Polybrominated dibenzo-p-dioxins and dibenzofurans and mixed polybrominated/chlorinated dibenzo-p-dioxins and dibenzofurans

Draft risk profile

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Contents

Executive summary3					
1.	Introduction		3		
	1.1	Chemical Identity	3		
	.2	Conclusion of the POPs Review Committee regarding Annex D information	6		
	.3	Data sources	6		
	.4	Status of the chemical under national or regional regulations	6		
2.	Summary of the information	relevant to the risk profile	7		
2	2.1	Sources	7		
	2.1.1	Production, trade, stockpiles	7		
	2.1.2	Uses1	0		
	2.1.3.	Releases to the environment1	1		
2	2.2.	Environmental fate1	5		
	2.2.1	Persistence1	5		
	2.2.2	Bioaccumulation1	7		
	2.2.3	Potential for long-range environmental transport1	8		
2	2.3	Exposure2	1		
	2.3.1	Environmental monitoring data2	1		
	2.3.2	Human exposure2	24		
2.4		Hazard assessment for endpoints of concern2	:6		
3.	Synthesis of information	2	9		
4.	Concluding statement	3	1		
5.	References		2		

Executive summary

1. Will be provided for a later version of the draft.

1. Introduction

2. In May 2024, Switzerland submitted a proposal to list polyhalogenated dibenzo-*p*dioxins and dibenzofurans in Annex C to the Stockholm Convention on Persistent Organic Pollutants. The proposal (UNEP/POPS/POPRC.20/5*) was submitted in accordance with Article 8 of the Convention and reviewed by the POPs Review Committee (POPRC) at its twentieth meeting in September 2024.

3. The scope of the evaluation covers polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and mixed polybrominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans (PBCDD/Fs), excluding polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), which are already listed in Annex C to the Convention.

1.1 Chemical Identity

4. There are 75 polybrominated dibenzo-*p*-dioxin (PBDD) and 135 polybrominated dibenzofuran (PBDF) congeners (Ballschmiter & Bacher, 1996). As polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are already listed in Annex C to the Convention, they are excluded from the scope of this risk profile. However, mixed polybrominated/chlorinated congeners are within the scope. There are 1550 mixed polybrominated/chlorinated dibenzo-*p*-dioxin (PBCDD) and 3050 mixed polybrominated/chlorinated dibenzofuran (PBCDF) congeners (WHO, 1998; L. Yang et al., 2021).

5. The general chemical structures of PBDD/Fs and PBCDD/Fs are shown in Figure1:



Figure 1. General chemical structures of polybrominated and mixed polybrominated/chlorinated dibenzo-p-dioxins (left) and polybrominated and mixed polybrominated/chlorinated dibenzofurans (right) (X = CI, Br; $1 \le m + n \le 8$; where Br ≥ 1 ; possible positions are indicated by blue numbers).

6. As there is no intentional production of PBDD/Fs and PBCDD/Fs other than for use as analytical standards (Kannan et al., 2012), there are no trade names or commercial names associated with these substances.

7. In this risk profile, special emphasis is given to those PBDD/F congeners for which the relative effect potency (REP) ranges in mammals were compared with the corresponding PCDD/F congeners in the review by van den Berg et al. (2013). Six

additional PBDD/F congeners were added to the list in *Table 1* to cover the mono- to octabrominated PBDD/Fs. WHO (1998) provides a more extensive list of CAS numbers for PBDD/F and PBCDD/F congeners.

Table 1. Commonly used names, acronyms and CAS Registry Numbers of selected PBDD/F congeners (additional congeners, not reviewed by van den Berg et al. (2013), are marked with an asterisk). The IUPAC names contain the terms "oxanthrene" and "dibenzo[b,d]furan" instead of "dibenzo-p-dioxin" and "dibenzofuran", respectively.

Name	Acronym	CAS RN
2-bromodibenzo- <i>p</i> -dioxin*	2-MoBDD	105906-36- 3
2,7-dibromodibenzo-p-dioxin*	2,7-DiBDD	39073-07-9
2,3,7-tribromodibenzo- <i>p</i> -dioxin	2,3,7-TrBDD	51974-40-4
2,3,7,8-tetrabromodibenzo-p-dioxin	2,3,7,8-TeBDD	50585-41-6
1,2,3,7,8-pentabromodibenzo- <i>p</i> - dioxin	1,2,3,7,8-PeBDD	109333-34-8
1,2,3,4,7,8-hexabromodibenzo- <i>p</i> -dioxin	1,2,3,4,7,8-HxBDD	110999-44-5
1,2,3,6,7,8-hexabromodibenzo- <i>p</i> -dioxin	1,2,3,6,7,8-HxBDD	110999-45-6
1,2,3,7,8,9-hexabromodibenzo- <i>p</i> - dioxin	1,2,3,7,8,9-HxBDD	110999-46-7
1,2,3,4,6,7,8-heptabromodibenzo- <i>p</i> -dioxin*	1,2,3,4,6,7,8-HpBDD	110999-47-8
octabromodibenzo-p-dioxin	OBDD	2170-45-8
2-bromodibenzofuran*	2-MoBDF	86-76-0
2,7-dibromodibenzofuran*	2,7-DiBDF	65489- 80-7
2,3,8-tribromodibenzofuran*	2,3,8-TrBDF	84761- 82-0
2,3,7,8-tetrabromodibenzofuran	2,3,7,8-TeBDF	67733-57-7
1,2,3,7,8-pentabromodibenzofuran	1,2,3,7,8-PeBDF	107555-93-1
2,3,4,7,8-pentabromodibenzofuran	2,3,4,7,8-PeBDF	131166-92-2
1,2,3,4,7,8- hexabromodibenzofuran	1,2,3,4,7,8-HxBDF	129880-08-6
1,2,3,4,6,7,8- heptabromodibenzofuran	1,2,3,4,6,7,8-HpBDF	107555-95-3
octabromodibenzofuran	OBDF	103582-29-2

8. PBCDD and PBCDF congeners with the same substitution pattern and with alternating chloro and bromo substituents were selected for closer evaluation (for structural formulae see UNEP/POPS/POPRC.21/INF/# Figure 1–4).

1.2 Conclusion of the POPs Review Committee regarding Annex D information

 At its twentieth meeting, the POPs Review Committee evaluated the proposal by Switzerland to list polyhalogenated dibenzo-*p*-dioxins and dibenzofurans in Annex C to the Stockholm Convention. The Committee concluded that PBDD/Fs and PBCDD/Fs meet the screening criteria specified in Annex D to the Convention (decision POPRC-20/4).

1.3 Data sources

- 10. The draft risk profile is based on the following data sources:
 - (a) The proposal to list polyhalogenated dibenzo-*p*-dioxins and dibenzofurans by Switzerland (UNEP/POPS/POPRC.20/5*);
 - (b) Information submitted by Parties and observers according to Annex E to the Convention and in response to the invitation for comments on the draft risk profile. Annex E information was provided by: Australia, Canada, Egypt, the European Union, Germany, Italy, Japan, Monaco, Netherlands, Norway, Oman, Peru, Spain, Sweden, United Kingdom, a best available techniques (BAT)/best environmental practice (BEP) expert, the Bromine Science and Environmental Forum (BSEF), the Cancer Prevention and Education Society, the International Pollution Elimination Network (IPEN) / Alaska Community Action on Toxics (ACAT) and Arnika;

(c) Peer-reviewed scientific journals, as well as information from reports and other grey literature.

1.4 Status of the chemical under national or regional regulations

11. In Germany, substances, mixtures and articles may not be placed on the market if they contain five PBDD and three PBDF specific congeners, respectively, above a defined threshold (Bundesrepublik Deutschland, 2017; EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2024; Kannan et al., 2012). These congeners are among those listed in *Table 1*. Further, in Germany, for specific installations processing pre-shredded material containing brominated flame retardants, annual measurements of PBDD/Fs in the exhaust gas are required (TA Luft, 2021).

12. In the Netherlands, PBDD/Fs are indicated as extremely hazardous substances: persistent, bioaccumulating and very toxic. Releases of such substances are bound to obligations related to minimize their emissions and releases to the environment (Ministerie van Binnenlandse Zaken en Koninkrijksrelaties, Nederlanden, 2018).

13. COP Decision SC-5/5 encouraged parties and other relevant stakeholders to implement where appropriate, taking into account national circumstances, the recommendations set out in the annex to decision POPRC-6/2 on the elimination from the waste stream of brominated diphenyl ethers that are listed in Annex A to the Convention. The recommendations included generating and collecting information on releases of PBDD/Fs in emissions to air and in the solid residues from thermal processes used in treating materials contaminated with brominated diphenyl ethers and to identify appropriate disposal options to ensure that brominated diphenyl ethers and/or PBDD/Fs

are not released (UNEP/POPS/COP.5/15, 2015). The POPRC discussed the toxicity and unintentional formation of PBDD/Fs and PBCDD/Fs and their presence in polybrominated diphenyl ethers (PBDEs) at POPRC 6 (UNEP/POPS/POPRC.6/2, 2010).

14. In the EU, emissions to air of PBDD/Fs are to be monitored once every six months in waste incineration plants. The monitoring only applies to the incineration of waste containing brominated flame retardants or to plants using boiler bromine addition with continuous injection of bromine. (European Commission, 2019).

2. Summary of the information relevant to the risk profile

2.1 Sources

2.1.1 Production, trade, stockpiles

15. There are several anthropogenic sources of PBDD/F emissions to the environment. For example, PBDD/Fs and PBCDD/Fs can be formed unintentionally when materials are heated or burnt, including in accidental or other types of uncontrolled fires, especially when brominated flame retardants (BFRs) or other brominated (and chlorinated) aromatics are present (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2024; Kannan et al., 2012; Secretariat of the Stockholm Convention, 2008). Since PBDD/Fs and PBCDD/Fs are formed unintentionally, they are neither traded, nor stockpiled with the exemption of small quantities for analytics and research purposes.

According to Yang et al. (2021), three dominant sources are (1) commercial PBDE 16. mixtures (presence as a by-product), (2) photolytic and thermal degradation of BFRs and (3) unintentional production in industrial thermal processes. PBDD/Fs and PBCDD/Fs can also be formed when mechanochemical non-combustion technologies are used to treat contaminated soil, depending on the temperature (Lu et al., 2017). Further, PBDD/Fs can be formed when plastics containing direct precursors such as PBDEs are subject to recycling processes such as extrusion and molding (Hamm et al., 2001; Weber & Kuch, 2003; Zennegg et al., 2014). Japan identified cement manufacturing facilities (due to waste incineration) and flame-retardant plastic manufacturing and processing facilities as main sources of PBDD/F emissions to the atmosphere as well as general and industrial waste incinerators, steelmaking electric furnaces, aluminium secondary refining facilities and sewage treatment plants (due to sludge incineration) as secondary sources. In regard to sources to water, Japan identified sewage treatment facilities and flame retardant manufacturing and handling facilities as main sources of PBDD/F emissions, as well as flame retardant fiber processing facilities, flame retardant plastic manufacturing and processing facilities, cement manufacturing facilities and flame retardant resin manufacturing facilities as secondary source (NIP Japan, 2016).

17. PBDD/Fs can be generated during the production of BFRs. Levels of PBDFs in commercial octa- and decaBDE mixtures were generally in the mg/kg range (Hanari et al., 2006; Ren et al., 2011; Suzuki et al., 2021). Tetrabrominated PBDDs can be formed as by-products during the synthesis of 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) (Ren et al., 2017). Two tetrabrominated congeners, namely 1,3,6,8- and 1,3,7,9-TeBDD, have been identified in commercial BTBPE with concentrations of 2.5 and 1.5 mg/kg, respectively (Ren et al., 2017). PBDD/Fs can also be present in other BFRs. Low levels of PBDD/Fs have been detected as impurities in TBBPA (European Commission, 2006). Since PBDD/Fs are present as impurities in commercial mixtures of BFRs, they

subsequently occur in household products and house dust (Neuwahl et al., 2019; Tue et al., 2019).

18. Several studies have investigated photolytical and thermal degradation of BFRs and BFR-containing products (e.g. incorporated in plastics) with a special focus on PBDEs as precursors for PBDD/Fs (Ebert, 2003). Moreover, it was experimentally determined that PBDFs are formed when a salmon sample spiked with decabromodiphenyl ether (decaBDE) is heated (Vetter et al., 2015). From a mechanistic point of view, the formation of PBDFs from PBDEs requires the intramolecular elimination of Br₂, HBr or H₂ for cyclization. For example, the elimination of two bromine substituents in the 2,2' position of BDE 209 could result in the formation of octabrominated PBDFs (Kajiwara et al., 2008). Wang et al. (2024) investigated mechanisms and kinetics of the formation of PBDD/Fs from PBDEs by pyrolysis and combustion using density functional theory calculation and determined that involvement of polymers and metals significantly reduces the energy barriers for the formation of PBDD/Fs. It was experimentally shown that during photodegradation of decaBDE incorporated into high-impact polystyrene (HIPS) PBDF concentrations increased by about 40 times after 1 week of exposure to natural sunlight while BDE 209 (the dominant congener found in commercial decaBDE mixtures) concentrations were decreasing (Kajiwara et al., 2008). In this study tri- to octabrominated PBDF congeners were found with hepta- and octabrominated congeners accounting for approximately 40% of the total PBDFs in the irradiated samples. PBDD/Fs are also formed when plastics containing PBDEs are heated at temperatures of 200 °C to 250 °C and subjected to treatment such as extrusion and molding as reported in a Swedish study (Ortuño et al., 2015).

19. PBDD/Fs can be formed as a result of the pyrolysis and combustion of tetrabromobisphenol A (TBBPA) which is another common BFR (Ebert, 2003). Ortuño et al. (2014) investigated combustion and pyrolysis of TBBPA at 650 and 850 °C in different atmospheres (nitrogen and air) and found a different prevalence of PBDD/F congeners formed depending on the process. The most abundant congeners were 2,4,6,8-TeBDF in pyrolysis and 1,2,3,7,8-PeBDF in combustion as the congener pattern was observed to be affected by oxygen presence. In addition, the total PBDD/F yields obtained in the combustion experiment were nearly forty times higher than those from pyrolysis (levels in the ppm range). An investigation of PBDD/F formation during combustion from polymer linked and from additively incorporated TBBPA at 600 °C in the presence of bromine revealed concentrations in the range of 17.5 to 19.6 mg PBDD/F per kg TBBPA applied (Wichmann et al., 2002). The PBDD/F congener pattern observed was highly depending on the reaction conditions and the plastic material. In general, PBDFs were found in much higher concentrations compared to PBDDs in both studies. Also, HBCD and products containing HBCD may release small amounts of PBDD/Fs during burning. Trace levels of PBDD/Fs have been measured during combustion of flame-retarded polystyrene materials containing HBCD (Desmet et al., 2005; Dumler et al., 1989). The most recent study by Huang et al. (2023) focused on the formation mechanisms of PBDD/Fs from 2,6-dibromophenol pyrolysis. The calculation results show that the 2bromophenoxy radical is a major decomposition product in initial pyrolysis of 2.6dibromophenol, and dimerization of bromophenoxy radicals occurs mainly through O-C coupling or C-C coupling. O-C coupling results in the formation of PBDD precursors, and C-C coupling results in the formation of PBDF precursors. The formation of PBDD/Fs proceeds mainly via H-abstraction or H-transfer, cyclization, and debromination or dehydroxylation. The energy barriers of the rate-determining steps in the formation of PBDDs are lower than those of PBDFs, so that the formations of PBDDs is predominant.

20. Bromine and chlorine can be present to varying degree depending on waste type (Österlund et al., 2009), bromine acts in a similar way to chlorine during combustion to form PBDD/Fs. The presence of both bromine and chlorine results in the formation of PBCDD/Fs. The ratio of bromine and chlorine in the combustion process largely corresponds to the ratio of bromine and chlorine in the PBCDD/Fs formed. During insufficiently controlled combustion processes, significant amounts of PBDD/Fs may be formed, including those with the most toxic dioxin-like properties. The origin of these PBDD/Fs may partly be explained by their presence as contaminants in the commercial PBDE flame-retardant mixtures in household waste, but de novo synthesis cannot be excluded. Another source of bromine in incineration processes is the use of techniques for the enhanced oxidation of mercury by means of high-temperature bromide injection (Neuwahl et al., 2019). Tu et al. (2011) detected PBDD/Fs in incineration residues and off gases of two MSWIs and a coal fired power plant. E.g. they found a concentration range for PBCDD/Fs between 0.021 to 0.167 ng/Nm³ in the stack flue gases of MSWIs and a coal fired power plant. As combustion processes generally take place in the presence of an excess of chlorine, PBCDD/Fs are usually formed predominantly. The total amounts of PBDD/Fs and PBCDD/Fs formed during thermal processes depend largely on the quality of the precursor compounds and the specific conditions of the thermal treatment (Altarawneh, 2022; Ebert, 2003; Hamm et al., 2001; Weber & Greim, 1997; Weber & Kuch, 2003). A positive correlation was found between PBDEs and both PBDD/Fs and mono-brominated PBCDD/Fs in the atmosphere. This suggests that atmospheric PBDD/Fs are linked to PBDEs, either as impurities in PBDE products or as byproducts formed during the production or combustion of plastics containing PBDEs. (Havakawa et al., 2004). For some metallurgical industries, PBDD/Fs and PBCDD/Fs were found to be emitted in similar or higher amounts than PCDD/Fs (Du et al., 2010). PBDD/Fs that were found to be formed during combustion and other anthropogenic processes are often furans and often with higher levels of substitution (tetra- to octa-) (Arnoldsson, 2012).

21. Research conducted in the Baltic Sea indicates that certain PBDD/Fs and PBCDD/Fs might originate from natural sources (Haglund, 2010; Haglund et al., 2007; Malmvärn et al., 2008; Unger et al., 2009). The congeners from natural sources are usually less brominated, ranging from mono- to penta-brominated. Primary producers such as cyanobacteria, algae or aquatic sponge could be potential sources of naturally occurring PBDDs, suggesting a biogenic formation (Arnoldsson, 2012; Unger et al., 2009). It has been postulated that natural condensation reactions involving bromophenol congeners could produce lower brominated PBDDs, with these bromophenols arising from the action of bromoperoxidase enzymes, which facilitate biobromination in the presence of bromide ions (Haglund et al., 2007). For tribrominated (TrBDDs) and tetrabrominated (TeBDDs) derivatives, no single pathway seems to fully account for the observed PBDD patterns. Instead, it is suggested that a range of potential formation mechanisms could come into play, such as enzymatic and light-induced coupling of widespread environmental bromophenols or hydroxylated diphenyl ethers (OH-PBDEs), alongside the debromination of PBDDs to create products with lower bromine content.(Haglund, 2010). Haglund et al. (2010) report PBDD and MeO-PBDE levels in perch for the timeframe between 1990 and 2005 to be in the range from 0.4 to 73 pg/g fresh weight and from 30 to 1100 pg/g fresh weight, respectively. In addition to PBDDs, Malmvärn et al. (2018) detected tri- to pentabrominated PBDFs (concentrations: 0.03) ng/g fresh weight for triBDDs) in red algae from the Baltic Sea. The study further presents mean detected levels of 10, 0.36 and 0.13 ng/g fresh weight for the sum of the OH-PBDEs, sum of the MeO-PBDEs and sum of the PCBs, respectively. In another study by Unger et al. (2009), di- to tetrabrominated PBDDs (3.2 ng/g extractable organic matter (EOM) 2,7/2,8-diBDD, 0.87 ng/g EOM 1,8-diBDD, 43 ng/g EOM 1,3,7-triBDD, 84 ng/g EOM

1,3,8-triBDD, 4.5 ng/g EOM 2,3,7-triBDD, 3.1 ng/g EOM 1,2,4,7/1,2,4,8-tetraBDD, 3.2 ng/g EOM 1,2,3,7-tetraBDD and 1.7 ng/g EOM 1,2,3,8-tetraBDD) and PBCDDs with unknown substitution patterns (USP) (CIBr_xDD, x = 2-3) (0.76 ng/g EOM CIBr₂DD_{USP 1}, 2.3 ng/g EOM CIBr₂DD USP 2, 1.3 ng/g EOM CIBr₂DD USP 3 and 1.9 ng/g EOM CIBr₂DD USP 6) were found in sponge from the Baltic Sea, but no PBDF congeners were present in concentrations higher than 0.5 ng/g EOM. The PBDD/Fs formed in anthropogenically related (combustion) processes are mostly PBDFs and highly brominated (tetra- to hepta-) congeners, whereas Baltic biota have very low PBDF content and PBDDs are mainly less brominated (mono- to tetra-) congeners (Arnoldsson, 2012). Goto et al. (2017) investigated the occurrence of mono- to octabrominated PBDD/Fs in Tokyo Bay, Japan, using ²¹⁰Pb-dated sediment cores covering the period 1895–2000. In the sediment cores, PBDF and PBDE concentrations increased drastically after the 1960s and reached the highest levels in the late 1990s. PBDD levels showed only marginal fluctuation over the past century, with the predominance of 2,7-/2,8-DiBDDs and 1,3,7-/1,3,8-TrBDDs in all the sediment layers. In the last decades, PBDF levels are higher than PBDD levels. It is noteworthy that the PBDD congeners were also found in the sediment layers corresponding to the pre-industrial era, supporting their natural formation in the coastal environment. The contribution of the anthropogenic PBDFs to the total TEQ increases consistently since their first occurrence. In the most recent sediment core samples from 1998, 1999 and 2000, the PBDF contribution to the total TEQ ranges from 0.29 to 1.03%.

2.1.2 Uses

22. No information was received indicating that there has been or there are any intentional uses of PBDD/Fs or PBCDD/Fs with the exemption of small quantities for analytics and research purposes.

PBDEs, which are precursors of PBDD/Fs or, when chlorine is present, of 23. PBCDD/Fs, are already restricted to a large extent as tetra-, penta-, hexa-, hepta- and decaBDE are listed in Annex A (Elimination) to the Stockholm Convention. Previously, commercial PBDE mixtures were used as additive flame retardants and had a variety of applications including in plastics/polymers/composites, textiles, adhesives, sealants, coatings and inks (UNEP/POPS/POPRC.4/15/Add.1. UNEP/POPS/POPRC.2/17/Add.1. UNEP/POPS/POPRC.10/10/Add.2). However, products containing PBDEs are still in use and PBDEs are present in consumer products made from plastics derived from electronic waste (P. Behnisch et al., 2023; Grechko et al., 2022; Petrlik et al., 2019), which show that, for example, in consumer products with PBDE concentrations between 169 and 593 mg/kg, PBDD/Fs ranged from 690 to 3,821 pg WHO-Toxic Equivalent (TEQ)/g (Petrlik et al., 2019). The toxicity of a mixture of dioxins and/or dioxin-like compounds can be expressed in a single number – the toxic equivalency (TEQ). It is a single figure resulting from the product of the concentration and individual toxic equivalency factors (TEFs) of each congener. TEFs express the toxicity of dioxins, furans and dioxin-like PCBs in terms of the most toxic form of dioxin, 2,3,7,8-TeCDD. Based on mechanistic considerations, PBDD/Fs and PBCD/Fs can be included in the TEF concept as other dioxin-like compounds. Several similar TEQ schemes have been developed and are used in scientific literature: BGA (BGA TEQ), NATO (I-TEQ), WHO (WHO2005-TEQ, WHO2005-TEQ, WHO2005-TEQ).

24. Other aromatic BFRs that can be precursor of PBDD/Fs or, when chlorine is present, of PBCDD/Fs are applied to a variety of polymers to produce a wide range of products with a lot of the reported uses being in textiles, electrical and electronic equipment and automotive articles (ECHA, 2024). For example, TBBPA can be used in

enhancing the fire resistance of electrical and electronic devices and systems that incorporate printed circuit boards, including household appliances like televisions, vacuum cleaners, and washing machines, as well as office and communication devices such as photocopy machines, computers, printers, and fax machines, alongside equipment used in automotive, aviation and entertainment sectors (Ortuño et al., 2014). Moreover, TBBPA has been detected at concentrations of hundreds of mg/kg in consumer products made from recycled plastics derived from electronic waste (P. Behnisch et al., 2023; Grechko et al., 2022). In some cases, concentrations have exceeded one to three thousand mg/kg (Petrlik, Bell, et al., 2022). PBDD/Fs can also be formed in the presence of other substances that contain bromine. This has for example been shown through studies on vehicle exhaust where it was linked to dibromoethane (Haglund et al., 1988). Many substances that have been used to replace PBDEs are also brominated (Cowell e al., 2017).

2.1.3. Releases to the environment

As the use of brominated flame retardants has become widespread over the past 25. 50 years (Cowell et al., 2017), it is no longer uncommon to find them in municipal incineration waste and with metals recycled by heat treatment in metallurgy. The emission of PBDD/Fs is influenced by many parameters, including the type of combustion and the type of material (INERIS, 2020). In a Swedish study, Remberger et al. (2014) concluded that the emission of PBDFs will take place both to air and water. PBDFs were generally found in samples from wastewater treatment plants (WWTPs), storm water, indoor air and dust, indicating that they may be emitted and transported to the environment via these sources and pathways. Therein, the authors conclude that BFRs and PBDFs emitted indoors to air and to settled dust may be transported to outdoor air via ventilation. The presence of these pollutants in influent, effluent and sludge from municipal WWTPs also indicates that diffusive emissions from household products occur and that these chemicals may be emitted to the environment from WWTPs. The occurrence of the BFRs and PBDD/Fs in storm water and fire extinguishing water shows that these may also be pathways to the environment (Remberger et al., 2014).

Based on the production and use of commercial PBDE mixtures in 2001, the 26. potential global annual emissions of PBDFs were calculated to be 2300 kg based on an annual global demand for commercial PBDE mixtures of 66,110 tonnes (Hanari et al., 2006). A similar calculation can be made for potential global annual emissions of PBDD/Fs from TBBPA. Evidence on impurities of PBDD/Fs in TBBPA is available in European Commission (2006). According to this source, several studies have investigated the levels of PBDD/Fs present in TBBPA. Some of them have indicated that the levels are low (often below detection limits). A few studies have occasionally indicated the presence of relevant amounts of some congeners. Highest levels where found in TBBPA which contained PeBDF to OBDF in a range between 1 and 31.5 µg/kg with a sum concentration of 63.6 µg/kg (Thoma et al., 1986a und Dummler et al., 1989b as cited in European Commission, 2006)). Global TBBPA consumption in 1999 was 121,300 tonnes. For a worst-case assessment, the sum concentration of 63.6 µg/kg PBDD/F and a global consumption of 121,300 tonnes can be used. The potential PBDD/F content which could be emitted from TBBPA results in an annual amount of 7,715 kg at that time (in 1999).

27. Plastics from cathode ray tube (CRT) casings containing PBDEs or other BFRs sampled in Nigeria were found to contain a mean concentration of 41,000 ng/g PBDD/Fs.

It was estimated that the CRT casings stockpiled in Nigeria contain between 2 and 8 tonnes of PBDD/Fs. PBDE-treated plastic contained ca. 1000 ppm of PBDD/Fs when related to the PBDE content. Taking into account the total global production of decaBDE (ca. 1.25 million tonnes) and c-octaBDE (ca. 110,000 tonnes), it is possible that the total quantity of PBDD/Fs in these products might be around 1000 tonnes. (Sindiku et al., 2015). PBDFs of different bromination degrees (60 to 80% octabrominated PBDF as predominant congener) from TV casing samples were observed during photodegradation of TV casings with BDE 209 incorporated in concentrations up to 10% by weight (Kajiwara et al., 2008). Plastics containing PBDEs or PBDD/Fs can thus contribute to releases to the environment.

28. Current global practice of plastic recycling might pose a risk that PBDD/Fs formed from BFRs can cross-contaminate new products and contribute to releases into the environment. The formation of PBDD/Fs has been observed in two South African e-waste recycling processes and under controlled laboratory conditions (Zennegg et al., 2014). In this study, formation rates of PBDFs between $2 \cdot 10^{-5}$ and $2 \cdot 10^{-4}$ per \sum PBDE/min were calculated during thermal exposure in the recycling processes and under laboratory conditions. The PBDF pattern was dominated in all samples by penta-, hexa- and heptabrominated congeners (Behnisch et al., 2023; Fernandes et al., 2023; Li et al., 2020). Emissions are especially high during informal e-waste recycling, however, large emissions have also been measured in controlled recycling facilities (Lundstedt, 2016). In 2022, PBDD/Fs were measured in raw and clean gases at a shredder plant in Germany, using refrigeration scrap and aluminium scrap as feedstock. PBDDs were not detected. PBDFs (tetra- to octa-congeners) were only detected in the raw gas at concentrations of 0.61 and 2.10 ng/Nm³ (Communication from the German EPA, 2025)

29. In some countries, people use plastic waste as an alternative fuel to wood, which produces a range of pollutants including PBDD/Fs and PBCDD/Fs (Gündoğdu, 2024). Uncontrolled thermal disposal of e-waste and dismantling/recycling of e-waste containing brominated and/or chlorinated flame retardants can also lead to the formation of PBDD/Fs and PBCDD/Fs (ECHA, 2023b) and has been reported to emit PBDD/Fs at levels up to 50–500 times higher than those of PCDD/Fs (Yang et al., 2021). Similar results were observed in a study by Ortuño et al. (2014), where PBDD/Fs were formed as a result of the pyrolysis and combustion of waste printed circuit boards, with a total content of eleven 2,3,7,8-substituted congeners (tetra- through heptaBDD/Fs) was 7240 and 3250 ng WHO₂₀₀₅-TEQ/kg sample before and after metal removal, respectively.

30. An incomplete and uncontrolled incineration of plastics containing BFRs, occurring in fire accidents in private residences, can form high amounts of PBDD/Fs, which can be released and endanger the environment and persons in contact with fire residues (Ebert, 2003). PBDD/Fs were also analyzed in waste incineration residues sampled in Southern Taiwan. Relatively high levels of up to 61 pg WHO-TEQ/g dw were measured in the samples of different locations (Bell et al., 2023).

31. In a one-year air sampling study around a large-scale municipal solid waste incinerator (MSWI), the concentrations of PBDD/Fs and PCDD/Fs showed spatially decreasing trends with the distance away from the MSWI. The corresponding inhalation carcinogenic risks at some MSWI-vicinal sites exceeded the acceptable threshold of 10^{-6} to 10^{-4} proposed by the U. S. EPA (Li et al., 2023).

32. During the investigation on the feasibility of thermal valorisation of automobile shredder residue with regard to different oxygen ratios a significant difference in PBDD/F

release could be found. The highest concentrations of PBDD/Fs found were at low oxygen ratios (λ =0.35) at 600 °C and highly brominated hepta- and octabrominated dibenzofurans were obtained in 10-50 times higher concentration than the lower brominated congeners. In comparison, at 850 °C PBDD/Fs were almost only found at over stochiometric amounts of oxygen (λ =1.5), but the concentrations were still lower by a factor of 100 compared to the highest concentrations found at 600 °C. (Rey et al., 2016). Another study evaluated the occurrence of PBDEs, PBDD/Fs in polyurethane foam (PUF) from car seats of end-of-life vehicles (ELVs). The results showed that specific PBDD congeners were in general below the detection limit or found in low concentrations in foam samples from ELVs. However, in the two samples with the highest PBDE concentrations, PBDD concentrations were about a thousand-fold higher for specific congeners compared to the other samples. The concentrations of PBDFs were even higher, about a thousand-fold higher than the corresponding PBDDs. Maximum TEQ PBDD/F concentrations of 2.4 ng TEQ/g and 0.62 ng TEQ/g were observed, representing total concentrations of PBDD/Fs of about 410 ng/g and 140 ng/g, respectively (Redin et al., 2017). Products containing PBDD/Fs can contribute to their releases.

33. Use of plastic waste as an alternative fuel to wood in some countries and burning of e-waste have reportedly led to soils contaminated with PBDD/Fs and PBCDD/Fs (Ma et al., 2009; Weber et al., 2015). The highest PBDD/F levels (300 pg (TEQ)/g fat) in free-range chicken eggs, which are sensitive indicators of POP contamination in soils/dust and represent an important human exposure pathway, were found in an e-waste and automotive waste scrap yard in Ghana (Gündoğdu, 2024; Petrlik, Bell, et al., 2022). High concentrations in such eggs were also found in the surroundings of e-waste recycling sites in Kalasin province, Thailand (Dvorská et al., 2023). PBCDD/Fs were also found to occur in e-waste sites at elevated levels. Moreover, PBCDFs were substantial TEQ contributors in open burning areas (Tue et al., 2019).

34. PBDD/Fs were monitored in a cement production plant, which used petroleum coke as primary fuel, but also alternative fuels such as solid recovered fuel, automotive shredder residue, sewage sludge, waste tires and meat and bone meal. The monitoring was performed over the period of a year. PBDD/F emission values found ranged from 0.01 to 0.44 pg I-TEQ/m³. Due to no availability of bromine in the cement plant, the observed values stem from the materials used as fuels. The congener distribution was also investigated, and it was apparent, that there was a clear predominance of octa-substituted species (both dioxin and furan) followed by the hepta-substituted dioxin. Further, in all samples the furan/dioxin ratio found was >1 (Conesa et al., 2016).

35. Metallurgical facilities including sinter plants, electric arc furnaces (EAFs), secondary aluminium smelters and secondary copper smelters were identified as a significant source of PBDD/Fs into their surrounding atmospheric environments in Taiwan (Wang et al., 2008). Metal smelters are treating high inputs of BFR-containing plastics (Wu et al., 2020). Also secondary copper smelting processes are a source of PBDD/F emissions (Lin et al., 2022; Wang et al., 2015). PBDD/Fs are formed during thermal metallurgical processes (Yang et al., 2021). Wang et al. (2010) calculated emission rates of PBDD/Fs from metallurgical processes, including EAFs) fly ash treatment plants and sinter plants. They found average emission rates from 25 to 750 μ g/h (corresponding to 0.46 to 6.67 μ g TEQ/h) for the investigated metallurgical facilities in Taiwan with the highest values for sinter plants. PBDD/Fs and PBCDD/Fs are released from the incineration of WEEE (Dresch et al., 2014) and co-disposal of HBCD in a municipal solid waste incinerator showed increased concentrations of PBDEs and PBDD/Fs after the air

pollution control devices (Xie et al., 2024). The review by (Mwangi et al., 2015) concluded that, based on the few studies available, it is evident that diesel vehicle emissions are a relevant source of PBDD/Fs, PBBs and PBDEs. The mass concentrations of PBDD/Fs (417 ng/Nm³) are relatively higher than those of chlorinated pollutants such as PCDD/Fs (156 pg/Nm³) and PCBs (267 pg/Nm³). These values point out the significance as well as the contribution of the less understood and investigated brominated pollutants in comparison to their chlorinated homologues.

36. Stack gases from EAFs in steel producing facilities in China have been analyzed to determine, whether they significantly contributed to the emissions of PBDD/Fs. Average emission rates during the preheating stages of the furnaces revealed average emissions of 271.1 to 9467.8 pg/Nm³ (corresponding to 10.8 to 791.2 pg/Nm³ TEQ). These concentrations were reduced to 261.9 pg/Nm³ (4.5 pg/Nm³ TEQ) during the smelting stage. The wide fluctuations were caused by different factors, such as feeding materials and the working temperature of the bag filters. Further the different feeding materials also led to different PBDD/F congener patterns (Shen et al., 2021). Mean PBDD/F concentrations were 0.14 ng WHO-TEQ/m³ (range = 0.03–0.39) in a UK iron ore sinter plant (Drage et al., 2014).

37. For the sources identified in Japan (see paragraph 16), emission of PBDD/Fs into the atmosphere and water were monitored in Japan from 2003 to 2020. The annual releases to the atmosphere amounted to 1.96 g TEQ/year. This value decreased after regulation of decaBDE (in 2018) to 1.48 g TEQ/year. In water, the annual release of 3.08 g TEQ/year decreased to 1.46 g TEQ/year (NIP Japan, 2016). Compared to PCDD/Fs emissions, these releases in terms of TEQ are lower. For example in 2014, total PCDD/F emissions in Japan into air and water amounted to 121 to 123 g-TEQ (NIP Japan, 2016). Using the annual releases before the decaBDE regulation as a basis for comparison, it can be concluded that the contribution of the PBDD/Fs to the total TEQ was about 4%. Multiple PBCDD/Fs congeners were found in leachate from an industrial landfill in Japan indicating that landfill might be an additional source for their release into the environment (Hashimoto et al., 2021).

38. The occurrence of PBDD/Fs was positively correlated with local development levels and sediments from highly urbanized/industrialized areas in China (Liu et al., 2023). PBDE-related products/industries were the greatest contributors to contamination with PBDD/Fs in this area, followed by bromo-phenol/benzene-related products/industries. These results indicate that main contamination sources of PBDFs were technical PBDE formulations, especially decaBDE (Goto et al., 2017). Significant correlation between PBDFs and PBDEs was also observed in sediment samples of British lakes, whereas sources of PBCDD/Fs were not related to PBDEs and differ from those of PBDFs (Peters et al., 2021).

39. Appropriate risk management measures such as BAT/BEP developed to limit the formation of PCDD/Fs can also limit the formation of PBDD/Fs and PBCDD/Fs. BSEF provides specific information indicating that BFRs can be handled during their end of life phase without formation of significant dioxin/furan levels (Annex E, BSEF, 2024; Brusselaers et al., 2006; Dresch et al., 2014; Vehlow et al., 2002). Information on technologies for the destruction or irreversible transformation of specific POP-BFR wastes, is provided in subsection IV.G.2 of the Basel Convention general technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with POPs (UNEP/CHW.16/6/Add.1/Rev.1, 2023).

40. A study carried out in the UK to determine the concentrations of key pollutants, including PBDD/Fs, in solid residues and air emissions of energy from waste facilities showed, that concentrations of PBDD/Fs as partial products of combustion no consistent trend. Quantifying PBDD/Fs as partial products of combustion had a minor impact on the overall outcome as they were only found at very low concentrations (WRC, 2024).

2.2. Environmental fate

2.2.1 Persistence

41. The photodegradation half-life of TeBDDs in a 5 mm layer of soil exposed to daylight was found to be between 3 and 6 months. However, photodegradation is unlikely to be relevant in deeper soil layers. The soil used came from a remote rural site and was air-dried at room temperature for 14 days and ground in a pestle and mortar. Portions of the soil were given in 5mm deep aluminium trays. The samples were spiked with 40 μL each of PBDD/PBCDD mixture in hexane. The blank (unspiked) sample, and one spiked sample were extracted immediately. Half of the remaining spiked samples were kept in the dark indoors at room temperature, the rest was placed outdoors in a position where it was exposed to full sun. Samples were removed from the outdoor site at intervals over a 3-month period. A sample that had been kept indoors was extracted at the same time. Extracts were subjected to multi-layer and Florisil column chromatography and GC-MS analysis. No significant degradation of PBDDs and PBCDDs was observed in soil kept in the dark indoors, which indicates poor degradability (Chatkittikunwong & Creaser, 1994).

42. The photolysis of PBDDs/PBDFs was studied in various environments, including organic solvents, quartz surfaces, soil, and soot particles. Photodegradation was fastest in organic solvents under UV or sunlight, leading to reductive debromination and formation of lower brominated congeners. In contrast, photolysis was significantly slower in soil and on airborne particles. The degradation rate depends on bromine substitution, with higher brominated congeners breaking down more rapidly. PBDD/Fs degraded faster than their chlorinated analogues, and photolytic degradation was more effective in controlled solutions than in real environmental conditions (WHO, 1998).

43. During photolysis, PBCDD/Fs preferentially lose their bromine atoms and therefore are transformed into PCDD/Fs. Consistently short photolytic half-lives (0.5-4 min) were observed for the mixed mono- and dibromotetrachloroDD/Fs tested, whereas the resulting tetraCDD/Fs were much more stable. Such a transformation of PBCDD/Fs to PCDD/Fs can also occur during incineration processes (WHO, 1998).

44. Biodegradation is more relevant than photolysis in many media, including sediment, deeper layers of soil and surface water. PBDD/Fs and PBCDD/Fs have been found in sediment cores from English lakes (Peters et al., 2021). Similarly, PBDD/Fs, including DiBDDs and TrBDDs, have been detected in sediment cores from Tokyo Bay (Goto et al. 2017). Their presence in slices that were deposited several decades ago point to their persistence under these conditions. To estimate biodegradation half-lives, BIOWIN3 scores were derived using the BIOWIN v4.10 module implemented in EPI Suite (US EPA, 2017) for the PBDD/F congeners listed in *Table 1* as well as for the analogous PBCDD/F and PCDD/F congeners. The scores were converted to half-lives in water using the equation derived by (Scheringer et al., 2012). Note that the use of the equation derived by Rorije et al. (2011) would result in half-lives that are higher by a factor of 1.69 to 2.19. The half-lives in water were converted to half-lives in water and soil are

greater than the threshold of two and six months, respectively, for all PBDD/F and PBCDD/F congeners analyzed (for numerical values see UNEP/POPS/POPRC.21/INF/#, Table 1 and Table 2). As there are uncertainties associated with the numerical values of these estimates, the persistence of PBDD/Fs and PBCDD/Fs was further evaluated on the basis of empirical data available for PCDD/Fs. The relative duration of the half-lives of analogue chemicals, which differ only in the type of halogen atoms, is considered to be better captured than their absolute values. As shown in Figure 2, the estimated half-lives of PBDD/F and PBCDD/F congeners are consistently higher than those of analogous PCDD/F congeners calculated by the same method. Therefore, the actual half-lives of PBDD/F and PBCDD/F congeners are likely to be at least as high as those determined for their analogue PCDD/F congeners. Half-lives of PCDD/F congeners relevant to the Baltic environment were derived based on data available in the literature (Sinkkonen & Paasivirta, 2000). These data agree quite well for water, although the agreement becomes worse for higher chlorinated congeners (see Figure 2 and UNEP/POPS/POPRC.21/INF/#, Table 2). For soil, on the other hand, the half-lives derived by Sinkkonen & Paasivirta (2000) are considerably higher than those estimated based on the BIOWIN3 scores. Another data set of PCDD/Fs half-lives in soil is available from a more recent study (Terzaghi et al., 2020). Data were derived from a greenhouse experiment performed with an aged contaminated soil under semi-field conditions in Northern Italy. These half-lives are closer to those estimated based on the BIOWIN3 scores but are mostly higher and do not show a clear trend.



Figure 2. Estimated biodegradation half-lives of PBDD/F and PBCDD/F congeners in water (left) and soil (right), compared to those of PCDD/Fs and grouped according to the number of halogen atoms. Empirically derived half-lives of PCDD/F congeners (Sinkkonen & Paasivirta, 2000; Terzaghi et al., 2020) are also displayed. Dashed lines represent the thresholds for persistence according to Annex D (60 and 180 days).

45. According to additional biodegradation predictions provided by the UK (Annex E, UK, 2024), PBDD/Fs and PCBDD/Fs are similar to PCDD/Fs not readily biodegradable in water, with the probability values for degradation in the range from 0 to 0.029 (calculated using BIOWIN2) or from 0.007 to 0.0702 (calculated using BIOWIN6) for PBDDs and from 0 to 0.051 (calculated using BIOWIN2) for PCBDD/Fs, respectively (for values see UNEP/POPS/POPRC.21/INF/#, Table 3 and Table 4).

46. In conclusion, tetra- to octahalogenated PBDD/Fs and PBCDD/Fs meet the criteria for persistence with high confidence. Di- and trihalogenated PBDD/Fs and PBCDD/Fs are also likely to meet the persistence criteria, but with less confidence. On the other

hand, monobrominated dibenzo-*p*-dioxins and dibenzofurans are unlikely to meet these criteria.

2.2.2 Bioaccumulation

47. The log *K*_{OW} values of the PBDD/F congeners, estimated using the KOWWIN v1.69 module implemented in EPI Suite (US EPA, 2017), range from 4.9 to 11.5, those of the analogous PBCDD/F congeners from 5.6 to 10.5 (see UNEP/POPS/POPRC.21/INF/#, Table 5). It is noted that the molecular weights of HpBDD, OBDD and OBDF are above the upper end of the values in the KOWWIN training set (720 g/mol), which might imply a somewhat lower accuracy for these compounds. The KOWWIN estimates are in line with other predicted values of 5.23 to 7.90 for mono- to tetra-brominated PBDD/Fs (Arnoldsson, 2012).

48. In fish, PBDD/Fs were found to generally have uptake and elimination patterns similar to those of the PCDD/Fs. The halogen substitution pattern influences the retention of these substances. PBDDs with unsubstituted vicinal positions are less strongly retained than other congeners in fish (Arnoldsson et al., 2012). Thereby, concentrations in fish were examined during a 6- or 12-week uptake period, and a 6-week elimination period via food uptake. Nominal concentrations of 1 ng congener per gram of feed were tested. Half-lives decreased in the order PCBs > PCDD/Fs > PBDD/Fs. For example, the half-life for 2,3,7,8-TeBDF was 5.0 days, the half-life for 2,3,7,8-TeBDD was 12 days and the half-life of 2,3,7,8-TeCDD was 36 days. Similar to OECD TG 305, fish were fed with 2% of their body weight each day. On the other hand, PBDDs appear to be more resistant to mammalian metabolism than PCDDs (Birnbaum et al., 2003; Bjurlid, Dam, et al., 2018).

49. Fernandes et al. (2023) found that the uptake of PBDD/Fs by chicken muscle tissue, liver and eggs from recycled bedding material. The average TEQ contribution from the brominated contaminants was 33% and 44% in eggs and tissues respectively (> 96% thereof was from PBDD/Fs).

50. PBDD/Fs have been found in organisms that are high up in the food web, including ringed seals (*Pusa hispida botnica*) from the Baltic Sea and pilot whales (*Globicephala melas*) caught around the Faroe Islands. 1,2,3,4,6,7,8-HpBDF was the most abundant congener in both studies. The concentration range for ∑PBDD/Fs was 0.080–71 pg/g l.w. (lipid weight) (median 3.6 pg/g l.w.) in 20 of 26 whale blubber samples, and 0.5–52.3 pg/g l.w. (median 8.6 pg/g l.w.) in the seal blubber (22 pooled samples from 68 seals). (Bjurlid, Dam, et al., 2018; Bjurlid, Roos, et al., 2018). In both species, no correlation was found between concentrations of PBDD/Fs and PBDEs, which indicates differences in exposure or tentatively differences in metabolism of PBDEs and PBDD/Fs (Bjurlid, Dam, et al., 2008; Hagberg et al., 2011; Lundstedt, 2016).

51. The elimination half-life in mice of TrBCDF is 5.6 days, followed by TeBDF and TeCDD (both approximately 8.8 days), and PeBDF, which was eliminated more slowly (13 days). The non-2,3,7,8-substituted TrBDF exhibited rapid elimination following two-phase kinetics (Tue et al., 2024).

52. Elimination half-lives for 2,3,7,8-TeBDD in rat liver, feces and adipose tissue were estimated to be 17, 18, and 58 days, respectively. They are similar to those reported for 2,3,7,8-TeCDD in liver and feces, but higher than those in adipose tissue. Despite

differences in early retention, half-lives of 2,3,7,8-TeBDF and 2,3,7,8-TeCDF in liver are comparable (WHO, 1998).

53. While 2,3,7,8-TeCDF is metabolized rather rapidly in rats and mice with a half-life of less than 2 days, 2,3,7,8-TeBDF appears to be much more resistant to metabolism, resulting in a longer half-life. In a study from Tue et al. (2024) the half-life of TeBDF in mice is 8.8 days. The elimination half-life of 2,3,7,8-TeBDD in rats is between 2 and 3 weeks, similar to that of 2,3,7,8-TeCDD. If the relationship between rat and human half-lives for 2,3,7,8-TeCDD holds for 2,3,7,8-TeBDD, this would suggest a half-life in the range of 5to 10 years in humans (Birnbaum et al., 2003). According to ECHA (2023b), an elimination half-life greater than 4 days in rats and/or greater than 50 days in humans is indicative of high bioaccumulation (vB).

54. Elimination half-lives ranging from 1.1 to 1.9 years and from 2.9 to 10.8 years have been determined for 2,3,7,8-TeBDF and 2,3,7,8-TeBDD, respectively, in workers assigned to the extrusion of plastic resins containing PBDEs (Zober et al., 1992). A chemist who had synthesized 2,3,7,8-TeBDD in 1956 was found to have markedly elevated blood levels 35 years after exposure (WHO, 1998). The estimated half-lives for humans are 3–11 years (mean: 5.9 years) for 2,3,7,8-TeBDD and of 1–2 years (mean: 1.5 years) for 2,3,7,8-TeBDF (WHO, 1998).

55. After rats were exposed via gavage, intratracheally or dermally, radiolabelled 2,3,7,8-TeBDD exhibited nonlinear oral and transpulmonary absorption kinetics with maximum absorption (~80%) occurring at dose \leq 10 nmol/kg, while dermal absorption of 2,3,7,8-TeBDD was low (~12%). The major tissue depots of radioactivity were liver, adipose tissue, and skin and the major route of excretion was the feces where between 30 and 80 % of the dose was found 72 hours after administration (Diliberto et al., 1993; Mennear & Lee, 1994).

56. The long elimination half-lives of PBDD/Fs in mammals, suggest that these substances are highly bioaccumulative. The detection in human tissues and in breast milk adds to the concern. PBCDD/Fs have physicochemical properties in the range between PCDD/Fs and PBDD/Fs, including a log *K*_{OW} at or greater than 5. Since both PCDD/Fs (as a recognized POP) and PBDD/Fs are bioaccumulative, it is very likely that this is also the case for PBCDD/Fs. Moreover, in combination with the high toxicity of PBDD/Fs and PBCDD/Fs (see below), even moderate bioaccumulation can lead to body concentrations that elicit adverse effects. Furthermore, PBCDD/Fs may photochemically be transformed to PCDD/Fs. Likewise, higher brominated PBDD/Fs may form lower brominated PBDD/F congeners (WHO 1998).

57. It can therefore be concluded that PBDD/Fs and PBCDD/Fs fulfil the criteria for bioaccumulation.

2.2.3 Potential for long-range environmental transport

58. PBDD/Fs and PBCDD/Fs undergo atmospheric oxidation by reaction with OH radicals. For PBDD/F congeners, the rate was found to be dependent on the bromination pattern (Zeng & Wang, 2018). The AOPWIN v1.92 module implemented in EPI Suite (US EPA, 2017) was applied to calculate the gas-phase half-lives of PBDD/F and PBCDD/F congeners, based on second-order rate constants for the reaction with OH radicals. A 24-hour average concentration of photochemically generated OH radicals in air of 7.5 × 10⁵ OH radicals/cm³ (as implemented in AOPWIN) was used. It is noted that the AOPWIN

training set contains 18 organobromine compounds including bromobenzene as well as various halogenated aromatics. The half-lives obtained are 1.8 to 504 days for PBDD/F congeners and 2.8 to 435 days for PBCDD/F congeners. These estimates are slightly higher than for the analogous PCDD/F congeners (see UNEP/POPS/POPRC.21/INF/# Table 6), which are recognized POPs. PBDD/Fs can undergo photolysis (Yang et al., 2021). However, due to their physicochemical properties, the PBDD/F and PBCDD/F congeners are expected to occur predominantly particle-bound in the atmosphere (WHO, 1998). As the sorbed fraction undergoes little or no atmospheric oxidation, the atmospheric half-lives will be higher than those calculated for the gas phase. The Annex D criterion of a half-life in air greater than two days is therefore met, at least for di- to octahalogenated PBDD/Fs and PBCDD/Fs.

59. A recent modelling study concludes that each of the investigated PBDD/F congeners (tetra- to heptabrominated) exceeds the threshold for POP-like accumulation in the remote region when emitted to air or water, but not to soil. For the modelling, selected brominated dioxins and furans (PBBD/Fs) were screened for their potential to be dispersed, transferred to, and accumulated in remote regions. The screening was carried out applying a set of LRTP metrics, collectively referred to as the emissions fractions approach (EFA), as implemented in a modified version of the OECD Pov and LRTP (long-range transport potential) Screening Tool. The Tool is parameterized to reflect the environmental characteristics of the global environment and it includes one air, one water, and one soil compartment. Input parameters were the log *K*_{OW}), the log K_{AW} and the degradation half-lives in air, water, and soil. Thresholds for POP-like behavior for each of the metrics were defined as the lowest values predicted for a set of 14 legacy POPs based on any of the three default emission scenarios (100% to air, 100% to water, and 100% to soil) (Breivik et al., 2023).

60. Another modelling study by Kawai et al. (2014) compared the long-range transport potential of groups of halogenated POPs and POP-like chemicals using a new metric, the global average of imported fractions in receptor regions (GIF). The authors used a 3D atmospheric transport model (FATE) to simulate the transport and fate of various chemicals, including PCBs, PCDDs, PCDFs, and PCDEs, and compared the performance of the new GIF metric with existing metrics. The GIF of PBDDs and PBDFs was 0.09 to 0.21 and 0.11 to 0.21, respectively, which overlap with the ranges obtained for PCDDs (0.17–0.22) and PCDFs (0.13–0.27). It should be noted that the number of congeners investigated for PBDDs (20) and PBDFs (31) was higher than for PCDDs (5) and PCDFs (13), respectively. The GIF is defined as a global average of imported fractions in receptor regions weighted by the contents.

61. PBDEs have been found to be transported to remote areas as additives in plastic debris in the oceans. There, they can be ingested by seabirds and other animals, leading to accumulation in their bodies (Andrade et al., 2021; Yamashita et al., 2021). As PBDD/Fs have been found to be present in plastics containing PBDEs or other BFRs, and they have similar physicochemical properties, it is likely that PBDD/Fs can also be transported to remote areas with plastics and accumulated in animals ingesting these plastics. Wang et al. (2021) found PBDD/Fs in plastic pellets from beaches in Taiwan in the ranges of up to 1388 pg/g for surficial adsorption, and from 3092 to 29,343 pg/g for total adsorption, respectively. In a more recent study, the authors studied the fate of PBDD/Fs in microplastics and seawater from Taiwanese sea ports. They calculated enrichment factors to show the concentration effect for PCDD/Fs, PBDD/Fs and dl-PCBs in microplastic in seawater and in suspended particulate matter in seawater. The enrichment factors are slightly higher for PBDD/Fs than for PCDD/Fs and dl-PCBs (Wang

et al., 2024). It could be concluded that PBDD/Fs (and probably PBCDD/Fs) are enriched in microplastics and can be transported in seawater to remote regions together with microplastics. The strong dominance of PBDFs, over PBDDs, in all studies supports the theory that most PBDD/Fs in the atmosphere, even in remote areas, originate from BFR-containing materials (Lundstedt, 2016). DecaBDE, for example, has also been found to be transported to remote areas by air. DecaBDE deposited to the Arctic environment is bioavailable to organisms living there and is widespread in Arctic food webs (UNEP/POPS/POPRC.10/10/Add.2, 2014). Kajiwara et al. (2008) have found formation of PBDD/Fs in flame-retarded plastics under natural sunlight. It can therefore be concluded that PBDD/Fs could be formed from flame-retarded plastics, once they reach remote areas.

62. Air concentrations of PBDD/Fs were similar in the city of Gothenburg on the Swedish west coast (number of samples: 4 in total; years of monitoring: 2011-2012; concentrations measured: 1.5–1.8 fg/m³ for Σ PBDD and 2.1–510 fg/m³ for Σ PBDFs) and in Råö (number of samples: 16; years of monitoring: 2011-2012; concentrations measured: 1.1–310 fg/m³ for Σ PBDD and 34–1200 fg/m³ for Σ PBDFs), the background monitoring station on the Swedish west coast. The concentration of PBDD/Fs in air samples from Pallas (number of samples: 2; years of monitoring: 2011–2012; concentrations measured: <LOD for Σ PBDDs and 39–91 fg/m³ for Σ PBDFs), a remote station in northern Finland was lower, but indicate long-range environmental transport (Lundstedt, 2016; Remberger et al., 2014). PBDDs where generally found at lower levels and were not found above detection limits in Pallas (Remberger et al., 2014). Another study indicating long-range transport of PBDD/Fs in air masses was conducted near Taiwan, where Chao et al. (2014) measured 0.0013 pg WHO-TEQ/m³ in the air over the ocean. Only the highly brominated PBDF congeners were detectable. 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and OBDF were found in the atmosphere over both the ocean and land. The mean PBDD/F concentration in the oceanic atmosphere was higher than in the ambient air of the rural area. The authors conclude that the halogenated POPs (note: including the PBDD/Fs) originated from Taiwan or the continental East Asia could easily reach remote ocean sites via atmospheric transport

63. As mentioned in paragraph 50 50, PBDD/Fs have been found in pilot whales (*Globicephala melas*) caught around the Faroe Islands (Bjurlid, Dam, et al., 2018), providing additional evidence that PBDD/Fs undergo long-range environmental transport.

64. PBDD/Fs were identified in lichens (5.7–16.2 pg/g), soils (0.25–2.62 pg/g), and ornithogenic soils (0.77–1.61 pg/g) in the Antarctic coastal environment (Mwangi et al., 2016). However, the authors extrapolated that the relatively elevated PBDD/F contents in samples from sampling sites near research bases could be from the burning of waste containing plastics used for generating electricity and domestic heating in the Antarctic research stations. No conclusions could be drawn on long-range transport potential of PBDD/Fs from this study.

65. Monitoring data for PBCDD/Fs in the environment and the human food chain are limited. This is mainly due to the complex analytical methods required and the lack of pure analytical standards (Kannan et al., 2012; van den Berg et al., 2013; Weber et al., 2015). New approaching workflows to screen PBCDD/Fs by two-dimensional gas chromatography/time-of-flight mass spectrometry and post-data processing has been suggested recently (Hashimoto et al., 2021). In Baltic wild salmon (*Salmo salar*), 3-B-2,7,8-tri-CDF was detected in the concentration range from 0.039 to 0.075 pg/g fresh weight (Zacs et al., 2013). *Salmon salar* is a migratory species and as such can

contribute to the long range transport. (Wania, 1998). 22 other PBCDD/Fs were not detected. The fish were sampled from two Latvian rivers.

66. In conclusion, PBDD/Fs and PBCDD/Fs fulfil the criteria for long-range environmental transport.

2.3 Exposure

2.3.1 Environmental monitoring data

67. Limited historical data on the occurrence of PBDD/Fs and PBCDD/Fs have been recorded, most of which confirm emissions from incineration processes containing chlorine and bromine in the raw materials (Wang et al., 2023; Wang et al., 2010). Goto et al. (2017) investigated the occurrence of mono- to octabrominated PBDD/Fs in Tokyo Bay, Japan, using ²¹⁰Pb-dated sediment cores covering the period 1895–2000. PBDDs were more abundant than PBDFs before the 1960s. PBDF levels were found to increase up to the most recent sediment layer. Peters et al. (2021) analyzed temporal trends of PBDEs, PBDD/Fs and PBCDD/Fs using ²¹⁰Pb-dated cores from English lakes between 1950 and 2015 and found that PBDEs increased towards the present and were significantly correlated (R = 0.88–0.98; p < 0.05) with concentrations of PBDFs ranging from 0 to 19,000 pg/g OC, whereas PBCDD/Fs concentrations decreased. (Peters et al., 2021).

68. Several researchers have investigated the distribution of PBDD/F contaminants in sediment samples from different global locations. Xiao et al. (2016) reported high mean concentrations in Chinese e-waste areas Longtang (527 pg/g), that correspond to the highest level found by Liu et al. (2022) in another Chinese e-waste area Guiyu (124-568 pg/g, mean: 355 pg/g). A level of 1,862 pg WHO-TEQ/g of PBDD/Fs was measured in sediment from a pond inside a dumpsite in Kalasin Province, Thailand, where electronic waste, including plastics, is burned (Dvorská et al., 2023). A very high PBDD/F concentration in sediment up to 10000 pg/g was found at a coastal area of Sweden adjacent to some metal smelters that partially used e-waste as feed stocks (Lundstedt, 2016). Edgbaston Pool, a lake in a highly populated area in the UK, had anomalously high levels up to 7100 pg/g (Peters et al., 2021). Levels from other industrialized regions show a great diversity suggesting different pollution profiles in different urban and industrial landscapes. Examples are South Korea Sea Coast (n.d. to 460 pg/g) (Terauchi et al., 2009), Hong Kong Coast (11.0-217 pg/g) (Terauchi et al., 2009) and Japan's Osaka Bay (2.4–590 pg/g) (Takigami et al., 2005) and Tokyo Bay (2.2–66 pg/g) (Goto et al., 2017), Baiyangdian (China) (n.d. to 280 pg/g) (Zhao et al., 2019) and the Pearl River Delta (China) (1.57–1300 pg/g) (Liu et al., 2023).

69. In seawater at Kaohsiung Harbor (Taiwan) total dioxin-like toxicity from PCDD/Fs, PCBs and PBDD/Fs ranged from 0.00936 to 0.167 pg WHO-TEQ/L, with PBDD/Fs accounting for 19 % of total toxicity. The authors state that PBDEs in seawater can transform into PBDD/Fs upon UV light exposure, highlighting another potential pathway for the persistence and spread of these harmful contaminants in the environment (Wardiani et al., 2024). The PBDD/F levels totaled 0.0169 and 0.00195 pg WHO-TEQ/L at KH-1 and KH-2, respectively, but ranged from 0.00224 to 0.0206 pg WHO-TEQ/L for KH-3, KH-4, and KH-5, with KH-5 predictably accounting for the maximum. PBDD/Fs have been found in a broad range of marine biota, including pilot whales, seals, fish, shellfish and mussels (Bjurlid, Dam, et al., 2018; Bjurlid, Roos, et al., 2018; A. Fernandes et al., 2009; Haglund et al., 2007). Bjurlid, Dam et al. (2018) analyzed brominated dioxins

PBDD/Fs in blubber from juvenile male Faroese pilot whales during the period 1997-2013. The concentration range for the sum of PBDD/Fs among the samples was 0.080-71 pg/g lipid weight. In addition, samples from the period 2010–2013 were analyzed for PBDEs. and its sum ranged from 140 to 1900 ng/g lipid weight. Bjurlid, Roos, et al. (2018) analyzed 22 pooled samples from 69 individuals of Baltic ringed seal for PBDD/Fs from 1974 to 2015. The sum of PBDD/Fs ranged from 0.5-52.3 pg/g lipid weight with 1,2,3,4,6,7,8-HpBDF contributing on average 61% to this sum. The sum of PCDD/Fs ranged from 103 to 1480 pg/g lipid weight with 1,2,3,6,7,8-HxCDD, 1,2,3,7,8-PeCDD, and 2,3,4,7,8-PeCDF showing the highest average concentrations. PBDD/Fs contributed on average 1.1% to the total TEQ. Fernandes et al. (2009) analyzed 60 samples of Pacific oysters (Crassostrea gigas), native oysters (Ostrea edulis), mussels (Mytilus edulis), scallops (Pecten maximus), and cockles (Cerastoderma edule) from different coastal regions in the UK between 2006 and 2007 for the occurrence of PBDD/Fs and PBDEs. The sum of 17 PBDEs ranged from 0.06 ng/g fresh weight to 3.23 ng/g fresh weight. The highest concentration of PBDE congeners was BDE-47 with 1.34 ng/g fresh weight. Haglund et al. (2007) analyzed PBDDs in marine fish, mussels, and shellfish collected from different locations in Sweden. The maximum total PBDD level was 4100 pg/g wet weight. In studies from UK, PBDFs occurred in most cases more frequently and generally at a higher levels than PBDDs (similar PBCDFs > PBCDDs) in marine fish and shellfish (mean concentrations indicate 0.25 pg/g fresh weight for 2,3,8-TrBDF and 0.13 pg/g fresh weight for 2,3,7-TrBDD in Scallops Gonad (A. Fernandes et al., 2009)) and contamination appeared to be consistent with the extent of local industrialization with lower levels observed in more remote areas such as the north of Scotland (A. Fernandes et al., 2009; Rose et al., 2015). In contrast, some species present in the Baltic Sea show a prevalence of less brominated congeners (mono- to penta-), which combined with an analysis of the spatial distribution, suggests local natural biogenic production, for example in red algae (Ceramium tenuicorne), blue mussels or aquatic sponge (Ephydatia fluviatilis) (Arnoldsson et al., 2012; Haglund et al., 2007; Unger et al., 2009). Higher brominated congeners like 1,2,3,4,6,7,8-HpBDF that was the predominant congener found in pilot whales from the Faroe Island (concentration ranges for Σ PBDD/Fs are reported from 0.080 to 71 pg/g lipid weight) (Bjurlid, Dam, et al., 2018) and in seals $(\Sigma PBDD/Fs ranged from 0.5 to 52.3 pg/g lipid weight) from the Baltic Sea (Bjurlid, Roos,$ et al., 2018) indicates that the PBDD/Fs found in these samples largely originated from anthropogenically related processes. 1,2,3,4,6,7,8-HpBDF was also found in cod liver derived products sourced from the Baltic Sea with levels up to 0.302 pg/g fat (Falandysz et al., 2020).

70. A temporal trend could be found for PBDD/Fs in seals from the Baltic Sea between 1974–2013 with concentrations ranging from 0.5 to 52.3 pg/g lipid weight (Bjurlid, Roos, et al., 2018). Visual inspection of the data showed decreasing concentrations for all compound groups except PBDD/Fs. A slight increase in the PBDD/Fs concentrations was observed from 2004 onwards. The authors noted that the generally low concentrations hampered interpretation of temporal trends. No trend was found in cod liver oil sourced from the Baltic Sea between 1972–2001 (Falandysz et al., 2020), however, this data is based on underestimates as the authors were only able to analyse a limited amount of PBDD/F congeners.

71. Wang et al. (2008) investigated PBDD/Fs in different atmospheric environments in Taiwan. The mean PBDD/F concentrations in the atmosphere of the rural, urban, industrial, and science park areas were 11, 24, 46, and 95 fg/Nm³, respectively. These values are rather low but according to the same authors, PBDF concentrations in stack flue gases of full-scale municipal solid waste incinerators (MSWIs) of 2.28 pg/Nm³ were

also low (L.-C. Wang & Chang-Chien, 2007). PBDFs were all much more dominant than PBDDs in the atmosphere, and their mass fractions increased with PBDD/F concentrations. In another study of atmosphere and bulk deposition in Kyoto, Japan also PBDFs were predominant and PBDDs were detected only at trace levels (Hayakawa et al., 2004).

Japan surveys since 2002 PBDD/Fs in exhaust gas, drainage and air inside 72. buildings of selected facilities focusing on the life cycle of products that contain BFRs. The facilities to be surveyed are selected each year. The results are published (in Japanese) (NIP Japan, 2016). Monitoring data from Japan starting from 2002 for PBDD/Fs in the surrounding areas of selected facilities focusing on the life cycle of products that contain BFRs found concentration ranges in the atmosphere from 0.10 to 990 pg/m³ (average 22 pg/m³) with higher concentrations around a flame-retardant resin manufacturing facility (2002) and flame-retardant manufacturing facilities (2003 and 2006). In dust fall, a range from 140 to 180,000 $pg/m^2/day$ (average 16,000 $pg/m^2/day$) was found with higher concentrations at a home appliance recycling facility (2002) and a flame-retardant resin manufacturing facility (2002). In public water bodies a range from ND to 7,400 pg/L (average 330 pg/L) was found with higher concentrations around a flame-retardant textile processing facility and around a sewage treatment facility. In public water sediments, a range from ND to 13,000 pg/g dry weight (average 630 pg/g) was found with higher concentrations around a flame-retardant resin manufacturing facility (TrBPhs end-treated TBBPA type epoxy resin), a flame-retardant resin manufacturing facility (TBBPA epoxy resin), a home appliance recycling facility and a flame-retardant textile processing facility (Annex E, MoE Japan, 2024). PBDD/F levels in dust from the Ban Nong Bua dumpsite reached 16,898 pg WHO-TEQ/g dw, while levels in ash from the same site were 17,458 pg WHO-TEQ/g dw. In the shredding plant at an e-waste site in Kalasin Province, Thailand, levels were slightly above 426 pg WHO-TEQ/g dw (Dvorská et al., 2023). At a different location near the e-waste processing plant in Khao Hin Son, Thailand, levels ranged from 4 to 10 pg WHO-TEQ/g dw (Petrlik, Boontongmai, et al., 2022).

73. PBDD/Fs have also been found in soil. (Amuah et al., 2024) summarized data from previous studies in Agbogbloshie, Ghana. Total PBDDs recorded levels of 3400–82,000 and 120–4000 (pg/g dry weight) in soil samples taken from non-e-waste, no-burning and burning sites (Tue et al., 2016). Tue et al. (2016) further indicated that PBDFs ranged between ND and 100, 2600 and 83,000, and 83,000 and 3,800,000 (pg/g dry weight) for the non-e-waste, no-burning and burning areas respectively. The total levels (ng/g) of PBDD/Fs (83–3800) > PCDD/Fs (18–520) > DL-PCBs (3.4–83) > DL-PCBs (3.4–83) were detected in the open burning areas of the Agbogbloshie e-waste site. The constituents in non-burning areas (PBDD/Fs: 2.6–83 ng/g; PCDD/Fs: 1.0–7.0 ng/g; DL-PCBs: 1.4–7.5 ng/g) were 1–2 orders lower than those in open burning areas, but about two orders higher than those in non-e-waste locations in Accra (ND to 100 ng/g; 8.0–300 ng/g and 2.7–290 ng/g)" (Amuah et al., 2024).

74. PBDD/Fs have also been found in soil, wastewater, sludge, fly ash, various animal and plant species, food and feed, indoor dust and humans (Altarawneh et al., 2019; Bell et al., 2023; Lundstedt, 2016; Ma et al., 2009).Bell et al. (2023) analyzed disposed waste incineration residues in Taiwan for PBDD/F residues. PBDD/Fs were only detected in ash samples from two of five sampled localities, with concentrations up to 61 pg WHO-TEQ/g dw. Ma et al. (2009) reported total PBDD/F (10 congeners) concentrations in leaves (n=6) (from a nearby e-waste recycling facility) of 113–818 pg/g dw, in an electronic shredder (n=5) of 392–18500 pg/g dw, in soil samples (n=10) of 716–800000 pg/g dw, in

workshop-floor dust (n=5) of 89600 –143000 pg/g dw, and in soil from a chemicalindustrial complex (n=12) up to 427 pg/g dw., PBDD/Fs were also found in blood, viscera and meat samples of cattle raised in one Indonesian landfill (n=2) with concentrations up to 38.59 pg/g fat in viscera with 1,2,3,4,6,7,8-HpBDD as the predominant congener (Ismawati et al., 2024). PBDD/F levels ranging from below the LOQ to 1.7 pg WHO-TEQ/g fresh weight were measured in apple snails from the vicinity of a dumpsite where e-waste is burned in Thailand (Dvorská et al., 2023). Apple snails are part of the diet for local community.

2.3.2 Human exposure

75. PBDD/Fs were found in children's plastic toys and other consumer products sampled from 26 countries around the world. These toys were likely manufactured using BFR-containing recycled plastics with high levels of PBDD/Fs. The samples included in this study contained significant levels of PBDD/Fs, PBDEs, TBBPA and other BFRs. It was estimated that the daily ingestion of PBDD/Fs from contaminated plastic toys could contribute substantially to the total daily PBDD/F intake of young children due to their mouthing habits (P. Behnisch et al., 2023; Budin et al., 2020).

In the serum of firefighters, levels of PBDD/Fs were found to be one order of 76. magnitude higher than those of PCDD/Fs (Shaw et al., 2013). Firefighters are exposed to flame retardants, PBDD/Fs and PCDD/Fs. PBDD/Fs were found in relatively higher concentrations in air and on surfaces of personal protection equipment than PCDD/Fs and thus may be of greater concern with regard to occupational exposures (Fent et al., 2020). Blood serum of Vietnamese women from the e-waste sector was analyzed for nine PBDD/F congeners. In non-recyclers (recruited from nearby commune), total PBDD TEQ accounted for 48.80% and PBDF TEQ for 28.06% of the total dioxin load, making PBDDs/PBDFs responsible for 76.86% of their total TEQ. In recyclers, PBDD TEQ contributed 43.78% and PBDF TEQ 26.03% of the total dioxin load, making PBDDs/PBDFs responsible for 69.81% of their total TEQ (Peecher et al., 2022). A chemist who had synthesized 2,3,7,8-TeBDD in 1956 was found to have markedly elevated blood levels 35 years after exposure (WHO, 1998). The results of the analyses of PBDD/Fs in indoor and outdoor air of gymnasiums in Taiwan showed that indoor-dust. indoor PM2.5, and outdoor PM2.5 levels of PBDD/Fs were 37.8 ± 13.7 pg WHO2005-TEQ g^{-1} and 0.00650 ± 0.00340 and 0.00469 ± 0.00101 pg WHO2005-TEQ m^{-3} , respectively (Su et al., 2022). A study by Tue et al. (2013) analyzed house dust from New York State for dioxin-like (DL) activities and dioxin-related compounds (DRCs), including polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs). PBDD/F concentrations varied widely (0.33–150 ng/g, median 2.1 ng/g), with contributions to CALUX-TEQs ranging from <1% to 21%.

77. According to several studies monitoring the occurrence of PBDD/Fs in human milk, their contribution to total TEQ levels varies. In Sweden, PBDD/Fs contributed an average of 40% to the TEQ (Bjurlid, 2018). In Germany, the median (95th percentile) concentrations of PBDD/F congeners were at 0.62 (2.69) pg WHO₂₀₀₅TEQ/g lipid weight contributing approximately 11% (Fromme et al., 2022). Shanghai samples contained three PBDF congeners (no PBDDs) – 2,3,7,8-TeBDF, 1,2,3,4,6,7,8-HpBDF, and OBDF – with mean concentrations of 3.2 pg/g (72.5%), 9.5 pg/g (100%) and 28 pg/g (67.5%), respectively (Y. Lin et al., 2021). In a global WHO monitoring study of 38 pooled samples from 28 countries, PBDD/F concentrations contributed about 10% to overall TEQ on average (Schächtele et al., 2023).

78. Additional human monitoring studies are focusing on PBDD/Fs in human adipose tissue. Hagberg et al. (2011) reported that ten human adipose tissue samples were analyzed for PBDD/Fs. In all samples, 2,3,7,8-TeBDF was present in levels ranging from 0.23 to 0.54 pg/g lipid and pentabrominated furans were present in nine out of ten samples. The levels of 2,3,7,8-TeBDF, 1,2,3,7,8- and 2,3,4,7,8-PeBDF were similar to those reported in the previous screening study (Ericson Jogsten et al., 2010). Similarly, Thatcher et al. (2015) examined PCDDs and PBDDs in the visceral and subcutaneous adipose tissue and liver biopsies, reporting that PBDD/F TEQ concentrations were relatively low, contributing less than 5% of adipose tissue TEQ and under 10% of liver TEQ, with 2,3,7,8-TeBDF and 2,3,4,7,8-PeBDF being the most frequently detected compounds. Another Swedish study found PBDFs in human adipose tissue at concentrations between 0.27 and 2.24 pg/g (Ericson et al., 2008).

79. PBDD/Fs are present in most commonly consumed foods contributing to the dietary intake of PBDD/Fs (A. R. Fernandes & Falandysz, 2021; Rose et al., 2010). Analysis of various food samples (eggs, milk, fish, shellfish, pork, beef and poultry) showed mean TEQs for the PBDD/Fs ranging from 0.15 to 0.48 pg/g fat upper bound in the animal products and 0.03–0.05 pg/g whole weight in shellfish and fish. The most frequently detected congeners were 2,3,7,8-TeBDF, 2,3,7,8-TeBDD as well as 1,2,3,4,6,7,8-HpBDD/F. 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF and OBDF were also detected in some samples (Ceci et al., 2022). In another study, PBDD/Fs were found at higher concentrations than their chlorinated analogues in lower-lipid food groups like bread, cereal, potatoes, and fresh fruit, with the most abundant congener being 1,2,3,4,6,7,8-HpBDF (Bramwell et al., 2017). In a Swedish study, the levels of PCDD/Fs decreased over time in breast milk samples from 1997 to 2011. In the same study, PBDD/Fs were found above the detection limit in only one sample from 2010, contributing with 1.6% to the total TEQ (Haglund et al., 2014). Levels of PBDD/Fs in Italian food showed that terrestrially raised food had low or nondetectable levels of contamination compared to fish and shellfish with concentrations of <0.001 to 4.58 pg/g in fish. The dietary exposure (upper bound) of different Italian population groups, resulting from these occurrence levels was estimated using TEQ approach that is commonly used for dioxin-like contaminants and ranged from 0.17 to 0.42 pg TEQ/kg bw/day (Diletti et al., 2020). Additionally, levels of PBDD/Fs in Polish food samples, including fish, meats, livers, milk, and eggs, ranged from 0.023 to 1.6 pg WHO-TEQ/g fat, with the highest concentrations detected in ostrich eggs. As observed in other studies PBDFs were more prevalent than PBDDs, with the most frequently found congeners 2,3,7,8-TeBDF, 2,3,4,7,8-PeBDF, 2,3,8-TeBDF and 1,2,3,4,6,7,8-HpBDF (Rose & Fernandes, 2010). In the research by Teebthaisong et al. (2021), fifteen pooled samples of free-range chicken eggs (from 14 hot spots around the world) and two reference samples from supermarkets were analyzed for PBDD/Fs. The highest level of PBDD/Fs were measured in eggs from Agbobloshie, Ghana (300 pg TEQ/g fat), an e-waste and end of life vehicles scrapyard followed by eggs from the vicinity of waste incinerators in Wuhan (27 pg TEQ/g fat). In the dietary study conducted by Mortimer et al. (2013), the total diet was estimated by measuring a range of contaminants in composites representing 19 food groups (such as bread, cereals, carcass mat, offal, poultry, fish, etc.) in the UK. Dietary exposures for average and high-level (97.5th percentile, P97.5) consumers were estimated by using the Intake Programme (software developed for the Food Standards Agency). The estimated dietary exposures to total PBDD/Fs for all age group (toddlers, children aged 4–6 years, children aged 7–10 years, children aged 11–14 years, youths, adults and the elderly) were in the range from 0.19 to 1.64 pg WHO₂₀₀₅ TEQ/kg bw/d. The highest dietary exposure estimates were found for toddlers (mean: 0.95, P97.5: 1.64 pg WHO₂₀₀₅ TEQ/kg bw/d) and children aged 4-6 years (mean: 0.84, P97.5: 1.29 pg WHO₂₀₀₅ TEQ/kg

bw/d). The contribution to the total TEQ from the PBDD/Fs was consistently around 30% for all age groups and for average and high consumers. The authors of the study concluded that brominated and probably also mixed halogenated dioxins, furans and biphenyls may make a significant contribution to dietary exposure to dioxin-like compounds.

80. In the EU there is an ongoing interlaboratory study on the determination of brominated contaminants in powdered infant milk that also includes PBDD/F and PBCDD/Fs (Annex E, BAT/BEP Expert, 2024).

2.4 Hazard assessment for endpoints of concern

81. The classic effects demonstrated for PCDD/Fs—lethality, wasting, thymic atrophy, teratogenesis, reproductive effects, immunotoxicity, enzyme induction, decreases in T_4 and vitamin A, and increased hepatic porphyrins—have also been observed for PBDD/Fs (Birnbaum et al., 2003; WHO, 1998).

82. The most toxic congeners are those substituted at positions 2, 3, 7 and 8. There are seven 2,3,7,8-substituted PBDDs and ten 2,3,7,8-substituted PBDFs, as well as 337 possible 2,3,7,8-substituted PBCDDs and 647 possible 2,3,7,8-substituted PBCDFs (WHO, 1998).

83. Like PCDD/Fs, PBDD/Fs and PBCDD/Fs have the ability to activate the aryl hydrocarbon receptor (AhR) signal (P. A. Behnisch et al., 2003) and to cross-react with dioxin antibodies (Samara et al., 2010). Binding to the AhR by PBDDs and PBCDDs varies with the number and position of the halogen atoms. While 2,3,7,8-TeBDD has a slightly lower binding affinity than 2,3,7,8-TeCDD, 2,8-di-B-3,7-di-CDD has twice the binding affinity of 2,3,7,8-TeCDD (Birnbaum et al., 2003).

84. The evidence shows that PBDD/Fs and PBCDD/Fs can induce developmental neurotoxicity (2,3,7,8-TeBDF) and neurobehavioral changes (2,3,7,8-TeBDF, 2,3,7-tri-B-8-CDF) in mouse offspring perinatally exposed (Kimura et al., 2020, 2023). Liver injury, such as an increase in liver size and disrupted gene expression has been reported in mice with TeBDF or TeCDD exposure (Kimura et al., 2022). Adult zebrafish being exposed to 2,3,7,8-TeBDD for 9-weeks via feed (nominal concentrations: 3, 30 and 300 ng/g food dw) showed a significant dose and time dependent reduced spawning success and significantly altered ovarian morphology (Norman Haldén et al., 2011). The high dose group (300 ng/g food dw) stopped spawning after one week of exposure and the medium group (30 ng/g food dw) after five weeks of exposure. The reduction of vitellogenic oocytes was significantly larger in the medium group than in the low dose group. Fish from the high dose showed highest mortality (23 %) and were therefore sampled three weeks before the other groups. Also, body weight was lower than the pre-exposure weight in the high and medium group.

85. The available evidence also shows that many relative potency factors (REPs) for PBDD/Fs in mammals are similar to, or at least within one order of magnitude of those for their chlorinated analogues. Similarly, based on embryo injection, the REPs for causing larval mortality in different strains of rainbow trout are mostly within one order of magnitude for PBDD/Fs and their corresponding PCDD/F congeners (van den Berg et al., 2013).

86. For tetra- to hexahalogenated PBCDDs, REPs ranging from 0.19 to 0.96 have been calculated (Eljarrat & Barceló, 2004). A higher toxicity of a PBCDF congener, 3,7,8-tri-B-2-CDF, compared to 2,3,7,8-TeCDD was observed *in vivo* in early-life stages of Japanese medaka (*Oryzias latipes*) using aqueous exposure with a REP_{water} of 3.3 and a REP_{egg} of 4.6 (Nakayama et al., 2022). Furthermore, PBCDD/Fs may photochemically be transformed to PCDD/Fs (WHO 1998) that are acknowledged POPs.

87. 2,3,7,8-TeBDD is a similarly powerful inducer of ethoxyresorufin *O*deethylase (EROD) in rat liver as 2,3,7,8-TeCDD after a single subcutaneous injection (Nagao et al., 1990). The induction of EROD was confirmed in in rats and zebrafish being exposed to 2,3,7,8-TeBDD (Mason et al., 1987; Mennear & Lee, 1994; Norman Haldén et al., 2011; Weber & Greim, 1997). AhR regulated genes were also induced in rats and zebrafish being exposed to 2,3,7,8-TeBDD with similar affinities like PCDDs (Mennear and Lee, 1994; Norman Haldén et al., 2011). Hepatic ethoxyresorufin-O-deethylase (EROD) activity and hepatic expression of AhR-regulated genes indicate if brominated dioxins can activate gene transcription through the AhR pathway (Norman Haldén et al., 2011).

88.

89. PBDD/Fs, like their chlorinated congeners, have the potential to cause dermal, hepatic and gastrointestinal carcinogenic effects. The comparative oral toxicity study of 2,3,7,8-TeCDF and TeBDF (Moore et al. 1979, cited in (Mennear & Lee, 1994) on male Hartley guinea pigs exposed to single doses of 0, 0.47, 1.58, 4.74, or 15.81 µg/kg of TeBDF or 0, 1, 5, 10, or 15 µg/kg of TeCDF showed similar effects such as decreased body weight gain after the lower doses (1.0 µg/kg for TeCDF and 4.74 µg/kg for TeBDF). Mason et al. (1987, cited in (Mennear & Lee, 1994)) demonstrated that a series of PBDDs and PBCDDs produced body weight loss and thymic atrophy in immature male Wistar rats. The compounds studied were 1,3,7,8-TeBDD; 2,3,7,8-TeBDD; 1,2,3,7,8-PeBDD; 1,2,4,7,8-PeBDD; 2,3-di-B-7,8-di-CDD; and 2-B-3,7,8-tri-CDD with no doses specified in the study, and the effects were observed for 14 days. Each of the compounds reduced body weight and caused thymic atrophy. The order and magnitude of potency for the induction of thymic atrophy were similar. Mason et al. (1987, cited in Mennear & Lee, 1994) compared the relative abilities of TeCDD and TeBDD to bind to rat liver cytosolic receptors and to induce AHH and EROD in vitro. The affinities of the compounds for receptor binding sites appeared to be equivalent, and the chlorine derivative appeared to be somewhat more potent as an inducer of AHH and EROD. Safe et al. (1989, cited in (Mennear & Lee, 1994)) studied a series of 27 PCDD, PCDF, PBDD, and PCB congeners and reported a high correlation coefficient between in vitro enzyme induction and the ED₅₀ for either body weight loss or thymic atrophy in rats. In the study by Hardy et al. (1990, cited in (Mennear & Lee, 1994)), TeBDF was administered orally to Sprague Dawley rats (5 days/week for 4 weeks) at 0, 1, 10, 50, 150, or 500 µg/kg/day. Animals at high doses (over 500 µg/kg/day) died; 70% of the animals receiving 150 µg/kg/day died, and those dosed with 50 µg/kg/day or more exhibited decreased body weight gain. Mean thymus weight (relative to body weight) was decreased in males by 150 µg/kg/day and in females by 10 and 50 µg/kg/day. Liver, kidney, spleen, adrenal gland, heart, and thymus from animals in the control, and 1, 10, and 50 µg/kg/day groups were observed with hepatic lesions characterized as panlobular hypertrophy of the hepatocytes with associated panlobular hepatocyte vacuolation and focal necrosis. An increase in triiodothyronine was seen in animals with doses of 1 or 3 µg/kg. The major effects noted in the 3 and 10 µg/kg groups included decreased body weight gain, poor general health, icterus, and after 12 weeks, increased plasma alkaline phosphate,

alanine aminotransferase, and aspartate aminotransferase in the 3 µg/kg group animals that survived to the scheduled termination of the study. Löser and Ivens (1989, cited in (Mennear & Lee, 1994)) conducted a 13-week study of the toxicity, storage, and elimination of TeBDD in male and female Wistar rats with oral doses of 0.01, 0.1, 1, 3, and 10 µg/kg for 91 days. The authors stated that animals dosed with either 0.01 or 0.1 µg/kg exhibited no treatment-related signs of toxicity; however, 0.1 µg/kg (or higher) produced decreases in serum thyroxin in both sexes. In addition to studying the brominated analogue of TeCDD, the developmental effects of TeBDF; 1,2,3,7,8-PeBDF; and 2,3,4,7,8-PeBDF were studied on pregnant C₅₇BL/6N mice on gestation day 10, with doses ranging from 0 to 192 μ g/kg for TeBDD and from 0 to 4000 μ g/kg for TeBDF, 1,2,3,7,8-PeBDF, and 2,3,4,7,8-PeBDF (Birnbaum et al. 1991, as cited in (Mennear & Lee, 1994)). All doses of each compound significantly increased liver weights in the dams but produced no other evidence of maternal toxicity. TeBDD and TeBDF caused doserelated increases in foetal weights, and 500 µg/kg or more of TeBDF significantly increased embryo/foetal mortality. The most sensitive measure of developmental toxicity was the induction of hydronephrosis. The incidence was increased by each compound, and ED₅₀ doses were estimated to be 9 µg/kg for TeBDD, 12 µg/kg for TeBDF, 340 µg/kg for 1,2,3,7,8-PeBDF, and 4347 µg/kg for 2,3,4,7,8-PeBDF. The authors estimated the ED₅₀ dose for TeCDD to produce hydronephrosis was 4 µg/kg. Thus TeBDD, as the most potent inducer of hydronephrosis among the brominated congeners tested, was estimated to be roughly one-half as potent as TeCDD in this regard. When molar doses are compared, TeBDD and TeCDD were approximately equipotent. All of the PBDDs and PBDFs also caused significant increases in the incidence of cleft palate, which the authors suggested may indicate these compounds produce their effects through the same mechanism. Given that the carcinogenicity of PCDD/Fs in animals is well established, it is reasonable to consider PBDD/Fs that could therefore be considered human carcinogens based on structural similarity and read-across since the carcinogenic potential of the PCDD/Fs in animals is established. However, there is no evidence from studies available to prove that PBDD/Fs are carcinogenic (Mennear & Lee, 1994; IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 1997).

90. In mammalian systems, the mechanism of action, type of toxicity and potency of 2,3,7,8-substituted PBDDs and PBDFs are similar to their chlorinated analogues. According to van den Berg et al. (2013), there is sufficient evidence to conclude that concentrations of 2,3,7,8-substituted PBDDs and PBDFs in human food, tissues and milk can contribute significantly to the total dioxin-like toxicity. Reported PBDD/F dietary intakes suggest that some population groups, in particular young children, may exceed the tolerable weekly intake for dioxin-like contaminants (2 pg TEQ/kg bw/week), even for mean consumption estimated with lower bound data (A. R. Fernandes & Falandysz, 2021). PBCDD/Fs may significantly contribute to the overall dioxin-like exposure (A. R. Fernandes et al., 2014; van den Berg et al., 2013). This is in line with another study which concluded that PBDD/Fs and probably also PBCDD/Fs may make a significant contribution to dietary exposure to dioxin-like compounds (Mortimer et al. 2013).

91. Due to their toxicity, which is similar to that of PCDD/Fs (Birnbaum et al., 2003; Bjurlid, 2018; Mennear & Lee, 1994), it can be concluded that PBDD/Fs and PBCDD/Fs fulfil the criteria for adverse effects.

3. Synthesis of information

92. There are several anthropogenic sources of PBDD/Fs and emissions to the environment including (1) commercial polybrominated diphenyl ether (PBDE) mixtures (presence of PBDD/Fs as by-product), (2) photolytic and thermal degradation of BFRs and (3) unintentional production in industrial thermal processes. PBDD/Fs and PBCDD/Fs can also be formed when mechanochemical non-combustion technologies are used to treat contaminated soil. PBDD/Fs can be formed when plastics containing direct precursors such as PBDEs are subject to recycling processes or as a result of photolytic and thermal degradation of BFRs and BFR-containing products. PBDD/Fs and PBCDD/Fs can form unintentionally during heating or burning, particularly when BFRs or other brominated/chlorinated materials are involved. PBDD/Fs and PBCDD/Fs can also form during the production of BFRs, such as BTBPE, and through degradation of PBDEs and TBBPA (another BFR) under various conditions. The presence of chlorine and bromine influences the ratio of PBDD/Fs to PBCDD/Fs formed. Research indicates that some PBDD/Fs and PBCDD/Fs might originate from natural sources like algae or cyanobacteria, where bromophenols undergo biobromination or other reactions. The corresponding congeners are usually less brominated, ranging from mono- to pentabrominated.

93. No evidence was received indicating any intentional uses of PBDD/Fs or PBCDD/Fs with the exception of small quantities for analytics and research purposes. The uses of PBDEs, which are precursors of PBDD/Fs or, when chlorine is present, of PBCDD/Fs, are already restricted to a large extent as tetra-, penta-, hexa-, hepta- and decaBDE are listed in Annex A (Elimination) to the Stockholm Convention. Other BFRs that can be precursors of PBDD/Fs or, when chlorine is present, of PBCDD/Fs are used in a variety of applications including printed circuit boards, electrical enclosures, automotive applications, building materials, and textiles for public buildings and specialized sectors like military and medical, aerospace adhesives, coatings, and structural parts of aircraft and rail vehicles.

Releases of PBDD/Fs and PBCDD/Fs can occur when materials are heated or 94. burnt, including in accidental or other types of uncontrolled fires, especially when BFRs or other brominated (and chlorinated) aromatics are present or in relation with the production and use of BFRs. PBCDD/Fs can also be found in landfill leachate. Appropriate risk management measures such as BAT/BEP developed to limit the formation of PCDD/Fs can also limit the formation of PBDD/Fs and PBCDD/Fs. Thermal disposal of e-waste can release PBDD/Fs at levels significantly higher than PCDD/Fs. Estimates based on production and use of PBDEs in 2001 suggest that global annual emissions of PBDFs could have reached 2300 kg. PBDD/Fs have been found in plastics from e-waste, like CRT casings, with stockpiled e-waste in places like Nigeria containing large amounts. Uncontrolled incineration of plastics with BFRs, including in private fires, can also produce harmful levels of PBDD/Fs. Recycling e-waste and materials like automobile shredder residue may lead to cross-contamination and environmental release of PBDD/Fs. Metallurgical facilities, such as steel plants and other non-ferrous smelting plants, have also been identified as significant sources of PBDD/F emissions. Other sources include landfills and industrial sites, especially in urbanized areas.

95. PBDD/Fs and PBCDD/Fs are persistent and bioaccumulative. Using QSARs, and subsequent extrapolation as well as analogies from empirical data for PCDD/Fs, the half-

lives in water and soil are estimated to be greater than the threshold of two and/or six months, respectively, for di- to octahalogenated PBDD/Fs and PBCDD/Fs. Elimination half-lives of PBDD/Fs in mammals are significantly longer than those of PCDDs. The estimated half-lives for humans range from 1 to 11 years. Additionally, a case of markedly elevated blood levels of 2,3,7,8-TeBDD were found after 35 years of exposure (WHO, 1998). The long elimination half-lives of PBDD/Fs in mammals, suggest that these substances are highly bioaccumulative. The detection in human tissues and in breast milk adds to the concern. PBDD/F and PBCDD/F have log $K_{OW} \ge 5$ (values ranging from 4.9 to 11.5) and, according to Annex D criteria, are considered likely to bioaccumulate. They exhibit similar uptake and elimination patterns to PCDD/Fs in fish and mammals, with halogen substitution influencing retention. PBCDD/Fs have physicochemical properties (such as molecular size, halogenation patterns, and metabolic stability) in the range between PCDD/Fs and PBDD/Fs. Since both PCDD/Fs (as recognized POPs) and PBDD/Fs are bioaccumulative, it is very likely that this is also the case for PBCDD/Fs. PBDD/Fs have been detected in high-trophic level species such as seals and whales, and human tissues in Japan and Sweden. These compounds show longer elimination half-lives compared to PCDDs, indicating their higher resistance to metabolism and a higher potential for bioaccumulation. Based on BIOWIN2, -3 and -6 QSARs, congeners of PBDD/Fs and PCBDD/Fs are predicted to have similarly low levels of biodegradation as congeners of PCDD/Fs.

96. PBDD/Fs and PBCDD/Fs have the potential for long-range environmental transport. Their estimated gas-phase half-lives range from 1.8 to 504 days. Due to their physicochemical properties, they are expected to occur predominantly particle-bound in the atmosphere. The atmospheric half-lives will therefore be higher than those calculated for the gas phase. The Annex D criterion of a half-life in air greater than two days is therefore met. A recent modelling study concludes that each of the investigated PBDD/F congeners (tetra- to heptabrominated) exceeds the threshold for POP-like accumulation in the remote region when emitted to air or water. Thresholds for POP-like behavior for each of the metrics were defined as the lowest values predicted for a set of 14 legacy POPs based on any of the three default emission scenarios (100% to air, 100% to water, and 100% to soil). As PBDD/Fs have been found to be present in plastics containing PBDEs or other BFRs, and they have similar physicochemical properties, it is likely that PBDD/Fs can also be transported to remote areas with plastics and accumulated in animals ingesting these plastics and as a consequence, birds or other wildlife that ingest plastic debris are exposed to these substances, as leaching is accelerated in warmblooded organisms and in hydrophobic fluids such as stomach oil, compared to leaching in water. PBDD/Fs are enriched in microplastic in seawater and may therefore be transported via microplastics to remote regions. Moreover, PBDD/Fs could be formed from PBDEs or other BFRs once they reach remote areas. PBDD/Fs have been found in pilot whales (Globicephala melas) caught around the Faroe Islands, providing additional evidence that PBDD/Fs undergo long-range environmental transport.

97. PBDD/Fs and PBCDD/Fs have been detected in various environmental compartments, including sediments, air and biota. Elevated concentrations are often linked to industrial activities such as related to the life cycle (manufacturing, use, disposal, recycling) of products that contain BFRs including e-waste processing and incineration. Studies show regional variation, with high levels in several countries in

places like e-waste and automotive scrap yards, e-waste recycling areas, areas adjacent to some metal smelters that partially used e-waste as feed stocks and open burning areas. PBDD/Fs have also been detected in high-trophic level species such as seals and whales. PBDD/Fs have also been found in soil, wastewater, sludge, fly ash, various animal and plant species, food and feed, indoor dust and in humans.

98. Exposure of the general population to PBDD/Fs takes place by consumption of food products. Further, oral uptake from children's toys made from recycled plastics containing brominated flame retardants, contributes to significant daily intake, especially through mouthing habits. Firefighters and workers in the e-waste sector show higher PBDD/F levels in their blood compared to PCDD/Fs. PBDD/Fs are also present in human milk, with varying contributions to the total TEQ levels across regions. Monitoring of human adipose tissue indicates low PBDD/F TEQ concentrations. PBDD/Fs are found in common foods like eggs, milk, fish, and meat, contributing to dietary exposure, with higher levels detected in food from industrial areas, such as e-waste and incinerator sites. Dietary exposure estimates for the UK range from 0.19 to 1.64 pg TEQ per kg body weight per day.

99. PBDD/Fs and PBCDD/Fs cause adverse effects similar to that of PCDD/Fs with similar REPs for causing adverse effects in mammals and fish. They can significantly contribute to the overall dioxin-like exposure. In mammalian systems, the mechanism of action, type of toxicity and potency of 2,3,7,8-substituted PBDDs and PBDFs are similar to their chlorinated analogues. There is sufficient evidence to conclude that concentrations of 2,3,7,8-substituted PBDDs and PBDFs in human food, tissues and milk can contribute significantly to the total dioxin-like toxicity. Reported PBDD/F dietary intakes suggest that some population groups, in particular young children, may exceed the tolerable weekly intake for dioxin-like contaminants (2 pg TEQ/kg bw/week).

4. Concluding statement

100. In conclusion, PBDD/Fs and PBCDD/Fs are released in significant quantities from anthropogenic sources. They are persistent in the environment for a long time, increasing the probability of exposure to the environment and humans and their bioaccumulation in biota, including humans. They are transported over long distances and PBDD/Fs have been detected in various environmental compartments including in marine mammals in remote regions. PBDD/Fs and PBCDD/Fs can significantly contribute to the overall dioxin-like exposure, and they may cause adverse effects also in remote regions.

101. Therefore, it is concluded that di- to octahalogenated PBDD/Fs and PBCDD/Fs are likely, as a result of their long-range environmental transport, to lead to significant adverse human health and/or environmental effects such that global action is warranted.

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