OBAFEMI AWOLOWO UNIVERSITY

INVESTIGATION OF POLYBROMINATED FLAME RETARDANTS AND POTENTIALLY TOXIC METALS IN SOIL, SEDIMENT AND WATER OF THE OBAFEMI AWOLOWO UNIVERSITY DUMPSITE AND ITS RECEIVING STREAM.

BY

GODWIN OLADELE OLUTONA
SCP11/12/R/0099
B.Sc. (Ed.) (Chemistry), Abuja; M.Sc. (Chemistry), Port-Harcourt; M.Phil. (Chemistry), Ife.

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY (Ph.D.) IN CHEMISTRY TO THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, OBAFEMI AWOLOWO UNIVERSITY ILE-IFE, NIGERIA.

2015

CERTIFICATION

This research work by Godwin Oladele Olutona was carried out under our supervision in partial fulfillment of the requirements for the award of Ph.D. Degree in Chemistry of the Obafemi Awolowo University, Ile-Ife, Nigeria.

____

Prof. A .O. Ogunfowokan

(Supervisor)

____

Dr. J. A. O. Oyekunle

(Co-Supervisor)

____

Prof. A. O. Ogunfowokan

Head of Department

DEDICATION

This research work is dedicated to my biological father, **Mr. Stephen Omotayo Oguntona,** who has always encouraged me to pursue education to the peak. To **MANY** that is **UNKNOWN** in the academic profession but are **PRECIOUS GEMS!** To those who have **STRUGGLED** and **SUFFERED** in this noble **PROFESSION**. I salute your courage with deep dedication.

ACKNOWLEDGEMENTS

The eternal source of all knowledge and wisdom; honour, majesty and adoration be to your Holy name for giving me the strength to accomplish the present feat in spite of all obstacles. *"For you, O God, tested me; you refined me like silver. You brought me into prison and laid burdens on my backs. You let men ride over my head, I went through fire and water but you brought me to a place of abundance" Psalms 66; 10-12 (NIV).* Hallowed be to your holy name.

Many people deserve special thanks for their contributions to this thesis. First of all, my sincerest gratitude and deepest respect are expressed to my Supervisor and Head of Department of Chemistry, Prof. A. O. Ogunfowokan and Co-Supervisor, Dr. J. A. O. Oyekunle, for all their help, supervision, dedication, invaluable comments, encouragement and patience in reading the thesis and throughout the course of this study. I feel extremely fortunate to have had an opportunity to work with such dedicated individuals. I also acknowledge the opportunity given to me by Prof. O. S. Fatoki of Cape Peninsula University of Technology, South Africa, to use his laboratory as a visiting doctoral candidate. Prof. D. J. Oyedele provided me the auger used throughout the sampling periods. I really appreciate your kindness sir.

To the Head of Department Chemistry and Industrial Chemistry, Bowen University, Associate Prof. (Mrs) M. O. Dawodu, Prof. J. A. Faniran, Prof. E. O. Odebunmi and Prof. C. O. Fakunle, I wish to say a big thank you for the motherly and fatherly roles played during the course of this study. The contributions of Eng. Remi Oluokun, Dr O .E. Atobatele, Dr. E. O. Akindele, Dr. O. S. Ayanda, Dr. Dayo Adeyi, Dr. Joshua Obisanya, Dr. S. O. Olatunji and Mr. A. R. Alashe towards the success of this work are highly appreciated.

To all my teachers who have taught me since childhood, I say thank you for being a part of what I am today and what I will be in future. To my academic colleagues and the technologists in the Department of Chemistry and Industrial Chemistry, Bowen University, your moral support is highly appreciated.

To those who walked beside me and lent me their time on the course of this study, I say thank you. I am very grateful to the Chaplain, Bowen University Rev. Kunle Popoola, Mr. E. A. Akintunde, Mr Femi Oduola, Mr. Gbenga Oke, Mr. A. A. Olanrewaju, Mr Taiwo Ogunwale and Mr Lekan Akindolani my fellow adventurers who tirelessly gave me their time and assisted me in one way or the other in the course of this study.

To my senior and colleagues in the ministry such as Pastors E.O. Adeoje, Moradeyo, Akinwumi, Lucky, Ali, Noah Morakinyo, James Olanipekun, Rev. Ben Adesina and Rev. Dr. Bayo Ademuyiwa, I say thank you all for your spiritual support. I also appreciate my biological father, siblings (Tunde, Folasade and Mojisola) and friend, Debola Odu-Onikosi, for their moral, financial and spiritual supports. To my wife (Kemi) and beloved daughters (Hephzibah and Emerald), thank you for your unquantifiable endurance following my long absence from home.

Godwin Oladele OLUTONA

2015

TABLE OF CONTENTS

TITLE
PAGE

Title page		i
Certification		ii
Dedication		iii
Acknowledgment		iv
Table of Contents		vi
List of Figures		x
List of Tables		xiii
Abbreviations and Symbols		xv
Abstract		xvii
CHAPTER ONE		
1.0	Introduction	1
1.1	Background to the Study	1
1.2	Scope of the Study	6
1.3	Justification for the Study	6
1.4	Aim and Objectives of the Study	7
1.5	Expected Contribution to Knowledge	7
CHAPTER TWO		
2.0	Literature Review	8
2.1	Environmental Pollution	8
2.2	Flame Retardants	9
2.3	Bromine	9
2.4	Brominated Flame Retardants	10
	2.4.1 Tetrabromobisphenol A (TBBPA)	11

2.4.2 Hexabromocyclododecane (HBCD) 12

2.4.3 Polybrominated Biphenyls (PBBs) 12

2.4.4 Polybrominated Diphenyl Ethers (PBDEs) 13

2.5 Chemistry and Characteristics of PBDEs 14

2.5.1 Global Production and Usage of PBDEs 16

2.6 Sources of Polybrominated Diphenyl Ethers in the Environment 25

2.7 Degradation of Brominated Flame Retardants 26

2.7.1 Chemical Degradation 27

2.7.2 Photochemical Degradation 27

2.7.2.1 Photochemical Degradation of PBDEs 27

2.7.3 Thermal Degradation 28

2.7.4 Biological Degradation 29

2.7.4.1 Biological Degradation of PBDEs 30

2.8 Environmental Occurrence of PBDEs 32

2.8.1 Abiotic Exposure 32

2.8.1.1 PBDEs in Air/Dust 32

2.8.1.2 Occurrence in Sediment 35

2.8.2 Biota Exposure 36

2.8.2.1 Human Exposure to PBDEs 37

2.8.2.2 Dietary Exposure to PBDEs 38

2.8.2.3 Levels of PBDEs in Fish and Shellfish 42

2.8.2.4 Levels of PBDEs in Meat Products and Eggs 42

2.8.2.5 Levels of PBDEs in Vegetables and Fruit 43

2.8.3 Occupational Exposure 44

2.9 Toxicology of PBDEs 45

2.10 Methods of Solid Waste Management 47

2.10.1 Landfilling 47

2.10.2 Recycling of Organic Waste 48

2.10.3 Aerobic Composting 48

2.10.4 Vermicomposting 49

2.10.5 Anaerobic Digestion (Biomethanation) 49

2.11 Thermal Treatment Techniques of MSW 50

2.11.1 Incineration 50

2.11.2 Gasification Technology 50

2.12 Soil 51

2.12.1 Heavy Metal 52

2.12.2 Heavy Metals in Soil 52

2.12.3 Heavy Metals in Bed Sediment 53

2.13 Potential Remediation Technologies for Potentially Toxic Metals and PBDEs 55

2.14 Previous Related Works on PBDEs in Africa 56

2.15 Previous Works on Heavy Metals in Dumpsite Soils and Aquatic Environment 64

2.16 Analytical Equipment 68

2.16.1 Inductive Couple Plasma-Optical Emission Spectrometry (ICP-OES) 68

2.16.1.1 ICP Operation and Characteristics 69

2.16.2 Gas Chromatography (GC) 74

2.16.2.1 Electron Capture Detector 76

2.16.2.2 Detection by Mass Spectrometry 77

2.17 Health Risk Assessment 77

CHAPTHER THREE

3.0 Materials and Methods 79

3.1 Determination of some Physicochemical Parametersin Water Samples 79

3.1.1 pH Determination 79

3.1.2 Electrical Conductivity (EC) and Temperature 79

3.2 Sterilization of Apparatus Purification 79

3.3 Choice of Target Analytes for PBDE Analysis 79

3.4 Description of the Study Area 80

3.5 Sample Collection, Handling and Preservation 85

3.6 Extraction of Water Sample for PBDE Analysis 86

3.7 Extract Clean -up Procedure for Water Samples 86

3.8 Extraction of Soil and Sediment Samples for PBDE Analysis 87

3.9 Extract Clean-up Technique for Soil and Sediment 87

3.10 Digestion of Soil and Sediment for Metal Analysis 87

3.11 Instrumental Analysis of Potentially Toxic Metals 88

3.12 Instrumental Determination of Brominated Flame Retardants 89

3.12.1 Optimization of GC Parameters 90

3.12.1.1 Injector Temperature 89

3.12.1.2 Instrumental Analyses 91

3.13 Quality Control and Quality Assurance 95

3.14 Linearity, Precision, Accuracy and Recoveries of Spiked Standards 95

3.14.1 Recovery Analysis of PBDEs in Water Samples 96

3.14.2 Recovery Analysis of PBDE in Soil and Sediment Samples 96

3.14.3 Recovery of Surrogate Standards 97

3.15 Calculations 99

3.16 Contamination Assessments of Dumpsite Soil and Sediment 99

3.16.1 Enrichment Factor (EF) 99

3.16.2 Determination of Geo-accumulation Index 98

3.16.3 Contamination Factor 101

3.16.4 Pollution Load Index 101

3.17 Health Risk Assessment for Potentially Toxic Metals 103

3.18 Statistical Analysis 104

CHAPTER FOUR

4.0 Results and Discussion 105

4.1 Selected Physicochemical Parameters of Asunle Stream 105

4.2 GC Chromatograms 106

4.2.1 Retention Time of the Targeted Compounds 111

4.2.2 Method Detection Limit (MDL) and Instrument detection Limit for PBDE 111

4.3 Environmental Levels of Target Compounds Investigated 114

4.3.1 PBDEs Occurrence in the Dumpsite Soil 114

4.3.2 Principal Component Analysis of PBDEs in the Dumpsite Soils 117

4.3.3 Seasonal Levels of PBDEs in the Dumpsite 117

4.3.4 Total Mean Levels of PBDEs in the Dumpsite Soil 120

4.3.5 Correlation Analysis of PBDEs in the Dumpsite 121

4.3.6 Vertical Migration of PBDEs in the Dumpsite Soil 124

4.4 Lateral Migration of PBDEs away from the Dumpsite to the Receiving Stream 126

4.4.1 Monthly Levels of PBDEs Lateral Migration of PBDEs away from the Dumpsite to the Receiving Stream 126

4.4.2 Vertico-Lateral Distribution of PBDEs from the Dumpsite to the Receiving Stream 128

4.4.3 Levels of PBDEs at Various Distances away from the Dumpsite 130

4.4.4 Seasonal Levels Lateral Distribution of PBDEs in Dumpsite Soil towards the Receiving Stream 130

4.4.5 Correlation Analysis of Lateral Distribution of PBDEs in the Dumpsite 133

4.5 Levels and Distribution of PBDEs in the Asunle Stream 133

4.5.1 Monthly Levels and Distribution of PBDEs in Stream Water Samples 135

4.5.2 Principal Component Analysis of PBDEs in Water Sample of Asunle Stream 136

4.5.3 Levels of PBDEs in Water Samples at Various Locations of Asunle Stream139

4.5.4 Seasonal Levels of PBDEs in Water Samples of Asunle Stream 140

4.5.5 Correlational Analysis of PBDEs in Water Samples of Asunle Stream 143

4.5.6 Comparison of PBDEs Levels in Water Samples with Various Countries Of the World 145

4.6 Levels and Distribution of PBDE Congeners in Bed Sediment of Asunle Stream 148

4.6.1 Monthly Levels of PBDEs in Bed Sediment 148

4.6.2 Levels of PBDEs in Bed Sediment of Asunle Stream at Various Locations 150

4.6.3 Seasonal variations of PBDE in Bed Sediment of Asunle stream 152

4.6.4 Principal Component Analysis of PBDEs in Bed Sediment of Asunle Stream 154

4.6.5 Correlational Analysis of PBDEs in Bed Sediment of Asunle Stream 154

4.6.6 Comparison of PBDE Levels in Sediment with Levels in other Countries 157

4.6.7 Potential Source of Target Compounds 158

4.7 Potentially Toxic Metals Analysis using ICP-OES 160

4.7.1 Validity of Analytical Method Adapted for Potentially Toxic Metal Analysis 160

4.7.2 Levels of Potentially Toxic Metals in the Soil Collected from the Dumpsite 162

4.7.3 Vertical Levels of Potentially Toxic Metals in the Dumpsite 171

4.7.4 Seasonal Levels of Potentially Toxic Metals in the Dumpsite Soil 174

4.7.5 Factor Analysis of Potentially Toxic Metals in the Dumpsite Soil 174

4.7.6 Geoaccumulation Index of Potentially Toxic Metals in the Dumpsite Soil 177

4.7.7 Enrichment Factor (EF) of Potentially Toxic Metals in the Dumpsite Soil 179

4.7.8 Contamination Factor or Index of Metals in the Dumpsite 181

4.7.9 Correlation Analysis of Metals in the Dumpsite Soil 183

4.8 Lateral Distribution and Levels of Potentially Toxic Metals in Soil toward the Receiving Stream 185

4.8.1 Seasonal Levels in Lateral Distribution of Potentially Toxic Metals Towards the Receiving Stream 191

4.8.2 PCA of Metals in Lateral Distribution of Metals towards the Receiving Stream 191

4.8.3 Geoaccumulation Index of Lateral Distribution of Potentially Toxic Metals 194

4.8.4 Enrichment Factor in Lateral Distribution of Potentially Toxic Metals Toward the Receiving Stream 194

4.8.5 Contamination Factor/Index of Lateral Distribution of Potentially Toxic Metals towards the Receiving Stream 197

4.8.6 Correlational Variation of Metals of the Lateral Sampling towards the Receiving Stream 200

4.9 Potentially Toxic Metals in Bed Sediment of Asunle Stream 202

4.9.1 Seasonal Levels of Potentially Toxic Metals in Bed Sediment of Asunle Stream 206

4.9.2 Principal Component Analysis of Potentially Toxic Metals in Bed Sediment of Asunle Stream 206

4.9.3 Geoaccumulation Index of Potentially Toxic Metals to Bed Sediment Of Asunle Stream 209

4.9.4 Enrichment Factor/Index of Potentially Toxic Metals to Bed Sediment Of Asunle Stream 209

4.9.5 Contamination Factor with Respect to Temporal Variation of Potentially Toxic Metals in Bed Sediments of Asunle Stream 212

4.9.6 Spatial Variation of Potentially Toxic Metals in Bed Sediment of

Asunle Stream 214

4.9.7 Contamination Factor of Potentially Toxic Metals with Respect to their Spatial Variation in Sediment of Asunle Stream 219

4.9.8 Pollution Load Index of the Bed Sediments 219

4.9.9 Correlation Analysis of Potentially Toxic Metals in Bed Sediment of Asunle Stream 222

4.10 Health Risk Assessment of Potentially Toxic Metals in the Dumpsite Soil 224

4.11 Health Risk Assessment of Potentially Toxic Metals in Bed Sediment of Asunle Stream 237

CHAPTER FIVE

5.0 Conclusion and Recommendations 248

5.1 Conclusion 248

5.2 Recommendations 249

REFERENCES 252

APPENDIX I Calibration Curves of PBDE standards 299

APPENDIX II Photograph Showing the Obafemi Awolowo University Dumpsite 302

LIST OF FIGURES

Figure	Title	Page
Fig 1.1:	Chemical Structure of Brominated Flame Retardants	3
Fig. 2.1:	Structure of Eight most Abundant PBDE Congeners	19
Fig. 2.2:	Consumption, Distribution of Bromine in the Final Products	21
Fig 2.3:	Debromination of Deca and Octa-BDE mixture by Anaerobic Bacteria *Sulfurospirillum multivorans* and *Dehalococcoides* species adapted from He *et al*., 2006	31
Fig. 2.4 :	PBDEs Debromination Pathway by Different Cultures	33

Fig. 2.5: Overview of Sources and Pathways of PBDEs 39

Fig. 2.6: Schematic Diagram of an ICP Torch (Source: Hou and Jones, 2000) 71

Fig. 2.7: Schematic Diagram of Three Types of Pneumatic Nebulizers (Source: Hou and Jones, 2000) 73

Fig. 3.1: Geological Map of Obafemi Awolowo University 82

Fig. 3.2: Map Showing the Sampling Locations 84

Fig. 3.3a &b: Specification and the Operating Condition of the GC-MS Employed 93-94

Fig. 4.1a&b: Chromatograms of PBDEs Congeners Mixed Standards (10&20 ng/ml) 108

Fig. 4.2 : Chromatograms Showing Elution of Target PBDE Congeners Standards 109

Fig. 4.3: PCA Component Plot for the Monthly Variation of BDE Collected from the Dumpsite 118

Fig. 4.4: Seasonal Variation of PBDEs in Dumpsite 119

Fig. 4.5: Annual Mean Concentrations of PBDEs in the Dumpsite 122

Fig. 4.6: Levels of PBDEs at Various Distances from the Dumpsite towards the Receiving Stream 131

Fig. 4.7: Seasonal Variation of the Lateral Distribution of PBDEs in the Dumpsite Soil 132

Fig. 4.8: PCA Analysis of PBDE Congeners in Water Samples of Asunle Stream 138

Fig. 4.9: Seasonal Variation in Levels of PBDE Congeners in Water Samples of Asunle Stream 142

Fig. 4.10: Seasonal Variation of PBDE Congeners in Bed Sediment of Asunle Stream 153

Fig. 4.11: PCA Analysis of PBDEs in Bed Sediment of Asunle Stream 155

Fig. 4.12 a&b: Seasonal Levels of Potentially Toxic Metals in the Dumpsite 175

Fig. 4.13: PCA of Potentially Toxic Metals in the Dumpsite Soil 176

Fig. 4.14: Principal Component Analysis of Lateral Distribution of Potentially Toxic Metals towards the Receiving Stream 193

Fig. 4.15: Seasonal Levels of Potentially Toxic Metals in Bed Sediment of Asunle Stream 207

Fig. 4.16: PCA of Potentially Toxic Metals in Bed Sediment of Asunle Stream 208

LIST OF TABLES

Page

Table 1.1: BFR volume Estimates in 2001 and 2003 in Metric Tonnes 6

Table 2.1 Physicochemical Properties of some PBDEs and PBBS Technical Formulations 15

Table 2.2: The Percentage Composition of PolyBrominated Diphenyl Ether (PBDE) Congeners in Technical Formulation (WHO, 1994) 20

Table 2.3: A Comparism of Annual Global Bromine Production in Tonnes 23

Table 2.4 Global Annual Production of Polymers in 2000 and their BFR Content 24

Table 2.5 Upper Bound Estimate of PBDEs Daily Intake for General Canadian Population 40

Table 2.6 PBDE Levels in Human Samples (ng/g lipid) from Different

Countries (Range in Parenthesis) 41
Table 3.1 Chemical Information of the Target Compounds (PBDEs Investigated) 82
Table 3.2 GC Operating Parameters Optimized for PBDE Analysis 90
Table 3.3 Percent Recoveries of Target Compounds for Different Matrices 98
Table 3.4 Classes of the Geoacculation Index 102
Table 4.1: Annual (mean±Sd) Values of Selected Physicochemical Parameters of Water Samples from Asunle Stream 107
Table 4.2: Target ions of Investigated PBDE Congeners Monitored with the GC-MS 112
Table 4.3: Method Detection Limit Values for Different Matrices Investigated 113
Table 4.4: Monthly Variation of Polybrominated Diphenyl Ethers in the Dumpsite Soil 116
Table 4.5: Correlation Analysis of PBDE of the Dumpsite 123
Table 4.6: Vertical Distribution of PBDE in the Dumpsite Soil 125
Table 4.7: Monthly Lateral Distribution of PBDEs in Soil Samples towards the Receiving Stream 127
Table 4.8: Variation by Depth of the Lateral Migration of PBDEs in Soil Samples 129
Table 4.9: Correlational Analysis of the Longitudinal Distribution of PBDEs in the Dumpsite 134
Table 4.10: Mean Concentrations of PBDEs in Water Sample Collected from Asunle Stream 137
Table 4.11: Mean Levels of PBDEs in Water Sample Collected from Asunle Stream at Different Locations 141
Table 4.12: Correlational Analysis of PBDEs in Water Samples of Asunle Stream 144
Table 4.13: Comparison of PBDE Levels in Water Samples with other Studies around the World 147
Table 4.14: Monthly Variation of PBDE in Bed Sediment of Asunle Stream 149
Table 4.15: Locational Variation in PBDEs in Bed Sediment of Asunle Stream 151
Table 4.16: Correlation Analysis of PBDE in Bed Sediment of Asunle Stream 156

Table 4.17: Comparison of PBDE Concentrations in the Sediment with other Studies across the World 159

Table 4.18: Validity of Analytical Procedure Employed in this Study 161

Table 4.19a&b: Monthly Levels of Potentially Toxic Metals in the Dumpsite soil 169-170

Table 4.20a&b: Depth Variation of Potentially Toxic Metals in the Dumpsite Soil 172-173

Table 4.21: Geoaccumulation Index of Potentially Toxic Metals in the Dumpsite 178

Table 4.22: Enrichment Factor of Potentially Toxic Metals in the Dumpsite Soil 180

Table 4.23: Contamination Factor/Index of Metals in the Dumpsite Soil 182

Table 4.24: Correlation Analysis of Potentially Toxic Metals in the Dumpsite 184

Table 4.25a&b: Monthly Variation of Potentially Toxic Metals in Longitudinal Sampling towards the Stream 189-190

Table 4.26: Seasonal Levels in Lateral Distribution of Potentially Toxic Metals 192

Table 4.27: Geo-accumulation Index of Lateral Distribution of Metals in the Dumpsite Soil 195

Table 4.28: Enrichment Factor of Lateral distribution of Potentially Toxic Metals towards Receiving Stream 196

Table 4.29a&b: Contamination Factor of Lateral Distribution of Potentially Toxic Metals towards the Receiving Stream 198-199

Table 4.30: Correlational Variation of Potentially Toxic Metals of the Longitudinal Sampling 201

Table 4.31: Monthly Levels of Potentially Toxic Metals in Bed Sediment of Asunle Stream 205

Table 4.32: Geoaccumulation Index of Metals in the Dumpsite Soils 210

Table 4.33: Enrichment Factor of Potentially Toxic Metals in Bed Sediment of

Asunle Stream 211

Table 4.34: Contaminant Factor of Potentially Toxic Metals in Bed Sediment of Asunle Stream 213

Table 4.35: Spatial Variation of Potentially Toxic Metals in Bed Sediment of Asunle Stream 218

Table 4.36: Contaminant Factor of Potentially Toxic Metals in Spatial Variation in Sediment of Asunle Stream 220

Table 4.37: Pollution Load Index of Potentially Toxic Metals across the Sampling Locations. 221

Table 4.38: Correlation Analysis of Metals in Bed sediment of Asunle Stream 223

Table 4.39: Chronic Daily Intake of Carcinogenic Risk (ingestion) for the Dumpsite Soil 230

Table 4.40: Cancer Risk for the Potentially Toxic Metals in the Dumpsite Soil 232

Table 4.41a&b: Chronic daily Intake (oral) for Non-Carcinogenic Risk for Children in the Dumpsite Soil 234

Table 4.42: Total Chronic Hazard Quotient Index ($x10^6$) of the Potentially Toxic Metals in the Dumpsite 236

Table 4.43: Chronic Daily Intake for Carcinogenic (oral) in Bed Sediment of Asunle Stream 241

Table 4.44: Cancer Risk Assessment of Potentially Toxic Metals in Bed Sediment of Asunle Stream 243

Table 4.45a&b: CDI for Non-Carcinogenic (oral) in Bed Sediment of Asunle Stream 245

Table 4.46: Total Chronic Hazard Quotient (x106) of the Potentially Toxic Metals in the Bed Sediment of Asunle Stream 247

ABBREVATIONS AND ACRONYMS

ACC	American Chemistry Council
ANOVA	Analysis of Variance
ATSDR	Agency for Toxic Substances and Disease Registry
BFR	Brominated Flame Retardant
BSEF	Bromine Science and Environment Forum
CDI	Chronic Daily Intake
CF	Contaminant Factor
DCM	Dichloromethane
EFSA	European Food and Safety Authority
GC	Gas Chromatography
EI^+	Electron impact ionization
IARC	International Agency for Research in Cancer
ICP-OES	Inductive Couple Plasma-Optical Emission Spectrometry
IPCS	International Programme on Chemical Safety
MRL	Minimal Risk Level
M/Z	Mass to Charge Ratio
OCP	Organochlorine Pesticides Residue
PBDEs	Polybrominated Diphenyl Ethers
PCA	Principal Component Analysis
RAIS	Risk Assessment Information System
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

ABSTRACT

ABSTRACT

This study investigated the occurrence and levels of polybrominated flame retardants and potentially toxic metals in soils, sediment and water of the Obafemi Awolowo University Dumpsite and its receiving stream. It also monitored the temporal, spatial and seasonal distribution of the analytes in the matrices and evaluated the health risk of the potentially toxic metals in soils and sediments of the study area. These were done with a view to evaluating the pollution status of the studied area with respect to polybrominated fire retardants and potentially toxic metals.

Sampling was done on seasonal basis comprising of May- August and November-February, respectively, for wet and dry seasons. Soil samples of the dumpsite and land space towards the stream were collected using an auger at 0-15 cm and 15-30 cm depths and 50 m away from each other. Water and sediment samples were collected from the receiving stream at six different points that included the upstream and downstream points. Extraction of polybrominated diphenyl ethers (PBDEs) from water, sediment and soil samples were done using liquid-liquid extraction and soxhlet extraction methods with dichloromethane as the extraction solvent. Clean-up of the extracted samples was done using multi-layer silica gel chromatography. The potentially toxic metals were analysed using Inductive Couple Plasma Optical Emission Spectrometry while Gas Chromatography Mass Spectrometry was employed for the quantification of the PBDEs.

The total mean values of PBDEs in the dumpsite soil ranged from 0.36 ± 0.34 ng/g BDE - 47 to 13.84 ± 28.18 ng/g BDE- 153. Total PBDEs indicated that concentrations in 0-15 cm layer were higher than those in the 15-30 cm layer. The concentration of Σ_6PBDEs in the stream

water ranged from 0.03 – 0.31 ng/ml while the values in the sediments ranged from 0.83 – 10.43 ng/g with BDE-153 occurring as the dominant congener in all the matrices analyzed. Seasonal variability of PBDEs in the matrices indicated that higher levels were found during the wet season in the dumpsite and the receiving stream. The mean values of potentially toxic metals in the dumpsite soil ranged between 3.12 mg/kg Ni and 15500 mg/kg Al. Geo-accumulation study indicated that the soil of the dumpsite and stream sediment were practically unpolluted with, Fe, Cr, Al and Si; strongly polluted with Zr; while the soil and sediment samples were polluted with respect to Se, As, Th, U and Y. Mean levels of the potentially toxic metals in the dumpsite were higher in wet season than dry season. The mean values (mg/kg) of potentially toxic metals in the sediment of Asunle stream ranged from 0.10 Sr to 7260 Fe. The health risk assessment of most of the potentially toxic metals in the dumpsite soil and sediments of Asunle stream revealed that their chronic daily intake for both carcinogenic and non-carcinogenic effects gave hazard quotient for exposure that exceeded the acceptable USEPA value of 1.0.

This study revealed that the environmental matrices of the area under investigation contained higher levels of PBDEs and potentially toxic metals than recommended by WHO and USEPA.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Advances in polymer science over the past 50 years have led to the introduction of a large number of polymers with different properties and applications. As a result, we are surrounded by a wide variety of polymers that have found applications in clothing, furniture, electronics, vehicles and computers. In fact modern cars contain in excess of 100 kg of various polymers. Most of these polymers are petroleum-based, and hence, are flammable.

Fire is a major cause of property damage, loss and even death throughout the history of mankind (Daso *et al*., 2013a). To circumvent these phenomenal losses as a result of fire accidents, a group of chemicals known as “flame retardants”have been incorporated into various polymer products to reduce the likelihood of ignition and burning in a wide range of textiles, plastics, building materials and electronic equipment used in commerce and residential homes (Alaee and Wenning, 2002). Brominated flame retardants (BFRs) are chemicals that are added to many consumer products including plastics, electronics, textiles, cushioning foams for furniture, automobile interiors and other materials to prevent fire (WHO/IPCS, 1994, 1997).

The idea of flame retardant materials dates back to about 450 BC, when the Egyptians used alum to reduce the flammability of wood. The Romans (about 200 BC) used a mixture of alum and vinegar to reduce the combustibility of wood (Hindersinn, 1990). Certain ammonium salts were also found to be effective for the protection of precious textiles in the early nineteenth century, a practice that continues today (Daso *et al.*, 2013a).

In the development of traditional building materials like wood and metal with plastics, the previously used inorganic salts could not be applied because they considerably reduce thermal stability (Vonderheide *et al*., 2008). The development of halogen-based organic flame retardants was a major advancement as they could be incorporated into plastic substance (Daso *et al*., 2011a). With the increasing usage of polymeric materials in construction, electronic and computer equipment, global market demand for the use BFRs continues to grow substantially. This scientific advancement has resulted in the production and use of several flame retardants broadly classified into three major groups, namely: brominated flame retardants (BFRs), phosphorous-based flame retardants and inorganic flame retardants (usually magnesium and aluminium hydroxides) (Minnesota Pollution Control Agency, 2008). Flame retardants could further be sub-divided into five major classes: brominated bisphenols, diphenyl ethers, cyclododecanes, phenols and phthalic acid derivatives (European Food Safety Authority, (EFSA, 2011). Among these three groups of chemicals, the halogenated organics and organophosphorous flame retardants are of great concern to the public due to their environmental persistence and toxicity (Daso *et al*., 2011a).

The halogenated organic flame retardants are generally classified as either chlorinated or brominated flame retardants. The brominated flame retardants (Fig 1.1) are extensively used due to their thermal stability, high bromine content and relatively low cost (Darnerud *et al*., 2001). The most used brominated flame retardants are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA) and polybrominated biphenyls (PBBs) (Odusanya *et al*., 2009). Depending on their mode of incorporation into the polymeric materials, two groups of BFRs exist, namely: reactive and additive BFRs. Reactive BFRs are those that are covalently bonded to the polymers, e.g, tetrabromobisphenol A and its derivatives. Additive BFRs, which include polybrominated biphenyls (PBBs), poly brominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), are not covalently bonded to the polymeric materials. However, they are more likely to diffuse out of the treated polymer during their lifetime (de Wit, 2002).

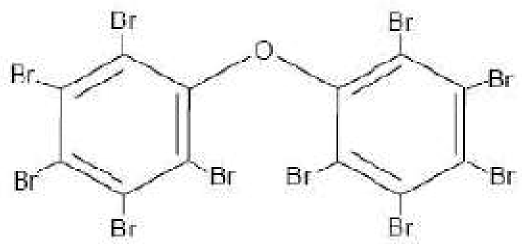

Fig. 1.1: Chemical Structure of Brominated Diphenyl Ethers used in Flame Retardants