United States Environmental Protection Agency

An Alternatives Assessment for the Flame Retardant Decabromodiphenyl Ether (DecaBDE)

Chapter 6

Considerations for Selecting Flame Retardants

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6 Considerations for Selecting Flame Retardants

Selecting an alternative chemical flame retardant involves considering a range of factors. Design for the Environment (DfE) chemical alternatives assessments provide extensive information on chemical hazards and provide a more general discussion of other factors relevant to substitution decisions, such as: use information and exposure and life cycle considerations. Decision-makers will likely supplement the human health and environmental information provided in this report with information on cost and performance that may vary depending on the supplier, the materials involved, and the intended application. Alternative flame retardants must not only have a favorable environmental profile, but also must provide satisfactory (or superior) fire safety, have an acceptable cost, and attain the appropriate balance of properties (e.g., mechanical, thermal, aesthetic) in the final product. Users of information in this report may wish to contact the manufacturers of alternative flame retardants for engineering assistance in designing their products with the alternatives.

This chapter outlines attributes that are appropriate for a decision maker to consider in choosing an alternative to decabromodiphenyl ether (decaBDE) and gives a summary of the results of this assessment including certain caveats specific to this assessment that the reader should consider. The chapter begins by describing five general attributes evaluated in this assessment that can inform decision-making about chemical hazards: (1) human health, (2) ecotoxicity, (3) persistence, (4) bioaccumulation potential and (5) exposure potential. The chapter gives special attention to discussion of data gaps in the full characterization of chemicals included in this assessment. The chapter also includes information on the social, performance, and economic considerations that may affect substitution and the chapter concludes by providing additional resources related to state, federal, and international regulations.

The scope of this assessment was focused on the human health and environmental hazards of potential flame retardant substitutes. The report does not include a review or analysis of any additional life-cycle impacts, such as energy and water consumption or global warming potential, associated with any of the baseline or alternative chemicals, or the materials in which they are used. If selection of an alternative flame retardant requires significant material or process changes, relevant life-cycle analyses can be applied to the potentially viable alternatives identified through this hazard-based alternatives assessment, and to the materials in which they are used. Manufacturers may also wish to analyze the life-cycle impacts of materials that do not require the use of a flame retardant, in order to select materials that pose the fewest life-cycle impacts.

6.1 Preferable Human Health and Environmental Attributes

This section identifies a set of positive attributes for consideration when formulating or selecting a flame retardant that will meet flammability standards. In general, a safer chemical has lower human health hazard, lower ecotoxicity, better degradability, lower potential for bioaccumulation and lower exposure potential. As described in Chapter 4, the toxicity information available for each of the alternatives varies. Some hazard characterizations are based on measured data, ranging from one study to many detailed studies examining multiple endpoints, doses and routes of exposures. For other chemicals, there is no chemical-specific toxicity information available, and in these cases either structure activity relationship (SAR) or professional judgment must be used. In Table 4-4, Table 4-5, and Table 4-6, the hazard designations based on SAR or professional judgment are listed in black italics, while those with hazard designations based on measured test data are listed in color. Readers are encouraged to review the detailed hazard assessments available for each chemical in Chapter 4.

Residual starting materials should be considered and ideally disclosed by the manufacturer in a hazard assessment. For example, several flame retardants are synthesized with bisphenol A or tetrabromobisphenol A. If residual monomers were identified as more than 0.1 percent of the product they were considered in the hazard assessment. It is possible DfE was not aware of/did not predict residuals for some products. The user/purchaser of the flame retardants can ask the manufacturer for detailed product certification to answer questions about residuals, oligomer content or synthesis by-products.

6.1.1 Low Human Health Hazard

The DfE alternatives assessment criteria address a consistent and comprehensive list of human health hazard endpoints. Chemical hazards to human health assessed in this report are: acute toxicity, carcinogenicity, genotoxicity, reproductive and developmental toxicity, neurotoxicity, repeated dose toxicity, skin sensitization, respiratory sensitization, eye irritation and dermal irritation. The DfE criteria describe thresholds to define low, moderate, and high hazard. As described in Chapter 4, where data for certain endpoints were not available or were inadequate, hazard values were assigned using data for structural analogs, SAR modeling and professional judgment. In some cases (e.g., respiratory sensitization) it was not possible to assign hazard values due to a lack of data, models or structural analogs.

For the flame retardant chemicals evaluated in the report, human health hazard endpoints varied due to the different chemistries of decaBDE and the 29 alternatives. Some general trends include the following:

1. Large polymers (greater than 1,000 daltons) were generally designated as low concern compared to discrete chemicals, because the large polymers generally cannot be absorbed or easily metabolized. Chemicals with molecular weights (MWs) close to 1,000 may have potential for absorption whereas those with MWs much larger than 1,000 have a much lower potential for absorption (U.S. EPA 2010). Without absorption there cannot be systemic effects. Although irritation can occur without absorption, it was not identified as a hazard for any of the large polymers and therefore was not a distinguishing characteristic in this assessment. The entire MW range of polymeric components was considered. All representative oligomers and low MW polymers were assessed and when they were responsible for the hazard designation, it was indicated as such using footnotes. The presence of oligomers and low MW polymers is dependent upon specific synthesis conditions and final MW range, can vary by application/trade product even for a given CAS Number.

2. Acute mammalian toxicity was low for decaBDE and all the alternatives except for tris(tribromoneopentyl) phosphate and the substituted amine phosphate mixture.

3. Irritation and sensitization endpoints were generally not distinguishing, but five chemicals had at least one designation of moderate, high, or very high for one or more irritation or sensitization endpoint, whereas decaBDE had low designations for these endpoints.

4. Carcinogenicity and mutagenicity hazards varied among the alternatives, with many low or moderate results. None of the chemicals had high concerns for carcinogenicity. Only zinc borate had a high concern for mutagenicity. DecaBDE was low for genotoxicity and moderate for carcinogenicity. For the alternatives, many of the moderate designations for carcinogenicity and mutagenicity result from a lack of data or SAR. DfE criteria are conservative for both of these endpoints in that a lack of data or SAR to designate the hazard as low triggers a default designation of moderate.

5. Reproductive, developmental, neurological, and repeated dose toxicity varied from very low to high across discrete chemicals. DecaBDE has high developmental toxicity and moderate repeated dose toxicity.

Examples of DfE Approaches for Neurotoxicity and Degradation Products

This assessment used the DfE hazard criteria that were published in 2011. The 2011 criteria do not specifically address two factors that were important for this assessment of flame retardants: developmental neurotoxicity in the face of incomplete data sets, and theoretical but undemonstrated degradation products. Special consideration, which is summarized below, was given to these factors and used to complement the hazard profiles where relevant.
Some of the alternatives have structures that result in questions about potential for degradation products. For example, some of the decaBDE alternatives are synthesized from TBBPA and contain a TBBPA backbone (e.g., tetrabromobisphenol A bis (2,3 dibromopropyl ether) (21850-44-0), brominated epoxy resin end-capped with tribromophenol (135229-48-0), brominated epoxy polymers (68928-70-1)). It is not evident that TBBPA will be released from these substances and the conditions necessary for such degradation are not known. If TBBPA is released through the degradation of these substances, the associated hazard profiles would be influenced by any toxicity associated with TBBPA[19]. There is a lack of data to determine if TBBPA might be a degradation product of, for example, TBBPA-bis (2,3 dibromopropyl) ether[20] under environmental conditions. Further testing is needed to answer this question. The chemical considerations section of the profiles for the brominated epoxy resin end-capped with tribromophenol and the brominated epoxy polymers describes the potential for low MW components to inform readers how this pathway was considered during the assessment process. For the profiles of the three substances identified above, formation of TBBPA was not explicitly considered when assigning the hazard designations.

There is also inadequate information to fully understand the neurotoxicity of decaBDE and its alternatives. There are two types of neurotoxicity: neurotoxicity which is a result of an exposure

[19] TBBPA has been evaluated in a 2-year carcinogenicity study at the National Toxicology Program (NTP) (NTP 2013b) and in the DfE's Partnership to Evaluate Flame Retardants in Printed Circuit Boards (U.S. EPA 2008b).
[20] TBBPA bis (2,3-dibromopropyl) ether has been nominated for consideration for a 2-year cancer bioassay at NTP (Haneke 2002; NTP 2013a).

to a substance during gestation or lactation, referred to as developmental neurotoxicity, and neurotoxicity as a result of exposure to a substance as an adult. Developmental neurotoxicity has been associated with decaBDE (European Chemicals Bureau 2002; U.S. EPA 2008a; Washington Department of Ecology 2008), and organophosphate esters as a class are associated with neurotoxicity. Therefore it is of interest to assess the developmental and adult neurotoxicity of the decaBDE alternatives. The assessment of the neurotoxicity hazard (developmental and adult) of the chemicals assessed in this report presented some challenges as outlined below.

For the highly brominated discrete organics, such as decabromodiphenyl ethane and ethylene bistetrabromophthalimide, data exist for developmental neurotoxicity for some substances but there are no data for adult neurotoxicity. Filling data gaps for neurotoxicity was challenging. One possible approach was to predict that any developmental neurotoxicant is also an adult neurotoxicant (or vice versa). While some substances can be both developmental and adult neurotoxicants, it is also possible for substances to be either developmentally neurotoxic or neurotoxic in adults and not both; therefore, this approach was not used. A second potential approach was to look for neurotoxicity data for a wide range of analogs for highly brominated compounds. Unfortunately, none of the analogs that U.S. Environmental Protection Agency (EPA) identified had any neurotoxicity data based upon adult exposures. The third approach, which was used for this assessment, was to use professional judgment to determine if there are structural alerts to consider highly brominated compounds to be adult neurotoxicants based upon the DfE hazard criteria (see Section 4.1.2). EPA determined there was no evidence of structural alerts and therefore gave the highly brominated discrete organics a hazard designation of estimated Low for adult neurotoxicity. For developmental toxicity, EPA gave substances analogous to decaBDE a hazard designation of High[21] based on measured developmental neurotoxicity data[22] for decaBDE.

Neurotoxicity was also considered for the phosphates as a group. Although many organic phosphates (“organophosphates”) are associated with neurotoxicity (e.g., tri-ortho cresyl phosphate and parathion, neither of which is included in this assessment), neurotoxicity data are limited for the organic phosphates in this report. The available data and physical-chemical properties of the discrete phosphate alternatives in this report do not suggest concern for neurotoxicity or developmental neurotoxicity. With some exceptions, phosphates and inorganics are estimated or measured Low for adult neurotoxicity and developmental toxicity in this report. Additional experimental data would help to verify EPA’s estimations.

6.1.2 Low Ecotoxicity

Ecotoxicity includes adverse effects observed in wildlife. An aquatic organism’s exposure to a substance in the water column has historically been the focus of environmental toxicity considerations by industry and government during industrial chemical review. Surrogate species of fish, aquatic invertebrates and algae are traditionally assessed to consider multiple levels of the aquatic food chain. Aquatic organisms are a focus also because the majority of industrial

[21] Measured data were available for decaBDE resulting in a measured High designation. DecaBDE is an analog for decabromodiphenyl ethane resulting in an estimated High designation.
[22] Developmental toxicity considers additional endpoints beyond neurotoxicity, such as teratogenicity. However, in the case of decaBDE the developmental neurotoxicity data informed the High hazard designation.

chemicals are released to water. Both acute and chronic aquatic toxicity should be considered in choosing a chemical flame retardant. It is common to have limited data on industrial chemicals for terrestrial wildlife. Some human health data (i.e., toxicity studies which use rodents) can be relevant to non-human vertebrates in ecotoxicity evaluations. When evaluating potential concerns for higher trophic level organisms (including humans), bioaccumulation potential (discussed in Section 6.1.4) is an important consideration in conjunction with toxicity for choosing a safer alternative.

For the flame retardant chemicals evaluated in the report, ecotoxicity hazards varied significantly due to the diverse chemistries of the alternatives. Some general trends include the following:

1. Large discrete chemicals and large polymers (both halogenated and non-halogenated) had generally low ecotoxicity hazards. The larger chemicals and compounds with high K_{ow} values are not expected to be bioavailable in the water column. Without absorption there cannot be systemic effects. For almost all the chemicals included in this assessment (including decaBDE) the hazard designation was based on professional judgment and/or SAR predicting ‘no effects at saturation’.

2. For inorganic compounds, aquatic toxicity varied from Low to High hazard. The metal species influences toxicity, as does the type of anion with which it is associated (e.g., a metal hydroxide). Metal compounds will have different solubilities depending on the anion involved, which will contribute to the level of toxicity of the metal compound. The aluminum, antimony and zinc compounds have Moderate to High aquatic toxicity hazard. For aluminum hydroxide, sufficient data are not available to rule out a Moderate concern. For magnesium hydroxide and red phosphorus, aquatic toxicity was Low based on predicted and measured data, respectively.

3. In addition to some of the inorganic compounds, some of the phosphorus and/or nitrogen-containing compounds also had High or Very High measured or predicted aquatic toxicity.

4. Ecotoxicity data for terrestrial species was limited or completely absent for the chemicals assessed. Therefore, potential for impacts of the alternatives on high trophic level and terrestrial wildlife is unclear and could not be fully assessed.

6.1.3 Readily Degradable: Low Persistence

Persistence describes the tendency of a chemical to resist degradation and removal from environmental media, such as air, water, soil and sediment. Chemical flame retardants must be stable by design in order to maintain their flame retardant properties throughout the lifetime of the product. Therefore, it is not surprising that all but two of the chemicals assessed in this report, including decaBDE, had a persistence value of high or very high. The alternatives without high concern for persistence were triphenyl phosphate, which is readily biodegradable (low persistence), as well as resorcinol bis-diphenyl phosphate (inherently biodegradable), which degrades slowly (moderate persistence).

The half-life for a given removal process is used to assign a persistence designation. The half-life measured or estimated to quantify persistence of organic chemicals is not a fixed quantity as is it for a linear decay process such as for the half-life of a radioisotope. Chemicals with half-lives that suggest low or no persistence can still present environmental problems. “Pseudo persistence” can occur when the rate of input (i.e., the emission rate) of a substance exceeds the rate of degradation in, or movement out of, a given area. Even though triphenyl phosphate is by definition not persistent, it demonstrates pseudo persistent properties (Waaijers 2013). With the current criteria, DfE did not address pseudo persistence in the assessment which should include analysis of volumes of production and release.

A number of the alternatives are high MW polymers (>10,000 daltons) that are predicted to be highly persistent because they are not bioavailable or assimilated by microorganisms. Highly persistent chemicals may ultimately degrade in the right environmental conditions, but time to degradation is much longer than other chemicals, often several months or years.

If the use of higher MW chemicals and polymers for flame retardant applications increases, there would be a need for further information regarding the environmental fate of these chemicals to understand how they behave in the environment, including their persistence in various environmental settings and the identity and toxicity of their degradation products. Environmental monitoring information exists for some of the (non-polymeric) alternatives, including the degradation products, which have been in the marketplace for more than a few years. However, no information was available for other alternative chemicals.

Environmental monitoring could bolster hazard assessments by confirming that environmental fate is as predicted. The lack of such information should not be taken as evidence that environmental releases are not occurring. Environmental detection is not equivalent to environmental persistence; detection in remote areas (e.g., the Arctic) where a chemical is not manufactured is considered to be a sign of persistence and transport from the original point of release. An ideal safer chemical would be stable in the material to which it is added and have low toxicity, but also be degradable at end of life of that material, i.e., persistent in use but not after use. This quality is difficult to achieve for flame retardants.

In addition to the rate of degradation or measured half-life, it is important to be aware of the byproducts formed through the degradation process. In some cases, degradation products might be more toxic, bioaccumulative or persistent than the parent compound. Some of these degradation products are discussed in the hazard profiles, but a complete analysis of this issue is beyond the scope of this assessment. This issue was discussed earlier, in Section 6.1.1 of this chapter, in the context of compounds with a TBBPA backbone that may not degrade to TBBPA. Experimental studies describing this degradation pathway were not available. The report did not consider toxicity from this potential degradation route.

Additionally, a group of three phosphate esters, resorcinol bis-diphenyl phosphate (125997-21-9 “RDP”), bisphenol A bis-(diphenyl phosphate) (181028-79-5 “BAPP”) and phosphoric acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol (1003300-73-9 “BPBP”), could theoretically release biphenol-type structures during degradation by alkaline hydrolysis. However, RDP and BAPP are poorly soluble substances possibly making hydrolysis a less prevalent degradation pathway. Both RDP and BAPP are in commerce and are used in plastics for electronics. Questions have been raised about whether these substances can release resorcinol and bisphenol A, respectively, during degradation. Experimental data on whether RDP or BAPP release resorcinol or bisphenol-A through degradation are not available. Resorcinol and bisphenol A are associated with endocrine activity; bisphenol A is a priority chemical for regulatory activity and research.

The BPBP alternative is a new to market substance. Applying the same questions and analysis to BPBP, this substance may also have a biphenol type degradant, 4, 4'-dihydroxybiphenyl, that based on its structure, may have potential for endocrine activity.

For the phosphate esters described above, DfE cannot determine the likelihood of release of degradates. DfE includes this information in the hazard profiles of relevant chemicals. Only degradants that were known or predicted to be likely were included in the hazard assessments in this report. Stakeholders are encouraged to conduct additional analyses of the degradation products of preferable alternatives using the assessment methods described in Chapter 4.

In general, metal-containing chemicals are persistent. This is because the metal moiety remains in the environment. Metal-containing compounds can be transformed in chemical reactions that could change their oxidation state, physical/chemical properties, or toxicity. A metal-containing compound may enter into the environment in a toxic (i.e., bioavailable) form, but degrade over time into its inert form. The converse may also occur. The chemistry of the compounds and the environmental conditions it encounters will determine its biotransformation over time. For metals, information relevant to environmental behavior is provided in each chemical assessment in Chapter 4 and should be considered when choosing an alternative.

6.1.4 Low Bioaccumulation Potential

The ability of a chemical to accumulate in living organisms is described by the bioconcentration, bioaccumulation, biomagnification, and/or trophic magnification factors. DecaBDE has high potential hazard for bioaccumulation, as do its break down products (lower brominated diphenyl ether congeners). Some of the alternatives assessed in this report also have a high level of potential for bioaccumulation, including the discrete brominated chemicals and, based on presence of oligomers below 1,000 daltons, also some of the phenyl phosphates. Based on structure activity relationships, the potential for a molecule to be absorbed by an organism tends to be lower when the molecule is larger than 1,000 daltons. This is reflected in the low hazard designations for bioaccumulation for the large polymeric flame retardants without low MW components below 1,000 daltons. The inorganic flame retardants assessed in this report do not have high potential to bioaccumulate. Note that care should be taken not to consider the 1,000 daltons size to be an absolute threshold for absorption – biological systems are dynamic and even relatively large chemicals might be absorbed under certain conditions. In the past, available data suggested that the large size of decaBDE would preclude transport across biological membranes and that its limited water solubility would decrease the potential for absorption (Toxicology Excellence for Risk Assessment 2003). Absorption of decaBDE is poor, whereas lower brominated polybrominated diphenyl ethers (PBDEs) are readily absorbed (ATSDR 2004). Subsequent studies using more sensitive analysis techniques have detected decaBDE in biological samples demonstrating its potential to be absorbed (Lorber 2008). DecaBDE has a MW of 959 daltons. This provides a basis to suggest that the potential for absorption and potential for bioaccumulation of large molecules around 1,000 daltons is not well understood. Furthermore the initial 1,000 Dalton threshold was established based on the consideration of BCFs. Corresponding thresholds for hazard assessments based on BAF have not yet been rigorously established.

Chemical manufacturers have reduced absorption and bioaccumulation potential of certain substances through the design of larger molecules. Making a molecule bigger (often by making large polymeric molecules) can reduce bioavailability, or minimize the likelihood of low MW components and residuals of concern. A larger polymeric flame retardant molecule may also impact performance properties of the material to which the flame retardant is added in positive or negative ways. A safer molecule also has to perform well in the intended application.

The test guidelines available to predict potential for bioaccumulation have some limitations. For example, they do not require the measurement for the BCFs of different components of a mixture, even if they are known to be present in the test material and sufficiently precise analytical methods are available. This situation often arises for lower MW oligomers or materials that have varying degree of substitution. Bioconcentration tests tend to be limited for chemicals that have low water solubility (hydrophobic), and many flame retardants have low water solubility. Even if performed properly, a bioconcentration test may not adequately measure bioaccumulation potential if dietary exposure dominates over respiratory exposure (i.e., uptake by fish via food versus via their gills). The Organisation for Economic Cooperation and Development program recently updated the fish bioconcentration test, in which dietary uptake is included for the first time (OECD 2012). Dietary uptake is of critical importance and may be a more significant route of exposure for hydrophobic chemicals.

6.1.5 Low Exposure Potential

For humans, chemical exposure may occur at different points throughout the chemical and product lifecycle; by dermal contact, by inhalation, and/or by ingestion; and is affected by multiple physicochemical factors that are discussed in Chapter 5. The DfE alternatives assessment assumes exposure scenarios to chemicals and their alternatives within a 'functional-use' class to be roughly equivalent. The assessment also recognizes that in some instances chemical properties, manufacturing processes, chemical behavior in particular applications, or use patterns may affect exposure scenarios. For example, some decaBDE flame retardant alternatives may require different loadings to achieve the same flammability protection. Stakeholders should evaluate carefully whether and to what extent manufacturing changes, lifecycle considerations, and physicochemical properties will result in markedly different patterns of exposure as a result of informed chemical substitution. For example, a replacement may leach out, or "bloom" out of the polymer it is flame retarding faster than decaBDE, thus increasing its relative exposure during use or disposal. The combination of high persistence and high potential for bioaccumulation makes an alternative less desirable. Even if human toxicity and ecotoxicity hazards are measured or estimated to be low, dynamic biological systems don't always behave as laboratory experiments might predict. High persistence, high bioaccumulation chemicals, or their degradation products, have high potential for exposure and unpredictable hazards following chronic exposures that may not be captured in the hazard screening process.

6.2 Considerations for Poorly or Incompletely Characterized Chemicals

Experimental data for hazard characterization of industrial chemicals are limited. As described in Chapter 4, for chemicals in this report without full data sets, analogs, SAR modeling, and professional judgment were used to estimate values for those endpoints lacking empirical data. No alternative chemical had empirical data for all of the hazard categories. Nine chemicals had no empirical data at all, and all of their respective endpoints were predicted; an additional six lacked data on at least 10 of the hazard endpoints. Several chemicals included in this analysis appear to have more preferable profiles, with low human health and ecotoxicity endpoints, although they are highly persistent, a frequent property for flame retardants (see Table 4-4, Table 4-5, and Table 4-6). There is less confidence in the results of some seemingly preferable chemicals in which the majority of hazard profile designations are based on estimated effect levels compared to chemicals with full experimental data sets. Empirical data would allow for a more robust assessment that would confirm or refute professional judgments and then support a more informed choice among alternatives for a specific use. Estimated values in the report can, therefore, also be used to prioritize testing needs.

Examples where data are lacking for endpoints reviewed for chemicals in this report include the following:

1. The environmental fate of large discrete or polymeric flame retardants (MW approaching or exceeding 1,000 daltons) is uncertain. This is true for both halogenated and non-halogenated chemicals. Polymeric flame retardants are assessed in this report. Some of these polymeric chemicals were designed to be safer alternatives to decaBDE. While SAR analysis shows these chemicals are anticipated to be associated with low hazard, chemical-specific data to support these predictions are lacking. In general, large polymeric flame retardants are predicted to have high persistence but low concern for toxicity or potential for bioaccumulation. Further research is needed to fully understand the environmental fate of polymers approaching or exceeding 1,000 daltons.

2. For discrete brominated chemicals with MW and (or) functional groups similar to decaBDE, e.g., decabromodiphenyl ethane and ethylene bistetrabromophthalimide, hazard designations were based on analogy to decaBDE. Because of reactivity, physicochemical and structural properties similar to those of decaBDE, chronic exposure studies are needed to rule out concerns similar to those that have been raised regarding long-term exposure to decaBDE.

3. Empirical data is needed to confirm low toxicity and bioaccumulation predictions. Flame retardants are usually highly persistent chemicals by design since they need to maintain their properties throughout the lifetime of the flame retarded product; however, the persistence can be less of a concern for chemicals with a preferable toxicity and bioaccumulation profile. Empirical data for several chemicals identifies them as high or very highly persistent but predicted information identifies them as having low toxicity and/or bioaccumulation hazards.

4. An evaluation of potential combustion by-products was not a hazard category in this alternatives assessment. When considering preferred substitutes, a product

manufacturer may wish to consider the types of combustion by-products that may occur when a flame retarded product burns.

In the absence of measured data, DfE encourages users of this alternatives assessment to be cautious in the interpretation of hazard profiles. Chemicals used at high volumes, or likely to be in the future, should be given priority for further testing. Decision-makers are advised to read the full hazard assessments for each chemical, available in Chapter 4, which may inform whether additional assessment or testing is needed. Contact DfE with any questions on the criteria included in hazard assessments or the thresholds, data, and prediction techniques used to arrive at hazard values (www.epa.gov/dfe).

Where hazard characterizations are based on measured data, there are often cases where the amount of test data supporting the hazard rating varies considerably between alternative chemicals. In Table 4-4, Table 4-5, and Table 4-6 the hazard characterizations based on SAR or professional judgment are listed in black italics, while those with hazard characterizations based on measured test data are listed in color. The amount of test data behind these hazard characterizations shown in color can vary from only one study of one outcome or exposure, to many studies in many species and different routes of exposure and exposure duration. In some instances, testing may go well beyond basic guideline studies, and it can be difficult to compare data for such chemicals against those with only a single guideline study, even though hazard designations for both chemicals would be considered "based on empirical data" and thus come with a higher level of confidence. Cases where one chemical has only one study but a second chemical has many studies are complex and merit careful consideration. For hazard screening assessments, such as the DfE approach, a single adequate study can be sufficient to make a hazard rating. Therefore, some designations that are based on empirical data reflect assessment based on one study while others reflect assessment based on multiple studies of different design. The hazard rating does not convey these differences – the full hazard profile should be consulted to understand the range of the available data.

6.3 Social Considerations

Decision-makers should be mindful of social considerations when choosing alternative chemicals. This section highlights occupational, consumer, and environmental justice considerations. Stakeholders may identify additional social considerations for application to their own decision-making processes.

Occupational considerations: Workers might be exposed to flame retardant chemicals from direct contact with chemicals at relatively high concentrations while they are conducting specific tasks related to manufacturing, processing, and application of chemicals (see Section 5.1.1). Many facilities have established risk management practices which are required to be clearly communicated to all employees. The National Institute for Occupational Safety and Health (NIOSH) has established a hierarchy of exposure control practices[23]. From best to worst, the practices are: elimination, substitution, engineering controls, administrative controls and personal protection. Switching from high hazard chemicals to inherently lower hazard chemicals can benefit workers by decreasing workplace risks through the best exposure control practices:

[23] http://www.cdc.gov/niosh/topics/engcontrols/

elimination and substitution of hazardous chemicals. While occupational exposures are different to consumer exposures, workers are also consumers and as such workers are relevant to both exposure groups.

Consumer considerations: Consumers are potentially exposed to flame retardant chemicals through multiple pathways described in Chapter 5. As detailed in Section 5.1.5, exposure research documents that people carry body burdens of flame retardants, including decaBDE and its breakdown products. These findings have created pressure throughout the value-chain for substitution, which impacts product manufacturers. DfE alternatives assessments can assist companies in navigating these substitution pressures.

In recent years there has been a greater emphasis on 'green' products. In addition to substituting in alternative chemicals, some organizations advocate for moving away from certain classes of chemicals entirely (e.g., halogenated flame retardants), with product re-design, to avoid future substitutions altogether. Product manufacturers should be mindful of the role of these organizations in creating market pressure for alternative flame retardant chemicals and strategies, and should choose replacement chemicals – or re-designs – that meet the demands of their customers.

Environmental justice considerations: At EPA, environmental justice concerns refer to the disproportionate impacts on people based on race, color, national origin, or income that exist prior to or that may be created by the proposed action. These disproportionate impacts arise because these population groups may experience higher exposures, are more susceptible in response to exposure, or experience both conditions. Factors that are likely to influence resilience/ability to withstand harm from a toxic insult can vary with sociodemographics (e.g., co-morbidities, diet, metabolic enzyme polymorphisms) and are therefore important considerations. Adverse outcomes associated with exposure to chemicals may be disproportionately borne by people of a certain race, national origin or income bracket. Insights into EPA's environmental justice policy can be accessed at: www.epa.gov/compliance/ej/resources/policy/considering-ej-in-rulemaking-guide-07-2010.pdf.

Some populations have higher exposures to certain chemicals in comparison to the average member of the general population. Low-income populations are over-represented in the manufacturing sector, increasing their occupational exposure to chemicals. Higher exposures to environmental chemicals may also be attributable to atypical product use patterns and exposure pathways. This may be due to a myriad of factors such as cultural practices, language and communication barriers, and economic conditions. The higher exposures may also be a result of the proximity of these populations to sources that emit the environmental chemical (e.g., manufacturing industries, industries that use the chemical as production input, hazardous waste sites, etc.), access to and use of consumer products that may result in additional exposures to the chemical, or higher employment of these groups in occupations associated with exposure to the chemical.

Some populations are disproportionately exposed to chemicals no longer manufactured in the U.S., including some flame retardants like the components of commercial octa- and pentabromodiphenyl ethers (Zota, Adamkiewicz et al. 2010). Low-income households may have older furniture and other consumer goods, leading to higher exposure to flame retardants as the materials break down over time and chemicals migrate out of products. It is possible that low-income households are less able than higher income households to replace their furniture with new products possibly containing less hazardous materials. Minorities and low income populations tend to live in low income housing, which is typically low quality housing stock and may be poorly ventilated and contain old carpeting, which is a significant source of household dust, and low-income populations may be less able to afford high quality vacuum cleaners to reduce levels of dust in the home. Also, research has documented that certain communities may have greater exposure to industrial waste, making them more exposed to releases from manufacturing facilities (United Church of Christ 1987; Faber and Krieg 2005; Bullard, Mohai et al. 2007; Mohai, Pellow et al. 2009). Finally, certain populations may experience high exposures to toxic chemicals due to geography, food sources, and cultural practices (Burger and Gochfeld 2011). There is research showing that Alaska Natives are disproportionately impacted by certain flame retardants and other persistent organic pollutants, both because of atmospheric transport of persistent chemicals and because of the biomagnification of chemicals in traditional subsistence food webs (Arctic Monitoring and Assessment Program 2009).

Considering environmental justice in the assessment of an alternative chemical may include exploring product use patterns, pathways and other sources of exposure to the substitute, recognizing how upstream factors such as socio-economic position, linguistic and communication barriers, may alter typical exposure considerations. One tool available to these populations is the Toxics Release Inventory (TRI), which was established under the Emergency Planning and Community Right-to-Know Act to provide information about the presence, releases, and waste management of toxic chemicals. Communities can use information reported to TRI to learn about facilities in their area that release toxic chemicals and to enter into constructive dialogue with those facilities. This information can empower impacted populations by providing an understanding about chemical releases and the associated environmental impacts in their community. Biomonitoring data for the alternative chemical, if available, can also signal the potential for disproportionate exposure among populations with EJ issues.

6.4 Performance Considerations

The DfE approach allows companies to examine hazard profiles of potential replacement chemicals so they can consider the human health and environmental attributes of a chemical in addition to cost and performance considerations. This is intended to allow companies to develop marketable products that meet performance requirements while reducing hazard. This section identifies some of the performance attributes that companies should consider when formulating or selecting a flame retardant, in addition to health and environmental consideration. Performance attributes are critical to the overall function and marketability of flame retardants and should be considered along with other factors. Chapter 2 includes a detailed discussion of the categories of materials, sectors, and products relevant to the chemicals in this assessment, along with a discussion of relevant flammability standards.

The ability of a product to meet required flammability standards is an essential performance consideration for all flame retardant chemicals. The fire safety requirements influence the amount and type of flame retardant, if any, that needs to be added to a resin. Formulations are optimized for cost and performance, so that in some instances it may be equally viable to use a small quantity of an expensive, highly efficient flame retardant or a larger quantity of a less expensive, less efficient chemical.

In addition to flame retardancy properties, the flame-retarded product must meet all required specifications and product standards (e.g., rigidity, compression strength, weight). The polymer/fire retardant combination used in many of the products which contain decaBDE may be complex chemical formulations. In some instances, replacements exist which could allow for relatively easy substitution of the flame retardant. However, a true “drop-in” exchange of flame retardants is rare; some adjustment of the overall formulation, product re-design, or use of inherently flame retardant materials is usually required. An alternative with similar physical and chemical properties such that existing storage and transfer equipment as well as flame retardant manufacturing technologies could be used without significant modifications. Unfortunately, chemicals that are closer to being “drop-in” substitutes generally have similar physical and chemical properties, and therefore are likely to have similar hazard and exposure profiles. Those seeking alternatives to decaBDE should work with flame retardant manufacturers and/or chemical engineers to develop the appropriate flame retardant formulation for their products.

6.5 Economic Considerations

This section identifies economic attributes that companies often consider when formulating or selecting a flame retardant. Economic factors are best addressed by decision-makers within the context of their organization. Accurate cost estimations must be company-specific; the impact of substituting chemicals on complex product formulations can only be analyzed in-house; and a company must determine for itself how changes will impact market share or other business factors. Cost considerations may be relevant at different points in the chemical and/or product lifecycle. These attributes are critical to the overall function and marketability of flame retardants and flame retarded products and should be considered jointly with performance attributes, social considerations, and human health and environmental attributes.

Substituting chemicals can involve significant costs, as industries must adapt their production processes, and have products re-tested for all required performance and product standards. Decision-makers are advised to see informed chemical substitution decisions as long-term investments, and to replace the use of decaBDE with a chemical they anticipate using for many years to come. This includes attention to potential future regulatory actions motivated by adverse human health and environmental impacts, as well as market trends. One goal is to choose from among the least hazardous options to avoid being faced with the requirement to substitute again.

Flame retardants that are either more expensive per pound or require more flame retardant per unit area to meet the fire safety standards will increase raw material costs. In this situation, a product manufacturer substituting away from decaBDE may pass the cost of a more expensive flame retardant on to customers (e.g., a television manufacturer), who subsequently may pass the cost on to retailers and consumers. In some cases the price premium significantly diminishes over the different stages of the value chain. However, market conditions, competing technologies, and intellectual property issues may influence flame retardant selection when replacing decaBDE.

Handling, disposal, and treatment costs, as well as options for mechanical recycling, may be important considerations when evaluating alternatives. Inherently high hazard chemicals may require special engineering controls and worker protections that are not required of less hazardous alternatives. Disposal costs for high hazard chemicals may also be much higher than for low hazard alternatives. High hazard chemicals may be more likely to result in unanticipated and costly clean-up requirements or enforcement actions should risk management protections fail or unanticipated exposures or spills occur. Also, some chemicals may require specific treatment technologies prior to discharge through wastewater treatment systems. These costs can be balanced against potentially higher costs for the purchase of the alternative chemical. Finally, initial chemical substitution expenses may reduce future costs of mitigating consumer concerns and perceptions related to hazardous chemicals.

It should be noted that, while some assessed alternative chemicals included in this report are currently manufactured in high volume, not all are currently available in quantities that would allow their widespread use immediately. However, prices and availability may change if demand increases.

6.6 Moving Towards a Substitution Decision

As stakeholders proceed with their substitution decisions for decaBDE, the functionality and technical performance of each product must be maintained, which may include product performance in extreme environments over a lifecycle of many years. Critical requirements, such as product safety during operation cannot be compromised. When alternative formulations are developed, the stakeholders should also consider the hazard profiles of the chemicals used to meet product performance, with a goal to drive towards safer chemistry on a path of continuous improvement.

When chemical substitution is the necessary approach, the information in this report can help with selection of safer, functional alternatives. The hazard characterization, performance, economic, and social considerations are all factors that will impact the substitution decision. When choosing safer chemicals, alternatives should ideally have a lower human health hazard, lower ecotoxicity, better degradability, lower potential for bioaccumulation, and lower exposure potential. Where limited data are available characterizing the hazards of potential alternatives, further testing may be necessary before a substitution decision can be made.

Switching to an alternative chemical is a complex decision that requires balancing all of the above factors as they apply to a particular company's cost and performance requirements. DecaBDE is used in a range of polymers and end products; it is therefore unlikely that a single alternative evaluated by this report will fulfill all of the current applications of decaBDE. This report provides hazard information about alternatives to decaBDE to support the decision-making process. Companies seeking a safer alternative should identify the alternatives that may be used in their product (see Table 3-2), and then apply the information provided in this report to aid in their decision-making process.

Alternative chemicals are often associated with trade-offs. For any chemical identified as a potential alternative, some endpoints may appear preferable while other endpoints indicate increased concern relative to the original chemical. A chemical may be designated as a lower concern for human health but a higher concern for aquatic toxicity or persistence. For example, in the case of high MW polymers, where health hazards and potential bioaccumulation are predicted to be low, one trade-off is high persistence. Additionally, there may be limited information about the polymer's combustion byproducts, or how the polymer behaves in the environment and eventually degrades.

Trade-offs can be difficult to evaluate, and such decisions must be made by stakeholders taking into account relevant information about the chemical's hazard, expected product use, and life-cycle considerations. For example, chemicals expected to have high levels of developmental or reproductive toxicity should be avoided for products intended for use by children or women of child-bearing age. Chemicals with high aquatic toxicity concerns should be avoided if releases to water cannot be mitigated. Nonetheless, even when certain endpoints are more relevant to some uses than others, the full hazard profile must not be ignored.

6.7 Relevant Resources

In addition to the information in this report, a variety of resources provide information on regulations and activities that include review or action on flame retardants at the state, national and global levels, some of which are cited in this section.

6.7.1 Resources for state and local government activities

University of Massachusetts at Lowell created a database which "houses more than 700 state and local legislative and executive branch policies from all 50 states from 1990 to the present. The online database makes it simple to search for policies that your state has enacted or introduced, such as those that regulate or ban specific chemicals, provide comprehensive state policy reform, establish biomonitoring programs, or foster "green" chemistry…" (National Caucus of Environmental Legislators 2008).
http://www.chemicalspolicy.org/chemicalspolicy.us.state.database.php

The Interstate Chemicals Clearinghouse (IC2) is an association of state, local, and tribal governments that promotes a clean environment, healthy communities, and a vital economy through the development and use of safer chemicals and products. The IC2 also created a wiki page to allow stakeholders and members of state organizations to share resources for conducting safer alternatives assessments.
http://www.newmoa.org/prevention/ic2/
http://www.ic2saferalternatives.org/

6.7.2 Resources for EPA regulations and activities

EPA's website has a number of resources regarding regulation development and existing regulations, along with information to assist companies in staying compliant. Some of these sites are listed below.

Laws and Regulations
http://www.epa.gov/lawsregs/

Office of Pollution Prevention and Toxics (OPPT): Information on PDBEs
http://www.epa.gov/oppt/pbde/

EPA – OPPT's Existing Chemicals Program
http://www.epa.gov/oppt/existingchemicals/index.html

America's Children and the Environment
http://www.epa.gov/ace/

Integrated Risk Information System (IRIS)
http://www.epa.gov/IRIS/

Design for the Environment Program (DfE)
http://www.epa.gov/dfe

6.7.3 Resources for global regulations

The European Union (EU)'s REACH (**R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emical substances) legislation was enacted in 2007 and has an "aim to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances" (European Commission 2011a). Their website contains information on legislation, publications and enforcement.
http://ec.europa.eu/environment/chemicals/reach/enforcement_en.htm

Under REACH, applicants for authorization are required to control the use of Substances of Very High Concern (SVHC). If a SVHC does not have available alternatives, applicants must carry out their own alternatives assessments. The European Chemicals Agency has published a guidance document for this application that provides direction for conducting an alternatives assessment, as well as creating a substitution plan.
http://echa.europa.eu/documents/10162/17229/authorisation_application_en.pdf

The EU also has issued the Restriction of Hazardous Substances directive which ensures that new electrical and electronic equipment put on the market does not contain any of the six banned substances: lead, mercury, cadmium, hexavalent chromium, poly-brominated biphenyls or PBDEs above specified levels (European Commission 2011b).
http://www.bis.gov.uk/nmo/enforcement/rohs-home

6.8 The ENFIRO project

ENFIRO, Life Cycle Assessment of Environment-Compatible Flame retardants: Prototypical Case Study (see http://www.enfiro.eu/), is a European Commission FP7 funded research project (Contract-No. 226563) that evaluates viable substitution options for a number of brominated flame retardants for better, safer alternatives (ENFIRO 2011). The consortium is a collaboration between industries, small and medium enterprises and universities. The project delivers a comprehensive dataset on viability of production and application, environmental safety, and a life cycle assessment (LCA) of the alternative flame retardants. Different combinations of the flame retardant with the product are studied in five applications: printed circuit boards, electronic components, injection-molded products, textile coatings, intumescent paint. Three types of halogen free flame retardants (metal-, phosphorous- and nanoclay-based) are investigated in relation to 1) environmental and toxicological risks, 2) viability of industrial implementation, i.e., production of the flame retardant, 3) fire safety, and 4) application of the flame retardant into the material. The fourteen flame retardants that were considered are: aluminum diethylphosphinate, aluminum trihydroxide, ammonium polyphosphate, bisphenol A bis(diphenyl phosphate), resorcinol bis(diphenyl phosphate), triphenyl phosphate, nanoclay, melamine polyphosphate, zinc borate, zinc stannate, zinc hydroxystannate, dihydro oxaphosphaphenantrene oxide, melamine cyanurate, and pentaerythritol. The project approach is based on the chemical substitution cycle in which the alternative flame retardants are evaluated regarding their environmental and toxicological properties, their flame retardant properties, and their influence on the function of products once incorporated. The main objectives of ENFIRO are 1) to deliver a comprehensive dataset on viability of production and application, environmental safety, and a LCA of the alternative flame retardants, and 2) to recommend certain flame retardant/product combinations for future study based on LCA, life cycle costing and risk assessment studies. The outcome of that assessment together with socio-economic information is used in a LCA. The ENFIRO approach and the results are useful for similar substitution studies, e.g., in REACH. An ENFIRO Stakeholder Forum with members representing flame retardant users (e.g., formulators and users of flame retardants, waste (processing) plants) and other institutes such as non-governmental organizations and policy-related ones, guide the project.

6.9 References

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