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Review

Brominated flame retardants and the formation of dioxins and furans in fires and combustion

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HIGHLIGHTS

- BFRs (PBDEs, HBCD and TBBP-A) are the main sources of PBDD/Fs in combustion process.
- Precursor formation is the most relevant pathway for PBDD/Fs formation.
- Adding bromine into combustion system can enhance the formation of PCDD/Fs.
- Primitive recycling of e-waste produces the largest amounts of PBDD/Fs.

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ABSTRACT

The widespread use and increasing inventory of brominated flame retardants (BFRs) have caused considerable concern, as a result of BFRs emissions to the environment and of the formation of both polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and mixed polybromochloro-dibenzo-*p*-dioxins and dibenzofurans (PBCDD/Fs or PXDD/Fs). Structural similarities between PBDD/Fs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) suggest the existence of comparable formation pathways of both PBDD/Fs and PCDD/Fs, yet BFRs also act as specific precursors to form additional PBDD/Fs. Moreover, elementary bromine (Br_2) seems to facilitate chlorination by bromination of organics, followed by Br/Cl-exchange based on displacement through the more reactive halogen. Overall, PBDD/Fs form through three possible pathways: precursor formation, de novo formation, and dispersion of parts containing BFRs as impurities and surviving a fire or other events. The present review summarises the formation mechanisms of both brominated (PBDD/Fs) and mixed dioxins (PXDD/Fs with X = Br or Cl) from BFRs, recaps available emissions data of PBDD/Fs and mixed PXDD/Fs from controlled waste incineration, uncontrolled combustion sources and accidental fires, and identifies and analyses the effects of several local factors of influence, affecting the formation of PBDD/Fs and mixed PXDD/Fs during BFRs combustion.

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1. Introduction

In order to protect the general public from accidental fires, flame retardants are widely used in numerous commodities and products, such as plastics, textiles, furniture, mattresses, electrical and electronic equipment (EEE) and other materials, reducing the flammability of combustible materials [1] and the likelihood of their ignition and propagation. There are more than 175 different types of flame-retardants in the market; at least 75 of them are brominated flame retardants (BFRs) [2]. A majority of studies on BFRs conducted to date have focused on three products or product classes: polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBP-A) and hexabromocyclododecane (HBCD) (Fig. 1) [3–5]. Once a common BFR, polybrominated biphenyls (PBBs) already in the 1970s drew public concern due to a poisoning accident in the US and were removed therefore from market supplies [6,7].

More than 200,000 metric tons of BFRs are produced each year, of which 56% are consumed in Asia [2]. With this high production rate and concomitant expanding inventory, large amounts of BFRs can be emitted to the environment all along their lifetime, from cradle to grave: during the manufacture of masterbatches with BFRs, the compounding and processing of flame-retardant materials, the useful lifetime of products containing BFRs, their dismantling, as well as during recycling of waste containing BFR, during incineration, or in a fire [8–10]. Since their introduction, BFRs have developed into widespread global contaminants, drawing great concern because of the markedly increasing BFRs levels observed in the environment (air, soil, water and sediment) [11–13], in biota, human tissues, blood, or mother milk [14–16]. Another reason for concern is the reported harmful effects caused by some BFRs (e.g., PBDEs, TBBP-A, HBCD, etc.) on human health and that of other mammals [17–20]. Therefore, some BFRs are listed in the Annex A of the Stockholm Convention and thus subjected to phase-out and prohibition [21].

Not only original BFRs, but also other groups of undesirable products are emitted into the environment, in particular during the processing, combustion and fires of materials containing BFRs. Several studies were devoted to the volatilisation of specific heavy metals in the presence of bromine or hydrogen bromide [22,23]. Metal bromides and chlorides alike volatilise in the fire and de-sublimate from the vapor phase onto the finest particles preferentially, given their high surface to volume ratio; this creates catalytic sites that are probably very active in both the de novo route and the precursor pathways [24].

Yet, polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and mixed polybromochloro-dibenzo-*p*-dioxins and dibenzofurans (PXDD/Fs) are among the most toxic by-products. Having a chemical structure similar to those of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), PBDD/Fs (Fig. 1) refer to a group of 135 polybrominated dibenzofurans (PBDFs) and 75 dibenzo-*p*-dioxins (PBDDs), the same species as for their chlorinated analogous. Theoretically, there are 4600 mixed bromochlorodibenzo-*p*-dioxin or dibenzofuran congeners (mixed PXDD/Fs), consisting of 3050 polybromochloro dibenzofurans (PXDFs) and 1550 polybromochloro-dibenzo-*p*-dioxins (PXDDs) [25].

Several PCDD/Fs and polychlorinated biphenyls (PCBs) have been shown to cause toxic and biological effects similar to those caused by 2,3,7,8-tetrachlorodibenzo-*p*-dioxins (TCDD), which is the most potent congener within these groups of compounds. These toxic effects include dermal damage (chloracne), immunotoxicity, carcinogenicity, and adverse effects on reproduction, development, and endocrine functions [26]. The toxic equivalency factors (TEFs) of 17 2,3,7,8-substituted PCDD/Fs congeners and 12 dioxin-like PCBs, determined by the relative effect potency (REP) values of these toxic PCDD/Fs and PCBs compounds compared with 2,3,7,8-TCDD as a reference compound [27], have been developed to facilitate risk assessment of exposure to these PCDD/Fs and PCBs [28,29]. PBDD/Fs and mixed PXDD/Fs are about comparable to PCDD/Fs in their persistence and toxicity [30]. Because toxic equivalency factors (TEFs) have not yet been determined for PBDD/Fs, the current TEFs of PCDD/Fs are generally applied for the corresponding congeners of PBDD/Fs [30,31].

PBDD/Fs have physical–chemical properties similar to those of PCDD/Fs, albeit they could be less volatile and thus bound more to particulate matter. Besides, the analogous chemical properties of chlorine and bromine suggest that the formation mechanism of PBDD/Fs and PCDD/Fs could follow comparable pathways [32]. Formation mechanisms of PCDD/Fs have been investigated during the last decades, in laboratory studies, pilot-scale experiments and under real combustion conditions [33–36]. However, PBDD/Fs and especially mixed PXDD/Fs are much less studied, due to the more advanced and complex techniques required for their GC/MS separation and quantification [37,38]. The sheer number of PXDD/Fs congeners precludes systematic analysis of individual congeners. Considering the differences in content of chlorine and bromine in common combustibles, their diverse origin and speciation, and analogies and distinctions in properties between chlorine and bromine, the formation mechanisms of PBDD/Fs, as well as those of PXDD/Fs should be discussed distinctly.

BFRs are clearly the chief source of bromine in Br-containing dioxins and furans [13,30]. Potentially, both PBDD/Fs and PXDD/Fs might be formed during the entire life cycle of BFRs materials and products, including their production [39,40], recycling [41], pyrolysis/gasification [32], controlled incineration [42], and – in particular – any uncontrolled combustion and fires [43]. Due to the structural similarities between BFRs (e.g., PBDEs, PBBs and TBBP-A, etc.) and PBBD/Fs, BFRs can easily form PBDD/Fs even under only mild thermal stress, through precursor pathways. The largest amounts of PBDD/Fs are reportedly formed at the end-of-life stages of BFRs products during primitive or rudimental recycling of electrical and electronic waste [4,44,45]. In developing countries (China, India, Pakistan, Nigeria, etc.) often open burning is conducted to remove plastic coverings and recycle metals leading to serious contamination not only of the recycling sites, but also of surrounding cities