0.21 (4.92)	0.22 (5.32)	1.57±0.01	
Point of discharge	Feb, '11	0.20±0.04	0.26±0.12	0.14±0.02	0.32±0.17	0.74±0.18	0.18±0.10	0.44±0.07	0.40±0.09	1.73±0.21	0.34 (8.05)	0.53 (12.70)	1.38±0.02	
	April, '10	3.04±0.24	3.24±0.28	3.24±0.28	2.46±0.15	0.27±0.12	0.19±0.10	4.03±0.55	3.14±1.11	1.30±0.79	2.45 (58.80)	2.59 (62.10)	3.77±0.03	
	June, '10	ND	27.77±0.59	ND	0.25±0.22	9.51±1.99	ND	0.07±0.02	0.37±0.05	0.17±0.03	4.75 (114)	4.77 (114)	3.63±0.03	
	Aug, '10	ND	29.45±1.21	ND	ND	ND	ND	0.07±0.01	0.31±0.24	0.07±0.02	3.73 (89.50)	3.74 (89.70)	3.08±0.01	
	Oct, '10	ND	53.20±11.40	9.89±15.91	13.30±19.50	0.75±0.55	0.63±0.53	1.73±1.11	0.62±0.39	0.10±0.01	11.40 (239)	9.95 (239)	5.43±0.04	

Table 4.22: Mean (±standard deviation) concentrations (ng/g) of selected PBDE congeners and BB 153 in sediment samples collected from the Kuils River

Downstream	Dec '10	2.34±0.78	3.73±0.99	3.81±0.59	2.43±0.60	1.89±0.20	1.01±0.15	4.97±0.85	2.77±0.86	0.58±0.22	3.13 (65.80)	2.81 (67.50)	3.64±0.01
	Feb. '11	1.53±0.22	2.94±0.66	0.97±0.16	1.22±0.09	1.45±0.60	0.93±0.12	2.75±0.24	4.52±0.52	3.50±0.31	2.04 (49.00)	2.36 (56.60)	5.04±0.002
	April '10	0.07±0.03	0.08±0.01	0.08±0.02	0.15±0.04	0.19±0.05	ND	0.36±0.34	0.11±0.05	1.44±0.11	0.13 (3.13)	0.31 (7.44)	3.02±0.01
	June '10	ND	35.74±1.58	ND	0.19±0.02	6.37±0.38	ND	0.03±0.05	0.65±0.40	0.10±0.02	5.37 (129)	5.38 (129)	2.81±0.02
	Aug. '10	ND	2.74±2.38	0.80±1.39	0.97±1.67	ND	ND	0.05±0.01	0.25±0.13	0.16±0.16	0.60 (14.40)	0.62 (14.90)	4.66±0.01
	Oct '10	ND	3.59±0.19	ND	0.42±0.73	ND	ND	ND	0.35±0.20	0.10±0.03	0.54 (13.10)	0.56 (13.40)	2.67±0.01
	Dec '10	2.78±0.77	3.62±0.76	3.08±1.47	2.46±0.07	2.30±0.62	1.21±0.23	9.93±0.49	10.20±0.14	1.13±0.48	4.91 (103)	4.44 (106)	4.17±0.01
	Feb. '11	0.06±0.01	0.09±0.02	0.13±0.01	0.15±0.02	0.28±0.06	0.08±0.01	0.20±0.05	0.19±0.05	1.39±0.15	0.15 (3.53)	0.31 (7.45)	4.24±0.01

values reported are mean and standard deviation of triplicate analyses; ND – not detected; values in parentheses represent the sum of PBDE congeners; $\sum_{PBDEs}$ denotes sum of tri-heptaBDEs investigated; $\sum_{PBDEs}$ denotes sum of all PBDE congeners, including BDE 209; TOC – total organic carbon.

With respect to the variation of these contaminants in both sample types at different sampling locations, only BDE 183 and 209 did not show statistically significant difference ($p > 0.001$) in their levels in both rivers. Furthermore, the statistical analysis further revealed that BDE 209 did not show any significant difference ($p > 0.001$) in its levels at different sampling regimes in both sample types collected in these rivers. This observation might be due to the uniform release of this congener from its point sources into the rivers. In this study, relatively high levels of BDE 209 were found in the treated effluent of most of the WWTPs investigated. This suggests that the discharge of treated effluent might constitute an important source of this congener into the rivers.

Although the overall mean concentrations of the total PBDEs were higher in the bottom sediment of the Kuils River, the impact of treated effluent discharges seemed to be more pronounced in the Diep River. This is because most of the penta-BDE congeners monitored were detected in the bottom sediment collected from the sampling locations. The penta-BDE technical formulation is mostly used to flame-retard household products, including furniture, carpets, textile, amongst others. Their release into the wastewater usually results during the cleaning and washing of these materials. Since a significant amount of the effluent received by most WWTPs investigated were derived from residential and commercial homes, it might be reasonable to attribute their occurrence in bottom sediment to treated effluent discharges.

The hydrodynamics of the rivers might also influence the distribution of these contaminants, especially during the summer season. The flow rates as well as the degree of turbulence could affect the settling rates of suspended solids and ultimately sediment deposition in the rivers (Forstner, 2004). For most of the rivers within the study area, effluent discharges play a vital role in their water chemistry, especially during the summer season. The overall contributions of these factors would determine the levels and distribution of pollutants in the rivers investigated. It is apparent that slightly higher levels of these contaminants were found during the summer season at nearly all the sampling locations. Relatively high levels of contaminants were also found at both the point of discharge and downstream sampling location than at the upstream location in the Kuils River.

An attempt was made to statistically establish possible relationship between target congeners and total organic carbon (TOC) in the bottom sediment of these rivers. The assessment was carried out to predict the possible roles of the TOC in the distribution of these contaminants in both rivers. The Pearson correlation showed that all the congeners were positively correlated with the TOC in the Kuils River. However, only BDE 99 had a significant correlation at 0.05 level (2-tailed) amongst the congeners with the TOC. In the Diep River, all the congeners, except BDE 209 showed a significantly strong positive

correlation with the TOC, even at 0.01 level (2-tailed). BDE 209 had a significant negative correlation with the TOC, thus suggesting that the presence of organic matter might not influence its levels in the river.

A comparison of the results obtained in this study with similar studies conducted around the world is shown in Table 4.23. The levels of the target compounds found in the bottom sediment of both investigated rivers were lower than those reported elsewhere. Although relatively high levels of these contaminants were found in the river water samples of these rivers, the observed trend could be explained by the discharge of treated WWTP effluent, which often influences their water chemistry, especially during the dry seasons of the year. Furthermore, it is a usual practice in most developed countries that effluent emanating from any industrial activities, which are capable of releasing considerable quantities of harmful organic contaminants be pre-treated before their discharge into the urban sewer systems (Peng *et al.*, 2009). Unfortunately, this is not the case for most of the WWTPs investigated in this study. The relatively high levels of these contaminants in the effluent and sludge samples might therefore be attributed to this observation.

Moreso, the rivers investigated in this study travel over a relatively short distance before emptying their contents into the adjacent oceans. The rate at which the suspended particles conveyed by these rivers settle along their courses could differ from those of the inland rivers to which they have been compared in this study. Since these rivers usually receive large quantities of treated WWTP effluent, which mostly determine their water levels during the dry seasons, the observed contaminant levels in the river water samples could be due to the influx of high loads of suspended particles from the discharged WWTP effluent. The high levels of these contaminants found in the river water samples, which were several orders of magnitude higher than those reported in other studies call for concerns. This is because the hydrogeological cycles could considerably contribute to the contamination of other surface water bodies as well as ground water sources.

Table 4.23: Comparisons of PBDE concentrations in the wastewaters (ng/l) and sewage sludge (ng/g, dw) with other studies across the world

Region/Country	Sample type	No. of WWTPs/Rivers	ΣPBDEs (tri-heptaBDE)	DecaBDE	References
North America					
USA	sludge	3	61 – 2290	1010 – 1440	North, 2004.
	influent/effluent	3	NS	29,032 ^a	
USA	biosolid	11	1100 – 2290	85 – 4890	Hale <i>et al.</i> (2001a)
Canada	sludge	1	1626 – 2698	NR	Song <i>et al.</i> (2006)
	influent/effluent	1	36 – 265	NR	
USA	sediment		0.72 – 148	NR	Samara <i>et al.</i> , (2006)
USA	sediment	Niagara River	<0.5 – 52.3	NR	Hale <i>et al.</i> , (2001b)
Europe					
Spain	sludge	14	5.3 – 177.3	785 – 18,032	Fabrellas <i>et al.</i> (2004)
Germany	sludge	11	12.5 – 286	97.1 – 2217	Knoth <i>et al.</i> (2007)
Sweden	sludge	22	ND - 450	ND – 390	Oberg <i>et al.</i> (2002)
Sweden	sediment	Viskan River	8 – 50	68 – 7100	Sellström <i>et al.</i> , (1998)
Spain	sediment	Cinca River	0.4 – 34.1	2.1 – 39.9	Eljarrat <i>et al.</i> , (2004)
United Kingdom	sediment	River Tees	0.5 – 16.8	0.6 – 119	Alchin and de Boer (2001)
Asia					
Kuwait	sludge	3	3.3 – 28.0	4.8 – 1595	Gevao <i>et al.</i> (2008)
China	sludge	26	6.2 – 57.0	ND – 1108	Wang <i>et al.</i> (2007)
China	sludge	2	8.5 – 96.2	150 – 22,894	Peng <i>et al.</i> (2009)
	influent/effluent	2	0.267 – 32.9	0.6 – 2412.6	
China	sediment	Zhujiang River	0.78 – 49.28	26.34 – 3575.33	Mai <i>et al.</i> , (2005)
	sediment	Dongjiang River	2.21 – 94.72	21.30 – 2923.85	
	sediment	Xijiang River	0.13 – 0.59	1.95 – 77.41	
China	surface water	Pearl River	0.344 – 68.0	0.335 – 65.237	Guan <i>et al.</i> , (2007)
Oceania					
Australia	sludge	16	NS	3.4 – 3780	Clarke <i>et al.</i> (2008)
	sludge	1	NS	220 – 460 ^a	Clarke <i>et al.</i> (2010)
	Influent/effluent	1	NS	0.058 – 100 ^a	
Africa					
South Africa	sludge	5	0.01 – 2640	ND – 34400	This study
	influent/effluent	5	0.42 – 41100	ND – 9770	
	bottom sediment	Diep/Kuils Rivers	0.04 – 5.37	ND – 3.50	
	River water	Diep/Kuils Rivers	0.25 – 21200	ND – 2310	

^a – average total PBDE concentration, including BDE 209; ND – not detected; NR – not reported; NS – not specified.

4.5 Potential sources of target compounds

This study attempted to provide insights into the possible sources of the target compounds into the Cape Town environment. The monitoring of these contaminants in different environmental matrices also assists in identifying important point and non-point sources of the analysed pollutants into the environment. Essentially, their various routes into the environment are linked with activities which are associated with the collection, transportation, disposal and treatment of various waste materials previously treated with these chemicals.

In this study, the discharge of treated effluent was identified as the most important point source of PBDEs into the aquatic environment. However, due to the poor performance in terms of effluent quality of some of the WWTPs within the City of Cape Town, considerable amounts of the analysed compounds are regularly discharged into the rivers. The re-use of treated effluent either for landscape and agricultural irrigation or for groundwater recharge could contribute significantly to contaminant re-distribution in the environment. According to the available records, about 10% (69.4 Mℓ/d) of treated effluent is currently being re-used in the City of Cape Town (CCT, 2007). Up to 10.5 Mℓ/d of this quantity is being used for agricultural purposes (Adewunmi *et al.*, 2010). Unfortunately, the use of treated effluent for irrigation purposes does not only lead to the build up of these contaminants in the underlying soil, but also contributes to the overall atmospheric burden of the analysed pollutants. Hence, this practice further results into widespread distribution of the analysed compounds in the environment. Considering the enormous quantity of the treated effluent used for irrigation on a daily basis, the inputs from this practice could be highly significant over time.

Several regulatory measures had been put in place internationally to control the use of certain technical formulations of PBDEs in some consumer products (UNEP, 2009). The huge reserve of these chemicals stored up in previously treated consumer products will continue to act as important sources of these contaminants in years to come. Unfortunately, most of these products eventually end up in the disposal sites. With the rising standard of living fuelled by the stable economic growth over the years, it is envisaged that the quantities of waste products containing these chemicals will continue to increase over time.

Presently, the solid waste treatment facilities in the City of Cape Town receive over 2 million tonnes of solid waste per annum (CCT, 2007), majority of which are landfilled. Leachate derived from these wastes contains a considerable amount of these contaminants. In the City of Cape Town, leachate are either treated on-site or channelled to a nearby WWTP for treatment. The treatment of leachate in WWTPs might contribute to increased aquatic contamination especially when the WWTPs are not functioning optimally during the treatment processes. Besides, the loss of volatile PBDEs, especially the lower

brominated congeners during waste compaction, vehicular movement on landfill sites could aggravate the rate at which these congeners are released into the environment.

Furthermore, the enormous quantity of grey water from several informal settlements scattered across the City of Cape Town might be notable sources of PBDEs into the aquatic environment. It is estimated that about half a million people live in informal settlements in the City of Cape Town (CCT, 2006b). Although some of these settlements are connected to the urban sewer system, majority of these are not (CCT, 2008). Hence, the greywater generated from these locations usually flow into the adjacent waterbodies from different points, thus constituting a non-point source of PBDEs into the aquatic environment.

The land application of WWTP derived sludge commonly used as compost in agricultural soils can release these contaminants into the environment. During heavy rainfall, some of the compost can be washed away by means of run-off, and are often transported into adjacent waterbodies (Eljarrat *et al.*, 2008). As observed in this study, WWTP sludge contains high levels of these contaminants (see: Tables 4.10 – 4.13). Their use as organic compost either for large scale farming or for ornamental plants cultivation in botanical gardens could considerably results in further contamination of aquatic environment, especially during heavy rainfall.

Another possible source of these contaminants, especially into the atmosphere is via incineration of waste materials. Although this method of waste disposal is not commonly practised in the City of Cape Town, a significant amount of these contaminants and other harmful by-products (furans and dioxins) could be released into the atmosphere via this method of waste disposal. There could be significant release of these contaminants from the transportation and manufacturing sectors. The wear and tear of different parts of several vehicles and machineries might represent important non-point sources of these contaminants into the environment (Polkowska *et al.*, 2001; Yisa *et al.*, 2011). Generally, the sources of these contaminants are numerous and most of them are inter-related. The tracking of these contaminants via periodic monitoring of different environmental matrices is essential. This will assist in the proper evaluation of several abatement measures put in place to control their release into the environment.

4.6 Congener profile of PBDEs in environmental samples

The tracking of individual PBDE congeners in a waste stream can provide information about their likely sources into the environment. This involves the estimation of the percentage composition of each of the PBDE congeners in different matrices investigated. A critical look at their relative contributions at different stages of any treatment facilities would also provide useful information about the effectiveness of treatment processes at removing different contaminants from the waste stream.

4.6.1 PBDE congener profile in landfill leachate samples

For ease of evaluation, the annual summation of the eight PBDE congeners was adopted for the estimation of the percentage composition of each congener. The total sum of the eight PBDE congeners were 80,900, 1,480, 47,000 and 10,600 ng/l for Bellville, Coastal Park, Vissershok (raw) and Vissershok (treated), respectively. The relative composition of each of the PBDE congeners is shown in Figure 4.14.

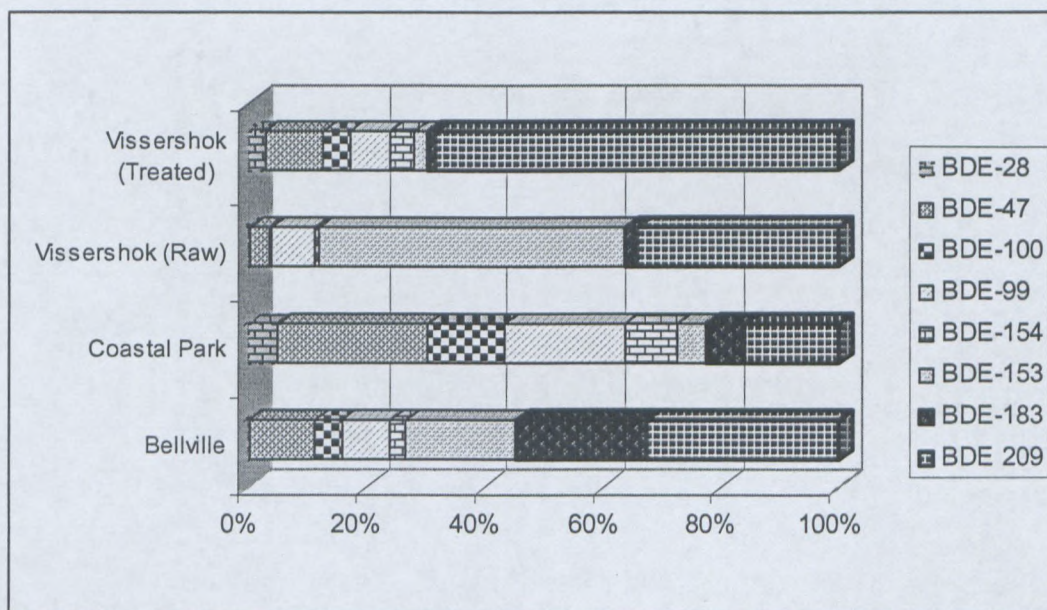


Figure 4.14: The annual percentage composition of PBDE congeners in landfill leachate samples

From this data, BDE 209 was the most dominant congener in most of the samples. This congener represented 16.1 – 68.2% of the total PBDEs in these samples. While BDE 47 was the most dominant congener accounting for 25.4% at the Coastal Park landfill site, BDE 153 dominated at the Vissershok site with a percentage composition of 51.8% of the total PBDE congeners.

Considering the relative contributions of each of the congeners representing the different technical formulations, it was evident that all the technical formulations were well represented at the Bellville site. However, the contribution of octa-BDE technical formulation at Coastal Park and Vissershok landfill sites were less significant. Congeners of both penta-BDE and deca-BDE dominated these sites where they account for over 60 and 15%, respectively. Interestingly, this study revealed that most of PBDE congeners were poorly removed by the LTP at the Vissershok site. Only BDE 99, 153 and 183 were effectively removed by the treatment process. This study further showed that the transfer of raw leachate to nearby

WWTP for treatment could represent important source of PBDEs in WWTPs and subsequently in the adjacent waterbodies.

4.6.2 PBDE congener profile in WWTP samples

The compositional profile of all the eight PBDE congeners in different WWTP effluent samples investigated is shown in Figure 4.15. According to this data, the congener composition of the raw effluent in all the WWTPs was dominated by BDE 47, 99, 183 and 209. The occurrence of these dominant congeners in the raw effluent suggests that their release might be associated with the widespread usage of their technical formulations or products previously treated with these chemicals in the study area. The congener profile of the primary and secondary effluents indicated the effectiveness of each type of treatment processes at removing these contaminants from the wastestream. For plants equipped with primary clarifiers, the lower brominated congeners (BDE 28 and 47) dominated in this unit, except at the Old Bellville plant where BDE 209 dominated.

BDE 47 dominated all other congeners in the secondary effluent contributing between 46.5 to 97.1% to the total PBDEs in all the WWTPs investigated. This observation is not surprising as this congener exhibits certain characteristics which favour its preferential solubility in the aqueous media (Tittlemier *et al.*, 2002). Consequently, its dominance in the final effluent of most of the WWTPs could be attributed to its high percentage composition in the penta-BDE technical formulation and its relatively high solubility. The percentage composition of BDE 209 in the treated final effluent was relatively low, except at the Zandvliet WWTP where it contributed up to 86.1% to the total PBDEs.

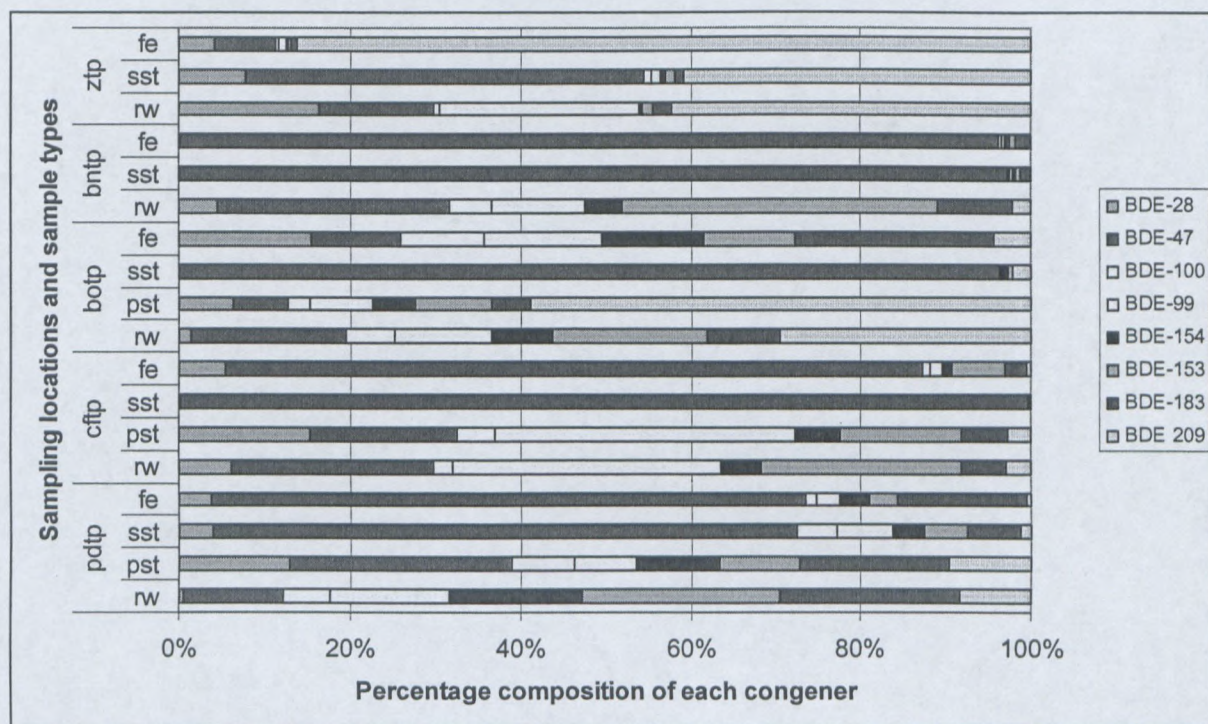


Figure 4.15: PBDE congener profile of different WWTP effluent samples

(*pdtp* – Potsdam WWTP; *cftp* – Cape Flats WWTP; *botp* – Old Bellville WWTP; *bntp* – New Bellville WWTP; *ztp* – Zandvliet WWTP; *rw* – raw water; *pst* – primary effluent; *sst* – secondary effluent; *fe* – final effluent)

Based on this observation, it seemed that the discharge of treated effluent would not significantly result into BDE 209 contamination of the receiving waterbodies. However, with due consideration of the enormous quantity of the treated effluent discharged on a daily basis, a significant contamination of the receiving water by this congener might result over time.

The PBDE congener profile of the different sludge types investigated in this study is shown in Figure 4.16. Unlike the effluent samples where lower brominated congeners had relatively high percentage composition, especially in the treated effluent; the congener profile of the different sludge types was entirely dominated by the highly brominated PBDE congeners. Ten out of the twelve sludge samples types from all the WWTPs investigated were dominated by BDE 209 where its percentage composition to the total PBDEs ranged from 11.4 to 98.6%. The other two samples types were dominated by BDE 183 contributing 40.8 to 49.1% to the total PBDEs. Amongst the penta-BDE congeners, only BDE 47 and 153 had significantly high percentage composition in the sludge samples. Each of these congeners generally had less than 35% of the total PBDEs in all the samples analysed.

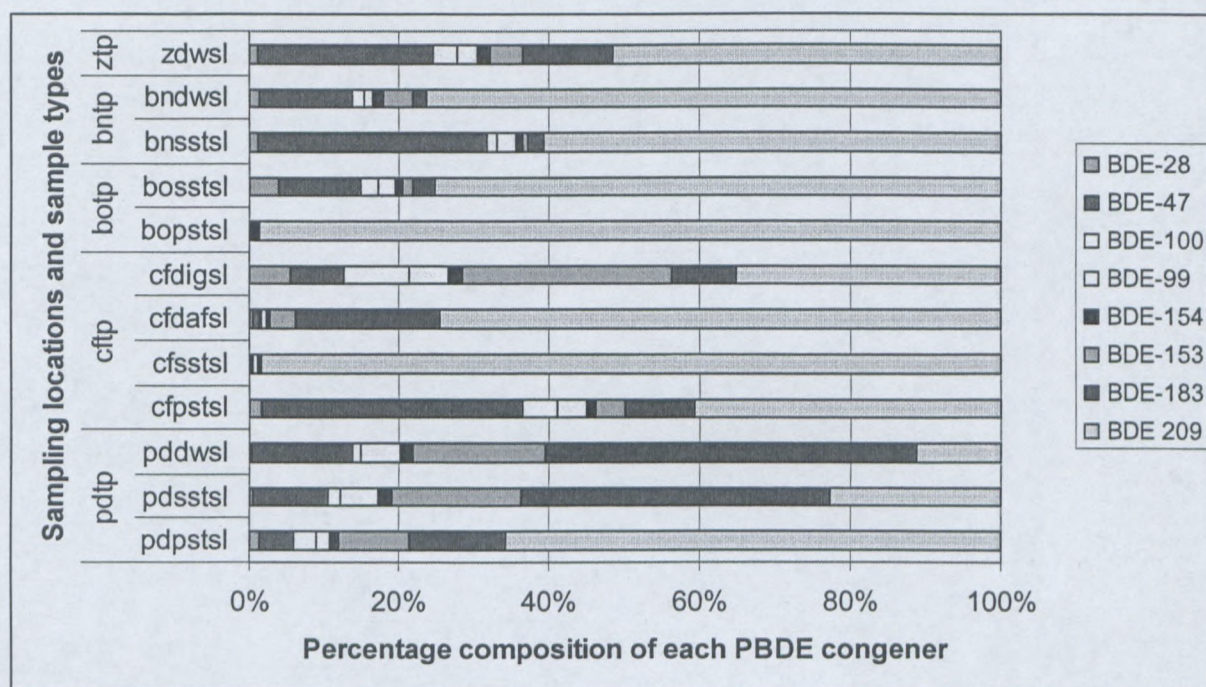


Figure 4.16: PBDE congener profile of different sludge samples collected from the WWTPs

(*pdtp* – Potsdam WWTP; *cftp* – Cape Flats WWTP; *botp* – Old Bellville WWTP; *bntp* – New Bellville WWTP; *ztp* – Zandvliet WWTP; *pdpstsl*, *pdsstsl*, *pddwsl* – Potsdam primary, secondary, de-watered sludge; *cfpstsl*, *cfsstsl*, *cfdafsl*, *cfdigsl* – Cape Flats primary, secondary, DAF, digested sludge; *bopstsl*, *bosstsl*, *bnsstsl*, *bndwsl* – Old Bellville primary, secondary, New Bellville secondary, de-watered sludge; *zdwsl* – Zandvliet de-watered sludge)

The congener profile of the dissolved air flotation (DAF) sludge was quite unique having over 93% of the total PBDEs contributed by BDE 183 and 209. Primarily, the function of DAF systems in WWTPs is to reduce the biochemical oxygen demand (BOD), total suspended solids (TSS) and fats, oil and grease (FOG) from the wastewater. This system can achieve between 90 to 99% removal of TSS and FOG and more than 85% of BOD from the wastestream (Al-Mutairi *et al.*, 2008; de Nardi *et al.*, 2008). However, the pattern observed in the digested sludge differs from those found in the DAF sludge. In this case, the congeners of penta-BDE nearly had a uniform percentage composition where BDE 153 had the highest (27.9%) contribution. This observed trend might be due to the possible degradation of the highly brominated congeners during the sludge digestion process.

4.6.3 PBDE congener profile in river water and bottom sediment samples

The congener profile of water samples from the Kuils and Diep Rivers was entirely dominated by BDE 47. Its dominance in these samples was more pronounced at the upstream and the point of discharge sampling points where it contributed up to 98% to the total PBDEs. As shown in Figure 4.17, a significant contribution to the total PBDEs by other congeners, especially BDE 209 was also observed. In the

downstream of both rivers, this congener contributed significantly to the total PBDEs, which were probably due to the high load of the congener in the discharged treated effluent.

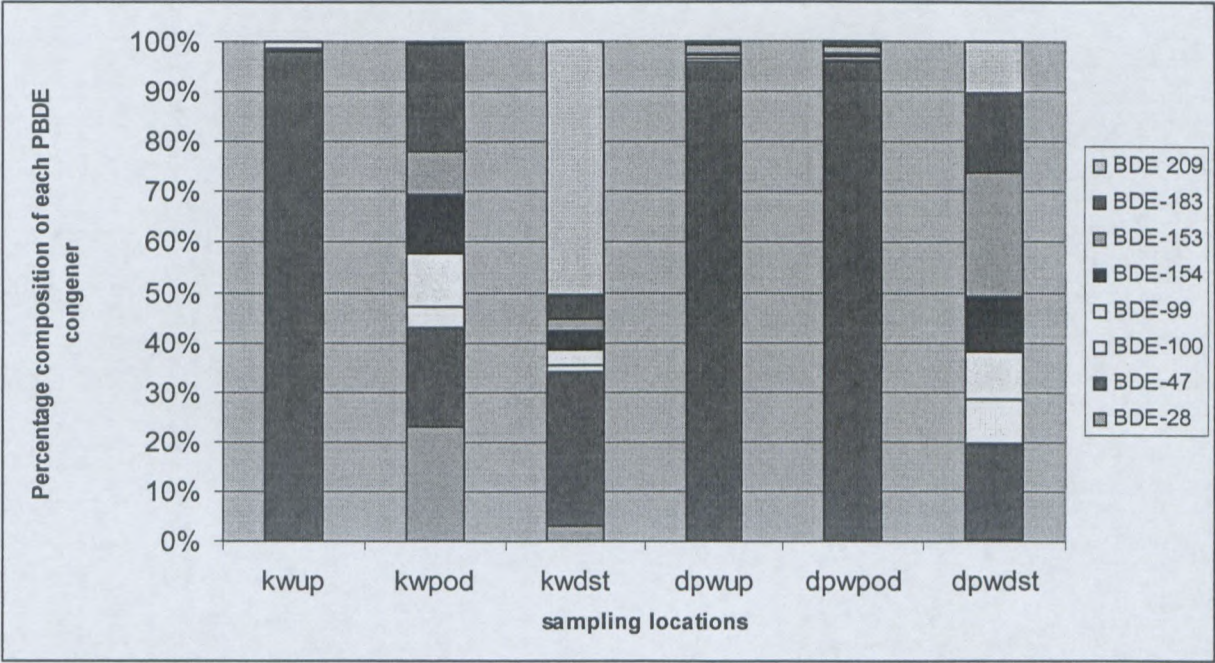


Figure 4.17: PBDE congener profile of the river water samples of the Kuils and Diep Rivers
(kwup – Kuils River water upstream; kwpod – Kuils River water point of discharge; kwdst – Kuils River water downstream; dpwup – Diep River water upstream; dpwpod – Diep River water point of discharge; dpwdst – Diep River water downstream)

The pattern assumed by the PBDE congeners in the final effluent of the Potsdam WWTP, which discharges into the Diep River was similar to those found in the river water samples collected from the point of discharge sampling point. These samples were entirely dominated by BDE 47, a trend that was also observed for river water samples collected from the upstream sampling point of the river. However, the congener profile observed further downstream suggests that other possible sources might be responsible for the PBDE contamination of the Diep River. In this case, all the congeners, except BDE 47 and 209 had 6 – 18-fold increase in terms of their relative percent composition at both the point of discharge and the downstream sampling points.

On the other hand, the percentage contribution of BDE 47 decreased from 95.6% at the point of discharge to 19.0% at the downstream site. The observed trend might be due to the possible dilution effect of the discharged effluent since relatively high levels of this congener was also observed at the upstream sampling point. BDE 209 was 515 times enriched at the downstream sampling point of the Diep River. This suggests that the discharge of treated effluent might represent an important pathway of BDE 209 contamination of the Diep River.

The congener profiles of the bottom sediment of both rivers as shown in Figure 4.18 were quite different from each other. BDE 47 was the dominant congener contributing between 49.3 and 73.1% to the total PBDEs in all the samples collected at different sampling points in the Kuils River. Although BDE 209 had the highest percentage contribution at the downstream sampling points, the relatively uniform distribution of all the congeners suggests that they might have a similar point source into the Diep River. The principal component analysis (PCA) performed on this data clearly showed that these congeners have a somewhat similar source into the rivers investigated.

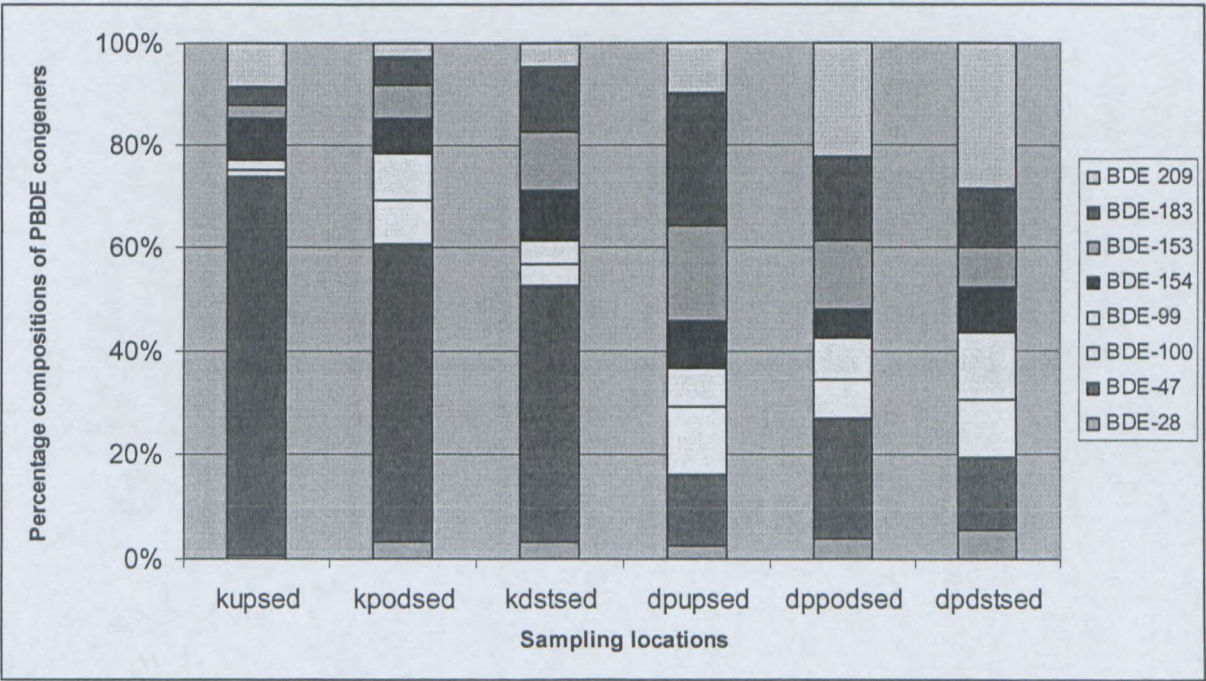


Figure 4.18: PBDE congener profile of the bottom sediment samples of the Kuils and Diep Rivers

(kupsed – Kuils River upstream bottom sediment; kpodsed – Kuils River point of discharge bottom sediment; kdtsed – Kuils River downstream bottom sediment; dpupsed – Diep River upstream bottom sediment; dppodsed – Diep River point of discharge bottom sediment; dpdtsed – Diep River downstream bottom sediment)

4.7 Seasonal variability of target compounds in different matrices investigated

The characterisation of the seasonal variations of the target compounds in different environmental matrices would normally require an extensive monitoring exercise for at least two years (Chapman, 1996). However, the estimation of the total PBDEs as well as BB 153 at different seasons of the year can possibly indicate their seasonal characteristics in these matrices. For this purpose, the entire study period was sectionalised into different seasons as follows: March – May (autumn), June – August (winter), September – November (spring) and December – February (summer). Since the sample collection began in April 2010, the sampling exercise for certain seasons spilled over into the following year. For instance,

certain samples were collected in the autumn of 2010 and some were also collected in the same season of the following year. This time difference in sampling could provide explanation for some differences observed in the seasonal variability assessment of the target compounds. Therefore, the average values of the total PBDEs (8 congeners) were estimated and compared across the different seasons of the year so as to counteract the possible effects of the inconsistencies in sample collection.

4.7.1 Seasonal variations of target compounds in leachate samples

All the landfill sites investigated in this study generated sufficient quantities of leachate throughout the sampling period. The assessment of the seasonal variability of the target compounds showed that the highest average values of the total PBDEs were found in the raw leachate during the spring season at nearly all the landfill sites. Similarly, BB 153 levels were highest during this season at the landfill sites. Therefore, the observed trend could have huge implications for the PBDEs levels found during this season in the influent of most of the WWTPs monitored in this study.

The Bellville landfill site had the highest level of 1120 ng/ℓ during this season. This might probably be due to the age of the landfill site as the site has been in operation since early 1960s. Generally, higher levels of these contaminants were found during winter than in summer, except at the Coastal Park landfill site. This observation was in agreement with those reported in a similar study where higher levels of these contaminants were found during winter than in summer (Odusanya, 2008). Although samples were not collected during autumn at the Vissershok site due to the delay in administrative approval of the permission request by the site managers, the levels of these contaminants found in other sites during this season were higher than those found during the summer season.

In this study, the lowest levels of these contaminants in raw leachate samples were found during summer. This might be due to the decreased rate of precipitation during this period, thus resulting in decreased leachate production within these sites. Generally, in this region of the country, the winter coincides with the period of high precipitation. The frequency decreases in spring and rarely occurs during autumn and summer seasons. The seasonal variability of these contaminants in leachate samples from the three landfill sites is shown in Figure 4.19.

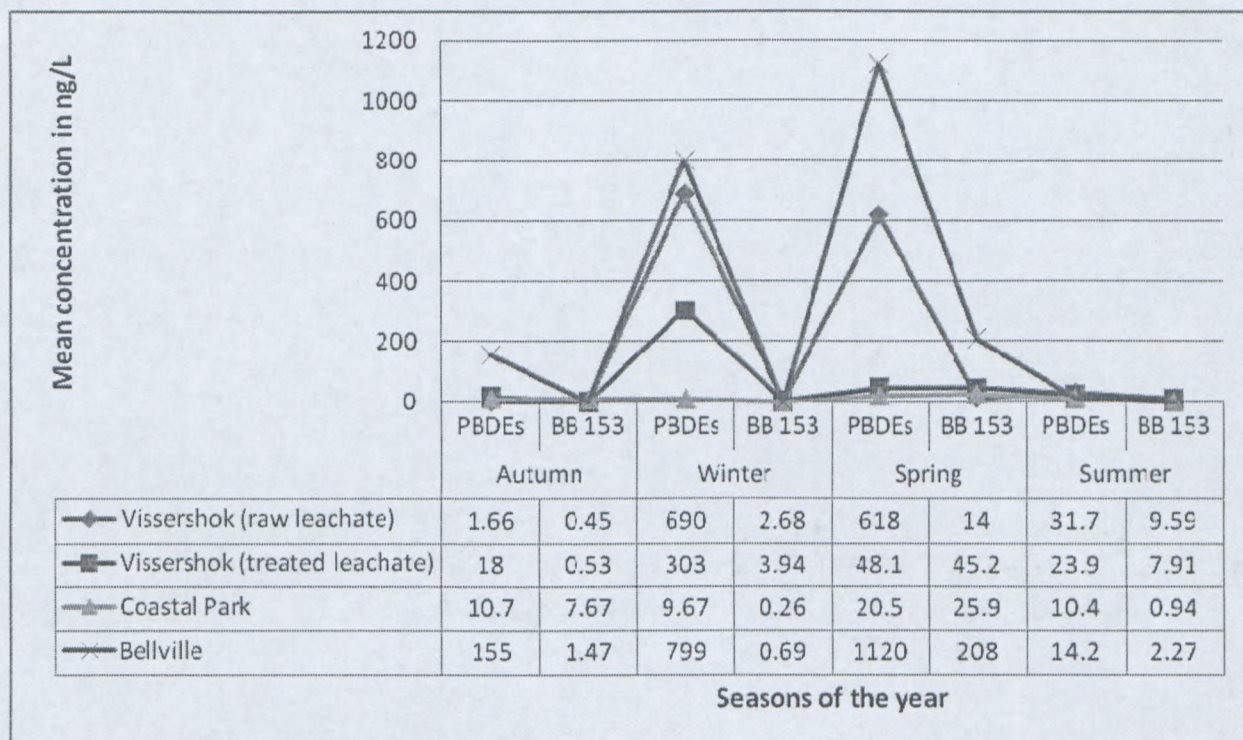


Figure 4.19: Seasonal variability of target compounds in leachate samples from different landfill sites

4.7.2 Seasonal variability of target compounds in WWTP samples

The WWTPs investigated in this study receives variable flows of influent at different periods of the year. Depending on the time of the day and the catchment area of the WWTP in question, the daily fluctuation in volume of wastewater reaching the WWTPs could sometimes double the average daily flow of each of these plants. A recent assessment of the average influent flow at all the WWTPs within the City of Cape Town was conducted between July 2009 and June 2010. Samson (2011) reported that the average dry weather flows into the WWTPs investigated in this study were 41.8, 174, 52.8 and 71.3 Mℓ/d for Potsdam, Cape Flats, Bellville (Old & New) and Zandvliet WWTPs, respectively. In this same study, the highest single day flows were 85.7, 355, 138 and 179 Mℓ/d for Potsdam, Cape Flats, Bellville (Old & New) and Zandvliet WWTPs, respectively. Going by these observations, it was envisaged that varying concentrations of the target compounds would also be found at different stages of the WWTPs at different seasons of the year.

A comparison of the evaluation of the target compounds' levels at different seasons showed that most of the WWTPs had the highest average total PBDEs levels in the raw water samples during the spring season. Only the New Bellville plant had its highest levels during the summer season. The average levels of the target compounds in the influent were generally comparable in most of the WWTPs investigated, except during the autumn season. The lowest levels of these contaminants were recorded in autumn in all

the WWTPs, except at the Zandvliet WWTP, where about 287 ng/ℓ of total PBDEs was found. Generally, higher levels of these contaminants in the influent were found in summer than in winter in nearly all the WWTPs investigated. The observed trend might be due to the possible dilution effects of the high precipitation on the waste stream reaching these plants during the winter season. Amongst the WWTPs monitored, the lowest average total PBDEs in the influent was found at the Potsdam WWTP, where up to 25-fold variation was recorded in contaminants levels in the wastewater reaching the plant. Unfortunately, the assessment of the seasonal variability of PBDEs in WWTP samples has not been widely investigated. Most of the studies conducted so far have focussed on the environmental fate, transport, distribution as well as the congener-specific characteristics of these contaminants in WWTP samples (de Boer *et al.*, 2003; Knoth *et al.*, 2007; Clarke *et al.*, 2008; Clarke *et al.*, 2010).

The observed seasonal variations of these contaminants in effluents within the WWTPs could be a reflection of several inter-related factors influencing their concentrations within the WWTP. Usually during the winter, there is high volume of influent reaching the WWTPs with its attendant high level of suspended solids. The increased influent volume could therefore result into poor settling of the suspended solids in the clarifiers. This could be responsible for the higher levels of contaminants detected in these matrices during the winter and spring seasons. The detection of extremely high PBDEs levels in the secondary effluent of the Cape Flats WWTP is not surprising. This is because several household products, which were analysed for PBDEs had been shown to contain as much as 15,107 and 1,603,343 ng/g for octa- and deca-BDE commercially derived PBDEs (Chen *et al.*, 2010). In another study, the predominance of BDE 209 over other PBDE congeners was observed. The level of this congener in indoor dust samples analysed for these contaminants showed that BDE 209 was as high as 45,000 ng/g (Harrad *et al.*, 2008). Therefore, activities such as recycling of previously treated products as well as vacuum cleaning of contaminated surfaces could result in the transfer of these contaminants into the wastewater stream. This, of course, would significantly influence the mass loading rates of these contaminants in these treatment facilities as well as into the adjacent rivers.

Furthermore, the nature and type of good house-keeping measures adopted in each WWTP could also play a significant role on the seasonal variations observed. Despite the extremely high levels of the target compounds found in the influent samples, some of the WWTPs were able to efficiently remove these contaminants from the waste stream. The removal efficiencies of the Zandvliet and New Bellville WWTPs were generally poor, especially during the autumn and spring seasons, respectively. Hence, the focus with respect to the seasonal variability of these contaminants might be better placed on their concentrations reaching the each WWTP at different seasons of the year. The aforementioned factors would also influence the seasonal variability of these contaminants in WWTP sludge samples analysed.

Unlike the WWTP effluent samples, the seasonal variability of these contaminants in sewage sludge samples did not follow a unique pattern. While the highest levels were generally found during autumn in sludge samples collected from the Cape Flats and Zandvliet WWTPs, a similar trend was observed at the Potsdam and Bellville (Old & New) WWTPs during the spring and winter seasons, respectively. Although there seems to be no distinct seasonal characterization of these contaminants amongst the different sludge types monitored, most of the WWTPs had relatively high levels of these contaminants in the secondary sludge than in the primary sludge in spring and summer seasons.

The irregular patterns of contaminants' distribution in different sludge types were not clearly understood. However, in a recent study, where the influence of WWTP characteristics (capacity, sludge rate and the type of treatment processes) was evaluated, a possible explanation for this trend was provided (De la Torres *et al.*, 2011). In their study, while there were no significant differences ($p < 0.05$) between PBDE concentrations and treatment capacity as well as with the sludge rate, a notable decrease in PBDE concentration was observed when biological N and P elimination treatment processes were employed. Consequently, the efficiency of WWTPs at removing these contaminants might not be largely dependent on the seasonal fluctuations in the waste streams reaching these plants but rather on the treatment processes employed. The seasonal variations of these target compounds in both WWTP effluent and sludge samples are presented in Table 4.24.

4.7.3 Seasonal variability of target compounds in bottom sediment and river water samples

Unlike the atmospheric samples, whose seasonal variability assessment of PBDEs levels have been widely studied, only few studies have focussed on the seasonal variations of PBDEs in the freshwater systems. Until recently, data indicating the presence of PBDEs in river water and other aqueous samples are generally scarce (Law *et al.*, 2008). This might be due to the hydrophobic properties of these contaminants, which make their assessment in these matrices less critical.

The observed seasonal variation of the target compounds in the investigated rivers followed a somewhat unique pattern. In both rivers, the average total PBDEs levels in the river water samples were highest during spring at all the sampling locations.

More so, an appreciable increase in the average total PBDEs at the downstream sampling locations of both rivers was observed in nearly all the seasons, except during the spring season. This trend, therefore suggests the possible influence of WWTP discharges on PBDE contamination of river water of these

rivers. The occurrence of extremely high levels of these contaminants in the upstream sampling locations of both rivers, especially during spring is indicative of other notable sources of PBDEs into the rivers.

Generally, in this present study, extremely high contaminants levels were found in spring in the WWTP effluents and water samples of the rivers investigated. This observation could imply that the discharge of WWTP effluent containing high loads of these contaminants is probably responsible for the trend observed in these rivers. Qiu *et al.* (2010) observed a similar trend in their analysis of lake water, where the increased PBDEs levels found in autumn and winter seasons were associated with the discharge of WWTP effluent containing high levels of these contaminants. The release of treated effluent into the upper reaches of the investigated rivers could significantly contribute to high levels of PBDEs observed in this study. Furthermore, the intrusion of grey water from informal settlements, which are generally scattered in different parts of the city, into these rivers could also influence the levels of these contaminants in these rivers. The use of combined sewer systems ensures that wastewater generated from different sources is treated together with urban run-off derived from stormwater. Unfortunately, in a city like Cape Town, where this technology is yet to be operational, urban run-off are usually emptied directly into the receiving waterbodies or via their tributaries. A huge amount of these contaminants could therefore be transported into the rivers via stormwater (Wepener *et al.*, 2011).

Table 4.24: Seasonal variability of target compounds in WWTP effluent, sludge, bottom sediment and river water samples

Location/Sample type	Season				Sample type	Season			
	Autumn	Winter	Spring	Summer		Autumn	Winter	Spring	Summer
Potsdam									
Raw water									
Primary effluent	32.5 (1.75)	76.80 (3.65)	819 (851)	175 (27.70)	Primary sludge	1.71 (0.25)	69.9 (3.73)	6.05 (ND)	1.03 (0.12)
Secondary effluent	127 (9.32)	40.50 (0.57)	163 (172)	22.70 (4.74)	Secondary sludge	127 (0.44)	1.20 (0.33)	407 (79.70)	1.19 (0.41)
Final effluent	14.80 (2.58)	38.90 (28.70)	195 (34.40)	5.57 (4.00)	De-watered sludge	29.20 (0.22)	10.20 (0.14)	258 (78.70)	3.89 (0.50)
	5.06 (0.34)	52.50 (14.30)	158 (19.50)	3.17 (1.19)					
Cape Flats									
Raw water									
Primary effluent	40.40 (13.60)	108 (47.30)	356 (127)	222 (14.20)	Primary sludge	185 (4.04)	15.7 (2.10)	12.8 (0.20)	6.08 (0.35)
Secondary effluent	34.60 (8.01)	130 (41.80)	253 (0.79)	179 (22.80)	Secondary sludge	-548 (1.45)	5.23 (0.13)	5.82 (ND)	
Final effluent	3.32 (1.41)	75.60 (62.60)	36000 (51.80)	30.10 (3.59)	DAF sludge	327 (0.65)	131 (7.80)	5.89 (ND)	13.80 (0.53)
	3.26 (ND)	1.45 (0.46)	209 (ND)	20.80 (12.30)	Digested sludge	13.00 (0.23)	4.38 (0.59)	8.98 (ND)	6.25 (1.05)
Old Bellville									
Raw water									
Primary effluent	62.80 (2.54)	118 (22.50)	503 (344)	193 (28.90)	Primary sludge ^a	2.50 (ND)	798 (1.05)	2170 (3.06)	1.01 (ND)
Secondary effluent	49.8 (2.77)	53.70 (28.30)	694 (201)	204 (34.30)	Secondary sludge ^a	2.87 (0.32)	106 (1.19)	9.62 (0.24)	4.67 (1.13)
Final effluent	8.80 (6.24)	8.13 (0.51)	7760 (113)	17.60 (20.00)	Secondary sludge ^b	1.34 (0.47)	234 (0.42)	122 (0.87)	2.85 (0.96)
	9.55 (8.67)	3.64 (0.75)	1.80 (0.30)	12.70 (10.20)	De-watered sludge ^{a,b}	1.75 (0.30)	52.30 (0.89)	55.30 (0.37)	10.90 (0.66)
New Bellville									
Raw water									
Secondary effluent	43.30 (3.32)	378 (41.50)	334 (597)	393 (27.50)	De-watered sludge	48.40 (7.32)	20.30 (0.71)	2.39 (ND)	3.70 (0.05)
Final effluent	15.40 (11.20)	5.84 (0.77)	3390 (84.60)	8.08 (7.18)					
	9.56 (4.14)	61.10 (41.60)	3410 (74.80)	8.84 (12.60)					
Zandvliet									
Raw water									
Secondary effluent	287 (0.98)	206 (7.33)	402 (5.26)	191 (9.53)					
Final effluent	35.70 (4.64)	124 (0.48)	278 (ND)	26.80 (4.49)					
	1240 (2.81)	153 (7.07)	116 (0.15)	44.00 (6.29)					
River water									
Kuils River									
Upstream					Upstream	0.29 (0.09)	1.25 (ND)	1.32 (ND)	0.38 (0.15)
Point of discharge	-	89.8 (10.60)	18500 (213)	43.8 (6.04)	Point of discharge	2.59 (0.19)	4.25 (ND)	9.95 (0.63)	2.59 (0.97)
Downstream	-	74.50 (35.00)	176 (232)	31.00 (7.33)	Downstream	0.31 (ND)	3.00 (ND)	0.56 (ND)	2.37 (0.65)
		229 (ND)	403 (281)	32.50 (5.86)					
Diep River									
Upstream					Upstream	0.19 (0.08)	2.47 (0.33)	0.20 (0.05)	0.87 (0.15)
Point of discharge	4.47 (0.32)	0.84 (ND)	5600 (311)	1.48 (0.19)	Point of discharge	0.29 (0.09)	0.58 (0.22)	0.90 (0.02)	0.48 (0.13)
Downstream	5.70 (2.84)	8.58 (6.14)	12100 (843)	9.25 (7.58)	Downstream	0.72 (0.33)	0.43 (0.27)	0.21 (0.05)	0.41 (0.10)
	12.40 (0.12)	70.10 (0.52)	291 (348)	4.74 (4.33)					

^{a,b} - represents sludge samples from the Old and New Bellville WWTP, respectively; ND - not detected; - not analysed; values in parenthesis represent the mean values of BB 153; reported values represent the mean of total PBDEs, including BDE 209 in ng/g for sediment and sewage sludge samples and ng/t for all the aqueous samples.

With respect to the bottom sediment samples, the observed seasonal variations differ in both rivers. The highest average total PBDEs as well as BB 153 levels was found at the upstream sampling point during winter in the Diep River. At the downstream point, these contaminants had their highest levels during autumn in the river. In the Kuils River, the pattern exhibited by these contaminants was almost similar to those observed in the Diep River. In this case, the highest average total PBDEs levels were found at the upstream and point of discharge sampling locations during the spring season. These levels were highest at the downstream point during winter. These seasonal trends might be indicative of the possible changes in the settling rates of the suspended solids, water level and volumes of these rivers at different seasons of the year. In a related study, Zhao *et al.* (2011) observed significantly high mean PBDEs concentrations in summer than those obtained in spring in the analysis of some sediment samples. Incidentally, the summer in the Daliao River watershed, where this study was conducted coincides with the rainy season which is in agreement with the trend observed in this present study. The seasonal variation of these contaminants in both bottom sediment and riverwater samples is presented in Table 4.24.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The assessment of the levels of selected PBDE congeners as well as BB 153 in different environmental matrices in this study showed some interesting outcomes about their environmental burden and potential sources into the Cape Town environment. Prior to their investigation in these matrices, the suitability of some analytical methods often employed for their determination was assessed. While the majority of these established analytical procedures gave acceptable results, certain improvements regarding the clean up of extracts were made.

A modified multi-layer silica gel column chromatographic clean up technique was developed. This involved the use of relatively small quantities of the different sorbent forms packed into a clean Pasteur pipette. The purification of the extract was effected with smaller volume of the eluting solvent. With this measure, the cost of procuring these materials and the overall time of analysis were significantly reduced. An important aspect of this study was the tracking of the potential point sources of these contaminants into the aquatic environment. The periodic monitoring of these contaminants in different WWTP effluent, sludge, leachate as well as riverwater and bottom sediment revealed that WWTP discharges constitute important sources of PBDEs into the Cape Town environment. Owing to the enormous quantities of both treated effluent and sludge being re-used for agricultural, industrial, sporting and other purposes, these sources might represent important pathways of PBDE contamination of other components of the environment.

The treatment of landfill leachate together with WWTP effluent could also contribute to high environmental burden especially when these facilities are not functioning optimally. Several other possible sources of these which could not be readily evaluated are also worth mentioning. The wear and tear of vehicle parts in the transportation sector as well as in the processing machineries in the industries are typical examples. These sources, including the possible release into the atmosphere during landscape and agricultural irrigation could be significant non-point sources of these contaminants into the Cape Town environment. Furthermore, the large quantities of greywater generated from the informal settlements across the city could also represent important non-point sources of these contaminants into the adjacent waterbodies.

With regard to the levels of these contaminants in different matrices investigated, the degree of pollution of the aquatic environment was comparable to those of the European countries. However, unlike in the EU and the North American regions where the environmental levels of these contaminants normally indicate the dominant use of a particular technical formulation, all the technical formulations were fully

represented in most of the matrices investigated. The seasonal variability of these contaminants in different matrices showed that high levels were generally found during the spring and winter seasons. In the WWTP samples, high levels of these contaminants in the influent samples were generally received during the spring and summer seasons. A similar trend was observed in the water samples of the rivers investigated, thus suggesting the possible influence of WWTP discharges on the river water quality. In contrast, these contaminants were more dominant in the bottom sediment of both rivers during the winter and spring seasons. The hydrodynamics of these rivers especially during these seasons might be responsible for the observed trend. The highest levels of these contaminants were found in leachate samples during the spring season at all the landfill sites. Increased leaching of contaminants from previously treated products as a result of the high precipitation during the winter might be responsible for the trend observed.

5.2 Recommendations

Although this study has established baseline information on the environmental levels of these selected PBDEs and BB 153 in different matrices within the City of Cape Town, the evaluation of the risk associated with exposure to the matrices containing these contaminants still need to be carried out. Further studies should be focussed on the assessment of these contaminants in different biological samples, including human specimens to ascertain the extent of bioaccumulation of these contaminants.

The effective management of wastewater and other aqueous matrices is critical to ensuring the safety of the receiving waterbodies as well as the public health. Several approaches, including the establishment of relevant institutional and regulatory frameworks have been adopted to achieve these objectives. The efforts made so far, by policy and decision-makers and their execution by the public servants with respect to wastewater management within the City of Cape Town are quite commendable. However, there are still avenues for greater improvement in this regard, and the following underlisted recommendations based on the findings and personal observations during this study might be useful.

- The general lack of information on the production volume and usage of the technical formulations of PBDEs should be addressed. The relevant government's agency must develop an inventory of chemicals, including PBDEs whose production and usage have been restricted by other countries.
- The national government must also put relevant regulatory measures in place to regulate and control the importation and use of these chemicals and products containing them.
- Relevant pre-treatment standards to forbid non-domestic or industrial users from discharging substances which are capable of interfering with the operations of WWTPs as well as the health status of the receiving waterbodies must be established. This measure can significantly improve

opportunities to recycle or reclaim both treated effluent and sewage sludge for other beneficial uses.

- Industries which are capable of generating and releasing large quantities of harmful organic chemicals into the sewer system must be identified. Effluent emanating from such industries must be subjected to initial pre-treatment before it could be released into the urban sewer system.
- The South African Wastewater Sludge Guidelines must be reviewed to incorporate emerging pollutants such as PBDEs as important part of the pollutant class to be considered for evaluation.
- The operators of the WWTPs must gather and keep good records of relevant data such as the physicochemical characteristics of the effluent and hydrodynamics data (in-flow and out-flow rates, HRTs and SRTs) for effective management of wastewater treatment plant.
- Periodic monitoring of persistent organic pollutants (POPs) as well as disinfection by-products should be carried out by experienced analysts.
- The annual loading rates of these pollutants should be estimated to check widespread contamination of the receiving waterbodies via WWTP discharges.
- Investment in the training of personnel at all levels saddled with the responsibility of ensuring efficient treatment of wastewater is essential.
- Embarking on public awareness and enlightenment programmes through both electronic and print media to educate people on the dangers of introducing pollutants which can interfere with the public health into urban sewers are also essential.
- The regular inspection of the treatment processes must be carried out to prevent unnecessary risks to human life. The maturation ponds and other treatment units should be cleared regularly for efficient removal of suspended solids.
- Appropriate sanctions must be levied on persons or groups that violate any established regulations aimed at ensuring the public safety.

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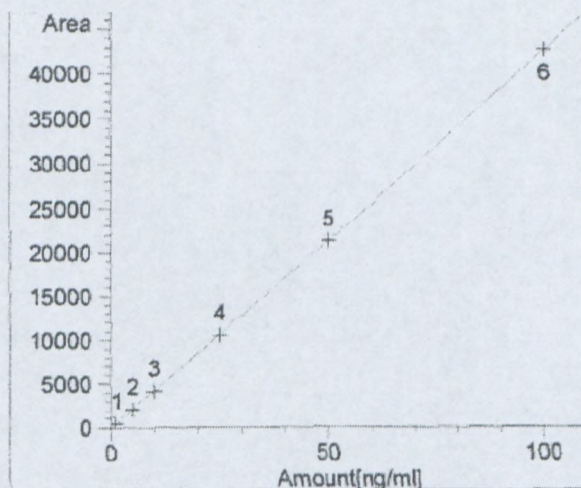
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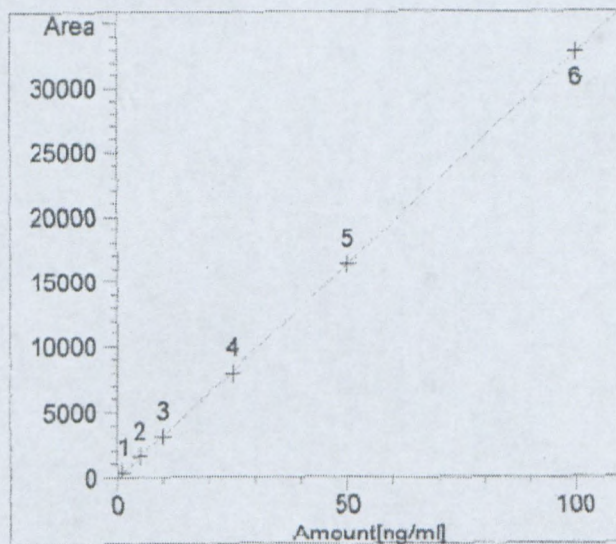
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APPENDICES

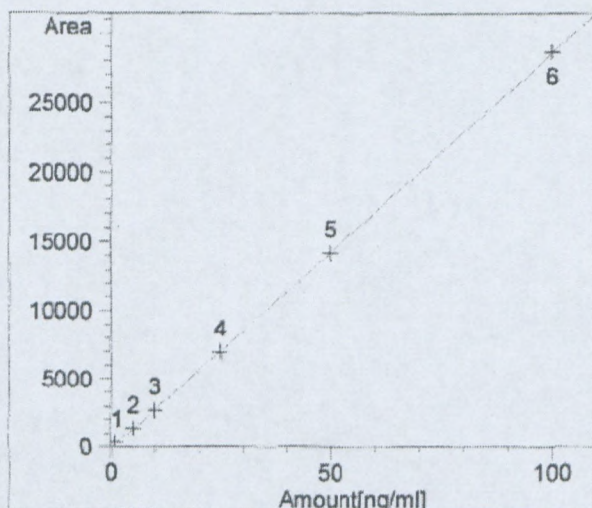
APPENDIX 1: Calibration curves of selected PBDE congeners and BB 153



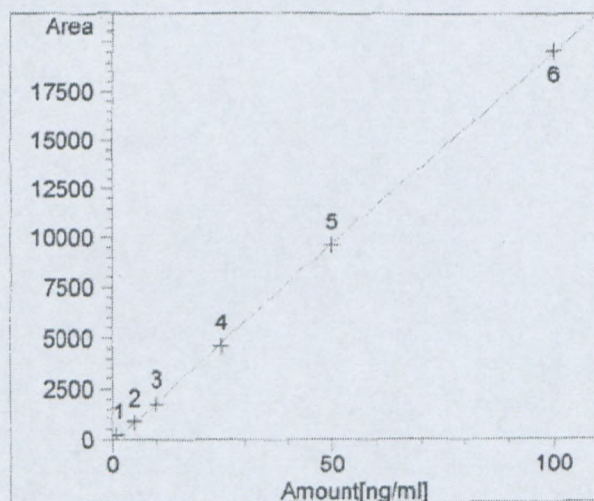
BDE 28 at exp. RT: 13.952
 ECD1 A,
 Correlation: 0.99998
 Residual Std. Dev.: 105.26501
 Formula: $y = mx + b$
 m: 428.61998
 b: -92.69940
 x: Amount [ng/ml]
 y: Area



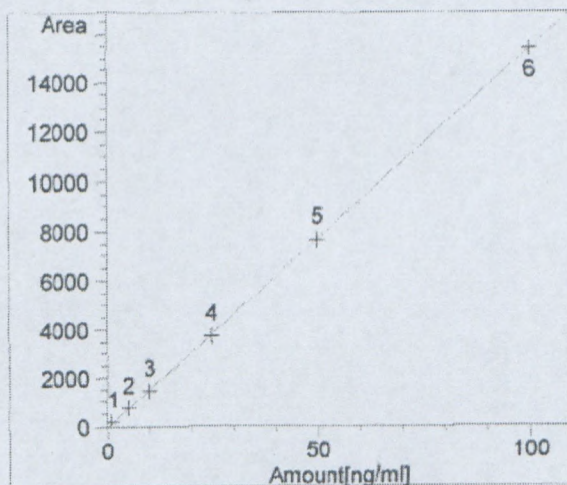
BDE 47 at exp. RT: 16.683
 ECD1 A,
 Correlation: 0.99997
 Residual Std. Dev.: 104.23541
 Formula: $y = mx + b$
 m: 327.62895
 b: -94.90243
 x: Amount [ng/ml]
 y: Area



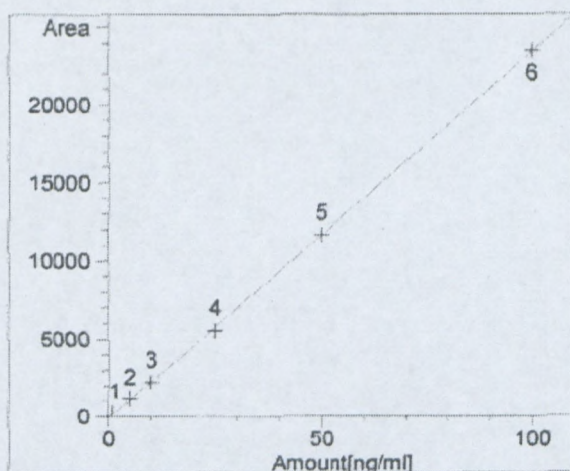
BDE 100 at exp. RT: 19.137
 ECD1 A,
 Correlation: 0.99998
 Residual Std. Dev.: 80.49836
 Formula: $y = mx + b$
 m: 286.76393
 b: -78.43329
 x: Amount[ng/ml]
 y: Area



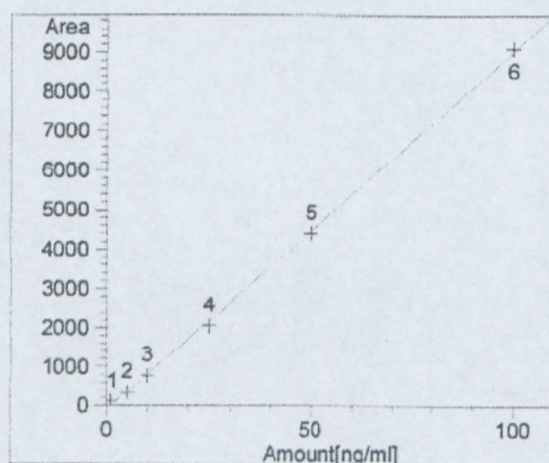
BDE 99 at exp. RT: 19.990
 ECD1 A,
 Correlation: 0.99986
 Residual Std. Dev.: 131.52842
 Formula: $y = mx + b$
 m: 196.27655
 b: -127.70203
 x: Amount[ng/ml]
 y: Area



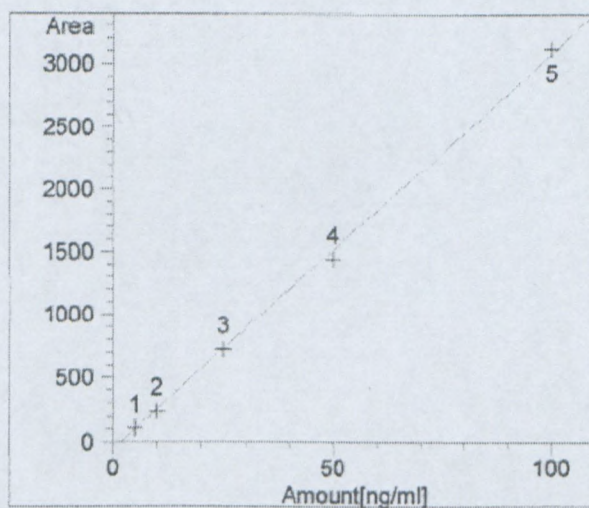
BDE 154 at exp. RT: 22.231
 ECD1 A,
 Correlation: 0.99995
 Residual Std. Dev.: 62.03173
 Formula: $y = mx + b$
 m: 154.33416
 b: -44.65929
 x: Amount[ng/ml]
 y: Area



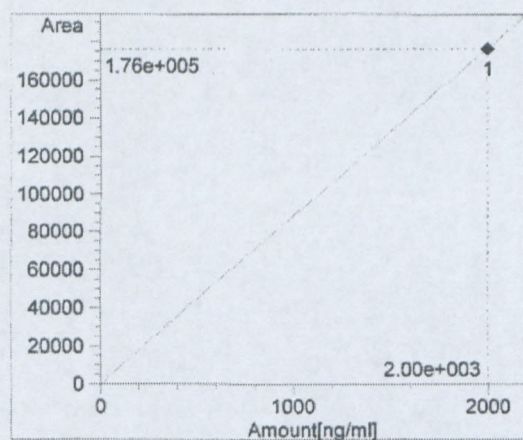
BB 153 at exp. RT: 22.290
 ECD1 A,
 Correlation: 0.99991
 Residual Std. Dev.: 128.07469
 Formula: $y = mx + b$
 m: 234.87149
 b: -78.25850
 x: Amount[ng/ml]
 y: Area



BDE 153 at exp. RT: 23.506
 ECD1 A,
 Correlation: 0.99961
 Residual Std. Dev.: 102.68688
 Formula: $y = mx + b$
 m: 91.25647
 b: -96.11559
 x: Amount[ng/ml]
 y: Area

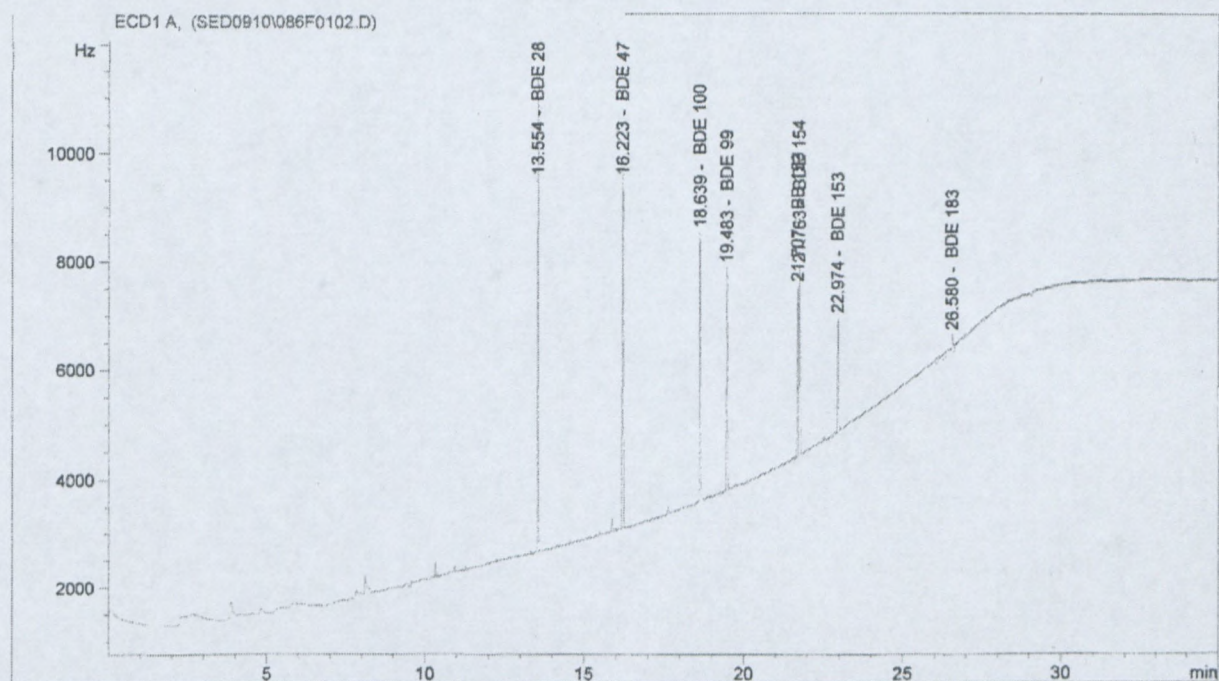


BDE 183 at exp. RT: 27.117
 ECD1 A,
 Correlation: 0.99928
 Residual Std. Dev.: 50.46366
 Formula: $y = mx + b$
 m: 31.35490
 b: -55.10710
 x: Amount[ng/ml]
 y: Area

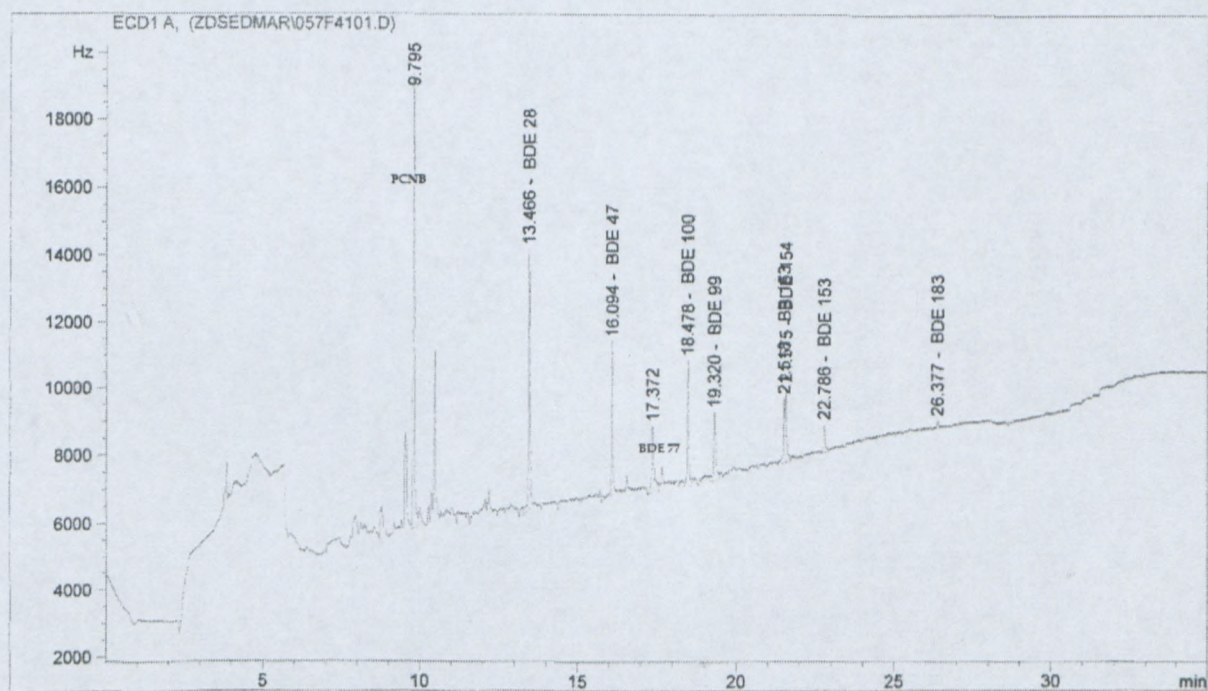


BDE 209 at exp. RT: 16.513
ECD1 A,
Correlation: 1.00000
Residual Std. Dev.: 0.00000
Formula: $y = mx + b$
m: 88.26659
b: 0.00000
x: Amount[ng/ml]
y: Area

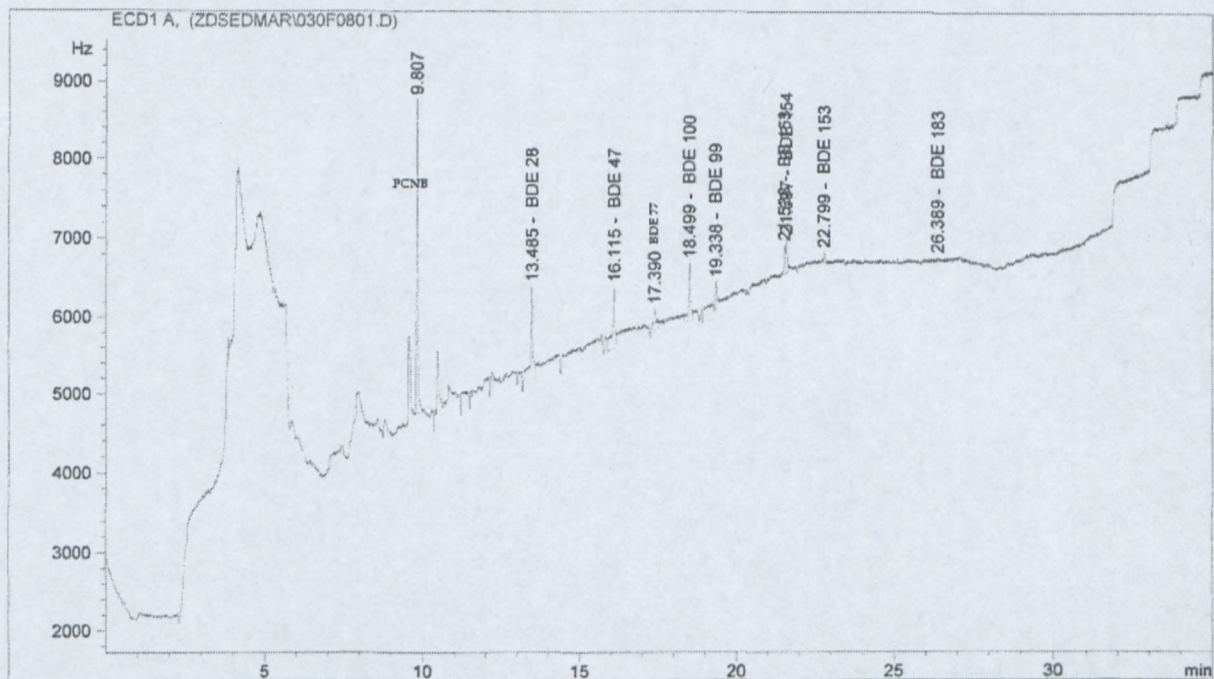
APPENDIX 2: Chromatograms of mixed PBDEs and BB 153 standards, spiked and unspiked samples



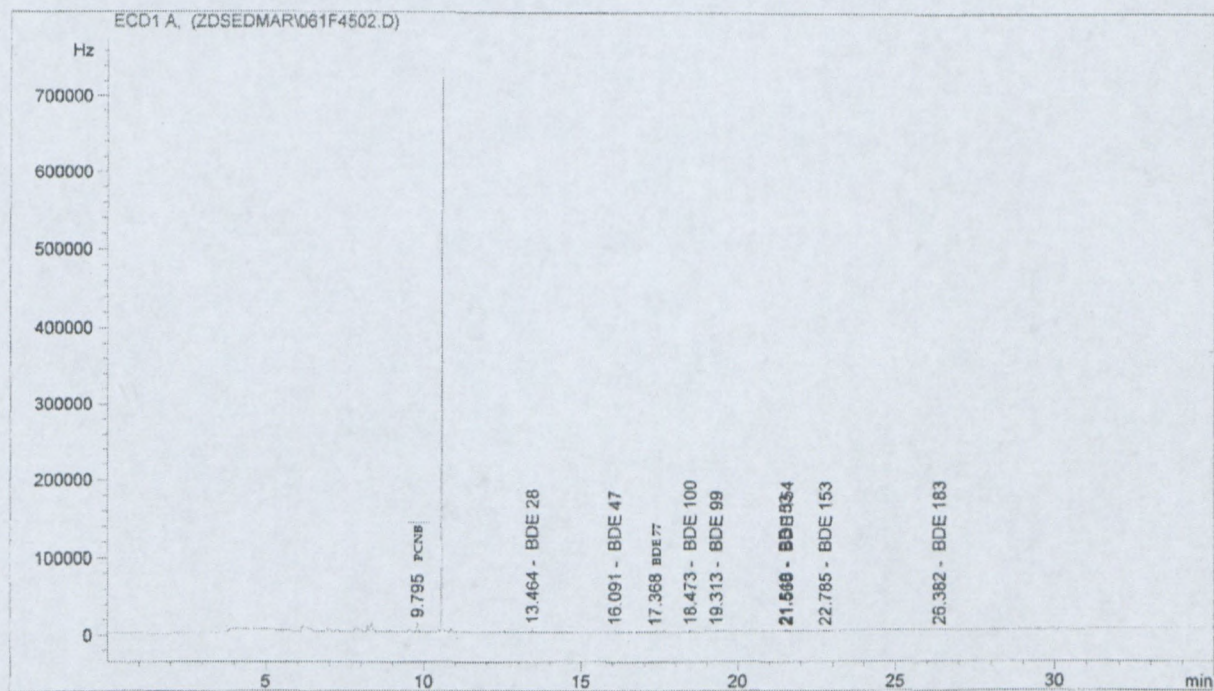
Chromatogram of mixed PBDEs and BB 153 standards representing the tri-heptaBDEs congeners



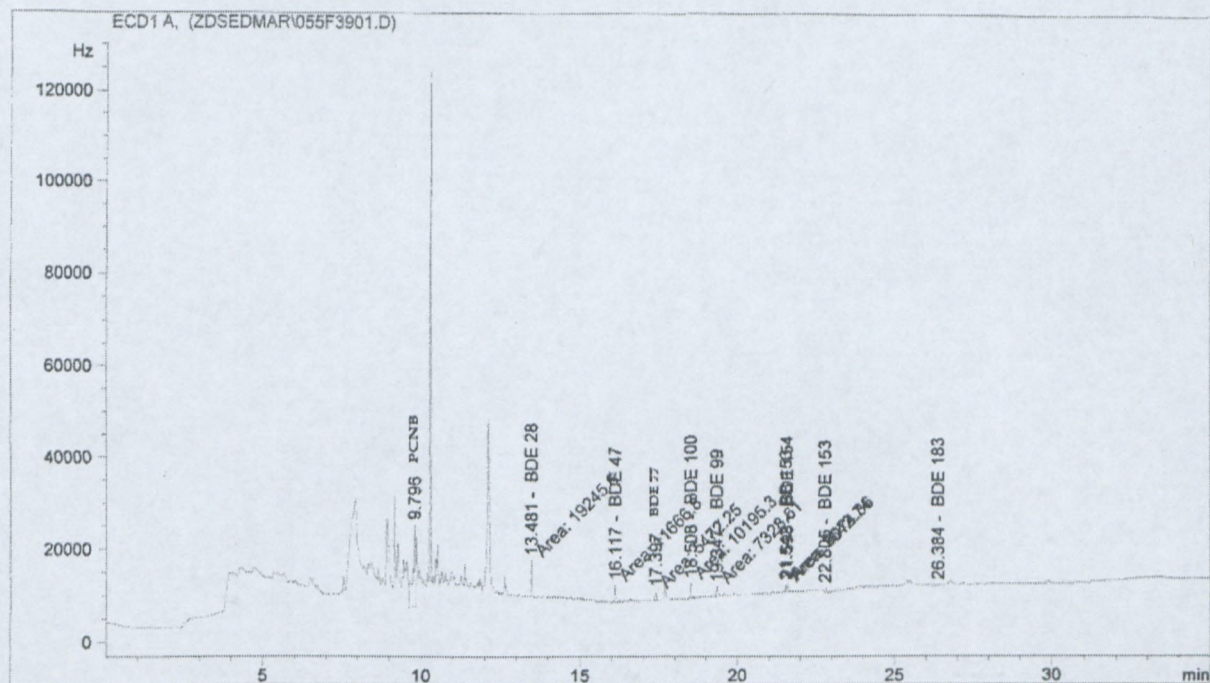
Chromatogram of target compounds and the surrogate standards in river water (Diep River upstream) sample



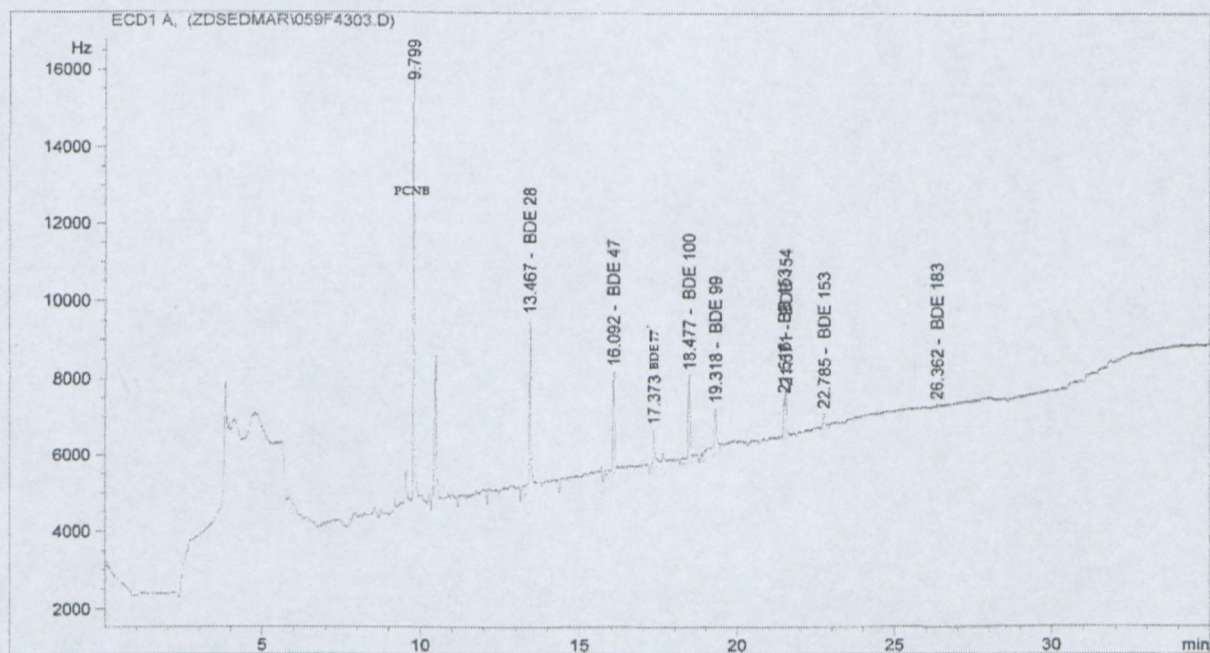
Chromatogram of target compounds and the surrogate standards in bottom sediment (Diep River upstream) sample



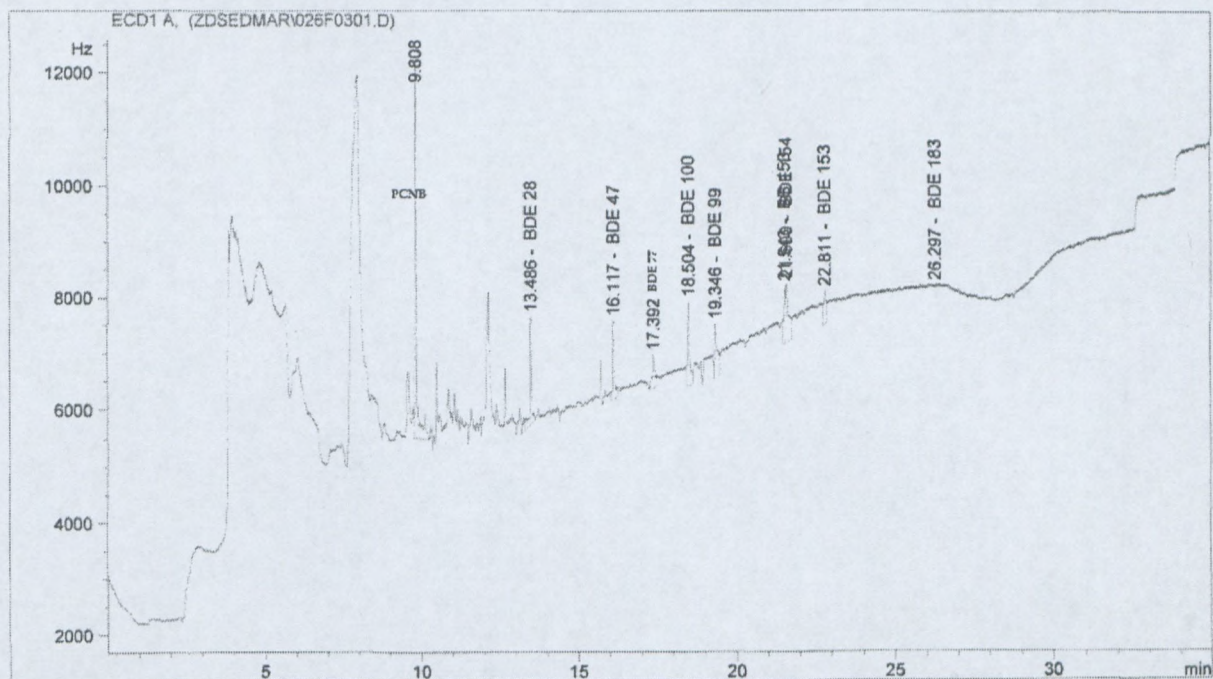
Chromatogram of target compounds and the surrogate standards in raw leachate (Vissershok) sample



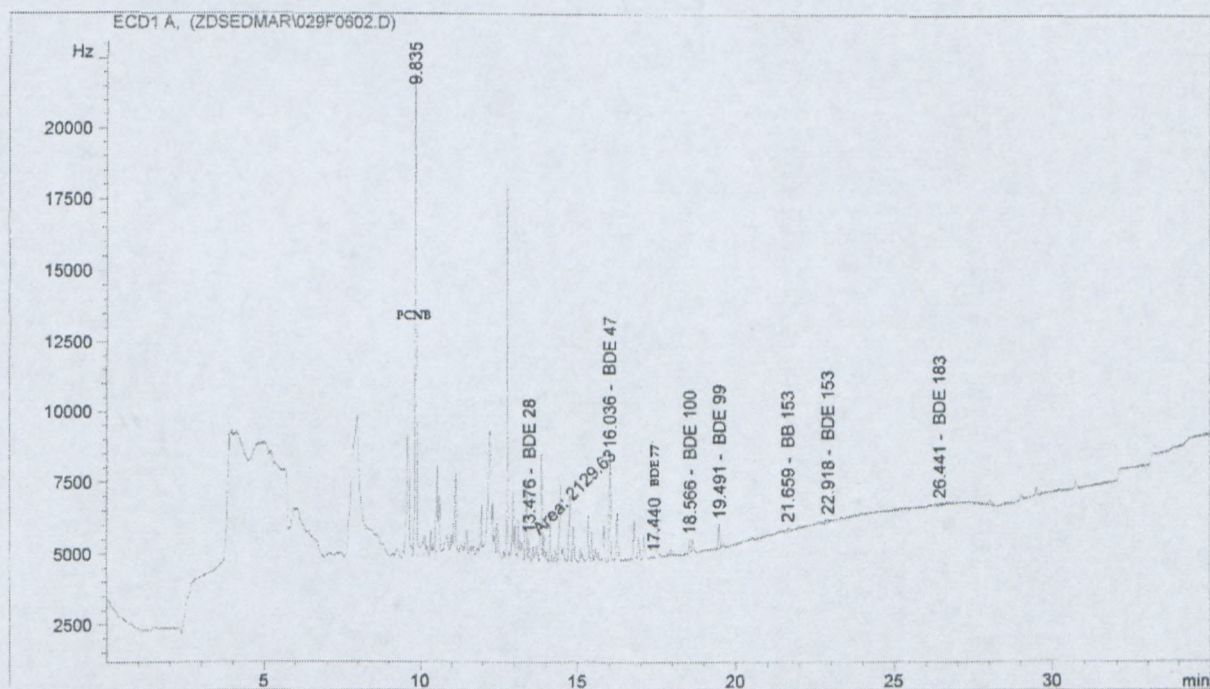
Chromatogram of target compounds and the surrogate standards in primary effluent (Old Bellville WWTP) sample



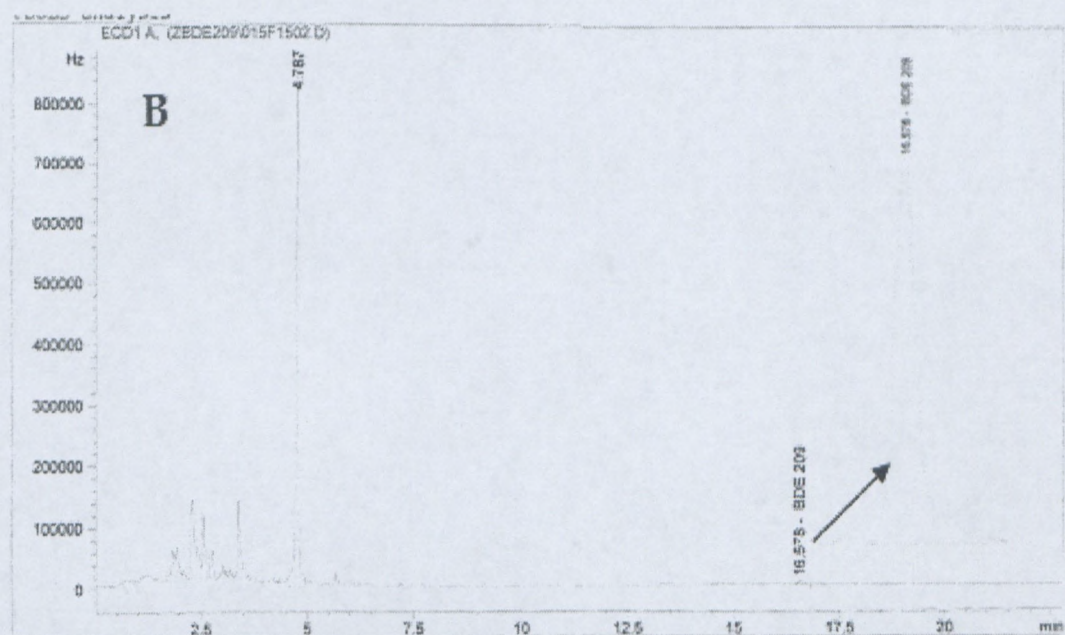
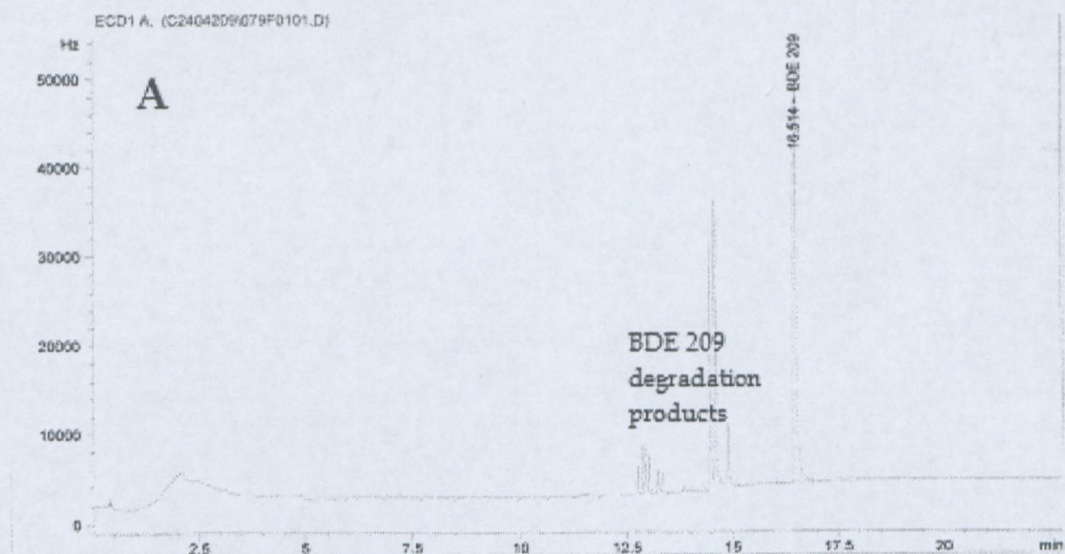
Chromatogram of target compounds and the surrogate standards in spiked MilliQ water sample



Chromatogram of target compounds and the surrogate standards in the spiked secondary sludge (Cape Flats WWTP) sample



Chromatogram of target compounds and the surrogate standards in the unspiked secondary sludge (Cape Flats WWTP) sample



Typical chromatograms of the target compounds [A] BDE 209 standard (2000 ng/ml) showing some of the degradation products of the congener [B] BDE 209 in a secondary sludge sample

BDEMix_STD_EO_6276

DP_SDS_OUTPUT_WL_110815_9

100

0

4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00

BDE 28

BDE 47

BDE 100

BDE 99

BDE 154+BB 153

BDE 153

BDE 183

9.37

9.30

11.51

11.54

15.12

15.12

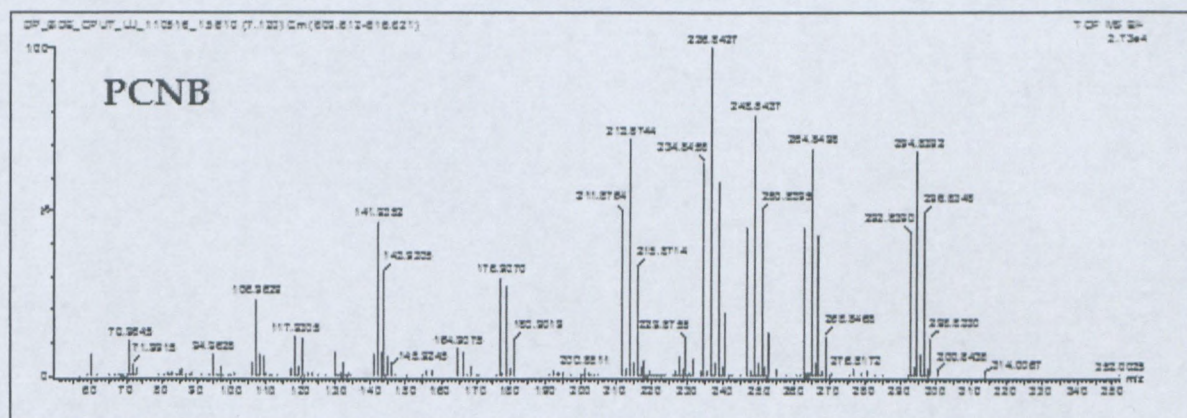
17.12

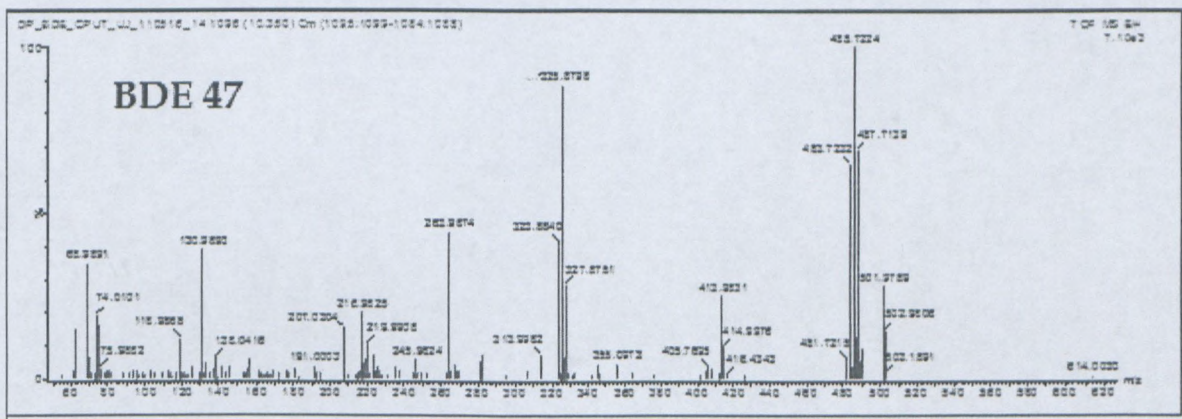
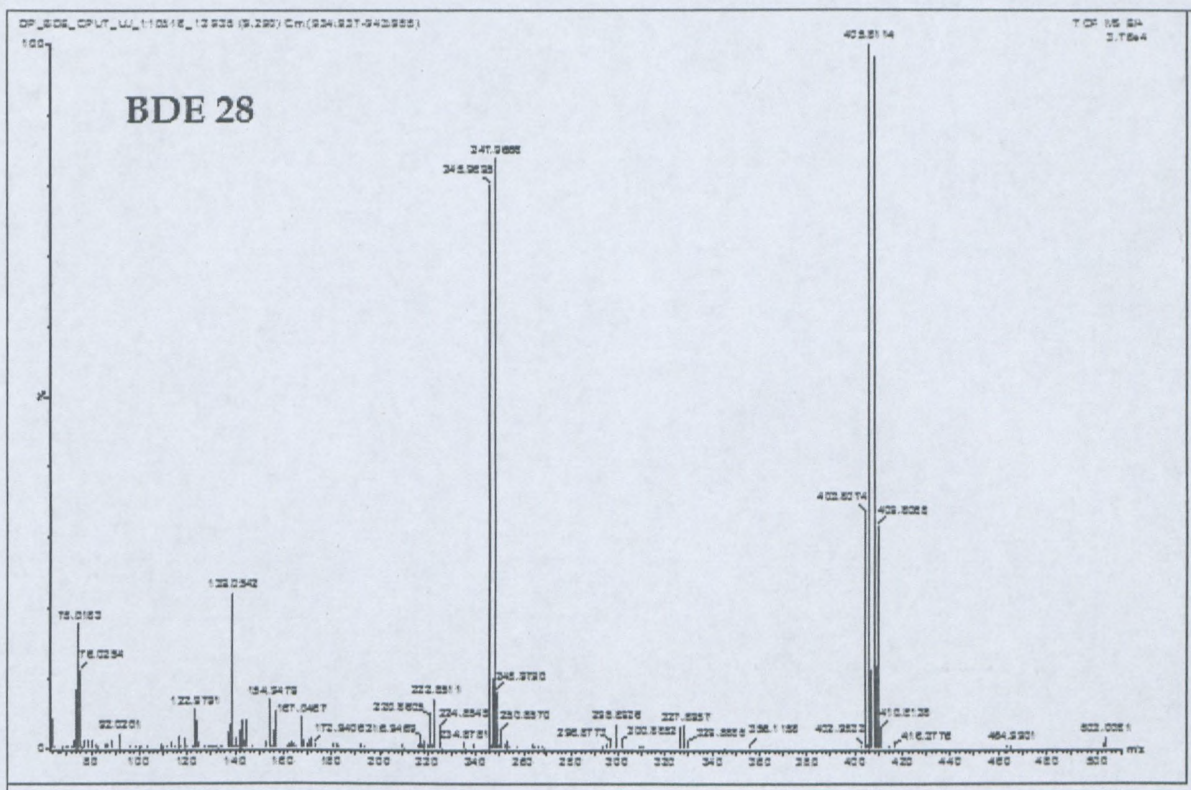
BDEMix_STD_EO_6276 NOT EXTRACTED

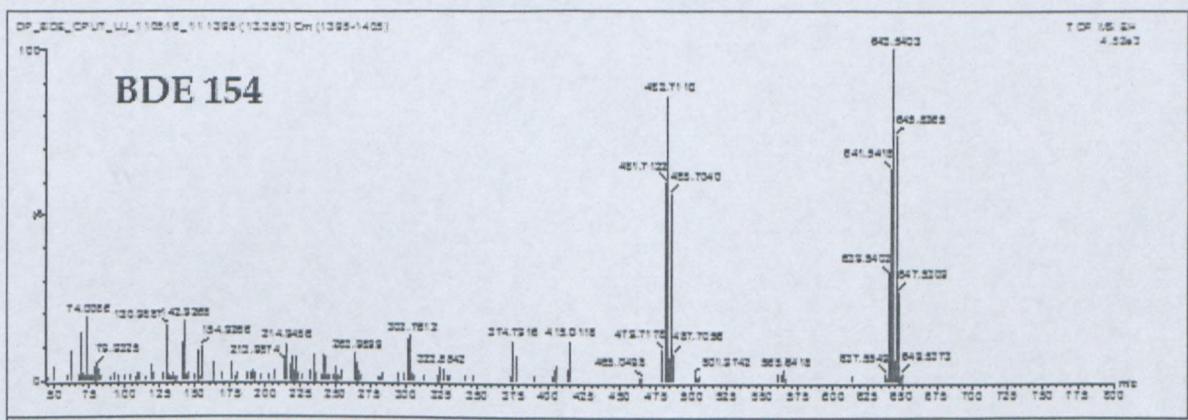
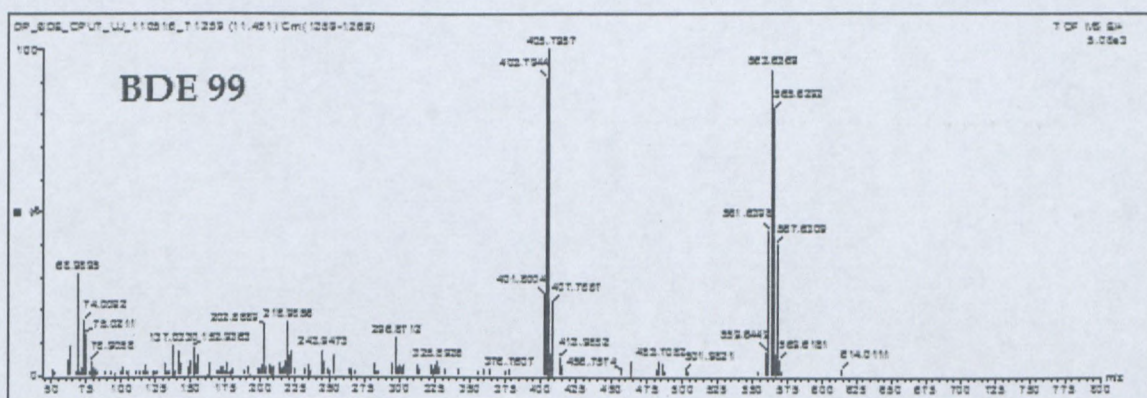
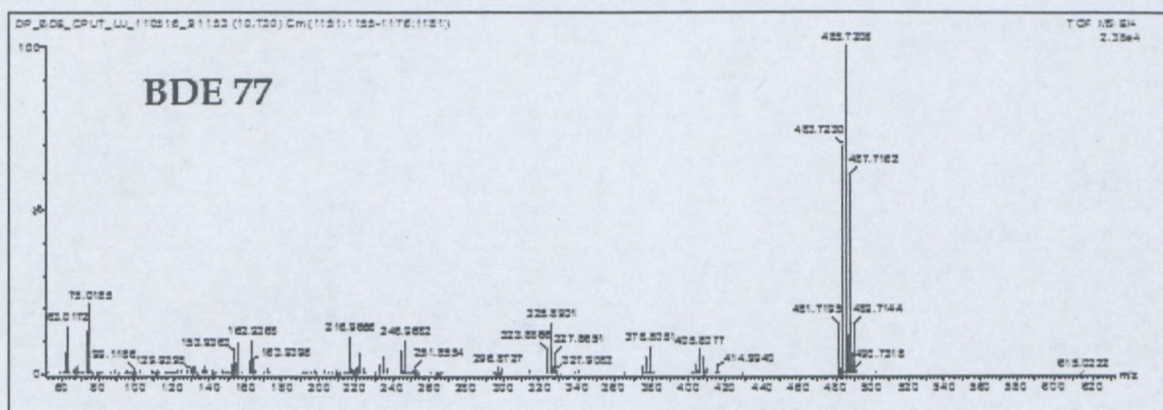
TOT MS EV

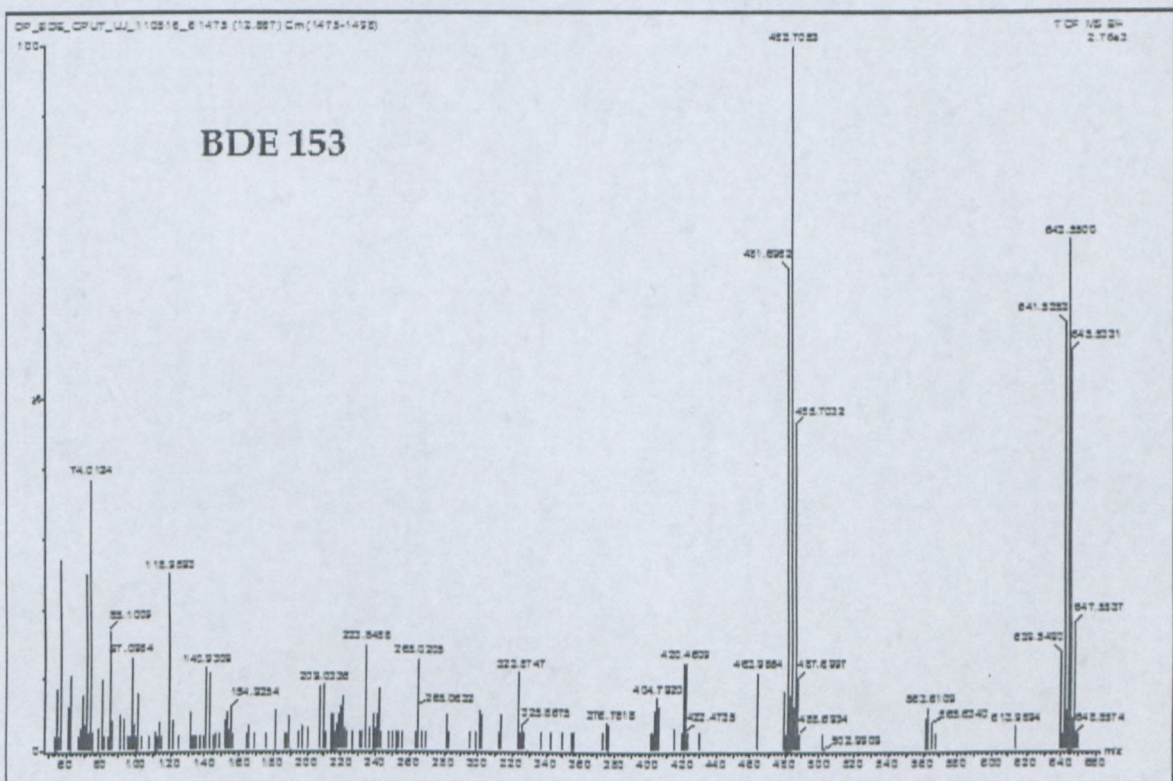
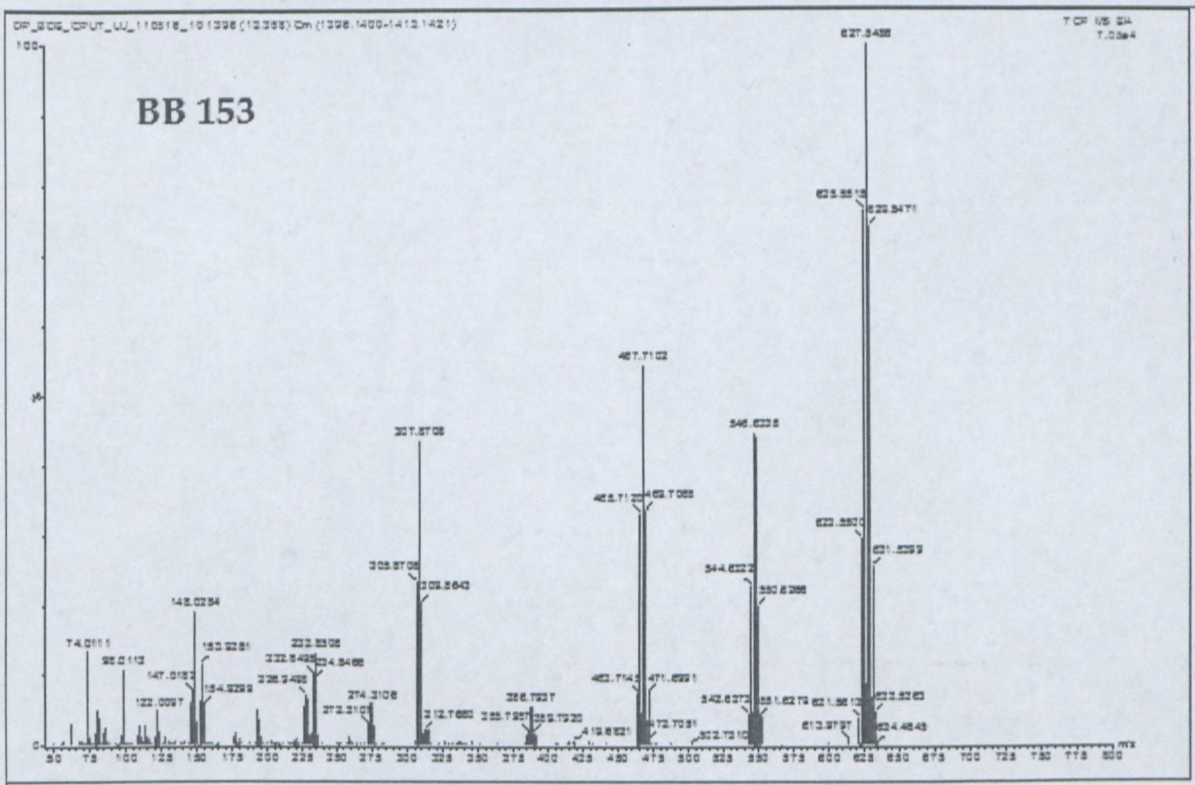
Sum 3.50E6

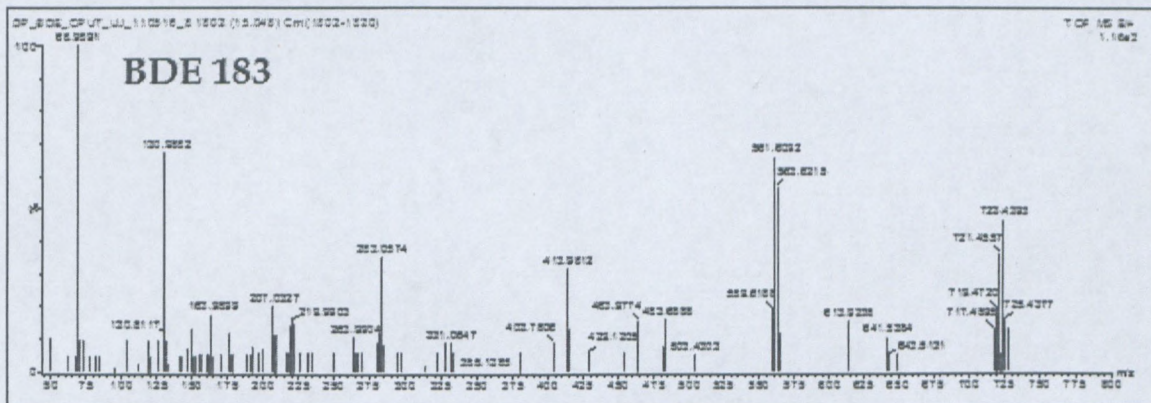
242



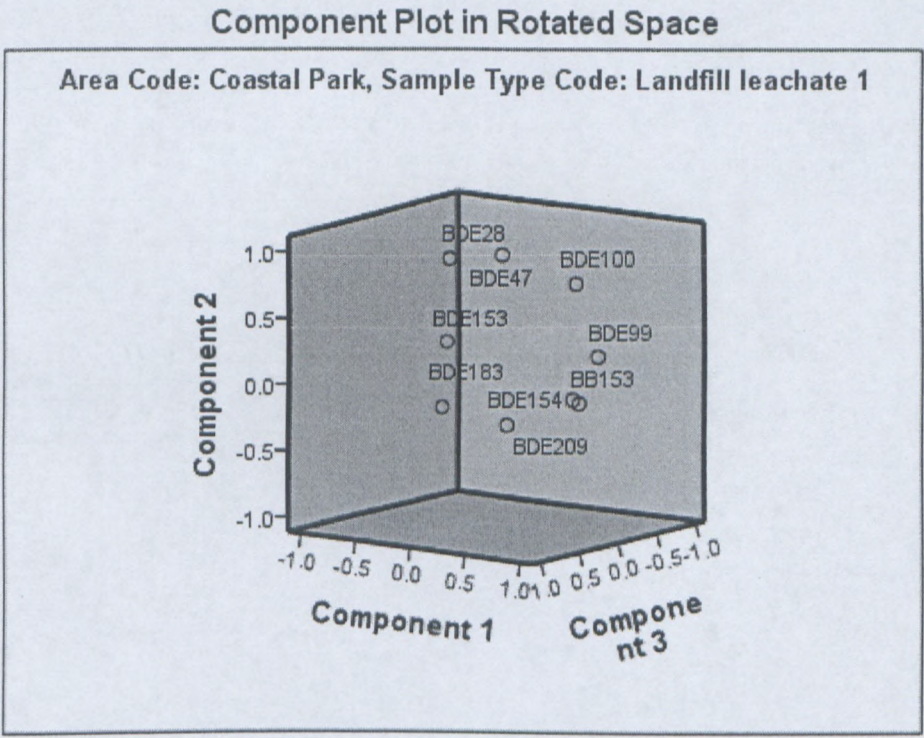
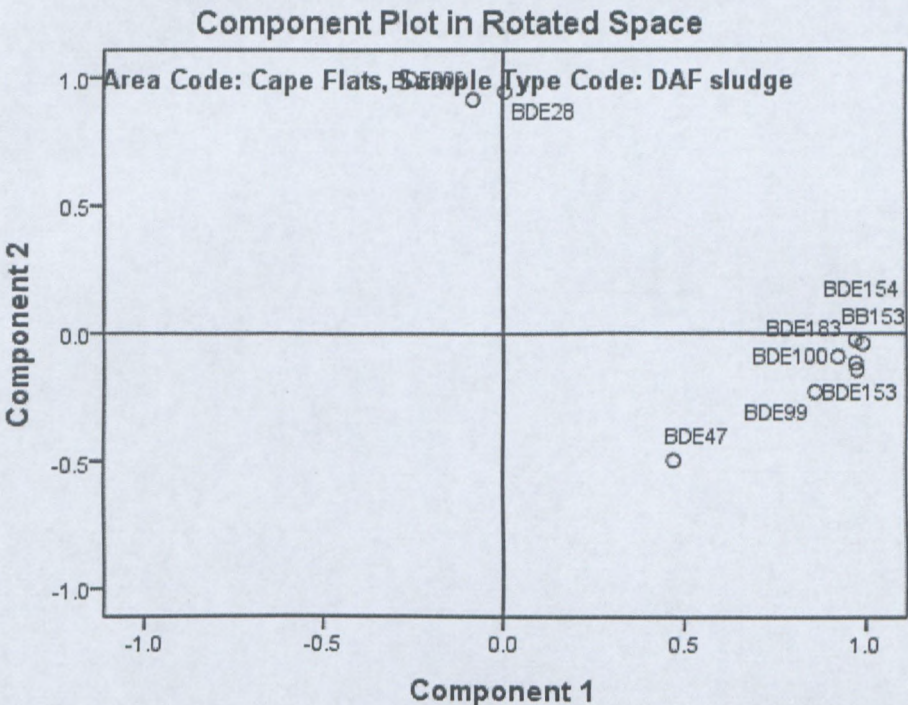






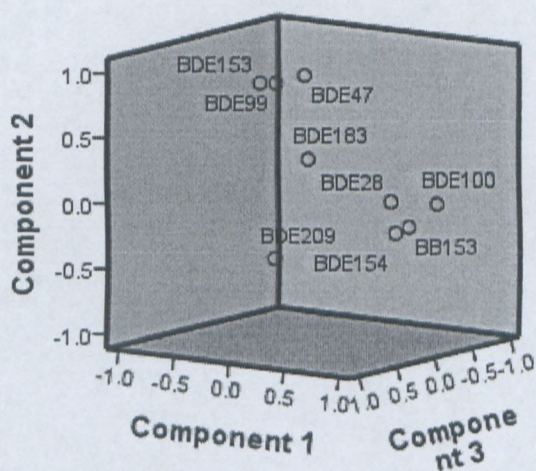


APPENDIX 4: Principal Component Analysis (PCA) plots for different sample types



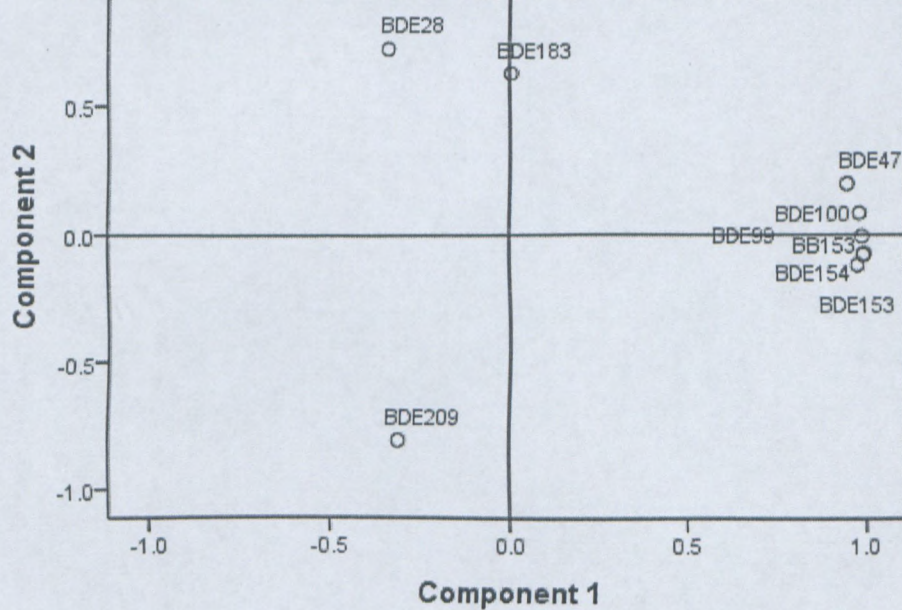
Component Plot in Rotated Space

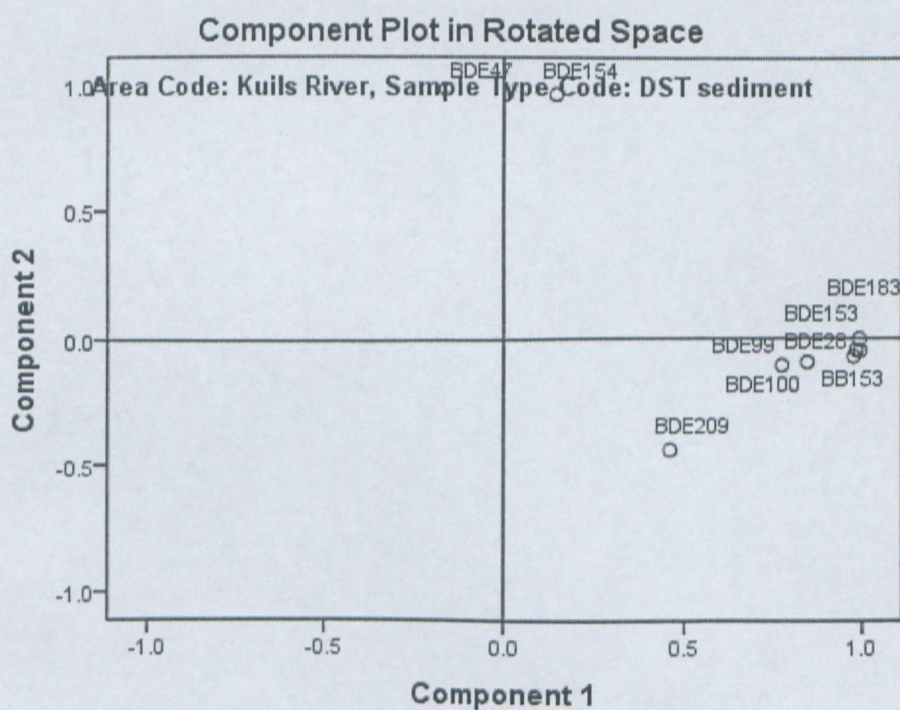
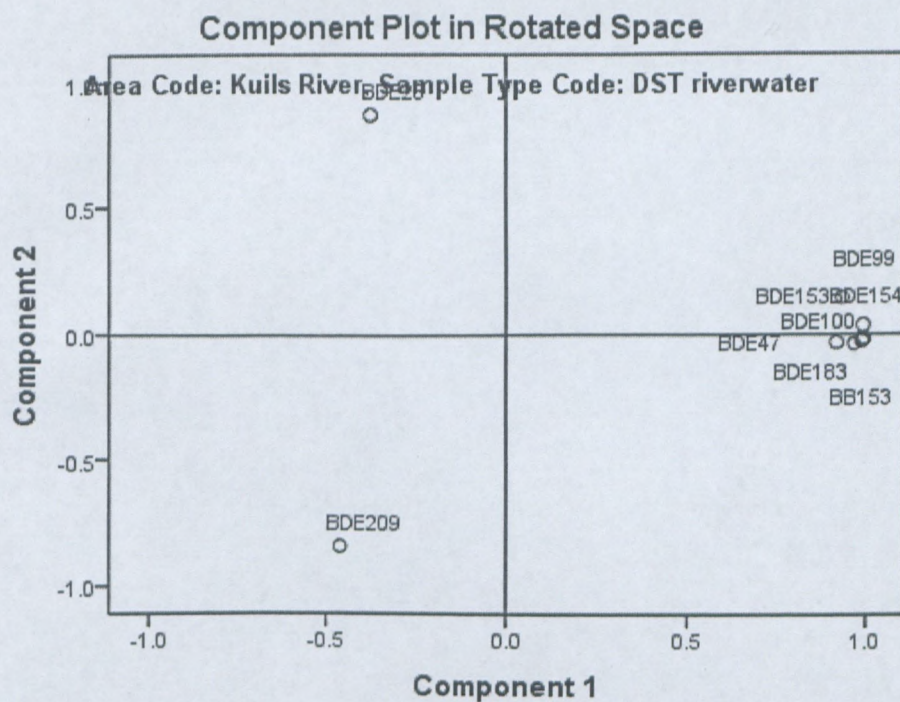
Area Code: Vissershok, Sample Type Code: Landfill leachate 1

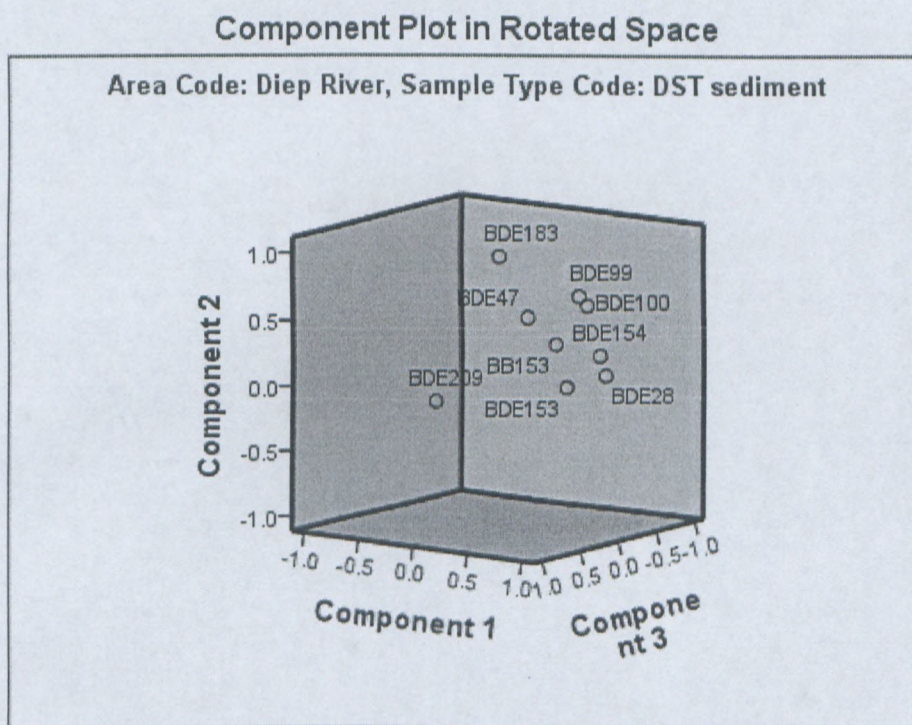
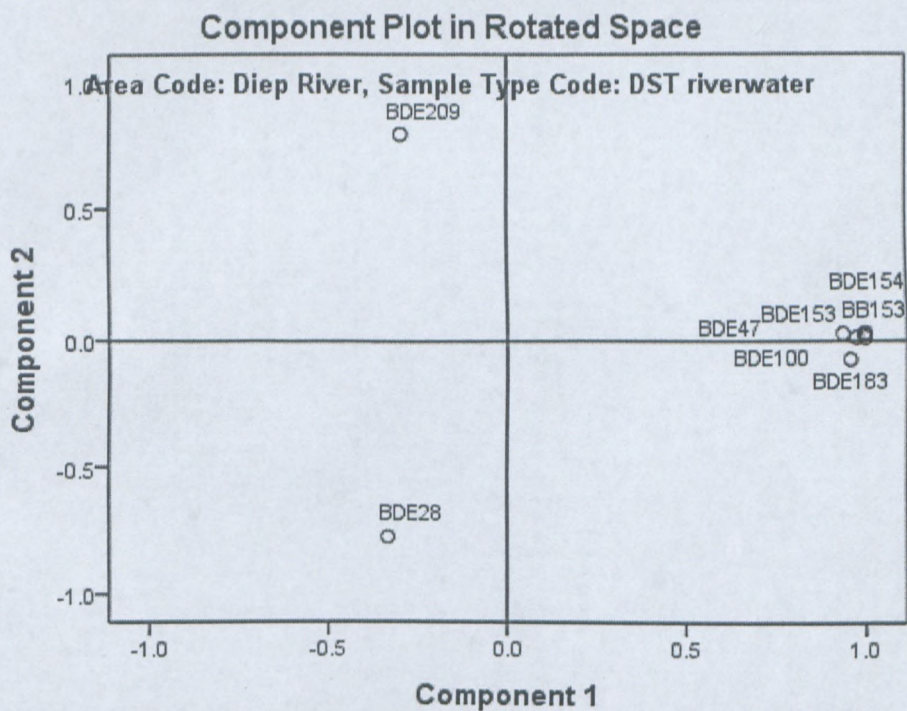


Component Plot in Rotated Space

Area Code: Vissershok, Sample Type Code: Landfill leachate 2







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