

**FLAME RETARDANTS USED IN FLEXIBLE  
POLYURETHANE FOAM:  
AN ALTERNATIVES ASSESSMENT UPDATE**



**SECTIONS 1-6**

August 2015

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## List of Acronyms and Abbreviations

ACR	Acute to chronic ratio
APP	Ammonium polyphosphate
ASTM	American Society for Testing and Materials
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BEARFTI	Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation
CASRN	Chemical Abstracts Service Registry Number
CDC	Centers for Disease Control and Prevention
CDR	Chemical Data Reporting
CFR	Code of Federal Regulations
CHO	Chinese hamster ovary cells
ChV	Chronic value
CPSC	Consumer Product Safety Commission
DecaBDE	Decabromodiphenyl ether
DfE	Design for the Environment
DMSO	Dimethyl sulfoxide
$E_bC_{50}$	Concentration at which 50% reduction of biomass is observed
$EC_{50}$	Half maximal effective concentration
ECHA	European Chemicals Agency
ECOSAR	Ecological Structure Activity Relationships
EDSP	Endocrine Disruptor Screening Program
EEC	European Economic Community
EPA	U.S. Environmental Protection Agency
EPI	Estimation Program Interface
$E_rC_{50}$	Concentration at which a 50% inhibition of growth rate is observed
EU	European Union
FFRP	Furniture Flame Retardancy Partnership
FPUF	Flexible polyurethane foam
GD	Gestation day
GHS	Globally Harmonized System of Classification and Labeling of Chemicals
GLP	Good laboratory practice
HPLC	High performance liquid chromatography
HPV	High Production Volume
HPVIS	High Production Volume Information System
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
$ID_{50}$	Median ineffective dose
IFR	Inherently flame retardant
IPTPP	Isopropylated triphenyl phosphate
IRIS	Integrated Risk Information System
IUCLID	International Uniform Chemical Information Database
$K_{oc}$	Sediment/soil adsorption/desorption coefficient

K <sub>ow</sub>	Octanol/water partition coefficient
LbL	Layer-by-layer
LC <sub>50</sub>	Median lethal concentration
LC <sub>100</sub>	Absolute lethal concentration
LCA	Life cycle assessment
LD	Lactation day
LD <sub>50</sub>	Median lethal dose
LD <sub>Lo</sub>	Lethal dose low
LFL	Lower limit of flammability
LOAEL	Lowest observed adverse effect level
LOEC	Lowest observed effect concentration
MF	Molecular formula
MITI	Japanese Ministry of International Trade and Industry
MSDS	Material Safety Datasheet
MW	Molecular weight
NAS	National Academy of Sciences
NCI	National Cancer Institute
NCP	New Chemicals Program
NES	No effects at saturation
NFPA	National Fire Protection Association
NGO	Non-governmental organization
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NOAEC	No observed adverse effect concentration
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration
NTP	National Toxicology Program
OECD	Organisation of Economic Cooperation and Development
OEHHA	California Office of Environmental Health Hazard Assessment
OPFR	Organophosphate flame retardant
OPP	Office of Pesticide Programs
OPPT	Office of Pollution Prevention and Toxics
PBDE	Polybrominated diphenyl ether
PBT Profiler	Persistent, Bioaccumulative, and Toxic Chemical Profiler
PentaBDE	Pentabromodiphenyl ether
PINFA	Phosphorus, Inorganic & Nitrogen Flame Retardants Association
PMN	Premanufacture Notification
ppm	parts per million
QSAR	Quantitative Structure Activity Relationship
REACH	<b>Registration, Evaluation, Authorisation and Restriction of Chemicals</b>
SAR	Structure Activity Relationship
SF	Sustainable Futures
SIDS	Screening Information Data Set
SMILES	Simplified Molecular-Input Line-Entry System
SNUR	Significant New Use Rule
TB	Technical Bulletin
TBB	Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester

TBPH	Di(2-ethylhexyl) tetrabromophthalate
TBPP	Tris (p-t-butylphenyl) phosphate
TCEP	Tris (2-chloroethyl) phosphate
TCP	Tricresyl phosphate
TCPP	Tris (2-chloro-1-methylethyl) phosphate
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate
TG	Test guidelines
TPP	Triphenyl phosphate
TSCA	Toxic Substances Control Act
UFAC	Upholstered Furniture Action Council
UFL	Upper limit of flammability
V6	Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P,P',P'-tetrakis(2-chloroethyl) ester
WAF	Water accommodated fraction

# 1 Introduction

## 1.1 The Furniture Flame Retardancy Partnership

The flame retardant pentabromodiphenyl ether (pentaBDE) was widely used as an additive in furniture foam and in other products to meet flammability requirements in the late 20<sup>th</sup> century. In the early 2000s, growing concerns over the possible environmental and public health impacts of pentaBDE led to a voluntary phase-out of the chemical by the sole U.S. manufacturer. At the end of 2004, industry voluntarily ceased production of pentaBDE, and U.S. Environmental Protection Agency (EPA) issued a regulation that prohibited further manufacture of the chemical without notification of EPA under the Toxic Substances Control Act (TSCA). The substitution likely to result from the move to alternatives to pentaBDE resulted in the need for evaluating flame retardants.

In 2003, EPA's Design for the Environment Program (DfE) convened a multi-stakeholder group to undertake an assessment of viable alternatives to pentaBDE. The Furniture Flame Retardancy Partnership (FFRP) included chemical manufacturers, furniture manufacturers, governmental representatives and environmental non-governmental organizations (NGOs). In 2005, EPA issued a report<sup>1</sup> based on the partnership's work assessing the human health and environmental profiles of alternatives to pentaBDE, indicating that a number of alternatives were available that appeared to pose a lower level of concern than was associated with pentaBDE. This DfE Alternatives Assessment update report identifies and evaluates flame retardants that may be used in flexible polyurethane foam (FPUF) products (as of 2013) and updates hazard profiles from the previous report.

Additional actions regarding pentaBDE were outlined in the EPA 2009 Action Plan for polybrominated diphenyl ethers (PBDEs) (U.S. EPA 2009).

## 1.2 Updating the 2005 Furniture Flame Retardancy Report

### Purpose and Scope of the Updated Report

The goal of the FFRP, as stated in its 2005 report, was to “identify and assess environmentally safer chemical alternatives to pentaBDE, and to investigate other technologies for improving furniture fire safety” (U.S. EPA 2005a). Since the publication of the 2005 FFRP report, the marketplace for flame retardants used in FPUF has changed significantly, with some flame retardant chemicals being withdrawn from the market, and others being introduced. This update is intended to identify all flame retardants either known to be used, or marketed to be used, in meeting fire safety requirements for upholstered consumer products containing FPUF. Also, DfE published updated hazard criteria in 2011 (see “Alternatives Assessment Criteria for Hazard Evaluation”), and data from the 2005 FFRP report were re-evaluated using the current criteria, and included in this report. The resulting hazard profiles allow a direct comparison among

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<sup>1</sup> Available at: <http://www2.epa.gov/saferchoice/environmental-profiles-chemical-flame-retardant-alternatives-low-density-polyurethane>.

substances found in the two DfE alternative assessment reports. It should be noted that, as in all DfE Alternatives Assessments, the term “alternative” is used to designate any chemical that can be used in the functional category, and does not designate preferability for environmental or health endpoints.

DfE is publishing the current update for several reasons, in addition to the marketplace changes and data developments described above. Public and media attention to flame retardants in recent years has led to new scrutiny of flame retardant chemistry. Also, both the State of California and the Consumer Product Safety Commission (CPSC) have established or are planning to establish updated flame retardancy standards for upholstered furniture (see Section 3 below). The impact of these changes in terms of flame retardant selection and use is as yet unknown; therefore, it is important that the most current information be available to decision makers, which requires an update of the chemicals and hazard data contained in the 2005 report. In addition, several chemicals in this category (notably benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester (TBB), di(2-ethylhexyl) tetrabromophthalate (TBPH), and tris (2-chloroethyl) phosphate (TCEP)) were identified by EPA as TSCA Work Plan chemicals for assessment beginning in 2013 (U.S. EPA 2013b). The full list of chemicals for assessment can be found here: [http://www.epa.gov/oppt/existingchemicals/pubs/assessment\\_chemicals\\_list.html](http://www.epa.gov/oppt/existingchemicals/pubs/assessment_chemicals_list.html). Updating the hazard and use information for these and related chemicals complements other assessment projects underway at EPA.

As mentioned above, this report by EPA’s DfE Program updates and supplements the previous alternatives assessment report developed by the FFRP (U.S. EPA 2005a). DfE identified 16 flame retardant chemicals, one non-proprietary mixture, and 2 proprietary mixtures to be evaluated in the update report. Additional information on polyurethane foam is available in the 2005 FFRP report (U.S. EPA 2005a).

The scope of this report was expanded to include all upholstered consumer products containing FPUF (i.e., not just furniture), including a number of flame retardants that have been identified in products such as car seats and nursing pillows (Stapleton, Klosterhaus et al. 2011). These products, like the furniture that was the subject of the 2005 report, are made from FPUF with a covering fabric, and, when flame retarded, are expected to rely on the same set of flame retardants. (Some upholstered FPUF products, particularly for babies and children, are exempt from flame retardancy requirements, but may still contain flame retarded foam.)

The 2005 report describes alternative methods of improving furniture fire safety; for example, the use of IFR upholstery, or the use of fire barriers between upholstery and foam. Since the 2005 report was published, one additional technology, known as layer-by-layer (LbL) assembled flame retardancy, has been in development, but is not yet commercialized. The hazards associated with this technology are not addressed in this update because it is nanoscale and not commercially available, and the DfE criteria have not been evaluated for suitability to assess nano-sized substances. The current update addresses the hazards associated with one alternative technology--expandable graphite (used in graphite impregnated foam), which may be commercially viable as a replacement for flame retardant chemicals in FPUF for some applications. All other alternatives are briefly described in Section 4. Because the DfE hazard criteria are developed for chemical-to-chemical comparison under a specific functional use,

rather than material-to-material comparison, a life cycle assessment (LCA) might be a better tool for evaluating and comparing alternative materials (see Section 1.3).

## **How to Use This Report**

Audiences for this report include stakeholders interested in chemical hazards and safer alternatives, including but not limited to chemical manufacturers, component manufacturers, product manufacturers, retailers, consumers, NGOs, consultants, and state and federal regulators. Three potential uses of this report include:

*Identification of potential substitutes.* This report allows stakeholders interested in chemical substitution to identify functional alternatives for flame retardants used in flexible polyurethane foam, which is commonly found in furniture. The two lists of potential alternatives includes chemicals identified by stakeholders as viable, functional alternatives, as well as chemicals that are not considered functional alternatives, and information on inherently flame retardant (IFR) polymers. The inclusion of a chemical in this assessment does not indicate environmental- or health-based preferability. By identifying potential functional alternatives, this report assists manufacturers in selecting chemicals for additional performance testing, and can identify a need for alternative approaches to fire safety such as barrier materials, as studied by the CPSC (CPSC 2013b). Although the alternatives identified in this report are additive flame retardants that can be used in barrier materials, an evaluation of the use of the identified chemicals in these technologies is outside of the scope of this report.

*Selection of alternative chemicals based on comparative chemical hazard assessment.* This report helps decision-makers understand and compare the hazards associated with potential alternatives to which they can supplement information on performance and cost. Some alternatives may be associated with hazard concerns similar to those of pentaBDE; others may be associated with different hazard concerns. Use of the hazard information in Section 2 may help businesses avoid the cost of repeated substitution. Section 7 contains a robust human health and environmental profile for each chemical that is based on empirical data when available, and enhanced with modeling and expert judgment to fill data gaps. The profiles can help decision-makers understand which potential alternatives may come under scrutiny in the future, and choose the safest possible alternative now to reduce future costs. In addition to reading the hazard comparison table, decision-makers should review the full hazard assessments for each chemical available in Section 7. The hazard assessments provide more information on hazard criteria, data interpretation, and information used to assign hazard values in each category, and ensure a complete understanding of the hazard profiles of each alternative.

*Use of hazard information for further analysis and decision-making.* The information in this report can be used to inform further analyses on preferred alternative chemicals, such as risk assessments or LCA. For example, a decision-maker could identify several functional alternatives with preferable hazard profiles, and conduct product-specific risk assessments based on exposure expectations along the product's life-cycle. A decision-maker could also conduct an assessment of the (non-hazard) environmental impacts associated with the life cycles of the alternatives (or any differences in environmental impacts of the product that may result from choosing one alternative over another). This type of supplementary information may be helpful



in guiding product-specific decision-making. In addition, information in this report can be used to identify the Very Persistent Very Bioaccumulative chemicals, PBT chemicals, and those with an “equivalent level of concern” targeted under European Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) policy. This report does not evaluate the relative hazards of alternatives, but GreenScreen® ([www.cleanproduction.org/Greenscreen.php](http://www.cleanproduction.org/Greenscreen.php)) is one tool that can be used for this purpose. The criteria used to develop the hazard assessments in this report can also be used to inform Green Chemistry design.

### **1.3 Alternatives Assessment as a Risk Management Tool**

The DfE Alternatives Assessment process was one of a suite of actions EPA chose to pursue to manage the potential risks associated with pentaBDE. The Agency chose this tool to inform the chemical substitution that may occur as an outcome of other risk management activities.

Chemical alternatives assessment compares chemicals within the same functional use group, and evaluates alternatives across a consistent and comprehensive set of hazard endpoints and environmental fate parameters. Information about chemical hazards derived from this type of comparative chemical hazard assessment, in combination with analyses of cost, performance, and other factors, can be used by industry and other decision-makers to select safer alternative chemicals for a particular use. (For details on DfE’s Hazard Assessment criteria, see “Alternatives Assessment Criteria for Hazard Evaluation,” available at <http://www2.epa.gov/saferchoice/design-environment-alternatives-assessments>.)

Alternatives assessment is most useful in identifying safer substitutes when available alternatives meet performance requirements and are expected to present lower hazards for human health and the environment. Alternatives assessments may identify scenarios in which there do not appear to be any preferable alternatives to the chemical being considered for replacement. In this case, the resulting information can be used to guide innovation, and the development of safer chemicals and products.

#### **Functional Use Approach and Chemical Fate**

DfE’s “functional use” approach to alternatives assessment orients chemical evaluations within a given product type and functionality. Under this approach, factors related to exposure scenarios, such as physical form and route of exposure, can be similar within a given functional use analysis and will fall out of the comparison, so that a reduction in hazard is equivalent to a reduction of risk. When less hazardous alternatives have different physical-chemical profiles or require different use levels, it may be appropriate to also conduct an exposure or risk assessment.

DfE Alternatives Assessments consider intrinsic properties of chemical substitutes that affect exposure potential, including absorption potential, persistence, and bioaccumulation. Under this approach, the health and environmental hazard profiles in the alternatives assessments become the key variable and source of distinguishing characteristics. Information on key properties that can be used to evaluate significant differences in environmental fate and transport, including persistence, bioaccumulation, and physical properties, are included in the hazard assessment.

Under conditions where fire or incineration occurs, a halogenated substance may contribute to halogenated dibenzodioxin and dibenzofuran formation, increase the generation of PAHs, and impact fire parameters such as smoke and carbon monoxide (Sidhu, Morgan et al. 2013). However, combustion reactions are complex and variable, and make inclusion of combustion byproducts in hazard assessment challenging. Both halogenated and non-halogenated flame retardants may yield other toxic by-products that would need to be compared, not only halogenated dioxins and furans. For these reasons, the pyrolysis transformation products are not assessed in this report.

## **DfE Alternatives Assessments Scope and Data Sources**

As described above, the DfE Alternatives Assessment process is intended to provide useful hazard and fate data on chemicals within a given functional class; it is not intended to describe exposure or risk, nor do alternatives assessments provide quantitative information on chemical performance in the product or cost, which are most appropriately conducted by manufacturers who have hands-on expertise in product cost and performance. DfE Alternatives Assessments provide complete hazard data according to a uniform set of criteria, in a format amenable to comparison among chemicals, and in a relatively quick timeframe. This information can contribute important information for decision makers, whether chemical manufacturers, product manufacturers, consumers, or NGOs.

As with other DfE Alternatives Assessments, this report summarizes available data from many sources, including information from experts on uses of flame retardants, and hazard and fate information from the scientific literature. Because EPA oversees the TSCA Premanufacture Notification (PMN) process, DfE also has access to hazard and fate information from confidential and non-confidential studies submitted to the Agency as part of a PMN chemical review. Furthermore, when little data are available on a chemical of interest, hazard and fate information may be derived from data on analog molecules, which may be confidential. Experts from DfE, from other groups within EPA's Office of Chemical Safety and Pollution Prevention (OCSPP), and from DfE's contractors, provide expert judgment on chemical hazard and fate for those chemicals. This report compiles existing data and does not include results of new research on chemical hazards; EPA did not undertake any testing for this report.

When reporting hazard data on available alternatives, DfE does not recommend specific flame retardants. It is the role of manufacturers to use the data provided, along with their own expert knowledge, to choose the safest chemicals possible, while also meeting their requirements for efficacy, price, and other criteria.

## **Green Chemistry Principles**

The DfE Alternatives Assessment approach is aligned with established green chemistry principles. Two of these principles are particularly relevant to the DfE approach:

- Principle 4: Design of safer chemicals – “Chemical products should be designed to affect their desired function, while minimizing their toxicity;” and

- Principle 10: Design for degradability – “Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment” (Anastas and Warner 1998).

DfE incorporates these two green chemistry principles in its criteria, and applies them in its assessment of chemical hazard and fate in the environment. This approach enables identification of safer substitutes that emphasize greener chemistry, and points the way to innovation in safer chemical design, where hazard becomes a part of a performance evaluation.

### **Alternatives, Life-Cycle, and Risk Assessments**

Alternatives assessment, life-cycle assessment (LCA), and risk assessment are tools that can be used to evaluate and improve the sustainability profiles of chemicals, products, and services. These tools, which can be complementary to one another, should be selected according to the ultimate decisions needing to be made, and other regulatory and policy considerations. DfE Alternatives Assessments establish a foundation that other tools, such as risk assessment and LCA, can build upon.

Risk assessment and alternatives assessment are both based on the premise that risk is a function of hazard and exposure. Risk assessment characterizes the nature and magnitude of hazard and exposure from chemical contaminants and other stressors. A DfE Alternatives Assessment evaluates and compares the nature of the chemical hazards, and reflects a view that when exposure is comparable, risk is reduced through the use of less hazardous chemicals. Alternatives assessment strives to decrease the reliance on exposure controls, thus reducing risk when exposure controls fail.

An LCA can create a robust picture of a variety of environmental impacts associated with the material and energy inputs and outputs throughout the life cycle (or part of a life cycle) of a product or service, and by doing so can identify opportunities for reducing those impacts. However, an LCA may not assess the inherent hazards of the chemical inputs and outputs for each life cycle stage. During decision-making, risk assessment or LCA can be applied to the lower-hazard or potentially preferable alternatives, to further distinguish between preferable substitutes, or to identify unintended consequences.

#### **1.4 DfE Alternatives Assessment and the Toxic Substances Control Act**

EPA’s DfE Program is administered by the Office of Pollution Prevention and Toxics (OPPT), which is charged with the implementation of the Toxic Substances Control Act (TSCA) and the Pollution Prevention Act (PPA).

Central to the administration of TSCA is the management of the TSCA Inventory. Section 8 (b) of TSCA requires EPA to compile, keep current, and publish a list of each chemical substance that is manufactured or processed in the United States. Companies are required to verify the TSCA status of any substance they wish to manufacture or import for a TSCA-related purpose. For more information, please refer to the TSCA Chemical Substance Inventory website: <http://www.epa.gov/opptintr/existingchemicals/pubs/tscainventory/basic.html>.

Substances selected for evaluation in a DfE Alternatives Assessment generally are subject to TSCA regulations, and therefore must be listed on the TSCA Inventory, or be exempt or excluded from reporting before being manufactured in or imported to, or otherwise introduced in commerce in, the United States. For more information see <http://www.epa.gov/oppt/newchemicals/pubs/whofiles.htm>.

To be as inclusive as possible, DfE Alternatives Assessments may consider substances that may not have been reviewed yet as new chemicals under TSCA, and therefore may not be listed on the TSCA Inventory. DfE has worked with stakeholders to identify and include chemicals that are of interest and likely to be functional alternatives, regardless of their TSCA status. Chemical identities are gathered from the scientific literature and from stakeholders and, for non-confidential substances, appropriate TSCA identities are provided.

Persons are advised that substances, including DfE-identified functional alternatives, may not be introduced into U.S. commerce unless they are in compliance with TSCA. Introducing such substances without adhering to the TSCA provisions may be a violation of applicable law. Those who are considering using a substance discussed in this report should check with the manufacturer or importer about the substance's TSCA status. If you have questions about the reportability of substances under TSCA, please contact the OPPT Industrial Chemistry Branch at 202-564-8740.

## 2 Hazard Evaluation Results for Flame Retardants Used in Flexible Polyurethane Foam

### 2.1 Hazard Comparison Table

The hazard comparison table is shown below, followed by the results described both by the chemical groupings found in the hazard comparison table and by type of hazard endpoint.

Other approaches to improving fire safety of upholstered FPUF products exist, including flame resistant cover fabrics and fire barriers, which could be comprised of chemically treated materials (e.g., treated cotton-based materials) or inherently flame retardant materials (e.g., wool, Kevlar), and nanoclay technologies (See Section 4). These alternative technologies are not assessed for hazard in this report. The DfE Hazard Evaluation Criteria (described in Section 5.1.2) are not amenable to assessing the hazard from the flame resistant cover fabrics and fire barriers. Additionally, the DfE Hazard Evaluation Criteria have not been evaluated for suitability to assess nano-sized substances. Further, layer-by-layer nanoclay technologies are currently in research and development and are not commercially available for use in upholstered FPUF products.

**Table 2-1. Screening Level Toxicity Hazard Summary**

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

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

\* Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. For Firemaster® mixtures there is no corresponding profile in Section 7.

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

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

Chemical (for full chemical name and relevant trade names see the individual profiles in Section 7)	CASRN	Human Health Effects										Aquatic Toxicity		Environmental Fate			
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation	
<b>Halogenated Flame Retardant Alternatives</b>																	
<b>Firemaster® 550 Components</b>																	
Firemaster® 550*	Mixture	L	M	M	H	H	H	H	M		L	L	VH	VH	H	H	
Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester (TBB)¥	183658-27-7	L	M	L	M	M	M	M	M		M	L	L	L	L	H	H
Di(2-ethylhexyl) tetrabromophthalate (TBPH) ^¥	26040-51-7	L	M	M	M	M	M	M	L		L	L	L	L	H	H	
Isopropylated triphenyl phosphate (IPTPP) ^	68937-41-7	L	M	L	H	H	H	H	L		L	L	VH	VH	M	H	
Triphenyl phosphate (TPP) ^	115-86-6	L	M	L	L	L	L	H	L		L	VL	VH	VH	L	M	
<b>Firemaster® 600</b>																	
Firemaster® 600*	Mixture; Proprietary	L	M	M	M	M	M	H	M		L	M	VH	VH	H	H	
<b>Chlorinated Phosphorus Alternatives</b>																	
Tris (2-chloroethyl) phosphate (TCEP)	115-96-8	H	H	M	M	H	M	M	L		L	L	H	H	M	L	
Tris (2-chloro-1-methylethyl) phosphate (TCPP)	13674-84-5; 6145-73-9	L	M	L	H	H	M	M	L		L	L	M	M	H	L	
Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)	13674-87-8	L	H	M	H	M	L	H	L		L	L	H	H	H	L	
Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P',P',P'-tetrakis(2-chloroethyl) ester	38051-10-4	L	M	L	M	H	L	M	L		L	L	M	M	H	L	

**Table 2-2. Screening Level Toxicity Hazard Summary**

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

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

♦ Expandable graphite commercial formulations are prepared using chemical washes that may be present in the final product as residues. The associated hazards vary depending on the specific wash chemicals used, and as a result, the hazards may change by manufacturer. One confidential wash has additional hazard concern as follows, based on experimental data: HIGH-Acute Toxicity, Eye Irritation, Dermal irritation. Other manufacturers may use a wash that contains chromic acid (CASRN 7738-94-5) with additional hazard concerns as follows, based on experimental data: HIGH-Acute Toxicity, Carcinogenicity, Genotoxicity, Reproductive, Repeated dose, Skin sensitization, Respiratory sensitization, Eye Irritation, Dermal irritation.

<sup>d</sup> This hazard designation would be assigned MODERATE for a potential for lung overloading if >5% of the particles are in the respirable range as a result of dust forming operations.

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

Chemical (for full chemical name and relevant trade names see the individual profiles in Section 7)	CASRN	Human Health Effects										Aquatic Toxicity		Environmental Fate		
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
<b>Non-Halogenated Flame Retardant Alternatives</b>																
<b>Inorganic/Other Alternatives</b>																
Ammonium polyphosphate (APP) <sup>‡</sup>	68333-79-9	L	L	L	L	L	L	L <sup>d</sup>	L		VL	L	L	L	VH	L
Expandable graphite <sup>‡</sup>	12777-87-6	L♦	M♦	L♦	L♦	L	L	M♦	L♦	♦	M♦	M♦	L♦	M♦	H	L
Melamine	108-78-1	M	M	M	H	M	L	M	L		L	VL	L	L	H	L

**Table 2-2. Screening Level Toxicity Hazard Summary (Continued)**

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

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

<sup>§</sup> Based on analogy to experimental data for a structurally similar compound.

<sup>d</sup> This hazard designation would be assigned MODERATE if >5% of the particles are in the respirable range as a result of dust forming operations.

<sup>†</sup> This component of Firemaster® 550 may be used alone or in other mixtures as an alternative. It can also be found in Table 2-1 of this report.

<sup>‡</sup> The highest hazard designation of any of the oligomers with MW <1,000.

\*Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value.

<sup>°</sup> Based on experimental test data for a residual impurity reported to be present in this substance at levels up to 5% by weight.

Chemical (for full chemical name and relevant trade names see the individual profiles in Section 7)	CASRN	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
<b>Non-Halogenated Flame Retardant Alternatives continued</b>																
<b>Phosphate Alternatives</b>																
Triphenyl phosphate (TPP) <sup>†</sup>	115-86-6	L	M	L	L	L	L	H	L		L	VL	VH	VH	L	M
Tricresyl phosphate (TCP) <sup>1</sup>	1330-78-5	M	L	L	H	M	M	H	M		L	L	VH	H	M	H
Isopropylated triphenyl phosphate (IPTPP) <sup>†</sup>	68937-41-7	L	M	L	H	H	H	H	L		L	L	VH	VH	M	H
Tris (p-t-butylphenyl) phosphate (TBPP)	78-33-1	L	M	L	M	L	M	H	M		L	M	VH	VH	M	H
Diethyl bis(2-hydroxyethyl)aminomethylphosphonate	2781-11-5	L	M	M	L	L	M	M	M		L	VL	M	L	H	L
Oligomeric ethyl ethylene phosphate	184538-58-7	L	L	M	L	M	M	L <sup>d</sup>	L		M	L	L	L	VH	L
Oligomeric phosphonate polyol	363626-50-0	L	M	M	L	M	M	L	L		L	VL	L	M	M	L
<b>New-to-Market Proprietary Mixtures</b>																
Emerald Innovation™ NH-1*	Proprietary	H	M	L	M	L	M	H	M		M	M	VH	VH	M	H
Confidential C	Confidential	H	M	L	M	VL	M	L	M		M	M	H	H	L	L
Confidential D	Confidential	L	M	L	L	L	L	H	L		L	VL	VH	VH	L	M
Confidential E	Confidential	L	M	L	L	L	M	M	M		VL	M	VH	VH <sup>°</sup>	M	H
Fyrol™ HF-5*	Proprietary	L	M <sup>§</sup>	M	L	M	M <sup>§</sup>	M <sup>d</sup>	L		M	L	VH	VH	VH	H <sup>‡</sup>
Confidential A	Confidential	L	L	M	L	L	M	L <sup>d</sup>	L		M	L	L	L	VH	L
Confidential B	Confidential	L	M <sup>§</sup>	L	L	M	M <sup>§</sup>	M	L		L	VL	VH	VH <sup>°</sup>	M	H <sup>‡</sup>

<sup>1</sup>This assessment also includes information for other methylated triphenyl phosphate isomers (phosphoric acid, bis(methylphenyl) phenyl ester (CASRN 26446-73-1) and phosphoric acid, methylphenyl diphenyl ester (CASRN 26444-49-5)).



## 2.2 Hazard and Fate Results by Chemical Group

The **components of Firemaster® 550**, thought to be one of the primary alternatives used since pentaBDE was phased out, are predicted to have Moderate to High hazards for reproductive, developmental, neurological and repeated dose toxicities. The phosphate components have inherently Very High hazard for aquatic toxicity, due to the phosphate ester structure and molecular weight (MW); all the components have Moderate or High potential to bioaccumulate, based on parent compound or degradation products. Similar to several of the alternatives evaluated, the components TBB and TBPH lack full data characterization necessary to adequately describe hazard and risk.

Firemaster® 600 is currently marketed for use in flexible polyurethane foams and other applications as a mixture of phosphorus and bromine based flame retardants (Great Lakes Solutions, 2010; Chemtura, 2014). Although the identity and composition of some of the ingredients in Firemaster® 600 are proprietary and cannot be disclosed in this report, the summary hazard designation profile is provided, based upon the mixture component with the highest hazard. The hazard designations for Firemaster® 600 are similar to Firemaster® 550.

The **chlorinated phosphorus alternatives** are tris (2-chloroethyl) phosphate (TCEP), tris (2-chloro-1-methylethyl) phosphate (TCPP), tris (1,3-dichloro-2-propyl) phosphate (TDCPP), and phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P,P',P'-tetrakis(2-chloroethyl) ester (V6), which are fairly well characterized with empirical test data. In addition to Firemaster® 550, TDCPP is also thought to be one of the primary alternatives used to replace pentaBDE in FPUF. The four chlorinated phosphate substances exhibit several distinguishing characteristics. They have Moderate to High hazard designations for at least four of the following human health endpoints: carcinogenicity, genotoxicity, reproductive toxicity, developmental/ neurodevelopmental toxicity, neurological toxicity, and repeated dose toxicity. TCEP is also acutely toxic. These four substances also have aquatic toxicity hazards in the Moderate to High range, but lack adequate characterization of chronic aquatic toxicity. Due to the structure and size of these substances they are not expected to bioaccumulate, but there is a potential for 'pseudo persistence.' Pseudo persistence is a term for chemicals that are observed to be continually present in the environment because they are released at a rate greater than or equal to their rate of removal.

The non-halogenated alternatives include two inorganics, the nitrogen substance melamine, and a collection of non-halogenated phosphate esters.

The hazard profiles for the **inorganics** ammonium polyphosphate (APP) and expandable graphite indicate lower levels of concern than the other profiles in this report. APP is a high MW polymer. Although APP is not well characterized with test data, it is predicted to be Low hazard based on its structure and very high MW. While it is not expected to be readily absorbed due to its MW, it is predicted to be highly persistent. Expandable graphite is not likely to bioaccumulate and has potentially Low to Moderate human health and aquatic toxicity, but there is low confidence in the hazard profile due to the lack of empirical data, and there is potential for the use of hazardous chemical washes in the production process.

The profile for **melamine** identifies key hazards in human health endpoints including acute toxicity, carcinogenicity, genotoxicity, reproductive and repeated dose toxicity. Bioaccumulation potential is low, aquatic toxicity is Low, and persistence is High, but with potential for degradation.

The **phosphorus-based non-halogenated alternatives** have varied designations for human health toxicity; several have Moderate to High hazard for reproductive, developmental, neurological, and repeated dose toxicity, in addition to insufficient data to characterize the potential for carcinogenicity. These human health hazards are compounded by the Very High aquatic toxicity associated with the phosphate esters of this size and structure. Trade-offs can be seen within this group: the more degradable (Low to Moderate persistence) phosphate esters triphenyl phosphate (TPP), tricresyl phosphate (TCP), isopropylated triphenyl phosphate (IPTPP) and tris (p-t-butylphenyl) phosphate (TBPP) have High to Very High aquatic toxicity and Moderate to High bioaccumulation potential, whereas the more persistent substances diethyl bis(2-hydroxyethyl)aminomethylphosphonate and oligomeric ethyl ethylene phosphate have Moderate to Low aquatic toxicity and bioaccumulation designations.

While there is uncertainty associated with the hazard profiles of diethyl bis(2-hydroxyethyl)-aminomethylphosphonate, the oligomeric ethyl ethylene phosphate, and the oligomeric phosphonate polyol, due to heavy reliance on analog or modeled data (especially for the two oligomers)--yielding conservative Moderate designations for several human health endpoints, they may be the most preferable out of all the chemicals assessed in this report. Of these three chemicals, the most preferable may be the oligomeric phosphonate polyol, which has Low to Moderate aquatic toxicity, Moderate persistence, and Low bioaccumulation potential. Human health and aquatic toxicity designations are Low or Moderate for this chemical. Also, the oligomeric phosphonate polyol is a component of the polyurethane foam, and as such may have no potential for release from the foam during product use. The combination of Low to Moderate hazard designations and its reaction into the polyurethane foam make oligomeric phosphonate polyol an alternative anticipated to be safer for use in upholstered polyurethane foam, when flame retardants are added to make the end-use product meet flammability standards.

Two proprietary mixtures that are new to the market were also reviewed. EPA knows the chemical identification, but cannot reveal it in this report due to regulations regarding confidential business information. The two mixtures have one or more components with highest hazards for aquatic toxicity, and the potential to bioaccumulate.

### **2.3 Hazard and Fate Results by Endpoint**

The following text describes results by class of endpoint: human health, aquatic toxicity, persistence, and bioaccumulation potential.

The human health endpoints evaluated in DfE Alternatives Assessments include acute toxicity, carcinogenicity, genotoxicity, reproductive toxicity, developmental toxicity, neurotoxicity, repeated dose toxicity, skin sensitization, respiratory sensitization, eye irritation, and dermal irritation. Acute mammalian toxicity was Low for all but four of the alternatives: tricresyl phosphate, melamine, TCEP, and Emerald Innovation NH-1. Carcinogenicity and genotoxicity hazards varied among the alternatives, with many Low or Moderate designations. Two of the

chemicals had High concerns for carcinogenicity: TCEP and TDCPP. Reproductive, developmental, neurological, and repeated dose toxicity varied from Low to High across the chemicals. Irritation and sensitization endpoints were generally not distinguishing, with many Low or Very Low designations, although a few substances had Moderate designations.

Aquatic toxicity hazards varied significantly, due to the diverse chemistries of the alternatives. The endpoints evaluated in DfE Alternatives Assessments include acute and chronic aquatic toxicity based on water column exposures, which may not be suitable tests for some of the poorly soluble substances.

Most flame retardants have High or Very High persistence designations, because they are expected to be stable by design in order to maintain their flame retardant properties throughout the lifetime of the product. Several of the flame retardant alternatives in this report were not designated as highly persistent, including TPP, which is readily biodegradable (low persistence). Also, TCP, IPTPP, TBPP, and TCEP are inherently biodegradable chemicals that degrade slowly (Moderate persistence); however, these substances have aquatic toxicity hazards, including deformities in fish and eutrophication from degradation to inorganic phosphates. There is an apparent trade-off between persistence and toxicity for diethyl bis(2-hydroxyethyl)-aminomethylphosphonate and the oligomeric ethyl ethylene phosphate that have High and Very High persistence but Low to Moderate toxicity. The oligomeric phosphonate polyol appears to remove this trade-off with only estimated Moderate persistence and estimated Low – Moderate toxicity. Predicting long-term fate in the environment is challenging, so there is an uncertainty as to how substances will eventually degrade, and whether some substances that are degradable in standard tests may be ‘pseudo persistent.’

The ability of a chemical to accumulate in living organisms is described by bioconcentration, bioaccumulation, biomagnification, and/or trophic magnification factors. Some of the alternatives assessed in this report also have a High potential for bioaccumulation, including the New-to-Market mixtures, the brominated alternatives, and some of the phosphate alternatives: TCP, IPTPP, and TBPP.

### 3 Flexible Polyurethane Foam Flame Retardants and Flammability Standards

This section provides an overview of flexible polyurethane foam (FPUF), discusses which flame retardants are used in FPUF, and summarizes the standards that drive their use. For more details about FPUF, and its manufacture and exposure potential during the manufacturing processes, see Chapter 3 of the 2005 FFRP report<sup>2</sup>.

#### 3.1 Flexible Polyurethane Foam

Numerous types of furniture and other products incorporate FPUF. Rigid polyurethane foams, by contrast, are used in insulation, construction, and other applications (ISOPA 2005), and are not assessed in this report update.

Flexible foam is made either in large slabs (“slabstock”) that are cut to shape, or in molds that have the shape of the finished product. The basic ingredients include polyols, isocyanates, blowing agents, and other additives (including flame retardants). In manufacturing slabstock, the ingredients are blended in a mixing head and deposited on a conveyor belt, where the polymerization reactions occur, and the foam is expanded by blowing agents into a large (e.g., 60 foot) “bun.” The buns are cured before being cut into shapes for a finished product. In molded foam, the polymerization reactions occur within the mold, and are heated to accelerate curing.

Furniture and other foam product manufacturers typically receive cured foam and do not directly handle flame retardant chemicals. Because slabstock is made in very large buns, uses requiring smaller pieces of foam may consist of off-cuts from larger buns. This may be why smaller polyurethane foam products may contain flame retardants, even when they are not required to do so by regulation.

#### 3.2 Flame Retardant Classification and Exposure Considerations

Flame retardants used in FPUF are typically classified as “additive.” Additive flame retardants are blended evenly into the foam, but remain unbound. Additive flame retardants are expected to be more mobile during the consumer use phase, for example, by volatilizing from the foam, by being washed from the foam or from the foam surface, or in dust as the foam itself is mechanically abraded. Reactive flame retardants are chemically bound to the polymer in the finished product and are used in rigid PUF; they are not typically used in FPUF.

Additive flame retardants have been widely identified in air, house dust, and handwipe samples (Stapleton, Allen et al. 2008; Dodson, Perovich et al. 2012; Stapleton, Eagle et al. 2012; van der Veen and de Boer 2012; Carignan, Heiger-Bernays et al. 2013), supporting the idea that additive flame retardants can mobilize from a plastic or foam into the local microenvironment. Furthermore, detection of additive flame retardants in blood and urine samples (Stapleton, Eagle

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<sup>2</sup> Available at: <http://www2.epa.gov/saferchoice/environmental-profiles-chemical-flame-retardant-alternatives-low-density-polyurethane>.

et al. 2012; Carignan, McClean et al. 2013) and *in vivo* studies (Patisaul, Roberts et al. 2012) demonstrate the bioavailability and absorption of several additive flame retardants.

Reactive flame retardants, because they are chemically bound to the foam polymer itself, are expected to have lower mobility, volatility, and bioavailability than additive flame retardants, especially in the consumer use phase of product life. However, reactive flame retardants may still be released from furniture, either because they are liberated from the polymer, or the original polymerization was incomplete (U.S. EPA 2005a). As such, exposure to reactive flame retardants could occur at all points in the life cycle, including manufacture, use, and disposal.

Under conditions where fire or incineration occurs, a halogenated substance may contribute to halogenated dibenzodioxin and dibenzofuran formation, increase the generation of PAHs, and impact fire parameters such as smoke and carbon monoxide (Sidhu, Morgan et al. 2013). However, combustion reactions are complex and variable, and make inclusion of combustion byproducts in hazard assessment challenging. Both halogenated and non-halogenated flame retardants may yield other toxic by-products that would need to be compared, not only halogenated dioxins and furans. For these reasons, the pyrolysis transformation products are not assessed in this report.

### **3.3 Sources of Data for Identifying Foam Flame Retardants**

#### **Published Data**

Publication of the 2005 FFRP report was one of a set of actions undertaken by EPA and other stakeholders in response to growing concerns about pentaBDE. After a voluntary phase-out of pentaBDE by the sole U.S. manufacturer in 2004, EPA issued a Significant New Use Rule (SNUR), effective August 14, 2006, to ensure that production could not re-commence in the United States without prior notice to EPA.

Recent data suggest that the pentaBDE phase-out has had the desired effect of decreasing the environmental prevalence of the flame retardant. A study of house dust in 16 California homes found an overall reduction in median values of pentaBDE components between 2006 and 2011; the declines in pentaBDE component concentrations were significantly associated with new (purchased between 2006 and 2011) furniture, electronics, and flooring (Dodson, Perovich et al. 2012). However, the changes were not uniform; two homes showed marked increases in pentaBDE congeners. In another study of 102 FPUF samples from residential couches purchased across the United States, including 24 percent from California, pentaBDE was identified in 16 of 41 samples purchased between 1985 and 2004, but in only one of the 61 samples dating from 2005 or later (Stapleton, Sharma et al. 2012).

These same studies, along with others, helped confirm the major flame retardants used to replace pentaBDE. In the study of residential couches, TDCPP was detected in 52 percent of foam samples dating from 2005 or later (Stapleton, Sharma et al. 2012). Firemaster® 550, identified by its brominated components, TBB and TBPH, was identified in 18 percent of post-phase-out samples, while alkylated triphenyl phosphates were identified in another 16 percent of samples. In only 2 of the 61 post-phase-out samples were flame retardants not identified. The high detection rate of flame retardants, even in couches purchased outside of California, suggested to

the authors that California's furniture flammability standard 1975 Technical Bulletin (TB) 117 (TB117; see Section 3.5 for more details on the recent update to this standard) "is becoming a de facto standard across the United States" (Stapleton, Sharma et al. 2012).

Several other flame retardants were identified in these studies. In a study of foam baby products, Stapleton et al. (2011) identified a chlorinated organophosphate flame retardant (OPFR) sold commercially as V6, previously thought to be used in automobiles; TCPP, a major flame retardant in FPUF in the United Kingdom, but expected to have limited use in the United States; and TCEP. All of these chemicals are included in the current report.

## **Stakeholder Information**

In the course of developing this report, DfE had conversations with several stakeholders from the 2005 FFRP, other stakeholders in the chemical and furniture industries, and academic researchers with expertise on flame retardancy. DfE developed a candidate list of chemicals known to be used in FPUF, including a number of flame retardants for which there was the possibility of use, but that were ultimately excluded from the report. Discussion of these lists with various stakeholders provided critical information about flame retardant use, including valuable information about the limitations of some flame retardants (e.g., that discolor or "scorch" the foam) that likely limit their use in the marketplace.

## **Process of Identifying Chemicals for Assessment**

Flame retardant chemicals assessed in this update were identified through the following approach:

1. ***Reviewed all chemicals from the 2005 report.*** Many of the chemicals were identified in the original report by proprietary placeholders (i.e., generic names). In some of these cases, the chemicals have since been publicly identified either by the manufacturer or by another party; for example, the brominated components of Firemaster® 550 were identified publicly by Stapleton et al. (2008). In these cases, the publicly available chemical names were used. Many of the compounds assessed in the 2005 report are no longer sold; manufacturer information as well as direct conversations with manufacturers was used to ascertain the current market status of these products.
2. ***Identified products advertised for use in FPUF.*** Website and promotional materials from the major U.S. manufacturers, as well as from the trade organization Phosphorus, Inorganic & Nitrogen Flame Retardants Association (PINFA), were reviewed. Manufacturers of proprietary formulations were also consulted to ensure that the candidate list included all chemical components.
3. ***Examined all PMN chemicals associated with FPUF that were identified by PMN submitters as being suitable for flame retardancy.*** New chemicals are required by TSCA to be submitted by the manufacturer through the PMN process before being produced in or imported into the United States. In some cases it was possible for these PMNs to be

associated with trade names, to ascertain whether they were sold for possible use in FPUF or limited to other markets (e.g., rigid polyurethane foam).

**4. Added flame retardants identified in furniture and other FPUF applications by external researchers.** In particular, all flame retardants recently identified in FPUF baby products by Stapleton et al. were included.

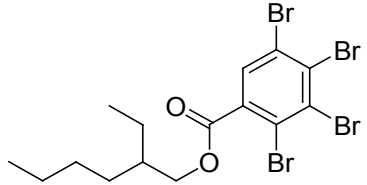
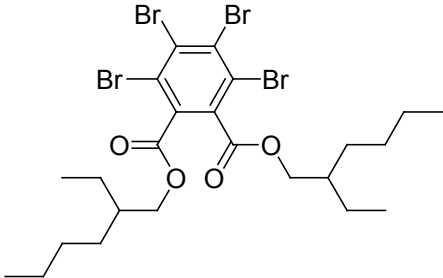
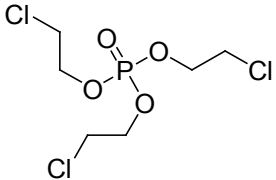
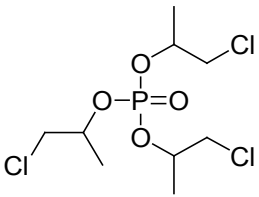
Chemicals identified through these sources were then grouped into two lists: chemicals known to be currently used in FPUF, which would therefore be assessed; and chemicals thought not to be used in FPUF (see Table 3-1 and Table 3-2, respectively). Stakeholders from the 2005 partnership and other experts were then contacted, and provided with the proposed lists of chemicals to be included and excluded. In some cases, each chemical on the lists was discussed to receive feedback on whether it was actually in use, or specific reasons its use had been halted.

When chemicals were excluded from the assessment, the reason for exclusion is given on that list. For example, some flame retardants were identified by manufacturers' promotional materials as being suitable for polyurethane foam, but were described by experts as suitable only for rigid polyurethane, lacking the appropriate characteristics for FPUF (e.g., unsuitable viscosity). Other chemicals had previously been identified as suitable for FPUF, but are no longer sold for that market.

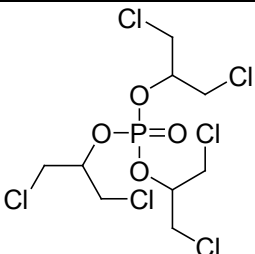
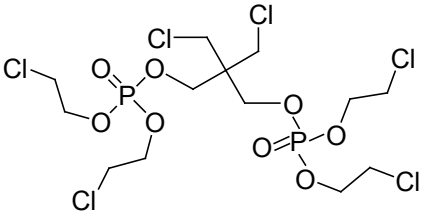
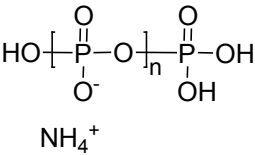
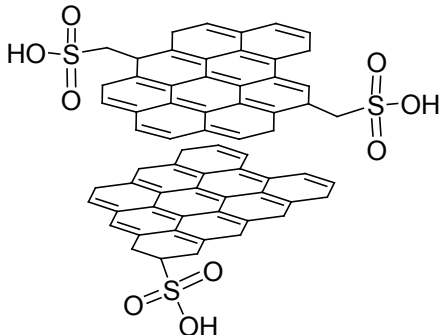
It is difficult to assess the precise number and volume of flame retardants used in furniture and other products. Although chemical manufacturers are required to periodically report the amount of raw chemicals manufactured in or imported into the United States, there is no general requirement for disclosure of the amount of chemicals contained in manufactured or imported articles.

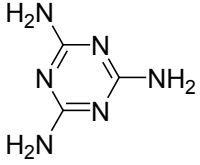
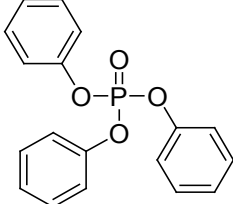
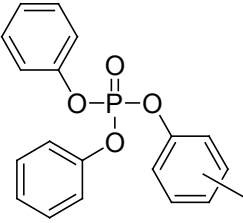
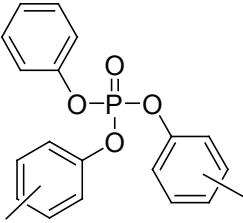
As mentioned above, chemical and FPUF manufacturers consulted for this report identified issues such as odor and scorch with particular flame retardant chemicals, and suggested that they are unlikely to be in use in the United States. Flame retardant chemicals phased out by U.S. manufacturers with odor or scorch issues are unlikely to be used in overseas manufacture as well.

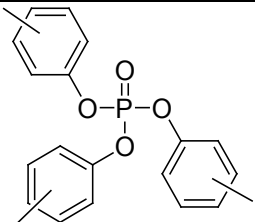
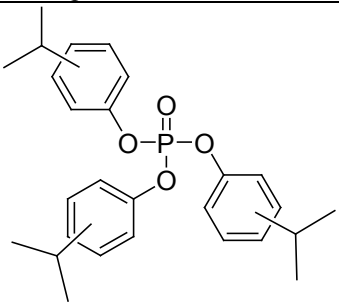
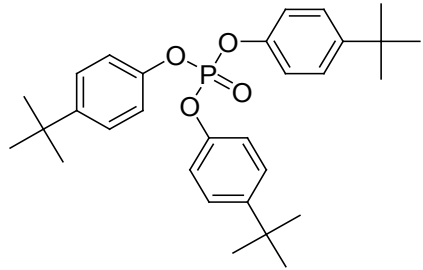
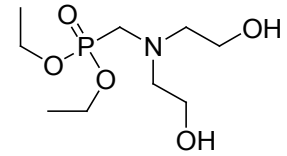
**Table 3-1. Flame Retardants Evaluated in the DfE Furniture Flame Retardancy Update**

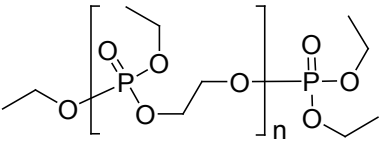
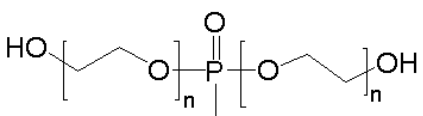
CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>b</sup>	Molecular Formula (MF)	Structure
<b>Brominated Alternatives</b>				
183658-27-7	Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester	TBB; EH-TBB	C <sub>15</sub> H <sub>18</sub> Br <sub>4</sub> O <sub>2</sub>	
26040-51-7	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1,2-bis(2-ethylhexyl) ester	TBPH; BEH-TEBP	C <sub>24</sub> H <sub>34</sub> Br <sub>4</sub> O <sub>4</sub>	
<b>Halogenated Phosphorus Alternatives</b>				
115-96-8	Ethanol, 2-chloro-, phosphate (3:1)	TCEP; Tris(2-chloroethyl) phosphate	C <sub>6</sub> H <sub>12</sub> Cl <sub>3</sub> O <sub>4</sub> P	
13674-84-5; 6145-73-9	2-Propanol, 1-chloro-, 2,2',2"-phosphate; 1-Propanol, 2-chloro-, 1,1',1"-phosphate	TCPP; Tris(2-chloro-1-methylethyl)phosphate; TCIPP	C <sub>9</sub> H <sub>18</sub> Cl <sub>3</sub> O <sub>4</sub> P	 Representative structure



CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>b</sup>	Molecular Formula (MF)	Structure
13674-87-8	2-Propanol, 1,3-dichloro-, phosphate (3:1)	TDCPP; Tris-(1,3-dichloro-2-propyl)phosphate; TDCIPP	C <sub>9</sub> H <sub>15</sub> Cl <sub>6</sub> O <sub>4</sub> P	
38051-10-4	Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P',P'-tetrakis(2-chloroethyl) ester	V6; BCMP-BCEP	C <sub>13</sub> H <sub>24</sub> Cl <sub>6</sub> O <sub>8</sub> P <sub>2</sub>	
<b>Inorganic/Other Alternatives</b>				
68333-79-9	Polyphosphoric acids, ammonium salts	APP; Ammonium polyphosphate	[NH <sub>4</sub> PO <sub>3</sub> ] <sub>n</sub>	 <p style="text-align: center;">NH<sub>4</sub><sup>+</sup> Representative structure</p>
12777-87-6	Sulfuric acid, compd. with graphite (1:?)	Expandable graphite	[C] <sub>n</sub> [SO <sub>3</sub> H] <sub>x</sub>	 <p style="text-align: center;">Representative structure</p>

CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>b</sup>	Molecular Formula (MF)	Structure
108-78-1	1,3,5-Triazine-2,4,6-triamine	Melamine	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub>	
<b>Phosphate Alternatives</b>				
115-86-6	Phosphoric acid, triphenyl ester	TPP; Triphenyl phosphate; TPHP	C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P	
26444-49-5	Phosphoric acid, methylphenyl diphenyl ester	Cresyl diphenyl phosphate; Methylphenyl diphenyl phosphate; Disflamoll DPK; MPHDPHP	C <sub>19</sub> H <sub>17</sub> O <sub>4</sub> P	 <p>Representative structure</p>
26446-73-1	Phosphoric acid, bis(methylphenyl) phenyl ester	Methylated triphenyl phosphates; Bis(methylphenyl) phenyl phosphate; MPHP	C <sub>20</sub> H <sub>19</sub> O <sub>4</sub> P	 <p>Representative structure</p>

CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>b</sup>	Molecular Formula (MF)	Structure
1330-78-5	Phosphoric acid, tris(methylphenyl) ester	Tricresyl phosphate; Disflamoll TKP; TMPHP	C <sub>21</sub> H <sub>21</sub> O <sub>4</sub> P	 <p>Representative structure</p>
68937-41-7	Phenol, isopropylated, phosphate (3:1)  Commercial product may include mono-, di-, tri- and higher substitutions with appropriate CASRNs.	IPPP; ITP; IPTPP; Isopropylated triphenyl phosphate; Isopropylated phenol phosphate; TIPPP	C <sub>27</sub> H <sub>33</sub> O <sub>4</sub> P  Formula for tri-propyl substitution	 <p>Representative structure</p>
78-33-1	Phenol, 4-(1,1-dimethylethyl)-, 1,1',1"-phosphate  Includes mono-, di-, tri-, and higher substitutions with appropriate CASRNs.	TBPP; tris(4-(tert-butyl)phenyl) phosphate; tert-butylphenyl diphenyl phosphate; bis(4-(tert-butyl)phenyl) phenyl phosphate; TTBPHP	C <sub>30</sub> H <sub>39</sub> O <sub>4</sub> P  Formula for tri-butylated substitution	 <p>Representative structure</p>
2781-11-5	Phosphonic acid, P-[[bis(2-hydroxyethyl)amino]methyl]-, diethyl ester	N,N-(bis)-hydroxyethyl-aminomethane phosphonic acid diethyl ester; BHEAMP-DE	C <sub>9</sub> H <sub>22</sub> NO <sub>5</sub> P	

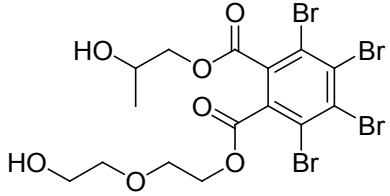
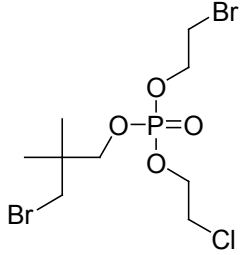
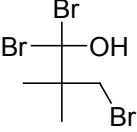
CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>b</sup>	Molecular Formula (MF)	Structure
184538-58-7	Phosphoric acid, triethyl ester, polymer with oxirane and phosphorus oxide (P <sub>2</sub> O <sub>5</sub> )	Oligomeric ethyl ethylene phosphate; Alkylphosphate oligomer	(C <sub>6</sub> H <sub>15</sub> O <sub>4</sub> P·C <sub>2</sub> H <sub>4</sub> O·O <sub>5</sub> P <sub>2</sub> ) <sub>n</sub>	 <p>Representative structure</p>
363626-50-0	Poly(oxy-1,2-ethanediyl), α,α' - (methylphosphinylidene)bis[ω-hydroxy-	Oligomeric phosphonate polyol; Bis(polyoxyethylene) methylphosphonate; Polyethylene glycol methylphosphonate (2:1)	CH <sub>5</sub> O <sub>3</sub> P·(C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub> ·(C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub>	
<b>New-to-Market Proprietary Mixtures</b>				
Proprietary	Halogen-free flame retardant	Emerald Innovation NH-1		--
Proprietary	Halogen-free phosphorus-based	Fyrol HF-5		--

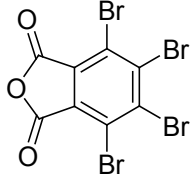
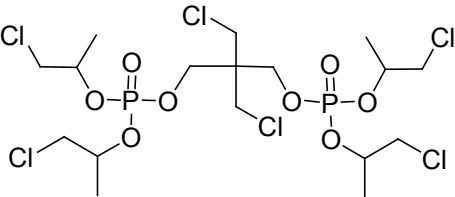
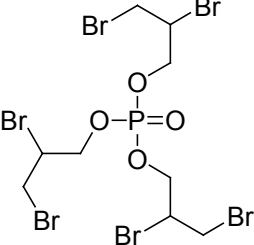
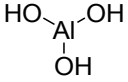
<sup>a</sup> The list of flame retardants evaluated in the Furniture Flame Retardancy update is based on publicly available information on product availability, public and confidential information on chemical production, and DfE's conversations with stakeholders. The inclusion of these chemicals in the DfE Alternatives Assessment does not denote environmental preference.

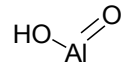
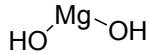
<sup>b</sup> The last acronym listed for each substance is the "practical abbreviation" according to Bergman et al. (2012)'s proposed standard approach for making acronyms for organic flame retardants. Bergman et al. 2012. *Environment International* 49: 57-82.

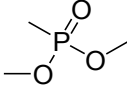
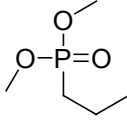
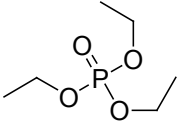
**Table 3-2. Flame Retardants That Were Not Evaluated in the DfE Furniture Flame Retardancy Update**

Flame retardants listed here have been identified as being used in polyurethane or other plastics, but are not thought to be used in flexible polyurethane foam (FPUF), or are not candidates for DfE's hazard assessment process.

CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>a</sup>	MF	Structure	Reason for Exclusion <sup>b</sup>
<b>Brominated Alternatives</b>					
77098-07-8; 20566-35-2	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol; 1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1-[2-(2-hydroxyethoxy)ethyl] 2-(2-hydroxypropyl) ester	Diester/ether diol of tetrabromophthalicanhydride; 2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate; HEEHP-TEBP	C <sub>15</sub> H <sub>20</sub> Br <sub>4</sub> O <sub>9</sub> ; C <sub>15</sub> H <sub>16</sub> Br <sub>4</sub> O <sub>7</sub>	 <p>Representative Structure</p>	Appears to be used in rigid polyurethane foams only.
125997-20-8	Phosphoric acid, mixed 3-bromo-2,2-dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters	BBDMP-CDMP-P	C <sub>9</sub> H <sub>18</sub> Br <sub>2</sub> ClO <sub>4</sub> P	 <p>Representative Structure</p>	Historical FR for polystyrene boards; no current production. Not reported in Chemical Data Reporting (CDR) <sup>c</sup> .
36483-57-5	1-Propanol, 2,2-dimethyl-, tribromo deriv.	Tribromoneopentyl alcohol; TBNPA	C <sub>5</sub> H <sub>9</sub> Br <sub>3</sub> O	 <p>Representative Structure</p>	Appears to have been an unsuccessful product.

CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>a</sup>	MF	Structure	Reason for Exclusion <sup>b</sup>
632-79-1	1,3-Isobenzofurandione, 4,5,6,7-tetrabromo-	Tetrabromophthalic anhydride; TEBP-Anh			Advertised for use in rigid foams.
1047637-37-5	Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P',P',P'-tetrakis(2-chloro-1-methylethyl) ester	U-OPFR; BCMP-BCMEP			Although identified in consumer products, there is no evidence of commercial production.
<b>Halogenated Phosphorus Alternatives</b>					
126-72-7	1-Propanol, 2,3-dibromo-, 1,1',1''-phosphate	TDBPP; Tris-(2,3-dibromopropyl)phosphate	C <sub>9</sub> H <sub>15</sub> Br <sub>6</sub> O <sub>4</sub> P		Historical FR identified in house dust, but no evidence of use in FPUF. Not reported listed in CDR <sup>c</sup> .
<b>Inorganic/Other Alternatives</b>					
21645-51-2	Aluminum hydroxide (Al(OH) <sub>3</sub> )	ATH; Aluminum trihydrate	Al(OH) <sub>3</sub>		Inefficient, requiring very high loadings. Probably not used in FPUF <sup>d</sup> .

CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>a</sup>	MF	Structure	Reason for Exclusion <sup>b</sup>
1318-23-6	Boehmite (Al(OH)O)	Aluminum oxide hydroxide	Al(OH)O		Inefficient, requiring very high loadings. Possible use in some niche applications.
1309-42-8	Magnesium hydroxide (Mg(OH) <sub>2</sub> )	Milk of magnesia	Mg(OH) <sub>2</sub>		Inefficient, requiring very high loadings. Probably not used in flexible polyurethane foam <sup>d</sup> .
	Nano: layers, clays, mesoporous silicate	Nano: layers, clays, mesoporous silicate	--	--	Research product; not yet commercially available.
68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with bentonite	Surface treated, Inorganic, mineral based FR synergist	--	--	Vendor described use in thermoplastic polyurethane; no other use data available.

CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>a</sup>	MF	Structure	Reason for Exclusion <sup>b</sup>
<b>Phosphate Alternatives</b>					
756-79-6	Phosphonic acid, P-methyl-, dimethyl ester	DMMP; Dimethyl methyl phosphonate	C <sub>3</sub> H <sub>9</sub> O <sub>3</sub> P		Used in rigid polyurethane foams. PINFA website lists as appropriate for FPUF; however, no evidence of such use is available.
18755-43-6	Phosphonic acid, P-propyl-, dimethyl ester	Dimethyl propane phosphonate DMPP; Levaguard DMPP	C <sub>5</sub> H <sub>13</sub> O <sub>3</sub> P		Thought to be used in rigid but not flexible polyurethane foam; however, not reported on listed on CDR <sup>c</sup> .
78-40-0	Phosphoric acid, triethyl ester	Triethyl phosphate; Levaguard TEP-Z	C <sub>6</sub> H <sub>15</sub> O <sub>4</sub> P		Used in rigid but not flexible polyurethane foam. Could be an impurity from other flame retardants.



CASRN	Preferred Chemical Abstract Index Name	Common Names and Acronyms <sup>a</sup>	MF	Structure	Reason for Exclusion <sup>b</sup>
<b>Proprietary Alternatives</b>					
--		Antiblaze PR82			For use in rigid foams.

<sup>a</sup> The last acronym listed for each substance is the “practical abbreviation” according to Bergman et al. (2012)’s proposed standard approach for making acronyms for organic flame retardants. Bergman et al. 2012. *Environment International* 49: 57-82.

<sup>b</sup> Flame retardants and use information were identified based on publicly available information on product availability, public and confidential information on chemical production, and DfE’s conversations with stakeholders.

<sup>c</sup> The CDR Rule requires manufacturers, including importers, to submit information on the chemical they produce domestically or import into the United States during the principal reporting year, subject to reporting requirements. <http://epa.gov/cdr/>. The last two reporting years were 2005 and 2011.

<sup>d</sup> This substance was assessed in the Alternatives Assessment for Decabromodiphenyl Ether (DecaBDE) Report, available at: <http://www2.epa.gov/saferchoice/partnership-evaluate-flame-retardant-alternatives-decabde>.

### 3.4 Notes on Specific Foam Flame Retardants

Notes on selected foam flame retardant chemicals included in the report follow.

- **TDCPP**, known to be a major flame retardant in FPUF and produced in a volume between 10 and 50 million pounds per year in 2011, was listed by California as a Proposition 65 chemical<sup>3</sup> in late 2011 for concerns about carcinogenicity (OEHHA 2011; U.S. EPA 2013a). The Proposition 65 listing may impact the TDCPP market because it requires relabeling products that contain TDCPP for sale in California, though labeling of TDCPP products for sale outside of California is not required. TDCPP was identified by Stapleton, Sharma et al. (2012) in more than half of couch samples tested since 2005. In 2012, the major U.S. manufacturer of TDCPP announced a voluntary phase-out of TDCPP production by 2015 (ICL Industrial Products 2012). New York State has banned TDCPP from use in children's products, including baby products, toys, car seats, nursing pillows, crib mattresses, strollers and other items intended for use by children under three years of age, effective December 1, 2015 (New York State Governor's Office 2014). Maryland has also prohibited importing, selling, or offering for sale any child care product containing more than one-tenth of 1% (by mass) of TDCPP intended for use by children under the age of three including baby products, toys, car seats, nursing pillows, crib mattresses, and strollers (State of Maryland 2014). The ban became effective on October 1, 2014, and does not contain a provision for phasing out existing stock.
- There has been recent opposition from consumer and environmental groups to the use of **halogenated flame retardants**, and this opposition may shape the market suitability of these flame retardants, regardless of hazard data. Some shift away from halogenated flame retardants appears to have already occurred. While the 2005 FFRP report assessed a number of brominated flame retardants, the two brominated components of Firemaster® 550 (TBB and TBPH) are the only **brominated flame retardants** included in the current update report.
- Although **TCEP** was previously not thought to be used in foam, it has been identified in upholstered FPUF products (Stapleton, Klosterhaus et al. 2011). TCEP was a TSCA work plan chemical for 2013-14, so the DfE Alternatives Assessment process is a useful contribution to other EPA activities on this compound (U.S. EPA 2013b). New York State banned the sale or offer for sale of children's products containing TCEP, effective December, 1, 2013 (State of New York 2011). Maryland also passed a law prohibiting the import, sale, or offer for sale of child care products containing more than one-tenth of 1% (by mass) of TCEP intended for use by children under the age of three, including baby products, toys, car seats, nursing pillows, crib mattresses, and strollers (State of Maryland 2014). The ban became effective on October 1, 2014, and does not contain a provision for phasing out existing stock.

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<sup>3</sup> A chemical known to the State of California to cause cancer or reproductive toxicity; businesses are required to provide a warning (e.g., label consumer products, distribute notices to residents) when exposure to a Proposition 65 chemical may occur.

- **TCPP and melamine** are the major flame retardants used in the United Kingdom to meet the stringent “Crib 5” standard (BS-5852; UK Parliament 1988), but use of this mixture is not known to be common in the United States. However, because TCPP was identified in FPUF products by Stapleton et al. (2011), it is included in this report.
- The larger molecule “**V6**” (CASRN 38051-10-4) has been used in automobile foam, due to its lower volatility, but was also identified by Stapleton et al. (2011) in baby products. V6 is a dimer of TCEP, and contains TCEP as an impurity.
- Researchers first experimented with the use of **expandable graphite** in FPUF in the 1980s, but performance limitations restricted its commercial adoption (Bhagat 2001). These limitations have been overcome (Wolska, Goździkiewicz et al. 2012; Wang, Ge et al. 2013), and expandable graphite is now considered viable in FPUF (PINFA 2012).
- A new molecule, “**U-OPFR**” (“unknown organophosphate flame retardant,” BCMP-BCMEP), a dimer of TCPP, was identified by Stapleton et al. (2011). This molecule is not in EPA’s CDR data on the manufacturing, processing, and use of commercial chemical substances and mixtures; however, it is possible that whole products with this molecule have been imported. Experts consulted by DfE were unfamiliar with this molecule, and no references to it beyond the Stapleton paper have been identified. U-OPFR was not assessed in this update, because there is no evidence of commercial production of this chemical.

### Flame Retardants as Mixtures

The assessment of flame retardant hazard properties is complicated by the fact that many flame retardant products are sold as mixtures. This may be the result of a deliberate mixing of diverse flame retardant chemicals for performance reasons, or as a natural result of the synthesis of the flame retardant molecules. For example, a number of flame retardant products now contain alkylated triphenyl phosphates with a number of different side chains in use (e.g., methyl, isopropyl, tert-butyl). As a natural result of the synthesis process, these mixtures are likely to contain the unalkylated TPP itself, along with mixtures of mono-, di-, tri-, and possibly higher alkyl substitutions. Each of these substitutions can also occur in numerous isomers (e.g., the substitution might occur on the *meta*, *ortho*, or *para* positions). A single product identified as IPTPP, therefore, may in fact consist of a large number of molecules of differing properties, making evaluation more difficult.

Deliberate mixtures of different molecules are also common. Most notably, Firemaster® 550 has been identified as a mixture of TBB, TBPH, TPP, and IPTPP (Stapleton, Allen et al. 2008); approximately 50% of the mixture is TBB and TBPH at a ratio of 4:1 by mass, while the remainder is comprised of the other two molecules. This constitutes a challenge to the DfE assessment process. Some of the toxicity studies available are of the Firemaster® 550 mixture itself; others are of the mixture of only the two brominated components (also sold as Firemaster® BZ-54), while some data exist for each component individually. Therefore, it is not always possible to attribute effects seen in toxicologic studies to an individual component. (Effects

resulting from additive, synergistic, or antagonistic interactions of a combination could complicate the analysis further.) It is likely that the composition of some commercial products varies from batch to batch. In addition, differential volatilization, degradation, or absorption may lead to different exposure patterns to the individual components at various points along the life cycle of the product.

DfE attempted to assess hazard profiles of the commercial products, where possible. For example, since mono- and tri-substituted cresyl triphenyl phosphate are sold as different products, DfE listed them separately in the list of substances for assessment, but for efficiency assessed the variety of substitutions of the cresyl phosphate in one profile “tricresyl phosphate.” Similarly, since IPTPP appears to be sold as a mixture of mono/di/tri-substitutions, that mixture was evaluated as a whole. In practical terms, little data are available for each component, and most available data are associated with a mixture. Where data on individual components do exist, DfE takes a conservative approach by using the highest hazard designation for any one component of the mixture as the hazard designation for the whole mixture.

In the case of mixtures of dissimilar molecules, DfE evaluated, as far as possible, both the components and the complete mixture. Here, again, DfE’s criteria were followed in assigning to each endpoint for the mixture the highest hazard call for a mixture component. (No attempt was made to assess synergistic or other interactions between component chemicals.) For example, Firemaster® 600 is a mixture of phosphorus and bromine-based flame retardants marketed for use in flexible polyurethane foams and other applications. Although the identity and composition of some of the ingredients in Firemaster® 600 are proprietary and cannot be described in this report, the summary hazard designations based upon the mixture component with the highest hazard are provided.

### **3.5 Standards that Influence the Use of Flame Retardants**

Several regulations currently drive the use of flame retardants in FPUF. As described below, changes to some of the standards have been proposed or passed. As these changes are implemented, this report will provide valuable information on available alternatives to enable informed substitution, should there be a continuing need for flame retardants in FPUF or upholstery fabric.

#### **California TB117**

In 1975, California’s Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation (BEARHFTI) (then the Bureau of Home Furnishings and Thermal Insulation) promulgated TB117. Meeting TB117 required a small, candle-sized flame to be applied directly to the uncovered foam for 12 seconds without igniting a fire (Cal/DCA 2000). Passing such a test required either an IFR foam or the use of flame retardants. The most common solution was the addition of flame retardants to FPUF (NRDC 2013). Since manufacturers generally prefer to make a single product for the U.S. market, the TB117 standard had to some extent become a national *de facto* standard. TB117 required labeling of compliant furniture in California, but labels did not always appear in other states.

In 2010, California amended TB117 to specifically exempt “juvenile furniture”: “strollers, infant carriers, and nursing pillows” (Cal/DCA 2010). However, as described above, FPUF is manufactured in large (60-foot) “buns,” which are then cut to shape. It is likely that most buns are made with flame retardants, in anticipation of being used in a mixture of TB117-compliant and -exempt products. Similarly, the flame retardants in FPUF “pit cubes” identified by Carignan, Heiger-Bernays, et al. (2013) in a study of gymnast exposure to flame retardants may have been the result of a manufacturing process that incorporates flame retardants to meet TB117 standards.

In 2013, California enacted changes to the TB117 standard. In contrast to the 1975 standard, the new TB117-2013 does not require open flame testing for filling materials used in upholstered furniture. TB117-2013 tests for smolder resistance by applying a lit cigarette to a miniature assembly of the cover fabrics, barrier materials, and filling materials that represents the finished piece of furniture (Cal/DCA 2013b). Fabric materials failing the smolder test can still be used if a fire blocker (inter-liner) layer is added. The new test is based on the voluntary American Society for Testing and Materials (ASTM) E1353 standard (Cal/DCA 2013b). Manufacturers were able to use the new testing requirements as of January 1, 2014, and required to be fully compliant by January 1, 2015 (California Governor’s Office 2013).

Although TB117-2013 does not regulate or mandate the use of flame retardant chemicals, BEARHFTI anticipates that the new standard will significantly reduce or eliminate manufacturers’ use of flame retardant chemicals in upholstered furniture, because these products may meet the new standards without the use of flame retardant chemicals (Cal/DCA 2013a). Many of the more common thermoplastic fabrics are likely to pass the smolder test, although some fabrics, primarily cellulosic, are likely to need modification before passing the test (CPSC 2008). Although not assessed for possible hazards in this report, Section 4 provides information on flame retardant technologies that may provide increased fire safety, with and without the use of flame retardant chemicals.

A number of other localities have passed flammability standards, which are often based on California standards; for example, the Boston Fire Code incorporates TB133 (Boston Fire Department 1995). How local standards will change as a result of revisions to TB117 remains an open question.

### **California TB133**

The more stringent TB133 standard, promulgated in 1991, was designed to increase fire safety in public spaces. Meeting TB133 requires a large open flame, provided by a gas burner, to be applied to the assembled piece of furniture for about 80 seconds without igniting a fire. TB133 has been used as the basis for legislation in other localities (TB133 compliance is often voluntary for sprinklered buildings, in which case TB117 still applies in California (PFA 1992)).

Detailed data on how products meet TB133 are not available, but two general approaches are possible: the use of flame-retardant fabrics and foams that together provide suitable flame resistance; alternatively, an intrinsically flame-retardant fire blocker or “inter-liner” layer can be used between the foam and the cover fabric (PFA 1992). Anecdotal evidence gathered from

manufacturers suggests that the foam components are typically TB117 compliant, and that a cover fabric back-coated with flame retardant is commonly used. No public data exist on which flame retardants are used in back-coatings.

### **Consumer Product Safety Commission**

In a March 4, 2008, notice of proposed rulemaking (NPR) published in the *Federal Register*, CPSC proposed a national standard addressing the risk of deaths and injuries associated with residential upholstered furniture fires<sup>4</sup> (CPSC 2008). The proposed rule focused primarily on fires ignited by smoldering cigarettes. The standard could be met by either using cover materials that are sufficiently smolder-resistant to meet a cigarette ignition performance test, or by using fire barriers (inter-liners) that meet smoldering and open flame resistance tests placed between the cover fabric and interior filling materials. In order to reduce reliance on additive flame retardants, the proposed rule did not contain performance requirements for filling materials. As such, CPSC specified a standard foam that did not include any flame retardant chemicals when testing cover materials, thereby removing additive flame retardants in the foam from consideration in order to meet the requirements of the flame resistance test. Technical challenges with the test methods in this approach prompted CPSC staff to investigate other approaches. Validation of the test methodology proposed in the NPR showed that furniture constructed with fire barriers and exposed to a small open flame produced a significantly less intense fire than furniture constructed without fire barriers. CPSC staff believes the fire barrier approach may have the potential to address nearly all of the upholstered furniture-related fires and save more lives each year than the 2008 proposed standard. Subsequently, in 2013, CPSC requested comments on a standard that would cover a wider range of ignition sources found in the home (CPSC 2013a).

It should be noted that other open flame standards, including the more stringent Crib 5 standard in the United Kingdom, which tests PUF covered with a standard fire-retarded polyester fabric but does not allow for the use of fire barriers, are typically met with a combination of additive flame retardants (NRDC 2013).

### **Other Standards and Laws**

The Upholstered Furniture Action Council (UFAC) has developed a voluntary industry standard for cigarette ignition, which is embodied in the ASTM E-1353 method. The revised California TB117-2013 follows this method, with modifications. CPSC estimates that 90% of currently produced furniture meets the voluntary UFAC standard, which does not address open flame ignitions (CPSC 2008).

In 2013, the New York State Assembly (the lower house of the Legislature) passed a bill (A06557 in the Assembly, introduced as S04780 in the Senate) that would establish an as-yet-undefined open flame standard for furniture (NY State Assembly 2013). The bill also prohibits the use of halogenated flame retardants in furniture. Also, as noted in Section 3.4, New York

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<sup>4</sup> This standard would apply to cushioned, upholstered seating products available for residential, home office, and/or dormitory use.

State has also passed a law (A4741/S3703-B) banning TDCPP from consumer products intended for use by children under three years of age, such as baby products, toys, car seats, nursing pillows, crib mattresses, and strollers, effective December 1, 2015 (New York State Governor's Office 2014). New York State banned the sale of children's products containing TCEP in 2011, effective December 1, 2013 (State of New York 2011).

As also noted in Section 3.4, Maryland passed a law prohibiting the importing, selling, or offering for sale any child care product containing more than one-tenth of 1% (by mass) of TDCPP and TCEP. Under the law, child care products are those intended for use by children under the age of three, including baby products, toys, car seats, nursing pillows, crib mattresses, and strollers (State of Maryland 2014). The ban became effective on October 1, 2014, and does not contain a provision for phasing out existing stock.

During its July 2013 meeting, the National Fire Protection Association (NFPA) Standards Council reviewed a request to consider establishing an open flame standard for upholstered furniture. In 2014, NFPA was accepting public comments on the need for a new standard, available resources on the issue, individuals who may be interested in participating in the development of a new standard, and organizations involved in furniture flame retardant standards (Durso 2013; NFPA 2013).

### **Other Product Sectors**

In addition to furniture, other products contain upholstered FPUF. Automobile and aircraft seating is constructed in a manner similar to furniture, with a need for stringent fire protection, as well as other requirements. For example, the flame retardant known as "V6" (Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P',P'-tetrakis(2-chloroethyl) ester) has a higher molecular weight (MW) and lower volatility, and has been identified in automobile applications, where window fogging is an important problem. Aircraft seating is less cost-sensitive than most consumer products, and has relied on more expensive flame barriers as well as additive flame retardants, including expandable graphite. This report includes all flame retardants that DfE identified as being used in these other sectors; this update does not address the flammability standards for these sectors.

### **Impacts of Changing Standards**

It is difficult to predict the impact of changes to these standards on the use of flame retardants. The recent changes to TB117, moving from an open flame to a smolder test, may lessen the need for flame retardant additives in foam; however, for some fabrics, TB117-2013 will still require flame retardant coatings or other modifications. The Consumer Product Safety Commission and New York State have indicated that they may issue a performance-based standard that is more difficult to meet than TB117 (e.g., an open flame test); if they do, it may need to be met either with flame retardant inter-liners or with higher loads of flame retardants in foam, a choice made by individual manufacturers and likely to be driven in many cases by costs.

## 4 Alternative Flame Retardant Solutions not Addressed in This Report

While the focus of recent public attention has been on additive flame retardant chemicals in FPUF, other methods can be used to provide increased fire safety. These methods are described briefly here; however, this update does not attempt to fully characterize these methods. A rigorous comparison of costs and benefits, particularly over the product life cycle, would require analysis beyond the scope of this report. More information on alternative methods is available in the 2005 FFRP report. Additionally, with the advent of changes to flammability standards, manufacturers may also consider whether the standards can be met without incorporating flame retardants to FPUF. In fact, several major furniture manufacturers have announced plans to produce furniture that does not contain flame retardants (Chicago Tribune 2015).

### Flame Resistant Cover Fabrics

In its 2008 proposal for a national furniture flame retardancy standard, CPSC estimated that about 14% of fabrics used at that time would fail the proposed smolder test (CPSC 2008); these fabrics could be coated with a flame retardant to meet a smolder test. Coating fabrics raises the issue of chemical safety in the coatings used; flame retardant chemicals used for coatings tend to differ from the flame retardant chemicals used in FPUF. Anecdotal information indicates that decaBDE, tetrabromobisphenol A, and hexabromocyclododecane – each one the subject of a DfE Alternatives Assessment (see <http://www2.epa.gov/saferchoice/design-environment-alternatives-assessments>) – have been used as fabric coatings (Stapleton July 2013, personal communication). The current report does not attempt to identify or assess flame retardants used in fabric coatings.

### Fire Barriers

To meet a more stringent test (e.g., an open flame test), a fire barrier may be used between the foam and the upholstery fabric. A fire barrier may be IFR (e.g., Kevlar or Nomex), or may be coated with a flame retardant chemical, possibly including the chemicals identified as alternatives in this report. Fire barriers have proven highly effective in aircraft seating, even in extreme fire situations (CPSC 2013b). A suitable fire barrier is likely to be able to achieve almost any flame retardancy standard; however, costs of such products are likely to be higher. Mattresses meeting the CPSC 1633 open flame standard most commonly use fire barriers, although designs of these barriers vary widely (Nazare, Davis et al. 2012).

### Polymers and Reactive Flame Retardants

The current report includes only one polymeric flame retardant (excluding expandable graphite). While polymers would be expected to have lower mobility, reducing exposures during the consumer use phase, they are difficult to use in the manufacture of FPUF. Polymeric and reactive flame retardants typically have high viscosities incompatible with flexible polyurethane, are not compatible with the extremely small pores used in the blending nozzle, and have difficulty blending with the polyol. Reactive products are available in other product sectors (e.g., in printed



circuit boards), and there is great interest in the manufacturing industry in finding reactive flame retardants for FPUF.

### **Nanoclays**

There has been recent interest in nanoclay flame retardants, which may slow or prevent the breakdown of materials and decrease the temperature of the flame, and have been shown to improve the mechanical properties of polyurethane foam (Betts 2008; Nayani, Gunashekar et al. 2013). Nanoclays can also be combined with other classes of flame retardants to improve their performance. These materials are currently in the research and development stage, but may become viable products in the near future. Layer-by-layer (LbL) coatings are nanocomposite structures assembled by an alternate deposition of anionic and cationic monolayers onto a substrate (Li, Schulz et al. 2009; Kim, Harris et al. 2012). The LbL deposition technique was discovered in 1966, and flame retardant LbL coatings have recently gained attention beyond the areas of academic research and development, with some industrial companies pursuing internal studies on the effectiveness of LbL coatings as flame retardants in commercial products (Apaydin, Laachachi et al. 2013). Research has shown that LbL coatings can be effective flame retardants for a number of different substrates including polyurethane foam (Kim, Harris et al. 2012; Laufer, Kirkland et al. 2012a) and cotton fabric (Li, Schulz et al. 2009; Laufer, Kirkland et al. 2012b).

## 5 Hazard Evaluation Methodology

This section summarizes the toxicological and environmental hazards of furniture flame retardants (FFRs) and each alternative chemical or proprietary mixture that was identified as a potential functional substitute for them. Evaluations of chemical formulations may also include associated substances (e.g., starting materials, byproducts, and impurities) if their presence is specifically required to allow that alternative to fully function in the assigned role. Otherwise, pure substances were analyzed in this assessment. Users of this DfE alternatives assessment should be aware of the purity of the trade product they purchase, as the presence of impurities may alter the assessment of the alternative. This report is a hazard assessment, not a risk assessment. Hazard assessment as a risk management tool is discussed in more detail in Section 1.3.

Toxicological and environmental endpoints included in the hazard profiles are discussed in Section 5.1, along with the criteria used to evaluate each hazard endpoint. Data sources and the review methodology are described in Section 5.2. The report then offers a detailed description of the utility of physical-chemical properties in understanding hazard in Section 5.3, and the process of evaluating human health and environmental endpoints in Sections 5.4 and 5.5, respectively. A discussion of the evaluation of endocrine activity is included in Section 5.6. The characteristics of each chemical included in the alternatives assessment are summarized in the comparative hazard summary table in Section 2. Lastly, the collected data and hazard profile of each chemical are presented in Section 7.

### 5.1 Toxicological and Environmental Endpoints

The assessment of endpoints with the intent to create hazard profiles for a DfE alternatives assessment follows the guidance of the *DfE Alternatives Assessment Criteria for Hazard Evaluation* (U.S. EPA 2011b). The definitions for each endpoint evaluated following these criteria are outlined in Section 5.1.1, and the criteria by which these endpoints are evaluated are outlined in Section 5.1.2. Lastly, there are endpoints that DfE characterizes but to which it does not assign criteria; these are summarized in Section 5.1.3.

#### 5.1.1 Definitions of Each Endpoint Evaluated Against Criteria

Hazard designations for each chemical discussed in this report were made by direct comparison of the experimental or estimated data to the *DfE Alternatives Assessment Criteria for Hazard Evaluation* (U.S. EPA 2011b). Table 5-1 provides brief definitions of human health toxicity, environmental toxicity, and environmental fate endpoints.

**Table 5-1: Definitions of Toxicological and Environmental Endpoints for Hazard Assessment**

Endpoint Category	Endpoint	Definition
Human Health Effects	Acute Mammalian Toxicity	Adverse effects occurring following oral or dermal administration of a single dose of a substance, or multiple doses given within 24 hours, or an inhalation exposure of 4 hours.

Endpoint Category	Endpoint	Definition
	<b>Carcinogenicity</b>	Capability of a substance to increase the incidence of malignant neoplasms, reduce their latency, or increase their severity or multiplicity.
	<b>Mutagenicity/Genotoxicity</b>	<p><i>Mutagenicity</i> - The ability of an agent to induce permanent, transmissible changes in the amount, chemical properties or structure of the genetic material. These changes may involve a single gene or gene segment, a block of genes, parts of chromosomes, or whole chromosomes. Mutagenicity differs from genotoxicity in that the change in the former case is transmissible to subsequent cell generations.</p> <p><i>Genotoxicity</i> – The ability of an agent or process to alter the structure, information content, or segregation of DNA, including those which cause DNA damage by interfering with normal replication process, or which in a non-physiological manner (temporarily) alter its replication.</p>
	<b>Reproductive Toxicity</b>	The occurrence of biologically adverse effects on the reproductive systems of females or males that may result from exposure to environmental agents. The toxicity may be expressed as alterations to the female or male reproductive organs, the related endocrine system, or pregnancy outcomes. The manifestation of such toxicity may include, but is not limited to: adverse effects on onset of puberty, gamete production and transport, reproductive cycle normality, sexual behavior, fertility, gestation, parturition, lactation, developmental toxicity, premature reproductive senescence or modifications in other functions that were dependent on the integrity of the reproductive systems.
	<b>Developmental Toxicity</b>	Adverse effects in the developing organism that may result from exposure prior to conception (either parent), during prenatal development, or postnatally to the time of sexual maturation. Adverse developmental effects may be detected at any point in the lifespan of the organism. The major manifestations of developmental toxicity include: (1) death of the developing organism, (2) structural abnormality, (3) altered growth, and (4) functional deficiency.
	<b>Neurotoxicity</b>	An adverse change in the structure or function of the central and/or peripheral nervous system following exposure to a chemical, physical or biological agent.

Endpoint Category	Endpoint	Definition
	<b>Repeated Dose Toxicity</b>	Adverse effects (immediate or delayed) that impair normal physiological function (reversible and irreversible) of specific target organs or biological systems following repeated exposure to a chemical substance by any route relevant to humans. Adverse effects include biologically significant changes in body and organ weights, changes that affect the function or morphology of tissues and organs (gross and microscopic), mortality, and changes in biochemistry, urinalysis, and hematology parameters that are relevant for human health; may also include immunological and neurological effects.
	<b>Respiratory Sensitization</b>	Hypersensitivity of the airways following inhalation of a substance.
	<b>Skin Sensitization</b>	A cell-mediated or antibody-mediated allergic response characterized by the presence of inflammation that may result in cell death, following an initial induction exposure to the same chemical substance (i.e., skin allergy).
	<b>Eye Irritation/Corrosivity</b>	Irritation or corrosion to the eye following the application of a test substance.
	<b>Skin Irritation/Corrosion</b>	Skin irritation- reversible damage to the skin following the application of a test substance for up to 4 hours. Skin corrosion- irreversible damage to the skin namely, visible necrosis through the epidermis and into the dermis following the application of a test substance for up to 4 hours.
<b>Environmental Toxicity</b>	<b>Environmental toxicity refers to adverse effects observed in living organisms that typically inhabit the wild; the assessment is focused on effects in three groups of surrogate aquatic organisms (freshwater fish, invertebrates, and algae).</b>	
	<b>Aquatic Toxicity (Acute)</b>	The property of a substance to be injurious to an organism in a short-term, aquatic exposure to that substance.
	<b>Aquatic Toxicity (Chronic)</b>	The property of a substance to cause adverse effects to aquatic organisms during aquatic exposures which were determined in relation to the life-cycle of the organism.
<b>Environmental Fate</b>	<b>Environmental Persistence</b>	The length of time the chemical exists in the environment, expressed as a half-life, before it is destroyed (i.e., transformed) by natural or chemical processes. For alternatives assessments, the amount of time for complete assimilation (ultimate removal) is preferred over the initial step in the transformation (primary removal).
	<b>Bioaccumulation</b>	The process in which a chemical substance is absorbed in an organism by all routes of exposure as occurs in the natural environment (e.g., dietary and ambient environment sources). Bioaccumulation is the net result of competing processes of chemical uptake into the organism at the respiratory surface and from the diet and chemical elimination from the organism, including respiratory exchange, fecal egestion, and metabolic biotransformation of the parent compound and growth dilution.

The hazard profile for each chemical contains endpoint specific summary statements (see Section 7). For each of the endpoints listed in Table 5-1, these summary statements provide the hazard designation, the type of data (experimental or estimated) and the rationale. The endpoint summaries may also include explanatory comments, a discussion of confounding factors, or an indication of the confidence in the data to help put the results in perspective.

### 5.1.2 Criteria

Table 5-2 summarizes the criteria that were used by DfE to interpret the data presented in the hazard evaluations. The *DfE Alternatives Assessment Criteria for Hazard Evaluation* underwent internal and public comment, and were finalized in 2011 (U.S. EPA 2011b). A hazard designation for each human health endpoint was not given for each route of exposure, but rather was based on the exposure route with the highest hazard designation. Data may have been available for some or all relevant routes of exposure.

The details as to how each endpoint was evaluated are described below and in the DfE full criteria document, *DfE Alternatives Assessment Criteria for Hazard Evaluation*, available at: <http://www2.epa.gov/saferchoice/alternatives-assessment-criteria-hazard-evaluation>.

**Table 5-2: Criteria Used to Assign Hazard Designations**

Endpoint	Very High	High	Moderate	Low	Very Low
<b>Human Health Effects</b>					
<b>Acute mammalian toxicity</b>					
Oral median lethal dose (LD <sub>50</sub> ) (mg/kg)	≤50	>50–300	>300–2,000	>2,000	–
Dermal LD <sub>50</sub> (mg/kg)	≤200	>200–1,000	>1,000–2,000	>2,000	–
Inhalation median lethal concentration (LC <sub>50</sub> ) - vapor/gas (mg/L)	≤2	>2–10	>10–20	>20	–
Inhalation LC <sub>50</sub> - dust/mist/fume (mg/L)	≤0.5	>0.5–1.0	>1–5	>5	–
<b>Carcinogenicity</b>					
Carcinogenicity	<i>Known or presumed human carcinogen</i>  (equivalent to Globally Harmonized System of Classification and Labeling of Chemicals (GHS) Categories 1A and 1B)	<i>Suspected human carcinogen</i>  (equivalent to GHS Category 2)	<i>Limited or marginal evidence of carcinogenicity in animals</i>  (and inadequate evidence in humans)	<i>Negative studies or robust mechanism-based Structure Activity Relationship (SAR)</i>  (as described above)	–

<b>Mutagenicity/Genotoxicity</b>					
Germ cell mutagenicity	GHS Category 1A or 1B: Substances known to induce heritable mutations or to be regarded as if they induce heritable mutations in the germ cells of humans	GHS Category 2: Substances which cause concern for humans owing to the possibility that they may induce heritable mutations in the germ cells of humans  OR	Evidence of mutagenicity supported by positive results in <i>in vitro</i> OR <i>in vivo</i> somatic cells of humans or animals	Negative for chromosomal aberrations and gene mutations, or no structural alerts.	--
Mutagenicity and genotoxicity in somatic cells		Evidence of mutagenicity supported by positive results in <i>in vitro</i> AND <i>in vivo</i> somatic cells and/or germ cells of humans or animals			
<b>Reproductive toxicity</b>					
Oral (mg/kg/day)	–	<50	50–250	>250-1,000	>1,000
Dermal (mg/kg/day)	–	<100	100–500	>500-2,000	>2,000
Inhalation - vapor, gas (mg/L/day)	–	<1	1–2.5	>2.5-20	>20
Inhalation - dust/mist/fume (mg/L/day)	–	<0.1	0.1–0.5	>0.5-5	>5
<b>Developmental toxicity</b>					
Oral (mg/kg/day)	–	<50	50–250	>250-1,000	>1,000
Dermal (mg/kg/day)	–	<100	100–500	>500-2,000	>2,000
Inhalation - vapor, gas (mg/L/day)	–	<1	1–2.5	>2.5-20	>20
Inhalation - dust/mist/fume (mg/L/day)	–	<0.1	0.1–0.5	>0.5-5	>5
<b>Neurotoxicity</b>					
Oral (mg/kg/day)	–	<10	10–100	>100	–
Dermal (mg/kg/day)	–	<20	20–200	>200	–
Inhalation - vapor, gas (mg/L/day)	–	<0.2	0.2–1.0	>1.0	–
Inhalation - dust/mist/fume (mg/L/day)	–	<0.02	0.02–0.2	>0.2	–
<b>Repeated-dose toxicity</b>					
Oral (mg/kg/day)	–	<10	10–100	>100	–
Dermal (mg/kg/day)	–	<20	20–200	>200	–

Inhalation - vapor, gas (mg/L/day)	–	<0.2	0.2–1.0	>1.0	–
Inhalation - dust/mist/fume (mg/L/day)	–	<0.02	0.02–0.2	>0.2	–
<b>Sensitization</b>					
Skin sensitization	–	High frequency of sensitization in humans and/or high potency in animals (GHS Category 1A)	Low to moderate frequency of sensitization in human and/or low to moderate potency in animals (GHS Category 1B)	Adequate data available and not GHS Category 1A or 1B	–
Respiratory sensitization	–	Occurrence in humans or evidence of sensitization in humans based on animal or other tests (equivalent to GHS Category 1A and 1B)	Limited evidence including the presence of structural alerts	Adequate data available indicating lack of respiratory sensitization	–
<b>Irritation/corrosivity</b>					
Eye irritation/corrosivity	Irritation persists for >21 days or corrosive	Clearing in 8–21 days, severely irritating	Clearing in ≤7 days, moderately irritating	Clearing in <24 hours, mildly irritating	Not irritating
Skin irritation/corrosivity	Corrosive	Severe irritation at 72 hours	Moderate irritation at 72 hours	Mild or slight irritation at 72 hours	Not irritating
<b>Endocrine activity</b>					
Endocrine Activity	<i>For this endpoint, High/Moderate/Low etc. characterizations will not apply. A qualitative assessment of available data will be prepared.</i>				
<b>Environmental Toxicity and Fate</b>					
<b>Aquatic toxicity</b>					
Acute aquatic toxicity – LC <sub>50</sub> or half maximal effective concentration (EC <sub>50</sub> ) (mg/L)	<1.0	1–10	>10–100	>100 or No Effects at Saturation (NES)	–
Chronic aquatic toxicity – lowest observed effect concentration (LOEC) or chronic value (ChV) (mg/L)	<0.1	0.1–1	>1–10	>10 or NES	–

<b>Environmental persistence</b>					
Persistence in water, soil, or sediment	Half-life >180 days or recalcitrant	Half-life of 60–180 days	Half-life <60 but ≥16 days	Half-life <16 days OR passes Ready Biodegradability test not including the 10-day window. No degradation products of concern.	Passes Ready Biodegradability test with 10-day window. No degradation products of concern.
Persistence in air (half-life days)	<i>For this endpoint, High/Moderate/Low etc. characterizations will not apply. A qualitative assessment of available data will be prepared.</i>				
<b>Bioaccumulation</b>					
Bioconcentration Factor (BCF)/Bioaccumulation Factor (BAF)	>5,000	5,000–1,000	<1,000–100	<100	–
Log BCF/BAF	>3.7	3.7–3	<3–2	<2	–

*Very High or Very Low designations (if an option for a given endpoint in Table 5-2) were assigned only when there were experimental data located for the chemical under evaluation. In addition, the experimental data must have been collected from a well conducted study specifically designed to evaluate the endpoint under review. If the endpoint was estimated using experimental data from a close structural analog, by professional judgment, or from a computerized model, then the next-level designation was assigned (e.g., use of data from a structural analog that would yield a designation of very high would result in a designation of high for the chemical in review). One exception is for the estimated persistence of polymers with an average MW >1,000 daltons, which may result in a Very High designation.*

### 5.1.3 Endpoints Characterized but Not Evaluated

Several additional endpoints were characterized, but not evaluated against hazard criteria. This is because the endpoints lacked a clear consensus concerning the evaluation criteria (endocrine activity), data and expert judgment were limited for industrial chemicals (persistence in air, terrestrial ecotoxicology), or the information was valuable for the interpretation of other toxicity and fate endpoints (including toxicokinetics and transport in the environment).

**Table 5-3: Definitions of Endpoints and Information Characterized but Not Evaluated Against Hazard Criteria**

<b>Toxicological Endpoint</b>	<b>Definition</b>
<b>Toxicokinetics</b>	The determination and quantification of the time course of absorption, distribution, biotransformation, and excretion of chemicals (sometimes referred to as <i>pharmacokinetics</i> ).
<b>Biomonitoring Information</b>	The measured concentration of a chemical in biological tissues where the analysis samples were obtained from a natural or non-experimental setting.
<b>Environmental Transport</b>	The potential movement of a chemical, after it is released to the environment, within and between each of the environmental compartments, air, water, soil, and sediment. Presented as a qualitative summary in the alternatives assessment based on physical-chemical properties, environmental fate parameters, and simple volatilization models. Also includes distribution in the environment as estimated from a fugacity model <sup>5</sup> .



Toxicological Endpoint	Definition
<b>Persistence in Air</b>	The half-life for destructive removal of a chemical substance in the atmosphere. The primary chemical reactions considered for atmospheric persistence include hydrolysis, direct photolysis, and the gas phase reaction with hydroxyl radicals, ozone, or nitrate radicals. Results are used as input into the environmental transport models.
<b>Immunotoxicology</b>	Adverse effects on the normal structure or function of the immune system caused by chemical substances (e.g., gross and microscopic changes to immune system organs, suppression of immunological response, autoimmunity, hypersensitivity, inflammation, and disruption of immunological mechanistic pathways).
<b>Terrestrial Ecotoxicology</b>	Reported experimental values from guideline and nonguideline studies on adverse effects on the terrestrial environment. Studies on soil, plants, birds, mammals, invertebrates were also included.
<b>Endocrine Activity</b>	A change in endocrine homeostasis caused by a chemical or other stressor from human activities (e.g., application of pesticides, the discharge of industrial chemicals to air, land, or water, or the use of synthetic chemicals in consumer products.)

<sup>1</sup>A fugacity model predicts partitioning of chemicals among air, soil, sediment, and water under steady state conditions for a default model “environment” (U.S. EPA 2011e).

## 5.2 Data Sources and Assessment Methodology

This section explains how data were collected (Section 5.2.1), prioritized and reviewed (Section 5.2.2) for use in the development of hazard profiles. High-quality experimental studies lead to a thorough understanding of behavior and effects of the chemical in the environment and in living organisms. Analog approaches and SAR-based estimation methods are also useful tools and are discussed throughout this section. Information on how polymers differ from discrete chemicals in terms of how they are evaluated is presented in Section 5.2.3.

### 5.2.1 Identifying and Reviewing Measured Data

For each chemical assessed, data were collected in a manner consistent with the *High Production Volume (HPV) Chemical Challenge Program Guidance* (U.S. EPA 1999) on searching for existing chemical information. This process resulted in a comprehensive search of the literature for available experimental data. For chemicals well characterized by experimental studies, this usually resulted in the collection of recent high-quality reviews or peer-reviewed risk assessments. These were supplemented by primary searches of scientific literature published after these secondary sources were released; this is explained in greater detail below. For chemicals that are not as well characterized, that is, where these secondary sources were not available or lacked relevant or adequate data, a comprehensive search of the primary scientific literature was done. Subsequently, these searches led to the collection and review of articles from the scientific literature, industrial submissions, encyclopedic sources, and government reports. In addition, data presented in EPA public databases (e.g., Integrated Risk Information System (IRIS); the High Production Volume Information System (HPVIS)) and confidential databases were obtained for this project. Generally, foreign language (non-English) reports were not used unless they provided information that was not available from other sources.

Chemical assessments were performed by first searching for experimental data for all endpoints in Table 5-2. For most alternatives assessed, high quality secondary sources were not available;

therefore a comprehensive search of the literature was performed to identify experimental data. In some cases, confidential studies submitted to EPA by chemical manufacturers were also available to support hazard designations. For those chemicals that were expected to form stable metabolites, searches were performed to identify relevant fate and toxicity information for the metabolite or degradation product.

### **Well Studied Chemicals – Literature Search Strategy**

As mentioned above, for chemicals that have been well characterized, the literature review focused primarily on the use of secondary sources, such as Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles or IRIS assessments. Using high-quality secondary sources maximized available resources and eliminated potential duplication of effort. However, more than one secondary source was typically used to verify reported values, which also reduced the potential for presenting a value that was transcribed incorrectly from the scientific literature. Although other sources might also contain the same experimental value for an endpoint, effort was not focused on building a comprehensive list of these references, as it would not have enhanced the ability to reach a conclusion in the assessment. When data for a selected endpoint could not be located in a secondary source for an otherwise well studied chemical, the primary literature was searched by endpoint and experimental studies were assessed for relevant information.

### **Making Predictions in the Absence of Measured Data**

In the absence of primary or secondary data, hazard designations were based on (1) Quantitative Structure Activity Relationships (QSAR)-based estimations from the EPA New Chemical Program's predictive methods; (2) analog data; (3) class-based assignments from the EPA Chemical Categories document, and (4) expert judgment by EPA subject matter experts.

For chemicals that lacked experimental information, QSAR assessments were made using either EPA's Estimation Programs Interface (EPISuite™) for physical-chemical property and environmental fate endpoints or EPA's Ecological Structure Activity Relationships (ECOSAR™) QSARs for ecotoxicity. For the cancer endpoint, estimates were also obtained from EPA's OncoLogic expert system. These estimation methods have been automated, and are available for free (U.S. EPA 2012c). Often analog data were used to support predictions from models. These approaches were described in the EPA Pollution Prevention (P2) Framework and Sustainable Futures (SF) program (U.S. EPA 2005b; U.S. EPA 2011e).

For some physical-chemical properties that could not be estimated using EPISuite™, such as acid/base dissociation constants, other available methods (e.g., the ACE acidity and basicity calculator website for dissociation constants) were used (ACE Organic 2013). All estimation methods employed were limited to those freely available in the public domain.

The methodology and procedures used to assess polymers are described in Section 5.2.3. In addition, the endpoints for impurities or oligomers with a MW >1,000 daltons were estimated using professional judgment and the results assessed for inclusion in the overall hazard

designation. This process is described, as appropriate, under the corresponding endpoints appearing in Section 5.3.

When QSAR models were not available, professional judgment was used to identify hazards for similar chemicals using the guidance from EPA's New Chemicals Categories (U.S. EPA 2010b). The categories identify substances that share chemical and toxicological properties and possess potential health or environmental concerns (U.S. EPA 2010a). In the absence of an identified category, analogs for which experimental data are available were identified using EPA's Analog Identification Methodology (AIM) or by substructure searches of confidential EPA databases (U.S. EPA 2012a). If a hazard designation was still not available, the expert judgment of scientists from EPA's New Chemical Program would provide an assessment of the physical-chemical properties, environmental fate, aquatic toxicity and human health endpoints to fill remaining data gaps.

Expandable graphite was a unique substance compared to the other alternatives in this report. Although expandable graphite has some structural features in common with carbon-based nanoparticles, its cross-section diameter is far greater, and it would be less likely to pass through biological membranes. As a result, it was not considered a nano-sized substance and available nanoparticle data were not used as analog data in the evaluation. At the time of this report, DfE is not using the hazard criteria to assess nanoparticles.

### **5.2.2 Hierarchy of Data Adequacy**

Once the studies were obtained, they were evaluated to establish whether the hazard data were of sufficient quality to meet the requirements of the assessment process. The adequacy and quality of the studies identified in the literature review are described in the Data Quality field of the chemical assessments presented in Section 7. The tiered approach described below represents a general preferred data hierarchy, but the evaluation of toxicological data also requires flexibility based on expert judgment.

1. One or more studies conducted in a manner consistent with established testing guidelines
2. Experimentally valid but nonguideline studies (i.e., do not follow established testing guidelines)
3. Reported data without supporting experimental details
4. Estimated data using SAR methods or professional judgment based on an analog approach
5. Expert judgment based on mechanistic and structural considerations

In general, data were considered adequate to characterize an endpoint if they were obtained using the techniques identified in the HPV data adequacy guidelines (U.S. EPA 1999). Studies performed according to Harmonized EPA or Organisation for Economic Cooperation and Development guidelines were reviewed to confirm that the studies followed all required steps.

Experimental studies published in the open literature were reviewed for their scientific rigor and were also compared and contrasted to guideline studies to identify potential problems arising from differences in the experimental design. Data from adequate, well-performed, experimental

studies were used to assign hazard designations in preference to those lacking in sufficient experimental detail. When multiple adequate studies were available for a given endpoint, any discrepancies that were identified within the set of data were examined further and addressed using a weight-of-evidence approach that was described in the data entry to characterize the endpoint whenever possible.

When available, experimental data from guideline or well-performed experimental studies were preferred (Items 1 and 2 in the hierarchy list). Information from secondary sources such as Material Safety Data Sheets (MSDSs), or online databases (such as the National Library of Medicine's Hazardous Substances Data Bank (HSDB), Item 3 in the hierarchy list) was considered appropriate for some endpoints when it included numerical values for effect levels that could be compared to the evaluation criteria.

### **5.2.3 Assessment of Polymers and Oligomers**

The methodology and procedures used to assess polymers were slightly different than those used for oligomers, discrete compounds and simple mixtures. Although experimental data for polymers were identified using the literature search techniques discussed above in Section 5.2.1, in the absence of experimental data, estimates were performed using professional judgment as presented in the literature (Boethling and Nabholz 1997). The polymers are a mixture of molecules with a distribution of components (e.g., different chain lengths) that depend on the monomers used, their molar ratios, the total number of monomeric units in the polymer chain, and the manufacturing conditions. To account for this variation, the average MW profile (also referred to as the number average molecular weight ( $MW_n$ )) was used in their assessment, as the individual chains rarely have the same degree of polymerization and weight, yet their physical, chemical, and environmental properties are essentially identical for the purposes of this assessment. The polymers evaluated as alternatives typically have average MWs ranging from >1,000 to <100,000 daltons.

For polymers with relatively low average MWs (i.e., those with average MWs generally less than 2,000), the alternatives assessment also determined the amount of oligomers and unchanged monomers (starting materials) in the MW profile with MWs <1,000 daltons. Special attention was paid to materials that have a MW <1,000 daltons, as these materials often have the highest hazard (potentially bioavailable substances) in the mixture. This type of assessment was similar to the evaluation of the hazards of impurities present in discrete chemical products. Methodological differences between the evaluation of discrete products and polymers are discussed in Section 5.3. Although the MW of expandable graphite is >1,000, it was not explicitly evaluated as a polymer. However, the chemical property and hazard designation cutoffs associated with polymers and other high MW materials were used in its evaluation.

For this alternatives assessment, there were chemicals that are mixtures of low MW oligomers comprised of 2 or 3 repeating units. The hazard assessment evaluated all oligomers present. From all the oligomers, the higher concern material was used to assign the hazard designation. This process is essentially identical to the evaluation of the hazards associated with impurities or byproducts present in discrete chemical products. As a result, the alternatives assessment process determined the amount of oligomers and unchanged monomers (starting materials) present, and considered their potential hazards in the alternatives designation.

### **5.3 Importance of Physical and Chemical Properties, Environmental Transport, and Biodegradation**

Physical-chemical properties provide basic information on the characteristics of a chemical substance, and were used throughout the alternatives assessment process. These endpoints provide information required to assess potential environmental release, exposure, and partitioning, as well as insight into the potential for adverse toxicological effects. The physical-chemical properties are provided in the individual chemical hazard profiles presented in Section 7. Descriptions of relevant physical-chemical properties and how they contribute to the hazard assessments are presented below.

#### **Molecular Weight (MW)**

MW informs how a chemical behaves in a physical or biological system, including bioavailability and environmental fate. In general, but not strictly, larger compounds tend to be less mobile in biological and environmental systems. Their large size restricts their transport through biological membranes and lowers their vapor pressure. Polymers and oligomers evaluated in this alternatives assessment were mixtures that contain a distribution of components, and they may not have a unique MW (see also Section 5.2.3). To account for variation in these mixtures, the average MW or  $MW_n$ , determined experimentally (typically using high pressure liquid chromatography, viscosity, or light-scattering), was used in the assessment of polymers. The assessment of polymers also includes oligomers and unchanged monomers (starting materials) that have MW of <1,000 daltons, as these were often the highest concern materials (bioavailable substances) in the mixture.

#### **Melting Point and Boiling Point**

These two properties provide an indication of the physical state of the material at ambient temperature. Chemicals with a melting point more than 25°C were assessed as a solid. Those with a melting point less than 25°C and a boiling point more than 25°C were assessed as a liquid, and those with a boiling point less than 25°C were assessed as a gas. The physical state was used throughout the assessment, such as in the determination of potential routes of human and environmental exposure. The melting and boiling points were also useful in determining the potential environmental fate, ecotoxicity, and human health hazards of a chemical. For example, organic compounds with high melting points generally have low water solubility and low rates of dissolution. These properties influence a material's bioavailability, and were therefore taken into account in both the assessment process and the evaluation of experimental studies. Similarly, chemicals with a low melting point also have a higher potential to be absorbed through the skin, gastrointestinal tract, and lungs.

In the absence of experimental data, the melting point value was not reported, and no estimations were performed. If a chemical decomposes before it melts, this information was included in the assessment. For boiling point, the maximum value reported in the assessment was 300°C for high boiling materials, including polymers (U.S. EPA 1999). Melting points for polymers and/or oligomers were not reported, as these materials typically reach a softening point and do not undergo the phase change associated with melting (i.e., solid to liquid).

## Vapor Pressure

Vapor pressure is useful in determining the potential for a chemical substance to volatilize to the atmosphere from dry surfaces, from storage containers, or during mixing, transfer, or loading/unloading operations. In the assessment process, chemicals with a vapor pressure less than  $1 \times 10^{-6}$  mm Hg have a low potential for inhalation exposure resulting from gases or vapors. Vapor pressure is also useful for determining the potential environmental fate of a substance. Substances with a vapor pressure more than  $1 \times 10^{-4}$  mm Hg generally exist in the gas phase in the atmosphere. Substances with a vapor pressure between  $1 \times 10^{-4}$  and  $1 \times 10^{-8}$  mm Hg exist as a gas/particulate mixture. Substances with a vapor pressure less than  $1 \times 10^{-8}$  mm Hg exist as a particulate. The potential atmospheric degradation processes described below in the reactivity section generally occur when a chemical exists in the gas phase. Gases in the atmosphere also have the potential to travel long distances from their original point of release. Materials in the liquid or solid (particulate) phases in the atmosphere generally undergo deposition onto the Earth's surface.

A maximum vapor pressure of  $1 \times 10^{-8}$  mm Hg was assigned for chemicals without experimental data, or for those substances that were anticipated by professional judgment to be nonvolatile (U.S. EPA 1999). The maximum vapor pressure of  $1 \times 10^{-8}$  mm Hg was also the default value reported for the vapor pressure of polymers and other high MW materials with a MW >1,000 daltons (U.S. EPA 1999).

## Water Solubility

The water solubility of a chemical provides an indication of its distribution between environmental media, potential for environmental exposure through release to aquatic compartments, and potential for human exposure through ingestion of drinking water. Water solubility was also used extensively to determine potential human health and ecotoxicity hazards. In general, chemicals with water solubility less than  $1 \times 10^{-5}$  g/L indicate a lower concern for both the expression of adverse effects and potential aquatic and general population exposure, due to their low bioavailability. However, chemicals with a low bioavailability also tend to be more environmentally persistent. Low bioavailability is different than no bioavailability, and the two should not be used interchangeably.

Within the context of this alternatives assessment, the following descriptors were used according to ranges of water solubility values: more than 10,000 mg/L was considered very soluble; 1,000–10,000 mg/L represents soluble; 100–1,000 mg/L represents moderately soluble, 1–100 mg/L represents slightly soluble, and less than 1 mg/L was considered to be insoluble, noting that these guidelines might not match what is used elsewhere within the scientific literature for other disciplines. Chemicals with higher water solubility are more likely to be transported into groundwater with runoff during storm events, be absorbed through the gastrointestinal tract or lungs, partition to aquatic compartments, undergo atmospheric removal by rain washout, and possess a greater potential for human exposure through the ingestion of contaminated drinking water. Chemicals with lower water solubility are generally more persistent, and have a greater potential to bioconcentrate.

The water solubility of a substance was also used to evaluate the quality of experimental aquatic toxicity and oral exposure human health studies, as well as the reliability of aquatic toxicity estimates. If the water solubility of a substance was lower than the reported exposure level in these experiments, then the study was likely to be regarded as inadequate, due to potentially confounding factors arising from the presence of un-dissolved material. For aquatic toxicity estimates obtained using SARs, when the estimated toxicity was higher than a chemical's water solubility (i.e., the estimated concentration in water at which adverse effects appear cannot be reached because it was above the material's water solubility), the chemical was described as having NES. An NES designation is equivalent to a low aquatic toxicity hazard designation for that endpoint.

While assessing the water solubility of a chemical substance, its potential to disperse in an aqueous solution was also considered. Ideally, a chemical's potential to disperse would be obtained from the scientific literature. In the absence of experimental data, the potential for dispersion can be determined from chemical structure and/or comparison to closely related analogs. There are two general structural characteristics that lead to the formation of dispersions in water: (1) chemicals that have both a hydrophilic (polar) head and a hydrophobic (nonpolar) tail (e.g., surfactants), and (2) molecules that have a large number of repeating polar functional groups (e.g., polyethylene oxide).

The potential for a chemical to disperse influences potential exposure, environmental fate, and toxicity. Dispersible chemicals have greater potential for human and environmental exposure, leachability, and aquatic toxicity than what might be anticipated based on the material's water solubility alone.

Chemicals without experimental data, or chemicals that were anticipated by professional judgment to be sufficiently insoluble and thus were not bioavailable, were assigned a water solubility maximum value of  $1 \times 10^{-3}$  mg/L (U.S. EPA 1999). A water solubility of  $1 \times 10^{-3}$  mg/L is the default value used for discrete organics, as well as non-ionic polymers with a MW > 1,000 daltons, according to information contained in the literature concerning polymer assessment (Boethling and Nabholz 1997). This assignment is consistent with an analysis of the chemicals used in the development of the water solubility estimation program in EPA's EPISuite™ software. The training set for this model included 1,450 chemicals with a MW range 27-628 daltons and experimental water solubility values ranging from miscible to  $4 \times 10^{-7}$  mg/L (Meylan, Howard et al. 1996; U.S. EPA 2011i). Given that water solubility decreases with MW, a default value of  $1 \times 10^{-3}$  mg/L is consistent with the limited bioavailability expected for materials with a MW >1,000 daltons.

### **Octanol/Water Partition Coefficient ( $K_{ow}$ )**

The octanol/water partition coefficient, commonly expressed as its log value (i.e.,  $\log K_{ow}$ ) is one of the most useful properties for performing a hazard assessment. The  $\log K_{ow}$  indicates the partitioning of a chemical between octanol and water, where octanol is used to mimic fat and other hydrophobic components of biological systems. Chemicals with a  $\log K_{ow}$  less than 1 are highly soluble in water (hydrophilic), while those with a  $\log K_{ow}$  more than 4 are not very soluble in water (hydrophobic). A  $\log K_{ow}$  more than 8 indicates that the chemical is not readily

bioavailable and is essentially insoluble in water. In addition, a log  $K_{ow}$  greater than approximately 8 may be difficult to obtain experimentally.

The log  $K_{ow}$  can be used as a surrogate for the water solubility in a hazard assessment, and is frequently used to estimate the water solubility if an experimental value is not available. It can also be used to estimate other properties important to the assessment, including bioconcentration and soil adsorption, and is a required input for SAR models used to estimate ecotoxicity values.

For chemicals without data, that are not within the domain of EPISuite™ or that were expected to be insoluble in water ( $WS < 1 \times 10^{-3}$  mg/L), a minimum value of 10 was assigned for the log  $K_{ow}$  (U.S. EPA 1999). Insoluble chemicals that could be run through EPISuite™ software may use a log  $K_{ow} > 10$  if the result appeared to be valid based on expert review. This assignment is consistent with an analysis of the chemicals (“training set”) used in the development of the octanol/water partition coefficient estimation program in the EPISuite™ software. The training set for this model included 10,946 chemicals with a MW range 18-720 daltons and experimental log  $K_{ow}$  values ranging from -3.89 to 8.70 (Meylan and Howard 1995; U.S. EPA 2011h). Given that log  $K_{ow}$  increases with MW, a default value of 10 is consistent with the limited bioavailability expected for materials with a MW  $> 1,000$  daltons. A maximum log  $K_{ow}$  of -2 was used for water soluble materials. For most polymers and other materials that are anticipated to be insoluble in both water and octanol, the log  $K_{ow}$  cannot be measured and was therefore not listed.

### **Flammability (Flash Point)**

The flash point of a substance is defined as the minimum temperature at which the substance emits sufficient vapor to form an ignitable mixture with air. Flash point can be used to identify hazards associated with the handling of volatile chemicals. Substances with a flash point above 37.8°C (100°F) were commonly referred to as non-flammable, as this is the flammability definition used in the shipping industry. There are exceptions to this definition, such as chemicals that may form explosive mixtures in the presence of air.

### **Explosivity**

Explosivity refers to the potential for a chemical to form explosive mixtures in air, and can be defined using the limits of flammability. The lower limit of flammability (LFL) is defined as the minimum concentration of a combustible substance that is capable of propagating a flame through a homogenous mixture in the presence of an ignition source. The upper limit of flammability (UFL) is similarly defined as the highest concentration that can propagate a flame. LFLs and UFLs are commonly reported as the volume percent or volume fraction of the flammable component in air at 25°C. If the ambient air concentration of the gas (or vapor) is between the upper and lower explosion limit, then the material has the potential to explode if it comes in contact with an ignition source. Knowledge regarding the explosivity of a given material in air is also useful in identifying potential hazards associated with the manufacture and use of that material.



## pH

The pH scale measures how acidic or basic a substance is on a range from 0 to 14. A pH of 7 is neutral. A pH less than 7 is acidic, and a pH greater than 7 is basic. This scale is used primarily to identify potential hazards associated with skin or eye contact with a chemical or its aqueous solutions. The corrosive nature of chemicals that form either strongly basic (high pH) or strongly acidic (low pH) solutions are generally likely to result in harm to skin and other biological membranes. For corrosive chemicals, some experimental studies, such as biodegradation tests, require additional analysis to determine if the tests were performed at concentrations that cause harm to microbes in the test (and, therefore, may result in incorrectly identifying a chemical as persistent in the environment). For chemicals that form moderately basic or acidic solutions in water, the pH of the resulting solution can be used in lieu of a measured dissociation constant.

## Dissociation Constant in Water (pKa)

The dissociation constant determines if a chemical will ionize under environmental conditions. The dissociation constant in water provides the amount of the dissociated and undissociated forms of an acid, base, or organic salt in water. Knowledge of the dissociation constant is required to assess the importance of the other physical-chemical properties used in the hazard assessment. As the percentage of ionization increases, the water solubility increases while the vapor pressure, Henry's Law constant, and octanol/water partition coefficient decrease. For acids and bases, the dissociation constant is expressed as the  $pK_A$  and  $pK_B$ , respectively.

## Henry's Law Constant

Henry's Law constant is the ratio of a chemical's concentration in the gas phase to that in the liquid phase (at equilibrium). In environmental assessments, the Henry's Law constant is typically measured in water at 25°C. The Henry's Law constant provides an indication of a chemical's volatility from water, which can be used to derive partitioning within environmental compartments and the amount of material removed by stripping in a sewage treatment plant. Henry's Law constant values less than  $1 \times 10^{-7}$  atm-m<sup>3</sup>/mole indicate slow volatilization from water to air (the Henry's Law constant for the volatilization of water from water is  $1 \times 10^{-7}$  atm-m<sup>3</sup>/mole) and values more than  $1 \times 10^{-3}$  atm-m<sup>3</sup>/mole indicate rapid volatilization from water to air. To aid in determining the importance of volatilization, the assessment uses two models based on the Henry's Law constant. These models determine the half-life for volatilization from a model river and a model lake. A maximum value of  $1 \times 10^{-8}$  atm-m<sup>3</sup>/mole for the Henry's Law constant was assigned for chemicals without experimental data or for those that were anticipated by professional judgment to be nonvolatile.

## Sediment/Soil Adsorption/Desorption Coefficient ( $K_{oc}$ )

The soil adsorption coefficient provides a measure of a chemical's ability to adsorb to the organic portion of soil and sediment. This provides an indication of the potential for the chemical to leach through soil and be introduced into groundwater, which may lead to environmental exposures to wildlife or humans through the ingestion of drinking water drawn from underground sources. Chemicals with high soil adsorption coefficients are expected to be

strongly adsorbed to soil and are unlikely to leach into ground water. The soil adsorption coefficient also describes the potential for a chemical to partition from environmental waters to suspended solids and sediment. The higher the  $K_{oc}$ , the more strongly a chemical is adsorbed to soil. Strong adsorption may impact other fate processes, such as the rate of biodegradation, by making the chemical less bioavailable.

The soil adsorption coefficient,  $K_{oc}$ , is normalized with respect to the organic carbon content of the soil to account for geographic differences. The assignments for the degree that a chemical is adsorbed to soil within the context of the assessment were described qualitatively as very strong (above 30,000), strong (above 3,000), moderate (above 300), low (above 30), and negligible (above 3). When determining the potential for a chemical to adsorb to soil and suspended organic matter, the potential for a chemical to form chemical bonds with humic acids and attach to soil also needs to be considered, although this process is generally limited to a small number of chemical classes.

A maximum value of 30,000 for the  $K_{oc}$  was assigned for chemicals without experimental data or for those that were anticipated by professional judgment to be strongly adsorbed to soil (U.S. EPA 2005b). A default  $K_{oc}$  of 30,000 was used for polymers and other high MW materials with a MW >1,000 daltons.

## **Reactivity**

The potential for a substance to undergo irreversible chemical reactions in the environment can be used in the assessment of persistence. The primary chemical reactions considered in an environmental fate assessment are: hydrolysis, photolysis, and the gas phase reaction with hydroxyl radicals, ozone, or nitrate radicals. The most important reaction considered in the hazard assessment of organic compounds is hydrolysis, or the reaction of a chemical substance with water. Because the rate of hydrolysis reactions can change substantially as a function of pH, studies performed in the pH range typically found in the environment (pH 5–9) were considered. The second reaction considered in the assessment is photolysis, the reaction of a chemical with sunlight. Both hydrolysis and photolysis occur in air, water, and soil, while only hydrolysis was considered in sediment. The half-lives for reactive processes, if faster than removal via biodegradation, were used to assign the hazard designation by direct comparison to the DfE persistence criteria.

For the atmospheric compartment, persistence also includes the evaluation of oxidative gas-phase processes. These processes include the reaction with ozone, hydroxyl radicals, and nitrate radicals. Since the average concentration of these oxidative species in the atmosphere has been measured, the experimental or estimated rate constants were converted to, and reported as, a half-life in the assessment using standard pseudo first-order kinetics (U.S. EPA 2011f; U.S. EPA 2011d).

For inorganic compounds, an additional chemical process was considered, the potential to be reduced or oxidized (undergo a redox reaction) under environmental conditions. Redox reactions change the oxidation state of the species through the transfer of electrons to form another compound (such as the reduction of Cr(VI) to Cr(III)). A change in the oxidation state of a metal

or inorganic species can result in significant changes in the material's hazard designation. In this example, going from Cr(VI) to Cr(III) makes the compound less toxic.

### **Environmental Transport**

The persistence of a chemical substance is based on determining the importance of removal processes that may occur once a chemical enters the environment. Chemicals with a half-life of less than 60 days are expected to be at most a Moderate hazard designation for persistence. Persistence does not directly address the pathways in which a chemical substance might enter the environment (e.g., volatilization or disposal in a landfill) and focuses instead on the removal processes that are expected to occur once it is released into air, water, soil, or sediment. Similarly, the persistence assessment does not address what might happen to a chemical substance throughout its life cycle, such as disposal during incineration of consumer or commercial products. Understanding the environmental transport of a chemical substance can help identify processes relevant to environmental assessment. For example, if a chemical is toxic to benthic organisms and partitions primarily to sediment, its potential release to water should be carefully considered in the selection of alternatives.

### **Biodegradation**

In the absence of rapid hydrolysis or other chemical reactions, biodegradation is typically the primary environmental degradation process for organic compounds. Determining the importance of biodegradation is, therefore, an important component of the assessment. Biodegradation processes are divided into two types. The first is primary biodegradation, in which a chemical substance is converted to another substance. The second is ultimate biodegradation, in which a chemical is completely mineralized to small building-block components (e.g., CO<sub>2</sub> and water). DfE persistence criteria use data that are reported as percent of theoretical ultimate degradation in the guideline Ready Biodegradability test or as a half-life in other experimental studies; both of these measurements can be compared directly to the DfE criteria in 5.1.2. When considering primary degradation, the assessment process includes an evaluation of the potential for the formation of metabolites that were more persistent than the parent materials. Chemical substances that undergo rapid primary degradation but only slow ultimate biodegradation were considered to have stable metabolites. In the absence of measured data on the substance of interest, DfE evaluated the potential for biodegradation for chemicals with a MW <1,000 daltons using the EPA EPISuite<sup>TM</sup> models. EPISuite<sup>TM</sup> estimates the probability for ready biodegradation as well as the potential for primary and ultimate removal, as described in Section 5.3. A default Very High persistence hazard designation was assigned for polymers and other high MW materials with a MW >1,000 daltons, according to information contained in the literature concerning polymer assessment (Boethling and Nabholz 1997).

## **5.4 Evaluating Human Health Endpoints**

After data collection and analysis of the physical-chemical properties for the chemicals being assessed, the comparison of the data against the hazard criteria can begin. Section 5.4.1 discusses how measured data are used to make hazard designations for human health endpoints and Section 5.4.2 presents the approach for filling in data gaps to make these hazard designations.

#### **5.4.1 Endpoints Characterized and Evaluated Against Criteria Based on Measured Data**

This section provides a short description of how measured data were used to designate the level of hazard for each endpoint. As a reminder, the criteria for the hazard designations are in Table 5-2.

For acute mammalian toxicity the median lethal doses or concentrations were used to assign the hazard designation. Four levels of hazard designation have been defined ranging from Low to Very High.

For cancer, the hazard designation was contingent on the level of evidence for increased incidence of cancer, and not potency. The definitions applied in DfE criteria are based on International Agency for Research on Cancer (IARC) levels of evidence (International Agency for Research on Cancer 2006). For example, a designation of Very High concern requires that the substance be characterized as a “known or presumed human carcinogen,” whereas a designation of Low concern requires either negative studies or robust SAR conclusions. A designation of Moderate was applied as a default value when there was an absence of data suggesting High carcinogenicity, and an absence of data supporting Low carcinogenicity (i.e., a lack of negative studies or weak SAR conclusions).

Similarly, the hazard designation for mutagenicity/genotoxicity was also based on the level of evidence rather than potency. Complete data requirements for this endpoint were both gene mutation and chromosomal aberration assays. For instances of incomplete or inadequate mutagenicity/genotoxicity data, a Low hazard designation cannot be given.

For chronic endpoints, such as reproductive, developmental, neurological, and repeated dose toxicity, the hazard designation was based on potency. The evaluation considers both lowest observed adverse effect levels (LOAELs) and identification of no observed adverse effect levels (NOAELs), when available. The LOAEL and the NOAEL are experimental dose levels, and their reliability is dictated by the study design. In studies for which the lowest dose tested resulted in an adverse effect (and therefore a NOAEL was not established), and in studies for which the highest dose tested was a NOAEL, a conservative approach using professional judgment was used to address uncertainty regarding the lowest dose or exposure level that might be expected to cause a particular adverse effect. For example, in the absence of an established a NOAEL, an identified LOAEL might fall within the range of a Moderate hazard; however, it is uncertain if a lower dose, such as one that falls within the range of High hazard exists because no lower doses were tested. In such cases, professional judgment was applied to assign a hazard designation, when possible. Some degree of uncertainty was evident in results from studies in which a NOAEL may fall within one hazard range (e.g., Moderate hazard) and the identified LOAEL falls within a different hazard range (e.g., Low hazard) because the true LOAEL may fall in either category, but there were not enough experimental data points to determine the true LOAEL. Professional judgment was also applied to these cases to assign a hazard descriptor, when possible, and the rationale used was described in the assessment. Developmental neurotoxicity was considered, and was evaluated using the developmental toxicity criteria, which are more stringent than the criteria for neurotoxicity and thus designed to be more protective (U.S. EPA 2011b).

The criteria for skin and respiratory sensitization, which are immune-based responses, consider the frequency and potency of the reactions. For skin sensitization, categories were based on the weight of evidence<sup>6</sup> from traditional animal bioassays, but *in vitro* alternative studies were also considered. At this time, there are no standard test methods for respiratory sensitization; as a result, there was often no designation for this endpoint.

The evaluation of skin and eye irritation and corrosivity were based on the time to recovery.

#### **5.4.2 SAR – Application of SAR and Expert Judgment to Endpoint Criteria**

If measured data pertaining to human health criteria were not available, potential adverse effects were estimated with SAR analysis. To make these estimates, DfE relied on the expertise of scientists in EPA's New Chemicals Program (NCP) who have reviewed thousands of chemicals and associated data using these methods. SAR uses the molecular structure of a chemical to infer a physicochemical property that can be related to specific effects on human health. These correlations may be qualitative ("simple SAR") or quantitative (QSAR). Information on EPA's use of SAR analysis has been published by U.S. EPA (1994). Public access to free validated quantitative SAR models for human health endpoints is far more limited than physical-chemical properties, environmental fate parameters, or ecotoxicology. Carcinogenicity was assessed using the OncoLogic expert system that provides a qualitative result directly applicable to the DfE criteria. For other endpoints that required SAR approaches, an analog approach using expert judgment was used as discussed in Section 5.2. All estimates obtained in this project were reviewed by EPA scientists having subject matter expertise. Estimates for the other human health endpoints were based on expert judgment using an analog approach, and not through the use of computerized SAR methodologies.

#### **Carcinogenicity**

The potential for a chemical to cause cancer in humans was estimated using the OncoLogic expert system. This program uses a decision tree based on the known carcinogenicity of chemicals with similar chemical structures, information on mechanisms of action, short-term predictive tests, epidemiological studies, and expert judgment.

#### **Polymer Assessment**

Estimates for polymers were obtained using information contained in the literature concerning polymer assessment based on the MW profile (Boethling and Nabholz 1997). Those polymers with MW >1,000 were assessed using an appropriate representative structure that has a MW less than or equal to the average MW. For polymers with an average MW >1,000 daltons and a significant amount of low MW material <1,000 daltons, the low MW components were also assessed for their environmental fate and potential toxicity in order to identify any possible hazards for the most bioavailable fraction. Similarly, the presence of unreacted monomers requires that the assessment consider these components for polymers of any MW range. The

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<sup>6</sup> Generally, weight of evidence is defined as the process for characterizing the extent to which the available data support a hypothesis that an agent causes a particular effect (U.S. EPA 1999; U.S. EPA 2002; U.S. EPA 2005b).

properties for polymers with an average MW >1,000 with no low MW components were generally evaluated as a single high MW material for each of the properties described below. In general, polymers with an average MW >1,000 were not amenable to the available SAR estimation methods, and based on the SF guidance are assumed to have low to no bioavailability. Polymers with MW >1,000 that were not degradable or reactive are also typically not bioavailable. Polymers with an average MW >10,000 have potential for adverse effects due to lung overloading when respirable particles are present (less than ten microns). There may be exceptions to the rules of thumb outlined above, and as such this guidance should not be held as absolute thresholds.

Polymers and oligomers with MWs <1,000 were assessed using a representative structure for all the MW species anticipated to be present in the mixture. The procedures were essentially identical to those employed for the evaluation of impurities or byproducts in discrete chemicals, although in this case the oligomer with the highest concern was used to drive the hazard designation. Unreacted monomers, if present, were also assessed and considered in the hazard evaluation.

## **5.5 Evaluating Environmental Toxicity and Fate Endpoints**

As with endpoints previously mentioned, the preferred method for the evaluation of environmental endpoints is the use of experimental data. In their absence, the alternatives assessment uses computerized QSAR models developed by EPA for the evaluation of environmental endpoints that can be directly compared to the DfE criteria. When measured data were unavailable, the hazard designation for aquatic toxicity was estimated using EPA's ECOSAR<sup>TM</sup> software, and the persistence designation was estimated using models in EPA's EPISuite<sup>TM</sup> software. As a direct result of the design of these models and their direct application to DfE criteria, the evaluation of environmental endpoints using experimental or estimated data was discussed together in the following subsections.

### **5.5.1 Aquatic Toxicity**

For environmental toxicity, the alternatives assessment focused on the hazard designations for acute and chronic studies on freshwater species of algae, invertebrates, and fish, (often referred to as the "three surrogate species"). Aquatic toxicity values were reported in the assessment as follows:

- Acute (estimated or experimental) - LC<sub>50</sub> in mg/L
- Chronic (experimental) - No observed effect concentration (NOEC) in mg/L
- Chronic (estimated) - ChV, or the geometric mean between the NOEC and the LOEC, in mg/L

Experimental data reported in the alternatives assessment also included information on the species tested. Test data on other organisms (e.g., worms) were included in the assessment if data were readily available. These data would be evaluated using professional judgment to support hazard designations assigned using the three surrogate species; however, they were not used by themselves to assign a hazard designation, as DfE criteria are not available. Poorly soluble

substances for which the water column exposures may not be adequate to describe sediment and particulate exposures will be identified by a footnote.

If an experimental or estimated effect level exceeded the known water solubility of a chemical substance, or if the log  $K_{ow}$  exceeded the estimated ECOSAR<sup>TM</sup> cut-off values for acute and chronic endpoints (which are class specific), NES were predicted for the aquatic toxicity endpoints. NES indicates that at the highest concentration achievable, the limit of a chemical's water solubility, no adverse effects were observed (or would be expected). In these cases, a Low hazard designation was assigned. In the cases where both an estimated water solubility and ECOSAR<sup>TM</sup> estimate were used, then an additional factor of ten was applied to the water solubility before a NES designation was assigned, to account for the combined uncertainty in the model estimates.

In the case where an experimental aquatic toxicity value was significantly higher than the chemical's water solubility, it was likely the result of a poorly conducted study. In this circumstance, which is generally more frequent for formulated products or mixtures, additional details were provided in the Data Quality section to describe why the reported values could not be used to assign a hazard designation.

EPA's ECOSAR<sup>TM</sup> estimation program uses chemical structure to estimate toxicity of a chemical substance using class-specific QSARs. ECOSAR<sup>TM</sup> automatically determines all of the classes that a chemical substance may belong to and, therefore, may provide a number of different ecotoxicity estimates for some or all of the species and durations estimated. Modeled results are dependent on the functional groups present on the molecule, as well as the diversity of chemicals with experimental data that were used to build the models. However, if the chemical substance is not anticipated to lie within the domain of the class-specific estimates provided by ECOSAR, or to undergo the same mode of action of the chemicals that appear in their training sets, then the narcosis (baseline toxicity) associated with the neutral organic class will be used. Experimental log  $K_{ow}$  values were used preferentially as input into ECOSAR<sup>TM</sup>. In their absence, estimated log  $K_{ow}$  values from EPISuite<sup>TM</sup> were used. ECOSAR<sup>TM</sup> is maintained and developed as a stand-alone program, but is also accessible through the EPA EPISuite<sup>TM</sup> program after it is installed; therefore, the Estimations Program Interface (EPI) program was cited for the ECOSAR<sup>TM</sup> values in this report.

The QSARs for ECOSAR<sup>TM</sup> were built using experimental data for several chemical classes. For a chemical class to be defined within ECOSAR<sup>TM</sup>, sufficient acute experimental data were required to build a QSAR for all three species included in the model. The equations in ECOSAR are derived from surrogate species of fish, zooplankton, and phytoplankton. While these surrogate species can comprise several genera as well as families, the equations are not intended to be species-specific, but rather estimates of toxicity to the general trophic levels they represent (fish, aquatic invertebrates, and aquatic plants). There were instances, however, where sufficient experimental data were not available to build a chronic QSAR for some of the three surrogate species. When ECOSAR<sup>TM</sup> did not provide chronic estimates, the acute value (experimental or estimated) was divided by an acute to chronic ratio (ACR) to arrive at the ChV. ACRs of 10 were used for fish and daphnid, and an ACR of 4 was used for algae (Mayo-Bean, Nabholz et al. 2011).

For phosphate esters and phosphonate esters in this report, alternative predictive methodologies such as data derived acute-to-chronic ratios (ACRs) and read across to analogous substances were reported to address data gaps, using a weight of evidence approach instead of ECOSAR predictions. Many of the chemicals and chemical mixture components in this assessment are phosphate or phosphonate esters, including Diethyl bis(2-hydroxyethyl)aminomethyl-phosphonate, Emerald Innovation™ NH-1, Fyrol™ HF-5, Isopropylated triphenyl phosphate, Oligomeric ethyl ethylene phosphate, Oligomeric phosphonate polyol, Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P,P',P'-tetrakis(2-chloroethyl) ester, Tricresyl phosphate, Triphenyl phosphate, Tris (1,3-dichloro-2-propyl) phosphate, Tris (2-chloro-1-methylethyl) phosphate, Tris (2-chloroethyl) phosphate, and Tris (p-t-butylphenyl) phosphate. ECOSAR v1.11 provides estimates for these compounds based on the esters, esters (phosphate), and neutral organic classes. These compounds are not well represented by ECOSAR v1.11 esters (phosphate) QSAR, which is based on underlying Log  $K_{ow}$  methodology that does not adequately distinguish weak-to-strong esterase inhibition, resulting in low correlation of the class members. Additionally, certain modes of action have been previously associated with phosphate ester chemicals (i.e., potential for esterase inhibition and alkylation); therefore, the ECOSAR v1.11 esters and neutral organics QSARs are also not well representative of these chemicals. The ECOSAR v1.11 esters estimated values are reported in the assessment for comparative purposes.

An estimate of NES is the default value used for organics, oligomers, or non-ionic polymers with a MW >1,000 daltons in the assignment of aquatic toxicity hazard. In EPA's New Chemical program, aquatic toxicity is not predicted for chemicals with a MW >1,000 daltons, as uptake has been found to decrease exponentially with MWs >600 daltons (Nabholz, Clements et al. 1993), due to a decrease in passive absorption through respiratory membranes (Mayo-Bean, Nabholz et al. 2011). This methodology was also used in the evaluation of expandable graphite, a large, insoluble material with a MW >1,000 daltons.

### **5.5.2 Bioaccumulation**

Bioaccumulation is a process in which a chemical substance is absorbed in an organism by all routes of exposure as occurs in the natural environment (e.g., from dietary and ambient environment sources). Bioaccumulation is the net result of the competing processes; this includes uptake, metabolism, and elimination of a chemical in an organism. Bioaccumulation can be evaluated using the BAF, the steady state ratio of a chemical in an organism relative to its concentration in the ambient environment, where the organism is exposed through ingestion and direct contact. Experimental BAFs have not been widely available in the scientific literature and, as a result, experimental BCFs are more commonly used to evaluate the bioaccumulation hazard. BCFs are defined as the ratio of the concentration of a chemical in an organism to the concentration of the chemical in the organism's surroundings; BCFs are typically measured for fish (in water) using guideline studies.

Experimental BAF or BCF values can be compared directly to the DfE criteria for this endpoint to assign a hazard designation. The BCF/BAF designations range from <100 for a Low designation to >5,000 for a Very High designation (see Section 5.1.2). If experimental values were available for both of these endpoints, and the BCF and BAF were >100 (i.e., above the Low designation), the largest factor was used to assign hazard designation. If experimental BCFs



<100 were available, the estimated upper trophic BAF from EPISuite™ was used preferentially if its use resulted in a more conservative hazard designation, and if the potential for metabolism was accurately accounted for within the model estimates.

In the absence of experimental data, evaluation of bioaccumulation potential can be done using the log  $K_{ow}$  and the log octanol/air partition coefficient  $K_{oa}$ , as estimated by EPISuite™. However, analysis using  $K_{oa}$  requires the use of metabolism data for higher trophic, air breathing organisms, which can be difficult to obtain from the scientific literature and cannot be readily estimated. BAFs and BCFs from EPISuite™ were, therefore, typically used for the bioaccumulation hazard designation when experimental data were lacking. These values can be compared directly to DfE criteria, and the most conservative result was used for the hazard designation. For chemicals that had estimated bioaccumulation data, available experimental monitoring data were used to provide insight into the reliability of the model results. For example, an estimated Low bioaccumulation potential may be increased to a Moderate designation if a chemical was routinely identified in samples from higher trophic levels, or a High designation if the chemical was routinely measured in animals at the top of the food chain.

An estimate of Low is the default value used for discrete organics with a MW >1,000 daltons in the assignment of bioaccumulation hazard. This assignment is consistent with an analysis of the chemicals used in the development of the bioconcentration and bioaccumulation estimation programs in the EPISuite™ software (U.S. EPA 2011g). The training sets for these models included 527 and 421 chemicals, respectively, with a MW range 68-992 daltons (959 daltons for BAF). Given that BCF and BAF reach a maximum and then decrease with increasing log  $K_{ow}$ , a default value of Low is, in general, consistent with the limited bioavailability expected for materials with a MW >1,000 daltons. DfE uses all available well-conducted studies when evaluating bioaccumulation potential for materials with a MW >1,000, including environmental biomonitoring data on higher trophic levels.

In general, for polymers and other materials with a MW >1,000 daltons, the default bioaccumulation designation of Low was assigned, arising from their predicted limited bioavailability (Boethling and Nabholz 1997). A more detailed analysis was performed for compounds at or near this bright line cutoff, as well as for polymers with components where residuals <1,000 had the potential to be present.

### **5.5.3 Environmental Persistence**

A chemical's persistence in the environment is evaluated by determining the type and rate of potential removal processes. These removal processes were generally divided into two categories: chemical and biological. Of the chemical degradation processes, an evaluation of environmental persistence includes the reaction of a chemical with water, also known as hydrolysis, because water is ubiquitous in the environment. Hydrolysis rate constants can be obtained from the literature or estimated, and the resulting half-lives can be compared directly to DfE criteria. For commercial chemicals, hydrolysis tends to be a slower environmental removal process than biodegradation. Direct and indirect photolysis also represents other potential chemical degradation processes that are considered in the alternative assessment, and they are discussed later in this section.

Biodegradation, the most prevalent biological removal process, was divided into two types. The first is primary biodegradation, in which a chemical substance is converted to another substance through a single transformation. The second is ultimate biodegradation, in which a chemical is completely degraded to CO<sub>2</sub>, water, and mineral oxides (such as phosphates for chemicals containing phosphorus). DfE criteria utilize ultimate biodegradation preferentially for the persistence hazard designation, although primary removal rates were informative in assigning hazard designations, particularly for materials that were transformed slowly, and to a lesser extent for those that are transformed rapidly.

If ultimate biodegradation data were not available, primary removal data were used in some cases. For primary removal processes, the potential for the formation of degradation products that are more persistent than the parent compounds must be considered in the hazard designation. When present, the persistent degradation products should be evaluated for fate and toxicity. Half-life data on the persistent degradation products, if available, were used to determine the assignment for the persistence designation. In the absence of persistent degradation products, primary biodegradation half-life data were compared directly to the DfE criteria to assign a hazard designation.

Biodegradation processes can be classified as either aerobic or anaerobic. Aerobic biodegradation is an oxidative process that occurs in the presence of oxygen. Anaerobic biodegradation is a reductive process that occurs only in the absence of oxygen. Aerobic biodegradation is typically assessed for soil and water, while anaerobic biodegradation is generally assessed in sediment. For determining the persistence hazard, the importance of both aerobic and anaerobic biodegradation, as well as partitioning and transport in the environment, were considered to determine what removal processes were most likely to occur. Anaerobic degradation may use any of several electron acceptors, depending on their availability in a given environment and the prevailing redox potential ( $E_h$ ). The biodegradative populations that are dominant in a given environment vary with the conditions, and so do their biodegradative capabilities.

One aspect of the assessment is to determine the potential for removal of a chemical substance, and especially removal attributable to biodegradation within a sewage treatment plant and other environments. In this assessment, the term “ready biodegradability” refers to a chemical’s potential to undergo ultimate degradation in guideline laboratory studies. A positive result in a test for ready biodegradability can be considered as indicative of rapid and ultimate degradation in most environments, including biological sewage treatment plants. Ready tests typically include a 10-day window, beginning when the biodegradation parameter (e.g., disappearance of dissolved organic carbon from test substance, or theoretical oxygen demand) reaches 10%. The 10-day window must occur within the 28-day length of the test. If the pass level of the test (60% for oxygen demand and CO<sub>2</sub> production; 70% for dissolved organic carbon disappearance) is met in the 10-day window, the chemical received a Very Low hazard designation. Those that did not pass the 10-day window criterion but met the pass level in 28 days received a Low hazard designation. If ready biodegradability test data were available but the chemical did not meet the pass level, the chemical was evaluated based on measured data using the DfE half-life criteria (Table 5-2). These half-life criteria were also used to assign a hazard designation for non-guideline ultimate biodegradation studies reported in the scientific literature.

In the absence of a reported half-life, experimental data were also used to approximate half-life, as appropriate. For example, a chemical that undergoes <5% removal in 30 days would be expected to have a half-life >60 days, and would be assigned a High persistence concern.

When experimental data on the biodegradation of a chemical substance were not available, the potential of that substance to undergo this removal process was assessed from the results of the EPISuite™ models. These models fall into one of four classes: rapid biodegradation models based on linear and non-linear regressions that estimate the probability that a chemical substance will degrade fast; expert survey models that estimated the rate of ultimate and primary biodegradation using semi-quantitative methods; probability of ready biodegradability in the OECD 301C test; and probability of rapid biodegradation under methanogenic anaerobic conditions. Each of these is discussed in the following paragraphs.

The first models (Biowin 5 and 6) used in the screening assessment estimated ready biodegradability in the OECD 301C test, and are also known as Japanese Ministry of International Trade and Industry (MITI) models. These models provided the probability that a material passes this standardized test. Those chemicals that were estimated to pass the ready biodegradability test received a Low persistence designation. If a chemical was not estimated to pass the MITI test, the results of the other EPISuite™ biodegradation models were used.

The rapid biodegradation potential models within EPISuite™ (Biowin 1 and 2) were useful for determining if a chemical substance was expected to biodegrade quickly in the environment. If a chemical was likely to biodegrade quickly, it was generally assigned a Low hazard designation for persistence. The results of the estimates from these models may be used in concert with the semi-quantitative output from a second set of models, which include ultimate and primary biodegradation survey models (Biowin 3 and 4) for evaluating persistence. These models provide a numeric result, ranging from 1 to 5, which relates to the amount of time required for complete ultimate degradation (Biowin 3) and removal of the parent substance by primary degradation (Biowin 4) of the test compound. The numeric result from Biowin 3 is converted to an estimated half-life for removal that can be compared directly to DfE criteria. If results from different models (other than the MITI models) led to a different hazard designation, then the ultimate biodegradation model results were used preferentially. If the transport properties indicate the potential for the material to partition to sediment, an anoxic compartment, then the results of the anaerobic probability model (Biowin 7) are also evaluated.

Half-lives for hydrolysis from experimental studies or EPISuite™ estimates were used in preference to biodegradation data when they suggested that hydrolysis is a more rapid removal process. Hydrolysis half-lives were compared directly to DfE criteria to assign the persistence designation. Similar to primary biodegradation, breakdown products resulting from hydrolysis were evaluated for fate and toxicity when they were expected to be more persistent than the parent compound.

Photolysis may also be an important environmental removal process. In general, environmental removal rates from photolysis do not compete with biodegradation or hydrolysis, although there are exceptions, such as iodides. Photolysis may be an important removal process for chemicals

that were not bioavailable because of their limited water solubility. Estimation methods for photolysis rates were not available using computerized SAR tools. If experimental or suitable analog data were available, the rate of photolysis was evaluated relative to other removal processes.

When evaluating the environmental persistence designation, it should be noted that chemicals with a High or Very High designation can degrade over time, although this process may occur at a very slow rate. As a result, a Very High designation may have been assigned if persistent degradates were expected to be produced, even at a very slow rate, in the absence of experimental biodegradation data for the parent substance.

Chemicals that contain a metal are assigned a High persistence designation in DfE alternatives assessments, as these inorganic moieties are recalcitrant. In this instance, an ‘R’ footnote is added to the hazard summary table to indicate that the persistence potential was based on the presence of a recalcitrant inorganic moiety. The assessment process also includes the evaluation of the potential chemical reactions of metal-containing and inorganic moieties to determine if they were potentially transformed to more or less hazardous forms. However, no alternatives that contain metals were evaluated in this updated assessment.

Polymers with a MW >1,000 generally received a Very High persistence designation due to their lack of bioavailability.

## 5.6 Endocrine Activity

Chemicals included in DfE alternatives assessments are screened for potential endocrine activity, consistent with the DfE Alternatives Assessment Criteria. **Endocrine activity** refers to a change in endocrine homeostasis caused by a chemical or other stressor. An **endocrine disruptor** is an external agent that interferes in some way with the role of natural hormones in the body, in a manner causing adverse effects. Relevant data are summarized in the hazard assessments for each chemical, located in Section 7. Data on endocrine activity were available for twelve of the chemicals included in this report. For chemicals without available data on endocrine activity, this was acknowledged with a “no data located” statement. When endocrine activity data were available, the data are summarized as a narrative. A unique hazard designation of Low, Moderate or High is not provided for this endpoint in Table 5-2, for reasons discussed below.

The document *Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis* describes EPA’s activities regarding the evaluation of endocrine disruption (U.S. EPA 1997). This report was requested by the Science Policy Council and prepared by EPA’s Risk Assessment Forum. This report states that “Based on the current state of the science, the Agency does not consider endocrine disruption to be an adverse endpoint per se, but rather to be a mode or mechanism of action potentially leading to other outcomes, for example, carcinogenic, reproductive or developmental effects, routinely considered in reaching regulatory decisions” (U.S. EPA 1997). The report also states that “Evidence of endocrine disruption alone can influence priority setting for further testing and the assessment of results of this testing could lead to regulatory action if adverse effects are shown to occur” (U.S. EPA 1997).

The 1996 Food Quality Protection Act (FQPA) directed EPA to develop a scientifically validated screening program to determine whether certain substances may cause hormonal effects in humans. In response, EPA established the Endocrine Disruptor Screening Program (EDSP) (U.S. EPA 2012b). The EDSP is developing requirements for the screening and testing of thousands of chemicals for their potential to affect the endocrine system. When complete, EPA will use these screening and testing approaches to set priorities and conduct further testing, when warranted. The science related to measuring and demonstrating endocrine disruption is relatively new, and validated testing methods at EPA are still being developed.

The EDSP proposes a two-tiered approach that includes initial screening followed by more in-depth testing, when warranted (U.S. EPA 2011a). The Tier 1 screening battery is intended to identify chemicals with the potential to interact with the estrogen, androgen, or thyroid hormone systems through any of several recognized modes of action. Positive findings for Tier 1 tests identify the potential for an interaction with endocrine systems, but do not fully characterize the nature of possible effects in whole animals. Tier 2 testing is intended to confirm, characterize, and quantify the effects for chemicals that interact with estrogen, androgen, and thyroid hormone systems. These test methods must undergo a four-stage validation process (protocol development, optimization/prevalidation, validation, and peer-review) prior to regulatory acceptance and implementation. Validation is ongoing for Tier 1 and Tier 2 methods<sup>7</sup>. Once validated test methods have been established for screening and testing of potential endocrine disruptors, guidance must be developed for interpretation of these test results using an overall weight-of-evidence characterization.

To assess the data on endocrine activity, DfE applies the weight of evidence approach developed by the EDSP (U.S. EPA 2011c). This process integrates and evaluates data, and always relies on professional judgment (U.S. EPA 2011c). To evaluate endocrine activity with this weight of evidence approach, DfE examined multiple lines of evidence (when available) and considered the nature of the effects within and across studies, including number, type, and severity/magnitude of effects, conditions under which effects occurred (e.g., dose, route, duration), consistency, pattern, range, and interrelationships of effects observed within and among studies, species, strains, and sexes, strengths and limitations of the *in vitro* and *in vivo* information, and biological plausibility of the potential for an interaction with the endocrine, androgen, or thyroid hormonal pathways.

Most test data for chemicals in this report consist of *in vitro* assays, but results of *in vitro* assays alone were not generally expected to provide a sufficient basis to support a hazard designation for endocrine disruption. EPA expects that *in vivo* evidence would typically be given greater overall influence in the weight of evidence evaluation than *in vitro* findings, because of the inherent limitations of such assays. Although *in vitro* assays can provide insight into the mode of action, they have limited ability to account for normal metabolic activation and clearance of the compound, as well as normal intact physiological conditions (e.g., the ability of an animal to compensate for endocrine alterations).

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<sup>7</sup> Information on the status of assay development and validation efforts for each assay in EPA's EDSP can be found at: <http://www.epa.gov/oscpmont/oscpendo/pubs/assayvalidation/status.htm>

As described in the DfE Alternatives Assessment Criteria, endocrine activity was summarized in a narrative, rather than by High, Moderate or Low hazard designation. The endocrine activity summaries can be found in the hazard profiles. This is an appropriate approach because there is no consensus on what constitutes high, moderate or low concern for this endpoint. The summary of endocrine activity largely relies on representative studies and expert review summaries.

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