

## Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks?

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**Abstract:** Since the 1970s, an increasing number of regulations have expanded the use of brominated and chlorinated flame retardants. Many of these chemicals are now recognized as global contaminants and are associated with adverse health effects in animals and humans, including endocrine and thyroid disruption, immunotoxicity, reproductive toxicity, cancer, and adverse effects on fetal and child development and neurologic function. Some flame retardants such as polybrominated diphenyl ethers (PBDEs) have been banned or voluntarily phased out by manufacturers because of their environmental persistence and toxicity, only to be replaced by other organohalogens of unknown toxicity. Despite restrictions on further production in some countries, consumer products previously treated with banned retardants are still in use and continue to release toxic chemicals into the environment, and the worldwide use of organohalogen retardants continues to increase. This paper examines major uses and known toxic effects of commonly-used organohalogen flame retardants, replacements for those that have been phased out, their combustion by-products, and their effectiveness at reducing fire hazard. Policy and other solutions to maintain fire safety while reducing toxicity are suggested. The major conclusions are: (1) Flammability regulations can cause greater adverse environmental and health impacts than fire safety benefits. (2) The current options for end-of-life disposal of products treated with organohalogens retardants are problematic. (3) Life-cycle analyses evaluating benefits and risks should consider the health and environmental effects of the chemicals, as well as their fire safety impacts. (4) Most fire deaths and most fire injuries result from inhaling carbon monoxide, irritant gases, and soot. The incorporation of organohalogens can increase the yield of these toxic by-products during combustion. (5) Fire-safe cigarettes, fire-safe candles, child-resistant lighters, sprinklers, and smoke detectors can prevent fires without the potential adverse effects of flame retardant chemicals. (6) Alternatives to organohalogen flame retardant chemicals include using less flammable materials, design changes, and safer chemicals. To date, before evaluating their health and environmental impacts, many flame retardant chemicals have been produced and used, resulting in high levels of human exposure. As a growing literature continues to find adverse impacts from such chemicals, a more systematic approach to their regulation is needed. Before implementing new flammability standards, decision-makers should evaluate the potential fire safety benefit versus the health and environmental impacts of the chemicals, materials, or technologies likely to be used to meet the standard. Reducing the use of toxic or untested flame retardant chemicals in consumer products can protect human and animal health and the global environment without compromising fire safety.

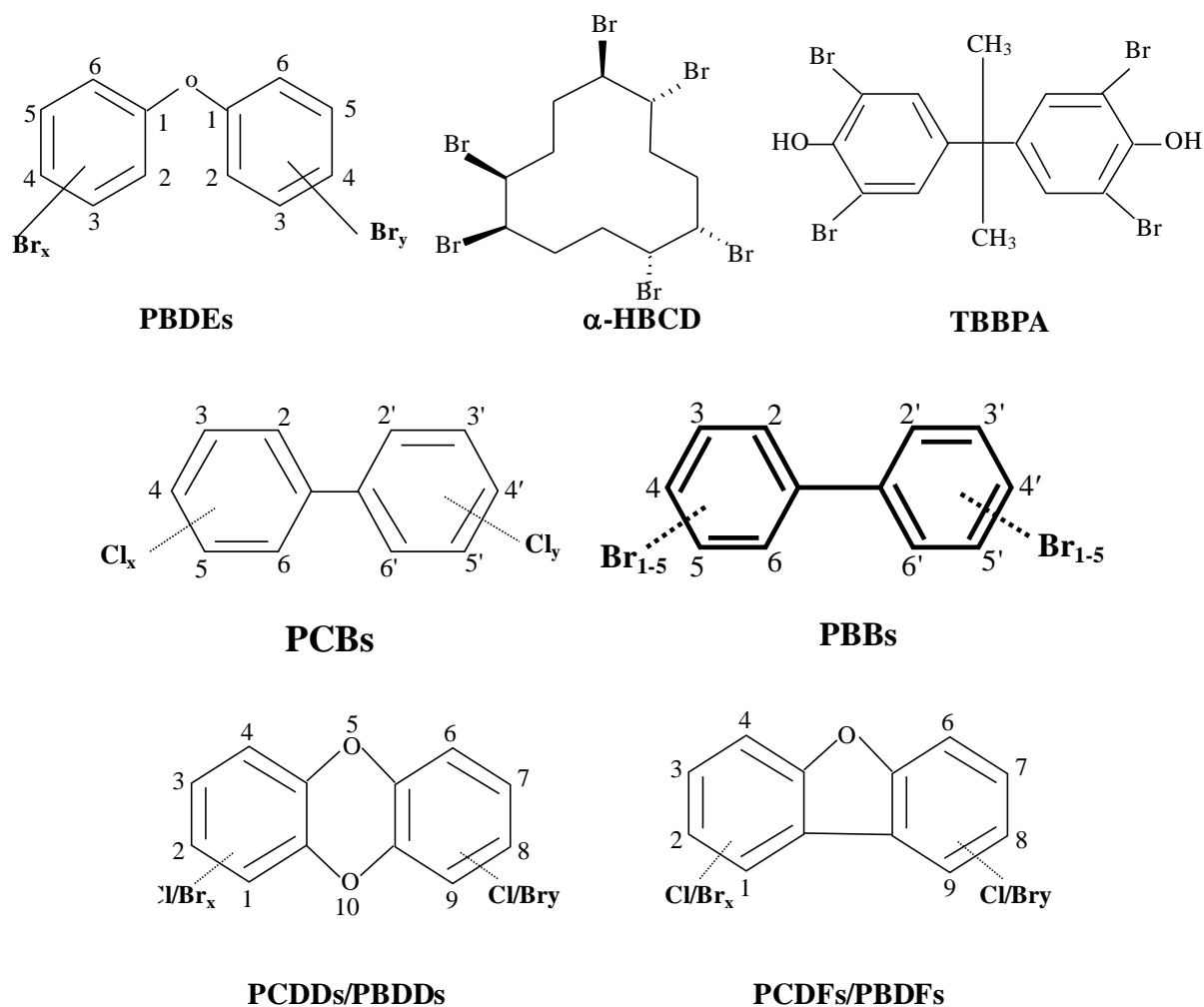
**Keywords:** Brominated flame retardants, chlorinated flame retardants, pentaBDE, octaBDE, decaBDE, PBDE, HBCD, TBBPA, PBDD/F, TDCPP, chlorinated Tris, brominated Tris, chlorinated paraffins, flammability standards, flame retardant regulations, fire safety, fire toxicity, replacement flame retardants, Technical Bulletin 117

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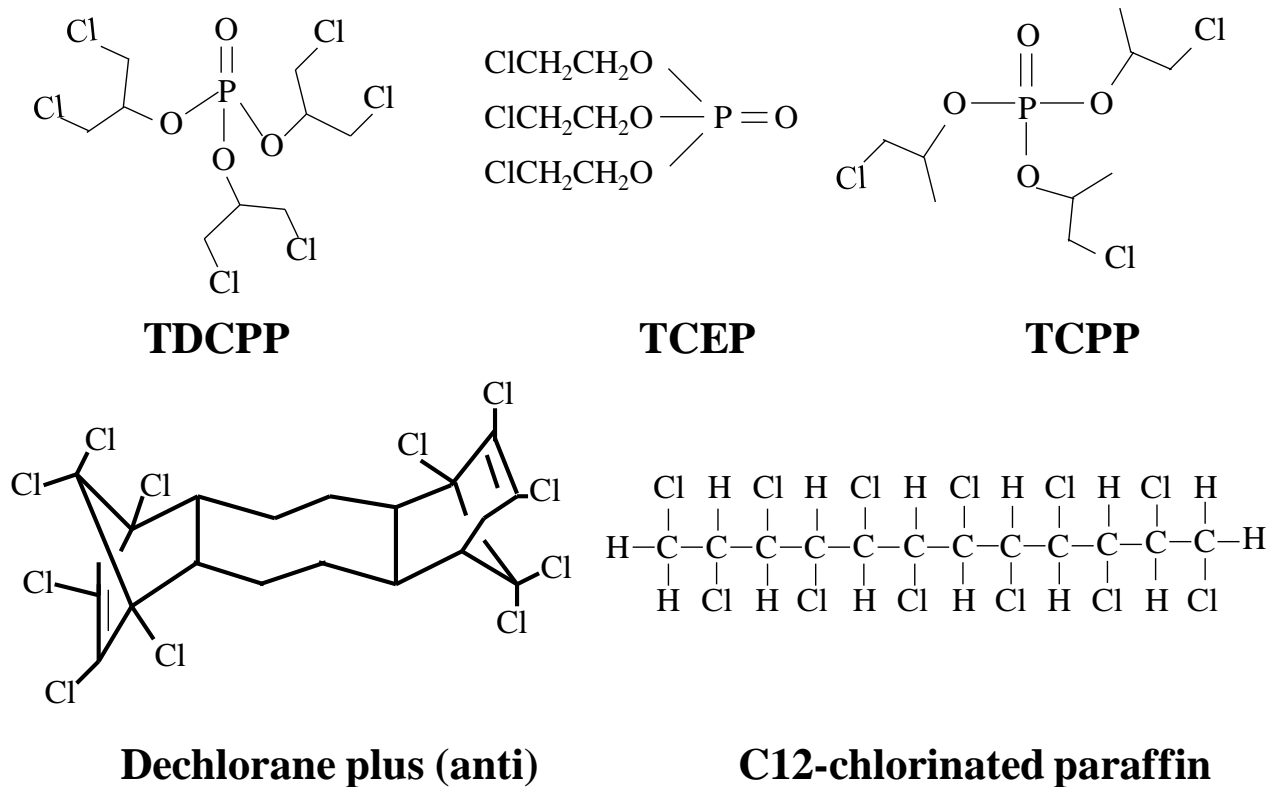
**Fig. 1:** Chemical structures of brominated flame retardants PBDEs, HBCD, and TBBPA, and related halogenated chemicals including the polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), and brominated/chlorinated dioxins and furans

## 1. INTRODUCTION

Since the 1970s, an increasing number of regulations have rapidly expanded the global usage of brominated and chlorinated flame retardants. Manufacturers add halogenated organic chemicals to a wide range of products to increase their flame ignition resistance [1]. Brominated and chlorinated chemicals are the least expensive way to meet flammability requirements. When the regulations leading to their use were implemented, the potential adverse health and environmental impacts of flame retardant chemicals were not recognized

or fully understood. Furthermore, when selecting flame retardant materials, the primary criteria of the manufacturer are cost and performance.

The five brominated flame retardants (BFRs) that have been used most extensively are tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and three commercial mixtures of polybrominated diphenyl ethers (PBDEs)—decabromodiphenyl ether (decaBDE), octabromodiphenyl ether (octaBDE), and pentabromodiphenyl ether (pentaBDE) (Figure 1). Although penta and octaBDE have been withdrawn from the market and decaBDE is being phased out, the



**Fig 2:** Chemical structures of chlorinated flame retardants in current use: TDCPP, [tris(1,3-dichloro-2-propyl) phosphate] also called TDCP or chlorinated Tris; TCEP or tris(2-chloroethyl) phosphate; TCPP or tris(1-chloro-2-propyl) phosphate, Dechlorane Plus, and chlorinated paraffins

overall production of halogenated flame retardants (HFRs) continues to rise rapidly /2,3/. Between 2001 and 2008, the volume of BFRs produced worldwide doubled from approximately 200,000 to 410,000 metric tons (mt) annually and between 2005 and 2008 CFRs increased from 82,000 to 190,000 mt /2,3/. In Asia, BFR output nearly doubled during 2005-2008, increasing from 139,000 to 246,000 mt and CFRs increased more than fivefold from 10,000 to 53,000 mt /3/.

The chlorinated flame retardants in current use in the United States (U.S.) include TDCPP, [tris(1,3-dichloro-2-propyl) phosphate] also called TDCP or chlorinated Tris; TCEP or tris(2-chloroethyl) phosphate; TCPP or tris(1-chloro-2-propyl) phosphate, Dechlorane Plus, and chlorinated paraffins /4-6/ (Figure 2). The Chemical Substance Inventory /7/ reports that between 10 and 50

million pounds of TDCPP were produced in 2006 in the U.S. The total chlorinated paraffin use in the U.S. is approximately 150 million pounds per year, divided among short chain (33 million pounds), medium chain (67 million pounds), and long chain (50 million pounds) /7/. In China the manufacture of chlorinated paraffins as flame retardants and for other uses is growing exponentially /8/.

Halogenated flame retardants enter the environment through multiple pathways, such as emission during manufacturing, from products in use, and combustion, leaching from landfills, or recycling at the end of the product's life. Since their introduction, HFRs have become widespread global contaminants and have been detected throughout the world in air, water, soil, sediment, sludge, dust, bivalves, crustaceans, fish, amphibians, reptiles, birds, mammals, and human

tissues /9-15/. The contamination patterns worldwide reflect the consumption patterns of various countries and regions. For example, North America has used 95% or more of the pentaBDE produced globally /16/, and pentaBDE levels in the North American general population and biota are the highest in the world /9,13/.

Exposure to HFRs is associated with a wide range of adverse effects in animals and humans, including endocrine disruption, immunotoxicity, reproductive toxicity, effects on fetal/child development, thyroid and neurologic function, and cancer /9,17-20/.

At the end of life, hazardous flame retardants are often exported to developing countries and countries in transition such as China in electronic waste (e-waste), second-hand electronics, and used cars. E-waste is frequently recycled with primitive technologies such as open burning, resulting in severe human and environmental contamination by PBDEs, other halogenated flame retardants, as well as their combustion products /21-24/. Firefighters are also exposed to such combustion products, especially during cleanup after fires. Studies show elevated rates of cancers that are thought to be related to dioxin exposure among firefighters /25,26/.

After 30 years of widespread use, several HFRs have been banned or phased out because of their environmental persistence and toxicity, only to be replaced by chemicals of similar structure and unknown toxicity /9,18/. Despite restrictions, flame-retarded consumer and household products will remain a reservoir for release into the environment for years to come, and some formulations, such as HBCD, TBBPA, and TDCP, are still in high-volume global production and use.

In this paper we review the major uses of halogenated flame retardants, their regulatory restrictions and chemical replacements, toxic effects related to human and animal exposure, hazards of toxic degradation products, end of life considerations, flammability standards and their

implementation, fire safety impacts, safer alternatives, and policy implications of continued use.

## 2. MAJOR USES, REGULATORY RESTRICTIONS AND REPLACEMENT FLAME RETARDANTS

### 2.1 Major Uses

The major uses of halogenated flame retardant chemicals in North America are in (1) electronics, (2) building materials, including insulation, (3) transportation, and (4) home furnishings /1,9,17/. The chemicals are commonly used at levels up to 5% of the weight of polyurethane foam in furniture and baby products and 20% or more of the weight of the plastic of electronic housings /27/. The highest-volume flame retardant worldwide, TBBPA, is used mainly as a reactive flame retardant in electronics, including printed circuit boards and several types of polymers /2/. HBCD is an additive flame retardant used in polystyrene foam insulation in buildings and to a lesser extent in upholstery, textile coatings, cable, latex binders, and electrical equipment /1/. Chlorinated paraffins are widely used as secondary plasticizers and flame retardants in plastics, primarily polyvinyl chloride (PVC) /7/. Other minor uses are as a plasticizer and flame retardant additive to rubber formulations, paints and other coatings, and adhesives and sealants /28/.

PentaBDE was added primarily to polyurethane foams in furniture, baby products, and automobile and aircraft interiors /1,17/. The main use of octaBDE was in a variety of thermoplastic resins, in particular ABS (acrylonitrile-butadiene-styrene) plastic, which can contain up to 12% by weight octa-BDE /29/. DecaBDE, the most widely used PBDE in all markets /2/, is added to various plastic polymers such as polyvinyl chloride, polycarbonates, and high-impact polystyrene, as well as back coating for textiles

(commercial furniture, automobile fabrics, and carpets) /1/. Because of their high-volume use in consumer products over decades, PBDEs are unique among toxic chemicals in that they can be found at pound levels in homes, public places, and transportation.

## 2.2 Regulatory Restrictions and Replacement Flame Retardant Chemicals

Because of their environmental persistence and toxicity, many HFRs have been banned or voluntarily phased out /9,17/. Manufacturers, however, often replace a banned chemical with another one having similar characteristics. For example, in 1977 the U.S. Consumer Product Safety Commission (CPSC) banned brominated Tris or Tris-BP/tris (2,3-dibromopropyl) phosphate/ from children's sleepwear after the chemical was found to be a mutagen /30/. Brominated tris was also found to be absorbed into children's bodies /31/. The main replacement for brominated Tris was chlorinated Tris or TDCPP. After being found to be a mutagen as well /32/, chlorinated Tris was voluntarily removed from use in sleepwear in 1978. Both compounds are also probable human carcinogens /33,34/. Nevertheless, chlorinated Tris or TDCPP is currently used to meet California Technical Bulletin 117 (TB117), a unique California flammability standard that requires polyurethane foam in furniture and juvenile products to withstand exposure to a small open flame for 12 seconds.

Previously, from the 1980s until 2004, pentaBDE was primarily used in furniture and juvenile product foam to meet the California standard TB117, as well as in transportation. PentaBDE and other PBDEs are structurally similar to known human toxicants including polybrominated biphenyls (PBBs), polychlorinated biphenyls (PCBs), dioxins, and furans (Figure 1). Because of environmental and public health concerns, the penta- and octaBDE commercial formulations were banned in California in 2003,

in Europe in 2004, and withdrawn from commerce in the U.S. in 2004 /35/. In May 2009, the principle congeners of the commercial products penta- and octaBDE were added to the Stockholm Convention list of persistent organic pollutants (POPs) /36/. These environmentally persistent, bioaccumulative, and toxic chemical mixtures are now banned from production. Furthermore, any remaining stockpiles must be eliminated or be subject to environmentally sound management.

DecaBDE, the third commercial PBDE, can break down into less brominated by-products that are more bioaccumulative and toxic /16,37-40/. DecaBDE was banned in Sweden in 2007, followed by partial bans in four U.S. states (Washington, Maine, Oregon, and Vermont), the European Union (2008), and Canada (2009). In December 2009, the U.S. Environmental Protection Agency (EPA) announced a negotiated three-year phase-out of this flame retardant in U.S. consumer products by three major global producers /41/.

Despite these restrictions, large amounts of upholstered furniture, juvenile products, and plastics containing PBDEs are still in use and must be disposed of after their lifetimes, creating outdoor reservoirs (e.g., landfills, wastewater treatment plants, electronic waste recycling facilities, or stockpiles of hazardous wastes) for the future dispersal of PBDEs to the environment. Moreover, large volumes of these materials are in the global recycling flow (e.g., plastic from waste electronics or polyurethane foam recycled to carpet padding) and will continue to be used in consumer products for a considerable time.

Major replacement chemicals for pentaBDE commercial mixtures in furniture and juvenile products (nursing pillows, baby carriers, high chairs) include Firemaster 550<sup>®</sup>, Firemaster 600<sup>®</sup> and TDCPP /4,42/. Firemaster 550<sup>®</sup>, contains: (1) triphenyl phosphate (TPP); (2) triaryl phosphate isopropylated; (3) 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB); and (4) Bis (2-ethyl

hexyl) tetrabromophthalate (TBPH) /43/. Two Firemaster 550<sup>®</sup> components, TBB and TBPH, have been detected in sewage sludge from wastewater treatment plants that discharge effluent into San Francisco Bay, California /44/, as well as in the blubber of dolphins and porpoises near flame retardant production facilities in south China /45/. Recent studies show that chlorinated Tris and Firemaster 550<sup>®</sup> components, as well as PBDEs, can migrate from foam products into indoor house dust /42/. These semi-volatile compounds can form thin films on walls and windows /46/. The inhalation and ingestion of contaminated dust has been shown to be a major route of human exposure, especially for children /42,47-49/.

A commonly used chlorinated flame retardant in the U.S. is chlorinated Tris or TDCPP, a pentaBDE replacement that was recently found in furniture and juvenile product foam, as well as in dust at similar levels to those of pentaBDE /42/. Other chlorinated phosphate flame retardants in use include TCEP or tris(2-chloro-ethyl) phosphate, which has been identified as a carcinogen by the World Health Organization /50/ and listed under Proposition 65 by the State of California /51/, and TCPP or tris(1-chloro-2-propyl) phosphate, a common replacement for TCEP in the EU. TCPP is over 200 times more volatile than TDCP or pentaBDE, and TCEP is 200 times more volatile than TCPP, making TCEP the most volatile of the three commonly used chlorinated phosphate flame retardants /52,53/. The volatility data suggest that the exposure risk is highest from TCEP, followed by TCPP.

Replacements for the octaBDE and decaBDE mixtures include 1,2-Bis(2,4,6-tribromophenoxy) ethane (BTBPE; trade named FF-680) and decabromodiphenylethane (DBDPE). Both BTBPE and DBDPE have been reported in air, water, sewage sludge, sediment, mussels, fish, and birds /14,54-56/, and in house dust from the U.S. /43/. Current concentrations of DBDPE in eggs of herring gulls from the Great Lakes are similar to

or higher than those of BDE-209 and appear to be increasing after a comparatively short period of usage /54/, suggesting that DBDPE may be more persistent and/or bioaccumulative than decaBDE. High concentrations of DBDPE have also been reported in captive pandas /57/ and waterbirds /58/ from China's Pearl River Delta, where many e-waste recycling facilities are located.

Another alternative to decaBDE in plastic enclosures is HBCD /59/. In recent years, the global demand for HBCDs has increased in Europe and Asia, and temporal studies show that the levels of the most persistent stereoisomer,  $\alpha$ -HBCD, are increasing in biota and humans /10,13,15,60/. HBCD is presently banned in Norway and was cited by the European Union (EU) as one of the chemicals for priority action /61/. In addition, the Stockholm Convention and regulators in Canada, Australia, and Japan are evaluating its hazards /8/.

TBBPA, the highest volume flame retardant worldwide, is primarily a reactive BFR (90%) covalently bound to the polymer structure and less likely to be released into the environment than are additive flame retardants. TBBPA is of high ecotoxicologic concern because of its acute and chronic toxicity in several biota /62/. TBBPA, however, can be rapidly metabolized by mammalian liver and eliminated in bile, urine and feces /63,64/ and therefore has a lower potential for bioaccumulation. Nevertheless, TBBPA has been detected in various environmental media and biota including air, soils, water, sediment, and bird muscle from e-waste regions of China /65,66/; in water and sediment from English lakes /67/ and in bottlenose dolphins and bull sharks from the Florida Coast /13/. TBBPA can serve as a source of environmental bisphenol A (BPA), a compound of increasing concern that has been shown to break down in marine sediments /68,69/. Currently, no restrictions are placed on the production and use of TBBPA.

Chlorinated paraffins are commonly used as flame retardants in plastics. Other minor uses are

as flame retardants in rubber formulations, paints and coatings, and adhesives and sealants /28/. Short-chain chlorinated paraffins (SCCPs), which have 10 to 13 carbons, are persistent, bio-accumulative, and toxic to aquatic organisms at low concentrations /7,70/. SCCPs have been measured in air, sediment, surface waters, and wastewater /70,71/, as well as in freshwater aquatic species, marine mammals, and avian and terrestrial wildlife. In addition, SCCPs have been detected in human breast milk from Canada and the United Kingdom, and in food from Japan and Europe /70/. Currently, the EPA is planning to ban or restrict the manufacture, import, processing, or distribution of SCCPs /7/. A global ban on SCCPs is being considered under the Stockholm Convention /70/.

The chlorinated flame retardant, Dechlorane Plus, used in electrical wires, cable coatings, hard connectors in computers and plastic roofing materials, is a replacement for the flame retardant Dechlorane, which is identical to the banned pesticide Mirex /72/. Dechlorane Plus has been widely detected in sediment and biota in the Great Lakes /72-74/ and has been measured in household dust /75,76/ raising concern about human exposure. Considered a high production volume (HPV) compound in the U.S, Dechlorane Plus is currently unregulated and therefore is subject to the U.S. EPA's HPV challenge. Dechlorane Plus is included among Canada's 50 top priority compounds of environmental concern /77/.

### 3. HEALTH EFFECTS OF HALOGENATED FLAME RETARDANTS IN ANIMALS AND HUMANS

Exposure to HFRs has been associated with and/or causally related to numerous health effects in animals and humans, including endocrine disruption, immunotoxicity, reproductive toxicity, effects on fetal/child development, and cancer /9,17,18/.

### 3.1 Polybrominated Diphenyl Ethers (PBDEs)

*3.1.1. Laboratory Animals.* Experimental data (both in vivo and in vitro) show that PBDEs have the potential to disrupt the endocrine system at multiple target sites in amphibians, birds, fish, mice, and rats, resulting in effects on thyroid, ovarian, and androgen function /17,18,78,79/. Like other BFRs, one of the primary toxic effects of PBDEs is thought to be disruption of thyroid hormone homeostasis, and several mechanisms have been proposed—interference in the transport of T<sub>4</sub> via competitive binding to thyroid transport proteins (TTR) and thyroid hormone receptors; induction of thyroid hormone metabolic activity; and/or interference with the hypothalamus-pituitary-thyroid axis /80/. The disruption of thyroid homeostasis during development is of special concern because small changes in maternal and fetal thyroid homeostasis cause neurologic impairments, including decreases in the IQ of offspring /17,18/.

Like other BFRs, many of the adverse health effects of PBDEs result from developmental exposure /9,17,18/. In rodent models, the toxic effects following prenatal or neonatal exposure include effects on liver enzymes /81,82/, endocrine disruption (altered thyroid hormone levels) /83/, reproductive damage /84-86/ immunotoxicity /87,88/, and neurotoxic effects /89,90/. Experiments conducted by Eriksson and co-workers in mice developmentally exposed either to penta- or higher BDEs /89-95/ and in rats exposed to BDE-209 /96/ during the period of rapid brain growth have shown neurotoxic effects, including an impairment of spontaneous behavior, cholinergic transmitter susceptibility, and habituation capability. The deficits in learning and memory persisted into adulthood and worsened with age. Rice et al. /97/ reported that neonatal exposure to decaBDE produces effects on behavioral performance in aging but not in younger mice, possibly as a result of increased impulsivity in older animals. An earlier study in



neonatal mice /98/ found that decaBDE exposure resulted in developmental delays, changes in spontaneous locomotor activity, and a dose-related reduction in serum  $T_4$  concentrations. The results of that study suggest that the neurodevelopmental effects of PBDEs might be related to perturbations in thyroid hormone homeostasis in the neonate. In male rats, hepatocellular degeneration is a high-dose effect of decaBDE exposure /99/. The developmental effects of PBDEs are exacerbated by co-exposure to PCBs in rats /100/.

As endocrine disruptors of adipocyte metabolism, PBDEs can predispose animals to obesity /101/. Exposure to pentaBDE results in increased lipolysis and reduced insulin-stimulated metabolism in rat adipocytes—the hallmark features of obesity, insulin resistance, and type 2 diabetes. Certain PBDEs are also potent anti-androgens /102,103/, which may explain delays in puberty and effects on gonads.

DecaBDE is the only PBDE that has been tested for carcinogenicity. In two-year studies in rats and mice, decaBDE exposure caused liver and thyroid tumors /104/. The National Toxicology Program is currently conducting two-year studies on DE-71, a commercial pentaBDE mixture /105/.

Dosing studies using captive mink (*Mustela vison*) indicate that mink are more sensitive than rodents to the reproductive, endocrine-disrupting, and developmental effects of PBDEs /106/. The effects of environmentally relevant doses of DE-71 on mink reproductive performance and the development of offspring exposed perinatally and post-weaning were recently investigated /107/. Dietary PBDE concentrations that caused no effects on reproduction in rodents ( $2.5\text{-}\mu\text{g g}^{-1}$  DE-71) resulted in complete reproductive failure in mink. Developmental effects in offspring were evident in 33-week-old juveniles, which were more sensitive to the effects than their respective dams. Juvenile thyroid hormone homeostasis was also much more sensitive to PBDE exposure in mink

than in rodents: a significant reduction of  $T_3$  was observed in all male and female mink, despite a compensatory increase of  $T_4$  in females /107/. Developmental immunotoxicity (increased splenic germinal center development and incidence of B-cell hyperplasia) was observed in ranch mink exposed to a high dose ( $10\ \mu\text{g g}^{-1}$ ) of DE-71 in the diet /88,107/. Significant body weight reductions were found in mink fed 5 and  $10\ \mu\text{g PBDE g}^{-1}$  /88/. The exposure doses of 5 and  $10\ \mu\text{g PBDE g}^{-1}$  diet for 8 weeks affected several immunologic endpoints, including lymphocyte counts, in mink /88/. Dietary exposure of mink to PBDEs resulted in accumulation in the brain, demonstrating that PBDEs can cross the blood-brain barrier /107/.

**3.1.2 Humans.** Human internal and external exposure to PBDEs has been recently reviewed /9,47,108/. About 20% of exposure to PBDEs in Americans is estimated to derive from the diet, with the highest levels found in butter, seafood, and meat /109/. The remaining 80% of exposure is assumed to derive from the ingestion/inhalation of PBDE-contaminated dust /48/. The PBDE concentrations in the North American general population—mean  $\sim 30\text{-}40\ \text{ng g}^{-1}$  lipid weight (lw) in serum—are 10 to 40-times higher than the concentrations reported for populations in Europe and other parts of the world /9,12,48,110-113/. The highest concentration of PBDEs ( $9630\ \text{ng g}^{-1}$  lw) in human adipose tissue was reported in a sample collected from New York /110/. In the U.S., infants are exposed at higher levels than adults through the ingestion of breast milk and by the ingestion of dust due to their frequent hand-to-mouth contact /114,115/. A significant positive correlation between PBDE concentrations in house dust and breast milk has been shown /49/. In California, populations have been shown to be disproportionately exposed to PBDEs, likely due to the state's unique fire regulation TB117 that has led to high usage of HFRs in furniture, mattresses, sleepwear, and baby products. In California, breast milk, serum, and house dust samples contain high concentrations of PBDEs

/76,116,117/. Serum PBDE levels in children are 2.5 times higher than those in similar-aged children across the U.S., 2-10 times higher than in U.S. adults, and 10-100 times higher than in similar aged children in Europe and Mexico /118/.

Numerous adverse effects have been associated with human exposure to PBDEs, including endocrine disruption, reproductive effects, diabetes, and effects on fetal/child somatic and neurodevelopment /9,17,119,120/. Increasing evidence suggests that PBDE exposure adversely affects the developing nervous system in children. In a recent study, exposure to pentaBDEs in umbilical cord blood was associated with substantial neurodevelopmental deficits /20/. Children in the highest 20% of the exposure distribution showed lower IQ performance scores (ranging from 5 to 8 points lower) at ages 1, 2, 3, 4, and 6. In Dutch children, prenatal exposure to pentaBDE and HBCDs was associated with significant adverse effects on motor, cognitive, and behavioral outcomes /121/. PentaBDE congeners appear to profoundly affect the development of fetal human neural progenitor cells via the endocrine disruption of cellular thyroid hormone signaling /122/. These studies are the first to provide biological plausibility for *in vivo* studies reporting behavioral and IQ deficits following developmental exposures.

Adverse human reproductive/developmental outcomes related to PBDE exposure have been recently reported. Harley et al. /19/ reported an association between PBDE exposure and reduced fertility in women from a predominantly Mexican-immigrant community in California. Increasing serum levels of pentaBDE were significantly associated with longer time to pregnancy. Prenatal PBDE exposure of the infants of these women was associated with low birth weight, altered cognitive behavior, and significantly reduced plasma levels of TSH /120/. A study by Wu et al. /123/ reported that elevated PBDE concentrations in umbilical cord blood were associated with adverse birth outcomes,

such as premature delivery, low birth weight, and stillbirth among the infants of pregnant women involved in e-waste recycling in Guiyu, China. Whereas most human tissues showed a pentaBDE 'signature' dominated by tetra-BDE-47, BDE-209 dominated the PBDE congener profiles in the Guiyu women. An earlier study reported that elevated levels of PBDEs in breast milk of pregnant Taiwanese women were significantly associated with adverse birth outcomes including weight, length, and chest circumference of their infants /124/. In both studies, the effects were observed at levels lower than the average PBDE levels in the adult U.S. population.

In a study of mother-son pairs from Denmark and Finland, elevated PBDE levels in breast milk correlated with cryptorchidism (undescended testicles) in the boys /125/. The PBDE levels associated with cryptorchidism were also positively correlated with serum luteinizing hormone (LH) concentrations in the infants, which suggested a possible compensatory mechanism to achieve normal testosterone levels and is consistent with the anti-androgenic effects of PBDEs observed in experimental animals. A pilot study conducted by Japanese researchers reported that elevated blood levels of BDE-153 correlated with decreased sperm count and decreased testes size /126/.

The importance of house dust as a major exposure route for PBDEs in humans has been highlighted /47,48,113/, and a recent study in the U.S. reported a relationship between altered hormone levels in men and PBDE levels in house dust /127/. The findings included significant inverse associations between PBDEs in house dust and serum concentrations of the free androgen index, LH, and follicle-stimulating hormone (FSH) and positive associations between PBDEs and sex-hormone binding globulin (SHBG) and free T<sub>4</sub>.

Significant relationships between PBDEs and elevated thyroid hormone levels have been reported in other human studies. Turyk et al. /128/

reported an association between PBDEs and elevated T<sub>4</sub> levels and thyroglobulin antibodies in the blood of adult male consumers of Great Lakes sport fish. The effects were observed at PBDE levels comparable to those found in the general U.S. population and were independent of PCB exposure and sport fish consumption. A recent study of Inuit adults /129/ reported that plasma concentrations of BDE-47 were related to increasing total T<sub>3</sub> levels. Yuan et al. /130/ found an association between serum levels of PBDEs and elevated TSH in persons living near or working at an electronic waste dismantling site in southeast China. Elevated TSH levels may be a compensation for the reduction of circulating thyroid hormones and are also indicative of stress on the thyroid system.

As endocrine-disruptors, some PBDEs are reported to cause disturbances in glucose and lipid metabolism in adipose tissue of Sprague-Dawley rats, which is characteristic of metabolic obesity and type-2 diabetes /101/, but few studies have examined the relationships between PBDEs and diabetes in humans. Turyk et al. /128/ reported a non-significant association between PBDE exposure and diabetes in Great Lakes sport fish consumers with hypothyroid disease. A recent study in U.S. adults examined the association between diabetes and PBDEs /119/. Serum concentrations of the hexaBDE congener-153 were significantly related to metabolic obesity syndrome and diabetes prevalence at background concentrations, suggesting that PBDEs may contribute to diabetes in the general population.

The carcinogenicity of PBDEs has not been adequately addressed in animals or humans. A study by Hardell et al. /131/ reported an association between BDE-47 concentrations and an increased risk for non-Hodgkin's lymphoma (NHL). In the highest risk/highest exposure group, BDE-47 was also significantly correlated with elevated titers to Epstein Barr IgG, a human herpes virus that has been associated with certain

subgroups of NHL. The incidence of thyroid cancer has been increasing in the U.S. during the past several decades, especially among women and in newborn babies (congenital hypothyroidism), and part of the observed increase in thyroid cancer rates is hypothesized to be related to the increasing population exposure to PBDEs and other thyroid hormone disrupting compounds /80,115/.

*3.1.3. Wildlife.* In North America, PBDE levels in wildlife are the highest in the world and are increasing /9,12,132-135/. In some areas, PBDEs are rivaling PCBs and organochlorine pesticides as the top contaminant in tissue /16/. Although the threshold levels for PBDE-related effects in wildlife are not understood, PBDE exposure at environmentally relevant levels has been associated with an array of adverse effects in numerous species /9/.

*3.1.3.1. Fish.* In fish, PBDE exposure may affect thyroid hormone homeostasis, sperm production, disease resistance, and neurodevelopment /9,136-138/. In juvenile lake trout (*Salvelinus namaycush*) exposed to 13 PBDE congeners at environmentally relevant levels, plasma T<sub>4</sub> levels were significantly reduced /138/. In male fathead minnows (*Pimephales promelas*), repeated oral exposure to BDE-47 reduced sperm production /139/. Low-dose embryonic exposure of killifish (*Fundulus heteroclitis*) to a pentaBDE mixture resulted in neurobehavioral effects and a subtle developmental asymmetry of tail curvature direction, with a J-shaped dose-response curve suggestive of thyroid hormone disruption /140/. Similarly, exposure of zebrafish (*Danio rerio*) embryos to high doses of BDE-47 resulted in developmental effects, including morphologic, cardiac, and neural deficits that impaired later survivorship in the fish larvae /141/. Juvenile zebrafish chronically exposed to ecologically relevant levels of BDE-47 exhibited altered locomotion behavior /137/. Dietary exposure of juvenile Chinook salmon (*Oncorhynchus tshawytscha*) to environmentally relevant levels of

PBDEs increased susceptibility to pathogenic microorganisms /136/.

**3.1.3.2 Birds.** PBDEs are detected at high concentrations in birds of prey, such as peregrine falcons (*Falco peregrinus*) and common kestrels (*F. tinnunculus*), and studies have shown that PBDEs may exert DDT-like endocrine-disrupting and reproductive effects in several species. In captive American kestrels (*F. sparverius*), Fernie et al. /142/ reported decreased plasma T<sub>4</sub> and vitamin A levels, as well as indications of oxidative stress in kestrels dosed with environmentally relevant levels of DE-71, both *in ovo* and post-hatch. In a separate study, DE-71 exposure had a negative impact on the timing and frequency of courtship behaviors that are essential for successful reproduction /143/. In a follow-up experiment, exposure to DE-71 and unintentional exposure to  $\alpha$ -HBCD resulted in delayed egg laying, reduced egg size, eggshell thinning, and reduced fertility and reproductive success in kestrels /144/. Egg laying was delayed with increasing concentrations of BDEs-153, -154, -28, and -17, and multiple effects of DE-71 exposure on egg quality (egg size and mass) were observed. Delayed egg laying, thinner eggshells, and poorer fledgling success were associated with BDE-153, the dominant congener recently found in kestrels and peregrine falcons /145/, whereas eggshell thinning was consistently inversely associated with the majority of congeners in the DE-71 mixture, especially BDE-153, and -154, and -28, as well as  $\alpha$ -HBCD. Fernie et al. /144/ concluded that these changes in the reproductive success of captive kestrels, particularly eggshell thinning associated with reduced hatching success, may partially explain the decline of American kestrels across North America. McKernan et al. /146/ reported decreased pipping and hatching success in American kestrel embryos following the air cell injection of DE-71 at concentrations of 10 and 20  $\mu\text{g g}^{-1}$ , suggesting that the observable effect level (LOEL) may be as low as 1800  $\text{ng g}^{-1}$  ww (based on the uptake rate). Similarly,

Johansson et al. /145/ reported a negative relationship between  $\Sigma$ PBDEs and reproductive success in peregrine falcons from Sweden. PBDE concentrations in eggs were negatively related to the average number of young produced from individual breeding females over a 2-7 year period. Van den Steen et al. /147/ observed negative effects of PBDEs on reproductive performance in European starlings (*Sturnus vulgaris*) implanted with silastic tubes containing environmentally relevant concentrations of PBDEs. A recent field study in the U.S. /148/ reported a negative relationship between reproductive performance and PBDEs in eggs of wild ospreys (*Pandion haliaetus*) at two locations in the highly contaminated Columbia River valley of Oregon and Washington, and suggested that concentrations of  $\sim 1000 \text{ ng g}^{-1}$  ww may reduce reproductive performance in ospreys. Many North American osprey populations have PBDE levels exceeding 1000  $\text{ng g}^{-1}$  ww and thus may be at increased risk for contaminant-induced reproductive impairment.

**3.1.3.4. Marine mammals.** Marine mammals are long-lived, apex predators that can accumulate extremely high concentrations of PBDEs and other POPs through the marine food chain. While the main exposure route for adults is the consumption of contaminated fish, placental and lactation exposure is significant for young animals. Marine mammals from the California coast contain the highest reported PBDE levels in the world /9/. The highest concentrations on record were detected in blubber of adult male California sea lions (mean 55300  $\text{ng g}^{-1}$  lw) /149/ and transient killer whales (*Orcinus orca*) (up to 12600  $\text{ng g}^{-1}$  lw), as well as in resident killer whales from the Puget Sound-Strait of Georgia Basin (mean 7500 and 6800  $\text{ng g}^{-1}$  lw in females and males, respectively) /150,151/. On the U.S. Atlantic coast, relatively high PBDE concentrations (mean 3000-4000  $\text{ng g}^{-1}$  lw) were reported in young harbor seals (*Phoca vitulina concolor*) /152/ and in juvenile bottlenose

dolphins from the Charleston Harbor estuary, North Carolina (mean 6000-8000 ng g<sup>-1</sup> lw) /153/. Adverse health effects in marine mammals co-exposed to PBDEs and PCBs have been reported, including thyroid hormone alterations in gray seals (*Halichoerus grypus*) /154/ and harbor seals (*Phoca vitulina*) /155/, and thymic atrophy and splenic depletion in harbor porpoises (*Phocoena phocoena*) from the North and Baltic Seas /156/. A study of infectious diseases in California sea otters (*Enhydra lutris*) co-exposed to PBDEs and PCBs suggested possible synergistic interactions between these contaminant groups /157/. A recent study reported, however, that PBDEs alone significantly reduced the probability of first year survival in gray seals /158/.

### 3.2 Tetrabromobisphenol A (TBBPA)

TBBPA, a cytotoxicant, immunotoxicant, and thyroid hormone agonist, has the potential to disrupt estrogen signaling /17,159/. TBBPA is toxic to primary hepatocytes, destroys mitochondria, and results in membrane dysfunction in liver cells and inhibition of a key mixed function oxidase enzyme (cytochrome P450 2C9) /160/. Studies of toxic effects using cell lines demonstrated that TBBPA interferes with cellular signaling pathways, reducing cell viability and proliferation /161/. TBBPA is also highly immunotoxic in vitro /162/ and inhibits T-cell activation by blocking the expression of CD25 proteins that are essential for the proliferation of activated T cells. Thus, TBBPA may have a profound effect on an organism's immune-mediated defense against bacteria, viruses, and possibly cancer. TBBPA is also neurotoxic in rat brain cells, where it causes oxidative stress, inhibits dopamine uptake, and generates free radicals /163/. Recent in vivo studies have shown that neonatal TBBPA exposure causes hearing deficits in rat offspring /164/, including changes in hearing latency and hearing threshold that are similar to changes observed following develop-

mental exposure to PCBs. Behavioral alterations were reported in perinatally exposed mice /165/.

TBBPA can act as an endocrine disruptor, and both estrogenic and androgenic effects have been reported. Hydroxylated TBBPA metabolites have been shown to inhibit estrogen sulfotransferase activity in vitro /166/, which could decrease estrogen clearance and result in elevated levels of circulating estrogens. Environmentally relevant TBBPA concentrations decreased reproductive success in zebra fish /167/ and inhibited estradiol metabolism in lake trout /168/.

Disruption of thyroid hormone homeostasis is proposed to be the primary toxic effect of TBBPA and many other BFRs. TBBPA has an even closer structural relation to thyroxine (T<sub>4</sub>) than PCBs, and TBBPA toxicity to the thyroid might be related to its effects on the transport of T<sub>4</sub> in the blood. In vitro assays demonstrated that the binding affinity of TBBPA to human transthyretin (TTR) is greater than that of T<sub>4</sub> (up to 10 times more potent than T<sub>4</sub>) /169,170/. TBBPA can act as a thyroid hormone agonist, antagonist, potentiator, or have no effect /169,172-174/. *Rana rugosa* tadpoles co-exposed to triiodothyronine (T<sub>3</sub>) and TBBPA exhibited suppression of T<sub>3</sub>-induced tail shortening, indicating a thyroid hormone antagonist effect /172/. A reproductive developmental feeding study in rats reported an increase in T<sub>3</sub> in TBBPA-exposed female rat offspring and a reduction in circulating total T<sub>4</sub> in both genders /175/. The developmental effects also included increased testis and pituitary weight.

### 3.3 Hexabromocyclododecane (HBCD)

Experimental evidence indicates that HBCD, the second most used flame retardant, exerts a range of endocrine disrupting and reproductive developmental effects in animals /10,17/. Although the acute toxic effects are low /176/, oral exposure to HBCD induces drug-metabolizing enzymes in rats and fish /177,178/ and can induce malignant transformation in

mammalian cells by a non-mutagenic mechanism /179/ HBCD isomers are endocrine disruptors with anti-androgenic properties that inhibit aromatase and interact with steroid hormone receptors /169,180/. Like other BFRs, HBCDs may disrupt thyroid hormone homeostasis /176/, resulting in decreased levels of T<sub>4</sub> and increased levels of thyroid stimulating hormone (TSH) /177,181-183/ and affect thyroid hormone receptor-mediated gene expression /184/.

Many effects of HBCDs occur during development. Low-dose reproductive developmental studies in rats have shown that HBCDs decrease bone density and retinoids, and enhance immune responses to sheep red blood cells /185/. Following neonatal exposure in rats, the developmental neurotoxic effects include aberrations in spontaneous behavior and learning, and memory deficits /186,187/. The HBCDs are neurotoxic to rat cerebellar granule cells /188/, inhibit the depolarization-evoked intracellular calcium and neurotransmitter release /189/, and alter the normal uptake of neurotransmitters in rat brain /190/. Lilienthal et al. /191/ reported that HBCD exposure caused hearing deficits in males and catalepsy (a dopamergic effect) in females. The effects differed from those observed after exposure to TBBPA or the pentaBDE-99.

The human health effects of HBCDs have not been studied. Although levels in humans are still relatively low, HBCD has the potential to bioaccumulate and persist in the environment. There is concern about the increasing levels of HBCD in wildlife and humans, especially in Asia /15/.

### 3.4 Short-Chain Chlorinated Paraffins (SCCPs)

SCCPs are recognized by the Stockholm Convention as highly toxic to aquatic organisms at low concentrations /70/. In rodent models, SCCPs are toxic to the liver and kidney, and thyroid gland, and carcinogenic in rats and mice of both genders /192,193/. SCCPs are also developmental toxins; studies have shown that

pre- and postnatal exposure resulted in reduced fetal body weight, reduced pup body weight, and reduced pup survival at higher doses /194/. Although they exhibit low acute toxicity in humans, SCCPs are classified as carcinogens under Proposition 65 by the State of California /51/. The National Cancer Institute lists SCCPs as reasonably anticipated to be human carcinogens, based on sufficient experimental evidence /193/. The SCCPs are classified by the IARC as Group 2B—possibly carcinogenic to humans /195/. The potential for SCCPs to exert adverse impacts on children and other vulnerable populations is currently under review /7/.

### 3.5 PentaBDE Replacements: Firemaster 550<sup>®</sup> Components and Chlorinated Tris (TDCPP)

Although replacement flame retardants, such as Firemaster 550<sup>®</sup> and chlorinated Tris, are in high-volume use, few studies have been conducted in animals or humans on the health effects of these chemicals. Firemaster 550<sup>®</sup> components TBB and TBPH are genotoxic in fish, causing significant DNA damage (increased DNA strand breaks from liver cells) in orally exposed fish /196/. Triphenyl phosphate (TPP) is toxic to aquatic organisms including *Daphnia* /197/, rainbow trout, and fathead minnows /198/. Triaryl phosphate isopropylated is a reproductive/ developmental toxin at mid- to high doses in rats /198/. Histopathologic changes were observed in female reproductive organs and adrenals at all doses.

Studies have reported that chlorinated Tris (TDCPP) is mutagenic /32,33/ and carcinogenic in rats /33,34/. TDCPP is also absorbed by humans /199/. The U.S. Consumer Product Safety Commission (CPSC) considers TDCPP a probable human carcinogen and estimates a lifetime cancer risk from TDCPP-treated furniture foam is up to 300 cancer cases/million /33/. However, we should note that this risk assessment focused entirely on dermal exposure and did not take into account exposure resulting from the escape of TDCPP from

products into dust. The U.S. EPA considers TDCPP a moderate hazard for cancer and reproductive/developmental effects /200/.

A recent study showed that men living in homes with high amounts of the organophosphate (OP) flame retardants TPP and TDCPP in household dust had reduced sperm counts and altered levels of hormones related to fertility and thyroid function /201/. High levels of TPP in dust were associated with a substantial (19%) reduction of sperm concentrations and a 10% increase in prolactin levels. Increased prolactin is considered a marker of decreased neuroendocrine/dopamine activity and may be associated with erectile dysfunction as well /202/. High levels of TDCPP in dust were associated with a 17% increase in prolactin and a 3% decline in free thyroid hormone levels. The possible synergistic or additive effects of the numerous flame retardant chemicals in use have not been studied in animals or humans.

#### **4. BROMINATED FLAME RETARDANTS UNINTENTIONALLY PRODUCE BROMINATED DIOXINS AND FURANS**

Brominated flame retardants, especially PBDEs, and PBBs, are a major source of toxic tetra- to octa-brominated dioxin and furan contamination /203-208/. Brominated dioxins and furans are unintentionally released during the entire life cycle of these flame retardants.

##### **4.1 Environmental, Food, and Human Contamination**

Brominated and mixed brominated-chlorinated dioxins and furans are major contaminants, both indoors and in the environment. Brominated furans have been found in house dust globally /22,207,209,210/. In Japan, brominated furans are the major contributors to dioxin-like toxicity in house dust and exceed the amount contributed by

chlorinated furans and dioxin-like PCBs /207, 208/. In the UK, brominated and brominated-chlorinated dioxins and furans contribute about 30% of the dioxin-like toxicity in food /211,212/. Brominated dioxins have been detected in human tissue /213-215/ and in biota /216,217/. A recent study of Swedish adipose tissue samples suggested that they contributed up to 14% of the total dioxin toxic equivalency (TEQ) /215/. Brominated dioxins also contribute to dioxin-like toxicity in human milk /214/, adding to the exposure of infants worldwide to chlorinated dioxins and furans and dioxin-like PCBs, which exceeds the WHO recommended tolerable daily intake by more than an order of magnitude /218/.

Workers involved in the production and recycling of BFRs are exposed to brominated dioxins and furans /219/. People living near primitive e-waste recycling facilities are also at high risk for exposure to HFRs and halogenated dioxins and furans /23,220,221/. Firefighters have elevated exposure to brominated and chlorinated dioxins and furans /222/, both during and while cleaning up after fires /26,223/. High levels are formed during accidental fires under uncontrolled combustion conditions in the presence of BFRs /204,224/. The significantly elevated rates of cancer reported in firefighters comprise four types that are potentially related to exposure to dioxins and furans—multiple myeloma, non-Hodgkin's lymphoma, prostate, and testicular cancer /25,26/.

##### **4.2 Toxicity of Brominated Dioxins and Furans**

Brominated dioxins and furans have toxicities similar to their chlorinated counterparts in human cell lines and mammalian species /222,225-227/. Thymic atrophy, wasting of body mass, lethality, teratogenesis, reproductive effects, chloracne, immunotoxicity, enzyme induction, decreases in T<sub>4</sub> and vitamin A, and increased hepatic porphyrins have been observed in animal studies of both brominated and chlorinated dioxins and furans /203,222,227/. In vitro responses are

similar, including enzyme induction, anti-estrogen activity in human breast cancer cells, and transformation of mouse macrophages into tumor cells /203/.

#### **4.3 Formation and Release of Brominated Dioxins and Furans during the Life Cycle of Brominated Flame Retardants**

Halogenated dioxins are formed unintentionally during the production of halogenated aromatic compounds. Brominated dioxins and furans have been found as contaminants in such commercial BFRs as PBDEs, decabromobiphenyl, 1,2-bis(tribromophenoxy)ethane, TBBPA, and bromophenols /203,228/. Brominated dioxins and furans are also formed in the production of BFR-retarded plastics in thermal processes like molding and extrusion /205,224,229/. For PBDEs, the levels of dioxin and furan contamination increase during the life span because of photolytic conversion, which can take place in plastic matrices /230/ or treated textiles /231/. The largest amounts are formed in the end-of-life stage during primitive recycling of e-waste /22,24,206/, secondary metal industry processes /232/, and during non-BAT (best available technology) incineration of e-waste /204,205/. The primitive recycling of thousands of tons of PBDEs contained in e-waste is estimated to release tons of brominated and brominated-chlorinated dioxin/furans into the environment /206/. In open burning e-waste areas in China, the measured levels of these compounds in soil exceeded allowable soil standards for dioxin worldwide /24/. PBDEs were shown to be the major precursor chemicals for this severe contamination /206/. Similarly, in industrial countries, brominated dioxins and furans are released from uncontrolled burning of BFR-containing wastes and the resulting emissions contribute substantially to total dioxin-like toxicity /204,233/.

### **5. END-OF-LIFE CONSIDERATIONS FOR HALOGENATED FLAME RETARDED MATERIALS**

The end-of-life management for products treated with PBDEs and other HFRs is critical /204,234/. The three main options are: (1) reuse/recycling, (2) incineration combustion, and (3) landfilling. Different management schemes are needed for different materials, such as flame-retarded plastic in e-waste or cars, polyurethane foam in furniture or cars, and textiles.

#### **5.1 Recycling of Brominated Flame-Retarded Materials**

From an energy efficiency life cycle perspective, the preferred method for end-of-life treatment of flame-retarded materials is mechanical recycling because it reduces the need for new materials /204,234/. Toxicity and potential health effects also have to be considered, however /204,234/. Materials containing halogenated flame retardants and other toxic chemicals are often exported to developing and transition countries to be recycled, resulting in environmental and human contamination /21,23, 220,235-237/. Similarly, workers in industrial countries can be exposed to high levels of PBDEs and other toxics during the recycling of e-waste or polyurethane foam /204,234,238,239/.

Another critical drawback of recycling PBDE-containing materials is the formation of brominated furans during the recycling operations such as extrusion and molding /205,229,240/. Recycled PBDE-containing plastics can be contaminated with brominated dioxins and furans, often exceeding allowable limits /204,241/. The chemical industry does not recommend the mechanical recycling of some of the bromine-containing plastic waste /241,242/.

Furthermore, some BFRs can degrade the mechanical properties of recycled engineering



plastics /243/. If the properties of recycled materials are not comparable to the original plastic, then the plastic will be 'downcycled' into less-demanding applications. Recent studies showing that PBDEs and other flame retardants are present in household goods /244/, videotape casings /245/, and children toys /246/ revealed that such downcycling is taking place without controlling BFR-contaminated plastic streams. Such practices lead to unnecessary human exposure to BFRs from recycled materials.

### **5.2 Combustion of Materials Containing Halogenated Flame Retardants**

A large proportion of BFR materials are eventually burned. Depending on the quality of combustion, high levels of brominated dioxins and furans can be formed and released /205,247/. In particular, the open burning of e-waste in developing and transition countries release large amounts of halogenated dioxins and furans /206/. Brominated dioxins and furans are also emitted from open burning of municipal waste /233/ and from accidental fires in houses, cars and other transport /224/. Large amounts of e-waste, cars, and other products containing BFRs are treated in melting furnaces for recovery of metals. These operations can include incomplete combustion processes resulting in the emission of halogenated dioxins and furans and HFRs /232,248/.

Brominated flame retardants can be destroyed with high efficiency in Best Available Techniques (BAT) incinerators operated according best environmental practice (BEP) /205,247,249/. For BAT incineration, however, the costs for incinerated material are about \$100/ton, hence such facilities are too costly for developing and transition countries /250/. Even in BAT grate incinerators, elevated brominated dioxin/furan levels were found in the bottom ashes /251/, most probably due to particle matter falling through the grate not subjected to a complete combustion. The

destruction of HFR materials in cement kilns and metal industry and associated releases needs further assessment.

### **5.3 Landfilling and Release of Halogenated Flame Retardants from Landfills**

A large portion of the products treated with HFRs ends up in landfills. This practice is common in developing, transition, and industrial countries that lack adequate thermal waste treatment options. For example, substantial amounts of flame-retarded waste are landfilled in California /252/ and in Australia, a country that has no waste incineration capacity. Brominated flame retardants leach from landfills to contaminate the environment /253-256/. Significant PBDE emissions in leachates have been detected from landfills in industrial countries /253,255,256/. In various regions of Canada, high concentrations of PBDEs were present in the soil adjacent to all landfills and dumpsites /253/. A mechanistic mass-balance model was developed to study the migration of PBDEs from waste streams to landfills and into the environment /257/. Recently, PBDE-contamination in ground-water has been reported at several South African landfill sites /254/.

With engineered landfills with bottom liners, leachates can be collected and treated to reduce the flow of contaminants to ground and surface water for some time /258/. Such treatments are expensive, however, and the resulting solids from the adsorption of pollutants need further treatment or deposition. Because of their persistence, PBDEs and other POPs will remain in landfills and leach into the environment for decades. Over these extended time frames, landfill engineering systems, including basal and capping liners, gas and leachate collection systems, will inevitably degrade and lose their ability to contain the contaminants /253,257,258/. Therefore, landfilling does not appear to be a sustainable solution for long-term containment of POP-containing waste.

All three above options for end-of-life treatments for HFR-containing materials result in environmental contamination and potential human exposure. The waste management of materials containing hazardous HFRs in current use must be globally addressed and significantly improved.

## **6. FLAMMABILITY STANDARDS AND THEIR IMPLEMENTATION**

Flame retardants are primarily used to meet flammability standards, commonly developed by standards bodies such as the International Electrotechnical Commission (IEC), International Organization for Standardization (ISO), Underwriters Laboratory (UL), International Codes Conference (ICC), American National Standards Institute (ANSI), and the American Society for Testing and Materials (ASTM). National, state, and local government agencies and bureaus such as the U.S. Consumer Product Safety Commission (CPSC), and the California Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation (the Bureau) may include compliance with one or more of these standards as part of the regulatory requirements for manufacturers.

Fires are complex and can vary enormously. A material's performance, as required to meet a flammability standard, will depend on the design of the standard, including the source of ignition and the duration and location of a flame or heat source. In some cases, the individual components of an article, such as the foam and the fabric are tested separately. Other 'composite tests' are performed on a whole manufactured article. A piece of furniture meeting a particular standard can behave in different ways under varied circumstances. For example, fires may strike different surfaces with different results. Standards that are designed to prevent a small open flame from igniting uncovered foam may not reflect the flammability of a complete upholstered chair /259/.

### **6.1 California Home Furniture Standards: Technical Bulletins 117 and 116**

California TB117, implemented in 1975, requires flexible polyurethane foam and other filling materials in furniture and juvenile products to withstand exposure to a small open flame for 12 seconds /260/. This standard is most economically and conveniently met by adding organohalogen flame retardant chemicals to the filling materials. Despite considerable research showing adverse health impacts from the halogenated chemicals commonly used to meet TB117 as described in Section 3, most national furniture manufacturers increasingly apply the standard for furniture sold across North America. For many juvenile products, such as nursing pillows, high chairs, strollers, and baby carriers, manufacturers make only one line of products and follow the California standard across the U.S. and Canada. Thus, TB117 is becoming a de facto national standard, with organohalogen flame retardants being found in many baby products containing polyurethane foam.

California Technical Bulletin 116 (TB116), the companion standard for fabric flammability, is a voluntary cigarette smolder test and rarely followed. In addition, TB117 requires that fabrics pass the Federal CS 191-53 flame-spread standard, a standard designed to remove the most dangerous flammable materials from the clothing market. According to some sources, this standard is so weak that tissue and newspaper can pass it /261/. As discussed in section 7.1, the lack of an effective fabric standard is one weakness of TB117.

### **6.2 California Technical Bulletin 133 (TB133) for Public Occupancies**

TB133 is a flammability standard for the composite testing of seating furniture for use in high risk public occupancies in California /262/. In most applications, TB133 compliance is not required in public buildings with active sprinkler

systems. In these buildings, compliance with TB117 is required. TB133 is a composite test, meaning that individual furniture components cannot be tested independently of other materials used in the furniture's construction. Compliance with this open-flame standard is typically achieved in one of two ways: (1) by inserting a fireproof barrier fabric or batting (such as fiberglass or "Kevlar" based materials) between foam and fabric; or (2) with a combination of fire-retarded upholstery fabric or inherently fire-retardant wool fabric and foam specifically designed for high risk use. The only domestically produced foam that fits this criterion is made with a high level of solid powered melamine (up to 45% by weight) along with organohalogen flame retardants /263/. Because the TB133 test burns full-size products and requires that all component variations be tested, the standard is not practical for residential furniture.

### 6.3 CPSC Staff Draft Furniture Standard

Smoldering ignition requirements for fabrics are also important as 90% or more of residential upholstered furniture fire deaths are caused by cigarette ignition /264/. In February 2008, the U.S. CPSC replaced a draft small open flame test standard for furniture foam (similar to California's TB117) with a draft 'smolder test' (or cigarette ignition resistance) standard for furniture fabric. This draft standard can be met with smolder-resistant cover fabrics or interior fire-resistant barriers rather than chemicals.

In a statement on the 2008 Notice of Proposed Rulemaking the CPSC, Commissioner Nancy Nord said the new standard would address furniture fires without requiring the use of fire-retardant chemicals /265/. This CPSC draft standard has been moving through the development process since 2008. If proposed and implemented, this standard, which regulates fabric flammability rather than foam flammability, could preempt California TB117 and greatly reduce the

use of flame retardants in furniture and baby products across North America.

### 6.4 CPSC Mattress Standard 16 CFR 1633

CPSC standard 16 CFR 1633 is a severe federal flammability standard for mattresses, implemented in 2007 /266/. The standard is commonly met with a barrier technology rather than the addition of flame retardants to foam. Typical barrier technologies include the use of ignition resistant fiber batting and/or the use of an ignition resistant fabric beneath the cover material.

During flammability testing, the vertical surface of the mattress is subjected to 50 seconds of intense flame exposure from large propane burners and the horizontal surface to 70 seconds. The standard requires that: (1) During the next 30 minutes, the peak rate of heat release for the mattress set must not exceed 200 kilowatts, and (2) the total heat release must not exceed 15 MJ during the first 10 minutes of the test. The barrier materials used by manufacturers to achieve compliance are primarily inherently combustion resistant polymeric fibers or boric acid-treated cotton. According to the polyurethane foam industry, flame retardant chemicals are not usually used in mattress foams in the U.S. Were barriers not used, achieving the level of flammability required by the standard would lead to very high levels of foam fire retardants, which could be expensive and could cause unacceptable characteristics in the mattress foam.

### 6.5 Standards for Electronics Enclosures

The current rigorous standards governing the safe internal functioning of electronic equipment prevent fires, electric shock, and other harm. Recently proposed 'candle' standards would have mandated that the outer housings of consumer electronic products be resistant to external ignition from a small open flame. Such requirements could

result in the addition of up to 30% by weight of organohalogen, antimony, or other flame retarding chemicals to the housings /267/.

For example, IEC-Standard 62368 *AudioVideo, Information and Communication Technology Equipment – Safety Requirements* developed by the International Electrotechnical Commission's (IEC) TC108 included such a candle flame requirement. The standard was voted down in 2008 by a majority of delegates from 31 countries, based on a lack of proven fire safety benefit, as well as health, environmental, and other concerns. Several other similar proposed candle flammability standards from the IEC, Underwriters Laboratory (UL) and the Canadian Standards Association (CSA) were also voted down in 2008. Nonetheless, a candle flame ignition requirement for television housings in the EU (CENELEC EN 60065) passed in 2009.

### **6.6 Building/Insulation Flammability Standards**

Polystyrene, polyisocyanurate, and polyurethane are insulation materials that increase energy efficiency and whose use in buildings, especially energy-efficient buildings, is growing rapidly. The ASTM International and the National Fire Protection Association (NFPA) set flammability standards for the ignition, burning, and combustion characteristics of insulation and other building materials. Chapter 26 of the Uniform Building Code 2603.3 (see test ASTM E 84 in section 1.5) states that foam plastic insulation shall have a flame-spread index of 75 or less and a smoke-developed index of 450 or less. These flammability standards are instrumental in the establishment of building codes, insurance requirements, and other fire regulations for building materials.

Flame retardant chemicals are added to insulation materials to meet such building codes. Polystyrene insulation in the U.S. is always treated with HBCD. Halogenated chemicals, such as 1-Bromopropane, Tris(1-chloro-2-propyl)

phosphate (TCPP), and other halogenated phosphate esters are often used with polyurethane and polyisocyanurate (polyiso) insulation. HBCD is a persistent organic pollutant, and the other organohalogens used with insulation have known toxic properties or lack adequate health data. The use of energy efficient insulation materials, such as polystyrene and polyurethane, treated with organohalogens, means that energy efficient 'green' buildings can contain toxic chemicals.

### **6.7 Motor Vehicle Standards**

The U.S. Federal Motor Vehicle Safety Standard (FMVSS 302), established in 1972, is an international flammability standard for the occupant compartments of motor vehicles. According to the National Highway Traffic Safety Administration, the purpose of the standard is to reduce deaths and injuries to motor vehicle occupants caused by vehicle fires, especially those from matches or cigarettes. Essentially the same test is embodied in ISO 3795, BS AU 169 [United Kingdom (U.K.)], ST 18-502 (France), DIN 75200 (Germany), JIS D 1201 (Japan), SAE J369 (automotive industry) and, dealing with plastics flammability, ASTM D 5132.

Studies of brominated flame-retardant levels of cars have indicated the presence of PBDEs, TBBPA, and HBCD in air and dust within the cabins and trunks in the U.K. /268/ and in Boston, Massachusetts in the U.S. /269/ where extraordinarily high levels of chlorinated tris or TDCP were also observed. Despite the use of halogenated flame retardants, motor vehicle flammability remains a serious problem /268/.

## **7. FIRE SAFETY BENEFITS OF HALOGENATED FLAME RETARDANTS IN CONSUMER PRODUCTS**

Flame retardants are used in a wide variety of products and assumed to provide a fire safety

benefit. As will be discussed below, this benefit has not been demonstrated for small open flame flammability standards for home furniture, baby products, and electronic enclosures, and some uses of building insulation.

**7.1 Home Furniture (Technical Bulletin 117)**

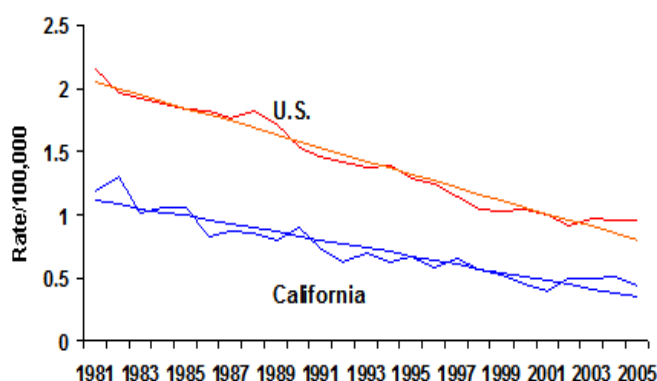
The California flammability standard TB117 has led to the use of pentaBDE and other organo-halogen flame retardants in consumer products for more than 30 years. Yet, whether this standard has been effective in preventing fires and fire deaths is not certain. An analysis of fire data from 1980 to 2005 by the NFPA shows that the rate of reduction of fire deaths in California is similar to that of seven other large population states that do not have a furniture flammability standard (Table 1). NFPA data comparing California with the entire U.S. does not show a greater reduction in the rate of fire deaths in California (Figure 3) between 1980 and 2005. According to the NFPA, U.S. fire data are not detailed or complete enough to show whether adding flame-retardant chemicals to furniture foam in California since 1980 has made a measurable difference in fire deaths in that state /270/. This report could be contrasted with an NFPA press release estimating that if fire safe cigarettes had been required 20 years earlier

**Table 1.** California’s decline in fire death rate from 1980-1984 to 2000-2004 was similar to that of the other seven largest states in the U.S., which do not have fire safety regulations for furniture /287/

State	% Reduction
California	40
Georgia	36
Illinois	45
Michigan	38
New York	48
Ohio	41
Pennsylvania	41
Texas	37

15,000 lives would have been saved /271/.

Laboratory research on TB117 supports this lack of measurable fire safety benefit. A study at the National Bureau of Standards in 1983 showed that following ignition, the important fire hazard indicators (peak heat release rate and the time to peak) were the same in TB117-compliant furniture where the foam was treated with chemical flame retardants and in non-treated furniture /272/. A small flame was able to ignite both regular furniture and furniture meeting the TB117 standard—once ignited, the fire hazard was essentially identical for both types /273/.



**Fig. 3:** Residential fire and flame death rates in the U.S. and California 1981-2005. Trend data and linear regression lines are shown /299/. Prepared by California Department of Public Health, EPIC Branch

A 1995 report from the Proceedings of the Polyurethane Foam Association provides further evidence that TB117 does not improve fire safety. Small open flame and cigarette ignition tests were performed separately on 15 fabrics covering TB117 type polyurethane foam, conventional polyurethane foam, and polyester fiber wrap between the fabric cover and the foam cores. The study found no improvement in ignition or flame spread from a small open flame or cigarette ignition propensity using TB117-compliant foam /274/.

Furthermore, CPSC research demonstrates that these types of small scale fire testing do not accurately predict large scale fire behavior. These researchers reported that *"The component tests in TB117 did not satisfactorily predict composite ignition behavior. Fabrics and fillings that comply with TB117 often ignited when tested as finished chairs. TB117 would not, if federally mandated, ensure a substantial reduction in the risk of small open flame ignition of finished articles of furniture"* /275/.

Ignition and fire-growth tests in the Babrauskas et al. /276/ study in 1988 provide the basis for a frequently quoted statement that flame retarded materials offer a 15-fold greater escape time for occupants during a fire. The Babrauskas study, however, did not examine any TB117 foam but rather only formulations of much higher percentage of added flame retardant chemicals than used to meet TB117. Furthermore, the room tests were fully-furnished rooms in which numerous combustibles were burned and not tests of upholstered furniture items alone. An earlier study by Babrauskas /273/ found the time-to-peak results for non-flame retarded and TB117 foams were identical, to within the data scatter of the apparatus.

Based on his research discussed above, Babrauskas /277/ concluded that TB117 is an ineffective test that does not accomplish its intended purpose of averting furniture ignitions from small flaming sources. The cumulative result

of research discussed above is that TB117 does not appear to increase fire safety. This outcome is not unexpected because in a fire, the fabric will ignite first, exposing the foam to a large flame. Because it is designed to resist small flames, TB117 does not prevent foam ignition from larger flames. A more effective flammability standard would address the flammability of the covering material and/or the structure of the upholstered furniture as opposed to considering only the impact of a small flame on the interior foam.

## 7.2 Standards for Electronic Enclosures

Proposals for flammability standards for plastic housings around television (TV) and other electronic equipment often cite papers by Simonson and colleagues /278-280/ showing a large fire-safety benefit from the use of flame retardant chemicals in TV enclosures. The Simonson model in these papers consists of a life-cycle study comparing TV sets with and without flame retardants. The model compares emissions from TV production, flame retardant production, and TV incineration, but does not include health or environmental effects of the chemical flame retardants themselves. For example, the model considers the chemicals emitted when a TV burns, but is limited to carbon dioxide, polycyclic aromatic hydrocarbons, dioxins, and furans. The model does not consider the effects of exposures that are due to the migration of flame retardants, such as decaBDE or HBCD, from the plastic TV enclosures into household dust, humans, animals, water, and the food chain /46,210/. In view of the recent significant increase in knowledge about the health and ecologic effects of flame retardants (Section 3), the Simonson model would benefit from considering other inputs across the life cycle of the products. These effects would include health effects from exposures occurring during manufacturing and use of the product, as well as toxicity to humans and the environment during and after disposal.

**Table 2.** Annual estimated TV fires per million TVs in the U.S. and Europe that breach the TV enclosure

Estimate	TV fires/million	Ignition Source	Reference
Europe - Simonson <sup>a</sup>	165	100 internal, 65 external	/274/
U.S. – Simonson <sup>b</sup>	13	internal, external	/275/
Europe - DTI <sup>c</sup>	18.2	12.2 internal, 6, external	/279/

<sup>a</sup> Based on 8 reported TV fires in a Stockholm suburb in 1994; <sup>b</sup> NFPA National 1990-1994 data based on fire department surveys and fire incident data from the U.S. Fire Administration; <sup>c</sup> UK Department of Trade and Industry (DTI) 1996 report based on fire brigade data and a review of fire statistics across Europe

As detailed in Table 2, the Simonson model also uses dissimilar data sources for comparing the annual fire rates in TV enclosures without flame retardants (Europe) and to those with flame retardants (U.S.). For Europe, the model input extrapolates from eight TV fire incidents during 1994 in one suburb of Stockholm, Sweden to an estimate of 165 TV fires per million TVs annually across all of Europe /278,279/. The 1994 in-depth review used a broad definition of a TV fire, which included very small fires. A detailed critique of extrapolating from such a small, unrepresentative sample to fire data for all of Europe has been previously published /281/.

Annual U.S. TV fire data as reported by the NFPA was based on fire-department surveys and fire- incident data from the U.S. Fire Administration from across the country /282/. The data were normalized to 13 TV fires per million TV sets, from both internal and external ignition /279/. The Simonson model then assumed that only a fraction of the U.S. TV fires reported by the NFPA were due to internal ignition and restricted further analysis to only the internal ignition fires (reducing the number of annual U.S. fires from 13 TV fires per million TVs to 5 TV fires per million TVs) /279,280/. In contrast, the model does not restrict European TV fires to internal ignition fires. The dissimilar data sources are based on different definitions and sizes of TV fires, potentially leading to an unrealistically high estimate for European television fires and a correspondingly low one for the U.S.

By comparison, a U.K. Department of Trade

and Industry (DTI) review of fire brigade data from across Europe found 12.2 European TV fires per million TVs by internal ignition plus 6 TV fires per million TVs by external ignition /283/. The Simonson estimate, based on data from one Stockholm suburb, gives results an order of magnitude higher than European fire brigade data, which are more representative and comparable to the U.S. data reported by the NFPA (Table 2).

The DTI review suggests a similar rate of TV fire incidents in Europe, where flame retardant chemicals have not been used, as that in the U.S., where TV enclosures contain decaBDE and other flame retardants.

The end-of-life emissions calculations in the Simonson model also used different inputs and methodologies for the U.S. and Europe. The model assumes that all disassembled TV enclosures will be incinerated, which overestimates the extent of incineration of European TVs. The non-treated plastics in European TVs can be reused repeatedly without degradation and account for 87% of recycled electronics plastics /243/. Plastic enclosures manufactured with flame retardants (U.S. TVs) are not recommended for recycling, as combining flame-retardant-containing recycled plastics with new product in manufacturing can result in dioxin and furan concentrations in the plastic enclosures above legal limits /242/. The model underestimates incineration emissions by assuming that 100% of incinerated plastic enclosures are used for energy recovery. In Europe and the U.S., only a small percentage of plastic waste (31% in Europe, 14% in the U.S.) is

incinerated with energy recovery /284/. Also not accounted for in the model are the emissions from uncontrolled incineration, such as landfill fires or open pit burning of plastic waste after disassembly. Such unregulated incineration of TVs treated with flame retardants emits toxic brominated dioxins and furans into the environment.

Conducting life-cycle analyses to evaluate the benefits and risks of adding flame retardants to plastic enclosures can provide useful information to policy makers. As described above, however, the Simonson analysis would benefit from incorporating public health and environmental impacts of commonly used flame retardant chemicals as well as using comparable data sources for the model inputs and end-of-life pollution related to disposal.

### 7.3 Building/Insulation Flammability Standards

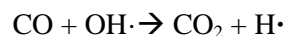
Insulation materials containing halogenated flame retardants can add to the toxicity of a building. The toxicity could be reduced by the use of such nonflammable materials as mineral or glass wool or by stopping the use of flame retardant chemicals in insulation materials in situations when no fire hazard exists. This includes insulation between building foundations and the soil, and between two outer wall layers of concrete. In these situations, despite the lack of fire danger, all polystyrene insulation is treated with HBCD. Having two well-labeled varieties of polystyrene, one that is flame retarded and one that is not, would reduce the use of HBCD for applications for which no fire hazard exists.

### 7.4 Effect of Halogenated Flame Retardants on Fire Effluent Toxicity

Most fire deaths and most fire injuries result from the inhalation of fire effluents, such as carbon monoxide, irritant gases, and soot /285/. Although the incorporation of halogenated flame retardants may reduce the ignitability and heat

release of a material, this practice can also increase the yield of such toxic fire effluents during combustion /286,287/.

Halogenated flame retardants act by replacing the most reactive hydrogen (H•) and hydroxyl (OH•) free radicals in a flame with more stable chlorine (Cl•) or bromine (Br•)-free radicals. The OH• radical, however, is required for the conversion of carbon monoxide to carbon dioxide.



In the presence of brominated or chlorinated flame retardants, this reaction is prevented, resulting in more carbon monoxide (CO) /288/. Thus, the same flame retardant action that reduces heat release is also responsible for much higher yields of CO. In addition, the flame-quenching action of Br• and Cl• radicals prevents the oxidation of other like hydrocarbons and aldehydes to carbon dioxide (CO<sub>2</sub>) and water, and significantly increases the smoke yield. Increased CO, incapacitating irritants, and smoke hinder an escape from the fire.

Fire effluents from the combustion of materials containing halogenated flame retardants will be more toxic for three reasons:

1. The effluents will contain more carbon monoxide.
2. The effluents will contain powerful irritant acid gases (hydrogen chloride or hydrogen bromide).
3. The effluents will contain a cocktail of respiratory irritants comprising unburned and partially burned hydrocarbons, resulting from stopping the burning process midway.

In addition, as discussed, combustion of organo-halogen compounds leads to the formation of brominated and chlorinated dioxins and furans.

When flame retardants are present, the reduced risk from increased time to ignition and reduced heat release rate during a fire should be balanced against the increased hazard from CO, irritant gases, and particulates like soot or smoke particles.



## 8. SAFER ALTERNATIVES TO CHEMICAL FLAME RETARDANTS

Reducing the sources of ignition can prevent fires without adding potentially hazardous chemicals to consumer products. A 60% decrease in fire deaths in the U.S. since 1980 parallels the decrease in per capita cigarette consumption /289,290/. An increased enforcement of improved building, fire, and electrical codes and increased use of smoke detectors and sprinkler systems in new construction have contributed to an increase in fire safety. An estimated 65% of reported home fire deaths in 2000-2004 resulted from fires in homes without working smoke alarms /291/.

### 8.1 Fire-Safe Cigarettes

The leading cause of fire fatalities in the U.S. is cigarette smoking. A large majority of residential fire deaths in which upholstered furniture was the first item ignited are caused by cigarette ignition /292/. Between 1980 and 2005, smoking-related fire deaths in the U.S. have declined from 2,000 to 800 annually /264/. The most recent data show a continued decline to 720 deaths in 2007 /292/. The reduction of smoking, through a combination of education, taxation, and location restriction policies has proven the single most effective fire safety strategy.

Smoking rates in the U.S. had declined to 21% by 2004. The recent passage in all 50 states of legislation requiring the manufacture and sale of reduced ignition propensity (RIP) or 'fire-safe' cigarettes /293/, should further reduce fire deaths. The ASTM E2187-09 test method for measuring the ignition propensity of cigarettes is referenced in laws of all 50 states. Many such laws are just beginning to be implemented. Fire-safe cigarettes contain internal 'speed bumps' of thicker paper that block the flow of oxygen to the rest of a lit cigarette that is no longer being smoked. If a cigarette is accidentally dropped on an ignitable

surface (for example, a couch or mattress), a fire-safe cigarette will normally extinguish itself in a few minutes when it reaches a speed bump of thicker paper, rather than smoldering for as long as 45 minutes and potentially starting a fire. Fire-safe cigarettes should reduce the potential benefit of flame retardants in furniture and other products.

### 8.2 Fire-Safe Candles

New voluntary safety standards for fire-safe candles have been adopted by the candle industries in the U.S. /294,295/. Research leading to these standards was initiated after U.S. candle consumption increased 350% from 1990 to 1998. Although candle-related fire injuries and deaths increased at much slower rates of 13% and 42%, respectively, improving candle fire safety became a joint objective of the candle industry and the CPSC.

The ASTM standards were developed to address candle fire safety issues based on research on the root causes of candle fires. The Society developed candle manufacturing standards for labeling about candle hazards, glass container material requirements to eliminate shattering due to candle heat, and improved candle design to minimize the four major causes of candle fires (excessive flame height, secondary ignition, end of useful life, and stability). Complying with these standards requires a manufacturer to produce candles (a) with warning labels, (b) with a maximum wick length, (c) without combustible decorative materials, (d) that will self-extinguish without incident when they have burned down, and (e) that will be proportioned not to tip over easily.

Ninety percent of U.S. candle manufacturers have pledged to comply with these standards. The ASTM is working with importers to ensure that these safety specifications are also met by imported candles. As a result, the ASTM estimates that the majority of all candles sold in the U.S. are in compliance with these fire safety standards. In

Europe, a committee for standardization (CEN) task force for candles in Europe is similarly defining standards and working with European candle producers to improve safety. The implementation of these standards should reduce candle fire injuries and deaths.

### 8.3 Alternate Designs and Materials

Design alternatives, such as making components of metal, glass, or ceramics instead of plastics, can reduce flammability without chemicals /36/. Fire-retardant barriers, usually made of polymeric materials like those used in mattresses, could be investigated for use around foam in furniture and juvenile products. Avoiding low density polyurethane foam, which is relatively flammable, will reduce the fire hazard from a small open flame. High-density foam and other filling materials such as polyester (which melts rather than flames) can sometimes meet TB117 without the addition of chemicals.

A discussion of the use of flame retardant chemicals in TV enclosures provides an example in which changes in technology have reduced flammability and the need for flame retardants. Such chemicals were first added to TV enclosures in the mid-1970s to meet UL 1410, which protected against internally-initiated fires /296/. The likelihood of such fires was far greater at that time with the very high voltages required by early cathode ray tube technology. Today's technology eliminates this hazard. High voltages are now contained in the ballast of fluorescent lamps that backlight the LCD display /297/ or within the individual cells of a plasma display /298/. The voltages are so low that arcing is not a potential hazard.

This new technology also eliminates such hazards as internal heat sources like the tube filaments, rectification and plate voltages that could reach as high as several hundred volts, and related high currents that were required in the

printed circuit boards to deliver (particularly) filament power. The benefits and costs of UL1410 could be revisited by evaluating the fire hazard from current TV technology, as well as the impact of the chemicals and materials used to meet this standard.

### 8.4 Safer Replacement Chemical Flame Retardants

Green chemistry—the design and use of safer materials and processes with minimal adverse impact on human health and the environment—should be used to design a new generation of alternative flame retardant chemicals that are not based on bromine or chlorine. Currently, several halogen-free compounds have been shown to be effective flame retardants, and almost all production polymers (such as nylon, polypropylene, polyester, or polyurethane) have halogen-free formulations that will meet current fire safety standards. The alternatives include mineral fillers, which absorb heat and give off water, such as aluminum trihydrate (ATH); low melting glasses and ceramics, which seal the surface from the flame; char promoters that protect the surfaces by the formation of a carbonaceous layer; and intumescent coatings, which swell to form a barrier some distance from the polymer surface.

Reactive flame retardants that are bonded to the substrate are safer substitutes than additive chemicals that are not bonded and can migrate out into the environment. Tetrabromobisphenol A, the most commonly used flame retardant, is found bonded to the substrate inside electronics to protect against internal fires. The use of reactive TBBPA inside electronics should present a lower health and environmental hazard than TBBPA used as an additive flame retardant in the plastic housing of electronics. Still, brominated dioxins and furans are produced upon combustion of electronics containing TBPPA. A life cycle approach should be used in evaluating replacement chemicals.

## 9. DISCUSSION: POLICY IMPLICATIONS AND SUGGESTIONS

Since the introduction of halogenated flame retardants in the 1970s, many hundreds of peer-reviewed scientific papers have documented the environmental persistence and toxicity of these compounds in animals and humans. After decades of high-volume use, pounds of halogenated flame retardants can be found in consumer products inside a typical home, school, or office. These semi-volatile chemicals leach out of products into dust, which is a major exposure route for humans and animals /48/.

All 21 chemicals banned by the Stockholm Convention are organohalogenes, and several are halogenated flame retardants or their degradation products. In the U.S., human levels of the banned flame retardant pentaBDE are approaching those that are known to cause harm in animals /85/. Of great concern is the increasing number of studies finding adverse health impacts associated with exposure, such as reduced IQ scores in children and increased time to conception in humans. Of further concern is the lack of necessary health information on PBDE replacements to determine if they are an improvement.

The fire safety benefit of using halogenated chemicals has not been well documented. Currently, fire deaths are decreasing. One could argue that the use of halogenated flame retardants in consumer products is contributing to this decrease; yet, no data exist to demonstrate a fire safety benefit from incorporating these chemicals. For example, according to NFPA data, states without a furniture flammability requirement show a similar decrease in fire deaths as that of California, which uniquely follows TB117 /291/. More likely is that the decrease in smoking, the increased use of smoke detectors and sprinklers, improved electrical product safety standards, a decrease in open fires and other lifestyle changes have been the major contributors to reduced fire deaths across the U.S.

When flammability regulations for consumer products were originally introduced in the 1970s, the health and environmental impacts of the chemicals being used to meet them were not well-known or considered. Nevertheless, the use of these chemicals increased 50% between 2005 and 2008 /3/, despite a growing knowledge of the adverse impacts of halogenated flame retardants on health and the environment. Alternative methods for achieving fire safety without the use of organohalogen flame retardants are available for most applications and should be considered when drafting new flammability standards.

### 9.1 Reevaluating California TB117 to Maintain Fire Safety while Reducing the Use of Halogenated Flame Retardants

After 35 years, California TB117 has not been proven to have increased fire safety. As previously discussed, however, pentaBDE and other flame retardants used to meet the standard are toxic and/or global pollutants. Thus, TB117 should be revised to consider the health and environmental impacts of the chemicals used to meet it. Furniture design, smolder resistant fabric, denser foam, and fire resistant barriers around the foam can all contribute to increasing fire safety with reduced toxicity. A revised TB117 could be modeled after the CPSC staff draft furniture standard for fabric, which maintains fire safety without the use of flame retardants in polyurethane foam /265/.

### 9.2 Reconsideration of Small Open-Flame Requirements for TV Sets in the EU and the U.S.

A new EU standard for small open-flame requirements for TVs enclosures (CENELEC EN 60065) and the current U.S. standard (UL60065) are met with flame retardant chemicals at levels up to 30% by weight. These standards should be evaluated for their fire safety benefit as well as

their effects on health, environment, and recycling.

Currently, in the U.S., TV sets are required to have fire-retardant enclosures due to internally initiated ignition threats rather than externally initiated ignition threats. After the earlier transition from vacuum tube to solid state technology occurred, cathode ray tube TVs are becoming nearly extinct and are being replaced by LCD panel and plasma display-based technology. The new technology has resulted in reduced and contained high voltage, lower power, and shallower products. New TV sets cannot function as shelves, nor can materials such as candles easily be placed to lean against them. The set can also be wall-mounted, further reducing an already low potential for candle ignition. Television manufacturers could further redesign their products to eliminate the use of fire retardants in the enclosures without compromising fire safety.

### **9.3 Production of Two Kinds of Polystyrene, With and Without Added HBCD**

One option for reducing the use of HBCD-treated polystyrene would be to remove the flame retardant for applications in which it is not needed. Currently, all polystyrene sold as building insulation carries at least a Class B designation for flame-spread and smoke development. This classification is required for above-grade applications, and many believe that the Class B category is a universal requirement. The International Residential Code and the International Building Code, however, appear to exempt foam insulation that will be separated from the building interior by at least one inch (25 mm) of masonry or concrete /299/. In below-grade, exterior applications, foam insulation may also be exempt from flammability standards. Manufacturers could offer non-treated polystyrene insulation for such below-grade installations. Polystyrene without flame retardants should cost less, but would require labeling and

care, so that the two sorts of polystyrene could be used appropriately. If building codes do not currently allow this exception, a reduced use of HBCD should be proposed. New, safer flame retardants should be developed for use with polystyrene as well as less flammable alternatives to plastic insulation materials.

### **9.4 Life Cycle Analysis before Using Flame Retardants**

Given the documented adverse health effects of halogenated flame retardants in consumer products, the authors believe that independent researchers at institutions such as the NAS, NIST, CPSC and/or universities should perform in-depth analyses of the fire safety benefits from the use of flame retardants, as well as the health and environmental costs. A life-cycle approach should be used, with emphasis on end-of-life issues, including the health and safety of workers, those living near chemical production facilities, and the general population, as well as ecological effects.

For example, new small open-flame and candle-ignition standards for electronic housings continue to be proposed despite an undocumented fire safety benefit. If implemented, such standards could result in the addition of large volumes of flame retarding chemicals to the plastic enclosures of electronics worldwide each year, thereby making recycling more difficult and expensive. A detailed life-cycle analysis of the impact of such candle standards should be conducted with significant input from the health and environmental effects communities, as well as the fire and combustion communities. This life-cycle analysis could determine the overall impact of the proposed standard to the entire envelope of materials and systems. In addition, such an analysis could foster communications among the health, environment, and fire safety communities and could serve as a platform for additional input from labor unions, occupational health organizations, water quality, and other environmental and community bodies.

### 9.5 Reducing Exposure, Legacy Problems, and Product End-of-Life for Flame Retardants

PentaBDE and octaBDE have not been produced in the U.S. since 2004, yet millions of pounds of these and other toxic or untested flame retardants mixed with foam and plastic are in consumer products. These flame retardants are semi-volatile and escape from products into dust. Hand washing, vacuuming with a HEPA filter, and wet mopping should reduce individual exposure to dust and the flame retardants it contains. Further research is needed on pathways of exposure and the effectiveness of dust reduction strategies.

The three current main end-of-life options for halogenated flame retardants mixed with foam or plastic are all problematic because: (a) combustion can create dioxins and furans; (b) the chemicals can leach from landfills into the environment and end up in the food supply; and (c) recycling can contaminate the non-flame retarded plastic stream with the chemicals and their combustion products. PBDE-containing products will remain a reservoir for releases for many years to come. According to the furniture industry, the average lifetime for foam-containing household furniture is 30 years, suggesting that only a fraction of the total PBDEs used in furniture has reached the outdoor environment. The indoor reservoir of PBDEs has been termed an environmental “time bomb” /300/. One prediction is that the main exposure route for humans will eventually shift from the indoor environment to the food supply /300/.

As pentaBDE-treated furniture continues to be replaced and the older, used furniture is purchased by low-income households, PBDE exposure could become an environmental justice issue. Already one study found that girls of color had higher PBDE levels than Caucasian girls /301/. Research is urgently needed to determine responsible methods of identifying and disposing of products containing PBDEs and other halogenated flame retardants.

### 9.6 Chemical Regulation

Several flame retardant chemicals have been produced and used with high levels of human exposure before evaluations of their health and environmental impact have been conducted. As the literature has grown on the adverse impact of such chemicals, a more systematic approach to their testing and regulation is needed. Such a policy is being initiated in Europe through the Registration, Evaluation, and Authorization of Chemicals initiative, or REACH. Current U.S. Congressional efforts, supported by a wide variety of non-government organizations (NGOs), users of chemicals, and other stakeholders to revise the Toxic Substance and Control Act (TSCA) should contribute to a sound and comprehensive U.S. chemicals policy. This policy could include provisions such as the following:

- Health and environmental data required before the use of chemicals;
- Disclosure and labeling of which chemicals are in products;
- Questioning replacement chemicals that are nearly identical to regulated toxics;
- Life-cycle analyses, including the impact on workers and the environment of chemical production, as well as end-of-life leaching and combustion products;
- Persistent, bioaccumulative, and/or toxic chemicals with high potential for human exposure, such as flame retardants in consumer products, should be prioritized for evaluation and regulation.

## 10. CONCLUSIONS

In the U.S., neither federal nor state environmental protection agencies have sufficient authority to require that manufacturers ensure that their flame retardant chemicals are safe for human health. Thus, in consumer products a series of brominated and chlorinated flame retardant

chemicals continue to be used without thorough consideration of their possible adverse effects. PBBs, PCBs, brominated tris, Halon, asbestos, and PBDEs are flame retardant materials that only after extensive use were found to have serious long-term negative effects on human health and/or the environment. Moreover, many of the current replacement chemicals are proprietary mixtures, protected by confidential business information regulations, whereas others lack adequate toxicity information, making difficult the accurate assessment of their potential hazards. Producers should be required to provide health and toxicity data about flame retardants and replacement chemicals before such materials are marketed.

Although pentaBDE is no longer being manufactured, a substantial fraction of the pentaBDE commercial mixtures ever produced is still present in furniture, carpet padding, automobiles, and seating in mass transportation. The identification and responsible disposal of pentaBDE-treated products is essential to prevent its future dispersal into the environment and the food supply. Already, PBDEs are widespread contaminants in remote areas, such as the polar regions and the deep oceans, and are considered an environmental 'time bomb' because the compounds continue to migrate from indoor reservoirs into the environment /9,300/. Furniture, electronics, and other products containing PBDEs must be identified and disposed of responsibly. The recent listing of pentaBDE and octaBDE as POPs under the Stockholm Convention should help with the tracking and phasing out of these chemicals from the global recycling flow /302/. Doing so will prevent the further PBDE contamination of food webs and human tissues worldwide.

Firemaster 550<sup>®</sup> and TDCPP, two commonly used pentaBDE replacements produced to meet California standard TB117, appear to share some of the persistence and toxic qualities of pentaBDE. Policy makers should consider the potential impact of contamination by pentaBDE and its replacements as they consider new

flammability standards, as well as possible modifications to current standards. The uncontrolled burning of products containing organohalogens should not be allowed because byproducts such as brominated and chlorinated dioxins and furans are often more toxic and persistent than the parent compounds. Landfills with major containment analogous to those required for radioactive waste constitute one possible solution. Complete destruction in waste-to-energy facilities, without the formation of significant quantities of brominated dioxins or furans, is another possible scenario. More research is urgently needed to develop and refine sustainable end-of-life solutions.

This paper raises questions about the validity of certain flammability tests that purport to show a benefit from flame retardants in preventing ignition or slowing fire growth. An additional study, such as a definitive review of the previous research, possibly accompanied by modeling, is needed. The authors question the use of halogenated flame retardants that lack a demonstrated fire safety benefit and that have a high potential for adverse effects on health and the environment.

For the future, flammability standards for manufactured household and commercial products could be designed to be met without added chemicals. Flame retardant chemicals can pose a potentially greater hazard than the risk from the fires they are supposed to prevent. Reducing the use of toxic and untested halogenated flame retardants will protect human and animal health and the global environment. Decision-makers should use peer-reviewed science to evaluate the fire safety benefits as well as the health and environmental risks before promulgating new requirements leading to the use of flame retardant chemicals.

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