UNIVERSITY OF BIRMINGHAM

EMISSIONS TO THE ENVIRONMENT OF BROMINATED AND ORGANOPHOSPHATE FLAME RETARDANTS IN THE WASTE STREAMS

by

Salim Ali Sakaroun

MSc, BSc

A thesis submitted to the University of Birmingham for the degree of

Doctor of Philosophy (PhD)

Division of Environmental Health and Risk Management
School of Geography, Environment, and Earth Sciences
College of Life and Environmental Sciences
University of Birmingham
United Kingdom

January 2017

Table of Contents

Table of Contents		i
List of Tables		v
List of Figures		vii
Acknowledgements		ix
Dedication		xi
Abstract		xii
Abbreviations		xiv
Symbols and Units		xviii

Chapter I: General Introduction

1.1.	Background	1
1.2.	Environmental Pollution	3
1.2.1.	Persistent Organic Pollutants (POPs)	5
1.2.2.	Stockholm Convention	6
1.3.	Role of Flame Retardants in Fire	7
1.4.	Flame Retardants Chemicals	12
1.4.1.	Brominated Flame Retardants (BFRs)	14
1.4.1.1.	Polybrominated diphenyl ethers (PBDEs)	15
1.4.1.2.	Production and Uses of PBDEs	18
1.4.2.	Novel Brominated Flame Retardants (NBFRs)	20
1.4.2.1.	Production and uses of NBFRs	21
1.4.3.	Organophosphate Flame Retardants (PFRs)	23
1.4.3.1.	Tris(1-chloro-2-propyl) phosphate (TCIPP)	25
1.4.3.2.	Triphenyl phosphate (TPhP)	25
1.4.3.3.	Production volumes of PFRs	26
1.4.4.	PFRs versus BFRs	27
1.5.	Physicochemical properties of FRs	29
1.6.	Review of FRs in Waste Stream	34
1.7.	Environmental and Health Impacts of FRs	38
1.7.1.	Transfer Processes of FRs from their Products in Waste Stream	40
1.7.2.	Environmental Source, Occurrence and Effects	42
1.7.3.	Exposure Pathways	46
1.7.3.1.	Occupational Exposure	49
1.7.4.	Health Effects	50

1.8. Analytical Method for Determining FRs in Environmental Samples 53
1.9. Aims and Objectives of this Study 54

Chapter II: Sampling and Analytical Methodology
2.1. Synopsis 56
2.3. Chemicals, Reagents and Materials 56
2.2. Sampling 58
2.3.1. Waste Polyurethane Foam (PUF) Samples 59
2.3.2. Passive Air Samplers (PAS) 59
2.3.2.1. Passive Sampling Uptake Profile and Equilibrium Sampling Device (ESD) 62
2.3.4. Region of Field Sampling 63
2.3.4.1. Soil Samples 66
2.3.4.2. Air Samples 67
2.4. Passive Sampling Rate (*R*) 68
2.4.3. Field Sampling Strategy 70
2.4.3.1. Soil Sampling 71
2.4.3.2. Air Sampling 71
2.5. Leaching Experimental 72
2.5.1. Preparation of Samples and Leaching Fluids 74
2.5.2. Leaching Experimental Design 74
2.5.3. Calculation of the Leaching Percentage of FRs 74
2.6. Extraction 75
2.6.1. Accelerated solvent extractions (ASE) 76
2.6.2. Soil and Air Samples Extraction 77
2.6.3. Leaching Samples Extraction 77
2.7. Purification (Clean-up) 78
2.7.1. Clean-up of Air and Soil Samples 80
2.7.2. Clean-up of Leaching Samples 81
2.7.3. Relative Recoveries of Calibration (CS) and Internal Standards (IS) 81
2.8. Quality Assurance and Quality Control (QA/QC) 83
2.8.1. Identification and Quantification Criteria 85
2.8.2. GC/MS Instrument Calibration 86
2.8.3. Field and method blanks for air samples 87
2.8.4. Limits of detection (LOD) and limits of quantification (LOQ) 90

2.8.5.	Accuracy and Precision	90
2.9.	Detection	93
2.9.1.	Gas Chromatography/ Mass Spectrometry (GC/MS) Instrument	93
2.10.	Analytical	93
2.10.1.	Quantitative and Qualitative of GC/MS Data	
2.10.2.	Statistical Analysis	

Chapter III: PBDEs concentrations in Air and Soil Surrounded Oman Landfills and Implications of Occupational Exposure

3.1.	Synopsis	94
3.2.	Concentrations of PBDEs in the Air of Oman	94
3.2.1	Statistical Analysis of PBDE Concatenations in the Air	97
3.2.2.	Comparison with worldwide PBDE concentrations in the Air	98
3.2.3.	Congener profile of PBDEs in Air	100
3.3.	Meteorology Role in the Sampling Areas	103
3.3.1.	Concentrations of PBDEs in the Soil from landfill sites in Oman	107
3.3.2.	Comparison of concentrations of PBDEs in soil from the vicinity of Omani landfills with other studies worldwide	111
3.4.	PBDE congener profile in soil	114
3.5.	Potential Occupational Exposures at Omani Landfills	116
3.5.1.	Daily exposure dose to PBDEs via air and soil	116

Chapter VI: NBFRs concentrations in Air and Soil Surrounded Oman Landfills and Implications of Occupational Exposure

4.1.	Synopsis	119
4.2.	Concentrations of NBFRs in the Air of Oman	119
4.2.1.	Profile of NBFRs homologues in the Air	124
4.2.2	Statistical Analysis of NBFR Concatenations in the Air	127
4.2.3.	Comparison with worldwide NBFR concentrations in the Air	128
4.3.	Periodical variability of NBFRs concentrations in the Air samples	130
4.3.1.	Meteorology Role in the Sampling Areas	130
4.4.	Concentrations of NBFRs in the Soil from landfill sites in Oman	133
4.4.1.	Comparison with worldwide NBFRs concentrations in the Soil	135
4.5.	Potential Occupational Exposures at Omani Landfills	
4.5.1.	Daily exposure dose to NBFRs via air and soil	137

137
Chapter V: Leaching of Flame Retardants from Waste PUF under Laboratory Conditions
5.1. Synopsis 143
5.2. Leaching experimental procedures 143
5.3. Initial FR concentrations in the PUF samples 144
5.3.1. Concentrations of BFRs and TPhP in the USA PUF samples 144
5.3.2. Preliminary TCIPP concentrations in the UK PUF sample 145
5.4. Results and discussion of the leaching experiments 146
5.4.1. Time contact and temperature effects 148
5.4.1.1. Time contact and temperature effects in PBDEs 150
5.4.1.2. Time contact effect in NBFRs 154
5.4.1.3. Time contact effect in PFRs 155
5.4.2. Agitation effect 157
5.4.3. DHM effects 159
5.4.4. Acidic and alkaline (pH 5.8 and 8.5) effects 161
5.4.5. Waste mass to leachate ratio 164
5.5. Leaching activities 165
5.6. Epilogue 166

Chapter IV: Summary, Conclusion and Recommendations
6.1. Summary 168
6.2. Conclusion and Recommendations 170
6.3. Research gaps and future work 170

References 172

Appendices 25
Appendix A 216
Appendix B 221
Appendix C 224

List of Tables

Chapter I: General Introduction

Table 1.1. Table 1.1: Types of FRs in this study 14
Table 1.2. Chemical congeners and basic details of prominent PBDEs of this study 16
Table 1.3. The general compositions of PBDE-based flame retardants given in percent (%) of BDE congeners present 17
Table 1.4. Global market demand for PBDEs technical mixtures between 1999 and 2003 with continental data of 2001 (metric tons; *t*) 17
Table 1.5. Examples of major PBDE applications 20
Table 1.6 The production of some NBFRs in the world[a] 22
Table 1.7. Chemical synonyms, Applications, uses and CAS number of NBFRs 23
Table 1.8. Production/usage volumes (*t*/year) of the studied PFRs 28
Table 1.9. Physicochemical properties affecting environmental behaviour of FRs 30
Table 1.10. Physicochemical properties of FRs in this study 33

Chapter II: Sampling and Analytical Methodology

Table 2.1. Specification of PAS contents that used in this study 60
Table 2.2. Universal Transverse Mercator (UTM) Co-ordinates of landfill sites, Oman 64
Table 2.3. Passive sampling rates (R) (m3 day-1) of the BFRs used in this study 71
Table 2.4. Conditions of ASE 350 for extraction and cleansing 75
Table 2.5. Average of TCIPP and d15-TPhP (IS) recoveries (%) in clean-up QA/QC trial experiment performed in duplicate (Stubbings, 2015) 79
Table 2.6. Average relative recoveries (SD) of the calibration and internal standards (CS and IS) for BFRs (n= 6) and PFRs (n= 3) in this study 80
Table 2.7. Concentrations of CS, IS and RDS of BFR and PFR compounds (pg µL-1) 84
Table 2.8. Instrument and sample detection limits (LOD and LOQ) in this study 88
Table 2. 9. Mean values and standard deviations (SD) (ng g-1 dust) of BFRs measured in NIST SRM 2585 (n= 5) 89
Table 2.10. Mean values and standard deviations (SD) (ng g-1 dust) of PFRs measured in NIST SRM 2585 in other studies 89
Table 2.11. Parameters for the GC/ECNI-MS and GC/EI-MS methods (Al-Omran and Harrad, 2015) 92

Chapter III: PBDEs concentrations in Air and Soil Surrounded Oman Landfills and Implications of Occupational Exposure

Table 3.1. Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target PBDEs in air from locations in the vicinity of Am and Ra landfills and the reference site in Oman 96

Table 3.2. Summary of Mean concentrations (pg m^{-3}) of BDE-209 and ΣPBDEs in the outdoor air around the world 102

Table 3.3. Summary of range and mean concentrations (pg m^{-3}) of ΣPBDEs in the ambient air in some vicinity of waste treatment facilities around the world 103

Table 3.4. Temporal variations in average ΣPBDEs concentrations (pg m^{-3}) and ambient air temperature at Am and Ra landfills (DGM, 2016) 104

Table 3.5. Summary of the descriptive statistics of PBDE concentrations in soil samples for a) the vicinity landfills (ng g^{-1} dw) and b) non-landfilled areas (pg g^{-1} dw), BDE-209 and ΣPBDEs concentrations (ng g^{-1} dw) in non-landfilled sites of Oman 109

Table 3.6. Summary of Mean concentrations (ng g^{-1} dw) of BDE-209 and ΣPBDEs in the soils around the world 115

Table 3.7. Estimated exposure of adults to PBDEs via Air inhalation and Soil ingestion (ng/kg bw/d) 118

Chapter VI: NBFRs concentrations in Air and Soil Surrounded Oman Landfills and Implications of Occupational Exposure

Table 4.1. Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target NBFRs in air from locations in the vicinity of Am and Ra landfills and the reference site in Oman 123

Table 4.2. Summary of Mean and/or range concentrations (pg m^{-3}) of NBFRs in air compartments from different regions worldwide 129

Table 4.3. Temporal variations in average ΣNBFR concentrations (pg m^{-3}) and ambient air temperature at Am and Ra landfills (DGM, 2016) 131

Table 4.4. Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target NBFRs in soil from locations in the vicinity of the landfills in Oman 134

Table 4.5. Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target NBFRs in soil from locations in the non-landfilled areas in Oman 134

Table 4.6. Some average and/or range concentrations of NBFRs in soil compartments from different regions worldwide 135

Table 4.7. Estimated exposure of adults to PBDEs via Air inhalation and Soil ingestion (ng/kg bw/d) 139

Chapter V: Leaching of Flame Retardants from Waste PUF under Laboratory Conditions

Table 5.1. Mean concentrations of FRs in USA PUF and TCIPP in UK PUF samples (n= 9; 3 for each PUF sample) in this study 145
Table 5.2. Congener composition (%) of PentaBDEs in PUF samples and commercial PentaBDE mixtures 145
Table 5.3. Concentrations of PBDEs and TCIPP in leachate of experimental studies 146
Table 5.4. Percentage (%) of each individual FRs in the leachate samples to its total concentration for the 5 contact times under different contact times and temperatures in the presence of agitation 149
Table 5.5. The comparison of FR concentrations in leachate samples in the agitated experiment at 60C with FR concentrations in the experiments at 60C without agitation 158
Table 5.6. FR concentrations (µg L^{-1}) in leachate using different DHM levels 160
Table 5.7. FR concentrations (µg L^{-1}) in leachate using different pH levels 161
Table 5.8. Comparison of a) the relationship of PL% for individual FRs for different contact times at 60°C at the standard waste: leachate ratio used in all experiments with contact times of 6, 24, 48, 72, and 96 h at 20°C, 60°C, and 80°C, using DDW (ph 6.5 and 0 mg L-1 DHM) with agitation, and b) the same previous experiments but with a waste: leachate ration that was 10% of standard ratio 163
Table 5.9. Average waste: leachate ratio (%) of the leaching experimental results of average FR concentrations under the contact time and 60ºC temperature effects 164

List of Figures

Chapter I: General Introduction

Figure 1.1. The global environmental system 4

Figure 1.2. Total fire fatalities in England 1981-82 to 2014-15 (UK National Statistics, 2015) 8

Figure 1.3. Total fires in US during years 1977 - 2014 (NFPA, 2015) 9

Figure 1.4. The stages of enclosure fire development with/without the presence of FRs compounds within burning materials (adapted from Cheng and Hadjisophocleous, 2011; de Jourdan, 2012) 10

Figure 1.5. Mechanism of action of BFRs in gaseous phase of flashover fire in a BFR-product (adapted from Abdallah, 2010) 12

Figure 1.6. Generic structure of PBDEs mixture (m and n= 1 to 5) 16

Figure 1.7. Annual global production of bromine between 1960 and 2005 (US GS, 2007) The chemical structures of the selected NFBRs 19

Figure 1.8. The chemical structures of the selected NFBRs 21

Figure 1.9. The chemical structures of the selected PFRs 24

Figure 1.10. A conceptual model of FRs contaminants release and movement within environment 34

Figure 1.11. Image of a mistake of E-waste disposed of in the landfill sites, Oman 35

Figure 1.12. Increasing in ΣPBDE concentrations in human blood, milk and tissue (*ng* g^{-1} lipid) in North America, Europe and Japan since 1970s (Hites, 2004) 40

Chapter II: Sampling and Analytical Methodology

Figure 2.1. PAS Configuration Deployed 61

Figure 2.2. Generalized uptake profile for a PAS (Mayer *et al*., 2003) 63

Figure 2.3. Sampling site locations in Oman 65

Figure 2.4. The aerial image of the Am landfill, Muscat with wind rose during the period of sampling campaign 66

Figure 2.5. The aerial image of the Ra landfill, Salalah with wind rose during the period of sampling campaign 67

Figure 2.6. Steps of clean-up procedure 78

Figure 2.7. Typical calibration curve of all native FRs compounds in this study 85

Figure 2.8. PTV method for FRs analysis 91

Figure 2.9. GC temperature programme 91

Chapter III: PBDEs concentrations in Air and Soil Surrounded Oman Landfills and Implications of Occupational Exposure

Figure 3.1. Concentration of ΣPBDEs in air Samples downwind (Dw) and upwind (Uw) sites of Am and Ra landfills and the reference sites (RS) in Oman 97

Figure 3.2. Box plot of the concentration of PBDEs in air Samples of Am landfill 99

Figure 3.3. Box plot of the concentration of PBDEs in air Samples of Ra landfill 100

Figure 3.4. Profiles of PBDE homologues (percentages, %) in Am and Ra landfills 101

Figure 3.5. Profiles of PBDE homologues in reference sites 102

Figure 3.6. Concentration of PBDEs in air samples of the reference sites 104

Figure 3.7. Average concentrations of ΣPBDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Am landfill compared with mean ambient temperature (°C) (red line) of Al- Amerat area 105

Figure 3.8. Average concentrations of ΣPBDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Ra landfill compared with mean ambient temperature (°C) (red line) of Raysut area 106

Figure 3.9. Average concentrations of Σtri-hexa BDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Am landfill compared with mean ambient temperature (°C) (red line) of Al- Amerat area 106

Figure 3.10. Average concentrations of Σtri-hexa BDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Ra landfill compared with mean ambient temperature (°C) (red line) of Raysut area 107

Figure 3.11. Box plot of the concentrations of PBDEs in soil samples from Am landfill 110

Figure 3.12. Box plot of the concentrations of PBDEs in soil samples from Ra landfill 110

Figure3.13. Dot plots of PBDE concentrations (ng g^{-1} dw) in soil samples (n=3) from Ni, So, Ib, and Bu landfills; sample 1 (blue circle), sample 2 (orange square) and sample 3 (green triangle) – note the log scale 112

Figure3.14. Dot plots of PBDE concentrations (ng g^{-1} dw) in soil samples (n=3) from Ni, So, Ib, and Bu reference sites; sample 1 (blue circle), sample 2 (orange square) and sample 3 (green triangle) – note the log scale 113

Figure 3.15. Profiles of tri-heptaBDE homologues in soil samples from Omani landfills 114

Figure 3.16. Profiles of tri-heptaBDE homologues in soil samples from Omani non-landfill reference locations 114

Chapter VI: NBFRs concentrations in Air and Soil Surrounded Oman Landfills and Implications of Occupational Exposure

Figure 4.1. Concentration of ΣNBFRs in air Samples downwind (Dw) and upwind (Uw) sites of Am and Ra landfills and the reference sites (RS) in Oman 124
Figure 4.2. Box plot of the concentration of NBFRs in air Samples of Am landfill 124
Figure 4.3. Box plot of the concentration of NBFRs in air Samples of Ra landfill 125
Figure 4.4. Profiles of NBFR homologues (percentages, %) in Am and Ra landfills 126
Figure 4.5. Profiles of NBFR homologues in reference sites 126
Figure 4.6. Concentration of NBFRs in air samples of the reference sites 132
Figure 4.7. Average concentrations of ΣNBFRs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Am landfill compared with mean ambient temperature (°C) (red line) of Al- Amerat area 132
Figure 4.8. Average concentrations of ΣNBFRs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Ra landfill compared with mean ambient temperature (°C) (red line) of Raysut area 133
Figure 4.9. Box plot of the concentrations of NBFRs in soil samples from Am landfill 136
Figure 4.10. Box plot of the concentrations of NBFRs in soil samples from Ra landfill 136

Chapter V: Leaching of Flame Retardants from Waste PUF under Laboratory Conditions

Figure 5.1. Average concentrations of PBDEs in the leachate samples under the time contact and temperature effects in the presence of agitation 152
Figure 5.2. Percentage (%) o PBDE congeners in the leachate samples under the contact time and temperature effects 153
Figure 5.3. Average concentrations of EH-TBB and BEH-TEBP in leachate samples under the contact time and temperature effects 154
Figure 5.4. Concentration percentage (%) of TCIPP and TPhP in the leachate samples under the contact time, temperature and agitation effects 157
Figure 5.5. FR compounds percentage (%) in leachate samples under the DHM (100 mg L^{-1}) DHM (1000 mg L^{-1}) effect 160
Figure 5.6. FR compounds percentage (%) in leachate samples under an acidic leachate samples (pH 5.8) and alkaline leachate samples (pH 8.5) 162
Figure 5.7. PLT values (logarithmic scale) of the time contact leaching experiments at a temperature of 60ºC with agitation 166
Figure 5.8. PLT values (logarithmic scale) of leaching experiments under no agitation effects at a temperature of 60ºC 166

Acknowledgments

First, of above all, praise is to Allah for health, guidance and inspiration throughout this work. The present study was carried out in the Environmental Health and Risk Management Division in Geography, Earth and Environmental Sciences School (GEES), University of Birmingham (UoB), United Kingdom (UK), during the years 2012 - 2016 under the supervision of Prof. Stuart Harrad, Professor of Environmental Chemistry.

I am delighted to say that this work could not have been completed without the help and support of several people and organizations. I am submitted my honest and humble thanks for all of them. First and foremost, I would like proudly to acknowledge gratefully the funding of my PhD studentship that granted by His Majesty Sultan Qaboos Bin Said, Sultan of Oman for the postgraduate scholarship programme that administered by Ministry of Higher Education (MOHE), Sultanate of Oman. As well, I am deeply grateful to my lead supervisor Prof. Stuart Harrad for giving me the opportunity to perform this work. It has been a great honour to be one of his PhD students. Many thanks for his understanding, encouragement and guidance throughout and he has always been available and ready to give me a constant help, support, follow-up, dedication and valuable scientific advice all over the whole project. Also, I offer my sincere thanks to my co-supervisor Prof. William Bloss, Professor of atmospheric science, GEES.

I would like to extend my thanks to all people and firm bodies in the government of Oman who have supported this study by providing moral support, useful technical advice, the financial means and even little effort to complete this project. I am much appreciated to Hilal Al-Azki, Nawal Al-Dehani in the Scholarship Dept., MOHE, Musalim Al-Amri, the cultural attaché and Yusura Al-Ismaili in Sultanate of Oman Embassy, London, UK. Alia Al-Gazali and her colleagues in Food and Water Monitoring Centre (FWMC), Muscat are kindly acknowledged. All friends and colleagues in the Ministry of Environment and Climate Affairs (MECA) and Directorate General of Environment and Climate Affairs, Dhofar Governorate, Oman, especially H.H. Mohammed Al-Toby, the minster, Najib Al-Rawas, the undersecretary, Dr. Ahmed Al-Saiari, the director general, Mohammed Al-Mashani, Ahmed Al-Zedjali, Mohammed Hardan, Paul Sharpless, Mohammed Al-Ghasini are warmly thanked. My ex-directors, Sheikh Salim A-Huzaili and Dr. Mahaad Shammas are deeply acknowledged.

I would like to thank all those, who helped me in a way or another during the preparation of this study. My deep thanks to all past and present PhD students and postdocs colleagues and all the entire staff members of GEES for helping, providing a good working environment, working assistance whenever necessary, and for sharing their scientific knowledge. Special thanks to UoB POPs research group. Dr. Mohammed Abdallah, Dr. Layla Al-Omran, Dr. William Stubbings, Dr. Yuning Ma and Dr. Alice Tao, they are much appreciated for their generous help,

support and advice. Dr. Maria Thompson, Emear Orgil, Dr. Daniel Drage, Dr. Salim Alam, Dr. Suad Al-Kindi, Dr. Temilola Oluseyi, Dr. Seth Newton, Gopal Pawar, Jiangmeng Kuang, Yessica Ortez, Ana Miralles-Marco Andrew Taunge, Leon Peter, Aristide Ghanci and Jennifer Anekwe were very acknowledged too and there are many others who I owe them thanks in GEES may forgive me if I am not mentioned. In addition, I offer great thanks to all members of Omani students' society, Birmingham (OSSB) for great practicing the cultural and traditional of Omani ways here in Birmingham.

Finally, I am immensely grateful to my parents, brothers and family for their continued love, support and encouragement. Especially thanks to my wife Muna and our children Abir, Ahmed, Musab, Noor and Zainab who were joining me on this journey to Birmingham, UK.

Dedication

To my parents, brothers, wife and our children, may Allah save and protect them, I dedicate this work to them all.

Abstract

Polybrominated diphenyl ethers (PBDEs), "novel" brominated flame retardants (NBFRs) and organophospate flame retardants (PFRs) are industrial chemicals widely used in consumer products to enhance their ignition resistance. The toxicity of some BFRs has led to concern about human exposure. The work carried out for this PhD thesis, focuses on brominated and organophospate flame retardants (FRs) emissions to the environment in the waste streams. It divided into 2 parts. First part was about taken the field measurements of the brominated FRs (BFRs) contaminants in the air and soil surrounded vicinity of six Oman landfills. The second part was about examining the potential for emissions of FRs from an end-of-life polyurethane furniture foams (PUF) via leaching experiments.

The analyses of samples in this study were performed according to the methodology and QA/QC procedures in the chapter (2). Therefore, a substantial amount of PBDEs were found emitted into the environment from landfills in high concentrations in comparison to non-landfilled areas. The percent ratio of BDE-209 in ∑PBDEs for all sampling locations in this study was particularly high as well as same of some percentages of other places in worldwide. Furthermore, PBDEs affected by different periodical variation trends. These were possibly mainly because the various types of PBDEs emitted from different varieties of BFR-containing waste and also were affected by various landfilling processes. The concentrations of ΣPBDEs in air samples in the vicinity of Oman landfills ranged from 176.38 - 1803.13 pg m^{-3}. Also, the concentrations of ΣPBDEs in soil ranged from 65 - 252 ng g^{-1} in Am landfill (mean 146 ng g^{-1}) and from 25 to 158 ng g^{-1} in Ra landfill (mean 91 ng g^{-1}). The average of other landfills was 199, 234, 246, and 174 ng g^{-1} for Ni, Ib, So, and Bu landfills, respectively. The ΣNBFR concentrations are lesser than that for PBDEs. They ranged in this study from 11 - 163 pg m^{-3} and from 4.5 - 13 pg m^{-3} at the vicinity of Oman landfills and reference sites, respectively. They ranged too from 20.5 – 47 ng g^{-1} and from nd – 1.29 ng g^{-1} in soil surrounded the landfills in Oman, respectiveley.

The leaching experiments of the FRs that were investigated in this study under the effect of a range of landfill relevant leaching fluids and parameters. The leaching concentrations of FRs from PUF wastes were determined. Thus, the most significant findings of these experiments are that

large concentrations of FRs can be created in leachate from PUF wastes in spite of their physicochemical properties like comparatively excessive hydrophobicity and moderately little water solubility.

The levels for the ΣPBDEs in these experiments were ranged from 1389 - 975325 µg L^{-1}, BEH-TEBP were ranged from 215 - 107800 µg L^{-1}, EH-TBB were ranged from 75 – 37730 µg L^{-1}, TCIPP was were covered from 6639 - 353326 µg L^{-1} and TPhP was range from 598 - 85608 µg L^{-1}. The ΣPBDEs concentrations are higher than the results of leaching experiments that prepared by Stubbings (2015) of ΣPBDEs in CRT plastics (ranged from 14000 – 200000 ng L^{-1}) but were comparable to a high of his study of TCIPP leaching fluids (13 - 130 mg L^{-1}). Henceforth, The NBFRs and TPhP were studied for the first time in this study.

The leaching experiments consisted of sequences of standardized trials that were accomplished to examine of FR leaching out from a flame retarded PUF waste, containing PUF samples from USA and UK. The leaching examinations were performed by using a range of leaching solutions, with the viewpoint of emulating of the features of actual landfill leachates. A four number of diverse analysis factors were inspected, for instance as variety of dissolved humic matter (DHM) densities, the pHs of 5.8, 6.5 and 8.5 which is relevant of landfill leachate, landfill proper temperatures, the effect of agitation, contact periods and measured the mass to leachate ratio. It is evident from these tests that even with the comparatively hydrophobic physicochemical properties of BFRs, they are capable of leaching out from waste materials at considerable concentrations.

Abbreviations

ABS	Acrylonitrile Butadiene-Styrene
AC	Acetone
Am	Al-Amerat landfill
ANOVA	Analysis of variance
ASE	Accelerated Solvent Extraction
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bio-concentration factors
BEH-TEBP	bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate
BFR(s)	Brominated flame retardants
Br	Bromine
BSEF	Bromine Science and Environmental Forum
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane
Bu	Al-Buraimi landfill
Bw	Body weight
CAS	Chemical Abstract Service
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CS_2	Carbon disulphide
CS	Calibration Standards
DBE-DBCH	Tetrabromoethylcyclohexane
DBDPE	decabromodiphenyl ethane
DCM	Dichloromethane
DDW	Deionized distilled Milli-Q water
DF	Detection frequently
DHM	Dissolved humic matter
GDM	General Directorate of Meteorological, Oman
Dw	Downwind
dw	Dry weight
EA	Ethyl acetate
EBFRIP	European Brominated Flame Retardant Industry Pane
ECNI	Electron capture negative ionisation
EEE	Electrical and electronic equipment
EFRA	European Flame Retardants Association
EFSA	European Food Safety Authority
EH-TBB	2-ethylhexyl-2,3, 4,5-tetrabromobenzoate

EI	Electron ionisation
ESD	Equilibrium sampling device
EU	European Union
e-waste	Electronic waste
FR	Flame Retardants
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GFFs	glass fibre filters
HBCDs	Hexabromocyclododecanes
H_c	Henry's Law Constant
HCl	Hydrochloric acid
Hex	n-Hexane
HIPS	High impact polystyrene
HPFRs	Halogenated PFRs
HPLC	High pressure liquid chromatography
HPV	High production volume
HVAS	High-volume air sampler
IDL	Instrumental detection limit
Ib	Ibri landfill
IS	Internal standard
IUPAC	International Union of Pure and Applied Chemistry
K_{oa}	Octanol-air partition coefficient
K_{oc}	Organic carbon water partitioning coefficient
K_{ow}	Octanol–water partition coefficients
LC	Liquid chromatography
LOD	Limit of detection
LOQ	The limit of quantification
LRAT	long-range atmospheric transport
m	Molecular mass
m/z	Ions of mass ratio or mass to charge ratio
MS	Mass spectrometry
MSW	Municipal Solid Waste management
MW	Molecular Weight
Na_2SO_4	Anhydrous sodium sulfate
NFPA	National Fire Protection Association
NGOs	non-governmental organisations
Ni	Nizwa landfill

NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NIST	National Institute of Standards and Technology
PAHs	Polycyclic aromatic hydrocarbons
PAS	Passive air samplers
PBBs	polybrominated biphenyls
PBDEs	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative and toxic
PBEB	pentabromo ethyl benzene
PCBs	Polychlorinated biphenyls
PFRs	Organophosphate Flame Retardants
PM	Particulate matter
PLE	Pressurized liquid extraction
PL	Percentage of leaching
PLT	Percentage leached relativized to time
PO_4	Phosphoric acid
P_4O_{10}	phosphorpentoxide
POPs	Persistent organic pollutants
PTV	Programmable temperature vaporiser
PUF	Polyurethane foam
PVC	Polyvinyl Chloride
QA/QC	Quality assurance/ quality control
R	Passive Sampling rate
Ra	Raysut landfill
RDS	Recovery determination standard
RfD	Reference dose
Rpm	Revolutions per minute
RRF	Relative response factor
RRT	Relative retention time
RSD	Relative standard deviations
R*t*	Retention time
SD	Standard deviation
SERw	Weight specific emission rate
S/N	Signal to noise ratio
So	Sohar landfill
SPE	Solid phase extraction
SRM	Standard reference material
SVOCs	Semi-volatile organic compounds
TBBPA	tetrabromobisphenol A

TBBPA-BDBPE	tetrabromobisphenol-A-bis(2,3-dibromopropylether)
TCIPP	Tris(1-chloro-2-propyl) phosphate
TPhP	triphenyl phosphate
TWA	Time-weighted average
UNEP	United Nations Environment Programme
Uw	upwind
UTM	Universal Transverse Mercator
USEPA	United States Environmental Protection Agency
V_p	Vapour pressure
WG84	World Geodetic System 1984
WHO	World Health Organization
W_s	Water solubility

Symbols and Units

S	second (time)
min	minute (time)
H	hour (time)
µm	micrometer
Mm	millimeter
Cm	centimeter
M	meter
m^2	square meter
m^3	cubic meter
T	ton(s)
G	gram
$mg\ kg^{-1}$	milligram per killogram
$\mu g\ g^{-1}$	microgram per gram
$ng\ g^{-1}$	nanogram per gram
$pg\ g^{-1}$	piqogram per gram
$\mu g\ m^{-3}$	microgram per cubic meter
$ng\ m^{-3}$	nanogram per cubic meter
$pg\ m^{-3}$	piqogram per cubic meter
°C	Celsius degree (temperature)
knots	Wind speed unit
$g\ cm^{-1}$	gram per centimeter (density)
$m^3\ day^{-1}$	cubic meter per day (*R*)
$ng\ cm^{-2}$	nanogram per square centimetre (dose)

Chapter I: General Introduction

1.1. Background

Fire from the earliest times has been regarded as one of the elemental forces shaping life on Earth (WFSC, 2010). Aristotle (384 – 322 BC) confirmed that fire is one of the essential elements of the universe along with earth (soil), water and air. The discovery of fire has given humans many advantages (de Jourdan, 2012). Using and controlling fire is one of the discoveries that have had a significant influence on the development of human life. This aptitude has been an elementary requirement for all civilizations as people have used fire to provide heat, to cook food, to extract metals from their ores (Voospoels, 2006) and many more activities. On the other hand, fires are adverse events with tangible costs to property and human life and it can also inflict adverse consequences on the natural environment (Martin *et al*., 2016). However, fire has been both a friend and an enemy of humankind throughout human history. Once a fire is out of human control, its deadly and devastating natural force becomes rapidly obvious. In the middle ages, open fire places and the use of candles and ovens easily caused fires in the overcrowded mainly wooden-constructed cities, the most well-known example being the Great Fire of London in 1666 (Porter, 1998).

In search of preventive measures to increase fire safety, Man has discovered the benefits of flame retardants (FRs). FRs are substances added or applied to a product in order to suppress, significantly reduce or delay the combustion of the material (van Esch, 1997). Such substances have been used to increase fire safety throughout centuries. As early as 360 BC, vinegar was used to protect wood from catching fire. The civilization of the ancient Greeks, Romans and Egyptians knew the use of alum to protect wooden objects from fire (Hindersinn, 1990;

Bourbigot *et al*., 2004). In more recent times, the first patent on a flame retardant was published in England in 1735 and that was aimed to flame retard canvas for use in theatres and public buildings just 70 years after the great fire of London (1666). Later, in 1789, the Montgolfier brothers used an alum coating on their hot air balloon (Bourbigot *et al*. 2004). Then, in the 18th and 19th centuries, inorganic salts, such as ferrous sulfate and ammonium phosphate were used as FRs. Louis XIV, the French King had the textiles in his castles treated with ammonium salts for fire protection (Hindersinn, 1990).

As the knowledge of fire and the burning process has evolved, chemicals are now incorporated in many materials and they are able to prevent ignition or to slow down the initial phase of a fire. FRs are less probable to have an influence on fires after their initial phase has commenced (Voorspoels, 2006). So, the principle of FRs is that they slow down the burning process as mentioned above, hence increasing the possibility of escaping from a burning site (Guerra *et al*., 2011). A fire retardant also decreases the amount of heat and toxic gases that are released and limits the amount of material that is actually burnt. Since the 20th century, the use of FRs has increased. This was connected with the increasing use of synthetic polymers i.e. plastics and synthetic products. These new materials were more flammable than e.g. wood or metal, because they have a much higher carbon-hydrogen content. Therefore, they would catch fire more easily, produce more heat, and once alight, combust more rapidly, giving people little time to escape. FRs gave a solution to this significant problem by substantially reducing the risk of fires and providing safety in dwellings and in public places. Furthermore, the increased use of electronics and soft furnishings, mostly polymer-based appliances, such as TVs, computers and polyurethane foam (PUF), as well as synthetic textiles and other products, has led to an enormous increase in the demand for FRs in our modern technological society (Voorspoels, 2006).

Many brominated flame retardants (BFRs) and organophosphate flame retardants (PFRs aka OPFRs) are found in quantifiable levels in humans, wildlife as well as in environmental components. Polybrominated diphenyl ethers (PBDEs) tend to persist in the environment and to linger in animal fat. They can travel long distances in the air and be deposited in places far from where they were released. They chemically and toxicologically resemble polychlorinated biphenyls (PCBs) (Schecter et al., 2005). So, since the restrictions and bans start in some countries from 2003 forward in especially on some types of PBDEs, then demand of new FRs products was increased (EU, 2003, Ali et al., 2012). Lately, 'Emerging' or 'Novel' BFRs (NBFRs) have received increasing attention due to their detection in some environmental constituents and biota samples (Shi et al., 2009; Ali et al., 2012). However, research gaps remain, but there are continuous efforts to fill these gaps and counter the lack of the knowledge about the effects of BFRs and PFRs on wildlife and man and identify how these chemicals move and are released from their products.

The recent global restrictions on the use and manufacture of two types of BFRs i.e. PBDEs and hexabromocyclododecanes (HBCDs) that have be situated used for many years, have directed chemical manufacturers to find alternatives. Some of those alternatives are NBFRs and PFRs (USEPA, 2005; Reemtsma *et al*., 2008; CEFIC, 2007; Stapleton *et al*., 2009). These BFR alternatives may be potential hazards to the environment and human health as they may be toxic, persistent, bioaccumulative and their capability of long-range transport (LRT).

1.2. Environmental Pollution

Why is so much concern being expressed about environmental contamination with FR compounds? Because these pollutants were found everywhere and they have potentially

negative effects. In the next sections, the selected compounds, the field of study and the state of art regarding their fate in the environment are described.

There are three most essential compartments on the earth which are water, soil and air while discussing the environmental pollution. The definition of environmental pollution is any material substances or energy -noise, heat, radiation or light- which discharged toward water, land or air. The contamination causes or may cause acute or chronic effects on the ecosystem and surrounding atmosphere, or it will lower the quality of life. Contaminants may have a directly or indirectly adverse impact on life or its quality. Figure 1.1 in next page presents the interaction between the biosphere, the hydrosphere, the lithosphere and the atmosphere of the globe and environmental pollution may be anything which affects them (Javaid, 2006).

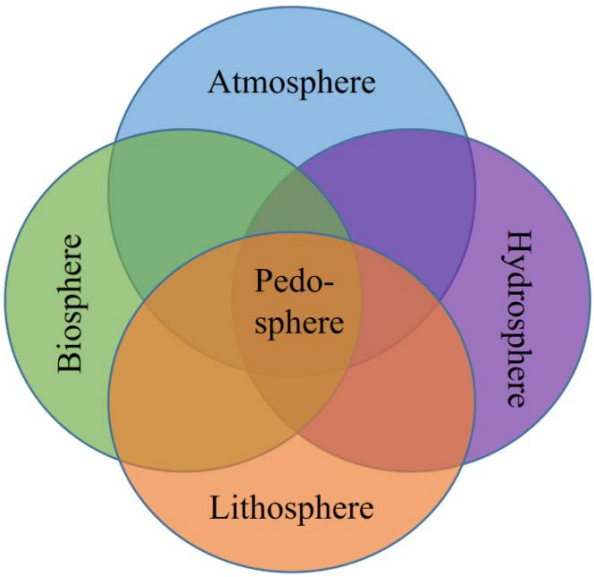


Figure 1.1: The global environmental system

In the last few decades, there was growing of global worry upon public health influences that attributed to environmental pollution. It became the industrial revolution that gave delivery to environmental pollutants as we recognize it today (Özkara *et al*., 2016). Environmental pollution ordinarily is the insertion of pollutants into the environments. It causes harm or anxiety to other

living creatures or destroy the surrounding environment, which can arise in the type of chemical materials or energy (Santos, 1990).

PBDEs are priority contaminants in Europe since they are regulated. NBFRs have been considered emerging contaminants, since their presence in several environmental compartments have been reported in the last decade. Although PFRs have been detected in the environment since 1970s, they considered as re-emerging contaminants because their use has increased after PBDE bans and also because their increasing levels in the environment (Cristale, 2013).

1.2.1. Persistent Organic Pollutants (POPs)

Chemicals have become an indispensable part of almost every aspect of human life in the 20th century, sustaining activities and development, preventing and controlling many diseases, increasing agricultural productivity, etc. In spite of their benefits, they may, especially when misapplied, lead to adverse effects on human health and environmental integrity. The widespread application of chemicals throughout the world raises the potential of adverse effects. The growth of chemical industries is predicted to continue to increase. In this context, it is recognized that the risk assessment and management of chemical exposure is amongst the critical priorities in practicing the sustainable development values (IPCS, 1998a).

There are more than 120 million organic and inorganic substances are recognized and recorded on the Chemical Abstract Service database in 2016 (CAS, 2016), which reflects of a typical boost of 4500 novel chemicals a day in despite the four million chemicals classified there since 1978 (Maugh, 1978). This fact was given the massive figure of anthropogenically manufactured chemical compounds while the limitations of existing analytical techniques which only capable of screening a small portion of organic contaminants in the tests are obstructed environmental experts and scientists to investigate these pollutants (Harrison et al., 2006). The emission of

organic substances toward the environment involves most life on Earth, inclusive people because a part of these chemicals that characterized as environmentally persistent. These mixtures mount up inside the organisms' tissues (bioaccumulation), are poisonous and some which include PBDEs can mimicking hormones in human body (Harden *et al*., 2005). Per the Stockholm Convention, the POPs term was setup to describe the persistence and accumulation of specific organic contaminants. The main POPs characteristics are as the following:

1. Naturally persistent, i.e. their half-life is greater than six months in soil.
2. Bioaccumulation capability (POPs accumulate in aquatic organisms' when their bio-concentration factors (BCF) > 5000 and/or an octanol-water partition coefficient, log K_{ow} > 5).
3. Long-Range atmospheric transport (LRAT).
4. Toxic to people and wildlife.

There are various POP compounds pose substantial threats to public health and the surrounding environment. Therefore, in 2001, the Stockholm Convention on POPs of the United Nations Environment Programme (UNEP) purposed to prohibit, limit and eventually reduce the POPs production, storage, use and discharge (POPs, 2004).

1.2.2. Stockholm Convention

The Stockholm Convention entered into force of 17th May 2004 and now it ratified by 180 states. This convention is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have harmful impacts on human health or on the environment (POPs, 2016).

1.3. Role of Flame Retardants in Fires

‘‘Fire is a rapid oxidation process, which is a chemical reaction resulting in the evolution of light and heat in varying intensities’’ (NFPA, 2014). It is described generally as an uncontrolled combustion, meaning a self-sustaining and exothermic process of oxidation of fuel accompanied with the evolution of heat and light; or smouldering combustion in its consolidated phase. This uncontrolled phenomenon involves numerous and complicated physical and chemical reactions in the solid, liquid and gas phases. It is predominantly associated with the release of smoke, which may contain nuisance gases and or corrosive species. The fire behaviour of materials is also particular to the thermal decomposition and the chemical nature of the material (Ngohang, 2014; NFPA, 2014). This subsection is a short discussion on fire and related parameters and the thermal decay of FRs materials.

Most synthetic or natural materials burn if exposed to temperatures that are sufficiently high. The response of these materials to fire depends on their formulation and configuration situation (Ebewele, 2000). Fire is a major source of loss of life, damage to properties and public expenses (Guerra *et al*, 2011). Every year, fires kill and injure more than 28,000 of people and result in assets damage exceeding an estimated £19 billion in the United States (US) and Europe (Karter, 2004; WFSC, 2008). In order to decrease the risks of fires and provide sufficient escape time during building fires, governments, product manufacturers and professional associations have promoted the use of FRs in consumer products and building materials likely to burn (Morose, 2006). Hence, these applications are in products with relatively high probabilities of accidental ignition (Callahan *et al*., 2012). For example, the increased use of FRs in consumer products has been attributed by some to the reduction in both total and smoke related fire deaths in the United Kingdom (Kolic *et al*., 2009). Fire incidence has dropped over the last six decades partly because of the fire prevention regulations requiring

action. This led to the use of FRs in many industrial products to reduce flammability (Birnbaum and Staskal, 2004; Clarke, 1999). Encouragingly, there has been a notable long-term downward trend in fire and smoke fatalities and casualties over the last 35 years in England, from a peak of 775 fire fatalities in 1981-92 to 258 fire deaths in 2014-15 (UK National Statistics, 2015). A numerical graph of total fire and smoke related deaths between 1981 and 2015 in England is given in Figure 1.2. Additionally, Figure 1.3 shows fires in the US have dropped from 3,264,500 in 1977 to 1,298,000 in 2014. These are reflected in the total civilian and firefighter death toll which in 1977 was 7,552 then declined steadily to be 3,339 in 2014. Also, civilian injuries which were 31,190 in 1977 decreased to 15,775 in 2014 (NFPA, 2015). This decrease in fatal fire incidences has been attributed to the fire prevention regulations requiring the presence of FRs in commonly used industrial products (Birnbaum and Staskal, 2004).

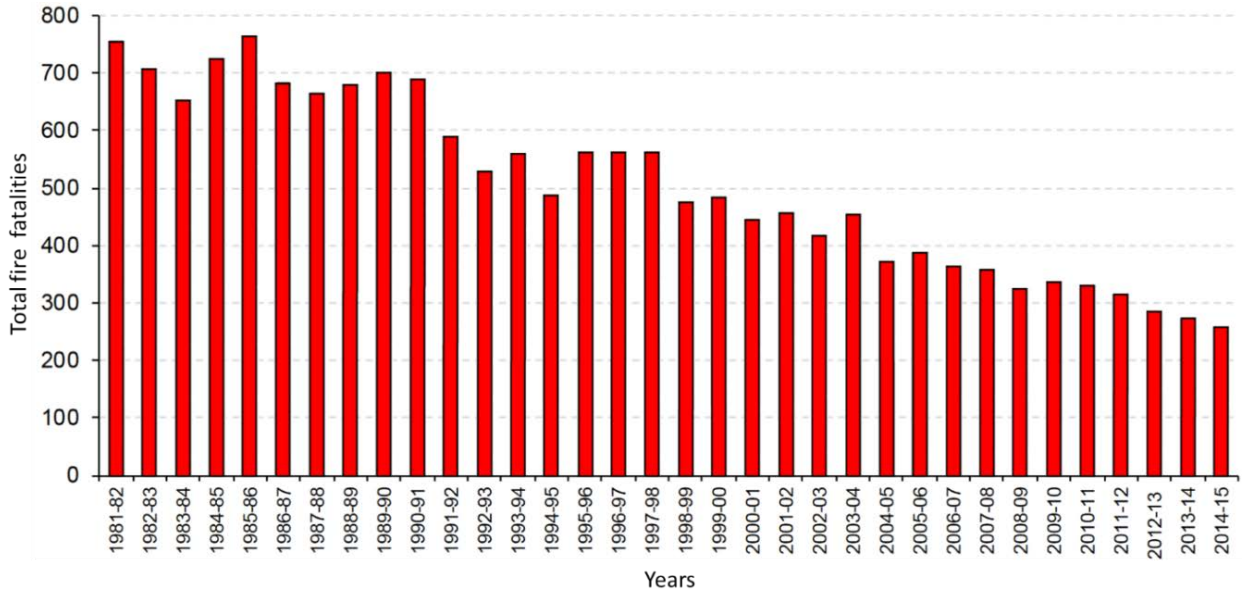


Figure 1.2: Total fire fatalities in England 1981-82 to 2014-15 (UK National Statistics, 2015)

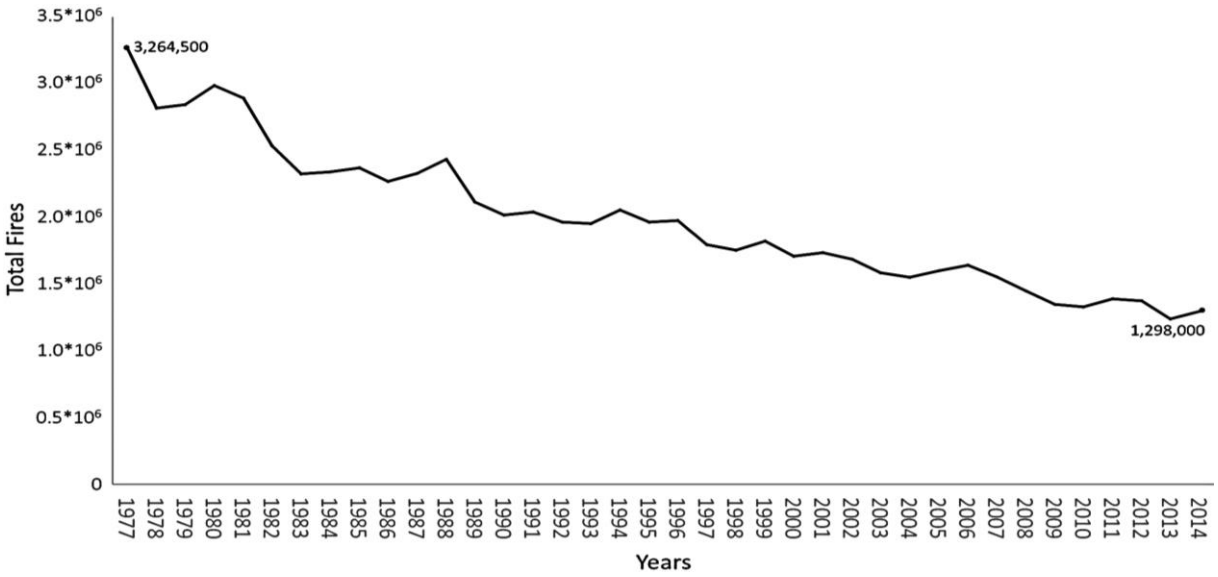


Figure 1.3: Total fires in US during years 1977 - 2014 (NFPA, 2015)

Fire has four phases; dormant, growth, developed fire and decay stages. When a flashover, which is the temperature point at which the heat in an area is great enough to ignite all combustible material simultaneously, FRs act to delay the spread of fire and increase the time to flashover, providing valuable time to mitigate loss to property and human life (de Jourdan, 2012).

Figure 1.4 depicts the phases of a fire and total fires without the presence of FR compounds within burning materials (solid curve), while the dashed curve shows the stages have shifted, with increased time until flashover, in the presence of an FR. This mechanism of using FRs helps in reducing the risks of fires and provides sufficient escape time to save lives.

The halogens are most active in the vapour phase; they act in the flame zone by forming a blanket of halogen vapour that interferes with the dispersal of the flame by disrupting the generation of high amount reactive free radicals, consequently tending to quench the flame. Others such as phosphorus operate in the condensed or solid phase, minimising the availability of fresh fuel (Ebewele, 2000). To interrupt or reduce fire combustion, FRs interact chemically in their gaseous phase with radicals formed in the fire process. This prevents the exothermic chain reactions from

occurring, resulting in a cooling down and a decrease of mass fluxes in the polymeric material undergoing thermal decomposition (Clarke, 1999; Simon *et al*., 2005). Once these flammable vapors burn by oxygen (O_2) in the air, then a flame will be visible. When this decay does not occur, hard materials will only smother slowly and maybe evenly self- extinguish, in particularly while a char performed, which further prevents of the fire access to the underlying objects. Hydrocarbon and hydroxide Radicals ($H^{\bullet}$ and $OH^{\bullet}$) that have a higher energy will sustain the vapors via decaying particles of carbon that can act in response with O_2 to produce high volume of CO_2 in a large exothermic reaction response (EFRA, 2013). In fact, the materials not burn immediately, they need to be decayed by heat source and release it to the fumes. These solid objects must be preheated due to an external source to be burn. Then they will break down by releasing heat to flammable gases. This situation leads to thermal decay (pyrolysis phase) of the solid materials and burnable gases releasing agent which subsequently reacts with atmospheric O_2. This thermal reaction formerly will make a visible flame and creates additional heat (combustion phase). If the produced high temperature is sufficient, the solid will decompose further, and the burning phase turns into self-diffusion (van Esch, 1997; EFRA, 2013).

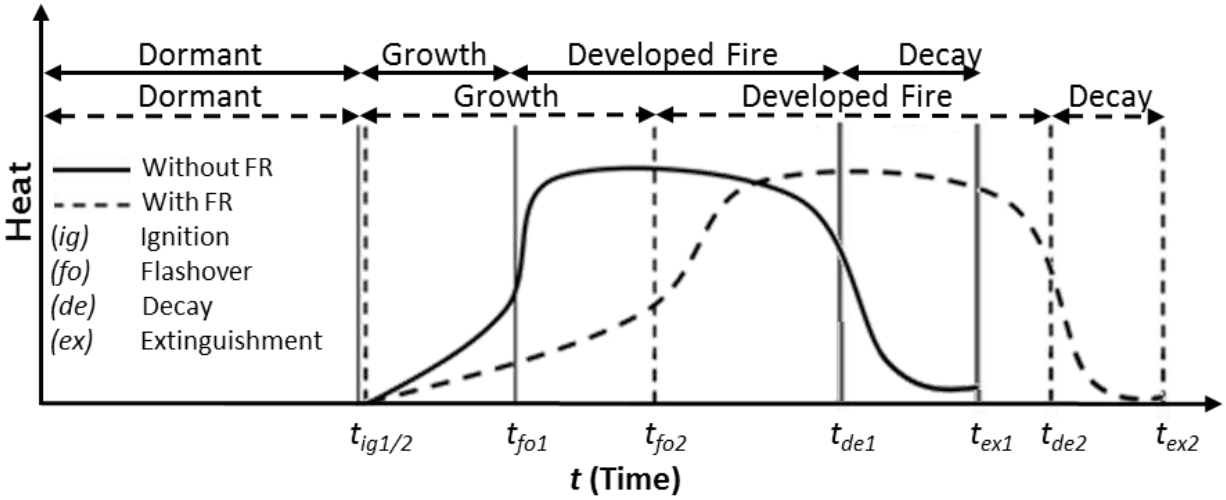


Figure 1.4: The stages of enclosure fire development with/without the presence of FRs compounds within burning materials (adapted from Cheng and Hadjisophocleous, 2011; de Jourdan, 2012)

Halogens are very effective in capturing free radicals (I>Br>Cl>F) that are produced throughout the combustion process and stopping the propagation of the flame. Thus, halogenated FR compounds have been designed to act as a storage and delivery system of halogens to products. However, not all of these elements are suitable for use in flame retardants. Fluorinated or iodinated compounds are stable or not stable and decompose at high or slightly elevated temperatures, respectively. Consequently, only chlorinated and brominated FR compounds have been found to be suitable, with BFRs being the most popular choice due to their higher trapping efficiency and lower decomposing temperature (Alaee *et al*., 2003; Birnbaum and Staskal, 2004).

BFR materials act through reducing or avoiding the flaming phase by decreasing fire creation and lowering production of more flammable vapors. While BFRs exposure to high temperatures, they liberate $Br^{\bullet}$ radicals which react with the $H^{\bullet}$ molecules of combustible gases to create HBr. The yielded HBr oxidizes with $H^{\bullet}$ and $OH^{\bullet}$ radicals to arise H_2O, H_2 and $Br^{\bullet}$ radicals. This let the cycle of BFR reaction to restart again and again surrounded the burning phase. The FR efficacy be influenced by on its number of bromine substance and its rule of bromine discharge. The bromine is get to release over a limited temperature series resulting in optimal concentrations in the blaze zone. In despite, the chlorine (Cl) is released within a wider heat range, which mean the chlorinated FR compounds are less efficient (van Esch, 1997). The inhibition mechanism of halogens in the gaseous phase is clarified in Figure 1.5.

The description of the PFRs reaction in one overall acting mechanism is unattainable (Schmitt, 2007). There is a further mechanism for halogenated PFRs (HPFRs) thru whose act as FRs. Furthermore, the HPFRs act in the gas stage to remove $OH^{\bullet}$ and $H^{\bullet}$ radicals from the fumes over a reaction with Cl molecules and forming the phosphoric acid (PO_4) char. This removal outcomes in a strike of the flaming development which aids to limit the extend of the fire. The

effectiveness of this process is affected by halogen molecules amount in the PFRs matter (van der Veen and de Boer, 2012). The HPFRs advantage is that both of halogen and phosphorus substances performance independently in the polymer structure contribution to more fire retardancy (van Esch, 1997). Also, in case of using non-halogenated PFRs such as triphenyl phosphate (TPhP), they only achievement retardancy in the solid part of the burning phase. The phosphorus atoms react when heated to provide a polymeric formula of PO_4. This acid causes the material to char, inhibiting the pyrolysis process (Verbruggen *et al*., 2005).

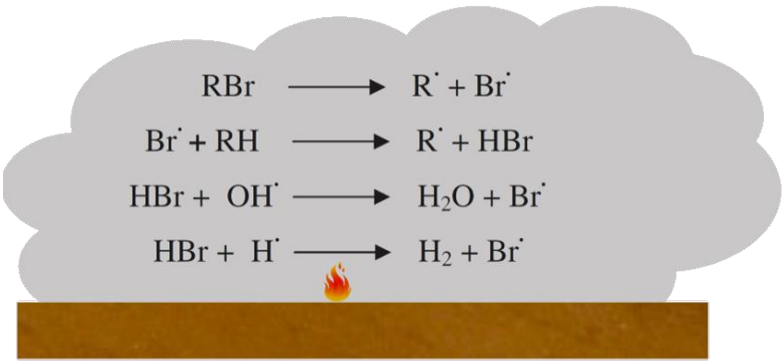


Figure 1.5: Mechanism of action of BFRs in gaseous phase of flashover fire in a BFR-product (adapted from Abdallah, 2010)

The radical trap mechanism described above is not the only mode of action of FRs. It has been demonstrated that halogenated FRs also have a physical effect on the combustion process; by virtue of their heat capacity and endothermic bond dissociation properties they can act as a heat sink (Larsen, 1980).

1.4. Flame Retardants Chemicals

Man has developed more sophisticated FRs. There are four major families of FR chemicals available on the market which are inorganic, halogenated organic, organophosphorus and

nitrogen based compounds. Inorganic FRs are salts, such as aluminum trihydrate, antimony trioxide, boric acid and others. Inorganic FRs make up 50% of the total amount of FRs produced worldwide. Organic FRs are either halogenated substances, corresponding to approximately 25% of the total amount of FRs produced, phosphorous and nitrogen containing organic substances, which are estimated to 20% and >5% respectively of the annual production demand of FRs (van Esch, 1997). Examples of phosphorous containing FRs are the PFRs that are used as plasticizers. Next to several non-halogenated PFRs that are in use, various PFRs are substituted with halogens (van Esch, 1997; IPCS, 1998b, 2000). The halogenated FRs i.e. BFRs, NBFRs, and PFRs groups will be discussed later in detail, in the sections (1.4.1), (1.4.2) and (1.4.3) respectively of this chapter.

FRs act to inhibit and/or stop the combustion reactions of polymers. A distinction is made between reactive FRs and additive FRs: reactive FRs are chemically grafted onto polymeric chains during the polymer synthesis, whereas additive FRs are incorporated into the polymer as filler. Depending on their nature, the elements in FRs can react chemically and/or physically with fire in their solid, liquid or gas phases (Laoutid *et al*., 2009). Although the use of reactive FRs is not excluded, additive FRs appear to be more convenient and currently represent the best compromise between process, cost and performance. There are more than 175 chemicals classified as FRs (Alaee *et al*., 2003). Two types of FRs, which are BFRs and PFRs, will be discussed in the following sections (Table 1.1). All details in this chapter will focus only on these kinds of FRs. It will cover and try to give an accurate description of them and contribute data about these FRs.

Table 1.1: Types of FRs in this study

Group	Type	Name/ Acronyms
BFRs	PBDEs congeners	BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209
	NBFRs	decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), tetrabromobisphenol-A-bis(2,3-dibromopropylether) (TBBPA-BDBPE), 2-ethylhexyl-2,3, 4,5-tetrabromobenzoate (EH-TBB, aka TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP, aka TBPH), pentabromo ethyl benzene (PBEB) and Tetrabromoethylcyclohexane (DBE-DBCH, aka TBECH)
PFRs	Halogenated phosphate ester	Tris(1-chloro-2-propyl) phosphate (TCIPP, aka TCPP)
	Aryl phosphate	triphenyl phosphate (TPhP, aka TPP)

1.4.1. Brominated Flame Retardants (BFRs)

There are approximately 75 different chemicals are used as BFRs (BSEF, 2007). They are divided into subgroups of PBDEs, polybrominated biphenyls (PBBs), tetrabromobisphenol A (TBBPA) and HBCDs (Alaee *et al*., 2003) and NBFRs as well. HFRs are currently receiving substantial attention because they are characterized by their POPs properties, such as persistence, lipophilicity, LRAT and toxicity (POPs, 2004). The majority of environmental studies conducted to date have focused on PBDEs and to some extent on TBBPA and HBCDs. Other brominated organic substances are also of concern, such as PBBs. Concern about PBBs was raised after a major poisoning accident in Michigan, US in 1973 (de Wit, 2002). However, coverage of PBBs, TBBPA and HBCDs is outside the scope of this study.

Despite their great efficacy, BFRs may have negative consequences for health and the environment and their use is disputed on these grounds by organisations and government bodies. In particular, a ban on the use of PBDEs has been in place since 2006, under the European Risk of Hazardous Substance directive. Furthermore, the degradation products of halogenated compounds are also known to produce corrosive and toxic by-products, i.e. there is solid

evidence of the degradation of BDE-209 over time, creating lesser brominated PBDEs with robust bioaccumulation marks and extreme toxicity (Danon-Schaffer, 2010; Kajiwara *et al*., 2014).

There are basically two methods by which FRs are combined into polymer products. First type is additive, in this case, the FR is delivered into the melted polymers. Such additive model scheme that the FR is not always chemically bound to the polymer backbone and because of this its start to leach out to the environment. So, its immigration is comparatively superficial. The alternate technique is in which the FR is covalently bound to the polymer through the reaction response. The FRs compounds release to the surroundings included over this reactive progression is comparatively limited (Law, 2010). Nevertheless, throughout the incorporation method into the handled product with FRs, a percentage of the applied reactive FR may will not polymerize, and this residual portion has the capacity potential to be out easily to the surrounding environment (de Wit, 2002). After each halogen and phosphorus compounds are present in a polymer product, they doing independently action and before acting the additive action of FRs (van Esch, 1997).

This is the reason for the increasing focus in research and development on zero halogenated additives (or halogen-free) FRs and their commercial application. This focus is also prompted by the growing demand, led by the industrial sector, for an alternative enabling it to avoid the problems that arise with halogenated FRs. Such alternatives are the use of NBFRs and PFRs.

1.4.1.1. Polybrominated diphenyl ethers (PBDEs)

Hoffmeister (1871) presented the very first report of the synthesis of a PBDE, which can be traced back to 1871. The synthesized congener was 4,4'-dibromodiphenyl ether (BDE-15) and it was obtained by adding elemental bromine (Br_2) to diphenyl ether using bromine in carbon

disulphide (CS_2). Subsequently, other methods of producing individual PBDE congeners have been reported. The commercial production of PBDEs as flame retardants started in the early 1960s, and they were widely used in a broad range of commercial and household products (NIWR, 2005).

The PBDEs are a group of chemical compounds in which up to 10 bromine atoms are attached to a diphenyl ether molecule (Muir *et al*., 2006). The PBDE generic structure is illustrated in Figure 1.6. There are theoretically 209 PBDE congeners and they are numbered according to the IUPAC system that is used for numbering PCBs based on the position of the halogen (chlorine or bromine) atoms on the rings (de Wit, 2002). They form different compounds depending on the number and position of the bromine atoms. Each one of the 209 possible compounds is called a congener and a set of these compounds can also be called homologues if they contain the same number of bromine atoms. The most common congeners are listed in Table 1.2.

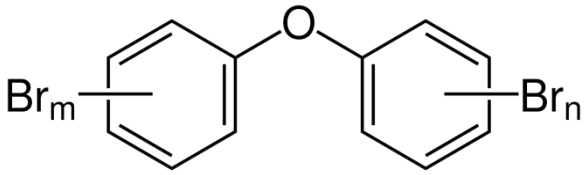


Figure 1.6: Generic structure of PBDEs mixture (m and n= 1 to 5)

Table 1.2: Chemical congeners and basic details of prominent PBDEs of this study

PBDE Synonyms	Homologue Groups	Chemical Name Br Substitution-Compound Name	IUPAC No.	CAS No.
BDE-28	Tri	,4,4'-tribromodiphenyl	28	41318-75-6
BDE-47	Tetra	,2',4,4'-tetrabromodiphenyl	47	5436-43-1
BDE-99	Penta	,2',4,4',5-pentabromodiphenyl	99	60348-60-9
BDE-100	Penta	,2',4,4',6-pentabromodiphenyl	100	189084-64-8
BDE-153	Hexa	,2',4,4',5,5'-hexabromodiphenyl	153	68631-49-2
BDE-154	Hexa	,2',4,4',5,6'-hexabromodiphenyl	154	207122-15-4
BDE-183	Hepta	,2',4,4',5',6-heptabromodiphenyl	183	207122-16-5
BDE-209	Deca	,2',4,4',5,5',6,6'-decabromodiphenyl	209	1163-19-5

PBDEs are mixtures of many congeners (Rahman *et al*., 2001; D'Silva *et al*., 2004). Technical PBDE products are produced by brominating diphenyl ether in the presence of a catalyst. The major technical products contain mainly penta-BDEs, octa-BDEs or deca-BDE, but contain other PBDEs as well (de Wit, 2002). These three commercial mixtures are Penta-BDE, Octa-BDE and Deca-BDE. The Penta-BDE mainly contains penta- and tetra-BDEs; towards to 40 and 60%, respectively (Sellstrom *et al*., 2005). Octa-BDE mixtures are mainly composed of hepta- and octa-BDEs; from around 44 and 35%, respectively and, to a lesser extent, hexa- and nona-BDEs; nearly 10% each (Sellstrom *et al*., 2005; MacDonald *et al*., 2009), whereas Deca-BDE, consists of nearly 100% BDE-209 (La Guardia *et al*., 2006). The general compositions of the technical products are given in Table 1.3 and typical products of them in Table 1.4.

Table 1.3: The general compositions of PBDE-based flame retardants given in percent (%) of BDE congeners present

Technical Product	Congener Percent						
	Tetra-BDEs	Penta-BDEs	Hexa-BDEs	Hepta-BDEs	Octa-BDEs	Nona-BDEs	Deca-BDEs
PentaBDEs	24 - 38	50 – 60	4 – 8				
OctaBDEs			10 – 12	44	31 - 35	10 - 11	<1
DecaBDEs						<3	97 - 98

Sources: IPCS, 1994.

Table 1.4: Global market demand for PBDEs technical mixtures between 1999 and 2003 with continental data of 2001 (metric tons; *t*)

PBDEs Technical Mixture	Total 1999	Continent, 2001					Total 2002	Total 2003
		North America[1]	Europe[1]	Asia[1]	Rest of World[2]	Total		
Deca-BDE	54,800	24,300	7,500	23,000	1,500	56,300	65,677	56,418
Octa-BDE	3,825	1,375	450	2,000	180	4,005	0	0
Penta-BDE	8,500	8,290	210	0	100	8,600	0	0

Sources: [1] BSEF, 2003; [2] BSEF, 2004.

PBDEs are hydrophobic and degradation resistant. The water solubility and vapor pressure of these compounds will reduction with expanding degree of bromination number. Correspondingly, a large quantity of bromine molecules contributes further to the hydrophobicity of the atom; the Br molecules increase in dimension without a polarity obtain. A study considered the Henry's law constants for PBDE congeners and found that there is a sturdy dependence on temperature. This dependence differs with the bromination grade and the bromines structural situation. The Henry's law values ranged from 0.04 to 4.83 Pa m^3 mol^{-1} at 25 °C, though the BDE-209 held the lowest value and BDE-28 held the highest (Cetin and Odabasi, 2005).

1.4.1.2. Production and Uses of PBDEs

BFRs are the most widely used because they are more compatible with modern manufacturing processes than any other compounds (Landry and Dawson, 2002). Moreover, BFRs represent the highest commercial use of bromine. Bromine is a member of group VII elements (halogens) and was discovered in 1826 by Antoine Balard. Since bromine is the principal ingredient for BFRs, it is necessary to review the production and applications of bromine as an industrial chemical (Alaee *et al*., 2003). The annual worldwide production of bromine between years 1996 to 2005 is given in (1.7).

The major companies producing BFRs are Eurobrom (Netherlands), Dead Sea Bromine (Israel), Great Lakes Chemical Corporation (USA and UK) and Ethyl Corporation (USA). Other companies include Nippo, Tosoh and Matsunagaall from Japan, Albemarle S.A. (Belgium), Warwick Chemicals (UK), Riedel de Haen (Hoechst Group), Potasseet Produit Chimiques (Rhone Poulenc Group) as well as Ceca (ATOCHEM, France) (KEMI, 1994; IPCS, 1994).

The total globe production of all BFRs is around 150,000 metric *t*/year. Their distribution are 40% to North America, 30% to the far East and 25% to Europe (KEMI, 1994). PBDEs have been broadly used for several decades in many commercial goods including rubbers, textiles, electronic components, plastics and building materials (Alaee *et al*., 2003; Hale *et al*., 2006).

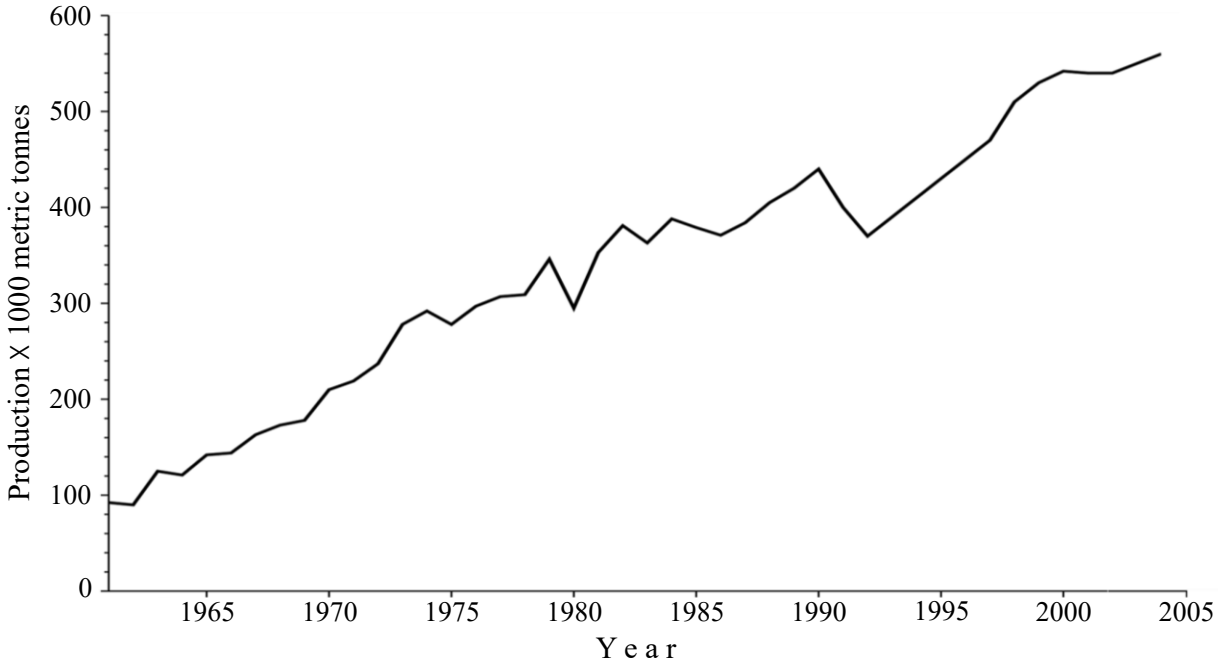


Figure 1.7: Annual global production of bromine between 1960 and 2005 (US GS, 2007)

The latest data of the annual world demand for PBDEs is for 2003, and it is only for the Deca-BDE technical product. The world market demand for total PBDEs in 1999, 2001, 2002 and 2003 is given in the previous Table 1.4. The production volumes of technical products of Pent-BDE, Octa-BDE and Deca-BDE in 2001 worldwide were 8,500, 3,825 and 54,800 t, correspondingly (BSEF, 2003; 2004). Ever after 2004, Penta-BDE and Octa-BDE technical mixtures have been forbidden in some countries. During the end of 2004, Great Lakes Chemical Corporation, the USA producer of Penta-BDE and Octa-BDE products, willingly ended their manufacturing of these products (USEPA, 2007). As well Canada barred all PBDEs production and the usage or selling of three PBDE technical products (Tetra-, Penta- and Hexa-BDE) in

2008. The technical mixtures of Penta-BDE and Octa-BDE were targeted, but not Deca-BDE, which is intended to be banned by 2013 (MacDonald et al., 2009). The European Union (EU) have forbidden Penta-BDE and Octa-BDE in all products in 2004 (USEPA, 2007). Stockholm Convention has listed both Penta-BDE and Octa-BDE in the POPs chemical list in May 2009 (POPs, 2008; 2009). Table 1.5 shows examples of major PBDE applications.

Table 1.5: Examples of major PBDE applications

Chemical Mixture	Typical Applications
Penta-BDE	Polyurethane foams: mattresses, seat cushions, other upholstered furniture and foam packaging. Carpet padding, imitation wood, paints, sound insulation panels, small electronic parts, fabric coatings, epoxy resins, conveyor belts
Octa-BDE	Acrylonitrile -butadiene - styrene (ABS) plastic: housings for fax machines, computers and other electronics. Automobile trim, telephone handsets, kitchen appliance casings, small electronics parts, audio/video equipment, remote control products
Deca-BDE	High-impact polystyrene (HIPS) plastic: housings for televisions, computers, stereos and other small electronics. Mobile phones and various plastics: polycarbonates, polyester resins, polyamides, polyvinyl chloride, polypropylenes, terephthalates (PBT and PET plastics) and rubber. Upholstery textiles (sofas, office chairs, backcoating), paints, rubber cables, lighting (panels, lamp sockets), smoke detectors, electrical equipment (connectors, wires, cables, fuses, housings, boxes, switches), stadium seats

Sources: Janssen, 2005 ; Mahesh *et al*., 2016.

1.4.2. Novel Brominated Flame Retardants (NBFRs)

The importance of BFRs is due to their efficiency, their good thermal stability even under severe conditions and also their strong contribution to reducing smoke toxicity under realistic fire conditions. As a further improvement to satisfy the market demand, new BFRs are being developed for more environmentally friendly applications (Smith *et al*., 1996). Figure 1.8 illustrates the chemical structures of the selected prominent NFBRs and their synonyms.

There are limited data around the production size, physicochemical characteristics, analytical methodologies, environmental destiny, behaviour and toxicity of NBFRs. In the lack of this knowledge, curiosity and concern arose from their similarity to structures of PBDEs. It was felt

that they might demonstrate of persistent, bioaccumulative and toxic (PBT) characteristics as well and may affect the human health and wildlife. Also, alike usage forms and structures, indicates that the typical pathways exposure of human to NBFRs are likely comparable to the legacy BFRs. The pathways exposure includes a sequence of diet, dust ingestion, dermal uptake and breathing (Harju *et al*., 2009).

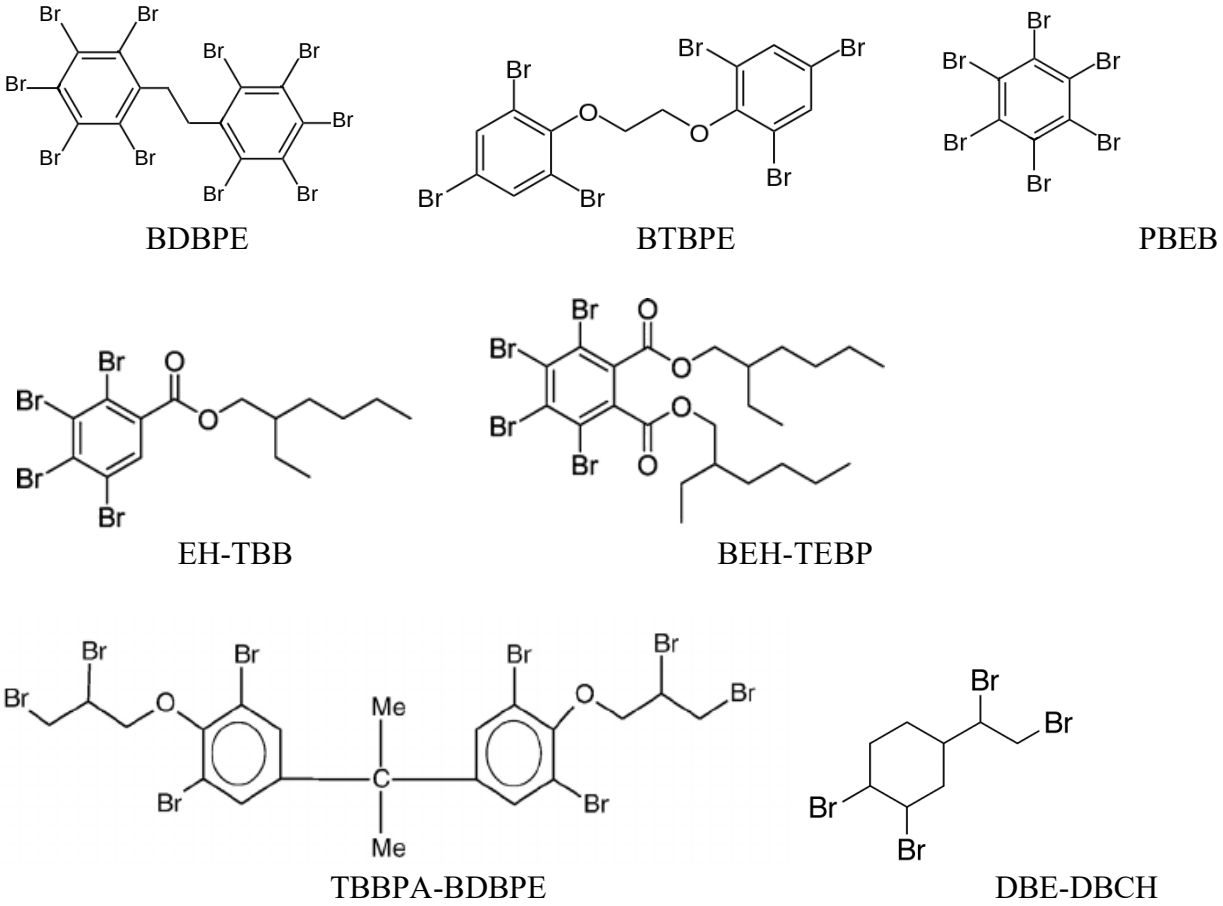


Figure 1.8: The chemical structures of the selected NFBRs

1.4.2.1. Production and uses of NBFRs

The accurate world production volume of NBFRs is unsure (Covaci *et al*., 2011) and their manufactured and used volume is difficult to stated (Harju *et al*, 2009). NCPA (2009)

recommended that we need more data about the most important NBFRs because the most up-to-date data from BSEF is still for 2003 and then to estimate the bulk of minor recognized BFRs. The HFRs are representative of about 25% by volume of the FRs production with a growing of about 5% annually (Covaci *et al*., 2011). The total consumption of BFRs in 2005 is 311,000 t worldwide, which is around 21% of the total use of FRs. Assuming that the manufacturing capacities not affected a lot upon the previous few years, the guesstimate of total NBFRs volume is about 180,000 t yearly (Sjödin *et al*., 2008; Hajru *et al*., 2009). Table 1.6 summarizes existing knowledge concerning of the application and usage of specific NBFR compounds and their CAS numbers. More particular detailed on production of NBFRs is required for there is a suggestion that their production has increased following the restriction upon the PBDEs. Table 1.7 shows the production of some NBFRs in the world.

Table 1.6: Chemical synonyms, Applications, uses and CAS number of NBFRs

Synonyms	Applications and uses	CAS No.
DBDPE	Acrylonitrile butadiene styrene (ABS), polycarbonate/ABS, HIPS/polyphenylene oxide and textiles[a].	84852-53-9
BTBPE	ABS, High impact polystyrenes (HIPS), thermoplastics, thermoset resins, polycarbonate and coatings[a].	37853-59-1
TBBP-A-DBPE	Plastic products, such as pipes, water barriers, kitchen hoods and electronics[a].	121850-44-2
EH-TBB	PUF applications[a].	183658-27-7
BEH-TEBP	PUF applications, polyvinylchloride (PVC) and neoprene, wire and cable insulation, film and sheeting, carpet backing, coated fabrics, wall coverings and adhesives[a].	1.26040-51-7
PBEB	Thermoset polyester resins (circuit boards, textiles, adhesives, wire and cable coatings, polyurethane foam)[a], unsaturated polyesters, styrene butadiene copolymers, textiles[b].	85-22-3
DBE-DBCH	Expandable PS beads for house insulation, extrudedpolystyrene, for adhesives in fabric, electrical cable coatings, high impact plastic in appliances and some construction materials[a].	3322-93-8

Source: [a] Covaci, *et al*., 2011; [b] Wu *et al*., 2011

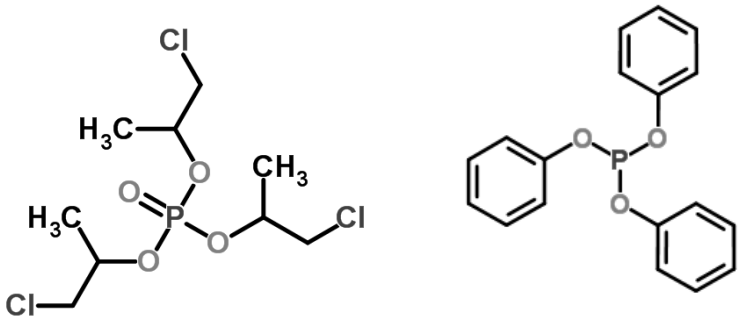
Table 1.7: The production of some NBFRs in the world[a]

NBFR	Production (*t*)	country	Year
DBDPE	1000 - 5000 (imports)	Europe (Germany)	2001
	12000	China	2006
BTBPE	4500 - 22500	USA	1986 – 1994
	450 - 4500	USA	1998
	16710	Worldwide	2001
BEH-TEBP	450 - 4500	USA	1990 - 2006
TBBPA-DBDPE	4000	China	2006
	< 4500	USA	2006
DBE-DBCH	4.5 - 230	USA	1986 - 2002

a) Covati et al., 2011.

1.4.3. Organophosphate Flame Retardants (PFRs)

Since the POPs properties of PBDEs and other BFRs have led to various bans on their production and usage as additive FRs worldwide (Reemtsma *et al*., 2008; Stapleton *et al*., 2009; Roberts *et al*., 2012; Besis and Samara, 2012) many of them are being replaced by PFRs (van der Veen and van Boer, 2012). PFRs comprised 20% of the FR consumption in 2006 in Europe. They have been applied in a wider range of polymer products like fiber types in textile and PUFs deployed in furniture, car upholstery and related products. They can be compatible with other processing chemicals and can be used easily (Powell, 1998). After the ban on some BFRs, PFRs are often proposed as alternatives. TCIPP is a potential substitute for BFRs (SCHER, 2007; van der Veen and van Boer, 2012). Another Penta-BDE replacement product named Firemaster 550 contains TPhP as one of its constituents (Stapleton *et al*., 2008) and it is additionally used as a lubricant in hydraulic fluids (Solbu *et al*., 2007). Figure 1.9 illustrates the structures of the selected PFRs.



TCIPP

TPhP

Figure 1.9: The chemical structures of the selected PFRs

According to the EFRA (CEFIC, 2007), the consumption of FRs in Europe in 2006 was 465,000 t in total; a 20% of this figure were PFRs. Various halogenated chemicals i.e. some BFRs and PCBs, have confirmed to be harmful to the environment, ecosystem and human. For more than sixty years, HFRs have been in the attention especially for preventing the public health. This concern was resulted in the forbidden of PCBs production in 1973 (Aresta *et al*., 2003). These days the manufacture and usage of BFRs are more constrained by the EU. As well the USA have phased out them voluntary (BSEF, 2011). For these reasons, PFRs are deemed as suitable replacements of BFRs. Since of the necessity for vapor-phase action, many of volatile PFRs as TPhP, have been recognized as possible substitutes for FR compounds that consists of bromine atoms i.e. to use in textile undercoats (Horrocks *et al*., 2007).

In production and use the TCIPP product is actually a reaction mixture containing four isomers, of which the individual isomers are not separated or produced as such. So far there are no emission or exposure controls that directly address TCIPP (EU, 2008). Total EU production of TCIPP in the years 1998 to 2000 was 30,000 to 40,000 t, produced at three sites in Germany and one in the UK. The consumption of TCIPP in the EU was 37,745 t in 2000. Over 98% of this amount is used as a flame retardant in the production of PUF for use in construction and furniture. TCPP can be added to polyols, which form PUF in reaction with di-isocyanates

(around 60%), or added directly at the point of foaming. Over 80% of PUF is used in rigid PUF foam for construction applications. The remaining PUF (more than 17%) is used in flexible foam for upholstery and bedding, but not for automotive applications (EC, 2004).

1.4.3.1. Tris(1-chloro-2-propyl) phosphate (TCIPP)

TCIPP or TCPP is a pure, colorless fluid (WHO, 1998), which is a HPFR, used as an additive FR (CEFIC, 2007). In Europe, approximately TCIPP acts for 80% of the chlorinated PFRs by the amount of the most essential PFR (Leisewitz *et al*., 2001). TCIPP has a solid-phase fire routine process as a gas-phase. In such mechanism, the phosphorus element is effective in the solid-phase and the chlorine is active in the gas-phase. When flame occur, carbon monoxide (CO), carbon dioxide (CO_2), phosphorous oxides such as phosphorpentoxide (P_4O_{10}) and hydrochloric acid (HCl) are created (KLIF, 2011).

Globally, TCIPP is consumed mostly in the solid PUFs, which may be distributed into blocks and sprayer schemes that used for construction insulation and fridge-freezer castings. Though, in the UK and Ireland, TCIPP is largely are used in soft PUFs for furnishing upholstery (WHO, 1998). It used for seat and chair pillows where are flame retarded (Lassen *et al*., 1999). In the UK, there is 80% of PUF production is flame treated with TCIPP (EU, 2008). It has also been used in PVC plastics in example that used as wall-paper (Ni *et al*., 2007). The registered TCIPP trade names are Amgard TMCP, Antiblaze 80, Fyrol PFC and Hostaflam OP 820 (ATSDR, 2012).

1.4.3.2. Triphenyl phosphate (TPhP)

TPhP, TPHP or TPP It is standout amongst the best active FRs for various consumers. TPhP is dense at room temperature and an aryl phosphate, an additive FR (Björklund *et al*., 2004). It is just

dynamic in the gas-phase (Pawlowski and Schartel, 2007) and it primarily being used as a FR in polymers (European Chemicals Bureau, 2002). This synthetic chemical is used in PUFs diffused in car upholstery, chairs, sofas and relative goods (Reemtsma *et al*., 2008; Stapleton *et al*., 2009; Marklund *et al*., 2003). It has been used commonly as plasticizer and a FR for a variety of materials, including electronic equipment, PVC, hydraulic fluids, glues and casting resins (Svara *et al.*, 2000; van der Veen and de Boer, 2012). Phase out of PBDEs may have increased the use of TPhP in recent years (Stapleton *et al*., 2009). TPhP used in plasticizer for cellulose acetate (Ferro, 2011) therefore, round 50% of the total TPhP manufacture is for usage as a FR plasticizer in PVC. Additional uses contain polymeric products (22%), circuit boards (11%), photography films (7%) and other minor uses of it includes hydraulic fluids, inks and adhesive coatings (OECD SIDS, 2002). The TPhP trademarks are Celluflex TPP, Disflamoll® TP, Phosplex® TPP, Reofoss® TPP and Reomol® TPP (Lassen *et al*., 1999; ATSDR, 2012). TPhP is present in all environmental compartments e.g., on average 23.2 ng m^{-3} in air (Danish EPA, 1999) and ranging from 21 - 180 ng g^{-1} in fish (Sundkvist *et al*. 2010). While TPhP thermally degradation, the PO_4 were formulated. This acid form reacts and creates pyro PO_4, which performances as heat transference obstacle in the solid-phase (Lee *et al*., 2002).

1.4.3.3. Production volume of PFRs

Manufacturing capacities in common are just accessible for the last decade subsequently. The Scandinavian countries of Sweden, Norway and Denmark are only countries that deliver a slight vision into the recent PFRs volumes data by their chemical database. Generally, TPhP and TCIPP are the most consumed PFRs. Table 1.7 in next page displays a summary of the accessible information on production volumes of PFRs.

The TCIPP production grew at 4% average each year from the mid-1960s to the late 1990s (WHO, 1998). Moreover, TCIPP in 2006 was greater than a third PFRs have being used and it was not lesser than 80% of chlorinated PFR that manufactured. This situation highlighting its importance as the main PFR products in Europe (Bayerisches Landesamt für Umwelt, 2006 cited in Brommer, 2014). The TPhP was used in the Penta-BDE replacement product "Firemaster 550" (Stapleton *et al*., 2008) could be a clarification for the excessive usage, particularly in the USA. The production and use volumes of PFR for the most extensively consumed PFRs i.e. TPhP and TCIPP, can be likened to those of PBDEs used (see Table 1.8 in next page). The figures in the data for Australia discloses relatively minimal PFR use, which might be due to no more chlorinated PFRs were produced in Australia since the year 2000. Furthermore, the data for other PFRs are not available for Australia and its main sources of FRs are the UK, Germany and Singapore (NICNAS, 2001).

Global production (excluding East Europe) was estimated to be 20,000 to 30,000 t. Of this production estimate, approximately 25% was made in Western Europe, 40% in the USA and 35% in Asia by 15 producers (OECD SIDS, 2002). TPhP is categorized as a high production volume (HPV) chemical in the EU (European Chemicals Bureau 2011). For the USA, the total annual production was given as 4,500 - 22,700 t in 2006 (USEPA, 2006).

1.4.4. PFRs versus BFRs

The consumption practice of PFRs, which have been consumed as FRs, because of them are diversify and integral role of their function in contrasted to BFRs (van der Veen and de Boer, 2012). Though, currently, PFRs are handled as substitutes for BFRs since the uses of the latter are more confined. There are some improvements of phosphorus combinations in the comparison to BFRs. As an example, there are toxic by-products created from BFRs over a fire

happened. But when using PFRs, the emissions are decreased, and in that way, the release of toxic gases from PFRs is furthest lower than of BFRs due to the char produced (McPherson *et al*., 2004).

Table 1.8: Production/usage volumes (*t*/year) of the studied PFRs

PFR	Production/ usage volume	Location	Year	Reference
TCIPP	22950	Europe	1995	SPIN Database, 2012
	2750	UK	1995	SPIN Database, 2012
	5000-6000	Germany	1997	BLU (Germany), 2006
	> 40000	Worldwide	1997	Green *et al*., 2008
	36000	EU	2000	EU, 2008
	7000-10500	Asia	2000	OECD SIDS, 2002
	5000-7500	West Europe	2000	OECD SIDS, 2002
	8000-12000	USA	2000	SPIN Database, 2012; Green *et al*., 2008
	50.5	Norway	2001	SPIN Database, 2012
	812.9	Finland	2001	SPIN Database, 2012
	704.2	Denmark	2001	SPIN Database, 2012
	145.0	Sweden	2001	SPIN Database, 2012
	290	Australia	2001	SPIN Database, 2012
	42.7	Norway	2008	SPIN Database, 2012
	177	Denmark	2008	SPIN Database, 2012
	16429	Finland	2008	SPIN Database, 2012
	132	Sweden	2008	SPIN Database, 2012
	199.5	Denmark	2010	SPIN Database, 2012
	84	Sweden	2010	SPIN Database, 2012
	43.3	Norway	2010	SPIN Database, 2012
TPhP	4500–22700	USA	1998	SPIN Database, 2012
	20000–30000	Europe (excl. Eastern Europe)	2000	SPIN Database, 2012
	7000- 10500	Asia	2000	OECD SIDS, 2002
	5000-7500!!!!	West Europe	2000	OECD SIDS, 2002
	8000- 12000	USA	2000	OECD SIDS, 2002; Green *et al*., 2008)
	4500–22700	USA	2002	SPIN Database, 2012
	55	Norway	2004	SPIN Database, 2012
	6.7	Norway	2005	SPIN Database, 2012
	1592	Sweden	2005	SPIN Database, 2012
	4500–22700	USA	2006	SPIN Database, 2012
	18.4	Norway	2008	SPIN Database, 2012
	2.3–16.7	Denmark	2004–2008	SPIN Database, 2012
	9.8–57.1	Finland	2004–2008	SPIN Database, 2012
	46.0–88.0	Sweden	2003–2008 (excl. 2005)	SPIN Database, 2012

Additionally, even as consuming PFRs, the burning gases are not polluted with other caustic gases i.e. HFRs released HBr or HCl in the flammable gases (Lenoir *et al*., 1994). The Chlorinated PFRs are confirmed to be carcinogenic, and there are acute health effects were found for TCIPP, which formulates those PFRs inappropriate as replacements for BFRs. Also, TPhP will not be suitable substitutes for BFRs, because they are toxic to aquatic organisms and potentially carcinogenic. There are other kinds of PFRs which possibly will be counted as appropriate substitutes for BFRs as opposed to using TPhP or TCIPP. That is based on the presently existing environmental and toxicity data (van der Veen and de Boer, 2012).

1.5. Physicochemical properties of FRs

Alternative BFRs share properties similar to those of the PBDE mixtures i.e. aromatic moieties, high bromination, low aqueous solubility, etc. Most are used as additives as opposed to reactive FRs. Hence, additive FRs are moulded in the material to be flame retarded (chemically bonded to the polymer) while reactive FRs are incorporated into or blended with the oligomers or polymers being manufactured (Danon-Schaffer, 2010; Bergman *et al*., 2012). As a result, it is plausible to hypothesize that the environmental fate and behaviour of many NBFRs may be similar to PBDEs (Stapleton *et al*., 2008). One of the most relevant comparatives between additive and reactive BFRs is that additive FRs are more likely to leach out of the product (Alaee *et al*., 2003).

There are some significant physicochemical properties which influence the availability for uptake of contaminants by plants and animals, routes of human exposure, their relative partitioning between different environmental compartments and their transport throughout the environment (Harrad, 2001). The physicochemical properties of legacy and novel BFRs pollutants are important in determining how they will be transferred to the environment (Lerche *et al*. 2002).

These important physicochemical properties include Octanol-water partition coefficient (K_{ow}), Octanol-air partition coefficient (K_{oa}), Organic carbon-water partition coefficient (K_{oc}) Henry's Law Constant (H_c), Vapour pressure (V_p) and Water solubility (W_s). Details of the physicochemical properties that govern the environmental fate and behaviour of BFRs and PFRs are given in Table 1.9. Chemicals with high K_{ow} values (log K_{ow} > 5) partition preferentially in octanol versus water in experimental tests, and often have a tendency to bioaccumulate in people and wildlife (Lerche *et al*. 2002). The concern of BFRs are because of their worldwide pollutants meanwhile they are toxic, persistent and depend to LRAT. They as well have the ability to bioaccumulate and biomagnify in the organisms. The physicochemical properties of BFRs have controlled their accumulation and magnification in ecosystems and even humans (Muenhor, 2011).

Table 1.9: Physicochemical properties affecting environmental behaviour of FRs

Parameter	Definition	Environmental Relevance
K_{ow} Octanol-water partition coefficient	Measurement of the equilibrium partition coefficient of a compound between water and octan-1-ol	Ability of a chemical to partition between water and lipids e.g between water and particle phase/soil/fish lipid
K_{oa} Octanol-air partition coefficient	Equilibrium partition coefficient of a chemical between air and octan-1-ol i.e. K_{OA} is the ratio of the octanol-water and air-water partition coefficient ($K_{OA}= K_{OW}/ K_{AW}$)	Ability of a chemical to partition from air to lipids e.g. between vapour and particle phase
K_{oc} Organic carbon water partition coefficient	Equilibrium partition coefficient of a chemical between water and natural organic carbon	Ability of a chemical to partition between organic matter and water
H_c Henry's Law Constant	Measurement of a compound's tendency to partition between a solution and the air above it	Tendency for a chemical to partition from aqueous solution to air e.g. between a lake and the overlying atmosphere
V_P Vapour pressure	The ability of a chemical to exist as a vapour	
W_S Water solubility	The solubility of a chemical in water	
Half-life or residence time	$T_{1/2}$ or τ	Persistence of the chemical; its resistance

Sources: Harrad, 2001; Desborough, 2011

Most of BFRs are extremely hydrophobic combinations with short vapor pressures and extraordinary log K_{ow} values. The vapor pressure and water solubility values together decline with cumulative bromine content number, while in difference, the log K_{ow} values are enlarges (Kierkegaard *et al*., 2007; Teclechiel, 2008). Consequently, with bromine content is increasing, there is raised of the BFRs propensity to be adsorbed by the soil, sediment and air constituents, more exactly than dissolved in water or partitioned to the vapor phase. The physicochemical properties differ significantly amongst the many BFRs. This will results in associated environmental alterations in their fate, behavior, distribution, exposure pathways and toxicological consequences (Hui-Ying *et al*., 2007; Kierkegaard *et al*., 2007). The physicochemical properties correspondingly regulate how PBDEs released from their products and will be transferred, spread, degraded and finally accumulated in numerous environmental partitions with humans. Strictly speaking, an exposure pathway is a physical course a chemical take from the source of release to the organism that is exposed. By comparison, the exposure route is a description of how the chemical gets into the body. The three primary exposure routes are inhalation, dermal absorption and ingestion e.g. dust or diet (USEPA, 2005).

The solubility of PFRs reduces by rising the molecular mass (*m*). Here in this case, their hydrolysis half-life could be equivalent to that of PFRs that with lesser masses and then they are more expected to be found in the aquatic nature than those with greater molecular masses. This is proven by the log K_{ow} rates of the PFRs. Maximum of the PFRs type distinguished by a positive value numbers of log K_{ow}, which leads them to be further lipophilic more than hydrophilic. TCIPP is extremely soluble in water with an aqueous solubility of 1.6 g L^{-1} (IPCS, 1998b); conversely, TPhP is 1.9 mg L^{-1} which means it is very poorly soluble in water at this value (Fisk *et al*., 2003). The log K_{ow} values show a discrepancy considerably among the diverse

PFR classes. The log K_{ow} values of TCIPP and TPhP are 2.59 and 4.59, respectively (IPCS, 1998b; van der Veen and de Boer, 2012). These log K_{ow} values contrast with the log K_{ow} rates of the BFRs of which range from 4.82 (TBECH) to 12.99 (TBBPA-BDBPE); log K_{ow} values of PBDEs are between these two values. Therefore, BFRs are considerable more lipophilic than PFRs. The vapor pressure of TCIPP and TPhP are 6.13×10^{-2} and 6.28×10^{-6} *mm* Hg, respectively. Thus, these less volatile PFRs will apportionment mainly to the particle phase, and in this situation, the inhalation will likely be irrelevant as an exposure pathway (SRC, 2013). Table 1.10 in next page show some of the descriptive data of the physicochemical properties that affect the environmental behaviour of FRs. The difference in the various physicochemical properties, seen in these two tables, controls the relative rate at which these compounds partition between environment and abiotic media (Jones and de Voogt, 1999).

Table 1.10: Physicochemical properties of FRs in this study

FRs Synonyms	Physicochemical Properties						
	Molecular Formula	Molecular Weight (g/mol)	W_S (mg/L)	$logK_{oa}$	H_c at 25 °C (Pa m^3 mol^{-1})	$logK_{ow}$	V_P (Pa at 21 °C)
PBDEs:							
BDE-28	$C_{12}H_6Br_3O$	406.89	0.421	9.7	4.83 ±0.67	5.94	1.57×10^{-3}
BDE-47	$C_{12}H_6Br_4O$	485.79	0.112	10.23	0.85 ±0.35	6.81	2.50×10^{-4}
BDE-99	$C_{12}H_6Br_5O$	564.69	0.077	11.28	0.6 ±0.11	7.32	5.00×10^{-5}
BDE-100	$C_{12}H_6Br_5O$	565.69	0.085	11.4	0.24 ±0.06	7.24	2.86×10^{-5}
BDE-153	$C_{12}H_6Br_6O$	643.58	0.031	12.15	0.26 ±0.08	7.9	5.80×10^{-6}
BDE-154	$C_{12}H_6Br_6O$	643.58	8.7×10^{-4}	12.18	0.08 ±0.04	7.82	2.85×10^{-8}
BDE-183	$C_{12}H_6Br_7O$	722.51	1.5×10^{-3}	12.89	0.19	8.27	4.68×10^{-7}
BDE-209	$C_{12}H_6Br_{10}O$	959.21	0.002	15.75	0.04 ±0.01	10.33	1.43×10^{-8}
NBFRs:							
DBDPE	$C_{14}H_4Br_{10}$	971.22	0.421	19.2	3.0×10^{-8}	11.1	6.0×10^{-15}
BTBPE	$C_{14}H_8Br_6O_2$	687.64	0.112	15.7	1.7×10^{-5}	8.31	2.91×10^{-12}
TBBPA-BDBPE	$C_{21}H_{20}Br_8O_2$	943.61	0.077	20.3	3.5×10^{-3}	12.99	2.85×10^{-7}
EH-TBB	$C_{15}H_{18}Br_4O_2$	549.92	0.16	12.3	103×10^{-3}	7.73	3.71×10^{-7}
BEH-TEBP	$C_{24}H_{34}Br_4O_4$	706.14	3.3×10^{-3}	16.9	3.3×10^{-6}	9.34	1.55×10^{-11}
PBEB	$C_8H_5Br_5$	500.65	3.2×10^{-4}	10.0	0.37	6.76	1.56×10^{-10}
TBECH	$C_8H_{12}Br_4$	427.8	5.92×10^{-5}	14.9	1.84×10^{-8}	4.82	2.97×10^{-3}
PFRs:							
TCIPP	$C_9H_{15}C_{13}0_4P$	327.5	1200	8.5	5.04×10^{-3}	4.70	7.52×10^{-3}
TPhP	$C_{18}H_{12}O_4P$	326	4.674	10.5	0.335	3.30	6.29×10^{-5}

Sources: Verbruggen *et al*., 2005; Covaci *et al*., 2011; Bergman *et al*., 2012; Cristale, 2013; USEPA, 2003, 2008abcd, 2013.

1.6. Review of FRs in Waste Stream

The waste streams are including landfills, incinerations, recycling plants etc. The landfills in many regions of the world have been actually historical the most communal way of disposed the waste. This method is still continuing worldwide. Therefore, they might comprise of wastes resulting from several periods of dumping and may decompose with a successive discharge of organic mixtures that might have affected the environment, wildlife and human health (Eggen *et al*., 2010). The historic dumping was often in badly engineered and unsuitably located landfill sites and dumps (Weber *et al*., 2011). Figure 1.10 show a conceptual model of FRs contaminants release and movement within environment.

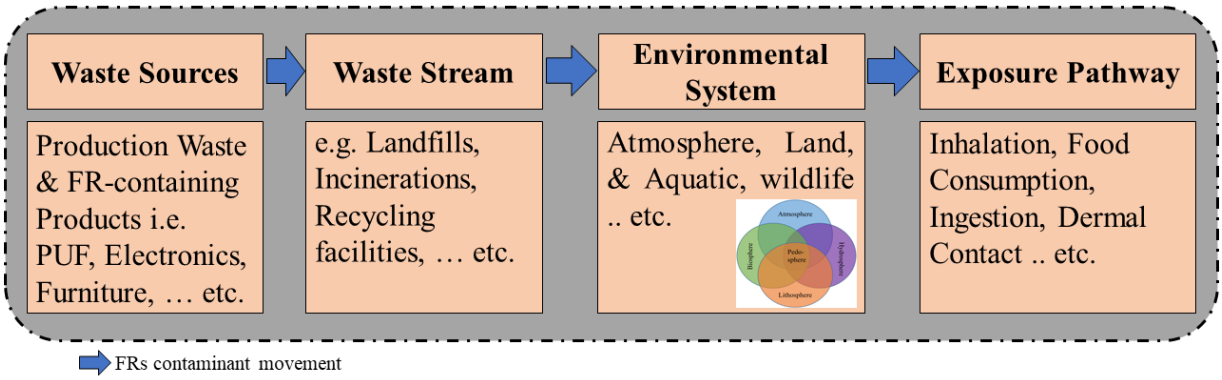


Figure 1.10: A conceptual model of FRs contaminants release and movement within environment

The FR products terminate in waste streams, which are treated in different ways in several countries due for the disparities of environmental policies and regulations, power demands and basic infrastructure. In some situations, entire waste, flammable or otherwise, reaches landfills untreated (Söderström, 2003). Figure 1.11 shows some of e-waste disposed in a landfill in Oman without any treatment.

Figure 1.11: Image of a mistake of E-waste disposed of in the landfill sites, Oman

Water filtering throughout these landfill sites can transport away of water-soluble mixtures and small particles that attached with alike these compounds, but typically, the polluted water ought to be remedied. Landfills are sometimes put on combustion situations, either fortuitously or intentionally to reduce garbage volumes (Söderström, 2003). Alongside refused plastics and electronic and electrical waste (e-waste), frequently comprise valued metals as like aluminum (Al), copper (Cu) or gold (Ag). That metals can be recovered from waste in various means, the simplest being to place these plastics and metallic items within the melted metal, upon which the plastic is directly burning. Nevertheless, the combustion productivity is inadequate in these conditions, and BFRs that could be existing can whichever evaporate or procedure toxic by-products such as HBr and dioxins (Sinkkonen *et al*., 2003).

BFRs are released into the environment through a variety of routes, among them volatilisation or leaching of pollutants during waste treatment at landfills (Osako *et al*, 2004). Landfill is a discrete area of land or an excavation that contains solid waste. Hence, landfills pose two major environmental threats; airborne and waterborne contaminant release. Airborne contaminants include fugitive dust or gases released or vented from the site. Landfill gases can migrate to remote locations, causing toxicity and explosion hazards. While most landfill air emissions consist of methane (CH_4) and carbon dioxide (CO_2) generated during decomposition, volatile chemicals may also be released. There is some evidence that methane may act as a carrier for polyhalogenated compounds and carcinogens. Additionally, landfill leachate (liquid releases) contains a variety of organic and inorganic contaminants. Without effective landfill liners, leachate collection and treatment systems, these pollutants can contaminate soil and groundwater (Schafish *et al*, 1995).

As confirmed by Basel convention, wastes are materials or substances which are either disposed of, on purpose to be disposed of or must be disposed of through the requirements of national regulations. The high technology thriving has carried with it another kind of waste, the e-waste, a type that scarcely occurred 25 years ago. Nowadays e-waste stand for the largest and rapidest growing waste (Basel Convention, 2004). The electronics become very predominant in each facet of community that they play the only biggest Municipal Solid Waste (MSW) management obstacle facing the world these days. They are growing three more times earlier than the typical growth of another trash types (Veleva and Sethi, 2004; Danon-Schaffer, 2010).

As an example, mobile phones were launched in 1984, and the market has been booming ever since. According to Nokia (the then largest mobile phone manufacturer), there would be 2 billion cell phone users worldwide in 2008 (Basel Convention, 2006). The present global manufacture

of e-waste alone is assessed to be 20 - 50 million *t*/year, by maximum of it being generated in Australasia, the United States and Europe. China, Latin America and Eastern Europe countries will come to be the main e-waste generators in the next few years (Robinson, 2009). E-waste is becoming a major environmental concern because of its high generation rate and the potential detrimental impact on the environment caused by the associated toxic chemicals (Wu *et al*, 2008).

In 2006, global production of furniture reached 271.9 billion Euros as monetary value. Of this massive figure, the EU countries produced 36.6% while the USA accounted for some 25%, China produced the equivalent of 15% and other countries were responsible for about 23.4% of the global production (WFC, 2012). Within this huge amount of furniture products, there are many different types of furniture and materials. According to UEA statistics (2005), approximately 8 - 10 million t of furniture waste is discarded annually in the EU. Of this 8 - 10 million t, 80 - 90% is incinerated or dumped in landfills (CREM, 2004). In 2009, the amount of discarded furniture waste reached 9.8 million t in the USA (USEPA, 2010). Globally, it is estimated that around 36 million t of that waste was part of 904.8 million t of MSW, according to the data for the latest year available in all of the countries (UNSD, 2011). This equates to 4% of the total MSW arising (CREM, 2004).

The huge quantity of E-waste and soft furnishings wastes and its potential for environmental contamination by chemicals, including BFRs and PFRs, has been reviewed recently and highlighted as a problem meriting serious and urgent attention by politicians, non-governmental organisations (NGOs), the scientific community and other bodies (Robinson, 2009). There is constant growth in the production of such goods and they become obsolete quickly; this generates huge amounts of BFR and PFR-containing wastes and causes significant problems for

their safe disposal and recycling. The most common method of treatment is thermal processing as it allows recycling and recovery of both the organic and inorganic fractions of the waste (Grabda *et al*. 2010). Landfills, as a reservoir of BFR-containing wastes, i.e. NBFRs can be regarded as a source of NBFRs to ambient air (Weinberg *et al*, 2011) and they may percolate through the soil to groundwater via leachate leakage. As well, PFR-containing e-waste could be a major source of pollution to the environment (Roth *et al*., 2012). Consistent with this, TPhP was identified at 0.4% and 0.2% w/w in two printed circuit boards (Ballesteros-Gómez *et al*., 2013) and it was the most common PFR detected in e-waste and consumer products (Ballesteros-Gómez *et al*., 2014).

1.7. Environmental and Health Impacts of FRs

The consumed products that comprising various kinds of additive FR materials with exceptional valuable advantage of their properties are in the everyday usage. Though, once these products are decayed, the additives will be released into the surroundings environment, part of them will be exposed to have adverse environmental effects. The novel and emerging of these constituents are always found in the environment because of bans or at least restrictions of some of these chemicals (Eggen *et al*., 2010). Several BFRs and PFRs are found in quantifiable levels in wildlife as well as in humans. However, there remains relatively little knowledge about the effects of BFRs and NBFRs in wildlife and man. Among the BFRs, the best environmental and human risk assessment data are available for PBBs and PBDEs. Interest in PBBs stems mainly from the contamination incident in Michigan in 1974 (IPCS, 1994). Regarding PBDEs, the high production volume (HPV) and the structural resemblance to other well-known environmental contaminants such as PCBs are two major reasons for environmental and health concern. The

concerns about PBDEs and other flame retardants have been rising in the recent past since measured concentrations have increased exponentially in people by a factor of ~100 during the last 30 years as shown in Figure 1.12 (Hites, 2004). There are a number of BFRs which are accumulated in biota, and in many cases the highest levels in wildlife are found in the aquatic environment (Darnerud, 2003).

Exposure to BFRs might be more harmful than previously thought (Wang *et al*, 2009). Certain commercial PBDE formulations i.e., Penta- and Octa-BDEs are listed under Stockholm Convention and have been banned in the EU, Japan, China and several states of the USA, due to various health and environmental threats posed by these BFRs (Darnerud, 2003; EU, 2003; Birnbaum and Staskal, 2004; Renner, 2004; Harrad *et al*., 2004, 2006; Thomas *et al*., 2006; Betts, 2008; Harrad *et al*., 2008; BSEF, 2010; Ali *et al*, 2011a). Moreover, the use of another major PBDE commercial formulation, i.e. Deca-BDE, in certain consumer products, has been banned in the EU since July 2008 (European Court of Justice, 2008; Ali *et al*, 2011a). These restrictions have led to an increased market demand for alternative flame retardants. Moreover, recent data from the USA indicates that restrictions on Penta- and Octa-BDEs have been having an effect and that the concentrations of PBDEs in the atmosphere are declining faster than those of other POPs (Salamova and Hites, 2011). As a result of the restrictions on PBDEs and HBCDs, it is thought likely that there has been an increased demand for alternative (or novel) flame retardants to meet flammability standards. Indeed, recent research has established the presence of these NBFRs in both indoor and outdoor environments which are published in several scientific articles (Ali *et al*, 2011a).

1.7.1. Transfer Processes of FRs from their Products in Waste Stream

The transfer processes or extent mechanism of FRs from their wastes to the environment remain a dynamic field of investigation (Stubbings, 2015). There are lack of knowledge on the level and potential processes of FRs emissions. There is evidence of FRs migration from waste materials and capable to go through a degradation and debromination processes during waste stream management and this may cause of spread more harmful compounds in the environment. For example, BDE-209 debrominates over time, forming lower brominated PBDEs with stronger bioaccumulation characteristics and higher toxicity (Stubbings and Harrad, 2014; Danon-Schaffer and Mahecha-Botero, 2010; Kajiwara *et al*., 2008, 2013; Schenker *et al*., 2008; Stapleton and Dodder, 2008). FRs that are used mainly as additives, and therefore migrate comparatively simply from their products into the environment (Deng *et al*., 2007) i.e. PBDEs in landfill leachate ranged from 0.05 ng L^{-1} (Oliaei *et al*., 2010) to 133,000 ng L^{-1} ng (Kwan *et al*., 2013).

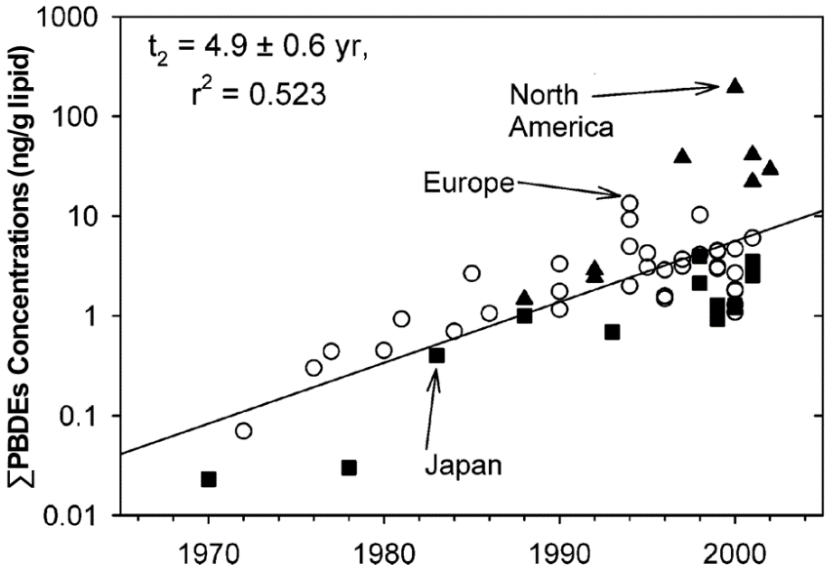


Figure 1.12: Increasing in ∑PBDE concentrations in human blood, milk and tissue (*ng g^{-1}* lipid) in North America, Europe and Japan since 1970s (Hites, 2004)

Also, the transport of waste materials to disposal sites and as well as their subsequent storage before sorting or deposition then the final disposal at landfills may prove exists that they be important emission pathways for FRs to the environment (Julander *et al*., 2005; Muenhor *et al*., 2010).

There are previous studies have conducted emission chamber and leaching experiments and tried to report the emissions of FRs via volatilization and leaching from a range of waste and consumer products. These investigations demonstrated that PBDE congeners are leached out in varied rates, controlled by their physiochemical characteristics i.e. the compounds by greater vapour pressures will detected at upper emissions (Kemmlein *et al*., 2003; Stubbings and Harrad, 2014). Kemmlein *et al*., (2003) has conducted volatilization chamber experiments to study BFRs and TCIPP emissions of a many products. He found that when raise temperature from 23 to 60°C, BDE-47 emissions increased a 500-fold. That is comparable with landfill conditions that the temperature may attain to more than 80°C because of aerobic degradation discharged more heat (Kjeldsen *et al*., 2002; EA, 2002). Therefore, a high unstable BFRs emissions of active landfills are perfectly reasonable, but then overlying layers of waste would limit their migration. Emission rates of FRs of aged products might alter due to their total concentrations inside the waste will reduces. As well, TCIPP emissions stated much greater than of BFRs (Stubbings, 2015).

There are many transfer processing of FRs to emitted from their sources to the environment like direct and indirect emissions i.e. emission, leaching and volatilization, debromination and degradation and abrasion and weathering. These mechanisms were studied in the field and lab experimental to find out more knowledge about the pollutants transferring. Furthermore, physicochemical characteristics and environmental conditions may affect the rates of transfer

processes of the FRs to environment media. However, it is worth to written in a separate chapter because it is a focus of debate how the FR contaminants transfer from their products in waste streams. Thus, it wills to focus only on the processes of direct emission, leaching and volatilization.

Finally, due to the many pathways that led FRs to leach out from their waste materials in the landfill. The most important of these transfer ways are firstly the leaching to the leachate of the landfills and the secondly is the volatilization. Subsequently, landfills should be monitoring via air, soil, leachate and groundwater samples regularly. The experimental lab studies were mimic the actual landfill conditions are the best tool to understanding more about this problem. However, the standardized experiments of leaching fluids or volatilization will produce accurate results and understanding of the significant role of the landfill as a source of environmental pollution.

1.7.2. Environmental Source, Occurrence and Effects

The concentrations of POPs compounds in the environment are highly variable depending on their source locations. For example, PBDE concentrations in river sediment collected from 11 different countries are ranged from undetectable to 7190 $ng\ g^{-1}$. There have been extensive industrial applications and they continue to be released from various products This has resulted in their ubiquitous distribution in the environment (Hites, 2004). In addition, the environmental fate and toxicity of BFRs can vary substantially (Nyholm, 2009). The largest issue in the environmental framework in conjunction with PFRs products is that they are regularly consumed as additives more exactly than have being a chemically bound toward the substances.

These consequences in further facile discharge in the environment after processed products wherever PFRs are combined additively (Brommer *et al*., 2012).

However, BFRs are added to many household, body care and many other products, they are now found everywhere in the environment. Since the last few decades, scientists have discovered BFR compounds in both wildlife and human tissues. Also, they found them as well as in the dust, sediments, landfill leachate, sewage sludge, water, atmosphere and soil specimens in many countries (de Wit, 2002; Alaee *et al*., 2003; Hale *et al*., 2003; Birnbaum and Staskal, 2004; Stapleton *et al*., 2005). Their types such as HBCD and PBDEs have been detected in air samples of the faraway regions as the Arctic and found in deep-seas mammals, indicating LRT of BFR components (Alaee *et al*., 2003; Remberger *et al*., 2004).

Soils can act as an important sink for POPs like PBDEs in the environment. POPs can be introduced to the soil either directly via point sources or indirectly via atmospheric transport (Jones and de Voogt, 1999). Moreover, volatilisation of PBDEs from soil to air is limited by the low volatility of PBDEs and strong adsorption of PBDEs to soil (ATSDR, 2015). Atmospheric POPs can accumulate in the surface environment via dry or wet deposition, even in remote mountain areas. In contrast, POPs in soil can be released to the atmosphere, surface water and groundwater through volatilisation, diffusion, leaching and surface runoff. Thus, POP-contaminated soils are a potential long-term source of environmental pollution (Jones and de Voogt, 1999).

Air pollution leads to exposure from contaminants that may be soaked by the lungs and gone into the other body organs. The leachate which is the percolated fluid that occurs as aquatic trickles underneath the polluted areas and it contains a leaching out chemicals. The landfill leachate can outcome in a leachate having a mixture of chemicals such as BFRs. The leachate

movement might affect the surface water, groundwater or soil by hazardous constituents. Contaminants in the water and soil can adversely impact the health of humans through inhaling, ingesting, or touching contaminated soil, as well as ingesting plants or animals that have accumulated soil contaminants (Basel Convention, 2004).

To date, at least 75 BFRs (Alaee *et al*., 2003) have been commercially produced. So far, studies have focused primarily on four groups: PBDEs, PBBs, HBCDs and TBBP-A (Covaci *et al*., 2011) i.e. the risk assessment has assigned HBCDs as having PBT properties (Abdullah, 2009) and it has been detected in air, sediments, freshwater and marine biota (de Wit *et al*., 2010) throughout the world.

One of the first reported environmental disasters related to these compounds arose when PBBs present in FireMaster^{TM} product were inadvertently added to animal feed instead of magnesium oxide in Michigan, USA in 1974. The ensuing contamination of farm animals resulted in the destruction of thousands of livestock and millions of chickens (IPCS, 1994; KLIF, 2010).

There is evidence that some NBFRs such as BTBPE, DBDPE and TBBPA-BDBPE may be persistent and can accumulate in the environment (Shi *et al*., 2009). Most BFRs, as well as NBFRs, are additive and can easily enter the environment during the production, usage and disposal of BFR-containing products (Hale *et al*., 2003, Shi *et al*, 2009). The latter types of alternative BFRs are more likely than legacy BFRs to leach from the finished products during use, disposal or recycling. Recently, concerns over the persistence, ability to bioaccumulate and potential for toxicity of some of the most widely used BFRs, like the PBDEs, have led to increasing regulation and restrictions on their production and use (Kemmlein *et al.*, 2009; Ashton *et al*, 2009; Papachlimitzou *et al*, 2012). Furthermore, de Wit *et al*. (2010) indicated that a number of NBFRs are of particular concern as they are being found in Arctic biota including

BTBPE, DBDPE, PBEB and TBECH, thereby, indicating long-range atmospheric transport (LRAT). PBEB was detected in glaucous gulls (Bjørnøya) while TBECH was found in beluga (Canada). Also, DBDPE was investigated for but not noticed in the ringed seals in Canada. These NBFRs results show that numerous of them are get into the Arctic and can pile in higher trophic ecosystems. For example, many of these compounds are being consumed as substitutes of PBDEs that have been prohibited or terminated, their occurrence in the Arctic is a cautionary sign for they may as well undergo LRAT. Furthermore, they are probably bioaccumulative and a rising use of these materials will drive to high concentrations of them in the nature environments with time.

While the inventories of environmental sources of PBDEs have not been completed, such sources are widely believed to include the leaching of these chemicals from a wide range of plastics, electronic equipment and textiles (de Wit, 2002). There is consequently a requirement to enhance the information of the dispersal of BFR combinations in the abiotic and biotic patterns, their spatial and temporal tendencies in the environment, and to provide a prove of they are undergoing LRT i.e. by testing the air samples of the remote locations (de Wit *et al*., 2010). Ultimately, there is an urgent research need to better identify sources of PBDEs, as well as to quantify emissions and document their potential environmental fate (Martin *et al*., 2004) as well as the other FRs contaminants.

The PFRs were found in the air samples of many remote marine regions, by this means they demonstrating a propensity of LRT (Möller *et al*., 2011, 2012). Additionally, air samples of Chicago and Cleveland cities presented greater concentrations contrasted to samples of the rural places in the US (Salamova *et al*., 2014). In particularly, TCIPP was the highest predominant PFR compounds exposed in rural and urban rainfall specimens. Bacaloni *et al*. (2008) concluded

that in three lakes water samples, the urban areas look further polluted by PFRs than the rural lake samples. PFR values in river water specify TCIPP concentrations in the UK to be significantly very abundant (Cristale *et al*., 2013) than the Italy concentrations (Bacaloni and Cavaliere, 2007; Bacaloni *et al*., 2008). Furthermore, TPhP has the uppermost vapor pressure of the aryl phosphates compounds, and has been detected in the remote air samples (Möller *et al*., 2011, 2012), a suggestion that it is has ability of travel over far distances (LRAT).

1.7.3. Exposure Pathways

The primary or most important pathway of exposure to BFRs for many people is through their diet, inhalation and ingestion i.e. indoor dust ingestion has been identified as an important source of exposure to legacy BFRs (Harrad *et al*., 2006). Furthermore, we cannot completely rule out dermal exposure, through absorption of BFRs from vapour or hand contact with dust or BFRs-containing products (Stapleton *et al.*, 2012).

Abdallah *et al*., (2016) have investigated the human dermal absorption of PFRs for the first time using human ex vivo skin and EPISKIN™ models. Results of human ex vivo skin experiments revealed 25% absorption of the applied dose (500 $ng\ cm^{-2}$, finite dose) of TCIPP after 24 h exposure. The EPISKIN™ model showed enhanced permeability values (i.e. weaker barrier), that were 11% for TCIPP compared to human ex vivo skin. However, this difference was not significant ($P > 0.05$). They also estimated dermal uptake of the studied PFRs via contact with indoor dust was higher in UK toddlers (median ΣPFRs = 36 $ng\ kg^{-1}$ bw day) than adults (median ΣPFRs = 4 $ng\ kg^{-1}$ bw day).

There are few data currently existing about the pathways exposure to NBFRs in human; though, according to their physicochemical properties, it is acceptable to propose when exposure of

BFRs, like PBDEs, HBCDs and TBBPA which happens through related pathways. The investigations that have indicated the NBFRs that found in the environment and foodstuff have been reviewed recently (Covaci *et al*., 2011). As a result, the environmental fate and behavior of many NBFRs is maybe a plausible hypothesis and they as well may be similar to those of "legacy" BFRs like PBDEs (Stapleton *et al*, 2008). That is for an arrangement to prepare an initial assessment of pathways exposure to NBFRs through indoor dust intake. There is an average level of adult and toddler ingestion of dust in the range of a 20 to 50 mg day^{-1}, and the highest dust digestion data that calculated for adults and toddlers is a 50 and 200 mg day^{-1} correspondingly. Many reasonable low-end, regular and high-end digestion exposure scenarios of the homes and mattress dust were guessed by gathering the floor and mattress dust concentrations. Also, using 5^{th} percentile, median and 95^{th} percentile in these data, respectively. These suppose a 12 kg body weight (bw) for toddlers and 70 kg bw for adults (Ali *et al*., 2012). The TCIPP pathway exposure estimation through breathing and dust digestion were at 4.1 and 2.1 ng day^{-1} kg bw^{-1} respectively. They are two and four times greater than the overestimation of the consumption water (Cequier *et al*., 2014). Nevertheless, the condition maybe dissimilar in the UK, values of a number of PFRs were measured in floor dust collected from UK living rooms, cars, classrooms and offices. While concentrations were overall broadly in the result zone of those studied earlier for North America, Japan and other European countries, median concentrations of TCIPP in all UK microenvironments exceeded those reported elsewhere in the world. Moreover, concentrations of TCIPP in 2 UK car dust samples were at 370 μg g^{-1} amongst the highest reported globally in indoor dust to date. When compared to concentrations of PBDEs determined previously in the classroom dust samples; concentrations of all target PFRs exceeded substantially those of those PBDEs that are the principal constituents of the

Penta- and Octa-BDE formulations. Moreover, while mass-based concentrations of BDE-209 exceeded those of most of target PFRs, they still fell below those of TCIPP (Brommer and Harrad, 2015).

As TCIPP concentrations in UK river water are up to 7.7 µg/L (Cristale *et al*., 2012), at minimum an order of magnitude greater than of them which stated in studies of Spain and Germany (Andresen *et al*., 2004; Rodil *et al*., 2012). Besides, the suggestions have been proposed that drinking water handling methods are not completely useful to remove the TCIPP compounds. Also remarkable that PBDEs concentration in the UK river water specimens were entirely under limits of detection (LOD). It is suggesting that exposure to PFRs via drinking water are likely more than for PBDEs (Cristale *et al*., 2012; Rodil *et al*., 2012). The Dust digestion has been presented to be a main pathways exposure of BFRs for adults and toddlers (Harrad *et al*., 2010). That pathways are probable likewise for PFRs, as their concentrations were exceeding significantly the PBDE concentrations in the similar samples of indoor dust (Dodson *et al*., 2012; Dirtu *et al*., 2012; Cequier *et al*., 2014). Correspondingly, the dust digestion was projected to cause of 54% of whole the children exposure to PFRs which have lesser vapor pressures properties (Cequier *et al*., 2014). It is believed that food that consumed by the human is the prime origin for exposure to numerous POP pollutants (Sjödin *et al*., 1999). In the Philippines samples, TPHP compounds discovered to be saturated in the aqueous particles, stabilize to surface sediments and cumulates via the benthic food chain (Kim *et al*., 2011).

In alike condition as adults exposed to PFRs, Children also are subjected to them even although they have smaller body weight. The fact, the children are very sensitive to health effects because

they still growing up. Based on this proof, consuming of mothers' milk by infants might be a serious exposure pathway for them (Brommer *et al*., 2012).

Alike to legacy BFRs, Cequier et al. (2004) described human exposure on NBFRs through air inhalation. This exposure was 1 – 2 orders of magnitude lesser than exposure to BFRs via dust ingestion. The leading exposure source of NBFRs via air (~80%) was the more volatile compounds in NBFRs i.e. DBE-DBCH the (Cequier et al., 2014).

1.7.3.1. Occupational Exposure

Through a variety of exposure routes, i.e. air inhalation, soil and dust ingestion, dermal uptake and food consumption, BFRs may enter the human body. High human's serum and breast milk PBDEs concentrations were correlated to high fish consumption (Sjödin et al., 2000). Workers exposed BFRs exposure through air inhalation and dust ingestion appearing throughout dealing with flame-retarded products, i.e. repairing furniture, electrical and electronic equipment. Jakobsson et al. (2002) observed that computer technicians take higher PBDE concentrations in their blood than computer clerks and hospital cleaners. This finding indicates that BFRs used in computers and electronics polluted the work environment and mount up in a worker's body. The is a correlation between some PBDE congeners and the period of computer work. So, assume that more computer duty work will lead to greater PBDE exposure (Julander et al., 2005).

There are very limited data on occupational exposure to NBFRs. Dust ingestion and air inhalation in the contaminated workplace is counted the primary exposure pathway for workers, particularly those working in e-waste recycling facilities. Large BTBPE concentrations in air of 0.1 - 10 pg m^{-3} were stated at BTBPE manufacturing site in the USA (Mandalakis et al., 2008). DBDPE Concentrations found in air and dust from electronic recycling plants, homes, offices,

cars and a hotel (Covaci et al., 2011). High concentrations of BTBPE and DBDPE were 29 ng m^{-3}, and 6.6 ng m^{-3} were observed in e-waste dismantling plant and dust samples close to an e-waste site (Shi et al., 2009). Also, concentrations of BTBPE and DBDPE were discovered to be 1900 and 9 times greater in the recycling facility's air than home air (Mandalakis et al., 2008), which might indicate a critical occupational exposure.

High concentrations NBFRs were found in air, and dust samples near NBFRs production factories or e-waste processing plants and the labours may be exposed to occupational exposure via air inhalation, dust ingestion, and dermal absorption. Hoh et al. (2005) analysed dust of e-waste area from China and found the concentrations of DBDPE and BTBPE were ~15 – 232 ng g^{-3} dw (average 107 ng g^{-3} dw) and 2 – 139 ng g^{-3} dw (average 107 ng g^{-3} dw), respectively. While BTBPE were found in two outdoor sites near BTBPE manufacture facility in the USA (70 and 19 pq m^{-3}). Also, BTBPE was found in e-waste recycling unit and the mean concentrations was 20000 pq m^{-3} (Hoh et al., 2005). BTBPE found at the mean of 5.8 pg m^{-3} in office air, which ca. 4000 times little than the recycling plant's concentrations. The superior levels detected in same recycling units are a hypothesis to arise because of bromine comprising additives to plastic products are emitted to the work environment from particle matter that generated by dismantling and shredding of FR-products (Sjödin et al., 2001).

1.7.4. Health Effects

Epidemiological studies generally focus on three main outcomes: endocrine disruption, neurotoxicity and reproductive toxicity. The available epidemiological studies tend to be based on key toxicological findings in laboratory studies (Wikoff and Birnbaum, 2011). The primary organs targeted by chronic exposure to PBDEs for children are the liver, kidney and thyroid

gland. These chemicals are endocrine disruptors and are known to block estrogen, progesterone and androgen receptors (Costa, 2008). However, most worrying is the fact that elevated PBDE blood levels have been linked to developmental neurotoxicity. This is because thyroid hormones play a crucial role in brain development. Studies have connected PBDE exposure and subsequent neurotoxicity with behavior changes and lowered cognitive function in infants and toddlers (Costa, 2007).

The IPCS (1994a) reported that environmental pollution caused by organic brominated compounds occurs and that their effects on the environment and human health is a cause of concern. In addition, there is the problem of polybrominated dibenzo-p-dioxins/dibenzofurans (PBDDs/DFs) formation as by-products in the process of manufacturing BFRs and during the combustion of products containing BFRs (Sakai *et al*, 2001).

BFR compounds pose a possibility hazard to the environment and human health. Many research papers have confirmed that these substances influence reversely on the on the thyroid hormones, endocrine systems, and neurobehavioral growth and they are the probable reason for a cancer tumor. (McDonald, 2002; Darnerud, 2003; Branchi *et al*., 2003; ATSDR, 2004; Herbstman *et al*., 2010; Muenhor *et al*, 2010). In an exposure study to NBFRs through dust digestion, the exposure concentrations for toddlers and adults together were several orders of magnitude lower than their corresponding reference dose (RfD) values. While this is reassuring, Ali *et al* (2011a) notes that the existing RfD values for NBFR compounds have been verified based on the old toxicological researches with a scarcity of strong or current information. Thus, the health influences of that exposures could not be wholly assessed now. For this reason, the existence of NBFRs in human micro-environments needs comprehensive investigations of the toxicological, which may be leading to revise of the RfD quantities (Ali *et al*, 2011a).

There is a lack of knowledge at present for NBFRs concentrations that will important in terms of body exposure. Accordingly, appreciation for human contact with their potential effects are based on the little information. Therefore, further data necessary demand to be collected; as well, biomonitoring investigations in human milk and blood, for example, are eligible. Furthermore, studies designed particularly to observe levels and scheme the pathway exposures. Connected with toxicological research studies, such will simplify NBFRs risk assessment from a humaneness perspective (Covaci *et al*, 2011).

An important exposure pathway of PFRs that has been deliberate might be air breathing, particularly surrounded the work environments. Human exposure to these substances through indoor air inhalation was small in indoor non-occupational areas (Bergh *et al*., 2011) in addition as well in outdoor atmosphere (Möller *et al*., 2011). In the comparison, an actual new Norwegian report (Cequier *et al*., 2014) points out that air considerably pays much towards human exposure to a greater vapor pressure of the PFRs. Specially, this research presented that the ingestion over breath of TCIPP compound was 49% of the whole intake of the PFRs. Additionally, the indoor atmosphere levels of PFRs were displayed to be about 2 orders of magnitude greater than BFRs within the same samples. Though, this study examined only living room therefore no findings could be illustrated on the over-all connection of the inhalation against dust digestion in the work environment. Whereas there is in a common absence of data about the health effects of TCIPP compound (Dodson *et al*., 2012), it is realized as possibly carcinogenic matter (van der Veen and de Boer, 2012). Furthermore, it could be accumulate in the liver and kidneys of wildlife, and it might a reasons of irritation in eyes and skin of the mice (Leisewitz *et al*., 2001).

1.8. Analytical Method for Determining FRs in Environmental Samples

Generally, the analytical methodology of the BFRs investigation in several abiotic samples contains of four main stages: sampling, extraction, purification and analytical procedures (Abdallah, 2009). The determination of FRs in environmental samples requires several steps and techniques. These compounds under consideration were chosen to represent wide variation in chemical properties (Nyholm, 2009). The NBFRs detection was frequently as collateral data following the examination of foremost BFRs. Hence there is a need to develop and improve the analytical approaches for NBFR elements to create a authoritative data. A current improvement is the usage of gas or liquid chromatography–mass spectrometry (GC-MS or LC-MS) built in systems for the instantaneous examination of many NBFR compounds. These methods require optimization, validation and application as an insistence situation (Covaci *et al*, 2011).

As most BFRs have the ability to bioaccumulate and a high degree of toxicity, monitoring their presence at or below $ng\ L^{-1}$ or $ng\ kg^{-1}$ concentrations is necessary. The analyses require highly sensitive and selective instrumentation as well as a large degree of analytical skill and expertise. GC-MS instruments can be used to analyse a number of BFRs and PFRs. Standards as well as reference materials are needed to obtain a proper assessment of the levels of these compounds in environmental matrices (Kolic *et al*, 2009).

Covaci *et al*. (2011) as well as Papachlimitzou *et al*. (2012) specifically focused and reviewed in detail the methodologies which have been used to date for the analysis of NBFRs in environmental samples, and make some recommendations regarding the need for further method development. The scheme is an example of a method where the emphasis is placed on sample clean-up and separation combined with low-resolution mass spectrometry (MS), rather than

relying on high-resolution MS techniques (Reeve, 2002). Also, this scheme is the framework of the analytical methodology in this study which will covered in Chapter (2).

1.9. Aims and Objectives of this Study

This thesis addresses some of the issues identified above. The overall goal is to increase the understanding of transfer, accumulation and transport of BFRs and PFRs from location to location and among different environmental media. The specific objectives are dictates the importance of investigating the hazardous effects of these compounds on humans and the environment. This study is an attempt to detect their residue in air and soil around landfills and to understand the mechanism of their leaching and volatilisation from the waste to the environment. Therefore, the general aim of this thesis is to generate data about the presence of BFRs in the environment and investigate in particular the ways of migration of PBDEs and PFRs from waste materials into the environment via laboratory experiments.

It is in this context that the present study was initiated, as part of efforts to find out more information about new and legacy BFRs concentration in soil and air within Oman landfills. Also, it will try to understand how the BFRs and PFRs leach out from waste.

The overall hypothesis tested in this study is that emission of BFRs and PFRs from landfilled consumer products and materials is resulting in contamination of the environment at concentrations that may be harmful to human health and wildlife. The primary objectives of this research are to:

1. Monitor the air and soil surrounding landfills in Oman to assess the potential emissions of BFRs from the waste stream.

2. Estimate the occupational exposure to BFRs via air inhalation and soil ingestion in surrounding lands of Oman and evaluate the implications of these exposure pathways to workers.
3. Elucidate the relative significance of possible pathway via which BFRs and PFRs may be emitted to the environment from waste streams via controlled laboratory leaching experiments under a variety of conditions.
4. To provide data and recommendations that can inform and motivate policy changes with respect to the management of BFRs and PFRs containing waste.

Chapter II: Sampling and Analytical Methodology

2.1. Synopsis

The analytical methodology that used in this study to investigate BFRs and PFRs concentrations in environmental and experimental samples is comprised of five major steps. They which are sampling, extraction, clean-up, The analytical methodology that used in this study to investigate BFRs and PFRs concentrations in environmental and experimental samples is comprised of five major steps which are sampling, extraction, clean-up, detection and finally data analysis. This chapter will clarify and discuss each of these procedures. Validation of the developed and applied analytical methods, as well as the quality assurance/quality control (QA/QC) protocol measures (Harrad, 2013), used to ensure the validity of the generated data will also be presented and explained. Many of useful computer software was used for carrying out of this study such as MS Offices, Thermo Xcalibur, Minitab 17 and Scrivener.

The sample types include soft furnishing Polyurethane foam (PUF) wastes, soil and air samples. The soil samples were collected according to Harrad and Hunter (2006) and Eguchi et al. (2013), and Air samples were picked as the method of Abdallah and Harrad (2010). The lab leaching experiment of this study used a single batch leaching procedure with similar conditions of a landfill.

2.2. Chemicals, Reagents and Materials

All chemicals, solvents, reagents and materials used for extraction and purification of this study samples were very high grade and supplied to the university by accredited companies. The

chemicals, solvents, reagents, materials and equipment details are as the following:

1. The solvents of HPLC analytical grade such as n-Hexane (Hex), Acetone (Ac), iso-octane, dichloromethane (DCM), methanol and Ethyl acetate (EA) were manufactured by Fisher Scientific, Loughborough, UK and the concentrated sulfuric acid purchased from Merck, Darmstadt, Germany.
2. The calibration (CS) and internal standards (IS) of individual PBDEs (BDEs 28, 47, 99, 100, 153, 154, 183 and 209), DBE-DBCH, TBP-DBPE, PBEB, BTBPE, DBDPE, EH-TBB, BEH-TEBP and labelled internal standards (IS) ^{13}C-BDE 209, ^{13}C-BTBPE and ^{13}C-BEH-TEBP were manufactured in Wellington Laboratories, Guelph, ON, Canada. TBBPA-BDBPE was purchased from Dr Ehrenstorfer, Essex, UK. BDEs 77 and 128 (IS) were gained from AccuStandard Inc., New Haven, CT, USA. TCIPP and TPhP were supplied by Chiron, Norway and d_{15}-TPhP as IS was purchased from Sigma Aldrich, UK. All these standard reagents were with the purity of more than 98%. The Recovery Standard Determination (RDS); PCB-129 in Hex was purchased from Greyhound Chromatography, UK.
3. The indoor dust NIST NIST dust standard reference material (SRM) 2585 was obtained from the US National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA.
4. The Florisil (particle size 60-100 mesh), silica gel (size 60Å, 70-320 mesh), anhydrous sodium sulfate (Na2SO4), humic acid (sodium salt) and sodium hydroxide solutions were supplied from Sigma Aldrich, Dorset, UK. The Hydromatrix™ was supplied by Varian Inc., UK.

   Activated florisil was baked at 450 C for an hour, cooled, cleansed once by ASE 350 (Table 2.4), dried, and stored in a clean sealed bottle glass. This prepared activated florisil should b used within the one-week maximum. Acidified silica (44% w/w) was prepared according to Method 1614 (USEPA, 2007).

5. The ISOLUTE® aminopropyl columns, solid phase extraction (SPE) cartridges and frits were purchased from Biotage, Uppsala, Sweden.
6. The deionized distilled Milli-Q water (DDW) was provided in the Public Health Laboratories, (PH, University of Birmingham, UK) and the oxygen-free nitrogen gas was supplied by BOC Gases, UK.
7. The equipment that used for sampling, preparing and analysing the samples in this research were as the Turbovap instruments (Zymark Turbovap® II (Hopkinton, MA, USA) and Biotage Turbovap® II) and as well as VWR™ Analog Vortex Mixer (VWR International, Germany), Carbolite oven, Fume Hoods, Agitation shaker, Maplelab Scientific hotplate, soil corer, scale, pH meter (Hanna, USA), freezers and cold stores (Polysec, UK). Also, there are a sort of plastics, glass fibre filter (GFFs) (12.5 cm diameter, 1 *μm* pore size, Whatman, UK and GC-50, 47 mm, 0.45 μm pore size, Advantec, Japan) and glassware and apparatus items were regularly used in samples collection and preparation.

2.3. Sampling

There are three sample categories considered and used for this study. These sampling methods were selected because they were having many benefits like they were practical and led to provide testable samples. Firstly, the soil samples were collected according to Harrad and Hunter, (2006) and Eguchi *et al*., (2009; 2013). Secondly, the air samples were picked by Passive Air Samplers (PAS) method that suitable for obtaining spatial data because of simplicity, low cost, effectively and electrical-free (Pozo et al., 2006; Abdallah and Harrad, 2010). Thirdly, the leaching experiments of this study are used the PUF waste samples in a series of triplicate standardized leaching experiments that developed and conducted to study FR

leaching from PUF wastes method (Stubbings, 2015) with adding some more parameters. These parameters were as dissolved humic matter (DHM) densities, the pHs of 5.8, 6.5 and 8.5, landfill temperatures, contact periods and measured the mass to leachate ratio. Also, these parameters were with the present of agitation (shaking at 200 rpm) and one part investigate the effect of no agitation.

Lastly, analysis of 44 soils, 32 air samples and 45 leaching samples in triplicate (n= 135) were conducted in this study. These methods were chosen to be conducted in this research work because of they are forceful and give good results.

2.3.1. Waste Polyurethane Foam (PUF) Samples

There are amount of three an end-of-life polyurethane foams (PUFs) were used widely in the UK and the USA for furniture especially upholstery in the couches, chairs and matrices. They were kindly donated from Dr. William Stubbings (UK PUF) and two PUF types from the Green Science Policy Institute (USA PUFs). The FR utilized by the manufacturer was unknown for all items prior to screening. These PUFs will be subjected in the leaching experiments in order to study how the behaviours of their FR-contents to leach out. Chapter 5 gives more details about the type of these PUF waste samples. Chapter 5 gives more details about the type of these PUF waste samples.

2.3.2. Passive Air Samplers (PAS)

Passive air sampling technology was demonstrated of truly quantitative since four decades (Palmes and Gunnison,1973), it has been widely used for environmental monitoring throughout the world. In many cases, it is the only practical means of determining pollution levels caused

by numerous anthropogenic chemicals. PAS today is practiced in various areas ranging from workplace exposure monitoring to global issues of climate change rising due to the presence of the different chemical compounds in the atmosphere (Seethapathy *et al*., 2008). PUF discs and GFFs were sheltered by two different size stainless steel housings (Table 2.1). PUF discs were washed in tap water, dried at room temperature and pre-extracted in ASE 350 for cleansing them (Table 2.4) while GFF filters were packed in Carbolite Furnace earlier to the field deployments. Shelters were cleaned carefully, and solvent rinsed to remove potential contamination.

As shown in Figure 2.1, PAS samplers consist of two pieces of sampling media; a PUF disc and a GFF filter entirely sheltered between two different size stainless steel housings. The opening holes in the bottom housing provide air and analyte movement in and out of the arrangement. On the subject of the advantageous properties of PUF disks, they have been applied as a receiving gas phase in the PAS while GFF filters have been employed as a particle phase receiver (Wilford *et al*., 2004; Hoh and Hites, 2009; Abdallah and Harrad, 2010; Drage *et al*., 2016).

Table 2.1: Specification of PAS contents that used in this study

Item	Description	Manufacturer/ Supplier
PUF disc	140 *mm* diameter, 12 *mm* thickness, 360.6 cm^2 surface area, 0.07 $g\ cm^{-1}$ density	PACS, Leicester, UK
GFF filter	12.5 *cm* diameter, 1 μm pore size	Whatman, UK
L-top housings	Stainless steel 23 *cm*	-
L-bottom housing	Stainless steel 18 *cm*	-

The PUF disc was mounted to the top of the shelter with only the downward face exposed to avoid any gravitational deposition of particles, as well as to eliminate ultraviolet radiation and minimize the effect of wind speed on the uptake in the case of the outdoor chamber. The reason of that because PUF has a high retention capacity for POPs compounds which are delivered by

air movement. The GFF was suspended in the middle of the housing (supported by a stainless-steel perforated disc mounted on the central screw) to trap the particulate matter. PBDEs can be particulate or gaseous phases i.e. BDE-209 is present predominantly in the particulate phase. This issue is in agreement with previous studies (Sjödin *et al*., 2001; Covaci *et al*., 2007; Seethapathy *et al*., 2008; Abdallah and Harrad, 2010). Therefore, a configuration of PAS was developed, calibrated, validated and used to monitor the concentrations of all the target PBDEs in air (Abdallah, 2010).

The advantages of using PAS is that it is firstly reusable, very slighter than high-volume air samplers (HVAS), further cost- efficient in contrast of active samplers, modest to deploy, visible and finally noiseless as no mechanical or power equipment is needed (Nothstein *et al*., 2000). These characteristics of PAS allow its extensive use in the ambient air without disrupting day-to-day activities (Muenhor, 2011). Furthermore, PAS characterized by allowing direct observing in more spatially distinguished places, do not want electricity and can deliver a time-weighted average (TWA) values that render them further suitable of chronic exposure valuation to the pollutants (Hazrati and Harrad, 2007).

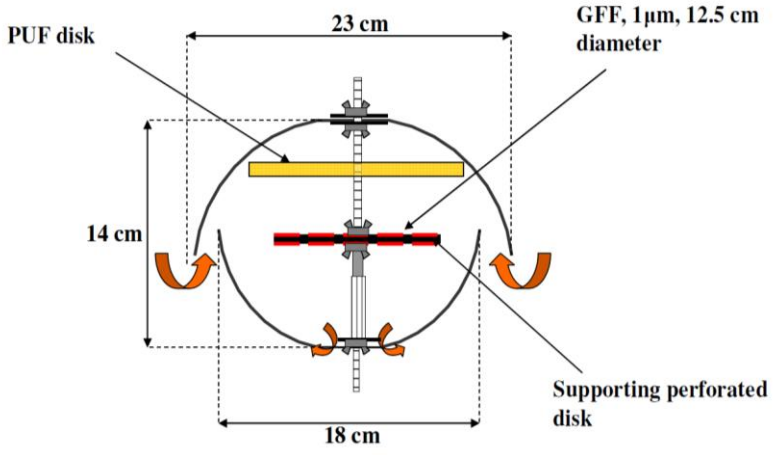


Figure 2.1: PAS Configuration Deployed

2.3.2.1. Passive Sampling Uptake Profile and Equilibrium Sampling Device (ESD)

The passive sampler runs in three regimes: kinetic, intermediate and near equilibrium. A first-order one-compartment model (Equation 1) is often used to fit experimental measurements. In principle, all PAS absorb contaminants from atmosphere as shown in Figure 2.4, which includes the generalized uptake profile according to the following Equation 1 (Mayer *et al*., 2003):

$$C_{\text{sampler}(t)} = C_{\text{medium}} * \frac{k_1}{k_2} * (1 - e^{-k1*t}) \quad (1)$$

Where $C_{\text{sampler(t)}}$ is the pollutant concentration on the sampler as a purpose of time, t, C_{medium} is the concentration of pollutant in the environment, and k_1 and k_2 are the uptake amount and the elimination rate constants, correspondingly.

In basis above, Figure 2.2 iin n next page demonstrate three likely scenarios. In the linear uptake regimen at moderately little sampling times, the C_{medium} could be assumed from the calculated $C_{\text{sampler(t)}}$ and the degree on which sampler is subjected to the average, rather stated as a volumes number that sampled each day per unit volume of the sampler (m^3 medium/ m^3 sampler). In the equilibrium scheme that put on at comparatively time-consuming sampling, an equilibrium segregating factor can be applied to conclude C_{medium} from C_{sampler} (Pawliszyn, 1997; Mayer *et al*., 2000, 2003). ESD refers to this regime requires sufficiently long sampling times to almost reach equilibrium (Mayer *et al*., 2003). However, this study was limited to two months sampling period to may be remain in the kinetic region in order for PAS to deliver concentration data.

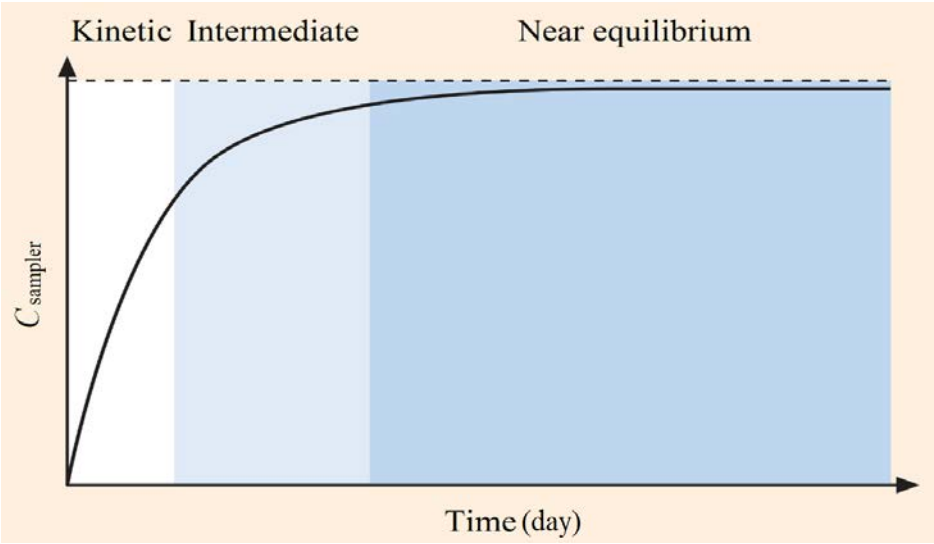


Figure 2.2: Generalized uptake profile for a PAS (Mayer *et al*., 2003)

2.3.3. Region of Field Sampling

Sultanate of Oman is located in the Middle East in the south-east of Arabian Peninsula. There are two landfills was chosen for air sampling study (Figure 2.3); one is Al-Amerat (Am) which serve some areas of Muscat, the capital of Oman and the another one is Raysut (Ra) in Salalah, a second large city in Oman. The sampling campaign took place in these landfills for 14 months for each one of these two landfills. The soil samples were taken from the vicinity and around of the six landfills which are Al-Amerat, Raysut, Nizwa (Ni), Sohar (So), Ibri (Ib), and Al-Buraimi (Bu) landfills (Table 2.2 and Figure 2.3). The soil sampling campaigns were between 2014 and 2015 and from other locations surrounding the landfills were in December 2015. The sample areas within the landfills far from their centres about 25 – 100 *m* and the samples areas outside these landfills far between 200 – 500 *m* even downwind or upwind. These sampling points regulated especially by the sites topographical and geological situations which are very complex in Oman. Because these landfills located far away from urban and located among hills or in desert areas.

Table 2.2: Universal Transverse Mercator (UTM) Co-ordinates of landfill sites, Oman

No.	Site/ Landfill	Co-ordinates		
		WGS84*	East (m E)	North (m N)
1	Al-Amerat (Am)	40 Q	649097.00	2582015.00
2	Raysut (Ra)	39 Q	814793.00	1880177.00
3	Nizwa (Ni)	40 Q	551677.00	2542722..00
4	Ibri (Ib)	40 Q	449507.00	2561267.00
5	Sohar (So)	40 R	462717.00	2677827.00
6	Al-Buraimi (Bu)	40 R	384631.00	2688828.00

* World Geodetic System 1984

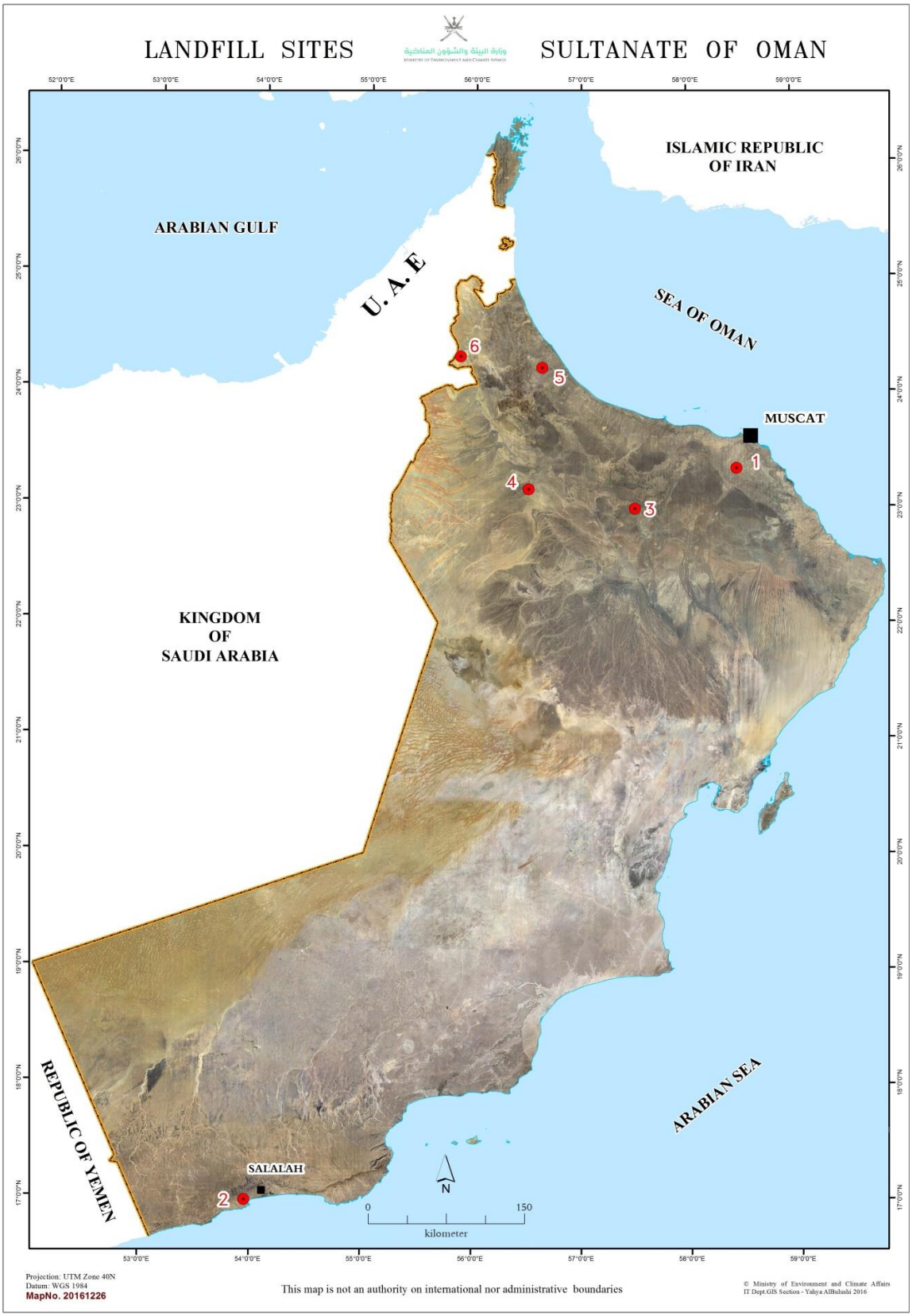


Figure 2.3: Sampling site locations in Oman

2.3.4. Field Sampling Strategy

There is coherent procedure to get accurate samples to assess the potential emissions of BFRs-containing waste to the environment from waste stream. Such wastes are discarded and final disposed at landfills as the last sink (Slack *et al*., 2004; Eggen *et al*., 2010; Weinberg *et al*., 2011). Air and soil samples were taken surrounding some of the landfills in Oman (Figure 2.3). Consequently, there are 28 air samples were collected for this study from Ra and Am landfills. Figure 2.4 and 2.5 show the aerial images of the Am and Ra landfills with wind rose during the period of sampling campaigns. The wind rose generated from the actual data of Directorate General of Meteorology (DGM) during sampling campaigns; June 2013 - July 2014 for Ra landfill and September 2014 - October 2015 for Am landfill (DGM, 2016).

Figure 2.4: The aerial image of the Am landfill, Muscat with wind rose during the period of sampling campaign

Figure 2.5: The aerial image of the Ra landfill, Salalah with wind rose during the period of sampling campaign

2.3.4.1. Soil Sampling

The soil texture types are mainly sandy-loam or loamy-sand in Oman (Hussain, 2005). These soil samples were collected surrounding six landfills in Oman between 2014 and 2015. Each sample was consisting of five subsamples that were taken using a soil corer to 5 cm surface depth from 20 m^2 areas located within and surrounded each studied landfill. The combo soil samples were pooled, transported back to the laboratory and immediately sieved through a 2 mm sieve, air dried, transferred to clean, solvent-rinsed, amber glass storage bottles, sealed, and stored at -20°C in food and water monitoring centre (FWMC), Muscat until analysis. Before extraction, soil samples were homogenized, an accurately weighed 50 g subsample was mixed with anhydrous sodium sulphate (20 g). The contaminants were then extracted from the soil

samples by ASE 350 in FWMC, Muscat. Final steps, each sample were placed in its CERTAN vial and then transported to Birmingham, UK. Later the vials saved into the freezer at 4˚C.

There are 22 soil samples were collected within six landfills in Oman between 2014 and 2015, and other 22 soil samples were collected from areas surrounding these landfills in December 2015. This total of 44 soil samples used to analysis of the concentrations of BFRs. Each sample was transferred to glass bottles and stored at -20^{o}C until extraction. At each sampling site, there were five subsamples were taken using a soil corer to 5 cm from 20 m^2 areas. Soil samples (n =44) were pooled, transported back to the laboratory and immediately sieved through a 2 *mm* sieve, air dried, transferred to clean, solvent-rinsed, amber glass storage bottles, sealed, and stored at -20°C until analysis. Before extraction, soil samples were homogenized, an accurately weighed 50 *g* subsample was mixed with anhydrous Na2SO4 (20 g).

2.3.4.2. Air Sampling

The air sampling techniques in this study were utilized depending on the physicochemical properties of the studied BFRs and the suitable technique is PAS in this study (Abdallah and Harrad, 2010). The PAS configuration deployed in the present study consisted of stainless-steel containers, will help in dampening the effects of wind speed on uptake rates, protect the sampling medium from coarse aerosol deposition, and prevent sunlight from reaching the PUF and GFF disks. Thereby it is minimizing the possibility of photo-degradation of target compounds (Shoieb and Harner, 2002; Gevao *et al*., 2006).

The air samples were collected from Am and Ra landfills using a PAS sampler in downwind and upwind locations of these landfills regarding to the dominant air direction in Oman. The campaign PAS were used to collect air samples over a two-month period. At end of each period

the PUF discs and GFF filters were replaced with new ones. Each period there are two points of sampling in a downwind and upwind of a landfill and each point contains 4 PASs. Later a 4 PUFs and 4 GFFs collected together to represent one sample calculated either downwind or upwind locations. The shelters were cleaned carefully and solvent rinsed to remove potential contamination every time of sampling. Moreover, before each deployment, a PUF disks were pre-cleaned in ASE 350 as in Table 2. 4 procedures (Page 69) and the GFF filters were backed by heating at 450°C for five h in Carbolite oven. The PUFs and GFFs were before and after each deployment wrapped with hexane rinsed aluminium foil and sealed in a polyethylene bags until analysis. Also, at each deployment, there was a field blank containing PUF and GFF discs as an air sample.

A total of 32 air samples obtained surrounding of two landfills in Oman using passive air samplers (PAS). There were two sampling points at each landfill, and each point contains 4 PASs assumed as one combo sample to prevent any loss or accident in these deployments. The campaign PAS were used to collect air samples over a two-month period between June 2013 - July 2014 for Ra landfill (n=14) and September 2014 - October 2015 for Am landfill (n=14). Further, four single air samples were collected in outside landfills as reference sites between July - August 2016. In each deployment period, the PUF discs and GFF filters were changed with new ones. Also, in each deployment, there was a field blank containing PUF and GFF discs as air samples were examined to check the levels of target pollutants. The shelters were cleaned carefully and solvent rinsed to remove potential contamination every time of sampling. The PUFs and GFFs were before and after each deployment wrapped with Hex rinsed aluminium foil and sealed in a polyethylene bags and they were stored at -20°C until analysis.

2.4. Passive Sampling Rate (*R*)

Passive Sampling Rate (*R*) (m^3 day^{-1}) was needed to know not only the mass of contaminant sequestered by the sampler over the course of its deployment but the volume of air sampled over the same period. It is necessary to conduct a calibration exercise to determine the passive air sampling rates for each of the studied compounds, and this approach was not one of the aims of this study. Thus, to achieve this, there is estimation to find suitable R values for ESD because there is no knowledge until a recent date for R data of NBFRs. Drage *et al*. (2016) were solved this problem that has been assumed equivalent sampling rates of them to PBDEs of similar in log Koa values which described in the physiochemical properties section in the previous chapter (section 1.5).

However, for more accurate, we assumed equivalent to literature R rates of similar in Bromine number, molecular weight, and physiochemical properties i.e. K_{OA} and K_{OW} values, will give more statistically significant R values of BFRs. This method has resulted in the next Table 2.3. however, in order to Quantitative data on airborne contaminant concentrations from PAS samplers, sampling rates R of PBDEs and NBFRs in the Table 2.3 were obtained from Abdallah and Harrad (2010) and Drage *et al*. (2016) which they use PAS and Hazarati and Harrad (2007) use PUF plugs only in their study. *R* values were calculated using the following Equation 2:

$$R = \frac{(R)_{L1} + (R)_{L2} + \cdots + (R)_{nL}}{Ln} \quad (2)$$

While,$(R)_{nL}$is sampling rates in literature; Ln: number of *R* readings in literatures which are Abdallah and Harrad (2010), Drage *et al*. (2016) and/or Hazarati and Harrad (2007) and Ln in this case are 1, 2 and or 3.

Table 2.3: Passive sampling rates (*R*) (m^3 day^{-1}) of the BFRs used in this study

BFR	*R* (this study)[d]	Br No.	Molecular Weight (g/mol)	Log K_{oa}	*R* in Literature
PBDEs:					
BDE-28	2.27	3	406.89	9.47	1.74[a], 2.80[c] (*R* of TBECH)
BDE-47	1.98	4	485.79	10.37	1.95[a,b], 2.00[c]
BDE-99	1.43	5	564.69	11.29	1.12[a], 1.57[b], 1.60[c]
BDE-100	1.52	5	565.69	11.26	1.34[a], 1.63[b], 1.60[c]
BDE-153	1.40	6	643.58	12.05	1.39[b], 1.40[c]
BDE-154	1.44	6	643.58	12.01	1.44[b]
BDE-183	1.12	7	722.51	12.47	1.14[b] ,1.10[c]
BDE-209	0.56	10	959.21	16.48	0.57[b] and 0.55[c]
NBFRs:					
TBECH	2.80	4	427.8	8.01	2.80[c]
EH-TBB	1.95	4	549.92	12.32	1.95[b] (*R* of BDE-47)
PBEB	1.63	5	500.65	9.95	1.63[b] (*R* of BDE-100)
BTBPE	1.39	6	687.64	15.35	1.39[b] (*R* of BDE-153)
BEH-TEBP	0.56	10	706.14	16.9	0.57[b] ,0.55[c]
DBDPE	0.56	10	971.22	19.11	0.57[b] ,0. 55[c] (*R* of BDE-209)
TBBPA-DBPE	0.56	10	943.61	20.70	0.57[b],0.55[c]

a) Hazrati and Harrad, 2007 b) Abdallah and Harrad, 2010 c) Drage *et al*., 2016.

2.5. Leaching Experimental

This section describes a series of standardized leaching tests that were conducted to study FR emissions from a PUF wastes. The leaching experiments were applied by using a variety of leaching fluids to mimic the real landfill leachates characteristics such as pH levels, humic matter, agitation, and step temperature.

2.5.1. Preparation of Samples and Leaching Fluids

In preparation for the leaching experiments, PUF samples were cut into small pieces (approximately 1 cm^3, equivalent to 0.5 g) from each of the three PUF samples and weighed accurately. When analyzing these samples to pre-determine initial analyte concentrations, small pieces of PUF (approximately 0.125 cm^3, equivalent to 50 mg) were taken each sample.

In this study, leaching fluids were prepared by mix up of the following materials;

1) DDW Milli-Q water,
2) Sodium hydroxide solutions to adjust the pH and
3) Dissolved humic matter (DHM) solution.

The solution was stirred for 5 minutes up until total dissolution then the pH was adjusted to the desired level before finally it was centrifuged at 2000 rpm for 1 min. Concentrations of DHM solutions used in experiments were 100 mg L^{-1} and 1000 mg L^{-1}. The pH levels were determined using a pH meter at 5.8 (acidic), 6.5 (slightly acidic) and 8.5 (alkaline). These levels were based on real landfilled leachates that lie in the range 5.8 - 8.5 (Renou *et al*. 2008).

2.5.2. Leaching Experimental Design

Triplicate distinct of single batch experimental scenarios on PUF wastes were undertaken to examine the effects of numbers of landfilled effect parameters and stages. These steps contain reviewed the contact time with the leaching fluids, pH levels and Ratio of the sample to leaching rate. They were conducted under the fundamental conditions of temperature and agitation.

These experiments willing to investigate the extent of leaching, its kinetics and how these are influenced by the factors of waste: leachate contact time; agitation; leachate temperature; DHM content of leachate; Leachate pH; and waste: leachate mass: volume ratio.

To address these goals of the study, the leaching experiments were conducted by single batch experiments and carried out in triplicate. They were done according to following stages;

1. Contact time: contact times of 6, 24, 48, 72 and 96 h at 20□C, using DDW Milli-Q, pH adjusted at 6.5 and DHM is 0 mg L^{-1} with agitation (200 rpm). This stage was repeated at 60 and 80□C. We use DHM 0 mg L^{-1} to make comparison later with different DHM levels.

2. Effect of Agitation: experiments in (a) were repeated at 60□C only without agitation.
3. Effect of DHM: experiments in (a) were repeated at 60□C only with agitation and were used (i) 100 mg L^{-1} DHM and (ii) 1,000 mg L^{-1} DHM.
4. Effect of pH: experiments in (a) were repeated at 60□C only with agitation, using (i) pH 5.8; and (ii) pH 8.5.
5. Effect of waste: leachate mass: volume ratio: experiments in (a) were repeated at 60□C only with agitation but with a waste: leachate ratio that is 10% of PUF that was used in the (a) experiments in 100 mL of DDW Milli-Q water.

The experiments were conducted in a triplicate single batch to get a confidence results. In the first setup, the treated sample is contacted once with the leaching fluids for a set programmed contact time of either, six h, 24 h (one day), two, three and four days. Then the leachate was extracted from the contact PTFE vessel via pouring or draining through a GC-50 GFF, in which the contact vessel was upturned for approximately 5 minutes to ensure all leachate fluids was removed as possible. Also, PUF was gently squeezed against the side of the contact bottle using a pre-cleaned stainless steel spatula to drain the retained leachate within the foam. The PTFE bottles (500 mL) were used as contact vessels during controlled leaching experiments. The whole volume of the contact vessel was not entirely filled with leaching liquids, and as a result, a headspace was present inside the contact vessel. A 1 g of PUF sample was contacted with 100 mL of DDW Milli-Q water giving a liquid-solid ratio of 100:1 (v/w). Subsequent addition of the sample and the leaching fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired contact time and temperature that regulated by hotplate.

2.5.3. Calculation of the Leaching Percentage of FRs

The percentage of leaching FRs present (*PL*) of the PUF waste that was leached into each leachate sample was calculated as follows Equation 3:

$$PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W}\right] \times 100\% \quad (3)$$

Where $C_{leachate}$ is Concentration of FR collected in leachate (mg L^{-1}); V is volume of leachate (L); C_{waste} is Concentration of FR in waste sample (mg kg^{-1}); W is total weight of waste sample (kg).

According to the previous Equation 3, the *PL* controlled by contact time. Then the Percentage leached relativized to time (*PLT*, % h^{-1}) is stated as the percentage of FR leached from the PUF waste per hour of contact time. *PLT* is calculated as the following Equation 4:

$$PLT = \frac{PL}{Ct} \quad (4)$$

Where *PL is* percentage leached (%); *Ct* = contact time (*h*).

2.6. Extraction

2.6.1. Accelerated solvent extractions (ASE)

Dionex ASE 350 (Dionex Inc., Europe, U.K.) instrument is a type of pressurized liquid extraction (PLE) or well known as accelerated solvent extraction (ASE). This device represents an exceptionally effective extraction technique compared to alternative methods (Balasubramanian and He, 2010). As well as (van den Eede *et al*., 2012) confirmed that a suitable method for both BFRs and PFRs using a mixture of Hex and Act (3:1, v/v). This method validation proved that accuracy, precision and limits of quantification are satisfying for most compounds and can save time of sample extraction. As well, the results of the SRM 2825

obtained with this method were in agreement with the previously reported and certified values for PBDEs and some NBFRs (Table 2.5). But there were no known SRMs data available for PBDEs, TCIPP and TPhP in aqueous solutions.

Using ASE 350 device with a mixture of Hex-Ac (3:1, v/v) method was implemented in this study for soil and air sample extraction and washing of PUF and Hydromatrix according to the parameters in the following Table 2.4.

Table 2.4: Conditions of ASE 350 for extraction and cleansing

Parameters	Extracting	Cleansing
Temperature (°C)	100	100
Pressure (psi)	1500	1500
Heating time (m)	5	5
Static time (m)	4	4
Purge time (s)	90	90
Flush volume (%)	60	60
Static cycle	3	1
Solvents	Hex-Ac (3:1, v/v)	Hex-Ac (1:1, v/v)
Cell type	Stainless steel 66 mL	Stainless steel 66 Ml

2.6.2. Soil and Air Samples Extraction

As indicated in the previous subsection (2.6.1) that using the Dionex ASE 350 extraction method is more robust than other extraction methods that used for extracting of POPs components. The soil and air samples for this study were selected to be extracted by this method. The soil samples, PUF discs and GFF filters were extracted by ASE 350 according to the method in the above Table 2.4. For air samples, PUFs and GFFs separately were put in the precleaned ASE 350 66 mL stainless steel cells containing prewashed hydromatrix to fill the void volume of the cells. Soil samples were well-homogenized prior to extraction using ASE 350. Accurately weighted aliquots (typically 50 *g*) were loaded into precleaned ASE 350 66 mL stainless containing 1.5 g

florisil and hydromatrix to fill the void volume of the cells. Then extracts were spiked with a mixture of 20 ng of each $^{13}C_{12}$-labelled BDE47, 99, 153, BTPE, BEH-TEBP and 40 ng of $^{13}C_{12}$-labelled BDE-209 in iso-octane as IS. They were evaporated to incipient dryness on Turbovap II, resolubilized in 1 mL of Hex and vorexed for 30 s. Afterwards, the extracted solutions of soil, air and leaching samples were following the purification steps in the next section (2.7).

2.6.3. Leaching Samples Extraction

Firstly, for predetermined the amount of FRs in the PUF samples, A 50 mg PUF sample and 5 mL of EA were put into a precleaned test-tube, swirled by vortex device for 1 min and then sonicated in the sonication bath for 5 mins in advance to be centrifuged for 2 mins at 2000 rpm. We selected EA because it is polar and can extracted PBDEs, NBFRs, and PFRs in high concentrations (Van den Eede et al., 2012). After that the above layer in the tube (the supernatant) was shifted to another tube. It will be refined more and all supernatants were collective together (10 mL total) and then swirled for 1 min. Afterwards a 1 mL of it was moved to a new tube and added 9 mL EA for dilution. Lastly, first diluted of 10 μL was relocated and added a 90 μL of methanol having a 90 ng d_{15}-labelled TPhP as IS (10,000 times dilution in total). These predetermination tests of PUF were analysed in triplicate.

Each experimental leachate was spiked with 50 ng each of $^{13}C_{12}$-labelled BDEs 47, 99 and 153 and 10 μg of d_{15}-labelled TPhP, as IS for PBDEs and TCIPP respectively. Then the collected filtrate was extracted in series using three times of 50 mL DCM by liquid-liquid extraction with mechanical shaking for 10 minutes each time. Approximately 5 - 10 mL 2% NaCl solution was used on these leachates which not containing DHM for enhancing separation after extraction.

Finally, the combined DCM crude extracts of the leachates were dried via filtration through 5 g Na_2SO_4 and they were following the purification procedures (Figure 2.6).

2.7. Purification (Clean-up)

The concentrated extracts in this study were subjected to the following clean-up methods:

2.7.1. Clean-up of Air and Soil Samples

In this study, SPE method was proposed because it is effectiveness and reliable clean-up method developed for BFRs compounds (Sahlstörm *et al*., 2012; Dirtu *et al*., 2013; Al-Omran and Harrad, 2015). The crude extract was evaporated to 0.5 mL using a Turbovap II and vortexed (speed 4, 30 s). Then, the concentrated extract was quantitatively transferred onto a SPE column packed with 2 g pre-washed and conditioned Florisil with 15 mL of Hex. Cautious was taken to assure the SPE columns were never out of solvent once conditioned (Al-Omran and Harrad, 2015). The sample fractionation was performed on SPE column and the analytes were eluted in two fractions as the following:

1. First fraction (F-I); PBDEs, DBDPE, TBBPA-DBPE, TBECH and PBEB were eluted with 12 mL of Hex.
2. Second fraction (F-II); BTBPE, EH-TBB and BEH-TEBP were eluted with 15 mL of EA.

Afterwards, F-I was evaporated to 1 mL under a gentle nitrogen stream and transferred onto a two g 44% w/w acidified silica SPE cartridge, pre-conditioned with 15 mL Hex, prior to elution with 15 mL Hex: DCM (1:1 v/v). F-II was evaporated to incipient dryness under a gentle nitrogen stream, resolubilized in 2-3 mL Hex, before the reduction in volume to 1 mL, and transfer onto an aminopropyl functionalized silica column (0.5 g, pre- washed with 6 mL Hex).

Then it was eluted with 12 mL Hex: DCM (1:1 v/v). Hence, the procedures are done to get F-I and F-II because each fraction has different compounds than others regarding the polarity of the targeted these compounds. F-I and F-II were combined and evaporated under nitrogen flow using a Turbovap II to incipient dryness, before re-solubilisation in 100 mL of iso-octane containing PCB-129 at 250 pg/mL and transferred to GC vial ready for GC-MS analysis. Figure 2.4 show a summary of clean up procedure that used in this research.

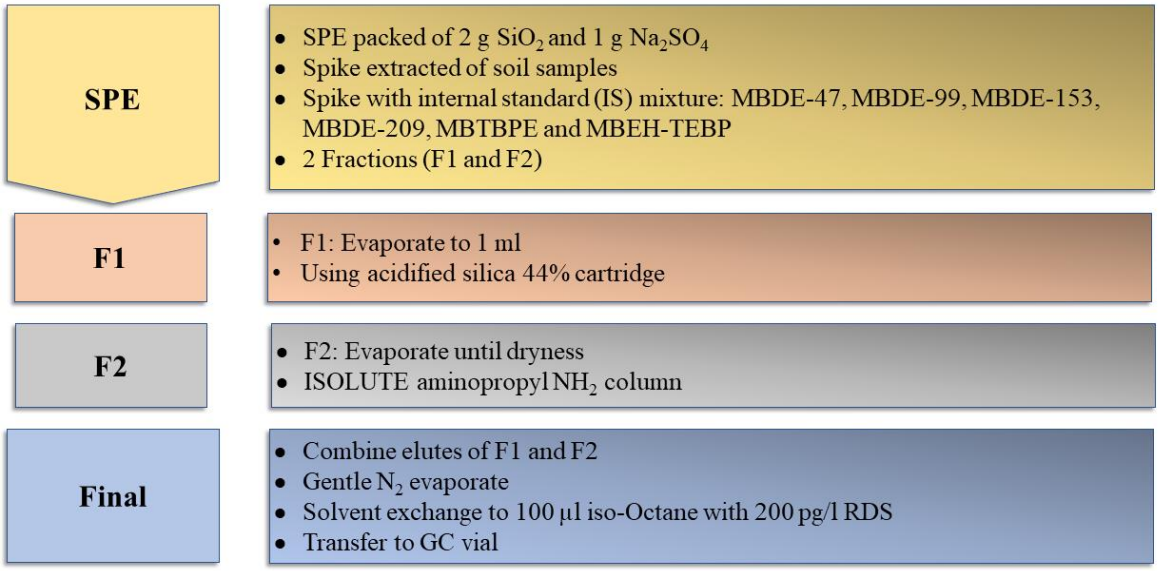


Figure 2.6: Steps of clean-up procedure

2.7.2. Clean-up of Leaching Samples

In the first step, the crude extract of leachate samples was concentrated to 0.5 mL using a Turbovap II with the solvent exchange to Hex (DCM was used in extraction) before being loaded onto a 2 g pre-cleaned, activated florisil SPE column and washed with 20 mL Hex; then the sample eluted using 30 mL EA. The eluate was evaporated to incipient dryness and then reconstituted to 100 µL with the addition of 25 ng d_{15}-labelled TPhP as recovery standards in methanol. The second step, portion of a 10 µL aliquot was taken from the previous step and

diluted with 990 µL of methanol, and then the action repeated to yield a 10,000 times dilution (dilution factor 1:10,000). Finally, there are two separately vials of the same sample. That was needed due to high TCIPP concentrations in the sample.

Stubbings (2015) has conduct a QA/QC trial experiment to assess the recovery efficiencies of native TCIPP and d_{15}-labelled TPhP IS. A 2 g pre-cleaned, activated florisil column was washed with 10 mL DCM before loading with 1 µg each of the above native and IS. The florisil was then washed with 20 mL Hex then eluted using two times of 15 mL EA. These three eluted were separately collected, evaporated and reconstituted in methanol for analysis. The average results of the collected Hex wash and two EA elutions are provided in Table 2.5. The quantity of recovered native TCIPP and IS in the Hex wash was < 2.1 % and the majority was eluted within the first step of EA (> 90%). It was necessary to dilute compounds in the sample prior to analysis. Therefore, due to the soaring of TCIPP concentrations in the samples, it was necessary that prior to analysis via GC/MS, the samples should undergo further stages of dilution. In which a 10 µL aliquot was taken and diluted with 990 µL of methanol and then the step repeated again to yield a 10,000 times dilution (Stubbings, 2015).

Table 2.5: Average of TCIPP and d_{15}-TPhP (IS) recoveries (%) in clean-up QA/QC trial experiment performed in duplicate (Stubbings, 2015)

Target analytes	Hex wash	**Recoveries (%)**		
		1st EA elution	2nd EA elution	Total
TCIPP	2.05	90.5	4.0	94.5
d_{15}-TPhP	1.08	92.5	3.2	95.7

2.7.3. Relative Recoveries of Calibration (CS) and Internal Standards (IS)

By using the previous clean-up method, relatively high satisfactory and reproducible results were achieved for almost target compounds. These results were satisfying recoveries with that were obtained when using an acid silica column of Ali *et al*. (2011) study. The acid processing is preferred for elute the non-polar solvent fraction to carried out via acidified silica (Ali et al., 2011; Van den Eede et al., 2012). Furthermore, the activated acid silica has a significant role to affect the degradation of some of the target compounds. The EH-TBB, BEH-TEBP and BTBPE have not to be subjected to acid treatment because of they may degraded (Sahlstrom et al., 2012; Ionas and Covaci, 2013). The smaller recoveries when using acidified silica may be attributed to longer contact times with acid and surface dependent reactions when using this reagent as opposed to neat acid (Guo *et al*., 2014). Table 2.6 in the next page show the average relative recoveries of FRs on the clean-up method in this study by using the Equation 5.

Table 2.6: Average relative recoveries (SD) of the calibration and internal standards (CS and IS) for BFRs (n= 6) and PFRs (n= 3) in this study

FRs	Recovery % (SD)	FRs	Recovery % (SD)
PBDEs:		NBFRs:	
BDE 28	83 (4)	DBDPE	95 (11)
BDE 47	97 (5)	DBE-DBCH	62 (5)
$^{13}C_{12}$-labeled BDE 47	95 (2)	PBEB	97 (3)
BDE 77	100 (7)	EH-TBB	100 (6)
BDE 99	95 (5)	BTBPE	98 (4)
BDE 100	94 (6)	$^{13}C_{12}$-labeled BTBPE	99 (13)
$^{13}C_{12}$-labeled BDE 99	100 (11)	$^{13}C_{12}$-labeled BEH-TEBP	96 (6)
BDE 128	100 (9)	BEH-TEBP	97 (4)
BDE 153	102 (10)	TBBPA-BDBPE	65 (7)
BDE 154	100 (8)	**PFRs:**	
$^{13}C_{12}$-labeled BDE 153	99 (12)	TCIPP	96 (5)
BDE 183	98 (7)	TPhP	97 (3)
BDE 209	101 (12)	d_{15}-labeled TPhP	97 (8)
$^{13}C_{12}$-labeled BDE 209	99 (5)		

SD is standard deviation

2.8. Quality Assurance and Quality Control (QA/QC)

Using of Organic Pollutants Research Group QA/QC Protocol in the Environmental Health and Risk Management Division (Harrad, 2013). This protocol document describes the generically applicable methods and procedures that followed in this study to ensure the reliability of the analytical data.

2.8.1. Identification and Quantification Criteria

To assess any losses or breakthrough of analytes associated sampling method used in this study, soil, PUF, GFF and leachate crude extracts were spiked with known quantities of IS (20 ng of each $^{13}C_{12}$-labelled BDEs 47, 99 and 209, BTBPE and BEH-TEBP and 40 ng of $^{13}C_{12}$-labelled BDE-209) prior to using of the SE 350. Also, crude extracts were spiked with known quantities of IS (50 ng each of $^{13}C_{12}$-labelled BDEs 47, 99 and 153 and 10 µg of d_{15}-labelled TPhP) before leaching experiment extraction procedures. The reason for using these ISs is because the detected ions for native and isotope isomers are different for these compounds and therefore there are no interferences between the fragmentation of them. In contrast, the BDEs 77 and 128 were used for quantification of other target compounds as the level of these two compounds in the environment are extremely low and will not affect their response when used as IS.

The IS Labelled analogues ($^{13}C_{12}$) of the FR analytes were utilized in this method to amend the analyte absence or breakthrough because of the extraction and clean-up methods, instrumental biases or matrix influences (signal suppression or improvement due to further elements existing in the sample). As per the isotope almost correspond the analyte in the natural chemical, shape and magnitude, they are predictable to tolerate the identical effect by any of these consequences. Therefore, a percentage of the reaction of an analyte on the IS stays the similar and refuses any

outcome. As of this proportion, the analyte rate could be assessed with larger assurance. Satisfactory recoveries of the IS are typically should be around 70%, but it can fall in the range between 30 to 150% (Harrad, 2013). The recovery that greater than 100% is likely because of instrumental bias, or matrix influences producing a signal improvement, creating a developed the detector reaction. For the IS, the signal to noise ratio (S/N) must be 20:1 for the highest zone to be categorized as suitable peak (Ambidge *et al*., 1990).

The recoveries of IS in the sample preparation were calculated using the RDS added to the samples in advance of GC-MS analysis. In this study, PCB-129 was used as RDS for IS for BFR and PFR compounds. The recoveries of the IS in each sample were calculated as in the following Equation 5:

$$\%\text{IS Recovery} = \left[\left(\frac{A_{IS}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{IS}}\right)_{STD} \times \left(\frac{C_{IS}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{IS}}\right)_S\right] x\ 100 \quad (5)$$

where $\left(\frac{A_{IS}}{A_{RDS}}\right)_S$ is the ratio of internal standard peak area to recovery determination standard peak area in the sample; $\left(\frac{A_{RDS}}{A_{IS}}\right)_{STD}$ is the ratio of RDS peak area to IS peak area in the CS (the average values calculated using two-CSs injected before and after this batch of samples); $\left(\frac{C_{IS}}{C_{RDS}}\right)_{STD}$ is the ratio of concentration of internal-standard to concentration of RDS in the calibration standard; and $\left(\frac{C_{RDS}}{C_{IS}}\right)_S$ is the ratio of concentration of RDS to concentration of internal-standard in the sample.

To confirm the specific retention time (R*t*) and the qualifier and quantifier ions of mass ratio (*m/z*) for each studied analyte, the pure individual standards of each of them was injected (1 ng on column) on the GC/MS in used method. Therefore, the chromatogram peak of a target pollutant in a sample was quantified by considering the following requirements:

1. Ratio of S/N must exceed 10:1.

2. The isotope ratios must not exceed ± 20% of the average value for the calibrations standards which were injected before and after the sample batch.
3. The relative retention time (RRT) of the peak in the sample necessity does not exceed ± 0.2% of the average value calculated for the same compound in the calibrations standards which injected before and after the sample batch.

2.8.2. GC/MS Instrument Calibration

A complete five-point calibration was conducted for each of the studied contaminants containing native analytes, labelled internal standards (IS) and labelled recovery determination standards (RDS), to assess the linearity of the MS response. Table 2.7 show the concentrations of the native and isotopes of PBDEs, NBFRs, TCIPP and TPhP (CS, IS and RDS) that were performed to get a well-defined calibration. Also, the typical five-point calibration curve was illustrated in Figure 2.4 it was nearly represented all analytes five-point calibration. The CS were run on the GS/MS for a short batch run list (i.e. ten samples), or before and after every 20-30 samples of a long batch isting, to evaluate any driftage of the instrumental during the investigation. The identical IS and RDS typical solutions applied for samples protection were exercised for the CS preparation. When a fresh RDS or IS standard was formulated, recent CS should equipped with it, that is to decrease somewhat inter-standard difference in the concentration. The CS was as well completed on a steady base (subject on instrument usage) in CERTAN vials then saved into the freezer at 4˚C once not in GC/MS analysis, to lower the degradation of analyte or inter-conversion produced by ultra violet radiation (UV) or the mixture age.

Table 2.7: Concentrations of CS, IS and RDS of BFR and PFR compounds (pg µL^{-1})

Standard	BFRs Natives	TBBPA-BDBPE	$^{13}C_{12}$-labeled BFRs (IS)	PFRs Natives	d_{15}-TPhP (IS)	PCB-128 (RDS)
A	25	1000	250	50	100	250
B	50	2000	250	100	100	250
C	200	6000	250	400	100	250
D	500	7500	250	1000	100	250
E	1000	10000	250	2000	100	250

The typical chromatograms of CS standard (C), showing the resolution of the analytes and isotopes of FRs compounds based on the calibrations of Table 2.7 above are presented in the next Figure 2.7.

The relative response factors (RRFs) is the instrument response for a unit amount of target pollutant relative to the instrument response obtained for the same amount of the internal standard (IS). The five-point calibration plot of ISs were used to calculate RRF for each of the target compounds by using the following Equation 6:

$$\text{RRF} = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{NAT}}{C_{IS}} \quad (6)$$

Where A_{NAT} is the peak area of the native compound (i.e. the ^{12}C or ^{1}H isotope of the target compound); A_{IS} is the peak area of the internal standard used for each analyte; C_{NAT} is the level of the native compound; and C_{IS} is the concentration of the IS. The relative standard deviation (RSD) percent of the RRFs calculated for studied compounds at the five-points of its calibration curves did not exceed 5%.

The standard (C) in previous Table 2.7 was injected before and after each batch of ten samples. The average RRFs of the target compounds from these two injections are calculated. These must be within ± 25% of the average RRFs obtained for that standards in the initial five-point

calibration curve and used for calculating the concentrations of the target compounds in samples of this batch using following Equation 7:

$$\text{Concentration} = \frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS} \quad (7)$$

Where A_{NAT} is peak area of target pollutant in sample; A_{IS} is peak area of internal standard in sample; RRF is relative response factor for the target pollutant; M_{IS} is a mass of IS added to sample (ng) and SS is a sample size (L or g). Hence, this Equation 7 was applied by Xcalibur software directly.

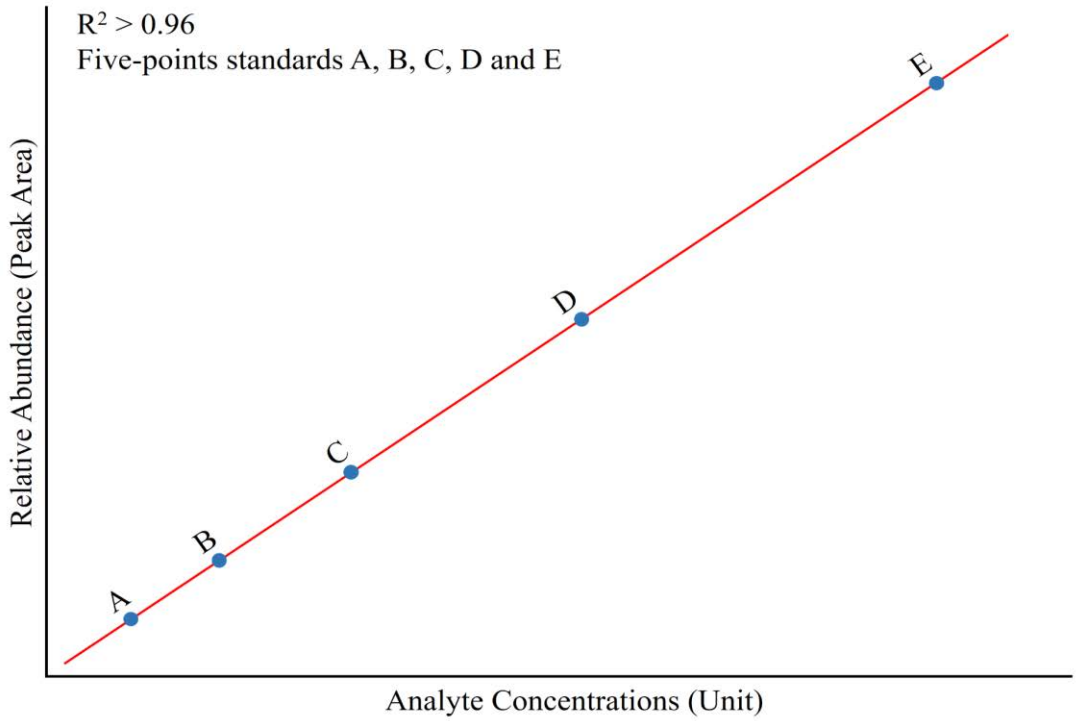


Figure 2.7: Typical calibration curve of all native FRs compounds in this study

2.8.3. Field and method blanks for air samples

There were field and method blank samples of air and soil surrounding the landfills during sampling campaign and lab analysis used as a control. Also, there were method or system blanks

of the lab leaching experiments. Field blanks are used to assess any cross contamination from the sampling situations at the sites, transport, handling and storage of the samples. Air field blanks (n=15) consisting of a pre-cleaned PUF and baked GFF disks for each air samples deployment and they were treated in identical fashion to those used for sampling, except that no air was aspirated through them. Soil field blanks (n=8) for soil samples consisting of precleaned Na_2SO_4 each five soil samples. Also, there were air (n=4) and soil (n=8) method blanks i.e. same as field blanks, but the disks or Na_2SO_4 were not transported to/from the sampling site. System blanks (n= 27) of the leaching experiments were used DWW Milli-Q as a leachate. Roughly, one method blank in the lab was prepared using the similar analytical method for each batch of five samples. According to the analytical procedures, if any of the pollutant concentration exceeds 5% - 20% mass of the amount found in samples from the same batch then it should be corrected by subtracted from the mass detected in this particular sample, prior to the calculation of concentrations. None of the target PBDE nor NBFR compounds concentrations was found in these samples, but if any, they were far smaller than 5% i.e. BDE-209 is < 5% in field and method blanks of this study. By this, the data are thus not corrected for blank concentrations. However, in the QA/QC protocol, if the pollutant concertation in the corresponding sample exceeds 20%, this sample analysis should be replaced. Accordingly, the result data are thus not corrected or replaced for blank concentrations.

2.8.4. Limits of detection (LOD) and limits of quantification (LOQ)

Instrumental limits of detection (LOD) and method limits of quantification (LOQ) were calculated for each target compound based on a (3:1) and (10:1) S/N ratio respectively. LOD and LOQ values for this study are shown in Table 2.8. Otherwise, LOQ was determined as the

lowest measurable concentration in the extracted sample. It is calculated according to the following Equation 8:

$$\mathrm{LOQ} = \frac{\mathrm{LOD\ x\ FEV}}{\mathrm{VFEI\ x\ SS}} \times \frac{100}{\%\mathrm{IS\ Recovery}} \quad (8)$$

Where FEV is the final extract volume (µL); VFEI is the volume of final extract injected (µL); SS is a sample size (g or m3); %IS Recovery is a percentage recovery of the IS used to quantify the target pollutant in a particular sample. None of the target compounds were found in method blanks for soils, or raw materials. However, BDE-209 was detected in field blanks for passive air samples. TCIPP was noticed in all samples and the LOQ was 324 ng L-1 based on LOD OF 2.12 ng on column, this may be regard to high concentrations in the leachate samples. Finally, according to the Table 2.8 in the next page, all of the studied FRs were below the LOQ values in field and method blanks. There were few concentration results of BFRs in air and soil samples were found less than LOQ. Otherwise, much of soil and air samples concentrations from non-landfilled areas were found under LOQ. But all of the leaching sample concentration results were above their LOQ values.

2.8.5. Accuracy and Precision

The measures to accuracy and precision of the method of this study was analysed on regular basis aliquots of the NIST SRM 2585. As an initial evaluation, 6 aliquots of SRM 2585 were analysed to validate the extraction and clean-up method developed for PBDEs and NBFRs in combination with GC/MS. The values obtained are compared with previously certified PBDE and indicative NBFR values as shown in the Table 2.9 and indicative PFR values as shown in the Table 2.10.

Table 2.8: Instrument and sample detection limits (LOD and LOQ) in this study

FRs		LOD (ng on column)	LOQ		
			Soil (ng g^{-1})	Air (pg m^{-3})	Leaching sample (ng L^{-1})
PBDEs:	BDE 28	0.06	0.21	0.25	-
	BDE 47	0.12	0.34	0.38	20
	BDE 100	0.22	0.26	0.21	12
	BDE 99	0.17	0.44	0.17	15
	BDE 154	0.32	0.61	0.52	29
	BDE 153	0.27	0.85	0.49	46
	BDE 183	0.17	0.48	1.06	-
	BDE 209	0.36	1.19	2.24	-
NBFRs:	DBDPE	0.04	1.6	8.82	-
	DBE-DBCH	0.08	0.77	1.45	-
	PBEB	0.06	0.09	0.13	-
	EH-TBB	0.76	0.08	0.09	17
	BTBPE	0.62	1.36	1.17	-
	BEH-TEBP	0.48	1.05	0.15	22
	TBBPA-BDBPE	0.43	1.3	6.72	-
PFRs:	TCIPP	2.12	-	-	324
	TPhP	0.93	-	-	27

The levels of five aliquots of SRM 2585 measured with the analytical method were comparable to the certified values except DBDPE which was very low than indicative values (Ali *et al*., 2011; Stapleton *et al*., 2008; van den Eede *et al*., 2012; Sahlström *et al*., 2012; Cristale and Lacorte, 2013; Lankova *et al*., 2015). Furthermore, the concentrations of EH-TBB, BTBPE and BEH-TEBP obtained in this study were similar to those reported previously but only BEH-TEBP level in Sahlström *et al*. (2012) was very high than levels of this and other studies. The SRM was analysed with every 20 soil samples as an ongoing method performance check. As mentioned above, the principal means of determining method accuracy is *via* analysis of a certified SRMs. There were no known SRMs available for PBDEs, NBFRs, TCIPP or TPhP in aqueous solutions nor in air. Lastly, PBEB was not detected in previous studies while it was found in this study.

Table 2. 9: Mean values and standard deviations (SD) (ng g^{-1} dust) of BFRs measured in NIST SRM 2585 (n= 5)

BFRs	This study	NIST certified	Indicative values					
			Stapleton *et al*., 2008	Ali *et al*., 2011	van den Eede *et al*., 2012	Sahlström *et al*., 2012	Cristale and Lacorte, 2013	Lankova *et al*., 2015
BDE 28	45.3 (5.2)	46.9 (4.4)	-	-	32.8 (1.1)	46 (5.1)	-	40.2 (4.8)
BDE 47	504 (51)	497 (46)	498 (46)	-	409 (11)	520 (62)	-	497 (53)
BDE 100	869 (77.4)	892 (53)	892 (53)	-	742 (23)	1,000 (120)	-	825 (73)
BDE 99	146.8 (14.2)	145 (11)	145 (11)	-	116 (3)	140 (18)	-	144 (13)
BDE 154	71.6 (5.1)	83.5 (2)	83.5 (2)	-	97 (2)	130 (15)	-	119 (12)
BDE 153	110.4 (6)	119 (1)	119 (1)	-	77.2 (2.7)	100 (12)	-	66.1 (7.1)
BDE 183	44.3 (3.2)	43 (3.5)	43 (3.5)	-	32.3 (4.8)	55 (13)	-	44.6 (8.7) 2
BDE 209	2788 (142)	2510 (190)	2510 (190)	-	2150 (231)	3400 (450)	-	(576)
DBDPE	0.6 (0.3)	-	-	< 20	< 7.1	< 10	n/a	-
BTBPE	28 (4)	-	<0.8	32	39 (14)	39 (4.9)	76 (4)	-
TBBPA-DBPE	14.9 (2.3)	-	n/a	< 20	-	-	-	-
EH-TBB	33.8 (5.1)	-	< 30	40	26 (2)	36 (2.4)	35 (6)	-
BEH-TEBP	621 (72)	-	n/a	652	574 (49)	1300 (94)	857 973)	-
PBEB	6 (2.3)	-	-	n/a	-	-	n/a	-

n/a = not available

Table 2. 10: Mean values and standard deviations (SD) (ng g^{-1} dust) of PFRs measured in NIST SRM 2585 in other studies

PFRs	This study	NIST certified	Indicative values					
			van den Eede *et al*., 2012	Bergh *et al*., 2012	Ali *et al*., 2012	Brandsma *et al*., 2014	Luongo and Östman, 2015	Harrad *et al*., 2016
TCIPP	-[a]	-	860 (70)	880 (160)	840 (20)	750 (40)	1260 (60)	900 (70)
TPhP	-[a]	-	1160 (140)	1100 (90)	1100 (80)	890 (50)	1520 (170)	980 (60)

a) not analysed in this study

2.9. Detection

The best-known technique to detect organic pollutants in the environmental compartments is GC/MS that can identify the little environmental consequence of compounds quantitatively and qualitatively with a concentration i.e. in water in the microgram/litre (μg L^{-1}) range or a smaller of these concentrations (Reeve, 2002).

2.9.1. Gas Chromatography/ Mass Spectrometry (GC/MS) Instrument

For analysis of BFRs and PFRs in this study, aliquots of sample extracts (2 mL) were injected into a state-of-the-art gas chromatograph (GC) (Thermo Trace 1310 GC) coupled to a Thermo mass spectrometer (MS) (ISQ™ LT Single Quadrupole); both are Thermo Fisher Scientific, USA. MS is operated either in negative ECNI or EI modes; ECNI mode was used for determination of BDE-209 and all target NBFRs (except PBEB), and EI mode was used for determination of other PBDEs, PBEB and PFRs. The GC instrument was equipped with a programmable temperature vaporizer (PTV) injector and fitted with a capillary fused silica GC column (RESTEK, USA, 15 *m* x 0.25 *mm* inner diameter, 0.1/0.25 *mm* film thickness). Later dispensed with the EI mode because the column with the film thickness of 0.25 *mm* and ECNI mode were detected all BFR target compounds, but it used for PFR compounds. The electron lens voltage was 15 V and emission current 50 μA. The ion source and transfer line temperature were 300˚C and 320˚C respectively. Table 2.11 shows the detailed information about GC/MS analysis parameters and selected masses.

A 2 μL of cleaned extract were injected into a GC column using solvent vent injection. The injection was performed under a pressure of 0.19 bar for 1 min and purge flow to split vent of 50 mL/min. The inlet temperature was set at 92°C, split flow 50 mL/min, splitless time 1 *m*

and purge flow 5 mL/min. The GC temperature program was 50°C, hold 0.50 min, ramp 20°C/min to 240°C, hold 5 min, ramp 5°C /min to 270°C, ramp 20°C/min to 305°C, hold 17 min. A carrier gas (Helium) was used with a starting flow rate of 1.5 mL/min, hold 22 min, ramp 1 mL/min to 2.5 mL/min, hold 13 min. The electron multiplier voltage was 1460 V. Methane was used as moderating/ standard reagent gas for ECNI. Figures 2.8 and 2.9 show the PTV method for FRs analysis and GC temperature programme, respectively.

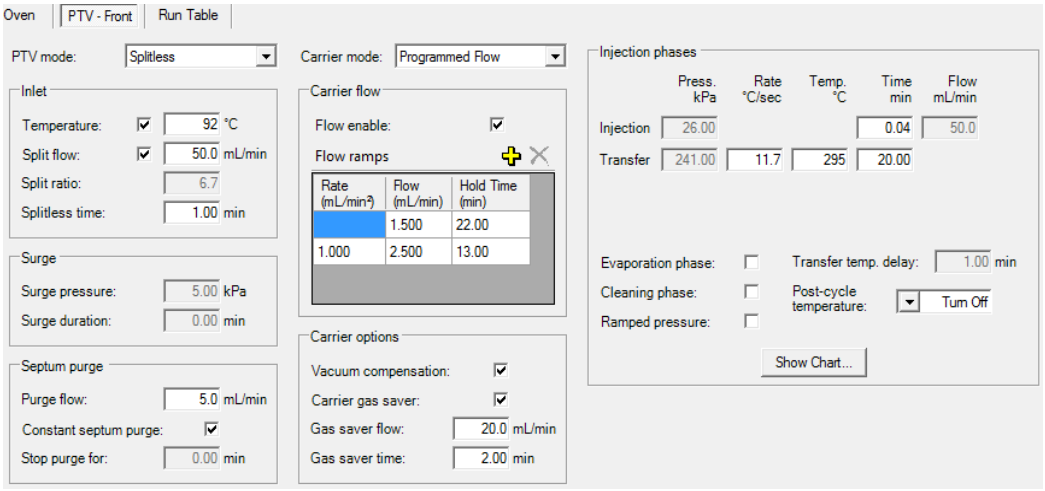


Figure 2.8: PTV method for FRs analysis

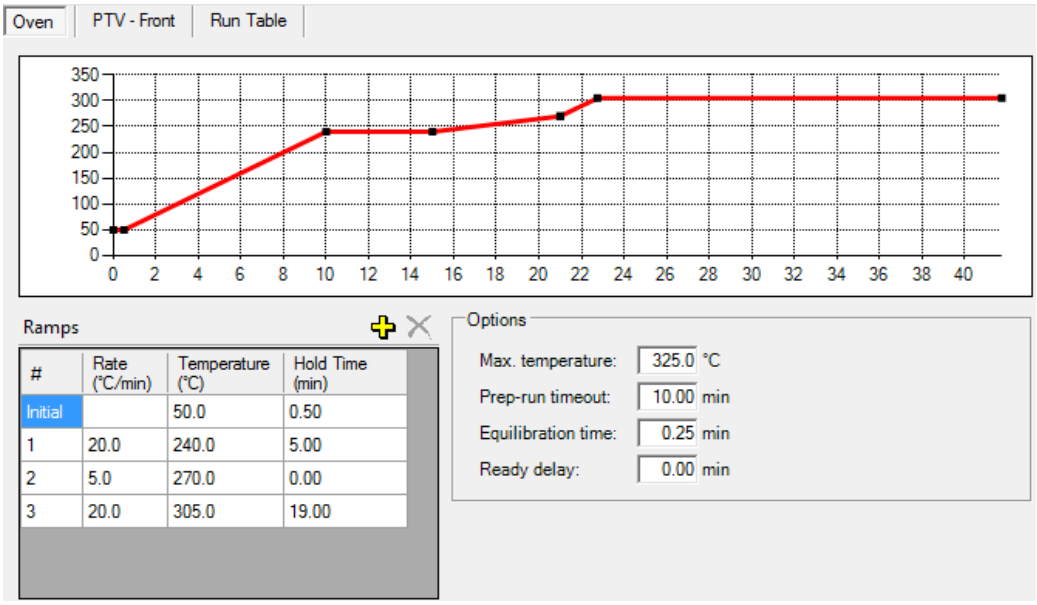


Figure 2.9: GC temperature programme

Table 2.11: Parameters for the GC/ECNI-MS and GC/EI-MS methods (Al-Omran and Harrad, 2015)

Categories		GC/ECNI-MS method			GC/EI-MS method		
Oven method	**-**	**Rate (ºC/min)**	**Temperature (ºC)**	**Hold Time (min)**	**Rate (ºC/min)**	**Temperature (ºC)**	**Hold Time (min)**
	Initial	-	50	5.00	-	110	2.00
	1	20.0	240	5.00	30.0	180	0.00
	2	5.00	270	0.00	20.0	260	0.00
	3	20.0	305	19.00	10.0	305	19.00
PTV Method		Inlet temperature	92ºC		Inlet temperature	92ºC	
		Split flow	50.0 mL/min		Split flow	50.0 mL/min	
		Splitless time	1.00 min		Splitless time	1.00 min	
		Purge flow	5 mL/min		Purge flow	5 mL/min	
		Gas saver flow	20 mL/min		Carrier mode	Constant	
		Gas saver time:	2 min		Carrier flow	1.200 mL/min	
		Injection Rate	0.04ºC/ sec		Gas saver flow	20 mL/min	
		Transfer Rate	11.70 min		Gas saver time	5 min	
		Transfer temperature	295ºC		Transfer Rate	5.00 min	
		Transfer time	20.00 min		Transfer Temperature	325°C	
MS Method		CI Flow	1.5 mL/min		Transfer time	20.00 min	
		CI Gas Type	Methane		Electron Lens Voltage	30 V	
		Electron Lens Voltage	15 V		Emission Current	35 µA	
		Emission Current	50 µA		MS Transfer Line	280.0°C	
		MS Transfer Line	320.0°C		Ion Source Temperature	250.0°C	
		Ion Source Temperature	300.0°C		Inlet temperature	92°C	

2.10. Analytical

2.10.1. Quantitative and Qualitative of GC/MS Data

The quantification of GC/MS chromatogram and *m/z* spectra were performed with MS Windows™ based Xcalibur™ 2.2 SP1 (Thermo Finnigan, San Jose, CA, USA). This software was helped to control and process data from Thermo Scientific™ GC/MS instrument during this study. It provides method setup and data processing and acquisition. The data that can be used, calculated and analysed through the QC/QA procedures along of this study.

2.10.2. Statistical Analysis

Data analysis of this research results was performed statistically by using MS Excel (Microsoft Office 365, 2016), IBM SPSS (21) and Minitab (17). The concentrations was revealed in all result sets to be distributed normally and calculate the descriptive statistics of the quantitative concentrations. The t-tests and ANOVA was conducted on log transformed data on Minitab 17. After all data sets were revealed to be log-normally distributed using the Kolmogorov-Smirnov test (similar to Shapiro-Wilk test) and all confidence limits were preset to 95% while p-value < 0.05 was regarded as indicating statistical significance (Stubbings, 2015; Al-Omran, 2016).

The statistical method was used to make the statistical analyses for compounds with detection frequencies (DF) ≥ 40%. In the concentrations of analyte were below LOQ value and the detection frequencies are higher than 50%, then the concentrations of this compound is stated as LOQ/2, and if the detection frequencies are lower than 50%, the concentration for each compound is reported as LOQ x DF. One-way ANOVAs with Tukey test analysis were performed to compare means looking for differences between dependent variables. Paired samples t-tests were employed when looking for significant differences in concentrations between different matrices (Stubbings, 2015). The data sets also were analysed by multiple linear regression in Minitab 17.

Chapter III: PBDE Concentrations in Air and Soil Surrounding Oman Landfills and Implications for Occupational Exposure

3.1. Synopsis

Polybrominated diphenyl ethers (PBDEs) have been extensively detected in environmental media such as air, soil, indoor dust, and sediment. In this chapter, concentrations of PBDEs in soil from the vicinity of six Omani landfills are reported, as well as concentrations of PBDEs in air surrounding two Omani landfills, specifically Al-Amerat (Am) and Raysut (Ra) (both upwind and downwind of the landfill) and four reference sites in other areas of Oman. PBDEs were detected in all air and soil samples in this study.

Levels of target PBDEs detected in samples from landfill and references sites are compared to each other and also with those reported in previous studies. Our results show BDE-209 was predominant with a mean concentration of 713 and 106 pg m^{-3} in the air of the landfills and reference sites, respectively. BDE-209 was also predominant in soil with mean concentrations of 170 ng g^{-1} and 2.6 ng g^{-1} in the landfill and non-landfilled sites, respectively. Finally, data from this study was used to estimate daily adult exposure to PBDEs via air inhalation and dermal absorption from the soil.

3.2. Concentrations of PBDEs in the Air of Oman

This study reports concentrations of PBDEs in air samples collected from the vicinity of two landfills and four reference outdoor locations in Oman. Each of the target PBDEs were detected in every sample in this study, which indicates that the landfills were polluted by these contaminants. As indicated by Figures 3.2 and 3.3, BDE-209 was the most abundant BDE congener in all air samples.

Table A.1 in Appendix A lists average, SD, minimum, maximum, median and 5th, 25th, 75th and 95th percentile concentrations of our target PBDEs in air from locations in the vicinity of both Am and Ra landfills; while Table A.2 summarises concentrations in air at reference locations within Oman. Concentrations of □PBDEs in air samples in the vicinity of our landfills ranged from 176 - 1803 pg m^{-3} at Am landfill and from 736 - 1675 pg m^{-3} at Ra landfill. This compares with concentrations at the reference sites that ranged from 56 - 165 pg m^{-3} (Table A.2). Figure 3.1 displays the concentrations of ΣPBDEs in air samples downwind (Dw) and upwind (Uw) sites of Am and Ra landfills (n=7 for each location category and landfill; thus total air samples at the 2 landfill sites combined = 28) and reference sites (n= 4). By comparison, Figures (3.2) and (3.3) are box and whisker plots of concentrations of individual PBDEs in air samples at both downwind and upwind locations at the two landfills; illustrating the congener pattern and the predominance of BDE-209.

We hypothesised that concentrations of ΣPBDEs in air at locations downwind of our landfills would exceed significantly those upwind and moreover that concentrations at our landfill locations would also exceed substantially those at our reference sites as a consequence of volatilisation of PBDEs from landfilled waste. Figure 3.1 and Table 3.1 show both these hypotheses to be proven. Specifically, concentrations of □PBDEs at the downwind locations of each landfill were shown by paired t-test comparison to significantly exceed ($p < 0.05$) those at the corresponding upwind location. Similarly, ANOVA comparison of concentrations in air samples from landfill locations exceeded significantly ($p < 0.05$) those at the reference locations.

Table 3.1: Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target PBDEs in air from locations in the vicinity of Am and Ra landfills and the reference site in Oman

PBDE congener	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	∑PBDEs
Am Downwind									
Average	2.6	25.7	56.1	12.3	61.8	39.8	105.3	1008.1	1311.7
SD	1.1	13.1	15.5	7.6	30.7	20.4	29.2	424.6	390.8
median	2.8	18.5	57.2	9.1	71.9	47.1	91.1	1178.3	1436.5
minimum	0.5	12	35.3	3	9.6	15.8	76.9	217.5	608.5
maximum	4.3	48.2	83.3	26.6	91.5	61.9	158.4	1494.7	1803
25th %ile	2.1	15.1	44.8	6.7	39	17.4	79.8	757.7	1072
75th %ile	3.3	35.5	63.6	16.8	90.7	59.7	125.5	1325.4	1594.9
Am Upwind:									
Average	1.2	2.1	5.4	1.5	7	4.2	9	178.8	209.2
SD	0.7	0.8	1.9	0.8	4.6	2.9	2.4	23.1	26.7
median	1.3	2.2	5.5	1.3	6.5	4.8	7.5	175.5	209
minimum	0.4	0.8	2.8	0.3	0.9	0.4	6.5	149.3	176
maximum	2.4	3.2	9	3.3	15.9	7.7	12.7	219.9	260.2
25th %ile	0.6	1.6	4	1.2	3.9	1.4	7	160.2	187.3
75th %ile	1.6	2.7	6.4	1.7	9.1	6.9	11.2	193.2	222.4
Ra Downwind:									
Average	4.1	19.5	41.4	18.8	55.2	38.3	104.8	928.6	1210.8
SD	2.1	5.8	12.7	9.1	32	21.3	32.5	242.6	288
median	3.1	19.9	46.9	13.4	64.7	47.2	109	781.8	1040.9
minimum	2.1	12.4	18	6	9	2.5	62.3	669	944
maximum	8.3	28.1	56.8	30.9	98.7	71.2	171.1	1357.4	1675
25th %ile	2.5	14	34	13	31.5	26.2	86.4	768.4	992.3
75th %ile	5	24.2	50.2	27.7	75.5	47.5	109.3	1077.7	1415.6
Ra Upwind:									
Average	11.7	15.7	40.6	16.9	40.5	30.8	88.4	737.1	981.8
SD	5.3	4.2	8.4	8	27.8	13.8	27	198.7	264.9
median	11.6	15.9	38.3	12.7	36.2	31.8	80.7	680.5	856
minimum	3.7	7.7	26.4	10.1	6.5	4.1	59.1	533.8	736
maximum	18.1	20.4	53.1	35.2	87.1	50.1	133.5	1095.8	1450.2
25th %ile	7.9	13.7	36.1	12.1	19.3	25.8	70.3	592	789
75th %ile	16.3	19.3	47.1	18.2	57.8	39	102.4	832.9	1126.1
Reference Sites:									
Average	0.5	1.8	3.8	1.5	4.9	3.1	8.7	81.4	105.6
SD	0.2	1	1.2	0.6	1.9	1.3	3.8	31.6	41.2
median	0.4	1.7	3.8	1.4	4.7	2.8	7.8	78	100.7
minimum	0.2	0.7	2.2	0.7	2.6	1.8	4.6	43.1	56
maximum	0.8	3.1	5.4	2.3	7.6	5.1	14.5	126.4	165
25th %ile	0.3	1	3	1.1	3.3	2.2	5.9	57.6	75.2
75th %ile	0.6	2.6	4.7	1.8	6.3	3.8	10.5	101.7	131.1

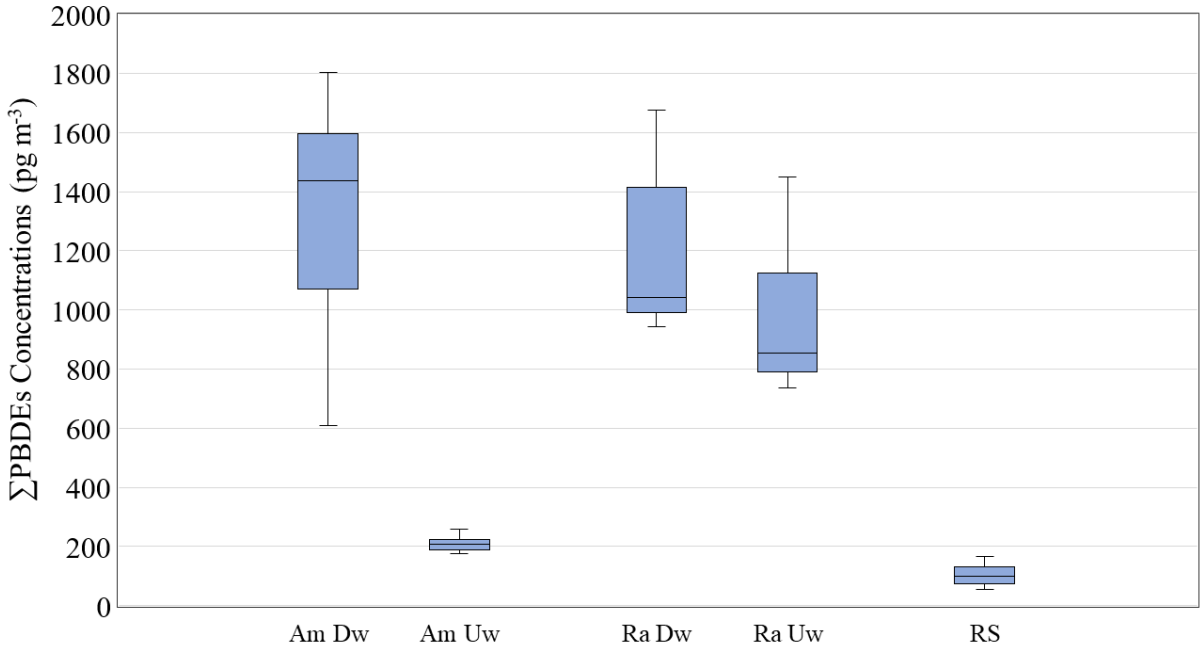


Figure 3.1: Concentration of ∑PBDEs in air Samples downwind (Dw) and upwind (Uw) sites of Am and Ra landfills and the reference sites (RS) in Oman

3.2.1 Statistical Analysis of PBDE Concatenations in the Air

Interestingly, the ΣPBDE concentrations at the other four non-landfilled sites are singifantly lower than the landfills levels ($p < 0.05$) (Figure 3.1). The possible reason for this is the non-landfilled outdoor sampling locations are likely to be influenced strongly by their proximity to landfills as point sources of the PBDE pollutants and as well may be influenced by the indoor environment because of these four sites located in urban areas (Table A.2).

The t-test of log-transformed PBDEs concentrations in air samples of both Am and Ra landfills show there were exceed significance ($p < 0.05$) of downwind to upwind concentrations and that refers to the source of these contaminants is the same landfill. However, the tri-heptaBDEs and BDE 209 were very high significance ($p < 0.01$).

Figures (3.2) and (3.3) show the concentration of ΣPBDEs in air Samples downwind and upwind sites of Am and Ra landfills. It illustrated that the downwind sites were more polluted

by these contaminants rather than upwind sites of these landfills. Also, in Am landfill, it was shown there was high significance ($p < 0.05$) between the concentrations of upwind and downwind sites.

There is different analysis performed to compare the levels and distribution of each compound in different sites. The first analysis used ANOVA and subsequent multiple comparisons to check the levels of compounds in Am and Ra landfills. The ANOVA results showed significant differences in compound levels in both sites, with $p = 0.00$ for Am landfill and $p = 0.00$ for Ra landfill. Multiple comparisons revealed unique significant differences. At Am landfill, there was a significant difference between the levels of compound BDE-28 and compound BDE-209 ($p < 0.000$), but no significant differences between BDE-28 and other compounds. Compounds BDE-47, BDE-153 BDE-154 BDE-183 were all significantly different from compound BDE-209, at $p= 0.000$, but not different from the other compounds. Correspondingly, compound BDE-209 was significantly different from all the compounds measured. At Ra landfill, all the compounds were significantly different from compound BDE-28 ($p < 0.000$) for all comparisons.

The paired sample T-test was used to see the differences in compound levels at different locations of the same landfills. The results showed that all the compounds were significantly different at location Upwind and Downwind ($p < 0.000$) for all the pollutants. Finally, the association between site and compound to the levels of each compound was investigated using multiple linear regression.

3.2.2. Comparison with worldwide PBDE concentrations in the Air

Comparison of the □PBDE concentrations detected in air samples in this study with those from other countries is difficult due to differences between studies with respect to factors such as: sampling method (passive or active), the number and identity of individual PBDE congeners

monitored and whether concentrations reported are for the vapour or particle phase only or for both combined (Besis and Samara, 2012).

Notwithstanding these potential issues, Table 3.1 summarises mean concentrations of BDE-209 and ΣPBDEs in our study with those reported at selected other global locations. The range of PBDE concentrations in our study was 176 - 1803 pg m^{-3} at Am landfill, and 736 - 1670 pg m^{-3} at Ra landfill. Inspection of Table 3.1 shows PBDE concentrations in this study to be at the high end of those reported elsewhere, with the exception of samples taken in the vicinity of e-waste handling activities.

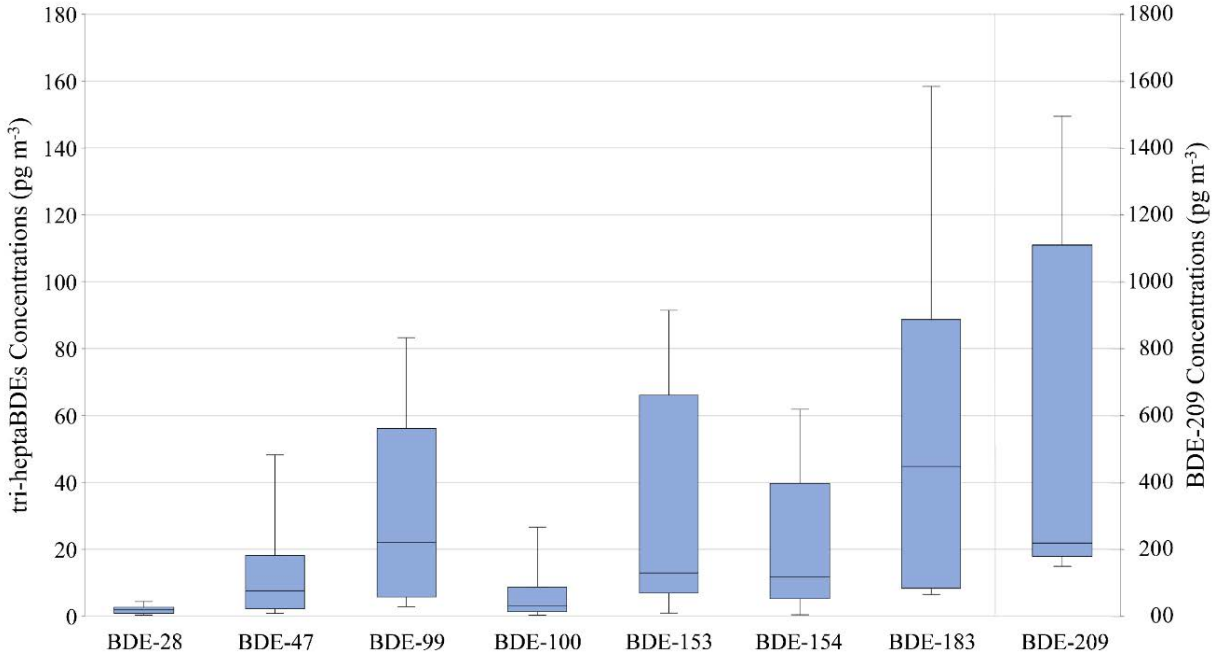


Figure 3.2: Box plot of the concentration of PBDEs in air Samples of Am landfill

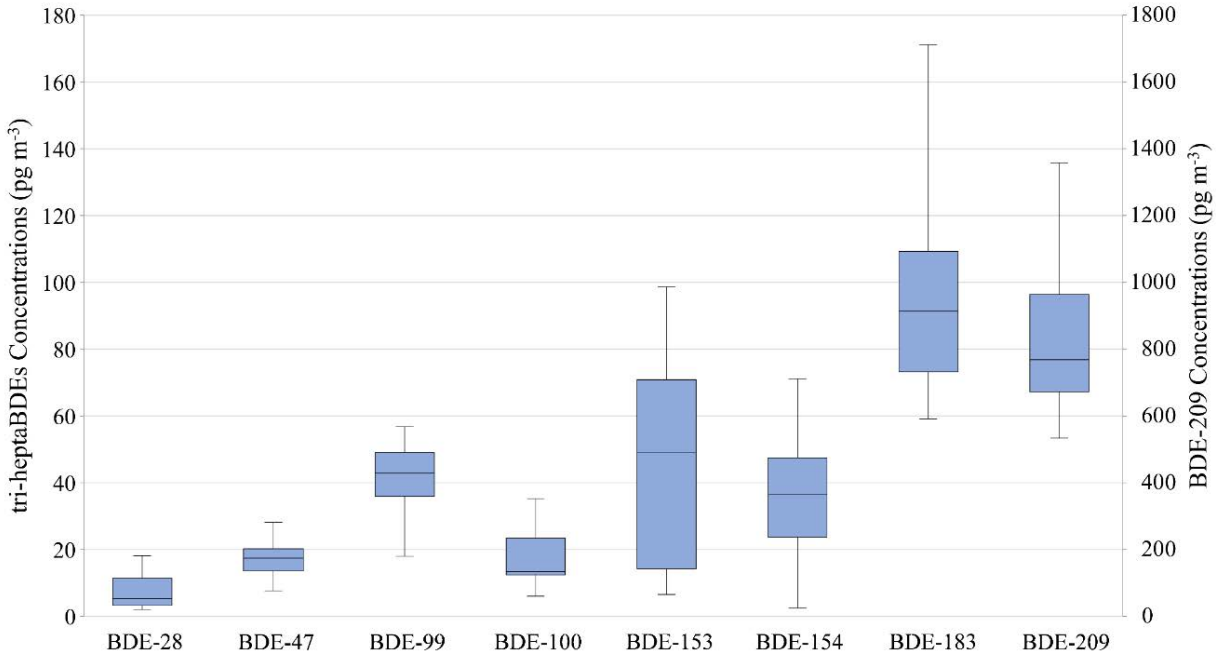


Figure 3.3: Box plot of the concentration of PBDEs in air Samples of Ra landfill

Moreover, concentrations of tri-hexaBDEs in Omani landfill-impacted air samples exceed those reported previously in rural and urban sites across Europe, i.e. Σtri-hexaBDEs ranged between 2.84 to 23.3 pg m^{-3} along an urban-rural transect in Birmingham, the UK in 2003 - 2004 (Harrad and Hunter, 2006).

3.2.3. Congener profile of PBDEs in Air

The profile of PBDE congeners in the atmosphere provide clues as to whether their sources are local or remote from the sampling location (Gevao et al., 2006). Figure 3.4 shows the average PBDE congener profiles at Am and Ra landfills, while Table 3.2 shows mean concentrations (pg m-3) of ΣPBDEs in the ambient air in the vicinity of waste treatment facilities around the world.

In general, the congener pattern at source locations (like landfills) is expected to be different from that at remote locations as a result of differences in volatility and reactivity in the atmosphere. In the discussion that follows, BDE-209 constituted ~76 and 78 % of ΣPBDEs in

the air at Ra and Am landfills, respectively. After this, BDE-183 comprised approximately 7.5 and 8.8% ΣPBDEs at the Am and Ra landfills, respectively. The sum of penta-BDEs, together constituted almost 14.2 and 14.7% ΣPBDEs with BDE-47, BDE-99 and BDE-100 contributing 1.8%, 4.1 and 0.91% ΣPBDEs at Am and 1.6%, 3.7% and 1.6% at Ra landfill, respectively. By comparison, BDE-153 contributed 4.3% and 4.4%, BDE-154 3.0 and 3.2% ΣPBDEs at the two landfills. By comparison, Figure 3.5 shows the PBDE congeners profile in air samples from the non-landfill areas (reference sites) in this study. In contrast with the above expectations, the texture profile shows the compatibility of reference sites with the landfill's profiles. So, mean BDE-209 founded to be ~77 % of ΣPBDEs in the air at reference sites. After this, BDE-183 covered approximately 8.16% ΣPBDEs. The sum of penta-BDEs together constituted almost 6.92 ΣPBDEs. By contrast, BDE-153 and BDE-154 contributed 4.57 and 3% of ΣPBDEs at the reference sites, respectively.

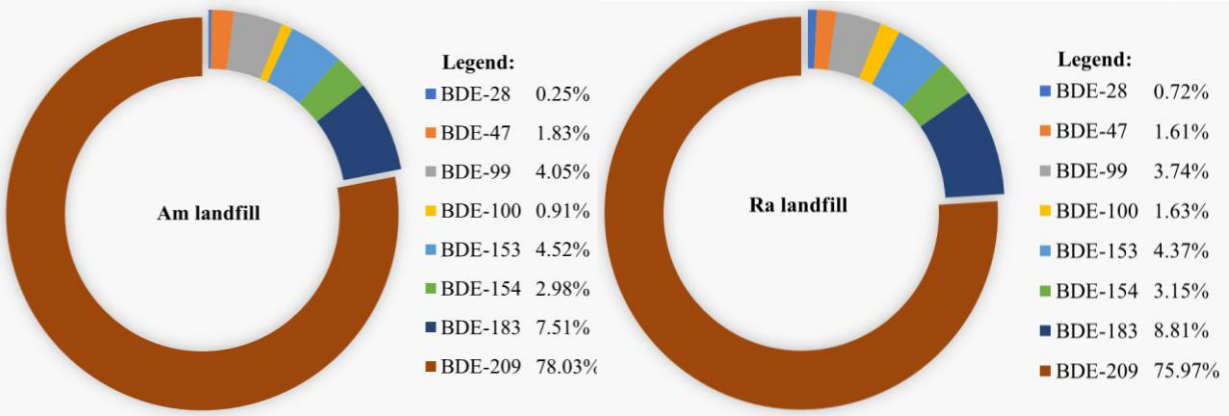


Figure 3.4: Profiles of PBDE homologues (percentages, %) in Am and Ra landfills

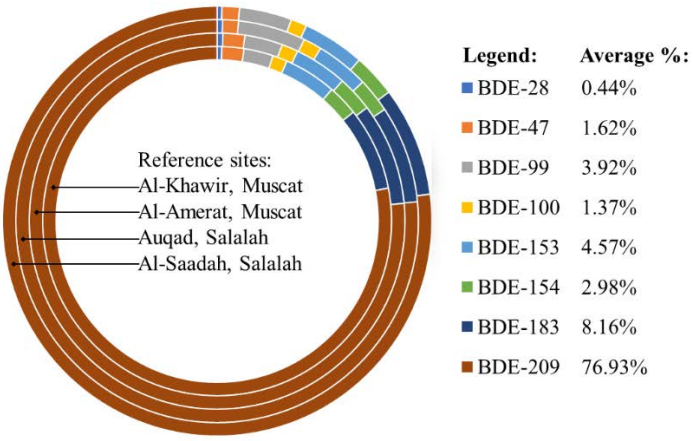


Figure 3.5: Profiles of PBDE homologues in reference sites

Table 3.2: Summary of Mean concentrations (pg m^{-3}) of BDE-209 and ΣPBDEs in the outdoor air around the world

Region (Year)	Type	n	BDE-209	ΣPBDEs	Reference
Oman	L	14	149 - 1494	176 - 1803	This study
Oman	NL	4	43 - 126	56 - 165	This study
France	U/I	13	133 - 196	158 - 230	Castro-Jiménez *et al*., 2011
Australia	U	2	3.6	1.7 – 6.8	Toms *et al*., 2009
China	E	-	1900	8900	Chen *et al*., 2009
China, Shundle	U	-	140 - 1233	195 - 1450	Zhang *et al*., 2009
China, Dongguan	U	-	55 -316	77 - 372	Zhang *et al*., 2009
China	I	9	13000	13890	Chen *et al*., 2008
Turkey	I	13	43	81 - 149	Cetin and Odabasi, 2008
Turkey	U/SU	47	7.5	11	Cetin and Odabasi, 2008
Italy	I	-	-	106	Vives *et al*., 2007
China	E	30	n/a	21000	Deng *et al*., 2007
China	E	-	1949	8862	Chen *et al*., 2006
China	I	16	1348	2431	Chen *et al*., 2006
USA	U	-	-	100	Hoh and Hites, 2005
Sweden	In	-	17	62	Agrell *et al*., 2004
Sweden	E	-	36000	64000	Agrell *et al*., 2004
Canada	SU	-	-	39 - 48	Shoeib *et al*., 2004
Japan	SU	7	n/a	58	Hayakawa *et al*., 2004
USA	U	12	0.3	52	Strandberg *et al*., 2001
USA	R	24	<0.10	7.2	Strandberg *et al*., 2001

Types: L: landfill; NL: non-landfilled, U: urban; R: rural; SU: suburban; E: e-waste; P: production area; D: dumping site; I: industrial; n/a: not available; In: Incineration facility

Table 3.3: Summary of range and mean concentrations (pg m^{-3}) of ΣPBDEs in the ambient air in some vicinity of waste treatment facilities around the world

Region (Year)	Type	ΣPBDEs	Reference
Oman	L	176 - 1803	This study
Sweden	WEEE-R	176 - 233	Julander *et al*., 2005
Thailand	WEEE-S	8 - 150	Muenhor *et al*., 2010
Germany	AL	1 - 11	Weinberg *et al*., 2011
Germany	CL	1 - 3	Weinberg *et al*., 2011
USA	CL	17300	Oliaei *et al*., 2010
Canada	AL	1.1-151.9	St-Amand *et al*., 2008
Canada	IP	2000	Alaee *et al*., 2001

Types: L: landfill; WEEE-R: e-waste recycling, WEEE-S: e-waste storage, AL: Active landfill, CL: closed landfill, IP: incineration plant

3.2.4. Meteorology Role in the Sampling Areas

Meteorological data obtained from the Oman Directorate General of Meteorology (DGM), during sampling campaigns (DGM, 2016) were used to try and explain any differences in PBDE concentrations in samples taken at different times of year. Table 3.3 displays the temporal variations of average ΣPBDEs concentrations (pg m^{-3}) and ambient air temperature at Am and Ra landfills.

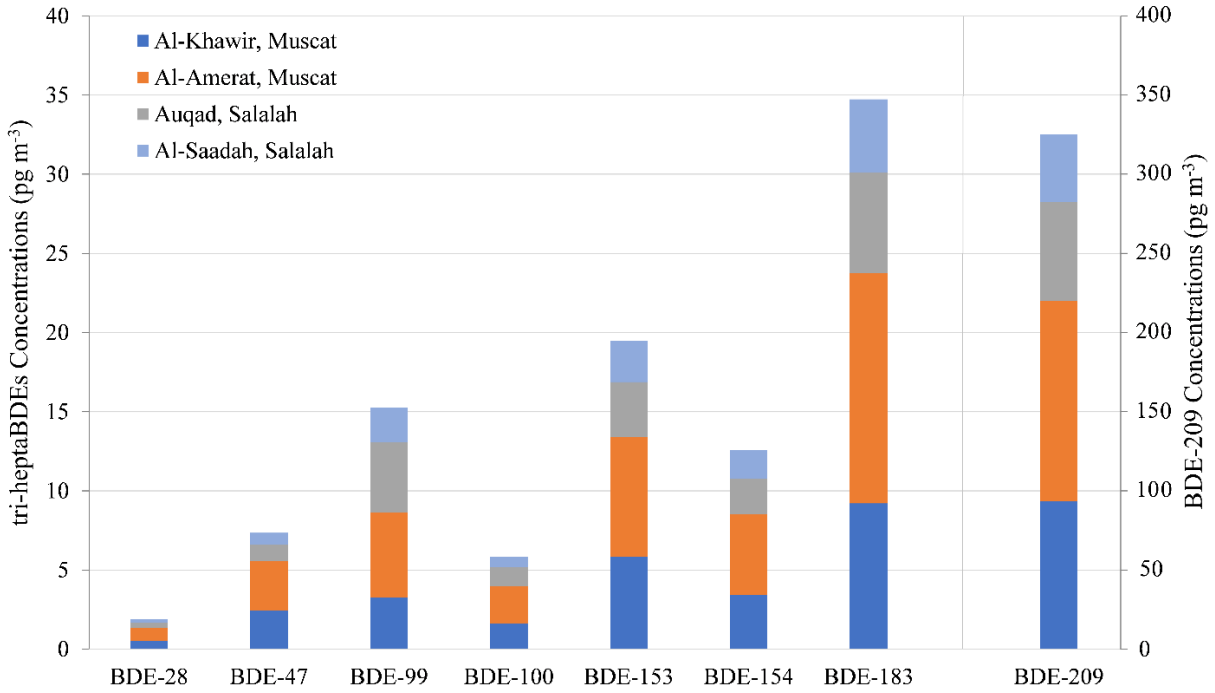


Figure 3.6: Concentration of PBDEs in air samples of the reference sites

Table 3.4: Temporal variations in average ΣPBDEs concentrations (pg m^{-3}) and ambient air temperature at Am and Ra landfills (DGM, 2016)

Sampling period	ΣPBDEs concentrations		Temperature		
	Upwind	Downwind	Mean	Max	Min
Am landfill:					
Sept. – Oct. 2014 (P1)	803	120	33	43	22
Nov. – Dec. 2014 (P2)	469	111	24	33	16
Jan. – Feb. 2015 (P3)	848	147	23	34	15
Mar. – Apr. 2015 (P4)	690	133	30	41	19
May – Jun. 2015 (P5)	368	67	35	46	26
Jul. – Aug. 2015 (P6)	751	127	35	49	25
Sept. – Oct. 2015 (P7)	575	114	33	44	22
Ra landfill:					
Jun. – Jul. 2013 (P1)	1618	1323	26	30	24
Aug. – Sept. 2013 (P2)	949	856	25	29	22
Oct. – Nov. 2013 (P3)	1036	736	27	33	21
Dec. 13 – Jan. 2014 (P4	944	929	24	31	17
Feb.– Mar. 2014 (P5)	1213	820	25	32	19
Apr. – May 2014 (P6)	1041	758	28	34	24
Jun. – Jul. 2014 (P7)	1675	1450	27	31	24

As mentioned before the period of sampling campaigns for both landfills were between June 2013 – July 2014 and September 2014 – October 2015 for Ra and Am landfills, respectively.

As well as Table 3.3, Figures 3.6, and 3.7 illustrate how average concentrations of ΣPBDEs vary with temperature at each of our two landfills. Linear regression between □PBDEs and average temperature revealed no significant correlation at either landfill, suggesting that volatilisation from landfill was not the only source of airborne PBDEs at the sites monitored in this study. Other possible sources could include dispersion of contaminated particulates. These would strongly preferentially favour emissions of less volatile PBDEs such as BDE-209 which as highlighted above, is the predominant PBDE congener detected in this study. In addition, Figures (3.8), and (3.9) show how average concentrations of high volatile PBDEs such as Σtri-hexa BDEs, fluctuate with temperature degrees at each landfill. Also, Linear regression between Σtri-hexa BDEs and average temperature shown no significant correlation at these landfills. Then, suggested same above suggestion that the volatilisation from landfill not alone to cause a source of airborne Σtri-hexa BDEs at the landfills monitored in this research.

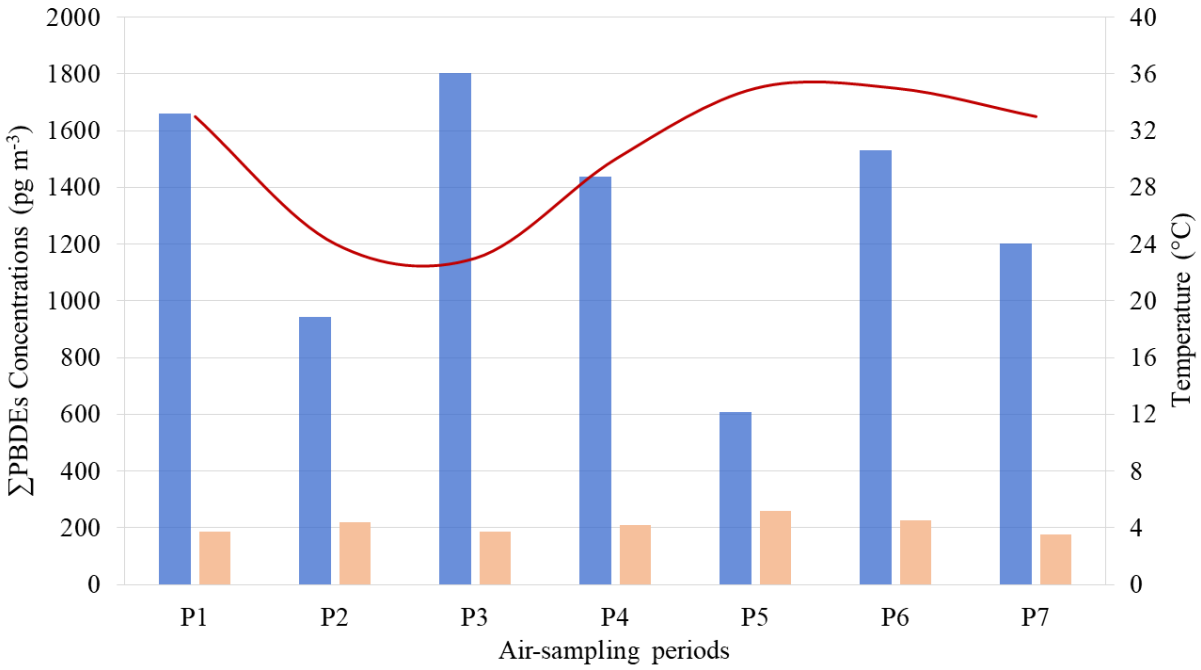


Figure 3.7: Average concentrations of ΣPBDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Am landfill compared with mean ambient temperature (°C) (red line) of Al- Amerat area

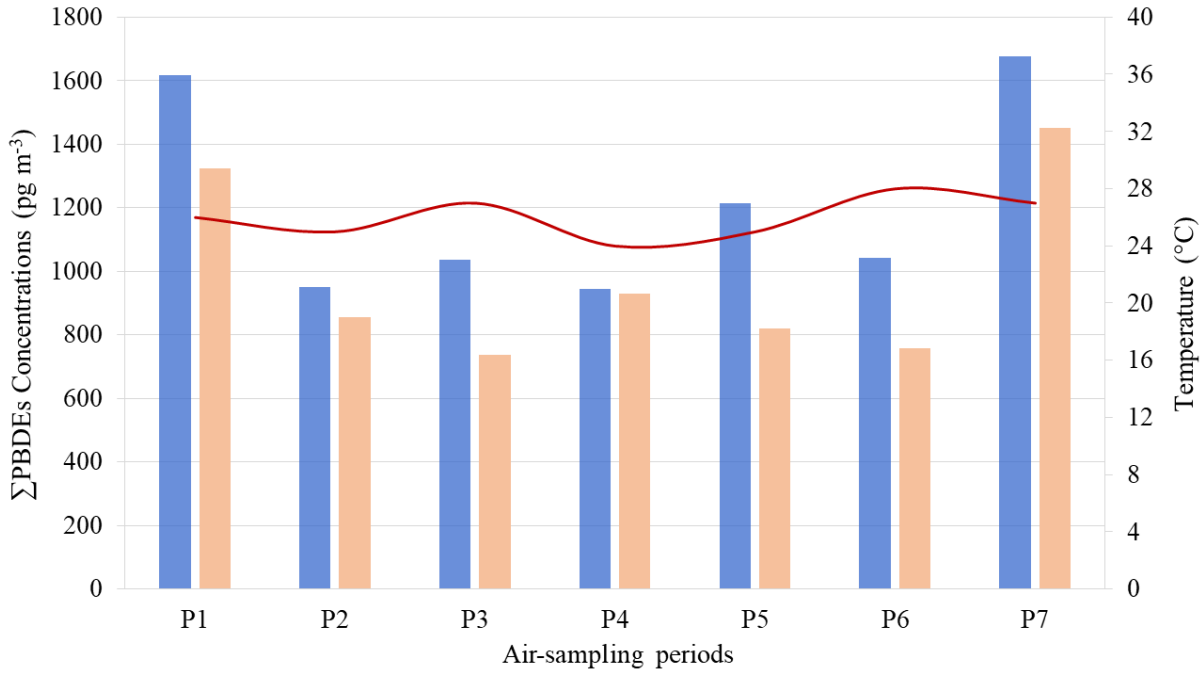


Figure 3.8: Average concentrations of ΣPBDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Ra landfill compared with mean ambient temperature (°C) (red line) of Raysut area

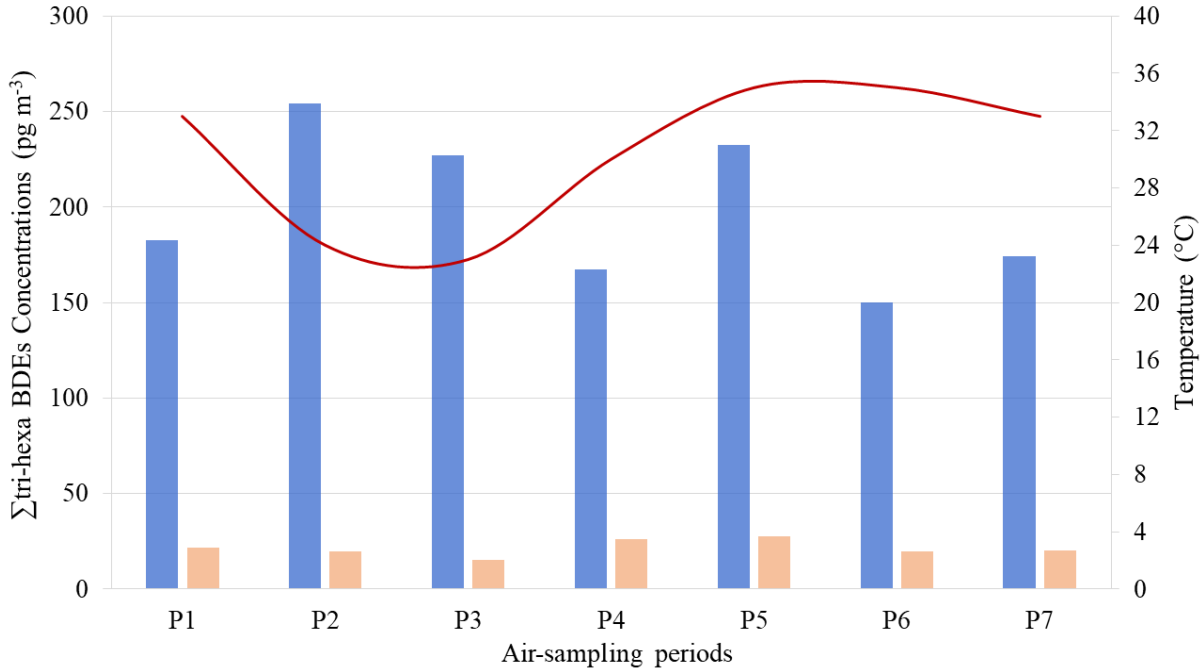


Figure 3.9: Average concentrations of Σtri-hexa BDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Am landfill compared with mean ambient temperature (°C) (red line) of Al- Amerat area

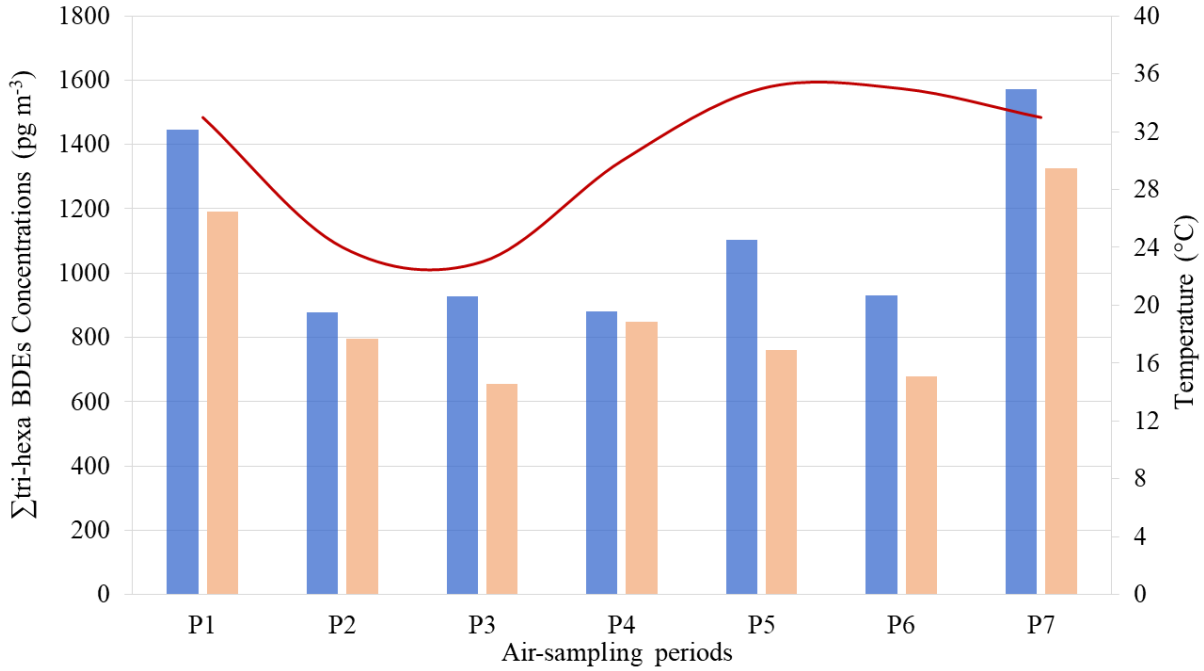


Figure 3.10: Average concentrations of Σtri-hexa BDEs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Ra landfill compared with mean ambient temperature (°C) (red line) of Raysut area

3.3. Concentrations of PBDEs in the Soil from landfill sites in Oman

A total of eight PBDE congeners were detected in all samples from the Omani landfill sites from which soil samples were collected. In total, soil was collected from the vicinity of 6 landfill sites in Oman. In addition to Am and Ra from which air samples were also collected, soil was collected from the following 4 additional landfills: Ni, So, Ib, and Bu landfills. Logistical considerations prevented the collection of air samples from all 6 landfills. In addition to landfill sites, soil samples were also collected from reference sites in Oman. Concentrations of PBDEs in soil samples from landfill locations were significantly higher than those in their respective reference sites ($p < 0.05$). With respect to the congener profile in soil samples, generally, BDE-209 congener was the predominant PBDE detected.

The descriptive statistics of PBDE concentrations in soil samples from each landfill are summarised in Table B.1 in Appendix B, with Table B2 providing the equivalent data for the reference non-landfill sites. Tables 3.4 show Summary of the descriptive statistics of PBDE

concentrations in soil samples for a) the vicinity landfills (ng g^{-1} dw) and b) non-landfilled areas (pg g^{-1} dw), BDE-209 and ∑PBDEs concentrations (ng g^{-1} dw) in non-landfilled sites of Oman. The soil concentrations of ΣPBDEs varied from 25 - 310 ng g^{-1} (mean 181 ng g^{-1}). The highest mean values were found in Ib landfill followed by the So landfill, with the lowest mean values were seen in Ra landfill.

The mean concentrations of ΣPBDEs for soil concentrations within the landfills ranged from 65 to 252 ng g^{-1} in Am landfill (mean 146 ng g^{-1}) and from 25 to 158 ng g^{-1} in Ra landfill (mean 91 ng g^{-1}). The average of other landfills was 199, 234, 246, and 174 ng g^{-1} for Ni, Ib, So and Bu landfills respectively. Figures (3. 10) and (3.11) are box plots of the concentrations of PBDEs in soil samples from Am and Ra landfills respectively.

Table 3.5: Summary of the descriptive statistics of PBDE concentrations in soil samples for a) the vicinity landfills (ng g^{-1} dw) and b) non-landfilled areas (pg g^{-1} dw), BDE-209 and ∑PBDEs concentrations (ng g^{-1} dw) in non-landfilled sites of Oman

a)	Landfills average concentrations (ng g^{-1} dw)										
BFRs	**Am**	**Ra**	**Ni**	**Ib**	**So**	**Bu**	**Mean**	**SD**	**Median**	**Min**	**Max**
BDE-28	0.61	0.27	0.44	0.41	0.57	0.58	0.48	0.33	0.37	0.26	3.95
BDE-47	0.53	0.41	0.46	0.53	0.66	0.57	0.53	0.32	0.42	0.32	2.63
BDE-99	0.68	0.67	1.18	0.97	1.04	0.82	0.89	0.41	0.53	0.71	2.18
BDE-100	0.44	0.43	0.75	0.7	0.62	0.66	0.6	0.33	0.38	0.47	3.68
BDE-153	0.69	0.88	1.04	0.9	1	1.14	0.94	0.43	0.69	0.42	3.21
BDE-154	0.56	0.78	1.1	0.57	0.92	1.11	0.84	0.63	0.71	0.67	2.95
BDE-183	1.57	1.78	2.21	1.87	2.33	1.77	1.92	0.97	1.20	0.82	11.49
BDE-209	140.53	85.31	191.42	240.27	226.99	166.9	175.24	74.98	84.39	24.32	419.16
∑PBDEs	145.61	90.53	198.6	246.22	234.13	173.55	181.44	101.71	88.68	28.00	449.25
b)	**Non-Landfills average concentrations**										
BFRs	**Am**	**Ra**	**Ni**	**Ib**	**So**	**Bu**	**Mean**	**SD**	**Median**	**Min**	**Max**
	Landfills average concentrations (pg g^{-1} dw)										
BDE-28	6.8	4.56	8.68	8.8	2.51	1.73	5.51	3.17	3.44	0.57	35.46
BDE-47	13.64	66.56	23.14	17.2	2.38	2.68	20.93	5.83	8.12	8.32	102.11
BDE-99	37.84	112.96	22.33	10.83	5.63	4.31	32.32	17.38	25.90	14.12	391.34
BDE-100	16.16	12.32	6.06	12.12	2.66	1.22	8.42	3.3	6.17	1.54	100.07
BDE-153	10.1	22.75	15.25	9.36	11.18	3.67	12.09	3.62	8.71	2.87	219.21
BDE-154	5.46	14.21	13.09	5.86	3.94	5.22	7.91	2.35	4.97	1.75	302.64
BDE-183	68.64	96.4	85.75	89.36	115.67	108.24	94.03	21.2	56.89	12.05	262.9
BDE-209	2966.25	3226.41	1876.78	1261.87	2358.92	2151.91	2307.02	1331.87	1507.39	200.5	3880.87
∑PBDEs	3124.89	3556.17	2051.08	1415.4	2502.89	2278.98	2488.23	1388.72	1621.58	241.72	5294.6
	Non-Landfills average concentrations (ng g^{-1} dw)										
BDE-209	2.97	3.23	1.88	1.26	2.36	2.15	2.31	1.33	1.51	2.01	3.88
∑PBDEs	3.12	3.6	2.05	1.42	2.50	2.28	2.49	1.39	1.62	2.42	5.29

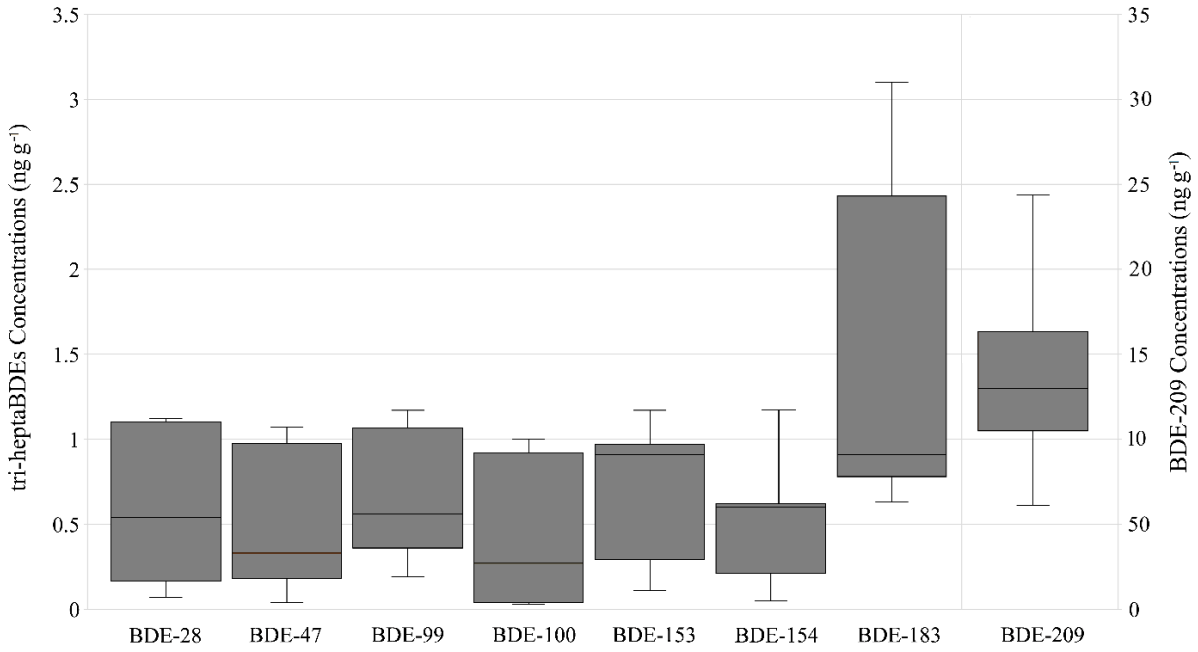


Figure 3.11: Box plot of the concentrations of PBDEs in soil samples from Am landfill

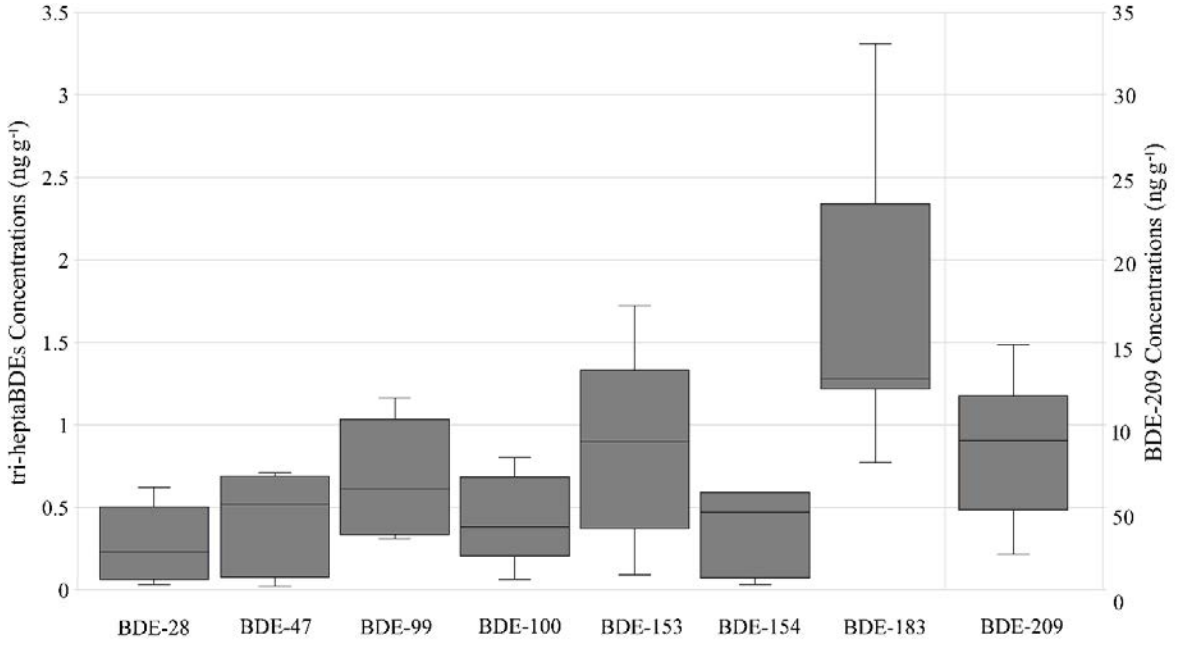


Figure 3.12: Box plot of the concentrations of PBDEs in soil samples from Ra landfill

Comparison of concentrations of PBDEs in soil samples taken in the vicinity of our landfills with those detected in soil from our non-landfill-impacted reference areas, shows those at landfill exceed significantly those in reference sites (t-test on log-transformed concentrations,

$p < 0.05$). These results are consistent with the hypothesis that landfill is a source of PBDEs to the environment. Figures (3.12) and (3.13) show the plates of dot plots of □PBDE concentrations (ng g^{-1} dw) in soil from Ni, So, Ib, and Bu landfills.

ANOVA was used and many subsequent comparisons to check the levels of contaminants in different locations, including the six landfills. The result revealed some significant differences. At non-landfilled areas at Am landfill, ΣBDEs was significantly different to BDE-209 ($p < 0.014$). Concentrations at non-landfilled areas of Ra, So and Bu landfills also showed significant differences between ΣBDEs and BDE-29 ($p < 0.05$). However, the remaining comparisons were not significantly different.

The paired sample t-test was used to see the differences in compound levels at different locations of the same site in this group of analysis. The results showed that all the PBDEs pollutants were significantly different at locations of the landfills and non-landfilled areas, with a $p= 0.004$. The association between site and pollutants to the levels of each pollutant in this group was also investigated using multiple linear regressions. The results showed that the concentrations not significant at a p-value of 0.299 and 0.197, respectively.

3.3.1. Comparison of concentrations of PBDEs in soil from the vicinity of Omani landfills with other studies worldwide

Table 3.5 compares concentrations of PBDEs in soil from both landfill and reference sites in this study with those in selected other studies worldwide. Concentrations at our landfill sites are consistent with those in the two other studies of PBDEs in soil around landfills, are at the high end of those reported for rural and urban locations, but are lower than those detected at e-waste impacted sites.

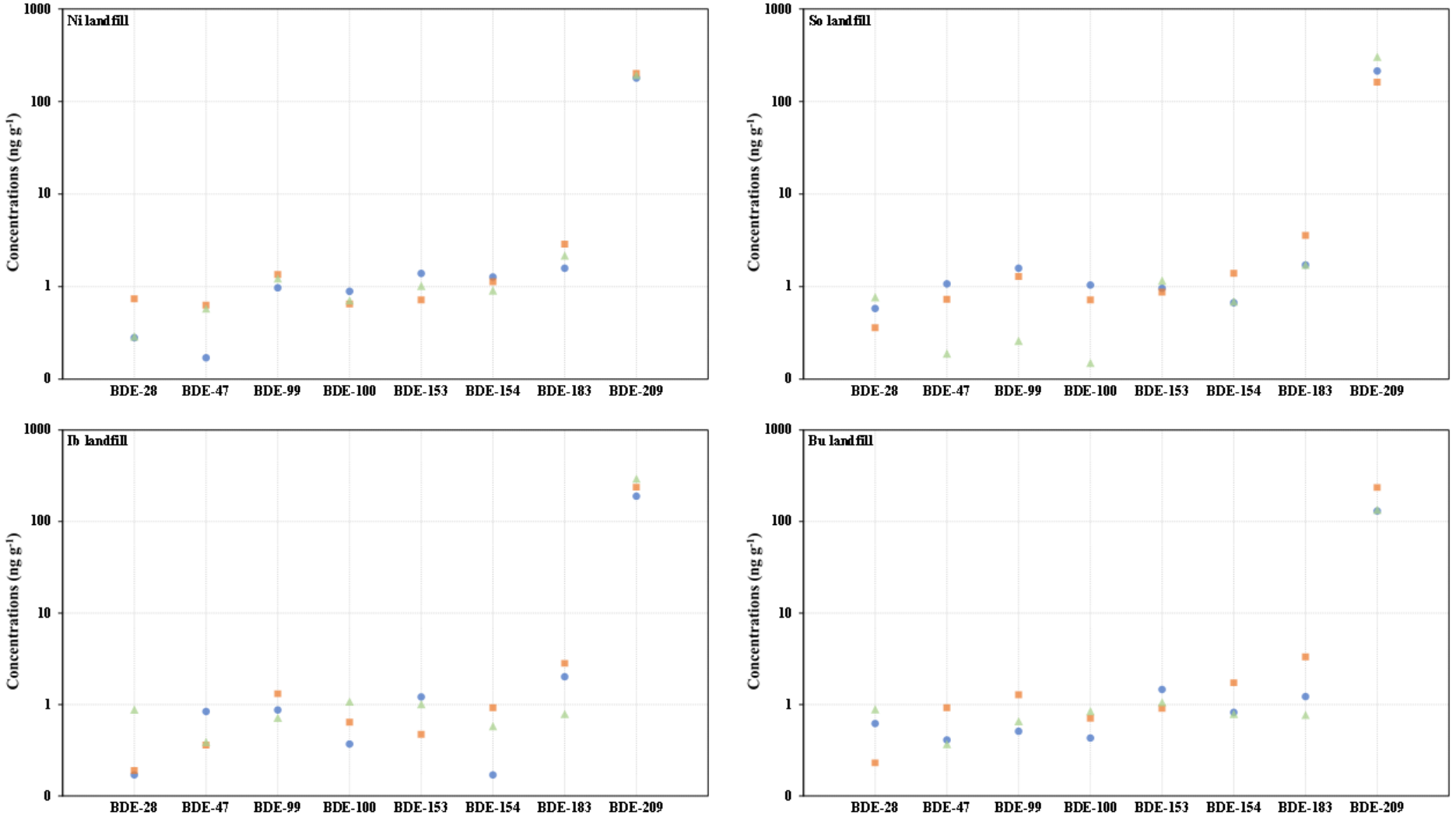


Figure 3.13: Dot plots of PBDE concentrations (ng g^{-1} dw) in soil samples (n=3) from Ni, So, Ib, and Bu landfills; sample 1 (blue circle), sample 2 (orange square) and sample 3 (green triangle) – note the log scale

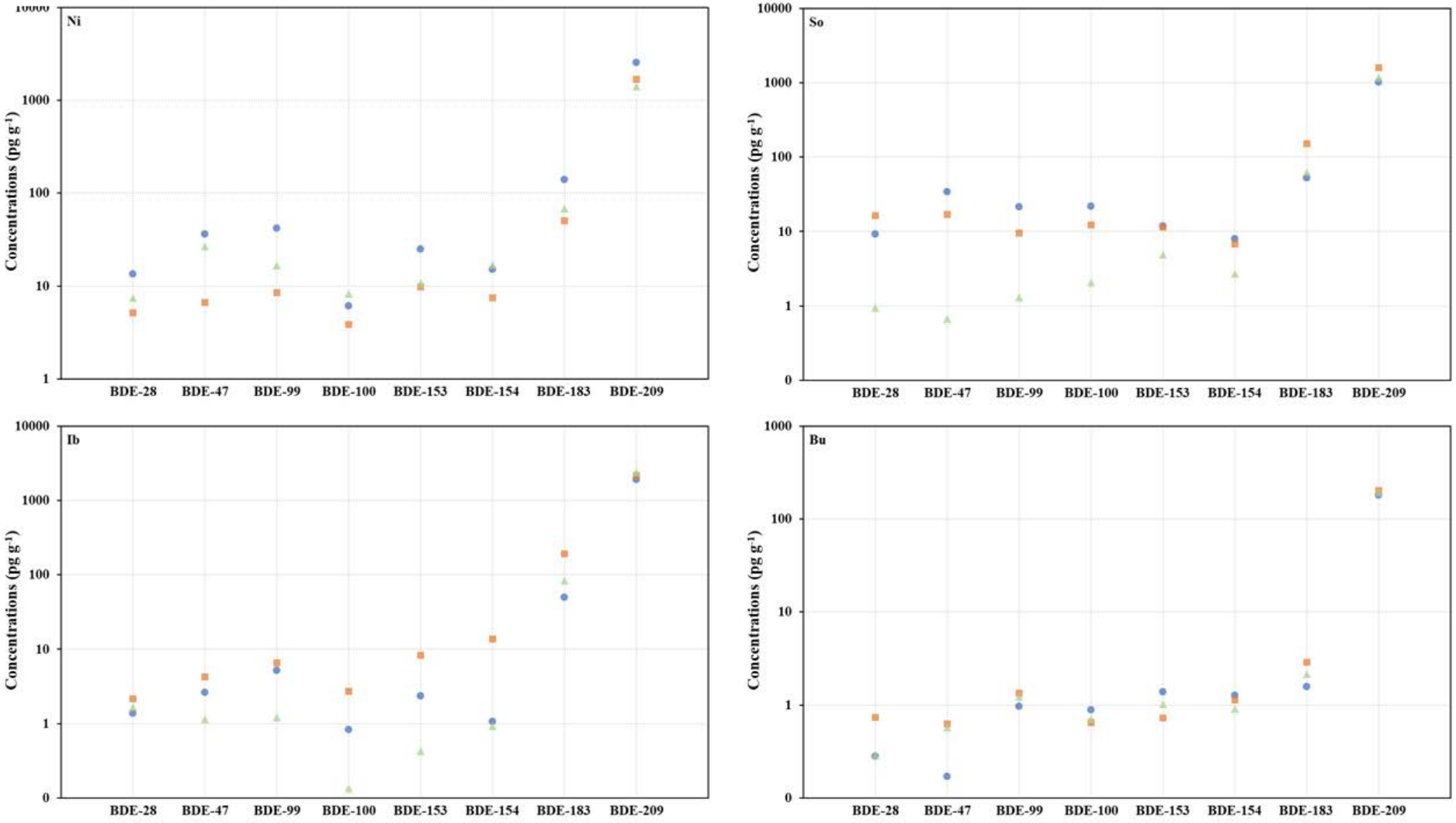


Figure 3.14: Dot plots of PBDE concentrations (ng g^{-1} dw) in soil samples (n=3) from Ni, So, Ib, and Bu reference sites; sample 1 (blue circle), sample 2 (orange square) and sample 3 (green triangle) – note the log scale

3.4. PBDE congener profile in soil

Figure 3.11 illustrates how BDE-209 contributed in the range of 80 to 98% □PBDEs in all landfill-impacted soil samples. Figures 3.14 and 3.15 further illustrate the congener profile of the 7 other PBDE congeners in soil from landfill and reference sites in this study. While the profiles at the landfill-impacted sites are all similar, there is a markedly different profile at the reference sites. Particularly striking is the predominance of BDE-183 in some of the reference site soils.

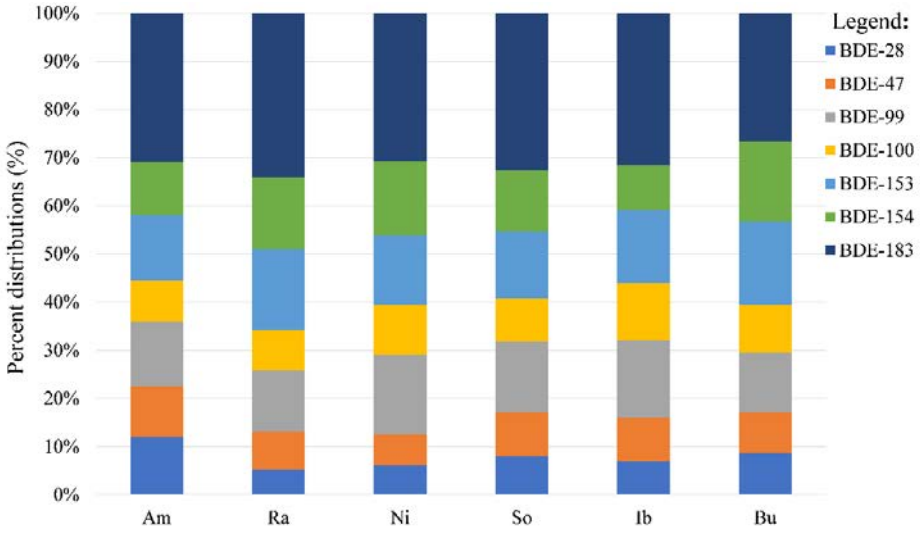


Figure 3.15: Profiles of tri-heptaBDE homologues in soil samples from Omani landfills

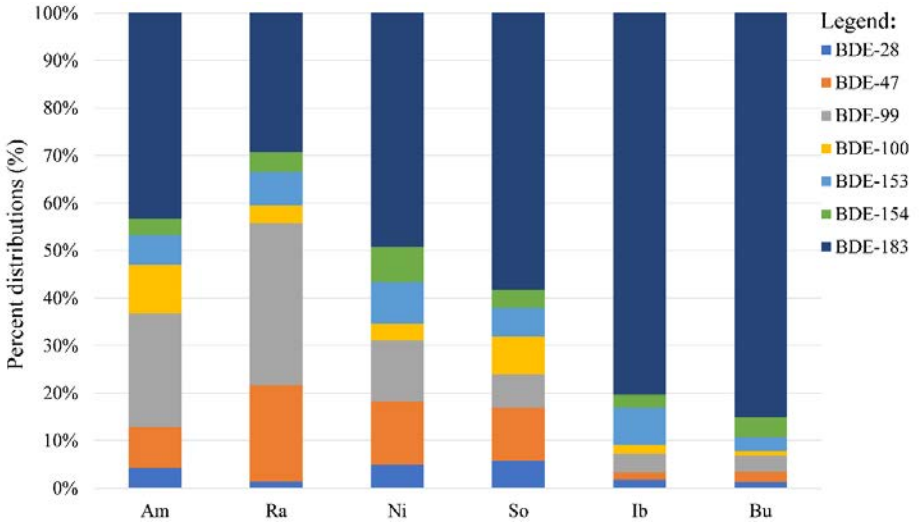


Figure 3.16: Profiles of tri-heptaBDE homologues in soil samples from Omani non-landfill reference locations

Table 3.6: Summary of Mean concentrations (ng g^{-1} dw) of BDE-209 and ΣPBDEs in the soils around the world

Region	Type	n	BDE-209	ΣPBDEs	Reference
Landfills, Oman	L	22	164	170	This study
Non-landfilled, Oman	R	22	2.45	2.6	This study
Vietnam (2014)	E	10	370	490	Matsukami et al., 2017
Vietnam (2013)	E	10	390	480	Matsukami et al., 2017
Vietnam (2012)	E	10	1100	1200	Matsukami et al., 2017
West Midland, UK	U, R	8	6	10	Drage et al., 2016
Melborne, US	I	5	164	171	McGrath et al., 2016
Qingyuan, China	R	16	162	165	Wang et al., 2015
Hung Yen, Vietnam	E	10	1700	1900	Matsukami et al., 2015
Shanghai, China	U	37	29	33	Wu et al., 2015
Shandong, China	I	23	51130	58679	Li et al., 2016
Guiyu, China	E	16	1946	2665	Zhang et al., 2014
Qingyuan, China	E	36	784	898	Wang et al., 2014
Zhaogezhuang, China	E	40	665	690	Tang et al., 2014
Yangtze River, China	U, R	33	9.5	10	Shi et al., 2014
Kocaeli, Turkey	U	49	22	26	Cetin et al., 2014
Shandong, China	I	38	1062	1127	Zhu et al., 2014
China	L	11	353	395	Huang et al., 2013
India	D	6	5	7	Eguchi et al., 2013
Vietnam	D	5	56	95	Eguchi et al., 2013
North China	U, R	87	188	202	Liu et al., 2013
China	E	9	25807	27302	Labunska et al., 2013
Yellow River Delta, China	R	8	104	121	Chen et al., 2013
Kuwait	U, R	11	16	17	Gevao et al., 2011
Surabaya, Indonesia	U	6	8	12	Ilyas et al., 2011
Surabaya, Indonesia	R	4	11	15	Ilyas et al., 2011
Laizhou Bay, China	P	5	576	687	Jin et al., 2011
Kolkata, India	D	3	41	49	Eguchi et al., 2009
Chennai, India	D	7	5	8	Eguchi et al., 2009
Phenom Penh, Cambodia	D	4	129	219	Eguchi et al., 2009
Can Tho, Vietnam	D	5	106	167	Eguchi et al., 2009
Kuala Lumpur, Malaysia	D	2	2	4	Eguchi et al., 2009
Bogor, Indonesia	D	2	7	37	Eguchi et al., 2009
Guangzhou, China	SU	4	67	72	Shi et al., 2009
Shanghai, China	E	10	1800	1910	Ma et al., 2009
Zhejiang, China	D	48	234	991	Wang et al., 2009
Shiawassee River, USA	R	10	11	14	Yun et al., 2008
Saginaw River, USA	R	10	2.8	3	Yun et al., 2008
Canada	L	13	62	131	Danon-Schaffer et al., 2008
Guiyu, China	D	3	510	1440	Leung et al., 2007
China	E	2	420	625	Leung et al., 2007
US	V	33	21	103	Offenberg et al., 2006

Types: L: landfill; NL: non-landfilled, U: Urban; R: Rural; SU: suburban; E: e-waste; P: production area; D: dumping site; I: Industrial; V: Various sites; OC: Organic Content.

3.5. Potential Occupational Exposures at Omani Landfills

Our data about concentrations of FRs in air and soil from the vicinity of landfill locations permit assessment of landfill workers' exposure (Seeberger et al., 2016). Occupational exposure has been demonstrated in workers of electrical dismantling facilities,who have been demonstrated to possess high PBDE levels in their blood (Sjodin et al., 1999). Even more pertinently to this study, PBDE exposures have also been reported for landfill workers (Wang et al., 2010). The people who work at these landfills may be exposed by inhalation, accidental ingestion of soil and dermal contact with soil. In this study, we estimate intake dose as multiples of the contact rates (e.g. m^3 air inhaled per day) and the PBDE concentration in the exposure media (air or soil) (USEPA, 2010). Table 3.5 show the estimated exposure (ng/kg bw/d) of adult to PBDEs via air inhalation, soil ingestion and dermal uptake from soil in this study.

3.5.1. Daily exposure dose to PBDEs via air and soil

A mean daily exposure dose (DED) to PBDEs via air inhalation and soil ingestion was estimated based on PBDEs concentrations in this study. Soil ingestion and air inhalation were assumed to arise pro-rata to typical activity patterns for adults – i.e. workers were assumed to spend 23.8% of time at the workplace (Harrad et al., 2004). Moreover, an average soil ingestion rate of 0.03 g/day was used for adults (Jones-Otazo et al. 2005; USEPA, 2011), with the assumed inhalation rate for adults being 16 m^3/day (USEPA, 2011). To calculate the daily exposure dose of inhalation or ingestion (DED_i) concentration (ng/kg bw/d) it can be using the following equation (9):

$$DED_i = \frac{C_{BDE} * IR * t}{bw} \quad (9)$$

Where C_{BDE} is the average concentration of individual BDE in air (ng/m^3) or soil (ng/g), IR is average inhalation rate (16.00 m^3/h or ng/h) or average ingestion rate (0.03 g/day), t is an exposure time (h) (8 h per day), and bw is the body weight of the exposed person (70 kg).

A range of exposures was calculated using 5th percentile (low), median (typical), and 95th percentile (high) concentrations of PBDEs. The exposed people were entirely adults. Table 3.6 presents the estimated exposure of adults to PBDEs via inhalation and soil ingestion (ng/kg bw/d).

An assessment of the human health risk arising from these estimated exposures was conducted by comparing exposure estimates with the reference doses for selected PBDE congeners (USEPA, 2011). The RfD values for BDE-47, BDE-99, BDE-153, BDE-209 are indicated in Table 3.6. Further inspection of Table 3.5 reveals that in all cases, our exposure estimates are substantially below the RfD values and suggest little concern about exposures arising from the pathways considered here.

To our knowledge, there are no comparable studies that assess human exposure to PBDEs associated with working at a landfill. Most previous exposure assessments focus on the indoor environment (Al-Omran and Harrad, 2015; 2016; Tao et al., 2016; Hassan and Shoeib, 2015; Fromme et al., 2014; Cequier et al., 2014;Thuresson et al., 2012; Tue et al., 2013; Ali et al., 2013; Kang et al., 2011; Zhu et al., 2013; Björklund et al., 2012; Shoeib et al., 2012; Sjödin et al., 2008a; Harrad et al., 2008b; 2006; 2004).

Table 3.7: Estimated exposure of adults to PBDEs via Air inhalation and Soil ingestion (ng/kg bw/d)

Exposure pathways		PBDE congeners								
		BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	tri-heptaBDEs	BDE-209
Air Inhalation (pg/kg bw/d):										
Landfill Air	Low	0.001	0.003	0.007	0.002	0.007	0.002	0.01	0.03	0.29
	Median	0.005	0.026	0.069	0.02	0.06	0.05	0.15	0.38	1.25
	High	0.03	0.067	0.12	0.06	0.17	0.11	0.27	0.82	2.48
Reference	Low	0.0004	0.0014	0.004	0.0014	0.005	0.0034	0.0089	0.025	0.08
Sites Air	Median	0.0008	0.0032	0.007	0.0026	0.0085	0.0052	0.0143	0.042	0.14
	High	0.0014	0.0055	0.0096	0.0041	0.0133	0.0089	0.0251	0.068	0.22
Soil Ingestion (ng/kg bw/d):										
RfD[a]		-	100	100	-	120	-	-	-	7000
Landfill Soil	Low	0.002	0.001	0.007	0.001	0.003	0.001	0.021	0.071	1.340
	Median	0.010	0.013	0.024	0.018	0.026	0.019	0.047	0.166	4.462
	High	0.029	0.029	0.037	0.028	0.040	0.047	0.091	0.249	8.013
Non-landfill	Low	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002	0.033
Soil	Median	0.000	0.000	0.001	0.000	0.000	0.000	0.002	0.004	0.057
	High	0.000	0.002	0.004	0.001	0.001	0.000	0.005	0.012	0.131

a) USEPA (2011a; b; c; d).

Chapter IV: NBFR Concentrations in Air and Soil Surrounding Oman Landfills and Implications for Occupational Exposure

4.1. Synopsis

Novel "emerging" brominated flame retardants (NBFRs) or "emerging flame retardants (EFRs)" have been considerably detected in environmental media such as air, soil, indoor dust, and sediment. NBFRs have more attention recently and there is a lack of data of these contaminants. In this chapter, concentrations of NBFRs in same soil and air samples of PBDE samples. NBFRs found in soil samples from the vicinity of six Omani landfills and in air surrounding two Omani landfills (Am and Ra landfills; both upwind and downwind of the landfill) and four reference sites in other areas of Oman. NBFRs were detected in all air and soil samples of landfills, 68% and 57**%** in the reference sites and in soil samples from non-landfilled areas respectively in this study.

Levels of target NBFRs detected in samples from landfill and references sites are compared to each other and with those reported in previous studies. Our results show DBE-DBCH was predominant with a mean concentration of 32.6 and 4.2 pg m^{-3} in the air of the landfills and reference sites, respectively. TBBPA-DBDPE was predominant in soil with mean concentrations of 34.8 ng g^{-1} and 12 ng g^{-1} in landfill and non-landfilled sites, respectively. Finally, data from this study was used to estimate daily adult exposure to PBDEs via air inhalation and dermal absorption from soil.

4.2. Concentrations of NBFRs in the Air of Oman

There have been little studies measuring NBFRs in outdoor air and soil, and to our knowledge, there are very little previous studies of concentrations of NBFRs in ambient air

and soil in the Middle East. This study reports concentrations of NBFRs in air samples collected from inside the vicinity of two landfills and four outdoor locations in Oman. Each of the target pollutants was high frequently detected in all samples with detection frequently (DF) of 100% for all compounds, which, indicates that the landfills were is polluted by these contaminants. Generally, DBE-DBCH congener was also often found and was the most abundant NBFR congener in all air samples profiles followed by DBDPE. Hence, sum of DBDPE and DBE-DBCH demonstrating 63 and 68% in average on Ra and Am landfills, respectively. Furthermore, NBFRs detected in 68% in air samples of reference sites. As indicated by Figures 4.2 and 4.3, DBE-DBCH was the most abundant NBFR congener in all air samples.

NBFRs are characterized as hydrophobic pollutants for especially the values of log K_{ow} > 5.0. Therefore, likened with soil and sediments specimens, observing BFRs in aquatic samples is fewer catchy due to the deficient concentrations (USEPA, 2010). In this study, the mean ∑NBFRs make up an average of 0.07 proportion of the mean ∑PBDEs content in the both Am and Ra landfills air samples.

In this chapter, concentrations of NBFRs in air of Oman's landfills will be reported for the first time. Levels of target NBFRs will be compared to each other and to those reported in previous studies. The NBFR compounds that low in concentrations among other contaminants were significantly generally lower than other BDE-209 concentrations in this study. These concentrations were eliminated from any statistical study for an independent contrast. Though, they were involved in the analysis of ΣNBFRs concentrations that mentions to the summation of these seven compounds.

Table B.1 in Appendix B lists average, SD, minimum, maximum, median and 5th, 25th, 75th and 95th percentile concentrations of our target NBFRs in air from locations in the vicinity of both Am and Ra landfills; while Table C.2 summarises concentrations in air at reference

locations within Oman. Concentrations of ΣNBFRs in air samples in the vicinity of our landfills ranged from 13 - 163 pg m^{-3} and from 11 - 135 pg m^{-3} at Am and Ra landfills, respectively. This compares with concentrations at the reference sites that ranged from 4.5 - 13 pg m^{-3} (Table 4.1). Figure 4.1 displays the concentrations of □NBFRs in air samples downwind (Dw) and upwind (Uw) sites of Am and Ra landfills (n=7 for each location category and landfill; thus, total air samples at the 2 landfill sites combined = 28) and illustrates the elevated concentrations downwind and upwind. By comparison, Figures 4.2 and 4.3 are box and whisker plots of concentrations of individual NBFRs in air samples at both downwind and upwind locations at the two landfills; illustrating the congener pattern and the predominance of DBE-DBCH.

Figure 4.1 show the concentration of NBFRs in air Samples downwind and upwind sites of Am and Ra landfills and reference sites. It illustrated that the downwind sites were more polluted by these contaminants rather than upwind of these landfills and reference sites. Also, in Am landfill it was shown there was high significance ($p < 0.05$) between upwind and downwind sites. So, we hypothesised that concentrations of NBFRs in air at locations downwind of our landfills would exceed significantly those upwind and moreover that concentrations at our landfill locations would also exceed substantially those at our reference sites as a consequence of volatilisation of NBFRs from landfilled waste. Figure 4.1 and Table C.1 show both these hypotheses to be proven. Specifically, concentrations of NBFRs at the downwind locations of each landfill were shown by paired t-test comparison to significantly exceed ($p < 0.05$) those at the corresponding upwind location. Similarly, ANOVA comparison of concentrations in air samples from landfill locations exceeded significantly ($p < 0.05$) those at the reference locations.

The results show that NBFR concentrations are higher than those outside locations, although the difference is not spectacular for these landfills (Table 4.1). These could be attributed to

meteorological and physical conditions, which might affect the NBFRs concentrations in the air. High average ambient temperatures (mean 31.1°C (± 6) in Al-Amerat station and 26°C (± 1.67) in Raysut, Salalah port station) during the sampling campaigns (2013 - 2015) and may also cause the wide distribution of NBFRs throughout the studied areas owing to high volatilisation. Also, the equilibrium sampling device (ESD) regime that applied in this study for air samples may be agreed with Mayer *et al*., (2003) hypothesis. However, the PAS sampling long period in this study (two-month campaign) remain in the kinetic region for PAS to deliver concentration data and may achieve ESD and their results caused to give high frequencies detected. Based on wind speed and direction data that measured in Al-Amerat and Raysut areas (DGM, 2016) during the sampling period for the landfill sites monitored, the downwind concentrations at two landfills exceed those analysed upwind (Figure 4.1). The winds in Oman blow predominantly to a north-northwest direction and at average speeds between 3 and 5 *knots*, with the maximum speed reaching 23 *knots* in the month of September 2015. Which suggests that ∑NBFRs concentrations may be affected the outer surrounding sites near to these landfills and it's indicating that these landfills represent a source of NBFRs to the outer environment. Interestingly, the ΣNBFR concentrations at the other four non-landfilled sites are slightly lower than these landfills levels ($p < 0.05$). The possible reason for this is the non-landfilled outdoor sampling locations are likely to be influenced strongly by their proximity to landfills as point sources of the NBFR pollutants and as well may be influenced by indoor environment because these four sites located in urban areas (Table 4.1). furthermore, Figures 4.2 and 4.3 show the box plots of the concentration of NBFRs in air Samples of Am and Ra landfills of this study.

Table 4.1: Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target NBFRs in air from locations in the vicinity of Am and Ra landfills and the reference site in Oman

NBFR congener	PBEB	EH-TBB	BEH-TEBP	BTBPE	TBBPA-DBPE	DBDPE	DBE-DBCH	∑NBFRs
Am Downwind:								
Average	1.72	3.12	10.49	11.07	12.88	23.28	64.41	126.96
SD	0.95	1.29	2.66	4.14	2.96	7.37	27.06	35.7
median	1.44	2.97	10.03	12.91	13.26	23.94	75.4	143.95
minimum	0.42	1.33	6.35	2.59	7.17	8.73	13.91	65.51
maximum	3.15	4.98	15.12	14.88	16.53	31.66	94.93	162.81
25th %ile	1.06	2.08	8.89	9.95	11.55	19.98	48.49	101.53
75th %ile	2.44	4.20	12.07	13.6	15.04	29.33	84.83	156.69
Am Upwind:								
Average	0.28	0.25	0.97	2.13	4.04	7.53	6.73	21.94
SD	0.16	0.09	0.41	0.95	1.32	3.66	3.84	5.45
median	0.29	0.3	1.03	2.47	3.26	7.49	6.02	21.86
minimum	0.09	0.13	0.41	0.49	2.65	2.63	2.02	13.30
maximum	0.57	0.36	1.69	3.36	6.43	12.66	13.32	29.37
25th %ile	0.15	0.16	0.66	1.48	3.01	4.47	3.39	18.43
75th %ile	0.37	0.33	1.16	2.82	4.97	10.5	9.47	26.08
Ra Downwind:								
Average	0.92	2.32	6.93	7.2	7.37	10.57	37.59	72.86
SD	0.59	1.05	2.64	3.48	4.56	7.67	20.69	35.95
median	0.71	1.90	7.32	4.85	6.43	10.29	37.97	68.99
minimum	0.29	0.87	2.81	3.36	0.01	2.58	8.31	23.84
maximum	1.77	4.18	11.02	12.38	15.38	26.59	65.42	135.12
25th %ile	0.4	1.63	5.04	4.43	5.27	4.39	20.78	46.67
75th %ile	1.45	3	8.65	10.46	9.6	12.88	54.93	94.36
Ra Upwind:								
Average	0.7	1.51	3.01	4.03	4.59	7.18	21.74	42.76
SD	0.42	0.61	1.24	1.83	2.57	4.19	11.58	17.75
median	0.62	1.48	2.96	3.81	4.84	7.68	17.64	37.78
minimum	0.14	0.5	0.49	2.09	0.08	1.30	3.76	11.21
maximum	1.35	2.52	4.54	7.22	8.14	14.17	40.59	66.8
25th %ile	0.41	1.18	2.68	2.27	3.04	3.66	14.9	35.18
75th %ile	0.98	1.85	3.86	5.28	6.5	9.89	30.2	56.58
Reference Sites:								
Average	0.10	0.42	1.25	0.76	0.57	1.95	4.24	9.29
SD	0.10	0.22	0.70	0.68	0.50	1.19	2.63	2.87
median	0.10	0.48	1.36	0.76	0.57	1.95	4.24	9.29
minimum	0	0	0	0	0	0	0	4.51
maximum	0.28	0.63	2.14	1.67	1.14	3.62	7.25	12.80
25th %ile	0	0.42	1.25	0	0.02	1.61	3.02	8.34
75th %ile	0.11	0.56	1.51	1.36	1.13	2.56	6.71	11.53

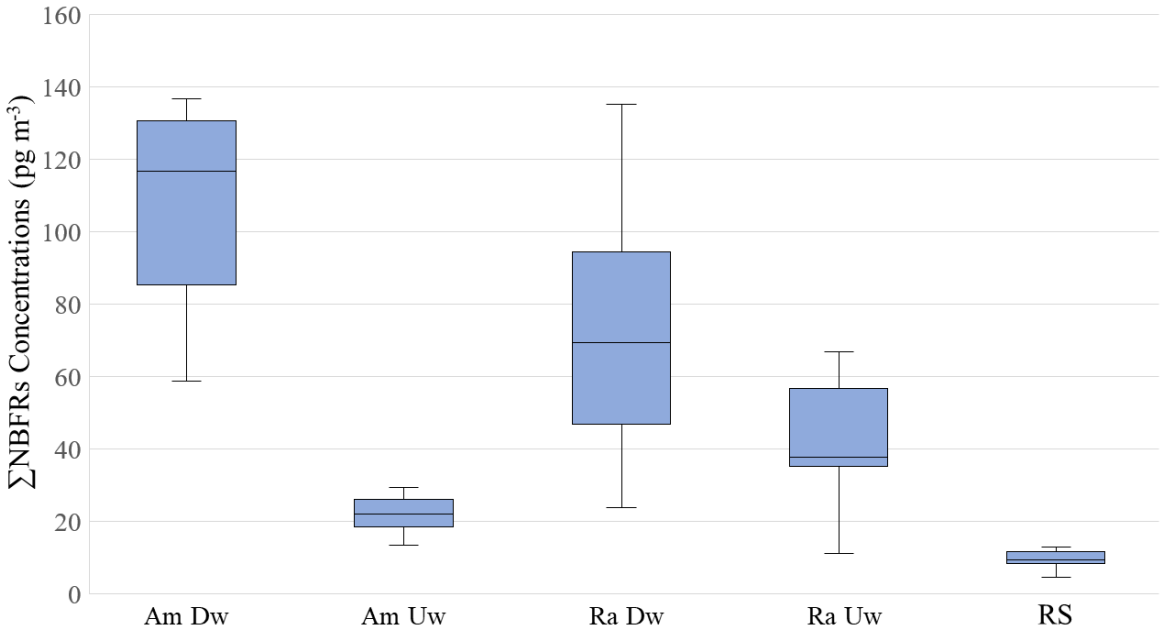


Figure 4.1: Concentration of ∑NBFRs in air Samples downwind (Dw) and upwind (Uw) sites of Am and Ra landfills and the reference sites (RS) in Oman

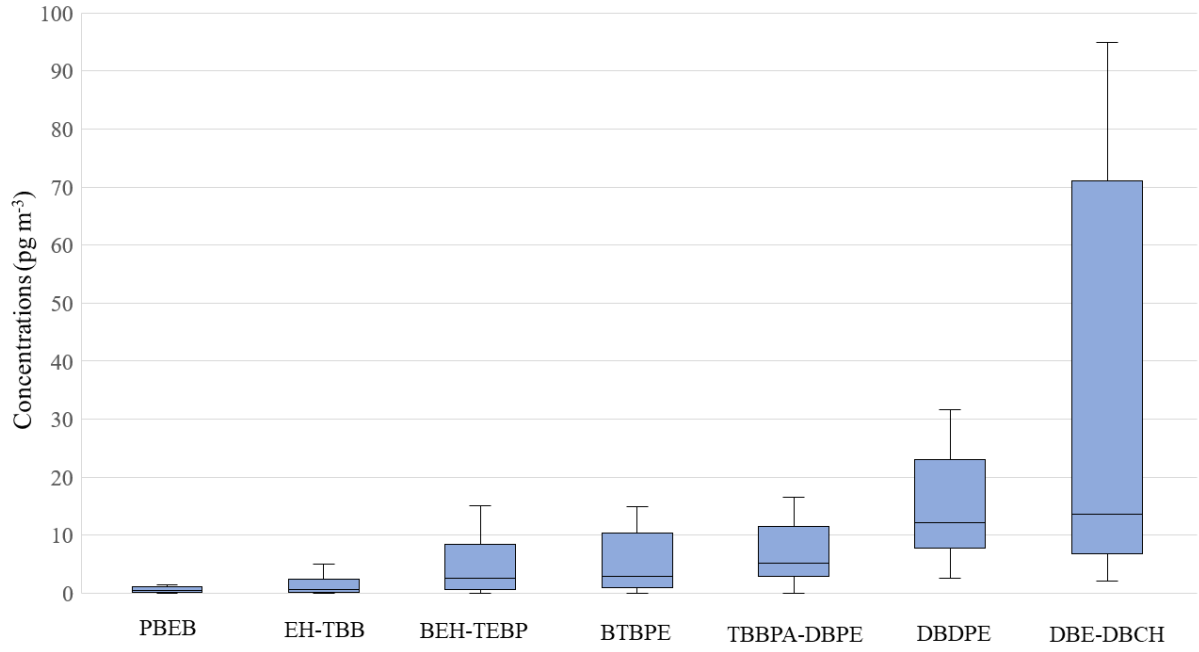


Figure 4.2: Box plot of the concentration of NBFRs in air Samples of Am landfill

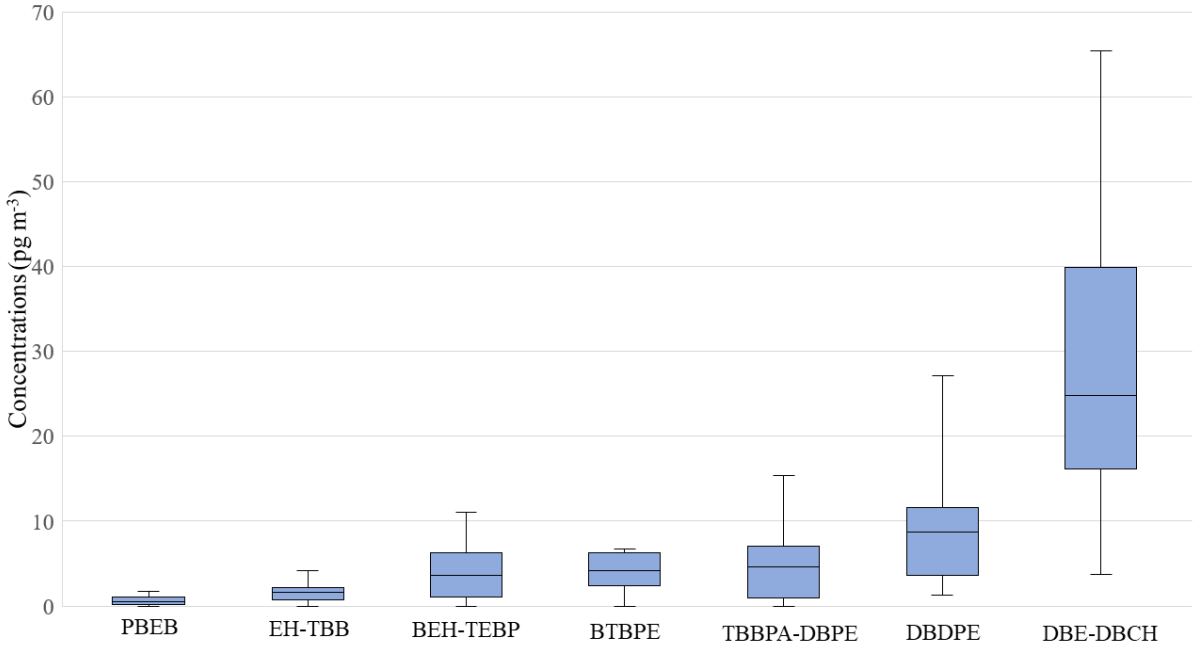


Figure 4.3: Box plot of the concentration of NBFRs in air Samples of Ra landfill

4.2.1. Profile of NBFRs homologues in the Air

The profile of NBFR congeners, as well as PBDEs in the atmosphere provide clues as to whether their sources are local or remote from the sampling location (Gevao *et al*., 2006). The range of NBFRs concentrations was 13 - 163 pg m^{-3} (mean 74.5 pg m^{-3}) and from 11 - 135 pg m^{-3} (mean 57.8 pg m^{-3}) at Am and Ra landfills, respectively. Figure 4.4 shows the profiles of NBFR homologues average concentrations in Am and Ra landfills. The profile of NBFR congeners in the atmosphere provide clues as to whether their sources are local or remote from the sampling location (Gevao et al., 2006). Figure 4.4 shows the average NBFR homologue profiles at Am and Ra landfills.

In general, the congener pattern at source locations (like landfills) is expected to be different from that at remote locations as a result of differences in volatility and reactivity in the atmosphere. In the discussion that follows, DBE-DBCH constituted 47.8 and 51.3% of ΣNBFRs in the air at Ra and Am landfills, respectively. After this, DBDBE comprised approximately 21 and 15.3 ΣNBFRs at the Am and Ra landfills, respectively. The sum of

five NBFRs (Σ_5NBFRs), together constituted almost 32 and 33.4% ΣNBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE, and TBBPA- DBPE contributing1.3, 2.3, 7.7, 8.9, and 11.4% and 1.3, 3.3, 8.6, 9.7, and 10.3% ΣNBFRs at Am and Ra landfills, respectively). By comparison, Figure 4.5 shows the NBFR congeners profile in air samples from reference sites in this study. In contrast with the above expectations, the texture profile shows the compatibility of reference sites with the landfill's profiles.

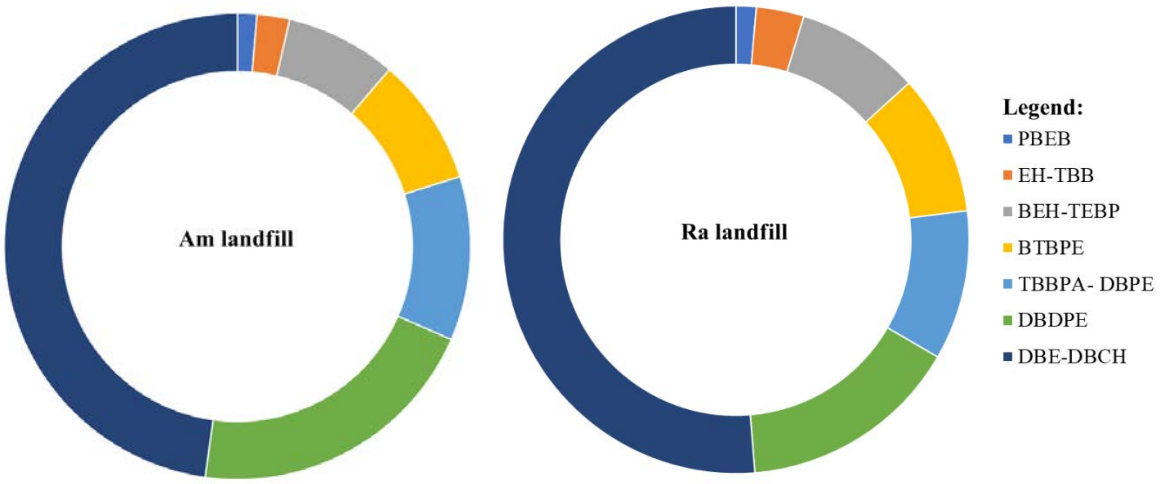


Figure 4.4: Profiles of NBFR homologues (percentages, %) in Am and Ra landfills

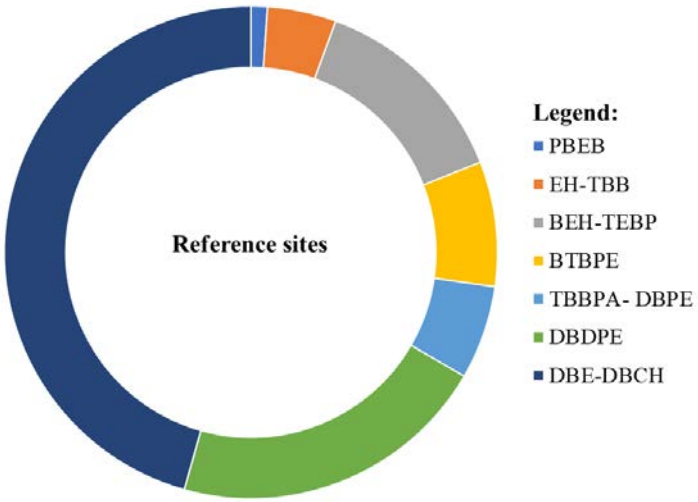


Figure 4.5: Profiles of NBFR homologues in reference sites

4.2.2 Statistical Analysis of NBFR Concatenations in the Air

Interestingly, the ΣNBFR concentrations at the other four non-landfilled sites are singifantly lower than the landfills levels ($p < 0.05$) (Figure 4.1). The possible reason for this is the non-landfilled outdoor sampling locations are likely to be influenced strongly by their proximity to landfills as point sources of the NBFR pollutants and as well may be influenced by the indoor environment because of these four sites located in urban areas (Table B.2). The t-test of log-transformed NBFR concentrations in air samples of both Am and Ra landfills show there were exceed significance ($p < 0.05$) of downwind to upwind concentrations and that refers to the source of these contaminants is the same landfill. However, NBFRs (without DBE-DBCH) and DBE-DBCH were high significance ($p < 0.05$).

Figures 4.2 and 4.3 show the concentration of ΣNBFRs in air Samples downwind and upwind sites of Am and Ra landfills. It illustrated that the downwind sites were more polluted by these contaminants rather than upwind sites of these landfills. Also, in Am landfill, it was shown there was high significance ($p < 0.05$) between the concentrations of upwind and downwind sites.

There is different analysis performed to compare the levels and distribution of each compound in different sites. The first analysis used ANOVA and subsequent multiple comparisons to check the levels of compounds in Am and Ra landfills. The ANOVA results showed significant differences in compound levels in both sites, with $p < 0.01$ for both Am and Ra landfills. Multiple comparisons revealed unique significant differences. At Am landfill, there was a significant difference between the levels of compound PBEB and compound DBE-DBCH ($p < 0.000$), also there is significant differences between PBEB and other NBFRs compounds. Other compounds (EH-TBB, BEH-TEBP, BTBPE, TBBPA-DBPE, and DBDPE) were all significantly different from compound DBE-DBCH ($p < 0.05$). Compound BTBPE was not significantly different from compound TBBPA-DBDPE and

BEH-TEBP ($p > 0.05$), but not different from the other compounds. Correspondingly, compound DBE-DBCH was significantly different from all the compounds measured. At Ra landfill, all the compounds were significantly different from compound DBE-DBCH ($p < 0.000$) for all comparisons.

The paired sample T-test was used to see the differences in compound levels at different locations of the same landfills. The results showed that all the compounds were significantly different at location Upwind and Downwind ($p < 0.000$) for all the pollutants. Finally, the association between site and compound to the levels of each compound was investigated using multiple linear regression.

4.2.3. Comparison with worldwide NBFR concentrations in the Air

The low concentrations of NBFRs were detected in air samples. In Sweden, Newton *et al*. (2015) reported that BEH-TEBP and DBDPE in indoor air ranged < 35 - 150 pg m^{-3} and < 90 - 250 pg m^{-3} with detection frequencies of 15% and 8% for BEH-TEBP and DBDPE respectively. Drage *et al*. (2016) were identified a DBE-DBCH, DBDPE and other FRs outdoor air collected from June 2012 to January 2013 on a rural-urban transect in West Midlands, UK. Compared to this study, the levels of DBE-DBCH in the landfills of this study were exceed significantly those in outdoor air of Birmingham ($p < 0.05$). Which support the hypothesis that suggested the landfills will be a source of contamination to the outdoor environment for those compounds. Table 4.2 shows the summary of Mean and/or range concentrations (pg m^{-3}) of NBFRs in air compartments from different regions worldwide.

Table 4.2: Summary of Mean and/or range concentrations (pg m^{-3}) of NBFRs in air compartments from different regions worldwide

NBFR	Air (pg m^{-3})	Region	Reference
DBDPE	1916	China	Shi *et al*., 2009
	up to 120	US	Hoh *et al*., 2005
	0.6	Sweden	Kierkegaard *et al*., 2004
	7	Sweden	Karlsson *et al*., 2006
	1842 (402 - 3578)	China	Shi *et al*., 2009
	23	China	Qiu *et al*., 2010
	0.27 (0.04 - 2.2)	Longyearbyen, Svalbard	Salamova *et al*., 2014
	1.0 - 22	USA, near Great Lakes	Venier and Hites, 2008
	0.15 (<0.12 - 0.33)	Sweden	Newton *et al*., 2015
	2.95 (<5.90 - 216)	East Africa	Arinaitwe *et al*., 2014
	nd - 2240	China, e-waste	Tian *et al*., 2011
	3.97 - 1370	China, rural area	Tian *et al*., 2011
BTBPE	0.1 - 10	US	Hoh and Hites, 2005
	30.7	China	Shi *et al*., 2009
	<0.6 - 39	Sweden	Pettersson-Julander *et al*., 2004
	5.6 - 67	Sweden	Sjödin *et al*., 2001
	30	Sweden	Karlsson *et al*., 2006
	6.7 (2.8 - 70)	USA	Hoh *et al*., 2005
	25.7 (3.83 - 67.4)	China	Shi *et al*., 2009
	0.4 - 1.8	USA	Ma *et al*., 2013
	0.73	China	Qiu *et al*., 2010
	0.044 (0.024 - 0.222)	Canada, Western sub-arctic	Yu *et al*., 2015
	0.03 (0.01 - 0.09)	Norway, Longyearbyen	Salamova *et al*., 2014
	0.5-1.2	USA, near Great Lakes	Venier and Hites, 2008
	<0.077 (<0.077 - 0.26)	Sweden	Newton *et al*., 2015
	1.26 (<0.06 - 90.5)	East Africa	Arinaitwe *et al*., 2014
	4.49 - 398	China, e-waste	Tian *et al*., 2011
	nd - 28.4	China, rural area	Tian *et al*., 2011
EH-TBB	2.2 (0.17 -58)	Canada, Western sub-arctic	Salamova *et al*., 2014
	0.03 (<0.06 - 1.19)	Longyearbyen, Svalbard	Arinaitwe *et al*., 2014
	0.143 (0.024 - 1.21)	Sweden	Yu *et al*., 2015
	0.13 (<0.029 - 0.47)	East Africa	Newton *et al*., 2015
BEH-TEBP	0.5 - 8	USA	Ma *et al*., 2013
	1.8 (0.27 - 14)	Canada, Western sub-arctic	Salamova *et al*., 2014
	0.35 (<0.69 - 64.2	Longyearbyen, Svalbard	Arinaitwe *et al*., 2014
	0.353 (0.028 - 5.55)	East Africa	Yu *et al*., 2015
TBBPA-BDBPE	371 (131 - 1240)	China	Shi *et al*., 2009
	528	China	
DBE-DBCH	0.46 (0.18 - 2.4)	Sweden	Newton *et al*., 2015
	2 (< 0.14 – 41)	UK	
PBEB	nd - 0.01	Canada	Gouteux *et al*., 2008
	0.29 - 867	Canada, Western sub-arctic	Tian *et al*., 2011
	0.10 - 4.80	Longyearbyen, Svalbard	Tian *et al*., 2011
	0.03 (0.01 - 0.24)	USA, near Great Lakes	Salamova *et al*., 2014
	0.03 (<0.06 - 1.83)	China, e-waste	Arinaitwe *et al*., 2014
	0.011 (0.002 - 0.078)	China, rural area	Yu *et al*., 2015

4.3. Periodical variability of NBFRs concentrations in the Air samples

The Periodical variations of NBFRs concentrations were investigated in the air samples of the Am and Ra landfills. As mentioned before the period of sampling campaigns for both landfills were between June 2013 - July 2014 and September 2014 - October 2015 in Ra and Am landfills, respectively. Due to the meteorological data that provided by GDM, Oman, the Table 4.3 shows the average concentrations of ΣNBFRs in the mentioned campaigns times. Also, it shows the impact of temperature periods that accompanied with sampling intervals in these landfills.

The seasonal variances of the average NBFR concentrations show that the period of Jul. – Aug. 2015 (96 pg m^{-3}) was the highest season that had high NBFR concentrations than other seasons in Am landfill. The lowest average concentrations were Jan. – Feb. 2015 (41 pg m^{-3}) in the same landfill. For Ra landfill, the average NBFR concentrations show that the period of February – March 2014 (101 pg m^{-3}) were the highest in the season of sampling and the lowest average concentrations were Oct. – Nov. 2013 (17.5 pg m^{-3}) in this landfill.

4.3.1. Meteorology Role in the Sampling Areas

Meteorological data obtained from the Oman Directorate General of Meteorology (DGM), during sampling campaigns (DGM, 2016) were used to try and explain any differences in NBFR concentrations in samples taken at different times of year. Table 4.3 displays the temporal variations of average ΣPBDEs concentrations (pg m^{-3}) and ambient air temperature at Am and Ra landfills.

As mentioned before the period of sampling campaigns for both landfills were between June 2013 – July 2014 and September 2014 – October 2015 for Ra and Am landfills, respectively. As well as Table 4.3, Figures 4.6, and 4.7 illustrate how average concentrations of ΣNBFRs vary with temperature at each of our two landfills. Linear regression between ΣNBFRs and average temperature revealed no significant correlation at either landfill, suggesting that

volatilisation from landfill was not the only source of airborne NBFRs at the sites monitored in this study. Other possible sources could include dispersion of contaminated particulates. These would strongly preferentially favour emissions of less volatile NBFRs such as BEH-TEBP, DBDPE, and TBBPA-DBDPE, which as highlighted above, is the predominant NBFR congener detected in air.

Table 4.3: Temporal variations in average Σ NBFR concentrations (pg m^{-3}) and ambient air temperature at Am and Ra landfills (DGM, 2016)

Sampling period	ΣPBDEs concentrations		Temperature		
	Upwind	Downwind	Mean	Max	Min
Am landfill:					
Sept. – Oct. 2014 (P1)	155.14	21.86	33	43	22
Nov. – Dec. 2014 (P2)	117.43	29.37	24	33	16
Jan. – Feb. 2015 (P3)	65.51	16.91	23	34	15
Mar. – Apr. 2015 (P4)	143.95	19.95	30	41	19
May – Jun. 2015 (P5)	158.23	23.41	35	46	26
Jul. – Aug. 2015 (P6)	162.81	28.75	35	49	25
Sept. – Oct. 2015 (P7)	85.63	13.30	33	44	22
Ra landfill:					
Jun. – Jul. 2013 (P1)	82.68	63.79	26	30	24
Aug. – Sept. 2013 (P2)	69.28	49.38	25	29	22
Oct. – Nov. 2013 (P3)	23.84	11.21	27	33	21
Dec. 13 – Jan. 2014 (P4)	106.03	37.10	24	31	17
Feb.– Mar. 2014 (P5)	135.12	66.80	25	32	19
Apr. – May 2014 (P6)	56.32	37.78	28	34	24
Jun. – Jul. 2014 (P7)	37.01	33.25	27	31	24

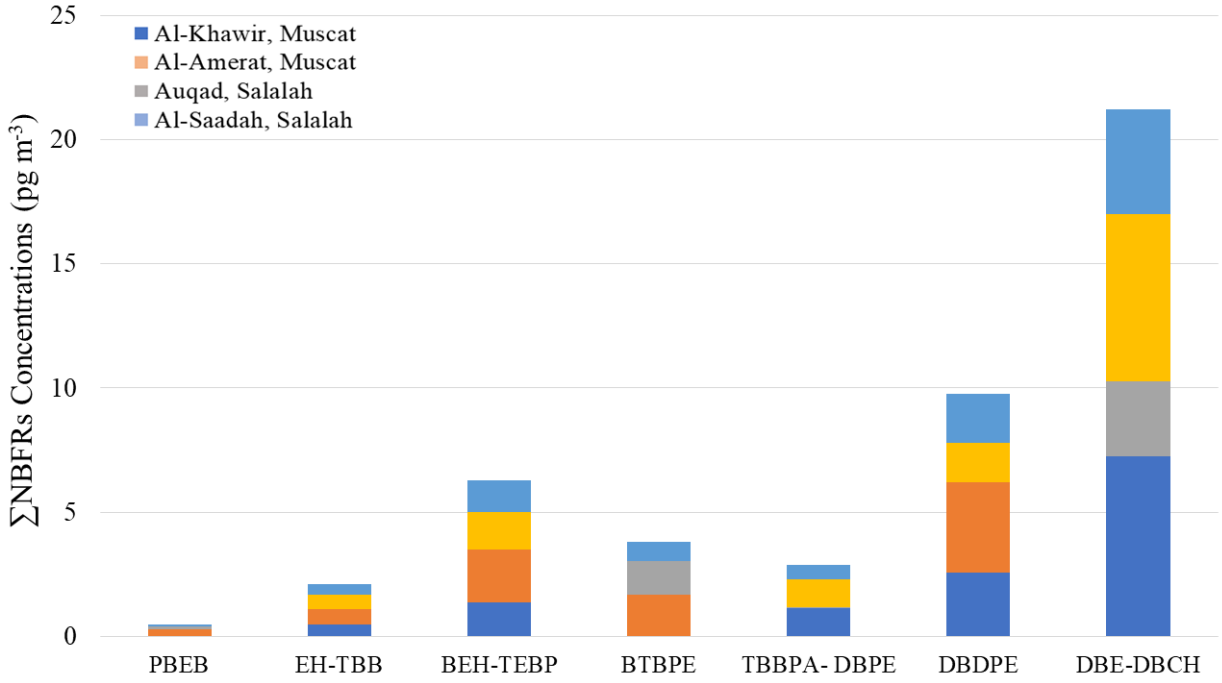


Figure 4.6: Concentration of NBFRs in air samples of the reference sites

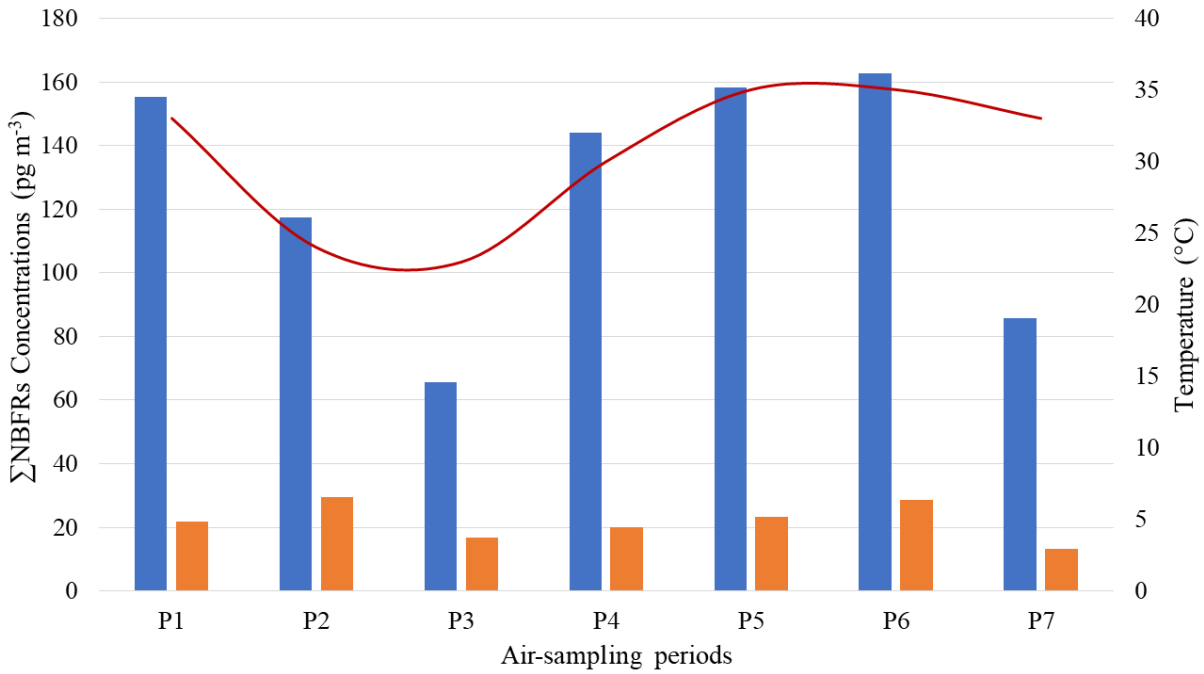


Figure 4.7: Average concentrations of ΣNBFRs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Am landfill compared with mean ambient temperature (°C) (red line) of Al- Amerat area

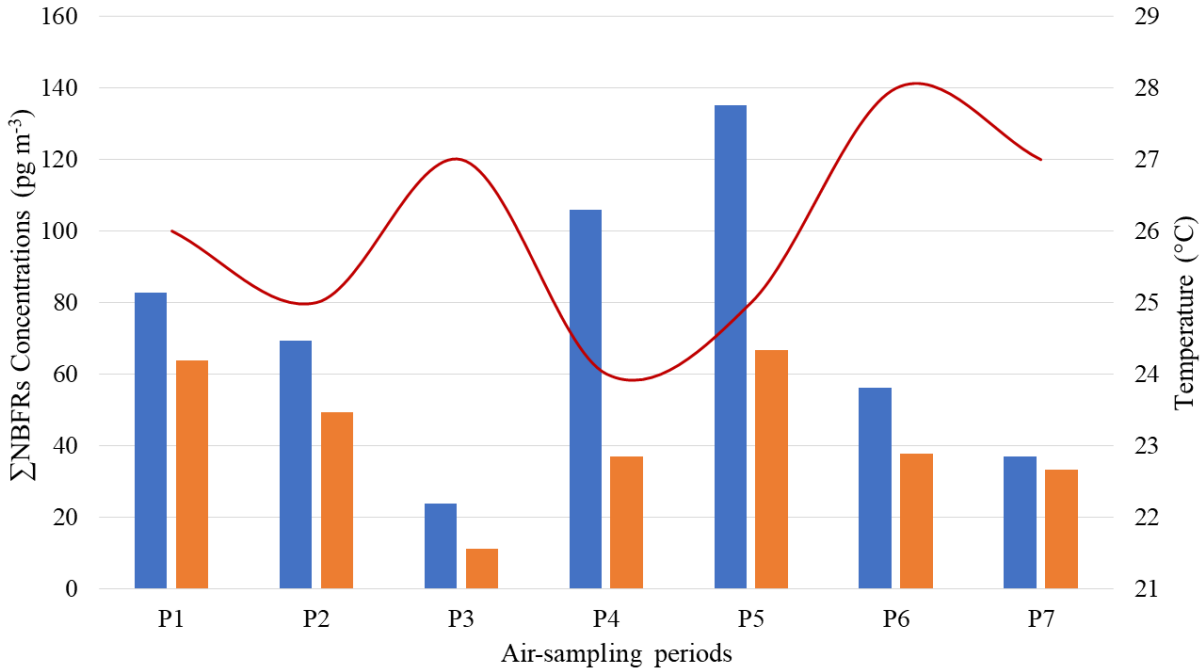


Figure 4.8: Average concentrations of ΣNBFRs in Dw (blue bars) and Uw (yellow bars) in the campaign's periods of the air samples of Ra landfill compared with mean ambient temperature (°C) (red line) of Raysut area

4.4. Concentrations of NBFRs in the Soil from landfill sites in Oman

This study reports concentrations of NBFRs in soil samples collected from surrounding of the vicinity of six landfills in Oman. The total of seven NBFR congeners were detected and quantified in all soil samples at significantly higher levels than that in their respective reference of non-landfilled sites ($p < 0.05$). The NBFRs were detected 57% in soil samples from non-landfilled areas in this study. Tables 4.4 and 4.5 show the Summary statistics of NBFRs concentrations in soil from the vicinity of landfills and non-landfilled areas of Oman. Occasionally, There is lack of NBFRs in the soil and air surrounding landfills worldwide. Table 4.6 show mean and range of concentrations (pg m^{-3}) of NBFRs in soil compartments from different regions worldwide.

Table 4.4: Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target NBFRs in soil from locations in the vicinity of the landfills in Oman

NBFR congener	PBEB	EH-TBB	BEH-TEBP	BTBPE	TBBPA-DBPE	DBDPE	DBE-DBCH	∑NBFRs
Am Downwind:								
Average	1.15	1.33	2.51	4.03	3.51	9.28	12.95	34.76
SD	1.15	0.87	1.67	3.26	1.59	4.06	4.61	7.90
median	0.66	1.06	2.08	2.81	3.50	8.47	12.93	35.41
minimum	0.04	0.16	0.65	0.48	0.87	2.10	5.10	20.49
maximum	3.39	4.02	6.09	12.05	7.11	17.15	22.24	47.03
25th %ile	0.25	0.81	1.07	1.93	2.48	6.33	9.55	28.87
75th %ile	1.92	1.72	3.82	6.15	4.11	11.81	16.99	38.69

Table 4.5: Average, SD, minimum, maximum, median, and 25th, and 75th percentile (%ile) concentrations of the target NBFRs in soil from locations in the non-landfilled areas in Oman

NBFR congener*	BTBPE	TBBPA-DBPE	DBDPE	DBE-DBCH	∑NBFRs
Am Downwind:					
Average	1.50	3.56	2.65	4.31	12.01
SD	0.26	1.24	0.66	1.70	3.85
median	6.44	2.06	5.36	7.41	21.27
minimum	1.03	0.46	1.98	3.18	6.66
maximum	3.29	3.49	3.69	5.66	16.13
25th %ile	1.50	3.56	2.65	4.31	12.01
75th %ile	0.26	1.24	0.66	1.70	3.85

* PBEB, EH-TBB, and BEH-TEBP not detected

A total of seven NBFR congeners were detected in all samples from the Omani landfill sites from which soil samples were collected. In total, soil was collected from the vicinity of six landfill sites in Oman. In addition to Am and Ra from which air samples were also collected, soil was collected from the following 4 additional landfills: Ni, So, Ib, and Bu landfills. In addition to landfill sites, soil samples were also collected from reference sites in Oman. Concentrations of NBFRs in soil samples from landfill locations were significantly higher than those in their respective reference sites ($p < 0.05$). With respect to the congener profile in soil samples, generally, DBE-DBCH congener was the predominant NBFR detected. The soil concentrations of ΣNBFRs varied from 20.5 - 47 ng g^{-1} (mean 34.8 ng g^{-1}).

4.4.1. Comparison with worldwide NBFRs concentrations in the Soil

There is lack of knowledge about physicochemical properties and environmental manner of NBFRs and there are no much data about NBFRs especially in landfill soils. The chemicals sorption into sediment or soil could be expected by K_{oc} rates. However, when K_{oc} degree is excessive, then a chemical will lead to adsorb into the soil. The ground soil signifies the main basin for countless organic contaminants. The NBFRs value concentrations in the rhizosphere (soil in the vicinity of plant roots) and non-rhizosphere were ranged between 11.6 - 70.8 ng g^{-1} in e-waste recycling area in South China i.e. they further fortified in the rhizosphere soils than non-rhizosphere soils. Total organic carbon was a more crucial factor for controlling the PBDEs more than NBFRs (Wang *et al*., 2016). For example, Zheng *et al*. (2015) confirmed that BDE-209 and DBDPE were the primary pollutants in forestry soil in China. The samples concentrations of BDE-209 went between < dl to 5,900 pg g^{-1} and those of DBDPE varied among 25 and 18,000 pg g^{-1}. In this investigation as well, the apportionment of most PBDEs and BEH-TEBP were substantially associated with population density. Moreover, the linkage between PBDEs and their substitute products designates same environmental conduct (Zheng *et al*., 2015). Table 4.6 show the concentrations of NBFRs in soil compartments from different regions worldwide.

Table 4.6: Some average and/or range concentrations of NBFRs in soil compartments from different regions worldwide

NBFR	Soil (ng g^{-1})	Region	Reference
DBDPE	0.91 (0.20-160)	Sweden	Newton *et al*., 2015
	28.1	China	Shi *et al*., 2009
BTBPE	0.05	China	Shi *et al*., 2009
TBBPA-BDBPE	<25-85.3	China	Qiu *et al*., 2010
DBE-DBCH	0.46 (0.18 - 2.4)	Sweden	Newton *et al*., 2015

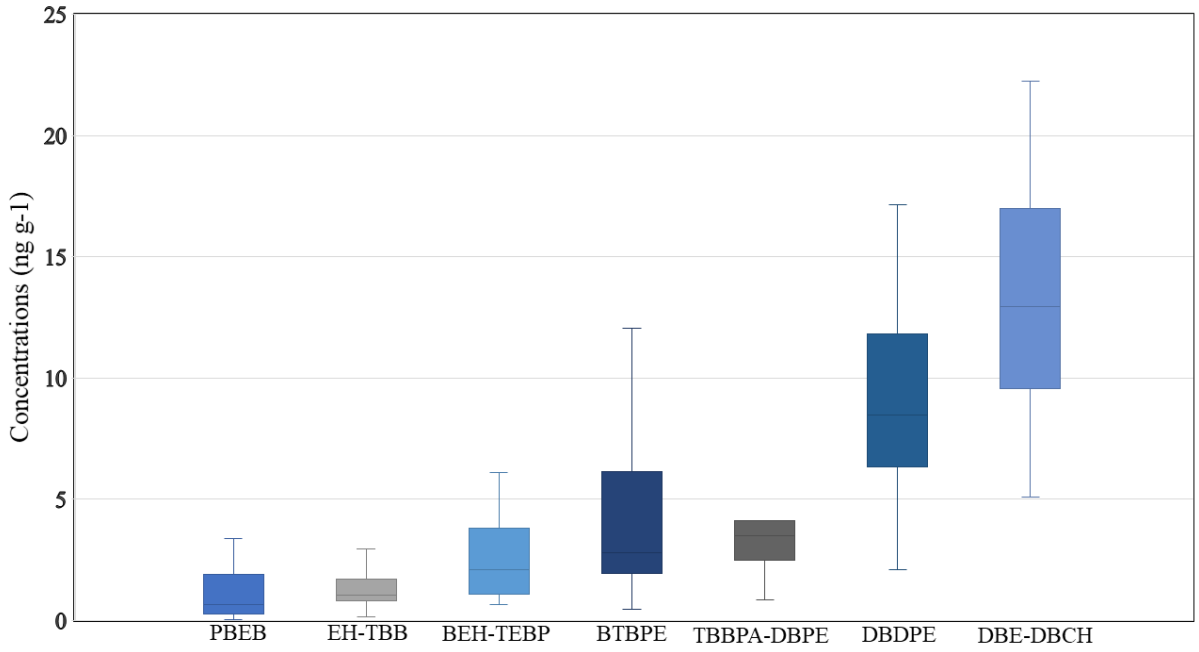


Figure 4.9: Box plot of the concentrations of NBFRs in soil samples from Am landfill

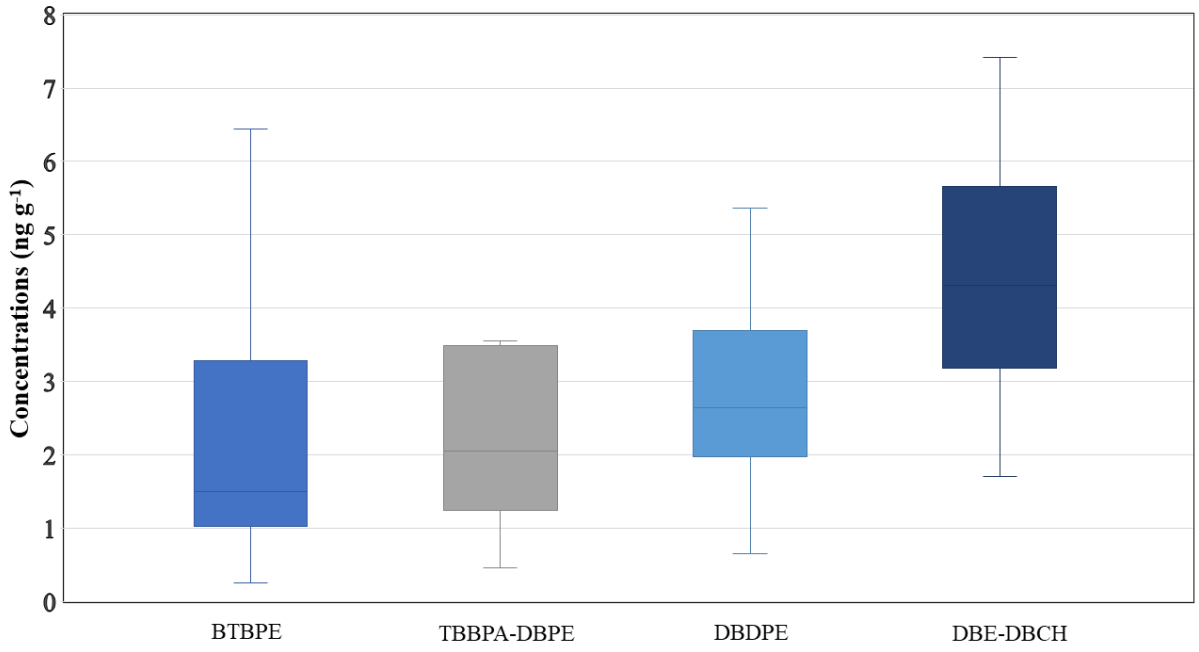


Figure 4.10: Box plot of the concentrations of NBFRs in soil samples from Ra landfill

Comparison of concentrations of NFBRs in soil samples taken in the vicinity of our landfills with those detected in soil from our non-landfill-impacted reference areas, shows those at

landfill exceed significantly those in reference sites (t-test on log-transformed concentrations, $p < 0.05$). These results are consistent with the hypothesis that landfill is a source of NBFRs to the environment (Figures 4.9).

ANOVA was used and many subsequent comparisons to check the levels of contaminants in different locations, including the six landfills. The result revealed some significant differences. At non-landfilled areas at Am landfill, ΣNBFRs was significantly different to DBE-DBCH ($p < 0.014$). Concentrations at non-landfilled areas of Ra, So and Bu landfills also showed significant differences between ΣNBFRs and DBE-DBCH ($p < 0.05$). However, the remaining comparisons were not significantly different.

The paired sample t-test was used to see the differences in compound levels at different locations of the same site in this group of analysis. The results showed that all the NBFR pollutants were significantly different at locations of the landfills and non-landfilled areas, with a $p= 0.004$. The association between site and pollutants to the levels of each pollutant in this group was also investigated using multiple linear regressions.

4.5. Potential Occupational Exposures at Omani Landfills

Here we will follow same role of section 3.4 in chapter III. Hence, the people who work at these landfills may be exposed by inhalation, accidental ingestion of soil and dermal contact with soil. In this study, we estimate intake dose as multiples of the contact rates (e.g. ng soil ingested per day) and the NBFRs concentration in the exposure media (air or soil) (USEPA, 2011). Table 4.7 show the estimated exposure (ng/kg bw/d) of adult to NBFRs via air inhalation, soil ingestion in this study.

4.5.1. Daily exposure dose to NBFRs via air and soil

A mean daily exposure dose (DED) to PBDEs via air inhalation and soil ingestion was estimated based on PBDEs concentrations in this study. Soil ingestion and air inhalation were assumed to arise pro-rata to typical activity patterns for adults. Moreover, an average soil ingestion rate of 0.03 g/day was used for adults (Jones-Otazo et al. 2005; USEPA, 2011), with the assumed inhalation rate for adults being 16 m^3/day (USEPA, 2011). To calculate the daily exposure dose of inhalation or ingestion (DED_i) concentration (ng/kg bw/d) it can be using the equation (9) in previous chapter III. A range of exposures was calculated using 5^{th} percentile (low), median (typical), and 95^{th} percentile (high) concentrations of NBFRs. The exposed people were entirely adults. Table 4.6 presents the estimated exposure of adults to PBDEs via inhalation and soil ingestion (ng/kg bw/d).

An assessment of the human health risk arising from these estimated exposures was conducted by comparing exposure estimates with the reference doses for selected NBFR congeners (USEPA, 2011). The RfD values for EH-TBB, BTBPE, BEH-TEBP, and DBDPE are indicated in Table 4.7. Further inspection of Table 4.7 reveals that in all cases, our exposure estimates are substantially below the RfD values and suggest little concern about exposures arising from the pathways considered here.

To our knowledge, there are no comparable studies that assess human exposure to NBFRs associated with working at a landfill. Most previous exposure assessments focus on the indoor environment.

Table 4.7: Estimated exposure of adults to PBDEs via Air inhalation and Soil ingestion (ng/kg bw/d)

Exposure pathways	NBFR			
	EH-TBB	, BTBPE	BEH-TEBP	DBDPE
Air Inhalation (pg/kg bw/d):				
RfD	20,000	243,000	20,000	333,333
Low	1.78	5.05	5.11	5.25
Typical	5.89	12.43	22.12	24.90
High	26.20	28.77	56.54	163.33
Soil Ingestion (ng/kg bw/d)				
Low	0.00	0.00	0.01	0.02
Typical	0.01	0.01	0.03	0.04
High	0.04	0.02	0.06	0.06

Chapter V: Leaching of Flame Retardants from Waste PUF under Laboratory Conditions

5.1. Synopsis

The investigation of the leaching behaviour of flame retardants (FRs) from PUF samples is carried out in this chapter. The concentrations (ng L^{-1}), percentage leached (PL, %) and percentage leached per unit time values (PLT, % h^{-1}) are presented for a range of landfill relevant leaching fluids. Concentrations of target FRs will be compared to those reported in landfill leachates from previous studies. More details of the experimental leaching programme can be found in section 2.5 of Chapter II. A brief summary is that experiments evaluate the impact of contact time, agitation, DHM and pH on FR leaching.

There are few previous studies of FR leaching experiments (Danon-Schaffer *et al*., 2009; Choi *et al*., 2013; Stubbings, 2015). For example, Stubbings (2015) developed a series of standardised leaching experiments to study FR leaching from a range of FR-containing waste including PUF used in furniture. These experiments demonstrated that PBDEs and particularly TCIPP are easily leached from PUF.

5.2. Leaching experimental procedures

Section 2.5 in chapter II describes a series of standardized leaching tests that were carried out in this study to finding out the FR emissions from waste PUF. The leaching experiments were applied by using a variety of leaching fluids to mimic the real landfill leachate characteristics such as pH and temperature under agitation. Aliquots of PUF pieces (3 x 0.5 g ~ 1 cm^3) were exposed to 100 mL leaching fluid for 6, 24, 48, 72 and 96 h respectively at 20, 60 and 80˚C. Hence, fresh PUF samples were used for each period. The effects of

different landfill relevant leaching fluids were explored and DHM contents of 0, 100 and 1000 mg L^{-1} and pH (5.8), (6.5) and (8.5) used in these tests. The leaching experiments were performed under agitation except for some experiments used to check the effect of agitation where no agitation was applied. Furthermore, a waste: leachate (mass: volume) ratio of 10% was used.

5.3. Initial FR concentrations in the PUF samples

The FR concentrations present in the PUF samples used in our leaching experiments were determined according to subsection 2.6.3 in the chapter II. The levels were compared with reference materials and previous studies.

In this study, the initial FR concentrations (Tables 5.1 and 5.2) in PUF samples are consistent with those present in commonly-used FR formulations, specifically PentaBDE, Firemaster® 550 (FM550) (Stapleton *et al*., 2009) and TCIPP. The brominated component of FM550 consists of 30, 8 and 17% of EH-TBB, BEH-TEBP and TPhP, respectively (Stapleton *et al*., 2009; Klosterhaus *et al*., 2010; McGee *et al*., 2012). TCIPP is an organophosphate flame retardant widely used as an additive FR in furniture PUFs and many other products (Cooper *et al*., 2016).

5.3.1. Concentrations of BFRs and TPhP in the USA PUF samples

Table 5.1 shows the average concentrations of FRs in USA and UK PUF samples used in this research. The percentage contribution of individual PBDE congeners was as shown in Table 5.2 and compared closely with the composition of the commercial Penta-BDE mixtures (DE-71) and Bromkal (70-5DE) (La Guardia *et al*., 2006).

Table 5.1: Mean concentrations of FRs in USA PUF and TCIPP in UK PUF samples (n= 9; 3 for each PUF sample) in this study

FR	Average Concentration (mg g^{-1}) ± SD [a]	RSD (%)	Water Solubility (mg L^{-1})[b]	Log K_{ow}[b]
PentaBDEs (USA PUF):				
BDE-47	8.10 ± 0.11	1.36	0.11	6.81
BDE-99	9.34 ± 0.23	2.46	0.08	7.32
BDE-100	2.09 ± 0.05	4.78	0.085	7.24
BDE-153	1.08 ± 0.07	6.48	0.031	7.90
BDE-154	0.72 ± 0.02	2.78	8.70×10^{-4}	7.82
NBFRs (USA PUF):				
EH-TBB	2.26 ± 0.11	4.87	3.2×10^{-4}	7.73
BEH-TEBP	10.25 ± 0.33	3.22	6.92×10^{-5}	9.34
PFRs				
TPhP (US PUF)	7.02 ± 0.67	9.54	4.67	4.76
TCIPP (UK PUF)	17.10 ± 0.41	2.40	1200	3.30

[a] SD is standard deviation; [b] Table 1.9 in the chapter I.

Table 5.2: Congener composition (%) of PentaBDEs in PUF samples and commercial PentaBDE mixtures

PentaBDE	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
This study	40.0	43.8	9.81	5.04	3.38	This study
DE-71	38.2	48.6	13.1	5.44	4.54	La Guardia *et al*., 2006
Bromkal (70-5DE)	42.8	44.8	7.82	5.32	2.68	

5.3.2. Preliminary TCIPP concentrations in the UK PUF sample

The TCIPP concentrations varied from 0.5 to 2.2% by weight in furniture foams from the USA (Stapleton et al., 2009). TCIPP is the major FRs used in the UK (WHO, 1998; USEPA, 2015). Its typically added to flexible PUF at 3 to 5% by weight (Leisewitz et al., 2001) or at 1 - 4 % by weight (Flexible Foam Research Ltd (BPF, UK) as cited on Stubbings, 2015). Flexible PUF as used in the furniture is made from a mixture of liquid starting materials individually pumped into a high-speed mixing head, and TCIPP added at this stage. Chlorinated phosphates such as TCIPP are liquids and can, therefore, be delivered directly

to the mixing head from storage tanks. TCIPP is blended evenly into the foam but remains unbound (Stubbings, 2015). The average of initial concentrations of TCIPP pre-determined in three 50 mg sub-samples of the UK PUF sample used in this study was 17,333 (± 246) mg kg^{-1}, and it is equal to (1.73 %) by weight (Table 5.1).

5.4. Results and discussion of the leaching experiments

In this study, there were 45 triplicate results (n= 135) from the lab leaching experiments. Table C.1 in appendix C summarise the average results of FR congener concentrations (µg L^{-1}) of FRs as well as their standard deviation (SD), mean of percentage of leaching (PL) and mean percentage leached relativized to time (PLT) values (% h^{-1}) in the leachate from triplicate batches of time contact and temperature leaching experiments. The PL and PLT values in leachate were explored in time contact periods. Table 5.3 show ranged concentrations of FRs in this study and Stubbings, (2015).

According to section 2.5 in the chapter II that described a series of standardized leaching tests using PUF waste, triplicate distinct of single batch experimental scenarios were prepared on PUF samples which were cut into small pieces (approximately 1 cm^3, equivalent to 0.5 g).

Table 5.3: Concentrations of PBDEs and TCIPP in leachate of experimental studies

Aqueous medium	FRs	Concentrations	country	Reference
Lab Leaching experiment	∑PBDEs	1389 - 975325 µg L^{-1}	UK and USA	This study
	∑NBFRs	204 - 145530 µg L^{-1}		
	TPhP	598 - 85608 µg L^{-1}		
	TCIPP	6639 - 353326 µg L^{-1}		
Lab Leaching experiment	∑PBDEs	14,000 - 200,000 ng L^{-1}	UK	Stubbings, 2015
	TCIPP	13 - 130 mg L^{-1}		

Furthermore, the leaching experiments were applied by using a variety of leaching fluids to mimic the real landfill leachates characteristics such as pH levels and step temperature

degrees. Most of these tests conducted under agitations by shaker device. The percentage of leaching FRs present (PL) of the PUF waste that was leached into each leachate liquid was calculated for each FR compound. After this point, the samples were extracted and followed by the analytical methodology for the determination of FRs via extraction, purification and GC/MS analysis. This work was conducted using standard QA/QC methods and procedures (Harrad, 2013).

According to many data gathered from the leaching experiments in this study for FR compounds in the PUF wastes (n= 405 records) (Table C.1), therefore, the different statistical analysis was performed for each compound based on the distribution of the experiments. In each subsection of this chapter, there are a supporting of analytical statistics. These leaching experiments were tried to elucidate the relative significance of possible pathways via which FRs may be emitted to the environment from waste streams. They aim to increase the understanding of transfer, accumulation and transport of FRs from location to location and among different environmental media. Though, the emission of FRs from landfilled consumer products and materials is resulting in contamination of the environment at concentrations that may be harmful to human health and wildlife.

The laboratory experiments of this research were not designed to investigate the volatilisation of FRs from PUF samples or its leachates. Volatilisation maybe occurs in these experiments regarding a mechanism that controlled by physiochemical properties FRs and the environmental conditions. Hence, due to the difficulties of determining low FR emissions and need for more extended period of volatilisation procedures and studies, there are few test-chamber emission studies of FRs from PUFs (Kemmlein et al., 2003; Wilford et al., 2003; Salthammer et al., 2003; Rauert et al., 2014; Stubbings, 2015). Then, volatilisation of FRs-containing PUF wastes needs more laboratory investigations with consideration of mimic a landfill condition. For examples, Wilford et al. (2003); Rauert et al. (2014) and

Stubbings (2015) carried out an air chamber tests to measure PBDE emissions from PUF products. This survey is concluded that PBDEs volatilisation from PUFs is a significant source of indoor air. Their conclusions indicated that different PBDE congeners are emitted at different rates, determined by their physical properties, i.e. higher emissions observed for congeners with higher vapour pressures. Also, Stubbings (2015) investigated the PFRs associated with the treatment of waste. He found that the conducted test chambers show TCIPP volatilisation from PUF wastes to be increasing exponentially with temperature.

5.4.1. Time contact and temperature effects

There were three experiments for the time effect at a temperature of 20, 60 and 80 ˚C. These experiments conducted in a 6, 24, 48, 72, 96 hours and were controlled by leaching fluids that contain only DWW and pH adjusted to 6.5 (slightly acidic). The influence of temperature on FR leaching was examined. Table 5.4 shows the FRs percentage (%) in the leachate samples under the contact time, temperature and agitation effects. Whereas, for each temperature in all period times together, the total of the leachate of individual FRs is ~100%. In the next Table 5.4, it is observed that the leaching concentration of PBDEs, NBFRs, and TPhP from the PUF at the start of leaching to end of the experiments had transferred into the leachate gradually. Whereas, they were increased in the range from 1.5 - 55.3% at 20°C, then ranged from 1.5 - 49% at 60°C, and varied between 1 - 53% at 80°C. But for TCIPP however, it was noted that the capability of leaching concentrations of TICPP from PUF has progressively moved with the decreasing extent to leachates from the beginning to end of the leaching experiments. Where the range of TCIPP concentration was reduced from 39.5 - 7% at 20°C, then the deficit ranged between 44 - 5.3% at 60°C, and finally decreased from 32.6 - 9.4% at 80°C.

Table 5.4: Percentage (%) of each individual FRs in the leachate samples to its total concentration for the 5 contact times under different contact times and temperatures in the presence of agitation

Temperature	Contact Time (*h*)	BDE-47 %	BDE-99 %	BDE-100 %	BDE-153 %	BDE-154 %	EH-TBB %	BEH-TEBP %	TPhP %	TCIPP %
	6 h	1.53	1.63	1.74	1.55	2.56	2.80	2.56	4.14	39.54
	24 h	4.61	4.77	4.55	4.66	5.13	4.99	5.13	7.11	27.98
20˚C	**48 h**	14.96	14.86	13.76	14.77	12.82	11.48	12.82	15.70	14.96
	72 h	25.75	25.42	24.69	25.65	25.64	26.41	25.64	24.68	10.47
	96 h	53.15	53.32	55.25	53.37	53.85	54.32	53.85	48.37	7.06
	6 h	1.52	1.51	1.51	1.51	1.51	1.59	1.50	3.83	44.24
	24 h	4.97	4.82	4.76	4.74	4.72	4.98	4.84	7.14	15.49
60˚C	**48 h**	16.28	15.15	14.75	14.54	14.41	14.85	15.11	15.95	14.87
	72 h	34.69	32.05	31.12	30.64	30.34	32.14	32.05	31.04	20.13
	96 h	42.55	46.47	47.86	48.58	49.01	46.44	46.49	42.04	5.27
	6 h	1.92	2.04	2.08	2.11	2.12	1.04	1.01	2.61	32.62
	24 h	7.27	7.52	7.62	7.68	7.71	3.60	3.73	5.64	24.34
80˚C	**48 h**	18.45	18.34	18.29	18.27	18.25	13.29	13.19	14.18	17.69
	72 h	29.74	29.34	29.19	29.11	29.06	29.24	29.09	28.71	15.99
	96 h	42.63	42.76	42.81	42.84	42.85	52.83	52.97	48.85	9.37

The amount leached decreases of TCIPP with increasing contact time concentrations in time contact periods maybe regard to volatilization in the air space in PTFE bottle (~80% air) or degradation by the temperature of agitation of this compound during the leaching experiments. By this misunderstanding of TCIPP volatilization and degradation thinking of behaviour, it needs to do more investigation in future work.

The time contact with temperature and agitation effect analysis used the data from each compound under time effect. Here, the data was analyzed twice using ANOVA, where the comparisons were made between 6, 24, 48, 72, 96 h for each temperature. The ANOVA results showed a significant difference between the percentages obtained from the same temperature at different times. Post HOC comparisons to find where the differences are showed time-dependent differences. Additional comparison of statistical analysis for the temperature effect was achieved by using the data in multiple linear regression analysis, and the results exposed numerous significant differences. The results revealed that some of these factors predict concentrations, including temperature effect ($p < 0.05$).

5.4.1.1. Time contact and temperature effects in PBDEs

The pentaBDE compounds (PBDEs or ΣPBDEs**)** were conveyed to the leaching fluid in gradually increasing manners with time contact periods and they were seen increased very high. The greatest concentrations of PentBDEs were when leaching fluid (Milli-Q water) was contacted at 80°C in 96 h. That may be the result of the agitation, temperature and long-time contact that cause leach out more easily of PBDEs during the experiments in these conditions. However, the concentrations of ΣPBDEs in the leachate were increased steadily with longer contact times and this may refer to no degradation effect of these compounds on agitation and

could attribute to the influencing of high temperature in increasing of leach out of these compounds from their products.

The maximum concentration that leached was observed for BDE-99 (averaged 48.4%) at 80°C, and the lowest concentration was for BDE-154 (averaged 0.42%%) at 20°C. The ΣPBDE concentrations in results of these experiments were ranged from 6931 to 975325 μg L^{-1}. As well the ΣPBDE concentrations were generally increased by 3 - 5 orders of magnitude from 6 h till 96 h time contact in these experiments. Figure 5.1 show the concentrations of PBDEs under the contact time and temperature effects in the presence of agitation in these experiments. Moreover, PBDE compounds were had similar activities manner through all experiments. Therefore, the profile of PBDEs mostly was similar in the three experiments of time contact with few differences among them, i.e. BDE-99 was predominant and ranged from 37.27 to 41.66% in the experiments of time contact. Those activities may reflect that the PBDE congeners were affected by time contact in this manner. Figure 5.1 show the average concentrations of PBDE homologues in the leachate samples under the time contact and temperature effects in these experiments. The order of these compounds consequently to their levels in leachates from high to low levels were BDEs 99, 47, 100, 153 and 154.

The next graph (Figure 5.1) presents a big transitional in the PBDEs concentrations in the leachate solutions among three contact periods, temperature and agitation effects in these leaching experiments of the time contact in these experiments as stated before in this subsection. Therefore, this especially seen in high transition at time contact at 80°C.

In otherwise, while Figure 5.1 shows the average concentrations of PBDEs in the leachate samples under the contact time and temperature effects. Also, Figure 5.2 which is a percentage of PBDE s values in Table 5.3, illustrates the PBDE congeners percentage (%) in the leachate samples according to the contact time, temperature and agitation effects. These profiles of PBDEs in Figures 5.2 and Table 5.3 represents that there is no statistically

significant (p > 0.05) in amount rates (%) of these compounds leaching from their products under the conditions of time contact, temperature and agitation. That justifies that the behaviour of PBDEs leaching from their products is reflecting their compositions percentage in the mixture (Table 5.2). Also, the graphs show BDE-99 is predominant in all leachates, and highest PBDEs leachate is at 96 h time contact at 80°C.

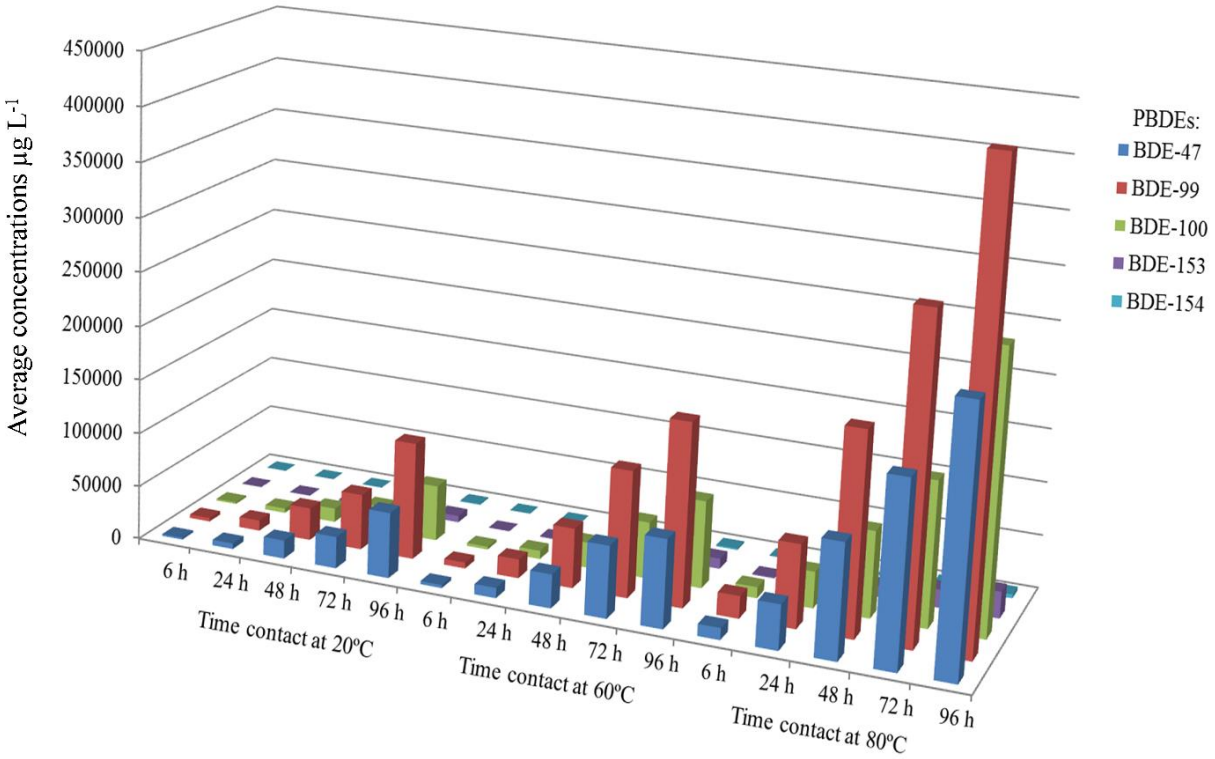


Figure 5.1: Average concentrations of PBDEs in the leachate samples under the time contact and temperature effects in the presence of agitation

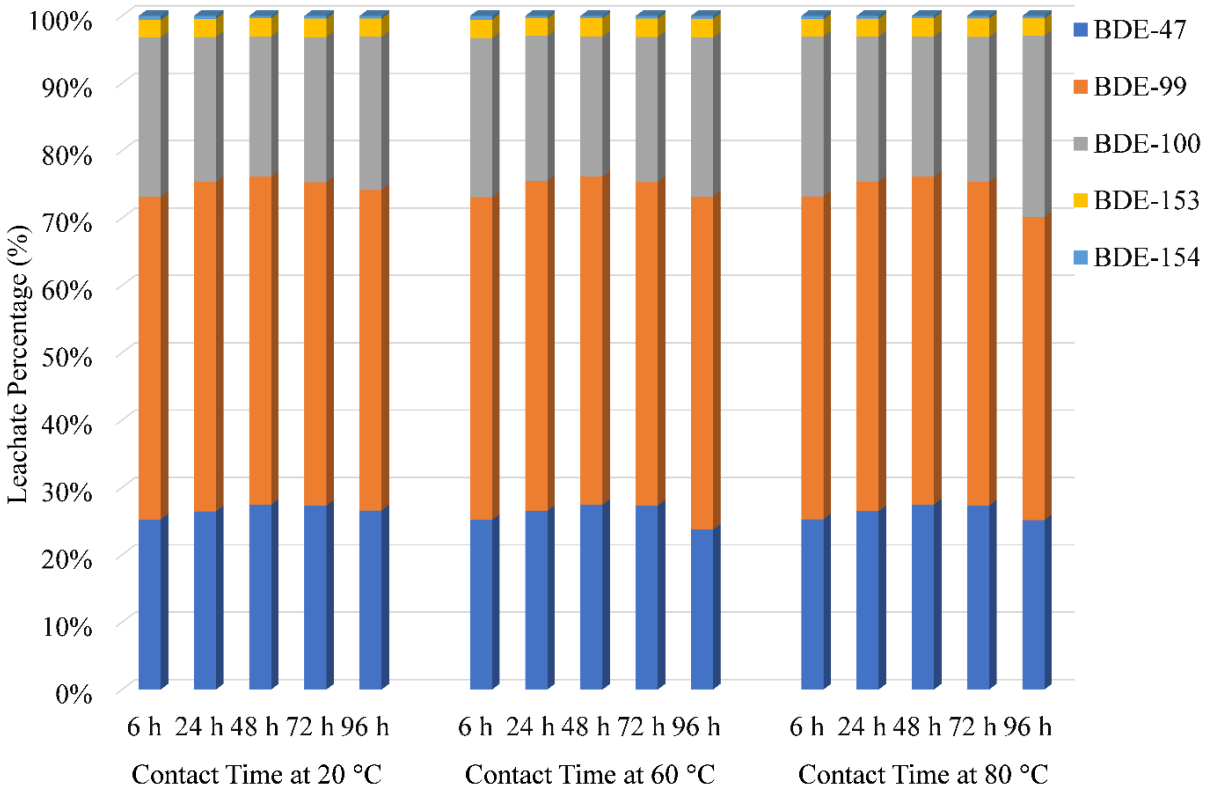


Figure 5.2: Percentage (%) o PBDE congeners in the leachate samples under the contact time and temperature effects

The PBDE Compounds showed similar significant ($p < 0.05$) increased in concentrations when the time increases for all the temperatures, but at the degree, 80 ˚C they had no significant ($p > 0.05$) differences from 6 h to 72 h. The 96 h in 80˚C was significantly higher than the other hours. Table C.2 in the appendix C show the Post Hoc Tukey tests for the non-significant results ($p > 0.05$) which were found of 74 among 270 records; the others were high to very high significant ($p < 0.05$).). Also, that most means of the FRs in these experiments were affected by time contact. It reflects may be in the real leachate of a landfill either by the increase or decrease the level of contaminants according to their effect by a long period.

The time effect data were subjected to further ANOVA analysis to compare temperature differences between each time point. The results revealed several significant differences between the temperatures and is contained in the Table C.3 in appendix C.

5.4.1.2. Time contact effect in NBFRs

The EH-TBB and BEH-TEBP compounds (NBFRs) were transferred to the leaching fluid in gradually increasing quantities with increasing time contact periods, and they were comprehended increased very high at a temperature of 80ºC for 96 h in similar of the pentBDEs trail. Which may be the result of agitation, temperature and long-time contact that cause leach out more easily of NBFRs during the experiments in these conditions. Though the concentrations of ΣNBFRs in the leachate were increased steadily with longer contact times, and this may refer to no degradation effect of these compounds on agitation and high temperatures. The BEH-TEBP has high concentrations than EH-TBB. BEH-TEBP and EH-TBB were ranged from 215 - 107800 µg L^{-1} and from 75 – 37730 µg L^{-1}, respectively in all three-time contact experiments. Figure 5.3 shows the concentrations of NBFRs under the contact time and temperature effects in these experiments.

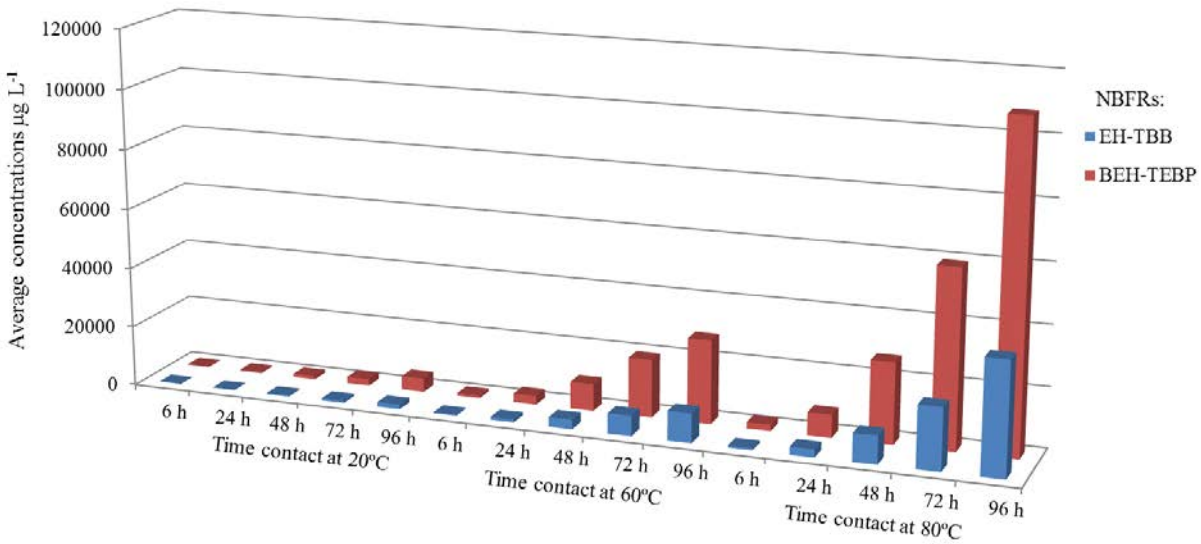


Figure 5.3: Average concentrations of EH-TBB and BEH-TEBP in leachate samples under the contact time and temperature effects

According to an average value of the NBFRs percentage (%) in the leachates under the contact time and temperature effects shown in Table 5.3, the profiles of them is similar to PBDEs.

These profiles represent that there is no statistically significant ($p > 0.05$) in comparing the amount rates (%) of these compounds leaching from their products under the conditions of time contact, temperature and agitation. That supports that the behaviour of NBFRs leaching from their products is reflecting their compositions percentage in the mixture at least (Table 5.2). So, the ratio of EH-TBB to BEH-TEBP is 26:74 which means that the leach rate of EH-TBB is slightly higher than BEH-TEBP while is compared with A and B the ratio in the mixture (Table 5.2). Although BEH-TEBP is predominant in all leachate fluids and very high at 96 h time contact at 80°C.

5.4.1.3. Time contact effect in PFRs

The PFR compounds were had different actions manner through all experiments. Though PFR compounds were carried to the leaching fluid in gradually increasing behaviours for TPhP and decreasing manners for TCIPP with time contact periods, and they were seen increased/ decreased very high at a temperature of 80ºC in 96 h. That may be the result of the agitation, temperature and long-time contact that cause leach out more easily of TPhP and less of TCIPP during the experiments in these conditions. However, the concentrations of TPhP in the leachate were increased steadily with longer contact times, and this may refer to no degradation effect of these compounds on agitation and high temperatures or long contact times.

The TPhP concentrations in results of these experiments were increased from 3088 µg L^{-1} at 6 h of 20ºC to 145664 µg L^{-1} at 96 h of 80ºC. But TCIPP concentrations were decreased from 248052 µg L^{-1} at 6 h of 20ºC to 17582 µg L^{-1} at 96 h of 80ºC. As well the TPhP concentrations were generally increased from 3 - 4 in spite of TCIPP concentrations were decreased from 5 - 4 orders of magnitude in the experiments of 6 h till 96 h time contact in these experiments. Figure 5.4 shows the concentration percentage (%) of TCIPP and TPhP in the leachate samples under the contact time and temperature effects in the leaching experiments. In these

experiments, the leaching quantity of TCIPP was found more substantial than other FRs in time contact of 6 h, but it was reduced when increased time contact 24, 48,72 and 96 h gradually. These reduced of TCIPP concentration maybe occurred because of degradation and/or volatilisation during of longer agitation (Stubbings, 2015) and increasing of temperatures at 80°C relative to those at 20°C and 60°C. In the contrary to TCIPP behaviour, the TPhP was increased gradually by time contact. This discovery suggests that TPhP compounds not degraded during longer agitation and rising of temperatures. Finally, TCIPP were found in high concentrations with fewer time contacts, and this maybe reflects a new landfill emitted more TCIPP contaminants more than the older landfill. As well, the reduced TCIPP concentrations present in leachates may be a result of enhanced TCIPP degradation and/or volatilisation at this higher temperature and long period contact with agitation. To establish evidence that TCIPP volatilisation from their PUF products, Stubbings (2015) for an example conducted a closed test chamber experiments to investigate the temperature effect on volatilisation of TCIPP compounds from PUF (Table 5.4). These experiments show exponentially volatilisation of TCIPP with increasing temperatures gradually. The weight specific emission rate (SERw) of TCIPP from PUF were 0.025, 0.495 and 2.0 mg kg^{-1} h^{-1} for 20, 60, and 80°C, respectively. These SERw values illustrated the potential for emissions of TCIPP from PUF wastes clearly. The concentrations of TCIPP show a significant reduction in percentages when the time increases for all the temperatures, but at the 80 ˚C it had no significant differences ($p > 0.05$) after 6 h. Concentrations of TPhP show a significant ($p < 0.05$) increase in percentages when the time increases for all the temperatures, but the 80 ˚C had no significant differences from 6 to 72 h. The 96 h (4 days) in the 80 ˚C was significantly higher than the other hours ($p < 0.01$). These may be agitation and temperature effects in the degradation of these compounds at high temperature and long-time contact.

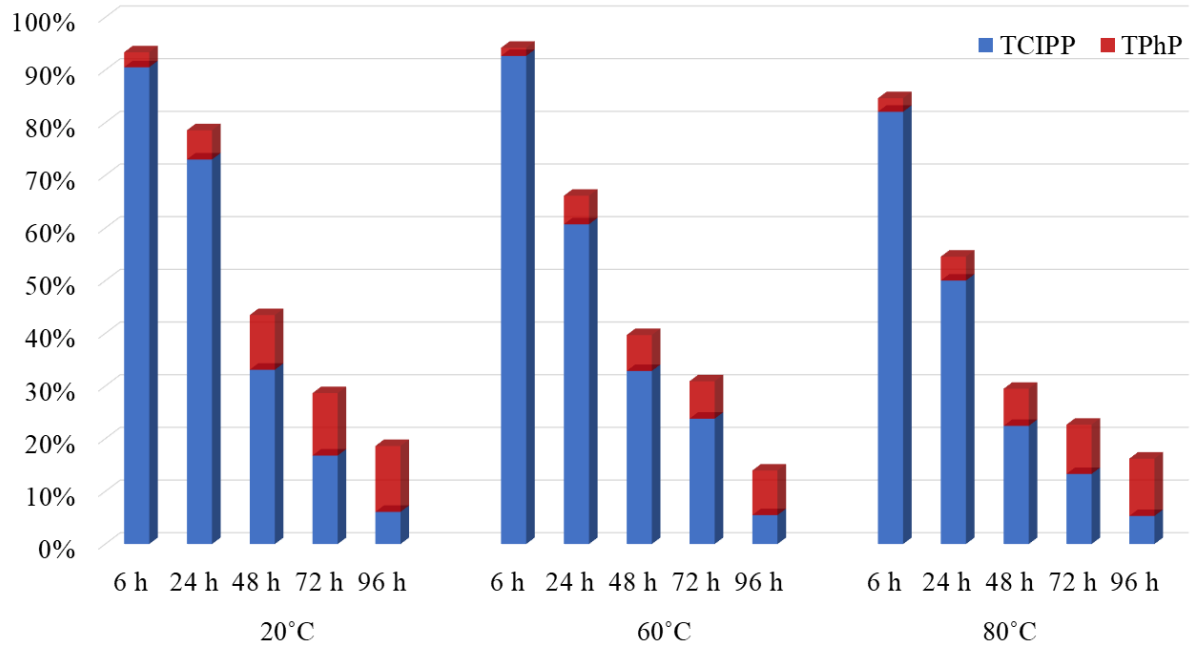


Figure 5.4: Concentration percentage (%) of TCIPP and TPhP in the leachate samples under the contact time, temperature and agitation effects

5.4.2. Agitation effect

All FRs were increased in the concentrations in the leaching fluids of no agitation experiments via time contact periods even TCIPP. It may be the effect of the temperature in releasing of FR compounds, and in TCIPP case it may show that it's affected by degradation with increased time contact and temperature under agitation. However, if no agitation effect there will be low degradation occurring in TCIPP levels. TABLE 5.5 show the FR compounds percentage (%) in leachate samples under no agitation effect during the periods of contact time. Table 5.5 show the comparison between concentrations in leachate in the agitated experiment at 60˚C with concentrations in the experiments at 60˚C without agitation.

No agitation operation was used in this contact time leaching experiments. Though, lower TCIPP concentrations were appeared when compared with an agitated 60 °C time contact leaching experiments ($p < 0.05$). However, if no agitation effect, there is no degradation will be occurred in TCIPP concentrations. Compared to other FRs, TCIPP show the lowest

concentrations in the leachates of these experiments. Also, the concentrations of PBDEs, NBFRs, TPhP have a steadily increased during the contact periods in the no agitation effect leaching experiments.

Table 5.5: FR concentrations (µg L^{-1}) concentrations in leachate in the agitated experiment at 60˚C with concentrations in the experiments at 60˚C without agitation

Effect	Time (*h*)				
	6 h	24 h	48 h	72 h	96 h
No Agitatation					
BDE-47	1903	7230	21040	36041	46812
BDE-99	3622	13351	37302	82390	86089
BDE-100	1787	5870	15966	36990	45996
BDE-153	209	702	2077	4695	4889
BDE-154	35	90	251	670	716
EH-TBB	287	946	2467	4151	6187
BEH-TEBP	785	2785	8988	19207	26562
TPhP	1624	3371	7806	17525	19516
TCIPP	15291	39884	52761	82723	102531
Agitation					
BDE-47	2910	9540	31245	66585	81670
BDE-99	5534	17632	55427	117289	170034
BDE-100	2730	7755	23700	52590	81300
BDE-153	315	945	3105	6705	9675
BDE-154	65	129	387	968	1419
EH-TBB	315	1015	3168	6720	9747.5
BEH-TEBP	900	2900	9050	19200	27850
TPhP	3424	6392	14272	27768	37608
TCIPP	204404	71542	68685	93021	24337

The comparison of agitation effect statistical analysis was performed using the corresponding data, and the results revealed several significant differences. The results revealed that some of these factors predict concentrations, including time contact (p-value= 0.00) in multiple linear regression analysis.

5.4.3. DHM effects

Relatively most FR compounds were increased in the concentrations in the leaching fluids of DHM experiments via time contact periods except TCIPP. Table 5.6 shows the FRs concentrations in leachate using different DHM levels. The FR concentrations are observed with increasing contact time for leaching fluids containing DHM at a concentrate of 100 and 1000 mg L^{-1}. For this reason, they may be affected by the temperature in releasing of FR compounds, and in TCIPP case it may show that it's affected by volatilisation and or degradation with increased time contact and temperature under agitation. Besides, DHM matter may be enhancing brominated and aryl phosphate FRs to leach out more. Therefore, the concentrations of PBDEs as in example, were consistently higher in the DHM (1000 mg L^{-1}) leaching fluid when compared to the concentrations found in the DHM (100 mg L^{-1}). That will support the hypothesis that larger DHM concentrations in the leaching fluid would enable more PBDEs to be present in leachate. Figure 5.5 show the average concentrations of FR compounds under DHM (100 mg L^{-1}) and (1000 mg L^{-1}), respectively.

The DHM effects analysis used the data from each compound under DHM effects (0, 100 and 1000 mg L^{-1}) (DHM 0 is the contact time experiment at 60ºC) and was analyzed twice using ANOVA and Paired Sample T-test. In the ANOVA analysis, there was a significant difference between the concentrations obtained from the same DHM at different times. Post HOC comparisons to find where the differences are, showed several time-dependent differences. In the paired T-test, each time points between DHM 0, 100 and 1000 were compared, and the results revealed significant differences between both concentrations at the same time point. Further comparison of DHM effect statistical analysis was performed using the particular data and the results revealed several significant differences. The results showed that some of these factors predict concentrations, including DHM effect (p-value= 0.00) in multiple linear regression analysis.

Table 5.6: FR concentrations (µg L^{-1}) in leachate using different DHM levels

Effect	Time (*h*)				
	6 h	**24 h**	**48 h**	**72 h**	**96 h**
DHM (100 mg L^{-1}):					
BDE-47	3260	10689	34998	74577	91471
BDE-99	6199	19750	62080	131364	190439
BDE-100	3058	8689	26548	589025	91057
BDE-153	353	1060	3479	7510	10836
BDE-154	72	145	434	1084	1590
EH-TBB	353	1139	3550	7527	10918
BEH-TEBP	1008	3248	10136	21504	31192
TPhP	3836	7167	15990	31103	42123
TCIPP	122181	98853	32363	18988	6639
DHM (1000 mg L^{-1}):					
BDE-47	5136	17048	56966	122149	153739
BDE-99	9561	30519	97152	206296	303317
BDE-100	4698	13391	41224	91674	143907
BDE-153	548	1652	5517	12092	17526
BDE-154	113	230	686	1723	2579
EH-TBB	563	1848	5895	12603	18105
BEH-TEBP	1569	5082	15961	34232	51870
TPhP	5997	11251	25867	51252	69637
TCIPP	188727	147088	77273	42223	18511

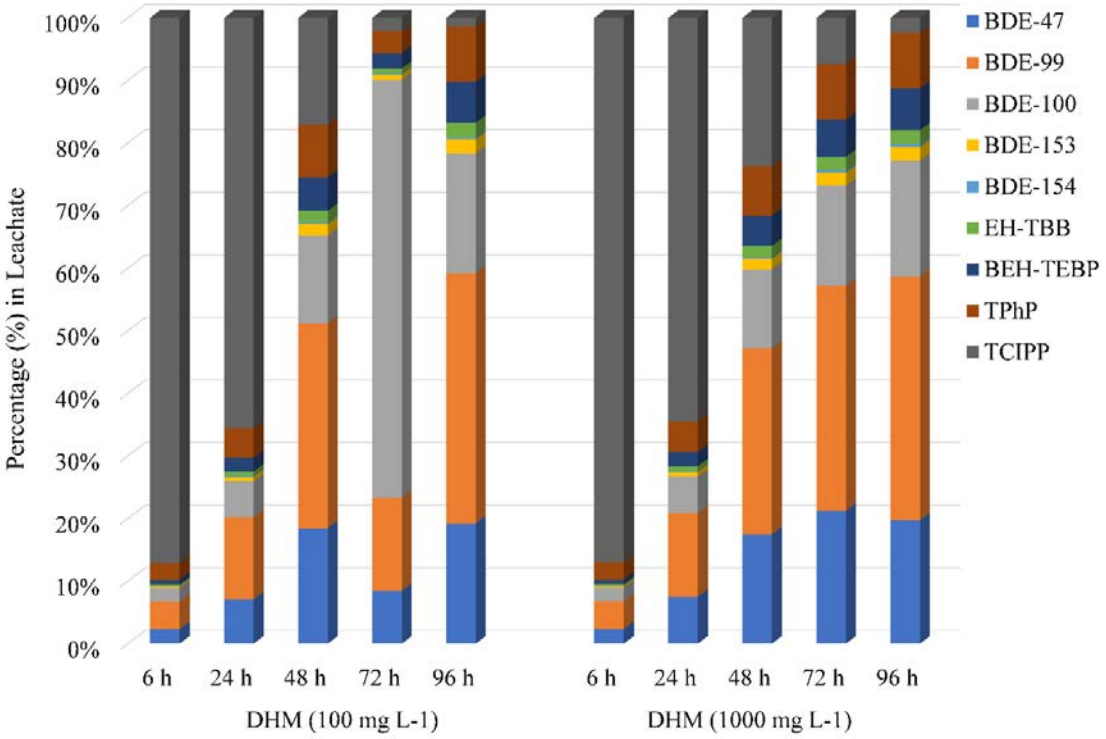


Figure 5.5: FR compounds percentage (%) in leachate samples under the DHM (100 mg L^{-1}) DHM (1000 mg L^{-1}) effect

5.4.4. Acidic and alkaline (pH 5.8 and 8.5) effects

The pH levels representing acidic leachate (pH 5.8) and alkaline leachate (pH 8.5) of FRs concentrations in leachate were explored in time contact periods. Table 5.7 shows the FRs concentrations in leachate using the target FRs experiments using different pH levels. There are variations in ΣPBDE concentrations in the leachate samples under the two pH levels examined in the study. The experiments with alkaline pH (8.5) leaching fluids yield the highest ΣPBDE concentrations than the acidic pH (5.8) levels inspected. The pH of the leaching fluid was found exceed significantly on the leachability levels of FRs ($p < 0.05$). Comparatively, most FR compounds were increased in the concentrations in the leaching fluids of pH experiments via time contact periods and agitation excluding TCIPP. Their concentrations are observed with increasing contact time for both acidic and alkaline leaching fluids. In this way, it's maybe the

Table 5.7: FR concentrations (µg L^{-1}) in leachate using different pH levels

Effect	**Time (*h*)**				
	6 h	**24 h**	**48 h**	**72 h**	**96 h**
pH (5.8):					
BDE-47	681	3222	17732	43529	94490
BDE-99	485	1738	10181	24548	55652
BDE-100	174	627	3095	7634	21081
BDE-153	37	138	844	2655	4711
BDE-154	9	26	94	275	742
EH-TBB	95	445	2338	5713	8353
BEH-TEBP	128	517	2082	6187	25474
TPhP	598	1274	7004	20728	30181
TCIPP	109091	78392	45455	39461	18382
pH (8.5):					
BDE-47	3591	12762	48977	110114	176160
BDE-99	6019	19370	65608	141837	225686
BDE-100	2904	8382	26795	60224	102381
BDE-153	343	1051	3754	8747	14386
BDE-154	71	149	459	1179	2161
EH-TBB	388	1358	4966	11114	18101
BEH-TEBP	1028	3417	11132	25387	53324
TPhP	4022	7666	21276	48496	67789
TCIPP	353325	242857	185847	112770	18611

effect of the temperature in releasing of FR compounds and in TCIPP case it may show that it's affected by degradation with increased time contact and temperature under agitation as stated in previous experiments that shown decreasing in TCIPP levels. Figure 5.6 shows the average concentrations of FR compounds under acidic and alkaline leachates, respectively.

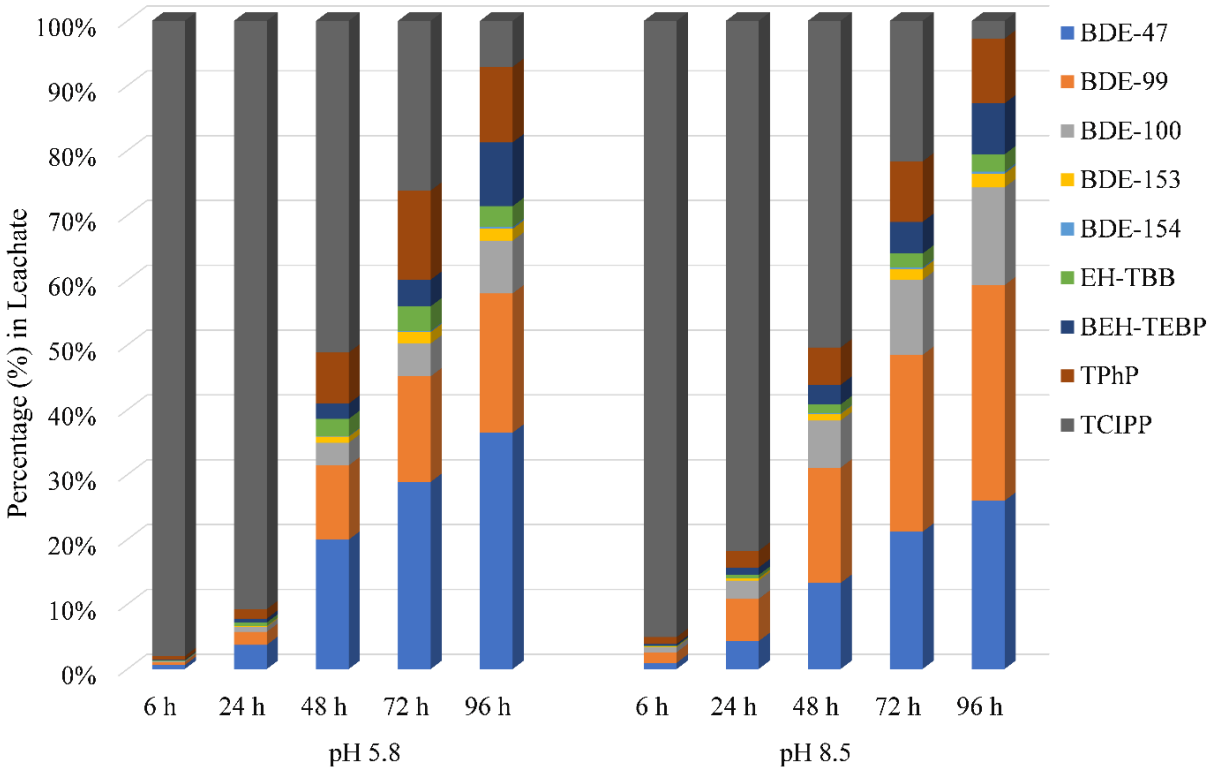


Figure 5.6: FR compounds percentage (%) in leachate samples under an acidic leachate samples (pH 5.8) and alkaline leachate samples (pH 8.5)

5.4.5. Waste mass to leachate ratio

The time contact experiments at 60ºC were repeated but using 10% of the mass of PUF samples. The FR concentration results were comparable with a range of 8.63 - 13.95% of that found the experiments of time contact at 60ºC. Table 5.8 shows the comparison of a) the relationship of PL% for individual FRs for different contact times at 60°C at the standard waste: lechate ratio used in all experiments with contact times of 6, 24, 48, 72, and 96 h at 20°C, 60°C, and 60°C, and

Table 5.8: Comparison of a) the relationship of PL% for individual FRs for different contact times at 60°C at the standard waste: leachate ratio used in all experiments with contact times of 6, 24, 48, 72, and 96 h at 20°C, 60°C, and 80°C, using DDW (ph 6.5 and 0 mg L-1 DHM) with agitation, and b) the same previous experiments but with a waste: leachate ration that was 10% of standard ratio

Temp.	20˚C					60˚C					80˚C				
Time (*h*)	6 h	24 h	48 h	72 h	96 h	6 h	24 h	48 h	72 h	96 h	6 h	24 h	48 h	72 h	96 h
a)	PL% at 60˚C to PL% at Waste: Leachate (Standard):														
BDE-47	1.82	1.82	1.73	2.28	1.35	1.00	1.00	1.00	1.00	1.00	3.50	4.33	3.47	2.59	3.02
BDE-99	1.66	1.81	1.83	2.27	1.57	1.00	1.00	1.00	1.00	1.00	3.78	4.38	3.40	2.57	2.58
BDE-100	1.67	1.90	1.84	2.25	1.57	1.00	1.00	1.00	1.00	1.00	3.85	4.26	3.39	2.56	3.22
BDE-153	1.81	1.76	1.77	2.21	1.55	1.00	1.00	1.00	1.00	1.00	3.47	4.32	3.50	2.58	2.56
BDE-154	1.50	1.50	1.80	2.23	1.57	1.00	1.00	1.00	1.00	1.00	3.33	5.00	3.22	2.54	2.53
EH-TBB	4.12	6.97	8.43	8.82	6.29	1.00	1.00	1.00	1.00	1.00	8.57	2.52	3.00	3.07	3.77
BEH-TEBP	4.40	6.67	8.46	8.55	6.36	1.00	1.00	1.00	1.00	1.00	2.27	2.64	2.95	3.09	3.79
TPhP	1.09	1.21	1.20	1.54	1.08	1.00	1.00	1.00	1.00	1.00	2.29	2.61	3.00	3.05	3.71
TCIPP	2.07	0.81	1.82	3.55	1.39	1.00	1.00	1.00	1.00	1.00	1.20	3.95	1.95	1.33	2.96
b)	PL% at Waste: Leachate (10%) to PL% at Waste: Leachate (Standard):														
BDE-47	0.15	0.22	0.18	0.24	0.15	0.09	0.12	0.11	0.10	0.11	0.09	0.12	0.11	0.10	0.11
BDE-99	0.17	0.16	0.20	0.20	0.19	0.10	0.09	0.11	0.09	0.12	0.10	0.09	0.11	0.09	0.12
BDE-100	0.16	0.24	0.18	0.25	0.19	0.10	0.13	0.10	0.11	0.12	0.10	0.13	0.10	0.11	0.12
BDE-153	0.18	0.24	0.19	0.21	0.19	0.10	0.14	0.11	0.10	0.12	0.10	0.14	0.11	0.10	0.12
BDE-154	0.17	0.13	0.19	0.19	0.17	0.11	0.09	0.10	0.09	0.11	0.11	0.09	0.10	0.09	0.11
EH-TBB	0.41	0.70	1.04	0.82	0.80	0.10	0.10	0.12	0.09	0.13	0.10	0.10	0.12	0.09	0.13
BEH-TEBP	0.40	0.62	0.90	0.90	0.81	0.09	0.09	0.11	0.11	0.13	0.09	0.09	0.11	0.11	0.13
TPhP	0.10	0.11	0.13	0.15	0.13	0.10	0.09	0.11	0.10	0.13	0.10	0.09	0.11	0.10	0.13
TCIPP	0.11	0.15	0.14	0.16	0.11	0.05	0.19	0.08	0.04	0.08	0.05	3.95	1.95	1.33	2.96

80°C, using DDW (ph 6.5 and 0 mg L-1 DHM) with agitation, and b) the same previous experiments but with a waste: leachate ration that was 10% of standard ratio. Also, Table 5.9 shows the average waste to leachate ratio (%) of the leaching experimental results of average FR concentrations under the contact time and 60°C temperature effects.

The waste mass (10%) to leaching fluids (100 mL) were useful things to determine if the leaching fluids are receiving equivalent density of each of the target compounds in this study. So, in the next Table 5.9, the percentage of all compounds set around the same initial 10% waste that used in time contact experiments at 60ºC (mean 10.68, SD 0.4, %).

Table 5.9: Average waste: leachate ratio (%) of the leaching experimental results of average FR concentrations under the contact time and 60ºC temperature effects

FRs	Time contacts				
	6 h	***24 h***	***48 h***	***72 h***	***96 h***
BDE-47	9.73	**12.06**	10.16	10.46	11.08
BDE-99	10.03	8.95	10.60	8.99	**12.40**
BDE-100	9.67	**12.71**	9.86	11.28	11.76
BDE-153	10.21	**13.95**	10.25	10.46	**12.29**
BDE-154	10.09	9.32	10.46	8.63	10.67
EH-TBB	9.77	10.03	**12.20**	9.43	**13.10**
BEH-TEBP	9.92	9.31	10.59	10.58	**13.17**
TPHP	9.61	8.99	10.63	10.42	**13.20**
TCIPP	9.70	**11.87**	11.31	10.30	10.47

In the above Table 5.8 shows some of the FR concentrations (bold) were slightly different than other FRs under time contact at 24, 48, and 96 hours even it is not statically significant ($p > 0.05$). The reason could be to the small ratio of these experiments (10%), but it recommends investigating more in similar future work.

5.5: Leaching activities

The PLT values were used to get more understanding of the activities of each compound in the leachates. These values were calculated from both the final concentrations in the leaching fluids and the initial amount of this compound in the specific time of the leaching experiments. It was easily calculated for each compound by using both equations 3 and 4 in the chapter II. The average of PLT ratios was calculated for further understanding of the FRs transfer from their products to the leaching fluids per specific time. Figure 5.7 shows the PLT values (logarithmic scale) of the time contact leaching experiments at a temperature of 60ºC with agitation. DHM, pH and mass to leachate ratio experiments were a similar movement to the scenario of Figure 5.7, but they differ in PLT percentage levels. At 24 h the PLT dropped down then increased after that to the end of time contact periods. It was explained as that at 6 h the leaching fluids received a higher amount of FR compounds per hour than the leaching fluids at 24 h time periods. These were caused by wash off of these contaminants when the leaching fluid is initially contacted. In point of view, the TCIPP had a unique PLT pathway after the 24 h, which it dropped down dramatically with time contact. This situation may be the degradation influences of temperature, agitation and long-time contact with leaching fluids. In the no agitation effect, the PLT of TCIPP levels were comparable with other FRs pathways as shown in Figure 5.8 that shows the PLT values (logarithmic scale) of leaching experiments under no agitation effects at a temperature of 60ºC. PLT for the experiments under no agitation effect. Also, all compounds were showed increasing at 72 h toward 96 h except BDE-47.

The PLT values of FRs were tested in paired to find which compound significantly with time contact experiments at 60ºC. They were all exceeded significant ($p < 0.05$) at 96 h. At contact time 6 h, BDEs 100 and 154 and BDE-47 and EH-TBB were substantial at 72 h. Furthermore, TPhP was exceeded significant, and BEH-TEBP was no significant ($p > 0.05$) at all-time contact intervals.

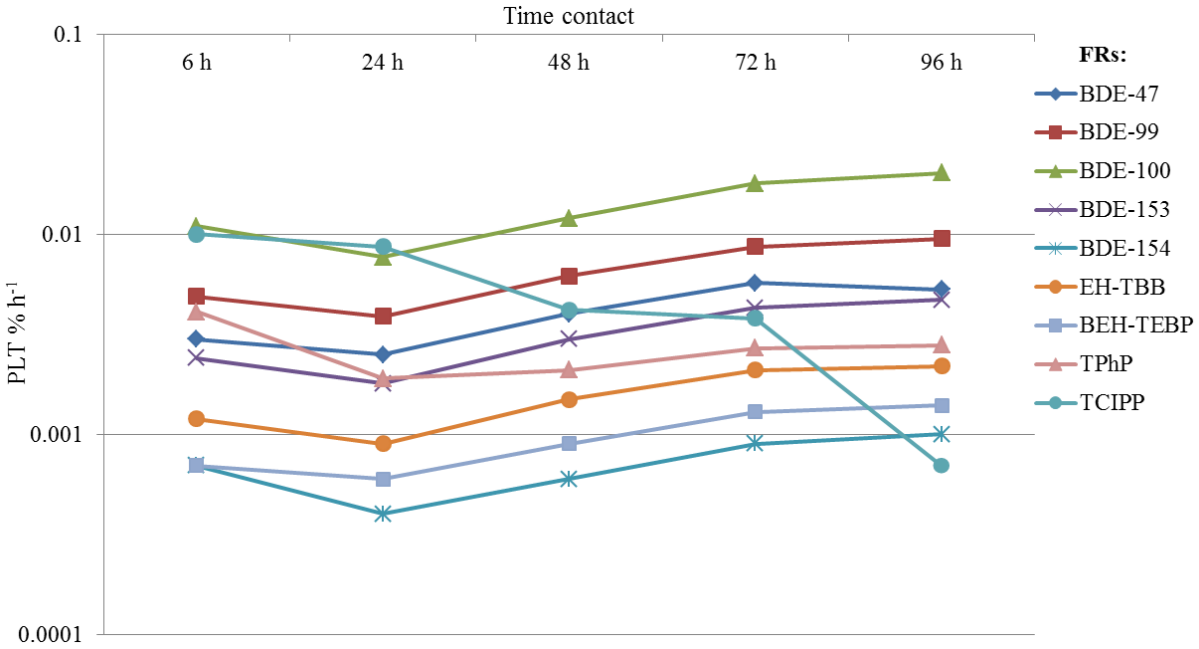


Figure 5.7: PLT values (logarithmic scale) of the time contact leaching experiments at a temperature of 60ºC with agitation

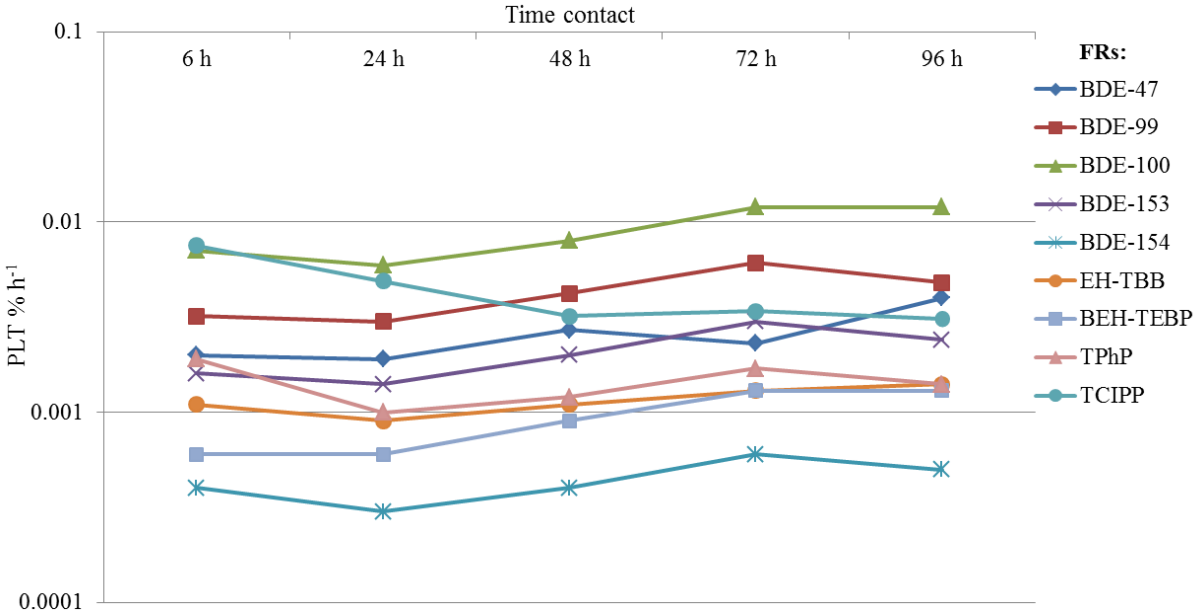


Figure 5.8: PLT values (logarithmic scale) of leaching experiments under no agitation effects at a temperature of 60ºC

5.6. Epilogue

In this follow-up research, the FRs were investigated under the effect of a range of landfill relevant leaching fluids and parameters. Afterwards, the leaching concentrations of FRs from

PUF wastes were determined. These compounds were regarded as a source of organic pollution of landfill sites.

While leaching, fluids are a second order process (Stubbings, 2015). Therefore, the most important findings of this study are that substantial concentrations of FRs can be generated in leachate from PUF wastes despite their physicochemical properties such as relatively high hydrophobicity and relatively low water solubility (Table 1.9 in the chapter I).

The concentrations for the ΣPBDEs were ranged from 1389 - 975325 μg L^{-1}. NBFR concentrations ranged from 204 – 145530 μg L^{-1} (BEH-TEBP and EH-TBB were ranged from 215 - 107800 μg L^{-1} and 75 – 37730 μg L^{-1}) and PFRs ranged from 7238 – 438934 μg L^{-1} (TCIPP was ranged from 6639 - 353326 μg L^{-1} and TPhP was range from 598 - 85608 μg L^{-1}). The concentrations of are higher than the results of leaching experiments that done by Stubbings (2015) of ΣPBDEs in CRT plastics (ranged from 14000 – 200000 ng L^{-1}), but were comparable to a high of his study of TCIPP (13 - 130 mg L^{-1}). Hence, The NBFRs and TPhP were studied for the first time in this study.

Chapter VI: Summary, Conclusion and Recommendations

6.1. Summary

Brominated and organophosphate flame retardants (BFRs and PFRs) are substances added or applied to a product i.e. electrical and electronic equipment, construction materials, textiles, fabrics and polyurethane foam used in furniture, beddings, and carpets. in order to suppress, significantly reduce or delay the combustion of the material (van Esch, 1997; BSEF, 2009). Such substances have been used to increase fire safety throughout centuries. The massive application and use of FRs has caused in a mounting scientific attention to study a potential consequence of these chemicals on the environment and human health. Many studies showed FRs can transfer into air, dust, soil and water throughout several phases of manufacture, use, recycle, and disposal. Such FRs contamination has accumulated in wildlife and humans (Hites, 2004; Covaci et al., 2006; 2009).

This study was thus to monitor which BFRs levels in air and soil within and surrounding landfills. As well as that it investigates the pathway via test the hypothesis that emissions of BFRs and PFRs leach out from treated end-of-life materials were constituted an important source to the environment. Also, in the function of this thesis, it gives for the first time BFR concentrations in Oman. It also marks a valuable contribution to the understanding of the mechanisms via which related FRs may transfer from landfilled waste to leachate. These leaching activities were found in the leaching experiments of this study. Furthermore, the leaching experiments were studied NBFR and TPhP flame retardants for the first time as well.

The main objective of this study was to shed light on the emissions to the environment of BFRs and PFRs in the waste streams. The key findings of this research are summarised as the following arguments:

- There is substantial amount of PBDEs were found emitted into the environment from landfills in high concentrations in comparison to non-landfilled areas. The percent ratio of BDE-209 in ∑PBDEs for all sampling locations in this study was particularly high as well as same of some percentages of other

places in worldwide. Furthermore, PBDEs affected by different periodical variation trends. These were possibly mainly because the various types of PBDEs emitted from different varieties of BFR-containing waste and also were affected by various landfilling processes. The concentrations of ΣPBDEs in air samples ranged from 176 - 1803 pg m^{-3} and ranged from 56 - 165 pg m^{-3} in the vicinity of Oman landfills and reference sites, respectively.

- Also, the concentrations of ΣPBDEs in soil sample of the landfills that monitoring was ranged from 65 - 252 ng g^{-1} in Am landfill (mean 146 ng g^{-1}) and from 25 to 158 ng g^{-1} in Ra landfill (mean 91 ng g^{-1}). The average of other landfills was 199, 234, 246, and 174 ng g^{-1} for Ni, Ib, So, and Bu landfills, respectively. The ΣNBFR concentrations are lesser than that for PBDEs. They ranged in this study from 11 - 163 pg m^{-3} and from 4.5 - 13 pg m^{-3} at_the vicinity of Oman landfills and reference sites, respectively. They ranged too from 20.5 - 47 ng g^{-1} ranged too from nd - 1.29 ng g^{-1} in soil surrounded the landfills in Oman, respectiveley.
- Soil ingestion and air inhalation were assumed to be a pathway exposure to workers at the landfills. A range of daily exposure dose was calculated using low, typical, and high levels of PBDE and NBFR concentrations in this study. An assessment of the human health risk arising from these estimated exposures was conducted by comparing exposure estimates with the reference doses for selected PBDE and NBFR congeners reveals that in all cases, our exposure estimates are substantially below the RfD values and suggest little concern about exposures arising from the pathways considered the landfills.
- The leaching experiments of the FRs that were investigated in this study under the effect of a range of landfill relevant leaching fluids and parameters. The leaching concentrations of FRs from PUF wastes were determined. The leaching fluids are a second order process. Thus, the most important findings of these experiments are that substantial concentrations of FRs can be generated in leachate from PUF wastes despite their physicochemical properties such as relatively high hydrophobicity and relatively low water solubility. The concentrations for the ΣPBDEs in these experiments were ranged from 1389 - 975325 µg L^{-1}, BEH-TEBP were ranged from 215 - 107800 µg L^{-1}, EH-TBB were ranged from 75 - 37730 µg L^{-1}, TCIPP was ranged from 6639 - 353326 µg L^{-1} and TPhP was range from 598 - 85608 µg L^{-1}.

6.2. Conclusion and Recommendation

Landfills signify as reservoirs of FR-containing waste e.g., used upholstery, furniture and e-waste etc. Therefore, integrated waste management must be implemented to prevent or reduce FRs emissions to the surroundings. Also, these types of waste must be demolished or treated eco-friendly. The current landfills need hard-work to control leachate during active or closed landfill. These procedures will assist to reduce FRs emissions.

To date, little research exists to FRs emissions within the waste stream. An emigrate mechanisms of FRs from waste streams is not fully recognized. But the few understandings is mostly established on the emission database of their products. In existence of DHM, the hydrophobic attribute of BFRs lead to enhance their leachability from wastes. So, further studies should conduct to increase comprehension of the influences of BFR and PFR emissions and degradation under landfill situations. While, the scientific and social attention has been on emissions from waste, then these priority investigations will increase the presently limited intellect of FR emissions from waste streams.

6.3. Research gaps and future work

In point of view, there is a lack of researches on FRs concentrations surrounded the waste streams. Though, there are essential study gaps which waiting to be classified. In specific, the most significant gaps are as the following:

- **Long-term monitoring study of legacy and emerging FRs in a landfill**

  Design a project plan to conduct a long-term monitoring study of legacy and emerging FRs in landfills' air, soil, leachate, groundwater and vented landfill gas samples at some active and closed landfill sites in Oman. These studies will allow us to gain more knowledge about these contaminants and their effects on the environment and public health of human.

- **Simulation a landfill condition for FRs vessel researches**

Many trails led FRs to leach out from their waste materials in the landfill. The most important of these transfer ways are such as leaching and volatilization, i.e. TCIPP needs more investigation of its volatilization and degradation thinking of behaviour. The experimental lab studies are the best tool for understanding more about this the actual landfill problem. However, these studies will produce accurate findings and a clear understanding of the significant role of the landfill as a source of environmental pollution.

References

1. Abdallah M. A. (2009). "Investigating the sources and magnitude of human exposure to halogenated organic pollutants using advanced methods for environmental analysis". PhD thesis. University of Birmingham, UK.

2. Abdallah M. A. , Pawar G. and Harrad S. (2016). "Human dermal absorption of chlorinated organophosphate flame retardants; implications for human exposure". Toxicology and Applied Pharmacology. 291: 28-37.

3. Abdallah M. A. and Harrad, S. (2010). " Modification and Calibration of a Passive Air Sampler for Monitoring Vapor and Particulate Phase Brominated Flame Retardants in Indoor Air: Application to Car Interiors" Environmental Science and Technology. 44: 3059–3065.

4. Abdallah, M. A., Pawar, G. and Harrad S. (2015a). "Effect of bromine substitution on human dermal absorption of polybrominated diphenyl ethers". Environmental Science and Technology. 49(18): 10976–10983.

5. Abdallah, M. A., Pawar, G. and Harrad S. (2015b). "Evaluation of 3D-human skin equivalents for assessment of human dermal absorption of some brominated flame retardants". Environment International. 84:64-70.

6. Agency for Toxic Substances and Disease Registry (ATSDR). (2004). "Toxicological profile for polybrominated biphenyls and polybrominated diphenyl ethers". [online] Available from: http://www.atsdr.cdc.gov/toxprofiles/tp68.pdf (Accessed January 2016).

7. Agrell C., ter Schure A. F. H., Sveder J., Bokenstrand A., Larsson P. and Zegers B. N. (2004). "Polybrominated diphenyl ethers (PBDEs) at a solid waste incineration plant I: Atmospheric concentrations". Atmospheric Environment, 38: 5139-5148.

8. Alaee M., Arias P., Sjödin A. and Bergman A. (2003). "An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release". Environment International. 29(6): 683-689.

9. Alaee M., Cannon C., Muir D., Blanchard P., Brice K. and Fellin P. (2001). "Spatial distribution and seasonal variation of PBDEs in Arctic and Great Lakes air". Organohalogen Compounds. 52: 26–29.

10. Ali N., Dirtu A., Van den Eede N., Goosey E., Harrad S., Neels H., Mannetje A., Coakley J., Douwes J., Covaci A. (2012). "Occurrence of alternative flame retardants in indoor dust from New Zealand: Indoor sources and human exposure assessment". Chemosphere. 88: 1276-1282.

11. Ali N., Harrad S., Muenhor D., Neels H. and Covaci A. (2011). "Analytical characteristics and determination of major novel brominated flame retardants (NBFRs) in indoor dust". Analytical and Bioanalytical Chemistry. 400(9): 3073-3083.

12. Ali, N., Van den Eede N., Dirtu A. C., Neels H. and Covaci A. (2012). "Assessment of human exposure to indoor organic contaminants via dust ingestion in Pakistan". Indoor Air. 22(3): 200-211.

13. Al-Omran L. S. (2016). "Factors Influencing Human Exposure Assessment of Legacy and “Novel” Brominated Flame Retardants via Indoor Dust Ingestion". PhD thesis. University of Birmingham, UK.

14. Al-Omran L. S. and Harrad S. (2015). Polybrominated diphenyl ethers and “novel” brominated flame retardants in floor and elevated surface house dust from Iraq: Implications for human exposure assessment. Emerging Contaminants. 2(1): 7-13.

15. Ambidge P. F., Cox E. A., Creaser C. S., Greenberg M., Gem M. G. de M., Gilbert J., Jones P. W. , Kibblewhite M. G., Levey J., Lisseter S. G., Meredith,T. J., Smith L., Smith

P., Startin J. R., Stenhouse I. and Whitworth M. (1990), "Acceptance criteria for analytical data on polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans". Chemosphere. 21: 999-1006.

16. Andresen J. a, Grundmann A. and Bester K. (2004). "Organophosphorus flame retardants and plasticisers in surface waters". The Science of the Total Environment, 332(1-3): 155-166.
17. Aresta M., Caramuscio P., De Stefano L., Pastore T. (2003). "Solid state dehalogenation of PCBs in contaminated soil using NaBH4". Waste Management. 23: 315–319.
18. Arinaitwe K., Muir D. C. G., Kiremire B. T., Fellin P., Li H. and Teixeira C. (2014). "Polybrominated diphenyl ethers and alternative flame retardants in air and precipitation samples from the northern Lake Victoria region, East Africa". Environmental Science and Technology. 48: 1458-16-44.
19. Ashton M., Kantai T., Kohlerm P.M., Roemer-Mahler A. and Templeton J., (2009). "Summary of the fourth conference of the parties to the Stockholm convention on persistent organic pollutants". International Institute for Sustainable Development.
20. ATSDR. (2012). "Toxicological Profile for Phosphate Ester Flame Retardants". [online]. Available from: http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=1119&tid=239 (Accessed January 2016).
21. ATSDR. (2015). "Toxicological Profile for Toxicological Profile for Polybrominated Diphenyl Ethers (PBDEs)". [online]. Available from: https://www.atsdr.cdc.gov/ toxprofiles /tp207-c6.pdf (Accessed January 2016).
22. Bacaloni A. and Cavaliere C. (2007). "Liquid chromatography/tandem mass spectrometry determination of organophosphorus flame retardants and plasticizers in drinking and surface waters". Rapid Communications in Mass Spectrometry. 21(7): 1123-1130.

23. Bacaloni A., Cucci F. and Guarino C. (2008). "Occurrence of organophosphorus flame retardant and plasticizers in three volcanic lakes of Central Italy". Environmental Science and Technology. 42(6): 1898-1903.

24. Balasubramanian R. and He J. (2010). "Trace Analysis of Persistent Organic Pollutants in the Air Using Accelerated Solvent Extraction". In: Zereini F., Wiseman C. (eds) Urban Airborne Particulate Matter. Environmental Science and Engineering (Environmental Engineering). Springer, Berlin, Heidelberg. Online ISBN 978-3-642-12278-1. pp 127-144.

25. Ballesteros-Gómez A., de Boer J. and Leonards P. E. G. (2013). "Novel Analytical Methods for Flame Retardants and Plasticizers Based on Gas Chromatography, Comprehensive Two-Dimensional Gas Chromatography and Direct Probe Coupled to Atmospheric Pressure Chemical Ionization-High Resolution Time-of-Flight-Mass Spectrometry". Analytical Chemistry. 85(20): 9572-9580.

26. Ballesteros-Gómez A., Brandsma S. H., de Boer J. and Leonards P. E. (2014). "Direct probe atmospheric pressure photoionization/atmospheric pressure chemical ionization high-resolution mass spectrometry for fast screening of flame retardants and plasticizers in products and waste". Analytical and Bioanalytical Chemistry. 406(11): 2503-2512.

27. Basel Convention (2004). "Vital Waste Graphics". UNEP/ The Basel Convention/ GRID-Arendal/ DEWA-Europe. Geneva, Switzerland.

28. Basel Convention (2006). "Vital Waste Graphics II". UNEP/ The Basel Convention/ GRID-Arendal. Geneva, Switzerland.

29. Bergh C., Luongo G., Wise S. and Ostman C. (2012). "Organophosphate and phthalate esters in standard reference material 2585 organic contaminants in house dust". Analytical and Bioanalytical Chemistry. 402: 51-59.

30.

31. Bergh C., Torgrip R., Emenius G. and Ostman C. (2011). "Organophosphate and phthalate esters in air and settled dust - a multi-location indoor study". Indoor Air. 21(1): 67-76.

32. Bergman A., Ryden A. , Law R. J. , de Boer J., Covaci A., Alaee M.; Birnbaum L., Petreas M., Rose M., Sakai S., Van den Eede N., van der Veen I. (2012). "A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals". Environmental International. 49: 57-82.

33. Besis A. and Samara C. (2012). "Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments--a review on occurrence and human exposure". Environmental Pollution. 169: 217-229.

34. Betts K. S. (2008). "New Thinking on flame retardants". Environmental Health Perspectives. 116(5): A210-A213.

35. Bierkens J., Van Holderbeke M., Cornelis C., Torfs R. (2011) . "Dealing with contaminated sites". Eds. Swartjes F. A. "Dealing with Contaminated Sites". Springer. 2011.

36. Birnbaum L. S. and Staskal D. F. (2004). "Brominated flame retardants: cause for concern?". Environmental Health Perspectives. 112(1): 9-17.

37. Björklund J., Isetun S. and Nilsson U. (2004). "Selective determination of organophosphate flame retardants and plasticizers in indoor air by gas chromatography, positive-ion chemical ionization and collision-induced dissociation mass spectrometry". Rapid Communications in Mass Spectrometry. 18 (24): 3079-3083.

38. Bourbigot S., Le Bras M. and Troitzsch J. (2004). "Chapter 1: Introduction". In: Troitzsch J., (Editor). "Plastics flammability handbook: Principles, regulations, testing and approval. 3rd Edition. Hanser Publisher, Munich, Germany. P. 3-7.

39. Branchi I., Capone F., Alleva E. and Costa L. G. (2003). "Polybrominated diphenyl ethers: Neurobehavioral effects following developmental exposure". Neuro Toxicology. 24: 449-62.

40. Brandsma S. H., Sell m U., de Wit C. A., de Boer J. and Leonards P. E. G. "Dust Measurement of Two Organophosphorus Flame Retardants, Resorcinol Bis(diphenylphosphate) (RBDPP) and Bisphenol A Bis(diphenylphosphate) (BPA-BDPP), Used as Alternatives for BDE209 ". Environmental Science and Technology. 47: 14434-14441.

41. Bromine Science Environmental Forum (BSEF). (2007). Fact Sheet: End-of-Life Management of Plastics Containing Brominated Flame Retardants. [online]. Available from: http://www.bsef.com/publications/index.php

42. Brommer S. (2014). "Characterising Human Exposure to Organophosphate Ester Flame Retardants ". PhD thesis. University of Birmingham, UK.

43. Brommer S. and Harrad S. (2012). "Comparison of organophosphate ester concentrations in surface/floor dust from UK and Germany". Organohalogen Compounds. 74: 1502-1505. 32nd International Symposium on Halogenated Persistent Organic Pollutants (Dioxin 2012), 26th- 31st August 2012, Cairns, Australia.

44. Brommer, S., Harrad S., Van den Eede N. and Covaci A. (2012). "Concentrations of organophosphate esters and brominated flame retardants in German indoor dust samples". Journal of Environmental Monitoring. 14(9): 2482-2487.

45. BSEF. (2001). "Major Brominated Flame Retardants Volume Estimates: Total Market Demand by Region". Brussels: Belgium. [online]. Available from: http://www.bsef-site.com/docs/BFR_vols_2001.doc

46. BSEF. (2003). "Major Brominated Flame Retardants Volume Estimates: Total Market Demand By Region in 2001". Brussels, Belgium. [online]. Available from: http://www.bsef-site.com/docs/BFR_vols_2001.doc
47. BSEF. (2004). Fact sheet. Brominated flame retardant: decabromodiphenyl ether (Deca-BDE). [online]. Available from: http://www.bsef.com
48. BSEF. (2010). Fact sheet. Brominated flame retardant: decabromodiphenyl ether (Deca-BDE). [online]. Available from:
49. http://www.bsef.com/uploads/Documents/documents/BSEF_Deca-BDE_08-10f.pdf
50. BSEF. (2013). About decabromo diphenyl ether (decaBDE). [online]. Available from: http.//www.bsef.com/our-substances/deca-bde/about-deca-bde
51. Callahan P., Roe S. and Hawthorne M. (2012). "Tribune watchdog: Playing with Fire". In Chicago Tribune, Chicago, USA. Sunday, May 6th 2012. [online]. Available from: http://media.apps.chicagotribune.com/flames/index.html
52. CAS. (2016). Chemical Abstract Service Home Page. [online] available from: http://www.cas.org (accessed October 2016).
53. Castro-Jiménez J., Mariani G., Vives I., Skejo H., Umlauf G., Zaldívar J. M., Dueri S., Messiaen G. and Laugier T. (2011). "Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France) ". Environmental Pollution. 159: 1948-1956.
54. CEFIC. (2007). "What are FRs? Flame Retardant Market Statistics". European Flame Retardants Association (EFRA).
55. Cequier E., Ionas A. C., Covaci A., Marcé R. M., Becher G. and Thomsen C. (2014). "Occurrence of a Broad Range of Legacy and Emerging Flame Retardants in Indoor Environments in Norway." Environmental Science and Technology. 48(12): 6827-6835.

56. Cetin B. (2014). " Soil concentrations and source apportionment of polybrominated diphenyl ethers (PBDEs) and trace elements around a heavily industrialized area in Kocaeli, Turkey ". Environmental Science Pollution Research. 21:8284-8293.

57. Cetin B. and Odabasi M. (2005). "Measurement of Henry's law constants of seven polybrominated diphenyl ether (PBDE) congeners as a function of temperature". Atmospheric Environment. 39: 5273-5280.

58. Cetin B.and Odabasi M. (2008). "Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey". Chemosphere. 71: 1067-1078.

59. Chen D., Bi X., Zhao J., Chen L., Tan J., Mai B., Sheng G., Fu J. and Wong M. (2009). "Pollution characterization and diurnal variation of PBDEs in the atmosphere of an e-waste dismantling region". Environmental Pollution. 157: 1051-1057.

60. Chen D., Martin P., Burgess N. M., Champoux L., Elliott J. E., Forsyth D. J., Idrissi A. and Letcher R. J. (2013). "European Starlings (Sturnus vulgaris) Suggest That Landfills Are anImportant Source of Bioaccumulative Flame Retardants to CanadianTerrestrial Ecosystems". Environmental Science and Technology. 47: 12238-12247.

61. Chen L. G., Mai B. X., Bi X. H., Chen S. J., Wang X. M., Ran Y., Luo X. J., Sheng G. Y., Fu J. M. and Zeng E. Y. (2006). "Concentration levels, compositional profiles and gasparticle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China". Environmental science and technology. 40(4): 1190-1196.

62. Chen L., Mai B., Xu Z., Peng X., Han J., Ran Y., Sheng G. and Fu J. (2008). "In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China". Atmospheric Environment. 42: 78-86.

63. Cheng, H. and Hadjisophocleous G. V. (2011). "Dynamic modeling of fire spread in building". Fire Safety Journal. 46: 211-224.

64. Choi K. I., Lee S. H. and Osako M. (2009). "Leaching of brominated flame retardants from TV housing plastics in the presence of dissolved humic matter". Chemosphere.74:460466.

65. Clarke F. B. (1999). "The Effects of Brominated Flame Retardants on the Elements of Fire hazard: A Re-examination of Earlier Results". Fire and Materials. 23:109-116.

66. Commonwealth of Australia National Industry Chemicals Notification and Assessment Scheme (NICNAS). (2001). "Trisphosphates Priority Existing Chemical Assessment Report No . 17". [online]. Available from:

67. http://www.nicnas.gov.au/__data/assets/pdf_file/0004/4378/PEC_17_Trisphosphates_Full_Report_PDF.pdf

68. Consultancy and Research for Environmental Management (CREM). (2004). Eco-label Furniture; Extension of the Scope Final report number 04.728 The Netherlands.

69. Cooper E. M., Kroeger G., Davis K., Clark C. R., Ferguson P. L. and Stapleton H. M. (2016). "Results from Screening Polyurethane Foam Based Consumer Products for Flame Retardant Chemicals: Assessing Impacts on the Change in the Furniture Flammability Standards". Environmental Science and Technology. 50(19): 10653-10660.

70. Costa L. G. and Giordano, G. (2007). "Developmental neurotoxicity of polybrominated diphenyl ether (PBDE) flame retardants". Neurotoxicology. 28(6): 1047-1067.

71. Costa L. G., G. Giordano S. Tagliaferri A. Caglieri and A. Mutti (2008). "Polybrominated diphenyl ether (PBDE) flame retardants: environmental contamination, human body burden and potential adverse health effects". Acta Bio-medica. 79(3): 172-183.

72. Covaci A., Gerecke A. C., Law R. J., Voorspoels S., Kohler M., Heeb N. V, Leslie H., Allchin C. R. and de Boer J., (2006). "Hexabromocyclododecanes (HBCDs) in the environment and humans: A Review". Environ. Sci. Technol. 40(12): 3679–3688.

73. Covaci A., Harrad S., Abdallah M. A., Ali N., Law R. J., Herzke D. and C. A. de Wit. (2011). "Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour." Environment International. 37(2): 532-556.

74. Cristale J. (2013). "Priority and emerging flame retardants in the aquatic environment: analytical development, occurrence and risk". PhD thesis University of Barcelona, Barcelona, Spain.

75. Cristale J. and Lacorte S. (2013). "Development and validation of a multiresidue method for the analysis of polybrominated diphenyl ethers, new brominated and organophosphorus flame retardants in sediment, sludge and dust". Journal of Chromatography A. 1305: 267-275.

76. Cristale J., Vázquez A. G., Barata C., Lacorte S. (2013). "Priority and emerging flame retardants in rivers: Occurrence in water and sediment, Daphnia magna toxicity and risk assessment". Environment International. 59: 232-243.

77. Cristale J., Quintana J., Chaler R., Ventura F. and Lacorte S. (2012). "Gas Chromatography/ Mass Spectrometry comprehensive analysis of organophosphorus, brominated flame retardants, by-products and formulation intermediates in water". Journal of Chromatography A. 1241: 1-12.

78. Danish EPA. (1999). "Brominated Flame Retardants: Substance Flow Analysis and Assessment of Alternatives". Environmental Project No. 494.

79. Danon-Schaffer M. N. (2010). "Polybrominated diphenyl ethers in landfills from electronic waste". PhD thesis 394. University of British Columbia, Vancouver, Canada.

80. Danon-Schaffer M. N. and Mahecha-Botero A. (2010). "Influence of chemical degradation kinetic parameters on the total debromination of PBDEs in a landfill system". Organohalogen Compounds.72: 47-50.

81. Danon-Schaffer M. N., Li L. Y., Ikonomou M. G., Grace J. R. (2012). "Occurrence of PFCs and PBDEs in landfill leachates from across Canada". Water Air Soil Pollution. 223: 365-3372.

82. Danon-Schaffer M.N., Mahech-B otero A., Grace J. R., Ikonomou M. G. (2013). "Transfer of PBDEs from e-waste to aqueous media". Science of the Total Environment. 447: 458-471.

83. Darnerud P. (2003). "Toxic effects of brominated flame retardants in man and in wildlife". Environment International. 29(6): 841-853.

84. Darnerud P. O., Eriksen G. S., Jóhannesson T., Larsen P.B. and Viluksela M. (2001). "Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology". Environmental Health Perspectives. 109: 49-68.

85. de Jourdan B. P. (2012). "Environmental Fate and Toxicity of Three Brominated Flame Retardants in Aquatic Mesocosms". PhD thesis. University of Guelph, Ontario, Canada.

86. de Wit C. A. (2002). "An overview of brominated flame retardants in the environment". Chemosphere. 46: 583-624.

87. de Wit C. A., Herzke D. and Vorkamp K. (2010). "Brominated flame retardants in the Arctic environment - trends and new candidates". Science of The Total Environment. 408: 2885-2918.

88. DeCarlo V. J. (1979). "Studies on brominated chemicals in the environment". Annals of the New York Academy of Sciences, 320: 678-681.

89. Deng W. J., Zheng J. S., Bi X. H., Fu J. M.,Wong M. H. (2007). "Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China". Environmental International. 33:1063-1069.

90. Desborough J. (2011). "Exploring the Utiity of Chiral Signatures to Further Understanding of Soil-to-Herbage Transfer of Persistent Organic Pollutants (POPs)". PhD thesis. University of Birmingham, UK.

91. Directorate General of Meterology (DGM). (2016). Meteoric Data of 2015 and 2016. Public Authority for Civil Aviation, Oman.

92. Dirtu A. C., Abdallah M. and Covaci A. (2013). "Advances in the sample preparation of brominated flame retardants and other brominated compounds". Trends in Analytical Chemistry. 43: 189-203.

93. Dirtu A. C., Ali N., Van den Eede N., Neels H. and Covaci A. (2012). "Country specific comparison for profile of chlorinated, brominated and phosphate organic contaminants in indoor dust. Case study for Eastern Romania, 2010". Environment International. 49: 1-8.

94. Dodson R. E., Perovich L. J., Covaci A., Van den Eede N., Ionas A. C., Dirtu A. C., Brody J. G. and Rudel R. A. (2012). "After the PBDE phase-out: a broad suite of flame retardants in repeat house dust samples from California". Environmental science & technology 46(24): 13056-13066.

95. Dong Y., Li L., Bie P., Jia S., Wang Q., Huang Z., Qiu X., Zhang J. and Hu J. (2014). "Polybrominated diphenyl ethers in farmland soils: Source characterization, deposition contribution and apportionment". Science of The Total Environment 466–467: 524-532.

96. Drage D. (2013). "Brominated micropollutants within the integrated steel-making process and their fate in the environment". PhD thesis. University of Birmingham, UK.

97. Drage, D. S., Newton S., de Wit C. A. and Harrad S. (2016). "Concentrations of legacy and emerging flame retardants in air and soil on a transect in the UK West Midlands". Chemosphere. 148: 195-203.

98. D'Silva K., Fernandes A. and Rose M. (2004). "Brominated organic micropollutants—igniting the flame retardant issue; Critical Review". Environmental science and technology. 34:141–207.

99. Ebewele R. O. (2000). "Polymer Science and Technology". Department of Chemical Engineering, University of Benin, Benin City, Nigeria. CRC Press LLC, New York, Boca Raton, Florida, USA.

100. Eggen T., Moeder M. and Arukwe A. (2010). "Municipal landfill leachates: A significant source for new and emerging pollutants". Science of The Total Environment. 408(21): 5147-5157.

101. Eggen T., Moeder M. and Aruwke A. (2010). "Municipal landfill leachates: a significant source for new and emerging pollutants". Science of the Total Environment. 408: 5147-5157.

102. Eguchi A., Isobe T., Ramu K., Tue N. M., Sudaryanto A., Devanathan G., Viet P. H., Tana R. S., Takahashi S., Subramanian A. and Tanabe S. (2013). "Soil contamination by brominated flame retardants in open waste dumping sitesin Asian developing countries". Chemosphere. 90: 2365-2371.

103. Eguchi A., Isobe T., Subramanian A., Sudaryanto A., Ramu K., Minh T. B., Chakraborty P., Minh N. H., Tana T. S., Viet P. H., Takahashi S. and Tanabe S. (2009). "Contamination by Brominated Flame Retardants in Soil Samples from Open Dumping Sites of Asian Developing Countries". Interdisciplinary Studies on Environmental Chemistry. TERRAPUB. 143-151.

104. Environment Agency (EA). (2002). Guidance on Monitoring of Landfill Leachate, Groundwater and Surface Water. [online]. Available from:

105. http://www.ehsdata.com/media/pdf/technical/monitoring%20guidancejune%2002%20v.3a.pdf (Accessed 1 February 2012).

106. EU (2003b) EU Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromo. Official Journal of the European Union. L (42): 45-46
107. European Court of Justice. (2008). "Cases C-14/06 and C-295/06, Judgement of the Court". [online]. Available from:
108. http://eur-lex.europa.eu/legalcontent/EN/TXT/?uri= CELEX%3A62006 CA0014.
109. European Flame Retardants Association (EFRA). (2013). "How do they work? ". [online]. Available from:
110. http://www.ceficefra.com/index.php?option=com_content&view=article&id=6&Itemid=11&lang=en
111. European Furniture Manufacturers Federation (UEA). Furniture in Europe. 2005.
112. European Union Risk Assessment Report, 2008. "Tris (2-chloro-1-methylethyl) Phosphate (TCPP) Final Risk Assessment". [online]. Available from: https://echa.europa.eu/documents/10162/.../trd_rar_ireland_tccp_en.pdf
113. Ferro Corporation (Ferro). (2011). "Plasticizer Product Profile Triphenyl phosphate". [online]. Available from:
114. http://www.ferro.com/Our+Products/Polymer+Additives/Products+and+Markets/Elastomer+Plasticizers/Triphenyl+Phosphate.htm
115. Fisk P. R., Girling A. E., Wildey R. J. (2003). "Prioritisation of flame retardants for environmental risk assessment". UK Environment Science Agency. pp. 1-129.
116. Gandhi N., Bhavsar S. P., Gewurtz S. B. and Tomy G. T. (2011). "Can Biotransformation of BDE-209 in lake trout cause bioaccumulation of more toxic, lower-brominated PBDEs (BDE-47, -99) over the long term?". Environment International. 37: 170-177.

117. Gevao B., Ghadban A. N., Uddin S., Jaward F. J., Bahloul M. and Zafa J. (2011). "Polybrominated diphenyl ethers (PBDEs) in soils along a rural-urban-ruraltransect: Sources, concentration gradients and profiles". Environmental Pollution. 159: 3666-3672.

118. Gevao, B., M. Al-Bahloul, A. N. Al-Ghadban, A. Al-Omair, L. Ali, J. Zafar and M. Helaleh (2006). "House dust as a source of human exposure to polybrominated diphenyl ethers in Kuwait." Chemosphere. 64(4): 603-608.

119. Gouteux B., Alaee M., Mabury S.A., Pacepavicius G. and Muir D.C.G. (2008). "Polymeric Brominated Flame Retardants: Are They a Relevant Source of Emerging Brominated Aromatic Compounds in the Environment?". Environmental Science and Technology. 42: 9039-9044.

120. Grabda M., Oleszek-Kudlak S., Shibata E., Nakamura T. (2010). Initial studies on possibility of simultaneous recycling BFR-containing waste plastics with EAF dust. Fifth International Symposium on Brominated Flame Retardants (BFR) Kyoto, Japan 7-9 April 2010.

121. Green N., Schlabach M., Bakke T., Brevik E. M., Dye C., Herzke D., Huber S., Plosz B., Remberger M., Schøyen M., Uggerud H. T. and Vogelsang C. (2008). "Screening of selected metals and new organic contaminants 2007 (2367/ 2008)". [online]. Available from: http://www.miljodirektoratet.no/old/klif/publikasjoner/2367/ta2367.pdf

122. Guerra P., Alaee M., Eljarrat E. and Barcelo D. (2011). "Introduction to Brominated Flame Retardants: Commercially Products, Application and Physicochemical Properties: Brominated flame retardants in the environment". Eds. Eljarrat E. and Barceló D. The Handbook of Environmental Chemistry. Springer. 16: 1–18.

123. Guo J., Li Z., Sandy A. L. and Li A. (2014). "Method development for simultaneous analyses of multiple legacy and emerging organic chemicals in sediments". Journal of Chromatography A. 1370: 1-8.

124. Hale R. C., Alaee M., Manchester-Neesvig J. B., Stapleton H. M. and Ikonomou M. G. (2003). "Polybrominated diphenyl ether flame retardants in the North American environment". Environmental International. 29: 771-779.

125. Hale R. C., La Guardia M. J., Harvey E., Gaylor M. O. and Mainor T. M. (2006). "Brominated flame retardant concentrations and trends in abiotic media". Chemosphere 64: 181–186.

126. Harden F., Muller J. and Toms, L. (2005). "Organochlorine Pesticides (OCPs) and Polybrominated Diphenyl Ethers (PBDEs) in the Australian Population: Levels in Human Milk.". Environment Protection and Heritage Council of Australia and New Zealand, Canberra.

127. Harju M., Heimstad E.S., Herzke D., Sandanger T., Posner S. and Wania F.(2009). "Emerging 'new' brominated flame retardants in flame retarded products and the environment". Oslo, Norway Norwegian Pollution Control Authority. SFT Report 2462: 113.

128. Harrad S. (2001). "Chapter 17 The environmental behaviour of persistent organic pollutants". Pollution Causes, Effects and Control edited by Harrison R. M. 4th Edition,. The Royal Society of Chemistry, UK.

129. Harrad S. (2013). "Organic Pollutants Research Group QA/QC Protocol in the Environmental Health and Risk Management Division". University of Birmingham, UK.

130. Harrad S., Brommer S. and Mueller J. F. (2016). "Concentrations of organophosphate flame retardants in dust from cars, homes, and offices: An international comparison". Emerging Contaminants 2(2): 66-72.

131. Harrad S. and Hunter S. (2006). "Concentrations of Polybrominated Diphenyl Ethers in Air and Soil on a Rural−Urban Transect Across a Major UK Conurbation". Environmental Science & Technology. 40(15): 4548-4553.

132. Harrad S., Goosey E., Desborough J., Abdallah M. A., Roosens L.and Covaci A. (2010). "Dust from U.K. primary school classrooms and daycare centers: the significance of dust as a pathway of exposure of young U.K. children to brominated flame retardants and polychlorinated biphenyls." Environmental science and technology. 44(11): 4198-4202.

133. Harrad S., Hazrati S. and Ibarra C. (2006). "Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: implications for human exposure." Environmental Science & Technology 40(15): 4633-4638.

134. Harrad S., Ibarra C., Abdallah M. A., Boon R., Neels H. and Covaci A. (2008). "Concentrations of brominated flame retardants in dust from United Kingdom cars, homes and offices: Causes of variability and implications for human exposure". Environment International. 34(8): 1170-1175.

135. Harrad S., Wijesekera R., Hunter S., Halliwell C. and Baker R. (2004). "Preliminary assessment of UK human dietary and inhalation exposure to polybrominated diphenyl ethers". Environmental science and technology. 38(8): 2345-2350.

136. Harrison E. Z., Oakes S. R., Hysell M. and Hay A. (2006). "Review: Organic chemicals in sewage sludges". Science of the Total Environment. 367: 481-497.

137. Hassanin A., Breivik K., Meijer S. N., Steinnes E., Thomas G. O. and Jones K. C. (2004) "PBDEs in European Background Soils: Levels and Factors Controlling Their Distribution". Environmental Science and Technology. 38:738-745.

138. Hayakawa K., Takatsuki H., Watanabe I. and Sakai S. (2004). "Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and

monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan". Chemosphere. 57: 343-356.

139. Hazrati S. and Harrad S. (2007). "Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinatedbiphenyls (PCBs) and polybrominateddiphenyl ethers (PBDEs): Factors influencing sampling rates". Chemosphere. 67: 448-455.
140. Herbstman J. B., Sjödin A., Kurzon M., Lederman S. A., Jones R. S., Rauh V., Needham L. L., Tang D., Niedzwiecki M., Wang R. Y. and Perera F. (2010). "Prenatal exposure to PBDEs and neurodevelopment." Environmental Health Perspectives. 118(5): 712-719.
141. Hindersinn R. R. (1990). "Historical aspects of polymer fire retardance". American Chemical Society (ACS). Fire and Polymers. Chapter 7. Symposium Series 425. 87-96.
142. Hites R. A. (2004). "Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations." Environmental Science Technology 38(4): 945-956.
143. Hoffmeister W. (1871). Über Phenyläther und Diphenylenoxyd. Annalen der Chemie und Pharmacie. 191-217.
144. Hoh E. and Hites R. A. (2005). "Brominated flame retardants in the atmosphere of the East-Central United States". Environmental Science and Technology. 39: 7794-7802.
145. Horrocks A, R., Davies P., Alderson A. and Kandola B. K. (2007). "The potential for volatile phosphorus-containing flame retardants in textile back-coatings", Journal of Fire Sciences. 25(6): 523-540.
146. Huang K., Guo J., Lin K. F., Zhou X. Y., Wang J. X., Zhou P., Xu F. and Zhang M. L. (2013). "Distribution and temporal trend of polybrominated diphenyl ethers in one Shanghai municipal landfill, China". Environmental Science Pollution Research. 20: 5299–5308.

147. Hui-Ying X., Jian-Wei Z., Qing-Sen Y., Yan-Hua W., Jian-Ying Z. and Hai-Xiao, J. (2007). "QSPR/QSAR models for prediction of the physicochemical properties and biological activity of polybrominated diphenyl ethers". Chemosphere. 66: 1998-2010.

148. Ilyas M., Sudaryanto A., Setiawan I. E., Riyadi A. S., Isobe T., Takahashi S. and Tanabe S. (2011). "Characterization of polychlorinated biphenyls and brominated flame retardants in sediments from riverine and coastal waters of Surabaya, Indonesia". Marine pollution bulletin. 62(1): 89-98.

149. IPCS. (1998a). "Polybrominated Dibenzo-p-dioxins and dibenzofurans, Environmental Health Criteria 205". WHO. ISBN 92-4-157205-1.

150. IPCS. (1998b). "Flame retardants: tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate, Environmental Health Criteria 209". WHO. ISBN 92-4-157209-4.

151. IPCS. (2000). "Flame retardants: tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) phosphate, tetrakis(hydroxymeth yl) phosphonium salts, Environmental Health Criteria 218". WHO. ISBN 92-4-157218-3.

152. Janssen S. (2005). "Brominated flame retardants rising levels of concern". Arlington: Health Care With Out Harm (HCWH). [online]. Available from: http://www.env-health.org/IMG/pdf/HCWH_BFR_Final_2005.pdf

153. Javaid S. (2006). "Development and Optimisation of Treatment Technologies for Environmental Pollution Control". PhD Thesis. Brunel University, London, UK.

154. Jin J., Wang Y., Liu W., Yang C., Hu J. and Cui J. (2011). "Polybrominated diphenyl ethers in atmosphere and soil of a production area in China: Levels and partitioning". Journal of Environmental Sciences. 23: 427-433.

155. Jones K. C. and Voogt P. (1999). "Persistent organic pollutants (POPs): state of the science". Environmental Pollution. 100: 209–221.

156. Julander A., Westberg,H., Engwall M. and van Bavel B. (2005). Distribution of brominated flame retardants in different dust fractions in air from an electronics recycling facility. Science of the Total Environment. 350: 151-60.

157. Kajiwara N., Desborough J., Harrad S. and Takigami H. (2013). "Photolysis of brominated flame retardants in textiles exposed to natural sunlight". Environmental Science: Processes Impacts. 15: 653-660.

158. Kajiwara N., Hirata O., Takigami H., Noma Y., Tachifuji A. and Matsufuji Y. (2014). Leaching of brominated flame retardants from mixed wastes in lysimeters under conditions simulating landfills in developing countries. Chemosphere. 116: 46-53.

159. Kajiwara N., Noma Y. and Takigami H. (2008). "Photolysis studies of technical decabromodiphenyl ether (DecaBDE) and ethane (DeBDethane) in plastics under natural sunlight". Environmental Science and Technology. 42: 4404-4409.

160. Karlsson M., Ericson I., van Bavel B., Jensen J. K. and Dam M. (2006). "Levels of brominated flame retardants in Northern Fulmar (Fulmarus glacialis) eggs from The Faroe Islands". Science of Total Environment. 367: 840-846.

161. Karter M. J. (2004). "Fire Loss in the United States During 2003". Fire Analysis and Research Division, National Fire Protection Association (NFPA).

162. Kemmlein S., Hahn and O. Jann O. (2003). "Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials." Atmospheric Environment. 37(39-40): 5485-5493.

163. Kemmlein S., Herzke D. and Law R. J. (2009). "Brominated flame retardants in the European chemicals policy of REACH-Regulation and determination in materials". Journal of Chromatography A. 1216(3): 320-333.

164. Kierkegaard A., Asplund L., de Wit C. A., McLachlan M. S., Thomas G. O., Sweetman A. J. and Jones K. C. (2007). "Fate of higher brominated PBDEs in lactating cows". Environmental Science and Technology. 41: 417-423.

165. Kierkegaard A., Bignert A., Sellström U., Olsson M., Asplund L., Jansson B. and de Wit C.A. (2004). "Polybrominated diphenyl ethers (PBDE) and their methoxylated derivatives in fish from Swedish waters with emphasis on temporal trends, 1967-2000". Environmental Pollution.130: 187-198.

166. Kim J., Isobe T., Chang K. H., Amano A., Maneja R. H., Zamora P. B., Siringan F. P. and Tanabe S. (2011) Levels and distribution of organophosphorus flame retardants and plasticizers in fishes from Manila Bay, the Philippines. Environmental Pollution. 159(12): 3653-3659.

167. Kjeldsen P., Barlaz M. A. , Rooker A. P., Baun, A., Ledin, A. and Christensen T. H. (2002). "Present and Long-Term Composition of MSW Landfill Leachate: A Review". Critical Reviews in Environmental Science and Technology. 32: 297-336.

168. KLIF. (2011). "Screening of organophosphor flame retardants". Det Norske Veritas(DNV), Umea University, Oslo, Norwegian. TA-2786/2011. (online). Available from: http://www.miljodirektoratet.no/old/klif/publikasjoner/2786/ta2786.pdf (Accessed February 2016).

169. Klosterhaus S., Stapleton H. M., La Guardia M., Davis E., Eagle S. and Blum A. (2010). "Recent Studies on the Identification and Occurrence of PentaBDE Replacement Chemicals in Indoor and Outdoor Environments". 5th International Symposium on Brominated Flame Retardants in Kyoto, Japan. 7-9 Apri, 2010.

170. Kolic T. M., Shen L., MacPherson K., Fayez L., Gobran T., Helm P., Marvin C. H., Arsenault G., Reiner E. J. (2009). "The Analysis of Halogenated Flame Retardants by

GC–HRMS in Environmental Samples". Journal of Chromatographic Science. 47: 83-91.

171. Kwan C. S., Takada H., Mizukawa K., Yamashita R., Torii M., Koike T., Saha M., Rinawati and Santiago E. C. (2013). "PBDEs in leachates from municipal solid waste dumping sites in tropical Asian countries: phase distribution and debromination". Environmental Science and Pollution Research. 20: 4188-4204.
172. La Guardia M. J., R. and Harvey E. (2006). Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa- and Deca-PBDE Technical Flame-retardant Mixtures. Environmental Science and Technology. 40: 6247-6254.
173. Labunska I., Harrad S., Santillo D., Johnston P. and Brigden K. (2013). "Levels and distribution of polybrominated diphenyl ethers in soil, sediment and dust samples collected from various electronic waste recycling sites within Guiyu town, southern China". Environmental Science: Processes and Impacts. Royal Society of Chemistry, UK.
174. Landry S. D., Dawson G. W. (2002). "Design for the Environment: Electrical and Electronic Equipment Sustainabe Fire Safety".. presented at the Electronic Products Recovery and Recycling (EPR2) Conference, Washington, DC, March 12-13, 2002.
175. Lankova D., Svarcova A., Kalachova K., Lacina O., Pulkrabova J. and Hajslova J. (2015). "Multi-analyte method for the analysis of various organohalogen compounds in house dust." Analytica chimica acta. 854: 61-69.
176. Laoutid F., Bonnaud L., Alexandre M., Lopez-Cuesta J. M. and Dubois Ph. (2009). "New prospects in flame retardant polymer materials: From fundamentals to nanocomposite". Materials Science and Engineering. 63: 100-125.

177. Larsen E. R. (1980). "Halogenated Flame Retardants". In: Krik-Othmer Encyclopedia of Chemical technology. Grayson M. and Eckroth D. (Eds.). John Willey and Sons Inc. New York, NY, USA. 3rd Edition, Volume 10: 373-395.

178. Lassen C., Løkke S. and Andersen L.I. (1999). "Brominated flame retardants; Substance flow analysis and assessment of alternatives". Danish Environmental Protection Agency (EPA), Ministry of Environment and Energy, Copenhagen, Denmark.

179. Law R. J. (2010). "Brominated Flame Retardants". In Harrad S. (2010). Persistent Organic Pollutants. Chichester: Wiley. 5-24.

180. Lee I. S., Kim K. S., Kim S. J., Yoon J. H., Choi K. H., Choi S. D. and Oh J. E. (2002). Evaluation of mono- to deca-brominated diphenyl ethers in riverine sediment of Korea with special reference to the debromination of DeBDE-209. Science of the Total Environment. 432: 128-134.

181. Leisewitz A., Kruse H. and Schramm, E. (2001). "Substituting environmentally relevant flame retardants: vol. I. Results and summary overview. vol. II: Flame-retardant finishings of selected products - application-focused analysis: state of the art, trends, alternatives". Federal Environmental Agency, Germany, Report no. UBA-FB 000171/1. [online]. Available from:

182. https://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/1988.pdf.

183. Lenoir D., Becker L., Thumm W., Kettrup, A., Hauk A., Sklorz M., Bergmann, G. Hutzinger, O. (1994). "Evaluation of ecotoxicological properties from incineration of new duroplastic materials without halogen as flame retardant". In: Conference on Flame Retardancy of Polymeric Materials, Stamford, Connecticut, USA.

184. Lerche D., van de Plassche E., Schwegler A. and Balk F. (2002). "Selecting chemical substances for the UN-ECE POP protocol". Chemosphere. 47: 617-630.

185. Li M., Liu Z., Gu L., Yin R., Li H., Zhang X., Cao T. and Jiang C. (2014). "Toxic effects of decabromodiphenyl ether (BDE-209) on human embryonic kidney cells". Frontiers in Genetics. 5: 118.

186. Li W. L., Liu L. Y., Zhang Z. F., Song W. W., Huo C. Y., Qiao L. N., Ma W. L. and Li Y. F. (2016). "Brominated flame retardants in the surrounding soil of two manufacturing plants in China: Occurrence, composition profiles and spatial distribution". Environmental Pollution 213: 1-7.

187. Luo Y., Luo X. J., Lin Z., Chen S. J., Liu J., Mai B. X. and Yang Z. Y. (2009). "Polybrominated diphenyl ethers in road and farmland soils from an e-waste recycling region in Southern China: concentrations, source profiles, and potential dispersion and deposition". Science of Total Environment. 407:1105–1113.

188. Luongo G. and Östman C. (2016). "Organophosphate and phthalate esters in settled dust from apartment buildings in Stockholm". Indoor Air. 26(3): 414-425.

189. Ma J., Addink R., Yun S. H., Cheng J. P., Wang W. H. and Kannan K. (2009). "Polybrominated dibenzo-p-dioxins/dibenzofurans and polybrominated diphenyl ethers in soil, vegetation, workshop-floor dust and electronic shredder residue from an electronic waste recycling facility and in soils from a chemical industrial complex in eastern China". Environmental Science and Technology. 43(19): 7350-7356.

190. Ma Y., Salamova A., Venier M. and Hites, R. A. (2013). "Has the Phase-Out of PBDEs Affected Their Atmospheric Levels? Trends of PBDEs and Their Replacements in the Great Lakes Atmosphere". Environmental Science and Technology. 47: 11457-11464.

191. MacDonald, E., Gue, L. and Cooper, K. (2009). "An overview of PBDEs and their regulation status in Canada". Ecojustice, David Suzuki Foundation and Canadian Environmental Law Association; Canada.

192. Mahesh P., Jena A., Kumar V.and Gasser M. (2016). WEEE plastic and brominated flame retardants: a report on WEEE plastic recycling. Toxic Link, India. (online) available from: http://toxicslink.org/docs/Report-WEEE-plastics.pdf

193. Marklund A., Andersson B. and Haglund P. (2003). "Screening of organophosphorus compounds and their distribution in various indoor environments". Chemosphere, 53(9): 1137-1146.

194. Martin D., Tomida M. and Meacham B. (2016). Environmental impact of fire. Fire Science Reviews. 5(5): 1-21.

195. Martin M., Lam P. K. S. and Richardson B. J. (2004). An Asian quandary: where have all of the PBDEs gone?". Marine Pollution Bulletin. 49:375-382.

196. Matsukami H., Suzuki G., Someya M., Uchida N., Tue N. M., Tuyen L. H., Viet P. H., Takahashi S., Tanabe S. and Takigami H. (2017). "Concentrations of polybrominated diphenyl ethers and alternative flame retardants in surface soils and river sediments from an electronic waste-processing area in northern Vietnam, 2012-2014". Chemosphere 167: 291-299.

197. Matsukami H., Tue N. M., Suzuki G., Someya M., Tuyen L. H., Viet P. H., Takahashi S., Tanabe S., Takigami H. (2015). "Flame retardant emission from e-waste recycling operation in northern Vietnam: environmental occurrence of emerging organophosphorus esters used as alternatives for PBDEs". Science of Total Environment. 514: 492-499.

198. Maugh T. H. (1978). "Chemicals: How Many Are There?". Science 199(4325): 162.

199. Mayer P., Tolls J., Hermens L. and Mackay D. (2003). "Equilibrium sampling devices". Environmental Science and Technology. 37(9):184A–191A.

200. McDonald T. A. (2002). "A perspective on the potential health risks of PBDEs". Chemosphere. 46: 745-755.

201. McGee S. P., Cooper E. M., Stapleton H. M. and Volz D. C. (2012). "Early zebrafish embryogenesis is susceptible to developmental TDCPP exposure". Environmental health perspectives. 120(11): 1585-1591.

202. McGrath T. J. Sandiford C. J., Ball A. S. and Clarke B. O. (2016). "Widespread polybrominated diphenyl ether (PBDE) contamination of urban soils in Melbourne, Australia". Chemosphere. 164: 225-232. McPherson A., Thrope B., Blake A. (2004). "Brominated Flame Retardants in Dust on Computers: The Case for Safer Chemicals and Better Computer Design". Clean Production Action Report. [online]. Available from: http://www.computertakeback.com/problem/bfr_report_pages1-43.pdf.

203. Meijer S. N., Harner T., Helm P. A., Halsall C. J., Johnston A. E. and Jones, K. C. (2001). "Polychlorinated naphthalenes in UK soils: Time trends, markers of source, and equilibrium status". Environmental Science and Technology. 35(21): 4205-4213.

204. Meuenhor D. Polybrominated Diphenyl Ethers (PBDEs) in Indoor and Outdoor Environments. PhD thesis, University of Birmingham, UK 2011

205. Möller A., Sturm R., Xie Z., Cai M., He J., Ebinghaus R. (2012). "Organophosphorus flame retardants and plasticizers in airborne particles over the Northern Pacific and Indian Ocean toward the Polar Regions: evidence for global occurrence". Environmental Science and Technology. 46: 3127-34.

206. Möller A., Xie Z., Sturm R. and Ebinghaus R. (2011). "Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic". Environmental Pollution. 159(6): 1577-1583.

207. Morose G. (2006). "An Overview of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD)". A Publication of the Lowell Center for Sustainable Production, University of Massachusetts – Lowell, Lowell, MA.

208. Muenhor D. (2011). "Polybrominated Diphenyl Ethers (PBDEs) in Indoor and Outdoor Environment". PhD thesis. University of Birmingham, UK.

209. Muenhor D., Harrad S., Ali N. and Covaci A. (2010). "Brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand". Environment international. 36(7): 690-698.

210. Muir D. C. G. and Howard P. H. (2006). "Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists". Environmental Science and Technology. 40: 7157-7166.

211. National Fire Protection Association (NFPA). (2014). "NFPA 921 Guide for Fire and Explosion Investigations". 2014 Edition. [online] Available from: http://www.nfpa.org/assets/files/AboutTheCodes/921/Errata_921_14_3.pdf (Accessed May 2016).

212. National Swedish Chemicals Inspectorate (KEMI). (1994). "The flame retardant project: a survey of brominated alternatives to brominated diphenyl ethers". PM 3/94. Solna, Sweden.

213. Newton S., Bidleman T., Bergknut M., Racine J., Laudon H., Giesler R. and Wiberg K. (2014). "Atmospheric deposition of persistent organicpollutants and chemicals of emerging concern at two sites in northern Sweden". Environmental Science: Processes and Impacts. 16: 298-305.

214. Newton, S., U. Sellström and C. A. de Wit (2015). "Emerging Flame Retardants, PBDEs and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden". Environmental Science and Technology. 49(5): 2912-2920.

215. NFPA. (2015). "Fire loss in the United Staee during 2014". (oline). Available from: www.nfpa.org/~/media/FD0144A044C84FC5BAF90C05C04890B7.ashx (Accessed April 2016).

216. Ngohang F. E. (2014). "Combination of mass loss cone, Fourier transform infrared spectroscopy and electrical low pressure impactor to extend fire behaviour characterization of materials". PhD Thesis. Lille1 University, France.

217. Ni Y., Kumagai K. and Yanagisawa Y. (2007). "Measuring emissions of organophosphate flame retardants using a passive flux sampler". Atmospheric Environment. 41(15): 3235-3240.

218. NIWR. (2005). "Concentrations and levels of POPs from long-range transboundary air pollution in freshwater fish and sediments". ICP Waters Programme Centre, Norwegian Institute for Water Research; Oslo, Norway.

219. Nothstein G. L., Hahne R. M. and Spence M.W. (2000). "Evaluation of the cost-effectiveness of various passive monitors and active monitors for industrial hygiene sampling". American Industrial Hygiene Association Journal. 61: 64-68.

220. Nyholm J. R. (2009). "Persistency, bioaccumulation and toxicity assessment of selected brominated flame retardants". PhD thesis, Umeå University, Sweden.

221. Offenberg J. H., Stapleton H. M., Strynar M. J., Lindstrom A. B. (2006). "Polybrominated Diphenyl Ethers in US soils". Organohalogen Compounds. 68: 1816-1819.

222. Oliaei F., King P. and Phillips L. (2010). "Occurrence and concentrations of polybrominated diphenyl ethers (PBDEs) in Minnesota environment". Organohalogen Compounds. 58:185-188.

223. Organization for Economic Co-operation and Development - Screening Information Dataset (OECD SIDS). (2002). "Guidelines for the testing of chemicals: Guideline 104". [online]. Available from: http://www.oecd.org/chemicalsafety/testing/2766281.pdf

224. Osako, M., Kim, Y. J. and Sakai, S.-I. (2004). "Leaching of brominated flame retardants in leachate from landfills in Japan". Chemosphere; 57: 1571-79.

225. Özkara A., Dilek Akyıl D. and Muhsin Konuk M. (2016). "Chapter 1: Pesticides, Environmental Pollution and Health". In Larramedy M. L. and Soloeski S. (2016). Environmental Health Risk - Hazardous Factors to Living Species. [Open Access] Available online from: https://www.intechopen.com/books/environmental-health-risk-hazardous-factors-to-living-species/pesticides-environmental-pollution-and-health.

226. Palmes E. D. and Gunnison A. F. (1973). "Personal monitoring device for gaseous contaminants". American Industrial Hygiene Association Journal. 34: 78-81.

227. Papachlimitzou A., Barber J. L., Losada S., Bersuder P. and Law R. J. (2012). "A review of the analysis of novel brominated flame retardants". Journal of Chromatography A. 1219:15-28.

228. Pawlowski K. H. and Schartel B. (2007). "Flame retardancy mechanisms of triphenyl phosphate, resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate) in polycarbonate/acrylonitrile-butadiene-styrene blends". Polymer International. 56: 1404-1414.

229. Perez-Vazquez F. J., Flores-Ramirez R. F., Ochoa-Martinez A. C., Orta-Garcia S. T., Hernandez-Castro B., eticia Carrizalez-Yañez L. and Pérez-Maldonado I. N. (2015). "Concentrations of persistent organic pollutants (POPs) and heavy metals in soil from San Luis Potosí, México". Environmental Monitoring and Assessment. 187: 4119.

230. Pettersson-Julander A., van Bavel B., Engwall M. and Westberg H. (2004). "Personal air sampling and analysis of polybrominated diphenyl ethers and other bromine containing compounds at an electronic recycling facility in Sweden". Journal of Environmental Monitoring. 6: 874-80.

231. POPs. (2008). "Risk management evaluation for commercial octabromodiphenyl ether". [online]. available from: http://chm.pops.int/portals/0/repository/poprc4/unep-pops-poprc.4-6.english.pdf.

232. POPs. (2009). "Stockholm Convention on Persistent Organic Pollutants (POPs): Text and Annexes". https://www.env.go.jp/chemi/pops/treaty/treaty_en2009.pdf.

233. POPs. (2016). United Nations Environment Programme (UNEP). http://chm.pops.int.

234. Porter R. (1998). "London, a Social History". Cambridge, MA: Harvard UP.

235. Pozo K., Harner T., Wania F., Muir D., Jnes K., Barrie L. (2006). "Toward a global network for persistent organic pollutants in Air: Results from the GAPS". Environ. Sci. Technol. 40(16): 4867-4873.

236. Powell, C. S. (1998). "Phosphorous-based flame retardants for textiles". American Dyestuff Reporter. 87: 51-53.

237. Qiu X. H., Zhu T. and Hu J.X. (2010). "Polybrominated Diphenyl Ethers (PBDEs) and Other Flame Retardants in the Atmosphere and Water from Taihu Lake, East China". Chemosphere 80: 1207-1212.

238. Rahman F., Langford K. H., Scrimshaw M. D. and Lester J. N. (2001). "Review: Polybrominated diphenyl ether (PBDE) flame retardants". The Science of the Total Environment. 275: 1-17.

239. Reemtsma T., Quintana J. B., Rodil R., Garcia-Lopez M. and Rodriguez I. (2008). "Organophosphorus flame retardants and plasticizers in water and air, Part I. Occurrence and fate. Trends in Analytical Chemistry. 27(9):727-737.

240. Reeve R. (2002). "Introduction to Environmental Analysis: Analytical Techniques of Science". John Wiley and Sons, Ltd. Chichester, UK.

241. Remberger M., Sternbeck J., Palm A., Kaj L., Strömberg K. and Brorström-Lundeon E. (2004). The environmental occurrence of hexabromocyclododecane in Sweden. Chemosphere. 54: 9-21.

242. Renner, R., 2004. "Government Watch: In US, flame retardants will be voluntarily phased out". Environmental Science and Technology. 38(1): 14a-14a.

243. Renou S., Givaudan J. G., Poulain S., Dirassouyan F. and Moulin P. (2008). "Landfill leachate treatment: Review and opportunity". Journal of Hazardous Materials. 150(3): 468-493.

244. Roberts S. C., Macaulay L. J. and Stapleton H. M. (2012). "In vitro metabolism of the brominated flame retardants 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl) 2,3,4,5 tetrabromophthalate (TBPH) in human and rat tissues". Chemical Research in Toxicology. 25: 1435-1441.

245. Robinson B. H. (2009). "E-waste: An assessment of global production and environmental impacts". Science of the Total Environment. 408: 183–191.

246. Rodenburg L. A., Meng Q, Yee D. and Greenfield B. K. (2014). "Evidence for photolytic and microbial debromination of brominated diphenyl ether flame retardants in San Francisco Bay sediment". Chemosphere. 106: 36-43.

247. Rodil R., Quintana J. B., Concha-Grana E., Lopez-Mahia P., Muniategui-Lorenzo S. and Prada-Rodriguez D. (2012). "Emerging pollutants in sewage, surface and drinking water in Galicia (NW Spain) ". Chemosphere. 86: 1040-1049.

248. Roth T., Urpi Bertran R., Pöhlein M., Wolf M. and van Eldik R. (2012). "Gas chromatographic determination of phosphate-based flame retardants in styrene-based polymers from waste electrical and electronic equipment". Journal of Chromatography A. 1262: 188-195.

249. Sahlström L., Sellström U. and de Wit C. A. (2012). "Clean-up method for determination of established and emerging brominated flame retardants in dust". Analytical and Bioanalytical Chemistry. 404(2): 459-466.

250. Sakai S., Watanabe J., Honda Y., Takatsuki H., Aoki I., Futamatsu M. and Shiozaki K. (2001). "Combustion of brominated flame retardants and behavior of its byproducts". Chemosphere. 42: 519-531.

251. Salamova A. and Hites R. A. (2011) "Discontinued and Alternative Brominated Flame Retardants in the Atmosphere and Precipitation from the Great Lakes Basin Environmental Science and Technology 45. 8698-8706.

252. Salamova A., Hermanson M. H. and Hites R. A. (2014). "Organophosphate and Halogenated Flame Retardants in Atmospheric Particles from a European Arctic Site". Environ. Sci. Technol.; 48: 6133-6140.

253. Santos M. A. (1990). "Managing Planet Earth: Perspective on Population, Ecoogy, and the Law". Bergin and Garvey, Westport, Connecticut, USA. pp. 33-44.

254. Schafish R. J., Kahl D. A., Strauss S. S. and Dowden L. (1995). "Solid Waste: Municipal Environmental Compliance Manual". Lewis Publishers. Boca Raton, USA.

255. Schecter A., Päpke O., Tung K. C., Joseph J., Harris T. R. and Dahlgren J. (2005). "Polybrominated diphenyl ether flame retardants in the U.S. population: current levels, temporal trends, and comparison with dioxins, dibenzofurans, and polychlorinated biphenyls". Journal of Occupational and Environmental Medicine. 47(3):199-211.

256. Schenker U., Soltermann F., Scheringer M. and Hungerbühler K. (2008). "Modeling the Environmental Fate of Polybrominated Diphenyl Ethers (PBDEs): The Importance of Photolysis for the Formation of Lighter PBDEs". Environmental Science and Technology. 42: 9244-9249.

257. Schmitt E. (2007). "Phosphorus-based flame retardants for thermoplastics". Plastics, Additives and Compounding. 9(3): 26-30.

258. Scientific Committee on Health and Environmental Risks (SCHER). (2007). SCHER Opinion on the risk assessment report on 2,2-bis(chloromethyl)trimethylene bis[bis(2-chloroethyl) phosphate] (V6). [online] available from: http://ec.europa.eu/health/ph_risk/committees/04_scher/docs/scher_o_067.pdf

259. Seethapathy S., Gorecki T. and Li X. J. (2008). "Passive sampling in environmental analysis". Journal of Chromatography A. 1184: 234-253.

260. Sellstrom U., de Wit C. A., Lundgren N. and Tysklind M. (2005). "Effect of sewage-sludge application on concentrationsof higher-brominated diphenyl ethersin soilsand earthworms". Environmental Science and Technology. 39: 9064-9070.

261. Shi S., Dong L., Yang W., Zhou L., Zhang L., Zhang X. and Huang Y. (2014). "Monitoring of Airborne Polybrominated Diphenyl Ethers in the Urban Area by Means of Road Dust and Camphor Tree Barks". Aerosol and Air Quality Research. 14: 1106-1113.

262. Shi T., Chen S. J., Luo X. J., Zhang X. L., Tang C. M., Luo Y., Ma Y. J., Wu J. P., Peng X. Z. and Mai B. X. (2009). "Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China". Chemosphere. 74(7): 910-916.

263. Shoeib M., Harner T., Ikonomou M. and Kannan K. (2004). "Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers". Environmental Science and Technology. 38(5): 1313-1320.

264. Shoieb M. and Harner T. (2002). "Characterization and comparison of three passive air samplers for persistent organic pollutants". Environmental Science and Technology. 36: 4142-4151.

265. Simon P.L., Scott S.K., Kalliadasis S., Merkin J.H. (2005). "The effect of a radical scavenger on the propagation of flames in an exothermic-endothermic system". Journal of Mathematical Chemistry. 38: 203-231.

266. Sinkkonen S., Lahtiperä M., Vattulainen A., Takhistov V. V., Viktorovskii I. V., Utsal V. A. and Paasivirta J. (2003). "Analysis of known and new types of polyhalogenated

aromatic substances in oven ash from recycled aluminum production". Chemosphere. 52:761-775.

267. Sjödin A., Carlsson H., Thuresson K., Sjölin S., Bergman Å. and Östman C. (2001). "Flame retardants in indoor air at an electronics recycling plant and at other work environments". Environmental Science and Technology. 35: 448-454.

268. Sjödin A., Hagmar L., Klasson-Wehler E., Kronholm-Diab K., Jakobsson E., Bergman A. (1999). "Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers". Environmental Health Perspective. 107: 643–648.

269. Sjödin A., Papke O., Mcgahee E., Focant J. F., Jones R. S., Plessmulloli T., Toms L. M. L., Herrmann T., Muller J., Needham L. L. and Patterson D. G. (2008). "Concentration of polybrominated diphenyl ethers (PBDEs) in household dust from various countries". Chemosphere. 73, S131-S136.

270. Slack R. J., Gronow J. R. and Voulvoulis N. (2004). "Hazardous components of household waste". Critical Reviews in Environmental Science and Technology. 34: 419-445.

271. Smith R., Georlette P., Finberg I. and Rezinck G. (1996). "Development of environmentally friendly multifunctional flame retadants for commodity and engineering plastics". Polymer Degradation and Stability. 54: 167-173.

272. Söderström G. (2003). "On the combustion and photolytic degradation products of some brominated flame retardants". Department of Chemistry, Environmental Chemistry, University of Umea, Sweden. ISBN 91-7305-516-6.

273. Söderström G., Sellström U., De Wit C. and Tysklind M. (2004). "Photolytic debromination of decabromodiphenyl ether (BDE 209) ". Environmental Science and Technology. 38: 127-132.

274. Solbu K., Thorud S., Hersson M., Overbo S., Ellingsen D. G., Lundanes E. and Molander P. (2007). "Determination of airborne trialkyl and triaryl organophosphates originating from hydraulic fluids by gas chromatography-mass spectrometry. Development of methodology for combined aerosol and vapor sampling". Journal of Chromatography A. 1161: 275-283.

275. Song W., Ford J. C., Li A., Sturchio N.C., Rockne K.J., Buckley D. R. and Mills, W. J. (2004). "Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie". Environmental Science Technology. 39: 5600-5605.

276. St-Amand A.; Mayer P. and Blais J. (2008). "Seasonal trends in vegetation and atmospheric concentrations of PAHs and PBDEs near a sanitary landfill". Atmospheric Environment. 42: 2948-2958.

277. Stapleton H. M. and Dodder N. G. (2008). "Photodegradation of decabromodiphenyl ether in house dust by natural sunlight". Environmental Toxicology and Chemistry. 27:306-312.

278. Stapleton H. M., Allen J. G., Kelly S. M., Konstantinov A., Klosterhaus S., Watkins D., McClean M. D. and Webster T. F. (2008). "Alternate and new brominated flame retardants detected in U.S. house dust". Environmental science & technology. 42(18): 6910-6916.

279. Stapleton H. M., Dodder N. G., Offenberg J. H., Schantz M. M. and Wise S. A. (2005). "Polybrominated diphenyl ethers in house dust and clothes dryer lint." Environmental science and technology. 39(4): 925-931.

280. Stapleton H. M., Eagle S., Sjödin A. and Webster T. F. (2012). "Serum PBDEs in a North Carolina toddler cohort: associations with handwipes, house dust, and socioeconomic variables". Environmental health perspectives. 120(7): 1049-1054.

281. Stapleton H. M., Klosterhaus S., Eagle S., Fuh J., Meeker J. D., Blum A. and Webster T. F. (2009). "Detection of organophosphate flame retardants in furniture foam and US house dust". Environmental Science and Technology. 43 (19). 7490-7495.

282. Stockholm Convention on Persistent Organic Pollutants (POPs). (2004). United Nations Environment Programme (UNEP). http://chm.pops.int.

283. Stockholm Convention on Persistent Organic Pollutants (POPs). (2004). United Nations Environment Programme (UNEP). http://chm.pops.int.

284. Strandberg B., Dodder N. G., Basu I. and Hites R. A. (2001). "Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air". Environmental Science and Technology. 35(6): 1078-1083.

285. Stubbings W. (2015). "Extent and Mechanisms of Brominated and Chlorinated Flame Retardants Emissions Associated with Furnishings and Building Materials". PhD thesis. University of Birmingham, UK.

286. Stubbings W. A. and Harrad S. (2014). "Extent and mechanisms of brominated flame retardant emissions from waste soft furnishings and fabrics: a critical review". Environmental International. 71: 164-175.

287. Sundkvist A. M., Olofsson U., Haglund P. (2010). "Organophosphorus flame retardants and plasticizers in marine and fresh water biota and in human milk". Journal of Environmental Monitoring. 12: 943-951.

288. Svara J., Weferling N. and Hofmann, T. (2000). "Phosphorus Compounds, Organic". In: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim.

289. Syracuse Research Corporation (SRC). (2013). "PhysProp Database". [online]. Available from: http://www.srcinc.com/what-we- do/databaseforms.aspx?id=386

290. Tang Z., Huang Q., Cheng J., Yang Y., Yang J., Guo W., Nie Z., Zeng N. and Jin L. (2014). "Polybrominated diphenyl ethers in soils, sediments, and human hair in a plastic

waste recycling area: a neglected heavily polluted area". Environmental Science and Technology. 48:1508-1516.

291. Teclechiel D., Sundström M. and Marsh G. (2008). "Synthesis of polybrominated diphenyl ethers via symmetrical tetra- and hexabrominated diphenyliodonium salts". Chemosphere. 74: 421-427.

292. The International Programme on Chemical Safety (IPCS). (1994). "Polybrominated Biphenyls, Environmental Health Criteria 152". World Health Organization (WHO). ISBN 924-157152-7.

293. The Norwegian Climate and Pollution Agency (KLIF). (2010). "Environmental screening of selected 'new' brominated flame retardants and polyfluorinated compounds 2009". Det Norske Veritas(DNV), Umea University, Oslo, Norwegian. TA-2625/2010. (online). Available from: http://www.miljodirektoratet.no/old/klif/publikasjoner/2625/ta2625.pdf (Accessed February 2016).

294. Thomas G. O., Wilkinson M., Hodson S. and Jones K. C. (2006). "Organohalogen chemicals in human blood from the United Kingdom". Environmental Pollution. 141: 30-41.

295. Tian M., Chen S. J., Wang J., Zheng X. B., Luo X. J. and Mai B. X. (2011). "Brominated Flame Retardants in the Atmosphere of E-Waste and Rural Sites in Southern China: Seasonal Variation, Temperature Dependence, and Gas-Particle Partitioning". Environmental Science and Technology. 45: 8819-8825.

296. Toms L.-M. L., Hearn L., Kennedy K., Harden F., Bartkow M., Temme C. and Mueller J. F. (2009). "Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air". Environment International. 35(6): 864-869.

297. UK National Statistics. (2015). Detailed analysis of fires attended by fire and rescue services in England. Home Office. http://www.uk.gov.

298. United Nation Statistics Division (UNSD). (2011). United Nation Statistics Division (UNSD). (2011). "Environmental Indicator: Waste". [online]. Available from: http://unstats.un.org/unsd/environment/wastetreatment.htm

299. USEPA. US Environmental Protection Agency. (2003) "Superfund Lead Contaminated Residential Sites Handbook". Office of Solid Waste and Emergency Response (OSWER) Final 9285.7-50. Lead Sites Workgroup: Washington DC, USA.

300. USEPA. (2005). "Furniture Flame Retardancy Partnership: Environmental Profiles of Chemical Flame Retardant Alternatives". Volume 2. EPA 742-R-05-002.

301. USEPA. (2006). "Toxicological review of 2,2′, 4,4′,5-Pentabromodiphenyl ether (BDE-99)". [online]. Available from:

302. https://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=474496

303. USEPA. (2007). "Method 1614 Brominated Diphenyl Ethers in Water Soil, Sediment and Tissue by HRGC/HRMS". [online]. Available from: http://nepis.epa.gov/Exe/ZyPDF.cgi/P10070D4.PDF?Dockey=P10070D4.PDF

304. USEPA. (2008a). "Toxicological Review of 2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)". [online]. Available from: http://www.epa.gov/iris/toxreviews/1010tr.pdf

305. USEPA. (2008b). "Toxicological Review of 2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)". [online]. Available from: http://www.epa.gov/iris/toxreviews/1009tr.pdf

306. USEPA. (2008c). "Toxicological Review of Decabromodiphenyl ether (BDE-209)". [online]. Available from: http://www.epa.gov/iris/toxreviews/0035tr.pdf

307. USEPA. (2008d) "Guidance for the Sampling and Analysis of Lead in Indoor Residential Dust for Use in the Integrated Exposure Uptake Biokinetic (IEUBK) Model". online]. Available from: http://nepis.epa.gov

308. USEPA. (2010). "An exposure assessment of polybrominated diphenyl ethers". [online]. Available from: http://www.epa.gov/ncea.

309. USEPA. (2015). Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update". [online]. Available from: http://www.epa.gov/sites/production/files/ 2015-08/ documents/ffr_final.pdf

310. van den Ede N., Dirtu A. C., Ali N., Neels H. and Covaci A. (2012). "Multi-residue method for the determination of brominated and organophosphate flame retardants in indoor dust". Talanta. 89: 292-300.

311. van der Veen I. and de Boer J. (2012). "Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis". Chemosphere, 88(10): 1119-1153.

312. van Esch G. J. (1997). "Flame Retardants: A General Introduction". Environmental Health Creteria 192. Internationa Programme on Chemical Saftey. WHO. Geneva, Swiss.

313. Veleva V. and Sethi S. (2004). "The Electronics Industry in a New Regulatory Climate: Protecting the Environment and Shareholder Value". International Journal for Sustainable Business. 11(9): 207-224.

314. Venier M. and Hites R.A. (2008). "Flame Retardants in the Atmosphere near the Great Lakes". Environmental Science and Technology. 42: 4745-4751.

315. Verbruggen E. M., Rila J. P., Traas T. P. Posthuma-Doodeman C.J.A.M. and Posthumus R. (2005) Environmental Risk Limits for several phosphate esters, with possible application as flame retardant RIVM report 601501024/2005 (online). Available from: http://rivm.openrepository.com/rivm/bitstream/10029/7383/1/601501024.pdf

316. Vives I., Canuti E., Castro-Jimenez J., Christoph E. H., Eisenreich S. J., Hanke G., Huber T., Mariani G., Mueller A., Skejo H., Umlauf G. & Wollgast J. (2007). "Occurrence of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated

biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Lake Maggiore (Italy and Switzerland)". Journal of Environmental Monitoring. 9: 589-598.

317. Voospoels S. (2006). "Environmental distribution of brominated flame retardants in Belgium". PhD thesis. University of Antwerp, Belgium.
318. Wang B. L., Pang S. T., Zhang X. l., Li X I., Sun Y. G., Lu X. M. and Zhang Q. (2015). "Levels of Polybrominated Diphenyl Ethers in Settled House Dust From Urban Dwellings With Resident Preschool-Aged Children in Nanjing, China". Archives of Environmental Contamination and Toxicology. 68(1): 9-19.
319. Wang H. M., Yu Y.J., Han M., Yang S.W., Li Q., Yang Y. (2009). "Estimated PBDE and PBB Congeners in Soil from an Electronics Waste Disposal Site". Bull Environmental Contaminants Toxicological. 83: 789-793.
320. Wang S., Zhang S., Huang H., Niu Z. and Han W. (2014). "Characterization of polybrominated diphenyl ethers (PBDEs) andhydroxylated and methoxylated PBDEs in soils and plants from ane-waste area, China". Environmental Pollution 184: 405-413.
321. Wang, S., Wang Y., Song M., Luo C., Li J. and Zhang G. (2016). "Distributions and compositions of old and emerging flame retardants in the rhizosphere and non-rhizosphere soil in an e-waste contaminated area of South China". Environmental pollution. 208: 619-625.
322. Weber R., Watson A., Forter M. and Oliae F. (2011). "Persistent organic pollutants and landfills - a review of past experiences and future challenges". Waste Management and Research .29(1): 107–121.
323. Weinberg I., Dreyer A. and Ebinghaus R. (2011). "Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air". Atmospheric Environment. 45: 935-941.

324. Weschler C. J. and Nazaroff W. W. (2010). "SVOC partitioning between the gas phase and settled dust indoors". Atmospheric Environment. 44(30): 3609-3620.

325. WFSC. (2010). Geneva Association Newsletter. World Fire Statistics N□ 26. [online] Available from: http://www.f-e-u.org/upload/statistics/worldfire/ WorldFireStatistics-26-October2010.pdf

326. WHO. (1998). "Environmental health criteria 208: Flame Retardants: tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate". Geneva, Switzerland.

327. Wikoff D. S. and Birnhum L. (2011). "Human Health Effects of Brominated Flame Retardants Brominated Flame Retardants". Hdb Environmental Chemistry. 16: 19-53.

328. Wilford B., Harner T., Zhu J., Shoeib M. and Jones K. (2004). "Passive Sampling Survey of Polybrominated Diphenyl Ether Flame Retardants in Indoor and Outdoor Air in Ottawa, Canada: Implications for Sources and Exposure". Environmental Science and Technology. 38: 5312-5318.

329. Wilford B., Thomas G., Alcock R., Jones K., and Anderson D. (2003). "Polyurethane Fom as a source of PBDEs to the Environment". Organohalogen Coumpounds. 61: 219-222.

330. World Fire Statistics Centre (WFSC). (2008). Geneva Association Newsletter. World Fire Statistics No. 24. [online] Available from: http://www.f-e-u.org/upload/statistics/ worldfire/WorldFireStatistics-24-October2008.pdf

331. World Furniture Confederation (WFC). (2012). Production in the world furniture industry. http://world-furniture-confederation.com

332. Wu J. P., Guan Y. T., Zhang Y., Luo X. J., Zhi H., Chen S. J. and Mai B. X. (2011). "Several current-use, nonPBDE brominated flame retardants are highly bioaccumulative: Evidence from field determined bioaccumulation factors". Environment International, 37, 210-215.

333. Wu J. P., Luo X. J., Zhang Y., Luo Y., Chen S. J., Mai B. X. and Yang, Z. Y. (2008). "Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China". Environment International. 34: 1109-1113.

334. Wu X. M., Bennett D. H., Moran R. E., Sjödin A., Jones R. S., Tancredi D. J., Tulve N. S., Clifton M. S., Colón M., Weathers W. and Hertz-Picciotto I. (2015). "Polybrominated diphenyl ether serum concentrations in a Californian population of children, their parents, and older adults: an exposure assessment study". Environmental Health 14:23.

335. Xiao Q., Hu B., Duan J., He M. and Zu W. (2007). "Analysis of PBDEs in Soil, Dust, Spiked Lake Water, and Human Serum Samples by Hollow Fiber-Liquid Phase Microextraction Combined with GC-ICP-MS". Journal of the American Society for Mass Spectrometry. 18: 1740-1748.

336. Yu Y., Hung H., Alexandrou N., Roach P.and Nordin K. (2015). "Multiyear Measurements of Flame Retardants and Organochlorine Pesticides in Air in Canada's Western Sub-Arctic". Environmental Science and Technology. 49(14): 8623-8630.

337. Yun S. H., Addink R., McCabe J. M., Ostaszewski A., Mackenzie-Taylor D., Taylor A. B. and Kannan K. (2008). "Polybrominated diphenyl ethers and polybrominated biphenyls in sediment and floodplain soils of the Saginaw River watershed, Michigan, USA". Archives of Environmental Contamination and Toxicology. 55(1):1-10.

338. Zhang S., Xu X., Wu Y., Ge J., Li W. and Huo X. (2014). Polybrominated diphenyl ethers in residential and agricultural soils from an electronic waste polluted region in South China: distribution, compositional profile, and sources. Chemosphere. 102:55-60.

339. Zhang X. L., Luo X. J., Chen S. J., Wu J. P. and Mai B. X. (2009). "Spatial distribution and vertical profile of polybrominated diphenyl ethers, tetrabromobisphenol A, and

decabromodiphenylethane in river sediment from an industrialized region of South China". Environmental Pollution. 157(6): 1917-1923.

340. Zheng Q., Nizzetto L., Li J., Mulder M. D., Sáňka O., Lammel G., Bing H., Liu X., Jiang Y., Luo C. and Zhang G. (2015). "Spatial Distribution of Old and Emerging Flame Retardants in Chinese Forest Soils: Sources, Trends and Processes". Environmental Science and Technology. 49(5): 2904-2911.

341. Zhu Z. C., Chen S. J., Zheng J., Tian M., Feng A. H., Luo X. J. and Mai B. X. (2014). Occurrence of brominated flame retardants (BFRs), organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs) in agricultural soils in a BFRmanufacturing region of North China". Science of Total Environment. 481: 47-54.

Appendices

Appendix A:

Table A.1: Summary descriptive statistics of the PBDE concentrations (pg m^{-3}) in the air samples of Am landfill;

1) Downwind

PBDE congeners	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	tri-hepta BDEs	∑PBDEs
Mean	2.63	25.72	56.09	12.25	61.78	39.85	105.29	1008.09	303.62	1311.71
Standard deviation	1.14	13.08	15.54	7.64	30.71	20.40	29.19	424.56	117.6942	390.76
Median	2.81	18.51	57.16	9.13	71.90	47.05	91.08	1178.27	297.64	1436.52
Minimum	0.53	12.02	35.25	3.01	9.62	15.80	76.93	217.48	153.16	608.51
Maximum	4.34	48.24	83.27	26.57	91.48	61.89	158.42	1494.73	474.21	1803.13
5th Percentile	0.94	12.33	35.66	3.92	15.53	16.18	77.30	335.48	205	708.58
25th Percentile	2.11	15.12	44.84	6.71	39.02	17.40	79.82	757.73	161.863	1072.00
75th Percentile	3.27	35.54	63.65	16.82	90.70	59.71	125.50	1325.37	395.165	1594.93
95th Percentile	4.12	45.48	78.17	24.07	91.44	61.43	149.35	1450.72	454.056	1759.86

2) Upwind

PBDE congeners	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	tri-hepta BDEs	∑PBDEs
Mean	1.22	2.10	5.43	1.53	7.03	4.18	8.99	178.76	30.47	209.23
Standard deviation	0.68	0.79	1.94	0.84	4.56	2.87	2.39	23.07	4.64	26.74
Median	1.29	2.20	5.50	1.30	6.50	4.75	7.50	175.50	28.25	208.67
Minimum	0.37	0.80	2.82	0.30	0.90	0.40	6.50	149.30	26.04	176.38
Maximum	2.38	3.20	9.00	3.30	15.90	7.70	12.70	219.90	40.33	260.23
5th Percentile	0.45	1.01	2.96	0.57	1.74	0.55	6.59	152.15	26.35	179.58
25th Percentile	0.64	1.55	4.00	1.20	3.90	1.35	6.95	160.15	27.20	187.30
75th Percentile	1.61	2.70	6.35	1.70	9.05	6.85	11.15	193.15	32.14	222.37
95th Percentile	2.24	3.14	8.22	2.85	14.10	7.52	12.31	213.30	38.18	249.73

Table A.2: Summary descriptive statistics of the PBDE concentrations (pg m^{-3}) in the air samples of Ra landfill;
1) Downwind

PBDE congeners	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	tri-hepta BDEs	∑PBDEs
Mean	4.06	19.55	41.45	18.82	55.16	38.32	104.82	928.60	282.19	1210.78
Standard deviation	2.06	5.78	12.73	9.12	32.02	21.28	32.53	242.63	57.11	287.98
Median	3.09	19.85	46.86	13.41	64.71	47.23	108.97	781.82	275.24	1040.86
Minimum	2.05	12.38	17.95	6.02	8.95	2.47	62.31	668.95	194.08	944.19
Maximum	8.27	28.11	56.78	30.92	98.65	71.17	171.09	1357.35	393.66	1674.83
5th Percentile	2.14	12.66	21.23	7.99	8.95	6.14	64.93	694.74	211.97	945.63
25th Percentile	2.52	14.04	34.05	13.00	31.46	26.18	86.40	768.35	256.38	992.25
75th Percentile	5.00	24.22	50.23	27.70	75.46	47.52	109.28	1077.68	299.78	1415.55
95th Percentile	7.43	27.37	55.05	30.82	93.80	64.08	152.55	1317.50	370.81	1657.84

2) Upwind

PBDE congeners	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	tri-hepta BDEs	∑PBDEs
Mean	11.69	15.72	40.61	16.93	40.55	30.77	88.37	737.14	244.64	981.77
Standard deviation	5.27	4.17	8.36	8.01	27.84	13.79	26.98	198.68	71.56	264.92
Median	11.63	15.94	38.29	12.74	36.20	31.76	80.72	680.49	202.96	855.74
Minimum	3.69	7.68	26.43	10.06	6.53	4.12	59.09	533.84	164.15	736.20
Maximum	18.14	20.37	53.14	35.17	87.06	50.11	133.54	1095.8	354.43	1450.23
5th Percentile	4.09	9.42	29.18	10.60	7.33	9.39	59.59	540.22	172.20	742.76
25th Percentile	4.09	9.42	29.18	10.60	7.33	9.39	59.59	540.22	172.20	742.76
75th Percentile	7.89	13.67	36.12	12.10	19.27	25.75	70.26	592.01	196.67	788.98
95th Percentile	17.80	20.21	51.54	30.33	82.44	47.90	130.59	1059.33	352.81	1412.13

A.3: Summary descriptive statistics of the concentrations of PBDE contaminants (pg m^{-3}) in the air in Reference samples

PBDE congeners	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	tri-heptaBDEs	∑PBDEs
Muscat:										
Mean	0.5	1.8	3.8	1.5	4.9	3.1	8.7	81.4	24.3	105.6
S D	0.2	1.0	1.2	0.6	1.9	1.3	3.8	31.6	9.6	41.2
Median	0.4	1.7	3.8	1.4	4.7	2.8	7.8	78.0	22.7	100.7
Minimum	0.2	0.7	2.2	0.7	2.6	1.8	4.6	43.1	12.9	55.9
Maximum	0.8	3.1	5.4	2.3	7.6	5.1	14.5	126.4	38.8	165.2
5th Percentile	0.2	0.8	2.4	0.7	2.8	1.9	4.9	46.0	13.8	59.8
95th Percentile	0.3	1.0	3.0	1.1	3.3	2.2	5.9	57.6	17.6	75.2

Table A.4: Summary statistics of PBDEs concentrations (ng g^{-1}) in soil from the vicinity of Oman landfills

	Landfills average concentrations										
BFRs	**Am**	**Ra**	**Ni**	**Ib**	**So**	**Bu**	**Mean**	**SD**	**Median**	**Min**	**Max**
BDE-28	0.61	0.27	0.44	0.41	0.57	0.58	0.48	0.33	0.37	0.26	3.95
BDE-47	0.53	0.41	0.46	0.53	0.66	0.57	0.53	0.32	0.42	0.32	2.63
BDE-99	0.68	0.67	1.18	0.97	1.04	0.82	0.89	0.41	0.53	0.71	2.18
BDE-100	0.44	0.43	0.75	0.7	0.62	0.66	0.6	0.33	0.38	0.47	3.68
BDE-153	0.69	0.88	1.04	0.9	1	1.14	0.94	0.43	0.69	0.42	3.21
BDE-154	0.56	0.78	1.1	0.57	0.92	1.11	0.84	0.63	0.71	0.67	2.95
BDE-183	1.57	1.78	2.21	1.87	2.33	1.77	1.92	0.97	1.20	0.82	11.49
BDE-209	140.53	85.31	191.42	240.27	226.99	166.9	175.24	74.98	84.39	24.32	419.16
∑PBDEs	145.61	90.53	198.6	246.22	234.13	173.55	181.44	101.71	88.68	28.00	449.25

Table A.5: Summary statistics of PBDEs concentrations (pg g^{-1} dw), BDE-209 and ∑PBDEs concentrations (ng g^{-1} dw) in soil from non-landfilled sites surrounded the vicinity of Omani landfills

BFRs	Am	Ra	Ni	Ib	So	Bu	Mean	SD	Median	Min	Max
	Landfills average concentrations (pg g^{-1} dw)										
BDE-28	6.8	4.56	8.68	8.8	2.51	1.73	5.51	3.17	3.44	0.57	35.46
BDE-47	13.64	66.56	23.14	17.2	2.38	2.68	20.93	5.83	8.12	8.32	102.11
BDE-99	37.84	112.96	22.33	10.83	5.63	4.31	32.32	17.38	25.90	14.12	391.34
BDE-100	16.16	12.32	6.06	12.12	2.66	1.22	8.42	3.3	6.17	1.54	100.07
BDE-153	10.1	22.75	15.25	9.36	11.18	3.67	12.09	3.62	8.71	2.87	219.21
BDE-154	5.46	14.21	13.09	5.86	3.94	5.22	7.91	2.35	4.97	1.75	302.64
BDE-183	68.64	96.4	85.75	89.36	115.67	108.24	94.03	21.2	56.89	12.05	262.9
BDE-209	2966.25	3226.41	1876.78	1261.87	2358.92	2151.91	2307.02	1331.87	1507.39	200.5	3880.87
∑PBDEs	3124.89	3556.17	2051.08	1415.4	2502.89	2278.98	2488.23	1388.72	1621.58	241.72	5294.6
	Landfills average concentrations (ng g^{-1} dw)										
BDE-209	2.97	3.23	1.88	1.26	2.36	2.15	2.31	1.33	1.51	2.01	3.88
∑PBDEs	3.12	3.6	2.05	1.42	2.50	2.28	2.49	1.39	1.62	2.42	5.29

Appendix B:

Table B.1: Summary descriptive statistics of the concentrations of NBFRs contaminants (pg m^{-3}) in the air samples in Am landfill in downwind and upwind

PBDE congeners	PBEB	EH-TBB	BTBPE	BEH-TEBP	DBDPE	TBECH	TBBPA-DBPE	∑NBFRs
Downwind:								
Mean	0.28	0.25	0.97	2.13	4.04	7.53	6.73	21.94
S D	0.16	0.09	0.41	0.95	1.32	3.66	3.84	5.45
Median	0.29	0.30	1.03	2.47	3.26	7.49	6.02	21.86
Minimum	0.09	0.13	0.41	0.49	2.65	2.63	2.02	13.30
Maximum	0.57	0.36	1.69	3.36	6.43	12.66	13.32	29.37
5th Percentile	0.15	0.16	0.66	1.48	3.01	4.47	3.39	18.43
25th Percentile	0.37	0.33	1.16	2.82	4.97	10.50	9.47	26.08
75th Percentile	0.09	0.14	0.45	0.71	2.70	2.71	2.41	14.38
95th Percentile	0.53	0.36	1.57	3.28	6.02	12.32	12.17	29.19
Upwind:								
Mean	0.03	0.04	0.29	0.13	0.53	0.10	0.75	1.87
S D	0.01	0.02	0.09	0.06	0.30	0.04	0.37	0.48
Median	0.03	0.04	0.23	0.15	0.47	0.11	0.75	1.80
Minimum	0.01	0.01	0.19	0.03	0.16	0.04	0.26	1.20
Maximum	0.04	0.08	0.46	0.21	1.04	0.17	1.27	2.55
5th Percentile	0.02	0.02	0.21	0.09	0.27	0.07	0.45	1.52
25th Percentile	0.03	0.06	0.36	0.18	0.74	0.12	1.05	2.25
75th Percentile	0.01	0.01	0.19	0.04	0.19	0.05	0.27	1.24
95th Percentile	0.04	0.08	0.43	0.20	0.95	0.16	1.23	2.52

Table B.2: Summary descriptive statistics of the concentrations of NBFRs contaminants (pg m^{-3}) in the air samples in Ra landfill in downwind and upwind

PBDE congeners	PBEB	EH-TBB	BTBPE	BEH-TEBP	DBDPE	TBECH	TBBPA-DBPE	∑NBFRs
Downwind:								
Mean	0.92	2.32	6.93	7.20	7.37	10.57	37.59	72.90
S D	0.59	1.05	2.64	3.48	4.56	7.67	20.69	35.95
Median	0.71	1.90	7.32	4.85	6.43	10.29	37.97	69.28
Minimum	0.29	0.87	2.81	3.36	0.01	2.58	8.31	23.84
Maximum	1.77	4.18	11.02	12.38	15.38	26.59	65.42	135.12
5th Percentile	0.40	1.63	5.04	4.43	5.27	4.39	20.78	46.67
25th Percentile	1.45	3.00	8.65	10.46	9.60	12.88	54.93	94.36
75th Percentile	0.30	1.07	3.37	3.60	1.47	2.79	11.95	27.80
95th Percentile	1.75	3.90	10.57	12.00	14.22	22.72	65.25	126.39
Upwind:								
Mean	0.70	1.51	3.01	4.03	4.59	7.18	21.74	42.76
S D	0.42	0.61	1.24	1.83	2.57	4.19	11.58	17.75
Median	0.62	1.48	2.96	3.81	4.84	7.68	17.64	37.78
Minimum	0.14	0.50	0.49	2.09	0.08	1.30	3.76	11.21
Maximum	1.35	2.52	4.54	7.22	8.14	14.17	40.59	66.80
5th Percentile	0.41	1.18	2.68	2.27	3.04	3.66	14.90	35.18
25th Percentile	0.98	1.85	3.86	5.28	6.50	9.89	30.20	56.58
75th Percentile	0.20	0.63	1.13	2.10	0.94	2.00	6.89	17.82
95th Percentile	1.33	2.33	4.45	6.67	7.87	12.93	37.99	65.89

Table B.3: Summary descriptive statistics of the concentrations of NBFRs contaminants (pg m^{-3})) in the air in Reference samples

PBDE congeners	PBEB	EH-TBB	BTBPE	BEH-TEBP	DBDPE	TBECH	TBBPA-DBPE	∑NBFRs
Mean	0.10	0.42	1.25	0.76	0.57	1.95	4.24	9.29
S D	0.10	0.22	0.70	0.68	0.50	1.19	2.63	2.87
Median	0.10	0.48	1.36	0.76	0.57	1.95	4.24	9.29
Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.51
Maximum	0.28	0.63	2.14	1.67	1.14	3.62	7.25	12.80
5th Percentile	0.00	0.42	1.25	0.00	0.02	1.61	3.02	8.34
95th Percentile	0.11	0.56	1.51	1.36	1.13	2.56	6.71	11.53

Appendix C:

Table C.1: 4.3: Leaching experimental results of average FR concentrations (µg L^{-1}) with SD, PL and PLT
a. The contact time and temperature effects

Temp.	20˚C					60˚C					80˚C				
Time (*h*)	6 h	24 h	48 h	72 h	96 h	6 h	24 h	48 h	72 h	96 h	6 h	24 h	48 h	72 h	96 h
BDE-47	1750	5260	17070	29390	60670	2910	9540	31245	66585	81670	11025	41800	106141	171062	245250
SD	73	139	903	1825	2036	576	379	1286	6376	4877	639	1358	3247	1130	27987
PL	0.011	0.033	0.11	0.18	0.37	0.02	0.06	0.19	0.41	0.50	0.07	0.26	0.66	1.06	1.51
PLT	0.0018	0.0014	0.0022	0.0025	0.0039	0.0030	0.0025	0.0040	0.0057	0.0053	0.011	0.011	0.014	0.015	0.016
BDE-99	3318	9724	30273	51780	108623	5534	17632	55427	117289	170034	20914	77256	188282	301337	439096
SD	212	270	1823	7632	2363	915	920	3154	2609	1339	1351	5140	2865	4731	51579
PL	0.0178	0.0521	0.1621	0.2772	0.5815	0.0296	0.0944	0.2967	0.6279	0.9102	0.1120	0.4136	1.0079	1.6132	2.3506
PLT	0.0030	0.0022	0.0034	0.0038	0.0061	0.0049	0.0039	0.0062	0.0087	0.0095	0.019	0.017	0.021	0.022	0.025
BDE-100	1640	4280	12940	23210	51940	2730	7755	23700	52590	81300	10350	33975	80513	135100	262438
SD	52	189	1186	5319	4566	394	396	1269	7689	5277	2165	1916	7402	8599	23836
PL	0.039	0.10	0.31	0.56	1.24	0.065	0.19	0.57	1.26	1.95	0.25	0.81	1.93	3.23	6.28
PLT	0.0065	0.0043	0.0064	0.0077	0.013	0.011	0.0077	0.012	0.018	0.0203	0.041	0.034	0.040	0.050	0.065
BDE-153	180	540	1710	2970	6180	315	945	3105	6705	9675	1125	4200	10578	17213	24930
SD	10	35	153	428	613	47	63	331	381	470	136	187	985	1044	2293
PL	0.0083	0.025	0.079	0.14	0.29	0.015	0.044	0.14	0.31	0.45	0.052	0.19	0.49	0.80	1.15
PLT	0.0014	0.0010	0.0016	0.0019	0.0030	0.0024	0.0018	0.0030	0.0043	0.0047	0.0087	0.0081	0.010	0.011	0.012
BDE-154	43	86	215	430	903	65	129	387	968	1419	215	645	1257	2419	3612
SD	3	4	11	83	124	3	6	25	20	112	21	25	120	63	431
PL	0.0030	0.0060	0.015	0.030	0.063	0.0045	0.0090	0.027	0.067	0.099	0.015	0.045	0.087	0.17	0.25
PLT	0.0005	0.0002	0.0003	0.0004	0.0007	0.0007	0.0004	0.0006	0.0009	0.0010	0.0025	0.0019	0.0018	0.0023	0.0026
EH-TBB	75	151	376	753	1580	315	1015	3168	6720	9747.5	717.5	2660	9398	20720	37730
SD	4	4	28	63	96	58	57	382	885	228	127	245	160	1061	3267
PL	0.0017	0.0033	0.0083	0.017	0.035	0.0070	0.023	0.070	0.15	0.22	0.06	0.058	0.21	0.46	0.83
PLT	0.0003	0.0001	0.0002	0.0002	0.0004	0.0012	0.0009	0.0015	0.0021	0.0022	0.0026	0.0025	0.0043	0.0064	0.0087
BEH-TEBP	215	430	1075	2150	4515	900	2900	9050	19200	27850	2050	7600	26850	59200	107800
SD	6	25	90	515	217	181	152	657	2403	1521	650	417	2729	5490	10028
PL	0.0010	0.0021	0.0052	0.011	0.022	0.0044	0.014	0.044	0.094	0.14	0.010	0.037	0.13	0.29	0.53
PLT	0.0002	0.0001	0.0001	0.0001	0.0002	0.0007	0.0006	0.0009	0.0013	0.0014	0.0017	0.0015	0.0027	0.0040	0.0055
TPhP	3088	5296	11696	18384	36040	3424	6392	14272	27768	37608	7784	16824	42296	85608	145664
SD	177	58	921	3291	2332	1038	299	944	3555	2098	1056	1471	3874	7815	11568
PL	0.022	0.038	0.083	0.13	0.26	0.024	0.046	0.10	0.20	0.28	0.055	0.12	0.30	0.61	1.038
PLT	0.0037	0.0016	0.0017	0.0018	0.0027	0.0041	0.0019	0.0021	0.0027	0.0028	0.0092	0.0050	0.0063	0.0085	0.011
TCIPP	98501	69710	37263	26074	17582	204404	71542	68685	93021	24337	248052	185115	134565	121578	71229
SD	4257	2701	1835	4924	1374	8905	4030	4203	12049	1246	4710	2048	11376	9996	6837
PL	0.29	0.26	0.11	0.076	0.051	0.60	0.21	0.20	0.27	0.071	0.72	0.83	0.39	0.36	0.21
PLT	0.048	0.011	0.0023	0.0011	0.0005	0.010	0.0087	0.0042	0.0038	0.0007	0.12	0.035	0.0082	0.0049	0.0022

b. The agitation and DHM effects of Time effect at 60˚C

Effect	Agitation					DHM (100 mg L^{-1})					DHM (1000 mg L^{-1})				
Time (*h*)	6	24	48	72	96	6	24	48	72	96	6	24	48	72	96
BDE-47	1903	7230	21040	36041	46812	3260	10689	34998	74577	91471	5136	17048	56966	122149	153739
SD	139	398	1493	2890	9636	558	455	4172	10711	6870	564	641	4865	8254	12039
PL	0.012	0.045	0.13	0.22	0.29	0.020	0.066	0.22	0.46	0.56	0.032	0.11	0.35	0.75	0.95
PLT	0.0020	0.0019	0.0027	0.0023	0.0040	0.0034	0.0027	0.0045	0.0064	0.0059	0.0053	0.0044	0.0073	0.011	0.0099
BDE-99	3622	13351	37302	82390	86089	6199	19750	62080	131364	190439	9561	30519	97152	206296	303317
SD	95	405	3086	22422	7756	796	627	3695	15679	12661	1697	1921	8084	14738	34365
PL	0.019	0.02	0.20	0.44	0.46	0.033	0.11	0.33	0.70	1.020	0.051	0.32	0.99	2.19	3.44
PLT	0.0032	0.0030	0.0042	0.0061	0.0048	0.0055	0.0044	0.0069	0.0098	0.011	0.0085	0.013	0.021	0.031	0.036
BDE-100	1787	5870	15966	36990	45996	3058	8689	26548	589025	91057	4698	13391	41224	91674	143907
SD	48	147	2367	8001	5289	130	351	-37	4973	6888	747	609	4279	5225	11577
PL	0.043	0.14	0.38	0.88	1.10	0.073	0.21	0.64	1.41	2.18	0.11	0.32	0.9	2.19	3.44
PLT	0.0071	0.0059	0.0080	0.012	0.012	0.012	0.0087	0.013	0.020	0.023	0.019	0.0133	0.021	0.03	0.036
BDE-153	209	702	2077	4695	4889	353	1060	3479	7510	10836	548	1652	5517	12092	17526
SD	8	26	167	965	462	38	58	331	727	926	114	84	423	30	1037
PL	0.0097	0.033	0.096	0.22	0.23	0.016	0.049	0.16	0.35	0.50	0.025	0.077	0.26	0.56	0.81
PLT	0.0016	0.0014	0.0020	0.0030	0.0024	0.0027	0.0020	0.0034	0.0048	0.0052	0.0042	0.0032	0.0053	0.0078	0.0085
BDE-154	35	90	251	670	716	72	145	434	1084	1590	113	230	686	1723	2579
SD	2	2	7	150	38	13	6	38	119	61	15	17	51	180	219
PL	0.0024	0.0062	0.018	0.047	0.050	0.0050	0.010	0.030	0.075	0.11	0.0078	0.016	0.048	0.12	0.18
PLT	0.0004	0.0003	0.0004	0.0006	0.0005	0.0008	0.0004	0.0006	0.0010	0.0011	0.0013	0.0007	0.0010	0.0017	0.0019
EH-TBB	287	946	2467	4151	6187	353	1139	3550	7527	10918	563	1848	5895	12603	18105
SD	26	29	116	900	489	68	70	387	966	412	34	121	369	1189	2113
PL	0.0064	0.01	0.055	0.092	0.14	0.0078	0.025	0.079	0.17	0.24	0.013	0.041	0.13	0.28	0.40
PLT	0.0011	0.0009	0.0011	0.0013	0.0014	0.0013	0.0011	0.0016	0.0023	0.0025	0.0021	0.0017	0.0027	0.0039	0.0042
BEH-TEBP	785	2785	8988	19207	26562	1008	3248	10136	21504	31192	1569	5082	15961	34232	51870
SD	42	33	656	4410	1718	213	151	782	3063	889	172	340	1579	2953	6621
PL	0.0038	0.014	0.044	0.094	0.13	0.0049	0.016	0.050	0.10	0.15	0.0077	0.0248	0.078	0.17	0.25
PLT	0.0006	0.0006	0.0009	0.0013	0.0013	0.0008	0.0007	0.0010	0.0015	0.0016	0.0013	0.0010	0.0016	0.0023	0.0026
TPhP	1624	3371	7806	17525	19516	3836	7167	15990	31103	42123	5997	11251	25867	51252	69637
SD	92	76	579	3484	2129	676	337	2225	5352	3643	1509	1012	2264	1371	7387
PL	0.012	0.024	0.056	0.12	0.14	0.027	0.051	0.11	0.22	0.30	0.043	0.080	0.18	0.37	0.50
PLT	0.0019	0.0010	0.0012	0.0017	0.0014	0.0046	0.0021	0.0024	0.0031	0.0031	0.0071	0.0033	0.0038	0.0051	0.0052
TCIPP	15291	39884	52761	82723	102531	122181	98853	32363	18988	6639	188727	147088	77273	42223	18511
SD	794	1710	1457	1256	2424	9891	1429	2057	1683	664	9348	7443	1797	108	2134
PL	0.045	0.12	0.15	0.24	0.30	0.36	0.29	0.095	0.056	0.019	0.5518	0.4301	0.2259	0.1235	0.0541
PLT	0.0075	0.0049	0.0032	0.0034	0.0031	0.060	0.0120	0.0020	0.0008	0.0002	0.0920	0.0179	0.0047	0.0017	0.0006

c. The pH (5.8, 8.5) effects and waste: leachate ratio concentration of Time effect at 60˚C

Effect	pH 5.8					pH 8.5					10% waste mass				
Time (*h*)	6	24	48	72	96	6	24	48	72	96	6	24	48	72	96
BDE-47	681	3222	17732	43529	94490	3591	12762	48977	110114	176160	283	1150	3174	6962	9053
SD	29	207	915	6946	12666	467	714	4213	9844	16274	21	113	261	575	1135
PL	0.0042	0.020	0.11	0.27	0.58	0.022	0.079	0.30	0.68	1.087	0.0017	0.0071	0.020	0.043	0.056
PLT	0.0007	0.0008	0.0023	0.0037	0.0061	0.0037	0.0033	0.0063	0.0094	0.0113	0.0003	0.0003	0.0004	0.0006	0.0006
BDE-99	485	1738	10181	24548	55652	6019	19370	65608	141837	225686	555	1577	5876	10544	21082
SD	14	87	416	4698	8769	768	1106	5919	8349	19033	96	85	553	135	1336
PL	0.0026	0.0093	0.055	0.13	0.30	0.032	0.10	0.35	0.76	1.21	0.0030	0.0084	0.032	0.056	0.11
PLT	0.0004	0.0004	0.0011	0.0018	0.0031	0.0054	0.0043	0.0073	0.0105	0.0126	0.0005	0.0004	0.0007	0.0008	0.0012
BDE-100	174	627	3095	7634	21081	2904	8382	26795	60224	102381	264	985	2337	5930	9561
SD	12	90	176	989	1300	357	455	1133	6567	8204	42	93	145	14	1034
PL	0.0042	0.015	0.074	0.18	0.50	0.070	0.20	0.64	1.44	2.45	0.0063	0.024	0.056	0.14	0.23
PLT	0.0007	0.0006	0.0015	0.0025	0.0053	0.0116	0.0084	0.0134	0.0200	0.0255	0.0011	0.0010	0.0012	0.0020	0.0024
BDE-153	37	138	844	2655	4711	343	1051	3754	8747	14386	32	131	318	701	1189
SD	5	22	46	428	322	40	57	379	525	574	6	9	25	29	103
PL	0.0017	0.0064	0.039	0.12	0.22	0.016	0.049	0.17	0.41	0.67	0.0015	0.0061	0.015	0.03	0.055
PLT	0.0003	0.0003	0.0008	0.0017	0.0023	0.0027	0.0020	0.0036	0.0056	0.0069	0.0002	0.0003	0.0003	0.0005	0.0006
BDE-154	9	26	94	275	742	71	149	459	1179	2161	6	12	40	83	151
SD	2	11	8	53	69	13	8	39	203	146	1	1	6	8	22
PL	0.0007	0.0019	0.0066	0.019	0.052	0.0050	0.010	0.032	0.082	0.15	0.0005	0.0008	0.0028	0.0058	0.011
PLT	0.0001	0.0001	0.0001	0.0003	0.0005	0.0008	0.0004	0.0007	0.0011	0.0016	0.0001	0.0000	0.0001	0.0001	0.0001
EH-TBB	95	445	2338	5713	8353	388	1358	4966	11114	18101	30	101	386	633	1277
SD	5	15	150	818	497	61	60	163	1673	1087	6	8	45	42	116
PL	0.0021	0.0099	0.052	0.13	0.18	0.0086	0.030	0.11	0.25	0.40	0.0007	0.0023	0.0086	0.014	0.028
PLT	0.0004	0.0004	0.0011	0.0018	0.0019	0.0014	0.0013	0.0023	0.0034	0.0042	0.0001	0.0001	0.0002	0.0002	0.0003
TBPH	128	517	2082	6187	25474	1028	3417	11132	25387	53324	89	269	958	2031	3668
SD	5	26	131	1367	1511	161	159	1478	3342	3704	6	23	98	195	371
PL	0.0006	0.0025	0.010	0.030	0.12	0.0050	0.017	0.054	0.12	0.26	0.0004	0.0013	0.0047	0.0099	0.0179
PLT	0.0001	0.0001	0.0002	0.0004	0.0013	0.0008	0.0007	0.0011	0.0017	0.0027	0.0001	0.0001	0.0001	0.0001	0.0002
TPhP	598	1274	7004	20728	30181	4022	7666	21276	48496	67789	329	574	1516	2893	4963
SD	37	24	311	4232	1684	542	393	2898	5347	3281	34	50	154	90	597
PL	0.0043	0.0091	0.050	0.15	0.22	0.029	0.055	0.15	0.35	0.48	0.0023	0.0041	0.011	0.020	0.035
PLT	0.0007	0.0004	0.0010	0.0021	0.0022	0.0048	0.0023	0.0032	0.0048	0.0050	0.0004	0.0002	0.0002	0.0003	0.0004
TCIPP	109091	78392	45455	39461	18382	353325	242857	185847	112770	18611	10582	13303	5140	4065	1924
SD	13094	3077	6447	2857	1118	1359	2490	1361	1768	1091	821	1188	569	136	212
PL	0.32	0.32	0.13	0.12	0.054	1.03	0.71	0.54	0.33	0.054	0.031	0.039	0.015	0.012	0.0056
PLT	0.053	0.013	0.0028	0.0016	0.0006	0.17	0.030	0.011	0.0046	0.0006	0.0052	0.0016	0.0003	0.0002	0.0001