Additional information relating to the draft risk profile for polybrominated dibenzo-*p*-dioxins and dibenzofurans and mixed polybrominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans

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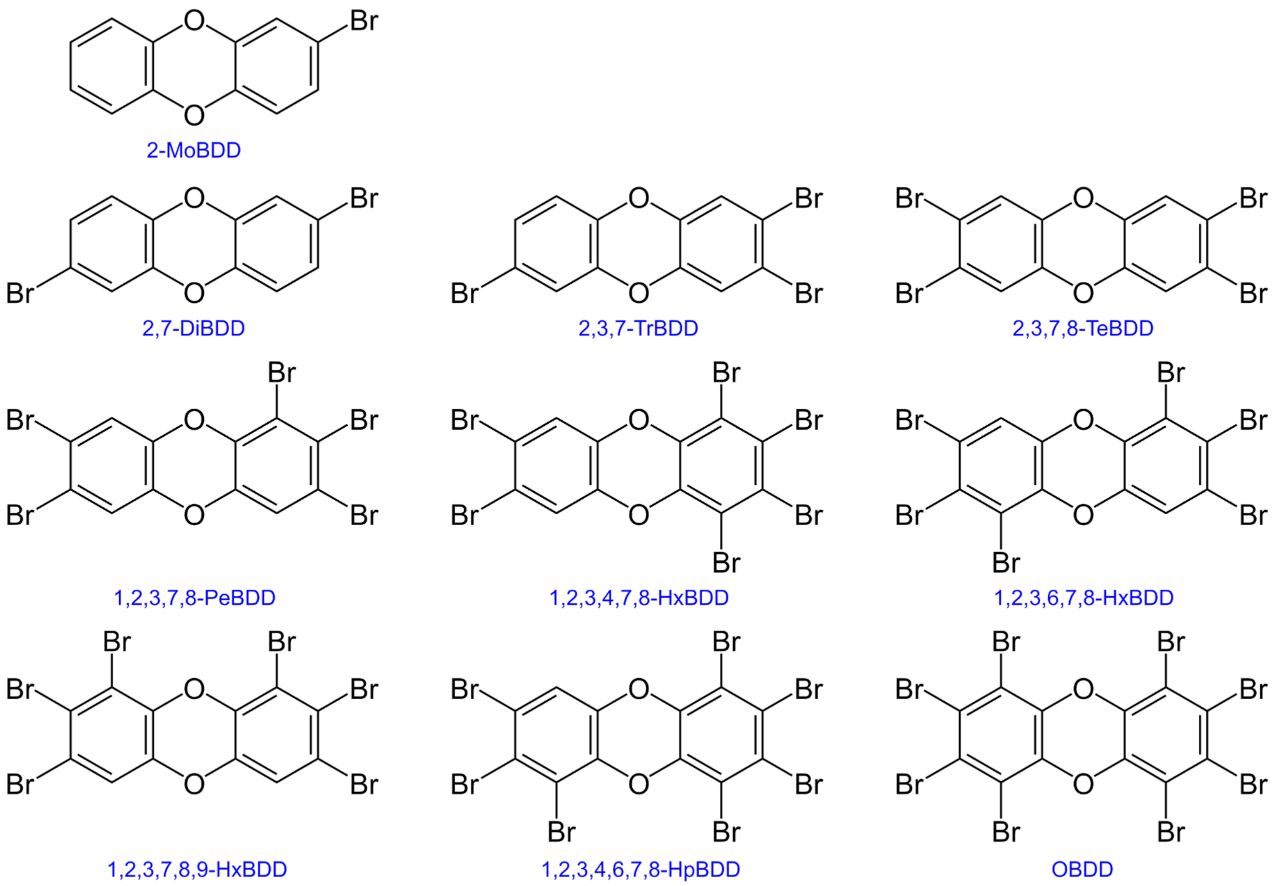


2-MoBDD

2,7-DiBDD

2,3,7-TrBDD

2,3,7,8-TeBDD

1,2,3,7,8-PeBDD

1,2,3,4,7,8-HxBDD

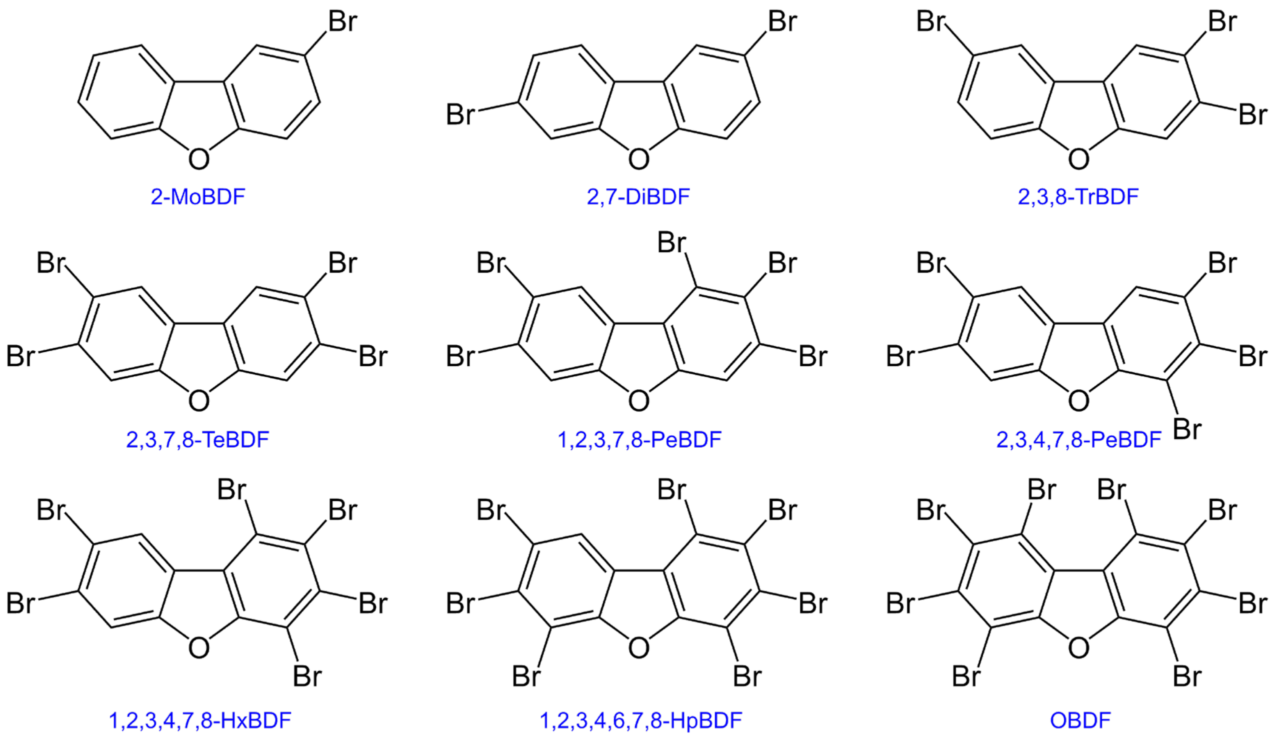
1,2,3,6,7,8-HxBDD

1,2,3,7,8,9-HxBDD

1,2,3,4,6,7,8-HpBDD

OBDD

Figure 1. Structural formulae of the polybrominated dibenzo-*p*-dioxin (PBDD) congeners contained in Table 1 of UNEP/POPS/POPRC.21/2.



2-MoBDF

2,7-DiBDF

2,3,8-TrBDF

2,3,7,8-TeBDF

1,2,3,7,8-PeBDF

2,3,4,7,8-PeBDF

1,2,3,4,7,8-HxBDF

1,2,3,4,6,7,8-HpBDF

OBDF

Figure 2. Structural formulae of the polybrominated dibenzofuran (PBDF) congeners contained in Table 1 of UNEP/POPS/POPRC.21/2.

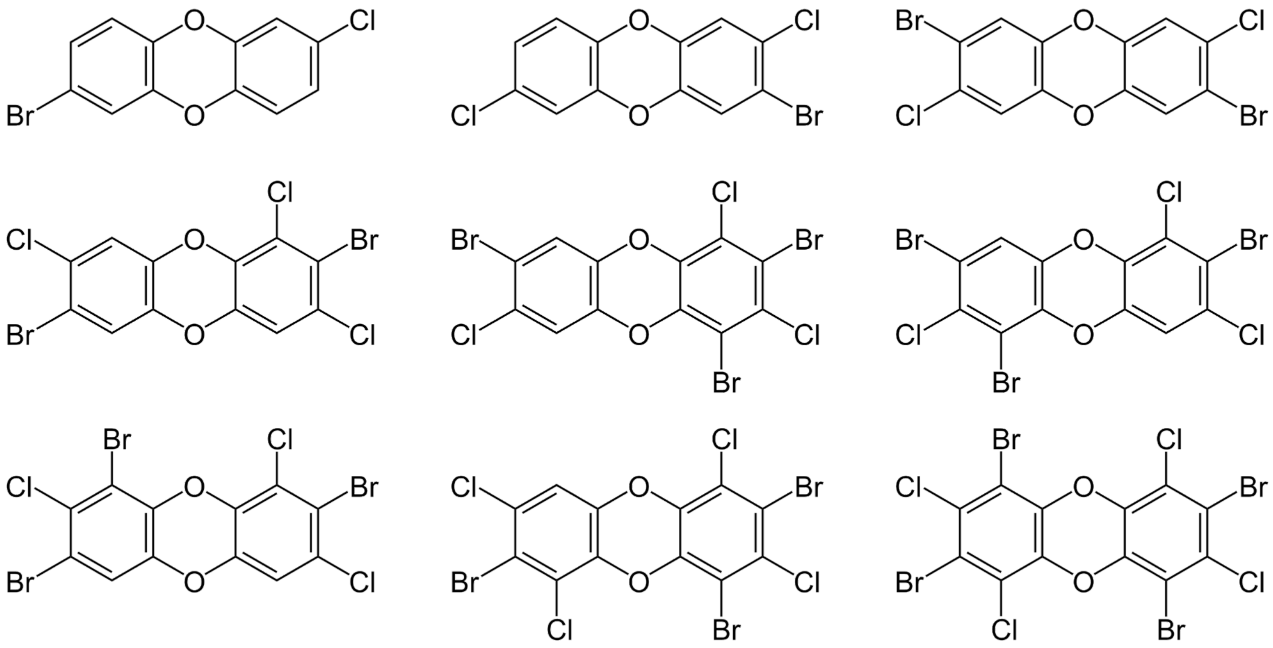


Figure 3. Structural formulae of mixed polybrominated/chlorinated dibenzo-*p*-dioxin (PBCDD) congeners with alternating chloro and bromo substituents. The substitution patterns correspond to those of the PBDD congeners in Table 1 of UNEP/POPS/POPRC.21/2.

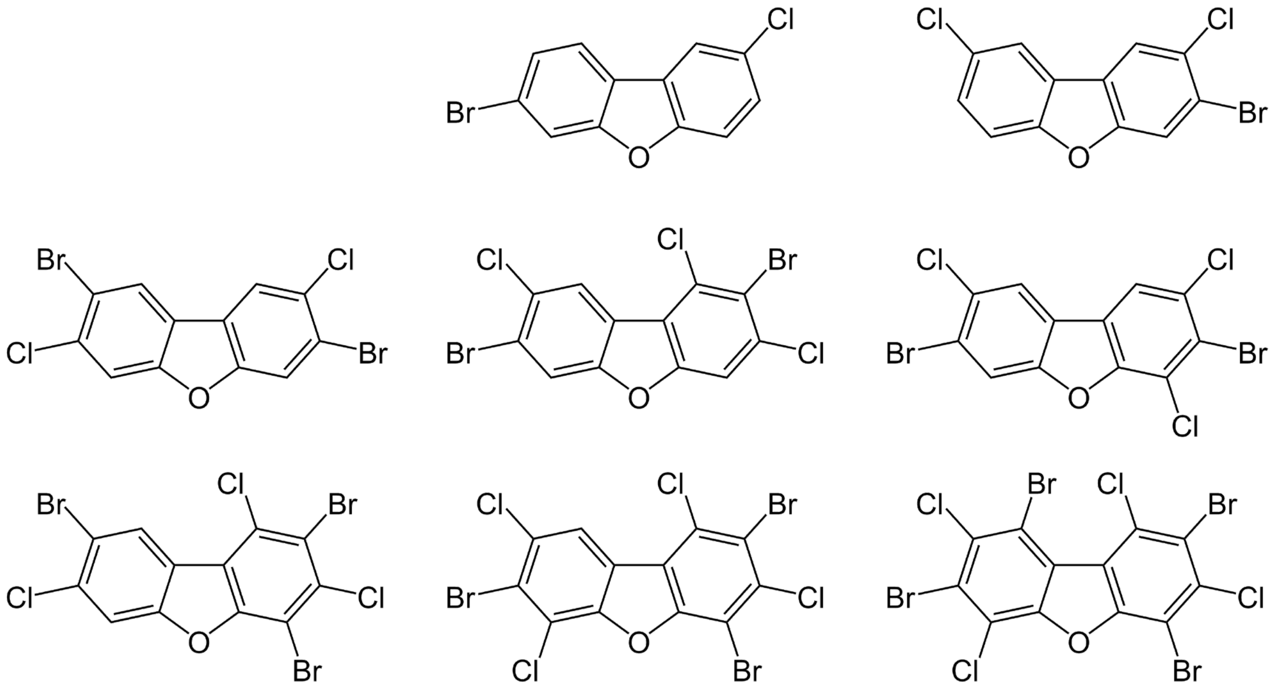


Figure 4. Structural formulae of mixed polybrominated/chlorinated dibenzofuran (PBCDF) congeners with alternating chloro and bromo substituents. The substitution patterns correspond to those of the PBDF congeners in Table 1 of UNEP/POPS/POPRC.21/2.

Table 1. Half-lives of PBDD/F and PBCDD/F congeners in water (values in days): Estimated based on the BIOWIN3 scores derived using the BIOWIN v4.10 module implemented in EPI Suite and the equation from Scheringer et al. (2012) and multiplied by a factor of 1.85 (Boethling et al., 1995). For comparison, half-lives of PCDD/F congeners estimated by same procedure as well as half-lives derived by Sinkkonen & Paasivirta (2000).

	Converted from BIOWIN3			Sinkkonen & Paasivirta (2000)
	Br	**Cl/Br**	**Cl**	**Cl**
2-MoXDD	41	n.e.	39	–
2,7-DiXDD	73	70	66	–
2,3,7-TrXDD	130	117	112	–
2,3,7,8-TeXDD	230	208	188	167
1,2,3,7,8-PeXDD	408	350	316	300
1,2,3,4,7,8-HxXDD	723	620	533	617
1,2,3,6,7,8-HxXDD	723	620	533	617
1,2,3,7,8,9-HxXDD	723	620	533	617
1,2,3,4,6,7,8-HpXDD	1280	1044	897	1250
OXDD	2267	1850	1509	3292
2-MoXDF	35	n.e.	33	–
2,7-DiXDF	62	59	56	–
2,3,8-TrXDF	109	99	94	–
2,3,7,8-TeXDF	194	175	158	267
1,2,3,7,8-PeXDF	343	295	266	550
2,3,4,7,8-PeXDF	343	295	266	550
1,2,3,4,7,8-HxXDF	608	522	448	1167
1,2,3,4,6,7,8-HpXDF	1078	879	755	2667
OXDF	1909	1557	1270	8000

n.e.: Non-existent.

See Table 1 of document UNEP/POPS/POPRC.21/2 for commonly used names, acronyms and CAS Registry Numbers of selected PBDD/F congeners.

Table 2. Half-lives of PBDD/F and PBCDD/F congeners in soil (values in days): Estimated based on the BIOWIN3 scores derived using the BIOWIN v4.10 module implemented in EPI Suite and the equation from Scheringer et al. (2012) and multiplied by a factor of 1.85 (Boethling et al., 1995). For comparison, half-lives of PCDD/F congeners estimated by same procedure as well as half-lives derived by Sinkkonen & Paasivirta (2000) and Terzaghi et al. (2020).

	Converted from BIOWIN3			Sinkkonen & Paasivirta (2000)	Terzaghi et al. (2020)
	Br	**Cl/Br**	**Cl**	**Cl**	**Cl**
2-MoXDD	77	n.e.	73	–	–
2,7-DiXDD	136	129	123	–	–
2,3,7-TrXDD	241	217	207	–	–
2,3,7,8-TeXDD	426	385	348	37500	927–1628
1,2,3,7,8-PeXDD	755	648	585	41667	1354–2113
1,2,3,4,7,8-HxXDD	1337	1148	985	100000	646–1095
1,2,3,6,7,8-HxXDD	1337	1148	985	22917	894–1606
1,2,3,7,8,9-HxXDD	1337	1148	985	29167	1325–3048
1,2,3,4,6,7,8-HpXDD	2368	1932	1659	37500	814–3230
OXDD	4195	3422	2792	54167	1219–1343
2-MoXDF	65	n.e.	61	–	–
2,7-DiXDF	114	109	103	–	–
2,3,8-TrXDF	203	183	174	–	–
2,3,7,8-TeXDF	359	324	293	22917	1573–2964
1,2,3,7,8-PeXDF	635	545	493	18750	1226–1967
2,3,4,7,8-PeXDF	635	545	493	22917	1456–2362
1,2,3,4,7,8-HxXDF	1125	966	829	25000	1314–2263
1,2,3,4,6,7,8-HpXDF	1994	1626	1396	14583	1186–3665
OXDF	3531	2881	2350	10416	960–2548

n.e.: Non-existent.

Table 3. QSAR predictions of probability of fast degradation in water using BIOWIN2 (nonlinear probability model).

BIOWIN2		*p* value	
	Br	Cl/Br	Cl
2,3,7-TrXDD	0.029	0.051	0.0676
2,3,7,8-TeXDD	0.0018	0.0033	0.0059
1,2,3,7,8-PeXDD	0.0001	0.0003	0.0005
1,2,3,4,7,8-HxXDD	0	0	0
1,2,3,6,7,8-HxXDD	0	0	0
OXDD	0	0	0
2,3,7,8-TeXDF	0.0002	0.0004	0.0008
1,2,3,7,8-PeXDF	0	0	0.0001
2,3,4,7,8-PeXDF	0	0	0.0001
1,2,3,4,7,8-HxXDF	0	0	0
1,2,3,4,6,7,8-HpXDF	0	0	0
OXDF	0	0	0

Does not biodegrade fast (probability <0.5), does biodegrade fast (probability > 0.5).

Table 4. QSAR predictions of probability of readily biodegradable in water using BIOWIN6 (MITI non-linear model prediction).

Substance	Probability from BIOWIN6
2,3,7-TrBDD	0.0702
2,3,7,8-TeBDD	0.0332
1,2,3,7,8-PeBDD	0.0153
1,2,3,4,7,8-HxBDD	0.007
1,2,3,6,7,8-HxBDD	0.007
OBDD	0.0015
2,3,7,8-TeBDF	0.0262
1,2,3,7,8-PeBDF	0.0121
2,3,4,7,8-PeBDF	0.0121
1,2,3,4,7,8-HxBDF	0.0055
1,2,3,4,6,7,8-HpBDF	0.0025
OBDF	0.0011

Does not biodegrade fast (probability <0.5), does biodegrade fast (probability > 0.5).

Table 5. Log *K*$_{OW}$ of PBDD/F and PBCDD/F congeners estimated using the KOWWIN v1.69 module implemented in EPI Suite. Estimated log *K*$_{OW}$ of PCDD/F congeners for comparison.

	Log *K*$_{OW}$		
	Br	**Cl/Br**	**Cl**
2-MoXDD	5.2	n.e.	5.0
2,7-DiXDD	6.1	5.9	5.6
2,3,7-TrXDD	7.0	6.5	6.3
2,3,7,8-TeXDD	7.9	7.4	6.9
1,2,3,7,8-PeXDD	8.8	8.1	7.6
1,2,3,4,7,8-HxXDD	9.7	9.0	8.2
1,2,3,6,7,8-HxXDD	9.7	9.0	8.2
1,2,3,7,8,9-HxXDD	9.7	9.0	8.2
1,2,3,4,6,7,8-HpXDD	10.6*	9.6	8.9
OXDD	11.5*	10.5	9.5
2-MoXDF	4.9	n.e.	4.7
2,7-DiXDF	5.8	5.6	5.3
2,3,8-TrXDF	6.7	6.2	6.0
2,3,7,8-TeXDF	7.6	7.1	6.6
1,2,3,7,8-PeXDF	8.5	7.8	7.3
2,3,4,7,8-PeXDF	8.5	7.8	7.3
1,2,3,4,7,8-HxXDF	9.4	8.7	7.9
1,2,3,4,6,7,8-HpXDF	10.3	9.3	8.6
OXDF	11.2*	10.2	9.2

n.e.: Non-existent.

* The molecular weights of 1,2,3,4,6,7,8-HpBDD (736 g/mol), OBDD (815 g/mol) and OBDF (799 g/mol) 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.

Table 6. Gas-phase half-lives of PBDD/F and PBCDD/F congeners obtained from the AOPWIN v1.92 module implemented in EPI Suite, based on estimated second-order rate constants for the reaction with OH radicals. Estimated half-lives of PCDD/F congeners for comparison.

	Gas-phase half-life (days)		
	Br	**Cl/Br**	**Cl**
2-MoXDD	1.8	n.e.	1.7
2,7-DiXDD	2.9	2.8	2.6
2,3,7-TrXDD	6.4	5.7	5.7
2,3,7,8-TeXDD	16	14	14
1,2,3,7,8-PeXDD	26	22	22
1,2,3,4,7,8-HxXDD	61	52	51
1,2,3,6,7,8-HxXDD	43	38	34
1,2,3,7,8,9-HxXDD	43	38	34
1,2,3,4,6,7,8-HpXDD	99	79	77
OXDD	256	205	197
2-MoXDF	2.4	n.e.	2.3
2,7-DiXDF	4.0	3.8	3.5
2,3,8-TrXDF	9.9	8.6	8.3
2,3,7,8-TeXDF	25	23	22
1,2,3,7,8-PeXDF	44	38	36
2,3,4,7,8-PeXDF	45	39	37
1,2,3,4,7,8-HxXDF	110	94	91
1,2,3,4,6,7,8-HpXDF	208	167	163
OXDF	504	435	389

n.e.: Non-existent.

Table 7. Summary of concentrations of PBDD/Fs and PCDD/Fs in marine biota from various studies.

Substance	**Concentration**	**Unit**	**Matrix**	**Additional information**	**Source**
11 PBDD/F congeners	0.080–71	pg/g lipid weight	Blubber of pilot whales	Sampled during 1997–2013	Bjurlid et al., 2018a
11 PBDD/F congeners	0.5–52.3	pg/g lipid weight	Baltic ringed seals	22 pooled samples collected during 1974–2015	Bjurlid et al., 2018b
17 PCDD/F congeners	103–1480	pg/g lipid	Baltic ringed seals	22 pooled samples collected during 1974–2015	Bjurlid et al., 2018b
2,3,7-TrBDD	up to 14.5	ng/kg	Oysters	60 samples collected during 2006–2007	Fernandes et al., 2009
10 PBDD congeners	up to 4100	pg/g wet weight	Marine fish, mussels, shellfish	26 composite samples	Haglund et al., 2007
2,3,8-TrBDF	0.25 (mean)	pg/g fresh weight	Scallop gonads		Fernandes et al., 2009
2,3,7-TrBDD	0.13 (mean)	pg/g fresh weight	Scallop gonads		Fernandes et al., 2009
1,2,3,4,6,7,8-HpBDF	up to 0.302	pg/g fat	Cod liver derived products		Falandysz et al., 2020

Additional information for paragraph 36 of the draft risk profile

"PBDD/Fs and/or precursors (e.g. bromophenols) can be formed as a result of pyrolysis and combustion of BFRs and materials containing BFRs such as TBBPA, tetrabromobisphenol A-bis(2,3-dibromopropyl ether) (TBBPA-BDBPE) or hexabromocyclododecane (HBCD)."

PBDD/Fs can be formed as a result of the pyrolysis and combustion of tetrabromobisphenol A (TBBPA), which is a common brominated flame retardant (BFR) (Ebert & Bahadir, 2003). During pyrolysis of acrylonitrile/butadiene/styrene with TBBPA, monobrominated (Mo-) to pentabrominated dibenzoburans (PeBDFs) were formed at a ng/g level. The optimum temperature for the formation of PBDDs and PBDFs was 600 °C (Luijk & Govers, 1992). Ortuño et al. (2014) investigated combustion and pyrolysis of TBBPA at 650 °C and 850 °C in different atmospheres (nitrogen and air) and found a different prevalence of PBDD/F congeners formed depending on the process. At 850 °C, the most abundant congeners were 2,4,6,8-TeBDF formed during pyrolysis, and 1,2,3,7,8-PeBDF under combustion conditions, indicating that the congener pattern is affected by the presence of oxygen. In addition, the total PBDD/F yields obtained from the combustion experiment were nearly forty times higher than those from pyrolysis (levels in the µg/g range). An investigation of PBDD/F formation during combustion at 600 ºC in the presence of bromine, using both polymer-linked and additively incorporated TBBPA, revealed concentrations in the range of 17.5 to 19.6 µg of PBDD/F per g TBBPA applied (Wichmann et al., 2002). The PBDD/F congener pattern observed depended heavily on the reaction conditions and the type of plastic material. In general, PBDFs were found in much higher concentrations compared to PBDDs in both studies.

Hexabromocyclododecane (HBCD) and products containing HBCD may also release PBDD/Fs during combustion. Bromophenols, which are precursors to PBDD/Fs, have been shown to be formed during the combustion of flame-retarded polystyrene materials containing HBCD (Desmet et al., 2005) and PBDD/Fs have been measured during combustion of flame-retarded polystyrene materials containing HBCD (Dumler et al., 1989). Decomposition products such as polycyclic aromatic hydrocarbons, biphenyls and their derivatives can serve as carbon sources for PBDD/F synthesis during co-disposal of HBCD containing waste in cement kilns. Emission factors of HBCD and PBDD/Fs were the highest in the clinker at 1.31×10^6 and 1.11×10^5 ng t^{-1}, respectively. Therefore, attention is needed for the potential secondary release of pollutants during the transportation and utilization of clinkers (Wang et al., 2024).

Furthermore, a more recent study reports on PBDD/Fs emitted during the thermal treatment of simulated polystyrene foam. It was demonstrated that the temperature, metal (metallic compound) content, and type of atmosphere are the key factors in the formation of PBDD/Fs. The total yield of PBDFs was greater than that of the PBDDs, and 1,2,3,7,8-PeBDF and 2,3,7,8-TeBDF were the predominant congeners emitted (Wang et al., 2018). A study by Huang et al. (2023) focused on the formation mechanisms of PBDD/Fs from the pyrolysis of 2,6-dibromophenol. The calculation results show that the 2-bromophenoxy radical is a major decomposition product in initial pyrolysis of 2,6-dibromophenol, 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, while 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, meaning that the formation of PBDDs is predominant. Liu et al. (2016) investigated the thermochemical decomposition pathway of decabromodiphenyl ethane (DBDPE) and tetrabromobisphenol A (TBBPA) containing electronic waste plastics. PBDD/Fs congeners were found in significant higher concentrations in the pyrolysis products of TBBPA plastics (14 ng/g) than those in the pyrolysis products of DBDPE contained electronic waste plastics (0.50 ng/g1), suggesting that the intramolecular oxygen atoms play a pivotal role in the formation of PBDD/Fs.

Tetrabromobisphenol A-bis(2,3-dibromopropyl ether) (TBBPA-BDBPE) is a BFR that has been widely used in electrical and electronic equipment (EEE) in recent years (Liu et al., 2025). In their study, the authors investigated the decomposition mechanisms of TBBPA-BDBPE pyrolysis to generate Br-containing products. The primary Br-containing products of TBBPA-BDBPE pyrolysis were HBr, 1,2,3-tribromopropane and bromophenols. During the initial stage of pyrolysis, TBBPA-BDBPE predominantly undergoes the homolysis of the C–O and C–Br bonds, resulting in the formation of 1,2,3-tribromopropane. Subsequently, Br radicals and H atoms can react with TBBPA-BDBPE and its intermediates to produce various Br-containing products, including HBr, 2,4,6-tribromophenol and 2,6-dibromophenol. Notably, the 2,6-dibromophenol radical serves as a critical precursor for the formation of PBDDs via C–O coupling reactions (Liu et al., 2025). 2,4,6-Tribromophenol that is also used as a BFR was found to form PBDD/Fs through thermal reaction (Die et al., 2022).

A review examining the pollutant emission behaviors of flame retardants during thermal treatment processes for energy conversion discusses the potential formation and releases of PBDD/Fs (Hsiao & Lin, 2025).

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