

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

Chapter 5

General Exposure Information and Other Life-Cycle Considerations



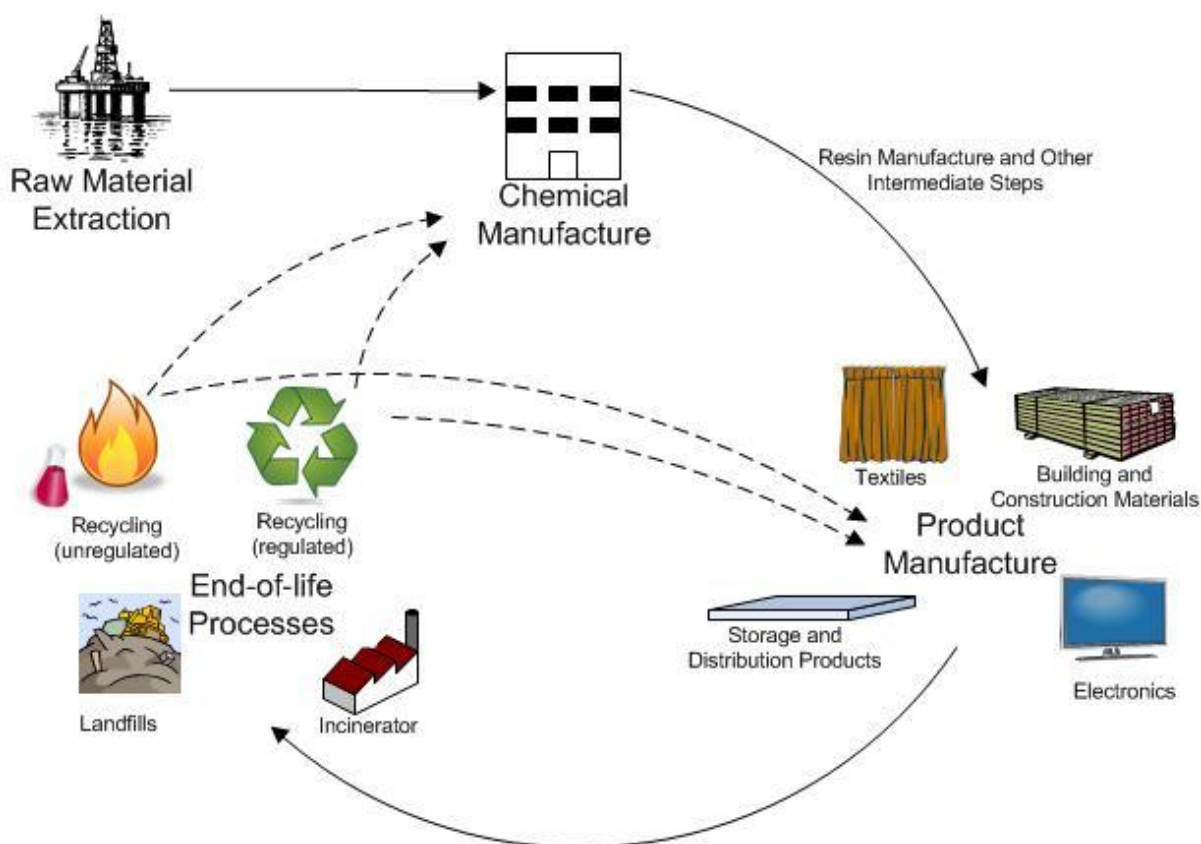
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5 General Exposure Information and Other Life-Cycle Considerations

The purpose of this chapter is to provide general information on exposure and life-cycle considerations for flame retardant chemicals. Section 5.1 includes an overview of exposure considerations and also includes data on some of the physical-chemical properties which impact the probability of exposure to decabromodiphenyl ether (decaBDE) and the alternatives included in the assessment. A quantitative exposure assessment is outside the scope of this project and is not necessary for a comparative hazard assessment. This discussion is framed in the context of five life-cycle stages: extraction (Section 5.2), chemical manufacture (Section 5.3), product manufacture (Section 5.4), product use (Section 5.5) and end-of-life (Section 5.6), as shown in Figure 5-1. Depending on the product type, intermediate steps between chemical and product manufacturing may be relevant; these are briefly discussed in Section 5.4. The chapter is intended to help the reader understand the factors that affect exposure to decaBDE and alternative flame retardants across the life-cycle.

Figure 5-1: Life Cycle Stages Included in this Chapter



5.1 Potential Exposure Pathways and Routes (General)

Exposure can occur at many points in the life cycle of a flame retardant chemical. Occupational

exposures may occur during raw material extraction, chemical and product manufacturing and at product end-of-life (i.e., reuse, refurbishing, recycling, incinerating or landfilling). Consumers may be exposed while the flame retarded product is being used. Exposures to the general population and environment may result from product manufacturing, use, storage, and end-of-life processes.

The risk associated with a given chemical or substance is influenced by how the exposure occurs. For example, the risk associated with inhaling a chemical can be different from the risk due to ingestion of the same chemical. As a result, exposure is typically characterized by pathway and route. An exposure pathway is the physical course a chemical takes from the source of release to the organism that is exposed. The exposure route is how a chemical gets inside the organism. The three primary routes of exposure are inhalation, dermal absorption, and ingestion. Each chemical's specific physical-chemical properties influence pathways and routes of exposure.

5.1.1 Occupational versus General Population Exposures

Exposures to the general population are different from exposures to workers and should be evaluated separately. Occupational exposures may be both acute and chronic because of direct contact with chemicals at relatively high concentrations while workers are conducting specific tasks such as manufacturing and processing of chemicals. However, certain occupations such as firefighting may result in unique occupational exposure scenarios. It may be more likely for consumers to be exposed chronically, over a long period, but to chemicals incorporated into products or released to the environment from a manufacturing facility. Information on sources of human exposure to decaBDE can be found in Section 5.1.5.

5.1.2 Inhalation Exposures

The physical state of the chemical during chemical manufacturing, downstream processing, incorporation into consumer products, and after release to the environment significantly influences the potential for inhalation exposure. In particular, there are three types of inhalation exposures that may be relevant for evaluation: dust, vapor, and/or mist.

Dust: “Dust is defined as solid particles of a substance or mixture suspended in a gas (usually air)” (United Nations 2011). Chemicals that are manufactured, processed, stored, or used as solids, have the potential to result in fugitive dust which may result in occupational exposures. The potential for fugitive dust formation depends on whether the solid chemical is handled in the crystalline form, as an amorphous solid, or as a fine powder. The particle size distribution and handling techniques can also impact the potential for fugitive dust. It is important to note the physical state of the chemical at the potential point of release and contact. For example, the pure chemical may be manufactured as a solid powder, indicating a potential occupational exposure to dust, but it may be formulated into solution before the majority of people come in contact with it, thereby eliminating inhalation exposure to dust as a possible exposure route. The material safety data sheet and best practice should inform the occupational worker when inhalation exposure to the chemical is likely to occur and what respiratory safety measures should be used. Furthermore, there is potential for a chemical to be released from a manufacturing facility and enter a home either through air, dirt or dust. For example, dirt or dust from a workplace may enter a home on a worker's clothing and be subsequently inhaled by other members of the

household. Additionally, certain chemicals may be released from a product during consumer use and become incorporated into indoor dust. Consumer exposures are dependent on how a chemical is incorporated into a product and on the chemical's physical-chemical properties.

If there is exposure to dust, particle size influences the degree to which the chemical enters the lungs. Particles less than 10 microns in diameter are “respirable” with potential to reach and attach to tissues in the respiratory tract and deep lung where they may be absorbed into the body. Once released into air or other media, the chemical can associate with particulate material through sorption onto particles or as particulates. For example, vapor phase chemicals can partition onto house dust and contribute to ingestion and dermal exposure pathways as well as inhalation.

Design of transfer facilities, engineering controls, and the use of personal protective equipment will have a greater impact on exposure potential in industrial settings than the size of the dust particles. However, the size of the particles in a manufacturing setting can be considered by individual decision-makers. Compounders may specify that the neat flame retardant be produced in a way that minimizes the low particle size fraction. Although manufacturer-specific, the particle size of the flame retardant chemical can be screened to remove the fine material that can then be returned to the manufacturing process. In residential settings, the flame retardants in electrical equipment and furniture, for example, may migrate to the surface of a material and escape from the polymer matrix, then likely becoming part of house dust. Exposure to flame retardants in house dust can be reduced by dusting frequently and using a vacuum cleaner with a HEPA filter.

Vapor: Vapor is defined as “the gaseous form of a substance or mixture released from its liquid or solid state” (United Nations 2011). Exposure to vapors can occur when chemicals volatilize during manufacturing, processing, storage, and use or are associated with particulates in air. Most chemical manufacturing operations occur in closed systems. However, fugitive emissions are expected during open mixing operations, transfer operations, and loading/unloading of raw materials. The more volatile the chemical the greater the fugitive releases and the higher occupational exposures are likely to be. Therefore, vapor pressure (a measure of volatility) is a key indicator of potential occupational exposures to vapors. Particulate exposures can result from the physical breakdown of products, erosion of materials from surfaces or other similar processes.

Mist: Mist is defined as “liquid droplets of a substance or mixture suspended in a gas (usually air)” (United Nations 2011). Both volatile and non-volatile liquids can result in inhalation exposure if manufacturing or use result in the formation of mist. Particle size is an important consideration in determining exposure to chemicals released as a mist. However, it is unlikely that flame retardant chemicals will be dispersed as a mist.

5.1.3 Dermal Exposures

Dermal exposure is also affected by the physical state of the chemical at the point of release and contact. Additionally, studies have shown that the amount of a chemical that is absorbed through the skin is dependent on where on the body the exposure occurs (U.S. EPA 1992). Dermal exposure is generally assumed to be proportional to the concentration of chemical in the

formulation (an exception would be if the solution contains ingredients that enhance dermal transfer). For example, the dermal exposure from contacting a pure chemical is greater than the exposure from contacting a solution that contains only 10 percent of the chemical. In addition to chemical concentration, the extent to which skin will absorb a chemical that it has to come in contact with depends on the chemical's lipophilicity, solubility, polarity volatility, structure and state (e.g., liquid, solid) (U.S. EPA 1992). To be successfully absorbed, compounds must be able to diffuse across both the aqueous pathways and lipid pathways in the skin. To do this, a chemical must first dissolve into the stratum corneum, a stable lipid barrier that is the outermost layer of the skin and the water-based portions of the skin and into the body, which is also water-based (U.S. EPA 2007a). Therefore, the best skin penetrants are "those that exhibit fat- and water-solubility and low levels of crystallinity" (p. 35 U.S. EPA 1992). Dermal exposure to volatile substances is unlikely to occur.

For occupational exposures, screening-level evaluations of dermal exposure can be based on the worker activities involving the chemical. For example, there may be exposure when workers handle bags of solid materials during loading and transfer operations. Maintenance and cleanup activities during shutdown procedures, connecting transfer lines, and sampling activities also result in potential for dermal exposures. For consumers, dermal exposure can occur if a chemical is released from a product that a consumer is handling or is in dust to which an individual comes into contact. Children may have higher dermal exposure because they crawl, roll, or sit on surfaces treated with chemicals and play with objects where residues may settle (U.S. EPA 2008). However, as stated above, absorption of a chemical through the skin is dependent on the properties of the chemical (U.S. EPA 1992).

5.1.4 Ingestion Exposures

Exposures via ingestion typically occur unintentionally when individuals eat food or drink water that has become contaminated with chemicals or ingest dust on hands. Several pathways should be considered. In regards to occupational exposures, often the primary pathway is poor worker hygiene (eating, drinking, or smoking with unwashed hands.) Additionally, dust particles may spread throughout the facility and settle (or deposit) on tables, lunchroom surfaces, or even on food itself. Vapors may similarly spread throughout the facility and may deposit near food or drinks. Another potential pathway for ingestion occurs from dust particles that are too large to be absorbed through the lungs. These "non-respirable particles" can be swallowed, resulting in exposures from this route. Consumers in the general population may also be exposed through ingestion if a chemical is released from a product and incorporated into dust, which can get on hands or deposit on food and thus be consumed inadvertently. This is an important route of exposure for children, particularly infants and toddlers, who may ingest dust and soil through repeated hand-to-mouth behavior (U.S. EPA 2008). Compared to inhalation and dermal exposures, ingestion is typically considered a less significant exposure pathway from an occupational health standpoint. However, ingestion can be an equally or more significant exposure pathway for the general population, especially children's ingestion of house dust, than inhalation and dermal exposures.

5.1.5 Human and Environmental Exposure to DecaBDE

This section summarizes the literature on occupational, consumer and environmental exposures to decaBDE. This information on decaBDE exposure can be instructive. Similar patterns of exposure may occur for alternative chemicals. However, exposure information and data are limited and only available for some of the alternatives (Stapleton, Allen et al. 2008; Betts 2009; Dodge, Pollock et al. 2009; Petito Boyce, Sax et al. 2009; Luo, Chen et al. 2010). Information on products and materials in which decaBDE has been used can be found in Chapter 2.

Human Exposures

According to U.S. Environmental Protection Agency (EPA)'s 2010 exposure assessment of polybrominated diphenyl ethers (PBDEs), individuals in occupations that would lead to higher exposures to specific congeners have higher concentrations of PBDE congeners in their blood than the general public (U.S. EPA 2010a). Workers involved in the manufacturing or recycling and disposal of products containing PBDE flame retardants have greater exposure to the chemical compared to the general population (Sjodin, Hagmar et al. 1999; Thomsen, Lundanes et al. 2001; Thuresson, Hoglund et al. 2006).

Consumer exposure to decaBDE is possible given that it can be released from common home products and become a component in house dust (Stapleton, Alaei et al. 2004; Takigamie, Suzuki et al. 2008) (for a list of products where decaBDE may be used, refer to Section 2.2). It is also possible that workers exposed to decaBDE may inadvertently carry particles containing the chemical home with them. This may lead to exposure to family members through household dust or direct contact, as has been proven with other hazardous chemicals such as pesticides and lead (Thompson, Coronado et al. 2003; Minnesota Department of Health 2010). DecaBDE has been found in dust within automobiles (Lagalante, Oswald et al. 2009) and automobile air (Mandalakis, Stephanou et al. 2008). The primary route of consumer exposure to decaBDE is through the ingestion of dust or, for infants, ingestion of breast milk, followed by food and water ingestion and dermal absorption (Lorber 2008; Petito Boyce, Sax et al. 2009; U.S. EPA 2010a). Inhalation may also be a relevant route of exposure (U.S. EPA 2010a). Children have higher levels of exposure to decaBDE than do adults (Petito Boyce, Sax et al. 2009) likely due to higher hand to mouth behavior.

Environmental Exposures

Environmental releases of decaBDE can occur during each stage of a product's life cycle, including chemical manufacturing, product manufacturing, product storage and use, and end-of-life handling (U.S. EPA 2009). In general, levels of PBDEs in humans and the environment are higher in North America than in other regions of the world, likely due to their greater use in North America (Trudel, Scheringer et al. 2011).

Empirical and predicted data indicate that all PBDEs (including decaBDE) are highly persistent in the environment (Environment Canada 2006) and decaBDE has been found in high and increasing concentrations in the sediment of lakes, rivers, streams and estuaries (Song, Li et al. 2005; Environment Canada 2006; Illinois Environmental Protection Agency 2006). Additionally, decaBDE has also been measured in ambient atmospheric particulates (Illinois Environmental

Protection Agency 2006) and in the Arctic environment, providing evidence that it is subject to long-range transport (Environment Canada 2006).

Laboratory studies demonstrate decaBDE's bioavailability and metabolism in fish (Illinois Environmental Protection Agency 2006). DecaBDE has been detected in some but not all species of fish studied (Dodder, Strandberg et al. 2002; European Chemicals Bureau 2002; Johnson-Restrepo, Kannan et al. 2005; Environment Canada 2009; Roberts, Noyest et al. 2011). Also, decaBDE has been measured in birds and their eggs (Lindberg, Sellström et al. 2004; Vorkamp, Thomsen et al. 2005) and in mammals including polar bears, seals, marmots and foxes (Christensen, MacDuffee et al. 2005; Illinois Environmental Protection Agency 2006; Voorspoels, Covaci et al. 2006; Environment Canada 2009). Further, terrestrial species tend to have higher levels of decaBDE than aquatic species for both birds (Jaspers, Covaci et al. 2006) and mammals (Christensen, MacDuffee et al. 2005). These observations indicate bioavailability of decaBDE to wildlife and human food sources with potential for bioaccumulation and biomagnification of decaBDE and/or its degradation products.

5.1.6 Physical-Chemical Properties for the Alternatives to DecaBDE included in this Assessment that May Impact Exposure

Table 5-1 highlights key physical-chemical properties that affect the likelihood of exposure along with the physical-chemical property's relevance to exposure. The properties included in the table are: the physical state of the chemical, vapor pressure, water solubility, dispersibility, log K_{ow} , bioaccumulation potential, and persistence. Descriptions of these properties and how they can be used to predict environmental behavior and hazard potential can be found in Section 4.3. More detailed information on the physical, chemical, and fate properties of each flame retardant chemical can be found in the full chemical summary assessments in Section 4.8.

Table 5-1: Key Physical/Chemical and Fate Properties of Flame Retardant Chemicals

Physical State of Chemical (ambient conditions)						
<i>Relevance to exposure:</i> Indicates if a chemical substance is a solid, liquid, or gas under ambient conditions. This is determined from the melting and boiling points. Chemicals with a melting point more than 25°C are considered solid. Those with a melting point less than 25°C and a boiling point more than 25°C are considered liquid and those with a boiling point less than 25°C are considered a gas. Physical state influences potential for dermal and inhalation exposure. For chemicals that exist as a gas, there is generally a potential for direct inhalation but not dermal exposure. For solids, there is potential for the inhalation and ingestion of dust particles and dermal contact. For liquids, there is potential for direct dermal contact but not for direct inhalation of the liquid (except in operations that produce aerosols).						
Decabromodiphenyl Ether	Aluminum Diethyl-phosphinate	Aluminum Hydroxide	Ammonium Polyphosphate	Antimony Trioxide	Bis (hexachlorocyclopentadieno) Cyclooctane	Bisphenol A bis-(diphenylphosphate)
Solid	Solid	Solid	Solid	Solid	Solid	Solid
Brominated Epoxy Polymer(s)	Brominated Epoxy Polymers	Mixture of Brominated Epoxy Polymer(s) and Bromobenzyl Acrylate	Brominated Epoxy Resin End-Capped with Tribromophenol	Brominated Polyacrylate	Brominated Poly(phenylether)	Brominated Polystyrene
Solid	Solid	Solid	Solid	Solid	Solid	Solid
Decabromodiphenyl Ethane	Ethylene bis-tetrabromophthalimide	Magnesium Hydroxide	Melamine Cyanurate	Melamine Polyphosphate	N-alkoxy Hindered Amine Reaction Products	Phosphonate Oligomer
Solid	Solid	Solid	Solid	Solid	Solid	Solid
Phosphoric Acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol	Polyphosphonate	Poly[phosphonate-co-carbonate]	Red Phosphorous	Resorcinol bis-diphenylphosphate	Substituted Amine Phosphate Mixture	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
Solid or Liquid ¹	Solid	Solid	Solid	Liquid	Solid	Solid
Triphenyl Phosphate	Tris (tribromoneopentyl) Phosphate	Tris (tribromophenoxy) Triazine	Zinc Borate			
Solid	Solid	Solid	Solid			

¹ Depends on the oligomer distribution

Vapor Pressure (mm Hg) at 25°C (unless otherwise noted)						
<i>Relevance to exposure:</i> Indicates the potential for a chemical to volatilize into the atmosphere. If a chemical has a vapor pressure leading to volatilization at room temperature or typical environmental conditions, then the chemical may evaporate and present the potential for inhalation of the gas or vapor. For a Design for the Environment (DfE) chemical alternatives assessment, inhalation exposure is assumed to occur if the vapor pressure is greater than 1×10^{-8} mm Hg. A default value of $<10^{-8}$ was assigned for chemicals without data that are anticipated to be non-volatile this is based on EPA HPV assessment guidance (U.S. EPA 2011b).						
Decabromodiphenyl Ether	Aluminum Diethyl phosphinate	Aluminum Hydroxide	Ammonium Polyphosphate	Antimony Trioxide	Bis (hexachlorocyclopentadiene) Cyclooctane	Bisphenol A bis-(diphenylphosphate)
3.5×10^{-8} at 21°C	$<10^{-8d}$	$<10^{-8c}$	$<10^{-8b}$	$<10^{-8}$	$<10^{-8c}$	$<9 \times 10^{-6a}$
Brominated Epoxy Polymer(s)	Brominated Epoxy Polymers	Mixture of Brominated Epoxy Polymer(s) and Bromobenzyl Acrylate	Brominated Epoxy Resin End-Capped with Tribromophenol	Brominated Polyacrylate	Brominated Poly(phenylether)	Brominated Polystyrene
$<10^{-8b}$	$<10^{-8d}$	$<10^{-8b}$	$<10^{-8b}$	$<10^{-8b}$	$<9.8 \times 10^{-7}$	$<10^{-8b}$
Decabromodiphenyl Ethane	Ethylene bis-tetrabromophthalimide	Magnesium Hydroxide	Melamine Cyanurate	Melamine Polyphosphate	N-alkoxy Hindered Amine Reaction Products	Phosphonate Oligomer
$<7.5 \times 10^{-7}$	1.7×10^{-6}	$<10^{-8b}$	$<10^{-8d}$	$<10^{-8d}$	$<10^{-8d}$	$<10^{-8b}$
Phosphoric Acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol	Polyphosphonate	Poly[phosphonate-co-carbonate]	Red Phosphorous	Resorcinol bis-diphenylphosphate	Substituted Amine Phosphate Mixture	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
4×10^{-7}	$<10^{-8b}$	$<10^{-8b}$	0.03 at 21°C	1.9×10^{-5} at 20°C	$<10^{-8c}$	$<10^{-8d}$
Triphenyl Phosphate	Tris (tribromoneopentyl) Phosphate	Tris (tribromophenoxy) Triazine	Zinc Borate			
6.28×10^{-6a}	$<10^{-8d}$	$<10^{-8d}$	$<10^{-8b}$			

^a Extrapolated. ^b Estimated based on polymer assessment literature (Boethling et al., 1997). ^c Estimated based on HPV guidance for nonvolatile compounds. ^d Estimated.

Water Solubility (mg/L)						
<i>Relevance to exposure:</i> Indicates the potential of a chemical to dissolve in water and form an aqueous solution. Water soluble chemicals present a higher potential for human exposure through the ingestion of contaminated drinking water (including well water). In general, absorption after oral ingestion of a chemical with a water solubility less than 10⁻³ mg/L is not expected. Water soluble chemicals are more likely to be transported into groundwater, absorbed through the gastrointestinal tract or lungs, partition to aquatic compartments, and undergo atmospheric removal by rain washout. A water solubility of 10⁻³ mg/L is used for large, high molecular weight non-ionic polymers according to the literature concerning polymer assessment (Boethling et al., 1997). A substance with water solubility at or below 10⁻³ mg/L is considered insoluble.						
Decabromodiphenyl Ether	Aluminum Diethyl phosphinate	Aluminum Hydroxide	Ammonium Polyphosphate	Antimony Trioxide	Bis (hexachlorocyclopentadieno) Cyclooctane	Bisphenol A bis-(diphenylphosphate)
<1.00×10 ⁻⁴	2.5×10 ³	1.5 at 20 °C	0.5% (w/w) at 25°C in 10% suspension	14 at 30 °C	4.4 x 10 ⁻⁵	0.389 – 0.462
Brominated Epoxy Polymer(s)	Brominated Epoxy Polymers	Mixture of Brominated Epoxy Polymer(s) and Bromobenzyl Acrylate	Brominated Epoxy Resin End-Capped with Tribromophenol	Brominated Polyacrylate	Brominated Poly(phenylether)	Brominated Polystyrene
<10 ^{-3c}	<10 ^{-3b}	<10 ^{-3c}	<10 ^{-3c}	<10 ^{-3c}	6.63×10 ⁻⁵ at 20°C	<10 ^{-3c}
Decabromodiphenyl Ethane	Ethylene bis-tetrabromophthalimide	Magnesium Hydroxide	Melamine Cyanurate	Melamine Polyphosphate	N-alkoxy Hindered Amine Reaction Products	Phosphonate Oligomer
7.2 x 10 ⁻⁴	<10 ^{-3b}	1.78 at 20°C, pH 8.3	2.7 at 20 °C	20,000	<10 ^{-3a}	0.0015 (for n=1) ^b ; <10 ⁻³ (for n≥2) ^b
Phosphoric Acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol	Polyphosphonate	Poly[phosphonate-co-carbonate]	Red Phosphorous	Resorcinol bis-diphenylphosphate	Substituted Amine Phosphate Mixture	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
<0.01	<10 ^{-3b}	<10 ^{-3c}	<10 ^{-3a}	1.05 at 20°C	>1×10 ^{6b}	<10 ^{-3b}
Triphenyl Phosphate	Tris (tribromoneopentyl) Phosphate	Tris (tribromophenoxy)Triazine	Zinc Borate			
1.9	0.9	<10 ⁻³	0.28%*			
*The water solubility of zinc borate is expressed as a percentage and is <0.28% at neutral pH. Its dissolution is pH dependent and will vary within the range 5-7 that is typically found in the environment. Good water solubility data for zinc borate are not available. ^a Estimated based on EPA High Production Volume assessment guidance. ^b Estimated. ^c Estimated based on polymer assessment literature (Boethling et al., 1997).						

Log K _{ow}						
<i>Relevance to exposure:</i> Indicates a chemical's tendency to partition between water and lipids in biological organisms. A high log K_{ow} value indicates that the chemical is more soluble in octanol (lipophilic) than in water, while a low log K_{ow} value means that the chemical is more soluble in water than in octanol. Log K_{ow} can be used to evaluate absorption and distribution in biological organisms, potential aquatic exposure, and potential general population exposure via ingestion. Generally, chemicals with a log K_{ow} <4 are water soluble and bioavailable, chemicals with a log K_{ow} ≥4 tend to bioaccumulate. Chemicals with a high log K_{ow} also tend to bind strongly to soil and sediment. Log K_{ow} cannot be measured for inorganic substances, polymers, and other materials that are not soluble in either water or octanol. This is indicated in the table with "No data".						
Decabromodiphenyl Ether	Aluminum Diethyl phosphinate	Aluminum Hydroxide	Ammonium Polyphosphate	Antimony Trioxide	Bis (hexachlorocyclopentadieno) Cyclooctane	Bisphenol A bis-(diphenylphosphate)
6.27	-0.44 ^a	No data	No data	No data	11 ^a	>10 ^a
Brominated Epoxy Polymer(s)	Brominated Epoxy Polymers	Mixture of Brominated Epoxy Polymer(s) and Bromobenzyl Acrylate	Brominated Epoxy Resin End-Capped with Tribromophenol	Brominated Polyacrylate	Brominated Poly(phenylether)	Brominated Polystyrene
No data	No data	No data	No data	No data	>9	No data
Decabromodiphenyl Ethane	Ethylene bis-tetrabromophthalimide	Magnesium Hydroxide	Melamine Cyanurate	Melamine Polyphosphate	N-alkoxy Hindered Amine Reaction Products	Phosphonate Oligomer
14 ^a	9.8 ^a	No data	<0 ^a	<-2 ^a	10	7.2 (n=1) ^a ; 11 (n=2) ^a
Phosphoric Acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol	Polyphosphonate	Poly[phosphonate-co-carbonate]	Red Phosphorous	Resorcinol bis-diphenylphosphate	Substituted Amine Phosphate Mixture	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
5.5	No data	No data	No data	4.93	<-2 ^a	12 ^a
Triphenyl Phosphate	Tris (tribromoneopentyl) Phosphate	Tris (tribromophenoxy)Triazine	Zinc Borate			
4.59	8.1 ^a	>10	No data			
^a Estimated data.						

Bioaccumulation Potential						
<i>Relevance to exposure:</i> Indicates the degree to which a chemical substance may increase in concentration within a trophic level. Bioconcentration describes the increase in tissue concentration relative to the water concentrations (environmental sources); bioaccumulation generally includes dietary and environmental sources. As chemicals bioconcentrate or bioaccumulate, there is a higher potential for them to reach a level where a toxic effect may be expressed. Estimated and/or measured bioconcentration and bioaccumulation values are presented as ranges based on relevant DfE hazard categories for each chemical. The DfE criteria for bioaccumulation designations are assigned by the bioaccumulation factor (BAF) or log BAF. The designations for bioaccumulation potential are as follows: Very High (VH) if the BAF (log BAF) is >5,000 (>3.7); High (H) if the BAF is between 5,000 (3.7-3) and 1,000; Moderate (M) if the BAF is between <1,000 and 100 (<3-2); and Low (L) if the BAF is <100 (<2) (U.S. EPA 2011a).						
Decabromodiphenyl Ether	Aluminum Diethyl phosphinate	Aluminum Hydroxide	Ammonium Polyphosphate	Antimony Trioxide	Bis (hexachlorocyclopentadieno) Cyclooctane	Bisphenol A bis-(diphenylphosphate)
High (1,000-5,000) ^b	Low (<100) ^a	Low (<100) ^a	Low (<100) ^a	Low (<100) ^a	High (1,000-5,000) ^b	High (1,000-5,000) ^b
Brominate Epoxy Polymer(s)	Brominated Epoxy Polymers	Mixture of Brominated Epoxy Polymer(s) and Bromobenzyl Acrylate	Brominated Epoxy Resin End-Capped with Tribromophenol	Brominated Polyacrylate	Brominated Poly(phenylether)	Brominated Polystyrene
Low (<100) ^c	Low (<100) ^c	Low (<100) ^c	Low (<100) ^b	Low (<100) ^c	Moderate (<1,000) ^a	Low (<100) ^c
Decabromodiphenyl Ethane	Ethylene bis-tetrabromophthalimide	Magnesium Hydroxide	Melamine Cyanurate	Melamine Polyphosphate	N-alkoxy Hindered Amine Reaction Products	Phosphonate Oligomer
High (1,000-5,000) ^d	High (1,000-5,000) ^b	Low (<100) ^a	Low (<100) ^a	Low (<100) ^a	High (1,000-5,000) ^b	High (1,000-5,000) ^b
Phosphoric Acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol	Polyphosphonate	Poly[phosphonate-co-carbonate]	Red Phosphorous	Resorcinol bis-diphenylphosphate	Substituted Amine Phosphate Mixture	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
Moderate (172) ^b	Low (<100) ^b	Low (<100) ^c	Low (<100) ^a	High (1,000-5,000) ^b	Low (<100) ^b	High (1,000-5,000) ^b
Triphenyl Phosphate	Tris (tribromoneopentyl) Phosphate	Tris (tribromophenoxy)Triazine	Zinc Borate			
Moderate (100-1,000)	Moderate (100-1,000) ^b	High (1,000-5,000) ^b	Low (<100) ^b			
^a Based on professional judgment. ^b Based on estimated data. ^c Estimated based on polymer assessment literature (Boethling et al., 1997). ^d Based on monitoring data.						

Persistence						
<i>Relevance to exposure:</i> Indicates the length of time required for a chemical substance to be completely converted to small building blocks including water, carbon dioxide, and ammonia (“ultimate degradation”). Persistence is typically expressed as a ‘half-life’, which is the time for the amount of the substance to be reduced by one half. For a DfE chemical alternatives assessment, persistent chemicals include those that have metabolic or degradation products that have long half-lives. The longer a chemical or its degradation/metabolism products exist in the environment, the higher the likelihood for human or environmental exposure. “Compartments” refer to those environmental media to which chemicals may partition and include soil, sediment, water and air as standard compartments for fate assessment. Persistence is considered Very High (VH) if the half-life is >180 days or recalcitrant; High (H) if the half-life is 60-180 days; Moderate (M) if the half-life is <60 days but ≥16 days; Low (L) if half-life is <16 days OR readily passes biodegradability test not including the 10- day window (see DfE Program Alternatives Assessment Criteria for Hazard Evaluation); and Very Low (VL) if passes biodegradability test with 10-day window (see DfE Program Alternatives Assessment Criteria for Hazard Evaluation).						
Decabromodiphenyl Ether	Aluminum Diethyl phosphinate	Aluminum Hydroxide	Ammonium Polyphosphate	Antimony Trioxide	Bis (hexachlorocyclopentadieno) Cyclooctane	Bisphenol A bis-(diphenylphosphate)
Very High (>180 days)	High (60-180 days) ^b	High (60-180 days) ^b	Very High (>180 days) ^c	High (60-180 days) ^b	Very High (>180 days)	High (60-180 days)
Brominate Epoxy Polymer(s)	Brominated Epoxy Polymers	Mixture of Brominated Epoxy Polymer(s) and Bromobenzyl Acrylate	Brominated Epoxy Resin End-Capped with Tribromophenol	Brominated Polyacrylate	Brominated Poly(phenylether)	Brominated Polystyrene
Very High (>180 days) ^c	Very High (>180 days) ^c	Very High (>180 days) ^c	Very High (>180 days) ^c	Very High (>180 days) ^c	Very High (>180 days) ^c	Very High (>180 days) ^c
Decabromodiphenyl Ethane	Ethylene bis-tetrabromophthalimide	Magnesium Hydroxide	Melamine Cyanurate	Melamine Polyphosphate	N-alkoxy Hindered Amine Reaction Products	Phosphonate Oligomer
Very High (>180 days)	Very High (>180 days)	High (60 – 180 days) ^b	Very High (>180 days)	High (60-180 days) ^b	High (60-180 days)	Very High (>180 days) ^a
Phosphoric Acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol	Polyphosphonate	Poly[phosphonate-co-carbonate]	Red Phosphorous	Resorcinol bis-diphenylphosphate	Substituted Amine Phosphate Mixture	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
High ^b	Very High (>180 days) ^a	Very High (>180 days) ^a	High (60-180 days)	Moderate (60 – 16 days)	High (60 – 180 days) ^b	Very High (>180 days)
Triphenyl Phosphate	Tris (tribromoneopentyl) Phosphate	Tris (tribromophenoxy)Triazine	Zinc Borate			
Low (<16 days)	High (60-180 days) ^a	Very High (>180 days)	High (60-180 days) ^b			
^a Based on results from biodegradation estimation model. ^b Based on professional judgment. ^c Estimated based on polymer assessment literature (Boethling et al., 1997).						

5.2 Extraction

This section describes the first step in manufacturing a flame retardant, extracting or synthesizing the basic components which make up the final chemical. As stated in Chapter 3, there are four main categories of flame retardants: inorganic (i.e., metal salts), halogenated (bromine or chlorine), phosphorous-based, or nitrogen-based. Descriptions by category are given below demonstrating how the basic elements of each of the flame retardants for this assessment are extracted, and some exposure considerations associated with extraction are also included. This report is not evaluating the synthesis and processing of each of these materials but is providing information on the primary source of each of their components. In general, the organic flame retardants are derived from petroleum and the inorganic flame retardants are derived from other naturally occurring mineral deposits.

5.2.1 Inorganic Flame Retardants

The inorganic flame retardants considered in this report include the following base elements:

Aluminum

Aluminum, used in aluminum hydroxide ($\text{Al}(\text{OH})_3$), is one of the most plentiful elements in the earth's crust and is usually present as bauxite ore. Bauxite can contain three different aluminum minerals, including gibbsite ($\text{Al}(\text{OH})_3$), böhmite, and diaspore (crystalline structures of $\text{AlO}(\text{OH})$). Bauxite ore also typically contains clay, silt, iron oxides, and iron hydroxides. The majority of bauxite is mined from surface deposits, but some is excavated from underground deposits (International Aluminium Institute 2007). Nearly all of the bauxite consumed in the United States is imported (USGS 2007). By refining bauxite ore using the Bayer process aluminum hydroxide can be made (U.S. EPA 1995b). This process requires mixing finely ground bauxite with sodium hydroxide to form a slurry that is then placed under steam pressure and heat (U.S. EPA 1995a). This creates a mixture of dissolved aluminum oxides and bauxite residues and precipitates out most of the impurities. The remaining slurry contains sodium aluminate that is flash cooled by evaporation and clarified to remove any other fine impurities (U.S. EPA 1995a). Lastly, the solution is sent to a precipitation tank where it is cooled and gibbsite "seeds" (usually from a previous cycle) are added to promote the precipitation of solid aluminum hydroxide crystals (U.S. EPA 1995a).

Magnesium

The mineral form of magnesium hydroxide ($\text{Mg}(\text{OH})_2$), also called brucite, is found throughout the world (Amethyst Galleries Inc 2008; USGS 2008). However, magnesium hydroxide is typically recovered from seawater and magnesite-bearing brines, which constitutes an even greater and more readily available resource than brucite. In 2007, magnesium oxide and other magnesite compounds (including magnesium hydroxide) were recovered from both seawater and well brines in the U.S. (USGS 2008).

Antimony

Antimony (Sb), used in antimony trioxide (Sb_2O_3), can be mined, recovered as a byproduct from the smelting of lead and silver-copper ores, or derived from scrap source materials, including lead-acid batteries (Carlin Undated). Six U.S. companies produce antimony metal and oxide using domestic and foreign feed material (Carlin Undated). However, recycling and domestic mine output supplied less than half of the estimated U.S. demand for antimony, meaning a significant amount of antimony in the U.S. is imported (Carlin Undated). Antimony is mined as a principal product and recovered as a byproduct of the smelting of base metal ores in 23 countries. China, Bolivia, Russia and South Africa account for more than 90 percent of mine production (Carlin Undated). More than 50 percent of available antimony is used in flame retardants (Carlin Undated).

Zinc

Zinc most often occurs in association with the sulfide mineral group as sphalerite (ZnS), which is the principal mineral mined to recover zinc. Other metals associated with sulfide ores include copper, iron, mercury, cadmium, silver and small quantities of gold (U.S. EPA 1994). These metals occur in varying amounts, and depend on the nature of the ore. Zinc ore is recovered from three types of deposits: strata-bound deposits, replacement deposits and vein deposits (U.S. EPA 1994). The largest and most productive deposits are associated with expansive, relatively flat lying sedimentary deposits. The strata-bound zinc ore in these deposits are restricted to well-defined stratigraphic units (a distinct layer of sedimentary or igneous rock), typically limestone, dolomite, or shale (U.S. EPA 1994). Replacement and vein type deposits make up a smaller portion of mined zinc. For the most part, zinc is mined in underground operations, although there are a few surface operations (U.S. EPA 1994).

5.2.2 Halogenated Flame Retardants

Bromine

Bromine is collected from salt brines in the United States and China, from the Dead Sea in Israel and Jordan, and from ocean water in Wales and Japan (Sjodin, Hagmar et al. 1999; Thuresson, Bergman et al. 2006; Bromine Science and Environmental Forum 2007; Qu, Bi et al. 2007). Bromine is typically isolated via a series of redox reactions involving chlorine, sulfur dioxide and acid (MIT 2003; The University of York). During these reactions the brine or seawater is acidified and then chlorinated to oxidize bromide to elemental bromine. At this stage, the bromine is volatilized from the seawater, but it is not concentrated enough for collection or liquefying, so sulfur dioxide is added to reduce the bromine to hydrobromic acid. Chlorine is then added to re-oxidize hydrobromic acid to bromine gas (Br_2). At this point, bromine gas is collected and condensed (Grebe, Bauman et al. 1942). While caustic substances are involved in these processes, they are typically contained in an enclosed tower to prevent worker exposure and environmental release.

Chlorine

Chlorine, one of the most abundant elements on earth (Kostick 2001), is found primarily as the chloride ion (Cl^-), which is a component of salt found deposited in the earth or dissolved in the oceans. Chlorine is produced industrially via the chloralkali process, which involves the electrolysis of an aqueous sodium chloride (a brine) through an ion exchanging membrane (ERG 2006). Chloride ions are oxidized at an anode on the membrane into chlorine. In addition to chlorine, this chloralkali process yields hydrogen gas (H_2) and sodium hydroxide (NaOH). The chloralkali process accounts for more than 95 percent of global chlorine production (ERG 2006).

5.2.3 Phosphorous-Based Flame Retardants

Phosphorus-based flame retardants are commonly synthesized from phosphate rock, which contains the mineral apatite (an impure tri-calcium phosphate). Phosphate esters can also be derived from yellow phosphorus. Large deposits of phosphate rock are found in Russia, Morocco, Florida, Tennessee, Utah, and Idaho (Lide 1993/94). Tri-calcium phosphate, the essential component of phosphate rock, is heated in the presence of carbon and silica in an electric furnace or fuel-fired furnace. Elementary phosphorus is liberated as vapor and may be collected underwater (Lide 1993/94). While elementary phosphorus can form a diatomic molecule with a triple bond, it more readily forms a tetrahedral P_4 molecule. At room temperature, phosphorus can exist in an amorphous or semi-crystalline state, called red phosphorus, which is produced from white phosphorus by extended heating in an inert atmosphere (Calvert 2004).

As for yellow phosphorous, approximately 80 percent of the global phosphorus is mined in China in the form of phosphate ore (Shigeru 2007). Extracting yellow phosphorus from phosphate ore also involves the co-extraction of arsenic, mercury, lead and other heavy metals as impurities that should be well controlled and treated before disposal of wastewater. If producers of yellow phosphorus appropriately treat their wastewater, then environmental releases and human exposures can be prevented. However, improperly treated wastewater can lead to major adverse environmental impacts (Shigeru 2007).

Predictions suggest that the world may be approaching ‘peak phosphorous’, or the point in time when the maximum production rate is reached. Phosphate-rich rocks are becoming harder to find and the demand for rock phosphate will soon exceed supply (Ulrich, Malley et al. 2009; Beardsley 2011). Depending on the calculation, predictions of peak phosphorous are broad (between twenty and several hundred years away), with some researchers predicting that peak extraction could occur as early as 2030 (Ulrich, Malley et al. 2009). This could have serious economic consequences in that it could raise the cost of products which use phosphorous (Ulrich, Malley et al. 2009) such as fertilizer or phosphorous-based flame retardants. It is suggested that there are ways to manage and mitigate peak phosphorous given that there is “an abundant but often ignored source of phosphorous” in human and animal waste (Beardsley 2011) but technology to extract and use phosphorous from these sources is still in its infancy (Ulrich, Malley et al. 2009).

5.2.4 Nitrogen-Based Flame Retardants

Nitrogen is the largest constituent of the earth's atmosphere and is also present in all living organisms, proteins, and nucleic acids (Kramer 2000). Anhydrous ammonia is produced commercially through the Haber-Bosch process, in which nitrogen and hydrogen react under high temperatures and pressure to produce ammonia (Kramer 2000). In this reaction, the source of nitrogen is air, which is almost 80 percent nitrogen. Additionally, small quantities of nitrates are mined from mineral resources principally in Bolivia and Chile (Kramer 2000). Although the U.S. produces most of its ammonia, the U.S. does import some ammonia mainly from Canada, Russia, and Trinidad and Tobago.

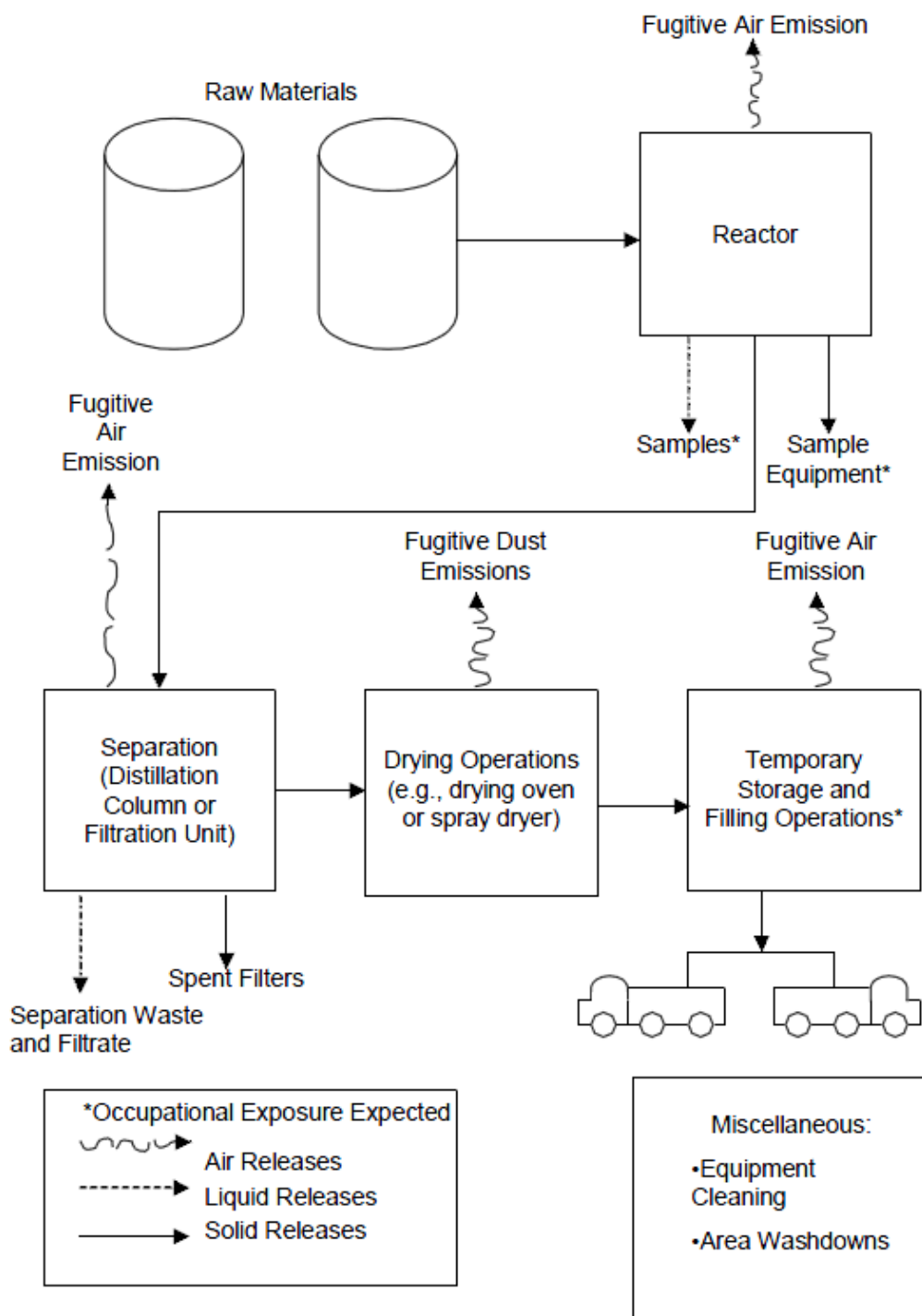
5.3 Chemical Manufacturing

After the extraction or synthesis of the flame retardant's basic components, the flame retardant chemical itself can be manufactured. Unit operations, operating conditions, transfer procedures, and packaging operations vary with the manufacture of different flame retardants and resin chemicals. Potential releases and occupational exposures will depend on each of these parameters. While it is outside the scope of this report to identify and quantify the releases and exposures associated with individual chemicals, this section presents a general description of typical chemical manufacturing processes and identifies potential releases.

Figure 5-2 is a generic process flow diagram for chemical manufacturing. Production volumes and batch sizes associated with flame retardants typically require the raw materials to be stored in large tanks or drums until use. The first step in most chemical manufacturing processes is to load or charge raw materials into some type of reactor or mix tank. Production volumes and batch sizes associated with flame retardant chemicals typically require the raw materials to be stored in large tanks or drums until use. Large-quantity liquids are typically pumped into the reactor, and solids are weighed and transferred via conveyorized, mechanical systems. Small-quantity raw materials may be manually introduced or carefully metered via automated systems. Releases and exposures that are expected from these operations are associated with the raw materials, not the finished flame retardant product (U.S. EPA 2005).

Throughout the chemical manufacturing process, there are several release points that may pose an opportunity for exposures to workers (see Figure 5-2) including packaging operations, leaks from pumps and tanks, fugitive emissions from equipment, cleaning of process equipment, and product sampling activities. Additionally, crude or finished products are often stored on-site in drums, day-tanks, or more permanent storage vessels until the chemical is packaged and shipped to the next user. The transfer and packaging operations, waste management activities, as well as any routine and unplanned maintenance activities, and spills or accidents may result in releases and exposures.

Figure 5-2: Generic Chemical Manufacturing Process Flow Diagram



Source: U.S. EPA 2005

Crude or intermediate products may be transferred through a series of reactors, distillation columns, filtration systems, drying ovens, spray dryers, and other unit operations. These processes typically occur in closed systems, with engineering controls that serve both to regulate operating parameters such as temperature and pressure as well as to minimize fugitive releases. However, there is potential for a variety of solid and liquid releases from these operations, from cleaning process equipment and from sampling activity. Additionally, crude or finished products may be stored on-site in drums, day-tanks, or more permanent storage vessels until the flame retardant formulation is packaged and shipped to customers (e.g., foam and textile manufacturers). The transfer and packaging operations, including storage, are expected to result in releases of the flame retardant chemicals. Finally, miscellaneous operations, such as routine and unplanned maintenance or waste management activities, can result in considerable releases and exposures (U.S. EPA 2005).

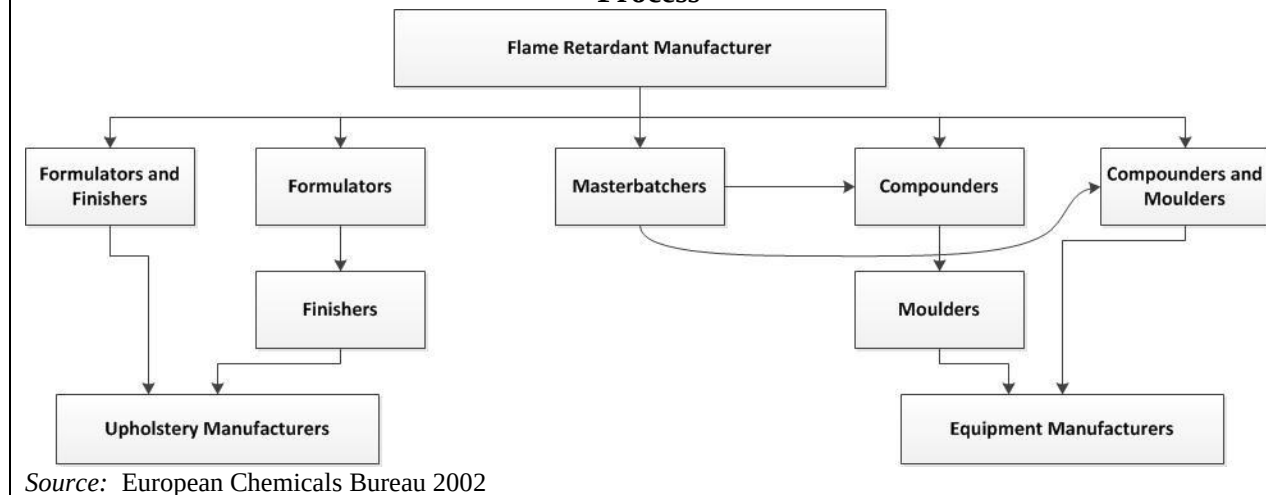
After the flame retardant is manufactured, it may need to be formulated into a solution, slurry, or mixture prior to its introduction into the commercial flame retardant formulation. For example, fine powders of a chemical may be formulated into an agglomerated powder or into a solution. The formulation steps usually occur at the chemical manufacturing facility, but additional mixing steps can occur at the formulator's manufacturing plant.

Release points from manufacturing and formulating can include: transfer and packaging operations involving handling a chemical product; routine and unplanned maintenance activities; leaks from pumps and pipelines; fugitive emissions from equipment; product sampling; waste management; and cleaning of equipment for transport and storage vessels.

5.4 Product Manufacturing

Given that decaBDE and its alternatives are used in a wide variety of products (see Chapter 2), this assessment does not include a discussion of the manufacturing process for each end-use product. However, a general discussion of how flame retardants are incorporated into plastics and textiles is included below in an attempt to understand where along the manufacturing process human or environmental exposures may occur. The production of flame retardants and their incorporation into a product is a complex process which involves multiple companies and specialties (European Chemicals Bureau 2002). With this in mind, the description of product manufacturing provided in this report is a generic one that understands that exposure is likely to vary at different facilities. Figure 5-3 displays the various steps flame retardants go through before they are incorporated into a final product for sale. The left side of the figure depicts the textile manufacturing process whereas the right side of the figure depicts the plastic manufacturing process (the plastic is subsequently used to make equipment such as televisions or computers). Supply chains may be more intricate for complex durable goods if materials or parts containing decaBDE are used to build subcomponents that are later aggregated into the final product. This type of assembly may also be considered when choosing chemical alternatives in complex finished goods.

Figure 5-3: Schematic of Flame Retardant Production and Incorporation into End Product Process



Depending on the processes and equipment used, exposure can occur at each stage of the manufacturing process. For non-textile based polymers (the right half of Figure 5-3) exposure can occur anywhere along the process such as during compounding¹⁴ or masterbatch¹⁵ production and these processes may or may not be carried out in the same facility. The type of polymer being manufactured does not affect release volumes; release is dependent on the type of system used (i.e., closed or open) and the amount of flame retardant used (European Chemicals Bureau 2002).

Exposure potential is highest during the handling of the raw flame retardant (European Chemicals Bureau 2002). For decaBDE, any losses during this stage will be to the air but it is expected that the dust will rapidly settle within the facility. Therefore, exposure may occur dermally or through inhalation. To understand the fate and potential exposure routes of the other alternatives, an understanding of their physical-chemical properties is essential (see Table 5-1). Additionally, compounding is prone to dust generation but losses are thought to be lower than the handling of the flame retardant itself. It is possible that losses may occur early in the mixing cycle and that localized containment may be used to recover the material (European Chemicals Bureau 2002). There may be releases to the air and to the atmosphere at this stage of the manufacturing process.

Textile manufacturing (the left half of Figure 5-3) is a complex process which involves fiber preparation, spinning, knitting, weaving, and dyeing among many other steps, all of which occur in the finishing or upholstery manufacturing steps. The addition of additive flame retardants in textiles occurs in the final stage of wet processing, which occurs before the product is cut and sewn. According to the International Agency for Research on Cancer (IARC), “textile workers are exposed to textile related dusts through the manufacturing process. During the spinning,

¹⁴ Blending of the polymer with various additives

¹⁵ Plastic compounds that contain high concentrations of additives which are subsequently mixed in the main polymer matrix.

weaving and knitting operations, exposure to chemicals is generally limited.” During the finishing processes when flame retardant chemicals are applied, IARC states that workers typically have exposures to multiple chemicals, including crease-resistance agents, antimicrobial agents, and flame retardants (IARC 1990).

When incorporating flame retardants into textiles, surface treatment is often used. There are two types of surface treatments: finishes and coatings. Finishes are applied by impregnating the fabrics in an aqueous solution of the chemical. Coatings are applied by incorporating a layer of flame retardant to the fabric, generating a heterogeneous fabric/polymer composite. Flame retardants used for finishes include phosphates and polyphosphates, phosphorous amides, phosphonium derivatives, antimony trioxide, borax and boric acid or halogenated flame retardants. Flame retardants used for coatings include phosphates, phosphonates, and brominated derivatives, which may be applied as backcoatings in the form of a paste or foam (GnoSys UK Ltd for the Department of Environment Food and Rural Affairs 2010). As of 2008, the leading flame retardant in backcoating on a wide range of fabrics including synthetic blends, is decaBDE, used with antimony oxide. New chemicals in development for textile coatings are polymers and copolymers of pentabromobenzyl acrylate (CAS Number: 59447-55-1). Additionally, insoluble ammonium phosphates have also been found to work well on charrable fabrics (Weil and Levchik 2008).

Flame retardants in textiles are classified according to their “laundry durability.” A non-durable flame retardant is washed off immediately when soaked in water, but may resist dry cleaning. Semi-durable flame retardants resist water soaking and possibly a few washes, while durable flame retardants resist 50 to 100 washes (Weil and Levchik 2008). Washing of flame retarded fabric could result in releases to waste water treatment plants and eventually to the environment.

Flame retardants based mostly on phosphate or phosphonate salts are typically used on infrequently washed or disposable goods given that they are non- or semi-durable. In regards to durable finishes, tetrakis(hydroxymethyl)phosphonium salts reacted with urea and cured with gaseous ammonia have been used for about 50 years in cellulosic fabrics. Other competitive wash-durable phosphorus-based finishes are also in development. Furthermore, polyesters are flame retarded with phosphonate or hexabromocyclododecane in a “thermosol¹⁶” process (Weil and Levchik 2008).

5.5 Use

As discussed in Chapter 2, decaBDE and its alternatives are used in a wide variety of polymers and products, allowing for potential release into a home, office or vehicle. Given that all of the flame retardants in this assessment are additive (as opposed to reacted into the polymer matrix), the potential for the flame retardant chemical to migrate or be released from a product is present. As discussed in Section 3.1, additive flame retardants are incorporated into the product through physical mixing and are not chemically reacted into the polymer. Empirical data on decaBDE

¹⁶ The thermosol process is the process of incorporating flame retardants into synthetic fibers. To run this process, liquid flame retardants are dissolved or dispersed in water (emulsion). Freshly spun hot fiber passes through this solution and the flame retardant penetrates the surface of the fiber because its affinity to the polymer is higher than to water. When the fiber cools down the flame retardant stays close to the surface.

and other PBDEs in house dust demonstrate that additive flame retardants are being released from products into the surrounding environment (Stapleton, Dodder et al. 2004). However, it is difficult to identify or quantify the primary sources of the additive flame retardants, given consumer products are not labeled or identified by specific treatments with flame retardant additives.

There are peer reviewed studies about PBDE and decaBDE exposures. For example, Trudel, Scherinder et al. (2011) found that the body burden¹⁷ of PBDE mixtures is generally higher in the United States and Canada than in other countries, likely due to the more stringent fire safety performance standards in North America and the greater number of consumer products containing these flame retardants. Again using PBDEs as an example, it has been shown that in the U.S., a primary exposure pathway for PBDEs among consumers is inhalation or ingestion of house dust (Johnson, Stapleton et al. 2010). In contrast, the diet constitutes a primary exposure pathway for consumers in Europe, China, and many other countries worldwide (Trudel, Scheringer et al. 2011). PBDE's have a tendency to bioaccumulate in the food chain, particularly in fatty tissues of animals. Consequently, meat and dairy products have higher concentrations of PBDEs than fruit and vegetables (Schechter, Haffner et al. 2010). Additionally, a large number of human samples have been analyzed and PBDE concentrations have increased by nearly a factor of 100 during the last 30 years (U.S. EPA 2009). The bioaccumulation potential of the other alternatives in this assessment is addressed in the Chapter 4 in each chemical's hazard profile.

Exposure levels and routes also vary by age group. Given children's predisposition to put hands and toys in their mouth, they can inadvertently ingest larger amounts of house dust than adults. Some children may be at a higher risk of exposure if family members work with PBDEs and bring dust containing the chemical home with them (Washington State Department of Labor & Industries Undated). The Agency for Toxic Substances and Disease Registry (2004) and the Child-Specific Exposure Factors Handbook (2008) both state that a child's exposure may differ from that of adults because children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface area in proportion to body volume. Additionally, it is possible for infants to be exposed to bioaccumulative chemicals through breast milk.

In addition to considering consumer exposures to a specific flame retardant, it is important to consider degradation products. For example, under certain conditions, decaBDE can degrade to less brominated congeners, which are potentially more toxic. Photolysis is expected to be the primary degradation process for decaBDE when it is significantly exposed to UV light (U.S. EPA 2009). DecaBDE can undergo photolytic debromination in house dust (Stapleton and Dodder 2008) and in organic films exposed to sunlight through automobile windshields (Ecology Center 2008), demonstrating that debromination may be possible within an automobile. Metabolic debromination of decaBDE can occur in fish, birds, cows, and rats, although its overall significance when compared with other degradation processes is unclear (U.S. EPA 2009). Uncertainty exists for the degradation products of some decaBDE alternatives. Debromination and other degradation processes may be relevant for some of the alternatives. Chapter 4 of this report provides a summary of the chemical-specific information available at the time of publication.

¹⁷ Body burden refers to the amount of a toxic substance present in the human body at a given time.

5.6 End-of-Life

When products reach their end-of-life, there are multiple pathways which they could take, including unregulated and/or regulated recycling (including reuse and refurbishment), landfilling, or incineration. The manner in which a product is handled after use contributes to its environmental and human health impacts. The following sections consider end-of-life issues for some of the types of products requiring flame retardants. Note that there may be overlap in the information presented for each product sector.

5.6.1 Electronics

The amount of used and end-of-life electronic equipment generated annually in the United States is growing rapidly. In 2010, the U.S. electronics recycling industry processed over 3.5 million tons of used and end-of-life electronic equipment (a large increase compared to the 650,000 tons processed in 2002) (Institute of Scrap Recycling Industries Inc 2011), whereas 3.2 million tons, predominately from households, is still sent to landfills (U.S. EPA 2010b). However, the amount being sent to landfills is likely to decline as there is a growing trend of state laws that requires the recycling of used and end-of-life electronics equipment (U.S. EPA 2010b).

Recycling Electronics

The U.S. electronics recycling industry has grown over the past ten years and has the capacity to handle additional tonnage. The biggest challenge is the need to educate households, businesses and government entities on the importance of responsibly recycling their used electronics equipment (Harris 2011; Institute of Scrap Recycling Industries Inc 2011).

The U.S. electronics recycling industry has seen a significant increase in the use of third-party certifications for electronic waste management and recycling (Harris 2011; Institute of Scrap Recycling Industries Inc 2011). Electronics recyclers may be certified to the *Responsible Recycling Practices for Use in Accredited Certification Programs for Electronics Recyclers* – better known as the “R2 Practices”, (or simply “R2”) or the *e-Stewards Standard for Responsible Recycling and Reuse of Electronic Equipment®*, (as known as “the e-Stewards Standard”).¹⁸ The e-Stewards Standard is another certification program by which electronics recyclers may be certified. The certification process helps to ensure that electronics recyclers use the best available practices to protect worker health by minimizing exposure.

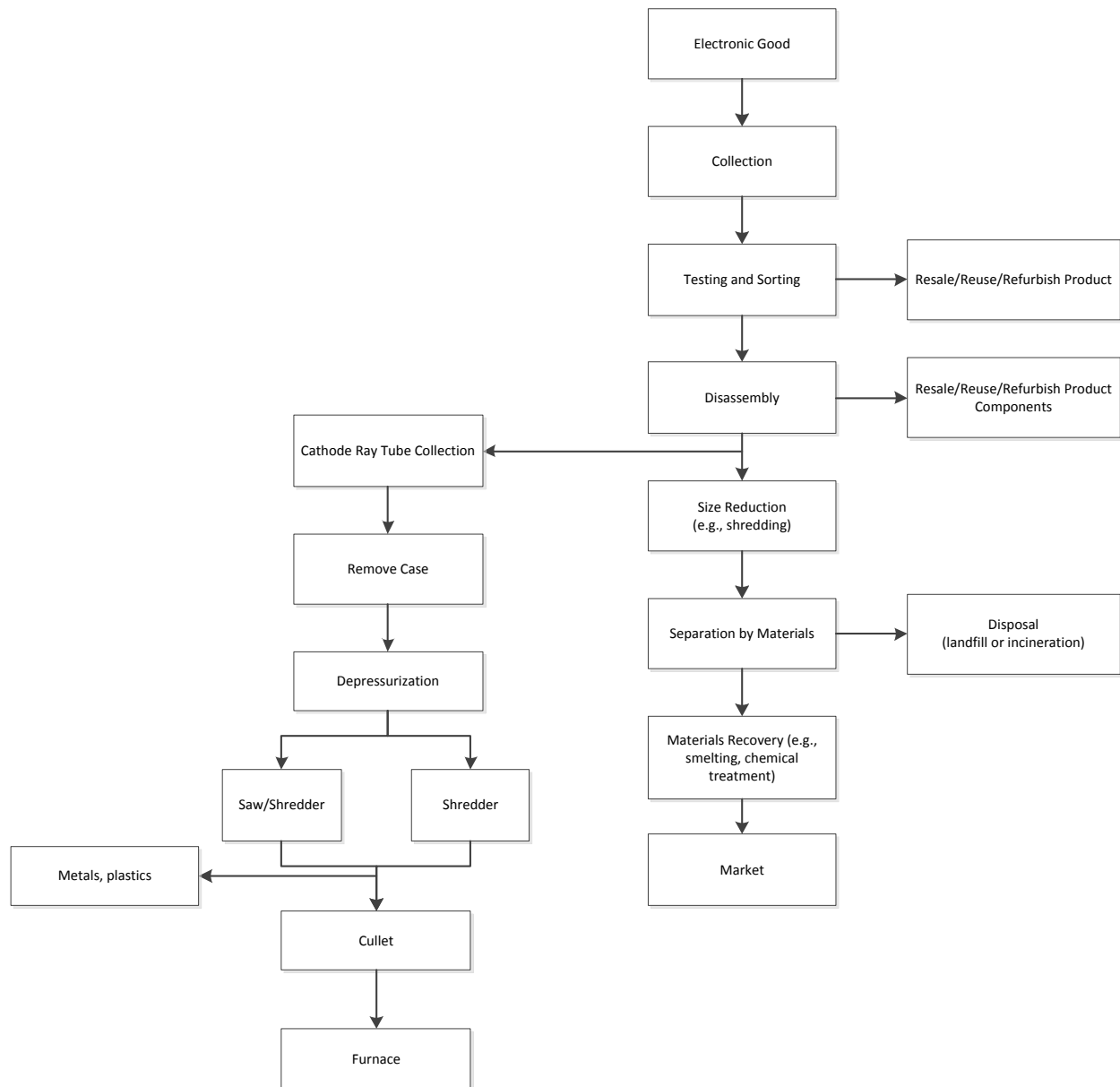
In the United States, used and end-of-life electronic equipment is typically collected by the recycling industry (i.e., collectors, repair/refurbishers, recyclers, and brokers). The collected equipment then undergoes a series of tests, or is "triaged", to determine its condition and market value, if any. If a device or component's key functions are in good working condition it can be resold directly as a used product or refurbished (e.g., updated operating systems or cosmetic changes) and then sold as a product on the domestic and global marketplace.

¹⁸ Information about electronics recycling facilities certified to the R2 Practices is available from R2 Solutions at www.R2Solutions.org. For more information about electronics recycling facilities certified to the e-Stewards Standard, go to www.e-stewards.org.

After the triage process, the remaining equipment is disassembled, either manually or mechanically, and segregated into commodity grade streams (e.g., steel, aluminum, plastic, glass, circuit boards that include copper, gold, silver, platinum, palladium, and rare earth oxides) that are then sold into the domestic and international commodities market. Many of the markets for processed raw materials are also outside of the U.S. and the manner in which used electronics are disposed of or recycled will affect the potential environmental and human health impacts.

Figure 5-4 is a depiction of the general electronic recycling process and shows that this process can involve both thermal processing, such as smelting to recover precious metals, and nonthermal processing, such as disassembly, shredding, separation, and chemical treatment (Kang and Schoenung 2005). The potential level of exposure to workers and the general population that results from these processes will vary depending on the management practices used within a facility.

Figure 5-4: Electronics Recycling Process



Source: Adapted from Kang and Schoenung 2005

The potential for emissions of halogenated dioxins and furans, mercury, lead, antimony, and other toxic substances exists with smelting operations that may be a part of the recycling process. In addition to the potential emission of toxic chemicals, high operating temperatures may create an occupational hazard and high loads of bromine or chlorine may induce corrosion of gas-cleaning equipment. In sensitive areas, a process step for halide recovery may need to be added (Lehrner 2008). Controlled smelting operations are able to handle high loads of halogenated electronic scrap and effectively control emissions.

Some post-use electronics are exported for reuse, refurbishment and recycling. Unfortunately, a number of these exported electronics end up in countries that do not have the technology to recycle the electronics in a way that does not pose exposure concerns. In the absence of proper practices, procedures and equipment, unregulated recycling processes may pose risks to workers and the public through exposure to toxic chemicals.

Additionally, a 2007 U.S. EPA study examined the waste management of computer, television, hard-copy devices, and cellular devices. The study indicated that 15 to 20 percent of post-use consumer electronics was recycled, and 80 to 85 percent was disposed of in landfills or through incineration (U.S. EPA 2007b).

The methods employed at unregulated recycling sites are sometimes crude and may include the open burning of printed circuit boards, cables, and plastics; acid or cyanide leaching of circuit boards; and gold recovery with cyanide salt leaching or nitric acid and mercury amalgamation (Williams, Kahhat et al. 2008; Sepúlveda, Schluep et al. 2010; Yu, Williams et al. 2010). These methods may pose concern for human and environmental health. Toxic substances released from these processes include leachates, particulate matter, fly and bottom ash, fumes, wastewater, and other effluents, which are released to the soil, groundwater, surface water, sediments, and air (Sepúlveda, Schluep et al. 2010). For example, the burning of electronic components containing flame retardants can produce a range of toxic by-products including halogenated dioxins and furans (U.S. EPA 1998; Tohka and Zevenhoven 2002).

Landfilling Electronics

More than 3.2 million tons of end-of-life electronics, predominately from households, are sent to landfills (U.S. EPA 2010b). Landfills in the United States are for the most part well managed and regulated, but in non-regulated and non-lined landfills, these post-use electronics can contribute to leachate (i.e., the mixture of rainwater and liquids within the waste). This leachate has the potential to seep into the ground or drain into nearby surface water, transporting chemicals where humans and wildlife may be exposed. Additive flame retardants have a higher potential than reactive flame retardants to be released from electronic products (KemI 1995). No reactive flame retardants were identified as alternatives to decaBDE.

To date, most leachability studies in the literature have focused on the potential for discarded electronic devices to release lead and other heavy metals. A small number of studies have investigated leaching potential of brominated flame retardants. For example, Osako et al, found that the levels of several PBDE congeners in both raw and treated leachate were below the limit of detection of 4,000 pg/L (Osako, Kim et al. 2004). Additionally, a study conducted by Beard and Marzi investigated the leachability potential of phosphorus-based and brominated flame retardants from thermoplastic polymers and found that small amounts of phosphorus and bromine, respectively, leached from the polymer (Beard and Marzi 2006). Osako et al. also concluded that the amount of leaching that occurs is dependent upon the chemical properties of the landfill (Osako, Kim et al. 2004).

Incineration of Electronics

According to EFRA, flame retarded plastics can be incinerated in municipal refuse incinerators as long as they are equipped with the proper gas cleaning devices (EFRA 2006). The flame retardant treatment will not prevent incineration at operating temperature.

EPA has done an alternatives assessment for flame retardants used in printed circuit boards, the final report of which will include data on combustion by-products for different burning scenarios. The final report will be posted to the DfE webpage:
<http://epa.gov/dfe/pubs/projects/pcb/index.htm>

5.6.2 Textiles

DecaBDE and its alternatives are often used in the textiles which make up office furniture, commercial grade carpet, or military supplies such as tents, tarps and uniforms. Below is a summary of information on the various textiles, specifically office furniture and commercial grade carpet, which may enter each end-of-life pathway.

Recycling Textiles

Only ten percent of the six billion pounds of carpet disposed of in 2010 was recycled, reconditioned, or reused (Carpet America Recovery Effort (CARE) 2010). As a response to the high rate of carpet disposal in landfills, members of the carpet industry, representatives of government agencies at the federal, state, and local levels (such as the U.S. EPA), and non-governmental organizations created a voluntary partnership in 2002 to increase the amount of post-consumer carpet reused, reconditioned, or recycled. The goal of the ten-year partnership is to reduce the amount of carpet discarded in landfills by 40 percent by 2012 by diverting the carpet to one of four routes: reuse, recycling, waste to energy (incineration technology that uses recovered carpet as a fuel source to generate electricity), or cement kilns (the use of a recovered carpet as an alternative fuel source and as an additive in cement production) (CARE 2006). In order to achieve this benchmark, the carpet industry created the CARE, which, with members of the carpet industry and government, is responsible for monitoring, evaluating, and assessing progress toward the negotiated goals (CARE 2006).

Landfilling Textiles

The frequent replacement of office furniture results in the increased production of products and leads to large volumes of furniture discarded in landfills. Landfilling is also the most common fate of used carpeting. Even though almost all of the components in carpet can be recycled or reused, the total estimated amount of U.S. carpet discarded in 2010 was six billion pounds (CARE 2010).

Research with the objective of investigating the release and transformation of additive and reactive flame retardants from textiles in simulated landfill environments was conducted in 2008 (Horsing 2008). The study found that the environmental conditions of a landfill (e.g., temperature, microbial activity, and pH), the way additives are applied (i.e., additive or reactive), and the nature of the material all affected the leaching of the flame retardants. Based on the

findings of the impact of the different landfill conditions on additive flame retardants, the author concluded that additive flame retardants may “leach and contribute to the contamination of water but not so much in new, well-managed landfills and in developed countries as in old landfills in countries where landfills are poorly managed” (Horsing 2008). Additionally, they found that the only leaching that occurred from products treated with reactive flame retardants was washout from unreacted manufacturing residuals.

Incineration of Textiles

Incineration of textile waste from production sites is difficult given that pieces of fabrics are too long and can cause fire outside the incinerator. The textiles are usually too strong to be ground prior to incineration. Therefore large amounts of textile waste from textile plants are landfilled instead of incinerated (Dahllof 2004). However, smaller flame-retarded textiles and foams can be incinerated. This method is preferred as long as the incinerators are equipped with the proper gas cleaning devices (EFRA 2006).

5.6.3 Storage and Distribution Products

A total of two to three billion storage and distribution pallets, composed of a variety of components including wood, plastic, aluminum, steel, corrugated paperboard, and composite wood, are believed to be in use in the United States (Buehlmann, Bumgardner et al. 2009; Pure Strategies Inc. for Maine Department of Environmental Protection 2010). Wood currently dominates the pallet market and is estimated to comprise 80 to 95 percent of pallets (Buehlmann, Bumgardner et al. 2009; Pure Strategies Inc. for Maine Department of Environmental Protection 2010). Wood’s overwhelming presence in the pallet market is due to its low material and production costs and its relative abundance as a raw material. However, the use of plastic pallets is becoming increasingly popular because plastic often is more durable, lighter, and more easily sanitized than wood. In 2010, over 900 million plastic pallets were estimated to be in use (Pure Strategies Inc. for Maine Department of Environmental Protection 2010).

Depending on the materials and construction, and the manner in which they are used, plastic pallets could have an expected lifetime of 20 years. Many plastic pallets are made from recycled plastic and are fully recyclable at the end of their lives (Pure Strategies Inc. for Maine Department of Environmental Protection 2010). When plastic pallets are no longer usable, they are removed from service and can enter a full recycling process (ERM 2008). One manufacturer of high-density polyethylene (HDPE) pallets shreds or grinds damaged pallets for reuse as a raw material, which, in turn, is molded into new pallets. Currently, new plastic pallets are sometimes made with a combination of recycled and new HDPE but the recycled content may increase in the long term. According to one producer of plastic pallets, small quantities of HDPE that might be trimmed or removed during fabrication, handling and processing of extruded plastic are collected for reuse at the pallet production facility.

5.7 References

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