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Determination of Flame Retardants and Poly- and Perfluoroalkyl Substances in Indoor Dust in Greater Cairo: Assessment of Human Exposure.

A thesis submitted in partial fulfillment of the requirements for the degree
of Master of Science in Chemistry

By

Yasmeen Hisham Hassan

Supervised by

Dr. Tamer Shoeib

May, 2015

Acknowledgments

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I would like to take the opportunity and thank the American University in Cairo for rewarding me the grant that made this all possible.

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Finally, this thesis is dedicated to my parents, my grandmother, family and friends who have always been of great support and inspiration through every step I take.

List of Publications

1. Hassan Y., Shoeib T.* Levels of polybrominated diphenyl ethers and novel flame retardants in microenvironment dust from Egypt: An assessment of human exposure. *Science of the Total Environment* 505 (2015) 47–55.

2. Shoeib T.*, Hassan Y., Rauert C. and Harner T. Poly- and perfluoroalkyl substances (PFASs) in indoor dust and food packaging materials in Egypt: Trends in developed and developing countries, *manuscript in preparation*.

Abstract

This thesis dissertation examines the presence and exposure of two classes of compounds; polybrominated diphenyl ethers (PBDEs) and polyfluorinated compounds (PFCs). Both classes are considered persistent organic pollutants as they are toxic, bio-accumulative and have a high susceptibility to be environmentally dispersed. The PBDEs are typically used as protective agents on household appliances and furniture to retard the startup of fires; PFCs on the other hand are used as oil and water repellants. Few studies have investigated the presence of polybrominated diphnely ethers (PBDEs), novel flame retardants (FRs / non-PBDEs) and poly- and perfluoroalkyl compounds in Africa and the Middle East. These compounds have become ubiquitous, not only found in humans but also in animals and wildlife. Researches have shown that these toxic compounds can cause cancer, affect neurodevelopment, growth and other possible health risk. The main aim of this thesis was to investigate the levels of these contaminants and assess their associated human health risk.

The levels of fourteen PBDE congeners and eleven non-PBDE flame retardants were investigated in 17 homes, 9 workplaces and 5 cars in the greater Cairo region. GC-MS was used for both the separation and quantification of the target analytes. Several parameters were calculated including the mean, median, minimum, maximum and four different percentiles. The median ΣPBDE concentrations were 57, 425 and 1608 ng g^{-1} in homes, workplaces and cars respectively. It was observed that congener 209 was dominant in all samples in the three different microenvironments with a median concentration of 40.2, 366 and 1,540 ng g^{-1} in homes, workplaces and cars respectively representing 70 to 95% of the total PBDEs. Several novel PBDEs were investigated including hexabromocyclododecane (HBCD), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis (2-ethyl-1-hexyl) tetrabromophthalate (TBPH), 1,2-bis (2,4,6-tribromophenoxy) ethane (TBPE), ally-2,4,6-tribromophenyl ether (ATE) and Dechlorane Plus (DP). The Σnon-PBDEs median concentrations were 8.30, 28.9 and 49.9 ng g^{-1} in homes, workplaces and cars respectively with HBCD predominating. Four groups of analytes were investigated in the PFCs including: fluorotelomer acrylates (FTA), fluorotelomer alcohols (FTOH), Methyl/Ethyl perfluorooctane sulfonamides (Me/Et FOSA), Methyl/Ethyl perfluorooctane sulfonamidoethanols (Me/Et FOSE). Concentration of the PFASs ranged from 1.3 to 69 ng g^{-1} with FTOHs being the dominant. The highest FTOH was 8:2 FTOH detected in all samples in the three microenvironments. Results show that levels of PBDEs, non-PBDEs and PFCs in the Egyptian dust were among the lowest worldwide. Different dust exposure scenarios using 5th percentile, median, 95th percentile and maximum levels were estimated for adult and children. The estimated dust intake results were several orders of magnitude lower than the oral reference dose values.

Motivation

The safety of human beings and the environment has been always a priority. Research has continuously revolved around the possible exposure to certain compounds and their consequent health risk. Dust is a non-escape pollutant that does not only exist outdoors but in the indoor environment as well. Several exposure pathways have been studied and dust has shown to be an important exposure route especially for toddlers that spend most of their times indoor, in addition to their significant floor to mouth action.

Technology and chemical production has increased recently and so did their toxicity to human. Several countries around the world especially industrial countries have had intensive research programs focused on the presence and the effects of these chemicals, which led to their regulation, restriction whether in production or in use as indicated above.

The main aim of this work was to determine the levels of these compounds in the Egyptian environment and to what extent they may show an adverse health effect. More specifically, we aim to:

1. Determine the levels of several classes of brominated flame retardants (BFRs) mainly, polybrominated diphenyl ethers (PBDEs) and their recent replacement which are used in electronics and TVs.
2. Determine the levels of several per-fluorinated and poly-fluorinated compounds (PFCs) used as water and oil repellant in many household items as non-stick cookware, anti-stain fabric and water and oil repellent coating textile.
3. To compare the levels of these target contaminants in Egypt to their levels in other geographical locations around the world.
4. To estimate the human exposure for adults and children to these contaminates in Egypt.

This is the first study to attempt to quantify these compounds in Egypt which provided us with the enthusiasm and motivation. This thesis comprises two results chapters: one focusing on PBDEs and another focusing on neutral PFCs. In the PBDE chapter, an overview of PBDEs and their different congeners along with an introduction to novel FRs is provided. This is followed by a description of the methodology used and the results obtained with a comparison with other published work from different geographic locations. The neutral PFCs chapter discussed the uses of these compounds, the differences between methodologies used for PFCs and PBDEs determination followed by the results obtained and a comparison with other studies.

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Abbreviations and Acronyms

10:2	10 carbons, 2 functional groups
102E (octa)	Octa trade name
^{13}C	Natural, stable isotope of carbon
6:2	6 carbons, 2 functional groups
8:2	8 carbons, 2 functional groups
Anti-stereoisomers	Groups added on different faces of the molecule
BC	Before Christ
BDE	Brominated diphenyl ether (used for congeners)
BFR	Brominated Flame Retardant
C8	Carbon 8
C_C	Contaminant concentration at cars
C_{dust}	Concentration of total contaminant
C-F bond	Carbon-Flourine bond
C_H	Contaminant concentration at homes
C-H	Carbon-Hydrogen bond
Congener	Compounds related by structure, function or origin
C_W	Contaminant concentration at workplaces
DB wax column	GC column
DB-5MS	Column used for GC-MS
DCM	Dichloromethane
DE	Diphenyl Ether
DE-60F (penta)	Penta trade name
DE-83R	Deca mixtures trade name
DL	Detection Limit
E_{Ingest}	Dust Ingestion Rate
EU	European Union
F_C	Average fraction of time spent in cars
F_H	Average fraction of time spent in homes
Firemaster 550	Flame retardant mixture
FR	Flame Retardant
FTOH	Fluorotelomer alcohol
F_W	Average fraction of time spent in workplaces
GC-MS	Gas chromatography-mass spectrometry
GC-NCIMS	Gas chromatography-negative chemical ionization mass spectrometry

GC-PCIMS	Gas chromatography-positive chemical ionization mass spectrometry
HBCD	Hexabromocyclododecane
IDL	Instrumental Detection Limit
Inc.	Incorporation
InjS	Injecting Standard
I_R	Ingestion Rate
IS	Internal Standard
LOD	Limit of detection
LOQ	Limit of quantification
m/z	Mass/charge
Ma, U.S.A.	Massachusetts, United States of America
MDL	Method Detection Limit
MeOH	Methyl Hydroxide
Non-PBDE	Non-Polybrominated diphenyl ethers
OSPAR	Oslo/Paris convention (for the Protection of the Marine Environment of the North-East Atlantic)
PBDEs	Polybrominated diphenyl ethers
PBT	Persistent, bio-accumulative, toxic
PFASs	A collective term for all per- and polyfluoroalkylated substances
PFCs	Per- and polyfluorinated compounds
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
POPs	Persistent Organic Pollutants
PVC	Polyvinyl chloride
QA	Quality Assurance
QC	Quality Control
Q_{dust}	Dust ingested rate
RfD	Reference dose
SD	Standard Deviation
SIM	Selective Ion Monitoring
Syn-stereoisomers	Groups added on the same face of the molecule
T3	Triiodothyronine
T4	Thyroxine
TBBPA	Tetrabromobisphenol A
TVs	Televisions
UK	United Kingdom

U.S.A.	United States of America (US for short)
US-EPA	United States – Environment Protection Agency
α	Alpha
β	Beta
γ	Gamma

Units of Measurement

$	Dollar
%	Percentage
˚C	Degrees Celsius
µL	microliter
µm	micrometer
cm	centimeter
g	gram
g/day	gram/day
kJ/mol	kilojoules/mol
m	meter
mg	milligram
mg/day	milligram/day
mg/h	milligram/hour
ml	milliliter
mm	millimeter
ng	nanogram
ng/day	nanogram/day
ng g^{-1}	nanogram/gram

pg	picogram
ppm	Parts per million
rpm	Rotation per minute
Σ	Sum
v/v	volume/volume
mg $(kgbw)^{-1}$ day^{-1}	milligram per kilogram of body weight per day
ng kg^{-1} day^{-1}	nanogram/kilogram/day
ng $(kgbw)^{-1}$ day^{-1}	nanogram per kilogram of body weight per day

Chapter 1: Introduction and Methodology

1.1 Environmental Science

The world is becoming more crowded everyday with more resources being used. The growing population is demanding a higher standard of living, which is adding more pressure on our environment. The increased industrialization has affected nature directly or indirectly leading to several unexpected consequences which have captured the attention of scientists. Relationships between compounds, their interactions with organisms and the environment are now a major concern.

Industrial chemicals like polybrominated diphenyl ethers (PBDEs) used as flame retardants to delay the ignition of fire [1], per-fluorinated and poly-fluorinated compounds (PFCs) used as water and oil repellant [4] have all been in strong demand in many applications for decades. Recently, these compounds have been clearly found to seriously affect the environment and human health. The majority of these compounds are known to be persistent in the environment, bio-accumulate in the food chain, toxic to human and wildlife, and possess long half-lives. Consequently, this led to these compounds being listed as persistent organic pollutants (POPs) by the Stockholm Convention; an international environmental treaty that aims to eliminate or restrict the production and use of POPs. Some compounds were phased out in the early 2000s while others are still manufactured until further restrictions are set. Alternative chemicals are being introduced to the market replacing the phased out compounds, such as a class of compounds called novel flame retardants which are to replace PBDEs [3-6].

Both classes of chemicals, FRs and PFCs, have been incorporated in a wide variety of consumer products and are released to the environment by abrasion, volatilization and when disposed at landfills at the end of their life cycle [7]. Repellant and flame retardant materials have been found to degrade from the items they initially were used to treat and get released to the environment. Human exposure has also been documented for these compounds and many health effects have been reported [8, 9]. These include positive correlations between PFCs levels and sperm quality, reduced birth weight and changes in adult thyroid hormone levels. Since the compounds are also reported to cross the placenta and are found in breast milk; exposures to these chemicals in infants and developing fetuses are of particular importance for brain development [10]. Recently, positive statistically associations between increasing PBDE concentrations in colostrum and a worse infant mental development were reported [11].

Exposure of dust in indoor environment takes place through several pathways such as inhalation, dust ingestion or skin absorption, yet the fate and effect of these pathways on humans and the environment remains unclear to date [12, 13].

1.2 Dust Collection, Extraction and Analysis

1.2.1 Dust collection and sampling criteria

The target sample collection locations were from three microenvironments; homes, workplaces and cars. Dust samples were collected during December 2013 from different places across the greater Cairo region and Giza by using a normal vacuum cleaner. A new vacuum bag was used every time during sample collection. The vacuum cleaner bag was emptied in a clean aluminum foil and then further sieved and sealed in a polyethylene bag and finally stored at 4 ˚C.

Home samples were collected from homes in different areas across Cairo and Giza. They were not only located on main roads but also side streets. The sampling from homes were conducted in bedrooms and living rooms, considering the high fraction time spent in both. The samples were collected from carpets or from floors in case the absence of carpets.

Car details were noted including the model and the manufacture year. Samples ranged from the year 1999 to 2012. Car models included Japanese cars like Honda and Toyota, American like Chevrolet, Chinese like Speranza and German like Volkswagen. The variety was important to examine if different origins would result in different levels of the target compounds; PBDEs/ non-PBDEs and neutral PFCs. Dust was collected from the chairs, roofs and dashboards but not from floors as it usually contains dirt and other particles obtained from the car exterior.

Work samples involved just offices in different locations with normal computer workstations. Samples were collected from carpets if found, otherwise from the floor. A detailed map presenting the home and work sample collection locations is presented in the Appendix.

1.2.2 Dust extraction and analysis

A general schematic figure for both the PBDEs and PFCs process analysis is shown below in Figure 1.1.

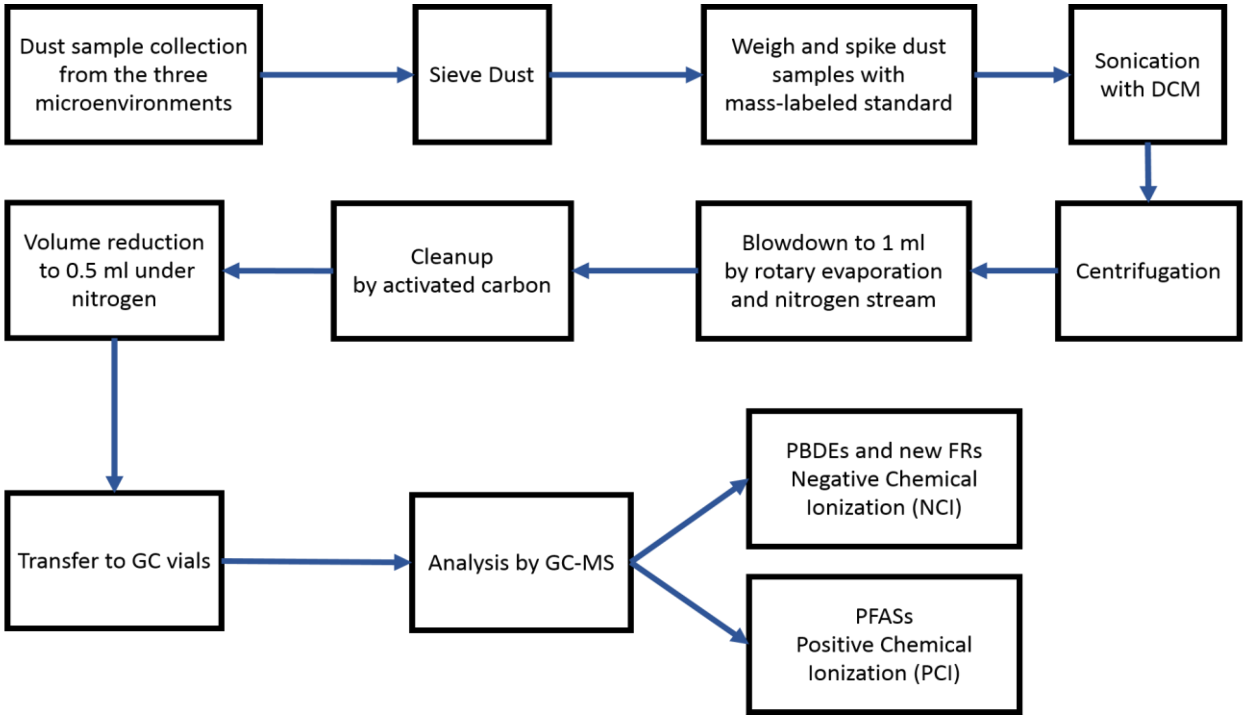


Figure 1.1: Schematic of dust analysis process.

The obtained dust passed through a sieve of 250 µm (USA Standard Testing Sieve). Sieved samples were weighed accurately to about 0.2 g and kept in polypropylene tubes with screw-caps wrapped in wax paraffin sheets as shown in Figure 1.2.

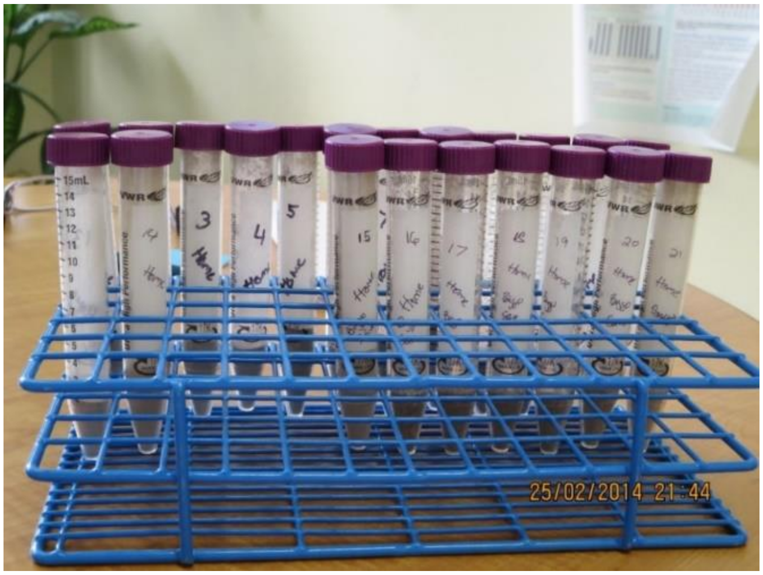


Figure 1.2: Sieved dust samples from the three microenvironments; homes, workplaces and cars.

Glassware used was baked beforehand at 350 ˚C for about an hour to maintain sterility and avoid any possible cross-contamination. Figure 1.3 shows the setup of the extraction equipment. Each sample was spiked with 100 µL of mass-labeled PFC standard as it does not interfere with the PBDE ions, yet provides the opportunity to analyze both the PBDEs and PFCs. In addition to that, this approach saved both time and sample as the sample collected was limited.

Complete adsorption of the Internal recovery Standard solution (IS) with the mass labeled PFCs (^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, d_3N-MeFOSA, d_7 N-MeFOSE, d_5 N-EtFOSA, d_9 N-EtFOSE) into the sample is essential; a step performed by using a vortex mixer for 1 minute and then the sample left to settle for 30 minutes. This method is known as 'Standard Addition Method', adding the labeled IS directly to every sample. This is a high-cost method but is best for the identification and quantification of analytes in a complex matrix, in our case dust as indicated below [14].

For extraction, 10 ml dichloromethane (DCM) were added to each sample then sonicated for 30 minutes using a water bath as shown on the right side of Figure 1.3, and then vortexed again to re-suspend the dust particles (homogenization). Vortexing and sonication are usually coupled together to obtain the best extraction results.

DCM or commonly known as methylene chloride, is the organic non-polar solvent (compared to other solvents like MeOH) of choice for most of the soil or dust extraction process [10]. The solvent is highly volatile with low boiling point. Despite being immiscible with water, it can dissolve a wide range of organic compounds which makes it a good solvent choice.

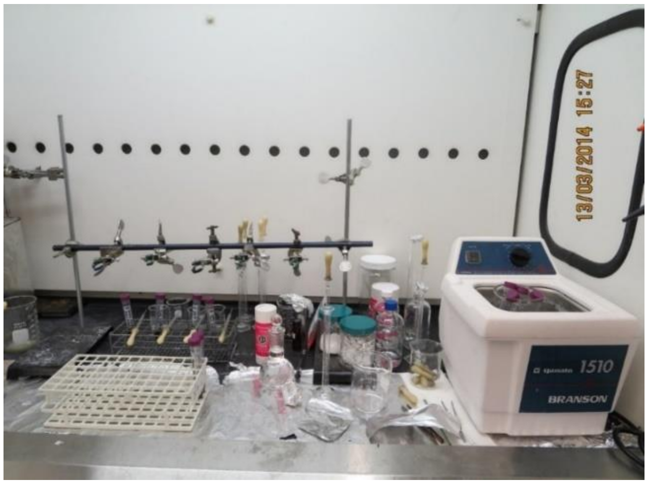


Figure 1.3: Lab setup for extraction.

The process was repeated a second time with a fresh 10 ml of DCM and the combined aliquots were centrifuged using a centrifuge as shown in Figure 1.4 at 3000 rpm to remove suspended fine dust particles and to obtain a clear supernatant to avoid blocking the GC column.

Figure 1.4: A lab centrifuge.

The extracts were subsequently down to ~ 0.5 ml under a gentle stream of dry nitrogen as shown in Figure 1.5 after being exchanged with ethyl acetate. Ethyl acetate is more polar than DCM and because of its relative higher water solubility; it tends to improve the partitioning of solvents like DCM into the aqueous phase. The use of nitrogen gas in particular is because of its cheap cost but this process could have been done by any other inert gas.

Figure 1.5: Nitrogen blowdown to downsize samples.

The extracts after that were ready for the cleanup process after being downsized to about 0.5 ml as shown in the figure below; Figure 1.6.

Figure 1.6: Samples downsized ready for cleanup.

The extracts were then cleaned-up using 0.1 g activated carbon (Supelclean ENVI-Carb 120/400) [15], pre-cleaned by 4 ml DCM followed by 4 ml of 20% (v/v) DCM in hexane, and then the samples were transferred quantitatively after being eluted with 4 ml of 20% (v/v) DCM in hexane. To ensure quantitative transfer, the tubes were washed twice with one ml of 20% (v/v) DCM in hexane. Preparation of the carbon columns involved the use of forceps, pipette and graduated cylinders that were all rinsed with acetone. Glass wool was inserted in a pipette but not too hard to avoid the movement blockage. The strong C-F bond in the fluorinated compounds needed a substance with strong absorbent property like charcoal in the cleanup process to effectively remove any possible interfering material and aids in obtaining better recoveries. Some specs of sodium sulphate were added to remove any residual moisture that could be present in the sample. The cleanup setup is shown in Figure 1.7.

Figure 1.7: Cleanup setup.

Significantly clearer samples were obtained as shown in Figure 1.8 after the cleanup process showing the difference between the samples before and after the cleanup. This step ensures that the samples will not destroy the GC column and will provide clean chromatogram with minimum interference from other compounds present in the dust matrix.

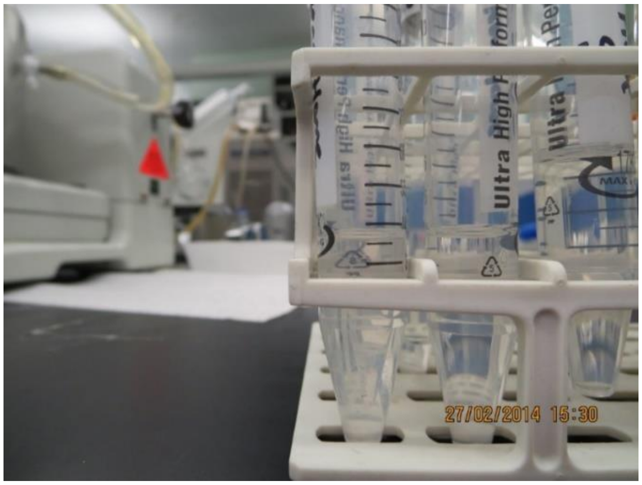


Figure 1.8: Clean, clear samples ready for GC-MS analysis.

The samples were further downsized by nitrogen blowdown as seen in Figure 1.5 until ~0.5 ml is obtained. Finally, each sample was quantitatively transferred to a GC vial after being spiked by 10 µl of an internal standard known as Mirex for PBDEs analysis and 10 µl NN MeFOA for PFCs analysis. The use of those internal standards for analysis has been documented in similar studies [10, 16]. Spiking with an internal standard is for volume correction; when slight volume difference occurs when processing and to calculate recovery of the labeled IS. Calibration curves were obtained based on the ratio between the internal standard and the analyte response to the different concentrations prepared beforehand, obtaining peaks from the concentration ratio. Any loss of the analyte through the process is tracked during the sample preparation and therefore can be corrected thus improving the quality, accuracy and precision of the data obtained.

Laboratory blank samples were prepared by pipetting 5 ml ethyl acetate and then spiking them with 100 µL recovery labeled standard like the other samples that were spiked during their preparation. The blank samples were then downsized, cleaned-up, downsized again via the nitrogen blowdown after adding ethyl acetate as a keeper and finally spiked with the internal standard, NN MeFOA and transferred to a GC vial for a GC-MS run.

1.2.3 Instrumentation Gas Chromatography-Mass Spectrometry

Identification and quantification of the target compounds; PBDEs, novel FRs and neutral PFCs was performed using a Hewlett-Packard 6890 GC-5973 in the selected ion monitoring mode. The GC-MS combines between two analytical techniques; gas chromatography and mass spectrometry. Separation of chemical mixtures is based on volatility where they travel through a column upon heat exposure with the aid of an inert gas. Consequently, identification of the components at the molecular level is based on their mass to charge ratios in the mass spectrometer. GC-MS is a reliable, very sensitive analytical apparatus popular in analyzing environmental samples. The apparatus is shown in Figure 1.9.

Figure 1.9: Gas Chromatography-Mass Spectrometry apparatus.

This separation apparatus choice is best for non-polar solvents and compounds that do not degrade easily in the injection port. The injections were splitless and were opened after 0.5 minutes. The fused silica representing the GC-MS column is shown in Figure 1.10 present in the GC-MS oven. The high oven temperature (~260 ˚C) allows the chemicals to be exchanged to gases, facilitating their transfer.

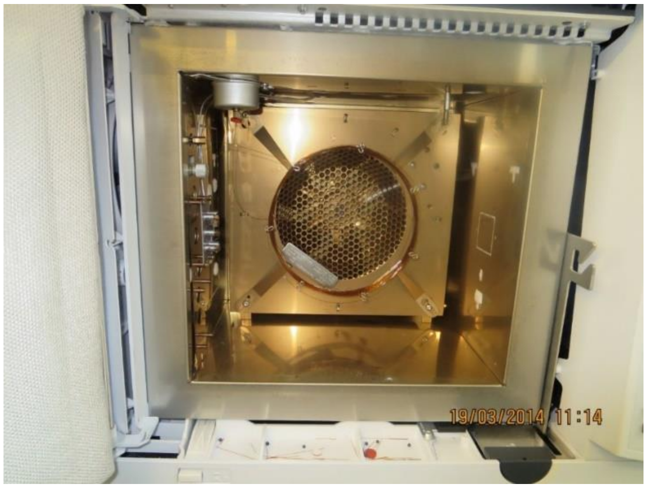


Figure 1.10: GC-MS oven.

Identification of the analytes is based on the comparison of retention times, quantified and qualified mass ratios between the sample and standard peaks. Quantification is based on the comparison of the signal intensity of the sample analyte ion against the signal intensity of the labeled counterpart internal standard (IS).

References

[1] Wilkie CA, Morgan AB (2010) Fire retardancy of polymeric materials. CRC, Boca Raton

[2] Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J. Perfluoroalkyl acids—a review of monitoring and toxicological findings. Toxicol Sci 2007;99:366–94.

[3] Eriksson, P., Viberg, H., Jakobsson, E., Orn, U., Fredriksson, A., 2002. A brominated flame retardant, 2, 20, 4, 40 , 5-pentabromodiphenyl ether: uptake, retention, and induction of neurobehavioral alterations in mice during a critical phase of neonatal brain development. Toxicol. Sci. 67, 98–103.

[4] Viberg, H., Fredriksson, A., Eriksson, P., 2003. Neonatal exposure to polybrominated diphenyl ether (PBDE 153) disrupts spontaneous behavior, impairs learning and memory, and decreases hippocampal cholinergic receptors in adult mice. Toxicol. Appl. Pharmacol. 192, 95–106.

[5] Hites, RA., 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ. Sci. Technol. 38, 945–956.

[6] Kodavanti, P.R.S., Ward, T.R., Ludewig, G., Robertson, L.W., Birnbaum, L.S., 2005. Polybrominated diphenyl ether (PBDE) effects in rat neuronal cultures: C-14- PBDE accumulation, biological effects, and structure-activity relationships. Toxicol Sci. 88, 181–192.

[7] Björklund, J.A., Thuresson, K., de Wit, C.A., 2009. Perfluoroalkyl Compounds (PFCs) in indoor dust: concentrations, human exposure estimates, and sources. Environ. Sci. Technol. 43, 2276–2281.

[8] Roosens, L., Abdallah, M.A.E., Harrad, S., Neels, H., Covaci, A., 2009a. Factors influencing concentrations of polybrominated diphenyl ethers (PBDEs) in students from Antwerp, Belgium. Environ. Sci. 43, 3535–3541.

[9] Roosens, L., Abdallah, M.A.E., Harrad, S., Neels, H., Covaci, A., 2009b. Exposure to hexabromocyclododecanes via dust ingestion, but not diet, correlates with concentrations in human serum. Environ. Health Perspect. 117, 1707–1712.

[10] Shoeib, M., Harner, T., Webster, GM., Lee, SC. Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: implications for human exposure. Environ Sci Technol 2011;45(19):7999–8005.

[11] 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. Environ. Health Perspect. 118: 712–719.

[12] Vestergren, R.; Cousins, I. T.; Trudel, D.; Wormuth, M.; Scheringer, M. Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA. Chemosphere 2008, 73, 1617–1624.

[13] Vestergren, R.; Cousins, I. T. Tracking the pathways of human exposure to perfluorocarboxylates. Critical review. Environ. Sci. Technol. 2009, 43, 5565–5575.

[14] Hassan Y, Shoeib T. Levels of polybrominated diphenyl ethers and novel flame retardants in microenvironment dust from Egypt: An assessment of human exposure. Science of the Total Environment 505 (2015) 47–55.

[15] Powley CR, George ST, Ryan TW, Buck RC. Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes. Anal Chem 2005;77:6353–8.

[16] Stapleton HM, Harner T, Shoeib M, Keller JM, Schantz MM, Leigh SD, et al. Determination of polybrominated diphenyl ethers in indoor dust standard reference materials. Anal Bioanal Chem 2006;384:791–800.

Chapter 2: PBDEs / non-PBDEs

2.1 Background

Fire is not only a source of damage to properties and public loss but can be catastrophic leading to loss of lives. In 2007, specifically in the United States, more than 1.5 million fire cases were reported resulting in 17675 injury cases, 3430 deaths and direct losses resulting in over $14 billion [1]. The increased demand for retarding fires and protecting materials started with the Ancient Egyptians around 450 BC using alum to reduce the flammability of wood [2]. In order to meet the flammability specifications and regulations, flame retardants are now manufactured to be applied on wood, plastic, textiles and paper such that the materials are made to increase their resistance to fire [3]. Polybrominated diphenyl ethers are added to products taking into account the temperature where the materials burn allowing the products to be more resistant. The introduction of technology and its increased usage have resulted in the use of synthetic polymers in households and office environments leading to the rise in the use of flame retardants as a safe measure against risks of potential fire hazards [4]. The origin of the flame retardants is a blend between organic and inorganic materials [5]. Flame retardants aim to *delay* not *prevent* fires, slowing down the onset of a fire giving time for people to escape, as opposed to fire proof material, that are designed to prevent the material from completely catching fire [4]. Flame retardants work by delaying combustion; a process involving the presence of a fuel source and oxygen utilizing vapor phase chemical reactions interfering in a certain step in the combustion process consequently leading to the delay and inhibition of the spread of fire. Bromine is regarded as the main active ingredient of brominated flame retardants [6]. This chapter aims to introduce polybrominated diphenyl ethers, their industrial use, the levels of these compounds in the Greater Cairo Region, in comparison with other countries and how these compounds have shown to have a direct effect on humans and the environment which have led to the banning of some of these compounds and the introduction of others, under the name: ‘Novel Flame Retardants’ which are also investigated in homes, workplaces and cars.

2.2 Introduction

Polybrominated diphenyl ethers (PBDEs); a class of synthetic chemical compounds, has been widely used as flame retardants (FRs) in consumer products like electronics, textiles and the plastics industry since 1970 [7]. This class of compounds has been commercially used to delay, not inhibit, the possibility of household items catching fire accounting for their name ‘flame retardants’. They are prevalent in everyday furniture, carpet pads and other electronic products including computers and television casings, polyurethane foams used in mattresses and car seats as well as textiles [8]. PBDEs have been found to be present in several microenvironments such as homes [9], work places [10], cars [11], schools [12] as well as in sea water [13] and landfill sites [14]. PBDEs were found to bio-accumulate in wildlife [15, 16] domestic animals [17], human serum [18-21], human tissues and breast milk [22, 23] being of high concern due to the possibility of being passed from mother to child.

PBDEs are a large class of compounds composed of 209 congeners in total [24]. The basic structure of PBDEs shown in Figure 2.1 can accommodate up to 10 bromines. The location of the bromines and their numbers determines the physical properties of the compound which vary from one congener to another [25].

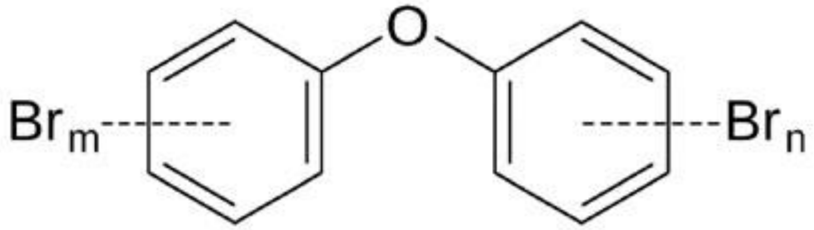
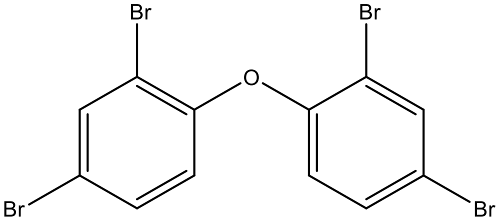
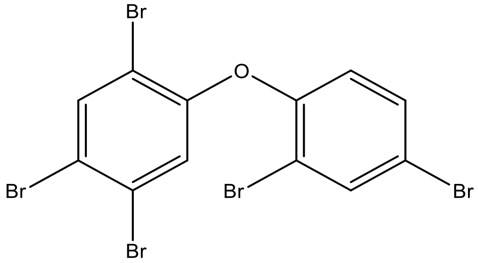
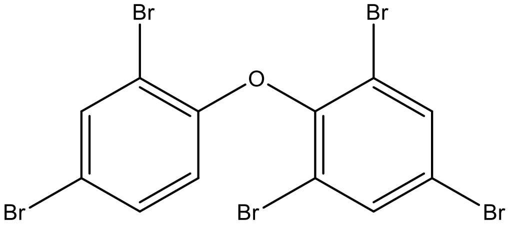
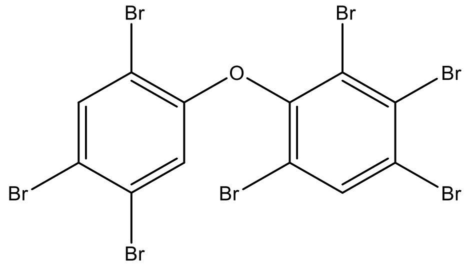
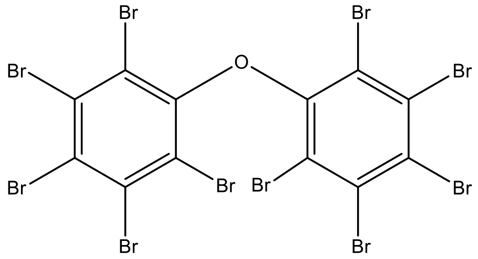


Figure 2.1: General structure of PBDEs [26].

The word ‘congener’ accounts for chemical substances being related to one another in terms of their structure, origin or function. Each congener is assigned a certain brominated diphenyl ether (BDE) number. The three most commercially popular formulations are the penta formulation, octa formulation and the deca formulation, having a bromine content of 70.8, 79 and 83% respectively [27-29]. The penta-BDE formulation is composed primarily of BDE 47, 99, 100, 153 and 154; both 47 and 99 accounting for around 50% of the penta-BDE formulation. The octa-BDE formulation which is a mixture between octa and deca congeners, is mainly composed of BDE 183 making up 40% of the formulation, yet it includes other congeners like BDE 153, 154, 196, 197, 203, 207 and 208. The third formulation; deca-BDE is primarily composed of BDE 209 representing 92-97% of the formulation [30-34]. Table 2.1 shows the main five BDE congeners that were the subject of this study. This table includes full name of the compounds, their commercial trade names and structures. Penta-BDE was more highly manufactured in North America than Europe and any other country. High restrictions have been placed on the production of these compounds [35]. The penta-BDE formulation is mainly used in baby products, mattresses and other cushioning, while the octa-BDE targets the plastic industry and finally the deca-BDE which is highly used in buildings, electronics, textiles and automotive industries [36]. The PBDEs are found in the market with trade names like DE-60F, DE-61, DE-62, DE-71 and DE-70-5 for penta-BDE congeners [28], DE-79 for the octa-BDE and finally Saytex 102E or DE-83R for the deca-BDE congener [29, 30].

Table 2.1: PBDEs Flame Retardants – Complete compound names, abbreviations and structures.

Number	Compound	Trade Name (Short form)	Structure
1	2,2′,4,4′-tetrabromodiphenyl ether	BDE 47	
2	2,2′,4,4′,5-pentabromodiphenyl ether	BDE 99	
3	2,2′,4,4′,6-pentabromodiphenyl ether	BDE 100	

Number	Compound	Trade Name (Short form)	Structure
4	2,2′,3,4,4′,5′,6-Heptabromodiphenyl ether	BDE 183	
5	2, 2’, 3, 3’, 4, 4’, 5, 5’, 6, 6’-decabromodiphenyl ether	BDE 209	

These compounds are known to be very persistent to physical, chemical and biological degradation, as well as being bio-accumulative and toxic to human health which soon caught the attention of researchers and accordingly led to their strict regulations [37]. Flame retardants are a class of compounds that can act either reactive or additive, either covalently bounded or not, respectively, to the materials they are applied upon. PBDEs in specific are considered as ‘additive’, not bounding to the materials they treat, enhancing their possibility to migrate from the material to the environment [38-40]. On the other hand, BDE 209 has a very low volatility at room temperature. The congeners volatilize differently depending on their physical-chemical properties [41].

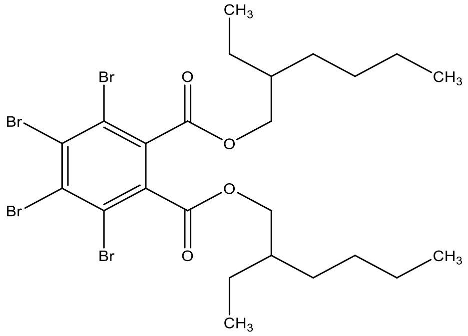
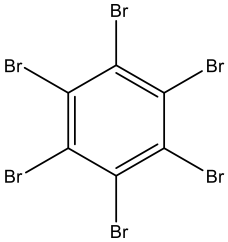
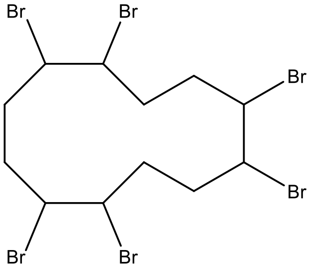
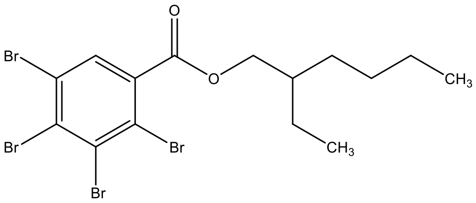
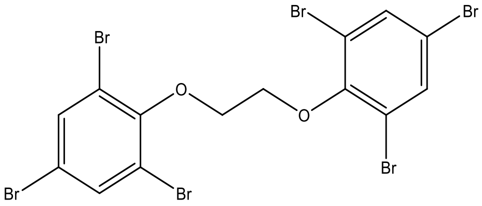
The production of the congeners penta-BDE and octa-BDE (both highly persistent) have been discontinued and banned in Europe [42] and voluntarily listed in 2004 in the U.S. [43]. Recently, the two formulations were added to the list of banned chemicals in Annex A of the Stockholm Convention as Persistent Organic Pollutants (POPs) in 2009 [44]. Deca-BDE is the only congener still in use globally and is expected to be phased out very soon in the U.S. [45] however, it is annulled from the European Union restriction in 2008 [46]. It was thought that the deca congener does not bio-accumulate but it has been found in both human and animal tissues [47-50].

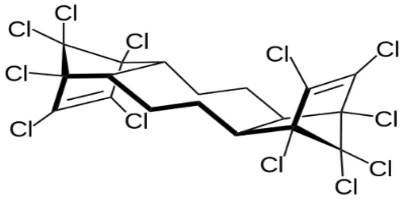
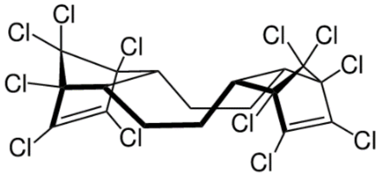
Deca 209 has showed to be nontoxic under laboratory conditions but tends to break down in the presence of sunlight into the penta and tetra forms of PBDEs [51].

Alternate flame retardants (FRs), known as halogenated FRs or non-PBDE FRs or novel FRs, were the alternative formulations used after the phase out of the brominated flame retardants (BFR) due to the risk they pose to humans, wildlife and the environment [52]. The new flame retardants represent 25% by mass of the flame retardant production with an increase of 5% per annum [53-54]. The compounds were to have similar properties to PBDEs and if added to a material like plastics, for example, the properties would not alter. These compounds include tetrabromobisphenol-A (TBBPA), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) among others. Bis-(2-ethylhexyl) tetrabromophthalate (TBPH) is also considered to be a very well-known non-PBDE, commercially sold as a mixture known as Firemaster 550 (Chemtura Corp., Middlebury, CT) [55].

Table 2.2 shows the main non-PBDEs discussed in this thesis. Hexabromocyclodecanes (HBCDs), one of the new FRs, found readily in the environment is highly used in polystyrene foams and other building insulation materials and in electrical equipment [56]. HBCD comes in three different formulations: α, β, and γ. HBCD makes it to the environment through different pathways including emissions and leaching out of the products [57]. The compound soon was recognized by the UK Chemical Stakeholders Forum as being persistent, bio-accumulative and toxic (PBT) like the penta-BDEs which led to the compound being listed in the OSPAR list of chemicals for an immediate action as well as the Stockholm Convention on Persistent Organic Pollutants on the 26th of November 2014 for elimination [58, 59]. Meanwhile, no restrictions have been placed on the production and consumption of HBCD in the U.S. [58].

Table 2.2: Non-PBDEs Flame Retardants – Complete compound names, abbreviations and structures.

Number	Compound	Trade Name (Short form)	Structure
1	Bis(2-ethylhexyl) 3,4,5,6-tetrabromophthalate	TBPH	
2	Hexabromobenzene	HBB	
3	1,2,5,6,9,10-Hexabromocyclododecane	HBCD	
4	2-ethylhexyl-2,3,4,5-tetrabromobenzoate	EH-TBB (Also known as TBB)	
5	1,2-bis(2,4,6-tribromophenoxy)ethane	BTBPE	

Number	Compound	Trade Name (Short form)	Structure
6	*Anti*-isomer of dechlorane plus	*anti*-DP	
7	*Syn*-isomer of dechlorane plus	*syn*-DP	

The compounds are highly used in PVC (polyvinyl chloride), wire insulations, wall coverings and coatings in fabrics, very much like the PBDEs. In 2006, the production of TBPH was about 450-4500 tons [60]. Like PBDEs they are not covalently bonded compounds, they are additive chemicals, allowing them to leach out from the products into the surrounding like air and dust. Humans then get exposed to these compounds despite them being banned or phased out, through the equipment and materials being treated with PBDEs which are still in use (like household equipment), or via inhalation of the dust, ingestion of contaminated food or dermal intake yet the dominant route is still unknown [35, 55, 61-64]. Researchers showed a link between the presence of BFR and their effect on human health due to the fact they are carcinogenic and have other neurotoxic effects [65]. Studies were extensive on breast milk and human blood [66, 67]. The inhalation of very fine dust with potentially high content of PBDEs is likely to reach the respiratory system. Other dust particles affect the digestive system [68]. A more in-depth insight of how PBDEs play a role in health risk will be discussed in this chapter.

2.3 PBDEs Health Effects

Several studies have linked the level of PBDEs to various aspects in human health affecting all body systems. The exposure of PBDEs were found to be not through dust only, but through diet, air, indoor environment [69-71] and dermal uptake [72] as mentioned earlier. Those compounds were found to be mostly prevalent in human tissues and approximately 90% of these accumulated compounds were the penta-congeners as well as hexa-BDE 153 and 154 [73, 74]. The chemicals found in PBDEs are known to be lipophilic endocrine disruptors [75]. According to a recent study, the levels of PBDEs were very significant in samples including breast milk and blood [76, 77]. It is noticeable that there is a declining level of PBDEs from the early 2000s, most probably due to the high restrictions of their production and the phase out of both the penta-BDE and octa-BDE congeners [78]. A recent study performed in 2014, examining the impact of PBDEs on the neurodevelopment and thyroid hormones showed that PBDEs results in disruptions in both despite that definitive proof was not provided especially in infants and toddlers. This is because the structure of PBDEs is greatly similar to those of the thyroid hormones, T3 and T4 which affects growth and differentiation [79-83]. Other studies concluded that upon exposure to both penta-BDE and octa-BDE, the liver becomes the main targeted organ that results in the inconsistency of its enzymatic activity, increase in its weight and alterations in its main function. Deca-209 has been found in high concentrations in blood samples from Korea and China [84-86]. Other studies have related the effect of exposure of PBDEs to the reproductive hormone levels in men [87]. The presence of PBDEs in maternal milk has been found in high amounts upon exposure to PBDEs in dust [88]. In 2005, the brominated flame retardants were estimated to be 311,000 metric tons and increased to 410,000 metric tons in 2008 [53]. The novel-PBDEs still hold several health risks affecting wildlife like dolphins in China Sea and passing through the fatty tissue of other species [89]. Other studies have shown that exposure to TBPH at about 20,000 ppm led to the decrease in body weight and decline of phosphorous and calcium levels as well as observed neurotoxicity in both toddlers and rodents. The non-PBDE compounds have caught a lot of attention as they have similar structures to PBDEs like halogenation and low aqueous solubility and are additive rather than reactive. They hold similar health risks including hepatic enzyme changes, affecting thyroid hormones leading to cancer [57].

Research interest in this field has increased exponentially since the 90’s. In this thesis, we examine for the first time levels of PBDEs in Egypt. Studies in this area have been extensive in Europe, U.S. and Canada while being very sparse in the Middle East. The weather conditions in Egypt for example are completely different than Europe and North America. Egypt is regarded as a warmer country that has very hot summers reaching to about 45 ˚C with a moderate cool winter. House dust is regarded as a pool for those contaminants and because people of different ages spend most of their time home this increases their exposure risk. Infants and toddlers for example are of higher risk due to their hand to mouth activity during crawling and also due to spending more time indoors than outdoors. Automobiles and workplace samples were investigated as well. Since regulations have not been placed in Asia, there has been an increase in the demand of PBDEs. Egypt, a country that imports more from countries in Asia like China and Taiwan, than any other country has high risk susceptibility to those compounds which is one of the reasons this work was undertaken.

2.4 Research Work

2.4.1 Chemicals and Reagents

A mixture of PBDEs 17, 28, 47, 49, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and the individual BDE 209 were obtained from the Cambridge Isotope Laboratories, Inc. Ma, U.S.A. Individual standards of non-PBDEs were purchased from Wellington Laboratories: Ally-2,4,6-tribromophenyl ether (ATE), beta-tetrabromoethylcyclohexane (β-TBECH), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), beta-1,2,5,6 tetrabromocyclooctane (β-TBCO), bis (2-ethyl-1-hexyl) tetrabromophthalate (TBPH), hexabromobenzene (HBB), gamma-Hexabromocyclododecane (γ-HBCD), 2-ethylhexyl-2,3,4,5-Tetrabromobenzoate (EH-TBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) and Dechlorane *Plus* in both its stereoisomers (*syn*-DP, *anti*-DP).

2.4.2 Gas Chromatography-Mass Spectrometry Methodology

Analysis was performed by GC-MS using negative chemical ionization having methane as the reagent gas and helium as the carrier gas. The gas chromatograph was fitted with a 15 m DB-5MS capillary column with 0.25 μm film thickness and 0.25 mm internal diameter (J&W Scientific, Folsom, CA). The 2 μl injections made in splitless mode and set at 265 °C. For PBDEs separation, the initial oven temperature was 80 °C, held for 2 minutes and then gradually increased by 10 °C per minute until reaching 285 °C which was held for 5 minutes allowing the chemicals to get exchanged to gases facilitating their transfer. For Non-PBDEs, the initial oven temperature was 100 °C held for 2 minutes and gradually increased by a rate of 6 °C per minute until reaching 250 °C and then increased to 310 °C by a rate of 20 °C per minute and temperature was held for 5 minutes [35]. The temperature of the source and quadrupole were 230 and 150 °C respectively.

Identification of the target PBDEs/non-PBDEs compounds was based on the retention time and the quantified base matching the bromine ion signal detected at m/z 79 and m/z 81; target ions. A target ion was characteristic for each target compound and distinguishes the specified compound from any other having similar retention times. Some non-PBDEs had different qualifier ions as shown in Table 2.3 like BTBPE, *syn*-DP and *anti*-DP that tend to increase the level of identification confidence and point out the possibility of an analytical problem.

Table 2.3: The m/z of target and qualifier ions used for the GC–MS detection employing the negative chemical ionization mode.

Analyte	Quantifier Ion m/z	Qualifier Ion m/z
Penta BDEs	79	81
Octa BDEs	79	81
Deca BDE	79	81, 486, 488
ATE	79	81, 464, 291
BTBPE	463.6	383.7, 512.9
BATE	79	81, 160
TBPH	79	81,160, 252
TBB	79	81, 160
HBB	79	81, 551.5, 471.6
HBCD	79	81, 160
β-TBCO	79	81, 160
β-TBECH	79	81
syn-DP	654, 463.6	654, 652, 547.8, 236.8
anti-DP	654, 463.6	654, 652, 547.8, 236.8

2.4.3 Quality Assurance / Quality Control

QA/QC is important as it qualifies the confidence level in the data. Quality control is usually the tool or equipment used for monitoring and regulating the process. While quality assurance is the process that verifies that the tools used are meeting the specifications set.

Sodium sulfate blanks were processed with each batch during the sieving process, stored and processed similarly to the other samples. This is important to eliminate the possibility of any contamination that could result from the various sources. The Method Detection Limit (MDL) obtained from the 5 sodium sulfate blanks was calculated to be three times the mean standard deviation of the blanks. Results have shown that the polypropylene tubes caused no contamination.

The method detection limit is defined as the detection of the lowest concentration of the reported substance with a 99% of confidence level.

The values are expressed as concentrations; dividing by an average dust amount of 0.2 g. For the compounds that were not detected in the blanks, $\frac{2}{3}$ of the instrumental detection limits (IDLs) were used for calculating the MDL. Instrumental detection limit is also known as the 'noise level'. The IDL is basically the analyte concentration required to produce a signal more than three times that of the standard deviation produced by the noise level.

The IDLs were calculated based on the instrument response, extrapolating to the lowest amount of analyte that would generate a signal to noise ratio of 3:1. As a matter of quality assurance and checking the efficiency of the procedure, the extraction process was repeated for the third and fourth time assuring that no PBDEs were present at all. This step was performed to ensure that the sonication process and the carbon cleanup were efficient. The efficiency of the activated carbon cleanup was tested using standard 50 ng solutions. BDE 190 was excluded due to their very minimal recovery as shown in Table 2.4, while an average recovery of 107 ± 6% was obtained for PBDEs and 107 ± 9 % was obtained for non-PBDEs. The recovery of individual compounds is shown in Table 2.4. The levels of the target compounds in sodium sulfate blanks were shown to be less than 2% than in other dust samples, therefore no blank corrections were applied to the results.

Table 2.4: Recoveries and standard deviation values all in percent of PBDEs and non-PBDEs after carbon cleanup.

Compound	Recovery Test 1	Recovery Test 2	Recovery Test 3	Mean Recovery	Standard Deviation
PBDEs					
BDE 17	115	114	108	113	4
BDE 28	120	112	107	113	7
BDE 71	125	109	105	113	11
BDE 47	125	109	105	113	10
BDE 66	127	108	104	113	12
BDE 100	128	107	105	114	13
BDE 99	129	108	104	114	14
BDE 85	129	106	105	113	14
BDE 138	128	106	104	113	13
BDE 154	114	99	96	103	9
BDE 153	122	102	102	109	12

Compound	Recovery Test 1	Recovery Test 2	Recovery Test 3	Mean Recovery	Standard Deviation
BDE 183	91	84	82	86	5
BDE 190	2	2	2	2	0.1
BDE 209	61	73	70	68	6
Non-PBDEs					
ATE	102	101	98	100	2
β-TBECH	101	104	105	103	2
BATE	121	111	119	117	5
β-TBCO	123	99	110	111	12
TBPH	157	138	152	149	10
HBB	96	85	93	91	6
HBCD	119	102	119	114	10
EH-TBB	121	78	108	102	22
BTBPE	111	87	102	100	12
anti-DP	112	89	106	102	12
syn-DP	87	86	103	92	10

2.5 Results and Discussion

2.5.1 Levels and congener profiles of PBDEs

Fourteen PBDE congeners were determined in the dust samples acquired from homes (n = 17), workplaces (n = 5) and cars (n = 9) from Cairo, Egypt. Six different standard concentrations known as ‘calibration samples’ were prepared in order to obtain a calibration curve. After preparing the calibration curve, quantifying the samples by integrating the peak areas was done using the program MassHunter (Workstation Software Version B.05.02/Build 5.2.365.0 for QQQ, Agilent Technologies). Figure 2.2 shows a representative chromatogram with the fourteen BDE congeners present in a prepared standard. Notice the presence of the internal standard, Mirex ensuring proper preparation.

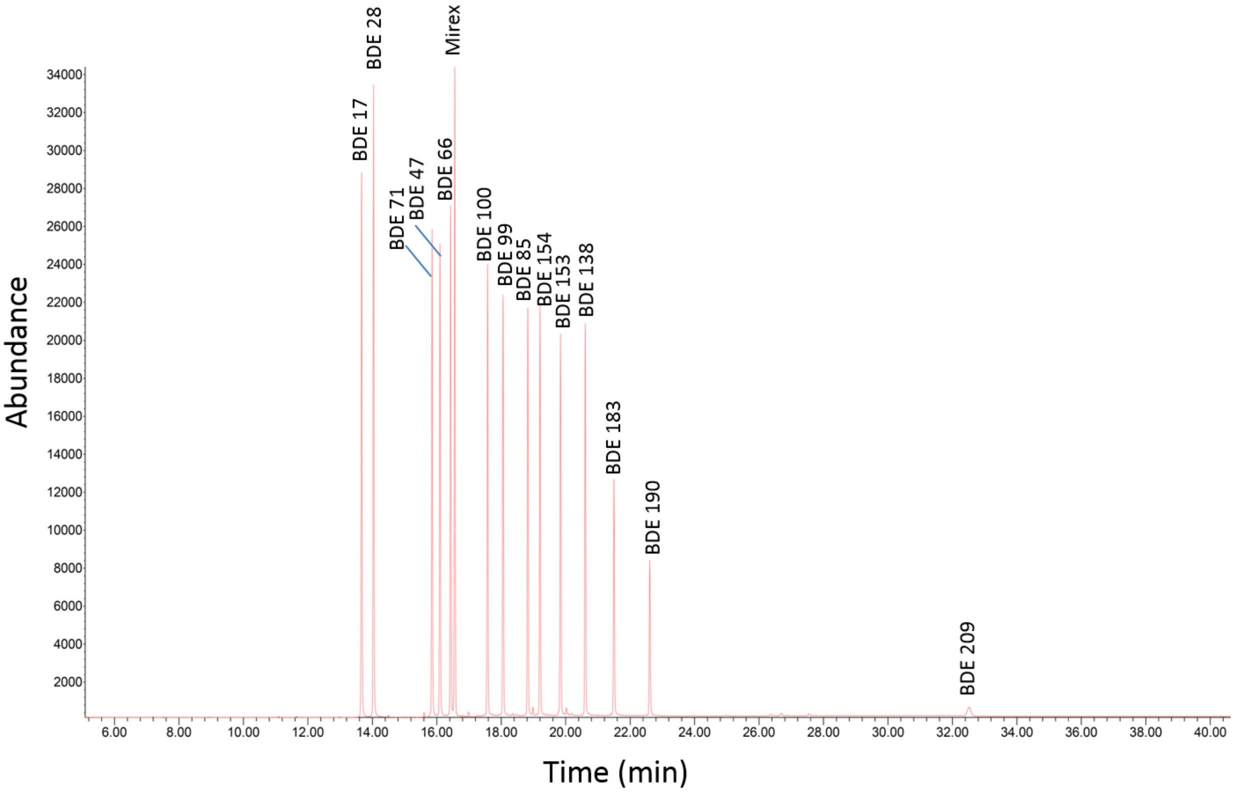


Figure 2.2: Representative chromatogram for PBDE standard mix.

Several parameters were calculated including mean, median, range, method detection limit, detection frequency as well as four different percentile distributions and the LOD of each congener, after quantifying the results which are all presented in Table 2.5. The percentile distribution of each congener was presented as shown in Figure 2.3. The contaminant level was reported in ng g^{-1}. Median of congeners representing the penta-BDE formulation (BDE 47, 99 and 100), the octa-formulation (BDE 183) and the deca-formulation (BDE 209) are all shown in Table 2.5, Figure 2.4 and Table 2.6 comparing this study to others. In Figure 2.4, the levels of the contaminants in the three microenvironments were illustrated to provide a better insight comparison of the concentration of the popular BDE formulations. In Figure 2.3, the three graphs represent the congener percentage in each of the three microenvironments: homes, workplaces and cars. The congeners were present in relatively high percentages between 94% - 100% except for congener 138 that was present in 71% in homes and 60% in workplaces.

Figure 2.3: Percent composition of PBDEs in homes (top panel), workplaces (middle panel) and cars (bottom panel). Values on the x-axis refer to the sample number and the percentage on the y-axis.

It is observed that BDE 209 is the dominant congener present in all samples; however other congeners were found with high variability. This is clearly illustrated in Figure 2.3 having BDE 209 being the dominant congener. The mean and median values for ΣPBDEs in this study were 248 and 57 ng g^{-1} respectively for home samples, 14993 and 425 ng g^{-1} for workplaces and finally 6943 and 1608 ng g^{-1} for car samples as shown in Table 2.5. A significant variation in the values gave an indication that the concentration level of PBDEs present in each microenvironment is different. Beginning with the mean values, BDE 47 and 99 were compared in the three different microenvironments as they showed a significant difference. In homes, BDE 47 and BDE 99 ranged between 0.34 to 375 and 0.53 to 510 ng g^{-1} respectively. The reason behind the variation can be due to several factors, but mostly due to new PBDE sources were introduced to the homes being sampled. The PBDE samples in workplaces and cars were of less variability. In car samples, congeners 47 and 99 were between 0.49 to 112 and 1.51 to 123 ng g^{-1} respectively while the least variation was in the workplaces having BDE 47 between the range of 0.75 and 23.52 and BDE 99 between 2.46 and 20.87 ng g^{-1} as shown in Table 2.5 [119].

Figure 2.4: Concentrations of selected PBDEs representing the penta, octa and deca formulations in different microenvironments shown in boxplot format. The lower and upper ends of the boxes are the 25th and 75th percentiles of the data. The lines separating the colors represent the median values while the whiskers define the minimum and maximum values.

Table 2.5: Concentration of PBDEs in ng g^{-1} determined in dust samples collected from 17 homes, 5 workplaces and 9 cars.

PBDE Congener	Method Detection Limit	% DF[a]	Mean	Median	Min	5th percentile	25th percentile	75th percentile	95th percentile	Max
Homes (n=17)										
17	0.023	100	2.62	1.70	0.21	0.44	1.18	2.70	7.51	14.3
28	0.021	100	0.70	0.34	0.15	0.19	0.23	0.42	2.61	4.12
47	0.029	100	29.0	1.69	0.34	0.41	0.54	2.51	126	375
66	0.036	100	1.37	0.64	0.23	0.24	0.42	1.02	5.34	7.49
71	0.029	100	3.31	1.35	0.40	0.45	0.73	3.54	12.0	16.8
85	0.046	100	3.64	0.23	0.04	0.05	0.10	0.84	26.4	28.9
99	0.044	100	34.9	2.70	0.53	0.55	2.02	7.81	124	509.8
100	0.030	100	7.18	0.37	0.07	0.11	0.16	0.53	27.8	97.7
138	0.062	71	1.67	0.25	<MDL[b]	0.00	0.09	0.62	8.31	12.3
153	0.032	100	27.8	6.26	0.54	2.32	3.10	18.5	95.0	194.7
154	0.048	94	4.94	0.38	<MDL[b]	0.09	0.17	0.97	20.9	60.1
183	0.042	100	1.67	1.05	0.27	0.35	0.09	2.11	5.12	5.23
209	7.32	100	129	40.2	2.20	3.22	12.1	161	422	591
ΣPBDEs	---	---	***248***	***57.1***	***5.04***	---	---	---	---	***1918***
Workplaces (n=5)										
17	0.023	100	3.74	3.82	0.67	0.74	1.03	6.21	6.82	6.97
28	0.021	100	0.98	0.39	0.27	0.30	0.38	1.66	2.18	2.21
47	0.029	100	7.41	2.33	0.75	0.86	1.32	9.15	20.7	23.5
66	0.036	100	1.55	1.45	0.45	0.63	1.34	1.72	2.56	2.77
71	0.029	100	7.33	6.03	2.49	2.50	2.54	9.55	14.8	16.0
85	0.046	100	2.48	0.17	0.04	0.04	0.07	0.38	9.49	11.8
99	0.044	100	11.2	7.11	2.46	3.28	6.52	18.9	20.5	20.9
100	0.030	100	1.01	0.60	0.16	0.18	0.26	2.00	2.02	2.03
138	0.062	60	3.95	1.68	<MDL[b]	0.90	1.25	5.52	8.59	9.35
153	0.032	100	30.0	32.9	2.89	5.73	17.1	42.5	52.4	54.9

PBDE Congener	Method Detection Limit	% DF[a]	Mean	Median	Min	5th percentile	25th percentile	75th percentile	95th percentile	Max
Workplaces (continued)										
154	0.048	100	5.61	0.83	0.18	0.19	0.25	0.95	20.8	25.8
183	0.042	100	3.31	2.34	0.82	0.83	0.87	5.69	6.62	6.85
209	7.32	100	14915	366	26.1	42.4	108	1978	58072	72096
ΣPBDEs	---	---	***14993***	***425***	***38.1***	---	---	---	---	***72279***
Cars (n=9)										
17	0.023	100	5.33	2.56	0.94	1.00	1.14	4.90	18.3	25.5
28	0.021	100	2.50	1.18	0.67	0.68	0.71	1.54	8.57	12.0
47	0.029	100	25.9	5.69	0.49	1.26	3.08	25.5	91.9	111
66	0.036	100	2.23	1.77	0.58	0.71	1.57	2.29	4.91	5.80
71	0.029	100	8.77	1.57	1.09	1.12	1.33	2.41	39.2	60.3
85	0.046	100	1.68	0.93	0.13	0.16	0.49	2.31	4.77	5.79
99	0.044	100	33.0	22.5	1.51	3.09	7.80	32.2	100	123
100	0.030	100	6.67	4.82	0.09	0.46	1.77	5.88	20.5	25.1
138	0.062	100	1.78	0.91	0.35	0.38	0.52	1.83	4.96	5.50
153	0.032	100	25.4	16.3	4.03	4.72	11.0	27.0	66.1	74.9
154	0.048	100	5.94	3.64	0.57	0.81	1.75	8.86	16.27	21.0
183	0.042	100	10.8	5.80	1.76	1.82	4.46	10.53	32.0	43.5
209	7.32	100	6813	1540	159	212	481	2643	28706	36927
ΣPBDEs	-	-	***6943***	***1608***	***171***	---	---	---	---	***37440***

a. Detection Frequency

b. Method Detection Limit

The median concentrations for ΣPBDEs in this study were 57, 425 and 1608 all in ng g^{-1} in homes, workplaces and cars respectively. The penta-BDE formulation median concentration (ΣBDE 47, 99 and 100) for the home samples, workplaces and cars were 4.76, 10.0 and 33.0 ng g^{-1} respectively. The octa-formulation, BDE 183, had a median concentration of 1.05, 2.34 and 5.80 for homes, workplaces and cars respectively. The median concentration for the deca congener, BDE 209, was 10 times higher than the penta congeners. Car samples had a median concentration of 1540, followed by the workplaces with a median 366 and the home samples with a median of 40, all values in ng g^{-1} [119]. The median values are shown in Table 2.5 and in Table 2.6 in which more details is provided including a comparison of our values to those obtained from other studies.

Similar studies were done in Kuwait, Pakistan, Korea, China, U.S., Canada and other countries. Comparing our penta-BDE formulation to another African country like South Africa showed very similar values [90]. Values in Canada and U.S. were higher than that of Asian counties. BDE 209 was highest in car samples more than work and homes as shown in our study (Figure 2.3, Figure 2.4 and Table 2.5) which is consistent with other studies.

Table 2.6 provides the median contaminant level as determined in this study, these are compared to other studies and are presented in more detail in Table 2.7 (see end of chapter), showing not only the median values but includes the minimum, maximum and average. Looking closer at the penta-formulation (BDE 47, 99 and 100) in home samples, some samples had high concentration amount in one of the BDE congeners. It is interesting to note that the samples with the highest penta-formulation involving the three congeners, BDE 47, 99 and 100 with an amount of 375, 97.7 and 510 ng g^{-1} respectively was obtained from the same home which had the second highest BDE 209 value being 379 ng g^{-1}. The highest BDE 209 value for all the home samples was 592 ng g^{-1} where in both instances new television sets were installed in the living rooms of both homes about a month before our sample collection. The home with the highest penta-congener values also had new imported drape fabrics installed alongside the new television set.

The octa-formulation, BDE 183, was present in all microenvironment samples with a detection frequency of 100% and a median of 1.05, 2.34 and 5.80 ng g^{-1} in homes, workplaces and cars respectively. BDE 183 (octa-BDE) was shown to be less abundant relative to the penta and deca formulations. In comparison with similar studies performed [9, 30, 62, 77, 98], results in this study were very much synchronized with the reported profiles in the three microenvironments. Table 2.6 shows the concentrations of the congener formulations in comparison to similar studies in different countries.

The deca congener, BDE 209, was the highest and most dominant amongst all congeners. This is clearly shown in Figures 2.3 and 2.4; where the percentage of BDE 209 is clearly significantly higher than any other constituent. Table 2.6 lists the relative concentration of the congener to be the highest among other congeners in homes, workplaces and offices. The median concentration for the home samples ranged from 2 to 591 ng g^{-1} and 26 to 72100 ng g^{-1} for workplaces. The car samples showed a median concentration range from 159 to 36927 ng g^{-1}. Table 2.5 gives an overview of the mean, median, minimum, maximum and the 5th, 25th, 75th and 95th percentile. The median concentration for BDE 209 was highest for cars, 1540 ng g^{-1} followed by 366 ng g^{-1} for workplaces and the least was for home samples with a median of 40 ng g^{-1} as shown in Tables 2.5 and 2.7. The maximum median value was obtained for a workplace sample corresponding to a computer room that had around 15 workstations. The room being small and densely populated with computers was also not routinely cleaned.

Table 2.6: Median concentration of PBDEs in ng g^{-1} reported from dust in homes, workplaces and cars.

Location[a]	BDE 47	BDE 99	BDE 100	BDE 183	BDE 209	Reference
Homes						
Egypt (Cairo)	1.7	2.7	0.37	1.1	40.2	This study [119]
South Africa (Pretoria)	2.6	2.6	<0.13	---	<1.8	[90]
Kuwait (Kuwait city)	9.5	12	2.3	1.9	310	[62]
Kuwait (Kuwait city)	2.7	3.4[b]	0.7	1.3	82.9	[72]
Pakistan (Faisalabad)	1.3	1.7	0.3	1.5	138	[62]
Pakistan (Faisalabad)	0.5[b]	0.6[b]	<0.2	0.8	19.7	[91]
China (Guangzhou)	8.4[b]	9.5[b]	1.3[b]	8.5[b]	2640	[30]
Taiwan	6.2[b]	10.0[b]	1.7[b]	6.3[b]	426	[77]
Japan	5.4	5.1	1.1	7.5	5500	[92]
Canada (Vancouver)	280	350	67	14	1300	[35]
Canada (Ottawa)	300	430	73	19	630	[71]
Canada (Toronto)	140	330	65	9	560	[98]

Location[a]	BDE 47	BDE 99	BDE 100	BDE 183	BDE 209	Reference
U.S. (California)	2300	2200	520	28	1400	[9]
U.S. (California)	1000	1100	240	18	1200	[9]
UK (Birmingham)	10	20	3.4	4.2	8100	[93]
Belgium	8	9	---	2	317	[94]
Sweden	*51*[d]	*79*	*24*	*4.8*	*470*	[95]
Poland	5.4	1.4	---	3.9	219	[96]
New Zealand (Wellington)	24	51	8.9	---	---	[98]
U.S. (Amarillo, Austin, TX)	410	820	160	16	1300	[98]
U.S.	644	676	119	17.6	1350	[70]
UK[c]	26	36	6.6	1.2	5000	[12]
UK (Birmingham)	13	23	4.2	13	2800	[98]
Workplaces						
Egypt (Cairo)	2.3	7.1	0.6	2.3	366	This study [119]
Japan	30.5	38	6.9[b]	20	1100	[92]
UK	23	65	3.2	8.3	6200	[93]
Belgium	21	45	---	24	443	[94]
U.S. (Boston)	*697* [d]	*915*	*195*	*81*	*4204*	[10]
Cars						
Egypt (Cairo)	5.7	23	4.8	5.8	1540	This study [119]
UK (Birmingham)	54	100	17	7.8	100000	[93]
U.S. (NJ and PA)	880	1130	211	73	48100	[32]
U.S. (PA)	588	613	79	3	8120	[97]
Kuwait	5.8	8.5	1.5	1	665	[62]
Pakistan	1.2	1.7	0.3	1.2	625	[62]

a. City or state is indicated in parenthesis when available.
b. Value rounded up for ease of comparison.
c. Dust samples collected from daycares.
d. Numbers in italics refer to mean values.

Table 2.7: Summary of concentrations (ng g^{-1}) of BDEs 47, 99, 100, 183 and 209 in house dust of this study and other studies.

Country	BDE 47	BDE 99	BDE 100	BDE 183	BDE 209	Reference
Homes						
Cairo, Egypt						**This Study [119]**
Min	0.3	0.5	0.1	0.3	2.2	
Max	375.1	509.8	97.7	5.2	591.5	
Median	1.69	2.7	0.37	1.05	40.16	
Mean	29.0	34.9	7.2	1.7	129.1	
Pretoria, South Africa						**[90]**
Min	-	-	-	-	-	
Max	48.2	71.1	16.6	-	78.9	
Median	2.6	2.6	< 0.13	-	<1.8	
Mean	1.32	1.84	0.09	-	3.47	
Kuwait, Kuwait						**[62]**
Min	1.3	1.4	0.3	0.5	81	
Max	4750	9390	2210	32	1250	
Median	9.5	12	2.3	1.9	310	
Mean	330	625	150	7.6	460	
Kuwait, Kuwait						**[72]**
Min	-	-	-	-	-	
Max	-	-	-	-	-	
Median	2.7	3.37	0.68	1.28	82.9	
Mean	-	-	-	-	-	
Faisalabad, Pakistan						**[62]**
Min	0.2	0.2	0.2	< 0.2	25	
Max	3.5	5.1	0.8	12	2140	
Median	1.3	1.7	0.3	1.5	138	
Mean	1.5	2.0	0.4	2.3	355	
Faisalabad, Pakistan						**[91]**
Min	-	-	-	-	-	
Max	-	-	-	-	-	
Median	0.57	0.60	< 0.2	0.75	19.7	
Mean	-	-	-	-	-	
Guangzhou, South China						**[30]**
Min	2.59	1.25	0.14	2.81	537	
Max	149	304	60.9	47.4	9600	
Median	8.42	9.49	1.26	8.46	2640	
Mean	18.3	24.5	3.97	10.9	3330	
Taiwan						**[77]**
Min	-	-	-	-	-	
Max	474	-	-	-	-	
Median	6.24	9.95	1.66	6.26	426	
Mean	178	445	141	16	1080	
Japan						**[92]**
Min	1.1	1.8	1.6	1.5	1000	
Max	220	390	5.7	500	26000	
Median	5.4	5.1	1.1	7.5	5500	
Mean	7.3	8.4	1.4	120	8200	

Country	BDE 47	BDE 99	BDE 100	BDE 183	BDE 209	Reference
Vancouver, Canada						**[35]**
Min	< 0.2	< 0.45	< 0.02	0.8	< 4.4	
Max	4900	7600	1300	270	43000	
Median	280	350	67	14	1300	
Mean	560	910	170	24	3000	
Toronto, Canada						**[98]**
Min	47	80	14	7	290	
Max	720	1800	420	30	1100	
Median	140	330	65	9	560	
Mean	300	510	120	13	670	
Wellington, New Zealand						**[98]**
Min	3.3	6.4	1.2	-	-	
Max	150	380	70	-	-	
Median	24	51	8.9	-	-	
Mean	36	87	16	-	-	
Ottawa, Canada						**[71]**
Min	21	19	4.1	< dl	74	
Max	33000	60000	21000	650	10000	
Median	300	430	73	19	630	
Mean	1100	1800	490	44	1100	
California, U.S.A.						**[9]**
Min	270	280	56	9	580	
Max	23000	24000	4900	770	15000	
Median	2300	2200	520	28	1400	
Mean	-	-	-	-	-	
California, U.S.A.						**[9]**
Min	140	190	37	3	110	
Max	17000	25000	11000	920	8500	
Median	1000	1100	240	18	1200	
Mean	-	-	-	-	-	
Amarillo, Austin, TX, U.S.						**[98]**
Min	82	150	33	4	530	
Max	3300	6000	840	170	3300	
Median	410	820	160	16	1300	
Mean	810	1400	240	28	1600	
U.S.A.						**[70]**
Min	103	162	25.9	1.3	162	
Max	7610	13800	2090	71.5	8750	
Median	644	676	119	17.6	1350	
Mean	-	-	-	-	-	
UK Daycare						**[12]**
Min	1.6	1.1	< 1	< 2	49	
Max	120	270	50	48	88000	
Median	26	36	6.6	1.2	5000	
Mean	32	54	10	5.1	8500	
Belgium						**[94]**
Min	0.5	0.6	-	0.1	15	
Max	307	748	-	262	5295	
Median	8	9	-	2	317	
Mean	21	37	-	11	604	

Country	BDE 47	BDE 99	BDE 100	BDE 183	BDE 209	Reference
Birmingham, UK						**[93]**
Min	1.2	2.8	< dl	< dl	< dl	
Max	58	180	17	550	2200000	
Median	10	20	3.4	4.2	8100	
Mean	15	36	5.6	71	260000	
Birmingham, UK						**[98]**
Min	1.2	2.8	0.53	2.0	120	
Max	160	320	50	550	520000	
Median	13	23	4.2	13	2800	
Mean	20	47	7	64	45000	
Sweden						**[95]**
Min	-	-	-	-	-	
Max	-	-	-	-	-	
Median	-	-	-	-	-	
Mean	51	79	24	4.8	470	
Poland						**[96]**
Min	< MDL	< MDL	< MDL	< MDL	7.1	
Max	51	4.8	< MDL	22	61.5	
Median	5.4	1.4	< MDL	3.9	219	
Mean	9.9	2.2	< MDL	7.5	241	
Workplaces						
Cairo, Egypt						**This Study [119]**
Min	0.75	2.46	0.16	0.82	26.1	
Max	145.5	20.9	2.02	6.85	72095.7	
Median	2.3	7.1	0.6	2.3	366	
Mean	31.8	11.2	1	3.32	14914.7	
Japan						**[92]**
Min	4.3	3.1	0.7	5.0	150	
Max	580	810	130	280	17000	
Median	30.5	38	6.85	20	1100	
Mean	110	170	30	81	2400	
Birmingham, UK						**[93]**
Min	2.6	4.2	< dl	< dl	620	
Max	380	490	79	24	280000	
Median	23	65	3.2	8.3	6200	
Mean	67	120	16	11	30000	
Belgium						**[94]**
Min	10	19	-	0.6	69	
Max	67	141	-	5464	11574	
Median	21	45	-	24	443	
Mean	26	58	-	578	1513	
Boston, MA						**[10]**
Min	37	< 0.4	13	15	912	
Max	19494	32831	8672	12970	106204	
Median	-	-	-	-	-	
Mean	697	915	195	81	4204	

Country	BDE 47	BDE 99	BDE 100	BDE 183	BDE 209	Reference
Cars						
Cairo, Egypt						**This Study [119]**
Min	0.49	1.5	0.09	1.77	159	
Max	111.5	122.7	25.1	43.4	3693	
Median	5.7	23	4.8	5.8	1540	
Mean	25.9	33	6.67	10.8	6813	
Birmingham, UK						**[93]**
Min	19	23	< dl	< dl	12000	
Max	7500	8000	2300	67	2600000	
Median	54	100	17	7.8	100000	
Mean	720	990	220	19	410000	
New Jersey and Pennsylvania, U.S.A.						**[32]**
Min	139	201	32	< 3.8	4380	
Max	13600	22900	3870	5650	3570000	
Median	880	1130	211	73	48100	
Mean	1233	1989	345	238	272119	
Villanova, Pennsylvania						**[97]**
Min	47	34	3.7	0	664	
Max	50900	64000	9590	568	322000	
Median	588	613	79	3	8120	
Mean	1950	2990	372	24	22900	
Kuwait City, Kuwait						**[62]**
Min	0.6	1.0	< 0.2	< 0.2	107	
Max	14.5	62	17	3.6	136900	
Median	5.8	8.5	1.5	1	665	
Mean	6.8	14.7	3.4	1.6	11950	
Pakistan						**[62]**
Min	< 0.2	0.4	< 0.2	< 0.2	25	
Max	7.5	8	1.5	8.5	260700	
Median	1.2	1.7	0.3	1.2	625	
Mean	1.8	2.5	0.4	3	30100	

2.5.2 Levels of non-PBDEs

Eleven non-PBDE flame retardants (ATE, β-TBECH, BATE, β−TBCO, TBPH, HBB, HBCD, EH-TBB, BTBPE, *anti*-DP and *syn*-DP) were investigated in the dust samples collected from each of the three microenvironments. Figure 2.5 provides a summary detailing the concentration of each non-PBDE in the three different microenvironments. A representative chromatogram for the non-PBDEs is shown in Figure 2.6. Table 2.8 lists the method detection limit, detection frequency, mean, median, minimum, 5th, 25th, 75th and the 95th percentile.

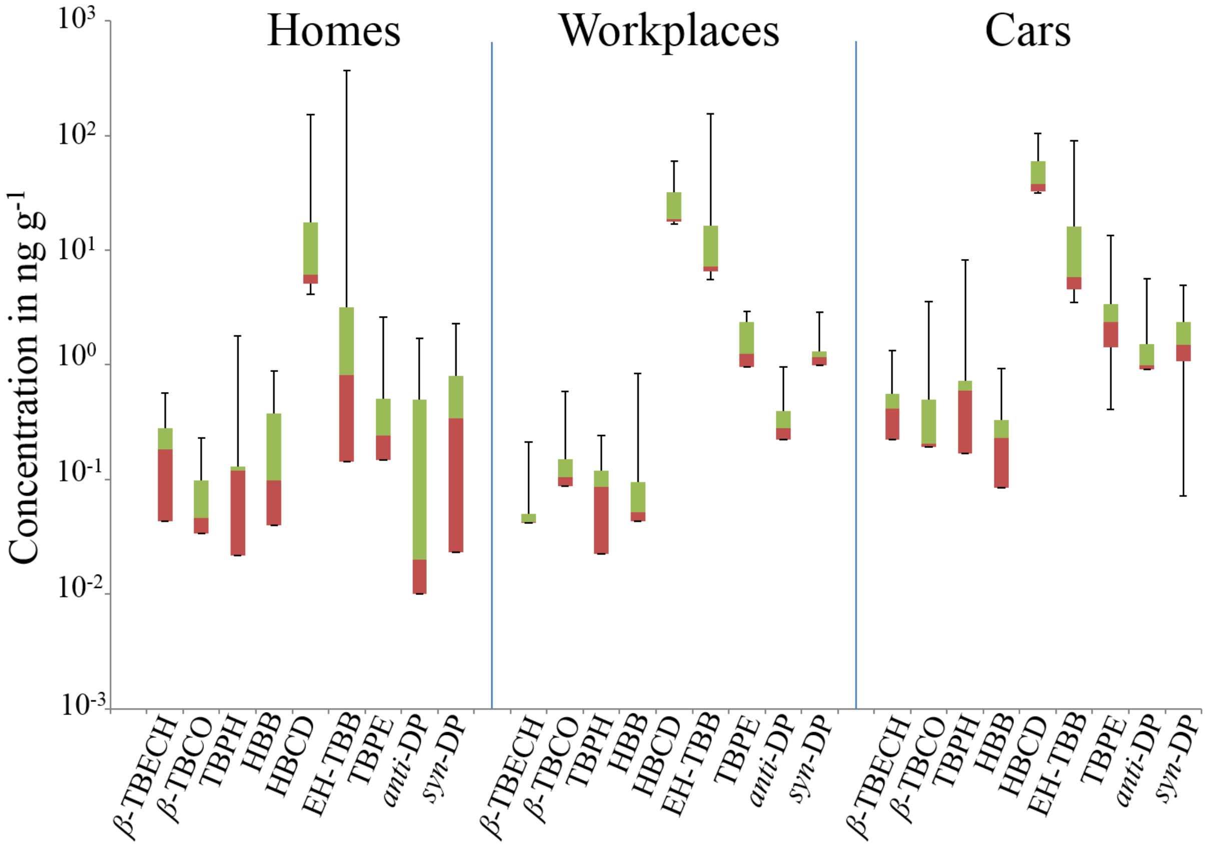


Figure 2.5: Concentrations of non-PBDEs with detection frequency above 50% in different microenvironments shown in boxplot format. The lower and upper ends of the boxes are the 25th and 75th percentiles of the data. The lines separating the colors represent the median values while the whiskers define the minimum and maximum values.

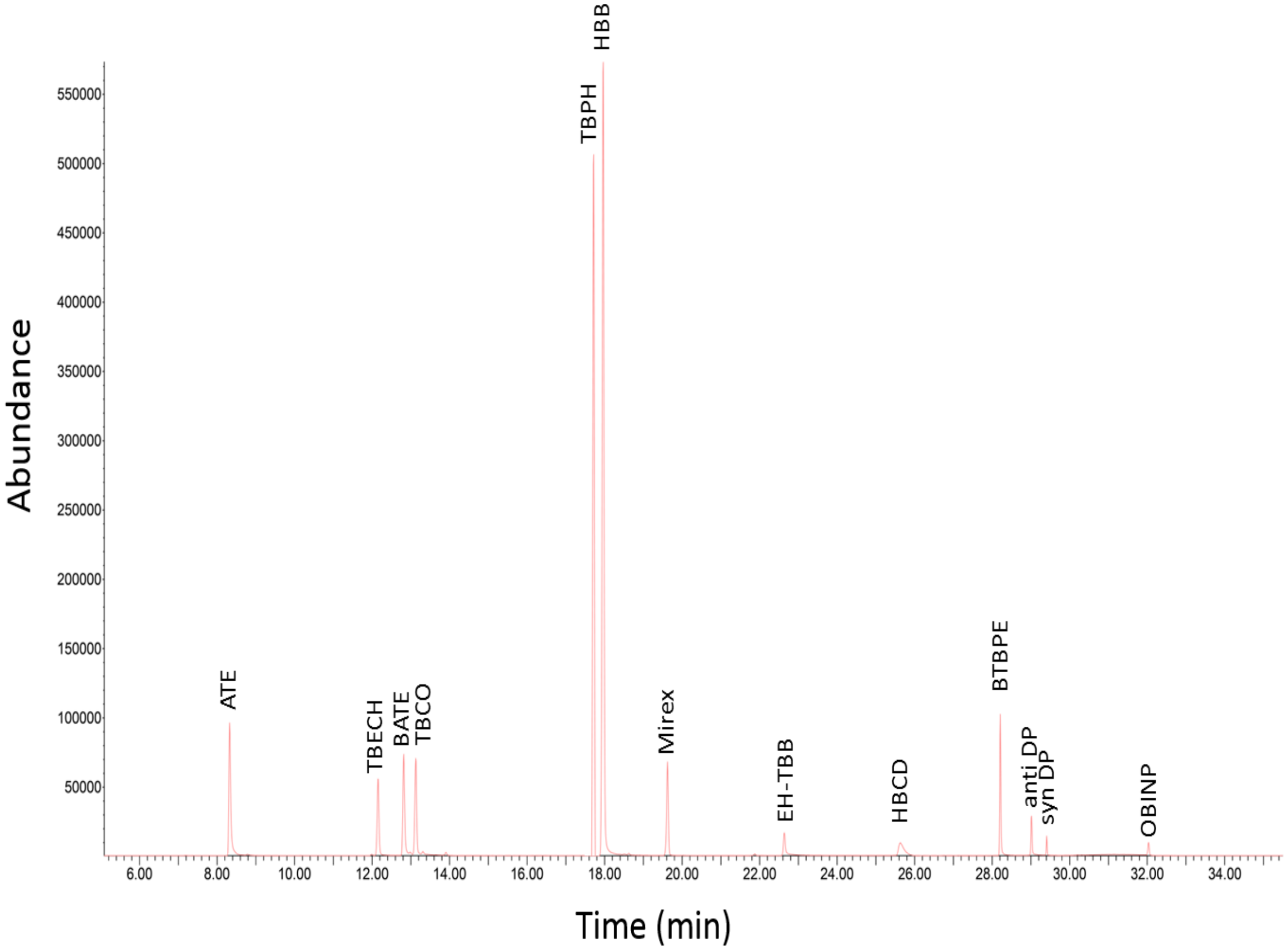


Figure 2.6: Representative chromatogram for non-PBDE standards

Table 2.8: Concentration of non-PBDE FRs in ng g^{-1} determined in dust samples collected from 17 homes, 5 workplaces and 9 cars.

Non-PBDEs	Method Detection Limit	% DF^{a}	Mean	Median	Min	5th percentile	25th percentile	75th percentile	95th percentile	Max
Homes (n=17)										
ATE	0.08	49	0.44	0.26	<MDL^{b}	0.08	0.08	0.79	1.19	1.59
β-TBECH	0.04	53	0.20	0.18	<MDL^{b}	0.04	0.04	0.28	0.51	0.56
BATE	0.09	88	0.07	0.04	<MDL^{b}	0.01	0.02	0.09	0.17	0.39
β-TBCO	0.03	94	0.07	0.05	<MDL^{b}	0.03	0.03	0.10	0.17	0.23
TBPH	0.10	59	0.19	0.12	<MDL^{b}	0.01	0.02	0.12	0.59	1.77
HBB	0.01	100	0.22	0.10	0.01	0.02	0.04	0.38	0.62	0.88
HBCD	0.16	100	20.7	6.15	1.39	1.70	5.15	17.4	78.1	153
EH-TBB	0.01	100	28.9	0.81	0.11	0.12	0.14	3.20	129	369
BTBPE	0.01	88	0.51	0.24	<MDL^{b}	0.01	0.15	0.51	1.84	2.63
anti-DP	0.01	53	0.39	0.01	<MDL^{b}	0.01	0.01	0.49	1.51	1.70
syn-DP	0.02	71	0.63	0.34	<MDL^{b}	0.02	0.02	0.80	2.09	2.28
ΣNon-PBDEs	---	---	***52.3***	***8.30***	***1.51***	---	---	---	---	***534***
Workplaces (n=5)										
ATE	0.08	40	0.54	0.08	<MDL^{b}	0.08	0.08	1.18	1.25	1.27
β-TBECH	0.04	80	0.08	0.04	<MDL^{b}	0.04	0.04	0.05	0.18	0.21
BATE	0.09	60	0.19	0.09	<MDL^{b}	0.05	0.05	0.09	0.54	0.66
β-TBCO	0.03	100	0.20	0.10	0.05	0.06	0.09	0.15	0.50	0.59
TBPH	0.10	80	0.10	0.09	<MDL^{b}	0.02	0.02	0.12	0.22	0.24
HBB	0.01	100	0.21	0.05	0.02	0.03	0.04	0.10	0.69	0.84
HBCD	0.16	100	27.6	18.6	9.95	11.5	17.9	32.1	53.9	59.3
EH-TBB	0.01	100	36.9	7.14	0.30	1.54	6.52	16.4	127	154
BTBPE	0.01	100	1.61	1.26	0.51	0.60	0.97	2.37	2.83	2.94
anti-DP	0.01	80	0.37	0.28	<MDL^{b}	0.05	0.22	0.34	0.84	0.95
syn-DP	0.02	100	1.42	1.17	0.73	0.78	0.99	1.32	2.57	2.88
ΣNon-PBDEs	---	---	***69.1***	***28.9***	***11.50***	---	---	---	---	***224***

Non-PBDEs	Method Detection Limit	% DF[a]	Mean	Median	Min	5th percentile	25th percentile	75th percentile	95th percentile	Max
Cars (n=9)										
ATE	0.08	56	0.93	0.08	<MDL[b]	0.07	0.08	1.198	2.871	3.04
β-TBECH	0.04	100	0.50	0.42	0.70	0.08	0.22	0.561	1.178	1.34
BATE	0.09	78	2.52	0.16	<MDL[b]	0.08	0.09	1.239	12.048	18.9
β-TBCO	0.03	100	0.68	0.20	0.11	0.13	0.19	0.502	2.438	3.57
TBPH	0.1	89	1.36	0.60	<MDL[b]	0.12	0.17	0.723	5.495	8.26
HBB	0.01	100	0.28	0.23	0.04	0.04	0.09	0.330	0.722	0.92
HBCD	0.16	100	47.7	37.5	17.39	18.5	32.6	59.717	94.161	105
EH-TBB	0.01	100	18.4	5.81	0.39	1.74	4.52	16.001	67.018	90.7
BTBPE	0.01	100	3.69	2.36	1.32	1.34	1.41	3.368	10.316	13.4
anti-DP	0.01	100	1.65	0.99	0.70	0.74	0.91	1.513	4.270	5.65
syn-DP	0.02	100	2.10	1.50	0.80	0.86	1.07	2.361	4.811	4.94
ΣNon-PBDEs	---	---	***79.8***	***49.9***	***20.8***	---	---	---	---	***255***

a. Detection Frequency

b. Method Detection Limit

Non-PBDEs were present in the three microenvironments sampled ranging from 40% detection frequency for ATE to 100% for HBB, HBCD and EH-TBB as shown in Table 2.8 and Figure 2.7. The highest concentration of non-PBDEs were attained in car samples followed by workplaces and home samples. The sum median concentrations of the non-PBDEs in the three microenvironments were 8.30, 28.9 and 49.9 ng g^{-1} for homes, workplaces and cars respectively. This shows the PBDEs median concentrations being higher than the non-PBDEs by approximately 7 times in homes, 15 times in workplaces and 55 in cars respectively as listed in Tables 2.5 and 2.8. The dominant non-PBDE in this study was HBCD as shown in Figure 2.7 relative to the other 10 non-PBDE compounds. HBCD was detected with 100% detection frequency indicating its presence in all samples in the three microenvironments.

Figure 2.7: Percent composition of non-PBDEs in homes (top panel), workplaces (middle panel) and cars (bottom panel). Values on the x-axis refer to the sample number and the percentage on the y-axis. TBECH and TCBO in the figure refer to *β*-TBECH and *β*-TCBO.

HBCD median concentration of the compounds was found to be 6.15, 18.6 and 37.5 ng g^{-1} in homes, workplaces and car samples respectively. This is clearly presented in Tables 2.8 and 2.9. It is worth mentioning that HBCD was highest in the very same sample that had both the highest penta-BDEs and second highest deca-BDE concentrations. The high percentage of HBCD indicates its high use in commercial products despite being categorized as a Persistent Organic Pollutant of the Stockholm Convention. The compound has similar properties to PBDEs namely being persistent, toxic and bio-accumulative. This compound is found in three diastereoisomers; α, β and γ. The γ-HBCD is considered the most abundant, ranging between 75-89% of the total HBCD followed by β-HBCD accounting for 10-13% and α-HBCD accounting for only 1-12% [99]. In this thesis, HBCD reported is the total of all three isomers as they were not separated during the analysis on the DB5 column and all co-eluted as one peak [55].

Another compound that was found in all samples is EH-TBB. The median concentrations for this species were 0.81, 7.14 and 5.81 ng g^{-1} in homes, workplaces and cars respectively. This compound as mentioned earlier, is a commercial product known as Firemaster® which was introduced to replace the penta-BDE [55]. The compound was determined to be 2 to 5 times lower in concentration than the penta-BDE found in this study. The compound HBB had a 100% detection frequency in all dust samples with a median concentration of 0.10 in homes, 0.05 in workplaces and finally 0.23 ng g^{-1} in cars. The concentrations were quite low and this has been the case in North America where the production volume of this chemical was not that high (2 tons per year in 1986 and 230 tons per year in 1998) [100]. The EU, on the other hand does not report HBB as a currently produced chemical [101].

Another compound that was frequently detected is TBPH, found with a detection frequency of 59% in homes, 80% in workplaces and 89% in cars. TBPH median concentration was not high relative to other detected non-PBDEs; being 0.12, 0.09 and 0.60 ng g^{-1} in homes, workplaces and cars respectively. The approximate ratio between EH-TBB and TPBH in the Firemaster-550® commercial mixture is 4:1 [55]. On the other hand, the observed compounds in this study had a noticeable variation to this ratio indicating that the sources of the compounds are most likely different.

Dechlorane plus (DP) is the commercial name of the only chlorinated compound investigated in this study. The technical DP formulation is known to contain about 65% chlorine by weight. It is considered an additive flame retardant used in different products like wire coatings and plastic roofing materials. The compound is used minimally in the automotive, electronics and the textile industries [102]. This chlorinated compound is present in two stereoisomers; *syn* and *anti*. Both stereoisomers have different physical and chemical properties leading to different environmental fates and persistence activities. Both *syn*- and *anti*-stereoisomers were detected in all car samples, which the workplace samples had a 20% decrease of the *anti*-stereoisomers. Both stereoisomers have reached 5.65 and 4.94 ng g^{-1} in both the *anti*-DP and *syn*-DP respectively in car samples. The percentage was lowest in the home samples having 47% and 71% in both *anti*-DP and *syn*-DP reaching a median of 0.01 and 0.34 ng g^{-1} respectively as shown in Table 2.8. The ratio between both stereoisomers varies within a range of 0.33 to 0.67 depending on the manufacturer [103].

The presence of the flame retardants is thought to be due to the breakdown of the chemicals from household items like computers and televisions when they heat up or materials such as cushions and curtains when used. The chemicals breakdown forming either dust particles that might release off gases to the indoor dust followed by partitioning to dust due to the low vapor pressures of PBDEs and HBCDs. This is thought to be a source of contamination to outdoor air from the PBDEs present indoor [104, 105].

House dust can act as a reservoir for PBDEs where the estimated release of PBDEs per house is about 4 mg/h in the U.S. where most of the released chemicals gets settled on floor dust [105]. To the best of our knowledge, in Egypt, the use of flame retardants is not regulated therefore, PBDEs and non-PBDEs can be obtained through imported consumer goods which consequently can lead to the release of the compounds when used [106].

2.6 Comparison of PBDEs and non-PBDEs to published data

Tables 2.6 and 2.9 lists the PBDE's and non-PBDE's median values respectively as detailed in this study in relation to similar reported studies from various countries. Data of the PBDEs were more abundant than those of novel flame retardants allowing a richer comparison of the three congeners; penta, octa and deca formulations.

The median concentration of the selected penta formulation congeners (ΣBDEs 47, 99, 100) for home samples in this study was 4.76 ng g^{-1} which was similar to other studies. This value is similar to that of South Africa which had a median concentration of < 5.33 ng g^{-1} [90]. Two studies in Kuwait in 2013 and 2006, report median values of 3 ng g^{-1} and 6.75 ng g^{-1} respectively [62, 72]. Pakistan on the other hand had a median concentration for the penta formulation of 3.3 ng g^{-1} in 2013 and < 1.37 ng g^{-1} in 2012 [62, 91].

Studies from Asia including South China [30], Taiwan [77] and Japan [92] reported median concentrations of the penta formulation congeners (ΣBDEs 47, 99, 100) 19.2 ng g^{-1}, 17.9 ng g^{-1} and 11.6 ng g^{-1} respectively. The values reported from Africa including this study are significantly lower than those from Asia and other countries from Europe and U.S. In Canada for example, the median concentration in a Vancouver study was shown to be 697 ng g^{-1} [35] and 803 ng g^{-1} in Ottawa for the three penta congener formulations [71]. The median concentration value was even higher in the U.S. being 5020 ng g^{-1} for the penta formulations in California [9]. In general, North America has the highest median concentrations of these compounds as listed in Table 2.6 [9, 35, 71, 107]. Values were also reported from countries like New Zealand [98], Belgium [94] and Poland [96]. It is very noticeable that the highest level of PBDEs is found in California due to their wide use of the formulation before being banned and due to its unique flammability standards legislation. The production of these two PBDE commercial mixtures were ceased by January 2005 in the U.S. [108]. Almost 70000 tons were produced every year in which approximately half the production was used in products sold in both U.S. and Canada [108]. The octa congener BDE 183 on the other hand was relatively low in all studies ranging from a median concentration of 0.75 ng g^{-1} in Pakistan [91], 1.05 ng g^{-1} in this study and highest in U.S.A., 28 ng g^{-1}. The median concentration of BDE 209 reported here for house dust is 40.2 ng g^{-1} which is considered the lowest worldwide apart from the other African study in South Africa that had a median < 1.8 ng g^{-1} [90] and in Pakistan 19.7 ng g^{-1} [91]. BDE 209 was highest in UK with a median concentration 8100 ng g^{-1} [93] followed by Japan at 5500 ng g^{-1} [92] South China at 2640 ng g^{-1} [30], U.S.A. [9, 107] and Canada [35] as shown in Table 2.6.

The above mentioned median concentrations were all home samples. In cars, PBDEs levels were similar to that of the home samples. The levels were among the lowest reported as shown in Table 2.6. This implies to the levels of BDE 209 too that had a median concentration of 1540 ng g^{-1}. A possible explanation for this is that Egypt is a very hot country with temperatures reaching up to 40 °C which might lead to higher volatilization of the FRs especially in cars. It has been mentioned earlier that BDE 209 is prone to degradation. This would also hold for the values of Pakistan and Kuwait being 625 and 665 ng g^{-1} respectively [62], proving the validity of the point stated as those countries are known for their elevated temperatures. Moving on to workplaces, Egypt still had lower median concentrations of BDE 209 being 366 ng g^{-1} this compares to Japan with values of 1100 ng g^{-1} [92] while the UK had the highest median concentration reported of 6200 ng g^{-1} [93].

The non-PBDEs data is very scarce with HBCD being the most monitored and most abundant novel flame retardant as shown in Table 2.9. The level of non-PBDEs in Egyptian dust were similar to that of PBDEs; both were among the lowest reported in literature. For example, HBCD in house dusts in Europe and U.S. were several orders of magnitude higher [35, 55, 63, 109]. The UK had the highest HBCD median concentration of 4100 ng g^{-1} [12]. The same applied to EH-TBB which was higher by 3 orders of magnitudes in Canada [35] and U.S. [9].

Table 2.9: Median concentration of non-PBDEs in ng g^{-1} reported from dust in homes, workplaces and cars.

Location[a]	TBPH	HBB	HBCD	EH-TBB	BTBPE	*anti*-DP	*syn*-DP	Reference
Homes								
Egypt (Cairo)	0.1	0.1	6	0.8	0.2	0.01	0.3	This study
CA (Vancouver)	1.5	3.7	270	120	0.3	4	2.8	[35]
UK (Birmingham)	---	---	730	---	---	---	---	[63]
CA (Toronto)	---	---	640	---	---	---	---	[63]
U.S. (Austin)	---	---	390	---	---	---	---	[63]
U.S. (Boston)	---	---	354[b],144[c]	---	---	---	---	[55]
UK	---	---	4100[d]	---	---	---	---	[12]
Sweden	---	---	100[e],45[f]	---	---	---	---	[64]
Germany	---	---	345	---	<10	---	---	[109]
U.S. (California)	<2	1	190	48	---	7.5	10	[9]
U.S. (California)	<2	<2	160	100	---	3	<2	[9]
Kuwait	---	1.2	0.8	---	6.8	---	---	[62]
Pakistan	---	0.2	0.4	---	15	---	---	[62]
Workplaces								
Egypt (Cairo)	0.09	0.05	19	7.1	1.3	0.3	1	This study
UK	---	---	650	---	---	---	---	[63]
Sweden	---	---	300	---	---	---	---	[64]
Cars								
Egypt (Cairo)	0.6	0.2	37	5.8	2.4	1	2	This study
Sweden	---	---	54	---	---	---	---	[64]
Kuwait	---	3	0.5	---	4	---	---	[62]
Pakistan	---	0.6	0.3	---	10.5	---	---	[62]

a) City or state is indicated in parenthesis when available. b) Value reported for living room. c) Value reported for bedroom. d) Value reported for day care. e) Value reported for homes. f) Value reported for apartments (same study reported a value of 340 for daycares)

The differences of the levels of PBDEs in indoor dust in different countries might account for the different fire safety regulations as stated earlier in the California studies. These regulations are more strict in Western Europe (in specific the UK) [110] and North America while in Egypt, to the best of our knowledge, there is a lack of fire safety regulations [106]. The presence of these compounds in dust may be due to the importation of goods that have PBDEs applied to them and subsequently being released into the microenvironments.

2.7 Implication for human exposure via dust ingestion

Studies have shown that ingestion of indoor dust is one of the significant exposure pathways to brominated flame retardants aside from air inhalation and diet [111, 112]. The measured concentrations of PBDEs and HBCD (which was the most significant non-PBDE compound studied here) were used to estimate the exposure of adults and toddlers via indoor dust ingestion in Cairo, Egypt. The sum of exposure via dust ingestion = $[(C_H F_H) + (C_W F_W) + (C_C F_C)] \times I_R$/body weight, is the equation previously used to calculate the total daily intake of PBDEs through dust ingestion [62]. The sum of exposure which is the total daily human exposure to PBDEs via dust ingestion here is expressed in ng (kg body weight)$^{-1}$ day^{-1}. PBDEs concentration of homes, workplaces and cars were expressed as C_H, C_W, C_C respectively having the unit ng g^{-1}. Moreover, the terms F_H, F_W, F_C are the average fraction of time spent in each of home, workplace and car microenvironment respectively; IR represents the daily dust ingestion in mg/day and the body weight of the target individual. The average body weights assumed are 70 kg for adults and 12 kg for toddlers [113]. Due to insufficient data on absorption, an assumption for the total absorption of contaminants for all congeners was set, leading to a possible overestimation of the exposure [61]. Recent studies have shown that less than 50% of PBDEs present in dust are usually bio-accessible in vitro digestion [114]. To our knowledge, there exists no comprehensive dataset that describes time-activity patterns for the Egyptian population. Therefore, overall exposure estimates are based on the assumption that dust ingestion occurs to typical activity patterns reported previously. It was estimated that adults spend 63.8% of their time at home, 22.3% at work and 4.1% in a car. On the other hand, for toddlers the time breakdown is quite different. They spend 86.1% at home and 4.1% in a car which is pretty much the same percentage as adults. The rest of the time for adults and toddlers were spent elsewhere in outdoors or other locations [115]. The mean and high exposure rates were estimated for adults to be 20 and 50 mg/day respectively and 50 and 200 mg/day respectively for toddlers [116]. Four concentration levels of the total PBDEs congeners were calculated for each of the three different microenvironments; 5th percentile, 25th, 75th and 95th. The 5th percentile represents the low exposed group, while the 25th represented the median where the majority of the population lies. The 95th percentile was the fourth and last percentile representing the high values while the maximum concentrations detected would be the worst case scenario. The calculated intake of ΣPBDEs and HBCD in ng (kgbw^{-1}) day^{-1} at these different exposure scenarios for adults and toddlers are shown in Table

2.10. The reference dose for oral exposure for PBDEs 47, 99, 153 and 209 are 100, 100, 200 and 7000 ng kgbw^{-1} day^{-1} respectively as listed by the US-EPA [117] and 0.2 mg kgbw^{-1} day^{-1} for HBCD [118]. Despite the assumptions made here and discussed earlier which may lead to overestimating the exposure, it is clear that the exposure levels for the ΣPBDEs and for HBCD calculated here are several orders of magnitude lower than their reference doses for oral exposure.

Table 2.10: Estimated human exposure in ng kg^{-1} day^{-1} of PBDEs and HBCD via dust ingestion from microenvironment based on mean and high dust intake rates for toddlers and adults.

	Adults		**Toddlers**	
	Total PBDEs[a]	**HBCD**	**Total PBDEs[a]**	**HBCD**
Average exposure				
5th percentile	0.01	0.001	0.07	0.009
Median	0.06	0.003	0.5	0.03
95th percentile	4.21	0.02	8.1	0.3
Max	5.39	0.03	13.3	0.6
High exposure				
5th percentile	0.02	0.003	0.3	0.04
Median	0.14	0.007	1.9	0.1
95th percentile	10.5	0.05	32.6	1.2
Max	13.5	0.08	53.1	2.3

a- For maximum tolerable dose (Reference dose) as listed by the US-EPA, see reference 117.

2.8 Correlations

Correlation analysis was performed between the different congeners to identify whether they originate from the same source and if they will experience similar fates. The Pearson correlations were calculated using SPSS version 17.0 for Windows. The Pearson correlations are statistically significant if the p value is < 0.05. Correlation calculations were performed only on compounds that were found in more than 90% in the samples. If values were not detected (or below DL) then they were automatically removed from the correlation calculation as in the case of BDE 190. Correlation showed that the penta-BDE congeners were positively correlated to one another ($p < 0.002$). The penta-BDE and the deca-formulation were not correlated ($p > 0.05$) indicating a high chance of originating from different sources. For the non-PBDEs, some compounds were positively correlated indicating the high possibility of originating from the same source. The two isomers *anti*- and *syn*-DP were positively correlated, which is expected given that they have the same primary source and similar properties that would most likely result in similar environmental fates. The correlation analysis is a statistical computational method to indicate whether the compounds have the same origin if they were positively correlated ($p < 0.05$) or have different sources of emissions leading to various environmental fates.

2.9 Conclusion

This chapter has reported the levels of PBDEs and non-PBDEs on the limited number of samples obtained from the greater Cairo region in Egypt where dust samples were collected from three microenvironments; homes, workplaces and cars in the winter season. The minimum, maximum, median and mean were calculated for fourteen BDE congeners and eleven non-PBDE flame retardants. The percentage composition of each congener was reported and based on the figures illustrated; the levels of BDE 209 were the most prevalent out of all having a median concentration of 40.2, 366 and 1540 ng g^{-1} in homes, workplaces and cars respectively. Based on the reported health risk of PBDEs, they were banned with the exception of BDE 209. This, has increased the demand for new compounds that could meet the flammability regulation which are termed non-PBDEs. The detection frequencies of some of these compounds in our study were between 40% and 100%. The ∑non-PBDEs median concentrations found here were 8.30, 28.9 and 49.9 ng g^{-1} in homes, workplaces and cars respectively. The level of non-PBDEs was significantly less than that of PBDEs. Positive correlations were present between PBDEs compounds and the same applied for non-PBDEs compounds concluding the same origin source. The case was different between the PBDEs compounds and the non-PBDEs resulting from distinguished different sources. Comparing the contaminant levels obtained here to other countries, indicate levels among the lowest reported therefore most likely there should be no immediate risks on human health through ingestion. However, chronic effects are yet unknown.

Further studies could involve periodical research performed on samples collected and analyzed in different seasons to examine the effects of temperature variation on the target analytes. Another factor that can be taken into consideration is the composition of dust particles, in this work, it was predominantly silica based; however it may be possible that different particle compositions may influence their adsorption properties thus reflecting on their respective target analyte levels.

References

[1] Karter MJ Jr (2008) Fire loss in the United States 2007. National Fire Protection Association, USA

[2] Alaee M, Arias P, Sjodin A, Bergman A˜ (2003) Environ Int 29:683

[3] WHO (1997) Environmental health criteria 192. Flame retardants: a general introduction. World Health Organization, Geneva

[4] Wilkie CA, Morgan AB (2010) Fire retardancy of polymeric materials. CRC, Boca Raton

[5] Kuryla WC, Papa AJ. Flame retardants in polymeric materials. New York: Marcel Dekker, 1991.

[6] Troitzsch J (ed) (1990) International plastics flammability handbook: principles, regulations, testings and approval. Hanser, Munich

[7] U.S. Environmental Protection Agency. Polybrominated diphenyl ethers (PBDEs); Washington, D.C.; 2010 [Accessed in 2010. Available from: http://www.epa.gov/oppt/pbde/].

[8] ATSDR. Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers (PBBs and PBDEs); Agency for Toxic Substances and Disease Registry: Atlanta, GA, 2004.

[9] Dodson RE, Perovich L, Covaci A, Van den Eeede N, Ionas A, Dirtu A, et al. After the PBDE phase-out: a broad suite of flame retardants in repeat house dust samples from California. Environ Sci Technol 2012;46:13056–66.

[10] Watkins DJ, McClean MD, Fraser AJ, Weinberg J, Stapleton H, Webster TF. Associations between PBDEs in office air, dust, and surface wipes. Environ Int 2013;59:124–32.

[11] Cunha SC, Kalachova K, Pulkrabova J, Fernandes JO, Oliveira MBPP, Alves A, et al. Polybrominated diphenyl ethers (PBDEs) contents in house and car dust of Portugal by pressurized liquid extraction (PLE) and gas chromatography–mass spectrometry. (GC–MS). Chemosphere 2010;78:1263–71.

[12] Harrad S, Goosey E, Desborough J, Abdallah MA, Roosens L, Covaci A. 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. Environ Sci Technol 2010;44(11):4198–202.

[13] Möller A, Xie Z, SturmR, Ebinghaus R. Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic. Environ Pollut 2011;159:1577–83.

[14] Odusanya DO, Okonkwo JO, Botha B. Polybrominated diphenyl ethers (PBDEs) in leachates from selected landfill sites in South Africa. Waste Manag 2009;29:96–102.

[15] Sonne C, Gustavson K, Rigét FF, Dietz R, Birkved M, Letcher RJ, et al. Reproductive performance in East Greenland polar bears (Ursus maritimus) may be affected by organohalogen contaminants as shown by physiologically-based pharmacokinetic (PBPK) modelling. Chemosphere 2009;77:1558–68.

[16] Vetter W, von der Recke R, Ostrowicz P, Rosenfelder N. Liquid chromatographic enantioseparation of the brominated flame retardant 2,3-dibromopropyl-2,4,6 tribromophenyl ether (DPTE) and enantiomer fractions in seal blubber. Chemosphere 2010;78(2):134–8.

[17] Venier M, Hites RA. Flame retardants in the serum of pet dogs and in their food. Environ Sci Technol 2011;45:4602–8.

[18] Fromme H, Körner W, Shahin N, Wanner A, Albrecht M, Boehmer S, et al. Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and biomonitoring in Germany. Environ Int 2009;35:1125–35.

[19] Johnson PI, Stapleton HM, Sjodin A, Meeker JD. Relationships between polybrominated diphenyl ether concentrations in house dust and serum. Environ Sci Technol 2010;44:5627–32.

[20] Toms LML, Harden F, Paepke O, Hobson P, Jake Ryan J,Mueller JF. Higher accumulation of polybrominated diphenyl ethers in infants than in adults. Environ Sci Technol 2008;42(19):7510–5.

[21] Roosens L, AbdallahMA-E, Harrad S, Neels H, Covaci A. Factors influencing concentrations of polybrominated diphenyl ethers (PBDEs) in students from Antwerp, Belgium. Environ Sci Technol 2009;43:3535–41.

[22] Thomsen C, Stigum H, Froshaug M, Broadwell SL, Becher G, Eggesbo M. Determinants of brominated flame retardants in breast milk from a large scale Norwegian study. Environ Int 2010;36:68–74.

[23] Frederiksen M, Vorkamp K, Thomsen M, Knudsen LE. Human internal and external exposure to PBDEs — a review of levels and sources. Int J Hyg Environ Health 2009;212:109–34.

[24] de Boer J, de Boer K, Boon JP (2000) Polybrominated biphenyls and diphenylethers. Springer, Berlin

[25] La Guardia, MJ; Hale, RC; Harvey, E. (2006) Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ Sci Technol 40:6247−6254.

[26] B. Keet, N. Giera; R. Gillett; and K. Verschueren (2010) Investigation of brominated flame retardants present in articles being used, recycled and disposed of in New Zealand

[27] EU (European Union). (2001) Risk assessment report: diphenyl ether, pentabromo derivative (pentabromodiphenyl ether). European Chemicals Bureau, Luxembourg. ISBN 92-894-0479-5.

[28] EU (European Union). (2002) Risk assessment report: bis(pentabromodiphenyl) ether). European Chemicals Bureau, Luxembourg, Belgium.

[29] EU (European Union). (2003) Risk assessment report: diphenyl ether, octabromo derivative (octabromodiphenyl ether). European Chemicals Bureau, Luxembourg.

[30] Chen L, Huang Y, Xu Z, Wen L, Peng X, Ye Z, et al. Human exposure to PBDEs via house dust ingestion in Guangzhou, South China. Arch Environ Contam Toxicol 2011;60:556–64.

[31] Li K. and Fu S., Polybrominated Diphenyl Ethers (PBDEs) in House Dust in Beijing, China. Bull Environ Contam Toxicol (2013) 91:382–385

[32] Lagalante AF, Oswald TD, Calvosa FC. Polybrominated diphenyl ether (PBDE) levels in dust from previously owned automobiles at United States dealerships. Environ Int 2009;35(3):539–44.

[33] Krol S, Zabiegała Z, Namieśnik J. Determination of polybrominated diphenyl ethers in house dust using standard addition method and gas chromatography with electron capture and mass spectrometric detection. J Chromatogr A 2012;1249:201-14.

[34] Krol S, Zabiegała Z, Namieśnik J. PBDEs in environmental samples: sampling and analysis. Talanta 2013;93:1–17.

[35] Shoeib M, Harner T, Webster G, Sverko E, Cheng Y. Legacy and current-use flame retardants in house dust from Vancouver, Canada. Environ Pollut 2012;169:175–82.

[36] Toms, L-M, Hearn, L., Kennedy, K., Harden, F. et al. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. Environment International 35 (2009) 864–869.

[37] Nordic Council of Ministers. Polybrominated Diphenyl Ethers: Food Contamination and Potential Risks; Report from an NNT project group; TemaNord: Copenhagen, Denmark, 1998; 1998: 503.

[38] de Wit, C.A., 2002. An overview of brominated flame retardants in the environment. Chemosphere 46, 583–624.

[39] Alaee, M., Arias, P., Sjodin, A., 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. Environ. Int. 29, 683–689.

[40] van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88, 1119–1153.

[41] Wania, F., Dugani, C.G. 2003. Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models. Environmental Toxicology and Chemistry 22, 1252-1261.

[42] Prevedouros K, Jones KC, Sweetman AJ. Estimation of the production, consumption, and atmospheric emissions of pentabrominated diphenyl ether in Europe between 1970 and 2000. Environ. Sci. Technol. 2004;38:3224–31.

[43] Ward J, Mohapatra SP, Mitchell A. An overview of policies for managing polybrominated diphenyl ethers (PBDEs) in the Great Lakes basin. Environ Int 2008;34:1148–56.

[44] Stockholm Convention text and annexes as amended in 2009. Available at http://chm.pops.int/Convention/tabid/54/language/en-US/Default.aspx#convtext, 2009. [Accessed 07/17/2014].

[45] U.S. EPA. Polybrominated diphenyl ethers (PBDEs) action plan summary. http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pbde.html, 2012. [Accessed 07/17/2004].

[46] European Court of Justice. Cases C-14/06 and C-295/06, Judgement of the Court, 1 April 2008, Directive 2002/95/EC and Commission Decision 2005/717/EC. http://curia.europa.eu, 2008. [accessed 07.10].

[47] Birnbaum, L.; Staskal, D. F. Brominated flame retardants: cause for concern? *Environmental Health Perspectives* **2004**, *112*, 9-16.

[48] Talsness, C. E. Overview of toxicological aspects of polybrominated diphenyl ethers: A flame-retardant additive in several consumer products. *Environmental Research* **2008**, *108*, 158-167.

[49] Stapleton, H. M. *Brominated Flame Retardants: Assessing DecaBDE Debromination in the Environment*; EEN: Brussels, Belgium, 2006.

[50] Hites, R. A.; Foran, J. A.; Schwager, S. J.; Knuth, B. A.; Hamilton, M. C.; Carpenter, D. O. Global Assessment of Polybrominated Diphenyl Ethers in Farmed and Wild Salmon. Environmental Science and Technology 2004, 38, 4945-4949.

[51] Schmidt, Charles. "PBDEs in breast milk: levels higher in United States than in Europe - Science Selections". *Environmental Health Perspectives*. Nov 2003.

[52] U.S. Environmental Protection Agency Environmental Profiles of Chemical Flame Retardant Alternatives for Low-Density Polyurethane Foam; United State Environmental Protection Agency, Design for the Environment, 2005.

[53] Fink U, Hajduk F, Wei Y, Mori H. Flame retardants. SRI Consulting SCUP Report Flame Retardants; 2008.

[54] Covaci, A., Harrad, S., Abdallah, M.A.-E., Ali, N., Law, R.J., Herzke, D., de Wit, C.A., 2010. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environment International 37, 532-556.

[55] Stapleton HM, Allen JG, Kelly SM, Konstantinov A, Klosterhaus S, Watkins D, et al. 2008. Alternate and new brominated flame retardants detected in U.S. house dust. Environ Sci Technol 42(18):6910–6916.

[56] Weil, E. D.; Levchik, S. V. Flame Retardants for Polystyrenes in Commercial Use or Development. J. Fire Sci. 2007, 25, 241–265.

[57] Covaci, A.; Gerecke, A. C.; Law, R. J; Voorspoels, S.; Kohler, M.; Heeb, N. V.; Leslie, H.; Allchin, C.; De Boer, J. Hexabromocyclododecanes (HBCDs) in the Environment and Humans: A Review. Environ. Sci. Technol. 2006, 40, 3679–3688.

[58] National Chemicals Inspectorate (KEMI). Draft of the EU Risk Assessment Report on Hexabromocyclododecane; Sundbyberg, Sweden, 2005.

[59] Stockholm Convention text and annexes as amended in 2014. Available at http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx, 2014. [Accessed 08/26/2014].

[60] Covaci A, Harrad S, Abdallah MA-E, Ali N, Law RJ, Herzke D, et al. 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ Int 37(2):532–556.

[61] de Wit CA, Björklund JA, Thuresson K. Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm microenvironments indoor sources and human exposure. Environ Int 2012;39:141–7.

[62] Ali N, Ali L, Mehdi T, Dirtu A, Al-Shammari F, Neels H, et al. Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan: implication for human exposure via dust ingestion. Environ Int 2013;55:62–70.

[63] Abdallah M, Harrad S, Ibarra C, Diamond M, Melymuk L, Robson M, et al. Hexabromocyclodocanes in indoor dust from Canada, United Kingdom and United States. Environ Sci Technol 2008;42:459–64.

[64] Thuresson K, Björklund JA, de Wit CA. Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm microenvironments 1: levels and profiles. Sci Total Environ 2012;414:713–21.

[65] Costa LG, Giordano G, Tagliaferri S, Caglieri A, Mutti A. 2008. Polybrominated diphenyl ether (PBDE) flame retardants: environmental contamination, human body burden and potential adverse health effects. Acta Biomed 79(3):172–183.

[66] Watkins DJ, McClean MD, Fraser AJ, Weinberg J, Stapleton HM, Sjödin A, et al. 2011. Exposure to PBDEs in the office environment: evaluating the relationships between dust, handwipes, and serum. Environ Health Perspect 119:1247–1252.

[67] Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey LE, et al. 2007. Human exposure to PBDEs: associations of PBDE body burdens with food consumption and house dust concentrations. Environ Sci Technol 41(5):1584–1589.

[68] Lippmann M (1977). Regional deposition of particles in the human respiratory tract. In Lee DHK, Murphy S (editors), *Handbook of Physiology: Section IV, Environmental Physiology*, 2nd edition. Williams and Wilkins, Philadelphia. Pp. 213-232.

[69] Jones-Otazo, H., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J.J. and Wilford, B. 2005. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. Environmental Science & Technology, 39: 5121-30.

[70] Stapleton HM, Dodder NG, Offenberg JH, Schantz MM, Wise SA (2005) Polybrominated diphenyl ethers in house dust and clothes dryer lint. Environ Sci Technol 39:925–931.

[71] Wilford BH, Shoeib M, Harner T, Zhu J, Jones KC. Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: Implications for sources and exposure. Environ Sci Technol 2005;39:7027–35.

[72] Gevao B, Al-Bahloul M, Al-Ghadban AN, Al-Omair A, Ali L, Zafar J, et al. House dust as a source of human exposure to polybrominated diphenyl ethers in Kuwait. Chemosphere 2006;64:603–8.

[73] Talsness CE. Overviewof toxicological aspects of polybrominated diphenyl ethers: a flame retardant additive in several consumer products. Environ Res 2008;108:158–67.

[74] Frederiksen M, Vorkamp K, Thomsen M, Knudsen LE. Human internal and external exposure to PBDEs — a review of levels and sources. Int J Hyg Environ Health 2009;212:109–34.

[75] EU (2001) European Union Risk Assessment Report (RAR): Diphenyl ether, pentabromo derivative (pentabromodiphenyl ether). EUR 19730 EN

[76] Schecter A, Paepke O, Ryan J, Tung K, Olson J, Harris TR (2005) PBDEs in US human milk, archived and recent blood, fetal liver, partitioning between milk and blood, cooked and uncooked food and environmental specimens. Organohalogen Compd 651–653.

[77] Chao HR, Shy CG, Huang HL, Koh TW, Tok TS, Chen SCC, Chiang BA, Kuo YM, Chen KC, Chien GPC. Particle-Size Dust Concentrations of Polybrominated Diphenyl Ethers (PBDEs) in Southern Taiwanese Houses and Assessment of the PBDE Daily Intakes in Toddlers and Adults. Aerosol Air Qual Res 2014;14:1299–309.

[78] European Environmental Bureau DECA Press Release. http://www.eeb.org/documents/010408-DECA-PRESS-RELEASE-FINAL.pdf. Accessed 20 July 2010.

[79] Eriksson P, Jakobsson E, Fredriksson A. Brominated flame retardants: a novel class of developmental neurotoxicants in our environment? Environ Health Perspect 2001; 109(9):903–8.

[80] Hallgren S, Sinjari T, Håkansson H, Darnerud PO. Effects of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) on thyroid hormone and vitamin A levels in rats and mice. Arch Toxicol 2001;75:200–8.

[81] Meerts IATM, Letcher RJ, Hoving S, Marsh G, Bergman Å, Lemmen JG, et al. In vitro estrogenicity of polybrominated diphenyl ethers, hydroxylated PBDEs, and polybrominated bisphenol A compounds. Environ Health Perspect 2001;109(4):399–407.

[82] McDonald TA. A perspective on the potential health risks of PBDEs. Chemosphere 2002;46:745–55.

[83] Lee SJ, Ikonomou MG, Park H, Baek SY, Chang YS. Polybrominated diphenyl ethers in blood from Korean incinerator workers and general population. Chemosphere 2007;67(3):489–97.

[84] Moon HB, Kannan K, Lee SJ, Choi M. Polybrominated diphenylethers (PBDEs) in sediment and bivalves from Korean coastal waters. Chemosphere 2007;66:243–51.

[85] Qu W, Bi X, Sheng G, Lu S, Fu J, Yuan J, et al. Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. Environ Int 2007;33:1029–34.

[86] Bi X, Thomas GO, Jones KC, Qu W, Sheng G, Martin FL, et al. Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls, and organochlorine pesticides in South China. Environ Sci Technol 2007;41:5647–53.

[87] Meeker JD, Johnson PI, Camann D, Hauser R (2009) Polybrominated diphenyl ether (PBDE) concentrations in house dust are related to hormone levels in men. Sci Total Environ 407(10):3425–3429.

[88] Lim YW, Kim HH, Lee CS, Shin DC, Chang YS, Yang JY. Exposure assessment and health risk of poly-brominated diphenyl ether (PBDE) flame retardants in the indoor environment of elementary school students in Korea. Science of the Total Environment 470–471 (2014) 1376–1389.

[89] Lam JCW, Lau RKF, Murphy MB, Lam PKS. 2009. Temporal trends of hexabromocyclododecanes (HBCDs) and polybrominated diphenyl ethers (PBDEs) and detection of two novel flame retardants in marine mammals from Hong Kong, South China. Environ Sci Technol 43(18):6944–6949.

[90] Kefani K, Okonkwo J, Botha B. Concentrations of polybromobiphenyls and polybromodiphenyl ethers in home dust: relevance to socio-economic status and human exposure rate. Sci Total Environ 2014;470–471:1250–6.

[91] Ali N, Van den Eede N, Dirtu AC, Neels H, Covaci A. Assessment of human exposure to indoor organic contaminants in Pakistan. Indoor Air 2012;22:200–11.

[92] Suzuki G, Nose K, Takigami H, Takahashi S, Sakai SI. PBDEs and PBDD/Fs in house and office dust from Japan. Organohalogen Compd 2006;68:1843–6.

[93] Harrad S, Ibarra C, Abdallah MA, Boon R, Neels H, Covaci A. Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and workplaces: causes of variability and implications for human exposure. Environ Int 2008;34:1170–5.

[94] Ali N, Harrad S, Goosey E, Neels H, Covaci A. “Novel” brominated flame retardants in Belgian and UK indoor dust: implications for human exposure. Chemosphere 2011;83:1360–5.

[95] Karlsson M, Julander A, van Bavel B, Hardell L. Levels of brominated flame retardants in blood in relation to levels in household air and dust. Environ Int 2007;33:62–9.

[96] Krol S, Namieśnik J, Zabiegata B. Occurrence and levels of polybrominated diphenyl ethers (PBDEs) in house dust and hair samples from Northern Poland; an assessment of human exposure. Chemosphere 2014;110:91–6.

[97] Lagalante AF, Shedden CS, Greenbacker PW. Levels of polybrominated diphenyl ethers (PBDEs) in dust from personal automobiles in conjunction with studies on the photochemical degradation of decabromodiphenyl ether (BDE-209). Environ Int 2011;37:899–906.

[98] Harrad S, Ibarra C, Diamond M, Melymuk L, Robson M, Douwes J, Roosens L, Dirtu AC, Covaci A. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States. Environment International 34 (2008) 232–238.

[99] Janak K, Covaci A, Voorspoels S, Becher G. Hexabromocyclododecane in marine species from the Western Scheldt Estuary: diastereoisomer- and enantiomer-specific accumulation. Environ Sci Technol 2005;39:1987–94.

[100] U.S. EPA. Unites States EPA inventory update rule. http://www.epa.gov/cgi/iursrch3_2002.cgi, 2002.

[101] Food Safety Authority of Ireland. Investigation into levels of chlorinated and brominated organic pollutants in carcass fat, offal, eggs and milk produced in Ireland. Monitoring and surveillance series, 2010; 2010.

[102] Weil ED, Levchik SV. Commercial flame retardancy of polyurethanes. J Fire Sci 2004;22:183–210.

[103] Zhu J, Feng YL, Shoeib M. Detection of dechlorane plus in residential indoor dust in the city of Ottawa, Canada. Environ Sci Technol 2007;41(22):7694–8.

[104] Abdallah MA-E, Harrad S. Modification and calibration of a passive air sampler for monitoring vapor and particulate phase brominated flame retardants in indoor air: application to car interiors. Environ Sci Technol 2010;44:3059–65.

[105] Batterman SA, Chernyak S, Jia C, Godwin C, Charles S. Concentrations and emissions of polybrominated diphenyl ethers from U.S. houses and garages. Environ Sci Technol 2009;43:2693–700.

[106] Abdallah MAE, Covaci A. Organophosphate flame retardants in indoor dust from Egypt: implications for human exposure. Environ Sci Technol 2014;48(9):4782–9.

[107] Whitehead TP, Brown FR, Metayer C, Park JS, Does M, Petreas MX, et al. Polybrominated diphenyl ethers in residential dust: sources of variability. Environ Int 2013;57–58:11–24.

[108] Stapleton HM. Instrumental methods and challenges in quantifying polybrominated diphenyl ethers in environmental extracts: a review. Anal Bioanal Chem 2006;386:807–17.

[109] Fromme H, Hilger B, Kopp E, Miserok M, Völkel W. Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and "novel" brominated flame retardants in house dust in Germany. Environ Int 2014;64:61–8.

[110] Zota AR, Rudel RA, Morello-Frosch RA, Brody JG. Elevated house dust and serum concentrations of PBDEs in California: unintended consequences of furniture flammability standards? Environ Sci Technol 2008;42(21):8158–64.

[111] Dirtu AC, Covaci A. Estimation of daily intake of organohalogenated contaminants from food consumption and indoor dust ingestion in Romania. Environ Sci Technol 2010;44:6297–304.

[112] Mercier F, Glorennec P, Thomas O, Le, Bot B. Organic contamination of settled house dust, a review for exposure assessment purposes. Environ Sci Technol 2011;45(16):6716–27.

[113] EFSA. Guidance on selected default values to be used by the EFSA Scientific Committee, Scientific Panels and Units in the absence of actual measured data European Food Safety Authority. EFSA J 2012;10(3):2579.

[114] Lepom P, Berndt M, Duffek A, Warmbrunn-Suckrow E. Oral bioaccessibility of PBDEs in dust using as in vitro gastrointestinal model. Sixth International Symposium on Flame Retardants, San Francisco, California; 2013. [April 7–10].

[115] Harrad S, Abdallah MAE. Brominated flame retardants in dust fromUK cars—within-vehicle spatial variability, evidence for degradation and exposure implications. Chemosphere 2011;82(9):1240–5.

[116] U. S. Environmental Protection Agency. Exposure factors handbook; EPA/600/P-95/002. Washington, DC: EPA; 1997.

[117] U.S. EPA. 2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47) (CASRN 5436-43-1) Integrated Risk Information System US Environmental Protection Agency. (Accessed 14-7-2013) http://www.epa.gov/iris/toxreviews/1010tr.pdf, 2008.

[118] Board on Environmental Studies, Toxicology. Board on Environmental Studies and Toxicology, Committee on Toxicology, Subcommittee on Flame-Retardant Chemicals, National Research Council, Division on Earth and Life Studies, Commission on Life Sciences. Toxicological Risks of Selected Flame-Retardant Chemicals National Academies Press, Jul 6, 2000; 2000.

[119] Hassan Y, Shoeib T. Levels of polybrominated diphenyl ethers and novel flame retardants in microenvironment dust from Egypt: An assessment of human exposure. *Science of the Total Environment* 505 (2015) 47–55.

Chapter 3: Neutral PFCs

3.1 Background

The increased amount of time spent indoors either at home, work or other places raises the attention to what humans are exposed to in these microenvironments [1-3]. Materials treated against water damage and fires have been increasingly used in curtains, furniture and some carpets. The compounds used for this treatment also have other wide industrial applications such as paper packaging, non-stick cookware and fire-fighting foams [4]. Due to these applications, the demand for this class of polyfluorinated and perfluorinated compounds (PFCs) has increased. PFCs can be released to the environment throughout their lifecycle, due to the handling and manufacturing of the chemicals, their use and disposal of the products which contain them. Recently, it was discovered that these compounds are persistent and are found in relatively high concentrations in the indoor environment and are even being linked to potential health hazards [1]. A direct link between the exposure of the compounds and human health has not yet been established as the data remains insufficient; however, the transport pathway and fate remain a concern [1-3]. This work aims to quantify the levels of neutral PFCs in dust samples from Egypt and estimate the human exposure to these chemicals.

3.2 Introduction

Poly- and perfluorinated compounds are man-made chemicals, known as PFCs, which have a hydrophilic group and a hydrophobic, aliphatic chain with different numbers of carbon-fluorine bonds. Such compounds containing only C-F bonds are named per-fluorinated compounds. However, when C-H bonds are present along with C-F bonds these compounds are called polyfluorinated compounds. Fluorine has unique properties with its electron withdrawing powers which gives these structures stability, high ionization energies, electron affinities and electronegativities. In fact, the C-F covalent bond has one of the strongest dissociation energies (around 450 kJ mol^{-1}) [5-11]. These compounds have been manufactured industrially for more than 50 years to the tune of thousands of tons per year [12]. This class of compounds has toxic, persistent properties and accumulates in humans and the environment [13-15]. Consequently, PFCs have been listed under the ‘Persistent Organic Pollutants’ (POPs) as being very toxic, resistant to degradation, prone to have long half-lives in humans and accumulate in food chains [16-17].

Among the most common surfactants found in the market are those made up from perfluoroalkyl acids (PFAAs) that do not easily break and are widespread in the environment [18-20]. PFCs are surfactants that cover two major classes; perfluoroalkly sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs). The most accumulated and persistent are the C8 perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) and perflurooctant sulfonate ($C_8F_{15}SO_3$, PFOS). The functional groups on these compounds known as ionic PFCs [21] determine their properties and thus their use. The structure of PFCs may be divided into three important parts, first is the hydrophobic or oleophobic tail which contains a high fluorine proportion. The second is the hydrophilic group that may include groups like sulfonates or carboxylates or phosphates, etc. The third part is the 'spacer' organic group that links both portions together; hydrophobic/oleophobic and hydrophilic moieties. The spacer which does not necessarily have to be present tends to provide space between the amphophiles that provides better activity of the surfactant through the optimizing of intermolecular interactions [6]. Figure 3.1 shows a PFC tree diagram with the most persistent compounds; PFOS and PFOA – the ionic PFCs.

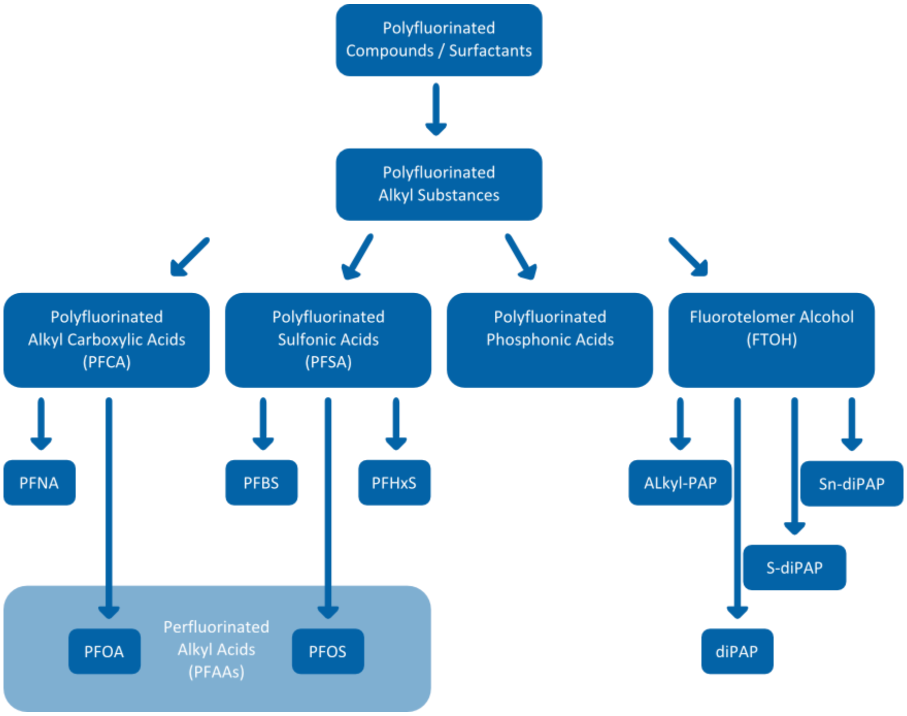
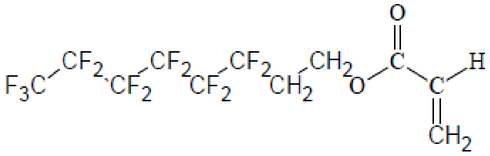
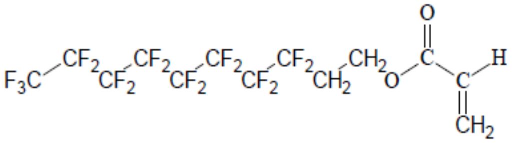
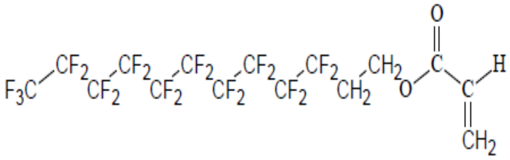
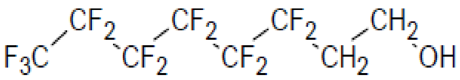
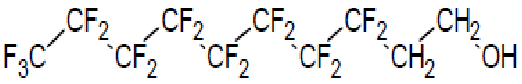
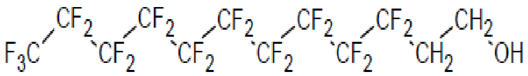
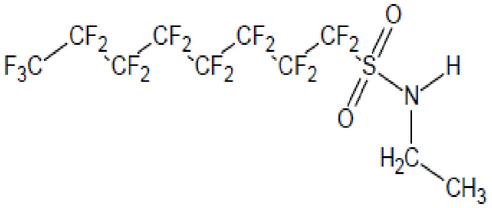
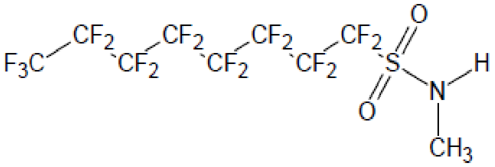
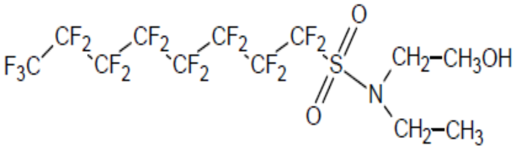
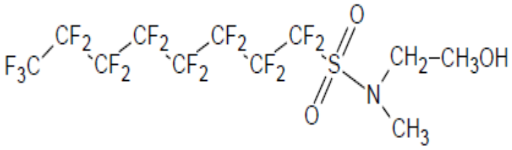


Figure 3.1: Polyfluorinated compounds tree diagram with the most persistent PFOS and PFOA appearing in the bottom blue box [22].

The production of fluorotelomer alcohols FTOH as shown in Figure 3.1 [22] results in the formation of compounds such as 8:2 FTOH, perfluorooctane sulfonamides and sulfonamidoethanols (FOSA/Es). These group of compounds which are typically called neutral PFCs are very volatile and are highly susceptible to be atmospherically oxidized and can transform biologically to form compounds like perfluorinated carboxylates (PFCAs) such as perfluorooctanoic acids (PFOA) and perfluorononanoic acids (PFNA) as well as perflurooctane sulfonates (PFOS). It is for this reason that neutral PFCs are typically referred to as precursor compounds [23]. Table 3.1 lists the full names, commercial trade names and structures of the major ten neutral PFCs compounds that were investigated in this study. PFOS and related compounds were originally produced by 3M. In 2002, 3M announced that certain PFCs were to be phased out due to concerns regarding their toxicity and environmental accumulation [24]. Currently, PFOS and related compounds are listed under the Annex B of the Stockholm Convention on Persistent Organic Pollutants, restricting their manufacture and use [25]. In this chapter, we focus on neutral PFCs. It is interesting to note that this is one of very few studies investigating these compounds in the Middle East.

Table 3.1: Neutral PFCs – Complete compound names, abbreviations and structures.

Number	Analytes	Acronym	Class	Structure
1	6:2 fluorotelomer acrylate	6:2 FTA	Fluorotelomer acrylates (FTAs)	
2	8:2 fluorotelomer acrylate	8:2 FTA		
3	10:2 fluorotelomer acrylate	10:2 FTA		
4	6:2 fluorotelomer alcohol	6:2 FTOH	Fluorotelomer alcohols (FTOHs)	
5	8:2 fluorotelomer alcohol	8:2 FTOH		
6	10:2 fluorotelomer alcohol	10:2 FTOH		

Number	Analytes	Acronym	Class	Structure
7	N-Ethyl perfluorooctane sulfonamide	Et FOSA	Perfluoroalkyl sulfonamids (FASAs)	
8	N-Methyl-perfluorooctane sulfonamide	Me FOSA		
9	N-Ethyl-perfluorooctane sulfonamido ethanol	Et FOSE	Perfluoroalkyl sulfonamide ethanols (FASEs)	
10	N-Methyl-perfluorooctane sulfonamido ethanol	Me FOSE		

PFCs have been very useful anthropogenic compounds. They have been used as surfactants reducing the surface tension due to the lipophilicity of the fluorocarbons having polar functional group [26]. This particular surfactant or non-stick characteristic has allowed PFCs to be popularly used in carpet treatments, textiles, floor polishes, cosmetics, cleaning agents, non-stick cooking utensils, fire-fighting foams as well as other industrial uses which prevent the sticking of stains to materials [27]. PFCs are also used in packaging materials such as oil resistant papers used in pizza boxes and in other food contact materials [4, 28] while EtFOSA, for example is used as an insecticide. Recently, PFCs were found to accumulate in the indoor environment leaving humans with high risk of exposure through inhalation and ingestion [4, 29, 30]. Dust ingestion is regarded as one route of exposure especially for toddlers through their floor to mouth action [31, 32].

3.3 PFCs Health Effects

Since their production in the early 1940s and as the market expanded with their diversity of use, questions about their safety have arisen. In the early 2000s, PFCs health effects have been a major concern [33] as these chemicals were found in nearly all studies investigating their presence in blood samples [34]. Perfluoroalkly sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs) particularly PFOS and PFOA were found to be in blood serum in both humans and animals around the world [35]. The increase of PFC levels in blood were reported and correlated with high cholesterol levels. Recently, several studies have documented several adverse effects for such compounds. For example, it was shown that chronic exposure to PFCs lowers body weight and increases liver mass. PFCs were also shown to cause elevations in the risk of tumors in organs like the pancreas, liver, testes and bladder [36-40]. The association between PFOS or PFOA levels and sperm quality, [41] reduced birth weight, [42] and changes in adult thyroid hormone levels [43] were reported. Because PFOS and PFOA cross the placenta [44] and are found in breast milk, [45] exposures to the developing fetuses and infants are of particular concern.

3.4 Research Work

3.4.1 Chemicals and Reagents

The target analytes include ten neutral PFC compounds that are presented in Table 3.1. The ten neutral compounds fall under four classes being: fluorotelomer acrylates (FTA), fluorotelomer alcohols (FTOH), Methyl/Ethyl perfluorooctane sulfonamides (Me/Et FOSA), Methyl/Ethyl perfluorooctane sulfonamidoethanols (Me/Et FOSE). In addition, mass labeled internal standards ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, d_3N-MeFOSA, d_7 N-MeFOSE, d_5 N-EtFOSA, d_9 N-EtFOSE, and injection standard N,N-dimethyl perfluorooctane sulfonamide (Me_2FOSA) were used for the PFCs analysis.

3.4.2 Gas Chromatography-Mass Spectrometry Methodology

Quantification was performed by the gas chromatography-positive chemical ionization-mass spectrometry (GC-PCI-MS) in the selective ion monitoring mode. Samples were spiked with mass-labeled standard, analytes were separated on a 30 m DB-wax column with 0.25 µm film thickness and 0.25 mm internal diameter. The oven temperature initially was 60 °C, which was held for 10 minutes and gradually increased by 8 °C per minute until reaching 150 °C. Then, the temperature was further increased by 10 °C per minute until reaching 210 °C. Methane was used as a reagent gas in this mode as well. The splitless 2 µL injections opening after 0.5 minute were kept at 200 °C. The temperature of the ion source and quadrupole were 250 and 106 °C respectively. Quantification of the PFASs was normalized against responses of their mass-labeled counterparts which were added prior to the extraction process. For example, the 6:2 FTOH was calibrated against counterparts ^{13}C 6:2 FTOH and 8:2 FTOH was against ^{13}C 8:2 FTOH. Table 3.2 shows each analyte with its corresponding target ion and qualifier ion.

Table 3.2: Details for target neutrals PFASs analyzed by GC/MS employing positive chemical ionization.

Analyte	Quantifier Ion	Qualifier Ion (PCI)	Allocation of the IS
Neutral PFASs			
6:2 FTOH	365.0	327.0	$^{13}C_2$, D_2-6:2 FTOH
8:2 FTOH	465.0	427.0	$^{13}C_2$, D_2-8:2 FTOH
10:2 FTOH	565.0	527.0	$^{13}C_2$, D_2-10:2 FTOH
6:2 FTA	432.9	461.0	$^{13}C_2$, D_2-6:2 FTA
8:2 FTA	518.9	547.0	$^{13}C_2$, D_2-8:2 FTA
10:2 FTA	618.9	647.0	$^{13}C_2$, D_2-10:2 FTA
MeFOSA	514.0	-	D_3-MeFOSA
EtFOSA	528.0	-	D_5-EtFOSA
MeFOSE	540.0	558.0	D_7-MeFOSE
EtFOSE	527.0	554.0	D_9-EtFOSE

Analyte	Quantifier Ion	Qualifier Ion (PCI)	Allocation of the IS
Labeled neutral PFASs			
2 perfluoro hexyl- [1,1 2H2 1,2 ^{13}C2]ethanol	369.0	331.0	^{13}C 6:2 FTOH
2 perfluoro octyl- [1,1 2H2 1,2 ^{13}C2]ethanol	469	431	^{13}C 8:2 FTOH
2 perfluoro decyl- [1,1 2H2 1,2 ^{13}C2]ethanol	569	531	^{13}C 10:2 FTOH
N ethyl D5 perfluoro octane sulfonamide	533	-	D5 N-EtFOSA
N methyl D3 perfluoro octane sulfonamide	517	-	D3 N-MeFOSA
2(N deuteriomethyl perfluoro 1-octane sulfonamido) 1,1,2,2 tetradeutorioethanol	547	565	D7 N-MeFOSE

3.4.3 Quality Assurance / Quality Control

Blank samples were prepared using sodium sulfate with the same procedure described previously as all samples and run between the initial set of calibration solutions and the samples as a verification step of absence to carry-over. The blank sample results were used to obtain the method detection limit (MDL) by obtaining the mean of the field blank values in addition to 3 standard deviations. Results have shown that no neutral PFCs were detected in the blank samples except for 8:2 FTOH and MeFOSE. In the case of compounds that were not detected in the blanks, $\frac{2}{3}$ of the instrumental detection limits (IDLs) were used for MDL calculation. Before the extraction, a standard was spiked into the samples to increase efficiency and compensate for any alteration that may occur to the resulting signals.

The limit of detection (LOD) was obtained from peaks of lowest calibration standard acquiring a signal to noise ratio of 3:1. The LOD ranged from 0.03 to 0.22 pg. To ensure stability of MS response, the calibration solution is run at the beginning, after each 10 samples and at the end of the analysis to correct any possible instrumental drift that may occur during analysis. Recovery of labeled IS fortified in each samples were calculated against the injection standard NN Me_2FOSA included just before the GC/MS analysis. Recovery ranged from 65 ± 8% for L6:2 FTOH to 120 ± 12 % for MeFOSE. All results were blank corrected.

3.5 Results and Discussion (Levels of neutral PFCs)

Ten neutral PFCs levels were calculated in the dust samples obtained from the three microenvironments; homes (n=17), workplaces (n=5) and cars (n=9) from Cairo, Egypt. Figure 3.2 represents an integrated chromatogram using MassHunter from a home sample for the analyte 8:2 FTOH. Its qualifier ion 465.0 is present. The sample has a clear peak with the same retention time as the mass-labeled IS added prior extraction.

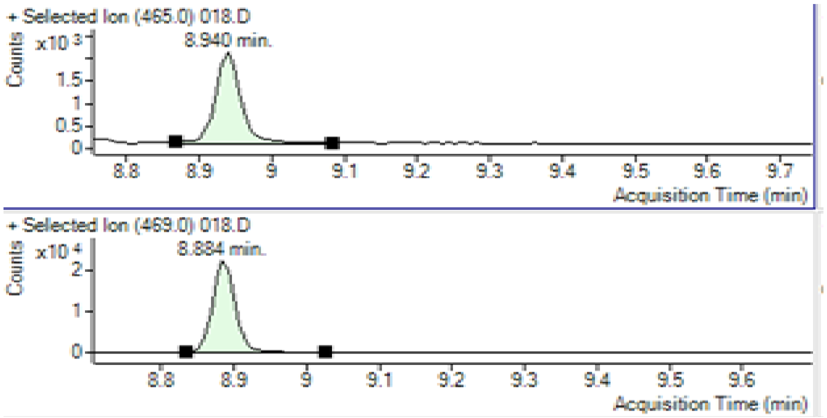


Figure 3.2: Representative chromatogram of 8:2 FTOH in a home sample with its corresponding labeled IS qualifier ions 465.

The mean, median, range, method detection limit and the four percentile distributions were all calculated and presented in Table 3.3. The percentile distribution of each analyte in the three microenvironments; homes, workplaces and cars was presented in Figure 3.3. The mean and median concentration levels of this study along with other countries are presented in Table 3.4. The contaminant level of the three microenvironments is combined and presented in Figure 3.4 giving space for better comparison. In Figure 3.3, the analytes were present in high percentages in the home samples ranging from 41% to 100% for 6:2 FTA and 10:2 FTOH respectively. FTOH was present in 88% of the home samples for 6:2 FTOH, 94% for 8:2 FTOH while 10:2 FTOH was found in all samples. On the other hand, the work samples had all analytes present in all samples except for the 8:2 FTA that was not present in any of the samples. The presence of the analytes in the car samples ranged from 11 to 100%. The dominant analyte was the 10:2 FTOH which was present in the three microenvironments. The car and workplace microenvironments had similar distribution patterns. The FTA was detected in fluctuating amount that might be due to its high volatility and low consumption in products.

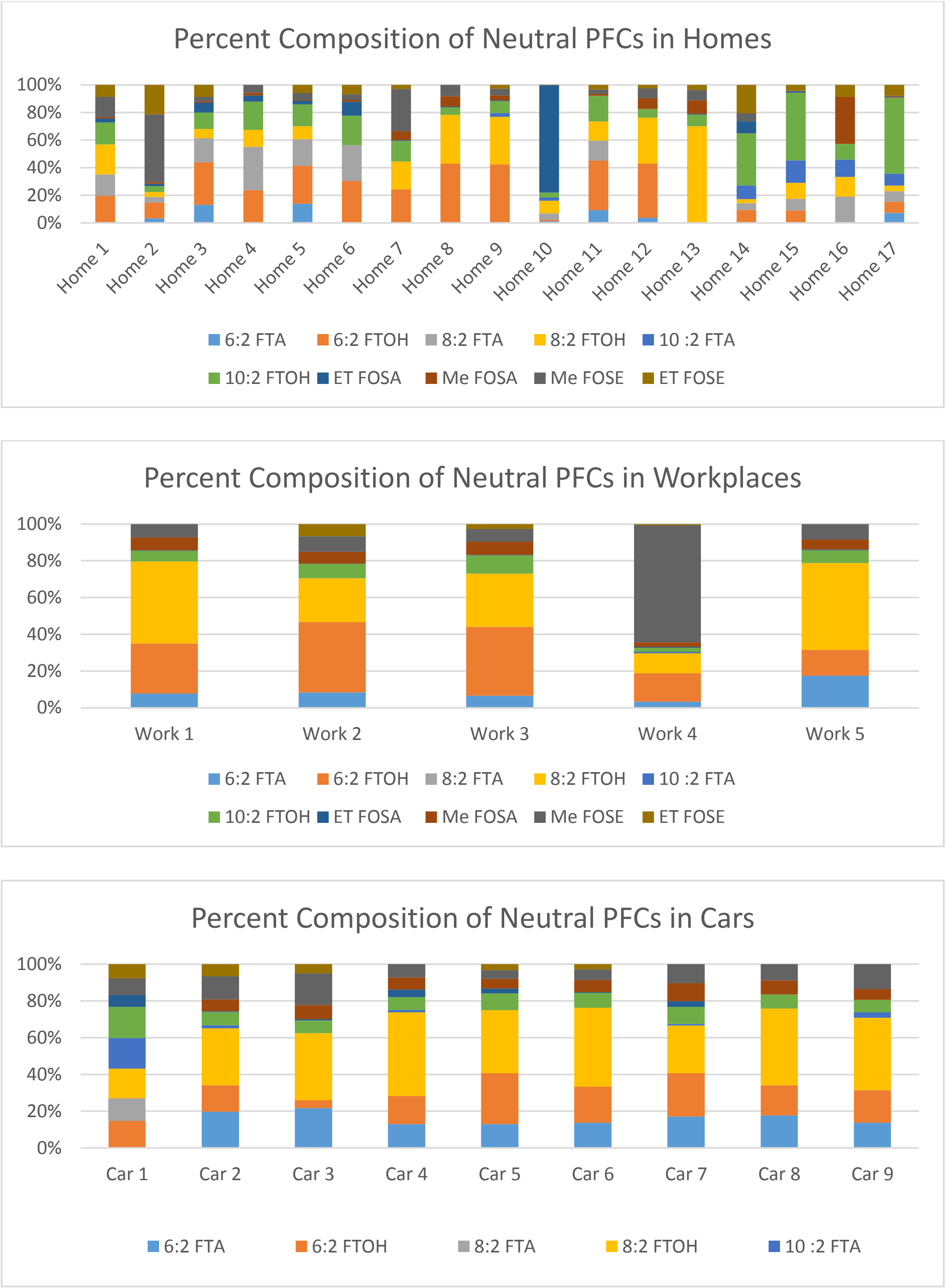


Figure 3.3: Percent composition of neutral PFCs in homes (top panel), workplaces (middle panel) and cars (bottom panel). Values on the x-axis refer to the sample number and percentage is represented on the y-axis.

Figure 3.4 shows the sum of each of the four neutral PFCs classes FTA, FTOH, FOSA and FOSE in the three microenvironments; homes, workplaces and cars. The dominant analyte is the FTOH being highest for the 8:2 FTOH followed by the 6:2 FTOH and the 10:2 FTOH as shown in Table 3.3 and Figure 3.4 giving an indication of its ongoing use in consumer goods. The FTOH analyte ranged from 0.71 to 10.2 ng g^{-1}. All analytes attained the highest levels in car samples.

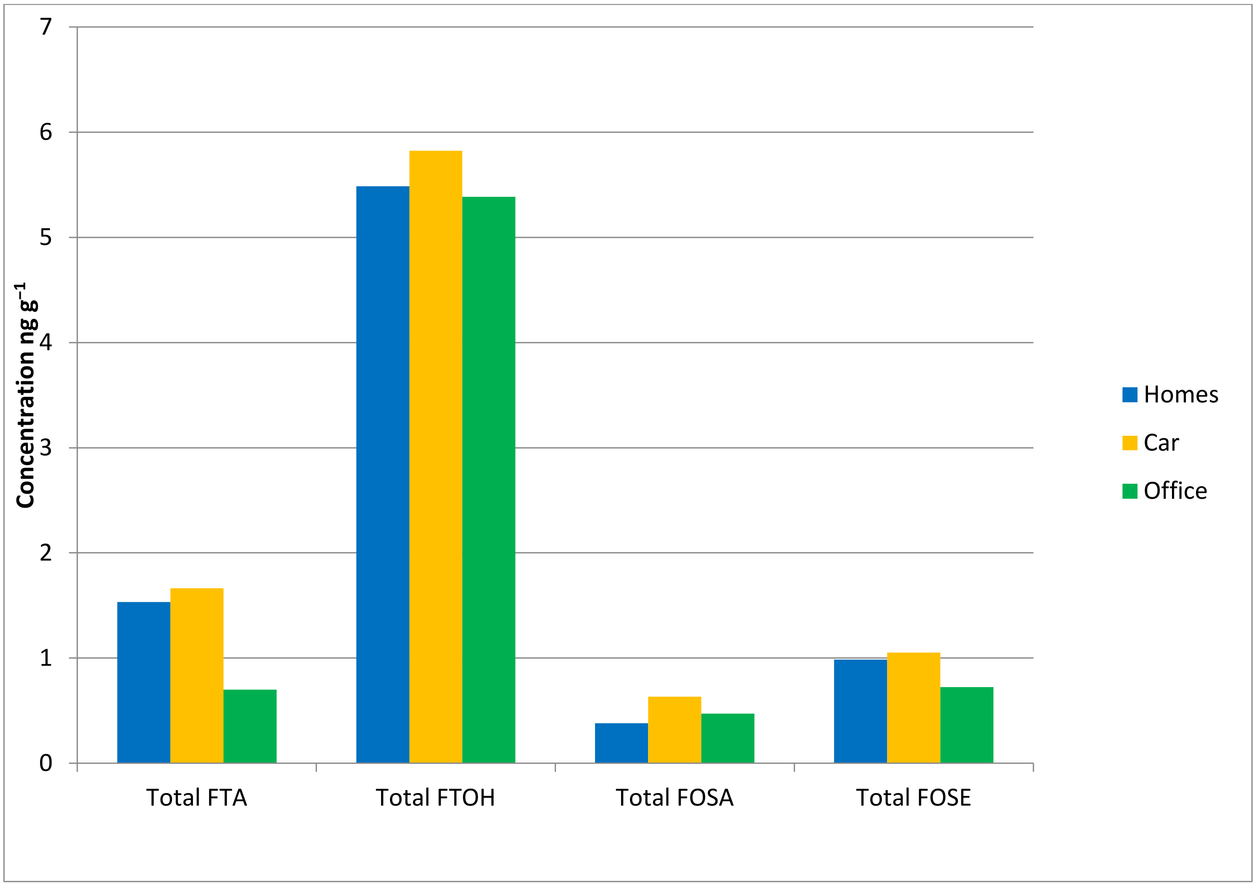


Figure 3.4: A comparative illustration of the contaminant level concentrations of selected neutral PFCs representing the total FTA, total FTOH, total FOSA and total FOSE in the three different microenvironments presented as a bar chart.

The mean and median values for ΣPFCs in this study were 13 ng g^{-1} and 7 ng g^{-1} respectively for home samples, 8 ng g^{-1} and 7 ng g^{-1} for workplaces and finally 12 ng g^{-1} and 9 ng g^{-1} for car samples as shown in Table 3.3. The levels between the three microenvironments were very similar in terms of the mean and median values indicating insignificant variation between them.

Table 3.3: Concentration of Neutral PFCs in ng g^{-1} determined in dust samples collected from 17 homes, 5 workplaces and 9 cars.

Neutral PFCs		% DF[a]	Mean	Median	Min	5th percentile	25th percentile	75th percentile	95th percentile	Max
Home (n=17)										
6:2 FTA		41	0.54	0.00	<MDL[b]	0.00	0.00	1.19	1.90	2.93
6:2 FTOH		88	2.69	2.26	<MDL	0.00	1.20	3.36	6.50	6.79
8:2 FTA		53	1.03	0.61	<MDL	0.00	0.00	1.14	4.53	4.74
8:2 FTOH		94	2.54	1.84	<MDL	0.30	0.82	3.75	6.74	9.12
10:2 FTA		29	0.52	0.00	<MDL	0.00	0.00	0.35	2.58	3.35
10:2 FTOH		100	2.31	1.34	0.38	0.38	0.89	3.01	5.85	10.13
ET FOSA		71	0.32	0.08	<MDL	0.00	0.00	0.60	1.19	1.55
ME FOSA		94	0.77	0.23	<MDL	0.03	0.06	0.48	2.29	9.05
ME FOSE		88	1.14	0.57	<MDL	0.00	0.25	0.76	4.18	9.81
ET FOSE		82	1.04	0.42	<MDL	0.00	0.19	1.90	2.93	4.28
ΣPFCs	***---***	***---***	***12.9***	***7.35***	***0.38***	***0.71***	***3.41***	***16.54***	***38.69***	***61.75***
ΣFTAs	***38.33***									
ΣFTOHs	***119.16***									
ΣFOSAs	***18.45***									
ΣFOSEs	***37.31***									
ΣPFCs	***213.25***									
Workplace (n=5)										
6:2 FTA		100	0.83	0.58	0.41	0.42	0.49	0.76	1.68	1.91
6:2 FTOH		100	2.37	2.33	1.51	1.56	1.73	2.67	3.41	3.59
8:2 FTA		0	0.00	0.00	<MDL	0.00	0.00	0.00	0.00	0.00
8:2 FTOH		100	2.79	2.51	1.66	1.69	1.81	2.82	4.68	5.15
10:2 FTA		20	0.03	0.00	<MDL	0.00	0.00	0.00	0.13	0.16
10:2 FTOH		100	0.55	0.55	0.37	0.39	0.49	0.62	0.72	0.75

Neutral PFCs		% DF[a]	Mean	Median	Min	5th percentile	25th percentile	75th percentile	95th percentile	Max
ET FOSA		100	0.04	0.02	0.01	0.01	0.01	0.05	0.10	0.12
ME FOSA		100	0.50	0.45	0.44	0.44	0.45	0.57	0.58	0.59
ME FOSE		100	0.78	0.58	0.44	0.44	0.46	0.93	1.36	1.47
ET FOSE		60	0.15	0.14	<MDL	0.00	0.00	0.16	0.41	0.47
ΣPFCs	**---**	**---**	***8.04***	***7.16***	***4.84***	***4.95***	***5.44***	***8.58***	***13.07***	***14.21***
ΣFTAs	***8.45***									
ΣFTOHs	***28.55***									
ΣFOSAs	***2.71***									
ΣFOSEs	***4.65***									
ΣPFCs	***44.36***									
Car (n=9)										
6:2 FTA		78	1.76	1.54	<MDL	0.32	1.01	3.01	3.39	3.49
6:2 FTOH		100	2.02	1.83	0.32	0.63	1.40	2.44	3.81	4.20
8:2 FTA		11	0.13	0.00	<MDL	0.00	0.00	0.00	0.69	1.15
8:2 FTOH		100	4.37	3.17	1.21	1.34	2.66	5.44	8.91	9.36
10:2 FTA		56	0.30	0.04	<MDL	0.00	0.00	0.24	1.22	1.56
10:2 FTOH		100	1.00	0.82	0.44	0.47	0.60	1.52	1.60	1.60
ET FOSA		78	0.19	0.08	<MDL	0.00	0.03	0.24	0.58	0.62
ME FOSA		100	0.74	0.55	0.01	0.19	0.47	0.99	1.47	1.53
ME FOSE		100	1.23	0.85	0.42	0.43	0.47	1.72	2.68	3.20
ET FOSE		56	0.29	0.21	<MDL	0.00	0.00	0.37	0.90	1.01
ΣPFCs	**---**	**---**	***12.03***	***9.09***	***2.4***	***3.38***	***6.64***	***15.97***	***25.25***	***27.72***
ΣFTAs	***28.18***									
ΣFTOHs	***66.52***									
ΣFOSAs	***8.33***									
ΣFOSEs	***13.67***									
ΣPFCs	***116.70***									

a. Detection Frequency b. Method Detection Limit

The total ΣPFCs were highest in the home samples (213.25 ng g^{-1}), followed by car samples (116.70 ng g^{-1}) and were lowest for workplaces samples being 44.36 ng g^{-1}. The ΣFTOHs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) showed the highest contaminant level in the three microenvironments of 119, 29 and 67 ng g^{-1} in homes, workplaces and cars respectively. The contaminant level of the analytes were very low in the three microenvironments, ranging between <MDL to 10.13 ng g^{-1} in home samples, <MDL to 5.15 ng g^{-1} in workplaces and <MDL to 9.36 ng g^{-1} in car samples showing no significant variation between the three microenvironments.

The median concentrations of the analytes in the home samples ranged from 0.08 ng g^{-1} for EtFOSA to 2.26 ng g^{-1} for 8:2 FTOH. PFCs were following the order ΣFTOHs > ΣFTAs > FOSEs > ΣFOSAs. The ΣFTAs were magnitudes lower than the other analytes. 6:2 FTOH dominated the pattern of the home dust samples with a mean of 2.69 ng g^{-1} and median 2.26 ng g^{-1} followed by 8:2 FTOH and 10:2 FTOH. The highest analyte found in the samples was 10:2 FTOH with a maximum of 10.13 ng g^{-1}. The dominant sulfonamide compound MeFOSE in home samples had a mean and median, 1.14 and 0.57 ng g^{-1} respectively followed by EtFOSE at 1.04 ng g^{-1} and 0.42 ng g^{-1} for the mean and median respectively. MeFOSA and EtFOSA showed mean and median of 0.77 and 0.23 ng g^{-1} and 0.32 and 0.08 ng g^{-1} respectively. FTOHs constituted around 60% of the total neutral PFASs giving an indication that they are likely still being used.

In addition, the workplace samples had the highest mean for the analyte 8:2 FTOH for 2.79 ng g^{-1}. The same sample was the highest among all the workplace samples with a maximum of 5.15 ng g^{-1}. MeFOSE had a median concentration of 0.58 ng g^{-1} for the workplaces and 0.85 ng g^{-1} for car samples. The same case applied in the car samples where the highest analyte found was 8:2 FTOH having 4.37 ng g^{-1} and 3.17 ng g^{-1} as the highest mean and median values respectively. Both the mean and median had an insignificant difference.

3.6 Comparison of neutral PFCs to published data

Similar studies were done in a few countries like Canada, UK, Spain, Germany, Australia, France, U.S.A. and Asian countries like Kazakhstan and Thailand. No studies were found in Africa. Table 3.4 shows the details of six neutral contaminants that were mostly common in research studies in comparison with this study. U.S. [46, 53] and Europe [47, 52] regions obtained the highest levels of neutral PFCs in comparison with the other countries. In home samples, Canada had the highest mean values for 6:2 FTOH, 8:2 FTOH and 10:2 FTOH, 311, 320, 205 ng g^{-1} respectively compared to 2.69, 2.54, 2.31 ng g^{-1} respectively in this study [48]. Spain had lower contaminant levels than Egypt [49]. The Asian countries, Kazakhstan and Thailand [47] had lower values than Europe, [47, 52] Canada [48] and U.S. [46] but not lower than Egypt and Spain [49]. EtFOSE reached to very high levels in Ottawa, Canada with about 75440 ng g^{-1} in both 2003 and 2005 [50, 51]. The analyte has reached 3900 ng g^{-1} in UK [47] and 3280 ng g^{-1} in Boston, U.S.A. [46, 53]. MeFOSE's mean and median values were accountably high. Research studies obtaining dust from workplaces and cars are scarce. In workplace samples, two other studies were found to compare their values to Egypt's. The maximum values for 6:2 FTOH, 8:2 FTOH and 10:2 FTOH in U.S. were found to be 2390, 3390 and 2050 ng g^{-1} respectively in comparison to 3.59, 5.15 and 0.75 ng g^{-1} respectively [46]. In addition, the mean values for MeFOSA, EtFOSA, MeFOSE and EtFOSE in this study were 0.50, 0.04, 0.78 and 0.15 ng g^{-1} respectively, having median values of 0.45, 0.02, 0.58 and 0.14 ng g^{-1} respectively. The same case applied to car samples where U.S. and UK were higher than Egypt. No contaminant level variation was reported for the three microenvironments.

Table 3.4: Summary of concentrations (ng g^{-1}) of 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, MeFOSA, EtFOSA, MeFOSE and EtFOSE in house dust of this study and other studies.

Country	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE	Reference
Homes								
Cairo, Egypt								**This Study**
Min	<MDL	<MDL	0.38	<MDL	<MDL	<MDL	<MDL	
Max	6.79	9.12	10.13	9.05	1.55	9.81	4.28	
Median	2.26	1.84	1.34	0.23	0.08	0.57	0.42	
Mean	2.69	2.54	2.31	0.77	0.32	1.14	1.04	
Vancouver, Canada[a]								**[48]**
Min	<MDL	9.0	5.7	0.9	<MDL	12	<MDL	
Max	4830	4670	2950	14	73	1676	1590	
Median	49	63	40	1.5	0.14	38	7.1	
Mean	311	320	205	2.2	0.68	111	55	
Ottawa, Canada								**[50]**
Min	2	3	2	0.7	<MDL	3	1	
Max	2500	16315	8176	44	<MDL	8860	75440	
Median	-	-	-	-	-	-	-	
Mean	156	410	233	14	<MDL	412	2200	
Ottawa, Canada								**[51]**
Min	-	-	-	0.7	<LOD	3.3	1.4	
Max	-	-	-	44	<LOD	8860	75440	
Median	-	-	-	-	-	-	-	
Mean	-	-	-	14	<LOD	412	2200	
Birmingham, UK								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	110	840	2500	3900	
Median	-	-	-	<0.1	40	93	34	
Mean	-	-	-	13	98	230	320	
Catalonia, Spain								**[49]**
Min	0.004	0.05	0.036	0.054	0.062	0.12	0.073	
Max	0.06	1.3	0.39	0.054	0.062	0.51	1.9	
Median	0.023	0.35	0.185	0.054	0.062	0.165	0.16	
Mean	0.027	0.409	0.199	0.054	0.062	0.218	0.368	

Country	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE	Reference
Bavaria, Germany[b]								**[52]**
Min	<MDL	2.4	1.0	-	-	-	-	
Max	246	256	232	-	-	-	-	
Median	3.7	13.1	6.6	-	-	-	-	
Mean	19.4	29.5	17.5	-	-	-	-	
Brisbane, New Castle, Sydney, Australia								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	3000	8600	400	440	
Median	-	-	-	<0.1	930	38	20	
Mean	-	-	-	360	2000	84	60	
Toronto, Canada								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	470	7900	47	66	
Median	-	-	-	<0.1	550	3.6	4.9	
Mean	-	-	-	32	1300	8.4	8.4	
Annecy, France								**[47]**
Min	-	-	-	<0.1	23	<0.22	<0.12	
Max	-	-	-	31	320	610	550	
Median	-	-	-	<0.1	130	130	140	
Mean	-	-	-	5.4	150	190	190	
Boston, U.S.A.								**[46]**
Min	<MDL	9.19	12.4	-	-	18.0	12.2	
Max	<MDL	136	46.4	-	-	488	3280	
Median[c]	-	-	-	-	-	-	-	
Mean	-	-	-	-	-	-	-	
Ohio, U.S.A.								**[53]**
Min	29.1	28.5	30.8	-	-	-	-	
Max	804	1660	883	-	-	-	-	
Median	23.5	32.9	30.6	-	-	-	-	
Mean	74.9	167	95.8	-	-	-	-	
Birmingham, UK[d]								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	<0.1	640	8400	13000	
Median	-	-	-	<0.1	30	660	370	
Mean	-	-	-	<0.1	65	1200	1300	

Country	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE	Reference
Augsberg and Michelstadt, Germany								**[47]**
Min	-	-	-	<0.1	36	<0.22	11	
Max	-	-	-	16	730	700	180	
Median	-	-	-	<0.1	120	38	120	
Mean	-	-	-	1.7	190	84	100	
Almaty and Astana, Kazakhstan								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	<0.1	570	73	24	
Median	-	-	-	<0.1	89	6.1	<0.12	
Mean	-	-	-	<0.1	150	12	5.7	
Bangkok and Nakhonsrithammarat, Thailand								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	13	940	140	350	
Median	-	-	-	<0.1	26	4.0	16	
Mean	-	-	-	1.6	140	14	59	
Boulder, CO, U.S.A.								**[47]**
Min	-	-	-	<0.1	41	58	44	
Max	-	-	-	130	380	310	700	
Median	-	-	-	<0.1	99	88	150	
Mean	-	-	-	15	140	120	210	
Workplaces								
Cairo, Egypt								**This Study**
Min	1.51	1.66	0.37	0.44	0.01	0.44	0	
Max	3.59	5.15	0.75	0.59	0.12	1.47	0.47	
Median	2.33	2.51	0.55	0.45	0.02	0.58	0.14	
Mean	2.37	2.79	0.55	0.50	0.04	0.78	0.15	
Boston, U.S.A.								**[46]**
Min	90.6	15.7	12.2	-	-	11.0	<MDL	
Max	2390	3390	2050	-	-	113	<MDL	
Median	-	-	-	-	-	-	-	
Mean	-	-	-	-	-	-	-	

Country	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE	Reference
Birmingham, UK[d]								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	1000	840	920	2600	
Median	-	-	-	<0.1	15.5	220	89	
Mean	-	-	-	61	120	250	290	
Cars								
Cairo, Egypt								**This Study**
Min	0.32	1.21	0.44	0.01	0	0.42	0	
Max	4.20	9.36	1.60	1.53	0.62	3.20	1.01	
Median	1.83	3.17	0.82	0.55	0.08	0.85	0.21	
Mean	2.02	4.37	1.00	0.74	0.19	1.23	0.29	
Boston, U.S.A.								**[46]**
Min	243	8.5	63.4	-	-	8.87	<MDL	
Max	243	82.4	63.4	-	-	23.1	<MDL	
Median	-	-	-	-	-	-	-	
Mean	-	-	-	-	-	-	-	
Birmingham, UK								**[47]**
Min	-	-	-	<0.1	<0.07	<0.22	<0.12	
Max	-	-	-	130	370	490	460	
Median	-	-	-	<0.1	40	82	55	
Mean	-	-	-	8.0	94	130	100	

a) ΣFTOHs (mean 836, median 152, min 14.7, max 12450)
ΣFOSAs (mean 169, median 46.8, min 12.9, max 3353)
b) ΣFTOHs (mean 66.4, median 26, min 4.8, max 734)
c) Geometric mean not Arithmetic mean
d) Samples taken from classrooms

The difference of neutral PFCs levels in the three microenvironments may account for the different regulations. The levels were low in Egypt suggesting that stain treated carpets and textiles are not very common.

3.7 Implication for human exposure via dust ingestion

Human exposure to PFCs through dust inhalation is not the only exposure pathway and is not considered the main one. An assumption for dust ingestion is estimated to the time spent by adults at the three microenvironments; homes, workplaces and cars accounting for 72%, 23.8% and 4.2% respectively. Children on the other hand have other measures taking into account more time spent at homes, classrooms and very minimal time in cars accounting for 75.5%, 20.1% and 4.2% respectively. A typical adult weight is regarded as 70 kg and 12 kg for a child. The PFCs concentrations in this study were used to calculate an estimate exposure of adults and children to the target neutral PFCs analytes. Two scenarios have been considered; first the mean and high scenario representing both the low and high uptake. Four concentration levels of the target compounds in dust were calculated; the 5th percentile, median, 95th percentile and maximum concentration representing the worst case scenario. The dust ingestion rate (E_{Ingest}, ng/day) was calculated using: E_{Ingest} = Cdust x Qdust where Cdust is the concentration of Σneutral PFCs in house dust (ng g^{-1}) and Qdust is the dust ingested rate (g/day) of 4.16 and 100 mg/day for the mean scenario, and 55 and 200 mg/day for the high scenario for adult and toddler, respectively (USEPA) [48, 54]. Therefore, overall exposure estimates are usually based on the dust concentration exposure through life activity. One scenario, if we assume that a child is living in a regularly cleaned home, therefore the exposure will be 0.887 ng/day and the worst case scenario would reach 21.3 ng/day. As for adults the minimum exposure dose is 11.73 ng/day and around 43 ng/day worst case scenario, these levels are within the safe margin.

3.8 Correlation

Correlation analysis was performed between the ten neutral PFCs aiming to identify if they originate from the same source or not. Compounds are significantly correlated when *p value is* < 0.05. There was positive correlation between some analytes like 6:2 FTA and 6:2 FTOH ($p = 0.024$), 6:2 FTA and 8:2 FTOH ($p = 0.004$), 8:2 FTA and 10:2 FTA ($p = 0.009$), 8:2 FTA and 10:2 FTOH ($p = 0.012$), 10:2 FTA and 10:2 FTOH ($p = 0.002$), 10:2 FTA and MeFOSA ($p = 0.00$), 10:2 FTOH and EtFOSA (*p* = 0.010), Et FOSA and EtFOSE (*p* = 0.015), MeFOSE and EtFOSE (*p* = 0.002). These positive correlations suggest common sources of origin for these compounds.

3.9 Conclusion

The research work conducted shows the levels of different neutral PFCs in Egyptian dust samples collected from homes, workplaces and cars. The contaminant levels reported were several magnitudes lower than those reported in Europe, Asia and U.S. The levels were highest more in cars relative to those in workplaces and homes. It has been shown that the dominant neutral PFCs compound is FTOH with no significant variation observed between the three microenvironments. To the best of our knowledge, this is the first study conducted in Egypt therefore; comprehensive and intensive research is required in order to collect more data. Variation in the results of this study in comparison to the others may be due to the different geographical locations, temperatures, regulations and lifestyles. Correlation has been significantly positive with several compounds like FTOH indicating that most probably they originated from the same source. The low contaminant level may suggest that Egypt is not heavy used of imported goods treated with these compounds.

References

[1] Björklund, J.A., Thuresson, K., de Wit, C.A., 2009. Perfluoroalkyl Compounds (PFCs) in indoor dust: concentrations, human exposure estimates, and sources. Environ. Sci. Technol. 43, 2276–2281.

[2] Roosens, L., Abdallah, M.A.E., Harrad, S., Neels, H., Covaci, A., 2009a. Factors influencing concentrations of polybrominated diphenyl ethers (PBDEs) in students from Antwerp, Belgium. Environ. Sci. 43, 3535–3541.

[3] Roosens, L., Abdallah, M.A.E., Harrad, S., Neels, H., Covaci, A., 2009b. exposure to hexabromocyclododecanes via dust ingestion, but not diet, correlates with concentrations in human serum. Environ. Health Perspect. 117, 1707–1712.

[4] Key, B.D., Howell, R.D., Criddle, C.S., 1997. Fluorinated organics in the biosphere. Environ. Sci. Technol. 31, 2454–2455.

[5] Kissa E (2001) Fluorinated surfactants and repellants. Surfactant Science Series 97. Marcel Dekker, New York

[6] Kissa E (1994) Fluorinated surfactants: synthesis-properties-applications. Surfactant Science Series 50. Marcel Dekker, New York

[7] Taylor CK (1999) Fluorinated surfactants in practice. Annu Surfact Rev 2:271-316

[8] Lehmler HJ (2009) Production of fluorinated surfactants by electrochemical fluorination. Surfact Sci Ser 142:301-321

[9] Lehmler HJ (2005) Synthesis of environmentally relevant fluorinated surfactants-a review. Chemosphere 58(11):1471-1496

[10] Schultz MM, Barofsky DF, Field JA (2003) Fluorinated alkyl surfactants. Environ Eng Sci 20(5):487-501

[11] Pabon M, Corpart JM (2002) Fluorinated surfactants: synthesis, properties, effluent treatment. J Fluorine Chem 114(2):149-156

[12] Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH (2006) Sources, fate and transport of perfluorocarboxylates. Environ Sci Technol 40:32–44

[13] Haukås, M., Berger, U., Hop, H., Gulliksen, B., Gabrielsen, G.W., 2007. Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. Environ. Pollut. 148, 360–371.

[14] Covaci, A., Roosens, L., Dirtu, A.C., Waegeneers, N., Van Overmeire, I., Neels, H., Goeyens, L., 2009. Brominated flame retardants in Belgian home-produced eggs: levels and contamination sources. Sci. Total. Environ. 407, 4387–4396.

[15] Yogiu, G.T., Sericano, J.L., 2009. Polybrominated diphenyl ether flame retardants in the US marine environment: a review. Environ. Int. 35, 655–666.

[16] Apelberg, B.J., Goldman, L.R., Calafat, A.M., Herbstman, J.B., Kuklenyik, Z., Heidler, J., Needham, L.L., Halden, R.U., Writter, F.R., 2007. Determinants of fetal exposure to polyfluoroalkyl compounds in Baltimore, Maryland. Environ. Sci. Technol. 41, 3891–3897.

[17] Van der Ven, L.T.M., Van de Kuil, T., Leonards, P.E.G., Slob, W., Lilienthal, H., Litens, S., Herlin, M., Håkansson, H., Cantón, R.C., Van den Berg, M., Visser, T.J., Van Loveren, Vos, J.G., Piersma, A.H., 2009. Endocrine effects of hexabromocyclododecane (HBCD) in a one-generation reproduction study in Wistar rats. Toxicol. Lett. 185,51–62.

[18] Lau C et al (2007) Perfluoroalkyl acids: a review of monitoring and toxicological findings. Tox Sci 99(2):366–394.

[19] Butt CM et al (2010) Levels and trends of poly- and perfluorinated compounds in the arctic environment. Sci Total Environ 408(15):2936–2965.

[20] Houde M et al (2006) Biological monitoring of polyfluoroalkyl substances: a review. Environ Sci Technol 40(11):3463–3473.

[21] Simons JH (1949) Electrochemical process for the production of fluorocarbons. J Electrochem Soc 95:47–59

[22] Wagner, C. (2013) Polyfluorinated chemicals. Food Packaging Forum. Last accessed: http://www.foodpackagingforum.org/food-packaging-health/polyfluorinated-compounds/chemistry

[23] White, S.S., et al. (2011). "Endocrine disrupting properties of perfluorooctanoic acid." The Journal of steroid biochemistry and molecular biology 127:16-26. http://www.sciencedirect.com/science/article/pii/S0960076011000549

[24] Paul, A. G.; Jones, K. C.; Sweetman, A. J. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ. Sci. Technol. 2009, 43 (2), 386–92.

[25] United Nations Environment Programme Report of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants on the work of its fourth meeting. http://chm.pops.int/Portals/0/Repository/COP4/UNEP-POPS-COP.4-38.English.pdf (accessed September 1, 2001).

[26] Dams R (1993) Fluorochemical surfactants for hostile environments. Spec Chem 13(1):4–6.

[27] Meng J (2006) Novel applications for fluorosurfactants in low VOC coatings. FutureCoat Proc:051/1–051/6

[28] Naturvernforbund (2007) Fluorerade milj€ogifter i impregneringsmedel. Rapport 9019009–2

[29] U.S. Environmental Protection Agency (2006) Meeting with Registrant on Perfluorinated Chemical (Masurf-FS-780, Fluowet PL 80-B, and Fluowet PL-80) Use as Inerts. Letter from the Office of Pollution Prevention and Toxics to the Office of Pesticide Programs. U.S. EPA Public Docket AR226-3804.

[30] U.S. Federal Register (2006) Inert Ingredient; Revocation of the Tolerance Exemption for Mono- and Bis-(1 H, 1 H, 2 H, 2 H-perfluoroalkyl) Phosphates Where the Alkyl Group is Even Numbered and in the C6-C12 Range. 71(153):45408–45411

[31] Strynar, M. J.; Lindstrom, A. B. Perfluorinated compounds in house dust from Ohio and North Carolina, USA. Environ. Sci. Technol. 2008, 42, 3751–3756.

[32] Bj€orklund, J. A.; Thuresson, K.; De Wit, C. A. Perfluoroalkyl compounds (PFCs) in indoor dust: Concentrations, human exposure estimates, and sources. Environ. Sci. Technol. 2009, 43, 2276–2281.

[33] Giesy, J. P.; Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. Environ. Sci. Technol. 2001, 35, 1339–42.

[34] Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Van Wouwe, N.; Yang, J. H.; Aldoust, K. M. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. Environ. Sci. Technol. 2004, 38, 4489–95.

[35] Giesy and Kannan (2001). Global distribution of perfluorooctane sulfonates in wildlife. Environ. Sci. Technol, 35:1339-1342.

[36] D'Hollander, W., Roosens, L., Covaci, A., Cornelis, C., Reynders, H., Van Campenhout, K., de Voogt, P. and Bervoets, L. (2010a) Brominated flame retardants and perfluorinated compounds in indoor dust from homes and offices in Flanders, Belgium. Chemosphere, 81, 478-487.

[37] Jones-Otazo, H. A., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J. J. and Wilford, B. (2005) Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. Environ. Sci. Technol., 39, 5121- 5130.

[38] 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. Environ. Sci. Technol., 40, 4548-4553.

[39] Ericson, I., Cid, R., Nadal, M., Van Bavel, B., Lindström, G. and Domingo, J. (2008) Human exposure to perfluorinated chemicals through the diet: Intake of perfluorinated compounds in foods from the Catalan (Spain) market. J. Agric. Food Chem., 56, 1787-1794.

[40] Vestergren, R., Cousins, I. T., Trudel, D., Wormuth, M. and Scheringer, M. (2008) Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA. Chemosphere, 1617-1624.

[41] Joensen, U. N.; Bossi, R.; Leffers, H.; Jensen, A. A.; Skakkebæk,N. E.; Jørgensen, N. Do Perfluoroalkyl compounds impair human semen quality?. Environ. Health Perspect. 2009, 117, 923–927.

[42] Nelson, J. W.; Hatch, E. E.; Webster, T. F. Exposure to polyfluoroalkyl chemicals and cholesterol, body weight, and insulin resistance in the general U.S. population. Environ. Health Perspect. 2010, 118, 197–202.

[43] Dallaire, R.; Dewailly, E.; Pereg, D.; Dery, S.; Ayotte, P. Thyroid function and plasma concentrations of polyhalogenated compounds in inuit adults. Environ. Health Perspect. 2009, 117, 1380–1386.

[44] Midasch, O.; Drexler, H.; Hart, N.; Beckmann, M. W.; Angerer, J. Transplacental exposure of neonates to perfluorooctanesulfonate and perfluorooctanoate: A pilot study. Int. Arch. Occup. Environ. Health 2007, 80, 643–648.

[45] Tao, L.; Ma, J.; Kunisue, T.; Libelo, E. L.; Tanabe, S.; Kannan, K. Perfluorinated compounds in human breast milk from several Asian countries, and in infant formula and dairy milk from the United States.Environ. Sci. Technol. 2008, 42, 8597–8602.

[46] Fraser, A.J.; Webster, T.F.; Watkins, D.J.; Strynar, M.J.; Kato, K.; Calafat, A.M.; Vieira, V.M.; McClean, M.D.Polyfluorinated compounds in dust from homes, offices, and vehicles as predictors of concentrations in office workers' serum. Environment International 60 (2013) 128–136.

[47] Goosey, E.; Harrad, S. Perfluoroalkyl compounds in dust from Asian, Australian, European, and North American homes and UK cars, classrooms, and offices. Environment International 37 (2011) 86–92.

[48] Shoeib M, Harner T, Webster GM, Lee SC. Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: implications for human exposure. Environ Sci Technol 2011;45(19):7999–8005.

[49] Jogsten, E.; Nadal, M; van Bavel, B.; Lindström, G.; Domingo, J.L. Per- and polyfluorinated compounds (PFCs) in house dust and indoor air in Catalonia, Spain: Implications for human exposure. Environment International 39 (2012) 172–180.

[50] Shoeib, M., Harner, T, Wilford, B.H., Jones, K.C., Zhu, J, Polyfluorinated Compounds in the Home: Levels in Air and Dust and Human Exposure, Poster 2003.

[51] Shoeib, M.; Harner, T.; Wilford, B. H.; Jones, K. C.; Zhu, J. Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: Occurrence, partitioning, and human exposure. Environ. Sci. Technol. 2005, 39, 6599-6606.

[52] Xu, Z.; Fiedler, S.; Pfister, G.; Henkelmann, B.; Mosch, C.; Völkel, W., Fromme, H., Schramm, K-W. Human exposure to fluorotelomer alcohols, perfluorooctane sulfonate and perfluorooctanoate via house dust in Bavaria, Germany. Science of the Total Environment 443 (2013) 485–490.

[53] Strynar MJ, Lindstrom AB. Perfluorinated compounds in house dust from Ohio and North Carolina, USA. Environ Sci Technol 2008;42:3751–6.

[54] U. S. Environmental Protection Agency. Exposure Factors Handbook; EPA/600/P-95/002; EPA: Washington, DC, 1997.

Appendix

Home and workplace sample locations from Cairo and Giza, expressed as yellow stars.