



Flame Retardants

A Report to the Legislature

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Flame Retardants

A Report to the Legislature

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Executive Summary

In 2014, the Washington State Legislature directed the Department of Ecology (Ecology) to review information on flame retardants, test products, and develop recommendations for bans or restrictions on the use of flame retardants in children's products and furniture. The Legislature requested specific information on tetrabromobisphenol A (TBBPA) and antimony, as well as other flame retardants detected in children's products and furniture. This report was prepared in response to this directive.

Ecology's Approach

Ecology's investigation first looked at general information on tetrabromobisphenol A (TBBPA) and antimony, with additional focus on their use in children's products and furniture. Second, the investigation looked at test results for the presence of a broader suite of flame retardants (including TBBPA and antimony) in children's products, household products, and furniture. This broader suite included flame retardants that are on the Children's Safe Product Act's chemicals of high concern to children reporting list, and others that have been commonly reported in children's products and furniture. Staff also considered the use of flame retardants in electronics because that is where most TBBPA is used and is a potential source of exposure for children.

As prescribed in the legislative directive, this report summarizes available information on flame retardants and contains the following chapters or sections:

- Classes
- Uses and product testing
- Product testing
- Hazards, health effects and exposures
- Environmental concerns

- Safer alternatives
- Existing regulatory programs
- End of life/disposal
- Key findings and recommendations

Ecology's approach included reviewing available scientific literature on flame retardants as well as conducting its own tests on a variety of products. Staff also analyzed information reported to Ecology under the Children's Safe Products Act (CSPA).

When considering potential health concerns, Ecology evaluated scientific literature that assessed the chemicals' toxicity (for example, if they were carcinogens, mutagens, irritants, or reproductive, developmental, or aquatic toxicants). Biomonitoring studies were evaluated to identify flame retardants already in people. The potential for people and the environment to be exposed to these chemicals was evaluated through review of studies on the presence of flame retardants in indoor dust, wastewater, fish and sediment.

Ecology staff also tested a variety of products for the presence of flame retardants. Types of products tested include:

- Baby carriers
- Tents
- Booster seats
- Changing pads/mats
- Furniture

- Children's furniture
- Carpet pads
- Small electronics
- Building products
- Clothing

Ecology staff also reviewed available alternatives assessments for flame retardants used in children's products, furniture, and electronics. An alternatives assessment is a process to improve decisions on replacements to toxic chemicals used in manufacturing processes and products. These assessments help avoid making "regrettable substitutions." A regrettable substitution occurs when a toxic chemical is replaced with another chemical of equal or greater toxicity.

Where there is strong evidence for concern about specific flame retardant chemicals and safer alternatives are available, Ecology's recommendations focus on eliminating use of those chemicals in order to reduce exposure, particularly for children. Where the evidence is less well established, Ecology recommends further study.

Background

Flame retardants are used in a wide variety of products including foam, plastics, and textiles. Many are high-production volume chemicals with more than one million pounds produced a year. Flame retardants are added to products to slow the spread of a fire and provide additional escape time. Over time, concerns have increased about the potential negative effects of many flame retardants on human health and the environment. Different flame retardants have different physical and chemical properties, which influence their effectiveness in specific applications.

One of the major classes of flame retardants is halogenated chemicals, which incorporates chlorine or bromine as a building block. TBBPA is an example of a halogenated chemical. This family of flame retardants also includes polybrominated diphenyl ethers, or PBDEs, which Washington banned beginning in 2008. Since the ban, studies have shown that alternatives, including other halogenated flame retardants, have replaced PBDEs. While the use of these replacement flame retardants in children's products and furniture is the subject of concern in this report, Ecology makes additional findings and recommendations on other uses of these chemicals.

There is a limit to what can be learned from product testing. Only *additive* flame retardants – those loosely bound to other ingredients in a product – can be identified. *Reactive* flame retardants cannot be extracted and analyzed since they are chemically bound to the base material. For example, TBBPA is used in both forms- it is added to plastics used in electronic enclosures, but in printed circuit boards, it is used in the reactive form. When testing results show the presence of TBBPA in a product, those results are just measuring the amount of unbound TBBPA. Another

difficulty is the availability of known standards for laboratory analysis. If a standard is not available, the laboratory will be unable to confirm the presence and amount of the flame retardant of interest.

It is also important to note that there is little available toxicity or use information for many flame retardants. While federal and state laws often target specific flame retardants in certain products, the safety of the alternatives is often not adequately assessed. Recent regulatory changes in California reduced the requirement for flame retardants in furniture and other foam products.

Flame Retardants in Certain Children's Products and Furniture

Use

- Many different flame retardants have been identified in a variety of children's products, including: car seats, changing table pads, sleep positioners, portable mattresses, nursing pillows, baby carriers, high chairs, and infant bath mats and slings.
- Halogenated flame retardants (those that contain bromine or chlorine) are often used in furniture in both flexible polyurethane foam and textiles.
- TBBPA and HBCD, both halogenated flame retardants, are occasionally used in fabric applications.

Testing

- Ecology tested children's products and furniture, including products such as baby changing mats, crib wedges, upholstered furniture, and carpet pad.
- Ecology's testing found a variety of flame retardants in children's products and furniture, including six halogenated flame retardants (TDCPP, TCEP, TCPP, V6, TBB, TBPH) and two phosphate-based chemicals (IPTPP and TPP). TBB, TBPH, IPTPP and TPP are used together as mixtures for commercial formulations. The remaining four flame retardants are used alone.
- TBBPA and HBCD were not detected in children's products and furniture at levels consistent with use as a flame retardant in products tested by Ecology.

Hazards and Health Effects

• The health effects of flame retardant chemicals include carcinogenicity, endocrine and reproductive effects, and neurological and developmental disorders.

- TBBPA may have moderate carcinogenicity and under certain conditions, can break down into bisphenol A, a chemical that is banned in Washington in baby bottles, sippy cups and sports bottles.
- HBCD can harm the liver and thyroid, and has reproductive and development toxicity.

Exposure

- Most of the flame retardants used in polyurethane foam and fabric have been found in indoor dust and many were found in people through biomonitoring.
- These flame retardants are additive, meaning they are not chemically bonded to the polymers or chemical materials used in the product (e.g. fabrics, plastic enclosures for TVs, computers, and other electronics). Additive flame retardants can migrate out of consumer products and collect in dust particles in the indoor environment.

Environmental Concerns

- In Washington, PBDE flame retardants have been found in many environmental media and appear to be ubiquitous in aquatic systems, but less information is available on flame retardants used in place of PBDEs.
- When textiles with indoor dust on them are washed, traces of these flame retardants are delivered to wastewater treatment plants. This is one of the major pathways for the release of flame retardants into the environment.
- Flame retardants have been found in air, water, soil, sediments, biota and wastewater treatment effluent. TDCPP, TCEP, TCPP, HBCD and TPP have all been found in Washington. TBB and TBPH were found in environmental studies conducted in other areas.

Safer Alternatives

- Ecology and the Washington Department of Health completed an alternatives assessment for upholstered furniture and found that chemical flame retardants are not necessary in these products. There are barrier fabrics or inherently flame-resistant materials that meet fire safety standards for furniture.
- The U.S. Environmental Protection Agency's (EPA's) Design for the Environment (DfE) program identified safer alternatives for chemical flame retardants used in flexible polyurethane foam. These include ammonium polyphosphate, polyphosphate, and magnesium hydroxide.
- There is evidence that other halogenated flame retardants now being used are examples of regrettable substitutes for PBDEs, which were banned or significantly restricted in the 2000s. One study found that TBB and TBPH concentrations in dust collected from California homes between 2006 and 2011 increased, consistent with their use as replacements for PBDEs.

Regulatory Programs

- California fire safety regulations for furniture have been a strong driver in the use of flame retardants in children's products and furniture. These regulations were revised in 2014, and chemical flame retardants are no longer needed to meet this standard in children's products and furniture.
- No flame retardants are required for children's products such as baby changing pads.

Conclusions

- Sufficient evidence exists to support enacting restrictions on the use of ten flame retardants in children's products and furniture that contain polyurethane foam and fabric. Each of these chemicals is toxic and there is potential for exposure. In many cases, exposures can already be documented in people and the environment. Many have been found in children's products and in furniture as well as in house dust. Many are produced in high volumes. Chemical flame retardants are not needed at all for children's products and most furniture applications. Safer alternatives are available.
- TBBPA is of most concern when used in the additive form rather than the reactive form. When used as an additive, TBBPA is much more likely to migrate out of the product and into people or the environment. Additive TBBPA is the form that could be used in textiles as part of children's products and furniture. Reactive TBBPA is of less concern because most of the TBBPA in these products is bound to the plastic and for the most part, is used in printed circuit boards, rather than in children's products or furniture.

Recommendations

1. Establish a limit of 1,000 parts per million (ppm) for each of the following flame retardants that are commonly used in children's products and furniture. This limit restricts use of these chemicals, but is sufficiently high enough to support continued recycling of products that contain them.

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a. TDCPP (CAS #13674-87-8) d. TCPP (CAS #13674-84-5) g. TBPH (CAS #26040-51-7) b. TPP (CAS #115-86-6) e. V6 (CAS #385051-10-4) h. IPTPP (CAS #68937-41-7) c. TCEP (CAS #115-96-8) f. TBB (CAS #183658-27-7)
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2. Establish a limit of 1,000 ppm for each of the following flame retardants that could be used in textiles in children's products and furniture. While these two chemicals are not commonly used in children's products and furniture, they could be introduced as regrettable substitutions. Restrictions on the use of TBBPA in children's products and furniture should be limited to the additive form.

- a. TBBPA (CAS # 79-94-7)
- b. HBCD (CAS # 25637-99-4 and CAS #3194-55-6)

Tetrabromobisphenol A (TBBPA)

Use

- TBBPA is a high production volume chemical (i.e. more than one million pounds of the chemical is produced every year in the U.S.).
- TBBPA is primarily used in plastics and is most often found in electronic products. The chemical is used in both reactive and additive forms. Each form presents different concerns.
- Eighty to ninety percent of all TBBPA is used in the reactive form as a polymer, where it is chemically bound to the plastic in products such as epoxy resins used in printed circuit boards. The remainder (ten to twenty percent) is additive.
- Under CSPA, TBBPA use as a flame retardant was reported in toy cars and in textiles in several baby products such as play pens and swings at levels indicating it is in the additive form.
- TBBPA use was also reported under CSPA at high levels for functions other than flame retardant, such as coloration, pigment, dyes, or inks.

Testing

- Ecology testing did not find TBBPA in children's products or furniture, but did find it in several electronic products, such as paper shredders and battery chargers.
- Studies in Europe and Australia identified TBBPA in electronics and a limited number of children's toys.
- TBBPA has been found at high levels in products made from recycled plastic such as Mardi Gras beads. It has also been found in camping tents and car seats.
- Test methods are not available for flame retardants used in the reactive form. Therefore, anytime TBBPA is found in a product it is either used as an additive, is present as a contaminant from the manufacturing process, or is from recycled content.

Hazards and Health Effects

- Studies documenting human health effects for TBBPA are not consistent. Some studies show
 potential endocrine effects and moderate carcinogenicity and others indicate no human health
 concern.
- Under certain conditions, TBBPA can break down into bisphenol A.

- When burned, TBBPA (both reactive and additive) can create toxic smoke containing chemicals such as dioxins.
- TBBPA is included on Washington's persistent, bioaccumulative, and toxic (PBT) list and on the list of chemicals of high concern for children under the CSPA.

Exposure

- In general, people are exposed to flame retardants through ingestion of contaminated food and dust
- Additive flame retardants are more easily released into house dust compared to reactive flame retardants.
- TBBPA is found in people at lower levels than other halogenated flame retardants. One study measured TBBPA at low levels in human breast milk.

Environmental Concerns

- TBBPA has both acute and chronic aquatic toxicity for a variety of fish species.
- Ecology tested for TBBPA but did not find it in fish tissue in Washington.
- TBBPA may have a lower bioaccumulation potential than some other halogenated flame retardants.

Safer Alternatives

- EPA has found safer alternatives for the use of the reactive form of TBBPA in circuit boards.
- EPA and the Department of Ecology both identified safer alternatives for the use of the additive form of TBBPA in furniture and in plastic enclosures for TVs, computers and other electronics.

Regulatory Programs

- TBBPA appears on several states' "chemicals of concern" lists such as California's Safer Consumer Products list, and Oregon's Toxics Focus List. There are currently no bans or restrictions on the use of TBBPA in consumer products.
- In the European Union, there are no ongoing processes under REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) for TBBPA.
- TBBPA is a chemical of high concern for children under the CSPA and manufacturers of children's products containing TBBPA must report their use to Ecology.

Conclusions

- Sufficient evidence does not exist at this time to support enacting restrictions in Washington on the use of the reactive form of TBBPA in children's products, furniture, or electronics. This form of TBBPA does not easily migrate out of the product and into people and the environment. The health impacts are less than for other halogenated flame retardants and it is not widespread in the environment. There are safer alternatives for some uses, but more information is needed to determine if restrictions would reduce exposures.
- Additional information is needed on the use of TBBPA used as an additive.

Recommendations

- 1. Require that manufacturers report to Ecology on their use of additive TBBPA in consumer products sold in Washington at levels exceeding 1,000 ppm. This requirement would not apply to manufacturers of children's products who already report their use of TBBPA under the CSPA.
- 2. Manufacturers should be encouraged to use identified safer alternatives to TBBPA.
- 3. Ecology should work with stakeholders to gather more information about the use of both reactive and additive TBBPA in electronics as well as other products where TBBPA is used.

Antimony as Antimony Trioxide (ATO)

Use

- The largest use of ATO is as a synergist with halogenated flame retardants to increase their
 overall effectiveness. A synergist is a chemical that combines with another chemical to act
 more efficiently than either chemical would individually. ATO does not have flame retardant
 properties.
- Other minor uses are as a plastic catalyst and as a pigment.
- ATO is mainly used in plastics, but can also be found in rubber, textiles, and adhesives. It is typically used in electrical equipment, wires, automotive parts, building materials and household products including furniture, carpets, mattress covers, and textiles.
- Use of antimony and antimony compounds has been reported to Ecology (through CSPA) in a few products at levels that indicate its use as a flame retardant synergist. Examples include battery-powered toy cars, play structures, bath toys, and baby changing mats.
- Most of the CSPA reports on antimony occur at low levels for functions other than as a flame retardant. These functions include catalyst, coloration agent, and plasticizer.

Testing

- Ecology's product testing work found antimony in electronics, small appliances, and a flameresistant tarp. Antimony was detected in these products at sufficient concentrations to suggest that some products contain antimony trioxide.
- Antimony was not found in foam or textiles, only plastic.
- Antimony results were most commonly found in products where bromine was also present, consistent with its use as a synergist with halogenated flame retardants.

Hazards and Health Effects

- Breathing high levels of antimony trioxide irritates the eyes and lungs, and leads to heart, lung, and digestive system effects.
- The International Agency for Research on Cancer has classified antimony trioxide as a possible human carcinogen and California has identified it as known to cause cancer.

Exposure

- According to the Centers for Disease Control and Prevention (CDC), people are exposed to antimony primarily through food and to a lesser extent from air and drinking water.
- Ecology did not find studies on the presence of antimony in indoor dust.
- High levels of antimony have also been found in dust from electronic waste recycling facilities.

Environmental Concerns

• EPA identifies antimony trioxide as having high acute aquatic toxicity.

Safer Alternatives

Ecology did not find any alternatives assessments for ATO when used as a synergist.

Regulatory Programs

- Antimony trioxide is included on California's Proposition 65 list as a carcinogen.
- The U.S. Consumer Product Safety Commission (CPSC) limits antimony in surface coatings for toys.
- The Occupational Safety and Health Administration established limits for antimony for occupational inhalation exposure.
- EPA has set limits for antimony in drinking water.
- Antimony and antimony compounds are chemicals of high concern for children under the Children's Safe Products Act. Manufacturers of children's products containing these compounds must report that use to Ecology.

Conclusions

Sufficient evidence does not exist at this time to support enacting restrictions in Washington
on using ATO in children's products or furniture. While ATO is quite toxic, there are
significant data gaps regarding exposure and safer alternatives have not been identified.
Additional information is needed on the use of ATO and the potential for people and the
environment to be exposed.

Recommendations

1. Require manufacturers to disclose their use of ATO in products (other than children's products where such reporting is already required).

Other Key Findings for Halogenated Flame Retardants

Other major uses of halogenated flame retardants include electronic products, building insulation, airplanes, autos and other vehicles, and gymnastic equipment. Large amounts of flame retardants (i.e. more than 1% by weight) are needed in many products to be effective. Flame retardants present in products at less than 0.1% (or 1,000 ppm) are likely due to contamination and not due to intentional use.

Ecology was able to identify some flame retardants in several small electronics such as battery chargers and power strips, but not all flame retardants could be identified. Bromine, an indicator for the presence of brominated flame retardants, was detected, but test results did not indicate the presence of known brominated flame retardants.

All halogenated flame retardants evaluated to date exhibit toxicity. Types of toxicity associated with known halogenated flame retardants include endocrine and reproductive effects, carcinogenicity, and neurological and developmental disorders. Toxicity evaluations are not available for all of the flame retardants currently in use. Many halogenated flame retardants are found in human urine, blood, and breast milk. Tests in children find higher levels of flame retardants compared to adults. Because children are still developing, they are more sensitive to adverse health effects from flame retardant exposure.

Indoor dust is a primary pathway for flame retardants to affect humans and the environment. Flame retardant chemicals have been found throughout the world. Some are ubiquitous in indoor and outdoor environments, having been found in homes, childcare centers, sediments, and wildlife.

Insufficient information is available on alternative flame retardants in the environment, primarily because few studies include analysis of a wide range of flame retardants. Based on limited sampling, a variety of toxic flame retardants including organophosphates, Dechlorane Plus,

HBCD, and chlorinated paraffins have been consistently detected in environmental samples collected in Washington.

Flame retardants can be released into the environment at the end of the product's life through chemical breakdown and/or burning of products. When incinerated, products containing halogenated flame retardants can release other highly toxic chemicals such as dioxins and furans. Flame retardants can also be passed on to new products through recycling.

Conclusion

Further study is needed to evaluate the potential impact of halogenated flame retardants on human health and the environment and to assess the availability of safer alternatives.

Recommendations

- 1. Ecology recommends that the Legislature direct Ecology to conduct a comprehensive chemical action plan on flame retardants used in electronics and other products known to contain halogenated flame retardants other than children's products and furniture. As a needed first step, the Legislature should require that manufacturers report to Ecology on their use of flame retardant chemicals in products sold in Washington (other than children's products and furniture) at levels that exceed 1,000 ppm.
- 2. Enact policies that provide incentives to use alternative assessments and safer alternatives in consumer products and manufacturing processes.
- 3. Ecology should work with the Washington Department of Health to identify key data gaps in understanding human exposure to flame retardant chemicals, including how biomonitoring could address these gaps and what studies should be performed.
- 4. Align state purchasing policies to support manufacturers that are using the safest identified alternatives.

Chapter 1: Background and Approach

In 2014, the Washington State Legislature directed the Department of Ecology (Ecology) to review information on flame retardants, test products, and develop recommendations for bans or restrictions on the use of flame retardants in children's products and furniture. The Legislature requested specific attention in the review and recommendations of tetrabromobisphenol A (TBBPA), antimony, and flame retardants detected in children's products and furniture. Below is the exact language of the budget proviso.

- (13) Within the environmental legacy stewardship account--state appropriation in this section, the department must use a portion of the funds to:
- (a) Review tetrabromobisphenol A, chemical abstracts service number 26 79-94-7 and antimony, chemical abstracts service number 7440-36-0 and their use in children's products and furniture as flame retardants. The department must consider available information on the hazards, uses, exposures, potential health and environmental concerns, safer alternatives, existing regulatory programs, and information from other governments or authoritative bodies. By December 31, 2014, the department must provide to the appropriate committees of the Legislature a summary of the data reviewed and recommendations on whether to ban or restrict antimony and tetrabromobisphenol A flame retardants in children's products and furniture; and
- (b) Test for the presence of flame retardants in children's products and furniture. By December 31, 2014, the department must report to the appropriate legislative committees on test results, available information on hazards, uses, exposures, safer alternatives, existing regulatory programs, potential health and environmental concerns, information from other governmental or authoritative bodies, and recommendations on whether to restrict or ban the flame retardants in children's products and furniture.

This report summarizes available flame retardant information on the classes, uses, exposures, potential health and environmental concerns, end of life, safer alternatives, and existing regulatory programs. This report is comprehensive but not exhaustive as there was not sufficient time to identify all uses and hazards for all flame retardants. Recommendations provided in this report are presented only where available information was sufficient to do so.

We used the GreenScreen® for Safer Chemicals (GreenScreen) to assess the hazard characteristics of various flame retardants. GreenScreen is a method for comparative chemical hazard assessment that can be used for identifying chemicals of high concern and safer alternatives (see Chapter 7 for more detail). This method provides a framework to research and gather data on eighteen human health and environmental hazard endpoints. The information is assessed and classified and chemicals are separated into four different groups or "Benchmarks." A chemical of high concern that should be avoided is a Benchmark 1, while a chemical that is preferred and considered a safe chemical is a Benchmark 4. An example of a chemical to be avoided are those that are persistent, bioaccumulative, and toxic (PBT), or carcinogenic.

The purpose of this comparative assessment is to help users identify alternatives that are safer thereby avoiding "regrettable substitutions." A regrettable substitution occurs when a toxic chemical is replaced with another chemical of equal or greater toxicity concern. A description of the benchmarks is presented below. Additional detail on the use of GreenScreen is provided in Chapter 7.

GreenScreen® Benchmarks

Benchmark 1: Avoid—Chemical of High Concern

Benchmark 2: Use—but search for Safer Alternatives

Benchmark 3: Use-but still Opportunity for Improvement

Benchmark 4: Prefer-Safer Chemical

We relied on biomonitoring (a method to assess a person's exposure to chemicals), house dust studies, and product testing to evaluate the potential for people to be exposed to toxic flame retardants. We know that if biomonitoring studies find toxic flame retardants in people they are already exposed, though these types of studies are rarely conducted. Measuring toxic chemicals in house dust is a less expensive way to demonstrate the potential for exposure, especially for children. Finding a toxic chemical in a household product indicates that exposure is possible.

We used available information from the scientific literature as well as data specific to Washington to assess environmental concerns.

Chapter 2: Flame Retardants - Overview and Classes

Flame retardants are added to products to slow the spread of a fire and provide additional escape time. Flame retardants typically function by separating into free radicals that absorb energy, thereby slowing combustion and propagation of fire. They are primarily used in percent levels (greater than ten grams per kilogram) in products.

Concerns about the potential negative effects of flame retardants on human health and the environment increased after the polybrominated biphenyl (PBB) accident in Michigan in 1973 (Fries 1985). In the late seventies, hazards of two flame retardants in children's pajamas, tris-(1,3-dichloro-2-propyl)phosphate (TDCPP, also known as Fyrol FR2) and tris-(2,3-dibromopropyl)phosphate (Tris-BP) were characterized (Blum 1977, Gold 1978).

Research conducted in Sweden analyzed the increase of flame retardants in breast milk over time and led to increased concerns of the potential negative effects of flame retardants on human health and the environment (Meironyte 1999). Subsequent studies raised questions about both the safety of these flame retardants and their effectiveness in certain applications (Shaw 2010).

Regulatory Drivers for the Use of Flame Retardants

Performance-based standards for flame resistance or flame retardancy exist for a wide variety of products in multiple jurisdictions. These regulatory drivers provided the impetus for the development and use of chemical flame retardants. Federal, state, and industry standards for products like furniture, electronics, car and airplane interiors, insulation, and carpet cushions all drove flame retardant usage.¹

Flame retardants are often an important component in product design and their use is sometimes driven by performance-based regulations. One important regulatory requirement that has greatly influenced the use of flame retardants in furniture and children's products sold in the United States is the <u>California Technical Bulletin 117</u> (TB-117) introduced in 1975.² This standard and additional regulatory flame resistance or retardancy standards are discussed below.

Furniture

California's TB-117 for upholstered furniture has been widely regarded as a strong driver for flame retardant use. The standard was unusually rigorous due to its open flame test for polyurethane foam materials, which made chemical flame retardants the only practical alternative to meet the standard. Because of the large market share represented by California's economy, furniture products that were sold nationally often met this standard to ensure they could be sold in California.³

More recently, concern about the unintended health consequences of flame retardants drove California to update its standard. Effective January 2014, the open flame test for filling materials was eliminated from the standard; therefore, chemical flame retardants are no longer needed in foam to meet the updated TB-117-2013 standard.⁴ In addition, the standard (which previously

¹ Cordner A, Mulcahy M, Brown P. (2013) Chemical Regulation on Fire: Rapid Policy Advances on Flame Retardants. Environ. Sci. Technol. 2013, 47, 7067–7076. Available at: dx.doi.org/10.1021/es3036237

² TB-117 was created by the California Department of Consumer Affairs, Bureau of Home Furnishings and Thermal Insulation

³ National Fire Protection Association. (2013) Hot Seat: A New Look at the Problem of Furniture Flammability and Home Fire Losses. NFPA Journal. Available at: www.nfpa.org/newsandpublications/nfpa-journal/2013/september-october-2013/features/old-problem-fresh-look

⁴ Chemical Watch (Subscription Required). (2013), California Approves New Upholstered Furniture Flammability Standards. Available at: http://chemicalwatch.com/17361/california-approves-new-upholstered-furniture-flammability-standards

was presumed to apply to furniture products intended for infants and very young children such as mats and pillows), was clarified to specifically exempt these items from future regulation.⁵

Electronics

Plastics used in electronic products are rated for their flame retardation capability using a voluntary standard identified by the National Fire Protection Association (NFPA) in conjunction with the Underwriters Laboratory Inc. that defines the specific method. Although the NFPA standards are voluntary, they are often cited by federal and state regulations as a definitive source for fire and combustion related technical information. In addition, products are typically manufactured to meet NFPA standards to minimize product liability concerns.⁶

Tents and Sleeping Bags

Outdoor items, such as camping tents and sleeping bags are often certified to flammability standards developed by the Industrial Fabrics Association International (IFAI), formerly the Canvas Products Association International (CPAI). CPAI-84 is the standard that applies to tents (also applies to play tents), and CPAI-75 applies to sleeping bags. The standards do not require the addition of flame retardants. Tents sold in California, Louisiana, Massachusetts, Michigan, Minnesota, New York, and New Jersey are required to meet CPAI-84. New Jersey also requires adherence to CPAI-75. There is no federal flammability standard for tents or sleeping bags. ⁷

Regulations Driving the Use of Flame Retardants

Regulation	Criteria	Notes		
California Technical Bulletin 117	Open flame test for polyurethane materials	Updated standard removed the flame test		
National Fire Protection Association	Electronic product plastics flame retardant standard	Voluntary standard		
Industrial Fabrics Association International	CPAI-84 flammability standard for tents	Required by some states		
Industrial Fabrics Association International	CPAI-75 flammability standard for sleeping bags	Required by some states		

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⁵ "5.Proposed to amend and clarify that the following products shall be exempt from the Bureau flammability requirements: Bassinets, booster seats, car seats, changing pads, floor play mats, highchairs, highchair pads, infant bouncers, infant carriers, infant mattresses, infant mattress pads, infant seats, infant swings, infant walkers, nursing pads, nursing pillows, playpen side pads, play yards, portable hook-on chairs, and strollers." Intertek (2013). U.S. – California Proposes to Amend Upholstered Furniture Flammability Regulation.

www.intertek.com/sparkles/2013/us-california-amend-furniture-flammability-regulation/

⁶ Washington Department of Ecology. (2009) Alternatives to Deca-BDE in Televisions and Computers and Residential Upholstered Furniture. https://fortress.wa.gov/ecy/publications/summarypages/0907041.html

⁷ Bureau Veritas. (2008) New Jersey Passes Law Requiring Tents and Sleeping Bags to Meet Flame Resistance Standards. https://outdoorindustry.org/pdf/ASTMBureauVeritasBulletin_08B-165.pdf

Additive and Reactive Flame Retardants

Flame retardants can be broadly classified into two types based on how they are incorporated into the material: additive and reactive.

Additive flame retardants are not chemically bonded to the polymers or chemical materials used in the product but are mixed in the product materials. These flame retardants maintain their chemical structure and are evenly dispersed throughout the product. They can also escape from their matrix through release to the air and accumulate in dust (Stapleton, 2008).

Reactive flame retardants chemically bond to the polymers or chemical materials used in the product and become an integral part of the product structure. Because these flame retardants are chemically bonded, they are much less likely to be released and potentially pose less of a threat to human health and the environment during consumer use. However, reactive flame retardants may still be released from products, either because they are liberated from the polymer (e.g., during a fire), or if the original polymerization was incomplete (U.S. EPA 2014e). Exposure over the life cycle of the product needs to be considered—from manufacturing, during use and recycling, and on to disposal.

Most flame retardants are only used in either the additive or reactive form. An exception is tetrabromobisphenol-A (TBBPA), which can be used in either form in specific applications. Reactive and additive forms of the same chemical have different physical and chemical properties so are not interchangeable.

Flame Retardant Classes

Currently, there is a wide variety of flame retardant chemicals used throughout the world in various types of materials. Many flame retardants are high production volume chemicals (HPV), which are classified as those produced or imported in the United States in quantities of one million pounds or more per year. Materials that commonly contain flame retardants include resins and polymers found in commercial products, such as furniture and electronics. Flame retardant chemicals are classified by their chemical makeup and most can be grouped into three common classes: halogenated, non-halogenated, and inorganic based. The makeup of the flame retardant affects its physical and chemical properties, which in turn affects its ability to be effective for a specific application. The classes of all of the flame retardants mentioned in this report are listed in Appendix 2. It is important to note that there are many other flame retardants being used but little information is available about them. As a result, they are not included in this report.

1. Halogenated Flame Retardants

Halogenated flame retardants are the largest class currently in use. The term 'halogenated' refers to one of the Group VIIA of related elements found in the periodic table (i.e., fluorine, chlorine, bromine, iodine, and astatine). Halogens are particularly effective at absorbing energy thereby slowing fire development and dispersal. Halogens also resist hydrolysis and biological and photolytic degradation resulting in a chemical that is persistent. Although any halogen can function as a flame retardant, the chemical characteristics of chlorine and bromine make them more effective as flame retardants.

Brominated and chlorinated flame retardants are the two most common classes of halogenated flame retardants used today and they can be used in either the additive and reactive forms. As their name indicates, chlorinated and brominated flame retardants use chlorine and bromine, respectively, as part of their chemical structure. These flame retardants all have a carbon-based backbone with attached halogens. Potential hazards for these two classes are discussed in detail in Chapter 4. Many halogenated flame retardants also include phosphorous in their structure as a secondary energy absorber.

Brominated Flame Retardants

Brominated flame retardants use the element bromine to absorb energy and slow fire propagation. There are many bromine-based flame retardants. The exact number of bromine-based flame retardants is unknown although the number is estimated to be over a hundred. Figure 1 shows the basic structure of polybrominated diphenyl ethers (PBDEs), which, prior to 2004, were one of the most commonly used flame retardant mixtures found in furniture and electronic products.

PBDE general structure

(m & n = 0 - 5 Br atoms on each benzene ring, total of 1 - 10 Br atoms in each PBDE congener)

(2-ethylhexyl-2,3,4,5-tetrabromobenzoate) Component of the mixture Firemaster® 550

Figure 1: Structure of several brominated flame retardants

Polybrominated diphenyl ethers (PBDEs) are persistent, bioaccumulative, and toxic (PBT). In 2001, the total PBDE volume produced worldwide was estimated at over 67,000 metric tons. PBDEs are only used as *additive* flame retardants, (not chemically bonded to the matrices of the products in which they are used).

Three PBDE mixtures, referred to as penta-, octa-, and deca-BDE, were used commercially in products. Each was used primarily in different applications. Penta-BDE was used in low-density polyurethane foam in products such as furniture. Octa-BDE was used in certain electronic applications such as housings for fax and answering machines, automobile trim, telephone handsets, and kitchen appliance casings. Deca-BDE's largest use was in electronic enclosures, particularly in computers and televisions (Ecology, 2006). Concerns about the effects of PBDEs on human health and the environment led many states, including Washington, to ban or restrict their use. These regulations are discussed further in Chapter 8. Manufacturers of penta-BDE and octa-BDE agreed to voluntarily stop producing these by the end of 2004 and in 2009, EPA announced a voluntary agreement with the three largest PBDE manufacturers to discontinue the manufacture of decaBDE (EPA, 2009).

Numerous other brominated flame retardants are still commonly used. Two brominated flame retardants that have garnered extensive scrutiny and concern are hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA), <u>Figure 1</u>. Both HBCD and TBBPA are identified as PBTs by Washington State (<u>Chapter 173-333 WAC</u>) and <u>chemicals of high concern to children</u> (CHCC) (<u>Chapter 173-334 WAC</u>). Manufacturers selling products containing CHCCs must report their use to Ecology.

In addition to deca-BDE, HBCD, and TBBPA, another common brominated flame retardant mixture is Firemaster[®] 550, which is frequently used as an alternative to penta-BDEs in flexible polyurethane foam (Stapleton 2008). Firemaster[®] 550 contains two brominated compounds, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH), and triphenyl phosphate (TPP) in addition to several isopropylated triaryl phosphate isomers (IPTPPs).

Chlorinated Flame Retardants

Chlorinated flame retardants use the element chlorine to absorb energy and slow fire propagation. There are many chlorine-based flame retardants; the exact number is unknown.

Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) is a chlorinated organophosphate commonly used as a flame retardant in polyurethane foam, both in children's products and upholstered furniture in the United States (Stapleton 2011, 2012a). Another commonly used chlorinated flame retardant is tris(2-chloroethyl) phosphate (TCEP).

Figure 2 shows the structure of a few chlorinated flame retardants. TCEP is also associated with a newer flame retardant mixture called Antiblaze[®] V6 (V6), which contains TCEP as a byproduct in the range from 4.5 to 7.5% (EU, 2007).

Figure 2: Structure of the chlorinated flame retardants TCEP, TDCPP, V6, and TCPP

A fourth chlorinated flame retardant compound, tris(1-chloro-2-propyl) phosphate (TCPP) has also generated concern. The Organization of Economic and Cooperative Development (OECD) indicates that TCPP is harmful to aquatic organisms (OECD, 2012). The similarity of this compound to TCEP and TDCPP, as seen in Figure 2, raises concerns about its widespread use. TCPP is also associated with a recently characterized flame retardant "U-OPFR" (unidentified chlorinated organophosphate flame retardant) that had not been identified in previous sampling efforts (Stapleton, 2011).

Another example of a group of chlorinated flame retardants are chlorinated paraffins. These chemicals are used as plasticizers and flame retardants in plastics, primarily polyvinyl chloride (EPA, 2009c). Chlorinated paraffins are complex mixtures of polychlorinated alkanes with varying carbon chain lengths and chlorine contents. The short-chain chlorinated paraffins (with a carbon chain length ranging from 10 to 13) are classified as PBT chemicals by Washington State (Chapter 173-333 WAC).

2. Non-halogenated Flame Retardants

A second major class of flame retardants is the non-halogenated. As the name implies, these flame retardants do not use any halogens in their structure but depend on other elements to absorb energy and slow fire propagation. Non-halogenated flame retardants can also function in either the additive or the reactive forms. Phosphorous and nitrogen are used as energy absorbers in the most common non-halogenated flame retardants. Figure 3 shows the structure of several non-halogenated flame retardants.

Figure 3: Several phosphate based non-halogenated flame retardant

With increased health concerns about halogenated flame retardants, discussed in <u>Chapter 4</u>, non-halogenated compounds are the fastest growing class as many manufacturers move away from halogenated flame retardants. While these chemicals are usually less persistent than the halogenated flame retardants, other factors such as toxicity to people and wildlife and whether they bioaccumulate need to be considered before they are identified as safer alternatives.

Like the halogenated flame retardants, these non-halogenated flame retardants can also be used in various mixtures. For example, triphenyl phosphate (TPP) is used as a flame retardant in halogenated and non-halogenated flame retardant mixtures (Stapleton 2009, 2012a). The two non-halogenated mixtures found by Stapleton contained TPP with either tris(4-(tert-butyl)phenyl) phosphate and several butylphenyl isomers, or with several methyl- or dimethylphenyl phosphate isomers. A halogenated mixture containing both TPP, a number of

isopropylphenyl phosphates (IPTPPs) and the halogenated compounds 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis-(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (TBPH), mentioned earlier is Firemaster[®] 550.

3. Inorganic Flame Retardants and Synergistic Additives

The final class of flame retardants is inorganic chemicals that can either be used as a flame retardant in their own right or appear as a "synergist" with other flame retardants. A synergist is a chemical that combines with another chemical to act more efficiently than either chemical would individually. Aluminum and magnesium hydroxides are the most common inorganic flame retardants. They release water, which absorbs energy, and cools and dilutes the flame zone. Aluminum trihydroxide is one of the most commonly used inorganic flame retardants.⁸ It is frequently used in a number of plastic applications.

Many flame retardant synergists do not have significant flame retardant properties by themselves but their addition increases the overall effectiveness of the flame retardant effect. Antimony trioxide (ATO) is one of the most commonly used synergists. It is primarily used as a synergist with halogenated flame retardants. Approximately 25 million pounds of ATO were used as a synergist for flame retardants in 2011 (EPA 2014g). As a synergist, ATO reacts with chlorine or bromine radicals formed during combustion to create antimony halides that scavenge free radicals. The exact mechanism of this synergistic action is not known (EU, 2008).

Chapter 3: General Uses and Product Testing Results

Flame retardant chemicals have been used for decades in various types of materials including resins and polymers found in commercial products ranging from construction materials, such as blown home insulation to consumer products including children's pajamas, computers, and televisions. Flame retardants can be identified in specific applications through manufacturing or producer reporting, product sampling, and testing. Use of flame retardants can also be identified through testing of specific media, such as indoor dust, though the specific application would not be identified. This chapter covers some common uses of TBBPA and ATO. It also reviews a number of product and house dust testing studies and results reported under the Children's Safe Products Act (CSPA).

Manufacturers or producers are not generally required to report the types and concentrations of flame retardants used in their products. Data from sampling and testing of products provide some of this information. Product testing not only provides information on specific chemical uses but can also be used to monitor compliance with regulatory reporting requirements and bans. Product testing results are limited as they do not account for all flame retardants used. Some of the reasons for these limitations include:

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⁸ www.pinfa.org/non-halogenated-pin-frs/inorganic-flame-retardants.html, accessed October 2014

- Only additive flame retardants can be identified. Reactive flame retardants cannot be extracted and analyzed since they are chemically bound to the insoluble base material.
- Almost all testing methods are targeted. While samples might contain multiple flame retardants, the sampling protocol defines a specific list of flame retardants to be identified. If products contain flame retardants not on this target list, they will not be reported.
- The structures of many flame retardants are not known except to the manufacturer and
 possibly the user. While laboratories can identify flame retardants that have not previously
 been reported (Stapleton 2011, Ballesteros-Gómez 2014), this is an arduous process and not
 routinely done.
- Analytical standards are not available. In order for a flame retardant to be identified and
 quantified, the laboratory must compare the sampling results with the analysis of a known
 standard. If the standard isn't available, the laboratory will be unable to confirm the presence
 of the flame retardant of interest.

An instrument that has been helpful for screening for bromine is the portable X-ray fluorescence (XRF) analyzer (Allen 2008, Stapleton 2011). This tool provides an estimate of the bromine content without destroying the product. If the XRF screens positive for bromine in the percent levels, it is likely that a brominated flame retardant is in the material. To date, XRF technology has not been found to be as effective for detecting chlorinated flame retardants (Stapleton 2011).

TBBPA and Antimony - General Uses

TBBPA is used primarily in the reactive form in the manufacture of flame-retarded epoxy and polycarbonate resins, for example, in printed circuit boards. TBBPA can also be used as an additive flame retardant in resins, (acrylonitrile-butadienestyrene [ABS] and high-impact polystyrene [HIPS] resins, for example), found in electronic enclosures of televisions and other products (Morose 2006). Additive usage accounts for approximately 10% to 18% of the total applications (ECHA 2006, Covaci 2009).

The largest use for antimony is as antimony trioxide (ATO) in flame-retarded products as a synergist with halogenated compounds. It is mainly used in plastics but can also be found in rubber, textiles, and adhesives. Typically, these products are used in electrical equipment, wires, automotive parts, building materials, and packaging and are used in both commercial and household products including furniture, carpets, mattress covers, textiles, and plastics (EC/HC, 2012). The relative abundance of ATO in the final (flame-retarded) product can range from 1.5 to 12%. It is also used as a plastic catalyst in manufacturing polyethylene terephthalate (PET) plastic in stabilizers and as a pigment (USGS, 2004).

Product Testing Results - Globally and Nationally

The study results below highlight some of the known and tested flame retardants used in products (these flame retardants are all alternatives to PBDEs). Table 1 below, summarizes the alternatives that have been measured in products purchased in Washington State, if they have been identified elsewhere, and the types of product classes where they have been identified. More details are discussed in this section.

Table 1: Commonly used flame retardants and where they have been detected in products

Children's Products			Furniture		Other Products		Dust	
Chemical	WA	US/ Global	WA	US/ Global	WA	US/ Global	WA	Global
ТВВРА		● ^{d,e}			• f	● b,d,e	x ^l	x ^{i,q,r}
TPP	● ^f	● ^a	r*	● ^g	• f	●b,o		X ^{c, i,o,p}
TCEP	r ^f	ra		r ^g	rf		x ^l	X ^{i,k,n,p,q}
Antimony trioxide (measured as Antimony)					•^			
ТСРР	● ^f	● ^a	rf	•c		•	x ^l	$\mathbf{X}^{c,i,o,p,q}$
TDCPP	● f	● ^a	• f	●c,g	• f	● b,o	x ^l	$\mathbf{X}^{c,i,k,o,p,q}$
HBCD	r ^f				• f	•	x ^l	x ^{c,i,q,r,s}
V6	• f	● ^a		● ^g	• f	•		x ⁿ
TBB	• ^	● ^a		● ^{c,g}		• 0	x ^l	X ^{c,i,k,o,q,s}
ТВРН	•^	● ^a		● ^{c,g}		•°	x ^l	X ^{c,i,k,o,q,s}

Note: Children's products include children's furniture, toys, and infant products.

- Detected as an additive above the percent level by weight
- r- Detected as an additive but less than 1% by weight
- x-Detected in dust

Stapleton 2011^a, Keller 2014^b, Stapleton 2009^c, Gallen 2014^d, Ballesteros-Gomez 2014^e, Ecology 2014^a, Stapleton 2012^g, Dodson 2012^h, Fromme 2014ⁱ, Bradman 2014^k, Schreder 2014^l, Fang 2013ⁿ, Caringan 2013^o, Brandsma 2014^p, Stapleton 2014^q, Abdallah 2008^r, Stapleton 2008^s

Flame Retardants in Foam

Recent studies have shown that with the phase-out of PBDEs, a more varied group of new and existing flame retardants are being used in consumer products. Stapleton et al. studied polyurethane foam in baby products purchased in the United States.

^{*}Washington sample in Stapleton 2012 study

[^] data from this report

Flame retardants were identified (Stapleton, 2011) in a wide range of products including:

- Car seats
- Changing table pads
- Sleep positioners
- Portable mattresses
- Nursing pillows
- Baby carriers
- High chairs
- Infant bath mats/slings

The most common flame retardant identified was TDCPP, followed by the mixture Firemaster[®] 550, which contains multiple chemicals including TBB, TBPH, IPTPP, and TPP. Two chlorinated organophosphate flame retardants were also found that had not previously been identified in the environment, V6 and "U-OPFR."

The most common class of flame retardant found in this study was chlorinated organophosphate flame retardants, which in addition to TDCPP, included TCEP, TCPP, V6, and "U-OPFR." Penta-BDE was found in a few of the products with TPP but the authors cautioned these were likely older products manufactured before specific bans were implemented (Stapleton, 2011). TPP was also found in one non-halogenated mixture sold commercially as AC073.

Stapleton's group did another study to address the question of the identity and frequency of chemical flame retardants being used in furniture since the phase-out of the penta-BDE mixture in 2005 (Stapleton, 2012a). In this study, Stapleton et al. collected and analyzed foam from couches purchased in the United States from 1985 to 2010. Prior to 2005, they found that PBDEs associated with the penta-BDE mixture were the most common flame retardants detected followed by TDCPP. In samples purchased during or after 2005, penta-BDE was successfully phased-out and the most common flame retardants identified were the same as the baby product study mentioned above. TDCPP was the most common followed by the mixture Firemaster® 550.

Some of the samples from 2005 or later contained one of two non-halogenated mixtures indicating that the use of non-halogenated flame retardants is increasing. The first mixture contained TPP, tris(4-(tert-butyl)phenyl phosphate (TBPP) and several butylphenyl phosphate isomers while the second contained TPP and several methyl- or dimethyl-phenyl phosphate isomers. While the products from these two Stapleton studies were sampled from various states, at least half of the products tested were from major brands that could also be found in the state of Washington (Heather Stapleton, email, 5/21/2014).

In addition to children's products and furniture, another study screened and tested foam used in gymnastic equipment (Carignan 2013b). Equipment was screened with XRF. Products where percent levels of bromine were found included pit cubes (3% to 6%), landing mats (0.005% to 3.6%), sting mats (0.8% to 2%) and the vault runway (0.5% to 0.9%). The pit cube samples were then analyzed in the laboratory and the presence of flame retardants in the foam was confirmed for all of the samples. PentaBDE was found in the majority of the samples and mixtures of TBB,

TBPH and TPP or TDCPP were found in the remainder. With the phase-out of pentaBDE, use of these alternative flame retardants may have become more common.

Flame Retardants in Plastics

In a 2013 report from New Zealand (Latimer 2013), electronic waste or e-waste samples were screened for bromine using XRF and a subset of samples were sent for laboratory analysis for TBBPA, select PBDEs, and screened for 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenylethane (DBDPE). The e-waste samples were manufactured in the late 1980s until 2012 and included products such as TVs, computers and peripherals, printers, photocopiers, refrigerators and toner cartridges. Of the 125 components from 63 products, 43 components contained greater than 10% bromine.

Many of the post-2005 samples (12 of 18) were much greater than 0.1% bromine suggesting that some type of brominated flame retardants are still being used in relatively new products for flame retardant purposes. Of the 15 samples that were sent to the lab:

- DecaBDE was detected in two cathode ray tube (CRT) computers (2.05%, 6.02%) respectively.
- TBBPA was detected in two TVs (one CRT at 8.3% and one LCD at 15.9%).
- BTBPE was found in a home office photocopier.
- DPDPE was found in a fridge, three TVs, (two LCD, one CRT), and a toner cartridge.
- Five samples, (three printer/copiers and two CRT TVs), which had high XRF-measured bromine levels but no positive laboratory results suggested alternative brominated flame retardants were likely used in the products.

In the Netherlands, a number of electronic products made from plastic were tested in 2012 and a novel flame retardant chemical 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) was identified for the first time (Ballesteros-Gómez 2014). None of the samples manufactured before 2006 contained TTBP-TAZ suggesting that it is one of the alternatives being used to replace banned octa- and deca-PBDE in certain plastics, such as ABS and high impact polystyrene (HIPS). In addition to testing for TTBP-TAZ, a subset of the samples (those purchased in 2012 and manufactured after 2006) was screened for a number of additional halogenated and phosphorous-based flame retardants. Analytes identified in the percent levels in one or more of the products were DBDPE, deca-BDE, TBBPA, and BTBPE. Of the thirteen electronics tested, TBBPA was found in the percent levels in six of the samples, an electrical power board, adaptors, heat sealer and two children's toys, indicating that it was being used in those samples as a flame retardant in additive form.

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⁹ TBBPA, DBDPE, BTBPE, (1,2-bis(2,4,6-tribromophenoxy)ethane), decaBDE, TPP, RDP, BDP, TBOEP, and TMPP

Consumer products containing plastic that were available for sale in 2012 were screened and tested for bromine, PBDEs, TBBPA, and HBCD in Australia (Gallen 2014). These products represented a broad range of product types including baby accessories, computers, televisions, small and large electronic appliances, furniture, and children's toys. Bromine was detected using XRF in the percent level in 10% of the products tested. These products were mainly small household appliances and electronics but included a few samples from computers, large household appliances, furniture, and toy plastic.

While bromine was detected in about half of the samples using XRF, most were at concentrations lower than what is required for use as a flame retardant. These findings suggest the use of recycled brominated flame retardant-containing plastic. Of these screened products, a subset was sent to a laboratory to be tested for selected PBDE congeners, TBBPA, and HBCD. The additive form of TBBPA was found in percent levels in power adaptors, small electronics, a plastic toy, and a television. HBCD was not detected. Deca-BDE was found in percent levels in televisions and power adaptors.

In a study from 2013, plastic Mardi Gras beads and Holiday Garlands purchased and collected after parades were screened using XRF (Gearhart 2013). The overall elemental composition of bead plastic was similar to the elemental composition of electronic waste and other plastic waste streams suggesting that recycled plastics including some with flame retarded plastics are likely being used in bead production. In this study, 51 of 87 samples had bromine XRF results above 400 ppm and the majority of those had levels between 1% and 2%. Chlorine was also found in many products, which is probably a combination of the use of polyvinyl chloride and chlorinated flame retardants.

A subset of samples (53) were further tested for TBBPA, BTBPE, DBDPE, decaBDE, TPP and 2,4,6- tributyl phosphate. Over 90% of the beads tested had greater than 100 ppm total flame retardants (one or more detected). The detected total analyte concentrations in the beads ranged from 100 ppm to 1% of the total bead by weight. The analytes found at the highest levels were TBBPA and deca-BDE (up to 0.6% of the total bead by weight). All of the flame retardants detected in this study were believed to be from recycled content (personal communication, Jeff Gearhart 12/16/14).

Flame Retardants in Textiles

Textiles, is another class of materials that has been tested for the presence of flame retardants in the United States. A study published earlier this year evaluated additive flame retardants being applied to camping tents (Keller 2014). Ten of eleven tents tested detected flame retardants in the percent level (0.9% to 3.9%). The flame retardants detected were deca-BDE, TDCPP, TBBPA, and TPP. While these products are not considered household furniture, many toy tents and tunnels designed

for children to use indoors meet the same flammability requirement (CPAI-84), which will be further discussed in Chapter 8.

It is unclear if the products would be treated with the same flame retardants but Stapleton's group tested ten children's play tents and tunnels purchased in 2011-2012 and found TDCPP and TCPP (0.1% to 1% by weight) in four of the products (Heather Stapleton, email, 8/21/2014). Their group also detected TBBPA in car seat fabrics (Heather Stapleton, email, 5/23/2014). Another study tested 11 upholstery textiles commercially available in Japan for HBCD, PBDEs, and DBDPE. With the exception of one sample, HBCD was found in all of the samples in percent levels (2.2% to 4.3%). These textiles were used mainly for manufacturing curtains in Japan (Kajiwara, 2009).

Specific Product Testing – Washington State

Ecology conducted several studies in Washington on flame retardants in consumer products, which are summarized below.

2011 Study

In 2011, Ecology tested 68 consumer product samples for PBDEs (Ecology 2012a). Samples were chosen for laboratory analysis based on XRF-measured bromine concentrations. Fourteen of the samples consisted of older electronics obtained from an e-waste recycling facility and one foam sample from a couch manufactured in the early 1990s. The remaining 54 samples were collected from new children's products purchased in 2011. The majority of samples containing XRF-measured bromine did not contain PBDEs above detection limits.

Results of XRF measurements showed high concentrations of bromine in all of the e-waste electronics and several pieces of children's furniture foam (about 2%), but none of these products contained lab-measured PBDEs at levels consistent with flame retardant application. The presence of high XRF-measured bromine levels and low PBDE concentrations suggested alternative brominated flame retardants were likely used in the products. Only the couch foam manufactured in the early 1990s contained PBDEs in levels.

2012/2013 Study

In 2012 and 2013, Ecology collected general consumer and children's products including seat cushions, mattresses, upholstered furniture for children, electronics, clothing, and baby carriers from local stores in the south Puget Sound area and online retailers (Ecology 2014a). These products were screened for bromine using XRF and components from 125 products were sent for laboratory analysis to evaluate the presence of PBDEs and selected alternative flame retardant chemicals.¹⁰ The majority of these components were plastic, foam, or fabric.

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¹⁰ DBDPE, TDCPP, tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP) and the non-halogenated phosphate triphenyl phosphate (TPP).

Results indicate that manufacturers have moved away from using PBDEs in products available to Washington State consumers but are using alternative flame retardants including some of the chemicals identified in Stapleton's studies (2011, 2012a). Some of these alternative chemicals are identified as chemicals of high concern to children (CHCC) and found at levels above the reporting limit established in the Children's Safe Product Act (CSPA). In



Sample of a children's product.

agreement with previous studies (Stapleton 2011, 2012a), TDCPP was the most common chlorinated phosphate detected in foam, indicating that alternative flame retardants are being used. TCEP, TCPP, and TPP were also detected. The majority of these samples were foam and many were children's products. A few of the components were plastic or fabric. Analyte results that were above 0.2% are listed in Table 9.

A subset of samples was tested for TBBPA, HBCD, and V6. All three flame retardants were found in a few of the samples analyzed. TBBPA was detected in four plastic electrical enclosure components in the percent levels indicating that it was used as an additive flame retardant. TBBPA was also found at low levels in two additional plastic samples, which would most likely be due to contamination from recycling plastics that contained TBBPA or residual of an unreacted monomer in a product containing reactive flame retardant. HBCD was detected in a plastic and a Styrofoam component. One sample, a safety glove, contained HBCD at percent levels and the other, a child's bean bag chair, was above the CSPA criteria for reporting HBCD in children's products but not found in percent levels. V6 was detected in a few children's products in percent levels. These products were also above the CSPA criteria for TCEP in children's products, which suggest that V6 was the source of TCEP. V6 was found in a tent sample at 0.2%. It was also found in trace levels in two bonded foam carpeting padding samples. This is most likely from recycled content as the products were made from pieces of shredded flexible polyurethane foam held together with a binder. All five carpet padding samples tested had trace amounts of multiple flame retardants.

Of seven samples with TPP above 0.2% (2,000 ppm), four had bromine levels above 1% by weight suggesting these products used halogenated mixtures. Three were children's furniture containing foam. The fourth was a plastic liquid crystal display (LCD) monitor. It was suspected that the three children's furniture samples contained a flame retardant mixture, likely Firemaster® 550 but this was not confirmed at the time due to the scope of the study (Ecology 2012b, Ecology 2014b). These three foam samples were added to the supplemental 2014 study discussed below.

Similar to the 2011 results, most samples (23 samples from 22 products) that screened positive for bromine in percent levels using XRF did not contain any of the brominated flame retardants tested for in the 2012-13 study. This result suggests that the bromine sources are likely either additive flame retardants that were not assessed in this study or reactive brominated flame retardants, which formed polymers and cannot be readily analyzed.

Supplemental 2014 Testing

In June 2014, Ecology initiated additional testing in support of the legislative proviso (Ecology 2014c). Due to time restrictions, only limited analytical methodologies could be performed. The additional testing included:

- Analyzing the three children's product samples from the 2012/2013 study suspected to contain Firemaster[®] 550 for TBB and TBPH.
- Reviewing the XRF results from the 2012/2013 samples for antimony and sending samples to the lab to be tested for antimony.
- Purchasing and testing ten new infant products to supplement the 2012/2013 study.

The three foam samples that were suspected to contain Firemaster[®] 550 were sent to a separate laboratory for analysis of flame retardants that contain TBB and TBPH. Two of the foam samples contained Firemaster[®] 550 and one sample contained Firemaster[®] 600, above 1% of the weight of the foam. Both of these commercial mixtures contain TBB, TBPH, TPP, and a number of isopropylphenyl phosphates (IPTPPs) but the ratios are different. The three samples consisted of inner polyurethane foam from children's upholstered chairs (Table 9).

Twenty-eight product components that were screened by XRF for the 2012/2013 study had antimony measurements greater than 0.2% (2000 ppm). All of these samples were plastic. In order to assess if XRF could be used as an effective screening tool for antimony, Ecology sent 16 samples that screened greater than 0.2% in addition to nine samples with low-level or non-detected XRF measurements for laboratory testing of antimony. Fourteen of the 16 samples sent to the laboratory that were screened greater than 0.2% antimony using XRF were confirmed to contain antimony at levels that would indicate its use as a flame retardant synergist (> 2,000 ppm) (Table 9).

Overall, the lab results agreed closely with the XRF measurements of antimony, indicating that the XRF analyzer can be used to qualitatively assess whether antimony is present in the product. Based on XRF results, no children's products or furniture screened in the 2012/2013 study contained antimony at levels where it would be used as a flame retardant synergist.

The 14 products confirmed to contain antimony in percent levels were all plastic components (plastic casings and cables for electronics and small appliances, such as space heaters, and a flame resistant plastic tarp). Bromine was measured by XRF alongside antimony at percent levels in all but three of the fourteen samples, supporting a conclusion that antimony is being used as a synergist with halogenated flame retardants. One of the samples that contained high levels of antimony also contained percent levels of TBBPA. Flame retardants from the 2012/2013 study were not detected in all products that contained high levels of antimony but screened positive for bromine in percent levels indicating that bromine sources are likely either additive flame retardants that were not assessed in this study or reactive flame retardants, which formed polymers and cannot be readily analyzed.

Ecology purchased ten new infant products (changing mats, changing pads, and sleep wedges) from four Washington stores and analyzed the inner polyurethane foam layer for the organophosphorous flame retardants—TCPP, TDCPP, TCEP, and TPP. Of the ten products tested, three (one changing pad and two changing mats) contained TCPP ranging from 0.7 to 3.6% by weight. These results are listed in <u>Table 9</u>. No other organophosphorous flame retardants were detected. Bromine was not detected by XRF in any of the products.

Two of the products that were tested during the 2012/2013 study were still on the market in 2014. The first product, a changing pad, still contained TCPP, whereas the second product, an infant sleep wedge that contained 2.5% TDCPP and 0.7% TCPP in 2012 did not contain any of the organophosphorous flame retardants tested for in 2014. The 2012/2013 study detected organophosphorous flame retardants in four out of five changing mats, changing pads, and sleep wedges. In contrast, only three of the ten similar products purchased in 2014 contained the organophosphorous flame retardants tested for. While neither study can be considered a statistically representative sample, the results suggest that either fewer manufacturers added flame retardants to infant foam products in 2014 or flame retardant usage has shifted to other chemicals.

Indoor Environment

In addition to testing products, another way to assess flame retardants in use is through the analysis of indoor dust. Researchers found a high correlation between the amount and type of consumer products present in the home and the amount of PBDEs found in house dust indicating that it can be used as a surrogate for identifying flame retardants used in products (Allen, 2008).

Since that study, multiple alternative flame retardants have been detected in house dust. This indicates that increasing numbers and different types of flame retardants are now being used.

Flame retardants measured in house dust include:

- HBCD
- BDF

BTBPE

- TBPH
- Dechlorane plus
- RDP (Resorcinol bis (diphenyl-phosphate)

- TCPP
- TBB

DBDPE

- TPP
- TDCPP
- TBBPA

- TTBP-TAZ
- V6

(Zhu 2007, Abdallah 2008, Stapleton 2008, 2009, Fang 2013, Brandsma 2013, Ballesteros-Gómez 2014)

Dodson et al. (2012) found an increase in TBB and TBPH concentrations in dust collected from California homes between 2006 and 2011, consistent with their use as replacements for PBDEs. These are components of Firemaster[®] 550, which was introduced as a replacement to PBDEs in polyurethane foam.

Flame retardants have also been detected in other indoor environments, such as child care facilities, gymnastic training facilities, offices, automobiles, and aircrafts (Bradman 2014, Carignan 2013a, Carignan 2013b, Fang 2013, Allen 2013, Brandsma 2014). For example, in a study of 39 early childhood education centers, 100% of dust samples contained TCEP, TDCPP, TBB, TBPH, and PBDEs (Bradman, 2014). Median concentrations of TCEP and TDCPP were higher than PBDE congeners, and levels were particularly elevated in centers with foam nap mats.

Reports Under the Children's Safe Products Act

Washington's Children's Safe Product Act (CSPA) requires manufacturers to report if <u>chemicals</u> of high concern to children (CHCCs) are present in children's products they manufacture. Manufacturers began reporting on a phased-in schedule based on product type and company size in August 2012, and report annually.

Table 2: Examples of information reported under CSPA

Present in a product	Present in a product	The function of the chemical				
category	component	in the product component				
Such as:	Such as:	Such as:				
 Puppets 	• Synthetic polymers	• Coloration/pigments/dyes/inks				
 Bracelets 	– plastic, foam, other	• Plasticizer/softener				
• Skirts	 Metals 	• Flame retardant				
• Cosmetics – nails	 Surface coatings 	• No function - contaminant				
 Baby changing mats 						

As of August 2014, manufacturers filed over 25,000 reports of a chemical in a product component and category. A minority (only 153) of those reports were for the function "flame retardant." Thirty one of these reports were for halogenated flame retardants. Of these 31 reports, only 10

indicated the chemical was used in the percent level, and all were reported to contain TBBPA. Of these ten reports, six were reported as synthetic polymers used in powered non-ride toy vehicles and four were reported as synthetic textiles used in the following products: a baby carrier, a baby play pen, a baby car/booster seat, and a baby swing. HBCD, deca-BDE, TCEP, and TDCPP with the function "flame retardant" were not reported in the percent levels. TDCPP was added to the list recently and the first reports for this chemical are not required until February 2015 so it might be underreported in comparison to the other chemicals. The majority (107 of 153) of these reports with a "flame retardant" function were less than 500 ppm indicating that they were likely a contaminant from recycled content, an impurity from another additive flame retardant, or residual un-reacted monomer from a reactive flame retardant.

The most frequently reported chemical group with the function "flame retardant" is antimony and antimony compounds (122 of 153 reports). Twenty-five of these reports were greater than 1,000 ppm (Figure 4) including four reports in the percent level.

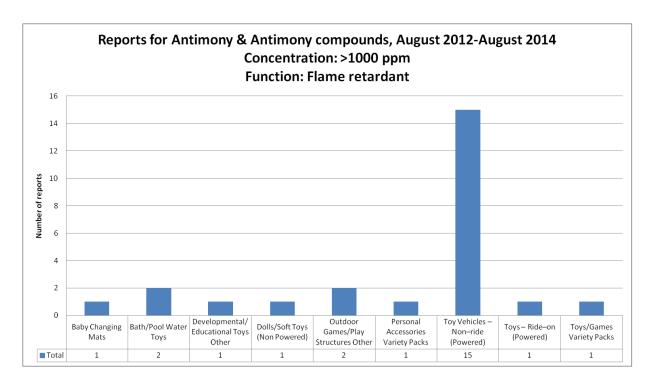


Figure 4: Reports for Antimony and Antimony Compounds

Antimony and antimony compounds have been reported 2,377 times, mostly at low levels for other functions, including a catalyst, a coloration agent, or plasticizer.

Some reports (103) noted that halogenated chemicals (TBBPA, HBCD, deca-BDE, TCEP, and TDCPP) were present for other functions, including contaminants, coloration agents, or plasticizers. Of these reports, only a small number submitted results in the percent levels with a

function other than "flame retardant." There were nine reports of TBBPA in the percent levels with the function of "Coloration/Pigments/Dyes/Inks" in Toy Vehicles-Non Ride (Powered) products.

In conclusion, the data reported under the CSPA does not indicate widespread use of halogenated flame retardants that require reporting in children's products.

Chapter 4: Known Potential Hazards/Health Effects and Exposures

Toxicity

Halogenated Flame Retardants

Brominated Flame Retardants

More than 75 brominated flame retardants are currently in use (Guerra, 2011) and very little is known about the hazards and exposures of most of them. Many brominated flame retardants in use are of concern due to their adverse effects, including those on the thyroid, liver, and reproductive system.

Endocrine disruption via thyroid hormones is the primary endpoint of concern for brominated flame retardants. PBDEs are structurally similar to triiodothyronine (T3) and thyroxin (T4) (Figure 5) and interfere with normal regulation by those hormones. Disruption of normal thyroid hormone function results in adverse effects on neurodevelopment and behavior.

Figure 5: Structure of the thyroid hormone, thyroxin (T4) and PBDE general structure (m & n = 0 - 5 Br atoms on each benzene ring, total of 1 - 10 Br atoms in each PBDE congener)

Most of what is known about the toxicity of flame retardants arises from animal studies and in vitro assays, especially as ethical concerns prevent controlled studies on human subjects. Some epidemiological studies exist on impacts from brominated flame retardants on humans. A recent review of those studies (Kim, 2014) found plausible outcomes associated with exposure to

brominated flame retardants (HBCD, polybrominated biphenyl [PBB], PBDEs, and TBBPA) include neurological and developmental disorders, cancer, reproductive health effects, and alteration of thyroid function.

PBDEs are believed to affect neurodevelopment and behavior adversely through effects on thyroid hormones (CDC, 2009; ATSDR, 2004). Exposure to PBDEs in utero and through lactation causes thyroid effects and neurobehavioral effects in animals. EPA has classified one PBDE congener, decaBDE also known as BDE-209, a possible human carcinogen based on the development of liver tumors in rodent feeding studies (EPA IRIS, 2008). EPA has also derived reference doses for several PBDE congeners for non-cancer effects.

Less is known about the toxicity of other halogenated flame retardants. However, some other flame retardants are thought to have similar toxic effects based on initial studies in animals and cell lines (Wikoff and Birnbaum, 2011; Roosens, 2009; Patisaul, 2013). For example, repeated dose HBCD studies in rodents show negative effects on the liver and thyroid. These results are supported by in vitro assays and neonatal HBCD exposure of rats, which led to adverse effects on neurodevelopment (Wikoff and Birnbaum, 2011). A Firemaster[®] 550 rat study showed endocrine disruption, including effects on thyroxine levels (Patisaul, 2013).

TBBPA has both acute and chronic aquatic toxicity for a variety of fish species and daphnia (EPA 2014f). Chronic toxicity in fish include effects on heart, trunk, and tail morphology (McCormick et al. 2010). Human health effects from TBBPA are less clear. The EU risk assessment found no consistent results on any endpoint and no human health concern was identified (Dekant 2010, ECHA 2006). The EU assessment notes some non-adverse effects on thyroid hormones. However, the EPA DfE hazard assessment (EPA 2014f) assigned more importance to those endocrine effects. Other endpoints were also unclear. For example, the DfE hazard assessment scored TBBPA as moderate for carcinogenicity based on rat studies. Some of the rat studies showed increased incidence of certain cancers in one or both sexes. DfE also scored TBBPA as moderate for developmental toxicity due to mixed results from different studies. The EU risk assessment determined that data was not sufficient to identify a concern. Both the DfE alternatives assessment and the EU risk assessment determined that TBBPA is persistent and not bioaccumulative.

The Washington State Departments of Ecology and Health published a Chemical Action Plan (CAP) for PBDEs in 2006 (Ecology 2006). The plan noted the reservoir of PBDEs in people and in the environment, negative effects on neurological development and thyroid hormone regulation, and people's exposure through indoor dust and foods. The PBDE CAP recommended, and the state later passed, a ban on the use of PBDEs in certain products, after safer alternatives were identified.

EPA published a chemical action plan for HBCD in 2010 (EPA 2010). The plan cites effects on thyroid hormones, learning and memory, and reproductive effects. Studies have detected HBCD in human tissue, and the general population is likely exposed through food, dust, and inhalation. EPA's concern is mostly based on its persistence, bioaccumulation, and aquatic toxicity, with some concern for the general population. Based on these concerns, the EPA recommends several rulemakings to gather more information on releases of HBCD, restrict some uses, and recommends an alternatives assessment. This EPA DfE alternatives assessment was completed in 2014 (EPA 2014d).

Chlorinated Flame Retardants

As mentioned previously, TCEP (<u>Figure 2</u>), TDCPP, TCPP, and V6 are part of a family of related chlorinated flame retardants (chlorinated alkyl phosphate esters). TCEP has also been identified as a byproduct in the flame retardant Antiblaze[®] V6. Cancer and reproductive effects are the primary concerns for chlorinated flame retardants (ATSDR, 2012).

Washington State identified TCEP as a CHCC due to its carcinogenicity and non-cancer effects on reproduction. TCEP is classified as a carcinogen by California and a reproductive hazard by the European Union. TDCPP was identified by the California Environmental Protection Agency as a chemical known to cause cancer and placed on the Proposition 65 list of toxic chemicals (Cal EPA 2014). Based on this concern, TDCPP was added to Ecology's CHCC list in 2013 (Chapter 173-334 WAC). The EU did not characterize a third compound, TCPP, as a hazard, but that is due to the assumption that the exposure is negligible due to its presence in foams that are enclosed (EU 2008). As mentioned in Chapter 3, TCPP has been detected in house dust. In repeated dose toxicity feeding studies in rats, there were effects on the liver and thyroid (EU 2008) and the similar structure suggests that TCPP will have similar effects as TCEP and TDCPP.

Non-halogenated Flame Retardants (TPP and RDP)

EPA's deca-BDE alternatives assessment (EPA, 2014) incorporated hazard assessments of possible alternatives including RDP and TPP. RDP has low to moderate human health effects. A two generation dietary reproduction study in rats detected delayed vaginal opening and preputial separation. TPP was found to have high human health effects for repeated dose toxicity based on effects of body weight in a rat study. The other human health endpoints for which there was data were considered a low level of concern.

Ecology and the Department of Health conducted an alternatives assessment for deca-BDE (2008) that included TPP and RDP. Neither flame retardant met Washington's PBT criteria. RDP was identified as a safer alternative as RDP was not found to cause the types of environmental or human health-related toxic effects observed for deca-BDE. These effects included developmental, reproductive, and neurological toxicity, based on limited studies in animals and its chemical structure. TPP was not identified as a safer alternative primarily based on its high aquatic toxicity.

Inorganic Antimony

Breathing high levels of antimony trioxide irritates the eyes and lungs, and leads to heart, lung, and digestive system effects (ATSDR, 1992; EPA, 2014g). Long-term, low-dose studies in animals showed similar effects, with additional effects on fertility. Antimony trioxide is also a highly acute aquatic toxic chemical (EPA, 2014). The International Agency for Research on Cancer (IARC) classified antimony as a possible human carcinogen and California identified it as known to cause cancer (Cal EPA, 2014). Antimony and antimony compounds are identified as CHCCs due to cancer from inhalation. There is no evidence of carcinogenicity from ingestion (EPA, 2014g).

Exposure

While some information is available on antimony and PBDE exposure, less is known about other flame retardants. For example, the National Health and Nutrition Examination Survey (NHANES), which provides an ongoing assessment of the exposure of the U.S. population to environmental chemicals via biomonitoring, reported levels of antimony and ten PBDE congeners, but does not measure other flame retardants (CDC, 2009).

In general, people are exposed to flame retardants through ingestion of contaminated food and dust, with dust being particularly important for children as their hands come in contact with dust through crawling and touching objects and they put their hands in their mouths (hand to mouth) (ATSDR, 2012; CDC, 2009; Toms, 2011). House dust accounts for 80% of total intake of PBDEs for Americans (Lorber 2008). Additive flame retardants are not covalently bound to materials and are more easily released into house dust compared to reactive flame retardants. Some workers are exposed to higher levels through inhalation and ingestion (ATSDR, 2012; CDC, 2009).

Brominated Flame Retardants

Levels of PBDEs in blood reflect cumulative exposure over the recent months to years of exposure. In the general population, levels in children tend to be higher than levels in adults (CDC, 2009; Butt, 2014; Stapleton, 2012). This is consistent with increased hand to mouth behavior in children. Levels of PBDEs in people are higher in the U.S. than in Europe (CDC 2009) and are higher within California than the rest of the U.S. (Zota, 2008). California's flame retardant standard TB-117, discussed in Chapter 2, resulted in increased use of chemical flame retardants, which may have contributed to the higher levels detected. Prior to 2004, when the flame retardant industry voluntarily ceased production, penta-BDE was the PBDE produced in the largest quantity. It is found in the NHANES study in all samples and at the highest levels compared with other PBDEs included in the study.

Firemaster[®] 550 is a mixture of triphenyl phosphate (TPP), isopropylated triphenyl phosphate isomers (ITPs), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), and bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH). Hoffman et al (2014) measured the main metabolite of TBB, 2,3,4,5-tetrabromobenzoic acid (TBBA), in human urine as a biomarker of Firemaster[®] 550

exposure. Unlike the other components, the use of TBB is thought to be specific to Firemaster[®] mixtures, so the TBB metabolite is a good indicator of exposure to Firemaster[®] 550. TBBA was detected in almost three quarters of the 64 urine samples, showing widespread and variable exposure. They also found a positive correlation between levels of TBB and TBPH in indoor dust and levels in handwipes. Additionally, levels of TBB in handwipes were positively correlated with urinary TBBA. This suggests indoor dust as an exposure pathway for Firemaster[®] 550, similar to PBDEs.

Carignan et al. (2012) measured TBBPA and HBCD in human breast milk and evaluated factors that could be used to predict the presence of TBBPA and HBCD. HBCDs were found in all samples and TBBPA in 35% of the samples tested. The lower concentrations and detection frequency of TBBPA compared to HBCD has been observed in other studies on breast milk and fat tissue. A positive correlation was found between HBCD levels and the number of electronics in the home, especially for stereo and video equipment. Other studies have also shown a correlation between HBCD levels in dust and serum (Roosens, 2009) and other halogenated flame retardants. Allen et al. (2008) found a correlation between bromine-containing consumer products and penta- and octa-BDEs in dust.

Roosens et al. (2009) compared HBCDs in food, dust, and serum. Dust concentrations correlated significantly with the concentrations in serum, while there was no such correlation between food and serum indicating that dust was the major route of exposure. Stapleton et al. (2012) used hand wipes to estimate exposure to PBDEs in house dust among toddlers. PBDEs were detected in all samples of house dust and serum and 98% of hand wipes. While the serum levels significantly correlated with both dust and hand wipes, the correlation was stronger for hand wipes, strengthening the conclusion that dust is the major route of exposure. Watkins et al. (2012) found a similar correlation between PBDEs levels in office dust and adult workers.

Chlorinated and Non-halogenated Flame Retardants

While no large representative study exists on the exposure of the U.S. population to chlorinated and non-halogenated flame retardants, exposure appears widespread and variable (Betts 2013). Two studies in the Boston area looked at TDCPP's main metabolite, bis(1,3-dichloro-2-propyl) phosphate (BDCPP). In one study, BDCPP was detected in the urine of all 24 female and 5 male office workers tested (Carignan, 2013a).

The second study found that 91% of 45 men had BDCPP and 96% had the TPP metabolite diphenyl phosphate (DPP) in their urine (Meeker, 2013). Meeker and Stapleton (2010) previously showed a relationship between TDCPP and TPP in house dust and hormone levels and semen quality in men. Hoffman et al. (2014) found the metabolites of TDCPP and TPP were widespread and variable in the urine of pregnant women (detected in 38/39 women).

Dodson et al. (2014) investigated the correlation of three chlorinated and four non-halogenated phosphate flame retardants (TCEP, TCPP, TDCPP, TPP, EHDPP, TBP, and TBOEP) in house dust and their metabolites in urine. The study looked at 16 California residents and their homes and is a follow up from earlier studies in 2006 and 2011 on flame retardants in house dust in California (Dodson 2012). BDCPP, the metabolite of TDCPP, was found most commonly, in 94% of the urine samples. The metabolites for TCEP, TDCPP, and TPP were found at the highest concentrations, up to 6.8 ng/mL. While data for comparison are limited, the results were in the range of previously reported results. There were some weak correlations between levels in dust and metabolite levels in urine. The lack of strong correlations could be due to the small sample size, shorter exposure times for urine compared to dust, or other exposure routes. There were stronger correlations among different metabolites in urine, meaning people tended to have similar levels of each phosphate flame retardant metabolite.

A correlation was found between levels of TCEP in both indoor air and dust in German daycare centers and the levels of its metabolite in the urine of children at the daycare centers (Fromme, 2014). Additional organophosphate flame retardants including TCPP were also detected in the children's urine. Bradman et al. (2014) estimated children's exposure to PBDEs and TDCPP based on their measured dust concentrations in daycares (see Chapter 3) and compared the estimated exposures to health risk levels. The authors concluded that the dose estimates of congener BDE-99, based on conservative non-dietary ingestion assumptions, exceeded the reference dose (RfD) in one facility for children less than 3 years old and that half of the centers had concentrations of TDCPP that exceeded the no significant risk levels. The RfDs used were the U.S. EPA reference doses for chronic oral ingestion of specific PBDE congeners and represent an exposure at which non-cancer effects may occur, but does not mean that health effects will occur. The no significant risk levels were developed by the California Office of Environmental Health Hazard Assessment (OEHHA) to determine a daily intake that corresponds to 1 in 10⁻⁵ lifetime excess cancer risk.

Organophosphate flame retardants have been found in human milk in Asian countries (Kim, 2014) and Sweden (Sundkvist, 2010). Kim evaluated levels of several organophosphorus flame retardants, including TDCPP, TCEP, and TPP. TCEP and TPP were detected in more than 60% of the samples. The authors also compared the estimated exposure of infants to TCEP via breast milk and found some individuals were close to the reference dose. The reference dose is the estimate of a daily oral exposure that is likely to be without appreciable risk of deleterious effects during a lifetime.

Inorganic Antimony

The NHANES reported on the levels of antimony in people in the U.S. population (CDC, 2009). According to the CDC, people are exposed to antimony primarily through food and, to a lesser extent, from air and drinking water. Because of the rapid elimination of antimony, levels of urinary antimony reflect recent exposure. Inhalation of airborne dust is the primary concern for

occupational exposure. The general population is primarily exposed to the less toxic pentavalent form of antimony through food and water (EPA, 2014g)

Occupational Exposure

Several studies have evaluated the levels of flame retardants, mostly for PBDEs, in certain occupational groups.

Sjödin et al. (1999) found elevated PBDEs in computer workers compared to cleaning personnel. Upon further evaluation, Jakobsson et al. (2002) found certain PBDE congeners were approximately five times higher in computer technicians compared to other clerks and cleaning personnel. Other studies did not find a clear relationship between exposure to flame retardant-containing equipment and office workers (Watkins, 2011).

Workers recycling foam and electronics are exposed to higher levels of flame retardants. Higher levels of PBDEs were found in recycling workers in the U.S. (Stapleton, 2005), China (Qu, 2007) and Sweden (Sjödin, 1999). The U.S. study looked at both foam recyclers and carpet pad installers, since carpet pads are often made from recycled materials. Both of those occupational groups had levels of PBDEs ten times higher than the control group. Sjödin et al. (1999) found levels of PBDEs in workers in an electronics dismantling plant were about five times higher than other workers.

Airplanes contain high levels of flame retardants to meet safety standards. PBDE levels were higher in aircraft maintenance personnel compared to pilots/cabin crew or a control group (Strid, 2014). Two congeners, BDE-153 and BDE-154, were also higher in the pilots and cabin crew compared to the control group.

Carignan et al. (2013b) found elevated levels of penta-BDE in collegiate gymnasts exposed to a lot of foam equipment. Flame retardant levels increased in hand wipe samples after practice compared with before practice.

Several studies evaluated occupational exposures and disease in firefighters, who are exposed to:

- Flame retardants
- Volatile organic compounds (VOCs)
- Polycyclic aromatic hydrocarbons (PAHs)
- Polychlorinated biphenyls (PCBs)
- Metals
- Various combustion by-products, including chlorinated and brominated dibenzo-pdioxins and dibenzofurans (PCDD/Fs and PBDD/Fs) formed during combustion of organic materials in the presence of precursors containing chlorine or bromine, including flame retardants.

California's biomonitoring program includes the <u>Firefighter Occupational Exposures (FOX)</u> <u>project</u>, a study of environmental chemical exposures in Southern California firefighters. High levels of <u>PBDE flame retardants</u> were measured in firefighters (particularly those who worked on front-line activities) and compared to the U.S. general population (using NHANES). Four percent of the samples exceeded the 95th percentile of NHANES (2003-2004) for both BDE-47 and BDE-153. Seventy-five percent of the samples exceeded the 50th percentile of NHANES (2003-04) for PBDE-47 and 90% for PBDE-153.

A smaller study sampled twelve California firefighters after a fire event. They found higher levels of PBDEs compared to the general population and the congener profiles were different, consistent with occupational exposure (Shaw et al, 2013). The study found higher exposures to PBDEs, PBDD/Fs, PCDD/Fs, and other chemicals. PBDEs were higher than in the general population, but lower than carpet layers, foam recyclers, and e-waste recyclers. TBBPA was not detected in any samples.

A meta-analysis of all the studies on cancer incidence in firefighters found twelve, about half of the cancers investigated, were significantly associated with firefighting (LeMasters et al, 2006). The National Institute for Occupational Safety and Health (NIOSH) funded a large study to look at 30,000 firefighters across the U.S. and found evidence of a relationship between firefighting and cancer that is consistent with earlier studies (Daniels et al. 2013).

Chapter 5: Flame Retardants in the Environment

Pathways for Environmental Release

PBDEs and other flame retardants migrate out of consumer products and collect in dust particles in the indoor environment (Allen, 2008). When textiles with indoor dust on them are washed, traces of these flame retardants are delivered to wastewater treatment plants (WWTPs), which is one of the major pathways for their release in Washington's environment (Ecology, 2011, Schreder and La Guardia 2014). Atmospheric deposition and surface runoff have also been identified as important pathways for PBDE contamination in Washington aquatic systems (Ecology, 2011; PNNL, 2010; Ecology, 2011). Similar pathways would be expected for other additive flame retardants that are found in dust and have similar physicochemical properties.

Global Contaminants

Halogenated flame retardants have been found in air, water, soil, sediments, biota, and WWTP effluents throughout the world (Covaci, 2011; van der Veen and de Boer, 2012). PBDEs, HBCD, BTBPE and other brominated flame retardants are persistent in the environment and can be transported long distances, making them ubiquitous in environmental media throughout the globe and as far away as the Arctic (de Whit, 2010). Organophosphorous flame retardants,

including TCPP, TDCPP, TCEP, and TPP, have also been detected in the air of remote Arctic regions (Salamova, 2014b). The presence of flame retardants in the Arctic is an indicator of persistence and bioaccumulation used by the Stockholm Convention on Persistent Organic Pollutants (de Whit, 2010).

Bioaccumulation

Certain PBDE congeners, such as PBDE-99, are highly bioaccumulative. Bioaccumulation refers to the buildup of a substance within an organism. These increasing concentrations are of concern. While studies have shown that deca-BDE does not bioaccumulate, lower brominated degradation products including lower substituted PBDEs bioaccumulate in organisms and concentrate in the environment (EPA, 2009c). HBCD has also been found to be highly bioaccumulative in aquatic organisms (Wu, 2011). Other brominated flame retardants, like TBBPA, BTBPE, TBB, and TBPH appear to have lower bioaccumulation potential than PBDEs and HBCD (La Guardia, 2012; Morris, 2004). However, modeled K_{ow} values suggest that many of the replacement brominated flame retardants may be bioaccumulative (Kuramochi, 2014), and many have been detected in wildlife, though at lower concentrations than PBDEs or HBCD (Covaci, 2011). Organophosphate flame retardants appear to be less likely to bioaccumulate than brominated flame retardants, but TPP in particular has been reported in several different trophic levels of wildlife (van der Veen and de Boer, 2012).



Fish sample collected during sampling event.

Alternative Flame Retardants Replacing PBDEs in the Environment

Recent air sampling in the Great Lakes and the Arctic found atmospheric concentrations of organophosphorous flame retardants one to three orders of magnitude higher than total PBDEs (Salamova, 2014a; Salamova, 2014b). Atmospheric TBB and TBPH concentrations are rising, while PBDEs are decreasing, suggesting an increase in the use of Firemaster[®] 550 and other formulations containing these chemicals as a replacement for penta-BDE (Salamova, 2014b; Ma, 2012). However, a later study by Ma et al. (2013) did not find the same pattern. Robson et al. (2013) analyzed PBDEs and emerging brominated flame retardants in wet deposition from the Great Lakes area and found concentrations of deca-BDE decreased while BDE-154 and BTBPE increased between 2004 and 2010. The authors suggested that the increase in BDE-154 might be due to debromination of deca-BDE in the environment, but that BTBPE was likely observed because of its use as a replacement for octaBDE.

A study assessing replacement flame retardants in the food web of San Francisco Bay found HBCD and Dechlorane Plus in sediments and wildlife, along with PBDEs (Klosterhaus, 2012). Other alternative flame retardants were detected infrequently at low concentrations or not at all. The authors suggested that samples collected soon after the phase-out of PBDEs might serve as a baseline for future monitoring.

There have been a few reports of TBBPA being detected at low levels in sharks and dolphins in Florida (Johnson-Restrepo, 2008) and in fish in China and Europe (Svhihlikova, 2014). Studies consistently find levels of TBBPA that are lower than HBCD, when TBBPA is detected. The detection limits were similar in the different studies.

Gauthier et al. (2009) reported concentrations of several brominated flame retardants in herring gull eggs and found that DBDPE levels were the highest and surpassed PBDEs in three of the sites studied. Similarly, a study of fish tissue in rivers influenced by textile manufacturing suggested that HBCD levels rose following the phase-out of penta-BDE (Chen, 2011).

The lack of any clear shift in environmental levels of flame retardants to reflect the use of replacement chemicals may arise from the short time period since the phase-out of PBDEs or the continued diffuse leaching of PBDEs from the large reservoir of products still in use.

Flame Retardants in Washington State

In Washington, PBDE flame retardants have been found in many different environmental media and appear to be a ubiquitous contaminant in aquatic systems (Ecology, 2006; Ecology, 2011). While PBDEs are well characterized, less information is available on the levels and occurrence of flame retardants used in place of PBDEs.

In the few studies conducted in Washington State, brominated and organophosphate flame retardants were consistently detected at low levels in WWTP effluent, river water, sediments, fish tissue, and osprey eggs. The following sections summarize these studies.

WWTP Effluent, Biosolids, and Stormwater

TCEP was detected in influent and effluent from WWTPs around the Puget Sound in 2008 at levels ranging from less than detection to 3,600 ng/L (Ecology, 2010). Concentrations of TCEP, the only flame retardant tested in the study, were higher in the Puget Sound influent and effluent samples than values reported in the literature from locations outside of Washington State (Ecology, 2010). TCEP was also detected in biosolids from one of the WWTPs at 1,480 ng/g. In effluent collected from Puget Sound WWTPs



Washington's Deer Lake

by Ecology (2010), 100% of samples contained TCEP, at lower levels (range = 70 to 430 ng/L).

Organo-phosphate flame retardants were consistently found in WWTP effluent measured in nine locations along the Columbia River, from Wenatchee to Longview during 2008-2009 (Morace, 2012). TCEP and TDCPP were detected in all samples, and all but one location contained tributyl phosphate (TBP) and TPP. Dechlorane Plus and Firemaster® 680 (BTBPE) were detected in solids filtered from WWTP effluent and stormwater runoff collected in the same municipalities. Pentabromotoluene was detected only in the stormwater runoff samples.

Puget Sound Tributaries

TCEP was found in surface water collected from tributaries and rivers draining to agricultural, commercial, residential, and forested land types in two Puget Sound watersheds (Ecology, 2011). Concentrations ranged from 60 to 210 ng/L.

Water and Sediment

A recent USGS study, along the lower Columbia River, analyzed several organo-phosphate flame retardants in passive samplers (Alvarez, 2014) and sediments (Counihan, 2014) between 2008 and 2010. TCPP and TDCPP were detected in passive samplers deployed along the lower Columbia River in spring 2010 (Alvarez, 2014). TPP, PBDEs and Dechlorane Plus were detected in sediment samples from the lower Columbia River as well, with TPP present in the highest concentrations (3.2 - 15.1 ng/g) (Counihan, 2014).

Sediment Cores

Freshwater sediment cores collected from three western Washington lakes showed increasing trends in concentrations of hexabromocyclododecane (HBCD) beginning in the 1960s and 1970s through recently deposited sediments (Ecology, 2014). HBCD concentrations in the upper sediments of two of the lakes – Kitsap and Sawyer Lakes – were higher than levels in ambient freshwater sediments collected outside of Washington State.

Freshwater Fish

HBCD, TBBPA, chlorinated paraffins, and PBDEs were measured in bottom-feeder fish from four freshwater locations in Washington State (Ecology, 2012). PBDEs and chlorinated paraffins were detected in all samples tested, with chlorinated paraffins in the highest amounts (320 to 1,670 ng/g) and PBDEs at lower levels (5 to 105 ng/g). HBCD was detected in all four water bodies at generally low concentrations.

TBBPA was not detected in any of the samples at reporting limits of 0.5 - 0.9 ng/g. A national probabilistic study of contaminants in fish tissue from U.S. lakes and reservoirs, which included many sites in Washington, also did not detect TBBPA in any of the fish samples (Stahl, 2009).

Osprey Eggs

Henny (2011) analyzed osprey eggs collected along the Columbia River, Spokane River, and reference lakes in Washington State and found several brominated flame retardants (including HBCD and BTBPE) at concentrations ranging from not detected to 4.3 ng/g.

Antimony in Washington State

Over 26,000 environmental samples have been analyzed for antimony in Washington State (EIM, accessed 1/22/15), primarily as part of clean-up studies or site investigations. In general monitoring studies, few water or tissue samples had antimony levels greater than the reporting limit. Antimony was detected more frequently in sediments, at levels ranging from less than 0.002 to 120 ppm (median = 0.28 ppm). The highest levels were seen in the Lower Duwamish Waterway and lakes in the northeastern part of the state. However, environmental levels of antimony are not directly related to antimony trioxide use as a flame retardant synergist. Antimony is released by humans to the environment through many sources, including combustion of fossil fuels, mining, and smelting activities (EPA, 2014g). Antimony trioxide used as a flame retardant synergist may enter the environment through wastewater treatment plant effluent and biosolids following the use and disposal of products, but no Ecology studies have been conducted to assess the contribution of this source to the environment.

Chapter 6: End of Life

Flame retardants used in products could be released to the environment at the end of the useful life of the product through the break-down and/or improper burning of the products. They could also be incorporated into new products made from recycled materials.

In Washington today, plastics and polyurethane foam probably contain the largest share of flame retardants in the waste stream (Table 5). Most of these products are landfilled. For example, auto fluff, which is mainly plastic and foam



Landfills are the final destination for many products containing flame retardants through the disposal of furniture, toys, electronics, and other items.

left over after metals have been separated from shredded scrap cars and other consumer products is used as a daily cover layer over waste in some municipal solid waste landfills.

Table 3: Waste composition analysis for the state of Washington, 2009

Waste Category	Percent of total municipal solid waste	Tons of municipal solid waste
Electronic waste	1.0	50,874
Furniture/mattresses	2.4	118,151
Carpet and carpet pad	2.7	134,290
Total percent of waste that	6.1	303,315
may contain flame retardants		

Some products are diverted for recycling, such as e-waste. Through Washington's E-Cycle program, e-waste is collected and separated into metals, plastics and glass (includes treated leaded glass) then sold as commodities to be reused as raw materials. In 2013, approximately 45 million pounds of e-waste was received. Ecology estimated that 89% of the material collected was recycled (including approximately 6.5 million pounds of plastic)

Globally, a large percentage of e-waste is sent to landfills or sent to smelting operations to recover metals. An unknown portion of the waste is recycled under unregulated conditions in certain developing countries, and the health implications of such practices are of concern (EPA 2008a).

Recycling Facilities and Recycled Products

Several studies have identified e-waste recycling facilities as "hot spots" of contamination. An unknown portion of the waste is recycled under unregulated conditions in certain developing countries, and the health implications of such practices are of concern (EPA 2008). For example, elevated concentrations of brominated flame retardants and dioxins and furans have been recorded in areas near the recycling operations (reviewed by Law and Herzke, 2011).

Concentrations of brominated dioxins and furans were also studied in a large electronics recycling facility and in surface soil surrounding a chemical production facility. Polybrominated dibenzofurans were found at elevated levels within the recycling plant and the surrounding environment for both facilities. These compounds were found to contribute significantly to toxic chemical levels affecting both workers and the environment (Ma, 2009).



What often happens to old carpet and padding when not managed appropriately.

High levels of antimony have also been found in dust from recycling facilities (Bi et al. 2011). While metals are the main incentive for e-waste recycling, plastics are also becoming increasingly recycled (Babayami, 2011). There are challenges in developing practical controls to flame retardants in the recycling system. Several studies demonstrate that flame retardants can also be introduced into products through the recycling system. These studies are mentioned in Chapter 3.

Incineration

Incineration of wastes containing halogenated compounds like flame retardants is an area of increasing concern. If burned at high temperatures, halogenated compounds are degraded to elemental compounds such as metal halides or halogen gases. These compounds can be intercepted before being released into the environment and disposed of appropriately. However, if high temperatures are not maintained, toxic halogenated compounds occur as byproducts of the combustion process. This is particularly



A computer enclosure inappropriately being used as a barbeque.

of concern during house fires and similar events where unintentional combustion occurs below the levels needed for complete destruction.

During these lower temperature combustion events, numerous halogenated compounds are formed, including halogenated dioxins and furans. Halogenated dioxins and furans have been shown to be some of the most toxic chemicals identified (Tuomisto, 2011). Dioxins and furans are highly toxic and can cause reproductive and developmental problems, damage the immune system, interfere with hormones, and cause cancer (WHO, 2014). Two commonly studied toxic dioxins and furans are shown in Figure 6.

Figure 6. Structures of two halogenated dioxins and furans

Widespread use of halogenated flame retardants have increased the formation of dioxins and furans, raising additional concerns about the impact they may have on human health and the environment. Hedman et al. (2006) found that burning chlorine-containing waste in residential stoves and boilers gave rise to high emissions of polychlorinated dioxins and furans. Wyrzykowska-Ceradini et al. (2011) found that the levels of polychlorinated and polybrominated dioxins and furans considerably increased under certain conditions at a municipal waste combustor.

Chapter 7: Safer Alternative Work

Flame retardants have been the subject of detailed scrutiny over recent years. This section discusses many of the relevant flame retardant projects but it is not intended to be an exhaustive review of all alternatives assessment (AA) work on flame retardants.

A complete alternative assessment process identifies and compares potential chemical and non-chemical alternatives currently in existence that can be used as substitutes to replace chemicals or technologies of high concern. An alternatives assessment is specific to the particular use of a chemical. Potential safer alternatives are not only products containing "drop in" safer chemicals

but also redesigned products that meet the same function. This includes redesigned products with safer alternatives and products that have designed out the need of a replacement to the chemical of concern. These assessments ensure that the safer alternatives are identified, which prevents "regrettable substitutions." A regrettable substitution occurs when a toxic chemical is replaced with another chemical of equal or greater toxicity concern.

DfE Alternatives Assessment Criteria and Process

The alternatives assessment process, the criteria used, and the hazard concern levels summarized in this report were developed by the EPA Design for the Environment (DfE) program. The DfE program was created to work '... with industry, environmental groups, and academia to reduce risk to people and the environment by finding ways to prevent pollution' (EPA, 2014a). DfE developed a seven step alternatives assessment process (EPA, 2014b):

- 1. Determine feasibility of an alternatives assessment.
- 2. Collect information on chemical alternatives.
- 3. Convene stakeholders.
- 4. Identify viable alternatives.
- 5. Conduct the hazard assessment.
- 6. Apply economic and life cycle context.
- 7. Apply the results in decision making for safer chemical substitutes.

Step 5, conduct the hazard assessment, is an important component of the AA process. To conduct a detailed hazard assessment, DfE identified a list of hazard criteria and how each hazard criterion can be separated into different levels of concern, ranging from very high to very low. DfE recently updated these criteria (EPA, 2011). Hazard assessment results are used to help decision makers evaluate the impact alternatives may have on human health and the environment with a goal of identifying a safer alternative.

One limitation of the DfE hazard screening methodology is that DfE does not compare alternatives or provide guidance on whether one alternative is 'safer' than another. DfE considers performance and cost and availability to identify alternatives for further analysis. DfE also assumes that the exposure potential for the alternatives is the same or less compared with the chemical under evaluation based upon experience and professional judgment. Companies using the DfE data should be sure that their proposed use does not contradict this assumption. DfE conducts the hazard assessment and provides the results but leaves any decision about whether one alternative is preferable over another to the assessor.

GreenScreen® Hazard Assessment

Clean Production Action (CPA), a small non-governmental organization, adapted the DfE hazard assessment steps into the GreenScreen[®] for Safer Chemicals. CPA added three endpoints (endocrine activity, reactivity, and flammability) to the original 15 hazard endpoints created by

DfE. In addition, CPA added the benchmarking process which separates chemicals into four different groups or benchmarks (Figure 7), from a chemical of high concern that should be avoided (Benchmark 1) to a chemical that is preferred and considered a safer chemical (Benchmark 4).

DfE does not make judgments on the chemicals in their alternatives assessment process but releases the assessment of each chemical and allows companies to reach their own conclusions. CPA through the benchmarking process standardized the review process and enabled users to separate alternatives into a hierarchy of increasing concern.

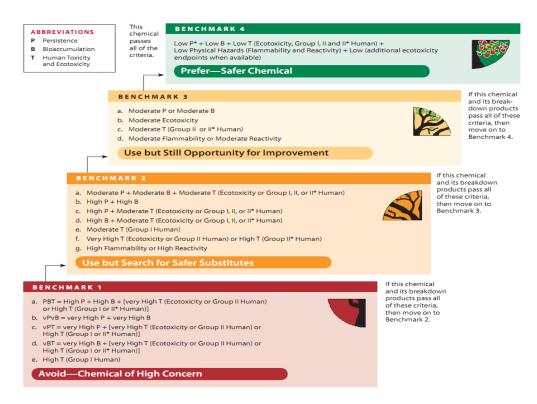


Figure 7: GreenScreen® Benchmarks

Each Benchmark is determined by analyzing specific combinations of hazard classifications. For example, the Benchmark 1 criteria align with the definition of a substance of very high concern (SVHC) under REACH. REACH identifies chemicals as SVHCs if they are persistent, bioaccumulative and toxic (PBT), carcinogenic, mutagenic or reproductive toxic (CMRs), very persistent and very bioaccumulative (vPvB), very persistent and toxic (vPT) or very bioaccumulative and toxic (vBT). 'Benchmark 1: Avoid-Chemicals of High Concern' meet one of these five criteria.

Ecology adopted the GreenScreen[®] as the primary chemical hazard assessment tool used in the alternatives assessment of the flame retardant, decabromodiphenyl ether (Ecology, 2008). This tool was chosen because it is based on the alternatives assessment work conducted by EPA's Design for the Environment program. It provides a detailed assessment of impacts on human

health and the environment and is sufficiently transparent that reviewers can understand the details behind the conclusions reached both for the toxic chemical and potential alternatives.

Alternative Assessments

Beginning in 2005, DfE conducted four alternatives assessments related to flame retardants:

- 1. An AA for the flame retardant decabromodiphenyl ether (DecaBDE),
- 2. Flame Retardant Alternatives for Hexabromocyclododecane (HBCD)
- 3. Flame Retardants Used in Flexible Polyurethane Foam: An AA Update
- 4. Flame Retardants in Printed Circuit Boards

Ecology also conducted an alternative assessment for DecaBDE using this process.

The results of some of the DfE hazard assessments were converted into GreenScreen[®] assessments by a toxicologist from Clean Production Action. The results are posted in the Interstate Chemicals Clearinghouse's (IC2) <u>Chemical Hazard Assessment Database</u> and are free to download and use (IC2, 2014). As noted previously, DfE does not pass judgment on alternatives to toxic chemicals but supplies the assessment results and allows each user to reach their own conclusion about the viability of an alternative. By converting the DfE assessment into a GreenScreen[®] Benchmark, assessors can identify the Benchmark for each chemical, and whether each chemical is a safer alternative to the toxic chemical of concern.

In addition to the certified GreenScreen® assessments, Ecology staff provided several provisional GreenScreen® Benchmark scores based on the DfE hazard assessments. Because of subtle differences between the DfE and GreenScreen® methodologies¹¹, a confirmed Benchmark cannot be assigned until the data has been reviewed by certified professionals familiar with the differences between the DfE and CPA methodologies and the appropriate GreenScreen® levels of concern assigned. Therefore, these provisional results should be used with caution.

Alternative assessments performed by Ecology and DfE and the certified and provisional GreenScreen[®] benchmark scores are discussed further in this section. The flame retardants selected included all the flame retardants detected in Washington products as well as a few examples of safer alternatives from the alternative assessment studies.

¹¹ The GreenScreen levels of concern (high, moderate, low, etc.) are assigned based on the Global Harmonized System (GHS) and the European Union's Classification and Labeling Program (CLP). DfE uses its own criteria and although these criteria are often similar to the GHS and CLP levels, there are subtle differences, which can impact the level of concern assigned in the GreenScreen[®] and the resulting Benchmark.

Washington Alternatives Assessment of decabromodiphenyl ether

In 2009, Ecology and the Washington Department of Health (Health) completed an alternatives assessment to identify safer alternatives to the brominated flame retardant deca-BDE in electronic enclosures and residential upholstered furniture (Ecology, 2009). Electronic enclosures are the housing that encloses the components of electronic products. The assessment fulfilled the requirements of Chapter 70.76 RCW, which gave Ecology the authority to ban the use of deca-BDE in electronics enclosures (particularly television and computer enclosures) and residential upholstered furniture if at least one safer alternative could be identified.



Ecology and Health limited their assessment to non-halogenated alternatives and identified at least one alternative, RDP or resorcinol bis(diphenyl phosphate), as a viable alternative to deca-BDE in electronic enclosures. RDP was identified as a certified GreenScreen[®] Benchmark 2. Use of RDP would require a product redesign-a change from HIPS or high impact polystyrene, the most common plastic used for electronic enclosures at that time, to a HIPS blend. However, Ecology was able to demonstrate that HIPS blends using RDP were being used in similar products on the market and provided equal performance while maintaining fire safety.

For residential upholstered furniture, a preferred alternative was identified that did not require chemical addition but instead could rely on barrier fabrics that also maintained performance and fire safety. Therefore, the identified safer alternative for upholstered furniture did not require the addition of flame retardants but a redesign of upholstered furniture.

DfE AA for deca-BDE

In 2014, DfE released the document, An Alternatives Assessment for the Flame Retardant Decabromodiphenyl Ether (EPA, 2014a). In the report, DfE evaluated '... 29 potentially functional, viable alternatives to deca-BDE for use in select polyolefins, styrenics, engineering thermoplastics, thermosets, elastomers, or waterborne emulsions and coatings.' The scope of this report was outlined in terms of categories of material rather than specific applications or end uses because decaBDE has been used in many different applications. Some of the applications include television enclosures, other electronic equipment, and textiles. In the report, DfE completed detailed hazard assessments of deca-BDE and 29 chemicals.

Table 4 provides provisional and certified Benchmarks for deca-BDE and four alternatives. Hazard assessments for these five chemicals appear in Appendix 2, Table 11. The DfE report

provides the full list of hazard assessments (EPA, 2014c.). DfE's report only included chemical alternatives. Alternative redesign solutions were not assessed.

Table 4: Provisional and certified GreenScreen® Benchmarks for deca-BDE and several alternatives (EPA, 2014c)

Chemical	CAS	Benchmark	Reason for Benchmark
Decabromodiphenyl Ethane	84852-53-9	1*	High PBT, vPT, High CMR
Decabromodiphenyl Ether	1163-19-5	1*	High PBT, vPT, High CMR
Ammonium polyphosphate (APP)	68333-79-9	3 ^a	Very high Persistence
Polyphosphonate	68664-06-2	3ª	Very high Persistence
Magnesium Hydroxide	1309-42-8	3ª	Very High Persistence, Moderate T

^{*}Provisional GreenScreen® result. Use with caution.

The eighteen non-halogenated alternatives identified in the DfE deca-BDE report were converted into GreenScreen® assessments and assigned Benchmarks (Figure 7). Five of the selected alternatives were 'regrettable substitutions', i.e., equally or more toxic than the chemical of concern. Eight alternatives were incrementally better (Benchmark 2) and three were considerably better (Benchmark 3). Two of the alternatives could not be assigned a Benchmark because there were too many important data gaps (Benchmark U for 'unspecified'). None of these alternatives attained a Benchmark 4 as all flame retardants had some level of concern. For those manufacturers seeking safer alternatives to toxic chemicals, all Benchmark 3 chemicals are safer alternatives.

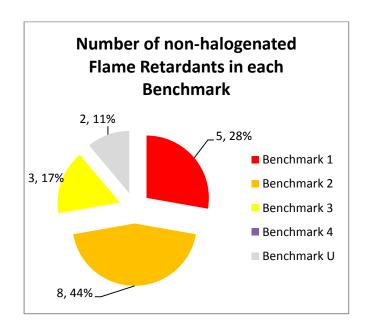


Figure 8: Benchmarks assigned to 18 of the 29 DfE deca-BDE alternatives

^a certified GreenScreen® assessments

ATO Chemical Hazard Assessment

From the deca-BDE report, ATO was converted into a GreenScreen® assessment. The summary table is shown in Figure 9. See <u>GreenScreen Assessment Acronyms</u> in <u>Appendix 1</u>.

•	Grou	roup I Human Group II Human				Group II Human								cotox	1	Fa	te	Physi	ical	
С	М	R	_	_	AT	S	ST	ı	N	SnS	SnR	IrS	lrE	AA	CA	Eo	D	В	Rx	_
1	IVI	H	ט	E	Ai	single	repeat	single	repeat	5115	SILH	ırs	IFE	AA	CA	EO	Р	В	HX	ļ
И	М	М	L	DG	L		н		L	L	DG	М	М	н	М		νH	νL	L	L

Figure 9: Certified GreenScreen® assessment of ATO

ATO was assigned a Benchmark 1, a chemical to avoid, based on its very high degree of persistence and high systemic toxicity, primarily from impacts on the lungs from inhalation of ATO particles. ATO also was assigned a high level of concern for acute aquatic toxicity. ATO is used extensively as a synergist with halogenated flame retardants, both additive and reactive.

Although ATO is in the DfE deca-BDE alternatives assessment in plastics, it was reviewed solely as a flame retardant synergist. Only one other synergist was included in the DfE assessment. An alternatives assessment is still needed to identify safer alternatives to ATO as a flame retardant synergist.

Flame Retardants Used in Flexible Polyurethane Foam

In 2014, DfE released an update of an alternatives assessment report on flame retardants used in polyurethane foam (EPA, 2014e). The assessment included all uses of flexible polyurethane foam such as upholstered furniture, child car seats, nursing pillows, and foam chairs in cars and airplanes. Nineteen alternatives were evaluated in this report: 16 individual flame retardants and three mixtures (one non-proprietary, and two proprietary). As with other reports, DfE includes a detailed hazard assessment, nine of which are shown in Table 5 but leaves any determination of whether one alternative is 'safer' than another to individual assessors. Non-chemical alternatives including product redesign were not assessed.

From the DfE report, APP, TPP, TCEP, TCPP, TDCPP, V6, IPTPP (a component of Firemaster[®] 550) were converted into GreenScreen[®] assessments. TBB and TBPH are provisional Benchmarks and identified as Benchmark 2. Firemaster[®] 550, TCEP, TDCPP, and V6 are listed in Table 5 and are certified either Benchmark 1 or Benchmark 2 chemicals (chemicals to be avoided or chemicals that should be discontinued as soon as safer alternatives are found). More information on carcinogenicity is needed to fully Benchmark TCPP. It is currently identified as a Benchmark U. Depending on the results of the carcinogenicity data, TCPP would either be a benchmark 1 or 2. It is a moderate concern for reproductive and developmental as well as a high concern for acute aquatic toxicity. All of these chemicals were found in children's products in Washington State (Ecology 2014). TCEP, for example, has a high concern for carcinogenicity, and acute aquatic

toxicity. TDCPP has a high level of concern for carcinogenicity, reproductive, and chronic aquatic toxicity. These high levels of concern indicate these alternatives are not safer flame retardants for use in polyurethane foam applications. (EPA, 2014e).

Table 5: Example Provisional and certified GreenScreen® Benchmarks for flame retardants used in Flexible Polyurethane foam (See Appendix 1 for acronyms.)

Chemical	CAS	Benchmark	Reason for Benchmark
Firemaster®550 (Mixtures of TBB, TBPH, IPTPP and TPP)	Mixture	2 ^a	Moderate PBT; High (P&B); High P, Moderate T; High B, Moderate T; Moderate CMR
ТВВ	183658-27-7	2 ^a	Moderate PBT; High (P&B); High P, Moderate T; High B, Moderate T; Moderate CMR
ТВРН	26040-51-7	2 ^a	Moderate PBT; High (P&B); High P, Moderate T; High B, Moderate T; Moderate CMR
IPTPP	68937-41-7	2 ª	Very High Aquatic Toxicity; High Systemic Toxicity, and Neurotoxicity; Moderate CMR
TPP	115-86-6	2 a	Moderate CMR
TCEP	115-96-8	1ª	High CMR (Carcinogenicity)
TCPP	13674-84-5/6145-73-9	U ^b	Lacking Carcinogenicity Data
TDCPP	13674-87-8	1 ^a	High CMR (Carcinogenicity); very High P, High T
V6	38051-10-4	2ª/1 ^{TP} **	Moderate CMR
APP	68333-79-9	3 a	Very High Persistence

^a certified GreenScreen[®] assessments

Flame Retardants Used in Expandable Polystyrene Foam for Insulation

In 2014, DfE released an alternatives assessment report on the use of the flame retardant HBCD (EPA, 2014d). DfE did not evaluate all uses of HBCD but limited its assessment to the use of HBCD as a flame retardant in expandable and extruded polystyrene foam building insulation (EPS and XPS, respectively), which accounts for more than 95% of HBCD use.

^b 'unspecified' for important hazard data missing so no Benchmark could be assigned.

^{**}Ecology reassigned the Benchmark to a 1_{TP} because TCEP is an impurity in V6. This data was not included in the EPA Alternative Assessment.

Due to the limited scope of HBCD use in the report, only three HBCD alternatives were evaluated because '...flame retardants for EPS and XPS foam must allow the material to comply with fire safety codes while not compromising the performance of the foam' (EPA, 2014d).

The HBCD hazard assessment and one of the alternatives is shown in <u>Table 6</u>. HBCD has a high level of concern for developmental toxicity and persistence, as well as both acute and chronic aquatic toxicity and ability to bioaccumulate. Although a GreenScreen[®] conversion has not been completed, HBCD would likely be assigned a Benchmark 1 based on the DfE results.

All three HBCD alternatives were brominated and two contained tetrabromobisphenol A (TBPPA) as a component of the polymer chain (reactive flame retardant compared with the additive flame retardant HBCD). Of the three flame retardants assessed, '...the hazard profile of the butadiene styrene brominated copolymer (CASRN 1195978-93-8) shows that this chemical is anticipated to be safer than HBCD for multiple endpoints.' DfE further indicated however, that '...this alternative is inherently persistent and its long-term behavior in the environment is not currently known' (EPA, 2014d).

Table 6 provides provisional Benchmarks assigned to HBCD and one of the alternatives.

Table 6: Provisional GreenScreen® Benchmarks for hexabromocyclododecane and an alternative from EPA, 2014d assessment results (See Appendix 1 for acronyms.)

Chemical	CAS	Benchmark	Reason for Benchmark
HBCD	25637-99-4/3194-55-6	1*	PBT; vBT; High CMR (Developmental)
Butadiene styrene brominated copolymer	1195978-93-8	2*	Very high P, Moderate T

^{*}Provisional GreenScreen® result. Use with caution.

Flame Retardants Used in Printed Circuit Boards

In 2014, DfE released a draft update to their 2008 report (EPA, 2014f) assessment of flame retardants in printed circuit boards. DfE assessed ten flame retardants that can be used in the manufacture of printed circuit boards. Table 9 in Appendix 2 lists the hazard assessments of TBBPA and two alternatives dihydrooxaphosphaphenanthrene (DOPO) and Fyrol PMP, an aromatic phophonate oligomer (EPA, 2014f). All three of these chemicals are used in the reactive form.

Using TBBPA data from DfE, results for the monomer were translated into a GreenScreen® assessment and assigned a Benchmark 1_{TP} based on concerns associated with bisphenol A, a Benchmark 1 chemical, as a potential degradation product which could occur under anaerobic conditions. Provisional GreenScreens indicate that DOPO and Fyrol PMP are likely to be identified as Benchmark 2 chemicals. Several other chemicals are likely to have a Benchmark higher than 1 indicating they are also likely to be safer alternatives to TBPPA. However, certified GreenScreen® assessments are required to confirm this assumption.

Table 7 provides provisional Benchmarks assigned for TBBPA and two alternatives.

Table 7: Provisional and certified GreenScreen® Benchmarks for for monomers of tetrabromobisphenol A and two alternatives (See <u>Appendix 1</u> for acronyms.)

Chemical	CAS	Benchmark	Reason for Benchmark
TBBPA	79-94-7	$1_{TP}{}^a$	High CMR Toxicity of degradation product BPA
DOPO	35948-25-5	2*	High P, Moderate T; High P, Moderate Ecotoxicity
Fyrol PMP	Proprietary	2*	Very high P, High B

^{*}Provisional GreenScreen® result. Use with caution. a certified GreenScreen® assessments

Additional Alternatives Assessments

As indicated previously, other alternatives assessments are available. However, many of these assessments are either based on the work described above or are sufficiently dated to have concerns about their current validity. As an example of the former, the non-governmental organization BizNGO conducted an alternatives assessment of deca-BDE to evaluate the ability of member companies to comply with the California Environmental Protection Agency's Safer Product Regulations (BizNGO, 2014). While some new cost and availability data was created as part of this assessment, all hazard information was taken from previous alternatives assessments.

The Danish Environmental Protection Agency conducted an alternatives assessment of deca-BDE in 2006 (DEPA, 2006). Although this assessment was important foundational work on deca-BDE alternatives assessments, subsequent work has provided substantive updates to concerns associated with deca-BDE.

Chapter 8: Existing Regulatory Programs

This section describes major existing regulations relevant to halogenated flame retardants and antimony trioxide at the federal, state, and international levels. While this section aims to summarize the most important regulations in this area, it is not an exhaustive review of all of the regulations pertinent to these chemicals.

Domestic Regulations on Halogenated Flame Retardants

Children's Sleepwear

Halogenated flame retardants began receiving regulatory attention in the 1970s when research raised concern about chemicals that were being used to meet flame retardant requirements for children's sleepwear. One chemical at issue (tris(2,3-dibromopropyl) phosphate (Tris-BP), commonly known as "brominated Tris,") was ultimately restricted by a Significant New Use Rule under the Toxic Substances Control Act (TSCA). TDCPP was used briefly as a replacement. While manufacturers voluntarily withdrew TDCPP from use in children's sleepwear, its use in other applications continued.¹²

U.S. Restrictions on Flame Retardant Use

Action	Flame Retardants
National voluntary agreements	pentaBDE, decaBDE, octaBDE
EPA restrictions	Tris-BP
U.S. State restrictions*	HBCD, pentaBDE, octaBDE, decaBDE, TBBPA, TCEP, TDCPP ATO

^{*} See Table 10. For more detailed information

PBDEs

More recently, concern about the safety of PBDEs led to a wave of regulatory activity. Washington joined a dozen other states in passing laws specifically addressing PBDEs, and was the first to restrict deca-BDE. Washington's law prohibits the use of penta- and octa-BDE, and places restrictions on deca-BDE in mattresses, residential upholstered furniture, and electronic enclosures for computers and televisions. He have required Ecology to issue a finding that safer alternatives to deca-BDE were available before the restrictions took effect. He

¹² Cordner A, Mulcahy M, Brown P. (2013) Chemical Regulation on Fire: Rapid Policy Advances on Flame Retardants. Environ. Sci. Technol. 2013, 47, 7067–7076. Available at: dx.doi.org/10.1021/es3036237

¹³ National Conference of State Legislatures. (2012) State Regulation of Flame Retardants in Consumer Products. Available at: www.ncsl.org/research/environment-and-natural-resources/flame-retardants-in-consumer-products.aspx

¹⁴ Washington Department of Ecology. Available at: www.ecy.wa.gov/programs/swfa/pbt/pbde.html

¹⁵ Washington Department of Ecology. Alternatives to Deca-BDE in Televisions and Computers and Residential Upholstered Furniture. Available at: https://fortress.wa.gov/ecy/publications/summarypages/0907041.html

Washington lists penta-BDE, octa-BDE, and deca-BDE as PBT chemicals. ¹⁶ Deca-BDE is listed as a CHCC under Washington's Children's Safe Product Act, which requires manufacturers to report if it is present in children's products. ¹⁷

PBDEs have also been addressed at the federal level through agreements with manufacturers. Manufacturers of penta-BDE and octa-BDE agreed to voluntarily stop producing these two forms of PBDEs by the end of 2004. In 2009, three major producers of deca-BDE arrived at an agreement with EPA to stop producing, importing, and selling deca-BDE by the end of 2012.¹⁸

Chlorinated Flame Retardants

Some of the flame retardant chemicals at issue in the 1970s controversy over children's sleepwear, notably TCEP and TDCPP, have recently re-emerged as a target for regulation. In 2013, Maryland¹⁹ barred the use of TCEP in certain children's products, while Vermont enacted restrictions on both TCEP and TDCPP in children's products, and required additional study of TCPP.²⁰ New York²¹ enacted restrictions on TCEP in 2013, and added restrictions on TDCPP to the law in 2014.

TDCPP in children's foam-padded sleeping products was named as one of three initial priority products for California's Safer Consumer Product regulations, which target chemical uses for safer alternatives assessment and substitution.²² This followed the listing of TDCPP as a carcinogen under the state's Proposition 65 law, which requires notification to citizens of exposures to chemicals known to the State of California to cause cancer, birth defects, or reproductive harm.²³ TCEP is also included on the Proposition 65 list as a carcinogen (Table 7).

TCEP and TDCPP are listed as CHCCs under Washington's Children's Safe Product Act, which requires manufacturers to report if they are present in children's products.²⁴

www.epa.gov/opptintr/existingchemicals/pubs/actionplans/deccadbe.html

http://mgaleg.maryland.gov/webmga/frmMain.aspx?pid=billpage&stab=03&id=hb0099&tab=subject3&ys=2013rs

¹⁶ Washington Department of Ecology. Available at: www.ecy.wa.gov/programs/swfa/pbt/list.html

¹⁷ Washington Department of Ecology. Available at: www.ecy.wa.gov/programs/swfa/cspa/chcc.html

¹⁸ U.S. Environmental Protection Agency. Available at:

¹⁹ State of Maryland. Available at:

²⁰ State of Vermont. Available at: www.leg.state.vt.us/database/status/summary.cfm?Bill=S%2E0081&Session=2014

²¹ State of New York. Available at: http://assembly.state.ny.us/leg/?term=2013&bn=S03703

²² California Department of Toxic Substances Control, Available at: www.dtsc.ca.gov/SCP/index.cfm

²³ California Office of Environmental Health Hazard Assessment. Available at: http://oehha.ca.gov/Prop65/prop65 list/102811list.html

²⁴ Washington Department of Ecology. Available at: www.ecy.wa.gov/programs/swfa/cspa/chcc.html

TBBPA

TBBPA is listed as a PBT chemical by the State of Washington²⁵ and as a CHCC.¹⁸ EPA identified TBBPA and related chemicals as candidates for potential future risk assessments under TSCA in its 2013 TSCA Work Plan.²⁶

HBCD

HBCD is listed as PBT chemical and a CHCC by the State of Washington. EPA released a chemical action plan in 2010 identifying regulatory actions it intends to pursue for HBCD under the Toxics Substances Control Act (TSCA), including adding HBCD to its list of chemicals of concern, adopting a significant new use rule for use in consumer textiles, adding HBCD to the toxics release inventory (TRI), or regulating it more comprehensively under TSCA Section 6(a). EPA's Design for the Environment (DfE) program released an alternatives assessment on HBCD in July 2014. 28

Regulations on Antimony

Antimony trioxide is included on the Proposition 65 list in California as a carcinogen (<u>Table 7</u>). The ASTM F963 Standard Consumer Safety Specification for Toy Safety, which manufacturers of toys are required to meet under regulations established by the U.S. Consumer Product Safety Commission (CPSC), includes a migration limit of 60 parts per million (ppm) for antimony.²⁹

The American Conference of Governmental and Industrial Hygienists and the Occupational Safety and Health Administration (OSHA) set limits for occupational inhalation exposure.³⁰ EPA has set a Maximum Contaminant Level (mcl) of six parts per billion (ppb) for antimony in drinking water.³¹

www.epa.gov/oppt/existingchemicals/pubs/2013wpractivities.html

²⁵ Washington Department of Ecology. Available at: www.ecy.wa.gov/programs/swfa/pbt/list.html

²⁶ U.S. Environmental Protection Agency. Available at:

²⁷ U.S. Environmental Protection Agency. Available at: www.epa.gov/oppt/existingchemicals/pubs/actionplans/hbcd.html

²⁸ U.S. Environmental Protection Agency. Available at: www.epa.gov/dfe/pubs/projects/hbcd/about.htm

²⁹ ASTM International. ASTM F963-11: Standard Consumer Safety Specification for Toy Safety. www.astm.org/Standards/F963.htm

 $^{^{30}}$ U.S. Environmental Protection Agency. Antimony Compounds. Available at: $\underline{www.epa.gov/ttnatw01/hlthef/antimony.html}$

³¹ U.S. Environmental Protection Agency. Basic Information about Antimony in Drinking Water. Available at: http://water.epa.gov/drink/contaminants/basicinformation/antimony.cfm

International Regulations on Halogenated Flame Retardants

European Union

The European Union's Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation evaluates chemical data provided by industry, assesses chemical risks, and makes decisions on appropriate use of specific chemicals of concern. REACH establishes a list of substances of very high concern (SVHCs) consisting of:

- Persistent, bioaccumulative, and toxic chemicals (PBTs).
- Carcinogenic, mutagenic, and reproductive toxicants (CMRs).
- Very persistent or very bioaccumulative toxic chemicals (vPT or vBT).
- Endocrine active chemicals.

Inclusion on the list of SVHCs is the first step of the authorization procedure, which ensures necessary controls on the use of chemical substances until they are ultimately replaced with safer substances. Substances may also become subject to a restriction (limit or ban on the manufacture or marketing of a substance). Currently the European Chemicals Agency (ECHA), the agency responsible for implementing REACH, has identified 155 SVHCs (as of June 16, 2014). At least four of these SVHCs (trixylyl phosphate, deca-BDE, TCEP and HBCD are used as flame retardants. (Table 5) A restriction proposal for deca-BDE was issued in August 2014. HBCD³⁴ and TCEP³⁵ have been proposed for phase-out by 2015, after which only authorized uses would be permitted. There are no ongoing processes under REACH for TBBPA.

The EU's RoHS (Restriction on Hazardous Substances) directive controls the use of certain chemical substances in electrical and electronic products. PBDEs were banned for use in these products in 2008.³⁷

TCEP, TDCPP, and TCPP are restricted in toys in the EU to 5 mg/kg under the EU Commission's Toy Directive. ³⁸

³² European Chemicals Agency. Available at: http://echa.europa.eu/web/guest/regulations/reach/authorisation

³³ European Chemicals Agency. Available at: http://echa.europa.eu/regulations/reach/restriction

³⁴ Bromine Science & Environmental Forum. Available at: www.bsef.com/regulation/europe

³⁵ Chemical Watch (Subscription Required). (2012) EU Commission Agrees on Eight Substances for Authorisation. Available at: http://chemicalwatch.com/9964/eu-commission-agrees-eight-substances-for-authorisation

³⁶ Bromine Science & Environmental Forum. Available at: www.bsef.com/regulation/europe

³⁷ European Commission. Directive 2011/65/EU. Available at: http://ec.europa.eu/enterprise/policies/european-standards/harmonised-standards/restriction-of-hazardous-substances/index en.htm

³⁸ European Commission. Directive 2014/79/EU. Available at: http://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=OJ:JOL 2014 182 R 0012&from=EN

International Restrictions on Flame Retardant Use

Regulatory Action	Flame Retardants
European directives (REACH or toys)	decaBDE, HBCD, PBDEs TCEP, TCPP, TDCPP
Stockholm or Rotterdam Conventions	pentaBDE and tetraBDE, HBCD, brominated Tris

International

The Stockholm Convention on Persistent Organic Pollutants is an international treaty that targets persistent organic pollutants (POPs), a synonym for persistent, bioaccumulative toxic chemicals for phase-out from production and use. Penta-BDE and tetra-BDE were added to the Stockholm Convention in amendments adopted in 2011.³⁹ HBCD is currently proposed for listing under the Convention.⁴⁰ The United States has not ratified the Stockholm Convention.

The Rotterdam Convention is a multilateral treaty to promote prior-informed consent and information exchange in the importation and exportation of chemicals. ⁴¹Brominated-Tris (tris (2,3,dibromopropyl) phosphate) is included in the Rotterdam Convention. ⁴² The United States has not ratified the Rotterdam Convention.

Chapter 9: Conclusions

- Flame retardants are used in a wide variety of products including foam, plastics, and textiles. Many are high production volume chemicals. There are many commercial flame retardant chemicals available and little public information is available for many of them on their use or expected impacts on human health and the environment.
- Manufacturers appear to have largely moved away from PBDEs and products are compliant
 with the Washington and other states and countries PBDE bans. Manufacturers are using
 alternative flame retardants to PBDEs, some of which are chemicals that are of equal or
 greater toxicity concern, known as regrettable substitutions.

www.pic.int/TheConvention/Overview/Howitworks/tabid/1046/language/en-US/Default.aspx

³⁹ Stockholm Convention. The New POPs under the Stockholm Convention. Available at: http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx#LiveContent[4-5-BDE]

⁴⁰ Stockholm Convention. Chemicals Proposed for Listing Under the Convention. Available at: http://chm.pops.int/TheConvention/ThePOPs/ChemicalsProposedforListing/tabid/2510/Default.aspx

⁴¹ Rotterdam Convention. Available at:

⁴² Rotterdam Convention. Annex III Chemicals. Available at: www.pic.int/TheConvention/Chemicals/AnnexIIIChemicals/tabid/1132/language/en-US/Default.aspx

- TBBPA is mainly used in plastics and is used in both the reactive and additive forms. It was not found in the children's products sampled in Washington. It was found in small electronics. Studies in Europe and Australia have identified TBBPA in electronics and a limited number of children's products.
- Antimony was found in electronics, small appliances, and a flame-resistant tarp purchased in Washington at sufficient concentrations to suggest that some products contain antimony trioxide. It was found in limited plastic samples and was mainly associated with halogenated flame retardants. Antimony has been reported in a few products through CSPA reporting at the levels that would be used as a flame retardant synergist.
- Some flame retardants are ubiquitous in the indoor and outdoor environment:
 - Brominated and organophosphate flame retardants such as TDCPP, TBPP, and TBPH are detected in indoor dust such as in homes and child-care centers.
 - Washington monitoring studies found PBDEs are widely present in both biological and physical media. Insufficient information is available on alternative flame retardants in the environment, primarily because few studies include analysis of a wide range of flame retardants. Based on limited sampling, organophosphates, Dechlorane Plus, HBCD, and chlorinated paraffins are consistently detected in environmental samples collected in Washington.
- Dust is an important pathway for human exposure to flame retardants. Children are
 particularly susceptible to toxic chemical exposure through indoor dust. Additional exposure
 potential exists as PBTs remain in the environment for many years beyond their predicted
 end-of-life.
- Additive flame retardants are more likely to be released into the environment, compared to reactive flame retardants.
- Many halogenated flame retardants are found in humans. Children have also been found to contain higher levels of flame retardants compared to adults. Children are more sensitive to the adverse health effects because they are still developing.
- Large amounts of flame retardants (i.e., more than 1% by weight) are needed in many products to be effective. Flame retardants present in products at less than 0.1% (or 1000 ppm) are likely due to contamination and not due to intentional use.
- Flame retardants are present in consumer and children's products purchased in Washington. Not all flame retardants used were identified. Of the nine flame retardants or mixtures

identified in Washington products in percent levels, six have been identified as certified or provisional GreenScreen® Benchmark 1 chemicals (Chemicals to avoid) and two have been provisionally identified as Benchmark 2 chemicals. More information on carcinogenicity is needed to fully assess the hazard characteristics of TCPP. Depending on the results of the carcinogenicity data, TCPP would either be a Benchmark 1 or 2. The reasons for the Benchmark scores are in Table 6.

Table 8: Summary of chemicals detected in WA products (bolded if detected in percent levels)

Chemical	Benchmark	Reason for Benchmark	Product type	Matrix
Firemaster*550/600, (Mixtures of TBB, TBPH, IPTPP and TPP)	2 ^a	Moderate PBT; High (P&B); High P, Moderate T; High B, Moderate T; Moderate CMR	Children's Product	Foam
ТВВРА	$1_{TP}{}^a$	CMR Toxicity of degradation product BPA	Electronics	Plastic
HBCD	1*	PBT; vBT; High CMR (Developmental)	Protective Clothing, Children's Products	Plastic, Styrofoam
Antimony Trioxide	1 ^a	vPT	Electronics	Plastic
TCEP	1 ª	High CMR (Carcinogenicity)	Children's Products	Foam
ТСРР	U ^b	Lacking Carcinogenicity data	Children's Product	Foam
TDCPP	1 ª	High CMR (Carcinogenicity); very High P, High T	Children's Product, Furniture, Carpet Padding, Tents	Foam, Fabric
V6	2ª/1 _{TP} **	Moderate CMR	Children's Product, Tent, carpet padding	Foam, Fabric
TPP	2 ^a	Moderate CMR	Children's Product, Electronics	Foam, Plastic

^{*}Provisional GreenScreen® result. Use with caution. a certified GreenScreen® assessments

Product type and matrix are bolded if analyte was found in the percent level.

^b 'unspecified' for important hazard data missing so no Benchmark could be assigned.

^{**}Ecology reassigned the Benchmark to a 1_{TP} based on TCEP being an impurity in V6. This data was not included in the EPA Alternative Assessment. TCEP is a CMR.

GreenScreen® Benchmarks

Benchmark 1: Avoid-Chemical of High Concern

Benchmark 2: Use-but search for Safer Alternatives

Benchmark 3: Use-but still Opportunity for Improvement

Benchmark 4: Prefer-Safer Chemical

- TBBPA has been identified as a GreenScreen® Benchmark 1_{TP}. The TP designation indicates the chemical is likely to break down into chemicals that would designate as Benchmark 1.
- Although antimony trioxide is not a PBT chemical, it is very persistent and has negative effects on human development and aquatic organisms. Through the GreenScreen[®] process, it has been scored a Benchmark 1 chemical, which is a chemical to avoid.
- All of the flame retardants found in percent levels in Washington products (Table 8) in foam have safer alternatives identified.
- Flame retardant standards and regulations have provided the impetus for the development
 and use of alternative chemical flame retardants. Federal and state laws have targeted specific
 flame retardants in certain products but the safety of the alternatives is not adequately
 assessed. Recent regulatory changes in California reduced the requirement for flame
 retardants in furniture and other foam products.
- Flame retardants can be released into the environment at their end of life through breakdown and/or burning of products. Products containing halogens that are incinerated can create other highly toxic PBT chemicals such as dioxins and furans. Flame retardants can also be found in products that use recycled content.

Chapter 10: Summary of Recommendations

Flame Retardants in Children's Products and Furniture

1. Establish a limit of 1,000 parts per million (ppm) for each of the following flame retardants that are commonly used in children's products and furniture. This limit restricts use of these chemicals, but is sufficiently high enough to support continued recycling of products that contain them.

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a. TDCPP (CAS #13674-87-8) d. TCPP (CAS #13674-84-5) g. TBPH (CAS #26040-51-7) b. TPP (CAS #115-86-6) e. V6 (CAS #385051-10-4) h. IPTPP (CAS #68937-41-7) c. TCEP (CAS #115-96-8) f. TBB (CAS #183658-27-7)
```

2. Establish a limit of 1,000 ppm for each of the following flame retardants that could be used in textiles in children's products and furniture. While these two chemicals are not commonly used in children's products and furniture, they could be introduced as regrettable substitutions. Restrictions on the use of TBBPA in children's products and furniture should be limited to the additive form.

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a. TBBPA (CAS # 79-94-7)b. HBCD (CAS # 25637-99-4 and CAS #3194-55-6)
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Tetrabromobisphenol A (TBBPA)

- 1. Require that manufacturers report to Ecology on their use of additive TBBPA in consumer products sold in Washington levels exceeding 1,000 ppm. This requirement would not apply to manufacturers of children's products who already report their use of TBBPA under the CSPA.
- 2. Manufacturers should be encouraged to use identified safer alternatives to TBBPA.
- 3. Ecology should work with stakeholders to gather more information about the use of both reactive and additive TBBPA in electronics as well as other products where TBBPA is used.

Antimony as Antimony Trioxide, or ATO

1. Require manufacturers to disclose their use of ATO in products (other than children's products where such reporting is already required).

Other General Recommendations for Flame Retardants

- 1. Ecology recommends that the Legislature direct Ecology to conduct a comprehensive chemical action plan on flame retardants used in electronics and other products known to contain halogenated flame retardants other than children's products and furniture. As a needed first step, Ecology further recommends that the Legislature should require that manufacturers report to Ecology on their use of flame retardant chemicals in products sold in Washington (other than children's products and furniture) at levels that exceed 1,000 ppm.
- 2. Enact policies that provide incentives to use alternative assessments and safer alternatives in consumer products and manufacturing processes.

- 3. Ecology should work with the Washington Department of Health to identify key data gaps in understanding human exposure to flame retardant chemicals, including how biomonitoring could address these gaps and what studies should be performed.
- 4. Align state purchasing policies to support manufacturers that are using the safest identified alternatives.

Appendix 1: Acronyms

Acronyms used in this document

	3.0 0 3.1 11.1 11.1 11.1 11.1 11.1 11.1
AA	Alternatives assessment
ABS	Acrylonitrile butadiene styrene
ASTM	American Society for Testing and Materials
В	Bioaccumulative
BDE209	Decabrominated diphenyl ether
CAP	Chemical action plan
CBCA	California Bureau of Consumer Affairs
CDC	Centers for Disease Control
CHCC	Chemical of High Concern to Children
CMR	Carcinogenic, mutagenic, and reproductive
СРА	Clean Production Action
CPAI	Canvas Products Association International (now IFAI)
CPSC	Consumer Product Safety Commission
CSPA	Children's Safe Product Act
DfE	Design for the Environment
ECHA	European Chemical Agency
DSL	Domestic substance list
EPA	Environmental Protection Agency
EU	European Union
HIPS	High impact polystyrene
HPV	High production volume
IARC	International Agency for Research on Cancer
IC2	Interstate Chemical Clearinghouse
IFAI	Industrial Fabrics Association International (formerly CPAI)
MCL	Maximum contaminant level
NFPA	National Fire Protection Association
NHANES	National Health and Nutrition Examination Survey
OECD	Organization of Economic and Cooperative Development
OSHA	Occupational Safety and Health Administration
Р	Persistent
PBT	Persistent, bioaccumulative, and toxic
POP	Persistent organic pollutants

nnh	Parts par hillian
ppb	Parts per billion
ppm	Parts per million
RCW	Revised Code of Washington
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RoHS	Restriction on Hazardous Substances
SVHC	Substances of Very High Concern
Т	Toxic
ТВ	Technical bulletin
TRI	Toxic Release Inventory
TSCA	Toxic Substances Control Act
UL	Underwriters Laboratory Inc.
"U-OPFR"	Unidentified chlorinated organophosphate flame retardant 2,2-bis(chloromethyl)propane- 1,3-diyl tetrakis(1-chloropropan-2-yl)bis(phosphate)
USEPA	United States Environmental Protection Agency
vBT	Very bioaccumulative toxic
vPT	Very persistent toxic
WAC	Washington Administrative Code
XRF	X-ray fluorescence

Chemical acronyms used in this report (name and CAS number)

Acronym	Chemical Name	CAS Number	Flame Retardant Class
APP	Ammonium polyphosphate	68333-79-9	Inorganic Flame Retardant
ATO	Antimony trioxide	1309-64-4	Synergist
BDCPP	bis(1,3-dichloro-2-propyl) phosphate	72236-72-7	Halogenated
BDE 153	2,2',4,4',5,5'-hexabromodiphenyl ether	68631-49-2	Halogenated
BDE 154	2,2',4,4',5,6'-hexabromodiphenyl ether	207122-15-4	Halogenated
BDE 99	2,2',4,4',5-pentabromodiphenyl ether	60348-60-9	Halogenated
BDP	Bisphenol A bis (diphenylphosphate)	5945-33-5	Non-Halogenated
ВТВРЕ	1,2-Bis(2,4,6-tribromophenoxy)ethane or FireMaster® 680	37853-59-1	Halogenated
DBDPE	Decabromodiphenylethane	84852-53-9	Halogenated
Deca-BDE	Decabrominated diphenyl ether (BDE 209)	1163-19-5	Halogenated
DOPO	6H-Dibenz(C,E)(1,2)oxaphosphorin-6-oxide	35948-25-5	Non-Halogenated

Acronym	Chemical Name	CAS Number	Flame Retardant Class
DP	Dechlorane Plus or bis(hexachlorocyclopentadieno)cyclooctane	13560-89-9	Halogenated
DPP	diphenyl phosphate	838-85-7	Non-Halogenated
EHDPP	2-ethylhexyl diphenyl phosphate	1241-94-7	Non-Halogenated
Fyrol			
HBCD	Hexabromocyclododecane	3194-55-6	Halogenated
HBCD	Hexabromocyclododecane	25637-99-4	Halogenated
HCDBCO	Hexachlorocyclopentadienyl- dibromocyclooctane	51936-55-1	Halogenated
IPTPP	Isopropylphenyl phosphate or Isopropylated triaryl phosphate or Isopropylated triphenyl phosphate	68937-41-7	Non-Halogenated
octa BDE	Octabrominated diphenyl ether	32536-52-0	Halogenated
PBB	Polybrominated biphenyl	N/A	Halogenated
PBDE	Polybrominated diphenyl ether	N/A	Halogenated
PBEB	Pentabromoethylbenzene	85-22-3	Halogenated
penta BDE	Pentabrominated diphenyl ether	32534-81-9	Halogenated
RDP	Resorcinol bis (diphenyl-phosphate)	57583-54-7	Non-Halogenated
SCCP	Short chain chlorinated paraffins (C10-13)	85535-84-8	Halogenated
TBB	(2-ethylhexyl)-2,3,4,5-tetrabromobenzoate	183658-27-7	Halogenated
TBBPA	Tetrabromobisphenol A	79-94-7	Halogenated
TBECH	Tetrobromoethylcyclohexane or 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	3322-93-8	Halogenated
TBOEP	Tris(2-butoxyethyl) phosphate	78-51-3	Non-Halogenated
TBP	Tributyl phosphate	126-73-8	Non-Halogenated
ТВРН	Bis(2-ethylhexyl)-2,3,4,5- tetrabromophthalate	26040-51-7	Halogenated
TBPP	tris(4-(tert-butyl)phenyl phosphate	78-33-1	Non-Halogenated
TCEP	Tris(2-chloroethyl) phosphate	115-96-8	Halogenated
TCP	Tri-para-cresyl phosphate	78-32-0	Non-Halogenated
TCPP	Tris(1-chloro-2-propyl) phosphate	13674-84-5	Halogenated
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	Halogenated
Tetra BDE	2,2',4,4',-tetrabromodiphenyl ether	5436-43-1	Halogenated
TPP	Triphenyl phosphate	115-86-6	Non-Halogenated

Acronym	Chemical Name	CAS Number	Flame Retardant Class
Tris-BP	Tris(2,3-dibromopropyl)phosphate Or "brominated Tris"	126-72-7	Halogenated
TTBP - TAZ	2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine	25713-60-4	Halogenated
V6	Antiblaze® V6 or 2,2- bis(chloromethyl)propane-1,3-diyltetrakis (2-chloroethyl) bisphosphate	385051-10-4	Halogenated
	Aluminum trihydroxide	21645-51-2	Inorganic Flame Retardant
	Chlorinated alkenes (C12-13)	71011-12-6	Halogenated
FM 550	Firemaster® 550 (mixture of TPP, TBPH, IPTPPs and TBB)	N/A	Halogenated Mixture

GreenScreen Assessment Acronyms

(AA)	Acute Aquatic Toxicity	(IrS)	Skin Irritation/Corrosivity
(AT)	Acute Mammalian Toxicity	(M)	Mutagenicity and Genotoxicity
(B)	Bioaccumulation	(N)	Neurotoxicity
(C)	Carcinogenicity	(P)	Persistence
(CA)	Chronic Aquatic Toxicity	(R)	Reproductive Toxicity
(Cr)	Corrosion/ Irritation (Skin/ Eye)	(Rx)	Reactivity
(D)	Developmental Toxicity	(SnS)	Sensitization- Skin
(E)	Endocrine Activity	(SnR)	Sensitization- Respiratory
(F)	Flammability	(ST)	Systemic/Organ Toxicity
(IrE)	Eye Irritation/Corrosivity		

Appendix 2: Other Tables

Table 9: Washington 2012-2013 samples – Analytes detected in products (children's products are denoted in blue)

derioted in blacy			
Sample	Matrix	Product Description	Analyte(s) Detected (greater
			than 0.2%)
2012-2013 Study Sa	mples		
CA002-F01	Fabric	Tent	TDCPP, V6
CA002-F02	Fabric	Tent	TDCPP
CA001-F01	Fabric	Tent Floor Liner	TDCPP
TR103-F01	Foam	Baby Carrier	V6, TCEP
TG027-F01	Foam	Booster Seat	TDCPP, TCPP
TG028-F02	Foam	Changing Pad	TDCPP, TCPP
TG024-F02	Foam	Changing Mat	TDCPP, TCPP
TR015-F01	Foam	Changing Pad	ТСРР
OS003-F03	Foam	Child's Chair	TDCPP, TCPP, TCEP
TR098-F01	Foam	Child's Chair	TDCPP, V6, TCPP, TCEP
OS001-F01	Foam	Child's Chair	V6, TCPP, TCEP
WM094-F01	Foam	Child's Chair	ТСРР
AM009-F01	Foam	Child's Chair	TPP
TG031-F01	Foam	Child's Chair	TPP, Bromine XRF, confirmed as Firemaster® 550 ²⁰¹⁴
AM008-F01	Foam	Child's Chair	TPP, Bromine XRF, confirmed as Firemaster® 550 ²⁰¹⁴
PB000-F01	Foam	Child's Chair	TPP, Bromine XRF, confirmed as Firemaster® 600 ²⁰¹⁴
OS002-F01	Foam	Child's Chair	TDCPP, TCPP
OS004-F01	Foam	Child's Chair Accessory	TDCPP
TR017-F01	Foam	Crib Wedge	TDCPP, TCPP
TR016-F01	Foam	Portable Crib Pad	TDCPP, TCPP
HD001-F01	Foam	Carpet padding	TDCPP, TPP
HD000-F01	Foam	Carpet padding	TDCPP
LW000-F01	Foam	Carpet padding	TDCPP
PO001-F01	Foam	Seat Cushion	TDCPP, TCPP
CT003-F01	Foam	Chair Pad	TDCPP, TCPP
LW001-F01	Foam	Carpet padding	TDCPP
GR003-F01	Plastic	Protective Glove	HBCD
WS002-F01	Plastic	Car charger	ТВВРА

Sample	Matrix	Product Description	Analyte(s) Detected (greater than 0.2%)
WM068-F03	Plastic	Heated mattress foot warming pad controller (bottom)	ТВВРА
OM003-F02	Plastic	Shredder	ТВВРА
OM000-F02	Plastic	Battery Charger	TBBPA , Antimony ²⁰¹⁴
OM005-F08	Plastic	LCD Monitor	TPP, Bromine XRF
WM066-F01	Plastic	Battery Charger	ТРР
BB000-F04	Plastic	Dehydrator	Antimony ²⁰¹⁴ , Bromine XRF
TG054-F01	Plastic	Power Strip	Antimony ²⁰¹⁴ , Bromine XRF
BL009-F02	Plastic	Electric Blanket controller	Antimony ²⁰¹⁴ , Bromine XRF
WM068-F02	Plastic	Heated mattress foot warming pad controller (top)	Antimony ²⁰¹⁴ , Bromine XRF
CT009-F03	Plastic	LED TV	Antimony ²⁰¹⁴ , Bromine XRF
BL005-F01	Plastic	Flat Iron	Antimony ²⁰¹⁴ , Bromine XRF*
TG056-F01	Plastic	Space Heater	Antimony ²⁰¹⁴ , Bromine XRF
FM043-F01	Plastic	Clothing Iron	Antimony ²⁰¹⁴ , Bromine XRF*
OM005-F02	Plastic	LCD Monitor power cord plug	Antimony ²⁰¹⁴
WM100-F05	Plastic	Popcorn Maker	Antimony ²⁰¹⁴
GR015-F01	Plastic	Flame Resistant Drainage Tarp	Antimony ²⁰¹⁴ , Bromine XRF
CT010-F04	Plastic	HDMI Cable	Antimony ²⁰¹⁴
BL004-F01	Plastic	Space Heater	Antimony ²⁰¹⁴ , Bromine XRF
2014 Study Samples	3		
TR-9-2-1	Foam	Changing Pad	ТСРР
TR-9-3-2	Foam	Changing Mat	ТСРР
TG-9-3-4	Foam	Changing Mat	ТСРР

Unbolded = analyte detected greater than 0.2% but less than 1%

 $bolded = analyte \ detected > 1\%$

²⁰¹⁴ Supplemental data from 2014 study

^{*}trace TBBPA detected, likely from contamination from recycling plastics or residual of an unreacted monomer of reactive flame retardant

Table 10: Selected Flame Retardants on "Lists"

		Washi	ngton	Minnesota	California		Maine	Oregon	European Union	Canada
CAS	Chemical	PBT	CSPA	Priority	Prop65	SCP	СНС	Focus List	SVHC	DSL
	Aluminum									
21645-51-2	trihydroxide									•
68333-79-9	APP									•
1309-64-4	ATO		•*		•	•				•
68631-49-2	BDE 153					•		•		
60348-60-9	BDE 99					•		•		
126-72-7	brominated Tris				•	•				
37853-59-1	BTBPE					•				
84852-53-9	DBDPE					•				
1163-19-5	Deca-BDE	•	•	•		•	•	•	•	
13560-89-9	DP					•				
3194-55-6	HBCD			•		•			•	•
25637-99-4	HBCD	•	•			•	•	•	•	
51936-55-1	HCDBCO					•				
32536-52-0	octa BDE	•				•				•
85-22-3	PBEB					•				
32534-81-9	penta BDE	•				•		•		•
85535-84-8	SCCP	•				•			•	•
183658-27-7	TBB					•				
79-94-7	TBBPA	•	•			•	•	•		•
3322-93-8	TBECH					•				
126-73-8	TBP							•		•

		Washington		gton Minnesota California Maine Oregon		Oregon	European Union	Canada		
CAS	Chemical	PBT	CSPA	Priority	Prop65	SCP	СНС	Focus List	SVHC	DSL
26040-51-7	TBPH					•		•		
115-96-8	TCEP		•		•	•	•	•	•	•
13674-84-5	TCPP					•				
13674-87-8	TDCPP		•		•	•		•		
5436-43-1	Tetra BDE					•		•		
115-86-6	TPP							•		

Note: The information from each list was limited to chemicals with CAS Numbers only, so a list that includes "Flame retardants" as a priority chemical with no CAS is not shown on this summary.

Legend

- CHC chemicals of high concern
- CSPA children's safe product act
- DSL domestic substance list

- PBT persistent, bioaccumulative, and toxic
- Prop65 proposition 65
- SCP safer consumer products
- SVHC substance of high concern

References for the lists in the table above are:

Washington State

- PBT Department of Ecology, <u>Persistent, Bioaccumulative, and Toxic (PBT)</u> chemicals (*Chapter 173-333 Washington Administrative Code: Persistent, Bioaccumulative, Toxins. Section 310 What chemicals or chemical groups are included on the PBT list?*)
 http://apps.leg.wa.gov/wac/default.aspx?cite=173-333-310
- CSPA Department of Ecology, Chemicals of High Concern to Children (CHCC) (Chapter 173-334 Washington Administrative Code: Children's Safe Products Reporting Rule. Section 130 The reporting list of chemicals of high concern to children (CHCC list))

 http://app.leg.wa.gov/WAC/default.aspx?cite=173-334-130

Minnesota

Priority – Department of Health, <u>Priority Chemicals List</u>: Toxic Free Kids Act, November 2012 Priority Chemicals list (*Minnesota Statutes, Chapter 116 Pollution Control Agency, § 9401 to § 9407 Chemicals of High Concern*)
 www.health.state.mn.us/divs/eh/hazardous/topics/toxfreekids/priority.html#chemicals

California

- **Prop65** Office of Environmental Health and Hazard Assessment List of <u>Proposition 65</u> chemicals, June 6, 2014 (*California Health and Safety Code, Division 20. Miscellaneous Health and Safety Provisions, Chapter 6.5. Hazardous Waste Control, Article 14*)

 www.oehha.ca.gov/prop65/prop65 list/Newlist.html
- SCP Department of Toxic Substances Control, <u>Safer Consumer Products</u> Candidate Chemicals List (*California Code of Regulations* **Title 22, Division 4.5,** *Chapter 55 Safer Consumer Products*) www.dtsc.ca.gov/SCP/ChemList.cfm

Maine

• **CHC** – Department of Environmental Protection, <u>Chemicals of High Concern</u> (*Chapter 38 Maine Revised Statutes Chapter 16-D: Toxic Chemicals in Children's Products*) <u>www.maine.gov/dep/safechem/highconcern/index.html</u>

Oregon

 Focus List – Oregon Department of Environmental Quality, <u>Toxics Focus List</u> 2010-2011 www.deq.state.or.us/toxics/docs/DEQFocusListCondensed.pdf

European Union

• **SVHC** - European Union Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) (*Regulation (EC) No 1907/2006 of the European Parliament and of the Council*) Candidate List of <u>Substances of Very High Concern for Authorisation</u> http://echa.europa.eu/web/guest/candidate-list-table

Canada

• **DSL** – Government of Canada <u>Domestic Substance List</u>, chemicals that meets the human health criteria *or* the environmental criteria (*Canadian Environmental Protection Act, 1999*) <u>www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=5F213FA8-1&wsdoc=D031CB30-B31B-D54C-0E46-37E32D526A1F</u>

Table 11: Hazard assessment for deca-BDE and several alternatives (EPA, 2014c)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned																
	based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgment.															
§ Based on analogy to experimental data for a structure																
This alternative may contain impurities. These impu								ant alter	native, I	3rominat	ted poly	(pheny	ylether), as fol	lows, base	d on
experimental data: HIGH for human health, HIGH for aquatic toxicity, and VERY HIGH for bioaccumulation.																
^T This chemical is subject to testing in an EPA consent order for this endpoint.																
		Human Health Effects Aquatic Environmental														
													Toxi	city	Fa	te
		>	Ţ					မ	Sensitization			Dermal Irritation				Bioaccumulation
		Toxicity	Carcinogenicity	₽.	Ĭ.	Developmental	- =	Repeated Dose	. <u>2</u> 2	× 1	<u>.5</u>	ita.				lat
		, ix	<u>5</u> 6	Genotoxicity	Reproductive	l ä	Neurological	Į p	is.	Respiratory Sensitization	Irritation	<u>F</u>			Persistence	
Chemical		T	<u>.</u>	1	∣ g	o do	용	ate	Ser	ira	Ë	7 8	•	Chronic	ste	5
(for full chemical name and relevant trade names see		Acute	2	2	l H	Ne	Ĕ) je	ı.ii	spi nsi	မ	E	Acute	2	-Si) ac
the individual profiles in Section 4.8)	CASRN	Ac	చ్	පී	№) a	×	Re	Skin	Re	Ey	Ď.	Ac	5	Pe	Bi
DecaBDE and Halogenated Flame Retardant Alter	natives															
	Deca	BDE a	and Dis	crete H	alogena	ted FR	Alterna	tives								
Decabromodiphenyl Ethane	84852-53-9	L	M [§]	L	L	H [§]	L	L	L		VL	VL	L	L	VH	H
	1									 						
Decabromodiphenyl Ether	1163-19-5	L	M	L	L	H	L	M	L		L	L	L	L	VH	H
Ammonium Polyphosphate	68333-79-9	L	L	L	L	L	L	L^{d}	L		VL	L	L	L	VH	L
Polyphosphonate	68664-06-2	L	L	L	L	L	L	La	L		L	L	L	L	VH	L
Magnesium Hydroxide	1309-42-8	L	L	L	L	L	L	L	L		M	L	L	L	H^{R}	L

GreenScreen® Chemical Hazard assessments for Ammonium Polyphosphate, Polyphosphonate and Magnesium Hydroxide are located at http://theic2.org/hazard-assessment.

GreenScreen® Chemical Hazard assessments for listed flame retardants listed in Table 12 are located at http://theic2.org/hazard-assessment.

Table 12: Hazard assessment for chlorinated phosphate flame retardants and several alternatives (EPA, 2014e) GreenScreen® Chemical Hazard assessments for listed flame retardants are located at http://theic2.org/hazard-assessment.

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (<math>VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgment.

^{*} Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

partition to sediment and particulates.	_															
									iatic icity		nmental ite					
Chemical (for full chemical name and relevant trade names see the individual profiles in Section 4.8)	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Halogenated Flame Retardant Alternatives Firemaster® 550 Components																
Firemaster® 550*	Mixture	т	M	naster@ M	B 550 C	Ompo	H	H	M		T	L	VH	VH	Н	Н
Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester (TBB)*	183658-27-7	L	M	L	M	M	М	М	M		L	L	L	L	H	Н
Di(2-ethylhexyl) tetrabromophthalate (TBPH) ^*	26040-51-7	L	M	M	M	M	M	M	L		L	L	L	L	Н	H
Isopropylated triphenyl phosphate (IPTPP)	68937-41-7	L	M	L	H	H	H	H	L		L	L	VH	VH	M	H
Triphenyl phosphate (TPP)	115-86-6	\mathbf{L}_{-}	M	L	L	L	L	H	L		L	VL	VH	VH	L	M
			Chlorina	ted Ph	osphor	$\overline{}$	rnative	es								
Tris (2-chloroethyl) phosphate (TCEP)	115-96-8	H	H	M	M	H	M	M	L		L	L	H	H	M	L
Tris (2-chloro-1-methylethyl) phosphate (TCPP)	13674-84-5; 6145-73-9	L	M	L	Н	Н	М	M	L		L	L	M	Н	Н	L
Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)	13674-87-8	L	H	M	H	M	L	H	L		L	L	Н	H	Н	L
Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P,P',P'-tetrakis(2-chloroethyl) ester (V6)	051-10-4	L	М	L	M	н	L	M	L		L	L	M	Н	н	L
Non-Halogenated Flame Retardant Alternatives			Y.,		N41 4	14										
1 1 1 (APP)*	222 70 0			ganic/(Jther A	Iterna		d	.	<u> </u>		, 1		,	****	
Ammonium polyphosphate (APP) [¥] 68	333-79-9 I	I	L		, <i>L</i>		. <i>L</i>	, d	L		VL	L	L	L	VH	L

^{*} This mixture is made up of four components contained in the hazard summary table. Hazard designations in bold and color are based on test data for the mixture, as summarized in the hazard profiles for the components. Hazard designations in italics are based on the most conservative results from one of the four components.

This component of Firemaster® 550 may be used alone or in other mixtures as an alternative.

Table 13: Hazard assessment for hexabromocyclododecane and an alternative (EPA, 2014d)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgment.

This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion byproducts are discussed in the report but not addressed directly in the hazard profiles. The caveats listed below must be taken into account when interpreting the information in the table.

d This hazard designation would be assigned MODERATE for a potential for lung overloading if >5% of the particles are in the respirable range as a result of dust forming operations. § Based on analogy to experimental data for a structurally similar compound.

¥ Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

		Human Health Effects												atic city	Environmental Fate	
Chemical For full chemical name and relevant trade names see the hazard profiles in Section 4.8	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Hexabromocyclododecane (HBCD)	25637-99-4; 3194-55-6	L	М	L	M	Н	M	M	L		VL	VL	VH	VH	Н	VH
Butadiene styrene brominated copolymer*								I		l						I
Butadrene styrene orominated copolymer	1195978-93-8	L	L	L	L	L	L	\mathbf{L}^d	L		M	L	L	L	VH	L

Table 14: Hazard assessment for tetrabromobisphenol A and two alternatives (EPA, 2014f). GreenScreen® GreenScreen® Chemical Hazard assessments for listed flame retardants are located at http://theic2.org/hazard-assessment.

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgment. This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion byproducts are discussed in the report but not addressed directly in the hazard profiles. The caveats listed below must be taken into account when interpreting the information in the table.

◆ TBBPA has been shown to degrade under anaerobic conditions to form bisphenol A (BPA; CASRN 80-05-7). BPA has hazard designations different than TBBPA, as follows: MODERATE (experimental) for reproductive, skin sensitization and dermal irritation. § Based on analogy to experimental data for a structurally similar compound. [‡]The highest hazard designation of any of the oligomers with MW <1,000. ¥ Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

			Human Health Effects											Aquatic Toxicity		ron- ntal ite	Exposure Considerations					
Chemical (for full chemical name and relevant trade names see the individual profiles in Section 4.9)	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation	Availability of flame retardants throughout the life cycle for reactive and additive flame-retardant chemicals and resins					
Reactive Flame-Retarda	eactive Flame-Retardant Chemicals																					
Tetrabromobisphenol A	79-94-7	\mathbf{L}	M	${f L}$	L♦	M	L	L	L♦		M	L♦	VH	Н	Н	M						
						•			•			•	•	•		•	Manufacture End-of-Life of of FR					
DOPO	35948-25-5	L	M	L	L [§]	M	M	L	M		M	VL	L	M	Н	L	Electronics Manufacture (Recycle, Disposal) of FR Resin					
								•		-				•	•		of Electronics Manufacture of Manufacture of PCB Laminate					
Fyrol PMP	63747-58-0	L	L§	L^{\S}	M [§]	M [§]	M [§]	M [§]	L		L	L	H^{\ddagger}	H^{\ddagger}	VH	$m{H}^{\ddagger}$	and Incorporation into Electronics					

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