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Brominated flame retardants: exposure routes, human impacts and status

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Brominated flame retardants (BFRs) are common organo-halogen components of polymers found in a wide range of consumer products such as plastics, textiles and electronics, where they are incorporated to reduce combustibility and fire risk (*1*). They are effective, cheap and have a negligible impact on the properties of the polymer (*2*). However, their toxicity, bioaccumulation and persistence in the environment have been established and several BFRs are included in the list of Persistent Organic Pollutants (POPs) (*2*).

The toxicity and persistence of BFRs stem from their ability to diffuse out of surfaces and undergo long range atmospheric transport (**Figure 1**). Given their widespread use and the variety of exposure pathways, BFRs have a lasting legacy that affects most global environmental compartments (*3*).

Recent history and status

There are more than 75 different commercial BFRs, grouped into four main classes: polybrominated diphenylethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA) (*4*). This variety of chemical structures results in a wide range of physiochemical properties (*1*).

General production of these chemicals started in the early 1970s with PBBs/PBDEs becoming commercially successful. Before long, the first major negative impacts were seen when accidental exposure to PBBs in rural environments in Michigan (US) led to degradation and adverse human health effects (*4*). As a result, in 1979, PBB production ceased in the US, and then in Europe in 2000 (*4*). PBDEs include 209 congeners, depending on the position and number of the bromine atoms. After a brief increase in production of PBDEs due to the PBB ban, these were also phased out in the US and banned in Europe by 2008, following risk assessments (*3*). HBCDs and TBBPA have since filled the gap left by the banned species, with the latter being the most highly produced BFR globally. Currently, HBCDs are listed as a 'substance of very high concern requiring authorisation' under EU legislation and have joined PBDEs in the list of persistent organic pollutants (POPs). The production and use of TBBPA is still unregulated (*3, 4*).

Most BFRs do not bind to the products they protect (with the partial exception of TBBPA). This means that their potential for leaching and volatilisation is very high. Consequently, BFRs have been found in breast milk, cord blood, fish, animal tissue, and in-house dust and sediments (*1, 3*).

Human impact

Human exposure to BFRs occurs mostly through in-

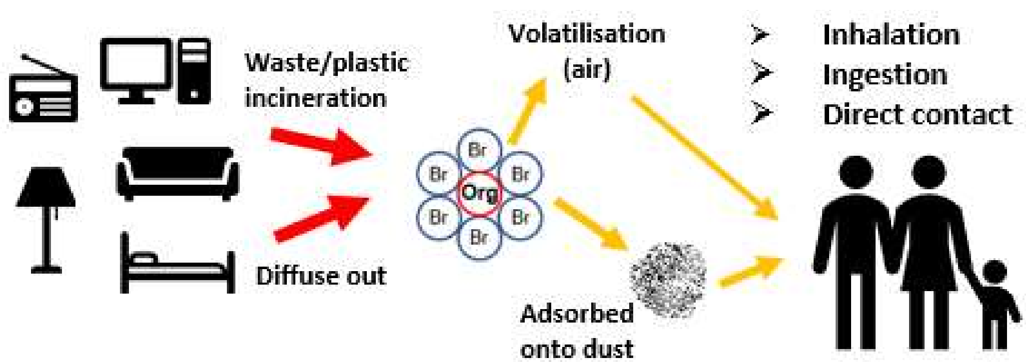

Figure 1. Graphical representation of BFRs diffusing out of materials or released upon incineration. Exposure pathways for people may occur from direct contact with the chemical species or from contact with contaminated dust.

house dust, but also from the ingestion of contaminated animal products and vegetables (*5*). Repeated studies have shown that PBDEs disrupt hormone homeostasis and neurological development, with lower birth weight and cancer among their consequences (*1, 6*). A study by Usenko *et al*. (2016) found high variability in the effects on humans exposed to the most commonly used BFRs (TBBPA, HBCD). They reported that exposure to TBBPA may pose a greater risk to human and environmental health than previously banned PBDEs (*1*). Indeed, subsequent studies (*5*) found TBBPA and HBCDs to have endocrine-disrupting properties and negative impact on neurological function and reproduction. Recently, two-year National Toxicology Program studies (designed to identify potential human carcinogens) found that mice exposed to TBBPA developed uterine and liver cancers (*6*).

BFRs are highly lipophilic and, as such, contaminated

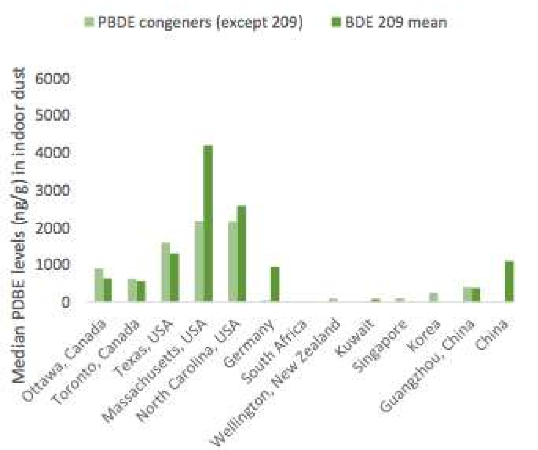

Figure 2. Comparison of PBDE levels (median) in indoor dust in the world (studies conducted 2006-2012, with BDE209 data missing for NZ) (STD error). Data from (7).

breast milk can contribute to up to 35 ng/kg bodyweight of BFRs in infants, whilst the average intake for toddlers through ingestion of dust has been estimated at 3 ng/kg bodyweight. Actions such as hand-to-mouth and object-to-mouth activity increase children's exposure to dust containing BFRs, leading to them being at much higher risk overall (*4, 5*).

Dust pathway

Studies have shown the main source of PBDEs found in human blood and milk to be indoor dust rather than dietary intake (*7*).

Concentrations of BFRs found in dust samples are much higher than those found in human blood/tissue and milk (**Figure 2**), and vary significantly across the globe. This reflects the large variance in worldwide market demand of BFR classes by region (e.g. US vs Asia), legislation prohibiting the use of particular compounds and voluntary cessation of production (*5*). For instance, average levels in US indoor dust (**Figure 2**) are significantly higher than in other countries. Concentrations of BFRs in fish, one of the most heavily contaminated food groups, show the clear disparity between contaminant levels in food and dust (**Table 1**) (*8*). This indicates that close proximity to materials containing BFRs where we live and work (desks, computers, phones, cars, upholstery, *etc*.) is a significantly more important exposure route than food.

Table 1: BFRs (ng/g) in sediment and fish (ng/g wet weight) from areas of high contamination globally (Great Lakes, Baltic Sea, Western Scheldt, etc) compared to concentrations found in indoor dust from EU, USA & China (Data from 8).

BFR	Sediment	Fish	Dust
BDE47	0.06	1.6	280
BDE209	20	0	1300
HBCD	0.6	0.5	270

Conclusion and foresight

BFRs have an important impact on the healthy function of a human body. They are detectable during prenatal development at relatively low concentrations, but this increases in children up to toddler age (who are at increased risk of exposure and accumulation). The lasting effect of legacy BFRs is apparent through their continued global persistence and high accumulation in dust. Of significant concern is the rise in 'novel' BFRs replacing banned ones, which has not been accompanied by data on their toxicity. Worryingly, a study in China has found that concentrations of novel BFRs found in food are similar or higher than those of legacy BFRs (*4*).

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