SCOPING STUDY ON THE SOURCES AND OCCURRENCE OF COMMON BROMINATED FLAME RETARDANTS IN SELECTED AREAS IN GAUTENG IN SOUTH AFRICA

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

BACKGROUND AND MOTIVATION

Brominated flame retardants (BFRs) are technical flame retardants containing brominated organic compounds which are applied to combustible materials such as plastics, wood, paper, electronics and textiles to meet fire safety regulations. The widespread production and use of BFRs, and strong evidence of increasing contamination of the environment by these chemicals, heighten the importance of identifying emerging issues and data gaps and of generating a future research agenda in South Africa. BFRs are relatively new environmental contaminants in developing countries such as South Africa and consequently information about their environmental fate and toxicity is scarce. It is, therefore, extremely important to monitor and manage these compounds.

With the exception of recent studies by Polder et al. (2008) and Odusanya et al. (2006 and 2009) who reported on the presence of PBDEs in bird eggs and landfill leachates respectively in South Africa, the authors are not aware of any report on the concentration of brominated flame retardants (PBBs and PBDEs) from any South African water system.

In the light of paucity of studies on the occurrences and levels of PBBs and PBDEs in landfill sites and groundwater located within the vicinity of landfill sites in South Africa, the present study was undertaken to investigate the existence of these emerging compounds in landfill leachates, sediment and groundwater. When seen in this light, an investigation was considered necessary in order to evaluate the current status of the South African environment with emphasis on landfill leachates, sediments and groundwater. This study is expected to show the presence of PBBs and PBDEs in the aforementioned environmental matrices as well as establish whether or not they are at levels that might raise public health concerns.

RESEARCH OBJECTIVES

The objectives of this study were:

1. To conduct a literature search on the legal status of BFRs control in South Africa as well as attempt to find the quantities, types and BFRs-containing products used in South Africa;

2. To determine the occurrence of common brominated flame retardants in landfill leachates, sediments and groundwater at selected areas in Gauteng, using established analytical methods and identify the potential sources of BFRs if present in and around the sites; and

3. To identify possible future research needs and actions to be taken if the results from the study indicate pollution of water resources.

The following tasks were undertaken in order to achieve the aforementioned objectives:

- An extensive literature search was undertaken on the legal status of BFRs control in South Africa as well as collate information on the quantities of BFRs in the country;

- Attempted to identify the major BFRs-containing products in the country;

- Searched for approved methods on sampling, extraction and analysis of BFRs from various sample matrices; and

- Extracted and analysed landfill leachates, sediment and groundwater for BFRs.

RESULTS AND CONCLUSIONS

The report by the South African Customs and Excise on imported and exported chemicals showed that in 2007 some 496 039 and 191 182 kg of polybrominated biphenyls (PBB) were imported and exported respectively and that in 2008 the figures were 60 963 and 34 555 kg. Information on products containing BFRs could not be obtained from any source. Furthermore, it was not clear from the information obtained from South African Customs and Excise whether other forms of BFRs were also imported or exported in 2007-2008.

With respect to legislation on the control of BFRs in South Africa, results show that there are two main Acts that are used to control the handling and management of chemicals and pesticides in South Africa, and these are: the Fertilizers, Farm Feeds and Agricultural Remedies and Stock Remedies Act No 36 of 1947 and the Hazardous Substances Act No15 of 1973. Several Government Notices and Regulations that address Fertilizers, Farm Feeds and Agricultural Remedies and Stock Remedies as well as Hazardous Substances stem from these two main Acts. Of particular interest is the Hazardous Substances Act which defines and provides four groups of hazardous substances to be declared by the Minister of Health and categorized according to their nature and the degree of danger they pose.

Although there is no specific legislation on the control of BFRs in South Africa at the moment, the aforementioned section 2 (1) (a) of the Hazardous Substances Act (Act 15 of 1973) can be seen to serve the purpose of controlling BFRs. Other legislation that may be used in controlling BFRs include: The National Water Act 36 of 1998 and The Customs and Excise Act 91 of 1964.

On the presence and concentrations of some BFRs in landfill sediment and leachates, two landfill sites, Kwaggasrand and Hatherley, were identified in Pretoria. Sediment and leachate samples were collected from the landfill sites in 2009 and extracted using accelerated solvent extraction and solid phase extraction respectively. Liquid-liquid extraction was used for groundwater. The extracts were cleaned by column chromatography and thereafter analysed using Agilent 6890 and 5975 series GC-MS fitted with auto-sampler and Chemstation software for data collection and analysis in electron ionization mode.

The limit of detection obtained ranged from 2.0-5.0 ng L^{-1} and 1.5-4.5 ng kg^{-1} for liquid and solid samples respectively. PBB-31, PBB-80 and PBB-155 were not detected in any of the samples. This was not the case with PBDEs where all the PBDEs were detected in at least one of the samples. The following PBBs and PBDEs were detected in all samples from the two sampling sites: PBB-4, PBB-10; PBDE-17 and PBDE-47. In addition to the aforementioned BFRs, PBB-49, PBDE-28, PBDE-66, PBDE-77, PBDE-100, PBDE-138, PBDE-153, PBDE-154 and PBDE-183 were detected in the leachate, sediment and groundwater samples as well. The detection of PBB-4, PBB-10, PBDE-17 and PBDE-47 in all the samples indicated that these were the most common BFRs in the samples analysed. One could, therefore, suggest that these congeners can be used as preliminary screening indicators of BFRs contamination in environmental matrices. PBDE-17 exhibited the highest concentrations for sediment and leachate samples from the two sites. For the BRFs detected, the concentrations of PBDEs are significantly higher than those of PBBs.

In general, sediment samples showed higher concentrations of PBBs and PBDEs than leachate samples. For Hatherley landfill site, leachate, sediment and groundwater accounted for 62.0%, 12.8% and 1.9% respectively of the total mass of BFRs detected. However, for Kwaggasrand landfill site the equivalent figures were 39.0%, 39.1% and 1.0% respectively. The highest BFRs concentration, 629.03±0.24 µg kg^{-1}, was recorded for PBDE-17 followed by PBB-10 and PBDE-47 with 471.4±1.38 µg kg^{-1} and 92.87±0.29 µg kg^{-1} respectively for sediment samples from Kwaggasrand site. Concentrations of 190.79±0.07 µg kg^{-1} and

89.0±0.14 μgL^{-1} were recorded for sediment and leachate samples respectively from Hatherley site. The highest concentration recorded for leachate sample, 89.0±0.1 μg L^{-1} in the present study is significantly higher than (not detected) – 0.004 μg L^{-1} , 0.029.0 μg L^{-1} and 0.0098 μg L^{-1} reported in landfill leachates from Japan, Minnesota and Pretoria by Osako et al. (2004), Oliaei et al. (2002) and Odusanya et al. (2009) respectively. PBDE-138 exhibited the highest concentration of 9.8±2.2 μg L^{-1} in groundwater. This was followed by PBDE-47 and PBDE-17 with concentrations of 8.4±2.1 μg L^{-1} and 5.3±0.4 μg L^{-1} respectively.

A significant correlation between the most common PBDEs in groundwater and landfill leachate for the two sites was observed: Hatherley (r: 0.84-0.94) and Kwaggasrand (r: 0.79-0.97). The concern, however, is that PBDEs are persistent new emerging chemicals, with relatively scarce information on their movement in the environment.

In conclusion, the present study has shown that to date there is no specific legislation on the control of BFRs in South Africa. However, the regulation under SANS10228 and section 2 (1) (a) of the Hazardous Substances Act, 1973 (Act 15 of 1973) can be used to control BFRs. Other legislations such as The National Water Act 36 of 1998 and The Customs and Excise Act 91 of 1964, may also be used to control BFRs. Furthermore, since South Africa is signatory to the Rotterdam Convention which has identified polybrominated biphenyl (PBB) as one of the chemicals that needs to be severely restricted or banned, the Convention can be invoked in the control of BFRs in South Africa.

The analyses of samples collected from two landfill sites have shown the presence of BFRs in landfill sediments, leachates and groundwater. Correlations between PBDEs in leachate and groundwater samples suggested that the groundwater contamination was as a result of the landfill. There is cause for concern about the levels of PBBs and PBDEs obtained in the present study.

RECOMMENDATIONS

The Stockholm Convention affirms the need to effectively control persistent and bioaccumulating chemicals. Establishing concentrations of contamination in environmental matrices such as landfill sites, as has been demonstrated in the present study, is an important way of verifying the environmental behaviour of chemicals approved for use. In order to estimate the extent to which the burden from various sources contribute to the total amount of BFRs released into the South African environment, investigations on more landfill sites, surface water, groundwater, sewage sludge and biota at regional and national levels need to be conducted. Pertinent questions such as the following need to be answered:

- What happens to flame retarded plastics in South Africa?
- What happens to polyurethane foams?
- Are polyurethane foams in mattresses, furniture and others treated with brominated flame retardants?
- What happens to car shredder material (plastic and seat material)?

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ACRONYMS & ABBREVIATIONS

APPA	Atmospheric Pollution Prevention Act 45 of 1965
ASE	Accelerated Solvent Extraction
AVCASA	Association of Veterinary and Crop Associations of South Africa
BFR	Brominated Flame Retardant
CAIA	Chemical and Allied Industries
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DEA	Department of Environmental Affairs
DoA	Department of Agriculture
DoH	Department of Health
ECA	Environmental Conservation Act
FFAS	Fertilizers, Farm Feeds and Agricultural Remedies and Stock Remedies
HBCD	Hexabromocyclododecane
HPLC	High Pressure Liquid Chromatography
NEAQA	National Environmental Management Air Quality
NEMA	National Environmental Management Act and Regulations
NGO	Non-Governmental Organization
PBBs	Polybrominated Biphenyls
PBDEs	Polybrominated Diphenyl Ethers
PCBs	Polychlorinated Biphenyls
SABS	South African Bureau of Standards
SANS	South African National Standards
SARS	South African Revenue Services
SPE	Solid Phase Extraction
TBBPA	Tetrabromobisphenol

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

The new methods in agriculture and forestry, the high demand in consumer products, the use of chemicals in health programmes, and the expansion of industrial processes, have contributed to the dramatic increase in the production of chemicals (Chandler, 2005). It is estimated that about 1 500 new chemicals are introduced into the global market every year (Chandler, 2005). It is, therefore, extremely difficult for governments to monitor and manage the many potentially dangerous substances going in and out of the country every day. This task is more challenging for developing countries where financial resources are lacking and building of adequate capacity remains a need. In response to this, the United Nations established three major conventions in order to protect human health and promote good environmental management of hazardous chemicals. These conventions are: the Rotterdam for chemicals of International Trade, the Stockholm Convention for Persistent Organic Pollutants, and the Basel Convention for the trans-boundary movement of hazardous wastes. These conventions aim to address the challenges posed by the use of hazardous chemicals in a cradle to grave approach, international trade including the transportation of chemicals, as well as the release of chemicals into the environment. One class of the emerging environmental contaminants is brominated flame retardants.

Brominated flame retardants (BFRs) are technical flame retardants containing brominated organic compounds which are applied to combustible materials such as plastics, wood, paper, electronics and textiles to meet fire safety regulations (Darnerud et al., 2001). Thus given the ubiquity of plastics in the modern world, it is not surprising that brominated flame retardants, particularly polybrominated diphenyl ethers (PBDEs) are being detected in all environmental compartments, including aquatic ecosystems (Allchin et al., 1999; de Boer et al., 1998). The estimated global consumption of BFRs shows that their usage is on the increase (de Boer et al., 1998). Being environmentally persistent compounds with high production volumes and lipophilic, polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) are among the most abundant BFRs detected in the environment.

Studies have shown that it is possible for BFRs, particularly polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) to leach from products into the environment if they are reactively added to those products (Darnerud et al., 2001). Recent reports have demonstrated that BFRs exist in the environment far from the locations where they are produced and/or used, and that the concentrations of some of the BFRs, both in the environment and in humans, are rapidly increasing. Consequently, the use of penta-BDE and octa-BDE mixtures has been banned in all applications in the European Union Market since August 2004 (European Union, 2004). The widespread production and use of BFRs, and strong evidence of increasing contamination of the environment by these chemicals, heighten the importance of identifying emerging issues and data gaps and of generating a future research agenda.

Studies conducted to date in some South African waters have shown the presence of organochlorinated pesticides (OCPs). Grobler (1994) investigated the presence of chlorinated hydrocarbon pesticide and polychlorinated biphenyl (PCB) residues in water, fish and sediment from Olifants River. PCBs and OCPs were analysed and were not detected in water and sediment although DDT (dichlorodiphenyltrichloroethane) was found in fish. Naude et al. (1998) studied the comparison of supercritical fluid extraction (SFE) and Soxhlet extraction (SE) for the determination of DDT and its metabolites DDD (dichlorodiphenyldichloroethane) and DDE (dichlorodiphenyldichloroethylene) in sediment samples from the Pongolo floodplain in KwaZulu-Natal and the Letaba River in Mpumalanga Province. London et al. (2000)

investigated the quality status of surface and groundwater in the rural Western Cape for OCPs. Also in the same year, Mentjies et al. (2000) analysed water samples from the Vaal River in the vicinity of Vereeniging and Vanderbijlpark for OCPs using SPE (solid phase extraction) and GC-ECD (gas chromatography – electron capture detector). Fatoki and Awofolu (2003) determined OCPs in water and sediment samples respectively in the Eastern Cape. Recently, Okonkwo et al. (2007) and Sibali et al. (2008) reported the presence of DDT and its metabolites (DDD and DDE) and other organochlorines in the Jukskei River Catchment Area. With the exception of recent studies by Polder et al. (2008) and Odusanya et al. (2006 and 2009) who reported on the presence of PBDEs in bird eggs and landfill leachates respectively in South Africa, the authors are not aware of any report on the concentration of brominated flame retardants (PBBs and PBDEs) from any South African water system.

In order to generate the required information on the presence of BFRs in South African environment, a scoping study is first required. From the scoping study, information on potential sources and occurrence of BFRs will be generated.

1.2 PROJECT AIMS

The following were the aims of the project:

1. To conduct a literature search on the legal status of BFRs control in South Africa as well as attempt to find the quantities, types and BFRs-containing products used in South Africa;

2. To determine the occurrence of common brominated flame retardants in landfill leachates, sediments and groundwater at selected areas in Gauteng, using established analytical methods and identify the potential sources of BFRs if present in and around the sites; and

3. To identify possible future research needs and actions to be taken if the results from the study indicate pollution of water resources.

CHAPTER 2: METHODOLOGY

2.1 EXPERIMENTAL

2.1.1 Materials

2.1.1.1 Chemicals and reagents

Polybromobiphenyls (PBBs) and polybromodiphenyl ethers (PBDEs) standards of the following congeners (BB-1,-2, -4, -10, -15, -26, -29, -30, -31, -38, -49, -80, -103, -153, -155, - 209) and (BDE-3, -15, -17, -28, -47, -66, -77, -85, -99, -100, -126, -138, -153, -154, -183, - 209) respectively were purchased from Wellington Laboratory, Canada. High Pressure Liquid Chromatography (HPLC) grade solvents and other chemicals such as the following: n-hexane, acetone, toluene, dichloromethane (DCM) and nonane, silica gel (100-200 mesh), sodium sulphate (99% purity) and glass wool were purchased from Sigma Aldrich.

2.1.1.2 Sampling sites

Figure 2.1 shows a map of all the landfill sites in Tshwane including the two landfill sites studied, while **Table 2.1** shows some details of the two landfill sites, Kwaggasrand and Hatherley.

Figure 2.1. Map of landfill sites in Tshwane including the two study sites.

Table 2.1. Details of Kwaggasrand and Hatherley landfill sites.

Landfill site	Year opened	Status	Address	Co-ordinates
Kwaggasrand	1965	Operational	Maunde Rd Pretoria West	25º46'30"S 28º06'34"E
Hatherley	1998	Operational	Hans Strydom North	25º44'16"S 28º24'26"E

2.1.1.3 Sediment sampling

Grab sediment samples were collected from about 0-5 cm below the surface of the leachate pool from Kwaggasrand and Hatherley landfill sites into wide mouth amber glass bottles and covered immediately after sampling. They were kept cool during transportation to the laboratory and later frozen below 4ºC prior to sample preparation and analysis. The sediment samples were air dried in the fume cupboard at room temperature for 2 days and homogenised thereafter before extraction.

2.1.1.4 Leachate sampling

About 2.5 L of raw leachate samples were collected from the aforementioned landfill sites from leachate shallow wells (**Figure 2.2**) by the grab sampling method using amber glass containers. After collection, the samples were stored in a cold room at 4ºC until pre-treatment for BFR analysis.

Figure 2.2. A view of the leachate pool from one of the landfill sites.

2.1.1.5 Groundwater sampling

Groundwater samples were collected from wells close to the landfill site. Thoroughly washed and oven-dried glass amber 2.5 L Winchester bottles were used for sample collection. Before use, the glass bottles were first rinsed with the groundwater samples and thereafter, immersed about 15 cm below the surface with the help of a string. After collection, the samples were acidified using analytical grade HNO_3 and then placed in a cooler bag and transported to the laboratory where they were stored in a cold room at 4ºC until pre-treatment and analysis.

2.2 METHODS

2.2.1 Introduction

In the present study the optimization of the Gas Chromatography - Mass Spectrometer (GC-MS) was conducted based on the variation of the following:

- Carrier gas and flow rate
- Injector temperature
- Oven temperature
- Column type
- Detector temperature

The presence of BFRs congeners in samples was confirmed using GC-MS. A standard mixture was first injected into the GC-MS to ascertain the elution times and therefore the resulting peaks. The peak profile and the retention time of each congener were then matched to those from the samples. For the determination of standard mixture, 1.0 µL of standard mixture containing 6-80 pg mL-1 of PBB and PBDE congener standards were injected into the GC.

2.2.2 Extraction

2.2.2.1 Accelerated solvent extraction (ASE)

Dried sediment samples as described earlier were extracted using ASE 350 accelerated solvent extractor (Dionex, Sunnyvale, CA, USA) equipped with 34 mL stainless steel cells. The extraction conditions used are presented in **Table 2.2** and the cell loading is as shown in **Figure 2.3**. Acetone and hexane (50:50 v/v) were used as extraction solvents. At the end of the extraction, anhydrous Na_2SO4 was added into the 60 mL collection vials to remove any traces of water from the extracts. Thereafter, nitrogen was blown into the solution and concentrated to about 30 mL of extract in toluene. An aliquot of 1 µL of the extract was injected into the GC-MS after column clean-up programme under the optimised instrumental condition.

Table 2.2. Accelerate solvent extraction operating conditions.

ASE conditions	ASE extraction coupled with online cleanup
Solvent	Hexane / Acetone (1:1 v/v)
Temperature	120ºC
Pressure	11 MPa
Static time (Min)	5
Static cycles	2
Flush	60%
Purge	90s

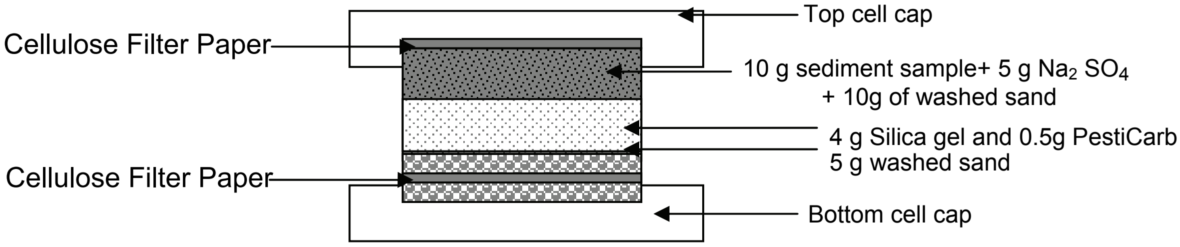


Figure 2.3. Packing of cell in accelerated solvent extraction.

2.2.2.2 Solid Phase extraction (SPE)

Leachate samples were first filtered (47 mm, GF1 filter paper) after which the pH level was adjusted to neutral for optimal extraction condition. The Nexus 6.0 mL cartridge was used. Before loading 1.0 L of sample via the manifold, the Nexus cartridge was washed with 4.0 mL of dichloromethane, soaked for 5 min and later drained and dried under vacuum for another 3 min, and then 4 mL of milli-RX-water was added and drained until the meniscus was just about the level of the top bed. After loading, the cartridge was allowed to dry for approximately 1.5 h under reduced vacuum and with a Pasteur pipette about 3.0 mL of DCM was used to wash the sample container and another 5.0 mL to elute the contents of the cartridge into a collection vial. A final 2.0 mL of hexane was used for elution before removing the vial for evaporation to near-dryness under nitrogen and then reconstituted by adding 1.0 mL of toluene. The vials were then transferred to the sample carousel of the GC where an aliquot of 1.0 µL of the extract was injected into the GC under the optimised instrumental condition.

2.2.2.3 Liquid-liquid extraction

About 100 mL of groundwater sample was placed in a 100 mL of separating funnel and the analyte extracted using 25 mL of dichloromethane by shaking manually. The extraction was repeated three times to ensure adequate extraction of the analyte from the matrix. The organic upper layers were collected in a weighed and thoroughly cleaned and dried flask. To the solvents collected from the combined organic extracts, anhydrous sodium sulphate was added to remove any traces of water, concentrated to about 2 mL by bubbling dry nitrogen gas through the solvent before passing through a column for clean up.

2.3 COLUMN CHROMATOGRAPHY

For clean up, a Pasteur pipette column 5 mm internal diameter was plugged with glass wool at the bottom and the column packed with pre-prepared chemicals from bottom to top in the following order: silica gel (0.25 g) , glass wool (for partition) and sodium sulphate (0.25 g) at the top were used. Each packed Pasteur pipette was first eluted with 20 mL of hexane/acetone mixture and later with 10 mL of hexane/acetone mixture. The clean up process was repeated at least two times and concentrated under a gentle flow of nitrogen to about 50 µL. Finally, the concentrated extract was diluted to 500 µL by toluene/nonane mixture 2:1 (v/v) and made ready for analysis.

2.4 INSTRUMENTATION (GC-MS)

Gas chromatograph coupled with mass selective detector was used, complete with all required accessories for split less injection and fitted with auto-sampler and Chemstation software for data collection and analysis. The Agilent 6890 and 5975 series GC-MS respectively was used for all the analyses with the following operating conditions:

- Injector temperature: 280ºC
- Programme Temperature: 100ºC, hold for 1 min, ramp at 30ºC/min to 300ºC, hold for 5 min and ramp at 10-30ºC /min to 310ºC, and hold 2 min (run time 15.67 min).
- Column flow 2.4 cm/s
- Helium carrier gas at average velocity of 58 cm/s
- Transfer line Temperature at 280ºC.
- Analytical capillary column: DB5, 30 m x 0.25 mm internal diameter x 0.25 um.
- Electron Impact Ionization mode.

2.5 QUALITY ASSURANCE AND QUALITY CONTROL

A solvent blank was extracted using the same condition as that of the samples as described earlier. After triplicate injection of each sample, a middle calibration standard was injected to control any change in retention time and concentration. In addition, before injection of a new sample, column cleaning was done at least twice using toluene/nonane mixture. Due to the unavailability of standard reference materials (SRM), addition of reagent standards to sediment and leachate samples was applied in the quality assessment and quality control processes for the validation of the analytical methods. To 5.0 g and 100 mL sediment and leachate respectively, 6.0-80 pg mL^{-1} of standard mixture of BDE-47 and BDE-99 were added and the extraction processes described earlier repeated. The extracts obtained were subjected to column chromatography as described earlier before analysis.

2.6 DATA ANALYSIS

The standard deviations for PBBs and PBDEs from replicate measurements were determined. For the general subsequent evaluation of the data, the mean values were used. The linear correlation coefficients of groundwater and landfill leachates for PBDEs were determined by calculating Pearson correlation coefficients using the equation shown below:

$$r^2 = \frac{\sum x_i y_i - \sum x_i \sum y_i}{\left[n\sum x^2 - \left(\sum x_i\right)^2\right]\left[n\sum y_i^2 - \left(\sum y_i\right)^2\right]}$$

CHAPTER 3: RESULTS AND DISCUSSION

3.1 REVIEW OF LEGISLATION

3.1.1 Introduction

Consultations were made (through phone calls, emails and visits) with the relevant authorities and institutions which deal with chemicals and pesticides management in South Africa. The legal documents pertaining to the control of chemicals and pesticides were obtained through the National Library of South Africa in Pretoria and some from the websites of the national departments. A search for the relevant literature was undertaken to find out whether there is any existing legislation on BFRs. The following Government Departments as well as NGOs were consulted:

- South African Bureau of Standards;
- Department of Agriculture;
- Department of Health;
- South African Revenue Services;
- Chemical and Allied Industries;
- Association of Veterinary and Crop Associations of South Africa;
- Provincial Environmental Health Departments;
- Dow Chemicals;
- Endangered Wildlife Foundation; and
- National Library of South Africa.

3.1.2 The Constitution

The Constitution of the Republic of South Africa is the supreme law of South Africa and it governs all other laws in the land. The law states that everybody has the right:

- to an environment that is not harmful to their health or well-being; and
- to have the environment protected for the benefit of present and future generations, through reasonable legislative and other measures that:
    - prevent pollution and ecological degradation;
    - promote conservation and
    - secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development.

The President of the Republic of South Africa is the custodian of the provisions of the constitution through various measures that ensure that the intentions of the constitution are realised in South Africa, including environmentally sound management of hazardous chemicals.

3.1.3 National Environmental Management Act

The Department of Environmental Affairs (DEA) is responsible for the National Environmental Management Act (NEMA). Through its principles for environmental management and the duty of care, NEMA is meant to address the right to an environment that is not harmful to the health or well being of organisms as enshrined in the South African Constitution. NEMA enables the Minister of DEA to draft Regulations to accommodate and adequately capture the provisions of the Multilateral Environmental Agreements that South Africa is a Party to, including the identification of any measures in need of environmental authorisation. Most NEMA principles, to a larger extent, capture the following:

- Participation of all interested and affected parties in environmental governance;
- That the social, economic and environmental impact of activities must be considered;
- That the rights of workers to refuse work that is harmful to human health or the environment must be respected and protected;
- That access to information must be provided; and
- That global and international responsibilities relating to the environment must be discharged in the national interest.

3.1.4 Environmental Conservation Act 73 of 1989

The Environmental Conservation Act (ECA) has been promulgated to address the effective protection and controlled utilisation of the environment. It empowers Government Institutions to issue directives to persons that carry out activities that cause damage to the environment; improper management of chemicals that could cause damage to the environment, and hazardous pesticide formulations that may also cause damage to the environment even when directions on use are followed.

3.1.5 National Laws on Hazardous Chemicals

South Africa has promulgated several laws that aim or partly aim to address the issue of hazardous chemicals management and these are as follows.

3.1.5.1 Atmospheric Pollution Prevention Act 45 of 1965 and the National Environmental Management Air Quality Act 39 of 2004

The Atmospheric Pollution Prevention Act (APPA) aims at the prevention of the pollution of the atmosphere. Hazardous chemical substances could be used during the undertaking of second schedule substances as listed in the Act. The National Environmental Management Air Quality Act (AQA) was promulgated to reform the legislation on air quality so as to protect the environment by making provisions for the prevention of pollution and ecological degradation. When the repeal provisions are enforced, APPA is to be repealed by AQA. The provisions of AQA such as the air management measures include the declaration of priority areas, listing of activities, controlled emitters and fuels, and offensive odours and others. Activities may be regarded as ‘controlled emitters’ by the Minister or MECs if they result in atmospheric emissions which through ambient concentrations, bioaccumulation, deposition or in any other way, present a threat to the health or the environment or are believed to present such a threat. Due to their chemical properties, the use of some of the chemicals that are listed in Annex III of the Rotterdam Convention that are used in the activities that are regarded as ‘control emitters’ could be regulated under this Act.

3.1.5.2 Customs and Excise Act 91 of 1964

The custodian of the Customs and Excise Act is the South African Revenue Services (SARS). The Act prohibits and controls the import, export, manufacture or use of certain goods. SARS has developed a list of prohibited and restricted substances that can be imported and exported. This Act could be used to strengthen the compliance and monitoring of hazardous chemicals.

3.1.5.3 Fertilizers, Farm feeds and Agricultural Remedies and Stock Remedies Act No 36 of 1947

The National Department of Agriculture is responsible for the Fertilizers, Farm feeds and Agricultural Remedies and Stock Remedies (FFAS) Act. The FFAS Act provides for the appointment of a Register of Fertilizers, Farm Feeds and Agricultural Remedies; for the registration of fertilizers, farm feeds, agricultural remedies, stock remedies, sterilizing plants and pest control operators, to regulate or prohibit the importation, sale, acquisition, disposal or use of fertilizers, farm feeds, agricultural remedies and stock remedies; to provide for the designation of technical advisers and analysts; and to provide for matters incidental thereto. ‘Agricultural remedies’ include chemical substances, biological remedies or any mixture or combination of any substance or remedy intended or offered to be used for, among others, pest destruction or control, but exclude any chemical substances, biological remedy or other remedy in so far as it is controlled under the Hazardous Substance Act. ‘Stock remedies’ are substances intended or offered to be used in connection with animals for the diagnosis, prevention, treatment or cure of any disease, infection or unhealthy condition, among other things, excluding substances in so far as they are controlled under the Medicines and Related Substances Control Act 101 0f 1965.

3.1.5.4 Hazardous Substances Act No 15 of 1973

The Department of Health is responsible for the Hazardous Substance Act. The Hazardous Substance Act provides for the control of substances which may cause injury or ill-health or death of human beings by reason of their toxic, corrosive, irritant, strongly sensitizing or flammable nature, and for the control of certain electronic products; to provide for the division of such substances or products into groups in relation to the degree of danger; to provide for the prohibition and control of the importation, manufacture, sale, use, operation, application, modification, disposal or dumping of such substances and products; and to provide for matters connected therewith. The Act provides for four groups of hazardous substances and makes reference to the South African National Standards (SANS) for the Group I and II hazardous substances.

Substances under Groups I and II are under strict control by this Act. For example, PCBs are Group I hazardous substances and are regulated under SANS10228. This regulation also applies to other Group I and II substances such as DDT, chlordane and heptachlor.

Group I substances are dangerous to humans due to their toxic nature. Group I is divided into categories A and B. Category A substances are listed in a Schedule in Regulations promulgated under the Act [GN R452 of 25 March 1977]. Category B hazardous substances are those substances which are specific in Annexes E and F of the South African National Standard Code 10228:2006 entitled Identification and Classification of Dangerous Goods for Transport (SANS Code 10228)[GN R452 of 25 March 1977]. Annex E contains an alphabetical list of pesticides while Annex F contains a list of generic shipping names.

Group II substances are dangerous to humans due to their toxic nature and with the exception of Class 1 and Class 7 substances of SANS Code 10228, all substances in SANS Code 10228 are Group I hazardous substances [GN R382 of 12 August 1994].

Group III substances concern electronic products and are listed in Regulations promulgated under the Act [GN R1302 of 14 June 1991]. For example, polychlorinated biphenyls (PCBs) would ordinarily be under

Group II but are also found in old electrical transformers which fall under Group III substances. PCBs could to some extent be regulated under Group III hazardous substances when in old electronic products such as old electrical transformers.

Group IV substances are radioactive and are defined in the Act.

3.1.5.5 Health Act 63 of 1977

The Department of Health is the custodian of the Health Act. The Act controls the conditions which may cause adverse effects unless immediately remedied and to which the provisions of the APPA are not applicable. This could be applicable to the production and the use of hazardous chemicals that could pose adverse effects to human health, the latter being more relevant to the provisions of the Rotterdam Convention.

3.1.5.6 National Environmental Management: Biodiversity Act 10 of 2004

The intention of the Biodiversity Act is to protect South Africa’s biodiversity, and that includes fauna and flora. It enables the Minister to identify any activity that may present threat to the environment in an ecosystem that is threatened or in need of protection, as a “threatening process” for which an Environmental Impact Assessment (EIA) is required.

3.1.5.7 National Environmental Management: Waste Management Act 39 of 2007

The provisions of the Waste Act of 2007 promote sharing of responsibility throughout the life cycle of a product and an environmentally sound disposal of wastes.

3.1.5.8 National Water Act 36 of 1998

The Act enables the commanding liability for the pollution of water resources, which could occur if proper measures are not put in place when trading in hazardous chemicals. To promote the protection of the environment, in this case, water being part of the environment, this Act can be used to control chemical substances such as BFRs.

3.1.5.9 Occupational Health and Safety Act 85 of 1993

The Act requires employers to maintain a working environment that is without risk to the health of employee and must ensure that employees’ exposure to hazardous chemicals is prevented or adequately controlled. Trade in hazardous chemical substances may present a hazard to the employees involved in the whole trade chain. The health of such employees can be protected through this Act.

3.1.6 Specific regulations

Table 3.1 shows some specific government regulations and associated chemicals and pesticides.

Table 3.1. Some government regulations addressing the management of chemicals and pesticides

Regulation	Chemicals listed
Department of Agriculture	
Reg. 384 of 25 February 1983	BHC, DDT, Arsenic, Mercury, Dieldrin or Aldrin, HCH (isomers)
Reg. 949 of 30 April 1987	2,4-D(dimethylamine salt), 2,4-D(iso-octyle ester), 2,4-D(sodium salt), MCPA(potassium and dimethylamine salt), MCPB (sodium salt), Dicamba, Picloram, Trichlopyr, 2,4,5-T
Reg. 1061 of May 1987	Chlorobenzilate, Camphechlor, gamma-BHC (Lindane)
Reg. 2370 of 27 September 1991	2, 4-D, MCPA, Dicamba
Department of Health	
Reg. 452 of 25 March 1977	Aldicarb, Arsenic phosphide, Azinphos-ethyl/methyl, Chlordane, Dieldrin, DNOC, Endosulfan, Methyl bromide, Parathion.
Reg. 1705 of 3 November 1995	Carbon tetrachloride

3.1.7 Overall legal framework

South Africa has numerous legislations relevant to the proper environmental management of hazardous chemicals that sit with various departments which have different mandates. Currently, there is no existing legislation specifically on brominated flame retardants in South Africa, although the Department of Environmental Affairs is aware that BFRs, particularly PBBs are listed in Annex III of the Rotterdam Convention as chemicals that need to be severely restricted or banned.

Results from the present study have shown that there are two main Acts that are used in controlling the handling and management of chemicals and pesticides in South Africa, and these are: the Fertilizers, Farm feeds and Agricultural Remedies and Stock Remedies Act No 36 of 1947 and the Hazardous Substances Act No 15 of 1973. Several Government Notices and Regulations (**Table 3.1**) that address Fertilizers, Farm Feeds and Agricultural and Stock Remedies as well as Hazardous Substances stem from these two main Acts. Of particular interest is section 2 (1) (a) of the Hazardous Substances Act, 1973 (Act 15 of 1973) which declares that any substance or mixture of substances which, in the course of customary or responsible handling or use including ingestion, might by reason of its toxic, corrosive, irritant, strongly sensitising or flammable nature or because it generates pressure through decomposition, heat or other means, cause injury, ill-health or death to human beings, to be a Group I or a Group II hazardous substance. Substances under Groups I and II are under strict control by this Act. The aforementioned section 2 (1) (a) of the Hazardous Substances Act, 1973 (Act 15 of 1973) can be seen to serve the purpose of controlling BFRs. Other legislations that may be used to control BFRs include: The National Water Act 36 of 1998 and the Customs and Excise Act 96 of 1964.

3.1.8 Imports and exports

Table 3.2 shows the quantities of PBBs imported and exported in 2007 and 2008 in South Africa. In trying to get data on the amounts of BFRs imported to, and/or exported from South Africa, it was noted from the PIC (Prior Informed Consent) database made available by DEA that no information was available on the chemicals that South Africa has exported to other countries. Furthermore, the information on imported and exported BFRs into and from South Africa from Customs and Exercise reports was not explicit. It is possible that other BFRs are imported into the country, though under license, but are grouped under PBBs. Efforts to get information from private companies on the type of BFRs currently in use failed.

The challenge with these legislative pieces is that they could be prone to different interpretations by different departments and may present challenges when one department has to enforce the legislation on behalf of another due to non-compliance as priorities of departments differ. Effective coordination remains a challenge for South Africa.

Table 3.2. Quantities of polybrominated biphenyls (PBBs) imported and exported in 2007 and 2008.

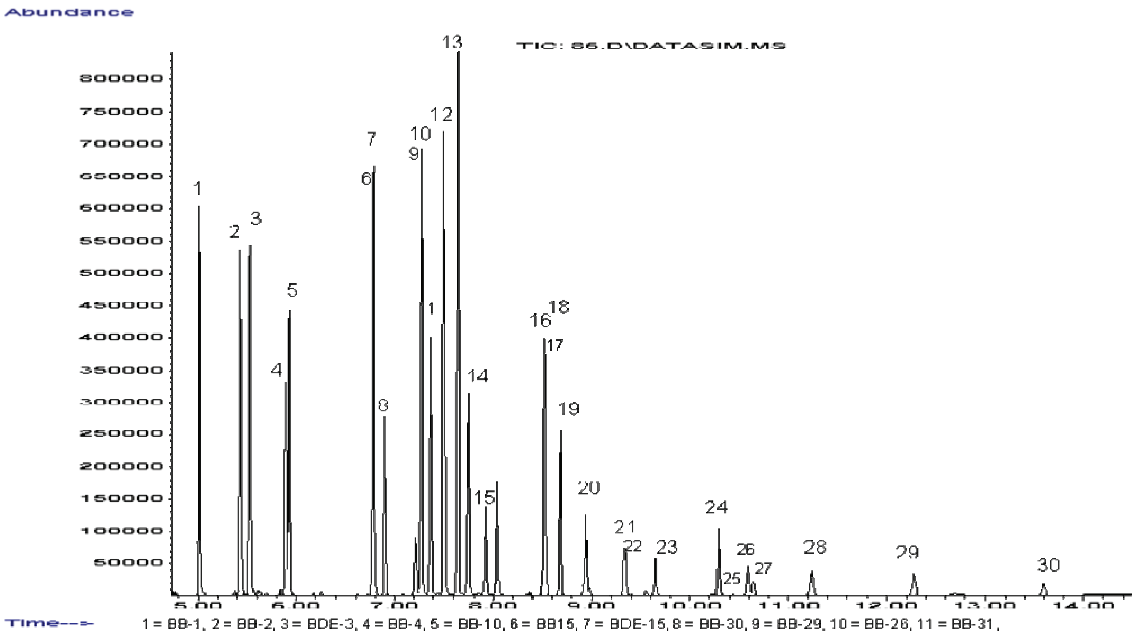
	Imported (kg)		Exported (kg)	
Harmonised code	**2007**	**2008**	**2007**	**2008**
29029000	496 039	191 182	60 963	34 555

Source: Customs and Excise (2009)

3.2 EXPERIMENTAL RESULTS

3.2.1 Chromatogram of standard mixtures

The chromatogram of PBDEs mixture of standard congeners is shown in **Figure 3.1**. As can be seen the peaks are fairly resolved and are similar to those reported by Ackerman et al. (2005). The limit of detection obtained ranged from 2.0-5.0 ng L^{-1} and 1.5-4.5 ng kg^{-1} for liquid and solid samples respectively. Limits of detection of 0.073–1.2 ng kg^{-1} and 2.5–5.0 ng kg^{-1} have been reported by Cramer, (1990); Kruger, (1988) and de Boer, (1999) respectively for different biological samples.



1 = BB-1, 2 = BB-2, 3 = BDE-3, 4 = BB-4, 5 = BB-10, 6 = BB15, 7 = BDE-15, 8 = BB-30, 9 = BB-29, 10 = BB-26, 11 = BB-31, 12= BDE-17, 13= BDE-28, 14 = BB-38, 15 = BB-49, 16 = BDE-47, 17 = BB-80,18 = BB-103, 19 =BDE-66, 20 = BDE-77, 21 = BDE-100, 22 = BB-155, 23 = BDE-99, 24 = BDE-85, 25 =BDE-126, 26 =BDE-154, 27 = BB-153, 28 = BDE-153, 29= BBDE-138, 30 = BDE-183

Figure 3.1. Chromatogram of BFR standards.

3.2.2 Recovery test

The mean percentage recoveries of the congeners, BDE-47 and BDE-99 ranged from 93.0 ± 6.7 to 102.9 ± 7.1. The mean recovery values obtained in the present study are higher than the values 67-88% and 89-94% reported by Meironyté et al. (2003) and Covaci et al. (2002b) respectively for congeners BDE-47,BDE-99 and BDE-100.

3.2.3 Concentrations of BFRs in samples

Identifications were carried out using full scan, by monitoring the presence of the mass spectra of molecular ion and two qualifier ions of the congeners at the elution retention time. Each congener was quantified against five level external standard calibration curves. Representative chromatograms of total ions for sediment, leachate, and groundwater are shown in **Figure 3.2**, **Figure 3.3** and **Figure 3.4** respectively, while the molecular spectra of some PBBs and PBDEs monitored are shown in the appendices A and B.

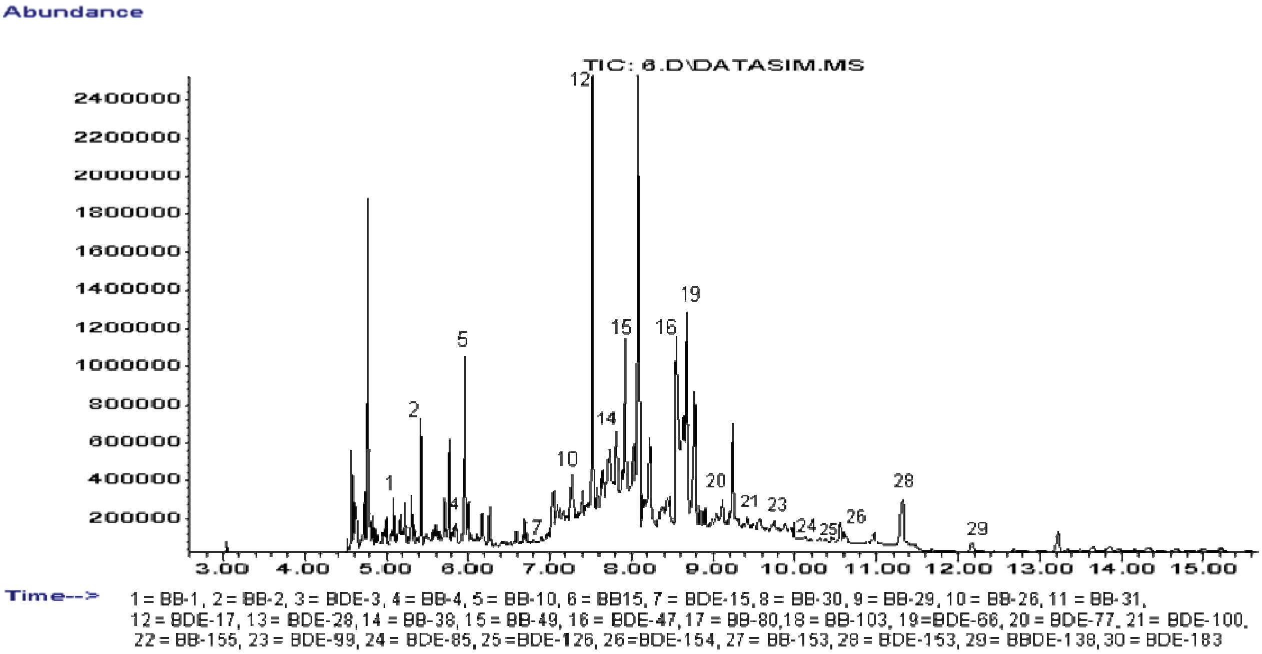


Figure 3.2. Representative chromatogram of BFRs in one sediment sample.

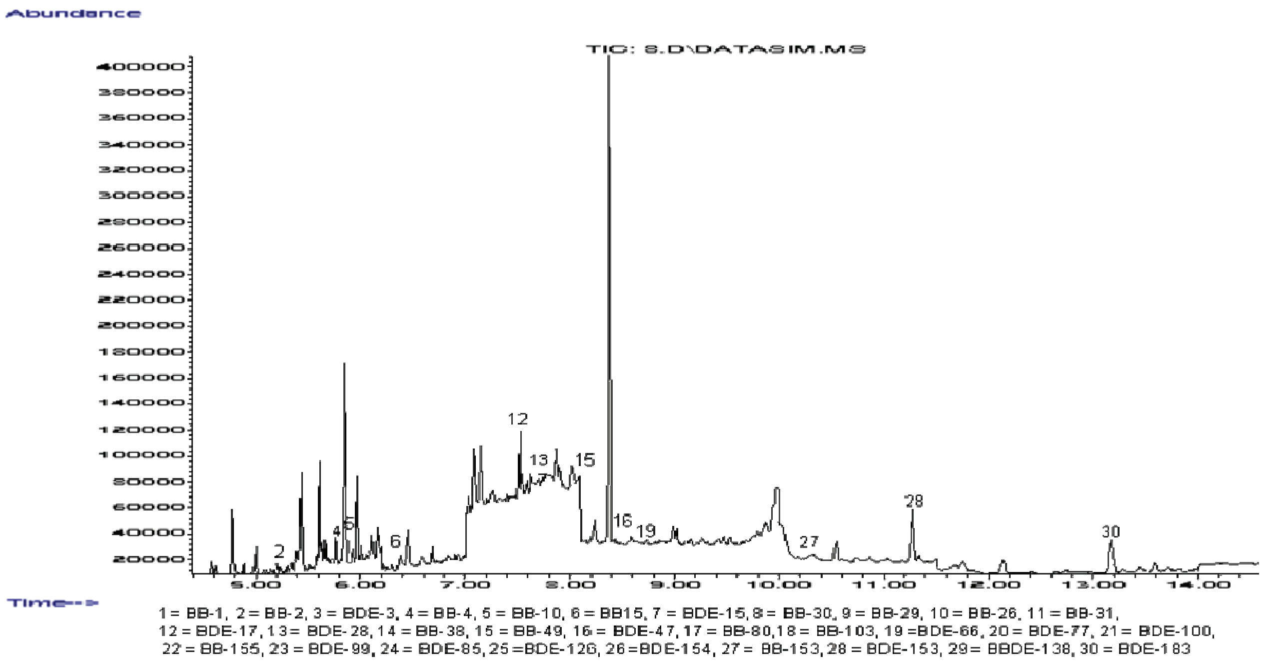


Figure 3.3. Representative chromatogram of BFRs in one leachate sample.

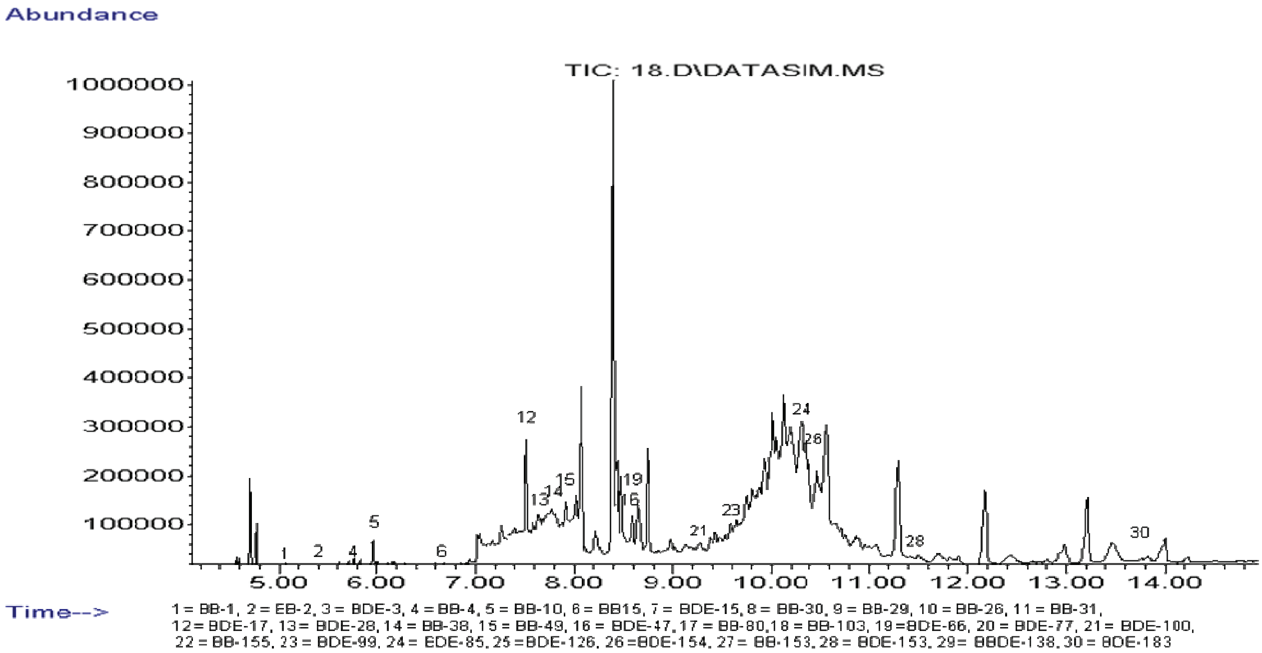


Figure 3.4. Representative chromatogram of BFRs in one groundwater sample.

The mean concentrations (obtained from triplicate measurements) of common PBBs and PBDEs congeners are shown in **Table 3.3**. As can be seen, PBB-31, PBB-80 and PBB-155, were not detected in any of the samples. This was not the case with PBDEs where all the PBDEs were detected in at least one of the samples. The following PBBs and PBDEs were detected in all the samples from the two landfill sites: PBB-4, PBB-10; PBDE-17 and PBDE-47. In addition to the aforementioned BFRs, PBB-49, PBDE-28, PBDE-66, PBDE-77, PBDE-100, PBDE-138, PBDE-153, PBDE-154 and PBDE-183 were detected in the leachate, sediment and groundwater samples as well. The detection of PBB-4, PBB-10, PBDE-17 and PBDE-47 in all the samples indicated that these were the most common BFRs in the samples analysed. One could, therefore, suggest that these congeners can be used as preliminary screening indicators of BFRs contamination in environmental matrices. Also from **Table 3.3**, PBDE-17 exhibited the highest concentrations for sediment and leachate samples from the two sites. For the BRFs detected, the concentrations of PBDEs are significantly higher than those of PBBs. It can also be seen from the table that in general, sediment samples showed higher concentrations of PBBs and PBDEs than leachate samples.

Table 3.3. Concentrations of BFRs (means and standard deviations) in the samples.

BFR	Landfill site					
	Hatherley			Kwaggasrand		
	leachate (µg/L)	sediment (µg/kg)	groundwater (µg/L)	leachate (µg/L)	sediment (µg/kg)	groundwater (µg/L)
PBB-1	nd	1.8±0.01	nd	0.02±0.01	0.02±0.01	nd
PBB-2	1.25±0.01	3.05±0.01	nd	0.02 ± 0.07	0.02 ± 0.07	nd
PBB-4	14.8±0.01	4.78±0.03	0.2±0.02	0.47±0.46	167.0±0.24	2.0±0.6
PBB-10	12.15±0.01	19.26±0.09	1.5±0.2	4.19±0.051	471.4±1.38	2.6±1.4
PBB-15	3.3±0.01	3.01±0.04	nd	0.14±0.19	1.2±0.11	nd
PBB-26	nd	5.0±0.01	nd	nd	0.09±0.01	nd
PBB-29	nd	3.3±0.01	nd	nd	0.09±0.01	nd
PBB-30	nd	2.2±0.01	nd	nd	nd	nd
PBB-31	nd	nd	nd	nd	nd	nd
PBB-38	nd	nd	nd	0.02±0.01	0.10±0.01	nd
PBB-49	6.6±0.01	2.19±0.04	nd	0.45±0.4	46.75±0.06	1.2±0.1
PBB-80	nd	nd	nd	nd	nd	nd
PBB-103	nd	8.42±0.01	nd	nd	9.63±0.07	nd
PBB-153	5.0±0.01	20.5±0.2	0.1±0.01	nd	0.03 ± 0.01	nd
PBB-155	nd	nd	nd	nd	nd	nd
PBDE-3	nd	2.25±0.01	nd	nd	1.44±0.01	nd
PBDE-15	nd	0.48 ± 0.01	nd	nd	1.09±0.01	nd
PBDE-17	89.0±0.14	190.79±0.07	2.5±0.5	11.06±1.82	629.03±1.8	5.3±0.4
PBDE-28	1.37±0.01	11.25±0.01	1.06±0.5	0.05±0.1	nd	3.0±1.2
PBDE-47	2.76±0.08	164.5± 0.23	7.4±1.1	0.64±0.21	92.87±0.29	8.4±2.1
PBDE-66	7.4±0.01	0.72±0.01	nd	1.33±0.08	20.97±1.78	0.60±0.2
PBDE-77	nd	nd	4.06±1.7	nd	0.23±0.01	0.56±0.2
PBDE-85	nd	6.9±0.01	23.26±2.5	0.03±0.01	0.88±0.01	nd
PBDE-99	nd	1.03±0.2	nd	0.1±0.01	3.51±0.07	nd
PBDE-100	nd	nd	nd	0.08±0.01	0.46±0.1	0.1±0.01
PBDE-126	nd	nd	nd	nd	4.55±0.02	0.15±0.3
PBDE-138	nd	1.6 ±0.01	11.81±3.2	nd	0.31±0.01	9.80±2.2
PBDE-153	56.0±0.2	20.5±0.2	nd	0.01±0.14	1.11±0.01	0.56±0.2
PBDE-154	nd	0.2 ± 0.01	18.30±2.1	0.1±0.01	0.9±0.01	4.3±0.5
PBDE-183	30.8±0.3	1.8±0.01	nd	0.02±0.01	0.95±0.01	1.4±4.1
∑BFRs	230.43	475.53	70.19	1454.22	1454.62	38.97

PBBs = polybrominated biphenyls; PBDEs = polybrominated diphenyl ether; nd = not detected

For Hatherley landfill site, leachate, sediment and groundwater accounted for 6.2.0%, 12.8% and 1.9% respectively of the BFRs detected. However, for Kwaggasrand landfill site, 39.0%, 39.1% and 1.0% was accounted for leachate, sediment and groundwater respectively. The highest BFRs concentration, 629.03±0.24 µg kg^{-1}, was recorded for PBDE-17 followed by PBB-10 and PBDE-47 with 471.4±1.38 µg kg^{-1} and 92.87±0.29 µg kg^{-1} respectively for sediment samples from the Kwaggasrand site. Concentrations of 190.79±0.07 µg kg^{-1} and 89.0±0.14 µgL^{-1} were recorded for sediment and leachate samples respectively from Hatherley site. The highest concentration recorded for leachate sample, 89.0±0.1 µg L^{-1} in the present study is significantly higher than nd–0.004 µg L^{-1}, 0.029 µg L^{-1} and 0.0098 µg L^{-1} reported in landfill leachates from Japan, USA and South Africa by Osako et al. (2004), Oliaei et al. (2002) and Odusanya et al. (2009) respectively. PBDE-138 exhibited the highest concentration of 9.8±2.2 µg L^{-1} in groundwater. This was followed by PBDE-47 and PBDE-17 with concentrations of 8.4±2.1 μg L^{-1} and 5.3±0.4 μg L^{-1} respectively. The concern, however, is that PBDEs are persistent new emerging chemicals, with relatively scarce information on their movement in the environment.

3.2.4 Possible source of PBDEs found in the groundwater

The correlation coefficient is used as a measure of the correlation between two variables. This tool has been employed to examine the relationship (with respect to possible sources) between trace metals and soil and vegetation (Harrison et al., 1981; Okonkwo et al., 2009). This tool was employed in the present study to attempt to evaluate the existence of PBDE in groundwater and landfill leachates from the selected sites. A significant correlation between the most common PBDEs in groundwater and landfill leachate for the sites was observed: Hatherley (r: 0.84-0.94) and Kwaggasrand (r: 0.79-0.97).

This suggests that the groundwater may be contaminated by the landfill sites in the vicinity.

CHAPTER 4: CONCLUSIONS & RECOMMENDATIONS

Currently in South Africa, there is no legislation specifically for regulating the handling of BFRs. However, the Hazardous Substance Act appears to cover hazardous substances such as BFRs in the absence of any specific law on these emerging environmental contaminants. Other legislations that may be used to regulate BFRs include: The National Water Act 36 of 1998 and the Customs and Excise Act 91 of 1964. There is a need for specific incorporation of the Rotterdam Convention into the South African legislative framework for effective compliance and monitoring to occur.

The present study has shown the presence of BFRs in landfill leachates, sediments and groundwater collected from two landfill sites. However, the concentrations obtained in the present study are significantly higher (more than three orders of magnitude) than some values reported in the literature. Correlations between PBDEs in leachate and groundwater samples suggested that the groundwater contamination was as a result of the landfill.

The Stockholm Convention affirms the need to effectively control persistent and bioaccumulating chemicals. Establishing concentrations of contamination in environmental matrices such as landfill sites, as has been demonstrated in the present study, is an important way of verifying the environmental behaviour of chemicals approved for use. In order to estimate the extent to which the burden from various sources contribute to the total amount of BFRs released into the South African environment, investigations on surface water, groundwater, sewage sludge and biota at regional and national levels needs to be conducted. Pertinent questions such as the following need to be answered:

1. What happens to flame retarded plastics in South Africa?
2. What happens to polyurethane foams?
3. Are polyurethane foams in mattresses, furniture and others treated with brominated flame retardants?
4. What happens to car shredder material (plastic and seat material)?

It is with hope that the identified gaps will pave the way for legislation to include BFRs in the list of hazardous compounds that need to be controlled in South Africa.

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APPENDIX A: MONITORED MASS SPECTRA FOR PBBS

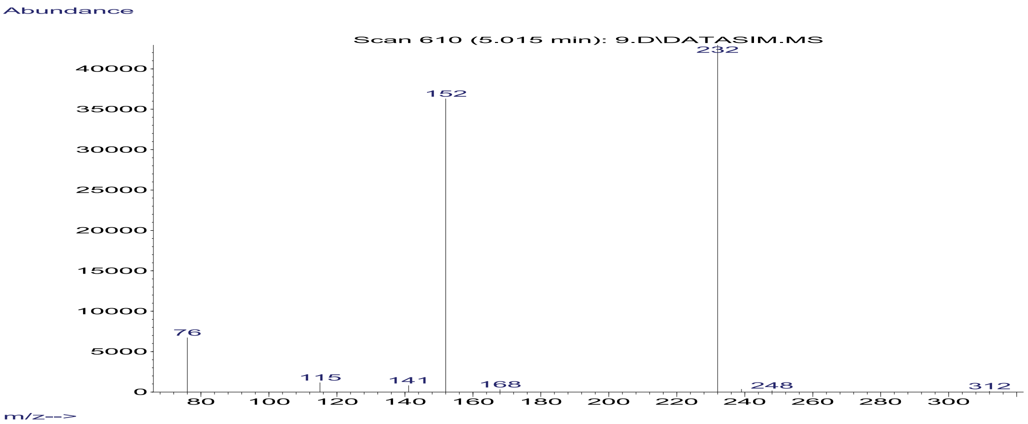

Figure A.1. Monitored mass spectra for PBB-1 and PBB-2.

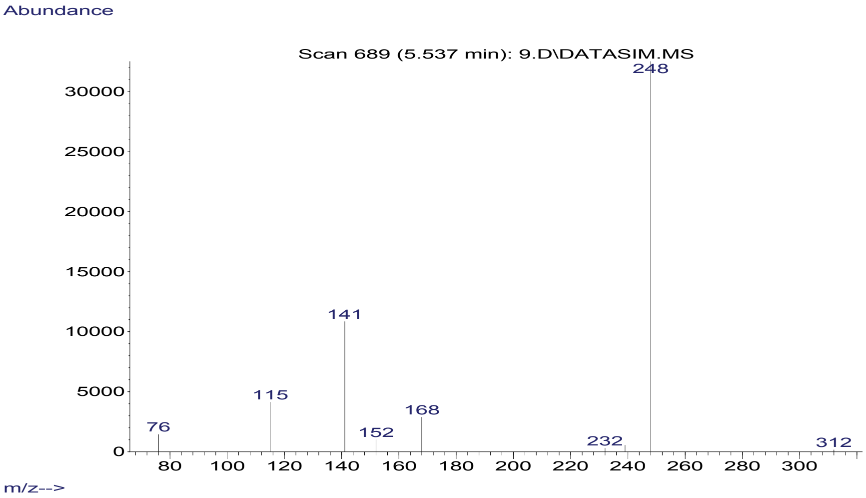

Figure A.2. Monitored mass spectra for BDE-3

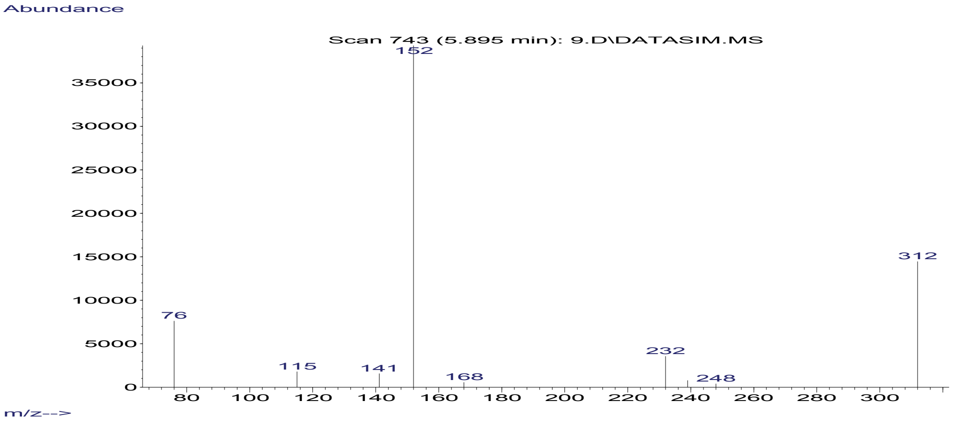

Figure A.3. Monitored mass spectra for PBB-4

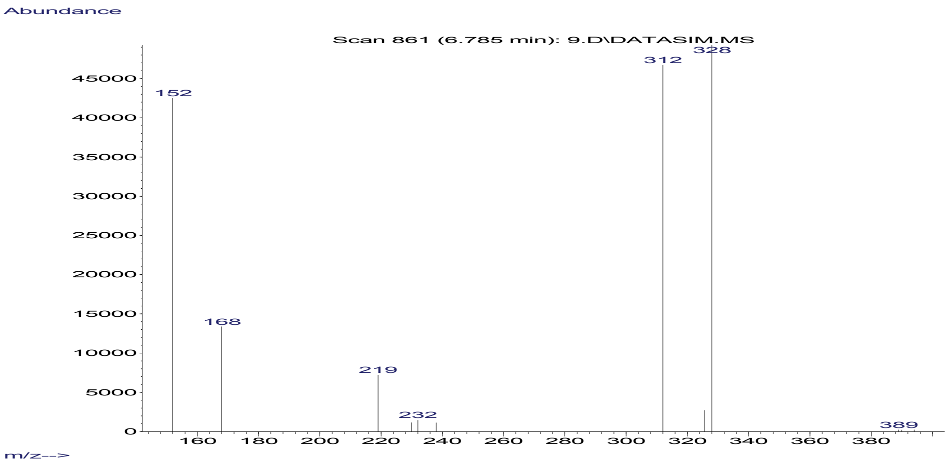

Figure A.4. Monitored mass spectra for PBB-15

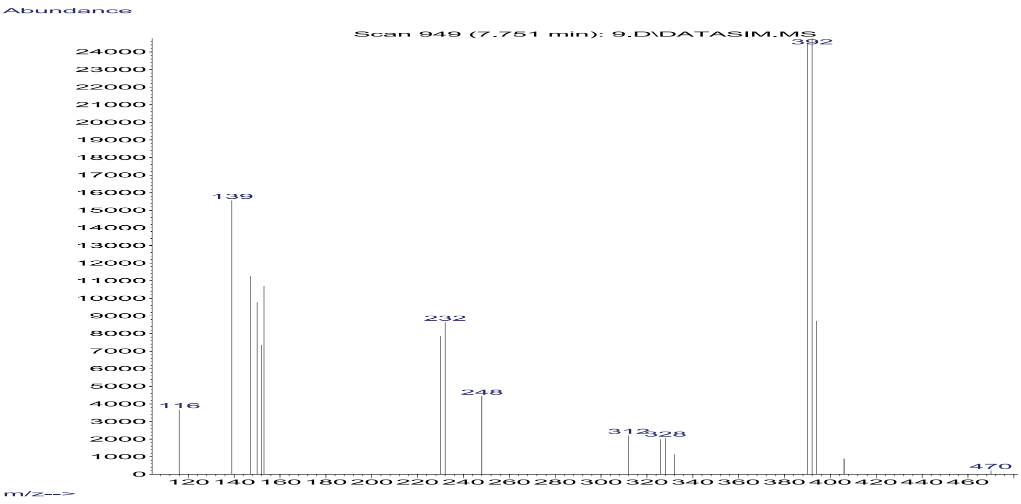

Figure A.5. Monitored mass spectral for PBB-38

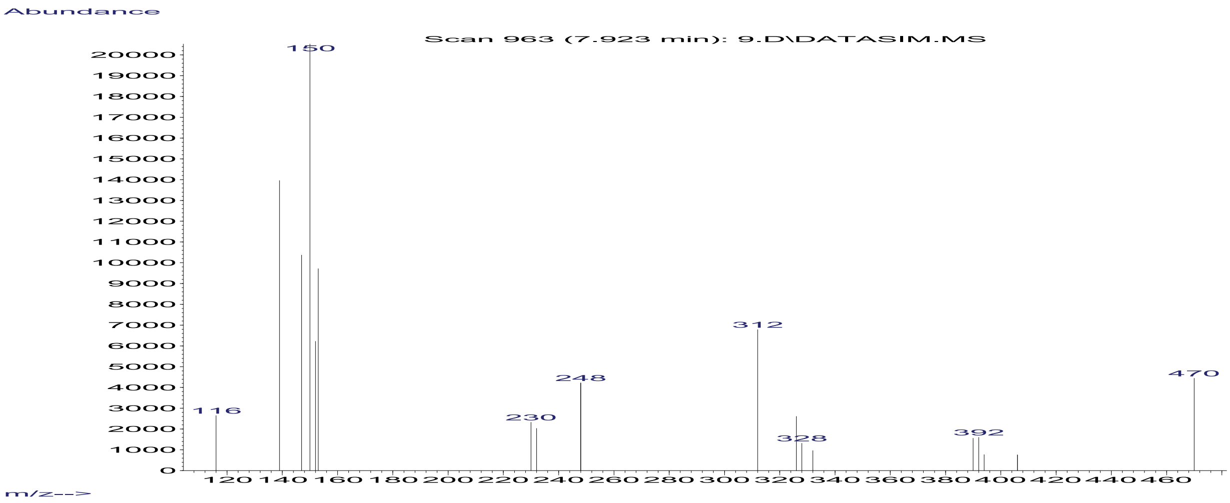

Figure A.6. Monitored mass spectral for PBB-49

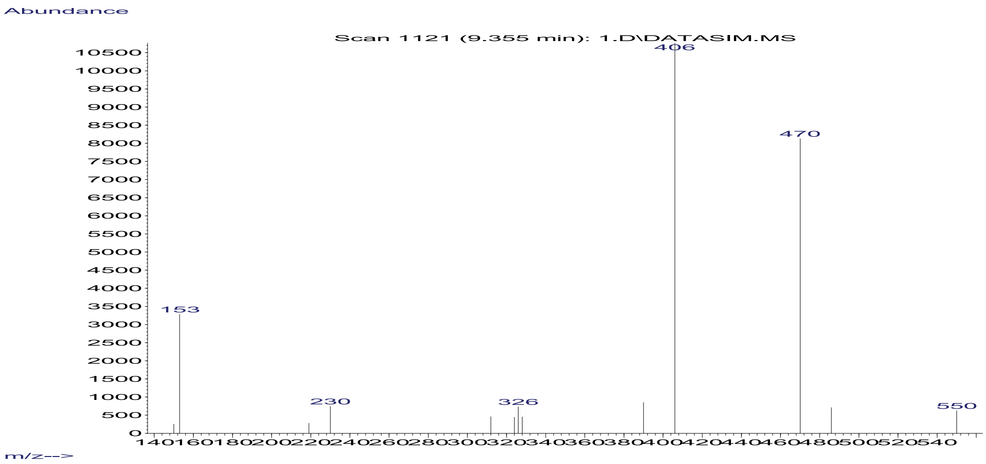

Figure A.7. Monitored mass spectra for PBB-153

APPENDIX B: MONITORED MASS SPECTRA FOR PBDES

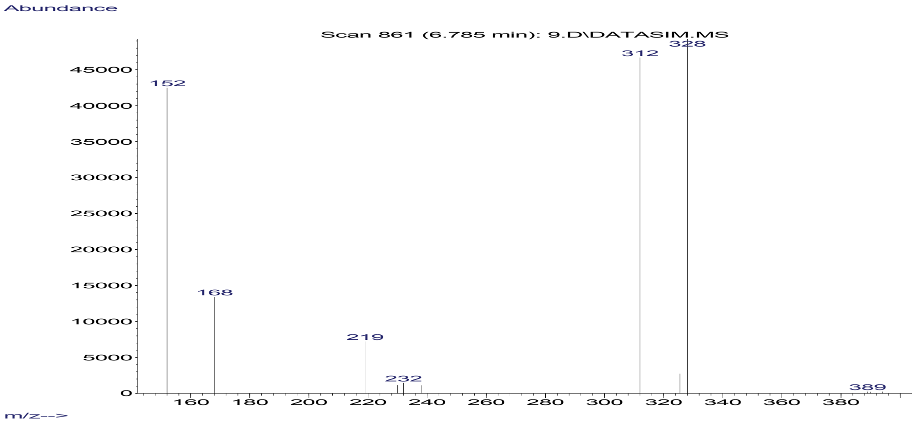

Figure B.1. Monitored mass spectra for BDE-15

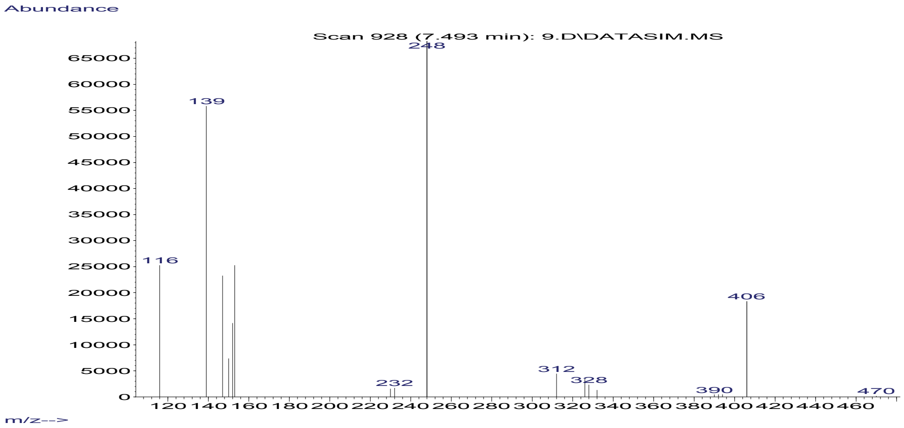

Figure B.2. Monitored mass spectra for BDE-17

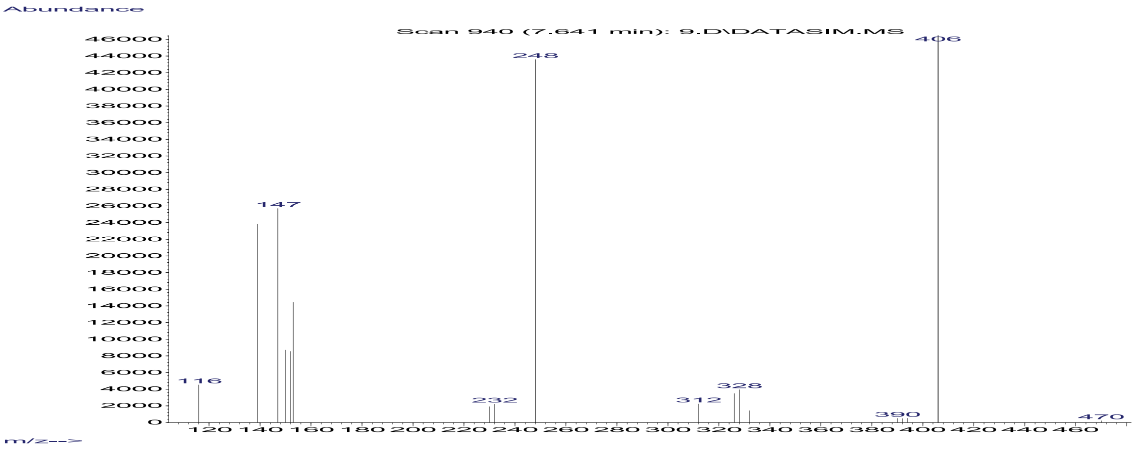

Figure B.3. Monitored mass spectra for BDE-28

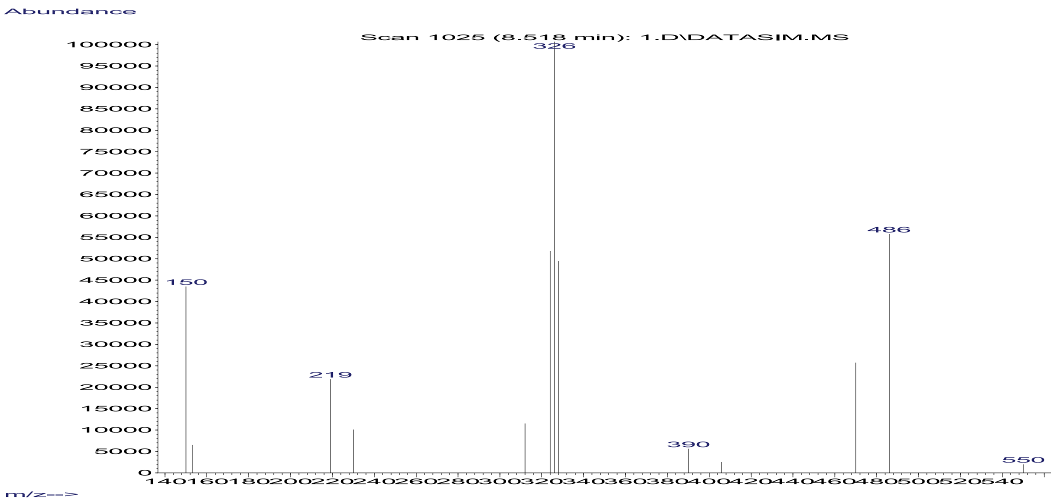

Figure B.4. Monitored mass spectra for BDE-47

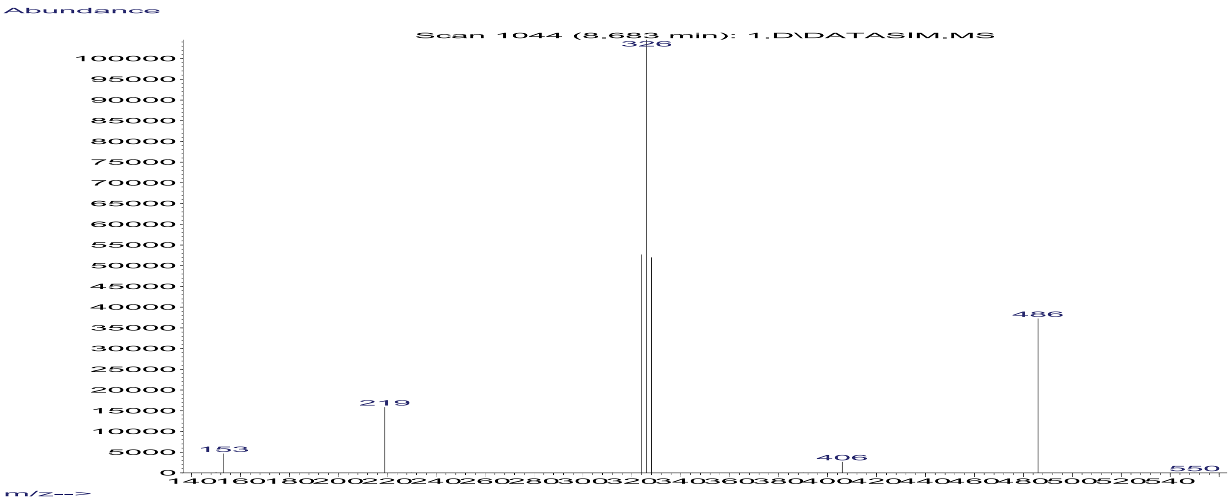

Figure B.5. Monitored mass spectra for BDE-66

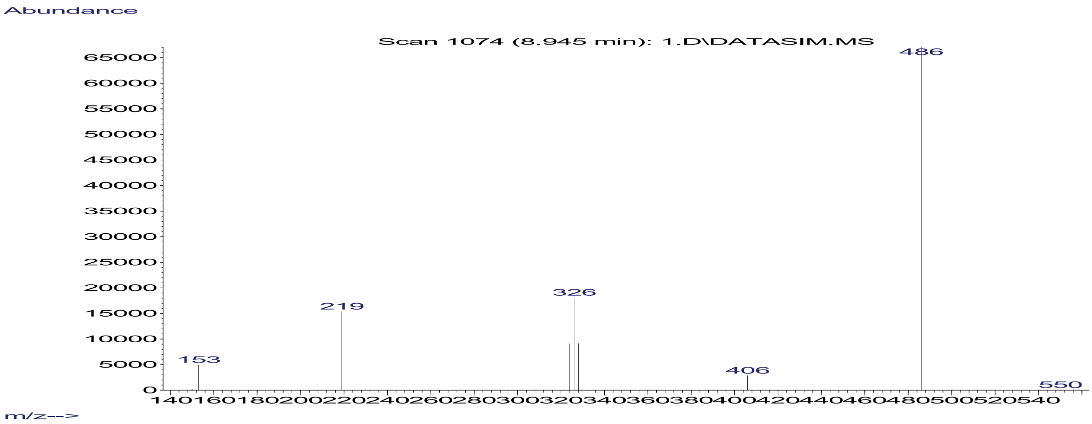

Figure B.6. Monitored mass spectra for BDE-77

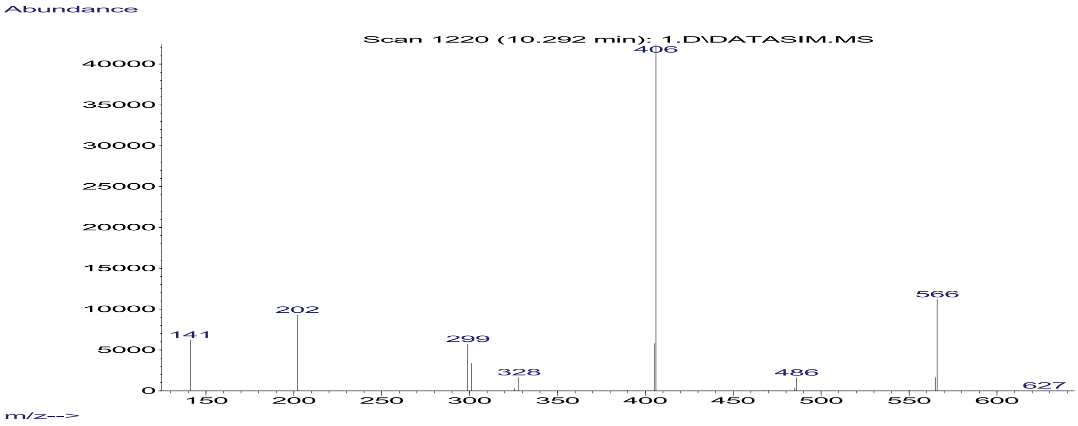

Figure B.7. Monitored mass spectra for BDE-85

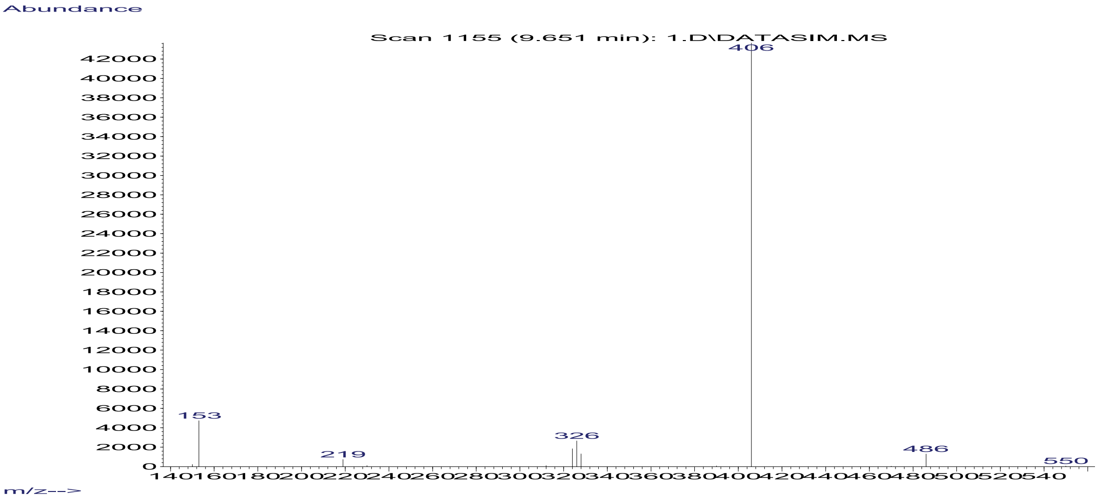

Figure B.8. Monitored mass spectra for BDE-99

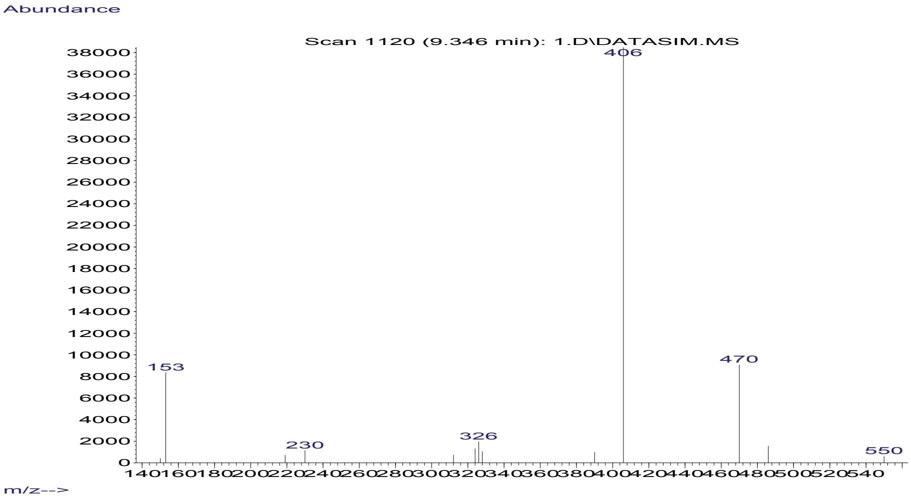

Figure B.9. Monitored mass spectra for BDE-100

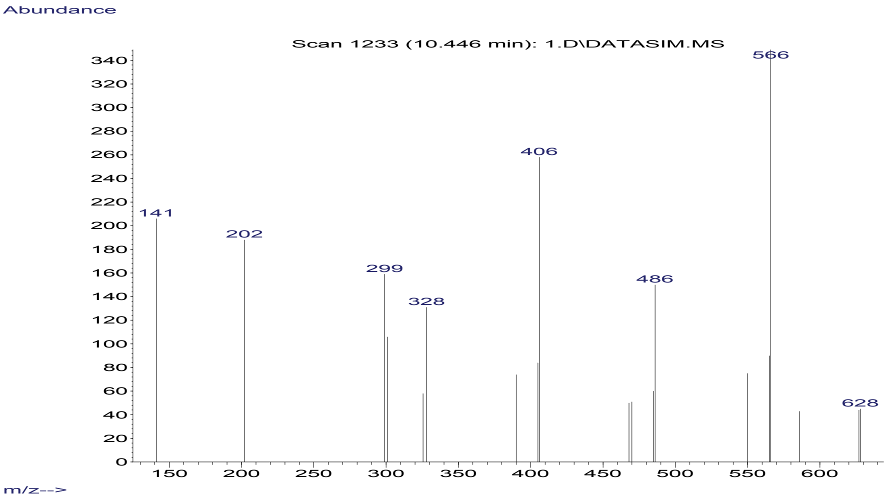

Figure B.10. Monitored mass spectra for BDE-126

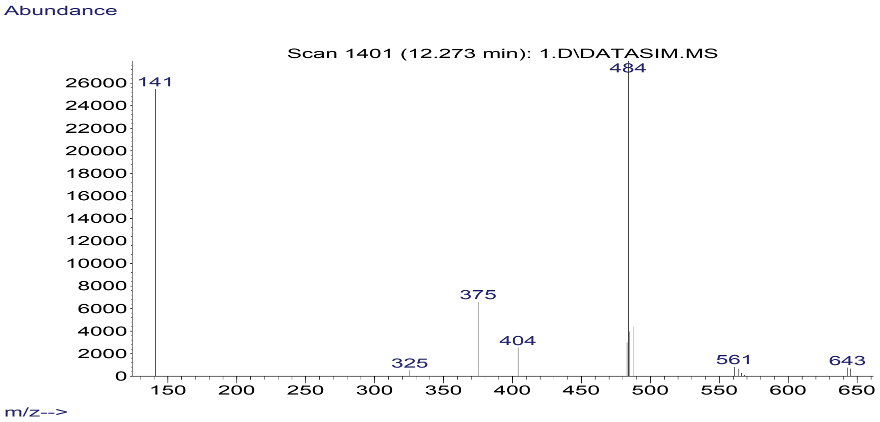

Figure B.11. Monitored mass spectra for BDE-138

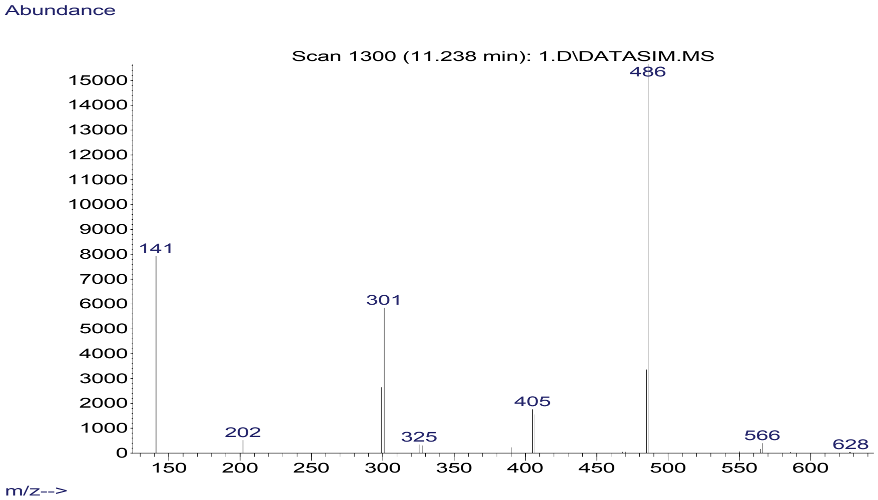

Figure B.12. Monitored mass spectra for BDE-153

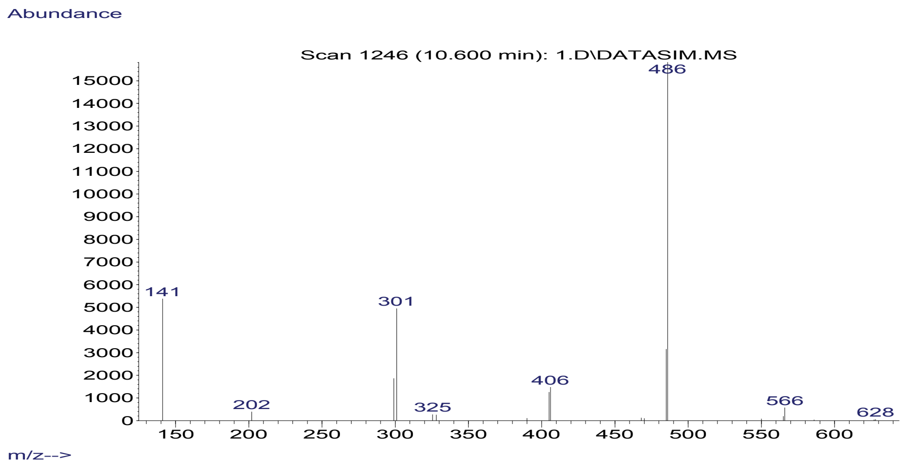

Figure B.13. Monitored mass spectra for BDE-154