ENVIRONMENTAL CONTAMINATION AND HUMAN EXPOSURE TO PBDEs AND OTHER HAZARDOUS CHEMICALS ARISING FROM INFORMAL E-WASTE HANDLING

by

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Abstract

The impact of improper e-waste handling on the environment at major informal e-waste recycling sites in China has been investigated with a focus on estimation of human exposure to polybrominated diphenyl ethers (PBDEs) and to other key contaminants via consumption of locally produced animal-derived foods. A method was developed and validated for GC/MS analysis of PBDEs in a variety of matrices (soil, dust, sediment, and 10 types of foodstuffs), represented by a total of 313 samples. Extensive environmental contamination by PBDEs is shown to arise as a result of improper e-waste handling in Guiyu, China, with open burning and circuit boards shredding operations identified as the most significant sources of PBDEs to soil and sediment. Elevated concentrations of selected key pollutants, including legacy and novel brominated flame retardants (NBFRs), polychlorinated biphenyls (PCBs), and metals/metalloids, were detected in a number of dietary samples from Taizhou e-waste recycling sites, confirming the hypothesis that improper e-waste handling is an important source of toxic contaminants to locally produced foods. Human exposure, of both adults and children, to key pollutants via diet was estimated, with results suggesting that children are particularly exposed to a range of toxic substances through a locally-sourced diet. This was especially evident in the case of PCBs, PBDEs, cadmium, and lead. Concentrations of, and/or routes of human exposure to, several contaminants (e.g., PBDEs in duck eggs, and compound-specific NBFRs in diet originating from Taizhou) are reported here for the first time. Application of a simple pharmacokinetic model to predict human body burden of PBDEs (based on estimated dietary intake) provided predicted PBDE body burdens that compared satisfactorily in most instances with those reported elsewhere in blood of adults from Taizhou e-waste sites (though BDE-209 was a notable exception). This research has highlighted the diversity and extent of dietary exposure to a number of toxic chemicals at informal e-waste recycling sites; the exposures that may be presenting considerable risks to human health.

Dedication

This dissertation is dedicated to the memory of my mother, Valentyna, who devotedly supported me throughout my life in my education and all my endeavours, helping me to find and realise my potential. Her strong belief that everything is possible to achieve if you work hard and you are confident in yourself, has helped me to find my way in life. Even during her last days she kept smiling in the face of pain and continued to encourage and inspire me to work on this dissertation. Her unconditional love will be always with me.

This work is also dedicated to my husband, Victor, and my daughter, Olga, whose moral support was priceless throughout the years of my PhD project. I am wholeheartedly grateful to both of you for being in my life and for your constant readiness to meet the challenges together.

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Conference presentations

OP = oral presentation; **PP** = Poster presentation; and **CA** = contributing author.

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Labunska, I., Abdallah, M.A.-E., Eulaers, I., Covaci, A., Tao, F., Wang, M., Santillo, D., Johnston, P., Harrad, S. (2015) Hazardous food: human dietary intake of organohalogen contaminants at e-waste recycling sites in eastern China. ***The 35th DIOXIN Symposium, 23 - 28 August 2015, Sao Paulo, Brazil. OP***

Abbreviations

ABS	Acrylonitrile-butadiene-styrene
AHVLA	Animal Health and Veterinary Laboratories Agency, UK
ASE	Accelerated solvent extraction
BAFs	Bioaccumulation factors
BEH-TEBP	bis-(2-ethylhexyl)-3,4,5,6-tetrabromophthalate
BFRs	Brominated flame retardant
BMDL$_{01}$	Benchmark dose lower confidence limit
BTBPE	1,2-bis-(2,4,6-tribromophenoxy)ethane
bw	Body weight
CBs	Chlorinated benzenes
CI	Chemical ionisation
DBDPE	Decabromodiphenyl ethane
Deca-BDE	Commercial PBDEs formulation almost exclusively consists of the decabrominated congener
DL-PCBs	Dioxin-like PCBs
DP	Dechlorane Plus
dw	Dry weight
ECNI	Electron capture negative ionisation
EDCs	Endocrine disrupting chemicals
EEE	Electrical and electronic equipment
EF	Enantiomer fraction
EH-TBB	2-ethylhexyl-2,3,4,5-tertabromobenzoate
FERA	Food and Environment Research Agency
FRs	Flame retardants
GC	Gas chromatography
GC/MS	Gas chromatography – mass spectroscopy
HBB	Hexabromobenzene
HBCDs	Hexabromocyclododecanes
HBLV	Health-based limit value
IDL	Instrument detection limit
IS	Internal standard
K$_{aw}$	Air/water partitioning coefficient
K$_{oa}$	Octanol/air partitioning coefficient
K$_{ow}$	Octanol/water partition coefficient
LOD	Limit of detection
LOQ	Limit of quantification
lw	Lipid weight
m/z	Mass to charge ratio
ML	Maximum level
MS	Mass spectrometer
NAEL	No Adverse Effect Level
NBFRs	Novel Brominated Flame Retardants
NDL-PCBs	Non-dioxin-like PCBs
NP	Nonylphenol
Octa-BDE	Commercial PBDEs formulation rich in octabrominated congeners
PAHs	Polycyclic aromatic hydrocarbons
PBBs	Polybrominated biphenyls
PBDD/Fs	Polybrominated dibenzo-*p*-dioxins & dibenzofurans

PBDEs	Polybrominated diphenyl ethers
PBEB	Pentabromoethylbenzene
PBT	Persistent, bioaccumulative and toxic
PCA	Principal Component Analysis
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-*p*-dioxins & dibenzofurans
PCNs	Polychlorinated naphthalenes
Penta-BDE	Commercial PBDEs formulation rich in pentabrominated congeners
PK	Pharmacokinetic
POPs	Persistent organic pollutants
PRD	Pearl River Delta
PTMI	Provisional tolerable monthly intake
QA/QC	Quality assurance/quality control
RDS	Recovery determination standard
RfD	Reference Dose
RRFs	Relative response factors
RRT	Relative retention time
RSD	Relative standard deviation
SD	Standard deviation
SDL	Sample detection limit
SIM	Selective ion monitoring
TBBPA	Tetrabromobisphenol A
TDI	Total dietary intake
TEQ	Dioxin-like toxicity equivalence
TMI	Tolerable monthly intake
TPP	Triphenyl phosphate
TWI	Tolerable weekly intake
U.S. EPA	United States Environment Protection Agency
UNEP	United Nations Environment Program
WEEE	Waste electrical and electronic equipment
ww	Wet weight

CHAPTER 1 INTRODUCTION

1.1 Consequences of electric and electronic wastes (e-waste) recycling

1.1.1 E-waste recycling – globally recognized problem

Over recent decades, countless units of electronic equipment have been produced, sold and disposed of worldwide. The lifetime of these devices is relatively short and decreasing as a result of rapid changes in the features and capabilities of electronic equipment. Computers, for example, are in use for about 3 years currently, whereas at the beginning of the 1980s a computer's lifetime was approximately 10 years (Yang et al., 2008; Perkins et al., 2014; Robinson, 2009; Williams et al., 2008). A similar situation is observed in the production of the mobile phones, which are being replaced every 2 years on average (Golev et al., 2016; Yin et al., 2014). Household electrical and electronic appliances are also discarded more frequently now than a few decades ago (Yang et al., 2008; Darby and Obara, 2005). This creates a large stream of obsolete items, referred to as waste electrical and electronic equipment (WEEE), or e-waste. The definition of e-waste is specified by the Directive 2012/19/EU of the European Parliament and of the Council (EU, 2012): '"waste electrical and electronic equipment" or "WEEE" means electrical or electronic equipment which is waste within the meaning of Article 3(1) of Directive 2008/98/EC, including all components, sub-assemblies and consumables which are part of the product at the time of discarding'. E-waste has also been defined by the Solving the E-Waste Problem (StEP) Initiative, a collaborative global project under the leadership of the United Nations University, which started in 2007: 'E-waste is a term used to cover items of all types of electrical and electronic equipment (EEE) and its parts that have been discarded by the owner as waste without the intention of re-use' (StEP, 2014).

As stated by the United Nations Environment Program (UNEP, 2015): 'About 41.8 million metric tonnes of e-waste was generated in 2014 and partly handled informally, including illegally'. Only a small part of the generated e-waste (6.5 million metric tonnes) is documented and treated formally to the highest standards. The United Nations University (Baldé et al., 2015) estimates that the top e-waste generators in 2014 were the United States and China, generating 7.1 and 6.0 million tonnes, respectively. By 2018, the global amount of e-waste is expected to grow to 49.8 million metric tonnes, with an annual growth rate of 4% to 5% (Baldé et al., 2015).

The conventional and primary disposal methods for e-waste are disposal in landfills and incineration. This creates serious risks to the environment and human health because the components of EEE contain a wide range of hazardous chemicals, including organic compounds (e.g., brominated flame retardants, phthalates, polychlorinated biphenyls, among others) and heavy metals (Grant et al., 2013b). As well as raising significant health and environmental concerns during the manufacture of electronic goods (EU, 2002, 2011b), the use of hazardous chemicals in EEE also presents major problems in handling, recycling and disposal of obsolete products.

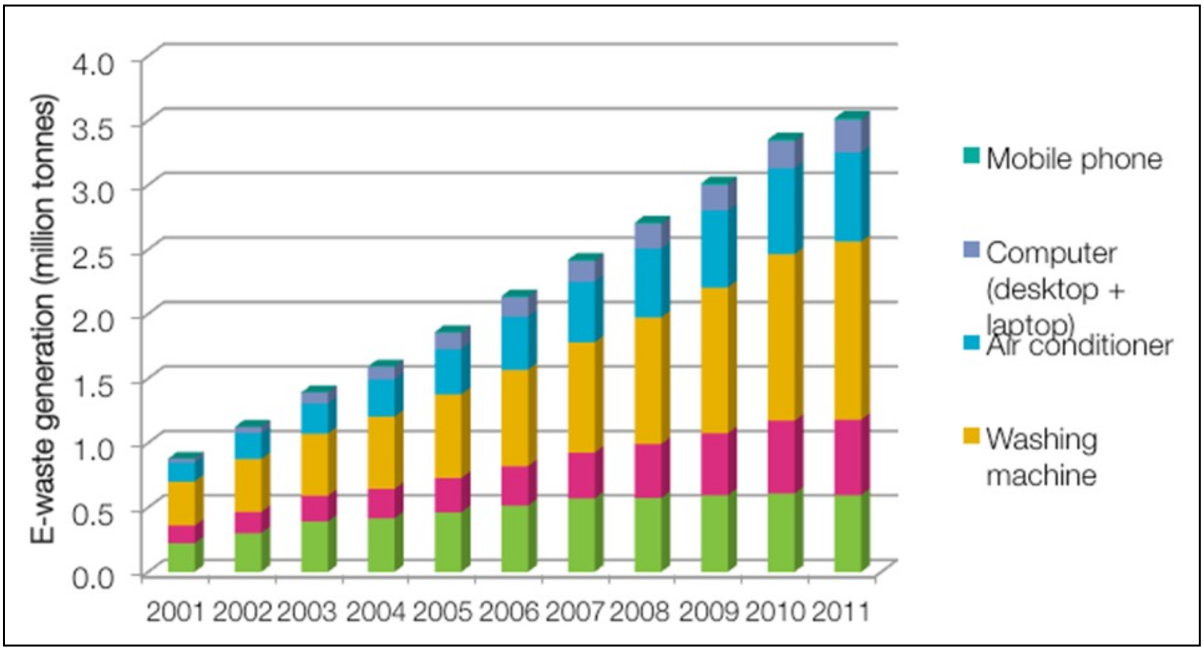
In response to global concern over the growing stream of e-waste, recycling schemes have been set up to recover some of the metals and plastics in the waste. Since the 1990s, such schemes have been in place in the European Union, Japan and some USA states. In Germany, Switzerland and Taiwan, legislation has been implemented requiring manufacturers to take back domestic EEE at the end of their lifespan.

Within the European community, two directives have been adopted, namely the directive of the European Parliament and the European Council on Waste Electrical and Electronic Equipment (WEEE) (EU, 2003a) that was last updated in 2012 (EU, 2012), and the directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) (EU, 2002, 2011b) . These directives necessitate, among other requirements, that Member States are responsible for ensuring that the producers set up systems for treatment and recovery of e-waste, as well as placing prohibitions on the use of certain hazardous substances (most uses of lead, cadmium, mercury and chromium (VI), as well as some brominated flame retardants) in the manufacture of EEE at the outset. The updated WEEE Directive (EU, 2012) states that countries have to meet collection rates for e-waste of 45% of EEE put on the market during the three preceding years from 2016 and 65% from 2019. Alternatively, the collection rate should account for 85% of e-waste generated on the territory of that Member State.

It remains the case, however, that many countries do not have the capacity to deal with the growing quantity of e-waste that they generate or with its content of hazardous chemical constituents. These countries began exporting e-waste to other countries, mainly in Asia, where the legislation and infrastructure to ensure the retrieval, safe and environmentally sustainable recycling, and disposal practices are lacking. For example, between 0.5 and 1.3 million tons of e-waste are shipped out of the European Union each year, accounting for between 16% and 38% of the e-waste collected (Baird et al., 2014).

In many cases, e-waste is exported out of developed countries under the guise of used goods, and it ultimately ends up in developing countries such as China, India, Vietnam, Pakistan, or Ghana, either at one of the informal e-waste recycling sites or simply dumped at landfills. At e-waste recycling sites, the products are dismantled, often in very rudimentary ways and with little regard for worker health and safety and environmental protection, with some materials recovered for reuse and the remainder disposed of to land or water courses.

Figure 1-1 Generation of e-waste in China 2001-2011 (Balde et al., 2015)



The two world’s largest informal e-waste recycling sites are located at Guiyu (Guangdong Province) and Taizhou (Zhejiang Province) in China. E-waste recycling activities had started at Guiyu in the late 1980s (Chan and Wong, 2013) while Taizhou has been recycling e-waste originally generated in China since the late 1970s (Chan et al., 2013; Chan and Wong, 2013) and started to process imported e-waste from the early 1990s (Chi et al., 2011). Gradually, these sites became the two major recipients of imported e-waste, mainly from the US and EU. During this time, the amount of domestic e-waste in China has grown significantly – (see Figure 1-1, data from Baldé et al. 2015) exacerbating the significant challenge to e-waste management in China.

There are 26 regulatory instruments concerning major aspects of e-waste management currently in place in China (StEP, 2016). Sinha-Khetriwal et al. (2006) and more recently Wei and Liu (2012) presented detailed overviews of the legislation and regulations concerning wastes, and e-waste in particular, implemented in China since the middle 1990s until 2011. The cited laws and regulations are aimed at:

- implementing stricter controls on the flow of obsolete EEE, both collected nationally and imported;
- banning illegal import of e-waste;
- restricting the use of certain hazardous chemicals (i.e., polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), lead, mercury, cadmium, and hexavalent chromium) in the whole lifecycle of EEE (production, sale, and import);
- introducing schemes for producer take-back;
- preventing pollution during processing of e-waste.

However, there are many loopholes and uncertainties in these legislative documents, such as an absence of specific stipulations on the implementation of an e-waste management system (Sinha-Khetriwal et al., 2006), an incomplete list of e-waste categories, and an incomplete list of regulated e-waste recycling activities, among others (Wei and Liu, 2012).

Hence, despite the existence of officially certified e-waste recycling enterprises and legislation on e-waste management in China (Liu et al., 2006), the informal e-waste recycling sector is blooming there. Chi et al. (2011) highlight the following reasons for this:

- a regular and sizeable bulk of e-waste is accumulated from both illegal imports and domestic individual collections;
- the highly contaminative recycling methods used are simple and cost effective;
- the highly specified dismantling process makes the separation of reusable components very efficient;
- there is a high and steady demand for the products of informal recycling workshops.

In addition, Chinese citizens have to pay for their e-waste to be treated at official recycling facilities and more than 90% are reluctant to spend money for recycling (Liu et al., 2006), preferring to sell e-waste to private collectors instead. Hence, about 60% of the e-waste generated in China is sold to private collectors that supply informal e-waste recycling workshops (Liu et al., 2006).

While cost effectiveness, sufficiency of e-waste flow and citizen fees associated with official recycling all contribute to continued informal e-waste recycling in China, the biggest contributor is arguably the lack of regulations ensuring proper and safe management of the e-waste lifecycle from collection to the final stages. The latter should include recovered products management and consider both environmental issues, to prevent contamination of the surroundings, and social and health-related issues, to ensure that e-waste recycling workers are protected from the impacts of hazardous chemicals and are able to maintain a healthy lifestyle. There are ways to change the informal e-waste recycling practices and gain more control on e-waste management. As shown in a recent study of an informal e-waste recycling site in Israel (Davis and Garb, 2015), cooperation between formal and informal e-waste recycling sectors may help workers to start operating in cleaner ways and reduce health impacts on themselves and on local communities but still retain their livelihoods. As an example, the authors provided a case study of a copper grinding facility installation at an e-waste site as an alternative to open burning of waste cables that was used previously.

Overall, there is an urgent need for a fundamental shift in thinking and emphasis by governments, the general public, and particularly those companies engaged in electronics production, recycling and disposal. It is vital to ensure that concerns regarding chemical and other raw material use, workplace exposure and waste management become a routine part of the EEE manufacturing industry’s planning, research and development cycles.

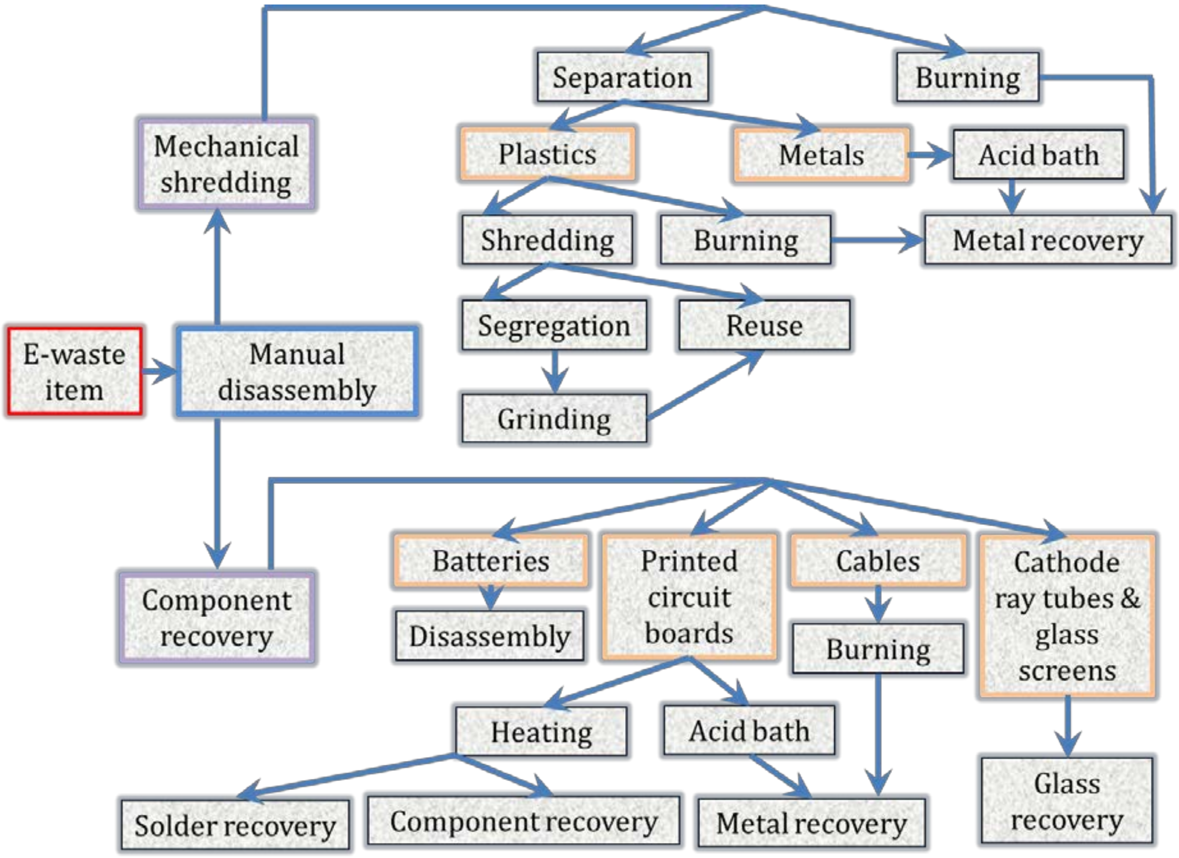
1.1.2 Main techniques of rudimentary e-waste recycling

The stages of informal e-waste recycling may vary slightly from site to site and from country to country; however, there are common main operations usually employed during such recycling. Fig. 1-2, adapted from Brigden et al.’s (2005) study, gives an example of the main stages of the operations utilized at e-waste workshops in China and India.

As noted in section 1.1.1 above, e-waste consists of a wide range of materials that can be recovered and reused. They could be divided roughly into three main groups: plastics, glass and metals. Of these, glass is not usually treated on site but rather sent away for further processing.

Hence, the first stage in recycling operations involves manually disassembly of an e-waste item as much as possible to recover components such as batteries, printed circuit boards, cathode ray tubes, glass screens, cables, and others. These components then undergo further treatment (see Fig. 1-2). The remainder of the item is then mechanically shredded or crushed helping to separate its metal and plastics parts. What cannot be separated in this manner is usually burnt to recover metals. The separated plastic fragments are roughly segregated by mixing in water and either directly re-used or ground to produce fine powders as a final recycling product.

Figure 1-2 Stages of informal e-waste treatment operations employed in China and India (adapted from Brigden et al. 2005)



Metal-containing parts are dissolved in strong acids in most cases, with further chemical recovering of metals from acidic solutions. The parts of the e-waste item that cannot be further separated after mechanical shredding (i.e., to plastics and metal-containing parts) as well as cables are simply burnt to recover metals. All the operations described above are usually performed in a very primitive manner without any regard for the health and safety of the workers and surrounding communities and with no consideration for environmental protection. All the wastes – both liquid and solid – formed during recycling operations are discharged in the immediate vicinity of the workshops, mainly to local watercourses, in some cases transferred to unofficial landfills or just left in heaps on-site. During the burning of cables and residual e-waste parts, more hazardous chemicals are formed creating additional threatto both the workers and the environment.

1.1.3 Overview of principal groups of contaminants released into environment as a result of e-waste recycling

Although the full diversity of chemicals released during e-waste recycling has never been documented, it has been reported that e-waste contains more than 1,000 different substances (Widmer et al., 2005), many of which have hazardous properties and present substantial concerns for human exposure as well as the environmental consequences of pollution of streams. Table 1-1 summarizes the main groups of chemicals released to environment during rudimentary e-waste recycling operations, their main uses in EEE, and the components of EEE they are incorporated in.

A diverse range of flame retardants (FRs) have been found in environmental samples around e-waste recycling sites including brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) (Han et al., 2010; Ma et al., 2011; Luo et al., 2009b; Brigden et al., 2005; Muenhor et al., 2010), decabromodiphenyl ethane (DBDPE) (Wang et al., 2010; Zheng et al., 2015b; Muenhor et al., 2010), hexabromocyclododecane (HBCD) (Tomko and McDonald, 2013; Zhang et al., 2012), tetrabromobisphenol A (TBBPA) (Shi et al., 2009; Huang et al., 2014), 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE) (Zheng et al., 2015a; Someya et al., 2016), as well as chlorinated (dechlorane plus (DP)) (Zhang et al., 2012; Zheng et al., 2015b; Someya et al., 2016), and phosphorus-containing (triphenyl phosphate (TPP)) FRs (Tsydenova and Bengtsson, 2011).

These FRs constitute ones already banned or restricted for use in EEE (e.g., penta- and octa-BDEs) as well as alternative or novel BFRs (NBFRs) introduced as replacements for discontinued FRs (e.g., DBDPE, BTBPE).

Table 1-1 Groups of environmental contaminants associated with rudimentary e-waste recycling. n/a – not applicable

Compounds/Elements	**Primary use in EEE**	**Component of e-waste**
Polybrominated diphenyl ethers (PBDEs)	BFR	Plastic casing of electronic equipment
Decabromodiphenyl ethane (DBDPE)	BFR	High-impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS), polypropylene
Hexabromocyclododecane (HBCD)	BFR	Expanded and extruded polystyrene foam (EPS & XPS), HIPS
Tetrabromobisphenyl A (TBBPA)	BFR	Printed circuit boards
1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE)	BFR	ABS, HIPS, thermoplastics & thermosetting resins, polycarbonate and coatings
Dechlorane Plus (DP, also known as Mirex)	Chlorinated FR	Thermoplastic & thermosetting resins, rubber, paint, electrical products
Triphenyl phosphate (TPP)	Phosphorous FR	Phenolic and phenylene-oxide based resins
Polychlorinated biphenyls (PCBs)	Insulators, transformer oil & capacitor additive	Transformers, insulators, capacitors, printing inks
Polychlorinated naphthalenes (PCNs)	Insulators, transformer oil & capacitor additive, byproduct of thermal processes involving chlorine	Transformers, insulators, capacitors
Chlorinated benzenes (CBs)	Solvent for PCB commercial formulations, antioxidant	Transformers, insulators, capacitors
Nonylphenol (NP)	Antioxidant	Plastics
Phthalate esters	Plasticizer	Flexible plastic (mostly PVC) components such as cables
Polychlorinated & polybrominated dibenzo-*p*-dioxins & dibenzofurans (PCDD/Fs & PBDD/Fs)	Burning or combustion byproduct	n/a
Polycyclic aromatic hydrocarbons (PAHs)	Burning or combustion byproduct	n/a
Dioxin-like PCBs	Burning or combustion byproduct	n/a
Lead	Solder, PVC stabilizer; as lead oxide – glass additive	Printed circuit boards, old-type CRTs, PVC plastics

Compounds/Elements	Primary use in EEE	Component of e-waste
Cadmium	Contact element, PVC stabilizer	Switches, solder joints, Ni-Cd batteries, printed circuit boards, old-type CRTs
Antimony	Flame retardant as antimony trioxide; dopant as antimony trihydride	Plastics and other polymers, semiconductors
Mercury	Contact & light enhancing element	Printed circuit boards, switches, relays, batteries, flat screen displays
Copper	High electrical conductivity element	Cables, wiring, alloys with beryllium
Zinc	Additive as zinc sulphide	Coating inside CRTs
Barium	Additive as barium oxide	CRTs front plate
Beryllium	Conductor of heat & electricity	Springs, relays, connections, printed circuit boards, usually as cooper-beryllium alloy
Nickel	High electrical conductivity, magnetic permeability & thermal conductivity element	Printed circuit boards, batteries, alloys with cooper
Lithium	Constituent of Lithium-polymer cell	Batteries

Similarly, both PCNs and their successor PCBs, which were used in the past in transformer oils and capacitors, are still detected at e-waste sites despite the long-standing restrictions on their production and use under the Stockholm Convention (Stockholm Convention, 2008).

Moreover, additional toxic chemicals can be formed during the uncontrolled burning or combustion of e-waste, including polychlorinated and polybrominated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs & PBDD/Fs), polycyclic aromatic hydrocarbons (PAHs), and dioxin-like PCBs (Zhang et al., 2012; Shen et al., 2009; Ren et al., 2014; Ma et al., 2008; Chan and Wong, 2013; Fujimori et al., 2016).

In addition, a wide range of metals and metalloids (see Table 1-1) are also released into the environment throughout many stages of e-waste processing in both solid and soluble forms, the former particularly evident at the stage of e-waste acidification to recover metals (Brigden et al., 2005; Song and Li, 2014b; Luo et al., 2011; Zheng et al., 2013; Tang et al., 2010; Liu et al., 2013).

Hence, informal e-waste recycling is one of the most significant point sources of the diverse range of both organic and inorganic pollutants in the environment. There is an urgent need to target the problem from its very beginning - to eliminate or minimize the use of toxic chemicals in EEE and develop plans and technologies for their safe and environmentally friendly recycling. Additionally, more control and proper recycling and treatment of the existing stockpiles of e-waste is needed to overcome environmental issues and to prevent further human exposure to hazardous chemicals.

1.1.4 Human health impacts from e-waste recycling

The full extent of effects on humans from exposure to the complex mixture of hazardous chemicals released during rudimentary e-waste recycling is still unknown. Many of these chemicals have been studied individually to determine their toxic effects (see Table 1-2). There are many pathways of exposure to hazardous chemicals around e-waste recycling sites including diet, dust and soil ingestion, inhalation, and dermal exposure (Zhao et al., 2009b; Song and Li, 2014a; Xing et al., 2011, 2009; Han et al., 2010).

Also, the exposure of workers and their families is ongoing (or chronic) and dynamic; hence, the scenario of the exposure might change on a daily basis depending on a number of factors such as involvement in e-waste recycling activities, the change in the type of e-waste processed, and dietary choices, among others. This combination of factors impacting populations around e-waste areas is unprecedented in terms of the diverse range of pollutants encountered – in many cases present at high concentrations – and the continuity of multi-pathway exposure. It can therefore be difficult to attribute an observed health effect to a single pollutant, because different pollutants may affect the same systems of the human body, exhibiting similar toxicological actions (see Table 1-2).

Table 1-2 Principal health effects in adults and children associated with key pollutants released during e-waste recycling

Health effect	Associated pollutants	Affected Cohort	Source
Developmental neurotoxicity	PBDEs, PAHs, PCDD/Fs, Pb, Hg, Cd, Cr (VI)	Children, foetuses	(Eskenazi et al., 2013; Chen et al., 2011; Zheng et al., 2008b; Dingemans et al., 2011; Liu et al., 2011; Chen et al., 2016)
Reproductive system toxicity	PBDEs, PCBs, PCDD/Fs, HBCDs, Cr (VI)	Children, adults	(Schecter et al., 2012; van Leeuwen et al., 2000; IARC, 2012)
Endocrine system toxicity	PBDEs, PCBs, PCDD/Fs, HBCDs, TBBPA, PAHs, Chlordane, As, Cd, Pb, Hg,	Children, adults	(Krivoshiev et al., 2016b; WHO-UNEP, 2013; Legler and Brouwer, 2003; Xu et al., 2015, 2014b; Yuan et al., 2008)
Immunotoxicity	PBDEs, TBBPA, HBCDs, PCBs	Children, adults	(Darnerud, 2003; Birnbaum and Staskal, 2004; Schecter et al., 2012)(U.S. EPA, 1997)
Adverse birth outcomes	PBDEs, Pb, Cr (VI)	Neonates	(Zhao et al., 2016; Xu et al., 2012; Xia et al., 2016)
Genotoxicity	PBDEs, Cr (VI)	Neonates, adults	(Zhao et al., 2016; Li et al., 2008; IARC, 2012)
Impaired physical development	Pb, Cd	Children	(Zheng et al., 2008b)
Carcinogenicity	PCDD/Fs, PAHs, Cr (VI),	Children, adults	(WHO-UNEP, 2013; IARC, 2012, 2010)
Reduced bone mineral density	HBCDs	Female offspring	(Yi et al., 2016)

Moreover, little is known about synergistic and cumulative effects that may also take place during multi-pollutant human exposure (Laborde, 2016). Beyond the empirical studies presented in Table 1-2 that focused on attributing selected health effects to specific pollutant exposure, a number of review studies highlighted a range of negative impacts on both adults and children observed within e-waste recycling communities (Grant et al., 2013a; Tsydenova and Bengtsson, 2011; Frazzoli et al., 2010; WHO, 2016; Suciu et al., 2013; Chen et al., 2010; Kim et al., 2014; Heacock et al., 2016) and raised several concerns in relation to the current health status of populations residing at e-waste recycling sites. Taken together, current research raises four main concerns summarised below.

1.1.4.1 Exposure of pregnant women adversely affects foetal development

A number of studies reported adverse growth and development effects to the foetus due to a placental transfer of pollutants accumulated in mothers' bodies including:

- PBDEs (Chen et al., 2014; Zhao et al., 2016; Jakobsson et al., 2012; Talsness, 2008; Xu et al., 2014a);
- Hydroxylated PBDE metabolites (Chen et al., 2016; Weijs et al., 2015; Meerts et al., 2001; Dingemans et al., 2011); and
- Toxic heavy metals (Guo et al., 2010b; EFSA, 2009; EFSA a, 2014; EFSA, 2012b; Xia et al., 2016), among others.

For example, prenatal exposure to mercury has been associated with reduced placental and foetal growth (Murcia et al., 2016); prenatal exposure to PCBs and dioxins (Murcia et al., 2016) has been linked with ovarian dysgenesis syndrome, the term used to characterise a number of effects that pollutants have on female reproductive development. Zhao et al. (2016) reported that adverse foetal growth such as changes in placental DNA methylation might be associated with *in utero* exposure to PBDEs. Prenatal exposure to high chromium concentrations may increase the risk of low body weight of neonates, females in particular (Xia et al., 2016).

1.1.4.2 Exposure of lactating women adversely affects neonates (and infants)

Many studies reported the transfer of toxic pollutants from mother to neonates and infants with breast milk. The transferred pollutants are similar to those specified in section 1.1.4.1:

- BFRs (Schecter et al., 2010b; Cui et al., 2012; Xu et al., 2014b; Abdallah and Harrad, 2014, 2011a; Bi et al., 2006; Sudaryanto et al., 2008; Harrad, 2015; Zhang et al., 2011a; Kim et al., 2014; Jin et al., 2009; Abdallah and Harrad, 2011b);
- PCDD/Fs (Shen et al., 2012; Sun et al., 2010; Song and Li, 2014a; Zheng et al., 2008a; WHO-UNEP, 2013; Xing et al., 2009; Ma et al., 2011; Zhang et al., 2007);
- PCBs (Tue et al., 2010; Inoue et al., 2006b; Shen et al., 2012; Asante et al., 2011; Inoue et al., 2006a; Song and Li, 2014a; Xing et al., 2009; EFSA, 2005; Zhang et al., 2011a); and
- Heavy metals (WHO-UNEP, 2013; EFSA, 2015).

Most worryingly, the internal exposure of neonates and infants during breastfeeding may by far exceed maternal exposure (Caspersen et al., 2016). Exposure to toxic pollutants at such an early age may trigger a number of adverse health effects (see Table 1-2) including damage to genetic, nervous, endocrine, and immune systems as well as inducing cancer.

1.1.4.3 Exposure of children causes long term adverse health effects

In addition to exposure *in utero* and during breastfeeding, developing children residing at e-waste sites may be exposed to pollutants listed in Table 1-1 via different routes, as follows:

- diet (Jiang et al., 2014; Tang et al., 2015; Yu et al., 2012; Fowler et al., 2015; Tao et al., 2016; Asante et al., 2011; Zhou et al., 2012; Zheng et al., 2013);
- ingestion of soil and dust (Man et al., 2013; Ma et al., 2008; Song and Li, 2014a; Chan and Wong, 2013; Jiang et al., 2014; Frederiksen et al., 2009);
- inhalation (Zhang and Wong, 2007; Song and Li, 2014a; Chan and Wong, 2013; Zheng et al., 2013); and
- dermal contact (Zheng et al., 2013; Ma et al., 2008; Song and Li, 2014a; Chan and Wong, 2013).

The review of Euling and Markis (2011) on children's health effects highlighted the crucial role of endocrine disrupting chemicals' (EDCs) impact on children due to their undeveloped mechanisms of protection from and elimination of toxic chemicals. The authors concluded that the most sensitive endpoints of endocrine disruption in children are associated with developmental effects including neurodevelopment, sexual differentiation, puberty timing, body size and obesity, and hormone levels. Similar observations have also been reported in other studies (Xu et al., 2014b; Lyche et al., 2015; Eskenazi et al., 2013; Talsness, 2008; WHO, 2003; Birnbaum and Staskal, 2004). Some pollutants (e.g., PBDEs and PCBs) may disrupt the endocrine system of children even at low doses (Vandenberg et al., 2012). Several developmental disorders observed in children are also recognised as risk factors for adult disease. It has been shown, for example, that male reproductive system disorders such as hypospadias and cryptorchidism in boys are linked to testicular cancer and sperm deficits in adult men (Main et al., 2007; Hardell et al., 2006); while early puberty in girls has been associated with higher risk of breast cancer in women (WHO-UNEP, 2013). It is often the case that, at informal e-waste recycling areas, children work alongside their parents as their small hands are considered ideal for the process of e-waste disassembling (Perkins et al., 2014; Robinson, 2009). Thus, child labour at informal e-waste recycling sites exacerbates children's exposure to pollutants.

1.1.4.4 Lack of comprehensive studies on health effects triggered by toxic pollutants

Finally, many studies raised concerns about the lack of sufficient data and full-scale investigations into human health effects associated with exposure to toxic pollutants. Euling et al. (2011), who reviewed children's health effects related to EDCs, concluded that more studies are needed to establish the underlying mechanisms linking exposure to EDCs with potential health effects on children that may cause diseases later in life. Other publications have echoed Euling et al.'s (2011) call for further studies into the effects of environmental pollutants on children's development (Fowler et al., 2012; Soechitram et al., 2017; Xu et al., 2012) and for prompt actions against continuous exposure of children to EDCs. Fowler et al. (2012) concluded that more comprehensive studies are needed that consider low dose exposures, pre- and postnatally, in the multiple pollutants exposure scenario, while Kim et al. (2014) stressed the importance of more studies taking into account long-term and chronic exposures (Kim et al., 2014).

The retrospective study (2001 – 2008) conducted in Guiyu, China (Xu et al., 2012) linked e-waste related pollution with adverse birth outcomes in children. The birth records of mothers from e-waste recycling areas in Guiyu were compared to those obtained for the control group of mothers residing in rural and suburban areas of Xiamen located away from e-waste areas. The main findings were:

- About four times higher risk of stillbirth in Guiyu than in Xiamen;
- Lower birth weight of singleton live births in Guiyu compared to Xiamen (mean: 91g);
- Higher risk of having low body weight or term low body weight in Guiyu;
- About five times higher cord blood concentration of lead (median: 10.78 µg/dL *vs* 2.25 µg/dL) in neonates from Guiyu compared to Xiamen;
- Significantly lower Apgar scores (i.e., a measure of the physical condition of a newborn) among Guiyu neonates;
- Higher rate of twin births and boys in Guiyu than those in Xiamen.

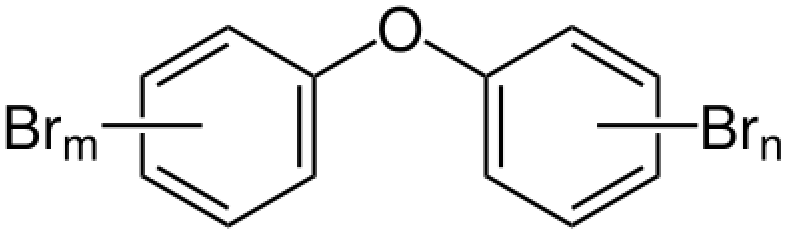
Xu et al.'s (2012) study has urged for more biomonitoring surveys conducted in e-waste affected areas to assess the levels of toxic pollutants in neonates that would enable the prediction of possible health effects in adulthood. It has also called for an introduction of safer practices of e-waste recycling, which would help to reduce the widespread release of toxic contaminants.

Overall, adverse human health effects associated with exposure to toxic chemicals are an ongoing problem at informal e-waste recycling sites. There is a clear need for more detailed estimation of human exposure – and children's exposure in particular – to toxic chemicals at these locations where such impacts are inevitable while rudimentary methods of e-waste treatment continue (see section 1.1.2). For instance, more research is needed to identify the extent and primary routes of exposure to key pollutants released at e-waste recycling areas (i.e., BFRs, PCBs and heavy metals) as these have been associated with a wide range of adverse health effects (see section 1.1.4) on both adults and children. Further investigations into simultaneous multi-pollutants exposures are important once we know more about the causal links between specific pollutants and health effects. This will allow more accurate prediction of possible health effects and, as a result, the timely prevention of health deterioration for many generations.

1.2 PBDEs - one of the key pollutants at e-waste recycling sites

Polybrominated diphenyl ethers (PBDEs) are one of several classes of brominated compounds in widespread use as flame retardant additives in plastics and foams, including plastic casings of electronic equipment (OECD, 2003). There are 209 different chemicals (congeners) included in this group, differing in the numbers and positioning of bromine atoms in the molecules (see Fig. 1-3). The production of PBDEs at industrial levels started in the 1970s in Germany (ATSDR, 2015). Those in common commercial use were "penta-BDE" (i.e. a mixture rich in pentabrominated congeners), "octa-BDE", (rich in octabrominated congeners) and "deca-BDE" (almost exclusively the decabrominated congener). Penta-BDE was used primarily as an additive flame retardant in flexible polyurethane foams. Octa-BDE was an additive to acrylonitrile-butadiene-styrene (ABS) plastic, which was used to manufacture casing for wide range of electric and electronic devices. Deca-BDE has been used in a variety of products including EEE, furniture, textiles, mattresses, as well as in vehicles, aircrafts and building materials (U.S. EPA, 2014a).

Figure 1-3 Chemical structure of PBDEs; m + n = 1 to 10



Both penta- and octa-BDE formulations were banned from manufacture and use in Europe from 2004 because some of the congeners of these mixtures are persistent, bioaccumulative and toxic (PBT) (EU, 2003b). The use of deca-BDE in EEE has also been banned by the European Court of Justice since 2008 (EU Court of Justice, 2008) on the same basis as penta- and octa-BDE. In 2010, the U.S. EPA announced a phase-out of deca-BDE by the end of 2013 (U.S. EPA, 2010c). However, large amounts of these BFRs will still be released into the environment – particularly in places that improperly handle used and obsolete EEE – due to their presence in various existing goods.

1.2.1 Properties of PBDEs

Compounds' physicochemical properties determine their behaviour in the environment, biota, and in the human body. In the case of commercial PBDE formulations, it is hard to specify such properties, as these formulations consist of complex mixtures of PBDE congeners that differ in their levels of bromination. Common compositions of selected commercial PBDEs formulations are presented in Table 1-3; however, differences in manufacturing processes may affect the nature and amounts of impurities in the final products. Advances in the mass-spectrometric analysis of PBDEs allowed the isolation of more compounds in commercial mixes including an additional 9 minor components in penta-BDE (DE-71) that have not been reported previously (BDEs 42, 48, 51, 91, 102, 104, 119, 149, and 155) (Konstantinov et al., 2008).

Table 1-3 Composition of three commercial PBDEs mixtures, in % by weight.[ǂ]

PBDEs	**Penta-BDE**			**Octa-BDE**			**Deca-BDE**	
	DE-71[a]	DE-71[c]	DE-71[b]	DE-79 [a]	DE-79 [c]	DE-79 [d]	Bromkal82-0DE [a]	DE-83[c]
tri-BDEs	0.32	0-1	0.4	-	-	-	-	-
tetra-BDEs	39.5	24-38	34-35	-	-	-	-	-
penta-BDEs	65.1	50-60	57	-	-	-	-	-
hexa-BDEs	7.1	4-8	7-9	1.9	<12	9	-	-
hepta-BDEs	0.1	-	0.1	45.5	<45	40	0.03	-
octa-BDEs	-	-	-	37.9	<33	34	0.07	3
nona-BDEs	-	-	-	13.1	<10	14	9.3	
deca-BDE	-	-	-	1.3	-	1	91.6	97

ǂ - These figures have been reproduced directly from the original articles and in some cases add up to >100%. No explanation has been given for this.
a - (La Guardia et al., 2006); b - (Konstantinov et al., 2008); c -(ATSDR, 2015); d - (Geller et al., 2008).

PBDEs are persistent and bioaccumulative chemicals (U.S. EPA, 2010a). Some of the physicochemical properties estimated for PBDE homologue groups and estimated or measured for the dominant PBDE congeners in each commercial formulation are provided in Table 1-4. Water solubility and vapour pressure, in general, decrease with the increase of the level of PBDE bromination. Logarithmic values of octanol/water partitioning coefficient (Log Kow) of PBDEs far exceed 2, thereby characterising these chemicals as lipophilic or hydrophobic (Connell, 1989). In addition, chemicals with Log Kow > 5 are specified as bioaccumulative under Annex D of the Stockholm Convention (UNEP, 2009), thus PBDEs have a potential to enter the food chain and the human body with a tendency to concentrate into lipid-rich biological compartments.

The octanol/air partitioning coefficient in logarithmic form (Log Koa) increases with increasing PBDE bromination level indicating that higher molecular weight BDEs are more likely to absorb into organic matter in soil, sediment or vegetation from the atmosphere than stay in vapour form (U.S. EPA, 2010a); moreover, that soils and sediments are generally considered as sinks for PBDEs (O'Driscoll et al., 2016).

Table 1-4 Selected physicochemical properties of the key PBDE congeners

Principal commercial formulation	PBDEs homologue groups and key congeners	Molecular weight (g/mol)	Water solubility (µg/L)	Vapour pressure, (Pa, 25°C)	Log K_{ow}	Log K_{oa} (25 °C)	Log K_{aw}
Penta-BDE	tetrabrominated	485.8	-	-	6.3^{a}	-	-3.2^{a}
	BDE-47		15^{b}	$1.9 \times 10^{-4\ f}$	6.8^{b} 6.4^{c}	10.5^{b} 10.4^{c}	-3.4^{c}
	pentabrominated	564.7	-	-	6.7^{a}	-	-3.5^{a}
	BDE-99		9^{b}	$1.8 \times 10^{-5\ f}$	7.3^{b} 6.8^{c}	$11.3^{b,c}$	-3.7^{c}
	BDE-100		40^{b}	$2.9 \times 10^{-5\ f}$	7.2^{b} 6.5^{c}	11.1^{b} 11.0^{c}	-3.8^{c}
	hexabrominated	643.6	-	-	7.1^{a}	-	-3.9^{a}
Octa-BDE	heptabrominated	722.5	-	-	7.7^{a} 7.5^{c}	12.8^{c}	$-4.2^{a,c}$
	BDE-183		2^{b}	$4.7 \times 10^{-7\ f}$	8.3^{b}	11.9^{b}	-
	octabrominated	801.4	-	-	8.1^{a} 7.5^{c}	13.6^{c}	-4.6^{a} -4.5^{c}
	nonabrominated	880.3	-	-	8.6^{a} 8.3^{c}	14.4^{c}	-4.9^{a} -4.8^{c}
Deca-BDE	BDE-209	959.2	$<0.1^{b}$	$9.0 \times 10^{-13\ g}$	9.0^{a} 8.8^{c} 11.2^{d} 6.3^{e}	15.3^{c}	-5.3^{a} -5.1^{c}

a – estimated values (Nordic Council of Ministers, 2004); b - (ATSDR, 2015); c – estimated values (Wania and Dugani, 2003); d – estimated value (Palm et al., 2002); e – measured value (EC, 2002); f - (Tittlemier et al., 2002); g – estimated value extrapolated to 25 °C (Fu and Suuberg, 2011).

1.2.2 Environmental levels of PBDEs around unofficial e-waste recycling sites in China

The use of PBDEs as additives in plastics and other polymers, in which they are not tightly bound to the polymer matrix, has led to their widespread presence in almost every part of the environment, particularly at places where e-waste is improperly recycled or dumped. Due to their hydrophobicity (see section 2.1.1), PBDEs are tightly bound to particulate matter, hence they accumulate in soil, sediment and dust.

1.2.2.1 Soil, sediment and dust

Studies reporting concentrations of e-waste-related PBDEs in soil, sediment and dust in China were mainly conducted within Taizhou City in Zhejiang Province (Fengjiang and Wenqiao) and in Guangdong Province (Guiyu, Longtang, Guangzhou, and Qingyuan) recycling areas. A summary of the findings of these studies is presented in Table 1-5. Most studies have focused on e-waste sites within Guangdong Province where extremely high concentrations of ∑PBDEs – up to 35700 ng/g dw and 160000 ng/g dw in soil and dust from Guiyu (Leung and Wong, 2007; Wang et al., 2010), respectively - have been reported. Two studies reported PBDE concentrations in soil and dust samples from Fengjiang (Ma et al., 2009; Wang et al., 2011c) that were lower than those reported for Guangdong Province e-waste sites; however, these samples were still quite contaminated (up to 82200 ng/g and 5710 ng/g dw for dust and soil samples, respectively). One of the dust samples collected from Wenqiao contained 334413 ng ΛPBDEs/g dw (Jiang et al., 2014). High concentrations of PBDEs have also been reported in uncontrolled e-waste sites in other countries, for example, in dust samples from Thailand (Muenhor et al., 2010) (range for 21 congeners, tri-deca: from 320 ng/g to 290000 ng/g dw) and from South Africa (Abafe and Martincigh, 2015) (range for 8 congeners, tri-deca: from 2632 ng/g to 44203 ng/g dw).

Sediments from both Guangdong and Taizhou e-waste sites were less frequently investigated for the presence of PBDEs than soils and dusts. Two studies reported PBDEs concentrations in sediments around Guangdong Province: from Longtang e-waste site (Wang et al., 2011d) and from Guiyu (Luo et al., 2007). Among these, pond sediments from Longtang contained PBDEs at a similar range of concentrations to those detected in sediments from 2 out of 3 rivers investigated in Guiyu but were significantly lower than sediments from the third river in Guiyu (see Table 1-5). In the Taizhou e-waste area, sediments from one of the canals running through

Fengjiang town contained PBDEs in a wide range of concentrations from about 10 ng/g to 60000 ng/g dw (Wang et al., 2011c).

Table 1-5 PBDEs concentrations in soil, dust and sediment from e-waste recycling sites in China, in ng/g dry weight. n/a – not available

Matrix	Area	Location	Nr. of samples	BDE-209 (range)	∑PBDEs (range)	Number of congeners	Source
Soil	Guangdong Province	Longtang	3	76 - 661	111 - 1031	19 (tri-deca)	(Liu et al., 2013)
		Longtang	5	67 – 284	151 – 533	8 (tri-deca)	(Wang et al., 2011d)
		Guiyu	29	105 - 5224	22 - 1853	19 (tri-deca)	(Gao et al., 2011)
		Guiyu	3	328 – 12700	398 – 35700	24 (mono-deca)	(Leung and Wong, 2007)
		Qingyuan	29	69 - 6320	191 - 9200	22 (mono-deca)	(Luo et al., 2009b)
		Qingyuan	31	779 - 8058	7 - 1188	19 (tri-deca)	(Gao et al., 2011)
		Qingyuan	36	5 - 11940	n/a	41 (mono-deca)	(Wang et al., 2014a)
	Zhejiang Province	Fengjiang	3	n/a	200 - 250	7 (tetra-deca)	(Wang et al., 2011c)
		Fengjiang	10	70 - 5530	72 - 5710	10 (tri-deca)	(Ma et al., 2009)
Dust	Guangdong Province	Guiyu	14	1770 – 232000	3520 – 23000	8 (tri-deca)	(Zheng et al., 2015b)
		Guiyu	39	105 - 140000	227 - 160000	28 (di-deca)	(Wang et al., 2010)
		Longtang	3	1194 - 4890	1332 - 5138	19 (tri-deca)	(Liu et al., 2013)
		Longtang	9 7 13	146 – 19100 385 – 73100 10200 - 195000	173 – 20010 414 – 48700 11000 - 196000	8 (tri-deca)	(Zheng et al., 2015b)
		Guangzhou	13	1900 - 23500	2700 - 28000	21 (tetra-deca)	(Zheng et al., 2011)
	Zhejiang Province	Fengjiang	5	5560 - 80600	6300 – 82200	10 (tri-deca)	(Ma et al., 2009)
		Wenqiao	64	597 - 323919	1375 - 334413	11 (tri-deca)	(Jiang et al., 2014)
Sediment	Guangdong Province	Longtang	6^a	3.2 - 200	4.8 - 386	8 (tri-deca)	(Wang et al., 2011d)
		Guiyu	6^a 6^b 5^b	16.9–62.2 13.9–53.9 15–57	4434 – 16088 55 – 445 52 – 365	14 (mono-deca)	(Luo et al., 2007)
	Zhejiang Province	Fengjiang	8^a	Max: 58400	10 - 60000	7 (tetra-deca)	(Wang et al., 2011c)

a – river or pond surface sediment; b – river bottom sediment

BDE-209 was the predominant congener in the majority of dust, soil and sediment samples with the exception of sediment samples from Nanyang River in Guiyu where the main congeners found in commercial penta-BDE formulations (i.e., BDE-47 and BDE-99) were predominant.

Taking into account that sediments may play an important role in assessing ecological risks of PBDEs to aquatic organisms and serve as a reservoir of pollutants that may enter the food chain; more studies are needed to investigate the load and distribution of PBDEs in freshwater sediments in both Taizhou and Guangdong e-waste recycling areas. Traditionally, people residing at e-waste sites in China raise poultry (ducks and chickens) close to or immediately on the banks of the ponds and watercourses in the area, as well as consuming locally caught fish and shrimp. Hence, investigating contamination of sediments and soils by PBDEs is an important factor in estimating indirect impacts on humans.

For comparison, PBDE concentrations in sediments from non-e-waste impacted areas in China are significantly lower than those reported in Table 1-5 for e-waste sites. For example:

- the range of PBDEs (8 congeners, from tri- to deca-BDE) detected in sediments from three main rivers in Shanghai was 11 ng/g to 64 ng/g dw (Wu et al., 2013);
- soils from urban areas in Shanghai (main roadsides, greenbelts, parks, residential, and commercial districts) ranged in PBDEs (29 congeners, from mono- to deca-BDE) concentrations from 24 ng/g to 3799 ng/g dw with BDE-209 as the main contributor (range: 1.3 to 2910 ng/g dw) (Jiang et al., 2010).
- agricultural soils in the Yangtze River Delta contained PBDEs in the range of < 1 ng/g to 382 ng/g dw (Sun et al., 2016);
- PBDEs in marine sediments from Sanggou Bay in the Yellow Sea ranged from 1.4 to 10.5 ng/g dw (Wang et al., 2016).

This comparison clearly shows the significance of uncontrolled e-waste recycling activities as sources of PBDEs resulting in severe contamination of the local environment. This has a wider regional and global impact as PBDEs may be transported across long distances by air particulates (Deng et al., 2007) as well as being distributed by land runoffs (Wang et al., 2016).

1.2.2.2 Biota

There are several studies reporting PBDEs in the biota at informal/illegal e-waste sites in China; however, making direct comparisons between them is complicated by a number of issues:

- They analyse for different PBDEs congeners and differing numbers of congeners, with some studies omitting BDE-209;
- They variously present PBDEs concentrations either on a wet weight or lipid weight basis;
- Different studies report PBDE concentrations in different formats. For example, some report PBDEs as a sum of all analysed congeners in addition to a few selected individual congeners rather than presenting results for all individual congeners. Such inconsistencies in reporting format hinders comparison of concentrations of specific individual congeners between studies;
- Data in some studies are reported in a graphical style that, on the one hand, makes the findings more visually apparent, but on the other hand, hinders comparison with non-graphical representations in other studies;
- The studies employ differing methods of statistical data interpretation (i.e., either arithmetic means, geometric means, median or range);

- The number of samples in certain studies is not representative, sometimes limited to 1 or 2 only.

Notwithstanding these caveats, these studies are important in understanding the ‘life-cycle’ of PBDEs starting from their release into the environment to entering the food chain and, finally, to entering the human body. As mentioned in section 1.2.1.1, the release of PBDEs during uncontrolled e-waste recycling causes significant contamination of environmental compartments including soils and the sediments of local watercourses. Such contamination may either result from direct discharge of wastes formed during various e-waste activities or be brought in with the runoff from contaminated soils surrounding e-waste workshops and with deposition of the particulate matter. In turn, both aquatic and land-based organisms also become contaminated because PBDEs may accumulate in lipid-containing tissues as was discussed in section 1.2.1. The next sections (1.2.2.2.1 and 1.2.2.2.2) present an overview of the main findings about concentrations of PBDEs detected in biota at informal e-waste recycling sites in China with specific focus on biota that form part of the human diet.

1.2.2.2.1 Aquatic organisms

There are several studies reporting levels of PBDEs in aquatic biota at e-waste recycling sites that, similarly to studies on environmental levels, were mostly conducted in and around Guangdong Province and Taizhou City, Zhejiang Province, in China.

Different parts of tilapia (n=9, abdomen muscle, back muscle and tail muscle) and bighead carp (n=6, abdomen muscle, back muscle, tail muscle and liver) from two rivers in Guiyu (Lianjiang River and Nanyang River) contained mean PBDE concentrations (11 congeners, tri-decabrominated) in the range of 67.8 ng/g wet weight (ww) in tilapia back muscle (Lianjiang River) to 2687 ng/g ww in liver of bighead carp (Nanyang River) (Luo et al., 2007). Though mean PBDE concentrations in abdomen muscle of bighead carp (1088 ng/g ww) were around double those in tilapia (483 ng/g ww), they were significantly higher than in samples of tilapia from control sites (range of means: nd – 115 ng/g ww), which clearly indicates the impact of e-waste recycling in the Guiyu area. A similar range of PBDEs concentrations has been reported in two further studies:

- in freshwater fish obtained from local markets in Guiyu (n=7, 22 congeners, mono-heptabrominated) with the mean of 2180 ng/g ww (Chan et al., 2013);
- and in fish (water snake, snakehead, mud carp, and crucian carp) from a reservoir surrounded by several informal e-waste recycling workshops in Longtang (Wu et al., 2008) that ranged from 316 ng/g ww in crucian carp (n=6, median value) to 1091 ng/g ww in water snake (n=2, median value). The latter study also reported PBDEs concentration in prawns from the same area at 253 ng/g ww (n=3, median value), which was much higher than that reported for coastal areas in South China (mean: 0.24 ng/g ww) (Guo et al., 2010a).

For Taizhou e-waste recycling sites, there is less consistency in the data: while Chan et al. (2013) reported mean PBDEs concentration at 60.4 ng/g ww in freshwater fish, another study observed much higher concentrations with the mean of 2755 ng/g ww (11 congeners, tri-through deca-brominated) (Jiang et al., 2014). Though Chan et al. (2013) did not analyse BDE-209, Jiang et al. (2014) reported BDE-209 in fish to be only a minor contributor to the total PBDEs, making it a less significant point of comparison in this instance. Both studies found BDE-47 to be the principal congener, which is consistent with the other studies mentioned above. Chan et al. (2013) also reported PBDE concentrations in marine fish and shellfish from both Guiyu and Taizhou that were significantly lower than that observed in freshwater fish.

Overall, in comparison to fish from non-e-waste impacted area in China, for example, in study from Nanjing (Su et al., 2012) and from 11 typical fishery-producing regions of Guangdong

Province (Meng et al., 2007a), all e-waste impacted aquatic organisms were more severally contaminated with PBDEs. Moreover, PBDEs may accumulate in organisms to levels exceeding those in the surrounding environment. This process is defined as bioaccumulation and expressed as bioaccumulation factors (BAFs) (i.e., the ratio of the observed concentration of the chemical in biota to the concentration in corresponding living media) that is presented logarithmically (Log BAF) in most cases. For example, Log BAFs have been reported for several PBDEs and several fish species from e-waste impacted areas in South China (Wu et al., 2008) ranging from 2.0 to 5.3 with the highest value calculated for BDE-154 in water snake. Additionally, the values for some congeners, including BDE-85 and BDE-99, were lower than expected, which authors attributed to metabolic processes in fish. Several studies have previously reported biotransformation of certain PBDEs in carp including debromination (Stapleton et al., 2004a, 2004b; Benedict et al., 2007) leading to the formation of lower-brominated congeners BDE-47 and BDE-154 from BDE-99 and BDE-183, respectively, while BDE-209 was shown to debrominate to nona- through penta-brominated BDEs (Stapleton et al., 2004a, 2006). Finally, biomagnification at each trophic level may lead to food chain magnification as it was shown in the study on fish from e-waste recycling sites in South China (Wu et al., 2009) that reported significant biomagnification for BDE-47, BDE-100, and BDE-154 in the studied fresh water food chain (snails - fish & prawns - predator fish).

1.2.2.2.2 Domestic fowl and their eggs

The data on PBDEs levels in domestic fowl originating from e-waste recycling sites in China is not extensive and varies most likely to reasons similar to those outlined in section 1.2.2.2. Again, as mentioned in sections 1.2.2.2 and 1.2.2.2.1, most studies investigating PBDEs in fowl were focused on e-waste sites around Guangdong Province and Taizhou City in Zhejiang Province. Chickens and, to a lesser extent, ducks and geese have been investigated in the studies discussed below as they represent the most consumed meat type in China (Luo et al., 2009a).

Guangdong Province. Various parts of chickens (n=12) that foraged at e-waste sites in South China were investigated for presence of PBDEs (12 congeners, tetra-decabrominated) including liver, muscle, heart, lung, fat, brain, stomach, intestine, ovary/testis, kidney and serum (Zheng et al., 2015a). The highest median concentrations of PBDEs were detected in chicken liver (1660 ng/g lw), followed by muscle (1450 ng/g lw) while the maximum concentration of PBDEs was detected in muscle (48200 ng/g lw). Zheng et al. (2015b) specified that BDE-209 and BDE-183 were the dominating congeners; however, no data were presented on their concentrations. A similar study conducted earlier in Longtong and Shijiao e-waste sites (Luo et al., 2009a) reported significantly lower concentrations of PBDEs than that in the study by Zheng et al. (2015b): (16 congeners, tri-decabrominated) in chicken muscle (16 male and 17 female) and duck muscle (9 males and females each) with median concentrations of 66 ng/g lw, 55 ng/g, 6.6 ng/g lw, and 3.9 ng/glw for male and female chickens and ducks, respectively. In the liver, median concentrations of PBDEs of 41 ng/g lw, 28 ng/g lw, 8.5 ng/g lw, and 6.3 ng/g lw were detected for the same respective matrices. BDE-209 was the principal congener in all samples, followed by BDE-207 with the exception of one male chicken muscle sample with a dominance of BDE-183 that was attributed to contamination of nearby road dust by technical octa-BDEs. Metabolic debromination of BDE-209 was suggested by Luo et al. (2009) as the reason for the high proportion of BDE-207 in bird tissues. A single sample of poultry and a fowl egg of unspecified origin collected from another e-waste site in Guiyu contained PBDEs at 8.95 ng/g ww and 8.21 ng/g ww, respectively (Chan et al., 2013); however, as data were presented on a wet weight basis, it is difficult to compare them to other studies. More recent study in Guangdong Province (Nie et al., 2015) reported mean PBDEs in chicken and goose samples from e-waste open burning sites as 4350 ng/g lw and 128 ng/g lw, respectively, which was in the same order of magnitude as reported by Zheng et al. (2015b) for chicken but not for goose samples. Again, BDE-209 was the dominating congener in both chicken and goose samples in the study by Nie et al. (2015), as was also reported by the majority of other studies in section 1.2.2.2.2.

Domestic fowl eggs have also been the subject of several studies investigating contamination by PBDEs. Chicken eggs (n=41) obtained from farmers at three e-waste sites in Qingyuan (Zheng et al., 2012) contained PBDEs (19 congeners, tri-decabrominated) ranging in mean values from 2640 ng/g lw to 14100 ng/g lw. Similar data were reported from 4 e-waste sites in Guiyu (Zeng et al., 2016): mean concentrations of PBDEs (17 congeners, tri-decabrominated) concentrations in two types of eggs, chicken (n=20) and goose (n=20), were in the range of 3500 ng/g lw to 14000 ng/g lw and 1200 ng/g lw to 2100 ng/g lw, respectively. The latter study also showed differences in habitat- and species-dependent accumulation of PBDEs reflected in the relative higher proportion of hepta- to deca-BDEs in goose eggs than in chicken eggs.

Taizhou City area. There are a limited number of studies reporting PBDEs in fowl from e-waste sites in Taizhou. The range of mean PBDEs (7 congeners, tetra-decabrominated) concentrations in various chicken parts (n=4) (fat, testis, kidney, lung, muscle, intestine, liver, blood, and brain) collected from the e-waste site in Wenling (Qin et al., 2011) was from 16 ng/g lw in brain to 3140 ng/g lw in fat. BDE-209 was the dominating congener in all investigated matrices with the highest mean concentrations of 2970 ng/g lw and 2490 ng/g lw in fat and blood, respectively. Qin et al. (2011) also reported mean PBDEs concentrations in chicken eggs (n=15) at 564 n g/g lw (38.3 ng/g ww), with BDE-209 again as the main contributor at 17.4 ng/g ww, followed by BDE-100 at 9.59 ng/g ww. Significantly higher PBDE concentrations than in the latter study were reported by Jiang et al. (2014) in Taizhou: mean ∑PBDEs in eggs and mixed meat at 2423 ng/g ww and 1799 ng/g ww, respectively. The lowest PBDE concentrations in the Taizhou area were reported by Chan et al. (2013) in a single sample of poultry and an egg (unspecified egg origin, at 1.16 ng/g ww and 1.23 ng/g ww, respectively (Chan et al., 2013).

As for aquatic organisms (discussed in section 1.2.2.2.1), biomagnification of several PBDEs in the terrestrial food chain has also been confirmed (Nie et al., 2015). Biomagnification factors (BMFs) that have been calculated in turtle dove food chains were the highest for BDE-154 (11.9), followed by BDE-202 (11.6), while BMFs for BDE-153 and BDE-209 accounted for 7.1 and 4.4, respectively.

1.2.3 Human exposure to PBDEs

There are three principal routes of human exposure to toxic chemicals (U.S. EPA, 2014b):

- Ingestion
- Inhalation
- Dermal absorption.

The physicochemical properties of PBDEs (discussed in section 1.2.1) determine their main routes of human exposure - ingestion of contaminated food, ingestion of dust and soil as well as dust inhalation (Ni et al., 2012; Frederiksen et al., 2009; U.S. EPA, 2010b; Law et al., 2008; Harrad and Abdallah, 2011; Trudel et al., 2011; Huwe et al., 2008; Muenhor et al., 2010). Dermal absorption of dust or soil, though contributing to the total human exposure to PBDEs, is thought to play a less significant role than their ingestion and inhalation (U.S. EPA, 2010b; Ni and Zeng, 2013; Abafe and Martincigh, 2015; Ni et al., 2012). To assess the human health effects stemming from exposure to PBDEs, health-based limit values for exposure to selected congeners or homologue groups have been promulgated (Table 1-6). However, not all of the studies discussed in the section below (see also Table 1-7) have reported estimated human exposure to those PBDEs for which health-based exposure limits are available, hence, limited comparison can be drawn. Moreover, as was mentioned in section 1.2.2.2, the comparison of these studies is challenging due to differences in the studies' scope, design, and reporting parameters.

Table 1-6 Health based limit values promulgated for PBDEs, in ng/kg bw/day

	Lower brominated PBDEs	**BDE-47**	**BDE-99**	**penta-BDE homologue**	**BDE-153**	**octa-BDE homologue**	**BDE-209**
RfD [a,b,c]	-	100	100	2000	200	3000	7000
oral slope factor for carcinogenic risk [a]	-	-	-	-	-	-	700
NAEL[d]	-	-	0.23 – 0.30	-	-	-	-
NAEL[e]	-	-	18.8 - 41.4	-	-	-	-
acute minimal risk level, oral exposure [f]	60	-	-	-	-	-	1000
intermediate minimal risk level, oral exposure [f]	3	-	-	-	-	-	200

a,b,c - Reference Dose (RfD) values promulgated by the U.S. EPA (U.S. EPA, 2008b, 2008c, 2008a); d,e - Expected human no adverse effect level (NAEL) for impaired spermatogenesis and for impaired neurodevelopmental toxicity (Bakker et al., 2008); f - (ATSDR, 2016).

For example, estimation of human exposure in some studies based only on a single type of matrix (Zheng et al., 2012; Zeng et al., 2016) or two types (Qin et al., 2011; Luo et al., 2009a) while other studies that considered a wider range of matrixes have sometimes insufficient sample population, limited in some cases to only one (Chan et al., 2013) or a few samples (Zhao et al., 2009b).

In addition, some of the studies reported estimated daily intake of PBDEs (in ng/day), but did not provide data normalised to a body weight, again, making the comparison between studies less efficient. Methodological differences in exposure estimation have also played an important role during comparison of the data from different studies. For example, while in the study by Zeng et al. (2016) the estimation of child exposure was calculated in a similar way as for adults (e.g., utilizing the data on local daily consumption rates and typical body weight of a child from the investigated area), in the study by Jiang et al. (2014) the assumption that child's intake of PBDEs via diet is approximately 57% of that for an adult was used resulting in child's exposure

Table 1-7 Estimated human exposure to PBDEs at e-waste recycling sites in China from published data

Location	Area	Samples categories (number of samples)	Main food category contributor	PBDE congeners	Mean ∑PBDEs intake, ng/day	Mean exposure, ng/kg bw/day				Source
						BDE-47	BDE-99	BDE-209	∑PBDE	
Guangdong Province	Guiyu	Fish (8), shellfish (1), pork (1), poultry (1), eggs (1), cereal (1), vegetables (5)	Fish	22 tri-hepta	55886	584	n/a	n/a	931	(Chan et al., 2013)
	Longtang	Chicken (33), duck (18)	Chicken	16 tri-deca	67.8	n/a	n/a	n/a	n/a	(Luo et al., 2009a)
	Guiyu	Chicken eggs (20)	-	17 tri-deca	19000	1.8 – 12.5[a] 7.7 – 54[b]	4.1 – 13 [a] 18 - 58 [b]	23 – 907 [a] 99 – 3900 [b]	55 – 1614 [a] 235 – 6943 [b]	(Zeng et al., 2016)
	Guiyu	Goose eggs (20)	-	17 tri-deca	5500	2.2 – 19.2 [a] 9.3 - 82 [b]	1.7 – 18 [a] 7.4 - 79 [b]	2.2 – 248 [a] 9.6 - 1067 [b]	14 – 462[a] 60 – 1988 [b]	(Zeng et al., 2016)
	Qingyuan	Chicken eggs (12) Chicken eggs (11) Chicken eggs (10)	-	19 tri-deca	6420 20000 4200	n/a	n/a	n/a	n/a	(Zheng et al., 2012)
Zhejiang Province	Taizhou	Eggs (6), pulses (2), fish (2), pork (unspecified), chicken (unspecified), rice, vegetables	Fish	12 tri-deca	196	n/a	n/a	n/a	n/a	(Zhao et al., 2009b)
	Taizhou	Fish (10), shellfish (9), pork (1), poultry (1), eggs (1), cereal (1), vegetables (14)	Fish	22 tri-hepta	2683	n/a	n/a	n/a	44.7	(Chan et al., 2013)
	Taizhou	126 samples in 6 categories: cereals, vegetables, beans, eggs, meat, fish & shrimp	Cereals	11 tri-deca	1671[a] 952[b]	n/a	n/a	n/a	n/a	(Jiang et al., 2014)
	Wenling	Chicken meat (4), chicken eggs (15)	Eggs	7 tetra-deca	810	1.81	0.69	7.24	13.5	(Qin et al., 2011)

a – range for adults; b – range for children; n/a – not available.

lower than adult's by default, which contradicted with finding of the study by Zeng et al. (2016) that reported childrens' exposure to PBDEs via chicken eggs to exceed that for adults.

Limited number of studies (presented in Table 1-7) reported body weight normalised exposures to individual BDEs (Zeng et al., 2016; Qin et al., 2011), however, they used a different style of data reporting, hence, it is difficult to compare data between studies as well as discuss them in relation to available health-based exposure limits.

Additionally, the exposure to PBDEs via breast milk is an important parameter in evaluation of these chemicals health impacts on infants residing at e-waste sites. For example, estimated daily intake of penta-BDEs in Taizhou e-waste site of infants via breast milk (mean: 572 ± 839 ng/kg bw/day) was significantly higher than that estimated for infants from a control site (mean: 10.1 ng/kg bw/day) (Leung et al., 2010). Moreover, the maximum infant exposure to PBDEs via breast milk in the study by Leung et al. (2240 ng/kg bw/day) exceeds the U.S. EPA's RfD for penta-BDE of 2000 ng/kg bw/day (see Table 1-6) indicating a potential danger to health. PBDEs express a number of toxic effects on developing organisms that may have life-long health implications (section 1.1.4). Studies estimating human exposure to PBDEs via dust ingestion and inhalation at e-waste sites in China are limited (Table 1-8). Again, due to differences in data reporting style (i.e., range, range of medians, and means of estimated PBDE exposure) comparison is complex. It was not possible to predict PBDE health impacts following exposure to dust reported in these studies (Table 1-8) as none estimated exposures to individual PBDE congeners. However, it was possible to compare two of the studies, revealing that childrens' exposure to PBDEs via dust is more significant than for adults: estimated exposure range for child from the e-waste site was reported at 20.3 – 817 ng/day (Wang et al., 2014b) while for a child from the general population in the PRD region ofChina it was 101 – 404 ng/day (Kang et al., 2011). This was consistent with other studies worldwide (de Wit et al., 2012; Frederiksen et al., 2009; Wu et al., 2015). No differences were observed in PBDE exposure estimates via dust for adults between the studies by Wang et al. (2014b) and by Kang et al. (2011).

Table 1-8 Estimated human PBDEs exposure via dust at e-waste recycling sites and among general population in China from published data

Area	Route of exposure	PBDE congeners	∑PBDEs intake, ng/day	Exposure ∑PBDEs, ng/kg bw/day	Source
Longtang, Guiyu	Ingestion	8 tri-deca	n/a	0.20–18.1^{c} 2.85–264^{d}	(Zheng et al., 2015b)
Guangzhou	Ingestion	28 di-deca	37^{e} 92.5^{f}	n/a	(Wang et al., 2010)
Guangzhou	Ingestion & Inhalation	26 mono-deca	5.1 – 228 ^{c} 20.3 - 817 ^{d}	n/a	(Wang et al., 2014b)
Taizhou	Inhalation	11 tri-deca	10.9 – 9077^{a} 138 – 17283^{b}	n/a	(Jiang et al., 2014)
PRD region, non-e-waste related	Ingestion	27 mono-deca	1.4 - 277 ^{c} 101 - 404 ^{d}	n/a	(Kang et al., 2011)

a– range for adults; b – range for children; c – range of median for adults; d – range of median for toddler; e- mean for adult; f – mean for child.

Nonetheless, existing information on human exposure via diet and dust ingestion around e-waste sites in China, though not extensive, is somewhat alarming. High daily PBDE intakes via ingestion of both local diet and dust and inhalation (see Tables 1-7 and 1-8) are of concern because they exceed significantly corresponding values obtained for reference or control sites in all studies discussed in this section. Other studies that estimated exposure to PBDEs in non-e-waste regions of China have also reported significantly lower exposure to PBDEs (Gong et al., 2015; Kang et al., 2011) than for e-waste sites, with the exception of the adult exposure via dust ingestion and inhalation reported by Wang et al. (2014b) (Guangzhou area, range: 5.1 – 228 ng/day) that was similar to PBDE exposure via dust ingestion for general population residing within PRD region in China (Kang et al., 2011). More comprehensive and systematic research in needed, which would consider both main matrices of human exposure (i.e., diet and dust), include all main types of food originating from e-waste sites, and have representative sample size. Finally, the inclusion of BDE-209 in analyses is also important as this congener appears to be the main contributor to total PBDEs in many investigated matrices (see sections 1.2.2). Body weight normalised exposure estimation is important also to allow comparison with health-based exposure limits, thereby facilitating human health impact assessment.

1.2.4 Body burden of PBDEs in humans

To better understand possible human health impacts of informal e-waste recycling, internal exposure to PBDEs (i.e., exposure to PBDEs accumulated in the human body) has also been investigated by the direct measurement of PBDEs concentrations in various body compartments. The main matrices analysed are as follows:

- Whole blood or blood serum of both adults and children;
- Breast milk;
- Human body tissues including adipose tissue, umbilical cord, and placenta;
- Hair.

As blood (whole blood or blood serum) is considered a very important compartment for biomonitoring of persistent organic pollutants (Porta et al., 2008), it was the most frequently investigated human body compartment for the content of PBDEs among population at e-wastes sites. Breast milk from women residing at e-waste sites has also been analysed for PBDEs, however, to a much lesser extent than blood. The main findings are summarised in Table 1-9. PBDE concentrations in human blood and blood serum varied greatly between different e-waste sites in China. The highest median ∑PBDEs concentration in adult serum was reported for a Guiyu e-waste site at 600 ng/g lw with BDE-209 predominant (median: 310 ng/g lw)(Bi et al., 2007).

Table 1-9 Concentrations (median, mean and range) of major PBDEs (ng/g lw) in humans residing at e-waste recycling cites in China. n/a – not analysed or not available, nd – not detected

Age group	Matrix	Location	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-197	BDE-207	BDE-209	∑PBDE	Source
Adult	Serum	Guangzhou	1.0 ^{med} 0.36 - 3.6	0.15 ^{med} 0.08 - 2.3	0.36 ^{med} 0.08 - 7.4	0.10 ^{med} 0.0 - 1.2	1.4 ^{med} 0.36 - 6.4	0.31 ^{med} 0.0 - 1.3	n/a	n/a	n/a	4.4 ^{med} 1.6 - 17	(Bi et al., 2006) [a]
	Serum	Guiyu	9.5 ^{med} 13 ^{mean} nd - 180	1.3 ^{med} 3.7 ^{mean} nd - 26	310 ^{med} 340 ^{mean} nd - 3100	2.3 ^{med} 5.3 ^{mean} nd - 31	18 ^{med} 37 ^{mean} 3.3 - 270	5.5 ^{med} 9.2 ^{mean} nd - 200	27 ^{med} 29 ^{mean} 0.3 - 2400	73 ^{med} 77 ^{mean} nd - 1400	310 ^{med} 340 ^{mean} nd - 3100	600 ^{med} 580 ^{mean} 140 - 8500	(Bi et al., 2007)[b]
	Serum	Guangdong	6.7 ^{med} 1.5 - 161	1.0 ^{med} 0.1 – 6.3	1.4 ^{med} 0.4 – 29.7	0.8 ^{med} 0.1 – 3.5	9.0 ^{med} 0.9 - 245	4.7 ^{med} 0.5 – 60.2	2.1 ^{med} 0.1 – 31.2	10.0 ^{med} 0.9 – 66.2	83.5 ^{med} nd - 3436	n/a	(Qu et al., 2007) [e]
	Serum	Wenling	0.97 ^{med} 4.0 ^{mean} nd - 177	0.12 ^{med} 0.69 ^{mean} nd - 30.1	0.33 ^{med} 1.36 ^{mean} nd – 60.6	0.41 ^{med} 0.82 ^{mean} nd – 7.33	2.54 ^{med} 5.84 ^{mean} 0.16 - 46	0.81 ^{med} 1.86 ^{mean} nd – 16.1	n/a	n/a	2.39 ^{med} 6.93 ^{mean} nd – 80.3	9.77 ^{med} 22.7 ^{mean} 0.4 - 370	(Lv et al., 2015) [f]
	Serum	Luqiao	6.2 ^{med} 9.6 ^{mean} 2.3 – 88.2	1.3 ^{med} 3.2 ^{mean} 0.2 – 37.6	3.6 ^{med} 12.5 ^{mean} 0.8 – 165	3.9 ^{med} 16.6 ^{mean} 1.2 – 161	14.9 ^{med} 54.8 ^{mean} 3.0 – 771	13.5 ^{med} 36.7 ^{mean} 0.5 – 240	n/a	n/a	n/a	51.6 ^{med} 139 ^{mean} 17.1 – 864	(Xu et al., 2015) [i]
	Serum	North China	0.5 ^{med} 0.2 – 0.9	0.14 ^{med} 0.09 – 0.21	0.08 ^{med} 0.05 – 0.13		1.45 ^{med} 0.9 – 2.4	0.53 ^{med} 0.34 – 1.21			5.73 ^{med} 1.8 – 12.3	23 ^{med} 10.9 – 34.8	(Yang et al., 2013)[k]
	Blood	Luqiao	3.6 ^{med} 5.8 ^{mean} 1.2 – 51	0.7 ^{med} 0.9 ^{mean} 0.1 – 4.9	1.1 ^{med} 2.0 ^{mean} 0.4 – 17.8	0.8 ^{med} 1.0 ^{mean} 0.1 – 6.1	10.5 ^{med} 14.6 ^{mean} 2.4 – 68.5	3.4 ^{med} 3.9 ^{mean} 1.0 – 11.6	n/a	n/a	64.5 ^{med} 87.2 ^{mean} 17.2 – 378	80.9 ^{med} 118 ^{mean} 39.9 – 396	(Zhao et al., 2010) [c]
	Blood	Wenling	25.3 ^{med} 44.7 ^{mean} 2.9 – 222	3.1 ^{med} 4.1 ^{mean} 0.6 – 21.2	5.7 ^{med} 7.9 ^{mean} 1.1 – 23.0	1.7 ^{med} 2.3 ^{mean} 0.5 – 12.6	21.9 ^{med} 26.1 ^{mean} 8.4 – 119	6.7 ^{med} 7.3 ^{mean} 2.6 – 22.8	n/a	n/a	172 ^{med} 210 ^{mean} 85 – 556	315 ^{med} 357 ^{mean} 132 – 714	(Zhao et al., 2010) [c]
	Blood	Southeast China	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	382 ^{med} 77 - 8452	(Yuan et al., 2008) [g]
	Breast milk	Guangzhou	1.3 ^{med} 0.7 - 4.7	0.19 ^{med} 0.07 - 0.53	0.23 ^{med} 0.09 - 0.78	0.11 ^{med} 0.01 - 0.22	0.80 ^{med} 0.35 - 1.8	0.18 ^{med} 0.0 - 0.40	n/a	n/a	n/a	3.5 ^{med} 1.7 - 7.2	(Bi et al., 2006) [a]
	Breast milk	Taizhou	27.5 2.0 - 109	1.6 0.2 – 5.6	10.8 0.8 – 45.6	1.0 0.1 – 3.9	16.9 1.0 – 60.8	1.5 0.3 – 4.4	n/a	n/a	n/a	117 ^{mean} 8.9 - 457	(Leung et al., 2010)[l]
	Breast milk	Wenling	1.8 ^{med} 3.1 ^{mean} 0.4 – 29.0	0.4 ^{med} 0.60 ^{mean} 0.1 – 2.8	0.8 ^{med} 1.0 ^{mean} 0.1 – 4.4	0.8 ^{med} 2.3 ^{mean} 0.3 – 22.2	3.4 ^{med} 8.9 ^{mean} 2.2 – 31.6	0.9 ^{med} 1.3 ^{mean} 0.4 – 4.5	n/a	n/a	5.5 ^{med} 7.4 ^{mean} nd – 45.0	19.5 ^{med} 25.7 ^{mean} 7.7 – 90.6	(Li et al., 2016) [m]
Foetus	Serum	Guangzhou	1.4 ^{med} 0.03 – 4.9	0.22 ^{med} 0.04-0.86	0.47 ^{med} 0.17-3.4	0.12 ^{med} 0.0-0.45	0.80 ^{med} 0.09-5.2	0.20 ^{med} 0.0-1.5	n/a	n/a	n/a	3.9 ^{med} 1.5-12	(Bi et al., 2006) [a]
Child	Blood	Luqiao	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	664 ^{mean}	(Han et al., 2011)[d]
	Blood	Luqiao	4.6 ^{med} 4.0 ^{mean} 0.7 – 5.5	2.9 ^{med} 2.7 ^{mean} 0.2 – 4.4	13.8 ^{med} 12.4 ^{mean} 0.5 – 17.1	1.4 ^{med} 1.8 ^{mean} 0.2 – 5.4	3.4 ^{med} 3.8 ^{mean} 2.1 – 8.0	1.5 ^{med} 1.5 ^{mean} 0.8 – 2.4	n/a	n/a	n/a	31.9 ^{med} 32.1 ^{mean} 8.1 – 65.2	(Xu et al., 2014b) [h]
	Blood	Luqiao	4.0 ^{mean} 0.7 – 5.5	2.7 ^{mean} 0.2 –4.4	12.4 ^{mean} 0.5 – 17.1	1.8 ^{mean} 0.2 – 5.4	3.8 ^{mean} 2.1 – 8.0	1.5 ^{mean} 0.8 – 2.4	n/a	n/a	n/a	32.1 ^{mean} 8.1 – 65.2	(Shen et al., 2010a) [j]

a – 21 samples of maternal and foetal blood samples as well as 27 breast milk samples collected from patients of Guangzhou Second People's Hospital, Guangdong Province, 7 P BDE congeners analysed from tri- through hepta-brominated;
b - 26 adults of Guiyu town, Shantou City, Guangdong Province, 16 PBDE congeners analysed from tri- through deca-brominated;
c - 27 adults of Luqiao (16 male, 11 female) and 23 adults of Wenling (7 male, 16 female) from Taizhou, Zhejiang, 8 PBDE congeners from tri- through deca-brominated;
d – 369 children aged 6-8 years old residing in Luqiao for ≥5 years, 15 PBDEs from mono- through hepta-brominated;
e - 20 workers from electronic waste dismantling region in Guangdong, 14 PBDE congeners, tri- through deca-brominated;
f – 64 women residing at e-waste sites in Wenling, Zhejiang Province; 8 PBDE congeners, tri- through deca-brominated;
g – 23 manual e-waste dismantling workers form southeast China, no information on the PBDE congeners analysed;
h – 21children of 8 years old from Luqiao e-waste site, 16 PBDE congeners, mono- through hepta-brominated;
i – 40 subject of 15 - 65 years old from Luqiao e-waste site, 9 PBDE congeners, tri- through hepta-brominated;
j – 21 children's (aged 5-11 years old) blood samples analysed in 7 pools, 16 PBDE congeners, tri- through hepta-brominated;
k – 35 e-waste dismantling workers and local residents from area about 50 km southwest of Tianjin in Northern China, 19 PBDE congeners, tetra- through deca-brominated;
l - 5 women from Taizhou e-waste sites, 36 congeners, tri- through hepta-brominated;
m – 25 women residing in Wenling e-waste site for more than 20 years but not involved into e-waste operations, 8 PBDE congeners from tri- through deca-brominated.

Similar levels of ∑PBDEs (mean: 664 ng/g lw) to that reported in the study by Bi et al. (2006) were determined in blood of children from Luqiao (Han et al., 2011), however, congener specific data were not available for this study. A further two studies, which reported ∑PBDE concentrations in the same order of magnitude as studies by Bi et al. (2007) and Han et al. (2011), were conducted in adults in Wenling (∑PBDEs median: 315 ng/g lw; BDE-209 median: 172 ng/g lw) (Zhao et al., 2010) and South East China (∑PBDEs median: 382 ng/g lw) (Yuan et al., 2008). The latter study, however, did not provide information on the PBDE congeners considered in the study. Some studies reported lower ∑PBDEs concentrations in adults' blood (Xu et al., 2015; Bi et al., 2006) than in studies mentioned above, most probably due to omission of BDE-209, which dominated when analysed in other studies. Two studies investigating blood of children from Luqiao e-waste site (Shen et al., 2010b; Xu et al., 2014b) reported identical results for mean ∑PBDEs (32.1 ng/g lw) as well as for other BDE congeners, however without BDE-209 analysed in both studies (see Table 1-9). In comparison, ∑PBDE concentrations (9 congeners, tetra-decabrominated) detected in blood of children from mountain area of Taizhou, Zhejiang Province, which has no impact of e-waste recycling, were reported at 7.2 ng/g lw (median for 58 children aged 9-12 years old, range: 2.7-32.2 ng/g lw) (Zhang et al., 2011c) with BDE-209 as the primary congener at median concentration of 1.7 ng/g lw. This was significantly lower than ∑PBDEs in blood of children residing at e-waste areas of Taizhou (Xu et al., 2014b) (median: 31.9 ng/g lw) even allowing for the omission of BDE-209 in the latter study.

Information on PBDE levels in breast milk from women residing around e-waste sites in China is limited. Two earlier studies by Bi et al. (2006) and by Leung et al. (2010) reported ∑PBDE at 3.5 ng/g lw (median of 27 samples) in milk from Guangzhou and 117 ng/g lw (mean of 5 samples) in milk from Wenling, respectively; BDE-209 was not analysed in either study. The most recent study by Li et al. (2016) - conducted in Wenling - included BDE-209 and reported concentrations of ∑PBDEs as 19.5 ng/g lw and 25.7 ng/g lw for median and mean, respectively. BDE-209 dominated in the latter study at concentrations of 5.5 ng/g lw and 7.7 ng/g lw for median and mean, respectively. Li et al.'s (2016) study also compared PBDE levels in milk of mothers residing at e-waste sites for a different duration of time (20 or more years vs 3 or less years) and concluded that women residing for a long time adjacent to e-waste recycling areas are more likely to contribute significantly to infants exposure to PBDEs via breast milk than women with short duration of living within e-waste areas. In comparison to non-e-waste recycling areas, PBDEs concentrations in breast milk from e-waste recycling sites were relatively high. For example, levels of PBDEs detected in human breast milk in urban areas (mean: 7.7 ng/g lw) and rural areas (mean: 4.7 ng/g lw) in China (Sudaryanto et al., 2008) were much lower than in breast milk from women at Taizhou e-waste sites (mean: 117 ng/g lw)

(Leung et al., 2010), but were within the range reported for breast milk from women at a Guangzhou e-waste site (median: 3.5 ng/g lw, range: 1.7 - 7.2 ng/g lw) (Bi et al., 2006), though the latter study was based on a cohort of non-occupationally exposed women.

Concentrations of PBDEs in hair of residents of e-waste sites in China have also been reported in several studies (Leung et al., 2010; Ma et al., 2011; Zhao et al., 2008; Zheng et al., 2011) with a maximum mean value of 157 ng/g dw detected in e-waste workers in Taizhou (Ma et al., 2011) that was higher than corresponding control cohort. Other human body compartments that showed elevated PBDE concentrations in residents of e-waste areas included adipose tissue (Lv et al., 2015), placenta (Xu et al., 2014a), as well as kidney, liver and lung of cancer patients (Zhao et al., 2009a).

Considering all studies discussed in the current section, it is clear that PBDE body burdens in people living at e-waste recycling areas is significantly higher, in most cases, than those reported for other areas in China that have no e-waste recycling operations. Most worryingly, it appears that children born to mothers living at e-waste sites have already been exposed to PBDEs via placental transfer (Xu et al., 2014a) and that they will be chronically exposed to these contaminants from the first days of their lives through PBDE-contaminated breast milk, dust, soil and locally produced foods. As mentioned above, children as young as 6-8 years old may already have PBDE body burdens as high as adults. While toxic effects for a limited number of PBDE congeners on children's health are already known, the action of a number of other PBDE congeners is still undiscovered. Therefore, we still do not know the full extent of the consequences of PBDE exposure and in particular the health outcomes that children chronically exposed to high PBDE levels may experience throughout their childhood and later life. Additionally, we still have insufficient knowledge about how the processes of PBDE biomagnification occur in humans and particularly at places with high levels of exposure to PBDEs. As discussed in section 1.2.2.2, PBDE biomagnification has been observed in both aquatic (Wu et al., 2009) and terrestrial organisms (Nie et al., 2015) and some differences have been observed in the preferential bioaccumulation of certain PBDEs. Hence, more research is needed to better understand the interrelation between PBDE exposure levels, body burdens, and human health outcomes.

1.3 Human exposure to PCBs, HBCDs and NBFRs as a result of improper e-waste handling

Additionally to PBDE human exposure discussed in section 1.2, people residing at e-waste sites are exposed to a range of other contaminants released during improper e-waste handling (see section 1.1.3). Among these, PCBs have been historically one of the most significant contaminants at e-waste sites due to their release from PCB-containing transformers, for example, at Luqiao where this type of e-waste has been treated since the 1970s (Zhao et al., 2010).

HBCDs have been introduced as a BFR to replace banned PBDEs formulation (in some applications) and have gradually become an ubiquitous contaminant in the environment including biotic and abiotic compartments (Law et al., 2006b). However, due to its environmental widespread and toxic properties, the European Commission proposed in 2013 to phase-out and effectively ban HBCDs from its applications (European Commission, 2013) with exemptions for its uses in buildings and construction materials. Finally, HBCDs have been listed as prohibited substances under the Stockholm Convention on P OPs since 2015 (Stockholm Convention, 2016). A number of other FRs have also been introduced to the market following the ban of PBDEs, the majority being brominated compounds. Such newly introduced FRs are collectively referred to as novel brominated flame retardants (NBFRs); though some publications refer to them as alternative brominated flame retardants (ABFRs) as well. What is worrying is that there are no specific regulations on the production or use of

NBFRs, which may lead to their uncontrolled use as replacements for regulated BFRs, hence, environmental releases of NBFRs might increase in the future with a potential to enter food chain.

Table 1-10 Estimated human exposure to PCBs, HBCDs, NBFRs and other halogenated FRs at e-waste recycling sites in China

Exposure matrix	**Location**	**Age group**	**PCBs**			**HBCDs**	**NBFRs and other FRs***		**Source**
			ng/day	**ng/kg bw/day**	**pg TEQ/kg bw/day**	**ng/day**	**ng/day**	**ng/kg bw/day**	
Chicken eggs	South China	Adults	n/a	n/a	n/a	80 – 490	970 - 4530	n/a	(Zheng et al., 2012) *[a]
Chicken eggs	Qingyuan	Adults	n/a	n/a	n/a	n/a	n/a	0.03 - 0.09	(Zheng et al., 2015c)
		Children						0.20 - 0.54	
Chicken eggs	South China	Adults	n/a	n/a	n/a	540 - 19600		n/a	(Zeng et al., 2016)*
Goose eggs	South China	Adults	n/a	n/a	n/a	80 - 6300		n/a	
Fish	Guiyu	Adults	264	n/a	n/a	n/a	n/a	n/a	(Xing et al., 2009) [b]
Diet[c]	Taizhou	Adults	4740	92.8	9.78	n/a	n/a	n/a	(Xing et al., 2010) [c]
Diet[d]	Taizhou	Adults	12372	n/a	196.6¥	n/a	n/a	n/a	(Zhao et al., 2009b) [d]
Diet[e]	Luqiao	n/a	n/a	n/a	13.4ǂ	n/a	n/a	n/a	(Song et al., 2011)

* - indication that other halogenated FRs have also been included in total intake or exposure value, such as Dechlorane Plus (DP);
¥ - expressed in pg TEQ/day;
ǂ - total value for PCDD, PCDF and twelve dioxin-like PCBs;
a – range of means for 3 e-waste sites, FRs: DBDPE, BTBPE, PTBX, HBB, PBEB, PBT, DP;
b - 37 PCBs from CB-18 through to CB-199;
c – diet included freshwater and marine fish, shellfish, meat, viscera, eggs, cereals, vegetables and fruits; 37 PCBs from CB-18 through to CB-199;
d - diet included vegetables, pork, chicken, rice, fish and shellfish, pulses, and hen eggs; 27 PCBs from CB-8 through to CB-206;
e - diet included vegetables, chicken, duck, rice, carp, and hen eggs.

The examples of some chemicals currently used as NBFRs are as follows: pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-

tetrabromobenzoate (EH-TBB), bis-(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TBP), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), tetrabromobisphenol A (TBBPA), and decabromodiphenyl ethane (DBDPE). There is already information available on toxic effects of some of the NBFRs and their ability to bioaccumulate (Saunders et al., 2013; Wu et al., 2011; Covaci et al., 2011). Taken all together, human exposure to PCBs, HBCDs, and NBFRs is also of great concern at e-waste recycling sites in China, similar to concerns about exposure to PBDEs. In general, food has been reported as main pathway of human exposure to a number of POPs in China (Ni et al., 2012; Xing et al., 2010; Yu et al., 2012; Zhang et al., 2013a; Lau et al., 2012; Wang et al., 2011a). However, very limited information exists in relation to human dietary exposure to HBCDs and NBFRs at e-waste sites in China. Furthermore, little comparison may be drawn among existing studies due to differences in type and number of compounds analysed as well as differences in the data reporting style. The main findings are summarised in Table 1-10.

Three studies reported human intake or human exposure to non-PBDE FRs within e-waste sites in China via fowl eggs. A study by Zheng et al. (2012) reported human intake of HBCDs (range: 80 – 490 ng/day) and other FRs including NBFRs and DP (reported as total sum, range: 970 – 4530 ng/day) via chicken eggs from e-waste sites in South China. Another study by Zheng et al. (2015c) has also estimated exposure to NBFRs via chicken eggs in Qingyuan, but reported data normalised to body weight for adults and children as a range of means of 0.03 - 0.09 ng/kg bw/day and 0.2 - 0.54 ng/kg bw/day, respectively. A more recent study estimated human intake of several halogenated FRs (DP, DBDPE, BTBPE, HBB, HBCDs, and TBBPA) (Zeng et al., 2016) via chicken and goose eggs, however, the data were reported only as a sum for all studied FRs (range for chicken eggs: 540 – 19600 ng/day; range for goose eggs: 80 - 6300 ng/ day), hence, it was not possible to distinguish the contribution of each FR and compare to other studies.

More comprehensive investigations than for HBCDs and NBFRs, though still a limited number of them, were carried out at e-waste sites in China to estimate dietary human exposure to PCBs. Three of the four identified studies (see Table 1-10) included a number of dietary products in consideration of human exposure to PCBs while one study's estimates were based on the contribution of fish consumption only (Xing et al., 2009). Again, the comparison between these studies was hindered by the different styles of data reporting. It was possible to directly compare the data on daily PCBs dietary intakes from two studies: those of Zhao et al. (2009b) at 12372 ng/day and Xing et al. (2010) at 4740 ng/day; both studies were conducted in Taizhou e-waste sites. The almost 3-fold difference in the reported data between these two studies, each of which have considered main food categories based on sufficient sample numbers, was not addressed in the study by Xing et al. (2010). All studies discussed in the current section have compared data obtained in relation to e-waste and to non-e-waste origin of the samples and reveal significantly higher exposure to PCBs via food impacted by e-waste recycling activities.

Overall, a more systematic approach in research is needed to obtain comparable data that would allow reliable assessment of the risks to human health associated with exposure to PCBs, HBCDs and NBFRs at e-waste sites.

The following gaps in knowledge that need to be address were identified on the basis of the literature review presented in sections 1.1 – 1.3:

1. Limited data exist on synergistic and cumulative effects to human health associated with multipollutant exposure at e-waste recycling sites; most of the published investigations have been carried out on individual chemicals to determine their toxic effects.

2. Lack of comprehensive studies that investigate multiple pathways human exposure that is a common place at informal e-waste recycling sites.

3. Lack of biomonitoring surveys conducted within informal e-waste recycling areas, particularly in case of children.

4. Limited data exist on dietary exposure to legacy and novel BFRs, among other pollutants, arising in locally produced foods as a result of e-waste recycling operations. Some of existing studies investigate a single type of food or a couple of products, have considered a small sample population, and/or focused on a single contaminant.

5. Difficulties in comparison of existing studies on human exposure to PBDEs due to differences in the studies' scope, design, and reporting parameters.

6. Inconsistency in values of estimated human half-lives that are available for selected PBDEs, and absence of such estimation for most of them.

7. Absence of estimation of human half-life of PBDE congeners in children.

8. Limited information on daily consumption rates for children in China; most of the studies utilise existent data for adults for estimation of dietary exposure.

9. Limited data exist on processes of PBDEs accumulation, distribution and elimination in humans, especially in the scenario of exposure to pollutants at high concentration. Most of the studies in this regard are based on animal, bird, and fish species investigation.

10. Absence of toxicity data for most of NBFRs as well as absence of health-based limit values with legislative standing for both HBCDs and most of NBFRs.

1.4 Final remarks

Overall, insufficient attention has been paid to the whole scope of problems related to informal e-waste recycling in China - starting from the illegal stream of imported e-waste, through to the rudimentary treatment practices employed at informal e-waste workshops that release an enormous number and quantity of toxic contaminants with most of them entering the food chain. Scientific groups in China and worldwide have conducted important but as yet insufficient research to identify and assess the impacts on workers and residents at e-waste sites and, most importantly, on children that live in the contaminated surroundings, consume contaminated food and are chronically exposed to a range of toxic chemicals. The time has come to re-evaluate the long-lasting legacy of informal e-waste recycling and to switch over to environmentally and human-friendly e-waste recycling techniques. Moreover, it is vital to properly assess alternative chemicals that are to be introduced in replacement of banned FRs before they are actually used in various goods, including in EEE, for their ability to bioaccumulate in biota and humans and their toxicity to living organisms. A recent review (Stieger et al., 2014) that assessed the persistence, bioaccumulation potential and toxicity of the 36 NBFRs highlighted that the chemical properties of 17 of them simply cannot be found through available databases. Other limitations on the uses of these NBFRs as alternative FRs are identified by Stieger et al. (2014) as follows:

- For 17 chemicals out of the 19 with existing data on their properties, the data are insufficient for reliable assessment of chemicals hazard and risk;
- Limited data exists on the degradability of these chemicals;
- Half-life estimates are available only for 11 of the chemicals considered, however, the data points for estimation are too few;
- In cases with sufficient number of data points, the data scatters widely, thereby hampering reliable assessment of chemical hazard and risk;
- There are indications that K_{ow} data for some of the chemicals considered are underestimated by several orders of magnitude, thereby resulting in inaccurate estimation of their baseline toxicity.

Finally, Stieger et al. (2014) concluded that the quality of currently available data on chemical properties of NBFRs requires improvement before they can be identified as safe replacements for banned FRs. At the same time, new data on toxicity of some NBFRs is emerging, for example, a recent study (Krivoshiev et al., 2016a) has shown that TBBPA and other alternative phosphorous FRs may affect endocrine function.

Looking back over the whole history of POPs, we can see the ever continual cycle: new chemical introduction to the market followed by its widespread distribution in the environment and wildlife through releases from manufacture, recycling and disposal processes; detection in humans and wildlife and assessment of toxic effects on both; culminating in restrictions or bans on production and uses due to the recognition of their toxic impacts on humans and wildlife. However, by following this route repeatedly, vast wildlife and human populations will be unnecessarily exposed to toxic substances that will result in health deterioration for many generations to come. Change to break this cycle is needed.

1.5 Aims of the study

Taking into account the research gaps in knowledge about the extend and diversity of the informal e-waste recycling impacts on the environments and on the human health mentioned above, the aims of the current study are as follows:

1. Develop and validate methods for the determination of PBDEs in a range of matrices.
2. Investigate the impact of the electronics manufacturing sector located along the Neva River, Russia, by determination of PBDE concentrations in river sediments.
3. Test the hypothesis that rudimentary techniques of e-waste recycling are a significant source of PBDEs to the environment by determination of PBDE concentrations in soil, sediment, dust and ash collected in the vicinity of e-waste recycling sites in Guiyu, China.

4. Investigate the impact of informal e-waste recycling on the biota by determination of PBDEs in duck eggs grown in the vicinity of e-waste recycling workshops in Taizhou, China, and estimate human exposure to PBDEs via the consumption of such eggs.

5. Estimate human exposure to PBDEs via wide range of foodstuffs originating from Taizhou, China, and produced from locally reared animals, including pigs, chickens, ducks, eggs from domestic fowl, culinary oils as well as fish and shrimp caught from ponds and rivers within e-waste recycling areas in Taizhou.
6. Test the hypothesis that transboundary transfer of PBDEs can occur via exported foodstuffs by conducting a small-scale pilot study to determine PBDE concentrations in foodstuffs exported from China for sale in the UK.
7. Estimate human exposure to key pollutants arising at e-waste recycling sites including HBCDs, NBFRs, PCBs, and metals/metalloids through consumption of the same foodstuffs originating from e-waste recycling sites in Taizhou, which were considered for estimation of human exposure to PBDEs.
8. Evaluate the accuracy of PBDE dietary exposure estimation utilizing a one-compartment pharmacokinetic (PK) model to predict the body burden of PBDEs in adults and children from Taizhou e-waste recycling areas based on estimated dietary PBDE intakes.

CHAPTER 2 SAMPLING AND METHODOLOGY

This chapter contains some text taken verbatim from the following publications:

Labunska, I., Harrad, S., Santillo, D., Johnston, P., & Brigden, K. (2013). Levels and distribution of polybrominated diphenyl ethers in soil, sediment and dust samples collected from various electronic waste recycling sites within Guiyu town, southern China. ***Environmental Science: Processes & Impacts***, *15*(2), 503–511.

Labunska, I., Harrad, S., Santillo, D., Johnston, P., & Yun, L. (2013). Domestic duck eggs: an important pathway of human exposure to PBDEs around e-waste and scrap metal processing areas in Eastern China. ***Environmental Science & Technology***, *47*(16), 9258–66.

Labunska, I., Harrad, S., Wang, M., Santillo, D., & Johnston, P. (2014). Human dietary exposure to PBDEs around e-waste recycling sites in Eastern China. ***Environmental Science & Technology***, *48*(10), 5555–5564.

Labunska, I., Abdallah, M. A.-E., Eulaers, I., Covaci, A., Tao, F., Wang, M., Santillo, D., Johnston, P., Harrad, S. (2015). Human dietary intake of organohalogen contaminants at e-waste recycling sites in Eastern China. ***Environment International***, *74*, 209–220.

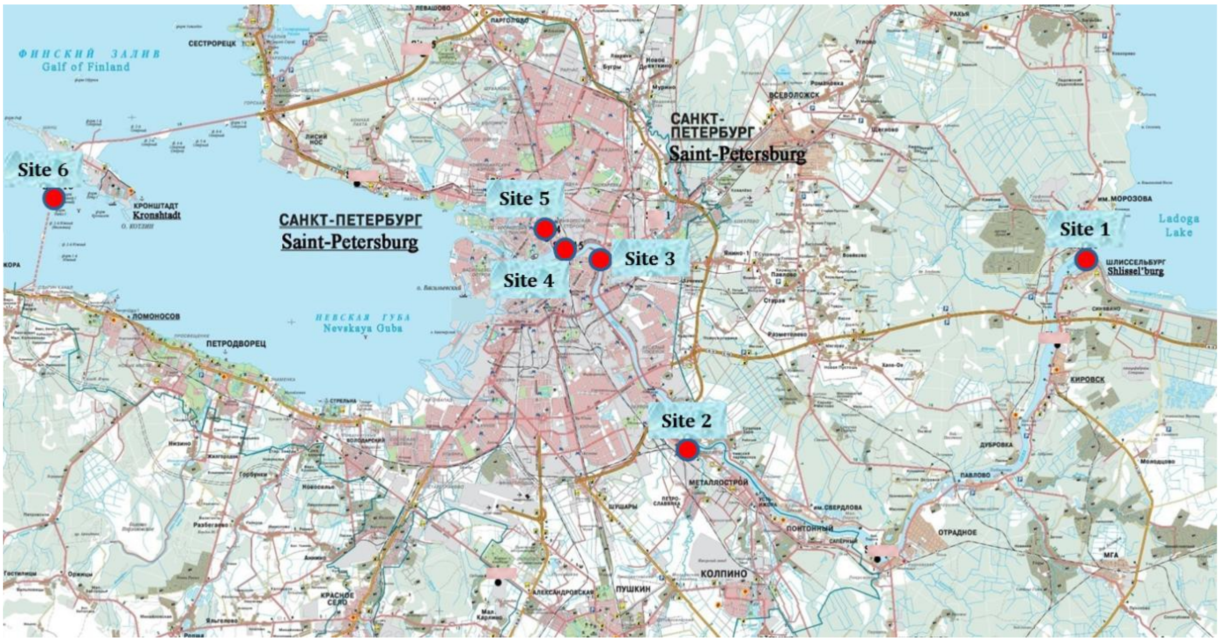
2.1 Sampling and sample pre-treatment

2.1.1 Environmental samples

2.1.1.1 Samples from Russia

These samples were part of a wider investigation of sediments collected from the Neva River in 2007 and included general screening analysis for the presence of a wide range of organic contaminants, including qualitative PBDEs analysis, as well as quantification of metals/metalloids (Labunska et al., 2008).

Figure 2-1 Location of the sampling sites, St-Petersburg, Russia, 2007



The current study was conducted in 2010 and aimed to apply a newly developed fully quantitative method to analyse congener-specific PBDEs in these samples as such data were not available at the time of the investigation. Samples of sediment from the Neva River and its tributaries were collected at five locations (Sites 1-3 & 5) stretching from the river's origin in Lake Ladoga down to St-Petersburg city (see Fig. 2-1).

Table 2-1 Description of sediment samples collected for PBDEs analysis from Neva River, St-Petersburg, Russia

Site	Sample Code	Description of the sample source
Site 1	RU07027	riverhead of the Neva River, right bank, in the vicinity of the wharf
	RU07028	left bank of the Neva River, 1.5 km downstream from Orekhovy Island, Shlisselburg
Site 2	RU07030	left bank of the Neva River, 1 km upstream of the Guyed Bridge, downstream of Slavyanka River
Site 3	RU07002	Neva River, 3-5 m from the bank, about 10 m downstream of the Bolsheokhtinsky bridge, 5 m water depth
	RU07003	Neva River, about 500 m downstream of the Bolsheokhtinsky bridge, Sverdlovskaya embankment
	RU07004	Okhta River junction with the Neva River, under the Bolsheokhtinsky bridge crossing Okhta River
Site 4	RU07023	non-operated discharge pipe located in front of Petrogradskaya Embankment Industrial Zone
Site 5	RU07006	Neva River, close to the left bank, just downstream of Liteyniy bridge
	RU07007	Neva River, close to the right bank, just downstream of Liteyniy bridge
Site 6	RU07017	Nevskaya Guba, Gulf of Finland, about 0.5 m offshore

Additionally, a single sediment sample was collected from inside an effluent pipe that discharges directly into the Neva River from Petrogradskaya embankment industrial zone (Site 4) located on the bank of the Neva River within the city of St-Petersburg. There are several plants operating in this zone, which maintains various types of printed circuit board production and soldering lines. Nearly every year, the Neva River rises and St-Petersburg suffers flooding, usually at the end of autumn.

This event is the result of a combination of climatic factors, including low-pressure air movement from the West, which in turn creates so-called ‘long waves’ that bring additional water into the Gulf of Finland and the mouth of the Neva River. Strong westerly winds then effectively block the flow of water from the Neva into the Gulf of Finland, and the river level is forced to rise, often by several metres. This may, in turn, cause surficial layers of sediments to move upstream from the lower part of the river towards the upper reaches.

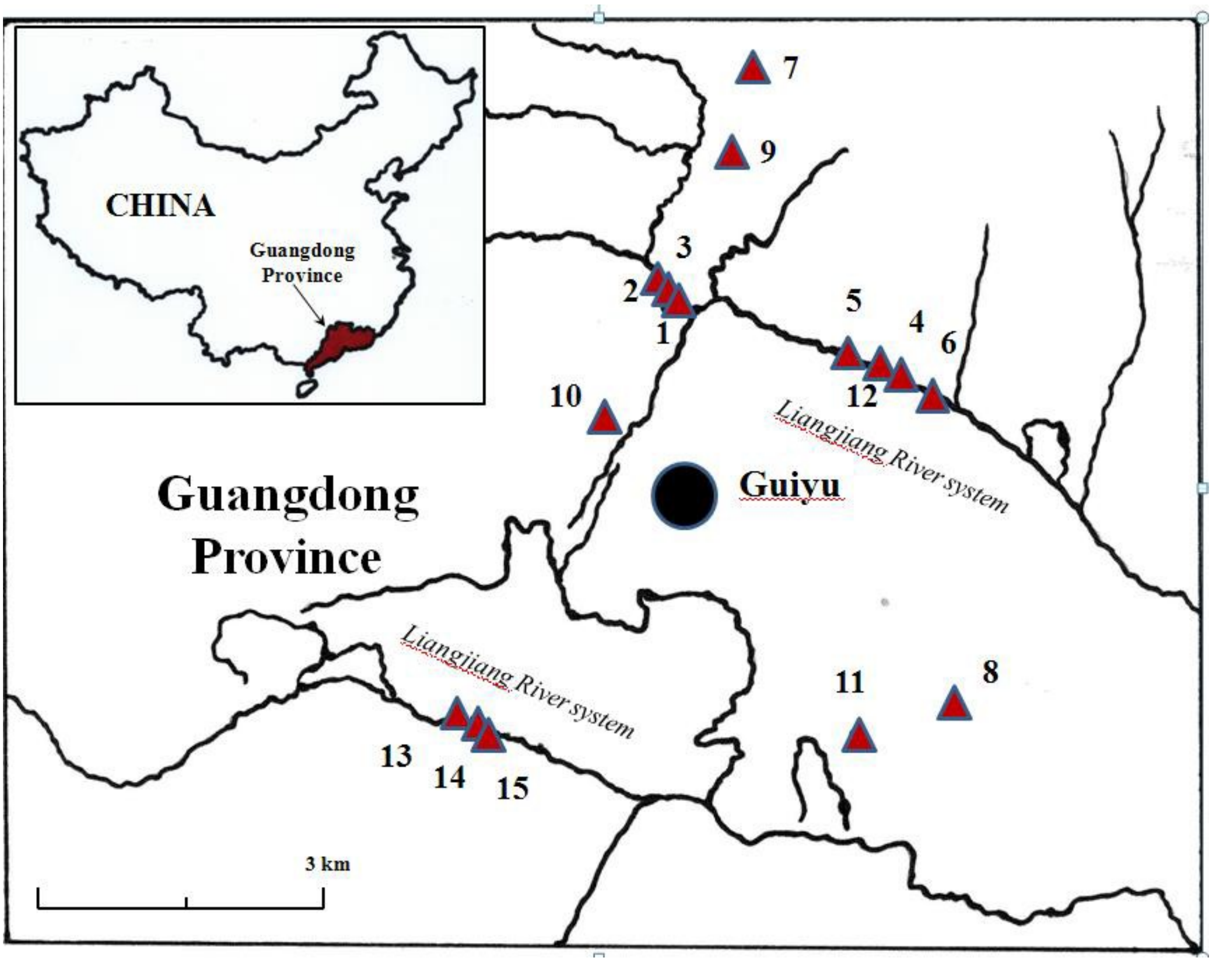
A description of the samples is presented in Table 2-1. Sediment samples were collected either from the river banks below the water line using a stainless steel spatula or by sediment grab deployed from a boat. All samples were stored in 100 mL pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all organic residues. All samples were kept cool and dark during transportation. On arrival at the laboratory, samples were air dried at ambient temperature in the dark and stored at -20 ˚C until removed for analysis.

2.1.1.2 Samples from China

This set of samples was obtained as part of a wider investigation conducted in 2005 around Guiyu town, Guangdong Province, in southern China. Samples of sediment, soil, surface dust and solid wastes were collected from a large e-waste recycling area and qualitatively analysed for the presence of organic contaminants, including PBDEs, in addition to quantitative analysis for metals/metalloids (Brigden et al., 2005). The current study was conducted in 2011 and aimed to perform newly developed fully quantitative congener-specific PBDE analysis in these samples. At the time of sample collection, dismantling and processing of e-wastes was being carried out in multiple small unregulated workshops, with many operations executed in the open air. Location of sampling sites is presented in Fig. 2-2. Prefixes assigned for samples are as follows: AP – acid processing, OB – open burning, PD – printers dismantling, SS –

separation and solder recovery from circuit boards, SH – shredding. Site 1 – AP01-AP03; Site 2 – AP04-AP06; Site 3 – OB05; Site 4 – AP07-AP10; Site 5 – AP11; Site 6 – AP12-AP14; Site 7 – AP15-AP16; Site 8 – OB01-OB04; Site 9 – PD01-PD02; Site 10 – SS01-SS03; Site 11 – SH01; Site 12 – SH02; Sites 13-15 – SH03-SH05. Detailed descriptions of the samples and sampling locations are presented in Table 2-2.

Figure 2-2 Location of sampling sites around Guiyu town, Guangdong Province, China.



Samples AP03 and AP11 represent control samples for acid processing activities as they were collected from sites located upstream from discharges of these operations. Samples of soil were collected to a depth of about 5 cm using a pre-cleaned stainless steel spatula or trowel. Sediment samples were collected from the river banks or wastewater pools below the water line using an unpainted wooden spoon or a stainless steel spatula.

Table 2-2 Description of sampling sites within Guiyu e-waste recycling area, China

Location	Code	Sample description
Longmen	AP01	soil/sediment from small pool connected to river adjacent to workshop 1
	AP02	soil from dry waste pit adjacent to workshop 1
	AP03	river sediment, upstream from workshop 1
	AP04	soil from 1 m deep waste pit A connected to river, workshop 2
	AP05	river sediment, downstream from workshop 2
	AP06	sediment from waste pit B connected to river, workshop 2
Liangjiang River	AP07	soil from waste ground area washed with acidic wastewater, workshop 3
	AP08	soil from waste ground area washed with acidic wastewater, workshop 3
	AP09	sediment from small river further from waste channel, close to workshop 3
	AP10	sediment from small river near waste channel, close to workshop 3
	AP11	sediment from upper part of small river away from workshop 3
	AP12	sediment from Lianjiang River, near workshop 4
	AP13	soil from dry discharge channel to Lianjiang River, workshop 4
	AP14	sediment from Lianjiang River, near workshop 4, closer to discharge than point AP12
Hua Mei	AP15	sediment from stream surrounding acidic waste sumps, away from working area
	AP16	sediment from stream surrounding acidic waste sumps, close to wastewater entry from sumps
Longgang	OB01	ash & soil at the place of burning, waste dumpsite
	OB02	ash & burnt e-wastes brought to dumpsite from elsewhere, in piles on ground
	OB03	ash & burnt e-wastes brought to dumpsite from elsewhere, in piles on ground
	OB04	ash & burnt e-wastes brought to dumpsite from elsewhere, in sacks on ground
Longmen	OB05	ash & burnt e-wastes from pile that was still burning on dumpsite
Nanyang	PD01	dust from floor of printers dismantling workshop 5
	PD02	soil/sediment from shallow pool outside printers dismantling workshop 5
Beilin	SS01	dust from floor of separation & solder recovery workshop 6
	SS02	dust from container at separation & solder recovery workshop 6
	SS03	dust from floor of separation & solder recovery workshop 7
Longgang	SH01	street dust/soil, between two plastic shredding workshops 8 & 9
Liangjiang River	SH02	sediment from wastewater gully from printed circuit boards shredding workshop 10
Liangjiang River	SH03	sediment from waste channel immediately before it enters Liangjiang River, 150m downstream from discharge from printed circuit boards shredding workshop 11
	SH04	sediment from waste channel at a point of discharge from printed circuit boards shredding workshop 11
	SH05	sediment from waste channel at a point of discharge from printed circuit boards shredding workshop 12

Dust samples were collected from the surface of the floor in workshops or ground surface on the street using a new nylon brush and stainless steel spatula for each sample. All samples were stored after collection in 100 mL screw-cap glass bottles for transportation. Prior to sample collection, bottles had been cleaned with detergent, rinsed with tap and deionised water followed by soaking in 10 % nitric acid, rinsing in deionised water and drying in an oven at about 100 °C, before rinsing three times with analytical grade pentane. Samples were kept cool and dark during transportation to the laboratory. On arrival at the laboratory, samples were air dried at ambient temperature in the dark and stored at -20 °C.

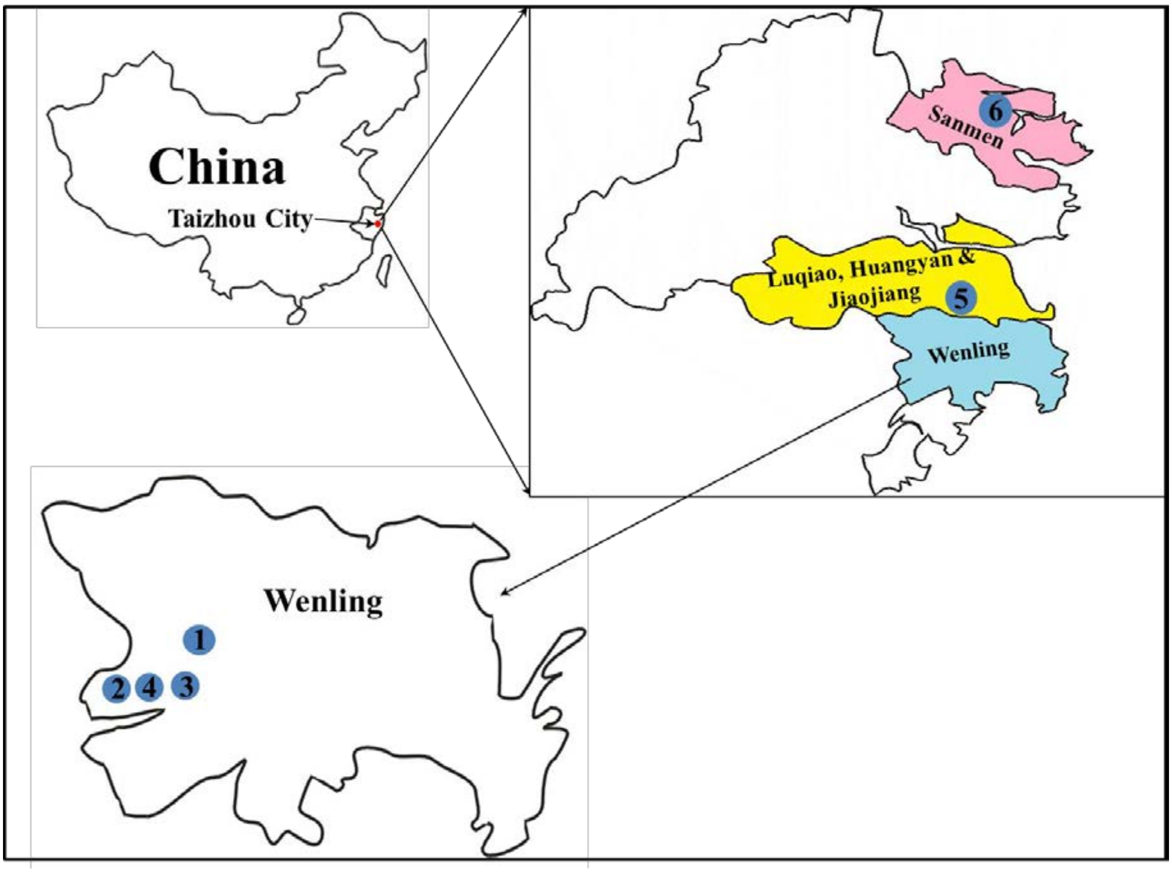
2.1.2 Diet samples

Diet samples were collected in China on three occasions: in November 2011 (duck eggs and duck feed), in November 2012 (pork, fish, shrimp, chickens, ducks, and chicken eggs), and in February 2013 (culinary oils). In the UK, diet samples were purchased in April-May 2013 from stores selling foodstuffs of Chinese origin in Birmingham and Exeter. These samples included: fish balls with pork filling, roasted duck, chicken powder, dried fish, and seafood.

2.1.2.1 Duck egg collection, storage and pre-treatment

Locations of sampling sites from which duck eggs were obtained are presented in Fig. 2-3. Fresh duck eggs were purchased from duck farm owners at five locations situated within 10 – 500 metres of e-waste and scrap metal recycling activities around Taizhou City, eastern China. A questionnaire was used to collect information about each sampling site (see Table 2-3). Four areas (sites 1 - 4) were located in Wenling district. While two of these locations (sites 1 and 2) remain actively involved in e-waste recycling, focusing mainly on printed circuit boards and other computer components, the number of e-waste recycling workshops has decreased in recent years at site 3. Site 4 is a former e-waste recycling site where operations ceased about six years prior to the collection of samples analysed in this study, while site 5 is located in Luqiao district, one of the main e-waste recycling areas in Taizhou, focusing mainly on dismantling scrap metal items including transformers, capacitors, motors, cables and wires.

Figure 2-3 Location of duck egg sampling sites: sites 1, 2, 3 and 4 - Wenling, site 5 – Luqiao, and site 6 - Sanmen, Zhejiang Province, China, 2011.



Family workshops in all areas have more than 10 years' history of e-waste or scrap metal recycling. The main types of recycling operations carried out at sites 1 - 5 include obsolete equipment dismantling, heating dismantled parts to recover precious metals and burning of plastics. Dump sites containing processed e-wastes are commonplace around villages and towns involved in e-waste recycling in Taizhou City.

Control duck egg samples were purchased from the Taobao web supermarket. These control eggs originated from an eco-farm in San Men County, north east Taizhou city, Zhejiang province (control - site 6), which is situated approximately 90 km and 60 km distant from the e-waste recycling sites (sites 1 - 4) and metal scrap reprocessing site (site 5), respectively. Eleven duck eggs were obtained from each site for analysis. In order to assess the possible impact of feed that ducks receive as a supplement to foraging; a sample of duck feed was obtained from each of sites 1-5. No feed sample was available from the control site 6.

Upon collection, the weight of each egg sample was recorded prior to storage overnight at 4 ˚C, followed by heat treatment. Prior to their shipment to the UK for the analysis, eggs were heat treated in order to fulfil the requirements of the UK's Animal Health and Veterinary Laboratories Agency (AHVLA) for the import of eggs from China. Heat treatment was conducted in a large pan filled with deionised water and placed on a temperature regulated heating plate. Heat treatment was conducted in batches, so only eggs from one sampling site were treated at the same time to ensure consistency.

After 30 min of heating at 56 ± 2 ˚C, eggs were removed from the water, placed on paper towels, cooled down at room temperature, and placed into a freezer at -20 ˚C until shipping. For express courier transportation to the UK, frozen eggs were packed carefully into plastic cool boxes containing frozen cooling blocks. On arrival at our laboratory, egg samples were immediately stored in a freezer at -20 ˚C until analysis.

Table 2-3 Description of duck eggs sampling sites, Taizhou City, Zhejiang Province, China, 2011.

Location	Site	Type of facility	Distance to recycling sites, m	Sampling site description	Number of ducks at facility	Type of duck feed	Number of eggs produced per month	Are eggs sold in local markets?	Who consumes duck eggs?
Wenqiao, Wenling, Taizhou City	Site 1	Private household	~40	Printed circuit boards recycling sites	Was 50 at the beginning of 2011, but only 5 at sampling time	Local corn	60 – 90	No	owner's family and local people
	Site 2	Private house	~30	Printed circuit boards recycling and damping sites	6 (2 ducks from 2009; 4 ducks from early 2011)	Local rice	90 - 180	No	owner's family and local people
	Site 3	Duck farm	~30	Printed circuit boards recycling sites	630	Mixture of local corn and commercial food pellets	8,400 – 10,500	Yes	owner's family and local people
	Site 4	Duck farm	~500	Former e-waste recycling site, currently no recycling operation in place	2200	commercial food pellets	46,200	Yes	Only market trade
Fenjiang, Luqiao, Taizhou City	Site 5	Private house	~10	Near metal scrap waste dismantling base	60	Local rice	300 - 450	Yes	owner's family and local people
San Men, Taizhou City	control samples Site 6	Super market, Taobao web	~90,000	Duck eco-farm	n/a	n/a	n/a	Yes	Only market trade

2.1.2.2 Collection, storage and pre-treatment of meat (pork, chicken and duck), fish, shrimp, chicken eggs and culinary oils

126 samples (including controls), covering pork, fish, shrimp, chicken eggs, chickens, ducks, and culinary oils were purchased between November 2012 and February 2013 from local farm owners, fishermen and families. Samples were procured from seven locations situated within 1 to 300 metres of present or former e-waste and scrap metal recycling facilities around Taizhou City, Eastern China. Sampling site locations are shown in Figure 2-4. Sampling sites 1-4 were located in Wenling district, within which three villages (Sites 1, 2 and 3) remain involved in recycling of printed circuit boards and other computer components, mainly in family workshops. At site 4, local residents advised that e-waste operations ceased around 5-6 years prior to sampling. Sites 5, 6 and 7 were located in Luqiao District, focusing mainly on dismantling of scrap metal items as well as transformers, capacitors, motors, cables, and wires.

Control samples of pork, fish, shrimp, chicken eggs, chickens, and ducks were purchased in Shanghai City and Nanjing City. Duck and chicken liver controls were purchased from a local market in Taizhou City, and were reported by vendors to be mixed livers from ducks or chickens from locations around Taizhou city not involved in e-waste recycling. Ten samples of culinary oils were purchased from supermarkets in Nanjing City. There is no production of culinary oils in e-waste areas of Taizhou, hence residents use oils from elsewhere in China. Details of sampling sites and samples are presented in Table 2-4. Chickens and ducks, purchased directly from local farm owners or individuals, were prepared by a local professional butcher to separate livers and muscle tissues.

Figure 2-4 Location of sampling sites for collection of dietary samples, November 2012 – February 2013, China.

Table 2-4 Description of e-waste related food samples and sampling sites, Taizhou City, Zhejiang Province, China. EG – chicken egg, CH – chicken meat, CHL – chicken liver, DK – duck meat, DKL – duck liver, PK – pork, FS – fish or shrimp.

Sites	**Sample code**	**Distance to e-waste recycling facility, m**	**Sampling site description**	**Number of chickens /ducksat holding**	**Type of chicken /duck feed**	**Conditions of chicken /duck living; where fish caught**	**Age of the birds**
Site 1	EG1205a&b CH1204 CHL1204 DK1205 DKL1205	~5 - 100	e-waste dismantling workshops area	17 chickens 13 ducks	corn from northern part of China	chickens restricted in a small hut; ducks mainly in a small nearby river	mixed: 1~4 years
Site 2	EG1201a&b CH1201 CH1202 CHL1201 CHL1202 DK1201 DK1202 DKL1201 DKL1202 PK1204 FS1202shrimp FS1208 carp FS1209 carp PK1301a&b	~1 - 30	e-waste dismantling workshops area near powdered e-waste disposal area	7 chickens 6 ducks	local rice and sometimes wheat from northern part of China	free range on nearby open area & rice farm; fish from small river nearby; pig restricted in small hut	unknown
	EG1211a&b CH1209 CH1210 CHL1209 CHL1210	~15	e-waste dismantling workshops area	13 chickens	local rice and sometime wheat (origin unknown)	free range in the forecourt of the owner's house	mixed: 1 ~ 4 or 5 years)
Site 3	EG1202a&b CH1203 CHL1203 DK1203 DKL1203	~50	e-waste dismantling workshops area	1 chicken, >22 ducks	local rice	free range on nearby rice farm and pond	2~3 years
	EG1203a&b PK1202	~300	e-waste dismantling workshops area	3 chickens	local vegetables and rice	restricted in the backyard of the owner's house	~2 years
	EG1204a&b DK1204 DKL1204	~10	e-waste dismantling workshops area	8 chickens, >1000 ducks	local rice	free range around the nearby pond	1~2 years
Site 4	FS1201 shrimp FS1210 carp FS1211 carp PK1201	unknown	former e-waste recycling site	n/a	n/a	local river	n/a

Sites	Sample code	Distance to e-waste recycling facility, m	Sampling site description	Number of chickens /ducksat holding	Type of chicken /duck feed	Conditions of chicken /duck living; where fish caught	Age of the birds
Site 5	EG1207a&b CH1206 CHL1206 FS1205 loach FS1206 shrimp FS1207 carp	~20	metal scrap recycling especially from copper wires & cables	8 chickens	local and purchased rice & locally caught fish	restricted in a small patch in front of the owner's house; fish & shrimp from small pond	1~2 years
	EG1208a&b PK1203	~150	metal scrap recycling especially from copper wires & cables	4 chickens	local rice	free range on the street in front of the owner's house	~1.5 years
Site 6	EG1209a&b CH1207 CH1208 CHL1207 CHL1208 DK1206 DK1207 DKL1206 DKL1207	~10	metal scrap, dismantling, and electric transformer recycling & processing workshops area	>10 chickens ~50 ducks	local vegetables and rice; local spiral shell	restricted in a small patch around a pond	~1 year
	EG1210a&b	~15	metal scrap, dismantling, and electric transformer recycling & processing workshops area	>10 chickens	rice & corn bought from nearby villages (origins unknown)	free range around a cowshed in front of the owner's house	~1 year
Site 7	EG1206a&b CH1205 CHL1205 FS1203 snakehead FS1204 carp	~20	metal scrap recycling especially from copper wires & cables	6 chickens	local and purchased rice & locally caught fish	chickens restricted in the small backyard of the owner's house; fish from local river	3 years

Raw pork samples were purchased from local markets, local shops and, in one case, from a local owner. A fisherman was hired to catch fish and shrimp from local waterways, while other fish were purchased locally. Chicken eggs were heat treated in China prior to freezing and storage at -20 ˚C as described in section 2.1.2.1 for duck eggs. Livers, gutted fish and meat (pork, chicken, and duck) were carefully washed in distilled water, wrapped in pre-cleaned aluminium foil and oven-cooked for 30 min at 200˚C to mimic food preparation. After cooking, samples (in foil) were cooled to room temperature, placed in plastic bags and frozen at -20 ˚C until shipment. Frozen samples were transported to the UK in cool boxes containing frozen cooling blocks to maintain low temperature. On arrival at our laboratory, still frozen samples were transferred to a freezer at -20 ˚C for storage until analysis.

2.1.2.3 Pooled dietary samples preparation

In order to measure a wider range of contaminants in dietary samples, pooled samples were prepared from 189 individual food samples from e-waste and non-e-waste impacted areas (see Table 2-5). To achieve this, portions of homogenised individual samples (pre-treated, if necessary, as described in sections 2.1.2.1 – 2.1.2.2) were combined according to food category (e.g. chicken eggs, duck meat etc.) and whether they originated from e-waste or non-e-waste impacted areas. Pooled samples were prepared by mixing equal amounts of each sample from each product type (2 g per sample for shrimp, 3 mL per sample for vegetable oils and 1 g per sample for all others). Pooled samples were then homogenised thoroughly using a Waring 32BL80 commercial blender, followed by further homogenisation using a mortar and pestle. Each homogenised pooled sample was sub-sampled into pre-cleaned extraction vials and stored at -20 ˚C until analysis. Pooled samples of meat, fish, shrimp and liver were prepared using individual samples from both Wenling and Luqiao districts combined. For chickens' eggs, separate pooled samples were prepared for Wenling and Luqiao district respectively, using individual yolks from each site. In the case of duck egg yolk, one pooled sample was prepared per location for each of the five e-waste locations monitored in Wenling and Luqiao.

One pooled control sample was prepared for each food category examined. Upon preparation, pooled samples were divided into four aliquots, which then were analysed as follows:

- The 1st aliquot was spiked with HBCD internal standards and extracted at the Greenpeace Research Laboratories as described in section 2.2.3; the extract was then sent to the University of Birmingham, UK, for HBCDs analysis as described in section 2.4;
- The 2nd, non-spiked, aliquot was transferred into a clean vial and sent to Antwerp University, Belgium, for PCB analysis as described in sections 2.2.4 and 2.3.4;
- The 3rd, non-spiked, aliquot was transferred into a clean vial and sent to University of Birmingham, UK, for NBFR analysis as described in sections 2.2.5 and 2.3.3;
- Finally, the 4th, non-spiked, aliquot was transferred into a clean vial and sent to the Food and Environment Research Agency (FERA), UK, for metals/metalloids analysis as described in sections 2.2.6 and 2.5.

2.2 Preparation of samples for analysis

In order to achieve optimum extraction efficiency for target compounds, an appropriate amount of sub-sample was extracted separately for the analysis of each class of investigated contaminants. Detailed descriptions of the extraction and clean up procedures employed are provided in sections 2.2.2 – 2.2.5. While PBDEs were the only subject for analysis of environmental samples (i.e. soil, sediment, and dust) in this study, diet samples were also investigated for the presence of a wider range of contaminants including other BFRs and PCBs.

Table 2-5 Description of pooled dietary samples. The codes of e-waste sites are as specified in Table 2-4

Sample type	№ of samples in a pool	Samples Code	Location of samples origin	E-waste Site	Description of sampling site
vegetable oil	10	GP01	Jiangsu, Shandong & Hebei Provinces	n/a	from areas not involved in e-waste recycling
fish control	4	GP02	Jiangsu & Shandong Provinces	n/a	from areas not involved in e-waste recycling
fish	8	GP03	Wenling & Luqiao, Taizhou, Zhejiang Province	Sites 2,4,5,7	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area
shrimp control	2	GP04	Jiangsu & Shandong Provinces	n/a	from areas not involved into e-waste recycling
shrimp	3	GP05	Wenling & Luqiao, Taizhou, Zhejiang Province	Sites 2,4,5	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area
chicken control	5	GP06	Jiangsu & Shandong Provinces	n/a	from areas not involved in e-waste recycling
chicken	10	GP07	Wenling & Luqiao, Taizhou, Zhejiang Province	Sites 1-3,5-7	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area
chicken liver control	5	GP08	Taizhou City, Zhejiang Province	n/a	from areas not involved in e-waste recycling
chicken liver	10	GP09	Wenling & Luqiao, Taizhou, Zhejiang Province	Sites 1-3,5-7	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area
duck control	5	GP10	Jiangsu & Anhui Provinces	n/a	from areas not involved in e-waste recycling
duck	7	GP11	Wenling & Luqiao, Taizhou, Zhejiang Province	Sites 1-3,6	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area
duck liver control	5	GP12	Taizhou City, Zhejiang Province	n/a	from areas not involved in e-waste recycling
duck liver	7	GP13	Wenling & Luqiao, Taizhou, Zhejiang Province	Sites 1-3,6	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area

Sample type	№ of samples in a pool	Samples Code	Location of samples origin	E-waste Site	Description of sampling site
pork control	5	GP14	Jiangsu, Anhui & Shandong Provinces	n/a	from areas not involved in e-waste recycling
Pork	5	GP15	Wenling & Luqiao, Taizhou, Zhejiang Province	Sites 2-4,5	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area
chicken eggs control	10	GP16	Jiangsu & Jilin Provinces	n/a	from areas not involved in e-waste recycling
chicken eggs	12	GP17	Wenling, Taizhou, Zhejiang Province	Sites 1-3	e-waste dismantling workshops area
chicken eggs	10	GP18	Luqiao, Taizhou, Zhejiang Province	Sites 5-7	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area
duck eggs control	11	GP19	San Men, Taizhou, Zhejiang Province	n/a	from areas not involved in e-waste recycling
duck eggs	11	GP20	Wenling, Taizhou, Zhejiang Province	Site 1	printed circuit boards recycling sites
duck eggs	11	GP21	Wenling, Taizhou, Zhejiang Province	Site 2	printed circuit boards recycling and damping sites
duck eggs	11	GP22	Wenling, Taizhou, Zhejiang Province	Site 4	former e-waste recycling site, currently no recycling operation in place
duck eggs	11	GP23	Wenling, Taizhou, Zhejiang Province	Site 3	printed circuit boards recycling sites; currently decreased e-waste operation
duck eggs	11	GP24	Luqiao, Taizhou, Zhejiang Province	Site 5	e-waste dismantling, metal scrap, and electric transformer recycling & processing workshops area

Additionally, a range of metals/metalloids, which potentially may arise in samples from e-waste recycling sites, were analysed in diet samples (see Table 2-6 for a full list of analysed compounds).

Table 2-6 Compounds analysed in this study.

Name of compound	Abbreviation	CAS #
PBDEs		
2,2’,4-tribromodiphenyl ether	BDE-17	147217-75-2
2,4,4’-tribromodiphenyl ether	BDE-28	41318-75-6
2,2’,4,4'-tetrabromodiphenyl ether	BDE-47	5436-43-1
2,3’,4,4’-tetrabromodiphenyl ether	BDE-66	189084-61-5
2,2’,3,4,4’-pentabromodiphenyl ether	BDE-85	182346-21-0
2,2’,4,4’,5-pentabromodiphenyl ether	BDE-99	60348-60-9
2,2’,4,4’,6-pentabromodiphenyl ether	BDE-100	189084-64-8
2,2’,3,4,4’,5’-hexabromodiphenyl ether	BDE-138	182677-30-1
2,2’,4,4’,5,5’-hexabromodiphenyl ether	BDE-153	68631-49-2
2,2’,4,4’,5,6’-hexabromodiphenyl ether	BDE-154	207122-15-4
2,2’,3,4,4’,5’,6-heptabromodiphenyl ether	BDE-183	207122-16-5
2,2’,3,3’,4,4’,6,6’-octaabromodiphenyl ether	BDE-197	117964-21-3
2,2’,3,3’,4,4’,5,6,6’-nonabromodiphenyl ether	BDE-207	437701-79-6
2,2’,3,3’,4,4’,5,5’,6,6’-decabromodiphenyl ether	BDE-209	1163-19-5
HBCDs		
α-hexabromocyclododecane	*α*-HBCD	134237-50-6
β- hexabromocyclododecane	*β*-HBCD	134237-51-7
γ- hexabromocyclododecane	*γ*-HBCD	134237-52-8
NBFRs		
Pentabromoethylbenzene	PBEB	85-22-3
Hexabromobenzene	HBB	87-82-1
2-ethylhexyl-2,3,4,5-tertabromobenzoate	EH-TBB	183658-27-7
bis-(2-ethylhexyl)-3,4,5,6-tetrabromophthalate	BEH-TEBP	26040-51-
1,2 bis (2,4,6-tribromophenoxy)ethane	BTBPE	37853-59-1
1,2-bis(pentabromophenyl)ethane	DBDPE	84852-53-9
PCBs		
2,2',5-trichlorobiphenyl	PCB-18	37680-65-2
2,4,4'-trichlorobiphenyl	PCB-28	7012-37-5
2,4',5-trichlorobiphenyl	PCB-31	16606-02-3
2,2',4,4'-tetrachlorobiphenyl	PCB-47	2437-79-8
2,2',4,5'-tetrachlorobipheny	PCB-49	41464-40-8
2,2',5,5'-tetrachlorobiphenyl	PCB-52	35693-99-3
2,3',4,4'-tetrachlorobiphenyl	PCB-66	32598-10-0
2,4,4',5-tetrachlorobiphenyl	PCB-74	32690-93-0
2,2',3,5',6-pentachlorobipheny	PCB-95	38379-99-6

Name of compound	Abbreviation	CAS #
2,2',4,4',5-pentachlorobiphenyl	PCB-99	38380-01-7
2,2',4,5,5'-pentachlorobipheny	PCB-101	37680-73-2
2,3,3',4,4'-pentachlorobiphenyl	PCB-105	32598-14-4
2,3,3',4',6-pentachlorobiphenyl	PCB-110	38380-03-9
2,3',4,4',5-pentachlorobipheny	PCB-118	31508-00-6
2,2',3,3',4,4'-hexachlorobiphenyl	PCB-128	38380-07-3
2,2',3,4,4',5'-hexachlorobiphenyl	PCB-138	35065-28-2
2,2',3,4',5,5'-hexachlorobiphenyl	PCB-146	51908-16-8
2,2',3,4',5',6-hexachlorobiphenyl	PCB-149	38380-04-0
2,2',3,5,5',6-hexachlorobiphenyl	PCB-151	52663-63-5
2,2',4,4',5,5'-hexachlorobiphenyl	PCB-153	35065-27-1
2,3,3',4,4',5-hexachlorobiphenyl	PCB-156	38380-08-4
2,3',4,4',5,5'-hexachlorobiphenyl	PCB-167	52663-72-6
2,2',3,3',4,4',5-heptachlorobiphenyl	PCB-170	35065-30-6
2,2',3,3',4,4',6-heptachlorobiphenyl	PCB-171	52663-71-5
2,2',3,3',4,5,6'-heptachlorobiphenyl	PCB-174	38411-25-5
2,2',3,3',4,5',6'-heptachlorobiphenyl	PCB-177	52663-70-4
2,2',3,4,4',5,5'-heptachlorobiphenyl	PCB-180	35065-29-3
2,2',3,4,4',5',6-heptachlorobiphenyl	PCB-183	52663-69-1
2,2',3,4',5,5',6-heptachlorobiphenyl	PCB-187	52663-68-0
2,2',3,3',4,4',5,5'-octachlorobiphenyl	PCB-194	35694-08-7
2,2',3,3',4,5,5',6'-octachlorobiphenyl	PCB-199	52663-75-9
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	PCB-206	40186-72-9
2,2’,3,3’,4,4’,5,5’,6,6’-decachlorobiphenyl	PCB-209	2051-24-3
METALS/METALLOIDS		
Arsenic	As	7440-38-2
Beryllium	Be	7440-41-7
Bismuth	Bi	7440-69-9
Cadmium	Cd	7440-43-9
Chromium	Cr	7440-47-3
Copper	Cu	7440-50-8
Mercury	Hg	7439-97-6
Nickel	Ni	7440-02-0
Lead	Pb	7439-92-1
Antimony	Sb	7440-36-0
Tin	Sn	7440-31-5
Yttrium	Y	7440-65-5
Zinc	Zn	7440-66-6

Due to the sensitivity of BDE-209 to degradation by UV light (Ahn et al., 2006), special attention was paid during both sample preparation and instrumental analysis of this compound.

This included use of amber glassware when applicable, and minimisation of sample exposure to direct light.

2.2.1 Chemicals

A list of the chemicals used in this study to extract and clean up samples during their analysis for PBDEs and HBCDs is provided in Table 2-7.

Table 2-7 Chemicals used in the current study for sample analysis

Chemical	Manufacturer	Grade/Specifications
Solvents		
Pentane	Rathburn Chemicals, UK	low haloform grade
Toluene	Rathburn Chemicals, UK	HPLC
Acetone	Fisher Scientific, UK	AR
iso-Propane	Fisher Scientific, UK	AR
Sorbents/media		
Florisil	Thames Restek, UK	60/100 mesh
Hydromatrix	Thames Restek, UK	30/40 mesh
Silica	Merck, Germany	0.063-0.200 mm
Reagents		
tetrabutylammonium hydrogen sulfate	Acros Organics, UK	98% purity
sodium sulfite, anhydrous	Sigma-Aldrich, UK	puriss. p.a.
sodium sulfate, anhydrous	Fisher Scientific, UK	AR grade
concentrated sulfuric acid	Fisher Scientific, UK	AR grade
Dionex ASE Prep CR Na+ form	Thermo Fisher Scientific, USA	0.6 – 0.8 mm
Internal Standards		
F-BDE-69 and F-BDE-160	Chiron, Norway	>98% purity
^{13}C-BDE-209, ^{13}C α-, β-, γ-HBCDs and α-HBCD-d_{18}	Wellington Laboratories, Canada	>98% purity
PCB-209	Thames Restek, UK	>98% purity
Native target compound standards		
α-, β-, and γ-HBCD	Cambridge Isotope Laboratories (USA)	>98% purity
BDE-17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 197, 207 and 209	Wellington Laboratories, Canada	>98% purity

2.2.2 Sample extraction and clean up for PBDE analysis

2.2.2.1 Choice of solvent for PBDEs extraction

There are a number of publications reporting various solvents that could be used for extraction of PBDEs from samples as summarised in Table 2-8. Dichloromethane, hexane, acetone, toluene and various combinations of these solvents have been traditionally used to efficiently extract PBDEs from samples. However, these solvents are toxic, with dichloromethane being of most concern.

Table 2-8 Published data on solvent choice for PBDEs extraction

Solvent	Sample type	Extraction technique	Reference
Dichloromethane	Soil, sediment, dust, biological tissues	Soxhlet extraction	(U.S. EPA, 2007)
Dichloromethane:hexane (9:1, *v/v*)	dust	pressurised liquid extraction	(Harrad and Abdallah, 2011)
Dichloromethane:hexane (3:1, *v/v*)	foodstuffs	Soxhlet extraction	(Schecter et al., 2010a)
hexane : acetone (3:1, *v:v*)	biological tissues	Soxhlet extraction	(Covaci et al., 2009; Eulaers et al., 2014)
Hexane : acetone (1:1, *v:v*)	soil	ultrasonic extraction	(Niu et al., 2014)
Toluene	fish	Soxhlet extraction	(Airaksinen et al., 2014)
Toluene:acetone (9:1, *v/v*)	sediment	Soxhlet extraction	(Guerra et al., 2014)

In the current study, we conducted experiments to compare extraction efficiencies of three main congeners of commercial Penta-, Octa-, and Deca-BDE formulations (BDE-47, BDE-99, and BDE-209) from self-prepared spiked soil using single solvents as well as their combinations (see Table 2-9) to achieve the following objectives:

- substitute, if possible, conventionally used solvents for the extraction of PBDEs with less toxic alternatives. It was decided to include pentane as one of the potential alternatives due to its lesser toxicity than the solvents mentioned above;
- decrease sample preparation time by using a more volatile solvent (e.g., pentane) or combination of solvents;
- maintain sufficient PBDE extraction efficiency with the chosen solvent.

Table 2-9 Results of the experiment examining BDE-47, BDE-99, and BDE-209 extraction from spiked soil using different solvents and their combinations.

Solvent	PBDE	Expected conc., ng/g	Average measured conc., ng/g	Standard deviation (SD), ng/g	RSD, %	Extraction efficiency, %
Pentane	BDE-47	20	21.5	1.0	4.7	108
	BDE-99	50	48.9	1.8	3.7	98
	BDE-209	50	53.0	4.6	8.7	106
Pentane:acetone 3:1, v:v	BDE-47	20	18.9	0.5	2.8	95
	BDE-99	50	52.1	0.9	1.8	104
	BDE-209	50	52.2	0.9	1.8	104
Pentane:toluene 95:5, v:v	BDE-47	20	22.0	4.7	21.4	110
	BDE-99	50	68.5	9.9	14.4	137
	BDE-209	50	61.9	10.1	16.3	124
Hexane	BDE-47	20	18.6	1.4	7.8	93
	BDE-99	50	57.7	4.4	7.5	115
	BDE-209	50	55.4	3.0	5.5	107

Clean garden soil from the suburbs of Exeter (Devon, UK) was used as a matrix for spiked sample preparation. To do so, about 300 g of soil was dried in the oven at 30 ˚C to constant weight, ground using a pre-cleaned pestle and mortar and sieved, firstly, through a 2 mm sieve and then through a 63 µm sieve to achieve thorough homogeneity of the sample. Three sub-samples of ground soil (1 g each) were analysed for PBDEs and showed no presence of them above detection limits. Then 20 g of clean soil was spiked with 400 ng, 1000 ng, and 1000 ng of BDE-47, BDE-99, and BDE-209 respectively, resulting in concentrations of 20 ng/g for BDE-47 and 50 ng/g for both BDE-99 & BDE-209 in spiked soil. Spiked soil was transferred into a clean bottle and thoroughly mixed for 24 hours on a rotating device.

Triplicate sub-samples (1 g each) were then extracted with the single solvent or mixture of solvents and analysed. Recoveries of the three target compounds and statistics were calculated – see results in Table 2-9.

In general, all tested combinations of solvents displayed satisfactory extraction efficiencies for the three BDEs, although the pentane:toluene combination had slightly higher relative standard deviations than the other combinations evaluated. Hence, pentane and pentane/acetone mixture were selected as the solvents for PBDE analysis in this study.

2.2.2.2 Soil, sediment and dust samples extraction procedure

Prior to analysis, samples were transferred into pre-cleaned crucibles, covered by a pre-cleaned aluminium foil, defrosted and dried in an oven at 30 ˚C until they reached constant weight. Each sample was thoroughly mixed and sieved through a 2 mm sieve to remove any visible plastic particles or stones, then ground and sieved through a 63 µm stainless steel sieve to ensure homogeneity.

In case of sediment samples from Neva River, Russia, 5 g of each sample was taken for analysis as earlier screening analysis showed these samples were not likely to be highly contaminated with PBDEs (Labunska et al., 2008). In contrast, samples of soil, sediment and dust from e-waste recycling sites in China were expected to contain high concentrations of PBDEs (Brigden et al., 2005). Experiments were therefore conducted to elucidate the optimum sample size required for analysis. Essentially, this equates to that sample size that provides an analyte signal that is sufficiently strong to permit reliable quantification but that does not exceed the linear range of the instrument, nor result in excessive co-extractives that could contaminate the GC (or LC)-MS.

The experiments conducted were:

- firstly, three different sample masses of SRM 2585 were extracted (1 g, 0.5 g and 0.05 g) and analysed as outlined below. The results were satisfactory in comparison with the certified values of SRM 2585 in all cases;
- it was decided to proceed further with the smallest tested amount of the SRM2585, i.e., 0.05 g, to check for the precision and accuracy of the analysis. For that, six replicates of SRM2585 at 0.05 g each were extracted and analysed for PBDEs. The results obtained from this experiment again compared favourably with the certified values of SRM2585 – see Fig. 2-6 in section 2.10.2;
- a triplicate experiment with two e-waste related samples was conducted, again using 0.05 g of the sample for extraction, and key PBDE congeners were quantified. Good reproducibility of analysis was achieved, illustrated by RSD of BDE-47, BDE-99, and BDE-209 at 3.9-9.0%, 5.8-14.4%, and 7.3-11.8% respectively;

Based on the outcomes of these experiments, it was decided that 0.05 g was the optimum sample size for all soil, sediment and dust samples from e-waste related sites.

The homogenized sample (5 g for sediments from Neva River, Russia, and 0.05 g for samples from e-waste related sites in China) was transferred into 34 mL stainless steel accelerated solvent extraction (ASE) cells filled with 2 g of Florisil and packed with Hydromatrix pre-cleaned with a 1:3 v/v mixture of acetone and pentane prior to sample loading. Samples were spiked with three IS: F-BDE-69, F-BDE-160, and ^{13}C-BDE-209. Samples were extracted with pentane using a Dionex 350 ASE system under the following conditions: temperature: 100°C;

pressure: 1500 psi; heating time: 5 min; static time: 4 min; flush volume: 60 %; purge time: 60 secs; static cycles: 3.

The resulting extract was concentrated to 0.5 mL under a stream of N_2 gas using a Zymark Turbovap II solvent concentrator. The concentrate was cleaned with 0.68 g of tetrabutylammonium hydrogen sulfate and 5 g of sodium sulfite dissolved in 20 mL deionized water together with 3 mL of iso-propanol to remove elemental sulfur. The extract was then cleaned further by column chromatography using 2 g of Florisil (activated at 250 ˚C overnight and pre-cleaned with pentane). PBDEs were eluted with pentane (25 mL) and the eluate concentrated to 0.5 mL. This concentrate was transferred into a 2 mL vial and 20 µL of toluene was added as a keeper solvent, prior to concentration to incipient dryness under a gentle stream of nitrogen and reconstitution with 200 µL of toluene containing 5 ng of PCB-209 as a recovery determination standard.

2.2.2.3 Duck egg samples

For egg samples, only egg yolks were taken for analysis as it has been shown previously by others that persistent organic pollutants (POPs) including PBDEs do not partition significantly to egg whites (Rawn et al. 2011). Therefore, frozen eggs were thawed at room temperature and the yolks separated from whites. Following weighing, the yolk was homogenised thoroughly using a clean spatula.

Similar experiments to that conducted for environmental samples were performed to determine the optimum sample mass of the yolk taken for analysis as well as to optimise the parameters of the extract in-cell clean up. For this set of experiments, duck eggs were purchased from a farm in Devon, UK, in July 2011.

Firstly, five 1 g aliquots of egg yolk were analysed for PBDEs. The analysis showed no target PBDEs above detection limits in these samples. However, a distorted peak was observed for one of the ISs (F-BDE-69) indicating insufficient removal of fat from the extract (fat is typically present in yolks at about 30-35 %). Hence, a duplicate series of lower weight samples of yolk (0.1 g, 0.2 g and 0.3 g), but this time spiked with 14 PBDEs, were extracted. Both the 0.1 g and 0.2 g sample aliquots showed good separation and complete removal of the fat by in-cell clean up (described below) while F-BDE-69 and also BDE-47 & BDE-66 were still affected by the presence of fat in the 0.3 g aliquot. Hence, a sample mass of 0.2 g yolk was selected for the analysis of further samples as described below.

An aliquot of 0.2 g of yolk was taken for extraction, placed into a pre-cleaned ceramic crucible, spiked with 5 ng, 5 ng, and 20 ng of internal (or surrogate) standards F-BDE-69, F-BDE-160, and 13C-BDE-209 respectively, covered with pre-cleaned aluminium foil and left to equilibrate for 15 min. The sample was then mixed with 2 g of pre-cleaned Hydromatrix and 2 g of anhydrous sodium sulfate (baked at 250 ˚C overnight and washed with pentane), until the mixture was friable, and then quantitatively transferred for extraction into a pre-cleaned "Dionium" ASE cell.

Cells were packed with the following layers to achieve in-cell extract clean-up (from top to bottom): pre-cleaned Hydromatrix; mixture of egg yolk, Hydromatrix and sodium sulfate; 10 g acidified silica; 4 g Florisil; 2 g silica; and 5 g neutralizing agent CR Na+ (Dionex).

Samples were extracted using an ASE 350 (Dionex) system with the following conditions: pentane solvent, pressure 1500 psi, temperature 100 °C, static time 5 min, 3 static cycles, flush 80 %, purge 60 seconds. The extract was concentrated to 0.5 mL using a TurboVap apparatus and transferred quantitatively into a 2 mL vial. Prior to evaporation to incipient dryness under nitrogen, 20 μL of toluene was added as a keeper solvent. Following evaporation, the concentrate was reconstituted immediately with 100 μL toluene, containing 5 ng of PCB-209 as a recovery determination (or syringe) standard (RDS), and analysed via GC/ECNI-MS.

2.2.2.4 Effect of heat treatment of duck eggs on PBDE concentrations

In order to determine the effect of egg heat treatment on the PBDE congener pattern in duck eggs, the following experiment was conducted. Duck egg yolks obtained from a farm in Devon, UK, were analysed for PBDEs, confirming that concentrations of all target PBDEs were below detection limits in these samples (n=5). A yolk sample from this "clean" source was spiked with six PBDEs (BDE-47, BDE-99, BDE-100, and BDE-153 at 4 ng each, plus BDE-183 at 8 ng and BDE-209 at 25 ng), mixed thoroughly using a stainless steel spatula and incubated in an ultrasound bath at room temperature for 15 min to ensure equilibration and homogeneity. The spiked yolk was then split in two; one half was frozen at -20 ˚C and the second half was placed into a pre-cleaned jar, sealed and heat treated at 56 ± 2 ˚C for 30 min before storage at -20 ˚C to mimic the pre-treatment procedure applied to duck eggs sampled in China. This process was conducted for 10 " clean" egg yolk samples, and concentrations of PBDEs determined in both the heat treated and non-heat treated egg yolk aliquots. While concentrations of most PBDEs in heat-treated aliquots exceeded slightly (<10%) those in the corresponding non-heated aliquots, paired t-test analysis confirmed that this increment was not significant ($p>0.05$). The one exception to this was BDE-209, for which concentrations were slightly (at most 10%) but significantly higher in heat treated aliquots ($p<0.05$). Overall, this exercise led us to conclude that our heat treatment of the Chinese eggs did not exert a substantial influence on the concentrations of PBDEs detected.

2.2.2.5 Duck feed samples

About 25 g of duck feed samples were placed into pre-cleaned crucibles, covered with clean aluminium foil and dried in an oven at 30 ˚C for 4 hours. After cooling in a desiccator, duck feed samples were ground using a Waring 32BL80 commercial blender. An aliquot (5 g) was taken for analysis, spiked with internal standards as for egg yolk samples, and extraction carried out as in section 2.2.2.3.

2.2.2.6 Other dietary samples (except culinary oils)

Excess fat and liquids exuded during cooking were excluded from analysis. Samples were freeze-dried and homogenised using a Waring 32BL80 commercial blender. To check the efficacy of sample homogenisation, 10 separately extracted aliquots from one of the homogenised pork samples were analysed. Results were satisfactory, with RSD values for concentrations of individual PBDEs ranging from 3.9 % for BDE-183 to 28.2% for BDE-100. A similar procedure, which was used for eggs, was applied for extraction of other food types, only larger sample masses were analysed (0.5 g for freeze dried samples) and a correspondingly increased quantity of acidified silica (20 g) employed to facilitate extract in-cell clean up.

2.2.2.7 Culinary oils

1 mL of culinary oil was taken for analysis and extracted in a similar procedure to that described in section 2.2.2.3.

2.2.3 Dietary samples extraction and clean up for HBCDs analysis

Extraction was carried out using a pressurised liquid extraction technique utilising an Accelerated Solvent Extractor ASE 350 (Dionex). An accurately weighed aliquot (~0.5 g) of each dried pooled sample was mixed with 5 g of anhydrous Na2SO4, transferred into a 33 mL stainless steel extraction cell half-filled with diatomaceous earth, spiked with 20 ng of each of 13C-labelled α-, β-, and γ- HBCD as internal (surrogate) standards, topped with diatomaceous earth, and extracted using the ASE 350 (temperature 90 °C, pressure 1500 psi, heating time 5 min, static time 4 min, purge time 90 s, flush volume 50 %, 3 static cycles, solvent pentane/acetone 3:1). A 2 mL aliquot of the resultant extract was used for gravimetric determination of lipid content. The remainder of the extract was evaporated to incipient dryness using a Turbovap system and reconstituted with 2 mL pentane.

Extracts were cleaned with 3 mL of concentrated sulfuric acid. After separation of phases, each extract was transferred to a glass column containing 2 g of Florisil topped with 0.5 g of anhydrous Na_2SO_4 and eluted with 25 mL of pentane/acetone (3:1 v/v). Cleaned extracts were evaporated to complete dryness using a gentle stream of nitrogen and reconstituted in 100 µL of α-HBCD-d18 (25 pg/µL in methanol) used as recovery determination (or syringe) standard.

2.2.4 Extraction and clean up of diet samples for PCBs (conducted by collaborators at Antwerp University, Belgium)

Pooled samples (typically 0.5 g) were weighed accurately, homogenised, mixed with anhydrous Na2SO4, and spiked with PCB-143 as internal standard, prior to automated hot Soxhlet extraction for 2 h with hexane:acetone (3:1, v:v). Sample lipid content was determined gravimetrically by drying 10% of the crude extract for 1 h at 100 °C. The remaining extract was purified by elution through acidified silica (8 g; 44% H2SO4) with 20 mL of hexane followed by 15 mL of dichloromethane. Eluates were concentrated to incipient dryness under a gentle nitrogen flow and reconstituted in 150 µL iso-octane.

2.2.5 Extraction and clean up of diet samples for NBFRs (conducted by collaborators at the University of Birmingham, UK)

An accurately weighed aliquot (~0.5 g) of pooled sample was loaded into an ASE cell (half-filled with pre-extracted Hydromatrix), spiked with internal standards (15 ng of each of BDE 77, BDE 128, 13C 12-BTBPE and 30 ng of 13C12-BDE 209), and extracted with hexane:acetone (3:1 v/v) using an ASE 350. After concentration to ~1 mL using the Turbovap system, extracts were eluted through activated Florisil (2 g) using 18 mL hexane (fraction 1) and 12 mL of DCM (fraction 2). Following evaporation to ~1 mL, fraction 1 was eluted through 44 % acidified silica (3 g) with 20 mL hexane:DCM (1:1 v/v). Fraction 2 was reduced to 0.5 mL and solvent exchanged to hexane, prior to loading onto an isolute NH2 cartridge and elution with hexane:DCM (1:1 v/v, 15 mL). The eluate from this cartridge was combined with that obtained by passing fraction 1 through Florisil. This combined eluate was concentrated under a gentle stream of nitrogen and solvent exchanged to iso-octane (200 µL) containing PCB 129 as recovery determination (or syringe) standard.

2.2.6 Extraction of diet samples for metals/metalloids (conducted by collaborators at FERA, UK)

Samples were prepared and analysed using UKAS accredited procedures (ISO17025). 0.25 g aliquots of samples and certified reference materials (ZC73013 Trace Elements in Spinach, NACIS, China; NRCDORM4 Fish Protein, LGC, UK; and SRM1548a Typical Diet, NIST, USA) were digested in a mixture of nitric acid and hydrochloric acid (5 mL, 4:1 ratio) using a high pressure microwave system (Ultrawave, Milestone, Italy). The digest solutions were transferred into graduated test tubes and made up to a volume of 10 mL with Milli-Q plus ultrapure deionized water (Millipore, Bedford, USA). An aliquot of each digest solution (1 mL) was added to diluted nitric acid (1 % v/v) containing an internal standard (rhodium, 10 µg/L). Calibration standards were prepared from NIST traceable single element solutions.

2.3 GC/MS analysis

2.3.1 Optimisation of GC/MS parameters for simultaneous determination of tri- to deca-BDEs using ENCI method in selective ion monitoring (SIM) mode

Determination of PBDEs is challenging, especially if BDE-209 is to be analysed simultaneously with other less brominated BDE congeners. Difficulties arise from the fact that BDE-209 is thermally unstable and can undergo degradation in both the hot injection port and GC oven (Covaci et al. 2003; H. M. Stapleton 2006b). In most cases, PBDE analysis is carried out utilising gas chromatography – mass spectroscopy (GC/MS) with either electron impact (EI) ionisation or electron capture chemical ionisation (ECNI) (de Boer et al. 2000; Covaci et al. 2003; Król et al. 2012; de Wit 2002). Detection of PBDEs using ECNI was particularly efficient in combination with low resolution MS, which allowed to obtain increased sensitivity for higher brominated congeners (Covaci et al. 2003). It was particularly evident for BDE-209, which was successfully detected by monitoring ions with m/z 486.6 & 484.6 (Björklund et al. 2003). At the same time, lower brominated PBDEs were successfully analysed utilising ECNI by monitoring bromide ions with m/z 78.9 & 80.9 (Ackerman et al. 2005; Król et al. 2012; H. Stapleton 2006). Hence, all samples in our study were analysed for PBDEs using ECNI GC/MS as described below.

PBDEs analysis was conducted using an Agilent 6890 Series gas chromatograph interfaced with an Agilent 5973 Inert MSD, using ECNI in the selected ion monitoring (SIM) mode and with methane as a reagent gas. Usage of a short thin film Restek Rtx-1614 column (15 m, 0.25 mm ID, 0.1 μm film thickness), which was specifically designed for PBDEs analysis, allowed to minimise thermal degradation of BDE-209 while maintaining satisfactory resolution of lower BDE congeners. It was reported that use of a Rtx-1614 column for PBDE analysis delivers higher response and better peak shape for high molecular weight PBDEs (Wei et al. 2010). To minimize active sites in the sample pathway and to reduce injection port discrimination, a Restek Drilled Uniliner inlet liner (with the hole near the top) was used, which connects to the analytical column via a press-tight seal, thereby eliminating sample contact with any part of the injector below the column inlet.

The GC/MS parameters were chosen with a focus on preventing degradation of BDE-209 while achieving satisfactory separation of all BDE congeners considered in our study. This was achieved by:

- Ensuring the oven temperature program did not exceed 295 ˚C, a critical temperature point for degradation of BDE-209 (Dirtu et al. 2008; Krumwiede et al. 2004);
- Supplying the He carrier gas in ramped flow mode. This allowed good separation of the lower brominated congeners during the first flow ramp (1 mL/min) while minimising the time spent at higher temperatures to reduce the potential for degradation of higher brominated BDEs;
- Auto injection of 1 µL of sample was conducted in pulsed splitless mode to achieve fast introduction of the extract on the column;
- GC inlet, MS ion source and MS quadrupole temperatures were set to values reported previously as optimum for PBDE analysis including BDE-209 (Hites 2008; Dirtu et al. 2008).

Taking into account the above, our optimised GC/MS parameters for PBDE analysis, applied for all samples in this study, are summarised in Tables 2-10 & 2-11.

Table 2-10 GC parameters for PBDE analysis

Parameter	Set points
Oven temperature program	Initial temperature 120 ˚C (held for 2 min), then raised to 295 ˚C at 25 ˚C/min (held for 8 min)
GC inlet temperature	280 ˚C
Pulsed splitless injection	Pressure 3.89 psi, pulse pressure 33.0 psi, pulse time 1 min
GC column	Restek Rtx-1614, 15 m, film 0.10 µm, ⌀ 250 µm
Column ramped flow (helium)	Initial 1 mL/min, hold 9.8 min, final 2 mL/min, hold 7.2 min
GC/MS interface temperature	280 ˚C
Injection volume	1 µL

Optimised GC/MS analysis parameters allowed a good response and satisfactory separation of all target PBDEs and ISs considered in this study as shown in Fig. 2-5.

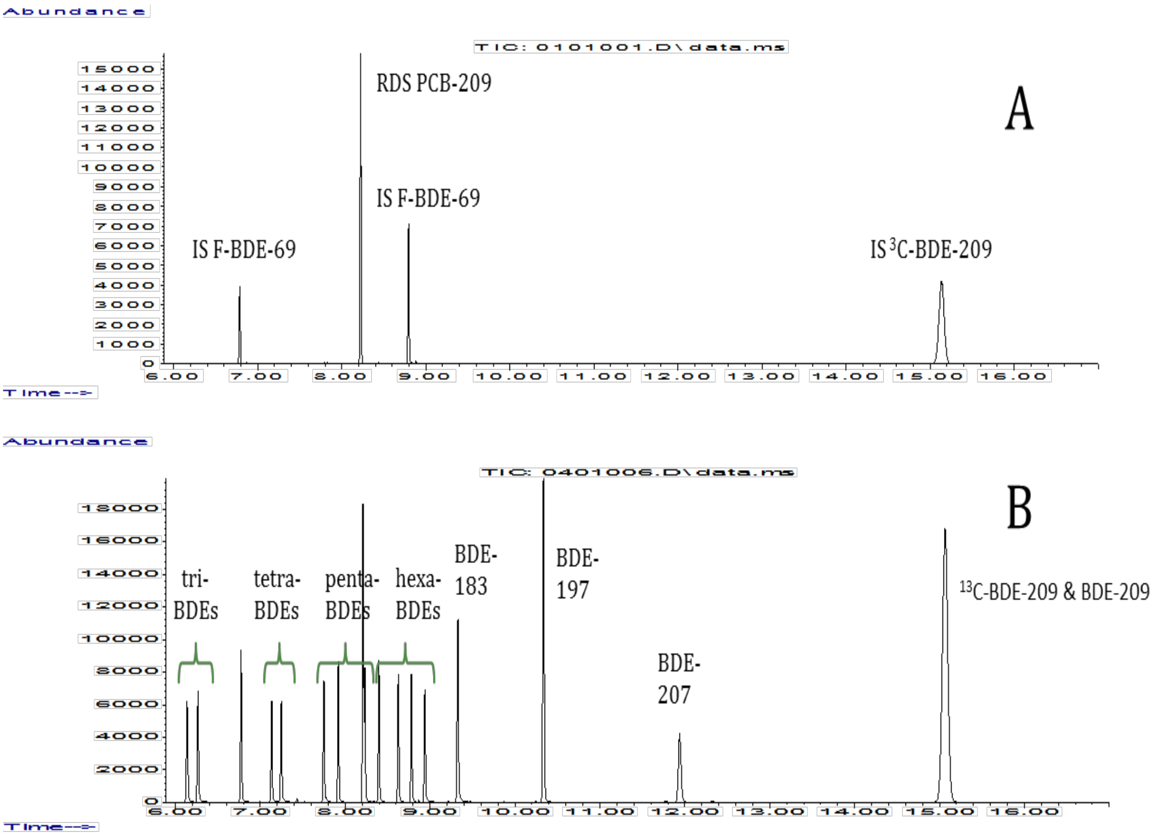
Table 2-11 MS parameters for PBDE analysis

Parameter	Value
Source type	CI
Ion source temperature, ˚C	200
Quadrupole temperature, ˚C	150
Emission current, µA	49
Electron energy, eV	188
Acquisition mode	SIM

2.3.2 PBDE quantification using internal standard technique

Two main ions of target compounds were used for PBDE quantification (see Table 2-12): bromide ions with m/z 78.9 & 80.9 for tri- to hepta-BDEs; ions with m/z 408.6 & 406.6 for BDE-197; and ions with m/z 486.6 & 484.6 for BDE-207 and BDE-209.

Figure 2-5 Chromatogram of ISs (A) and native PBDEs together with ISs (B); retention times of all compounds are provided in Table 2-12



It is important to note that ion 488.7, which is one of the most abundant ions formed for BDE-209 during ECNI analysis, was not monitored because it overlaps with an ion formed from

13C-BDE-209. For the fluorinated ISs, F-BDE-69 and F-BDE-160, bromide ions were also used for quantitation, while for isotope labelled ^{13}C-BDE-209, ions 494.6 & 496.6 were utilized. The recovery determination standard (RDS) PCB-209 produced very distinctive ions 495.7 & 497.7 in ECNI GC/MS analysis, which were used to calculate IS recoveries. Additional qualifier ions were monitored for most target compounds, which helped to distinguish between BDEs belonging to different homologue groups as well as ISs.

Quantification of all PBDEs was carried out via the internal standard method, using F-BDE-69 as an IS for tri- to penta-BDEs, F-BDE-160 as IS for hexa- to nona-BDEs, and ^{13}C-BDE-209 as IS for BDE-209 quantification. Six-point calibration solutions were prepared and analysed in duplicates.

Table 2-12 PBDE retention times (RT) and quantitation and qualifier ions monitored. n/a – not applicable

Compound	RT, min	Quantitation ions	Qualifier ions
BDE-17	6.137	78.9 & 80.9	326.8
BDE-28	6.266	78.9 & 80.9	326.8
BDE-47	7.134	78.9 & 80.9	324.8
BDE-66	7.247	78.9 & 80.9	324.8
BDE-100	7.748	78.9 & 80.9	402.7
BDE-99	7.919	78.9 & 80.9	404.7
BDE-85	8.232	78.9 & 80.9	402.7
BDE-154	8.398	78.9 & 80.9	561.5
BDE-153	8.625	78.9 & 80.9	561.5
BDE-138	8.937	78.9 & 80.9	563.5
BDE-183	9.325	78.9 & 80.9	561.5
BDE-197	10.336	408.6 & 406.6	n/a
BDE-207	11.941	486.6 & 484.6	n/a
BDE-209	15.067	486.6 & 484.6	n/a
F-BDE-69	6.774	78.9 & 80.9	342.7
F-BDE-160	8.780	78.9 & 80.9	501.5
^{13}C-BDE-209	15.064	494.6 & 496.6	n/a
PCB-209	8.212	495.7 & 497.7	n/a

Table 2-13 presents the scheme used for standard solution preparation in this study for PBDE quantification in duck eggs - as an illustration. In the case of quantitation of PBDEs in environmental samples from China, higher concentrations of both target and ISs have been used to be able to accurately calculate extremely high levels of PBDEs in these samples. Areas of quantitation ions were obtained using Agilent Enhanced MSD ChemStation version D.03.00.611 custom reporting and exported into Excel for further calculations.

Table 2-13 Standard solutions for six-point calibration for PBDEs quantification via the internal standard method

PBDEs standard solution	Concentration, ng/mL		
	tri- to hexa-BDEs	hepta- to nona-BDEs	deca-BDE
Standard 1	10	20	100
Standard 2	20	40	200
Standard 3	40	80	300
Standard 4	60	120	400
Standard 5	80	160	500
Standard 6	100	200	600

All further calculations were done using an automation program, called “EasyBDE”, especially designed for the current project. This program incorporated equations (1, 2, 5) used for relative response factors (RRFs) calculation and determination of PBDEs concentrations in the samples as well as for quantitation quality control. This automation dramatically decreased time for calculations and minimised human error in data manipulations. Short description of the EasyBDE program is provided in the Appendix 1.

Mean areas of quantitation ions obtained from duplicate analysis of calibration solutions were used for calculation of relative response factors (RRFs) for each of the target PBDEs as follows:

$$RRF = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{IS}}{C_{NAT}} \qquad \text{(Equation 1)}$$

Where:

A_{NAT} - peak area of the target compound in the standard;

A_{IS} - peak area of the IS in the standard;

C_{NAT} – concentration of the target compound in the standard;

C_{IS} – concentration of the IS in the standard.

Typical relative standard deviations of RRFs calculated for PBDEs quantification were satisfactory and did not exceed 10% throughout the study, an example of one of the calibration statistics is given in Table 2-14.

Table 2-14 Calculated mean RRFs of six-point calibration, their range, standard deviation (SD) and relative standard deviation (RSD,%) obtained for PBDE quantification

Congener	Mean RRF	Range	SD	RSD, %
BDE-17	0.98	0.94 – 1.02	0.04	4.0
BDE-28	1.01	0.98 – 1.04	0.03	2.7
BDE-47	0.83	0.79 – 0.87	0.03	3.6
BDE-66	0.83	0.78 – 0.89	0.04	4.9
BDE-85	0.76	0.70 – 0.80	0.04	5.0
BDE-99	0.85	0.80 – 0.93	0.05	5.5
BDE-100	0.89	0.83 – 0.96	0.04	4.8
BDE-138	1.18	1.11 – 1.25	0.06	4.7
BDE-153	1.38	1.28 – 1.45	0.08	5.6
BDE-154	1.60	1.45 – 1.72	0.13	7.9
BDE-183	1.05	0.94 – 1.17	0.08	7.9
BDE-197	1.72	1.57 – 1.84	0.10	6.1
BDE-207	0.71	0.65 – 0.77	0.05	6.5
BDE-209	0.93	0.88 – 0.97	0.03	3.7

Standard 3 (see Table 2-13) was run before and after each batch of the samples and the average RRFs obtained from these two runs were used for calculating PBDEs concentrations in the samples, as long as these RRFs fell within ±25 % of the RRFs obtained for that standard in the initial six-point calibration. When average RRFs obtained for a particular batch failed the required parameters, which could be due to a several reasons including loss of sensitivity in the GC/MS system due to the ion source contamination, a new full calibration procedure was repeated after appropriate GC/MS system maintenance. In all such cases, the average RRFs obtained for the subsequent full calibration had to fall within ±10% of the RRFs obtained for that standard in the initial six-point calibration for the new calibration to be deemed satisfactory. PBDE concentrations in samples were calculated via Equation 2:

$$Conc = \frac{A_{NAT}}{A_{IS}} \times \frac{M_{IS}}{SS} \times \frac{1}{RRF} \qquad \text{(Equation 2)}$$

Where:

A_{NAT} - peak area of the target compound in sample;

A_{IS} - peak area of the IS in sample;

RRF – relative response factor for the target compound (see equation 1);

M_{IS} – mass of the IS added to sample;

SS – sample size.

2.3.3 NBFRs analysis

This analysis was conducted by Dr. Mohamed Abdallah and Dr. Fang Tao at the University of Birmingham, UK. Target analytes were quantified using a TRACE™ 1310 G as Chromatograph coupled to ISQ™ single quadrupole mass spectrometer (ThermoScientific, Austin, TX, USA) operated in negative ion chemical ionisation mode. Chromatographic resolution of NBFRs was achieved on a HP5-MS capillary column (15 m x 0.25 mm x 0.1 µm; Agilent, CA, USA) according to a previously described method (Van den Eede et al., 2012). Recoveries of the internal standards ranged from 74 to 102 % in all samples. LOQs for the method ranged from 0.54 ng/g for HBB to 1.61 ng/g for DBDPE, based on the lipid weight.

2.3.4 PCBs analysis

Analysis of samples for PCBs was conducted by Dr. Igor Eulaers led by Prof. Adrian Covaci, at Antwerp University, Belgium. PCBs were quantified using a mass spectrometer (Agilent MS 5973, Palo Alto, CA, USA) coupled to a gas chromatograph (Agilent GC 6890, Palo Alto, CA, USA) equipped with a HT-8 capillary column (30 m x 0.22 mm x 0.25 µm; SGE Analytical Science, Zulte, Belgium) operated in electron ionisation mode. Recoveries of the internal standard ranged from 81 to 106% (RSD =10%) in all samples. For every tenth sample, a procedural blank and certified reference material (SRM 1945 whale blubber) were analysed. The LOQ was defined either as three times the standard deviation of the procedural blanks or, for analytes not detectable in blanks, as S:N = 10:1.

2.4 LC–MS/MS analysis

Determination of HBCDs in diet samples was conducted by Dr. Mohamed Abdallah and co-workers at the University of Birmingham, UK. In brief, analysis was carried out using an LC-MS/MS system composed of a dual pump Shimadzu LC-20AB Prominence liquid chromatograph equipped with a SIL-20A autosampler and a DGU-20A3 vacuum degasser, coupled to a Sciex API 2000 triple quadrupole mass spectrometer. Details of the methodology, LC columns and mass spectrometric conditions for both chiral and achiral separation and quantification of HBCDs can be found elsewhere (Abdallah and Harrad, 2011b). Regular analysis of method blanks (1 blank for every 5 samples) revealed no detectable interferences from target compounds. Method limits of detection (LOD) and quantification (LOQ) were estimated based on 3:1 and 10:1 signal:noise (S:N) ratios respectively. LOQ for *α*-, *β*-, and *γ*-HBCD was 0.02 ng/g lipid weight each. Good recoveries (60 - 109 %) of the ^{13}C-labelled internal standards were obtained for *α*-, *β*-, and *γ*-HBCDs.

2.5 ICP–MS analysis for metals/metalloids

Metal/metalloid analysis was conducted by Dr. Malcolm Baxter and co-workers at the Food and Environment Research Agency (FERA), York, UK. Obtained extracts were subject to inductively coupled plasma – mass spectrometry (ICP-MS) analysis using an Agilent 7500ce with a collision cell. Reagent blanks and samples spiked with known amount of analyte were analysed with the test samples for recovery estimation. The recoveries were in range from 92% (for Sn) to 102% (for Be). The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as 3 and 10 times, respectively, of standard deviation of reagent blank values adjusted for dilution and sample weight. The range of LOQs obtained for measured metals/metalloids was from 0.01 mg/kg (Be, Y, Cd, Hg, Pb, and Bi) to 0.5 mg/kg for Zn. The data for analysis of certified reference materials NCS ZC73013 “Trace elements in spinach” (National Analysis Centre for Iron & Steel (NACIS), China), NRCDORM4 “Trace elements in fish protein” (LGC, UK), and SRM 1548a “Typical diet” (NIST, USA) were satisfactory.

2.6 Total fat analysis in dietary samples

For duck egg samples, the lipid content of egg yolks was determined according to the European Standard procedure (European Standard EN 1528-2-1996, 1996). In brief, 1 g of homogenised egg yolk was ground with 2 g of Hydromatrix and 4 g of anhydrous sodium sulfate, before transfer to a 30 cm glass column (0.5 cm diameter) containing 2 cm of anhydrous sodium sulfate. Lipids were eluted with 30 mL of pentane:acetone (2:1 v/v). After solvent evaporation, the eluate was oven-dried at 32 ˚C for 2 hours, and allowed to cool before gravimetric lipid determination.

For meat, liver, fish and chicken egg samples, the lipid content was determined by sub-sample extraction using an ASE 350 utilising 34 mL stainless steel cells. Cells were filled with 1 g sample mixed thoroughly with Hydromatrix and, in the case of chicken egg yolks, anhydrous sodium sulfate, for moisture retention. Extracts obtained were transferred into evaporation dishes, covered with aluminium foil and left at room temperature to permit solvent evaporation. Subsequently, the eluate was oven-dried at 32 ˚C for 2 hours and cooled before gravimetric lipid determination.

2.7 Total organic carbon analysis in soil, sediment, and dust samples

Clean crucibles were dried in an oven at 105 ˚C overnight, cooled in a desiccator for 30 min and their weight recorded. Air dried samples were added to the crucibles and dried in the oven at 105 ˚C overnight (to ensure constant final weight), before being cooled in a desiccator and the weight of crucibles with samples recorded. Subsequently, crucibles with samples were placed in a furnace at 500 ˚C for 4 hours before the final weights of the cooled crucibles and ash was recorded. %TOC was calculated as in Equation 3:

$$\%TOC = \frac{loss\ on\ ignition(g)}{sample\ weight(g)} x\ 100 \qquad \text{(Equation 3)}$$

2.8 Statistical analysis

Principal component analysis (PCA) was performed on PBDE data using IBM SPSS Statistics version 19.0.0 for Windows XP. All other statistical calculations were conducted using Microsoft Office Excel 2007 or Microsoft Office Excel 2010. Results were considered significant at $p<0.05$. The variables used for PCA analysis were fractional contributions of each congener to the sum of all congeners detected in a sample. For congeners present in samples below detection limits, the concentration taken for statistical analysis was assumed to equal half the detection limit. The same variables were also calculated for commercial Penta-, Octa-, and Deca-BDE formulations, using information reported previously (La Guardia et al., 2006). Samples, which had only three or fewer congeners for which concentrations were above detection limits, were excluded from PCA.

2.9 Estimation of total dietary intake (TDI)

The weight of eggs used for calculating daily intakes of PBDEs via duck egg consumption was corrected for the eggshell weight. The average shell weight (11 % total egg weight) was consistent with previously reported values of 9–12 % total duck egg weight (Chen, 2000;

Shafey, 2001). As we measured PBDE concentrations in egg yolk only, concentrations on a whole egg basis were calculated as follows:

$$C_{egg} = C_{yolk} \times \frac{W_{yolk}}{W_{egg}} \qquad \text{(Equation 4)}$$

Where:

C_{egg} - ∑PBDE or individual congener concentration in whole egg, ng/g, wet weight;

C_{yolk} - ∑PBDE or individual congener concentration in yolk, ng/g, wet weight;

W_{yolk} – wet weight of yolk, g;

W_{egg} – wet weight of egg corrected for the eggshell weight, g.

Although official figures on daily consumption of duck eggs in China, and in the Taizhou area in particular, are not available, a number of publications have reported values for egg consumption in general. We have used the most recent available publication on daily dietary consumption figures for Taizhou, China (Zhuang et al., 2012) that reports an average daily consumption rate for eggs (type unspecified) of 24 g per person, consistent with an earlier report for Taizhou of 25 g/day (Xing et al., 2010).

However, this latter value was for chicken eggs only, and hence we selected an average daily consumption rate of 24 g/person. Moreover, information from duck farm owners during our sampling program indicated high-end egg consumers from our study area consumed an average of one egg per day, while low-end egg consumers ate one egg every three days. Based on the average duck egg weight in our study (58.7 g, n=66) our low-end and high-end exposure factors are 19.6 g and 58.7 g/person/day respectively.

Table 2-15 Published data and data used in current study on daily consumption rates for food products

Food type	Daily consumption rate, g/day			
	Published data		Daily rate used in current study calculations	
	Adult	Child	Adult	Child
Fish & shrimp	-	40 – 50[a]		
freshwater fish	25[b]	-	25	20
shrimp	22[b]	-	22	20
Poultry & meat	-	30 - 40[a]		
pork	30[b]	-	30	10[d]
chicken	16[b]	-	16	10[d]
duck	12[b]	-	12	10[d]
Liver	11[b]	-		
chicken liver	-	-	5.5[c]	5[d]
duck liver	-	-	5.5[c]	5[d]
Egg	60[a]			
chicken egg	-	-	30	30
duck egg	-	-	30	30
Culinary oil	25 - 30[a]		30	30

a - (Chinese Nutrition Society, 2007); b - (Xing et al., 2010); c - derived from assumption that liver intake (i.e., 11 g/day) is split equally between chicken and duck liver; d - derived from assumption that poultry & meat intake for children (i.e., 40 g/day) is split equally between chicken, pork, duck and liver, and that liver intake is further split equally between chicken and duck liver.

All other diet samples (with the exception of culinary oils) were cooked before analysis. PBDE concentrations measured in freeze dried samples were converted to wet weight to permit calculation of daily intakes. For calculation of intakes via culinary oils, PBDE concentrations were reported on as consumed basis. Daily consumption rates for various food products considered in our study were drawn from the most appropriate information, summarised in Table 2-15.

Dietary exposure was calculated thus:

$$TDI = \sum_{i=1}^{10} \left(\frac{C_i \, x \, CR_i}{BW}\right) \qquad \text{(Equation 5)}$$

Where:

TDI – estimated total dietary intake, ng/kg bw/day;

C_i – ∑PBDE or individual congener concentration in a food sample, ng/g, wet weight;

CR_i – consumption rate, g/day;

BW – body weight, kg.

2.10 Method validation and QA/QC

2.10.1 Internal Standards (ISs) and Recovery Determination Standard (RDS)

The use of the internal standard quantification method in our study eliminated the need for correction of concentrations for recovery. However, the recoveries of ISs have been calculated for each sample as a QA/QC measure using equation 6:

$$\%\,IS\ Recovery = \left[\left(\frac{A_{IS}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{IS}}\right)_{STD} \times \left(\frac{C_{IS}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{IS}}\right)_S\right] \times 100 \qquad \text{(Equation 6)}$$

Where:

$(A_{IS}/A_{RDS})_S$ – ratio of IS peak area to RDS peak area in the sample;

$(A_{RDS}/A_{IS})_{STD}$ – ratio of RDS peak area to IS peak area in the calibration standard (the average of values obtained for both calibration standards run for a batch of samples is used);

$(C_{IS}/C_{RDS})_{STD}$ – ratio of concentration of IS to concentration of RDS in the calibration standard;

$(C_{RDS}/C_{IS})_S$ – ratio of concentration of RDS to concentration of IS in the sample (assuming 100% recovery).

Table 2-16 presents values for mean recoveries and standard deviation of ISs used for PBDE analysis of all environmental and diet samples in the current study.

Table 2-16 Mean, standard deviation (SD) and relative standard deviation (RSD, %) of recoveries of the ISs used for PBDEs analysis

IS	Type of samples	Number of samples	Mean recovery, %	SD, %	RSD, %
F-BDE-69	Sediment, soil, dust	54	73	11	16
	Diet samples	259	88	10	11
F-BDE-160	Sediment, soil, dust	54	83	16	19
	Diet samples	259	99	10	10
^{13}C-BDE-209	Sediment, soil, dust	54	61	8	13
	Diet samples	259	64	12	19

Recoveries of ISs were satisfactory, however, for environmental samples (range 61 – 83%) they were slightly lower than those obtained for diet samples (range 64 – 99%) most probably due to the differences in the clean up procedures between the two methods.

2.10.2 SRMs and self-prepared materials for evaluation of the accuracy and precision of analytical procedures

To determine the accuracy and reproducibility of the methods used, two certified reference materials (SRM) and one self-prepared material were used for evaluation of analyses in the current study:

- SRM2585 "Organic contaminants in house dust" (NIST, USA) was analysed alongside environmental samples (sediments, soils and dust);
- SRM2974A "Organics in freeze-dried mussel tissue (Mytilus edulis)" (NIST, USA) was used for evaluation of PBDE and HBCD analyses in diet samples;
- A self-prepared homogenate of duck egg yolk was used to evaluate PBDE analysis in duck eggs. Preparation of this material is described in section 2.2.2.4.

Figure 2-6 Results of SRM2585 analysis (n=6) for PBDEs. Error bar – SD. Note: to enhance visualisation, the values for some congeners were multiplied by the following factors: BDE-100, 154 & 135 by 10; BDE-28 & 85 by 20; BDE-17 & 138 by 100; and BDE-183 by 200

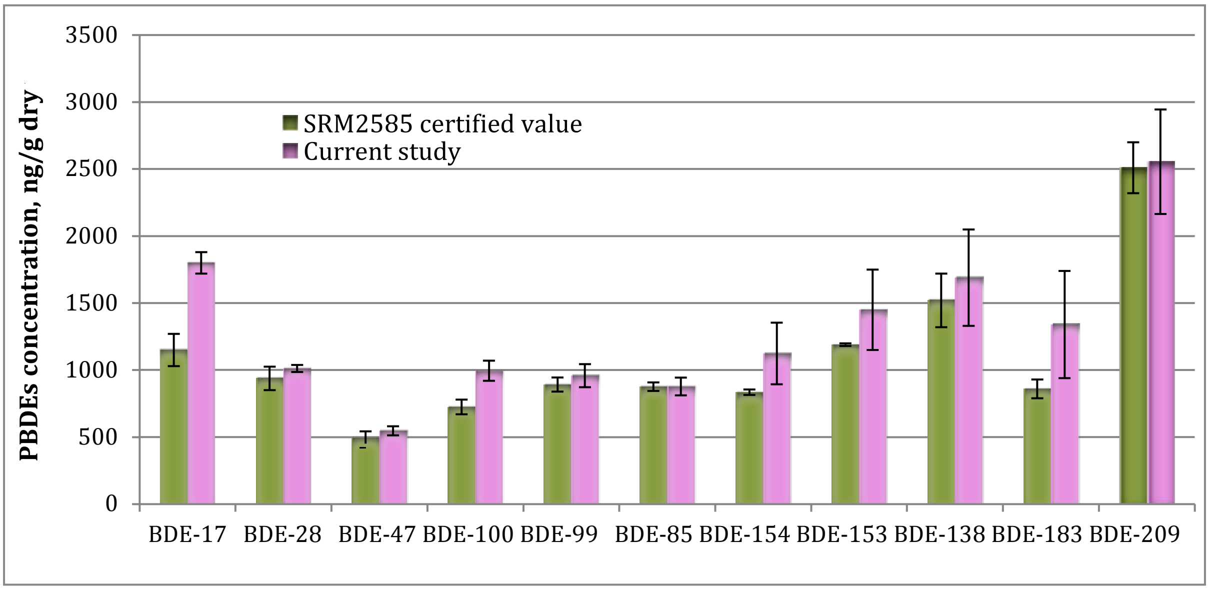
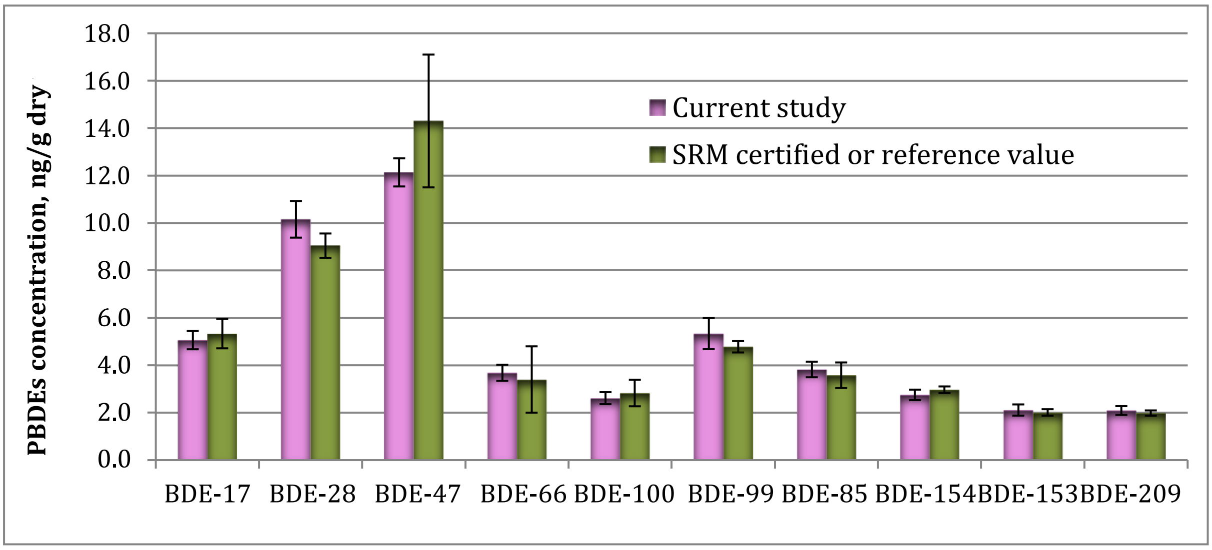


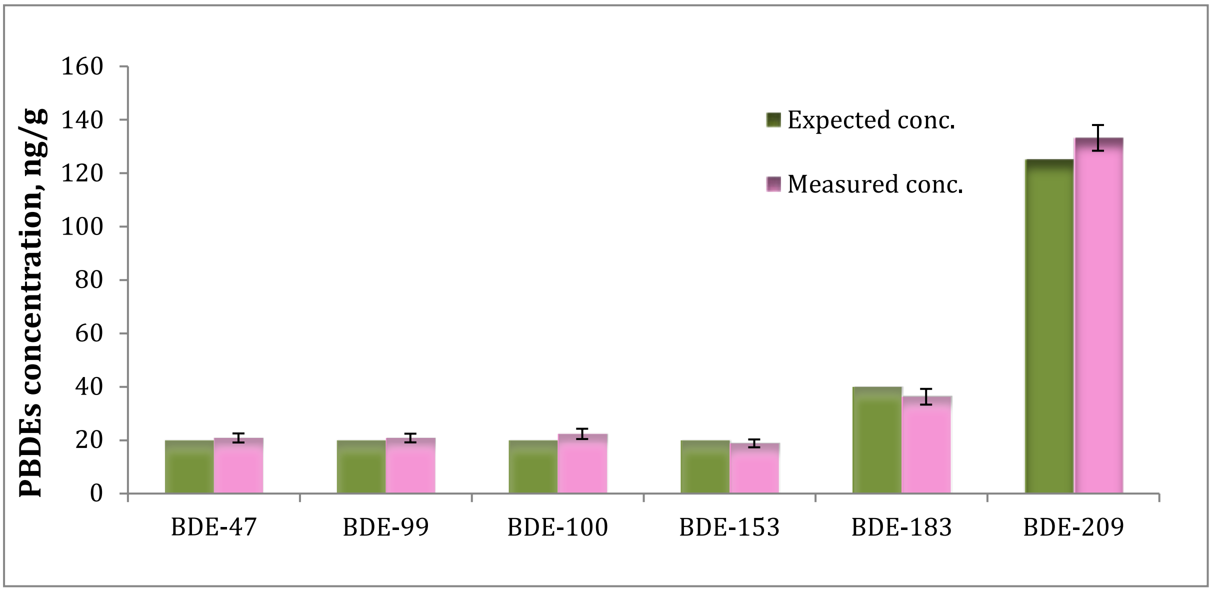
Figure 2-7 Results of SRM 2974A analysis for PBDEs (n=5). Error bar – SD. Note: to enhance visualisation, the values for BDE-17, 28, 66, 85, 153, and 154 were multiplied by a factor of 10



The concentrations determined agree well with the certified values, with satisfactory reproducibility illustrated by the standard deviation – see Fig 2-6 – 2-9. These SRMs were also used as an ongoing check on accuracy by analysis of one aliquot of appropriate SRM for every 20 samples. In all cases, satisfactory data were obtained with RSD values not exceeding 30%.

Figure 2-8 Results of SRM 2974A analysis for HBCDs (n=4). Error bar – SD

Figure 2-9 Expected and measured PBDE concentrations in self-prepared QA/QC of duck yolk homogenate (n=10). Error bar – SD



2.10.3 Analysis of procedural blanks and duplicates

One procedural blank was analysed for every 5 samples, which were subject to PBDE analysis, throughout the study. The majority of the blanks contained <5% of the PBDE concentration in all samples; data, therefore, were not blank-corrected in such instances. However, in several cases the amount of PBDEs in a method blank was 5-20% of that detected in samples in the same batch, and in such cases the blank concentration was subtracted from the concentration determined in that batch of samples. For e-waste related environmental samples from China, blank concentration subtraction was carried out in one case for BDE-154, in two cases for BDE-66 and BDE-153, three cases for BDE-99, four cases for BDE-47 and 7 cases for BDE-100. The sample detection limit for those PBDEs was set therefore as the concentration detected in the blank. Additionally, BDE-47 was present in a duck egg blank at 5 to 7% of the concentrations detected in samples from the same batch, so the blank concentration was subtracted from the concentrations of BDE-47 determined in that batch of samples.

Good precision of the applied methods was also demonstrated by the satisfactory values of RSD (typically < 20%) obtained through the analysis of duplicates, triplicates, and 10 replicates of the same pork sample (see section 2.2.2.6), as well as by the analysis of two sets of 10 replicates each of the self-prepared reference material (duck egg yolk homogenate, see section 2.10.2).

2.10.4 Instrument detection limit (IDL, pg/injection) and sample detection limit (SDL, ng/g)

Two categories of the detection limits were calculated in the study:

- Instrument detection limit (IDL)
- Sample detection limit (SDL)

The IDL, defined as the amount of the target compound that gives a signal to noise ratio of 3:1, was calculated using the data obtained for the calibration standard with the lowest concentration of target compounds (see Table 2-13). The SDL then was calculated as in equation 7:

$$SDL = \frac{IDL \times FEV}{VFEI \times SS} \times \frac{100}{\%\, IS\ Recovery} \text{ (Equation 7)}$$

Where:

FEV – final extract volume (µL);

VFEI – volume of final extract injected (µL);

SS – sample size (g);

% IS Recovery – percentage of internal standard recovery used to quantify the target compound in a particular sample.

Table 2-17 presents IDL and SDL for the different samples analysed in the current study.

Table 2-17 Instrument detection limits (IDL, pg/injection) and sample detection limits (SDL, ng/g) for environmental and dietary samples in the current study

PBDEs	Environmental samples				Diet samples			
	Sediments, Russia		Sediments, soils, dusts, China		Duck eggs, China		Meat, fish, shrimp, chicken eggs, oils, China	
	IDL	SDL	IDL	SDL	IDL	SDL	IDL	SDL
BDE-17	0.08	0.002	0.02	0.1	0.02	0.01	0.02	0.002
BDE-28	0.17	0.005	0.04	3.8	0.04	0.03	0.02	0.002
BDE-47	0.02	0.001	0.02	16.3	0.04	0.02	0.04	0.004
BDE-66	0.25	0.008	0.05	3.8	0.03	0.02	0.02	0.003
BDE-100	0.21	0.006	0.01	29.4	0.02	0.01	0.03	0.003
BDE-99	0.19	0.006	0.06	8.9	0.02	0.02	0.03	0.003
BDE-85	0.09	0.003	0.10	0.6	0.05	0.03	0.05	0.005
BDE-154	0.25	0.005	0.06	0.4	0.05	0.03	0.02	0.002
BDE-153	0.86	0.015	0.10	13.0	0.02	0.01	0.04	0.004
BDE-138	0.26	0.005	0.17	1.1	0.04	0.02	0.03	0.003
BDE-183	0.74	0.013	0.07	6.8	0.07	0.04	0.04	0.004
BDE-197	0.68	0.012	0.01	0.1	0.02	0.01	0.02	0.002
BDE-207	0.25	0.004	0.24	1.6	0.08	0.04	0.03	0.003
BDE-209	0.53	0.009	0.09	10.3	0.06	0.05	0.04	0.007

The higher values of SDLs obtained for the environmental samples from China than obtained for samples from Russia reflected both differences in the sample size analysed (5 g and 0.05 g respectively) as well as the detection of the target compounds in some of the procedural blanks analysed for the Chinese samples as described in section 2.10.3.

CHAPTER 3 CONCENTRATIONS OF PBDES IN ENVIRONMENTAL SAMPLES AFFECTED BY MANUFACTURE, RECYCLING AND DISPOSAL OF ELECTRIC AND ELECTRONIC GOODS

This chapter contains some text taken verbatim from the following publications:

Labunska I, Harrad S, Santillo D, Johnston P, Brigden K. 2013. Levels and distribution of polybrominated diphenyl ethers in soil, sediment and dust samples collected from various electronic waste recycling sites within Guiyu town, southern China. ***Environmental Science: Processes & Impacts.*** 15(2):503–11

Labunska I, Brigden K, Santillo D, Kiselev A, Johnston P. 2008. Russian refuse: PBDEs and other contaminants arising from production, recycling and disposal of electrical and electronic equipment in St-Petersburg area, Russia. ***Greenpeace Research Laboratories, Technical Report 07/2008. Exeter, UK***

3.1 PBDEs in sediment samples from the Neva River, Russia

Effluent pipe located in front of JSC "Ladoga", discharging into the Neva River, St-Petersburg, Russia, 2007

3.1.1 Introduction and aim of the study

Discharges of wastewater from the electronics manufacturing sector are possible sources of contamination of river sediments by persistent organic compounds including PBDEs (Labunska et al., 2007). A number of industrial sites involved in electronics production are known to discharge wastewaters directly into the Neva River, which runs through the city of St-Petersburg, Russia. A small study was conducted with the aim of investigating sediments collected from the Neva River for the presence of PBDEs as such data were not available at the time of the investigation. At the same time, this was the first application to environmental samples of the method developed for PBDE analysis. A description of the samples and sampling programme is provided in section 2.1.1.1. Location of sampling sites is presented in Fig. 2-1.

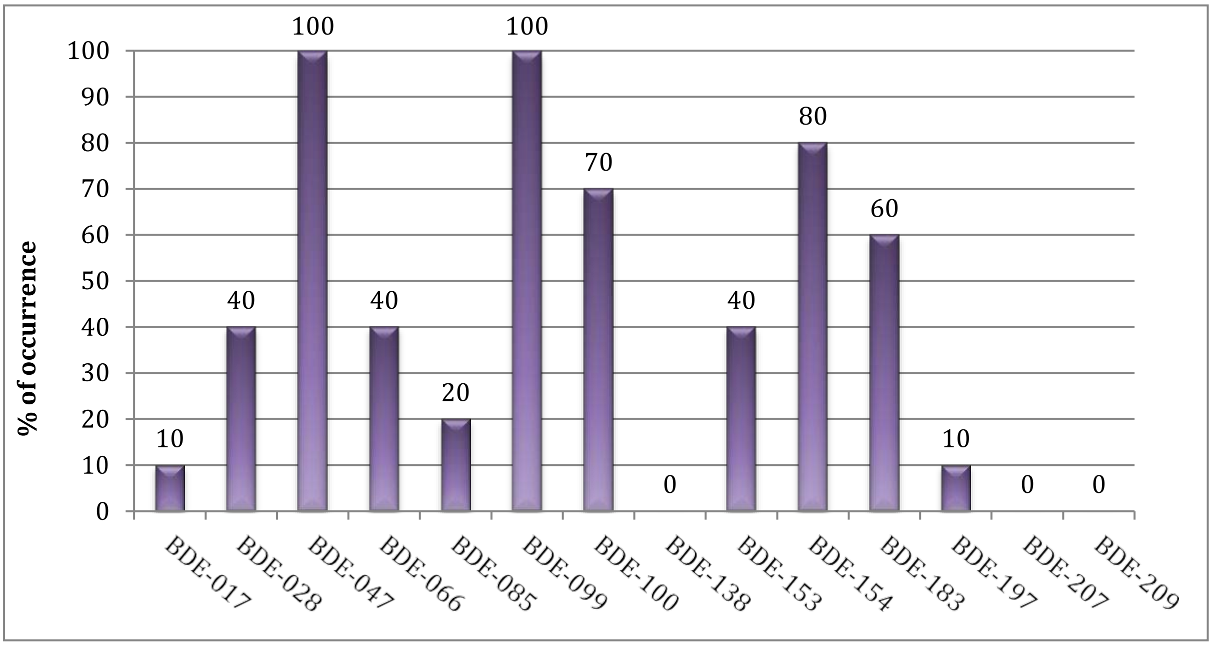
Table 3-1 PBDE concentrations in sediment samples, in ng/g dry weight, Neva River, Russia

	Site 1		**Site 2**	**Site 3**			**Site 4**	**Site 5**		**Site 6**
Code	**RU07027**	**RU07028**	**RU07030**	**RU07002**	**RU07003**	**RU07004**	**RU07023**	**RU07006**	**RU07007**	**RU07017**
BDE-17	<0.002	<0.002	0.022	<0.002	0.139	<0.002	<0.002	<0.002	<0.002	<0.002
BDE-28	0.046	0.012	0.017	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.016
BDE-47	0.013	0.009	0.043	0.043	0.272	0.166	0.215	0.050	0.843	0.004
BDE-66	<0.008	<0.008	0.124	<0.008	<0.008	0.495	0.209	<0.008	0.267	<0.008
BDE-100	0.016	0.015	<0.006	<0.006	0.091	0.174	0.138	<0.006	0.143	0.016
BDE-99	0.028	0.130	0.130	0.059	0.356	0.804	0.482	0.024	1.124	0.011
BDE-85	<0.003	<0.003	0.040	<0.003	<0.003	<0.003	<0.003	<0.003	0.078	<0.003
BDE-154	<0.005	0.005	0.012	0.008	0.016	0.033	0.022	0.009	0.076	0.006
BDE-153	<0.015	<0.015	<0.015	<0.015	0.039	0.052	0.044	0.015	<0.015	<0.015
BDE-138	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
BDE-183	<0.013	<0.013	0.020	<0.013	0.040	0.055	0.032	0.022	0.557	<0.013
BDE-197	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	0.337	<0.012
BDE-207	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
BDE-209	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009
∑PBDEs	0.10	0.17	0.41	0.11	0.95	1.78	1.14	0.12	3.43	0.05

Table 3-1 presents data on congener specific PBDE concentrations detected in sediment samples collected from the Neva River, including the sum of total PBDEs detected in each sample, ranging from 0.1 to 3.4 ng/g dry weight.

The presence of PBDEs in all sediment samples starting from the very beginning of the Neva River down to its delta in the Nevskaya Guba, part of the Gulf of Finland, may indicate long term discharge of these chemicals into the river and, possibly, even into the Ladoga Lake from which the Neva River originates. Two PBDE congeners, BDE-47 (tetra-BDE) and BDE-99 (penta-BDE) were the most prominent in all samples quantified in this study, suggesting that technical mixtures of commercial penta-BDE (La Guardia et al., 2006) were important contributors to overall PBDE burden in the investigated area (see Fig. 3-1). Three of the congeners considered in our study (BDE-138, BDE-207 and BDE-209) were present at concentrations below corresponding detection limits, which may suggest that investigated area was not impacted by higher brominated commercial formulations, such as Octa- and Deca-BDE.

Figure 3-1 PBDE detection frequency (%) in sediment samples from Neva River, Russia



The lowest ∑PBDE concentrations were detected in the two samples collected at the river source (outflow from Ladoga Lake) at 0.10 ng/g dw and in a single sample collected from Nevskaya Guba, Gulf of Finland, at 0.05 ng/g dw. In contrast, the highest PBDE concentrations were detected in samples collected downstream from the main industrial area of St-Petersburg with a maximum of 3.43 ng/g dw (Fig. 2-1, site 5). A sample collected from a discharge pipe located in front of the Petrogradskaya Embankment Industrial Zone (Fig. 2-1, site 4), contained a total PBDE concentration of 1.14 ng/g dw, which was one order of magnitude higher than detected in sediment at the riverhead. Therefore, this may indicate that this discharge point is one of the possible sources of PBDEs into the Neva River.

It is important to note, however, that the Neva is a tidal river, which means that it is difficult, if not impossible, to identify specific point sources of contaminants through the analysis of river sediments alone. Furthermore, even at specific single locations (e.g., Fig. 2-1, sites 3 and 5), the variation in PBDE concentrations between individual samples can be quite significant. Nonetheless, the fact that the most contaminated sediments were found in the vicinity of industrial discharges and industrialised tributaries of the Neva River, indicates the likely importance of industrial discharges as a source of PBDEs.

In general, the levels of PBDEs detected in this study were within the middle of the range reported for river and coastal sediments in various parts of the world. It is important to note, however, that most such studies that investigated a similar range of major PBDE congeners to those in our study, detected BDE-209 as the main contributor to ∑PBDEs. Therefore, it was not always possible to make a direct comparison as deca-BDE was found below the detection limit in samples from Neva River in our study. Nevertheless, ∑PBDE concentrations in Neva River sediments were higher than reported for sediments from the Northern Arabian Gulf at

0.164 ± 0.09 pg/g dw (Gevao et al., 2014), and comparable to those detected in creek and subtidal sediments in Korea (range: 0.18 – 13.95 ng/g dw) (Lee et al., 2014), and in marine sediments of Thermaikos Gulf, Greece (range: 0.26 - 4.92 ng/g dw) (Dosis et al., 2011) despite BDE-209 being the most abundant congener detected in the above studies. The sum of seven main lower brominated PBDEs (BDE-28, 47, 100, 99, 154, 153, and 183) detected in sediments in our study (range: 0.1 – 2.7 ng/g dw) was slightly higher than reported for sediments from principal watersheds of Shanghai, China (range: 0.05 to 0.61 ng/g dw) (Wu et al., 2013), but lower than in coastal sediments from the eThekwini Metropolitan Municipality, South Africa (range: not detected - 358 ng/g dw) (La Guardia et al., 2013).

As Nevskaya Guba is a predominantly sandy bay, relatively low levels of PBDEs were detected in sediment samples at this location (Site 16). In addition, despite the fact that the Neva is the third largest river in Europe in terms of average water flow, significant dilution of the contaminant load it carries is inevitable once the river reaches Nevskaya Guba bay. However, given that PBDEs are persistent and bioaccumulative chemicals (ATSDR, 2015), their initial dispersion through the bay does not eliminate the significance of the Neva River as an ongoing source of such pollutants to the Gulf of Finland and the Baltic Sea.

3.2 PBDEs in soil, sediment and dust within major e-waste recycling site at Guiyu town, southern China

Obsolete printed circuit boards at e-waste recycling sites in Guiyu, Guangdong Province, China, 2005

3.2.1 Introduction and aim of the study

Electronic waste recycling operations in some parts of Asia are conducted using rudimentary techniques which result in workplace and environmental contamination with toxic metals and persistent organic pollutants. An earlier study (Brigden et al., 2005), reveals that PBDEs were among the most frequently detected organic contaminants in environmental samples collected around e-waste recycling workshops in Guiyu, southern China, which were engaged in common activities such as: dismantling, shredding, solder recovery, acid processing and open burning. The aim of the current study was to determine the concentrations of 14 PBDEs, from tri- to deca-brominated, in 31 samples of soil, sediment, dust or ash collected in the vicinity of e-waste recycling sites in Guiyu, and to test the hypothesis that such rudimentary techniques of e-waste recycling are a significant source of PBDEs to the environment. We also compared the levels of PBDEs detected in samples associated with different types of processing activities and/or type of wastes processed, to better understand the processes responsible for elevated PBDE concentrations. A description of the samples and sampling procedure is provided in section 2.1.1.2.

3.2.2 PBDE concentrations

Table 3-2 presents concentrations of selected PBDEs in each environmental sample collected from e-waste recycling and reprocessing sites at Guiyu, China. Concentrations are expressed on both a dry weight and organic carbon content basis. Frequency distribution and cumulative percentage of key PBDEs in environmental samples (soil, sediment, and dust) effected by e-waste recycling operations are presented in Fig. 3-2. For comparison, Table 3-2 also includes concentrations of PBDEs that have been reported in urban soils (Jiang et al., 2010) and lake sediments (Wu et al., 2012) from sites in China which were not directly impacted by e-waste recycling activities. A full list of concentrations of all PBDEs monitored in all samples in this study (expressed on a dry weight (dw) basis) is provided in Appendix 2.

Average concentrations of all PBDEs detected in our study in soil and sediment samples exceeded by several orders of magnitude those previously reported for Chinese urban soils and Chinese lake sediments (see Table 3-2). BDE-209 displayed the highest average concentration (35,000 ng/g dw) of the PBDEs monitored, as well as the highest concentration detected in an individual sample, 320,000 ng/g dw in sample OB05 (Fig. 2-2 sampling site 3), a mixture of ash and burnt e-waste components, collected from an open burning site in the Longmen area.

Soil sample AP02 (Fig. 2-2 sampling site 1), collected from a dry waste pit adjacent to a Longmen workshop involved in acid processing of e-wastes, had the second highest BDE-209 concentration in our study, at 150,000 ng/g dw.

Table 3-2 Concentration of selected PBDEs, in ng/g dry weight (and ng/g organic carbon content, in parentheses) in samples collected from e-waste recycling sites in Guiyu, China

Code	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE-183	BDE-207	BDE-209
AP01 soil	62 (490)	350 (2,700)	140 (1,100)	360 (2,900)	380 (3,000)	1,400 (11,000)	2,800 (22,000)	6,900 (55,000)	18,000 (150,000)
AP02 soil	67 (780)	<16.3 (<190)	<29 (<340)	110 (1,300)	61 (710)	120 (1,400)	380 (4,400)	23,000 (270,000)	150,000 (1,700,000)
AP03 control	<3.8 (<51)	<16.3 (<220)	<29 (<380)	34 (450)	<0.4 (<5)	<13 (<170)	<6.8 (<91)	28 (370)	260 (3,500)
AP04 soil	<3.8 (<15)	<16.3 (<65)	<29 (<120)	<8.9 (<35)	<0.4 (<2)	<13 (<52)	19 (75)	820 (3,300)	12,000 (48,000)
AP05 sediment	2,600 (10,000)	15,000 (58,000)	1,300 (5,300)	17,000 (67,000)	2,500 (9,900)	9,300 (37,000)	1,500 (6,000)	2,800 (11,000)	19,000 (77,000)
AP06 sediment	<3.8 (<42)	<16.3 (<180)	<29 (<320)	<8.9 (<98)	<0.4 (<4)	790 (8,600)	1,100 (12,000)	1,500 (16,000)	2,600 (29,000)
AP07 soil	36 (96)	170 (440)	<29 (<78)	200 (540)	15 (40)	45 (120)	45 (120)	130 (350)	1,800 (4,800)
AP08 soil	23 (73)	<16.3 (<51)	<29 (<91)	97 (310)	21 (66)	48 (150)	48 (150)	110 (340)	1,200 (3,800)
AP09 sediment	<3.8 (<19)	<16.3 (<83)	<29 (<150)	<8.9 (<45)	6 (30)	<13 (<66)	<6.8 (<35)	17 (86)	96 (490)
AP10 sediment	7 (56)	57 (460)	<29 (230)	60 (480)	<0.4 (<3)	22 (176)	53 (420)	30 (240)	370 (3,000)
AP11 control	11 (180)	38 (620)	<29 (480)	36 (590)	<0.4 (<7)	<13 (<21`0)	<6.8 (<110)	<1.6 (<26)	<10 (<160)
AP12 sediment	310 (2,700)	2,000 (17,000)	180 (1,600)	2,200 (19,000)	130 (1,100)	460 (3,900)	73 (620)	110 (910)	2,700 (23,000)
AP13 soil	24 (150)	210 (1,300)	84 (520)	240 (1,500)	9 (55)	59 (360)	<6.8 (42)	94 (580)	530 (3,300)
AP14 sediment	170 (1,400)	1,300 (11,000)	<29 (<240)	1,500 (13,000)	77 (640)	260 (2,200)	34 (280)	110 (880)	1,800 (15,000)
AP15 sediment	<3.8 (<40)	<16.3 (<170)	<29 (<300)	<8.9 (<93)	<0.4 (<4)	<13 (<140)	30 (310)	48 (500)	1,100 (11,000)
AP16 sediment	<3.8 (<21)	<16.3 (<88)	<29 (<160)	36 (200)	120 (640)	1,100 (5,900)	2,900 (16,000)	1,600 (8,600)	8,100 (44,000)
OB01 ash/soil	20 (84)	62 (260)	<29 (<120)	69 (290)	6 (25)	25 (110)	32 (140)	46 (190)	630 (2,700)
OB02 ash/burnt waste	3,200 (1,600)	220 (1,100)	<29 (<150)	210 (1,100)	<0.4 (<2)	52 (270)	90 (460)	78 (400)	780 (4,000)
OB03 ash/burnt waste	520 (1,000)	510 (990)	210 (420)	760 (1,500)	200 (380)	640 (1,300)	1,600 (3,100)	890 (1,700)	8,100 (16,000)
OB04 ash/burnt waste	330 (720)	1,000 (2,200)	200 (430)	500 (1,100)	170 (360)	1100 (2,300)	2,600 (5,500)	14,000 (30,000)	31,000 (66,000)
OB05 ash/burnt waste	1,600 (2,200)	9,500 (13,000)	1,000 (1,400)	11,000 (15,000)	1,800 (2,400)	4,600 (6,300)	7,100 (9,700)	25,000 (34,000)	320,000 (440,000)

Code	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE-183	BDE-207	BDE-209
PD01 dust	<3.8 (<6)	670 (1,000)	170 (250)	850 (1,300)	73 (110)	170 (250)	450 (680)	190 (280)	2,000 (3,000)
PD02 soil/ sediment	<3.8 (<16)	480 (2,000)	170 (730)	1,700 (7,100)	160 (690)	420 (1,800)	490 (2,100)	490 (2,100)	8,500 (36,000)
SS01 Dust	820 (3,500)	2,800 (12,000)	550 (2,300)	3,000 (13,000)	2,100 (9,100)	8,400 (36,000)	7,300 (31,000)	2,000 (8,500)	25,000 (11,000)
SS02 dust	98 (1,200)	530 (6,700)	170 (2,200)	650 8,300)	530 (6,700)	1,700 (22,000)	4,100 (52,000)	3,100 (39,000)	14,000 (18,000)
SS03 dust	250 (1,300)	1,000 (5,100)	230 (1,200)	890 (4,500)	710 (3,600)	5,300 (27,000)	6,500 (33,000)	5,100 (26,000)	19,000 (96,000)
SH01 dust/soil	<3.8 (<76)	<16.3 9<330)	<29 (<580)	33 (66)	24 (480)	110 (2,200)	540 (11,000)	1,400 (29,000)	15,000 (290,000)
SH02 sediment	12,000 (51,000)	21,000 (85,000)	5,100 (21,000)	19,000 (79,000)	8,500 (35,000)	20,000 (80,000)	8,500 (35,000)	25,000 (100,000)	120,000 (490,000)
SH03 sediment	5,700 (39,000)	20,000 (130,000)	2,400 (16,000)	21,000 (140,000)	7,600 (51,000)	26,000 (170,000)	7,700 (52,000)	6,500 (44,000)	48,000 (320,000)
SH04 sediment	9,200 (30,000)	38,000 (120,000)	3,800 (12,000)	41,000 (130,000)	3,700 (12,000)	13,000 (41,000)	1,600 (5,100)	7,800 (25,000)	120,000 (390,000)
SH05 sediment	5,700 (21,000)	18,000 (66,000)	1,200 (4,700)	17,000 (63,000)	1,900 (7,400)	7,500 (28,000)	1,400 (5,300)	14,000 (53,000)	54,000 (210,000)
Current study, soils average (n=6), d/w	26 ± 24	150 ± 190	50 ± 60	390 ± 630	45 ± 60	120 ± 150	160 ± 210	4,100 ± 9,200	28,000 ± 58,000
Current study, sediments average* (n=13), d/w	2,800 ± 4,200	8,800 ± 12,200	1,100 ± 1,700	9,200 ± 13,000	1,900 ± 3,000	6,100 ± 8,500	2,100 ± 2,800	5,100 ± 7,300	31,000 ± 44,000
China, urban soil, average [a]	0.0033 ± 0.0043	0.0364 ± 0.0491	0.0199 ± 0.0179	0.0193 ± 0.0256	0.0030 ± 0.0025	0.0053 ± 0.0056	0.0116 ± 0.0139	n/a	0.477 ± 0.648
China, lake sediments, average [b]	∑PBDE tri-hepta 0.176 ± 0.102			1.261 ±1.181			8.163 ±13.311		

* excluding two control samples AP03 and AP11;

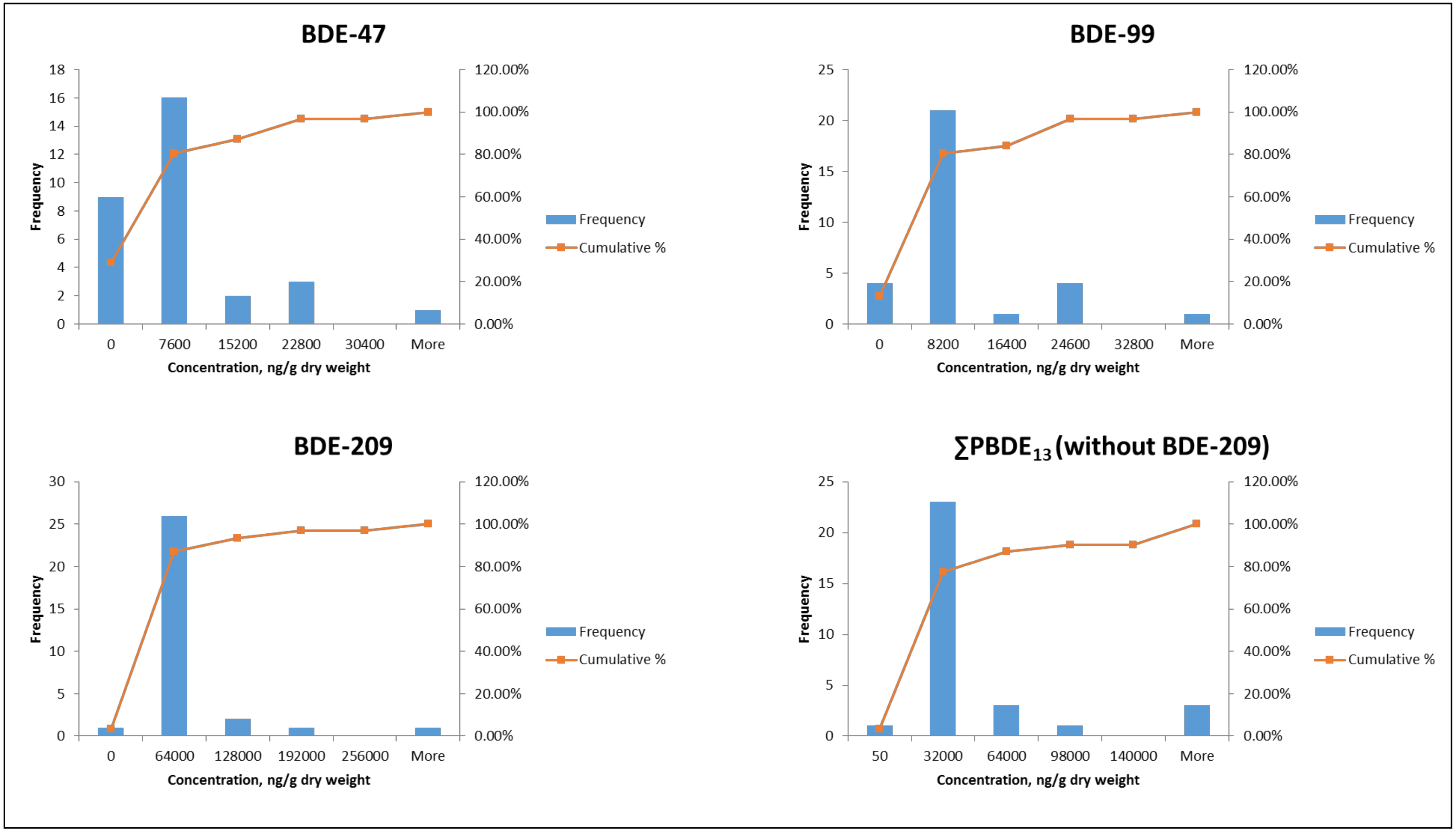
± – standard deviation;

n/a – not analysed;

a - (Jiang et al., 2010)

b - (Wu et al., 2012)

Figure 3-2 Frequency distribution and cumulative percentage of key PBDEs in environmental samples (soil, sediment, and dust) effected by e-waste recycling operations in Guiyu, China

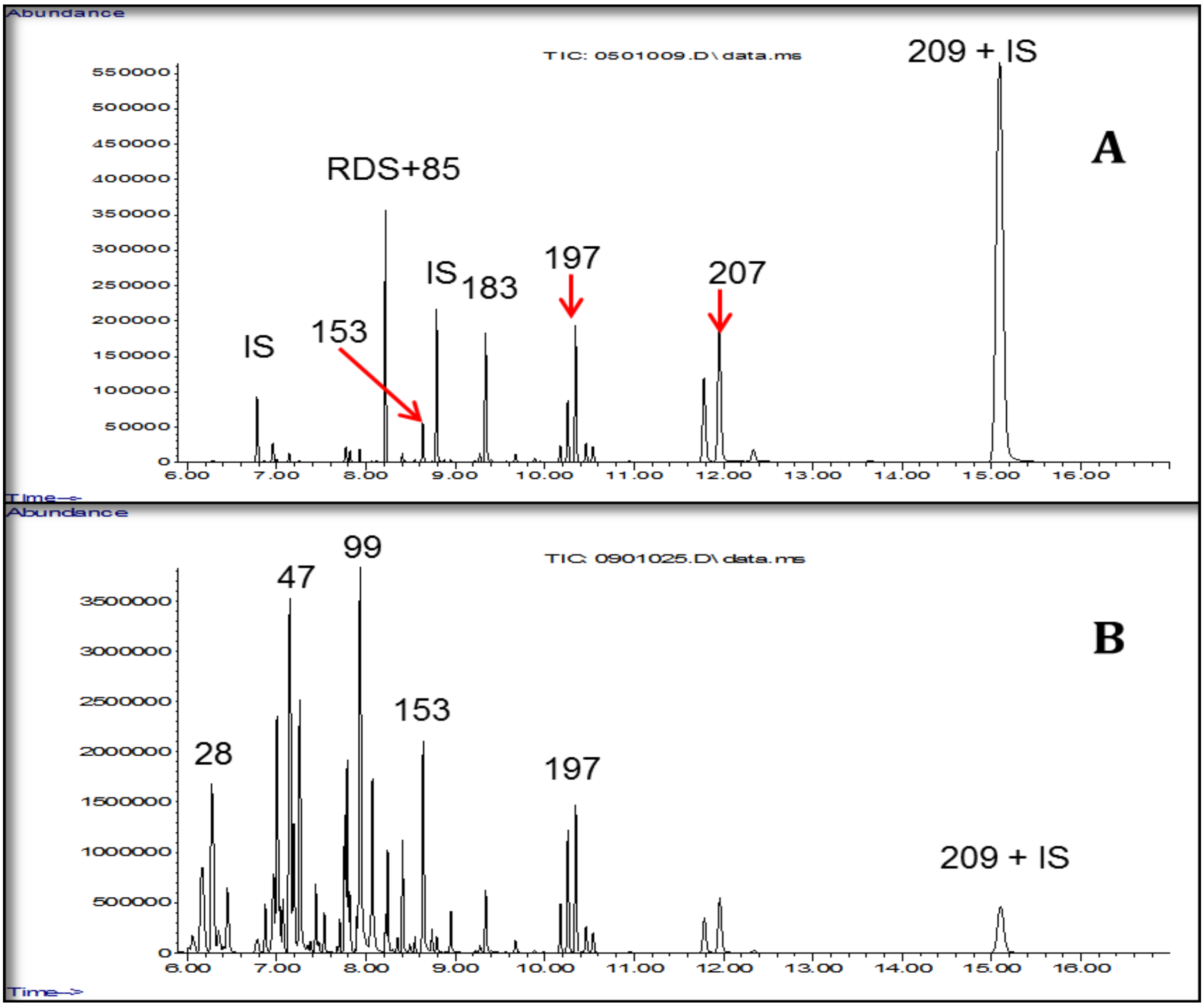


Moreover, the low organic carbon content of this sample meant that, when normalised to organic carbon, it displayed the highest concentration of BDE-209 in this study at 1,700,000 ng/g TOC. In contrast, the control river sediment sample AP03 (e.g., an upstream sample which was not visually affected by e-waste activities in the area at the time of sampling) (Fig. 2-2 sampling site 1) collected upstream of an acid processing workshop in Longmen, contained concentrations (BDE-209 = 260 ng/g dw, ∑PBDEs = 330 ng/g dw) that were several orders of magnitude lower than in samples collected either adjacent to (soil samples AP01, AP02, and AP04; and sediment sample AP06) or downstream from the workshop (sediment sample AP05).

Similarly, sediment sample AP11 (Fig. 2-2 sampling site 5) (assigned as a control sample due to its location away and upstream from acid processing area on sites 4 and 6), which was collected from a small river near the road between Guiyu and Nanyang towns crossing over Liangjiang River; had the lowest concentrations of PBDEs among the samples collected from that area. It was also the only sample in our study in which the concentration of BDE-209 was below our limit of detection. The total PBDE concentration in sample AP11 was 99 ng/g dw, two orders of magnitude lower than those detected in all soil samples around workshops at this acid processing area (AP07, AP08, and AP13, Fig. 2-2 Sites 4 & 6).

Sediment samples collected close to, or downstream from, this area (AP09, AP10, AP12 and AP14, Fig. 2-2 Sites 4 & 6), also displayed total PBDE concentrations that exceeded, by between 1.4 and 92 times, those in the corresponding control sample AP11. Moreover, the ∑PBDE concentration in the sediment sample collected immediately behind a workshop at sampling site 4 (AP10) was approximately 5 times higher than in the associated sample AP09 collected further away from the same workshop.

Figure 3-3 Chromatograms of PBDEs in street dust/soil sample (A) around plastic shredding workshop, Longgang, and sediment sample (B) from Liangjiang River receiving wastes from printed circuit boards shredding workshop

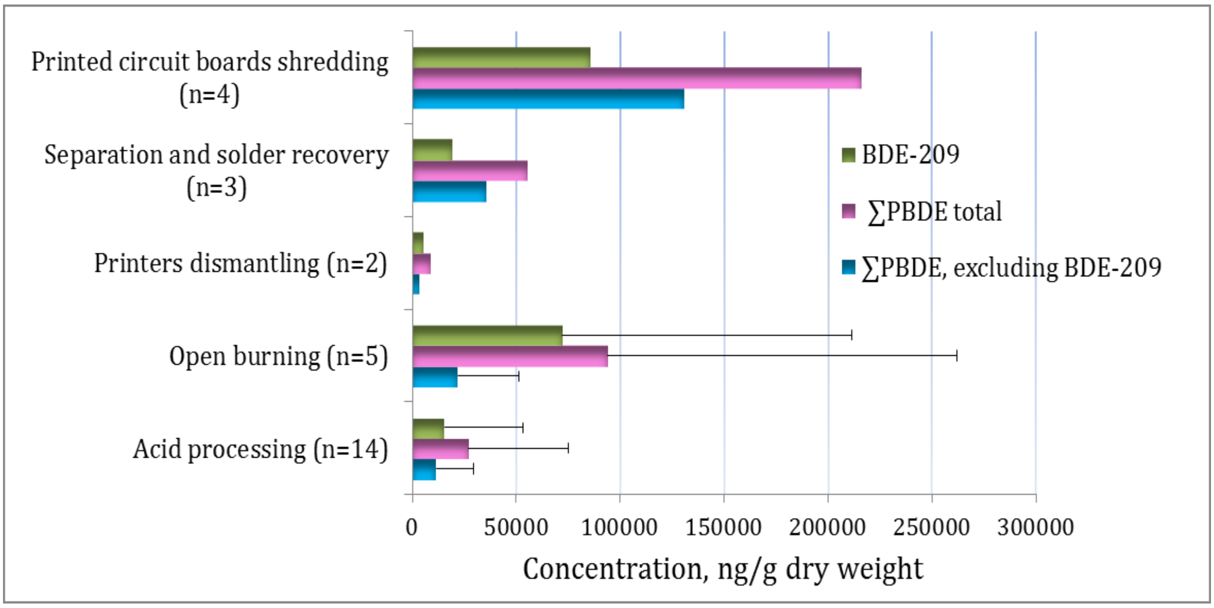


This is consistent with our hypothesis that such workshops are a significant source of PBDEs to the environment. The highest concentrations of congeners other than BDE-209 were detected in sediment samples collected around workshops with the prefix SH, denoting that their primary activity was the shredding of components (plastics or printed circuit boards) – see Fig. 3-3. Sample SH02, collected in the vicinity of a circuit boards workshop located by the Liangjiang River (Fig. 2-2 sampling site 12), contained the highest levels in our study of BDE-28, BDE-100, BDE-154, BDE-183, and BDE-207, at concentrations of 12,000; 5,100; 8,500; 8,500; and 25,000 ng/g dw respectively. The highest concentrations of BDE-47 and BDE-99 (i.e. 38,000 and 41,000 ng/g dw, respectively) were found in sample SH04 (Fig. 2-2 sampling site 14) collected close to a workshop located on the bank of Liangjiang River. The highest concentration of BDE-153 (26,000 ng/g dw) was found in sample SH03, also in the vicinity of a workshop at sampling site 13. Concentrations of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-197, expressed on an organic carbon content normalised basis, were also highest in samples associated with printed circuit board shredding and ranged from 16,000 ng/g for BDE-100 (in sample SH03) to 170,000 ng/g for BDE-153 (also in sample SH03). Moreover, concentrations of BDE-209 were also very high in samples collected around printed circuit boards shredding workshops, particularly in samples SH02 and SH04, which both contained BDE-209 at concentration of 120,000 ng/g dw.

Comparison of ∑PBDE concentrations in samples associated with different types of processing activities and/or type of wastes processed (Fig. 3-4) reveals the highest concentrations of PBDEs to be associated with samples taken near workshops shredding printed circuit boards (average 220,000 ng/g dw), followed by samples obtained from areas conducting open burning of e-wastes (average ~100,000 ng/g dw) and samples associated with the separation and recovery of solder from printed circuit boards (average ~ 50,000 ng/g dw). These levels exceed by several orders of magnitude those reported for urban soils (Jiang et al., 2010) and lake sediments (Wu et al., 2012) from sites in China not known to be impacted by e-waste processing activities.

It is also apparent that PBDE concentrations in samples associated with open burning and acid processing activities displayed markedly greater variability than those in samples associated with treatment of printed circuit boards. We believe that this reflects both the wider range of waste materials processed and different matrices sampled at the former site categories.

Figure 3-4 Average concentrations (ng/g dw) of BDE-209 and ∑PBDEs in samples collected from various sectors of e-waste recycling in Guiyu, China. Error bar - standard deviation; n - number of samples



It is also evident that, while BDE-209 was the principal contributor to total PBDEs in samples associated with acid processing, open burning and printer dismantling activities, the sum of other PBDEs was greater in samples associated with printed circuit board processing. BDE-47, BDE-99, BDE-183 and BDE-197 were detected at particularly high concentrations in these latter samples. This may reflect the greater influence of Penta- and Octa-BDE commercial formulations known to have been used in printed circuit board components (EU, 2003c); however, this is based on a very small sample size.

3.2.3 Pattern and distribution of PBDEs

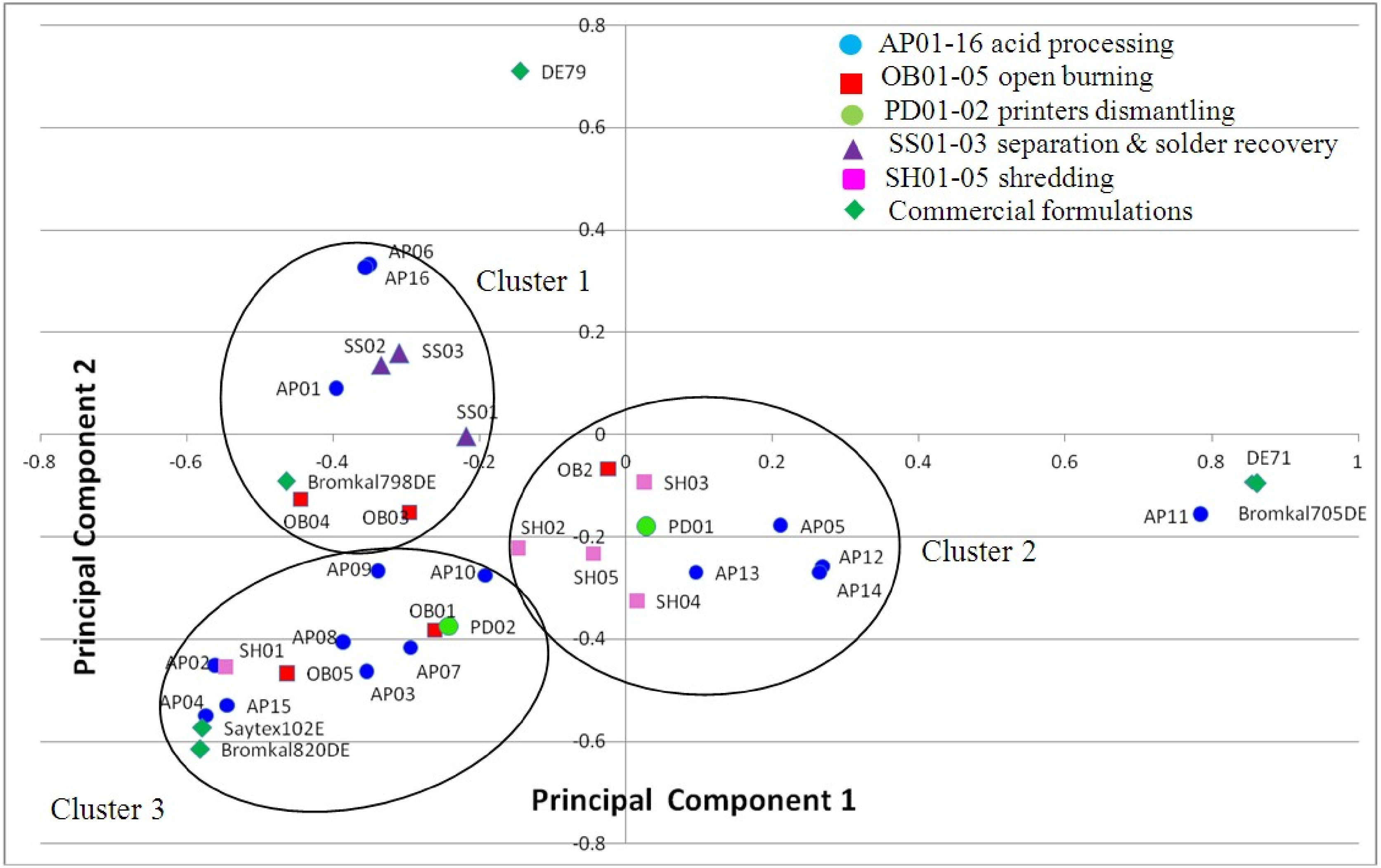
Principal Components Analysis (PCA) was conducted in order to examine congener patterns of PBDEs released by processes commonly used in e-waste recycling operations at the various sites sampled in Guiyu. Principal Component 1 (PC1) and Principal Component 2 (PC2) accounted for 35% and 20%, respectively, of the total variance within the data set. Highly positive PC1 values were attributed to elevated contributions from tri- to hexa-BDE congeners, mainly representative of Penta-BDE commercial formulations (DE-71 and Bromkal70-5DE).

Positive PC2 values were displayed by Bromkal 79-8DE, one of the Octa-BDE commercial formulations, though these scores were pulled in a slightly negative direction by the fact that this formulation (and, by extrapolation, samples impacted by it) also contains a relatively high content of BDE-209. Highly negative values for both PC1 and PC2 reflect the presence of BDE-209, the main congener of Deca-BDE commercial formulations (Saytex 102E and Bromkal 820-DE).

Fig. 3-5 shows the plot of PC1 versus PC2 scores calculated for each sample and for six commercial formulations entered into PCA for comparison. Scores for the commercial formulations were calculated based on data published elsewhere (La Guardia et al., 2006). There was clear separation of some of the samples, particularly for those associated with e-waste separation and solder recovery (SS01-SS03) in Cluster 1 and printed circuit board shredding (SH02-SH05) in Cluster 2, both occupying an area of component space also occupied by Octa-BDE formulation Bromkal 79-8DE. Cluster 1 also contained samples from open burning (OB03, OB04) and acid processing (AP06, AP16) sites, indicating that Octa- BDE formulations were an important influence on these four samples.

Cluster 2 displayed more positive PC1 scores than Cluster 1, most likely due to a presence of Penta-BDE formulations in Cluster 2 samples. Similarly, more negative PC2 values for samples in Cluster 2 in comparison to Cluster 1 may indicate the influence of the Deca-BDE formulation in Cluster 2 samples. Therefore, Cluster 2 samples, which also included several samples from acid processing and one sample from a printer dismantling site, appear influenced by a combination of all three commercial PBDE formulations, occupying a region of component space that is roughly equidistant from each of the three main formulations.

Figure 3-5 Plot of PC1 versus PC2 for principal component analysis of the samples associated with various e-waste recycling techniques employed in Guiyu, China



Finally, Cluster 3, which was characterized by strongly negative values of both PC1 and PC2, mainly contained samples associated with acid processing sites, indicating that this recycling activity in particular, can constitute a significant source of Deca-BDE to the local environment.

Although the majority of samples from acid processing sites displayed a pattern closely resembling that of Deca-BDE, others showed apparently greater influences from Octa- and Penta- formulations (including one sample, AP11, with a congener pattern very close to that of commercial Penta-BDE formulations DE71 and Bromkal 70-5DE). This spread of points, along with the lack of clustering apparent in samples from open burning sites, is suggestive of a wider diversity of e-waste materials being subjected to these two relatively non-specific treatment processes compared to shredding, dismantling and solder recovery operations, as may be expected. Many different types of electronic equipment (including cables, casings and component parts) are burnt in the open to recover metals in a batch-processing manner. As a result, localised contamination is likely to vary considerably from place to place, even over relatively short distances depending on precisely what has been burnt. Similarly, acid leaching processes may be applied to wastes which are relatively unsegregated in comparison to workshops dedicated to circuit board solder recovery or shredding. In these cases, therefore, the pattern of observed contamination depends less on the type of recycling process involved than on the type of the waste processed which, when diverse as in these instances, results in contamination that reflects inputs from more than one PBDE formulation.

Furthermore, given the particularly aggressive nature of acid leaching and open burning of e-wastes as treatment methods, it is also possible that partial degradation/debromination of PBDEs in parent materials (Stapleton, 2006) contributes to the greater diversity in congener patterns apparent in the residues sampled from sites in which these practices were commonplace. Further investigation would be required to determine the significance of these treatment methods in influencing congener profiles.

3.2.4 Comparison with previously reported data

The total PBDE concentrations detected in some samples in our study are among the highest reported to date, even when compared to other areas known to be influenced by e-waste recycling activities (see Table 3-3). The highest level of ∑PBDEs (390,000 ng/g dw), was detected in a sample collected from the sampling site 3 used for open burning ofe-waste. This concentration exceeded (though was of the same order of magnitude as) that reported previously for indoor dust from an e-waste storage site in Thailand (290,000 ng/g dw) (Muenhor et al., 2010), indoor dust from private houses in Guiyu, China (160,000 ng/g dw) (Wang et al., 2010) and in shredded e-waste residues from Taizhou, China (163,000 ng/g dw) (Ma et al., 2009). Moreover, it was significantly higher than that detected previously in soil from open burning sites in Guiyu (63,300 ng/g dw) (Leung and Wong, 2007) and in road soil near an e-waste dismantling site in Qingyuan (9,200 ng/g dw) (Luo et al., 2009b). Moreover, the peak BDE-209 concentration of 320,000 ng/g dw and the average total PBDEs concentration of 66,000 ng/g dw detected in our study are also, to our knowledge, the highest reported.

Those levels were about one order of magnitude higher than those previously reported for six surface soils collected specifically from e-waste recycling sites in Guiyu (Gao et al., 2011) and more than double (for average of ∑PBDEs) those detected in dust samples collected beneath fans in workshops involved in printed circuit boards heating in Guiyu (Leung et al., 2011). The extremely high PBDE levels detected in certain samples in our study along with wide variation of PBDE concentrations most probably arise from a combination of various factors including location of sampling points, proximity to the source of contamination, type of e-wastes processed as well as e-waste treatment techniques, among others.

Table 3-3 Concentrations of PBDEs (in ng/g dw) in current study and previously reported as being detected in samples collected from e-waste related sites in China and Thailand. n - number of samples

Location	Site description or recycling process	Matrix analysed	BDE-209 (range)	∑PBDEs (range)	Average $^{(av)}$ or median $^{(md)}$ ∑PBDEs	Number of congeners	Source
Guiyu, Guangdong, China, current study	all sites investigated	soil, sediment, dust, ash, burnt e-wastes	96 – 320,000	140 – 390,000	66,000^{av} 15,000^{md} (n=29)*	14 (tri-deca)	Current study
Four sites in Thailand	e-wastes storage	indoor dust	250 - 250,000	320 - 290,000	43,000^{av} 28,000^{md} (n=25)	21 (tri-deca)	(Muenhor et al., 2010)
Guiyu, Guangdong, China	private houses	indoor dust	105 - 140,000	150 - 160,000	7,300^{av} 1,400^{md} (n=23)	28 (di-deca)	(Wang et al., 2010)
Fengjiang, Taizhou, China	printed circuit boards & plastics shredding	shredded residues	977 - 6,390	997 - 163,000	45,500^{av} (n=5)	10 (tri-deca)	(Ma et al., 2011)
Guiyu, Guangdong, China	open burning site	soil	328 - 48,600	398 – 63,300	21,200^{av} (n=3)	24 (mono-deca)	(Leung and Wong, 2007)
Qingyuan, Guangdong, China	e-wastes dismantling site	road soil	69 - 6,320	191 - 9,200	2,700^{av} (n=29)	22 (mono-deca)	(Luo et al., 2009b)
Fengjiang, Taizhou, China	e-wastes workshop floors	indoor dust	5,560 - 80,600	6,300 - 82,200	30,700^{av} (n=5)	10 (tri-deca)	(Ma et al., 2011)
Guiyu, Guangdong, China	various e-waste recycling sites	surface soils	105 – 5,220	130 – 7,100	2,910^{av} (n=6)	19 (tri-deca)	(Gao et al., 2011)
Guiyu, Guangdong, China	printed circuit boards heating	dust underneath fans	n/a	n/a	24,900^{av} (n=3)	27 (mono-deca)	(Leung et al., 2011)

However, similar situation with wide scatter of the data for PBDEs levels in environmental samples, including dust, affected by e-waste recycling operations has reported in previous studies in other countries including in Thailand (Muenhor et al., 2010), Africa (Abafe and Martincigh, 2015), Vietnam (Tue et al., 2013) as well as at other locations in China (Luo et al., 2009b; Ma et al., 2011). Therefore, such variation could well be a feature common to, and typical of, contamination patterns associated with e-waste recycling operations including contamination of local biota and locally produced foodsTaken together, these data reaffirm the significance of poorly controlled 'e-waste' recycling operations as sources of hazardous wastes and of resulting environmental contamination which is locally severe and undoubtedly regionally significant.

Indeed, the concentrations of PBDEs determined for the wastes, dusts, sediments and soils sampled include some of the highest levels reported to date. For example, a median PBDE concentration ($\sum_{14}$PBDEs) of 220,000 ng/g dw was recorded for four sediment samples from an area used for shredding of printed circuit boards, while maximum values of 390,000 ng/g dw and 170,000 ng/g dw were found in a sample of uncontained ash from an open burning site and of soil from the site of an acid-processing works respectively. In addition to contamination of the workplace, these results indicate that the crude recycling and disposal methods routinely employed within the areas studied at the time of sampling (including acid leaching, open burning and shredding operations) have also given rise to contamination of soils and river sediments in the vicinity, suggesting that these areas may be acting as significant point sources of wider environmental pollution. Principal components analysis applied to TOC-normalised data confirms a diverse and complex picture of PBDE congener distribution amongst the samples collected, with those data relating to some recycling activities showing what appear to be more consistent patterns of orientation than others. Further sampling and analysis would be valuable, particularly aimed at extending data sets for areas surrounding shredding and solder recovery workshops, in order to discern with greater detail and confidence the relative contributions of different input waste material and specific processing method used to the spread of PBDE congener patterns observed.

CHAPTER 4 DUCK EGGS AS AN IMPORTANT SOURCE OF HUMAN EXPOSURE TO PBDES IN AREAS IMPACTED BY E-WASTE RECYCLING AND/OR DISPOSAL, TAIZHOU, EASTERN CHINA


Duck farm at e-waste recycling sites in Taizhou, Zhejiang Province, China, 2011

This chapter contains some text taken verbatim from:

Labunska I, Harrad S, Santillo D, Johnston P, Yun L. 2013. Domestic duck eggs: an important pathway of human exposure to PBDEs around e-waste and scrap metal processing areas in Eastern China. ***Environmental Science & Technology.*** 47(16):9258–66

4.1 Introduction and aim of the study

Although consumption of local foods is recognised as an important pathway of human exposure to PBDEs in areas of China involved in rudimentary recycling of electronic waste, dietary intake studies to date have not considered the contribution from consumption of duck eggs, despite them being a common dietary component. During the collection in 2005 of environmental samples around e-waste recycling sites in Guiyu, China, many small and medium size private duck farms were observed. We thus in 2011, re-visited e-waste recycling sites at Guiyu aiming to collect duck eggs for investigation. However, we found that the majority of duck farming had ceased there, as surrounding land had been identified in the interim as inappropriate for farming due to extensive contamination resulting from recycling activities. Hence, we visited another major e-waste recycling site in China located in Taizhou City, Zhejiang Province (Eastern China), with an operational history dating back around 30 years (Chan and Wong, 2013). It specialises in various e-waste recycling processes including: manual dismantling, circuit boards processing, acid treatment to recover metals, open burning, and dumping of processed wastes. In Taizhou e-waste processing areas, domestic bird farming was still active in 2011, similar to that observed in Guiyu in 2005. The aim of the current study was therefore to analyse duck eggs obtained from places involved in e-waste recycling in Taizhou City and to estimate human exposure to PBDEs via the consumption of such eggs, using duck eggs from control locations to place those estimates into context. Fresh duck eggs (n=11) were collected from each of five farms located within 500 m of e-waste recycling workshops in the Wenling and Luqiao districts of Taizhou City, Eastern China, in November 2011, along with eggs from a control site located 90 km to the north-east. Details of the sampling procedure and description of sampling locations are presented in section 2.1.2.1.

4.2 PBDE concentrations in duck egg yolk samples

Concentrations of individual PBDEs calculated on a lipid weight (lw) basis along with % fat contents detected in duck egg yolk samples are presented in Tables 4-1 and 4-2. Values are calculated for 11 samples from each site; with levels below detection limits assigned zero values for calculation of averages (means). The average fat content in yolk samples varied from 29.7 ± 2.3 % to 39.4 ± 7.7 %; this is similar to the 36.7 ± 2.0 % reported elsewhere for duck egg yolks (Sinanoglou et al., 2011). Average concentrations (lw) of key congeners of the three commercial BDE formulations (BDE-99 in Penta-BDE, BDE-183 in Octa-BDE, and BDE-209 in Deca-BDE) are presented in Fig. 4-1.

Figure 4-1 Average concentrations of key congeners of commercial PBDE formulations (BDE-99, BDE-183 and BDE-209) in duck egg samples (n=11 from each site, ng/g lw), Taizhou City, Zhejiang Province, China. Error bar – SD

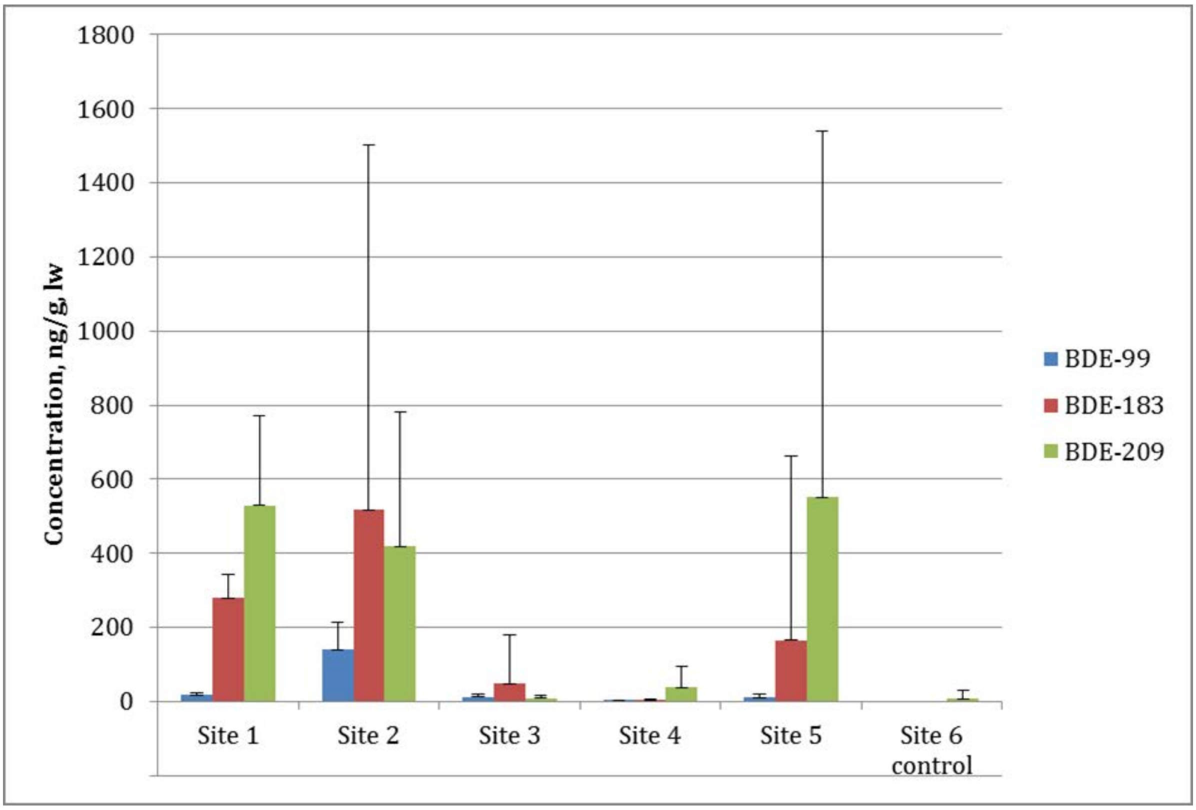


Table 4-1 PBDE concentrations (ng/g lipid weight) and lipids content (%) in duck egg yolk samples collected from sites 1 - 3 involved in e-waste recycling; n – number of samples

	Site 1 (n=11)				**Site 2 (n=11)**				**Site 3 (n=11)**			
	average	**SD**	**median**	**max**	**average**	**SD**	**median**	**max**	**average**	**SD**	**Median**	**max**
Lipids, %	39.4	7.7	34.8	52.8	29.7	2.3	30.5	32.9	32.6	2.2	32.1	35.8
BDE-17	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
BDE-28	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
BDE-47	8.5	6.8	12.4	15.2	110.6	43.2	107.9	168.9	12.1	6.1	10.6	24.3
BDE-66	<0.06	<0.06	<0.06	<0.06	2.4	2.6	2.7	6.3	<0.06	<0.06	<0.06	<0.06
BDE-100	4.7	3.9	6.2	9.9	10.5	6.9	12.2	21.0	0.6	1.0	<0.04	3.2
BDE-99	16.5	7.7	19.1	26.0	140.6	72.2	141.9	269.2	12.7	5.6	9.7	21.0
BDE-85	<0.09	<0.09	<0.09	<0.09	4.7	3.5	5.6	11.1	<0.09	<0.09	<0.09	<0.09
BDE-154	13.8	2.8	14.1	18.1	25.1	25.4	16.1	99.8	2.5	1.8	2.1	7.2
BDE-153	91.0	21.8	89.9	124.1	141.8	187.4	73.3	687.6	24.0	56.6	5.2	193.4
BDE-138	8.5	1.9	8.3	11.8	11.8	12.9	7.4	50.0	1.2	3.4	<0.07	11.5
BDE-183	279.8	63.8	288.5	368.6	517.4	986.1	250.3	3415.4	47.8	131.6	3.7	442.0
BDE-197	54.5	15.3	58.1	77.4	273.1	564.2	121.2	1942.1	6.2	15.7	1.1	53.1
BDE-207	44.1	20.0	39.9	74.9	120.2	214.0	46.0	749.0	0.3	1.1	<0.13	3.8
BDE-209	529.7	242.0	506.9	871.5	419.9	360.5	400.2	1234.9	9.0	6.3	10.7	17.6
∑PBDE	1051.1	356.3	1054.9	1553.5	1778.2	1967.5	1167.7	7389.2	116.5	214.6	47.0	754.9

Table 4-2 PBDE concentrations (ng/g lipid weight) and lipids content (%) in duck egg yolk samples collected from sites 4 - 5 involved in e-waste recycling and control site 6; n – number of samples

	Site 4 (n=11)				**Site 5 (n=11)**				**Site 6 (control) (n=11)**			
	average	**SD**	**median**	**max**	**average**	**SD**	**median**	**max**	**average**	**SD**	**median**	**max**
Lipids, %	32.7	1.9	32.5	35.7	30.9	1.6	31.1	33.6	35.6	4.1	34.9	42.0
BDE-17	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
BDE-28	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
BDE-47	2.0	2.4	<0.07	6.0	7.4	4.0	5.4	17.5	<0.07	<0.07	<0.07	<0.07
BDE-66	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
BDE-100	<0.04	<0.04	<0.04	<0.04	2.7	2.2	1.8	7.9	<0.04	<0.04	<0.04	<0.04
BDE-99	2.3	1.7	2.2	4.9	11.7	6.8	8.8	28.2	<0.05	<0.05	<0.05	<0.05
BDE-85	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
BDE-154	0.4	0.7	<0.08	1.9	9.0	16.0	4.6	56.9	<0.08	<0.08	<0.08	<0.08
BDE-153	1.9	1.8	2.2	5.4	47.5	119.9	11.4	408.6	<0.03	<0.03	<0.03	<0.03
BDE-138	<0.07	<0.07	<0.07	<0.07	3.1	10.1	<0.07	33.5	0.1	0.2	<0.07	0.8
BDE-183	2.6	2.6	2.3	8.9	165.9	497.0	17.3	1663.9	<0.12	<0.12	<0.12	<0.12
BDE-197	1.1	1.6	0.6	5.6	81.8	233.5	12.6	785.4	<0.04	0.2	<0.04	0.5
BDE-207	3.5	6.4	1.2	21.8	58.6	80.0	27.0	224.4	<0.13	<0.13	<0.13	<0.13
BDE-209	39.0	55.0	26.4	189.4	551.7	986.6	166.0	2738.0	7.9	22.0	<0.14	73.5
∑PBDE	52.7	69.5	33.2	243.4	939.4	1312.2	380.1	3361.5	8.0	21.9	0.0	73.5

Average ∑PBDE concentrations (sum of 14 congeners) in duck yolk samples collected from e-waste recycling sites ranged from 52.7 ng/g lw at site 4 to 1780 ng/g lw at site 2; while for control samples (site 6, obtained from ducks bred on an eco-farm located about 90 km from e-waste recycling sites in Taizhou), the average concentration was only 8 ng/g lw.

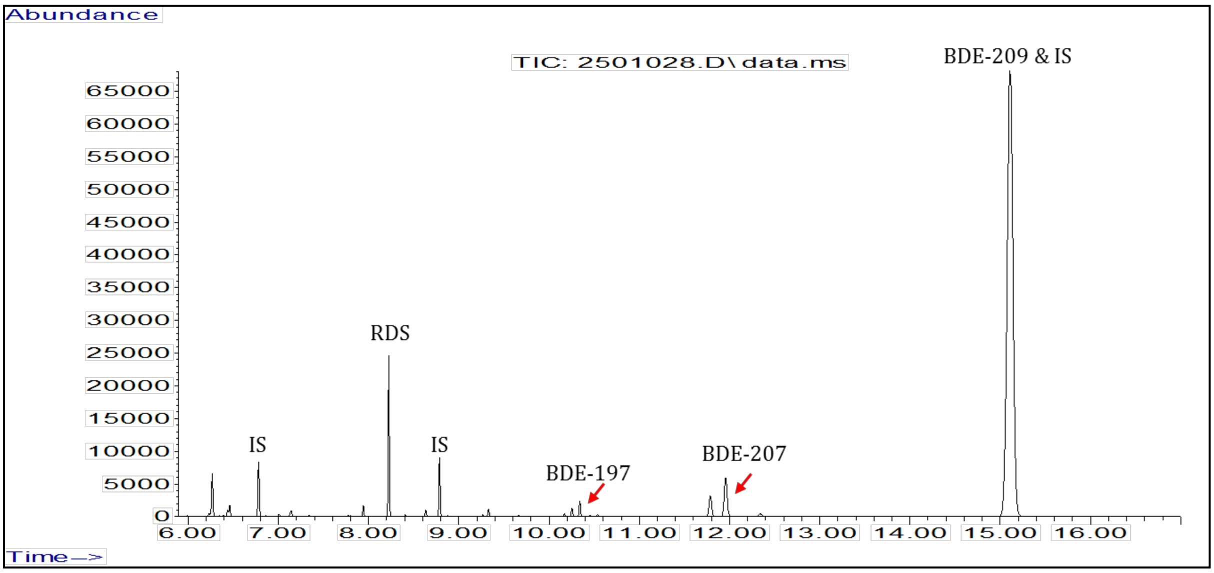
Among the samples collected within e-waste recycling sites, the lowest average concentration (52.7 ng/g lw) was detected for samples from an area which ceased e-waste recycling operations about six years prior to sample collection (site 4), though these lower concentrations may also be attributable to the increased distance between the farm and the former e-waste treatment workshops, which was about 500 m at site 4 compared to 10 – 40 m at other sites – see Table 2-3.

An intermediate average ∑PBDE concentration of 116.5 ng/g lw was found in eggs from site 3, at which e-waste recycling activities remain ongoing but have diminished recently. Conversely, average concentrations at sites 1, 2 and 5, at which e-waste recycling was still practiced extensively at the time of sample collection, significantly exceeded those detected at sites 3 and 4 (by approximately one and two orders of magnitude respectively, $p \ll 0.05$, single factor ANOVA). The highest concentration of 7,400 ng/g lw was detected in a sample from site 2.

It is also interesting to note that the variability of PBDE concentrations observed at a given site differed substantially between sites. For example, while for site 1 the relative standard deviation (RSD) of ∑PBDEs in egg yolks was 34 %, eggs from site 2, which contained similar levels of ∑PBDEs, displayed an RSD of 110 %. This was possibly due to differing age profiles of the ducks: all ducks from site 1 were of the same age (born 2010), while ducks from site 2 were of different ages, hatched between 2009 and early 2011. Hence, the larger variability in concentrations at site 2 may reflect the enhanced bioaccumulation of PBDEs in older ducks observed previously in bird species (Chen and Hale, 2010).

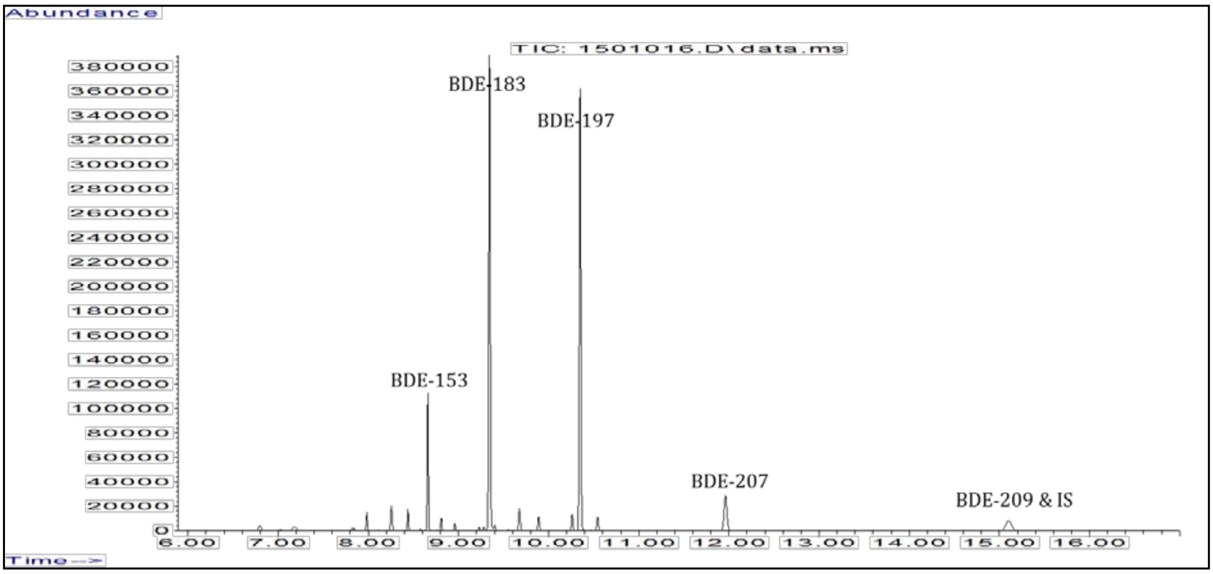
In the majority of the samples, BDE-209 was the most abundant congener (62%). Samples from sites 1, 2 and 5 had very similar average BDE-209 concentrations of about 500 ng/g lw (accounting for about 50 %, 24 % and 59 % of the corresponding ∑PBDE concentrations respectively). The highest individual BDE-209 concentration in this study (2,700 ng/g lw) was detected at site 5 - see Fig. 4-2. BDE-183 was the second most abundant congener in samples from sites with active e-waste recycling (average concentrations: 280 ng/g lw, 517 ng/g lw, and 166 ng/g lw for sites 1, 2, and 5 respectively). At site 2, the average BDE-183 concentration exceeded that of BDE-209, with one sample from site 2 displaying the highest BDE-183 concentration at 3,400 ng/g lw – see Fig. 4-3.

Figure 4-2 Chromatogram of PBDEs in the duck egg yolk sample containing the maximum BDE-209 concentration



BDE-99 was unusually prominent in samples from site 3, accounting for about 10 % of the average ∑PBDE concentration in eggs from this location. At site 3, BDE-153 contributed quite significantly to the average ∑PBDE concentration (21%). These apparent spatial variations in congener pattern are analysed further using PCA in section 4.3.

Figure 4-3 Chromatogram of PBDEs in the duck egg yolk containing maximum BDE-183 & BDE-197 concentrations



To assess the influence of commercial feed supplements to the foraging diet of ducks in our study, a sample of duck feed was analysed from each e-waste recycling site. BDE-209 was detected (0.19 - 5.12 ng/g dw) in feed samples from all but one of the printed circuit board recycling locations (site 5), whereas other PBDEs were detected only in the sample from site 2 (BDE-47, BDE-99 and BDE-100 at 0.36, 0.28 and 0.01 ng/g dw respectively).

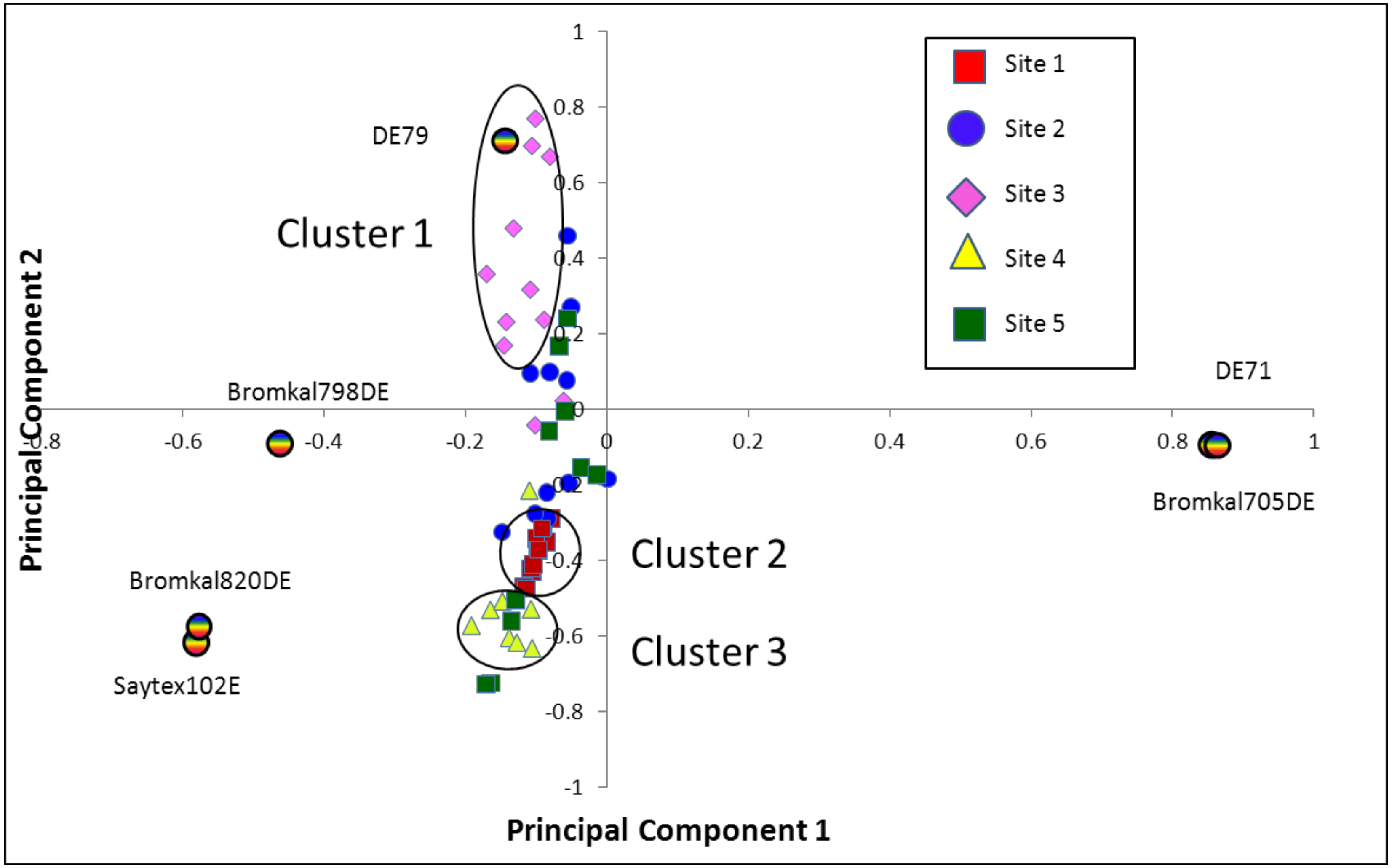
In comparison, PBDEs have been reported at very high concentrations in soils and sediments from e-waste recycling sites in Taizhou, ranging from 997 to 163,000 ng/g dry weight with an average of 45,500 ng/g dry weight for the sum of ten PBDE congeners (from tri- to deca-BDE) (Ma et al., 2009). This, coupled with the significantly higher concentrations detected in eggs from villages adjacent to operating e-waste treatment sites, leads us to conclude that the locally-foraged component of the ducks' diet is the principal source of contamination in eggs. This is consistent with the suggestion from another study (Luo et al., 2009a) that habitat and foraging habits are likely more important influences than feed supplements in determining the PBDE burden in farm birds.

4.3 PBDEs congener profiles in duck egg samples

To evaluate differences in PBDE congener profiles in duck eggs from different e-waste recycling sites, Principal Components Analysis (PCA) was conducted. Principal Component 1 (PC1) and Principal Component 2 (PC2) accounted for 37% and 26%, respectively, of the variation within the data set.

Fig. 4-4 shows the plot of PC1 versus PC2 scores calculated for each sample and for six commercial formulations entered into PCA for comparison. Some samples separate clearly on these component axes, particularly samples from site 1 (closely aggregated in Cluster 2) and site 4 (for which most samples fall within Cluster 3). By comparison, samples from site 3 disperse widely within Cluster 1. Samples from sites 2 and 5 displayed the most variable congener patterns, and could not be assigned to a specific cluster. When compared to the commercial formulations, Cluster 1 (site 3) appears strongly influenced by one or both Octa-BDE formulations, while Cluster 2 (site 1) and particularly Cluster 3 (site 4) bear strong similarities to the Deca-BDE mixture. Site 1 (Cluster 2) also displayed some similarity to the Octa-BDE formulations, given its more positive PC2 values than Deca-BDE. Moreover, Clusters 2 and 3 displayed positive PC1 scores, indicating an influence of the Penta-BDE formulation and/or a possible enhanced contribution of the less brominated congeners from debromination of BDE-209 (Van den Steen et al., 2007; Luo et al., 2009b). The diverse patterns in samples from sites 3 and 5 suggest a wide range of e-waste categories are processed at these locations. This is particularly so for site 5, where both metal scrap and e-waste recycling workshops are located.

Figure 4-4 Plot of PC1 versus PC2 for principal component analysis of duck egg samples collected near e-waste recycling sites in Taizhou, China



4.4 Comparison with previous reports on PBDEs in farm bird eggs

To the author's knowledge, this study is the first report of the levels of PBDEs in eggs from domesticated ducks from areas affected by e-waste recycling. A recent study (Ni et al., 2012) investigated levels of PBDEs in both chicken and duck eggs, but did not report results for duck eggs separately. Therefore, to place our data in context, we compared our findings with studies reporting PBDE concentrations in domestic chickens' eggs, focusing on studies which monitored both BDE-209 and lower brominated congeners (Table 4-3). Average ∑PBDE concentrations in eggs from both types of current recycling activities in our study area (printed circuit boards and scrap metal recycling) were similar, at 982 ± 1319 ng/g lw and 939 ± 1312 ng/g lw respectively. These concentrations were several orders of magnitude higher than those in chicken eggs available on the Canadian market (Rawn et al., 2011), up to four orders of magnitude higher than those in eggs (chicken and duck eggs reported together) from Shenzhen, China (Ni et al., 2012), and up to three orders of magnitude greater than concentrations detected in eggs from free-foraging chickens in Belgium (Covaci et al., 2009) and eggs from Taiwanese supermarkets (Chen et al., 2012). Moreover, concentrations in our samples from e-waste recycling locations, far exceeded those detected (all below detection limits) during method development in duck eggs from farms in Devon, UK. Comparison with previous studies reveals that PBDE concentrations in duck eggs in our study exceeded slightly those found in chicken eggs from Wenling, Taizhou City (564 ± 340 ng/g lw) (Qin et al., 2011), but were, in some cases, lower than those reported for chicken eggs from Quingyuan, Guangdong (Zheng et al., 2012), another major e-waste recycling site. The latter study reported average ∑PBDE concentrations in samples from two sites (wires and components recycling) of the same order of magnitude as those in our study, while concentrations in eggs collected near workshops recycling household appliances were one order of magnitude higher than those reported here.

Table 4-3 Concentrations of PBDEs (ng/g lw) in domestic poultry egg samples from various countries (n = number of samples)

Location	Samples or sampling site description	Year of collection	Type of egg samples	Number of congeners	Concentrations (ng/g lw)	Source
British Colombia, Quebec and Maritime provinces, Canada	Four main categories of eggs on the Canadian market: conventional, omega-3 enriched, free range and organic	2005 - 2006	chicken	23 (tri-deca)	0.018 – 20.9^{a} 1.28 – 5.83^{b} (n=162)	(Rawn et al., 2011)
Shenzhen, China	eggs purchased in supermarkets	2009	chicken and duck	8 (tri-deca)	0.559^{f} (n=10)	(Ni et al., 2012)
Ten locations in Belgium	Eggs from free-foraging chicken held by private owners	2006 -2007	chicken	13 (tri-deca)	Autumn eggs: 3.51 ± 4.01^{c} Spring eggs: 7.77 ± 12.5^{c} (n=10)	(Covaci et al., 2009)
Taiwan	Eggs purchased in markets or supermarkets	2009	not specified	8 (tri-deca)	8.6 ± 2.9^{c} (n=12)	(Chen et al., 2012)
Quingyuan, Guangdong, China	E-waste recycling sites: a) electrical wires b) household appliances c) electrical components	2010	chicken	19 (tri-deca)	a) 4010 ± 683^{c} (n=12) b)14100±3220^{c} (n=11) c) 2640 ± 626^{c} (n=10)	(Zheng et al., 2012)

Location	Samples or sampling site description	Year of collection	Type of egg samples	Number of congeners	Concentrations (ng/g lw)	Source
Wenling village, Taizhou City, China	Various e-waste recycling sites	n/a	chicken	7 (tetra-deca)	564 ± 340[c] (n=15)	(Qin et al., 2011)
Wenling, China (sites 1-3)	Printed circuit board recycling and dumping sites	2011	duck	14 (tri-deca)	982 ± 1319[d] (n=33)	Current study
Luqiao, China (site 5)	Metal scrapping sites	2011	duck	14 (tri-deca)	939 ± 1312[c] (n=11)	Current study
Wenling, China (site 4)	Former printed circuit board recycling sites	2011	duck	14 (tri-deca)	53 ± 70[c] (n=11)	Current study
Sanmen, China (site 6)	Eco-farm	2011	duck	14 (tri-deca)	8 ± 22[c] (n=11)	Current study
Devon, UK	Private farm	2011	duck	14 (tri-deca)	All below detection limit (n=10)	Current study

a – range; b – median; c – average (mean); d - average for three sites: site 1, site 2 and site 3 with current e-waste recycling activities; f – based on wet weight; ± - SD; n - number of samples.

The differences between the concentrations of PBDEs in chicken eggs from Guangdong, China and those in our study of duck eggs likely reflect various factors including: accessibility of domestic birds to contaminated locations, proportion of time spent foraging in such locations, species-specific differences in habitat preferences (ducks spend a substantial proportion of time in local watercourses while chickens are essentially terrestrial) as well as inter-site differences in soil/sediment contamination. We have shown previously (see section 3.2) that sediments from e-waste recycling sites in Guangdong, China had one of the highest PBDE levels ever reported (average 220000 ng ∑PBDE/g dw), and thus free-foraging chickens in such areas are likely exposed to elevated concentrations. It has also been reported (Luo et al., 2009a) that concentrations of PBDEs in free range chickens from e-waste recycling areas in Guangdong exceed substantially those in tissues of free range ducks from the same areas, which was attributed to different living and feeding habitats. It is thus likely that duck eggs will contain lower PBDE concentrations than chicken eggs from the same location.

4.5 Estimation of daily intake of PBDEs from duck egg consumption

Methodology for PBDEs estimation is presented in section 2.9. Normalization to body weight was calculated based on a standard Chinese male with average body weight of 63 kg (Zhou et al., 2012); and on a standard Chinese 3 year old male child living in a rural area of 14.65 kg (MHC, 2012). Table 4-4 presents our estimates of daily exposure to ∑PBDEs from duck egg consumption for each site, as well as relevant previously reported data.

Initially, we calculated lower, median and upper bound estimates of daily exposure to ∑PBDEs at each site, assuming that non-detects were zero, half the detection limit or at detection limit respectively. However, given that at all sites except the control site, there were very few non-detects, these daily exposure estimates were only marginally influenced by the way in which non-detected congeners were treated. Hence, we report here only those estimates derived by assuming non-detected congeners were present at half the detection limit. On this basis, our estimated average daily ∑PBDE intake via duck egg consumption at the e-waste recycling sites ranged from 159 ng/day at site 4 to 5124 ng/day at site 2, and only 27 ng/day at control site 6.

As we are unaware of any previous estimates of exposure to PBDEs via duck egg consumption, we compared our data with the available (albeit limited) information for chicken eggs. Our estimates of average daily intakes from consumption of duck eggs from sites 1, 2, and 5 were three orders of magnitude higher than those reported to arise from eating chickens' eggs in market-basket studies in Belgium (3.1 ng/day) (Voorspoels et al., 2007) and Spain (2.2 ng/day) (Bocio et al., 2003). Our estimates also exceed that derived from consumption of chickens' eggs from e-waste sites in Wenling, China (4.8 ng/day) (Zhao et al., 2009b), though BDE-209 was not reported in that study. Another study of Wenling e-waste recycling sites (Qin et al., 2011) estimated average daily ∑PBDE intake via chicken egg and muscle consumption at 810 ng/day. This is lower than estimated here for sites 1, 2 and 5, but slightly higher than those for sites 3 and 4. Moreover, our ∑PBDE exposure estimates for sites 1 and 2 were similar to those obtained for chicken eggs from an e-waste recycling site in Guangdong, China (4200 ng/day) (Zheng et al., 2012), but about 5 times lower than for another site in the same study (20000 ng/day). Additionally, for a high-end duck egg consumer, the average daily ∑PBDE intake obtained for site 2 (12532 ng/day) was of similar magnitude to the highest average value for chicken eggs from various sites in Guangdong (Zheng et al., 2012).

The highest average daily intake estimates for BDE-47 and BDE-99 were obtained for samples from site 2 (339 and 424 ng/day respectively). Those were four orders of magnitude higher than reported for egg consumption in a study estimating dietary intake of the general Netherlands population (Bakker et al., 2008). Table 4-4 compares our daily exposure estimates for ∑PBDE and BDE-47, -99, -183, and -209 with relevant previous reports.

Table 4-4 Estimated intakes of PBDEs via consumption of duck eggs from e-waste recycling sites in Wenling (sites 1 – 4), Luqiao (site 5), and control site in Sanmen (site 6), Taizhou City, Zhejiang Province, China; and previously reported data

	∑PBDE intake, ng/day		**Exposure dose, ng/kg bw/day**									
	Medium bound intake[e]	**High-end consumer intake[f]**	**BDE-47**		**BDE-99**		**BDE-183**		**BDE-209**		**∑PBDE**	
	Adult[a]	Adult[a]	Adult[a]	Child[b]	Adult[a]	Child[b]	Adult[a]	Child[b]	Adult[a]	Child[b]	Adult[a]	Child[b]
RfD[c]	n/a	n/a	100		100		n/a		7000		n/a	
NAEL[d]	n/a	n/a	n/a		0.23 - 0.30[c] 18.8 – 41.4[d]		n/a		n/a		n/a	
Site 1	3520	8609	0.44	1.98	0.89	4.03	15.09	68.12	27.87	125.8	55.87	252.3
Site 2	5124	12532	5.38	24.30	6.74	30.42	22.57	101.9	20.63	93.15	81.33	367.2
Site 3	325	796	0.56	2.54	0.58	2.60	2.08	9.40	0.40	1.81	5.17	23.32
Site 4	159	389	0.10	0.44	0.11	0.49	0.13	0.57	1.85	8.38	2.52	11.40
Site 5	2802	6854	0.34	1.53	0.54	2.42	7.34	33.13	27.10	122.4	44.48	200.9
Site 6	27	65	0.002	0.01	0.001	0.01	0.003	0.01	0.39	1.78	0.42	1.91
Sites 1, 2 & 5 average	3815	9332	2.05	9.3	2.72	12.3	15.00	67.7	25.20	113.8	60.56	273.5
Wenling, China[i]	810	n/a	1.81	n/a	0.69	n/a	0.35	n/a	7.24	n/a	13.50	n/a
Shenzhen, China[j]	13	n/a	0.01	n/a	0.01	n/a	0.004	n/a	0.15	n/a	0.18	n/a

[a] Based on medium bound daily intake (non-detects assigned 1/2 LOD value), consumption of 24 g duck eggs/day (Zhuang et al., 2012), and an adult male weight of 63 kg (Zhou et al., 2012); [b] Based on authors own high-end consumption figure of 25.2 g duck eggs/day assuming that a 3 year old male child with average weight of 14.65 kg (Zhou et al., 2012) consumes 3 duck eggs per week; average egg weight from our study is 58.7 g (n = 66). [c] Expected human no adverse effect level (NAEL) for impaired spermatogenesis. [d] Expected human no adverse effect level (NAEL) for impaired neurodevelopmental toxicity. [e] Non-detects assigned 1/ 2 LOD value. [f] Based on consumption of one egg per day, non-detects assigned 1/2 LOD value. [g] Reference Dose values promulgated by the US EPA (U.S. EPA, 2008c, 2008b, 2008a); [h] Bakker et al. 2008; [i] Mean estimated daily intake of PBDEs through chicken muscle and egg consumption (Qin et al., 2011) . [j] Mean estimated daily intake of PBDEs through chicken eggs (n = 8) and duck eggs (n = 2) consumption (Zheng et al., 2012). n/a − not applicable

Importantly, our exposure estimates do not exceed the reference dose (RfD) values promulgated by the U.S. EPA (U.S. EPA, 2008c, 2008b, 2008a) for BDE-47 (100 ng/kg/day), BDE-99 (100 ng/kg/day) and BDE-209 (7000 ng/kg/day). In contrast, our estimates of exposure to BDE-99 (for men) for all but sites 4 and 6 exceeded substantially (by over 20 times for site 2) the no adverse effect level (NAEL) for impaired spermatogenesis of 0.23 – 0.30 ng/kg bw/day proposed by Netherlands researchers (Bakker et al., 2008). Moreover, our exposure estimates are based only on consumption of duck eggs, and inhabitants of our study locations will receive additional dietary and non-dietary exposure.

Furthermore, children will have much higher exposure doses that those estimated for adults when normalised to body weight. Indeed, based on assumed consumption rates, our estimate of exposure to BDE-99 for a typical 3 year old male child from site 2 (30.4 ng/kg bw/day) falls within the range of the NAEL for impaired neurodevelopmental toxicity (18.8 – 41.4 ng/kg bw/day) (Bakker et al., 2008). This is of concern, as it has been shown (Verner et al., 2011; Eskenazi et al., 2013) that PBDEs can have adverse impacts on c hild neurobehavioural development. Moreover, the average dose estimates for children at sites 1, 2 and 5 (12.3 ng/kg bw/day) were only just below the lower range of this NAEL. Another study (Shen et al., 2010b) has confirmed that concentrations of PBDEs in children residing around e-waste recycling areas at Luqiao, Zhejiang province, were significantly higher than the case control areas in the same province ($p<0.001$). As the children involved were not occupationally exposed, the authors suggested intake via contaminated food (e.g. duck eggs as shown here) was a likely important exposure pathway.

Our average estimates of exposure (for male adults) to individual congeners for those sites where e-waste recycling activity remains on-going (1, 2 and 5) are from 1.1 times (BDE-47) to 42 times (BDE-183) higher than reported previously for consumption of chicken meat and eggs combined from e-waste sites in Wenling (Qin et al., 2011) and between three times (for BDE-

99 & BDE-183) and two orders of magnitude higher (for BDE-47, BDE-209 & ∑PBDEs respectively) than reported for consumption of chicken and duck eggs from Shenzhen, China (Ni et al., 2012). Additionally, average exposure to ∑PBDEs via duck egg consumption alone (60.56 ng/kg bw/day) for our sites 1, 2, and 5 exceeded by two orders of magnitude that estimated for egg consumption from three USA locations (Schecter et al., 2010a) and was one order of magnitude higher than the estimated exposure of adults in Shenzhen, China to ∑PBDEs (tri- to deca-BDE, 8 congeners) via food, air, soil, and dust (Ni et al., 2012). We stress the importance of conducting exposure assessments on a representative number of samples, given the significant variation between samples collected simultaneously at sites 2 and 5.

CHAPTER 5 CONCENTRATIONS OF SELECTED BFRS, PCBS, AND METALS/METALLOIDS IN HUMAN FOODSTUFFS FROM AN E-WASTE PROCESSING AREA IN EASTERN CHINA: IMPLICATIONS FOR HUMAN EXPOSURE

This chapter contains some text taken verbatim from:

Labunska I, Harrad S, Wang M, Santillo D, Johnston P. 2014. Human dietary exposure to PBDEs around E-waste recycling sites in Eastern China. ***Environmental Science & Technology***, 48(10):5555–64;

Labunska I, Abdallah MA-E, Eulaers I, Covaci A, Tao F, et al. 2015. Human dietary intake of organohalogen contaminants at e-waste recycling sites in Eastern China. ***Environment International,*** 74:209–20.

5.1 Introduction and aim of the study

The findings of our investigation into human exposure to PBDEs via duck eggs foraged at e-waste recycling sites around Taizhou City, led us to conduct a more comprehensive study into dietary exposure to other chemical pollutants at the same locations. It has been shown previously that fish and animal-based foodstuffs, in most cases, are the primary dietary routes of human exposure to organohalogen pollutants including PBDEs (Jiang et al., 2014; Domingo, 2012; Ni et al., 2013, 2012; Chan et al., 2013), PCBs (Song and Li, 2014a; Asante et al., 2011; Xing et al., 2009; Song et al., 2011; Xing et al., 2010), hexabromocyclododecane (HBCD) (Zheng et al., 2012; He et al., 2013) and “novel” BFRs (NBFRs) (Zheng et al., 2012). Dietary exposure to metals and metalloids have also been reported (Zheng et al., 2013; Pizzol et al., 2010). Despite this, data on human dietary exposure to BFRs and PCBs associated with e-waste recycling are still limited. Thus, we conducted the following study comprising three strands, specifically:

1) Estimation of human exposure to PBDEs via wider range of the foodstuffs at e-waste sites in Taizhou produced from locally reared animals, including pigs, chickens and ducks, as well as eggs from domestic fowl. Fish and shrimp caught in local ponds or rivers, and consumed by local people on a regular basis, were also included. Culinary oils are not produced locally at e-waste recycling sites in Taizhou, therefore we included in our study oils identified as the most popular in the area to assess any additional contribution of PBDEs to the local diet. Combined, these categories of food cover the main potential routes of human dietary exposure to PBDEs in rural areas involved in e-waste recycling. 126 samples (including controls) were procured from seven locations situated within 1 to 300 metres of present or former e-waste and scrap metal recycling facilities around Taizhou. Sampling site locations and samples descriptions are provides in section 2.1.2.2.
2) Determination of PBDE concentrations in samples of animal-based foodstuffs originating from China and sold in the UK to investigate the hypothesis of intercontinental transfer of POPs - PBDEs in our case - via exported foodstuffs. To

conduct this small-scale pilot study, 12 dietary samples were purchased in April-May 2013 from stores selling foodstuffs of Chinese origin in Birmingham and Exeter. It is necessary to mention that origin of the samples was purely based on the product labelling. Only those foodstuffs which clearly stated that they originated from China were obtained for analysis. These samples included cooked duck meat, mixed meat products, frozen fish, dried fish/sea products, and chicken powder.

3) Estimation of human exposure to HBCDs, NBFRs, PCBs, and metals/metalloids through a consumption of the same foodstuffs originating from e-waste recycling sites in Taizhou, which were investigated for estimation of human exposure to PBDEs. To achieve this, we prepared 24 pooled samples from 189 individual food samples collected in this study, which included both e-waste related and control samples. Preparation of pooled samples is provided in section 2.1.2.3. A list of all target compounds is provided in Table 2-6.

5.2 Human dietary exposure to PBDEs around e-waste recycling sites

5.2.1 Concentrations of PBDEs in food samples

Table 5-1 presents the average, median and range of concentrations for selected PBDEs in food samples originating from e-waste recycling areas in Taizhou, as well as in culinary oils and control samples. To enable comparison with previously published data, ∑PBDE are reported on both a lipid weight (lw) and wet weight (ww) basis.

All samples collected from locations close to e-waste activities contained concentrations of PBDEs significantly higher than those detected in corresponding control samples, most markedly in fish, for which samples from e-waste areas contained on average, lipid weight ∑PBDE concentrations around three orders of magnitude higher than in fish from control sites. Full data on PBDE concentrations in control samples are provided in Appendix 3.

Average ∑PBDE concentrations expressed on a lipid weight basis (lw) were highest in samples of fish (4180 ng/g), followed by samples of chicken meat (1160 ng/g), chicken eggs (656 ng/g) and chicken liver (459 ng/g). On a wet weight basis (ww), however, chicken meat showed the highest average concentrations (349 ng/g), followed by chicken eggs (77.8 ng/g), chicken liver (48.7 ng/g) and fish (44.4 ng/g). The maximum ∑PBDE lipid weight concentration (12600 ng/g lw) was recorded for a sample of fish, while the maximum wet weight concentration (1220 ng/g ww) was in a chicken sample. While BDE-209 was the biggest contributor to ∑PBDE in chicken, chicken liver and egg samples, BDE-47 predominated in fish, followed by BDE-100.

5.2.1.1 Chicken meat, liver and eggs

Average ∑PBDE concentrations for chicken meat (1160 ng/g lw; 349 ng/g ww), chicken liver (459 ng/g lw; 48.7 ng/g ww), and chicken eggs (656 ng/g lw; 77.8 ng/g ww) were among the highest reported for these foodstuffs. Concentrations in this study exceeded, by a considerable margin, those reported for chicken samples from Nanjing, China, (0.064 ng/g ww) (Su et al., 2012), the USA (0.3 ng/g ww) (Schecter et al., 2010a), Spain (0.25 ng/g lw) (Bocio et al., 2003) and Taiwan (13 ng/g lw) (Chen et al., 2012). They also exceeded, to a lesser degree, those reported for chicken samples obtained from e-waste recycling sites in China including: Wenling (5.9 ng/g ww) (Qin et al., 2011), Qingyuan (cockerel muscle median: 66 ng/g lw and cockerel liver median: 41 ng/g lw) (Luo et al., 2009a), and Guiyu (8.6 ng/g ww, for mono-hepta BDEs only) (Chan et al., 2013). Chan and co-authors (Chan et al., 2013) reported the concentration of mono- to hepta-BDEs in chicken meat from e-waste sites in Taizhou (0.67 ng/g ww) to be three orders of magnitude lower than the corresponding average in the current study (181 ng/g ww).

Table 5-1 Average, median and range of concentrations of selected PBDE congeners (in ng/g lw) and of ∑PBDEs (in ng/g lw and, in parentheses, ng/g ww) detected in food samples originated from e-waste and control sites. n = number of samples; n/a – not applicable

Location	**E-waste recycling sites**										**Control sites**
PBDEs	**BDE-47**	**BDE-100**	**BDE-99**	**BDE-154**	**BDE-153**	**BDE-183**	**BDE-197**	**BDE-207**	**BDE-209**	**∑PBDEs***	**∑PBDEs***
Chicken (n=10)											
average	55.0	9.5	30.9	16.0	31.4	328	107	81.6	484	1160 (349)	2.3 (0.19)
median	10.1	4.5	17.9	6.2	31.4	19.4	6.2	10.4	110	354 (38.7)	0.07 (0.005)
range	1.3 - 200	0.60- 28.0	1.0 – 86.6	1.0 - 65.6	1.4 - 813	1.2 - 1514	0.5 - 484	1.0 - 316	8.8 – 1960	18.2 – 3970	<0.018 - 10.7
Chicken liver (n=10)											
average	35.8	9.3	17.9	4.5	33.9	85.3	25.9	21.2	242	459 (48.7)	3.3 (0.12)
median	9.4	3.3	3.8	3.9	17.5	7.9	5.9	9.5	145	230 (16.8)	4.1 (0.11)
range	1.1 -129	<0.015 - 31.8	<0.015- 59.6	0.7 - 10.5	0.2 - 117	1.0 - 414	0.4 - 127.8	1.5 - 79.2	15.4 - 723	24.5 - 1473	0.9 – 4.6
Chicken egg (n=22)											
average	40.1	4.9	24.3	5.6	18.1	19.8	6.8	31.5	503	656 (77.8)	7.0 (2.1)
median	10.9	2.1	11.2	4.3	7.1	8.8	4.7	12.8	136	307 (42.2)	4.8 (1.4)
range	<0.014 – 178	<0.010 - 16.9	<0.010 - 86.1	<0.007 - 26.5	<0.014 - 48.1	<0.014 - 67.2	<0.007 - 17.6	<0.010 - 197	<0.024 - 3400	<0.024 - 3620	2.8 – 23.6
Duck (n=7)											
average	11.4	2.4	9.9	3.3	16.9	46.7	13.6	6.6	35.3	150 (40.9)	10.0 (0.74)
median	13.3	2.6	10.9	2.1	4.7	7.1	2.5	2.8	16.1	66.7 (16.1)	11 (0.84)
range	1.1 -23.0	0.3 - 5.2	1.4 – 19.6	0.2 - 10.6	0.6 - 73.3	1.0 - 231	0.5 - 64.4	0.6 - 26.6	5.0 - 121	11.2 - 593	4.1 – 15.5
Duck liver (n=7)											
average	7.7	1.5	5.9	1.8	9.7	30.1	13.3	13.4	172	256 (11.4)	18.2 (1.52)
median	10.6	1.1	6.8	1.2	3.3	4.5	2.2	5.8	64.7	110 (4.5)	19.6 (1.65)
range	2.3 – 12.1	<0.024 - 4.3	1.0 -15.0	<0.016 - 6.0	<0.032 - 41.1	<0.032 - 160	0.8 - 72.5	<0.024 - 64.5	12.5 - 766	16.6 - 1150	13.3 – 20.8
Pork (n=5)											
average	27.8	1.1	11.4	0.7	2.5	0.9	0.6	0.4	3.0	53.8(7.9)	<0.036(<0.02)
median	6.1	0.6	2.6	0.3	0.4	0.6	0.5	0.4	3.3	16.0 (1.4)	<0.036(<0.02)
range	<0.020 – 114	<0.015 - 3.9	<0.015- 45.9	<0.010 - 2.6	<0.020 - 9.8	<0.020 - 2.7	<0.010 - 1.5	<0.015 - 0.8	2 - 3.8	4.2 - 205	<0.036(<0.02)
Fish (n=8)											
average	2915	308	26.8	612	234	22	7.3	2.3	5.9	4180 (44.2)	2.5 (0.29)
median	1799	109	1.5	233	119	8.3	1.5	<0.070	<0.163	2130 (37.9)	1.0 (0.29)
range	358 - 9660	39.9 - 1140	<0.070- 133	125 - 1420	56.4 - 576	<0.093 - 88.0	<0.047 - 43.2	<0.070 - 18.6	<0.163 – 47.3	702 - 12600	0.15 – 7.8
Shrimp (n=3)											
average	26.1	<0.083	<0.083	1.2	0.7	<0.111	<0.056	<0.083	<0.194	28.0 (0.3)	<0.056
median	20.1	<0.083	<0.083	<0.056	<0.111	<0.111	<0.056	<0.083	<0.194	25.8 (0.4)	<0.056
range	<0.111 - 58.1	<0.083	<0.083	<0.056 - 3.5	<0.111 - 2.1	<0.111	<0.056	<0.083	<0.194	<0.194 – 58.1	<0.056
Oil (n=10)											
average	0.5	<0.003	0.1	0.01	<0.004	0.03	0.01	0.05	1.0	1.7	n/a
median	0.7	<0.003	0.3	<0.002	<0.004	<0.004	<0.002	<0.003	<0.007	1.1	
range	<0.004 – 1.0	<0.003	<0.003- 0.3	<0.002 - 0.07	<0.004	<0.004 - 0.1	<0.002 - 0.06	<0.003 - 0.3	<0.007 – 3.2	<0.007 – 4.7	

Median ∑PBDE levels previously reported for chicken liver sourced from an e-waste site in Qingyun, China, (Luo et al., 2009a) ranged from 28 to 41 ng/g lw for hens and male fowl respectively, one order of magnitude lower than the median for chicken liver in our study (230 ng/g lw). In our samples, both average and median ∑PBDE concentrations in chicken meat samples exceeded those in chicken liver, consistent with previous observations (Luo et al. 2009; Voorspoels et al. 2006) that attributed this finding to greater metabolic activity in liver than in muscle. However, other studies report no significant difference between PBDE concentrations in liver and muscle tissues (Chen et al., 2007; Qin et al., 2011). For ducks, liver contained median ∑PBDE concentrations around 1.5 times higher on a lipid weight basis than in meat, though on a wet weight basis, concentrations were higher in meat than liver.

For chicken eggs, concentrations of ∑PBDEs for areas not affected by e-waste recycling have been reported as 0.3 ng/g ww (Schecter et al., 2010a), 1.1 ng/g lw (Rawn et al., 2011), 7.8 ng/g lw (Covaci et al., 2009), and 8.6 ng/g lw (Chen et al., 2012). For samples originating from e-waste recycling sites, the average ∑PBDE concentration in our study (656 ng/g lw) was slightly higher than that reported for Wenling village in Taizhou City, China (563 ng/g lw) (Qin et al., 2011). This suggests contamination arising from e-waste recycling persists at this location. Another study on chicken eggs from a major e-waste recycling site in Guangdong Province, China, (Zheng et al., 2012) reported average ∑PBDE concentrations between 2640 ± 626ng/g lw and 14100 ± 3220ng/g lw for samples associated with various e-waste recycling activities. Our data for chicken eggs (656 ± 864 ng/g lw) and for duck eggs from the same study area in Taizhou(982 ± 1320ng/g lw) (see section 4.2) indicate slightly lower levels of PBDEs in these samples compared to those found in Guangdong. It is important to note, however, that e-waste recycling sites in Guangdong had amongst the highest PBDE concentrations reported for soil (average 28000 ± 58000 ∑PBDE ng/g dw) (see section 3.2.2) and which exceed those in Taizhou soils (average 1910 ∑PBDE ng/g dw) (Ma et al., 2009). Free-foraging chickens and ducks in Guangdong e-waste recycling areas are thus likely more exposed to PBDEs than in Taizhou.

5.2.1.2 Duck meat and liver

∑PBDE concentrations in duck and duck liver samples in our study were lower than in chicken meat and chicken liver samples respectively, most probably due to a combination of species-specific differences in habitat preferences and differences in soil and sediment contamination. Limited information exists on concentrations of PBDEs in ducks. In comparison to other studies, average or median ∑PBDE concentrations in duck samples in this study (40.9 ng/g ww and 16.1 ng/g ww respectively) were about two orders of magnitude higher than those previously reported for ducks from Nanjing, China (average: 0.3 ng/g ww) (Su et al., 2012), and one order of magnitude higher than in male ducks from e-waste areas in Guangdong, China (median: 6.6 ng/g lw) (Luo et al., 2009a). The median ∑PBDE concentration in duck liver samples in our study (median: 110 ng/g lw) was also one order of magnitude higher than in male duck liver from Guangdong (median: 8.5 ng/g lw) (Luo et al., 2009a).

5.2.1.3 Fish and shrimp

The highest ∑PBDE concentration detected in the current study was in a sample of fish from site 4, at 12600 ng/g lw (98.2 ng/g ww). Average and median ∑PBDE concentrations in fish were 4180 ng/g lw (44.2 ng/g ww) and 2130 ng/g lw (37.9 ng/g ww) respectively. These are slightly lower than values reported previously for freshwater fish from Taizhou (60.4 ng/g ww), but substantially lower than in fish from Guangdong e-waste sites (2180 ng/g ww) (Chan et al., 2013). However, concentrations of PBDEs detected in fish samples in the current study were between one to three orders of magnitude higher than previously reported for fish from non-e-waste-related sites in China (Meng et al. 2007; Luo et al. 2009; Su et al. 2012; Gao et al. 2009), Hong Kong (Wang et al., 2011b),USA (Schecter et al., 2010a), UK (Jürgens et al., 2013), and Taiwan (Peng et al., 2007). Shrimp samples had much lower concentrations of PBDEs (average

28 ng/g lw, 0.3 ng/g ww) than fish samples. Nonetheless, concentrations in our shrimp samples exceed by one order of magnitude those in river prawns from Nanjing, China (mean: 0.052 ng/g ww) (Su et al., 2012), are about twice those in shrimp from the Yangtze River, China, (Gao et al. 2009) and are similar to those in shrimp from Taizhou, China (average: 0.25 ng/g ww) (Chan et al., 2013).

The EU have proposed (European Commission, 2012) an Environmental Quality Standard (EQS) of 8.5 ng/kg ww for PBDEs in fish (sum of six congeners: BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154). Average concentrations in our study for these six PBDEs in shrimp and fish (0.32 ng/g and 42.8 ng/g ww respectively) far exceed this EQS.

5.2.1.4 Pork

Average (and median) ∑PBDE concentrations in pork samples were 53.8 ng/g lw (7.9 ng/g ww) and 16.0 ng/g lw (1.4 ng/g ww) respectively; significantly higher than previously reported for pork from Nanjing, China (average: 0.11 ng/g ww) (Su et al., 2012) , Spain (0.17 ng/g ww) (Bocio et al., 2003) and Taiwan (average: 0.55 ng/g ww) (Chen et al., 2012). Our data on pork were, however, comparable albeit slightly higher than those previously reported for sites associated with e-waste recycling in Taizhou (average: 4.57 ng /g ww) and Guangdong (average: 10.0 ng/g ww) (Chan et al., 2013).

5.2.1.5 Culinary oils

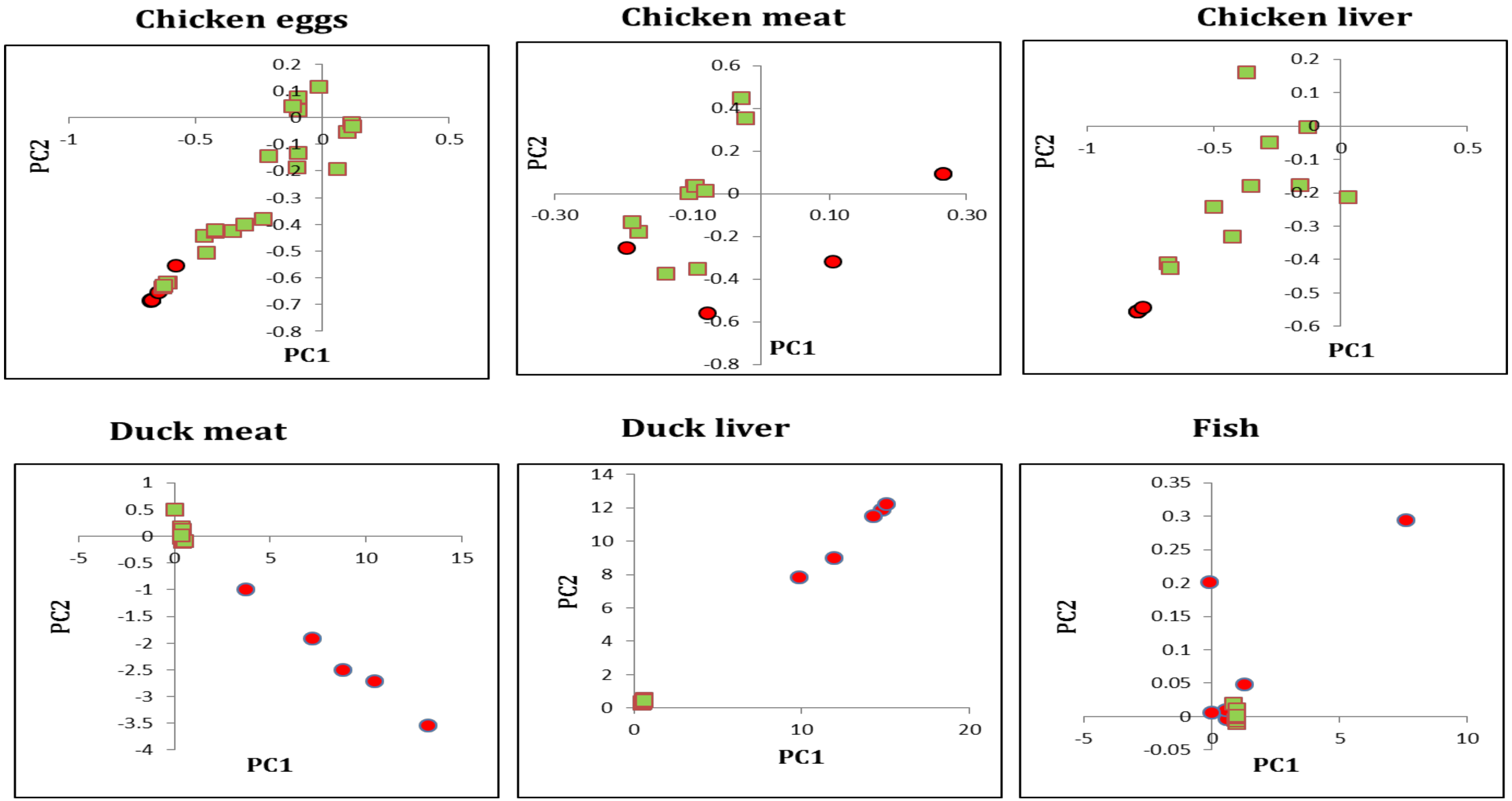
The culinary oils analysed here contained only low concentrations of PBDEs compared to other foods analysed. The average and median ∑PBDE concentration was 1.1 ng/g for both parameters. The following PBDEs were present above detection limits: BDE-47 and BDE-99 in six samples, BDE-183, BDE-197 and BDE-209 in three samples, and BDE-154 in one sample out of the 10 samples analysed.

5.2.2 PCA analysis of PBDE patterns

Principal Component Analysis (PCA) was conducted to evaluate differences in PBDE congener profiles in food samples collected from e-waste recycling sites as well as to compare those profiles with corresponding patterns in control samples. Overall, PCA indicates that food samples collected from Taizhou e-waste recycling areas display PBDE congener patterns that differ substantially from those in corresponding control samples. Principal Component 1 (PC1) and Principal Component 2 (PC2) accounted for 25% and 19%, respectively, of the variation within the data set. Fig. 5-1 plots principal component 1 (PC1) versus principal component 2 (PC2) scores for food samples from e-waste sites and control samples.

For chicken eggs, for example, all control samples were closely located in an area of the plot with high negative values for both PC1 and PC2, while only 4 (18%) of the samples associated with e-waste recycling showed a similar pattern. For the majority of other foodstuffs, controls showed similarly close clustering in patterns distinct from non-control samples, with the latter displaying comparatively more diverse congener patterns. In the case of chicken meat samples, two of the five controls were located close to non-control samples in the PC1 versus PC2 plot, though in these control samples, all PBDE concentrations were below detection limits, such that the apparent similarity of control and non-control samples in this case is likely an artefact. For fish, two of the control samples showed significant dissimilarity with non-control samples, while the other two, with BDE-47 as the main congener detected, oriented much closer to the non-control samples.

Figure 5-1 Plots of PC1 versus PC2 scores calculated for food samples associated with e-waste recycling sites vs corresponding control samples. n = number of samples



🟩 e-waste related samples; for chicken eggs n=22, chicken meat and liver n=10, for duck meat and liver n=7, for fish n=8

🔴 control samples; n=5 for each type (except fish and chicken eggs where n=6 and n=10, respectively)

Overall, PCA indicated that food samples collected from Taizhou e-waste recycling areas are heavily influenced by contamination from waste recycling and disposal activities. In addition, the various food matrices sampled in this study show marked differences in PBDE patterns which most probably, arise from a combination of several factors. These include: exposure of organisms to a diverse range of e-wastes containing distinct PBDE congener patterns, as well as differences in metabolic processes between species.

5.2.3 Estimation of daily intake of PBDEs

Table 5-2 and Table 5-3 present estimates of ∑PBDE intakes for key PBDE congeners, for adults and children, respectively, via consumption of foodstuffs originating from the vicinity of e-waste recycling sites in Taizhou City. Food consumption rates assumed for each type of food considered in our study are drawn from other published studies (see Table 2-15). It should, however, be noted that information on food consumption rates for children in China is limited or, in case of specific region, is absent. Therefore, we used the best available data at the time of the current study on balanced dietary guidelines consumption rates for Chinese children (from 3 years old up to 6-7 years old) (Chinese Nutrition Society, 2007). The more recent publication (Yu et al., 2016), which was not available at the time of this part of the current study publication (Labunska et al., 2014), reported data on 24-hour dietary recall among infants and children from urban areas of China (mean ± SD for 2.9 years old child) including eggs (48.7 ± 3.1 g/day), pork/ham (33.2 ± 3.0 g/day), and fish/shrimp/shellfish (15.5 ± 3.3 g/day). Though consumption rates for children we used in the current study (each for duck and chicken eggs: 30 g/day; pork: 10 g/day; fish/shrimp: 20 g/day) were somewhat different in comparison with data by Yu et al. (2016), the variations in food consumption rates for children within Chinese provinces and/or between urban and rural communities cannot be ruled out. Hence, though it is difficult to speculate about the extent of uncertainty of the estimations we made based on available published parameters, it could be the case that some of our exposures are under- or overestimated. Low, median, and high-end estimates of daily Σ PBDE intakes were calculated by multiplying 5th, 50th, and 95th percentile concentrations, respectively, by average food consumption rates.

In addition to dietary exposure, (Ma et al., 2009) reported indoor dust at e-waste recycling sites in Taizhou to contain very high PBDE concentrations, that constitute additional sources of PBDE intake, particularly for children spending significant periods in or around their parents' workplace (often immediately adjacent to or even part of the family house). Estimates of exposure via dust ingestion based on these data are included in Tables 5-2 and 5-3. We, therefore, calculated daily PBDE intake via ingestion of dust based on concentration data from Ma and co-authors (Ma et al., 2009) and dust consumption rates of 0.03 and 0.06 g/day for adults and children respectively (U.S. EPA, 2011). Estimated adult daily median ∑PBDE intakes from foodstuffs in our study decreased in the following order: duck eggs>chicken eggs>fish>chicken meat>pork>duck meat>chicken liver>duck liver>culinary oils>shrimp.

A similar order, with only slight variations, was estimated for children: duck eggs>chicken eggs>fish>chicken meat >duck meat>pork >chicken liver>duck liver>shrimp >culinary oils.

The highest estimated contributions to median daily ∑PBDE intake from consumption of locally produced food were: via adult consumption of duck eggs (3880 ng/day), followed by adult consumption of chicken eggs (1090 ng/day) and fish (792 ng/day).

Estimated daily intake via consumption of duck eggs was three times higher than for chicken eggs. This could be due to a combination of factors including differences in: PBDE concentrations of soil/sediment at the locations in which the birds foraged; the proportion of time each species had access to such areas; habitat and feeding preferences; and inter-species differences in absorption, metabolism and/or partitioning of PBDEs.

Table 5-2 Estimated adult intakes of PBDEs via consumption of food originated from e-waste recycling sites in Taizhou City, Zhejiang Province, China; and estimated PBDEs intake via dust based on previously reported data

Food type	**∑PBDE intake, ng/day**			**Exposure dose[d], ng/kg bw/day**													
	Low[a]	**Median[b]**	**High[c]**	**BDE-47**		**BDE-99**		**BDE-153**		**BDE-154**		**BDE-183**		**BDE-209**		**∑PBDE**	
				Median[b]	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**
Chicken meat	41.0	530	20100	0.21	16.8	0.66	7.70	0.92	41.1	0.26	3.32	0.69	84.4	4.76	112.8	8.41	319
Chicken liver	10.2	78.6	897	0.04	1.55	0.02	0.73	0.12	0.93	0.02	0.12	0.04	2.40	0.89	6.89	1.25	14.2
Chicken eggs	107	1090	6370	1.61	6.32	1.30	3.88	1.64	3.09	0.28	0.53	1.95	4.46	8.68	76.4	17.3	101
Duck meat	45.2	240	1520	0.79	1.07	0.64	0.92	0.31	2.94	0.15	0.43	0.34	9.28	1.05	4.89	3.81	24.2
Duck liver	6.5	23.5	205	0.04	0.06	0.03	0.05	0.02	0.12	0.01	0.02	0.02	0.45	0.23	2.17	0.37	3.26
Duck eggs[e]	155	3880	27300	2.02	19.8	3.20	26.3	8.69	33.0	1.74	4.29	9.27	111.4	28.2	159	61.6	433
Pork	45.4	254	1220	0.23	0.31	0.16	0.28	0.10	0.70	0.03	0.10	0.13	2.67	3.06	12.9	4.03	19.4
Fish	104	792	2600	8.77	26.2	0.004	1.08	0.75	2.73	1.94	6.00	0.04	0.68	<0.003	0.33	12.6	41.2
Shrimp	0.7	7.0	13.6	0.11	0.19	<0.001	<0.001	<0.001	0.01	<0.001	0.02	<0.001	<0.001	<0.002	<0.002	0.11	0.22
Culinary oils	<0.003	19.4	102	0.35	0.46	0.09	0.14	<0.002	<0.002	<0.002	0.02	<0.002	0.05	<0.003	1.52	0.31	1.63
Total diet	514	6920	60300	14.2	72.8	6.1	41.1	12.5	84.6	4.4	14.8	12.5	216	46.8	377	110	957
Dust (Ma et al., 2009)	303	1330	2350	0.14	0.24	0.13	0.23	0.03	0.05	0.01	0.01	n/a	n/a	20.5	36.6	21.1	37.3
Total	817	8250	62700	14.3	73.1	6.2	41.4	12.6	84.7	4.4	14.9	12.5	216	67.4	414	131	995

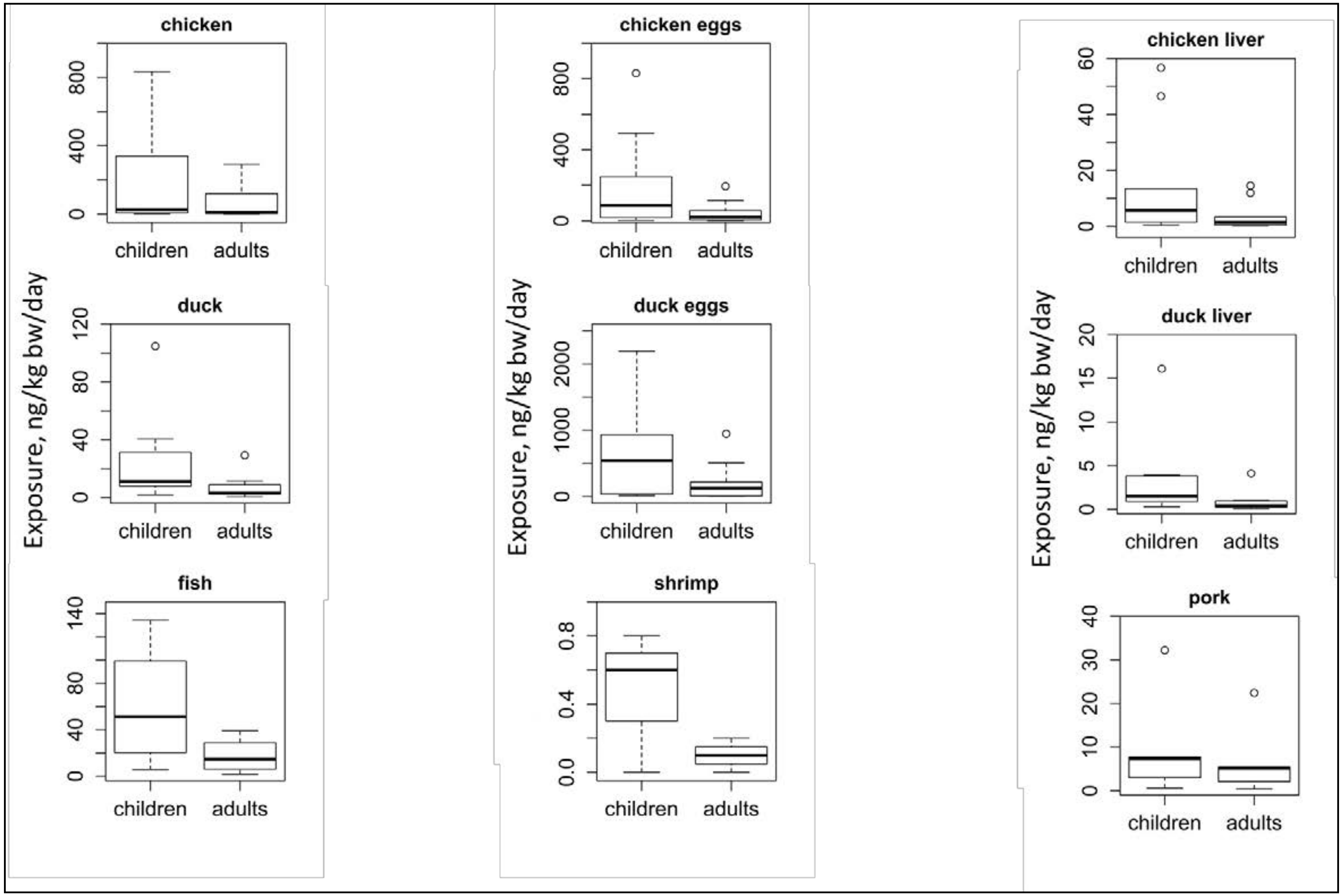
a - low end exposure, 5th percentile; b – medium exposure, 50th percentile; c - high end exposure, 95th percentile; d - based on a standard Chinese male with an average body weight of 63 kg (Zhou et al., 2012); e - based on a set of 33 duck eggs collected in 2011 (see Chapter 4) from the same e-waste areas as chicken eggs (sites 1, 2, 3, & 5).

Table 5-3 Estimated child intakes of PBDEs via consumption of food originated from e-waste recycling sites in Taizhou City, Zhejiang Province, China; and estimated PBDEs intake via dust based on previously reported data

Food type	**∑PBDE intake, ng/day**			**Exposure dose, ng/kg bw/day**													
	Low[a]	**Median[b]**	**High[c]**	**BDE-47**		**BDE-99**		**BDE-153**		**BDE-154**		**BDE-183**		**BDE-209**		**∑PBDE**	
				Median[b]	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**	**Median[b]**	**High[c]**
Chicken	25.6	331	12500	0.57	45.2	1.77	20.7	2.47	110.5	0.71	8.91	1.87	227	12.8	303	22.6	856
Chicken liver	9.2	71.5	816	0.16	6.07	0.09	2.87	0.47	3.65	0.08	0.46	0.16	9.38	3.49	26.9	4.88	55.7
Chicken eggs	107	1091	6370	6.90	27.2	5.59	16.7	7.04	13.3	1.21	2.28	8.38	19.2	37.3	329	74.5	435
Duck	37.6	200	1270	2.82	3.84	2.29	3.31	1.11	10.5	0.52	1.54	1.23	33.3	3.75	17.5	13.7	86.7
Duck liver	5.9	21.3	187	0.17	0.22	0.10	0.20	0.06	0.47	0.02	0.07	0.08	1.75	0.89	8.49	1.46	12.7
Duck eggs[e]	155	3880	27300	8.69	85.3	13.8	113	37.37	142	7.47	18.5	39.9	479	121	685	265	1863
Pork	15.1	84.7	407	0.34	0.44	0.23	0.40	0.15	1.01	0.05	0.15	0.18	3.83	4.38	18.5	5.78	27.8
Fish	83.0	634	2080	30.2	90.2	0.01	3.70	2.57	9.41	6.66	20.7	0.13	2.34	<0.01	1.14	43.3	142
Shrimp	0.6	6.3	12.3	0.43	0.73	<0.004	<0.004	<0.005	0.04	<0.003	0.07	<0.005	<0.005	<0.01	<0.01	0.43	0.84
Culinary oils	<0.01	0.9	4.9	1.51	1.97	0.38	0.61	<0.008	<0.008	<0.008	0.08	<0.008	0.21	<0.01	6.53	1.32	6.99
Total diet	439	6320	51000	51.8	261	24.2	162	51.2	291	16.7	52.7	51.9	776	184	1400	433	3490
Dust (Ma et al., 2009)	606	2660	4700	1.23	2.08	1.10	1.99	0.27	0.42	0.08	0.11	n/a	n/a	176	315	181	321
Total	1040	8980	55700	53.0	263	25.3	164	51.5	291	16.8	52.8	51.9	776	360	1710	614	3810

a - low end exposure, 5th percentile; b – median exposure, 50th percentile; c - high end exposure, 95th percentile; d - based on a standard Chinese 3 year old male child living in a rural area of 14.65 kg (MHC, 2012); *e* - based on a set of 44 duck eggs collected in 2011 from the same e-waste areas (reported in Chapter 4) as chicken eggs (sites 1, 2 , 3, & 5).

Figure 5-2 Box and whisker plot summarising estimated exposure (ng/kg bw/day) of children and adults to ∑PBDE via different type of foods. The bottom and top of the boxes represent the 25th and 75th percentiles of the values, respectively. The solid horizontal line within each box represents the median value. The upper and lower whisker are equal to the maximum and minimum values. ○ – outliers.



Conversely, median ∑PBDE intake via chicken meat was about twice that estimated from duck meat. This suggests that inter-species differences in accumulation of PBDEs may be particularly important. Estimated high-end daily ∑PBDE intakes for adults via chicken meat and duck eggs were the highest recorded contributions in our study (20100 ng/day and 27300 ng/day respectively), underlining the importance of these foodstuffs for human dietary exposure to PBDEs. Consumption of both duck and chicken livers resulted in lower median ∑PBDE intakes than for the corresponding meat, due to lower concentrations in livers than meat.

Estimated daily median ∑PBDE intake through fish consumption (792 ng/day for adults and 634 ng/day for children) was the second highest contribution in our study, after food products of avian origin (with the exception of livers). Consumption of pork also contributes considerably to daily ∑PBDE intake in these areas, though more substantially for adults (254 ng/day) than children (84.5 ng/day).

Taking all analysed foodstuffs into account, median dietary ∑PBDE intakes (6920 ng/day and 6320 ng/day for adults and children respectively) were significantly higher in this study than in a previous estimate for Taizhou e-waste sites of 195 ng/day (Zhao et al., 2009b) and more than double that from another more recent study in Taizhou at 2863 ng/day (Chan et al., 2013). However, our estimates were one order of magnitude lower than estimates of total dietary intake for e-waste-impacted locations in Guangdong province (Chan et al., 2013), despite the exclusion of BDE-209 from the latter study.

Including exposure via ingestion of contaminated dust at e-waste recycling sites increases our median ∑PBDE daily intakes by approximately 19% for adults and 42% for children (see Tables 5-2 & 5-3). While this highlights the potential importance of dust ingestion at the most contaminated locations; dietary exposure remains the principal exposure pathway in most circumstances.

Normalised to a body weight, median ∑PBDE exposure via diet and dust ingestion combined is 131 ng/kg bw/day for adults and 614 ng/kg bw/day for children. Box and whisker plot summarising estimated exposure (ng/kg bw/day) of children and adults to ∑PBDE via different type of foods is presented in Fig. 5-2. Compared with previous estimates of dietary exposure to PBDEs in Taizhou of 44.7 ng/kg bw/day without BDE-209 (Chan et al., 2013), our estimates excluding BDE-209 amount to 63.5 ng/kg bw/day for adults and 254 ng/kg bw/day for children. Furthermore, if high end exposure is considered, the difference in estimated PBDE exposures between our study and that of Chan et al. (2013) would increase further.

Our median estimates of exposure to individual key PBDE congeners (BDE-47, BDE-99 and BDE-209) for adults and children did not exceed the reference dose (RfD) values promulgated by the U.S. EPA of 100 ng/kg bw/day, 100 ng/kg bw/day, and 7,000 ng/kg/day, respectively, (U.S. EPA, 2008b, 2008c, 2008a). However, high-end exposure estimates for BDE-47 and BDE-99 in children were approximately 2.5 and 1.5 times the RfDs, respectively, while for adults, high-end exposure estimates approached the RfD for BDE-47. Moreover, our estimates of median exposure to BDE-99 (6.2 ng/kg bw/day and 25.3 ng/kg bw/day for adults and children, respectively), exceeded substantially (by around 20 times for adults and over 80 times for children) the no adverse effect level (NAEL) for impaired spermatogenesis of 0.23 – 0.30 ng/kg bw/day proposed by Netherlands researchers (Bakker et al., 2008). Furthermore, for children, estimates were close to the NAEL for impaired neurodevelopmental toxicity (18.8 – 41.4 ng/kg bw/day) proposed by the same Netherlands researchers (Bakker et al., 2008), while the high end exposure estimates (41.4 ng/kg bw/day and 164 ng/kg bw/day for adults and children respectively), exceeded both NAELs. This highlights the potential for adverse human health impacts arising from exposure to PBDEs at e-waste recycling sites in Taizhou.

5.3 Concentrations of PBDEs in food samples exported from China to the UK for sale

Concentrations of PBDEs detected in diet samples originating from China and sold in the UK are presented in Table 5-4. BDE-209 was the most frequently detected congener in our study (64% frequency of occurrence) at concentrations ranging from 0.68 ng/g lw in boneless roasted duck to 9.67 ng/g lw in frozen fish (Cut Beltfish). BDE-47 was the second frequentlydetected congener (55% frequency of occurrence) at concentrations ranging from 0.14 ng /g lw in boneless roasted duck to 4.63 ng /g lw in sample of dried white fish. The frequency of occurrence of other BDE congeners in these samples was decreasing in the following order: BDE-154>BDE-153=BDE-187=BDE-197>BDE-99=BDE-207>BDE-28. Five congeners, BDE-17, BDE-66, BDE-100, BDE-85, and BDE-138, were present below sample detection limits (SDLs) in all 12 dietary samples. Two samples (shredded squid and fish strips with white sesame topping), contained all BDEs considered in our study below corresponding SDLs.

Concentrations of ∑PBDE in these samples ranged from 0.90 ng/g lw (chicken powder) to 12.66 ng/g lw (frozen fish, Cut Beltfish). BDE-209 was the main contributor to ∑PBDE in the majority of the samples, which was consistent with findings of previous study in China (Luo et al. 2009) except for chicken powder and one fish sample where BDE-47 was detected at the highest concentrations. Interestingly, two of the five fish samples from this study contained unusually high levels of BDE-209 relative to BDE-47, the congener typically most abundant in fish (EFSA, 2011b) including samples from China, as shown in section 5.2. This phenomenon was observed in frozen but not dried fish samples in this study and may indicate additional input of BDE-209 during fish handling and transportation from the catch area to the facility where it was finally sealed in packs and frozen.

Table 5-4 Concentrations of PBDEs in foods exported from China to the UK (ng/g, lipid weight)

Sample type	BDE-17	BDE-28	BDE-47	BDE-66	BDE-100	BDE-99	BDE-85	BDE-154	BDE-153	BDE-138	BDE-183	BDE-197	BDE-207	BDE-209	∑PBDEs
chicken powder	<0.002	<0.002	0.69	<0.003	<0.003	0.21	<0.005	<0.002	<0.004	<0.003	<0.004	<0.002	<0.003	<0.007	0.90
fish balls with pork filling	<0.002	<0.002	0.18	<0.003	<0.003	0.18	<0.005	0.09	0.17	<0.003	0.26	0.24	0.25	4.92	6.28
crispy aromatic duck	<0.002	<0.002	<0.004	<0.003	<0.003	<0.003	<0.005	<0.002	<0.004	<0.003	0.14	0.12	0.25	2.81	3.33
boneless crispy duck	<0.002	<0.002	<0.004	<0.003	<0.003	<0.003	<0.005	<0.002	0.17	<0.003	0.22	0.12	<0.003	2.08	2.58
boneless roasted duck	<0.002	<0.002	0.14	<0.003	<0.003	<0.003	<0.005	<0.002	<0.004	<0.003	<0.004	0.05	<0.003	0.68	0.87
frozen fish (Cut Beltfish)	<0.002	<0.002	2.20	<0.003	<0.003	<0.003	<0.005	0.77	<0.004	<0.003	<0.004	<0.002	<0.003	9.69	12.66
frozen fish (Yellow Croaker)	<0.002	<0.002	2.50	<0.003	<0.003	<0.003	<0.005	1.55	0.66	<0.003	<0.004	<0.002	<0.003	2.87	7.59
fish strips with white sesame	<0.002	<0.002	<0.004	<0.003	<0.003	<0.003	<0.005	<0.002	<0.004	<0.003	<0.004	<0.002	<0.003	<0.007	<0.046
dried anchovy	<0.002	3.33	<0.004	<0.003	<0.003	<0.003	<0.005	<0.002	<0.004	<0.003	<0.004	<0.002	<0.003	<0.007	3.33
dried white fish	<0.002	<0.002	4.63	<0.003	<0.003	<0.003	<0.005	1.27	<0.004	<0.003	<0.004	<0.002	<0.003	<0.007	5.90
boiled & dried small shrimp	<0.002	<0.002	<0.004	<0.003	<0.003	<0.003	<0.005	0.74	<0.004	<0.003	<0.004	<0.002	<0.003	3.42	4.16
shredded squid	<0.002	<0.002	<0.004	<0.003	<0.003	<0.003	<0.005	<0.002	<0.004	<0.003	<0.004	<0.002	<0.003	<0.007	<0.046

Average ∑PBDE concentrations in duck meat (n=3) in our study (0.66 ng/g ww and 2.26ng/g lw) was comparable to that previously reported for ducks from Nanjing, China (average: 0.3 ng/g ww) (Su et al., 2012), but lower than in ducks from e-waste areas in Guangdong, China (median: 6.6 ng/g lw) (Luo et al., 2009a), and much lower than in ducks from e-waste areas in Taizhou (average: 40.9 ng/g ww) as reported in section 5.2. Average ∑PBDE concentrations (n=5) in fish (0.27 ng/g ww and 5.61 ng/g lw) in this study were also much lower than we detected in fish from e-waste sites in Taizhou (average: 44.2 ng/g ww and 4180 ng/g lw – see section 5.2), and than reported in other studies on fish from e-waste related sites in China (Chan et al., 2013), but were comparable to those detected previously for non-e-waste related areas in China (Meng et al. 2007; Su et al. 2012; Gao et al. 2009) and Hong Kong (Wang et al., 2011b).

Overall, it was apparent from this small study that foodstuffs exported from China to the UK for sale were less contaminated with PBDEs as foodstuffs originating from e-waste related sites in Taizhou. Our results did not confirm our hypothesis, in this case, that substantial transboundary transfer of PBDEs can occur via exported foodstuffs. However, as this study was based on a very limited number of samples, further investigation would be useful to confirm our findings.

5.4 Human dietary intake of organohalogen contaminants (OHCs) and metals/metalloids at e-waste recycling sites in Eastern China

5.4.1 Concentrations of contaminants in dietary samples

5.4.1.1 NBFRs

Concentrations of NBFRs in e-waste related samples in this study generally exceeded concentrations in the corresponding control samples by substantial margins (Table 5-5), indicating a discernible influence of e-waste treatment on concentrations of these contaminants in locally produced foods.

Table 5-5 Concentrations of OHCs in composite food samples from e-waste recycling (Taizhou) and control sites in Eastern China

Sample type		**Site Category (Control /E-waste)**	**Lipid%**	**Concentration, ng/g lipid weight**							
				∑HBCDs	**∑PCBs**	**PBEB**	**HBB**	**EH-TBB**	**BEH-TBP**	**BTBPE**	**DBDPE**
Vegetable oil		Control	100	0.10	<1.00	<0.17	<0.15	<0.20	<0.25	<0.35	<0.45
Muscle	Fish	Control	23.4	5.90	79.0	<0.17	<0.15	4.00	1.90	2.10	<0.45
		E-waste	5.70	310	75400	<0.17	6.49	62.2	15.5	6.83	<0.45
	Shrimp	Control	4.50	5.70	240	<0.17	0.97	11.7	9.32	<0.35	9.19
		E-waste	4.50	<0.06	1170	6.81	<0.15	36.8	16.3	9.07	45.3
	Chicken	Control	19.0	0.09	<1.00	<0.17	<0.15	2.66	1.78	<0.35	<0.45
		E-waste	38.6	78.7	500	<0.17	0.41	24.7	8.97	1.46	<0.45
	Duck	Control	18.2	2.40	33.0	1.16	<0.15	2.74	<0.25	1.87	<0.45
		E-waste	48.1	26.4	1320	0.87	0.56	24.2	7.23	4.57	<0.45
	Pork	Control	24.6	3.10	<1.00	<0.17	<0.15	2.14	1.37	2.69	<0.45
		E-waste	18.4	<0.06	<1.00	<0.17	0.41	38.2	12.4	5.40	<0.45
Liver	Chicken	Control	14.9	2.30	<1.00	2.66	<0.15	5.00	2.61	3.38	<0.45
		E-waste	20.9	42.5	410	2.30	<0.15	35.0	10.6	15.0	<0.45
	Duck	Control	21.5	29.9	3.00	<0.17	<0.15	8.20	1.69	3.27	<0.45
		E-waste	14.5	5.70	570	3.37	<0.15	38.4	13.7	11.7	<0.45
Egg	Chicken	Control	29.6	1.70	<1.00	<0.17	<0.15	1.73	<0.25	<0.35	<0.45
		E-waste	28.5	47.5	740	<0.17	<0.15	4.86	0.94	2.02	<0.45
		E-waste	26.5	37.7	1180	<0.17	<0.15	4.73	1.37	3.84	<0.45
	Duck	Control	32.7	0.50	<1.00	<0.17	<0.15	1.21	<0.25	<0.35	<0.45
		E-waste	32.0	9.30	740	<0.17	<0.15	3.09	0.97	1.11	<0.45
		E-waste	27.0	3.00	62.0	<0.17	<0.15	5.42	1.65	3.07	<0.45
		E-waste	31.0	17.5	140	<0.17	<0.15	3.67	1.24	2.15	<0.45
		E-waste	28.8	2.20	59.0	<0.17	<0.15	4.40	0.81	<0.35	<0.45
		E-waste	29.6	14.7	2860	<0.17	<0.15	3.56	0.88	<0.35	<0.45

EH-TBB and BEH-TBP were detected in all e-waste related samples, with BTBPE detected in 86% of samples. Less frequently detected were PBEB and HBB (>LOQ in 36% of e-waste related samples) while DBDPE was detected only in shrimp. The highest concentration among NBFRs was found for EH-TBB (fish: 62.2 ng/g lw) followed by DBDPE (shrimp: 45.3 ng/g lw). Consistent with previous findings for water birds from e-waste recycling sites in South China (Zhang et al., 2011b), concentrations of EH-TBB, BEH-TBP, BTBPE and PBEB in avian livers in this study (chicken: 35.0, 10.6, 15.0, and 2.3 ng/g lw; duck: 38.4, 13.7, 11.7, and 3.4 ng/g lw, respectively) exceeded those in corresponding muscle samples (chicken: 24.7, 9.0, 1.5, and <0.17 ng/g lw; duck: 24.2,7.2, 4.6, and 0.9 ng/g lw, respectively). In contrast, in both chickens and ducks, HBB was detected in muscle but not liver.

Finally, while concentrations of PBEB, HBB, and DBDPE were all <LOQ in chicken and duck eggs, EH-TBB and BEH-TBP were detected in all e-waste related egg samples (average: 4.3 and 1.1 ng/g lw, respectively). No information related to the concentrations of BEH-TEBP, EH-TBB, BTBPE, DBDPE, PBEB and HBB in food samples was identified in a meta-analysis conducted by the European Food Safety Authority (EFSA, 2012a). However, we are aware of two studies of chicken eggs (Zheng et al., 2012) and chicken and goose eggs (Zeng et al., 2016) from e-waste recycling sites in South China which reported concentrations of NBFRs. The study by Zheng et al. (2012) reported BTBPE, DBDPE, HBB and PBEB to be present at mean concentrations of 37.2–264, 5.97–37.9, 7.32–25.7, and 0.63–0.78, ng/g lw, respectively, compared to those in chicken eggs in our study (range: <0.35 – 3.84 ng/g lw) (see Table 5-5). At the same time, the study by Zeng et al. (2016) reported concentrations of BTBPE in chicken eggs (mean from site 2: 1.1 ng/g lw,) that were comparable to those detected in our study (2.02 and 3.84 ng/g lw) while chicken eggs from site 1 showed higher concentrations of BTBPE (mean: 24 ng/g lw) than our chicken egg samples.

More recently, a study has been conducted on human exposure to NBFRs through consumption of a wider range of foodstuffs originating from e-waste recycling site in Vietnam (Tao et al., 2016). Interestingly, the patterns of NBFR contamination recorded by Tao et al. (2016) for fish, pork and chicken muscle, liver and eggs were quite different from those recorded in our study. For example, although we did not record the presence of DBDPE at levels above detection limit for any of the abovementioned foodstuffs, this BFR was found in samples of pork, chicken muscles and eggs from an e-waste recycling site in Vietnam, at mean concentrations of 2.5, 6.9, and 280 ng/g lw, respectively. Conversely, BEH-TBP was detected in all samples in our study (range for five food categories: 0.94 – 15.5 ng/g lw) while it was present only in chicken eggs (mean: 2.0 ng/g lw) in the study by Tao et al. (2016). Such differences are not unexpected and may largely reflect the diversity of e-waste materials that are processed at each particular recycling site, as well as levels of contamination of surrounding environment, which is accessible to domestic birds. Another study (Fernandes et al., 2009) reported concentrations of three of our target NBFRs (HBB, BTBPE and DBDPE) in a wide range of foodstuffs in the UK, with BTBPE being the only NBFR detected above LODs and ranging from 0.1 ng/g lw (in beef burger) to 3.33 ng/g lw (in lemon sole). As well as the presence of a much wider range of NBFRs; concentrations of BTBPE in our study exceeded those in UK foods. For example, BTBPE was detected in our pooled chicken liver sample at 15.0 ng/g lw, compared to 0.75 ng/g lw in the UK study, while it was present at 6.83 and 9.07 ng/g lw in our fish and shrimp samples respectively, exceeding the concentrations reported in UK fish (range: 0.26 – 3.33 ng/g lw).

5.4.1.2 HBCD

Amongst pooled samples, the highest concentration of ∑HBCD was detected in fish muscle (310 ng/g lw) followed by chicken muscle, chicken egg, and chicken liver (79, 47 and 43 ng/g lw, respectively) (Table 5-5). Concentrations of HBCD in all analysed samples are provided in

Table 5-6. HBCDs in most of the e-waste related samples exceeded those in corresponding controls by 1-3 orders of magnitude. However, HBCDs were <0.06 ng/g lw in e-waste related pork and shrimp samples, while the corresponding control samples contained 3.1 and 5.7 ng/g lw ∑HBCD, respectively.

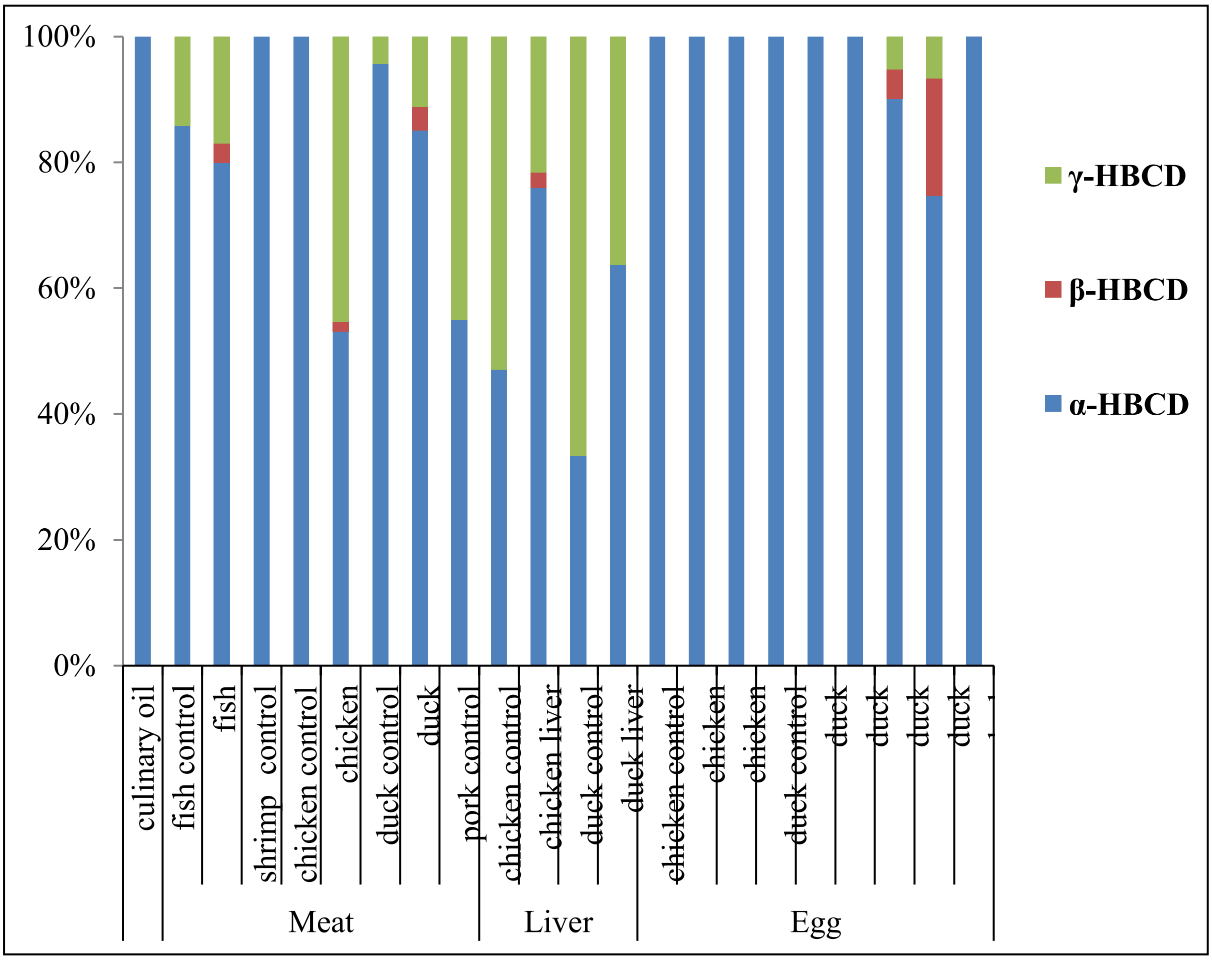
Table 5-6 Concentration of HBCD isomers (in ng/g lw) in pooled food samples from e-waste and control sites in China

Sample type		**Control/ E-waste**	**Code**	***α*-HBCD**	***β*-HBCD**	***γ*-HBCD**	**ΣHBCDs**
Vegetable oil		Control	GP01	0.1	<0.02	<0.02	0.1
Meat	Fish	Control	GP02	5.1	<0.02	0.8	5.9
		E-waste	GP03	250	9.9	53.0	313
	Shrimp	Control	GP04	5.7	<0.02	<0.02	5.7
		E-waste	GP05	<0.02	<0.02	<0.02	<0.06
	Chicken	Control	GP06	0.1	<0.02	<0.02	<0.06
		E-waste	GP07	41.8	1.2	35.7	78.7
	Duck	Control	GP10	2.3	<0.02	0.1	2.4
		E-waste	GP11	22.5	1.0	3.0	26.4
	Pork	Control	GP14	1.7	<0.02	1.4	3.0
		E-waste	GP15	<0.02	<0.02	<0.02	<0.06
Liver	Chicken	Control	GP08	1.1	<0.02	1.2	2.3
		E-waste	GP09	32.3	<0.02	9.2	42.5
	Duck	Control	GP12	10.0	<0.02	19.9	29.9
		E-waste	GP13	3.6	<0.02	2.1	5.7
Egg	Chicken	Control	GP16	1.7	<0.02	<0.02	3.0
		E-waste	GP17	47.4	<0.02	<0.02	47.4
		E-waste	GP18	37.7	<0.02	<0.02	37.7
	Duck	Control	GP19	0.5	<0.02	<0.02	0.5
		E-waste	GP20	9.3	<0.02	<0.02	9.3
		E-waste	GP21	3.0	<0.02	<0.02	3.0
		E-waste	GP22	15.8	0.8	0.9	17.5
		E-waste	GP23	1.6	0.4	0.1	2.2
		E-waste	GP24	14.7	<0.02	<0.02	14.7

Moreover, concentrations of ∑HBCD in the duck liver control sample exceeded five-fold that detected in duck livers from e-waste-impacted locations. A previous study from the Pearl River Delta in South China (Sun et al., 2012) reported higher concentrations of HBCDs in the muscle and stomach of three species of passerine birds collected from urban sites than in those from e-waste recycling sites. That difference was attributed to higher releases of HBCD from textile and construction applications in urban areas. This may also help explain the higher concentrations of ∑HBCD in our control samples, which were all obtained from urban areas distant from e-waste recycling sites. Furthermore, as the main application of HBCDs is in thermal insulation boards and construction materials (Covaci et al., 2006), a more widespread presence of this compound may be expected in urban areas, with no particular association expected with proximity to e-waste recycling sites. Nevertheless, e-waste-impacted samples of duck muscle, as well as of chicken muscle and liver displayed significantly higher concentrations of ∑HBCDs than corresponding controls. We hypothesise this occurs because chicken and duck housing at the Taizhou e-waste sites are often constructed from potentially HBCD-containing recycled construction materials, as well as containing old furniture and textiles that may also have been treated with HBCDs. This might also explain the higher concentration of ∑HBCD in chickens than in ducks from e-waste sites in our study as chickens spend more time in their housing, though a significant contribution to the patterns from differences in feeding habits between ducks and chickens cannot be also ruled out.

A similar combination of factors may account for our observation that e-waste-impacted chicken eggs contained higher concentrations of ∑HBCDs (47.4 and 37.7 ng/g lw for Wenling and Luqiao e-waste sites respectively) than duck eggs from the same locations (range: 3.0 – 17.5 ng/g lw; average: 9.35 ng/g lw). To the author's knowledge, there are no previously reported data on HBCD concentrations in domestic duck eggs. Interestingly, while the lowest ∑HBCD concentration was detected in a pooled duck egg sample from a site in the Wenling district at which e-waste activity has decreased substantially recently, the highest concentration was found in a sample from a site in the same district where e-waste recycling had only recently ceased. The farm on this former e-waste recycling area was the largest in our study with 2,200 ducks onsite, and which contained several large duck shelters thickly covered with recycled textile and construction materials that potentially may contain substantial amounts of HBCDs (Alaee et al., 2003). This highlights the importance of sources of HBCDs other than e-waste treatment to our samples. Diastereomer profiles of HBCDs in pooled samples are presented in Fig. 5-3. In general, α-HBCD was the predominant HBCD congener contributing on average 77±31% ∑HBCDs in all our samples (from e-waste areas and controls). This accords with previous reports of the predominance of α-HBCD in biota as opposed to the higher contribution of γ-HBCD found in commercial formulations and abiotic matrices (Marvin et al., 2011).

Figure 5-3 α-, β- and γ-HBCD diastereomer profiles in composite food samples containing concentrations above LOQ



This has been attributed to several factors, including preferential biotransformation of the *β*- and *γ*-isomers (Abdallah et al., 2014) in addition to higher bioavailability and higher bioaccumulation potential of α-HBCD (Fournier et al., 2012; Abdallah et al., 2012; Szabo et al., 2011a).

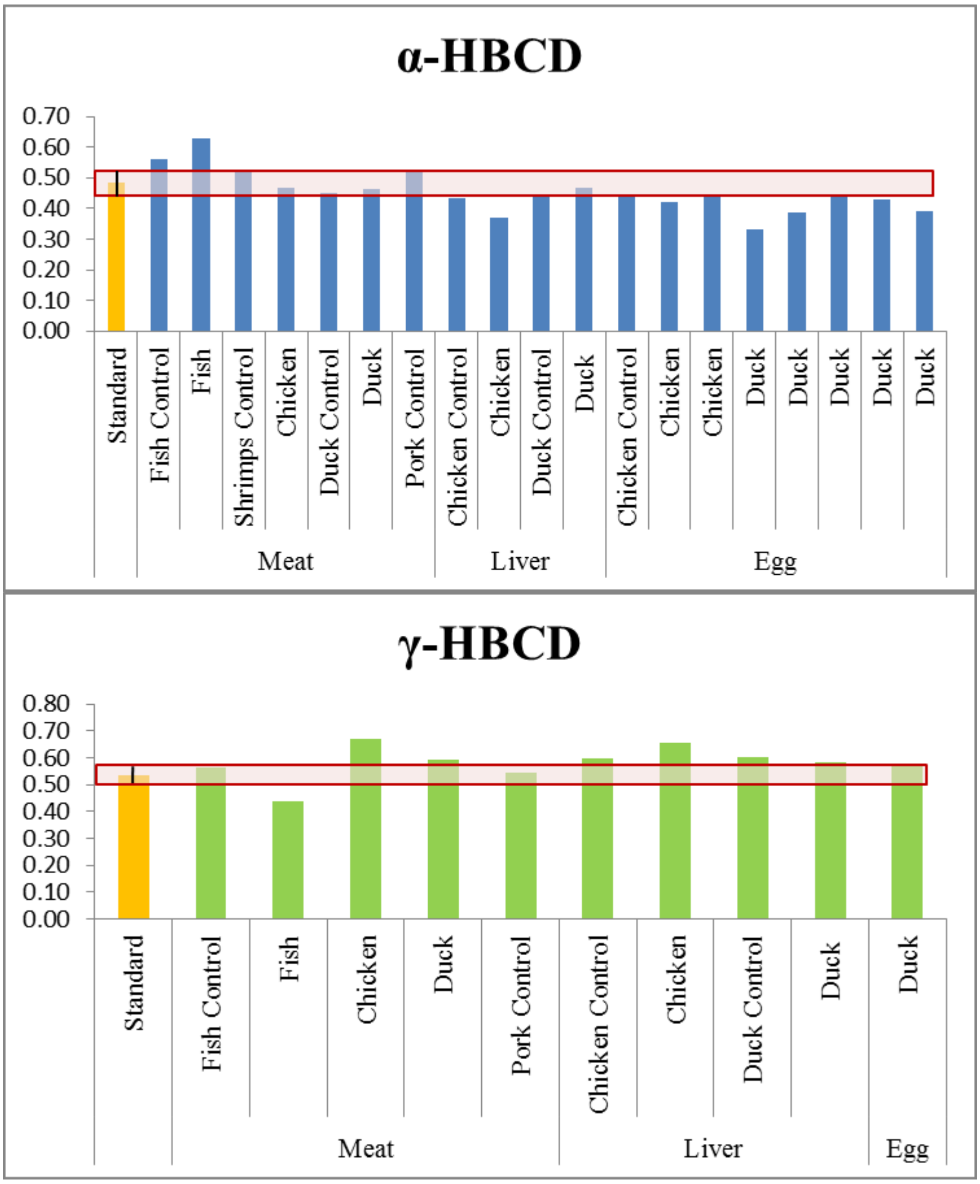
Moreover, *in vivo* metabolic isomerisation of β- and γ-HBCDs to the α-isomer was also suggested (Law et al., 2006a; Luo et al., 2013). Interestingly, while γ-HBCD comprised only 22% and 36% ∑HBCD, respectively, in chicken and duck livers from e-waste related sites, in control samples of the same matrices, γ-HBCD contributed 53% and 67% of ∑HBCD respectively. This suggests exposure of the control birds to a comparatively "fresh" HBCDs source.

Table 5-7 Concentrations of HBCDs (ng/g lw) in individual samples of fish, and paired samples (muscle and liver) of chickens and ducks

Sample Type		Location	α-HBCD	β-HBCD	γ-HBCD	ΣHBCDs
Fish	carp	Wenling, Taizhou, Site 4	1530	56.0	350	1940
	loach	Luqiao, Taizhou, Site 5	490	30.0	190	710
	snakehead	Luqiao, Taizhou, Site 7	620	14.6	39.4	670
	bream	Shanghai supermarket, control sample	1.20	2.20	7.40	10.8
	perch	Nanjing supermarket, control sample	20.1	3.30	11.9	35.3
Duck	meat	Wenling, Taizhou, Site 1	19.2	0.50	5.60	25.3
	liver		3.10	3.50	11.9	18.5
	meat	Wenling, Taizhou, Site 2	1.60	0.10	0.90	2.60
	liver		0.20	0.40	2.50	3.10
	meat	Wenling, Taizhou, Site 2	1.70	0.20	0.90	2.80
	liver		0.70	0.20	2.70	3.70
Chicken	meat	Wenling, Taizhou, Site 2	7.60	1.20	5.10	14.0
	liver		1.90	3.50	12.8	18.3
	meat	Wenling, Taizhou, Site 1	490	9.00	150	640
	liver		190	4.40	190	390
	meat	Wenling, Taizhou, Site 2	14.4	1.40	5.40	21.1
	liver		5.40	1.80	5.70	12.9

In comparison, some e-waste related food samples from the study in Vietnam (Tao et al., 2016) contained HBCD concentrations (chicken liver and eggs: average ∑HBCD: 3200 ng/g lw and 3600 ng/g lw, respectively) higher than those detected in our study, with the exception of fish (average ∑HBCD: 3.4 ng/g lw) and chicken muscle (average ∑HBCD: 39 ng/g lw), which were lower than in our study. Also, α-HBCD was the main isomer in all our e-waste related food samples, indicating accumulation from less recent exposure. In contrast, γ-HBCD contributed significantly to ∑HBCD in chicken liver and eggs from Vietnamese e-waste site (1500 ng/g lw and 700 ng/g lw, respectively) but not in chicken muscles (5.3 ng/g lw), which may suggest some level of ongoing exposure to new sources of HBCDs.

Figure 5-4 Enantiomer fractions (EF) of α-HBCD and γ-HBCD in pooled food samples containing concentrations above LOQ. Error bar – SD for a racemic standard



Analyses also revealed different HBCD diastereomer profiles in liver and muscle tissues taken from individual birds (Table 5-7), similar to those reported recently for predatory birds in Belgium (Eulaers et al., 2014). Moreover, such intra-bird variation was exceeded still further by the variation in profiles between duck and chicken tissues. Notably, γ-HBCD was the dominant diastereomer in some avian liver samples compared to the predominance of α-HBCD in muscle tissue from the same birds. We hypothesise this predominance of γ-HBCD in some avian liver samples reflects the profile to which the bird is exposed, as the liver is the first organ exposed after the gastrointestinal tract.

In contrast, the diastereomer profile in muscle tissue reflects more the chronic exposure after metabolism and is thereby skewed towards α-HBCD, due to the latter's enhanced bioaccumulation potential and resistance to enzymatic metabolism (Szabo et al., 2011b; Fournier et al., 2012).

HBCD enantiomer fractions (EFs) are presented in Fig. 5-4. Generally, muscle and eggs from ducks and chickens displayed significant enrichment of the (-)-α-HBCD and (+)-γ-HBCD enantiomers. This is in agreement with previous reports for terrestrial bird samples from e-waste, urban and rural locations in South China (Sun et al., 2012; He et al., 2010) and eggs of predatory birds from Northern Europe (Janak et al., 2008).

Fish samples showed variable EF values with enrichment of (+)-α-HBCD in loach, carp and bream, (-)-γ-HBCD in loach, and (+)-γ-HBCD in bream. Our results are consistent with previous studies reporting species-specific variation in EFs in fish (Janak et al., 2005; He et al., 2013; Köppen et al., 2010). These findings indicate potential enantioselective processes associated with absorption, biotransformation and/or excretion of HBCDs in the fish and bird species studied, and that such processes are species-specific.

5.4.1.3 PCBs

With the exception of pork, concentrations of ∑PCB in our e-waste related food samples were all higher than in corresponding control samples (see Table 5-5). Results for individual PCB congeners in all samples are presented in Appendix 4. PCBs can arise in environmental samples from both primary and secondary sources and, because of their persistence and long-range transport, they are widely distributed environmental contaminants.

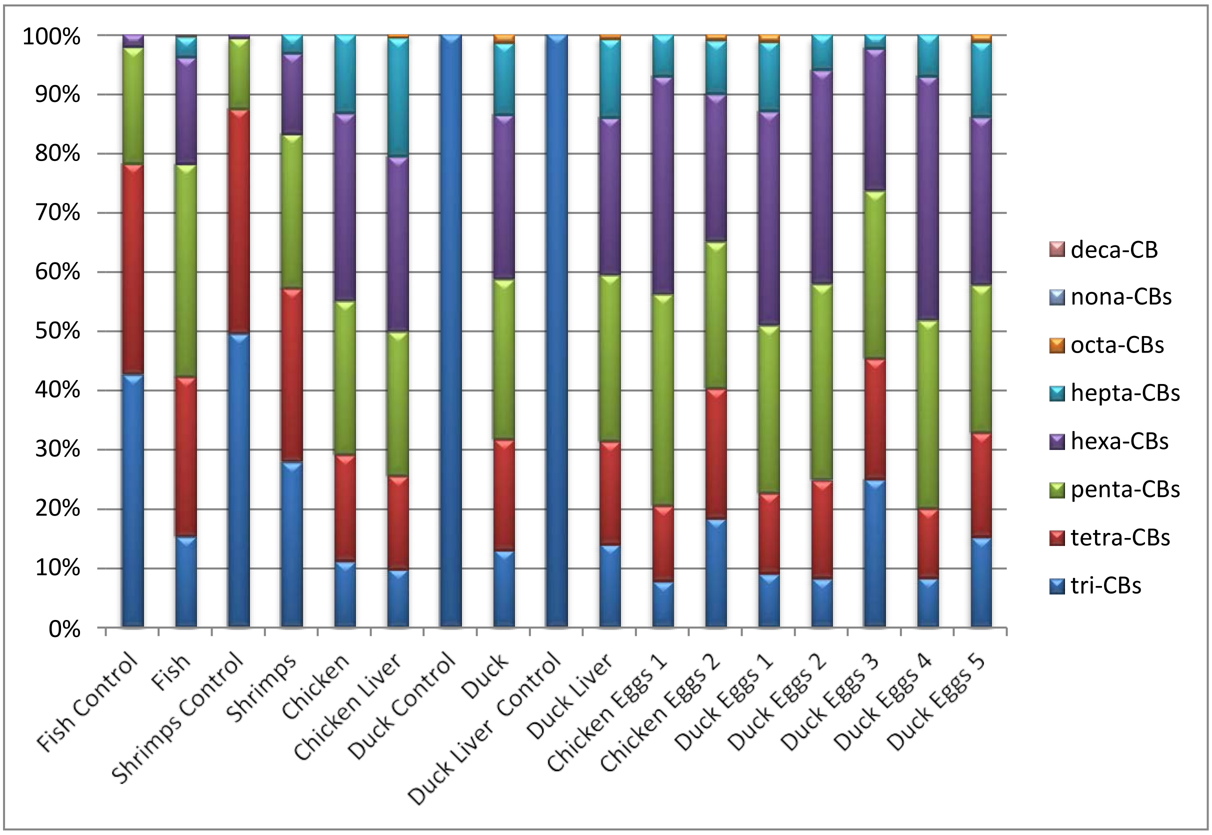
The relatively high levels of PCBs in many of the pooled food samples from e-waste areas are, however, suggestive of primary contributions from local point sources, such as recycling and disposal of obsolete transformers, an activity widely practised in Luqiao (Xing et al. 2011; Zhang et al. 2012) as well as handling of other electrical and electronic waste.

In view of the history of transformer treatment at Luqiao, it is thus unsurprising that concentrations of ∑PCB from samples obtained from this site were the highest in this study. Of the species considered, concentrations were highest in fish (75416 ng/g lw or 1168 ng/g ww), followed by those in duck eggs (site 5: 2857 ng/g lw and 846 ng/g ww), duck muscle (1322 ng/g lw and 276 ng/g ww) and chicken eggs (1179 ng/g lw and 312 ng/g ww). Consistent with previous studies (Xing et al., 2010; Rajaei et al., 2010) and possibly attributable to higher metabolic activity in liver than muscle, concentrations of ∑PCB in livers of both ducks and chickens were lower than in the corresponding muscle samples. It is also interesting to note that, while the concentration of ∑PCB in duck muscle exceeded approximately three-fold that in chicken muscle (276 ng/g ww and 88 ng/g ww, respectively), concentrations were similar in both duck and chicken livers at ~30 ng ∑PCB/g ww. This may reflect species-specific differences in metabolism.

Concentrations of ∑PCB in duck meat (276 ng/g ww), duck liver (32 ng/g ww) and eggs (average in chicken and duck eggs was 109 and 91.2 ng/g ww respectively) substantially exceeded those reported previously for e-waste-related sites in Taizhou (13.8, 2.1 and 7.9 ng/g ww, respectively) (Xing et al., 2010).

The homologue pattern of PCBs in avian-related samples originating from our e-waste sites (see Fig. 5-5) were dominated by hexa-PCBs (from 28% ∑PCBs in duck meat to 41%∑PCBs in duck eggs), followed closely by penta-PCBs. In contrast, tetra- and penta-PCBs were more prominent in aquatic species. Penta-PCBs comprised 36% ∑PCB in fish and 26% ∑PCB in shrimp, with tetra-PCBs contributing 27% ∑PCB in fish and 29% ∑PCB in shrimp.

Figure 5-5 PCB profiles in pooled food samples originating from e-waste site in Taizhou, Zhejiang, and from control sites in China



While these homologue patterns are consistent with previous observations for Taizhou (Xing et al., 2010); those in our e-waste impacted fish samples differed from patterns observed in Europe, in which hexa-PCBs (mostly PCB-153 and PCB-138) are dominant in fish (Malarvannan et al., 2014; Roosens et al., 2008). The different patterns seen in our e-waste-associated samples may reflect influences from multiple local sources at e-waste recycling sites. These include releases from PCB-containing transformers and/or capacitors as well as unintentional formation of some PCBs during poorly-controlled combustion processes (Shen et al., 2009).

Concentrations of NDL-PCBs and DL-PCBs are compared in Table 5-8 to the maximum levels (ML) promulgated by the European Commission for certain contaminants in foodstuffs (EU, 2011a).

Table 5-8 Concentrations of indicator PCBs, ∑NDL-PCB and ∑DL-PCB in food originating from Taizhou, China; and maximum levels (ML) for these contaminants in foodstuffs (EU 2011)

Sample category	**∑PCB, indicator[c]**	**∑NDL-PCB[d]**	**ML, ∑NDL-PCB[e]**	**∑DL-PCB-TEQ[f]**	**ML,∑DL-PCB-TEQ[g]**
	ng/g			**pg/g TEQ**	
Fish	34456 [a]	441[b]	125 [b]	4.32 [b]	3.0 [b]
Shrimp	569 [a]	5.82 [b]		0.09 [b]	
Chicken muscle	270 [a]	206 [a]	40 [a]	3.07 [a]	1.25 [a]
Duck muscle	698 [a]	530 [a]		7.74 [a]	
Chicken liver	180 [a]	137 [a]	40 [a]	2.09 [a]	5.5 [a]
Duck liver	288 [a]	225 [a]		3.15 [a]	
Chicken egg	518 [a]	388 [a]	40 [a]	6.41 [a]	2.5 [a]
Duck egg	428 [a]	336 [a]		5.38 [a]	

[a] expressed on a lipid weight basis; [b] expressed on a wet weight basis; [c] sum of PCB28, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180; [d] sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180; [e] maximum levels for sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180; [f] sum of PCB105, PCB118, PCB156 and PCB167; [g] maximum levels for sum of twelve dioxin-like PCBs derived by subtraction of value for the sum of dioxins (WHO-PCDD/F-TEQ) from the sum of dioxins and DL-PCBs (WHO-PCDD/F-PCB-TEQ).

The sum of seven indicator PCBs (PCB-28, 52, 101, 118, 138, 153 and 180) in fish (534 ng/g ww) in our study exceeded the Chinese maximum residue limit of 500 ng/g ww for aquatic organisms and aquatic products (MOH, 2012). Additionally, with the exception of chicken liver, all samples of avian origin from e-waste sites in our study exceeded the maximum level of 200 ng/g lw set by the European Commission (EC, 1999), for the sum of these seven indicator PCBs in products including eggs and poultry.

Another EC Regulation No. 1881/2006 (EC, 2006) established maximum levels (ML) for dioxins and DL-PCBs in a range of foodstuffs. This was amended recently (EU, 2011a) to include limits for the sum of six marker NDL-PCBs (see Table 5-8). This ML for ∑NDL-PCB was exceeded by at least an order of magnitude for foodstuffs of avian origin in our study and 3.5 times in case of fish. Moreover, while only four DL-PCBs were measured in this study (PCB-105, 118, 156, and 167), Table 5-8 shows that based on the contribution of these four congeners alone, the corresponding EU ML was exceeded for all foodstuffs studied except for livers.

5.4.1.4 Metals and metalloids

Concentrations of metals and metalloids in food samples (expressed on a wet weight basis) are presented in Table 5-9. The vegetable oil sample analysed contained all metals considered in our study below corresponding LODs, indicating no additional input of these contaminants through cooking processes.

Arsenic (As) was detected above LOQ in four out of ten food types in our study with shrimp from e-waste sites containing the highest concentration of As at 0.94 mg/kg, which was also two times higher than corresponding control. In contrast, our control fish sample contained As at 0.36 mg/kg, which was four times higher than that from the e-waste sites, which suggests exposure of our control fish to other As sources. In general, fish and seafood have been shown to be amongst the main dietary sources of arsenic as was reported in a Hong Kong total diet study (Wong et al., 2013b). Both chicken meat and liver from e-waste sites contained higher As concentrations than corresponding controls (up to 8 times for chicken liver) while this was not the case for duck meat and liver. Pork and avian eggs in our study contained As concentrations below LODs.

Cadmium (Cd) concentrations in e-waste related duck and chicken liver were the highest amongst all food samples (2.19 and 1.32 mg/kg respectively) and exceeded significantly corresponding controls for up to 44 times for chicken liver. Moreover, avian liver samples exceeded substantially the maximum contaminant limit (MCLs) of 0.5 mg/kg for Cd in food set up by both Chinese (MOH, 2012) and European Union (EU, 2006; EC, 2014) regulations. Concentrations of Cd in e-waste related duck and chicken meat (~0.01 and 0.05 mg/kg respectively) were considerably lower than those for the corresponding livers, which was consistent with previous studies (Marettová et al. 2012; White & Finley 1978; Ismail & Abolghait 2013). However, the Cd concentration in chicken meat (0.05 mg/kg) was equal to the MCL according to European regulations (EC, 2014). Though the difference between e-waste and control samples of duck and chicken meat was not as prominent as for the livers, our finding still suggests that e-waste recycling activities are a substantial source of Cd to avian species breeding in the vicinity of the local workshops. Comparable concentrations of Cd to that detected in our study have previously been reported in another study for e-waste related chicken meat at 0.01 - 0.04 mg/kg (Zheng et al., 2013).

At the same time, slightly higher concentrations were reported in the latter study for Cd in pork (<0.01 - 0.03 mg/kg) and fish (0.01 - 0.03 mg/kg) than detected in our study. Despite elevated levels in avian liver and meat, cadmium was not detected in any samples of egg yolk, which was consistent with previously reported findings of restricted Cd transfer to eggs from laying hens exposed to Cd (Sato et al., 1997). Among aquatic species from e-waste sites, shrimp but not fish had elevated Cd concentrations in comparison to control samples.

Chromium (Cr) concentrations in chicken egg yolk from two e-waste sites (0.96 and 5.6 mg/kg) were the highest among other foods in our study and exceeded considerably the Cr concentration in the corresponding control by over 100 times for the sample containing the highest concentrations of this metal (sample GP18 from Luqiao). Concentrations of Cr in duck egg yolk (range: 0.15 - 0.41 mg/kg) were lower than in chicken egg yolk, but still exceeded the concentration in the corresponding control sample by up to 4 times.

Similarly, while the concentration of Cr in chicken meat and liver samples from e-waste sites were 2 and 4 times higher than corresponding controls, duck meat and liver samples from both e-waste and control sites were detected at comparable concentrations. These data may reflect the diversity of contamination patterns in areas impacted by e-waste recycling activities (Tang et al., 2010) as well as differences in intake routes of Cr for chickens and ducks. The e-waste related pork sample contained Cr at a slightly higher concentration than detected in the corresponding control. Furthermore, Cr concentrations in chicken meat and in pork exceeded the MCL for food in China (1 mg/kg) (MOH, 2012). In contrast, both shrimp and fish samples from control sites exceeded those from e-waste related sites, which may be for various reasons including the exposure of our control aquatic species to a different source or sources of this metal. Additionally, it was previously reported for fresh water fish (Ciftci et al., 2010) that muscle tissue has a moderate ability for Cr accumulation compared to the gut and kidney which accumulate Cr more efficiently. Therefore, as our aquatic related samples were muscle tissue only, they may not fully reflect the accumulation of Cr by aquatic organisms in e-waste recycling areas.

Copper (Cu) concentrations were higher in e-waste related duck liver compared to the control (by just over two times), though this pattern was not observed for chicken liver, nor for duck and chicken meat.

Table 5-9 Concentrations of metals/metalloids in foodstuffs, mg/kg wet weight. Results marked ~ fall below LOQ but were above LOD

Sample type		Category	Code	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Sn	Y	Bi	Be	Sb
Vegetable oil		Control	GP01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.2	<0.01	<0.5	<0.2	<0.01	<0.01	<0.01	<0.02
Meat	Fish	Control	GP02	0.36	<0.003	0.55	0.29	0.02	0.3	~0.003	7.6	<0.006	<0.003	<0.003	<0.006	<0.003
		E-waste	GP03	0.08	<0.003	0.32	0.43	0.07	~0.16	0.05	15.4	<0.005	<0.003	<0.003	<0.005	<0.003
	Shrimp	Control	GP04	0.42	0.08	0.65	10.32	<0.003	0.3	~0.006	17.7	<0.006	<0.003	<0.003	<0.006	<0.003
		E-waste	GP05	0.94	0.16	0.28	23.03	0.01	0.4	0.02	20.0	<0.006	~0.01	<0.003	<0.006	<0.003
	Chicken	Control	GP06	~0.01	<0.003	0.50	0.96	<0.003	~0.18	0.03	21.4	~0.01	<0.003	<0.004	<0.007	<0.003
		E-waste	GP07	0.04	0.05	1.09	0.86	<0.003	0.5	0.04	18.6	<0.009	<0.003	<0.005	<0.009	<0.003
	Duck	Control	GP10	~0.01	<0.003	1.00	3.39	<0.003	0.5	0.04	46.1	<0.009	<0.003	<0.004	<0.009	<0.003
		E-waste	GP11	~0.02	~0.01	0.83	2.48	~0.003	0.4	0.06	25.2	<0.009	<0.003	<0.004	<0.009	<0.003
	Pork	Control	GP14	<0.007	<0.003	0.96	0.91	<0.003	0.4	0.02	37.4	<0.009	<0.003	<0.004	<0.009	<0.003
		E-waste	GP15	<0.007	<0.003	1.18	1.06	<0.003	0.7	0.05	31.8	<0.011	<0.003	<0.006	<0.011	<0.003
Liver	Chicken	Control	GP08	<0.007	0.03	0.23	4.75	0.02	~0.25	0.04	74.6	<0.007	<0.003	<0.004	<0.007	<0.003
		E-waste	GP09	0.06	1.32	0.89	3.68	~0.01	0.4	1.32	45.4	<0.007	<0.003	<0.004	<0.007	<0.003
	Duck	Control	GP12	<0.007	0.14	0.78	26.5	~0.003	0.3	0.03	72.2	<0.009	~0.01	<0.004	<0.009	<0.003
		E-waste	GP13	<0.007	2.19	0.77	66.9	0.05	0.4	1.27	76.2	<0.008	<0.003	<0.004	<0.008	<0.003
Egg yolk	Chicken	Control	GP16	<0.02	<0.01	~0.05	1.20	<0.01	<0.2	<0.01	34.0	<0.2	<0.01	<0.01	<0.02	<0.01
		E-waste	GP17	<0.02	<0.01	0.96	1.40	<0.01	~0.4	0.15	36.0	<0.2	<0.01	<0.01	<0.02	<0.01
		E-waste	GP18	<0.02	<0.01	5.60	1.40	<0.01	2.7	~0.03	33.0	<0.2	<0.01	<0.01	<0.02	<0.01
	Duck	Control	GP19	<0.02	<0.01	~0.09	1.20	<0.01	<0.2	<0.01	34.0	<0.2	<0.01	<0.01	<0.02	<0.01
		E-waste	GP20	~0.03	<0.01	0.41	1.20	<0.01	<0.2	0.53	40.0	<0.2	<0.01	<0.01	<0.02	<0.01
		E-waste	GP21	<0.02	<0.01	~0.15	1.20	<0.01	<0.2	0.07	35.0	<0.2	<0.01	<0.01	<0.02	<0.01
		E-waste	GP22	<0.02	<0.01	<0.05	1.30	<0.01	<0.2	~0.01	35.0	<0.2	<0.01	<0.01	<0.02	<0.01
		E-waste	GP23	<0.02	<0.01	0.30	1.40	<0.01	<0.2	~0.03	37.0	<0.2	<0.01	<0.01	<0.02	<0.01
		E-waste	GP24	<0.02	<0.01	0.34	1.30	<0.01	~0.2	0.19	34.0	<0.2	<0.01	<0.01	<0.02	<0.01

E-waste related shrimp samples also contained a higher Cu concentration compared to the control, which may contribute to the difference observed between duck and chicken livers, as the diet of ducks likely includes shrimp. All egg yolk samples considered in our study (including controls) contained similar concentrations of Cu.

Mercury (Hg) concentrations in fish and shrimp samples (0.07 and 0.01 mg/kg respectively) were between 3 and 4 times those in the respective control samples. Fish samples were within the range detected previously in fish from e-waste impacted coastlands in Zhejiang province (range: 0.04 – 1.1 mg/kg) (Zhang and Wong, 2007), but exceeded those in seafood products (average: 0.016 mg/kg) from the industrial area of Huludao, northeast of China (Zheng et al., 2007). Hence, rudimentary e-waste recycling techniques of mercury-containing equipment, such as batteries, clocks, pocket calculators, switches, and LCDs (Tiwari and Dhawan, 2014), may result in environmental contamination by mercury, which subsequently enters into the food chain. This was further confirmed by the analysis of food samples from avian species. Duck liver, though not chicken liver, samples from e-waste sites also displayed mercury concentrations (0.05 mg/kg) above that of the controls, by over 10 times. This difference between duck and chicken concentrations may reflect the influence of the diet which includes aquatic biota for ducks, a pattern which was also observed for copper. The Hg concentration in e-waste related duck liver in our study was comparable to that reported for chicken liver in another recent study conducted in Taizhou (0.059 ± 0.023 mg/kg) (Tang et al., 2015). However, samples of fish, chicken egg and pork in the latter study (0.23, 0.05 and 0.05 mg/kg respectively) contained higher Hg concentrations than detected in our study. This difference may be attributed to a site specific pattern and extent of environmental contamination, which may vary dramatically from site to site in e-waste recycling areas (see section 3.2.2).

Nickel (Ni) concentrations were the highest in e-waste related chicken egg yolk samples (~0.4 - 2.70 mg/kg) for which they exceeded those in the corresponding control by over 10 times (for the sample GP18 from Luqiao). In contrast, Ni levels in duck egg yolk samples were similar to those in the control. Similarly, while e-waste impacted chicken meat and liver samples contained Ni at 0.5 and 0.4 mg/kg respectively, i.e. about two times higher than the corresponding controls; no such difference was observed between e-waste related and control samples of duck meat and liver. It has been previously reported that both chicken and duck eggs may contain similar trace levels of Ni (at 0.059 and 0.058 mg/kg respectively) (Nisianakis et al., 2009), which was significantly lower that it has been found in our study for chicken eggs. Also, levels of Ni in chicken meat in our study were five times higher than reported for chickens from e-waste sites in South China (Zheng et al., 2013). Thus, our data may indicate that chickens in our study have been exposed to the source of nickel in investigated areas, which most probably arose as a result of e-waste recycling activities. Our pork e-waste related sample had a Ni concentration (0.7 mg/kg) about two times higher than displayed by the corresponding control, which also was about 5 times higher than reported for pork in study for e-waste sites in South China (range: <0.01 – 0.13 mg/kg) (Zheng et al., 2013). At the same time, our data on Ni levels in fish (~ 0.16 mg/kg) were comparable to those detected in the latter study (range: 0.02 – 0.12 mg/kg).

Lead (Pb) was detected in e-waste related duck and chicken liver samples at relatively high concentrations (1.27 and 1.32 mg/kg respectively) that exceeded those in the corresponding controls by between 42 and 33 times. Similar to the observation for cadmium, avian liver samples also exceeded the maximum contaminant limit (MCL) of 0.5 mg/kg for Pb in food set by both Chinese (MOH, 2012) and European Union (EU, 2006) regulations. Concentrations of Pb in e-waste related chicken and duck meat (0.04 and 0.06 mg/kg respectively) were considerably lower than those for the corresponding livers, though were higher than the corresponding meat control samples. These results were consistent with previous findings of primary accumulation of Pb in the chicken liver, but not in the muscle (Ismail & Abolghait

2013; Trampel et al. 2003). Pb concentrations in e-waste related shrimp and fish (0.02 and 0.05 mg/kg, respectively) exceeded those in the corresponding controls (by 3 and 16 times respectively). Similarly, Pb concentrations in duck and chicken egg yolks (range: ~0.01 - 0.53 and ~0.03 - 0.15 mg/kg, respectively) were higher than in the corresponding controls (<0.01 mg/kg), an exceedance particularly evident for chicken and duck eggs from Wenling (samples GP17 and GP20). Nevertheless, in comparison to other studies, e-waste related chicken meat, fish and pork samples in this study had slightly lower concentrations of Pb than previously reported for e-waste sites in South China (Zheng et al., 2013).

Zinc (Zn) concentrations in all e-waste related samples were similar to, or lower than, those for the corresponding control samples, with the exception of fish for which the zinc concentrations were double that of the control. However, for some e-waste related samples the zinc concentration was around half that in the corresponding control, and therefore the relatively small differences between e-waste related and control samples may be due to a variability unrelated to influence by e-waste processing.

Beryllium, antimony and bismuth were present at concentrations below LODs in all samples while yttrium (in e-waste related shrimp and control duck liver) and tin (in control chicken meat) were present above respective LODs but below LOQs.

5.4.2 Estimation of daily intakes

Our estimated exposures of both adults and children to halogenated organic contaminants via the consumption of a range of frequently-consumed local foodstuffs in e-waste recycling sites of Taizhou are presented in Table 5-10. The contributions to total dietary exposures for organic contaminants from different types of food are presented in Fig. 5-5.

Table 5-10 Estimated adult and child exposure to selected organohalogen contaminants (ng/kg bw/day) via different types of food at e-waste recycling sites in Taizhou, China. n/e – not estimated

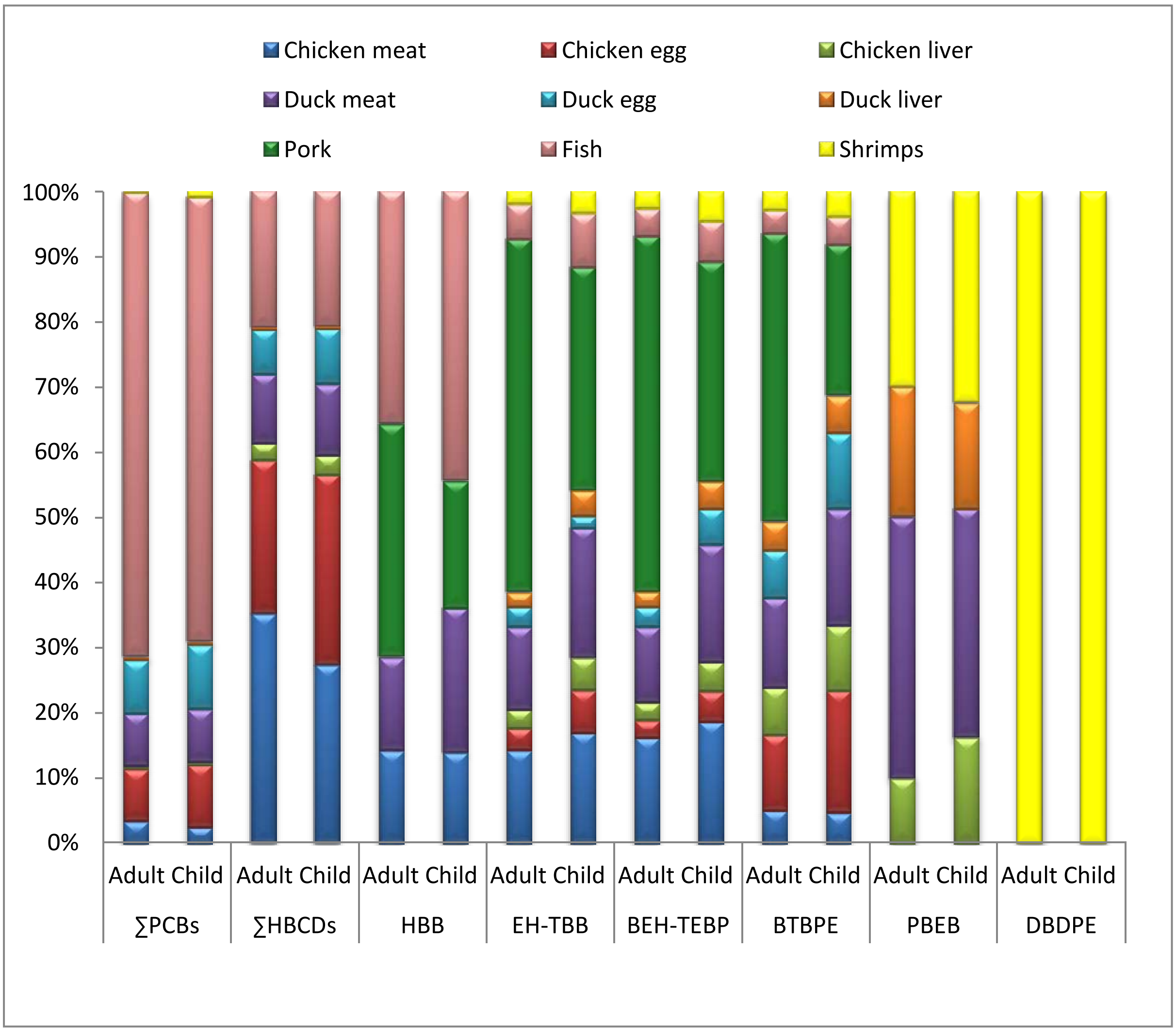
Contaminant/age group		**Meat**					**Liver**		**Egg**		**TDI**
		Fish	**Shrimp**	**Chicken**	**Duck**	**Pork**	**Chicken**	**Duck**	**Chicken**	**Duck**	
∑HBCD	Adult	2.18	n/e	3.67	1.10	n/e	0.28	0.03	2.44	0.71	10.4
	Child	7.49	n/e	9.86	3.95	n/e	1.08	0.11	10.5	3.06	36.1
∑PCB	Adult	460	1.23	22.3	52.6	n/e	2.70	2.76	51.9	53.5	650
	Child	1590	22.0	60.0	190	n/e	10.5	10.8	220	230	2340
PBEB	Adult	n/e	0.03	n/e	0.04	n/e	0.01	0.02	n/e	n/e	0.10
	Child	n/e	0.12	n/e	0.13	n/e	0.06	0.06	n/e	n/e	0.37
HBB	Adult	0.05	n/e	0.02	0.02	0.05	n/e	n/e	n/e	n/e	0.14
	Child	0.16	n/e	0.05	0.08	0.07	n/e	n/e	n/e	n/e	0.36
EH-TBB	Adult	0.43	0.16	1.15	1.01	4.34	0.23	0.18	0.27	0.25	8.02
	Child	1.49	0.62	3.09	3.62	6.22	0.89	0.71	1.18	0.32	18.1
BEH-TEBP	Adult	0.11	0.07	0.42	0.30	1.41	0.07	0.06	0.07	0.08	2.59
	Child	0.37	0.28	1.12	1.08	2.02	0.27	0.25	0.28	0.33	6.00
BTBPE	Adult	0.05	0.04	0.07	0.19	0.61	0.10	0.06	0.16	0.10	1.38
	Child	0.16	0.15	0.18	0.68	0.88	0.38	0.22	0.71	0.44	3.80
DBDPE	Adult	n/e	0.20	n/e	n/e	n/e	n/e	n/e	n/e	n/e	0.20
	Child	n/e	0.77	n/e	n/e	n/e	n/e	n/e	n/e	n/e	0.77

5.4.2.1 NBFRs

Estimated total dietary exposure to NBFRs considered in our study decreased in the following order: EH-TBB > BEH-TEBP > BTBPE > DBDPE > PBEB > HBB (Table 5-10).

EH-TBB had the highest estimated exposures for both adults and children (8.03 and 18.9 ng/kg bw/day respectively) followed by BEH-TEBP (2.6 and 6.0 ng/kg bw/day, respectively).

Figure 5-6 Contributions to total dietary exposures for organic contaminants from different types of food originating from Taizhou, China



The main source of both EH-TBB and BEH-TEBP to dietary exposure was via pork consumption (54 and 34% for adults and children respectively). Consumption of pork was also the principal contributor to dietary exposure to BTBPE (44 and 23% for adults and children respectively). For HBB, fish was the main contributor for children (44%), while for adults, both pork and fish each contributed 36% of dietary exposure. Duck muscle and duck liver combined contributed over 50% of PBEB dietary exposure for both adults and children, while shrimp were the only food type in our study found to result in exposure to DBDPE.

To our knowledge, this study is the first report of dietary exposures to NBFRs in Eastern China. One study has reported daily intakes of several NBFRs via chicken eggs from e-waste sites in South China (Zheng et al., 2012), but presented their dietary estimates as the sum of all monitored NBFRs, in contrast to our compound-specific approach. Moreover, the main contributor to exposure to NBFRs in the Zheng et al. (2012) study was Dechlorane Plus (DP), which was not investigated in our study. Hence, it was not possible to make a direct comparison between the two studies. Moreover, to our knowledge - with the exception of HBB - no health based limit values (HBLVs) with legislative standing exist for the NBFRs considered in our study. For HBB, our exposure estimates are reassuringly well below the U.S. Environmental Protection Agency's (U.S. EPA, 1988) reference dose (RfD) of 2000 ng/kg bw/day.

5.4.2.2 HBCDs

As with the NBFRs, we are unaware of any HBLV of legislative standing for HBCDs. However, we were able to compare our dietary exposure estimate with those reported in other studies. Estimated dietary exposure of both adults and children to ∑HBCD in our study (10.4 and 36.1 ng/kg bw/day) was significantly higher than reported previously for a Swedish market basket study (0.14 ng/kg bw/day) (Törnkvist et al., 2011), as well as for the Belgian population (0.37 ng/kg bw/day) (Goscinny et al., 2011). Chicken muscle and eggs were the main contributors to ∑HBCDs exposure for both adults and children at e-waste sites in Taizhou accounting for over 50% of the dietary exposure combined (Fig. 5-6).

This contrasted with two studies from Sweden (Törnkvist et al., 2011; Remberger et al., 2004) in which fish was the main contributor to dietary intake of HBCDs. Such differences likely reflect both differences in local dietary preferences and variations in environmental contamination of the study areas. Our estimate of daily ∑HBCD intake from chicken egg consumption (154 ng/day) was similar to that reported for chicken eggs at e-waste sites in South China (range: 80 – 490 ng/day) (Zheng et al., 2012), but exceeded significantly that reported for the general population in Romania (0.02 ng/day) (Dirtu and Covaci, 2010).

Our exposure estimates for adults and children to ∑HBCD via consumption of chicken eggs (2.44 and 10.5 n g/kg bw/day respectively), exceeded significantly those reported for the Belgian population (0.004 ng/kg bw/day) (Goscinny et al., 2011).

Fish contributed a further 21% to our estimate of dietary exposure to ∑HBCD for both adults and children, at 2.18 and 7.49 ng/g bw/day, respectively; values that exceeded those reported for the populations of nine Chinese coastal cities (range: 0.004 – 1.00 ng/kg bw/day) (Xia et al., 2011). Interestingly, while chicken muscle and eggs were the main contributors to ∑HBCD exposure (adults: 35 and 23 %, respectively), duck muscle and eggs contributed greatly to ∑PBDE exposure (adults: 3 and 56, % respectively) – see section 5.2.3. Our estimate also exceeded that of rural residents of Tianjin, China (1.64 ng/kg bw/day) but was similar to that reported for urban residents (6.16 ng/kg bw/day) (Zhang et al., 2013b). In comparison to other countries, our estimate of exposure to ∑HBCD via fish consumption was in line with the average estimate for Japanese adults (range: 1.3 – 3.7 ng/g bw/day) (Nakagawa et al., 2010). The contribution of duck muscle and eggs to ∑HBCD exposure was lower than that from chicken muscle and eggs. Consistent with other studies (Goscinny et al. 2011), of the avian tissues studied, liver made the lowest contribution to our estimated dietary intake of ∑HBCD.

5.4.2.3 PCBs

Dietary exposure to PCBs (650 and 2340 ng/kg ∑PCBs bw/day for adults and children, respectively) was the highest of all of the contaminants considered in this study and exceeded that for PBDEs (see section 5.2.3) of the individual samples from which the pooled samples analysed here were taken Moreover, it exceeded substantially the Minimal Risk Level (MRL) for ∑PCB of 20 ng/kg bw/day derived by the Agency for Toxic Substances & Disease Registry (ATSDR, 2000). Fish was the major contributor to total dietary exposure to PCBs (Fig. 5-5) followed by eggs (both duck and chicken) and duck muscle. Additionally, we estimated dietary intake of the four DL-PCBs measured in our study (i.e. PCB-105, 118, 156 and 167) based on their dioxin-like toxicity equivalence (TEQ) (Van den Berg et al., 2006; EU, 2011a) (see Table 5-11). While adult intake (2.83 pg TEQ/kg bw/day) was within the range of tolerable daily intake (TDI) for dioxin-like chemicals of 1 – 4 pg TEQ/kg bw/day established by the World Health Organisation (WHO) (van Leeuwen et al., 2000); estimated intake for children at 10.22 pg TEQ/kg bw/day was 2.5 times the WHO TDI upper limit for all 12 DL-PCBs combined.

Moreover, DL-PCBs-TEQ monthly intakes in our study (84.9 and 307 pg TEQ/kg bw/month for adults and children, respectively) exceeded the provisional tolerable monthly intake (PTMI) of 70 pg TEQ/kg bw, which was established by Joint FAO / WHO Expert Committee on Food Additives (JECFA, 2002).

We also compared our estimates with those reported elsewhere. Specifically, a study at an e-waste recycling site in Luqiao, Eastern China (Song et al., 2011) reported the estimated dietary intake of adults to PCDD/Fs and DL-PCBs combined to be 402 pg TEQ/kg bw/month, via consumption of six types of local food (rice, vegetable, chicken, chicken eggs, duck, and crucian carp). Although this exceeded our exposure estimate, it is important to emphasise that our DL-PCB-TEQ exposure estimates are based on exposure to only 4 out of the 12 PCB congeners deemed to display dioxin-like toxicity.

Table 5-11 Concentrations of four DL-PCBs (pg TEQ/g ww) and dietary intake (pg TEQ/kg bw/day) by adults and children from e-waste recycling sites in Eastern China

Food type	Concentration, pg TEQ/g ww					Intake, pg TEQ/kg bw/day	
	PCB 105	PCB 118	PCB 156	PCB 167	∑PCB	Child	Adult
Fish	1.16	2.79	0.24	0.13	4.32	5.89	1.71
Shrimp	0.02	0.06	0.00	0.00	0.09	0.12	0.03
Chicken meat	0.14	0.34	0.03	0.03	0.54	0.37	0.14
Duck meat	0.41	1.05	0.10	0.05	1.62	1.10	0.31
Chicken Liver	0.04	0.10	0.01	0.00	0.16	0.05	0.01
Duck Liver	0.06	0.11	0.01	0.00	0.18	0.06	0.02
Chicken Egg	0.45	0.20	0.03	0.06	0.74	1.51	0.35
Duck Egg	0.34	0.14	0.02	0.03	0.54	1.11	0.26
Total						**10.22**	**2.83**

Moreover, the exposure estimates of Song et al (2011) are calculated using WHO-1988 TEFs (Van den Berg et al., 1998), compared to the current re-evaluated WHO-2005 TEFs (Van den Berg et al., 2006) used in our study. The use of the WHO-1998 TEFs to our data raises our estimated monthly dietary intake of DL-PCBs to 332 and 1197 pg TEQ/kg bw/month for adults and children respectively. Our data thus suggest dietary exposure to PCBs and, potentially, other related contaminants in the study area is of substantial health concern, particularly for children.

5.4.2.4 Metals and metalloids

We estimated adult and child dietary intakes for those metals and metalloids (Table 5-12), which were detected at significant concentrations in the investigated foods. Daily intake was not estimated for foods containing target analytes below corresponding detection limits. Table 5-13 presents adult and child daily, weekly and monthly dietary intakes of key metals and metalloids to enable comparison with available established tolerable intakes and/or reference doses.

Estimated **cadmium** adult and child daily dietary intakes in our study, 0.38 and 1.47 μg/kg bw/day respectively, were higher than reported from a duplicate diet study conducted in area remote to e-waste recycling in Taizhou (rural farmlands, Jinhu county, China) (Liu et al., 2010) (0.21 and 0.38 μg/kg bw/day, respectively). The higher levels in our study were particularly evident for child intakes, despite the fact that the earlier study included a much wider range of foodstuffs for intake estimation.

At the same time, our estimate of Cd dietary intake was similar to that estimated for pork, fish and chicken for e-waste sites in South China (Zheng et al., 2013). Moreover, both adult and child weekly dietary intakes in our study of 2.67 and 10.3 μg/kg bw/week, respectively (Table 5-13), exceeded the tolerable weekly intake (TWI) of 2.5 μg/kg bw/week established by the EFSA Panel on Contaminants in the Food Chain (CONTAM) (EFSA, 2011a). However, in comparison to the less strict tolerable monthly intake (TMI) of 25 μg/kg bw/month established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA b, 2011), adult's Cd intake in our study (11.6 μg/kg bw/month) was below this JECFA value, while our estimate of children's monthly Cd intake (44.7 μg/kg bw/month) was almost double the JEFCA limit.

Estimates for daily intakes of **Lead** were 0.39 and 1.38 μg/kg bw/day for adults and children respectively. Weekly lead intakes (2.67 and 10.3 μg/kg bw/week for adults and children, respectively) were lower than reported for the Jinhu area in China (Liu et al., 2010), in contrast to cadmium intakes, which were higher in our study. This difference may be attributed to the high proportion of non-animal-based foods considered in Liu et al.'s study (2010) contributing to the total diet lead concentration as well as to relatively high cadmium levels in animal-based foods originating from e-waste recycling areas in Taizhou (range <0.003 – 2.19 mg/kg) in comparison to those from Jinhu area (range: 0.05 – 0.199 mg/kg).

Table 5-12 Estimated adult and child daily intakes (µg/kg bw/day) of selected metals via different foods originating from Taizhou, China. n/e – not estimated

Metal / age group		**Meat**					**Liver**		**Egg**		**Total diet**
		Fish	**Shrimp**	**Chicken**	**Duck**	**Pork**	**Chicken**	**Duck**	**Chicken**	**Duck**	
Cd	Adult	n/e	0.06	0.01	0.002	n/e	0.12	0.19	n/e	n/e	0.38
	Child	n/e	0.22	0.04	0.01	n/e	0.45	0.75	n/e	n/e	1.47
Pb	Adult	0.02	0.01	0.01	0.01	0.02	0.12	0.11	0.03	0.06	0.39
	Child	0.06	0.02	0.02	0.04	0.03	0.45	0.43	0.1	0.23	1.38
Hg	Adult	0.03	0.003	n/e	0.001	n/e	0.001	0.01	n/e	n/e	0.05
	Child	0.10	0.01	n/e	0.003	n/e	0.003	0.02	n/e	n/e	0.14
Cr	Adult	0.13	0.10	0.28	0.16	0.56	0.08	0.07	1.28	0.09	2.75
	Child	0.44	0.38	0.74	0.56	0.80	0.30	0.26	5.52	0.37	9.37
Ni	Adult	0.08	0.15	0.14	0.08	0.34	0.03	0.03	0.76	n/e	1.61
	Child	0.30	0.58	0.37	0.27	0.48	0.13	0.13	3.28	n/e	5.41
As	Adult	0.03	0.33	0.09	n/e	n/e	0.01	0.001	n/e	n/e	0.46
	Child	0.11	1.30	0.02	n/e	n/e	0.02	0.003	n/e	n/e	1.45

The joint FAO/WHO Expert Committee on Food Additives (JECFA b, 2011) estimated that the previously established provisional TWI (PTWI) of 25 µg Pb/kg bw/week, corresponding to a daily intake of 3.6 µg/kg bw/day, is associated with a decrease of at least 3 IQ points in children and an increase in systolic blood pressure of 3 mmHg. Later, the CONTAM Panel concluded that the current PTWI of 25 µg/kg bw is no longer appropriate as there is no evidence for a threshold for critical lead-induced effects (EFSA, 2013) and it was therefore withdrawn. In any case, our estimates for weekly adult and child lead intake (2.73 and 9.99 µg/kg bw/week, respectively) were below this former PTWI.

Mercury daily dietary intakes for both adult and child for e-waste related samples in our study (0.05 and 0.14 µg/kg bw/day, respectively) were lower than reported for corresponding foodstuffs (sum of fish, meat and egg: 0.27 and 0.44 µg/kg bw/day, respectively) from Baifengao village, a former e-waste recycling site in Taizhou, China (Tang et al., 2015).

Table 5-13 Adult and child daily, weekly and monthly diet intakes of key selected metals/metalloids compared to available established dietary intake limit values

Metal / age group		**Daily intake, µg/kg bw/day**	**Weekly intake, µg/kg bw/week**	**Monthly intake, µg/kg bw/month**	**Established contaminant dietary intake limit values**
Cd	Adult	0.38	2.67	11.6	2.5 µg/kg bw/week (a) 25 µg/kg bw/month (b)
	Child	1.47	10.3	44.7	
Pb	Adult	0.39	2.73	11.9	Currently not established (c)
	Child	1.38	9.66	41.9	
Hg	Adult	0.05	0.32	1.37	1.3 µg/kg bw/week (d) 0.1 µg/kg bw/day (e)
	Child	0.14	0.95	4.13	
Cr	Adult	2.75	19.3	83.6	300 µg/kg bw/day (f)
	Child	9.37	65.6	285	
Ni	Adult	1.61	11.3	48.9	2.8 µg/kg bw/day (g)
	Child	5.41	38.8	168	
As	Adult	0.46	3.23	14.0	0.3 µg/kg bw/day (h)
	Child	1.45	10.2	44.2	

a – tolerable weekly intake (TWI) established by EFSA Panel on Contaminants in the Food Chain (CONTAM) (EFSA, 2011a);
b - tolerable monthly intake (TMI) established by Joint FAO/WHO Expert Committee on Food Additives (JECFA b, 2011);
c - The CONTAM Panel concluded that the current PTWI of 25 µg/kg bw is no longer appropriate as there is no evidence for a threshold for critical lead-induced effects (EFSA, 2013);
d - tolerable weekly intake (TWI) established by EFSA Panel on Contaminants in the Food Chain (CONTAM) (EFSA, 2012b);
e – U.S. EPA reference dose (RfD) (U.S. EPA, 2001b) for methylmercury;
f - tolerable daily intake (TDI) established by EFSA Panel on Contaminants in the Food Chain (CONTAM) (EFSA a, 2014);
g - tolerable daily intake (TDI) established by EFSA Panel on Contaminants in the Food Chain (CONTAM) (EFSA, 2015);
h - U.S. EPA reference dose (RfD) (U.S. EPA, 1997).

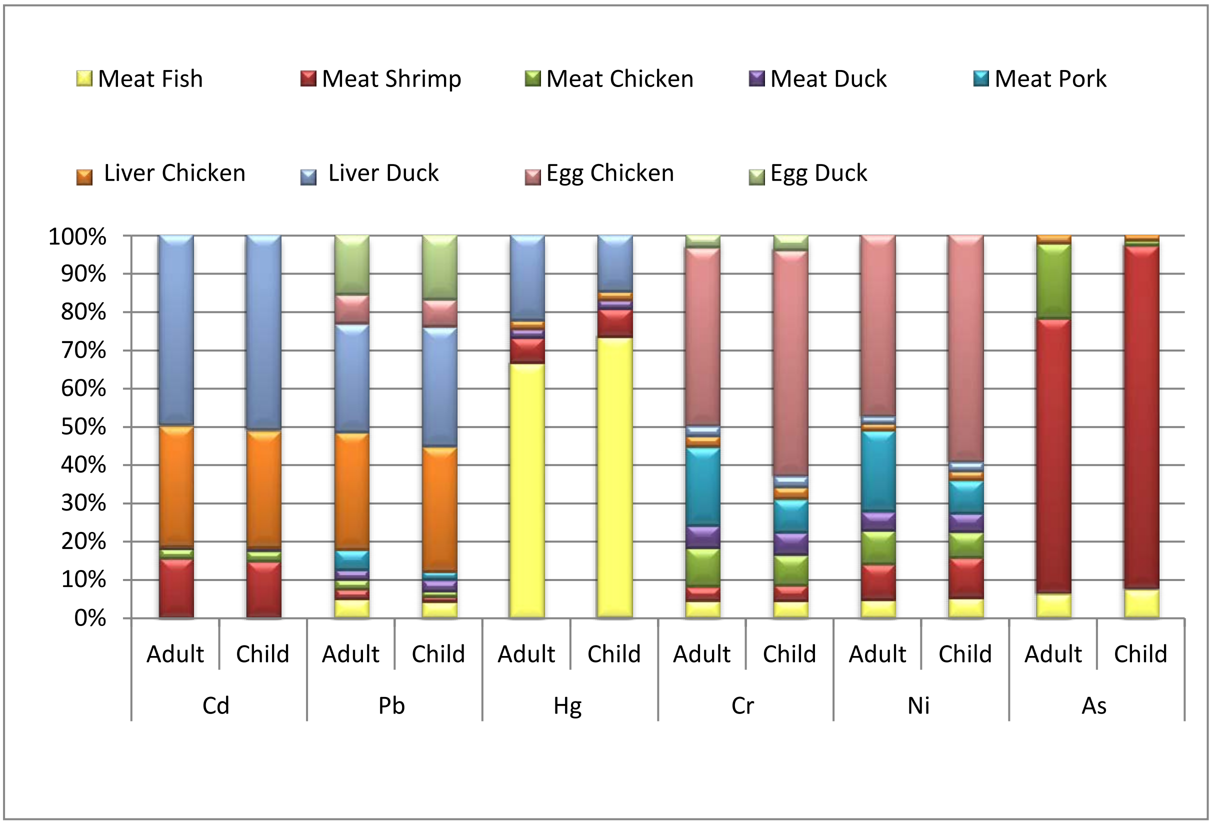
The difference may be attributed to the type of e-waste recycled at various areas of Taizhou as well as to the resulting level of environmental contamination caused by e-waste recycling activities, which may vary significantly. Mercury dietary intake in our study did not exceed the TWI established by the EFSA Panel on Contaminants in the Food Chain of 1.3 µg/kg bw/week (EFSA, 2012b). However, our estimated children's intake (0.95 µg/kg bw/week) fell just below this value. Moreover, our estimated children's daily mercury intake exceeded the U.S. EPA RfD of 0.1 µg/kg bw/day (U.S. EPA, 2001a).

Both adult and child daily dietary intakes of **Chromium** (2.75 and 9.37 µg/kg bw/day, respectively) fell far below the TDI established by the EFSA Panel on Contaminants in the Food Chain (EFSA a, 2014) of 300 µg/kg bw/day. This may indicate that samples that we collected were from households that experienced limited influence from recycling of chromium-containing e-waste. As mentioned in section 5.4.1, our control and e-waste related samples contained relatively similar concentrations of Cr or, in some cases, concentrations in controls exceeded those in e-waste related samples. It is important to note though, that Cr concentrations in soil have been reported previously to vary by an order of magnitude in Wenling (Tang et al., 2010), which could contribute to high variability in Cr levels in locally produced animal-based foods and, in turn, dietary Cr intake via consumption of those foods. At the same time, Cr intake from e-waste sites in our study was comparable to that reported for animal-based foods obtained from markets in Shanghai, one of the biggest industrial cities in Eastern China (Lei et al., 2013). We are not aware of other studies estimating Cr dietary from animal-based foods at e-waste recycling sites.

Adult daily dietary intakes of **Nickel** in our study (1.61 µg/kg bw/day) were below the corresponding TDI of 2.8 µg/kg bw/day (EFSA, 2015) while our estimated daily dietary Ni intake for children (5.41 µg/kg bw/day) was almost twice this value. Interestingly, both adult and child daily dietary intakes of Ni in this study exceeded significantly those reported for e-waste sites in South China (0.13 and 0.17 µg/kg bw/day, respectively) for animal based foods (Zheng et al., 2013), while intakes of cadmium were comparable in both cases. This may again highlight the influence of the type of the wastes processed at each site as well as the extent of the resulting environmental contamination.

Arsenic daily dietary intakes were quite high for both adults and children in our study (0.46 and 1.45 µg/kg bw/day, respectively) exceeding, for children, the U.S. EPA reference dose (RfD) of 0.3 µg/kg bw/day (U.S. EPA, 1997) by around 5 times.

Figure 5-7 Contributions to total dietary exposures for selected metals/metalloids from different types of food originating from Taizhou, China

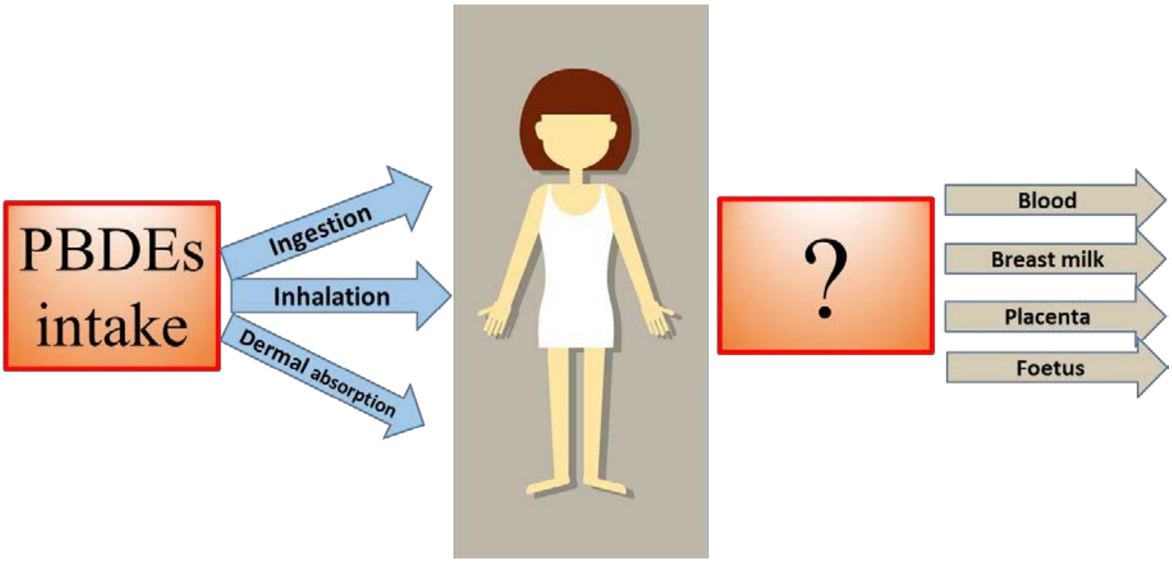


In 2009, EFSA Panel on Contaminants in the Food Chain has concluded that the provisional tolerable weekly intake (PTWI) of 15 µg/kg bw for As is no longer appropriate and introduced the $BMDL_{01}$ values for the relevant health endpoints, such as skin lesions, cancers of the skin, urinary bladder and lung, that ranged from 0.3 to 8 µg/kg bw/day (EFSA, 2009). Alarmingly, both adult and child As intakes in our study were within the proposed range.

The foodstuffs providing the principal contribution to the total dietary intakes, were different for individual metals/metalloids (Fig. 5-7). For cadmium and lead, the main dietary contribution was from chicken liver and duck liver, which together contributed between 62% (Pb) and 80% (Cd) of total intake. Duck eggs and shrimp have also contributed significantly (15% each) to the total dietary lead intake. The total contribution for mercury was dominated by fish (75%), and that for arsenic was dominated by shrimp (87%). Chicken eggs provided the major contribution for both chromium (47%) and nickel (47%), with pork also providing a significant contribution for both (20-21%).

Overall, dietary intakes of cadmium, mercury, nickel and arsenic via animal-based foods produced in our study area suggest that a number of health related issues may arise among the population consuming food contaminated by these metals/metalloids, with particular concerns existing for children.

CHAPTER 6 PHARMACOKINETIC MODELLING



6.1 Introduction and aim of the study

We have estimated that diet is the primary route of human exposure to PBDEs at e-waste recycling sites in Taizhou (see section 5.2.3), which may result in adverse human health impacts, particularly in children. To evaluate the accuracy of our PBDE dietary exposure estimation, we used a one-compartment pharmacokinetic (PK) model to predict the body burden of PBDEs in adults and children from Taizhou e-waste recycling areas based on their dietary PBDE intakes, and compared the data thus obtained with previously reported human body burdens in these locations.

Due to the high lipophilicity of PBDEs (de Wit, 2002), body lipids have been selected as the single compartment in our model of PBDE human body burdens. Estimation of PBDE body burden was conducted as previously reported (Lorber, 2008) using the following equation:

$$C_{BDE} = \frac{D_{BDE} \times ABS_{BDE}}{k_{BDE} \times BL} \quad (Equation\ 8)$$

Where:

C_{BDE} is the lipid-based concentration of the specific PBDE congener (ng/g lw),

D_{BDE} is the daily dietary intake of the specific congener (ng/day),

ABS_{BDE} is the absorption fraction,

BL is the body lipid mass (g),

and k_{BDE} is the congener-specific first order dissipation rate in the body (day^{-1}).

Table 6-1 Estimated PBDE daily dietary intakes (ng/day)

Congener	**Dietary daily intake, ng/day**			
	Adult, 20 – 26 years old		**Child, 5 – 11 years old**	
	median	**range**	**median**	**range**
BDE-47	890	94 - 4600	760	73 - 3800
BDE-66	10	0.56 - 170	8.7	0.51 - 140
BDE-100	110	10 - 590	96	7.9 - 480
BDE-99	390	81 - 2600	360	77 - 2400
BDE-85	3.2	0.89 - 74	2.8	0.8 - 72
BDE-154	280	41 - 940	250	36 - 770
BDE-153	790	57 - 5300	750	54 - 4300
BDE-138	74	0.96 - 220	71	0.84 - 190
BDE-183	790	38 - 14000	760	36 - 11000
BDE-197	260	9.5 - 5300	250	7.6 - 4600
BDE-207	380	17 - 3200	360	14 - 2700
BDE-209	3000	170 - 24000	2700	140 - 20000

The calculation of dietary intake was conducted separately for male and female adults and male and female children in this exercise to allow comparison of predicted PBDE body burdens between genders within the age group (see Table 6-1). We have also selected specific age cohorts for both adults (20 – 27 years old) and children (5 – 11 years old) in order to make more accurate comparison of predicted PBDEs body burdens with published measured values. Data on body weight and lipid content in adults were used from a recent study on Chinese males and females (Hung et al., 2016); while the corresponding data for children were taken from a study reporting body composition of Chinese boys and girls (Xiong et al., 2012). Hence, dietary intakes presented in Table 6-1 are slightly different than those calculated in section 5.2.3 where only body weight of a standard Chinese male and a standard Chinese 3-year-old boy were used for intakes estimation.

To provide an idea of the range of likely exposures, 5th, 50th, and 95th percentile PBDE concentrations in each food category (see section 5.2.1) were used to calculate the low, median and high end of dietary intake, respectively. Calculated values of dietary intakes obtained in such manner were used to predict corresponding body burden for each congener.

Half-lives of BDE-47, 99, 100, 153, and 154 of 1.8, 2.9, 1.6, 6.5, and 3.3 years, respectively, which were estimated previously from daily intake and human total body burden of these BDEs in non-occupationally exposed adult humans (Geyer et al., 2004), were used in our study for body burden prediction. We assigned the median value for the half-life of these five congeners (2.9 years) as half-life for BDE-66 and BDE-138 due to the lack of half-life data for these congeners. For the higher molecular weight congeners BDE-183, 207, and 209, we used half-lives of 0.26, 0.11, and 0.04 years, respectively, as reported in another study (Thuresson et al. 2006). Again, due to the lack of data on the human half-life of BDE-197, we assigned a value of 0.11 years (the median for BDE-183, 207, and 209) for this congener.

6.2 Prediction of PBDE body burdens using the PK model and comparison with PBDE concentrations in individuals residing at the e-waste recycling area in Taizhou

Table 6-2 presents our prediction of PBDE body burdens for adults and children, respectively. Estimated adult PBDE body burdens were, in general, lower than those calculated for children. Interestingly, while young adult females (20 – 26 years old) had noticeably lower estimated concentrations for most congeners than males of the same age, among 5-11-year-old children, no such gender-related differences were apparent. In general, previous studies have also reported little or no significant gender-related differences in PBDEs body burden (Harrad and Porter, 2007; Garí and Grimalt, 2013; Arbuckle, 2006).

BDE-153 and BDE-47 were the dominant congeners in our estimated body burdens accounting, on average for all age groups 56% and 20%, respectively, of the ∑PBDE followed by BDE-99 and BDE-154. Estimated body burdens of the higher brominated congeners BDE-197, BDE-207 and BDE-209 were, in general, lower.

Table 6-2 Predicted PBDE body burdens (ng/g lw) using PK model

Congener	Predicted PBDEs body burden, ng/g, lw							
	Adult				Child			
	median		range		median		range	
	male	female	male	female	boy	girl	boy	girl
BDE-47	40	33	4.2 - 200	3.5 - 170	60	62	5.8 - 300	5.9 - 300
BDE-66	0.5	0.43	0.03 -8.6	0.02 - 7.2	0.78	0.81	0.05 - 13	0.05 - 13
BDE-100	4.1	3.5	0.36 - 21	0.3 - 18	6.1	6.3	0.5 - 31	0.52 - 32
BDE-99	19	16	4.1 - 130	3.4 - 110	32	33	6.9 - 210	7.1 - 220
BDE-85	0.16	0.13	0.04 - 3.8	0.04 - 3.2	0.25	0.26	0.07 – 6.4	0.07 - 6.6
BDE-154	13	11	1.8 - 42	1.6 - 35	20	20	2.8 - 61	2.9 - 63
BDE-153	110	88	7.6 - 710	6.4 - 600	180	180	13 - 180	13 - 1000
BDE-138	3.7	3.1	0.05 - 11	0.04 - 9.5	6.4	6.6	0.08 - 17	0.08 - 18
BDE-183	3.8	3.2	0.19 - 66	0.16 - 56	6.6	6.8	0.31 - 98	0.32 - 100
BDE-197	0.51	0.43	0.02 - 10	0.02 - 8.6	0.86	0.88	0.03 - 15	0.03 - 16
BDE-207	0.73	0.61	0.03 - 6.1	0.03 - 5.2	1.2	1.26	0.05 -9.1	0.05 - 9.4
BDE-209	0.70	0.59	0.04 - 5.7	0.03 - 4.8	1.1	1.17	0.06 -8.6	0.06 - 8.9

To compare our estimates of PBDE human body burdens to those directly measured in humans, we identified several potential studies reporting PBDE concentrations in human body compartments. The main criteria for our selections were: the closest match to our study area - Luqiao and Wenling e-waste recycling sites in Taizhou, China; availability of the data reporting PBDEs concentrations on a lipid weight basis; and that the populations sampled were representative. On this basis, we selected two studies, which satisfied our criteria, to provide a point of detailed comparison to our predicted body burdens (see Table 6-3):

- Zhao et al.'s (2010) study that reported PBDE concentrations in the blood of adults from Luqiao (male 16, female 11) and Wenling (male 7, female 16); and
- Shen et al.'s (2010) study that reported PBDE concentration in the blood of children (21 boys and girls in total) from Luqiao analysed as 7 pooled samples.

Table 6-3 Comparison of predicted PBDE body burdens (ng/g lw, this study) with reported PBDE concentrations in blood of adults and children from Luqiao and Wenling e-waste sites, Taizhou, China. n/a – not analysed

Congener	**Adult**					**Child**		
	Our study*	**Luqiao** (Zhao et al. 2010)		**Wenling** (Zhao et al. 2010)		**Our study***	**Luqiao** (Shen et al. 2010)	
	median	range	median	range	median	median	range	median
BDE-47	36.5	1.22 – 51.2	3.64	2.88 – 222	25.3	60.6	0.66 – 5.51	4.60
BDE-100	3.80	0.08 – 4.98	0.66	0.64 – 21.2	3.12	6.23	0.16 – 4.42	2.86
BDE-99	17.9	0.44 – 17.8	1.06	1.14 – 23.0	5.74	32.3	0.54 – 17.1	13.8
BDE-154	11.5	0.14 – 6.12	0.78	0.54 – 12.6	1.70	19.8	0.23 – 5.37	1.39
BDE-153	96.7	2.38 – 68.5	10.5	8.40 – 119	21.9	179	2.10 – 8.04	3.43
BDE-138	3.43	n/a	n/a	n/a	n/a	6.45	0.12 – 12.1	0.60
BDE-183	3.52	1.00 – 11.6	3.44	2.60 – 22.8	6.72	6.66	0.83 – 2.40	1.45
BDE-209	0.65	17.2 – 378	64.5	84.5 – 556	172	1.16	n/a	n/a

* The median values presented here are average of median values calculated separately for males and females that presented in Table 6.2.

An additional study (Xu et al., 2014b) that reported data on PBDE body burdens of children from Luqiao included data that had already been reported in Shen's et al. (2010), including the average and range of PBDEs concentrations but not the median, which was available from the Xu et al. (2014) study. Hence, we have chosen to represent both studies as a single dataset in Table 6-3. We included in Table 6-3 only those congeners from our study that were also reported in the selected two studies. To match our estimations maximally to the data in the selected studies that reported PBDEs concentrations in blood for males and females combined, we calculated average of median values for males and females estimated in our study that presented in Table 6-2.

We also identified some other studies that met our criteria to some degree, for example, the study (Han et al., 2011) that reported PBDEs in samples of blood from 6-8-year-old children residing in Luqiao, as the sum of 15 congeners (di- to heptabrominated) at concentration of 664.28 ± 262.38 ng/g lw. However, no congener-specific concentrations were presented, which made it difficult to compare with our data. Other studies presented the levels of PBDEs in matched serum-adipose tissue samples from expectant mothers living at e-waste recycling sites in Wenling (Lv et al., 2015) and in the breast milk, placenta and hair of women residing in Luqiao (Leung et al., 2010). However, the latter study has limited number of samples (n=5), which probably was one of the factors resulting in high differences in PBDEs body burden within the dataset; for example, the sum of PBDE in breast milk measured in this study (36 congeners, from di- to heptabrominated) was in the range of 8.89 – 457 ng/g lw.

It is also important to mention that physiological processes of child-bearing or breastfeeding woman are more complex in comparison to a non-child-bearing or non-breastfeeding woman that may lead to a different pattern of body contaminants redistribution not only within their body compartments but also due to the transfer of contaminants to the child via placenta or milk (Chen et al., 2014; Leung et al., 2010). Moreover, differential PBDE partitioning into blood and milk in mothers of neonates has been reported and thus concentrations in the serum of such women may not accurately reflect body burdens (Schecter et al., 2010b; Inoue et al., 2006a; LaKind et al., 2009). The pattern of PBDEs in milk may also change markedly during the first month of lactation while it is not so prominent in maternal serum (Jakobsson et al., 2012). Therefore, the concentrations of some PBDEs in mothers' blood serum and milk are dependent on many factors including the time of sample collection, which may influence heavily both the levels of PBDEs and the their pattern in an investigated matrix. These factors may help to explain why some studies have good agreement between predicted and measured PBDEs body burdens, for example, in breast milk (Abdallah and Harrad, 2014) while in other cases there is less agreement (Lorber, 2008); this is discussed further in section 6.2.1.

6.2.1 Predicted PBDEs body burden *vs* measured PBDEs in adult blood

In general, median body burdens estimated in our study were for most individual congeners higher than those reported in previous biomonitoring studies of adults for both Luqiao and Wenling; although for all congeners other than BDE-209, estimated concentrations fell well within the range of those reported for the Wenling cohort. Most of the estimated median body burdens for other brominated congeners were within the range reported for the Luqiao cohort, with the exception of BDE-154 and BDE-153 for which our predicted median values exceeded observed maximum concentrations in adults. Our predicted median value for BDE-209 was markedly lower than reported values for both sites. In contrast, our forecast body burden for BDE-100 (3.80 ng/g lw) was similar to the median concentration measured for Wenling at 3.12 ng/g lw, with similar observations for BDE-183 (estimated 3.52 ng/g lw, compared to measured values for Luqiao at 3.44 ng/g lw). In general, therefore, the comparison of estimated body burden and biomonitoring data for all congeners supports our hypothesis that, other than for BDE-209, dietary intake is one of the most – if not *the* most - important source of human exposure to PBDEs in informal e-waste treatment areas.

It is important to mention that while blood has traditionally been used as a representative matrix to investigate human body burdens of a range of contaminants, there may still be some limitations in this approach, particularly as concentrations in blood lipid might not be a good predictor of concentrations in other compartments. It was reported in the recent study investigating PBDEs in matched samples of adipose tissue and serum from e-waste recycling areas in Wenling (Lv et al., 2015) that BDE-47, BDE-153 and BDE-209 were the dominant congeners in both adipose tissue and serum. Conversely, while the tri- to pentabrominated congeners (BDE-28, BDE-47, BDE-100 and BDE-99) and BDE-209 were more abundant in the serum than adipose tissue; the hexa- to octabrominated congeners (BDE-153, BDE-154 and BDE-183) were more prominent in adipose. The relatively long half-life of BDE-153 in the human body, coupled with its tendency to accumulate in adipose tissue rather than in blood, could explain why the body burdens estimated by our PK model exceeded measured values in human blood.

To assess the possible contribution of BDE-209 from sources additional to diet that may explain the high concentrations of this congener in human blood, we predicted the contribution of dust ingestion to estimated BDE-209 body burdens using similar approach for daily intake calculation as discussed in section 5.2.3. T here are a number of studies reporting that contaminated dust ingestion is one of the most significant pathways of human exposure to this congener (Muenhor et al., 2010; Al-Omran and Harrad, 2016; Zheng et al., 2015b; Kim et al., 2016; Wang et al., 2010; Lorber, 2008). We have also shown in section 5.2.3 that ingestion of dust around e-waste sites in Taizhou, in comparison to dietary exposure, may increase BDE-209 median exposure by over 40% for adults and by 95% for children.

However, even when additional exposure via dust ingestion was incorporated into our PK model, our predicted BDE-209 body burdens still fell short of those reported in adults (see

Table 6-4) despite relatively high adult daily PBDE intake via both diet and dust ingestion (median for combined diet and dust: 4242 ng/day, range 170 – 23760 ng/day).

Table 6-4 Predicted body burdens of BDE-209 for adults and children from Taizhou e-waste recycling sites based on the previously reported data of PBDE concentrations in dust (Ma et al., 2009) from e-waste recycling sites in Taizhou and combined (based on both dust and diet – this study - contributions). n/a – not analysed

Age group	**Gender**	**Dust daily intake, ng/day**		**Body burden, dust contribution, ng/g lw**		**Body burden, diet & dust, ng/g lw**	**PBDEs in blood, ng/g lw** (Zhao et al. 2010)
		median	**range**	**median**	**range**	**median**	**median**
Adult	male	1292	279 - 2305	0.31	0.07- 0.55	1.01	64.5 (Luqiao) 172 (Wenling)
	female			0.26	0.06 - 0.46	0.85	
Child	boy	2585	559 - 4611	1.09	0.24 - 1.94	2.23	n/a
	girl			1.13	0.24 - 2.01	2.30	

While the definitive reasons for such a discrepancy are unknown, we can speculate as to a number of possibilities for why our estimates of BDE-209 body burdens are low. First of all, due to the quite short half- life of this congener (15 days) (Thuresson et al. 2006) in comparison to the other, lower brominated congeners, that we used in our calculations. Specifically, a recent study on PBDE bioaccumulation in ducks in semi-field experiments conducted over one year at an e-waste recycling village in Taizhou (Liu et al., 2015), suggested that higher brominated congeners (e.g., BDE-153, BDE-183, and BDE-209) may have longer half-lives than lower brominated congeners (tri- to pentaBDEs), particularly in fatty tissues. The authors hypothesised that higher brominated PBDEs were more accumulative in fat tissue in relation to metabolism and excretion than in other tissues, which resulted in a subsequent increase in these BDEs concentrations in fat tissue.

There are, however, other published studies that have reported relatively close comparisons between measured and estimated BDE-209 body burdens. For example, a study utilizing a one-compartment pharmacokinetic model, the same approach as in our study, predicted BDE-209 body burden based on its intake by adults in the UK via inhalation, diet and dust ingestion (Abdallah and Harrad, 2014), which were quite closely comparable to those observed in human breast milk (estimated median of 0.27 ng/g *vs* observed in milk at 0.24 ng/g lw). In contrast, predicted BDE-209 body burden among general population of the USA (Lorber, 2008) based on several routes of exposure (water, soil, indoor dust, indoor and outdoor air, and diet) was about one order of magnitude lower than those measured in human blood and milk (predicted: 0.1 ng/g lw; measured: 1.4 and 0.8 ng/g lw for blood and milk, respectively). However, the differences between predicted and observed BDE-209 body burden in Lorber's (2008) study were still less prominent than in our study. This may indicates that other factors should be taken into account for more accurate prediction of human BDE-209 body burden at e-waste recycling sites. It has been shown, for example, that the transfer of PBDEs from other tissues to fat may with time lead to an increase of PBDE concentrations in lipids in ducks grown at Taizhou recycling sites (Liu et al., 2015). Hence, it might be possible that the levels of BDE-209 in fat are increasing over time through redistribution within the body parts, and not purely due to BDE-209 intake.

Moreover, the discrepancies between PBDEs body burden estimates based on intakes and PBDEs biomonitoring data have already been recognised (Wong et al. 2013). The main reasons are reported to be: underestimation of PBDE half-lives, underestimation of intakes, or a combination of both. Wong et al. (2013) also proposed a scenario for half-life estimation based on a model fitted to biomonitoring data only, which yields half-lives for BDE-47, BDE-99, BDE-100, and BDE-153 of 0.37, 8.2, 2.0, and 3.5 years, respectively. If we were to use these in our study for PBDEs body burden prediction (based only on a dietary intake), the median values for BDE-47, BDE-99, BDE-100, and BDE-153 would be 7.50, 4.75, 50.6, and 51.9 ng/g lw, respectively. In this case, our estimation would fit more closely within the range of measured concentrations in blood for BDE-47 and BDE-153, but will exceed maximum values reported for BDE-99 and BDE-100. Similarly, use of other proposed values for half-lives of BDE-47, BDE-100, BDE-99, BDE-154, and BDE-153 estimated on the basis of measured half-lives in rats (Geyer et al., 2004); would yield predicted body burden for these congeners even higher than those presented in Table 6-3. More investigation is needed to clarify values for half-lives of PBDEs in humans to maintain consistency between different studies, which would help to produce comparable results.

Due to the fact that the residents of e-waste recycling sites are exposed to PBDEs daily for a prolonged time through a variety of pathways, the concentration of PBDEs in a human at a particular time (e.g. at the time of blood sampling) may depend on a number of parameters. Those include the extent of the background contamination, duration of exposure, participation of the person in e-waste recycling handling, the type of e-waste that the person is exposed to, individual differences in the rate of metabolic processes, differences in dietary preferences, among the others. As these parameters are dynamic processes, we suggest that if the elimination rate of a particular PBDE from the body is lower than the rate of input (i.e., daily ‘chronic exposure’), a higher PBDE body burdens may be expected despite relatively low half- lives in human for some BDE congeners. As a result, it might be that actual concentrations of some PBDEs in humans are higher than those we can predict utilising simple pharmacokinetic models. It might be interesting to investigate this in future studies utilizing more complex pharmacokinetic models.

It is possible that some of the inconsistency between our estimation of BDE-209 body burden and measured BDE-209 bodily concentrations occurs due to application of a steady state PK model, whereas in practice, within the complex dynamic scenario of e-waste recycling, steady state assumptions may not properly represent actual patterns of exposure. Furthermore, it might then be the case that lower brominated congeners that have longer half-lives are influenced less by the application of a steady state PK model than those with shorter half-lives (e.g., BDE-209). However, this hypothesis needs to be investigated further.

Additionally, PBDEs metabolic debromination processes may simultaneously increase concentrations of lower PBDEs while decreasing those of higher brominated congeners in living organisms. This was shown, for example, in carp where higher brominated congeners may debrominate as follows: BDE-99 to BDE-47, BDE-183 to BDE-154, and BDE-209 to BDE-197 (Stapleton et al., 2004b, 2006; Benedict et al., 2007; Zeng et al., 2012). Similarly, a study of debromination of eleven PBDEs (tri- to deca-BDE) in three different fish species (carp, salmon and trout) concluded that metabolic debromination of PBDEs is species-specific and may lead to a different scenario of preferential metabolic PBDEs accumulation: while carp are most likely to accumulate BDE-47 and BDE-154, in trout and salmon, BDE-99 and BDE-154 will be preferentially accumulated (Roberts et al., 2011). We hypothesise that genetically driven differences in the PBDE metabolic pathways and accumulation may also exist between human populations.

6.2.2 Predicted PBDE body burdens *vs* measured PBDE concentrations in children's blood

The comparison of our estimated PBDE body burdens in children with those measured in children's blood from Luqiao (Shen et al., 2010a) is presented in Table 6-3. BDE-209 was not reported in the latter study, hence no comparison was possible with our estimations for this congener. Median predicted body burdens of all BDE congeners exceeded those reported in children's blood, particularly so for BDE-153 (179 ng/g *vs* 3.43 ng/g), BDE-47 (60.6 ng/g *vs* 4.60 ng/g), BDE-154 (19.8 ng/g *vs* 1.39 ng/g), and BDE-99 (32.3 ng/g *vs* 3.43 ng/g). Moreover, our predicted median concentrations were above the maximum reported in children's blood for all congeners.

It is difficult to pinpoint why a greater discrepancy occurred between predicted and observed body burdens for children compared to adults. One possibility is that the children studied by Shen (2010) were not representative of the e-waste-impacted notional population forecast by our PK model. As mentioned in section 6.2, another study of PBDEs in children's blood from Luqiao (Han et al., 2011) reported the ∑PBDE concentrations to be 664.28 ± 262.38 ng/g lw (15 congeners, from BDE-8 through to BDE-183), which is over 20 times higher than that reported by Shen (2010) at 32 ± 18 ng/g lw for the same range of BDE congeners. Unfortunately, Han et al. (2011) did not provide congener-specific BDE concentrations, but we note that our median estimated ∑PBDE body burden of 312 ng/g lw matches much more closely to the value reported by Han et al (2011).

Alternatively, we can hypothesise that PBDE absorption, accumulation, metabolic and elimination processes in children may differ from those in adults in a fashion similar to that shown (Fernandez et al., 2011) for the pharmacokinetics of pharmaceuticals. Fernandez at al's. (2011) study highlighted that anatomical, physiological and biochemical changes that occur from birth affect pharmacokinetics/pharmacodynamics and hence the bioavailability of drugs. Therefore, we do not know, for example, if it is justified to assume that half-lives of PBDEs estimated for adults are correct for infants and children as well. Further studies are needed to clarify this.

Overall, this exercise has supported our hypotheses that the dietary intake is the primary contributor to PBDEs body burden for all our target BDEs with the exception of BDE-209 in the case of adults. More comprehensive pharmacokinetic modelling is needed to support better prediction of BDE-209 body burden. The importance of dust ingestions as the second pathway is also clear. In the same time, our exercise raises a number of questions that are important to answers in order to have more detailed and deeper understanding of all the processes of distribution, accumulation and elimination of PBDEs once they enter the human body:

- Is there a difference in the metabolic processes in adults and children that may lead to different half-lives of PBDEs in children than that in adults?
- Is there a difference in the metabolic processes in child-bearing or lactating woman in comparison to non-child-bearing or non-lactating woman that may lead to different PBDEs distribution in body parts and effect accumulation processes?
- Are there genetically driven differences in human populations that may affect the processes of PBDEs metabolism, accumulation and elimination?
- Would half-lives of PBDE congeners, and BDE-209 in particular, estimated for high end chronic human exposure (i.e., at uncontrolled e-waste recycling sites) be different than that estimated previously for non-occupationally exposed adult humans?

Finally, we stress that informal e-waste recycling is a serious and on-going threat to human health in the Taizhou area. The introduction of proper industrial hygiene practices may reduce the risks to workers as shown in a study of workers in an electronics dismantling plant in Sweden (Thuresson et al., 2006a). In that study, the introduction of measures to improve industrial hygiene reduced workers' exposure to BDE-183 and BDE-209 notwithstanding an increase in the quantity of BFR-containing recycled goods between 1997 and 2000. As a result, concentrations of BDE-209 in the workers' serum were similar to those observed in the general population, although concentrations of hexa- to nona-BDEs in the same samples remained elevated above those in non-occupationally exposed adults.

CHAPTER 7 SUMMARY AND CONCLUSIONS

The current study aims to bring more attention to the environmental contamination resulting from improper e-waste handling in China with the main focus on human dietary exposure of both adults and children to selected key contaminants through a consumption of locally grown animals, domestic fowl and fish from local watercourses. The main findings and outcomes of this study are summarised below.

7.1 Main findings and outcomes

1. The main operations of rudimentary e-waste recycling that resulted in the highest environmental contamination by PBDEs within informal e-waste recycling sites in Guiyu, China, were identified as e-waste open burning and circuit boards shredding. The concentrations of PBDEs in soils and sediments from e-waste open burning sites, with the maximum of 390000 ng/g dw, were among the highest reported to date. The decrease in PBDE concentrations in soil observed with increasing distance from workshops confirmed the hypothesis that improper e-waste handling is a significant source of PBDEs to the environment. Principal components analysis indicated a complex PBDE congener distribution, suggesting contamination of soils by two or more commercial formulations of different PBDE bromination levels that reflected the diverse range of e-wastes processed.
2. Eggs of domestic ducks reared within e-waste recycling areas in Taizhou, China, have been shown to be important pathway of human exposure to PBDEs that was not considered hitherto. Duck egg samples from 5 e-waste recycling sites (n=11 from each site) contained average ∑PBDE concentrations from 7 to over 200 times higher than the corresponding samples (n=11) from the control site (an eco-farm in Sanmen located 90 km away from e-waste sites). A maximum average ∑PBDE concentration of

1778 ng/g lipid weight (lw) was similar to the highest mean values reported in previous studies for chicken eggs from Taizhou e-waste recycling areas. Estimated average daily ∑PBDE intake via duck egg consumption alone at the e-waste recycling sites in Taizhou ranged from 159 ng/day to 5124 ng/day compared to only 27 ng/day at the control site. While exposure estimates for both adults and children fall below the U.S. EPA RfDs for PBDEs, the estimates of typical exposure for both adults and children to BDE-99 (average: 2.72 and 12.3 ng/kg bw/day, respectively) exceeded substantially the no adverse effect level (NAEL) for impaired spermatogenesis of 0.23 – 0.30 ng/kg bw/day proposed by Netherlands researchers. Moreover, estimated exposure to BDE-99 for a typical 3–year-old male child from one of the sites (30.4 ng/kg bw/day) falls within the range of the NAEL for impaired neurodevelopmental toxicity (18.8 – 41.4 ng/kg bw/day).

3. The hypothesis that food is the major pathway of human exposure to PBDEs at e-waste recycling sites in Taizhou was further supported. Following the findings that consumption of duck eggs from e-waste impacted areas around Taizhou is an important overlooked pathway of human exposure to PBDEs, a more comprehensive estimation of dietary exposure to PBDEs through foodstuffs produced locally was conducted. Over 120 samples (including controls) comprising of 10 types of staple food were analysed for the presence of PBDEs. Average ∑PBDE concentrations in chicken meat, eggs, and liver (1160, 656, and 459 ng/g lw, respectively) and duck eggs, liver and meat (982, 256 and 150 ng/g lw, respectively) were among the highest reported globally to date. The main contributors to estimated dietary PBDE intake were duck eggs (median for adults and children: 61.6 and 265 ng/kg bw/day, respectively), followed by chicken eggs (median for adults and children: 17.3 and 74.5 ng/kg bw/day, respectively) and fish (median for adults and children: 12.6 and 43.3 ng/kg bw/day, respectively).

Inclusion of previously published estimates for ingestion of contaminated dust increased ∑PBDE daily intakes from diet by approximately 19% for adults and 42% for children. High-end estimates of exposure for young children to BDE-47 (261 ng/kg bw/day) and to BDE-99 (162 ng/kg bw/day) exceeded corresponding U.S. EPA RfDs by approximately 2.5 and 1.5 times, respectively. Estimates for median exposure to BDE-99 for adults (6.1 ng/kg bw/day) and children (24.21 ng/kg bw/day) exceeded by around 20 and 80 times, respectively, the NAEL for impaired spermatogenesis proposed by Netherlands researchers. For children, median exposure estimates to BDE-99 were also close to the NAEL for impaired neurodevelopmental toxicity, whereas the high end exposure estimates exceeded both NAELs.

4. Given the limited number of samples, it was not possible to fully test the hypothesis that foods exported from China to the UK for sale may contribute to transboundary transfer of PBDEs. The limited evidence gathered here suggests that any such transboundary transfer is likely not substantial.
5. Food produced at e-waste recycling sites in Taizhou from locally grown animals and locally caught fish and shrimp has been also shown to be an important route of human exposure to legacy contaminants (e.g., PCBs and HBCDs) and newly introduced chemicals such as novel brominated flame retardants (NBFRs).
6. PCBs were particularly conspicuous contaminants in food samples from e-waste sites in Taizhou, which possibly relates to a long history of PCB-containing transformers being recycled in the area. Fish was the foodstuff considered here that was most contaminated by PCBs, at a mean concentration of 75400 ng/g lw (or 1168 ng/g ww), followed by duck eggs (from site 5: 2857 ng/g lw and 846 ng/g ww), duck muscle (1322 ng/g lw and 276 ng/g ww) and chicken eggs (1179 ng/g lw and 312 ng/g ww). The PCB homologue pattern in avian-related samples was dominated by hexa-PCBs, followed

closely by penta-PCBs, while tetra- and penta-PCBs were more prominent in aquatic species. Such patterns of PCB contamination may reflect releases from PCB-containing transformers and/or capacitors, as well as unintentional formation of some PCBs from other chlorinated chemical precursors during poorly-controlled combustion processes and species-specific variation in metabolism of PCBs. Concentrations of PCBs in several foods in the current study exceeded a number of legislative limits:

- the sum of seven indicator PCBs (PCB-28, 52, 101, 118, 138, 153 and 180) in fish (534 ng/g ww) exceeded the Chinese maximum residue limit of 500 ng/g ww for aquatic organisms and aquatic products;
- all e-waste impacted samples of avian origin (with the exception of chicken liver) exceeded the maximum level of 200 ng/g lw set by the European Commission for the sum of seven indicator PCBs in products including eggs and poultry;
- the sum of six marker non dioxin-like (NDL)-PCBs (PCB-28, 52, 101, 138, 153 and 180) exceeded limits set up by EU Regulation for these congeners in food by at least an order of magnitude for foodstuffs of avian origin and 3.5 times in the case of fish;
- based on the contribution of only four dioxin-like PCBs measured in the current study (PCB-105, 118, 156, and 167), the corresponding EU MLs were exceeded for all foodstuffs studied except for livers and shrimp.

Children may receive especially high daily PCBs intakes via foods, in addition to other possible sources, and may therefore be at particularly high risk. Notably, children's estimated dietary exposure to only four DL-PCBs, at 10.22 pg TEQ/kg bw/day, exceeded the WHO limit of 1-4 pg TEQ/kg bw/day; fish and eggs were the main contributors to estimated dietary exposure to DL-PCBs. DL-PCBs-TEQ monthly intakes in our study (84.9 and 307 pg TEQ/kg bw/month for adults and children, respectively) exceeded the provisional tolerable monthly intake (PTMI) of 70 pg TEQ/kg bw, which was established by Joint FAO / WHO Expert Committee on Food Additives.

7. This study has shown that NBFRs have already entered the food chain at e-waste recycling sites in Taizhou. E-waste recycling operations in Taizhou appear to be a significant source of NBFR contamination of locally produced foods, especially by EH-TBB, BEH-TEBP, BTBPE & DBDPE; the patterns of contamination varied with the food type. Concentrations of NBFRs in e-waste impacted food samples generally exceeded concentrations in the corresponding controls by substantial margins (up to one order of magnitude for PBEB and DBDPE in shrimp), indicating a discernible influence of e-waste treatment on levels of these contaminants in locally produced foods. Among NBFRs considered in this study, EH-TBB gave rise to the highest estimated exposures for both adults and children (8.03 and 18.9 ng/kg bw/day respectively), followed by BEH-TBP (2.6 and 6 ng/kg bw/day respectively), which mostly arose through the consumption of pork. Consumption of pork was also the principal contributor to dietary exposure to BTBPE (44 % and 23% for adults and children, respectively), while duck meat and liver combined contributed greatly (over 50%) to PBEB exposure. Fish was the main contributor to HBB exposure for children (44%) while fish and pork accounted for 36% of adults' exposure. No health risk assessment could be made in connection with most of the NBFRs in the current study due to the absence of health-based limit values (HBLV) with legislative standing for them - with the exception of that for HBB, for which the exposure estimates in the current study (0.14 and 0.36 ng/kg bw/day for adults and children, respectively) are well below the U.S. EPA RfD of 2000 ng/kg bw/day. This study reported estimated human dietary exposures to compound-specific NBFRs in Taizhou for the first time.

8. For HBCDs, the link to e-waste as a contributory source to contamination levels in locally produced foods was less clear, especially for avian samples. These results suggest a diversity of sources for this compound group in investigated areas, including non-e-waste related sources (for example, old textiles). The highest ∑HBCD concentrations recorded in the current study were detected in fish from e-waste sites (313 ng/g lw), at levels about two orders of magnitude higher than in fish collected from the control site. E-waste impacted duck eggs contained lower HBCDs concentrations than chicken eggs; however, both were higher than corresponding controls. This is the first report on HBCDs concentrations in domestic duck eggs. For both adults and children, major contributors to estimated HBCDs exposure were chicken meat and eggs (over 50% combined), followed by fish. Again, as for NBFRs, there are no HBLVs of legislative standing for HBCDs to compare with the estimations made in the current study.
9. Consumption of locally produced foods has also resulted in human exposure to toxic metals/metalloids. Estimated dietary intakes of cadmium, mercury, nickel, arsenic and lead via animal-based foods produced in the studied area are high enough to give rise to health-related concerns for populations consuming these foods, with particular concerns existing for children. The categories of foods that were most prominent in contamination by metals/metalloids in the current study are as follows:
   - avian liver samples, which contained Cd (duck liver: 2.19 mg/kg; chicken liver: 1.32 mg/kg) and Pb (duck liver: 1.27 mg/kg; chicken liver: 1.32 mg/kg) in concentrations that exceeded substantially the maximum contaminant limit (MCLs) of 0.5 mg/kg for these metals in food set up by both Chinese and EU regulations;

- chicken meat and pork that contained Cr at concentrations of 1.09 mg/kg and 1.18 mg/kg, respectively that exceeded the MCL for food in China (1 mg/kg).

In terms of dietary intakes, the estimates for both adult and child weekly dietary intake of Cd at 2.67 and 10.3 μg/kg bw/week, respectively, exceeded the TWI of 2.5 μg/kg bw/week established by the EFSA Panel on Contaminants in the Food Chain. Estimated children's monthly intake of Cd at 44.7 μg/kg bw/month also exceeded TMI of 25 μg/kg bw/month established by the Joint FAO/WHO Expert Committee on Food Additives. Estimated children's daily dietary Hg intake (0.14 μg/kg bw/week) exceeded the U.S. EPA RfD of 0.1 μg/kg bw/day. Arsenic estimated daily dietary intakes were quite high for both adults and children in the current study (0.46 and 1.45 μg/kg bw/day, respectively) exceeding, for children, the U.S. EPA RfD of 0.3 μg/kg bw/day by around 5 times. In addition, both adult and child estimated arsenic intakes in the current study (0.46 and 1.45 μg/kg bw/day, respectively) were within the proposed range of $BMDL_{01}$ values for the relevant health endpoints (0.3 to 8 μg/kg bw/day), such as skin lesions, cancers of the skin, bladder and lung. Estimated dietary intakes for Pb, Cr, and Ni were below corresponding limits established in the EU and China.

10. The comparison of predicted PBDEs body burdens, estimated using a one-compartment PK model, with reported measured PBDEs concentrations in adults blood supported the hypothesis that, other than for BDE-209, dietary intake is one of the most important sources of human exposure to PBDEs in informal e-waste recycling areas, if not the most important. The PK model was used to predict the body burden of PBDEs in adults and children from two villages in Taizhou (Wenling and Luqiao) e-waste recycling areas, based on their dietary PBDE intakes. PBDEs intake via ingestion of contaminated dust has also been estimated from previously reported data and considered in the current study. However, predicted values of BDE-154 and BDE-153 for the Luqiao cohort

exceeded observed maximum concentrations in adults, while the predicted median value for BDE-209 was markedly lower than reported values for both cohorts. In contrast, median predicted body burdens of all BDE congeners exceeded those reported in children's blood and were also higher than the corresponding maximums. Several possible reasons for such a discrepancy are discussed in Chapter 6, including the following:

- scatter in the published estimates of PBDEs half-lives;
- absence of estimation data on PBDEs half-lives for children;
- lack of PBDEs monitoring data in cohorts with representative e-waste-impacted notional population;
- limitations of steady state modelling applied to dynamic processes taking place at e-waste recycling areas that mayresult in misrepresentation of actual patterns of exposure to some congeners; more complex PK modelling would be beneficial in this case;
- absence of data on differences in preferential metabolic PBDEs pathways and accumulation between human populations.

11. In advance of addressing the wider problems associated with improper e-waste recycling, it would be valuable to have greater emphasis on simple measures that local people can take in order to reduce exposure of the animals and, therefore, themselves to these harmful contaminants (e.g., better segregation of livestock from areas impacted by e-waste recycling; pay more attention to material that used for housing of livestock, and improve occupational hygiene).

7.2 Developments

1. A method was developed and validated for GC/MS analysis of PBDEs in a variety of matrices (soil, dust, sediment, and 10 types of animal-derived foodstuffs). This method

allowed the achievement of satisfactory extraction of 14 PBDE congeners using environmentally friendly (non-halogenated) extraction solvent n-Pentane, utilizing the Accelerated Solid Extraction (ASE) technique with in-cell sulphuric acid impregnated Silica clean-up of biological matrices. Optimised parameters for GC/MS analysis permitted simultaneous determination of tri- to deca-BDEs in a single column using ENCI method with methane that resulted in good separation of all target BDEs with minimal degradation of BDE-209 during the GC/MS run. This set of selected 14 PBDEs was quantified in all samples considered in the current study.

2. The program "EasyBDE" was designed to conduct calculations automatically for PBDEs quantification in this study. This program handles calibration data, utilizing appropriate relative response factors, including calibration verification, performs calculation of PBDEs concentrations in the samples, and calculation of extraction efficiency for internal standards. A short summary report is produced as well in Excel format. This automation dramatically decreased time for calculations and minimised human error in data handling. A short description of the EasyBDE program is provided in the Appendix 1.

7.3 Further research perspectives

A number of gaps in research have been identified during the current study that would be important to address in order to better understand the whole complex of toxic chemicals behaviour in the environment and in biological systems, including humans. Prospective further research directions are summarised below.

1. Investigate low dose exposures (e.g., non-occupational) and high dose exposures (e.g., within e-waste recycling sites) to BFRs and other POPs in the multiple pollutants

exposure scenario, taking into account long-term or chronic exposures, considering all possible pathways of human exposure and studying representative population cohort.

2. Investigate human health effects resulted from simultaneous multi-pollutants exposures.
3. Identify and map hotspots of environmental pollution caused by improper e-waste handling (e-waste hotspots) in order to prevent entry of toxic pollutants to the food chain.
4. For PBDEs analysis, the inclusion of BDE-209 is important during investigation of PBDEs in environments impacted by e-waste recycling and in human body compartments due to widespread of this congener in such areas.
5. Standardised reporting of findings (e.g., use of common units and normalisation) is essential to allow comparison between studies and with health-based exposure limits.
6. Estimate half-lives of PBDEs in different age cohorts (e.g., infants, children, and adults) and in different exposure scenario (e.g., low and high exposure).
7. Estimate and compare half-lives of PBDEs in genetically different populations.
8. Predict PBDEs body burden using multicomponent PK models and evaluate the results in comparison with PBDEs body burden predictions using simple one-compartment PK model.
9. Investigate further the hypothesis that transboundary transfer of POPs can occur via exported foodstuffs.

10. Investigate if pH of different human body matrices (e.g., milk, plasma) plays a significant role in preferential accumulation of BDE congeners with different level of bromination.

Appendices

Appendix 1 Description of EasyBDE program

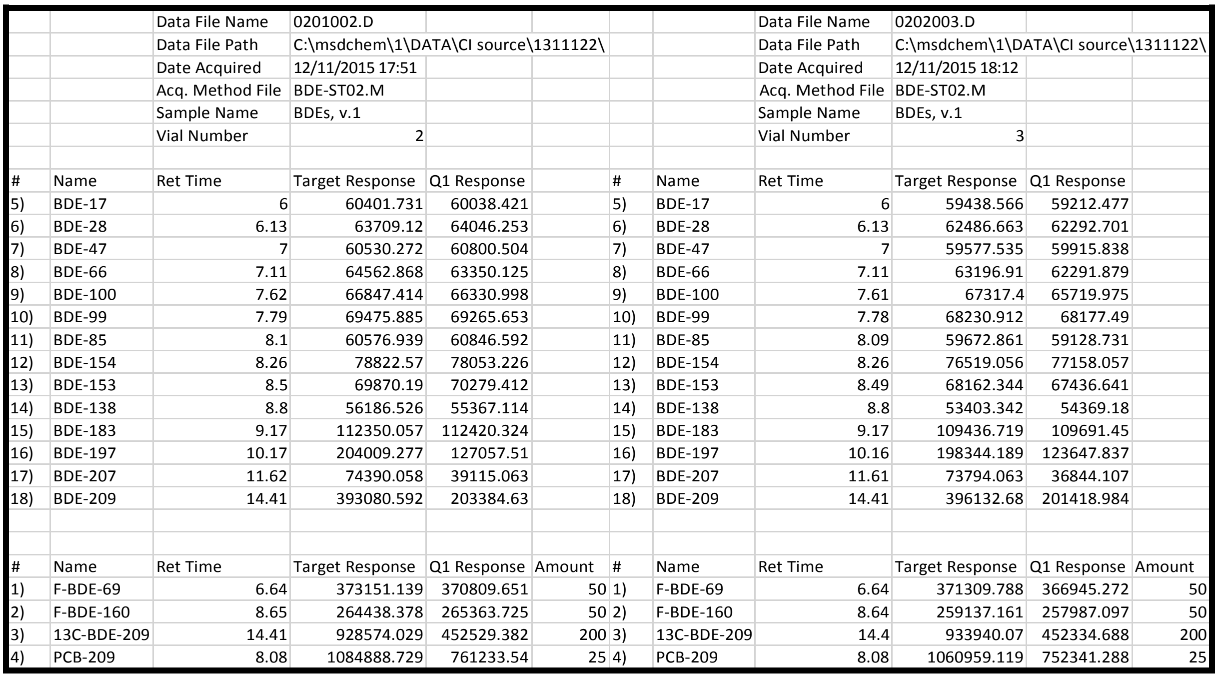
EasyBDE is an Excel automation application developed with Visual Basic 6 programming language. Algorithms used in this application allows quickly and efficiently perform calculations of the following:

- relative response factors (RRFs) based on initial 6-point calibration data;
- the on-going accuracy check;
- concentrations of analytes in the sample;
- IS recoveries.

Preparation of calibration data file

6-point calibration (in duplicates) to be analysed for 14 target BDEs in SIM method and results of the analyses to be organised through a custom report application of the Agilent ChemStation software as shown in Fig.1 for the initial calibration concentration (BDEs, v.1). Repeat to enter data for remaining 5 calibration standards (in duplicates).

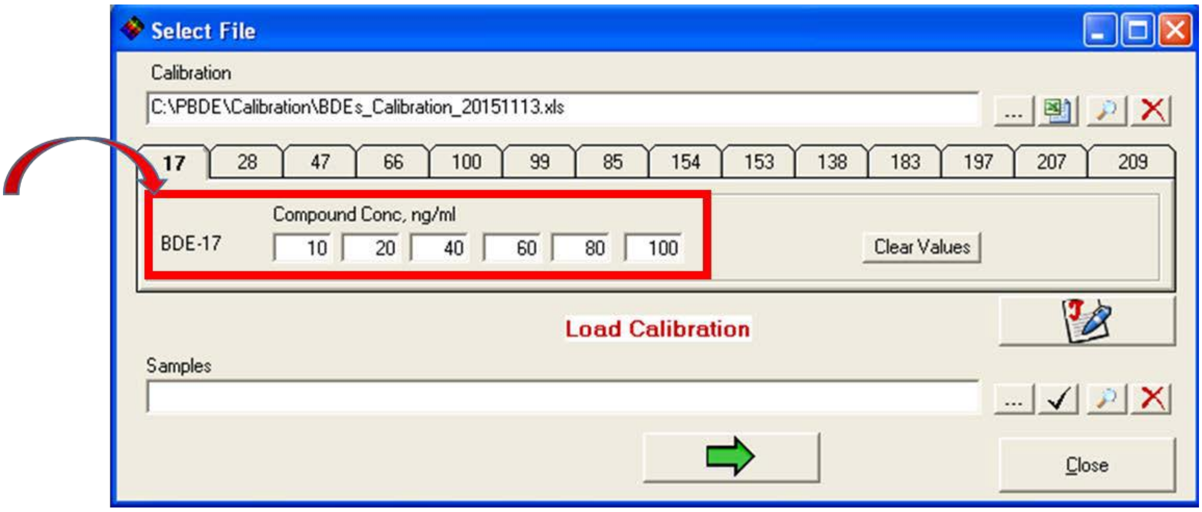
Figure 1. Example of custom reporting for 6-point PBDEs calibration



		Data File Name	0201002.D					Data File Name	0202003.D		
		Data File Path	C:\msdchem\1\DATA\CI source\1311122\					Data File Path	C:\msdchem\1\DATA\CI source\1311122\		
		Date Acquired	12/11/2015 17:51					Date Acquired	12/11/2015 18:12		
		Acq. Method File	BDE-ST02.M					Acq. Method File	BDE-ST02.M		
		Sample Name	BDEs, v.1					Sample Name	BDEs, v.1		
		Vial Number	2					Vial Number	3		
#	Name	Ret Time	Target Response	Q1 Response		#	Name	Ret Time	Target Response	Q1 Response	
5)	BDE-17	6	60401.731	60038.421		5)	BDE-17	6	59438.566	59212.477	
6)	BDE-28	6.13	63709.12	64046.253		6)	BDE-28	6.13	62486.663	62292.701	
7)	BDE-47	7	60530.272	60800.504		7)	BDE-47	7	59577.535	59915.838	
8)	BDE-66	7.11	64562.868	63350.125		8)	BDE-66	7.11	63196.91	62291.879	
9)	BDE-100	7.62	66847.414	66330.998		9)	BDE-100	7.61	67317.4	65719.975	
10)	BDE-99	7.79	69475.885	69265.653		10)	BDE-99	7.78	68230.912	68177.49	
11)	BDE-85	8.1	60576.939	60846.592		11)	BDE-85	8.09	59672.861	59128.731	
12)	BDE-154	8.26	78822.57	78053.226		12)	BDE-154	8.26	76519.056	77158.057	
13)	BDE-153	8.5	69870.19	70279.412		13)	BDE-153	8.49	68162.344	67436.641	
14)	BDE-138	8.8	56186.526	55367.114		14)	BDE-138	8.8	53403.342	54369.18	
15)	BDE-183	9.17	112350.057	112420.324		15)	BDE-183	9.17	109436.719	109691.45	
16)	BDE-197	10.17	204009.277	127057.51		16)	BDE-197	10.16	198344.189	123647.837	
17)	BDE-207	11.62	74390.058	39115.063		17)	BDE-207	11.61	73794.063	36844.107	
18)	BDE-209	14.41	393080.592	203384.63		18)	BDE-209	14.41	396132.68	201418.984	
#	Name	Ret Time	Target Response	Q1 Response	Amount	#	Name	Ret Time	Target Response	Q1 Response	Amount
1)	F-BDE-69	6.64	373151.139	370809.651	50	1)	F-BDE-69	6.64	371309.788	366945.272	50
2)	F-BDE-160	8.65	264438.378	265363.725	50	2)	F-BDE-160	8.64	259137.161	257987.097	50
3)	13C-BDE-209	14.41	928574.029	452529.382	200	3)	13C-BDE-209	14.4	933940.07	452334.688	200
4)	PCB-209	8.08	1084888.729	761233.54	25	4)	PCB-209	8.08	1060959.119	752341.288	25

To create calibration file, open EasyBDE program and load file with custom report obtained for 6-point calibration. Click on tab BDE-17 and enter concentrations used for calibration points – see Fig. 2. Repeat for the rest of BDEs by clicking on the each corresponding BDE tab and entering values for calibration points.

Figure 2. Example of concentration input for 6-point calibration



Calibration: C:\PBDE\Calibration\BDEs_Calibration_20151113.xls

BDE-17 Compound Conc, ng/ml: 10 20 40 60 80 100

After concentration points have been entered for all congeners, click “Process Calibration” button to create calibration file. Calibration than be loaded and ready to use for samples quantification. The calibration file name will be created and saved automatically. Calibration can be loaded and used for further data quantification as necessary.

Preparation of samples analysis data file

Prepare and analyse a sequence that consists of:

- middle range calibration PBDEs standard – to be analysed at the beginning and at the end of the sequence;
- laboratory and procedural blanks;
- samples for PBDEs quantification;
- and appropriate SRM, if required.

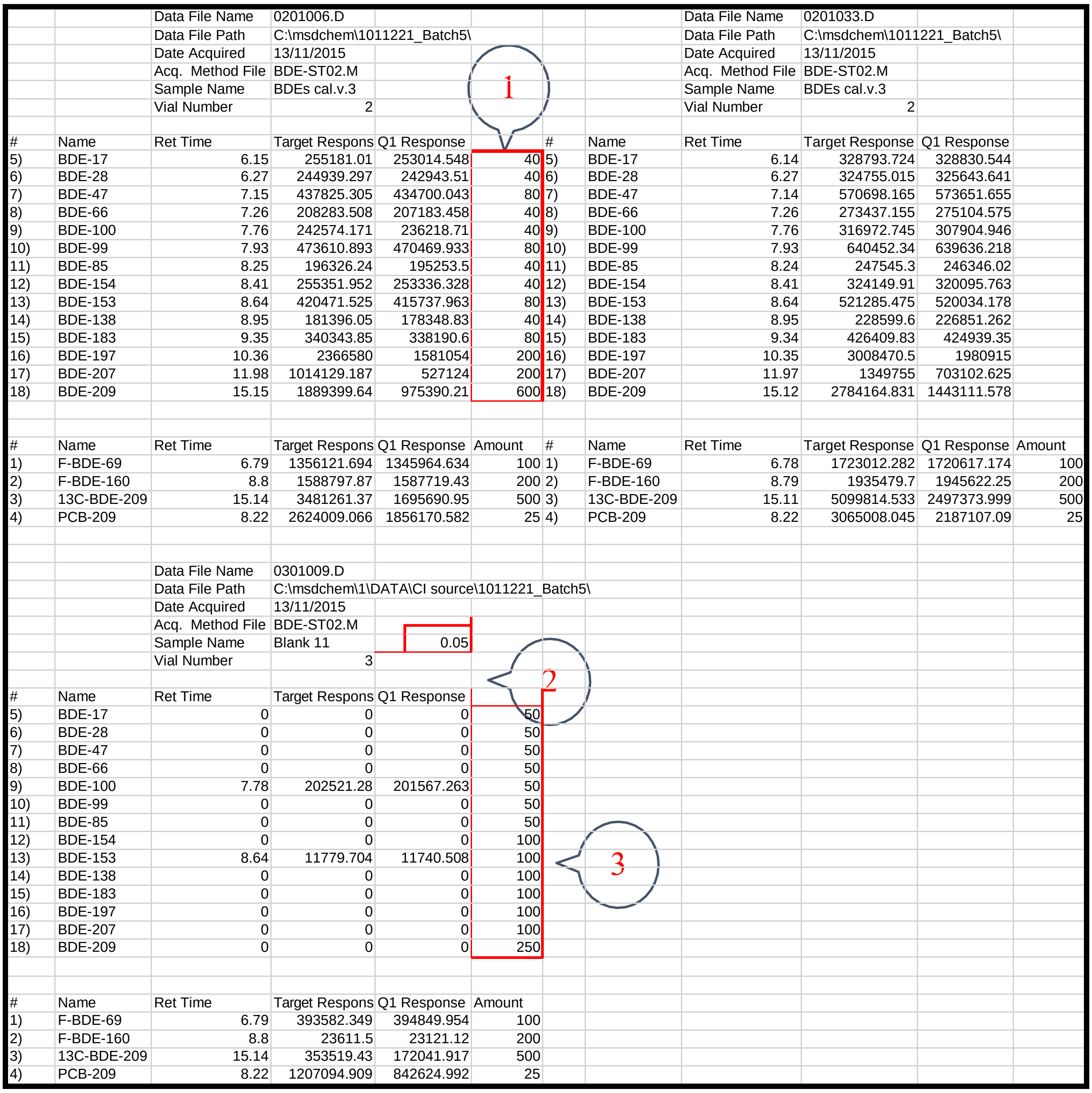
Organise analysis data using Agilent ChemStation custom report application as shown in Fig. 3 starting data of middle range calibration PBDEs standard followed by all required samples data analysis. Enter the following data at appropriate places as shown on Fig. 3:

1. Concentration of each native BDE in PBDEs standard analysed at the beginning and at the end of the sequence.
2. Sample weight, in g.
3. Concentration of appropriate IS used for each BDE quantification.

Performing PBDEs quantification in samples

Make sure that appropriate calibration file is loaded (file name appears on the top line of the window). Load samples analysis data file – file name should appear on the second line. Click green arrow button to process data quantification (see Fig. 4).

Figure 3. Example of custom reporting for samples quantification



Data File Name	0201006.D
Data File Path	C:\msdchem\1011221_Batch5\
Date Acquired	13/11/2015
Acq. Method File	BDE-ST02.M
Sample Name	BDEs cal.v.3
Vial Number	2

#	Name	Ret Time	Target Respons	Q1 Response	
5)	BDE-17	6.15	255181.01	253014.548	40
6)	BDE-28	6.27	244939.297	242943.51	40
7)	BDE-47	7.15	437825.305	434700.043	80
8)	BDE-66	7.26	208283.508	207183.458	40
9)	BDE-100	7.76	242574.171	236218.71	40
10)	BDE-99	7.93	473610.893	470469.933	80
11)	BDE-85	8.25	196326.24	195253.5	40
12)	BDE-154	8.41	255351.952	253336.328	40
13)	BDE-153	8.64	420471.525	415737.963	80
14)	BDE-138	8.95	181396.05	178348.83	40
15)	BDE-183	9.35	340343.85	338190.6	80
16)	BDE-197	10.36	2366580	1581054	200
17)	BDE-207	11.98	1014129.187	527124	200
18)	BDE-209	15.15	1889399.64	975390.21	600

#	Name	Ret Time	Target Respons	Q1 Response	Amount
1)	F-BDE-69	6.79	1356121.694	1345964.634	100
2)	F-BDE-160	8.8	1588797.87	1587719.43	200
3)	13C-BDE-209	15.14	3481261.37	1695690.95	500
4)	PCB-209	8.22	2624009.066	1856170.582	25

Data File Name	0201033.D
Data File Path	C:\msdchem\1011221_Batch5\
Date Acquired	13/11/2015
Acq. Method File	BDE-ST02.M
Sample Name	BDEs cal.v.3
Vial Number	2

#	Name	Ret Time	Target Response	Q1 Response
5)	BDE-17	6.14	328793.724	328830.544
6)	BDE-28	6.27	324755.015	325643.641
7)	BDE-47	7.14	570698.165	573651.655
8)	BDE-66	7.26	273437.155	275104.575
9)	BDE-100	7.76	316972.745	307904.946
10)	BDE-99	7.93	640452.34	639636.218
11)	BDE-85	8.24	247545.3	246346.02
12)	BDE-154	8.41	324149.91	320095.763
13)	BDE-153	8.64	521285.475	520034.178
14)	BDE-138	8.95	228599.6	226851.262
15)	BDE-183	9.34	426409.83	424939.35
16)	BDE-197	10.35	3008470.5	1980915
17)	BDE-207	11.97	1349755	703102.625
18)	BDE-209	15.12	2784164.831	1443111.578

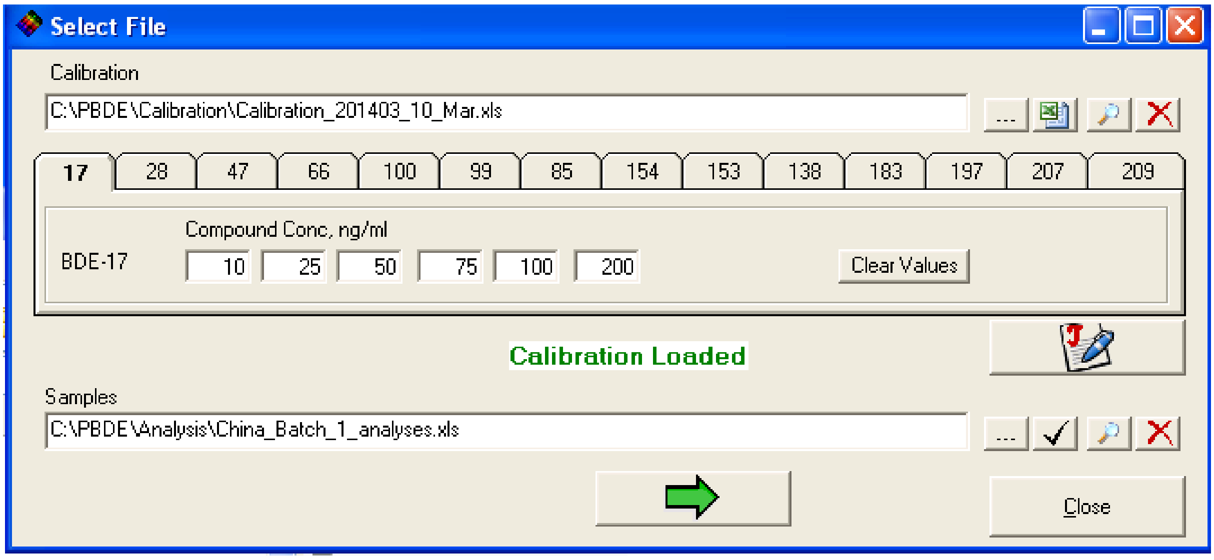
#	Name	Ret Time	Target Response	Q1 Response	Amount
1)	F-BDE-69	6.78	1723012.282	1720617.174	100
2)	F-BDE-160	8.79	1935479.7	1945622.25	200
3)	13C-BDE-209	15.11	5099814.533	2497373.999	500
4)	PCB-209	8.22	3065008.045	2187107.09	25

Data File Name	0301009.D	
Data File Path	C:\msdchem\1\DATA\CI source\1011221_Batch5\	
Date Acquired	13/11/2015	
Acq. Method File	BDE-ST02.M	
Sample Name	Blank 11	0.05
Vial Number	3	

#	Name	Ret Time	Target Respons	Q1 Response	
5)	BDE-17	0	0	0	50
6)	BDE-28	0	0	0	50
7)	BDE-47	0	0	0	50
8)	BDE-66	0	0	0	50
9)	BDE-100	7.78	202521.28	201567.263	50
10)	BDE-99	0	0	0	50
11)	BDE-85	0	0	0	50
12)	BDE-154	0	0	0	100
13)	BDE-153	8.64	11779.704	11740.508	100
14)	BDE-138	0	0	0	100
15)	BDE-183	0	0	0	100
16)	BDE-197	0	0	0	100
17)	BDE-207	0	0	0	100
18)	BDE-209	0	0	0	250

#	Name	Ret Time	Target Respons	Q1 Response	Amount
1)	F-BDE-69	6.79	393582.349	394849.954	100
2)	F-BDE-160	8.8	23611.5	23121.12	200
3)	13C-BDE-209	15.14	353519.43	172041.917	500
4)	PCB-209	8.22	1207094.909	842624.992	25

Figure 4. Example of data input for samples quantification



Calibration: C:\PBDE\Calibration\Calibration_201403_10_Mar.xls

BDE-17 Compound Conc, ng/ml: 10, 25, 50, 75, 100, 200

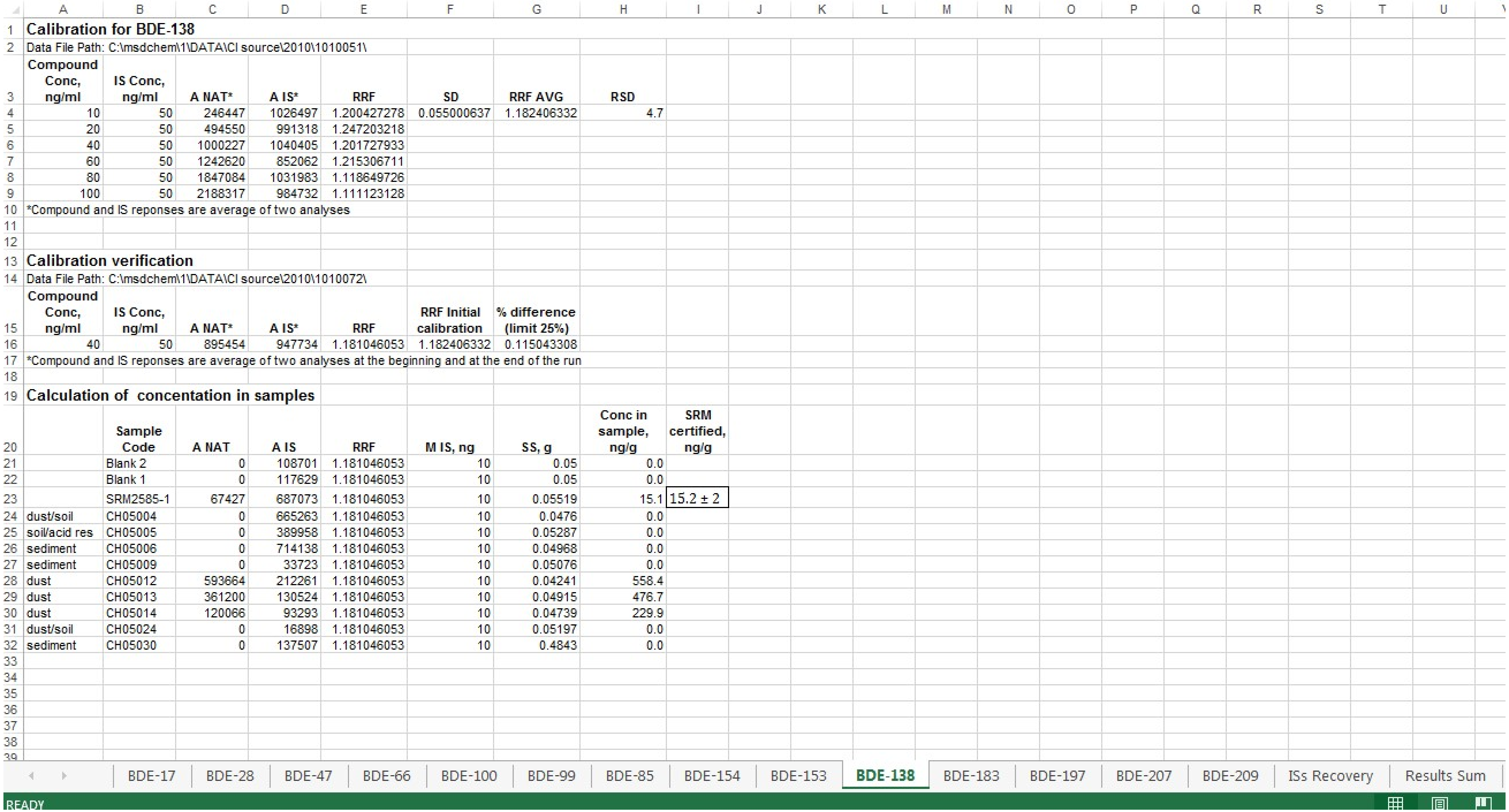
Calibration Loaded

Samples: C:\PBDE\Analysis\China_Batch_1_analyses.xls

Program performs calculations (as described in section 2.3.2) and creates Excel file with:

- 14 worksheets showing initial calibration data for the corresponding BDE, calibration verification with the PBDEs standard analysed at the beginning and at the end of the sequence, and calculation of BDE concentration in samples, blanks and SRM (see example - Fig. 5);
- ISs recovery determination;
- Summary of the PBDEs quantification in samples, blanks and SRM.

Figure 5. Example of Excel spreadsheet showing results for BDE-138 quantification in samples



Calibration for BDE-138

Data File Path: C:\msdchem\1\DATA\CI source\2010\1010051\

Compound Conc, ng/ml	IS Conc, ng/ml	A NAT*	A IS*	RRF	SD	RRF AVG	RSD
10	50	246447	1026497	1.200427278	0.055000637	1.182406332	4.7
20	50	494550	991318	1.247203218			
40	50	1000227	1040405	1.201727933			
60	50	1242620	852062	1.215306711			
80	50	1847084	1031983	1.118649726			
100	50	2188317	984732	1.111123128			

*Compound and IS reponses are average of two analyses

Calibration verification

Data File Path: C:\msdchem\1\DATA\CI source\2010\1010072\

Compound Conc, ng/ml	IS Conc, ng/ml	A NAT*	A IS*	RRF	RRF Initial calibration	% difference (limit 25%)
40	50	895454	947734	1.181046053	1.182406332	0.115043308

*Compound and IS reponses are average of two analyses at the beginning and at the end of the run

Calculation of concentation in samples

	Sample Code	A NAT	A IS	RRF	M IS, ng	SS, g	Conc in sample, ng/g	SRM certified, ng/g
	Blank 2	0	108701	1.181046053	10	0.05	0.0	
	Blank 1	0	117629	1.181046053	10	0.05	0.0	
	SRM2585-1	67427	687073	1.181046053	10	0.05519	15.1	15.2 ± 2
dust/soil	CH05004	0	665263	1.181046053	10	0.0476	0.0	
soil/acid res	CH05005	0	389958	1.181046053	10	0.05287	0.0	
sediment	CH05006	0	714138	1.181046053	10	0.04968	0.0	
sediment	CH05009	0	33723	1.181046053	10	0.05076	0.0	
dust	CH05012	593664	212261	1.181046053	10	0.04241	558.4	
dust	CH05013	361200	130524	1.181046053	10	0.04915	476.7	
dust	CH05014	120066	93293	1.181046053	10	0.04739	229.9	
dust/soil	CH05024	0	16898	1.181046053	10	0.05197	0.0	
sediment	CH05030	0	137507	1.181046053	10	0.4843	0.0	

Appendix 2 Concentration of PBDEs (ng g^{-1} dry weight) in samples collected from e-waste recycling sites in Guiyu, China

Code	BDE17	BDE28	BDE47	BDE66	BDE100	BDE99	BDE85	BDE154	BDE153	BDE138	BDE-183	BDE-197	BDE-207	BDE-209	$\sum PBDE_{13}$	$\sum PBDE_{14}$
AP01	37	62	350	110	140	360	15	380	1400	240	2800	15000	6900	18000	28000	46000
AP02	<0.1	67	<16.3	<3.8	<29	110	<0.6	61	120	<1.1	380	3800	23000	150000	27000	170000
AP03	6	<3.8	<16.3	<3.8	<29	34	<0.6	<0.4	<13	<1.1	<6.8	4	28	260	72	330
AP04	<0.1	<3.8	<16.3	<3.8	<29	<8.9	<0.6	<0.4	<13	<1.1	19	26	820	12000	870	13000
AP05	1700	2600	15000	5300	1300	17000	1100	2500	9300	1200	1500	1900	2800	19000	63000	82000
AP06	9	<3.8	<16.3	<3.8	<29	<8.9	<0.6	<0.4	790	<1.1	1100	5500	1500	2600	8800	11000
AP07	23	36	170	72	<29	200	14	15	45	<1.1	45	28	130	1800	780	2600
AP08	20	23	<16.3	35	<29	97	3	21	48	18	48	31	110	1200	450	1600
AP09	2	<3.8	<16.3	<3.8	<29	<8.9	1	6	<13	<1.1	<6.8	22	17	96	48	140
AP10	<0.1	7	57	20	<29	60	<0.6	<0.4	22	<1.1	53	25	30	370	270	650
AP11	<0.1	11	38	14	<29	36	<0.6	<0.4	<13	<1.1	<6.8	<0.1	<1.6	<10	99	99
AP12	180	310	2000	710	180	2200	130	130	460	52	73	25	110	2700	6500	9200
AP13	<0.1	24	210	64	84	240	<0.6	9	59	<1.1	<6.8	26	94	530	820	1300
AP14	88	170	1300	390	<29	1500	73	77	260	28	34	13	110	1800	4100	5900
AP15	<0.1	<3.8	<16.3	<3.8	<29	<8.9	<0.6	<0.4	<13	<1.1	30	11	48	1100	89	1200
AP16	<0.1	<3.8	<16.3	<3.8	<29	36	<0.6	120	1100	<1.1	2900	17000	1600	8100	22000	30000
OB01	<0.1	20	62	48	<29	69	<0.6	6	25	<1.1	32	16	46	630	320	960
OB02	80	3200	220	79	<29	210	84	<0.4	52	<1.1	90	44	78	780	4100	4900
OB03	49	520	510	<3.8	210	760	47	200	640	170	1600	1600	890	8100	7200	15000
OB04	100	330	1000	230	200	500	29	170	1100	99	2600	6300	14000	31000	27000	57000
OB05	980	1600	9500	3100	1000	11000	360	1800	4600	1100	7100	4600	25000	320000	71000	390000
PD01	13	<3.8	670	<3.8	170	850	47	73	170	16	450	210	190	2000	2900	4900
PD02	110	<3.8	480	200	170	1700	65	160	420	46	490	230	490	8500	4500	13000
SS01	440	820	2800	970	550	3000	240	2100	8400	560	7300	13000	2000	25000	43000	68000
SS02	66	98	530	140	170	650	27	530	1700	480	4100	13000	3100	14000	25000	39000
SS03	140	250	1000	320	230	890	38	710	5300	230	6500	19000	5100	19000	40000	59000
SH01	3	<3.8	<16.3	<3.8	<29	33	<0.6	24	110	<1.1	540	310	1400	15000	2400	17000
SH02	7900	12000	21000	14000	5100	19000	7600	8500	20000	7100	8500	6700	25000	120000	160000	280000
SH03	3900	5700	20000	9900	2400	21000	2100	7600	26000	3700	7700	17000	6500	48000	130000	180000
SH04	5600	9200	38000	15000	3800	41000	3100	3700	13000	1600	1600	630	7800	120000	140000	270000
SH05	3300	5700	18000	7500	1200	17000	1100	1900	7500	890	1400	3400	14000	54000	8200	140000

Appendix 3 Average, median and range of concentrations (in ng/g lw) of selected PBDE congeners detected in control food samples originated from China. n = number of samples

	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-197	BDE-207	BDE-209	∑PBDEs*
Chicken (n=5)										
average	<0.010	<0.008	<0.008	0.04	0.1	0.2	0.1	0.4	1.6	2.3
median	<0.010	<0.008	<0.008	<0.005	<0.010	<0.010	0.07	<0.008	<0.018	0.07
range	<0.010	<0.008	<0.008	<0.005 – 0.2	<0.010 - 0.3	<0.010 - 0.6	<0.005 - 0.4	<0.008 - 1.5	<0.018 - 7.8	<0.018 - 10.7
Chicken liver (n=5)										
average	<0.020	<0.015	<0.015	<0.010	<0.020	<0.020	<0.010	<0.015	3.3	3.3
median	<0.020	<0.015	<0.015	<0.010	<0.020	<0.020	<0.010	<0.015	4.1	4.1
range	<0.020	<0.015	<0.015	<0.010	<0.020	<0.020	<0.010	<0.015	0.9 – 4.6	0.9 – 4.6
Chicken egg (n=10)										
average	<0.014	<0.010	<0.010	<0.007	<0.014	<0.014	0.02	0.2	6.8	7.0
median	<0.014	<0.010	<0.010	<0.007	<0.014	<0.014	<0.007	<0.010	4.8	4.8
range	<0.014	<0.010	<0.010	<0.007	<0.014	<0.014	<0.007- 0.23	<0.010 - 1.0	2.8 – 22.6	2.8 – 23.6
Duck (n=5)										
average	<0.008	<0.006	<0.006	0.04	0.1	0.4	0.3	0.7	8.1	10.0
median	<0.008	<0.006	<0.006	<0.004	<0.008	0.2	0.2	0.7	7.8	11
range	<0.008	<0.006	<0.006	<0.0040.21	<0.008 - 0.4	<0.008 - 1.1	0.2 – 0.6	0.3 – 1.1	3.6 – 11.9	4.1 – 15.5
Duck liver (n=5)										
average	<0.032	<0.024	<0.024	<0.016	<0.032	0.3	0.3	0.8	16.4	18.2
median	<0.032	<0.024	<0.024	<0.016	<0.032	0.3	0.3	0.8	17.9	19.6
range	<0.032	<0.024	<0.024	<0.016	<0.032	<0.032 - 0.7	<0.016 - 0.4	0.4 – 1.1	12.8 – 19.0	13.3 – 20.8
Pork (n=5)										
average	<0.020	<0.015	<0.015	<0.010	<0.020	<0.020	<0.010	<0.015	<0.036	<0.036
median	<0.020	<0.015	<0.015	<0.010	<0.020	<0.020	<0.010	<0.015	<0.036	<0.036
range	<0.020	<0.015	<0.015	<0.010	<0.020	<0.020	<0.010	<0.015	<0.036	<0.036
Fish (n=4)										
average	1.3	0.3	0.2	0.4	0.1	<0.093	0.1	<0.070	<0.163	2.5
median	0.7	<0.070	<0.070	0.2	<0.093	<0.093	<0.047	<0.070	<0.163	1.0
range	<0.093 - 3.8	<0.070 - 0.9	<0.070 - 0.9	<0.047 – 1.3	<0.093 - 0.4	<0.093	<0.047 - 0.4	<0.070	<0.163	0.4 – 7.8
Shrimp (n=2)										
average	0.2	<0.083	<0.083	0.1	<0.111	<0.111	<0.056	<0.083	<0.194	0.3
median	0.2	<0.083	<0.083	0.1	<0.111	<0.111	<0.056	<0.083	<0.194	0.3
range	<0.111 - 0.4	<0.083	<0.083	<0.056 – 0.2	<0.111	<0.111	<0.056	<0.083	<0.194	<0.194– 0.6

Appendix 4 Concentrations of PCBs, ng/g lw, in pooled food samples originating from e-waste sites in Taizhou, Zhejiang, and from control sites in China. Sample codes are as referred to in Table 2-5

Sample	**GP-01**	**GP-02**	**GP-03**	**GP-04**	**GP-05**	**GP-06**	**GP-07**	**GP-08**	**GP-09**	**GP-10**	**GP-11**	**GP-12**	**GP-13**	**GP-14**	**GP-15**	**GP-16**	**GP-17**	**GP-18**	**GP-19**	**GP-20**	**GP-21**	**GP-22**	**GP-23**	**GP-24**
CB 18	<1.0	15.6	2220	48.9	79.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
CB 31	<1.0	6.2	2980	31.8	59.7	<1.0	1.8	<1.0	1.2	<1.0	6.6	1.4	9.7	<1.0	<1.0	<1.0	<1.0	5.7	<1.0	2.5	<1.0	3.5	<1.0	16.6
CB 28	<1.0	12.0	6350	40.2	188	<1.0	54.3	<1.0	39.3	2.0	166	1.2	69.7	<1.0	<1.0	<1.0	57.4	211	<1.0	64.7	5.2	31.4	4.9	420
CB 52	<1.0	15.2	6660	41.3	77.9	<1.0	<1.0	<1.0	<1.0	<1.0	16.0	<1.0	3.5	<1.0	<1.0	<1.0	4.6	8.7	<1.0	6.7	<1.0	4.2	<1.0	15.5
CB 49	<1.0	6.0	3870	27.6	37.2	<1.0	<1.0	<1.0	<1.0	<1.0	8.6	<1.0	3.0	<1.0	<1.0	<1.0	<1.0	5.7	<1.0	3.2	<1.0	<1.0	<1.0	15.1
CB 47	<1.0	7.0	2084	14.0	54.6	<1.0	23.5	<1.0	17.8	<1.0	66.2	<1.0	28.8	<1.0	<1.0	<1.0	18.7	53.5	<1.0	9.4	1.9	3.9	<1.0	68.8
CB 74	<1.0	<1.0	3030	<1.0	81.9	<1.0	26.4	<1.0	18.5	<1.0	60.7	<1.0	22.9	<1.0	<1.0	<1.0	30.0	74.1	<1.0	38.9	3.4	8.3	2.3	158
CB 66	<1.0	<1.0	4670	9.7	91.5	<1.0	40.1	<1.0	28.7	<1.0	95.1	<1.0	40.4	<1.0	<1.0	<1.0	40.8	117	<1.0	42.0	4.9	12.1	4.5	246
CB 95	<1.0	4.3	3440	10.3	20.0	<1.0	3.2	<1.0	3.4	<1.0	18.4	<1.0	4.2	<1.0	<1.0	<1.0	6.8	7.2	<1.0	6.8	<1.0	2.4	<1.0	13.9
CB 101	<1.0	4.8	6120	9.3	27.2	<1.0	1.7	<1.0	1.9	<1.0	20.0	<1.0	13.8	<1.0	<1.0	<1.0	9.3	9.0	<1.0	11.1	<1.0	2.6	1.3	34.0
CB 99	<1.0	1.9	2920	4.4	32.2	<1.0	29.1	<1.0	21.5	<1.0	75.5	<1.0	29.6	<1.0	<1.0	<1.0	53.7	66.5	<1.0	38.4	4.7	8.2	4.8	159
CB 110	<1.0	2.9	6060	<1.0	20.3	<1.0	4.6	<1.0	12.2	<1.0	8.3	<1.0	10.3	<1.0	<1.0	<1.0	12.0	11.0	<1.0	5.2	<1.0	<1.0	1.6	14.7
CB 118	<1.0	1.7	6000	5.1	147	<1.0	64.0	<1.0	43.3	<1.0	168	<1.0	63.9	<1.0	<1.0	<1.0	127	134	<1.0	103	10.7	18.4	10.9	345
CB 105	<1.0	<1.0	2500	<1.0	59.6	<1.0	27.3	<1.0	18.4	<1.0	65.3	<1.0	36.4	<1.0	<1.0	<1.0	54.1	63.0	<1.0	44.2	5.2	8.0	<1.0	143
CB 151	<1.0	<1.0	501	<1.0	<1.0	<1.0	<1.0	<1.0	4.7	<1.0	5.1	<1.0	<1.0	<1.0	<1.0	<1.0	2.7	3.8	<1.0	3.7	<1.0	<1.0	<1.0	5.5
CB 149	<1.0	<1.0	2460	<1.0	<1.0	<1.0	7.2	<1.0	8.2	<1.0	30.7	<1.0	10.3	<1.0	<1.0	<1.0	12.9	15.2	<1.0	13.8	<1.0	2.8	<1.0	51.3
CB 146	<1.0	<1.0	482	<1.0	10.8	<1.0	6.0	<1.0	10.2	<1.0	16.0	<1.0	7.6	<1.0	<1.0	<1.0	9.8	11.8	<1.0	10.7	<1.0	1.2	<1.0	41.1
CB 153	<1.0	1.7	4020	1.4	79.6	<1.0	61.8	<1.0	41.9	<1.0	130	<1.0	53.5	<1.0	<1.0	<1.0	88.6	109	<1.0	103	11.4	11.1	11.1	301
CB 138	<1.0	<1.0	4320	<1.0	32.1	<1.0	60.3	<1.0	39.4	<1.0	132	<1.0	58.6	<1.0	<1.0	<1.0	105	108	<1.0	95.6	8.3	12.0	10.5	289
CB 128	<1.0	<1.0	1020	<1.0	26.3	<1.0	12.6	<1.0	9.7	<1.0	29.4	<1.0	16.2	<1.0	<1.0	<1.0	24.6	24.1	<1.0	20.9	2.7	3.8	2.6	67.1
CB 167	<1.0	<1.0	284	<1.0	<1.0	<1.0	5.1	<1.0	1.8	<1.0	8.5	<1.0	<1.0	<1.0	<1.0	<1.0	9.3	7.7	<1.0	6.7	<1.0	<1.0	<1.0	24.5
CB 156	<1.0	<1.0	509	<1.0	10.1	<1.0	6.0	<1.0	6.1	<1.0	15.9	<1.0	4.8	<1.0	<1.0	<1.0	18.1	14.7	<1.0	13.2	<1.0	2.7	<1.0	32.0
CB 187	<1.0	<1.0	440	<1.0	10.7	<1.0	11.0	<1.0	39.1	<1.0	30.1	<1.0	17.9	<1.0	<1.0	<1.0	5.5	18.3	<1.0	12.2	1.4	<1.0	1.3	65.8
CB 183	<1.0	<1.0	228	<1.0	4.1	<1.0	6.5	<1.0	3.8	<1.0	12.4	<1.0	5.4	<1.0	<1.0	<1.0	5.5	9.9	<1.0	8.0	<1.0	<1.0	<1.0	32.6
CB 174	<1.0	<1.0	287	<1.0	<1.0	<1.0	2.5	<1.0	<1.0	<1.0	9.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.0	3.5	<1.0	3.3	<1.0	<1.0	<1.0	16.8
CB 177	<1.0	<1.0	181	<1.0	<1.0	<1.0	5.0	<1.0	18.9	<1.0	11.2	<1.0	18.0	<1.0	<1.0	<1.0	4.2	7.6	<1.0	5.1	<1.0	<1.0	<1.0	25.1
CB 171	<1.0	<1.0	116	<1.0	<1.0	<1.0	4.0	<1.0	<1.0	<1.0	6.2	<1.0	<1.0	<1.0	<1.0	<1.0	2.5	4.6	<1.0	3.4	<1.0	<1.0	<1.0	13.8
CB 180	<1.0	<1.0	997	<1.0	18.1	<1.0	27.9	<1.0	14.5	<1.0	64.9	<1.0	25.5	<1.0	<1.0	<1.0	20.9	43.9	<1.0	37.9	2.3	3.3	2.8	150.1
CB 170	<1.0	<1.0	436	<1.0	4.7	<1.0	9.7	<1.0	6.6	<1.0	26.5	<1.0	8.6	<1.0	<1.0	<1.0	12.2	19.2	<1.0	17.1	<1.0	<1.0	<1.0	58.9
CB 199	<1.0	<1.0	110	<1.0	<1.0	<1.0	<1.0	<1.0	2.1	<1.0	12.0	<1.0	3.9	<1.0	<1.0	<1.0	<1.0	6.4	<1.0	4.6	<1.0	<1.0	<1.0	20.6
CB 194	<1.0	<1.0	84.1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	6.3	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	4.9	<1.0	4.4	<1.0	<1.0	<1.0	14.1
CB 206	<1.0	<1.0	22.7	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
CB 209	<1.0	<1.0	12.8	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
∑PCBs	**<1.0**	**79**	**75420**	**244**	**1170**	**<1.0**	**502**	**<1.0**	**413**	**2.0**	**1320**	**2.6**	**566**	**<1.0**	**<1.0**	**<1.0**	**737**	**1179**	**<1.0**	**740**	**62**	**140**	**57**	**2860**

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