



Determination of PBDDs and PBDFs in emission samples

Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) are the brominated analogues of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). PBDD/Fs are classified as persistent organic pollutants (POPs)—toxic substances that can persist and bioaccumulate across environmental and biological compartments, with adverse effects on human and animal health. Because they may occur at trace levels yet build up over time, accurate analysis is essential for exposure assessment, trend monitoring, and identifying emissions from thermal and waste-related activities, including processes involving brominated flame retardants.



1: Illustrative picture

PBDD/F Introduction

PBDD/Fs are not intentionally manufactured, with the exemption of the production of small quantities for analytical and research purposes. However, the chemicals are formed unintentionally when materials are heated or burnt in the presence of brominated flame retardants (BFRs) or other brominated organic compounds. Furthermore, PBDD/Fs can also be formed as by-products during the production of BFRs such as polybrominated diphenyl ethers (PBDEs). After their formation, the release of PBDD/Fs from several anthropogenic sources (e.g. waste incinerators and metallurgical facilities) into the environment is documented.

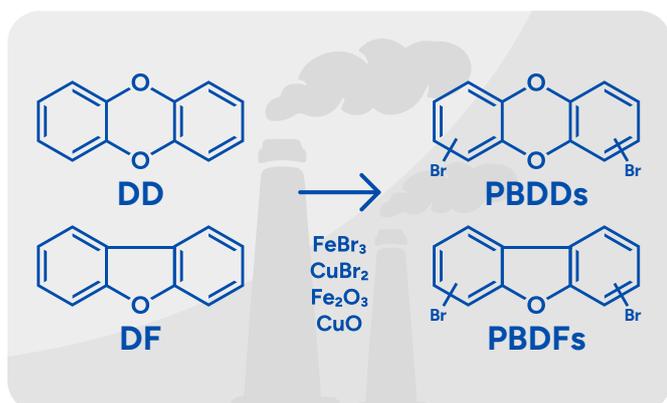


Figure 2: The formation and emission of PBDD/Fs

PBDFs are almost planar tricyclic aromatic compounds, vary in the number of bromine atoms and the positions of halogenation. There are eight positions on both the dibenzo-p-dioxin and the dibenzofuran molecules where halogen substitution can occur. The positions are numbered as shown in Fig. 3. Theoretically, 75 PBDDs and 135 PBDFs are possible (Table 1). The most toxic congeners are those substituted at positions 2, 3, 7 and 8.

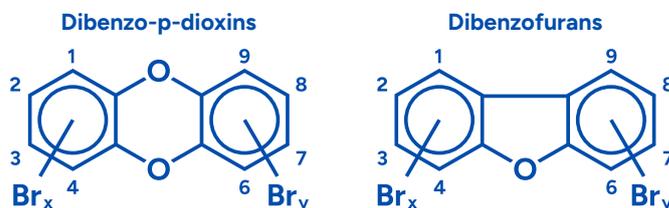


Figure 3: PBDD and PBDF structural formulas

Table 1. Number of possible PBDD and PBDF congeners

| Compound | Substitution | Di | Tri | Tetra | Penta | Hexa | Hepta | Octa | Total |
|---------------|--------------|----|-----|-------|-------|------|-------|------|------------|
| PBDD | 2 | 10 | 14 | 22 | 14 | 10 | 2 | 1 | 75 |
| PBDF | 4 | 16 | 28 | 38 | 28 | 16 | 4 | 1 | 135 |
| Total: | | | | | | | | | 210 |

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(PBDD/F Introduction)

In comparison to their chlorinated relatives (PCDD/Fs), brominated dioxins and furans have higher molecular weights, higher melting points, lower vapor pressures, and lower water solubility.

PBDD/Fs are persistent, based on their predicted half-lives in water and soil. Additionally, PBDD/Fs were found in sediment cores, in layers where they were deposited decades ago, showcasing the compounds' persistence. The elimination half-lives of PBDD/Fs in mammals are significantly longer than those of PCDDs, suggesting that the brominated substances are also highly bioaccumulative. PBDD/Fs have the potential for long-range environmental transport, mainly particle-bound in the atmosphere. The detection of PBDD/Fs in pilot whales around the Faroe Islands provides an example of the long-range transport of the chemicals.

Human Health Risks Associated with PBDD/F

PBDD/Fs are being detected in the environment (e.g. in sediments, air and wildlife) and in humans. The public is exposed to PBDD/Fs via food (e.g. eggs, milk, fish, and meat), indoor dust and consumer products made of recycled plastics (e.g. toys).

PBDD/Fs cause adverse effects similar to those of PCDD/Fs, including for example immunotoxicity, carcinogenicity, reproductive and developmental toxicity, and thus contribute to the overall dioxin-like exposure of humans and wildlife. The high toxicity of PBDD/Fs is especially concerning in combination with the potential for bioaccumulation.

National or regional regulations

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 BFRs or to plants using boiler bromine addition with continuous injection of bromine (European Commission, 2019). Additionally, the presence in products and the release of several PBDD/Fs are currently already regulated in Germany and the Netherlands, respectively.

Brominated dioxins are highly toxic, persistent substances that accumulate in the environment and the food chain. Due to their adverse effects on human health and ecosystems, they are currently under review for listing under the Stockholm Convention on Persistent Organic Pollutants.

Determination of PBDD/F in ALS Laboratories

At ALS Czech Republic we use the most modern analytical method for the determination of PBDD/Fs in emission matrices. Target congeners of PBDDs and PBDFs are listed in Table 2.

Table 2. The list of PBDD/Fs compounds analyzed by ALS Czech Republic

| Number of Br atoms | Target analytes | |
|--------------------|-------------------------------------------------------------|----------------------------------------------------------------------------------|
| | PBDDs | PBDFs |
| 4 | 2,3,7,8-TBDD | 2,3,7,8-TBDF |
| 5 | 1,2,3,7,8-PeBDD | 1,2,3,7,8-PeBDF 2,3,4,7,8-PeBDF |
| 6 | 1,2,3,4,7,8-HxBDD 1,2,3,6,7,8-HxBDD 1,2,3,7,8,9-HxBDD | 1,2,3,4,7,8-HxBDF 1,2,3,6,7,8-HxBDF 1,2,3,7,8,9-HxBDF 2,3,4,6,7,8-HxBDF |
| 7 | 1,2,3,4,6,7,8-HpBDD | 1,2,3,4,6,7,8-HpBDF 1,2,3,4,7,8,9-HpBDF |
| 8 | OBDD | OBDF |

For these purposes, we use gas chromatography coupled with high-resolution mass spectrometry (GC-HRMS) or gas chromatography coupled with tandem mass spectrometry with a triple quadrupole (GC-MS/MS). Both techniques use electron ionization and analytical methods are based on the isotope dilution using ¹³C isotope-labeled standards, ensuring high accuracy and reliability of results. The developed method achieves limits of quantification in ranges 0.005-0.300 ng/sample depending on congener, for making it suitable for the intended purposes. To translate quantitative GC-MS data into relevant toxicity information, the TEQ (toxic equivalent) values for the PBDD/Fs were calculated according to the World Health Organization (WHO) recommendation for human and mammalian toxic equivalency factors (TEF) with recommendation to use the same as for PCDD/F congeners.



Figure 4: GC-MS/MS and GC-HRMS instrumentation used for PBDD/Fs analyses

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