# Assessing polybrominated diphenyl ethers (PBDEs) in indoor environments: Concentrations in dust, human serum and the effect of regulations

**A thesis Submitted for the Degree of Doctor of Philosophy in the Faculty of Science and Technology**
**By**

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**July 2019**

# Abstract

Polybrominated diphenyl ethers (PBDEs) are synthetic chemicals used in consumer products as additive flame retardants. There has been concern about these substances amongst regulators and policy makers as a result of their persistence in the environment and bioaccumulation in human and wildlife, as well as their ability to undergo long range atmospheric transport. PBDE contamination has been reported in most parts of the outdoor environment (such as sediment, soil, air, water and wildlife), as well as the indoor environment (dust and air) and human body (blood, breast milk, hair and so on). These chemicals have also raised concerns as they are human toxicants since they have been reported to affect thyroid hormones, neurobehavioural development, disruption to endocrine systems and possibly causing cancer. The overall hypothesis for this study was that the government regulatory intervention has differed between regions and countries. This has led to variations in the use of consumer goods containing PBDEs which directly affects contaminant levels in indoor environments which may be detrimental to human health with different timing and severities. The aims of the study were to discuss the development of regulations in Europe, North America and China, and through a sampling campaign and investigation, determine concentrations of PBDEs in the indoor environment of private homes across China. The final part of the study investigated the possible correlation between human serum concentrations and thyroid hormone function.

In the initial part of this study, previously published studies of PBDEs in indoor environments and human exposure were used to summarize and compare temporal and spatial patterns across Europe, the USA and China. This was followed by the collection of dust samples in private homes in December, 2016 to January 2017, from five main cities in China, Dalian, Beijing, Shanghai, Xiamen and Guangzhou. Serum samples were collected from patients diagnosed with thyroid function abnormalities in Kunming, China. All samples were analyzed by gas chromatography and mass spectrometry (GC/MS).

As a result of the variation in regional restrictions of the production/usage of commercial PBDEs, the concentration and PBDE profile composition were found to be different between Europe, the USA and China. Data from this study also showed variations in PBDE concentration between cities, within a city region and within individual dwellings. For example, a significant positive correlation was found between total PBDE concentration in dust collected from air conditioner (AC) filters and floor dust samples, which suggests they have a common source. AC filters may be a good place to collect samples in future as it represents the status of the general indoor environment. However, no significant association was found between total PBDEs in dust collected from foam furniture and floor dust. Differences were also observed between urban, suburban and rural locations. Serum samples from patients with abnormal thyroid function from Kunming were evaluated for PBDE contamination to assess exposure and possible interactions. The results identified BDE47 to be the major congener present in human serum. The concentrations of $\sum_7$PBDE were similar to those from previous studies for general population groups including both adults and children, and at the same order of magnitude as European data, but lower than in the USA. Multiple linear regressions were used to examine the associations between PBDE congeners and the 5 thyroid hormone parameters. BDE153 showed significant positive correlation with Thyroxine (T4) and a negative correlation with Triiodothyonie (T3), whilst BDE47 showed a negative correlation with Free Thyroxine (FT4). The $\beta$-coefficients also suggested that a log-unit increase in $\sum_7$PBDE was associated with

an increase of FT4 and T4 levels and a decrease of TSH, T3 and free triiodothyonine (FT3). Further research is required, preferably using an increased sample size from thyroid patients, to investigate this possible relationship.

# Acknowledgement

I really appreciate and respect my supervisors, Dr. Andy Sweetman and Dr. Hong Li, who provide guidance, help, invaluable comments, encouragement and patience on my thesis from draft to final version during the four years. Andy and Hong teach me a lot, how to design and tell a professional science story, how to set up a logical outline, and how to position contents clearly, concise and powerful in article. I learned much more from Andy and Hong on data analysis, how to use clearly figures to express my opinions and support the conclusion of papers. Andy always provide me constructive suggestion on science and help me to polish language. Hong help me to set up collaboration with Dr Zhang Xian in Institute of Urban Environment, Chinese Academy of Sciences, so that I could finish field work and lab work. I really thank them to encourage and make me have more confident in my PhD study life.

I also appreciate Dr. Xian Zhang, who supervised me when was studying in Institute of Urban Environment, Chinese Academy of Sciences, and Xu Liao, Liang Chen and Bin Lin. Thank you for training me the laboratory skills and discussing the experiments with me. I am grateful to Dr. Xian Zhang, who help me overcome challenges and assist me at the stage of lab work. My sincerely thanks also should be expressed to Xu Liao, who teach me technical skills and analysis on GC/MS

I would like to express my gratitude to my father Mr. Ruwen Yang and mother Mrs. Yangfang Li. They always give me unconditional love, continuous encouragement and support. I could not finish my PhD without both of you.

Finally, I would like to thank to Prof. Kevin Jones, Prof. Hao Zhang and Dr. Hong Li, who take care of me, provide help on daily life and make me delightful in the UK. I also feel very lucky to have lots of friends to encourage me and provide the warmest companionship during my difficult stage, Yujie Zeng, Hanbing Li, Yanying Li, Ying

Zhu, Naifu Jin, Wenjuan Yu, Chun Lin, Yaping Guo, Ran Tian, Jianhua Lei, Xiaoliang Sun and Yangyang Qu. Thank you for accompanying me and sharing the laughs, delicious meals and talks together.

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# Abbreviation

| | |
|---|---|
| ABS | Acrylonitrile-butadiene-styrene |
| AC | Air conditioner |
| AF | Fraction of PBDEs adsorbed |
| ATSDR | Agency for toxic substances and disease registry |
| BDE | Brominated diphenyl ether |
| BDE209 | Decabromodiphenyl ether |
| BFRs | Brominated flame retardants |
| BMI | Body mass index |
| BSA | Body surface area |
| BSEF | Bromine science environmental forum |
| BSEF | Bromine science and environmental forum |
| BW | Body weight |
| C-decaBDE | Commercial decaBDE |
| CEPA | Canadian environmental protection act |
| CHOL | Total cholesterol |
| C-octaBDE | Commercial octaBDE |
| C-pentaBDE | Commercial pentaBDE |
| CTD | Characteristic travel distance |
| DAS | Dust adhered to the skin |
| DCM | Dichloromethane |
| $DED_{ai}$ | Daily exposure dose through air inhalation |
| $DED_{da}$ | Daily exposure dose through dermal absorption |
| $DED_{di}$ | Daily exposure dose through dust ingestion |
| DIR | Daily intake of dust (g/day) |
| DL | Detection limit |
| DW | Dry weight |
| EC | European commission |
| EPA | Environment protection agency |
| EU | European union |
| E-waste | Electronic waste sites |
| FD | Floor dust |

| | |
|---|---|
| FF | Furniture foam |
| FRSs | Fire and rescue services |
| FT3 | Free triiodothyronine |
| FT4 | Free thyroxine |
| GC/MS | Gas chromatographic/Mass spectrometer |
| GDP | Gross domestic product |
| GM | Geometric mean |
| GPC | Gel permeation chromatography |
| HBCD/HBCDD | Hexabromocyclododecane |
| He | Helium |
| HIPS | High-impact polystyrene |
| IEF | Indoor exposure fraction |
| IPCS | International programme on chemical safety |
| IRIS | Integrated risk information system |
| IUPAC | International union of pure and applied chemistry |
| $K_{OA}$ | Octanol-air partition coefficient |
| $K_{OC}$ | Soil organic carbon-water coefficient |
| $K_{OW}$ | Octanol-water partition coefficient |
| LOD | The limit of detection |
| LOQ | The limit of quantification |
| LRAT | Long-range atmospheric transport |
| LRTAP | Long range transboundary air pollution |
| M/Z | Mass to charge ratio |
| MDL | Method detection limit |
| mmHg | Millimeter of Hg |
| NCI | Negative chemical ionization |
| nd | Not detected |
| OH-PBDE | Hydroxylated polybromodiphenyl ethers |
| $P_a$ | Pascals |
| PBB | Polybrominated biphenyl |
| PBDD | Polybrominated dibenzodioxins |
| PBDEs | Polybrominated diphenyl ethers |
| PBDF | Polybrominated dibenzofurans |

| | |
|---|---|
| PCA | Principal component analysis |
| PCBs | Polychlorinated biphenyls |
| POPs | Persistent organic pollutants |
| PUF | Polyurethane foam |
| QA | Quality assurance |
| QC | Quality control |
| RA | Rural areas |
| RDS | Recovery determination standard |
| RoHS | Restriction of hazardous substances |
| S/N | Signal to noise ratio |
| SA | Suburban areas |
| SD | Standard deviation |
| SIM | Selected ion monitoring |
| SNUR | Significant new use rule |
| SPE | Solid phase extraction |
| SPSS | Statistical product and service solutions |
| T3 | Triiodothyonine |
| T4 | Thyroxine |
| TBBPA/TBBP-A | Tetrabromobisphenol A |
| TBG | Thyroxine-binding globulin |
| TG | Triglycerides |
| TL | Total lipids |
| TSH | Thyroid-stimulating hormone |
| TTR | Transthyretin |
| UA | Urban areas |
| UNECE | United nations economic commission for europe |
| UNEP | United nations environment programme |
| USA | United state america |
| UV | Ultraviolet |
| $V_P$ | Vapor pressure |
| WHO | World health organization |
| WS | Water solubility |
| ww | Weight by weight |

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# Chapter 1 General Introduction

## 1.1 Introduction

Fire has become one of the most significant elements of damage, injury and death hence synthetic polymers became widely used in household products. According to a report from Fire Department of the Ministry of Public Security in China, 312,000 fires occurred during 2016/2017, resulting in 1065 injuries, 1582 deaths and losses of ￥37.2 billion Renminbis (Security, 2017). In the UK, Fire and Rescue Services (FRSs) attended 161,770 fire related incidents and 261 fatalities occurred in 2016/2017 due to fire from the report: Fire and Rescue Incident Statistics, issued by Home Office, England in April 2016 to March 2017, Home Office (HomeOffice, 10 August, 2017). In order to mitigate these losses, the development of fire safety standards has become very important especially for items of furniture, electrical equipment and plastic products. As a result of such standards, flame retardants have been added into a wide range of plastic and daily use products to allow more time for people to escape before the fire spreads. Brominated flame retardants (BFRs) have been readily added to products as they have been demonstrated to be effective and can be manufactured at a relatively low cost. As one of the main groups of BFRs, polybrominated diphenyl ethers (PBDEs) were first introduced as additive retardants for use in a range of consumer products in the 1970s. The global market demand of BFRs in 2001 was estimated 203,470 tons, of which PBDEs accounted for 33%, 67,440 tons for total

PBDE commercial products (Janssen, 2005).

Although flame retardants have played an important role in public safety, brominated flame retardants have been detected widely in outdoor environments such as sediments and sewage, water resources, indoor environments such as indoor air and indoor dust and even in human tissues such as breast milk and blood (de Boer et al., 2003; Lake et al., 2011; Guan et al., 2009; Hirai et al., 2012; Daniels et al., 2010; Abb et al., 2011; Allen et al., 2006; Darnerud et al., 2015). They have been classified as toxic chemical contaminants with the chemical characteristics of low water solubility, high lipid solubility, semi-volatility and resistance to degradation (Janssen, 2005). Additionally, PBDEs also have the potential for long-range atmospheric transport (LRAT) via deposition and revolatilization dependent on seasonally and fluctuating temperatures that results in their transport from their emission regions to remote areas)(Hale et al., 2008; Review, 2014). These characteristics can result in their accumulation and magnification in humans and wildlife. Previous studies have addressed the toxicity of PBDEs to human health since they have been reported to affect thyroid hormones, endocrine systems and neurobehavioural development, as well as being suspected carcinogens (Arkoosh et al., 2010; Abdelouahab et al., 2009; Allen et al., 2016; Branchi et al., 2003).

## 1.2 Overview of Polybrominated diphenyl ethers (PBDEs)

### 1.2.1 Brominated Flame retardants (BFRs)

The history of flame retardant usage dates back to 450 BC, when the Egyptians used alum to reduce the flammability of wood. In a 200 BC, the Romans used a mixture of alum and vinegar to reduce the combustibility of wood (Alaee et al., 2003). Early study indicated flame retardant can be achieved the target by four ways: 1. produce non-combustible products to dilute the flame oxygen supply; 2. format a barrier to hinder the supply of oxygen; 3. trap the active radicals in the vapor phase; 4. reduce the thermal conductivity of the material to limit heat transfer (Lomakin and Zaikov, 1996). There are currently more than 175 different flame retardants (Alaee and Wenning, 2002) which are used in daily life, and all of them can be classified into four groups: Inorganic compounds, Halogenated Organic compounds, Nitrogen-based compounds and Organophosphorous compounds (Alaee and Wenning, 2002). Among them, the halogenated organics can be divided into two classes, those containing either chlorine or bromine. During combustion, halogenated organics flame retardant released bromine or chlorine to remove high energy OH and H radicals by a chemical interfering with the radical chain mechanism (Cagnetta et al., 2016). It is illustrated below and the active chain carriers are replaced with the less active Br • radical in order to slow the rate of energy production resulting in flame extinguishing (Cagnetta et al., 2016).

$$H\bullet + HBr \rightarrow H_2 + Br\bullet$$

$$\bullet OH + HBr \rightarrow H_2O + Br\bullet$$

Brominated flame retardants (BFRs) are used more widely as they have the advantage of being more effective and cheaper to produce (de Wit, 2002). As an important group of chemical flame retardants, the Brominated Flame Retardant (BFRs) can be used in wide range of products to reduce product flammability. The application of BFRs has been widespread, such as their use in plastics and electronic equipment (televisions, air conditioners etc.), in electronic accessories such as cables and wires, but also in textiles, e.g. carpets, clothes and curtains.

More than 70 different types of brominated flame retardant have been produced. They are divided into four groups depending on the mode of incorporation (Figure 1.1) (de Wit, 2002): brominated cycohydrocarbons such as hexabromocyclododecane (HBCD or HBCDD), polybrominated diphenyl ethers (PBDEs), polybrominated biphenyl (PBB), and tetrabromobisphenol A ( TBBPA or TBBP-A). Usually, TBBPA is bonded into the plastics as a reactive flame retardant, whilst PBDEs, PBB and HBCDD are blended with the polymers as additive flame retardants (Alaee et al., 2003).

Additive flame retardants are thought to be more readily lost from the polymer during product use. Polybrominated biphenyls (PBBs) were used as flame retardants from the early 1970s. In 1974, PBBs were accidentally mixed into dairy cattle feed, as well as poultry feed in Michigan, USA. The widespread contamination of PBBs in the milk, meat, eggs and Michigan farm products resulted in human exposure to the toxicant

(Alaee et al., 2003) which led to the ban of PBBs use in the USA. By 1979 the production of PBBs ceased in North America. In Europe, commercial PBB mixtures were produced until 2000 (Luross et al., 2002). Tetrabromobisphenol A (TBBPA) is widely used as a reactive flame retardant added into plastics and electronic circuit boards. Since the molecular structure of TBBPA is similar to the thyroid hormone, previous studies suggested TBBPA may affect renal and immune function as well as disrupt thyroid hormone homeostasis (Darnerud, 2003; Law et al., 2008). Hexabromocyclododecane (HBCDD) is used as an additive flame retardant in polyurethane foams, textile coatings and electronic equipment. There are few studies investigating the adverse effects of HBCDD on human health. A study by (Darnerud, 2003) suggested there was a potential for interference with the function of thyroid hormones.

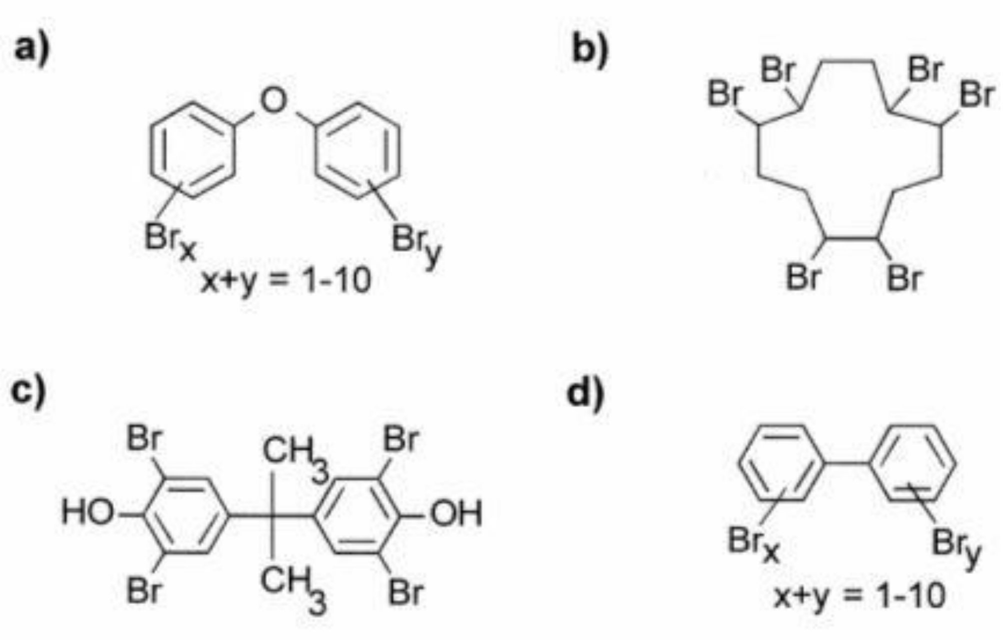


**Figure 1.1** Chemical structures of four group brominated flame retardants (BFRs): (a) Polybrominated diphenyl ethers (PBDEs); (b) Hexabromocyclododecane (HBCD); (c)

Tetrabromobisphenol A (TBBPA); (d) Polybrominated biphenyls (PBBs). x and y are the number of bromine atoms and substitution positions on the diphenylether structure. The sum of bromine atoms is from 1 to 10.

### 1.2.2 Structure of PBDEs

Polybrominated diphenyl ethers (PBDEs) are a group of synthetic organohalogens used worldwide as additive flame retardants in a range of consumer products, such as textiles, furniture, electrical equipment and household appliances. PBDEs do not occur naturally in the environment, and they are produced by bromination of diphenyl ether in the presence of a Friedel-Craft catalyst such as $AlCl_3$ in a solvent such as dibromomethane (Alaee et al., 2003).

There are 209 PBDE compounds, each termed a congener, which can be distinguished by the number of bromine atoms and substitution positions on the diphenylether structure. The family of PBDEs can be divided into 10 homologue groups according to the degree of bromination, ranging from monobromodiphenyl ether to decabromodiphenyl ether: mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and deca- (Rahman et al., 2001). Homologues are defined as the congeners with the same number of bromine atoms (de Wit, 2002). Each congener is assigned a specific brominated diphenyl ether (BDE) number. Table 1.1 contains the name and congener numbering system for PBDEs. They are numbered according to the International Union of Pure and Applied Chemistry (IUPAC) system. Table 1.2 shows the IUPAC number, name and chemical structure of main PBDE congeners. When a product containing

PBDEs is burned, bromine atoms are released which displace the oxygen needed for a fire to burn, generating a very thin protective layer of bromine gas on the surface of the treated product which restricts access of the fire to fuel sources (USEPA 2005).

$$\text{PBDE} = C_{12}H_{(10\text{-}X)}Br_xO \quad (x=1, 2, 3, \ldots, 10 = m + n)$$

Chemical structure of PBDEs:

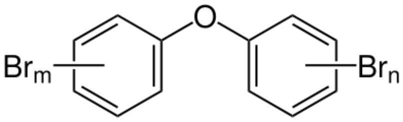


**Table 1.1** 10 homologue groups of PBDEs: congener name and congener number

| PBDE congener name | Congener Number |
|---|---|
| **Mono-BDE** | BDE-1 to BDE-3 |
| **Di-BDE** | BDE-4 to BDE-15 |
| **Tri-BDE** | BDE-16 to BDE-39 |
| **Tetra-BDE** | BDE-40 to BDE-81 |
| **Penta-BDE** | BDE-82 to BDE-127 |
| **Hexa-BDE** | BDE-128 to BDE-169 |
| **Hepta-BDE** | BDE-170 to BDE-193 |
| **Octa-BDE** | BDE-194 to BDE-205 |
| **Nona-BDE** | BDE-206 to BDE-208 |
| **Deca-BDE** | BDE-209 |

**Table 1.2** Congener name, homologue name, chemical structure and bromine atoms number of eleven main PBDE congeners.

| Congener | Homologue | Bromine Atoms # |
|---|---|---|
| **BDE-28** | 2,4,4'-tribromodiphenyl ether | 3 |
| **BDE-47** | 2,2',4,4'-tetrabromodiphenyl ether | 4 |
| **BDE-85** | 2,2',3,4,4'-pentabromodiphenyl ether | 5 |
| **BDE-99** | 2,2',4,4',5-pentabromodiphenyl ether | 5 |
| **BDE-100** | 2,2',4,4',6-pentabromodiphenyl ether | 5 |
| **BDE-153** | 2,2',4,4',5,5'-hexabromodiphenyl ether | 6 |
| **BDE-154** | 2,2',4,4',5,6'-hexabromodiphenyl ether | 6 |
| **BDE-183** | 2,2',3,4,4',5',6-heptabromodiphenyl ether | 7 |
| **BDE-197** | 2,2',3,3',4,4',6,6'-octabromodiphenyl ether | 8 |
| **BDE-206** | 2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether | 9 |
| **BDE-209** | 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether | 10 |

### 1.2.3 Production and application of PBDEs

Commercial PBDE manufacture began in the 1970s (de Wit, 2002) and were produced as three commercial formulations, commercial penta-BDE (c-pentaBDE), commercial octa-BDE (c-octaBDE) and commercial deca-BDE (c-decaBDE)(de Boer et al., 2003). In this study, the abbreviation c-pentaBDE, c-octaBDE and c-decaBDE will be used for the commercial PBDEs products, while PentaBDE, OctaBDE and DecaBDE refer to the homologue groups. PBDEs within commercial formulations are not a single product but a mixture. Table 1.3 lists the components of the three commercial mixtures and shows the typical application for each of the commercial PBDE products (de Wit, 2002; La Guardia et al., 2006; Chen et al., 2007).

C-pentaBDE (commercially known as DE-71 and Bromkal 70-5DE) is a viscous liquid. It contains a mixture of 40% tetra-, 50-60% penta-, and 6% hexa-BDE. Among them, the dominant pentaBDE congener from commercial mixtures is 2,2',4,4',5-pentaBDE (BDE99) with some 2,2',4,4',6 - pentaBDE (BDE100). The most abundant tetra-BDE congener is 2,2',4,4' - tetra-BDE (BDE47), and main hexa-BDEs consist of congeners of BDE153 and BDE154. BDE47 and BDE99 account for almost 75% of the total c-pentaBDE. Usually, c-pentaBDE was added into polyurethane foams such as mattresses, foam packaging, but also in carpet padding and fabric coatings.

C-octaBDE (commercially known as DE-79 and Bromkal 79-8DE) is a white powder. It is a mixture of 30-40% octaBDE, 30-45% heptaBDE and 10% nonaBDE and hexaBDE. The major congener in c-octaBDE is 2,2',3,4,4',5',6-hepta-BDE (BDE183). C-octaBDE was manufactured primarily as an acrylonitrile-butadiene-styrene (ABS) additive and found in items such as kitchen appliance casings, small electronics parts and telephone handsets

C-decaBDE (commercially known as Bromkal 82-0DE and Saytex 102E) is also a white powder, which contains 97-98% 2,2',3,3',4,4',5,5',6,6'-deca-BDE (BDE209), with a minor quantity of nona-BDEs (< 3%). Previous studies have reported a high degree of impurities have been found in c-decaBDE produced in China, which contains 8.2% OctaBDE and 10.4% NonaBDE (Chen et al., 2007). C-decaBDE was used in plastic polymers, including high-impact polystyrene plastic and various

**Table 1.3** Composition, foam and typical application of three commercial PBDE mixtures (c-pentaBDE, c-octaBDE and c-decaBDE).

| Mixture | Form | Components | Applications |
|---|---|---|---|
| **c-pentaBDE** | Liquid | 0.022% BDE17, 0.11% BDE28, 37% BDE47, 0.22% BDE66, 1.6% BDE85, 35% BDE99, 6.8% BDE100, 0.41% BDE138, 3.9% BDE153. 2.5% BDE154 | polyurethane foams in mattresses, seat cushions, other upholstered furniture and foam packaging. Also: carpet padding, imitation wood, small electronic parts, fabric coating |
| **c-octaBDE** | Solid | 40% BDE183, 21% BDE197, 5-35% BDE203, 8% BDE196, 10% BDE208, 7% BDE207, 5-10% BDE153, 1-5% BDE154, 1% BDE190, 0-3% BDE209 | Acrylonitrile-butadiene-styrene (ABS) plastic: such as kitchen appliance casings, small electronics parts, audio/video equipment, remote control products and telephone handsets; |
| **c-decaBDE** | Solid | EU and the USA: 97.5% BDE209, 2.2% BDE206, 0.24% BDE207, 0.06% BDE208<br>China: 81.4% BDE209, 8.2% OctaBDE, 10.4% NonaBDE | High-impact polystyrene (HIPS) plastic<br>Various plastics<br>Upholstery textiles (sofas, chairs), paints, rubber cables, lighting, smoke detectors, electrical equipment, stadium seats |

plastics (Alaee et al., 2003). According to the Bromine Science Environmental Forum (BSEF), C-decaBDE occupied over 80% of the total PBDE production market globally in 2001.

The major companies that produced brominated flame retardants were Albemarle Corporation (US), Dead Sea Bromine Corporation (Israel) and Chemtura Corporation (US), which occupied the 78% flame retardant market in 2006 (Danish EPA 2006). After c-pentaBDE and c-octaBDE were banned in USA and Europe in 2003 and 2004, the c-decaBDE product began to dominate the flame retardant market with most of the manufacturing moving to China. In 2014, three companies accounted for 40% of c-decaBDE production in China, WeiDong Chemical Industry Company (ShanDong Province, China), RunKe Chemical Industry Company (ShanDong Province, China) and Shenyang Research Institute of Chemical Industry (LiaoNing Province, China) (China Flame Retardant Society). Another six companies in China occupied the rest of flame retardant market. China never produced c-octaBDE and may haveproduced c-pentaBDE. However, no data for c-pentaBDE production are available (Chen et al., 2012).

### 1.2.4 Physicochemical properties of PBDEs

PBDEs can leach or volatilize out from products containing commercial PBDE during usage, production and recycling process, and then persist and bioaccumulate once in the environment (EPA/600/R-08/086F). The reason for the persistence can be explained by their physicochemical properties. Table 1.4 summarizes typical physical and chemical properties of three commercial PBDEs (Agency for Toxic Substances and Disease Registry (ATSDR), 2004, 2015).

**Water solubility** (WS) is used to describe how readily chemical compound dissolves in water. The chemical compounds are classified to have low, medium or high solubility with water solubility value at the range of <0.1, 0.1-10, or >10 mg/L (measured temperature at 25℃) (NAS, 2001).

**Octanol-water partition coefficient** ($K_{OW}$) is another important chemical property for organic chemicals to present the ratio of the concentration in n-octanol and the concentration in water. The higher water solubility value, the lower $K_{OW}$ value. The $K_{OW}$ coefficient is usually expressed as the logarithm, base 10 of the ratio value. Generally speaking, with the log $K_{OW}$ coefficient equal or greater than 5, organic chemicals have very hydrophobic and bioaccumulation (EPA/600/R-08/086F).

**Vapor Pressure** ($V_P$) presents the force per unit area (pressure) exerted by chemicals in vapor phase. $V_P$ is usually expressed in units of Pascals (Pa) or millimeter of Hg (mmHg). Volatile compounds are defined with solid phase vapor pressure >10 Pa, while semi-volatile organic compounds have solid phase vapor pressures <1 Pa (Environment Canada, 2004).

**Octanol-air partition coefficient** ($K_{OA}$) is the ratio of the concentration of the chemical in air versus the concentration in octanol. The log $K_{OA}$ value suggests the environment cycling of semi-volatile compounds between the air and organic phases such as soil particles, air particles and vegetation (Kierkegaard, 2007).

PBDEs are very hydrophobic compounds with low vapor pressures and high octanol-water partition coefficient (log $K_{OW}$) values. As the bromine content increases, vapor pressure and water solubility decreases, while the log $K_{OW}$ increases (Sellstrom et al., 1993). Therefore, PBDEs sorb strongly to soil, sediment and atmospheric particles, rather than dissolve in water. Higher brominated congeners are more hydrophobic, lower volatility and higher log $K_{OW}$ values than lower brominated congeners, which results in the differences in their environmental fate. The USA environment protection agency (EPA) concluded the tetra- and pentaBDE congeners distribute more atmospheric particles than the mono-, di-, triBDE, which present in vapor phase. The hexa- and heptaBDE may be present in the particle phase and BDE209 is associated with airborne particles (EPA/600/R-08/086F). Along with persistence in the environment, PBDEs also have demonstrated a potential to undergo long-range atmospheric transport (LRAT). Previous studies have shown that PBDEs have been detected in wildlife such as polar bears (Kirkegaard et al., 2005; Krieger et al., 2016). Since lower brominated PBDEs are more volatile and transported in water and air, they have a higher potential for LRAT compared to higher brominated congeners. Because of low vapor pressures, low water solubility and high log $K_{OW}$ values, PBDEs enter in the environment and bind to the organic particle such as soils and sediments, only small amounts in water and air, so that the soils and sediments will serve for PBDE emission during LRAT (La Guardia et al., 2006). Previous study estimated the characteristic travel distance (CTD) for tetraBDE (range from 1,113 to 2,483 km), pentaBDE (range from 608 to 1,349 km) and decaBDE (range from 480 to 735 km) (Wania and Dugani, 2003).

**Table 1.4** Physical and chemical properties of three commercial PBDE products (c-pentaBDE, c-octaBDE and c-decaBDE).

| **Property** | **C-pentaBDE** | **C-octaBDE** | **C-decaBDE** |
|---|---|---|---|
| **Water solubility (mg/L)** | 0.013 | 0.002 to 0.005 | <0.001 |
| **Boiling point (℃)** | Over 300 | Over 330 | Over 320 |
| **Melting point (℃)** | -7 to -3 | 85 to 89 | 290 to 306 |
| **Vapor pressure (mm Hg)** | $2.2 * 10^{-7}$ to $5.5 * 10^{-7}$ | $9 * 10^{-10}$ to $1.7 * 10^{-9}$ | $3.2 * 10^{-8}$ |
| **Octanol-water partition coefficient (log $K_{OW}$)** | 6.64 to 6.97 | 6.29 | 6.265 |
| **Soil organic carbon-water coefficient (log $K_{OC}$)** | 4.89 to 5.1 | 5.92 to 6.22 | 6.8 |
| **Octanol-air partition coefficient (log $K_{OA}$)** | 9.5 to 11.66 | 11.82 to 12.15 | 13.21 |

## 1.3 Timeline of PBDEs production, usage and regulation within selected regions

### 1.3.1 Production

PBDEs have been launched to commercial market since the 1960s to 1970s. With the growth of electronics and other household in the 1980s, the demand for PBDEs grew substantially (BSEF 2000). Annual production of c-pentaBDE, c-octaBDE and c-decaBDE worldwide was estimated to around 4,000, 6,000 and 30,000 metric tons (the total 40,000 tons) in 1990 respectively, and the total world production of the three commercial PBDEs increased to approximately 67,125 metric tons in 1999 (de Wit, 2002). Due to the usage restriction of c-pentaBDE and c-octaBDE in EU and the USA, c-decaBDE demand increased and occupied 83.3% PBDEs global market in 2001, followed by c-pentaBDE, 11.1% and c-octaBDE, 5.6% (La Guardia et al., 2006).

The major companies producing brominated flame retardants worldwide are Albemarle Corporation (US), Dead Sea Bromine Corporation (Israel) and Chemtura Corporation (US), which were responsible for 78% of the flame retardant market in 2006 (Danish EPA 2006). The other production companies include Ceca (France), Warwick Chemicals (UK) and Albermarle S.A (Belgium), as well as Nippo, Tosoh and Matsunaga (all from Japan) (WHO/ICPS, 1994b). After c-pentaBDE and c-octaBDE were banned in the USA and Europe in 2003 and 2004, c-decaBDE became the predominant product in the brominated flame retardant market and most of the manufacturing companies moved to China. In 2014, three Chinese companies accounted for 40% of the c-decaBDE production in Chinese market, WeiDong Chemical Industry Company, Brother Chemical Industry Company and Shenyang Research Institute of Chemical Industry (China Flame Retardant Society). Another major six companies in China accounted for the rest of flame retardant market. China has never produced the c-octaBDE in official record, but it is available to produce c-pentaBDE. However, there is no c-pentaBDE production data available (Chen et al., 2012) and c-decaBDE has been the most important product in China (China Flame Retardant Society). Table 1.5 summarized the main years of commercial PBDE mixture production in three regions.

### Production of PBDEs in the USA and Europe

From 1990 to 1994, three commercial PBDE production in EU and the USA occupied the major flame retardant worldwide. However, In 1997, c-pentaBDE production ceased in Europe (UNEP, 2006, 2010b), followed in 1998 by c-octaBDE and 1999 by c-decaBDE production. After stopped production, commercial PBDEs product, especially c-decaBDE still imported into Europe in considerable quantities (UNEP 2010b, ECB2002, ECHA 2012a). In the USA, Great Lakes Chemical Corporation, the sole domestic producer of c-pentaBDE and c-octaBDE were voluntarily ceased these two mixture products production at the end of 2004 (Tullo A. Chemical & Engineering News 10 November, 2003). After 2004, most of PBDE manufacturing relocated to China, with a small amount of c-decaBDE production remaining in the USA. In 2005, 8215 metric tons of c-decaBDE were produced in the USA (US EPA 2010). By 2013, c-decaBDE was completely stopped production in the USA (UNEP/POPS/POPRC.10/10/Add.2, USEPA).

### Production of PBDEs in China

China began to produce commercial PBDE products in 1999 and with increasing production until a peak in 2006. After 2006, there have been a series of related regulations about PBDE intervention. C-decaBDE was the major product in the Chinese market. C-octaBDE was never been produced in China and there is only limited information for c-pentaBDE production. Only in 1999, a patent of c-pentaBDE about technical mixture containing was issued for China, but no production data (UNEP/POPS/POPRC.3/20/Add.1) (Chen et al., 2012). In 2014, the production of c-pentaBDE were stopped by the Ministry of Environmental Protection of China (000014672/2014-00289, China MEP, 2014)

From 2000 to 2004 the production of c-decaBDE in China increased from 10,000 metric tons to 25,000 tons, and the consumption of the c-decaBDE amounted to 30,000 tons in 2005 (Mai et al., 2005; Li et al., 2010; Xiang et al., 2007; Zou et al., 2007). The production of c-decaBDE declined in China, from 80,000 tons in 2006 to 21,000 tons in 2013 (Chen et al., 2012). During the period 2004 to 2013, the production of c-decaBDE in China covered domestic consumption and exports, but no detailed data are available.

**Table 1.5** The production periods (from beginning year to end) of c-pentaBDE, c-octaBDE and c-decaBDE in EU, the USA and China respectively.

| | **European Union** | **The USA** | **China** |
|---|---|---|---|
| **C-pentaBDE** | 1960 - 1997 | 1970 - 2004 | 1999 - 2014 |
| **C-octaBDE** | 1960 - 1998 | 1970 - 2004 | Never |
| **C-decaBDE** | 1980 - 1999 | 1980 - 2013 | 1999 - now |

### 1.3.2 Regulation and legislative actions on PBDEs

Potential health risks were first identified in Sweden with Brominated Flame Retardants (BFRs) being detected in sediment and fish along the Viskan river system (Andersson and Blomkvist, 1981). Because of this discovery, in 1987, PBDEs were specifically suggested as contaminants for the first time (Jansson et al., 1987). As they were reported in tissue samples from birds and marine mammals. In 1991, further concerns were raised as PBDEs were detected in human's tissues, blood and breast milk (Stanley et al., 1991; Daniels et al., 2010). Figure 1.2 showed the important regulation and control of PBDEs in EU, the USA and China from 2004 to 2017.

**Regulation and legislative actions on PBDEs in the USA and Europe**

In 1999, the Swedish government commissioned the National Chemicals Inspectorate to investigate PBDEs, and their report suggested that the government should prohibit the usage of PBDE, including other products containing PBDEs (The Swedish National Chemicals Inspectorate, 1999). In the same year, polybrominated biphenyl (PBB) was stopped manufacturing and prohibited to use in Sweden. After the action, Sweden continues to make efforts for an Europe wide prohibition of PBDEs. In 2001, the Council of the European Union discussed the control of marketing and use of the c-pentaBDE with a maximum content of 0.1% allowed in materials and formulations. (European Directive 76/769/EWG, 2001). In February 2003, EU banned to use c-pentaBDE and c-octaBDE by the European Parliament and Council of the EU and entered into force on 15th August 2004. However, c-decaBDE was exempt from this ban (Directive 2003/11/EC). In 2003, according to Restriction of Hazardous Substances (RoHS) which was adopted in February 2003 by the European Union as directive on the restriction of the use of six hazardous substances (Pb, Hg, Cd, $Cr^{6+}$, PBB, PBDE) in electrical and electronic equipment, c-decaBDE was banned to use in electrical and electronic goods (EU 2002/95/EC). However, this ban was reinstated in 2005 because of the practicalities of c-decaBDE cited by the member of the European Parliament (EU/2005/717/EC). In July 2003, the State of California firstly banned to use or distribute c-pentaBDE and c-octaBDE and took effect in 2006 (PBDEs Project Plan, March 2006, USEPA). Then, the USEPA promulgated a Significant New Use Rule (SNUR) which required notification prior 90 days for anyone who wanted to restart production or usage, and the rule was effective on 14th August, 2006 (rule at 40 CFR Part 721.10000) (La Guardia et al., 2006). In December, 2006, the importation of these two commercial mixtures (c-pentaBDE and c-octaBDE) were also banned on manufacture, use, sale and import in Canada by the Canadian Environmental Protection Act (CEPA) and took effect in Fall, 2007, but no restrictions were placed on the usage of c-decaBDE (MacDonald et al., CEPA, March 27, 2009). In August, 2006, Sweden banned to stop the use of c-decaBDE in textiles, furniture and electronic/electrical products by Ministry of Sustainable Development, and entered into force on 1st January, 2007 (#547, EMFacts Consultancy, 2006). In April to June , 2007, Washington States, Maine States and other eleven US states banned to use c-decaBDE in mattress, upholstered furniture, televisions and computers and entered into force on 2008, 2011 and 2010 separately (Washington State, 2007; NCEL, 2005; NCEL, 2007; Illinois EPA, 2006; CalEPA, 2006). In April, 2008, the use of c-decaBDE in electronics and electrical applications was prohibited by the European Commission (European Court of Justice, 2008) and became effective on the 1st June,

2008. In March, 2009, Canada prohibited c-pentaBDE and c-octaBDE in all of products and c-decaBDE in electronics and electrical equipment, and the regulation entered in force in 2011 (CEPA, March 2009). In May 2009 c-pentaBDE and c-octaBDE were listed as persistent organic pollutant (POPs) in the Annexes A of the Stockholm Convention (UNEP/POPS/COP.7/20). In 2014, The European Chemicals Agency (ECHA) proposed a restriction on the manufacturing, use and placing on the market of c-decaBDE, and entered in force on 17th March 2015 (ANNEX XV Restriction report, ECHA, August, 2014). In 2017 c-decaBDE was added to the Stockholm Convention Annex A on 5th May 2017 at the eighth Convention of the Parties (UNEP/POPS/COP.8/32) and cannot be manufactured or placed on the market as a substance on its own after 2 March 2019 (REACH ANNEX XVII).

### Regulation and legislative actions on PBDEs in China

In China, there have been a series of related regulations on three commercial PBDEs products dating from 2006. In November 2006, the Ministry of Information Industry of the People's Republic of China determined that concentrations of c-pentaBDE and c-octaBDE should be no more than 0.1% w/w in electronic products (Requirements for concentration limits for certain hazardous substances in electronic information products, SJ/T 11363-2006). In January 2010, China Environmental Protection Agency indicated that waste wires, cables and plastics containing PBDE should be separated during collection and disposed with other e-waste products, and the rules took effect on April 2010 Technical specifications of pollution control for processing waste electrical and electronic equipment, HJ527-2010).. In January 2016, People's Republic of China Ministry of Information Industry launched restriction of the use of c-decaBDE in electronic products followed by four standards (SJ/T 11364-2014*, GB/T 26572-2011**, GB/T 26125-2011*** and GB/T 29783-2013****) and entered into force on July 2016 (Management methods for the restriction of the use of hazardous substances in electrical and electronic products, January 2016).

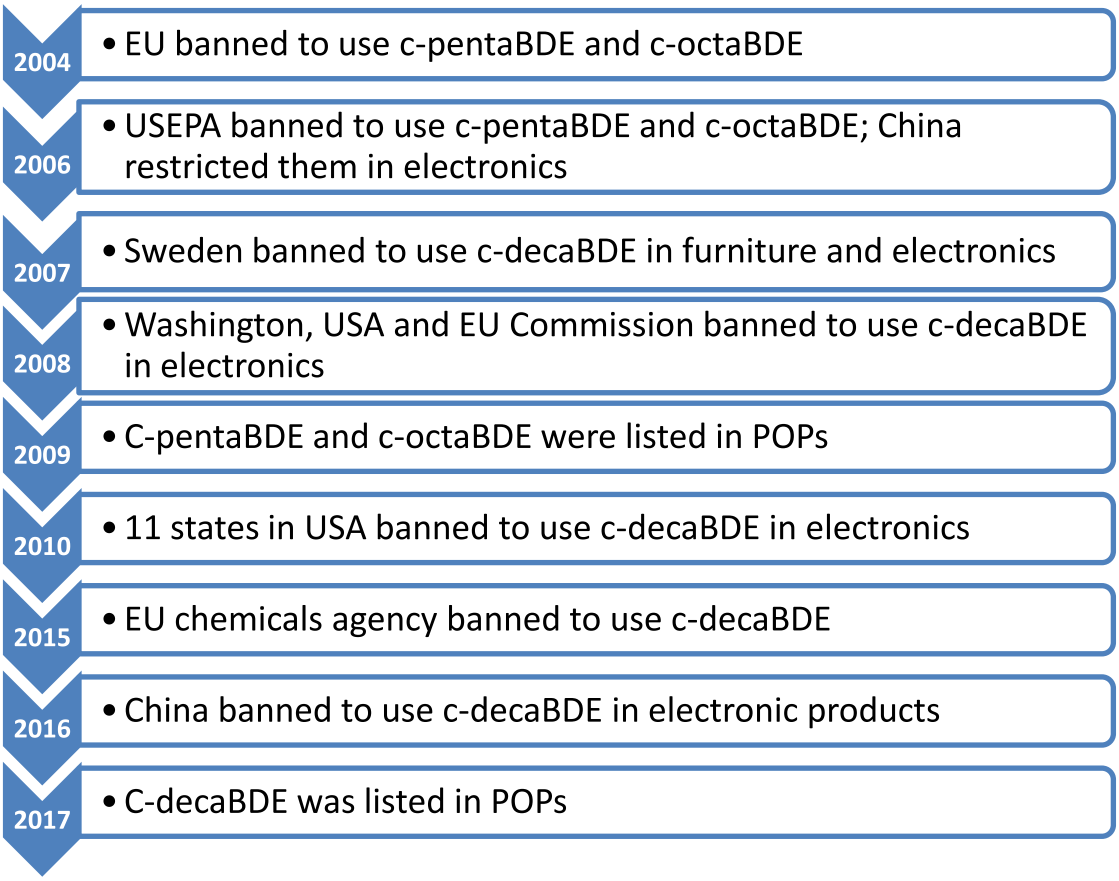
Notes:

* Marking for the restricted use of hazardous substances in electronic and electrical products.

** Requirements of concentration limits for certain restricted substances in electrical and electronic products.

*** Determination of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyl, polybrominated diphenyl ethers).

**** Determination of chromium (VI) in electrical and electronic products - Atomic fluorescence spectrometry.



2004
- EU banned to use c-pentaBDE and c-octaBDE

2006
- USEPA banned to use c-pentaBDE and c-octaBDE; China restricted them in electronics

2007
- Sweden banned to use c-decaBDE in furniture and electronics

2008
- Washington, USA and EU Commission banned to use c-decaBDE in electronics

2009
- C-pentaBDE and c-octaBDE were listed in POPs

2010
- 11 states in USA banned to use c-decaBDE in electronics

2015
- EU chemicals agency banned to use c-decaBDE

2016
- China banned to use c-decaBDE in electronic products

2017
- C-decaBDE was listed in POPs

**Figure 1.1** the timeline of important regulation and control of PBDEs in EU, the USA and China from 2004 to 2017.

### 1.3.3 Comparison timelines of PBDEs in China, Europe and the USA

Since commercial PBDE production and use began in China in 1999, for the purposes of this study, it is supposed the production of c-octaBDE and c-pentaBDE in Europe and USA were for domestic consumption only, with potentially limited export to China. Over the period 2000 to 2004, production of commercial PBDEs began to decrease in the USA and cease in EU, whilst production in China began to increase. In 2001, 83% of all commercial PBDEs consumed around the whole world was c-decaBDE, followed by c-pentaBDE, 11% and c-octaBDE, 6% (Hites, 2004). It means that Europe and USA imported considerable amounts of c-decaBDE from China. After 2004, nearly all of the

PBDE manufacturers ceased production in Europe and USA, with only small amount of c-decaBDE still produced in USA. At the same time production in China increased for both domestic consumption in China and export to Europe and the USA. Figure 1.3 shows the production of commercial PBDE formulation (metric tons) in Europe, the USA and China over the period 1990 to 2014. No production data was available during 1994 to 1998, so dashed lines represent potential trends of production during these periods. The same meaning of dashed lines were used to describe the production situation from 2006 to 2013. As shown in Table 1.6, the general time plots of PBDE usage and restriction action are presented.

**Table 1.6** Time plot of PBDEs usage and restriction in EU, the USA and China

| | | **C-pentaBDE** | **C-octaBDE** | **C-decaBDE** |
|---|---|---|---|---|
| **EU** | Began | 1960 | 1960 | 1980 |
| | Stop production | 1997 | 1998 | 1999 |
| | Stop usage | 2004 | 2004 | 2015 |
| **USA** | Began | 1970 | 1970 | 1980 |
| | Stop production | 2004 | 2004 | 2013 |
| | Stop usage | 2006 | 2006 | 2010(electronics) |
| **China** | Began | 1999 | - | 1999 |
| | Stop production | 2014 | - | - |
| | Stop usage | 2014 | 2014 | 2016(electronics) |

**Figure 1.3** Production amount (metric tons) of commercial PBDE products in EU, the USA and China from 1990 to 2014. Dashed lines represent potential trends of production during 1994 to 1998 and 2006 to 2013 as lack of available data.

## 1.4 Environment fate of PBDEs

### 1.4.1 Generalized life cycle of PBDEs

In general, there are three main stages of PBDEs life cycle: manufacturing, usage and disposal or recycling. It begins with the PBDE commercial formulation production, then launches to market as flame retardants, and added in consumer products, and finally disposes and recycles when the products containing PBDEs reach obsolescence. Releases to environment of PBDEs occur in each of the three stages (EPA/600/R-08/086F). Previous reports addressed PBDEs could leach out during the process when PBDEs are added in products, which includes various methods such as mixing, compounding, molding, extrusion and spinning (Environment Canada, 2011; EPA, 2010). Assessment report of PBDEs issued by US. EPA in 2009 estimated the total environmental releases from production and manufacturing reached the peak at 53.9 million tons in 1999, then decreased to 21.7 million tons in 2007 (U.S.EPA, 2009a).

Since PBDEs are additive flame retardant and not bonded chemically to the matrix, releases of PBDEs can occur through the process of volatilization during product usage stage. Several studies have measured furniture or appliances to test the concentration of PBDEs in indoor environment. Kemmlein et al. (Kemmlein et al., 2003) tested old panel of television casing and PBDE congeners including BDE28, 47, 66, 100 and 99 were detected in the air. It also concluded that older products emitted more PBDEs and continued for long time. Hazrati and Harrad also measured the older and newer PC in office and observed the concentration of PBDEs in indoor air decreased when only newer PC used (Hazrati and Harrad, 2006). Prevedouros et al. estimated the volatilization flux of BDE47 from products and consumed in the United Kingdom (Prevedouros et al., 2004). They concluded the air emissions of BDE47 with higher consumption rates was higher than the value with lower consumption occurred in 1997 in United Kingdom. It also assumed the average lifetime of consumer products was 10 years.

When the consumer products containing PBDEs reached their end-life, they were discarded in landfills, incinerators or recycled. PBDEs pollution occurred during the process at disposal sites. Previous studies showed the concentration of PBDEs in outdoor air and dust at landfill, electronic and electrical equipment (EEE) waste site and incineration areas, as well as the association with occupational exposure (An et al., 2011; Qu et al., 2007; Jiang et al., 2014).

### 1.4.2Environmental debromination of PBDEs

The breakdown of PBDEs including debromination, degrading and transforming. The process of debromination is defined as higher brominated congeners degrading to lower brominated congeners. Transforming of PBDEs occurs during production or recycling process and results in the formation of polybrominated dibenzodioxins (PBDD) and polybrominated dibenzofurans (PBDF) under thermal condition (Zheng et al., 2014; Tue et al., 2010). Degrading is shown to occur through aerobic and anaerobic bacteria metabolism, as well as through metabolism in several species such as fish, birds, rats and cows (Kodavanti et al., 2010; Tomy et al., 2004)

#### Debromination

The photolysis of BDE209 has been observed in various solutions under experimental conditions. DecaBDE has been shown to debrominate to pentaBDE and heptaBDE via nonaBDE (Gevao et al., 2010) when it is dissolved in solvent and subjected to artificial ultraviolet (UV) irradiation. DecaBDE also can photolytically debrominate into lower brominated PBDEs when present in soil and sediment (Rodenburg et al., 2014).

Another debromination study indicated the process of photolytical debromination can also occur in indoor dust (Stapleton et al., 2008a). The authors exposed dust spiked with BDE209 to sunlight for more than a week and found evidence of the formation of heptaBDE, octaBDE and nonaBDE congeners. These previous studies suggest PBDE debromination can happen both in outdoor and indoor environments (Stapleton et al., 2008a).

### Transformation

The combustion of PBDE can lead to the formation of Polybrominated dibenzofurans (PBDFs) and Polybrominated dibenzodioxins (PBDDs) in the smoke. When the combustion temperature of BDE209 is at 500 ℃ and octaBDF and heptaBDF are emitted (EPA/600/R-08/086F). When BDE47 and BDE153 are heated for 5 to 10 minutes at 250 to 500 ℃ they will be chemically transformed (Takigami et al., 2008) to form PBDDs and PBDFs and emitted during the combustion of PBDEs containing products. A study in China collected air samples from electronic waste (e-waste) processing sites and found the concentration of PBDD and PBDF were significantly high, so did the concentration of octaBDE and nonaBDE. The authors suggested the e-waste recycling may be the one of the sources of halogenated organic pollutants of human exposure (Ren et al., 2014).

### Biodegradation

Biodegradation occurs in microorganisms, humans and wildlife through PBDE metabolism (Kodavanti et al., 2010; Guo et al., 2007; Hale et al., 2006). These previous studies have shown BDE209 was reduced to lower congeners and may have harmful impacts on wildlife and human health. The process of degradation also occurs through environment media such as soil, sediment and sand. Environmental debromination may lead to the concentration of lower brominated congeners increasing in the environment from the presence of higher brominated congeners (Rahman et al., 2001). Previous study has shown the estimated degradation half-lives of PBDE congeners is the longest in sediment (5,760 to 14,400 hours), followed by soil (1,440 to 3,600 hours) and water (1,440 to 3,600 hours). In air, the half-lives for low PBDEs (BDE28, BDE47, BDE99, BDE100, BDE153 and BDE183) were the shortest, 128 to 1,540 hours, but long in BDE209, 7,620 hours (Wania and Dugani, 2003).

### 1.5 Pathways of human exposure to PBDEs

PBDEs have been identified as representing a potential risk to human health and the environment as a result of their high lipophilicity, high resistance to degradation processes and bioaccumulation. Human exposure is determined by a combination of intake, which can be calculated by the amount of chemical entering the human body via a range of pathways, and body burden. Body burden can be estimated through external exposure and biomonitoring routes (Figure 1.2). External exposure pathways include diet (meat/fish/egg/vegetables/fruits) and inhalation (indoor air/dust and outdoor air/particulates. Biomonitoring can be used to assess body burdens through human tissue measurements such as breast milk, blood, serum, tissues and hair (Bramwell et al.,

2016) which takes into account absorption/excretion and metabolism.

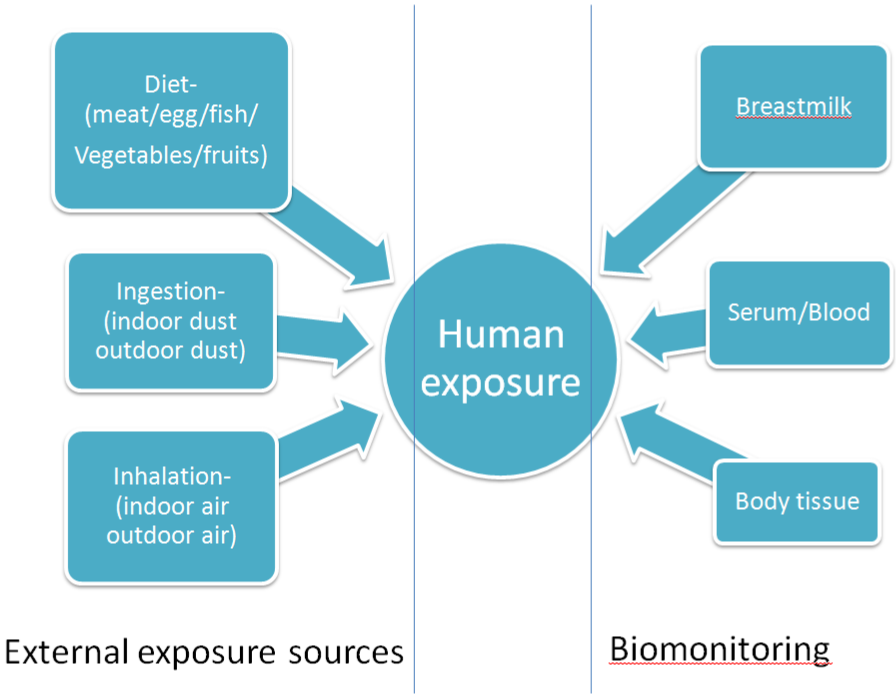


**Figure 1.4** External exposure sources (diet, ingestion and inhalation) and biomonitoring pathway (tissue measurement) of human exposure to PBDEs

### 1.5.1 External exposure sources

#### Dust ingestion

Previously published studies have addressed indoor dust as an important route of human exposure to PBDEs since there was evidence of a positive correlation between concentrations of PBDEs in indoor dust and breast milk, as well as for blood and serum (Wu et al., 2007; Harrad et al., 2006; Petreas et al., 2011; Johnson et al., 2010; Sjodin et al., 2008; Allen et al., 2008; Stapleton et al., 2005; Wilford et al., 2005). House dust contributes to 82% and 77% of the USA adult and toddler exposure, with more than 80% for Canadian children, and 37% for adults and 69% for toddlers in the UK and 71% of

Chinese adult exposure (Johnson-Restrepo and Kannan, 2009; Jones-Otazo et al., 2005; Harrad et al., 2006; Jin et al., 2010). Infants are especially at risk to exposure from PBDEs in dust because of their hand-to-mouth behavior while playing on the floor and touching toys (Kelly et al., 2008; Bradman et al., 2014; Frederiksen et al., 2009; Jeong et al., 2014). These studies indicated that the ingestion of dust accounted for over 80% of daily PBDE intake in children.

### Air inhalation

Inhalation of air is also a pathway for human exposure, although it has been estimated that inhalation only contributed to 4% of daily PBDE human intake (Wilford et al., 2004). Indoor air inhalation is more important than outdoor air inhalation because the median of PBDE concentration is higher than outdoor air.

### Diet

Since PBDEs can accumulate in the lipid rich tissues of animals, they have been found in fatty foods of animal origin. Diet thus represents an important route of exposure in humans through eating fish, meat, eggs, fatty foods and dairy products. Some of the highest concentrations of PBDEs have been found in freshwater fish, followed by meat. Previous study measured 62 food samples and detected BDE17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183 and 209. The results showed the three highest mean value of total PBDE concentrations reported in fish, meat and dairy products, approximately 1,000 pg/g, 400 pg/g and 100 pg/g respectively (Schecter et al., 2006). Other studies indicated the mean concentrations of total PBDEs between countries were 1,120 ng/kg ww (BDE17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183 and 209), 634 ng/kg ww (BDE28, 47, 99, 100, 153, 154, 183 and 209), and 231 ng/kg ww (BDE28, 47, 99, 100, 153, 154, 183 and 209) for the USA, Swedish and Chinese fishes, respectively (Schecter et al., 2006; Ni et al., 2013; Darnerud and Risberg, 2006). The authors concluded that fish was a main dietary source for human exposure to PBDEs. A comparison of the concentration of BDE47 in serum samples from two fish consumer groups, a high fish intake and no fish intake group showed that the high fish intake group had higher concentrations of BDE47 in serum, with a median value of 2.1 ng/g lipid weight, while it was only 0.4 ng/g lipid weight for the no fish intake group(de Wit, 2002).

The consumption of meat and eggs can also be an important exposure route. In the USA, the median concentration of PBDEs (BDE17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183 and 209) was 85 pg/g wet weight in eggs and 383 pg/g wet weight in meat. In China, there were few studies on consumption of meat and eggs. One published study focused on e-waste sites (Schecter et al., 2006; Ni et al., 2013). The latest study measured 14 food groups in 2017 in Birmingham, UK and the results showed the highest mean value of PBDE (BDE28, 47, 100, 99, 154, 153 and 209) concentration in fish, 1800 pg/g ww, followed by meat, 600 pg/g ww and eggs, 200pg/g. Compared to the record data by UK Food Standards Agency in 2006 and resulted PBDEs concentration were in fish, 600 pg/g ww; in meat, 200 pg/g ww and in eggs 100 pg/g ww) (Tao et al., 2017). The authors suggested it may be attributable a lagged time of

PBDEs from indoor environment to outdoor environment and may increase the concentration of PBDEs in food samples temporally, because they also showed the decline of PBDE (BDE209, 47 and 99) concentration in indoor dust and indoor air (Tao et al., 2017).

The PBDE content of vegetables and fruits is lower than other food types because of low fat content and greater water content in vegetables and fruits. The concentration range of PBDEs (BDE28, 47, 99, 100, 153, 154, 183 and 209) has been reported to range from 8 to 17 ng/kg ww in vegetables and 4.2 to 6 ng/kg ww in fruits in EU countries (Trasande et al., 2015; Fernandes et al., 2008; Law et al., 2008).

### 1.5.2 Biomonitoring

Biomonitoring has become an important tool for human intake assessment in recent years. PBDE concentrations in breast milk, blood and other human tissues have been investigated in the USA and European countries for several years. In China, studies into body burdens have been conducted later than in western countries, and has mostly focused on e-waste areas, appliance recycling sites and PBDEs production areas.

**Breast milk**

Several studies have reported the level of PBDE (BDE47, 99, 100, 153, 154 and 183) concentration in breast milk in China, for example; 2.5 ng/g (lipid weight) in TianJing (Zhu et al., 2009), 7.1 ng/g lw in Nanjing (Sudaryanto et al., 2008), 3.71 ng/g lw in Shijiazhuang (Sun et al., 2010), 3.42 ng/g lw in Tianjing (Sun et al., 2010). These results suggest that the concentration of PBDEs in breast milk in the cities in China for women were the same order of magnitude to their counterparts from European countries (median value of PBDEs (BDE47, 99, 100, 153, 154 and 183) was 4.33 ng/g lw) (Bramwell et al., 2017; Bjorklund et al., 2012; Darnerud et al., 2015), but lower than that the USA (median value was 62.5 ng/g lw) (Daniels et al., 2010; Schecter et al., 2003). However, PBDE concentrations in breast milk collected in a prominent E-waste recycling area (Jin et al., 2009; Leung et al., 2010) were much higher than the samples from general places in China, with concentration value of PBDEs (BDE47, 99, 100, 153, 154 and 183) at 59.3 ng/g lw in Taizhou place and 33.9 ng/g lw in Laizhou Bay place separately. The results indicated that the significant correlations occurred between the PBDEs contamination environmental levels and human exposure.

Table 1.7 shows the average concentration of total PBDEs (including BDE209) (ng/g lipid weight) in breast milk for China, the USA and Europe, respectively, from 2003 to 2014. The supporting information provides concentration data for PBDEs in breast milk from several countries. Data from the USA showed the highest concentrations of PBDEs, followed by samples collected from around the China E-waste recycling areas. In addition to many presented studies of PBDEs in the indoor and natural environment, other researches have discussed the presence of PBDEs in human breast milk. Breast milk plays an important role on the biomonitoring of PBDEs since it reflects an infant's potential exposure (Antignac et al., 2009). A literature reveiew found 7 studies focused on Europe, 9 studies in China, and 6 studies in the USA. Several studies in China and

Europe have reported PBDEs concentration in breast milk that were lower than the breast milk samples from the USA. In the USA, PBDE concentrations measured in breast milk were 10 to 100 times greater than in EU and China. For European countries, the levels of PBDEs in human milk have remained stable. Although the EU countries banned commercial PBDE mixture production early in 1999 in environment, there was evidence of the lagged decreasing trend of PBDEs in human body (Bramwell et al., 2017; Bjorklund et al., 2012; Darnerud et al., 2015), For China, the concentration of PBDEs in breast milks from non-e-waste recycling centers were of the same order of magnitude as EU samples. However, PBDE concentration in breast milk collected in a prominent E-waste recycling areas (Jin et al., 2009; Leung et al., 2010) were much higher, with the total PBDE concentration including BDE209 at 59.3 ng/g lw in Taizhou area and 33.9 ng/g lw in Laizhou Bay area. The results indicated that correlations existed between the PBDEs contamination level in the environment and human exposure.

**Table 1. 5** The average value of PBDEs concentration (ng/g lipid weight) in breast milk based on the median PBDE value from individual published study from EU (n=9), the USA (n=7) and China (n=6) separately from 2002 to 2014.

| | China | EU | North America |
|---|---|---|---|
| 2002 | | | 34 |
| 2003 | | 5.4 | 55.8 |
| 2004 | 1.08 | | 55.8 |
| 2006 | 2.5 | | |
| 2007 | 3.3 | | |
| 2008 | 2.67 | | |
| 2009 | | 5.2 | 36.8 |
| 2010 | | 5.25 | |
| 2011 | 1.47 | 5.09 | 60 |
| 2012 | | | 36.8 |
| 2013 | | | |
| 2014 | | 5.8 | |

**Serum**

Human serum has also been increasingly used for the assessment of human exposure. The median concentrations of PBDEs (BDE17, 28, 47, 66, 99, 100, 153, 154 and 183) in human serum samples from the USA have been reported at 61 ng/g lipid (Makey et al., 2016; Johnson et al., 2010; Anderson et al., 2008) which is higher than samples from European countries 6.83 ng/g lipid (Bramwell et al., 2017; Thomas et al., 2006; Bramwell et al., 2014; Darnerud et al., 2015) and in China 5.74 ng/g lipid (Wang et al., 2013; Wang et al., 2016; Liu et al., 2017). However, the concentrations of PBDEs in serum samples from workers at electrical appliance factories were much higher than non-e-waste workers, 165 ng/g lipid (BDE17, 28, 47, 66, 99, 100, 153, 154 and 183) for carpet and foam manufacturing workers in USA; 254 ng/g lipid (BDE28, 47, 99, 100, 153, 154, 183 and 209) for PBDE production area in Laizhou Bay, China (Jin et al., 2009; Zheng et al., 2017; Stapleton et al., 2008b).

### 1.5.3 Occupational exposure

Occupational exposure occurs when people who work in the manufacturing of goods containing PBDEs, working in an e-waste area or recycling of materials and products containing PBDEs. They are often subject to higher exposure through air inhalation, dust ingestion and dermal absorption in developing countries such as China, India, Vietnam, where illegally exported electronic waste from developed industrial countries and received for manufacturing, recycling or disposal (UNEP/POPS/COP 4/38). Deng et al (Deng et al., 2007) reported concentrations of PBDEs (BDE28, 47, 99, 100, 153, 154, 183 and 209) in serum samples from workers at an e-waste recycling facility in Southern China which ranged from 140 to 8,500 ng/g lipid weight, with a median value of 600 ng/g lwt. Jin et al (2007) also collected serum samples at c-decaBDE production areas from the southern coastal area of Laizhou Bay in China. The concentrations were similar to those in the e-waste region, with a median value of PBDEs (BDE28, 47, 99, 100, 153, 154, 183 and 209) at 613 ng/g lwt (Jin et al., 2009). Some studies have suggested that gender is a factor that influences PBDEs concentrations, although with little explanation. Females had higher concentrations of PBDEs in serum than males, especially for BDE209, with 2.33 times greater than in male serum from Laizhou Bay (Jin et al., 2009). Conversely, another studies reported higher PBDEs concentration in serum from males than from females in Korea and 1.24 times in New Zealand (Moon et al., 2007; Harrad and Porter, 2007), but t-test revealed $p>0.1$ and no statistically insignificant.

## 1.6 PBDEs in indoor environment in EU, the USA and China

PBDEs have been identified as representing a potential risk to human health and the environment as a result of their high lipophilicity, high resistance to degradation processes, and bioaccumulation, therefore, human exposure to PBDEs has been a great concern. Human exposure pathways for PBDEs can be assessed through quantifying external pathways and biomonitoring. Previously published studies have addressed indoor dust an important exposure pathway for PBDEs since there was a significant correlation between indoor dust and human milk and blood and PBDE concentrations (Wu et al., 2007; Harrad et al., 2006; Petreas et al., 2011). In this present study, the levels of PBDEs in indoor dust and indoor air are compared separately as main exposure routes, and finally summarizes the concentration of PBDEs in human blood and breast milk.

### 1.6.1 Inclusion and exclusion criteria

This study aims to summarize and compare the previous published studies which have assessed PBDE exposure. The following database selection criteria were considered avoiding false data and specialty sampling location: the studies must be in English and published in a scientific journal from 2003 to 2016, and the samples collected must be only from private house in general city regions, excluding office, E-waste, hospitals, etc.

### 1.6.2 PBDEs in indoor dust

As one of the most important exposure pathways, indoor dust inhalation studies have been mainly conducted in houses exclusively, not in other indoor microenvironments. The supporting information lists PBDE concentration data from previously published studies on indoor dust in the USA, Europe and China. Detailed information on the sampling method, sampling location and detected PBDE congeners are listed. All of the data represented were collected in living rooms and bedrooms from private houses in different cities in the three selected regions. In total, there were 22 published studies from China, 21 studies from Europe and 18 studies from the USA. Using these data sets, the average value of PBDE concentration including BDE209 have been estimated and shown in Figure 1.6 for each year from the three regions. Each bar value represents the average value of PBDE concentration in China, USA and UK in a given year based on the median PBDE concentrations from previously published study. The median value of PBDEs in the UK was higher than the rest of Europe for each year. This may be because of the stricter fire regulations in Britain compared to other countries in Europe, and therefore higher BFR content in home furniture, as well as the greater use of carpets (Kalantzi and Siskos, 2011). For North America, although the median value of PBDE concentrations decreased slightly year by year, the concentration was higher than

Europe and China from 2008 to 2010. After 2011, the concentration in China began to increase, with levels in Europe being the lowest.

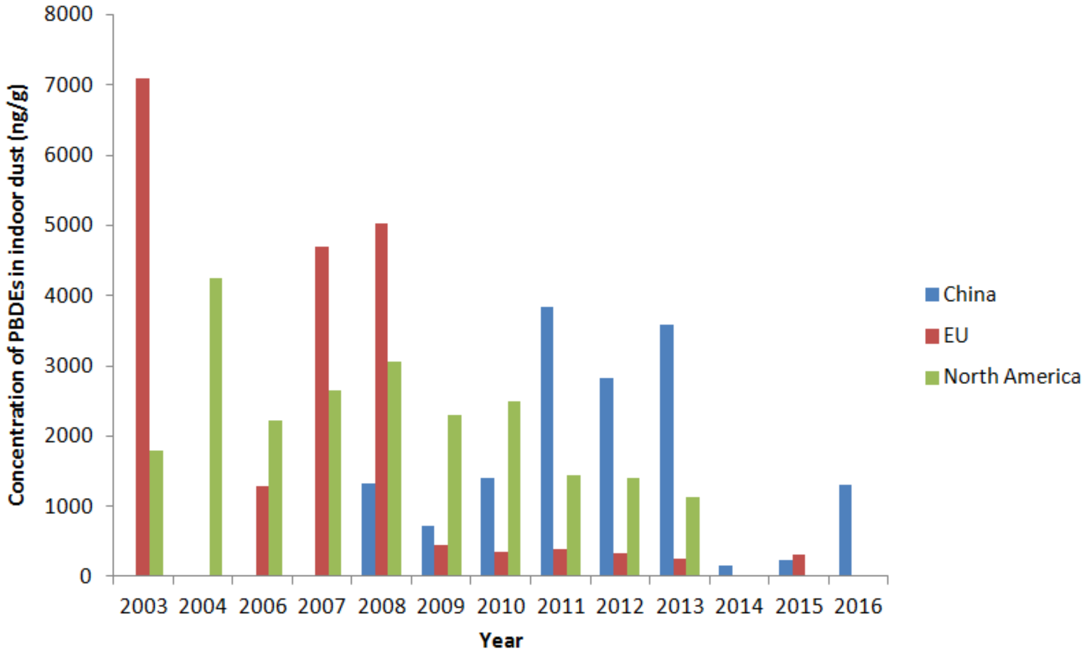


**Figure 1.5** The average value of PBDEs concentration (ng/g) in indoor dust based on the median PBDE value from each published study from EU (n=21), the USA (n=18) and China (n=22) separately from 2003to 2016.

### 1.6.3 PBDEs in indoor air

Unfortunately, researchers have not measured indoor air as much as they did for indoor house dust in EU and North America. Compared with indoor dust sample, studies of measuring indoor air were fewer, only 27 studies in total were found in literature search , 8 studies from China, 11 studies from Europe and 8 studies from North America. This may possibly be due to the easier sampling technique of indoor dust than that of indoor air (EPA/600/R-08/086F) (Malliari and Kalantzi, 2017). The average values for PBDE concentrations in indoor air are shown in Table 1.8 The supporting information also lists PBDE concentration data in indoor air from published studies in the USA, Europe and China. Detailed information on the sampling method, sampling location and detected PBDE congeners are listed. The highest concentration of PBDEs (BDE47, 99, 100, 153 and 154) in indoor air was observed in UK in 2003 at 1622 pg/m$^3$ (Harrad et al., 2004), and in the USA the highest median concentration of PBDEs (BDE28, 47, 66, 77, 85, 99, 100, 118, 138, 153, 154, 183, 203, 207 and 209) was 760 pg/m$^3$ in 2006 and the maximum was 3980 pg/m$^3$ (Johnson-Restrepo and Kannan, 2009). Low PBDE concentrations in China were reported during 2008 to 2013, but after 2013, the concentration of PBDEs began to increase. One previous review summarized indoor air samples across the world and concluded BDE47 and BDE99 accounted for 60% to 80% of PBDEs in indoor air, with BDE17 being detected in high abundance in the vapor phase because of the atmospheric debromination process of BDE209 by sunlight (Besis and Samara, 2012). However, limited data for indoor air were collected, hence more future work may be needed on the indoor air quality as PBDEs may continue to volatilize from these products resulting in emission to indoor air throughout the lifetime of a product (UNEP, 2007).

**Table 1. 6** The average value of PBDEs concentration (pg/m$^3$) in indoor air based on the median PBDE value from each published study in EU (n=11), the USA (n=8) and China (n=8) separately from 2003to 2016.

|  | China | EU | North America |
|---|---|---|---|
| **2003** |  | 26.85 | 255 |
| **2004** |  | 75.5 |  |
| **2006** |  | 18 | 760 |
| **2007** |  | 194 | 559.2333 |
| **2008** |  | 275 |  |
| **2009** | 126 |  | 760 |
| **2010** |  | 37.8 | 530 |
| **2011** | 82.45 | 5 |  |
| **2012** |  |  |  |
| **2013** | 81.1 | 170 |  |
| **2014** | 119 |  |  |
| **2015** | 68.5 |  | 47 |

## 1.7 Discussion of PBDEs in indoor environment and human burdens in EU, the USA and China

In this study, concentration data for PBDEs in indoor air, indoor dust and breast milk in the USA, UK and China were collated over the period from 2003 to 2016. These results were then compared to production trends of three commercial PBDE products and the influence of regulatory controls as already discussed in this study. Correlations connecting PBDE production and regulation with PBDEs concentrations in indoor environments were evident, which would have implications for changing human exposure patterns. First of all, (Alaee et al., 2003) indicated that PBDEs can be released from electrical and electronic equipment, textiles, plastic components and other furniture into the indoor environment hence contributing to indoor air and dust pollution. Secondly, previous studies have suggested that there was a positive correlation between the concentration of PBDEs in indoor dust and the concentrations in human breast milk and blood (Johnson et al., 2010; Allen et al., 2008; Jones-Otazo et al., 2005; Wu et al., 2007) with indoor dust being an important pathway to human exposure, accounting for 80% of exposure for both adults and children (Johnson-Restrepo and Kannan, 2009). Hence the above analysis and data including table 1.7, table 1.8 and figure 1.6showed:

1). Despite production having ceased before 2004, PBDE concentrations in indoor dust in the USA and Europe were still much higher than that of China until 2008, since the usage and import of commercial PBDE products were not stopped at the same time as production. A previous study came to the same conclusion that although production and manufacturing have stopped domestically, the concentration of PBDEs in indoor environments were still high until the limits on PBDEs added into consumer products came into force (Janssen, 2005). After the limitation on PBDE usage in consumer products, the concentration of PBDEs in indoor dust began to decrease slowly.

2). The decreasing trends of PBDE concentrations in indoor environments were slowly and slightly after being banned production and usage. It is suggested the old furniture and household appliances kept using in daily life and emission PBDEs continually. Generally, the lifetimes of furniture and consumer house hold products may be ten years (UNEP/POPS/POPRC.10/10.Add.2), Also, It addressed the PBDEs have long persistence and half-life character (de Wit et al., 2012).

3). Previous studies (Harrad et al., 2008a; Stapleton et al., 2005) indicated that the peak median value of total PBDEs including BDE209 in dust was 4250 ng/g in the USA in 2004, and the peak of PBDE median concentration in China was 4000 ng/g in 2011(Kang et al., 2011). It is suggested that PBDE concentration trends were similar between developed countries and China. The usage of commercial PBDE history in developed countries were earlier than in China, and the peak of PBDE pollution also reached earlier in developed countries than in China.

However, it is clear that the PBDE mixture compositions were different between developed countries and China. A number of previous studies from China (Chen et al., 2011; Huang et al., 2010) concluded that BDE209 was the dominant congener in indoor environments in China, accounting for over 90%, and other low PBDE congeners have been reported to be less than 10%. Opposite results were observed from the studies in USA and UK (Allen et al., 2008; Harrad et al., 2008b; Shoeib et al., 2012), which showed that BDE209 accounted for 60% to 80%. The results may be explained because c-pentaBDE and c-octaBDE were widely used in the USA and UK before the phase out. While in China, the majority of PBDE commercial products were c-decaBDE with its main component being BDE209. Another potential contributing factor may be from the difference in life-styles in which more carpets are used in the USA and the UK than in China. So BDE47, BDE99 and BDE100 were usually the most dominant congeners in indoor dust in Europe and the USA, since c-pentaBDE were widely used in foams, and textiles and carpets (Kang et al., 2011; Alaee et al., 2003; de Wit, 2002).

4). On-going emissions of PBDEs from products still in use has been predicted to be zero by 2020 in UK (Birgul et al., 2012). In China, it only took four years to reduce the concentrations of total PBDEs including BDE209 from the peak of PBDE concentration in 2011. A possible reason was the limited fire regulations in China which required use of flame retardants. A lower peak value than USA and EU may be an evidence. As c-decaBDE products were expensive, only products due for export were treated with sufficient flame retardant materials to reach the standards required in the receiving country. For the domestic market, only household furniture was made with flame retardant materials (PUF and POP blog in Chinese website). Owing to the low levels of PBDE incorporation into products, emissions to the environment were lower.

5). As shown in Table 1.7, human exposure to PBDEs in the USA was much higher than either the UK or China. The main reasons may be dietary behavior and more commercial PBDE production and usage in the USA. There are many concerns that dietary intake of PBDEs have affected human health (Bramwell et al., 2016). Cultural and dietary behavior differences between the USA, UK and China may result in different PBDE concentrations and profiles being present in breast milk. Schecter et al. (2006) suggested that the highest PBDE concentrations were found in fish, followed by meat and dairy products. In the USA, fish consumption was reported to be a predominant dietary intake pathway for PBDEs (Zuurbier et al., 2006; Thomas et al., 2017).

For the USA, the long-term usage and production of PBDEs from early 1970 to the late of 2013 led to the higher concentrations of PBDEs in breast milk than that of EU countries (Daniels et al., 2010) (Janssen, 2005). For China, the concentration of PBDEs in human breast milk kept increasing slightly because of five year lag for human exposure compared with indoor environment. Previous studies also suggested it may take several years from bioaccumulation to degradation and then the PBDE pollution decreased in human body such as indoor environment situation (Buttke et al., 2013; Daniels et al., 2010).

## 1.8. Statement and objectives of the thesis.

### 1.8.1 Aim of this study

As an important role in the global market of PBDE manufacture, the production of c-decaBDE in China has increased rapidly over the past 20 years (Chen et al., 2012). In 2001, the production of c-decaBDE accounted for 93.3% of commercial PBDEs products, however, no specific data confirmed that c-pentaBDE and c-octaBDE were produced in China (Chen et al., 2007). Compared with PBDEs produced in developed countries, the history of usage in China was shorter than in the EU or USA. PBDEs had been launched for use in developed countries in 1970s, it was until 30 years later that they entered into the Chinese market (de Wit, 2002; Chen et al., 2012). Additionally, the amounts of each commercial PBDE products used were different. C-pentaBDE and c-octaBDE were produced and used widely in the EU and USA over a long-time period, but only c-decaBDE was used in the majority products in China. As a result, the concentrations of PBDE and congeners profiles were different among EU countries, the USA and China.

Previous studies suggested that indoor dust was a significant pathway of human exposure since there was a positive correlation between the concentration of PBDEs in indoor dust and concentrations in human breast milk and blood (Johnson et al., 2010; Allen et al., 2008; Jones-Otazo et al., 2005; Wu et al., 2007). However, compared with the abundant studies in indoor environments in developed countries, only limited studies have been conducted in China. Previously published studies in China largely covered industrial or E-waste regions, or only focused on the specific key cities such as Beijing, Shanghai and Guangzhou (An et al., 2011; Ding et al., 2016; Chan et al., 2013; Chen et al., 2009; Deng et al., 2014; Guan et al., 2009; Labunska et al., 2014; Zheng et al., 2011; Zheng et al., 2015; Wang et al., 2018; Yu et al., 2018; Sun et al., 2016b; Li et al., 2015; Peng et al., 2017). These cities have larger populations and higher degree of urbanization than other cities in China, with higher levels of contamination of the outdoor environment expected compared to other cities, which could influence indoor PBDE concentrations. Another data gap is the lack of spatial distribution investigations for PBDEs in China, considering climate, urbanization and life style.

Only limited studies have been conducted for spatial distribution in indoor environment in China. For example, 78 indoor dust samples were collected from 23 provinces in 2015 (Zhu et al., 2015) and the range of total PBDEs (BDE17, BDE28,

BDE47, BDE49, BDE66, BDE85, BDE99, BDE100, BDE138, BDE153, BDE154, BDE183, BDE190 and BDE209) was 8.92 to 37,500 ng/g with a median value of 1110 ng/g. The study suggested that samples from eastern China (2120 ng/g) were higher than other parts of China (847 ng/g) because of more factories and production field in eastern part.

Another study collected 76 indoor dust samples from Guangzhou city, Wuhan city and Haikou city in China in 2010 (Huang et al., 2010). The concentration of total PBDEs in house dust including BDE28, BDE47, BDE49, BDE85, BDE99, BDE100, BDE153, BDE154, BDE183 and BDE209 varied from 186.6 to 9654 mg/g with a median value of 1867 ng/g. The study suggested Guangzhou may experience higher emissions than the other two cities because of higher temperatures and more industrial activities.

He et al. (He et al., 2017) collected 78 indoor dust samples from e-waste recycling, rural and urban regions in South China in 2017. The results showed that concentration of PBDEs (BDE47, 99, 100, 153, 154, 183, 206, 207, 208 and 209) were 30,100 ng/g, 4810 ng/g and 2360 ng/g for e-waste, rural and urban areas separately, suggesting that e-waste regions had higher levels of PBDE contamination which are mostly present in South China especially derived from c-decaBDE mixture.

However, there were still limitation in these studies that the dust samples and sampling locations were insufficient or only covered few cities. Also, these studies only focused on northern cities of China or southern ones, lack of spatial distribution from south to north and comparison of dust sources within indoor environment, lack of spatial distributions between rural, suburban and urban araes in particular.

Studies concerning contamination of human blood are also limited in China, especially connected with thyroid hormone parameters. Further to this there is a complete lack of analysis of human exposure for China compared to developed countries, since the source, concentration and fate of PBDEs in indoor environments are different.

Based on the above concerns and data gaps, the aims of the study were:

1. to compare the concentrations, legacy activities, time trends and congener profiles of PBDEs in the EU, the USA and China;
2. to investigate the spatial concentration of PBDEs across five key cities (Dalian, Beijing, Shanghai, Xiamen and Guangzhou) in China from North to South and discuss the potential indoor sources of PBDEs and analyze spatial characteristics in urban, suburban and rural regions in each target city;
3. to develop the initial methods on analyzing the concentrations of PBDEs in serum from patients with abnormal thyroid hormones, and to conduct a pilot investigation of the potential correlation between PBDEs and thyroid hormones parameters.

### 1.8.2. Objectives of this study

The sampling and analytical methodology in **Chapter 2** describes the sampling methods and analytical techniques used in this thesis including sample collection, extraction, GC/MS analysis, as well as the quality control (QC), quality assurance (QA), and statistics software chosen.

**Chapter 3** describes a study into indoor dust contamination across private homes in Xiamen, analyzes the concentrations of PBDEs, and characterizes congener profiles. The study discusses how the presence of consumer products could affect PBDE concentrations. Estimated human exposures based on dust concentration and activity are calculated.

**Chapter 4** focuses on PBDEs in indoor dust in China across a number of important cities from North to South. 141 indoor dust samples were collected from five cities. For each city, the sampling locations included urban, suburban and rural areas. Daily human exposure was calculated for each city using indoor dust concentration and activity.

**Chapter 5** describes a study which analyzed 40 serum samples in abnormal thyroid hormone function patients and discusses the link between PBDE concentrations in serum and thyroid hormone function. The results provided a comparison with the PBDEs exposure levels for people with abnormal thyroid function and explored the correlation between PBDEs congeners and five thyroid hormones parameters including T4 (thyroxine), T3 (triiodothyronine), FT4 (free thyroxine), FT3 (free triiodothyronine) and TSH (thyroid-stimulating hormone), as well as human basic characteristics such as age, gender and BMI.

**Chapter 6** summaries the conclusions of this thesis and discuss the limitation gap for current research and the possibilities of the future work.

## Supporting information

Table S1 Concentrations of PBDEs in indoor dust, indoor air and breast milk in selected regions, Europe, the USA and China (ng/g)

| # | City | Sampling Year | Sample Size | PBDE congeners | Median (ng/g) | Range (ng/g) | Reference |
|---|---|---|---|---|---|---|---|
| **Indoor dust in China (n=22)** | | | | | | | |
| 1 | Guangzhou | 2011 | N = 5 | BDE-28, 71, 47, 66, 100, 99, 85, 154, 153, 156, 184, 183, 197, 196, 207, 206 and 209 | 3930 | 685 to 18,385 | (Kang et al., 2011) |
| 2 | Shenzhen | 2011 | N = 5 | BDE-28, 71, 47, 66, 100, 99, 85, 154, 153, 156, 184, 183, 197, 196, 207, 206 and 209 | 4563 | | (Kang et al., 2011) |
| 3 | HongKong | 2011 | N = 13 | BDE-28, 71, 47, 66, 100, 99, 85, 154, 153, 156, 184, 183, 197, 196, 207, 206 and 209 | 4169 | | (Kang et al., 2011) |
| 4 | Shanghai | 2008 | N = 44 | BDE-17, 28, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190 and 209 | 695.7 | 131.6 to 3,886.7 | (Yu et al., 2012) |
| 5 | Guangzhou | 2008 | N = 46 | BDE-28, 47, 66, 100, 99, 85, 154, 153, 183 and 209 | 2686 | 564.3 to 9654 | (Chen et al., 2011) |
| 6 | Haikou | 2008 | N = 20 | BDE-28, 47, 66, 100, 99, 85, 154, 153, 183 and 209 | 1088 | 186.6 to 8285 | (Huang et al., 2010) |
| 7 | Wuhan | 2008 | N = 10 | BDE-28, 47, 66, 100, 99, 85, 154, 153, 183 and 209 | 844.4 | 302.9 to 1356 | (Huang et al., 2010) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 8 | Shanghai (living room) | 2016 | N = 15 | BDE-28, 47, 49,66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 201, 202, 203, 206, 207, 208 and 209 | 1900 | 800 to 12,300 | (Peng et al., 2017) |
| 9 | Shanghai (Bedroom) | 2016 | N = 15 | BDE-28, 47, 49,66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 201, 202, 203, 206, 207, 208 and 209 | 1000 | 200 to 11,200 | (Peng et al., 2017) |
| 10 | Multiple cities (23 cities) | 2010 | N = 78 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 190 and 209 | 1110 | 8.92 to 37,500 | (Zhu et al., 2015) |
| 11 | Hangzhou | 2015 | N = 10 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 239 | 56.5 to 2207 | (Sun et al., 2016b) |
| 12 | Guangzhou (Rural region) | 2013 | N = 28 | BDE-47, 99, 100, 153, 154, 183, 206, 207, 208 and 209 | 4810 | 372 to 16,800 | (He et al., 2017) |
| 13 | Guangzhou (Urban region) | 2013 | N = 30 | BDE-47, 99, 100, 153, 154, 183, 206, 207, 208 and 209 | 2360 | 186 to 20,400 | (He et al., 2017) |
| 14 | Harbin | 2010 | N = 14 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 190 and 209 | 1700 | 240 to 9270 | (Zhu et al., 2013) |
| 15 | Beijing | 2012 | | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 190 and 209 | 2820 | | (Chen et al., 2014b) |
| 16 | Shanghai (bacony) | 2016 | N = 15 | BDE-28, 47,49, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 201, 202, 203, | 1000 | 200 to 11,200 | (Peng et al., 2017) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | 206, 207, 208 and 209 | | | |
| 17 | Beijing | 2014 | N = 30 | BDE-28, 47, 100, 99, 154, 153, 183 and 209 | 155 | 90.1 to 428 | (Wang et al., 2018) |
| 18 | Guangzhou | 2011 | N = 46 | BDE-28, 47, 99, 100, 153, 183 and 209 | 2690 | 564 to 9650 | (Chen et al., 2011) |
| 19 | Shanghai (Spring) | 2009 | N = 44 | BDE-17, 28, 47, 66, 99, 100, 85, 153, 154, 183, 190 and 209 | 972.1 | 151 to 1921 | (Yu et al., 2012) |
| 20 | Shanghai (Summer) | | | | 930.7 | 440.7 to 3886 | |
| 21 | Shanghai (Autumn) | | | | 275.1 | 131.6 to 2410.4 | |
| 22 | Shanghai (Winter) | | | | 704.8 | 182.9 to 3562.9 | |
| **Indoor dust in EU (n=21)** | | | | | | | |
| 1 | West Midlands (UK) | 2005 | N = 8 | Tetra-, Penta-, HexaBDE | 87.1 | 16.2 to 625.4 | (Harrad et al., 2006) |
| 2 | Sweden | 2006 | N = 10 | BDE-28, 47, 99, 100, 153, 183 and 209 | 510 | 53 to 4000 | (Thuresson et al., 2012) |
| 3 | Sweden (Apartment) | 2006 | N = 34 | BDE-28, 47, 99, 100, 153, 183 and 209 | 1400 | 13 to 100,000 | (de Wit et al., 2012) |
| 4 | Newcastle (UK) | 2008 | N = 10 | BDE-47, 99, 100, 153, 154, 183, 209 | 10,000 | 950 to 54,000 | (Sjodin et al., 2008) |
| 5 | Birmingha | 2006 | N = 28 | BDE-47, 99, 100, 153, 154, 183, 209 | 2900 | 360 to 520,000 | (Harrad et al., |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | m |  |  |  |  |  | 2006) |
| 6 | West Midlands | 2007 | N = 30 | BDE-47, 99, 100, 153, 154, 183, 209 | 8500 | 12 to 2200,000 | (Harrad et al., 2008c) |
| 7 | Germany (from 6 cities) | 2008 | N = 10 | BDE-47, 99, 100, 153, 154, 183, 209 | 74 | 17 to 550 | (Sjodin et al., 2008) |
| 8 | West Midlands | 2007 | N = 30 | BDE-47, 99, 100, 153, 154, 183, 209 | 5100 | 72 to 89,000 | (Harrad et al., 2008c) |
| 9 | UK (various regions) | 2003 | N = 10 | BDE- 28, 47, 99, 100, 153, 154, 183, 209 | 7100 | 3800 to 19,000 | (Santillo et al., 2003) |
| 10 | Poland (3 cities) | 2012 | N = 12 | BDE- 28, 47, 99, 100, 153, 154, 183, 209 | 232 | 0.01 to 701 | (Krol et al., 2014) |
| 11 | Romania | 2007 | N = 18 | BDE-28, 47, 100, 99, 154, 153, 183, 197, 203, 196 and 209 | 495 |  | (Dirtu et al., 2012) |
| 12 | Czech Republic | 2009 | N = 25 | BDE-28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207 and 209 | 501 | 84 to 5896 | (Kalachova et al., 2012) |
| 13 | Germany | 2009 | N = 34 | BDE-28, 47, 66, 99, 100, 153, 154, 183and 209 | 386 | 36.5 to 1580 | (Fromme et al., 2009) |
| 14 | Romania | 2010 | N = 47 | BDE-28, 47, 66, 99, 100, 153, 154, 183and 209 | 295 | 45 to 6800 | (Dirtu et al., 2012) |
| 15 | Sweden | 2010 | N = 27 | BDE-28, 47, 99, 100, 153, 183 and 209 | 418 | 184 to 310,000 | (Sahlstrom et al., 2015) |
| 16 | Portugal | 2011 | N = 28 | BDE-28, 47, 99, 100, 153, 154, 183 | 340 | 38 to 9600 | (Coelho et al., |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | and 209 |  |  | 2016) |
| 17 | Germany | 2011 | N = 20 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 420 | 10 to 3748 | (Fromme et al., 2014) |
| 18 | Norway | 2012 | N = 48 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 426 | MDL to 5125 | (Cequier et al., 2014) |
| 19 | Sweden (Houses) | 2006 | N = 10 | Penta-, Octa- and DecaBDE | 330 | 72 to 1400 | (de Wit et al., 2012) |
| 20 | Norwegian | 2013 | N = 10 | BDE-28, 47, 66, 85, 100, 153, 154, 183 and 209 | 258 | 98 to 3654 | (Kademoglou et al., 2017) |
| 21 | Turkey | 2015 | N = 40 | BDE-28, 47, 66, 85, 100, 153, 154, 183 and 209 | 316.1 | 29.32 to 4790 | (Civan, 2016) |
| **Indoor dust in North America (n=18)** |  |  |  |  |  |  |  |
| 1 | Canada | 2003 | N = 74 | BDE-28, 47, 66, 85, 100, 153, 154, 183 and 209 | 1800 | 170 to 170,000 | (Wilford et al., 2005) |
| 2 | Washington and Charleston | 2004 | N = 17 | BDE-28, 47, 66, 85, 100, 153, 154, 183 and 209 | 4250 | 780 to 30,100 | (Stapleton et al., 2005) |
| 3 | Canada (Toronto) | 2006 | N = 10 | BDE-47, 99, 100, 153, 154, 183, 209 | 950 | 750 to 3500 | (Harrad et al., 2008c) |
| 4 | Amarillo and Austin, Texas | 2006 | N = 20 |  | 3500 | 920 to 17,000 |  |
| 5 | Chicago, USA | 2007 | N = 4 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 3100 | 533 to 6944 | (Wei et al., 2009) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 6 | Canada | 2007 | N = 116 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 2200 | 10 to 61,000 | (Shoeib et al., 2012) |
| 7 | Albany, New York | 2008 | N = 12 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 1910 | 380 to 9340 | (Johnson-Restrepo and Kannan, 2009) |
| 8 | Atlanta (GA, USA) | 2008 | N = 10 | BDE-47, 99, 100, 153, 154, 183, 209 | 4200 | 520 to 29,000 | (Sjodin et al., 2008) |
| 9 | California, USA (swip) | 2009 | N = 88 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 1900 | | (Bennett et al., 2015) |
| 10 | California, USA (vacuum cleaner ) | 2009 | | | 2400 | | |
| 11 | North California | 2009 | N = 81 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 2574 | 441 to 76,130 | (Stapleton et al., 2012) |
| 12 | California | 2010 | N = 203 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 2500 | | (Whitehead et al., 2013) |
| 13 | California | 2011 | N = 39 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 1442.5 | MDL to 16,792 | (Bradman et al., 2014) |
| 14 | USA (4 states) | 2012 | N = 30 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 1400 | 152 to 74,560 | (Stapleton et al., 2014) |
| 15 | New York (Winter) | 2013 | N = 25 | BDE-47, 99, 100, 153, 154 and 209 | 1504.6 | | (Cowell et al., 2017) |
| 16 | New York | | | | 1470.1 | | |

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|---|---|---|---|---|---|---|---|
| | (Spring) | | | | | | |
| 17 | New York (Summer) | | | | 349.5 | | |
| 18 | New York (Autumn) | | | | 1171.4 | | |
| **Indoor air in China (n=8)** | | | | | | | |
| 1 | Shanghai, China (Summer) | 2008 | N = 20 | Tri-, Tetra-, Penta-, Hexa-, Hepta-, and BDE209 | 188 | 45 to 813 | (Han, 2016) |
| 2 | Shanghai, China (Winter) | | | | 64 | 18 to 271 | |
| 3 | HongKong, China | 2010 | N = 12 | BDE-47, 99, 100, 153, 154 and 209 | 20.9 | 0.25 to 160 | (Wang et al., 2014) |
| 4 | Guangzhou, China | | N = 60 | BDE-47, 99, 100, 153, 154 and 209 | 144 | 52.9 to 2030 | |
| 5 | Hangzhou, China | 2013 | N = 33 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 119 | 38 to 184 | (Sun et al., 2016b) |
| 6 | Taiwan | 2012 | N = 3 | BDE-47, 99, 100, 153, 154 and 209 | 81.1 | 13.1 to 156 | (Shy et al., 2015) |
| 7 | China (multiple cities) | 2009 | N = 15 | BDE-17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 232 | 11 to 838 | (Yang et al., 2013) |
| 8 | Guangzhou | 2014 | N = 72 | Penta-, Octa- and DecaBDE | 68.5 | 1.43 to 537 | (Ding et al., 2016) |
| **Indoor air in EU (n=11)** | | | | | | | |

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|---|---|---|---|---|---|---|---|
| 1 | Norway | 2012 | N = 47 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 170 | MDL to 2100 | (Cequier et al., 2014) |
| 2 | West Midlands (UK) | 2003 | N = 31 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 5 | 4 to 245 | (Harrad et al., 2006) |
| 3 | Sweden | 2006 | N = 10 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 330 | 72 to 1400 | (Thuresson et al., 2012) |
| 4 | Sweden | 2006 | N = 44 | BDE-28, 47, 99, 100, 153, 154, 183 and 209 | 58 | 1.3 to 990 | (de Wit et al., 2012) |
| 5 | Manchester, UK | 2003 | N = 16 | BDE-47, 99, 49, 100, 119, 154, 153, 138 and 183 | 48.7 | | (Birgul et al., 2012) |
| 6 | Manchester, UK | 2010 | | | 5 | | |
| 7 | Manchester, UK | 2004 | | | 23 | | |
| 8 | Manchester, UK | 2005 | N = 16 | | 18 | | (Birgul et al., 2012) |
| 9 | Denmark | 2007 | N = 43 | BDE-17,28, 47, 99, 66, 85, 100, 154 and 153 | 275 | 107 to 953 | (Vorkamp et al., 2011) |
| 10 | Germany | 2009 | N = 34 | BDE-28, 47, 66, 99, 100, 153, 154, 183and 209 | 37.8 | 8.24 to 477 | (Fromme et al., 2009) |
| 11 | UK | 2004 | | BDE-47, 99, 100, 153, 154 | 128 | 60to 1622 | (Harrad et al., 2004) |
| **Indoor air in North America (n=8)** | | | | | | | |
| 1 | Albany, | 2008 | N = 12 | BDE-17, 28, 47, 49, 66, 85, 99, 100, | 760 | 210 to 3980 | (Johnson-Restrepo |

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|---|---|---|---|---|---|---|---|
| | New York | | | 138, 153, 154, 183 and 209 | | | and Kannan, 2009) |
| 2 | Boston, USA | 2006 | N = 20 | BDE-28, 47, 99, 100, 153, 183 and 209 | 765.7 | 230.2 to 2684.4 | (Allen et al., 2007) |
| 3 | Boston, USA (Bedroom) | 2006 | N = 20 | BDE-28, 47, 99, 100, 153, 183 and 209 | 460.4 | 174.5 to 1532.6 | (Allen et al., 2007) |
| 4 | Boston, USA (Living room) | | | | 452.8 | 224.1 to 3538.4 | |
| 5 | California | 2009 | N = 88 | BDE-17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 and 209 | 530 | | (Bennett et al., 2015) |
| 6 | Canada | 2003 | | BDE-17, 28, 71, 47, 66, 99, 100, 85, 154 and 153 | 100 | 2 to 3600 | (Wilford et al., 2004) |
| 7 | Toronto, Canada | 2003 | N = 10 | BDE-17, 28, 47, 85, 99, 100, 153 and 154 | 410 | 76 to 2088 | (Shoeib et al., 2004) |
| 8 | Ottawa, Canada | 2015 | N = 19 | BDE-17, 28, 49, 71, 47, 99 | 47 | | (Okeme et al., 2018) |
| **Human breast milk in China (n=9)** | | | | | | | |
| 1 | Taiwan | 2007 | N = 20 | BDE-17, 28, 47, 66, 85, 99, 100, 138, 153, 154 and 183 | 3.3 | | (Chao et al., 2007) |
| 2 | Beijing | 2005 | N = 205 | BDE-47, 99, 100, 153, 154 and 183 | 1.08 | | (Li et al., 2008) |
| 3 | Tianjin | 2006 | N = 80 | BDE-28, 47, 99, 100, 153, 154 and 183 | 2.5 | 1.7 to 4.5 | (Zhu et al., 2009) |

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| 4 | Tianjin | 2006 | N = 50 | BDE-15, 28, 49, 47, 66, 77, 100, 99, 85, 154, 153, 184, 183, 197, 196, 207 and 209 | 2.62 | 1.66 to 10.82 | (Sun et al., 2010) |
| 5 | Shijiazhuang | 2007 | N = 48 |  | 2.24 | 0.87 to 22.9 |  |
| 6 | Yantai | 2007 | N = 60 |  | 4.05 | 2.62 to 6.28 |  |
| 7 | China | 2011 | N = 32 | BDE-28, 47, 99, 100, 153, 154 and 183 | 1.47 |  | (Zhang et al., 2017) |
| 9 | Zhejiang | 2008 | N = 74 | BDE-15, 28, 47, 99, 100, 118, 153, 154 and 183 | 2.67 | 1.54 to4.99 | (Shen et al., 2012) |
| **Human breast milk in EU (n=7)** |  |  |  |  |  |  |  |
| 1 | UK | 2010 | N = 25 | Tri-, Tetra-, Penta-, Hexa- and DecaBDE | 5.25 | 0.2 to 26.1 | (Tao et al., 2017) |
| 2 | UK | 2014 | N = 25 |  | 5.8 | 1.7 to 14 |  |
| 3 | Sweden | 2009 | N = 36 | BDE-47, 99, 100, 153 and 209 | 5.2 |  | (Darnerud et al., 2015) |
| 4 | Sweden | 2003 | N = 93 | BDE47, 99, 100, 153 and 154 | 3.15 | 0.91 to 28.2 | (Lind et al., 2003) |
| 5 | Olomouc region | 2003 | N = 103 | BDE-28, 47, 49, 66, 85, 99, 100, 153, 154 and 183 | 1.59 |  | (Kazda et al., 2004) |
| 6 | UK | 2003 | N = 54 | BDE-17, 28, 32, 35, 37, 47, 49, 71, 75, 85, 99, 100, 119, 153 and 154 | 6.3 | 0.3 to 69 | (Kalantzi et al., 2004) |
| 7 | UK | 2011 | N = 10 | BDE-47, 99, 153 | 5.09 |  | (Harrad and Abdallah, 2015) |
| **Human breast milk in North America (n=6)** |  |  |  |  |  |  |  |
| 1 | California, USA | 2003 | N = 82 | Tri-, Tetra-, Penta-, Hexa- and DecaBDE | 55.8 | 10.1 to 1310 | (Guo et al., 2016) |
| 2 | CA, USA | 2005 |  |  |  |  |  |

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| 3 | CA, USA | 2009 | N = 66 |  | 36.8 | 11.2 to 435 |  |
| 4 | CA, USA | 2012 |  |  |  |  |  |
| 5 | USA | 2002 | N = 47 | BDE-17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183 and 209 | 34 |  | (Schecter et al., 2003) |
| 6 | USA | 2011 | N = 13 | BDE-28, 47, 99, 100, 153, 183 and 209 | 60 | MDL to 625.9 | (Darrow et al., 2017) |

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# Chapter 2 Sampling and analytical methodology

## 2.1 Indoor dust sampling

### 2.1.1 Sampling location

In this thesis, indoor dust samples were collected from five key cities in China from north to south; Dalian (n=30), Beijing (n=33), Shanghai (n=33), Xiamen (n=53) and Guangzhou (n=26) using a Midea MV-WJ12Q2 vacuum cleaner. Figure 2.1 showed these five cities locations on the map of China from five provinces including Liaoning, Beijing, Shanghai, Fujian and Guangdong. Among the samples in Xiamen, 19 samples were floor dust, 19 samples were collected from air conditioner filters and 15 samples from furniture foam. For each city, the sample locations were chosen to include urban areas, suburban areas and rural areas. Figure 2.2 to Figure 2.6 showed the details of the three sampling areas from five cities. The following descriptions were defined urban areas, suburban areas and rural areas. Table S2.1 showed the each sampling site with longitude and latitude in supporting information.

**Urban areas:** the districts near the city center with the highest population density and high gross domestic product (GDP)

**Suburban areas:** the districts connect to the rural areas and urban areas

**Rural areas:** the districts located at and surround the edge of suburban areas with low population density and often rudimentary living facilities.

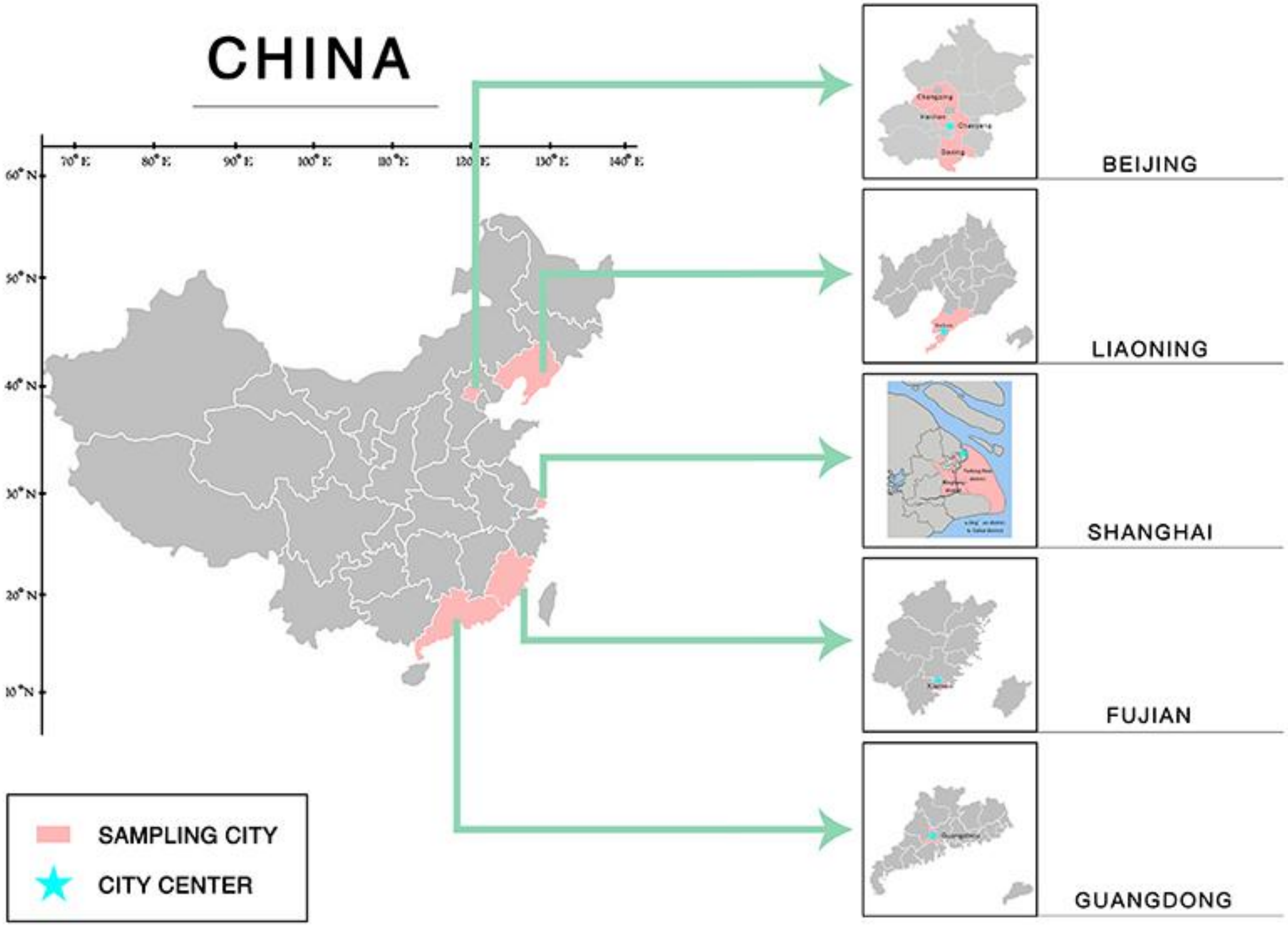


**Figure 2. 1** The locations of five key cities on the map of China from five provinces

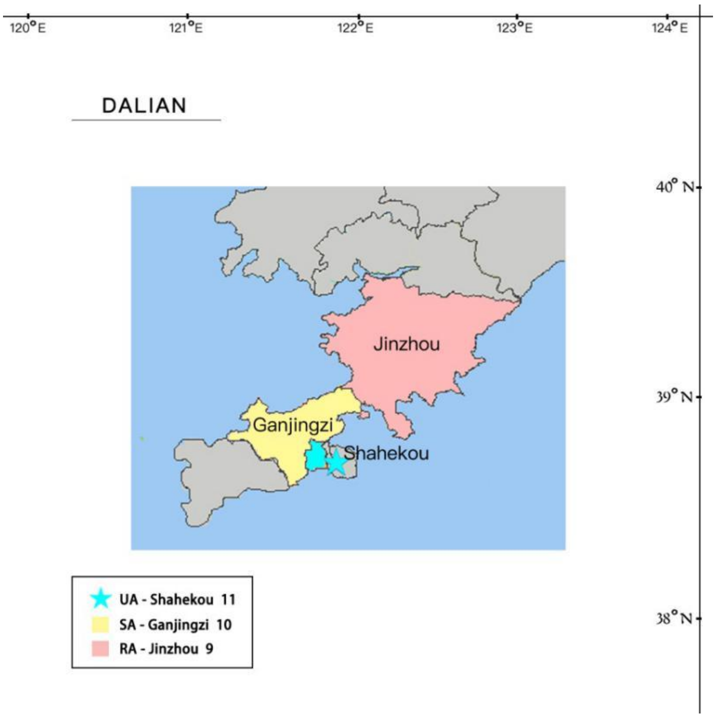


**Figure 2. 2** The details of sampling sites in Dalian (9 samples from rural areas, 10 samples from suburban areas, 11samples from urban areas)

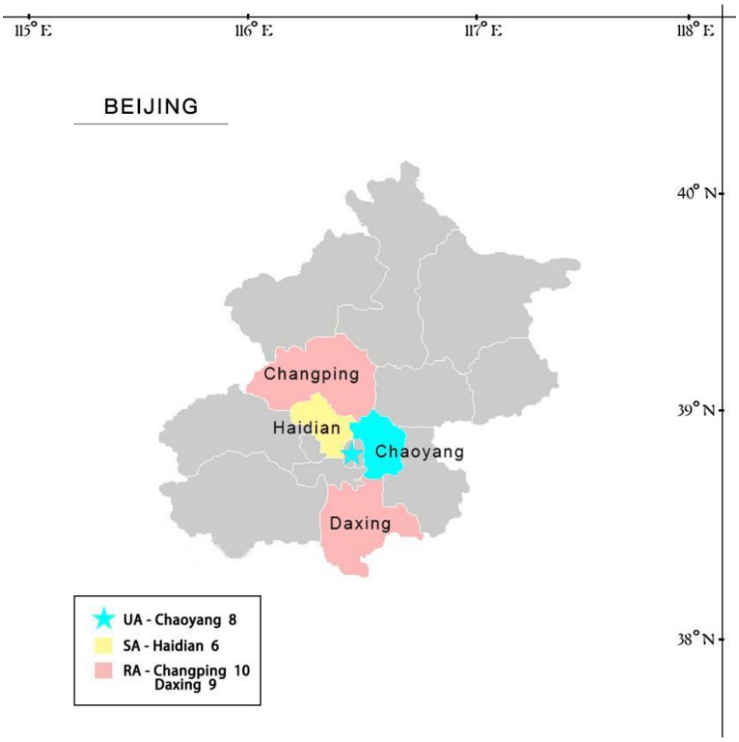


**Figure 2. 3** The details of sampling sites in Beijing (19 samples from rural areas, 6 samples from suburban areas, 8 samples from urban areas)

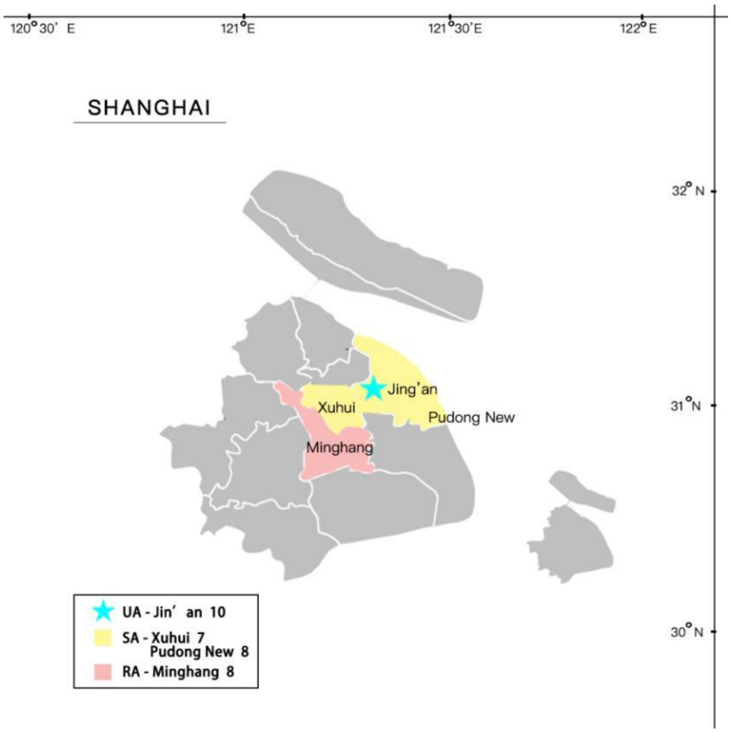


**Figure 2. 4** The details of sampling sites in Shanghai (8 samples from rural areas, 15 samples from suburban areas, 10 samples from urban areas)

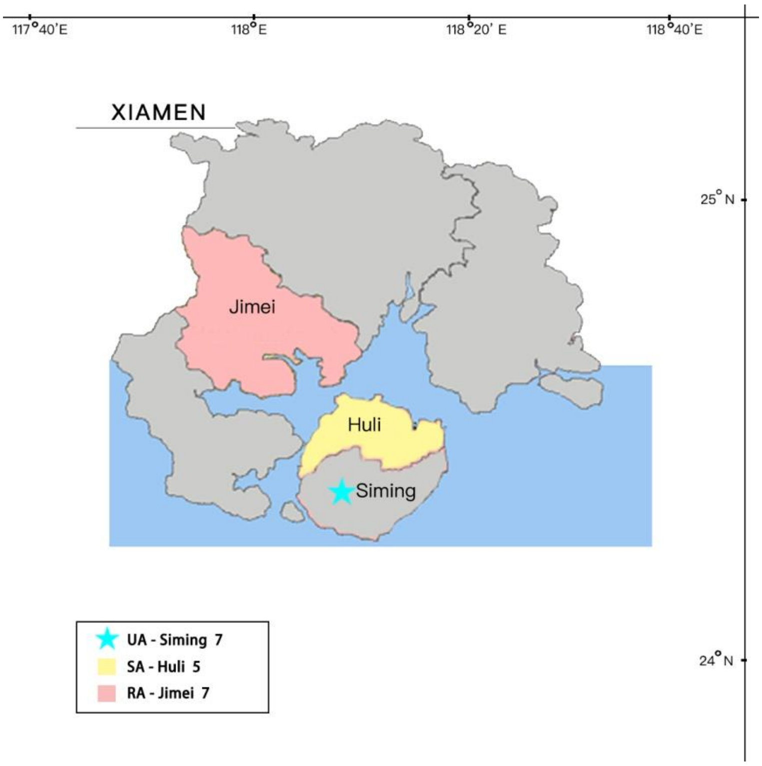


**Figure 2. 5** The details of sampling sites in Xiamen (7 samples from rural areas, 5 samples from suburban areas, 7 samples from urban areas)

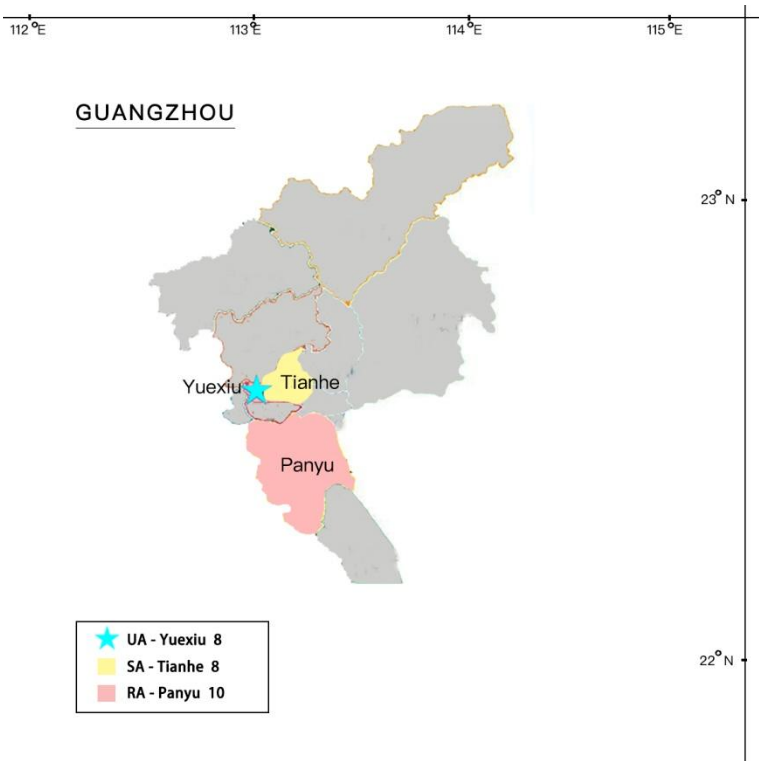
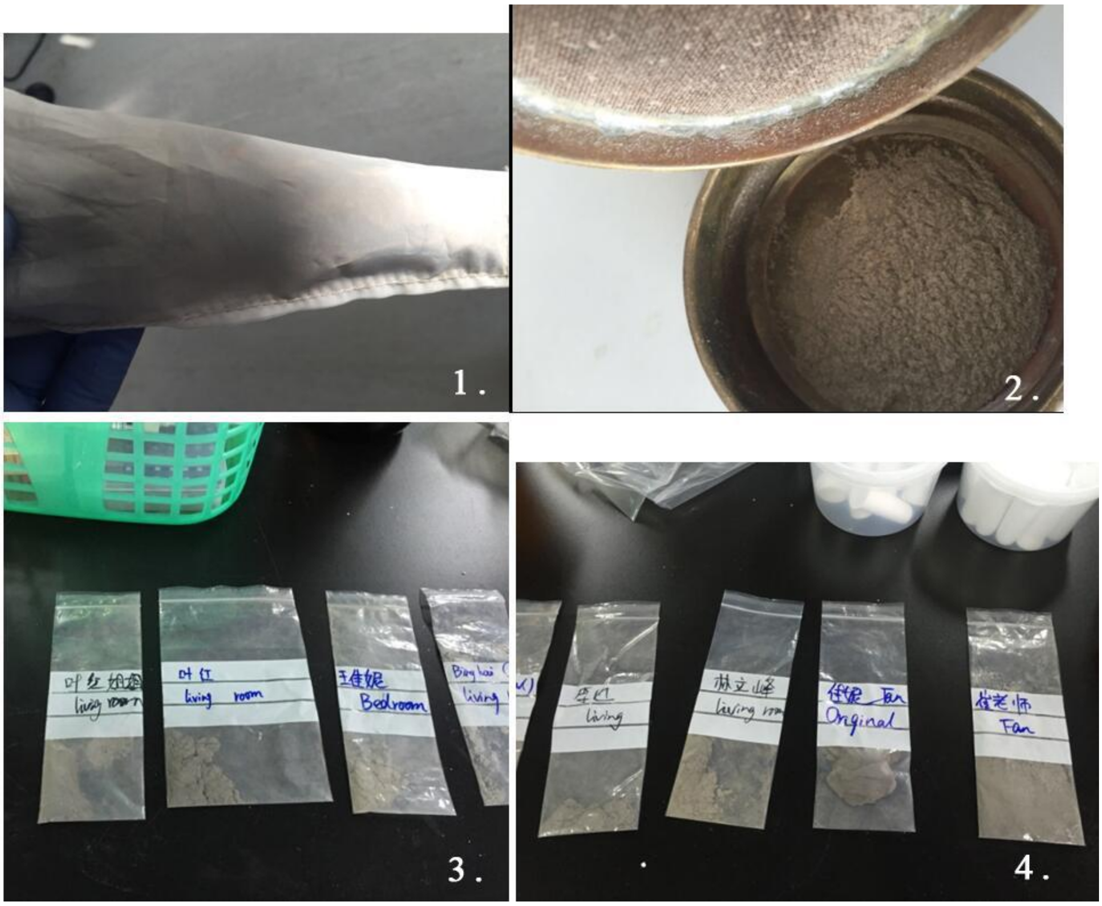


**Figure 2. 6** The details of sampling sites in Guangzhou (10 samples from rural areas, 8 samples from suburban areas, 8 samples from urban areas).

### 2.1.2 Sampling and extraction methodology

Dust samples were collected using a vacuum cleaner with a nylon sample sock (25μm pore size) mounted on the end of the suction tube. The tube and socks were cleaned with acetone and hexane between sample collections to prevent cross contamination. Each sock was used only for one sample. After sampling, each sample was passed through a 500μm sieve to remove larger debris and solid objects such as hairs and fibers. The dust samples were sealed in aluminum foil and stored in a freezer at -20° C. Sampling questionnaires were used to collect basic information (such as the age of house, room flooring and number of appliances) and listed in **Chapter 3** and **Chapter 4**. Field blanks consisted of sodium sulfate powder on a clean aluminum foil surface collected using the same method as a sample.

The following pictures were taken during the field sampling campaign (1. original dust collected in sock by vacuum cleaner; 2. target dust passed through sieve; 3-4. kept target dust in sealed bag and labeled name)



The extraction and purification method in this thesis is based on a previous study by (Birgul et al., 2012) with some modifications to replace gel permeation chromatography (GPC) clean-up step. Soxhlet equipment was pre-extracted for 8h to 10h by hexane. 1g dust sample was weighed, mixed with sodium sulphate and spiked with a mixture of $^{13}$C-PCB-141 and $^{13}$C -BDE-77 as recovery standards. Samples were extracted in 150 ml hexane for 16h to 18h. A combined silica and alumina column was used for sample clean-up. The column was packed in the following order starting from the bottom layer: 6cm alumina, 2cm activated silica, 6cm basic silica (25%), 2cm activated silica, 6cm acid silica (44%) and 1cm sodium sulphate.

**Acid silica:** Baked silica at 550℃ for 6 hours, then 100g Silica mixed with 44g $H_2SO_4$.

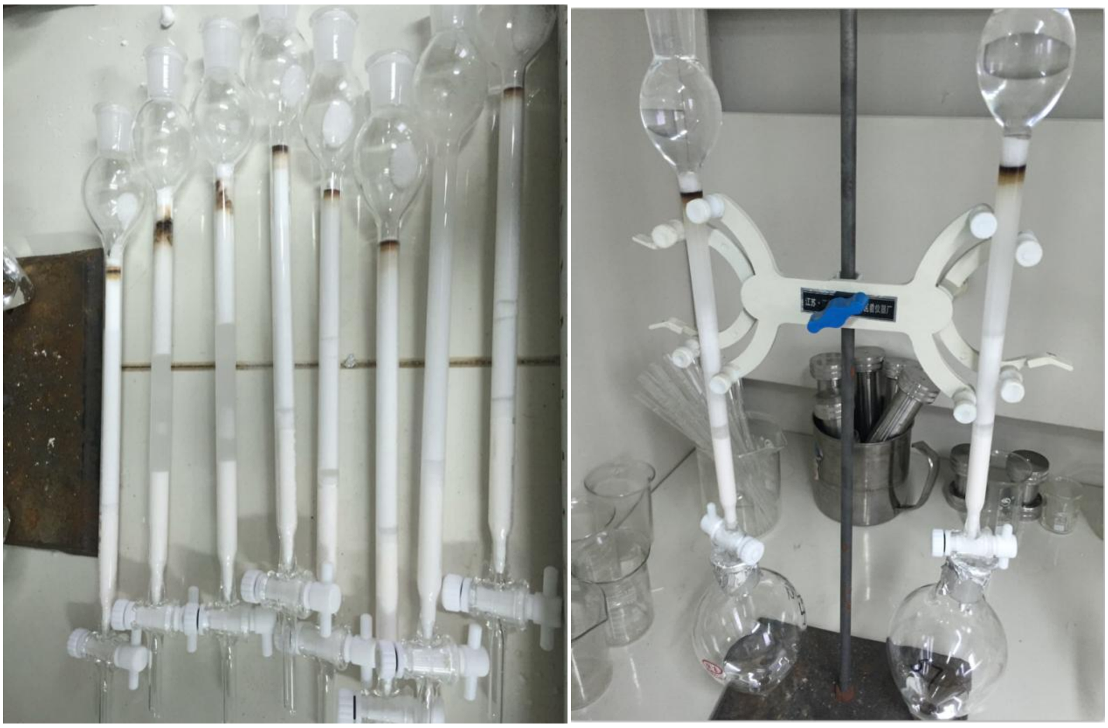
**Basic silica:** Baked silica at 550℃ for 6 hours, then 100g Silica mixed with 25g NaOH (4g solid NaOH dissolved into 100 ml Milli-Q water)

**$Na_2SO_4$:** Baked for 8 hours before used at 660℃

**$Al_2O_3$:** Baked for 8 hours before used at 660℃

The target compounds were eluted with 70 ml of hexane/DCM (1:1). Finally, the sample was evaporated to 0.1 ml under a gentle nitrogen gas flow. $^{13}$C-PCB-208 was added as an internal standard to the samples before GC/MS analysis.

The following pictures show some of the clean up process.



## 2.2 Human serum sampling

### 2.2.1 Sampling location

Blood samples were collected from the 28 females and 12 males at the Disease Control and Prevention Centre of Kunming, China in July 2016. Kunming was selected as the study city, which is the capital city of Yunnan province located in the southwest of China. Figure 2.7 showed the location of Yunnan provinces, as well as Kunming city.

The province borders Guangxi, Guizhou, Sichun provinces and the countries Vietnam, Laos and Myanmar. Yunnan is one of the major production bases for copper, lead, zinc tin and aluminum in China. The main reason was there was long-term electrical cable production history in Kunming. Kunming Cable Group Co., Ltd., built in 1936, is the first wire and electrical cable manufacturer in China, and also is the birthplace of China's first wire (Kunming Cable Group Co., Ltd. website). Hence, there also are commercial PBDE products manufacturing in Kunming to add in cable.

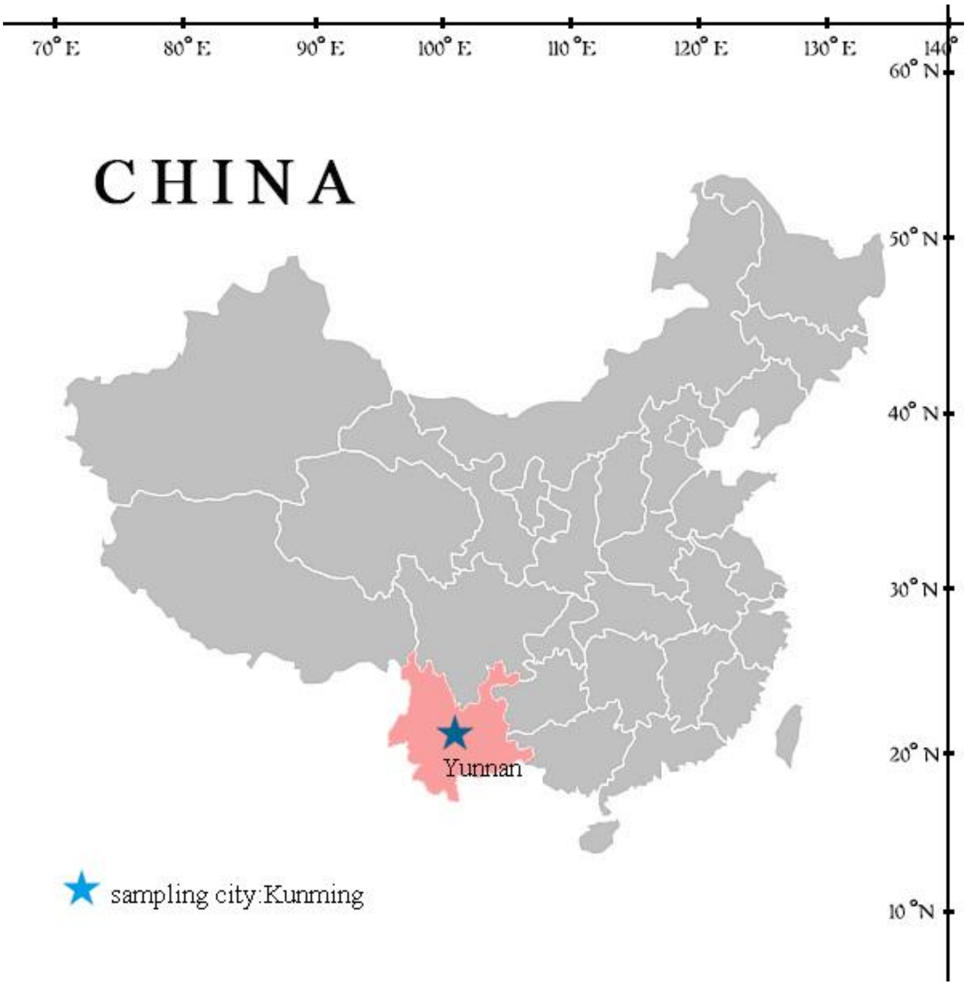


**Figure 2. 7** The location of Yunnan provinces, as well as Kunming city.

### 2.2.2 Sampling and extraction methodology

Fasting bloods were required. 5 ml of blood from a cubical vein were collected into a sterile serum tube without anticoagulants, the serum was separated by centrifugation at

4000 rpm for 5 min using a high-speed centrifuge (Thermo Fisher Scientific, Waltham, MA) and then transferred to a new tube. All the serum samples were kept at -20° C until further analysis. $^{13}$C-BDE77 and $^{13}$C-PCB141 were added to the 1 ml serum sample in a 15 ml centrifuge tube which was cleaned before using acetone and hexane. Samples were placed in an ultrasonic bath for 10 minutes and allowed to equilibrate overnight. After equilibrium, 2 ml of formic acid and acetonitrile (2:1, v/v), as well as 5ml ultra-pure water, were placed in an ultrasonic bath for 10 minutes to achieve denaturation and dilution. The samples were extracted using an Oasis HLB cartridge. The method was described in previous studies (Liu et al., 2017; Brasseur et al., 2014). Before extraction, the cartridge was cleaned with 3ml DCM and conditioned with 3ml MeOH and 3ml ultra-pure water. The samples were eluted with 4ml of isopropanol and water (1:19, v/v). 200μl of sulfuric acid was added to remove lipids and other contaminant, and then diluted with ultra-pure water until the pH value of solution was neutral. This was further cleaned using 2ml of MeOH and water (9:1, v/v), after which the cartridge was dried. The cartridge was then eluted with 4ml DCM, to collect the target compounds. After $N_2$ reduction, the extract was transferred to 100μl hexane. An internal standard $^{13}$C-PCB208 was added and quantification was carried out using GC-MS.

The following pictures were 40 serum samples in sterile serum tube and solid phase extraction (SPE) process using Oasis HLB cartridge.

## 2.3 GC/MS analysis of PBDEs

### 2.3.1 Chemicals and standards

A standard mixture of 39 PBDE congeners (including BDE-7, -11, -8, -12, -15, -32, -30, -17, -25, -33, -28, -35, -37, -75, -49, -47, -66, -100, -119, -99, -116, -118, -155, -85, -126, -154, -153, -138, -166, -183, -181, -190) and BDE-209, were purchased from AccuStandard, Inc. (New Haven, CT, USA). $^{13}$C-PCB208, $^{13}$C-PCB141 and $^{13}$C-BDE77 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) as recovery standard and internal standard respectively. Acetone, dichloromethane (DCM) and n-hexane were obtained from Fisher Chemical (MA, USA).

### 2.3.2 GC/MS methodology

All of the samples were prepared and analyzed in Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China. 33 PBDE congeners were investigated (BDE7, 11, 8, 12, 15, 32, 30, 17, 25, 33, 28, 35, 37, 75, 49, 47, 66, 100, 119, 99, 116, 118, 155, 85, 126, 154, 153, 138, 166, 183, 181, 190 and 209). All PBDE analyses were performed on an Agilent 7890A gas chromatograph with negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. Original methodology (Jakobsson et al., 2002; Tan et al., 2007; Harrad et al., 2008) separated PBDE congeners by two columns. Low bromine substituent were measured by long column (30 m * 250 μm * 0.25 μm ) and short column (15m * 250 μm * 0.1 μm) was used for DecaBDE, since DecaBDE would decompose when the long column took long time to separate PBDE congeners. Advanced methodology (Brasseur et al., 2014; Liu et al., 2017; Bu et al., 2018; Jin et al., 2019) was improved that one short column (15m * 250 μm * 0.1 μm) was used for both low bromine congeners and DecaBDE in order to reduce the running time. Table 2.1 listed the differences of these two methodologies to compare the instrument conditions and results.

**Table 2. 1** The differences of two methodologies using Agilent GC/MS to compare the instrument conditions and results.

| | **Two columns** | **One column** |
|---|---|---|
| **Instrument** | Agilent 6890N | Agilent 7890A |
| **Column** | 30m * 250 μm * 0.25 μm<br>15m * 250 μm * 0.1 μm | 15m * 250 μm * 0.1 μm |
| **Mode** | NCI | NCI |
| **Heating program** | **Long column:** from 130° C held for 1 min to 155° C at 12° C/min, then to 215° C at 4° C/min and to 300° C at 3° C/min (held for 10 min)<br>**Short column:** from 80° C held for 2 min to 220° C at 25° C/min, then to 315° C at 5° C/min (held for 10 min) | from 100° C held for 1 min to 200° C at 25° C/min, then to 280° C at 5° C/min and to 315°C at 15°C/min (held for 4 min) |
| **Total time** | 57 min + 38 min | 28 min |
| **Recoveries** | 90±12% | 98±3.65% |
| **MDL** | 0.032 ng/g | 0.0134 ng/g |
| **Reference** | (Gevao et al., 2006) | (Jin et al., 2019) |

In this study, gas chromatography was performed on a DB-XLB 15m * 250 μm * 0.1 μm column with the following oven program: from 110° C held for 0.5 min to 200° C at 60° C/min, then to 280° C at 5° C/min (held for 0.5 min) and to 310° C at 60° C/min (held for 8 min) (Jin et al., 2019). The total operation time was 28 minutes. BDE-209 was quantified by using m/z 486.6 and 488.6; $^{13}$C-PCB-141was monitored through m/z 371.9 and 373.9; $^{13}$C-PCB-208 was monitored through m/z 473.8 and 475.8; and $^{13}$C-BDE-77 was monitored through m/z 471.8 and 473.8. The other congeners were quantified by the bromide ions, m/z 79 and 81. Helium (purity > 99.999%) was used as the carrier gas at flow rate of 1 ml/min and methane (purity > 99.99%) was used as a chemical ionization moderating gas.

### 2.3.3 Quality assurance, quality control and analysis

In order to assess the MS response over the concentration range of PBDEs in dust samples, five point calibration curves were carried out for each target compound with excellent linearity to analysis each indoor dust sample. $^{13}$C-PCB-208, $^{13}$C-PCB-141 and $^{13}$C-BDE-77 kept at 20μl 100ppb through all of the 5 points, 5ppb, 10ppb, 25ppb, 50ppb and 100ppb for 32 low PBDE congeners. The 5 points for BDE209 were 75ppb, 100ppb, 1ppm, 5ppm and 10ppm.

The correlation coefficient of the calibration was from 0.996 to 0.999. Table 2.2 lists the coefficient for each target compound. Figure 2.8 shows the total ion chromatograms (TIC) of the internal and recovery standards. Figure 2.9 shows the TIC of 33 PBDE standards and BDE209. Instrumental limits of detection (LOD) and method limits of quantification (LOQ) were calculated for target compound based on 3:1 and 10:1 signal to noise ratio respectively. The method blank (1 g sodium sulfate) was prepared using the same analytical method for each batch of 10 samples. Field blanks were collected from each sampling location and were analyzed by the same method. None of target compounds were detected in method blanks, but BDE209 was detected in the majority of field blanks, although the level was less than 5% of PBDE concentration in dust samples. The limits of detection (LODs) of the low PBDE congeners ranged from 0.002 to 0.016ng/g, and BDE209 was 0.33 ng/g. The average recovery of three internal standards were: 92.8% ± 8.1% for $^{13}$C-PCB-208; 86.6% ± 9.2% for $^{13}$C-PCB-141 and 89.2% ± 11.3% for $^{13}$C-BDE-77. The detection frequency for each target compound also was listed in table 2.1.

**Table 2. 2** The correlation coefficient ($R^2$) of five points calibration and retention time for 33 target PBDE congeners. The range of $R^2$ was from 0.996 to 0.999.

| Congener | $R^2$ | RT[a] | DF[b](%) | Congener | $R^2$ | RT | DF(%) |
|---|---|---|---|---|---|---|---|
| **BDE209** | 0.9999 | 25.11 | 100 | BDE47 | 0.9989 | 6.74 | 100 |
| **BDE7** | 0.9998 | 3.17 | 85 | BDE66 | 0.9985 | 7.10 | 100 |
| **BDE11** | 0.9997 | 3.25 | 94 | BDE100 | 0.9985 | 8.65 | 100 |
| **BDE8** | 0.9972 | 3.28 | 79 | BDE119 | 0.9970 | 8.88 | 100 |
| **BDE12** | 0.9991 | 3.32 | 100 | BDE99 | 0.9997 | 9.36 | 100 |
| **BDE15** | 0.9969 | 3.47 | 100 | BDE116 | 0.9986 | 9.54 | 98 |
| **BDE32** | 0.9972 | 3.90 | 96 | BDE118 | 0.9984 | 9.98 | 98 |
| **BDE30** | 0.9981 | 4.31 | 92 | BDE155 | 0.9983 | 10.54 | 100 |
| **BDE17** | 0.9997 | 4.43 | 97 | BDE85 | 0.9985 | 10.68 | 100 |
| **BDE25** | 0.9960 | 4.48 | 100 | BDE126 | 0.9978 | 10.96 | 100 |
| **BDE33** | 0.9976 | 4.64 | 100 | BDE154 | 0.9995 | 11.05 | 100 |
| **BDE28** | 0.9995 | 4.73 | 100 | BDE153 | 0.9995 | 12.24 | 100 |
| **BDE35** | 0.9965 | 4.84 | 97 | BDE138 | 0.9988 | 13.73 | 100 |
| **BDE37** | 0.9965 | 5.08 | 100 | BDE166 | 0.9986 | 13.85 | 97 |
| **BDE75** | 0.9989 | 6.14 | 100 | BDE183 | 0.9990 | 15.14 | 100 |
| **BDE49** | 0.9998 | 6.32 | 100 | BDE181 | 0.9965 | 16.94 | 100 |
|  |  |  |  | BDE190 | 0.9978 | 17.23 | 100 |

RT[a]: Retention time

DF[b]: Detection frequency collected from dust samples in Chapter 4 and Chapter 5. Detection frequency of serum samples was listed in Chapter 6.

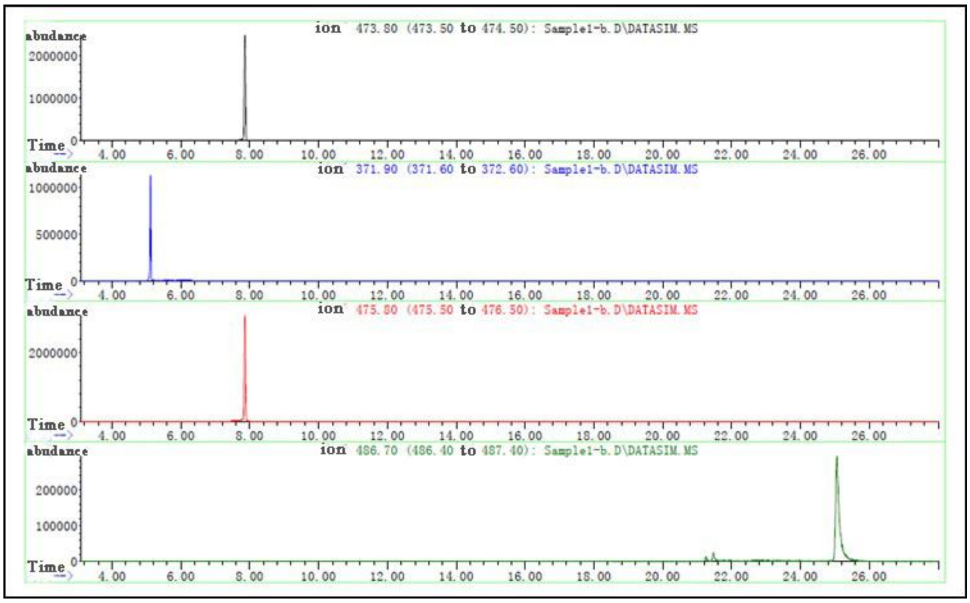


**Figure 2. 8** Total ion chromatography (TIC) of three internal and recovery standards and BDE209 (BDE-209 m/z: 486.6 and 488.6; $^{13}$C-PCB-141: 371.9 and 373.9; $^{13}$C-PCB-208: 473.8 and 475.8; and $^{13}$C-BDE-77: 471.8 and 473.8).

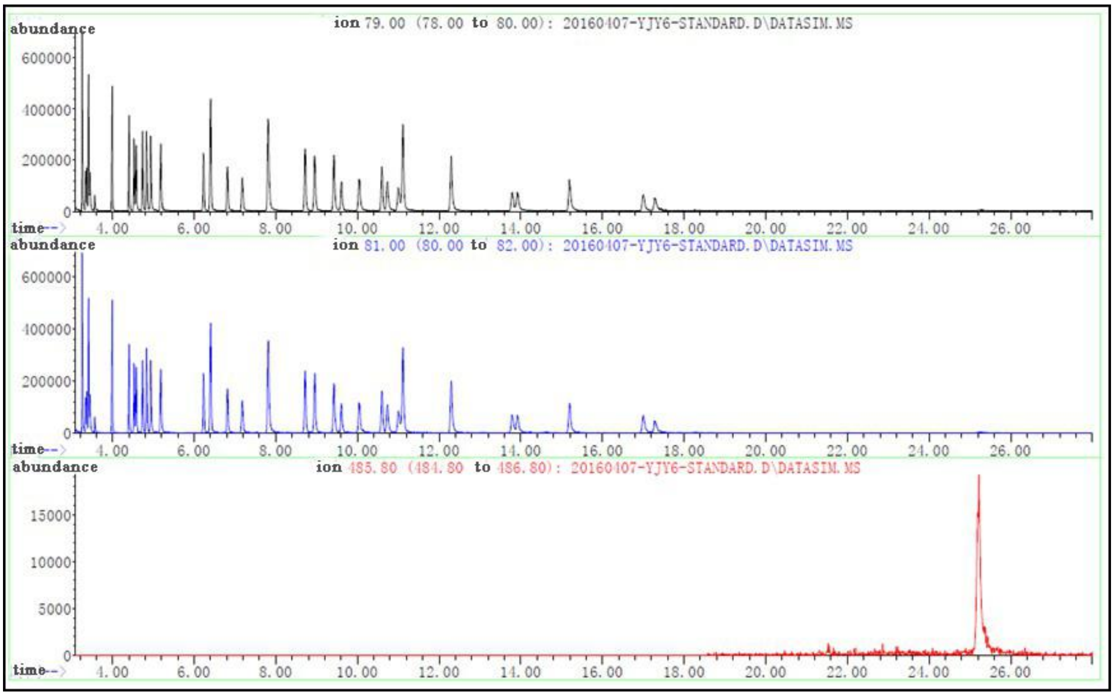


**Figure 2. 9** Total ion chromatography (TIC) of 33 PBDE (BDE7, 11, 8, 12, 15, 32, 30, 17, 25, 33, 28, 35, 37, 75, 49, 47, 66, 100, 119, 99, 116, 118, 155, 85, 126, 154, 153, 138, 166, 183, 181, 190 and 209) congeners standards. Retention time listed in table 2.1

## 2.4 Statistical analyses

Throughout the thesis, statistical analyses were carried out using SPSS version 23 software (IBM Co, Armonk, NY, USA). Probability values less than 0.05 ($p<0.05$) were considered as statistically significant. The normality test (Shapiro-Willk test) and Student t-test were utilized. Correlation between parameters and total PBDEs were evaluated by the Spearman's test. Multiple linear regression analysis and principal component analysis (PCA) were used for data set.

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## Supporting information

| | | | | | |
|---|---|---|---|---|---|
| Shanghai (Suburban area) | | | | | |
| 1.<br>121.561679,31.228379 | 2.<br>121.561221,31.23002 | 3.<br>121.563301,31.229534 | 4.<br>121.558535,31.226662 | 5.<br>121.566997,31.231475 | 6.<br>121.566997,31.231475 |
| 7.<br>121.566997,31.231475 | 8.<br>121.566997,31.231475 | 9.<br>121.566997,31.231475 | 10.<br>121.446032,31.191738 | 11.<br>121.446032,31.191738 | 12.<br>121.446032,31.191738 |
| 13.<br>121.452104,31.198986 | 14.<br>121.452104,31.198986 | 15.<br>121.452104,31.198986 | | | |
| Shanghai (Urban area) | | | | | |
| 1.<br>121.452104,31.198986 | 2.<br>121.452104,31.198986 | 3.<br>121.452104,31.198986 | 4.<br>121.452104,31.198986 | 5.<br>121.452104,31.198986 | 6.<br>121.455392,31.240402 |
| 7.<br>121.455392,31.240402 | 8.<br>121.455392,31.240402 | 9.<br>121.455392,31.240402 | 10.<br>121.455392,31.240402 | | |
| Shanghai (Rural area) | | | | | |
| 1.<br>121.412004,31.10789 | 2.<br>121.413769,31.125763 | 3.<br>121.39925,31.113414 | 4.<br>121.399475,31.115598 | 5.<br>121.401105,31.109554 | 6.<br>121.40071,31.113345 |
| 7.<br>121.399556,31.11542 | 8.<br>121.404407,31.11816 | | | | |
| Beijing (Suburban area) | | | | | |
| 1.<br>116.312444,39.994013 | 2.<br>116.313068,39.993674 | 3.<br>116.313535,39.993138 | 4.<br>116.314568,39.9927 | 5.<br>116.315274,39.993764 | 6.<br>116.316244,39.99356 |
| Beijing (Urban area) | | | | | |
| 1.<br>116.455688,39.923274 | 2.<br>116.456029,39.923243 | 3.<br>116.456186,39.922886 | 4.<br>116.455863,39.922693 | 5.<br>116.455158,39.922762 | 6.<br>116.454843,39.922668 |
| 7 .<br>116.453667,39.9228 | 8.<br>116.453334,39.922956 | | | | |
| Beijing (Rural area) | | | | | |
| 1.<br>116.33439,39.742333 | 2.<br>116.335027,39.74225 | 3.<br>116.334192,39.741986 | 4.<br>116.334192,39.741591 | 5.<br>116.335108,39.741612 | 6.<br>116.335957,39.742593 |
| 7. | 8. | 9. | 10. | 11. | 12. |

| | | | | | |
|---|---|---|---|---|---|
| 116.335957,39.74226 | 116.335921,39.741882 | 116.336761,39.741868 | 116.247946,40.22539 | 116.249284,40.222856 | 116.249688,40.22331 |
| 13. 116.250551,40.223317 | 14. 116.24967,40.223641 | 15. 116.249365,40.223868 | 16. 116.249311,40.224254 | 17. 116.24879,40.225046 | 18. 116.250596,40.22499 |
| 19. 116.248943,40.225438 | | | | | |
| Guangzhou (Urban area) | | | | | |
| 1. 113.273895,23.141495 | 2. 113.274155,23.141474 | 3. 113.274155,23.14172 | 4. 113.274263,23.141927 | 5. 113.275525,23.141707 | 6. 113.275004,23.141811 |
| 7. 113.27588,23.14194 | 8. 113.274775,23.141852 | | | | |
| Guangzhou (Suburban area) | | | | | |
| 1. 113.374918,23.126989 | 2. 113.375385,23.127043 | 3. 113.375318,23.12681 | 4. 113.374864,23.126719 | 5. 113.375439,23.126573 | 6. 113.37459,23.126549 |
| 7． 113.375354,23.126345 | 8. 113.375286,23.12595 | | | | |
| Guangzhou (Rural area) | | | | | |
| 1. 113.39932,22.93768 | 2. 113.398629,22.937356 | 3. 113.399518,22.937185 | 4. 113.398921,22.937173 | 5. 113.398984,22.936636 | 6. 113.399482,22.936183 |
| 7. 113.398876,22.935713 | 8. 113.399716,22.935708 | 9. 113.398966,22.935243 | 10. 113.399545,22.93503 | | |
| Xiamen (Rural area) | | | | | |
| 1. 118.06987,24.614121 | 2. 118.114196,24.590576 | 3. 118.115265,24.589331 | 4. 118.112916,24.587701 | 5. 118.102177,24.596206 | 6. 118.112382,24.591919 |
| 7. 118.115301,24.589303 | | | | | |
| Xiamen (Urban area) | | | | | |
| 1. 118.105993,24.445286 | 2. 118.106262,24.445035 | 3. 118.106532,24.445524 | 4. 118.106779,24.445088 | 5. 118.106748,24.444895 | 6. 118.105795,24.445697 |
| 7． 118.106869,24.445631 | | | | | |
| Xiamen (Suburban area) | | | | | |
| 1. 118.188898,24.467265 | 2. 118.185849,24.483269 | 3. 118.186316,24.482657 | 4. 118.18464,24.483471 | 5. 118.18464,24.483471 | |

| | | | | | |
|---|---|---|---|---|---|
| Dalian (Suburban area) | | | | | |
| 1. 121.535373,38.962079 | 2. 121.535984,38.9621 | 3. 121.535966,38.961764 | 4. 121.535346,38.961441 | 5. 121.536648,38.962002 | 6. 121.536693,38.961666 |
| 7. 121.537205,38.962086 | 8. 121.53663,38.96102 | 9. 121.537358,38.961034 | 10. 121.536612,38.960698 | | |
| Dalian (Urban area) | | | | | |
| 1. 121.602409,38.914367 | 2. 121.603073,38.914381 | 3. 121.602355,38.914089 | 4. 121.602979,38.914097 | 5. 121.602292,38.913721 | 6. 121.603006,38.913861 |
| 7. 121.603276,38.913616 | 8. 121.60408,38.914493 | 9. 121.604071,38.914188 | 10. 121.604911,38.913949 | 11. 121.604219,38.913609 | |
| Dalian (Rural area) | | | | | |
| 1. 121.79572,39.051303 | 2. 121.796474,39.051559 | 3. 121.79664,39.051131 | 4. 121.796218,39.050932 | 5. 121.796218,39.050932 | 6. 121.79709,39.050834 |
| 7. 121.797579,39.050511 | 8. 121.798684,39.050368 | 9. 121.799528,39.050161 | | | |

# Chapter 3 Polybrominated diphenyl ethers (PBDEs) in the indoor dust in Xiamen, an ecological city in China: Concentration, composition and human exposure.

## 3.1. Introduction

Polybrominated diphenyl ethers (PBDEs), are a group of organic compounds containing bromine that have been used as flame retardants in consumer products, such as electronic equipment (television set, air conditioner), polyurethane foams, textiles and plastics (de Wit, 2002). Three major PBDEs commercial formulations were produced containing a mixture of several PBDE congeners: c-pentaBDE, c-octaBDE and c-decaBDE. C-pentaBDE contains a mixture of TetraBDE, PentaBDE and HexaBDE; c-octaBDE is a mixture of OctaBDE, HeptaBDE, NonaBDE and HexaBDE, and c-decaBDE is dominated by BDE209. Previous studies reported a high degree of impurities have been found in c-decaBDE produced in China, which contained 8.2% OctaBDE and 10.4% NonaBDE (Chen et al., 2007). Details of congeners composition of three commercial products including c-pentaBDE, c-octaBDE and c-decaBDE used in China usage are shown in Figure 3.1.

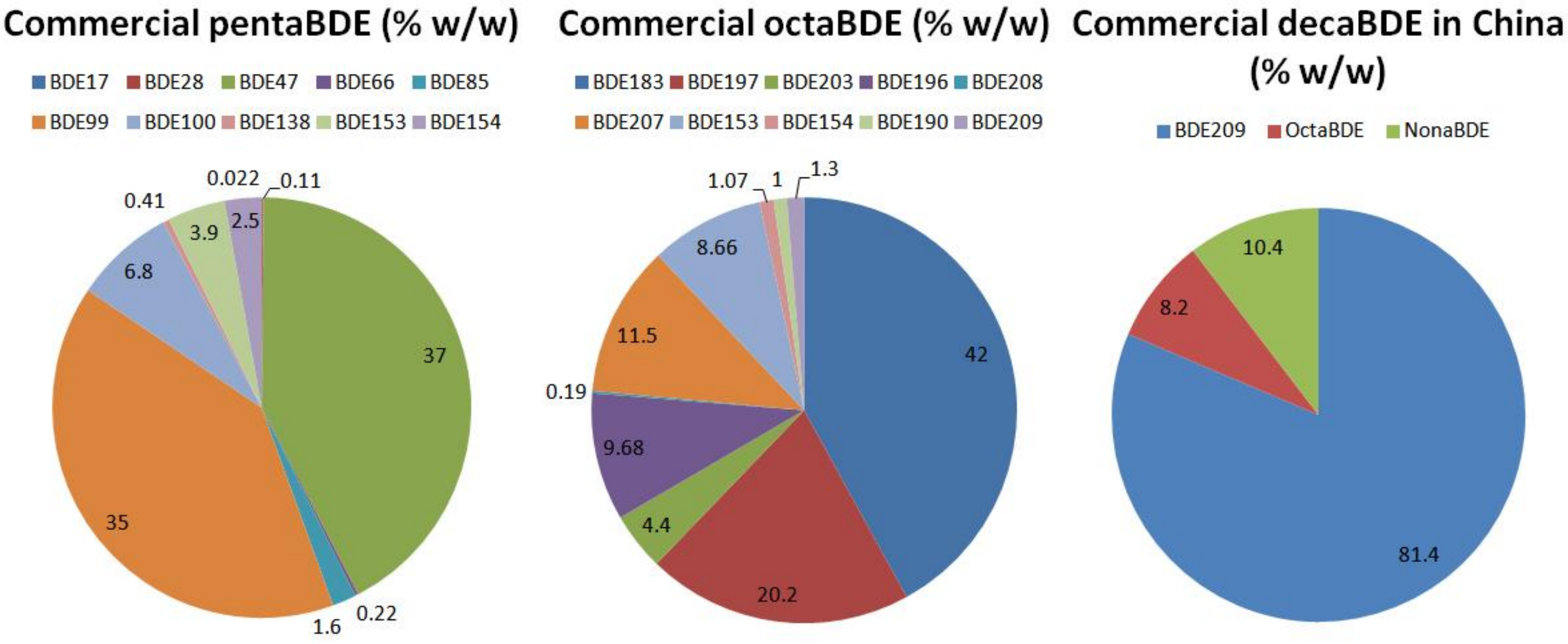

**Figure 3. 1** Composition profile of three commercial PBDE mixtures (c-pentaBDE, c-octaBDE and c-decaBDE) used in China market.

Although PBDEs played a beneficial role as a group of widely used flame retardants, environmental concerns were raised about their characteristics such as hydrophobicity, lipophilicity, resistant to degradation processes, bioaccumulation and potential for long-range transport (LRT). As a result, PBDEs have been detected throughout the environments such as sediments, lakes, indoor air and dusts, as well as in human hair, blood and breast milk (de Boer et al., 2003; Allchin et al., 1999; Baron et al., 2014; Guan et al., 2009; Li et al., 2016; Birchmeier et al., 2005; Moon et al., 2012; Song et al., 2005; Wang et al., 2015; Daniels et al., 2010; Buttke et al., 2013; Chen et al., 2014a; Coakley et al., 2013; Lyche et al., 2015; Wang et al., 2012; Kang et al., 2011).

Several studies have found significant positive associations between PBDE concentrations in house dust and the concentration in human serum or breast milk (Johnson et al., 2010; Bondy et al., 2011). Some studies have suggested that higher exposure occurs in infants and children compared to adults as indoor dust was one of the most important pathway for children (Bradman et al., 2014; Canbaz et al., 2016). Previous studies have carried out and provided concentrations of PBDEs in indoor dust in developed countries like UK, Canada, the USA, and Germany, but fewer are available in China.

The significance of PBDE exposure to humans through indoor environments has been recognized in China (Chen et al., 2011; Huang et al., 2010; Wang et al., 2014). Most of the studies concerning PBDEs in indoor environment in China have focused on providing concentration data for indoor air and indoor dust. However, previous published studies in China concerned more attention on production industry or E-waste regions, or only focused on the specific key cities such as Beijing, Shanghai, Guangzhou (An et al., 2011; Ding et al., 2016; Chan et al., 2013; Chen et al., 2009; Deng et al., 2014; Guan et al., 2009; Labunska et al., 2014; Zheng et al., 2011; Zheng et al., 2015; Wang et al., 2018; Yu et al., 2018; Sun et al., 2016b; Li et al., 2015; Peng et al., 2017). These first tier cities have larger population, advanced urbanization than other cities in China, and higher air pollution in general than other cities, which would have higher input from outdoor environment into indoor environment and may masked the indoor sources of PBDEs exposure. In order to observe the pollution level of PBDEs in indoor environment and differentiate sources in indoor sources of PBDE, a smaller city size and less industrialization would be ideal.

Xiamen was selected as a study location because it is a key second tier city in China, less pollution sources from industrial or factories than Guangzhou, better air quality than Beijing such as the concentration of PM2.5 concentration in Beijing was 64.6 ug/m$^3$ in 2017, while only 28.5 ug/m$^3$ in Xiamen in 2017 (China statistic data). So the influence from outdoor environment would be less and smaller than in Beijing. Because it has long periods of hot weather with high temperature and humidity so that the electrical appliances especially air conditioners are widely used during eight months of the year from April to November. Xiamen's rapid industrial, commercial and urban development over the past 30 years have gradually expanded from the inner island to outer-island which covers an area of 158 square kilometers and a population of 1,861,289 (China statistic data).

Based on the above concerns, the aims of this study were to 1). investigate the concentrations of PBDEs in indoor dust in a range of indoor environments considering factors, such as house age and location within the city; 2) to evaluate the correlation between the house dust concentrations with presence of furniture and electrical appliances, etc. and to explore the potential sources to the PBDE emission in indoor environment; 3) to compare the composition of PBDE in dust collected from different locations within the indoor environment such as general floor dust, furniture foam dust and appliance dust. To achieve the target of this research, nineteen private homes were selected in urban, suburban and rural regions across Xiamen separately, and for each house, floor dust, dust present of furniture foam and inner filters from air conditioners in living room were sampled.

## 3.2. Materials and methods

### 3.2.1 Sample collection

Samples from 19 private homes were collected across the main Bus Rapid Transit route (BRT) which connects the rural region (Jimei district), suburban region (Huli district) and urban region (Siming district) of Xiamen. Seven homes from the urban area, five from suburban regions, and seven from rural areas. For each private home, floor dust, air conditioner filter dust and foam furniture dust were collected. Across the 19 homes, house sizes were different, with floor areas ranging from 60 to 240 square meters. The information from questionnaire including the sampling site location, building ages, the home size, the amount of furniture and air conditioner, the hours of air conditioner operation and the frequency of the house cleaning have been included in the supporting information. Figures 3.2 and 3.3 show the location of the city of Xiamen and the districts within Xiamen where samples were collected. Dust samples were collected using a vacuum cleaner fitted with a hexane pre-cleaned nylon sample sock (25 µm pore size) mounted on the attachment tube of the vacuum cleaner. The tube and socks were cleaned with acetone and hexane before using. Each sock was used only for one sample. Indoor dust samples were collected from three areas within the living room in each house including the floor, the air conditioner filter and the sofa cushions. After collection, each sample was passed through the 500 µm mesh sieve to remove debris and solid objects like hair and fibres. The dust was then sealed in aluminum foil and stored in freezer at -20° C. For field blanks, sodium sulfate powder on the clean aluminum foil surface was vacuum collected on site.

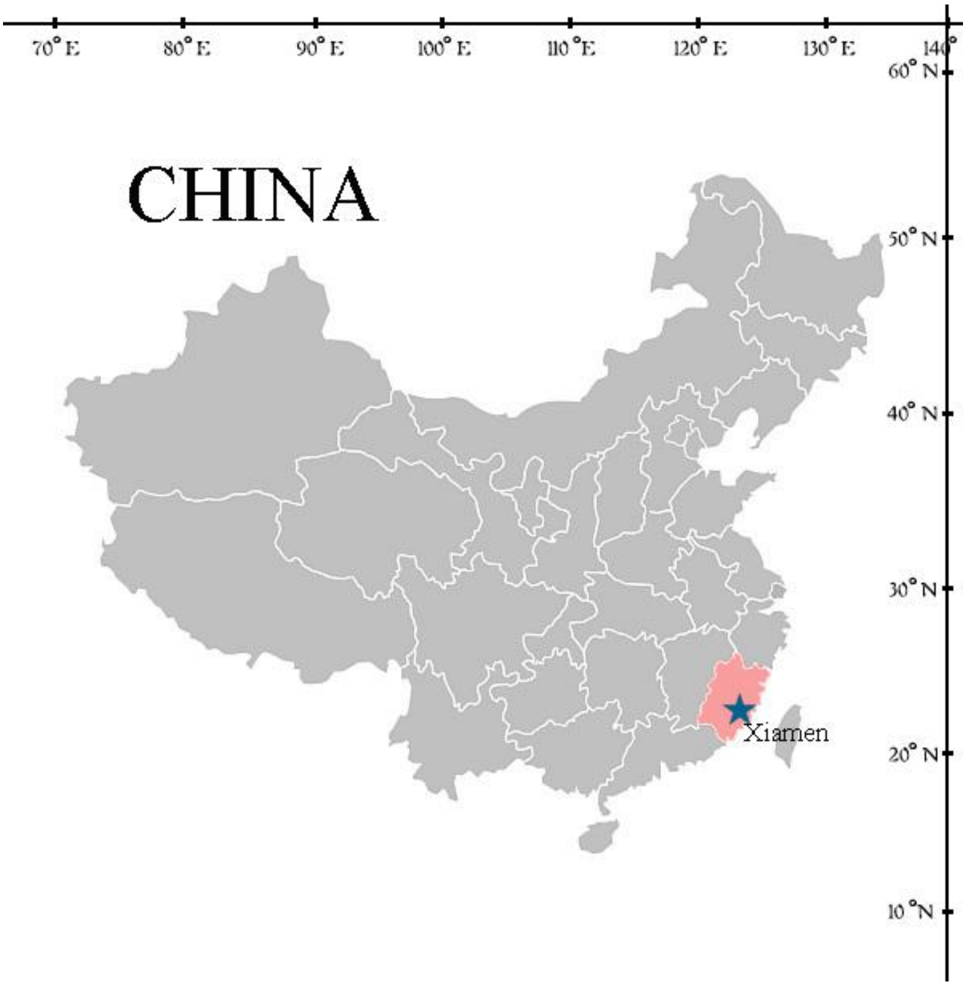

**Figure 3. 2** The location of Xiamen city

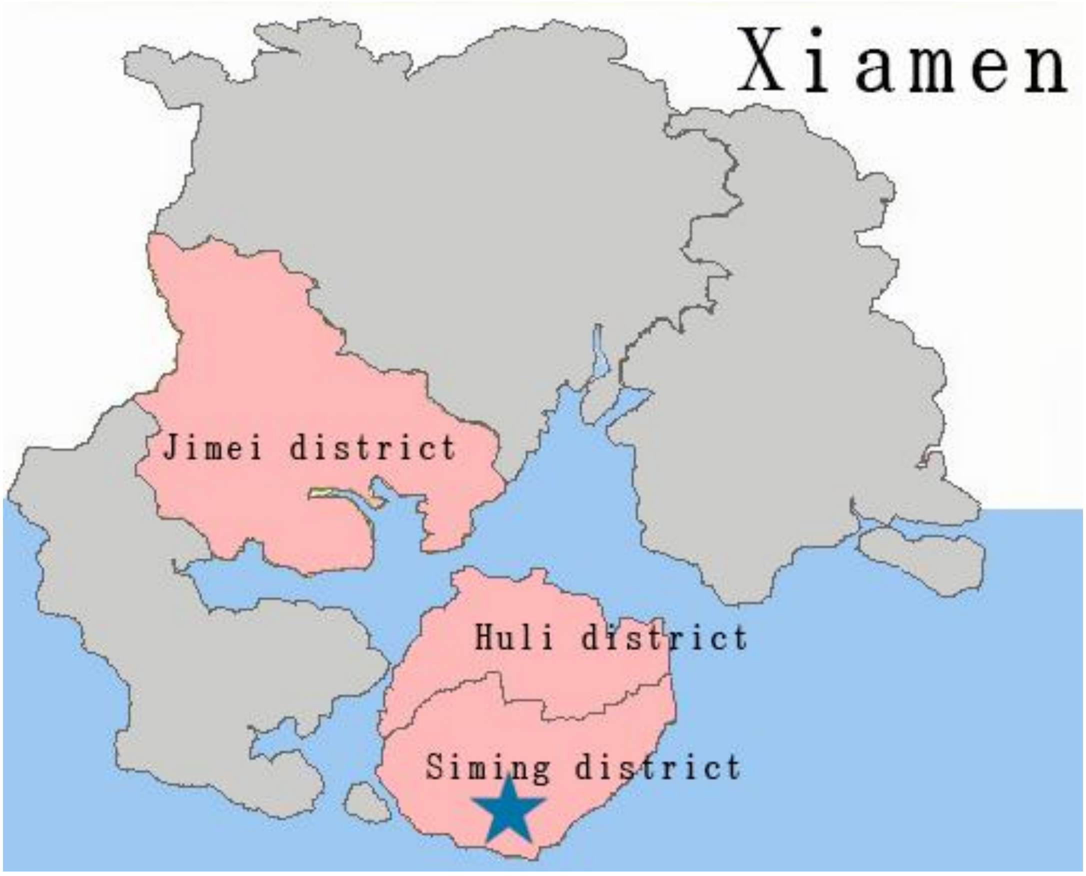

**Figure 3. 3** The sampling location map: urban area (Siming district), suburban area (Huli district) and rural area (Jimei district). The blue star shows the location of the city Centre.

### 3.2.2 Chemicals and standards

A standard mixture of 39 PBDEs (including BDE-7, -11, -8, -12, -15, -32, -30, -17, -25, -33, -28, -35, -37, -75, -49, -47, -66, -100, -119, -99, -116, -118, -155, -85, -126, -154, -153, -138, -166, -183, -181, -190) and BDE-209 were produced by AccuStandard, Inc. (New Haven, CT, USA). $^{13}$C-PCB208, $^{13}$C-PCB141 and $^{13}$C-BDE77 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) as recovery standard and internal standard respectively. Acetone, dichloromethane (DCM) and n-hexane were obtained from Fisher Chemical (MA, USA). Anhydrous sodium sulfate was baked at 660° C for 6h which from Puhui Chemical Co., Ltd., Hangzhou, China Silica gel and alumina were activated at 550° C for 6h and 660° C for 6h respectively.

### 3.2.3 Sample extraction

All extraction equipment was pre-cleaned for 8h to 10h. 1g dust samples were weighed, mixed with sodium sulphate and spiked with a mixture of $^{13}$C-PCB-141 and BDE-77 in. Samples were Soxhlet extracted in 150 ml hexane for 16h to 18h. A combined silica and alumina column was used for sample clean-up. The column was packed in the following order starting from the bottom layer; 6cm Alumina, 2cm activated silica, 6cm basic silica (25%), 2cm activated silica, 6cm acid silica (44%) and 1cm sodium sulphate. The target compounds were eluted with 70 ml of hexane/DCM (1:1). Finally, the sample was evaporated to 0.1 ml under a gentle nitrogen gas flow. $^{13}$C-PCB-208 as internal standard was added to the sample before analysis.

### 3.2.4 Analysis

The samples were analyzed using an Agilent 7890A gas chromatograph with mass selective detector using negative chemical ionization in the selected ion monitoring (SIM) mode. BDE-209 was quantified by monitoring through m/z 486.6 and 488.6, while $^{13}$C-PCB-141was monitored through m/z 371.9 and 373.9, $^{13}$C-PCB-208 was monitored through m/z 473.8 and 475.8, and $^{13}$C-BDE-77 was monitored through m/z 471.8 and 473.8. The other congeners were quantified by the bromide ions, m/z 79 and 81. Helium (purity > 99.999%) was used as the carrier gas at flow rate of 1 ml/min and methane (purity > 99.99%) was used as a chemical ionization moderating gas. Gas chromatographic was performed on a DB-XLB 15m * 250 um * 0.1 um with the following oven program: starting from 110° C held for 0.5 min to 200° C at 60° C/min, then to 280° C at 5° C/min (held for 0.5 min) and to 310° C at 60° C/min (held for 8 min). The total operation time was 28 mins.

### 3.2.5 QA/QC

One field blank was collected at each sampling location. Sodium sulfate from a sheet of foil was collected using the same vacuum cleaner used for samples. The field blank was used to check for contamination from the equipment. Internal and recovery standards were used to monitor the contaminant recovery during the processes of sample analysis. Detailed information had been discussed in **Chapter 2.**

## 3.3. Results

### 3.3.1 PBDEs concentration in floor dust, air conditioner filter and furniture foam

Concentrations of the main PBDE congeners for samples collected across Xiamen are summarized in Table 4.1. For this study, 33 PBDEs congeners were detected, among them BDE28, BDE47, BDE100, BDE99, BDE154, BDE153, BDE183 and BDE209 were identified as main congeners, which accounted for over 90% to the total 33 PBDEs congeners, and the detection frequency were 100% in all of the dust samples. Hence the total eight congeners were discussed in **this chapter** and **Chapter 4**

The mean, median and range values in dust samples from the air conditioners (AC) are listed in Table 3.1. Concentrations of total PBDEs (the sum of 7 major PBDEs congeners not including BDE209) for AC ranged from 0.23 ng/g to 424.18 ng/g, with a median value of 47.43 ng/g. The concentration order of other main congeners found in AC samples were BDE183 (15.35 ng/g) > BDE47 (10.25ng/g) > BDE99 (8.23ng/g) > BDE100 (8.12 ng/g) >BDE153 (3.16 ng/g) > BDE28 (1.18 ng/g) > BDE154 (1.15 ng/g). The average, median and range of each congener in floor dust (FD) are also listed in Table 3.1. The range of BDE209 concentration was from 138.00 ng/g to 2450.29 ng/g, and the median value was 754.69 ng/g. The total PBDE concentration of 7 major congeners was 6.39 ng/g to 228.31 ng/g and the median value was 45.27 ng/g. The seven most abundant congeners in floor dust were BDE47 (11.55 ng/g) > BDE183 (10.78 ng/g) > BDE99 (10.37 ng/g) > BDE100 (5.02 ng/g) > BDE154 (3.28 ng/g) > BDE153 (2.1 ng/g) > BDE28 (1.16 ng/g). The concentration of BDE209 in furniture foam (FF) ranged from 1.76 ng/g to 35.25 ng/g. The average value and the median value concentration were 12.57 ng/g and 6.31 ng/g respectively. The most abundant PBDE congeners in FF excluding BDE209 were BDE47 (0.91 ng/g), followed by BDE99 (0.61 ng/g).

### 3.3.2 PBDE congener profiles across the dust samples

Congener profiles of PBDEs across the three types of dusts were analyzed. BDE209, the main congener in c-decaBDE mixtures, was the most abundant congener in all dust sample types, and contributed 79.9%, 94.55% and 94.23% of total PBDEs by weight in FF, FD and AC dusts. Of the other seven lower brominated $\Sigma_7$PBDE, BDE47, BDE99 and BDE183 were the most abundant congeners. The proportions of these congeners across the three types of dusts are shown in the figure 4.3. For samples collected from air conditioner units, BDE183 had the highest concentration of $\Sigma_7$PBDE, followed by BDE-47and BDE-99. The congener profile of PBDEs in FD followed the same pattern as with AC. After the BDE209, the BDE47, BDE99 and BDE183 were the most dominant three major congeners in $\Sigma_7$PBDE, representing 25%, 22% and 23%. Significant differences were evident in FF samples, notably, BDE47 was higher in comparison with other two types of dusts, and accounted for over 50% of the $\Sigma_7$PBDE concentration, followed by BDE99, over 35%, the other five

**Table 3. 1** PBDE concentration (ng/g) in furniture foam dust (n=15), floor dust (n=19) and air conditioner filter dust (n=19) from Xiamen in 2016

| | **Furniture foam (FF), n=15** | | | **Floor dust (FD), n=19** | | | **Air conditioner filter (AC), n=19** | | |
|---|---|---|---|---|---|---|---|---|---|
| | mean | median | range | mean | median | range | mean | median | range |
| **BDE28** | 0.43 | 0.03 | 0.01-1.88 | 1.45 | 1.16 | 0.19-3.78 | 4.34 | 1.18 | 0.02-31.16 |
| **BDE47** | 2.80 | 0.91 | 0.10-6.03 | 19.91 | 11.55 | 1.05-70.52 | 6.82 | 10.25 | 0.05-60.58 |
| **BDE100** | 0.02 | 0.02 | 0.01-0.06 | 6.19 | 5.02 | 1.32-18.43 | 0.23 | 8.12 | 0.02-22.18 |
| **BDE99** | 0.39 | 0.61 | 0.06-0.83 | 15.22 | 10.37 | 0.68-51.35 | 5.69 | 8.23 | 0.03-76.83 |
| **BDE154** | 0.03 | 0.02 | 0.01-0.06 | 8.15 | 3.28 | 0.18-31.35 | 0.19 | 1.15 | 0.02-30.47 |
| **BDE153** | 0.06 | 0.04 | 0.01-0.24 | 6.88 | 2.10 | 0.20-32.96 | 0.31 | 3.16 | 0.02-36.57 |
| **BDE183** | 0.13 | 0.05 | 0.01-0.73 | 12.49 | 10.78 | 1.03-34.35 | 10.48 | 15.35 | 0.06-166.38 |
| **BDE209** | 12.57 | 6.31 | 1.76-35.25 | 926.49 | 754.69 | 138.00-2450.29 | 1144.34 | 754.69 | 108.07-5740.85 |
| **$\sum_7$PBDE** | 3.87 | 1.68 | 0.19-9.83 | 70.29 | 45.27 | 6.39-228.21 | 28.05 | 47.43 | 0.23-424.18 |
| **$\sum_8$PBDE** | 16.44 | 7.98 | 1.95-45.07 | 996.78 | 798.18 | 163.59-2536.06 | 1172.39 | 823.26 | 108.30-6165.03 |

$\sum_7$PBDE: the sum of BDE28, 47, 100, 99, 154, 153, 183

$\sum_8$PBDE: the sum of BDE28, 47, 100, 99, 154, 153, 183 and 209 remaining congeners ranged from 1% to 3% in foam samples.

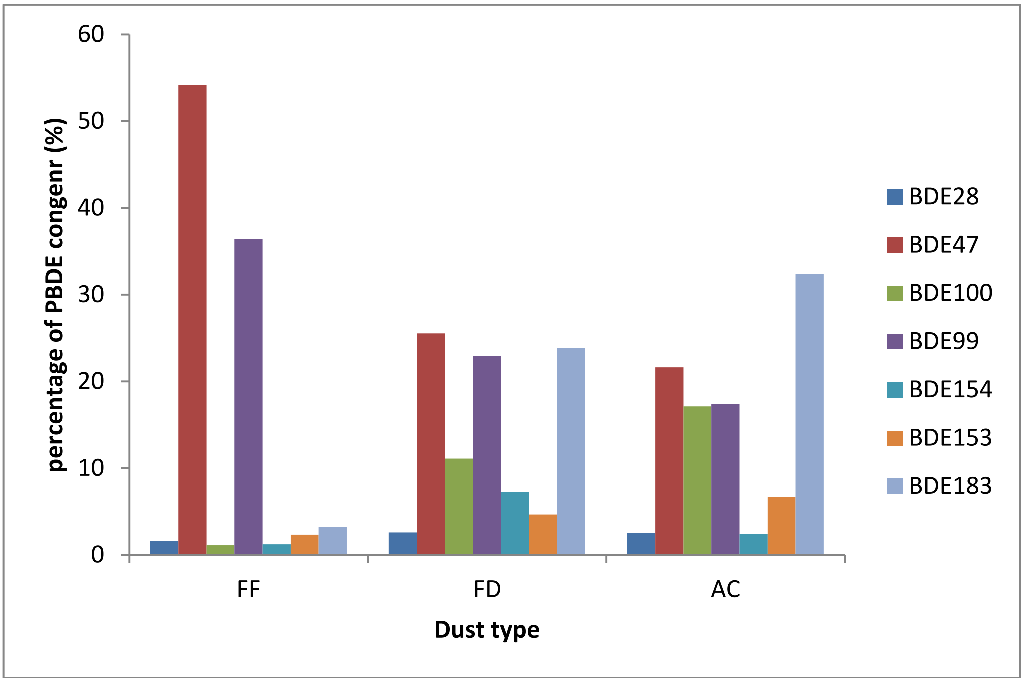

**Figure 3. 4**The percentile distribution (%) of seven PBDE congeners (BDE28, 47, 100, 99, 154, 153 and 183) in furniture foam (FF), floor dust (FD) and air conditioner filter in houses in Xiamen, China (AC)

## 3.4 Discussion

### 3.4.1 Comparison of PBDE contamination in floor dust samples collected in Xiamen to other cities in China and worldwide

PBDE concentrations data in indoor dust samples collected across the world were compared with present study to provide links to possible sources and regional differences in production and use. The median concentration of BDE 209 in the present study was 754.69 ng/g, which was similar to 550 ng/g reported in Japan, (Tue et al., 2013), Ottawa, Canada, 630 ng/g (Wilford et al., 2004), New Zealand, 598 ng/g, (Coakley et al., 2013), Toronto, Canada, 560 ng/g (Harrad et al., 2008a), but lower than in Texas, USA, 1,300 ng/g, (Harrad et al., 2008c), Vancouver, Canada, 1350 ng/g

(Shoeib et al., 2012), Birmingham, UK, 8100 ng/g (Harrad et al., 2008c), and higher than in Poland, 219 ng/g (Krol et al., 2014). Compared with other cities in China, the concentration of BDE209 in indoor dust in Xiamen was lower than that of in Beijing, which was 961 ng/g (Chen et al., 2014b), Wuhan, 810 ng/g (Huang et al., 2010), Guangzhou, 3407 ng/g (Huang et al., 2010), Haikou, 1873 ng/g (Huang et al., 2010), Shanghai, 948 ng/g (Yu et al., 2012) and Guangzhou, 6875 ng/g (Wang et al., 2010), but higher than in Hangzhou, 228 ng/g (Sun et al., 2016b).

The concentrations of PBDEs excluding BDE209 were lower than those in South Korea, Canada and the USA. This is expected as the c-pentaBDE and c-octaBDE consumption across North America were higher than in China, while c-decaBDE was the main flame retardant product used and production in China (Huang et al., 2010; Sun et al., 2016b). The present study suggested that the concentrations of PBDEs in Xiamen were either similar or at lower level compared with that of most of the cities in the world, also lower than that of most mage cities in China.

For the foam furniture samples, the median concentration for the seven lower brominated PBDE, $\Sigma_7$PBDE congeners including BDE28, BDE47, BDE99, BDE100, BDE154, BDE153 and BDE183 from the present study was 1.68 ng/g, which was lower than 3.74 ng/g in foam samples collected in the USA (Hammel et al., 2017). Although few data are available for samples collected from furniture foam, the reported concentrations of PBDEs were different from each country but the congener pattern was similar. BDE47 accounted for approximately 50% of $\Sigma_7$PBDE (excluding BDE209) as was found by Hammel in Duke (Hammel et al., 2017) and Redin in Sweden (Redin et al. 2017).

The concentration of $\Sigma_8$PBDE (including BDE209) in dust collected from air conditioner filters was 823 ng/g, which was higher than the levels of 477 ng/g in

Shenzhen, China (Ni et al., 2011) , 359 ng/g in Hangzhou, China (Sun et al., 2016b), but much lower than 2779 ng/g in Shanghai, China (Yu et al., 2013).

The congener profiles in three kinds of dust samples in this study matched well with the composition of commercial mixtures. As mentioned in the introduction and shown in figure 3.1, the composition of three commercial products was compared with the congener profile of PBDEs across the different types of dust. Usually c-pentaBDE was added into polyurethane foams present in mattresses, foam packaging and fabric coatings in the world; c-octaBDE was found in electric appliances, such as appliance casings, electronics parts and telephone handsets and manufactured as an additive to acrylonitrile-butadiene-styrene (ABS). While c-decaBDE was used widely in China and added into furniture such as sofas, chairs, but also in cables and other electronics parts (Alaee et al., 2003). The composition profile can be used to explain the congener composition in AC, FD and FF separately. For example, FF samples congener profile contained dominated BDE47 and BDE99 pattern, reflecting significant contributions of c-pentaBDE congeners profiles. This pattern distinguished well from that of floor dust profile. Although lack of data available on c-pentaBDE production in China, the Ministry of Environmental Protection of China announced, in August, 2013, to phased out the production, use and import of c-pentaBDE and c-octaBDE in China since 2014 (China MEP, 2014). The announcement suggested that c-pentaBDE and c-octaBDE were used and imported in China prior to 2014. The direct evidence of c-pentaBDE was used in China was seen in the foam dust samples congeners profiles identified in this study and elsewhere. In fact, the flame retardant used in foam production was largely c-pentaBDE. This is in agreement to our findings in FF samples. For AC samples, the main PBDE congeners were the same as the major components of c-octaBDE such as BDE183. This was in line with the usage nature of the type of flame retardants in house hold product in China. However, several studies have reported that BDE209 can be de-brominated to lower brominated PBDE congeners such as BDE28, BDE47 and BDE99 (Jiang et al., 2011). Figure 3.1 shows the composition of c-pentaBDE and c-octaBDE, which can be used for comparison with Figure 3.3.

### 3.4.2 Correlation analysis for Xiamen dust samples

#### 3.4.2.1 Correlation analysis between PBDE concentration, house location and age

The results in this study suggests some relationships existed between concentration of total PBDE (including BDE209) in floor dust samples and the age of the house, see Figure 3.4 and Figure 3.5. Flame retardant use in China began at the end of the 1990s although production volumes were lower than in the UK and USA (EPA/600/R-08/086F, 2010). In the year 1999, PBDEs manufacturers ceased production in the EU and the USA, moving production to China (Chen et al., 2012). However, with the restriction of PBDE usage and the development of replacements PBDEs, production capacity began to decrease (Peng et al., 2017). Figure 3.4 showed the pilot of concentration change of total PBDEs, including BDE209, against the build year of the house, and figure3.5 showed the concentrations of total PBDEs in urban, suburban and rural areas. Figure 3.4 shows that the trend of concentration increased sharply between the mid-1990s and then decreased slightly until 2005. This trend could be explained by the usage history of PBDEs in China. However, due to the small sample size, the trend in PBDEs concentration is not clear and more samples are required to confirm. De Wit (de Wit et al., 2012)) also suggested that significant negative correlations were observed between total PBDE concentration in indoor environments and the building construction year in Sweden (de Wit et al., 2012). An interfering factor, however, comes from sampling location. Previous studies have suggested that the concentration of PBDEs in indoor dust in urban areas was higher than suburban and rural areas (Zheng et al., 2011; He et al., 2017; Zhu et al., 2015). This means that although the houses were built earlier in the rural area, the PBDEs concentrations in floor dust detected were lower than in urban house built in later years. This suggests that the indoor consumer products and PBDEs emission sources had a greater effect than the age of the house. In the present study, the result indicates the lowest concentration of $\Sigma_8$PBDE were measured in the newly built houses in 2014 in the rural areas.

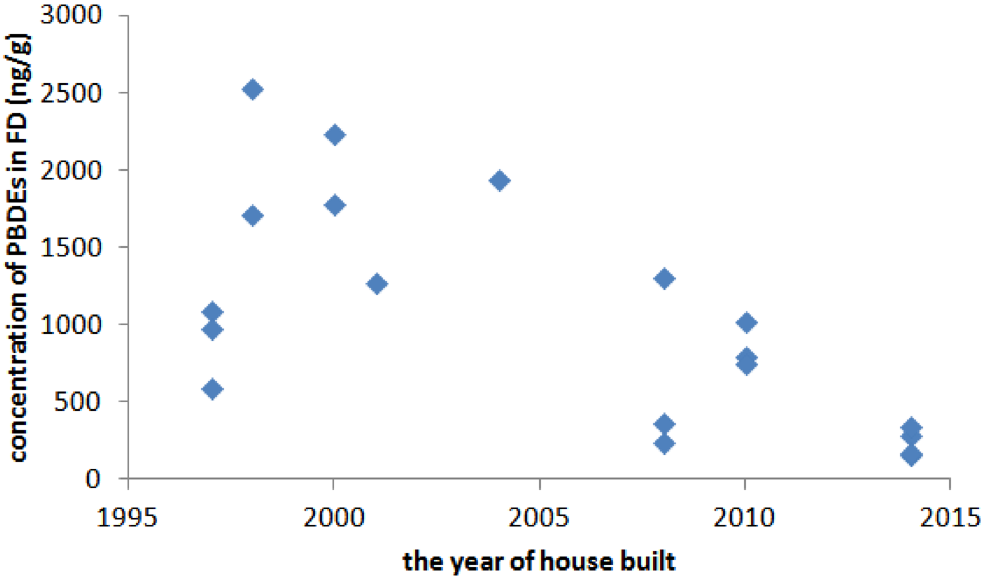

**Figure 3. 5** Correlation among the PBDEs ($\sum_8$PBDE) concentration (ng/g) in floor dust (n=19) and the year the house was built (Xiamen from 1995 to 2015.)

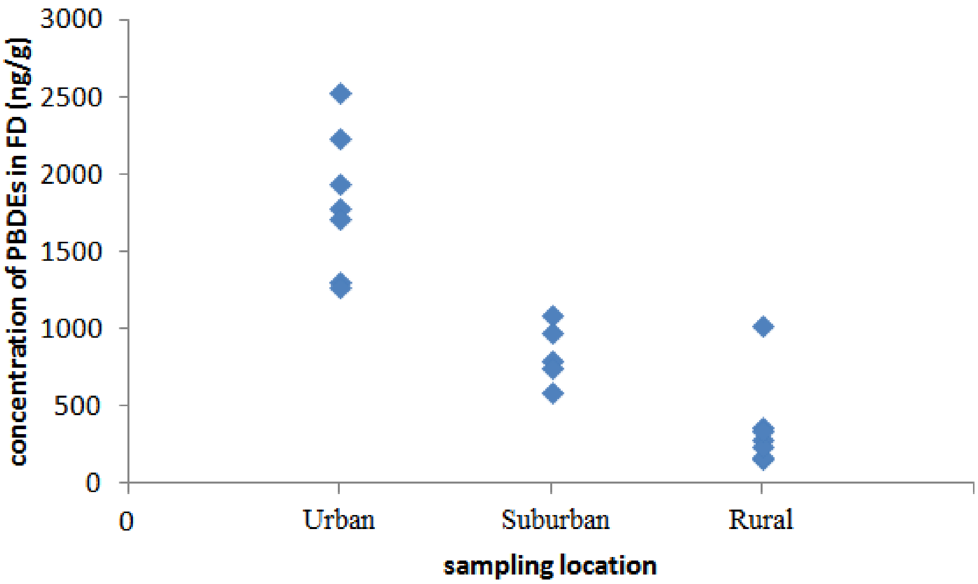

**Figure 3. 6** Correlation among the PBDEs ($\sum_8$PBDE) concentration (ng/g) in floor dust (n=19) and the sampling location, urban, suburban and rural areas.

#### 3.4.2.2 Potential impact of electric appliances usage on the indoor environment

In the present study, no relationship was found between indoor dust concentrations and the number of house hold consumer products, as well as the operating hours. This may have been due to the lack of significant variation of the number of pieces of appliances and other sources of PBDEs between locations and the size of sampling. According to the questionnaires, there were only 3 to 5 air conditioners in each volunteer private home, and majority of them operated from 6 to 8 hours per day.

By far, there is no strong evidence suggested that PBDEs concentration in indoor dust is associated with the operating hours of electric appliances. However, Sun et al. (Sun et al., 2016b) reported a significant positive correlation ($r=0.82$, $p<0.01$) between the daily operating hours of air conditioners and the PBDE concentration in indoor air. They also collected dust samples from the inner filter of the air conditioner units. It was suggested that the high operating temperature of the air conditioners accelerated the volatilization of PBDEs from materials to the air and so longer operating hours should have increased indoor air concentrations. Previous studies suggested that a number of house hold products in indoor environments could influence PBDE concentrations in air and dust. It has been reported that there is a significant positive correlation between the concentration of PBDEs in indoor air and the number of electrical devices (Harrad et al., 2004). Another research detected PBDEs widely in indoor environment including indoor air and dust was reported by De Wit et al.(de Wit et al., 2012) who indicated that a significant positive correlation was seen between the number of presence of foam furniture and electronics to the indoor dust concentrations, but a negative correlation with PBDE concentrations in indoor air. De Wit et al (2012) suggested that in a room with numerous pieces of furniture the foam was found to act as a sink instead of a source.

### 3.4.2.3 Correlation analysis among floor dust, furniture foam dust and air conditioner filter dust

Figure 3.6 and Figure 3.7 showed the associations between PBDE concentrations in floor dust, AC dust and foam furniture dust. The association between floor dust and air conditioner dust concentrations is shown in figure 4.6, suggesting a significant positive correlation for $\Sigma_8$PBDE between two types of samples ($r=0.56$, $p<0.05$). The ratios of $\Sigma_8$PBDE concentration in AC filter dust to floor dust ($C_{AC}/C_{floor}$) ranged from 0.2 to 7.9, and the 70 % ratios of comparison samples are close to 1. This result suggests that there are common PBDE sources to both the air conditioner filter and indoor dust. A previous study suggested that dust captured on the air conditioner filter could be used to represent the indoor dust concentrations more broadly (Ni et al., 2011). Figure 3.7 shows no statistically correlation between floor dust and foam furniture dust was evident ($r=-0.03$, $p=0.57$). Although the dust collected from foam furniture might represent the foam itself, the amount of foam could influence the concentrations of PBDEs in indoor environment (de Wit et al., 2012). A previous study indicated BDE47 concentrations were higher in rooms with more foam furniture than in those with less ones. It was also noted that higher concentrations were detected in serum in those people who had a greater number of pieces of furniture (Hammel et al., 2017). Of course, if the sofa or foam furniture does not contain PBDEs, it can't be the source of PBDE emission (Ni et al., 2011).

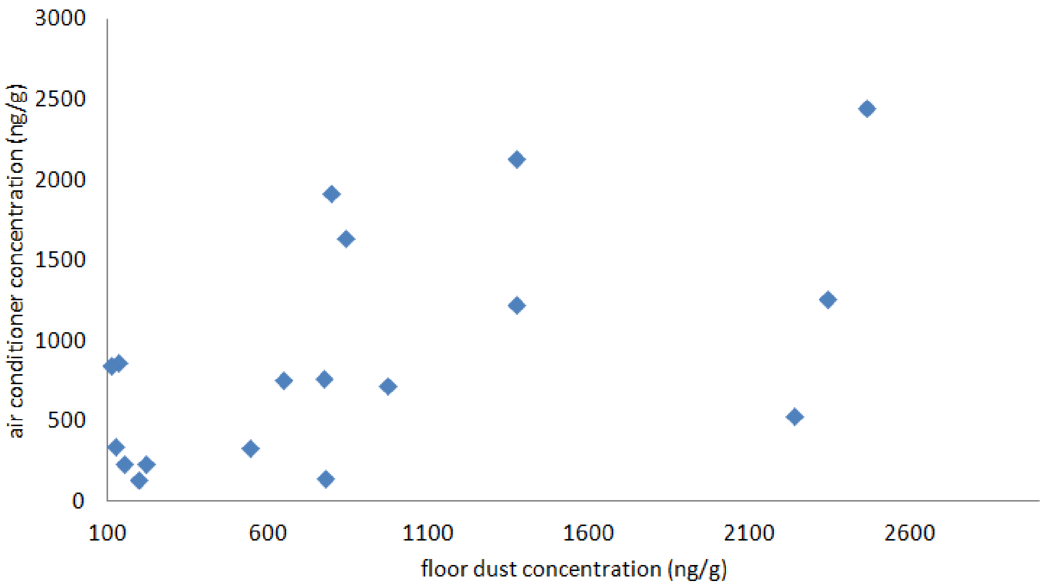

**Figure 3. 7** Scatter plots of positive associations for $\sum_8$PBDE concentration in floor dust and air conditioner filter dust (r=0.56, p<0.05)

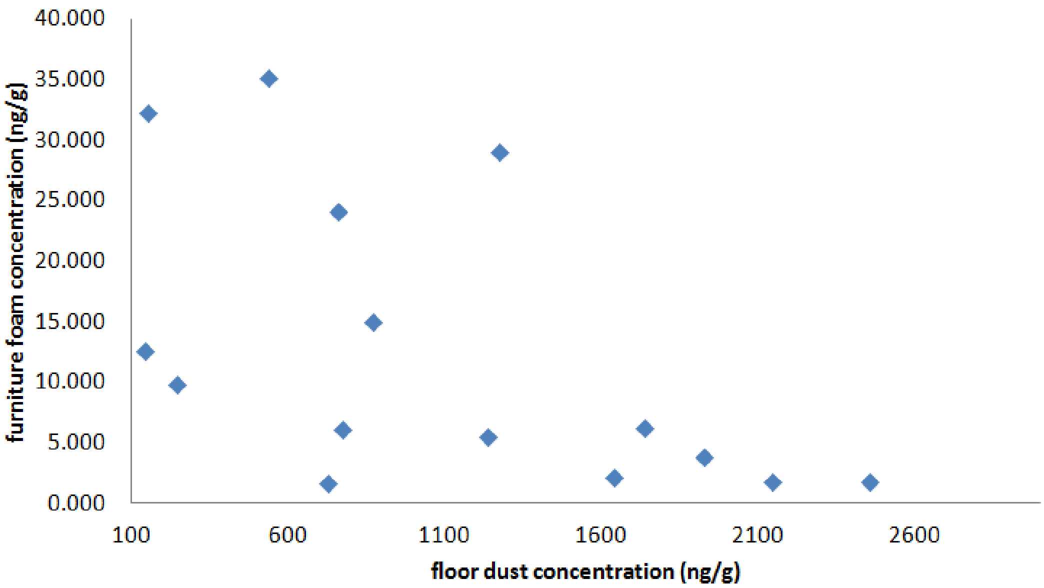

**Figure 3. 8** Scatter plots of associations for $\sum_8$PBDE concentration in floor dust and furniture foam dust (r=-0.03, p=0.57). No statistically correlation.

### 3.4.3 Human exposure to PBDEs from the indoor environment

Human exposure can be estimated by biomonitoring and external exposure assessment. The external exposure pathways include diet and inhalation of air and dust, whilst biomonitoring can be analyzed through body tissue measurements. Exposures to PBDEs were estimated using data from this study using questionnaire information on the hours people spent per day in their living rooms, the age of family members living in the work and the measured concentration of PBDEs in floor dust. Dust ingestion and dermal absorption are the two major pathways for human exposure to PBDEs via indoor dust Previous studies estimated that dust ingestion contributed to 37% for adults and 69% for toddlers in the UK; 82% and 77% of the USA adult and toddler, as well as 80% of exposure for Canadian children. (Gevao et al., 2006; Johnson-Restrepo and Kannan, 2009; Wilford et al., 2005,(Harrad et al., 2006).

The daily intake of PBDEs exposure dose through dust ingestion ($DED_{di}$) and dust dermal absorption ($DED_{da}$) (ng/kg bw day) were calculated by the following equations

(Johnson-Restrepo and Kannan, 2009):

$DED_{di}$=C * DIR *IEF / BW

$DED_{da}$ = C * BSA * DAS* AF * IEF / BW * 1000

$DED_{T}$ = $DED_{i}$ + $DED_{da}$

where C is the concentration of PBDEs in indoor dust (ng/g); DIR is the daily intake of dust (g/day); IEF is indoor exposure fraction (time fraction spent in indoor environments per day); BW is body weight (kg); BSA is body surface area ($cm^2$ ); DAS is dust adhered to the skin ($mg/cm^2$ ), and AF is the fraction of PBDEs adsorbed by skin.

Based on the information in the questionnaire from each sampling site, daily intake including dust ingestion and dermal absorption of PBDEs in indoor dust across five age groups: infants (<1 year), toddlers (1-5 year), children (6-11 year), teenagers (12-19 year) and adults (>19 years) were calculated. Supporting information supplied more details and the process of calculation, as well as the standers for each parameters.

The present study concluded that higher PBDE exposures in children than in adults. which was similar to previous studies (Toms et al., 2008; Schecter et al., 2006; Sun et al., 2016b). The highest dust exposure was observed in infants and toddlers, 12.34 and 11.63 ng/kg bw day separately. These results can be explained that infants spent most time at home and had hand-to-mouth contact behavior (Toms et al., 2008). Although adults and teenagers had low exposure on dust at home, 4.90 and 4.76 ng/kg bw day, they spent more time in the office. Future work should aim to estimated PBDE exposure from office dust.

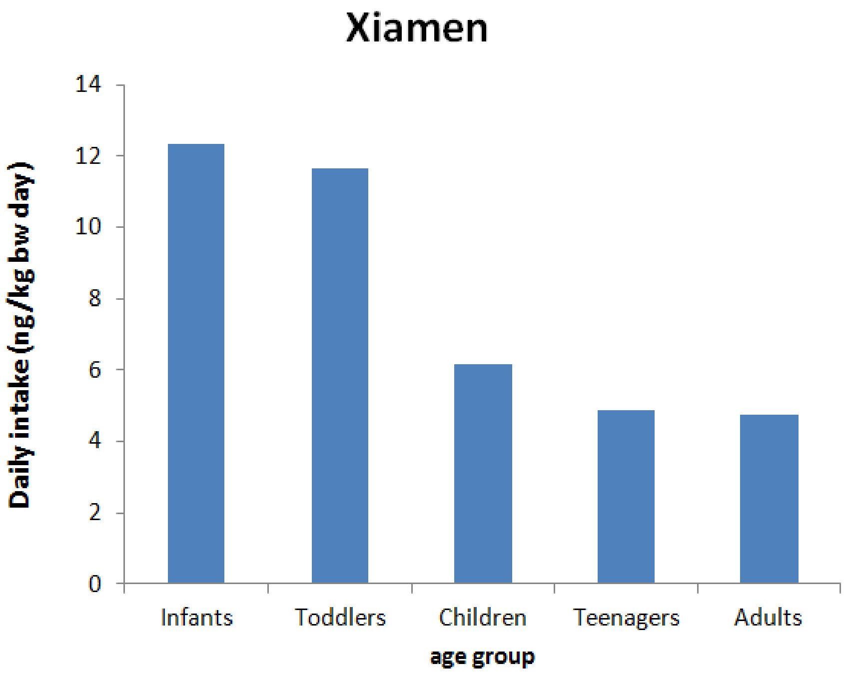

**Figure 3. 9** Estimated daily intake (ng/kg bw day) of PBDEs through dust ingestion and dust dermal absorption in five age groups in Xiamen, China.

### 3.4.4 Limitation

The volunteers in this study were selected from the Institute of Urban Environment in Xiamen. All of them were researchers aged 35 to 45 years old, therefore the results from the study are not representative of the whole population as these volunteer samples have similar age and socio-economic status, house, the style of decoration, the family members and the living habit. The details of the volunteers' house were listed in supporting infomarion. Thus, this study is exploratory research to develop a methodology to sample for these compounds and obtain initial results on PBDE emission and human exposure. Also, this study was the first one to use advanced instrument methodology (one column) to measured foam dust, indoor dust and air conditioner filter dust at the same time.

However, the sample size was too small to discuss the relationship among the age of house, location and exposure to PBDE products. In future work, a large random sample size should be involved, not only enlarged other age groups, but also the other representative samples of the whole population, to compare the different living habit and decoration.

## 3.5. Conclusion

This study provided information on PBDEs in indoor environments focusing on dust collected from homes in Xiamen city, China. Compared to previous studies, reported concentrations of PBDEs in indoor dust from other countries/regions in the world, the concentrations in this study are relatively low. BDE209 exceeded 90% of the total PBDE in floor dust, air conditioner dust and foam furniture dust. The fact that older houses contained higher concentrations of PBDE suggested a higher exposure potential for people living in these. A significant positive correlation was found between total PBDEs in dust from air conditioner filters and floor dust samples, which suggests that they have a common source of PBDEs. AC filters may be a good sample source to estimated indoo dust concentration where AC is used . No significant association was found between total PBDEs for foam furniture dust and floor dust. Compared with c-pentaBDE, c-octaBDE and c-decaBDE profile, the results indicate that c-decaBDE was the major PBDE products used in consumer products in China. PBDE exposure via dust ingestion and dust dermal absorption were higher in infants than adults suggesting that hand to mouth behavior and more time spent in home may lead to increased exposures.

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## Supporting information

Table S1 Summary the questionnaires basic information from 19 selected volunteer home

| House# | Region | Built Year | Number of air conditioner | AC purchased year | AC operating hours | Number of furniture foam | Floor square (m) | Clean frequency |
|---|---|---|---|---|---|---|---|---|
| 1 | Urban | 2000 | 3 | 2000 | 8 | 1 | 80 | one day |
| 2 | Urban | 1998 | 2 | 1998 | 8 | 2 | 80 | one day |
| 3 | Urban | 2004 | 5 | 2004 | 10 | 3 | 240 | one day |
| 4 | Urban | 1998 | 3 | 1998 | 6 | 3 | 80 | one day |
| 5 | Urban | 2000 | 3 | 2000 | 8 | 2 | 80 | one day |
| 6 | Urban | 2008 | 3 | 2008 | 8 | 2 | 120 | one day |
| 7 | Urban | 2001 | 3 | 2001 | 8 | 1 | 120 | one day |
| 8 | Suburban | 1997 | 3 | 1997 | 6 | 3 | 60 | one day |
| 9 | Suburban | 1997 | 3 | 1997 | 6 | 3 | 60 | one day |
| 10 | Suburban | 1997 | 3 | 1997 | 6 | 3 | 60 | one day |
| 11 | Suburban | 2010 | 4 | 2010 | 8 | 1 | 120 | one day |
| 12 | Suburban | 2010 | 4 | 2010 | 8 | 1 | 120 | one day |
| 13 | Rural | 2010 | 3 | 2010 | 8 | 3 | 120 | one day |
| 14 | Rural | 2014 | 3 | 2014 | 8 | 3 | 120 | one day |
| 15 | Rural | 2014 | 3 | 2014 | 8 | 2 | 120 | one day |
| 16 | Rural | 2008 | 4 | 2008 | 8 | none | 135 | one day |
| 17 | Rural | 2014 | 3 | 2014 | 8 | none | 120 | one day |
| 18 | Rural | 2008 | 3 | 2008 | 8 | none | 135 | one day |
| 19 | Rural | 2014 | 3 | 2014 | 8 | none | 120 | one day |

Table S2 Eight PBDE congeners concentration (ng/g) for air conditioner (AC, n=19) from 19 selected homes in Xiamen, China in 2016.

| | House# | BDE209 | BDE28 | BDE47 | BDE99 | BDE100 | BDE154 | BDE153 | BDE183 |
|---|---|---|---|---|---|---|---|---|---|
| AC | 1 | 5740.85 | 13.45 | 0.20 | 0.23 | 0.21 | 0.44 | 0.08 | 0.84 |
| | 2 | 2459.34 | 31.16 | 160.58 | 76.83 | 2.18 | 0.32 | 2.57 | 66.38 |
| | 3 | 790.70 | 6.37 | 56.89 | 21.16 | 0.25 | 0.11 | 0.81 | 31.71 |
| | 4 | 835.90 | 11.45 | 0.82 | 0.56 | 0.07 | 0.34 | 0.18 | 44.53 |
| | 5 | 1366.52 | 0.53 | 0.17 | 0.24 | 0.08 | 0.19 | 0.23 | 31.91 |
| | 6 | 2337.57 | 6.59 | 0.62 | 1.73 | 0.23 | 0.47 | 0.16 | 19.78 |
| | 7 | 1368.21 | 0.87 | 7.16 | 2.38 | 0.12 | 0.05 | 0.35 | 0.71 |
| | 8 | 2233.53 | 0.02 | 1.08 | 0.23 | 0.23 | 0.03 | 0.20 | 0.28 |
| | 9 | 129.87 | 0.27 | 0.32 | 0.11 | 0.12 | 0.25 | 0.14 | 0.35 |
| | 10 | 641.90 | 3.98 | 12.96 | 0.14 | 0.06 | 0.21 | 0.09 | 0.31 |
| | 11 | 768.60 | 0.09 | 0.32 | 0.14 | 0.06 | 0.18 | 0.16 | 0.30 |
| | 12 | 965.54 | 7.20 | 0.76 | 1.37 | 0.14 | 0.15 | 0.24 | 0.35 |
| | 13 | 108.07 | 0.07 | 0.05 | 0.07 | 0.02 | 0.13 | 0.07 | 0.22 |
| | 14 | 194.71 | 0.04 | 0.10 | 0.11 | 0.07 | 0.05 | 0.28 | 0.53 |
| | 15 | 148.10 | 0.25 | 0.26 | 2.37 | 0.23 | 0.42 | 0.03 | 0.18 |
| | 16 | 541.76 | 0.05 | 0.61 | 0.03 | 0.07 | 0.05 | 0.13 | 0.35 |
| | 17 | 775.83 | 0.03 | 0.14 | 0.09 | 0.02 | 0.03 | 0.02 | 0.16 |
| | 18 | 214.73 | 0.10 | 0.35 | 0.11 | 0.02 | 0.02 | 0.08 | 0.06 |
| | 19 | 120.77 | 0.04 | 0.17 | 0.13 | 0.12 | 0.07 | 0.07 | 0.12 |

Table S3 Eight PBDE congeners concentration (ng/g) for floor dust (FD, n=19) from 19 selected homes in Xiamen, China in 2016.

| | House# | BDE209 | BDE28 | BDE47 | BDE99 | BDE100 | BDE154 | BDE153 | BDE183 |
|---|---|---|---|---|---|---|---|---|---|
| FD | 1 | 1732.79 | 0.25 | 4.25 | 4.10 | 7.28 | 1.58 | 1.59 | 31.22 |
| | 2 | 2450.29 | 2.61 | 20.50 | 11.72 | 4.30 | 11.08 | 11.61 | 23.96 |
| | 3 | 1920.54 | 0.26 | 4.48 | 4.81 | 3.15 | 1.60 | 1.08 | 10.16 |
| | 4 | 1636.68 | 1.26 | 19.50 | 10.35 | 5.02 | 11.04 | 10.63 | 21.56 |
| | 5 | 2139.14 | 2.87 | 26.88 | 21.21 | 6.43 | 21.15 | 1.53 | 18.88 |
| | 6 | 1266.86 | 1.45 | 10.04 | 11.81 | 2.53 | 2.80 | 2.55 | 14.71 |
| | 7 | 1229.50 | 1.36 | 11.83 | 11.19 | 9.61 | 3.68 | 1.17 | 6.44 |
| | 8 | 532.24 | 1.05 | 21.83 | 21.72 | 9.65 | 1.08 | 2.17 | 10.78 |
| | 9 | 864.78 | 3.56 | 66.18 | 51.35 | 18.43 | 31.35 | 32.96 | 21.35 |
| | 10 | 754.69 | 3.78 | 70.52 | 50.62 | 7.28 | 31.00 | 30.66 | 34.35 |
| | 11 | 769.26 | 0.22 | 7.74 | 5.36 | 2.78 | 1.32 | 1.38 | 10.13 |
| | 12 | 722.30 | 0.19 | 4.55 | 4.55 | 3.66 | 2.30 | 1.32 | 10.85 |
| | 13 | 149.42 | 2.56 | 58.71 | 45.90 | 14.25 | 20.61 | 20.38 | 10.85 |
| | 14 | 138.00 | 0.91 | 5.06 | 0.68 | 8.99 | 4.13 | 3.41 | 2.41 |
| | 15 | 239.14 | 1.95 | 19.85 | 10.37 | 5.14 | 3.37 | 1.29 | 2.95 |
| | 16 | 333.67 | 0.96 | 10.22 | 10.73 | 2.95 | 2.25 | 3.65 | 2.61 |
| | 17 | 143.18 | 1.16 | 11.55 | 10.36 | 2.48 | 3.28 | 2.10 | 1.03 |
| | 18 | 236.90 | 0.94 | 3.52 | 1.07 | 1.32 | 1.07 | 1.09 | 1.94 |
| | 19 | 344.03 | 0.19 | 1.05 | 1.21 | 2.36 | 0.18 | 0.20 | 1.20 |

Table S4 Eight PBDE congeners concentration (ng/g) for furniture foam (FF, n=15) from 19 selected homes in Xiamen, China in 2016.

| | House# | BDE209 | BDE28 | BDE47 | BDE99 | BDE100 | BDE154 | BDE153 | BDE183 |
|---|---|---|---|---|---|---|---|---|---|
| FF | 1 | 6.31 | 0.09 | 4.15 | 0.54 | 0.02 | 0.06 | 0.24 | 0.29 |
| | 4 | 1.92 | 0.03 | 0.14 | 0.42 | 0.02 | 0.02 | 0.04 | 0.03 |
| | 5 | 3.92 | 0.02 | 0.90 | 0.80 | 0.06 | 0.02 | 0.06 | 0.05 |
| | 6 | 2.22 | 0.02 | 0.20 | 0.06 | 0.01 | 0.02 | 0.02 | 0.01 |
| | 7 | 1.92 | 0.01 | 0.91 | 0.46 | 0.05 | 0.05 | 0.02 | 0.11 |
| | 8 | 29.07 | 1.54 | 2.80 | 0.83 | 0.03 | 0.01 | 0.10 | 0.73 |
| | 9 | 5.64 | 0.01 | 0.10 | 0.28 | 0.01 | 0.01 | 0.01 | 0.02 |
| | 10 | 35.25 | 0.04 | 1.13 | 0.31 | 0.04 | 0.02 | 0.05 | 0.07 |
| | 11 | 15.13 | 0.01 | 0.29 | 0.27 | 0.01 | 0.00 | 0.03 | 0.05 |
| | 12 | 24.26 | 1.88 | 1.34 | 0.38 | 0.01 | 0.06 | 0.05 | 0.20 |
| | 13 | 6.24 | 1.41 | 0.62 | 0.15 | 0.02 | 0.03 | 0.03 | 0.05 |
| | 14 | 1.76 | 0.01 | 0.19 | 0.31 | 0.00 | 0.02 | 0.03 | 0.04 |
| | 15 | 32.33 | 0.80 | 26.03 | 0.27 | 0.01 | 0.01 | 0.04 | 0.02 |
| | 16 | 12.68 | 0.01 | 1.61 | 0.71 | 0.02 | 0.02 | 0.02 | 0.21 |
| | 17 | 9.96 | 0.64 | 1.64 | 0.09 | 0.01 | 0.05 | 0.14 | 0.10 |

Table S5 summary the age group of population in 19 selected volunteer home

| House# | Infants | Toddlers | Children | Teenagers | Adults |
|---|---|---|---|---|---|
| 1 | | | | | 4 |
| 2 | | | | 1 | 2 |
| 3 | | | 1 | | 2 |
| 4 | 1 | | | | 4 |
| 5 | | | | 1 | 2 |
| 6 | | | | | 3 |
| 7 | | 1 | | | 3 |
| 8 | | | 1 | | 2 |
| 9 | | | | 1 | 2 |
| 10 | | | | | 2 |
| 11 | 1 | 1 | | | 4 |
| 12 | | | 1 | | 3 |
| 13 | | 1 | | | 3 |
| 14 | 1 | | | | 3 |
| 15 | 1 | | | | 3 |
| 16 | | | | | 2 |
| 17 | | | | | 2 |
| 18 | | | 1 | | 3 |
| 19 | | | | | 3 |

Table S6 Estimated daily exposure dose of PBDEs from house dust (ng/kg bw day) for five age groups

| | Infants | Toddlers | Children | Teenagers | Adults |
|---|---|---|---|---|---|
| Age | <1 | 1-5 | 6-11 | 12-19 | >19 |
| BW (kg) | 5 | 16 | 29 | 52 | 65 |
| IEF | 0.88 | 0.79 | 0.79 | 0.88 | 0.88 |
| IEF/BW | 0.176 | 0.049375 | 0.027241 | 0.016923 | 0.013538 |
| BSA($cm^2$/day) | 801 | 2564 | 3067 | 3692 | 4615 |
| SAS(mg/$cm^2$) | 0.096 | 0.096 | 0.096 | 0.096 | 0.096 |
| di | 0.176 | 0.049375 | 0.027241 | 0.016923 | 0.013538 |
| da | 0.01191 | 0.009601 | 0.006336 | 0.005278 | 0.005278 |
| $DED_{da}$ | 9.527722 | 7.680924 | 5.069104 | 4.222648 | 4.222648 |
| DIR | 0.02 | 0.1 | 0.05 | 0.05 | 0.05 |
| $DED_{di}$ | 2.816 | 3.95 | 1.089655 | 0.676923 | 0.541538 |
| TotalDED | 12.34372 | 11.63092 | 6.158759 | 4.899571 | 4.764187 |

DIR is the daily intake of dust (g/day);

IEF is indoor exposure fraction (hours/24);

BW is body weight (kg);

BSA is body surface area ($cm^2$);

SAS is soil adhered to the skin (mg/$cm^2$),

AF is the fraction of PBDEs adsorbed by skin.

# Chapter4 Spatial distribution of polybrominated diphenyl ethers (PBDEs) in indoor dusts from districts in five cities in China

## 4.1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of bromine containing organic compounds that are used in wide range of materials to reduce product flammability, such as electronic equipment (televisions, air conditioners), polyurethane foams, textiles and plastics (de Wit, 2002). Three major PBDE commercial formulations were produced which were not single component products, but mixtures of several PBDE congeners: commercial pentaBDE (abbreviation c-pentaBDE) comprised of 0-1% triBDE, 24%-38% tetraBDE, 50%-62% pentaBDE and 4%-12% hexaBDE congeners; commercial octaBDE (abbreviation c-octaBDE) comprised of 0.5% pentaBDE, 12% hexaBDE, 45% heptaBDE, 33% octaBDE, 10% nonaBDE and 0.7% decaBDE; and commercial decaBDE (abbreviation c-decaBDE) which was almost entirely decaBDE (97% - 99%) with less than 3% nonaBDE (de Boer et al., 2003). Among these three commercial PBDE products, c-pentaBDE was largely used in polyurethane foams, c-octaBDE was added to electronics parts and plastic casings for appliances, and c-decaBDE was widely used in high-impact polystyrene plastics (Alaee et al., 2003). Figure 5.1 presents the details of three commercial PBDEs products composition.

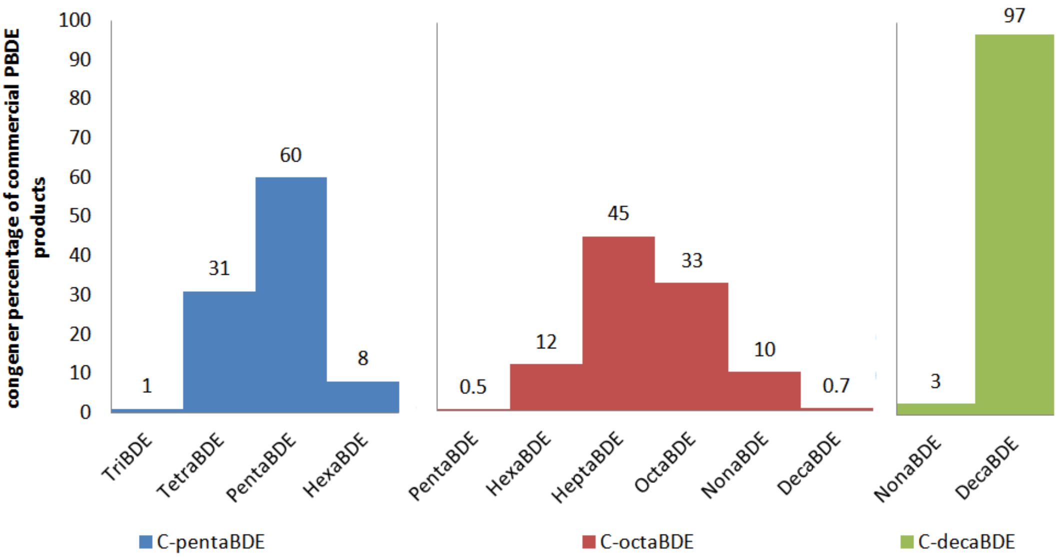


**Figure 4. 1** Each PBDE congeners percentage of c-pentaBDE, c-octaBDE and c-decaBDE (weight/weight %)

Although PBDEs have played a beneficial role in the flame retardant market and have become prevalent in people's daily life, they have been found in most parts of the environment, and even in humans (de Boer et al., 2003; Guan et al., 2009; Hirai et al., 2012). As a result, PBDEs were subject to regulation in Europe and North America and then globally under the Stockholm Convention. C-pentaBDE and c-octaBDE formulations have been banned from use in California since 2003 and in Europe since 2004 according to Restriction of Hazardous Substances (RoHS). In May 2009, the c-pentaBDE and c-octaBDE products were added into the Annexes of the Stockholm Convention on POPs (UNEP/POPS/COP.4/38). The use of c-decaBDE has also been restricted in the USA (US EPA IRIS, 2013) and c-decaBDE was added to the Stockholm Convention Annexes A on 5th May 2017 at the eighth Convention of the Parties (UNEP/POPS/COP.8/32) and shall not be manufactured or placed on the market as a substance on its own after 2 March 2019 (REACH ANNEX XVII).

In the early 2000s, the global production of PBDEs were approximately 70,000 tons (de Wit, 2002). After production ceased in the USA and EU in 2004, China became one of the largest manufactures with a peak PBDE production of 80,000 tons in 2006. In China, the usage of c-decaBDE has occupied the majority of the flame retardant market in 2001, which accounted for 93.3% of commercial PBDEs products, followed by c-octaBDE (6.1%) and c-pentaBDE (<1%) in 2001 (Chen et al., 2007). The production of c-decaBDE reached a peak of 80,000 tons in 2006 in China (Chen et al., 2012).

Previous studies have suggested that indoor dust can be a significant pathway of human exposure since there was a positive correlation between the concentration of PBDEs in indoor dusts and the concentrations in human breast milk and blood (Johnson et al., 2010; Allen et al., 2008; Jones-Otazo et al., 2005; Wu et al., 2007). Following the regulation of PBDEs in Europe and North America, studies began to focus on the significance of PBDE exposure from indoor environments and adverse human health effects in China (Chen et al., 2011; Huang et al., 2010; Wang et al., 2014). However, many published studies in China placed greater emphasis on specific areas such as e-waste recycling sites and industrial manufacturing site (Chan et al., 2013; Ding et al., 2016; Jiang et al., 2014). Other studies have focused on PBDEs in indoor dust from main cities such as Beijing, Shanghai and Guangzhou, which have larger populations, higher urbanization development and are wealthier than other cities in China (Sun et al., 2016b; Chen et al., 2011; Zhu et al., 2013; Peng et al., 2017). However, there is only a limited number of studies on other cities, as well as data on the spatial distribution of PBDE concentrations within the indoor environment, as well as lack of comparison between urban, suburban and rural regions in given city environment.

The main objectives of this study were to investigate the spatial distribution of concentrations and composition of PBDEs in indoor dust from north to south China; to investigate the PBDE contamination levels in different urban, suburban and rural districts of the cities; to explore associations between PBDE concentration and the possible indoor sources, and finally to estimate the daily human exposure dose to PBDEs for Chinese population. To achieve above objectives, five cities were selected, including Guangzhou, Xiamen, Shanghai, Beijing and Dalian, which are key cities in China in the order of south to north cross 2856 kilometers, and with differences in city scale, climate, life style, urbanization level, economic development and population density.

## 4.2. Materials and methods

### 4.2.1 Sample collection

In total, 141 indoor dust samples were collected from five cities, Dalian, Beijing, Shanghai, Guangzhou and Xiamen from December 2016 to January 2017. The number of samples collected from each city are shown in Table 5.1, with all of the samples were classed into three groups: urban areas (UA), suburban areas (SA) and rural areas (RA). The figure 4.2 showed the details of sampling sites.

In this study, the districts near the city center, with highest population density and high gross domestic product (GDP) are defined as urban areas; the districts surrounding the urban areas are defined as suburban areas. In China, suburban areas always connect to the rural areas and urban areas, also industrial developments often develop here. Rural areas located and surround the edge of suburban areas, and are characterized with low population density and often rudimentary living facilities.

In Beijing, Chaoyang district represents an urban area and is a shopping and business center, Haidian district is a suburban region with a number of electronics companies, universities, and factories, Daxing and Changping districts are rural areas.

In Dalian, Shahekou district, is an urban area near the city center, Gangjinzi district is suburban region and Jingzhou district is a rural area. Jingzhou district is being developed as an industrial development zone.

In Shanghai, Jing'an district is an urban region within the city and contains a shopping district, as well as the oldest town region, Xuhui and Pudong districts are newly developing suburban areas. Pudong represents the financial district and Xuhui is becoming a transportation hub which is connected to the city center of Shanghai and surrounding rural areas; Minghang district is suburban region.

For Guangzhou, Yuexiu district is an urban area, representing the city center and the oldest part of downtown; Tianhe district is newly built suburban centre and financial district, with many electronics companies and factories. Panyu district is a rural region with fewer factories.

In Xiamen, Siming district is the oldest part of the city center; Huli district is a newly built suburban area and Jimei district is rural areas with fast development of university and college campuses and institutes.Table 4.1 lists the number of samples collected from urban, suburban and rural areas in each city, and supporting information lists basic information including population density and gross domestic product for each district.

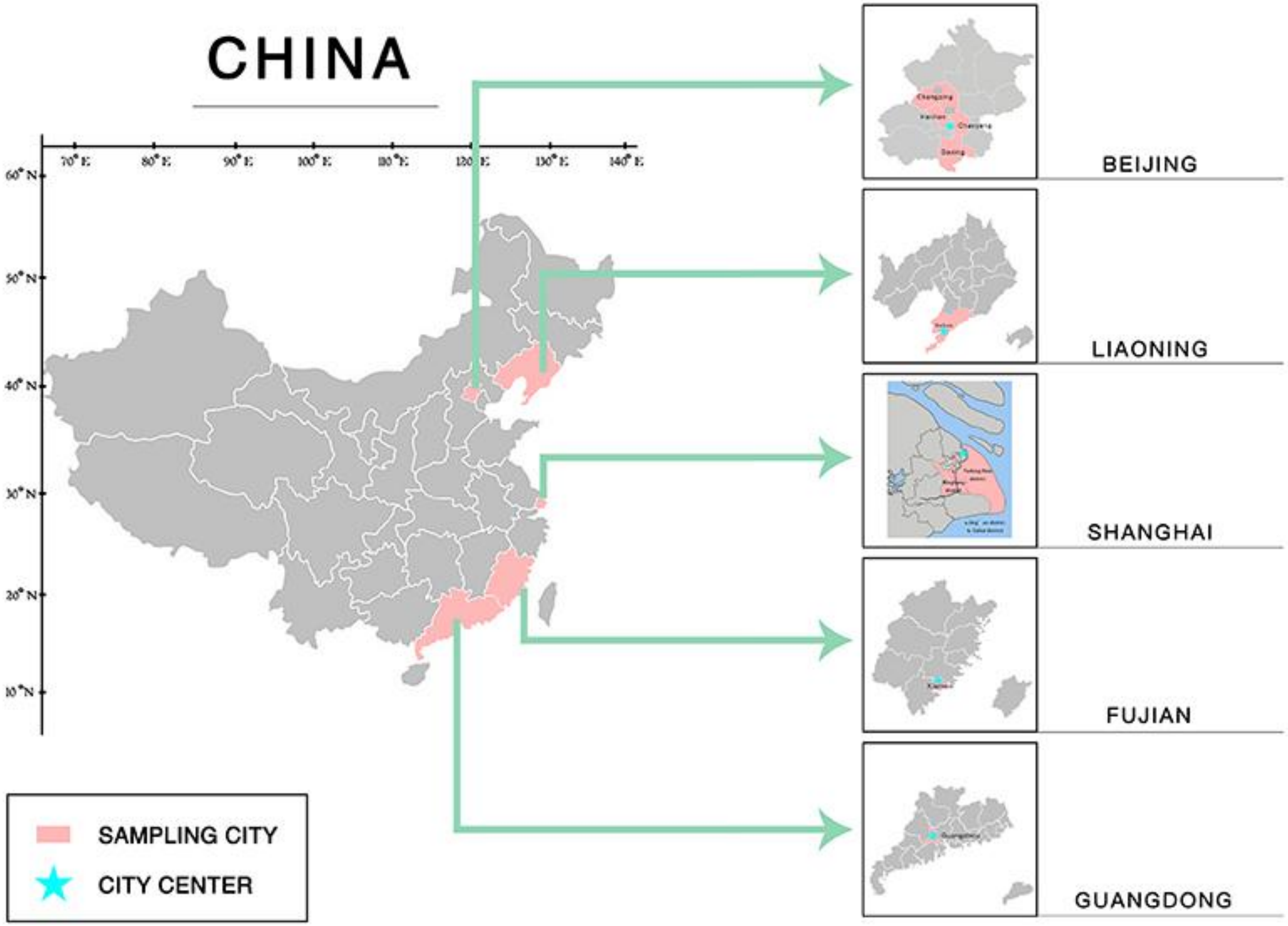


**Figure 4. 2** The details of sampling site of five cities (Dalian, Beijing, Shanghai, Xiamen and Guangzhou). Blue stars indicate the city center

**Table 4. 1** Number of samples collected from five target cities in urban, suburban and rural areas. In total 141 samples were collected

| | Dalian | Beijing | Shanghai | Xiamen | Guangzhou |
|---|---|---|---|---|---|
| **Urban** | 11 | 8 | 10 | 7 | 8 |
| **Suburban** | 10 | 6 | 15 | 5 | 8 |
| **Rural** | 9 | 19 | 8 | 7 | 10 |

Dust samples were collected from the living room from each private home, using a vacuum cleaner with a nylon sample sock (25 μm pore size) mounted on the end of the suction tube. The tube and socks were cleaned with acetone and hexane before and after each use. Each sock was used only for one sample. After sampling, each sample was passed through a 500 μm sieve to remove larger debris and solid objects such as hairs and fibers. The dust samples were sealed in aluminum foil and stored in a freezer at -20° C. Field blanks consisted of sodium sulfate powder on a clean aluminum foil surface collected using the same method as a sample. **Chapter 2** had discussed the sampling, method and instrument analysis.

### 4.2.2 Chemicals and standards

A standard mixture of 39 PBDEs (including BDE-7, -11, -8, -12, -15, -32, -30, -17, -25, -33, -28, -35, -37, -75, -49, -47, -66, -100, -119, -99, -116, -118, -155, -85, -126, -154, -153, -138, -166, -183, -181, -190) and BDE-209 were produced by AccuStandard, Inc. (New Haven, CT, USA). The $^{13}$C labeled PCB 208, $^{13}$C-PCB 141 and $^{13}$C-BDE77 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) as recovery standard and internal standard respectively. Acetone, dichloromethane (DCM) and n-hexane were obtained from Fisher Chemical (MA, USA).

### 4.2.3 Sample extraction

All equipment was pre-extracted for 8h to 10h. 1g dust sample was weighed, mixed with sodium sulphate and spiked with a mixture of $^{13}$C-PCB-141 and $^{13}$C-BDE-77 as recovery standards. Samples were extracted in 150 ml hexane for 16h to 18h. A combined silica and alumina column was used for sample clean-up. The column was packed in the following order starting from the bottom layer; 6cm Alumina, 2cm activated silica, 6cm basic silica (25%), 2cm activated silica, 6cm acid silica (44%) and 1cm sodium sulphate. The target compounds were eluted with 70 ml of hexane/DCM (1:1). Finally, the sample was evaporated to 0.1 ml under a gentle nitrogen gas flow. $^{13}$C-PCB-208 was added as an internal standard to the samples before analysis.

### 4.2.4 Analysis

The samples were analyzed using an Agilent 7890A-5975C gas chromatograph-mass spectrometer (GC/MS) with negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. BDE-209 was quantified by monitoring ions m/z 79, 81, 486.6 and 488.6, while $^{13}$C-PCB-141was monitored using m/z 371.9 and 373.9, $^{13}$C-PCB-208 was monitored using m/z 473.8 and 475.8, and $^{13}$C-BDE-77 was monitored using m/z 471.8 and 473.8. The other congeners were quantified by the bromide ions, m/z 79 and 81. Helium (purity > 99.999%) was used as the carrier gas at a flow rate of 1 ml/min and methane (purity > 99.99%) was used as a chemical ionization moderating gas. The gas chromatography column was a DB-XLB 15m * 250 μm * 0.1 μm with the following oven program: the initial column temperature started from 110° C held for 0.5 min, and then ramped to 200° C at 60° C/min, then to 280° C at 5° C/min (held for 0.5 min) and to 310° C at 60° C/min (held for 8 min). The total operation time was 28 min.

### 4.2.5 Quality assurance and quality control

One field blank was collected at each sampling location. Sodium sulfate from a sheet of foil was collected using the same vacuum cleaner used for samples. The field blank was used to check for contamination from the equipment. Internal and recovery standards were used to monitor the contaminant recovery during the processes of sample analysis. Details information had been discussed in **Chapter 2.**

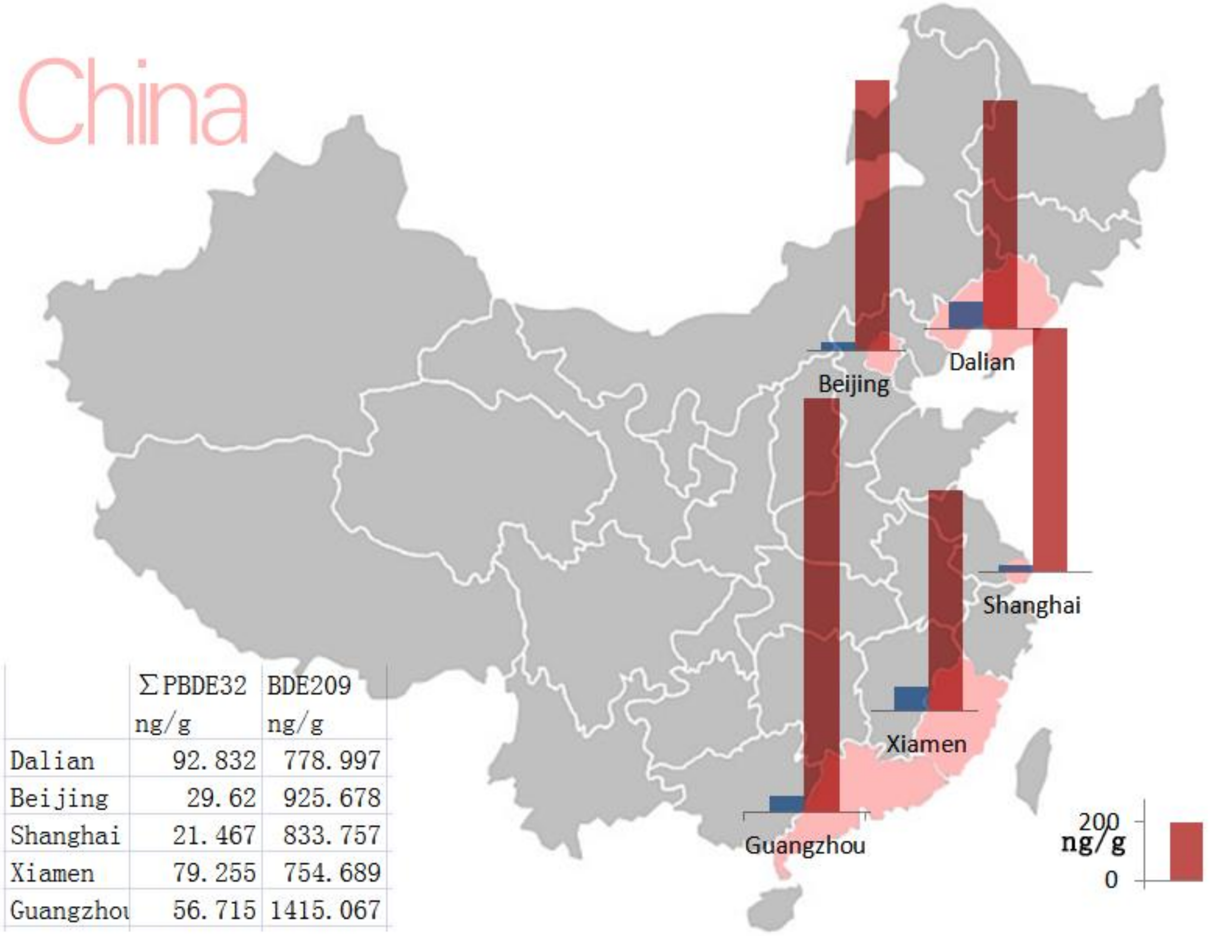
## 4.3. Results

### 4.3.1 PBDEs in indoor dust from cities across China

#### 4.3.1.1 Concentrations of PBDEs in five cities in China

The spatial distribution of PBDEs including 32 congeners and BDE209 in indoor dust samples collected across China is presented in figure 4.3. The concentration of PBDEs from each sampling city are summarized in Table4.2. All 33 congeners including BDE209 were detected and detailed data are contained in supplementary information. In Table 4.2, only the main eight congeners accounted for over 90% of total 33 PBDE concentration have been included to illustrate typical concentrations for each city. The median $\Sigma_{33}$PBDEs for 33 congeners including BDE209 in indoor dust from Dalian, Beijing, Shanghai, Xiamen and Guangzhou were 836, 971, 1017, 815 and 1455 ng/g respectively, representing geographical locations from north to south. The highest concentrations of $\Sigma_{33}$PBDEs including BDE209 were found in Guangzhou, which ranged from 263 to 7072 ng/g, followed by Shanghai, 151 to 4704 ng/g. Samples from Beijing, ranging from 328 to 2968 ng/g, were higher than Dalian and Xiamen. Dalian was higher than Xiamen, ranging from 236 to 3712 ng/g, but much lower than other three developed cities. The lowest concentrations of $\Sigma_{33}$PBDEs was in dust from

Xiamen, ranging from 187 to 2611 ng/g. BDE209 was the most important congener in all samples collected across China, and the median concentration of BDE209 was 778, 925, 833, 754 and 1415 ng/g for Dalian, Beijing, Shanghai, Xiamen and Guangzhou respectively.



| | ΣPBDE32 ng/g | BDE209 ng/g |
|---|---|---|
| Dalian | 92. 832 | 778. 997 |
| Beijing | 29. 62 | 925. 678 |
| Shanghai | 21. 467 | 833. 757 |
| Xiamen | 79. 255 | 754. 689 |
| Guangzho | 56. 715 | 1415. 067 |

**Figure 4. 3** Concentration of 33 PBDE congeners in indoor dust samples from Dalian, Beijing, Shanghai, Xiamen and Guangzhou in China (n=141).

**Table 4. 2** Eight main congeners of PBDEs (ng/g) in the indoor dust samples for five target cities in China in 2016.(n=141)

| | | BDE209 | BDE28 | BDE47 | BDE99 | BDE100 | BDE154 | BDE153 | BDE183 | $\sum_7$PBDE | $\sum_8$PBDE |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Beijing | Mean | 1006.28 | 0.25 | 13.08 | 13.68 | 2.08 | 2.31 | 1.94 | 7.68 | 41.01 | 1047.29 |
| | Median | 925.68 | 0.11 | 3.47 | 1.10 | 0.69 | 0.51 | 1.44 | 4.40 | 15.58 | 941.34 |
| | Minimum | 311.97 | 0.01 | 0.37 | 0.10 | 0.07 | 0.11 | 0.02 | 0.45 | 2.33 | 323.82 |
| | Maxmum | 2892.00 | 0.93 | 89.56 | 100.44 | 17.55 | 17.77 | 7.82 | 40.41 | 214.85 | 3006.51 |
| Shanghai | Mean | 1275.40 | 0.53 | 21.65 | 23.16 | 3.73 | 1.79 | 2.83 | 29.72 | 83.42 | 1358.81 |
| | Median | 833.76 | 0.25 | 3.41 | 1.40 | 1.54 | 1.40 | 1.67 | 0.32 | 11.17 | 1083.71 |
| | Minimum | 129.10 | 0.01 | 0.39 | 0.08 | 0.32 | 0.11 | 0.29 | 0.10 | 3.11 | 139.22 |
| | Maxmum | 4682.79 | 5.66 | 174.32 | 220.20 | 23.12 | 9.69 | 9.89 | 445.32 | 674.06 | 4695.76 |
| Guangzhou | Mean | 1924.90 | 2.60 | 19.76 | 25.21 | 4.09 | 4.47 | 5.45 | 13.59 | 75.16 | 1996.86 |
| | Median | 1415.07 | 1.48 | 3.83 | 5.56 | 2.14 | 1.60 | 2.63 | 10.13 | 27.74 | 1445.93 |
| | Minimum | 239.39 | 0.25 | 0.58 | 0.71 | 0.35 | 0.16 | 0.57 | 1.18 | 8.78 | 249.04 |
| | Maxmum | 6950.23 | 11.17 | 191.75 | 196.87 | 17.19 | 34.14 | 17.37 | 56.21 | 506.79 | 7028.63 |

Table continued

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dalian | Mean | 1378.88 | 1.91 | 18.81 | 18.71 | 11.06 | 5.22 | 3.01 | 28.85 | 87.58 | 1466.46 |
| | Median | 779.00 | 1.55 | 5.57 | 6.02 | 4.08 | 4.84 | 1.82 | 12.24 | 51.30 | 811.64 |
| | Minimum | 167.95 | 0.21 | 0.24 | 0.53 | 0.23 | 0.70 | 0.17 | 1.09 | 14.13 | 209.98 |
| | Maxmum | 3667.08 | 4.86 | 90.65 | 97.72 | 69.53 | 16.16 | 16.44 | 136.66 | 331.72 | 3685.17 |
| Xiamen | Mean | 926.49 | 1.45 | 19.91 | 15.22 | 6.19 | 8.15 | 6.88 | 12.49 | 70.29 | 996.78 |
| | Median | 754.69 | 1.16 | 11.55 | 10.37 | 5.02 | 3.28 | 2.10 | 10.78 | 45.27 | 798.18 |
| | Minimum | 138.00 | 0.19 | 1.05 | 0.68 | 1.32 | 0.18 | 0.20 | 1.03 | 6.39 | 163.59 |
| | Maxmum | 2450.29 | 3.78 | 70.52 | 51.35 | 18.43 | 31.35 | 32.96 | 34.35 | 228.21 | 2536.06 |

$\sum_7$PBDE includes BDE28, 47, 99, 100, 154, 153 and 183;

$\sum_8$PBDE includes BDE28, 47, 99, 100, 154, 153, 183 and BDE209;

### 4.3.1.2 Congeners profile of PBDE pollution in five cities in China

BDE209 was the most abundant congener in all dust samples, contributing to 96%, 95%, 92%, 90% and 89% of the PBDE composition of house dust for Beijing, Guangzhou, Shanghai, Dalian and Xiamen, respectively. Figure 5.4 presents BDE209 contribution to the concentration of $\sum_8$PBDE. The proportions of the other 7 main PBDE congeners in indoor dust from the five cities are presented in Figure 5.5. BDE47, BDE99 and BDE183 were the most important congeners for $\sum_7$PBDE (excluding BDE209), followed by BDE100, BDE154 and BDE153. The lowest brominated congener detected was BDE28. Among these five cities, BDE183 accounted for 32% and 29% of the total in Dalian and Guangzhou separately, higher than BDE47 and BDE99. While for Shanghai, Beijing and Xiamen, BDE47 and BDE99 contributed more than BDE183.

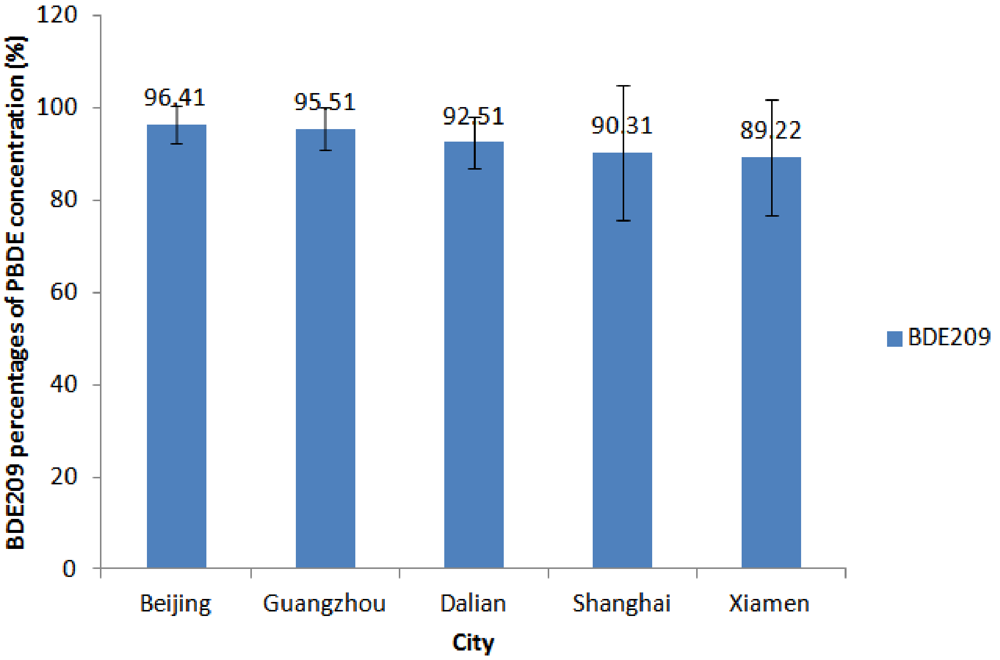


**Figure 4. 4** The percentage of BDE209 in $\sum_8$PBDE in indoor dust from Dalian, Beijing, Shanghai, Xiamen and Guangzhou in China. Error bar were calculated from the standard deviation (SD) of samples from each city.

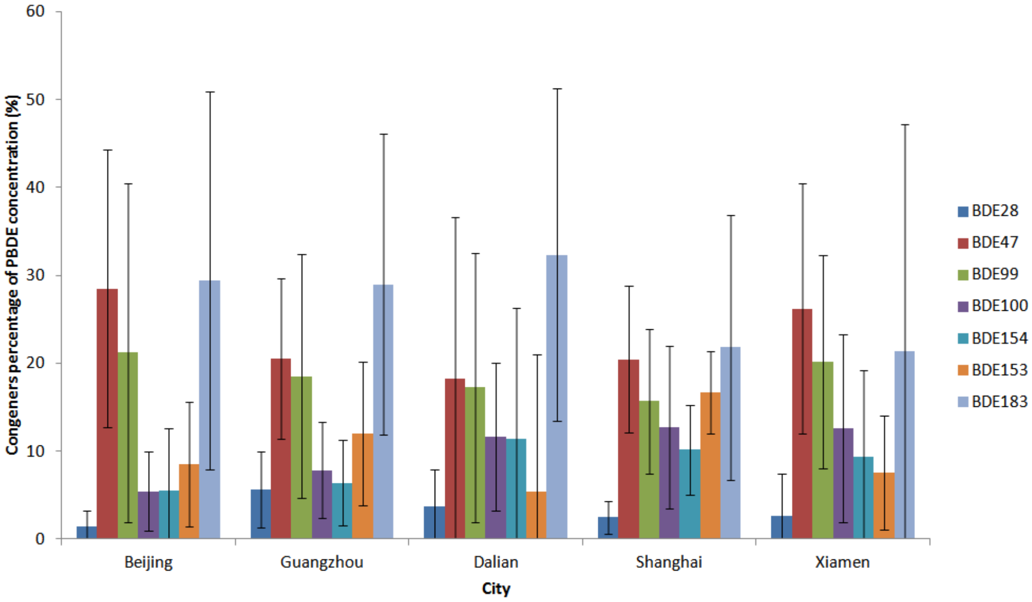


**Figure 4. 5** The percentage of each congener in $\sum_7$PBDE in indoor dust from Dalian, Beijing, Shanghai, Xiamen and Guangzhou in China. Error bar were calculated from the standard deviation (SD) of samples from each city.

#### 4.3.1.3 Correlation analysis of major PBDEs congeners in indoor dust in China

Table4.3 shows Spearman's correlations between the concentrations of congeners in all samples. BDE47 strongly correlated with BDE99, BDE100, BDE28, BDE154 and BDE153 at the $p<0.01$ level. BDE209 shows no related with other congeners, and only weak correlation with BDE28, BDE153, BDE154 and BDE183 at the $p<0.05$ level. BDE183 showed only weak correlations with other congeners at the $p<0.01$ level. Another strong correlation was evident between BDE154 and BDE153 at the $p<0.01$ level.

**Table 4. 3** Spearman's correlations among the eight main congeners in 141 samples from five target cities in China

| | | BDE209 | BDE28 | BDE47 | BDE99 | BDE100 | BDE154 | BDE153 |
|---|---|---|---|---|---|---|---|---|
| BDE28 | r | .294* | | | | | | |
| | P | 0.02 | | | | | | |
| BDE47 | r | 0.09 | .655** | | | | | |
| | P | 0.29 | 0.00 | | | | | |
| BDE99 | r | 0.11 | .603** | .923** | | | | |
| | P | 0.20 | 0.00 | 0.00 | | | | |
| BDE100 | r | 0.08 | .387** | .520** | .479** | | | |
| | P | 0.35 | 0.00 | 0.00 | 0.00 | | | |
| BDE154 | r | .182* | .577** | .590** | .488** | .359** | | |
| | P | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | | |
| BDE153 | r | .211* | .530** | .537** | .476** | .387** | .762** | |
| | P | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| BD183 | r | 0.204* | 0.212* | .253** | .341** | .228** | 0.21** | 0.211** |
| | P | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

**. Correlation is significant at the 0.01 level p<0.01

*. Correlation is significant at the 0.05 level p<0.05.

### 4.3.2 PBDEs pollution level in indoor dust from different districts across China.

#### 4.3.2.1 PBDEs concentration in indoor dust from urban, suburban and rural areas

The concentrations of PBDEs in different regions for each city were analyzed. The median concentrations of BDE209 and $\sum_7$PBDE from urban, suburban and rural sites are presented in supporting information. Urban sites had the highest median value for BDE209 and $\sum_7$PBDE, followed by suburban sites and rural sites. The different concentrations indicated that indoor dust in urban and suburban sites were much more contaminated by PBDEs than rural sites in China. Figure 5.6 indicates that the concentration of $\sum_7$PBDE in samples from suburban areas was 327.64 ng/g, which is higher than urban areas (276.33 ng/g), with the lowest concentration of 120.06 ng/g being found in rural areas. For BDE209, data presented in Figure 5.7 shows that the concentrations in urban areas were highest, followed by the suburban areas with the lowest concentrations in rural areas. For urban areas, Guanghzou has the highest concentration of BDE209, measured at 3542.2 ng/g, followed by Dalian, 2863.57 ng/g and Shanghai, 2645.955 ng/g. For suburban areas, Guangzhou also exhibits the highest concentration at 1480.3 ng/g, with Beijing at 1185.5 ng/g.

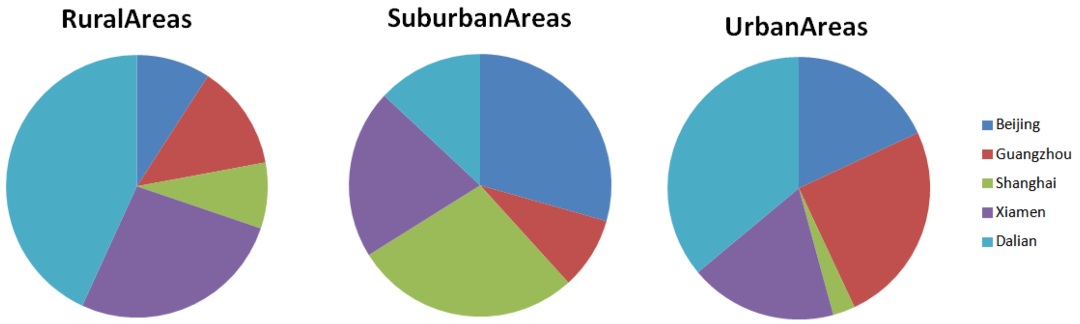


**Figure 4. 6** Concentration of $\sum_7$PBDE (ng/g) in urban, suburban and rural areas from Dalian, Beijing, Shanghai, Xiamen and Guangzhou, China

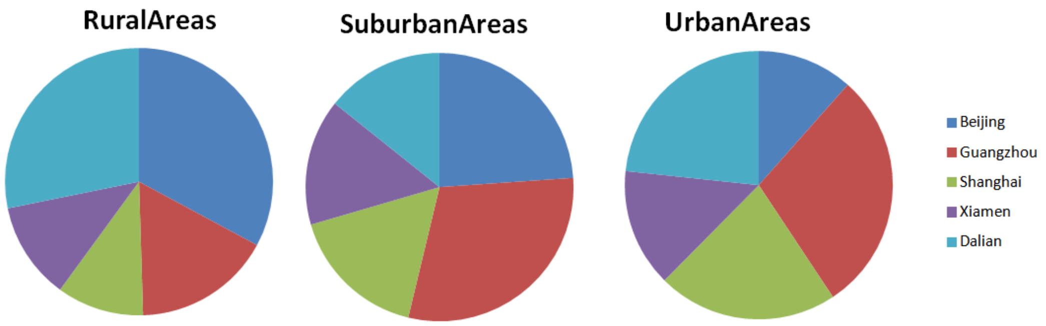


**Figure 4. 7** Concentration of BDE209 (ng/g) in urban, suburban and rural areas from Dalian, Beijing, Shanghai, Xiamen and Guangzhou

### 4.3.2.2 Congener profiles of PBDEs in indoor dust from rural, suburban and urban areas

Figure 4.8 shows the composition profiles of $\sum_7$PBDE congeners in indoor dust from rural, suburban and urban areas. BDE209 accounted for 92% in rural areas, 93% in suburban areas and 95% in urban areas. For $\sum_7$PBDE congeners, excluding BDE209, the composition was similar in these three regions. In rural areas, BDE183 was the dominant congener, contributing up to 35.79%, followed by BDE47 and BDE99 at 20% and 16%, respectively. Very similar results were found in suburban areas where BDE183 accounted for 31% of the$\sum_7$PBDE, followed by BDE47 at 21% and BDE99 at 13%. For urban areas, the contribution of BDE183 to $\sum_7$PBDE was lower than for the suburban and rural area at 24%, with BDE47 accounting for 19% of the total. BDE28 always the lowest contributing congener in these three areas.

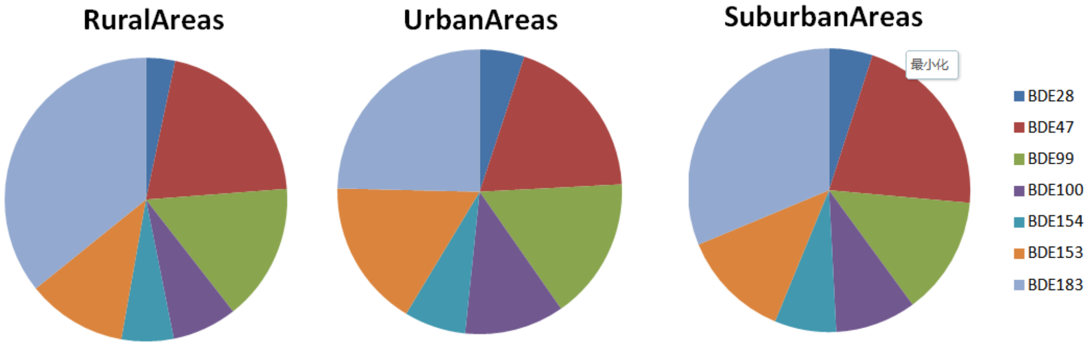


**Figure 4. 8** Composition profiles (%) of $\sum_7$PBDE in indoor dust from rural, suburban

and urban areas in China

## 4.4 Discussion

### 4.4.1 Concentrations of PBDEs in dust collected from China and worldwide comparisons.

In this study median concentrations of BDE 209 was 925, 833, 1415, 778 and 754 ng/g for Beijing, Shanghai, Dalian, Guangzhou and Xiamen, respectively. These data are in the same order of magnitude as those from Haikou, 1069 ng/g (Huang et al., 2010), Toronto, 560 ng/g, (Harrad et al., 2008c), Texas, 1300 ng/g (Harrad et al., 2008a), Singapore, 1000 ng/g (Tan et al., 2007), Korea, 1200 ng/g (Lee et al., 2013), Australia, 730 ng/g (Sjodin et al., 2008), although higher than Hokkaido, 360 ng/g (Takigami et al., 2009), Flanders, 313 ng/g (D'Hollander et al., 2010), Hangzhou, 228 ng/g (Sun et al., 2016b), Queensland, 291 ng/g (Toms et al., 2009), Germany, 63 ng/g (Sjodin et al., 2008). The concentration of total PBDEs including low PBDEs and BDE209 in this study were significantly much lower than samples collected from E-waste sites in Guangzhou, 4039 ng/g (Wang et al., 2010), Guiyu, 55,100 ng/g, Longtang, 11,000 ng/g, Dali, 6470 ng/g (Zheng et al., 2015), North Carolina, USA, 2574 ng/g (Stapleton et al., 2009b), Birmingham, UK, 8100 ng/g, (Harrad et al., 2008a).

However, the concentration of $\sum_7$PBDEs excluding BDE209 in China were much lower than those in Canada, USA, Korea and UK, (Harrad et al., 2006; Harrad et al., 2008a; Harrad et al., 2008b; Lee et al., 2013; Stapleton et al., 2009b), These results were expected as c-pentaBDE and c-octaBDE were used to a greater extent in North America and Europe compared to China, while c-decaBDE was widely used across the world, usage was especially high in China. Regulations have banned the use of c-pentaBDE and c-octaBDE in North America and Europe since 2004, although related compounds are still being detected in indoor dust because of on-going emissions from furniture and other common products used in the home.

### 4.4.2 Spatial characteristics and analysis of pollutant sources

In China, unbalanced economic development in Eastern and Western regions of China is a problem. Eleven provinces from Eastern regions account for 79.6% of total GDP, while only 20.4% from western regions (China Index Academy). Also 80% people live in Eastern cities. In order to prevent the big differences of human activity and consumption mode across west to east, five sampling cities were only selected from eastern region. Among the five sampled cities, Beijing is the capital; Shanghai is the largest international financial center in China; Dalian has become an important industrial centre after the last World War, and it is also the 6th largest port in China. Guangzhou, is the largest industrial city, particularly for electronics and contains one of the largest E-waste sites. Over the past 30 years, the Xiamen's economic special zone has developed rapidly, and real estate development has become the 4th most rapid in the country, after Beijing, Shanghai and Guangzhou (China Index Academy).

From data contained in Figure 4.3, the highest $\sum_{33}$PBDEs concentrations were found in Guangzhou, followed by Beijing, Shanghai, Dalian and Xiamen. One explanation of this trend may be the level of development in each city. A report written by Chinese government statistic group referred to industrial big data provided the consumption level per capita from these five cities in 2016, Guangzhou was the highest RMB 120,000, followed by Beijing RMB 50,703. The lowest consumption occurred in Xiamen and Dalian, RMB 30,866 and RMB 35,889, respectively (www.chyxx.com). A significant positive correlation was observed between $\sum_{33}$PBDEs (including BDE209) concentration and consumption level ($r=0.9$, $p<0.05$). Logically it appears that at higher levels of consumer product consumption, more products may contain PBDEs will be present in home, so that the higher PBDE concentrations would be observed in indoor dust. It also suggests that consumer products in indoor environments were the dominant source of PBDE contamination.

Another possible explanation could be due to climate differences. In this study, sampling work was conducted during December 2016 to January 2017. The average of winter temperature in Guangzhou was the highest, 22 ℃ (China Statistical Yearbook), followed by Beijing and Dalian, which were using heating system and kept the room temperature around 18 ℃ to 20 ℃. Previous studies have suggested lower emissions of PBDEs occurs at lower temperatures (Huang et al., 2010; Zhu et al., 2015). One modeling study suggested that temperature was the most influential parameter for emission rates since it directly affects vapor pressure and $K_{OA}$ (Zhang et al., 2009). Yu et al also reported that PBDEs in indoor dust were the highest in the summer, followed by winter, spring and autumn. It is not surprising the temperature in the summer in indoor environment is the highest, even the air conditioners were used in Guangzhou, where the average room temperature could normally be kept at 30℃ degree for private house and the air conditioner may not be used for 24 hours. The residents in Shanghai also open windows to ventilate their houses during spring and autumn, so the lowering down the total PBDEs concentrations in indoor dust. (Yu et al., 2012).

In the present study, based on the data from Chinese Year Big Data (www.bigdata.cn), Supporting information lists descriptive information for each city including population, area and gross industrial output value in 2016. A significant positive correlation (r=0.783, $p<0.01$) was found between PBDE concentration and population density, whilst a poor correlation (r=0.157, $p<0.05$) was observed between PBDE concentration and gross industrial output value. Compared to previous studies, significant correlations were observed between population density and PBDEs including low PBDEs (BDE28, 47, 99, 100, 153, 154, 183) and BDE209 concentrations ($r=0.403$, $p<0.01$) (Zhu et al., 2015). Few studies have been conducted into possible correlations between PBDEs in indoor dust and population density, although some studies have suggested a strong correlation between PBDEs and outdoor air. Yang et al (2013) published the result indicated a significant correlation ($r=0.69$, $p<0.05$) between population density with PBDEs level in outdoor air (Yang et al., 2013). Zhao et al (2013) and even suggested that population density could be used as a surrogate parameter for nonpoint sources to illustrate PBDE contamination because of a strong correlation ($r=0.52$, $p<0.01$) (Zhao et al., 2013). The evidences also supported that Guangzhou had the highest concentration contaminant level may be because of the highest population density compared to other four cities. Supporting information listed related data.

### 4.4.3 PBDE concentrations in dust from urban, suburban and rural areas

The present results indicates that the concentration of BDE209 and PBDE in dust collected from urban areas was the highest, followed by suburban areas and rural areas. There are two potential reasons that could explain the observed differences between urban, suburban and rural samples. First of all, houses in urban and suburban areas tend to have more furniture and electric appliances than rural areas related to the occupant’s higher disposable income. In this study, according to the questionnaire, the average number of electronic items in urban and suburban areas was higher than rural areas. A strong positive correlation was observed between concentration of PBDEs in these three regions and the number of household appliances ($r=0.73$, $p<0.05$). Also, the surface area and number pieces of foam containing furniture such sofas in urban and suburban areas were higher than rural areas. A positive correlation between number of items of foam containing furniture and PBDE concentration in dust from urban, suburban and rural areas was observed ($r=0.87$, $p<0.05$). Previous studies have also reported the same positive correlation between number of electrical items in room and PBDE concentrations in indoor dust (de Wit et al., 2012; Allen et al., 2008; Sun et al., 2016b). These unsurprising results indicate that consumer products used in room were likely to be important sources of brominated flame retardants to dust.

Another possible consideration could be the floor surface area ($m^2$) and level of human activity such as the frequency of furniture change and the ability of new consumer products purchase. In China, urban areas were found to be the most advanced and developed region, followed by suburban, finally rural areas (Ying et al., 2017). Therefore, houses built in urban areas were generally smaller than those built in suburban areas. Rural areas were generally developed last, and so the floor surface areas were larger than urban and suburban areas, although with simple decoration and fewer household appliances (www.chyxx.com). At the same time, suburban areas in China often contain electronic factories and industrial developments (China Statistical Data), so the concentration of contaminants also would be attributed to these factories emission.

### 4.4.4 Congener patterns of PBDEs in floor dust

The data from this study agree with a previous study from East China where BDE209 contributed to between 90% and 99% of the total concentration of PBDEs in dust (Zhu et al., 2015; Huang et al., 2010; Sun et al., 2016a; Zhu et al., 2013). Excluding BDE209, higher concentrations of the BDE183, BDE47 and BDE99 in samples could be explained by the fact that these congeners were the main composition of the c-pentaBDE and c-octaBDE, which were mainly added into furniture and electric appliances and electronics. As mentioned previously showed in Figure 5.1 that BDE28 accounted for 0.11%, BDE47 37%, BDE99 35%, BDE100 6.8%, BDE153 3.9% and BDE154 2.5% of the total with minor contributions from BDE17, BDE66 and BDE138. These congeners were present in c-pentaBDE, whilst BDE183 was the dominate congener of c-octaBDE (Krol et al., 2014). The profile in the samples may reflect different usages of PBDE mixtures and formulation in China that c-decaBDE occupied the mainly flame retardant market (including production and usage)in China, whilst there was no record showed ever c-pentaBDE and c-octaBDE produced in China which had been discussed in introduction section.

The data in Table 4.3 shows significant correlations were found among BDE47, 99, 100, 154 and 153, which suggests these congeners are emitted from common sources. These congeners represent major constituents of the c-pentaBDE product. Although there was no data that China has manufactured c-pentaBDE, it might be imported from Europe and America and were used in the products. However, BDE183 showed poor correlations with other congeners which suggests it come from different sources of commercial products. BDE183 is a component of the c-octaBDE product, which has evidence of being produced in China. BDE209 has weak correlations with BDE28, BDE183 and other congeners. This agrees with commercial production history in China as BDE209 is the component of commercial product c-decaBDE, which was massly produced and used in China. As shown in table 5.3, poor correlations ($r=0.2$, $p<0.05$)between HexaBDE or HeptaBDE (including BDE153, BDE154, BDE183) and BDE209 was observed, however, there were no statistically correlation between low PBDE congeners (such as BDE47, BDE99, BDE100) and BDE209 ($r=0.2$, $p>0.05$). This could be explained that BDE209 would debrominated to high PBDE congeners

(Hexa- and HeptaBDE). The same conclusion agreed with a previous study, which detected the stronger correlation ($r=0.5$, $p<0.01$) between BDE183 and BDE209 and it also suggested BDE209 may be a debromination product of BDE209 (Birgul et al., 2012),.

To investigate the spatial characteristics of the contaminant sources, principal component analysis (PCA) was adopted for the three commercial PBDE formulations and composition profile of PBDEs in dust from urban, suburban and rural areas shown in figure 5.9 and figure 5.10. The first two principal components PC1accounted for 52% and PC2 accounted for 15% of the total variance, respectively. Different congeners were categorized according to their loadings on both factors, and the factor score plot exhibited information of the three commercial PBDE mixtures and the 141 samples distribution for both factors in Figure4.10.

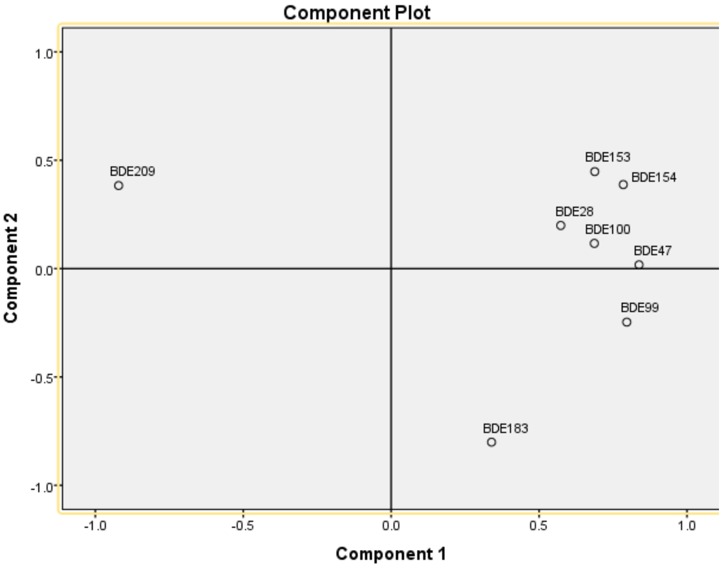


**Figure 4. 9** Factors loading of BDE28, 47, 99, 100, 153, 154, 183 and 209 on component 1(52%) and component 2 (15%)

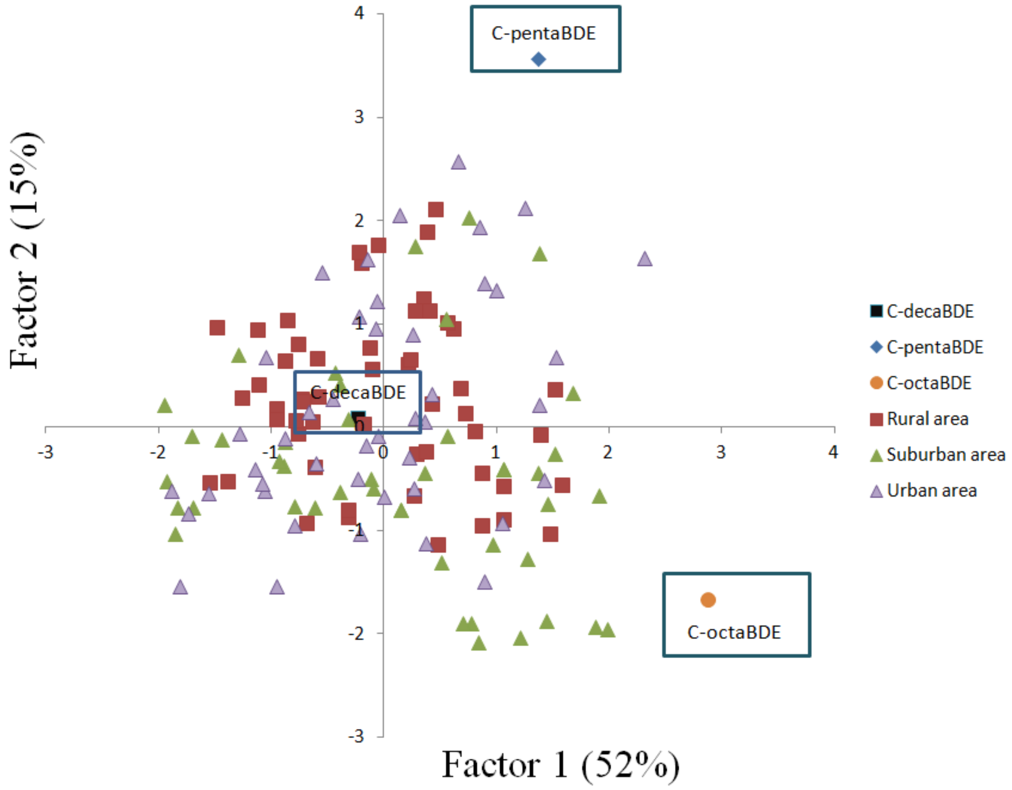


**Figure 4. 10** Factor score plot of three commercial PBDE mixture and 141 samples collected in 2016 from urban, suburban and rural regions in China

The first two principal components accounted for 52% and 15% of the total variance within the dataset. PBDE congeners were separated into three clusters in figure 4.9. Cluster 1 consisted of BDE28, BDE47, BDE99, BDE100, BDE153 and BDE154, which were the major components in c-pentaBDE and was used in China. Because of the physical and chemical properties which listed in Chapter1 were the similar, these congeners grouped together. Cluster 2 included BDE209, the major component in c-decaBDE, and cluster 3 included BDE183, the main component of c-octaBDE. Cluster 1 displayed higher value in factor 1 and lower absolute value in factor 2 relative to BDE183; BDE183 had highest absolute value in factor 2 and lower absolute value in factor1incomparision with cluster 1; while BDE209 had high absolute value in factor 2, and also the highest absolute value in factor 1. The well separated three clusters may be indicative of sources differentiation. The results indicated factor 1 was heavily influenced by c-decaBDE products, followed by c-pentaBDE, and reflected the sources of PBDE concentration in indoor dust were mostly from furniture, foam and general construction and decoration materials. Factor 2 was heavily influenced by c-octaBDE products, as well as c-decaBDE, which reflected the electronics and house appliances such as air conditioner and TV set were the secondly sources of PBDE contaminant in indoor dust.

Factor score plot (figure 4.10) showed the scores of 141 samples on PC1 and PC2. All of the samples were distributed around c-decaBDE, which strongly indicates that c-decaBDE may be the main commercial PBDEs product used in the Chinese market. This is true with the production and usage data in background review (Chapter 1). Compared with rural samples, urban and suburban samples were widely scattered and with a tendency towards c-pentaBDE and c-octaBDE commercial products positions, which showed some indication of c-octaBDE and c-pentaBDE influenced urban and suburban areas more than rural areas. The more spread data distribution in PC1 and PC2 plot in figure 4.10 may also indicate the diverse source of urban and suburban samples, which may be true that urban dwellers may not only tend to have more furniture electronic appliances, but also using diverse types of other products including foam, mattress and so on. All the samples from three regions distributed with more separations away from c-pentaBDE , which suggested the influence of c-pentaBDE was lower than c-octaBDE and c-decaBDE in China. A previous study has suggested c-decaBDE was used widely in China, and c-octaBDE also had both produced and used, but C-pentaBDE never produced and rarely used in China. The PCA charts also confirmed that BDE209 was the dominant congener in indoor dust in China, followed by BDE183 (35.79%), BDE47 and BDE99 at 20% and 16% separately.

### 4.4.5 Human exposure to PBDEs

Human exposure to PBDEs from the inhalation of the indoor air and particulates, along with dermal absorption from indoor dust were estimated from the hours of people spent per day and the measured concentrations of PBDEs. Previous studies calculated human exposure per day from indoor air and dust. The present study calculates human exposure using data from the questionnaires including how many hours people spent in each room, the age of group of family members etc.

Dust ingestion and dermal absorption are the two major pathways for human exposure to PBDEs via indoor dust. Previous studies and **Chapter 3** had addressed dust ingestion contributed to 69% to 82% of exposure for worldwide adults and children. (Gevao et al., 2006; Johnson-Restrepo and Kannan, 2009; Wilford et al., 2005,(Harrad et al., 2006).The daily intake of PBDEs exposure dose through dust ingestion ($DED_{di}$) and dermal absorption ($DED_{da}$) were calculated by the following equations, the same as in **Chapter3**, and supporting information listed parameters for five target cities:

$DED_{di}=C * DIR *IEF / BW$

$DED_{da} = C * BSA * DAS* AF * IEF / BW * 1000$

$DED_{T} = DED_{i} + DED_{da}$

Since the indoor dust samples were collected during the winter period, people in Dalian are exposed to the highest levels of PBDE, followed by Guangzhou and Xiamen, the lowest being in Beijing and Shanghai. This is because people in North China spend a longer amount of time in indoor environments during winter. For Beijing and Shanghai, since the speed of life and work is busy, people especially teenager and adults spend less time in home.

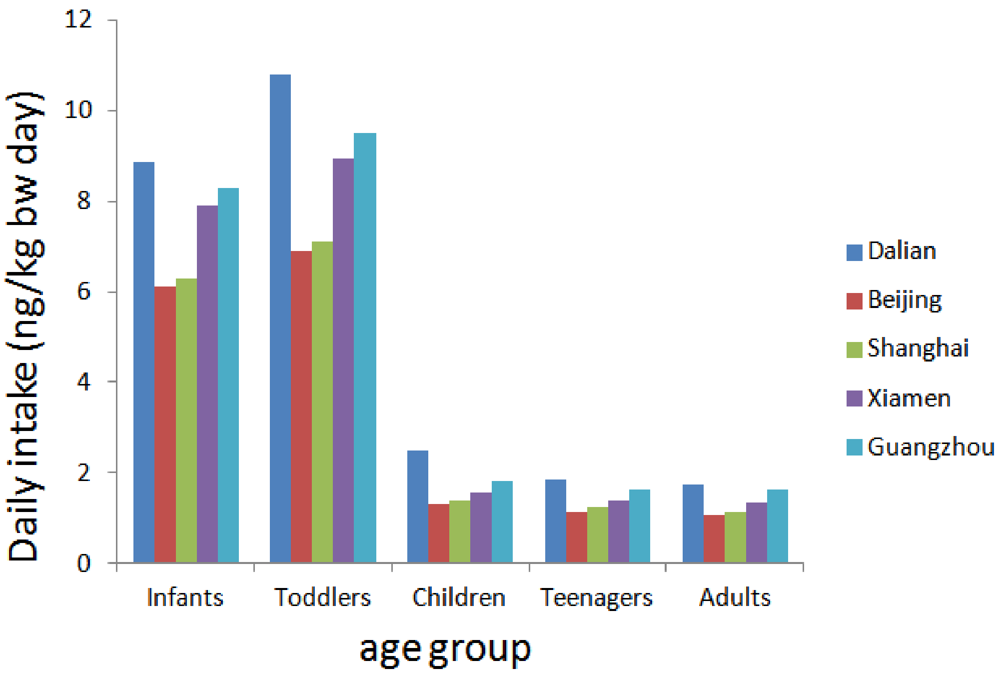


**Figure 4.11** The value of daily intake of PBDEs through dust exposure in different age of group in Beijing, Guangzhou, Dalian, Shanghai and Xiamen in China

### 4.5 Conclusion

This study focused on the presence of PBDEs in indoor dust across 5 cities in China from north to south and between urban, suburban and rural areas. The data demonstrated that BDE209 was the most abundant congener in China, accounting for over 90 % of PBDE in indoor dust samples. Different amounts of other major congeners present in the technical PentaBDE and OctaBDE were found between sampling sites and cities. An assessment of the data suggested that differentiation of both concentration and congener pattern across different districts of the city is possible. PBDE concentrations were generally lower in rural areas than in urban and suburban areas. Samples from areas that have experienced dynamic urban development with electronic goods production and use, such as science parks and new town areas, tended to show a dominance of BDE209. This suggested that there could be an effect of social economic development on PBDE concentrations in indoor dusts. It is likely that populations that live in different cities and different areas within a city may be exposed to different levels of flame retardants and also to different kinds of flame retardants.

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## Supporting information

Table S1 Comparison of PBDEs levels (median value, ng/g) in indoor dust in the world

| Sampling site | Congeners | Median of ∑PBDE without BDE209 | Median value of BDE209 | References |
|---|---|---|---|---|
| Beijing, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 29 | 975 | Present study |
| Shanghai, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 11 | 833 | Present study |
| Dalian, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 67 | 787 | Present study |
| Guangzhou, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 41 | 1059 | Present study |
| Xiamen, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 45 | 769 | Present study |
| Flanders, Belgium | BDE28, 47, 100, 99, 154, 153, 183, 197, 196, 203 and 209 | 27 | 313 | (D'Hollander et al., 2010) |
| Toronto, Canada | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 620 | 560 | (Harrad et al., 2008c) |
| Texas, USA | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 1600 | 1300 | (Harrad et al., 2008b) |
| Wellington, New Zealand | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 96 | NA | (Harrad et al., 2008b) |
| Singapore | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 98 | 1000 | (Tan et al., 2007) |
| Korea | BDE17,28,47,49,66,71,77,85,99,100,119,126,138,153,154,183,184,191,196,197,206,207 and 209 | 240 | 1200 | (Lee et al., 2013) |
| North Carolina, USA | BDE47, 99, 100, 153 and 209 | 2153 | 2574 | (Stapleton et al., 2009b) |
| Guangzhou, China | BDE11,12,13,15,17,25,28,32,33,47,66,85,99,100,119,138,153,154,183,196,197,202,203,206,207,208 and 209 | NA | 4039 | (Wang et al., 2010) |
| Haikou, China | BDE28, 47, 66, 100, 99, 85, 154, 153, 183 and 209 | 16 | 1069 | (Huang et al., 2010) |
| Guangzhou, China | BDE28, 47, 66, 100, 99, 85, 154, 153, 183 and 209 | 38 | 2637 | (Huang et al., 2010) |

| | | | | |
|---|---|---|---|---|
| Birmingham, UK | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 59 | 2800 | (Harrad et al., 2008b) |
| Heilongjiang, China | BDE17,28,49,47,66,100,99,85,154,153,138,183,190 and 209 | 25 | 1700 | (Zhu et al., 2013) |
| Guangzhou, China | BDE28, 47, 66, 85, 99, 100, 153, 154, 183 and 209 | 38 | 2690 | (Chen et al., 2011) |
| Washington DC, USA | BDE17, 33, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, 197, 196, 207, 206, 208 and 209 | 1680 | 1350 | (Stapleton et al., 2005) |
| Hokkaido, Japan | BDE28, 47, 66, 100, 99, 154, 153 and 209 | 9 | 390 | (Takigami et al., 2009) |
| Birmingham, UK | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 46 | 8100 | (Harrad et al., 2008a) |
| Longtang, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 11,000 | (Zheng et al., 2015) |
| Dali, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 6470 | (Zheng et al., 2015) |
| Guiyu, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 55,100 | (Zheng et al., 2015) |
| Hangzhou, China | BDE28, 47, 99, 100, 154, 153, 183 and 209 | 11 | 228 | (Sun et al., 2016b) |
| Queensland, Australia | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 291 | (Toms et al., 2009) |
| Germany | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 63 | (Sjodin et al., 2008) |
| Australia | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 730 | (Sjodin et al., 2008) |
| Newcastle, UK | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 10,000 | (Sjodin et al., 2008) |
| Atlanta, USA | BDE28, 47, 99, 100, 154, 153, 183 and 209 | NA | 2,000 | (Sjodin et al., 2008) |

Table S2 population, gross industrial output value and area for 5 cities, 17 districts.

| City | District | Population | Gross industrial output value | population density | area | ∑PBDE33 |
|---|---|---|---|---|---|---|
| **Beijing** | ChaoYang | 395 | 4587 | 0.838641189 | 471 | 1492.746 |
| | HaiDian | 359.3 | 5036.8 | 0.84342723 | 426 | 1329.900 |
| | DaXing | 169.4 | 510.2 | 0.164306499 | 1031 | 573.123 |
| | ChangPing | 201 | 708.6 | 0.148668639 | 1352 | 766.297 |
| **Shanghai** | Pudong New | 504.443 | 7898.35 | 0.416895041 | 1210 | 1369.427 |
| | Jing'an | 109.71 | 1480 | 2.965135135 | 37 | 2660.891 |
| | Xuhui | 108.51 | 1300 | 1.972909091 | 55 | 572.923 |
| | Minghang | 242.93 | 1964.71 | 0.654797844 | 371 | 234.167 |
| **Dalian** | Ganjingzi | 132.18 | 1051 | 0.263306773 | 502 | 829.500 |
| | Shahekou | 69.31 | 450 | 1.434395695 | 48.32 | 3051.939 |
| | Jinzhou | 68.2 | 523 | 0.050423647 | 1352.54 | 680.819 |
| **Guangzhou** | Yuexiu | 115.68 | 2694.88 | 3.505454545 | 33 | 4016.340 |
| | Tianhe | 154.57 | 3432.79 | 1.610104167 | 96 | 1535.525 |
| | Panyu | 154.41 | 1608.78 | 0.291339623 | 530 | 365.823 |
| **Xiamen** | Siming | 99.1 | 1056.36 | 1.179761905 | 84 | 1823.603 |
| | Huli | 97.1 | 699.78 | 1.316253219 | 73.77 | 815.072 |
| | Jimei | 60.4 | 422.7 | 0.219636364 | 275 | 341.566 |

# Chapter 5 Potential association of polybrominated diphenyl ethers (PBDEs) concentrations in serum with thyroid function in thyroid abnormal patients--a pilot study

## 5.1 Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of flame retardant chemicals which have been widely used in consumer products such as home electronics (televisions, computers), textiles (carpeting, drapery) and furniture to ensure they meet fire safety standards (Alaee et al., 2003). There have been three commercial formulations of PBDEs, which are mixture of congeners and named as c-pentaBDE, c-octaBDE and c-decaBDE in this study (de Boer et al., 2003).

Although PBDEs have been widely used around the world, they are lipophilic, persistent in the environment and bio-accumulative in wildlife and have been reported in human serum, breast milk, hair, and human tissues (de Boer et al., 2003; Guan et al., 2009; Hirai et al., 2012; Kang et al., 2011; Bansal et al., 2014; Leonetti et al., 2016). Over recent years the majority of studies on human exposure to PBDEs originated from North America and Europe (Harrad and Porter, 2007; Zuurbier et al., 2006; Allen et al., 2016; Butt et al., 2016; Harley et al., 2010; Zota et al., 2013; Aschebrook-Kilfoy et al., 2015; Guo et al., 2016) . There have been several studies on PBDEs in human serum in China which have mostly focused on key cities such as Shanghai, Zhejiang, Dalian (Chen et al., 2014b; Wang et al., 2016; Wang et al., 2012; Liang et al., 2016; Qu et al., 2007). Previous studies using experimental animals have concluded that PBDEs could have a wide range of adverse health effects including interfering metabolic processes, sexual dimorphism and interference with the function of thyroid hormones (Lilienthal et al., 2006; Darnerud et al., 2005; Kuriyama et al., 2007; He et al., 2011; Macaulay et al., 2015). The associations between PBDEs and thyroid function have also been widely reported in animals and these findings raise more concerns about the influence of PBDE exposure in humans.

The thyroid regulates basic metabolism and growth, especially for healthy brain development in young children. Five parameters are used to examine the level of thyroid function: triiodothyronine (T3), free triiodothyronine (FT3), free thyroxine (FT4), thyroid-stimulating hormone (TSH) and thyroxine (T4). For example, thyroid-stimulating hormone (TSH) and thyroxine (T4) would influence language ability, memory and executive processing skills (Jacobson et al., 2016). Due to the structural similarities between PBDEs and the two major thyroid hormones T4 and triiodothyronine T3, some concerns have been expressed that PBDEs could potentially interfere with thyroid function (Ibhazehiebo et al., 2011). TSH is produced by the pituitary gland in response to low T4 levels, which stimulate the thyroid to secrete more T4. A previous study by (Zota et al., 2013) demonstrated that PBDEs may disrupt this system and that TSH can be down regulated when T4 levels are high. In addition to interfering with thyroid hormone transport, it was suggested they may bind to transthyretin, which can lead to decreased FT4 concentrations in serum (Makey et al., 2016). However, epidemiological evidence is presently unclear with studies showing positive, negative and no associations between PBDE exposure and thyroid function (Makey et al., 2016; Abdelouahab et al., 2013; Bloom et al., 2008; Stapleton et al., 2011; Zota et al., 2011; Chevrier et al., 2011)

Previous studies have demonstrated that PBDEs induce decreased T4 levels and its metabolically active unbound free form T4, combined with increased TSH levels in rats, mice or rodents (Hallgren et al., 2001; Zhou et al., 2001; Darnerud et al., 2005; Stoker et al., 2004). In humans, some studies also have shown that PBDE exposure in humans was associated with changes to thyroid hormone concentration in adults, pregnant women and young children (Jacobson et al., 2016; Abdelouahab et al., 2013; Turyk et al., 2008; Makey et al., 2016; Huang et al., 2014; Zhang et al., 2010). Makey et al. (2016) concluded that a significant decrease in T4 levels occurred alongside increasing levels of BDE47 exposure (Makey et al., 2016). Stapleton et al. (2011) (Stapleton et al., 2011) reported a positive association between PBDE exposure and T4 and FT4 levels in women after 34 weeks of gestation. However, limited studies on the association between PBDEs and thyroid function have been carried out in China. Only two studies have been reported by Liu et al. and Zheng et al. (Zheng et al., 2017; Liu et al., 2017). Liu et al. (2017) investigated the association of PBDEs in serum with thyroid function in thyroid cancer patients (Liu et al., 2017), and suggested that OH-PBDEs and PBDEs would result in reduced levels of FT4, with elevated TSH concentrations. Zheng et al. (2017) (Zheng et al., 2017) collected serum samples from e-waste workers to observe any associations with PBDE concentrations and thyroid function. They concluded that T3 and T4 significantly and positively correlated with low PBDE concentrations including BDE47, BDE66 and BDE85.

The aim of this study was to examine possible associations between PBDE exposure and patients with abnormal thyroid hormone levels whose thyroid function parameters were over normal ranges. The data could then be explored to investigate the profile of PBDE congeners in patients serum, and to discuss any correlations between PBDEs congeners and five thyroid hormone parameters including T4 (thyroxine), T3 (triiodothyronine), FT4 (free thyroxine), FT3 (free triiodothyronine) and TSH (thyroid-stimulating hormone).

Kunming was selected as the study city, which is the capital city of Yunnan province located in the southwest of China. The province borders Guangxi, Guizhou, Sichun provinces and the countries Vietnam, Laos and Burma. Yunnan is one of the major production bases for copper, lead, zinc tin and aluminum in China. The main reason was there was long-term cable production history in Kunming. Kunming Cable Group Co., Ltd., built in 1936, is the first wire and cable manufacturer in China, and also is the birthplace of China's first wire (Kunming Cable Group Co., Ltd. website). Hence, there also are commercial PBDE products manufacturing in Kunming to add in cable.

## 5.2 Materials and methods

### 5.2.1 Sampling

In this study, 40 serum samples were collected from abnormal thyroid hormone patients at the Disease Control Centre in Kunming (see map in Chapter 2 -figure number?)for location)**.** For a range of thyroid hormone parameters there are normal ranges for healthy people defined by the hospital. Any one of parameters outside of these normal ranges the patient would have been assessed as having abnormal thyroid function. For example, if FT3 and FT4 increased, clinical symptoms would manifest as hyperthyroidism, conversely FT3 and FT4 are decreased when hypothyroidism is diagnosed. Increased TSH levels can be seen in patients with primary hypothyroidism; T3 and T4 are the specific diagnostic indicators of chronic lymphatic thyroiditis. All of volunteers included in this study had these five thyroid hormone parameters measured in hospital and had two or three factors outside normal ranges. Thyroid hormone levels were measured by Chemiluminescence Enzyme Immunoassay in the Kunming Municipal Hospital of Traditional Chinese Medicine. Five thyroid parameters including T3, T4, FT3, FT4 and TSH were recorded. The normal range of T3 is 1.34 - 2.73 nmol/L, T4 is 78.4 - 157.4 nmol/L, FT3 is 2.77 - 6.31 pmol/L, FT4 is 10.44 - 24.38 pmol/L and TSH is 0.34 - 5.6 mIU/L separately. 40 human serum samples were collected, 28 from female patients with an age range between 16 and 83, and 12 samples from male with the age range of 19 to 82. The samples had reported ranges for T3, T4, FT3, FT4 and TSH of 1.3 - 16.99 nmol/L, 78 -353.4 nmol/L, 0.691 - 37.72 pmol/L, 10.812 - 74.266 pmol/L and 0.005 - 15.641 mIU/L, respectively. The distribution of characteristics are shown in Table 6.1. Supporting materials included some basic information about the volunteers and clinical diagnosis.

All blood samples were collected from the 28 females and 12 males at the Disease Control and Prevention Centre of Kunming in July 2016. All participants in this study were informed as volunteers and gave written consent. These samples were collected on the same date, at the same clinical room and the same preservation method. Fasting bloods were required. 5 ml of blood from a cubical vein were collected into a sterile serum tube without anticoagulants, the serum was separated by centrifugation at 4000 rpm for 5 min using a high-speed centrifuge (Thermo Fisher Scientific, Waltham, MA) and then transferred to a new tube. All the serum samples were kept at -20° C until further analyzed. A questionnaire for each volunteer was completed including gender, age, family history of thyroid, other diseases, height and weight. The detail information was listed in supporting information.

### 5.2.2 Standards

A standard mixture of 39 PBDEs (including BDE-7, -11, -8, -12, -15, -32, -30, -17, -25, -33, -28, -35, -37, -75, -49, -47, -66, -100, -119, -99, -116, -118, -155, -85, -126, -154, -153, -138, -166, -183, -181, -190) and BDE-209 were produced by AccuStandard, Inc. (New Haven, CT, USA). The $^{13}$C labeled PCB 208, $^{13}$C-PCB 141 and $^{13}$C-BDE77 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) as recovery standard and internal standard respectively.

Acetone, dichloromethane (DCM) and n-hexane were obtained from Fisher Chemical (MA, USA). Anhydrous sodium sulfate was baked at 660° C for 6h which from Puhui Chemical Co., Ltd., Hangzhou, China). Silica gel and alumina were activated at 550° C for 6h and 660° C for 6h respectively.

### 5.2.3 Sample extraction

$^{13}$C-BDE77 and $^{13}$C-PCB141 were added to the 1ml serum sample in a 15ml centrifuge tube which was cleaned using acetone and hexane. Samples were placed in an ultrasonic bath for 10 minutes and allowed to equilibrate overnight. After equilibrium, 2ml of formic acid and acetonitrile (2:1, v/v), as well as 5ml ultra-pure water, were placed in an ultrasonic bath for 10 minutes to achieve denaturation and dilution. The samples were extracted using an Oasis HLB cartridge. Before extraction, the cartridge was cleaned with 3ml DCM and conditioned with 3ml MeOH and 3ml ultra-pure water. The samples were eluted with 4ml of isopropanol and water (1:19, v/v). 200ul of sulfuric acid was added to remove lipids and other contaminant, and then diluted with ultra-pure water until the pH value of solution was neutral. This was further cleaned using 2ml of MeOH and water (9:1, v/v), after which the cartridge was dried. The cartridge was then eluted with 4ml DCM, to collect the target compounds. After $N_2$ reduction, the extract was transferred to 100 μl hexane. An internal standard $^{13}$C-PCB208 was added and quantification was carried out using GC-MS. All of the samples were prepared and analyzed in Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China.

### 5.2.4 Analysis

The samples were analyzed using an Agilent 7890A gas chromatograph with negative chemical ionization in the selected ion monitoring (SIM) mode. BDE-209 was quantified by using m/z 486.6 and 488.6, while $^{13}$C-PCB-141was monitored through m/z 371.9 and 373.9, $^{13}$C-PCB-208 was monitored through m/z 473.8 and 475.8, and $^{13}$C-BDE-77 was monitored through m/z 471.8 and 473.8. The other congeners were quantified by the bromide ions, m/z 79 and 81. Helium (purity > 99.999%) was used as the carrier gas at flow rate of 1 ml/min and methane (purity > 99.99%) was used as a chemical ionization moderating gas. Gas chromatographic was performed on a DB-XLB 15m * 250 um * 0.1 m with the following oven program: from 110° C held for 0.5 min to 200° C at 60° C/min, then to 280° C at 5° C/min (held for 0.5 min) and to 310° C at 60° C/min (held for 8 min). The total operation time was 28 min.

### 5.2.5 Quality assurance/Quality control

PBDE measurements below the MDL were assigned a value of MDL/2. Statistical analysis were implemented when the detection frequencies of compounds were over 50%. Quality control was performed by regular analysis of procedural blanks, by random injection of standards and solvent blanks. The average recoveries of target compounds were above 90% with relative standard deviation from 0.56% to 8.57%. No PBDEs were detected in the procedure and instrument blanks. The limit of detection (LOD) was defined as three times signal to noise, and the limit of quantification (LOQ) was defined as ten times signal to noise. The limits of detection (LODs) of the low PBDE congeners ranged from 0.002 to 0.016ng/ml.

### 5.2.6 Statistical analyses

The normality test (Shapiro-Willk test) and Student t-test were utilized. If the data showed logarithmic normal distribution, the data were log transformed before analysis. Correlation between parameters and total PBDEs were evaluated by the Spearman's test. Multiple linear regressions were conducted to explore the associations between PBDE concentrations and thyroid hormone levels after adjusting for socio-demographic characteristics known as age, sex, BMI, lipids, etc. Statistical analyses were carried out using the SPSS version 23 software (IBM Co, Armonk, NY, USA). The levels of significance were $p<0.05$.

## 5.3 Result

### 5.3.1 Sociodemographic characteristics of the participants

Table 5.1 presents the sociodemographic characteristics of the 40 participants. The study population consisted of 28 females and 12 males classified by four age groups. 42% of the participants had lower BMI, $< 24$ kg/m$^2$. For each participant, 5 thyroid hormone parameters were measured, then classified into two groups separately, in the normal range or over it.

**Table 5. 1** Sociodemographic characteristics (gender, BMI, age, thyroid hormones parameters) of 40 volunteer participants collected from Kunming in 2016

| Characteristics | Number (%) |
|---|---|
| Sex | |
| Female | 28 (70%) |
| Male | 12 (30%) |
| Age (years) | |
| <20 | 4 (10%) |
| 20 - 39 | 16 (40%) |
| 40 - 59 | 9 (23%) |
| 60 - 85 | 11 (27%) |
| BMI (kg/m$^2$) | |
| Normal weight (<24) | 17 (42%) |
| Overweight or obesity (≧24) | 23 (58%) |
| Thyroid hormones parameters | |
| T3<br>Normal range (NR): 1.34 - 2.73 nmol/L | In the NR: 21 (52%) |
| | Not in the NR: 19 (48%) |
| T4<br>Normal range: 78.4 - 157.4 nmol/L | In the NR: 12 (30%) |
| | Not in the NR: 28 (70%) |
| FT3<br>Normal range: 2.77 - 6.31 pmol/L | In the NR: 20 (50%) |
| | Not in the NR: 20 (50%) |
| FT4<br>Normal range: 10.44 - 24.38 pmol/L | In the NR: 24 (60%) |
| | Not in the NR: 16 (40%) |
| TSH<br>Normal range: 0.34 - 5.6 mIU/L | In the NR: 22 (55%) |
| | Not in the NR: 18 (45%) |

### 5.3.2 Total PBDE concentrations in human serum

The concentration of PBDEs were expressed on the wet weight basis (ng/ml serum) and adjusted to a lipid weight basis (ng/g lipid). Following analysis would use lipid weight basis. Total cholesterol (CHOL) and triglycerides (TG) were determined enzymatically in a separate aliquot of serum in the same hospital along with the thyroid hormone parameters. Total lipids (TL) were calculated by the following formula: TL (g/l) = 2.27 * CHOL + TG + 62.3 (Jacobson et al., 2016).

In this study 33 PBDE congeners were detected, but only those with detection frequencies over 50% will be discussed. BDE28, BDE47, BDE99, BDE100, BDE153, BDE154 and BDE183 were detected in approximately 79%, 100%, 98%, 83%, 65%, 89%, and 82% respectively. Table 6.2 and Figure 6.1 contain both serum and lipid-adjusted values, detection frequencies, ranges, median values and geometric mean (GM). $\sum_7$PBDE (including BDE28, BDE47, BDE99, BDE100, BDE153, BDE154 and BDE183) concentrations ranged from 2.23 ng/g lipid to 18.71 ng/g lipid, and the median value was 7.50 ng/g lipid. BDE47 was found at the highest median concentration in serum with 3.63 ng/g lipid and range from 0.56 ng/g lipid to 11.01 ng/g lipid, followed by BDE99 at the second highest median value 1.20 ng/g lipid, BDE183 with 0.87 ng/g lipid and BDE153 with 0.55 ng/g lipid. For the profile of congeners measured in human serum, Figure 6.2 showed the percentage contribution of each PBDE congener in serum samples in 40 samples. BDE47 was the predominant serum congener and accounted for 43.04%, followed by BDE99 and BDE183 with 16.61% and 15.75% separately.

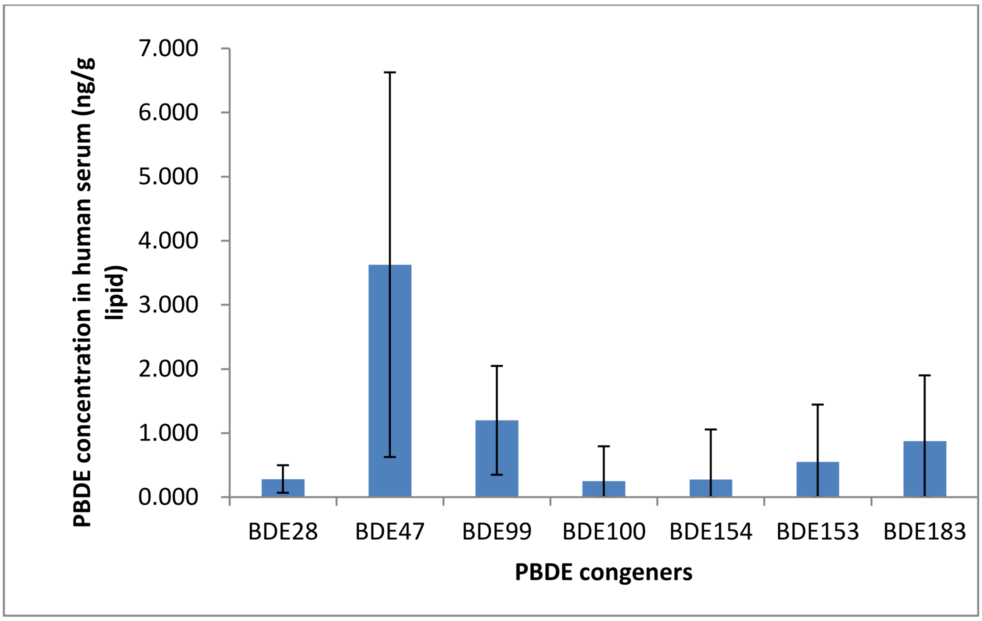

**Figure 5. 1** Concentration of $\sum_7$PBDE (BDE28, 47, 99, 100, 154, 153 and 183) measured in 40 volunteer serum samples (ng/g lipid) from Disease Control Centre in Kunming in 2016. Error bars were calculated from the standard deviation of 40 serum samples

**Table 5. 2** Total PBDEs concentration in human serum (ng/ml serum and ng/g lipid), age, BMI and thyroid function in participants (N=40)

| | minimum | maximum | median | GM[a] | R(%)[b] |
|---|---|---|---|---|---|
| Age (years) | 1 | 83 | 40 | 40 | |
| BMI (kg/m$^2$) | 16.65 | 30.86 | 23.77 | 23.02 | |
| Lipid (g/L) | 5.50 | 12.50 | 9.05 | 8.62 | |
| $\sum_7$PBDE concentration (ng/ml serum) | | | | | |
| BDE28 | nd[c] | 0.01 | nd | nd | 79 |
| BDE47 | 0.01 | 0.11 | 0.03 | 0.02 | 100 |
| BDE99 | nd | 0.03 | nd | 0.01 | 98 |
| BDE100 | nd | 0.03 | nd | nd | 83 |
| BDE154 | nd | 0.05 | nd | nd | 65 |
| BDE153 | nd | 0.04 | nd | 0.01 | 89 |
| BDE183 | nd | 0.04 | 0.01 | 0.01 | 82 |
| $\sum_7$PBDE | 0.02 | 0.17 | 0.06 | 0.06 | 100 |
| Thyroid function | | | | | |
| TSH (mIU/L) | 0.01 | 15.64 | 0.89 | 0.31 | |
| T4 (ug/dl) | 6.06 | 27.46 | 14.45 | 13.56 | |
| FT4 (pg/ml) | 8.32 | 57.13 | 16.12 | 19.54 | |
| T3 (ng/ml) | 0.84 | 11.03 | 1.65 | 1.95 | |
| FT3 (pg/ml) | 0.45 | 24.45 | 3.82 | 4.65 | |
| $\sum_7$PBDE concentration lipid-adjusted (ng/g lipid) | | | | | |
| BDE28 | nd | 0.86 | 0.28 | 0.23 | 79 |
| BDE47 | 0.562 | 11.01 | 3.63 | 2.77 | 100 |
| BDE99 | nd | 4.18 | 1.20 | 1.00 | 98 |
| BDE100 | nd | 3.14 | 0.25 | 0.27 | 83 |
| BDE154 | nd | 5.00 | 0.28 | 0.28 | 65 |
| BDE153 | nd | 4.72 | 0.55 | 0.58 | 89 |
| BDE183 | nd | 4.27 | 0.87 | 0.90 | 82 |
| $\sum_7$PBDE | 2.232 | 18.71 | 7.5 | 7.27 | 100 |

[a] GM: geometric mean

[b] R: detection frequency

[c] nd: not detected

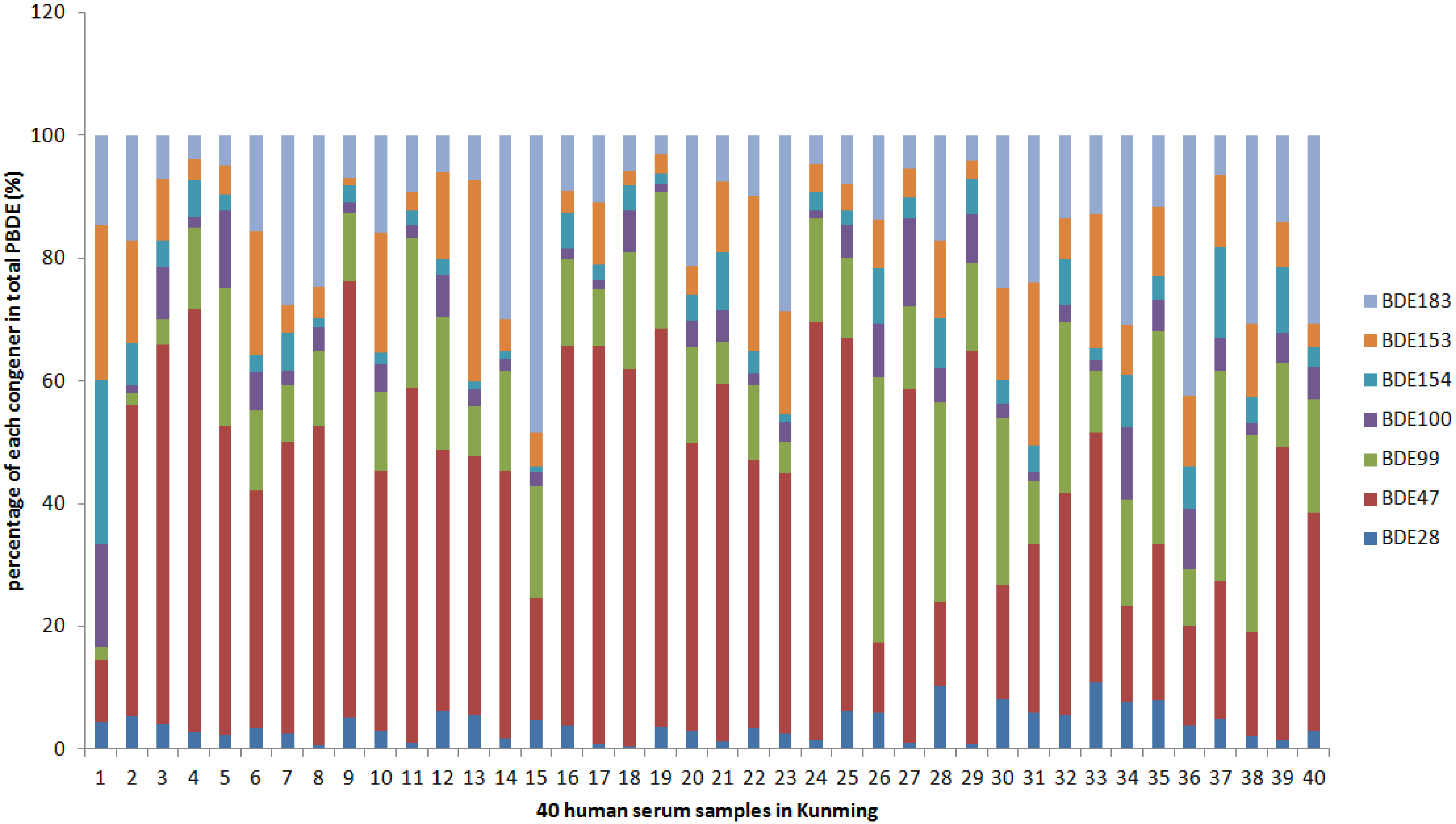

**Figure 5. 2** Percentage of each PBDE congener (BDE28, 47, 99, 100, 154, 153 and 183) in 40 serum samples in 2016 from Kunming (%)

### 5.3.3 Spearman's correlation between total PBDE concentration and thyroid function parameters

Correlations between basic characteristics, five thyroid function factors and concentrations of $\sum_7$PBDE were evaluated using the Spearman's test. Table 6.3 shows correlations between PBDE concentration, age, BMI, lipid and thyroid hormone parameters (T3, T4, FT3, FT4 and TSH) in 40 human serum samples. In this study, lipid contents had positive correlations with each PBDE congener and $\sum_7$PBDE at $p<0.05$ level, but not for the thyroid function parameters. BDE28, BDE47, BDE99 and BDE100 and $\sum_7$PBDE were significant and positive correlated ($r=0.2$-$0.8$, $p<0.01$), whereas slightly weaker correlations were found with BDE154 and BDE153 ($r=0.3$, $p<0.05$). However, BDE154 and BDE153 had positive correlations with each other ($r=0.44$, $p<0.01$). For the five thyroid function parameters, there were strong positive correlations among TSH, T4, T3, FT3 and FT4 ($r=0.4$-$0.8$, $p<0.01$), which could be explained by T3 being the more metabolically active hormone produced from T4. T4 is deiodinated by three deiodinase enzymes to produce the more active T3 (Mehmetcik et al., 2012). Nevertheless, no correlations were observed between concentrations of total PBDEs to ages and BMI ($p>0.05$).

## 5.4 Discussion

### 5.4.1 Status of BDE209 in human serum

In this study, BDE209 was found to be lower than the LOD (0.1 ng/ml) in all of the human serum samples. This is probably due to its short half- life of 15 days in humans (Stapleton et al., 2009a), higher detection limits (Johnson et al., 2010) and being less accumulative in biota because of its large molecular size and high octanol-water partition coefficient (Boon et al., 2002; Mazdai et al., 2003). U.S. Environmental Protection Agency suggested that BDE209 had a rapid half-life of under 10 days in human serum (EPA/600/R-08/086F). The estimated half-life of BDE47 was on average 3 years, with a range of 1.9 to 4.2 years, and BDE99 also had long half-life on 5 years, with the range of 3.5 to 7.2 years (EPA/600/R-08/086F). However, BDE209 only had an approximate half-life of 15 days with a range of 11 to 18 days in human blood (Thuresson et al., 2006; Jin et al., 2009). Thuresson et al. (2006) suggested that the apparent half-lives of decaBDE to pentaBDE in serum increased with decreasing number of bromine substituent

The results from this study were similar to those reported from other countries, as well as previous studies in China (Johnson et al., 2010; Makey et al., 2016; Wang et al., 2016; Jacobson et al., 2016; Liu et al., 2017). In these studies, BDE209 was either not detected, or even if BDE209 was measured the levels were low (around 5 ng/g lipid). Also, these previous studies suggested that debromination and metabolism of highly brominated congeners to lower brominated congeners was occurring, resulting in increased concentrations of BDE47, BDE28 and BDE99.

Previous studies have also showed that BDE209 was the most dominant congener for human serum, but all of them were conducted at production sites or e-waste processing areas (Johnson et al., 2010; Cao et al., 2017; Wang et al., 2012; Zheng et al., 2017; Deng et al., 2007). An explanation for this was provided by Zheng. et al (2017) (Zheng et al., 2017) related the high concentrations of BDE209 detected in worker's serum were a result of widespread application of commercial decaBDE mixtures in obsolete electronics in e-waste areas. Other studies conducted in China at e-waste processing sites in Guiyu, China (Deng et al., 2007) and electrical appliance factories site in Wenzhou, China (Wang et al., 2012) also suggested that the BDE209 were measured in worker's serum due to the high concentration of BDE209 in air, lake or food samples, and continuously exposed high level of BDE209 to blood level at rapid turnover rate.

Some human epidemiological studies have focused on the associations between the presence of higher brominated PBDEs and thyroid function (Shy et al., 2012; Liu et al., 2017; Zota et al., 2011; Jacobson et al., 2016). DecaBDE, which contains ten bromine atoms, is thought to have limited affinity to bind non-covalently with thyroid hormone transport proteins compared to triBDE and pentaBDE congeners, which are more structurally similar to T3 and T4. In addition, Liu et al. (2017) also suggested that the larger molecular mass and shape of decaBDE had difficulty interacting directly with the thyroid hormone receptor (Liu et al., 2017).

### 5.4.2 Concentration and congener profile of total PBDE in human serum from China and worldwide comparisons

The mean concentration of $\sum_7$PBDE across all samples in this present study was 7.5 ng/g lipid. This result was similar to those reported in blood samples in other cities in China such as in Dalian, 5.56 ng/g lipid (Wang et al., 2016), from thyroid papillary cancer patients in Dalian, 4.46 ng/g lipid (Liu et al., 2017), in HongKong, 5.36 ng/g lipid (Wang et al., 2013), but much lower than the worker serum samples from electrical appliance factories in Liushi and Wenzhou, 1.69 ng/ml serum (0.061ng/g serum in present study) (Wang et al., 2012), serum samples from Laizhou Bay, which is the one of main brominated flame retardants (BFRs) production areas in China, 613 ng/g lipid (Jin et al., 2009), the e-waste recycling workers from south China, 724 ng/g lipid (Zheng et al., 2017). Compared to other countries, the concentrations in human serum samples in the present study is lower than serum samples from the USA which ranged from 22 ng/g lipid to 40 ng/g lipid (Makey et al., 2016; Johnson et al., 2010;

Anderson et al., 2008), but similar to the UK and European samples, which ranged from 2.4 ng/g lipid to 5.6 ng/g lipid (Bramwell et al., 2017; Thomas et al., 2006; Bramwell et al., 2014; Darnerud et al., 2015). However, the samples in the present study were from abnormal thyroid hormone function patients including two groups hyperthyroidism and hypothyroidism, whilst those samples from other countries where from thyroid cancer patients or special E-waste workers.

In this study, BDE47 comprised about 50% of the total concentration in serum, followed by BDE99 and BDE153 with 16.61% and 15.75% separately. This result is similar to other countries including the USA and European countries, as well as other studies in China (Johnson et al., 2010; Wang et al., 2012; Wang et al., 2016; Darnerud et al., 2015; Bramwell et al., 2016). The situation for BDE209 with low detection rates or low concentrations was observed in several previous studies from different countries. It suggests that PBDE composition profiles in human serum are similar worldwide, because low PBDEs (such as pentaBDE and HexaBDE) have long half-life in humans (Wang et al., 2016; Jacobson et al., 2016; Bramwell et al., 2014).

### 5.4.3 Associations between PBDEs, thyroid hormones and human characteristics

In this study, no significant correlations were observed between concentration of PBDE with age, gender (Table S2) and BMI, which is consistent with some previous studies (Wang et al., 2016; Wang et al., 2012; Frederiksen et al., 2009; Toms et al., 2009), although several studies reported different findings (Jin et al., 2009; Harrad and Porter, 2007). Jin et al. (2009) reported that female groups had higher PBDE concentrations compared to males in Shandong, China, although they did not provide an explanation for this finding. Although Harrad and Porter et al.(2007) (Harrad and Porter, 2007) reported PBDE concentrations in male serum were higher than in females in Wellington, New Zealand, a t-test revealed the difference to be statistically insignificant ($p>0.1$). Jacobson et al. (2016) (Jacobson et al., 2016) found that PBDE concentrations in serum from children were higher than those from adults which could be explained by the transformation processes in adults being more efficient than in children.

Based on Spearman's correlations provided in Table 5.3 (** presents Correlation is significant at the 0.01 level. * presents Correlation is significant at the 0.05 level), no significant correlations were observed between PBDE congeners and thyroid hormones. To examine significant associations, multiple linear regressions were needed after adjusting for sociodemographic characteristics. Since T4, TSH, FT4, FT3, T3 and PBDE congener concentrations were not normally distributed, the data was log-transformed prior to regression analysis. Figures showing untransformed and log transformed data for the hormone factors and PBDE congeners have been included in the appendix.

Table 5.4 contains the associations between the major PBDE congeners and the five thyroid function parameters examined by multiple linear regressions after log-transformation. The regression results suggest that BDE153 had significant positive correlation with T4 and a negative correlation with T3 at the $p<0.05$ level, whilst BDE47 had a negative correlation with FT4 ($p<0.05$). However, other PBDE congeners had weak and non-statistical correlations with thyroid function parameters ($p>0.05$). The β-coefficients (beta coefficients) could be used and estimated to compare the trend of thyroid function indexes. A log-unit increase in $\sum_7$PBDE was associated with an increase of FT4 and T4 and a decrease of TSH, T3 and FT3.

**Table 5. 3** Spearman's correlations between PBDE and thyroid parameters (T3, T4, FT3, FT4 and TSH) in 40 serum samples

| | age | TSH (mIU/L) | T4 (ug/dl) | FT4 (pg/ml) | T3 (ng/ml) | FT3 (pg/ml) | Lipid | BDE28 | BDE47 | BDE99 | BDE100 | BDE154 | BDE153 | BDE183 | $\sum_7$ **PBDE** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| age | 1.000 | | | | | | | | | | | | | | |
| TSH (mIU/L) | .050 | 1.000 | | | | | | | | | | | | | |
| T4 (ug/dl) | -.260 | -.474** | 1.000 | | | | | | | | | | | | |
| FT4 (pg/ml) | -.213 | -.692** | .634** | 1.000 | | | | | | | | | | | |
| T3 (ng/ml) | -.153 | -.467** | .790** | .577** | 1.000 | | | | | | | | | | |
| FT3 (pg/ml) | -.259 | -.630** | .714** | .890** | .746** | 1.000 | | | | | | | | | |
| Lipid | -.019 | -.045 | -.292 | .054 | -.183 | -.062 | 1.000 | | | | | | | | |
| BDE28 | .080 | .049 | -.051 | -.168 | -.099 | -.156 | .226 | 1.000 | | | | | | | |
| BDE47 | -.059 | -.064 | -.032 | .001 | .104 | .013 | .191 | .437** | 1.000 | | | | | | |
| BDE99 | -.028 | .042 | .080 | .084 | .098 | .125 | .234 | .364** | 0.399** | 1.000 | | | | | |
| BDE100 | .006 | .039 | -.103 | .044 | -.120 | .039 | .357* | .369** | 0.221** | .453** | 1.000 | | | | |
| BDE154 | .064 | -.100 | .064 | .096 | -.143 | -.024 | .489** | 0.203* | 0.306* | 0.201* | 0.154* | 1.000 | | | |
| BDE153 | -.208 | -.135 | .167 | .103 | .109 | .064 | .339* | 0.141* | .286* | .243* | .156* | .444** | 1.000 | | |
| BDE183 | -.145 | -.054 | -.042 | -.028 | -.097 | -.053 | .470** | .855** | .457** | .568** | .525** | .462** | .468** | 1.000 | |
| Total PBDE | -.038 | -.083 | -.041 | .005 | -.112 | -.042 | .317* | .496** | .823** | .501** | .585** | .781** | .533** | .645** | 1.000 |
| BMI | .059 | .219 | -.053 | -.095 | -.164 | -.097 | .224 | .060 | -.189 | -.327* | -.027 | -.053 | -.044 | .036 | -.147 |

**Table 5. 4** Multiple linear regressions with thyroid function parameter, individual PBDE congener and total PBDEs concentration after log transformation.

| β(95%CI) | logTSH β(95%CI) | logFT4 β(95%CI) | logT3 β(95%CI) | logFT3 β(95%CI) | logT4 β(95%CI) |
|---|---|---|---|---|---|
| logBDE28 | -0.11(-0.29, 0.07) | 0.69(-0.42, 1.81) | -0.14(-0.92, 0.63) | -0.43(-1.24, 0.38) | -0.93(-2.07, 0.20) |
| logBDE47 | -0.05(-0.26, 0.16) | **-0.37(-1.69. 0.95)** [a] | -0.23(-1.14, 0.68) | 0.01(-0.96, 0.96) | 0.56(-0.78, 1.89) |
| logBDE99 | -0.05(-0.20, 0.11) | 0.47(-0.50, 1.45) | 0.29(-0.38, 0.97) | -0.37(-1.01, 0.34) | -0.50(-1.49, 0.48) |
| logBDE100 | 0.10(-0.10, 0.30) | 0.13(-1.13, 1.34) | -0.05(-0.92. 0.82) | 0.35(-0.56, 1.26) | -0.16(-1.43, 1.11) |
| logBDE153 | -0.05(-0.22, 0.13) | 0.05(-1.06, 1.16) | **-0.97(-1.74, -0.20)**[a] | 0.05(-0.76, 0.85) | **1.11(-0.1, 2.23)**[a] |
| logBDE154 | 0.08(-0.11, 0.28) | -0.10(-1.32, 1.12) | -0.56(-1.40, 0.29) | 0.51(-0.38, 1.4) | 0.22(-1.02, 1.46) |
| logBDE183 | -0.06(-0.23, 0.11) | 0.56(-0.50, 1.62) | 0.13(-0.60, 0.86) | -0.71(-1.49, 0.06) | 0.47(-0.60, 1.55) |
| log$\sum_7$PBDE | -0.04(-0.16, 0.09) | -0.06(-0.75, 0.88) | -0.17(-0.74, 0.40) | -0.12(-0.72, 0.48) | 0.21(-0.62, 1.04) |

[a] Correlation is significant at the 0.05 level

The same result was reported by Makey et al. (2016) (Makey et al., 2016) with the samples from the USA, which also observed that BDE153 had an inverse association with T3 ($\beta=-0.27$, $p<0.01$) and a positive correlation with FT4 ($\beta=0.03$, $p<0.01$). Other previous studies showed similar results on the effect of PBDEs to thyroid function. Liu et al. (2017) suggested high concentrations of OH-PBDEs (hydroxylated PBDE metabolites) and PBDEs would results in reduced FT4 levels, but elevated TSH values in serum from thyroid cancer patients. Zheng et al. (2017) observed that T3 and T4 had significantly and positively correlated with low PBDE concentrations including BDE47, BDE66 and BDE85 from e-waste workers' serum samples in China. Jacobson et al. (2016) suggested that higher total PBDE concentrations (including BDE47, BDE99, BDE100 and BDE153) correlated with lower T4, higher FT3 and higher TSH levels. A similar result was also found by Zota (Zota et al., 2011), who showed a positive association between TSH levels and low brominated PBDE concentrations in pregnant women from California. However, opposite results have been reported by (Turyk et al., 2008) who found that serum PBDE concentrations were significantly correlated with T4 and FT4 levels, but inversely with TSH. Shy et al. (2012) reported that cord blood levels of FT3 were negatively correlated with BDE183, but FT4 had positive association with BDE197 and BDE207.

In this study, lipid content had a significantly positive correlation with PBDE congener concentration. As PBDEs accumulate in lipid and serum PBDEs were expressed on a lipid basis (ng/g lipid) and the concentration of PBDEs were adjusted for lipids before being compared (Hirai et al., 2012; Chevrier, 2013).

### 5.4.4 Limitation

This study only collected 40 hyperthyroidism and hypothyroidism patients and measured by one short column. It was the first study to focus on hyperthyroidism and hypothyroidism patients. Previous studies paid much more attention on E-waste workers, general people or thyroid cancer patients. Up to now, hyperthyroidism and hypothyroidism patients increased year by year since the usage of chemical decoration in house and unhealthy living habit with pressure. These two groups of patients are not seriously as e-waste worker or cancer, but still occupy the most of general people. Compared the result with previous studies, the conclusion had advanced progress, also it concluded the extraction and analysis methods were available for abnormal thyroid function patients. However, the limitation of this study was lack of control group of PBDE concentration data for human serum samples with normal thyroid hormone factor ranges in Kunming to allow a comparison between the two groups (normal ranges and abnormal ones). Thus, in future work, three more test work should be involved. The first task will connect the relationship between the indoor environment such as indoor dust and hyperthyroidism and hypothyroidism groups. The second research is preferable using an increased sample size from patients, and the last work is to compare normal control group and hyperthyroidism & hypothyroidism groupds to evaluated the PBDEs concentration level in human serum.

## 5.5 Conclusions

In this study, serum samples from abnormal thyroid hormone patients from Kunming were evaluated for PBDE concentrations to assess exposure and possible interactions. The results identified BDE47 as the major congener present in human serum. The concentrations of $\sum_7$PBDE were similar to those from previous studies for general population groups including both adults and children, and at the same order of magnitude as European data, but lower than in the USA. Multiple linear regressions were used to examine the associations between PBDE congeners and the 5 thyroid hormone parameters. BDE153 had significant positive correlation with T4 and negative correlation with T3, whilst BDE47 had negative correlation with FT4. The β-coefficients also suggested that a log-unit increase in $\sum_7$PBDE was associated with an increase of FT4 and T4 levels and a decrease of TSH, T3 and FT3. Further research is required, preferable using an increased sample size from thyroid patients, to investigate this possible relationship further.

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## Supporting information

Table S1 The serum hormone levels including T3, T4, FT3, FT4 and TSH and patients' age, gender

| | | | mIU/L | nmol/L | pmol/L | nmol/L | pmol/L |
|---|---|---|---|---|---|---|---|
| Order# | gender | age | TSH | T4 | FT4 | T3 | FT3 |
| 1 | female | 27 | 0.019 | 187.9 | 25.61 | 1.95 | 6.36 |
| 2 | female | 19 | 15.641 | 184.04 | 29.47 | 2.10 | 7.25 |
| 3 | male | 19 | 1.933 | 169.88 | 21.49 | 1.98 | 5.39 |
| 4 | female | 54 | 8.230 | 172.46 | 16.09 | 1.97 | 3.90 |
| 5 | male | 39 | 0.001 | 238.1 | 72.72 | 6.67 | 30.72 |
| 6 | female | 28 | 1.408 | 171.17 | 10.81 | 2.10 | 3.00 |
| 7 | female | 62 | 3.385 | 205.92 | 13.51 | 2.20 | 0.69 |
| 8 | female | 26 | 1.061 | 157.01 | 11.46 | 2.12 | 3.56 |
| 9 | female | 34 | 1.626 | 162.16 | 14.42 | 1.69 | 3.69 |
| 10 | female | 40 | 0.004 | 169.88 | 36.68 | 3.61 | 12.18 |
| 11 | female | 62 | 0.063 | 153.15 | 18.15 | 1.47 | 3.53 |
| 12 | female | 29 | 1.605 | 166.02 | 12.36 | 2.40 | 3.27 |
| 13 | female | 53 | 0.002 | 334.62 | 74.27 | 8.59 | 30.72 |
| 14 | female | 38 | 0.340 | 157.01 | 18.15 | 1.95 | 4.67 |
| 15 | male | 49 | 0.005 | 189.4 | 48.28 | 3.77 | 13.49 |
| 16 | female | 45 | 0.720 | 192.6 | 21.24 | 2.52 | 5.4 |
| 17 | female | 19 | 1.890 | 204.6 | 19.28 | 2.80 | 4.4 |
| 18 | female | 47 | 0.010 | 221.9 | 34.94 | 4.17 | 11.14 |
| 19 | male | 75 | 0.005 | 213.1 | 41.92 | 2.92 | 8 |
| 20 | male | 24 | 0.010 | 188.4 | 64.54 | 5.02 | 20.37 |
| 21 | female | 24 | 0.930 | 222.3 | 30.51 | 3.28 | 10.14 |
| 22 | male | 54 | 0.005 | 249.7 | 37.47 | 3.16 | 8.69 |
| 23 | female | 22 | 0.010 | 204.9 | 18.2 | 3.80 | 12.21 |
| 24 | male | 27 | 0.010 | 234.7 | 73.6 | 5.00 | 20.6 |
| 25 | female | 33 | 0.005 | 245.2 | 56.72 | 5.85 | 19.96 |
| 26 | female | 16 | 5.400 | 194.7 | 20.21 | 3.63 | 13.21 |
| 27 | male | 32 | 0.002 | 244.2 | 52.83 | 6.12 | 22.2 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 28 | female | 37 | 0.005 | 348.3 | 56.26 | 5.27 | 18.41 |
| 29 | female | 48 | 0.120 | 353.4 | 70.64 | 16.99 | 37.72 |
| 30 | male | 75 | 2.096 | 226.4 | 14.33 | 13.46 | 6.94 |
| 31 | male | 82 | 1.55 | 80 | 14.82 | 4.46 | 3.91 |
| 32 | female | 23 | 2.56 | 131.8 | 20.66 | 2.21 | 5.16 |
| 33 | female | 66 | 1.24 | 93.4 | 16.56 | 1.36 | 3.41 |
| 34 | female | 83 | 0.7 | 95.1 | 18.41 | 1.65 | 4.25 |
| 35 | female | 70 | 1.18 | 78 | 16.14 | 1.48 | 4.12 |
| 36 | female | 47 | 1.15 | 161.8 | 21.69 | 2.55 | 4.13 |
| 37 | male | 37 | 0.84 | 110 | 22.00 | 1.30 | 6.64 |
| 38 | female | 64 | 2.58 | 102.2 | 16.00 | 1.66 | 4.05 |
| 39 | male | 68 | 2.49 | 112.7 | 16.10 | 1.98 | 4.47 |
| 40 | female | 66 | 2.75 | 112.4 | 16.99 | 2.03 | 4.59 |

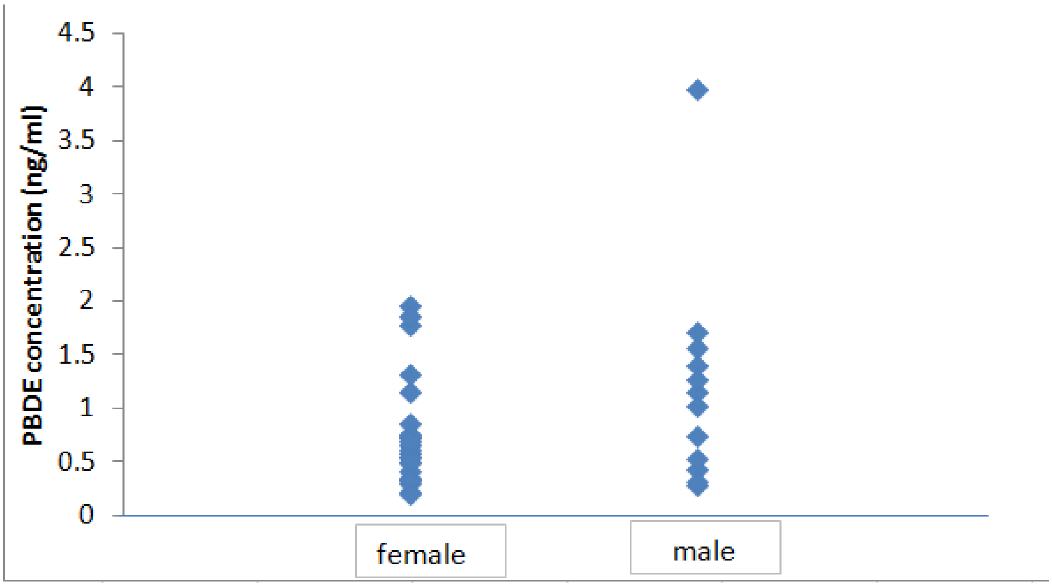

Figure S2 correlation between PBDE concentration of 7 PBDE congeners (ng/ml) and gender.

# Chapter 6: Conclusions and Future work

## 6.1 Conclusions

This study has attempted to assess human exposure to PBDEs in China from indoor environments by collecting and analyzing indoor dust and human serum samples and assessing exposures. A comparison between the time trend of PBDE production, regulations and concentration of PBDEs in indoor dust, indoor air, and human breast milk in North America, Europe and China was made. Production changed in line with changes in the regulation banning the use of PBDEs. The measured concentrations of PBDEs in indoor dust in the USA and EU decreased from the peak on 2004 and are predicted to continue declining as old furniture containing these products are disposed off.. Similar trends have been found in China albeit lagging by five years. Compared with previous studies the concentrations of PBDEs measured in this study were relatively low. BDE209 exceeded 90% of the total PBDE in floor dust, air conditioner dust and foam furniture dust, while only 60% to 80% in EU and the USA. After measuring PBDEs in dust samples collected throughout China, it appeared that there was a correlation with the age of the house sampled. Older houses contained higher concentrations of PBDE suggesting a higher exposure potential for people living in these houses. An assessment of the data suggested that differentiation of both concentration and congener pattern across different districts in one city was evident. PBDE concentrations were generally lower in rural areas than in urban and suburban areas. This suggested that there could be an effect of social economic development on PBDE concentrations in indoor dusts. It is likely that populations that live in different cities and different areas within a city may be exposed to different levels of flame retardants and also to different kinds of flame retardants. A significant positive correlation was found between total PBDEs in dust from air conditioner filters and floor dust samples, which suggests they have a common source. AC filters may be a good place to collect samples in future as it represents the general indoor environment dusts status. No significant association was found between total PBDEs for foam furniture dust and floor dust. The concentrations of PBDEs in breast milk were observed to be higher in the USA than in EU and China since the more commercial PBDE production activity in the USA and the differences in usage patterns. The concentration of PBDEs in breast milk would decrease as did concentrations in indoor air and indoor dust but lagged for several years. Serum samples collected from abnormal thyroid hormone patients from Kunming were evaluated for PBDE concentrations to assess exposure and possible interactions. The results identified BDE47 as the major congener present in human serum. The concentrations of $\sum_7$PBDE were similar to those from previous studies for general population groups including both adults and children, and at the same order of magnitude as European data, but lower than in the USA. Multiple linear regressions were used to examine the associations between PBDE congeners and five thyroid hormone parameters. BDE153 had significant positive correlation with T4 and a negative correlation with T3, whilst BDE47 had a negative correlation with FT4. The β-coefficients also suggested that a log-unit increase in $\sum_7$PBDE was associated with an increase of FT4 and T4 levels and a decrease of TSH, T3 and FT3.

## 6.2 Future work

This study is the first to measure PBDEs level in indoor dust and human serum from six cities in China using one short column methodology at the same time. It is also the first study to measure the PBDEs level in human serum from hyperthyroidism and hypothyroidism patients.

Results highlight the fact that the spatial distribution of PBDEs in indoor dust in China depends on the social economic development of the area sampled. PBDE concentrations were lower in rural areas than in urban and suburban areas. However, this study lacked enough samples from urban area, suburban area and rural area to explain PCA analysis more clearly, only 33 samples in Beijing, 33 from Shanghai, 30 from Dalian, 26 from Guangzhou and 19 in Xiamen. Future work would enlarge the population sampled and theindoor dust samples collected.

PBDE concentrations were measured for 40 hyperthyroidism and hypothyroidism patients from Kunming in China.The results are preliminary as it involved a limited number of samples and no controls. OH-PBDE metabolites were not measured, which have been suggested to have binding affinities for thyroxine-binding globulin (TBG) and interact with the serum thyroid hormone binding protein transthyretin (TTR). Also, the sample size was too small to illustrate statistically any correlations between PBDE congeners and thyroid function parameters or for reliable assessment by multiple liner regression. Another limitation of this study was lack of control group of PBDE concentration data for human serum samples with normal thyroid hormone factor ranges in Kunming to allow a comparison between the two groups (normal ranges and abnormal ones). Further research is required, preferable using an increased sample size from thyroid patients, and compared with normal control group to be able to properly evaluate the PBDEs concentration level in human serum. Future work also may consider these particular chemicals such as OH-PBDE in development studies. In addition, more concerns is needed on the relationship of human exposure and indoor environment with flame retardants.