Polybrominated dibenzo-\textit{\textit{p}}-dioxins and furans
Till Dalia, Ellen och Ludvig
Polybrominated dibenzo-\(\rho\)-dioxins and furans: from source of emission to human exposure
© Filip Bjurlid, 2018

Title: Polybrominated dibenzo-p-dioxins and furans: from source of emission to human exposure
Publisher: Örebro University 2018
www.oru.se/publikationer-avhandlingar

Print: Örebro University, Repro 12/2017

ISSN 1651-4270
Abstract


Brominated flame retardants (BFRs), which are ubiquitous in modern life and the environment, are the major source for polybrominated dibenzo-p-dioxins and furans (PBDD/Fs). The knowledge about PBDD/Fs is limited compared to other environmental pollutants, even though PBDD/Fs show similar toxicity as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) which are considered to be among the most toxic man-made substances. The aim of the thesis was to provide a better understanding of PBDD/Fs by investigating the occurrence and distribution of PBDD/Fs in the following matrices: soot and gas from an accidental fire site which is a typical source of emission, blubber from marine mammals living in both far remote areas as well as areas close to anthropogenic sources, and finally in human milk from ten nursing mothers.

PBDD/Fs was detected in blubber from pilot whales sampled around Faroe Islands, which proved the occurrence in marine mammals in a far remote area. The findings of PBDD/Fs in blubber from Baltic ringed seals showed slightly higher concentrations compared to the pilot whales, which is expected since the Baltic Sea is among the world’s most contaminated water areas. In the pilot whales and the ringed seals, the average contribution from PBDD/Fs to the total (PCDD/F+PBDD/F) Total Equivalent Quantity (TEQ) was low, (1-8%). In gas and soot samples from the accidental fire site, PBDD/Fs were detected in all samples and the contribution of PBDD/Fs to the total TEQ was close to 100%. In the human milk samples, PBDD/Fs were detected in all samples and the average contribution of PBDD/Fs to the total TEQ was 40%. The results indicate that PBDD/Fs are of concern for human exposure, and should be monitored together with PCDD/Fs in future studies. Moreover, the occurrence at accidental fire sites indicate that PBDD/Fs are a source for occupational exposure for firefighters and other professionals. The impact from PBDD/Fs on marine mammalians seems to be of less concern.

Keywords: PBDD/Fs, PCDD/Fs, marine mammal, combustion, fire, human milk, occupational exposure

Filip Bjurlid, School of Science and Technology, Örebro University, SE-701 82 Örebro, Sweden, filip.bjurlid@oru.se
Sammanfattning

Konsekvenserna av giftiga och långlivade organiska föroreningar är många och allvarliga, och de påverkar både miljön och människans hälsa. Ett av de giftigaste ämnena som existerar är klorerade dioxiner och furaner (PCDD/Fs). Det finns även bromerade dioxiner och furaner (PBDD/Fs) men studierna av dessa, och därmed även kunskapen, är begränsade trots att PBDD/Fs och PCDD/Fs uppvisar liknande toxiska egenskaper. Den dominerande källan till PBDD/Fs är förbränningsrelaterade processer av material innehållande bromerade flamskyddsmedel.

Syftet med denna avhandling var att öka kunskapen om PBDD/Fs genom att undersöka förekomsten av PBDD/Fs i olika miljöer och matriser, och studierna spänner över lägenhetsbränder, till marina däggdjur och till ammande kvinnor. I delarbete 1 studerades förekomsten av PBDD/Fs i gas och sot då olika släcktekniker används för att bekämpa lägenhetsbränder. Lägenhetsbränderna representerade förekomsten av PBDD/Fs vid en känd punktkälla. Resultaten från försöken visade högre koncentrationer av PBDD/Fs än av PCDD/Fs, vilket också indikerar att PBDD/Fs är en relevant grupp av kemikalier att inkludera vid riskbedömning för yrkesgrupper som återkommande arbetar vid olycksbränder. I delarbete 2 undersöktes hur PBDD/Fs finns spridda till marina däggdjur. Genom att fastställa att PBDD/Fs finns spridda till grindvalar från vattnet utanför Färöarna, indikerar att PBDD/Fs har förmåga att transporteras över stora sträckor samt har de persistenta och bioackumulerande egenskaper som är karaktäristiska för traditionella miljögifter. I delarbete 3 studerades förekomsten av PBDD/Fs i vikare (ringsäl) från Östersjön, under perioden 1974-2015. Förekomsten av PBDD/Fs i vikare kan även ses som en indikator för spridningen av PBDD/Fs till näringskedjan i Östersjön. I delarbete 4 studerades människors exponering för PBDD/Fs genom att undersöka förekomsten i bröstmjölk. Resultaten visade så pass höga koncentrationer av PBDD/Fs i mjölken att den genomsnittliga toxiska effekten från dessa var nästan lika hög som från PCDD/Fs. Då spädbarn är känsliga för exponering av miljögifter, är de höga koncentrationerna av PBDD/Fs i bröstmjölen oroväckande. Sammanfattningsvis visar denna avhandling att PBDD/Fs är förekommande i olika miljöer och matriser, och att det primärt är människors exponering som är oroande. Dels handlar det om risken för den generella exponeringen av människan som fynden i bröstmjölk indikerar, men även om den yrkesrelaterade exponeringen som brandmän m.fl. kan utsättas för.
List of papers

This thesis is based in the following papers:

Paper 1
Bjurlid, Filip; Kärrman, Anna; Ricklund, Niklas; Hagberg, Jessika
DOI: 10.1016/j.scitotenv.2017.05.087

Paper 2
Bjurlid, Filip; Dam, Maria; Hoydal, Katrin; Hagberg, Jessika
Occurrence of polybrominated dibenzo-p-dioxins, dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs) in pilot whales (Globicephala melas) caught around the Faroe Islands. Under review in Chemosphere.

Paper 3
Bjurlid, Filip; Roos, Anna; Ericson Jogsten, Ingrid; Hagberg, Jessica
Temporal trends of PBDD/Fs, PCDD/Fs, PBDEs and PCBs in ringed seals from the Baltic sea (Pusa hispida botnica) between 1974 and 2014. Science of the Total Environment, accepted for publication.
DOI: 10.1016/j.scitotenv.2017.10.178

Paper 4
Bjurlid, Filip; Hagberg, Jessika
Under review in Environmental International.

Papers not included in the thesis:

Henriksson, Sara; Bjurlid, Filip; Rotander, Anna; Engwall, Magnus; Lindström, Gunilla; Westberg, Håkan; Hagberg, Jessika
Uptake and bioaccumulation of PCDD/Fs in earthworms after in situ and in vitro exposure to soil from contaminated sawmill site. Science of the Total Environment, 580 (2017) 564-571. DOI: 10.1016/j.scitotenv.2016.11.213
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ah</td>
<td>Aryl hydrocarbon receptor</td>
</tr>
<tr>
<td>BFRs</td>
<td>Brominated flame retardants</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibromophenol</td>
</tr>
<tr>
<td>DDE</td>
<td>Dichlorodiphenyl dichloroethylene</td>
</tr>
<tr>
<td>EROD</td>
<td>Ethoxyresorufin-O-deethylase</td>
</tr>
<tr>
<td>HBr</td>
<td>Hydrogen bromide</td>
</tr>
<tr>
<td>HRGC/HRMS</td>
<td>High-resolution gas chromatography high-resolution mass spectrometry</td>
</tr>
<tr>
<td>OCPs</td>
<td>Organochlorine pesticides</td>
</tr>
<tr>
<td>PBDD</td>
<td>Polybrominated dibenzo-(p)-dioxin</td>
</tr>
<tr>
<td>PBDEs</td>
<td>Polybrominated Diphenyl ethers</td>
</tr>
<tr>
<td>PBDF</td>
<td>Polybrominated dibenzofuran</td>
</tr>
<tr>
<td>PBT</td>
<td>Pentabromotoluene</td>
</tr>
<tr>
<td>PCBs</td>
<td>Polychlorinated biphenyls</td>
</tr>
<tr>
<td>PCDD</td>
<td>Polychlorinated dibenzo-(p)-dioxin</td>
</tr>
<tr>
<td>PCDF</td>
<td>Polychlorinated dibenzofuran</td>
</tr>
<tr>
<td>POPs</td>
<td>Persistent Organic Pollutants</td>
</tr>
<tr>
<td>PTV</td>
<td>Programmed Temperature Vaporiser</td>
</tr>
<tr>
<td>SIR</td>
<td>Selective ion recording</td>
</tr>
<tr>
<td>TEF</td>
<td>Toxic Equivalence Factor</td>
</tr>
<tr>
<td>TEQ</td>
<td>Toxic Equivalent Quantity</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WTC</td>
<td>World Trade Center</td>
</tr>
</tbody>
</table>
# Table of Contents

1 INTRODUCTION .......................................................................................... 13  
  1.1 Aim of the thesis ........................................................................... 14  
  1.2 POPs – Persistent Organic Pollutants ........................................... 15  
  1.3 Brominated Flame Retardants..................................................... 16  
  1.4 PBDD/F - Polybrominated dibenzo-\(p\)-dioxins and polybrominated dibenzofurans ................................................................. 18  
    1.4.1 Characteristics of PBDD/Fs .................................................. 20  
    1.4.2 Sources and formation of PBDD/Fs ..................................... 22  
    1.4.3 Environmental distribution and concentrations of PBDD/Fs ... 24  
    1.4.4 Toxicological and health effects of PBDD/Fs ................. 27  
      1.4.4.1 Toxicity of chlorinated dioxins and furans ................. 28  
      1.4.4.2 Toxicity of brominated dioxins and furans ............... 29  
      1.4.4.3 Toxic Equivalence Factors – TEFs ............................ 29  
2 METHODS ............................................................................................... 31  
  2.1 Extraction and clean-up of PBDD/Fs ........................................... 32  
  2.2 Instrumental analysis and quantification of PBDD/Fs ............... 34  
  2.3 Quality assurance and quality control ........................................ 36  
3 RESULTS AND DISCUSSION ............................................................... 37  
  3.1 Occurrence of PBDD/Fs at an accidental fire site – a typical point source (Paper I) ................................................................. 37  
    3.1.1 Background information about the tests ......................... 37  
    3.1.2 Results from the fire phase .............................................. 43  
    3.1.3 Results from the extinguishing phase .............................. 47  
    3.1.4 Comparing results from fire and extinguishing phase .......... 48  
    3.1.5 Final remarks on the occurrence of PBDD/Fs at an accidental fire site .............................................................................. 49  
  3.2 PBDD/Fs in marine mammals living in far remote areas (Paper II) 50  
  3.3 PBDD/Fs in marine mammals living near anthropogenic sources (Paper III) ........................................................................... 55  
  3.4 PBDD/Fs in human breast milk (Paper IV) ............................... 60  
4. CONCLUSIONS AND FUTURE PERSPECTIVE .................................. 67  
5. ACKNOWLEDGEMENT ........................................................................ 71  
6. REFERENCES ....................................................................................... 73
1 Introduction

Modern society has given man the ability to create and produce a countless number of chemical compounds, and in addition to this, numerous compounds are formed unintentionally. These unintentionally produced substances are generally formed in chemical processes and at high process temperatures, as by-products, waste or degradation products (Naturvårdsverket, 2007). Unintentionally produced substances usually exhibit both persistent and lipophilic properties (Naturvårdsverket, 2011). Organic compounds that exhibit toxic properties and resist natural degradation are classified as POPs, Persistent Organic Pollutants (Wikoff et al., 2012). The implications of POPs are many and serious, and they affect both the environment and human health (Wikoff et al., 2012). In an effort to globally protect human health and environment, the Stockholm Convention on Persistent Organic Pollutants was signed in 2001 to restrict and eliminate the production and use of some of the most harmful compounds (Wikoff et al., 2012). The first substances that ended up on the list were called the dirty dozen. In 2010, additional substances were added to the list (Wikoff et al., 2012). In 2017, 181 countries had ratified the Stockholm Convention (Stockholm Convention, 2017). According to the Stockholm Convention, member states must take measures to eliminate, restrict and reduce the production and use of the chemicals on the list. One of the substances listed on the Stockholm convention list is polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), which are among the most toxic substances that exist (Birnbaum, 1994).

There are also polybrominated dibenzo-p-dioxins and furans (PBDD/Fs), but the knowledge and studies of these are limited compared to their chlorinated analogues. Based on the current knowledge, brominated dioxins and furans have similar toxic properties as the chlorinated dioxins and furans (Birnbaum et al., 2003; Olsman et al., 2007; van den Berg et al., 2013). Despite this, brominated dioxins and furans are not on the Stockholm Convention list. The predominant sources of brominated dioxins and furans are brominated flame retardants, BFRs (Ebert and Bahadir, 2003; Kannan et al., 2012). Brominated dioxins and furans may be formed in various ways such as in industrial processes, during photolysis of BFRs and from natural formation (Ebert and Bahadir, 2003; Haglund et al., 2007; Kannan et al., 2012), but the most common source to PBDD/Fs is combustion of plastics containing brominated flame retardants (Li et al., 2007). During combustion, PBDD/Fs are emitted to the surrounding air and are spread over vast
areas through the major transport pathway; atmospheric transport (Li et al., 2008). Many modern products consist largely of plastic, which is a highly flammable material. To meet fire safety requirements, brominated flame retardants can be added to the plastic (Zhu et al., 2007). Regulation and restrictions regarding the use of BFRs have increased, since several of these substances exhibit bioaccumulative and toxic properties (Papachristitou et al., 2012). The occurrence of PBDD/Fs and its effects are not sufficiently studied to determine whether they pose such a threat towards human health and the environment that they should be included on the Stockholm Convention List or not.

1.1 Aim of the thesis
The overall aim of this thesis was to increase the current knowledge about PBDD/Fs, by studying the occurrence of PBDD/Fs in matrices representing one potential source of emission, provide evidence for PBDD/Fs' occurrence in marine mammals living in far remote areas as well as in areas close to anthropogenic sources and finally examine the levels of PBDD/Fs in human milk. All of this, in order to provide a better understanding of the occurrence of PBDD/Fs from source of emission to human exposure.

Specific aims of the papers included in this thesis are described below:

Paper I. The aim was to compare the amount of PBDD/Fs, and to some extent also PCDD/Fs, in gas and on soot particles formed during firefighting using different firefighting methods. To study how the different firefighting methods affected the formation of PBDD/Fs and PCDD/Fs, the study design featured replicated scenarios of accidental fires in defined apartment environments where furnishings were identical.

Paper II. The aims were to investigate the occurrence of PBDD/Fs in pilot whales caught around the Faroe Islands during 1997-2013, and also investigate the correlation between PBDD/Fs and PBDEs. A secondary aim was to assess a possible time trend for PBDEs in pilot whales.

Paper III. The aim was to investigate the occurrence of primarily PBDD/Fs and also other POPs in Baltic ringed seals caught in the Swedish waters of the Baltic Sea during 1974 to 2015, in order assess possible time trends.

Paper IV. The aim was to investigate the occurrence of primarily PBDD/Fs and also other POPs in breast milk from ten Swedish women. Moreover, the effects of breastfeeding duration on the concentrations of the studied compounds were evaluated.
1.2 POPs – Persistent Organic Pollutants

Chemicals play an important economic role in our society, and have contributed to improved standards of living as well as human well-being. But the awareness, that some chemicals have an adverse effect on the environment and on human health, has increased (Secretariat of the Stockholm Convention, 2011).

There is a group of chemicals that share four characteristics in a particularly dangerous combination:

- they are persistent, and have the ability to withstand degradation and thus remain intact over long periods of time (Wikoff et al., 2012).
- they have the capacity to spread over great distances because they are semi-volatile and can travel either as vapor, or by being adsorbed onto other particles (Wikoff et al., 2012).
- they mostly exhibit lipophilic properties, thus accumulate in fat-containing food and body tissue (Wikoff et al., 2012).
- they are highly toxic (Secretariat of the Stockholm Convention, 2011).

Chemicals exhibiting the properties listed above, are classified as Persistent Organic Pollutants, POPs. Emissions of POPs originate from accidental emissions or from human activities such as industrial emissions, waste disposal, combustion, traffic and so on (Colles et al., 2008). POPs can be transported over long distances, and have been found even in the Antarctic. Thus, the problem is not geographically limited to the immediate surroundings of the emission source (Perrini et al., 2005), and POPs have become ubiquitous in the environment (Colles et al., 2008).

POPs accumulate in fat tissue owing to their chemical and physical properties, which can lead to biomagnification in top predators in the food chain. There are examples of substances that biomagnify up to 70,000-fold, which results in relatively high exposure of the top predators/consumers (Wikoff et al., 2012). For humans, diet is the predominant source of exposure, but there are other exposure routes such as from occupational exposure and from the surrounding environment exposure. Some examples of environmental exposures are ingestion of contaminated dust particles and inhalation of POPs in the air (Wikoff et al., 2012).
Substances classified as POPs are toxic, both to humans and animals. They have the capability of causing severe health outcomes even at low level exposure, for example cancer, endocrine disruption, nervous-system damage, memory problems, liver damage, cardiovascular disease, birth defects and reproductive problems (Secretariat of the Stockholm Convention, 2011).

1.3 Brominated Flame Retardants

New materials such as plastics, and increased used of materials, have placed new demands on fire safety, and flame retardants have emerged as one solution. Flame retardants are added to all kinds of materials we have at home, e.g. electronic components, plastic materials, clothing, furniture etc., to improve their resistance to fire (Zhu et al., 2007). BFRs are commonly used owing to effective flame retardation and low cost (Sakai et al., 2001).

When a polymer containing BFRs are subjected to thermal stress, hydrogen bromide, HBr, is released. HBr is the active component of the flame retardant property of chemicals used as BFRs (Ebert and Bahadir, 2003).

During the combustion process, free radicals (highly oxidizing agents) are produced. The free radicals are crucial elements for the flame to propagate (Eljarrat and Barceló, 2011). Vital steps of the chain reaction in the combustion process involves the highly reactive ·OH and H· radicals. The bromine-containing compounds interrupt the chain reaction by replacing the ·OH and H· radicals by the less reactive bromine radical, i.e. Br·. The following reaction takes place (where R-Br represents the flame retardant and P-H represents the polymer):

\[
\begin{align*}
R-\text{Br} + P-\text{H} & \rightarrow H-\text{Br} + R-P \\
H-\text{Br} + H· & \rightarrow H_2 + Br· \\
H-\text{Br} + ·OH & \rightarrow H_2O + Br·
\end{align*}
\]

By diverting the energy of the ·OH radicals by capturing, the thermal balance of the combustion process is changed and the combustion rate is strongly reduced (Troitzsch, 2004).

Bromine is the major component of BFR, thus, there is no precise restriction on the structure of the backbone (Troitzsch, 2004). More than 80 different compounds have been registered as brominated flame retardants (Eljarrat
Examples of brominated flame retardants are 2,4-Di-bromophenol (DBP), Pentabromotoluene (PBT) and PBDEs.

In the early 2000s, it was reported that bromine containing compounds were ubiquitous in homes, workplaces and public places. The reason for this could be found in the increasing use of BFRs in consumer products, such as in electrical equipment, building foams, furniture, upholstery and plastic heat insulation (Weber and Kuch, 2003). Studies showed the same results for sediment and biota; BFRs were found everywhere (de Wit, 2002). Brominated flame retardants were also found in humans. During a thirty-year period, starting in the early 1970s, the concentration of a number of BFRs was measured in human milk from Swedish women. During this period, the concentrations doubled about every five years. Not unexpectedly, the trend coincided with an increasing production and use of brominated flame retardants (Brown et al., 2004).

A number of restrictions have been introduced to control and restrict a number of BFRs and replace them with alternative flame retardants, but reports still show relatively high levels of the BFRs in both indoor air and house dust. Although a certain brominated flame retardants are banned and replaced with an alternative compound, products containing the banned substance can still be found in homes, households and waste streams for 5-20 years, i.e. the normal life span of products (Ericson Jogsten et al., 2010).

Referring to the volume, approximately 25% of all flame retardants contain bromine (Eljarrat and Barceló, 2011). Plastic can comprise of up to 20 weight percent of BFRs (Ebert and Bahadir, 2003). In polyurethane foam, the content of BFRs can be as high as 30% of the product weight (Hanari et al., 2004).

The global use of BFRs in 2005 was 311,000 metric tons, which accounted for 21% of the total consumption of flame retardants, and in 2008 the consumption had increased to 410,000 tons. The increased use can primarily be explained by the growing market in Asia (Covaci et al., 2011).

In 2016 the global production of bromine was approximately 500 000 metric tons, and the leading applications for bromine containing compounds were in the production of flame retardants and industrial uses such as pesticides and pharmaceuticals, drilling fluid, and water treatment (Boldyryev and Varbanov, 2015; US Department of Interior, 2017).
Different BFR compound groups mediate various types of toxicities, and the concentration levels at which adverse health outcomes occurs vary (Darnerud, 2003). PBDEs are one of the most used compound groups of brominated flame retardants, and it is also one of the most studied. PBDEs are suggested to impact thyroid hormone levels; thyroid, liver, and kidney morphology; liver ethoxyresorufin-O-deethylase (EROD) activity; neurodevelopment and behavior; reproductive success, as well as fetal toxicity/teratogenicity (Domingo, 2012). Babies and young children are particularly vulnerable, and there are indications that PBDEs may act as neurotoxicants and endocrine disruptors (Costa L.G, 2008). However, information on the potential mechanisms of PBDE toxicity is still limited (Domingo, 2012).

1.4 PBDD/F - Polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans

**Figure 1.** 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TeCDD)

In more general terms, *dioxin* refer to one, or more, of the polychlorinated dibenzo-\(p\)-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), see Figure 1 (Wikoff et al., 2012). However, dioxins are not only open to chlorine substitution but also bromine substitution (WHO, 1998). Thus, the term *dioxin* can also include polybrominated dibenzo-\(p\)-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) (Figure 2). In the following text, the term dioxin will be used to describe PBDD/Fs.

**Figure 2.** The molecular structure of PBDD (left) and PBDF (right).
Dioxins have eight different positions available for bromination, and the abbreviations for the PBDD/F isomers with different degrees of bromination can be seen in Table 1).

Table 1. Abbreviations of PBDD/Fs.

<table>
<thead>
<tr>
<th>Number of bromine atoms</th>
<th>Dioxins (BDD)</th>
<th>Furans (BDF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoBDD</td>
<td>MoBDF</td>
</tr>
<tr>
<td>2</td>
<td>DiBDD</td>
<td>DiBDF</td>
</tr>
<tr>
<td>3</td>
<td>TriBDD</td>
<td>TriBDF</td>
</tr>
<tr>
<td>4</td>
<td>TeBDD</td>
<td>TeBDF</td>
</tr>
<tr>
<td>5</td>
<td>PeBDD</td>
<td>PeBDF</td>
</tr>
<tr>
<td>6</td>
<td>HxBDD</td>
<td>HxBDF</td>
</tr>
<tr>
<td>7</td>
<td>HpBDD</td>
<td>HpBDF</td>
</tr>
<tr>
<td>8</td>
<td>OBDD</td>
<td>OBDF</td>
</tr>
</tbody>
</table>

Compounds belonging to the same chemical family, and only differ in number and position of the same substituent are called congeners (Baird, 1999). Since dioxins are open to substitution at eight different positions, there exist a large number of congeners – theoretically 75 PBDDs and 135 PBDFs are possible. Dioxins can also be substituted by both chlorine and bromine atoms at the same time, which means that the number of theoretically possible congener becomes even higher, 1550 PXDDs and 3050 PXDFs (WHO, 1998). The numbers of isomers for the eight homologous groups of PBDD/Fs are listed in Table 2.
Table 2. Number of isomers for PBDDs and PBDFs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of isomers</th>
<th>Compound</th>
<th>Number of isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoBDD</td>
<td>2</td>
<td>MoBDF</td>
<td>4</td>
</tr>
<tr>
<td>DiBDD</td>
<td>10</td>
<td>DiBDF</td>
<td>16</td>
</tr>
<tr>
<td>TrBDD</td>
<td>14</td>
<td>TriBDF</td>
<td>28</td>
</tr>
<tr>
<td>TeBDD</td>
<td>22</td>
<td>TeBDF</td>
<td>38</td>
</tr>
<tr>
<td>PeBDD</td>
<td>14</td>
<td>PeBDF</td>
<td>28</td>
</tr>
<tr>
<td>HxBDD</td>
<td>10</td>
<td>HxBDF</td>
<td>16</td>
</tr>
<tr>
<td>HpBDD</td>
<td>2</td>
<td>HpBDF</td>
<td>4</td>
</tr>
<tr>
<td>OBDD</td>
<td>1</td>
<td>OBDF</td>
<td>1</td>
</tr>
</tbody>
</table>

1.4.1 Characteristics of PBDD/Fs

Dioxins are a group of almost planar, tricyclic aromatic chemicals with similar structure and chemical properties (WHO, 1998). In the following section, emphasis will be given to compare characteristics of PBDD/Fs and PCDD/Fs, as these in a later section will be compared with respect to their toxicity.

Despite the structural similarities, PBDD/Fs have slightly different behavior than PCDD/Fs, owing to the bromine atom being bigger than chlorine atom, and the bromine-carbon bond being weaker in strength than the chlorine-carbon bond (Birnbaum et al., 2003). Some of the known differences between PBDD/Fs and PCDD/Fs analogues are listed in Table 3.
Table 3. Comparison of the characteristics of PCDD/Fs and PBDD/Fs.

<table>
<thead>
<tr>
<th>Type</th>
<th>PCDD/Fs</th>
<th>PBDD/Fs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-halogen bond</td>
<td>Stronger (379 kJ/mol)</td>
<td>Weaker (276 kJ/mol)</td>
</tr>
<tr>
<td>(Kannan et al., 2012)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>(Li et al., 2005)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lipophilic</td>
<td>Generally less</td>
<td>Generally more</td>
</tr>
<tr>
<td>(Jackson et al., 1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensitive to UV-degradation</td>
<td>Less</td>
<td>More</td>
</tr>
<tr>
<td>(Birnbaum et al., 2003)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioaccumulative</td>
<td>Somewhat more</td>
<td>Somewhat less</td>
</tr>
<tr>
<td>(Diliberto et al., 1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Half-life</td>
<td>In general longer</td>
<td>In general shorter</td>
</tr>
<tr>
<td>(Ivens et al., 1990)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Even though PBDD/Fs are less water-soluble and more lipophilic than PCDD/Fs, it seems like the brominated dioxins are less environmentally persistent. The reason for this might be because bromine is a better leaving group than chlorine, and possibly, the higher UV-sensitivity for brominated dioxins can also be explained by bromine being a better leaving group (Birnbaum et al., 2003). The biochemical properties, such as susceptibility to enzymatic attacks, are also affected by the bigger size of the bromine atom (Birnbaum et al., 2003). Bromine shows lower resistance to photolytic reactions, and as a consequence, a lower portion PBDD/Fs will be persistent in soil, sediment and biota compared to PCDD/Fs (Naturvårdsverket, 2007). Brominated dioxins seem, nevertheless, to be more persistent towards mammalian metabolism (Birnbaum et al., 2003). According to Kannan et al (2012), there are no studies on how PBDD/Fs behave in the food chain. However, based on the properties of PCDD/Fs, brominated dioxins probably biomagnifies in the food chain.

PBDD/Fs have higher molecular weight and lower vapor pressure than analogous PCDD/Fs, which presumably means that they are less suited for atmospheric transport than PCDD/Fs (Kannan et al., 2012). Because of the low volatility, brominated dioxins also show high affinity to dust (Takigami et al., 2008).
1.4.2 Sources and formation of PBDD/Fs

PBDD/Fs are typical examples of unintentionally produced substances, and have no known commercial use (Wikoff et al., 2012). PBDD/Fs are unintentionally produced in various ways and at different conditions, depending on the precursors and the prerequisites. PBDD/Fs are formed during different stages of the lifecycles of several products and in various production processes.

For instance, PBDD/Fs are formed via bromide production (Li et al., 2007) and other industrial processes such as metallurgical industries (Wang et al., 2010b) and textile industries (Sedlak et al., 1998). PBDD/Fs can also be formed during the production and processing of some BFR mixtures, where PBDFs are the predominant congeners formed (Hanari et al., 2006; Ren et al., 2011). Even though e-waste recycling processes are on the latter stage of the life cycle of BFR treated products, it can be seen as an industrial source where formation and release of PBDD/Fs take place (Ma et al., 2009).

When plastic is subjected to treatment such as extrusion and molding, a thermal stress occurs. If the plastic contain some direct precursors, such as PBDEs, PBDD/Fs can be formed during thermal stress (Weber and Kuch, 2003). BFR-protected products can in itself be a source of PBDD/Fs through release of the unintentionally produced compounds, and PBDD/Fs can evaporate into the environment. For instance, when products such as TVs and hairdryers containing BFR become warm during use, PBDD/Fs evaporate (Sakai et al., 2001). PBDD/Fs are also formed via photo degradation which occur when plastic materials containing brominated flame retardants (i.e. PBDEs) are exposed to UV radiation. The dominant congeners formed from photo degradation processes are different kinds of PBDFs (Kajiwara et al., 2008).

Combustion of plastics containing brominated compounds, typically brominated flame retardants, is a major source of PBDFs (Li et al., 2007). The term combustion in this aspect can be divided into controlled combustion (or incineration) and insufficient combustion. The conditions of the combustion process are of great importance for the amount of PBDD/Fs formed (Weber and Kuch, 2003).

During controlled combustion, BFRs can be destroyed and can not act as precursors for PBDD/Fs. For achieving controlled combustion, the temperature must be above 850°C, and the residence time must be a little bit less than 2 seconds with a sufficient turbulence for mixing oxygen and gas in the combustion area. During controlled combustion, the precursor pathway
is expected to have little effect on the formation of PBDD/Fs. However, PBDD/Fs will still be formed, primarily by fly ash catalyzed de novo synthesis (Weber and Kuch, 2003). In the de novo synthesis, PBDD/Fs are formed from fragments of precursor BFR-molecules or from pure elements. This is a long pathway of reactions, resulting in small amounts of dioxins (Lundstedt, 2009). The incineration of electronic waste (TV sets, circuit boards, cables) is a particularly distinctive source of emission of PBDD/Fs (Sakai et al., 2001). In industrial areas specializing in manufacture of electric machines and equipment, the proportion of PBDD/Fs relative to PCDD/Fs in ambient air increases, which strengthens the relationship between PBDD/Fs and BFRs (Li et al., 2008; Wang et al., 2008). During combustion, or other anthropogenically related processes, the brominated dioxins formed are mostly PBDFs and highly substituted (tetra- to hepta) congeners (Kannan et al., 2012).

Accidental fires and uncontrolled combustion is referred to the term insufficient combustion. Although insufficient combustion may involve incomplete destruction of halogenated brominated compounds, it is assumed that the formation of PBDD/Fs is similar to the pathways in controlled combustions (Weber and Kuch, 2003). Accidental fires can produce considerable amounts of PBDD/Fs yielding foremost local contamination (Ebert and Bahadir, 2003; Litten et al., 2003; Söderström and Marklund, 1999; Zhang et al., 2016) where the concentrations of PBDD/Fs can be significantly higher than the concentration of PCDD/Fs (Lundstedt, 2009). The emissions from accidental fires can also make way for atmospheric transportation. Recycling activities, such as open burning of e-waste for recovery of metals, in developing and transition countries, are sources of emission to take into consideration (Sindiku et al., 2015).

Depending on the molecular appearance of the brominated flame retardant, the formation pathways will be different. A summary of different formation pathways is shown in Figure 3.
There are also studies reporting on PBDD/Fs in the Baltic Sea originating from natural formation in marine environment. The naturally formation of brominated dioxins yield mainly di-tetraBDDs (Haglund et al., 2007; Löfstrand et al., 2010; Malmvärn et al., 2005; Malmvärn et al., 2008; Unger et al., 2009). Even though these congeners are formed in a natural way, they may still exhibit toxic properties and have an effect on human health (Haglund et al., 2007).

1.4.3 Environmental distribution and concentrations of PBDD/Fs
In comparison to other POPs, information about PBDD/Fs in the environment is limited. The first publication on the occurrence of PBDD/Fs in the environment came in the early 1990s (Wiberg et al., 1992). Although the current knowledge may be somewhat limited, brominated dioxins have been found in several matrices such as in ambient air, plastics, flue gas, fly ash, sediments, diet samples, shellfish and fish, adipose tissue, human milk and in blood from people with occupational exposure (Kannan et al., 2012).
A summary of the findings of PBDD/Fs in selected matrices are given in the following text:

**Water.** The levels of PBDD/Fs were measured in the lower part of Hudson River, New York, after the World Trade Center (WTC) disaster in 2001. It is the only study that reports on levels of brominated dioxins in water. In runoff water samples from the WTC site (n=2), the concentration ranged from 263 to 5300 (mean 2 780) pg/L. In the Hudson River, the total concentration of tetra- to hexa-BDD/Fs in ambient water (n=15) ranged from 0.06 to 5.2 (mean: 1.4) pg/L. In both measurement sites, the concentration of PBDF was higher than PBDD (Litten et al., 2003).

**Air (outdoor).** There are several studies reporting on the presence of brominated dioxins in outdoor air. Studies conducted in rural, urban and industrialized areas in Taiwan showed air concentrations of tetra-hexa-BDD/Fs ranging from 0.01-0.10 pg/m³ (Wang et al., 2008), and in air around municipal solid waste incinerators was the average concentration 0.42 pg/m³ (Wang et al., 2010a; Wang et al., 2008; Wang et al., 2010b). Studies in Japan showed that PBDFs were the predominant compounds in ambient air, and that PBDDs were detected at only trace levels (Hayakawa et al., 2004). A study in Shanghai reported that 2,3,7,8-TeBDD was detected in 72% of the air samples (Li et al., 2008).

**Air (indoor).** Measurements carried out in rooms containing electronic equipment (i.e. computers, TV sets etc.), showed levels of PBDFs in concentrations ranging from 0.23 to 1.27 pg/m³ (WHO, 1998), and occurrence of PBDD/Fs has also been reported in air samples from car interior (Mandalakis et al., 2008).

**Indoor dust.** PBDD/Fs have been detected in indoor dust from offices, homes and e-waste facilities (Ma et al., 2009; Suzuki et al., 2010; Takigami et al., 2008), where the possible sources were emissions from electronic equipment. A study of plastic components (cabinets and circuit boards) from TV sets showed an average concentration of 9600 ng/g of PBDFs, and 460 ng/g of PBDDs. In the same study, the average concentration of PBDFs in dust from inside the TVs was 410 ng/g (Takigami et al., 2008). The levels of brominated dioxins in indoor dust were lower than in dust from electronic appliances, but despite this, it is possible that indoor dust is a major exposure pathway of PBDD/Fs to humans (Kannan et al., 2012).

**Soil.** Studies of soil from various areas indicate that local sources are critical for the levels of brominated dioxins detected in soil. Possibly, photo-
degradation of PBDD/Fs can also affect the concentrations in soil. Examination of the soil at an e-waste recycling facilities and at a chemical-industrial complex, both in China, showed high levels of PBDFs and lower levels of PBDDs. In contrast, the same studies presented results for soil from urban and rural areas in China that showed no detectable concentrations of PBDD/Fs (Ma et al., 2009; Ma et al., 2008).

**Sediment.** There are reports from several countries showing PBDD/Fs in sediments, and they exhibit similar degree of contamination. The highest concentration were found in sediments near industrialized areas, and there were also places where PBDD/Fs were not detected at all (Haglund, 2010; Litten et al., 2003; Ren et al., 2009; Terauchi et al., 2009; Unger et al., 2009). Sediment from Tokyo Bay, Japan, was analyzed for PBDD/Fs and the highest concentration was 0.27 pg TEQ/g dry weight (Goto et al., 2017).

**Biota and food.** There are several examples where PBDD/Fs have been detected in various biological samples; shellfish, blue mussels, shrimps, brown algae, cyanobacteria, sponge, milk and eggs. Samples were taken in China, Japan, United Kingdom, Ireland and the Baltic Sea showing that PBDD/Fs seem to have a wide geographical distribution (Ashizuka et al., 2008; Ashizuka et al., 2005; Fernandes et al., 2008; Haglund, 2010; Miyake et al., 2008; Skinner, 2011). Some of the concentrations, e.g. in Chinese seafood, were so high that they may pose health risks to consumers (Miyake et al., 2008). Studies in the Baltic Sea indicate that lower brominated PBDDs (di-tetra) are naturally produced, but even if these substances have a natural origin they may affect organisms (Arnoldsson, 2012). A report from the Swedish Environmental Protection Agency showed that PBDFs was detected in almost all samples of biota (Naturvårdsverket, 2011).

**Human exposure.** There are studies on PBDD/Fs exposure of the general population, but they are relatively few in number so the information is limited. One of the earliest reports describe the concentration of 2,3,7,8-TeBDD in a blood sample from a chemist who 34 years earlier had synthesized 2,3,7,8-TBDD in laboratory experiments. The samples showed concentrations of 2,000 ppt 2,3,7,8-TBDD (Schecter and Ryan, 1990). In a German factory, the employees exposure to PBDD/Fs during extrusion blending of resins containing PBDEs were studied by Zober et al. (1992), and the results showed that concentrations in blood from the 42 participants ranged from non-detectable to 112 ppt for 2,3,7,8-TBDF, and from non-detectable to 448 ppt for 2,3,7,8-TBDD. In a Japanese study the concentrations of PBDD/Fs in human adipose tissue between 1970 (n=9) and 2000 (n=7) were compared, where the sum of 2,3,7,8-TeBDD, 2,3,7,8-
TeBDF and 2,3,4,7,8-PeBDF showed a range from 3.4-8.3 pg/g lipid weight in 1970 and 1.9-5.3 pg/g lipid weight in 2000. According to the study, it was not possible to see any significant correlation between the concentrations of PBDD/Fs and the increased use of PBDEs during the period 1970-2000 (Choi et al., 2003). In a Swedish study, it was possible to detect PBDFs in all human adipose tissue samples (n=9), while PBDDs were below the detection limit. The highest concentration was found for 2,3,7,8-TeBDF, ranging from 0.3-2.4 pg/g lipid weight (Ericson Jogsten et al., 2010). In a study from Germany, blood samples from 42 randomly selected study participants were analyzed for PBDD/Fs and showed a median of 2.8 pg PBDD/Fs TEQ/g lipid weight (Fromme et al., 2016). In human breast milk, PBDD/Fs have been detected in samples from Vietnam, Ireland, Belgium, Sweden and Japan (Brorström-Lundén et al., 2010; Croes et al., 2013; Ohta et al., 2004; Pratt et al., 2013; Tue et al., 2014). PBDD/Fs were also detected in a study analyzing a pooled sample comprising of human milk samples from 17 countries (Kotz et al., 2005). The reported concentrations varied in the studies, for instance Tue et al. (2014) presented a maximum ΣPBDD/F concentration of 1.5 pg/g l.w. while Ohta et al. (2004) presented an average ΣPBDD/F concentration of 269 pg/g l.w.

When comparing the prevalence of PBDD/Fs in abiotic samples (water, air, dust, soil, sediment), the presence of PBDFs were higher than of PBDDs, and lower brominated congeners (mono-to tri-BDD/Fs) had a relatively moderate contribution to the total PBDD/Fs concentrations (Kannan et al., 2012). Samples from biota showed a dominance of tetra and penta substituted PBDD/Fs, even though the proportion between each homologous group varies for different organisms and animals, which may be owing to different metabolic effects (Kannan et al., 2012). In human samples, the PBDFs are more common compared to PBDDs, and 2,3,7,8-TeBDF, 1,2,3,4,6,7,8-HpBDFs and 2,3,7,8-TeBDD are typically the most common congeners (Choi et al., 2003; Croes et al., 2013; Ericson Jogsten et al., 2010; Kotz et al., 2005; Ohta et al., 2004; Pratt et al., 2013; Tue et al., 2014).

1.4.4 Toxicological and health effects of PBDD/Fs

PBDD/Fs exhibit similar toxicity as their chlorinated analogues (Birnbaum et al., 2003). However, the chlorinated dioxins are more studied and their effects are described more, so this section will describe both chlorinated and brominated dioxins.
1.4.4.1 Toxicity of chlorinated dioxins and furans

Chlorinated dioxins are considered as one of the most toxic man-made substances, because of the low dose required to cause lethality (even though not leading to an instant death) (Birnbaum, 1994). When dioxin and its toxic properties are discussed, the 2,3,7,8-TeCDD congener is used as a model compound since it is the most toxic congener (Devito, 2012). Exposure to dioxins can cause several serious health outcomes such as severe wasting, thymic atrophy, teratogenesis, reproductive effects, chloracne, immunotoxicity, enzyme induction, decreases in T4 and vitamin A, and increased hepatic porphyrins (Birnbaum, 1994; Birnbaum et al., 2003). One effect of severe dioxin exposure is chloracne, a condition that is extremely persistent and easily identified. There are examples of chloracne which lasted for more than 30 years (Birnbaum, 1994). According to Birnbaum (1994), the biochemical effects of 2,3,7,8-TeCDD can be grouped into three classes:

- altered metabolism resulting from changes in enzyme levels.
- altered homeostasis resulting from changes in hormones and their receptors.
- altered growth and differentiation resulting from changes in growth factors and their receptors (Birnbaum, 1994).

The various symptoms of the diseases caused by exposure to chlorinated dioxins are mediated through the Aryl hydrocarbon (Ah) receptor pathway (Birnbaum, 1994). The Ah receptor is an ubiquitous, high affinity protein that responds to planar aromatic ligands (e.g. 2,3,7,8-TeCDD) by forming an active complex (McFadyen et al., 2003). The activated complex binds to a specific position on DNA, and probably function as transcriptional enhancers (Birnbaum, 1994). Several parts of the normal growth, development and differentiation, as well as hypoxia, aging and circadian rhythms are regulated by the Ah receptor (Wikoff et al., 2012).

Dioxin is absorbed in the gastrointestinal tract and transported into the systematic circulation. It then binds into lipid rich tissue, accumulates and/or is eliminated. The elimination of dioxin is affected by the amount of body fat (the less body fat the faster elimination) and metabolism. Degradation rate varies among species and even within species (Wikoff et al., 2012).
1.4.4.2 Toxicity of brominated dioxins and furans
Chlorinated dioxins and brominated dioxins have many similar characteristics, and this also applies to their affinity to the Ah receptor (Mennear and Lee, 1994). Although the studies and knowledge of the toxic properties of PBDD/Fs are limited, the toxic properties shown – e.g. lethality, wasting, thymic atrophy, teratogenesis, reproductive effects, chloracne, immunotoxicity, enzyme induction, decreases in T4 and vitamin A, and increased hepatic porphyrins – are the same as for chlorinated dioxins (Birnbaum et al., 2003).

The most toxic congeners have four bromine substituents in the 2,3,7,8-positions. The toxicity of PBDD/Fs increases from none to four brominated substituents, and decreases from five to eight bromine substituents (Kannan et al., 2012).

If comparison of the toxicity between 2,3,7,8-TeBDD and 2,3,7,8-TeCDD is based on mass, it turns out that 2,3,7,8-TeCDD is approximately twice as potent as 2,3,7,8-TeBDD. But if the comparison is based on a molar basis, it appears that 2,3,7,8-TeCDD and 2,3,7,8-TeBDD are equally potent (Nagao et al., 1990).

1.4.4.3 Toxic Equivalence Factors – TEFs
There are major challenges in assessing risks of chemicals, and usually there are a number of uncertainties involved. It is also complex to estimate the exposure of a substance, as it may involve different pathways, such as dietary, dermal, inhalation and the rate of this exposure (Devito, 2012).

To be able to conduct risk evaluations of PCDD/Fs, the method of Toxic Equivalence Factors (TEFs) was developed (Safe, 1990). The model is based on the relationship between congeners and their ability to mediate biological and toxic effects in various in vitro and in vivo test systems (Kannan et al., 2012). In order to grade the toxicity of PCDD/Fs, relative potency factors (REP) were determined for individual PCDD/F congeners. The relative potency factors estimates a relative potency compared with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the prototypical congener for this class (Devito, 2012).

According to Kannan et al (2012), the TEF values are estimated according to the following guidelines:

TEF values have been calculated by comparing the ratio of the molar dose of TCDD to produce a 50% effect for a given toxic or biochemical end point to the molar dose of the chemical required to generate a 50% effect.
A panel of experts assesses the REP values and gives the substance a specific TEF value, which is used to more easily compare the toxicity of different dioxins. The TEF values and method have been evaluated and corrected since the late 1980s. Table 4 shows the WHO 2005 TEF values (Devito, 2012).

Table 4. Toxic Equivalency Factors. According to WHO 2005 (Devito, 2012)

<table>
<thead>
<tr>
<th>PCDDs</th>
<th>WHO 2005 TEFs</th>
<th>PCDFs</th>
<th>WHO 2005 TEFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3,7,8-TCDD</td>
<td>1</td>
<td>2,3,7,8-TCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>1</td>
<td>1,2,3,7,8-PeCDF</td>
<td>0.03</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDD</td>
<td>0.1</td>
<td>2,3,4,7,8-PeCDF</td>
<td>0.3</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDD</td>
<td>0.1</td>
<td>1,2,3,4,7,8-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
<td>0.1</td>
<td>1,2,6,7,8-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.01</td>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>OCDD</td>
<td>0.0003</td>
<td>2,3,4,6,7,8-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OCDF</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

In a mixture of different congeners, it is relevant to provide an estimate of the total potential toxicity, and because of that the term toxic equivalent quantity (TEQ) was introduced. With 2,3,7,8-TeCDD being the model congener, the total potency of a mixture of dioxins can be expressed as:

\[
\text{TEQ} = \sum (\text{Compound}_1 \times \text{TEF}_1 + \text{Compound}_2 \times \text{TEF}_2 + \ldots + \text{Compound}_n \times \text{TEF}_n)
\]

(Kannan et al., 2012)

The TEF model has its limitations and challenges. The TEF methodology uses a single TEF value for all end points and for all mammals, including humans. Some argue that it is unlikely that a single factor can describe the relative potency of a chemical for all end points and all species. In addition, there is a discussion about the fact that the TEF methodology only provides an estimation of the potential health effects of dioxin or dioxin-like chemical. It does not take into account exposure to any other chemicals, and the health effects different combinations may cause (Devito, 2012). On the basis of current knowledge, for human risk assessment it is recommended to use similar Toxic Equivalent Factors for both brominated and chlorinated congeners (van den Berg et al., 2013).
2 Methods

To achieve the aim of the thesis, i.e. to provide a better understanding of the occurrence of PBDD/Fs from source of emission to human exposure, a number of matrices were selected.

In Paper I, gas and soot particles were considered as relevant matrices for studying the occurrence of PBDD/Fs during firefighting of replicated scenarios of accidental fires. Besides providing information about the occurrence of PBBD/F at a point source of emission, gas and soot particles can also give an indication of PBDD/Fs’ availability for atmospheric transport. Moreover, it is relevant to analyse the concentration of PBDD/Fs in soot particles as they remain on surfaces after the accidental fire is extinguished, and may cause occupational exposure to persons who regularly work on the site of an accident fire, such as firefighters, demolition workers and cleaners.

In marine mammals, the lipid reserves serves as depositories for lipophilic compounds, and more than 90% of the total body load of lipophilic contaminants can be found in the blubber (Nyman et al., 2003; Yordy et al., 2010). Therefore, blubber was considered suitable for studying the occurrence of PBDD/Fs in pilot whales (Paper II) and ringed seal (Paper III). Findings of PBDD/Fs in pilot whales around Faroe Islands can possibly verify that PBDD/Fs are transported long distances to far remote areas via atmospheric transport. Moreover, since pilot whales are a part of the Faroese traditional diet (Hoydal et al., 2015), findings of PBDD/Fs provide information about human exposure. The findings of PBDD/Fs in Baltic ringed seal can provide important information about the occurrence of PBDD/Fs in marine food webs near anthropogenic sources and that are related to human food webs.

In Paper IV, human milk was chosen to study the human exposure to PBDD/Fs. One reason why human milk was considered a relevant matrix, is that the concentration of lipophilic POPs in human milk gives an estimation about the accumulated concentrations in the adipose tissue of the breast-feeding mothers (Norén and Meironyté, 2000). Moreover, for breast-fed babies, the human milk is a major source of exposure to lipophilic POPs (Barr et al., 2005; Ingelido et al., 2007; Lakind et al., 2000; Pratt et al., 2013).
2.1 Extraction and clean-up of PBDD/Fs

Before extraction, all samples were spiked with $^{13}$C-labelled internal standards. In Paper I, the gas and soot samples from the fire tests were extracted with toluene during a 24 h reflux in Soxhlet extractors. In Paper II and Paper III, the blubber from pilot whales and ringed seals were homogenized with anhydrous Na$_2$SO$_4$, and the homogenate was transferred to open columns, and the lipids were extracted using a volume of approximately 150 ml of n-hexane:dichloromethane (1:1). In Paper IV, K$_2$C$_2$O$_4$-saturated ethanol was mixed with the milk, followed by liquid-liquid extraction (three times) with diethyl ether/n-hexane (7:10). In Paper II-IV, the amounts of lipids were determined gravimetrically, and was used for lipid adjustment of the PBDD/F concentrations. In Paper I, the sampled gas volume (m$^3$) and the area wiped for soot (m$^2$) were used for adjustment of the PBDD/F concentration. Regardless of the extraction applied, the same clean-up procedure was adapted for all samples.
Figure 4. Schematic overview of the clean-up procedure.

The schematic overview of the clean-up process is shown in Figure 4, and the composition of the used open columns is shown in Figure 5.
During extraction and clean-up, amber colored glassware or glassware covered with aluminum foil, was used to avoid photolytic degradation of the brominated compounds. Addition of $^{13}$C-labelled recovery standards was performed prior to instrumental analysis. The extracts were kept in toluene and stored in a freezer (-20°C) before analysis.

### 2.2 Instrumental analysis and quantification of PBDD/Fs

For PBDD/Fs, high-resolution gas chromatography high-resolution mass spectrometry (HRGC/HRMS) analysis was performed on a Micromass Autospec Ultima operating at 10 000 resolution using electron ionisation at 35 eV. The source temperature was 250°C, the trap current 500 μA, the detector voltage 450 V and the transfer line temperature 280°C. All measurements were performed in the selective ion recording mode (SIR), monitoring the two most abundant ions of the molecular bromine cluster. Quantification was performed using the isotope dilution method. The method is based on the assumption that the labeled standard and the analyte exhibit identical chemical and physical behavior at all stages during the analysis.
PBDD/Fs are sensitive to high temperatures, so the analytical method was adapted to minimize thermal degradation. By using columns with a thin stationary phase, a lower elution temperature can be achieved, and the analyte spends less time in the heated stationary phase. Even injection techniques need to be adapted to counteract degradation, and to meet this, Programmed Temperature Vaporiser (PTV) was used. The starting point for the PTV is simple: by increasing the sample volume, the detection limits of analytical methods can be improved (Engewald et al., 1999). Usually, volumes injected in split/splitless and on-column injectors are around 1-3 µl. The PTV can inject volumes up to 10 ml (Tollbäck et al., 2003). PTV is basically structured like a classic split/splitless injector, but is also equipped with a fast and efficient cooling and heating system. In the PTV injection, the sample is injected at a temperature that is below the boiling point of the solvent. Thereafter, the PTV is heated rapidly to a defined temperature, high enough to completely evaporate the entire sample (Engewald et al., 1999). As the analytes vaporize, they are transferred into the column in the order of boiling points, where they are focused into a sharp starting band. The gradual heating minimizes decomposition of sensitive sample components (Björklund, 2003).

For analysis of PBDD/Fs, PTV injection was used to apply 7 µL of extract onto a 15 meter (0.25 mm i.d, 10 µm) DB-5MS column (J&W Scientific; Folsom, CA, USA). The oven temperature program proceeded as follows: initial temperature of 100°C (held for 1.25 minutes) followed by several temperature increases: 13°C/min to 170°C; 35°C/min to 240°C; 10°C/min to 300°C; and finally 20°C/min to 325°C followed by a constant temperature for 4.20 minutes. The PTV settings were as follows: an initial temperature of 110°C (held for 0.25 minutes) followed by an increase of 700°C/min to 325°C (held for 5 minutes). By using columns with relatively short lengths, i.e. 15 m, there was a risk of co-elution and possibly overestimation of some congeners. However, essentially all traces for dioxin congeners detected in the samples corresponded to their matching internal standards. Therefore, the risk of overestimation owing to co-elution was considered low.

All concentrations from Paper I-IV refer to lower bound concentrations, which means that for concentrations below limit of detection, a value of zero was used. Upper bound concentrations are shown in the supplementary material for Paper I-IV.
2.3 Quality assurance and quality control

Isotope ratios and retention time match were used to confirm the identity of the analytes. For two ions of a molecular ion cluster, the isotope ratio was set to be within ±15% for positive identification. For retention time match, the retention time for native compounds had to be within ±2 s compared to the internal standard. Ideally, the recovery of the internal standard should be within 50-120% range, but for a few congeners, this criterion was not met and concentrations for these congeners are highlighted with their corresponding recovery can be found in the supplementary material for Paper I-IV. Method detection limits were calculated based on a signal-to-noise ratio of 3. An extraction blank was prepared and analyzed for every batch of samples extracted, and the number of samples in each batch ranged from 5-8. The contribution from PBDD/Fs in the blanks were too low to affect the results, therefore no consideration had to be taken to the content of PBDD/Fs in the blanks. In Paper IV, an in-house reference sample was included in each batch. For the in-house reference samples, the relative standard deviation ranged from 1-41% for PBDD/Fs. The wide range of relative standard deviation identified for PBDD/Fs was related to low concentrations of some congeners, which approached the limit of detection and cause substantial uncertainty. The MTM Research Centre regularly takes part in inter-laboratory comparison studies of PCDD/Fs, PCBs, PBDEs and OCPs in biological and environmental samples to ensure the quality of analysis. In the Interlaboratory Comparison Study UNEP 2016, MTM Research Centre obtained 81% satisfactory results for the 168 reported DL-POPs and 91% satisfactory results for the 32 reported PBDEs. For the UNEP 2016 test material, satisfactory results deviated ±25% from assigned values.
3 Results and discussion

The extraction and clean-up of PBDD/Fs is relatively extensive, and it provides the possibility to include traditional environmental compounds in the same process. In all four papers, legacy environmental pollutants were included to be able to verify their concentrations compared to the scientific literature and to investigate whether there were correlations between PBDD/Fs and other compound groups. However, in this thesis, the results and discussion will focus mainly on PBDD/Fs. For result and discussion concerning other POPs, see Paper I-IV. In addition to PBDD/Fs, the following legacy environmental pollutants were included in the studies:

- Paper I – PCDD/Fs.
- Paper II – PCDD/Fs and PBDEs.
- Paper III – PCDD/Fs, PBDEs and polychlorinated biphenyls (PCBs)
- Paper IV – PCDD/Fs, PCBs, BDE #47 and organochlorine pesticides (OCPs).

3.1 Occurrence of PBDD/Fs at an accidental fire site – a typical point source (Paper I)

3.1.1 Background information about the tests

Four different firefighting methods were evaluated in Paper I:

- Nozzle, using water spray.
- Compressed Air Foam System (CAFS) using foam intended for fibrous fires.
- Cutting extinguisher system (see Figure 7)
  - using water only
  - using water with an extinguishing additive.

In total, five tests were performed. The cutting extinguisher system using water with extinguishing additive was repeated once, with the aim to identify variables that might differ owing to external circumstances rather than firefighting method. See Table 5 for further details regarding the tests.
Table 5. Test ID, information and descriptive data from the five fire tests.

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Firefighting method</th>
<th>Extinguishing agent</th>
<th>Extinguishing additive</th>
<th>Volume (litres)/Number of re-ignitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>Nozzle</td>
<td>Water – spray</td>
<td>-</td>
<td>121/22</td>
</tr>
<tr>
<td>Test 2</td>
<td>Cutting extinguisher</td>
<td>Water – fog</td>
<td>-</td>
<td>65/4</td>
</tr>
<tr>
<td>Test 3</td>
<td>Compressed air foam system</td>
<td>Foam</td>
<td>-</td>
<td>45/1</td>
</tr>
<tr>
<td>Test 4</td>
<td>Cutting extinguisher</td>
<td>Water – fog</td>
<td>X-FOG</td>
<td>21/0</td>
</tr>
<tr>
<td>Test 5</td>
<td>Cutting extinguisher</td>
<td>Water – fog</td>
<td>X-FOG</td>
<td>28/0</td>
</tr>
</tbody>
</table>

Since the aim of Paper I was to compare different firefighting methods’ ability to rapidly decrease flue gas temperatures during firefighting and also the formation of dioxins, each test was divided into a fire phase and extinguishing phase (see Figure 6). Gas and soot were sampled both during fire phase and extinguishing phase. The combustion gases were sampled using glass tubes filled with XAD-2 adsorbent connected to pumps, and a prefilter before the adsorbent made sure that no soot particles got into the adsorbent. Soot particles were sampled from stainless steel plates.
Figure 6. Graph from Test 5 exemplifies how the temperature (°C) evolves in relation to time from ignition. The “fire phase” was defined as the time from ignition to flashover, while the “extinguishing phase” was defined as the time from approximately ten seconds after the flashover, when the extinguishing started, and lasted for five minutes.
Figure 7. The cutting extinguisher system, in standby and in use. In the picture to the right, note the heat camera mounted on the tripod that was used to determine the extinguishing progress. Also, in the picture to the right, note the plate in the upper left corner that was used for soot sampling. Within seconds after the photo was taken, the plate was placed in the upper part of the container opening to collect soot particles during the extinguishing phase. Photos: Mikael Linder, In to Fire & Water.
To compare the firefighting methods, containers with identical set up of furniture, interior and electronic equipment were used to resemble a small living room in an apartment (Figure 8).

Figure 8. Identical set up of combustible material was used in all five tests. To the right of the picture is a bottle of ignition fluid, which was only used to set fire to the ignition wood block. In each test, the ignition block was placed underneath the front right corner of the sofa. Photo: Mikael Linder, In to Fire & Water

The change in temperature during the tests are shown in Figure 9, and also the application of extinguishing agent. The time from ignition to flashover differed between the tests, see Table 6. In Figure 9, the time is normalized against the start of extinguishing to simplify the graphical comparison between the tests, i.e. the start of the extinguishing is set to t=0. The temperature zone from 250-350°C is of special interest due to possible formation of PBDD/Fs through de novo synthesis (Huang and Buekens, 1995; Ortuño et al., 2014; Stieglitz, 1998; Weber, 2002), and is therefore marked in Figure 9.
Figure 9. Temperature changes in flue gases in the containers during the tests, normalized to the start of the extinguishing phase. Due to technical difficulties, the temperature at the point of flashover could not be properly measured. Red symbols represent application of extinguishing agent. The grey field highlights the temperature span 250-350°C, where de novo synthesis is probably the dominant formation pathway.
3.1.2 Results from the fire phase

The results from the fire phase showed that even though major efforts were made to create identical conditions for the tests, the concentrations varied between the tests. In the gas samples, the concentrations of $\Sigma$PBDD/Fs ranged from 4000-18700 pg/g m³, while the soot samples ranged from 220-390 pg/g m² (Table 6). One explanation to the wide range is that fires are turbulent and dynamic processes, and compounds and concentrations can vary even within a smoke plume (Blomqvist, 2005), and it is therefore hard to characterize emissions from fires. Moreover, the tests indicate an association between the wind direction and concentrations of PBDD/Fs. It is reasonable to assume that if the wind direction is heading into the container, the wind enhances the supply of oxygen and thereby increase the progress of the fire. The wind direction in relation to the container opening and the concentrations of $\Sigma$PBDD/Fs for all five tests are shown in Table 6. As seen in Table 6, the two tests with the wind direction heading into the container opening (test 3 and 4), had the highest concentration of $\Sigma$PBDD/Fs of all gas samples collected during fire phase. The concentration of $\Sigma$PBDD/Fs in gas during fire phase was approximately five times higher in test 4 compared to test 1. Table 6 also shows that the wind direction seems to affect the time from ignition to flashover, where test 3 and 4 had the shortest time from ignition to flashover. It is notable that the fire progress was approximately twice as fast in test 4 compared to test 1. In total, this suggest that when the wind direction was heading into the container opening it increased the fire’s growth rates which in turn resulted in increased concentrations of PBDD/Fs.

Comparing the results from the fire phase, using visual inspection of the data, there was no correlation between the gas and soot samples. A possible explanation is related to the placing of the plates used for soot sampling. During the fire phase, the plate was placed in the upper part of the container opening. Since the last part of the fire phase consisted of a few seconds of flashover, the plate was hit by heat and flames that broke out of the container opening, see Figure 7. It is reasonable to assume that some of the compounds condensed on the plate during the fire phase, was degraded owing to the flames that hit the plate the last part of the fire phase.

When comparing congener distribution, see Figure 10, the furans were the predominant congeners. In the gas samples, 1,2,3,4,6,7,8-HpBDF was the dominant congener while it was the second most dominant congener in the soot samples. In total, the congener distribution was similar in gas and soot samples with 1,2,3,4,6,7,8-HpBDD as an exception. While
1,2,3,4,6,7,8-HpBDD wasn’t detected at all in the gas samples, it was the dominant congener in the soot samples. A possible explanation to the different occurrence of PBDD/Fs in the gas and soot samples during fire phase, is that the plate, where the soot was sampled, enabled formation of 1,2,3,4,6,7,8-HpBDD via de novo synthesis.
Table 6. ΣPBDD/Fs for gas (pg/m³) and soot (pg/m²) samples and descriptive data from all tests.

<table>
<thead>
<tr>
<th></th>
<th>Gas, fire phase (pg/m³)</th>
<th>Gas, extinguishing phase (pg/m³)</th>
<th>Soot, fire phase (pg/m²)</th>
<th>Soot, extinguishing phase (pg/m²)</th>
<th>Wind direction in relation to container opening</th>
<th>Time from ignition to flashover (s)</th>
<th>Temperature drop, time from 350-250°C (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>4000</td>
<td>13500</td>
<td>390</td>
<td>4100</td>
<td>Varying, partly away</td>
<td>460</td>
<td>25</td>
</tr>
<tr>
<td>Test 2</td>
<td>4900</td>
<td>9600</td>
<td>280</td>
<td>1500</td>
<td>Varying, partly towards</td>
<td>446</td>
<td>14</td>
</tr>
<tr>
<td>Test 3</td>
<td>12100</td>
<td>6500</td>
<td>340</td>
<td>3300</td>
<td>Towards</td>
<td>344</td>
<td>10</td>
</tr>
<tr>
<td>Test 4</td>
<td>18700</td>
<td>7400</td>
<td>220</td>
<td>290</td>
<td>Towards</td>
<td>235</td>
<td>8</td>
</tr>
<tr>
<td>Test 5</td>
<td>7300</td>
<td>5400</td>
<td>250</td>
<td>1100</td>
<td>Calm</td>
<td>446</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 10. A box plot representation of congener distribution of PBDD/Fs detected in gas and soot samples during fire and extinguishing phase. Dark grey and light grey bars show lower and upper quartiles, respectively. The line between dark and light grey bars shows the median. Max and min concentrations are shown by whiskers. *1,2,3,4,7,8/1,2,3,6,7,8-HxBDD
3.1.3 Results from the extinguishing phase

During the extinguishing phase, the concentration of $\Sigma$PBDD/Fs ranged from 5400-13500 pg/m$^3$ in the gas samples, and from 1100-4100 pg/m$^2$ in the soot samples (Table 6). The different firefighting methods showed different results regarding how fast the temperature dropped from the start of extinguishing (see Figure 9), which also affected the temperature drop from 350-250°C (see Table 6). Test 1 showed the slowest temperature drop from 350-250°C, and the highest concentrations of $\Sigma$PBDD/Fs in both gas and soot samples were detected in Test 1. Studies suggests that the formation through de novo synthesis have the highest outcome when the temperature is around 300°C (Huang and Buekens, 1995; Ortuño et al., 2014; Stieglitz, 1998; Weber et al., 2002). A faster temperature drop from 350-250°C results in a reduced amount of time in the temperature zone 350-250°C where dioxin formation are favoured. A hypothetical assumption is that a faster temperature drop decreases the time when formation of PBDD/Fs through de novo synthesis is most efficient, and as a result decreasing amounts of PBDD/Fs formed is expected. In contrast to the results from Test 1, the tests that showed the fastest temperature drop from 350-250°C (Test 3, 4, 5), showed concentrations that were considerable lower. It is also worth noting that the gas samples from Test 1 during fire phase showed the lowest concentrations of all tests, but during extinguishing phase Test 1 showed the highest concentrations.

Since the number of tests are limited, the data should be interpreted with caution. However, using visual inspection of the data it is possible to identify an association between the temperature drop from 350-250°C and the concentration of $\Sigma$PBDD/Fs. It is possible that not all differences can be explained by the temperature drop from 350-250°C and the de novo synthesis, but it is reasonable to assume that the difference in concentrations can partly be explained by the temperature drop.

The congener profiles during extinguish phase, Figure 10, shows that furans are the dominants congeners in both gas and soot samples, and 1,2,3,4,6,7,8-HpBDF had the highest concentrations. In the gas samples, the concentrations of 2,3,7,8-TeBDD were comparable to concentrations of 2,3,7,8-TeBDF. Even though detected in low concentrations, 1,2,3,4,6,7,8-HpBDD was detected in low concentrations in four out of five soot samples. In the gas samples, 1,2,3,4,6,7,8-HpBDD was only detected in one sample. A possible explanation to the different congener profiles is that the plate used for soot sampling provided an effective condensation surface.
3.1.4 Comparing results from fire and extinguishing phase

The dominant congeners in the gas samples, both during fire and extinguishing phase, were 1,2,3,4,6,7,8-HpBDF, 2,3,7,8-TeBDF and 2,3,7,8-TeBDD. The concentration ranges of $\Sigma$PBDD/Fs in gas samples showed similar results during fire phase and extinguishing phase, 4000-18700 and 5400-13500 pg/m$^3$, respectively. High concentrations during fire phase didn’t correspond to high concentrations during extinguishing phase. For the gas samples collected during fire phase, the differences in PBDD/F concentrations were probably greatly influenced by the wind direction during the tests. However, during the extinguishing phase, the different firefighting methods were probably the main reason to the observed differences in PBDD/F concentrations between the tests. These assumptions are supported by the following observations regarding the gas samples; as seen in Table 6, Test 3 & 4 with the wind direction heading into the container opening, had concentrations during fire phase that were approximately three to four times higher compared to the corresponding concentrations in Test 1 & 2 that had a low impact from the wind direction. But during the extinguishing phase, Test 3 & 4 that had a fast temperature drop from 350-250°C, had concentrations that were approximately half to three quarters compared to corresponding concentrations in Test 1 & 2 that had a slow drop from 350-250°C.

In the soot samples, the congener profiles were similar during fire and extinguishing phase. The concentration of 1,2,3,4,6,7,8-HpBDD were comparable in fire and extinguishing phase, while the concentrations of furans were 3-16 times as high during the extinguishing phase. The concentrations of $\Sigma$PBDD/Fs in the soot samples were 4-13 times as high in the extinguishing phase compared to the fire phase. As mentioned earlier, an explanation to the low concentrations during fire phase is probably the last part of the phase when heat and flames hit the plate. The heat exposure of the plates is probably also the reason to why there was no association between wind direction and $\Sigma$PBDD/Fs in the soot samples during fire phase.

However, the effect of the wind direction can probably partly explain the different concentrations of PBDD/Fs detected in soot during the extinguishing phase. As seen in Figure 9 and Table 6, Test 3, 4, 5 showed similar temperature drop from 350-250°C, but the concentration of $\Sigma$PBDD/Fs were higher in Test 3 and 4. The wind direction in Test 3 and 4 was heading into the container opening, while the wind was calm during test 5. Possibly,
when the wind was heading into the container opening, it increased the turbulence of gases in the container and thereby possibly increased the production rate of the monitored compounds. Another possible explanation is that when wind headed into the container, more gas was pushed out of the container and as the gas hit and interacted with the plate, condensation processes increased.

3.1.5 Final remarks on the occurrence of PBDD/Fs at an accidental fire site

Even though the concentrations varied between samples, PBDD/Fs were detected in both gas and soot samples in all tests, during both fire and extinguishing phase. The dominant congener was 1,2,3,4,6,7,8-HpBDF, which showed the highest concentrations and was detected in all samples. When using the WHO 2005 TEFs, the contribution from PBDD/F TEQ to the total (PCDD/F+PBDD/F) TEQ ranged from 75-100% with an average of 97%.

The high contribution from PBDD/F TEQ to the total TEQ points out that accidental fires are a source of concern for PBDD/Fs, both regarding spreading to the environmental and occupational exposure. As PBDD/Fs are formed and emitted to the surrounding air during accidental fires, it is likely that both short and long range atmospheric transport of PBDD/Fs results from these kind of fires, as well as creating local PBDD/F contaminated hotspots close to the fire site. Moreover, the occurrence of PBDD/Fs indicate that firefighters, demolition workers and other professionals working at accidental fire sites should be made aware of the toxicity and characteristics of PBDD/Fs, to prevent or reduce occupational exposure.

The intention of the test design and the combustible material was that it would resemble a living room, but it is reasonable to assume that there are more chlorine-containing materials in a real living room, such as electrical outlet covers, plastic window frames and floorings containing plastic. Therefore, the contribution from PBDD/F TEQ to the total TEQ must be interpreted with caution. The use of extinguishing additive and foam induced a faster temperature drop from 350-250°C in the flue gases which seems to decrease the formation of PBDD/Fs. If only considering exposure to heat and dioxins, the use of extinguishing methods using additive or foam seems to be favourable in reducing firefighters’ occupational exposure. The wind direction seems to affect the growth rate of the fire. In turn, this may affect the formation processes of PBDD/Fs in gas, and thereby affecting the concentration of PBDD/Fs. However, it doesn't seem like the wind influenced the congener profile.
3.2 PBDD/Fs in marine mammals living in far remote areas (Paper II)

The study of PBDD/Fs in pilot whales (Paper II) was the first study concerning PBDD/Fs in marine mammals. Blubber from pilot whales were sampled around Faroe Islands (Figure 11) in connection with the traditional whale hunt, between 1997 and 2013. To restrict the variability in the data related to sex and age, thus simplifying comparison between the samples, only juvenile males were included in the study. When a male is shorter than 494 cm, it is classified as a juvenile male (Desportes et al., 1994). In total, 26 blubber samples from pilot whales (Globicephala melas) was analyzed (see Table 7) with a length range of 290-446 cm, which corresponds to immature males of approximately 7-8 years of age (Bloch et al., 1993).

Figure 11. Map showing sampling location of the pilot whales.
Table 7. Sample information regarding the pilot whales sampled around Faroe Islands.

<table>
<thead>
<tr>
<th>Sampling year</th>
<th>Length, median (cm)</th>
<th>Length, range (cm)</th>
<th>Sample information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>412</td>
<td>403-420</td>
<td>3 pooled samples, 5-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>individuals in each pool</td>
</tr>
<tr>
<td>2006</td>
<td>397</td>
<td>396-398</td>
<td>3 pooled samples, 5-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>individuals in each pool</td>
</tr>
<tr>
<td>2010</td>
<td>424</td>
<td>380-443</td>
<td>5 individual samples</td>
</tr>
<tr>
<td>2011</td>
<td>430</td>
<td>352-435</td>
<td>5 individual samples</td>
</tr>
<tr>
<td>2012</td>
<td>411</td>
<td>365-446</td>
<td>5 individual samples</td>
</tr>
<tr>
<td>2013</td>
<td>342</td>
<td>290-360</td>
<td>5 individual samples</td>
</tr>
</tbody>
</table>

Brominated dioxins and furans were detected in 20 of the 26 samples (Table 8). The samples in which PBDD/Fs were detected showed a wide concentration range of $\Sigma$PBDD/Fs, i.e. 0.08-71 pg/g l.w., with an average and median concentration of 6.6 and 1.9 pg/g l.w., respectively. Findings of PBDD/Fs have been reported in several studies concerning the marine environment, even though not in marine mammals (Fernandes et al., 2008; Fernandes et al., 2009; Miyake et al., 2008; Rose et al., 2015; Roszko et al., 2015; Skinner, 2011; Zacs et al., 2013).
Table 8. Concentrations of ΣPBDD/Fs in all pilot whale samples. Sample ID is given by the digit combination X:Y, where X represents the sampling year and Y represents the samples’ given number for that year.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>ΣPBDD/Fs (pg/g l.w.)</th>
<th>Sample ID</th>
<th>ΣPBDD/Fs (pg/g l.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997:1</td>
<td>0.08</td>
<td>2011:3</td>
<td>1.9</td>
</tr>
<tr>
<td>1997:2</td>
<td>0.09</td>
<td>2011:4</td>
<td>1.3</td>
</tr>
<tr>
<td>1997:3</td>
<td>ND</td>
<td>2011:5</td>
<td>ND</td>
</tr>
<tr>
<td>2006:1</td>
<td>0.27</td>
<td>2012:1</td>
<td>0.39</td>
</tr>
<tr>
<td>2006:2</td>
<td>8.7</td>
<td>2012:2</td>
<td>ND</td>
</tr>
<tr>
<td>2006:3</td>
<td>5.5</td>
<td>2012:3</td>
<td>ND</td>
</tr>
<tr>
<td>2010:1</td>
<td>71</td>
<td>2012:4</td>
<td>ND</td>
</tr>
<tr>
<td>2010:2</td>
<td>0.93</td>
<td>2012:5</td>
<td>0.41</td>
</tr>
<tr>
<td>2010:3</td>
<td>1.9</td>
<td>2013:1</td>
<td>6.1</td>
</tr>
<tr>
<td>2010:4</td>
<td>16</td>
<td>2013:2</td>
<td>6.6</td>
</tr>
<tr>
<td>2010:5</td>
<td>0.69</td>
<td>2013:3</td>
<td>4.8</td>
</tr>
<tr>
<td>2011:1</td>
<td>ND</td>
<td>2013:4</td>
<td>2.3</td>
</tr>
<tr>
<td>2011:2</td>
<td>0.42</td>
<td>2013:5</td>
<td>2.3</td>
</tr>
</tbody>
</table>

ND – Not Detected

One sample, 2010:1, showed very high concentrations (Table 8). For whales, higher concentrations of POPs are related to young age, but the juvenile male corresponding to sample 2010:1 is relatively long and is therefore not among the youngest whales in the study population. Neither can this whale’s higher concentrations of PBDD/Fs be explained by the area it was caught, as many of the studied whales included in Paper II was caught
at the same location. A possible explanation to the high concentration detected could be that this whale has been exposed through its diet or been suckled by a young mother with a high body-burden.

Figure 12. Congener distribution of PBDD/Fs in pilot whales shown as a box plot of the detected congeners. Dark grey and light grey bars show lower and upper quartile, respectively. The line between dark and light grey bars shows the median. Max and min concentrations are shown by whiskers. The detection frequencies are shown in brackets.

The PBDFs dominated the congener profiles, and 1,2,3,4,6,7,8-HpBDF was the most common congener and showed the highest concentrations (Figure 12). The fact that the most abundant congener was only detected in less than half of the samples, exemplifies the fact that PBDD/Fs was not ubiquitously occurring in the pilot whales. Even though PBDFs were the dominant congeners, 1,2,3,4,6,7,8-HpBDD was the second most common congener.
and also showing the second highest average concentrations. Several studies concerning PBDD/Fs in the marine environment have shown similar congener profiles (Fernandes et al., 2008; Fernandes et al., 2009; Rose et al., 2015; Roszko et al., 2015; Skinner, 2011; Zacs et al., 2013), and the profiles detected in the pilot whales are probably originating from combustion-related processes (Duan et al., 2011; Lundstedt, 2009; Sakai et al., 2001; Wang and Chang-Chien, 2007; Wang et al., 2010a).

The PBDD/F concentrations were low, often close to the limit of detection, which causes an uncertainty when interpreting the data. Moreover, since the number of samples are limited and they cover a wide time span, it is difficult to draw general conclusions concerning temporal and spatial trends. The samples from 1997 showed lower concentrations compared to the samples from 2006 and 2010-2013, which might indicate increasing concentrations in pilot whales during the studied period.

PCDD/Fs were analyzed in 10 samples, and the analyzed samples showed similar concentrations of PCDD/Fs and PBDD/Fs, however, due to differences in congener profiles the TEQ differed widely. The contribution of PBDD/F TEQ to total (PCDD/F+PBDD/F) TEQ ranged from 0-49% with an average and median contribution of 8.2% and 1.6%, respectively. PBDEs were analyzed in the samples from 2010-2013, and no association was seen between the concentrations of PBDD/Fs and PBDEs.

To summarize, the findings of PBDD/Fs in blubber from pilot whales sampled around the Faroe Islands, proves that PBDD/Fs are occurring among marine mammals in far remote areas. Moreover, the findings indicating that PBDD/Fs, as their chlorinated analogues, have the ability to be spread over vast areas owing to long range atmospheric transport. The limited number of samples and low concentrations, often close to limit of detection, hampers the possibility to draw general conclusions regarding temporal trends. Possibly, an increase of PBDD/Fs concentration could be observed between 1997 and around 2010. The low concentrations of PBDD/Fs in the sampled pilot whales implies that PBDEs and PCDD/Fs can cause a more serious threat to the pilot whales studied. Since pilot whales are a part of traditional Faroese diet, the findings of PBDD/Fs indicate that the human exposure through pilot whales should be investigated further.
3.3 PBDD/Fs in marine mammals living near anthropogenic sources (Paper III)

As a result of geographical and hydrological characteristics, the Baltic Sea is vulnerable to anthropogenic input (Szlinder-Richert et al., 2009), and it is considered to be the world’s most contaminated brackish water area (Koistinen et al., 2008). The concentration of POPs in aquatic ecosystems increases along the food chain and can reach high concentrations in top predators such as seals (Nyman et al., 2002). Concentrations of pollutants in Baltic ringed seal, a marine mammal and top predator, can be used as an indicator of pollutants concentrations in the Baltic region. The study of PBDD/Fs in ringed seal (Pusa hispida), Paper III, was the first study concerning PBDD/Fs in marine mammals from the Baltic Sea. In total, blubber from 43 female and 26 male ringed seals were gathered between April and December from 1974-2015 at different areas along the Swedish east coast (see Figure 13), and the blubber were pooled into 22 samples. The weight of the seals ranged from 20-49 kg, with an average weight of 33 kg.

![Map showing the four sampling areas from where the ringed seals were sampled from 1974-2015. The majority of the ringed seals were sampled in the Bothnian Sea and Bothnian Bay.](image)

Brominated dioxins and furans were detected in all samples, and £PBDD/Fs ranged from 0.5-52 pg/g l.w., with an average and median concentrations of 14 and 8.6 pg/g l.w., respectively. The £PBDD/Fs for all samples and the number of individuals in each pool are shown in Figure 14.
Two different pools from 2012.

Figure 14. The sum of PBDD/Fs in the Baltic ringed seal sampled from 1974-2015. The numbers above the bars are the $\Sigma$PBDD/Fs for the corresponding samples. The number of seals in each pool is shown in brackets.
The most common congeners were 1,2,3,4,6,7,8-HpBDF, 2,3,7,8-TeBDF and 2,3,7,8-TeBDD (see Table 9 for detailed information). The congeners showing the highest concentrations were 1,2,3,4,6,7,8-HpBDF followed by 1,2,3,4,6,7,8-HpBDD, even though the abundance of 1,2,3,4,6,7,8-HpBDD appeared to be sporadic. There was no obvious temporal trend of the congener profiles during 1974-2015. A number of studies concerning PBDD/Fs in fish and shellfish reported that 1,2,3,4,6,7,8-HpBDF was the most abundant congener (Rose et al., 2015; Skinner, 2011; Zacs et al., 2013) and several studies showed that furans were more abundant than dioxins (Fernandes et al., 2008; Fernandes et al., 2009; Roszko et al., 2015). This is consistent with the results of Paper III, and the congener distribution indicate that the PBDD/Fs detected largely originate from combustion related processes (Duan et al., 2011; Lundstedt, 2009; Sakai et al., 2001; Wang and Chang-Chien, 2007; Wang et al., 2010a).

Table 9. Detection frequencies, medium and average concentrations (pg/g l.w.) for individual congeners detected in blubber from Baltic ringed seal.

<table>
<thead>
<tr>
<th>Congener</th>
<th>Detection frequencies (n=22)</th>
<th>Range</th>
<th>Average/ Median</th>
<th>Average/ Median</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(pg/g l.w.)</td>
<td>(pg/g l.w.)</td>
</tr>
<tr>
<td>2,3,7,8-TeBDF</td>
<td>18</td>
<td>0.23-2.4</td>
<td>0.73 / 0.64</td>
<td>0.60 / 0.62</td>
</tr>
<tr>
<td>1,2,3,7,8-PeBDF</td>
<td>3</td>
<td>2.1-3.3</td>
<td>2.5 / 2.2</td>
<td>0.35 / 0.0</td>
</tr>
<tr>
<td>2,3,4,7,8-PeBDF</td>
<td>3</td>
<td>1.4-2.1</td>
<td>1.7 / 1.6</td>
<td>0.23 / 0.0</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxBDF</td>
<td>4</td>
<td>1.4-2.8</td>
<td>2.1 / 2.2</td>
<td>0.39 / 0.0</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpBDF</td>
<td>19</td>
<td>2.8-30</td>
<td>10 / 6.3</td>
<td>8.7 / 6.1</td>
</tr>
<tr>
<td>2,3,7,8-TeBDD</td>
<td>14</td>
<td>0.23-1.4</td>
<td>0.52 / 0.46</td>
<td>0.33 / 0.31</td>
</tr>
<tr>
<td>1,2,3,7,8-PeBDD</td>
<td>10</td>
<td>0.23-1.7</td>
<td>0.73 / 0.64</td>
<td>0.33 / 0.0</td>
</tr>
<tr>
<td>1,2,3,4,7,8 /</td>
<td>6</td>
<td>0.62-1.8</td>
<td>1.1 / 1.1</td>
<td>0.3 / 0.0</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxBDD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxBDD</td>
<td>4</td>
<td>0.58-2.0</td>
<td>1.1 / 0.86</td>
<td>0.2 / 0.0</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpBDD</td>
<td>9</td>
<td>2.1-15</td>
<td>6.4 / 6.6</td>
<td>2.6 / 0.0</td>
</tr>
<tr>
<td>∑PBDD/Fs</td>
<td>0.5-52</td>
<td>14 / 8.7</td>
<td>14 / 8.7</td>
<td></td>
</tr>
</tbody>
</table>

* Including only concentrations >LOD

b Concentrations <LOD replaced by zero
Concentrations close to the limit of detection, the different number of individuals in the pooled samples and the low number of samples covering a time range of 40 years, causes an uncertainty concerning the interpretation of a temporal trend for PBDD/Fs. Tentatively, concentrations of PBDD/Fs in seals showed a decreasing trend from 1974 to around the 2000s, followed by a number of samples with somewhat higher concentrations between 2007 and 2015, see figure 14. A hypothetic explanation to the slightly higher concentrations detected during the end of the study period could be that larger amounts of bromine containing waste are being incinerated, and thereby causing elevated emissions and environmental levels of PBDD/Fs. However, the study showed that all Baltic Ringed seals included in Paper III were exposed to PBDD/Fs during the whole study period between 1974 and 2015, and possibly, the concentrations of PBDD/Fs increased during 2007-2015. The other compound groups included in Paper III showed decreasing concentrations during the whole period (PCDD/Fs, PCBs) or from 2000s and onwards (PBDEs). PBDD/Fs showed no correlation with PCDD/Fs and PBDEs.

When comparing the results from the Baltic ringed seal to the results from the pilot whales in Paper II, it appears that the ∑PBDD/Fs ranges were similar. But the average ∑PBDD/Fs was twice as high in blubber from the Baltic ringed seals compared to pilot whales, and the median was four times as high in the ringed seals compared to the pilot whales. A possible explanation for this difference is that the Baltic Sea is more polluted compared to the Atlantic.

The PBDD/F TEQ in blubber from ringed seals ranged from 0.1-4.8 pg TEQ/g l.w., with an average concentration of 0.7 pg TEQ/g l.w. and median concentration of 1.0 pg TEQ/g l.w. The contribution of PBDD/F TEQ to the total (PBDD/F+PCDD/F) TEQ ranged from 0.04-5.9%, with an average and median contribution of 1.1 and 0.6%, respectively. In pilot whales, the contribution of PBDD/F TEQ to the total TEQ was found to be 0-49%, and the average contribution of PBDD/F TEQ to the total TEQ was eight times as high as in the ringed seals. As mentioned above, the concentration range of PBDD/Fs in ringed seals and pilot whales were similar, but since the concentrations of PCDD/Fs were higher in the ringed seals, the PBDD/F TEQ contribution in ringed seal was lower. PBDD/Fs have been detected in several species of fish and shellfish (Ashizuka et al., 2008; Fernandes et al., 2009; Food Standards Agency, 2006; Miyake et al., 2008; Rose et al., 2015; Skinner, 2011). Most of these studies reported that 1,2,3,4,6,7,8-HpBDF
was the most abundant congener (Rose et al., 2015; Skinner, 2011; Zacs et al., 2013), and several studies showed that furans were more abundant than dioxins (Fernandes et al., 2008; Fernandes et al., 2009; Roszko et al., 2015), which is consistent with the result from the Baltic ringed seals in Paper III.

To summarize, the findings of PBDD/Fs in blubber from ringed seals samples 1974-2015 show that PBDD/Fs were occurring during the whole period. The concentrations vary and some of the detected congeners had concentrations close to the detection limit, which hampers the possibility to draw general conclusions. However, in comparison to the other compound groups included in Paper III, PBDD/F do not show a general decreasing temporal trend. Using visual inspection of the data, a slight increase of the concentrations of PBDD/Fs can be observed during 2007-2015. Moreover, the findings in Paper III show that the Baltic ringed seal (Figure 15), a top predator, are exposed to PBDD/Fs which also indicates that PBDD/Fs are present in the marine food chain in the Baltic Sea. Indirectly, this points towards that fish from the Baltic Sea may be a pathway of human exposure to PBDD/Fs.

Figure 15. Baltic ringed seal. Photo: Anna Roos.
3.4 PBDD/Fs in human breast milk (Paper IV)

Lipophilic POPs can accumulate in adipose tissue, and owing to our position in the top of the food web and consumption of contaminated food we accumulate lipophilic POPs in our body fat (Polder et al., 2008). Lipophilic compounds are transferred to the human milk that has a relatively high fat content (Norén and Meironyté, 2000), and human milk is a major source of exposure to lipophilic POPs for breast-fed babies (Barr et al., 2005; Ingelido et al., 2007; Lakind et al., 2000; Pratt et al., 2013). The concentration of lipophilic POPs in human milk gives an indication of the accumulated concentrations in the adipose tissue in the mothers (Norén and Meironyté, 2000), and also indicates how exposed breastfeeding babies are to lipophilic POPs (LaKind et al., 2004; Lignell et al., 2009; Raab et al., 2008). Even though human milk is a major source of lipophilic POPs for breast-fed babies and PBDD/Fs are assigned the same Toxic Equivalence Factors as PCDD/F when performing human risk assessment (van den Berg et al., 2013), there are just a few more than a handful of publications concerning PBDD/Fs in human milk.

To study the occurrence of PBDD/Fs in human milk, ten mothers living in the vicinity of Örebro volunteered to provide human milk samples at three, six and twelve months postpartum. By providing samples at several occasions, effects of breastfeed duration could be evaluated. However, only two mothers could provide a large enough sample volume at 12 months postpartum. The age of the mothers ranged from 29-40 years (average 34 years), and the weight at the date of birth ranged from 73-113 kg (average 82 kg). Six of the mothers gave birth for the first time, and the remaining four gave birth for the second time.

PBDD/Fs were detected in all samples, and the range of $\Sigma$PBDD/Fs were between 2.3 and 51 pg/g l.w. (Figure 16). The average and median $\Sigma$PBDD/Fs were 12 and 8.3 pg/g l.w., respectively. Other studies concerning PBDD/Fs in human milk reported concentrations that were both lower and higher compared to Paper IV (Brorström-Lundén et al., 2010; Croes et al., 2013; Kotz et al., 2005; Ohta et al., 2004; Pratt et al., 2013; Tue et al., 2014; Wiberg et al., 1992).
Figure 16. Concentrations of $\Sigma$PBDD/Fs (pg/g l.w.) in human milk samples from 10 women sampled at three, six and twelve months postpartum.

The most common congener was 1,2,3,4,6,7,8-HpBDF that was detected in all samples, followed by 2,3,7,8-TeBDF that was detected in all samples but one (Table 10). The congener with the highest contribution to $\Sigma$PBDD/Fs was 1,2,3,4,6,7,8-HpBDF, which in average accounted for approximately one-third of $\Sigma$PBDD/Fs. As furans were the dominant congeners detected in the milk, the congener profiles indicate that the PBDD/Fs detected originate largely from incineration and combustion related sources (Duan et al., 2011; Lundstedt, 2009; Sakai et al., 2001; Wang and Chang-Chien, 2007; Wang et al., 2010a; Zhang et al., 2016). The other studies concerning PBDD/Fs in human milk showed similar congener profiles (Brorström-Lundén et al., 2010; Croes et al., 2013; Kotz et al., 2005; Pratt et al., 2013; Tue et al., 2014; Wiberg et al., 1992).

Milk from one of the mothers, mother number five, showed deviating results. In comparison to the other milk samples included in Paper IV, milk from mother number five showed low concentrations of PCDD/Fs, PCBs, OCPs and BDE #47 but higher concentrations of PBDD/Fs. Mother number five is multiparous and breastfed her first baby for more than 24 months.
Moreover, she had previously donated milk when breastfeeding her first born and she was still actively donating breastmilk to the local hospital during the sample collection period of Paper IV, a fact that may explain the low concentrations of POPs in her milk. However, it is difficult to explain why milk from mother number five showed higher concentrations of PBDD/Fs when all of the other analyzed compounds were found at low concentrations. Through an interview with participant number five, two sources of exposure were identified. Participant number five had previously been working at a newspaper for one year and her main function had been to wrap piles of newspapers in plastic. After the wrapping, the bundles of wrapped newspapers were sent through an oven to let the plastic shrink. The other source of exposure identified by participant five was that she previously had eating large amounts of vegetables from a vegetable patch, which had been fortified with ashes generated from burning wood and plastic food contact materials in a wood boiler. Since there may be a risk that plastic food contact materials and plastics are treated with BFRs (Schecter et al., 2011; Shaw et al., 2014), it is possible that PBDD/Fs were formed during combustion of these materials and were present in the ash used for fertilizing the vegetable patch or when heating the plastics used for wrapping the newspaper stacks. Lipophilic compounds as PBDD/Fs do not enrich in vegetables, but possibly vegetables such as carrots and potatoes were only rinsed before eating them and small amounts of soil and ash particles contaminated with PBDD/Fs were consumed while eating them. Possibly, the elevated concentrations of PBDD/Fs observed in the milk samples from mother number five are resulting from working at the newspaper or from consumption of vegetables from the tentative contaminated vegetable patch.

Although no formal interviews regarding exposure and nutrition were performed, it became clear during the project that the participants are well aware of environmental pollutants and try to limit their exposure to POPs. The awareness concerning POPs and the fact that all participants volunteered for the study, make it possible that the participants’ exposure to POPs, diet and concentrations of POPs in their human milk are not representative of the general population.
Table 10. Detection frequencies, medium and average concentrations (pg/g l.w.) for individual congeners detected in 22 human milk samples from 10 women.

<table>
<thead>
<tr>
<th>Congener</th>
<th>Detection frequencies (n=22)</th>
<th>Rangea</th>
<th>Average/Mediana</th>
<th>Average/Mediana (pg/g l.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3,7,8-TeBDF</td>
<td>21</td>
<td>0.8-2.7</td>
<td>1.4 / 1.2</td>
<td>1.3 / 1.2</td>
</tr>
<tr>
<td>1,2,3,7,8-PeBDF</td>
<td>9</td>
<td>0.6-5.6</td>
<td>2.3 / 2.5</td>
<td>0.9 / 0.0</td>
</tr>
<tr>
<td>2,3,4,7,8-PeBDF</td>
<td>11</td>
<td>0.5-5.2</td>
<td>1.9 / 1.7</td>
<td>1.0 / 0.3</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxBDF</td>
<td>8</td>
<td>0.8-5.5</td>
<td>3.2 / 3.2</td>
<td>1.2 / 0.0</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpBDF</td>
<td>22</td>
<td>0.7-12</td>
<td>3.6 / 2.9</td>
<td>3.6 / 2.9</td>
</tr>
<tr>
<td>2,3,7,8-TeBDD</td>
<td>17</td>
<td>0.2-2.3</td>
<td>0.7 / 0.5</td>
<td>0.6 / 0.5</td>
</tr>
<tr>
<td>1,2,3,7,8-PeBDD</td>
<td>4</td>
<td>0.6-5.0</td>
<td>2.5 / 2.3</td>
<td>0.5 / 0.0</td>
</tr>
<tr>
<td>1,2,3,4,7,8 /</td>
<td>13</td>
<td>0.5-7.1</td>
<td>3.0 / 2.8</td>
<td>1.8 / 0.6</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxBDD</td>
<td>5</td>
<td>0.5-1.4</td>
<td>0.9 / 0.9</td>
<td>0.2 / 0.0</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxBDD</td>
<td>4</td>
<td>2.1-15</td>
<td>5.9 / 3.4</td>
<td>1.1 / 0.0</td>
</tr>
<tr>
<td>∑PBDD/Fs</td>
<td>2.3-52</td>
<td>12 / 8.2</td>
<td>12 / 8.2</td>
<td></td>
</tr>
</tbody>
</table>

*a Including only concentrations >LOD
b Concentrations <LOD replaced by zero

As seen in Figure 16, the concentration of PBDD/Fs varied between the sampling occasions, even though there was no significant difference between 3 and 6 months postpartum. The results for the other compound groups included in Paper IV showed that decreased concentrations corresponded to breastfeeding duration for PCDD/Fs and DDE, while there was no such association for PCBs and BDE #47.

There was no correlation between concentration of PBDD/Fs and the mothers’ weight. However, for PCBs, DDE and BDE #47, there was a correlation between higher weight of the mother and lower milk concentrations. The same association have been reported in other studies (Croes et al., 2013; Lignell et al., 2009; Lignell et al., 2016).

Regarding the age of the mothers, there was no correlation with concentration of PBDD/Fs or with the concentrations of any other compound groups in Paper IV. A positive association between concentration of POPs and the age of the mothers was shown in studies by Croes et al. (2013) and Schade and Heinzow (1998).

There was no association between weight loss and concentration of PBDD/Fs, nor to any other compound group in the study. Some published studies showed no correlation between the weight loss of the mothers and concentrations of POPs (Dewailly et al., 1996; Ennaceur and Driss, 2013; LaKind et al., 2004; Lignell et al., 2005), while other studies reported a
positive correlation between weight loss and concentration of POPs (Croes et al., 2013; Lignell et al., 2016).

As the only compound group in Paper IV, the concentration of PBDD/Fs were significantly higher in the milk from the multiparous mothers compared to the primiparous mothers. No other compound groups showed associations between concentration and parity. Some studies concerning lipophilic POPs have shown a negative association between concentration and parity (Lignell et al., 2016; Schade and Heinzow, 1998; Takekuma et al., 2011; Vaz et al., 1993), while Croes et al. (2013) showed no association between parity and concentration.

Since a limited number of samples were included in the study and there is an uncertainty caused by the fact that some of the PBDD/F concentrations reported in Paper IV were close to the detection limit, the correlations or lack of correlations should be interpreted with caution.

There was no correlation between concentration of PBDD/Fs and concentrations of the other compound groups included (PCDD/Fs, PCBs, DDE, BDE #47). Moreover, using visual inspection of the data, there was a tendency that PBDD/Fs behaved in a different way compared to the other compound groups. When the concentration of PBDD/Fs increased between the sampling occasions, the other compound groups tend to show decreased concentrations, and vice versa. The data set was too limited to draw any general conclusions, but possibly the routes of human exposure to PBDD/Fs differs from the other compound groups.

The PBDD/F TEQ ranged from 0.2-8.4 pg TEQ/g l.w., with an average and median of 1.8 and 1.1 pg TEQ/g l.w., respectively. The contribution of PBDD/F TEQ to the total (PBDD/F+PCDD/F) TEQ ranged from 7-99%, with an average and median contribution of 40 and 33%, respectively. Even though the average and median ∑PCDD/Fs were approximately three times higher compared to corresponding concentrations of ∑PBDD/Fs, the different congener profiles between PCDD/Fs and PBDD/Fs resulted in higher PBDD/F TEQ. For example, the dominant chlorinated congener was OCDD, a congener with a low TEF. In contrast, 2,3,7,8-TeBDD, the PBDD/F congener with the highest TEF, was detected in 17 of the samples while the chlorinated analogue was only detected in 8 samples. This is the highest contribution of PBDD/F to the total TEQ ever published in human
milk. As this result derives from a single study with a limited number of participants, further studies are necessary to verify this finding.

Finally, it is important to note that a vast majority of the present knowledge agrees that the benefits, for both the infant and the mother, of breastfeeding far outweigh the toxicological risks associated with certain POPs (van den Berg et al., 2017).
4. Conclusions and future perspective

The ambition of this thesis was to improve the current knowledge of the occurrence of PBDD/Fs, from source of emission to human exposure.

The study of gas and soot particles from the replicated fire scenarios in defined apartment environments, showed that PBDD/Fs were formed during accidental fires since they were detected in all samples. The detection of PBDD/Fs congeners in gas and soot samples indicate that the PBDD/Fs formed during accidental fires are available for atmospheric transport. The findings imply that an accidental fire site should be considered as a potential source of occupational exposure to PBDD/Fs, both during and after the fire has been extinguished. The firefighting methods using additive or foam were most effective in reducing flue gas temperatures during firefighting, and when using these methods lower concentrations of PBDD/Fs were formed.

PBDD/Fs were detected in the blubber from pilot whales sampled around the Faroe Islands which proves that PBDD/Fs are occurring in marine environments in far remote areas, even though the reported concentrations were low and PBDD/Fs were not detected in all pilot whales. The findings of PBDD/Fs in pilot whales from the Faroe Islands implies that PBDD/Fs undergo long range atmospheric transport. PBDD/Fs were detected in all samples of blubber from Baltic ringed seals. The concentrations were slightly higher compared to the pilot whales, which is reasonable since the Baltic Sea is closer to anthropogenic sources and considered to be among the world’s most contaminated water areas. The findings of PBDD/Fs in a marine mammal from the Baltic Sea showed that PBDD/Fs are probably present in the marine food web of the Baltic Sea, and humans consuming fish from this area might therefore be exposed to PBDD/Fs. Considering human exposure, it is also likely that the Faroese population are exposed to PBDD/Fs as blubber from pilot whales is part of the traditional Faroese diet.

The occurrence of PBDD/Fs in humans were studied by analysing human milk. PBDD/Fs were detected in all human milk samples, which proved that humans are exposed to PBDD/Fs and that human milk is a route of exposure to PBDD/Fs for breastfed babies.

The congener profiles from the accidental fire showed that PBDFs dominated the congener distribution, and 1,2,3,4,6,7,8-HpBDF was overall the most common congener and was detected in the highest concentrations. Similar congener profiles were detected in the marine mammals and the human milk, which strongly indicates that the detected congeners originate from combustion related processes.
The contribution of PBDD/F TEQ to the total (PCDD/F+PBDD/F) TEQ showed different levels. The average contribution of PBDD/F TEQ in the pilot whales and ringed seals were low, 8.2 and 1.1%, respectively, which implies that PBDD/Fs are of minor concern for the marine mammals included in this thesis. However, the contribution of PBDD/Fs to total TEQ in samples from the accidental fires were in average 97% and the average contribution in human milk was 40%. This indicates that PBDD/Fs are of major concern for human exposure, both in more general terms (Paper IV), and more specifically, in occupationally related terms for professionals such as firefighters (Paper I).

This thesis has proved the occurrence of PBDD/Fs in different matrices, from soot at an accidental fire site to human milk. The results from this thesis show that PBDD/Fs are formed in substantial concentrations, in relation to PCDD/Fs, during accidental fires, and that PBDD/Fs are occurring in blubber from marine mammals in far remote areas as well as close to anthropogenic sources, and finally in human milk. The findings in this thesis indicate that the omnipresence of PBDD/Fs are related to combustion related processes, and that humans are more exposed compared to the marine mammals studied in this thesis.

Based on the results of this thesis, a number of future studies have emerged:

- It is of importance to study the occurrence of PBDD/Fs in human milk to further investigate the PBDD/Fs contribution to the total TEQ. Moreover, it is also of interest to further evaluate any association between concentrations of PBDD/Fs in human milk and covariate data such as breastfeeding duration, diet, weight and occupational exposure.

- Occupational exposure to PBDD/Fs related to accidental fires needs to be investigated further, both for firefighters but also for other occupational groups such as restoration and demolition workers. Further studies are needed to investigate whether certain firefighting methods using additive or foam generates lower emissions of PBDD/Fs compared to other methods.

- Human exposure to PBDD/Fs through diet from the Baltic marine food web needs to be investigated further. Since pilot whales are a
part of Faroese traditional diet, it is of interest to study the human exposure to PBDD/Fs in the Faroese population.

- The results from this thesis implies that environmental levels of PBDD/Fs are increasing. Therefore, it is of importance that environmental monitoring of PBDD/Fs are continued.
5. Acknowledgement

There are lots of people who have helped me during my time at MTM, but my first and biggest thanks go to my supervisor Jessika Hagberg. I am very grateful that you gave me the opportunity to start my PhD at MTM, even though my knowledge in analytical chemistry was a bit rusty at that time. You have happily shared your thorough knowledge and experience, and I am deeply impressed by your commitment to my studies. Your ability to laugh and create a good mood has been highly appreciated during the years. To summarize, you are the role model of an excellent supervisor.

Big thanks to Bert van Bavel, who gave me the chance to start my PhD at MTM and was my co-supervisor during the first years. Ingrid Ericson Jogsten, assistant co-supervisor during the last years, thank you for your energy, useful questions that made me think twice and your wise advice concerning both scientific issues and life itself.

Thanks to Niklas Ricklund at AMM, which was a big part in the fact that the fire project was not only hard work but also a lot of laughter. Big thanks to the other external co-authors of the manuscripts; Anna Roos, Maria Dam and Katrin Hoydal.

Most of the time here, I have happily shared office with two fantastic persons; Dawei, a big thank you for many laughs, all the answers you gave to my (stupid) questions and for introducing me to the white rabbit; Jordan, my GC friend, thank you all the happy moments, laughter, good conversations about life and finally for sharing my frustration over the ever-troubled Autospec.

Ulrika, I really appreciate that you have taken your time to answer my questions. Moreover, you really are my role model when it comes to being a credible person. Thank you Samira for taking the time to be encouraging, it has been appreciated! If you need some encouragement when it comes to your future construction projects, just call me! Anna K, thank you for sharing your enormous knowledge and still have the energy to care for everyone in your surroundings.

Thank you Monika and Christine for happy moments, laughter and teaching me useful German words like nickerchen and pfülen. And thank you
for letting me introduce you to the best of all – svenskt lösgodis. I know you love it!

In addition to the above-mentioned people, there are a lot of amazing persons who have made my time joyful through sharing life, laughter and wisdom in a great mix, and some of them are Alf, Anna G, Anna R, Erik, Florian, Heidi, Helena, Jenna, Josefín, Jörgen, Kristina, Leo, Lottie, Magnus, Maria B, Mattias, Maria L, Ola, Owe, Petr, Stefan, Steffen, Thanh, Tuulia and Ulf.

Big thanks to friends and family who have been there, even when I been too focused on my studies.

My warmest thanks goes to my amazing wife Evelina. You are incredible, and I could not have finished my thesis without you. Love you.

Thanks to my wonderful children Ludvig, Ellen and Dalia! To come home after a too long day, and be met by three happy children have truly been a blessing.

Thank you!
6. References


Domingo JL. *Polybrominated diphenyl ethers in food and human dietary exposure: A review of the recent scientific literature*. Food and Chemical Toxicology 2012; 50: 238-249.

Duan H, Li J, Liu Y, Yamazaki N, Jiang W. *Characterization and inventory of PCDD/Fs and PBDD/Fs emissions from the incineration of waste printed circuit board*. Environmental Science and Technology 2011; 45: 6322-6328.


Ericson Jogsten I, Hagberg J, Lindström G, Bavel Bv. *Analysis of POPs in human samples reveal a contribution of brominated dioxin of up to 15% of the total dioxin TEQ*. Chemosphere 2010; 78: 113-120.


Hayakawa K, Takatsuki H, Watanabe I, Sakai S-i. Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan. Chemosphere 2004; 57: 343-356.


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


Litten S, McChesney DJ, Hamilton MC, Fowler B. *Destruction of the World Trade Center and PCBs, PBDEs, PCDD/Fs, PBDD/Fs, and Chlorinated Biphenylenes in Water, Sediment, and Sewage Sludge.* Environmental Science & Technology 2003; 37: 5502-5510.


Nyman M, Koistinen J, Fant ML, Varttainen T, Helle E. *Current levels of DDT, PCB and trace elements in the Baltic ringed seals (Phoca hispida baltica) and grey seals (Halichoerus grypus)*. Environmental Pollution 2002; 119: 399-412.


Roszko M, Szymczyk K, Rzeptowska M, Jedzzejczak R. *Preliminary study on brominated dioxins/furans and hydroxylated/methoxylated PBDEs in Baltic cod (Gadus morhua) liver. Comparison to the levels of analogue chlorinated co-occurring pollutants.* Marine Pollution Bulletin 2015; 96: 165-175.
Safe S. Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). Critical Reviews in Toxicology 1990; 21: 51-88.


Schecter A, Ryan JJ. Chlorinated and Brominated Dioxin Levels in the Blood of a Chemist Who Became Ill after Synthesizing 2,3,7,8-TCDD and 2,3,7,8-TBDD. Organohalogen compd 1990; 4.


Skinner LC. Distributions of polyhalogenated compounds in Hudson River (New York, USA) fish in relation to human uses along the river. Environmental Pollution 2011; 159: 2565-2574.


Wang LC, Hsi HC, Wang YF, Lin SL, Chang-Chien GP. Distribution of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) in municipal solid waste incinerators. Environmental Pollution 2010a; 158: 1595-1602.


Wang LC, Wang YF, Hsi HC, Chang-Chien GP. Characterizing the emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from metallurgical processes. Environmental Science and Technology 2010b; 44: 1240-1246.


Zacs D, Rjabova J, Bartkevics V. *Occurrence of brominated persistent organic pollutants (PBDD/DFs, PXDD/DFs, and PBDEs) in Baltic Wild Salmon (Salmo Salar) and Correlation with PCDD/DFs and PCBs*. Environmental Science and Technology 2013; 47: 9478-9486.


Publications in the series
Örebro Studies in Chemistry

1. Bäckström, Mattias, On the Chemical State and Mobility of Lead and Other Trace Elements at the Biogeosphere/Technosphere Interface. 2002.


18. Eriksson, Ulrika, *Contribution of polyfluoroalkyl phosphate esters (PAPs) and other precursor compounds to perfluoroalkyl carboxylates (PFCAs) in humans and the environment*. 2016

19. Riddell, Nicole, *Packed Column Supercritical Fluid Chromatography: Applications in Environmental Chemistry*. 2017