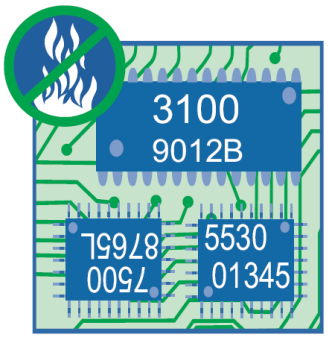
United States Environmental Protection Agency

Design for the Environment U.S. EPA

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS



UPDATED DRAFT REPORT

December 2014

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This document addresses environmental and human health issues associated with the production, use, and disposal of Flame Resistant 4 (FR-4) printed circuit boards using current and emerging flame retardant technologies. The report provides an evaluation of the environmental and human health hazards associated with flame-retardant chemicals during manufacturing and use of the FR-4 boards and a discussion and identification of end of life issues. The report also presents experimental data from the investigation of the thermal breakdown of boards and the by-products formed under different combustion and pyrolysis conditions. These data may provide further insight into any issues that may arise, including possible end of life disposal issues.

For More Information

To learn more about the Design for the Environment (DfE) Flame Retardant in Printed Circuit Board Partnership or the DfE Program, please visit the DfE Program website at: www.epa.gov/dfe.

To obtain copies of DfE Program technical reports, pollution prevention case studies, and project summaries, please contact:

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This document was produced as part of the DfE Flame Retardants in Printed Circuit Boards Partnership under the direction of the partnership's steering committee, including: Ray Dawson, BSEF; Lauren Heine, Clean Production Action; Art Fong, IBM; Steve Tisdale, Intel; Fern Abrams, IPC; Mark Buczek, Supresta; Adrian Beard, Clariant and HFFREC; and Clive Davies, Kathleen Vokes, and Melanie Adams, U.S. EPA DfE. The partnership's technical committee also provided technical input, research, and other support. This project could not have been completed without their participation.

The Flame Retardants in Printed Circuit Boards Partnership includes representatives from the following organizations:


isola


lenovo


WORLDWIDE PARTNER


NAN YA


PURDUE
UNIVERSITY


supreSTA
BUILT-IN DEFENSE


TTM Technologies
Time-To-Market Interconnect Solutions


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Executive Summary

Background

In 2006, U.S. Environmental Protection Agency (EPA)'s Design for the Environment (DfE) Program and the electronics industry convened a multi-stakeholder partnership to identify and evaluate commercially available flame retardants in Flame Resistant 4 (FR-4) printed circuit boards (PCBs). The majority of PCBs are classified as FR-4, indicating that they meet certain performance criteria, as well as the V0 requirements of the UL (Underwriters Laboratories) 94 flammability testing standard. Over 90 percent of FR-4 PCBs used epoxy resins containing the reactive flame retardant tetrabromobisphenol A (TBBPA) to meet flammability standards when the partnership was convened. Because little information existed concerning the potential environmental and human health impacts of the materials being developed as alternatives to the brominated epoxy resins being used in PCBs, the partnership developed information to improve understanding of new and current materials that can be used to meet the flammability requirements. This information was published in a 2008 draft report titled *Partnership to Evaluate Flame Retardants in Printed Circuit Boards*. In addition to this written draft report, experimental testing was conducted as part of this project to learn more about the combustion by-products released during end-of-life disposal processes of PCBs.

In this version of the report, the hazard profiles in Chapter 4 and the accompanying methodology were updated to ensure that most recent information was used for hazard assessment. Each human health and environmental endpoint was evaluated using the 2011 DfE Criteria for Hazard Assessment. The information on the physical-chemical and fate properties of the alternatives in Table 5-2 of Chapter 5 and text in Chapter 7 were also updated. Chapter 6 was revised to describe the results of the combustion testing experiments. Additional edits have been made throughout the report as appropriate in response to public comments received on the 2008 draft report.

Goal of the Partnership and This Report

The partnership, which includes members of the electronics industry, flame retardants industry, environmental groups, academia, and others, developed the information in the report *Partnership to Evaluate Flame Retardants in Printed Circuit Boards* to advance understanding of the human health and environmental impacts of conventional and new flame-retardant materials that can provide fire safety for PCBs. Participation of a diverse group of stakeholders has been critical to developing the information for this partnership. The multi-stakeholder nature of the partnership led to a report that takes into consideration many diverse viewpoints, making the project richer both in approach and outcome.

This partnership report provides objective information that will help members of the electronics industry more efficiently factor human health and environmental considerations into decision-making when selecting flame retardants for PCB applications. This report can also serve as a step toward developing a more comprehensive understanding of the human health and environmental implications of flame-retardant chemicals by noting gaps in the existing human health and environmental literature. For example, future studies could be directed at key human health and environmental toxicological endpoints that are not yet adequately characterized. Additional

testing could also be directed at improving understanding of fate and transport of flame-retardant chemicals during the most relevant life-cycle phases.

The objective of the partnership is not to recommend a single best flame retardant for PCB applications or to rank the evaluated flame retardants. In addition to information on environmental and human health impacts, performance, and cost are critical in the final decision. The information in this report could be used in decision-making frameworks that address these critical elements. When using these flame-retardant chemical profiles, it is important to consider other life-cycle impacts, including exposure considerations.

Fire Safety for Printed Circuit Boards (PCBs) and Flame Retardants Evaluated

PCBs are commonly found in consumer and industrial electronic products, including computers and mobile phones. Manufacturers commonly produce PCBs with flame-retardant chemicals to help ensure fire safety. In 2008, the majority of PCBs produced worldwide met the V0 requirements of the UL 94 fire safety standard. This standard was usually achieved through the use of brominated epoxy resins in which the reactive flame retardant TBBPA forms part of the polymeric backbone of the resin. These UL 94 V0 compliant boards are referred to as FR-4 boards, which must meet performance specifications as well as the fire safety standard. While alternative flame-retardant materials are used in only a small percentage of FR-4 boards, in 2008, the use of alternatives was increasing and additional flame-retardant chemicals and laminate materials were under development. In 2008, TBBPA was used to make the epoxy resin base material in more than 90 percent of FR-4 boards while alternative flame-retardant materials were used in only 3 to 5 percent of FR-4 boards.

The partnership originally evaluated nine commercially available flame retardants or resins for FR-4 laminate materials for PCBs: TBBPA, DOPO, Fyrol PMP, aluminum hydroxide, Exolit OP 930, Melapur 200, silicon dioxide (amorphous and crystalline), and magnesium hydroxide. Three reaction products of epoxy resin with flame retardants (TBBPA, DOPO, and Fyrol PMP) were also evaluated for a total of 12 hazard profiles. These chemicals were identified through market research and consultation with industry and iNEMI (the International Electronics Manufacturing Initiative) as potentially viable options for PCBs. The reaction products of TBBPA, DOPO, Fyrol PMP, and other reactive flame retardants are present during the manufacturing process, and trace quantities may be locked in the PCB polymer matrix. Chemical components making up less than 1 percent by weight of the flame-retardant formulation were not considered in this assessment.

For this updated report, ten flame-retardant chemicals and resins for FR-4 laminate materials for PCBs were evaluated. One of the alternatives from the 2008 draft report – "reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin" – was not reassessed in the updated Chapter 4 because the product is not known to be on the market. In the 2008 draft report, there were two profiles for silicon dioxide – amorphous and crystalline; for this update, the two were combined into one profile that accounts for the differences between the two forms. The ten revised hazard profiles and their accompanying methodology are located in the updated Chapter 4 of the alternatives assessment report. A summary of the hazard assessment results by chemical group are summarized in this updated executive summary.

Hazard Assessment Results

The level of available human health and environmental information varies widely by flame-retardant chemical. Little information exists concerning many of the alternative flame-retardant materials included in this report. TBBPA and silicon dioxide are more fully characterized. To help address this discrepancy, and to increase the usefulness of this report, EPA used the tools and expertise developed for the New Chemicals Program to estimate the potential impacts of flame retardants when no experimental data were available.

Hazard profiles for the **reactive flame retardant alternatives** TBBPA, DOPO, and Fyrol PMP vary; all three have High to Very High persistence. TBBPA is relatively well characterized with empirical data while DOPO and Fyrol PMP have a limited data set and therefore many hazard designations based on analogs, structural alerts, or estimation models. The primary hazard for TBBPA is aquatic toxicity (High to Very High). TBBPA has Moderate potential for bioaccumulation based on measured bioconcentration and estimated bioaccumulation factors. Human health hazard designations for TBBPA are Low to Moderate; Moderate designations were determined for carcinogenicity, developmental toxicity, and eye irritation. Comparatively, DOPO has Low hazard for acute
aquatic toxicity and bioaccumulation potential but similar estimated hazards for carcinogenicity, developmental toxicity, neurotoxicity, and eye irritation. DOPO is estimated to have Low bioaccumulation potential due to hydrolysis in aqueous conditions. Fyrol PMP, with the least amount of empirical data, has potential for Low to Moderate human health effects and High aquatic toxicity. Fyrol PMP also has High potential for bioaccumulation based on presence of low molecular weight oligomers.

The **reactive flame retardant resins** D.E.R. 500 Series (TBBPA-based resin) and Dow XZ-92547 (DOPO-based resin) are poorly characterized. The hazard profiles for these alternatives identify Low acute mammalian toxicity. A High skin sensitization designation was assigned based on empirical data and Moderate respiratory sensitization was estimated for Dow XZ-92547. Moderate hazard was estimated for carcinogenicity, genotoxicity, reproductive toxicity, developmental effects, neurotoxicity, and repeated dose toxicity. Acute and chronic aquatic toxicity are estimated to be Low for D.E.R. 500 Series; chronic aquatic toxicity is estimated to be High for Dow XZ-92547. Bioaccumulation potential is estimated High and persistence estimated to be Very High for both reactive flame retardant resins.

The **additive flame retardant alternatives** aluminum diethylphosphinate, aluminum hydroxide, magnesium hydroxide, melamine polyphosphate, and silicon dioxide have varied hazard designations for human health effects. The majority of the endpoints range from Very Low to Moderate hazard with the exception of High repeated dose toxicity for silicon dioxide, which is based upon inhalation of particles less than 10 μm in size. Aluminum diethylphosphinate has Moderate aquatic toxicity hazard while the other four additive flame retardants have Low designations for these endpoints. Persistence is expected to be High for all five of the additive flame retardant alternatives and bioaccumulation potential is expected to be Low. The four additive flame retardant alternatives that contain a metal (aluminum diethylphosphinate, aluminum hydroxide, magnesium hydroxide, and silicon dioxide) were assigned High persistence designations because these inorganic moieties are recalcitrant.

A hazard comparison summary table (presented below as Table ES-1 and Table ES-2) is also presented in Chapter 4. The tables show relative hazard levels for eleven human health endpoints, two aquatic toxicity endpoints, and two environmental fate endpoints. The tables also highlight exposure considerations through the chemical life cycle. Selected flame retardants are presented according to their reactive or additive nature. An explanation of EPA's chemical assessment methodology and more detailed characteristics of the chemicals in each formulation are presented in Chapter 4.

Life-Cycle Thinking and Exposure Considerations

In addition to evaluating chemical hazards, this partnership agreed it was important to apply life-cycle thinking to more fully understand the potential human health and environmental impacts of evaluated flame retardants. Human health and environmental impacts can occur throughout the life cycle: from raw material extraction and chemical manufacturing, to laminate, PCB, and electronic product manufacturing, to product use, and finally to the end of life of the material or product. Factors such as occupational best practices and raw material extraction and subsequent flame-retardant and laminate manufacturing, together with the physical and chemical properties of the flame retardants, can serve as indicators of a chemical's likelihood to pose human health and environmental exposure concerns. During later stages of the life cycle, from PCB manufacturing to end-of-life, human health and environmental exposure potential is highly dependent upon whether the flame retardant was incorporated additively or reactively into the resin system. Chapter 5 explores the exposure considerations of these flame retardants and other life-cycle considerations. The detailed chemical assessments in this report are focused only on the flame-retardant chemicals. Other chemicals, such as feedstocks used to make the flame retardants; chemicals used in manufacturing resins, laminate materials, and PCBs; and degradation products and combustion by-products are only mentioned in the process descriptions.

Combustion Testing Results

As part of this life-cycle thinking, the partnership decided that experimental testing of FR-4 laminates and PCB materials was necessary to better understand the potential by-products during thermal end-of-life processes. The combustion by-products of four epoxy laminates alone and with PCB components added were identified and compared. The four laminates tested were: a brominated flame retardant epoxy laminate (BFR), an additive phosphorus-based flame retardant epoxy laminate (PFR1), a reactive phosphorus-based flame retardant epoxy laminate (PFR2), and a non-flame retardant epoxy laminate (NFR). PCB components designed for conventional boards were provided by Seagate and combined with the laminates as homogeneous powders to simulate a circuit board. A standard halogenated component (SH) blend and a low-halogen component (LH) blend were created and combusted with the various laminates. The two end-of-life processes simulated by a cone calorimeter in this testing were open burning (50 kW/m^2 heat flux) and incineration (100 kW/m^2 heat flux). Halogenated dioxins and furans as well as polyaromatic hydrocarbons (PAHs) emitted during combustion were measured using gas chromatography-mass spectrometry. Cone calorimetry data on CO, CO_2, particulate matter, smoke, and heat release were also recorded. The results of the combustion testing, completed in 2012, are summarized here. A more detailed description of the testing methods, results, and conclusions can be found in Chapter 6 with full study reports in the Appendices.

Analysis of halogenated dioxins and furans was conducted only for the BFRs because initial testing indicated that PFR1 and PFR2 contained low levels of bromine and therefore would not generate detectable levels of polybrominated dibenzo-p-dioxins/furans (PBDD/Fs). Detectable levels of PBDD/Fs were emitted for all BFRs combusted. For the BFRs without components, nearly 40 percent more PBDD/F emissions were generated in open burn conditions compared to incineration conditions. PBDD/Fs were detected in the BFRs containing low-halogen components but could not be quantitated in the samples containing standard halogen components due to significant interference with the standard. Polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) were quantified in the initial testing but could not be quantified in the final studies due to an ineffective quality control standard.

PAH emissions were measured and detected in all laminate types. Of the laminates without components, BFR emitted over three times the amount of PAHs of PFR1 in incineration conditions; BFRs emitted almost three times more PAHs than PFR1 and almost two times more PAHs than PFR2 in open burn conditions. BFR emitted over eight times more PAHs than NFR in open burn conditions, while PFR1 and PFR2 emitted nearly three times and five times the PAHs of the NFR, respectively. In incineration conditions, BFR1 emitted over three times the PAHs of PFR1. Of the samples with standard halogen components in open burn conditions, BFR generated nearly twice the amount of PAHs compared to PFR2 and PFR1; a similar emissions trend was observed for the samples containing low-halogen components.

Data on smoke, particulate matter, CO and CO_2 releases, and heat release were collected for all laminate types. Smoke release was nearly twice as high for BFRs compared to PFR1 and PFR2 for laminates without components in both combustion scenarios. A similar trend was observed for smoke release from laminates with standard halogen components. Particulate matter emissions for PFR1 without components were nearly twice that of NFR in open burn conditions. Of the samples containing standard halogen components, BFRs emitted over 25 percent more particulate matter than PFR2; BFRs emitted over 50 percent more particulate matter than PFR2 in samples containing low-halogen components. However, particulate matter trends did not always align with smoke release emissions. While differences in CO release between samples were negligible, CO_2 emissions varied depending on laminate type. Heat release results showed flame retardant laminates to have lower peak heat releases compared to the non-flame retardant laminates in open burn scenarios. In incineration conditions, the BFRs lowered heat release compared to the NFRs. PFR1 emitted heat at levels about equal or slightly higher than the NFRs; heat release was not measured for PFR2 in incineration conditions.

Selecting Flame Retardants for PCBs

The partnership recognizes that the human health and environmental impacts are important factors in selecting a flame-retardant chemical or formulation to provide fire safety in a PCB. However, the partnership also believes other factors are important, such as flame retardant effectiveness, electrical and mechanical performance, reliability, cost, and impacts on end-of-life emissions. These factors are discussed as considerations for selecting flame retardants in Chapter 7. While the report focuses on human health and environmental attributes of each flame-retardant chemical, it is important to note that many of these flame-retardant chemicals must be used together in different combinations to meet the performance specifications. It is also important to note that performance requirements will vary depending on the use of the PCB. Performance testing for commercially available halogen-free flame-retardant materials to determine their key

electrical and mechanical properties has been the focus of several separate but complementary projects conducted by iNEMI. This partnership worked closely with iNEMI to develop this alternatives assessment, as well as the High Density Packaging User Group (HDPUG). HDPUG completed a project in 2011 to build a database of existing information on halogen-free materials, including halogen-free flame retardants – both commercially available and in research and development.[1]

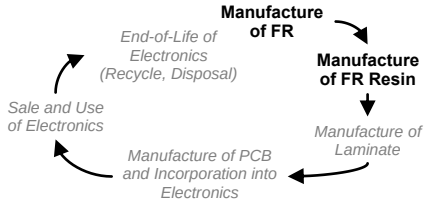
[1] http://hdpug.org/content/completed-projects#HalogenFree

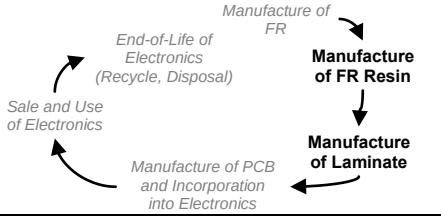
ES-1. Screening Level Hazard Summary for Reactive Flame-Retardant Chemicals & Resins

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

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

Chemical (for full chemical name and relevant trade names see the individual profiles in Section 4.9)	**CASRN**	**Human Health Effects**										**Aquatic Toxicity**		**Environ-mental Fate**		**Exposure Considerations**
		Acute Toxicity	**Carcinogenicity**	**Genotoxicity**	**Reproductive**	**Developmental**	**Neurological**	**Repeated Dose**	**Skin Sensitization**	**Respiratory Sensitization**	**Eye Irritation**	**Dermal Irritation**	**Acute**	**Chronic**	**Persistence**	**Bioaccumulation**	**Availability of flame retardants throughout the life cycle for reactive and additive flame-retardant chemicals and resins**
Reactive Flame-Retardant Chemicals																
Tetrabromobisphenol A	79-94-7	L	M	L	L♦	M	L	L	L♦		M	L♦	VH	H	H	M
DOPO	35948-25-5	L	*M*	L	*L*[§]	*M*	*M*	L	M		M	VL	L	*M*	*H*	*L*
Fyrol PMP	63747-58-0	L	*L*[§]	*L*[§]	*M*[§]	*M*[§]	*M*[§]	*M*[§]	L		L	L	*H*[‡]	*H*[‡]	*VH*	*H*[‡]
Reactive Flame-Retardant Resins																
D.E.R. 500 Series[¥]	26265-08-7	*L*	*M*	*M*	*M*	*M*	*M*	*M*	H		*M*[‡]	*M*[‡]	*L*	*L*	*VH*	*H*[‡]
Dow XZ-92547[¥]	Confidential	L	*M*[‡]	*M*[§]	*M*[‡]	*M*[‡]	*M*[‡]	*M*[‡]	H	*M*[‡]	VL	L	*L*	*H*	*VH*	*H*[‡]



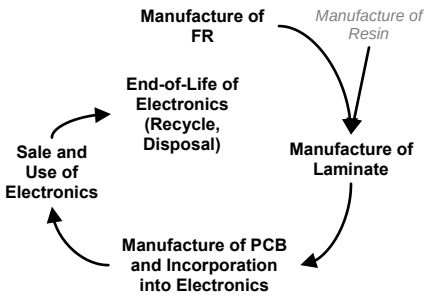


ES-2. Screening Level Hazard Summary for Additive Flame-Retardant Chemicals

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[R] Recalcitrant: Substance is comprised of metallic species (or metalloids) that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions. [§] Based on analogy to experimental data for a structurally similar compound. [¤]Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter. [^] Depending on the grade or purity of amorphous silicon dioxide commercial products, the crystalline form of silicon dioxide may be present. The hazard designations for crystalline silicon dioxide differ from those of amorphous silicon dioxide, as follows: VERY HIGH (experimental) for carcinogenicity; HIGH (experimental) genotoxicity; MODERATE (experimental) for acute toxicity and eye irritation. [¥] 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 4.9)	CASRN	Human Health Effects											Aquatic Toxicity		Environ-mental Fate		Exposure Considerations
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation	Availability of flame retardants throughout the life cycle for reactive and additive flame-retardant chemicals and resins
Additive Flame-Retardant Chemicals																	
Aluminum Diethylphosphinate[¥]	225789-38-8	L	*L*[§]	L	L	*M*[§]	*M*[§]	*M*[§]	L		L	VL	M	M	*H*[R]	*L*	
Aluminum Hydroxide[¥]	21645-51-2	L	*L*[§]	L	*L*[§]	L	M	*M*[§]	L		VL	VL	L	L	*H*[R]	*L*	
Magnesium Hydroxide[¥]	1309-42-8	L	L	L	L	L	*L*	L	M		M	L	*L*	*L*	*H*[R]	*L*	
Melamine Polyphosphate[1¥]	15541-60-3	L	*M*	*M*	*H*	*M*	*M*	*M*	*L*		L	VL	L	L	*H*	*L*	
Silicon Dioxide (amorphous)	7631-86-9	L[^]	L[^]	L[^]	L	L	*L*[§]	H[¤]	L		L[^]	VL	L	*L*	*H*[R]	*L*	



[1] Hazard designations are based upon the component of the salt with the highest hazard designation, including the corresponding free acid or base.

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List of Acronyms and Abbreviations

ACR	Acute to chronic ratio
AIM	Analog Identification Methodology
ATH	Aluminum trihydroxide (a.k.a. Alumina trihydrate)
BAF	Bioaccumulation Factor
BAN	Basel Action Network
BCF	Bioconcentration factor
BFR	Brominated flame retardant epoxy laminate
BPA	Bisphenol A
BSEF	Bromine Science and Environmental Forum
CCL	Copper clad laminate
ChV	Chronic value
DfE	Design for the Environment
Dicy	Dicyandiamide
EASE	Estimation and Assessment of Substance Exposure
ECOSAR	EPA's Ecological Structure Activity Relationships estimation program
EDSP	Endocrine Disruptor Screening Program
EETD	Economics, Exposure, and Technology Division
EHS	Environmental, health, and safety
EMT	Environmental Monitoring Technologies, Inc.
EPA	U.S Environmental Protection Agency
EPIWIN	Estimations Program Interface for Windows
EU	European Union
E-waste	Electronic waste
FR-4	Flame Resistant 4
GHS	Globally Harmonized System of Classification and Labeling of Chemicals
GS-MS	Gas chromatography-mass spectrometry
HDPUG	High Density Packaging User Group
HPV	High Production Volume
HSDB	Hazardous Substances Data Bank
HSE	Health and Safety Executive
IC2	Interstate Chemicals Clearinghouse
iNEMI	International Electronics Manufacturing Initiative
IRIS	Integrated Risk Information System
ISO	International Organization for Standardization
K_{oc}	Sediment/soil adsorption/desorption coefficient
K_{ow}	Octanol/water partition coefficient
LER	Liquid epoxy resin
LFL	Lower limit of flammability
LH	Low-halogen components
LOAEL	Lowest observed adverse effect level
LOEC	Lowest observed effect concentration
MITI	Japanese Ministry of International Trade and Industry
MW	Molecular weight
NES	No effects at saturation

NFR	Non-flame retardant laminate
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration
OECD	Organisation for Economic Cooperation and Development
OPPT	Office of Pollution Prevention and Toxics
ORD	Office of Research and Development
P2	Pollution prevention
PAH	Polycyclic aromatic hydrocarbon
PBDD/Fs	Polybrominated dibenzo-p-dioxins/furans
PCB	Printed circuit board
PCDD/Fs	Polychlorinated dibenzo-p-dioxins/furans
PEC	Predicted environmental concentration
PFR1	Additive phosphorus-based flame retardant epoxy laminate
PFR2	Reactive phosphorus-based flame retardant epoxy laminate
Prepreg	Pre-impregnated material
PTFE	Polytetrafluoroethylene
QSAR	Quantitative structure activity relationship
SAR	Structure activity relationship
SF	Sustainable Futures
SH	Standard halogen components
SMILES	Simplified molecular input line entry specification
SVTC	Silicon Valley Toxics Coalition
TBBPA	Tetrabromobisphenol A
T_d	Decomposition temperature
T_g	Transition temperature
TSCA	Toxic Substances Control Act
UDRI	University of Dayton Research Institute
UFL	Upper limit of flammability
UK	United Kingdom
UL	Underwriters Laboratories
VECAP	Voluntary Emissions Control Action Programme
XRF	X-ray fluorescence

1 Introduction

The electronics industry engaged in a multi-stakeholder partnership with the U.S. Environmental Protection Agency (EPA)'s Design for the Environment (DfE) Program to identify and evaluate commercially available flame retardants and their environmental, human health and safety, and environmental fate aspects in Flame Resistant 4 (FR-4) printed circuit boards (PCBs). The majority of PCBs are classified as FR-4, indicating that they meet certain performance criteria, as well as the V0 requirements of the UL (Underwriters Laboratories) 94 flammability testing standard.[2] For more than 90 percent of FR-4 PCBs, the UL 94 V0 requirement is met by the use of epoxy resins in which the reactive flame retardant tetrabromobisphenol A (TBBPA) forms part of the polymeric backbone of the resin.

As of 2008, alternative flame-retardant materials were used in only 3 to 5 percent of FR-4 boards, but additional alternative flame-retardant materials are under development. Little information existed at the time the partnership was convened concerning the potential environmental and human health impacts of the materials that are being developed as alternatives to the brominated epoxy resins. Environmental and human health impacts can occur throughout the life cycle of a material, from development and manufacture, through product use, and finally at the end of life of the material or product. In addition to understanding the potential environmental and human health hazards associated with the reasonably anticipated use and disposal of flame-retardant chemicals, stakeholders have expressed a particular interest in understanding the combustion products that could be formed during certain end-of-life scenarios.

A risk assessment conducted in 2006 by the European Union did not find significant human health risk associated with reacted TBBPA in PCBs.[3] However, the potential environmental and health impacts of exported electronic waste (e-waste) are not fully understood. A large percentage of e-waste is sent to landfills or recycled through smelting to recover metals. An unknown portion of the waste is recycled under unregulated conditions in certain developing countries, and the health implications of such practices are of concern.

This report aims to increase understanding of the potential environmental and human health impacts of PCBs throughout their life cycle. Information generated from this partnership will contribute to more informed decisions concerning the selection and use of flame-retardant materials and technologies and the disposal and recycling of e-waste.

1.1 Purpose of the Flame Retardant Alternatives Assessment

The partnership committee identified the overall purpose of this assessment as follows:

[2] FR-4 refers to the base material of the printed circuit board; namely, a composite of an epoxy resin reinforced with a woven fiberglass mat. UL 94 is an Underwriters Laboratories standard for flammability of plastic materials. Within UL 94, V0 classification entails one of the highest requirements.

[3] The EU results, while noteworthy, will not form the basis of this assessment, but rather should be viewed in conjunction with the independent conclusions drawn in this assessment.

- To identify and evaluate current and alternative flame retardants and their environmental, human health and safety, and environmental fate aspects in FR-4 PCBs.

- To allow industry and other stakeholders to consider environmental and human health impacts along with cost and performance of circuit boards as they evaluate alternative materials and technologies.

1.2 Scope of the Flame Retardant Alternatives Assessment

The partnership will incorporate life-cycle thinking into the project as it explores the potential hazards associated with flame retardants and potential exposures throughout the life cycle of flame retardants used in FR-4 PCBs. While the report focuses on flame retardants used in FR-4 PCBs, these flame retardants may also be applicable in a wide range of PCBs constructed of woven fiberglass reinforced with thermoset resin.

As appropriate, the scope will include aspects of the life cycle where public and occupational exposures could occur. For example, consideration of exposures from open burning or incineration at the end of life will be included, as will exposures from manufacturing and use.

The following investigations were considered within the scope of the project:

- An environmental, health, and safety (EHS) assessment of commercially available flame-retardant chemicals and fillers for FR-4 laminate materials;

- An assessment of environmental and human health endpoints (environmental endpoints include ecotoxicity, fate, and transport);

- A review of potential life-cycle concerns; and

- Combustion testing to compare the potential by-products of concern from commercially available FR-4 laminates and PCB materials during thermal end-of-life processes, including open burning and incineration.

The project's scope will be limited to flame-retardant chemicals used in bare (i.e., unpopulated) FR-4 PCBs. Other elements of PCBs (such as solder and casings) and chemicals in components often attached to PCBs to make an electronic assembly (such as cables, capacitors, connectors, and integrated circuits) will not be assessed.

The report is intended to provide information that will allow industry and other stakeholders to evaluate alternatives for flame retardants in PCBs. The report is organized as follows:

- *Chapter 1 (Introduction):* This chapter provides background to the Flame Retardants in Printed Circuit Boards partnership project including the purpose and scope of the partnership and of this report.

- *Chapter 2 (FR-4 Laminates):* This chapter describes the characteristics, market for, and manufacturing process of FR-4 laminates and investigates possible next generation developments.

- *Chapter 3 (Chemical Flame Retardants for FR-4 Laminates):* This chapter describes chemical flame retardants generally, as well as those specific flame retardants used in FR-4 laminates. The next generation of flame-retardant chemicals is also discussed.

- *Chapter 4 (Hazard Evaluation of Flame Retardants for Printed Circuit Boards):* This chapter explains the chemical assessment methodology used in this report and summarizes the assessment of hazards associated with individual chemicals.

- *Chapter 5 (Potential Exposure to Flame Retardants and Other Life-cycle Considerations):* This chapter discusses reasonably anticipated exposure concerns and identifies potential exposure pathways and routes associated with flame-retardant chemicals during each stage of their life cycle.

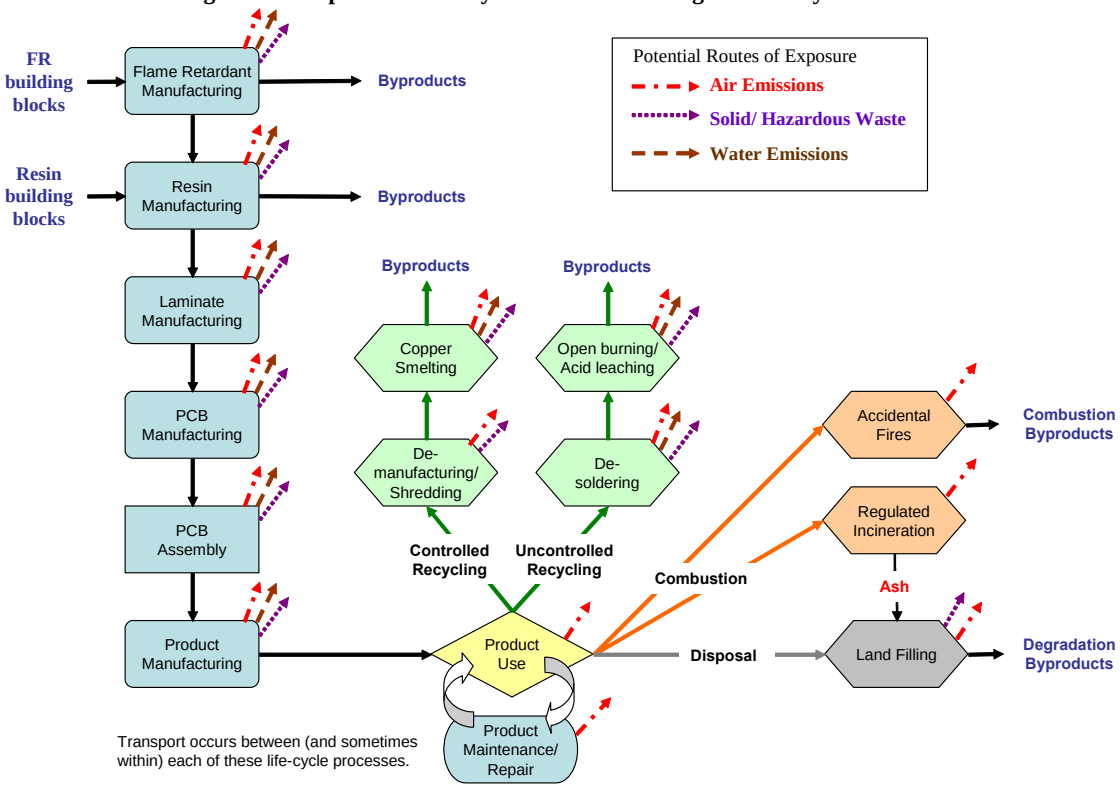
- *Chapter 6 (Combustion and Pyrolysis Testing of FR-4 Laminates):* This chapter describes the rationale and methods for combustion and pyrolysis testing of PCB materials.

- *Chapter 7 (Considerations for Selecting Flame Retardants):* This chapter addresses considerations for selecting alternative flame retardants based on environmental, technical, and economic feasibility.

1.2.1 Life-Cycle Stages Considered

Figure 1-1 shows the life-cycle stages of a PCB and the associated potential exposure pathways that will be examined in this report. In brief, the flame-retardant chemical is manufactured and then incorporated, either reactively or additively, into the epoxy resin. The epoxy resin is then applied to a woven fiberglass mat and hardened. Layers of copper foil are attached to both sides of the reinforced resin sheet to form a laminate. Next, a PCB is manufactured by combining several laminate layers that have had conductive pathways (i.e., circuits) etched into the copper foil. The layers are then laminated together, and holes are drilled to connect circuits between layers and hold certain electronic components (e.g., connectors or resistors). Once assembled, PCBs are incorporated into various products by original equipment manufacturers. When the product is no longer in use, there are several end-of-life pathways that the product may take: landfilling, regulated incineration, unregulated incineration (or open burning), and recycling. All of these life-cycle stages will be discussed in further detail in the subsequent chapters of this report.

Figure 1-1. Exposure Pathways Considered During the Life Cycle of a PCB



1.2.2 Aspects Beyond the Scope of This Assessment

Although the assessment will explore hazard data associated with potential exposure scenarios, the partnership does not intend to conduct a full risk assessment, which would require a full exposure assessment along with the hazard assessment. Likewise, the project will not be a complete life-cycle analysis, which inventories inputs and outputs from processes throughout the life cycle and evaluates the environmental impacts associated with those inputs and outputs.

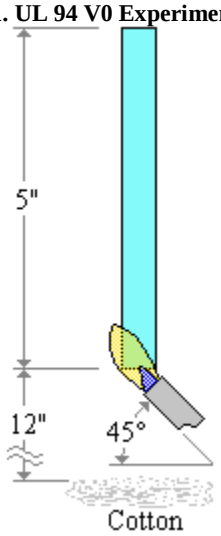
Process chemicals (i.e., etching or washing solutions used in manufacturing PCBs) are not included in the scope of this assessment. Although PCBs come in many varieties, the scope of this assessment is limited to FR-4 boards which meet the V0 requirements of the UL 94 standard. Boards of this type are used in consumer products such as computers and cell phones and make up a large portion of the PCBs used in consumer products. The assessment may be useful beyond FR-4 boards to the extent that the same flame retardants are used in other laminates constructed of woven fiberglass reinforced with other thermoset resins such as phenolics.

Finally, this assessment is not a technical evaluation of key electrical and mechanical properties of halogenated and halogen-free materials. These properties have been explored in parallel assessments conducted by iNEMI (International Electronics Manufacturing Initiative) that are described in greater detail in Section 2.3 and Section 7.6.4 of this report. Together, these resources will provide information on both the performance and environmental properties of the various materials being evaluated.

2 FR-4 Laminates

Flame Resistant 4 (FR-4) laminates are flame-retardant systems of woven glass reinforced with epoxy-like resin, notable for their resistance to heat, mechanical shock, solvents, and chemicals. Unlike lower grade laminates, a finished FR-4 laminate can obtain a V0 rating in the UL (Underwriters Laboratories) 94 test, a vertical burning test for flammability. The UL 94 V0 test is typically conducted using a 5-inch by 0.5-inch test specimen (thickness may vary) (RTP Company, 2014). The specimen is fastened vertically with a holding clamp at the top so that the 5-inch side is perpendicular to the ground (Figure 2-1). A cotton indicator is located 12 inches below the bottom of the specimen to capture any flaming dripped particles from the specimen (Figure 2-1). A burner flame is applied at a 45° angle to the bottom of the specimen in two intervals. The burner is first applied for 10 seconds and is removed until all flaming stops (UL, 2014). The burner is then reapplied for an additional 10 seconds (UL, 2014). Two sets of five specimens are tested (UL, 2014). In order to meet the UL 94 V0 flammability standard: (1) the specimens must not burn with flaming combustion for more than 10 seconds after the burner is removed; (2) the total flaming combustion time for each set of five specimens must not be greater than 50 seconds; (3) any flaming or glowing combustion must not burn up to the holding clamp; (4) flaming dripped particles from the specimens must not ignite the cotton indicator; and (5) glowing combustion must not exceed 30 seconds after the second burner flame is removed from the specimen (UL, 2014).

Figure 2-1. UL 94 V0 Experimental Setup



Source: UL, 2014

FR-4 laminates can be categorized as (1) high glass transition temperature (T_g) FR-4 laminates,[4] (2) middle T_g FR-4 laminates,[5] and (3) low T_g FR-4 laminates.[6] Within each of those categories, individual FR-4 laminates are differentiated through reference to their physical properties (e.g., rate of water absorption, flexural strength, dielectric constant, and resistance to heat). With the

[4] High glass transition temperature laminates have a T_g above 170°C.
[5] Middle glass transition temperature laminates are usually considered to have a T_g of approximately 150°C.
[6] Low glass transition temperature laminates are usually considered to have a T_g of 130°C and below.

introduction of halogen-free FR-4 materials,[7] a similar segmentation is emerging (e.g., high T_g halogen-free, low T_g halogen-free), leading to a multiplication of the number of FR-4 materials available (Beard et al., 2006; Bergum, 2007). As different formulations (different flame-retardant systems and different resin chemistries) result in different laminate properties, there can be different materials within one class (e.g., low T_g) having different performance (e.g., dielectrics, mechanics), thus addressing the different market needs. Such differences in performance are not specific to halogen-free materials and may also exist among brominated grades of the same T_g class.

2.1 Overview of FR-4 Laminates Market (Prismark, 2006)

In 2006, global printed circuit board (PCB) production exceeded $45 billion. PCBs are fabricated using a variety of laminate materials, including laminate, pre-impregnated material, and resin-coated copper. In 2006, $7.66 billion of laminate materials were consumed globally. Laminate materials can be sub-segmented according to their composition, and include paper, composite, FR-4, high T_g FR-4, and specialty products (polytetrafluoroethylene (PTFE) and high-performance materials).

- Paper and composite laminates represent 17.1 percent of the global laminate market in value (Figure 2-2). These materials are used as the basic interconnecting material for consumer applications. The materials are low in cost, and their material characteristics are adequate for use in mainly low-end consumer products.

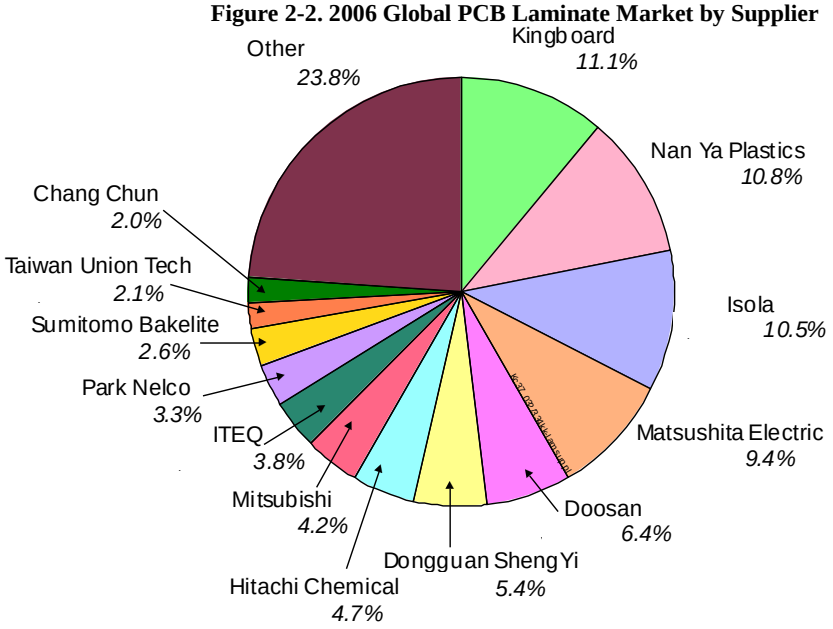
- The workhorse laminate for the PCB industry is FR-4. In terms of value, approximately 70.4 percent of the material used in the industry is FR-4 glass-based laminate (including high T_g and halogen-free) (Figure 2-2). This material provides a reliable and cost-effective solution for the vast majority of designs.

- Many laminators offer halogen-free FR-4 laminate materials. These materials are typically designed to be drop-in replacements for current halogenated materials, but they carry a price premium. Halogen-free materials have been slowly gaining acceptance on a regional basis.

- There are special applications that call for laminate materials with characteristics beyond the capability of FR-4. These materials consist of special integrated circuit packaging substrates and materials for use in wireless or high-speed digital applications, including laminate containing bismaleimide-triazine resins, poly(p-phenylene oxide), high-performance PTFE, and polyimide.

[7] In accordance with IEC-61249-2-21, this report defines "halogen-free materials" [illegible]erials that are ≤900ppm by weight chlorine; ≤900ppm by weight bromine; and ≤1,500ppm maximum total halogens.

Figure 2-2. 2006 Global PCB Laminate Market by Supplier

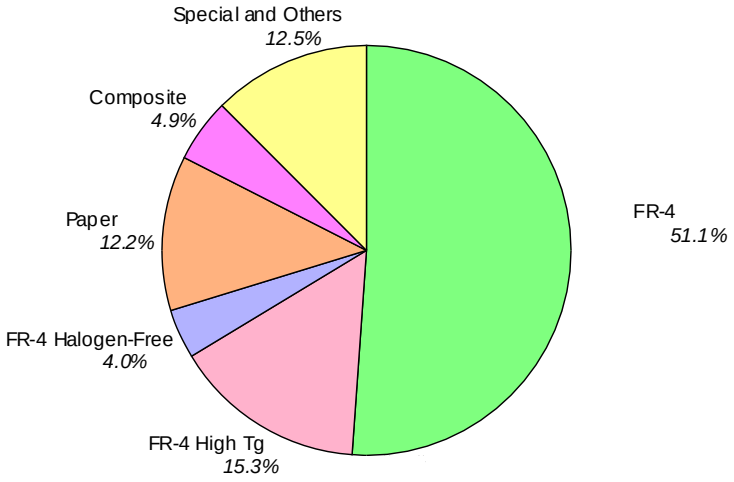


TOTAL: $7.66Bn

Note: This market includes prepreg and RCC values.

PCB LAMINATE MARKET 2006 BY MATERIAL TYPE

Figure 2-3. 2006 Global PCB Laminate Market by Material Type



TOTAL: $7.66Bn

Note: Includes prepreg

Global sales of laminate materials in 2006 were estimated at $7.66 billion. In terms of area production, it is estimated that more than 420.2 million square meters of laminate was manufactured to support the PCB industry in 2006. The distribution of laminate sales geographically and the leading suppliers to each region are shown in Figure 2-4 and Figure 2-5.

Figure 2-4. 2006 Regional Laminate Sales

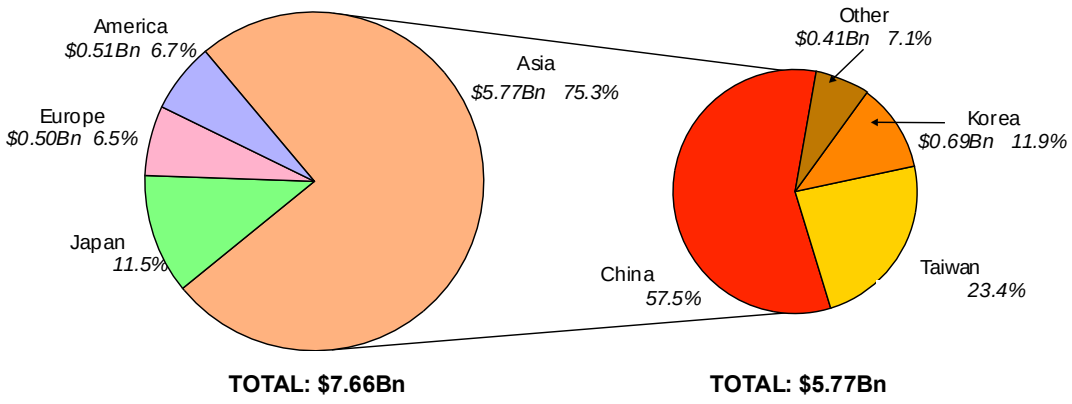
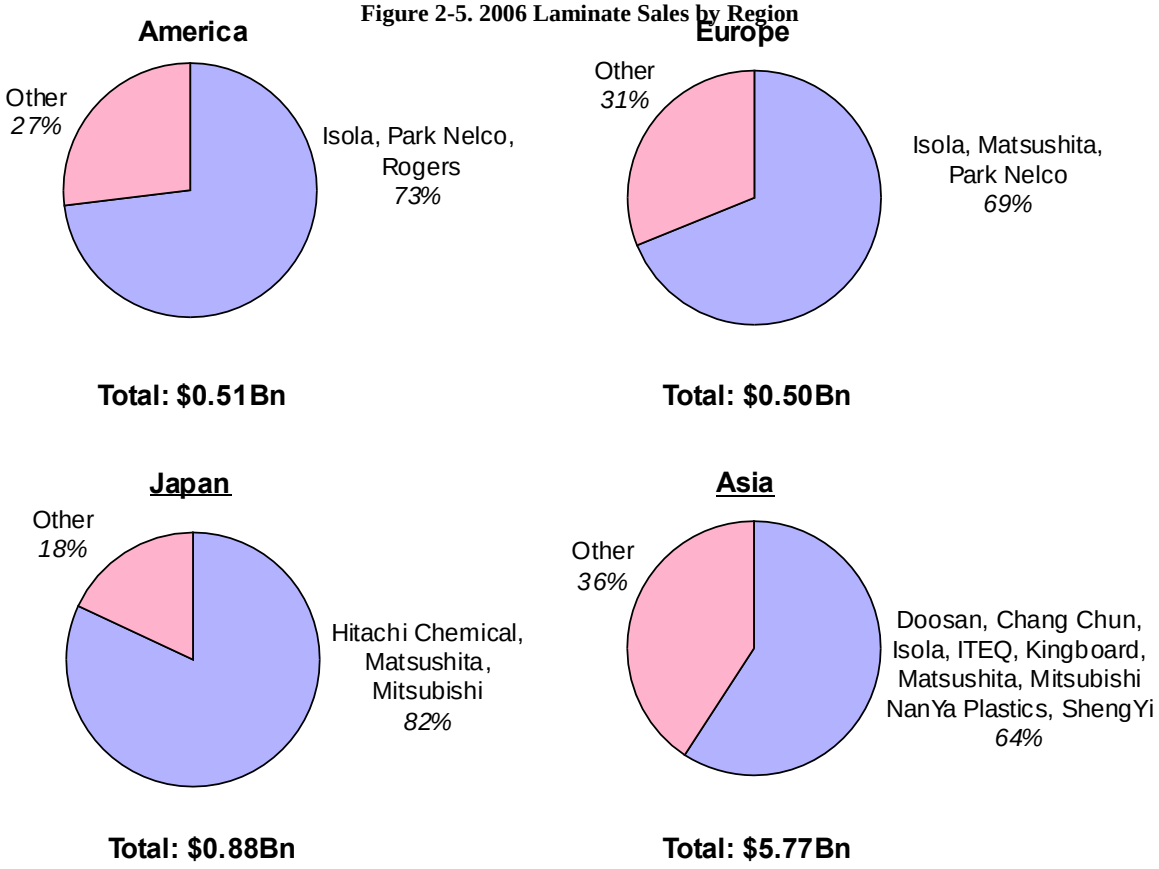


Figure 2-5. 2006 Laminate Sales by Region



2.2 Halogen-Free Laminate Market

There has been a continuous increase in the demand for halogen-free material over the past few years. In 2003, the global halogen-free laminate market was approximately $60 million. In 2004 this market grew to $161 million, in 2005 it reached $239 million, and it is estimated at $307 million for 2006.

Most laminate suppliers now include halogen-free materials in their portfolio. Pricing for halogen-free laminate is still higher than conventional material by at least 10 percent, and often by much more. Tallying the production volumes of such leading laminate manufacturers as Hitachi Chemical, NanYa, Matsushita, ITEQ, Isola, Park Nelco, and others, Prismark has constructed a market segmentation, shown in Figure 2-6.

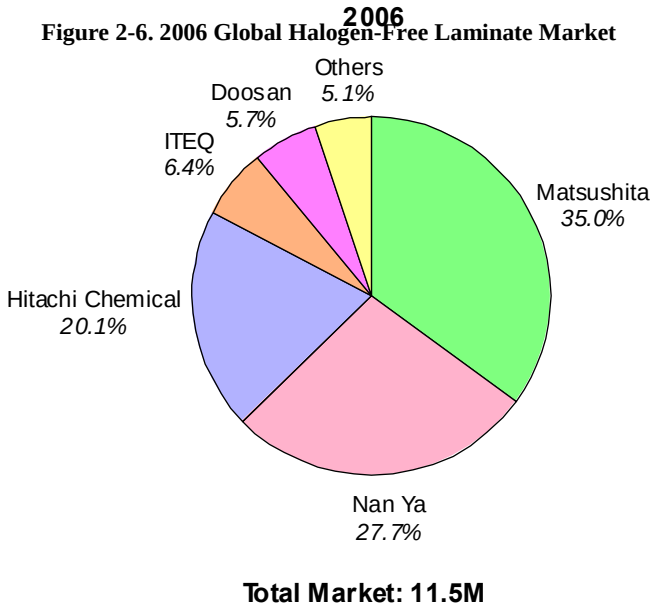


Figure 2-6. 2006 Global Halogen-Free Laminate Market

2.3 Past Research Efforts

While demand for halogen-free laminates is increasing, there was a lack of information regarding their performance and environmental impact when this partnership was convened. The International Electronics Manufacturing Initiative (iNEMI) and the High Density Packaging User Group (HDPUG) have taken on separate but complementary roles in helping to fill information gaps.

iNEMI has carried out a series of projects to determine the key performance properties and the reliability of halogen-free flame-retardant PCB materials. Each project has observed different outcomes, with the latest findings indicating that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of traditional brominated laminates. Technology improvements, especially those that optimize the polymer/fire retardant combinations used in PCBs, have helped shift the baseline in regards to the performance of halogen-free flame-retardant laminates.

In 2009, iNEMI completed a project focused on performance testing of commercially available halogen-free materials to determine their electrical and mechanical properties. In 2008 when this alternative assessment was first published, the list of laminate materials identified by iNEMI for further study include nine laminate materials from seven different suppliers:

- NanYa NPG-TL and NPG-170TL
- Hitachi BE-67G(R)
- TUC TU-742

- Panasonic R1566W
- ITEQ IT140G and IT155G
- Shengyi S1155
- Supresta FR Laminate

While not in the final list for further study, the following laminates were also identified as promising candidates by iNEMI:

- Isola DE156 and IS500
- TUC TU-862
- ITEQ IT170G
- Nelco 4000-7EF

The results of the testing and evaluation of these laminate materials were made public in 2009.[8] The overall conclusions from the investigation were (1) that the electrical, mechanical, and reliability attributes of the halogen-free laminate materials tested were not equivalent to FR-4 laminates and (2) that the attributes of the halogen-free laminates tested were not equivalent among each other (Fu et al., 2009). Due to the differences in performance and material properties among laminates, iNEMI suggested that decision-makers conduct testing of materials in their intended applications prior to mass product production (Fu et al., 2009).

iNEMI also conducted two follow-on projects to its HFR-free Program Report: (1) the HFR-Free High-Reliability PCB Project and (2) the HFR-Free Leadership Program. The focus of the HFR-Free High-Reliability PCB Project was to identify technology readiness, supply capability, and reliability characteristics for halogen-free alternatives to traditional flame-retardant PCB materials based on the requirements of the high-reliability market segment (e.g., servers, telecommunications, military) (iNEMI, 2014). In general, the eight halogen-free flame-retardant laminates tested outperformed the traditional FR-4 laminate control (Tisdale, 2013). The other project, the HFR-Free Leadership Program, assessed the feasibility of a broad conversion to HFR-free PCB materials by desktop and laptop computer manufacturers (Davignon, 2012). Key electrical and thermo-mechanical properties were tested for six halogen-free flamed-retardant laminates and three traditional FR-4 laminates. The results of the testing demonstrated that the computer industry is ready for a transition to halogen-free flame-retardant laminates. It was concluded that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of brominated laminates and that laminate suppliers can meet the demand for halogen-free flame-retardant PCB materials (Davignon, 2012). A "Test Suite Methodology" was also developed under this project that can inform flame retardant substitution by enabling manufacturers to compare the electrical and thermo-mechanical properties of different laminates based on testing (Davignon, 2012).

In contrast to the iNEMI project, HDPUG collected existing data on halogen-free flame-retardant materials; no performance testing was conducted. HDPUG created a database of information on the physical and mechanical properties of halogen-free flame-retardant materials, as well as the environmental properties of those materials. The HDPUG project, completed in 2011, broadly examined flame-retardant materials, both ones that are commercially viable and in research and

[8] http://thor.inemi.org/webdownload/newsroom/Presentations/SMTA_South_China_Aug09/HFR-Free_Report_Aug09.pdf

development (R&D). For more information about the database and other HDPUG halogen-free projects, visit: http://hdpug.org/content/completed-projects#HalogenFree.

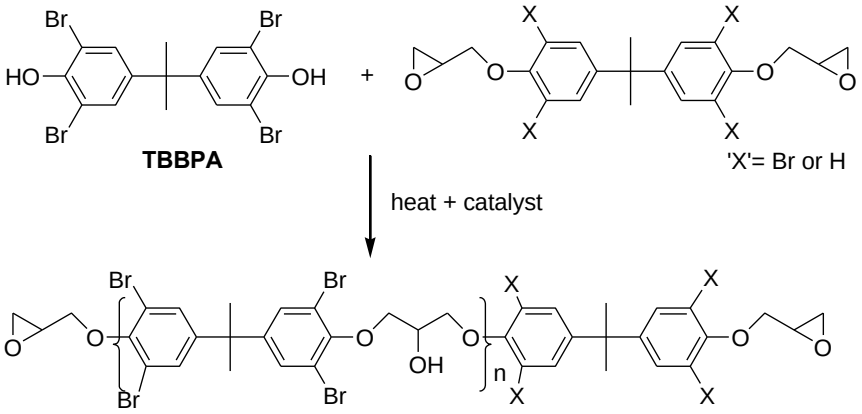
Even though they are taking on different roles, HDPUG and iNEMI have been in contact with each other, as well as this DfE partnership project, to ensure minimal duplication in scope. The results of their efforts help inform companies that want to select halogen-free laminate materials.

2.4 Process for Manufacturing FR-4 Laminates

This section describes general processes for manufacturing epoxy resins and laminates. Specific chemicals and process steps can differ between manufacturers and intended use of the product.

2.4.1 Epoxy Resin Manufacturing

The process for making brominated epoxy resins that are used to make FR-4 laminates is shown below. Two different classes of oligomers (low molecular weight (MW) linear polymers) are in common use. The simplest are prepared by reacting TBBPA with a "liquid epoxy resin" ("X" is hydrogen in this case). The products (for example D.E.R. 500 Series) have an M_n (number average MW) of 800-1,000 g/mole and contain about 20 percent bromine by weight After the oligomers are prepared, they are dissolved in a variety of solvents such as acetone or methyl ethyl ketone (2-butanone) to reduce the viscosity. The M_w (average MW) is typically about 2,000 g/mole. An excess of the epoxy resin is used, and therefore essentially all of the TBBPA is converted.



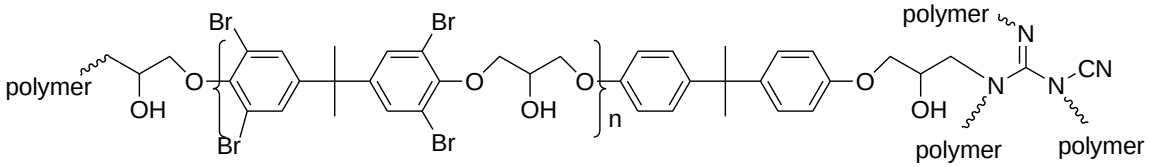
In cases where it is desired to have an oligomer with a higher concentration of bromine, the liquid epoxy resin (LER) is replaced with a brominated epoxy resin ("X" = Br in the above structure). The products (D.E.R.™ 560 is a typical example) have similar MWs, but the content of bromine is higher (about 50 percent bromine by weight). These "high-brominated" resins are typically used when other non-brominated materials must be added to the formulation (or "varnish").

In the past a large majority of laminate varnishes would be prepared by simply combining the 20 weight percent brominated resin with 3 percent weight "dicy" (dicyandiamide) as a curing agent, along with additional solvent. After the solvent was removed and the laminate pressed, the thermoset matrix would contain about 20 percent bromine by weight. This is sufficient bromine

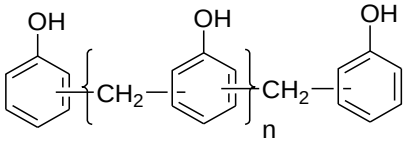
to allow the thermoset matrix to pass the V0 performance requirements in the standard UL 94 test. The cure chemistry of dicy is very complex and poorly understood. However, it is known to be capable of reacting with 4, 5, or even 6 epoxy groups.

"Catalysts" such as 2-methylimidazole are used to increase the cure rate. Imidazoles are not true catalysts: they initiate polymer chains, and become covalently bound to the matrix.

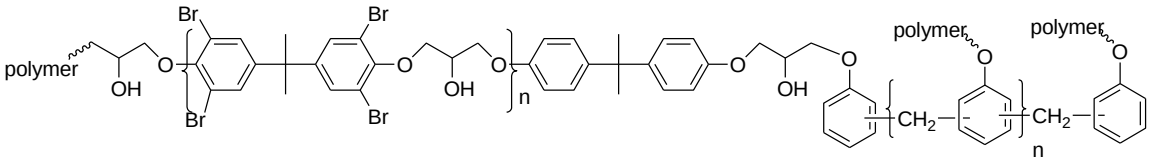
A simplified representation of the final thermoset is shown below. In a properly cured laminate all of the resin has become one molecule, meaning every atom is covalently linked into one three-dimensional structure. This is desirable because it means that there are no leachable (or volatile) materials that can be released during the various procedures used to make a final PCB.



With the advent of lead-free solders that melt at higher temperatures, phenolic hardeners (in place of dicy) are becoming more common. Such formulations typically have higher decomposition temperatures. A common phenolic hardener is an oligomer prepared from phenol and formaldehyde that has the structure shown below. These "novolaks" typically have 2.5 to 5.5 phenolic groups per molecule, which translates to M_ns of 450 to 780 g/mole. Bisphenol A novolak is also becoming increasingly common to boost the glass T_g.



The cross-linked matrix formed in this case is represented below. The use of phenolic hardeners in the formulation has the effect of reducing the bromine concentration in the final cured resin. In some cases additional flame retardant is needed to meet the UL 94 V0 classification. This is typically a solid additive such as alumina trihydrate or other fillers. Other methods are to mix in a fraction of the fully brominated resin that contains 50 percent bromine by weight. Finally, additional TBBPA and LER can be mixed into the crosslinked matrix to increase the bromine concentration of the final cured resin, although it is unclear how common this practice is among epoxy resin manufacturers (Mullins, 2008).



This description does not cover all of the formulations used by laminate producers to meet their product specifications. Various epoxy novolaks can be added.

The process of making epoxy resins containing alternative flame retardants is similar to the process used for making brominated epoxy resins. In the case of phosphorus-based flame retardants, the epoxy resin is produced by reacting diglycidyl ether of bisphenol A or an epoxy

novolak with a stoichiometric deficiency of phosphorus flame retardant. This produces a new resin containing both an epoxy group and covalently bound phosphorus. Alternatively, a phosphorus-containing hardener can be prepared by condensing a phenolic compound with a phosphorus-containing flame retardant. For example, hydroquinone can condense with phosphorus-containing flame retardants in the presence of an oxidizing agent to give a hydroquinone-phosphorus compound. The laminator uses this hardener in conjunction with an epoxy resin (such as an epoxy novolak) and catalysts. A laminate can also be made halogen-free by using solid inorganic flame retardants (or fillers) to achieve the V0 requirement of the UL 94 fire safety standard. A phosphorus content of about 4 to 5 percent by weight in the laminate is generally sufficient to achieve the V0 requirement of the UL 94 fire safety standard.

2.4.2 Laminate Manufacturing

Most PCBs are composed of 1 to 16 conductive layers separated and supported by layers (substrates) of insulating material. In a typical four-layer board design, internal layers are used to provide power and ground connections with all other circuit and component connections made on the top and bottom layers of the board. The more complex board designs have a large number of layers necessary for different voltage levels, ground connections, and circuit package formats.

The basic layer of the PCB is a woven fiberglass mat embedded with a flame-resistant epoxy resin. A layer of copper is often placed over this fiberglass/epoxy layer, using methods such as silk screen printing, photoengraving, or PCB milling to remove excess copper. Various conductive copper and insulating dielectric layers are then bonded into a single board structure under heat and pressure. The layers are connected together through drilled holes called vias, typically made with laser ablation or with tiny drill bits made of solid tungsten carbide. The drilled holes can then be plated with copper to provide conductive circuits from one side of the board to the other (How Products Are Made, 2006).

Next, the outer surfaces of a PCB may be printed with line art and text using silk screening. The silk screen, or "red print," can indicate component designators, switch setting requirements, test points, and other features helpful in assembling, testing, and servicing the circuit board. PCBs intended for extreme environments may also be given a conformal coat made up of dilute solutions of silicone rubber, polyurethane, acrylic, or epoxy, which is applied by dipping or spraying after the components have been soldered. This coat will prevent corrosion and leakage currents or shorting due to condensation.

Once printed, components can be added in one of two ways. In through-hole construction, component leads are electrically and mechanically fixed to the board with a molten metal solder, while in surface-mount construction, the components are soldered to pads or lands on the outer surfaces of the PCB. The parts of the circuit board to which components will be mounted are typically "masked" with solder in order to protect the board against environmental damage and solder shorts. The solder itself was traditionally a tin-lead alloy, but new solder compounds are now used to achieve compliance with the Restriction of Hazardous Substances directive in the European Union, which restricts the use of lead. These new solder compounds include organic surface protectant, immersion silver, and electroless nickel with immersion gold coating (Oresjo and Jacobsen, 2005). Tin-silver-copper alloys have also been developed, some containing small amounts of an additional fourth element (IPC, 2005; Lasky, 2005).

After construction, the PCB's circuit connections are verified by sending a small amount of current through test points throughout the board. The PCB is then ready to be packaged and shipped for use (Electronic Interconnect, 2007).

2.5 Next Generation Research and Development

Most R&D is oriented around improving the performance of FR-4 laminates. For example, manufacturers are seeking to improve the glass T_g of FR-4 laminates in order to produce laminates better able to withstand heat. A higher T_g is generally compatible with the use of lead-free solder, which often requires a higher soldering temperature (Thomas et al., 2005). Manufacturers often consider T_g together with the decomposition temperature (T_d) when assembling lead-free assemblies. T_d is the temperature at which material weight changes by 5 percent. Due to marketplace concerns over potential environmental impacts of TBBPA, such as the generation of halogenated dioxins and furans during combustion, as supported by this project's combustion testing (Chapter 6), the development of non-halogen flame retardants (discussed in Section 3.2) has also been a priority of manufacturers. However, concerns over the human health and environmental impact, as well as the expense and performance of laminates containing these non-halogen flame retardants, are still an issue.

There are many types of FR-4 laminates under development that have a resin design different from the epoxy-based construction described above. These typically include more thermally stable inflexible structures (such as biphenyl or naphthalene groups) and/or nitrogen heterocyclic structures (such as reacted-in triazine, oxazoline, or oxazine rings). Another alternative to epoxy resin, polyimide resin, can be produced through condensation reactions between aromatic dianhydrides and aromatic diamines (Morose, 2006). IF Technologies has manufactured an aliphatic LER system produced from epoxidized plant oils and anhydrides that reduces emissions, decreases toxicity, and replaces bisphenol A and epichlorohydrin. Other technologies in development use substances such as keratin, soybean oil, or lignin in the manufacturing process.

Improvements in the lamination process are also being developed. Technologies may soon enable the formation and multi-layering at room temperature of ceramic film on resin circuit boards, allowing for further multi-functionality, miniaturization, and cost reduction of electronic devices (PhysOrg, 2004). Laser drilling techniques will allow for the production of smaller microvias, which may allow for the creation of smaller circuit boards (Barclay, 2004). Lasers can also be used for direct copper ablation, as they can quickly vaporize copper without damaging the epoxy and glass substrate (Lange, 2005).

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3 Chemical Flame Retardants for FR-4 Laminates

This chapter summarizes the general characteristics of flame retardants and associated mechanisms of flame retardancy. The flame-retardant chemicals currently used in printed circuit boards (PCBs) are also briefly introduced, with more detailed information about their potential exposure pathways, toxicity, and life-cycle considerations presented in later chapters.

3.1 General Characteristics of Flame-Retardant Chemicals

Fire occurs in three stages: (a) thermal decomposition, where the solid, or condensed phase, breaks down into gaseous decomposition products as a result of heat, (b) combustion chain reactions in the gas phase, where thermal decomposition products react with an oxidant (usually air) and generate more combustion products, which can then propagate the fire and release heat, and (c) transfer of the heat generated from the combustion process back to the condensed phase to continue the thermal decomposition process (Hirschler, 1992; Beyler and Hirschler, 2002).

In general, flame retardants decrease the likelihood of a fire occurring and/or decrease the undesirable consequences of a fire (Lyons, 1970; Cullis and Hirschler, 1981). The simplest way, in theory, of preventing polymer combustion is to design the polymer so that it is thermally very stable. Thermally stable polymers are less likely to thermally degrade, which prevents combustion from initiating. However, thermally stable polymers are not typically used due to cost and/or other performance issues such as mechanical and electrical properties incompatible with end-use needs for the finished part/item. As a result, manufacturers use other methods, such as using flame-retardant chemicals, to impart flame-retardant properties to polymers.

Flame retardants typically function by decreasing the release rate of heat (Hirschler, 1994), thus reducing the burning rate or flame spread of a fire, or by reducing smoke generation (Morose, 2006). In the gas phase, flame retardants can interfere with free radical chain reactions, thereby reducing the tendency of the fire to propagate and spread. Flame retardants can also act in the gas phase by cooling reactants and thereby decrease the rate of combustion. In the condensed phase, flame retardants can act by forming a solid char (or a glassy layer), which interferes with the transfer of heat back from the gas phase to the condensed phase. This inhibits or prevents further thermal decomposition.

Typically, flame retardants contain one of the following seven elements: chlorine, bromine, aluminum, boron, nitrogen, phosphorus, or antimony (Lyons, 1970; Cullis and Hirschler, 1981; Hirschler, 1982). There are, however, a number of replacements and synergists that are also effective. For example, aluminum (which is most often used as an oxide or hydroxide) can be replaced with magnesium hydroxide or by a magnesium salt. In addition, some elements, such as zinc (often used as zinc borate or zinc stannate) and molybdenum (often used as ammonium molybdates), are effective primarily as smoke suppressants in mixtures of flame retardants.

3.1.1 Flame Retardant Classification

Flame retardants are generally incorporated throughout the polymeric material, although they can also be coated on the external surface of the polymer to form a suitable protective barrier. Flame

retardants can be classified, broadly speaking, into two types according to the method of incorporation:

- *Reactive:* Reactive flame retardants are incorporated into polymers via chemical reactions. The production of existing polymers is modified so that one or more unsubstituted reactant monomers is replaced with a substituted monomer containing flame-retardant heteroelements. The substituted monomers and their heteroelement components become an integral part of the resulting polymer structure. Reactive flame retardants must be incorporated at an early stage of manufacturing, but once introduced they become a permanent part of the polymer structure. Once they are chemically bound, reactive flame-retardant chemicals cease to exist as separate chemical entities. Reactive flame retardants have a greater effect than additive flame retardants on the chemical and physical properties of the polymer into which they are incorporated.

- *Additive:* Additive flame retardants are incorporated into the compounds via physical mixing. Compounds containing flame-retardant elements are mixed with existing polymers without undergoing any chemical reactions. As a result, the polymer/additive mixture is less susceptible to combustion than the polymer alone. Since additive flame retardants can be incorporated into the product up until the final stages of manufacturing, it is typically simpler for manufacturers to use additive flame retardants than reactive flame retardants.

Due to the differing physical and chemical properties of flame-retardant chemicals, most are used exclusively as either reactive or additive flame retardants. Both reactive and additive flame retardants can significantly change the properties of the polymers into which they are incorporated. For example, they may change the viscosity, flexibility, density, and electrical properties, and may also increase the susceptibility of the polymers to photochemical and thermal degradation.

Flame retardants can also be classified into four main categories according to chemical composition (IPC, 2003; and Morose, 2006):

- *Inorganic*: This category includes silicon dioxide, metal hydroxides (e.g., aluminum hydroxide and magnesium hydroxide), antimony compounds (e.g., antimony trioxide), boron compounds (e.g., zinc borate), and other metal compounds (molybdenum trioxide). As a group, these flame retardants represent the largest fraction of total flame retardants in use.

- *Halogenated*: These flame retardants are primarily based on chlorine and bromine. Typical halogenated flame retardants are halogenated paraffins, halogenated alicyclic and aromatic compounds, and halogenated polymeric materials. Some halogenated flame retardants also contain other heteroelements, such as phosphorus or nitrogen. When antimony oxide is used, it is almost invariably used as a synergist for halogenated flame retardants. The effectiveness of halogenated additives, as discussed below, is due to their interference with the radical chain mechanism in the combustion process of the gas phase. Brominated compounds represent approximately 25 percent by volume of the

global flame retardant production (Morose, 2006). Chemically, they can be further divided into three classes:

- Aromatic, including tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers, and polybrominated biphenyls;
- Aliphatic; and
- Cycloaliphatic, including hexabromocyclododecane.

- *Phosphorus-based*: When this partnership was convened, the current information showed that this category represented about 20 percent by volume of the global production of flame retardants and includes organic and inorganic phosphates, phosphonates, and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states. There are also halogenated phosphate esters, often used as flame retardants for polyurethane foams or as flame-retardant plasticizers but not commonly used in electronics applications (Hirschler, 1998; Green, 2000; Weil, 2004).

- *Nitrogen-based*: These flame retardants include melamine and melamine derivatives (e.g., melamine cyanurate, melamine polyphosphate). It is rare for flame retardants to contain no heteroatom other than nitrogen and to be used on their own. Nitrogen-containing flame retardants are often used in combination with phosphorus-based flame retardants, often with both elements in the same molecule.

3.1.2 Flame Retardant Modes of Action

The burning of polymers is a complex process involving a number of interrelated and interdependent stages. It is possible to decrease the overall rate of polymer combustion by interfering with one or more of these stages. The basic mechanisms of flame retardancy will vary depending on the flame retardant and polymer system.

Flaming Combustion

Chemical Inhibitors – Some flame retardants interfere with the first stage of burning, in which the polymer undergoes thermal decomposition and releases combustible gases. Interference during this stage alters polymer breakdown in such a way as to change either the nature of released gases or the rate at which they are released. The resulting gas/oxidant mixture may no longer be flammable.

Fillers – A completely different mode of action is that exerted by inert solids incorporated into polymers. Such materials, known as fillers, absorb heat and conduct heat away by virtue of their heat capacity and thermal conductivity, respectively. As a result, fillers keep polymers cool and prevent them from thermally decomposing. The temperature is kept down even more effectively if the fillers decompose endothermically. Since fillers act predominantly via a physical rather than a chemical process, large levels of fillers are needed.

Protective Barriers – Some flame retardants cover the flammable polymer surface with a non-flammable protective coating. The coating helps insulate the flammable polymer from the source

of heat, thus preventing the formation of combustible breakdown products and their escape into the gas phase. The non-flammable coating may also prevent gaseous oxidants (normally air or oxygen) from contacting the polymer surface. Intumescent compounds, which swell as a result of heat exposure, lead to the formation of a protective barrier in which the gaseous products of polymer decomposition are trapped. Alternatively, a non-flammable layer can be directly applied to the surface of the polymer to form a non-intumescent barrier coating. Many phosphorus-containing compounds form such non-intumescent surface chars.

Gaseous Phase Mechanisms – Flame-retardant chemicals can also inhibit combustion of the gaseous products of polymer decomposition. These reactions are known as the gaseous flame reactions. As for condensed phase inhibition, there are several rather distinct possible modes of action.

In some cases, flame retardants lead to the release of reactive gaseous compounds into the combustion zone, which can replace highly active free radicals with less reactive free radicals. The less reactive free radicals slow the combustion process and reduce flame speed. In other cases, flame retardants can cause the evolution of a small particle "mist" during combustion. These small particles act as "third bodies" that catalyze free-radical recombination and hence chain termination. This mode of action is typical of halogenated flame retardants, which usually act by decomposing at high temperature to generate hydrogen chloride or hydrogen bromide. These compounds react with oxygenated radicals and inhibit gas phase combustion reactions (Cullis and Hirschler, 1981; Hirschler, 1982; Georlette et al., 2000).

Flame-retardant chemicals can also operate by releasing relatively large quantities of inert gas during decomposition, which can change the composition and temperature of gaseous polymer decomposition products. The resulting mixture of gaseous products and surrounding gaseous oxidants are no longer capable of propagating flame. In some systems, when the polymer burns the flame-retardant chemical is released chemically unchanged as a heavy vapor, which effectively "smothers" the flame by interfering with the normal interchange of combustible gaseous polymer decomposition products and combustion air or oxygen. This mode of action is typical of metal hydroxides, such as aluminum or magnesium hydroxide (Horn, 2000).

Melting and Dripping – Some flame-retardant chemicals inhibit combustion by interfering with the transfer of heat from combustion back to the polymer. Certain chemicals may promote depolymerization, which lowers the molecular weight of the polymer and facilitates melting. As the burning melt drips away from the bulk of the polymer it carries with it a proportion of the heat that would otherwise contribute to polymer decomposition and volatilization. By reducing the release of volatile decomposition products into the gas phase, these flame retardants reduce the amount of gaseous decomposition products available to feed the flame. While enhanced melting should decrease flammability in theory, in practice droplets of burning molten polymer may help spread a fire to other combustible materials.

Ablation – Combustion can also be retarded by coating or constructing the polymer in such a way that, when it burns, incandescent sections disintegrate from the original polymer and remove with them heat from the combustion zone. This mechanism of action, known as ablation, is in a sense the solid phase parallel of liquid phase melting and dripping. A surface char layer is

frequently formed, which isolates the bulk of the polymer material from the high temperature environment. This charry layer remains attached to the substrate for at least a short period while a degradation zone is formed underneath it. In this zone, the organic polymer undergoes melting, vaporization, oxidation, or pyrolysis. The ablative performance of polymeric materials is influenced by polymeric composition and structure, as well as environmental factors, such as atmospheric oxygen content. Higher hydrogen, nitrogen, and oxygen content of the polymer increases the char oxidation rate; higher carbon content decreases the char oxidation rate (Levchik and Wilkie, 2000).

Smoldering (Non-Flaming) Combustion

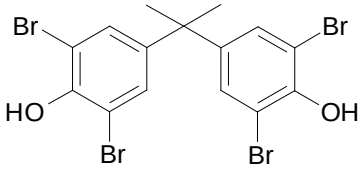
Smoldering (non-flaming) combustion and the closely related phenomenon of glowing combustion occur primarily with high-surface area polymeric materials that break down during combustion to form a residual carbonaceous char (typically cellulosic materials). In general, it is possible to inhibit non-flaming combustion either by retarding or preventing the initial breakdown of the polymer to form a char, or by interfering with the further combustion of this char. Boric acid and phosphates are the primary flame retardants used for preventing non-flaming combustion of organic polymers.

3.2 Flame-Retardant Chemicals Currently Used in FR-4 Laminates

Over the last several years, the electronics industry has been increasingly focused on researching and developing halogen-free alternatives to TBBPA, due in large part to environmental concerns and the anticipation of possible regulatory actions in the European Union. Several flame-retardant chemicals are commercially available to meet fire safety standards for Flame Resistant 4 (FR-4) laminates. As of 2008, the halogenated flame retardant TBBPA is used in approximately 90 percent of FR-4 PCBs. The majority of halogen-free alternatives to TBBPA are based on phosphorus compounds that are directly reacted into the epoxy resin or combined with aluminum trioxide or other fillers (De Boysère and Dietz, 2005). This section briefly discusses TBBPA, dihydrooxaphosphaphenanthrene (DOPO), Fyrol PMP, and four commonly used halogen-free fillers: aluminum hydroxide, melamine polyphosphate, metal phosphinate, and silica. In this report, these four fillers are also referred to as additive flame retardants.

Reactive Flame-Retardant Chemicals

TBBPA

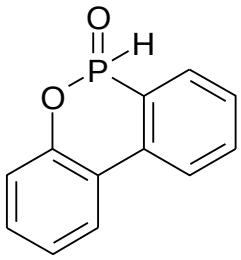


TBBPA is a crystalline solid with the chemical formula $C_{15}H_{12}Br_4O_2$. TBBPA increases the glass transition temperature (T_g) of the epoxy resins and enables the resin to achieve a UL (Underwriters Laboratories) 94 V0 flammability rating. TBBPA is most commonly reacted into the epoxy resin through "chain extension," meaning TBBPA is reacted with a molar excess of diglycidyl ether of bisphenol A, or other similar epoxy. Once the TBBPA is chemically bound,

the finished epoxy resin typically contains about 18 to 21 percent bromine (Weil and Levchik, 2004).

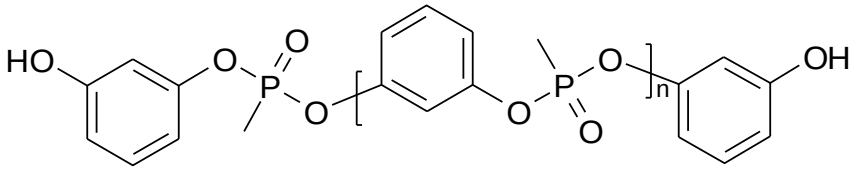
TBBPA is produced by several flame retardant manufacturers. According to High Density Packaging User Group International (2004) and Morose (2006), TBBPA's market dominance is due primarily to its moisture resistance, thermal stability, cost-effectiveness, compatibility with the other components of PCBs, and ability to preserve the board's physical properties. Aside from PCBs, another primary application of TBBPA is its use as an additive flame retardant in the acrylonitrile-butadiene-styrene resins found in electronic enclosures of televisions and other products.

DOPO



DOPO is a hydrogenphosphinate made from *o*-phenyphenol and phosphorus trichloride. Similar to TBBPA, it can be chemically reacted to become part of the epoxy resin backbone. DOPO was originally developed as a flame retardant for polyester textile fibers and also has applications as an antioxidant-type stabilizer (Weil and Levchik, 2004). Due to DOPO's higher cost (nearly four times as much as TBBPA at the time this partnership was convened), its use has been limited by laminate manufacturers. To decrease the cost of their formulations, some laminate manufacturers are using DOPO in combination with less expensive materials such as alumina trihydrate (ATH) and/or silica (Thomas et al., 2005) or along with more cost-effective compounds like metal phosphinates (De Boysère and Dietz, 2005).

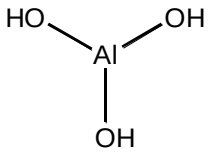
Fyrol PMP



Fyrol PMP is an aromatic phosphonate oligomer with high phosphorus content (17 to 18 percent). Similar to TBBPA and DOPO, Fyrol PMP can be chemically reacted to become part of the epoxy resin backbone. When reacted into a phenol-formaldehyde novolak epoxy, Fyrol PMP provides good flame retardancy at loadings as low as 20 percent (Weil, 2004).

Flame-Retardant Fillers

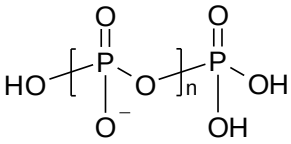
Aluminum Hydroxide

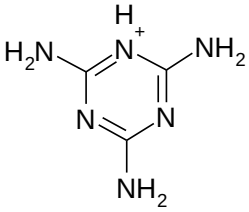


While the use of aluminum hydroxide ($Al(OH)_3$) in FR-4 PCBs was relatively low several years ago, it was the largest volume flame retardant used worldwide, with an estimated 42 percent volume market share in 2006 (BCC, 2006). Aluminum hydroxide is commonly referred to as ATH and has been used to impart flame retardancy and smoke suppression in carpet backing, rubber products, fiberglass-reinforced polyesters, cables, and other products. It is also used in the manufacture of a variety of items – antiperspirants, toothpaste, detergents, paper, and printing inks – and is used as an antacid.

ATH is difficult to use alone to achieve the FR-4 rating of laminates, and as a result, high loadings relative to the epoxy resin, typically up to 60 to 70 percent by weight, are needed (Morose, 2006). ATH is most commonly used in FR-4 PCBs as a flame-retardant filler, in combination with DOPO or other phosphorus-based compounds. When heated to 200-220°C, ATH begins to undergo an endothermic decomposition to 66 percent alumina and 34 percent water (Morose, 2006). It retards the combustion of polymers by acting as a "heat sink" – i.e., by absorbing a large portion of the heat of combustion (HDPUG, 2004).

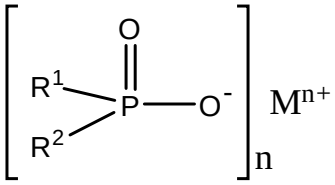
Melamine Polyphosphate





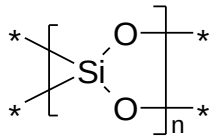
Melamine polyphosphate, an additive-type flame retardant based on a combination of phosphorus and nitrogen chemistries, is typically used as crystalline powder and in combination with phosphorus-based compounds. Its volume market share in 2006 was slightly more than 1 percent (BCC, 2006) but is expected to increase as the demand for halogen-free alternatives increases. Similar to ATH, melamine polyphosphate undergoes endothermic decomposition but at a higher temperature (350°C). It retards combustion when the released phosphoric acid coats and therefore forms a char around the polymer, thus reducing the amount of oxygen present at the combustion source (Special Chem, 2007). Melamine polyphosphate does not negatively impact the performance characteristics of standard epoxy laminates, and functions best when blended with other non-halogen flame retardants (Kaprinidis, 2008). Melamine polyphosphate dissociates in water to form melamine cations and phosphate anions.

Metal Phosphinates



Flame retardants based on phosphinate chemistry were a relatively new class of halogen-free flame retardants on the market at the time this partnership was convened. One such phosphinate-based flame retardant – aluminum diethylphosphinate – is a fine-grained powder with high phosphorus content (23 to 24 percent) used as a filler in FR-4 laminates (De Boysère and Dietz, 2005). It is designed primarily for use in FR-4 laminate materials with T_g greater than 150°C (mid-range and high T_g applications). Like most phosphorus-based compounds, metal phosphinates achieve flame retardancy by forming a char barrier upon heating, thereby cutting off access to the oxygen needed for the combustion process. Due to its low density and high surface area, aluminum diethylphosphinate cannot be used alone. It is typically used as a powerful synergist in combination with modified resins and sometimes other filler-type flame retardants.

Silica



Also known as silicon dioxide (SiO_2), silica is characterized by its abrasion resistance, electrical insulation, and high thermal stability. Silica is not a flame retardant in the traditional sense. It dilutes the mass of combustible components, thus reducing the amount of flame retardant necessary to pass the flammability test. Silica is most commonly used in combination with novolak-type epoxy resins. For example, silica clusters can be reacted with phenolic novolak resins (the resin bonds to hydroxyl groups on the silica cluster) to form a silica-novolak hybrid resin (Patent Storm, 2002). It can be used as an inert, low expansion material in both the epoxy resin and electronic circuit. One drawback is its abrasiveness, which affects drilling operation during the PCB manufacturing process.

Magnesium Hydroxide

Magnesium hydroxide is functionally similar to ATH, in that it endothermically decomposes at high temperatures to produce an oxide (MgO) and water. The absorption of heat retards the combustion of polymers, and the release of water may create a barrier that prevents oxygen from supporting the flame (Huber, 2007). However, whereas ATH undergoes thermal decomposition at 200-220°C, magnesium hydroxide decomposes at approximately 330°C. This allows manufacturers to use magnesium hydroxide when processing temperatures are too high for ATH (Morose, 2006). Similar to ATH, high loadings of magnesium hydroxide are required to achieve

the FR-4 rating. In many polymer systems, in order to reduce loadings, magnesium hydroxide is sometimes combined with more effective flame retardants, such as phosphorus (Morose, 2006).

Other Chemicals

Following is a brief description of other chemicals that can be used as flame retardants in FR-4 PCBs but are not evaluated in this paper.

Ammonium Polyphosphate

Ammonium polyphosphate is an intumescent flame retardant, meaning that it swells when exposed to heat, and can be used in epoxies. However, it is not commonly used in electronic applications. At high temperatures (>250°C), ammonium polyphosphate decomposes into ammonia and polyphosphoric acid. When exposed to water, polyphosphate reacts to form monoammonium phosphate, a fertilizer (Chemische Fabrik Budenheim, 2007).

Red Phosphorus

Red phosphorus is produced from white phosphorus by heating white phosphorus in its own vapor to 250°C in an inert atmosphere. It is fairly stable and is used in the manufacture of several products, such as matches, pesticides, and flame retardants (Lide, 1993; Diskowski and Hofmann, 2005). Its main use as a flame retardant is in fiberglass-reinforced polyamides. Although it does function in epoxy resins, it is not recommended for electronic applications, because red phosphorus can form phosphine (PH_3) and acidic oxides under hot and humid conditions (Clariant, 2002). The oxides can lead to metal corrosion, and hence electric defects can occur (Clariant, personal communication 2007).

Antimony Oxide

Antimony oxide, typically antimony trioxide (Sb_2O_3), can be used as a flame retardant in a wide range of plastics, rubbers, paper, and textiles. Antimony trioxide does not usually act directly as a flame retardant, but as a synergist for halogenated flame retardants. Antimony trioxide enhances the activity of halogenated flame retardants by releasing the halogenated radicals in a stepwise manner. This retards gas phase chain reactions associated with combustion, which slows fire spread (Hastie and McBee, 1975; Hirschler, 1982; Chemical Land 21, 2007).

Melamine Cyanurate

Melamine cyanurate is relatively cheap and highly available. However, it is a poor flame retardant and requires high dosage (>40 percent weight) (Albemarle, 2007).

3.3 Next Generation Research and Development of Flame-Retardant Chemicals

Some companies are already offering halogen-free alternatives to TBBPA. In 2008, JJI Technologies, for example, is developing new activated, non-halogen flame-retardant formulations for PCBs – both additive and reactive. An activated flame retardant is one that provides enhanced flame retardancy through the incorporation of an activator, which may consist of either a char-forming catalyst or phase-transfer catalyst or both. Activated flame retardants may improve flame-retardant features, including faster generation of char, higher char yield,

denser char, self-extinguishing performance, thermal insulation, and lower smoke emissions (JJI Technologies, 2007).

In addition to halogen-free alternatives to TBBPA, flame retardant manufacturers have beenexploring ways to achieve a V0 rating in the UL 94 fire test result through the redesign of flame-retardant chemicals and epoxy resin systems. One of the largest areas of research and development involves the use of nanotechnology to impart flame retardancy and increased functionality to PCBs and other electronics products. However, their technical and commercial viability is still limited, and their future use in commercial settings remains unknown. So far, only combinations of nano flame retardants with traditional flame retardants have met performance requirements. In addition, these new nano-traditional flame-retardant combinations are only usable in certain polymer systems.

One type of halogen-free nano flame retardant is being developed through the synthesis of ethylene-vinyl acetate copolymers with nanofillers (or nanocomposites) made of modified layered silicates (Beyer, 2005). Nanofillers are incorporated into the olefin polymer during the polymerization process by treating the surface of the nanofiller to induce hydrophobic tendencies. The hydrophobic nanofiller disperses in the olefin monomers, which then undergo polymerization and trap the nanofillers (Nanocor, 2007). Nanocomposites can also incorporate aluminum into their structures, and can be combined with additive flame retardants, such as ATH, leading to a reduction of the total ATH content and a corresponding improvement in mechanical properties (Beyer, 2005).

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4 Hazard Evaluation of Flame Retardants for Printed Circuit Boards

This chapter summarizes the toxicological and environmental hazards of each flame-retardant chemical that was identified for potential functional use in printed circuit boards (PCBs) laminates. Evaluations of chemical formulations may also include associated substances (e.g., starting materials, by-products, 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 the alternative assessments should be aware of the purity of the trade product they purchase, as the presence of impurities may alter the hazard of the alternative.

Toxicological and environmental endpoints included in the hazard profiles are discussed in Section 4.1 along with the criteria used to evaluate each hazard endpoint. Data sources and the review methodology are described in Section 4.2. The report then offers a detailed description of the utility of physical-chemical properties in understanding hazard in Section 4.3 and the process of evaluating human health and environmental endpoints in Section 4.4 and Section 4.5, respectively. A discussion of the evaluation of endocrine activity is included in Section 4.6. The characteristics of each chemical included in the alternatives assessment are summarized in the comparative hazard summary table in Section 4.8. Lastly, the collected data and hazard profile of each chemical are presented in Section 4.9.

4.1 Toxicological and Environmental Endpoints

The assessment of endpoints with the intent to create hazard profiles for a Design for the Environment (DfE) alternatives assessment follows the guidance of the *DfE Program Alternatives Assessment Criteria for Hazard Evaluation* (U.S. EPA, 2011b). The definitions for each endpoint evaluated following these criteria are outlined in Section 4.1.1 and the criteria by which these endpoints are evaluated are outlined in Section 4.1.2. Lastly, there are endpoints which DfE characterizes but does not assign criteria to and these are summarized in Section 4.1.3.

4.1.1 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 Program Alternatives Assessment Criteria for Hazard Evaluation* (U.S. EPA, 2011b). Table 4-1 provides brief definitions of human health toxicity, environmental toxicity and environmental fate endpoints.

Table 4-1. 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
	Carcinogenicity	Capability of a substance to increase the incidence of malignant neoplasms, reduce their latency, or increase their severity or multiplicity.
	Mutagenicity/Genotoxicity	*Mutagenicity* - 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. *Genotoxicity* – 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.
	Reproductive Toxicity	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.
	Developmental Toxicity	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.
	Neurotoxicity	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
	Repeated Dose Toxicity	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.
	Respiratory Sensitization	Hypersensitivity of the airways following inhalation of a substance.
	Skin Sensitization	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.
	Eye Irritation/Corrosivity	Irritation or corrosion to the eye following the application of a test substance.
	Skin Irritation/Corrosion	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.
Environmental Toxicity	**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).**	
	Aquatic Toxicity (Acute)	The property of a substance to be injurious to an organism in a short-term, aquatic exposure to that substance.
	Aquatic Toxicity (Chronic)	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.
Environmental Fate	**Environmental Persistence**	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 alternative assessments, the amount of time for complete assimilation (ultimate removal) is preferred over the initial step in the transformation (primary removal).
	Bioaccumulation	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, metabolic biotransformation of the parent compound and growth dilution.

The hazard profile for each chemical contains endpoint specific summary statements (see Section 4.9). For each of the endpoints listed in Table 4-1, 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.

4.1.2 Criteria

Table 4-2 summarizes the criteria that were used by the U.S. Environmental Protection Agency (EPA) DfE Program to interpret the data presented in the hazard evaluations. The *DfE Program 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 Program Alternatives Assessment Criteria for Hazard Evaluation*, available at: http://www.epa.gov/dfe/alternatives_assessment_criteria_for_hazard_eval.pdf.

Table 4-2. Criteria Used to Assign Hazard Designations

Endpoint	Very High	High	Moderate	Low	Very Low
Human Health Effects					
Acute mammalian toxicity					
Oral median lethal dose (LD_{50}) (mg/kg)	≤50	>50–300	>300–2000	>2000	–
Dermal LD_{50} (mg/kg)	≤200	>200–1000	>1000–2000	>2000	–
Inhalation median lethal concentration (LC_{50}) - vapor/gas (mg/L)	≤2	>2–10	>10–20	>20	–
Inhalation LC_{50} - dust/mist/ fume (mg/L)	≤0.5	>0.5–1.0	>1–5	>5	–
Carcinogenicity					
Carcinogenicity	*Known or presumed human carcinogen* (equivalent to Globally Harmonized System of Classification and Labeling of Chemicals (GHS) Categories 1A and 1B)	*Suspected human carcinogen* (equivalent to GHS Category 2)	*Limited or marginal evidence of carcinogenicity in animals* (And inadequate evidence in humans)	*Negative studies or robust mechanism-based Structure Activity Relationship (SAR)* (As described above)	–

Endpoint	Very High	High	Moderate	Low	Very Low
Mutagenicity/Genotoxicity					
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 *in vitro* OR *in vivo* 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 *in vitro* AND *in vivo* somatic cells and/or germ cells of humans or animals			
Reproductive toxicity					
Oral (mg/kg/day)	–	<50	50–250	>250-1000	>1000
Dermal (mg/kg/day)	–	<100	100–500	>500-2000	>2000
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
Developmental toxicity					
Oral (mg/kg/day)	–	<50	50–250	>250-1000	>1000
Dermal (mg/kg/day)	–	<100	100–500	>500-2000	>2000
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
Neurotoxicity					
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	–
Repeated-dose toxicity					
Oral (mg/kg/day)	–	<10	10–100	>100	–

Endpoint	Very High	High	Moderate	Low	Very Low
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	–
Sensitization					
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	–
Irritation/corrosivity					
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
Endocrine activity					
Endocrine Activity	*For this endpoint, High/Moderate/Low etc. characterizations will not apply. A qualitative assessment of available data will be prepared.*				
Environmental Toxicity and Fate					
Aquatic toxicity					
Acute aquatic toxicity – LC_{50} or half maximal effective concentration (EC_{50}) (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	–
Environmental persistence					

Endpoint	Very High	High	Moderate	Low	Very Low
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)	*For this endpoint, High/Moderate/Low etc. characterizations will not apply. A qualitative assessment of available data will be prepared.*				
Bioaccumulation					
Bioconcentration Factor (BCF)/Bioaccumulation Factor (BAF)	>5000	5000–1000	<1000–100	<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 4-2) 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 molecular weight (MW) >1,000 daltons, which may result in a Very High designation.

4.1.3 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 4-3. Definitions of Endpoints and Information Characterized but Not Evaluated Against Hazard Criteria

Toxicological Endpoint	Definition
Toxicokinetics	The determination and quantification of the time course of absorption, distribution, biotransformation, and excretion of chemicals (sometimes referred to as *pharmacokinetics*).
Biomonitoring Information	The measured concentration of a chemical in biological tissues where the analysis samples were obtained from a natural or non-experimental setting.
Environmental Transport	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 alternative 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[1].
Persistence in Air	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.

Toxicological Endpoint	Definition
Immunotoxicology	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).
Terrestrial Ecotoxicology	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.
Endocrine Activity	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.)

[1]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).

4.2 Data Sources and Assessment Methodology

This section explains how data were collected (Section 4.2.1), prioritized and reviewed (Section 4.2.2) 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 4.2.3.

4.2.1 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, 1999b) 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 U.S. Environmental Protection Agency (EPA) public databases (e.g., integrated risk information system (IRIS); the High Production Volume Information System) 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 4-2. 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 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 Relationship (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 Program 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, 2005; 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 4.2.3. 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 4.3.

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, 2010c). 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.

4.2.2 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 4.9. 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, 1999b). Studies performed according to Harmonized EPA or Organisation for Economic Cooperation and Development (OECD) 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, or online databases (such as the National Library of Medicine's

Hazardous Substances Data Bank, 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.

4.2.3 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 4.2.1, in the absence of experimental data, estimates were performed using professional judgment as presented in the literature (U.S. EPA, 2010b). 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 alternative 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 4.3.

For the 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 by-products 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.

4.3 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 4.9. For information on how key physical-chemical properties of alternatives can be used to address the potential for human and environmental exposure, please refer to Table 5-2.

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 4.2.3). 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, as described in Chapter 5. 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, 1999b). 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 (see Section 5.2). In the assessment process, chemicals with a vapor pressure less than 1×10^{-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 x 10^{-4} mm Hg generally exist in the gas phase in the atmosphere. Substances with a vapor pressure between 1 x 10^{-4} and 1 x 10^{-8} mm Hg exist as a gas/particulate mixture. Substances with a vapor pressure less than 1 x 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 Earth's surface.

A maximum vapor pressure of 1 x 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, 2011e). The maximum vapor pressure of 1 x 10^{-8} mm Hg was also the default value reported for the vapor pressure of and other materials polymers with a MW >1,000 daltons (U.S. EPA, 2010b).

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 x 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 represents insoluble, noting that these guidelines might not match what is used elsewhere within the scientific literature for other disciplines. Chemicals with higher water solubility were 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 chemicals 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 1×10^{-3} mg/L (U.S. EPA, 2011e). A water solubility of 1×10^{-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 (U.S. EPA, 2010b). 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 4×10^{-7} mg/L (Meylan, Howard et al., 1996; U.S. EPA, 2011i). Given that water solubility decreases with MW, a default value of 1×10^{-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 x 10^{-3} mg/L), a minimum value of 10 was assigned for the log K_{ow} (U.S. EPA, 2011e). 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 1×10^{-7} atm-m^3/mole indicate slow volatilization from water to air (the Henry's Law constant for the volatilization of water from water is 1×10^{-7} atm-m^3/mole) and values more than 1×10^{-3} atm-m^3/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 1×10^{-8} atm-m^3/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 absorbed to soil (U.S. EPA, 2011e). A default K_{oc} of 30,000 was used for polymers and other 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. As noted in Section 4.3, 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_2 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 Section 4.1.2. 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™ models. EPISuite™ estimates the probability for ready biodegradation as well as the potential for primary and ultimate removal, as described in Section 4.3. A default Very High persistence hazard designation was assigned for polymers and other materials with a MW >1,000 daltons according to information contained in the literature concerning polymer assessment (U.S. EPA, 2010b).

4.4 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 4.4.1 discusses how measured data are used to make hazard designations for human health endpoints and Section 4.4.2 presents the approach for filling in data gaps to make these hazard designations.

4.4.1 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 4-2.

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 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[9] 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.

[9] 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, 1999a).

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

4.4.2 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 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 4.2. 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 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 (U.S. EPA, 2010b). 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 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 literature 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). The potential for fibrosis or cancer are not assumed with high MW compounds. 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 by-products 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.

4.5 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 not available, the aquatic toxicity was estimated using EPA's ECOSAR™ software and the persistence designation was estimated using models in EPA's EPISuite™ software. The hazard designation was determined by applying the criteria to these estimates. 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.

4.5.1 Aquatic Toxicity

For ecological 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_{50} 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 where 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™ 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™ 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™ estimation program uses chemical structure to estimate toxicity of a chemical substance using class-specific QSARs. ECOSAR™ 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 (their training set). The hazard profiles report every estimated value returned from ECOSAR™. Narcosis classes (neutral organics) are only provided for comparative purposes if class-specific QSARs are available; the latter will be used preferentially. If multiple class-specific QSARs are available, the hazard designation was based on the most conservative ECOSAR™ estimate, unless expert judgment suggested that an individual substance was better represented by a specific class based on analysis of the operative mode of action. 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™. In their absence, estimated log K_{ow} values from EPISuite™ were used. ECOSAR™ is maintained and developed as a stand-alone program but is also accessible through the EPA EPISuite™ program after it is installed; therefore the Estimations Program Interface (EPI) program was cited for the ECOSAR™ values in this report.

The QSARs for ECOSAR™ were built using experimental data for several chemical classes. For a chemical class to be defined within ECOSAR™, 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 are not available to build a chronic QSAR for some of the three surrogate species. When ECOSAR™ 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).

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).

4.5.2 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 4.1.2). 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 will use 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 (U.S. EPA, 2010b). 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.

4.5.3 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_2, 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 percent. The 10-day window must occur within the 28-day length of the test. If the pass level of the test (60 percent for oxygen demand and CO_2 production; 70 percent 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 4-1). These half-life criteria were also used to assign a hazard designation for nonguideline 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 percent 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 provided 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 was 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) will also be 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 were assigned a High persistence designation in the assessment, as these inorganic moieties are recalcitrant. In this instance, an ‘R’ footnote was 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 included 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.

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

4.6 Endocrine Activity

Chemicals included in DfE alternatives assessments were screened for potential endocrine activity, consistent with the *DfE Program Alternatives Assessment Criteria for Hazard*

Evaluation. **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 4.9. Data on endocrine activity were available for two of the alternatives 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 4-2, 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 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[10]. 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.

[10] 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.

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).

As described in the *DfE Program Alternatives Assessment Criteria for Hazard Evaluation*, 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.

Chemical Alternatives 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 U.S. 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.

TSCA and DfE Alternatives Assessments

Substances selected for evaluation in a DfE Alternatives Assessment generally fall under the 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 U.S. For more information see http://www.epa.gov/oppt/newchems/pubs/whofiles.htm.

To be as inclusive as possible, DfE Alternatives Assessments may consider substances that may not have been reviewed 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 reportability of substances under TSCA, please contact the OPPT Industrial Chemistry Branch at 202-564-8740.

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4.8 Hazard Summary Table

Table 4-4. Screening Level Hazard Summary for Reactive-Flame Retardant Chemicals & Resins

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

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

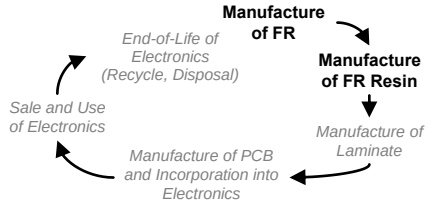
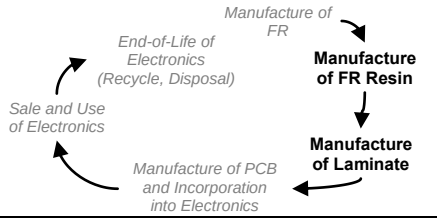
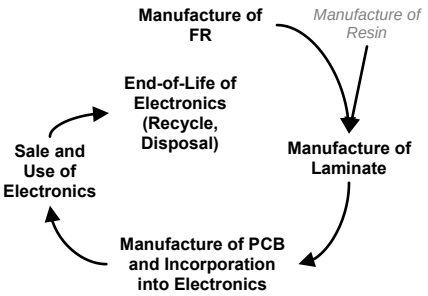
Chemical (for full chemical name and relevant trade names see the individual profiles in Section 4.9)	**CASRN**	**Human Health Effects**											**Aquatic Toxicity**		**Environ-mental Fate**		**Exposure Considerations**
		Acute Toxicity	**Carcinogenicity**	**Genotoxicity**	**Reproductive**	**Developmental**	**Neurological**	**Repeated Dose**	**Skin Sensitization**	**Respiratory Sensitization**	**Eye Irritation**	**Dermal Irritation**	**Acute**	**Chronic**	**Persistence**	**Bioaccumulation**	**Availability of flame retardants throughout the life cycle for reactive and additive flame-retardant chemicals and resins**
Reactive Flame-Retardant Chemicals																	
Tetrabromobisphenol A	79-94-7	L	M	L	L♦	M	L	L	L♦		M	L♦	VH	H	H	M	
DOPO	35948-25-5	L	*M*	L	*L*[§]	*M*	*M*	L	M		M	VL	L	*M*	*H*	*L*	
Fyrol PMP	63747-58-0	L	*L*[§]	*L*[§]	*M*[§]	*M*[§]	*M*[§]	*M*[§]	L		L	L	*H*[‡]	*H*[‡]	*VH*	*H*[‡]	
Reactive Flame-Retardant Resins																	
D.E.R. 500 Series[¥]	26265-08-7	*L*	*M*	*M*	*M*	*M*	*M*	*M*	H		*M*[‡]	*M*[‡]	*L*	*L*	*VH*	*H*[‡]	
Dow XZ-92547[¥]	Confidential	L	*M*[‡]	*M*[§]	*M*[‡]	*M*[‡]	*M*[‡]	*M*[‡]	H	*M*[‡]	VL	L	*L*	*H*	*VH*	*H*[‡]	

Table 4-5. Screening Level Hazard Summary for Additive Flame-Retardant Chemicals

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[R] Recalcitrant: Substance is comprised of metallic species (or metalloids) that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions. [§] Based on analogy to experimental data for a structurally similar compound. [¤]Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter. [^] Depending on the grade or purity of amorphous silicon dioxide commercial products, the crystalline form of silicon dioxide may be present. The hazard designations for crystalline silicon dioxide differ from those of amorphous silicon dioxide, as follows: VERY HIGH (experimental) for carcinogenicity; HIGH (experimental) genotoxicity; MODERATE (experimental) for acute toxicity and eye irritation. [¥] 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 4.9)	CASRN	Human Health Effects											Aquatic Toxicity		Environ-mental Fate		Exposure Considerations
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation	Availability of flame retardants throughout the life cycle for reactive and additive flame-retardant chemicals and resins
Additive Flame-Retardant Chemicals																	
Aluminum Diethylphosphinate[¥]	225789-38-8	L	*L*[§]	L	L	*M*[§]	*M*[§]	*M*[§]	L		L	VL	M	M	*H*[R]	*L*	
Aluminum Hydroxide[¥]	21645-51-2	L	*L*[§]	L	*L*[§]	L	M	*M*[§]	L		VL	VL	L	L	*H*[R]	*L*	
Magnesium Hydroxide[¥]	1309-42-8	L	L	L	L	L	*L*	L	M		M	L	*L*	*L*	*H*[R]	*L*	
Melamine Polyphosphate[1¥]	15541-60-3	L	*M*	*M*	*H*	*M*	*M*	*M*	*L*		L	VL	L	L	*H*	*L*	
Silicon Dioxide (amorphous)	7631-86-9	L[^]	L[^]	L[^]	L	L	*L*[§]	H[¤]	L		L[^]	VL	L	*L*	*H*[R]	*L*	

[1] Hazard designations are based upon the component of the salt with the highest hazard designation, including the corresponding free acid or base.

4.9 Hazard Profiles

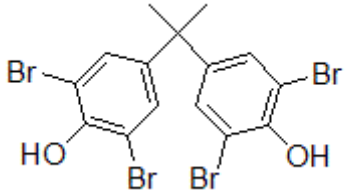
Tetrabromobisphenol A

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

♦ TBBPA has been shown to degrade under anaerobic conditions to form bisphenol A (BPA; CASRN 80-05-7). BPA has hazard designations different than TBBPA, as follows: MODERATE (experimental) for reproductive, skin sensitization and dermal irritation.

		Human Health Effects											Aquatic Toxicity		Environmental Fate	
Chemical	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Tetrabromobisphenol A	79-94-7	L	M	L	L♦	M	L	L	L♦		M	L♦	VH	H	H	M

Tetrabromobisphenol A



CASRN: 79-94-7

MW: 543.88

MF: $C_{15}H_{12}Br_4O_2$

Physical Forms: Solid
Neat: Solid

Use: Flame retardant

SMILES: Oc(c(cc(c1)C(c(cc(c(O)c2Br)Br)c2)(C)C)Br)c1Br

Synonyms: Tetrabromobisphenol A; TBBPA; TBBP-A; 4,4'-Isopropylidenebis(2,6-dibromophenol); 2,2-bis(3,5-dibromo-4-hydroxyphenyl) propane; 3,3',5,5'-tetrabromobisphenol-A; phenol, 4,4'-isopropylidinebis, (dibromo-); 4,4'-(1-methylethylidene)bis(2,6-dibromophenol); 2,2',6,6'-Tetrabromobisphenol A; 2,2-Bis(3,5-dibromo-4-hydroxyphenyl)propane; 2,2-Bis(4-hydroxy-3,5-dibromophenyl)propane

*Trade names:*BA-59P; F-2016; F-2400; F-2400E; FR-1524; Fire Guard FG2000; Firemaster BP 4A; Saytex RB-100; Saytex RB 100PC; Tetrabrom; Tetrabromodian; Bromdian

Chemical Considerations: This is a discrete organic chemical with a MW below 1,000. EPI v 4.11 was used to estimate physical/chemical and environmental fate values in the absence of experimental data. Measured values from experimental studies were incorporated into the estimations. TBBPA is produced by bromination of bisphenol A (BPA). (HSDB, 2013).

Polymeric: No
Oligomeric: Not applicable

Metabolites, Degradates and Transformation Products: TBBPA-glucuronic acid conjugates (mono, di and a mixed glucuronide-sulfate conjugate); TBBPA-sulfate ester conjugates; tribromobisphenol A and glucuronide of tribromobisphenol A were identified as metabolites in experimental studies.

4-isopropyl-2,6-dibromophenol, 4-isopropylene-2,6-dibromophenol and 4-(2-hydroxyisopropyl)-2,6-dibromophenol were identified as major degradation products by UV light photolysis; other reported products include di- and tribromobisphenol A, dibromophenol, 2,6-dibromo-4-(bromoisopropylene)phenol, 2,6-dibromo-4-(dibromoisopropylene)phenol and 2,6-dibromo-1,4-hydroxybenzene. Polybrominated dibenzofurans (PBDF) and dibenzodioxins (PBDD) were identified by pyrolytic degradation. Debromination of TBBPA to tribrominated-BPA, dibrominated-BPA and BPA has been demonstrated in experimental anaerobic biodegradation studies. (Eriksson and Jakobsson, 1998; Eriksson et al., 2004; Ravit et al., 2005; EU, 2006; ACC, 2006b; Roper et al., 2007; Environment Canada, 2013; NTP, 2013)

Analog: None

Analog Structure: Not applicable

Structural Alerts: Phenols, neurotoxicity (EPA, 2010).

Risk Phrases: 50/53 - Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (ESIS, 2012).

Hazard and Risk Assessments: Risk assessments were completed for TBBPA by the European Union in 2006 and Canada in 2013. (EU, 2006; Environment Canada, 2013).

Tetrabromobisphenol A CASRN 79-94-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	179 (Measured)	Ashford, 1994; HSDB, 2013	Reported in a secondary source.
	181 Reported as a range 181-182°C (Measured)	EU, 2006	Study details and test conditions were not stated.
	178 (Measured)	EU, 2006	Reported in a secondary source. Details and test method were not stated.
	181 (Measured)	WHO, 1995; ACC, 2006b	The measurement was performed on a commercial product which was not 100% pure.
	178.35 Reported as 451.5 ± 0.5 K using differential scanning calorimeter (Measured)	Kuramochi et al., 2008	Adequate study details provided. Consistent with other reported values.
Boiling Point (°C)	316 Decomposes (Measured)	Stenger, 1978; WHO, 1995	TBBPA will decompose before boiling based on measurements on a commercial product, which may not have been 100% pure.
	>300 (Estimated)	EPI v4.11; EPA, 1999	Cutoff value for high boiling materials according to HPV assessment guidance.
Vapor Pressure (mm Hg)	4.7×10^{-8} at 25°C Reported as 6.24×10^{-6} Pa (Measured)	BRE, 2009	Valid study with limited details reported.
	$<8.9 \times 10^{-8}$ at 20°C Organisation for Economic Co-operation and Development (OECD) Guideline 104 "Vapor Pressure Curve" Spinning rotor gauge method; reported as $<1.19 \times 10^{-5}$ Pa (Measured)	Lezotte and Nixon, 2001 (as cited in EU, 2006; ACC, 2006b)	Value reported is based on the limit of quantification of the method. The vapor pressure was below the limit of quantification of the method.
	3.54×10^{-11} Reported as 4.72×10^{-9} Pa at 298K using Knudsen effusion method (Measured)	Kuramochi et al., 2008	Adequate study details provided.
	<1	WHO, 1995; Hardy and Smith,	Sufficient study details were not

Tetrabromobisphenol A CASRN 79-94-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	(Measured)	1999	available to assess the quality of this study.
Water Solubility (mg/L)	4.16 (Measured)	Danish EPA, 1999	Limited study details provided.
	0.171 ±0.004 at pH 3.05 4.15 ±0.36 at pH 7.56 30.5 ±1.8 at pH 7.99 228 ±6 at pH 8.48 1,510 ±60 at pH 8.91 27,900 ±400 at pH 9.50 (Measured)	Kuramochi et al., 2008	Reported in a primary source; demonstrates the relationship between the pH conditions and the water solubility of TBBPA as an ionized and non-ionized compound.
	0.72 at 15°C 4.16 at 25°C 1.77 at 35°C (Measured)	WHO, 1995	Study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.
	0.082 at pH 7.6-8.1 (Measured)	Submitted confidential study (as cited in NOTOX, 2000)	The measured water solubility was dependent on the flow rates through the column. The cause of the flow rate dependency is unknown. The flow rate dependency is not caused by a failure to reach equilibrium, since higher flow rates gave higher solubility. The samples were centrifuged to remove dispersed TBBPA.
	0.148 at pH 5 1.26 at pH 7 2.34 at pH 9 (Measured)	Submitted confidential study (as cited in MacGregor and Nixon, 2002; EU, 2006)	Submitted confidential study. The samples were not assessed for the presence of colloidal material before analysis.
Log K_{ow}	4.54 (Measured)	EU, 2006	Reported in a secondary source.
	Generator column method used to evaluate D_{ow}: pH 3.05 = 6.53 ±0.12 (considered non-ionic form) pH 7.53 = 4.75 ±0.07	Kuramochi et al., 2008	Reported in a primary source; demonstrates the relationship between the pH conditions and the octanol-water partition coefficient (log K_{ow}) of TBBPA as an ionized

Tetrabromobisphenol A CASRN 79-94-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	pH 8.12 = 3.00 ±0.03 pH 9.18 = 1.25 ±0.01 pH 10.19 = -0.293 ±0.020 pH 10.95 = -0.769 ±0.023 pH 11.83 = -1.22 ±0.00 (Measured)		and non-ionized compound.
	4.5 (Measured)	Danish EPA, 1999	Valid study reported in a secondary source.
	<4 (Measured)	EU, 2006	Reported in a secondary source. Study details and test conditions were not available.
	6.4 HPLC method (Measured)	EU, 2006	Reported in a secondary source. Limited study details available.
	3.25 (Measured)	EU, 2006	Reported in a secondary source.
	5.903 Reported as 5.90 ± 0.034; method based on USEPA Product Properties Test Guideline OPPTS 830.7560. (Measured)	MacGregor and Nixon, 2001 (as cited in EU, 2006)	Reported in secondary source.
	5.3 Reported as a range: 4.5-5.3 (Measured)	WHO, 1995	Study details and test conditions were not available.
Flammability (Flash Point)	Not flammable (Measured)	ICL, 2013	Reported in safety datasheet and based on its use as a flame retardant.
Explosivity	Dust Explosivity: Maximum Explosion Pressure (P_{max}) = 7.7 bar; Maximum Rate of Pressure Rise (dP/dt)max = 379 bar/s; K_{st} value = 103 bar.m/s (weak explosion) (Measured)	Churchwell and Ellis, 2007	Adequate supporting information provided.

Tetrabromobisphenol A CASRN 79-94-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Pyrolysis	Under certain high temperature pyrolysis conditions, TBBPA can form and release brominated dibenzofurans (PBDF) and dibenzo-p-dioxins (PBDD). (Measured)	EU, 2006	Adequate.
	Purified TBBPA was pyrolyzed in open quartz tubes for 10 minutes resulting mainly in mono-, di-, tri- and tetra-PBDD and PBDF. The formation of PBDD and PBDF occurred at 0.02, 0.16, and 0.1% for 700, 800, and 900°C. (Measured)	WHO, 1995	Adequate.
pH			No data located.
pK_a	9.4 Method based on OECD Guideline 112. (Measured)	Lezotte and Nixon, 2002; EU, 2006; ACC, 2006b	Adequate guideline study.
	pK_{a1} = 7.5 pK_{a2} = 8.5 (Measured)	WHO, 1995; EU, 2006	Study details and test conditions were not available. Reported in a secondary source.
Particle Size			No data located.

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Toxicokinetics		**A laboratory study using human skin indicates TBBPA is not well absorbed dermally. The results indicated 0.73% of the applied dose penetrated through the skin. Oral administration to rats showed that TBBPA is rapidly metabolized and eliminated in the feces (>80%). TBBPA and metabolites were detected in plasma and traces of TBBPA and metabolites were detected in urine (glucuronic acid and sulfate ester conjugates). The estimated bioavailability following oral dosing is 1.6%. Human volunteers had no detectable TBBPA in plasma following ingestion of low doses; however, TBBPA metabolites (TBBPA-glucuronide, TBBPA-sulfate) were detected. TBBPA-glucuronide (25% of the administered dose) was the only metabolite detected in the urine. TBBPA has been detected in breast milk; although a study in pregnant rats indicates that there is no significant transfer of TBBPA or its metabolites to the fetus (total amount of radioactivity in the fetus was approximately 0.34% of the administered dose).**		
Dermal Absorption *in vitro*		Human split-thickness skin: Absorbed dose = 0.73% applied dose (14.06 µg/cm^2); Dermal delivery = 1.60% applied dose (32.05 µg/cm^2)	Roper, 2005; Roper et al., 2007	Sufficient study details reported in primary source.
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	Distribution of TBBPA and its conjugates was observed in pregnant rats fed 0, 100, 1,000 or 10,000 ppm from gestational day (GD) 0-16. Free-TBBPA detected in blood, liver and kidney of dams and amniotic fluid on GD10 and in the placenta and amniotic fluid in fetuses on GD16. Free-TBBPA was also found in the stomach of suckling pups from dams in the high dose group. Conjugated TBBPA was detected in the liver and kidney and suckling pups.	Fujitani et al., 2007	Insufficient study details; study is in Japanese with English abstract.
		Male rats exposed to TBBPA via i.v. injection (20 mg/kg), single oral bolus (2, 20 or 200 mg/kg) or repeated daily oral doses (20 mg/kg for 5-10 days). TBBPA is absorbed from the intestinal tract, but is extracted and metabolized by the liver to glucuronides that are exported into the bile.	Solyom et al., 2006	Sufficient study details reported in primary source.

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Intravenous injection: half-life in blood was 82 minutes at a clearance rate of 2.44 mL/min. Major route of elimination was the bile/feces; 82% eliminated within 36 hours; 0.5% eliminated in the urine. Single oral bolus: 90-106% eliminated in feces within 72 hours; 2% in urine. Repeated dose: 85-98% eliminated in feces		
		In an intraperitoneal injection study in rats, peak concentrations of ^{14}C-TBBPA were found in all tissues within an hour; highest concentrations found in fat followed by the liver, sciatic nerve, muscles, and adrenals. A small amount of the administered dose was retained after 72 hours in fatty tissue and muscle (3-6% and 11-14%, respectively). It has also been observed that unmetabolized TBBPA is rapidly excreted in feces (51-95% of the administered dose) following single exposure (route not specified).	Birnbaum and Staskal, 2004	Adequate study details reported in a secondary source.
		The half-life of TBBPA was estimated to be 2 days in Swedish workers engaged in the recycling process.	Sjodin et al., 2003	Adequate study details reported in a secondary source.
		TBBPA was poorly absorbed in the gastrointestinal tract in rats following single oral administration. Approximately 95% of the administered dose was eliminated in feces and <1% was eliminated in urine within 72 hours. Levels in tissues were highest in the liver and gonads. The maximum half-life in	WHO, 1995	Summary information from an unpublished study.

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		any tissue was <3 days.		
		Placental transfer of hydroxylated BFRs was observed in rats orally dosed with test compounds (including TBBPA) on gestation days (GDs) 10-16. There were no associated developmental effects at the dose used in the study (25 mg/kg).	Buitenhuis et al., 2004	Sufficient study details reported in primary source.
		TBBPA has been detected in breast milk, although a study in pregnant rats indicates that there is no significant transfer of TBBPA or its metabolites to the fetus (total amount of radioactivity in the fetus was approximately 0.34% of the administered dose).	EU, 2006	Summary of various studies in a secondary source.
		Only an extremely small percentage of TBBPA particles are expected to be small enough (1-2 µm) to be deposited into the rat lung following inhalation. Particles that do not reach the alveolar region are expected to be exhaled. The remainder will deposit in the respiratory tract, will be swallowed and absorbed by the gastrointestinal tract (70% absorbed by gastrointestinal tract, <4% absorbed through the lungs).	EU, 2006	General information summarized in a secondary source.
		Recovery of TBBPA (measured as radioactivity) following single oral administration to rats: Feces: 90-95% Urine: <1% Tissues: 0.4% (Measured) Recovery of TBBPA (measured as radioactivity) following repeated oral administration to rats (1, 5 or 10 days): Feces: 82-98%	ACC, 2006b; Kuester et al., 2007	Sufficient study details reported in primary source.

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Urine: <0.5% Tissues: <1% Unexcreted intestinal contents: 1-10%. The rats were sacrificed 24 hours after the last dose. (Measured) Following oral administration of ^{14}C-TBBPA to rats, 47% and 51% of the dose was excreted in the bile within 2 hours, primarily as 2 metabolites: TBBPA-glucuronide and TBBPA-diglucuronide. Estimated systemic bioavailability after oral dosing: 1.6%		
		In a single dose study in rats, TBBPA was rapidly metabolized following oral administration of 300 mg/kg. Primary metabolites were TBBPA-glucuronide and TBBPA-sulfate. Diglucuronide of TBBPA (a mixed glucuronide-sulfate conjugate of TBBPA), tribromobisphenol A, and the glucuronide of tribromobisphenol A were also present in low concentrations. A peak plasma concentration of 103 µmol/L was achieved within 3 hours with an elimination half-life of 13 hours. Fecal excretion of unchanged TBBPA was the major excretory pathway with (>80%).	Schauer et al., 2006 (as cited in ACC, 2006b)	Sufficient study details reported in primary source.
		In a single dose study in humans (3 males, 2 females), TBBPA was rapidly metabolized following oral administration via gel capsule of 0.1 mg/kg. Primary metabolites were TBBPA-glucuronide and TBBPA-sulfate. Only TBBPA-glucuronide was detected in the urine; approximately 25% of the administered	Schauer et al., 2006 (as cited in ACC, 2006b)	Sufficient study details reported in primary source.

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		dose was eliminated in urine.		
		In a single oral dose and bile-cannulated rat study, TBBPA was readily absorbed, metabolized and eliminated within 72 hours after dosing of male Sprague-Dawley rats. Excretion in oral dosing study: 91.7% in feces, 0.3% in urine. Residue in tissue was 2% of dose (Primarily large and small intestines). Excretion in bile-duct cannulated rat: 26.7% in feces, 71.3% in bile, <1% residue in tissues. Primary metabolites: Glucuronic acid and sulfate ester conjugates. Over 95% of extractable fecal ^{14}C was parent TBBPA.	Hakk et al., 2000 (as cited in ACC, 2006b; EU, 2006; NTP, 2013)	Sufficient study details reported in primary source.
		Rapid clearance of [^{14}C]-labeled TBBPA from the blood of male F344 or female Wistar Han rats; single oral or intravenous administration. T_{max} of ^{14}C in blood was observed at 32 ± 19 minutes in male rats (200 mg/kg fasted) and 114 ± 42 minutes in females (250 mg/kg nonfasted). Terminal half-lives were > 5 hours and systemic bioavailability was < 5%.	Knudsen et al., 2013 Kuester et al., 2007 (as cited in NTP, 2013)	Sufficient study details reported in NTP technical report.
		No accumulation of TBBPA in tissues of male Sprague-Dawley rats receiving 1,000 mg/kg for 14 consecutic ve days.	Kang et al., 2009 (as cited in NTP, 2013)	Sufficient study details reported in NTP technical report.
	Other	TBBPA was present in breast milk, and both maternal and fetal serum samples in two studies, indicating a possible risk of overexposure of newborns through breastfeeding.	Antignac et al., 2008; Cariou et al., 2008	Sufficient information in primary sources.
		In bile-cannulated rats, 71% of administered TBBPA was excreted in the	Birnbaum and Staskal, 2004	Sufficient information in review.

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		bile. Metabolites found in bile were a diglucuronide, a monoglucuronide, and a glucuronide-sulfate ester.		
Acute Mammalian Toxicity		**LOW: Experimental studies indicate TBBPA, administered orally to rats and mice at levels up to 50,000 and 10,000 mg/kg, respectively, and TBBPA administered dermally to rabbits at levels up to 10,000 mg/kg does not produce substantial mortality. Data from located inhalation studies are not sufficient to consider for the hazard designation.**		
Acute Lethality	**Oral**	Rat oral LD_{50} >50 mg/kg (range finding study in rats (2 rats/group) administered 0.5 - 50 mg/kg)	Sterner, 1967c	Limited study details reported in an unpublished study.
		Rat oral LD_{50} >2,000 mg/kg - >50,000 mg/kg	Doyle and Elsea, 1966; WHO, 1995; EU, 2006	Sufficient study details reported.
		Mouse oral LD_{50} 3,200 mg/kg - >10,000 mg/kg	Dean et al., 1978b (as cited in WHO, 1995; EU, 2006)	Limited information in secondary sources. Sufficient information in unpublished study.
		Rat oral LD_{50} >5,000 mg/kg	Mallory et al., 1981b (as cited in EU, 2006; ECHA, 2013)	Sufficient data in unpublished study conducted in accordance with good laboratory practices (GLP).
		Mouse oral LD_{50} >7,000 mg/kg	ECHA, 2013	Pre-dates standard guidelines and GLP; no analytical verification of test material; unequal amounts of vehicle administered; no vehicle control.
		Mouse oral LD_{50} >10,000 mg/kg	ECHA, 2013	Pre-dates standard guidelines and GLP; no analytical verification of test material; unequal amounts of vehicle administered; no vehicle control.
	Dermal	Rabbit dermal LD_{50} >2,000 mg/kg	WHO, 1995	Limited study details reported in a secondary source.
		Guinea pig dermal LD_{50} >1,000 mg/kg	WHO, 1995	Limited study details reported in a secondary source.
		Rabbit dermal LD_{50} >2 g/kg (2,000 mg/kg)	ECHA, 2013	Sufficient information in an unpublished study conducted in

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				accordance with GLP.
		Rabbit dermal LD_{50} >10,000 mg/kg	Doyle and Elsea, 1966 (as cited in EU, 2006; ECHA, 2013)	Sufficient study details reported in unpublished studies.
	Inhalation	Rat, mouse, guinea pigs 8-hour aerosol inhalation $LC_{50} \geq 0.5$ mg/L (whole-body, aerosol)	Sterner, 1967b (as cited in EC, 2000; EU, 2006)	Inadequate unpublished study, due to short observation period (2 days) and because the particle size of the aerosol was not measured.
		Rat 1 hour inhalation LC_{50} >57 mg/L (whole body, vapor)	ECHA, 2013	No GLP data; methodology predates or was not conducted according to standardized guidelines; no analytical verification of test compound concentrations.
		Rat 1-hour inhalation LC_{50} >1,267 ppm (whole-body)	Doyle and Elsea, 1966 (as cited in EU, 2006)	Inadequate, methodological deficiencies (lack of analysis of the test atmosphere and stability of the test compound) raise uncertainties as to the reliability of this study.
Carcinogenicity		**MODERATE: There is evidence of increased incidences of tumors of the uterus in female rats and interstitial cell adenoma of the testes in male rats orally exposed to TBBPA for up to 105 weeks. There were also increased incidences of tumors in male mice (hepatoblastoma and combined incidence of hepatocellular carcinoma or hepatoblastoma of the large intestine and hemangiosarcoma in all organs); however, there was no evidence of carcinogenicity reported in female mice. In addition, a marginal concern was estimated based on structure-activity relationships and functional properties. The mechanism of action of TBBPA carcinogenicity is not clearly understood. While there was some evidence of carcinogenicity in animals (in male and female rats and male mice, but not in female mice), there is inadequate evidence of carcinogenicity in humans.**		
	OncoLogic Results	Marginal; likely to have equivocal carcinogenic activity.	OncoLogic, 2008	Estimated by OncoLogic based on structure-activity relationships and functional properties.
	Carcinogenicity (Rat and Mouse)	2-year oral gavage carcinogenicity study; B6C3F1/N mice (50/sex/dose) were administered 0, 250, 500, or 1,000 mg/kg-day 5 days/week for up to 105 weeks. Survival was decreased at 1000 mg/kg-day, and therefore, effects are not reported	NTP, 2011; NTP, 2012; NTP, 2013	Sufficient study details reported.

Tetrabromobisphenol A CASRN 79-94-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		for this dose. There was an increase in incidence of multiple hepatocellular adenomas in male mice in the 500 mg/kg-day dose group. Increased incidence of hepatoblastoma and combined incidence of hepatocellular carcinoma or hepatoblastoma were reported in male mice in the 250 mg/kg-day dose group when compared to controls. Also, a significant increased positive trend in the incidence of adenoma or carcinoma (combined) was seen in the large intestine in males. In addition, there was a significant trend for increased incidence of hemangiosarcoma in all organs in male mice. There was no evidence of carcinogenicity in female mice.		
		2-year oral gavage carcinogenicity study; Wistar Han rats (50 or 60/sex/dose) were administered 0, 250, 500, or 1,000 mg/kg-day 5 days/week for up to 105 weeks. There was a slight increase in incidence of interstitial cell adenoma of the testis in male rats (1/50 at 500 mg/kg-day; 3/50 at 1,000 mg/kg-day) as compared to controls (0/50). There was a significant increase in the incidences of adenomas and carcinomas of the uterus in female rats at 500 and 1,000 mg/kg-day compared to controls. There was also an increased combined incidence of adenoma, adenocarcinoma, and malignant mixed Mullerian tumor of the uterus at these dose groups (3/50, 7/50, 11/50, 13/50 in the 0, 250, 500, and 1,000 mg/kg-day	NTP, 2013	Sufficient study details reported.

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		groups, respectively).		
	Combined Chronic Toxicity/Carcinogenicity			No data located.
	Other	Negative in a tumor promotion study in male F344 rats exposed *in utero* and directly via drinking water for 2 weeks after weaning.	CCRIS, 2013	Limited study details reported in a secondary source.
Genotoxicity		**LOW: Experimental studies indicate that TBBPA is not genotoxic to bacterial, mammalian, or yeast cells *in vitro*. TBBPA was negative in a micronucleus test in mice *in vivo*.**		
	Gene Mutation *in vitro*	Negative, *Salmonella typhimurium* strains TA98, TA100, TA1535, or TA1537, or *E. coli* strain WP2 *uvr*A/pKM101, with or without metabolic activation.	NTP, 2013	Sufficient study details reported in NTP technical report.
		Negative, several Ames assays in *Salmonella typhimurium* strains TA92, TA98, TA100, TA1535, TA1537 and TA1538 with and without metabolic activation. Positive controls responded as expected.	Brusick and Weir, 1976; Jagannath and Brusick, 1977; Simon et al., 1979; Curren et al., 1981; WHO, 1995; EC, 2000; Darnerud, 2003; EU, 2006	Sufficient information in secondary sources and unpublished reports.
		Negative, several gene mutation assays in yeast (*Saccharomyces cerevisiae* D3 and D4) with and without metabolic activation. Positive controls responded as expected.	Brusick and Weir, 1976; Jagannath and Brusick, 1977; Simon et al., 1979; WHO, 1995	Sufficient information in secondary sources and unpublished reports.
		Negative, induction of intragenic recombination in two *in vitro* mammalian cell assays. No information was provided regarding positive controls.	Simonsen et al., 2000; Darnerud, 2003	Limited data in secondary sources.
	Gene Mutation *in vivo*			No data located.
	Chromosomal Aberrations *in vitro*	Negative, chromosomal aberration in human lymphocytes. Positive controls responded as expected.	Gudi and Brown, 2001 (as cited in EU, 2006)	Sufficient information in primary source.

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	Chromosomal Aberrations *in vivo*	No increases in micronucleated normochromatic erythrocytes in B6C3F1/N mice administered TBBPA via oral gavage for 3 months.	NTP, 2013; NTP, 2012	Sufficient study details reported in NTP technical report.
	DNA Damage and Repair			No data located.
	Other			No data located.
Reproductive Effects		**LOW: Experimental studies indicate TBBPA, administered orally to rats, produces no adverse effects on reproductive performance or outcomes at levels up to 3,000 mg/kg-day. In some studies there were changes in testis weights at low doses; the significance of these changes on testicular function is unclear given the limitations of the studies.**		
	Reproduction/Developmental Toxicity Screen	In a dietary study, pregnant rats (8/group) were fed 0, 100, 1,000, or 10,000 ppm (~17, 149, and 1,472 mg/kg-day) TBBPA (>98% pure) on GD 10 until day 20 after delivery. There was no evidence of maternal toxicity during the study. Treatment with TBBPA did not affect the number of implantation sites. No other reproductive endpoint was assessed. NOAEL: 10,000 ppm (~1,472 mg/kg-day, highest dose tested) LOAEL: Not established	Saegusa et al., 2009	Sufficient study details reported in primary source, but limited reproductive data. Doses are TWA for mean intakes of TBBPA during GD 10-20, PND 1-9, and post natal days [PND10-20) estimated by the investigators.
		In a dietary study, rats (8-13 males and 6-10 females/group) were fed 0, 3, 10, 30, 100, 300, 1,000 and 3,000 mg/kg-day TBBPA (98% pure) for 11 weeks (males) or 2 weeks during premating and throughout pregnancy and lactation (females). Dosing continued in F_1 offspring after weaning until necropsy at approximately 6 weeks of age. Decreased body weight in dams at highest dose. No adverse effect on number of litters, number of implantation sites or number of	Van der Ven et al., 2008	Sufficient details provided in the primary source. Doses were estimated by the investigators. As stated in the study, dose-response analysis of effects based on external dosing (mg/kg-day) was done using a nested family of purely descriptive (exponential) models with the PROAST software. The method enables integrated evaluation of the complete data set. From the best fitted curve, indicated by

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		pups per litter. Increased testicular and pituitary gland weights in F_1 males (with BMDL values of 0.5 and 0.6 mg/kg-day). No other effect on F_1 gonads wes seen. Other reproductive-related effects in offspring were seen only at high doses (e.g., decrease in anogenital distance in females seen at day 7 only but not at day 4 or day 21; number of days until vaginal opening). BMDLs for these effects are 2736 and 2745 mgkg-day, respectively.		significance at the 5% level, a critical effect dose (CED) was calculated most often using a critical effect size of 10%; there has been some criticism of the modeling and methodology used for this study along (Banasik et al. 2009).
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects	20-Week, 2-generation reproductive assay, rats (30/sex/group), administered TBBPA via oral gavage at 0, 10, 100 or 1,000 mg/kg-day. No effects on reproductive performance or outcomes. NOAEL: 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	ACC, 2002	Sufficient details provided in primary source.
		2-generation drinking water study in mice administered TBBPA dissolved in water at a concentration of 200 µg/L. This provided a dose of 0.035 mg TBBPA/kg-day (reagent grade) based on body weight and daily water consumption (estimated by the investigators). In the parental generation, only females were exposed during gestation; In the F_1 generation,	Zatecka et al., 2013	Study is inadequate because only one dose level was tested. Unknown toxicological significance of alterations reported; therefore, study was not used for hazard classification.

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		pups were exposed to TBBPA during gestation, lactation, pre-pubertal and pubertal period, and up to adulthood. No adverse effect on progeny or sex ratio in either generation. Significantly reduced testicular weight, increased prostate and seminal vesicle weight. No visible abnormalities or pathological changes in the morphology of seminiferous tubules. Significantly increased number of apoptotic cells in the testes and increased expression pattern of genes encoding proteins important during spermatogenesis (F_1 generation).		
	Other	Male rats were administered 0, 10, 100 and 1,000 µg/kg (0, 0.01, 0.1, 1 mg/kg) TBBPA via subcutaneous injection on postnatal day (PND) 1-10. Increased preputial gland weight; decreased averages of preleptotene spermatocyte, pachytene spermatocyte and round spermatid; decreased cauda epididymal sperm reserves. These effects were not statistically different from controls.	Tada et al., 2005	Study in Japanese with English summary.

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Developmental Effects		**MODERATE: Based on several studies reporting potentially adverse effects in the range of moderate to high hazard designations with effects on kidney, liver, thyroid and brain endpoints. Some of the studies with effects in moderate to high hazard range have limitations in experimental design and/or statistical methods but cannot be completely dismissed. A number of studies indicate no effects up to relatively high oral or dietary doses of TBBPA. Based on this weight of evidence, a moderate hazard designation is assigned.** **Evidence of potential for moderate or high developmental toxicity:** **Nonstandard experimental studies indicate TBBPA, administered orally, produces adverse hepatic effects (very slight focal hepatocyte necrosis and enlargement of hepatocytes) at 140.5 mg/kg-day (NOAEL = 15.7 mg/kg-day) in mouse pups and kidney effects (polycystic lesions associated with the dilatation of the tubules) at 200 mg/kg-day (NOAEL = 40 mg/kg-day) in rats postnatally exposed from PND 4-21. Increased hearing latencies (most likely related to impairment of the development of the upper (apical) part of the cochlea) were reported in a dietary 1-generation study at a $BMDL_{10}$ of 8 mg/kg-day. There were also changes in plasma thyroid hormone levels (decreased TT4 at $BMDL_{10}$ of 30-60 mg/kg-day, and increased TT3 at $BMDL_{10}$ of 5 mg/kg-day) in rat fetuses. Alterations in pup development were observed following administration of TBBPA in the diet to pregnant rats at a dose of 10,000 ppm (NOAEL = 1,000 ppm). These effects included increase in interneurons in the dentate hilus-expressing reelin suggestive of aberration of neuronal migration. Cholinergic effects were observed in neonatal NMRI mice administered TBBPA at doses up to 11.5 mg/kg body weight (highest dose tested) on postnatal (PND) 10.** **Evidence of low developmental toxicity:** **Six oral exposure studies with rats and one with mice using standard exposure scenarios showed no effects in a range of endpoints including body weight, clinical signs, organ weights, alterations in development of the fetus, neonatal viability and growth, onset of puberty, estrous cycles, organ histology and brain morphometry at doses ranging from 1,000 to 10,000 mg/kg-day. Two studies with rats using oral exposure to relatively low doses (<10 mg/kg-day) of TBBPA showed no changes in thyroid and sperm endpoints.**		
	Reproduction/ Developmental Toxicity Screen			No data located.

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	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen	20-Week, 2-generation developmental neurotoxicity and neuropathology assay, rats, administered TBBPA via oral gavage at 0, 10, 100 or 1,000 mg/kg-day. Treatment with TBBPA did not induce significant alterations in F_1 or F_2 pups regarding body weight, clinical signs, survival to weaning, or organ weight data. F0 rats exhibited a decrease in T3 at 1000 mg/kg. Decreases in T4 were seen in F0 rats and in F1 offspring at 100 and 1000 mg/kg-day. NOAEL (developmental): 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	ACC, 2002	Sufficient study details provided in primary source.

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	Prenatal Development	In a nonstandard assay for gestational and lactational exposure, mice (6/group) were fed 0, 0.01, 0.1 or 1.0% TBBPA (99.1% pure) in the diet from GD 0 to postnatal day (PND) 27. Approximate daily doses were 15.7, 140.5 or 1,639.7 mg/kg-day for gestational period (GD0-17) and 42.1, 379.9 or 4,155.9 mg/kg-day for lactational period (PND0-21). No standard developmental effects. Very slight focal hepatocyte necrosis and enlargement of hepatocytes (female pups) were seen at 140.5 / 379.9 mg/kg-day and higher. NOAEL: 15.7 mg/kg-day during gestation and 42.1 mg/kg-day during lactation LOAEL: 140.5 mg/kg-day during gestation and 379.9 mg/kg-day during lactation based on very slight focal hepatocyte necrosis and enlarged hepatocytes	Tada and Fujitani, 2006	TWA doses can be estimated for the combined gestational and lactational periods as 32, 287, and 2,614 mg/kg-day for the 0.01, 0.1, and 1% dietary groups, respectively. The TWA developmental LOAEL would be 287 mg/kg-day. Study limitations include statistical deficiencies due to the failure to control for litter effects. Littermates were utilized as independent variables for the experimental and statistical analysis. The tendency of littermates to respond more similarly to one another than non-litter mates was not taken into account.
		In a dietary study, pregnant rats were fed 0, 100, 1,000, or 10,000 ppm (~17, 149, and 1,472 mg/kg-day) TBBPA on GD 10 until day 20 after delivery. Treatment with TBBPA did not result in maternal toxicity. Maternal exposure to TBBPA did not affect the number of live offspring, birth weight, anogenital distance (AGD) on postnatal day (PND) 1, neonatal viability and growth, or organ histology on PND 20, onset of puberty (males and females), estrous cycle, or organ histology and brain morphometry on post-natal week 11.	Saegusa et al., 2009	Sufficient details provided in primary source. Doses are TWA for mean intakes of TBBPA during GD 10-20, PND 1-9, and PND 10-20) estimated by the investigators.

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		NOAEL (developmental): 10,000 ppm (~1,472 mg/kg-day, highest dose tested) LOAEL: Not established		
		Pregnant rats (25/group) were orally administered 0, 100, 300 and 1,000 mg/kg TBBPA by gavage on gestation days (GDs) 0-19; sacrifices were conducted on GD 20. There were no toxicologically significant maternal effects and no adverse developmental effects. NOAEL (maternal and developmental): 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	MPI Research 2001 (as cited in EU, 2006)	Sufficiently detailed summary of results in secondary source.
		Pregnant rats were orally administered 0, 280, 830 and 2,500 mg/kg-day TBBPA by gavage throughout gestation. No toxicologically significant maternal effects were observed. There were no significant alterations in the development of fetuses examined on GD 20 or on pups monitored up to postnatal day (PND) 21. NOAEL (maternal and developmental): 2,500 mg/kg-day (highest dose tested) LOAEL: Not established	Noda et al., 1985 (as cited in EU, 2006)	Sufficiently detailed summary of results in secondary source.
		Pregnant rats (5/group) were orally administered 0, 30, 100, 300, 1,000, 3,000 and 10,000 mg/kg TBBPA by gavage on GDs 6-15. Sacrifices were conducted on GD 20. Maternal deaths occurred with the highest dose, but there were no adverse developmental effects. NOAEL (maternal): 3,000 mg/kg-day	Goldenthal et al., 1978 (as cited in EC, 2000; Simonsen et al., 2000)	Sufficiently detailed summary of results in primary source.

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		LOAEL (maternal): 10,000 mg/kg-day based on mortality NOAEL (developmental): 10,000 mg/kg-day (highest dose tested) LOAEL (developmental): Not established		
		Pregnant rats were orally administered ^{14}C-TBBPA (5 mg/kg) on gestation days (GDs) 10-16 and were sacrificed on GD 20. No effect on plasma total and free T4 levels in dams and fetuses and on maternal total and T3 levels. Significant increase (196%) in TSH levels in fetuses' plasma (but not in dams). TBBPA did not seem to bind to transthyretin (TTR) *in vivo*.	Darnerud, 2003	Limited scope study. Use of a single dose level precludes drawing firm conclusions.
	Postnatal Development	In a nonstandard assay for postnatal exposure, newborn rats (6/sex/group) were orally administered 0, 40, 200 and 600 mg/kg-day TBBPA (99.5% pure) by gavage from day 4-21 after birth and were sacrificed after the last dose. Kidney effects (polycystic lesions associated with dilatation of the tubules) evident at ≥ 200 mg/kg-day. NOAEL: 40 mg/kg-day LOAEL: 200 mg/kg-day (based on polycystic lesions, dilation of tubules in kidneys)	Fukuda et al., 2004	Sufficient details in primary source.
		Male rats were administered 0, 10, 100 and 1,000 µg/kg (0, 0.01, 0.1, 1 mg/kg) TBBPA via subcutaneous injection on postnatal days (PNDs) 1-10. Increased preputial gland weight; decreased averages of preleptotene spermatocyte,	Tada et al., 2005	Study in Japanese with English abstract.

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		pachytene spermatocyte and round spermatid; decreased cauda epididymal sperm reserves. These effects were not statistically different from controls. NOAEL: 1 mg/kg bw-day (highest dose tested) LOAEL: Not established		
		In 5-week old rats administered 0, 2,000 or 6,000 mg/kg-day TBBPA for 18 days, no adverse effects were observed. NOAEL: 6,000 mg/kg-day (highest dose tested) LOAEL: Not established	Fukuda et al., 2004	Sufficient study details reported in a primary study.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity	Pregnant Sprague Dawley rats were exposed to 0, 100, 1,000 or 10,000 ppm TBBPA in the diet from GD 10 through day 20 after delivery (weaning). Alterations in pup brain development on postnatal day (PND) 20 (increase in interneurons in the dentate hilus-expressing reelin suggestive of aberration of neuronal migration) in pups from the high dose group. NOAEL: 1,000 ppm (~80 mg/kg-day) LOAEL: 10,000 ppm (~800 mg/kg-day) based on alterations in pup brain development	Saegusa et al., 2012 (as cited in NTP, 2013)	Sufficient study details reported in NTP technical report. Doses were reported as ppm in the diet but were converted to mg/kg/day using EPA 1988 reference values for body weight and food consumption.
		Newborn rats (6/sex/group) were administered 0, 40, 300, or 600 mg/kg-day TBBPA (99.5% pure) by gavage on postnatal days (PNDs) 4 through 21. No	Fukuda et al., 2004	Qualitative observations only.

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		significant effects on a variety of reflexes tested on postnatal day 21. NOAEL: 600 mg/kg-day (highest dose tested) LOAEL: Not established		
		TBBPA administered to male neonatal NMRI mice at single oral doses of 0, 0.75, or 11.5 mg/kg body weight on postnatal (PND) 10; No neurotoxicity, changes in spontaneous motor behavior, or clinical signs of dysfunction; however, cholinergic effects were observed. NOAEL: 0.75 mg/kg LOAEL: 11.5 mg/kg (based on cholinergic effects)	Viberg and Eriksson, 2011 (as cited in NTP, 2013)	Sufficient study details reported in NTP technical report. Study limitations include statistical deficiencies due to the failure to control for litter effects.
		Sprague-Dawley rats administered TBBPA at doses of 0, 100, 1,000 or 10,000 ppm in a soy-free diet from GD 10 - postnatal day (PND) 20. Slight decrease in serum T3 concentrations in pups on PND 20; however, no evidence for developmental brain effects. NOAEL: 10,000 ppm (~1,472 mg/kg-day; highest dose tested) LOAEL: Not established	Saegusa et al., 2009	Sufficient study details reported in primary source.
		In a dietary study, rats (8-13 males and 6-10 females/group) were fed 0, 3, 10, 30, 100, 300, 1,000, or 3,000 mg/kg-day TBBPA (98% pure) for 11 weeks (males) or 2 weeks during premating and throughout pregnancy and lactation for females (doses estimated by the investigators). After weaning, dosing of F_1	van der Ven et al., 2008; Lilienthal et al. (2008)	As stated in the study, dose-response analysis of effects based on external dosing (mg/kg-day) was done using a nested family of purely descriptive (exponential) models with the PROAST software. The method enables integrated evaluation of the complete data set.

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		continued for life. Neurobehavioral testing was conducted between postnatal days (PNDs) 50 and 140. Increase in hearing latencies were seen, with a $BMDL_{10}$ calculated to be 8 mg/kg-day. Other changes in auditory responses using other types of measures resulted in higher BMDL values. Changes in plasma thyroid hormone levels were seen, with decreased T4 at $BMDL_{10}$ of 30.8 mg/kg-day (males) and 16.1 mg/kg-day (females). Increased T3 levels were seen in female offspring, with a $BMDL_{10}$ of 2.3 mg/kg-day. Increases in pituitary gland and testis weights were seen in male F1 offpring (with BMDLs of 0.6 and 0.5 mg/kg-bw/day, respectively). Other offspring effcts (e.g., changes in body weight) were seen at much higher doses and not necessarily seen throughout the study.		From the best fitted curve, indicated by significance at the 5% level, a critical effect dose (CED, also referred as Benchmark Dose) was calculated most often using a critical effect size of 10%; there has been some criticism of the modeling and methodology used for this study along with noted study limitations not consistent with recommended study guidelines (Banasik et al. 2009; Strain et al. 2009; comparison with OPPTS 870.6855).
		20-Week, 2-generation developmental neurotoxicity and neuropathology assay, rats, administered TBBPA via oral gavage at 0, 10, 100 or 1,000 mg/kg-day. No significant neurobehavioral or neuropathological alterations in F_2 pups identified at various times up to postnatal day 60. NOAEL: 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	ACC, 2002	Sufficient study details in primary source.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Other			No data located.
Neurotoxicity		**LOW: An experimental study in rats produced no adverse neurotoxic effects in adults at levels up to 1,000 mg/kg-day. In an acute exposure study, TBBPA, administered orally to mice, resulted in neurobehavioral effects; these effects were not clearly dose-dependent. Although one study with limitations appears to result in neurobehavioral effects, a well-designed subchronic duration study did not identify any adverse neurological effects. Based on study quality, a Low hazard designation was assigned.**		
	Neurotoxicity Screening Battery (Adult)	In a 90-day study, rats (10-15/sex/dose) were administered daily doses of 0, 100, 300 or 1,000 mg/kg-day TBBPA via in corn oil. A detailed functional observational battery (FOB) was conducted pre-test and at week 12. Motor activity (MA) was also assessed at week 12. No neurobehavioral effect of treatment with TBBPA was evident. NOAEL: 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	MPI Research, 2002 (as cited in EU, 2006)	Sufficient study details in secondary source.
		Male mice (14-15/group) were administered 0, 0.1, 5, or 250 mg/kg-day TBBPA (99% pure) by gavage 3 hours before a series of neurobehavioral tests (open field test, Y-maze test or training of contextual fear conditioning paradigm). No gross abnormalities. No significant differences in the number of rearing and grooming behaviors. Increased horizontal movement activities (5 mg/kg-day), increased freezing behavior in fear conditioning paradigm (0.1 or 5 mg/kg-day), increase in spontaneous alternation behavior in Y-maze test at the low dose, but no adverse effects occurred at higher doses. Elevated levels of TBBPA were detected in the striatum region of the brain	Nakajima et al., 2009	Sufficient details in primary source. Difficult to establish a NOAEL/LOAEL due to lack of dose-response relationships; acute study duration is not a standard methodology for a neurotoxicity screening study.

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		at lower doses (0.1 or 5 mg/kg-day). At the highest dose tested (250 mg/kg-day), there was non-specific accumulation of TBBPA in the brain.		
	Other	Potential for neurotoxic effects based on a structural alert for phenols (Estimated)	Professional judgment	Estimated based on a structural alert and professional judgment.

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Repeated Dose Effects	**LOW: Based on a weight of evidence indicating that effects occur at doses >100 mg/kg-day. Mice administered 500 mg/kg-day TBBPA for 3 months were reported to have increased liver weight and kidney effects in males (NOAEL=100 mg/kg-day). There was decreased serum alanine aminotransferase and sorbitol dehydrogenase activity at week 14 in male and female rats at 100 mg/kg-day following oral exposure for 3 months. Increased liver weights and decreased spleen weight were reported in male rats in the 500 and 1,000 mg/kg-day dose group, though no treatment-related histopathologic lesions were observed. Experimental studies indicate that TBBPA, administered orally to mice, produced effects on the liver (inflammatory cell infiltration) at ≥ 350 mg/kg-day (lowest dose tested). In a dietary study in mice, changes in hematology and clinical chemistry (decreased red blood cells, hemoglobin, hematocrit, serum triglycerides and total serum proteins) and decreased body weight gain occurred at 2,200 mg/kg-day (NOAEL: 700 mg/kg-day) while mortality was reported at the highest dose tested (7,100 mg/kg-day). In a 2-year oral gavage carcinogenicity study in mice, renal tubule cytoplasmic alteration and effects on the forestomach (ulcer, mononuclear cell cellular infiltration, inflammation, and epithelium hyperplasia) were observed at ≥ 250 mg/kg-day (lowest dose tested). Mean body weight was reduced by at least 10% in this study at 1,000 mg/kg-day. In a 2-year oral gavage carcinogenicity study in rats, mean body weight was reduced by at least 10% following exposure to ≥ 500 mg/kg-day and at 1,000 mg/kg-day. Thymus weight was reduced and liver weight was also increased in this study. Clinical signs of toxicity (excessive salivation and nasal discharge) were evident in rats following inhalation exposure at levels of 6 mg/L (NOAEC: 2 mg/L). Very slight dermal erythema was present in rabbits following application of 100 mg/kg-day TBBPA; however, this occurred in the absence of any systemic effects (NOAEL: 2,500 mg/kg-day).**		

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		3 month oral gavage study in F344/Ntac rats (10/sex/dose); rats were administered 0, 10, 50, 100, 500, or 1,000 mg/kg-day, 5 days/week for 14 weeks. Dose-related decrease in total thyroxine concentrations were reported on day 4 at the final week of the study at 500 and 1,000 mg/kg-day, but not consistently in the 100 mg/kg-day dose group in males and female rats. There was a small decrease in hematocrit levels, hemoglobin concentrations, and erythrocyte counts in female rats in the 500 and 1,000 mg/kg-day dose groups by week 14. There was also decreased serum alanine aminotransferase and sorbitol dehydrogenase activity at week 14 in males and females of the 100 mg/kg-day. Increased liver weights and decreased spleen weight were reported in male rats in the 500 and 1,000 mg/kg-day dose group. Although enzyme changes are seen at lower doses, it is uncertain if this is linked to any of the observed adverse endpoints. No treatment-related histopathologic lesions were observed. NOAEL: 100 mg/kg-day LOAEL: 500 mg/kg-day (based on decreased serum enzyme activity)	NTP, 2013	Sufficient study details reported in NTP technical report
		3 month oral gavage study in B6C3F1/N mice (10/sex/dose); Mice were administered 0, 10, 50, 100, 500, or 1,000 mg/kg-day, 5 days/week for 14 weeks. There was no mortality reported. Final mean body weight of treated mice in all	NTP, 2013	Sufficient study details reported in NTP technical report.

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		dose groups was similar to controls. Liver weights were significantly greater in male mice in the 500 and 1,000 mg/kg-day dose groups as compared to controls. Increased spleen weights and decreased kidney weights were reported in the male 1,000 mg/kg-day dose group. Increased incidence of renal tubule cytoplasmic alteration in the kidney at 500 and 1,000 mg/kg in male mice (greater severity at 1,000 mg/kg). NOAEL: 100 mg/kg-day LOAEL: 500 mg/kg-day (based on alterations in the kidneys in male mice)		
		In a 28-day dietary study, rats (25/sex/group) were fed a diet containing TBBPA at 0, 1, 10, 100 and 1,000 ppm (~ 0.07, 0.7, 7.2 and 75 mg/kg-day in males, and 0.07, 0.77, 7.4 and 72 mg/kg-day in females). No changes in general appearance, behavior, body weight or food consumption. No compound-related mortality, gross or microscopic lesions in the liver, kidneys, and thyroid. NOAEL: 1,000 ppm (75 or 72 mg/kg-day in males and females, respectively; highest dose tested) LOAEL: Not established	Sterner, 1967c (as cited in Wazeter et al., 1972); Simonsen et al., 2000; ACC, 2006b; EU, 2006; ECHA, 2013	Study limited by histological examination of only the liver, kidneys, and thyroid.
		28-day repeated-dose study, rat, diet, no treatment-related effects. NOAEL: ~ 98 mg/kg-day (0.1%, highest dose tested) LOAEL: Not established	Wazeter et al., 1972	Inadequate, the high dose was relatively low and failed to elicit toxicity.

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		In a 90-day repeated-dose study, rats were fed 0.3, 3, 30 or 100 mg/kg-day TBBPA in the diet. No toxicologically significant effects. NOAEL: ~ 100 mg/kg-day (highest dose tested) LOAEL: Not established	Quast et al., 1975	Sufficient details in a primary source. However, it was tested at relatively low doses.
		In a 14-day oral study, male mice (7-8/group) were dosed by gavage with 0, 350, 700 or 1,400 mg/kg-day TBBPA (99.1% pure) in olive oil. No clinical signs or mortality. Significant increase in absolute and relative liver weight in high-dose mice. Slight enlargement of hepatocytes at ≥ 700 mg/kg-day, inflammatory cell infiltration at ≥ 350 mg/kg-day, and focal necrosis of hepatocytes at 1,400 mg/kg-day. In treated mice the liver appeared swollen and the pancreas looked slightly enlarged and edematous. NOAEL: Not established LOAEL: 350 mg/kg-day (lowest dose tested)	Tada et al., 2007	Sufficient details in primary source.
		In a 14-day oral study, male rats (6/group) were administered 0, 200, 500 or 1,000 mg/kg TBBPA (98% pure) by gavage in corn oil. No significant adverse effects on body weight, clinical chemistry parameters, or enzymes' activities indicative of lipid peroxidation in the kidneys. NOAEL: 1,000 mg/kg-day (highest dose	Kang et al., 2009	Study of limited toxicological scope. There was no histological examination of the kidneys.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		tested) LOAEL: Not established		
		B6C3F1 mice (10/sex/group) were fed TBBPA in the diet at 0, 71, 700, 2,200 or 7,100 mg/kg-day for 3 months. All animals receiving 7,100 mg/kg-day died, but no deaths occurred at lower doses. Decreased body weight gain at the two highest doses with no change in food consumption. Decreased red blood cells, hemoglobin, hematocrit, serum triglycerides and total serum proteins at 2,200 mg/kg-day. Increased spleen weight with blood observed outside the red pulp. No other organ weight or pathological changes. NOAEL: 700 mg/kg-day LOAEL: 2,200 mg/kg-day	IPCS, 1995; WHO, 1995; HSDB, 2013; NTP, 2013	Sufficient study details reported in a secondary source.
		In a 90-day repeated-dose study, rats were administered TBBPA via oral gavage at 0, 100, 300 or 1,000 mg/kg-day. No deaths. No effect on clinical signs, body/organ weight, histopathology, urinalysis, ophthalmology, or serum chemistries. NOAEL: 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	MPI Research, 2002 (as cited in EU, 2006)	Sufficient details in a secondary source.
		10-day developmental study, rats orally gavaged with 0, 30, 100, 300, 1,000, 3,000 and 10,000 mg/kg TBBPA-day. Maternal clinical signs, mortality and reduced body weight gain at the high dose only (10,000 mg/kg-day). No effects at 3,000 mg/kg-day or less.	Goldenthal et al., 1978	Sufficient details in primary source.

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		NOAEL: 3,000 mg/kg-day LOAEL: 10,000 mg/kg-day		
		In an oral study, 5-week old rats were administered 0, 2,000 or 6,000 mg/kg-day TBBPA (99.5% pure) by gavage for 18 days. There were no changes in general behavior, body weight or kidney weight. Microscopic examination of the kidneys showed no abnormalities. NOAEL: 6,000 mg/kg-day (highest dose tested) LOAEL: Not established	Fukuda et al., 2004	Limited scope study; only the kidneys were examined.
		In a 28-day dietary study, rats (10/sex/group) were fed 0, 30, 100 and 300 mg/kg-day TBBPA (98% pure). Decreased circulating T4 and increased T3 levels in males (BMDLs = 48 and 124, respectively). No histopathological changes in the thyroid or pituitary gland.	Van der Ven et al., 2008	As stated in the study, dose-response analysis of effects based on external dosing (mg/kg-day) was done using a nested family of purely descriptive (exponential) models with the PROAST software. The method enables integrated evaluation of the complete data set. From the best fitted curve, indicated by significance at the 5% level, a critical effect dose (CED, also referred as Benchmark Dose) was calculated at a default critical effect size of 10%.
		2-year oral gavage carcinogenicity study; Wistar Han rats (50 or 60/sex/dose) were administered 0, 250, 500, or 1,000 mg/kg-day 5 days/week for up to 105 weeks. Survival was similar to controls. Decreased mean body weight (by at least 10% compared to controls) after week 25 in males in the 500 and 1,000 mg/kg dose	NTP, 2013	Sufficient study details reported in NTP technical report.

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		groups. At the 3-month interim sacrifice, there were no treatment-related lesions in either sex. However, thymus weight was decreased and liver weight was increased at 1,000 mg/kg. NOAEL: 250 mg/kg LOAEL: 500 mg/kg (based on decreased mean body weight in males)		
		2-year oral gavage carcinogenicity study; B6C3F1/N mice (50/sex/dose) were administered 0, 250, 500, or 1,000 mg/kg-day 5 days/week for up to 105 weeks. Reduced survival in males and females in the 1,000 mg/kg dose group. Decreased mean body weight (by at least 10% compared to controls) after week 25 in females at 1,000 mg/kg. Increase in the incidence of renal tubule cytoplasmic alteration in 250 and 500 mg/kg males. Significant increase in the incidences of ulcer, mononuclear cell cellular infiltration, inflammation, and epithelium hyperplasia in the forestomach in males at 500 mg/kg and in females at 250 and 500 mg/kg. NOAEL: Not established LOAEL: 250 mg/kg (based on effects in the forestomach in females)	NTP, 2013	Sufficient study details reported in NTP technical report.
		21-day repeated-dose study in rabbits with dermal application of 0, 100, 500 and 2,500 mg/kg TBBPA to the intact or abraded back 6 hours/day, 5 days/week. Very slight erythema (≥ 100 mg/kg-day). No compound-related changes in body	Sterner, 1967c (as cited in Goldenthal et al., 1979; Simonsen et al., 2000; EU, 2006; ECHA, 2013)	Sufficient details in secondary source.

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		weights, hematologic and biochemical parameters and urinalysis. No compound induced gross or microscopic lesions in any of the tissues examined. No compound-related organ weight variations occurred. NOAEL: 2,500 mg/kg-day (highest dose tested) LOAEL: Not established		
		In a 14-day inhalation study, rats (4/sex/group) were exposed whole-body to 0, 2, 6 or 18 mg/L TBBPA as dust 4 hours/day, 5 days/week. No significant effects on body weight gain, food consumption, hematology and clinical chemistry parameters or urinalysis. No deaths and no gross or microscopic lesions. Excessive salivation at 2 mg/L; excessive salivation, nasal discharge and lacrimation at ≥ 6 mg/L. NOAEC: 2 mg/L LOAEC: 6 mg/L	Sterner, 1967c (as cited in Wazeter et al., 1975; Simonsen et al., 2000; EC, 2000; ECHA, 2013)	No information regarding how the exposure atmosphere was generated or regarding analytical measurements of exposure concentrations.
Skin Sensitization		**LOW: TBBPA is not a skin sensitizer in humans or guinea pigs.**		
	Skin Sensitization	Non-sensitizing, human volunteers In a modified Draize Multiple Insult test.	Sterner, 1967c; Dean et al., 1978a; WHO, 1995; EC, 2000; EU, 2006; ECHA, 2013	Sufficient study details in secondary sources.
		Non-sensitizing, guinea pigs No irritation was elicited at either induction or challenge in the group exposed to TBBPA.	Mallory et al., 1981c (as cited in EU, 2006)	Sufficient study details in a primary source.
		Not sensitizing, guinea pigs Three treated animals showed a mild skin reaction at the induction site, no treated	Dean et al., 1978c (as cited in EU, 2006)	Sufficient study details in a primary source.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		animal showed a skin reaction at the challenge site.		
Respiratory Sensitization		**No data located**		
	Respiratory Sensitization			No data located.
Eye Irritation		**MODERATE: Slight pain, conjunctivitis and corneal damage lasting for three days were reported in rabbits administered TBBPA in a 10% solution. In addition, moderate conjunctival erythema, clearing within 72 hours, was also reported following application of TBBPA to the eyes of rabbits.**		
	Eye Irritation	Application of the test material to the eye of rabbits produced no irritation in one rabbit, mild conjunctival erythema in eight rabbits, and moderate conjunctival erythema in the remaining three rabbits. Effects diminished in intensity or subsided completely during subsequent 72 hours.	Doyle and Elsea, 1966 (as cited in EU, 2006)	Sufficient details in primary source.
		Irritating, range-finding study in rabbits. Undiluted test material caused very slight immediate conjunctivitis (disappearing within 48 hours). TBBPA administered as 10% solution in water caused slight pain, conjunctivitis and corneal damage (lasting for 3 days and then returning to normal within a week).	EU, 2006	Sufficient details in secondary source.
		Non-irritating, rabbits	Sterner, 1967a (as cited in Mallory et al., 1981a; WHO, 1995; EU, 2006)	Sufficient study details in secondary sources.
Dermal Irritation		**LOW: Slightly irritating to rabbits in a 21-day dermal repeated dose study.**		
	Dermal Irritation	Irritating, rabbits 21-day repeated dermal toxicity assay with very slight dermal erythema persisting for 1-3 days.	Sterner, 1967c; Goldenthal et al., 1979; EU, 2006	Sufficient details in primary sources.
		Non-irritating, rabbits Undiluted test material was applied to intact and abraded skin.	Doyle and Elsea, 1966; Sterner, 1967c; Mallory et al., 1981d; EC, 2000; EU, 2006	Sufficient details in primary sources.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Non-irritating, human volunteers In a modified Draize Multiple Insult test.	Sterner, 1967c; Dean et al., 1978a; EC, 2000; EU, 2006	Sufficient details in primary source.
Endocrine Activity		**Both whole animal and *in vitro* studies indicate that TBBPA may exhibit thyroid endocrine activity. In a one-generation reproduction study in rats, TBBPA decreased circulating thyroxine (T4) and increased circulating T3 levels in males. TBBPA was negative for agonistic and antagonistic estrogenic responses following oral exposure and subcutaneous injection at doses up to 1,000 mg/kg-day in an uterotrophic assay with adult female ovariectomized mice. TBBPA has a high potency in competing with thyroxine (T4) for binding to transport protein transthyretin (TTR) in *in vitro* animal studies. In addition, TBBPA exhibited significant thyroid hormonal activity towards rat pituitary cell line GH3, which releases growth hormone in a thyroid hormone-dependent manner. TBBPA produced only mild effects during long-term treatment on larval development using the amphibian *Xenopus laevis*; however, short-term exposure revealed indirect evidence that TBBPA can function as a TH antagonist. There were no adverse effects on tail resorption in tadpoles that were microinjected with TBBPA during development. TBBPA did not induce Vitellogenin in immature rainbow trout after intraperitoneal injection.**		
		TBBPA did not exhibit thyroid hormonal activity in a thyroid hormone-responsive reporter assay using a Chinese hamster ovary cell line (CHO-K1) transfected with thyroid hormone receptor alpha1 or beta1. TBBPA showed significant anti-thyroid hormone effects on the activity of T3 in the concentration range of $3x10^{-6}$ to $5x10^{-5}$ M. In addition, TBBPA (in the concentration range of $1x10^{-8}$ to $1x10^{-6}$ M showed suppressive action on T3 enhancement of tadpole tail shortening.	Kitamura et al., 2005a	Sufficient study details reported in a primary source.
		One-generation reproduction study in Wistar rats fed TBBPA at doses of 0, 3, 10, 30, 100, 300, 1,000 and 3,000 mg/kg-day. Decreased circulating thyroxine (T4) and increased circulating T3 levels in males. BMDL: 31 (male) and 16 (female) mg/kg-day	Van der Ven et al., 2008	Sufficient study details summarized in a primary source.

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	There were no adverse effects on tail resorption in tadpoles microinjected with TBBPA at doses up to 60 µg at developmental stage 58 (hind limbs emerged; forelimbs formed, but not emerged).	HSDB, 2013	Sufficient study details summarized in a secondary source.
	TBBPA inhibited the binding of triiodothyronine (T3; $1x10^{-10}$ M) to thyroid hormone receptor in the concentration range of $1x10^{-6}$ M to $1x10^{-4}$ M. The thyroid hormonal activity of TBBPA was also examined using rat pituitary cell line GH3 cells. TBBPA enhanced the proliferation of GH3 cells and stimulated their production of growth hormone (GH) in the concentration range of $1x10^{-6}$ M to $1x10^{-4}$ M. TBBPA did not show antagonistic action (did not inhibit the hormonal activity of T3 to induce growth and GH production of GH3 cells). TBBPA enhanced the proliferation of MtT/E-2 cells (growth is estrogen-dependent).	Kitamura et al., 2002	Sufficient study details in a primary source.
	TBBPA gave a positive response in an *in vivo* uterotrophic assay using ovariectomized mice but was inactive for effects on the androgenic activity of 5alpha-dihydrotestosterone in mouse fibroblast cell line NIH3T3. TBBPA exhibited significant thyroid hormonal activity towards rat pituitary cell line GH3, which releases growth hormone in a thyroid hormone-dependent manner.	Kitamura et al., 2005b	Sufficient study details in a primary source.
	In a uterotrophic assay with adult female ovariectomized mice, TBBPA was administered by oral gavage and	Ohta et al., 2012 cited in Environment Canada, 2013	Sufficient study details in a secondary source.

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	subcutaneous injection daily for 7 days. TBBPA was negative for agonistic and antagonistic estrogenic responses by both routes of exposure at concentrations up to 1,000 mg/kg-day.		
	Positive for thyroid hormone agonist activity in a yeast two-hybrid assay incorporating human thyroid hormone with and without metabolic activation. Metabolic activation by rat liver S9 significantly increased the agonist/antagonist potential.	HSDB, 2013	Sufficient study details summarized in a secondary source.
	Negative for estrogenic activity in yeast two-hybrid assay. REC_{10}(M) $>1x10^{-5}$ compared to $3x10^{-10}$ for E2.	Nishihara et al., 2000	Sufficient study details reported in a primary source.
	In vitro competition binding assays of T4 to TTR using human plasma samples; the competing potency of TBBPA was 5 times greater than T4.	Bergman et al., 1997	Sufficient study details reported in a primary source.
	The human adrenocortical carcinoma cell line (H295R cell line) was used to assess possible effects of TBBPA on the activity of adreno cortical enzyme CYP17. A maximum of 2-fold induction of CYP17 activity occurred after 24 hours of incubation. TBBPA was a potent inducer of CYP17 activity, causing 50% induction at the lowest concentration tested (0.01µM).	Canton et al., 2004	Sufficient study details reported in a primary source.
	In a 14-day oral study, male mice (7-8/group) were dosed by gavage with 0, 350, 700 or 1,400 mg/kg-day TBBPA (99.1% pure) in olive oil. No clinical signs or mortality. In treated mice the liver appeared swollen and the pancreas	Tada et al., 2007	Sufficient details in primary source.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	looked slightly enlarged and edematous. NOAEL: Not established LOAEL: 350 mg/kg-day (lowest dose tested)		
	Negative, thyroid hormone receptor (TR)-binding activity of TBBPA using a yeast two-hybrid assay; REC_{10}(M) >$3.0x10^{-4}$ compared to $2.1x10^{-8}$ for T3.	Kitagawa et al., 2003	Sufficient study details reported in a primary source.
	Hormonal effects of TBBPA were investigated *in vitro* on recombinant yeasts and *in vivo* on mosquitofish (*Gambusia affinis*). TBBPA had a weak androgenic activity with recombinant yeast systems carrying human androgen receptor (hAR). Following 60-days of exposure in mosquitofish, significant up-regulation of vitellogenin (Vtg), and estrogen receptor (ER-alpha and ER-beta) mRNAs was observed in the liver (500 nM of TBBPA). The lowest concentration (50 nM) markedly induced Vtg, ER-beta and AR-beta mRNA expression in the testes and significantly inhibited AR-alpha expression. TBBPA did not produce histopathological alterations in the liver or testis.	Huang et al., 2013	Sufficient study details reported in a primary source.
	TBBPA did not have anti-androgenic activity in a recombinant cell-based *in vitro* bioassay using the Chinese hamster ovarian cell line (CHO K1).	Roy et al., 2004	Sufficient study details reported in a primary source.
	In a transcriptional activation assay, TBBPA suppressed the thyroid replacement element (TRE) mediated transcriptional activity of T3 on the human HeLaTRDR4-luc cell line.	Sakai et al., 2003	Sufficient study details reported in a primary source.

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	ER-, DR-CALUX® and T4-TTR competitive binding assays; TBBPA did not show estrogenic/antiestrogenic or dioxin-like/anti-dioxin activity. TBBPA was more potent than to thyroxine (T4) in binding to transport protein transthyretin (TTR).	Legler et al., 2002	Sufficient study details reported in a primary source.
	Vitellogenin induction in immature rainbow trout after intraperitoneal injection of TBBPA was studied. Exposure to TBBPA did not induce vitellogenin synthesis.	Christiansen et al., 2000	Sufficient study details reported in a primary source.
	The estrogen-dependent human breast cancer cell line MCF-7 was used to characterize estrogen-like profiles of high volume chemicals. The EC_{50} for the displacement of radiolabeled 17 β-estradiol from the estrogen receptor = 2.5 (+/- 1.29) x 10^{-5}; Relative binding affinity (RBA) = 0.013.	Olsen et al., 2003	Sufficient study details reported in a primary source.
	Tadpoles were exposed to TBBPA at concentrations ranging from 2.5 to 500 µg/L for 21 days. Larval development was inhibited only at the highest concentration level. The TH receptor beta-mRNA was not affected. Conversely, short-term exposures to TBBPA slightly increased the expression of TH receptor beta- and basic region leucin zipper transcription factor b/Zip-mRNA but inhibited their T3-induced elevation in a dose-dependent manner indicating that TBBPA can function as a TH antagonist.	Jagnytsch et al., 2006	Sufficient study details reported in a primary source.
	Short (24 h) exposures of TBBPA modulated the expression of a number of TH target genes implicated in neural stem	Fini et al., 2012	Sufficient study details reported in a primary source.

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	cell function and neural differentiation. TBBPA also reduced cell proliferation in the brain of *Xenopus laevis* (African clawed frog).		
	Thyroid hormone (TH) disrupting activity of TBBPA was investigated in the rat pituitary cell line GH3. The effect of a strong antiestrogen, ICI (10^{-9} M), was also analyzed on E2 and TBBPA. TBBPA stimulated GH3 cell growth but could not counteract the inhibiting growth effect of 10^{-9} M ICI at the tested concentrations. These data indicate that the effect of TBBPA is TH-like and ER-mediated.	Ghisari and Bonefeld-Jorgensen, 2005	Sufficient study details reported in a primary source.
	In vitro bioassay with phenobarbital-induced rat liver microsomes. TBBPA and TBBPA-DBPE significantly increased TTR-binding potencies and E2SULT-inhibiting potencies after biotransformation. TBBPA-DBPE became a more potent AR-antagonist after biotransformation. TBBPA and TBBPA-DBPE enhanced GH3 cell proliferation in the T-Screen test.	Hamers et al., 2008	Sufficient study details reported in a primary source.
	TBBPA binded to crystal structures of the hormone-metabolizing enzyme, estrogen sulfotransferase (SULT1E1), and has the potential to cause endocrine disruption.	Gosavi et al., 2013	Sufficient study details reported in a primary source.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Immunotoxicity		**The data located had limited experimental details. TBBPA inhibits expression of CD25, which is essential for proliferation of activated T lymphocyte cells, at concentrations ≥ 3 µM. In a disease challenge study, TBBPA administered to mice (1% in diet for 28 days; approximately 1,800 mg/kg-day) produced irregular changes in cytokine production and immune cell populations, which were suggested to cause exacerbation of pneumonia in respiratory syncytial virus-infected mice. Determination of significance of the response to RSV infection is limited by the study design having only one, particularly high, dose of TBBPA. In an *in vitro* study, TBBPA decreased the level of cell surface proteins, possibly interfering with NK cell function.**		
	Immune System Effects	TBBPA is immunotoxic in culture; inhibits expression of CD25 at concentrations at ≥ 3 µM; CD25 is essential for proliferation of activated T cells and is commonly used as a marker for T-cell activation.	Birnbaum and Staskal, 2004	Limited information in a secondary source.
		In a 90-day oral study in mice, there were no adverse effects at doses up to 700 mg/kg-day; however, 2,200 mg/kg-day produced increased spleen weight and reduced concentrations of red blood cells, serum proteins and serum triglycerides. NOAEL: 700 mg/kg-bw LOAEL: 2,200 mg/kg-bw	Tobe et al., 1986; WHO, 1995; Simonsen et al., 2000; Darnerud, 2003	Limited details in secondary sources.
		In vitro study in natural killer (NK) cells; TBBPA (5 µM) decreased the level of cell surface proteins, possibly interfering with NK cell function.	Hurd and Whalen, 2011 (as cited in NTP, 2013)	Sufficient study details reported in NTP technical report.
		TBBPA administered to mice as 1% in diet for 28 days. Irregular changes in cytokine production and immune cell populations were suggested to cause exacerbation of pneumonia in respiratory syncytial virus-infected mice.	Watanabe et al., 2010 (as cited in NTP, 2013)	Sufficient study details reported in NTP technical report.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ECOTOXICITY			
ECOSAR Class	Phenols, Poly		
Acute Aquatic Toxicity	**VERY HIGH: Based on measured LC_{50} values <1 mg/L in fish, daphnia and algae.**		
Fish LC_{50}	Freshwater fish (*Salmo gairdneri*) 96-hour LC_{50} = 0.40 mg/L (Experimental)	Calmbacher, 1978 (as cited in Simonsen et al., 2000)	Insufficient information in primary source.
	Freshwater fish (*Lepomis macrochirus*) 96-hour LC_{50} = 0.51 mg/L (Experimental)	EC, 2000	Insufficient information in secondary source.
	Freshwater fish (*Pimephales promelas*) 96-hour LC_{50} = 0.54 mg/L: 144-hour LC_{50} = 0.49 mg/L; 144-hour NOEC = 0.26 mg/L; Flow-through test conditions; test concentrations: 0.63, 0.45, 0.32, 0.26, and 0.19 mg active substance/L (Experimental)	Suprenant, 1988 (as cited in EC, 2000; ECHA, 2013)	Sufficient study details in primary source.
	Freshwater fish (*Cyprinus carpio*) 96-hour LC_{50} = 0.71 mg/L 48-hour LC_{50} = 0.80 mg/L Static conditions; test concentrations: 0.42, 0.65, and 1.0 mg/L (nominal) (Experimental)	ECHA, 2013	Sufficient study details in a secondary source; GLP study following standard guidelines; however, no analytical verification of test compound concentrations.
	Freshwater fish (*Pimephales promelas*) 96-hour LC_{50} = 710 µg/L (0.71 mg/L) (Experimental)	ECOTOX, 2012	Sufficient study summary reported in a secondary source.
	Freshwater fish (*Pimephales promelas*) 96-hour LC_{50} = 1,040 µg/L (1.04 mg/L) (Experimental)	ECOTOX, 2012	Sufficient study summary reported in a secondary source.
	Freshwater fish (*Oncorhynchus mykiss*) 96-hour LC_{50} = 1.1 mg/L 96-hour NOEC <1.1 mg/L; flow-through conditions; test concentrations: 1.1 and 1.7 mg/L	Blankenship et al., 2003a; ECHA, 2013	Sufficient information in primary source.

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	(measured); 1.2 and 1.8 mg/L (nominal) (Experimental)		
	Freshwater fish (*Danio rerio*) 96-hour EC_{50} = 1.1 mg/L (*Danio rerio*) larvae 96-hour LC_{50} = 5.27 mg/L (Experimental)	Chow et al., 2013	Insufficient study details reported in a primary source. EC_{50} is based on hatching of zebrafish embryos. Inconsistent with most other LC_{50} values reported for this compound.
	Freshwater fish (*Danio rerio*) LC_{100} = 1.5 mg/L Exposure concentrations were 0, 0.002, 0.01, 0.05, 0.25, 0.75, and 1.5 mg/L; nearly 100% of animals survived at concentrations <1.5 mg/L, but some embryos were malformed at 0.75 mg/L (Experimental)	Hu et al., 2009	Sufficient information in primary source.
	Freshwater fish (*Lepomis macrochirus*) 96-hour NOEC = 0.1 mg/L (Experimental)	Simonsen et al., 2000	No study details in secondary source.
	Freshwater fish (*Salmo gairdneri*) 96-hour NOEC = 0.18 mg/L (Experimental)	Simonsen et al., 2000	No study details in secondary source.
	Freshwater fish (*Danio rerio*) 96-hour LC_{50} = 1.5 µg/L (0.0015 mg/L) (Experimental)	ECOTOX, 2012	Insufficient study summary reported in a secondary source.
	Freshwater fish (*Pimephales promelas*) 96-hour LC_{50} = 60 µg/L (0.06 mg/L) (Experimental)	ECOTOX, 2012	Insufficient study summary reported in a secondary source.
	Freshwater fish (*Pimephales promelas*) 96-hour NOEC = 0.26 mg/L (Experimental)	Simonsen et al., 2000	No study details in secondary source.
	Freshwater fish (*Oryzias latipes*) 48-hour LC_{50} = 8.2 mg/L (Experimental)	MITI, 1992 (as cited in EC, 2000)	No study details in secondary source.
	Freshwater fish 96-hour LC_{50}= 0.89 mg/L	ECOSAR v1.11	

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	(Estimated) ECOSAR: Phenols, Poly		
	Freshwater fish 96-hour LC_{50} = 2.3 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid LC_{50}	*Daphnia magna* 48-hour EC_{50} = 0.60 mg/L (Experimental)	Waaijers et al., 2013	Sufficient study details reported in a primary source.
	Daphnia magna 48-hour LC_{50} = 0.96 mg/L; NOEC <0.32 mg/L (Experimental)	Morrissey et al., 1978; Simonsen et al., 2000; EC, 2000; Anonymous, 2003	Sufficient information in primary source.
	Daphnia magna 48-hour LC_{50} >0.9 - <1.2 µg/L (>0.0009 - <0.0012 mg/L) (Experimental)	ECOTOX, 2012	Sufficient details reported in a secondary source.
	Daphnia magna 24 and 48-hour LC_{50} >1.8 mg/L 48-hour NOEC = 1.8 mg/L flow-through test conditions Test concentrations: 1.2 and 1.8 mg a.i./L (nominal); average measured concentration: 1.2 and 1.8 mg a.i./L (Experimental)	Blankenship et al., 2003b; ECHA, 2013	Sufficient information in primary source. GLP study, following standard guidelines, with analytical verification of test compound concentrations.
	Daphnia magna 48-hour LC_{50} = 7,900 µg/L (7.9 mg/L) (Experimental)	ECOTOX, 2012	Sufficient details reported in a secondary source.
	Saltwater Mysid shrimp 96-hour LC_{50} = 0.86-1.2 mg/L (in 1, 5 or 10 day old shrimp, respectively) (Experimental)	Goodman et al., 1988 (as cited in EC, 2000)	Sufficient information in primary source.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Daphnia magna 48-hour LC_{50}= 2.6 mg/L (Estimated) ECOSAR: Phenols, Poly	ECOSAR v1.11	
	Daphnia magna 48-hour LC_{50} = 1.7 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Green Algae EC_{50}	Green Algae (*Skeletonema costatum*) 72-hour EC_{50} = 0.09 - 0.89 mg/L (Experimental)	Walsh et al., 1987; EC, 2000; Simonsen et al., 2000; ACC, 2006b	Limited details in secondary sources.
	Green Algae (*Skeletonema costatum*) 72-hour EC_{50} = 0.09 - 1.14 mg/L (Experimental)	Walsh et al., 1987; ACC, 2006b	Sufficient details in primary source.
	Green Algae (*Thalassiosira pseudonana*) 72-hour EC_{50} = 0.13-1.0 mg/L (Experimental)	Walsh et al., 1987 (as cited in ACC, 2006b)	Sufficient details in primary source.
	Green Algae (*Pseudokirchneriella subcapitata*) 96-hour EC_{50} >5.6 mg/L 96-hour NOEC = 5.6 mg/L; Static test conditions; Test concentrations: 0.60, 1.2, 2.4, 4.8, and 9.6 mg/L (nominal); Mean measured concentration: 0.34, 0.76, 1.5, 3.0, and 5.6 mg/L. (Experimental)	Giddings, 1988; Anonymous, 2003; ACC, 2006b; ECHA, 2013	Sufficient study details in secondary sources. The effect levels are greater than the water solubility of 4.16 mg/L; no effects at saturation (NES) are predicted.
	Green algae 96-hour EC_{50} = 1.6 mg/L (Estimated) ECOSAR: Phenols, poly	ECOSAR v1.11	
	Green algae 96-hour EC_{50} = 3.3 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Chronic Aquatic Toxicity	**HIGH: Based on experimental LOECs and/or NOECs <1.0 mg/L in fish and daphnia.**		
Fish ChV	Freshwater fish (*Pimephales promelas*) 35 day NOEC = 0.16 mg/L; LOEC = 0.31 mg/L; MATC = 0.22 mg/L Flow-through test conditions Test concentrations: 0.025, 0.05, 0.1, 0.2, and 0.4 mg a.i./L (nominal); 0.024, 0.04, 0.084, 0.16, and 0.31 mg a.i./L. (measured) (Experimental)	Surprenant, 1989; EC, 2000; ACC, 2006b; ECHA, 2013; Weltje et al., 2013	Sufficient information in secondary sources.
	Freshwater fish (*Platichthys flesus*) 105 day NOEC >0.8 µM (435 ng/mL or 0.000435 mg/L) Test concentrations: 0; 0.001; 0.01; 0.1; 0.2; 0.4 and 0.8 µM (0, 0.54, 5.4, 54.4, 109, 218, 435 ng/mL) No adverse effect on behavior, survival, growth rate, relative liver and gonad weight. Increased levels of thyroid hormone thyroxin (T4) with no signs of altered thyroid gland activity. (Experimental)	Kuiper et al., 2007a	Sufficient details in primary source.
	Zebra fish (*Danio rerio*) 28-day LC_{100} (embryonic exposure) = 0.8 mg/L Edema and hemorrhage, decreased heart rate, edema of the trunk, tail malformation Test concentrations: 0.27, 0.4, 0.54, 0.8, 1.6 mg/L (Experimental)	McCormick et al., 2010	Sufficient details in primary source.
	Freshwater fish (*Danio rerio*) 30-day	Kuiper et al., 2007b	Sufficient study details reported in a

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	partial life cycle test; LC_{100} = 1.5 µM (0.816 mg/L) Exposure to 0, 0.023, 0.094, 0.375 and 1.5 µM. Reduced egg production (all exposure groups) and hatching ratios (all groups other than 0.375 µM). All larvae died in the high dose group (1.5 µM) and mortality was preceded by retardation of development. (Experimental)		primary source.
	Freshwater fish ChV = 0.33 mg/L (Estimated) ECOSAR: Phenols, poly	ECOSAR v1.11	
	Freshwater fish ChV = 0.30 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid ChV	*Daphnia magna* 21 day EC_{50} >0.96 mg/L 21-day NOEC = 0.38 mg/L 21-day MATC >0.3 <0.98 mg/L Flow-through test conditions. Test concentrations: 0.13, 0.25, 0.5, 1.0, 2.0 mg/L (nominal); 0.037 - 0.078, 0.068 - 0.13, 0.14 - 0.26, 0.19 - 0.29, 0.65 - 1.3 mg/L (measured) (Experimental)	ECHA, 2013	Sufficient study details in a secondary source. GLP study with analytical verification of test compound concentrations; methodology employed is well described and designed specifically to meet US EPA requirements.
	Daphnia magna 21 day EC_{50} >0.98 mg/L MATC = 0.54 mg/L Flow-through test conditions. Test concentrations: 0, 0.13, 0.25, 0.5, 1.0 and 2.0 (nominal) (Experimental)	Suprenant, 1989 (as cited in EC, 2000; ACC, 2006b)	Sufficient study details

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Daphnia magna ChV = 0.82 mg/L (Estimated) ECOSAR: Phenols, poly	ECOSAR v1.11	
	Daphnia magna ChV = 0.31 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Green Algae ChV	Green algae ChV: 0.31 mg/L (Estimated) ECOSAR: Phenols, poly	ECOSAR v1.11	
	Green algae ChV = 5.6 mg/L (Experimental)	Giddings, 1988	The effect level is greater than the water solubility of 4.16 mg/L; no effects at saturation (NES) are predicted.
	Green algae ChV = 1.5 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
ENVIRONMENTAL FATE			

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Transport		**Level III fugacity models incorporating available physical and chemical property data indicate that at steady state, TBBPA is expected to be found primarily in soil and to a lesser extent, sediment. TBBPA is expected to have low mobility in soil based on its calculated K_{oc}. Therefore, leaching of TBBPA through soil to groundwater is not expected to be an important transport mechanism. Estimated volatilization half-lives for a model river and lake indicate that it will have low potential to volatilize from surface water. In the atmosphere, TBBPA is expected to exist primarily in the particulate phase. Particulate phase TBBPA will be removed from air by wet or dry deposition.**		
	Henry's Law Constant (atm-m^3/mole)	$1.47x10^{-10}$ at 298K (Measured)	Kuramochi et al., 2008	Based on the measured enthalpy of fusion and melting point used to calculate the sub-cooled liquid vapor pressure and infinite dilution activity coefficient.
		$<10^{-8}$ (Estimated)	EPI v4.11; EPA, 2012	Cutoff value for nonvolatile compounds.
	Sediment/Soil Adsorption/Desorption - K_{oc}	$1.1x10^5$ at 6.8% organic carbon; $2.0x10^5$at 2.7% organic carbon; $2.3x10^6$ at 0.25% organic carbon (Measured)	Breteler et al., 1989	The K_{oc} values were calculated from the reported K_d values and the percent organic carbon for each sediment sample.
		TBBPA is shown to adsorb to soil based on laboratory soil mobility tests. TBBPA was not eluted from the soil column after 11 pore volumes were displaced. No quantitative values for the rate of soil migration were measured. (Measured)	Larsen et al., 2001 (as cited in ACC, 2006a; ACC, 2006b)	Nonguideline study reported in a secondary sources.
		>30,000 (Estimated)	EPI v4.11; EPA, 2004	Estimated value is greater than >30,000 using the K_{ow} method from KOCWIN v2.00; the high estimated soil adsorption coefficient is consistent with nonmobile compounds.
	Level III Fugacity Model	Air = 0% Water = 1.4% Soil = 64% Sediment = 35% (Estimated)	EPI v4.11	EPI v 4.11 was used to estimate environmental fate values in the absence of experimental data. Measured values (log K_{ow}) from experimental studies, were

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				incorporated into the estimations.
Persistence		**HIGH: Experimental aerobic and anaerobic biodegradation studies in soil and sediment indicate that the aerobic primary biodegradation half-life is less than 180 days, but not less than 60 days. Mineralization under both aerobic and anaerobic conditions in soil and sediment is low, indicating that persistent degradation products are formed. An experimental photolysis half-life of 24 minutes at pH 7.4 in water indicates that TBBPA may photolyze rapidly to 4-isopropyl-2,6-dibromophenol, 4-isopropylene-2,6-dibromophenol and 4-(2-hydroxyisopropyl)-2,6-dibromophenol; however, it is not anticipated to partition significantly to water. Although adequate experimental data are not available, degradation of TBBPA by hydrolysis is not expected to be significant as the functional groups present on this molecule do not tend to undergo hydrolysis. The atmospheric half-life for the gas phase reactions of TBBPA is estimated at 3.6 days, though it is expected to exist primarily as a particulate in air.**		
Water	**Aerobic Biodegradation**	Passes Ready Test: No Test method: OECD TG 301C: Modified MITI Test (I) No biodegradation was observed according to a Japanese MITI test using TBBPA (100 mg/L) in activated sludge (30 mg/L) for 2 weeks. (Measured)	MITI, 1992; ACC, 2006a; ACC, 2006b; CERIJ, 2007	Guideline study reported in a secondary source.
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI v4.11	EPI v 4.11 was used to estimate environmental fate values in the absence of experimental data. Measured values (log K_{ow}) from experimental studies, were incorporated into the estimations.
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI v4.11	EPI v 4.11 was used to estimate environmental fate values in the absence of experimental data. Measured values (log K_{ow}) from experimental studies, were incorporated into the estimations.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Soil	**Aerobic Biodegradation**	Study results: 50%/65-93 days Test method: Other Half-life values reported for two aerobic series using activated or digested sludge. An aerobic soil half-life of 65 days was calculated for TBBPA in the experiment with activated sludge and 93 days in the experiment with digested sludge. (Measured)	Nyholm et al., 2010	Adequate guideline study.
		Aerobic biodegradation of TBBPA was measured in three soil types. After 64 days, the amount of TBBPA in the soil ranged from 43.7 to 90.6%. 0.5 to 2.5% of the applied radioactivity was recovered as CO_2, suggesting only partial biodegradation. (Measured)	Fackler et al., 1989b (as cited in ACC, 2006a)	Nonguideline study reported in a secondary source.
		Study results: 17.5%/6 months Test method: Other A transformation study in soil calculated an aerobic DT_{50} of 5.3-7.7 days for the soil extracts. The disappearance appears to be predominantly due to binding to soil and not due to biodegradation. Insufficient material was extracted to identify the transformation products. After 6 months, 17.5-21.6% of the dose was mineralized in the aerobic soils. (Measured)	Schaefer and Stenzel, 2006c (as cited in Environment Canada, 2013)	DT_{50} values were calculated for the soil extracts; however, the majority of the material remained bound to soil and was not extracted. The non-extractable (bound) radioactivity or residues in the soil were not characterized as called for in the OECD guidelines. The abiotic degradation rate under sterile conditions was not estimated as called for in the OECD guidelines.
	Anaerobic Biodegradation	12-18% complete mineralization of TBBPA in different soil types observed after 4 months and 3-9% complete mineralization observed after six months in two separate series of anaerobic biodegradation experiments.	Schaefer and Stenzel, 2006c (as cited in Environment Canada, 2013)	Nonguideline studies reported in a secondary source. Full anaerobic conditions were not used throughout the duration of the study in soil.
		Study results: 50%/430 days Test method: Other Using a testing method similar to OECD	Nyholm et al., 2010	Adequate guideline study.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Test Guideline 307. (Measured)		
		Study results: >43.7%/64 days Test method: CO_2 Evolution Anaerobic biodegradation of TBBPA was measured in three soil types. After 64 days, the amount of TBBPA remaining in the soils ranged from 43.7 to 90.6%. Less than 0.5% applied radioactivity was recovered as CO_2, suggesting only partial biodegradation. (Measured)	Fackler et al., 1989b	Adequate guideline study.
		Study results: 100%/45 days Test method: Other Under anaerobic conditions the results initially reported TBBPA was mostly dehalogenated within 10 days, and complete dehalogenation to BPA was achieved after 45 days. The resulting BPA was not degraded anaerobically after 3 months. Di- and tribromobisphenol A were observed as intermediates. Under aerobic conditions, BPA was degraded to 4-hydroxybenzoic acid and 4-hydroxyacetophenone. (Measured)	Ronen and Abeliovich, 2000 (as cited in ACC, 2006a; ACC, 2006b)	Nonguideline study reported in a secondary report.
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation	50%/84 days Half-lives of 48 to 84 days were determined in anaerobic natural river sediment/water test system using ^{14}C-TBBPA. Less than 8% applied radioactivity was recovered as CO_2, suggesting only partial biodegradation. (Measured)	Fackler et al., 1989a (as cited in ACC, 2006a; ACC, 2006b)	Adequate guideline study reported in a secondary source.
		TBBPA was reductively dehalogenated to BPA with tribromobisphenol A and	Ravit et al., 2005 (as cited in Environment Canada, 2013)	Adequate, nonguideline study.

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		dibromobisphenol A formed as intermediates in sediment samples through two species of salt marsh macrophyte. (Measured)		
		An anaerobic mineralization and transformation study in freshwater aquatic sediment systems calculated an anaerobic DT_{50} of 24-28 days for the whole system. Very little mineralization was observed. The transformation products included BPA and 3 (Measured)	Schaefer and Stenzel, 2006a; ACC, 2006b	Adequate nonguideline study.
		An anaerobic mineralization and transformation study in digester sludge calculated an anaerobic DT_{50} of 19 days. Very little mineralization was observed. The transformation products included BPA and 3 unidentified materials. (Measured)	Schaefer and Stenzel, 2006b	Adequate nonguideline study.
		Estuarine sediment; under methanogenic conditions half-life was estimated to be about 28 days. Under sulfate-reducing conditions half-life was estimated to be 40 days. (Measured)	Voordeckers et al., 2002 (as cited in ACC, 2006b)	Nonguideline study reported in a secondary source.
Air	**Atmospheric Half-life**	3.6 days assuming 12-hr day/sunlight (Estimated)	EPI v4.11	EPI v 4.11 was used to estimate environmental fate values in the absence of experimental data. Measured values (log K_{ow}) from experimental studies, were incorporated into the estimations.
Reactivity	**Photolysis**	50%/24 minutes Photolysis half-lives in water of 16, 24, and 350 minutes at pH values 10, 7.4, and 5.5, respectively, were measured under fluorescent UV radiation representing environmental wavelengths. Major	Eriksson et al., 2004 (as cited in ACC, 2006a; ACC, 2006b; NTP, 2013)	Adequate nonguideline study.

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		degradation products were 4-isopropyl-2,6-dibromophenol, 4-isopropylene-2,6-dibromophenol and 4-(2-hydroxyisopropyl)-2,6-dibromophenol. Other products include di- and tribromobisphenol A, dibromophenol, 2,6-dibromo-4-(bromoisopropylene)phenol, 2,6-dibromo-4-(dibromoisopropylene)phenol and 2,6-dibromo-1,4-hydroxybenzene. (Measured)		
		50%/33 hour Photolysis of TBBPA in the presence of UV light and hydroxyl radicals has also been reported; TBBPA was no longer detected after 5-6 days with an estimated 33 hour half-life. TBBPA decomposition produced 2,4,6-tribromophenol and other bromine containing compounds that were not fully identified. (Estimated)	Eriksson and Jakobsson, 1998 (as cited in ACC, 2006a; ACC, 2006b)	Reported in a secondary source.
		A study of TBBPA on silica gel was reported. The wavelength studied was too short to derive any environmental conclusions. (Measured)	WHO, 1995 (as cited in ACC, 2006a)	Study details and test conditions were not available. Reported in a secondary source.
		Reported half-lives in water of 6.6, 10.2, 25.9, and 80.7 days during summer, spring, fall and winter, respectively. (Measured)	WHO, 1995 (as cited in ACC, 2006a; NTP, 2013)	Study details and test conditions were not available. Reported in a secondary source.
	Hydrolysis	Not a significant fate process (Estimated)	Wolfe and Jeffers, 2000; Professional judgment	The substance does not contain functional groups that would be expected to hydrolyze readily under environmental conditions.
Environmental Half-life		360 days (Estimated)	PBT Profiler v1.301; EPI v4.11	Half-life estimated for the predominant compartment (soil), as determined by EPI methodology. Measured values from experimental

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				studies, were incorporated into the estimations.
Bioaccumulation		**MODERATE: The measured fish BCF and estimated BAF values are greater than 100 but less than 1,000.**		
	Fish BCF	485 *Cyprinus carpio* BCF ranges of 30 to 341 and 52 to 485 were measured in carp during an 8-week study at concentrations of 80 µg/L and 8 µg/L, respectively. (Measured)	MITI, 1992 (as cited in HSDB, 2013)	Adequate guideline study reported in secondary source.
		300 *Pimephales promelas* A BCF of 1,200 was measured based on total ^{14}C radioactivity; however, extraction and thin layer chromatograph of the residue in the body of the fish determined that only 24.9% of the ^{14}C radioactivity was due to TBBPA, with the remainder due to metabolites, giving a BCF of 300 for TBBPA. Elimination half-life <24 hours for total ^{14}C radioactivity. (Measured)	Dionne et al., 1989; ACC, 2006b	Adequate nonguideline study reported in secondary source.
		170 *Lepomis macrochirus* Bluegill sunfish were exposed to ^{14}C-TBBPA for 28 days to 0.0098 mg/L (flow-through) followed by a 14-day withdrawal period. The bioconcentration factor (BCF) in edible tissue was 20 and 170 in visceral tissue. These BCF values were based on ^{14}C-residues and therefore represent the sum total of parent compound, any retained metabolites and assimilated carbon. (Measured)	ACC, 2006b	Adequate nonguideline study reported in secondary source.
		1,200 in Fathead minnows (*Pimephales promelas*) Reported for the BCF wet weight; BCF value for lipid weight = 24,000; 24 days	Geyer et al., 2000	The BCF value includes all the metabolites of the test substance, as well as the test substance, ^{14}C-labeled chemical was used.

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		uptake (Measured)		
		960 in Zebrafish; reported as BCF wet weight BCF value for lipid weight = 28,300; kinetic approach in outdoor experiment at pH 7.5. (Measured)	Geyer et al., 2000	Adequate nonguideline study reported in secondary source.
	Other BCF	<3,190 in *Chironomus tentans* BCF values of 243-511 (6.8% organic carbon sediment); 487-1,140 (2.7% organic carbon sediment) and 646-3,190 (0.25% organic carbon sediment). (Measured)	ACC, 2006b	Reported in a secondary source. This is nonguideline study using a non-standard test species and is not able to be evaluated with the assessment criteria.
		148 in Eastern oyster (Measured)	ACC, 2006b	Adequate nonguideline study reported in secondary source with limited study details.
	BAF	130 (Estimated)	EPI v4.11	EPI v 4.11 was used to estimate environmental fate values in the absence of experimental data. Measured values (log K_{ow} of 4.54) from experimental studies, were incorporated into the estimations.
	Metabolism in Fish			No data located.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL MONITORING AND BIOMONITORING			
Environmental Monitoring	TBBPA has been detected in the air of electronic recycling plants, although its presence in the air of this facility likely arises from products where it was used as an additive flame retardant. Studies on the release of TBBPA from PCBs after disposal in landfills were not available but would likely be low due to the low levels of unreacted TBBPA. TBBPA was reported in air and marine sediment samples collected from several locations in the Arctic. TBBPA was reported in indoor dust and air, soil, and food in Europe and the United States. It has been reported in surface water in Japan, Germany, France, and the United Kingdom (Sellstrom and Jansson, 1995; Sjodin et al., 2001; Sjodin et al., 2003; PBS Corporation, 2006; Environment Canada, 2013).		
Ecological Biomonitoring	TBBPA was reported in eel, salmon, perch, pike, cod, whiting, starfish, whelk, hermit crab, bottlenose dolphin, bull shark, sharpnose shark, cormorant, harbour porpoise blubber, predatory birds, tern eggs and moss samples from Norway. (Environment Canada, 2013)		
Human Biomonitoring	TBBPA was detected in human umbilical cord, blood/serum, adipose, milk and hair samples (DeCarlo, 1979; Thomsen et al., 2002; Peters, 2005; NTP, 2013).		

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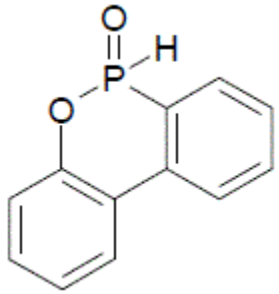
DOPO

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[§] Based on analogy to experimental data for a structurally similar compound.

		Human Health Effects											Aquatic Toxicity		Environmental Fate	
Chemical	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
DOPO	35948-25-5	**L**	***M***	**L**	***L***[§]	***M***	***M***	**L**	**M**		**M**	**VL**	**L**	***M***	***H***	***L***

DOPO



CASRN: 35948-25-5

MW: 216.18

MF: $C_{12}H_9O_2P$

Physical Forms:
Neat: Solid

Use: Flame retardant

SMILES: O=P1c2ccccc2c3ccccc3O1

Synonyms: DOP; DOPPO; 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; 6H-dibenz[c,e][1,2]oxaphosphorin 6-oxide

Chemical Considerations: This is a discrete organic chemical with a MW below 1,000. EPI v 4.11 was used to estimate physical/chemical and environmental fate values in the absence of experimental data. Measured values from experimental studies were incorporated into the estimations. As described in the *DfE Program Alternatives Assessment Criteria for Hazard Evaluation*, stable degradation products of the alternatives are evaluated. Therefore the hydrolysis product of DOPO was evaluated in this assessment for endpoints typically obtained in the presence of water; based on a submitted guideline water solubility study reporting that 2-(2'-hydroxyphenyl)phenyl phosphonic acid is readily formed by deesterification of DOPO in water. Although there were no separate experimental studies available for the hydrolysis product, it was considered in the evaluation of the human health designations using structural alerts and professional judgment (ECHA, 2013).

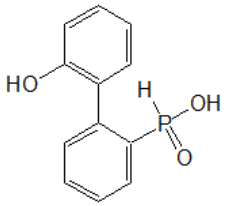
Polymeric: No
Oligomeric: Not applicable

Metabolites, Degradates and Transformation Products: [2-(2'-Hydroxyphenyl)phenyl]phosphonic acid by hydrolytic deesterification (ECHA, 2013)

Analog: [2-(2'-Hydroxyphenyl)phenyl]phosphonic acid (the hydrolysis product of DOPO)

Endpoint(s) using analog values: Endpoints typically obtained in the presence of water for [2-(2'-Hydroxyphenyl)phenyl]phosphonic acid, the hydrolysis product of DOPO

Analog Structure:



Structural Alerts: Phosphinate esters - environmental toxicity (aquatic toxicity); Organophosphorus compounds - neurotoxicity; Phenols (for the hydrolysis product) - neurotoxicity (EPA, 2010; EPA, 2012).

Risk Phrases: R43 - May cause sensitization by skin contact (ECHA, 2013).

Hazard and Risk Assessments: None located.

DOPO CASRN 35948-25-5			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	122 According to Organisation for Economic Co-operation and Development (OECD) 102 (Measured)	Chang et al., 1998 (as cited in ECHA, 2013)	Adequate guideline study.
	117 (Measured)	Chernyshev et al., 1972	Consistent with other measured values.
Boiling Point (°C)	359 (Extrapolated)	McEntee, 1987	The boiling point at 760 mmHg was extrapolated from the measured boiling point at reduced pressure using a computerized nomograph.
	200 at 760 mmHg pressure reported as 5 Torr (Measured)	International Resources, 2001	Value was obtained at a reduced pressure, no further study details reported.
	>300 at 5 mmHg (Estimated)	EPI v4.11; EPA, 1999	Estimated value is greater than the cutoff value, >300°C, according to HPV assessment guidance.
Vapor Pressure (mm Hg)	0.000022 at 25°C (Extrapolated)	McEntee, 1987	The vapor pressure was extrapolated from the measured boiling point at reduced pressure using a computerized nomograph.
	5 at 200°C (Measured)	International Resources, 2001	Value reported at an elevated temperature.
	0.000012 (Estimated)	EPI v4.11	
	$1.1x10^{-8}$ for [2-(2'-hydroxyphenyl)phenyl] phosphonic acid (Estimated)	EPI v4.11	This value is applicable to the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.

DOPO CASRN 35948-25-5			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Water Solubility (mg/L)	3,574 at 25°C according to OECD 105 study. DOPO is readily converted to [2-(2'-hydroxyphenyl)phenyl] phosphonic acid by deesterification in water; however, the rate of hydrolysis and pH conditions were not reported. (Measured)	ECHA, 2013	The reported water solubility is measured for the hydrolysis product of DOPO, in this guideline water solubility study.
	460 (Estimated)	EPI v4.11	
Log K_{ow}	1.87 (Estimated)	EPI v4.11	This compound hydrolyzes in aqueous conditions.
	1.33 for [2-(2'-hydroxyphenyl)phenyl] phosphonic acid (Estimated)	EPI v4.11	This value is applicable to the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
Flammability (Flash Point)	Not readily combustible solid EU Method A.10 Flammability (Solids). Fine powder sample melted to a clear liquid and no ignition was observed. (Measured)	ECHA, 2013	Guideline study reported in a secondary source.
	Flash point: 222°C Cleveland open tester (Measured)	ECHA, 2013	Nonguideline study reported in a secondary source.
Explosivity	Lower explosive limit: 980 g/m^3 Considered non explosive. Vertical tube test. (Measured)	ECHA, 2013	Nonguideline study reported in a secondary source.
Pyrolysis			No data located.
pH	Not applicable (Estimated)	Professional judgment	The substance does not contain functional groups that would be expected to ionize; although this compound hydrolyzes in aqueous conditions.

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
pK_a		Not applicable (Estimated)	Professional judgment	The substance does not contain functional groups that would be expected to ionize. Although this is compound hydrolyzes in aqueous conditions.
Particle Size				No data located.
HUMAN HEALTH EFFECTS				
Toxicokinetics		**Absorption of neat solid is expected to be negligible through skin. Absorption in solution is expected to be moderate through skin, and moderate through lungs and gastrointestinal tract.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**			No data located.
	Other	Absorption of neat solid negligible through skin. Absorption in solution moderate through skin. Absorption moderate through lungs and GI tract. (Estimated)	Professional judgment	Estimated based on physical/chemical properties
Acute Mammalian Toxicity		**LOW: Based on experimental oral and dermal LD_{50} data in rats. No inhalation data were located.**		
Acute Lethality	**Oral**	Mouse (male) oral LD_{50} = 6,490 mg/kg, Mouse (female) oral LD_{50} = 7,580 mg/kg	International Resources, 2001	Study details and test conditions were not available.
		Rat oral LD_{50} > 2,000 mg/kg; Observation period was 14 days. No deaths occurred.	ECHA, 2013	Sufficient information in secondary source. Study conducted in accordance with OECD Guideline 401 and good laboratory practices (GLP). Test substance was CASRN 35948-25-5 named Ukanol DOP 95 in study report. Primary reference not identified; purity of test substance not provided.
	Dermal	Rat dermal LD_{50} > 2,000 mg/kg (semi-occlusive). Observation period was 14 days. No deaths occurred.	ECHA, 2013	Sufficient information in secondary source. Study conducted in accordance with OECD guideline 402 and GLP. Test substance was CASRN 35948-25-5 named HCA in study report. Primary reference not

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				identified. Neat test substance (99.5% pure).
	Inhalation			No data located.
Carcinogenicity		**MODERATE: OncoLogic estimates a low concern for carcinogenicity for the organophosphates chemical class; However, there is uncertainty based on the lack of data and carcinogenic effects cannot be ruled out.**		
	OncoLogic Results	Low; although the structure of DOPO is not fully represented by the phosphate and phosphinate skeletons provided in the program. (Estimated)	OncoLogic, 2008	Estimated for the aryl phosphinate-type compound.
	Carcinogenicity (Rat and Mouse)			No data located.
	Combined Chronic Toxicity/Carcinogenicity			No data located.
	Other			No data located.
Genotoxicity		**LOW: Experimental studies indicate that DOPO was not mutagenic to bacteria or mammalian cells and did not cause chromosomal aberrations *in vitro*.**		
	Gene Mutation *in vitro*	Negative in Ames assay; in Salmonella typhimurium strains TA1535, TA97a, TA98, TA100, and TA102 with and without metabolic activation. Tested up to 5,024 µg/plate (purity >99%). Positive controls responded as expected.	ECHA, 2013	Sufficient study details reported in a secondary source. Study conducted in accordance with OECD guideline 471 and GLP. Test substance was CASRN 35948-25-5 named Ukanol GK-F in study report. Primary reference not identified.
		Negative in Ames assay in *Salmonella typhimurium* strains TA97, TA98, TA100, and TA102 and *Escherichia coli* WP2 *uvr* A pKM 101 with and without metabolic activation. Tested up to 5,000 µg/plate (purity, industrial grade). Positive controls responded as expected.	Hachiya, 1987 (as cited in ECHA, 2013)	Sufficient study details reported in a secondary source. Not GLP study, but adequate as supporting data.
	Gene Mutation *in vivo*			No data located.

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Chromosomal Aberrations *in vitro*	Negative in Chinese hamster lung cells with and without activation. Tested up to 216 µg/mL (purity not provided). Positive controls responded as expected.	Ryu et al., 1994 (as cited in ECHA, 2013)	Sufficient study details reported in a secondary source. Study equivalent to OECD Guideline 473; not GLP study.
	Chromosomal Aberrations *in vivo*			No data located.
	DNA Damage and Repair			No data located.
	Other			No data located.
Reproductive Effects		**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties, as well as professional judgment.**		
	Reproduction/Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects			No data located.
	Other	Low potential for reproductive effects. (Estimated by analogy)	Professional judgment	Estimated based on analogy to a structurally similar compound and professional judgment.
Developmental Effects		**MODERATE: There is uncertain concern for developmental neurotoxicity based on the potential for cholinesterase (ChE) inhibition in dams that may result in alterations of fetal neurodevelopment. There is an estimated Low potential for developmental effects based on closely related analogs with similar structures, functional groups, and physical/chemical properties, as well as professional judgment. There were no experimental data for the developmental or neurodevelopmental endpoints.**		
	Reproduction/ Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Prenatal Development			No data located.
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity	Uncertain concern for developmental neurotoxicity based on the potential for cholinesterase (ChE) inhibition in dams that may result in alterations of fetal neurodevelopment. (Estimated)	Professional judgment	Estimated based on a structural alert for organophosphates for the neurotoxicity endpoint.
	Other	Low potential for developmental effects. (Estimated by analogy)	Professional judgment	Estimated based on analogy to a structurally similar compound and professional judgment.
Neurotoxicity		**MODERATE: There is uncertain potential for neurotoxic effects based on a structural alert for organophosphates. There is also uncertain potential for neurotoxic effects for the hydrolysis product of DOPO [2-(2'-hydroxyphenyl)phenyl] phosphonic acid based on the phenols structural alert and professional judgment.**		
	Neurotoxicity Screening Battery (Adult)			No data located.
	Other	Potential for neurotoxic effects based on a structural alert for organophosphates. (Estimated by analogy)	Professional judgment	Estimated based on a structural alert for organophosphates and professional judgment.
		Potential for neurotoxic effects based on a structural alert for phenols. Estimated for the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid. (Estimated by analogy)	Professional judgment	Estimated based on a structural alert for phenols and professional judgment for the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Repeated Dose Effects		**LOW: Based on no significant effects on multiple endpoints in a 16-week dietary study in rats at doses up to 1,094 mg/kg-day.**		
		Male and female Wistar rats (20/sex/dose) were fed diets containing 0, 0.24, 0.6, or 1.5% HCA (0, 159, 399, or 1,023 mg HCA/kg-day to males; 0, 177, 445, or 1,094 mg HCA/kg-day to females) for 16 weeks (purity of test substance not provided). There were no significant effects on body weight, food consumption, hematology, limited clinical chemistry, urinalysis, organ weight, and gross and microscopic examination of major organs. NOAEL= 1,023 mg/kg-day (males), 1,094 mg/kg-day (females); highest dose tested LOAEL= Not established	ECHA, 2013	Sufficient information in secondary source; data lacking regarding detailed clinical observations and neurobehavioral examination. Study equivalent to OECD guideline 408. Study pre-dates GLP. Test substance identified as HCA in study report. Primary reference not identified.
Skin Sensitization		**MODERATE: Limited data were available to categorize this compound; however, because an SI of 4.2 was seen at a 5% concentration, this compound is considered to have a Moderate concern for skin sensitization. Because the test concentrations started a 5%, there is uncertainty as to if there would be skin sensitization at a concentration < 2% resulting in an SI of 3 which would warrant a High hazard designation.**		
	Skin Sensitization	Local lymph node assay conducted in female CBA/J Rj mice. HCA tested at 5, 10, and 25% (w/v); four mice/treatment group. Test substance >98% pure. Significant lymphoproliferative response was noted for HCA at concentrations of 10% (SI 4.4) and 5% (SI 4.2). SI for positive control was 16.6. HCA was a sensitizer under the conditions of the study.	ECHA, 2013	Sufficient information in secondary source. Study conducted in accordance with OECD guideline 429 and GLP. Test substance was CASRN 35948-25-5 named HCA in study report. Primary reference not identified.
		Risk phrase: R43: May cause sensitization by skin contact	ECHA, 2013	Reported in a secondary source.

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.
Eye Irritation		**MODERATE: Based on moderate signs of eye irritation in rabbits that cleared in 7 days.**		
	Eye Irritation	Neat test material (0.1 mL) was instilled in left eye of 3 female albino rabbits. Eyes were monitored for up to 7 days. Moderate signs of eye irritation that cleared in 7 days were observed among the rabbits.	ECHA, 2013	Sufficient information in secondary source. Study conducted in accordance with OECD guideline 405 and GLP. Test substance was CASRN 35948-25-5 named Ukanol DOP in study report. Primary reference not identified.
Dermal Irritation		**VERY LOW: Based on no skin reactions in semi-occlusive test in rabbits.**		
	Dermal Irritation	Not irritating. Neat test material (0.5 mL) was applied in gauze patches to a clipped skin area of 3 female albino rabbits; patches were secured for 4 hours. Skin was examined from 1 to 72 hours after patch removal and skin washing. No skin reactions were noted at any time point.	ECHA, 2013	Sufficient information in secondary source. Study conducted in accordance with OECD guideline 404 and GLP. Test substance was CASRN 35948-25-5 named Ukanol DOP in study report. Primary reference not identified.
Endocrine Activity		**No data located.**		
				No data located.
Immunotoxicity		**Estimated by professional judgment to have low potential for immunotoxic effects based on closely related analogs with similar structures, functional groups, and physical/chemical properties.**		
	Immune System Effects	Low potential for immunotoxic effects. (Estimated by analogy)	Professional judgment	Estimated by analogy to a structurally similar compound and professional judgment.

DOPO CASRN 35948-25-5			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ECOTOXICITY			
ECOSAR Class	Phenols class; only the hydrolysis product [2-(2'-hydroxyphenyl)phenyl]phosphonic acid was assessed in ECOSAR because DOPO hydrolyzes in water based on data from a water solubility study		
Acute Aquatic Toxicity	**LOW: Based on experimental acute aquatic toxicity values > 100 mg/L in fish, daphnia, and algae. DOPO will hydrolyze in water; therefore only the hydrolysis product, [2-(2'-hydroxyphenyl)phenyl]phosphonic acid, was assessed in ECOSAR, which is represented by the phenols class.**		
Fish LC_{50}	Freshwater fish (*Danio rerio*) 96-hour LC_{50} >100 mg/L; 96-hour NOEC = 100 mg/L; The study was conducted under static conditions. (Experimental)	ECHA, 2013	Sufficient study details reported in a secondary source. Study was conducted in accordance with OECD guideline 203. GLP deviations were not considered critical. Primary reference not identified; test substance purity >99%; Test substance concentrations were kept within 20% of initial concentrations.
	Oryzias latipes 48-hour LC_{50} = 370 mg/L (95% CI, 280-500 mg/L) Limit test conducted under static conditions. (Experimental)	ECHA, 2013	Test substance purity not reported; sufficient study details reported in a secondary source. The study follows the methodology presented in the Japanese Industrial Standard JIS K 0102-1986 No 71. Primary reference not identified.
	96-hour LC_{50} = 130 mg/L (Estimated) ECOSAR: Phenols	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions.
	Fish 96-hour LC_{50} = 770 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by

DOPO CASRN 35948-25-5			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid LC_{50}	*Daphnia magna* 48-hour EC_{50} >100 mg/L; 48-hour NOEC = 100 mg/L Limit test conducted under static conditions. Concentrations of test substance were stable during study. Test substance purity >99%. (Experimental)	ECHA, 2013	Sufficient study details reported in a secondary source. Study was conducted in accordance with OECD guideline 202. GLP deviations were not considered critical. Primary reference not identified.
	Daphnia magna 48-hour EC_{50} = 240 mg/L (unbuffered); no effect up to 289 mg/L when buffered to pH 7.5 Test conducted under static conditions. Test substance purity =98%. Concentrations of the test substance were measured at the beginning and end of the test. (Experimental)	Waaijers et al., 2013	Sufficient study details reported in a primary source, Study was conducted in accordance with OECD Guideline 202 and GLP.
	48-hour LC_{50} = 29 mg/L (Estimated) ECOSAR: Phenols	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions.
	48-hour LC_{50} = 410 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.

DOPO CASRN 35948-25-5			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Green Algae EC_{50}	Green algae (*Desmodesmus subspicatus*) 72-hour ErC_{50} = 110 mg/L; 72-hour EbC_{50} = 100 mg/L; EyC_{50} = 98 mg/L; all nominal concentrations; concentrations of test substance were stable during study). EyC_{50} = biomass at the end of exposure period minus biomass at the start of the exposure period. Test substance purity >99%. (Experimental)	ECHA, 2013	Sufficient study details reported in a secondary source. Study was conducted in accordance with OECD guideline 201 and GLP. Primary reference not identified.
	96-hour EC_{50} = 140 mg/L (Estimated) ECOSAR: Phenols	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions.
	96-hour EC_{50} = 240 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Chronic Aquatic Toxicity	**MODERATE: Based on estimated chronic aquatic toxicity values for the primary degradation product [2-(2'-hydroxyphenyl)phenyl]phosphonic acid of 5.6 mg/L for daphnid. DOPO will hydrolyze in water; therefore only the hydrolysis product was assessed in ECOSAR, which is represented by the phenols class.**		
Fish ChV	Fish ChV = 12 mg/L (Estimated) ECOSAR: Phenols	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions.
	Fish ChV = 70 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimation is for the hydrolysis product; This compound hydrolyzes in aqueous conditions.

DOPO CASRN 35948-25-5			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid ChV	Daphnid ChV = 5.6 mg/L (Estimated) ECOSAR: Phenols	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions.
	Daphnid ChV = 34 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Green Algae ChV	Green algae ChV = 68 mg/L (Estimated) ECOSAR: Phenols	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions.
	Green algae ChV = 54 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimation is for the hydrolysis product; this compound hydrolyzes in aqueous conditions. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				ECOSAR classes that have a more specific mode of action relative to narcosis.
ENVIRONMENTAL FATE				
Transport		**Under aqueous conditions, DOPO is expected to hydrolyze to [2-(2'-hydroxyphenyl)phenyl] phosphonic acid based on data from a water solubility study. Therefore, the transport and mobility of DOPO and the hydrolysis product of DOPO are evaluated. Level III fugacity models incorporating available physical and chemical property data indicate that at steady state DOPO and [2-(2'-hydroxyphenyl)phenyl] phosphonic acid are expected to be found primarily in soil and to a lesser extent, water. DOPO and [2-(2'-hydroxyphenyl)phenyl] phosphonic acid are expected to be highly mobile in soil based on an experimental K_{OC} value; these compounds have the potential to migrate from soil into groundwater. The estimated Henry's Law constant indicates that the hydrolysis product, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid will not significantly volatilize from water to the atmosphere. Volatilization from dry surfaces is also not expected. In the atmosphere, DOPO is expected to exist in both the vapor and particulate phase, based on its vapor pressure and [2-(2'-hydroxyphenyl)phenyl] phosphonic acid is expected to exist primarily in the particulate phase. Vapor-phase DOPO is expected to have limited potential for photodegradation. Particulates will be removed from air by wet or dry deposition.**		
	Henry's Law Constant (atm-m^3/mole)	$<10^{-8}$ for [2-(2'-hydroxyphenyl)phenyl] phosphonic acid (Estimated)	EPI v4.11	This compound hydrolyzes in aqueous conditions. This value is applicable to the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
		5.4×10^{-8} (Estimated)	EPI v4.11	Estimated by the HENRYWIN Bond SAR model.
	Sediment/Soil Adsorption/Desorption - K_{oc}	36 According to OECD 121 (Measured)	ECHA, 2013	Adequate guideline study reported in a secondary source. This study was performed in acetonitrile and water; it is unclear if this value is for DOPO or the hydrolysis product since DOPO is expected to hydrolyze in water based on data from a water solubility study.
		120 (Estimated)	EPI v4.11	This compound hydrolyzes in aqueous conditions. This value is

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				applicable to the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
	Level III Fugacity Model	Air = 0.3% Water = 18.9% Soil = 80.6% Sediment = 0.1% (Estimated)	EPI v4.11	
		Air = 0% Water = 16% Soil = 84% Sediment = 0.2% (Estimated) for [2-(2'-hydroxyphenyl)phenyl] phosphonic acid	EPI v4.11	This compound hydrolyzes in aqueous conditions. These values are applicable to the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
Persistence		**HIGH: The persistence designation of DOPO is High considering ultimate degradation based on an estimated environmental half-life of 75 days in soil. An intermediate, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid, is formed by hydrolysis of DOPO in aqueous environments. This primary degradation product is expected to resist further environmental degradation based on an estimated half-life of 75 days in soil. The rate of hydrolysis is expected to be dependent on pH, with increasing alkalinity resulting in increasing rates of hydrolysis. A guideline OECD 301B Ready Biodegradability study indicated that DOPO is not biodegradable under test conditions with activated sludge; however data from this protocol are insufficient to determine a persistence designation. QSARs of aerobic and anaerobic biodegradation estimate primary aerobic biodegradation in days-weeks and ultimate aerobic degradation in weeks-months for both DOPO and the hydrolysis product. DOPO is not expected to undergo direct photolysis by sunlight as it does not contain chromophores that absorb at wavelengths >290 nm. The atmospheric half-life for the gas phase reactions of DOPO is estimated at 1.8 days, though it is not anticipated to partition significantly to air.**		
Water	**Aerobic Biodegradation**	Passes Ready Test: No Test method: OECD TG 301B: CO_2 Evolution Test 0% degradation after 28 days using an activated sludge inoculum. (Measured)	ECHA, 2013	Adequate guideline study reported in a secondary source; this value is expected to apply to both DOPO and the hydrolysis product since DOPO is expected to hydrolyze in water based on data from a water solubility study.
		Days-weeks (Primary Survey Model)	EPI v4.11	This compound hydrolyzes in

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Weeks-months (Ultimate Survey Model) (Estimated)		aqueous conditions. These values are applicable to DOPO and for the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI v4.11	This compound hydrolyzes in aqueous conditions. These values are applicable to DOPO and for the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI v4.11	This compound hydrolyzes in aqueous conditions. These values are applicable to DOPO and for the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
Soil	**Aerobic Biodegradation**			No data located.
	Anaerobic Biodegradation	Not probable (Anaerobic-methanogenic biodegradation probability model)	EPI v4.11	
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	1.8 days (Estimated)	EPI v4.11	
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment; Mill, 2000	The substance does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	DOPO is readily converted to [2-(2'-hydroxyphenyl)phenyl]phosphonic acid by deesterification in water; however, the rate of hydrolysis and pH conditions were	ECHA, 2013	Summary statement reported in a modified OECD 105 guideline water solubility study; however, the rate of hydrolysis and pH conditions was

DOPO CASRN 35948-25-5				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		not reported. (Measured)		not reported.
		Phosphinate esters hydrolyze in water and their rate of hydrolysis is correlated to pH; increasing alkalinity results in increasing rates of hydrolysis. (Estimated)	EPA, 2010	Adequate summary statement from guidance document.
Environmental Half-life		75 days (Estimated)	PBT Profiler v1.301	Half-life estimated for the predominant compartment (soil), as determined by EPI methodology. This value is applicable to DOPO and for the hydrolysis product of DOPO, for [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
Bioaccumulation		**LOW: The bioaccumulation hazard designation is based on the estimated BCF and BAF values that are <100 for DOPO and the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl]phosphonic acid.**		
	Fish BCF	7.9 (Estimated)	EPI v4.11	This compound hydrolyzes in aqueous conditions.
		3.5 for [2-(2'-hydroxyphenyl)phenyl]phosphonic acid (Estimated)	EPI v4.11	This value is applicable to the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
	Other BCF			No data located.
	BAF	7.7 (Estimated)	EPI v4.11	This compound hydrolyzes in aqueous conditions.
		2.9 for [2-(2'-hydroxyphenyl)phenyl]phosphonic acid (Estimated)	EPI v4.11	This value is applicable to the hydrolysis product of DOPO, [2-(2'-hydroxyphenyl)phenyl] phosphonic acid.
	Metabolism in Fish			No data located.
ENVIRONMENTAL MONITORING AND BIOMONITORING				
Environmental Monitoring		No data located.		
Ecological Biomonitoring		No data located.		
Human Biomonitoring		This chemical was not included in the NHANES biomonitoring report. (CDC, 2013).		

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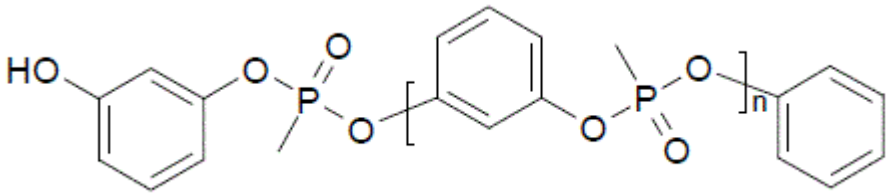
Fyrol PMP

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[§] Based on analogy to experimental data for a structurally similar compound. [‡] The highest hazard designation of any of the oligomers with MW <1,000.

		Human Health Effects										Aquatic Toxicity		Environmental Fate	
Chemical	**CASRN**	**Acute Toxicity**	**Carcinogenicity**	**Genotoxicity**	**Reproductive**	**Developmental**	**Neurological**	**Repeated Dose**	**Skin Sensitization**	**Respiratory Sensitization**	**Eye Irritation**	**Dermal Irritation**	**Acute**	**Chronic**	**Persistence**	**Bioaccumulation**
Fyrol PMP	63747-58-0	**L**	***L*[§]**	***L*[§]**	***M*[§]**	***M*[§]**	***M*[§]**	***M*[§]**	**L**		**L**	**L**	***H*[‡]**	***H*[‡]**	***VH***	***H*[‡]**

Fyrol PMP



Representative Structure

CASRN: 63747-58-0

MW: >1,000; with a significant percentage of components having MW <1,000

MF: $(C_{13}H_{13}O_3P \cdot C_6H_6O_2)_x$

Physical Forms: Solid
Neat: Solid

Use: Flame retardant

SMILES: c1(OP(C)(=O)Oc2cc(O)ccc2)cc(OP(C)(=O)Oc2ccccc2)ccc1 (n=1);
c1(OP(C)(=O)Oc4cc(OP(C)(=O)Oc3cc(O)ccc3)ccc4)cc(OP(C)(=O)Oc2ccccc2)ccc1 (n=2);
c1(OP(C)(=O)Oc5cc(OP(C)(=O)Oc3cc(OP(C)(=O)Oc4cc(O)ccc4)ccc3)ccc5)cc(OP(C)(=O)Oc2ccccc2)ccc1 (n=3);
c1(OP(C)(=O)Oc6cc(OP(C)(=O)Oc3cc(OP(C)(=O)Oc4cc(OP(C)(=O)Oc5cc(O)ccc5)ccc4)ccc3)ccc6)cc(OP(C)(=O)Oc2ccccc2)ccc1 (n=4)

Synonyms: Phosphonic acid, P-methyl-, diphenyl ester, polymer with 1,3-benzenediol; Phosphonic acid, methyl-, diphenyl ester, polymer with 1,3-benzenediol; 1,3-Benzenediol, polymer with diphenyl methylphosphonate; Diphenyl methylphosphonate-resorcinol copolymer; Aryl alkylphosphonate; Poly(m-phenylene methylphosphonate)
Trade Name: Fyrolflex PMP

CASRN 124933-95-5 was identified by literature searches based on name as a related alternative. CASRN 124933-95-5 has a slightly different structure, and no other applicable data were found for this CASRN.

Chemical Considerations: This alternative is a polymer consisting of oligomers with MWs above and below 1,000 daltons according to commercial product datasheets.
The oligomers with a MW >1,000, where n≥5, are assessed using the available polymer assessment literature.
The components with a MW <1,000 are evaluated with four representative structures, where n=1, 2, 3 and 4, as indicated in the SMILES entry. The low MW components are assessed with EPI v4.11 and ECOSAR v1.11 estimates due to an absence of publicly available experimental physical/chemical, environmental fate and aquatic toxicity values. A typical phosphorus content of 17.5% was reported from the commercial product literature. (Hsu, 2013; ICL, 2013).

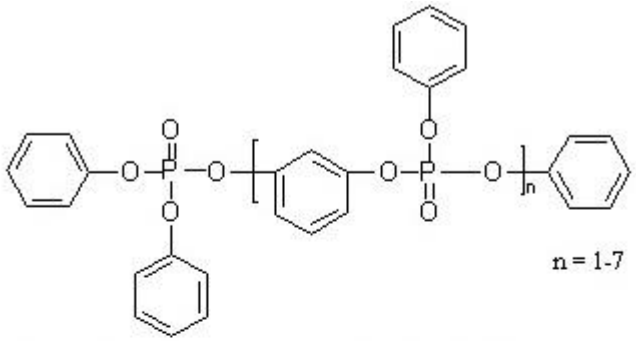
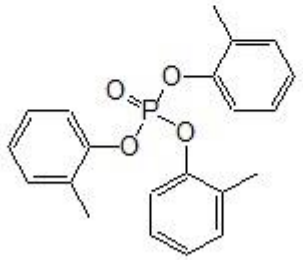
Polymeric: Yes
Oligomeric: This polymer is terminated with either resorcinol and/or phenyl groups based on the starting materials. The repeating units of this polymer are m-phenylene methylphosphonate. A representative structure for n=1 is identified in the SMILES section above.

Metabolites, Degradates and Transformation Products: None identified. Environmental degradation of Fyrol PMP has not been demonstrated in experimental studies. Degradation of Fyrol PMP by sequential dephosphorylation could produce phosphinates, phenol (CASRN 108-95-2) or resorcinol (CASRN 108-46-3). The importance of dephosphorylation relative to possible competing pathways has not been demonstrated in a published study. (Professional judgment)

Analog: Resorcinol bis-diphenylphosphate (RDP; CASRN 125997-21-9); tricresyl phosphate (TCP; CASRN 1330-78-5);and confidential analogs

Endpoint(s) using analog values: Carcinogenicity, genotoxicity, reproductive,

Analog Structure:

developmental, repeated dose	 n = 1-7 Resorcinol bis-diphenylphosphate (RDP; CASRN 125997-21-9)  Phosphoric acid, tris(methylphenyl) ester (CDP; CASRN 1330-78-5) Representative structure
Structural Alerts: Phenols - neurotoxicity; Organophosphorus compounds - neurotoxicity. (EPA, 2012).	
Risk Phrases: Not classified by Annex VI Regulation (EC) No 1272/2008 (ESIS, 2012).	
Hazard and Risk Assessments: None located.	

Fyrol PMP CASRN 63747-58-0			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	52 (Measured)	ICL, 2010	Reported in a material safety datasheet.
Boiling Point (°C)	>300 (Estimated)	EPA, 1999; EPI v4.11	Estimate based on four representative structures with MW <1,000. Also estimated for oligomers with MWs >1,000. Cutoff value according to HPV assessment guidance and cutoff value used for large, high MW solids.
Vapor Pressure (mm Hg)	$<10^{-8}$ for n=1-4 (Estimated)	EPA, 1999; EPI v4.11	Estimates based on the representative structures with MW <1,000. Cutoff value for nonvolatile compounds according to HPV assessment guidance.
	$<10^{-8}$ (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Cutoff value for large, high MW polymer components.
Water Solubility (mg/L)	8.4 for n=1 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1.
	0.1 for n=2 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=2.
	0.001 for n=3 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=3.
	$1.3x10^{-5}$ for n=4 (Estimated)	EPI v4.11; EPA, 1999	Estimates based on representative oligomer where n=4. Values are less than the cutoff value, <0.001 mg/L, for non-soluble compounds according to HPV assessment guidance.
	<0.001 for the n≥5 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Cutoff value for large, high MW non-ionic polymer components.
	<0.01% (Measured)	ICL, 2010	Reported in a material safety datasheet.

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Log K_{ow}		3.4 for n=1 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1.
		4.4 for n=2 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=2.
		5.3 for n=3 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=3.
		6.3 for n=4 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=4.
Flammability (Flash Point)		Not flammable (Measured)	ICL, 2010	Reported in safety datasheet and based on its use as a flame retardant.
Explosivity		Not expected to form explosive mixtures with air. (Estimated)	Professional judgment	No experimental data located; based on its use as a flame retardant.
Pyrolysis				No data located.
pH				No data located.
pK_a				No data located.
Particle Size				No data located.
HUMAN HEALTH EFFECTS				
Toxicokinetics		**No experimental data were located. Based on professional judgment, absorption is expected to be poor by all routes for the low MW (<1,000) fraction. There is no absorption expected for any route of exposure for the MW >1,000 components.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	Absorption is expected to be negligible by all routes for the neat material and poor by all routes for the low MW fraction if in solution.	Professional judgment	Estimated based on professional judgment.
	Other			No data located.
Acute Mammalian Toxicity		**LOW: Experimental data indicates that the LD_{50} are >2,000 mg/kg when administered orally and dermally to rats. Experimental data for the analog, phosphoric trichloride, polymer with 1,3-benzenediol, phenyl ester (CASRN 125997-21-9) indicates an LC_{50} > 4.14 mg/L.**		
Acute Lethality	**Oral**	Rat LD_{50} >2,000 mg/kg in a 75% DMSO solution	ICL, 2010	Reported in a material safety datasheet with limited study details.
	Dermal	Rabbit LD_{50} >5,000 mg/kg	ICL, 2010	Reported in a material safety

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				datasheet with limited study details.
	Inhalation	Rat inhalation LC_{50} > 4.14 mg/L	EPA, 2010	Estimated by analogy to Phosphoric trichloride, polymer with 1,3-benzenediol, phenyl ester (CASRN 125997-21-9)
Carcinogenicity		**LOW: Estimated based on analogy to tricresyl phosphate (TCP). There was no evidence of carcinogenicity in rats or mice following dietary exposure to a commercial mixture of TCP for 2 years. There were no experimental data located for this substance.**		
	OncoLogic Results			This polymer is not amenable to available estimation methods.
	Carcinogenicity (Rat and Mouse)			No data located.
	Combined Chronic Toxicity/Carcinogenicity	2-Year dietary study in Fischer 344/N rats (95/sex/concentration) Test substance concentrations: 0, 75, 150, 300 ppm (approximately 0, 3, 6, and 13 mg/kg bw-day for males and 0, 4, 7, and 15 mg/kg bw-day for females) Chronic toxicity: NOAEL = 13 mg/kg bw-day (males); 4 mg/kg bw-day for females LOAEL = 26 mg/kg bw-day (males) and 7 mg/kg bw-day (females) for cytoplasmic vacuolization of adrenal cortex No evidence of carcinogenic activity (Estimated by analogy)	NTP, 1994	Estimated based on analogy to tricresyl phosphate (TCP); study details reported in a reliable primary source; test substance: Tricresyl phosphate (CASRN 1330-78-5) as a commercial product comprised of 18% dicresyl phosphate esters (unconfirmed isomeric composition) and 79% tricresyl phosphate esters (21% confirmed as tri-m-cresyl phosphate, 4% as tri-p-cresyl phosphate, and no detectable tri-o-cresyl phosphate [<0.1%]).
		2-Year dietary study in B6C3F1 mice (95/sex/concentration) Test substance concentrations: 0, 60, 125, 250 ppm (approximately 0, 7, 13, and 27 mg/kg bw-day for males and 0, 8, 18, and 37 mg/kg bw-day for females)	NTP, 1994	Estimated based on analogy to tricresyl phosphate (TCP); study details reported in a reliable primary source; test substance: Tricresyl phosphate (CASRN 1330-78-5) as a commercial product comprised of

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		chronic toxicity NOAEL = 18 mg/kg bw-day for females, not established for males LOAEL: 7 mg/kg bw-day (males) and 37 mg/kg bw-day (females) for ceroid pigmentation of adrenal cortex No evidence of carcinogenic activity (Estimated by analogy)		18% dicresyl phosphate esters (unconfirmed isomeric composition) and 79% tricresyl phosphate esters (21% confirmed as tri-m-cresyl phosphate, 4% as tri-p-cresyl phosphate, and no detectable tri-o-cresyl phosphate [<0.1%]).
	Other			No data located.
Genotoxicity		**LOW: Based on results from an Ames assay, analogy to RDP (CASRN 125997-21-9) and professional judgment. The test substance was reported to be negative for gene mutations in an Ames assay; however, there were no experimental chromosomal aberrations data for the test substance. The analog RDP did not cause gene mutations or chromosomal aberrations *in vitro* and did not produce an increase in micronuclei in mice *in vivo*.**		
	Gene Mutation *in vitro*	Negative, Ames assay	ICL, 2010	Reported in a material safety datasheet with limited study details.
		Negative in *Salmonella typhimurium* (strains not indicated) with and without metabolic activation at concentrations up to 5,000 µg/plate. No cytotoxicity was evident. (Estimated by analogy)	EPA, 2010; Pakalin et al., 2007	Estimated based on analogy. Guideline study. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9).
		Negative in *Escherichia coli* (strains not indicated) with and without metabolic activation at concentrations up to 5,000 µg/plate. No cytotoxicity was evident. (Estimated by analogy)	EPA, 2010; Pakalin et al., 2007	Estimated based on analogy. Guideline study. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9).
	Gene Mutation *in vivo*			No data located.

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Chromosomal Aberrations *in vitro*	Negative in chromosomal aberration test (cultured human lymphocytes) with and without metabolic activation at concentrations up to 625 µg/mL. Cytotoxicity data not indicated. (Estimated by analogy)	EPA, 2010; Pakalin et al., 2007	Estimated based on analogy. Guideline study. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9).
	Chromosomal Aberrations *in vivo*	Negative in mammalian erythrocyte micronucleus test (Swiss mice) following a single oral dose of 5,000 mg/kg-bw. (Estimated by analogy)	EPA, 2010; Pakalin et al., 2007	Estimated based on analogy. Guideline study. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9).
		Negative in mammalian erythrocyte micronucleus test (mice) following single oral dose of 500 mg/kg-bw. (Estimated by analogy)	Submitted confidential study	Estimated based on analogy. Reported in a submitted confidential study for the analog RDP (CASRN 125997-21-9) conducted in accordance with GLP and OECD Guideline 474.
	DNA Damage and Repair			No data located.
	Other	Limited bioavailability expected for the high MW (>1,000) components. (Estimated for n ≥5 oligomers)	Boethling and Nabholz, 1997; Professional judgment	Based on polymer assessment literature.
Reproductive Effects		**MODERATE: Based on data for a confidential analog and professional judgment. There were no experimental data located for the substance Fyrol PMP. There is potential for reproductive toxicity based on data for a confidential analog reporting reduced litter size and weight at 250 mg/kg-day (NOAEL: 50 mg/kg-day) a An experimental study for the analog RDP indicated no adverse effects on reproductive performance or fertility parameters at doses up to 1,000 mg/kg-day (highest dose tested) in a two generation dietary study in parental rats. Developmental changes effecting the reproductive system were also reported in F_1 female rats at 250 mg/kg-day. In the absence of experimental data for this substance, and conflicting results for analogs, a conservative approach was used to assign a Moderate hazard designation.**		
	Reproduction/Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity	Two generation dietary reproduction study in rats. Sprague-Dawley rats (30/sex/dose) were fed 0, 50, 500, or	EPA, 2010; Pakalin et al., 2007	Estimated based on analogy. Guideline study. Data are for a commercial polymeric mixture of

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Screen	1,000 mg/kg-day to the analog RDP in the diet for 10 weeks. There were no reproductive or systemic effects reported in parental rats at doses as high as 1,000 mg/kg-day. Developmental changes affecting the reproductive system (delayed vaginal opening and preputial separation) were reported in F_1 female rats at 500 and 1,000 mg/kg-day. This effect was considered by study authors to be secondary to reduction of body weight in F_1 generation during week 1 (treated animals had decreased body weights compared to controls during week 1, reportedly due to an initial aversion to taste of diet) Parental systemic and reproductive toxicity: NOAEL: ≥1,000 mg/kg-day (highest dose tested) LOAEL: Not established Offspring (developmental) reproductive toxicity: NOAEL(F_1generation): 50 mg/kg-day LOAEL (F_1generation): 500 mg/kg-day (for vaginal opening and preputial separation) (Estimated by analogy)		the analog RDP (CASRN 125997-21-9).

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Reproduction and Fertility Effects	Potential for reproductive toxicity; no pregnancies (1,000 mg/kg-day); reduced litter size and weight (250 mg/kg-day). NOAEL: 50 mg/kg-day LOAEL: 250 mg/kg-day (Estimated by analogy)	Professional judgment; Submitted confidential study	Estimated by analogy to confidential analog.
	Other	Limited bioavailability expected. (Estimated for n ≥5 oligomers)	Boethling and Nabholz, 1997; Professional judgment	Based on cutoff value for large, high MW non-ionic polymers.
Developmental Effects		**MODERATE: Based on analogy to RDP (CASRN 125997-21-9) and professional judgment. There were no experimental data for the substance Fyrol PMP. An experimental study for the analog RDP reported a NOAEL of 50 mg/kg-day in a two generation dietary reproduction study in rats. Adverse effects included delayed vaginal opening and preputial separation at a dose of 500 mg/kg-day. Though the changes are considered by the study authors to be secondary to reduced body weight in the F_1 generation, reported data were insufficient to determine if this was a secondary effect. No adverse developmental effects were observed in rabbits following oral administration of the analog RDP at doses up to 1,000 mg/kg-day. There were no data located for the developmental neurotoxicity endpoint. The analog RDP (CASRN 125997-21-9) has been shown to cause cholinesterase inhibition which may be an indicator of potential developmental neurotoxicity.**		
	Reproduction/ Developmental Toxicity Screen			No data located.

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen	Two generation dietary reproduction study in rats. Sprague-Dawley rats (30/sex/dose) were fed 0, 50, 500, or 1,000 mg/kg-day to the analog RDP in the diet for 10 weeks. Vaginal opening and preputial separation were delayed at 500 and 1,000 mg/kg-day. This effect was considered by study authors to be secondary to reduction of body weight in F_1 generation during week 1 (treated animals had decreased body weights compared to controls during week 1, reportedly due to an initial aversion to taste of diet). NOAEL(F_1generation): 50 mg/kg-day LOAEL (F_1generation): 500 mg/kg-day (for vaginal opening and preputial separation) (Estimated by analogy)	EPA, 2010; Pakalin et al., 2007	Estimated based on analogy. Guideline study. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9); limited study details reported to determine if the developmental effect is secondary to reduced body weight in F1 rats.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Prenatal Development	Pregnant rabbits; oral gavage; gestation days (GDs) 6-28; 0, 50, 200 or 1,000 mg/kg-day test material containing the analog RDP No clinical signs of toxicity. No adverse effects on maternal food consumption, body weight gain or organ weights. No adverse effects on fetal body weights, viability, or any developmental endpoint measured. NOAEL (maternal and developmental toxicity): >1,000 mg/kg-day (highest dose tested) LOAEL: Not established (Estimated by analogy)	EPA, 2010; Environment Agency, 2009	Estimated based on analogy. Guideline study reported in a secondary source. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9).
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity	There were no data located for the developmental neurotoxicity endpoint. As a result, there is uncertain potential for developmental neurotoxicity for this substance. The analog RDP (CASRN 125997-21-9) has been shown to cause cholinesterase inhibition which may be an indicator of potential developmental neurotoxicity. (Estimated)	Professional judgment	Estimated by analogy to RDP (CASRN 125997-21-9).
	Other	Limited bioavailability expected. (Estimated for n≥5 oligomers)	Boethling and Nabholz, 1997; Professional judgment	Based on cutoff value for large, high MW non-ionic polymers.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Neurotoxicity		**MODERATE: Based on data for the analog RDP (CASRN 125997-21-9) and professional judgment. There were no experimental data for the substance Fyrol PMP. A study for the analog RDP reported a 28-day inhalation LOAEL of 0.5 mg/L for inhibition of plasma ChE in rats (NOAEL = 0.1 mg/L). The neurotoxicity criteria values are tripled for 28-day studies to correlate to the criteria values based on 90-day repeated dose studies; the LOAEL and NOAEL of 0.5 mg/kg-day and 0.1 mg/kg-day, respectively, lie within the MODERATE hazard range from 0.06 - 0.6 mg/L. There is also potential for neurotoxicity based on the presence of the phenol and organophosphorus structural alerts.**		
	Neurotoxicity Screening Battery (Adult)	28-day inhalation study in rats with the analog RDP (CASRN 125997-21-9); 0, 0.1, 0.5 and 2.0 mg/L (aerosol) Significant inhibition of plasma cholinesterase (ChE) (0.5 and 2.0 mg/L). No clinical signs suggestive of neurotoxic effect. ChE was not affected after study termination. NOAEL: 0.1 mg/L LOAEL: 0.5 mg/L (plasma ChE inhibition) (Estimated by analogy)	Environment Agency, 2009	Estimated based on analogy to RDP (CASRN 125997-21-9). Study details reported in a secondary source; study was not designed to assess all neurological parameters; criteria values are tripled for chemicals evaluated in 28-day studies; the LOAEL of 0.5 mg/kg-day falls within the Moderate hazard criteria (0.06-0.6 mg/L).
		28-day oral (gavage) study in mice with the analog RDP (CASRN 125997-21-9); 0, 500, 1,500, 5,000 mg/kg-day. Dose-related decrease in plasma ChE compared to controls, which was no longer apparent after the 60 day recovery period. No NOAEL/LOAEL determined. (Estimated by analogy)	Environment Agency, 2009	Estimated based on analogy. Study details reported in a secondary source; study was not designed to assess all neurological parameters; cannot rule out all neurotoxicity.
	Other	Limited bioavailability expected. (Estimated for n≥5 oligomers)	Boethling and Nabholz, 1997; Professional judgment	Based on cutoff value for large, high MW non-ionic polymers.
		Potential for neurotoxic effects based on a	EPA, 2012; Professional	Estimated based on a structural alert

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		structural alert for phenol and organophosphorus compounds.	judgment	for phenols and organophosphorus compounds and professional judgment.
Repeated Dose Effects		**MODERATE: Based on analogy to RDP (CASRN 125997-21-9), a confidential analog and professional judgment. There were no experimental data for the test substance Fyrol PMP. A 4-week inhalation exposure study in rats to 0.5 mg/L of the analog RDP as an aerosol resulted in alveolar histiocytosis (NOAEC = 0.1 mg/L- day). No other exposure-related gross or microscopic pathology was identified in any organ in this study. The repeated dose criteria values are tripled for 28-day studies to correlate to the criteria values based on 90-day repeated dose studies; this study lies in the MODERATE hazard range from 0.06 - 0.6 mg/L. There is also potential for liver toxicity based on a confidential analog (NOEL = 300 mg/kg-day).**		

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		In a 4-week inhalation study Sprague-Dawley rats (10/sex/group) were exposed (aerosol, nose only) to 0, 100, 500 or 2,000 mg/m^3 (0, 0.1, 0.5, or 2 mg/L) of the analog RDP. No deaths or clinical signs of toxicity. Decreased body weight and food consumption in males. Significant inhibition of plasma cholinesterase in females at 500 and 2,000 mg/m^3 and in males at 2,000 mg/m^3. White foci in the lungs at 2,000 mg/m^3 and alveolar histiocytosis at 500 and 2,000 mg/m^3. Although lung changes are relevant, they were not considered to be a reflection of a specific toxic response to the analog RDP; these changes are characteristic of exposure to non-cytotoxic water-insoluble materials. No other gross or microscopic pathology in any organ. NOAEC: 100 mg/m^3 (0.1 mg/L) LOAEC: 500 mg/m^3 (0.5 mg/L; based on alveolar histiocytosis) (Estimated based on analogy)	EPA, 2010; Environment Agency, 2009	Estimated based on analogy. Guideline study reported in a secondary source. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9).
		28-day oral study, rats Potential for liver toxicity. NOEL: 300 mg/kg-day (Estimated based on analogy)	Submitted confidential study; Professional judgment	Estimated based on analogy to confidential analog.
		Limited bioavailability expected for the high MW (>1,000) components. (Estimated for n ≥5 oligomers)	Boethling and Nabholz, 1997; Professional judgment	Based on polymer assessment literature.
	Immune System Effects	Negative, oral gavage study in mice.	EPA, 2010	Estimated based on analogy.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Female B6C3F1 mice (50/group) were exposed via oral gavage to 0, 500, 1,500, or 5,000 mg/kg-day of the analog RDP for 28 days. No deaths, clinical signs of toxicity, or effects on body or organ weights. No adverse histopathological changes or necropsy findings. No treatment-related changes in peritoneal cell numbers or cell types, peritoneal macrophage phagocytic activity or host susceptibility to infection. No adverse effect on splenic natural killer cell activity, lymphocyte blastogenesis, or antibody-forming cell function. There were significant decreases in erythrocyte cholinesterase activity and plasma pseudocholinesterase activity in all dose groups, but both enzyme activities returned to control levels at the end of the 60 day recovery period.		Guideline study reported in a secondary source. Data are for a commercial polymeric mixture of the analog RDP (CASRN 125997-21-9).
Skin Sensitization		**LOW: Negative for skin sensitization in guinea pigs.**		
	Skin Sensitization	Non-sensitizing, guinea pigs	Submitted confidential study	Adequate confidential study
		Not a sensitizer, Modified Buehler Method	ICL, 2010	Reported in a material safety datasheet with limited study details.
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.
Eye Irritation		**LOW: Fyrol PMP was mildly irritating to rabbit eyes.**		
	Eye Irritation	Mild, rabbits	ICL, 2010	Reported in a material safety datasheet with limited study details.
		Negative, rabbits	Submitted confidential study	Study details and test conditions were not available.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Dermal Irritation		**LOW: Fyrol PMP was mildly irritating to rabbit skin.**		
	Dermal Irritation	Mild irritant, rabbit	ICL, 2010	Reported in a material safety datasheet with limited study details.
Endocrine Activity		**No experimental data were located to evaluate and determine if Fyrol PMP affects endocrine activity. However, resorcinol, a metabolite of the analog RDP (CASRN 125997-21-9) and a starting material in Fyrol PMP synthesis, is listed as a suspected endocrine disruptor by the EU.**		
		Resorcinol (CASRN 108-46-3) is listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors. (Estimated by analogy)	European Commission, 2012	Estimated by analogy. "Potential for endocrine disruption. In vitro data indicating potential for endocrine disruption in intact organisms. Also included effects in-vivo that may, or may not, be endocrine disruption-mediated. May include structural analyses and metabolic considerations".

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Immunotoxicity		**The analog, RDP (CASRN 125997-21-9), had no effect on immunological parameters at doses up to 5,000 mg/kg-day (highest dose tested) in an oral gavage study in mice. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for immunotoxicity.**		
	Immune System Effects	Negative, oral gavage study in mice. Female B6C3F1 mice (50/group) were exposed via oral gavage to 0, 500, 1,500, or 5,000 mg/kg-day for the analog RDP for 28 days. No deaths, clinical signs of toxicity, or effects on body or organ weights. No adverse histopathological changes or necropsy findings. No treatment-related changes in peritoneal cell numbers or cell types, peritoneal macrophage phagocytic activity or host susceptibility to infection. No adverse effect on splenic natural killer cell activity, lymphocyte blastogenesis, or antibody-forming cell function. There were significant decreases in erythrocyte cholinesterase activity and plasma pseudocholinesterase activity in all dose groups, but both enzyme activities returned to control levels at the end of the 60 day recovery period.	EPA, 2010	Estimated based on analogy. Guideline study reported in a secondary source. Data are for the analog, a commercial polymeric mixture of RDP (CASRN 125997-21-9).
		Limited bioavailability expected for the high MW (>1,000) components. (Estimated for n ≥5 oligomers)	Boethling and Nabholz, 1997; Professional judgment	Based on polymer assessment literature.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ECOTOXICITY			
ECOSAR Class	Phenols		
Acute Aquatic Toxicity	**HIGH: Based on estimated acute aquatic toxicity values for fish, daphnia, and green algae using the phenols SAR for a representative structure, where n=1, with a MW <1,000. The high MW components, with a MW>1,000 have low water solubility and are expected to have no effects at saturation (NES).**		
Fish LC_{50}	Freshwater fish 96-hour LC_{50}: 6.2 mg/L (ECOSAR class: Phenols); 19 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimate based on representative oligomer n=1. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Freshwater fish 96-hour LC_{50}: n=2: 1.6 mg/L (ECOSAR class: Phenols); 3.6 mg/L (ECOSAR class: Neutral organic SAR) n=3: 0.39 mg/L (ECOSAR class: Phenols); 0.64 mg/L (ECOSAR class: Neutral organic SAR) n=4: 0.09 mg/L (ECOSAR class: Phenols); 0.11 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimates based on representative oligomers n=2 through n=4. The corresponding estimated effects exceed the water solubilities (0.1 mg/L for n=2, 0.001 mg/L for n=3, and 0.00001 mg/L for n=4) by more than 10x. The log K_{ow} of 5.3 for n=3, and 6.3 for n=4 for these oligomers exceed the Neutral organic SAR limitation for the log K_{ow} of 5.0. NES are predicted for these endpoints. Narcosis classes (neutral organics)

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
Daphnid LC_{50}	*Daphnia magna* 48-hour LC_{50}: 3.5 mg/L (ECOSAR class: Phenols); 12 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimate based on representative oligomer n=1. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Daphnia magna 48-hour LC_{50}: n=2: 1.4 mg/L (ECOSAR class: Phenols); 2.5 mg/L (ECOSAR class: Neutral organic SAR)	ECOSAR v1.11	Estimates based on representative oligomers n=2 through n=4. The corresponding estimated effects exceed the water solubilities (0.1

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	n=3: 0.52 mg/L (ECOSAR class: Phenols); 0.49 mg/L (ECOSAR class: Neutral organic SAR) n=4: 0.18 mg/L (ECOSAR class: Phenols); 0.09 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		mg/L for n=2, 0.001 mg/L for n=3, and 0.00001 mg/L for n=4) by more than 10x. The log K_{ow} of 5.3 for n=3, and 6.3 for n=4 for these oligomers exceed the Neutral organic SAR limitation for the log K_{ow} of 5.0. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Green Algae EC_{50}	Green algae 96-hour EC_{50}: 14 mg/L (ECOSAR class: Phenols); 16 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimate based on representative oligomer n=1. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Green algae 96-hour EC_{50}: n=2: 5.1 mg/L (ECOSAR class: Phenols); 4.7 mg/L (ECOSAR class: Neutral organic SAR) n=3: 1.7 mg/L (ECOSAR class: Phenols); 1.3 mg/L (ECOSAR class: Neutral organic SAR) n=4: 0.55 mg/L (ECOSAR class: Phenols); 0.35 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimates based on representative oligomers n=2 through n=4. The corresponding estimated effects exceed the water solubilities (0.1 mg/L for n=2, 0.001 mg/L for n=3, and 0.00001 mg/L for n=4) by more than 10x. The log K_{ow} of 5.3 for n=3, and 6.3 for n=4 for these oligomers exceed the Neutral organic SAR limitation for the log K_{ow} of 5.0. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
Chronic Aquatic Toxicity	**HIGH: Based on estimated chronic aquatic toxicity values for fish, daphnia, and green algae using the phenols SAR for representative structure, where n=1, with a MW <1,000. The high MW components, with a MW>1,000 have low water solubility and are expected to have no effects at saturation (NES).**		
Fish ChV	Freshwater fish ChV: 0.77 mg/L (ECOSAR class: Phenols); 2.1 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimate based on representative oligomer n=1. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Freshwater fish ChV: n=2: 0.23 mg/L (ECOSAR class: Phenols); 0.46 mg/L (ECOSAR class: Neutral organic SAR) n=3: 0.06 mg/L (ECOSAR class: Phenols); 0.09 mg/L (ECOSAR class:	ECOSAR v1.11	Estimates based on representative oligomers n=2 through n=4. The estimated effect for n=2 exceeds the water solubility of 0.1 mg/L, but not by 10x as required to be considered NES by ECOSAR. The chemical

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Neutral organic SAR) n=4: 0.02 mg/L (ECOSAR class: Phenols); 0.02 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		may not be soluble enough to measure the predicted effect. The corresponding estimated effects for n=3 and n=4 exceed the water solubilities (0.001 mg/L and 0.00001 mg/L, respectively) by more than 10x. NES are predicted for these oligomers. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid ChV	Daphnia magna ChV: 0.67 mg/L (ECOSAR class: Phenols); 1.7 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimate based on representative oligomer n=1. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Daphnia magna ChV: n=2: 0.27 mg/L (ECOSAR class: Phenols); 0.46 mg/L (ECOSAR class: Neutral organic SAR) n=3: 0.1 mg/L (ECOSAR class: Phenols); 0.11 mg/L (ECOSAR class: Neutral organic SAR) n=4: 0.03 mg/L (ECOSAR class: Phenols); 0.03 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimates based on representative oligomers n=2 through n=4. The estimated effect for n=2 exceeds the water solubility of 0.1 mg/L, but not by 10x as required to be considered NES by ECOSAR. The chemical may not be soluble enough to measure the predicted effect. The corresponding estimated effects for n=3 and n=4 exceed the water solubilities (0.001 mg/L and 0.00001 mg/L, respectively) by more than 10x. NES are predicted for these oligomers. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
Green Algae ChV	Green algae ChV: 6.5 mg/L (ECOSAR class: Phenols); 5.5 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimate based on representative oligomer n=1. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Green algae ChV: n=2: 2.4 mg/L (ECOSAR class: Phenols); 2 mg/L (ECOSAR class: Neutral organic SAR) n=3: 0.78 mg/L (ECOSAR class: Phenols); 0.68 mg/L (ECOSAR class: Neutral organic SAR) n=4: 0.25 mg/L (ECOSAR class:	ECOSAR v1.11	Estimates based on representative oligomers n=2 through n=4. The corresponding estimated effects exceed the water solubilities (0.1 mg/L for n=2, 0.001 mg/L for n=3, and 0.00001 mg/L for n=4) by more than 10x. NES are predicted for these endpoints.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Phenols); 0.22 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis. ECOSAR also provided results for the Esters, and Esters (phosphate) classes; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
		NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
ENVIRONMENTAL FATE				
Transport		**The estimated negligible water solubility and estimated negligible vapor pressure indicate that this polymer is anticipated to partition predominantly to soil and sediment. The estimated Henry's Law Constant of $<10^{-8}$ atm-m^3/mole indicates that it is not expected to volatilize from water to the atmosphere. The estimated K_{oc} of >30,000 indicates that it is not anticipated to migrate from soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant (atm-m^3/mole)	$<10^{-8}$ for the n≥5 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	High MW polymers are expected to have low vapor pressure and are not expected to undergo volatilization.
		$<10^{-8}$ for n=1-4 (Estimated)	EPI v4.11	
	Sediment/Soil Adsorption/Desorption - K_{oc}	>30,000 for n=1-4 (Estimated)	EPI v4.11; Professional judgment	Estimated value based on representative structures with MW <1,000. Cutoff value for nonvolatile compounds.
		>30,000 for the n≥5 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the n≥5 oligomers; cutoff value used for large, high

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				MW polymers. High MW polymers are expected to adsorb strongly to soil and sediment.
	Level III Fugacity Model	Air = 0% Water = 4.8% Soil = 57% Sediment = 39% (Estimated) for n=1	EPI v4.11	Estimates based on a representative structure where n=1. No data located for the high MW component of the polymers.
Persistence		**VERY HIGH: Although experimental data are not available, the high MW components of this polymer (n≥5; MW>1,000) are expected to be recalcitrant to biodegradation. Estimated half-lives for ultimate aerobic biodegradation are >180 days for the n=1 oligomer, representing MW <1,000 components of the polymer. Degradation of this polymer by hydrolysis or direct photolysis is not expected to be significant as the functional groups present do not tend to undergo these reactions under environmental conditions. The atmospheric half-life is estimated to be <1 day; however, the polymer is not anticipated to partition significantly to air.**		
Water	**Aerobic Biodegradation**	Days-weeks (Primary Survey Model) Weeks-months (Ultimate Survey Model) (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1.
		Recalcitrant for n≥5 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	High MW polymers are expected to be non-biodegradable.
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI v4.11; Professional judgment	Estimated value based on representative structures with MW <1,000. Also, the high MW polymer components are anticipated to be nonvolatile.
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI v4.11; Professional judgment	Estimated value based on representative structures with MW <1,000. Also, the high MW polymer components are anticipated to be nonvolatile.
Soil	**Aerobic Biodegradation**			No data located.
	Anaerobic Biodegradation	Not probable (Anaerobic-methanogenic biodegradation probability model) for n=1-4	EPI v4.11	Estimates based on representative oligomer where n=1-4.

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		Recalcitrant for n≥5 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	High MW polymers are expected to be resistant to removal under anoxic conditions due to their limited bioavailability.
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	<0.15 days (Estimated)	EPI v4.11	Estimated value based on four confidential representative structures with MW <1,000.
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Mill, 2000; Professional judgment	This polymer does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	>1 year (Estimated)	Professional judgment	Given the limited solubility estimated for this material, hydrolysis is not anticipated to occur to an appreciable extent.
		>1 year at pH 6 68 days at pH 7 6.8 days at pH 8 16 hours at pH 9 (Estimated for n=1)	EPI v4.11	Hydrolysis rates are expected to be pH-dependent and may be limited by the low water solubility of this compound. Under basic conditions, sequential dephosphorylation reactions may occur.
Environmental Half-life		>75 days Half-life estimated for representative structure where n=1; in the predominant compartment, soil, as determined by EPI and the PBT Profiler methodology (Estimated)	PBT Profiler v1.301; EPI v4.11	Half-life estimated for the predominant compartment, soil, as determined by EPI and the PBT Profiler methodology.

Fyrol PMP CASRN 63747-58-0				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Bioaccumulation		**HIGH: The estimated BCF and BAF for the low MW components (n=1-4; MW<1,000) result in a High bioaccumulation designation. The higher MW oligomers that may be found in the polymeric mixture (n≥5; MW>1,000) are expected to have Low potential for bioaccumulation based on their large size and low water solubility according to the polymer assessment literature and professional judgment.**		
	Fish BCF	6,600 for n=4 (Estimated)	EPI v4.11	Estimates based on representative structure where n=4.
		1,500 for n=3 (Estimated)	EPI v4.11	Estimates based on representative structure where n=3.
		360 for n=2 (Estimated)	EPI v4.11	Estimates based on representative structure where n=2.
		85 for n=1 (Estimated)	EPI v4.11	Estimates based on representative structure where n=1.
		<100 (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the oligomers with a MW >1,000. Cutoff value for large, high MW, insoluble polymers according to polymer assessment literature.
	Other BCF			No data located.
	BAF	$2.1x10^6$ for n=4 (Estimated)	EPI v4.11	Estimates based on representative structure where n=4.
		$3.2x10^4$ for n=3 (Estimated)	EPI v4.11	Estimates based on representative structure where n=3.
		1,200 for n=2 (Estimated)	EPI v4.11	Estimates based on representative structure where n=2.
		170 for n=1 (Estimated)	EPI v4.11	Estimates based on representative structure where n=1.
	Metabolism in Fish			No data located.
ENVIRONMENTAL MONITORING AND BIOMONITORING				
Environmental Monitoring		No data located.		
Ecological Biomonitoring		No data located.		
Human Biomonitoring		No data located.		

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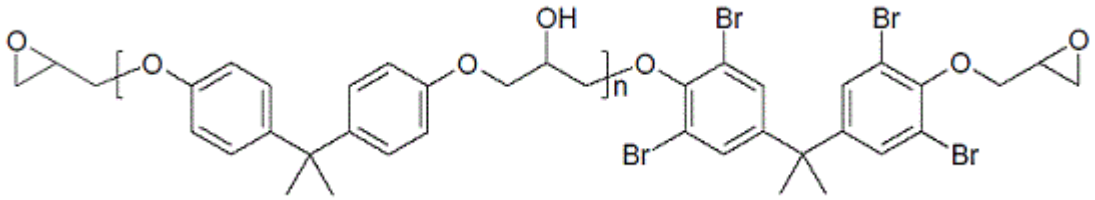
D.E.R. 500 Series

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

‡ The highest hazard designation of any of the oligomers with MW <1,000. ¥ Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

		Human Health Effects											Aquatic Toxicity		Environmental Fate	
Chemical	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
D.E.R. 500 Series¥	26265-08-7	***L***	***M***	***M***	***M***	***M***	***M***	***M***	**H**		***M*‡**	***M*‡**	***L***	***L***	***VH***	***H*‡**

D.E.R. 500 Series



CASRN: 26265-08-7

MW: Average MW 900 (Measured)

MF: $C_{39}H_{40}Br_4O_7$ as shown with n=1; MW=940

Physical Forms: Solid
Neat:

Use: Flame retardant

SMILES: O1CC1COc2ccc(cc2)C(C)(C)c3ccc(cc3)OCC(O)COc4c(Br)cc(cc4Br)C(C)(C)c5cc(Br)c(c(Br)c5)OCC6CO6 as shown with n = 1

Synonyms: Phenol, 4,4'(1-methylethylidene)bis[2,6-dibromo-, polymer with (chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol] (The reaction product of TBBPA), bisphenol A, epichlorohydrin and tetrabromobisphenol A polymer; Brominated epoxy resin; Epichlorohydrin, tetrabromobisphenol A polymer
Trade names: D.E.R.® 500 series epoxy resin; D.E.R. 538; Epikote 1145-B-70; EPON Resin 1123 (polymer of tetrabromobisphenol A epoxy resin, bisphenol A diglycidyl ether, and epichlorohydrin)

The D.E.R. 500 series epoxy resin product literature also lists CASRN 40039-93-8, Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with 2-(chloromethyl)oxirane; or Bisphenol A diglycidyl ether, brominated. This compound is a very close structural analog to Phenol, 4,4'(1-methylethylidene)bis[2,6-dibromo-, polymer with (chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol] (CASRN 26265-08-7).

Chemical Considerations: The D.E.R. 500 Series of polymers consist of components with MWs above and below 1,000 daltons.
The low MW components (MW <1,000) are expected to be present at levels requiring their assessment. The MW <1,000 components are assessed with EPI v4.11 and ECOSAR v1.11 estimates due to an absence of publicly available experimental physical/chemical, environmental fate and aquatic toxicity values. These include the n=1 component as shown in the SMILES entry and the n=0 component, as represented by the discrete organic 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2).
The n≥2 oligomers have a MW >1,000 and are assessed using the available polymer assessment literature.

Polymeric: Yes
Oligomeric: This is a tetrabromobisphenol A (TBBPA)-based epoxy resin; the oligomers are produced by reacting epichlorohydrin with bisphenol A (BPA) and TBBPA (Dow, 2009).

Metabolites, Degradates and Transformation Products: None identified (Professional judgment)

Analog: None **Endpoint(s) using analog values:** Not applicable	**Analog Structure:** Not applicable

Structural Alerts: Polyhalogenated aromatic hydrocarbons: immunotoxicity; epoxy groups/epoxides: dermal sensitization, cancer, reproductive effects, developmental toxicity (EPA, 2012; EPA, 2010).
Risk Phrases: Not classified by Annex VI Regulation (EC) No 1272/2008 (ESIS, 2012).
Hazard and Risk Assessments: None identified.

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)			No data located.
Boiling Point (°C)	>300 (Estimated)	EPI v4.11; EPA, 1999	Estimates based on a representative oligomer where n=1 and for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture with a MW <1,000. Also estimated for oligomers where n≥2 with MWs >1,000. Cutoff value according to HPV assessment guidance and cutoff value used for large, high MW solids.
Vapor Pressure (mm Hg)	$<10^{-8}$ for MW <1,000 components (Estimated)	EPI v4.11; EPA, 1999	Estimates based on representative oligomer where n=1 and for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. Cutoff value for nonvolatile compounds according to HPV assessment guidance.
	$<10^{-8}$ for the n≥2 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Cutoff value for large, high MW polymers.
Water Solubility (mg/L)	$3.3x10^{-5}$ for a component (Estimated)	EPI v4.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
	$1.7x10^{-9}$ for n=1 (Estimated)	EPI v4.11; EPA, 1999	Estimates based on representative oligomer where n=1. Values are less than the cutoff value, <0.001 mg/L, for non-soluble compounds according to HPV assessment guidance.
	<0.001	Boethling and Nabholz, 1997;	Cutoff value for large, high MW

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	for the n≥2 oligomers (Estimated)	Professional judgment	non-ionic polymers.
Log K_{ow}	7.4 for a component (Estimated)	EPI v4.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
	11 for n=1 (Estimated)	EPI v4.11; EPA, 1999	Estimates based on representative oligomer where n=1. Estimated value is greater than the cutoff value, >10, according to methodology based on HPV assessment guidance.
	No data located; for n≥2 oligomers (Estimated)		Polymers with a MW >1,000 are outside the domain of the available estimation methods.
Flammability (Flash Point)	Not flammable (Estimated)	Professional judgment	No experimental data located; based on its use as a flame retardant.
Explosivity	Not expected to form explosive mixtures with air (Estimated)	Professional judgment	No experimental data located; based on its use as a flame retardant.
Pyrolysis			No data located.
pH	Not applicable (Estimated)	Professional judgment	Does not contain functional groups that are expected to ionize under environmental conditions.
pK_a	Not applicable (Estimated)	Professional judgment	Does not contain functional groups that are expected to ionize under environmental conditions.
Particle Size			No data located.

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Toxicokinetics		**No experimental data were located. Based on professional judgment, absorption is expected to be poor by all routes for the low MW (<1,000) fraction. There is no absorption expected for any route of exposure for the large MW >1,000 components.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	Absorption is expected to be poor by all routes for the low molecular weight fraction. There is no absorption expected for any route of exposure for the large, high molecular weight (>1,000) fraction. (Estimated)	Professional judgment	Estimated based on professional judgment.
	Other			No data located.
Acute Mammalian Toxicity		**LOW: Estimated based on experimental data for a component of D.E.R., professional judgment and by analogy to structurally similar polymers. The large MW components, with a MW >1,000, are expected to have limited bioavailability and therefore have low potential for acute mammalian toxicity. There was no data located regarding the inhalation route of exposure.**		
Acute Lethality	**Oral**	Rat oral LD_{50} > 2,000 mg/kg	ECHA, 2014	Study details reported in a secondary source; test substance identified as F-2200HM (CASRN 3072-84-2) a component of the polymeric mixture; purity: 100%; conducted according to OECD 423.
		Rat oral LD_{50} = 7,160 mg/kg	Ash and Ash, 2009	Limited study details reported in a secondary source; data are for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
		Rat oral LD_{50} >3,663 mg/kg (Estimated by analogy)	Submitted confidential study; Professional judgment	Based on closely related confidential analogs with similar structures, functional groups, and physical/chemical properties.
	Dermal	Rat LD_{50} >2,000 mg/kg (Estimated by analogy)	ECHA, 2014	Estimated based on analogy; Study details reported in a secondary

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				source for the test substance bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), a very close structural analog.
		Rabbit LD_{50} >2,000 mg/kg (Estimated by analogy)	Submitted confidential study; Professional judgment	Based on closely related confidential analogs with similar structures, functional groups, and physical/chemical properties.
	Inhalation			No data located.
Carcinogenicity		**MODERATE: There is uncertainty due to lack of data for this substance. In addition, there is potential for carcinogenicity based on a structural alert for epoxy groups/epoxides though this concern may be mitigated by the high molecular weight; carcinogenic effects cannot be completely ruled out.**		
	OncoLogic Results			Not amenable for OncoLogic modeling.
	Carcinogenicity (Rat and Mouse)			No data located.
	Combined Chronic Toxicity/Carcinogenicity			No data located.
	Other	There is potential for carcinogenicity based on a structural alert for epoxy groups/epoxides; however, the concern may be mediated by the high molecular weight. (Estimated)	Professional judgment; EPA, 2010	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Genotoxicity		**MODERATE: There is uncertainty regarding the potential for genotoxicity due to the lack of sufficient data for this substance. Conflicting results were reported for gene mutations; the test substance was reported to be negative for gene mutations in one study, while there were positive results for gene mutations in Ames and mouse lymphoma assays. There were also mixed results for sister chromatid exchanges for analogs. There was no experimental chromosomal aberrations data for the test substance located. Genotoxic effects cannot be completely ruled out; an estimated Moderate hazard designation was assigned.**		
	Gene Mutation *in vitro*	Negative, *Salmonella typhimurium* strains TA98, TA100, TA1535, TA1537 and TA1538 and *E. coli* strain WP2 *uvrA* pKM101 with and without metabolic activation.	Willett, 1991	Study details reported in the primary source. Test substances reported as Epikote 1145-B-70.
		Negative, *Salmonella typhimurium* strains TA98, TA100, TA1535, TA1537 and *E. coli* strain WP2 *uvrA* pKM101 with and without metabolic activation. (Estimated by analogy)	ECHA, 2014	Estimated based on analogy; study details reported in a secondary source for the test substance bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), a very close structural analog; conducted according to OECD 471.
		Positive, Ames assay (Estimated by analogy)	Submitted confidential study	Limited study details reported in a confidential study submitted to EPA. Estimated based on a confidential analog.
		Positive, mouse lymphoma test (Estimated by analogy)	Submitted confidential study	Limited study details reported in a confidential study submitted to EPA. Estimated based on a confidential analog.
	Gene Mutation *in vivo*			No data located.
	Chromosomal Aberrations *in vitro*	Negative, chromosomal aberration test in human lymphocytes with and without metabolic activation (Estimated by analogy)	ECHA, 2014	Estimated based on analogy; study details reported in a secondary source for the test substance bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), a very close structural analog; conducted according to OECD 473.

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Positive, chromosomal aberration test in human lymphocytes (Estimated by analogy)	Submitted confidential study	Limited study details reported in a confidential study submitted to EPA. Estimated based on a confidential analog.
	Chromosomal Aberrations *in vivo*			No data located.
	DNA Damage and Repair			No data located.
	Other			No data located.
Reproductive Effects		**MODERATE: There is potential for reproductive toxicity for the low MW oligomers of the polymer (<1,000) based on a structural alert for epoxy groups/epoxides.**		
	Reproduction/Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects			No data located.
	Other	There is potential for reproductive toxicity based on a structural alert for epoxy groups/epoxides. (Estimated)	Professional judgment; EPA, 2010	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.
Developmental Effects		**MODERATE: There is potential for developmental toxicity for the low MW oligomers of the polymer (<1,000) based on a structural alert for epoxides.** **There were no data located for the developmental neurotoxicity endpoint.**		
	Reproduction/ Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Prenatal Development			No data located.
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity	No data was located for the developmental neurotoxicity endpoint.		No data located.
	Other	There is potential for developmental toxicity based on a structural alert for epoxy groups/epoxides (Estimated)	Professional judgment; EPA, 2010	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.
Neurotoxicity		**MODERATE: There is potential for neurotoxicity for the lower MW components based on professional judgment.**		
	Neurotoxicity Screening Battery (Adult)			No data located.
	Other	Potential for neurotoxicity (Estimated)	Professional judgment	Estimated based on the lower MW components and professional judgment.
Repeated Dose Effects		**MODERATE: Estimated to have potential for immunotoxicity based on a structural alert for polyhalogenated aromatic hydrocarbons and liver effects for the lower MW components. A 28-day oral study in rats for a very close structural analog, bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8) indicated effects in males (reduced body weight gain) at a dose of 1,000 mg/kg bw-day (NOAEL = 300 mg/kg bw-day).**		
		Potential for liver effects (Estimated)	Professional judgment	Estimated based on the lower MW components and professional judgment.
		Potential for immunotoxicity based on structural alert for polyhalogenated aromatic hydrocarbons. (Estimated)	Professional judgment; EPA, 2012	Estimated based on structural alert for polyhalogenated aromatic hydrocarbons and professional judgment.
		28-day oral (gavage) study in male and female Wistar rats; 30, 300 and 1,000 mg/kg bw-day Reduced body weight gain in males at	ECHA, 2014	Study details reported in a secondary source for the test substance bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), a

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		1,000 mg/kg bw-day. Microscopic liver changes (centrilobular hypertrophy) and metabolic blood chemical changes (increases in alanine aminotransferase, aspartate aminotransferase or bile acids) in males at 300 and 1,000 mg/kg bw-day were not considered to be adverse health effects. NOAEL = 300 mg/kg bw-day (males) LOAEL = 1,000 mg/kg bw-day (males, based on reduction in body weight gain)		very close structural analog. Conducted according to GLP and OECD guideline 407.
Skin Sensitization		**HIGH: Positive for skin sensitization in guinea pigs. In addition, there is an estimated potential for skin sensitization based on a structural alert for epoxy groups/epoxides.**		
	Skin Sensitization	Strong sensitizer, guinea pigs, maximization test. 19/20 test animals showed positive responses 24 hours after removal of challenge patches and 16 continued to have positive response at 48 hours.	Willett, 1990	Adequate primary source; Test substance reported as Epikote 1120-B-80.
		Not sensitizing, mouse local lymph node assay (LLNA)	ECHA, 2014	Estimated based on analogy; Study details reported in a secondary source for the test substance bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), a very close structural analog.
		There is potential for skin sensitization based on a structural alert for epoxy groups/epoxides. (Estimated)	Professional judgment	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Eye Irritation		**MODERATE: Estimated based on mixed results for studies using the component F-2200HM (2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2)). The structural analog, bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), was not an eye irritant in rabbits.**		
	Eye Irritation	Mildly irritating in rabbit eyes; reported eye irritation was resolved within 72 hours.	ECHA, 2014	Study details reported in a secondary source; test substance identified as the component F-2200HM (2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2)); purity: 100%; conducted according to OECD 404.
		Eye irritant	Ash and Ash, 2009	Reported in a secondary source with limited details for the component 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2).
Dermal Irritation		**MODERATE: Estimated based on mixed results for studies using the component F-2200HM (2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2)).**		
	Dermal Irritation	Not a skin irritant in rabbits	ECHA, 2014	Study details reported in a secondary source; test substance identified as the component F-2200HM (2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2)); purity: 100%; conducted according to OECD 404.
		Skin irritant	Ash and Ash, 2009	Limited study details reported in a secondary source for the component 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2).
Endocrine Activity		**No data located.**		
				No data located.

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Immunotoxicity		**Estimated to have potential for immunotoxicity based on a structural alert for polyhalogenated aromatic hydrocarbons.**		
	Immune System Effects	Potential for immunotoxicity based on structural alert for polyhalogenated aromatic hydrocarbons. (Estimated)	Professional judgment; EPA, 2012	Estimated based on structural alert for polyhalogenated aromatic hydrocarbons and professional judgment.
ECOTOXICITY				
ECOSAR Class		Epoxides, Poly		
Acute Aquatic Toxicity		**LOW: Non-ionic polymers with a MW >1,000 and negligible water solubility are estimated to display no effects at saturation (NES). These polymers display NES because the amount dissolved in water is not anticipated to reach a concentration at which adverse effects may be expressed. Guidance for the assessment of aquatic toxicity hazard leads to a low potential for those materials that display NES. The estimated acute toxicity values for fish, daphnid, and algae for the low MW components of the polymer (<1,000) also suggest no effects at saturation (NES).**		
Fish LC_{50}		NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
		Freshwater fish 14-day LC_{50}= 0.008 mg/L (Estimated) ECOSAR: Epoxides, Poly	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$mg/L by more than 10x. NES are predicted for these endpoints.
		Freshwater fish 96-hour LC_{50} = $1x10^{-5}$ mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$mg/L by more than 10x.

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish 14-day LC_{50} = 0.08 mg/L (Estimated) ECOSAR: Epoxides, poly	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. NES: The log K_{ow} of 7.4 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $3.26x10^{-5}$mg/L by more than 10x. NES are predicted for these endpoints.
	Freshwater fish 96-hour LC_{50} = 0.008 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2). NES: The log K_{ow} of 7.4 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $3.26x10^{-5}$mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid LC_{50}	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
	Daphnia magna 48-hour LC_{50}= 0.00065 mg/L (Estimated) ECOSAR: Epoxides, poly	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints.
	Daphnia magna 48-hour LC_{50}=$1.28x10^{-5}$ mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			narcosis.
	Daphnia magna 48-hour LC_{50} = 0.036 mg/L (Estimated) ECOSAR: Epoxides, poly	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. NES: The log K_{ow} of 7.4 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by more than 10x. NES are predicted for these endpoints.
	Daphnia magna 48-hour LC_{50} = 0.007 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2). NES: The log K_{ow} of 7.4 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0. In addition, the estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Green Algae EC_{50}	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Green algae 96-hour EC_{50} = 0.00027 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 6.4. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae 96-hour EC_{50} = 0.041 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. NES: The log K_{ow} of 7.4 for this chemical exceeds the SAR limitation for the log K_{ow} of 6.4. In addition, the estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			ECOSAR classes that have a more specific mode of action relative to narcosis.
Chronic Aquatic Toxicity	**LOW: Non-ionic polymers with a MW >1,000 and negligible water solubility are estimated to display NES. These polymers display NES because the amount dissolved in water is not anticipated to reach a concentration at which adverse effects may be expressed. Guidance for the assessment of aquatic toxicity hazard leads to a low potential for those materials that display NES. The estimated chronic toxicity values for fish, daphnid, and algae for the low MW components of the polymer (<1,000) also suggest no effects at saturation (NES).**		
Fish ChV	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
	Freshwater fish ChV = $2.7x10^{-5}$ mg/L (Estimated) ECOSAR: Epoxides, poly	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 8.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish ChV =$2.5x10^{-6}$ mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			8.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish ChV = 0.0008 mg/L (Estimated) ECOSAR: Epoxides, poly	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. The estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by 10x. NES are predicted for these endpoints.
	Freshwater fish ChV = 0.0013 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2). The estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			specific mode of action relative to narcosis.
Daphnid ChV	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
	Daphnia magna ChV: = $3.2x10^{-5}$ mg/L (Estimated) ECOSAR: Epoxides, poly	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 8.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints.
	Daphnia magna ChV = $1.2x10^{-5}$ mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimate based on representative oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log Kow of 8.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Daphnia magna ChV = 0.002 mg/L (Estimated) ECOSAR: Epoxides, poly	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2). The

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by more than 10x. NES are predicted for these endpoints.
	Daphnia magna ChV = 0.003 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. The estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	21-day EC_{50} >23 µg/L Considered effects on *Daphnia magna* immobility and reproduction Static conditions; 1.9, 3.8, 7.5, 15, 30 µg/L (nominal concentration). (Estimated by analogy)	ECHA, 2014	Reported for bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), a close structural analog. Study was conducted in accordance with OECD Guideline 211; *Daphnia magna* Reproduction Test and GLP. The estimated effect exceeds the water solubility by 10x. NES are predicted for these endpoints.
Green Algae ChV	NES (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES for the MW >1,000 components.
	Green algae ChV: 0.00044 mg/L	ECOSAR v1.11	Estimate based on representative

D.E.R. 500 Series CASRN 26265-08-7			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	(Estimated) ECOSAR: Neutral Organic SAR		oligomer n=1. NES: The log K_{ow} of 11 for this chemical exceeds the SAR limitation for the log K_{ow} of 8.0. In addition, the estimated effect exceeds the water solubility of $1.68x10^{-9}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae ChV = 0.033 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. The estimated effect exceeds the water solubility of $3.26x10^{-5}$ mg/L by more than 10x. NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	72-hour EC_{50} >30 µg/L	ECHA, 2014	Reported for bisphenol A diglycidyl

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Considered effects on area under the growth curve, yield and growth rate relative to the negative control group in *Pseudokirchneriella subcapitata* Static conditions; 1.8, 3.9, 7.6, 15, 24, 30 µg/L (nominal concentration). (Estimated by analogy)		ether, brominated (CASRN 40039-93-8) a close structural analog. Study was conducted in accordance with OECD Guideline 201 (Alga, Growth Inhibition Test) and GLP. The estimated effect exceeds the water solubility by 10x. NES are predicted for these endpoints.
ENVIRONMENTAL FATE				
Transport		**The estimated negligible water solubility, the estimated negligible vapor pressure and the estimated K_{OC} of >30,000 indicate the components of this polymer are anticipated to partition predominantly to soil and sediment and these components are not anticipated to migrate from soil into groundwater. The estimated Henry's Law constant values of $<10^{-8}$ atm-m^3/mole indicate that the polymer components are not expected to volatilize from water to the atmosphere.**		
	Henry's Law Constant (atm-m^3/mole)	$<10^{-8}$ for MW <1,000 components by Bond SAR Method. (Estimated)	EPI v4.11; Professional judgment	Estimates based on representative oligomer where n=1 and for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. Cutoff value for nonvolatile compounds.
		$<10^{-8}$ for the n≥2 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	High MW polymers are expected to have low vapor pressure and are not expected to undergo volatilization.
	Sediment/Soil Adsorption/Desorption - K_{oc}	>30,000 for MW <1,000 components (Estimated)	EPI v4.11; Professional judgment	Estimates based on representative oligomer where n=1 and for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. Cutoff value for nonmobile compounds.
		>30,000 for n≥2 (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the n=2 oligomers; cutoff value used for large, high MW polymers. High MW polymers are expected to adsorb strongly to

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				soil and sediment.
		215,000 for n=1 >430,000 for n=2 and 3 Reported for components of the mixture. According to OECD Guideline 121; Estimation of the Adsorption Coefficient on Soil and on Sewage Sludge using High Performance Liquid Chromatography (HPLC). (Estimated by analogy)	ECHA, 2014	Adequate guideline study reported for bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8). The three components in this study are close structural analogs to the components of D.E.R. 500 Series (CASRN 26265-08-7).
	Level III Fugacity Model	Air = 0% Water = 3.3% Soil = 88% Sediment = 8.4% (Estimated)	EPI v4.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
		Air = 0% Water = 3% Soil = 60% Sediment = 37% (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Persistence		**VERY HIGH: Experimental data are not available. Estimated half-lives for ultimate aerobic biodegradation are >180 days for the n=1 oligomer and 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), representing MW <1,000 components of the polymeric mixture. Polymeric components with a MW >1,000 are expected to have negligible water solubility and poor bioavailability to microorganisms indicating that neither biodegradation nor hydrolysis are expected to be important removal processes in the environment. Although debromination by photodegradation of polybrominated benzenes has been observed, this process is not anticipated to lead to ultimate removal of the polymer. The estimated degradation half-life by hydrolysis is also expected to be >1 year. Degradation of this polymer by direct photolysis is not expected to be significant as the functional groups present do not tend to undergo these reactions under environmental conditions. The atmospheric half-life is estimated to be <2 days; however, the polymer is not anticipated to partition significantly to air.**		
Water	**Aerobic Biodegradation**	Passes Ready Test: No Test method: OECD TG 301B: CO_2 Evolution Test -2.4% degradation after 28 days in activated sludge. (Estimated by analogy)	ECHA, 2014	Adequate guideline study reported for bisphenol A diglycidyl ether, brominated (CASRN 40039-93-8), a very close structural analog.
		Months (Primary Survey Model) Recalcitrant (Ultimate Survey Model) (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1 and 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
		Recalcitrant for the n=2 oligomers (Estimated)	Boethling and Nabholz, 1997	Estimated for the n≥2 oligomers; high MW polymers are expected to have low vapor pressure and are not expected to undergo volatilization.
		Microbial toxicity/inhibition: Water-leachates of the polymer inhibited bacterial growth by 8%. (Measured)	Willett, 1990	The study was performed on water-leachates of the polymer, and not on the polymer itself. Given the low water solubility of the polymer, it is not anticipated to be present in the leachate.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1 and for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1 and for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
Soil	**Aerobic Biodegradation**			No data located.
	Anaerobic Biodegradation	Not probable (Estimated)	Holliger et al., 2004	The estimated value addresses the potential for ultimate biodegradation. However, there is potential for primary anaerobic biodegradation of the lower MW (<1,000) haloaromatic compounds by reductive dehalogenation.
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	1.4 hours (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1. This compound is anticipated to exist as a solid particulate in the atmosphere, degradation by gas-phase reactions are not expected to be important removal processes.
		0.6 days (Estimated)	EPI v4.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric

D.E.R. 500 Series CASRN 26265-08-7				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				mixture. This compound is anticipated to exist as a solid particulate in the atmosphere, degradation by gas-phase reactions are not expected to be important removal processes.
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment	Bromine substituents may be susceptible to photolysis in the environment; however, this is expected to be a relatively slow process for a high MW brominated epoxy polymer and is not anticipated to result in the ultimate degradation of this substance.
	Hydrolysis	50%/>1 year at pH 7 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1 and for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture. The estimated hydrolysis rate is for the epoxide functional group; hydrolysis is not expected to be an important fate process for other parts of the polymer.
Environmental Half-life		>180 days for the n≥2 oligomers (Estimated)	Professional judgment	Estimated for the n≥2 oligomers; the substance is a high MW polymer and is not anticipated to be assimilated by microorganisms. Therefore, biodegradation is not expected to be an important removal process. It is also not expected to undergo removal by other degradative processes under environmental conditions.
		>1 year in soil; for the n=1 oligomer (Estimated)	PBT Profiler v1.301	Half-life estimated for the n=1 oligomer for the predominant

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				compartment, soil, as determined by EPI and the PBT Profiler methodology.
Bioaccumulation		**HIGH: The estimated BCF and BAF for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture and BAF for the n=1 component are >1,000 resulting in a High bioaccumulation designation. The higher MW oligomers that may be found in this mixture (n≥2) are expected to have Low potential for bioaccumulation based on their large size and low water solubility according to the polymer assessment literature and professional judgment.**		
	Fish BCF	8,400 for a component (Estimated)	EPI v4.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
		100 for n=1 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1.
		<100 for the n≥2 oligomers (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the n≥2 oligomers. Cutoff value for large, high MW, insoluble polymers according to polymer assessment literature.
	Other BCF			No data located.
	BAF	$9.7x10^6$ for a component (Estimated)	EPI v4.11	Estimated for 2,2',6,6'-tetrabromobisphenol A diglycidyl ether (CASRN 3072-84-2), a component of the polymeric mixture.
		69,000 for n=1 (Estimated)	EPI v4.11	Estimates based on representative oligomer where n=1.
	Metabolism in Fish			No data located.
ENVIRONMENTAL MONITORING AND BIOMONITORING				
Environmental Monitoring		No data located.		
Ecological Biomonitoring		No data located.		
Human Biomonitoring		This chemical was not included in the NHANES biomonitoring report. (CDC, 2013).		

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VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[§] Based on analogy to experimental data for a structurally similar compound. [‡] The highest hazard designation of any of the oligomers with MW <1,000. [¥] Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

Chemical	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
Dow XZ-92547[¥]	Confidential	**L**	***M*[‡]**	***M*[§]**	***M*[‡]**	***M*[‡]**	***M*[‡]**	***M*[‡]**	**H**	***M*[‡]**	**VL**	**L**	***L***	***H***	***VH***	***H*[‡]**

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	CASRN: Confidential CASRN
	MW: >1,000; with a significant percentage of components having MW <1,000
	MF: Confidential MF
	Physical Forms: Solid **Neat:**
	Use: Flame retardant
SMILES: Confidential SMILES notations for representative structures of the MW <1,000 components	
Synonyms: Reaction product of an epoxy phenyl novolak with DOPO	
Chemical Considerations: This alternative is a polymer consisting of components with MWs above and below 1,000 daltons. Lower MW components are expected to be present at a level requiring their assessment. The components with a MW <1,000 are evaluated as four proprietary representative structures. In general, the representative structures are different combinations of epoxy phenyl novolak and DOPO. These are assessed with EPI v4.11 and ECOSAR v1.11 estimates due to an absence of publicly available experimental physical/chemical, environmental fate and aquatic toxicity values. The oligomers with a MW >1,000 and are assessed using the available polymer assessment literature.	
Polymeric: Yes **Oligomeric:** This polymer contains oligomers that are formed by the reaction of an epoxy phenyl novolak with DOPO.	
Metabolites, Degradates and Transformation Products: None	
Analog: None **Endpoint(s) using analog values:** Not applicable	**Analog Structure:** Not applicable
Structural Alerts: Phosphinate esters - environmental toxicity; Epoxy groups/epoxides - dermal sensitization, cancer, reproductive effects, developmental toxicity; Organophosphorus compounds - neurotoxicity. (EPA, 2010; EPA, 2012).	
Risk Phrases: Not classified by Annex VI Regulation (EC) No 1272/2008 (ESIS, 2012).	
Hazard and Risk Assessments: None located.	

Dow XZ-92547			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	89 (Measured)	Submitted confidential study	Adequate, measured value from submitted study.
Boiling Point (°C)	>300 (Estimated)	EPI v4.11; EPA, 1999	Estimate based on four representative structures with MW <1,000. Also estimated for oligomers with MWs >1,000. Cutoff value according to HPV assessment guidance and cutoff value used for large, high MW solids.
Vapor Pressure (mm Hg)	$<10^{-8}$ (Estimated)	EPA, 1999; EPI v4.11	Estimates based on four confidential representative structures with MW <1,000. Cutoff value for nonvolatile compounds according to HPV assessment guidance.
	$<10^{-8}$ (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Cutoff value for large, high MW polymer components.
Water Solubility (mg/L)	0.62 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 1 with MW <1,000.
	0.0023 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 2 with MW <1,000.
	$7.7x10^{-6}$ (Estimated)	EPI v4.11; EPA, 1999	Estimates based on confidential representative structure 3 with MW <1,000. Estimated value is less than the cutoff value, <0.001 mg/L, for non-soluble compounds according to HPV assessment guidance.
	0.0082 (Estimated)	EPI v4.11; EPA, 1999	Estimates based on confidential representative structure 4 with MW <1,000.
	<0.001 (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Cutoff value for large, high MW non-ionic polymer components.

Dow XZ-92547			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Log K_{ow}	3.7 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 1 with a MW <1,000.
	5.3 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 2 with a MW <1,000.
	7 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 3 with a MW <1,000.
	4.8 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 4 with a MW <1,000.
Flammability (Flash Point)	Not flammable (Estimated)	Professional judgment	No experimental data located; based on its use as a flame retardant.
Explosivity	Not expected to form explosive mixtures with air (Estimated)	Professional judgment	No experimental data located; based on its use as a flame retardant.
Pyrolysis			No data located.
pH	Not applicable (Estimated)	Professional judgment	Does not contain functional groups that are expected to ionize under environmental conditions.
pK_a	Not applicable (Estimated)	Professional judgment	Does not contain functional groups that are expected to ionize under environmental conditions.
Particle Size			No data located.

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Toxicokinetics		**Based on the physical/chemical properties of this polymer, the higher MW fraction (>1,000) is estimated to have limited bioavailability. Based on the physical/chemical properties, absorption is expected to be negligible by all routes for the neat material and poor by all routes for the low molecular weight fraction if in solution.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	Absorption is expected to be negligible by all routes for the neat material and poor by all routes for the low MW fraction if in solution. (Estimated)	Professional judgment	Estimated based on professional judgment.
	Other			No data located.
Acute Mammalian Toxicity		**LOW: Based on experimental data that reported LD_{50} >2,000 mg/kg when administered orally and dermally to rats. There were no data located for the inhalation route of exposure. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for acute toxicity.**		
Acute Lethality	**Oral**	Estimated to have a low potential for acute toxicity for the high MW component. Limited bioavailability expected. (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the high MW component (MW >1,000) based on cutoff value for large, high MW non-ionic polymer components.
		Rat, oral LD_{50} >2,000 mg/kg.	Submitted confidential study	Limited study details reported in a confidential study.
	Dermal	Rat, dermal LD_{50} >2,000 mg/kg.	Submitted confidential study	Study details reported in a confidential study.
		Rat, dermal LD_{50} >2,000 mg/kg.	Submitted confidential study	Limited study details reported in a confidential study.
	Inhalation			No data located.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Carcinogenicity		**MODERATE: There were no experimental data located for this substance. Carcinogenic effects cannot be ruled out; therefore, uncertainty due to lack of data for this substance results in a Moderate designation. In addition, there is an estimated potential for carcinogenicity based on a structural alert for epoxy groups/epoxides and for the low MW components (MW < 1,000). The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for carcinogenicity.**		
	OncoLogic Results			No data located.
	Carcinogenicity (Rat and Mouse)			No data located.
	Combined Chronic Toxicity/Carcinogenicity			No data located.
	Other	Potential for carcinogenicity based on a structural alert for epoxy groups/epoxides. (Estimated)	Professional judgment; EPA, 2010	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.
		Potential for carcinogenicity for the low MW components. (Estimated)	Professional judgment	Estimated for the low MW components based on professional judgment.
		Estimated to have a low potential for carcinogenicity for the high MW component. Limited bioavailability expected. (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the high MW component (MW >1,000) based on professional judgment and the cutoff value for large, high MW non-ionic polymer components.

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Genotoxicity		**MODERATE: Estimated based on positive gene mutation results for a confidential analog of the low MW components (MW < 1,000) reported in a submitted confidential study. There were no gene mutation or chromosomal aberrations data located for this substance. Negative results for mutagenicity and chromosomal aberrations *in vitro* were reported in experimental data for the analog DOPO (CASRN 35948-25-5). In the absence of data for this substance and conflicting results reported for two analogs, a conservative approach is used to assign a Moderate designation. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for genotoxicity.**		
	Gene Mutation *in vitro*	There is potential for mutagenicity for the low MW components. Positive in Ames assay. (Estimated by analogy)	Professional judgment; Submitted confidential study	Estimated based on experimental data for a confidential analog for the low MW components; reported in a submitted confidential study and professional judgment.
		Negative in Ames assay in *Salmonella typhimurium strains* TA97, TA98, TA100, and TA102 and *Escherichia coli* WP2 uvr A pKM 101 with and without metabolic activation. Tested up to 5,000 µg/plate (purity, industrial grade). Positive controls responded as expected. (Estimated by analogy)	ECHA, 2013	Estimated based on analogy to DOPO (CASRN 35948-25-5). Sufficient study details reported in a secondary source. Non-GLP study, but adequate as supporting data.
		Negative in Ames assay; in *Salmonella typhimurium* strains TA1535, TA97a, TA98, TA100, and TA102 with and without metabolic activation. Tested up to 5,024 µg/plate (purity >99%). Positive controls responded as expected. (Estimated by analogy)	ECHA, 2013	Estimated based on analogy to DOPO (CASRN 35948-25-5). Sufficient study details reported in a secondary source. Study conducted in accordance with OECD guideline 471 and GLP. Test substance was CASRN 35948-25-5 named Ukanol GK-F in study report. Primary reference not identified.
	Gene Mutation *in vivo*			No data located.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Chromosomal Aberrations *in vitro*	Negative in Chinese hamster lung cells with and without activation. Tested up to 216 µg/mL (purity not provided). Positive controls responded as expected. (Estimated by analogy)	ECHA, 2013	Estimated based on analogy to DOPO (CASRN 35948-25-5). Sufficient study details reported in a secondary source. Study equivalent to OECD Guideline 473; not a GLP study.
	Chromosomal Aberrations *in vivo*			No data located.
	DNA Damage and Repair			No data located.
	Other	Estimated to have a low potential for genotoxicity for the high MW component. Limited bioavailability expected. (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the high MW component (MW >1,000) based on professional judgment and the cutoff value for large, high MW non-ionic polymer components.
Reproductive Effects		**MODERATE: There is an estimated potential for reproductive toxicity based on a structural alert for epoxy groups/epoxides and an estimated potential for male reproductive toxicity for the low MW components (MW < 1,000) based on professional judgment. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for reproductive toxicity.**		
	Reproduction/Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects			No data located.
	Other	There is potential for reproductive toxicity based on a structural alert for epoxy groups/epoxides. (Estimated)	Professional judgment; EPA, 2010	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.
		There is potential for male reproductive toxicity for the low MW components. (Estimated)	Professional judgment	Estimated for the low MW components based on professional judgment.
		Estimated to have a low potential for	Boethling and Nabholz, 1997;	Estimated for the high MW

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		reproductive effects for the high MW component. Limited bioavailability expected. (Estimated)	Professional judgment	component (MW >1,000) based on professional judgment and the cutoff value for large, high MW non-ionic polymer components.
Developmental Effects		**MODERATE: There is an estimated potential for developmental toxicity based on a structural alert for epoxy groups/epoxides and an estimated potential for developmental toxicity for the low MW components (MW < 1,000) based on professional judgment. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for developmental toxicity. There is uncertain concern for developmental neurotoxicity based on the potential for cholinesterase (ChE) inhibition in dams that may result in alterations of fetal neurodevelopment. No experimental data were located for this substance.**		
	Reproduction/ Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Prenatal Development			No data located.
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity	Uncertain concern for developmental neurotoxicity based on the potential for cholinesterase (ChE) inhibition in dams that may result in alterations of fetal neurodevelopment.	Professional judgment	Estimated based on a structural alert for organophosphates for the neurotoxicity endpoint.
	Other	There is potential for developmental toxicity based on a structural alert for epoxy groups/epoxides. (Estimated)	Professional judgment; EPA, 2012	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.
		Estimated to have a low potential for developmental effects for the high MW component. Limited bioavailability	Boethling and Nabholz, 1997; Professional judgment	Estimated for the high MW component (MW >1,000) based on professional judgment and the cutoff

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		expected. (Estimated)		value for large, high MW non-ionic polymer components.
Neurotoxicity		**MODERATE: There is an estimated potential for neurotoxicity based on a structural alert for organophosphorus compounds and professional judgment. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for neurotoxicity. There were no experimental data located for this substance.**		
	Neurotoxicity Screening Battery (Adult)			No data located.
	Other	There is potential for neurotoxicity based on the structural alert of organophosphorus compounds. (Estimated)	Professional judgment; EPA, 2012	Estimated based on a structural alert for organophosphorus compounds and professional judgment.
		Estimated to have a low potential for neurotoxicity for the high MW component. Limited bioavailability expected. (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the high MW component (MW >1,000) based on professional judgment and the cutoff value for large, high MW non-ionic polymer components.
Repeated Dose Effects		**MODERATE: There is an estimated potential for repeated dose effects for the low MW components (<1,000) for the inhalation and dermal routes of exposure. Experimental data for the analog DOPO (CASRN 35948-25-5) indicated a Low hazard designation with a reported NOAEL of 1,023 mg/kg-day (highest dose tested) in a 16-week dietary study in rats. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for repeated dose effects. There were no experimental data located for this substance.**		
		There is potential for repeated dose effects for the low MW component for the inhalation and dermal routes of exposure.	Professional judgment	Estimated for the low MW component based on professional judgment.
		Male and female Wistar rats (20/sex/dose) were fed diets containing 0, 0.24, 0.6, or 1.5% HCA (0, 159, 399, or 1,023 mg HCA/kg-day to males; 0, 177, 445, or 1,094 mg HCA/kg-day to females) of the analog DOPO for 16 weeks (purity of test substance not	ECHA, 2013; Professional judgment	Estimated based on analogy to DOPO (CASRN 35948-25-5). Sufficient information in secondary source; data lacking regarding detailed clinical observations and neurobehavioral examination. Study equivalent to OECD guideline 408.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		provided). There were no significant effects on body weight, food consumption, hematology, limited clinical chemistry, urinalysis, organ weight, and gross and microscopic examination of major organs. NOAEL: 1,023 mg/kg-day (males), 1,094 mg/kg-day (females); highest dose tested LOAEL: Not established (Estimated based on analogy)		Study pre-dates GLP. Test substance identified as HCA in study report. Primary reference not identified.
		Estimated to have a low potential for repeated dose effects for the high MW component. Limited bioavailability expected. (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the high MW component (MW >1,000) based on professional judgment and the cutoff value for large, high MW non-ionic polymer components.
Skin Sensitization		**HIGH: Positive for skin sensitization in guinea pigs; reported in a submitted confidential study for the low MW components (MW < 1,000). In addition, there is an estimated potential for skin sensitization based on a structural alert for epoxy groups/epoxides.**		
	Skin Sensitization	Sensitizing, guinea pigs	Submitted confidential study	Data reported in a submitted confidential study.
		Positive for skin sensitization for the low MW component.	Submitted confidential study	Data reported in a submitted confidential study for the low MW component.
		There is potential for skin sensitization based on a structural alert for epoxy groups/epoxides. (Estimated)	Professional judgment; EPA, 2012	Estimated based on a structural alert for epoxy groups/epoxides and professional judgment.
Respiratory Sensitization		**MODERATE: There is an estimated potential for respiratory sensitization for the low MW component (MW < 1,000) based on professional judgment.**		
	Respiratory Sensitization	There is potential for respiratory sensitization for the low MW component. (Estimated)	OSHA, 1999; Professional judgment	Estimated based presence of epoxides and professional judgment for the low MW component.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Eye Irritation		**VERY LOW: Based on a submitted confidential study, the polymer did not produce eye irritation in rabbits.**		
	Eye Irritation	Negative, rabbits	Submitted confidential study	Limited study details reported in a confidential study.
Dermal Irritation		**LOW: Negative for skin irritation in rabbits reported in a submitted confidential study. One study reported positive results for skin irritation, but did not contain adequate study details for assessment.**		
	Dermal Irritation	Positive for skin irritation for the low MW component.	Submitted confidential study	Inadequate study details reported in a submitted confidential study for the low MW component.
		Negative, rabbits	Submitted confidential study	Data reported in a submitted confidential study.
Endocrine Activity		**No data located.**		
				No data located.
Immunotoxicity		**Estimated to have a low potential for immunotoxic effects based on expert judgment. The higher MW components of this polymer (MW >1,000) are expected to have limited bioavailability and have low potential for immunotoxicity.**		
	Immune System Effects	Low potential for immunotoxic effects for the low MW component. (Estimated)	Expert judgment	Estimated based on expert judgment.
		Estimated to have a low potential for immunotoxic effects for the high MW component. Limited bioavailability expected.	Boethling and Nabholz, 1997; Professional judgment	Estimated for the high MW component (MW >1,000) based on professional judgment.
ECOTOXICITY				
ECOSAR Class		Epoxides, mono; Esters (Phosphinates)		
Acute Aquatic Toxicity		**LOW: Based on estimated acute aquatic toxicity values for fish, daphnia, and green algae, which all exceed the water solubility. No Effects at Saturation (NES) are predicted for these endpoints.**		
Fish LC_{50}		NES (Estimated)	Professional judgment	Estimations for the oligomers with a high MW; limited bioavailability and low water solubility suggest there will be NES.
		Freshwater fish 96-hour LC_{50}:	ECOSAR v1.11	Estimations for confidential

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	1.7 mg/L (ECOSAR class: Esters, phosphinate); 10.4 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		representative structure 1. The estimated values exceed the water solubility (0.62 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish 96-hour LC_{50}: 0.87 mg/L (ECOSAR class: Epoxides, mono); 0.74 mg/L (ECOSAR class: Esters phosphinates); 0.49 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 2. NES: The log K_{ow} of 5.3 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0; NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish 14-day LC_{50}: 0.13 mg/L (ECOSAR class: Epoxides, poly); Freshwater fish 96-hour LC_{50}: 0.28 mg/L (ECOSAR class: Esters phosphinates);	ECOSAR v1.11	Estimations for confidential representative structure 3. NES: The log K_{ow} of 6.9 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0 or 6.0; NES are predicted for these endpoints.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Freshwater fish 96-hour LC_{50}: 0.021 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish 96-hour LC_{50}: 1.7 mg/L (ECOSAR class: Epoxides, mono); 1.1 mg/L (ECOSAR class: Esters phosphinates); 1.5 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 4. The estimated values exceed the water solubility (0.0082 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid LC_{50}	NES (Estimated)	Professional judgment	Estimations for the oligomers with a high MW; limited bioavailability and low water solubility suggest there will be NES.
	Daphnid 48-hour LC_{50}: 1.2 mg/L (ECOSAR class: Esters, phosphinate); 6.9 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 1. The estimated values exceed the water solubility (0.62 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Daphnid 48-hour LC_{50}: 0.69 mg/L (ECOSAR class: Epoxides, mono); 0.56 mg/L (ECOSAR class: Esters phosphinates); 0.38 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 2. The log K_{ow} of 5.3 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0; NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Daphnid 48-hour LC_{50}: 0.071 mg/L (ECOSAR class: Epoxides, poly); 0.24 mg/L (ECOSAR class: Esters phosphinates); 0.019 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 3. NES: The log K_{ow} of 6.9 for this chemical exceeds the SAR limitation for the log K_{ow} of 5.0; NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Daphnid 48-hour LC_{50}: 1.6 mg/L (ECOSAR class: Epoxides, mono); 0.78 mg/L (ECOSAR class: Esters phosphinates); 1.1 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 4.The estimated values exceed the water solubility (0.0082 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Green Algae EC_{50}	NES (Estimated)	Professional judgment	Estimations for the oligomers with a high MW; limited bioavailability and low water solubility suggest there will be NES.
	Green algae 96-hour EC_{50}: 9.6 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 1. The estimated value exceeds the water solubility (0.62 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae 96-hour EC_{50}: 0.34 mg/L (ECOSAR class: Epoxides,	ECOSAR v1.11	Estimations for confidential representative structure 2. The

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	mono); 0.99 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		estimated values exceed the water solubility (0.0023 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae 96-hour EC_{50}: 0.093 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 3. NES: The log K_{ow} of 6.9 for this chemical exceeds the SAR limitation for the log K_{ow} of 6.4; NES are predicted for these endpoints. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae 96-hour EC_{50}: 0.9 mg/L (ECOSAR class: Epoxides, mono); 2.3 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 4. The estimated values exceed the water solubility (0.0082 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics)

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Chronic Aquatic Toxicity	**HIGH: Based on estimated chronic aquatic toxicity values for the confidential representative structures 1 and 4 for fish and daphnia.**		
Fish ChV	NES (Estimated)	Professional judgment	Estimations for the oligomers with a high MW; limited bioavailability and low water solubility suggest there will be NES.
	Freshwater fish ChV: 0.041 mg/L (ECOSAR class: Esters, phosphinate); 1.2 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 1. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish ChV: 0.003 mg/L (ECOSAR class: Epoxides, mono); 0.008 mg/L (ECOSAR class: Esters phosphinates); 0.069 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 2. The estimated values exceed the water solubility (0.0023 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish ChV: 0.0014 mg/L (ECOSAR class: Epoxides, poly); 0.0016 mg/L (ECOSAR class: Esters phosphinates); 0.004 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 3. The estimated values exceed the water solubility ($7.7x10^{-6}$). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Freshwater fish ChV: 0.004 mg/L (ECOSAR class: epoxides, mono); 0.02 mg/L (ECOSAR class: Esters phosphinates); 0.20 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 4. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid ChV	NES (Estimated)	Professional judgment	Estimations for the oligomers with a high MW; limited bioavailability and low water solubility suggest there will be NES.
	Daphnid ChV: 0.042 mg/L (ECOSAR class: Esters,	ECOSAR v1.11	Estimations for confidential representative structure 1.

Dow XZ-92547			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	phosphinate); 1.03 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Daphnia ChV: 0.064 mg/L (ECOSAR class: Epoxides, mono); 0.012 mg/L (ECOSAR class: Esters phosphinates); 0.086 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 2. The estimated values exceed the water solubility (0.0023 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Daphnid ChV: 0.005 mg/L (ECOSAR class: Epoxides, poly); 0.003 mg/L (ECOSAR class: Esters phosphinates); 0.007 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 3. The estimated values exceed the water solubility ($7.7x10^{-6}$). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by

Dow XZ-92547			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			ECOSAR classes that have a more specific mode of action relative to narcosis.
	Daphnid ChV: 0.15 mg/L (ECOSAR class: Epoxides, mono); 0.02 mg/L (ECOSAR class: Esters phosphinates): 0.22 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 4. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Green Algae ChV	NES (Estimated)	Professional judgment	Estimations for the oligomers with a high MW; limited bioavailability and low water solubility suggest there will be NES.
	Green algae ChV: 3.6 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 1. The estimated values exceed the water solubility (0.62 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae ChV: 0.69 mg/L (ECOSAR class: Epoxides, mono);	ECOSAR v1.11	Estimations for confidential representative structure 2. The estimated values exceed the water

Dow XZ-92547			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	0.51 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)		solubility (0.0023 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae ChV: 0.068 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 3. The estimated value exceeds the water solubility ($7.7x10^{-6}$). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
	Green algae ChV: 1.5 mg/L (ECOSAR class: Epoxides, mono); 1.0 mg/L (ECOSAR class: Neutral organic SAR) (Estimated)	ECOSAR v1.11	Estimations for confidential representative structure 4. The estimated values exceed the water solubility (0.0082 mg/L). The chemical may not be soluble enough to measure the predicted effect. Narcosis classes (neutral organics) are provided for comparative

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
ENVIRONMENTAL FATE				
Transport		**The estimated negligible water solubility and estimated negligible vapor pressure indicate that this polymer, including the low MW and high MW components, is anticipated to partition predominantly to soil. The estimated Henry's Law Constant of $<10^{-8}$ atm-m^3/mole indicates that it is not expected to volatilize from water to the atmosphere. Although estimates for one confidential representative structure results in a moderate absorption coefficient of 1,596, the estimated K_{oc} of >30,000 for the high MW components and 3 other confidential representative substances indicate that the majority of this polymeric mixture is not anticipated to migrate from soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant (atm-m^3/mole)	$<10^{-8}$ Bond SAR Method (Estimated)	EPI v4.11; Professional judgment	Estimated value based on four confidential representative structures with MW <1,000. Cutoff value for nonvolatile compounds.
		$<10^{-8}$ (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the MW >1,000 oligomers. High MW polymers are expected to have low vapor pressure and are not expected to undergo volatilization.
	Sediment/Soil Adsorption/Desorption - K_{oc}	1,595 (Estimated)	EPI v4.11; Professional judgment	Estimate based on confidential representative structure 1.
		>30,000 (Estimated)	EPI v4.11; EPA, 1999	Estimated values for confidential representative structures 2, 3 and 4. Cutoff value for nonmobile compounds according to HPV assessment guidance.
		>30,000 (Estimated)	Boethling and Nabholz, 1997; Professional judgment	Estimated for the oligomers with MW >1,000; cutoff value used for large, high MW polymers. High

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				MW polymers are expected to adsorb strongly to soil and sediment.
	Level III Fugacity Model	Air = 0% Water = 12% Soil = 88% Sediment = 1% (Estimated)	EPI v4.11	Estimates based on confidential representative structure 1. No data located for the high MW component of the polymers.
Persistence		**VERY HIGH: The persistence designation for this polymer is based on its higher MW components (MW >1,000). The higher MW components are expected to have Very High persistence because of their low water solubility and poor bioavailability, indicating that neither biodegradation nor hydrolysis are expected to be important environmental fate processes. The lower MW oligomers (MW <1,000) of this polymer have higher estimated water solubility and increased bioavailability to microorganisms and therefore would be expected to have lower persistence. This polymer does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths. Evaluation of these degradation values suggest a half-life of >180 days.**		
Water	**Aerobic Biodegradation**	Days-weeks (Primary Survey Model) Weeks-months (Ultimate Survey Model) (Estimated)	EPI v4.11	Estimates based on confidential representative structure 1.
		Recalcitrant for MW >1,000 components (Estimated)	Professional judgment; Boethling and Nabholz, 1997	High MW polymers are expected to be non-biodegradable.
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI v4.11; Professional judgment	Estimated value based on four confidential representative structures with MW <1,000; the high MW polymer components are anticipated to be nonvolatile.
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI v4.11; Professional judgment	Estimated value based on four confidential representative structures with MW <1,000; the high MW polymer components are anticipated to be nonvolatile.
Soil	**Aerobic Biodegradation**			No data located.
	Anaerobic Biodegradation	Recalcitrant for MW >1,000 components (Estimated)	Professional judgment; Boethling and Nabholz, 1997	High MW polymers are expected to be resistant to removal under anoxic conditions due to their limited bioavailability.

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	<0.19 days (Estimated)	EPI v4.11	Estimated value based on four confidential representative structures with MW <1,000.
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment; Mill, 2000	This polymer does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	50%/>1 month (Estimated)	Professional judgment	While this polymer contains a functional group with the potential to hydrolyze, this group does not readily hydrolyze under environmental conditions. The low water solubility of this polymer will further decrease the rate of hydrolysis.
		50%/>1 year (Estimated)	EPI v4.11	Estimated value based on confidential representative structures 2, 3 and 4 with MW <1,000.
Environmental Half-life		75 days in soil (Estimated)	PBT Profiler v1.301; EPI v4.11	Half-life estimated for confidential representative structure 1; in the predominant compartment, soil, as determined by EPI and the PBT Profiler methodology.

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Bioaccumulation		**HIGH: The bioaccumulation designation is based on the estimated BCF and BAF values >1,000; these values are estimated using confidential representative structures of lower MW components (MW <1,000) of Dow XZ-92547. The higher MW oligomers that may be found in this mixture are expected to have low potential for bioaccumulation based on their large size and low solubility according to polymer assessment literature.**		
	Fish BCF	9,900 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 3 with MW <1,000.
		610 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 4 with MW <1,000.
		820 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 2 with MW <1,000.
		68 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 1 with MW <1,000.
		<100 (Estimated)	Professional judgment	Estimated for the oligomers with a MW >1,000. Cutoff value for large, high MW, insoluble polymers.
	Other BCF			No data located.
	BAF	620 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 4 with MW <1,000.
		2,300 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 3 with MW <1,000.
		600 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 2 with MW <1,000.
		180 (Estimated)	EPI v4.11	Estimates based on confidential representative structure 1 with MW <1,000.

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Metabolism in Fish			No data located.
ENVIRONMENTAL MONITORING AND BIOMONITORING				
Environmental Monitoring		No data located.		
Ecological Biomonitoring		No data located.		
Human Biomonitoring		This chemical was not included in the NHANES biomonitoring report (CDC, 2013).		

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EPI Estimation Programs Interface (EPI) Suite, Version 4.11. Washington, DC: EPIWIN/EPISUITE. U.S. Environmental Protection Agency. http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm.

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PBT Profiler Persistent (P), Bioaccumulative (B), and Toxic (T) Chemical (PBT) Profiler, Version 1.301. Washington, DC: U.S. Environmental Protection Agency. www.pbtprofiler.net.

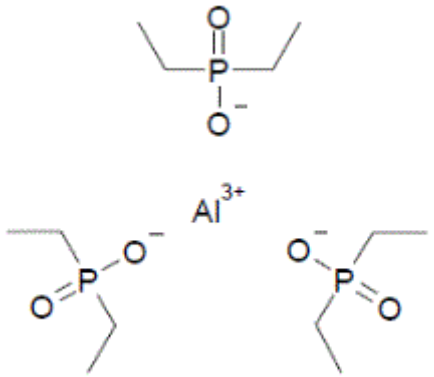
Aluminum Diethylphosphinate

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[§] Based on analogy to experimental data for a structurally similar compound. [R] Recalcitrant: Substance is comprised of metallic species (or metalloids) that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions. [¥] 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	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
Aluminum Diethylphosphinate[¥]	225789-38-8	L	*L*[§]	L	L	*M*[§]	*M*[§]	*M*[§]	L		L	VL	M	M	*H*[R]	*L*

Aluminum Diethylphosphinate



CASRN: 225789-38-8

MW: 390.27

MF: 3 $C_4H_{11}PO_2 \cdot Al$

Physical Forms:
Neat: Solid

Use: Flame retardant

SMILES: CCP(=O)(CC)O[Al](OP(=O)(CC)CC)OP(=O)(CC)CC

Synonyms: Exolit OP 930, Aluminium diethylphosphinate, Aluminium tris(diethylphosphinate)

Chemical Considerations: This alternative is an inorganic compound and in the absence of experimental data, professional judgment using chemical class and structural considerations were used to complete this hazard profile.

Polymeric: No
Oligomeric: Not applicable

Metabolites, Degradates and Transformation Products: Aluminum and diethylphosphinic acid may dissociate (Australia, 2005)

Analog: Confidential aluminum metal salts; aluminum hydroxide; phosphate esters

Endpoint(s) using analog values: Absorption, distribution, metabolism & excretion, carcinogenicity, developmental toxicity, immunotoxicity, neurotoxicity, repeated dose effects

Analog Structure: Not applicable

Structural Alerts: Not applicable

Risk Phrases: Not classified by Annex VI Regulation (EC) No 1272/2008 (ESIS, 2011).

Hazard and Risk Assessments: Hazard assessment in Design for the Environment Alternatives Assessment for Flame Retardants in Printed Circuit Boards, Review Draft, November 8, 2008 (EPA, 2008).

Aluminum Diethylphosphinate CASRN 225789-38-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	Decomposes at 315 (Measured)	Submitted confidential study	Adequate.
	Decomposes at 300 (Measured)	Submitted confidential study	Adequate.
	>400 according to EU Method A.1 using differential scanning calorimetry (Measured)	ECHA, 2013; Submitted confidential study	Adequate.
	Decomposes at 330 (Measured)	DeBoysère and Dietz, 2005	Sufficient details were not available to assess the quality of this study.
	Decomposes at > 300 (Measured)	Clariant, 2007	Sufficient details were not available to assess the quality of this study.
	>400 (Measured)	Australia, 2005	Sufficient details were not available to assess the quality of this study. Reported for a commercial formulation.
Boiling Point (°C)	Expected to decompose before boiling (Estimated)	Professional judgment	Based on available data for melting point.
Vapor Pressure (mm Hg)	$<10^{-8}$ (Estimated)	EPA, 1999; Professional judgment	Cutoff value for nonvolatile compounds according to HPV assessment guidance.
Water Solubility (mg/L)	$2.5x10^{3}$ (Measured)	Submitted confidential study	Sufficient details were not available to assess the quality of this study. Aluminum diethylphosphinate has low wettability and very slow dissolution. This gives a kinetically controlled solubility of <1 mg/L by guideline 92/69/EEC A.6. If aluminum diethylphosphinate is formed by precipitation of a soluble salt, the remaining equilibrium solubility of 2.5×10^{3} mg/L is found. This can be assumed to be the true limit of solubility under ideal conditions.
	<1	ECHA, 2013; Submitted	Guideline study; aluminum

Aluminum Diethylphosphinate CASRN 225789-38-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	According to EU Method A.6 (Measured)	confidential study	diethylphosphinate has low wettability and very slow dissolution. If aluminum diethylphosphinate is formed by precipitation of a soluble salt, the remaining equilibrium solubility of 2.5×10^{3} mg/L is found, which can be assumed to be the true limit of solubility under ideal conditions.
	<1 According to EU Method A.6 (Measured)	Australia, 2005; Submitted confidential study	Reported in a secondary source for a commercial formulation.
Log K_{ow}	-0.44 (Estimated)	Beard and Marzi, 2005; Stuer-Lauridsen et al., 2007	Reported in a secondary source with limited study details; it is unclear whether this value reflects the chemical's low water solubility or its lipophobicity.
Flammability (Flash Point)	No self-ignition below 402°C (Measured)	ECHA, 2013; Submitted confidential study	Adequate.
	Not readily combustible according to guideline 96/69/EEC, test A.10. (Measured)	Submitted confidential study	Guideline study.
Explosivity	Not expected to form explosive mixtures with air (Estimated)	Professional judgment	No data located; based on its use as a flame retardant.
Pyrolysis	Major products are diethylphosphinic acid, ethylphosphonic acid, phosphoric acid, and their respective salts (Measured)	Beard and Marzi, 2005	Study details and test conditions were not available.

Aluminum Diethylphosphinate CASRN 225789-38-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
pH	pH of an aqueous suspension was 4.0; aluminum diethylphosphinate completely dissociated within 24 hours at pH 4.5 during Japanese Ministry of International Trade and Industry (MITI) test. (Measured)	Beard and Marzi, 2005; Australia, 2005	Inadequate. Although this compound does not contain acidic protons, the reference indicates that the acidity results from equilibria involving the dissociated species in solution. Study details and test conditions were not available. Available data for commercial formulations suggest that this compound is likely to dissociate under environmental conditions. However, dissociation is expected to vary as a function of pH to a degree that will have a significant influence on its environmental fate. Available data are not adequate to assess its dissociation under typical environmental conditions.
pK_a			No data located.
Particle Size	D10 = mean ca. 0.4 ≤ 2 µm D50 = mean ca. 0.4 ≤ 29 µm According to Laser-Diffraction method. (Estimated)	ECHA, 2013	Nonguideline study reported in a secondary source.

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Toxicokinetics		**Based on estimates of physical and chemical properties, analogs, and professional judgment, aluminum diethylphosphinate is determined to not be readily absorbed through skin but may be absorbed through the inhalation of dust and oral exposure. Absorption is estimated to be good through the gastrointestinal tract based on physical/chemical properties and analogs; however, only a small amount of administered dose was reported to be absorbed in the gastrointestinal tract in a submitted confidential rat study. Elimination was reported primarily in the feces in a confidential study, while in contrast, elimination was reported to occur primarily in the urine within 12 hours of oral administration in another study.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	Absorption as neat solid expected to be negligible through skin. Absorption good through lungs. Absorption good through gastrointestinal tract. (Estimated)	Professional judgment	Estimates based on physical/chemical properties and confidential analogs.
		Following oral administration, excretion was almost quantitative via the urine within 12 hours.	Stuer-Lauridsen et al., 2007	Study details reported in a secondary source
		Male rats (2/dose group) administered (unradiolabeled) test substance via single oral gavage at 180 and 1,000 mg/kg-day. Only a small amount of the administered dose was absorbed by the gastro-intestinal tract. The major route of elimination was in the feces (unabsorbed fraction) and a small amount of free test substance was detected in the urine. After 36 hours, no test substance was detected.	Submitted confidential study	Study details from an abstract reported in a confidential submission; study conducted according to OECD 417; small number of animals tested.
	Other			No data located.
Acute Mammalian Toxicity		**LOW: Experimental studies indicate that oral and dermal routes to rats do not produce mortality at oral and dermal doses up to 2,000 mg/kg. No lethality data was located for inhalation exposure.**		

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Acute Lethality	**Oral**	Rat oral LD_{50} >2,000 mg/kg	Australia, 2005; Submitted confidential study	Reported in a secondary source for a commercial formulation. Test substance was Exolit OP 930. Conducted according to OECD TG 401.
	Dermal	Rat dermal LD_{50} >2,000 mg/kg	Australia, 2005; Submitted confidential study	Reported in a secondary source for a commercial formulation. Test substance was Exolit OP 930. Conducted according to OECD TG 402.
	Inhalation			No data located.
Carcinogenicity		**LOW: Aluminum diethylphosphinate is estimated to be of low hazard for carcinogenicity based on comparison to analogous metal salts and professional judgment.**		
	OncoLogic Results			No data located.
	Carcinogenicity (Rat and Mouse)	Not expected to be carcinogenic. (Estimated)	Professional judgment	Estimated based on analogy to confidential metal salts.
	Combined Chronic Toxicity/Carcinogenicity			No data located.
	Other			No data located.
Genotoxicity		**LOW: Experimental studies indicate that aluminum diethylphosphinate does not cause gene mutations in bacteria or chromosomal aberrations in mammalian cells.**		
	Gene Mutation *in vitro*	Negative, *Salmonella typhimurium* strains TA1535, TA1537, TA1538, TA98 and TA100 with and without metabolic activation	Australia, 2005; Stuer-Lauridsen et al., 2007; Submitted confidential study	Reported in a secondary source for a commercial formulation. Conducted according to OECD TG 471.
	Gene Mutation *in vivo*			No data located.
	Chromosomal Aberrations *in vitro*	Negative, chromosomal aberrations in Chinese hamster lung cells with and without metabolic activation	Australia, 2005; Submitted confidential study	Reported in a secondary source for a commercial formulation. Conducted according to OECD TG 473.

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Chromosomal Aberrations *in vivo*	Negative, mammalian erythrocyte micronucleus test in NMRI mice; oral (unspecified)	Submitted confidential study	Study reported in a submitted confidential study; Study conducted according to OECD Guideline 474 (Mammalian Erythrocyte Micronucleus Test).
	DNA Damage and Repair			No data located.
	Other			No data located.
Reproductive Effects		**LOW: Changes (characterized as minor) in the number of days of pre-coital interval and a reduction in copulation plugs were reported in a submitted confidential study at 1,000 mg/kg-day. The study-reported NOAEL is on the margin of the Low to Very Low hazard designation; therefore a Low hazard designation was assigned. Aluminum diethylphosphinate is also estimated to be of low hazard for reproductive effects based on professional judgment and comparison to analogous metal salts.**		
	Reproduction/Developmental Toxicity Screen	Expected to have low hazard potential for reproductive effects. (Estimated)	Professional judgment	Estimated based on analogy to confidential metal salts.
		Rats (Sprague Dawley); oral administration of 250 and 1,000 mg/kg bw-day; 15 days prior to mating and throughout gestation and lactation up to post-partum Day 3. Parental effects: No clinical signs of toxicity or change in food consumption. Slight reduction in body weight and body weight gain (both sexes, 1,000 mg/kg-day); Reduced terminal body weight and absolute and relative kidney weights (males, 1,000 mg/kg-day). No adverse effect on oestrus cycle, implantation, gestation length, corpora lutea or sex ratios. No effect on sperm (motility, morphology, concentration). Increase in the number of days of pre-coital interval and a reduction in copulation plugs (1,000 mg/kg-day);	Submitted confidential study	Study reported in a submitted confidential study; Study conducted according to OECD Guideline 421 (Reproductive/Developmental Toxicity Screening Test).

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		these changes were reported as "minor" No treatment-related macroscopic anomalies in pups dying or sacrificed at term. NOAEL: 1,000 mg/kg-day (highest dose tested) LOAEL: Not established		
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects			No data located.
	Other			No data located.
Developmental Effects		**MODERATE: There were no developmental effects reported in a reproduction/developmental toxicity screen in rats at doses up to 1,000 mg/kg-day. There is moderate hazard for aluminum diethylphosphinate given exposure may result in neurodevelopmental effects based on the presence of a phosphinate; there were no experimental studies specifically designed to evaluate the neurodevelopmental endpoint located. The potential for neurodevelopmental effects cannot be ruled out.**		
	Reproduction/ Developmental Toxicity Screen	Expected to have a moderate hazard potential for developmental and neurodevelopmental effects resulting from the presence of a phosphinate. (Estimated)	Professional judgment	Estimated based on analogy to phosphate esters and associated cholinesterase inhibition.
		Rats (Sprague Dawley); oral administration of 250 and 1,000 mg/kg bw-day; 15 days prior to mating and throughout gestation and lactation up to post-partum Day 3. Parental: No clinical signs of toxicity or change in food consumption. Slight reduction in body weight and body	Submitted confidential study	Study details reported in a confidential submission; Study conducted according to OECD Guideline 421 (Reproductive/Developmental Toxicity Screening Test).

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		weight gain; reduced terminal body weight and absolute and relative kidney weights (males, 1,000 mg/kg-day). No adverse effect on estrus cycle, implantation, gestation length, corpora lutea or sex ratios. No effect on sperm (motility, morphology, concentration). Increase in the number of days of pre-coital interval and a reduction in copulation plugs (1,000 mg/kg-day). No treatment-related macroscopic anomalies in pups dying or sacrificed at term. NOAEL = 1,000 mg/kg-day		
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Prenatal Development			No data located.
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity			No data located.
	Other			No data located.

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Neurotoxicity		**MODERATE: Aluminum diethylphosphinate is expected to be of Moderate hazard for based on analogy to aluminum hydroxide and professional judgment. Exposure to the analog resulted in impaired learning in a labyrinth maze test in a 90-day oral study in rats at 35 mg Al/kg/day as aluminum hydroxide with citric acid. Impaired learning in a labyrinth maze test was also reported in rats orally exposed to 300 mg Al/kg/day (only dose tested) as the analog aluminum hydroxide (without citric acid). There is uncertainty in the threshold of response; the possibility that effects occur at doses <100 mg/kg/day (In the Moderate – High hazard designation range) cannot be ruled out.**		
	Neurotoxicity Screening Battery (Adult)	Expected to have a moderate hazard potential for neurotoxic effects resulting from the presence of bioavailable metal species. (Estimated)	Professional judgment	Estimated based on professional judgment and analogy to aluminum hydroxide.
		28-day, Rat, oral gavage, 0, 62.5, 250 or 1,000 mg/kg bw-day. No treatment-related changes in behavior or appearance, no changes in body weight, food consumption, blood chemistry or organ weight. No alterations in gross or microscopic tissue examination. Rat NOAEL >1,000 mg/kg (highest dose tested).	Beard and Marzi, 2005; Stuer-Lauridsen et al., 2007	Reported in a secondary source; study details and test conditions were not available.
		90-day Rat, oral gavage, impaired learning in a labyrinth maze test. NOAEL: Not established LOAEL: 35 mg Al/kg-day as aluminum hydroxide with citric acid (only dose tested) (Estimated by analogy)	Bilkei-Gorzo, 1993 (as cited in ATSDR, 2008)	Reported in a secondary source; dose reported as 35 mg/kg-day as aluminum hydroxide with citric acid; citric acid was added to increase absorption; it is not proven that negative effects only related to aluminum hydroxide and not based on citric acid; also, the background aluminum content of the diet fed to rats was not reported; only one dose tested.
		90-day Rat, oral gavage, impaired learning in a labyrinth maze test. NOAEL: Not established	Bilkei-Gorzo, 1993	The background aluminum content of the diet fed to rats was not reported; only one dose tested

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		LOAEL: 300 mg Al/kg-day as aluminum hydroxide (only dose tested) (Estimated by analogy)		(aluminum hydroxide without citric acid); study description lacks sufficient details on individual results.
	Other	Oral exposure to aluminum is usually not harmful. Some studies show that people exposed to high levels of aluminum may develop Alzheimer's disease, but other studies have not found this to be true. It is not known for certain that aluminum causes Alzheimer's disease.	ATSDR, 2008	Summary statement from a secondary source.
Repeated Dose Effects		**MODERATE: Estimated to be of moderate hazard for immunotoxicity, due to the presence of a bioavailable metal species, based on comparison to analogous metal salts and professional judgment. Experimental studies indicate that oral exposure to rats produces no adverse effects at levels up to 1,000 mg/kg-day.**		
		28-day, Rat, oral gavage, 0, 62.5, 250 or 1,000 mg/kg bw-day. No treatment-related changes in behavior or appearance, no changes in body weight, food consumption, blood chemistry or organ weight. No alterations in gross or microscopic tissue examination. 28-day NOAEL >1,000 mg/kg-day, rats.	Australia, 2005; Stuer-Lauridsen et al., 2007; Submitted confidential study	Reported in a secondary source for a commercial formulation. Test substance was Exolit OP 930.
		Expected to have a moderate hazard potential for immunotoxicity effects resulting from the presence of bioavailable metal species. (Estimated)	Professional judgment	Estimated based on analogy to confidential metal salts.
Skin Sensitization		**LOW: Negative for skin sensitization in guinea pigs.**		
	Skin Sensitization	Non-sensitizing, guinea pigs.	Australia, 2005; Submitted confidential study	Reported in a secondary source for a commercial formulation. Conducted according to OECD TG 406.

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.
Eye Irritation		**LOW: Aluminum diethylphosphinate is slightly to non-irritating in rabbit eyes.**		
	Eye Irritation	Slightly irritating, rabbits.	Australia, 2005	Reported in a secondary source for a commercial formulation. Conducted according to OECD TG 405.
		Not irritating, rabbits.	Submitted confidential study	Study reported in a submitted confidential study.
Dermal Irritation		**VERY LOW: Aluminum diethylphosphinate is not irritating to rabbit skin.**		
	Dermal Irritation	Non-irritating, rabbit.	Australia, 2005; Submitted confidential study	Reported in a secondary source for a commercial formulation. Conducted according to OECD 404.
Endocrine Activity		**No data located.**		
				No data located.
Immunotoxicity		**Aluminum diethylphosphinate is estimated to be of moderate hazard for immunotoxicity, due to the presence of a bioavailable metal species, based on comparison to analogous metal salts and professional judgment.**		
	Immune System Effects	Expected to have a moderate hazard potential for immunotoxicity effects resulting from the presence of bioavailable metal species. (Estimated)	Professional judgment	Estimated based on analogy to confidential metal salts.
ECOTOXICITY				
ECOSAR Class		Not applicable		
Acute Aquatic Toxicity		**MODERATE: The measured green algae EC_{50} is between 50 and > 180 mg/L. For fish and *Daphnia*, LC_{50} values could not be determined because there were no effects at the highest concentrations tested.**		
Fish LC_{50}		*Danio rerio* (Zebra fish) 96-hour LC_{50} >11 mg/L (Experimental)	Australia, 2005	Reported in a secondary source for a commercial formulation.
		Danio rerio (Zebra fish) 96-hour LC_{50} >9.2 mg/L	Submitted confidential study	Study reported in a submitted confidential study.

Aluminum Diethylphosphinate CASRN 225789-38-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	(Experimental)		
	Danio rerio (Zebra fish) 96-hour LC_{50} >100 mg/L (Experimental)	Submitted confidential study	Study reported in a submitted confidential study; Study conducted according to EU Method C.1 (Acute Toxicity for Fish).
Daphnid LC_{50}	*Daphnia magna* 48-hour LC_{50} >33.7 mg/L. (Experimental)	Australia, 2005	Reported in a secondary source for a commercial formulation.
	Daphnia magna 48-hour LC_{50} >33 mg/L. (Experimental)	Submitted confidential study	Study reported in a submitted confidential study.
	Daphnia magna 48-hour EC_{50} >100 mg/L 48-hour NOEC = 100 mg/L. (Experimental)	Submitted confidential study	Study reported in a submitted confidential study; Study conducted according to OECD Guideline 202 (Daphnia sp. Acute Immobilization Test).
Green Algae EC_{50}	*Scenedesmus subspicatus* 72-hour E_bC_{50} of 60 mg/L; *Scenedesmus subspicatus* 72-hour E_rC_{50} of 76 mg/L. (Experimental)	Australia, 2005	Reported in a secondary source for a commercial formulation.
	72-hour EC_{50} = 50 mg/L. (Experimental)	Submitted confidential study	Study reported in a submitted confidential study.
	Scenedesmus subspicatus 72-hour EC_{50} >180 mg/L. (Experimental)	Submitted confidential study	Study details reported in a confidential submission; Study conducted according to EU Method c.3 (Algal Inhibition Test).
Chronic Aquatic Toxicity	**MODERATE: An experimental value for green algae is 1.8 mg/L, while measured toxicity values for fish and *Daphnia* are >10 mg/L.**		
Fish ChV	ChV = 48 mg/L. (Estimated) (Estimated)	Submitted confidential study	Study reported in a submitted confidential study.
	Danio rerio (Zebra fish) 28-day NOEC = 100 mg/L; LOEC >100 mg/L. (Experimental)	Submitted confidential study	Study reported in a submitted confidential study; Study conducted according to OECD Guideline 215 (Fish, Juvenile Growth Test).

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid ChV		*Daphnia magna* 21-day EC_{50} = 22.3 mg/L for immobility *Daphnia magna* 21-day EC_{50} = 46.2 mg/L for reproduction *Daphnia magna* 21-day LOEC = 32 mg/L for immobility and reproduction *Daphnia magna* 21-day NOEC = 10 mg/L for immobility and reproduction (Experimental)	Australia, 2005; Submitted confidential study	Reported in a secondary source for a commercial formulation.
Green Algae ChV		Green algae ChV = 1.8 mg/L. (Experimental) (Experimental)	Submitted confidential study	Study reported in a submitted confidential study.
ENVIRONMENTAL FATE				
Transport		**Although the behavior of metal salts under environmental conditions is dependent on the characteristics of the local environment (predominately pH), transport of both the metal species and the organic anion is anticipated to be dominated by leaching through soil, runoff to aqueous environments, adsorption and/or precipitation of the metal ion onto soil or sediment, and wet and dry deposition of dust particulates in air to land or surface water. Volatilization of this ionic compound from either wet or dry surfaces is not expected to be an important fate process. Nevertheless, the environmental fate of this organic salt will be dependent on its pH-dependent dissociation, and adequate data are not available.**		
	Henry's Law Constant (atm-m^3/mole)	$<10^{-8}$ (Estimated)	Professional judgment	Cutoff value for nonvolatile compounds.
	Sediment/Soil Adsorption/Desorption - K_{oc}	Approximately 0.38 according to OECD Guideline 121 (Measured)	ECHA, 2013; Submitted confidential study	Guideline study.
	Level III Fugacity Model			This substance is not amenable to the model.

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Persistence		**HIGH: For the organic counter-ion, estimates indicate that the half-life for ultimate aerobic biodegradation in water is less than 60 days, which converts to moderate potential for persistence. However, the metal ion is recalcitrant to biodegradation or other typical environmental removal processes.**		
Water	**Aerobic Biodegradation**	Passes Ready Test: No Test method: OECD TG 301F: Manometric Respirometry Test (Measured)	ECHA, 2013; Submitted confidential study	Guideline study.
		Not readily biodegradable (Measured)	Australia, 2005	Reported in a secondary source for a commercial formulation
		Not readily biodegradable (Measured)	Stuer-Lauridsen et al., 2007	Sufficient details were not available to assess the quality of this study.
		Organic counter-ion: Days-weeks (primary survey model) Weeks (ultimate survey model) (Estimated)	EPI v4.10	
		Metal ion: Recalcitrant (Estimated)	Professional judgment	Metal ions will not degrade in the environment.
		Study results: Not indicated Test method: 302C: Inherent - Modified MITI Test (II) Not inherently biodegradable (Measured)	ECHA, 2013; Submitted confidential study	Guideline study.
		Not inherently biodegradable (Measured)	Stuer-Lauridsen et al., 2007	Sufficient details were not available to assess the quality of this study.
	Volatilization Half-life for Model River	>1 year Not a significant fate process (Estimated)	Professional judgment	Based on the magnitude of the estimated Henry's Law constant.
	Volatilization Half-life for Model Lake	>1 year Not a significant fate process (Estimated)	Professional judgment	Based on the magnitude of the estimated Henry's Law constant.
Soil	**Aerobic Biodegradation**			No data located.
	Anaerobic Biodegradation	No degradation according to ISO/DIS 14853	Stuer-Lauridsen et al., 2007	Guideline study reported in a secondary source.

Aluminum Diethylphosphinate CASRN 225789-38-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	Not a significant fate process (Estimated)	Professional judgment	This chemical is expected to exist entirely in particulate form in air.
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Mill, 2000; Professional judgment	The substance does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	Metal salts form a variety of hydroxylation products as a function of pH. Hydrolysis of the organic counter-ion is not expected to be a significant fate process (Estimated)	Professional judgment; Wolfe and Jeffers, 2000	The organic counter ion does not contain functional groups that would be expected to hydrolyze readily under environmental conditions.
Environmental Half-life		**Organic counter-ion:** <60 days **Metal ion:** Recalcitrant (Estimated)	EPI v4.10; Professional judgment	Based on estimated biodegradation half-lives for the organic counter-ion and metal ions will not degrade in the environment.
Bioaccumulation		**LOW: Aluminum diethylphosphinate is not expected to have potential for bioaccumulation.**		
	Fish BCF	<100 (Estimated)	Professional judgment	Available data suggests this chemical will dissociate under environmental conditions. The estimated log K_{OW} and limited lipophilicity are indicative of a lower potential for bioconcentration.
	Other BCF			No data located.
	BAF			No data located.
	Metabolism in Fish			No data located.

Aluminum Diethylphosphinate CASRN 225789-38-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL MONITORING AND BIOMONITORING			
Environmental Monitoring	No data located.		
Ecological Biomonitoring	No data located.		
Human Biomonitoring	This chemical was not included in the NHANES biomonitoring report (CDC, 2011).		

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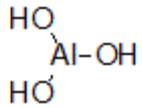
Aluminum Hydroxide

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[§] Based on analogy to experimental data for a structurally similar compound. [R] Recalcitrant: Substance is comprised of metallic species (or metalloids) that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions. [¥] Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

		Human Health Effects											Aquatic Toxicity		Environmental Fate	
Chemical	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Aluminum Hydroxide[¥]	21645-51-2	L	*L*[§]	L	*L*[§]	L	M	*M*[§]	L		VL	VL	L	L	*H*[R]	*L*

Aluminum hydroxide

	**CASRN:** 21645-51-2
	MW: 78.01
	MF: AlH_3O_3
	Physical Forms: **Neat:** Solid
	Use: Flame retardant

SMILES: O[Al](O)O	
Synonyms: Aluminum hydroxide ($Al(OH)_3$), Gibbsite, Bayersite, Nordstrandite, Aluminum trihydrate	
Chemical Considerations: This alternative is an inorganic compound and in the absence of experimental data, professional judgment using chemical class and structural considerations were used to complete this hazard profile.	
Polymeric: No **Oligomeric:** Not applicable	
Metabolites, Degradates and Transformation Products: None	
Analog: Unspecified analogous aluminum compounds were discussed in the structural based professional judgment rationale **Endpoint(s) using analog values:** Carcinogenicity, reproductive effects, immunotoxicity	**Analog Structure:** Not applicable
Structural Alerts: Aluminum compounds (EPA, 2010).	
Risk Phrases: Not classified by Annex I Directive 67/548/European Economic Community & IUCLID (Pakalin et al., 2007).	
Hazard and Risk Assessments: Risk assessment completed for aluminum hydroxide by the National Research Council Subcommittee on Flame-Retardant Chemicals (NRC, 2000). Hazard assessment completed for Design for the Environment Alternatives Assessment for Flame Retardants in Printed Circuit Boards, Review Draft, November 8, 2008. (EPA, 2008; NRC, 2000).	

Aluminum Hydroxide CASRN 21645-51-2			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	Decomposes at approximately 200 (Measured)	European Commission, 2000	Adequate.
	Decomposes at approximately 150-220 to Al_2O_3 and H_2O (Measured)	European Commission, 2000	Adequate.
	Decomposes (loses water) at 300 (Measured)	Lewis, 2000	Adequate.
Boiling Point (°C)	The substance is expected to decompose before boiling. (Estimated)	Professional judgment	Based on the values included in the melting point section of this assessment.
Vapor Pressure (mm Hg)	$<10^{-8}$ (Estimated)	EPA, 1999; Professional judgment	Cutoff value for compounds that are anticipated to be nonvolatile accorded to HPV assessment guidance
Water Solubility (mg/L)	≤ 0.09 at 20°C, pH 6-7 Organisation for Economic Cooperation and Development (OECD) Guideline 105 Purity calculated based on aluminum oxide (Measured)	ECHA, 2013	Guideline study reporting non-specific value that is in agreement with other experimental values indicating poor solubility.
	0.0117 to 0.0947 at pH 7.5-8.1 and 21-24°C Reported as 11.7 to 94.7 µg/L $Al(OH)_3$ and 4.06 to 32.75 µg/L Al 100 mg of $Al(OH)_3$ was dissolved in 100 mL distilled water or test media prepared according to OECD 201, 202 or 211, filtered, and then analyzed using Graphite Furnace Atomic Absorption Spectrometry (GF AAS) and Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Measured)	Submitted confidential study	Reported in a nonguideline study done to prepare for toxicity testing.
	1.5 at 20°C at pH 7 (Measured)	European Commission, 2000	Measured values were not consistently reported, but are sufficient for subsequent components of the hazard assessment.
	$1.5x10^{-2}$ at 20°C at pH 8-9 (Measured)	European Commission, 2000	Measured values were not consistently reported, but are sufficient for subsequent

Aluminum Hydroxide CASRN 21645-51-2			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			components of the hazard assessment.
	Insoluble in water (Estimated)	Lide, 2006	Measured values were not consistently reported, but are sufficient for subsequent components of the hazard assessment.
	Practically insoluble in water (Estimated)	Lewis, 2000; O'Neil et al., 2001	Measured values were not consistently reported, but are sufficient for subsequent components of the hazard assessment.
Log K_{ow}			No data located. This inorganic compound is not amenable to available estimation methods.
Flammability (Flash Point)	Not flammable (Measured)	ECHA, 2013	Reported in a secondary source and based on its use as a flame retardant.
Explosivity	Not explosive (Estimated)	European Commission, 2000	Adequate.
Pyrolysis	Not flammable (Estimated)	European Commission, 2000	Adequate.
pH	pH of a saturated solution in water was 6 to 7 (Measured)	ECHA, 2013	Determined in a water solubility study.
pK_a	Not applicable (Estimated)	Professional judgment	Determination of dissociation constant is not possible due to the insolubility of the test substance.
Particle Size	<100 µm; 88% for the fine unground hydrate and 52-61% for the coarse unground hydrate < 2 µm; 1.3-2% for the fine unground hydrate and 1% for the coarse unground hydrate According to OECD Guideline 110 (Particle Size Distribution / Fibre Length and Diameter Distributions) (Measured)	ECHA, 2013	Guideline study reported in a secondary source.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Toxicokinetics		**Toxicokinetic data suggest that aluminum hydroxide is not readily absorbed in humans following oral exposure. Excretion occurs primarily through feces, and less so in urine. Animal studies indicated that aluminum accumulated in intestinal cells but was not found in other tissues.**		
Dermal Absorption *in vitro*				No data located.
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	^{26}Al labeled aluminum hydroxide (in water suspension) was administered to rats by oral gavage. The mean fractional uptake (absorption) into the bloodstream of ^{26}Al from aluminum hydroxide was 0.025±0.041%. Compared to the uptake into the bloodstream of rats injected with 0.19 ng ^{26}Al labeled aluminum citrate in solution, aluminum hydroxide as an insoluble compound is less bioavailable than soluble compounds (mean fractional uptake of ^{26}Aluminum citrate: 0.079 ±0.0057%; ^{26}Aluminum hydroxide: 0.025±0.041%).	ECHA, 2013	Reported in a secondary source. Adequate, performed in accordance with OECD guidelines and Good Laboratory Practices (GLP); Aluminum hydroxide, was suspended in water with added 1% carboxymethylcellulose (to maintain a suspension).
		After rats were exposed to aluminum hydroxide in drinking water for 10 weeks, aluminum accumulated in intestinal cells but not in other tissues.	HSDB, 2013	Reported in a secondary source, study details and test conditions were not provided.
		In metabolic studies in humans, 12% of an oral load of aluminum hydroxide was retained, but absorption was not calculated.	HSDB, 2013	Reported in a secondary source, study details and test conditions were not provided.
		The absorbed fraction of aluminum hydroxide in two human males dosed orally was 0.01%.	HSDB, 2013	Reported in a secondary source, study details and test conditions were not provided.
		Adult humans with renal failure who ingested 1.5-3.0 g aluminum hydroxide per day for 20-32 days absorbed between 100 and 568 mg aluminum per day (7-19% of the dose).	HSDB, 2013	Reported in a secondary source, study details and test conditions were not provided.
		Adult humans taking aluminum antacids had a 3-fold increase of aluminum levels in the	ATSDR, 2008	Reported in a secondary source, study details were not provided.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		urine; minimal aluminum was absorbed and was mostly excreted in the feces.		
	Other	Certain complexing agents such as citric acid and lactic acid can increase the bioavailability/absorption of aluminum hydroxide.	Gomez et al., 1991; Bilkei-Gorzo, 1993; Colamina et al., 1994; Professional judgment.	Based on studies using citric acid and lactic acid in conjunction with aluminum hydroxide and professional judgment.
Acute Mammalian Toxicity		**LOW: Aluminum hydroxide has low acute toxicity based on oral LD_{50} > 2,000 mg/kg in rats.**		
Acute Lethality	**Oral**	Rat oral LD_{50} >5,000 mg/kg	European Commission, 2000	Reported in a secondary source, study details and test conditions were not provided.
		Rat oral LD_{50} >2,000 mg/kg	ECHA, 2013	Reported in a secondary source. Performed in accordance with OECD guidelines and GLP.
	Dermal			No data located.
	Inhalation			No data located.
Carcinogenicity		**LOW: Aluminum hydroxide is estimated to be of low hazard for carcinogenicity based on professional judgment and comparison to analogous aluminum compounds.**		
	OncoLogic Results			No data located.
	Carcinogenicity (Rat and Mouse)	Low potential for carcinogenicity (Estimated)	Professional judgment	Estimated based on professional judgment and comparison to analogous aluminum compounds.
	Combined Chronic Toxicity/Carcinogenicity			No data located.
	Other			No data located.
Genotoxicity		**LOW: Aluminum hydroxide did not cause mutations in mammalian cells *in vitro* and did not result in an increased incidence of micronuclei in rats *in vivo*.**		
	Gene Mutation *in vitro*	Negative in mouse lymphoma cells with and without metabolic activation	ECHA, 2013	Adequate, performed in accordance with OECD guidelines and GLP.
	Gene Mutation *in vivo*			No data located.
	Chromosomal Aberrations *in vitro*			No data located.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Chromosomal Aberrations *in vivo*	Negative for induction of micronuclei in polychromatic erythrocytes of bone marrow in Sprague-Dawley rats	ECHA, 2013	Adequate, performed in accordance with OECD guidelines and GLP.
	DNA Damage and Repair			No data located.
	Other			No data located.
Reproductive Effects		**LOW: Aluminum hydroxide is estimated to be of low hazard for reproductive effects based on professional judgment and comparison to analogous aluminum compounds.**		
	Reproduction/Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects	Low potential for reproductive effects (Estimated)	Professional judgment	Estimated based on professional judgment and comparison to analogous aluminum compounds.
	Other			No data located.
Developmental Effects		**LOW: Aluminum hydroxide does not show developmental toxicity when administered orally to rats or mice at dose levels up to 266 mg/kg-day. There were no data located regarding developmental neurotoxicity.**		
	Reproduction/ Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Prenatal Development	Rat (Sprague-Dawley), oral (gavage), 384 mg/kg/day $Al(OH)_3$ alone or 384 mg/kg/day $Al(OH)_3$ concurrent with 62 mg/kg/day citric acid on GD 6-15. No significant differences between controls and Al-treated rats on pre- or postimplantation loss, number of live fetuses per litter, or sex ratio. Reduced fetal body weight and increased incidence of skeletal variations in groups receiving $Al(OH)_3$ and citric acid.	Gomez et al., 1991	Study details reported in a primary source. Citric acid was added to increase absorption; it is not proven that effects are solely related to aluminum hydroxide and not based on citric acid.
		Swiss mice, oral (gavage), 166 mg/kg $Al(OH)_3$ alone or 166 mg/kg $Al(OH)_3$ concurrent with 570 mg/kg lactic acid on GD 6-15. Maternal toxicity was evident in groups treated with $Al(OH)_3$ and lactic acid. There were no embryotoxic effects in any group. There was a non-statistically significant increased incidence of skeletal variations in groups receiving $Al(OH)_3$ and lactic acid.	Colomina et al., 1992	Study details reported in a primary source Lactic acid was added to increase absorption; it is not proven that effects are solely related to aluminum hydroxide and not based on lactic acid.
		Rat (Sprague-Dawley), oral (gavage), 0 or 384 mg/kg-day on GD 6-15 There were no significant changes in pre- or post-implantation losses, number of live fetuses per litter, sex ratio, fetal body weight, incidence of malformations, or skeletal variations. NOAEL: 384 mg/kg-day (only dose tested) LOAEL: Not established	Gomez et al., 1991	Study details reported in a primary source; only one dose tested.
		Mouse, oral, no developmental effects. NOAEL: 266 mg/kg-day (highest dose tested)	Domingo et al., 1989	Adequate.
		Mouse, oral, no developmental effects. NOAEL: 268 mg/kg-day (highest dose tested)	Gomez et al., 1989	Abstract only.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Mouse, oral, no developmental effects. NOAEL: 300 mg/kg-day (only dose tested)	Colamina et al., 1994	Abstract only.
		Rat, oral (gavage), 192, 384, 768 mg/kg-day on GD 6-15 There were no significant changes in the number of litters, corpora lutea, total implants, pre- or post-implantation losses, and live fetuses per litter. There were also no significant differences in the sex ratio, fetal body weight, or fetal malformations. NOAEL: 768 mg/kg-day (highest dose tested) LOAEL: Not established	Gomez et al., 1990	Study details reported in a primary source.
		Rat, oral, no developmental effects. NOAEL: 384 mg/kg-day (only dose tested)	Llobet et al., 1990	Abstract only.
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity	Low potential for developmental neurotoxicity (Estimated)	Professional judgment	Estimated based on analogy to structurally similar compounds.
	Other			No data located.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Neurotoxicity		**MODERATE: Aluminum hydroxide is expected to be of moderate hazard for neurotoxicity. Impaired learning in a labyrinth maze test was reported in a 90-day oral study in rats at 300 mg Al/kg/day as aluminum hydroxide (only dose tested; a NOAEL was not identified). Impaired learning in a labyrinth maze test was also reported in rats orally exposed to 100 mg Al/kg/day as aluminum hydroxide in combination with 30 mg/kg-day citric acid (only dose tested; a NOAEL was not identified). There is uncertainty in the threshold of response for this effect for exposure to aluminum hydroxide alone and in combination with citric acid. The possibility that effects occur at doses <100 mg/kg/day (in the Moderate - High hazard designation range) cannot be ruled out; therefore a Moderate hazard designation was assigned.**		
	Neurotoxicity Screening Battery (Adult)	30-day Rat, oral diet, no significant effects noted. NOAEL: 1,252 mg Al/kg-day (highest dose tested)	Thorne et al., 1986; Thorne et al., 1987; ATSDR, 2008	Reported in a secondary source.
		90-day Rat, oral gavage, impaired learning in a labyrinth maze test NOAEL: not established LOAEL: 300 mg/kg-bw (only dose tested)	Bilkei-Gorzo, 1993	The background aluminum content of the diet fed to rats was not reported; only one dose tested; study description lacks sufficient details on individual results. Exposure to 100 mg /kg-day as aluminum hydroxide combined with 30 mg/kg-day citric acid (only dose tested) was also investigated for which impaired learning was observed; citric acid was added to increase absorption; it is not proven that negative effects only related to aluminum hydroxide and not based on citric acid.
		Low potential for repeated dose effects but moderate potential for immunotoxicity. (Estimated)	Professional judgment	Estimated based on professional judgment and comparison to analogous aluminum compounds.
	Other	Oral exposure to aluminum is usually not harmful. Some studies show that people exposed to high levels of aluminum may develop Alzheimer's disease, but other studies have not found this to be true. It is not known for certain that aluminum causes Alzheimer's disease.	ATSDR, 2008	Summary statement from a secondary source.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Repeated Dose Effects		**MODERATE: Aluminum hydroxide is estimated to have potential for immunotoxicity based on professional judgment and comparison to analogous aluminum compounds. Aluminum hydroxide is of low hazard for other repeated dose effects based on an experimental study indicating no adverse effects in rats following oral doses up to 14,470 ppm (302 mg/kg-day). In addition, a low potential for repeated dose effect is estimated based on professional judgment and comparison to analogous aluminum compounds.**		
		Low potential for repeated dose effects but moderate potential for immunotoxicity (Estimated)	Professional judgment	Estimated based on professional judgment and comparison to analogous aluminum compounds.
		28-day Rat (male), oral diet, no systemic effects noted. NOAEL: 14,470 ppm/diet (302 mg aluminum/kg-day; highest dose tested).	Hicks et al., 1987	Study details from primary source.
	Immune System Effects	6-Week human, oral. LOAEL: 25 mg Al/kg-day (Reduction in primed cytotoxic T-cells, only dose tested).	ATSDR, 2008	Study details reported in a secondary source.
		Moderate potential for immunotoxicity. (Estimated)	Professional judgment	Estimated based on professional judgment and comparison to analogous aluminum compounds.
Skin Sensitization		**LOW: Aluminum hydroxide is not a skin sensitizer.**		
	Skin Sensitization	Low potential for skin sensitization. (Estimated)	Professional judgment	Estimated based on professional judgment and comparison to analogous aluminum compounds.
		Not sensitizing to guinea pigs in an *in vivo* maximization test	ECHA, 2013	Reported in a secondary source; conducted in accordance with OECD guidelines and GLP.
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.
Eye Irritation		**VERY LOW: Aluminum hydroxide is not irritating to rabbit eyes.**		
	Eye Irritation	Not irritating, rabbits.	ECHA, 2013	Reported in a secondary source; Conducted in accordance with OECD guidelines and GLP.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Dermal Irritation		**VERY LOW: Aluminum hydroxide is not irritating to skin.**		
	Dermal Irritation	Not irritating, rabbits.	ECHA, 2013	Reported in a secondary source. Conducted in accordance with OECD guidelines and GLP.
		Not irritating, rabbits, mice and pigs	ECHA, 2013	Reported in a secondary source; nonguideline studies.
Endocrine Activity		**No data located.**		
				No data located.
Immunotoxicity		**Aluminum hydroxide is estimated to have potential for immunotoxicity based on professional judgment and comparison to analogous aluminum compounds.**		
	Immune System Effects	Moderate potential for immunotoxicity. (Estimated)	Professional judgment	Estimated based on professional judgment and comparison to analogous aluminum compounds.
		6-Week human, oral. LOAEL: 25 mg Al/kg-day (Reduction in primed cytotoxic T-cells, only dose tested).	ATSDR, 2008	Reported in a secondary source.
ECOTOXICITY				
ECOSAR Class		Not applicable		
Acute Aquatic Toxicity		**LOW: Effect values from experimental studies for fish, daphnia and algae indicate no effects at the saturation limit (NES).**		
Fish LC_{50}		*Salmo trutta* 96-hour NOEC >100 mg/L (Experimental)	European Commission, 2000	Reported in a secondary source. The effect concentration is greater than the measured water solubility.
Daphnid LC_{50}		*Daphnia magna* 48-hour EC_{50} = NES static test conditions. (Experimental)	Tóthová and Šimo, 2013a	Study details reported in an unpublished study; conducted according to OECD 202; no effects at test substance saturation limit (> 0.079 mg/L).
		Daphnia magna 48-hour NOEC >100 mg/L (Experimental)	European Commission, 2000	Reported in a secondary source. Study details and test conditions were not available and the effect concentration is greater than the measured water solubility.
		Daphnia magna 48-hour NOEC > 0.135	ECHA, 2013	Study conducted with aluminum powder.

Aluminum Hydroxide CASRN 21645-51-2			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	mg/L (Experimental)		
	Daphnia magna 48-hr EC_{50} = 0.8240 mg/L (Experimental)	TSCATS, 1996	Study incorrectly cited in source; results are for a different test substance, vanadium hydroxide oxide.
Green Algae EC_{50}	*Desmodesmus subspicatus* 72-hour EC_{50} = NES (Experimental)	Tóthová and Šimo, 2013c	Study details reported in an unpublished study; conducted according to OECD 201; no effects at test substance saturation limit (> 0.078 mg/L).
	Selenastrum capricornutum 72-hour NOEC >100 mg/L (Experimental)	European Commission, 2000	Reported in a secondary source. The effect concentration is greater than the measured water solubility.
	Selenastrum capricornutum 96-hour EC_{50} = 0.6560 mg/L (Experimental)	TSCATS, 1996	Study incorrectly cited in source; results are for a different test substance, vanadium hydroxide oxide.
	Pseudokirchneriella subcapitata 96-hour EC_{50} = 0.46 mg/L (Experimental)	ECHA, 2013	Reported in a secondary source. EC_{50} range: 0.57 mg/L at pH of 7.6 and 0.46 mg/L at pH of 8.2. The water solubility of aluminum hydroxide under basic pH conditions is not available; experimental details are not sufficient to address the confidence limits of these data points.
	Pseudokirchneriella subcapitata 72-hour NOEC = 0.004 - 0.052 mg/L (Experimental)	ECHA, 2013	Reported in a secondary source. DfE criteria are based on LC and EC_{50} values; therefore a NOEC value is not sufficient to determine a hazard designation.
Chronic Aquatic Toxicity	**LOW: Experimental data for daphnia indicate NES. Although there were no experimental data for fish or algae located, the available chronic toxicity data for daphnia suggests low chronic toxicity for fish and algae.**		
Fish ChV	*Pimephales promelas* 42-day NOEC = 0.102 mg/L, LOEC = 0.209 mg/L (Experimental)	TSCATS, 1996	Study incorrectly cited in source; results are for a different test substance, vanadium hydroxide oxide.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid ChV		Daphnia magna 21-day ChV = NES semi-static test conditions (Experimental)	Tóthová and Šimo, 2013b	Study details reported in an unpublished study; conducted according to OECD 211; no effects at test substance saturation limit (> 0.076 mg/L).
		Daphnia magna 21-day NOEC = 0.091 mg/L, LOEC = 0.197 mg/L (Experimental)	TSCATS, 1996	Study incorrectly cited in source; results are for a different test substance, vanadium hydroxide oxide.
Green Algae ChV				No data located.
ENVIRONMENTAL FATE				
Transport		**Although the behavior of aluminum salts under environmental conditions is dependent on the characteristics of the local environment (predominately pH), transport of the aluminum (III) species is anticipated to be dominated by leaching through soil; runoff to aqueous environments; adsorption and/or precipitation of the metal ion onto soil or sediment; and wet and dry deposition dust particulates in air to land or surface water. Volatilization of this ionic compound from either wet or dry surfaces is not expected to be an important fate process. Under acidic pHs typically encountered in the environment, it may form insoluble polymeric aluminum hydroxide colloids while under basic conditions; anionic aluminum hydroxide is expected to predominate. Other factors influencing its behavior include the presence of dissolved organic matter, the extent of absorption on suspended particles, and the presence of other aluminum species.**		
	Henry's Law Constant (atm-m^3/mole)	$<10^{-8}$ (Estimated)	Professional judgment	Cutoff value for nonvolatile compounds.
	Sediment/Soil Adsorption/Desorption - K_{oc}	>30,000 (Estimated)	EPA, 2004; Professional judgment	Cutoff value for nonmobile compounds.
	Level III Fugacity Model			No data located.
Persistence		**HIGH: As an inorganic material, aluminum hydroxide is not expected to biodegrade or oxidize under typical environmental conditions. Aluminum hydroxide does not absorb light at environmentally relevant wavelengths and is not expected to photolyze. No degradation processes for aluminum hydroxide under typical environmental conditions were identified.**		
Water	**Aerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	Substance is or contains inorganic elements, such as metal ions or oxides, that are expected to be found in the environment >180 days after release.
	Volatilization Half-life for Model River	>1 year (Estimated)	Professional judgment	Based on the magnitude of the estimated Henry's Law constant.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Volatilization Half-life for Model Lake	>1 year (Estimated)	Professional judgment	Based on the magnitude of the estimated Henry's Law constant.
Soil	**Aerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	Substance contains inorganic elements.
	Anaerobic Biodegradation	Recalcitrant	Professional judgment	Substance contains inorganic elements.
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	>1 year (Estimated)	Professional judgment	Substance contains inorganic elements.
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment	Aluminum hydroxide does not absorb UV light at environmentally relevant wavelengths and is not expected to undergo photolysis.
	Hydrolysis			Dissociation of aluminum hydroxide in environmental waters is dependent both on the pH and the local concentration of other aluminum species; dissociation will not occur unless in highly acidic waters, e.g., pH 3.
Environmental Half-life				No data located. Inorganic compounds are outside the estimation domain (EPI).
Bioaccumulation		**LOW: Aluminum hydroxide is not expected to bioaccumulate.**		
	Fish BCF	<100 (Estimated)	Professional judgment	Aluminum hydroxide is an inorganic compound and is not anticipated to bioaccumulate or bioconcentrate. This inorganic compound is not amenable to available quantitative structure activity relationship (QSAR) models.
	Other BCF			No data located.

Aluminum Hydroxide CASRN 21645-51-2				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	BAF	<100 (Estimated)	Professional judgment	Aluminum hydroxide is an inorganic compound and is not anticipated to bioaccumulate or bioconcentrate. This inorganic compound is not amenable to available QSAR models.
	Metabolism in Fish			No data located.
ENVIRONMENTAL MONITORING AND BIOMONITORING				
Environmental Monitoring		No data located.		
Ecological Biomonitoring		No data located.		
Human Biomonitoring		This chemical was not included in the NHANES biomonitoring report. (CDC, 2011).		

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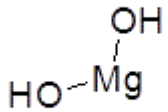
Magnesium Hydroxide

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[R] Recalcitrant: Substance is comprised of metallic species (or metalloids) that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions. [¥] 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	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
Magnesium Hydroxide[¥]	1309-42-8	L	L	L	L	L	*L*	L	M		M	L	*L*	*L*	*H*[R]	*L*

Magnesium Hydroxide



CASRN: 1309-42-8

MW: 58.32

MF: MgH_2O_2

Physical Forms:
Neat: Solid

Use: Flame retardant

SMILES: O[Mg]O

Synonyms: Magnesium hydroxide ($Mg(OH)_2$); Brucite, Milk of Magnesia; Alcanex NHC 25, Asahi Glass 200-06, Baschem 12, Combustrol 500, Duhor, Duhor N, Ebson RF, FloMag H, FloMag HUS, Hydro-mag MA, Hydrofy G 1.5, Hydrofy G 2.5, Hydrofy N, Kisuma 4AF, Kisuma 5, Kisuma 5A, Kisuma 5B, Kisuma 5B-N, Kisuma 5BG, Kisuma 5E, Kisuma 78, Kisuma S 4, Kyowamag F, Lycal 96 HSE, Mag Chem MH 10, Magnesia hydrate, MagneClear 58, Magnesia magma, Magnesiamaito, Magnesium dihydroxide, Magnesium hydroxide gel, Magnesium(II) hydroxide, Magnifin H 10, Magox, Marinco H, Marinco H 1241, Martinal VPF 8812, Milmag, Mint-O-Mag, Nemalite, Oxaine M, Phillips Magnesia Tablets, Phillips Milk of Magnesia Liquid, Reachim, Star 200, Versamag

Chemical Considerations: This alternative is an inorganic compound. In the absence of experimental data, professional judgment using chemical class and structural considerations were used to complete this hazard profile.

Polymeric: No
Oligomeric: Not applicable

Metabolites, Degradates and Transformation Products: Not applicable

Analog: No analogs; Mg^{2+} ions are expected to form when $Mg(OH)_2$ and other magnesium containing compounds dissociate in aqueous conditions. Studies included in this assessment include other sources of Mg^{2+} like $MgCl_2$.

Endpoint(s) using analog values: Not applicable

Analog Structure: Not applicable

Structural Alerts: None

Risk Phrases: Not classified by Annex VI Regulation (EC) No 1272/2008 (ESIS, 2011).

Hazard and Risk Assessments: Risk assessment completed for magnesium hydroxide by the National Academy of Sciences in 2000 (NAS, 2000).

Magnesium Hydroxide CASRN 1309-42-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	Decomposes at 350 (Measured)	Hodgman, 1959; Lewis, 1997; Lewis, 2000	MgO and H_2O are decomposition products.
	Decomposes at 380 (Measured)	IUCLID, 2000	MgO and H_2O are decomposition products.
	350 (Measured)	Lide, 2000; Aldrich Chemical Company, 2006	MgO and H_2O are decomposition products.
Boiling Point (°C)	Will decompose before boiling (Measured)	IUCLID, 2000	Decomposition occurs upon melting as described in additional sources above.
Vapor Pressure (mm Hg)	$<10^{-8}$ (Estimated)	EPA, 1999; Professional judgment	Cutoff value for nonvolatile compounds according to HPV assessment guidance. This inorganic compound is not amenable to available estimation methods.
Water Solubility (mg/L)	1.78 at 20°C, pH 8.3 According to Organisation for Economic Cooperation and Development (OECD 105) Column elution method. (Measured)	ECHA, 2013	Guideline study; results are in agreement with other experimental values.
	9 at 18°C (Measured)	Hodgman, 1959; IUCLID, 2000	Measured values, which span a relatively narrow range, are consistently reported in numerous sources.
	1 at 20°C (Measured)	IUCLID, 2000	Measured values, which span a relatively narrow range, are consistently reported in numerous sources.
	6 at 20°C (Measured)	IUCLID, 2000	Measured values, which span a relatively narrow range, are consistently reported in numerous sources.
	<8 at 20°C (Measured)	IUCLID, 2000	Measured values, which span a relatively narrow range, are consistently reported in numerous

Magnesium Hydroxide CASRN 1309-42-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			sources.
	40 at 100°C (Measured)	Hodgman, 1959	Value obtained at an elevated temperature.
Log K_{ow}			No data located; inorganic compounds are outside the estimation domain of EPI.
Flammability (Flash Point)	Not flammable (Measured)	IUCLID, 2000	Reported in a secondary source and based on its use as a flame retardant.
Explosivity	Not explosive (Estimated)	IUCLID, 2000	Adequate.
Pyrolysis	Not applicable (Estimated)	Professional judgment	Inorganic compounds do not undergo pyrolysis.
pH	pH of a saturated solution in water was 8.3 (Measured)	ECHA, 2013	Reported in a secondary source, determined from a water solubility study.
	9.5-10.5 (Measured)	O'Neil et al., 2011	Reported in a secondary source, limited study details provided.
pK_a			No data located.
Particle Size	D10 = mean 2.013 µm D50 = mean 13.915 µm D90 = mean 154.107 µm According to OECD Guideline 110 (Particle Size Distribution / Fibre Length and Diameter Distributions). (Estimated)	ECHA, 2013	Guideline study reported in a secondary source.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Toxicokinetics		**Some magnesium hydroxide is absorbed following ingestion and is excreted primarily in urine.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	The magnesium ion is poorly absorbed; when taken orally, only 5-15% of the magnesium from a dose of magnesium hydroxide is absorbed and this magnesium is readily excreted in the urine, if kidney function is normal.	IUCLID, 2000	Reported in a secondary source, limited study details provided.
	Other			No data located.
Acute Mammalian Toxicity		**LOW: Acute lethality values suggest that magnesium hydroxide is of low concern for acute toxicity for oral exposure. There were no data located regarding acute dermal exposure.**		
Acute Lethality	**Oral**	Rat oral LD_{50} = 8,500 mg/kg	Lewis, 2000	Reported in a secondary source, limited study details provided.
		Mouse oral LD_{50} = 8,500 mg/kg.	Lewis, 2000	Reported in a secondary source, limited study details provided.
		Human infant oral TD_{Lo} (behavioral) = 2,747 mg/kg.	Lewis, 2000	Reported in a secondary source, limited study details provided.
		Probable human oral lethal dose = 5-15 g/kg.	HSDB, 2003	Reported in a secondary source, limited study details provided.
	Dermal			No data located.
	Inhalation	Rat inhalation 4-hour LC_{50} >2.1 mg/L (whole-body inhalation to aerosol)	ECHA, 2013	Reported in a secondary source. There was no mortality at the highest dose tested (2.1 mg/L); conducted according to OECD 403.
Carcinogenicity		**LOW: Experimental studies indicate low concern for carcinogenicity based on results from studies on magnesium hydroxide and the related magnesium chloride.**		
	OncoLogic Results			Structure could not be evaluated by OncoLogic.
	Carcinogenicity (Rat and Mouse)	5-week, repeated-dose/carcinogenicity study, oral (diet), rat; Decreased number of carcinogen-induced DNA synthesis in	BIBRA, 1993	Reported in a secondary source, limited study details provided; study duration insufficient as a cancer

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		the large bowel epithelial cells. NOAEL: 2,000 ppm (approximately 100 mg/kg-day, highest dose tested)		study.
	Combined Chronic Toxicity/Carcinogenicity	96-week chronic toxicity/carcinogenicity study on $MgCl_2$, oral, mouse; no significant differences in tumor incidence between treated and control animals except for dose-related decrease in the incidence of hepatocellular carcinomas in males.	Kurata et al., 1989	Sufficient study details reported in a primary source; test substance: magnesium chloride.
		227-day, chronic toxicity/ carcinogenicity study, oral (diet), rat; decreased number of colon tumors in rats pretreated with a known colon carcinogen. NOAEL: 50 mg/kg-day (highest dose tested).	BIBRA, 1993	Reported in a secondary source, limited study details provided; study duration insufficient as a cancer study.
		16-week carcinogenicity study, oral (diet), rat; inhibitory effects on colon carcinogenesis, carcinogen-induced expression of c-myc proto-oncogene and cell proliferation. NOAEL: 0.2% in diet (highest concentration tested)	Wang et al., 1993	Sufficient study details reported in a primary source; study duration insufficient as a cancer study.
		Inhalation exposure of male rats to short (4.9 x 0.31 mm) or long (12 x 0.44 mm) $MgSO_4/5Mg(OH)_2 \cdot 3H_2O$ filaments for 6 hour/day, 5 day/week for up to 1 year did not increase the incidence of any tumor types in animals sacrificed 1 day or 1 year after cessation of exposure.	NAS, 2000	Reported in a secondary source, limited study details provided; study duration insufficient as a cancer study.
	Other			No data located.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Genotoxicity		**LOW: Experimental studies indicate that magnesium hydroxide is not mutagenic to bacteria or mammalian cells *in vitro* and does not cause chromosomal aberrations in human lymphocytes *in vitro*.**		
	Gene Mutation *in vitro*	Negative, Ames Assay in *Salmonella* and *Escherichia coli*.	BIBRA, 1993	Reported in a secondary source, limited study details provided. Only 3 strains of *Salmonella* were tested; current regulatory guidelines suggest that at least 4 strains be used in Ames tests.
		Negative; mouse lymphoma assay, L5178Y cells; with and without metabolic activation.	ECHA, 2013	Reported in a secondary source.
	Gene Mutation *in vivo*			No data located.
	Chromosomal Aberrations *in vitro*	Negative; did not induce chromosomal aberrations in human lymphocytes; with and without metabolic activation.	ECHA, 2013	Reported in a secondary source.
	Chromosomal Aberrations *in vivo*			No data located.
	DNA Damage and Repair			No data located.
	Other			No data located.
Reproductive Effects		**LOW: There were no reproductive effects observed in rats in a repeated dose toxicity study with the reproduction/developmental toxicity screen at doses of magnesium hydroxide as high as 1,000 mg/kg-day.**		
	Reproduction/Developmental Toxicity Screen			No data located.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen	Repeated dose toxicity study with the reproduction/developmental toxicity screen; rat, oral (gavage), 0, 110, 330, 1,000 mg/kg-day magnesium hydroxide. Males exposed for 29 days: 2 weeks prior to mating, during mating and up to termination; females exposed for 41-45 days: 2 weeks premating, during mating, post coitum, and 4 days of lactation. There were no reproductive effects observed in any dose group. NOAEL: 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	ECHA, 2013	Reported in a secondary source. Study conducted according to OECD 422.
	Reproduction and Fertility Effects			No data located.
	Other			No data located.
Developmental Effects		**LOW: Magnesium hydroxide is expected to be of low concern for developmental effects based on a nonstandard experimental study indicating magnesium chloride produces no adverse effects on developmental outcomes at levels up to 96 mg/kg/day of Mg^{2+} ion and an experimental study from a secondary source showing no effect on human newborns.**		
	Reproduction/ Developmental Toxicity Screen			No data located.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen	Repeated dose toxicity study with the reproduction/developmental toxicity screen; rat, oral (gavage), 0, 110, 330, 1,000 mg/kg-day. Males exposed for 29 days: 2 weeks prior to mating, during mating and up to termination; females exposed for 41-45 days: 2 weeks premating, during mating, post coitum, and 4 days of lactation. There were no developmental effects observed in any dose group. NOAEL:1,000 mg/kg-day (highest dose tested) LOAEL: Not established	ECHA, 2013	Reported in a secondary source. Study conducted according to OECD 422.
		Repeated-dose/developmental study (fetal exposure at unspecified dose levels during 3rd trimester), 27 hypertensive women treated with magnesium hydroxide, no effect on newborns except slightly increased body weight and hypermagnesiumemia. Cord serum Mg levels reported to be 70-100% of maternal levels after treatment (potentially causing neurological depression in neonate, characterized by respiratory depression, muscle weakness, decreased reflexes). Prolonged magnesium treatment during pregnancy may be associated with maternal and fetal hypocalcemia and adverse effects on fetal bone mineralization.	HSDB, 2003	Reported in a secondary source, limited study details provided. Maternal treatment doses not specified.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Prenatal Development	10-day (GD 6-15) reproductive/developmental study on $MgCl_2$, oral, rat; no treatment-related effects. NOAEL: 96 mg/kg-day for Mg^{2+} ion (highest dose tested) LOAEL: Not established	NAS, 2000	Reported in a secondary source, limited study details provided.
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity			No data located.
	Other			No data located.
Neurotoxicity		**LOW: Magnesium hydroxide is expected to be of low hazard for neurotoxicity based on expert judgment.**		
	Neurotoxicity Screening Battery (Adult)	Low potential for neurotoxicity. (Estimated)	Expert judgment	Estimated based on expert judgment.
	Other			No data located.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Repeated Dose Effects		**LOW: Experimental studies indicate magnesium ions produce no adverse systemic effects in rats or mice at levels ≥ 1,000 mg/kg-day of magnesium hydroxide.**		
		96-week repeated-dose study for $MgCl_2$, oral (0, 0.5, 2% in the diet), mouse; decreased body weight gain, increased food/water consumption and increased relative brain, heart and kidney weights in high dose (2%) females, no effects in males. Female: NOAEL: 87 mg/kg-day for Mg^{2+} ion LOAEL: 470 mg/kg-day for Mg^{2+} ion Male: NOAEL: 336 mg/kg-day for Mg^{2+} ion (highest dose tested) LOAEL: Not established	Kurata et al., 1989	Adequate, primary source.
		90-day repeated-dose study for $MgCl_2$, oral, mouse (M: 73, 146, 322, 650, 1,368 mg/kg-day for Mg^{2+} ion; F: 92, 190, 391, 817, 1,660 mg/kg-day for Mg^{2+} ion); decreased body weight gain in males and females at highest dose tested (1,660 mg/kg-day); renal tubular vacuolation in males administered 650 mg/kg-day for Mg^{2+} ion. Female: NOAEL: 817 mg/kg-day for Mg^{2+} ion LOAEL: 1,660 mg/kg-day for Mg^{2+} ion Male: NOAEL: 322 mg/kg-day for Mg^{2+} ion LOAEL: 650 mg/kg-day for Mg^{2+} ion	NAS, 2000	Reported in a secondary source, no study details provided.
		90-day repeated-dose study in B6C3F1 mice; $MgCl_2$ administered orally at doses	NAS, 2000	Reported in a secondary source, no study details provided.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		of 0.3, 0.6, 1.25 and 2.5% in the diet. Effects included decreased body weight gain and renal tubular vacuolation in males in the high-dose group (840 mg/kg-day). Female: NOAEL: 587 mg/kg-day for Mg^{2+} ion Male: NOAEL: 420 mg/kg-day for Mg^{2+} ion LOAEL: 840 mg/kg-day for Mg^{2+} ion		
		32-week repeated-dose study, diet, rat; no effects on body weight or liver weight. NOAEL: 1,000 ppm (approximately 50 mg/kg-day, highest dose tested) LOAEL: Not established	BIBRA, 1993	Reported in a secondary source, no study details provided.
		Repeated dose toxicity study with the reproduction/developmental toxicity screen; rat, oral (gavage), 0, 110, 330, 1,000 mg/kg-day $MgOH_2$. Males exposed for 29 days: 2 weeks prior to mating, during mating and up to termination; females exposed for 41-45 days: 2 weeks premating, during mating, post coitum, and 4 days of lactation. There were no toxicologically relevant changes in any of the parental parameters examined. NOAEL: 1,000 mg/kg-day (highest dose tested) LOAEL: Not established	ECHA, 2013	Reported in a secondary source. Study conducted according to OECD 422.
		4-week repeated-dose study, oral, human; caused diarrhea, abdominal discomfort,	BIBRA, 1993	Reported in a secondary source, no study details provided.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		and increased serum magnesium levels. NOAEL: Not established LOAEL: 400 mg/kg-day (only dose reported)		
		Inhalation exposure of male rats to short (4.9 x 0.31 mm) or long (12 x 0.44 mm) $MgSO_4/5Mg(OH)_2 3H_2O$ filaments for 6 hour/day, 5 day/week for up to 1 year (concentration not specified) exhibited a slight increase in the incidence of pulmonary lesions 1 year after cessation of exposure. Histopathological examination revealed a slight increase in segmental calcification of the pulmonary artery and thickening of the lung pleura in rats exposed to both short and long filaments for 4 weeks or 1 year. There were no effects on survival or body, lung, liver, kidney and spleen weights of animals sacrificed 1 day or 1 year following a 1-year exposure period.	NAS, 2000	Reported in a secondary source, no study details provided.
		Human systemic effects: chlorine level changes, coma, somnolence in a neonate.	Lewis, 2000	A case study of intoxication after oral exposure to magnesium in a neonate. Reported in a secondary source; no study details provided.
		Repeated oral exposure in humans may cause rectal stones composed of magnesium carbonate and magnesium hydroxide (rare occurrence).	IUCLID, 2000	Reported in a secondary source, no study details provided.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Skin Sensitization		**MODERATE: Magnesium hydroxide was sensitizing in a mouse local lymph node assay.**		
	Skin Sensitization	Sensitizing in a mouse local lymph node assay (LLNA); application of 10, 25 or 50% w/w $MgOH_2$ in propylene glycol to the ears. Very slight erythema in all animals treated with 50% $MgOH_2$, staining on the ears at 10, 25 and 50%. SI (stimulation index) at 10, 25 and 50% was 2.0, 3.6 and 5.9, respectively. Dose response and EC3 value >/= 3.	ECHA, 2013	Well documented secondary source; GLP study conducted according to guidelines. $MgOH_2$, purity not stated
		Does not cause skin sensitization. (Estimated)	Professional judgment	Estimated by professional judgment.
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.
Eye Irritation		**MODERATE: Based on irritation and damage to the corneal epithelium in rabbits that cleared within 2-3 days.**		
	Eye Irritation	Moderately irritating to rabbit eyes.	IUCLID, 2000	Reported in a secondary source, limited study details provided.
		Administration of milk of magnesia twice a day for 3-4 days caused damage to corneal epithelium of rabbit eyes; however, effects disappeared within 2-3 days.	HSDB, 2003	Reported in a secondary source, limited study details provided. Milk of magnesia is a mixture containing magnesium hydroxide and inactive ingredients.
Dermal Irritation		**LOW: An experimental study indicates that magnesium hydroxide is not an irritant to rabbit skin.**		
	Dermal Irritation	Moderate potential for dermal irritation based on experimental aqueous pH values. (Estimated)	Expert judgment	Estimated based on expert judgment.
		Not corrosive in an *in vitro* human skin corrosion test.	ECHA, 2013	Reported in a secondary source. Study conducted according to OECD guideline 431.
		Not irritating in an *in vitro* skin irritation test.	ECHA, 2013	Reported in a secondary source. *In vitro* skin irritation: reconstructed

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				human epidermis model test.
		Not irritating, rabbits.	Submitted confidential study	Reported in a submitted confidential study.
Endocrine Activity		**No data located.**		
				No data located.
Immunotoxicity		**Magnesium hydroxide is expected to have low potential for immunotoxicity based on expert judgment.**		
	Immune System Effects	Low potential for immunotoxicity. (Estimated)	Expert judgment	Estimated based on expert judgment.
ECOTOXICITY				
ECOSAR Class		Not applicable		
Acute Aquatic Toxicity		**LOW: Estimated LC_{50} values for all of the standard toxicity test organisms are greater than 100 mg/L. Experimental LC_{50} values are much greater than the anticipated water solubility, suggesting no effects at saturation (NES).**		
Fish LC_{50}		96-hour LC_{50} = $MgCl_2$: 2,120 mg/L $MgSO_4$: 2,820 mg/L (Estimated)	Mount et al., 1997	Estimated based on analogy to $MgCl_2$ and $MgSO_4$; expected to display NES because this amount of test substance is not anticipated to dissolve in water at a concentration at which adverse effects may be expressed.
		Pimephalis promelas 96-hour LC_{50} = 511 mg/L; static conditions. (Experimental)	ECHA, 2013	Reported in a secondary source. Test material diluted to 61% in aqueous suspension.
		Onchorinchus mykiss 96-hour LC_{50} = 775.8 mg/L; static conditions. (Experimental)	ECHA, 2013	Reported in a secondary source. Test material diluted to 61% in aqueous suspension.
Daphnid LC_{50}		*Daphnia magna* 48-hour LC_{50} = $MgCl_2$: 1,330 mg/L $MgSO_4$: 1,820 mg/L (Estimated)	Biesinger and Christensen, 1972; Mount et al., 1997	Estimated based on analogy to $MgCl_2$ and $MgSO_4$; expected to display NES because this amount of test substance is not anticipated to dissolve in water at a concentration at which adverse effects may be expressed.

Magnesium Hydroxide CASRN 1309-42-8			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Daphnia magna 48-hour LC_{50} = 284.76 mg/L; static conditions. (Experimental)	ECHA, 2013	Reported in a secondary source. Test material diluted to 61% in aqueous suspension.
	Gammarus lacustris LC_{50} = 64.7 mg/L. (Experimental)	O'Connell et al., 2004	Reported in a secondary source, study details and test conditions were not provided. Not a standard test species.
Green Algae EC_{50}	*Scenedesmus subspicatus* and *Selenastrum capricornutum* 72-hour EC_{50} >100 mg/L (for growth and biomass). (Experimental)	ECHA, 2013	Reported in a secondary source.
Chronic Aquatic Toxicity	**LOW: Estimated chronic values (ChV) are all >10 mg/L and exceed the anticipated water solubility, suggesting NES.**		
Fish ChV	Fish ChV: 50-80 mg/L (Experimental)	ECHA, 2013	An acute to chronic ratio of 10 was applied to experimental acute data for *Pimephalis promelas* and *Onchorinchus mykiss*. Reported in a secondary source. Test material diluted to 61% in aqueous suspension.
	Freshwater fish ChV = 403 mg/L. (Estimated)	Professional judgment	Estimated using an acute to chronic ratio of 3:3; expected to display NES because this amount of test substance is not anticipated to dissolve in water at a concentration at which adverse effects may be expressed.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid ChV		Daphnia ChV = 82 mg/L (Estimated)	Suter, 1996	Estimated based on analogy to the measured ChV for Mg^{2+} ion; based on tests that were not standard but were judged to be of good quality; expected to display NES because this amount of test substance is not anticipated to dissolve in water at a concentration at which adverse effects may be expressed.
Green Algae ChV		Green algae NOEC: 980 mg/L LOEC: 1,230 mg/L (Estimated)	ECOTOX, 2012	Estimated based on analogy to $MgSO_4$; expected to display NES because this amount of test substance is not anticipated to dissolve in water at a concentration at which adverse effects may be expressed.
ENVIRONMENTAL FATE				
Transport		**The low water solubility, the estimated vapor pressure of <1x10^{-8} mm Hg, estimated K_{OC} of >30,000 and estimated Henry's Law constant of <1x10^{-8} atm-m^3/mole indicate that magnesium hydroxide will be relatively immobile in the environment. Magnesium hydroxide is a mineral occurring naturally in the environment.**		
	Henry's Law Constant (atm-m^3/mole)	<10^{-8} (Estimated)	Professional judgment	Cutoff value for nonvolatile compounds.
	Sediment/Soil Adsorption/Desorption - K_{oc}	>30,000 (Estimated)	EPA, 2004; Professional judgment	Cutoff value for nonmobile compounds.
	Level III Fugacity Model			Not all input parameters for this model were available to run the estimation software (EPI).

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Persistence		**HIGH: As an inorganic compound, magnesium hydroxide is not expected to biodegrade, oxidize in air, or undergo hydrolysis under environmental conditions. Magnesium hydroxide does not absorb light at environmentally relevant wavelengths and is not expected to photolyze. Magnesium hydroxide is recalcitrant and it is expected to be found in the environment >180 days after release. As a naturally occurring compound, it may participate in natural cycles and form complexes in environmental waters.**		
Water	**Aerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	Substance is or contains inorganic elements, such as metal ions or oxides, that are expected to be found in the environment >180 days after release.
	Volatilization Half-life for Model River	>1 year (Estimated)	Professional judgment	Based on the magnitude of the estimated Henry's Law constant.
	Volatilization Half-life for Model Lake	>1 year (Estimated)	Professional judgment	Based on the magnitude of the estimated Henry's Law constant.
Soil	**Aerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	This inorganic compound is not amenable to available estimation methods.
	Anaerobic Biodegradation	Recalcitrant (Estimated)	Professional judgment	This inorganic compound is not amenable to available estimation methods.
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	>1 year (Estimated)	Professional judgment	Substance does not contain functional groups amenable to atmospheric degradation processes.
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment	Magnesium hydroxide does not absorb UV light at environmentally relevant wavelengths and is not expected to undergo photolysis.
	Hydrolysis	Not a significant fate process (Estimated)	Professional judgment	Substance does not contain functional groups amenable to hydrolysis.

Magnesium Hydroxide CASRN 1309-42-8				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Environmental Half-life				Not all input parameters for this model were available to run the estimation software (EPI).
Bioaccumulation		**LOW: Magnesium hydroxide is not expected to bioaccumulate based on professional judgment.**		
	Fish BCF	<100 (Estimated)	Professional judgment	This inorganic compound is not amenable to available estimation methods.
	Other BCF			No data located.
	BAF	<100 (Estimated)	Professional judgment	This inorganic compound is not amenable to available estimation methods.
	Metabolism in Fish			No data located.
ENVIRONMENTAL MONITORING AND BIOMONITORING				
Environmental Monitoring		Magnesium hydroxide is a mineral that occurs naturally in the environment (HSDB, 2003).		
Ecological Biomonitoring		No data located.		
Human Biomonitoring		This chemical was not included in the NHANES biomonitoring report (CDC, 2013).		

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Melamine Polyphosphate

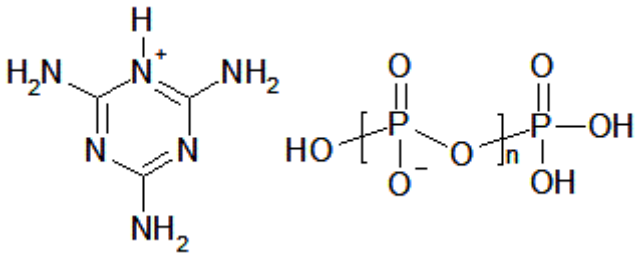
VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[¥] 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	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
Melamine Polyphosphate[1¥]	15541-60-3	L	*M*	*M*	*H*	*M*	*M*	*M*	*L*		L	VL	L	L	*H*	*L*

[1]Hazard designations are based upon the component of the salt with the highest hazard designation, including the corresponding free acid or base.

Melamine Polyphosphate



	CASRN: 15541-60-3
	MW: >1,000
	MF: $C_3H_6N_6 \cdot (H_3PO_4)_n$
	Physical Forms: **Neat:** Solid
	Use: Flame retardant

SMILES: n(c(nc(n1)N)N)c1N(H)(H)OP(=O)(O)OP(=O)(O)O (n =1) SMILES for the representative structure was created using the methodology described in the EPI help file.

Synonyms: Diphosphoric acid, compound with 1,3,5-triazine-2,4,6-triamine; Polyphosphoric acids, compounds with melamine.

The CASRN for the compound melamine pyrophosphate is 15541-60-3. The CASRN 218768-84-4 is associated with the product Melapur 200, not the chemical melamine polyphosphate.

Chemical Considerations: This alternative contains a polymeric moiety. Although the chain length of the polyphosphoric acid is not specified, the smaller, water-soluble polyphosphate ions were used in assessment (generally as the diphosphate ion, n=1). Melamine polyphosphate will freely dissociate under environmental conditions based on professional judgment. Measured values from studies on the dissociated components were used to supplement data gaps as appropriate and EPI v 4.10 was used to estimate physical/chemical and environmental fate values in the absence of experimental data. Measured values from experimental studies were incorporated into the estimations.

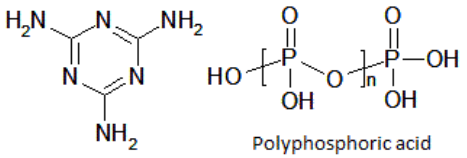
Polymeric: Yes
Oligomeric: Melamine polyphosphate is a complex mixture consisting of melamine and polyphosphate chains of varying length.

Metabolites, Degradates and Transformation Products: Melamine (CASRN 108-78-1)

Analog: Confidential structurally similar polymers; Polyphosphoric acid (CASRN 8017-16-1) and melamine (CASRN 108-78-1) are the dissociated components of this salt

Endpoint(s) using analog values: Reproductive effects, neurotoxicity, immunotoxicity

Analog Structure:



Structural Alerts: Aromatic amine, genetic toxicity (EPA, 2012).
Risk Phrases: Not classified by Annex I Directive 67/548/European Economic Community (EEC) & IUCLID (Pakalin et al., 2007).
Hazard and Risk Assessments: Australian Safety and Compensation Council National Industrial Chemicals Notification and Assessment Scheme (NICNAS), October 30, 2006 (Australia, 2006).

Melamine Polyphosphate CASRN 15541-60-3			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	>400 (Measured)	Submitted confidential study	Adequate; value for the melamine polyphosphate salt.
	>400 (Measured)	Australia, 2006	Adequate; value for the melamine polyphosphate salt.
Boiling Point (°C)	>300 (Estimated)	EPI v4.10; Professional judgment	As an organic salt, it is expected to decompose before boiling.
	225 Decomposes Reported for activated melamine pyrophosphate (CASRN 15541-60-3) (Measured)	New Line Safety, 2011	No study details reported in an MSDS.
Vapor Pressure (mm Hg)	$<10^{-8}$ (Estimated)	EPI v4.10; Boethling and Nabholz, 1997	Cutoff value for nonvolatile compounds.
Water Solubility (mg/L)	20,000 (Measured)	Submitted confidential study	Adequate; value for the melamine polyphosphate salt.
	20,000 (Measured)	Australia, 2006	Adequate.
Log K_{ow}	<-2 (Estimated)	EPI v4.10	Cutoff value for highly water soluble substances.
Flammability (Flash Point)	Not highly flammable (Measured)	Submitted confidential study	Reported in a secondary source and based on its use as a flame retardant.
Explosivity	Not a potential explosive (Measured)	Australia, 2006	Adequate.
	Not a potential explosive (Measured)	Submitted confidential study	Adequate.
Pyrolysis	May produce carbon monoxide, ammonia, oxides of nitrogen, and oxides of phosphorus by thermal decomposition. Reported for activated melamine pyrophosphate (CASRN 15541-60-3). (Estimated)	New Line Safety, 2011	No study details reported in an MSDS.
pH	7 Reported for activated melamine pyrophosphate (CASRN 15541-60-3) (Measured)	New Line Safety, 2011	No study details reported in an MSDS.

Melamine Polyphosphate CASRN 15541-60-3			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
pK_a	**Pyrophosphoric Acid:** pK_{a1} = 0.85 pK_{a2} = 1.96 pK_{a3} = 6.78 pK_{a4} = 10.39 (Estimated)	ECHA, 2014	Reported for pyrophosphoric acid (CASRN 2466-09-3); study reported in a secondary source.
	Melamine: pK_{b1}= 7.3; pK_{b2}= 11.4 according to OECD 112 (Measured)	ECHA, 2013	Guideline study reported for melamine in a secondary source.
	Melamine: pK_{b1} = 9 There are several amino groups that result in basic properties. pK_{b1} = 9 pK_{b2} = 14 K_{b1}= $1.1x10^{-9}$ K_{b2} = $1.0x10^{-14}$ at 25°C (Measured)	Baynes et al., 2008	Reported from a nonguideline study for melamine.
	Melamine: pK_{b1} = 9 pK_{b2} = 14 K_{b1}= $1.1x10^{-9}$ K_{b2} = $1.0x10^{-14}$ at 25°C (Measured)	Crews et al., 2006	For melamine; study details were not available.
	Melamine: Considered a weak base Neutral at pH values of 6 to 13; Cation formation at the triazine ring nitrogen at pH values of 1 to 4 (Measured)	OECD SIDS, 1998	Supporting information provided in a secondary source for melamine.
	Melamine: 5 (Measured)	HSDB, 2008; Weber, 1970	Reported in a secondary source for melamine, value is assumed to be the pK_b.
Particle Size			No data located.
HUMAN HEALTH EFFECTS			

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Toxicokinetics		**No toxicokinetic data were located for melamine polyphosphate or polyphosphoric acid; limited data for melamine indicate that melamine was rapidly absorbed, distributed to body fluids, cleared from plasma and excreted mainly via urine in monkeys. In rats, melamine was distributed to the stomach, small intestine, cecum, and large intestine, and found in blood and urine. Following a single oral exposure to pregnant rats, melamine was detected in the maternal serum, breast milk, whole foetus, amniotic fluid, neonatal serum and neonatal kidney. There is evidence that Melamine passed through the placenta, reached the fetus and accumulated in the lactating mammary gland. Excretion occurred through the placenta of the fetus and the kidneys of neonates and was later excreted into amniotic fluid. Melamine was transferred quickly to fetal circulation in studies where placentas from mothers following caesarean section or normal delivery were perfused with melamine. Melamine was readily cleared by the kidney in pigs administered melamine intravenously; distribution may be limited to the extracellular fluid compartment. There was no concern for binding in tissues. The half-life was reported as 4.04 hours. In monkeys, the half-life in plasma was ~4.41 hours. Other data for the melamine indicate an elimination phase half-life of 2.7 hours from plasma and 3 hours for urine.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	**Melamine:** Distributed to stomach, small intestine, cecum, and large intestine, and found in blood, and urine of rats.	ECHA, 2011b	Study details reported in a secondary source.
		Melamine: The elimination phase half-life calculated from plasma data was 2.7 hours, and the urinary half-life was 3.0 hours. The renal clearance was determined to be 2.5 mL/minute. (Measured)	Mast et al., 1983	For melamine; adequate, nonguideline study.
		Melamine polyphosphate: Low for all routes (Estimated)	Professional judgment	Estimates based on physical/chemical properties.
		Rhesus monkeys were orally administered melamine at a single dose of 1.4 mg/kg bw. Melamine was rapidly absorbed, distributed to body fluids, rapidly cleared from plasma and excreted mainly via urine. The half-life in plasma was ~4.41 hours. There was no correlation (concentration-time curve in plasma and urine) between melamine and	Liu et al., 2010	Adequate, primary source

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		cyanuric acid, suggesting that melamine may not be metabolized to cyanuric acid *in vivo*.		
		Pregnant Sprague-Dawley rats were administered a single oral dose of melamine (~6-7 mg in <2 ml water) on gestation day 17. Melamine was also administered to neonates at postnatal day 14 (~0.3-0.6 mg in <0.2 ml in water). Melamine was detected in the maternal serum, breast milk, whole foetus, amniotic fluid, neonatal serum and neonatal kidney. This is evidence that Melamine passed through the placenta, reached the fetus and accumulated in the lactating mammary gland. Excretion occurred through the placenta of the fetus and the kidneys of neonates and was later excreted into amniotic fluid.	Chu et al., 2010	Adequate primary source
	Other	Pigs (5 weanling) were administered Melamine intravenously at a dose of 6.13 mg/kg. Melamine is readily cleared by the kidney; distribution may be limited to the extracellular fluid compartment. No concern for binding in tissues. Half-life: 4.04 hours; clearance: 0.11 L/h/kg; volume distribution: 0.61 L/kg.	Baynes et al., 2008	Adequate primary source
		Placentas from mothers following caesarean section or normal delivery were perfused with 0 mM or 1 mM melamine, or 10 mM melamine with 10 nM cyanuric acid (CYA). Melamine (34-45%) was transferred quickly to fetal circulation (0.12-1.34% within 5 minutes, 34% within 4 hours); addition of CYA had no	Partanen et al., 2012	Adequate, primary study

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		effect. Functionality of the placental tissue was not affected. Viability of BeWo cells was decreased. It is concluded that melamine may be fetotoxic.		
Acute Mammalian Toxicity		**LOW: Melamine polyphosphate is expected to be of low hazard for acute toxicity based on experimental evidence for melamine polyphosphate, phosphoric acids and melamine with LD50s > 1,000 mg/kg following oral and dermal exposure. One inhalation study reported an LC_{50} of 3.25 mg/L; however, the reported study details were too limited to consider for the hazard designation.**		
Acute Lethality	**Oral**	**Melamine polyphosphate:** Rat (Gavage) LD_{50} >2,000 mg/kg	Ciba, 2005 (as cited in Australia, 2006)	Sufficient study details reported.
		Melamine polyphosphate: Rat LD_{50} >2,000 mg/kg	NOTOX BV, 1998 (as cited in Australia, 2006)	Limited study details reported.
		Melamine polyphosphate: Rat (Gavage) LD_{50} >2,000 mg/kg	Submitted confidential study	Study details reported in a confidential study.
		Melamine polyphosphate: Rat LD_{50} >2,000 mg/kg	Submitted confidential study	Limited study details reported in a confidential study.
		Polyphosphoric acid: LD_{50} = 4,000 mg/kg (species unknown)	ARZNAD, 1957	Limited study details reported. The test substance was identified as polyphosphates, and was described as containing 1/3 Kurrol's potassium salt and 2/3 pyrophosphate.
		Melamine: Rat LD_{50} = 3,161 mg/kg (male), 3,828 mg/kg (females)	NTP, 1983b; Melnick et al., 1984	Sufficient study details reported.
		Melamine: Mouse LD_{50} = 3,296 mg/kg (male), 7,014 mg/kg (female)	NTP, 1983b; Melnick et al., 1984	Sufficient study details reported.
		Melamine: Mouse LD_{50} = 4,550 mg/kg	American Cyanamid Company, 1955; May, 1979; Trochimowicz et al., 2001	Limited study details reported.
		Melamine: Rat LD_{50} = 3,160 mg/kg (male) and 3,850 mg/kg (female)	Trochimowicz et al., 2001	Limited study details reported.
		Melamine: Rat LD_{50} >6,400 mg/kg	BASF, 1969 (as cited in OECD SIDS, 1999; IUCLID, 2000a)	Limited study details reported.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine: $LD_{50} \approx 4{,}800$ mg/kg	Hoechst, 1963 (as cited in IUCLID, 2000a)	Limited study details reported.
	Dermal	**Melamine:** Rabbit LD_{50} >1,000 mg/L	Unknown, 1990	Limited study details reported.
	Inhalation	**Melamine:** Rat LC_{50} = 3.25 mg/L	Ubaidullajev, 1993 (as cited in IUCLID, 2000a)	Limited study details reported in a secondary source.
Carcinogenicity		**MODERATE: Estimated based on the dissolution product melamine. There is experimental evidence that oral melamine exposure to high doses of melamine causes carcinogenicity in animals. However, there is no evidence for carcinogenicity to humans. In addition, Oncologic estimated a marginal concern that is consistent with a Moderate hazard designation using DfE criteria. Tumor formation in animals appeared to be due to mechanical irritation by bladder calculi/stones. IARC classifies melamine as Group 3: *not classifiable as to its carcinogenicity to humans*.**		
	OncoLogic Results	**Melamine:** Marginal (Estimated)	OncoLogic, 2008	
	Carcinogenicity (Rat and Mouse)	**Melamine:** Group 3: melamine is not classifiable as to its carcinogenicity to humans; there is inadequate evidence in humans for the carcinogenicity of melamine, and there is sufficient evidence in experimental animals for the carcinogenicity of melamine under conditions in which it produces bladder calculi.	IARC, 1999	IARC classification statement.
		Melamine: Significant formation of transitional cell carcinomas in the urinary bladder of male rats and significant chronic inflammation in the kidney of dosed female rats were observed. Carcinoma formation was significantly correlated with the incidence of bladder stones. A transitional-cell papilloma was observed in the urinary bladder of a single high dose male rat, and compound related lesions were observed in the urinary tract of dosed animals.	NTP, 1983b; Huff, 1984; Melnick et al., 1984	Sufficient study details reported.
		Melamine: Increased incidence of acute and chronic inflammation and epithelial	NTP, 1983b; Huff, 1984; Melnick et al., 1984	Sufficient study details reported.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		hyperplasia of the urinary bladder was observed in male mice. Bladder stones and compound-related lesions were observed in the urinary tract of test animals. Melamine was not considered carcinogenic.		
		Melamine: Melamine-induced proliferative lesions of the rat urinary tract were directly due to the irritant stimulation of calculi, and not to molecular interactions between melamine or its metabolites with the bladder epithelium.	Okumura et al., 1992	Sufficient study details reported.
		Melamine: Water intake, used as an index of urinary output, was increased by NaCl treatment. Calculus formation resulting from melamine administration was suppressed dose-dependently by the simultaneous NaCl treatment. The main constituents of calculi were melamine and uric acid (total contents 61.1- 81.2%). The results indicate that melamine-induced proliferative lesions of the urinary tract of rats were directly due to the irritation stimulation of calculi, and not molecular interactions between melamine itself or its metabolites with the bladder epithelium.	Ogasawara et al., 1995	Sufficient study details reported.
		Melamine: As an initiator, melamine caused no significant increase in papillomas per mouse when compared to controls.	Perrella and Boutwell, 1983	Nonguideline study.
		Melamine: Diffuse papillary hyperplasia of the bladder epithelium and bladder calculi were observed in all melamine treated rats. Elevated	Matsui-Yuasi et al., 1992	Nonguideline study.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		spermidine/spermine N1-acetyltransferase activity following melamine treatment was considered to be an indicator of cell proliferation.		
		Melamine: Decreased antitumor activity was correlated with increasing demethylation; melamine was considered inactive as an antitumor drug.	Rutty and Connors, 1977	Limited study details reported.
		Melamine: In an *in vitro* cytotoxicity study in cultured ADJ/PC6 plasmacytoma ascites tumor cells, the ID50 was 470 µg/mL after 72 hours of treatment.	Rutty and Abel, 1980	Limited study details reported.
	Combined Chronic Toxicity/Carcinogenicity	**Melamine:** No effects were observed in rats fed 1,000 ppm of melamine. 4 of the 10 rats fed 10,000 ppm melamine had bladder stones associated with the development of benign papillomas.	Anonymous, 1958 (as cited in Wolkowski Tyl and Reel, 1992)	Limited study details reported.
		Melamine: Increased incidence of urinary bladder stones (6/20 rats) was noted in the 10,000 ppm dose group, and was associated with an increase in benign papillomata. The NOAEL was determined to be 1,000 ppm (67 mg/kg-day).	American Cyanamid Company, 1955	Limited study details reported.
	Other			No data located.
Genotoxicity		**MODERATE: Melamine polyphosphate is estimated to be a moderate hazard for genotoxicity based on a weight of evidence from multiple studies for melamine. For melamine, positive results were observed for *in vivo* chromosome aberration and sister chromatid exchange assays conducted by National Toxicology Program (NTP) in 1988 and 1989. Available in vitro genotoxicity testing was conducted with metabolic activation systems from the liver. NTP suggests this may not account for potential activation from bladder epithelial cells, which is the target organ. Proposed genotoxicity testing using a metabolic activation system from bladder epithelial cells (NTP, 1983) was never conducted (Personal Communication, 2007; 2008).**		
	Gene Mutation *in vitro*	**Melamine:** Bacterial forward mutation assay: Negative with and without liver activation	Haworth et al., 1983; NTP, 1983a	Sufficient study details reported.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine: Bacterial forward mutation assay: Negative	Seiler, 1973	Limited study details reported.
		Melamine: Bacterial reverse mutation assay: Negative with and without liver activation	Lusby et al., 1979	Limited study details reported.
		Melamine: Bacterial reverse mutation assay: Negative with and without unspecified metabolic activation	Mast et al., 1982b	Limited study details reported.
		Melamine: *In vitro* mouse lymphoma test: Negative with and without liver activation	NTP, 1983a; McGregor et al., 1988	Sufficient study details reported.
		Melamine: Chinese hamster ovary (CHO) cells/hypoxanthine-guanine phosphoribosyl-transferase forward mutation assay: Negative with and without liver activation.	Mast et al., 1982b	Limited study details reported.
	Gene Mutation *in vivo*			No data located.
	Chromosomal Aberrations *in vitro*	**Melamine:** *In vitro* chromosomal aberrations test: Negative in CHO with and without liver activation.	NTP, 1983a; Galloway et al., 1987	Sufficient study details reported.
		Melamine: *In vitro* sister chromatid exchange assay: Negative in CHO with and without liver activation.	NTP, 1983a; Galloway et al., 1987	Sufficient study details reported
		Melamine: *In vitro* sister chromatid exchange assay: Negative in CHO with and without liver activation.	Mast et al., 1982b	Limited study details reported.
	Chromosomal Aberrations *in vivo*	**Melamine:** *In vivo* mouse micronucleus test: The initial test gave a positive trend (P = 0.003) for chromosomal damage; however, both peripheral blood smears and the repeat bone marrow test were negative. The overall conclusion was that melamine does not induce chromosomal damage.	NTP, 1983b; Shelby et al., 1993	Sufficient study details reported.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine: *In vivo* mouse micronucleus test: Negative	Mast et al., 1982c	Limited study details reported.
		Melamine: *In vivo* chromosome aberrations test in mice: Positive	NTP, 1983a	Sufficient study details reported.
		Melamine: *In vivo* sister chromatid exchange assay in mice: Positive	NTP, 1983a	Sufficient study details reported.
	DNA Damage and Repair	**Melamine:** *In vivo* and *in vitro* unscheduled DNA synthesis (UDS) test: None of the tested chemicals, including melamine, were genotoxic hepatocarcinogens in the *in vivo* assay, and melamine was negative for UDS in the *in vitro* assay.	Mirsalis et al., 1983	Limited study details reported.
		Melamine: SOS/*umu* test: Negative for its ability to result in DNA damage and induce the expression of the *umu* operon.	Reifferscheid and Heil, 1996	Nonguideline study.
		Melamine: DNA synthesis-inhibition test in Hela S3 cells: Inhibits DNA synthesis by 50% at greater than 300 µM.	Heil and Reifferscheid, 1992	Limited study details reported.
	Other	**Melamine:** Sex-linked recessive lethal/reciprocal translocation: Results were considered equivocal based on 0.18% and 0.36% total lethal following oral and injection exposure, respectively, compared to control total lethal of 0.07% for oral and 0.09% for injection.	NTP, 1983a	Sufficient study details reported.
		Melamine: *Drosophila* Muller-5 test: Negative for mutagenicity	Rohrborn, 1959	Limited study details reported.
		Melamine: *Drosophila melanogaster* Sex-linked recessive lethal: No mutagenic effects were observed	Luers and Rohrborn, 1963	Limited study details reported.
		Melamine: *In vitro* flow cytometric DNA repair assay: Negative for genotoxic effects	Seldon et al., 1994	Nonguideline study.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine: Microscreen assay: Positive for genetic toxicity in *E. coli* WP2 cells	Rossman et al., 1991	Nonguideline study.
		Melamine: Growth and genotoxic effects to bacteria (*Salmonella typhimurium*) and yeast (*Saccharomyces cerevisiae*): Non-mutagenic in *S. typhimurium* with or without S-9 mix. The growth of eight out of nine strains tested was delayed by 10 mM melamine during 24 hour cultivation. *S. cerevisiae* strain was tested, and did not recover its growth following 48 hour cultivation.	Ishiwata et al., 1991	Limited study details reported.
		Proposed genotoxicity testing using a metabolic activation system from bladder epithelial cells (NTP, 1983) was never conducted.	Lehner and Vokes, 2008; Shigeru, 2007	Supporting information.
Reproductive Effects		**HIGH: Estimated based on experimental data for melamine. A NOAEL of 10 mg/kg-day (LOAEL of 50 mg/kg-day) for increased apoptotic index of spermatogenic cells was reported in male mice orally administered melamine for 5 days. In addition, altered epididymal sperm morphology and damage of testicular DNA were reported at a dietary dose of 412 mg/kg-day (lowest dose tested). No experimental data were located for melamine polyphosphate.**		
	Reproduction/Developmental Toxicity Screen	Rat, oral; potential for reproductive toxicity (Estimated by analogy)	Professional judgment	Estimated based on analogy to confidential analog; LOAEL not identified; study details not provided.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects	**Melamine:** In a 5-day study, male mice (8/group) were orally administered melamine only at doses of 0, 2, 10 and 50 mg/kg-day or melamine in combination with cyanuric acid at doses of 0, 1, 5 and 25 mg/kg-day. Sperm abnormalities were evaluated in a	Yin et al., 2013	Adequate, primary study

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		separate select group of mice (8/group), which were fed melamine only at doses of 0, 412, 824, and 1,648 mg/kg-day, or melamine in combination with cyanuric acid at doses of 0, 206, 412, or 824 mg/kg-day. No deaths in mice fed 2, 10 and 50 mg/kg-day melamine or 1 and 5 mg/kg-day melamine and cyanuric acid; 3 deaths in co-administration group fed 25 mg/kg/day. Grossly enlarged, pale yellow kidneys in all mice that survived. Increase in apoptotic index of spermatogenic cells in mice fed 50 mg/kg-day melamine-only; more severe apoptosis in co-administered mice at 5 and 25 mg/kg-day. NOAEL: 10 mg/kg-day LOAEL: 50 mg/kg-day (increased apoptotic index of spermatogenic cells) Sperm abnormality group: no deaths in mice administered melamine-only; all co-administered mice died before day 6 and exhibited anorexia, decreased activity and hunched posture. Altered epididymal sperm morphology (particularly the head abnormality) and damage of testicular DNA in all melamine-only treatment groups. NOAEL: Not established LOAEL: 412 mg/kg-day (altered epididymal sperm morphology; damage of testicular DNA)		

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine: There were no treatment-related macroscopic or microscopic effects on mammary glands, ovaries, prostate, seminal vesicles, testes and uterus in rats and mice up to dietary concentrations of 18,000 ppm in a 13-week study.	Melnick et al., 1984 (as cited in OECD SIDS, 1999)	Limited study details reported in a secondary source.
		Melamine: Reproductive dysfunction was observed at 0.5 mg/m^3 and included effects on spermatogenesis (genetic material, sperm morphology, motility, and count), effects on the embryo/fetus (fetal death), pre-implantation mortality (reduction in the number of implants per female), and total number of implants per corpora lutea.	Ubaidullajev, 1993	Study details, if present, were not translated into English.
	Other			No data located.
Developmental Effects		**MODERATE: Estimated based on a structural alert for aromatic amines. Limited experimental data for melamine indicated no developmental effects in rats exposed during gestation to doses up to 1,060 mg/kg-day. This experimental data is insufficient to determine a hazard designation for this endpoint. There was no data located for the developmental neurotoxicity endpoint for this substance or its analogs.**		
	Reproduction/ Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Prenatal Development	**Melamine:** Signs of maternal toxicity at 136 mg/kg b.w. included decreased body weight and feed consumption, hematuria (23/25 rats), indrawn flanks (7/25 rats), and piloerection (1/25 rats). No adverse effects on gestational parameters and no signs of developmental toxicity were noted. NOAEL ≥ 1,060 mg/kg-day (highest concentration tested); LOAEL: Not established	Hellwig et al., 1996 (as cited in OECD SIDS, 1999)	Sufficient study details reported.
	Postnatal Development	**Melamine:** Only minor effects on the fetuses or litters, including a non-significant increase in resorptions in the group treated on the 4th and 5th days of gestation, were observed.	Thiersch, 1957	Sufficient study details were not available.
	Prenatal and Postnatal Development			No data located.
	Developmental Neurotoxicity	There was no data located for the developmental neurotoxicity endpoint.		No data located.
	Other	Potential for developmental toxicity based on a structural alert for aromatic amines. (Estimated)	Professional judgment	Estimated based on a structural alert for aromatic amines and professional judgment.
Neurotoxicity		**MODERATE: Estimated based on experimental data for melamine. Several neurological effects were reported for different endpoints in 28-day studies evaluating mode of action in the brain. Impaired memory abilities and cognition deficits were mediated by alterations of the pathways affecting the hippocampus at a dose of 300 mg/kg-day (only dose tested). Design for the Environment (DfE) Alternatives Assessment criteria values are tripled for chemicals evaluated in 28-day studies; the LOAEL of 300 mg/kg-day falls on the threshold between Moderate and LOW hazard criteria. A NOAEL was not established and it is assumed that effects would occur at a dose within the Moderate-High hazard criteria range; due to this uncertainty, a Moderate hazard designation was assigned.**		
	Neurotoxicity Screening Battery			
		Melamine: In a 28-day study, male	An et al. 2011	Sufficient study details reported in

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	(Adult)	Wistar rats (control group n = 8, treatment group n = 10) were orally administered melamine only at doses of 0, or 300 mg/kg-day. A significant deficit of learning and memory in a Morris water maze test was reported in the treated group. In addition significantly lower field excitatory postsynaptic potential (fEPSPs) slopes were determined in a long term potentiation (LTP) test from Schaffer collaterals to CA1 region in the hippocampus in the treated group compared to the control group. Authors concluded that melamine had a toxic effect on hippocampus resulting in deficits of learning and memory in rats associated with impairments of synaptic plasticity. NOAEL: Not established LOAEL: 300 mg/kg-day		primary source; only one dose tested.
		Melamine: In a 28-day study, male Wistar rats (10/group) were orally administered melamine only at doses of 0, or 300 mg/kg-day. A significant deficit of learning and memory in a Morris water maze test was reported in the treated group. In addition significantly lower field excitatory postsynaptic potential (fEPSPs) slopes were determined in a long term potentiation (LTP) test in the treated group compared to the control group. Decreased frequencies of spontaneous EPSCs and minitura EPSCs were observed in a long-time potentiation test,	Yang et al., 2011	Sufficient study details reported in primary source; only one dose tested.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		though there was no change in the amplitude or kinetics of spontaneous or minitura EPSCs suggesting melamine's influence on glutamatergic transmission likely occurred presynaptic. NOAEL: Not established LOAEL: 300 mg/kg-day		
		Melamine: In a 28-day study, male Wistar rats (8/group) were orally administered melamine only at doses of 0, or 300 mg/kg-day. A significant deficit of learning and memory in a Morris water maze test was reported in the treated group. Increased levels of superoxide anion radical, hydroxyl free radical and malonaldehyde were reported. There was also decreased superoxide dismutase and glutathione peroxidase activity in the treated group compared to the control. Hippocampal energy metabolism analysis showed significantly decreased adenosine-triphosphate (ATP) content suggestive of reduced energy synthesis in the hippocampal neurocytes possibly associated with oxidative damage. NOAEL = Not established LOAEL = 300 mg/kg-day	An et al., 2012	Sufficient study details reported in primary source; only one dose tested.
		Melamine: In a 28-day study, male Wistar rats (8/group) were orally administered melamine only at doses of 0, or 300 mg/kg-day.	An et al., 2013	Sufficient study details reported in primary source; only one dose tested.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		A significant deficit of learning and memory in a Morris water maze test was reported in the treated group. Increased field excitatory postsynaptic potential slopes was reported in the treated group. There was decreased Ach levels and increased AChE activity suggesting damage to the function of cholinergic system. NOAEL = Not established LOAEL = 300 mg/kg-day		
		Melamine: In a 28-day study, male Wistar rats (8/group) were orally administered melamine only at doses of 0, or 300 mg/kg-day. Impaired memory abilities were reported in treated rats in the Morris water maze tests compared to the control group. Cognition deficits consistent with reduced long-term potentiation in the CA1 area of the hippocampus were induced. Phase locking values showed reduced synchronization between CA3 and CA1 in theta and LG rhythms. Decreased unidirectional indices for theta and LG rhythms were reported in treated rats suggesting that alterations of neural information flow on CA3-CA1 pathway in the hippocampus mediated cognitive impairment in treated rats. NOAEL = Not established LOAEL = 300 mg/kg-day	Xu et al., 2013	Sufficient study details reported in primary source; only one dose tested.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Other	Potential for neurotoxicity is expected to be low. (Estimated)	Professional judgment	Estimated based on analogy and professional judgment.
Repeated Dose Effects		**MODERATE: Melamine polyphosphate is expected to be a moderate hazard for repeated dose effects based on the data for melamine. Stones and diffuse epithelial hyperplasia in the urinary bladders were observed in male rats at doses as low as 700 ppm (72 mg/kg-day; lowest dose tested). Exposure to melamine has been associated with toxicity in humans.**		
		Polyphosphoric Acid: Rat Repeated-Dose Toxicity Study: An oral repeated-dose toxicity test in rats resulted in a TD_{Lo} of 450 mg/kg. The test substance was identified as polyphosphates, and was described as containing 1/3 Kurrol's potassium salt and 2/3 pyrophosphate. Toxic effects included changes in liver weight, changes in tubules (including acute renal failure, acute tubular necrosis), and weight loss or decreased weight gain.	ARZNAD, 1957	Sufficient study details were not available.
		Melamine: Rat 28-day dietary toxicity study: Clinical signs included a dose-related increase in pilo-erection, lethargy, bloody urine spots in the cage and on the pelage of animals, and chromodacryorrhea. The incidence of urinary bladder calculi and urinary bladder hyperplasia in treated animals was dose-dependent, with a significant relationship between the calculi and hyperplasia. Calculi composition indicated the presence of an organic matrix containing melamine, phosphorus, sulfur, potassium, and chloride. Crystals of dimelamine monophosphate were identified in the urine.	RTI, 1983	Sufficient study details reported.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		NOAEL: estimated to be 2,000 ppm (240 mg/kg/day), excluding the observed increase in water consumption and the incidence of crystalluria. LOAEL: 4,000 ppm (475 mg/kg/day) based on the formation of calculi.		
		Melamine: Rabbit and dog 28-day dietary toxicity study: No significant rise in the body temperature of rabbits was noted. Gross histological examination of the heart, lung, liver, spleen, thyroid, pancreas, intestines, kidneys and bladder did not show pathological changes. A zone of fat was found in the inner part of the renal cortex in two dogs, but also in the kidneys of 3 control dogs.	Lipschitz and Stokey, 1945	Sufficient study details were not available.
		Melamine: Rat 28-day dietary toxicity study: Incidence and size of bladder stones were directly related to the amount of substance administered. The larger stones were found to be unchanged melamine in a matrix of protein, uric acid and phosphate. Lowest effective dose: 1,500 ppm (~125 mg/kg-day) in males	American Cyanamid Company, 1984	Sufficient study details were not available.
		Melamine: Rat 90-day dietary toxicity study: one male rat receiving 18,000 ppm and two males receiving 6,000 ppm died. Mean body weight gain and feed consumption were reduced. Stones and diffuse epithelial hyperplasia in the urinary bladders were observed in male rats of all treatment groups. Focal epithelial hyperplasia was observed in	NTP, 1983b; Melnick et al., 1984; ECHA, 2011a	Sufficient study details reported.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		only 1 male. A second and third 13-week repeated dose toxicity study was conducted in rats at a dose range of 750 to 18,000 ppm; bladder stones were observed at all dose levels. LOAEL: 700 ppm (72 mg/kg/day)		
		Melamine: Mouse 90-day Dietary Toxicity Study: A single female mouse died after receiving 9,000 ppm. Mean body weight gain relative to controls was depressed. The incidence of mice with bladder stones was dose-related and was greater in males than in females. Sixty percent of mice having bladder ulcers also had urinary bladder stones. Bladder ulcers were multifocal or associated with inflammation (cystitis). Epithelial hyperplasia and bladder stones were observed together in 2 mice. Also, epithelial cell atypia was seen. NOAEL: 6,000 ppm (600 mg/kg-day) LOAEL: 9,000 ppm (900 mg/kg-day)	NTP, 1983b; Melnick et al., 1984	Sufficient study details reported.
		Melamine: Increased incidence of acute and chronic inflammation and epithelial hyperplasia of the urinary bladder was observed in mice following oral (feed) exposure for up to 103 weeks. There was also increased incidence of bladder stones in male mice. LOAEL: 2,250 ppm (~380 mg/kg bw-day; lowest dose tested)	NTP, 1983b; ECHA, 2011b	Repeated dose effects described in a carcinogenicity bioassay study.
		Melamine: Dog 1-year dietary toxicity study: crystalluria started 60 to 90 days into treatment, and persisted during the study period. No other effects attributable to melamine were observed.	American Cyanamid Company, 1955	Sufficient study details were not available.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine: Rat 30-month dietary toxicity study: neither accumulation of calculi nor any treatment-related urinary bladder lesions were found.	Mast et al., 1982a (as cited in Wolkowski Tyl and Reel, 1992)	Sufficient study details were not available.
		Melamine: Rat 24- to 30-month dietary toxicity study: a dose related trend for dilated glands in glandular gastric mucosa and inflammation in non glandular gastric mucosa was observed. Urinary bladder calculi formation was not observed.	American Cyanamid Company, 1983 (as cited in OECD SIDS, 1999)	Sufficient study details were not available.
		Melamine: Children affected by melamine contaminated milk for approximately 3 to 6 months before the onset of kidney stones. The highest content of melamine ranged from 0.090 to 619 mg/kg milk powder. A total of 52,857 children had received treatment for melamine-tainted milk. 99.2% of the children were younger than 3 yr. Some children were asymptomatic; however irritability, dysuria, difficulty in urination, renal colic, hematuria, or stone passage, hypertension, edema, or oliguria were also reported. Mortality occurred in four cases.	Hau et al., 2009	Summary of toxic effects from food contamination.
		Melamine: Renal damage is believed to result from kidney stones formed from melamine and uric acid or from melamine and cyanuric acid. Cyanuric acid can be produced in the gut by microbial transformation of melamine. The bacteria *Klebsiella terrigena* was shown to convert melamine to cyanuric acid and rats colonized by *K. terrigena* showed exacerbated melamine-induced nephrotoxicity.	Zheng et al., 2013	Supporting information about the renal toxicity of melamine.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Skin Sensitization		**LOW: Melamine polyphosphate is not expected to be a skin sensitizer based on the data for melamine.**		
	Skin Sensitization	**Melamine:** No evidence of primary dermal irritation or sensitization in a human patch test	American Cyanamid Company, 1955; Trochimowicz et al., 2001	Limited study details reported.
		Melamine: Non-sensitizing to guinea pigs	Fasset and Roudabush, 1963 (as cited in OECD SIDS, 1999; Trochimowicz et al., 2001)	Limited study details reported.
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.
Eye Irritation		**LOW: Melamine polyphosphate is slightly irritating to eyes.**		
	Eye Irritation	**Melamine polyphosphate:** Slightly irritating	NOTOX BV, 1998 (as cited in Australia, 2006)	Limited study details reported.
		Melamine polyphosphate: Slightly irritating	Submitted confidential study	Limited study details reported.
		Melamine: Non-irritating to rabbit eyes	BASF, 1969 (as cited in OECD SIDS, 1999; IUCLID, 2000a)	Limited study details reported.
		Melamine: Non-irritating to rabbit eyes following 0.5 mL of 10% melamine	American Cyanamid Company, 1955; Trochimowicz et al., 2001	Limited study details reported.
		Melamine: Mild irritant to rabbit eyes following exposure to 30 mg of dry powder	American Cyanamid Company, 1955; Trochimowicz et al., 2001	Limited study details reported.
		Melamine: Slightly irritating to rabbit eyes	Marhold, 1972 (as cited in IUCLID, 2000a; RTECS, 2009)	Limited study details reported.
Dermal Irritation		**VERY LOW: Melamine polyphosphate is not a skin irritant.**		
	Dermal Irritation	**Melamine polyphosphate:** Not irritating	NOTOX BV, 1998 (as cited in Australia, 2006)	Limited study details reported.
		Melamine polyphosphate: Not irritating	Submitted confidential study	Limited study details reported.
		Melamine: Not irritating to rabbit skin	Rijcken, 1995 (as cited in OECD SIDS, 1999)	Organisation for Economic Cooperation and Development (OECD) 404 guideline study.
		Melamine: Not irritating to rabbit skin	BASF, 1969 (as cited in OECD SIDS, 1999; IUCLID, 2000a)	Limited study details reported.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine: Not irritating to rabbit skin	American Cyanamid Company, 1955; Trochimowicz et al., 2001	Limited study details reported.
		Melamine: Not irritating to rabbit skin	Fasset and Roudabush, 1963 (as cited in OECD SIDS, 1999; Trochimowicz et al., 2001)	Limited study details reported.
Endocrine Activity		**There were insufficient data located to describe the effect of melamine polyphosphate on the endocrine system. In one study, melamine did not exhibit estrogenic activity *in vitro* in a yeast two-hybrid assay.**		
		Melamine: Showed no estrogenic activity (no change in B-galactosidase activity) in an *in vitro* yeast two-hybrid assay in *Saccharomyces cerevisiae* Y 190	ECHA, 2011b	Reported in a secondary source. Nonguideline study.
Immunotoxicity		**Potential for immunotoxic effects based on analogy to structurally similar polymers and professional judgment.**		
	Immune System Effects	Potential for immunotoxicity	Professional judgment	Estimated based on confidential analogs and professional judgment.
		Melamine: Did not inhibit the mitogenesis of B- and T- lymphocytes in an *in vitro* mouse lymphocyte mitogenesis test.	ECHA, 2011a	Data from a secondary source.
ECOTOXICITY				
ECOSAR Class		Melamines		
Acute Aquatic Toxicity		**LOW: Melamine polyphosphate is expected to be of low hazard for acute toxicity to aquatic organisms based on experimental data for melamine polyphosphate and experimental data for melamine. For melamine, the weight of evidence suggests that the acute values are >100 mg/L. For melamine polyphosphate, no effects were observed in algae at the highest concentration tested (3.0 mg/L). Melamine polyphosphate is not predicted to cause eutrophication based on laboratory testing.**		
Fish LC_{50}		**Melamine polyphosphate:** Freshwater fish 96-hour LC_{50} = 100 mg/L (Experimental)	Ciba, 2005 (as cited in Australia, 2006)	Reported in a secondary source, study details and test conditions were not reported.
		Melamine: *Leuciscus idus melanotus* 48-hour LC_{50} >500 mg/L (Experimental)	OECD SIDS, 1999	Study details reported in secondary source.
		Melamine: *Oryzias latipes* 48-hour LC_{50}	OECD SIDS, 1999	Study details reported in secondary

Melamine Polyphosphate CASRN 15541-60-3			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	= 1,000 mg/L (Experimental)		source.
	Melamine: *Poecilia reticulata* 96-hour LC_{50} >3,000 mg/L (Experimental)	OECD SIDS, 1999	Study details reported in secondary source.
	Melamine: *Poecilia reticulata* 4,400 mg/L dose lethal to <10% (Experimental)	OECD SIDS, 1999	Study details reported in secondary source.
	Melamine: Fish 96-hour LC_{50} = 2,680 mg/L (Estimated) ECOSAR: Anilines (amino-meta)	ECOSAR v1.11	ECOSAR provided results for the Anilines (amino-meta) class; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Melamine: Fish 96-hour LC_{50} = 391 mg/L (Estimated) ECOSAR: Melamines	ECOSAR v1.11	
	Melamine: Fish 96-hour LC_{50} = 14,272 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid LC_{50}	**Melamine polyphosphate:** *Daphnia magna* 48-hour EC_{50} >100 mg/L (Experimental)	Ciba, 2005 (as cited in Australia, 2006)	Reported in a secondary source, study details and test conditions were not reported.
	Melamine: *Daphnia magna* 48-hour LC_{50} >2,000 mg/L (Experimental)	OECD SIDS, 1999	Study details reported in secondary source.
	Melamine: Daphnid 48-hour LC_{50} = 6.23 mg/L	ECOSAR v1.11	ECOSAR provided results for the Anilines (amino-meta) class;

Melamine Polyphosphate CASRN 15541-60-3			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	(Estimated) ECOSAR: Anilines (amino-meta)		however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Melamine: Daphnid 48-hour LC_{50} = 144.34 mg/L ECOSAR: Melamines (Estimated)	ECOSAR v1.11	
	Melamine: Daphnid 48-hour LC_{50} = 4,805 mg/L ECOSAR: Neutral organics (Estimated)	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Green Algae EC_{50}	**Melamine polyphosphate:** *Selenastrum capricornutum* 96-hour EC_{50} >3.0 mg/L; 96-hour NOEC = 3.0 mg/L (Experimental)	Submitted confidential study	No effects observed at highest concentration tested.
	Melamine polyphosphate: *Selenastrum capricornutum* 96-hour EC_{50} >3.0 mg/L; 96-hour NOEC = 3.0 mg/L (Experimental)	Australia, 2006	Reported in a secondary source, study details and test conditions were not provided; no effects observed at highest concentration tested.
	Melamine polyphosphate: In a 96-hour control growth test (*Selenastrum capricornutum*), melamine polyphosphate causes increased algal growth, but growth is 95% less than growth in standard medium with adequate phosphorous. This indicates that melamine polyphosphate is not a good source of phosphorous for algal growth and does not cause eutrophication.	Submitted confidential study	Sufficient study details reported in a confidential study.

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	(Experimental)		
	Melamine: *Scenedesmus pannonicus* 4-day EC_{50} = 940 mg/L; 4-day NOEC = 320 mg/L (Experimental)	OECD SIDS, 1999	Reported in a secondary source, study details and test conditions were not provided.
	Melamine: Green algae 96-hour EC_{50} = 2.79 mg/L (Estimated) ECOSAR: Anilines (amino-meta)	ECOSAR v1.11	ECOSAR provided results for the Anilines (amino-meta) class; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Melamine: Green algae 96-hour EC_{50} = 325 mg/L (Estimated) ECOSAR: Melamines	ECOSAR v1.11	
	Melamine: Green algae 96-hour EC_{50} = 4,396 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Chronic Aquatic Toxicity	**LOW: Melamine polyphosphate is expected to be of low hazard for chronic toxicity to aquatic organisms based on experimental data for melamine. For melamine, the weight of evidence suggests that the chronic values are >10 mg/L.**		
Fish ChV	**Melamine:** *Jordanella floridae* 35-day NOEC ≥ 1,000 mg/L (Experimental)	OECD SIDS, 1999	Reported in a secondary source, study details and test conditions were not provided.
	Melamine: *Salmo gairdneri* NOEC (macroscopic) = 500 mg/L; NOEC (microscopic) <125 mg/L (Experimental)	OECD SIDS, 1999	Reported in a secondary source, study details and test conditions were not provided.
	Melamine: Fish ChV = 263 mg/L	ECOSAR v1.11	ECOSAR provided results for the

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PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	(Estimated) ECOSAR: Anilines (amino-meta)		Anilines (amino-meta) class; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Melamine: Fish ChV = 1,102 mg/L (Estimated) ECOSAR: Melamines	ECOSAR v1.11	
	Melamine: Fish ChV = 1,076 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
Daphnid ChV	**Melamine:** *Daphnia magna* 21-day LC_{50} = 32-56 mg/L, 21-day LC_{100} = 56 mg/L, 21-day NOEC = 18 mg/L (Experimental)	OECD SIDS, 1999	Reported in a secondary source, study details and test conditions were not provided.
	Melamine: Daphnid ChV = 0.078 mg/L (Estimated) ECOSAR: Anilines (amino-meta)	ECOSAR v1.11	ECOSAR provided results for the Anilines (amino-meta) class; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
	Melamine: Daphnid ChV = 14.85 mg/L (Estimated) ECOSAR: Melamines	ECOSAR v1.11	
	Melamine: Daphnid ChV = 343.93 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				specific mode of action relative to narcosis.
Green Algae ChV		**Melamine:** Green algae ChV = 0.70 mg/L (Estimated) ECOSAR: Anilines (amino-meta)	ECOSAR v1.11	ECOSAR provided results for the Anilines (amino-meta) class; however, professional judgment indicates that this compound does not lie within the domain of the ECOSAR model.
		Melamine: Green algae ChV = 81.26 mg/L (Estimated) ECOSAR: Melamines	ECOSAR v1.11	
		Melamine: Green algae ChV = 313.17 mg/L (Estimated) ECOSAR: Neutral organics	ECOSAR v1.11	Narcosis classes (neutral organics) are provided for comparative purposes; DfE assessment methodology will use the lowest estimated toxicity value provided by ECOSAR classes that have a more specific mode of action relative to narcosis.
ENVIRONMENTAL FATE				
Transport		**Melamine polyphosphate has a high measured water solubility of 20 g/L and its Henry's Law constant and vapor pressure are below cutoff values. It is expected to partition predominately to water and soil. It may migrate from soil into groundwater. As a salt, volatilization from either wet or dry surfaces is not expected to be an important fate process.**		
	Henry's Law Constant (atm-m^3/mole)	$<10^{-8}$ (Estimated)	EPI v4.10; Professional judgment	Cutoff value for nonvolatile compounds.
	Sediment/Soil Adsorption/Desorption - K_{oc}	**Melamine polyphosphate:** 13 (Estimated)	EPI v4.10	
	Level III Fugacity Model	Air = 0% Water = 37% Soil = 63% Sediment = 0% (Estimated) for Melamine Polyphosphate	EPI v4.10	

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Persistence		**HIGH: Melamine polyphosphate is expected to show high persistence in the environment based on the data for melamine. Melamine polyphosphate is expected to be fully dissociated under environmental conditions. The weight of evidence suggests that melamine will biodegrade at rates consistent with a High hazard designation. Although pure culture studies showed evidence of biodegradation by enzymatic hydrolytic deamination in less than 10 days, an original MITI test detected less than 30% degradation after 14 days and two separate guideline OECD 302B studies observed no degradation after 28 days and 16% degradation after 20 days. This results in an expected environmental persistence half-life between 60 and 180 days. Degradation of melamine or its cation by hydrolysis or direct photolysis is not expected to be significant as the functional groups present on this molecule do not tend to undergo these reactions under environmental conditions. Polyphosphoric acid is expected to have low persistence in the environment. The weight of evidence suggests that polyphosphoric acid will hydrolyze under environmental conditions. The phosphates formed are expected to participate in natural cycles and be readily assimilated.**		
Water	**Aerobic Biodegradation**	**Melamine polyphosphate:** Weeks (Primary survey model) Months (Ultimate survey model) (Estimated)	EPI v4.10	
		Melamine: 16% removal after 20 days with activated sludge, 14% removal after 10 days with adapted sludge (Measured)	OECD SIDS, 1999	These values are for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
		Melamine: 0% removal after 28 days with activated sludge (Measured)	OECD SIDS, 1999	These values are for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
		Melamine: 0% removal after 14 days with activated sludge (Measured)	OECD SIDS, 1999	These values are for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
		Melamine: <30% removal after 14 days with activated sludge (Measured)	OECD SIDS, 1999	These values are for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
		Melamine: <1% removal after 5 days with an adapted inoculum (Measured)	IUCLID, 2000a	These values are for the dissociated component, melamine. Reported in a secondary source, study details and

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				test conditions were not provided.
		Melamine: 0% removal after 14 days with activated sludge (Measured)	IUCLID, 2000a	These values are for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
		Melamine: <30% removal after 14 days with activated sludge (Measured)	IUCLID, 2000a	These values are for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
		Melamine: <20% removal after 20 days, 14% removal after 10 days with adapted inoculum (Measured)	IUCLID, 2000a	These values are for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
		Study results: 100%/<10 days Test method: Pure culture study **Melamine:** Bacterium, *Nocardioides sp.* Strain ATD6 rapidly degraded melamine and accumulated cyanuric acid and ammonium ion, via the intermediates ammeline and ammelide. (Measured)	Takagi et al., 2012	Melamine degradation was found to occur in species specific biodegradation studies.
	Volatilization Half-life for Model River	>1 year for **Melamine polyphosphate** (Estimated)	EPI v4.10	Based on the magnitude of the estimated Henry's Law constant.
	Volatilization Half-life for Model Lake	>1 year for **Melamine polyphosphate** (Estimated)	EPI v4.10	Based on the magnitude of the estimated Henry's Law constant.
Soil	**Aerobic Biodegradation**	Study results: 0%/28 days Test method: 302B: Inherent - Zahn-Wellens/EMPA Test **Melamine:** Not readily biodegradable: 0% biodegradation detected after 2 weeks with 100 ppm in 30 ppm activated sludge (OECD TG 301C) (Measured); 0% degradation after 28 days with 100 mg DOC/L in activated sludge (Zahn-Wellens test, OECD 302B) (Measured)	MITI, 1998; OECD SIDS, 1999	Adequate values from guideline studies for the dissociated component, melamine.

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Study results: 100%/4 days Test method: Pure culture study **Melamine:** Bacterium, *A. citrulli* strain B-12227 rapidly degraded melamine and accumulated cyanuric acid, ammeline and ammelide, via the intermediates ammeline and ammelide. (Measured)	Shiomi and Ako, 2012	Melamine degradation was found to occur in species specific biodegradation studies.
		Melamine: A set of soil bacteria has been identified whose members rapidly metabolize melamine as their source of nitrogen to support growth; these bacteria contain an enzyme which hydrolytically deaminates melamine. (Measured)	Cook and Hutter, 1981; Cook and Hutter, 1984	Melamine degradation was found to occur in species specific biodegradation studies.
	Anaerobic Biodegradation	Study results: <8.9%/28 days Test method: Other **Melamine:** 0-8.9% nitrification was observed after 28 days incubation with bacteria in Webster silty clay loam under anaerobic conditions. (Measured)	IUCLID, 2000a	This value is for the dissociated component, melamine. Reported in a secondary source, study details and test conditions were not provided.
	Soil Biodegradation with Product Identification	**Melamine:** Nitrification of melamine occurs in soil at a low rate (0.7% organic N found as NO_3-N in week 10, and 0 % in week 28). (Measured)	ECHA, 2011b; ECHA, 2011a	Non guideline studies for the dissociated component, melamine.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	**Melamine polyphosphate:** 21 days (Estimated)	EPI v4.10	
Reactivity	**Photolysis**	**Melamine polyphosphate:** Not a significant fate process (Estimated)	Professional judgment; Mill, 2000	The substance does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	**Polyphosphoric acid:** The half-life for the hydrolysis to phosphoric acid is several days at 25°C (Measured)	Gard, 2005	This value is for the dissociated component, polyphosphoric acid. These studies indicate polyphosphoric acid would undergo

Melamine Polyphosphate CASRN 15541-60-3				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				hydrolysis under environmental conditions to phosphate ions. Reported in a secondary source, study details and test conditions were not provided.
		Polyphosphoric acid: Hydrolysis occurs in 2 months at 20°C (Measured)	IUCLID, 2000b	This value is for the dissociated component, polyphosphoric acid. Reported in a secondary source, study details and test conditions were not provided available.
Environmental Half-life		**Melamine polyphosphate:** 120 days (Estimated)	PBT Profiler v1.301	Half-life estimated for the predominant compartment, as determined by EPI and the PBT Profiler methodology.
Bioaccumulation		**LOW: Based on the relatively high water solubility of melamine polyphosphate (20 g/L) and an estimated BCF of 3.2. In addition, the experimental bioconcentration values for the melamine component are low, BCF <3.8, and BAF <1.**		
	Fish BCF	**Melamine polyphosphate:** 3.2 (Estimated)	EPI v4.10	
		Melamine: <0.38 in carp (*Cyprinus carpio*) after 6 weeks at 2.0 ppm concentration; <3.8 in carp (*Cyprinus carpio*) after 6 weeks at 0.2 ppm concentration (OECD 302B) (Measured)	MITI, 1998	Adequate values from guideline studies for the dissociated component, melamine.
	Other BCF			No data located.
	BAF	**Melamine polyphosphate:** 0.9 (Estimated)	EPI v4.10	
		Melamine: 0.9 (Estimated)	EPI v4.10	
	Metabolism in Fish	**Melamine:** Uptake, bioaccumulation and elimination study with ^{14}C-melamine in fathead minnow and rainbow trout: BCFs <1 (Measured)	ECHA, 2011b; ECHA, 2011a	Non guideline studies that support the low potential for bioaccumulation of this substance.
ENVIRONMENTAL MONITORING AND BIOMONITORING				

Melamine Polyphosphate CASRN 15541-60-3			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Environmental Monitoring	No data located.		
Ecological Biomonitoring	No data located.		
Human Biomonitoring	This chemical was not included in the NHANES biomonitoring report (CDC, 2011).		

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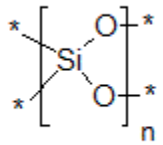
Silicon Dioxide (amorphous)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion 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.

[§] Based on analogy to experimental data for a structurally similar compound. [R] Recalcitrant: Substance is comprised of metallic species (or metalloids) that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions. [¤]Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter. [^] Depending on the grade or purity of amorphous silicon dioxide commercial products, the crystalline form of silicon dioxide may be present. The hazard designations for crystalline silicon dioxide differ from those of amorphous silicon dioxide, as follows: VERY HIGH (experimental) for carcinogenicity; HIGH (experimental) genotoxicity; MODERATE (experimental) for acute toxicity and eye irritation.

		Human Health Effects										Aquatic Toxicity		Environmental Fate	
Chemical	CASRN	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Silicon Dioxide (amorphous)	7631-86-9	L[^]	L[^]	L[^]	L	L	*L*[§]	H[¤]	L		L[^]	VL	L	*L*	*H*[R]	*L*

Silicon Dioxide (amorphous)



* indicates repeating units with indeterminate structure

CASRN: 7631-86-9

MW: 60.09 (for SiO_2)

MF: $(SiO_2)_n$

Physical Forms:
Neat: Solid

Use: Flame retardant

SMILES: Not applicable

Synonyms: Silica (CASRN 7631-86-9)
Silicon dioxide, amorphous: Silica, amorphous fumed, crystalline-free (CASRN 112945-52-5); Pyrogenic (fumed) amorphous silica (CASRN 112945-52-5); Silica, vitreous (CASRN 60676-86-0); Amorphous silica gel, crystalline-free (CASRN 112926-00-8); Silica gel, precipitated, crystalline-free (CASRN 112926-00-8); Silica, amorphous, diatomaceous earth (CASRN 61790-53-2); Silica, amorphous, flux-calcined diatomaceous earth (CASRN 68855-54-9)
Silicon dioxide, crystalline: Silica, crystalline, cristobalite (CASRN 14464-46-1), Silica, crystalline, tripoli (CASRN 1317-95-9); Silica, crystalline, tridymite (CASRN 15468-32-3); Quartz (CASRN 14808-60-7); Sand

Trade names:
Silicon dioxide, amorphous: Aerosil, Art Sorb, Baykisol, Bindzil, Biogenic silica, Britesorb, Cab-O-Sil, Celatom, Celite, Clarcel, Colloidasilica, Decalite, Diamantgel, Diatomaceous earth (flux-calcined), Diatomaceous earth (uncalcined), Diatomite, Fina/Optima, FK, Fused silica, Gasil, HDK, Hi-Sil, Hispacil, KC-Trockenperlen, Ketjensil, Kieselguhr, Lucilite, Ludox, Nalcoag, Neosyl, Nipsil, Nyacol, Opal, Precipitated silica, Quartz glass, Reolosil, Seahostar, Sident, Silcron, Silica fibres (biogenic), Silica-Perlen, Silica-Pulver, Sipernat, Skamol, Snowtex, Spherosil, Suprasil, Sylobloc, Syloid, Sylopute, Syton, TAFQ, Tixosil, Tripolite, Trisyl, Ultrasil
Silicon dioxide, crystalline: Agate, Chalcedony, Chert, Clathrasil, Coesite, alpha, beta Cristobalite, CSQZ, DQ 12, Flint, Jasper, Keatite, Min-U-Sil, Moganite, Novaculite, Porosil, alpha-Quartz, alpha, beta Quartz, Quartzite, Sandstone, Sil-Co-Sil, Silica sand, Silica W, Snowit, Stishovite, Sykron F300, Sykron F600, alpha, beta1, beta2 Tridymite, Zeosil

Chemical Considerations: Silicon dioxide (also known as silica) is an inorganic compound that exists in several physical forms. This report assesses silicon dioxide for flame retardant applications, in which amorphous silicon dioxide is more commonly used. Commercial products may contain crystalline silicon dioxide, depending on the purity and grade.

Silicon dioxide, amorphous consists of randomly arranged rings of silicon dioxide that form a complex structure of roughly spherical particles. Silicon dioxide, crystalline; however is a general term that refers to the many distinct crystal structures or polymorphs of silicon dioxide. Crystalline silicon dioxide includes naturally occurring quartz (CASRN 14808-60-7), cristobalite (CASRN 14464-46-1), and tridymite (CASRN 15468-32-3).

The structural form of silicon dioxide is evaluated in this assessment as it influences the hazards posed to human health. It may be difficult for supply chains to know the difference between the structural forms. Therefore, the hazard designations in this report are based on the amorphous form and a summary of the hazards associated with the crystalline form is provided in the hazard summary table as a footnote (^) for reference, in case the crystalline form is present in the commercial formulation. Concerns based on the nanoscale material were not included in this assessment; however, the potential health concerns from the inhalation of finely divided particulates that are generally less than 10 microns in diameter were considered for human health endpoints.

Although not all literature entries identified which form of silicon dioxide was being discussed, this information was provided whenever available. In the absence of experimental data, structural considerations associated with this mineral were used to complete this hazard profile (IARC, 1997; HSDB, 2009; Waddell, 2013).	
Polymeric: No **Oligomeric:** Not applicable	
Metabolites, Degradates and Transformation Products: None identified.	
Analog: Confidential analogs; a general silicon dioxide CASRN is used to represent all forms of silicon dioxide (CASRN 7631-86-9). Other CASRN for specific silicon dioxide forms are listed in the synonyms section and noted in the data quality column for relevant entries. **Endpoint(s) using analog values:** Neurotoxicity	**Analog Structure:** Not applicable
Structural Alerts: Respirable, poorly soluble particulates - Human health, limited to effects on the lung as a result of inhaling the particles (EPA, 2010).	
Risk Phrases: Not classified by Annex VI Regulation (EC) No 1272/2008 (ESIS, 2012).	
Hazard and Risk Assessments: An Organisation for Economic Co-operation and Development (OECD) Screening Information Dataset Initial Assessment Profile (SIAP) for silicon dioxide was completed in 2004. Silicon dioxide is included in the International Agency for Research on Cancer (IARC) monographs on the evaluation of carcinogenic risks to humans - summaries and evaluations. (IARC, 1997; OECD SIDS, 2004a).	

Silicon dioxide (amorphous) CASRN 7631-86-9			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	1,710 (Measured)	Lewis, 1999; EC, 2000a	Reported in multiple sources. Test substance form not specified.
	Crystalline silicon dioxide: 1,400-2,000 (Measured)	EC, 2000b	A range of values reported in a secondary source. Study details and test methods were not provided.
Boiling Point (°C)	2,230 (Measured)	Lewis, 1999; EC, 2000a; EC, 2000b	Reported in multiple sources. Test substance form not specified.
Vapor Pressure (mm Hg)	**Amorphous and crystalline silicon dioxide:** $<1x10^{-8}$ (Estimated)	Professional judgment	This substance is a high-boiling solid, so the vapor pressure is estimated to be negligible.
	9.98 at 1,732°C Reported as 13.3 hPa at 1,732°C. (Measured)	EC, 2000a	Reported in secondary source at an elevated temperature. Study details not provided. Test substance form not specified.
Water Solubility (mg/L)	**Amorphous silicon dioxide:** 120 (Measured)	Alexander et al., 1954	Study details and test methods were not provided.
	Amorphous silicon dioxide: 70 mg/L (Measured)	KEMI, 2006	Study details and test methods were not provided.
	Amorphous and crystalline silicon dioxide: Insoluble (Estimated)	Lide, 2000	Adequate, non-quantitative value provided.
	Amorphous and crystalline silicon dioxide: Insoluble for fumed, amorphous and crystalline silica (Estimated)	Lewis, 1999	Adequate, non-quantitative value provided.
	Crystalline silicon dioxide: 6.4-18 The water solubility of SiO_2 minerals is a function of temperature, pH, particle size, and the presence of a disrupted surface layer. The slow rate of dissolution is due to the high activation energy required to hydrolyze the Si-O-Si bond. (Measured)	OECD SIDS, 2011	Reported in a secondary source.
	Reported as ~0.15 wt% SiO_2 at 673 K and 100 MPa for pure water (Measured)	Flörke et al., 2000	Study details and test methods were not provided. Test substance form not specified.

Silicon dioxide (amorphous) CASRN 7631-86-9			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Practically insoluble (Estimated)	Merck, 1996	Adequate, non-quantitative value provided. Test substance form not specified.
Log K_{ow}			No data located.
Flammability (Flash Point)	**Amorphous silicon dioxide:** Used as a fire-extinguishing agent, not combustible, stable (Measured)	Daubert and Danner, 1989 (as cited in ECHA, 2013)	Reported in a secondary source for Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5) and Silica gel, precipitated, crystalline-free (CASRN 112926-00-8).
Explosivity	**Amorphous and crystalline silicon dioxide:** Silicon dioxide is a fully oxidized inorganic material and is not expected to be explosive. (Estimated)	Professional judgment	No experimental data located; based on its chemical structure and use as a flame retardant.
Pyrolysis	**Amorphous and crystalline silicon dioxide:** Not applicable (Estimated)	Professional judgment	Inorganic compounds do not undergo pyrolysis.
pH	3.5-9 for 5% aqueous suspension of wet process silica. (Measured)	EC, 2000a	Adequate values reported in a secondary source. The values of 20 different types of wet process silica, identified only by trade names, fall within this range.
	3.6-4.5 for 4% aqueous suspension of fumed silica. (Measured)	EC, 2000a	Adequate value reported in a secondary source for fumed silica.
pK_a			No data located.

Silicon dioxide (amorphous) CASRN 7631-86-9			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Particle Size	**Amorphous silicon dioxide:** D10 = <103 µm D50 = <211 µm D99 = <610 µm According to ISO 13320-1 (Part 1): Particle size analysis - Laser diffraction methods; OECD guideline 110: Particle size distribution / fibre length and diameter distributions and EN 481 (1993): Workplaces atmospheres; size fraction definitions for measurement of airborne particles. (Measured)	ECHA, 2013	Adequate guideline study reported for the commercial product Zeosil 45, Silica gel, precipitated, crystalline-free; (CASRN 112926-00-8).
	Amorphous silicon dioxide: D10 = <230 µm D50 = <615 µm D99 = <1,668 µm According to ISO 13320-1 (Part 1): Particle size analysis - Laser diffraction methods; OECD guideline 110: Particle size distribution / fibre length and diameter distributions and EN 481 (1993): Workplaces atmospheres; size fraction definitions for measurement of airborne particles. (Measured)	ECHA, 2013	Adequate guideline study reported for the commercial product Cab-O-Sil M5: CAS-Name: Silica, amorphous, fumed, crystalline-free; (CASRN 112945-52-5), purity ca. 100 %.
	Amorphous silicon dioxide: 13-27 µm mean distribution according to ISO 13320-1 (Part 1): Particle size analysis - Laser diffraction methods. (Measured)	ECHA, 2013	Reported for HDK T30: >99.8 % SiO_2 with limited study details.
	Amorphous silicon dioxide: D10 = <375 µm D50 = <680 µm D99 = <1,210 µm According to ISO 13320-1 (Part 1): Particle size analysis - Laser diffraction methods; OECD guideline 110: Particle	ECHA, 2013	Adequate guideline study reported for Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).

Silicon dioxide (amorphous) CASRN 7631-86-9			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	size distribution / fibre length and diameter distributions and EN 481 (1993): Workplaces atmospheres; size fraction definitions for measurement of airborne particles. (Measured)		
	Amorphous silicon dioxide: D13 = 200 µm D45.8 = 315 µm D90.6 = 2,000 µm According to ISO 13320-1 (Part 1): Particle size analysis - Laser diffraction methods; OECD guideline 110: Particle size distribution / fibre length and diameter distributions and EN 481 (1993): Workplaces atmospheres; size fraction definitions for measurement of airborne particles. (Measured)	ECHA, 2013	Adequate guideline study reported for the commercial product HDK T30: >99.8 % SiO_2, Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
	Amorphous silicon dioxide: D10 = <214 µm D50 = <480 µm D99 = <1,414 µm According to ISO 13320-1 (Part 1): Particle size analysis - Laser diffraction methods; OECD guideline 110: Particle size distribution / fibre length and diameter distributions and EN 481 (1993): Workplaces atmospheres; size fraction definitions for measurement of airborne particles. (Measured)	ECHA, 2013	Reported for Syloid 74, CAS-Name: Silica gel, crystalline-free; (CASRN 112926-00-8), purity ca. 100 %.
	Amorphous silicon dioxide: D14.04 = <0.64 µm D100 = <10.23 µm Using Anderson 7-stage cascade impactor (Measured)	ECHA, 2013	Non guideline study reported for HDK T30: >99.8 % SiO_2; Silica, amorphous, fumed, crystalline-free; (CASRN 112945-52-5).
	Amorphous silicon dioxide: Typical size ranges of:	ECHA, 2013	Reported for Silica, amorphous, fumed, crystalline-free (CASRN

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		0.1 - 1 µm for aggregates; 1 - 250 µm for Agglomerates (Measured)		112945-52-5).
		Amorphous silicon dioxide: Typical size ranges of: 0.1 - 1 µm for aggregates; 1 - 250 µm for Agglomerates 1 - 20 µm for silica gel aggregates (Measured)	ECHA, 2013	Reported for Silica gel and amorphous silica, precipitated, crystalline-free (CASRN 112926-00-8) with limited study details.
HUMAN HEALTH EFFECTS				
Toxicokinetics		**Amorphous silicon dioxide (CASRNs 7631-86-9, 112945-52-5, 112926-00-8) is rapidly eliminated from the lung tissue. Disposition in the mediastinal lymph nodes is substantial during and after prolonged inhalation exposures in experimental animals; however the involvement of lymphatic elimination is not as relevant following short exposure periods. Intestinal absorption of amorphous silicon dioxide is limited in animals and humans, and there is evidence of ready renal elimination of the bioavailable fractions of silica. In contrast, crystalline silicon dioxide forms tend to accumulate and persist in the lung and lymph nodes.**		
Dermal Absorption *in vitro*				
Absorption, Distribution, Metabolism & Excretion	**Oral, Dermal or Inhaled**	**Amorphous silicon dioxide:** After prolonged exposure of rats to high concentrations of amorphous silica (40-50 mg/m^3), overall elimination was high and was not found to accumulate in the lung: only 5-6% of respirable material was found after 120 exposure days. On the other hand, following prolonged exposure, there was substantial transfer to mediastinal lymph nodes with about 31% of total deposit = 1.5- 2% of the respirable material. The involvement of lymphatic elimination after short exposures is not as relevant, particularly when there is a lower body burden of amorphous silica.	OECD SIDS, 2004b	Sufficient study details reported in a secondary source. Aerosil 150, pyrogenic silica (CASRN 112945-52-5).
		Amorphous and crystalline silicon dioxide: Crystalline forms of silicon dioxide have a tendency to accumulate	OECD SIDS, 2004a; OECD SIDS, 2004b	Sufficient study details reported in a secondary source. Data are for synthetic amorphous silica and

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		and persist in the lung and lymph nodes. Intestinal absorption of silicon dioxide is insignificant in animals and humans. There is evidence of renal elimination of the bioavailable fractions		crystalline silica.
		Amorphous silicon dioxide: Female Sprague-Dawley rats exposed via inhalation to HDK V15 dust at a concentration of 50 - 55 mg/m^3 (nominal, respirable about 30 mg/m^3 with aerodynamic diameter of ≤7 µm) for 12 months. No substantial increase in the SiO_2 deposition in the lung and the mediastinal lymph nodes were observed between exposure of 18 weeks and of 12 months. About 90 % of the SiO_2 was cleared from the lungs and 50 - 60% from the mediastinal lymph nodes within 5 months. This corresponds to an approximate half-life of 7 weeks, based on first-order elimination kinetics.	ECHA, 2013	Sufficient study details reported in a secondary source. HDK V15: >99.8 % SiO_2, 150 m^2/g (BET), CAS-Name: Silica, amorphous fumed, crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: Fischer 344 rats exposed via inhalation to Aerosil 200 dust at a concentration of 50.4 mg/m^3 6 hours/day, 5 days/week for 13 weeks. Lung burdens during treatment were as follows: 755.9 µg at 6.5 weeks and 88.27 µg at 13 weeks of exposure. Lung burdens following treatment were 156.0 µg at 12 weeks and 92.6 µg at 32 weeks post- exposure (during the recovery phase).	ECHA, 2013	Sufficient study details reported in a secondary source. Aerosil 200: CAS-Name: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: Wistar rats exposed via inhalation to Aerosil 200 at concentrations of 0, 1.3, 5.9 or 31 mg/m^3 for 90 days. Half-life was rapid from the	ECHA, 2013	Sufficient study details reported in a secondary source. Aerosil 200: Silica, amorphous, fumed, crystalline-free (CASRN 112945-

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		lungs; No bioaccumulation potential based on study results.		52-5).
		Amorphous silicon dioxide: Rats receiving 20 daily oral doses of 100 mg HDK V15 per animal (about 500 mg/kg bw) each; tissue values (SiO_2) apparently were very slightly increased in liver and kidney: in liver 4.2 µg (control value 1.8 µg), in the spleen 5.5 µg (7.2 µg) and in the kidneys 14.2 µg (7.8 µg).	ECHA, 2013	Sufficient study details reported in a secondary source. HDK V15: >99.8 % SiO_2, 150 m^2/g (BET), CAS-Name: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: Human subjects (10 males and 2 females per test article) were given Aerosil or FK 700 as 0.5% suspensions in apple juice. Urinary excretion for both test substances was <0.5 % of the dose within 4 days. Overall, increases in excretion of SiO_2 after oral ingestion were not unequivocally detectable.	ECHA, 2013	Sufficient study details reported in a secondary source. Aerosil, CAS-Name: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5); or FK 700, Silica gel, precipitated, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Silicon dioxide is slowly absorbed from dusts deposited in lungs, or from material taken orally.	HSDB, 2009	Limited data reported in a secondary source for amorphous silica.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Other	**Amorphous silicon dioxide:** Amorphous silica (HDK V15), 10 mg subcutaneously injected in 0.3 mL water in female Sprague-Dawley rats, was rapidly removed from the site of injection: mean recovery 24 h post-treatment 6.90 mg, after one month 0.65 mg (approx. 10 % left) and after two months 0.30 mg (less than 5 % left) Similar results were obtained in rats after subcutaneous application of 30, 40, and 50 mg AEROSIL 150 as suspension in water or in 0.5% Tween or as dry powder (operative, subcutaneous): after 6 weeks 95 - 97 % of the substance was eliminated.	OECD SIDS, 2004b	Sufficient study details reported in a secondary source. HDK V15: >99.8 % SiO_2, 150 m^2/g (BET), CAS-Name: Silica, amorphous, fumed (CASRN 112945-52-5).
Acute Mammalian Toxicity		**LOW: Amorphous silicon dioxide is not acutely toxic when administered via oral, dermal, or inhalation routes. If the crystalline form of silicon dioxide is present, the hazard designation is Moderate based on an oral LD_{50} of 500 mg/kg and lung effects following short-term inhalation exposure.**		
Acute Lethality	**Oral**	**Amorphous silicon dioxide:** Mouse oral LD_{50} >3,160 mg/kg	ECHA, 2013	Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: Rat oral LD_{50} >3,300 - >20,000 mg/kg	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Silica, precipitated, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Rat oral LD_0 >3,300 - >40,000 mg/kg	EC, 2000a	Sufficient study details reported in a secondary source. Amorphous (CASRN 7631-86-9) or Silica, precipitated, crystalline-free (CASRN 112926-00-8).
		Crystalline silicon dioxide: Rat oral LD_{50} = 500 mg/kg	EC, 2000b	Study details reported in a secondary source; particle size of quartz was 100-200 µm.
	Dermal	**Amorphous silicon dioxide:** Rabbit	EC, 2000a; Waddell, 2013	Sufficient study details reported in a

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		dermal LD_{50} >2,000 - >5,000 mg/kg		secondary source. Silica, precipitated, crystalline-free (CASRN 112926-00-8).
	Inhalation	**Amorphous silicon dioxide:** Rat 4-hour inhalation LC_{50} >58.8 mg/L (nominal, nose only, dust); 4-hour LC_0 >58.8 mg/L (nominal)	ECHA, 2013	Sufficient study details reported in a secondary source. Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5), purity ca. 100 %.
		Amorphous silicon dioxide: Rat 4-hour inhalation LC_0 >0.139 - >0.69 mg/L (nose only, dust); Rat 1-hour inhalation LC_0 >0.139; Rat 7-hour inhalation LC_0 >0.139 - >3.1 mg/L	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Silica, precipitated, crystalline-free (CASRN 112926-00-8) or Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: Rat 1-hour inhalation LC_{50} >2.2 mg/L	ECHA, 2013	Insufficient study; significant methodological deficiencies. Silica gel, crystalline-free (CASRN 112926-00-8).
		Crystalline silicon dioxide: 3-day inhalation study in rats exposed to 0, 10, or 100 mg/m3 of cristobalite (6 hours/day). Increased granulocytes and other markers of cytotoxicity from the lung lavage fluid were reported in all treated animals. LOAEC: 10 mg/m^3 (0.01 mg/L)	OECD SIDS, 2011	Limited study details reported in a secondary source; test substance identified as cristobalite; an LC_{50} was not calculated for this study, but supports a Moderate hazard designation for the inhalation route.
Carcinogenicity		**LOW: Based on the weight of evidence, amorphous silicon dioxide has a Low potential for carcinogenicity. Amorphous silicon dioxide was not carcinogenic in rats or mice following dietary administration for 103 or 93 weeks, respectively. Amorphous silicon dioxide is not classifiable as to its carcinogenicity to humans. Crystalline silicon dioxide was carcinogenic in several inhalation studies in rats and was shown to have an excess cancer risk following workplace exposure in several epidemiology studies. In addition, estimation software predicts a high-moderate carcinogenic risk for crystalline silicon dioxide. If the crystalline form of silicon dioxide is present, a VERY HIGH hazard designation would be assigned based on the weight of evidence that indicates sufficient evidence of carcinogenicity in humans.**		

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	OncoLogic Results	**Amorphous silicon dioxide:**	OncoLogic, 2008	This compound is not amenable to available estimation methods.
		Crystalline silicon dioxide: High-moderate; there is clear evidence that crystalline silica is a human and animal carcinogen via the inhalation route. (Estimated)	OncoLogic, 2008	Estimated based on silica, crystalline (CASRN 14808-60-7).
	Carcinogenicity (Rat and Mouse)	**Amorphous silicon dioxide:** In a 103 week study, Fischer 344 rats (40/sex/dose) were fed 0, 0.125, 2.5 and 5% Syloid 244 in the diet daily. The mean daily intake was 143.46, 279.55 and 581.18 g/rat in males and 107.25, 205.02 and 435.33 g/rat in females, respectively. The tumor response was not statistically different from controls.	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: In a 93-week study, B6C3F1 mice (40/sex/group) were fed 0, 1.25, 2.5 and 5 % Syloid 244 in the diet daily. The mean cumulative intake after 93 weeks was 38.45, 79.78 and 160 g/mouse in males and 37.02, 72.46 and 157.59 g/mouse in females, respectively. No significant difference in survival rats or behavior was observed. No dose-related alteration in hematologic parameters or organ weights. Malignant lymphoma/leukemia, which occurred in 7/20 females in the 2.5% dose group, was not statistically different than controls. Non-neoplastic lesions were considered to be of no toxicological significance.	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Intrapleural implantation of synthetic amorphous	IARC, 1997	Reported in a secondary source; test substance specified as amorphous

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		silica was negative for tumorigenesis.		silica.
		Amorphous silicon dioxide: Oral administration of food-grade, micronized, amorphous silica to rats and mice was negative for tumorigenesis.	IARC, 1997	Reported in a secondary source; test substance specified as amorphous silica.
		Amorphous silicon dioxide: Slightly increased incidence of intra-abdominal lymphosarcomas was reported after intraperitoneal injection of diatomaceous earth to mice. Subcutaneous and oral administration in mice produced no increase in tumors.	IARC, 1997	Reported in a secondary source; test substance specified as amorphous silica.
		Crystalline silicon dioxide: Several epidemiological investigations have shown an excess cancer risk following workplace inhalational exposure to dust containing respirable crystalline silica. Lung cancer incidence tended to increase with cumulative exposure; increased duration of exposure; peak intensity of exposure; presence of radiographically defined silicosis; and length of follow-up time from date of silicosis diagnosis.	IARC, 1997; OECD SIDS, 2011	Reported in a secondary source; test substance specified as crystalline silica.
		Crystalline silicon dioxide: Study with Balb/x mice (8 hours/day, 5 days/week in three groups of 6 to 16 mice at a concentration of 475 mg/m^3 for 150 days, 1,800 mg/m^3 for 300 days or 1,950 mg/m^3 for 570 days. There was no statistically significant difference in the number of pulmonary adenomas reported in the control or treated groups.	EC, 2000b	Limited study details reported in a secondary source.
		Crystalline silicon dioxide: 2-year study with F344 rats (50/sex), exposed via whole body inhalation for 6 hours/day, 5	EC, 2000b; OECD SIDS, 2011	Limited study details reported in a secondary source.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		days/week at a concentration of 1 mg/m^3. Inhalation exposure caused primary lung tumors (majority were adenocarcinomas) in 18 animals (12 in females, 5 in males). Mean mass of particles in the lungs at the end of the exposure period was 0.91 mg/lung.		
		Crystalline silicon dioxide: Four experiments in rats by inhalation of quartz and four experiments in rats by intratracheal instillation of quartz produced increased incidences of adenocarcinomas and squamous-cell carcinomas of the lungs. Animals that developed tumors also showed fibrosis. For the intratracheal instillation studies, doses ranged from 4 to 57 mg/kg-bw (7, 12 or 20 mg/animal of Min-U-Sil (5) quartz or 20 mg/animal of novaculite quartz). Exposure ranged from single instillation with observation for up to two years, to weekly instillation for 10 weeks. There was an increased incidence of silicotic granulomas after 3 weeks and lung tumors after 11 months following single intratracheal administration of a 95% pure quartz particles (<5 µm).	IARC, 1997; OECD SIDS, 2011	Reported in a secondary source; test substance specified as crystalline silica.
		Crystalline silicon dioxide: Thoracic and abdominal malignant lymphomas, primarily of the histiocytic type (MLHT) were found following intrapleural or intraperitoneal injections of several types of quartz to rats.	IARC, 1997	Reported in a secondary source; test substance specified as crystalline silica.
	Combined Chronic Toxicity/Carcinogenicity			No data located.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Other	**Amorphous silicon dioxide:** Amorphous silica is not classifiable as to its carcinogenicity to humans (Group 3: This category is used most commonly for agents for which the evidence of carcinogenicity is inadequate in humans and inadequate or limited in experimental animals. Exceptionally, agents for which the evidence of carcinogenicity is inadequate in humans but sufficient in experimental animals may be placed in this category when there is strong evidence that the mechanism of carcinogenicity in experimental animals does not operate in humans. Agents that do not fall into any other group are also placed in this category. An evaluation in Group 3 is not a determination of non-carcinogenicity or overall safety. It often means that further research is needed, especially when exposures are widespread or the cancer data are consistent with differing interpretations).	IARC, 1997	Summarized from a secondary source.
		Crystalline silicon dioxide: Crystalline silica inhaled in the form of quartz or cristobalite from occupational sources is carcinogenic to humans (Group 1: This category is used when there is sufficient evidence of carcinogenicity in humans. Exceptionally, an agent may be placed in this category when evidence of carcinogenicity in humans is less than	IARC, 1997	Summarized from a secondary source.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		sufficient but there is sufficient evidence of carcinogenicity in experimental animals and strong evidence in exposed humans that the agent acts through a relevant mechanism of carcinogenicity).		
Genotoxicity		**LOW: Based on the weight of evidence, amorphous silicon dioxide was negative both *in vitro* and *in vivo* gene mutation and chromosome aberration assays. If crystalline silicon dioxide is present, the hazard designation is assigned a HIGH based on weight of evidence from multiple studies. Crystalline silicon dioxide induced gene mutations *in vivo* and chromosomal aberrations in several *in vitro* and *in vivo* studies in experimental animals. In addition, crystalline silicon dioxide induced cell transformation in mice and hamsters *in vitro*.**		
	Gene Mutation *in vitro*	**Amorphous silicon dioxide:** Negative in *Escherichia coli* WP2 with and without metabolic activation. Test concentrations: 0.033 - 10 mg/plate, suspended in DMSO.	IARC, 1997; EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Silcron G-190 (SCM Glidden): Silica gel, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Negative in HGPRT assay in Chinese hamster ovary (CHO) cells with and without metabolic activation. Test concentrations: 10, 50, 100, 150, and 250 µg/mL (without S9) and 100, 200, 300, 400, and 500 µg/mL (with S9).	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Cab-O-Sil EH-5: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: Negative in *Saccharomyces cerevisiae* strains TA98, TA100, TA1535, TA1537 and TA1538 with and without metabolic activation. Test concentrations: 667, 1,000, 3,333, 6,667, and 10,000 µg/plate	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Silcron G-190 (SCM Glidden): Silica gel, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Negative in *Salmonella typhimurium* and *Escherichia coli* mutagenicity assay.	IARC, 1987	Study details reported in a secondary source; test substance amorphous silica.
		Crystalline silicon dioxide: Direct treatment of rat lung epithelial cells with	IARC, 1987	Study details reported in a secondary source; test substance

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		quartz *in vitro* did not cause HPRT mutation.		crystalline silica.
		Crystalline silicon dioxide: Negative; *Salmonella typhimurium* reverse mutation assay (with or without metabolic activation)	EC, 2000b	Limited study details reported in a secondary source.
	Gene Mutation *in vivo*	**Amorphous silicon dioxide:** Negative; alveolar type-II cells isolated from rats exposed via whole body inhalation to 50-mg/m^3 Aerosil 200 showed no increased mutation frequency. Exposure was for 6 hours/day, 5 days/week for 13 weeks. Crystalline silica was examined simultaneously as a positive control.	ECHA, 2013	Sufficient study details reported in a secondary source. Aerosil 200: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: Negative, gene mutations in host mediated assay; male ICR mice orally gavaged with 1.4, 14, 140, 500 and 5,000 mg/kg suspended in 0.85 % saline and then injected with *Salmonella typhimurium* or *Saccharomyces cerevisiae*.	ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
		Crystalline silicon dioxide: Epithelial cells from the lungs of rats intratracheally exposed to quartz showed HPRT gene mutations.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.
	Chromosomal Aberrations *in vitro*	**Amorphous silicon dioxide:** Negative for chromosomal aberrations in human embryonic lung cells (Wi-38) without metabolic activation. Test concentrations: 0.1, 1.0, and 10 µg/mL.	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Negative for chromosomal aberrations in CHO cells with and without metabolic activation; Test concentrations: 38, 75, 150, 300	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		µg/mL (without S9) and 250, 500, 750, 1,000 µg/mL (with S9).		
		Crystalline silicon dioxide: Tridymite induced sister chromatid exchange in co-cultures of human lymphocytes and monocytes.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.
		Crystalline silicon dioxide: Induces micronuclei in Syrian hamster embryo cells, Chinese hamster lung V79 cells, and human embryonic lung Hel 299 cells *in vitro*, but negative for inducing chromosomal aberrations.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.
		Crystalline silicon dioxide: Induced micronuclei in Syrian hamster embryo cells	EC, 2000b	Limited study details reported in a secondary source; route and duration of exposure were not specified.
	Chromosomal Aberrations *in vivo*	**Amorphous silicon dioxide:** Negative, chromosomal aberration dominant lethal assay in rats orally gavaged with 1.4, 14.0, 140, 500 and 5,000 mg/kg suspended in 0.85 % saline.	ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
		Crystalline silicon dioxide: Induced chromosomal aberrations in human peripheral blood lymphocytes following *in vivo* exposure to dust containing crystalline silica.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.
		Crystalline silicon dioxide: Positive, induced sister chromatid exchange in human peripheral blood lymphocytes following *in vivo* exposure to dust containing crystalline silica.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.
		Crystalline silicon dioxide: Quartz did not induce micronuclei in mice *in vivo*.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Crystalline silicon dioxide: Negative; did not cause sister chromatid exchange or aneuploidy in Syrian hamsters exposed to 2 µg *in vivo*.	EC, 2000b	Limited study details reported in a secondary source; route of administration, exposure duration was not specified.
		Crystalline silicon dioxide: Negative; did not cause sister chromatid exchanges in Chinese hamsters	EC, 2000b	Limited study details reported in a secondary source; route of administration and exposure duration were not specified.
		Crystalline silicon dioxide: DQ 12 quartz did not induce micronuclei in polychromatic erythrocytes of bone marrow of mice at 500 mg/kg bw.	EC, 2000b	Limited study details reported in a secondary source.
		Negative for chromosomal aberrations in two assays following single and subacute oral gavage administration to rats.	IARC, 1997	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report. Test substance unspecified silica.
	DNA Damage and Repair			No data located.
	Other	**Crystalline silicon dioxide:** Five quartz samples induced transformation in BALB/c-3T3 cells *in vitro*.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.
		Crystalline silicon dioxide: Two quartz samples induced morphological transformation in Syrian hamster cells *in vitro*.	IARC, 1997	Study details reported in a secondary source; test substance crystalline silica.
		Negative, unscheduled DNA synthesis assay in primary rat hepatocytes.	EC, 2000a	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report. Test substance unspecified silica.
		Negative in two dominant lethal assays in rats following oral gavage administration.	EC, 2000a	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report. Test substance

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				unspecified silica.
Reproductive Effects		**LOW: There was no indication of adverse reproductive effects in an unpublished one-generation oral study in rats administered amorphous silica, fumed. It is estimated that crystalline silicon dioxide, if present, is not likely to produce reproductive effects based on analogy to amorphous silicon dioxide and professional judgment.**		
	Reproduction/Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Reproduction and Fertility Effects	**Amorphous silicon dioxide:** In a one-generation oral dietary study, Wistar rats (5 females, 1 male/dose) were fed test substance at doses of 0, 497 mg/kg bw (males) or 509 mg/kg bw (females) in the diet daily. In parents: no clinical signs of toxicity, no mortality, no abnormalities in body-weight gain and feed consumption, no hematological findings. In pups: no behavioral or developmental/structural abnormalities. NOAEL (parental and offspring): 497 mg/kg-day (males); 509 mg/kg bw-day (females) (highest concentrations tested) LOAEL: Not established	EC, 2000a; ECHA, 2013	Significant methodological deficiencies, acceptable as screening. Aerosil, not further specified, hydrophilic: CAS-Name: Silica, amorphous, fumed, crystalline free (CASRN 112945-52-5).
	Other	**Crystalline silicon dioxide:** There is low potential for reproductive effects based on analogy to amorphous silicon dioxide. (Estimated by analogy)	Professional judgment	Estimated based on analogy to amorphous silicon dioxide and professional judgment; no experimental data located.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Developmental Effects		**LOW: Amorphous silicon dioxide did not produce adverse developmental effects in rats, mice, rabbits or hamsters following oral administration at doses up to 1,600 mg/kg bw-day during gestation. It is estimated that crystalline silicon dioxide, if present, is not likely to produce developmental effects based on analogy to amorphous silicon dioxide and professional judgment. There were no data located for the developmental neurotoxicity endpoint.**		
	Reproduction/ Developmental Toxicity Screen			No data located.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data located.
	Prenatal Development	**Amorphous silicon dioxide:** Pregnant CD-1 mice (21-26 females/group) were administered Syloid 244 via oral gavage at doses of 0, 13.4, 62.3, 289 and 1,340 mg/kg bw-day from gestation days 6-15. The number of abnormalities seen in either soft or skeletal tissues of the test groups did not differ from the number occurring spontaneously in controls. NOAEL (maternal and fetal): 1,340 mg/kg-day (highest dose tested) LOAEL: Not established	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Pregnant Wistar rats (20/25 females/group) were administered Syloid 244 via oral gavage at doses of 0, 13.5, 62.7, 292 and 1,350 mg/kg bw-day from gestation days 6-15. No observable effects on maternal or fetal survival or development. The number of abnormalities seen in either soft or skeletal tissues of the test groups did not	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		differ from the number occurring spontaneously controls. NOAEL (maternal and fetal): 1,350 mg/kg-day (highest dose tested) LOAEL: Not established		
		Amorphous silicon dioxide: Pregnant Dutch rabbits (10-14/dose) were administered Syloid 244 via oral gavage at doses of 0, 16.0, 74.3, 345 and 1,600 mg/kg bw-day from gestation days 6-18. No adverse effect on maternal or fetal survival. The number of abnormalities seen in either soft or skeletal tissues of the test groups did not differ from the number occurring spontaneously in controls. NOAEL (maternal and fetal): 1,600 mg/kg bw-day (highest dose tested) LOAEL: Not established	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Pregnant Syrian hamsters (21-22 females/group) were administered Syloid 244 via oral gavage at doses of 0, 16.0, 74.3, 345 and 1,600 mg/kg bw-day from gestations days 6-10. The number of abnormalities seen in either soft or skeletal tissues of the test groups did not differ from the number occurring spontaneously in controls. NOAEL (maternal and fetal): 1,600 mg/kg-day (highest dose tested) LOAEL: Not established	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica gel, crystalline-free (CASRN 112926-00-8).
	Postnatal Development			No data located.
	Prenatal and Postnatal Development			No data located.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Developmental Neurotoxicity	No data were located for the developmental neurotoxicity endpoint.		No data located.
	Other	**Crystalline silicon dioxide:** There is low potential for developmental effects based on analogy to amorphous silicon dioxide. (Estimated by analogy)	Professional judgment	Estimated based on analogy to amorphous silicon dioxide and professional judgment; no experimental data located.
Neurotoxicity		**LOW: Both amorphous and crystalline silicon are estimated to have low potential for neurotoxic effects based on analogy to a similar compound and professional judgment.**		
	Neurotoxicity Screening Battery (Adult)			No data located.
	Other	Low potential for neurotoxic effects. (Estimated by analogy)	Professional judgment	Estimated for crystalline and amorphous silica based on analogy to a structurally similar chemical compound and professional judgment.
Repeated Dose Effects		**HIGH: Based on the weight of evidence, the hazard designation for both amorphous and crystalline silicon dioxide is High. Extended workplace exposure to amorphous and crystalline silica dust induced silicosis in humans. Effects on the lungs, such as increased weight, focal interstitial fibrosis, pulmonary inflammation and/or granuloma, macrophage accumulation, lesions in the bronchi, and hypertrophy/hyperplasia of the bronchiolar epithelium were observed following inhalation exposures to amorphous and crystalline silica dust or aerosol at concentrations as low as 0.001 mg/L in rats.**		
		Amorphous and crystalline silicon dioxide: Silicosis in humans following extended workplace exposure.	NIOSH, 1978a; NIOSH, 1978b	Test substance amorphous silica and crystalline silica.
		Amorphous silicon dioxide: 27-Month inhalation study, rabbit. Dyspnea, cyanosis, shortness of breath, emphysema, vascular stenosis, alveolar cell infiltration, sclerosis, granulomatous, lesions in the liver, spleen, and kidney. LOAEL: 28 mg/m^3 (0.028 mg/L)	EC, 2000a	Secondary source, test substance amorphous silica, study details, test concentrations, exposure protocol, and test conditions were not provided. The original study was in an unpublished report.
		Amorphous silicon dioxide: 1-Year inhalation study, rabbits. Progressive	EC, 2000a	Secondary source, test substance amorphous silica, study details and

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		functional incapacitation, emphysema, pulmonary vascular obstruction, blood pressure changes, mural cellular infiltration, peribronchiolar cellular catarrh, perivascular cellular nodules, ductal stenosis. LOAEL: <53 mg/m^3 (0.053 mg/L)		test conditions were not provided. The original study was in an unpublished report.
		Amorphous silicon dioxide: 13-Week inhalation study, rats. LOAEC: 1 mg/m^3 (0.001 mg/L), increased lung weight, focal interstitial fibrosis, pulmonary inflammation, and pulmonary granulomas.	Reuzel et al., 1991	Test substance amorphous silica; test concentrations and exposure protocol are unspecified.
		Amorphous silicon dioxide: In a 13-week inhalation study, Wistar rats (70/sex/dose) were exposed whole-body to SiO_2 at concentrations of 0, 1.3, 5.9 or 31 mg/m^3 6 hours/day, 5 days/week. Swollen and spotted lungs and enlarged mediastinal lymph nodes. Increased collagen content in the lungs (5.9 and 31 mg/m^3). Accumulation of alveolar macrophages and granular material, cellular debris, polymorphonuclear leucocytes, increased septal cellularity. Accumulation of macrophages was seen in the mediastinal lymph nodes. Treatment-related microscopic changes in the nasal region. NOAEC: 1.3 mg/m^3 (0.0013 mg/L) LOAEC: 5.9 mg/m^3 (0.0059 mg/L)	ECHA, 2013	Sufficient study details reported in a secondary source. Comparative study including Aerosil 200, Aerosil R 974 (pyrogenic, hydrophobic), Sipernat 22S (precipitated, hydrophilic) as well as quartz (crystalline silica at a concentration of 58 mg/m^3) as a positive control).
		Amorphous silicon dioxide: In a 13-week inhalation study, Wistar rats	ECHA, 2013	Sufficient study details reported in a secondary source. Comparative

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		(70/sex/dose) were exposed whole-body to SiO_2 at concentrations of 0 or 35 mg/m^3 6 hours/day, 5 days/ week. Slight mean increase in relative lung weight. Swollen and spotted lungs and enlarged mediastinal lymph nodes. Accumulation of alveolar macrophages, intra-alveolar polymorphonuclear leukocytes, and increased septal cellularity. Treatment-related microscopic changes in the nasal region. Slightly increased collagen content in the lungs at the end of the exposure period. Changes were nearly all reversed during the recovery period. NOAEC: Not established LOAEC: 35 mg/m^3 (0.035 mg/L; only dose tested)		study including Aerosil 200, Aerosil R 974 (pyrogenic, hydrophobic), Sipernat 22S (precipitated, hydrophilic) as well as quartz (crystalline silica at a concentration of 58 mg/m^3) as a positive control.
		Amorphous silicon dioxide: In a 13-week inhalation study, male Fischer 344 rats were exposed whole body to Aerosil 200 dust at a concentration of 0 or 50 mg/m^3 for 6 hours/day, 5 days/week. Quartz (crystalline silica) was used as positive control. Invasion of neutrophils and macrophages into alveoli after both amorphous and crystalline silica exposure; more pronounced with the amorphous type after 6.5 weeks but decreased during post-exposure period. Fibrosis was present in the alveolar septae, but subsided during recovery. NOAEC: Not established LOAEC: 50 mg/m^3 (0.05 mg/L; only concentration tested)	ECHA, 2013	Sufficient study details reported in a secondary source. Aerosil 200: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Amorphous silicon dioxide: In 13 and 18 month inhalation studies, male monkeys (10/group) were exposed whole body to 15 mg/m^3 (total dust, pyrogenic and precipitated; 15.9 mg/m^3 total dust silica gel; 6.9 - 9.9 mg/m^3 (respirable fraction) for 6 hours/day, 5 days/week. Histopathological examination of the lung revealed Incipient fibrosis, inflammatory response: aggregation of great amounts of macrophages, physiological impairment of lung function. NOAEC: Not established LOAEC: ≈ 15 mg/m^3 (0.015 mg/L) (nominal; only dose tested) LOAEC (related to respirable fraction) ≥ 6 ≤ 9 mg/m^3 air (analytical)	ECHA, 2013	Sufficient study details reported in a secondary source. Three silica subclasses: Cab-O-Sil type (pyrogenic), named "fume" silica (Silica F), (CASRN 112945-52-5): commercial quality; Hi-Sil (precipitated): silica P (CASRN 112926-00-8) commercial quality; silica gel: silica G (CASRN 112926-00-8) commercial quality.
		Amorphous silicon dioxide: In a 14-day inhalation study, Wistar rats (40/sex/group) were exposed to Aerosil 200 at concentrations of 0, 17, 44 or 164 mg/m^3 for 6 hours/day, 5 days/week. Respiratory distress, increased lung weight, decreased kidney and liver weights, dose-dependent changes in lung characteristics (pale, spotted, spongy, alveolar interstitial pneumonia, early granulomata). NOAEL: Not established LOAEL: <17 mg/m^3 (<0.017 mg/L, lowest concentration tested)	EC, 2000a; ECHA, 2013	Secondary source, test substance identified as Aerosil 200: >99.8 % (SiO_2): CAS-Name: Silica, amorphous, fumed, crystalline-free; CASRN: 112945-52-5; limited study details and test conditions provided. The original study was in an unpublished report.
		Amorphous silicon dioxide: In a 14-day inhalation study, Wistar rats were exposed whole body to Sipernat 22S at	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. SIPERNAT 22S >98 % (SiO_2): CAS-Name: Silica,

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		concentrations of 46, 180 or 668 mg/m^3. Respiratory distress, increased lung weight, decreased liver weights, dose-dependent changes in lung characteristics (pale, spotted, spongy, alveolar interstitial pneumonia, early granulomata), accumulation of alveolar macrophages and particulate material in lungs. NOAEC: Not established LOAEC: <46 mg/m^3 (<0.046 mg/L, lowest concentration tested)		precipitated, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: In a 5-day inhalation study, male Wistar rats (10/dose) were exposed whole body to Syloid 74 at concentrations of 0, 1, 5, and 25 mg/m^3 for 6 hours/day. Quartz (crystalline silica) was examined as a positive control. Significant mean increase in lung weight, very slight hypertrophy of the bronchiolar epithelium, accumulation of alveolar macrophages accompanied by a few granulocytes/neutrophils at high dose. NOAEC: 5.13 mg/m^3 (0.00513 mg/L) LOAEC: 25.1 mg/m^3 (0.0251 mg/L)	ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 74, CAS-Name: Silica gel, crystalline-free (CASRN 112926-00-8), purity ca. 100%.
		Amorphous silicon dioxide: In a 5-day inhalation study, Wistar rats (10/sex/group) were exposed nose-only to Zeosil 45 aerosol at concentrations of 0, 1, 5, 25 mg/m^3 for 6 hours/day. Slight increases in lung weights of the high-dose group, increase in relative weights of tracheobronchial lymph nodes in females. Increased absolute numbers of	ECHA, 2013	Sufficient study details reported in a secondary source. ZEOSIL 45: CAS name, Silica, precipitated, crystalline-free (CASRN 112926-00-8); impurities: Na (1.9 %), S (0.8 %), Al (0.045 %), Fe (0.02 %), Ca 0.06 %.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		neutrophils, hypertrophy and hyperplasia of the bronchiolar epithelium at high dose. NOAEC: 5.39 mg/m^3 (0.00539 mg/L) LOAEC: 25.2 mg/m^3 (0.0252 mg/L)		
		Amorphous silicon dioxide: In a 5-day inhalation study, male Wistar rats (10/group) were exposed nose-only to CAB-O-SIL M5 at concentrations of 0, 1.39, 5.41 and 25 mg/m^3 for 6 hours/day. Significant mean increases in relative and absolute lung weights of the mid- and high-dose groups. Very slight hypertrophy of the bronchiolar epithelium (mid and high dose) and slight hypertrophy (high dose). Accumulation of alveolar macrophages accompanied by a few granulocytes/neutrophils (mid and high dose). Accumulation of macrophages accompanied by infiltration of polymorphonuclear leukocytes (high dose). Very slight macrophage accumulation still present following 3 months of recovery (high dose). NOEC: 1.39 mg/m^3 (0.00139 mg/L) LOAEC: 5.41 mg/m^3 (0.00541 mg/L)	ECHA, 2013	Sufficient study details reported in a secondary source. CAB-O-SIL M5: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5), purity ca. 100%.
		Amorphous silicon dioxide: In a 103 week study, Fischer 344 rats (40/sex/group) were fed Syloid 44 continuously in the diet at concentrations of 1.25, 2.5 and 5%. Interim sacrifice of 10/sex after 6 and 12 months. Reduced liver weight in females after 12 and 24 months is not considered to be treatment-	ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica, precipitated, crystalline-free (CASRN 112926-00-8).

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		related. There were no other treatment-related effects. NOAEL: 5% (~ 2,000 mg/kg bw-day for average of male and female; highest dose tested) LOAEL: Not established		
		Amorphous silicon dioxide: In a 93 week study, B6C3F1 mice (40/sex/dose) were fed Syloid 244 continuously in the diet at concentrations of 0, 1.25, 2.5 or 5%. Interim sacrifice of 10/sex after 6 and 12 months. Transient retardation in body weight gain was not biologically relevant. No other adverse treatment-related effects. NOAEL: 5% (4,500 or 5,800 mg/kg bw-day for average of male/female, respectively; highest dose tested) LOAEL: Not established	ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica, precipitated, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: In a 6-month study, Charles River rats (12/sex/group) were fed Syloid 244 in the diet daily at doses of 0, 2,170 and 7,950 mg/kg bw-day (males) or 0, 2,420 and 8,980 mg/kg bw-day (females). There were no treatment-related effects. Isolated pathological findings were not related to test substance. NOAEL: 7,950 mg/kg bw-day (males) or 8,980 mg/kg bw-day (females) (highest doses tested) LOAEL: Not established	ECHA, 2013	Sufficient study details reported in a secondary source. Syloid 244: Silica, precipitated, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: In a 13-	ECHA, 2013	Silica, amorphous, fumed,

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		week study, Charles River rats were fed Cab-O-Sil(fluffy) (>99 % SiO_2) continuously in the diet at concentrations of 1, 3, and 5% (mean estimated dose: 700, 2,100, and 3,500 mg/kg bw-day). No clinical signs of toxicity. No gross pathological or histopathological treatment-related changes. NOAEL: 5% (~ 3,500 mg/kg bw-day; highest dose tested) LOAEL: Not established		crystalline-free (CASRN 112945-52-5).
		Amorphous silicon dioxide: In a 13-week dietary study, Wistar rats (10/sex/dose) were fed SiO_2 continuously in the diet at concentrations of approximately 0, 0.05, 2 and 6.7% (mean estimated doses: 300-330, 1,200-1,400, 4,000-4,500 mg/kg-day). Slightly increased mean food intake at high dose, with no corresponding body weight gain. No clinical signs of toxicity or other findings (hematological, blood-chemical and urinary parameters). Gross and microscopic examination did not reveal any treatment-related changes. NOAEL: 6.7% (4,000-45,000 mg/kg bw-day (nominal, highest dose tested) LOAEL: Not established	ECHA, 2013	Sufficient study details reported in a secondary source. Silica, precipitated, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: Biogenic silica fibers induced ornithine decarboxylase activity of epidermal cells in mice following topical application.	IARC, 1997	Test substance amorphous silica.
		Crystalline silicon dioxide: 2-Year inhalation (whole body) study, rats	Rice, 2000; OECD SIDS, 2011	Test substance identified as crystalline silica (DQ-12 quartz,

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		(50/sex) exposed to air or 1 mg/m^3 6 hours/day, 5 days/week). Subpleural and peribronchial fibrosis, focal lipoproteinosis cholesterol clefts, enlarged lymph nodes, granulomatous lesions in the walls of large bronchi. LOAEL: 1 mg/m^3 (0.001 mg/L; only dose tested)		containing 74% respirable quartz.
		Crystalline silicon dioxide: Silicotic nodules with reticulin fibrosis was reported by day 220 and dense, rounded collagenous nodules were reported on day 300 in rats following inhalation exposure (18 hours/day, 5 days/week) of 30,000 particles/mL (40% < 0.5 microns) for up to 420 days.	EC, 2000b	Limited study details reported in a secondary source.
		Crystalline silicon dioxide: 6-Month inhalation study, rats. Increased collagen and elastin content in the lungs, induced type II cell hyperplasia in alveolar compartment and intralymphatic microgranulomas around bronchioles. NOAEL: Not established LOAEL: 2 mg/m^3 (0.002 mg/L)	Rice, 2000	Test substance identified as crystalline silica (quartz); test concentrations not specified.
		Crystalline silicon dioxide: 13-week inhalation study in male rats exposed to 0 or 3 mg/m^3 (6 hours/day, 5 days/week). Treated rats presented with pulmonary inflammation and fibrosis. NOAEL: Not established LOAEL: 3 mg/m^3 (0.003 mg/L; only dose tested)	OECD SIDS, 2011	Study details reported in a secondary source; test substance identified at cristobalite.
		Crystalline silicon dioxide: 4-week	OECD SIDS, 2011	Study details reported in a

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		inhalation study in female rats exposed to 0, 0.1, 1, or 10 mg/m^3 (6 hours/day, 5 days/week). Evaluation of bronchoalveolar lavage fluid occurred on weeks 1, 8, and 24 following exposure. Significantly increased levels of granulocytes and increased levels of lactate dehydrogenase and beta-glucuronidase were reported at 24 weeks post exposure at a concentration of 1 mg/m^3. NOAEL: 0.1 mg/m^3 (0.0001 mg/L) LOAEL: 1 mg/m^3 (0.001 mg/L)		secondary source; test substance identified at quartz.
		Crystalline silicon dioxide: 9-day inhalation study in mice Minimal interstitial thickening, accumulation of mononuclear cells, and slight lymphoid hypertrophy in the lungs were reported. NOAEL: Not established LOAEL: 10 mg/m^3 (0.01 mg/L)	OECD SIDS, 2011	Limited study details reported in a secondary source; test concentrations were not specified.
		Crystalline silicon dioxide: 3-day inhalation study in rats exposed to 0, 10, or 100 mg/m^3 of cristobalite (6 hours/day). Increased granulocytes and other markers of cytotoxicity from the lung lavage fluid were reported in all treated animals. NOAEL: Not established LOAEL: 10 mg/m^3 (0.01 mg/L; lowest dose tested)	OECD SIDS, 2011	Limited study details reported in a secondary source; test substance identified as cristobalite.
		14-Day oral dietary study, rats. No clinical signs or other findings.	EC, 2000a	Secondary source, test substance unspecified silica, study details and

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		NOAEL: 24,200 mg/kg-day (highest dose tested) LOAEL: Not established		test conditions were not provided. The original study was in an unpublished report.
		6-Month oral dietary study, rats. No clinical signs or other findings. NOAEL: 497 mg/kg-day (highest dose tested) LOAEL: Not established	EC, 2000a	Secondary source, test substance unspecified silica, study details and test conditions were not provided. The original study was in an unpublished report.
		13-Week oral dietary study, rats. No clinical signs or other findings. NOAEL: 8% diet (highest dose tested) LOAEL: Not established	EC, 2000a	Secondary source, test substance unspecified silica, study details and test conditions were not provided. The original study was in an unpublished report.
		Up to 1 year inhalation study, rats. Enlarged and discolored lymph nodes, perivascular and peribronchiolar dust cell granuloma, necrotic cells. NOAEL: Not established LOAEL: <0.045 mg/L (lowest concentration tested)	EC, 2000a	Secondary source, test substance unspecified silica, study details and test conditions were not provided. The original study was in an unpublished report.
		4-Week oral dietary study, dog. No clinical signs or other findings. NOAEL 800 mg/kg-day (highest dose tested) LOAEL: Not established	EC, 2000a	Secondary source, test substance unspecified silica, study details and test conditions were not provided. The original study was in an unpublished report.
		In a 3-week dermal study, SiO_2 was applied to the intact and abraded skin of rabbits (2/sex/group) at doses of 0, 5,000, 10,000 mg/kg bw-day (nominal) for 18 hours/day, 5 days/week. No evidence of systemic toxicity or of gross or	ECHA, 2013	Unassignable. 21-Day dermal exposure study using a prolonged daily exposure regimen (18 h/d, 5 d/wk) instead of 6 h/d. Test substance form not specified.

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PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		microscopic pathology. NOAEL: ≥ 10,000 mg/kg bw-day (highest dose tested) LOAEL: Not established		
	Immune System Effects	**Amorphous silicon dioxide:** In a 12-month study, male Hartley Guinea pigs (20/dose) were exposed whole body to concentrations of 15 mg/m^3 (total dust, pyrogenic and precipitated); 15.9 mg/m^3 (total dust silica gel) and 6.9 - 9.9 mg/m^3 (respirable <4.7 µm) for 5.5 - 6 hours/day, 5 days/week. A few macrophages containing particles of amorphous silica were observed in the lungs and lymph nodes. NOAEC: ≥ 6 ≤ 9 mg/m^3 (≥ 0.006 ≤ 0.009 mg/L) LOAEC: Not established	ECHA, 2013	Sufficient study details reported in a secondary source. Three silica subclasses: Cab-O-Sil type (pyrogenic), named "fume" silica (Silica F), (CASRN 112945-52-5): commercial quality; Hi-Sil (precipitated): silica P (CASRN 112926-00-8) commercial quality; silica gel: silica G (CASRN 112926-00-8) commercial quality.
		Crystalline silicon dioxide: 15- or 27-week inhalation study in mice exposed to 0 or 5 mg/m^3 (6 hours/day, 5 days/week). Increased spleen weight and formation of plaque in the spleen was reported. NOAEL: Not established LOAEL: 5 mg/m^3 (0.005 mg/L; only dose tested)	OECD SIDS, 2011	Study details reported in a secondary source; test substance identified as quartz.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Skin Sensitization		**LOW: Amorphous silicon dioxide was not a dermal sensitizer in guinea pigs or humans. No experimental data were located for crystalline silicon dioxide. It is estimated that crystalline silicon dioxide, if present, is not likely to be a skin sensitizer based on analogy to amorphous silicon dioxide and professional judgment.**		
	Skin Sensitization	**Amorphous silicon dioxide:** Not sensitizing in a guinea pig maximization test.	EC, 2000a	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Amorphous silicon dioxide: Not sensitizing, humans (occupational surveys)	ECHA, 2013	Not assignable (no further details). Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5) or Silica gel, precipitated, crystalline-free. (CASRN 112926-00-8).
		Crystalline silicon dioxide: There is low potential for skin sensitization based on analogy to amorphous silicon dioxide. (Estimated by analogy)	Professional judgment	Estimated based on analogy to amorphous silicon dioxide and professional judgment; no experimental data located.
Respiratory Sensitization		**No data located.**		
	Respiratory Sensitization			No data located.
Eye Irritation		**LOW: Amorphous silicon dioxide was not irritating to slightly irritating in rabbits and slightly irritating in humans. If present, crystalline silicon dioxide would be assigned a Moderate hazard designation based on a study reporting fibrotic nodules in rabbit eyes.**		
	Eye Irritation	**Amorphous silicon dioxide:** Slightly irritating, rabbits	EC, 2000a	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Amorphous silicon dioxide: Slightly irritating, humans	EC, 2000a	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Amorphous silicon dioxide: Not irritating, rabbits (several studies)	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Silica, precipitated, crystalline-free

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				(CASRN 112926-00-8) or Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).
		Crystalline silicon dioxide: Quartz was reported to cause fibrotic nodules in rabbit eyes.	EC, 2000b	Limited study details reported in a secondary source; the severity and duration of the irritation was not specified. Irritation may be a result of mechanical mechanisms and scratching of the eye.
Dermal Irritation		**VERY LOW: Amorphous silicon dioxide was not irritating to the skin of rabbits or humans. No experimental data was located for crystalline silicon dioxide for this endpoint. It is estimated that crystalline silicon dioxide, if present, is not likely to be a skin irritant based on analogy to amorphous silicon dioxide and professional judgment.**		
	Dermal Irritation	**Amorphous silicon dioxide:** Not irritating, rabbits (several studies)	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. Silica, precipitated, crystalline-free (CAS-No. 112926-00-8) or Silica, amorphous, fumed, crystalline-free (CAS-No. 112945-52-5).
		Amorphous silicon dioxide: Not irritating, humans	EC, 2000a	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Crystalline silicon dioxide: There is low potential for skin irritation based on analogy to amorphous silicon dioxide. (Estimated by analogy)	Professional judgment	Estimated based on analogy to amorphous silicon dioxide and professional judgment; no experimental data located.
Endocrine Activity		**No data located.**		
				No data located.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Immunotoxicity		**Subjects that develop silicosis following exposure to crystalline silica have increased numbers of macrophages in the lungs. Effects on the lungs, such as inflammatory response, accumulation of alveolar macrophages, and infiltration of polymorphonuclear leukocytes were observed following inhalation exposures to amorphous and crystalline silica dust or aerosols in experimental animals.**		
	Immune System Effects	**Amorphous silicon dioxide:** In a 5-day inhalation study, male Wistar rats (10/group) were exposed nose-only to CAB-O-SIL M5 at concentrations of 0, 1.39, 5.41 and 25 mg/m^3 for 6 hours/day. Accumulation of alveolar macrophages accompanied by a few granulocytes/neutrophils (mid and high dose). Accumulation of macrophages accompanied by infiltration of polymorphonuclear leukocytes (high dose). Very slight macrophage accumulation still present following 3 months of recovery (high dose). NOAEC: 1.39 mg/m^3 (0.00139 mg/L) LOAEC: 5.41 mg/m^3 (0.00541 mg/L)	ECHA, 2013	Sufficient study details reported in a secondary source. CAB-O-SIL M5: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5), purity ca. 100%.
		Amorphous silicon dioxide: In a 13-week inhalation study, male Fischer 344 rats were exposed whole body to Aerosil 200 dust at a concentration of 0 or 50 mg/m^3 for 6 hours/day, 5 days/week. Quartz (crystalline silica) was used as positive control. Invasion of neutrophils and macrophages into alveoli after both amorphous and crystalline silica exposure; it was more pronounced with the amorphous type after 6.5 weeks but decreased during post-exposure period. Fibrosis was present in the alveolar septae, but subsided during recovery.	ECHA, 2013	Sufficient study details reported in a secondary source. Aerosil 200: Silica, amorphous, fumed, crystalline-free (CASRN 112945-52-5).

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		NOAEC: Not established LOAEC: 50 mg/m^3 (0.05 mg/L; lowest concentration tested)		
		Amorphous silicon dioxide: In a 13-week inhalation study, Wistar rats (70/sex/dose) were exposed whole-body to SiO_2 at concentrations of 0, 1.3, 5.9 or 31 mg/m^3 6 hours/day, 5 days/week. Swollen and spotted lungs and enlarged mediastinal lymph nodes. Accumulation of alveolar macrophages and granular material, cellular debris, polymorphonuclear leucocytes, increased septal cellularity. Accumulation of macrophages was seen in the mediastinal lymph nodes. Treatment-related microscopic changes in the nasal region. NOAEC: 1.3 mg/m^3 (0.0013 mg/L) LOAEC: 5.9 mg/m^3 (0.0059 mg/L)	ECHA, 2013	Sufficient study details reported in a secondary source. Comparative study including Aerosil 200, Aerosil R 974 (pyrogenic, hydrophobic), Sipernat 22S (precipitated, hydrophilic) as well as quartz (crystalline silica at a concentration of 58 mg/m3 was used as a positive control).
		Amorphous silicon dioxide: In a 13-week inhalation study, Wistar rats (70/sex/dose) were exposed whole-body to SiO_2 at concentrations of 0 or 35 mg/m^3 6 hours/day, 5 days/ week. Swollen and spotted lungs and enlarged mediastinal lymph nodes. Accumulation of alveolar macrophages, intra-alveolar polymorphonuclear leukocytes, and increased septal cellularity. NOAEC: Not established LOAEC: 35 mg/m^3 (0.035 mg/L; lowest concentration tested)	ECHA, 2013	Sufficient study details reported in a secondary source. Comparative study including Aerosil 200, Aerosil R 974 (pyrogenic, hydrophobic), Sipernat 22S (precipitated, hydrophilic) as well as quartz (crystalline silica at a concentration of 58 mg/m^3 was used as a positive control).
		Amorphous silicon dioxide: In a 14-Day inhalation study, Wistar rats were	EC, 2000a; ECHA, 2013	Sufficient study details reported in a secondary source. SIPERNAT 22S

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		exposed whole body to Sipernat 22S at concentrations of 46, 180 or 668 mg/m^3. Dose-dependent changes in lung characteristics (pale, spotted, spongy, alveolar interstitial pneumonia, early granulomata), accumulation of alveolar macrophages and particulate material in lungs. NOAEC: Not established LOAEC: <46 mg/m^3 (<0.046 mg/L; lowest concentration tested)		>98 % (SiO_2): CAS-Name: Silica, precipitated, crystalline-free (CASRN 112926-00-8).
		Amorphous silicon dioxide: In a 12-month study, male Hartley Guinea pigs (20/dose) were exposed whole body to concentrations of 15 mg/m^3 (total dust, pyrogenic and precipitated); 15.9 mg/m^3 (total dust silica gel) and 6.9 - 9.9 mg/m^3 (respirable ≤4.7 µm) for 5.5 - 6 hours/day, 5 days/week. A few macrophages containing particles of amorphous silica were observed in the lungs and lymph nodes. NOAEC: ≥ 6 ≤ 9 mg/m^3 (≥ 0.006 ≤ 0.009 mg/L) LOAEC: Not established	ECHA, 2013	Sufficient study details reported in a secondary source. Three silica subclasses: Cab-O-Sil type (pyrogenic), named "fume" silica (Silica F), (CASRN 112945-52-5): commercial quality; Hi-Sil (precipitated): silica P (CASRN 112926-00-8) commercial quality; silica gel: silica G (CASRN 112926-00-8) commercial quality.
		Amorphous silicon dioxide: In 13 and 18 month inhalation studies, male monkeys (10/group) were exposed whole body to 15 mg/m^3 (total dust, pyrogenic and precipitated); 15.9 mg/m^3 (total dust silica gel); and 6.9 - 9.9 mg/m^3 (respirable <4.7 µm) for 6 hours/day, 5 days/week. Inflammatory response: aggregation of great amounts of macrophages,	ECHA, 2013	Sufficient study details reported in a secondary source. Three silica subclasses: Cab-O-Sil type (pyrogenic), named "fume" silica (Silica F), (CASRN 112945-52-5): commercial quality; Hi-Sil (precipitated): silica P (CASRN 112926-00-8) commercial quality; silica gel: silica G (CASRN 112926-

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		physiological impairment of lung function. NOAEC: Not established LOAEC: ca. 15 mg/m^3 (0.015 mg/L) (nominal, lowest concentration tested)		00-8) commercial quality.
		Crystalline silicon dioxide: Human subjects with silicosis have increased macrophages and lymphocytes in the lungs, but minimal increases in neutrophils.	IARC, 1997	Test substance crystalline silica.
		Crystalline silicon dioxide: Exposure of rats to high concentrations of quartz leads to recruitment of neutrophils, marked persistent inflammation, and proliferative responses of the epithelium.	IARC, 1997	Test substance crystalline silica.
		Crystalline silicon dioxide: *In vitro* studies show that crystalline silica can stimulate the release of cytokines and growth factors from macrophages and epithelial cells; some evidence exists that these effects occur *in vivo* (species not specified).	IARC, 1997	Test substance crystalline silica.
		Crystalline silicon dioxide: Crystalline silica results in inflammatory cell recruitment in a dose-dependent manner (species not specified).	IARC, 1997	Test substance crystalline silica.
		Crystalline silicon dioxide: Crystalline silica deposited in the lungs causes macrophage injury and activation (species not stated).	IARC, 1997	Test substance crystalline silica.
		Crystalline silicon dioxide: 15- or 27-week inhalation study in mice exposed to 0 or 5 mg/m^3 (6 hours/day, 5 days/week). Increased spleen weight and formation of	OECD SIDS, 2011	Study details reported in a secondary source; test substance identified as quartz.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		plaque in the spleen was reported. NOAEL: Not established LOAEL: 5 mg/m^3 (0.005 mg/L; only dose tested)		
ECOTOXICITY				
ECOSAR Class		Not applicable		
Acute Aquatic Toxicity		**LOW: Amorphous silicon dioxide experimental LC_{50} and EC_{50} values for fish, daphnia and green algae are all >100 mg/L. The large MW, limited bioavailability and low water solubility suggest there will be no effects at saturation (NES). It is estimated by professional judgment that crystalline forms of silicon dioxide will also have low acute aquatic toxicity based on analogy to amorphous silicon dioxide. For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.**		
Fish LC_{50}		**Amorphous silicon dioxide:** Freshwater fish *Brachydanio rerio* 96-hour LC_{50} = 5,000 mg/L (Experimental)	EC, 2000a	Secondary source; test substance form, study details and test conditions were not provided.
		Amorphous silicon dioxide: Freshwater fish *Brachydanio rerio* 96-hour LC_{50} >10,000 mg/L; static test conditions; nominal concentrations: 1,000 and 10,000 mg/L (Experimental)	ECHA, 2013	Sufficient study details reported in a secondary source. GLP guideline study. Data are for amorphous silica.
		Amorphous and crystalline silicon dioxide: Freshwater fish LC_{50} >100 mg/L (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES. For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.

Silicon dioxide (amorphous) CASRN 7631-86-9			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid LC_{50}	**Amorphous silicon dioxide:** *Daphnia magna* 24-hour effect level based on mobility EL_{50} >10,000 mg/L (Experimental)	ECHA, 2013	Sufficient study details reported in a secondary source. Guideline study with acceptable restrictions (24 h instead of 48 h). Data are for Silica, amorphous.
	Amorphous silicon dioxide: *Ceriodaphnia dubia* $EC_{50} \approx$ 7,600 mg/L (Experimental)	EC, 2000a	Secondary source; test substance form, study details and test conditions were not provided. The original study was in an unpublished report.
	Amorphous and crystalline silicon dioxide: *Daphnia magna* LC_{50} >100 mg/L (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES. For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.
Green Algae EC_{50}	**Amorphous silicon dioxide:** Green algae *Selenastrum capricornutum* EC_{50} = 440 mg/L (Experimental)	EC, 2000a	Secondary source; test substance form, study details and test conditions were not provided. The original study was in an unpublished report.
	Amorphous and crystalline silicon dioxide: Green algae EC_{50} >100 mg/L (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES. For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.

Silicon dioxide (amorphous) CASRN 7631-86-9			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Chronic Aquatic Toxicity	**LOW: No experimental chronic data were located. The large MW, limited bioavailability and low water solubility suggest there will be no effects at saturation (NES). It is estimated by professional judgment that crystalline forms of silicon dioxide will also have low chronic aquatic toxicity based on large MW, limited bioavailability and low water solubility suggesting there will be no effects at saturation (NES). For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.**		
Fish ChV	**Amorphous and crystalline silicon dioxide:** Freshwater fish ChV >10 mg/L (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES. For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.
Daphnid ChV	**Amorphous and crystalline silicon dioxide:** Daphnia magna ChV >10 mg/L (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES. For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.
Green Algae ChV	**Amorphous and crystalline silicon dioxide:** Green algae ChV >10 mg/L (Estimated)	Professional judgment	The large MW, limited bioavailability and low water solubility suggest there will be NES. For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building some cell walls, skeletal structures or shells.
ENVIRONMENTAL FATE			

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Transport		**Silicon dioxide is a component of sand, soil, and sediment. Silicon dioxide has low water solubility and as a solid, it is expected to have a negligible estimated vapor pressure; these two factors correspond to an expected low Henry's Law constant. Amorphous forms of silicon dioxide will be relatively immobile in the environment with the exception of silicon dioxide dust in the atmosphere. Crystalline forms of silicon dioxide are expected to behave similarly in the environment and be relatively immobile with the exception of dust particulates.**		
	Henry's Law Constant (atm-m^3/mole)	**Amorphous and crystalline silicon dioxide:** $<10^{-8}$ (Estimated)	Professional judgment	Cutoff value for nonvolatile compounds based on professional judgment. This substance contains inorganic compounds that are outside the estimation domain of EPI.
	Sediment/Soil Adsorption/Desorption - K_{oc}	**Amorphous and crystalline silicon dioxide:** Not applicable (Estimated)	Professional judgment	As a component of sand, soil, and sediment, the soil-water partition coefficient is not applicable for silicon dioxide.
	Level III Fugacity Model			No data located.
Persistence		**HIGH: Amorphous silicon dioxide is expected to have high persistence in the environment because silicon dioxide is a recalcitrant, fully oxidized, inorganic substance and therefore will not biodegrade, oxidize in air, or undergo hydrolysis under environmental conditions. Silicon dioxide does not absorb light at environmentally relevant wavelengths and is not expected to photolyze. No degradation processes for silicon dioxide, under typical environmental conditions, were identified. It is also estimated that in the environment crystalline forms of silicon dioxide will behave similarly and have high persistence based on professional judgment.**		
Water	**Aerobic Biodegradation**	**Amorphous and crystalline silicon dioxide:** Recalcitrant (Estimated)	Professional judgment; OECD SIDS, 2004a	
	Volatilization Half-life for Model River	>1 year for both amorphous and crystalline silicon dioxide (Estimated)	Professional judgment	
	Volatilization Half-life for Model Lake	>1 year for both amorphous and crystalline silicon dioxide (Estimated)	Professional judgment	
Soil	**Aerobic Biodegradation**			No data located.
	Anaerobic Biodegradation	**Amorphous and crystalline silicon dioxide:** Recalcitrant (Estimated)	Professional judgment	

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Soil Biodegradation with Product Identification			No data located.
	Sediment/Water Biodegradation			No data located.
Air	**Atmospheric Half-life**	**Amorphous and crystalline silicon dioxide:** >1 year (Estimated)	Professional judgment	
Reactivity	**Photolysis**	**Amorphous and crystalline silicon dioxide:** Not a significant fate process (Estimated)	Professional judgment	Silicon dioxide does not absorb UV light at environmentally relevant wavelengths and is not expected to undergo photolysis.
	Hydrolysis	**Amorphous and crystalline silicon dioxide:** >1 year (Estimated)	Professional judgment	Silicon dioxide is a fully oxidized, insoluble, inorganic material and is not expected to undergo hydrolysis.
Environmental Half-life				Not all input parameters for this model were available to run the estimation software (EPI). This substance contains inorganic compounds that are outside the estimation domain of EPI.
Bioaccumulation		**LOW: Amorphous silicon dioxide is not expected to bioaccumulate based on professional judgment. Also based on professional judgment crystalline forms of silicon dioxide are not expected to bioaccumulate. Although for some organisms in marine habitats, silica and silicates are used as nutrients. They are used for building some cell walls, skeletal structures or shells.**		
	Fish BCF	**Amorphous and crystalline silicon dioxide:** <100 (Estimated)	Professional judgment	This inorganic compound is not amenable to available estimation methods.
	Other BCF	For some organisms in marine habitats, silica and silicates are used as nutrients; they are used for building skeletal structures or shells. For example, diatoms absorb soluble silica from water and metabolize it for an external skeleton.	EC, 2000b; OECD SIDS, 2004a; HSDB, 2009	Supporting information about the bioaccumulation of this compound in marine environments. Some organisms in marine habitats use silica and silicates as nutrients; they are used for building some cell walls, skeletal structures or shells.

Silicon dioxide (amorphous) CASRN 7631-86-9				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	BAF	**Amorphous and crystalline silicon dioxide:** <100 (Estimated)	Professional judgment	This inorganic compound is not amenable to available estimation methods.
	Metabolism in Fish			No data located.
ENVIRONMENTAL MONITORING AND BIOMONITORING				
Environmental Monitoring		Silicon dioxide is a ubiquitous mineral that occurs naturally in the environment as sand and quartz (HSDB, 2009).		
Ecological Biomonitoring		No data located.		
Human Biomonitoring		No data located.		

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5 Potential Exposure to Flame Retardants and Other Life-Cycle Considerations

Many factors must be considered to evaluate the risk to human health and the environment posed by any flame-retardant chemical. Risk is a function of two parameters, hazard and exposure. The hazard associated with a particular substance or chemical is its potential to impair human health, safety, or ecological health. While some degree of hazard can be assigned to most substances, the toxicity and harmful effects of other substances are not fully understood. The exposure potential of a given substance is a function of the exposure route (inhalation, ingestion, and dermal), the concentration of the substance in the contact media, and the frequency and duration of the exposure.

The purpose of this chapter is to identify the highest priority routes of exposure to flame-retardant chemicals used in printed circuit boards (PCBs). Section 5.1 through Section 5.4 provide general background regarding potential exposure pathways that can occur during different life-cycle stages, discuss factors that affect exposure potential in an industrial setting, provide process descriptions for the industrial operations involved in the PCB manufacturing supply chain (identifying the potential primary release points and exposure pathways), and discuss potential consumer and environmental exposures. Following this general discussion, Section 5.5 highlights life-cycle considerations for the ten flame retardants evaluated by this partnership. The chapter is intended to help the reader identify and characterize the exposure potential of flame-retardant chemicals based on factors including physical and chemical properties and reactive versus additive incorporation into the epoxy resin. The information presented in this chapter should be considered with the chemical-specific hazard assesment presented in Chapter 4.

Exposure can occur at many points in the life cycle of a flame-retardant chemical. There is a potential for occupational exposures during industrial operations; exposure to consumers while the flame-retardant product is being used; and exposure to the general population and environment when releases occur from product disposal or end-of-life recycling. Figure 5-1 presents a simplified life cycle for a flame-retardant chemical used in a PCB, and Table 5-1 summarizes the potential exposure routes that can occur during each of these life-cycle stages. The remaining sections of Chapter 5 discuss the information summarized in Figure 5-1 and Table 5-1 in more detail.

Figure 5-1. Life Cycle of Flame-Retardant Chemicals in PCBs (example with Tetrabromobisphenol A (TBBPA) as reactive FR)

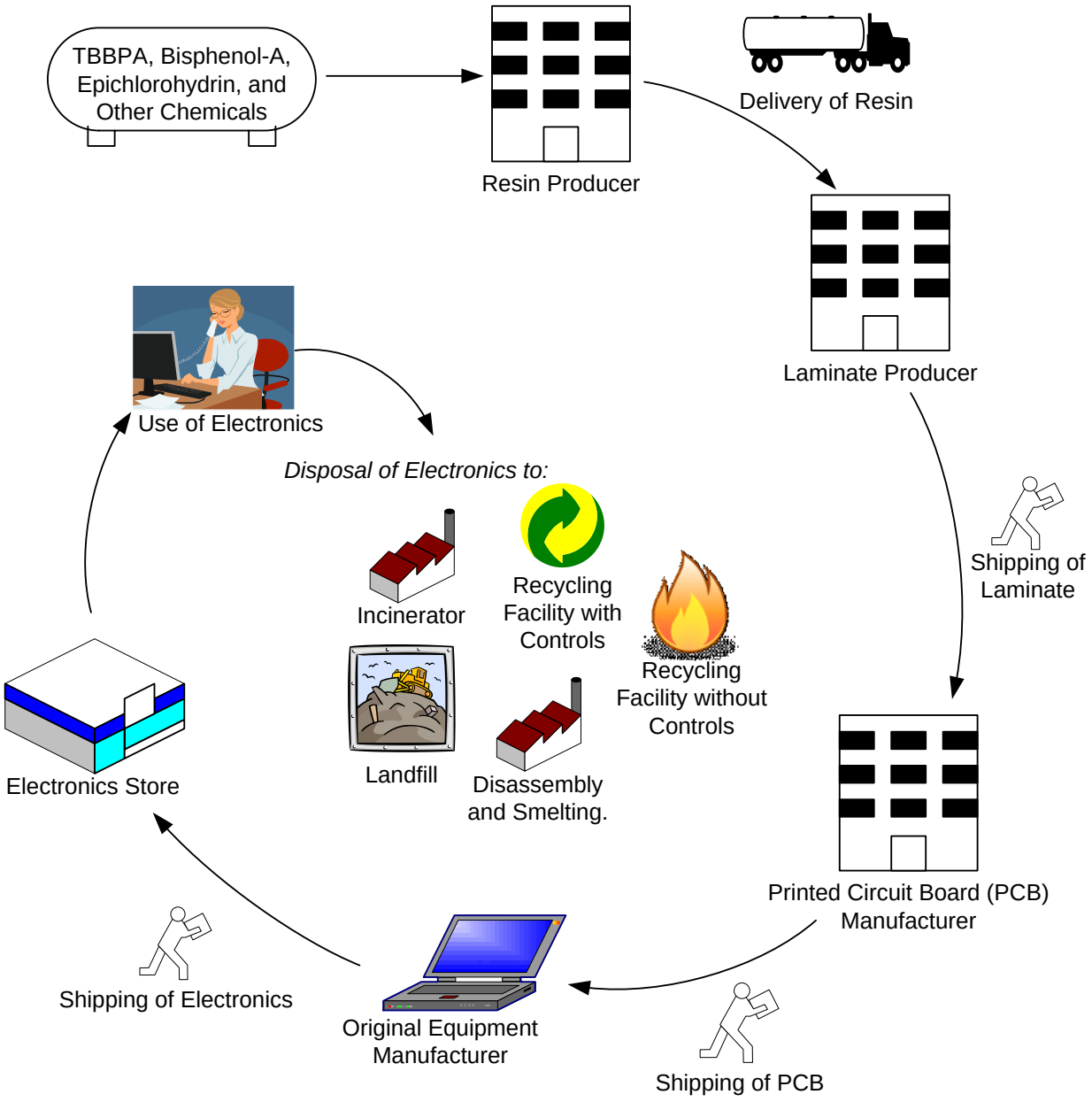


Table 5-1. Potential Exposure to Flame-Retardant Chemicals throughout Their Life Cycle in PCBs

Life Cycle Stage	Potential Exposure
Reactive Flame Retardants	
Manufacture: Chemical manufacture, resin formulation	Manufacture emissions will vary based on manufacturing practices and physical/chemical properties; direct exposure is possible because the neat chemical is handled.
Pre-impregnated material (prepreg) and laminate production	Cutting of material can release minor amounts of dust that contains epoxy resin. Reactive flame retardants are part of the polymer (chemically bound), and only trace amounts of unreacted flame retardant are anticipated to remain in the polymer matrix. Trace quantities are currently unknown* and/or will vary based on manufacturing methods and processes.
PCB manufacturing and assembly	Remaining, unreacted flame retardant may offgas; PCB manufacturing processes, such as drilling, edging, and routing, cut into the base material. In electronic assembly, some soldering processes could induce thermal stress on resins, which could yield degradation products. Testing is needed to determine the potential for formation of these products.
Use	Only residual unreacted flame retardant is available to offgas during use. In order for exposure to occur, offgassing from residual unreacted flame retardant would have to escape product casing. Testing is needed to determine exposure potential.
End of Life	*Disassembly/Recycling:* Disassembling electronics and shredding PCBs can release dust that contains epoxy resin. Reactive flame retardants are chemically bound to the polymer; however, levels of exposure and any subsequent effects of exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, are unknown. *Landfill*: Testing needs to be conducted to determine exposure potential from leaching from PCBs. *Incineration*: Combustion by-products need to be considered (see combustion experiments). *Open Burning*: Combustion by-products need to be considered (see combustion experiments). *Smelting*: Combustion by-products need to be considered.
Additive Flame Retardants	
Manufacture: Chemical manufacture, resin formulation	Manufacture emissions will vary based on manufacturing practices and physical/chemical properties; direct exposure is possible because the neat chemical is handled.
Prepreg and laminate production	Cutting of material can release minor amounts of dust that contains epoxy resin. Additive flame retardants are not chemically bound to the polymer, and their potential to offgas or leach out of the product is not known. Physical/chemical properties, such as vapor pressure and water solubility, may contribute to the potential for exposure to these chemicals.
PCB manufacturing and assembly	Additive flame retardant may offgas; PCB processes, such as drilling, edging, and routing, cut into the base material. In electronic assembly, reflow or wave soldering processes could induce thermal stress on resins, which could yield offgas products. Physical/chemical properties, such as vapor pressure and water solubility, may contribute to the potential for exposure to these chemicals.
Use	Although flame retardants are embedded in the polymer matrix, testing needs to be conducted to better understand the offgassing potential of additive flame retardants. Dermal exposure is not anticipated since the flame retardants are embedded in the polymer matrix.
End of Life	*Disassembly/Recycling:* Disassembling electronics and shredding PCBs can release dust that contains epoxy resin. Additive flame retardants are not chemically bound to the polymer and can be released through the dust. Physical/chemical properties, such as vapor pressure, may contribute to the potential for exposure to these chemicals. *Landfill*: Testing needs to be conducted to determine exposure potential from leaching from PCBs. *Incineration*: Combustion by-products need to be considered (see combustion experiments). *Open Burning*: Combustion by-products need to be considered (see combustion experiments). *Smelting*: Combustion by-products need to be considered.

*For TBBPA, Sellstrom and Jansen (1995) found about 0.7 micrograms of residual (or "free") TBBPA per gram of PCB.

5.1 Potential Exposure Pathways and Routes (General)

The risk associated with a given chemical or substance is largely dependent on how the exposure potentially occurs. For example, the toxicological effects associated with inhaling the chemical are different from those associated with ingesting the chemical through food or water. As a result, exposure is typically characterized by different pathways and routes.

An exposure pathway is the physical course a chemical takes from the source of release to the organism that is exposed. The exposure route is how the chemical gets inside the organism. The three primary routes of exposure are inhalation, dermal absorption, and ingestion. Depending on the hazard of the chemical, exposure from only one or perhaps all three routes may result in risk.

Expected environmental releases and potential exposure routes of chemicals are dependent upon their physical and chemical properties. For example, a highly volatile liquid can readily evaporate from mix tanks, potentially resulting in fugitive air releases and potential exposures to workers who breathe the vapors, while chemicals manufactured as solids may expose workers to fugitive dust that may be generated, but are unlikely to generate vapors. Each potential exposure route, along with appropriate endpoints, should be evaluated independently. Endpoints are the specific toxicological effect, such as cancer, reproductive harm, or organ/tissue damage. There are circumstances when a chemical has serious effects for a given endpoint, but due to physical and chemical properties as well as environmental fate, there is minimal potential for the chemical to be transported from the release point to the endpoint. This may essentially eliminate the potential pathway and route of exposure and, therefore, eliminate the associated risk.

Table 5-2 highlights key physical, chemical, and fate properties that affect the likelihood for exposure to occur: the physical state of the chemical, vapor pressure, water solubility, log K_{ow}, bioaccumulation potential, and persistence. The relevance of each physical, chemical, and fate property, as well as its impact on exposure potential, is summarized in Table 5-2. Detailed descriptions of these properties and how they can be used to assess potential environmental release, exposure, and partitioning, as well as insight into a chemical's likelihood to cause adverse toxicological effects, can be found in Chapter 4. More detailed information on physical, chemical, and fate properties of each flame-retardant chemical can be found in the full chemical hazard profiles in Section 4.9.

Table 5-2. Key Physical/Chemical and Fate Properties of Flame-Retardant Chemicals

Physical State of Chemical (ambient conditions)

Relevance to exposure: Indicates if a chemical substance is a solid, liquid, or gas under ambient conditions. This is determined from the melting and boiling points. Chemicals with a melting point more than 25°C are considered solid. Those with a melting point less than 25°C and a boiling point more than 25°C are considered liquid and those with a boiling point less than 25°C are considered a gas. Physical state influences potential for dermal and inhalation exposure. For chemicals that exist as a gas, there is generally a potential for direct inhalation but not dermal exposure. For solids, there is potential for the inhalation and ingestion of dust particles and dermal contact. For liquids, there is potential for direct dermal contact but not for direct inhalation of the liquid (except in operations that produce aerosols).

TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphos-phinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid

Vapor Pressure (mm Hg) at 25°C

Relevance to exposure: Indicates the potential for a chemical to volatilize into the atmosphere. If a chemical has a vapor pressure leading to volatilization at room temperature or typical environmental conditions, then the chemical may evaporate and present the potential for inhalation of the gas or vapor. For a Design for the Environment (DfE) chemical alternatives assessment, inhalation exposure is assumed to occur if the vapor pressure is greater than 1×10^{-8} mm Hg. A default value of $<10^{-8}$ was assigned for chemicals without data that are anticipated to be nonvolatile this is based on EPA HPV assessment guidance (U.S. EPA 1999).

TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphos-phinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
4.7×10^{-8}	$<10^{-8b,c}$	2.2×10^{-5a}	$<10^{-8b,c}$	$<10^{-8b,c}$	$<10^{-8c}$	$<10^{-8c}$	$<10^{-8d}$	$<10^{-8d}$	$<10^{-8c}$

[a] Extrapolated. [b] Estimated based on polymer assessment literature (Boethling and Nabholz, 1997). [c] Estimated based on HPV guidance for nonvolatile compounds. [d] Estimated.

Water Solubility (mg/L)

Relevance to exposure: Indicates the potential of a chemical to dissolve in water and form an aqueous solution. Water soluble chemicals present a higher potential for human exposure through the ingestion of contaminated drinking water (including well water). In general, absorption after oral ingestion of a chemical with a water solubility less than 10^{-3} mg/L is not expected. Water soluble chemicals are more likely to be transported into groundwater, absorbed through the gastrointestinal tract or lungs, partition to aquatic compartments, and undergo atmospheric removal by rain washout. A water solubility of 10^{-3} mg/L is used for large, high molecular weight (MW) non-ionic polymers according to the literature concerning polymer assessment (Boethling and Nabholz, 1997). A substance with water solubility at or below 10^{-3} mg/L is considered insoluble.

TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphos-phinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
4.16	$<0.001^{a,b,c}$	$3{,}574^{e}$	$\leq 0.62^{d}$ $<0.001^{c}$	8.4 (n=1)[b] 0.1 (n=2)[b] ≤ 0.001 (n≥3)[a,b,c]	≤0.09 at 20 °C, pH 6-7	2.5×10^{3}	2.0×10^{4}	120	1.78 at 20°C, pH 8.3

[a] Estimated based on EPA High Production Volume assessment guidance. [b] Estimated. [c] Estimated based on polymer assessment literature (Boethling and Nabholz, 1997). [d] Estimated based on proprietary components with MW <1,000. [e] Measured value for the hydrolysis product of DOPO.

Table 5-2. Key Physical/Chemical and Fate Properties of Flame-Retardant Chemicals (Continued)

Log K_{ow}

Relevance to exposure: Indicates a chemical's tendency to partition between water and lipids in biological organisms. A high log K_{ow} value indicates that the chemical is more soluble in octanol (lipophilic) than in water, while a low log K_{ow} value means that the chemical is more soluble in water than in octanol. Log K_{ow} can be used to evaluate absorption and distribution in biological organisms, potential aquatic exposure, and potential general population exposure via ingestion. Generally, chemicals with a log K_{ow} <4 are water soluble and bioavailable, chemicals with a log K_{ow} ≥4 tend to bioaccumulate. Chemicals with a high log K_{ow} also tend to bind strongly to soil and sediment. Log K_{ow} cannot be measured for inorganic substances, polymers, and other materials that are not soluble in either water or octanol. This is indicated in the table with "No data".

TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphos-phinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
4.54	7.4 (n=0)[a] 11 (n=1)[a] No data (n≥2)	1.87[a]	3.7-7[b]	3.4 (n=1)[a] 4.4 (n=2)[a] 5.3 (n=3)[a] 6.3 (n=4)[a]	No data	-0.44[a]	<-2[a]	No data	No data

[a] Estimated. [b] Estimated based on proprietary components with MW <1,000.

Bioaccumulation Potential

Relevance to exposure: Indicates the degree to which a chemical substance may increase in concentration within a trophic level. Bioconcentration describes the increase in tissue concentration relative to the water concentrations (environmental sources); bioaccumulation generally includes dietary and environmental sources. As chemicals bioconcentrate or bioaccumulate, there is a higher potential for them to reach a level where a toxic effect may be expressed. Estimated and/or measured bioconcentration and bioaccumulation values are presented as ranges based on relevant DfE hazard categories for each chemical. The DfE Alternatives Assessment criteria for bioaccumulation potential considers both the bioaccumulation factor (BAF) and bioconcentration factor (BCF) values, as follows: Very High (VH) if BAF (log BAF) or BCF (log BCF) is >5,000 (>3.7); High (H) if BAF or BCF is between 5,000 (3.7-3) and 1,000; Moderate (M) if BAF or BCF is between <1,000 and 100 (<3-2); and Low (L) if BAF or BCF is <100 (<2) (see *DfE Program Alternatives Assessment Criteria for Hazard Evaluation*).

TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphos-phinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
Moderate (100-<1,000)	High (1,000-5,000)[b]	Low (<100)[b]	High (1,000-5,000)[b]	High (1,000-5,000)[b]	Low (<100)[a]	Low (<100)[a]	Low (<100)[b]	Low (<100)[a]	Low (<100)[a]

[a] Based on professional judgment. [b] Based on estimated data.

Table 5-2. Key Physical/Chemical and Fate Properties of Flame-Retardant Chemicals (Continued)

Persistence									
Relevance to exposure: Indicates the length of time required for a chemical substance to be completely converted to small building blocks including water, carbon dioxide, and ammonia ("ultimate degradation"). Persistence is typically expressed as a "half-life", which is the time for the amount of the substance to be reduced by one half. For a DfE chemical alternatives assessment, persistent chemicals include those that have metabolic or degradation products that have long half-lives. The longer a chemical or its degradation/metabolism products exist in the environment, the higher the likelihood for human or environmental exposure. "Compartments" refer to those environmental media to which chemicals may partition and include soil, sediment, water and air as standard compartments for fate assessment. Persistence is considered Very High (VH) if the half-life is >180 days or recalcitrant; High (H) if the half-life is 60-180 days; Moderate (M) if the half-life is <60 days but ≥16 days; Low (L) if half-life is <16 days OR readily passes biodegradability test not including the 10-day window; and Very Low (VL) if passes biodegradability test with 10-day window (see *DfE Program Alternatives Assessment Criteria for Hazard Evaluation*).									
TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphos-phinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
High (60-180 days)	Very High (>180 days)[c]	High (60-180 days)[a]	Very High (>180 days)[c]	Very High (>180 days)[c]	High (60-180 days)[b]	High (60-180 days)[b]	High (60-180 days)[b]	High (60-180 days)[b]	High (60-180 days)[b]
[a] Based on results from biodegradation estimation model. [b] Based on professional judgment. [c] Estimated based on polymer assessment literature (Boethling and Nabholz, 1997).									

5.2 Potential Occupational Releases and Exposures

The unit operations associated with each part of the PCB manufacturing supply chain result in a unique set of potential release points and occupational exposures to flame-retardant chemicals. This section provides a general overview of occupational pathways and routes of exposure, and then identifies the specific processes and corresponding potential release and exposure points for the unit operations associated with the manufacturing of flame retardants, epoxy resins, laminates, and PCBs. It should be noted that many of the potential occupational exposures identified here have been reduced or eliminated by the use of engineering controls and personal protective equipment. Also, the level of exposure will vary considerably between workers and the general population. Some releases will only result in exposure for workers, while other releases result in exposures for the environment and the general population.

Inhalation Exposures

The physical state of the chemical during chemical manufacturing and downstream processing significantly affects the potential for inhalation exposure of workers. In particular, the physical state can result in three types of inhalation exposures that should be evaluated.

Dust: Chemicals that are manufactured, processed, and used as solids have the potential to result in occupational exposure to fugitive dusts. The potential for fugitive dust formation depends on whether the solid chemical is handled in the crystalline form, as an amorphous solid, or as a fine powder, as well as the particle size distribution and solids handling techniques. If there is exposure to dust, the level of exposure is directly proportional to the concentration of chemical in the particulate form. Therefore, a flame retardant that is used at a lower concentration results in a decreased exposure from this pathway and route (assuming that an equivalent amount of dust is inhaled).

When assessing occupational exposures to flame-retardant chemicals, it is important to note the physical state of the chemical at the potential point of release and contact. The pure chemical may be manufactured as a solid powder, indicating a potential exposure to dust. However, it may be formulated into solution before any workers come in contact with it, thereby eliminating inhalation exposure to dust as a potential route. It is also important to note that the size of the dust particles may have a profound influence on the potential hazards associated with inhalation exposures for those materials that are not anticipated to be absorbed in the lungs. For these materials, the potential hazards are typically associated with smaller, respirable particles (generally those less than 10 microns in diameter).

Vapor: Exposure to vapors can occur when liquid chemicals volatilize during manufacturing, processing, and use. Most chemical manufacturing operations occur in closed systems that contain vapors. However, fugitive emissions are expected during open mixing operations, transfer operations, and loading/unloading of raw materials. More volatile chemicals volatilize more quickly and result in greater fugitive releases and higher occupational exposures than less volatile chemicals. Therefore, vapor pressure is a key indicator of potential occupational exposures to vapors.

Mist: Both volatile and nonvolatile liquids can result in inhalation exposure if manufacturing or use operations result in the formation of mist. It is unlikely that flame-retardant chemicals used in PCBs will be applied as a mist.

Dermal Exposures

Occupational dermal exposure is also affected by the physical state of the chemical at the point of release and contact. For example, the likelihood of liquids being splashed or spilled during sampling and drumming operations is different than for similar operations involving polymerized solids, powders, or pellets. Dermal exposure is also generally assumed to be proportional to the concentration of chemical in the formulation. For example, the dermal exposure from contacting a pure chemical is greater than the exposure from contacting a solution that contains only 10 percent of the chemical. Screening-level evaluations of occupational dermal exposure can be based on the worker activities involving the chemical. For example, there may be significant exposure when workers handle bags of solid materials during loading and transfer operations. Maintenance and cleanup activities during shutdown procedures, connecting transfer lines, and sampling activities also result in potential dermal exposures.

Ingestion Exposures

Occupational exposures via ingestion typically occur unintentionally when workers eat food or drink water that has become contaminated with chemicals. Several pathways should be considered. Often the primary pathway is poor worker hygiene (eating, drinking, or smoking with unwashed hands). First, dust particles may spread throughout the facility and settle (or deposit) on tables, lunchroom surfaces, or even on food itself. Vapors may similarly spread throughout the facility and may adsorb into food and drinking water. Another potential pathway for ingestion occurs from dust particles that are too large to be absorbed through the lungs. These "non-respirable particles" are often swallowed, resulting in exposures from this route. While ingestion is considered to be a realistic route of exposure to workers, it is often considered less significant when compared to inhalation and dermal exposures, based on the relative exposure quantities. On the other hand, ingestion during consumer use and to the general population is often as significant as or more important than the inhalation and dermal routes. If persistent and bioaccumulative compounds get into the environment and build up in the food chain, they can become a significant exposure concern.

5.2.1 Flame Retardant and Epoxy Resin Manufacturing

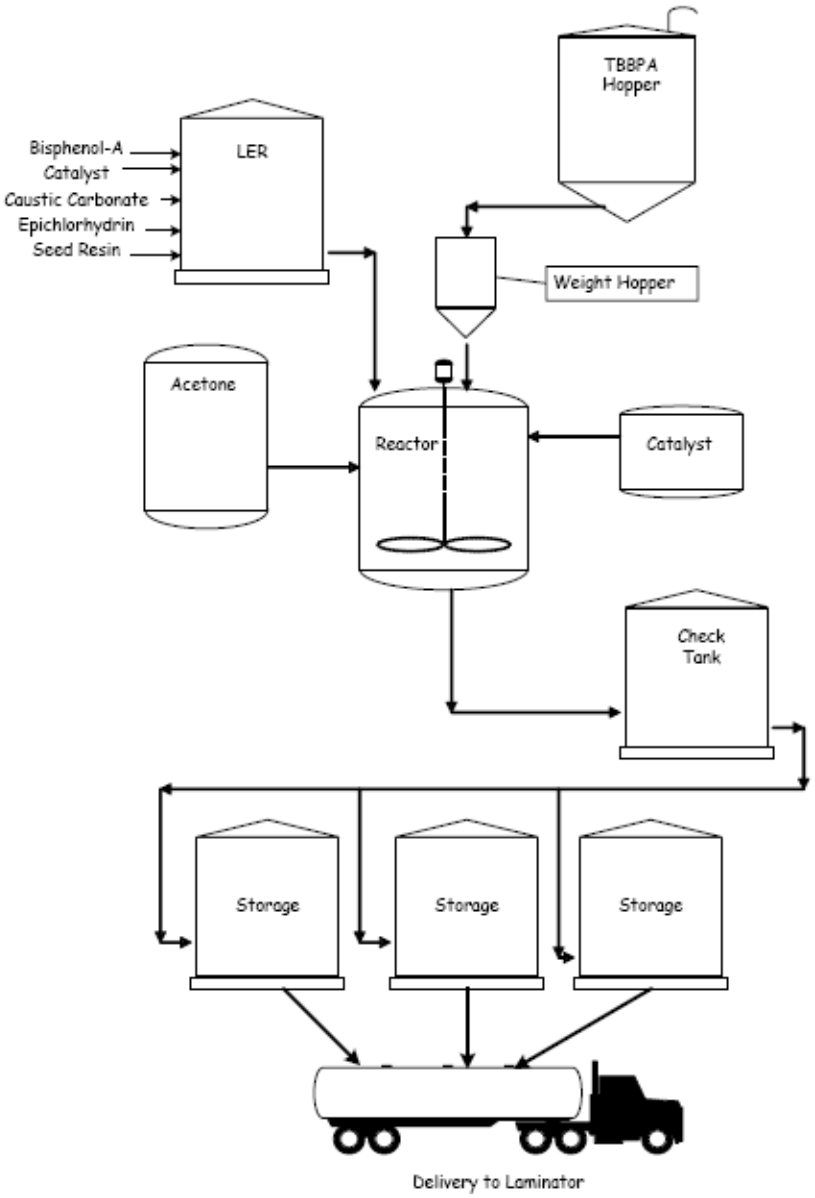
The specific unit operations, operating conditions, transfer procedures, and packaging operations vary with the manufacture of different flame-retardant and resin chemicals. Potential releases and occupational exposures will depend on each of these parameters. While it is outside the scope of this report to identify and quantify the releases and exposures associated with individual chemicals, this section presents a general description of typical chemical manufacturing processes and identifies potential releases.

Figure 5-2 presents a generic process flow diagram for epoxy resin manufacturing. Production volumes and batch sizes associated with flame-retardant and epoxy resin chemicals typically require the raw materials to be stored in large tanks or drums until use. The first step in most

epoxy resin manufacturing processes for standard Flame Resistant 4 materials is to load the raw materials into some type of reactor or mix tanks – as shown in Figure 5-2, the tanks labeled as liquid epoxy resin and reactive flame retardant (e.g. TBBPA) hopper. Next, large-quantity liquids are typically pumped into the reactor, and small-quantity raw materials may be manually introduced or carefully metered via automated systems. Releases may occur from these operations, but occupational exposure potential is typically small due to the number of safety procedures and engineering controls in place.

Throughout the resin manufacturing process, there are several release points that may pose an exposure risk to workers: packaging operations, leaks from pumps and tanks, fugitive emissions from equipment, cleaning of process equipment, and product sampling activities. Additionally, crude or finished products are often stored on-site in drums, day-tanks, or more permanent storage vessels until the flame-retardant epoxy resin is packaged and shipped to the laminator. The transfer and packaging operations, as well as any routine and unplanned maintenance activities, may result in releases of and exposures to hazardous chemicals.

Figure 5-2. Epoxy Resin Manufacturing Process (example with TBBPA as reactive FR)



5.2.2 Laminate and Printed Circuit Board Manufacturing

The laminate and PCB manufacturing processes, summarized in Figure 5-3 and Figure 5-4, can result in occupational exposures to process chemicals if protective measures are not put in place. The potential release of flame-retardant chemicals from laminates is not known, but is probably very low, if there is any at all. As shown in Figure 5-3, the laminator combines the flame-retardant epoxy resin with a curing agent (or hardener) and a catalyst in a mix tank as a first step of the laminate manufacturing process. From there, woven fiberglass mats are embedded with the epoxy resin, resulting in prepreg sheets. A copper clad laminate (CCL) is then assembled by layering the prepreg sheets with copper sheets and stainless steel caul plates, as shown in Figure 5-3. The finished CCL is then shipped to the PCB manufacturing facility.

As summarized in Figure 5-4, PCB manufacturing involves numerous chemical and electrochemical processes to cut, drill, clean, plate, and etch conductive pathways. Almost all of these processes involve immersion of equipment or work pieces into a series of process baths, with each bath followed by a rinsing step. For example, the process of drilling holes in the PCB involves a series of individual steps, including cleaning (or desmearing) the holes with chemicals or gas plasma and plating the holes with copper, and each step requires at least one process bath and rinsing.

Many PCB manufacturers have implemented relatively simple techniques to reduce the amount of chemicals that enter wastewater, such as withdrawing equipment from tanks slowly to allow maximum drainage back into the process tank (CA EPA, 2005). Most manufacturing facilities prevent worker exposure through use of engineering controls, personal protective equipment, and safe work practices.

Figure 5-3. Laminate Manufacturing Process

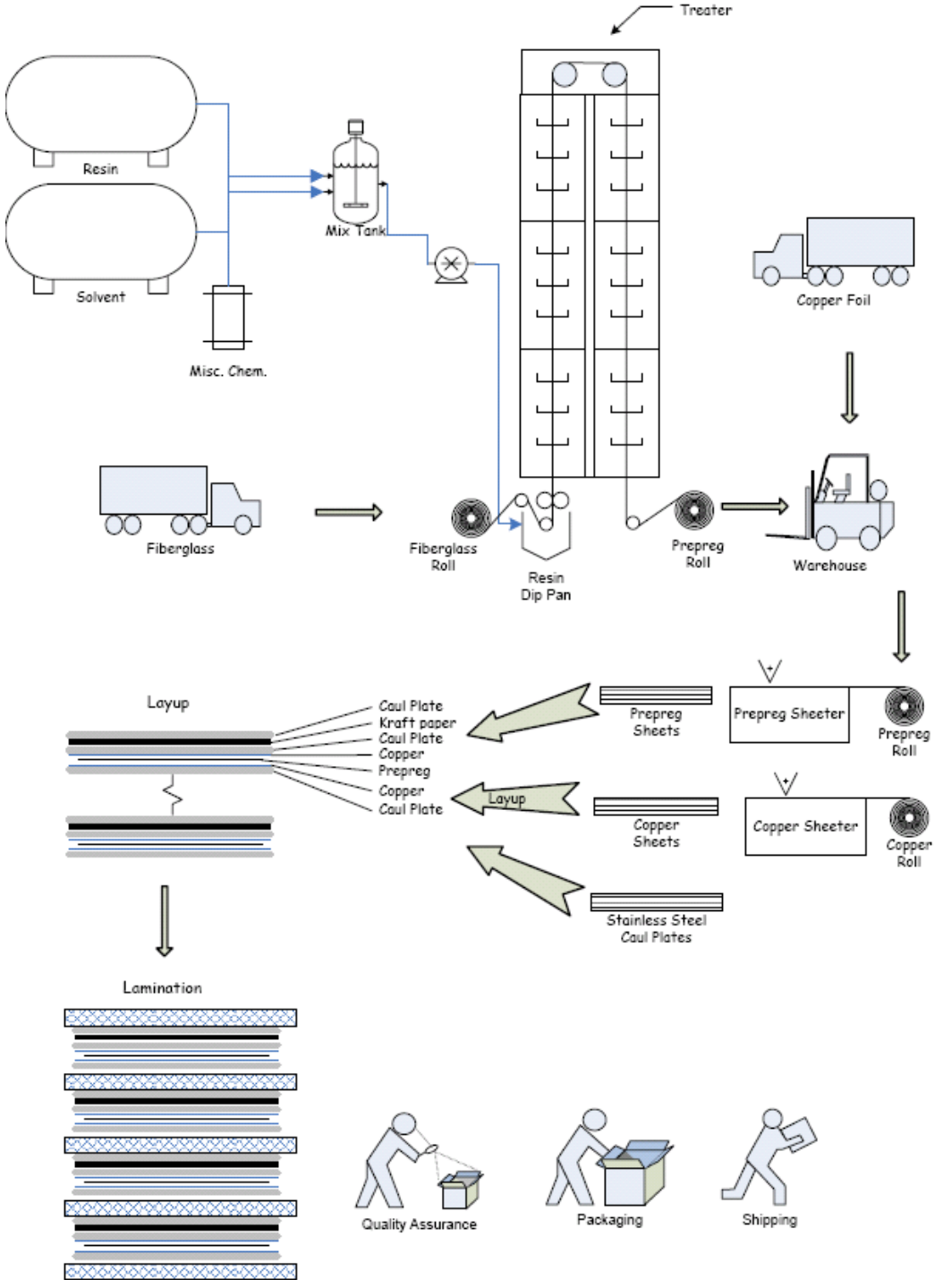
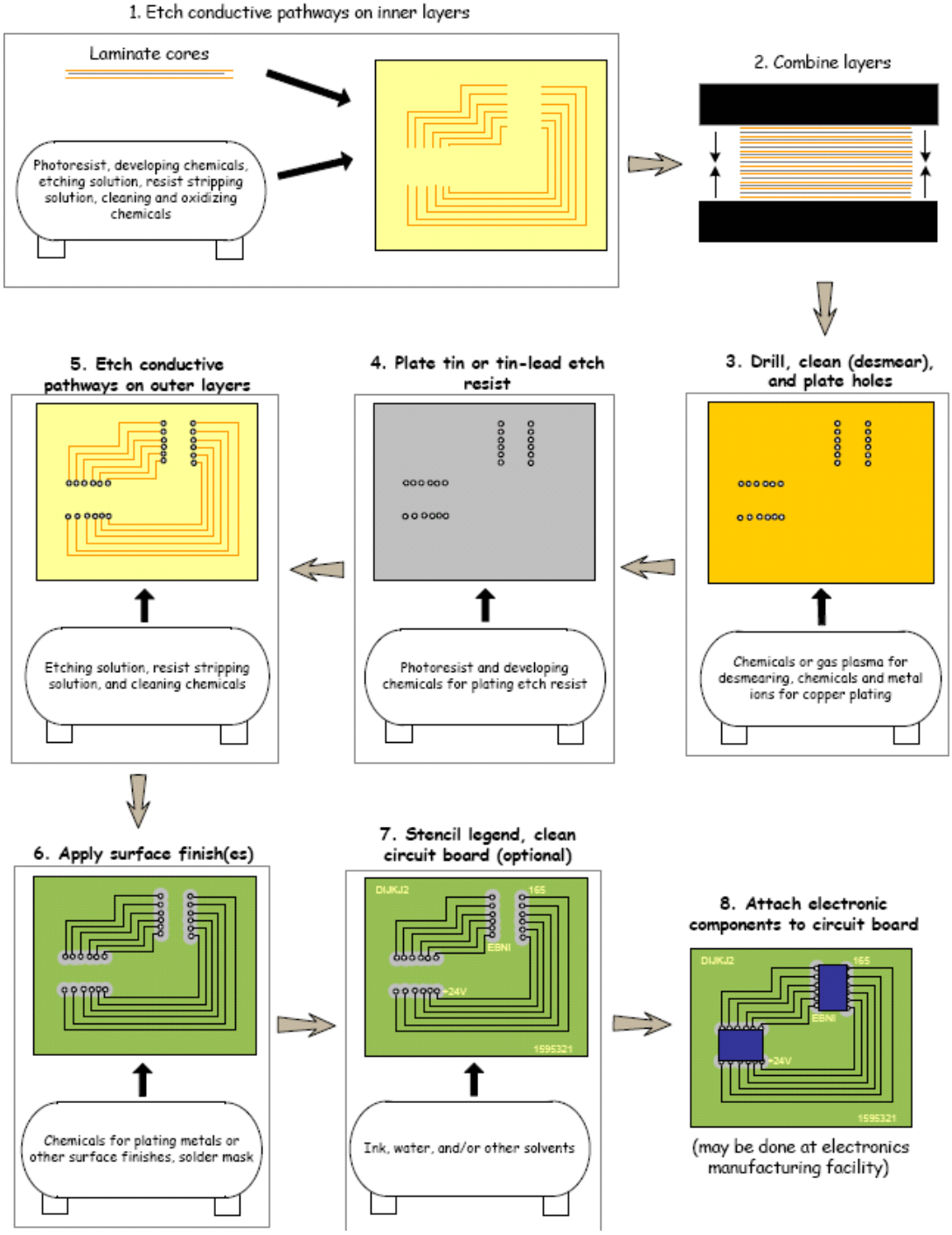


Figure 5-4. Printed Circuit Board Manufacturing Process



5.2.3 Best Practices

Incorporating best practices into the manufacturing process can reduce the potential for exposure. The Bromine Science and Environmental Forum (BSEF) set up the Voluntary Emissions Control Action Programme (VECAP) "to manage, monitor and minimize industrial emissions of brominated flame retardants into the environment through partnership with Small and Medium-sized Enterprises." The program started with decabromodiphenyl ether in Europe. VECAP members follow six central steps to continually improve their processes and reduce emissions: (1) commitment to the VECAP code of good practices; (2) self-audit; (3) mass balance; (4) baseline emissions survey; (5) emissions improvement plan; and (6) implementation and continuous improvement (BSEF, 2007).

ISO, the International Organization for Standardization, has also developed a series of environmental management standards under the 14000 label. ISO 14000 standards establish a "holistic, strategic approach" for continually reducing negative environmental impacts. They are intended to cover a wide range of operations, and thus are not specific to brominated flame retardants (ISO, 2007).

5.3 Potential Consumer and General Population Exposures

Exposures to consumers and the environment are different from exposures to workers and should be evaluated separately for a number of reasons. Occupational exposures typically result from direct contact with chemicals at relatively high concentrations while workers are conducting specific tasks. Conversely, consumers may be exposed over a much longer period, but to a much smaller level because the chemical is incorporated into the product. Also, the general population and the environment will be exposed via different pathways and routes from workers and consumers. For example, a person who does not own a product containing a flame-retardant PCB may still be exposed if the chemical leaches from the disposed product into the drinking water supply. Once in the water supply, groundwater, or surface water, it can be ingested by people or consumed by fish and other animals. Similarly, if the chemical is released to the atmosphere during manufacture, use, or disposal, it may settle out on food crops and be ingested directly by people, or by cattle or other livestock. If the chemical is bioaccumulative, it may concentrate in the animal and reach people through the food chain. For these reasons, exposure to the environment and the general population should be assessed independently from occupational exposure.

A quantitative exposure assessment is outside the scope of this report. However, the primary pathways and routes from environmental, general population, and consumer exposures are discussed in the following sections. Important chemical-specific factors that may help the reader compare potential exposure between various flame-retardant alternatives are also discussed.

5.3.1 Physical and Chemical Properties Affecting Exposures

As previously discussed, the physical and chemical properties of a chemical often determine the pathways and routes of exposure. In addition, the physical and chemical properties will affect how the chemical becomes distributed in the environment once it is released, which will, in turn, influence the potential for the chemical to be transported from the release point to the receptor.

Information about persistence, bioaccumulation, and physical and chemical properties affecting transport in the environment is presented in Section 4.3 of this report as well as Table 5-2.

As discussed in Chapter 3, flame-retardant chemicals can be classified as either additive or reactive and this distinction may affect exposure. Additive flame retardants are added to a manufactured product without bonding or reacting with the product, whereas reactive flame retardants are chemically reacted into the raw materials that are used to make the final product. As of 2008, most PCBs use reactive TBBPA, which loses the identity of the starting monomer material during polymerization. Because they are chemically bound to PCBs, reactive flame retardants are much less likely to pose occupational, consumer, or environmental exposure concerns than additive flame retardants. Moreover, the polymerization processes are typically conducted in totally enclosed systems, thus minimizing the potential for occupational exposure. It should be noted, however, that reactive chemicals or close analogs could be released from the finished product if a portion of the chemicals is not completely reacted during the polymerization process. According to a 1995 study, a trace amount of starting TBBPA material is unreacted after polymerization (4 micrograms per gram) (Sellstrom and Jansson, 1995).

5.3.2 Consumer Use and End-of-Life Analysis

Consumer Use

The nature of exposure to PCBs during use will vary with the composition of the product and the manner in which the product is used. However, little information existed in the literature in 2008 about the emissions potential of alternative flame retardants from the use of electronic products. Similarly, little to no research has addressed whether the type of flame retardants used in PCBs potentially affects these emissions.

Several studies have examined the potential of brominated flame retardants to volatilize or offgas from electronic devices. A study conducted by the German laboratory ERGO, which investigated offgassing potential of TBBPA from computers under both real-world conditions and chamber conditions, found that all emissions of TBBPA were associated with the housing material (additive application of TBBPA), none with the printed circuit boards (reactive application of TBBPA) (HDPUG, 2004). The German Federal Institute of Materials Testing also conducted chamber emission testing of flame retardants from electronic articles and construction products. They found very low emissions, even at the elevated operating temperatures of computers (Kemmlein et al., 2003). Beard and Marzi (2006) investigated the offgassing potential of thermoplastic polymers containing phosphorus-based and brominated flame retardants by simulating extreme indoor car heat conditions as a worst case scenario; the study found very low levels of volatilization (0 to 6 mg/kg).

Without further information on the exposure potential associated with printed circuit board use, the differences between flame-retardant alternatives cannot be estimated. Additive flame retardants, which are not commonly used in PCBs, are more likely to generate emissions than reactive flame retardants. However, for additive flame retardants the potential for offgassing is directly related to the volatility of the chemical (vapor pressure), which again is related to molecule size and weight.

End-of-Life Pathways

The amount of electronic waste (e-waste) generated annually in the U.S. is growing rapidly. According to an EPA study, the amount of electronic products either recycled or disposed of annually increased from an estimated 1.1 million tons in 1999 to 2.2 million tons in 2005 (OSW 1, 2007). While electronics represent less than 2 percent of the total municipal solid waste stream, electronics contain many toxic substances that can adversely affect the environment and human health (OSW 1, 2007).

In the U.S., used electronic goods are typically purchased by equipment handlers, such as brokers and liquidation or auction services, or by equipment processors, such as refurbishers and recyclers. Most used electronic goods then undergo a series of tests to determine their condition. If a device is in good condition, it is reused either in part or in whole. Devices not in satisfactory condition become e-waste, and are sent to demanufacturing and destruction facilities where raw materials are either disposed of or recycled.

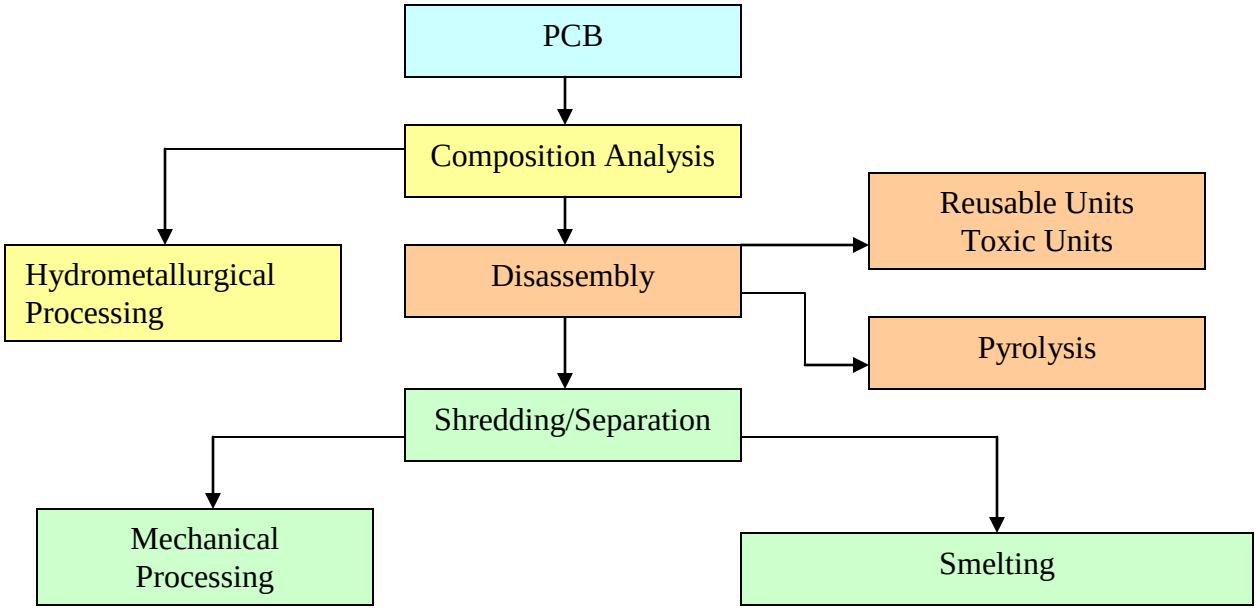
The manner in which electronic waste is disposed of or recycled determines the potential environmental and human health impacts.[11] An EPA study indicates that 15 to 20 percent of e-waste is recycled, and 80 to 85 percent is disposed of (includes landfill and incineration) (OSW 1, 2007). Of the e-waste that is recycled, a portion is shipped overseas. For example, 61 percent, or 107,500 tons of cathode ray tubes were shipped overseas in 2005 for remanufacture or refurbishment (OSW 2, 2007). Of the e-waste shipped overseas, an unknown portion is disassembled and recycled under largely unregulated conditions. The following sections describe disassembly and recycling practices typical of unregulated overseas conditions and summarize the nature of their potential impact.

Recycling

As Figure 5-5 shows, the PCB recycling process can involve both thermal processing, such as smelting to recover precious metals, and nonthermal processing, such as disassembly, shredding, separation, and chemical treatment. The potential level of exposure to workers and the general population that results from these processes will vary depending on the type of operation employed. Many recycling operations employ these methods in safe conditions that minimize the potential for exposure, and recover valuable metals that are part of finished boards.

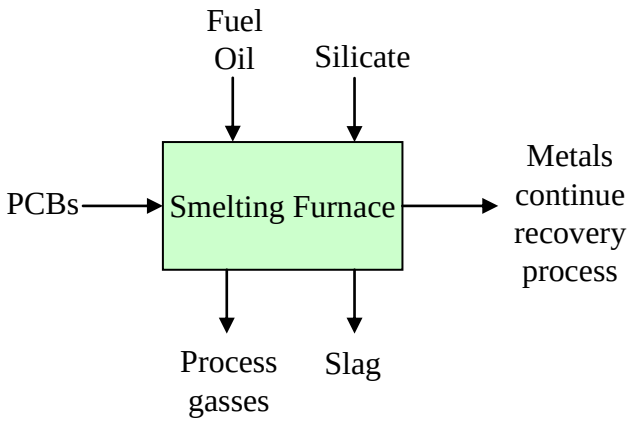
[11] According to a 2005 UN report, up to 50 million metric tons of e-waste is generated annually. In the U.S., the amount of e-waste is increasing at three times the rate of general waste. http://www.rrcap.unep.org/policy2/13-Annex%204a-e-wastes%20SEPD2.pdf

Figure 5-5. Sketch of the PCB Recycling Process (Li et al., 2004)



The thermal process of smelting separates valuable metals, such as gold, silver, platinum, palladium, selenium, and copper, from impurities in PCBs (Figure 5-6). The process operates by heating PCBs in a furnace to about 1,200 to 1,250°C in the presence of a reducing agent, which is usually carbon from fuel oil or the organic portion of PCBs. Silicate, such as silicon dioxide, is also added to help control reaction temperatures, and excess process gases are burned and purified to remove contaminants (Kindesjo, 2002). Therefore, silicon dioxide-based flame retardants are beneficial to the smelting process (Lehner, 2008).

Figure 5-6. Smelting Process (Kindesjo, 2002)



The smelting process generates two layers inside the furnace, a top layer of slag and a bottom layer of "black copper." The bottom black copper layer can be directly sent to a copper recovery unit, such as a copper converter or leaching and electrowinning facility (Umicore, 2007). The top layer of slag is further processed to separate metals from impurities. After slag processing is complete, leftover slag is deposited in impoundment areas (Kindesjo, 2002).

In the absence of proper control equipment, the smelting process may pose risks to workers and the public through exposure to toxic chemicals. Halogenated flame retardants, for example, can lead to the formation of dioxins during the smelting process if proper safety measures are not installed (Tohka, 2002). However, the three primary smelters in the world as of 2008 – Boliden, Umicore, and Noranda – have learned how to operate with high loads of halogenated electronic scrap and effectively control emissions of dioxins and furans, mercury, antimony, and other toxic substances. In addition to the potential emission of toxic chemicals, high operating temperatures may create occupational hazards. High loads of bromine or chlorine may induce corrosion of gas-cleaning equipment. In sensitive areas, a process step for halogenide recovery may need to be added (Lehner, 2008).

In contrast to the recycling practices described above, a large portion of the e-waste shipped overseas to China, India, Pakistan, and other developing countries is subjected to unregulated recycling practices that may pose significant exposure concerns. Much of the PCB waste in unregulated operations is subject to open burning and acid leaching to recover precious metals. The Basel Action Network (BAN), which has visited open burning sites in Asia, reports that the general approach to recycling a circuit board first involves a de-soldering process. The PCBs are placed on shallow wok-like grills that are heated underneath by a can filled with ignited coal. In the wok-grill is a pool of molten lead-tin solder. The PCBs are placed in the pooled solder and heated until the chips are removable, and then the chips are plucked out with pliers and placed in buckets. The loosened chips are then sorted between those valuable for re-sale and those to be sent to the acid chemical strippers for gold recovery. After the de-soldering process, the stripped circuit boards go to another laborer who removes small capacitors and other less valuable components for separation with wire clippers. After most of the board is picked over, it then goes to large scale burning or acid recovery operations. It is this final burning process that potentially emits substantial quantities of harmful heavy metals, dioxins, beryllium, and polycyclic aromatic hydrocarbons (PAHs) (BAN and SVTC, 2002). The chemicals released through these processes can be inhaled by workers or could leach into the soil and water surrounding the area. In 2005, Greenpeace collected industrial wastes, indoor dusts, soils, river sediments, and groundwater samples from more than 70 industrial units and dump sites in Guiyu, China, and New Delhi, India, and found elevated levels of lead, tin, copper, cadmium, antimony, polybrominated diphenyl ethers, and polychlorinated biphenyls (Greenpeace, 2005).

In terms of the size of the population potentially at risk from open burning practices, the local government website of Guiyu reported that the city processes 1.5 million tons of e-waste every year, resulting in $75 million in revenue (Johnson, 2006). The *People's Daily*, the state-run newspaper, reported in 2007 that Guiyu's more than 5,500 e-waste businesses employed more than 30,000 people, and state media estimated that almost 9 out of 10 people in Guiyu suffered from problems with their skin, nervous, respiratory, or digestive systems, which may be linked to these practices (Chisholm and Bu, 2007).

In order to better understand the effects of combustion processes, the relationship between specific combustion scenarios and the release of specific quantities of harmful substances has been further analyzed as part of this project. The results of these tests are presented in Chapter 6.

Landfills

E-waste sent to a landfill can lead to the creation of leachate (i.e., the mixture of rainwater and liquids within the waste). This leachate has the potential to seep into the ground or drain into nearby surface water, where it could affect the environment and have a negative impact on food and water supplies.

Most leachability studies as of 2008 in the literature have focused on the potential for discarded electronic devices to leach lead and other heavy metals. A relatively small number of these studies have investigated leachability potential of brominated flame retardants, and in general, have found either no or very small concentrations of brominated compounds in the leachate. When brominated flame retardants are added versus reacted into the resin system, the potential for the brominated flame retardants to leach from PCBs is much greater (KemI, 1995).

A study conducted by Beard and Marzi (2006) investigated the leachability potential of phosphorus-based and brominated flame retardants from thermoplastic polymers and found that small amounts of phosphorus and bromine respectively leached from the polymer. Another study (Yoneda et al., 2002) reported that a small amount of phosphate ions leached from a Fujitsu-developed dielectric material consisting of a bisphenol A epoxy with an additive type organic phosphate in hot water and aqueous alkaline solutions. When Fujitsu developed and tested a dielectric material consisting of a naphthalene-based epoxy with reactive-type organic phosphate, no phosphate ions leached from the material.

Aside from the studies referenced above, little information exists in the literature about the leachability potential of alternative flame retardants in landfill environments. Similarly, little to no research has addressed whether the type of flame retardants used in PCBs potentially affects the leachability of heavy metals.

5.4 Methods for Assessing Exposure

The European Union (EU)'s risk assessment of TBBPA offers insight into how personal and environmental exposure can be evaluated for flame-retardant chemicals. The EU risk assessment consists of two parts: the human health assessment, which was finalized in 2006, and the environmental assessment, which remains in draft form. As part of the human health and environmental risk assessments, exposure assessments have been conducted to estimate the levels of TBBPA released in occupational settings and in the general environment. In both, the EU differentiated between reactive and additive TBBPA and considered different stages of the life cycle when estimating releases. While the results of the EU risk assessment are not being used as part of this partnership project, Table 5-3 and Table 5-4 highlight some of the key methods and assumptions used to estimate emissions of TBBPA used as a reactive flame retardant in epoxy and other resins.

In the human health exposure assessment, the term exposure is used to denote personal exposure without the use of any personal protective equipment. The EU used both measured and predicted exposure data. Given the lack of TBBPA exposure data, the United Kingdom (UK) Health and Safety Executive (HSE) commissioned sampling studies within the UK at four sites: two sites involved in the production of polymers where TBBPA is incorporated into the finished product

(one of which manufactures resin laminates), and two sites where polymer products are recycled. The EU supplemented the measured exposure data with predicted data from the EASE (Estimation and Assessment of Substance Exposure) model, which is widely used across the EU for occupational exposure assessment of new and existing chemicals.

Table 5-3. Human Health Exposure Assessment (EU Risk Assessment, 2006)

Life-Cycle Stage	Key Methods/Assumptions	Source of Data
Production of laminates	Inhalation exposure: HSE visited a manufacturing facility of copper/resin laminates used for PCBs in 2002 to measure personal inhalation exposure. Used one personal sampler during the bromination step and multiple personal and static samplers during other steps of the laminate process. Due to uncertainty surrounding the measured estimates, EU used EASE model to estimate "typical" and "worst-case" inhalation values for bromination and other laminate production steps. Dermal exposure: EASE model used to estimate "typical" and "worst-case" dermal values for bromination and other laminate production steps.	Sampling results from 2002 study at UK laminate manufacturing facility; EASE model
Computer recycling	Inhalation exposure: HSE visited recycling facility where PCBs are shredded and exported for recovery of precious metals in 2002. Used personal and static samplers during shift. EU used EASE model to estimate "typical" and "worst-case" inhalation exposures. Dermal exposure: EASE model used to estimate dermal exposure values. Predicted to be very low; consequently, dermal exposure values not used by EU in exposure assessment.	Sampling results from 2002 study at UK recycling facility; EASE model
PCB Assembly	Inhalation exposure: Results of Sjodin et al., 2001 study, which measured levels of TBBPA in a factory that assembles PCBs, used to establish "typical" and "worst-case" inhalation values. Dermal exposure: Dermal exposure assumed to be negligible given the low levels of free TBBPA in PCBs.	Sjodin et al., 2001; professional judgment of risk assessors
Office environment	Inhalation exposure: Results of Sjodin et al., 2001 study, which measured levels of TBBPA in a factory that assembles PCBs, used to establish "typical" and "worst-case" inhalation values. Dermal exposure: Dermal exposure assumed to be negligible given the low levels of free TBBPA in PCBs.	Sjodin et al., 2001; professional judgment of risk assessors
Plastic recycling	Inhalation exposure: EASE model used to predict "typical" and "worst-case" inhalation values. Dermal exposure: EASE model predicted dermal exposure to be very low; consequently, dermal exposure values not used by EU in exposure assessment.	EASE model
Consumer exposure	EU concluded that consumer exposure to TBBPA is likely to be insignificant, and that any attempt to quantify it would result in significant errors due to the small exposure levels anticipated.	Professional judgment of risk assessors
Indirect exposure via environment	EUSES 2.0 model used to estimate the concentrations of TBBPA in food, air, and drinking water.	EUSES 2.0 model

In the environmental exposure assessment, the EU estimated environmental releases using industry-specific information, supplemented by defaults for life-cycle stages where sufficient industry-specific information was unavailable. These are used together with fate and behavior data to derive predicted environmental concentrations (PECs) in different media. The specific

methods used in the PEC calculations are described in the EU's Technical Guidance Document on Risk Assessment, last revised in 2003 (EU Technical Guidance Document, 2003).

Table 5-4. Environment Exposure Assessment (EU Risk Assessment, 2007 draft)

Life-Cycle Stage	Key Methods/Assumptions	EU Data Source
Production	Emissions associated with production not considered in the risk assessment since no TBBPA is currently produced in the EU.	--
Use/ Processing	Total amount of TBBPA used in the EU estimated at 6,500 tonnes per year, of which 90% (or 5,850 tonnes per year) assumed to be reactive flame retardant in epoxy and other resins.	2003 consumption data from EFRA and EBFRIP
	Default emissions factor of 0.001% to air and 0.001% to water used due to a lack of specific release information for EU sites.	Technical Guidance Document 2003
	Levels of residual TBBPA present in finished epoxy resins assumed to be <0.02% by weight of the resin, or <0.06% of the amount of TBBPA used to make the resin.	Information reported by Industry as part of survey; no references provided
Lifetime of Products	Releases associated with finished products based on estimated volume of TBBPA used as a reactive flame retardant in finished products, as well as estimate that 0.06% of the amount of TBBPA used to make epoxy resin is present, or free, for release.	Information reported by Industry as part of survey; no references provided
	Amount leached from products over their lifetime is assumed to be very low for purposes of this risk assessment.	Professional judgment of EU risk assessors
	A yearly emission factor of 8.0×10^{-5} % (of the residual amount of TBBPA in polymers) due to volatilization used. Assumed that reactive flame retardants volatilize at same release factor as additive flame retardants.	Emissions data from ERGO 2002
	No loss of residual TBBPA through wear and weathering is assumed over the lifespan of products where TBBPA is used as a reactive flame retardant	Professional judgment of EU risk assessors
Recycling and Disposal	Emissions of TBBPA from the collection, separation, and regrinding of PCBs (or other plastics where TBBPA is used as a reactive flame retardant) assumed to be limited.	Professional judgment of EU risk assessors

5.5 Chemical Life-Cycle Considerations

This section discusses the environmental and human health impacts for each of the ten flame retardants that can occur throughout the life cycle: from raw material extraction and manufacture, through product use, and finally at end of life of the material or product. For each stage of the chemical's life cycle, this section addresses potential exposure concerns for workers, the general population, and the environment. It should be noted that a greater level of information exists for TBBPA as compared to the more recently developed flame-retardant alternatives.

5.5.1 TBBPA

TBBPA is used as both an additive and reactive flame retardant in a wide variety of electronic equipment. As discussed in Section 3.2, TBBPA is most commonly used as a reactive flame retardant in PCBs and is incorporated through chemical reactions with the epoxy resin.

Raw Material Extraction

Bromine is produced from salt brines in the United Stated and China, from the Dead Sea in Israel and Jordan, and from ocean water in Wales and Japan (BSEF, 2007). Bromine is typically isolated via a series of redox reactions involving chlorine, sulfur dioxide and acid (MIT, 2003; York, 2007). During these reactions the seawater is acidified and then chlorinated to oxidize bromide to elemental bromine. At this stage, the bromine is not concentrated enough to practically collect and liquefy, so sulfur dioxide is added to reduce the bromine to hydrobromic acid. Chlorine is then added to re-oxidize hydrobromic acid to elemental bromine. At this point, bromine gas is collected and condensed (Grebe et al., 1942). While caustic substances are involved in these processes, they are typically contained in an enclosed tower, which mitigates worker exposure and environmental release.

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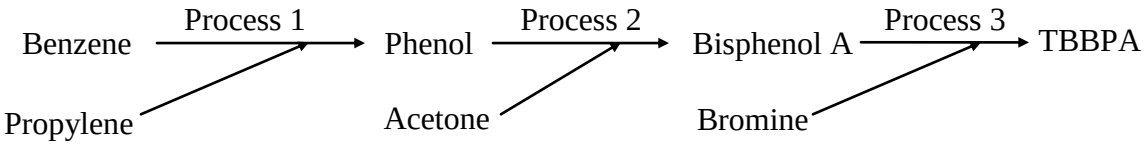
TBBPA is produced by brominating bisphenol A (BPA) in the presence of solvent. This reaction is highly exothermic, and no catalyst is required. Co-products will depend on the solvent used and the process conditions. The use of some solvents results in co-products, while the use of other solvents does not result in co-products. Co-products are typically either sold as products or disposed of as wastes.

Methanol and n-propanol are two examples of solvents that lead to the formation of co-products. Use of methanol produces methyl bromide, and use of n-propanol produces n-propyl bromide (Noonan, 2000). These co-products are typically removed through purification processes that can include the use of caustic neutralizers.

In 2008, TBBPA was commercially produced by Albemarle Corporation (Magnolia, AR) and Chemtura (El Dorado, AR). At that time, both corporations used proprietary processes that did not yield methyl bromide (Haneke, 2002).

While commercially employed bromination processes are proprietary, most involve bromination of BPA. Figure 5-7 gives a general overview of the main chemicals and reactions involved in TBBPA production. Please note that Figure 5-7 is a general outline of processes involved, and is not a complete list of chemicals or process steps.

Figure 5-7. Common Reactants and Processes Involved in TBBPA



Process (1): Cumene hydroperoxide rearrangement involving benzene and propylene to form phenol – this is the most common industrial process for producing phenol, accounting for approximately 97 percent of phenol production. Acetone is also formed as a coproduct (Plotkin, 2006). Process (2): Condensation reaction between phenol and acetone to produce bisphenol A. Process (3): Bromination of bisphenol A to produce TBBPA. In the absence of an oxidant, HBr would be produced as a coproduct. Hydrogen peroxide can be used to convert HBr back to Br_2, forming water and avoiding this problem.

While Figure 5-7 presents an overview of common reactants and processes involved in TBBPA production, there are also other processes that can be involved in producing TBBPA. To analyze the hazards associated with the production of any given TBBPA product, one would have to trace the line of production and identify which methods were used and what chemicals were involved, including catalysts, solvents, and other reagents.

Potential exposure to or release of TBBPA particulates may occur during manufacture or subsequent loading/unloading, transfer, or mixing operations (those that occur before its incorporation into the epoxy resin). When TBBPA is used as a reactive flame retardant, there may be unreacted (or free) TBBPA left over in the resin, leading to the presence of free TBBPA in the laminate and subsequently produced PCBs. The amount of free TBBPA is anticipated to be relatively low when it is used as a reactive flame retardant, although quantitative data on the amount of free TBBPA present in PCBs was limited at the time of report publication. Sellstrom and Jansson (1995) found approximately 0.7 micrograms per gram in a basic extraction of PCB filings from an off-the-shelf product purchased in Sweden (approximately 4 micrograms per gram TBBPA used). Studies have been conducted by Nelco to investigate the amount of residual TBBPA, but the results have not yet been published (PSB Corporation, 2006). One complication is that it is possible to add TBBPA to the varnish rather than pre-reacting it with an epoxy (as is done to make D.E.R. 500 Series). Even though all of the TBBPA should react, there is more potential to have unreacted TBBPA present when it is added to the varnish. It is not known how common this practice is.

D.E.R. 500 Series, the reaction product of TBBPA with an epoxy resin, may be released to the environment from its use in PCBs through dust-forming operations during its manufacture or subsequent loading/unloading, transfer, or mixing operations (those that occur before its incorporation into the laminate or PCB). Increased health hazards for this reaction product arise from the epoxy functional groups present on the polymer molecules. There may be unreacted D.E.R. 500 Series present in the laminate and, subsequently, the PCBs produced. The amount of free D.E.R. 500 Series is generally anticipated to be low given that it is incorporated as a reactive flame retardant, although quantitative data on the amount of free material that may be present are currently not available.

BPA, the unbrominated precursor to TBBPA, may also pose potential hazards to human health and the environment. The EU's risk assessment of BPA in 2003 concluded that for occupational exposures, "there is a need for limiting the risk" to workers based on eye and respiratory tract irritation, effects on the liver, and reproductive toxicity (effects on fertility and on development) during the manufacture of BPA and epoxy resins, as well as concerns for skin sensitization in all occupational exposure scenarios where there is a potential for skin contact (EU, 2003). For workers, consumers, and the general public, the EU concluded that further information and/or testing is needed in relation to developmental toxicity at low doses. The EU also assessed environmental hazards, concluding that further information is needed on the risk of BPA production to aquatic and terrestrial organisms, as well as the risk of epoxy resin production on aquatic organisms (EU, 2003). Steps have also been taken in the U.S. in recent years to identify the hazards associated with BPA. For uses under the Toxic Substances Control Act, U.S. EPA issued the BPA Action Plan[12] in March 2010, which summarized hazard, exposure, and use

[12] http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/bpa_action_plan.pdf

information, and identified actions to address BPA in the environment based on concerns for potential effects on aquatic species.[13] The Action Plan states that dermal exposure to BPA may occur in workers producing flame retardants during the loading/unloading of BPA from containers, and that occupational exposure via inhalation is not expected (U.S. EPA, 2010). As part of the Action Plan, U.S. EPA tasked its Design for the Environmental Program with conducting an alternatives assessment for BPA in thermal paper. BPA and 19 potential chemical alternatives in thermal paper were evaluated on their human health effects, ecotoxicty, and environmental fate. A final version of this alternatives assessment was released in January 2014.[14] The report also contains information on general exposure and lifecycle information on BPA, and can be used to inform decision-making and to guide the development of new alternatives. More information about the Agency's current efforts to address BPA can be found at: http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/bpa.html.

Use and End of Life

Since TBBPA is reacted with an epoxy resin to form D.E.R. 500 Series, which is then reacted with a hardener to form a crosslinked polymer, low levels of unreacted TBBPA and D.E.R. 500 Series may remain in trace concentrations in PCBs; release of these low levels could theoretically occur during the use and disposal of PCBs. Because TBBPA is difunctional[15], there is less potential for release compared to DOPO, which is monofunctional, and more potential for release compared to Fyrol PMP, which is tetrafunctional. TBBPA has been detected in the air of electronic recycling plants (Sjodin et al., 2001, 2003), although these facilities also recycled products where TBBPA is used as an additive flame retardant. Although its water solubility is low under neutral conditions, free TBBPA could also be released from PCBs in landfills that come in contact with basic leachate. However, unlike other brominated flame retardants, TBBPA is not very stable in air under basic conditions. In addition, there is potential for emissions of brominated dioxins and furans or other by-products when products containing TBBPA are combusted during end-of-life processes. Levels of exposure and any subsequent effects of exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, are unknown.

5.5.2 DOPO

Raw Material Extraction

Phosphorus is usually obtained from phosphate rock, which contains the mineral apatite, an impure tri-calcium phosphate. Large deposits of phosphate rock are found in Russia, Morocco, Florida, Tennessee, Utah, Idaho, and elsewhere (Lide, 1993). By one process, tri-calcium phosphate, the essential ingredient of phosphate rock, is heated in the presence of carbon and silica in an electric furnace or fuel-fired furnace. Elementary phosphorus is liberated as vapor

[13] The U.S. Food and Drug Administration (FDA) is expected to take the lead on assessing potential human health impacts associated with exposure to BPA. See http://www.fda.gov/NewsEvents/PublicHealthFocus/ucm064437.htm.
[14] http://www.epa.gov/dfe/pubs/projects/bpa/about.htm
[15] A molecule with two reactive sites.

and may be collected under water (Lide, 1993). While elementary phosphorus can form a diatomic molecule with a triple bond, it more readily forms a tetrahedral P_4 molecule. P_4, also called white or yellow phosphorus, exists in the gas phase and also as a waxy solid and viscous liquid. The degree of purity determines the "whiteness" of the phosphorus. At room temperature, phosphorus can exist in an amorphous or semi-crystalline state, called red phosphorus, which is produced from white phosphorus by extended heating in an inert atmosphere (Calvert, 2004).

Some phosphorus-based flame retardants are based on phosphate esters derived from yellow phosphorus. Approximately 80 percent of the global phosphorus is mined in China in the form of phosphate ore (Shigeru, 2007). Yellow phosphorus produced from phosphorus ore co-produces arsenic, mercury, lead and other heavy metals as impurities that should be well controlled and treated before disposal of wastewater. If Chinese producers of yellow phosphorus appropriately treat their wastewater, then there is little concern for environmental and human health effects. However, improperly treated wastewater can lead to major adverse environmental impacts (Shigeru, 2007).

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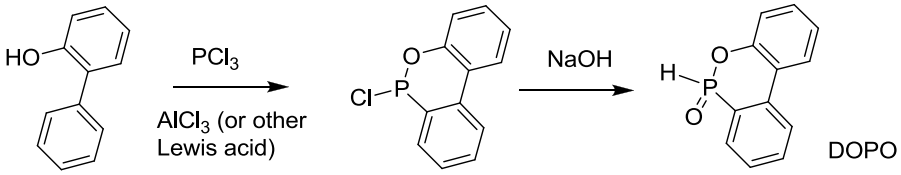
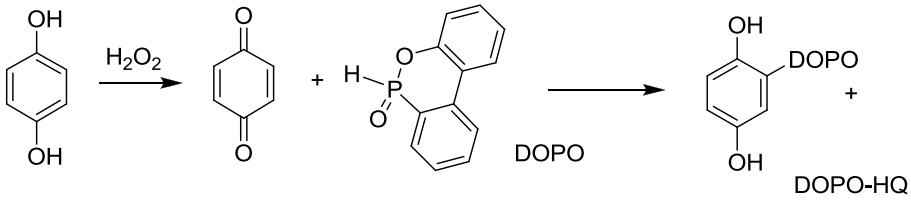
Chemistry that can be used to make DOPO is shown below. The by-products of this chemistry are salts of the Lewis acid (such as aluminum chlorohydrates) and NaCl from the second step.



Further chemistry must be performed to react DOPO into the thermoset backbone. The largest manufacturer of organophosphorus flame retardants for electrical laminates at the time this partnership was convened was Tohto-Kasei. The details of their product are not known, but it is widely thought that their product is "DOPO-HQ", or the adduct of DOPO with hydroquinone as shown below. This phenolic is then combined with an epoxy novolak and a catalyst in a solvent to make a varnish suitable for electrical laminates. Fillers are typically added to these formulations primarily to reduce costs.



Potential human and environmental exposure to DOPO may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations.

Dow XZ-92547, the reaction product of DOPO with an epoxy phenyl novolak, may be released from PCBs as a fugitive emission during manufacture of resins and laminates, or during subsequent loading/unloading, transfer, or mixing operations. The amount of Dow XZ-92547 that may be released from laminates or PCBs during their production and operational stages has

not been determined quantitatively; however, the low vapor pressure of Dow XZ-92547 indicates that it is not likely to undergo direct volatilization. Increased health hazards for this reaction product arise from the epoxy functional groups present on the polymer molecules.

Use and End of Life

As a reactive flame retardant, DOPO is not expected to be released from laminates. Its vapor pressure suggests that it has at least some potential to volatilize at elevated temperatures. Potential releases of DOPO particulates from PCBs may arise during the disposal phase of the life cycle via shredding or other operations where it may become mobilized. DOPO's water solubility suggests that it may migrate from PCBs deposited in landfills if contact with water ensues. Release of DOPO during the open burning of PCBs may also lead to environmental exposures. Because it is monofunctional, there is more potential for release compared to TBBPA, which is difunctional. DOPO may be released from PCBs during disposal or recycling, and potentially through dust-forming operations, such as PCB shredding. Leaching of Dow XZ-92547 from PCBs deposited in landfills is not likely given its low water solubility, high MW and functionality. Leaching of DOPO is more likely given its relatively low MW and because it is bound to the polymer by only one covalent bond. DOPO also oxidizes to a species containing a P-OH group in place of the P-H group. The toxicological properties of this species are unknown. Levels of exposure and any subsequent effects of exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, are unknown.

5.5.3 Fyrol PMP

Raw Material Extraction

For a description of phosphorus extraction, please refer to the above entry for DOPO.

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No information regarding the manufacture of Fyrol PMP was available at the time of publication due to the chemical's proprietary nature.

Use and End of Life

As a reactive flame retardant, Fyrol PMP is not expected to be released from laminates, and its low vapor pressure indicates that it is not likely to undergo direct volatilization. When PCBs are openly burned, it is possible that high temperatures could break the phosphorous-carbon bonds that hold Fyrol PMP to the crosslinked resin, which may result in the release of Fyrol PMP to the environment. Because it is tetrafunctional, Fyrol PMP is less likely to be released than TBBPA or DOPO, which are, respectively, difunctional and monofunctional. Even so, Fyrol PMP may be released from PCBs during its disposal or recycling, potentially through dust-forming operations, such as the shredding of PCBs. However, it is possible that methyl phosphonate may leach out of PCBs due to hydrolysis of phenol-phosphonate bonds. Exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, is unknown.

5.5.4 Aluminum Diethylphosphinate

Raw Material Extraction

For a description of phosphorus extraction, please refer to the above entry for DOPO.

Manufacture of Flame Retardant, Laminate, and PCB

Potential human and environmental exposure to aluminum diethylphosphinate may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations. No additional information regarding the manufacture of aluminum diethylphosphinate was available at the time of publication in 2008 due to the chemical's proprietary nature.

Use and End of Life

As an additive flame retardant, aluminum diethylphosphinate may also be released from laminates and PCBs. After incorporation into the resin and/or the laminate, potential releases of aluminum diethylphosphinate during the useful life cycle of PCBs is not anticipated, except by an extractive processes upon contact with water. Potential releases of aluminum diethylphosphinate particulates during the disposal of PCBs may arise during the disposal phase of the life cycle via shredding or other operations where it may become mobilized. Its water solubility suggests that it may also migrate from PCBs deposited in landfills upon contact with water.

5.5.5 Aluminum Hydroxide

Raw Material Extraction

Aluminum is one of the most plentiful elements in Earth's crust, and is usually present as bauxite ore. Bauxite can contain three different aluminum minerals, including gibbsite ($Al(OH)_3$), and böhmite and diaspore (different crystalline structures of AlO(OH)). Bauxite ore also typically contains clay, silt, iron oxides, and iron hydroxides. The majority of bauxite is mined from surface deposits, but some is excavated from underground deposits (International Aluminium, 2000). Nearly all of the bauxite consumed in the U.S. is imported (EPA, 2007).

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Once bauxite is recovered from deposits and broken into manageable pieces, it is shipped to a processing facility where it goes through the Bayer process. During this process, the bauxite ore is washed, ground, and dissolved with caustic sodium hydroxide. While the end product of the Bayer process is alumina (Al_2O_3), aluminum hydroxide ($Al(OH)_3$) can be isolated following the precipitation step (see process steps below) (International Aluminium, 2000). In the past, more than 90 percent of domestic bauxite conversion to alumina occured at refineries in Louisiana and Texas (EPA, 2007).

Bayer process steps:

1) Digestion—bauxite ore treated with heated sodium hydroxide solution to form sodium aluminate:

   Gibbsite: $Al(OH)_3 + NaOH \rightarrow Na^+ Al(OH)_4^-$
   and
   Böhmite and Diaspore: $AlO(OH) + NaOH + H_2O \rightarrow Na^+ Al(OH)_4^-$

2) Clarification—insoluble impurities (red mud) are separated from the suspension.

3) Precipitation—aluminum hydroxide crystals are added to the solution to seed the precipitation of aluminum hydroxide crystals:

   $Na^+ Al(OH)_4^- \rightarrow Al(OH)_3 + NaOH$

4) Calcification—the agglomerates of aluminum hydroxide are calcinated to produce pure alumina. (Note that while this step is included in the Bayer process, it is not relevant to the production of aluminum hydroxide; however, this is the reaction that occurs when aluminum hydroxide acts as a flame retardant.)

   $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

During clarification, clay, silt, iron oxides, iron hydroxides, and other non-aluminum components are removed from the bauxite ore. These components are disposed of as "red mud," which is highly alkaline (pH ≈ 13), and can be hazardous to human health and the environment. Red mud is viewed as a corrosive and hazardous substance requiring careful handling (Liu et al., 2007). While there are methods to reduce the hazard of red mud, its disposal can still be problematic.

Use and End of Life

Once aluminum hydroxide is produced, it can be released into the environment as a fugitive emission during loading/unloading, transfer, or mixing operations. After incorporation into a PCB resin and/or the laminate, potential exposure to finely divided aluminum hydroxide particulates is not expected during the remainder of the operational stages of the PCB life cycle. Aluminum hydroxide particulates may also be released during the disposal phase of the life cycle where they can become mobilized through direct intervention processes (such as shredding operations). The impact of aluminum hydroxide in smelting operations needs to be investigated further due to concerns about impacts on slags. Aluminum hydroxide thermally degrades to alumina in the smelting process. Alumina has a limited solubility in smelter slags. If large concentrations are added, this may lead to either increased slag volumes or higher operational temperatures, which lead to increased energy consumption (Lehner, 2008).

5.5.6 Magnesium Hydroxide

Raw Material Extraction

There are several million tons of mineral magnesium hydroxide, called brucite, in Earth's crust around the world (USGS, 2008; Amethyst, 2008). However, magnesium hydroxide is typically recovered from seawater and magnesia-bearing brines, which constitutes an even greater and more readily available resource than brucite. In 2007, magnesium oxide and other magnesia compounds (including magnesium hydroxide) were recovered from seawater by three companies in California, Delaware, and Florida; from well brines by two companies in Michigan; and from lake brines by two companies in Utah (USGS, 2008).

Manufacture of Flame Retardant, Laminate, and PCB

Recovering magnesium hydroxide from brine and seawater typically involves the addition of lime calcined dolime ($CaO \cdot MgO$), which is obtained from a mineral source such as dolomitic limestone ($CaMg(CO_3)_2$). Magnesium-bearing brine and seawater contain varying concentrations of calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$), which are mixed with appropriate concentrations of calcined dolime and water (if necessary) to facilitate the following reaction (Martin, 2008):

$$CaCl_2 + MgCl_2 + (CaO \cdot MgO) + 2H_2O \rightarrow 2Mg(OH)_2 + 2CaCl_2 + H_2O$$

The resulting magnesium hydroxide exists as solid particles suspended in an aqueous phase containing dissolved calcium chloride. The magnesium hydroxide particles settle to the bottom of the aqueous suspension, where they are separated, filtered, and washed to remove chlorides (Martin, 2008).

Hydrated lime ($Ca(OH)_2$) can also be used to precipitate magnesium hydroxide via the following reaction (NIEHS, 2001):

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 + CaCl_2$$

Potential human and environmental exposure to magnesium hydroxide may occur through dust-forming operations from its manufacture, or during loading/unloading, transfer, or mixing operations. As an additive flame retardant, it may also be released from laminates and PCBs.

Use and End of Life

After incorporation into the resin and/or the laminate, potential exposure to finely divided magnesium hydroxide particulates is not expected during the remainder of the operational stages of the PCB life cycle. Magnesium hydroxide particulates may also be released during the disposal phase of the life cycle where they can become mobilized through direct intervention processes, such as shredding operations. The impact of magnesium hydroxide in smelting operations needs to be investigated further due to concerns about impacts on slags. Magnesium hydroxide thermally degrades to magnesium oxide in the smelting process. However, magnesium oxide has a limited solubility in smelter slags. If large concentrations are added, this may lead to either increased slag volumes or higher operational temperatures, which lead to increased energy consumption (Lehner, 2008).

5.5.7 Melamine Polyphosphate

Raw Material Extraction

For a description of phosphorus extraction, please refer to the above entry for DOPO.

Manufacture of Flame Retardant, Laminate, and PCB

A two-step process is typically used to prepare melamine polyphosphate (Patent Storm, 2002). In the first step, melamine, urea, and an aqueous orthophosphoric acid solution (containing at least 40 wt percent orthophosphoric acid) are combined, mixed, and dehydrated to produce a powdery product. In the second step, this powdery product is heated to between 240 and 340°C for 0.1 to 30 hours to obtain melamine polyphosphate (Patent Storm, 2002)

Potential human and environmental exposure to melamine polyphosphate may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations. As an additive flame retardant, it may also be released from laminates and PCBs.

Use and End of Life

After incorporation into the resin and/or the laminate, potential releases of melamine polyphosphate during the useful life cycle of PCBs is not anticipated, except by an extractive process upon contact with water. Potential releases of melamine polyphosphate particulates during the disposal of PCBs may arise during the disposal phase of the life cycle via shredding or other operations where it may become mobilized. Its water solubility suggests that it may also migrate from PCBs deposited in landfills upon contact with water.

5.5.8 Silicon Dioxide

Raw Material Extraction and Manufacture

Silicon dioxide, or silica (sand), is a naturally occurring compound. It is usually mined with open pit or dredging mining methods, which have limited environmental impact (USGS, 2007). Silicon dioxide can also be made synthetically in autoclaves under pressures ranging from 1,500 to 20,000 pounds per square inch and at temperatures of 250°C to 450°C (Lujan, n.d.). In some cases, silicon dioxide is synthesized by adding an acid to a wet alkali silicate solution to precipitate amorphous silicate, which is then filtered, washed, and dried (Degussa, 2007). The conditions in which silicon dioxide is formed, such as temperature and pressure, determine its structural properties, such as whether it is amorphous or crystalline. The structure of silicon dioxide, in turn, affects its potential to cause harm to the environmental and human health.

Potential health concerns arise from the inhalation of finely divided particulates that are generally less than 10 microns in diameter. The potential health concerns for silicon dioxide, a poorly soluble respirable particulate, arise from effects on the lungs as well as other effects that may be linked to an adverse effect on the lungs. Assessment of the life cycle for the use of this compound in PCBs suggests that inhalation exposure to finely divided silicon dioxide

particulates may potentially occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations.

Use and End of Life

After incorporation into the resin and/or the laminate, potential inhalation exposure to finely divided silicon dioxide particulates is not anticipated during the remainder of the operational stages of the PCB life cycle. Finely divided silicon dioxide particulates that are less than 10 microns may also be released to the air during the disposal phase of the life cycle, where they can become mobilized through direct intervention processes (such as shredding operations). In the smelting process, silicon dioxide-based flame retardants are preferred since silicon dioxide is used as a flux in the process (Lehner, 2008).

5.6 References

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6 Combustion and Pyrolysis Testing of FR-4 Laminates

6.1 Background and Objectives

End-of-life pathways for electronic waste (e-waste) include recycling via thermal or non-thermal processing as well as landfilling. There has been increased demand to recycle e-waste for the recovery of precious metals used in electronic products. Incineration is one popular and cost-effective e-waste recycling technique. This type of thermal processing burns off the polymeric components of the e-waste and leaves behind inorganic ash that can be further smelted and refined to isolate reusable precious metals. When incineration is not conducted properly, the combustion of polymeric components creates toxic by-products that can be released into the environment. Unregulated incineration of electronics in developing countries has led to concerns about exposure to such toxic by-products. This issue may be attributable to the exportation of used electronics to developing countries that lack the capacity to manage them safely.

Little information exists about the combustion and pyrolysis products that could be formed during thermal end-of-life scenarios of printed circuit boards (PCBs). The presence of flame retardants in PCBs influences the emissions of the e-waste when burned. Flame retardants are added to PCBs by manufacturers to help products to meet flammability standards. They protect flammable polymers used in electronic products from potential ignition and help minimize fire risk. The primary fire risk that flame retardants protect against in PCBs is that of an electrical fault or short circuit ignition that can cause the polymers to ignite. An ignition site has the potential to lead to flame spread across the PCB and can cause its electronic casing to also ignite, and potentially propagate the flame into the electronic product's surrounding environment such as a home, vehicle, or mass transport structure.

The stakeholders of this partnership decided that testing of Flame Resistant 4 (FR-4) laminates and PCB components was warranted to learn more about potential by-products during thermal end-of-life processes (e.g., open burning and incineration). While it would also be informative to assess FR-4 laminates for leachability and offgassing during product use, these tests were not possible with available resources. This chapter gives an overview of the rationale and methods for combustion and pyrolysis testing of FR-4 laminates and PCB components. This section provides background information and a rationale for why the combustion testing was conducted. Section 6.2 offers an overview of Phase 1 of the combustion testing and information on how Phase 1 informed Phase 2 of the testing. The section also describes the process of selecting materials for Phase 2 and Section 6.3 summarizes Phase 2 conclusions, methods, and results.

The University of Dayton Research Institute (UDRI) led the combustion testing. UDRI has been involved in studying thermal processes for the last three decades and has experience with the flame retardants used in PCB manufacturing. The U.S. Environmental Protection Agency (EPA)'s Office of Research and Development (ORD) supplemented UDRI's testing with sample extraction and halogenated dioxins and furan analysis. The testing was completed in 2012.

The following stakeholders funded the combustion testing and provided materials:

- Albemarle
- Boliden
- BSEF (Bromine Science and Environmental Forum)
- Chemtura
- Clariant
- Ciba Specialty Chemicals
- Dell
- Environmental Monitoring Technologies, Inc. (EMT)
- Fujitsu-Siemens
- Hewlett-Packard
- IBM
- ICL-IP America, Inc.
- Intel
- Isola
- ITEQ
- Nabaltec
- Panasonic
- Seagate
- Sony
- Supresta

The overall goal of this combustion testing project was to compare the combustion by-products from FR-4 laminates and PCB components during potential thermal end-of-life processes, including open burning and incineration. The results from this testing will help advance decision making on the selection of flame-retardant materials and environmentally acceptable end-of-life thermal disposal processes.

This study was conducted in two phases. Phase 1 testing was a pilot study designed to evaluate the ability of proposed test methods to predict thermal degradation products of laminates. Phase 1 was also intended to help establish experimental methods and conditions for Phase 2 testing. The goal of the Phase 2 testing was to understand the potential emissions of halogenated dioxins, halogenated furans, and polyaromatic hydrocarbons (PAHs) of a standard tetrabromobisphenol A (TBBPA) laminate compared to different halogen-free laminates in precious metal recovery scenarios with and without typical circuit board components. A secondary goal of the Phase 2 testing was to expand cone calorimeter testing to other candidate laminates.

The laminates for testing in Phases 1 and 2 were selected to ensure a broad range of compositions. In Phase 1, three laminates were tested: a standard TBBPA laminate (BFR), a non-flame-retardant control laminate (NFR), and a halogen-free flame-retardant laminate (PFR1). PFR1, which was provided by ISOLA, contains an additive blend of flame retardants assessed in Chapter 4 of this report. At least one component of this blend contains phosphorus.

After Phase 1 was completed, UDRI reviewed the results with the partnership to determine the best way to proceed with Phase 2. The three laminates from Phase 1 were selected for Phase 2 testing as well as one additional halogen-free flame-retardant laminate (PFR2) for a total of four (see Table 6-2). PFR2, which was provided by Panasonic, contains a reactive phosphorus-based flame retardant that is also assessed in Chapter 4 of this report. In Phase 2, PCBs were simulated by combining the four laminates with homogeneous powders of components designed for conventional boards. These component mixtures were provided by Seagate. Further details about Phase 2 methods are located in Section 6.3.2 of this report. The suppliers of the phosphorus-based flame retardant laminates preferred not to disclose the exact chemical identity of the flame retardants in their laminates.

6.2 Phase 1 Methods and Results

The methodology for the two phases of the combustion testing was developed through ongoing collaboration among EPA, UDRI, and the stakeholders of this partnership. Phase 1 evaluated the ability of proposed test methods to predict thermal decomposition products of a small number of laminates (with TBBPA, an additive phosphorus flame retardant, or no flame retardant) and established experimental methods and conditions. The laminates in Phase 1 were tested under a number of different temperature and atmospheric conditions to predict combustion and pyrolysis products that could occur across various end-of-life scenarios.

A more detailed description of the Phase 1 methods is available in the following documents attached as appendices to this report:

- Appendix A – Yamada, Takahiro; Striebich, Richard. Open-burning, Smelting, Incineration, Off-gassing of Printed Circuit Board Materials Phase I Flow Reactor Experimental Results Final Report. Environmental Engineering Group, UDRI. August 11, 2008.

  This report summarizes flow reactor combustion tests conducted by UDRI. A quartz reactor was used to conduct controlled pyrolysis and oxidation experiments for the three different laminates at four different temperature/atmospheric conditions. The results were analyzed using gas chromatography-mass spectrometry (GC-MS). Aromatic hydrocarbons, specifically benzene, toluene, naphthalene, and xylene, were the principal combustion by-products for all three types of laminates. Bromophenol and dibromophenol were the brominated organic products unique to the brominated flame-retardant laminates. No phosphorus-containing organic compounds were observed for any of the laminates. The primary by-products of the phosphorus-containing flame-retardant laminates were various PAHs. The by-products of the phosphorus-containing flame-retardants were very similar to the by-products of the non-flame-retardant laminates.

- Appendix B – Sidhu, Sukh; Morgan, Alexander; Kahandawala, Moshan; Chauvin, Anne; Gullett, Brian; Tabor, Dennis. Use of Cone Calorimeter to Estimate PCDD/Fs and PBDD/Fs Emissions From Combustion of Circuit Board Laminates. US EPA and UDRI. March 23, 2009.

  This report by UDRI summarizes methods and emissions results from the combustion of PCB laminates using cone calorimetry. The compounds examined were polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and polybrominated dibenzo-p-dioxins and furans (PBDD/Fs). The emissions samples were analyzed using GC-MS. No chlorinated dioxin/furan congeners were detected in the combustion exhaust of any of the three types of laminates. Brominated dioxin/furan congeners were found in the brominated flame-retardant laminates, informing the researchers of what compounds to look for in Phase 2 of the combustion testing. The report also includes data on heat release and fire behavior for each type of laminate.

Laminates from the following companies were considered for testing under Phase 2.

- NanYa
- Hitachi
- Isola
- TUC
- Panasonic
- ITEQ
- Nelco
- Shengyi
- Supresta

A non-flame-retardant laminate provided by Isola was tested in both phases to serve as a control. Data on the elemental composition of laminates used in Phase 1 from NanYa, Isola, Panasonic, and ITEQ are reported in Appendix C and Appendix D.

Before the combustion and pyrolysis testing began in Phase 2, EPA ORD conducted X-ray fluorescence (XRF) analysis of each laminate to determine its elemental composition. To account for concerns among the partnership over the limitations of XRF analyses, follow-up analyses were done by Dow and ICL Industrial Products (ICL-IP). Dow tested for bromine and chlorine using neutron activation. ICL-IP tested for aluminum, calcium, magnesium, and phosphorus using inductively coupled plasma-optical emission spectroscopy (ICP-OES), bromine using titration, and chlorine using ion chromatography. Results from these analyses are summarized in:

- Appendix C – U.S. EPA. Analysis of Circuit Board Samples by XRF. Original Report - July 28, 2008. Revised Report - March 23, 2009. Prepared by Arcadis.

  This report summarizes the elemental analysis of circuit board samples by U.S. EPA ORD. XRF spectrometry was used to investigate the elemental makeup of two sets of circuit board samples. In Phase 1 of the experiment, a non-flame-retardant laminate, a bromine flame-retardant laminate, and a phosphorus flame-retardant laminate were cored from a circuit board at random locations and analyzed using XRF. The data from Phase 1 were of low quality so a second test phase was conducted in an effort to achieve more reliable results. In Phase 2 of the experiment, four halogen-free laminates were homogenized, powdered, and pelletized prior to XRF analysis. The results of the XRF elemental analysis can be found in Appendix D.

- Appendix D – U.S. EPA. Flame Retardant in Printed Circuit Boards Partnership: Short Summary of Elemental Analyses. DRAFT. December 9, 2009.

  This report summarizes the elemental analysis of circuit board samples by ICL-IP and Dow. ICL-IP used ion chromatography to test for chlorine, titration to test for bromine, and ICP-OES to test for aluminum, calcium, magnesium, and phosphorus. Dow used neutron activation to test for bromine and chlorine. ICL-IP's results suggest that the source of the aluminum, calcium, and magnesium detected in the samples was from glass fiber or glass treatment and not from a flame-retardant filler. Phosphorus was found in the largest quantities in the phosphorus flame-retardant laminates. Bromine quantities were highest in the

brominated flame-retardant laminate and existed in trace levels in the halogen-free laminates. Chlorine values differed greatly from the XRF results. Similar chlorine levels were detected in all laminates in small amounts along the order of $1/100^{th}$ to $1/10^{th}$ of a percent by weight. This summary presents information on the elemental analyses from the following memos:

ICL Industrial. JR 22 – Br and Cl Analysis in Copper Clad Laminates – part II. February 12, 2009.

ICL-IP Analysis of Laminate Boards. Memo from Stephen Salmon. November 16, 2009.

Dow. Analysis of Chlorine and Bromine. November 2, 2009.

Table 6-1 summarizes the methodology for Phase 1 and Phase 2 of the combustion and pyrolysis testing. This table can be used to compare the experiments conducted in both phases and illustrates how the Phase 1 experiments influenced Phase 2.

Table 6-1. Summary of Combustion Testing Methodology

	Phase 1	**Phase 2**
Goal:	To evaluate the suitability of test methods to produce and measure thermal degradation products of laminates, and to establish experimental methods/conditions for Phase 2 testing.	To understand the combustion by-products and fire characteristics of a standard TBBPA laminate compared to different laminates containing halogen-free flame retardants. To evaluate the effects of circuit board components in various precious metal recovery scenarios. To expand cone calorimeter testing to other candidate laminates.
Test Methods:	Thermogravimetric analysis to determine pyrolysis temperatures for establishing experimental methods for Phase 2 (performed by UDRI) Pyrolysis/quartz tube reactor system and cone calorimeter to evaluate the suitability of test methods to produce and measure thermal degradation products (performed by UDRI) XRF to determine elemental composition for establishing experimental methods for Phase 2 (performed by EPA ORD) Neutron activation to determine	Cone calorimeter

	Phase 1	Phase 2
	elemental composition for establishing experimental methods for Phase 2 (performed by Dow) ICP-OES, titration, and ion chromatography to determine elemental composition for establishing experimental methods for Phase 2 (performed by ICL-IP)	
Test Materials:	TBBPA laminate (BFR) Non-flame-retardant laminate (NFR) Phosphorus-based flame-retardant laminate (PFR1) (Several different laminates of each type were analyzed to inform the selection of Phase 2 laminates)	TBBPA laminate (BFR) Non-flame-retardant laminate (NFR) Phosphorus-based flame-retardant laminate (PFR1) Phosphorus-based flame-retardant laminate (PFR2) Plus 6 combinations of components and laminates
Size of Sample Material:	For quartz tube: 1.5-2 mm x 10 mm For cone calorimeter: ~100 cm^2 square pieces up to 50 mm thick	For cone calorimeter: ~100 cm^2 square pieces approximately 50 mm thick
Test Conditions:	For quartz tube: 7 different temperature/atmosphere conditions 300°C & 0% O_2 300°C & 21% O_2 700°C & 0% O_2 700°C & 10% O_2 700°C & 21% O_2 900°C & 0% O_2 900°C & 21% O_2 For cone calorimeter: Moderately high power (50 kW/m^2) and air atmosphere	Moderately high power (50 kW/m^2) and air atmosphere; and highest possible power (100 kW/m^2) and air atmosphere
Analytical Method:	GC-MS analysis for dioxins/furans (performed by EPA ORD) GC-MS analysis for PAHs (performed by UDRI) Cone calorimetry data on CO, CO_2, PM, smoke, and heat release	GC-MS analysis for dioxins/furans (performed by EPA ORD) GC-MS analysis for PAHs and organophosphorus compounds (performed by UDRI) Cone calorimetry data on CO, CO_2, PM, smoke, and heat release

6.3 Phase 2

Phase 2 identified the by-products of four laminates alone and with PCB components added through use of cone calorimetry and GC-MS analysis. Phase 1 results informed the methodology

and experimental conditions used in Phase 2 of the combustion testing. The research conducted in Phase 2 was also influenced by available funding, stakeholder input, and difficulties associated with novel equipment design. This section will summarize the conclusions, methods, and results of the Phase 2 testing. The full Phase 2 report is available in:

- Appendix E – University of Dayton Research Institute. Use of Cone Calorimeter to Identify Selected Polyhalogenated Dibenzo-P-Dioxins/Furans and Polyaromatic Hydrocarbon Emissions from the Combustion of Circuit Board Laminates. October 22, 2013.

The sample abbreviations used and order of the data presented in the figures in Section 6.3 of this report differ from those in Appendix E (full Phase 2 report). These minor changes are intended to increase the clarity of the Phase 2 findings for readers.

6.3.1 Phase 2 Conclusions

This section summarizes the main conclusions from Phase 2 testing. The methods used in the Phase 2 combustion testing are described in Section 6.3.2 followed by detailed results in Section 6.3.3.

Table 6-2 presents the sample combinations of laminates and components burned during Phase 2 testing, as well as the combustion scenarios (open burn and incineration) and the combustion emissions tested. A summary of the Phase 2 results is provided in Table 6-3 and Table 6-4 at the end of this section.

Table 6-2. Overview of Phase 2 Testing Methodology and Associated Abbreviations

Laminates Burned	TBBPA laminate (BFR) Non-flame-retardant laminate (NFR) Phosphorus-based flame-retardant laminate (PFR1) Phosphorus-based flame-retardant laminate (PFR2)
Laminate/Component Combinations Burned	BFR + standard halogen components (BFR + SH) BFR + low-halogen components (BFR + LH) PFR1 + standard halogen components (PFR1 + SH) PFR1 + low-halogen components (PFR1 + LH) PFR2 + standard halogen components (PFR2 + SH) PFR2 + low-halogen components (PFR2 + LH)
Scenarios (Heat Flux)	Open Burn (50 kW/m^2) (Laminate abbreviation-50) Incineration (100 kW/m^2) (Laminate abbreviation-00)
Analytes Tested	Polybrominated dibenzo-p-dioxins/furans (PBDD/Fs) Polyaromatic hydrocarbons (PAHs) Screening for organophosphorus degradation products

As presented in Table 6-3, PBDD/F analysis was only done for the laminate containing TBBPA because results from the Phase 1 elemental analyses revealed that PFR1 and PFR2 contained low levels of bromine (<0.04 percent by weight) and therefore would not generate detectable levels of PBDD/Fs. In comparison, the elemental analyses of BFR revealed levels of bromine between

6.1 and 8.1 percent by weight. Detectable levels of PBDD/Fs were emitted for all BFR laminates combusted. For the BFR laminate without components, higher levels of PBDD/Fs were generated in open burn conditions (3.04 ng/g) compared to incineration conditions (2.20 ng/g). PBDD/Fs were detected in the BFR laminates containing low-halogen components (1.88 ng/g) but could not be quantitated in the samples containing standard halogen components due to significant interference with the standard.

Although there was an attempt to measure chlorinated dioxins and furan emissions for the BFR laminates, the inability to detect the pre-sampling surrogate for some of the samples did not allow for effective quantification of the PCDD/Fs. It should be noted that detectable levels of PCDD/Fs were not found in any of the laminates when these compounds were quantified in Phase 1.

As shown in Table 6-4, PAHs were emitted by all materials. Of the laminates without components, BFRs emitted the highest levels of PAHs in both open burn (5.22 g/kg) and incineration (5.08 g/kg) conditions. The NFR in open burn conditions had the lowest levels of PAH emissions of the laminates without components (0.624 g/kg). PFR1 without components had the lowest levels among laminates in incineration conditions (1.51 g/kg). Of the samples with standard halogen components in open burn conditions, BFR generated the greatest amount of PAHs (3.93 g/kg), followed by PFR2 (2.24 g/kg), and PFR1 (2.04 g/kg); a similar emissions trend was observed for the samples containing low-halogen components.

In addition to the PBDD/F and PAH analyses, data on smoke, particulate matter, CO and CO_2 releases, and heat release were also collected during Phase 2. Smoke release was greatest for BFRs both with and without components. Particulate matter values for laminates without components were highest for PFR1 in open burn conditions. With the exception of the NFR laminate, samples without components emitted lower levels of particulate matter when combusted in incineration conditions compared to open burn conditions. The NFR laminates without components generated the lowest amount of particulate matter in both combustion scenarios compared to the other samples. Of the samples containing standard halogen components, BFR laminates emitted the greatest levels of particulate matter and PFR2 laminates generated the least; this particulate matter emissions trend was also observed in samples containing low-halogen components. However, particulate matter trends did not always align with smoke release emissions. While differences in CO release between samples were negligible, CO_2 emissions varied depending on laminate type.

Table 6-3. Summary of Phase 2 PBDD/Fs Results

Sample	PBDD/Fs	Quantity of PBDD/Fs detected (ng/g)
BFR-100	Present	2.20
BFR-50	Present	3.04
BFR + SH-50	Not quantified	N/A
BFR + LH -50	Present	1.88

Sample size: n=2. PBDD/Fs were only tested for the brominated laminates.

Table 6-4. Summary of Phase 2 PAH Results

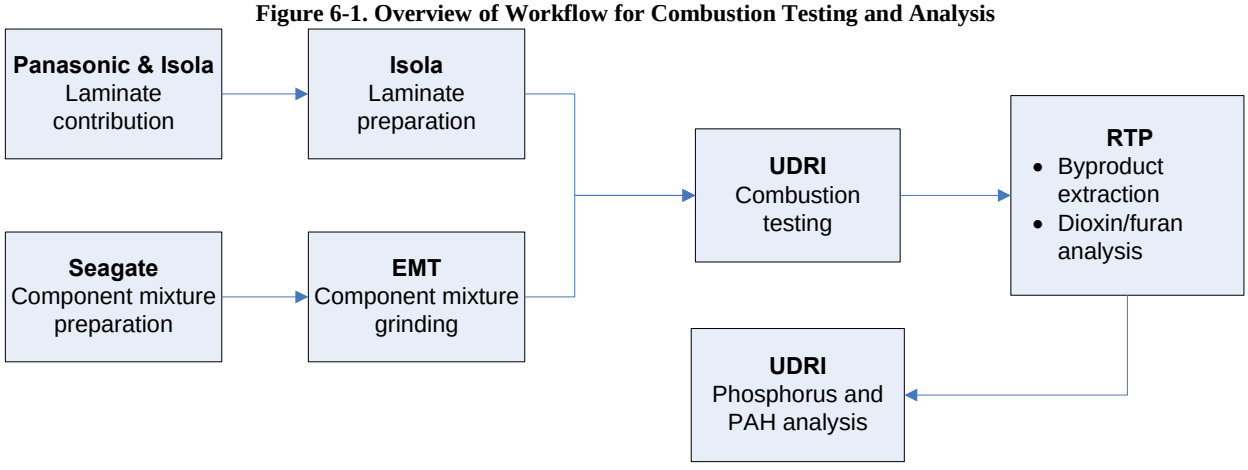
Sample	Quantity of PAHs detected (g/kg)
Incineration (100 kW/m^2)	
BFR-100	5.08
PFR1-100	1.51
NFR-100	1.95
Open burn (50 kW/m^2)	
BFR-50	5.22
PFR1-50*	1.74
PFR2-50	2.93
NFR-50*	0.624
Open burn (50 kW/m^2) with standard halogen components	
BFR + SH-50	3.93
PFR1 + SH-50	2.04
PFR2 + SH-50	2.24
Open burn (50 kW/m^2) with low-halogen components	
BFR + LH-50	3.69
PFR1 + LH-50	1.75
PFR2 + LH-50	2.11

Sample size: n=2 except for samples with asterisk for which n=1.

6.3.2 Phase 2 Methods

The combustion testing for Phase 2 was possible through the collaboration of many entities (Figure 6-1). Isola prepared the copper clad laminates in accordance with the laminate preparation procedures established in Phase 1 of the testing. A copper surface area of ~33 percent was pressed on each laminate to simulate real-world conditions of PCBs.

Figure 6-1. Overview of Workflow for Combustion Testing and Analysis



Seagate prepared the circuit board components. The component mixture simulated materials found in standard disk drive boards and included integrated circuits, resistors, capacitors, connectors (main source of plastic housing), shock sensors, and accelerometers. Both a low-halogen component mixture and a standard halogen component mixture were prepared by

Seagate. The partnership agreed to grind up the components prior to combustion testing to provide a more inclusive sample, have a more uniform sample preparation, and have more reliable results. EMT ground up the components and sent them to UDRI for combustion testing.

UDRI led the Phase 2 combustion testing. The laminate samples were tested under conditions mimicking open burning and incineration operations. Gases from combustion were collected in filters and polyurethane foam (PUF) cartridges contained in the cone calorimeter exhaust duct. The PUFs were cleaned and prepared with a pre-sampling spike of PBDD/F and PCDD/F quality controls to confirm that gases were being retained in the collection system and not lost through handling and extraction processes. A modified cone calorimeter was used to measure the emissions of particulate matter, CO, CO_2, and smoke from the samples and collect the combustion gases because it could mimic burning conditions of interest while providing quantitative emission information from complex circuit board samples. Heat release information and total mass burned were also measured; heat release information can reveal a material's flammability performance, while the total mass of each sample burned is used to determine emission factors.

The original experimental plan included a third combustion scenario for low-oxygen combustion to mimic smelting conditions. When UDRI initially burned samples under the simulated smelting conditions, combustion gases escaped from the top of the cone calorimeter apparatus. The outflow of these gases could have led to more complete combustion when exposed to more oxygen, which would have yielded inaccurate results. As a result, UDRI and the partnership collectively decided to exclude the low-oxygen combustion test condition from the study due to time and budget needed to modify the cone calorimeter system.

After the laminates were burned by UDRI, the PUFs and filters were shipped to EPA ORD for extraction, cleanup, and fractionation. Prior to extraction, the samples were spiked with internal standard mixtures for quality control purposes. The internal standards allow quantification of the native targets in the sample as well as help determine the overall method efficiency or "recovery" of the target. The dioxin and furan analysis carried out in Phase 2 focused on 2,3,7,8-substituted congeners of PCDD/Fs and their brominated counterparts. The target analytes included 17 PCDD/F congeners and only 13 PBDD/Fs congeners due to limited availability of commercial standards. Quality control for the dioxin and furan analysis was monitored using labeled pre-sampling (surrogate standards), pre-extraction (internal standards), and pre-injection (recovery standards) spiking solutions.

The PUFs and filters were extracted for PBDD/Fs using sequential Soxhlet extraction. The sequential Soxhlet extraction of the PUFs and filters required a 16-hour extraction with methylene chloride followed by another 16-hour extraction using toluene. The sampling train was also rinsed first with methanol, then methylene chloride, and lastly toluene after each run to collect any by-products that were not collected in the PUFs and filters. Once it was discovered that less than ten percent of the PBDD/Fs were found in the sample rinses, extraction for PBDD/Fs was only done for the PUFs and filters and the sampling train rinses were kept at UDRI for PAH analysis.

One portion of the Soxhlet-extracted samples was cleaned and fractionated for PBDD/F analysis at EPA. Clean-up of the extracts was required and done by washing the samples through a sequence of acidic and multilayer silica, carbon, and alumina columns. This multi-column liquid chromatography clean-up system was performed to ensure that combustion-related matrices would not interfere with the results of the analysis of the target compounds. EPA then analyzed the extracts using GC-MS for target PCDD/Fs and PBDD/Fs.

Another portion of the Soxhlet-extracted samples was sent back to UDRI for analysis of PAHs and organophosphorus compounds. (The extracts for PAH analysis did not undergo the same cleanup procedure as the extracts for dioxin and furan analysis.) The sampling train rinses were also used in the measurement of PAHs by UDRI. Liquid-liquid extraction using the methylene chloride rinse on the methanol rinse was performed. The four sample media tested for the presence of PAHs were: the methylene chloride from the methanol and methylene chloride rinses, the toluene rinse, the methylene chloride Soxhlet extraction of the PUF and filter, and the toluene Soxhlet extraction of the PUF and filter. UDRI used GC-MS to analyze the extracts for target PAHs and organophosphorus compounds. The PAHs targeted in the analysis were the 16 EPA priority PAHs. The organophosphorus analysis was conducted by doing a library scan of the chromatograms from the PAH analysis. Organophosphorus compounds were not quantified because the internal calibration standards necessary to conduct the analysis have not yet been commercially established.

Detailed information about the methods used for Phase 2 combustion testing can be found in Appendix E of this report.

6.3.3 Phase 2 Results

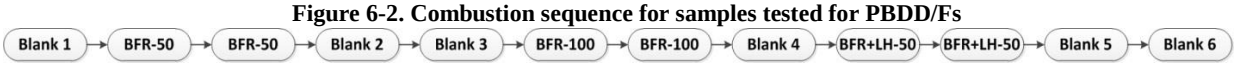
Halogenated Dioxin and Furan Analysis

Halogenated dioxins and furans were only analyzed for the samples containing BFRs. These samples were tested without components at incineration conditions, and both with and without components at open burn conditions. Although UDRI's combustion testing generated 42 samples for analysis, only a subset of samples were selected for halogenated dioxin and furan testing. Nine samples were selected for PCDD/Fs analysis, and 14 samples selected for PBDD/Fs analysis. As explained in Section 6.3.1, lack of detection of the pre-sampling quality control spike prevented the analysis of PCDD/F emissions.

Of the 14 samples chosen for PBDD/F analysis, testing was not carried out for the two samples intended to be burned under simulated smelting conditions (low oxygen). As explained in Section 6.3.2, all low-oxygen tests were excluded from this experiment due to the inability to yield reliable results. Of the 12 samples left to be analyzed after excluding the low-oxygen tests, six blanks were added for a total of 18 samples to be analyzed for PBDD/Fs. PBDD/F emissions could not be quantified for the six BFR-SH samples due to significant interference that caused the internal standards to be unusable. After excluding the six BFR-SH samples, PBDD/Fs were able to be quantified in 12 samples: 2 BFR-50, 2 BFR + LH, 2 BFR-100, and 6 blanks. Figure 6-2 presents the order of the blanks and brominated laminates combusted in the cone calorimeter that were tested for PBDD/Fs, but does not include samples not tested for PBDD/Fs that may

have been combusted within this sequence of 12 samples; other samples not analyzed for PBDD/Fs may have been combusted within this scheme.

Figure 6-2. Combustion sequence for samples tested for PBDD/Fs



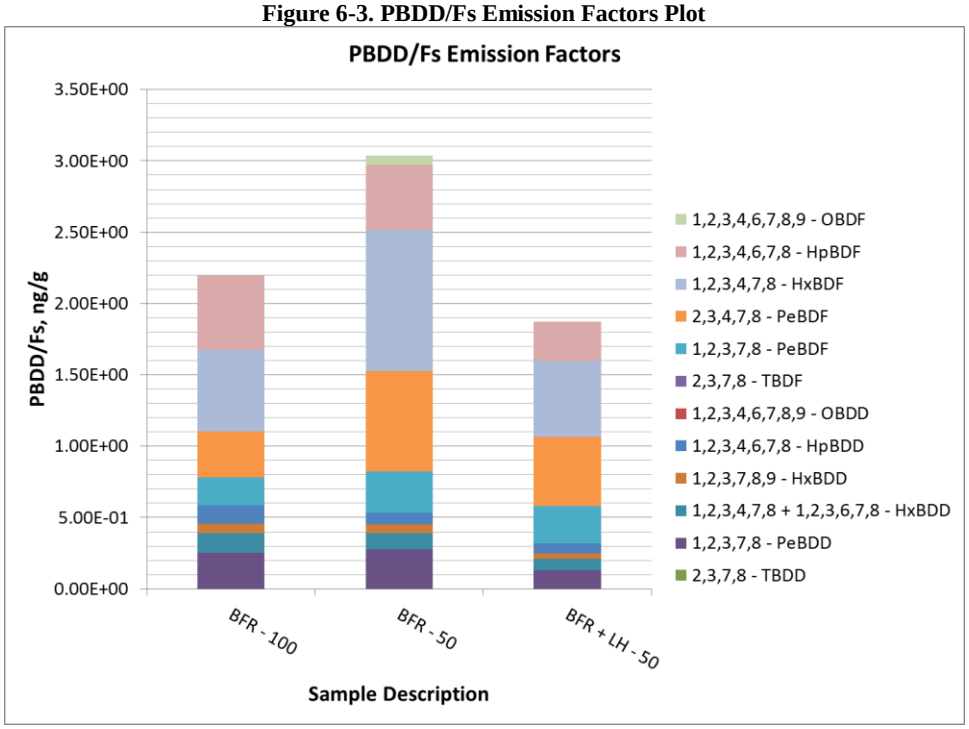
PBDD/Fs were detected and quantified in all six BFR samples (Figure 6-3); five of the six blanks had significantly lower levels of PBDD/Fs compared to the laminate samples. For example, the detection of 1,2,3,4,6,7,8 - HpBDF ranged from 4 to 9 ng/train for the six BFR laminate samples compared to not detected to 0.3 ng/train in all but the first combustion blank.

PBDD/Fs were detected in the first blank at levels as high as 11.7 ng/train. The subsequent samples are still considered valid because the congener pattern detected in the first blank differed greatly from the congener patterns detected in the subsequent samples and blanks. The first blank had large amounts of HpBDF and OBDF compared to the other samples and blanks analyzed for PBDD/Fs. The levels of HpBDF and OBDF detected from the combustion of the two laminate samples following the first blank (Figure 6-2) were about half of that detected in the first blank. The levels of tetra- through hexaBDF detected in the two laminate samples following the first blank were much higher than the levels detected in the first blank. Therefore, it is unlikely that laminate samples tested after the first blank and before the second blank were impacted by the tetra- through hexaBDF levels in the first blank. A conservative interpretation of the PBDD/F data for the first three tests would be to dismiss only the HpBDF and OBDF values for the first two laminates tested. The second blank tested had very low levels of HpBDF and OBDF detected. Therefore, no concerns about the levels of PBDD/Fs detected were raised by the investigators for the samples following the second blank. Although the ductwork and sampling train were cleaned, the detection of low concentrations of PBDD/Fs in the combustion blanks may be due to cross-contamination in the cone calorimeter duct. This cross-contamination is likely an outcome of the complexity of the cone calorimeter system and the reuse of many parts to create it. The difference in the amount of PBDD/Fs detected between the combustion blank samples and the BFR samples was as large as a factor of 100.

Higher chlorine levels were detected in the standard halogen components compared to the low-halogen components based on elemental analyses of the component mixtures (Appendix E). The difference in the levels of certain elements and molecules in the component mixtures may impact some endpoints including the production of chlorinated dioxins and furans, which could not be quantified in this study.

Figure 6-3 presents the sum of the target PBDD/F analytes emitted from the cone calorimeter experiments.

Figure 6-3. PBDD/Fs Emission Factors Plot



The BFR + SHs could not be quantitated due to significant interference with the standard. Data are an average of results from two tests.

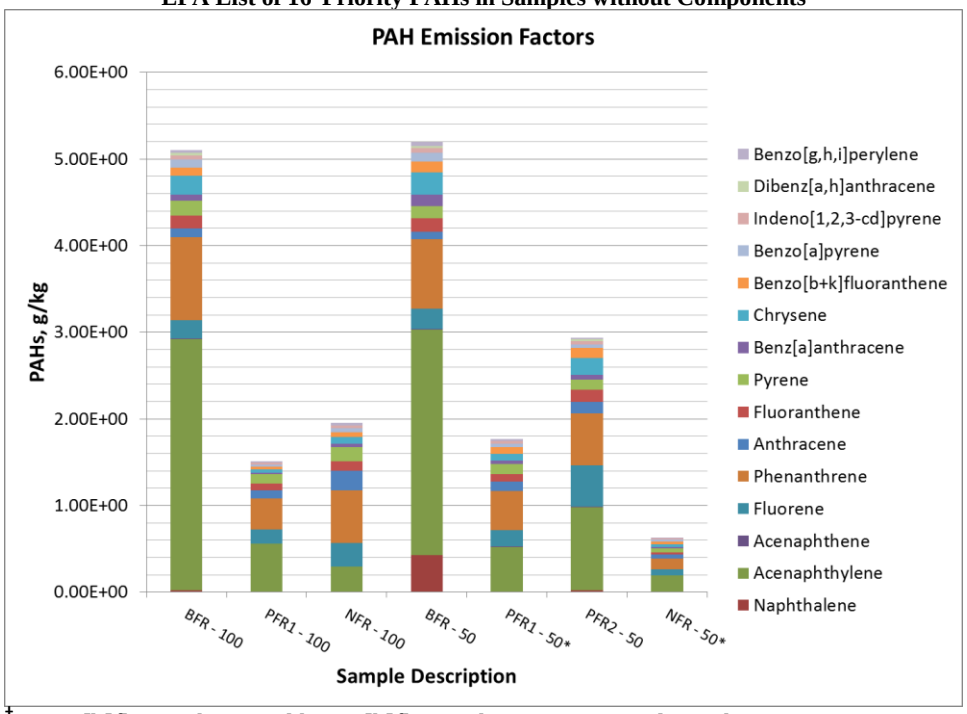
Polyaromatic Hydrocarbon Analysis

PAHs were detected and quantified in all samples. EPA's 16 priority PAHs were the target compounds for this analysis. It should be noted that PAH analysis from the PUF sampling was not expected to capture the light PAHs (i.e., PAHs containing ≤4 fused benzene rings). Therefore, the levels of light PAHs could be under reported. Figure 6-4 presents the PAH emission factors for samples without components. Of these samples, the BFRs combusted at both heat fluxes had the highest total PAH emissions – about twice the emissions of the non-brominated laminates. The NFR in open burn conditions had the lowest PAH emissions of all sample types. PFR2 was only tested in open burn conditions.

Figure 6-5 presents the PAH emission factors for samples with components. BFR laminates emitted the highest levels of PAHs among the different flame-retardant laminates with components. PAH emissions were similar between standard halogen and low-halogen components when compared within the same flame retardant laminate.

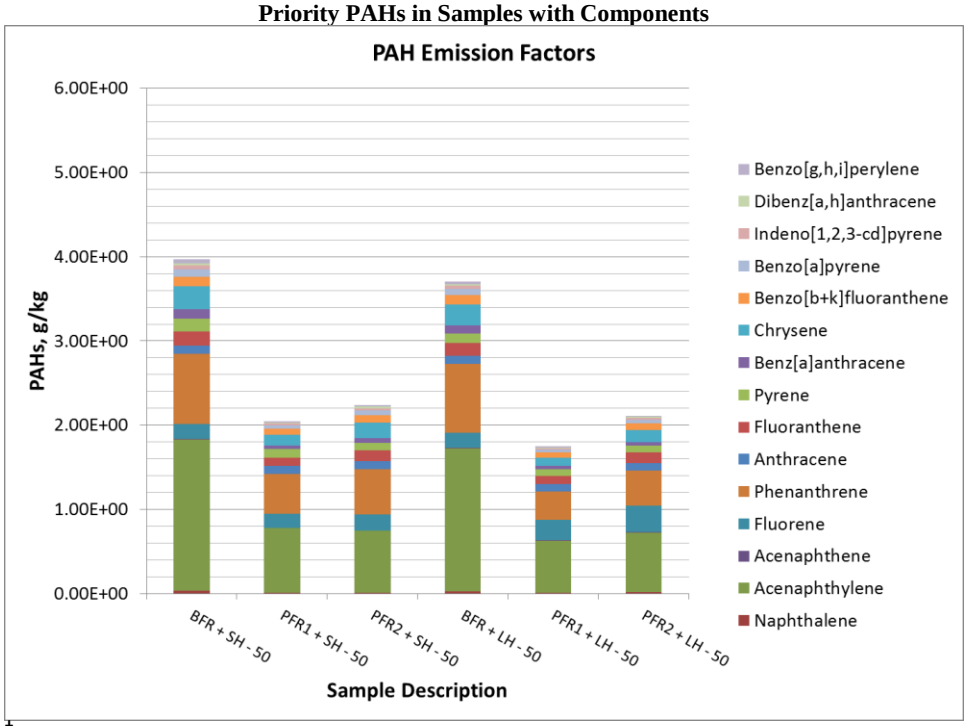
The flame retardant chemistry of each laminate type helps to characterize the PAH emission factor trends. TBBPA is a flame retardant that inhibits combustion in the vapor phase, which therefore yields more incomplete combustion products. On the other hand, the flame retardant systems used by PFR1 and PFR2 are phosphorus-based, which uses a condensed phase mechanism to form a char on the sample's surface. The char formation binds up potential PAH structures, resulting in fewer incomplete combustion products compared to the mechanism employed by TBBPA. Effects of flame retardant mechanisms on PAH emissions are generally reflected in Figure 6-4 and Figure 6-5.

Figure 6-4. PAH Emission Factors Plotted for Naphthalene and Higher Molecular Weight (MW) PAHs Detected from the EPA List of 16‡ Priority PAHs in Samples without Components



‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together
*Based on a single test; data without asterisks are an average of results from two tests.

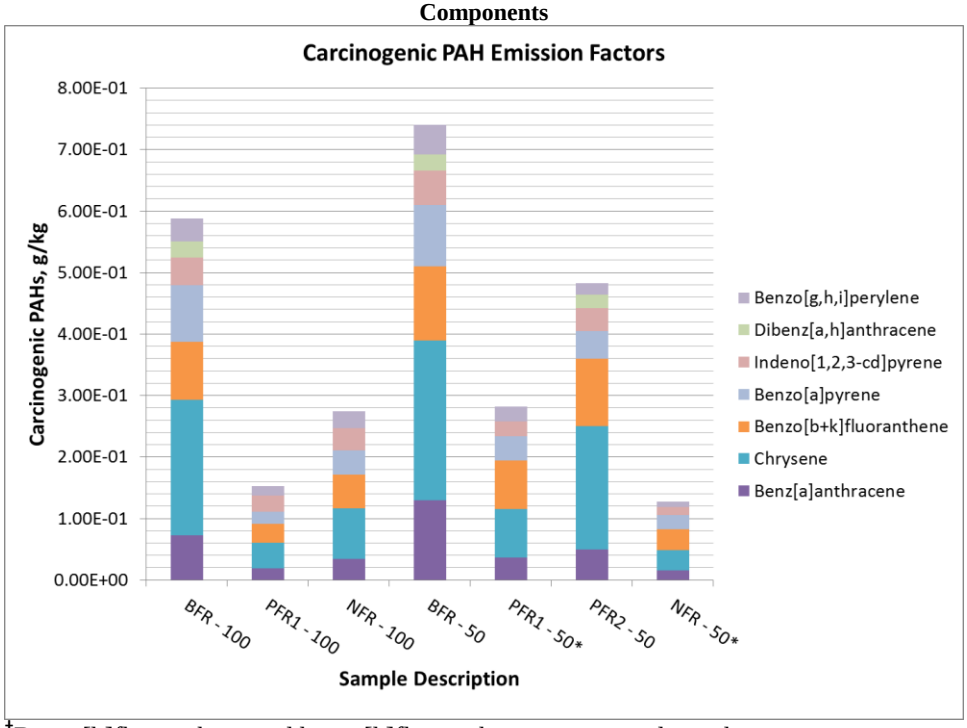
Figure 6-5. PAH Emission Factors Plotted for Naphthalene and Higher MW PAHs Detected from the EPA List of 16‡ Priority PAHs in Samples with Components



‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together
Data are an average of results from two tests.

Figure 6-6 presents the total emissions for the known carcinogenic PAHs for the samples without components and Figure 6-7 presents the total emissions for the known carcinogenic PAHs for samples with components. The emissions trends for the known carcinogenic PAHs for samples without components in Figure 6-6 follow similar emissions trends to the 16 priority PAHs without components presented in Figure 6-4; parallel trends are also observed between the samples with components presented in Figure 6-7 and Figure 6-5. Carcinogenic PAH emissions for samples without components were greatest for the BFR laminates in both combustion scenarios, with emissions being slightly higher in open burn conditions than in incineration conditions. Of the halogen-free flame-retardant laminates without components, PFR1 had lower carcinogenic PAH emissions compared to PFR2. For all flame-retardant laminates (BFR, PFR1, PFR2) without components, carcinogenic PAH emissions were greater in open burn conditions compared to incineration conditions. The NFR laminates without components had the lowest carcinogenic PAH emissions of all samples. Of the samples with components, BFR laminates with standard and low-halogen components had the highest carcinogenic PAH emissions – about twice the emissions of the PFRs. Samples with standard halogen components emitted only slightly higher levels of carcinogenic PAHs for all laminate types (BFR, PFR1, PFR2) compared to low-halogen components.

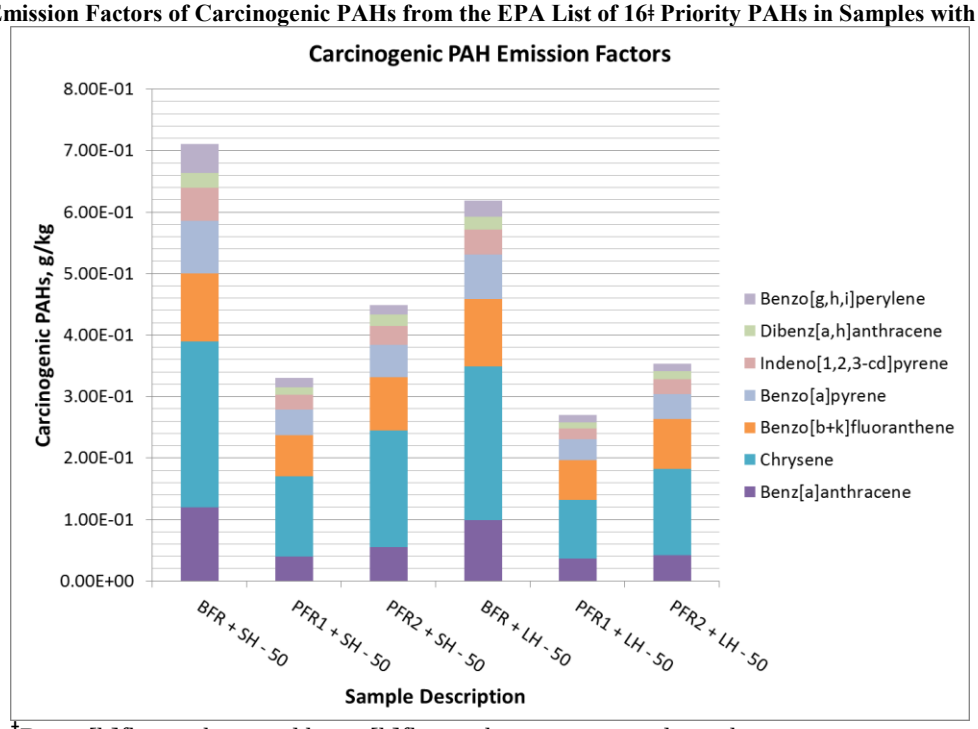
Figure 6-6. Emission Factors of Carcinogenic PAHs from the EPA List of 16[‡] Priority PAHs in Samples without Components



[‡]Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

*Based on a single test; data without asterisks are an average of results from two tests.

Figure 6-7. Emission Factors of Carcinogenic PAHs from the EPA List of 16‡ Priority PAHs in Samples with Components



‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together
Data are an average of results from two tests.

Because PCDD/Fs were unable to be quantified, attempts were made to determine the presence of other chlorinated benzenes and phenols known to be PCDD/F precursors. No chlorinated benzenes or phenols were detected at the concentrations analyzed in the PAH analysis. Although the absence of PCDD/F precursors in the PAH analysis may indicate that PCDD/Fs would not have been created under the combustion conditions tested in this study, this is merely a hypothesis.

Organophosphorus Analysis

Because PFR1 and PFR2 were phosphorus-based, UDRI conducted a spectral library scan for organophosphorus compounds in the laminate emissions. The human health and environmental impacts of exposure to these compounds were not assessed and are outside the scope of this report. It was assumed that the detection of organophosphorus compounds would indicate the presence of a vapor phase flame retardant, while the detection of no organophosphorus emissions would indicate the presence of a condensed phase flame retardant. Organophosphorus compound levels were unable to be quantified because the internal calibration standards vital to the quality control of the analysis have not yet been commercially developed. For this reason, the organophosphorus analysis in this report is limited strictly to a spectral library match.

Organophosphorus compounds were detected in all samples (Table 6-5). However, different compounds were detected from the repeat burn of the same laminate type. Some of the compounds detected are likely to be products of the flame retardant mechanism while others may be post-combustion reaction products or products of reactions between either PFR1 or PFR2 and

the circuit board components. Compounds containing silicon, for example, were likely the result of reactions between e-glass in the component mixture and the flame retardant. Compounds containing phosphonic or phosphinic acids are likely the decomposition products of phosphorus flame retardants.

Table 6-5. Organophosphorus Compounds Detected

Laminate Description	Organophosphorus Compounds Detected	Area %
BFR -100	Ethylphosphonic acid, bis(tert-butyldimethylsilyl) ester	8.33
BFR -100	Methylenebis(phosphonic acid), tetrakis(3-hexenyl) ester	0.29
BFR -50	1-Ethyl-1-hydridotetrachlorocyclotriphosphazene	0.04
BFR -50	Silanol, trimethyl-, pyrophosphate	0.51
	Phosphonic acid, methylenebis-, tetrakis(trimethylsilyl) ester	0.17
BFR + SH -50	O,O'-(2,2'-Biphenylylene)thiophosphoric acid	0.38
BFR + SH -50	Bis(4-methoxyphenyl)phosphinic acid	0.10
PFR1 +SH-50	Phosphonic acid, phenyl-, diethyl ester	0.25
	Phosphorane, 11H-benzo[a]fluoren-1-ylidenetriphenyl-	0.43
PFR2 + SH -50	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.53
	Silanol, trimethyl-, pyrophosphate(4:1)	0.08
	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.61
	4-Phosphaspiro[2.4]hept-5-ene, 4-methyl-5,6-diphenyl-	0.15
BFR + LH-50	Bis(4-methoxyphenyl)phosphinic acid	0.15
BFR + LH-50	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.23
PFR1 + LH-50	(2-Bromo-3-methylphenyl) diphenylphosphine	0.34
PFR1 + LH-50	Phosphine imide, P,P,P-triphenyl-	0.30
PFR2 + LH-50	Phosphine imide, P,P,P-triphenyl-	0.21

Smoke Release Analysis

Total smoke release for samples without components is presented in Figure 6-8. BFRs had the highest total smoke release among all samples without components, with releases being slightly greater in open burn conditions than in incineration conditions. The higher smoke release for the brominated flame-retardant laminate is likely due to its flame retardant mechanism that works by inhibiting vapor phase combustion, which creates more smoke. Total smoke release for the BFRs was less in incineration conditions compared to open burn conditions. PFR1 and PFR2 had lower total smoke release than the BFRs but only slightly higher total smoke release than the NFRs. It is likely that less smoke was emitted from PFR1 and PFR2 than the BFRs due to differences in the way each type of flame retardant works. PFR1 and PFR2 use a condensed phase char formation mechanism, which creates less smoke than a vapor phase mechanism. The char formation mechanism may also give insight into why an increase in PFR1's smoke release was observed when the heat flux was increased. The PAHs in the char of PFR1 and PFR2 may have become pyrolyzed when the heat flux rose, causing soot and condensed phase soot precursors to form. However, interpretations should consider the fact that the increase in smoke release is

within the percent error of the smoke measurement device (± 10 percent). The NFRs had the lowest total smoke release overall, but was within the percent error of PFR1 and PFR2.

Total smoke release for samples with components is presented in Figure 6-9. BFRs had the highest total smoke release among all samples with components, with releases being greater in the presence of standard halogen components compared to low-halogen components. In fact, higher smoke releases were observed for all laminate types (BFR, PFR1, PFR2) in the presence of standard halogen components compared to low-halogen components. While smoke data are important for determining incomplete combustion, smoke release is measured by light obscuration. For this reason, smoke release measurements cannot be directly correlated to the other emissions of concern investigated in this combustion testing project.

Figure 6-8. Total Smoke Release Plot for Samples without Components

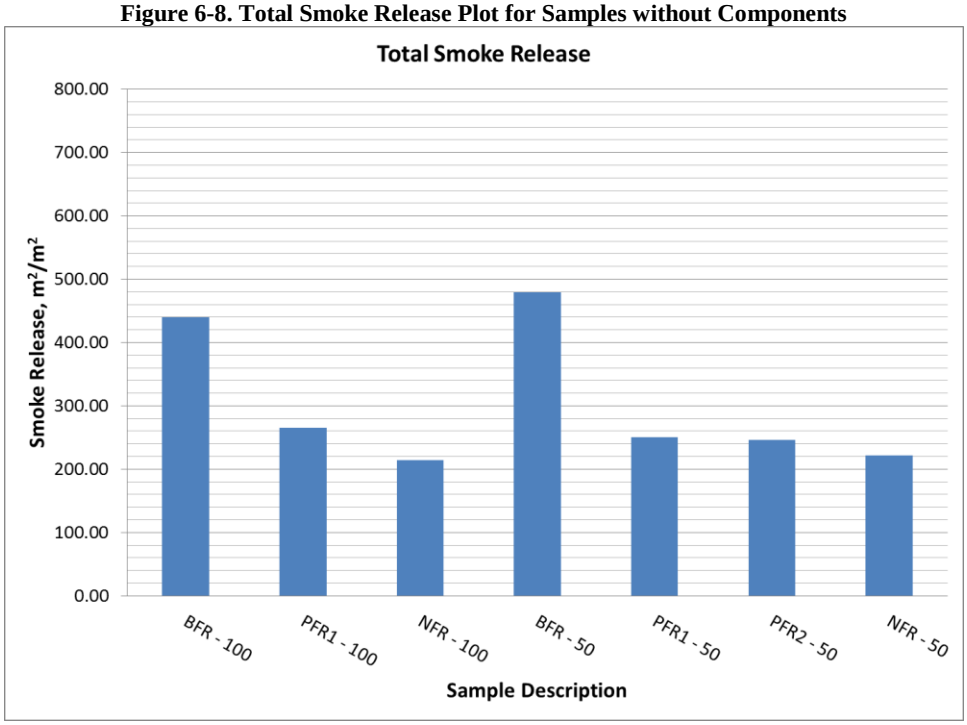
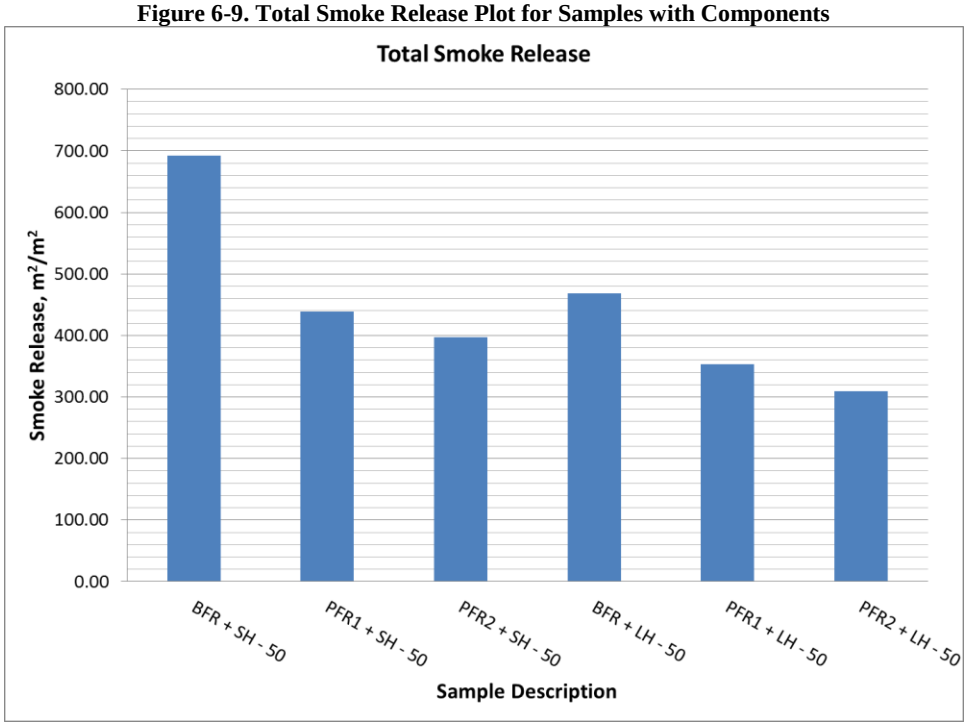


Figure 6-9. Total Smoke Release Plot for Samples with Components



Particulate Matter Release Analysis

The particulate matter results do not directly correlate with smoke release. For example, total smoke release was greatest for the samples containing the BFRs, while particulate matter was not always highest for the samples containing the BFRs. Differences between smoke release and particulate matter may be explained by smoke's chemical complexity; it is a substance that is composed of solid particles, liquid vapors, and gases. It is possible that the organic vapors released from the combustion of the BFRs were not captured by the filters measuring particulate matter but successfully obscured the light in the smoke release measurements.

Particulate matter emissions for samples without components are presented in Figure 6-10. Particulate matter emissions were higher in open burn conditions for all laminate types except the NFR. PFR1 in open burn conditions had the greatest particulate matter releases of all laminate types without components and were higher than the BFRs combusted in the same atmospheric conditions. The char phase flame retardancy mechanism can account for the higher particulate matter release; higher levels of particulate matter emissions may be the result of the pyrolyzation of the charred and cross-linked polymer components. Figure 6-11 presents particulate matter emissions for samples with components. Differences between BFR and PFR for particulate matter emissions appear negligible for the three laminate types with components. Particulate matter emissions were greater in the presence of standard halogen components than low-halogen components for all laminate types.

Figure 6-10. Particulate Matter Emission Factors for Samples without Components

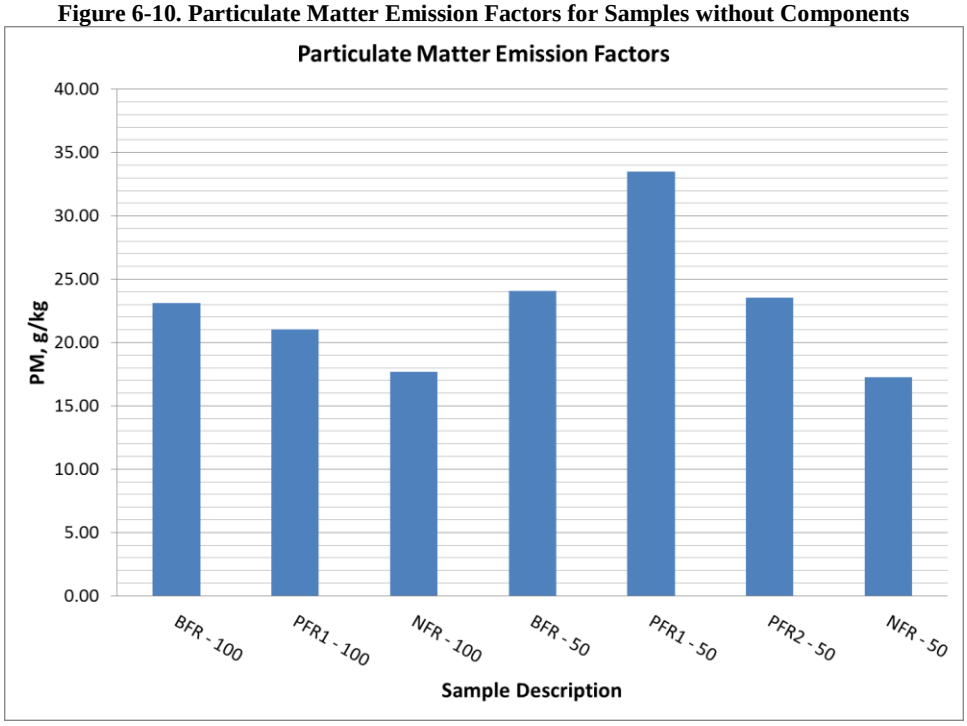
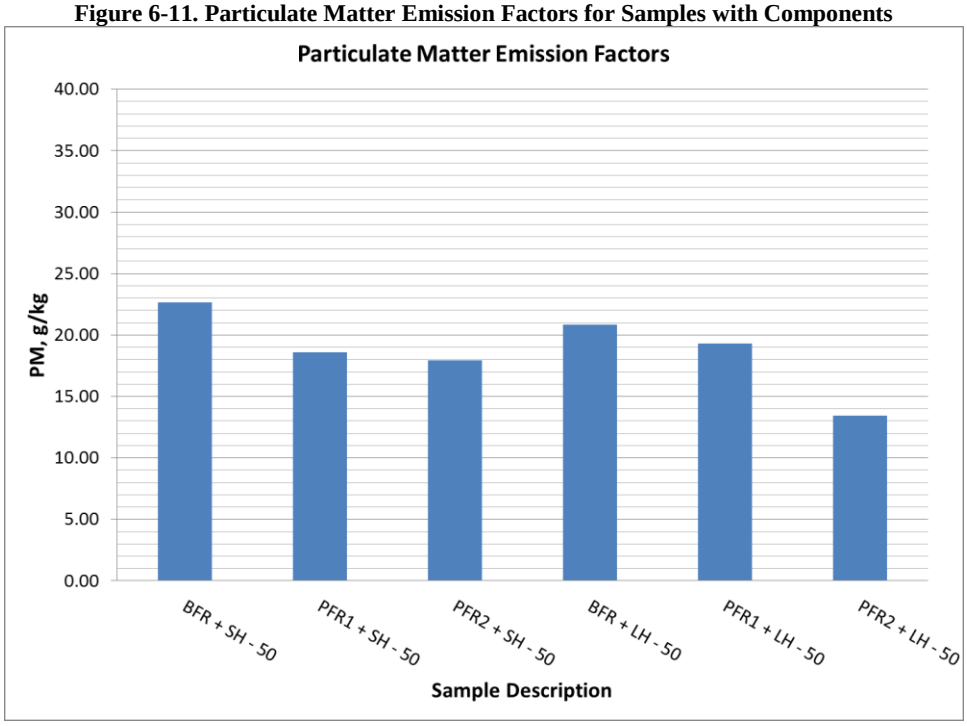


Figure 6-11. Particulate Matter Emission Factors for Samples with Components



CO/CO_2 Release Analysis

Figure 6-12 presents CO/CO_2 emissions for samples without components. In both combustion scenarios, BFRs without components had the lowest CO_2 emissions of all laminate types. CO_2

emissions were also lowest for BFRs of the samples with components presented in Figure 6-13. The comparatively lower CO_2 emissions for the BFR laminates is likely due to the inhibition of total combustion by bromine, which prevents carbon from converting to CO_2. However, a decrease in CO_2 emissions is not always accompanied by an increase in CO release as evidenced by the emissions trends for samples with (Figure 6-13) and without (Figure 6-12) components. PFR1 and PFR2 have CO emissions similar to the BFRs but higher CO_2 emissions. More CO_2 may be emitted when phosphorus-based flame retardants form char because less carbon is combusted. Halogenated flame retardants, in contrast, interfere with combustion in the vapor phase, leading to incomplete combustion and lower CO_2 yields. CO_2 yields were highest for the NFRs but their CO emissions were similar to or higher than the other laminate types in open burn conditions. While potential carbon in flame-retardant laminate systems is present as PAHs and soot, it is partly oxidized in the non-flame-retardant systems. CO and CO_2 emissions are best explained by combustion chemistry, flame retardant type and the presence of components.

Figure 6-12. CO/CO_2 Emission Factors Plot for Samples without Components

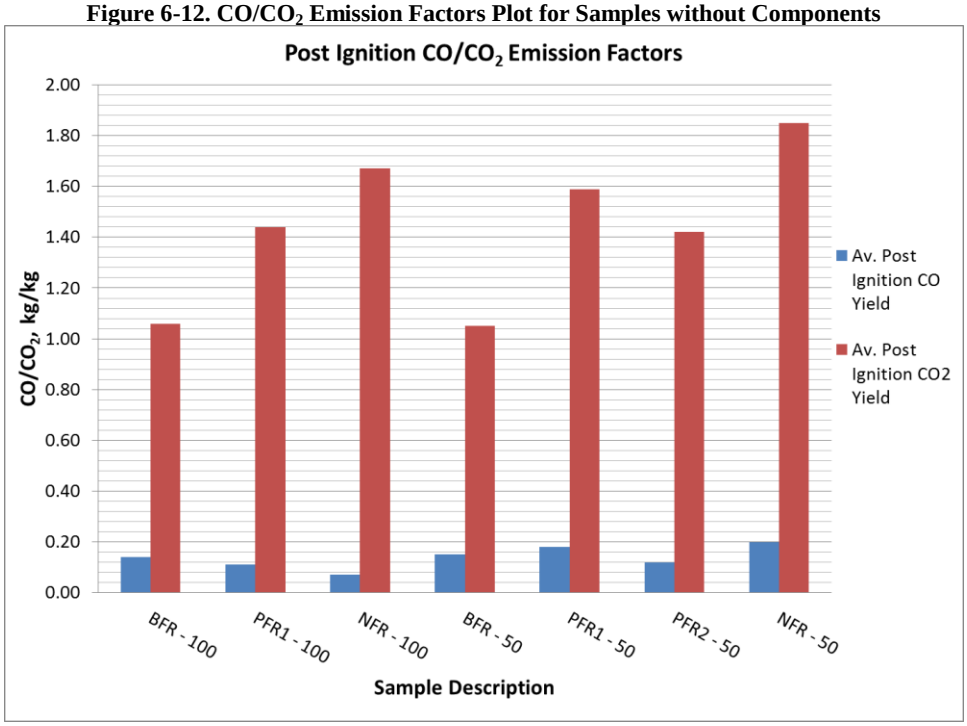
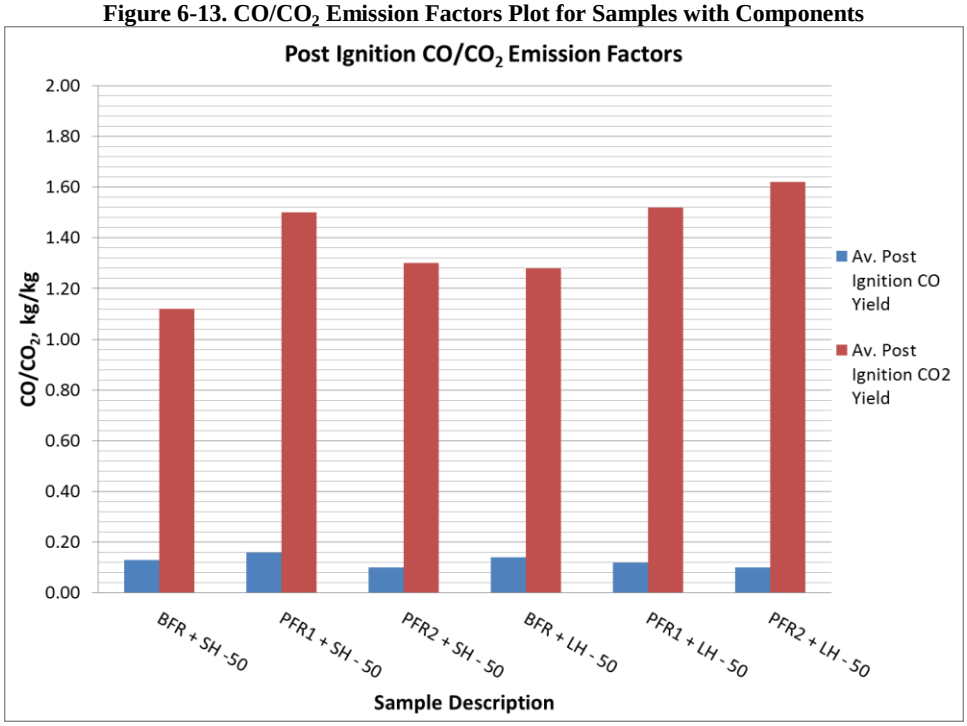


Figure 6-13. CO/CO_2 Emission Factors Plot for Samples with Components



Heat Release Results

Although flammability and fire safety were not the main focus of Phase 2 combustion testing, heat release information for each sample was captured using the cone calorimeter. Detailed information on heat release results can be found in Appendix E of this report. The heat release information gathered in this combustion testing study should not be used to infer the fire safety of the product, as each fire test used for regulating flame retardant materials is tailored for a specific fire risk scenario. Therefore, the cone calorimeter data in this study are best used to understand how much heat an object gives off when burned in a situation where it is well ventilated and a robust heat source is present.

In open burn scenarios, the flame-retardant laminates had lower peak heat releases compared to the laminates that did not contain flame retardants. Components generally increased total heat release, but had differing effects on peak heat release. In incineration conditions, the BFRs lowered heat release compared to the NFRs. PFR1 emitted heat at levels about equal or slightly higher than the NFRs; heat release was not measured for PFR2 in incineration conditions.

7 Considerations for Selecting Flame Retardants

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

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

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

7.1 Preferable Human Health and Environmental Attributes

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

used. In Table 4-4 and Table 4-5, the hazard designations based on SAR or professional judgment are listed in black italics, while those with hazard designations based on measured test data are listed in color. Readers are encouraged to review the detailed hazard assessments available for each chemical in Chapter 4.

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

7.1.1 Low Human Health Hazard

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

7.1.2 Low Ecotoxicity

Ecotoxicity includes adverse effects observed in wildlife. An aquatic organism's exposure to a substance in the water column has historically been the focus of environmental toxicity considerations by industry and government during industrial chemical review. Surrogate species of fish, aquatic invertebrates and algae are traditionally assessed to consider multiple levels of the aquatic food chain. Aquatic organisms are a focus also because the majority of industrial chemicals are released to water. Both acute and chronic aquatic toxicity should be considered in choosing a chemical flame retardant. It is common to have limited data on industrial chemicals for terrestrial wildlife. Some human health data (i.e., toxicity studies which use rodents) can be relevant to non-human vertebrates in ecotoxicity evaluations. When evaluating potential concerns for higher trophic level organisms (including humans), bioaccumulation potential (discussed in Section 7.1.4) is an important consideration in conjunction with toxicity for choosing a safer alternative.

7.1.3 Readily Degradable: Low Persistence

Persistence describes the tendency of a chemical to resist degradation and removal from environmental media, such as air, water, soil and sediment. Chemical flame retardants must be stable by design in order to maintain their flame retardant properties throughout the lifetime of the product. Therefore, it is not surprising that all ten of the chemicals assessed in this report had a persistence value of High or Very High.

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

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

In addition to the rate of degradation or measured half-life, it is important to be aware of the by-products formed through the degradation process. In some cases, degradation products might be more toxic, bioaccumulative or persistent than the parent compound. Some of these degradation products are discussed in the hazard profiles, but a complete analysis of this issue is beyond the scope of this assessment. The report did not consider toxicity from this potential degradation route.

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

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

7.1.4 Low Bioaccumulation Potential

The ability of a chemical to accumulate in living organisms is described by the bioconcentration, bioaccumulation, biomagnification, and/or trophic magnification factors. Some of the alternatives assessed in this report have a high level of potential for bioaccumulation, including Fyrol PMP and the two reactive flame retardant resins. Based on SAR, the potential for a molecule to be absorbed by an organism tends to be lower when the molecule is larger than

1,000 daltons. The inorganic flame retardants assessed in this report have low potential to bioaccumulate. Note that care should be taken not to consider the 1,000 daltons size to be an absolute threshold for absorption – biological systems are dynamic and even relatively large chemicals might be absorbed under certain conditions. Furthermore the initial 1,000 dalton threshold was established based on the consideration of bioconcentration factors (BCFs). Corresponding thresholds for hazard assessments based on bioaccumulation factor have not yet been rigorously established.

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

7.1.5 Low Exposure Potential

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

Even if a chemical has negative human health and environmental attributes, concerns may be mitigated if the chemical is permanently incorporated into a commercial product. In this case, the potential for direct exposure to the chemical is greatly decreased or eliminated. Reactive flame retardants are incorporated into the PCB laminate during the early stages of manufacturing. In the case of TBBPA, it is reacted into the epoxy resin to form a brominated epoxy before the

laminate production process begins. This brominated epoxy is the actual flame retardant that provides the fire safety to the PCBs. Studies have shown that levels of free, unreacted TBBPA in the brominated epoxy are extremely low. As referenced earlier in the report, one study by Sellstrom and Jansson extracted and analyzed filings from a PCB containing a brominated epoxy based on TBBPA. The study found that only 4 micrograms of TBBPA were unreacted for each gram of TBBPA used to make the PCB (Sellstrom and Jansson, 1995).

7.2 Considerations for Poorly or Incompletely Characterized Chemicals

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

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

Where hazard characterizations are based on measured data, there are often cases where the amount of test data supporting the hazard rating varies considerably between alternative chemicals. In Table 4-4 and Table 4-5, the hazard characterizations based on SAR or professional judgment are listed in black italics, while those with hazard characterizations based on measured test data are listed in color. The amount of test data behind these hazard characterizations shown in color can vary from only one study of one outcome or exposure, to many studies in many species and different routes of exposure and exposure duration. In some instances, testing may go well beyond basic guideline studies, and it can be difficult to compare data for such chemicals against those with only a single guideline study, even though hazard designations for both chemicals would be considered “based on empirical data” and thus come with a higher level of confidence. Cases where one chemical has only one study but a second chemical has many studies are complex and merit careful consideration. For hazard screening assessments, such as the DfE approach, a single adequate study can be sufficient to make a hazard rating. Therefore, some designations that are based on empirical data reflect assessment based on one study while others reflect assessment based on multiple studies of different design.

The hazard rating does not convey these differences – the full hazard profile should be consulted to understand the range of the available data.

7.3 Social Considerations

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

Occupational considerations: Workers might be exposed to flame retardant chemicals from direct contact with chemicals at relatively high concentrations while they are conducting specific tasks related to manufacturing, processing, and application of chemicals (see Section 5.2). Many facilities have established risk management practices which are required to be clearly communicated to all employees. The National Institute for Occupational Safety and Health (NIOSH) has established a hierarchy of exposure control practices[16]. From best to worst, the practices are: elimination, substitution, engineering controls, administrative controls and personal protection. Switching from high hazard chemicals to inherently lower hazard chemicals can benefit workers by decreasing workplace risks through the best exposure control practices: elimination and substitution of hazardous chemicals. While occupational exposures are different to consumer exposures, workers are also consumers and as such workers are relevant to both exposure groups.

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

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

Environmental justice considerations: At EPA, environmental justice concerns refer to the disproportionate impacts on people based on race, color, national origin, or income that exist prior to or that may be created by the proposed action. These disproportionate impacts arise because these population groups may experience higher exposures, are more susceptible in response to exposure, or experience both conditions. Factors that are likely to influence resilience/ability to withstand harm from a toxic insult can vary with sociodemographics (e.g., co-morbidities, diet, metabolic enzyme polymorphisms) and are therefore important considerations. Adverse outcomes associated with exposure to chemicals may be

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

disproportionately borne by people of a certain race, national origin or income bracket. Insights into EPA's environmental justice policy can be accessed at: www.epa.gov/compliance/ej/resources/policy/considering-ej-in-rulemaking-guide-07-2010.pdf.

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

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

7.4 Other Considerations

This section identifies performance and economic attributes that companies should consider when formulating or selecting a flame retardant for use in PCBs. These attributes are critical to the overall function and marketability of flame retardants and PCBs and should be considered jointly with the human health and environmental attributes described above.

7.4.1 Flame Retardant Effectiveness and Reliability

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

The ability of a product to meet required flammability standards is an essential performance consideration for all flame retardant chemicals. The primary purpose of all flame retardants is to prevent and control fire. According to the National Fire Protection Association, there were 1,602,000 fires reported in the U.S. in 2005, causing 3,675 civilian deaths, 17,925 civilian injuries, 87 firefighter deaths, and $10.7 billion in property damage (NFPA, 2007). Effective flame retardants are needed to further reduce fire incidents and associated injuries, deaths, and property damage. The fire safety requirements (e.g., a classification like UL (Underwriters Laboratories) 94 V0) determine the necessary level of flame retardant that needs to be added to a resin. Formulations are optimized for cost and performance, so that in some instances it may be equally viable to use a small quantity of an expensive, highly efficient flame retardant or a larger quantity of a less expensive, less efficient chemical.

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

Reliability is another aspect to consider in choosing a flame retardant. PCBs are used for many purposes, including telecommunications, business, consumer, and space applications. The environmental stresses associated with each application may be different, and so an ideal flame retardant should be reliable in a variety of situations. Resistance to hydrolysis and photolysis, for example, can influence the long-term reliability of a chemical flame retardant. For some applications, it may be necessary for the flame retardant to be resistant against acidic, alkali, and oxidative substances. These chemically demanding requirements have a direct effect on the persistence of flame retardants (see Section 7.1).

7.4.2 Epoxy/Laminate Properties

Small changes in a flame-retardant formulation can significantly affect the manufacturability and performance of PCB epoxies and laminates. In choosing a flame retardant for use in a PCB, it is important to consider how the flame retardant will affect key properties of the PCB epoxy and laminate, including glass transition temperature (T_g), mechanics (e.g., warpage, fracture toughness, flexural modulus), electrics, ion migration, water uptake (moisture diffusivity), resin-glass or resin-copper interface, color, and odor.

The glass Tg, for example, is particularly important for manufacturing lead-free PCBs. Due to the higher soldering temperatures required for lead-free PCBs, epoxy and laminate glass T_gs

must be high enough to prevent delamination of the PCB. Mechanical properties can also alter the manufacturing process by impacting the ability to drill through the laminate.

Changes in a flame-retardant formulation can also affect overall epoxy and laminate performance. Increased moisture diffusivity, for example, can reduce both the laminate and overall PCB reliability. Changes to moisture diffusivity, as well as any other parameter that may affect the electrical properties of the PCB should be considered. If the PCB cannot operate properly, any benefits associated with less hazardous flame retardants are irrelevant. As referenced in Section2.3, iNEMI (International Electronics Manufacturing Initiative) has conducted a series of performance testing of commercially available halogen-free materials to determine their electrical and mechanical properties.

7.4.3 Economic Viability

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

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

To ensure economic viability, flame retardants must be easy to process and cost-effective in high-volume manufacturing conditions. Ideally the alternative should be compatible with existing process equipment at PCB manufacturing facilities. If it is not, the plants will be forced to modify their processes and potentially to purchase new equipment. The ideal alternative would be a drop-in replacement that has similar physical and chemical properties such that existing storage and transfer equipment as well as PCB production equipment can be used without significant modifications.

The four steps in the Flame Resistant 4 (FR-4) manufacturing process that typically differ between halogenated and halogen-free materials are pressing, drilling, desmearing, and solder masking (Bergendahl, 2004). As a result, manufacturing and processing facilities may need to invest in new equipment in order to shift to alternatives flame retardants. In addition, daily operation costs may be different for the new process steps required to manufacture PCBs with alternative flame retardants.

Flame-retardants that are either more expensive per pound or require more flame retardant per unit area to meet the fire safety standards will increase the PCB's raw material costs. In this situation, a PCB manufacturer will attempt to pass the cost on to its customers (e.g., computer manufacturers), who will subsequently pass the cost on to consumers. However, the price premium significantly diminishes over the different stages of the value chain. For an alternative laminate, the price may be up to 20 to 50 percent higher per square meter, but for the final product (e.g., a personal computer), the price premium can be less than 1 percent.

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

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

7.4.4 Smelting Practices

Changes in flame-retardant formulation may also have implications for smelting processes. Smelters have had to adapt their practices over time to respond to changing compositions and types of electronic scrap as well as regulatory requirements (e.g., Waste Electrical and Electronic Equipment directive). As discussed in Section 5.3.2, smelters process PCB materials through complex, high-temperature reactions to recover precious and base metals (e.g., gold, silver, platinum, palladium and selenium, copper, nickel, zinc, lead). Primary smelters in the world (e.g., Boliden, Umicore, and Noranda) have learned how to operate with high loads of halogenated electronic scrap and effectively control emissions of dioxins and furans, mercury, antimony, and other toxic substances.

The consequences associated with the increased use of alternative flame retardants in FR-4 PCBs from a smelting perspective are largely unknown. For example, the flame-retardant fillers silicon dioxide and aluminum hydroxide are not expected to pose problems given that smelters routinely process silicon dioxide and aluminum hydroxide because they are found in other feedstock. Silicon dioxide is also beneficial in that it is used to flux the slag formed through the smelting process. Aluminum oxide, derived from either metallic aluminum or from aluminum oxide or hydroxide, can be tolerated in limited amounts. However, aluminum oxides are less effective than brominated flame retardants, so a greater load of aluminum oxide is needed to achieve similar flame retardancy. Whereas brominated flame retardants are typically found at 3 percent of feedstock weight, aluminum hydroxide flame retardants can account for 15 percent of

feedstock weight (Lehner, 2008). Since the slag used in base metals metallurgy have a limited solubility for Al_2O_3, completely replacing brominated flame retardants with aluminum oxide flame retardants would challenge the smelters' recovery or energy balance. A substantial increase in aluminum load would force smelters to use higher temperatures to overcome higher liquid temperatures, or experience higher slag losses as a result of adding slag for dilution. The added slag contains small, but measurable, contents of precious and base metals.

Phosphorus-based flame retardants are not expected to significantly change the composition of the slag product or cause significant problems. However, formation of phosphine (PH_3) from phosphorus-based flame retardants, and acrolein, hydrogen cyanide, and PAH from nitrogen-based flame retardants, is possible since most smelters operate under highly reducing conditions. Furthermore, little to no information is available in the literature on the combustion byproducts of phosphorus-based flame retardants under normal combustion conditions or elevated temperatures approaching those found in incinerators or smelters. As is standard practice, smelters will need to continuously evaluate if and how changes in flame-retardant formulation, as well as the overall composition of PCBs, will affect their operating procedures and health and safety practices.

7.5 Moving Towards a Substitution Decision

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

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

Switching to an alternative chemical is a complex decision that requires balancing all of the above factors as they apply to a particular company's cost and performance requirements. This report provides hazard information about alternatives to TBBPA to support the decision-making process. Companies seeking a safer alternative should identify the alternatives that may be used in their product, and then apply the information provided in this report to aid in their decision-making process.

Alternative chemicals are often associated with trade-offs. For any chemical identified as a potential alternative, some endpoints may appear preferable while other endpoints indicate increased concern relative to the original chemical. A chemical may be designated as a lower concern for human health but a higher concern for aquatic toxicity or persistence. For example,

in the case of high MW polymers, where health hazards and potential bioaccumulation are predicted to be low, one trade-off is high persistence. Additionally, there may be limited information about the polymer's combustion by-products, or how the polymer behaves in the environment and eventually degrades.

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

7.6 Relevant Resources

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

7.6.1 Resources for State and Local Government Activities

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

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

7.6.2 Resources for EPA Regulations and Activities

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

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

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

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

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

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

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

7.6.3 Resources for Global Regulations

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

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

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

7.6.4 Resources from Industry Consortia

iNEMI is a consortium of electronics manufacturers, suppliers, associations, government agencies, and academics. iNEMI has carried out a series of projects to determine the key performance properties and the reliability of halogen-free flame-retardant PCB materials. Each project has observed different outcomes, with the latest findings indicating that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of traditional brominated laminates. Technology improvements, especially those that optimize the polymer/fire

retardant combinations used in PCBs, have helped shift the baseline in regards to the performance of halogen-free flame-retardant laminates.

At the time the 2008 draft report was released, iNEMI was conducting performance testing for commercially available halogen-free flame-retardant materials to determine their key electrical and mechanical properties under its HFR-free Program Report. The results of the testing and evaluation of these laminate materials were made public in 2009.
The overall conclusions from the investigation were (1) that the electrical, mechanical, and reliability attributes of the eleven halogen-free laminate materials tested were not equivalent to FR-4 laminates and (2) that the attributes of the halogen-free laminates tested were not equivalent among each other (Fu et al., 2009). Due to the differences in performance and material properties among laminates, iNEMI suggested that decision-makers conduct testing of materials in their intended applications prior to mass product production (Fu et al., 2009).
http://thor.inemi.org/webdownload/newsroom/Presentations/SMTA_South_China_Aug09/HFR-Free_Report_Aug09.pdf

iNEMI also conducted two follow-on projects to its HFR-free Program Report: (1) the HFR-Free High-Reliability PCB Project and (2) the HFR-Free Leadership Program.

The focus of the HFR-Free High-Reliability PCB Project was to identify technology readiness, supply capability, and reliability characteristics for halogen-free alternatives to traditional flame-retardant PCB materials based on the requirements of the high-reliability market segment (e.g., servers, telecommunications, military) (iNEMI, 2014). In general, the eight halogen-free flame-retardant laminates tested outperformed the traditional FR-4 laminate control (Tisdale, 2013).
http://www.inemi.org/project-page/hfr-free-high-reliability-pcb

The HFR-Free Leadership Program assessed the feasibility of a broad conversion to HFR-free PCB materials by desktop and laptop computer manufacturers (Davignon, 2012). Key electrical and thermo-mechanical properties were tested for six halogen-free flamed-retardant laminates and three traditional FR-4 laminates. The results of the testing demonstrated that the computer industry is ready for a transition to halogen-free flame-retardant laminates. It was concluded that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of brominated laminates and that laminate suppliers can meet the demand for halogen-free flame-retardant PCB materials (Davignon, 2012). A “Test Suite Methodology” was also developed under this project that can inform flame retardant substitution by enabling manufacturers to compare the electrical and thermo-mechanical properties of different laminates based on testing (Davignon, 2012).
http://www.inemi.org/project-page/hfr-free-leadership-program
http://thor.inemi.org/webdownload/Pres/APEX2012/Halogen-Free_Forum/HFR-Free_PCB_Materials_Paper_022912.pdf

HDPUG is a trade organization for companies involved in the supply chain of producing products that utilize high-density electronic packages. HDPUG created a database of information on the physical and mechanical properties of halogen-free flame-retardant materials, as well as the environmental properties of those materials. The HDPUG project, completed in 2011, broadly examined flame-retardant materials, both ones that are commercially viable and in

research and development. For more information about the database and other HDPUG halogen-free projects, visit: http://hdpug.org/content/completed-projects#HalogenFree.

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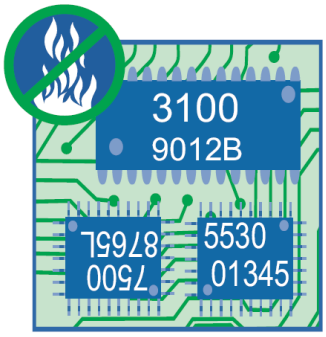
United States Environmental Protection Agency

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS



APPENDICES

December 2014

UPDATED DRAFT REPORT

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX A

Yamada, Takahiro; Striebich, Richard. Open-burning, Smelting, Incineration, Off-gassing of Printed Circuit Board Materials Phase I Flow Reactor Experimental Results Final Report. Environmental Engineering Group, UDRI. August 11, 2008

Open-burning, Smelting, incineration, off-gassing of printed circuit board materials, Phase I Flow Reactor Experimental Results Final Report (August 11, 2008)

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1. Introduction and Background

In this study we investigated the controlled exposure of various printed circuit boards (PCBs) laminates to high temperature conditions. This work, combined with more realistic combustion studies (Cone Calorimeter) will allow us to better understand the mechanisms of PCB thermal destruction. This information will be used to evaluate existing and candidate flame retardants used in the manufacturing of the PCBs. The combination of better controlled experiments with actual combustion experiments will allow researchers and manufacturers to determine whether candidate flame retardant material is better or worse than the existing formulations.

2. Experimental Setup

Figures 1 and 2 show an overview photo and a schematic of the experimental setup designed for the project. A straight 28.5" long quartz reactor with 9.5×7mm o.d.×i.d. (QSI, Fairport Harbor, OH) was used for pyrolysis experiments, and same reactor with 3×1mm i.d.×o.d. stem attached to the straight main reactor at 5 ¼" from the reactor inlet end (QSI, Fairport Harbor, OH, custom order) was used for the oxidation experiments. The narrow tubing was installed to introduce oxygen for the combustion tests. Figure 3 shows detailed design of the modified reactor. New reactor was used for each sample for pyrolysis experiments (100% N_2). The same reactor was used for the experiment with 10 and 21% O_2 and N_2 as bath gas. The samples were gasified under pyrolytic condition for all experiments as seen in Figure 2. Blank experiments were performed for each experiment, both pyrolysis and oxidation, to ensure that there was no carry over from the previous experiments. The reactors were installed into 3-zone temperature controlled furnace, ¾" diameter and 24" length, SST-0.75-0-24-3C-D2155-AG S-LINE (Thermocraft, Winston-Salem, NC.).

Figure 1. Overview of experimental Setup

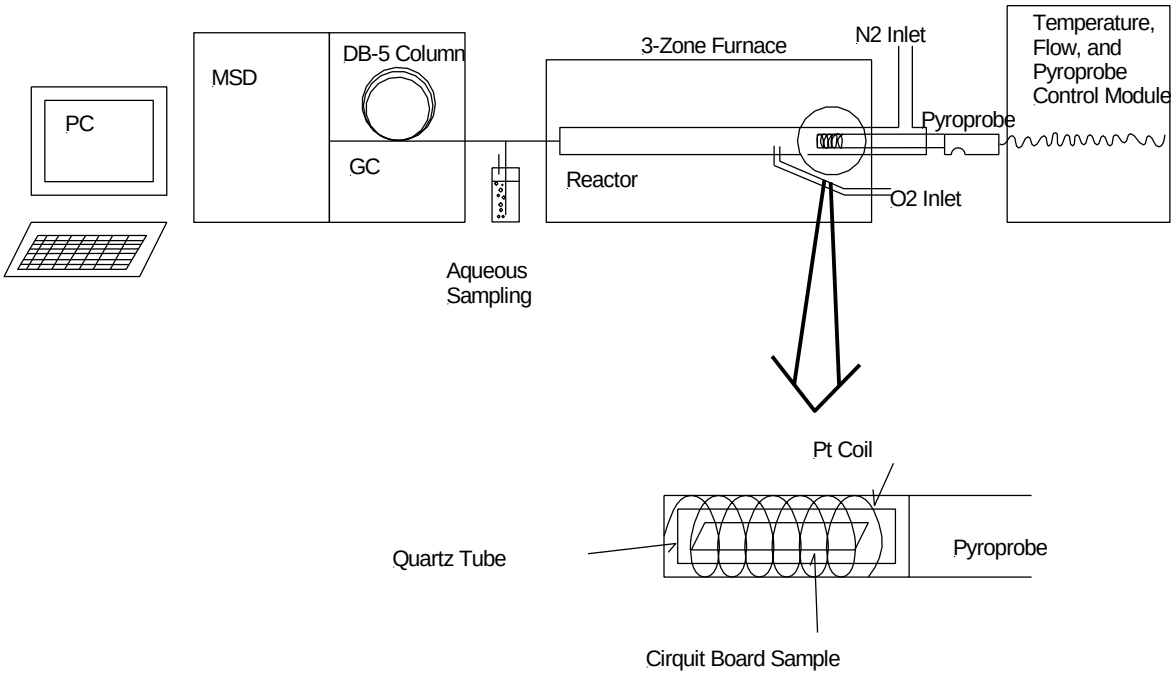

Figure 2. Schematic of experimental setup used for this project

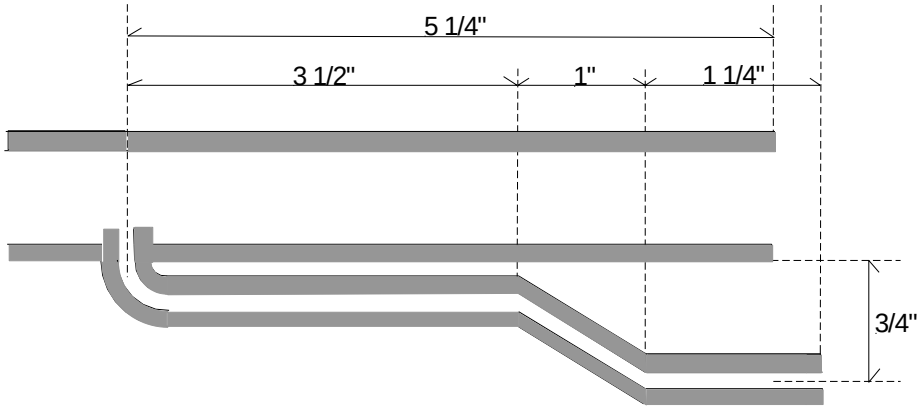

Figure 3. Detailed schematic of reactor inlet

Figure 4 shows the reactor temperature profiles at 300, 700, and 900ºC. Based on the profiles, effective length was determined to be 18" (from 6" to 24"). The effective length was used to set gas flow rate to maintain 2 sec. of residence time for each temperature. The transfer line between the reactor and GC oven was heated above 250ºC.

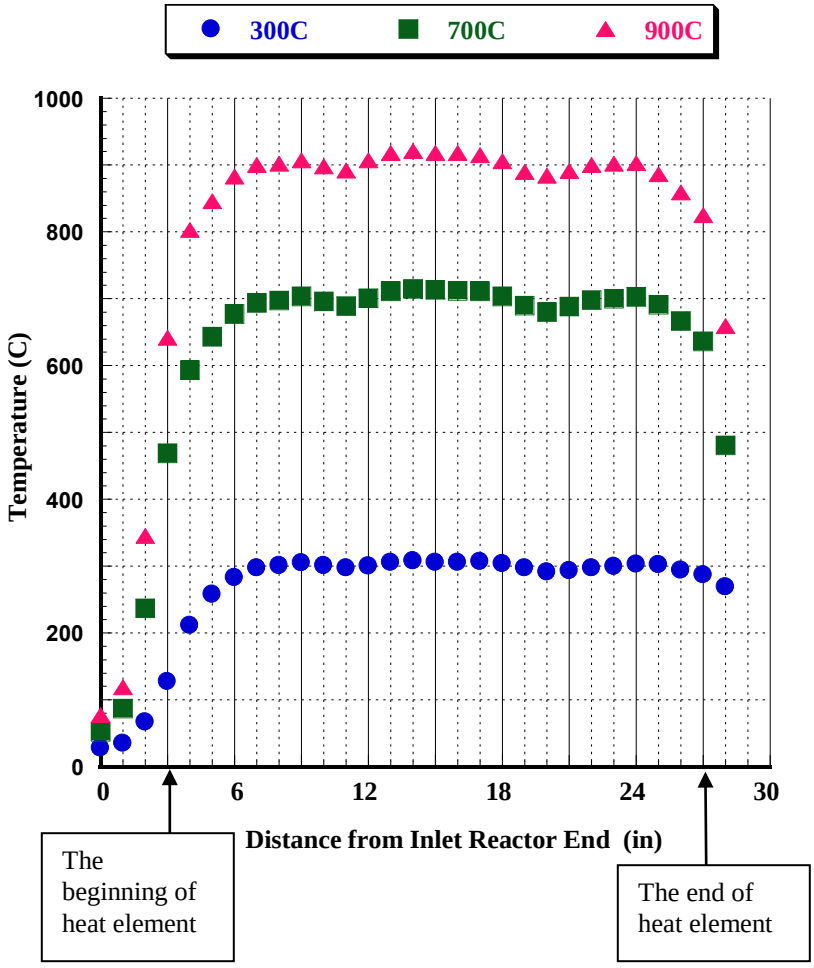

Figure 4. Reactor temperature profiles for 300, 700, and 900ºC

As shown in Figure 5, samples were gasified using a pyroprobe, CDS 120 Pyroprobe (CDS analytical Inc., Oxford, PA). The sample (circuit board laminate) was cut into a small piece, 1.5 - 2 mm wide × 1cm long, and inserted into quartz cartridge, 3×4mm i.d.×o.d. 1" length (CDS analytical Inc. Oxford, PA) as shown in Figure 6. The cartridge was then inserted into pyroprobe for the gasification. When the sample was gasified, the pyroprobe temperature was increased from room temperature to 900ºC with a 20ºC/ms ramp rate and held for 20 sec. at the final temperature. The gasification process was repeated 3 times to ensure complete gasification. The exhaust gas was passed through an impinger containing 20mL HPLC grade ultra-pure water (Alfa Aesar, Ward Hill, MA) in a 40mL amber vial (WHEATON Industries Inc., Millville, NJ). A small part of gas (1mL/min. flow rate) was introduced to Gas chromatograph / Mass Spectrometer (HP 5890/5970 GC/MSD, Hewlett Packard, Pasadena, CA). The GC column used for the analyte separation was DB-5MS, 30m length, 0.25mm i.d., 0.25µm thickness (Agilent J&W, Foster City, CA).

Figure 5. Pyroprobe Pt filament

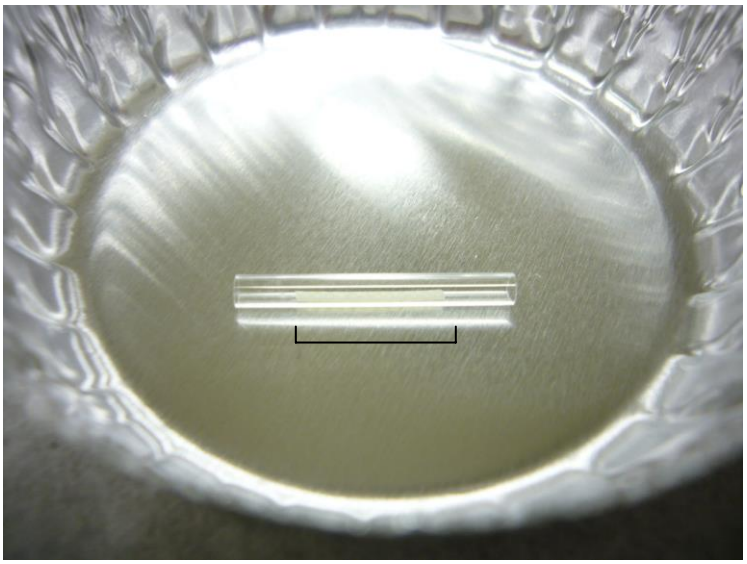

Figure 6. Pyroprobe cartridge with sample

3. Experimental Conditions

Table 1 and 2 show the experimental conditions that were investigated in Phase I of the flow reactor study. For the sample without copper laminate both pyrolysis and oxidation experiments were performed. The samples with copper laminate were only subject to pyrolysis. Selected experiments were repeated for pyrolysis at 700ºC and 21% O_2 at 900ºC. The oxygen concentrations of 10 and 21% were obtained by mixing nitrogen with 50% oxygen. The tables describe experiments conducted on a "no Flame Retardant" sample (NFR), a conventional "Brominated Flame Retardant" sample (BrFR), and candidate phosphorus sample (PFR).

Table 1 Experimental condition for the samples without Cu laminate (Unit: ºC)

Sample	N_2	10% O_2	21% O_2
NFR	300, 700, 900	700	700, 900
BrFR	300, 700	700	300, 700, 900
PFR	300, 700	700	300, 700, 900

Table 2 Experimental condition for the samples with Cu laminate (Smelting) (Unit: ºC).

Sample	N_2
NFR w/Cu	900
BrFR w/Cu	900
PFR w/Cu	900

Table 3 shows N_2 and O_2 (50%) flow rates for each temperature and oxygen concentration. The flow rate was set to obtain 2 sec. residence time in the flow reactor, 18" length × 7mm i.d.

Table 3 N2, O2, and total flow rate used for each experimental condition (Unit: mL/min).

Temperature	O_2 Conc. (%)	N_2	O_2 (50%)	Total
300	0	274	0	274
	21	159	115	274
700	0	162	0	162
	10	130	32	162
	21	94	68	162
900	0	134	0	134
	21	78	56	134

4. Results

4.1 TGA

Prior to the flow reactor incineration tests, thermogravimetric analysis (TGA) was conducted to determine final gasification temperatures. TGA for all samples in N2 and air environments are shown in Tables A1 to A6 of Appendix A. Table 4 shows initial and final gasification temperatures for each sample in N_2 and air environments. The gasification initial and final gasification temperatures vary for each sample. Those temperatures were lower when air was used for the gasification in general. No weight loss was observed over 900ºC for all samples; therefore, pyroprobe final gasification temperature was set to 900ºC.

Table 4 Sample gasification starting and final temperatures, and its weight loss

Sample	Gasification Environment	Approx. Starting Temperature (ºC)	Approx. Final Temperature (ºC)	Weight Loss (%)
Non-flame Retardant w/Cu	N_2	350	900	15.0
Non-flame Retardant	N_2	350	900	31.5
Non-flame Retardant	Air	300	650	45.9
Bromine Flame Retardant w/Cu	N_2	300	800	22.5
Bromine Flame Retardant	N_2	300	900	39.4
Bromine Flame Retardant	Air	250	650	48.4
Phosphorous Flame Retardant w/Cu	N_2	350	900	18.6
Phosphorous Flame Retardant	N_2	350	900	32.0
Phosphorous Flame Retardant	Air	350	750	47.3

4.2 Major Combustion Byproduct Analysis

The major peaks of the total ion chromatograms (TIC) were identified for the each flame retardant sample and experimental condition. Samples were introduced into the GC oven at a flow rate of 1mL/min., and cryogenically trapped at -30ºC during combustion tests. After the sample gasification and combustion, helium was introduced into the system for 3 minutes to sweep the reactor system and pressurize GC column. The oven was, then, heated at 20ºC/min ramp rate up to 300ºC and held 10 minutes. The results are shown in Figure B1 to B27 in Appendix B. Some of the experiments were repeated to examine the consistency of the experimental device. The repeatability experiments were conducted for the pyrolysis at 700ºC, and combustion with 21% O_2 at 900ºC for each of three samples. The results from these experiments are shown in Figure 3B, 8B, 12B, 17B, 22B, and 27B in Appendix B. Most of the compounds identified were aromatics. The most prevalent compounds from most pyrolysis and oxidation experiments were benzene, toluene, xylene and its isomers, phenol, methylphenol and its isomers, dimethyl phenol and its isomers, styrene, benzofuran and its derivatives, dibenzofuran and its derivatives, xanthene, naphthofuran and its derivative, naphthalene, biphenyl, biphenylene, fluorine, phenanthrene/anthracene. Major brominated compounds found from the brominated flame retardant include bromo - and dibromo-phenols and hydrogen bromide. Five largest peaks for each sample are listed in Table 5 for each temperature and oxygen concentration. Phenol, methylphenol, toluene, xylene, and benzene were often observed as major products. Dibromophenol was observed for brominated flame retardant at low temperature, and HBr was major brominated compound at the high temperature. Combined with TIC shown in Appendix B, it is observed that in the pyrolytic environment (100%N_2) brominated flame retardant reduces number of byproducts at all temperatures, especially effective at low

temperature (300ºC). In the oxidative environment (10 and 21% O_2) the brominated flame retardant also reduces both number of combustion byproducts and their amount at all temperatures. Phosphorous flame retardant reduces amount of combustion byproducts. Increased oxygen level reduces number and amount of combustion byproducts. Increased temperature also reduces number and amount of combustion byproducts, and byproducts are decomposed to smaller compounds at the high temperature. Number of brominated compounds were found at the trace level, and the identification of these compounds is described in Section 4.3. No phosphorous containing combustion byproducts were identified from the major peak of phosphorous flame retardant combustion test. Phosphorus flame retardant combustion tests at 900C with 21% oxygen were repeated after the completion of a series of combustion tests which produced skeptical results. When experiments were conducted under this condition initially, only water was observed with very minor combustion byproduct peaks. When experiments were repeated later, combustion byproducts were observed. TICs shown in Figure B26 and 27 are results from the repeated experiments. The reason why only water was observed is still unknown; however, problems with the mass selective detector (MSD) at that time could have caused poor sensitivity. Byproducts observed in these most recent experiments were more consistent with similar conditions and reactant feeds. Table 6 summarizes amount of sample gasified and its weight loss.

Table 5. Major Combustion Byproducts under Different Experimental Conditions

Temp. (ºC)	Environment	Major Combustion Byproducts (5 largest peaks in this order, top to bottom) and Remarks		
		Non-FR	Br-FR	P-FR
300	Pyrolysis	Phenol Methylphenol Toluene Xylene Xanthene	Phenol Methylethylphenol Methylphenol Dibromophenol Toluene (only mono-ring aromatics as a major peaks)	Phenol Methylphenol Dimethylpehnol Toluene Benzene
	Oxidation (21%)	N.A.	Benzene Methylethylphenol Bromophenol Dibromophenol Tetramethylbenzene	Phenol Methylphenol Dimethylphenol Toluene Xylene
700	Pyrolysis	Phenol Methylphenol Toluene Xylene Benzene	Phenol Toluene Benzene Methylphenol Methylbenzofuran (HBr observed)	Phenol Methylphenol Toluene Benzene Xylene

Table 5. Major Combustion Byproducts under Different Experimental Conditions (Cont'd)

Temp. (°C)	Environment	Major Combustion Byproducts (5 largest peaks with this order, top to bottom) and Remarks		
		Non-FR	Br-FR	P-FR
700	Oxidation (10%)	Phenol Benzene Toluene Methylphenol Styrene	Benzene Phenol Toluene Styrene Naphthalene (next biggest is bromophenol, then HBr)	Phenol Benzene Toluene Methylphenol Styrene
700	Oxidation (21%)	Benzene Phenol Benzofuran Toluene Styrene	Phenol Benzene HBr Dibenzofuran Naphthalene	Benzene Phenol Toluene Styrene Methylbenzofuran
900	Pyrolysis	Benzene Toluene Naphthalene Biphenylene Benzofuran	Benzene Toluene Naphthalene Styrene Indene	Benzene Naphthalene Toluene Biphenylene Anthracene
	Oxidation (21%)	Benzene Naphthalene Benzofuran Toluene Biphenylene (Benzene and naphthalene are the major products, others are minor)	Benzene Naphthalene HBr Phenanthrene Benzonitrile	Benzene Naphthalene Phenanthrene Toluene Biphenylene

Table 6. Amount of Samples Gasified and Their Gasification Rates

Sample	O_2 Conc. (%)	Temp. (C)	Sample Loaded (g)	Amount Gasified (g)	Gasification % by weight	Remarks
NFR	0	300	0.013644	0.005086	37.3	
		700	0.013336	0.005013	37.6	
			0.014391	0.005431	37.7	Duplicate
		900	0.013610	0.005175	38.0	
	10	700	0.012586	0.004722	37.5	
	21	700	0.013780	0.005072	36.8	
		900	0.013405	0.004966	37.0	
			0.012944	0.004566	35.3	Duplicate
NFR w/Cu	0	900	0.022023	0.004382	19.9	

Table 6. Amount of Sample Gasified and its Gasification Rate (Cont'd)

Sample	O_2 Conc. (%)	Temp. (C)	Sample Loaded (g)	Amount Gasified (g)	Gasification % by weight	Remarks
BrFR	0	300	0.012237	0.004501	36.8	
		700	0.013009	0.005157	39.6	
			0.012614	0.004855	38.5	Duplicate
	10	700	0.014123	0.005989	42.4	
	21	300	0.010710	0.003761	35.1	
		700	0.012087	0.004404	36.4	
		900	0.012065	0.004564	37.8	
			0.011910	0.004450	37.3	Duplicate
BrFR w/Cu	0	900	0.021360	0.004209	19.7	
PFR	0	300	0.013881	0.004689	33.8	
		700	0.014427	0.005010	34.7	
			0.013556	0.004717	34.8	Duplicate
	10	700	0.013486	0.004553	33.8	
	21	300	0.013447	0.004108	30.5	
		700	0.013447	0.004378	32.6	
		900	0.013853	0.004564	32.9	
			0.013318	0.004447	33.4	Duplicate
PFR w/Cu	0	900	0.022780	0.005374	23.6	

4.3 Detailed Brominated Flame Retardant Combustion Byproducts Analysis

Product yields

The major products generated at each temperature for each material are readily identified by GC-MS analysis. However, because the samples after pyrolysis or oxidation are so complex, additional analysis must be performed to examine the brominated byproducts constituents for each sample. Since analysis of the products using standards is difficult due to the fact that there is a thermal reactor in front of the GC-MS, the concentrations of the major compounds were estimated. At 300ºC in 0% oxygen atmosphere, the monobromophenol yield was estimated to be 1.2% of the mass of the board used. This estimate was calculated from the percentage of the laminate gasified (37% from Table 5), and the area percentage of chromatographic response from monobromophenol compared to the entire chromatographic run response (3.3%). The yield of the other major product (dibromophenol) was estimated to be 0.67% of the weight of the board exposed. These yields of the major products give an idea of the probable yield of the minor products.

The major products reported for the brominated flame retardants were the mono and dibrominated phenols. On the trace level (estimated as less than 1% of the total gaseous product mixture), a wide variety of compounds were formed as shown in Table 7. Various brominated aliphatic compounds were observed in small amounts, but the majority of compounds observed were brominated aromatics. Generally aromatic compounds are more stable, so this observation is appropriate.

Fate of brominated combustion byproducts

It is clear that some of the compounds reported for trace brominated organics were probably formed as products of incomplete combustion. This can be deduced because bromobenzene was not observed at 300ºC reactor temperature, but was observed in high amounts (on the trace level) at higher temperatures. We suspect that the bromophenols are relatively stable at 300ºC, but do degrade at higher temperatures to form bromobenzenes and in one case, trace amounts of bromobenzene diol. Even at reactor temperatures of 900ºC in an air atmosphere, there was some indication of the survival of these compounds through the reactor. At 900ºC, the four brominated compounds that could be observed were bromobenzene, bromobenzene diol, monobromophenol and dibromophenol. Blank runs (no sample) were conducted between analyses for many of the samples, and specifically between the 700ºC oxidation experiment and the 900ºC oxidation experiment. None of the major or minor compounds were observed in these blank experiments.

Even trace concentrations of brominated compounds were a surprise at these conditions. Oxidation at 900ºC should have been sufficient to completely oxidize the entire sample. It could be explained as follows: The sample was gasified instantaneously using pyroprobe. Because the amount of gas generated was relatively large compared to the carrier gas, it might have created oxygen deficit environment locally, and also there might not be enough time for gasified sample to be mixed with oxygen. Less surprising was the survival of the bromobenzene and the bromobenzene diol which were not present at temperatures of 300ºC and were present at 700 and 900ºC experiments. These clearly were formed as products during their time in the reactor, and the degradation of these compounds was not completed by the time these compounds escaped the high temperature reactor. From all this, we have learned that even at 2 seconds residence time in an air atmosphere, there is a small amount of bromine which will not be converted to HBr. The great majority of the brominated compounds, at these high temperatures, do convert to HBr. However, on the trace level, there is good evidence that compounds are surviving the exposure. This experimental system, because of its small sample size and short sampling time are not appropriate to observe the formation of brominated dibenzodioxins and brominated dibenzofurans. These types of compounds will be investigated in the larger scale systems.

Table 7 Identified Brominated Byproducts

		Area counts (x10E-06) from the Total Ion Current for each compound							
		pyrolysis (N2 atmosphere)				oxidation (21% O2 atmosphere)			
MW, g/mol	compound	300	700	900	blank	300	700	900	blank
		2-1-2	2-1-4	2-18-3	2-18-2	4-3-2	4-3-4	4-3-6	4-3-5
120	Br propene	**4.9**	ND	ND	ND	**0.2**	**0.1**	ND	ND
122	Br propane	**1.0**	ND	ND	ND	ND	ND	ND	ND
136	Br butane	**25.5**	ND	ND	ND	**6.6**	ND	ND	ND
172	Br phenol	**101.0**	**84.0**	ND	ND	**130.0**	**147.0**	**31.1**	ND
250	Br2 phenol	**55.0**	**27.7**	ND	ND	**93.0**	**69.6**	**7.5**	ND
206	Br naphthalene	ND	ND	ND	ND	ND	ND	ND	ND
262	Br dibenzodioxin	ND	ND	ND	ND	ND	ND	ND	ND
246	Br dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND
156	Br benzene	**0.1**	**4.7**	ND	ND	ND	**14.0**	**10.0**	ND
234	Br2 benzene	ND	**0.0**	ND	ND	ND	**1.1**	**1.4**	ND
214	Br propyl phenol	**3.5**	**3.4**	ND	ND	**14.0**	**0.1**	**0.2**	ND
292	Br2 propyl phenol	ND	ND	ND	ND	ND	ND	ND	ND
290	Br2 propenyl phenol	**2.3**	ND	ND	ND	**2.1**	ND	ND	ND

4.4 Phosphorous Flame Retardant Combustion Byproducts Analysis

With regard to phosphorous-containing trace organic compounds, we were not able to observe, even on the trace level, any phosphorus containing organic compounds. Several different phosphorous compounds were selected which were aromatic phosphorus containing compounds, including phenylphosphine, dimethyl phenylphosphine, phenylphosphinic acid, C3 phenyl phosphine, phenylphosphonic acid, hydroxyphenylphosphonic acid, and C4 phenylphosphine. The major ions from these compounds were checked for the phosphorous containing laminate materials, and none of these compounds were observed, even on the trace level.

The literature suggests that radical capture is not the mechanism of flame retardancy in phosphorous containing materials as it is with the brominated materials. Levchik and Weil[1] report some good information about these flame retardant materials. In our sample, we suspect that a aminophenyl phosphorous compound was used in the formulation as we do observe, on a trace level, the compound aniline as one of the compounds formed at 300ºC. Since many of the phosphorous retardants work by forming phosphate on the surface of the material they are protecting and "crusting" up the surface, we would expect aromatic formation from phenyl groups in the flame retardant formulation and the phenol degradation to take place. We do observe more polycyclic aromatic hydrocarbon (PAH) formation in this retardant than in the brominated retardant. The mechanism by which phosphorous FRs retard flame (surface complexes and PO_2 interaction with H/OH) prohibits incorporation of phosphorus with stable organic compounds. Thus, the phosphorous compounds could not be observed downstream of the reactor.

4.5 Hydrogen Chloride Analysis

During the course of experiments we were informed by the EPA that at least some (if not all) of the samples contained chlorine. Standard epoxies used for the laminate contain 1000 to 2500 ppm (0.1 to 0.25 wt %) chlorine. Therefore, we also examined if exhaust gas contained hydrogen chloride. Hydrogen chloride was found from brominated flame retardant pyrolysis and combustion tests, and phosphorus flame retardant pyrolysis tests. No hydrogen chloride was found from non-flame retardant pyrolysis and combustion tests. We did not look for chlorinated organics, such as polychlorinated dibenzodioxin, in these samples as there was an extremely low possibility of forming these organics at measurable levels with a flow reactor..

4.6 Aqueous Sample Analysis

The aqueous samples collected from combustion tests of BrFRs (w/o Cu) at 900ºC with 21% oxygen, and pyrolysis of BrFRs (w/o Cu) at 900ºC, were analyzed for bromine ion concentration. Results are shown in Table 8 and Figure C1 and C2 in Appendix C.

The samples were analyzed using a colorimetric method called Flow Injection Analysis (FIA)[2,3]. In this analysis, bromine ions react with reagents to form a colored complex which absorbs at 590 nm. The absorbance measured at 590 nm is directly proportional to the bromine ion concentration of the sample. Standards of 1, 2, 5, and 10 ppm are used for comparison to the sample solutions ($R^2 = 0.9995$). Figures C1 and C2 show the results of these two analyses. The sample labeled Blank 30 did not generate a peak as would be expected. The sample labeled BrFRCuP -1 (bromine flame retardant with Cu laminate) produced a negative peak, which was observed in both runs. It is believed that some other ion in the sample matrix may have reacted with method reagents to create a colored complex with a lower absorbance than the carrier solution. A TIC taken at the same time (Figure B9) also showed no HBr and no other brominated compounds. It is possible that Br reacted with copper in the pyroprobe to form $CuBr_2$, and it could have been condensed elsewhere on the reactor wall and transfer line. The aqueous samples from the Br flame retardant without Cu laminate showed bromine ion in it. Based on the XRF analysis, averaged Br concentration in the flame retardant sample was 6.17%. The expected Br ion concentration from two brominated flame retardant combustion tests were 14.0 and 13.8 ppm if all bromine converted to HBr. 63 and 51% bromine was recovered as HBr from the aqueous samples. The TIC taken at the same time (Figure B21 and B22) also consistently showed a large HBr peak.

Table 8 Aqueous sample analysis for Br ion concentration

Sample	Br Ion Concentration (ppm)	
	Run 1	Run 2
Br flame retardant w/o Cu 1st run (BrFR921-1)	8.77	8.87
Br flame retardant w/o Cu 2nd run (BrFR921-2)	7.06	7.14
Br flame retardant w/ Cu (BrFCuP1)	Not detected	Not detected

After the flow reactor combustion test, Br transport efficiency test was conducted using tetrabromobisphenol A (TBBPA) (Aldrich, St. Louis, MO) as a Br source. TBBPA was

dissolved into methylene chloride and dried in the quartz cartridge that was used for sample gasification. TBBPA was gasified in same manner as PCB samples. Reactor temperature was set at 700ºC, and gasified TBBPA was carried by N2 through reactor at the residence time of 2 sec. Sample was purged through a 40cc vial that contained 20cc HPLC grade ultrapure water. Results were summarized in Table 9. Br recovery rate was 33.2%. At 700ºC TBBPA will most likely decompose to HBr, or dissociated Br atom may react with the quartz reactor tube. The surface analysis and/or extraction of the reactor and transport line between reactor and vial could be further performed to elucidate the Br recovery rate if funding situation allows us to do so. Also our water impinger may not be sufficient to capture all HBr.

Table 9 Br transport test using TBBPA as a Br source

Sample	Br Introduced as TBBA (mg)	Expected Br if all Br converted to HBr (ppm)	Br recovered from aqueous sample (ppm)	Recovery Rate as Br (%)
TBBPA	0.393	11.5	3.82	33.2

5. Literature Review and Comparison

Relevant literature data for Br flame retardant circuit board and TBBPA pyrolysis and combustion experiments was reviewed after the experiment to better understand our experimental results. Grause et al.[4] conducted the pyrolysis of TBBPA containing paper laminated printed circuit board (PCB). The major constituents and their wt% of TBBA containing PCB are C (57.0%), H (6.3%), and Br (3.64%). The sample was pyrolised in a quartz glass reactor. The sample was heated from 50 to 800ºC with a heating rate of 10K/min. and a N2 flow of 100mL/min. The volatile products were gathered in four gas washbottles each containing 50mL of methanol. HBr content was determined by ion-chromatography (IC), and organic products were analyzed by GC-MS. Methylated phenols and methylated benzene derivatives were the most prominent degradation products after phenol. Also brominated phenols were found among the degradation products of TBBA, with main products being 2-bromophenol, 2,4- and 2,6-dibromophenols, and 2,4,6-tribromophenol. Most of the bromine was released in the form of HBr (87%), another 14% was bound in organic compounds, and about 1.8% of original bromine content was left in the residue. The release of the brominated aromatics was completed below 400ºC. However, only 50% of the bromine was released as HBr at this temperature. Another 37% of HBr was released from the resin between 400 and 700ºC. Barontini et al.[5,6] investigated thermal decomposition products and decomposition pathways of electronic boards containing brominated flame retardants using thermogravimetric (TG) FTIR and laboratory-scale fixed bed tubular batch reactor coupled with GC-MS/FID. The major constituents and their wt% are C (22.1~27.4%), H (2.0~2.4%), and Br (6.0~ 6.9%). The degradation products identified includes non-brominated aromatics (phenol, biphenyl, anthracene/phenanthrene, dibenzofuran, dibenzo-p-dioxin, bisphenol A), brominated benzene, phenols, and dibenzofurans and dioxins. Chien et al. [7] studied behavior of Br in pyrolysis of the printed circuit board waste. Pyrolysis of the printed circuit board wastes was carried out in a fixed bed reactor at 623-1073K for 30 min. in N_2. Condensable product gases were analyzed using FTIR, and non-condensable gases were scrubbed with NaOH solution. The main constituents and their wt% are C (52.2%), H (6.11%),

Br (8.53%), and copper (9.53%). Approximately 72.3% of total Br in the printed circuit board waste was found in product gas mainly as HBr and bromobenzene. Cu-O and Cu-(O)-Cu species were observed in the solid residues. No Cu-Br species was found in the solid residue. Barontini et al.[8,9] also conducted TBBPA decomposition product analysis. The analytical technique applied was similar to the one they conducted for Br flame retardant containing electronic boards. Major products formed were HBr, phenol, mono, di, and tribromophenols, bisphenol A, and brominated bisphenol A.

Our results show small amount of HBr for brominated flame retardant pyrolysis at 700ºC, and oxidation with 21% O_2 at 300ºC, and large amount of HBr for the oxidation with 10 and 21% O_2 at 700ºC and 21% O_2 at 900ºC. Our HBr recovery rate could have been greater, if multiple series of impingers and more water were used. Also if samples were captured using methanol impingers and analyzed using GC-MS as Grause et al. performed, instead of cryogenical trap, more brominated organic could have been identified, even though we had also identified many brominated organic compounds at the trace level. Experimental setup and analytical procedure will be reconsidered and redesigned for Phase II experiment for the better sample identification and bromine mass balance.

6. Conclusions

In this work, the controlled thermal exposure of flame-retardant and non-flame retardant laminates was examined. Results for brominated flame retardant laminates showed that bromophenol and dibromophenol were the main brominated organic products, with estimated yields of 1.2% for methylbromophenol and 0.67% for the dibromophenol. The responses for methylbromophenol and Dibromophenol decreased with increasing temperature, and were below detectable levels for oxygen free experiments. However, oxidation experiments indicated that even at 900ºC, some amounts of organic bromine containing compounds survived. In addition, bromobenzene and substituted bromophenols were formed at high temperatures, even though they were not formed at the 300ºC exposure (in both oxidation and pyrolysis). It is possible that these bromophenols and bromobenzenes will be sources for the formation of products in the cone calorimeter experiments, such as dioxins and furans.

Organic phosphorus compounds were not observed in the reactor exhaust gases during phosphorus FR experiments. When phosphorus containing flame retardants are used, the product distribution is similar to the non-flame retardant laminate experiments, in that there is a wide variety of polycyclic aromatic hydrocarbons (PAHs) such as benzene, toluene, xylene, and naphthalene. The results from this study suggests that cone calorimeter experiments will generate a large amount of PAH type compounds for all of the laminate systems but that the brominated system is likely to yield brominated dioxins and furans because of the relatively high yields of brominated phenols observed at high temperatures in this study. In addition, the compounds we should expect in the cone calorimeter are higher yields of methylbromophenol, dibromophenol, bromobenzene (mono and di) as well as brominated and nonbrominated fragments of bisphenol A, such as C_3 substituted bromophenol, bromomethylphenol and the like. All of the laminates formed large amounts of phenol and alkyl substituted phenols.

These experiments did not use enough mass of laminate to perform dioxin and furan analysis on-line. The investigation of these compounds should be performed with larger masses of sample and using off-line analysis as it is being performed for the cone calorimeter experiments. The lab scale experiments indicate that even under well controlled conditions, it is difficult to completely degrade the brominated phenols, even at 900ºC. While most of the bromine is converted to HBr, its conversion is not complete unless very well controlled mixing is available to expose all of the gaseous products to 21% oxygen.

References:

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2. Anagnostopoulu, P. I.; Doupparis, M. A. Anal. Chem. 1986, 58, 322-326.
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4. Grause, G.; Furusawa, M.; Okuwaki, A.; Yoshioka, T. Chemosphere 2008, 71, 872-878.
5. Barontini, F.; Cozzani, V. J. Anal. Appl. Pyrolysis 2006, 77, 41-55.
6. Barontini, F.; Marsanich, K.; Petarca, L.; Cozzani, V. Ind. Eng. Chem. Res. 2005, 44, 4186-4199.
7. Chien, Y.-C.; Wang, Y. P.; Lin, K.-S.; Huang, Y.-J.; Yang, Y. W. Chemosphere 2000, 40, 383-387.
8. Barontini, F.; Cozzani, V.; Marsanich, K.; Raffa, V.; Petarca, L. J. Anal. Appl. Pyrolysis 2004, 72, 41-53.
9. Barontini, F.; Marsanich, K.; Petarca, L.; Cozzani, V. Ind. Eng. Chem. Res. 2004, 43, 1952-1961.

Appendix A
Thremogravimetric Analysis (TGA)

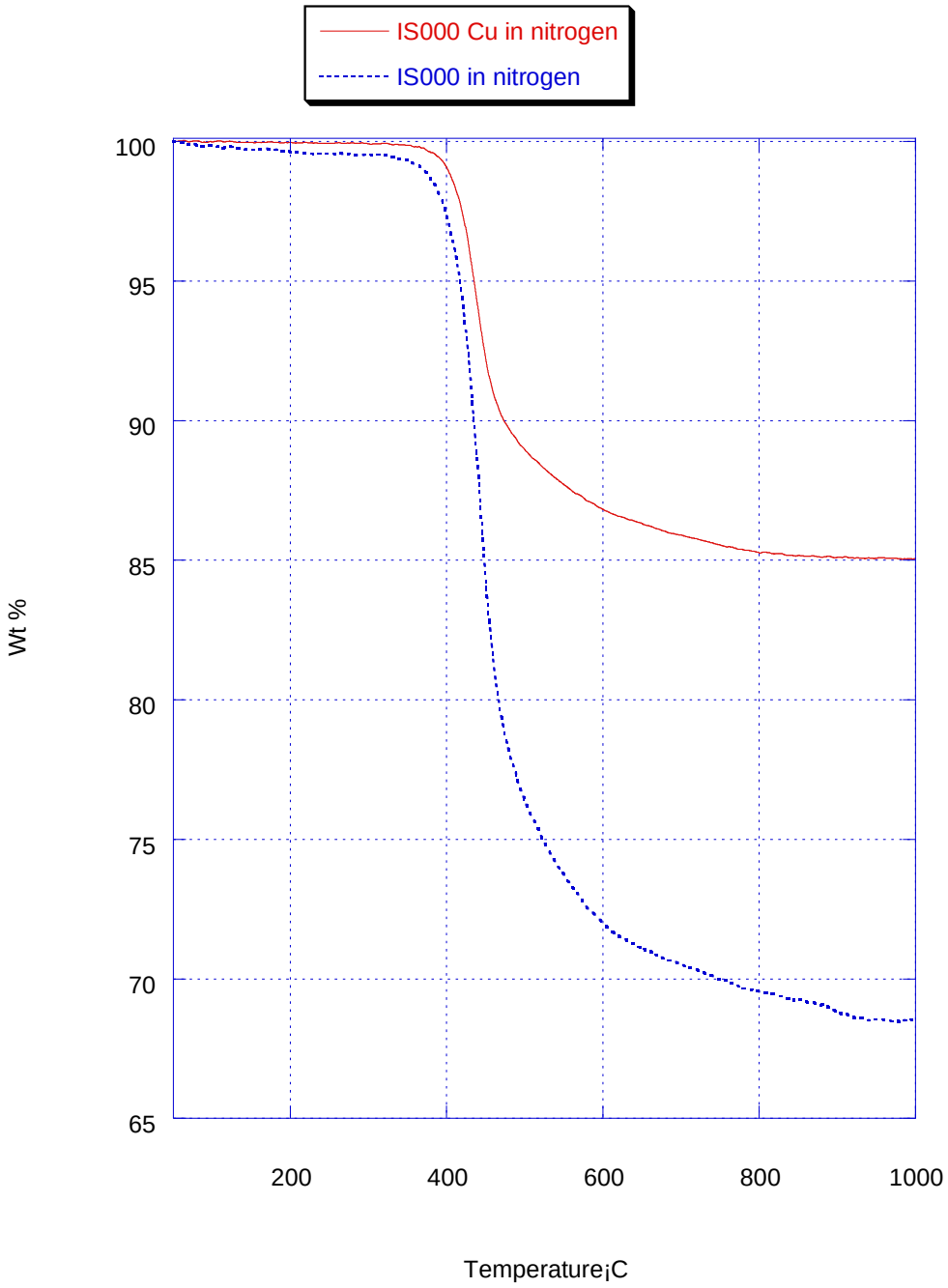


Figure A1. TGA in N_2 for Non-flame Retardant Sample with and without Cu Laminate

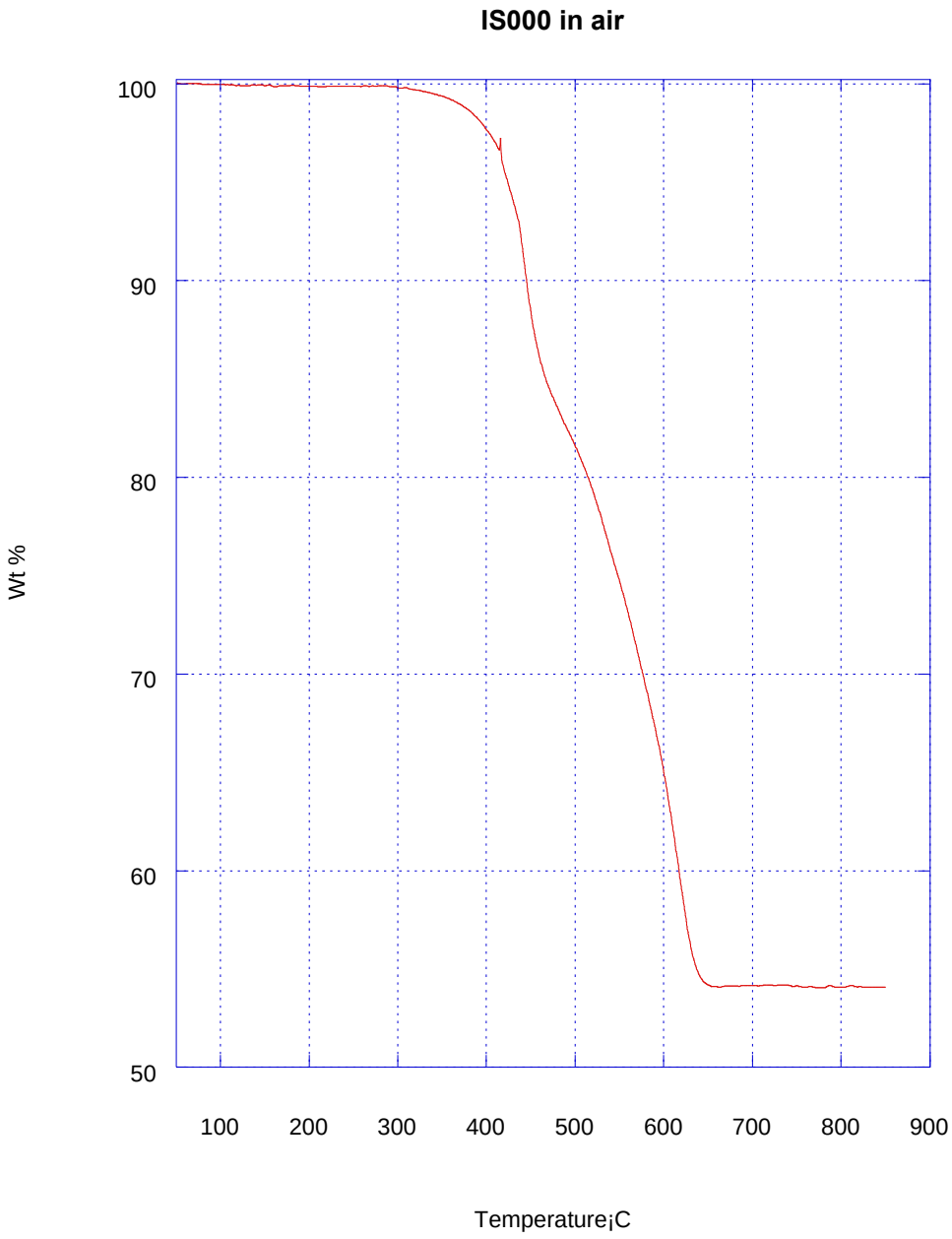


Figure A2. TGA in Air for Non-flame Retardant Sample without Cu Laminate

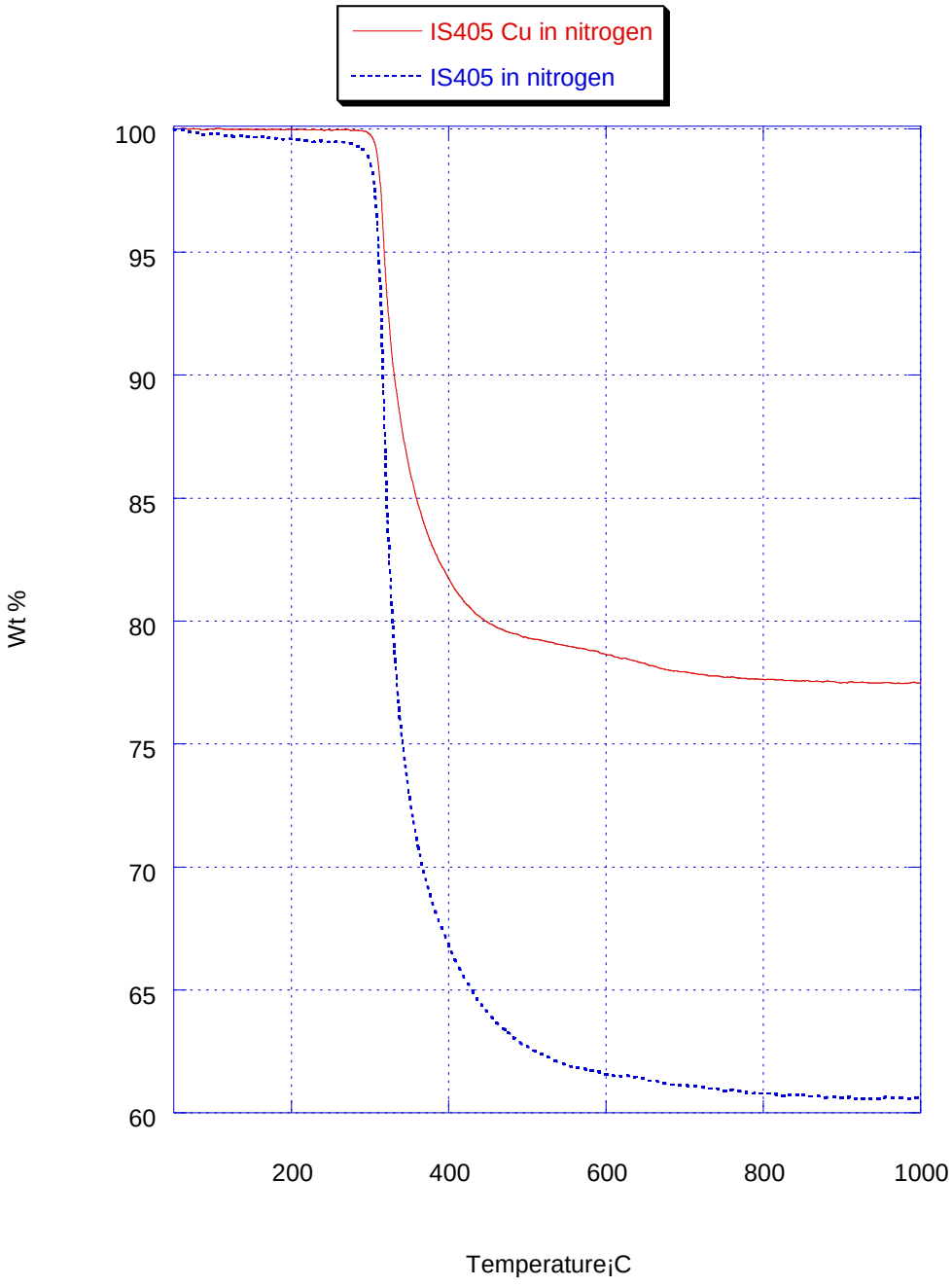


Figure A3. TGA in N_2 for Brominated Flame Retardant Sample with and without Cu Laminate

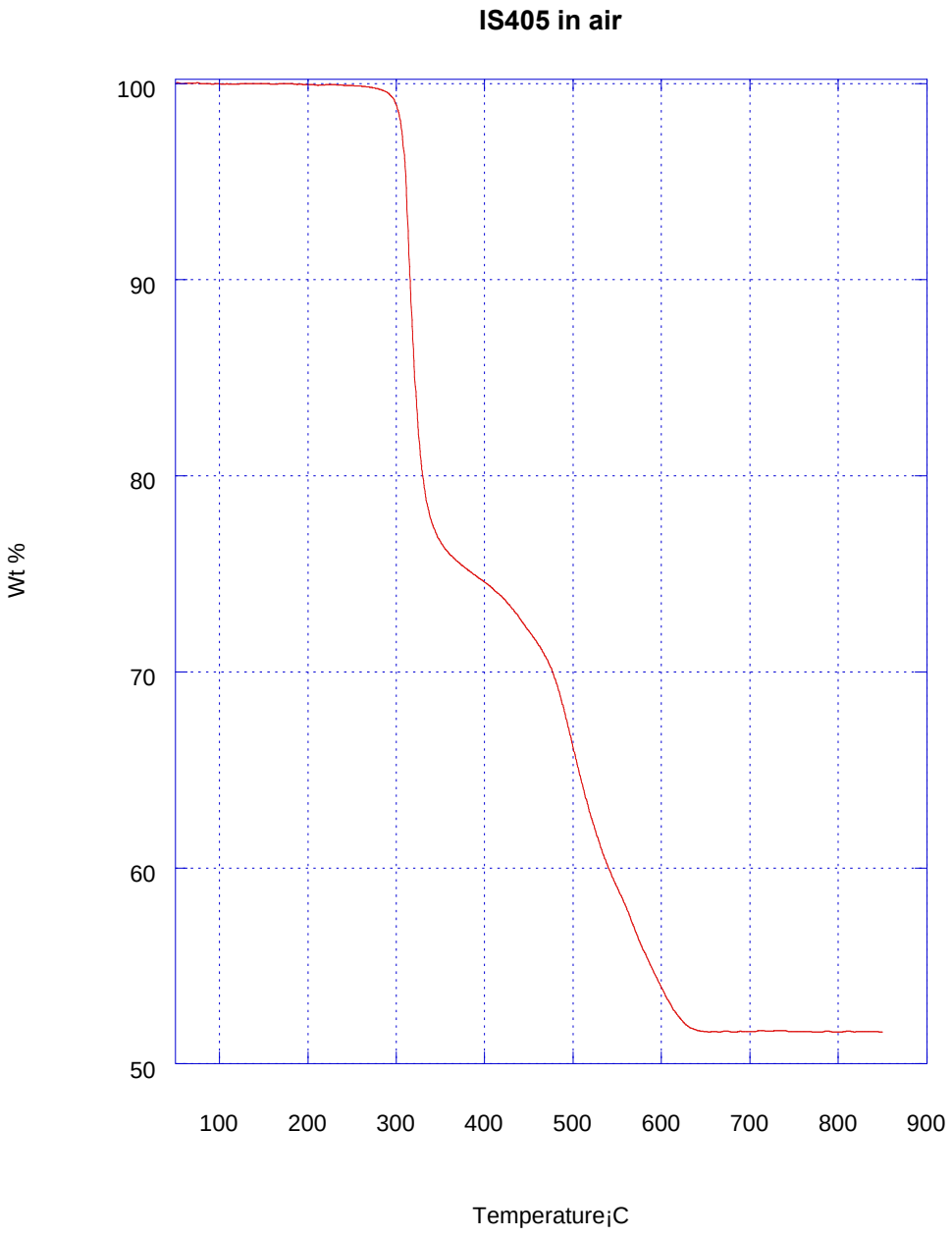


Figure A4. TGA in Air for Brominated Flame Retardant Sample without Cu Laminate

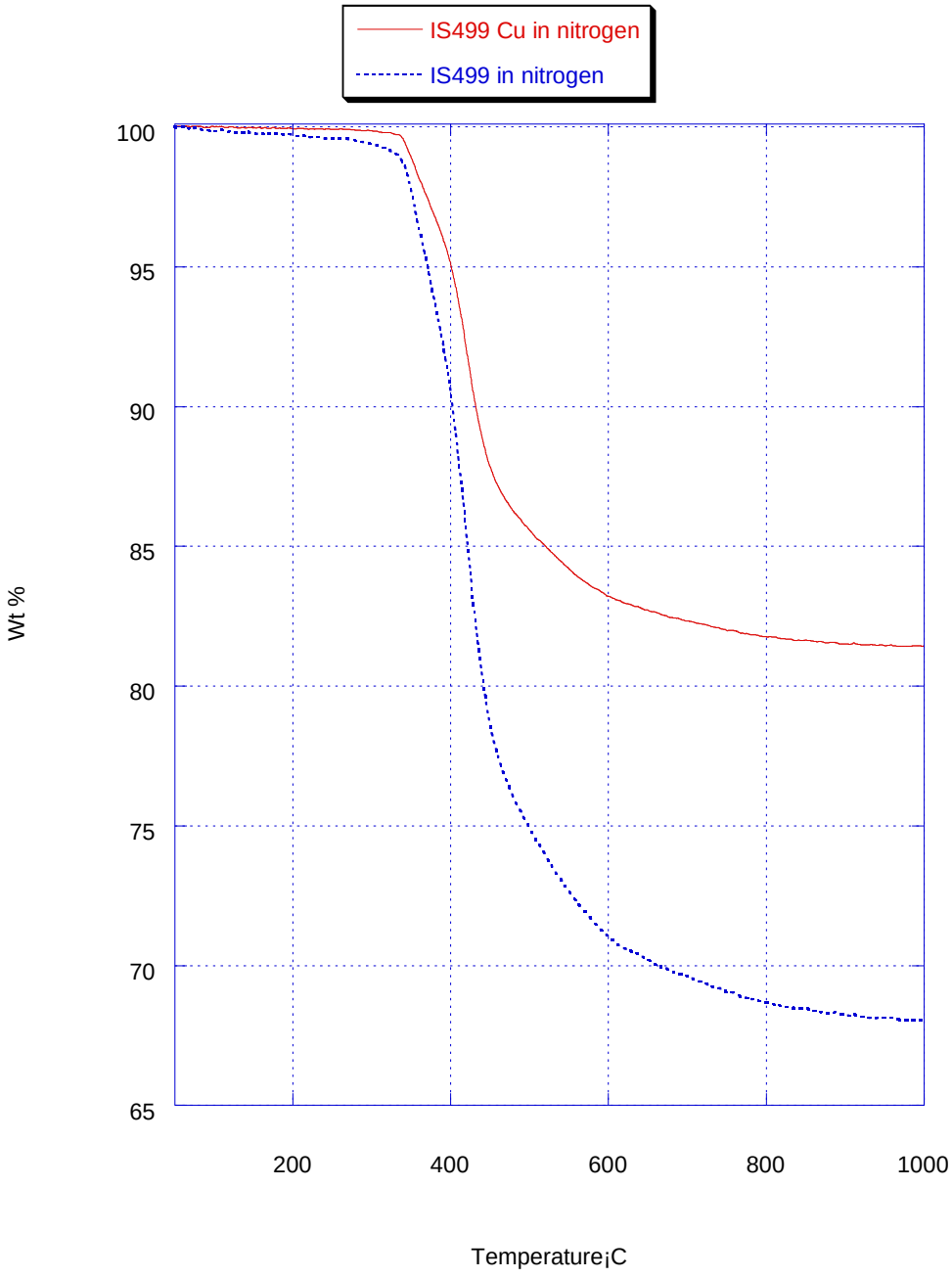


Figure A5. TGA in N_2 for Phosphorous Flame Retardant Sample with and without Cu Laminate

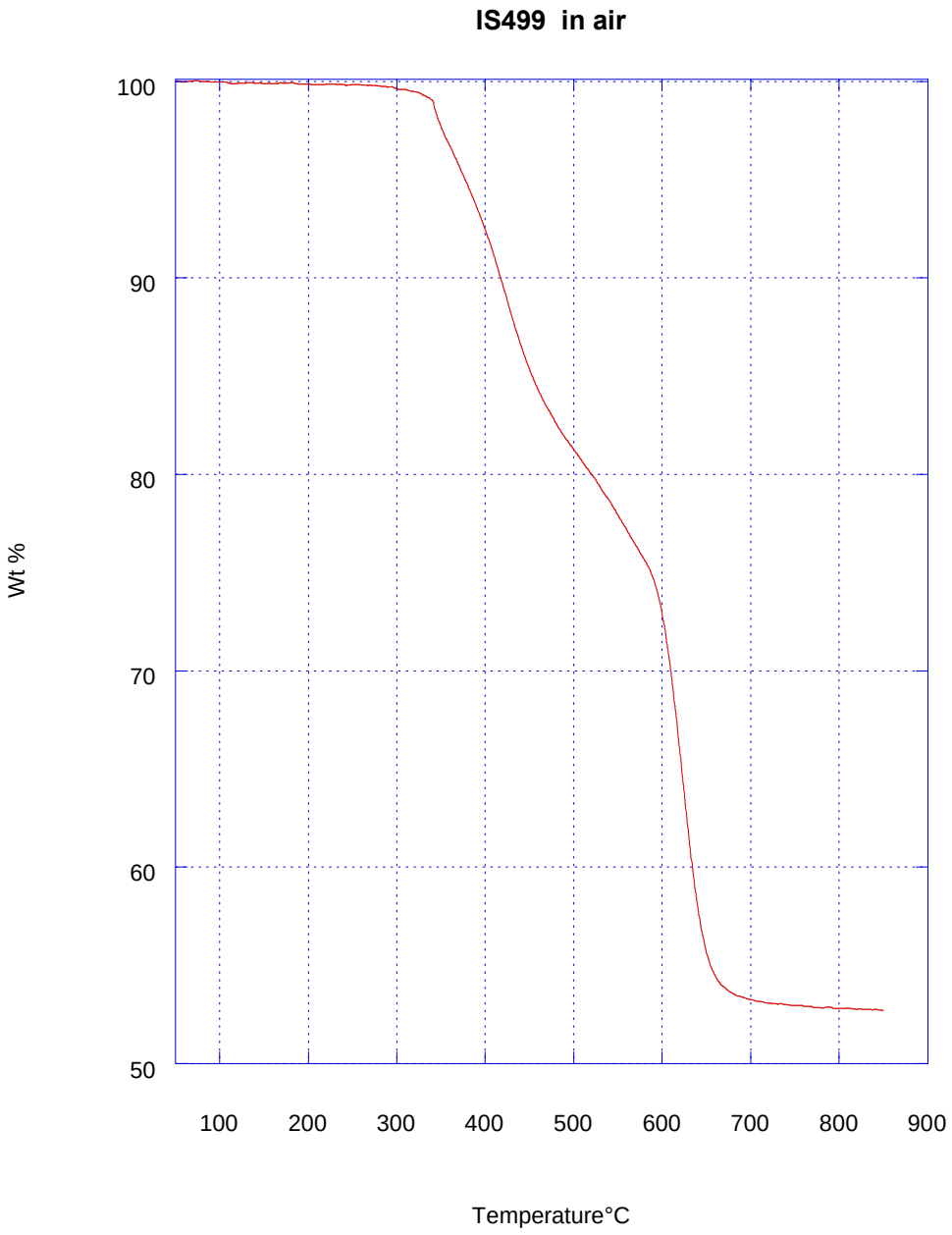


Figure A6. TGA in Air for Phosphorous Flame Retardant Sample without Cu Laminate

Appendix B
Total Ion Chromatogram Obtained from Circuit Board Combustion Byproducts Analysis

Table B1 Chemical Name – Structure Reference Table

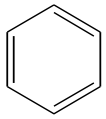
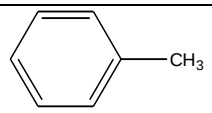
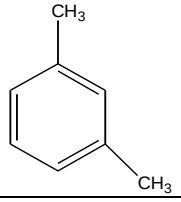
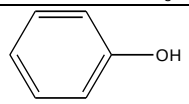
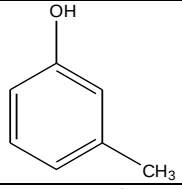
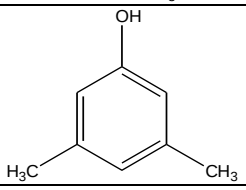
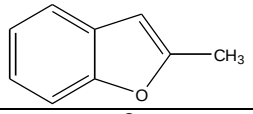
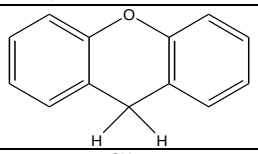
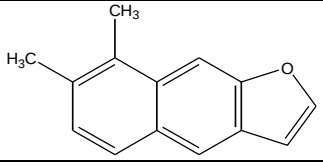
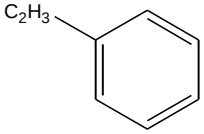
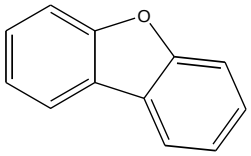
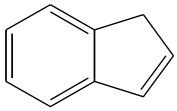
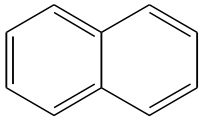
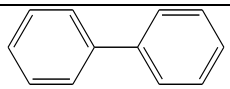
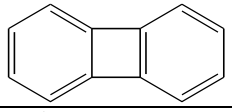
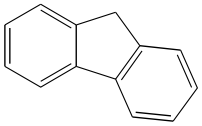
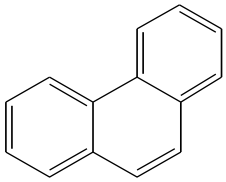
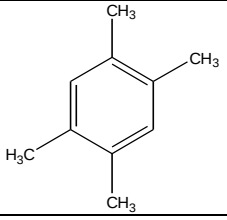
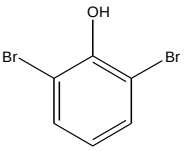
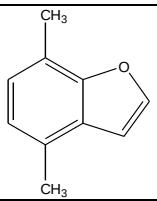
Chemical Name	Chemical Structure
Benzene	
Toluene	
Xylene (one of isomers)	
Phenol	
Methylphenol (one of isomers)	
Dimethylphenol (one of isomers)	
2-methylbenzofuran	
Xanthene	
1,2-dimethyl-naphthofuran	
Styrene	

Table B1 Chemical Name – Structure Reference Table (Cont'd)

Dibenzofuran	
Indene	
Naphthalene	
Biphenyl	
Biphenylene	
Fluorene	
Phenanthrene	
Tetramethylbenzene (one of isomers)	
Dibromophenol (one of isomers)	
Dimethylbenzofuran (one of isomers)	

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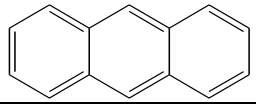
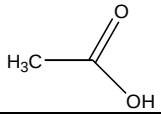
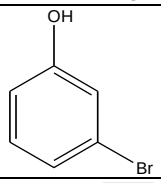
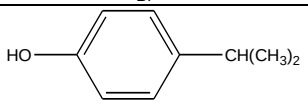
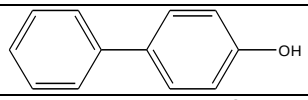
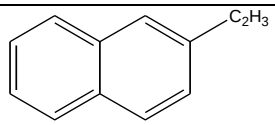
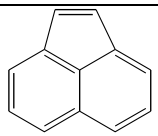
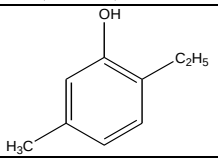
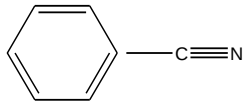
Anthracene	
Acetic Acid	
Bromophenol (one of isomers)	
Methylethylphenol (one of isomers)	
Hydroxybiphenyl (one of isomers)	
Ethenylnaphthalene (one of isomers)	
Acenaphthylene	
Methylethylphenol (one of isomers)	
Benzonitrile	

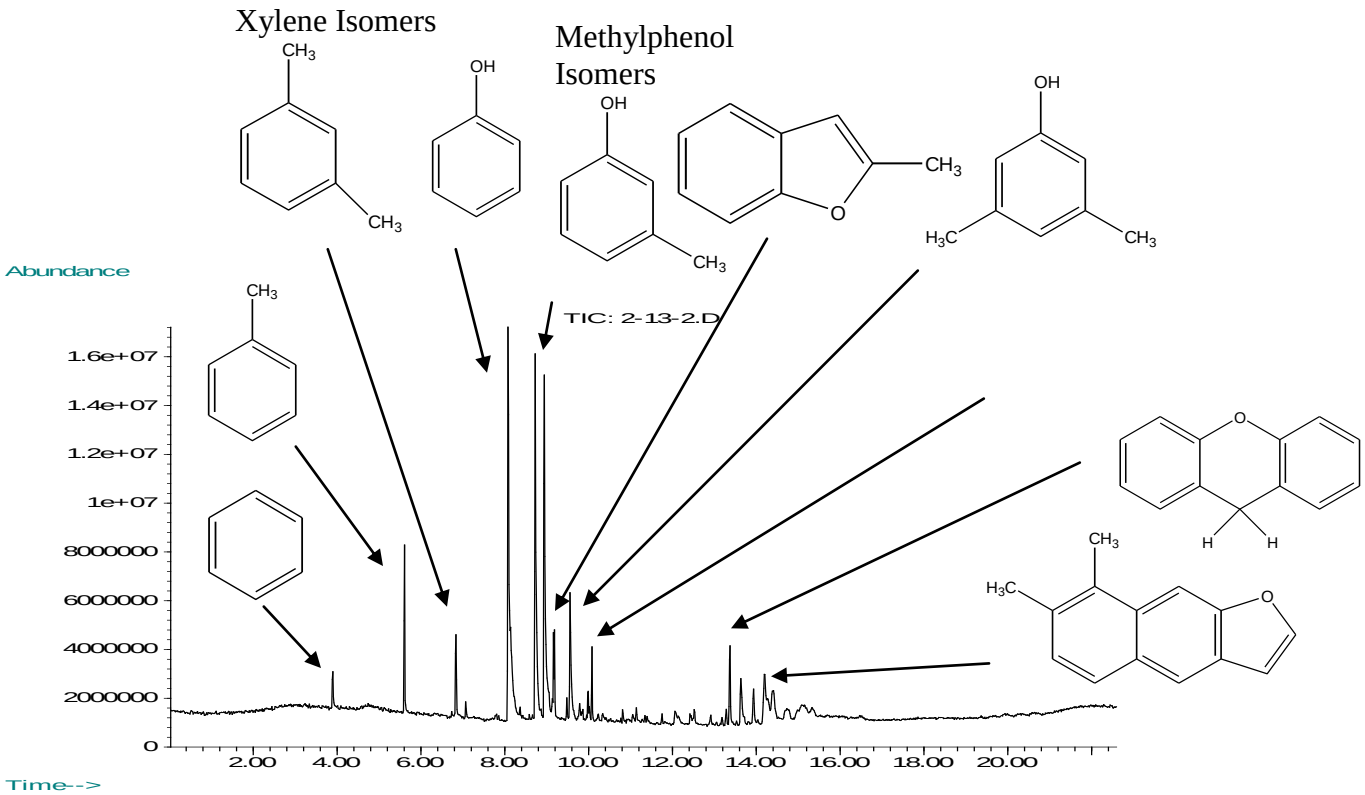


Figure B1. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under Pyrolysis Condition at 300°C

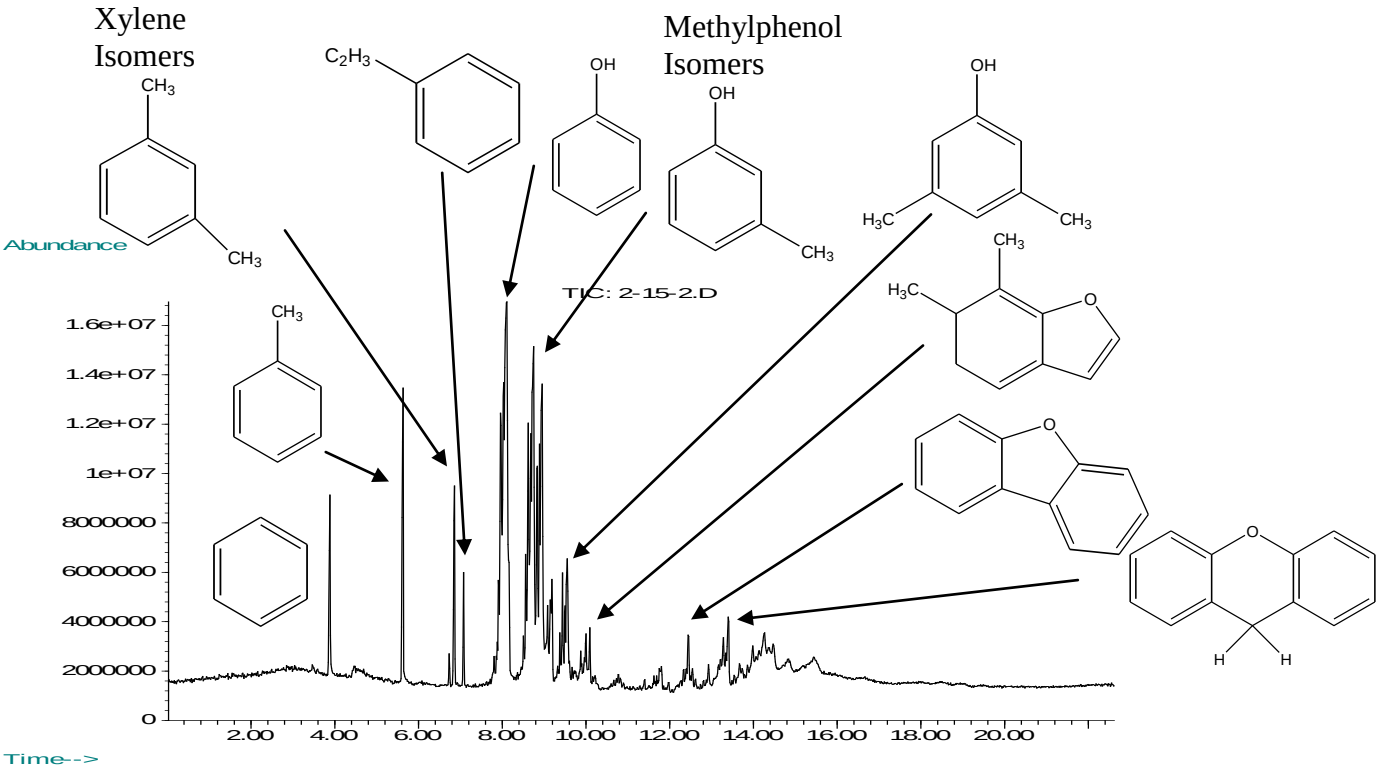


Figure B2. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under Pyrolysis Condition at 700°C

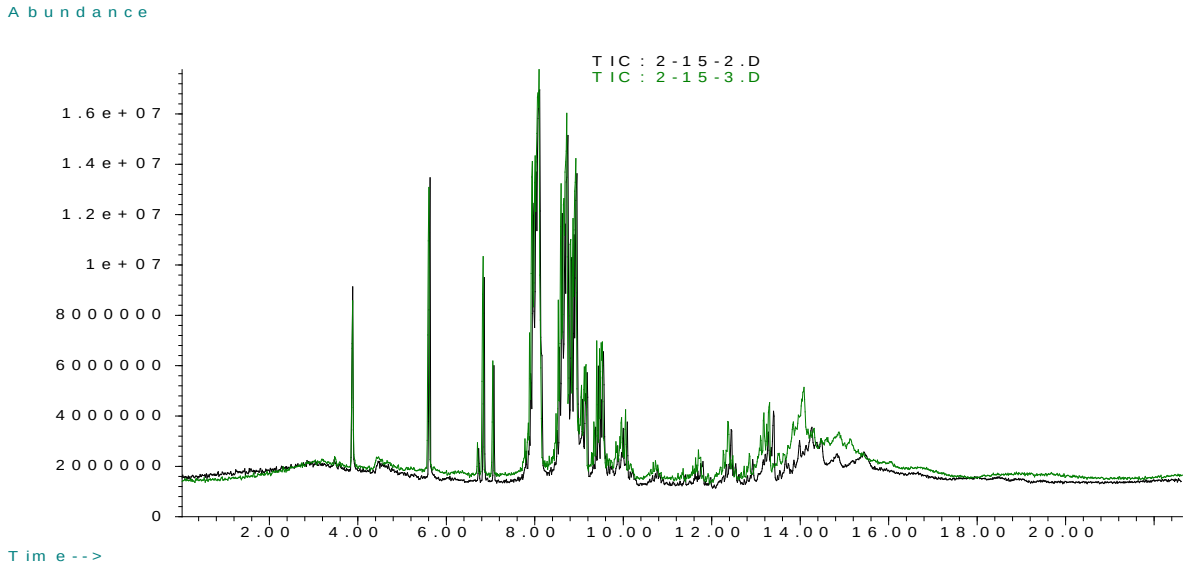


Figure B3. Overlaid TIC for Repeated Experiment (Non-flame Retardant Sample under Pyrolysis Condition at 700°C)

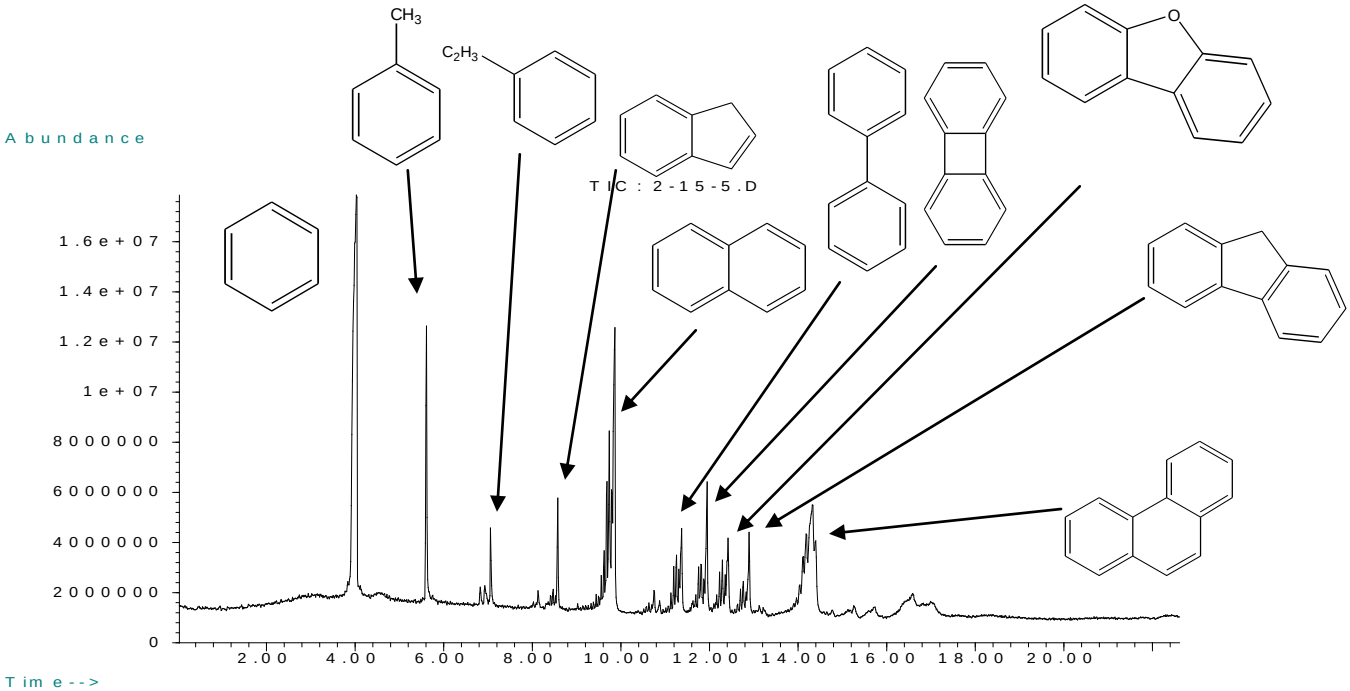


Figure B4. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under Pyrolysis Condition at 900°C

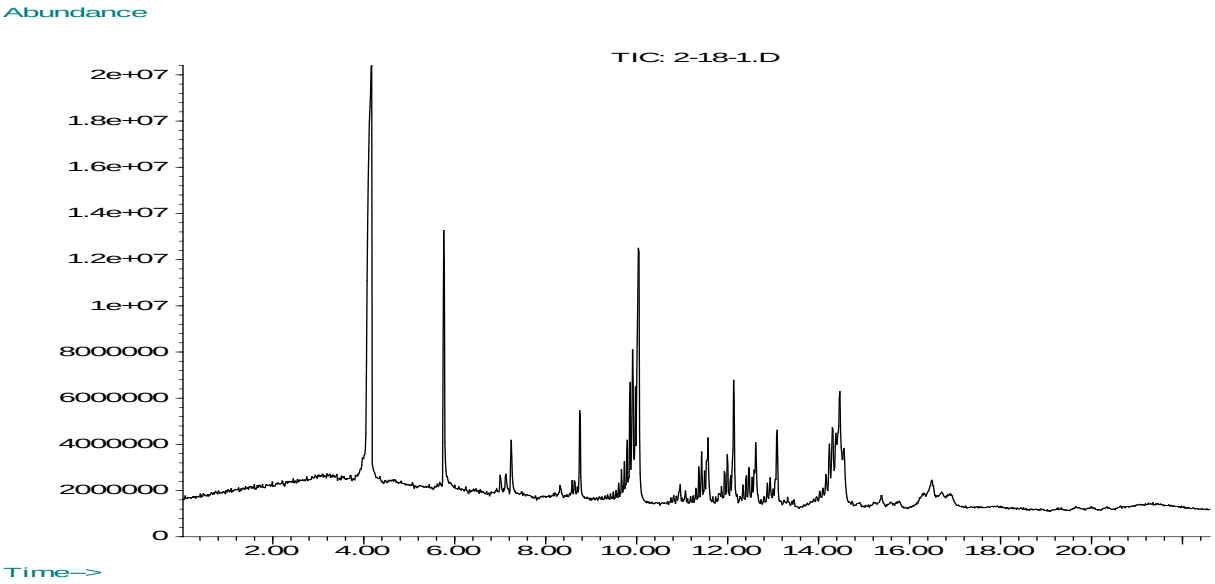


Figure B5. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample with Cu Laminate under Pyrolysis Condition at 900°C. Peak identifications are same as above (Figure B4).

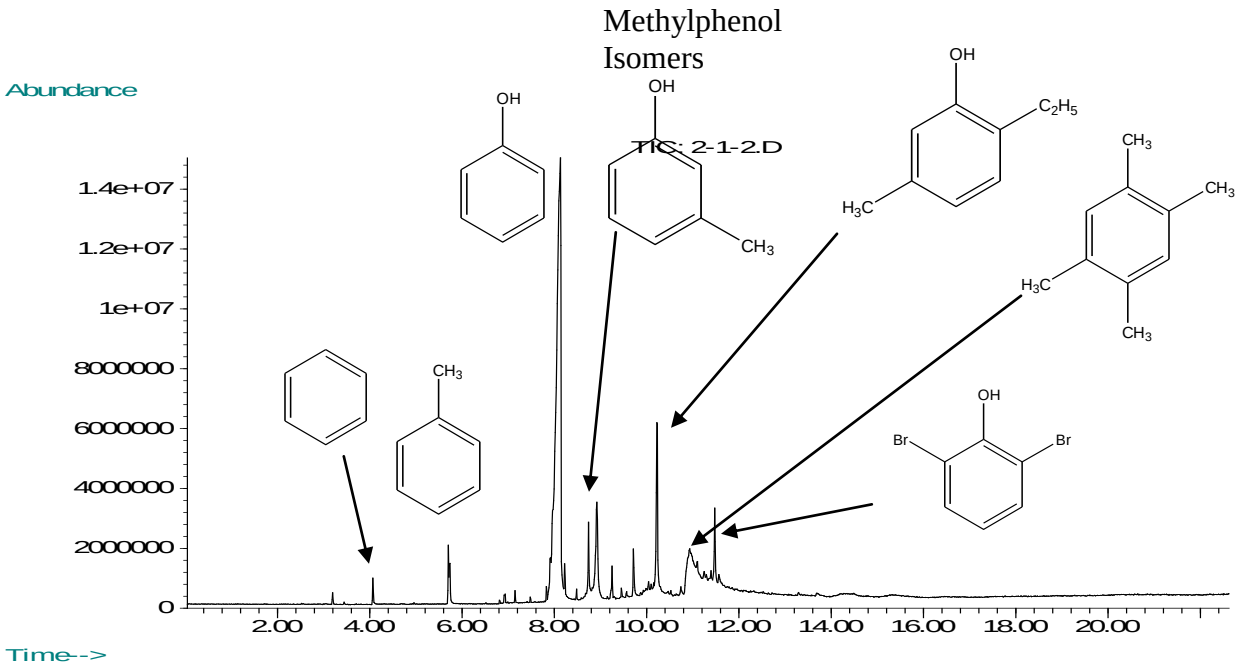


Figure B6. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under Pyrolysis Condition at 300°C

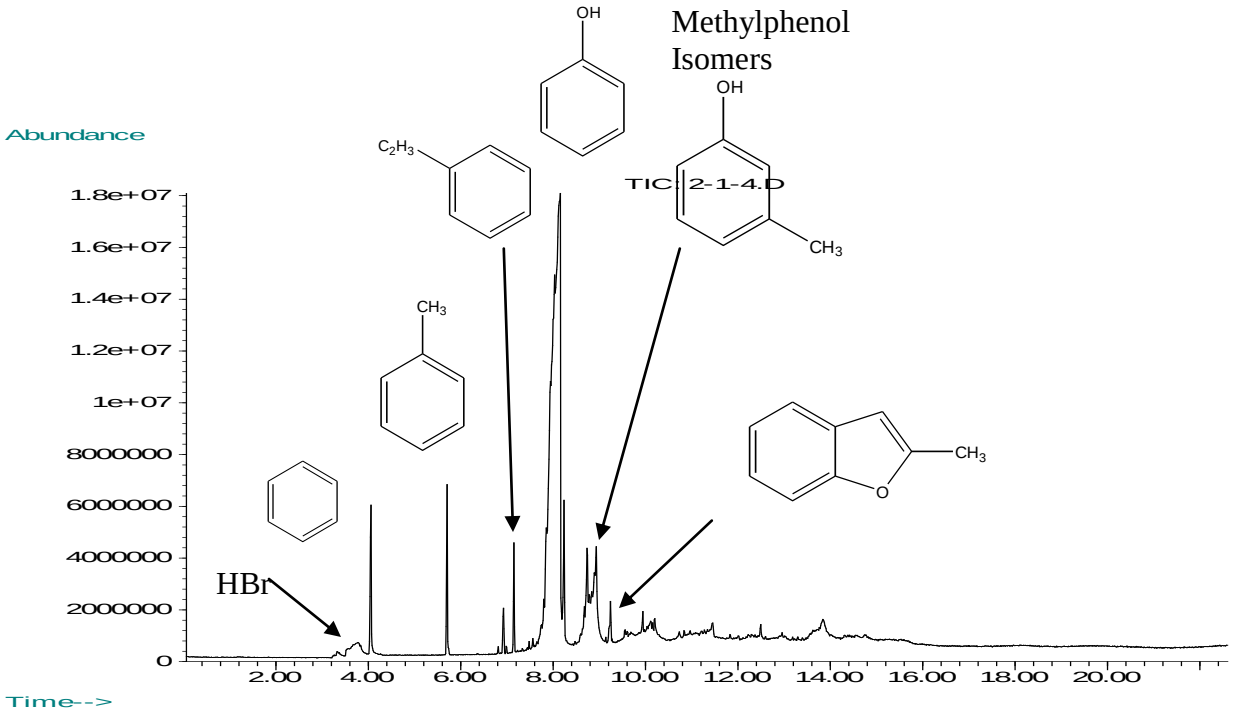


Figure B7. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under Pyrolysis Condition at 700ºC

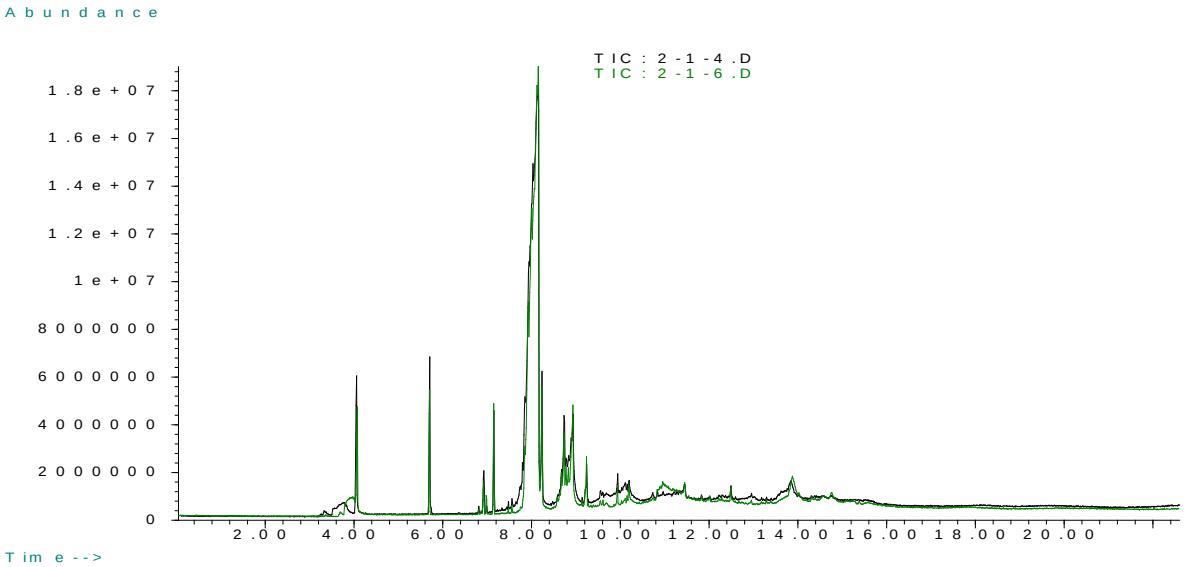


Figure B8. Overlaid TIC for Repeated Experiment (Brominated Flame Retardant Sample under Pyrolysis Condition at 700°C)

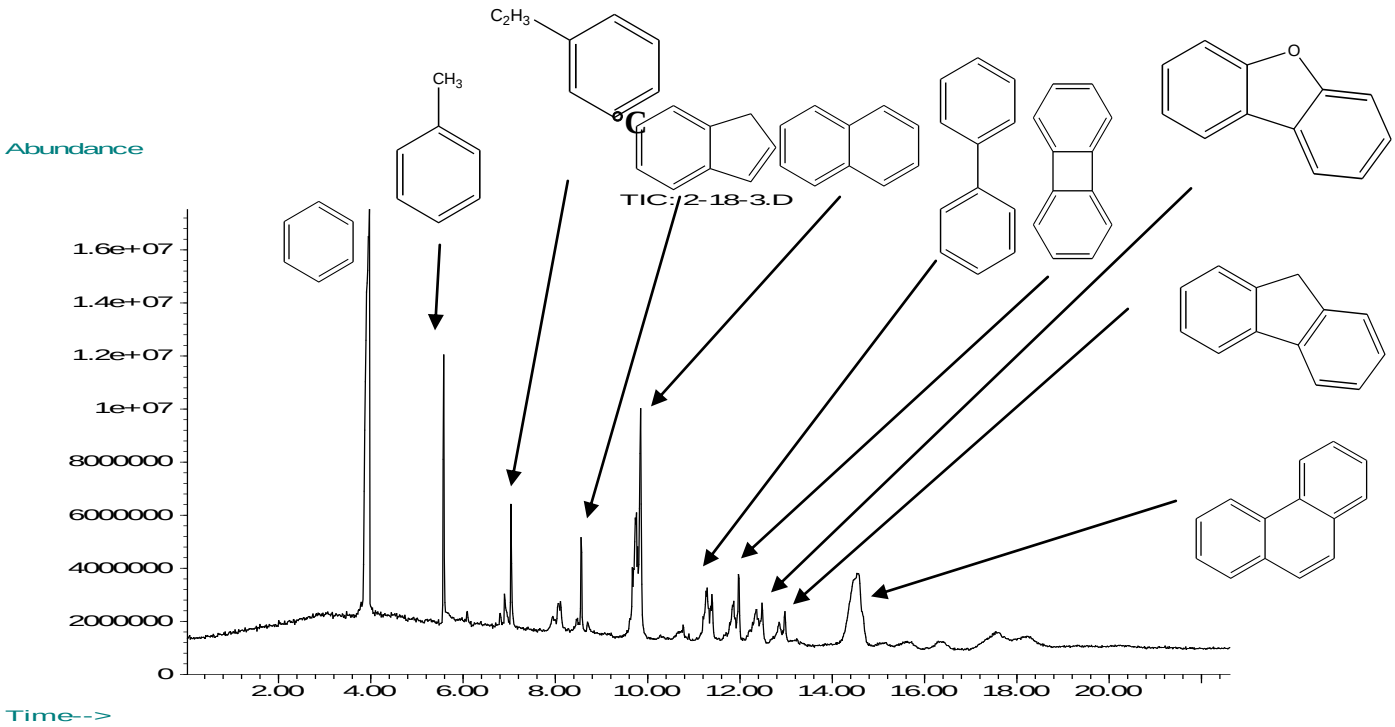


Figure B9. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample with Cu Laminate under Pyrolysis Condition at 900°C

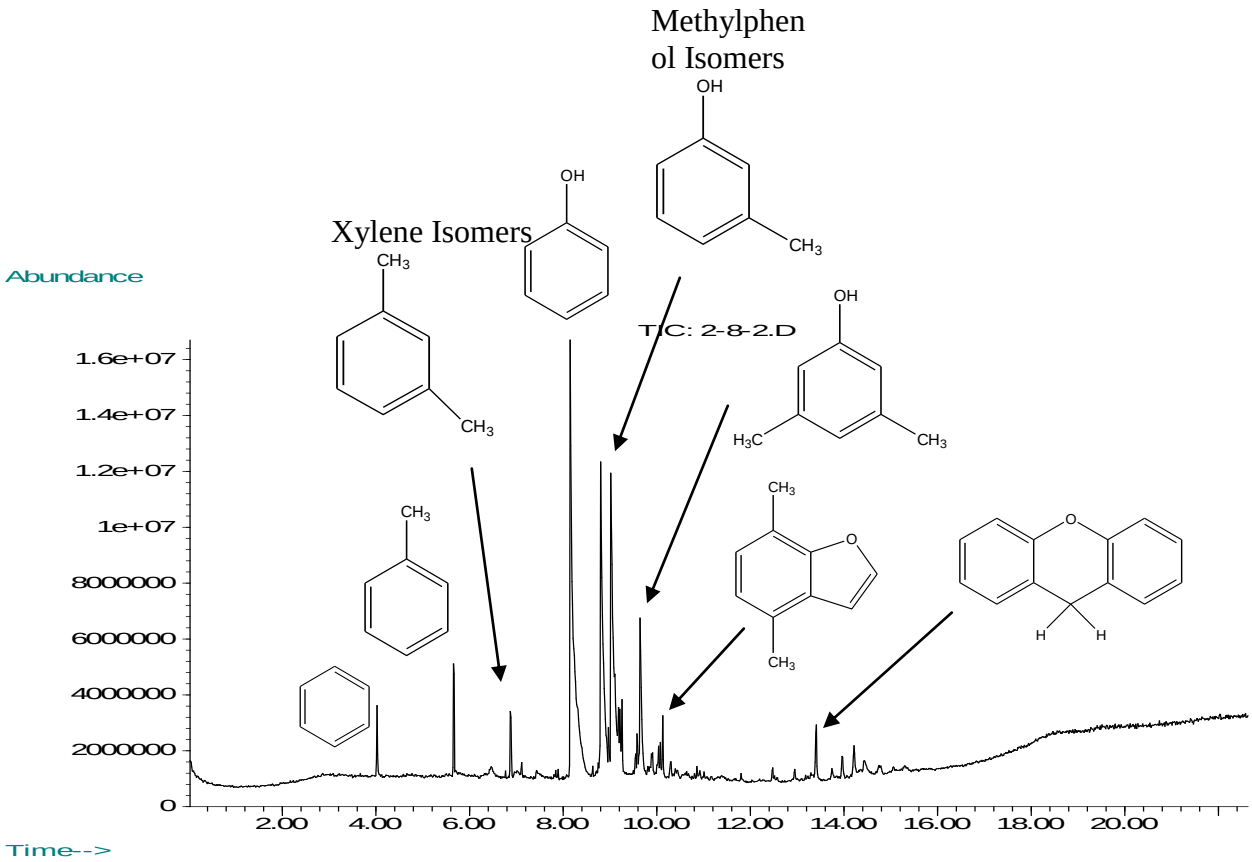


Figure B10. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under Pyrolysis Condition at 300°C

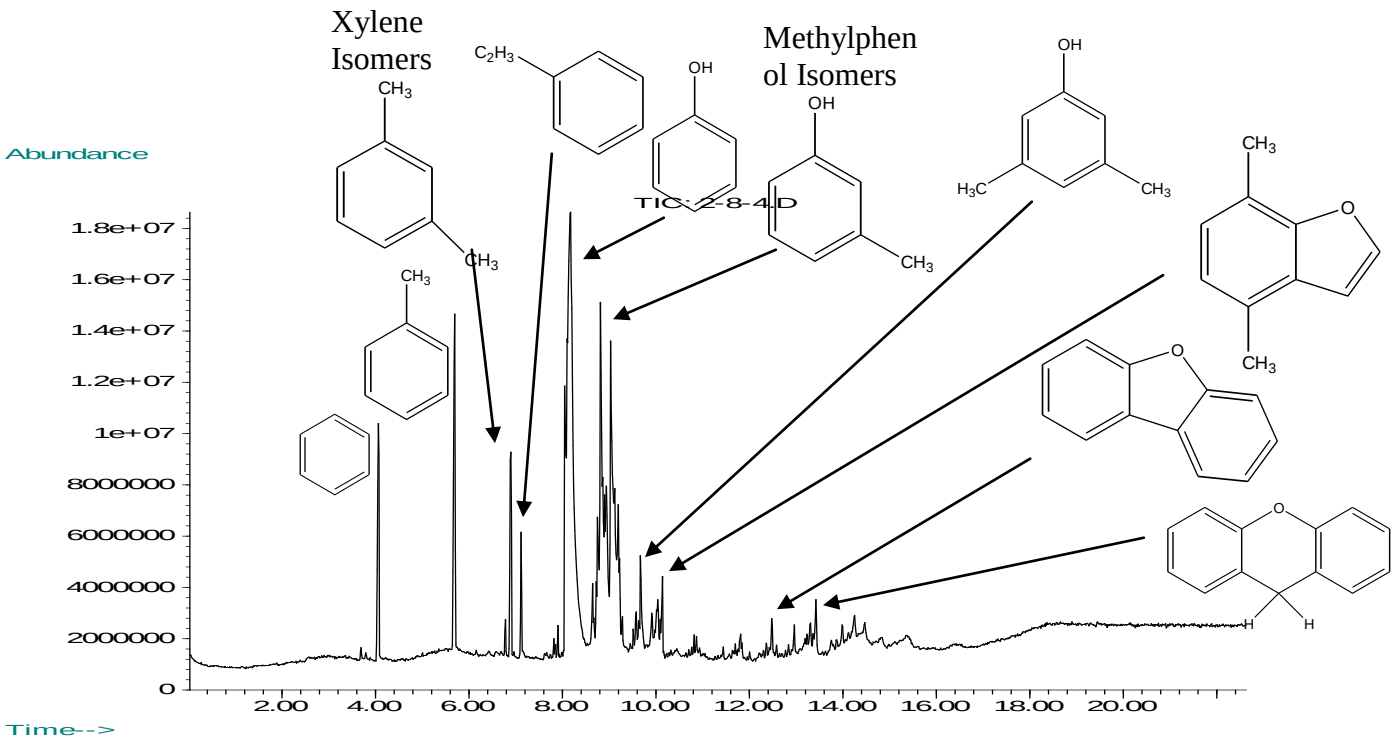


Figure B11. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under Pyrolysis Condition at 700°C

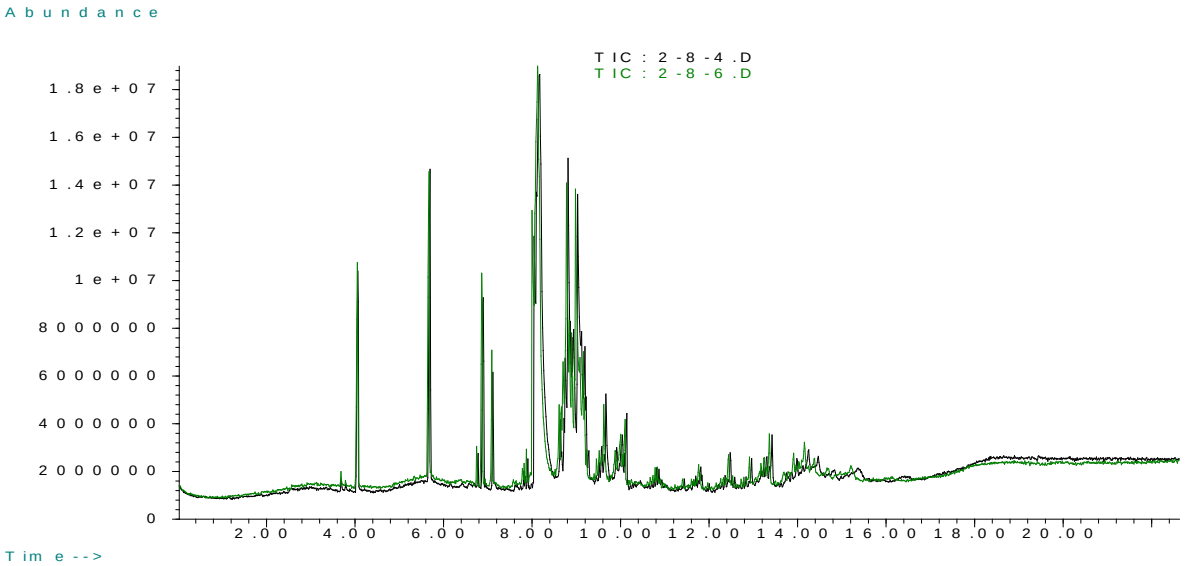


Figure B12. Overlaid TIC for Repeated Experiment (Phosphorous Flame Retardant Sample under Pyrolysis Condition at 700°C)

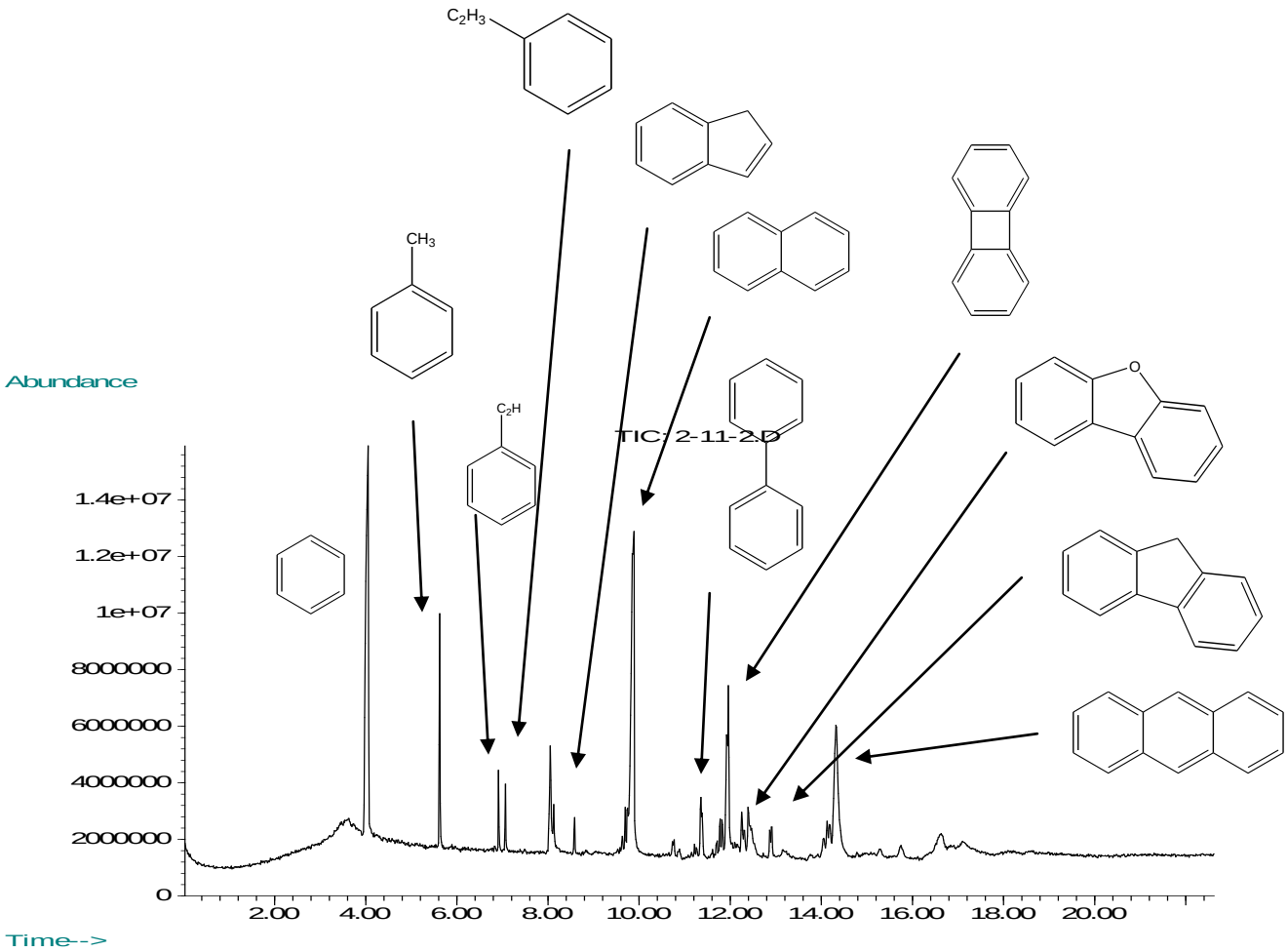


Figure B13. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample with Cu Laminate under Pyrolysis Condition at 900°C

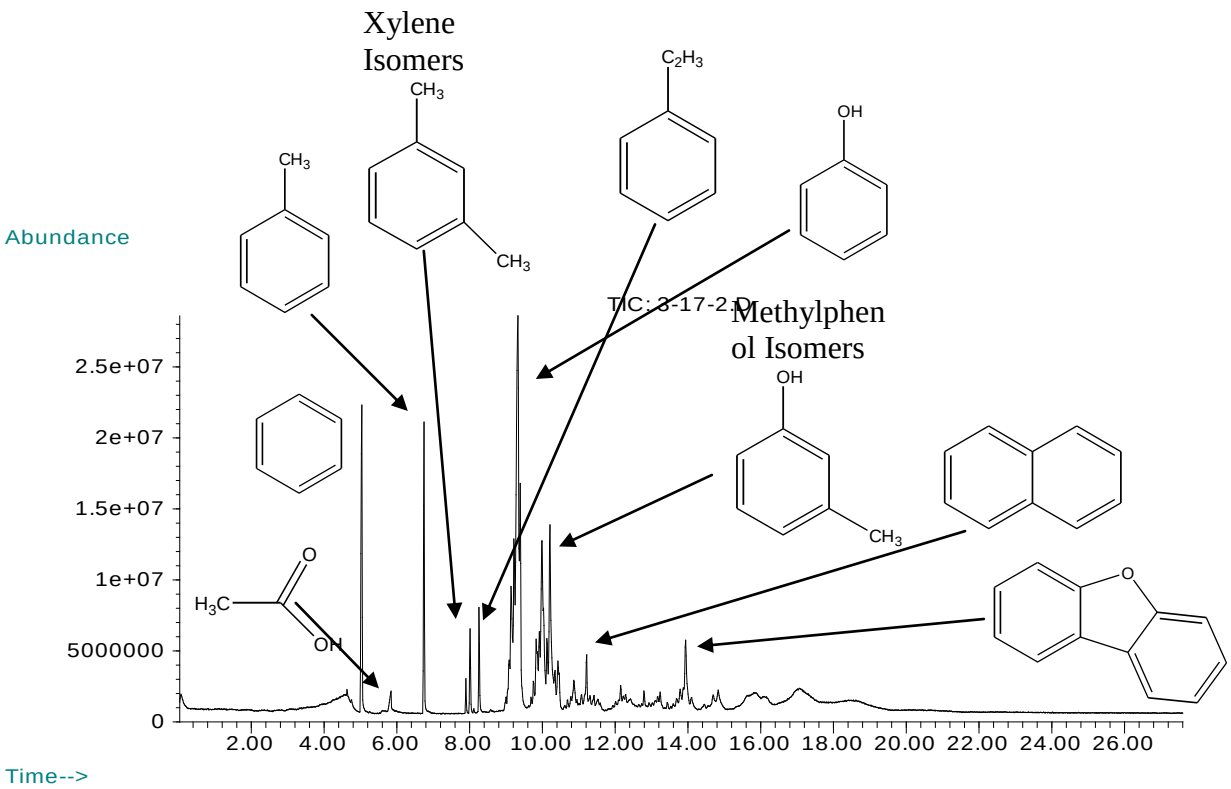


Figure B14. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under 10% O2 Condition at 700°C

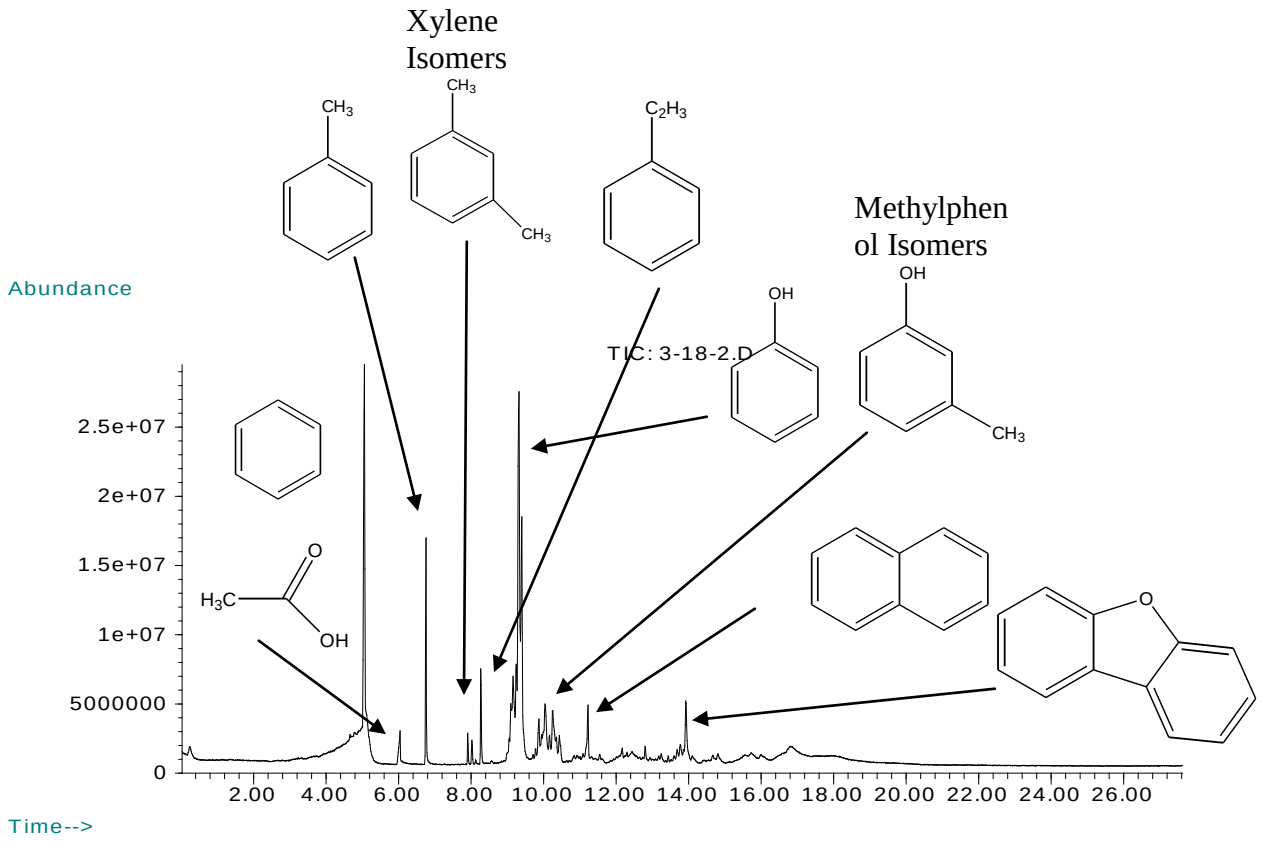


Figure B15. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under 21% O2 Condition at 700°C

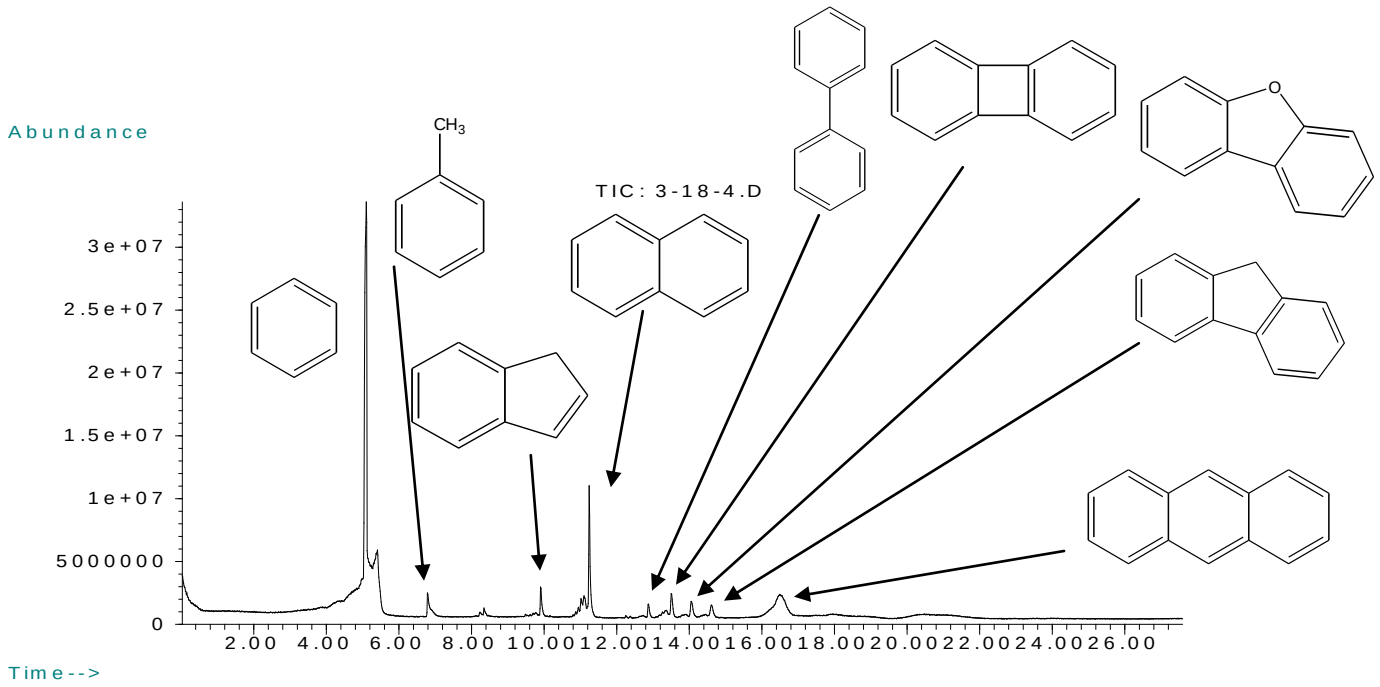


Figure B16. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under 21% O2 Condition at 900°C

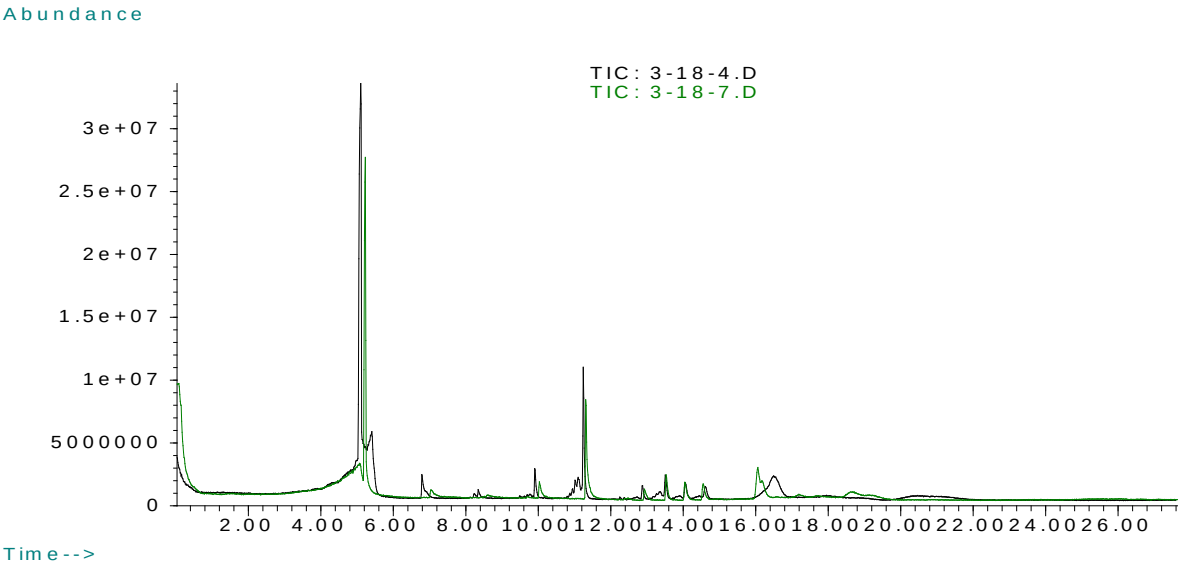


Figure B17. Overlaid TIC for Repeated Experiment (Non-flame Retardant Sample under 21% O2 Condition at 900°C)

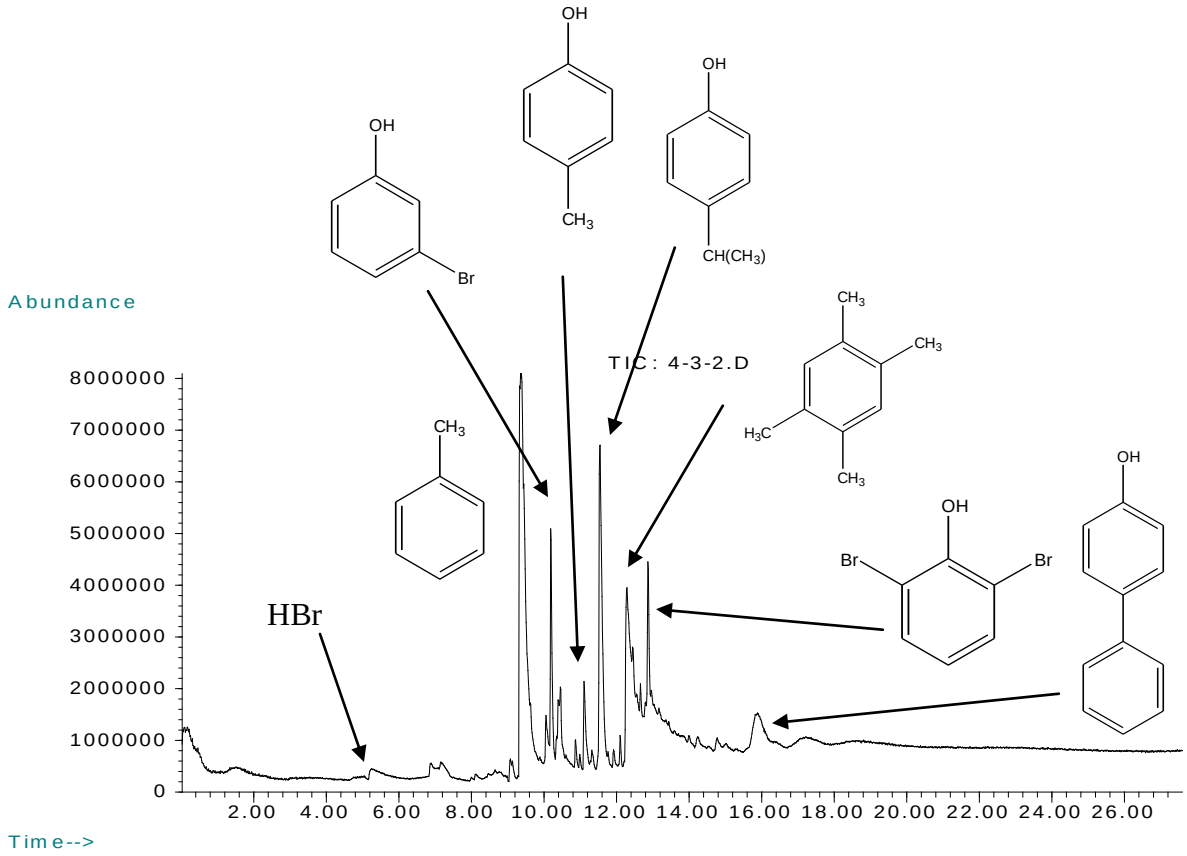


Figure B18. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 21% O2 Condition at 300°C

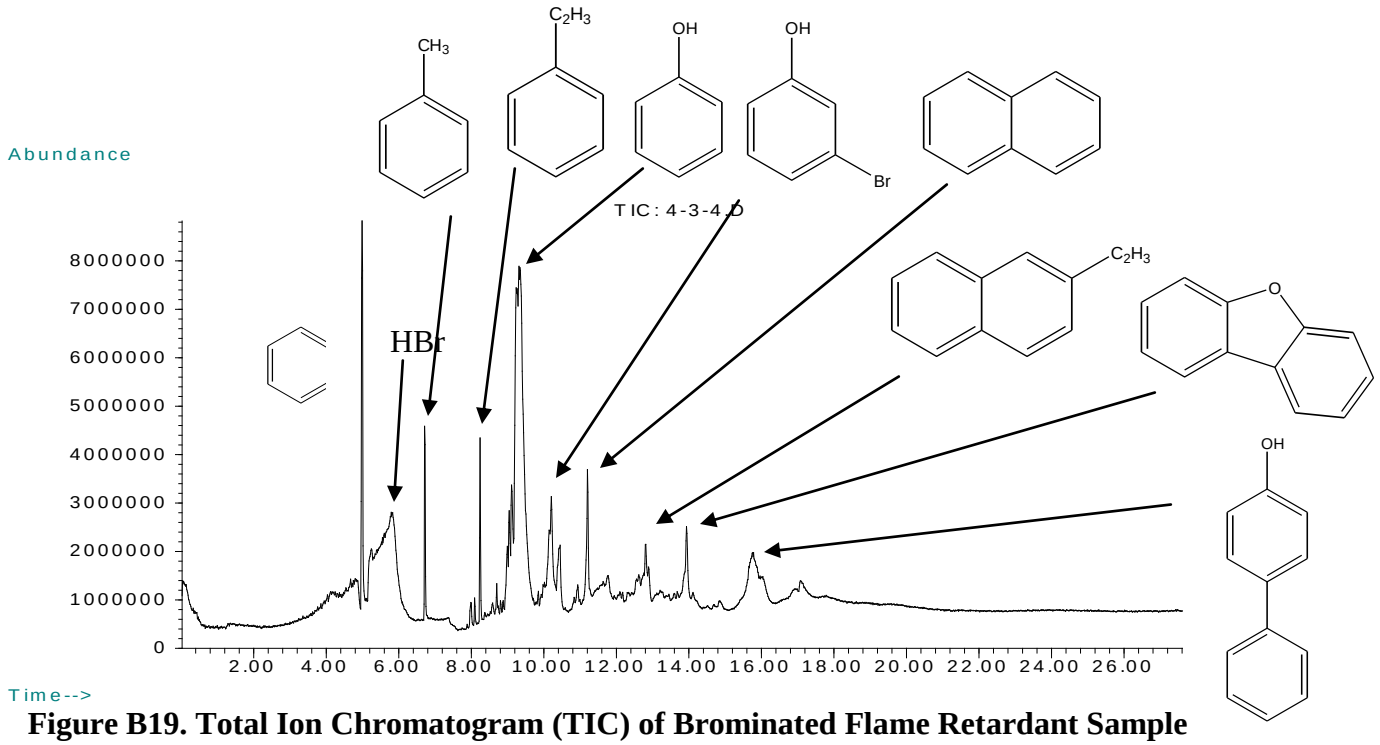


Figure B19. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 10% O2 Condition at 700°C

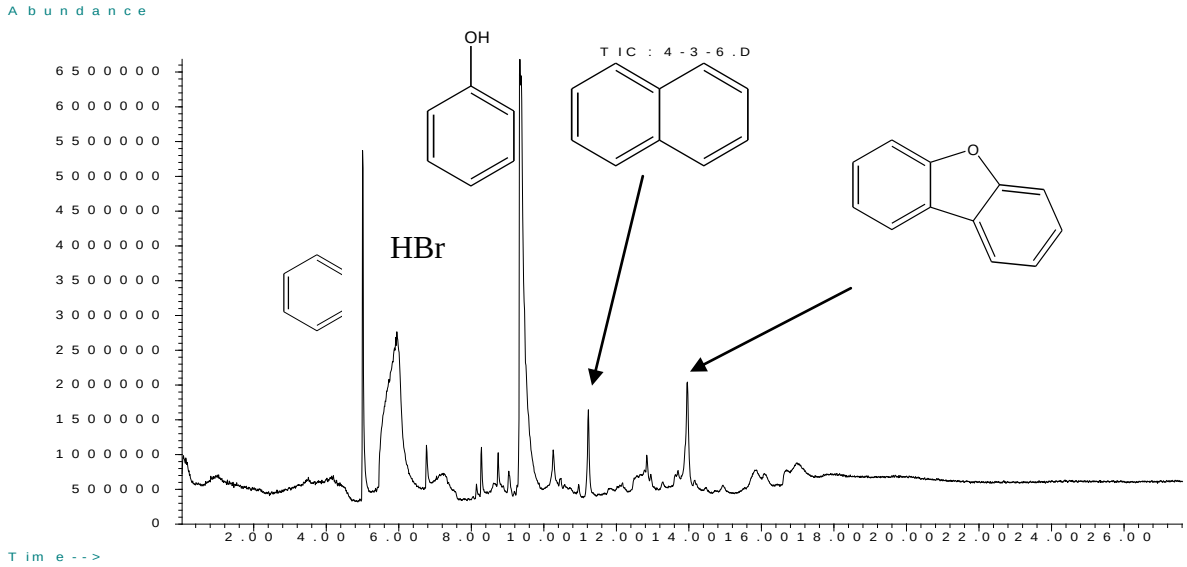


Figure B20. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 21% O2 Condition at 700°C

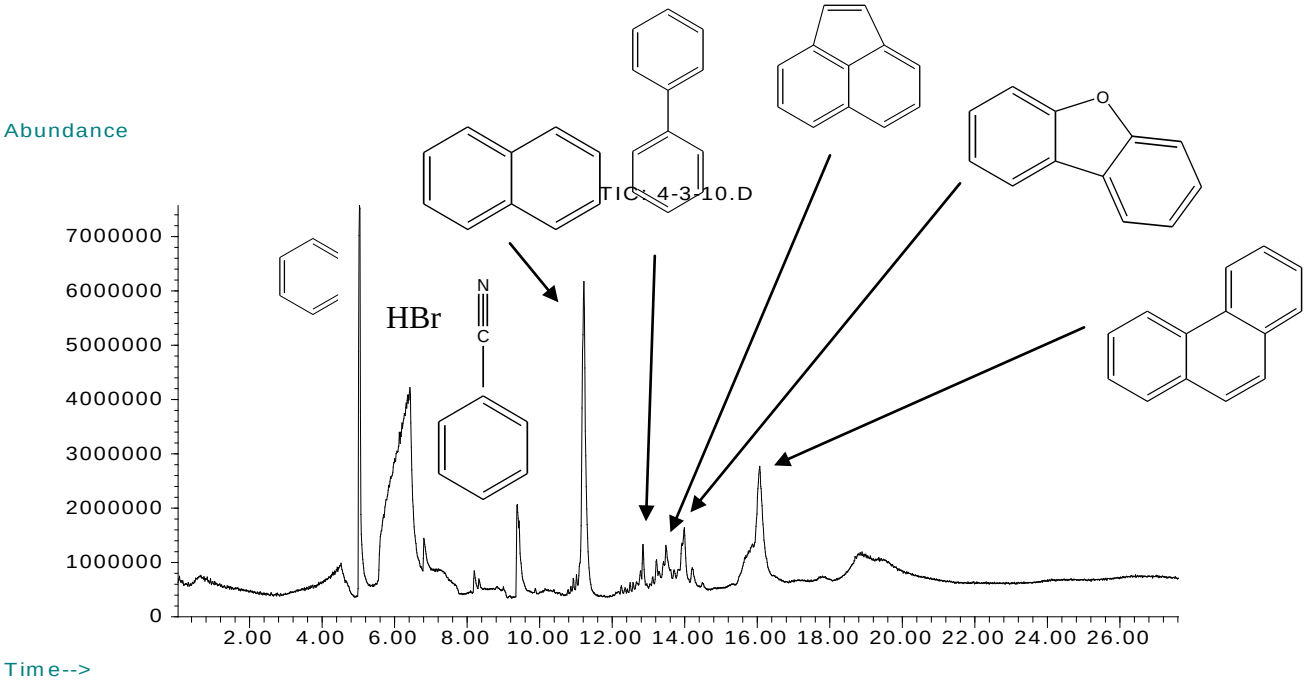


Figure B21. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 21% O2 Condition at 900°C

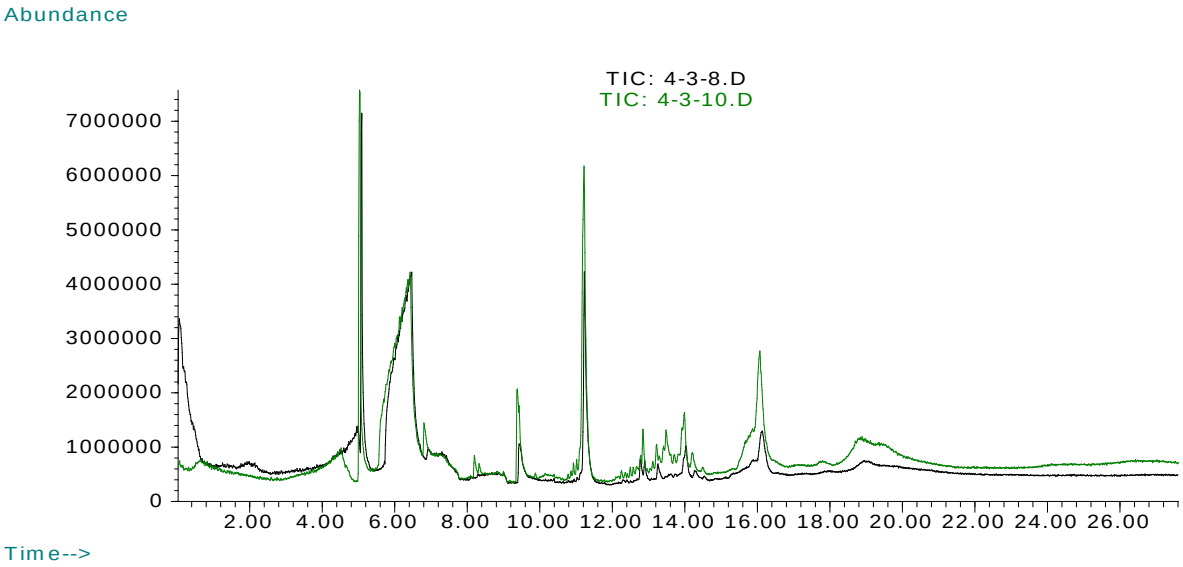


Figure B22. Overlaid TIC for Repeated Experiment (Brominated Flame Retardant Sample under 21% O2 Condition at 900°C)

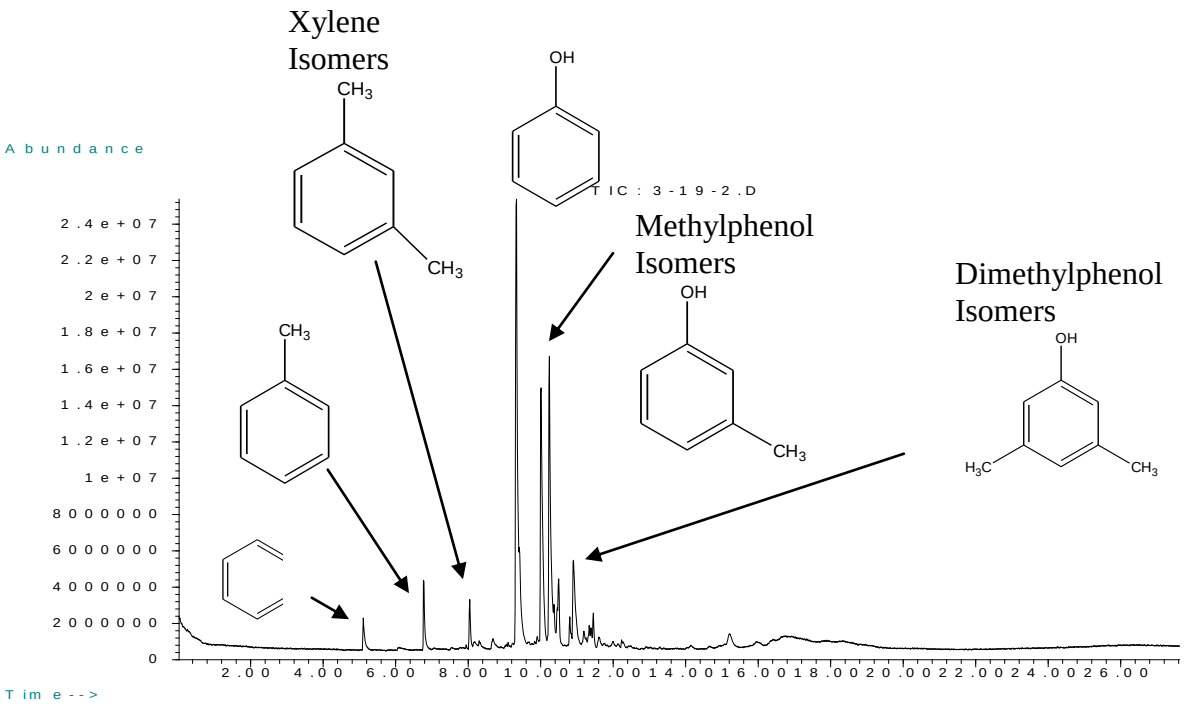


Figure B23. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 21% O2 Condition at 300°C

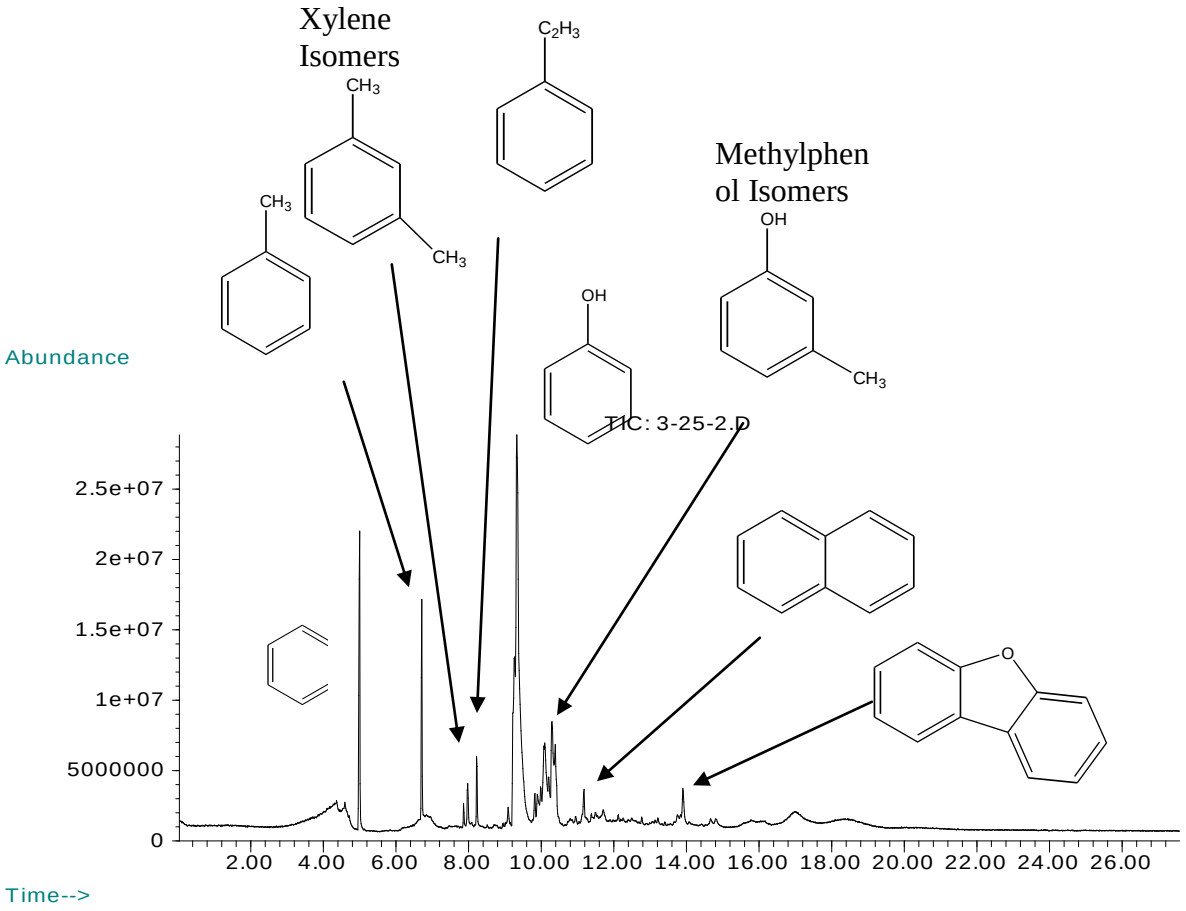


Figure B24. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 10% O2 Condition at 700°C

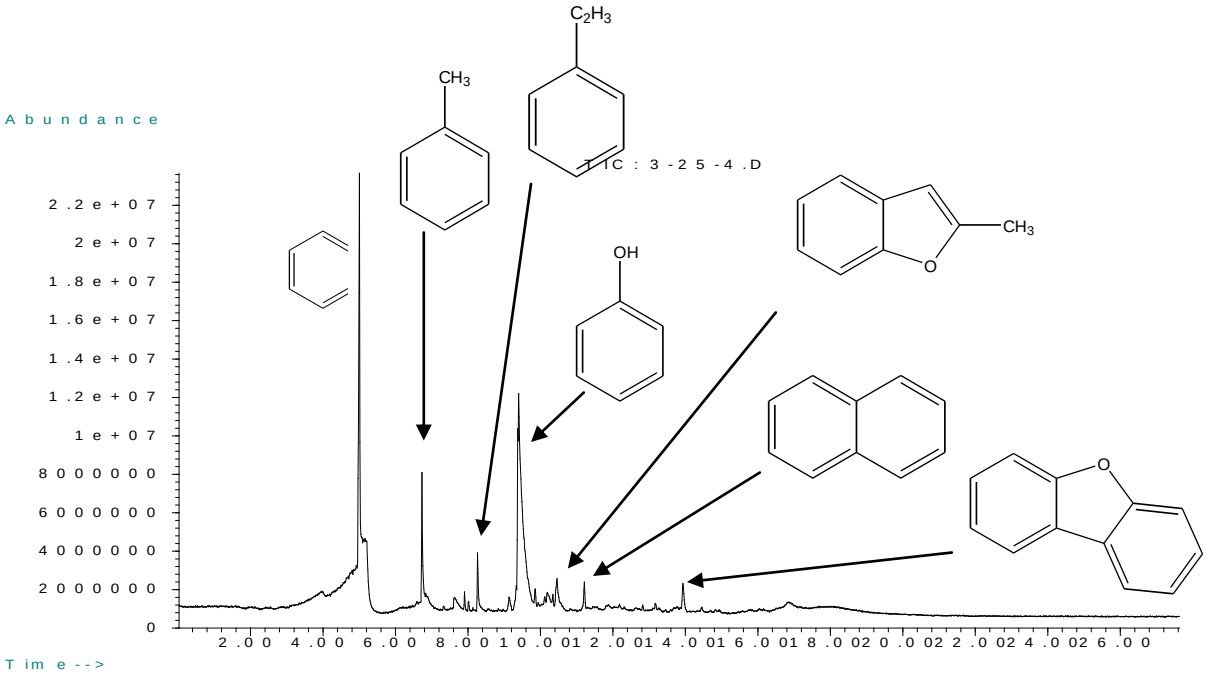


Figure B25. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 21% O2 Condition at 700°C

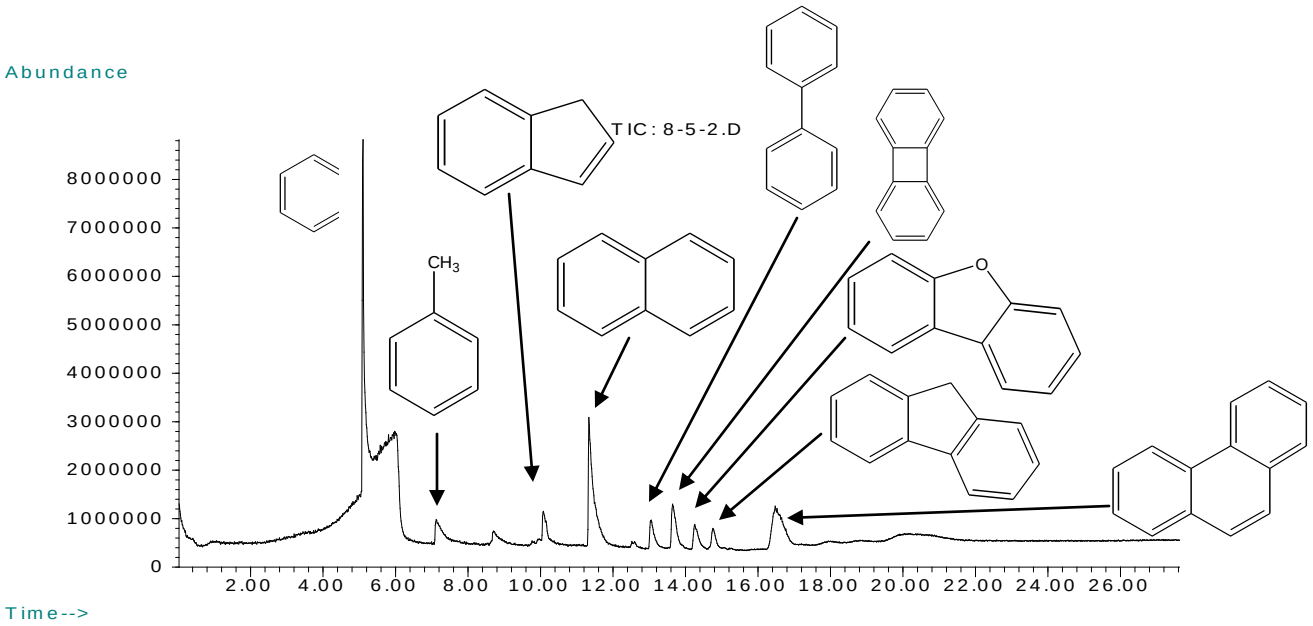


Figure B26. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 21% O2 Condition at 900°C

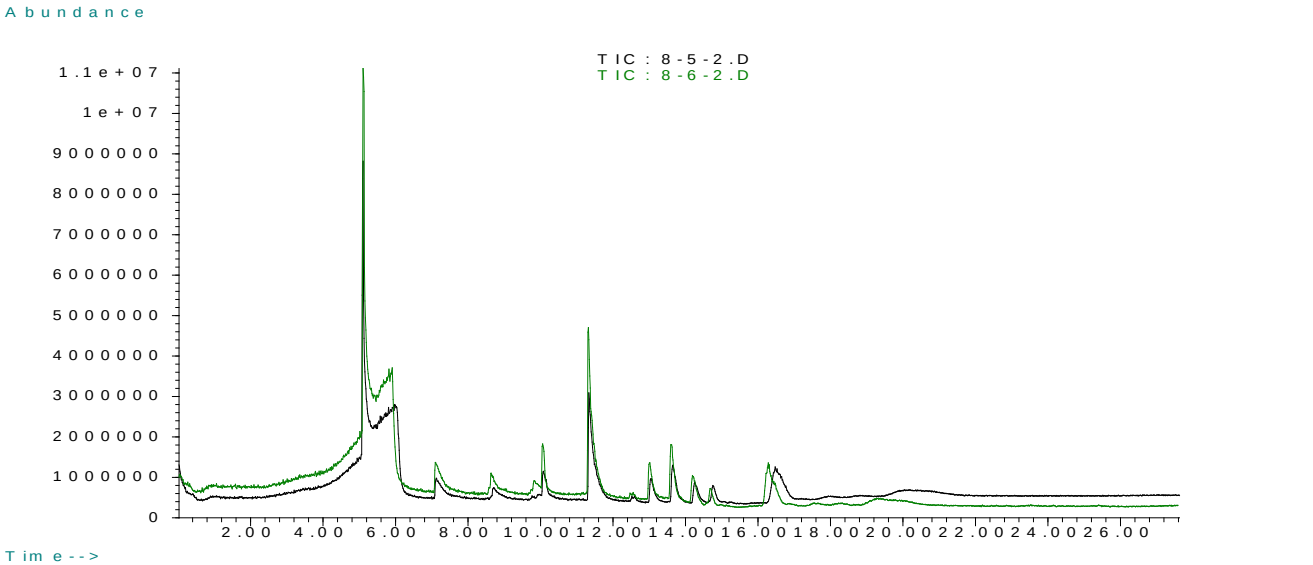


Figure B27. Overlaid TIC for Repeated Experiment (Phosphorous Flame Retardant Sample under 21% O2 Condition at 900°C)

Appendix C
Aqueous Sample Ion Chromatogram Analysis

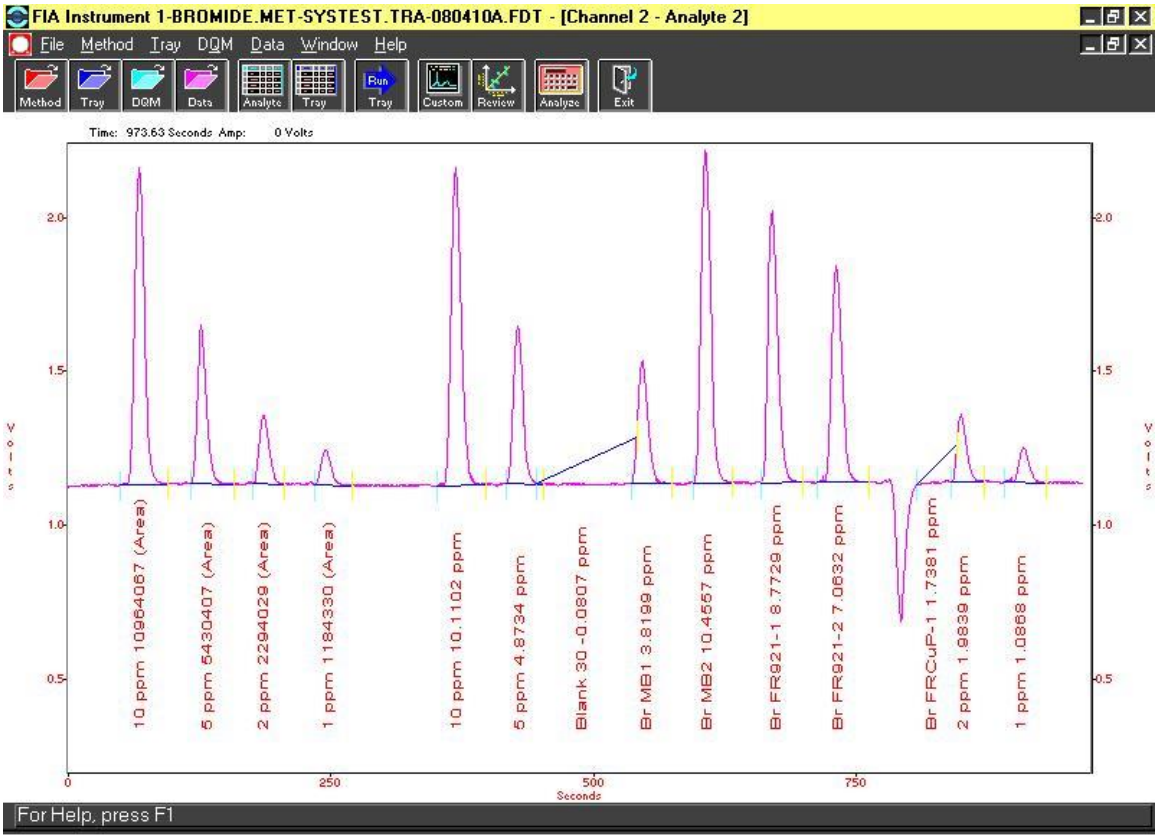


Figure C1. FIA Analysis of Aqueous Samples Run 1

Blank 30: Blank Sample
BrMB1: Aqueous sample for TBBA standard used for Br mass balance test.
BrMB2: Bromide standard for cross check
BrFR921-1: Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2.
BrFR921-2: Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2, repeated.
BrFRCuP1: Aqueous sample for Br flame retardant with Cu laminate combustion test at 900ºC in pyrolysis.

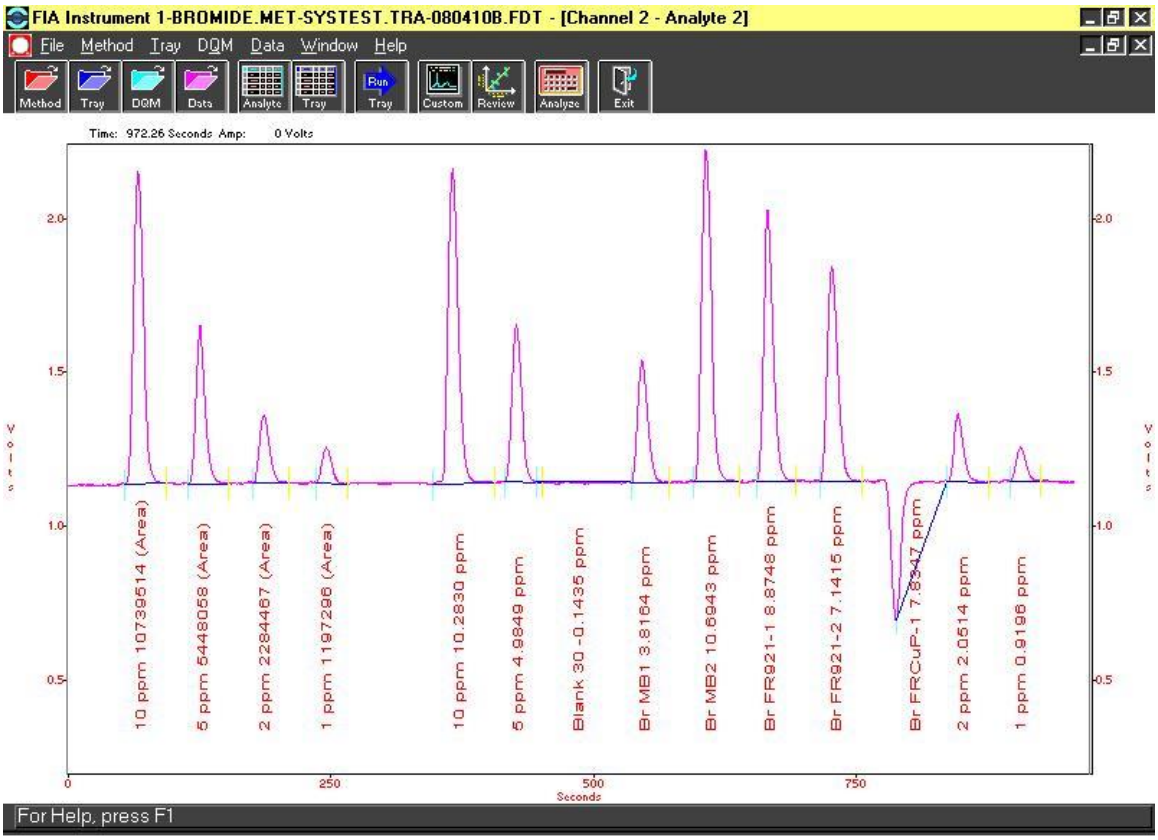


Figure C2. FIA Analysis of Aqueous Samples Run 2

Blank 30:	Blank Sample
BrMB1:	Aqueous sample for TBBA standard used for Br mass balance test.
BrMB2:	Bromide standard for cross check
BrFR921-1:	Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2.
BrFR921-2:	Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2, repeated.
BrFRCuP1:	Aqueous sample for Br flame retardant with Cu laminate combustion test at 900ºC in pyrolysis.

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX B

Sidhu, Sukh; Morgan, Alexander; Kahandawala, Moshan; Chauvin, Anne; Gullett, Brian; Tabor, Dennis. Use of Cone Calorimeter to Estimate PCDD/Fs and PBDD/Fs Emissions From Combustion of Circuit Board Laminates. U.S. EPA and UDRI. March 23, 2009

USE OF CONE CALORIMETER TO ESTIMATE PCDD/Fs AND PBDD/Fs EMISSIONS FROM COMBUSTION OF CIRCUIT BOARD LAMINATES

Sukh Sidhu, Alexander Morgan, Moshan Kahandawala,

Anne Chauvin, Brian Gullett, Dennis Tabor

UDRI and EPA

March 23, 2009

The purpose of this study was to use a cone calorimeter to measure emissions from fully ventilated combustion of printed circuit board laminates. The cone calorimeter (FTT Dual Cone Calorimeter) was modified in order to allow for isokinetic sampling of the exhaust gas. USEPA method 23 was used to sample and analyze Polychlorinated Dibenzo-p-Dioxins and Furans (PCDD/Fs) and Polybrominated Dibenzo-p-Dioxins and Furans (PBDD/Fs) from combustion of circuit board laminates. The cone calorimeter experiments were conducted at the University of Dayton Research Institute (UDRI). The exhaust gas samples were extracted and analyzed at the EPA Research Triangle Park laboratory. This report presents and discusses experimental and analytical data from both institutions.

BrFR or BFR or BR FR = laminate containing brominated flame retardant

PFR = laminate containing phosphorous based flame retardant

NFR = laminate without a flame retardant

MATERIAL AND METHODS

Cone Calorimeter

The cone calorimeter is a fire testing instrument that measures the inherent flammability of a material through the use of oxygen consumption calorimetry [1]. It is based on the principle that the net heat of combustion of any organic material is directly related to the amount of oxygen required for combustion [2]. The cone calorimeter is a standard technique under ASTM E-1354/ISO 5660 [3, 4] and is commonly used as a fire safety engineering tool. Under the ASTM E-1354/ISO 5660 method, small samples (100 cm^2 squares up to 50-mm thick) of combustible materials are burned and a wide range of data can be obtained. Through oxygen consumption calorimetry, heat release rate data can be obtained and sensors on the cone calorimeter can measure smoke release, CO/CO_2 production rates, mass loss rate and several other flammability properties such as time to ignition and fire growth rate.

A schematic of the UDRI cone calorimeter apparatus is shown in Figure 1. At the core of the equipment is a radiant cone heater, hence the name 'cone calorimeter'. A sample is placed at the center of the cone heater on the sample holder with dimensions of 100 mm x 100 mm. The cone heater provides a constant heat flux to the sample. Ignition of the sample is provided by a spark igniter located above the sample. The exhaust gas contains smoke and products of combustion. The constant ventilation is maintained by the blower. The cone calorimeter mimics a well-ventilated forced combustion of an object being exposed to a constant heat source and constant ventilation [5, 6].

Several measurements can be obtained from the cone calorimeter. A load cell continuously measures the mass loss of the sample as it burns. Gases from the fire are carried past a laser photometer beam to measure smoke density and to a sampling ring which carries the gases to a combined $CO/CO_2/O_2$ detector. Once the gases from the sampling ring have been analyzed, one can obtain CO and CO_2 production rates as a function of time which can give insight into the heats of combustion for the material, as well as combustion efficiency. Oxygen consumption is measured in the exhaust stream using an oxygen sensor (paramagnetic). The heat release rate is determined from oxygen consumption calorimetry. Temperature and pressure measurements are also taken at various locations in the exhaust duct.

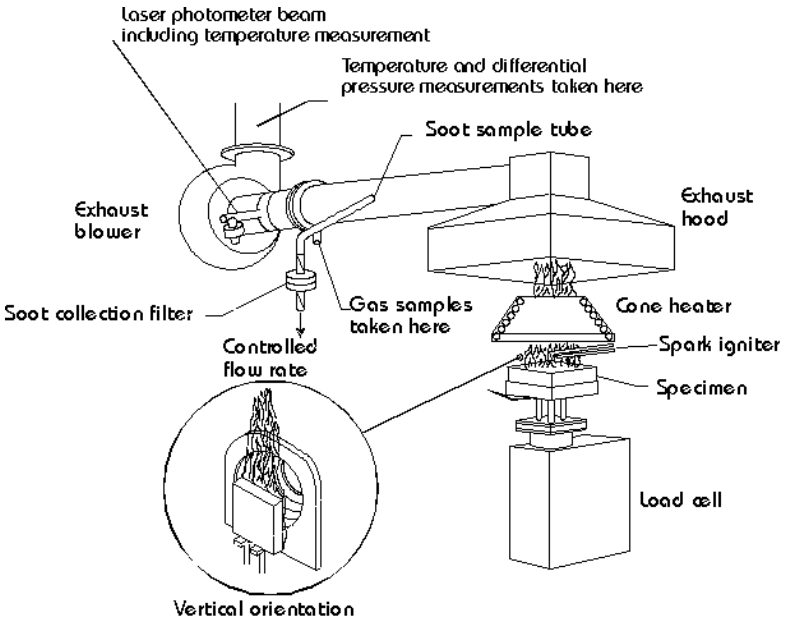


Figure 1. Schematic of Cone Calorimeter used at UDRI

The Cone calorimeter data collected during a test can reveal scientific information about material flammability performance. All measured data are defined below:

- Time to ignition (Tig): Measured in seconds, this is the time to sustained ignition of the sample. Interpretation of this measurement assumes that shorter times to ignition mean that samples are easier to ignite under a particular heat flux.
- Heat Release Rate (HRR): The rate of heat release, in units of kW/m^2, as measured by oxygen consumption calorimetry.
- Peak Heat Release Rate (Peak HRR): The maximum value of the heat release rate during the combustion of the sample. The higher the peak HRR, the more likely that flame will self-propagate on the sample in the absence of an external flame or ignition source. Also, the higher the peak HRR, the more likely that the burning object can cause nearby objects to ignite.
- Time to Peak HRR: The time to maximum heat release rate. This value roughly correlates the time it takes for a material to reach its peak heat output, which would in turn sustain flame propagation or lead to additional flame spread. Delays in time to peak HRR are inferred to mean that flame spread will be slower in that particular sample, and earlier time to peak HRR is inferred to mean that the flame spread will be rapid across the sample surface once it has ignited.
- Time to Peak HRR – Time to Ignition (Time to Peak HRR – Tig): This is the time in seconds that it takes for the peak HRR to occur after ignition rather than at the start of the test (the previous measurement). This can be meaningful in understanding how fast the sample reaches its maximum energy release after ignition, which can suggest how fast the fire grows if the sample itself catches fire.

- Average Heat Release Rate (Avg HRR): The average value of heat release rate over the entire heat release rate curve for the material during combustion of the sample.
- Starting Mass, Total Mass Lost, Weight % Lost. These measurements are taken from the load cell of the cone calorimeter at the beginning and end of the experiment to see how much total material from the sample was pyrolyzed/burned away during the experiment.
- Total Heat Release (THR). This is measured in units of MJ/m^2 and is basically the area under the heat release rate curve, representing the total heat released from the sample during burning. The higher the THR, the higher the energy content of the tested sample. THR can be correlated roughly to the fuel load of a material in a fire, and is often affected by the chemical structure of the material.
- Total Smoke Release: This is the total amount of smoke generated by the sample during burning in the cone calorimeter. The higher the value, the more smoke generated either due to incomplete combustion of the sample, or due to the chemical structure of the material.
- Maximum Average Heat Rate Emission (MAHRE): This is a fire safety engineering parameter, and is the maximum value of the average heat rate emission, which is defined as the cumulative heat release (THR) from t=0 to time t divided by time t [7]. The MAHRE can best be thought of as an ignition modified rate of heat emission parameter, which can be useful to rank materials in terms of ability to support flame spread to other objects.
- Fire Growth Rate (FIGRA): This is another fire safety engineering parameter, determined by dividing the peak HRR by the time to peak HRR, giving units of kW/m^2 per second. The FIGRA represents the rate of fire growth for a material once exposed to heat, and higher FIGRA suggest faster flame spread and possible ignition of nearby objects [1].

Isokinetic Sampling

In this project, the cone calorimeter was utilized to combust the various circuit board laminates and collect products released during their combustion. The USEPA method 23 was used to isokinetically sample a portion of the exhaust gases flowing through the exhaust duct. The cone calorimeter was modified to allow for the isokinetic sampling device to be inserted into the exhaust duct.

The main characteristic of isokinetic sampling is that the extraction of the gas sample from the main gas stream is at the same velocity as the gas travelling through the stack. This sampling method is easily adaptable and is commonly used to test for many organic pollutants such as polychlorinated biphenyls (PCBs), dioxins/furans and polycyclic aromatic hydrocarbons (PAHs) [8]. The compounds of interest are retained in a glass fiber filter and Amberlite XAD-2 adsorbent resin.

Apex Instruments Model MC-500 Series Source Sampler Console and Isokinetic System were used for this experiment and contained five main components: the source sampler console, the external vacuum pump unit, the probe assembly, the modular sample case and the umbilical cables. A picture of the Apex instrument isokinetic source sampling equipment is shown in Figure 2.

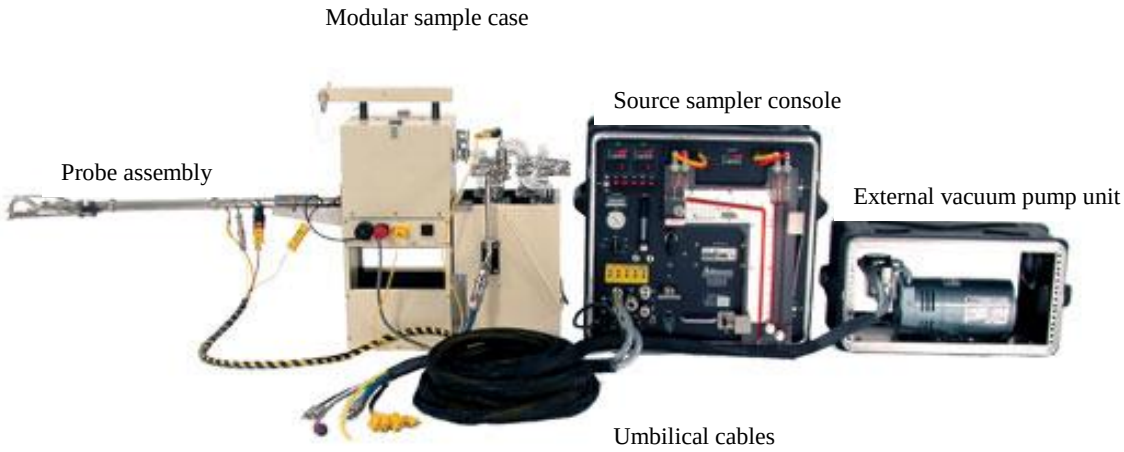


Figure 2. Isokinetic Sampling train used at UDRI

The modular sample case contained a heated box for the filter assembly and a cold box for the impinger glassware and condenser. The sampling nozzle of the heated transfer line was inserted into the exhaust duct, which was modified by adding holes into the side to allow for the device to be inserted. Figure 3 shows the modifications made to the exhaust system of the cone calorimeter. A picture of the cone calorimeter and the isokinetic sampling system assembly is shown in Figure 4.

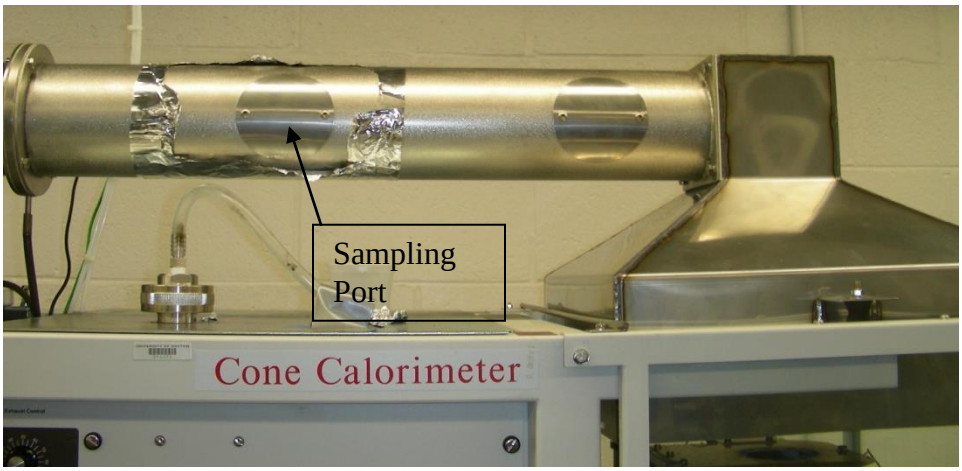


Figure 3. Modification of duct and sampling port of the UDRI cone calorimeter

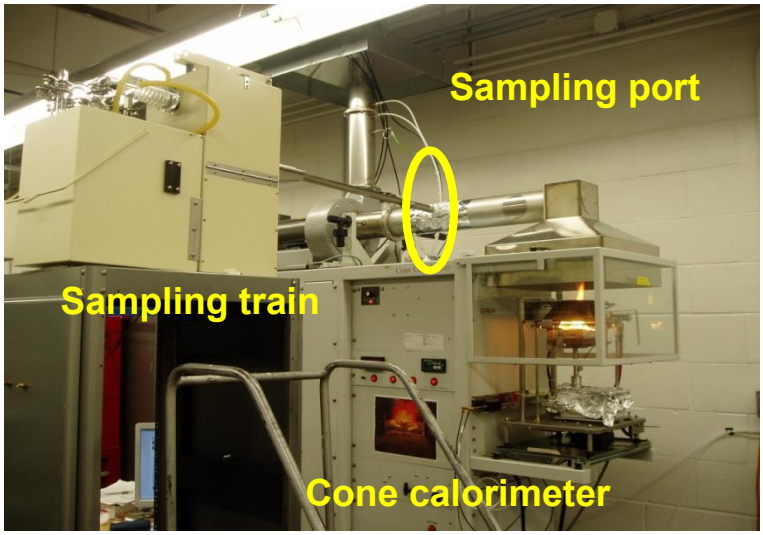


Figure 4. Cone calorimeter and isokinetic sampling system assembly

The heated probe connected the nozzle to the filter assembly where the soot was retained. The mass of the filter before and after sampling was recorded to obtain the mass of soot formed during the combustion of the samples (see data in the Appendix, Table 1). The filter assembly was also connected to a condenser followed by an adsorbent trap and a series of four impingers. The moisture formed in the condenser deposited as droplets in the first empty impinger and therefore could not be quantified. The adsorbent trap contained about 40 g of hydrophobic resin XAD-2, glass wool and 100 µL of surrogate standard solution. The surrogate standard solution contained $^{13}C_{12}$ labeled standards of PCDD/Fs to evaluate the method. Due to lack of standards for PBDD/Fs, no $^{13}C_{12}$ labeled standards of PBDD/Fs were spiked into the samples prior to sampling. XAD-2 was used to absorb the soluble organic compounds from the effluent gas. The second impinger contained about 100 mL of water, the third one was empty and the fourth one contained about 200 g of silica gel and was connected to a thermocouple. All three impingers were used to collect any extra moisture in the effluent gas. The mass of silica gel was recorded

before and after sampling to obtain the mass of moisture content in the effluent gas (see data in Appendix, Table 1). The third impinger appeared to stay dry throughout the experiment (few water droplets on the sides could not be quantified). The amount of water in the second impinger was recorded before and after sampling (see data in Appendix, Table 1) and appeared to decrease. This might be explained by the fact that some of the water could have been carried away by the effluent gas and was collected in the fourth impinger with the silica gel.

After assembling the sampling train, the system had to be checked for leaks. Throughout the runs, the temperature inside the probe and inside the filter was controlled and maintained at 120°C from the source sampler console. The cold box temperature was maintained under 20°C by adding ice water to it. The pump flow rate was maintained at 0.1104 L/s and the exhaust flow rate was maintained at 15 L/s throughout the experiment. The flow rate through the probe was controlled and maintained steady by adjusting the flow rate through the stack and therefore a pitot tube was not necessary.

After sampling, the filter and soot, as well as the soot in the probe, nozzle and front half of the filter holder, XAD-2 resin and water from the second impinger were combined for a single analysis. The filter was placed in container No.1. Container No. 2 contained the soot deposited in the nozzle, transfer probe and front half of filter holder as well as all the methylene chloride and acetone rinses. Container No. 3 contained the same material as container No. 2 with toluene as the rinse solvent. The water was also placed in a container for analysis and the silica gel was discarded. After sampling, the duct and exhaust hood were dismantled and thoroughly cleaned with hexane to avoid any risk of contamination from combustion of one type of circuit board to the next. The sampling method and sample recovery followed the USEPA method 23 for the

determination of emissions of PCDD's and PCDF's from stationary sources (9). A schematic of the isokinetic sampling train is shown in Figure 5.

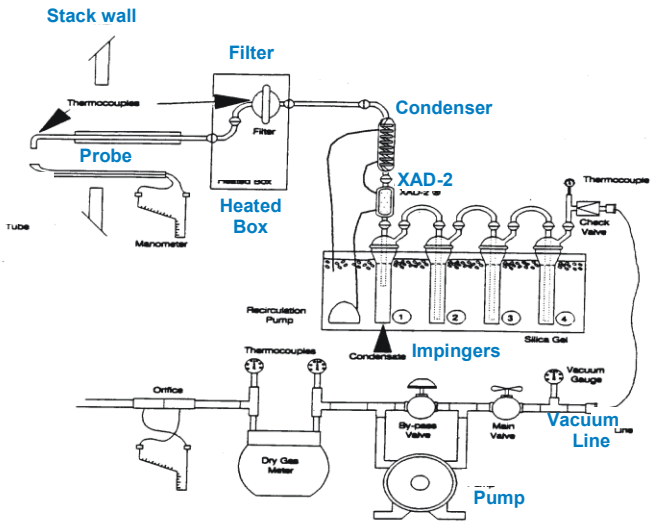


Figure 5. Schematic of isokinetic sampling train

For the first set of experiments (combustion of BrFR laminate), the temperature inside the stack dropped below 100°C before it even reached the sampling probe. The temperatures below 100°C can lead to condensation inside the stack; therefore, to prevent condensation inside the stack and ensure proper transport of gaseous organic compounds formed, a heating tape was wrapped around the stack to maintain the temperature inside the stack between 100°C and 130°C during combustion. In order to monitor the temperature inside the stack during combustion of the samples, a thermocouple was placed on the inside wall of the stack right behind the nozzle. Two other thermocouples were added to the outside wall. Please see Appendix, Table 3 for inside wall temperature data. Note that for the first set of experiments (BrFR) the cone calorimeter did not have the heating tape and thermocouples. However, a repeat run was made for the BrFR laminate which included the heating tape around the stack and thermocouples.

Samples tested

Three types of circuit board samples were provided: laminates containing brominated flame retardant, non-halogen flame retardant (Phosphorous- based) and no-flame retardant. The laminates were very thin (~0.4mm thick) and contained copper strips. They were made of a mixture of epoxy resin and e-glass [1]. The three types of circuit board are summarized in Table 1.

Table 1. Circuit Board Types

Circuit Board types	Description	Picture
BrFR	Circuit board containing Brominated Flame Retardant	
NFR	Circuit board without Flame Retardant	
PFR	Circuit Board containing Phosphorous Flame Retardant	

Preparation of Samples

Since the laminates provided were too large to be tested as is in the cone calorimeter, the samples were cut into roughly 100 cm^2 square pieces for cone calorimeter testing. Samples were not conditioned in any way prior to testing. Depending upon how the original laminates were cut, the samples had 1 or 2 copper strips as shown in Figure 6.

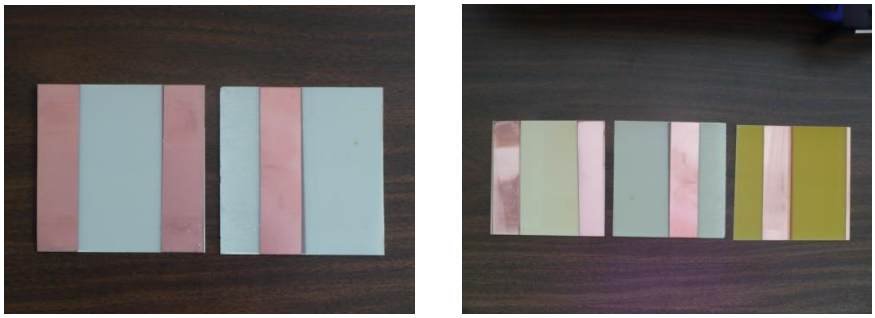


Figure 6. Two-strip and one-strip circuit boards

Initially, it was estimated that 6 thin laminates had to be stacked and burned together in order to reach a temperature inside the duct of about 120°C during combustion (120°C is the USEPA method 23 recommended transfer line temperature); this was also the maximum number of laminates per stack for which the exhaust gas flow rate was sufficient to remove the smoke produced during combustion (if the number of laminates per stack was increased, smoke came into the lab). The laminate pieces were selected and configured in six layer stacks where 2 x two-strip laminates and 4 x one-strip laminates where stacked together. The stacking sequence ensured that each test sample had the same amount of copper metal in similar configuration. One single one-strip laminate as well as one single two-strip laminate were also burned separately to determine the effect of copper on burning patterns and smoke emissions. Each

sample was wrapped in aluminum foil such that only the upper side was exposed to the constant heat flux. The aluminum foil helped to keep the samples together as they burned (preventing them from falling from the sample holder) and directed the smoke and flames toward the exhaust hood. Figure 7 shows a sample wrapped in aluminum foil.

Figure 7. Sample wrapped in aluminum foil

Five runs were conducted in series for each circuit board type where the first three runs consisted of 6- layer samples and the last two runs consisted of 1 one-strip laminate and 1 two-strip laminate sample. The combustion products for all five runs were collected for a single analysis for a given type of circuit board. The initial mass of each sample wrapped in aluminum foil was recorded for each run and is summarized in Table 2. Table 2 also summarizes the sequence in which the samples were burned.

Table 2. Description of Samples

Circuit Board Type	Date sampled	Run	Number of laminates	Description (one or two-strip laminate)	Sample ID
BrFR	06/05/08	1	6	2 two-strip and 4 one-strip	Br FR Epoxy Laminate, 6 plies, run 1
		2	6	2 two-strip and 4 one-strip	Br FR Epoxy Laminate, 6 plies, run 2
		3	6	2 two-strip and 4 one-strip	Br FR Epoxy Laminate, 6 plies, run 3
		4	1	one-strip	Br FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4
		5	1	two-strip	Br FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5
NFR	06/16/08	1	6	2 two-strip and 4 one-strip	No FR Epoxy Laminate, 6 plies, run 1
		2	6	2 two-strip and 4 one-strip	No FR Epoxy Laminate, 6 plies, run 2
		3	6	2 two-strip and 4 one-strip	No FR Epoxy Laminate, 6 plies, run 3
		4	1	one-strip	No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4
		5	1	two-strip	No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5
PFR	06/17/08	1	6	2 two-strip and 4 one-strip	Non Hal FR Epoxy Laminate, 6 plies, run 1
		2	6	2 two-strip and 4 one-strip	Non Hal FR Epoxy Laminate, 6 plies, run 2
		3	6	2 two-strip and 4 one-strip	Non Hal FR Epoxy Laminate, 6 plies, run 3
		4	1	two-strip	Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4
		5	1	one-strip	Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5
(Repeat BrFR)	06/18/08	1	6	2 two-strip and 4 one-strip	Br FR Repeat run 1
		2	6	2 two-strip and 4 one-strip	Br FR Repeat run 2
		3	6	2 two-strip and 4 one-strip	Br FR Repeat run 3
		4	1	one-strip	Br FR Repeat run 4
		5	1	two-strip	Br FR Repeat run 5

Sampling

The cone calorimeter experiments were conducted on a FTT Dual Cone Calorimeter following the ASTM E-1354-04 method at one heat flux (50 kW/m^2), but some modifications were made to the method: the isokinetic sampling system was added to sample the exhaust gas and the heating tape was wrapped around the duct for the NFR, PFR, BrFR and BrFR (repeat) samples. A constant heat flux of 50 kW/m^2 was maintained by setting the cone temperature at about 759°C. Samples were tested in triplicate without frame and grid, with the back side of each sample wrapped in aluminum foil and an exhaust flow was maintained at 15 L/s. All samples were tested copper side up [3]. The initial and final ambient conditions during the combustion of samples were recorded and are summarized in Table 3.

Table 3. Ambient conditions during experiment

	BrFR		NFR		PFR		BrFR (repeat)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Temperature (°C)	26.5	27.5	26.5	NA	24	28	24	24
Humidity (%)	46	45	33	32	35	29	35	34
Pressure (mbar)	1088	1088	1084	1084	1091	1089	1087	1086

Each sample was ignited and allowed to burn until the flames disappeared. For the 6-layer Non Hal FR Laminate run 2 and 3, and Br FR Laminate repeat run 3, the flame had to be re-ignited shortly after initial ignition. The burning times for each sample as well as the initial mass, mass burnt and volumes of gas sampled were recorded and are summarized in Table 4.

Table 4. Data taken during Combustion of Samples

Sample ID	Starting mass (g)	Mass lost (g)	Total sampling time (s)	Volume sampled (ft3)	Comments
Br FR Epoxy Laminate, 6 plies, run 1	61.8	19.2	426	10.1	No heating tape around cone calorimeter duct
Br FR Epoxy Laminate, 6 plies, run 2	62.2	18.5	400		
Br FR Epoxy Laminate, 6 plies, run 3	60.4	17.6	374		
Br FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	11.9	2.5	99		
Br FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	10.2	2.8	89		
No FR Epoxy Laminate, 6 plies, run 1	61.5	16.6	512	12.4	Heating tape
No FR Epoxy Laminate, 6 plies, run 2	64.5	15.9	622		
No FR Epoxy Laminate, 6 plies, run 3	63.8	17.6	534		
No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	12.6	3.4	129		
No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	11.0	3.5	110		
Non Hal FR Epoxy Laminate, 6 plies, run 1	63.3	14.3	670	13.9	Heating tape; Run 2 and 3 were re-ignited after 4 min
Non Hal FR Epoxy Laminate, 6 plies, run 2	64.3	14.9	668		
Non Hal FR Epoxy Laminate, 6 plies, run 3	64.5	13.8	652		
Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4	12.6	2.2	179		
Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5	11.0	2.8	145		
Br FR Repeat run 1	61.64	19.1	360	10.5	Heating tape; Run 3 was re-ignited after 1 min
Br FR Repeat run 2	60.03	18.5	300		
Br FR Repeat run 3	61.25	18.7	300		
Br FR Repeat run 4	10.65	1.3	60		
Br FR Repeat run 5	12.15	3.4	60		

All conditions during the combustion of the samples and collection of organic compounds are summarized in Table 5.

Table 5. Summary of Conditions during Combustion of Samples

Parameters	Conditions
Heat Flux (kW/m^2)	50
Stack Gas Flow Rate (L/s)	15
Sampling Flow Rate (L/s)	0.1104
Pump Flow Rate (L/s)	0.1104
Probe Temperature (°C)	120
Filter Temperature (°C)	120
Cold Box Temperature (°C)	<20
Cone Temperature (°C)	759

Extraction and Analysis

After sampling, Container No. 1 (filter), Container No. 2 (soot deposited in the nozzle, transfer probe and front half of filter holder as well as all the methylene chloride and acetone rinses), Container No. 3 (same material as container No. 2 with toluene as the rinse solvent), and an another container containing the XAD-2 and glass wool were sealed and recorded on a chain of custody form. All containers were sent to the EPA Research Triangle Park laboratory for extraction and analysis.

The EPA Research Triangle Park laboratory received the samples from UDRI and confirmed them against the chain of custody form. The samples had been spiked at UDRI with PCDD/F pre-sampling spikes to confirm the sampling process. The samples were spiked again just before extraction with PBDD/F surrogates and internal standards for both the PCDD/F and

PBDD/F. The samples were then extracted with methylene chloride for 3.5 hours and then with toluene overnight. The cooler methylene chloride extraction is used in low light conditions to extract the majority of the brominated compounds due to concerns that they could degrade due to light exposure, the higher extraction temperature of toluene, and longer extraction times. The toluene extraction procedure was used to ensure that the standard method of extraction (EPA Method 23 for Dioxin Analysis) was also completed. After extraction, the extracts were concentrated with a Snyder column and then filtered. The final volume was 1 milliliter. The extracts were very dark so only one quarter of the extract was used for further clean-up and analysis. Equal portions of the methylene chloride and toluene extracts were combined and diluted with hexane for the clean-up. The extracts were then processed through acidic, neutral, and basic silica gel, and then adsorbed onto basic alumina and washed with dilute methylene chloride in hexane. The target compounds were then transferred to carbon/celite with 50/50 methylene chloride/hexane, washed with benzene/ethyl acetate and then eluted from the carbon celite with toluene. The final fraction was concentrated to 100 microliter and analyzed with high resolution gas chromatography/high resolution mass spectrometry [10].

The samples were analyzed using an isotope dilution method where isotopically labeled internal standards and surrogate standards were incorporated prior to sampling and extraction. The surrogate standards were spiked prior to sampling and their recoveries gave a measure of the sampling process efficiency. The internal standards were spiked prior to extraction and allowed quantifying the PCDD/Fs and PBDD/Fs present in the samples. According to the USEPA method 23, recoveries of the pre-extraction standards must be between 40 and 130 percent for tetra- through hexachlorinated compounds and 25 to 130 percent for the hepta- and

octachlorinated homologues. All recoveries for PCDD/Fs pre- sampling surrogate standards must be between 70 and 130 percent [9]. Percent recovery limits for PBDD/Fs are not available at the moment. Overall, it was found that PCDD/Fs pre-sampling and pre-extraction surrogate standard recoveries fell within the acceptable range (see Appendix 2 for recoveries data). Standard recoveries never fell below the lowest limit, but for the isotopes $13C^{12}$ 2,3,7,8 - TeCDF in the BrFR run and 13 C^{12} 1,2,3,4,7,8,9 - HpCDF in the PFR run, the percent recovery was slightly above the highest limit, which means that there was a possibility of breakthrough in the sampling train.

A blank run sample was also analyzed for PCDD/Fs and PBDD/Fs analysis to demonstrate that no contamination was contributed by laboratory instruments (see Appendix 2 for data).

RESULTS AND DICUSSION

CO/CO_2 production/ O_2 consumption data

The gas sampled in the sampling ring was analyzed by a $CO/CO_2/O_2$ detector which allowed measurement of CO/CO_2 production rates and O_2 consumption rate as a function time. The total production rates and consumption rates per initial sample mass are presented in Table 6. Note that for the repeat run for BrFR samples, $CO/CO_2/O_2$ data is not provided because it is not affected by the temperature of exhaust duct.

Table 6. Total CO/CO_2 production rate and O_2 consumption rate data

Sample ID	Total CO_2 produced (g)	Total CO_2 produced (g)/ starting mass (g)	Total O_2 consumed (g)	Total CO produced (g)
Br Epoxy Laminate, 6 plies, run 1	23.7	0.4	18.3	2.7
Br Epoxy Laminate, 6 plies, run 2	23.4	0.4	17.9	2.5
Br Epoxy Laminate, 6 plies, run 3	20.3	0.3	15.1	2.6
Br Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	8.0	0.7	2.9	0.8
Br Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	6.9	0.7	2.3	0.7
No FR Epoxy Laminate, 6 plies, run 1	35.9	0.6	26.6	1.4
No FR Epoxy Laminate, 6 plies, run 2	39.3	0.6	28.6	2.3
No FR Epoxy Laminate, 6 plies, run 3	37.4	0.6	28.1	1.7
No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	14.6	1.2	5.4	1.0
No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	14.2	1.3	5.3	1.2
Non Hal FR Epoxy Laminate, 6 plies, run 1	29.2	0.5	20.5	2.7
Non Hal FR Epoxy Laminate, 6 plies, run 2	31.7	0.5	22.5	2.7
Non Hal FR Epoxy Laminate, 6 plies, run 3	30.0	0.5	21.0	2.7
Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4	13.0	1.0	3.7	1.4
Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5	11.2	1.0	3.3	1.5

PCDD/Fs and PBDD/Fs Data

For each type of circuit board laminates, combustion product samples from five runs were combined and analyzed to determine total dioxin concentration. The emission levels of Polychlorinated Dibenzo-p-Dioxins and DibenzoFurans (PCDD/Fs) are reported using both ng per Kg of laminate and as ng- Toxic equivalent (TEQ) per Kg of laminate. The TEQ concentration expresses the overall toxicity of a dioxin mixture relative to the toxicity of 2,3,7,8-TeCDD. Each dioxin congener is assigned a toxic equivalent factor (TEF) value based on its relative toxicity to the toxicity of 2,3,7,8- TeCDD [11]. The WHO 2005 TEF values for all 7 dioxin and 10 furan chemical compounds analyzed are presented in Table 7 [12].

Table 7. Toxic Equivalent Factors of Chlorinated Congeners

Isomer.	**2005 WHO (Mammals/Humans) Toxicity Equiv. Factor**
2,3,7,8 - TeCDD	1
1,2,3,7,8 - PCDD	1
1,2,3,4,7,8 - HxCDD	0.1
1,2,3,6,7,8 - HxCDD	0.1
1,2,3,7,8,9 - HxCDD	0.1
1,2,3,4,6,7,8 - HpCDD	0.01
1,2,3,4,6,7,8,9 - OCDD	0.0003
2,3,7,8 - TeCDF	0.1
1,2,3,7,8 - PCDF	0.03
2,3,4,7,8 - PCDF	0.3
1,2,3,4,7,8 - HxCDF	0.1
1,2,3,6,7,8 - HxCDF	0.1
2,3,4,6,7,8 - HxCDF	0.1
1,2,3,7,8,9 - HxCDF	0.1
1,2,3,4,6,7,8 - HpCDF	0.01
1,2,3,4,7,8,9 - HpCDF	0.01
1,2,3,4,6,7,8,9 - OCDF	0.0003

The total TEQ was calculated by summing the multiplication of each congener concentration in the flue gas by its corresponding TEF. The congener concentration (in ng/kg) was calculated from the data obtained from the HRGC/HRMS analysis (in ng/train) and based on the basis of total sampling as shown:

$$Concentration\left(\frac{ng}{kg}\right) = \frac{Total\ flow\ rate\ in\ duct}{Flow\ through\ sampling\ line} \times \frac{Total\ congener\ in\ extract\ (ng/train)}{Initial\ mass\ of\ circuit\ board\ (kg)}$$

Congeners concentrations below the limit of detection were regarded as zero and reported as less than limit of detection (<LOD).

Due to lack of standards for the analysis of Polybrominated Dibenzo-p-Dioxins and DibenzoFurans (PBDD/Fs) results are semi-quantitative, at best. Since TEFs for PBDD/Fs are not available, the PBDD/F data is only shown in ng per Kg of laminate units.

The results obtained from the analysis of emissions for PCDD/Fs concentrations in the extracts are presented in Table 8 and 9. Most chlorinated congener concentrations were reported as less than the limit of detection. The detected targets appeared to be a carry over from a standard. As expected, the results showed that no chlorinated dioxin/furan congeners were present in combustion exhaust. This confirmed the fact that since chlorine was not present in significant levels in the circuit board laminates, no chlorinated compounds were observed during combustion of the circuit board laminates.

Table 8. Results showing PCDD/Fs concentration in ng- Toxic equivalent (TEQ) per Kg of laminate in the emission samples from combustion of circuit board samples

Isomer.	**TEQ (ng/kg)**			
	PFR Epoxy laminate	BR FR Epoxy laminate	BR FR Epoxy laminate, repeat run	NFR Epoxy laminate
2,3,7,8 - TeCDD	<LOD	<LOD	<LOD	<LOD
1,2,3,7,8 - PCDD	<LOD	<LOD	13.3	<LOD
1,2,3,4,7,8 - HxCDD	<LOD	<LOD	1.9	<LOD
1,2,3,6,7,8 - HxCDD	<LOD	<LOD	1.3	<LOD
1,2,3,7,8,9 - HxCDD	<LOD	<LOD	2.1	<LOD
1,2,3,4,6,7,8 - HpCDD	<LOD	<LOD	0.3	0.2
1,2,3,4,6,7,8,9 - OCDD	<LOD	<LOD	0.0	0.0
2,3,7,8 - TeCDF	0.8	<LOD	2.7	1.3
1,2,3,7,8 - PCDF	<LOD	<LOD	0.7	<LOD
2,3,4,7,8 - PCDF	<LOD	<LOD	6.7	<LOD
1,2,3,4,7,8 - HxCDF	<LOD	<LOD	3.1	<LOD
1,2,3,6,7,8 - HxCDF	<LOD	<LOD	2.8	<LOD
2,3,4,6,7,8 - HxCDF	<LOD	<LOD	3.7	<LOD
1,2,3,7,8,9 - HxCDF	<LOD	<LOD	4.3	<LOD
1,2,3,4,6,7,8 - HpCDF	<LOD	0.3	0.5	0.1
1,2,3,4,7,8,9 - HpCDF	<LOD	<LOD	0.5	<LOD
1,2,3,4,6,7,8,9 - OCDF	<LOD	<LOD	0.0	<LOD
Total TEQ (ng/kg)	**0.8**	**0.3**	**43.9**	**1.6**

LOD= Limit of Detection
Additional Comments:
PFR Epoxy laminate: detected target appeared to be carry over from a standard
BR FR Epoxy laminate: Sample rerun; elevated standard recoveries were due to a large interfering peak causing reduced signal on the TeCDD recovery standard
BR FR Epoxy laminate, repeat run: All detected targets appeared to be carry over from a standard
NFR Epoxy laminate: All detected targets appeared to be carried over from a standard

Table 9. Results showing PCDD/Fs concentration (in ng/Kg of laminate) in the emission samples from combustion of circuit board samples

Isomer.	**Conc. (ng/kg)**			
	PFR Epoxy laminate	BR FR Epoxy laminate	BR FR Epoxy laminate, repeat run	NFR Epoxy laminate
2,3,7,8 - TeCDD	<LOD	<LOD	<LOD	<LOD
1,2,3,7,8 - PCDD	<LOD	<LOD	13.3	<LOD
1,2,3,4,7,8 - HxCDD	<LOD	<LOD	19.2	<LOD
1,2,3,6,7,8 - HxCDD	<LOD	<LOD	13.3	<LOD
1,2,3,7,8,9 - HxCDD	<LOD	<LOD	20.7	<LOD
1,2,3,4,6,7,8 - HpCDD	<LOD	<LOD	34.0	21.1
1,2,3,4,6,7,8,9 - OCDD	<LOD	<LOD	63.5	33.8
2,3,7,8 - TeCDF	8.1	<LOD	26.6	12.7
1,2,3,7,8 - PCDF	<LOD	<LOD	22.2	<LOD
2,3,4,7,8 - PCDF	<LOD	<LOD	22.2	<LOD
1,2,3,4,7,8 - HxCDF	<LOD	<LOD	31.0	<LOD
1,2,3,6,7,8 - HxCDF	<LOD	<LOD	28.1	<LOD
2,3,4,6,7,8 - HxCDF	<LOD	<LOD	36.9	<LOD
1,2,3,7,8,9 - HxCDF	<LOD	<LOD	42.9	<LOD
1,2,3,4,6,7,8 - HpCDF	<LOD	25.6	51.7	9.9
1,2,3,4,7,8,9 - HpCDF	<LOD	<LOD	48.8	<LOD
1,2,3,4,6,7,8,9 - OCDF	<LOD	<LOD	81.3	<LOD
Total conc. (ng/kg)	**8.1**	**25.6**	**555.6**	**77.5**

LOD= Limit of Detection
Additional Comments:
PFR Epoxy laminate: detected target appeared to be carry over from a standard
BR FR Epoxy laminate: Sample rerun; elevated standard recoveries were due to a large interfering peak causing reduced signal on the TeCDD recovery standard
BR FR Epoxy laminate, repeat run: All detected targets appeared to be carry over from a standard
NFR Epoxy laminate: All detected targets appeared to be carried over from a standard

The results obtained from the analysis of emissions for PBDD/Fs concentrations in the extracts are presented in Table 10. For the PFR laminates and NFR laminates, no brominated congener was detected. The OcBDD and OcBDF compounds were not reported for all circuit boards types because OcBDD/F needed separate clean-up and the $^{13}C_{12}$ labeled OcBDD surrogate standard did not elute from the carbon column during extraction procedure. The data for the BR FR laminates BrFR (first run and repeat run) were consistent. For the first set of experiments, it was found that 3213.8 ng PBDD/Fs per kg of laminates was produced. For the repeat run, it was found that 3389.7 ng PBD/Fs per kg of laminates was produced. No published data on PBDD/Fs concentrations in ng per kg of combustible material burned where found to compare the results.

Table 10. Results showing PBDD/Fs concentration (in ng/Kg of laminate) in the emission samples from combustion of circuit board laminates

Isomer.	**Concentration (ng/kg)**			
	PFR Epoxy laminate	BR FR Epoxy laminate	BR FR Epoxy laminate, repeat run	NFR Epoxy laminate
2,3,7 TrBDD*	ND	24.4	ND	ND
2,3,7 TrBDF*	ND	ND	ND	ND
2,3,7,8 TeBDD	ND	112.4	88.7	ND
2,4,6,8 TeBDF	ND	172.3	173.0	ND
2,3,7,8 TeBDF	ND	855.4	536.6	ND
1,2,3,7,8 PeBDD	ND	ND	ND	ND
1,2,3,7,8 PeBDF	ND	325.1	300.1	ND
2,3,4,7,8 PeBDF	ND	163.7	112.3	ND
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	ND	ND	ND	ND
1,2,3,7,8,9 HxBDD	ND	ND	ND	ND
1,2,3,4,7,8 HxBDF	ND	107.5	96.1	ND
1,2,3,4,6,7,9 HpBDD*/**	ND	ND	ND	ND
1,2,3,4,6,7,8 HpBDD*/**	ND	ND	ND	ND
1,2,3,4,6,7,8 HpBDF	ND	1453.0	2082.9	ND
OcBDD	NR	NR	NR	NR
OcBDF	NR	NR	NR	NR
Total conc. (ng/kg)	**-**	**3213.8**	**3389.7**	**-**

*Not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

**Assignment based on the elution order of HpCDD congeners on the DB5 column.

ND= not detected

NR= not reported (OcBDD/F would need separate clean-up; ^{13}C OcBDD did not elute from carbon column)

Heat release data and fire behavior

The combined cone calorimeter heat release data are shown in Table 11. Data for the 6-ply laminate stacks was not reproducible in all aspects of heat and smoke release due to erratic physical effects of burning, which are described below. Data from single ply laminates with one or two strips was also difficult to compare to each other, since the amount of copper metal had some effects on the amount of heat released. It should be noted that for the repeat run for BrFR, heat release data and fire behavior are not provided as they are not impacted by heating of the exhaust duct.

Table 11. Combined Heat Release Rate data

Description	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m2)	Time to Peak HRR (s)	Time to Peak HRR - Tig (s)	Average HRR (kW/m2)	Starting Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m2)	Total smoke Release (m2/m2)	Avg. Effective Heat of Comb. (MJ/kg)	MAHRE (kW/m2)	FIGRA
Br Epoxy Laminate, 6 plies, run 1	3.1	12	242	178	166	68	61.9	19.2	31.0	23.8	2394	12.35	93	1.36
Br Epoxy Laminate, 6 plies, run 2	2.9	14	204	222	208	69	62.2	18.5	29.8	23.4	2019	12.63	75	0.92
Br Epoxy Laminate, 6 plies, run 3	3.0	13	237	208	195	63	60.4	17.6	29.1	19.6	2046	11.06	68	1.14
Br Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	0.4	8	171	20	12	53	11.9	2.5	21.0	3.8	449	15.12	83	8.55
Br Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	0.5	10	185	25	15	43	10.2	2.8	27.4	3.2	424	10.94	76	7.39
No FR Epoxy Laminate, 6 plies, run 1	3.1	14	173	240	226	79	61.5	16.6	27.0	35.5	1401	21.40	96	0.72
No FR Epoxy Laminate, 6 plies, run 2	3.3	15	177	250	235	72	64.5	15.9	24.6	37.9	1350	23.83	85	0.71
No FR Epoxy Laminate, 6 plies, run 3	3.2	17	196	288	271	80	63.8	17.6	27.6	37.5	1310	21.37	88	0.68
No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	0.5	13	379	24	11	97	11.0	3.5	31.9	7.2	329	19.98	138	15.77
No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	0.6	15	265	50	35	81	12.6	3.4	27.0	7.4	353	21.46	111	5.29
Non Hal FR Epoxy Laminate, 6 plies, run 1	3.1	190	152	262	72	64	63.3	14.3	22.6	27.1	1310	18.90	57	0.58
Non Hal FR Epoxy Laminate, 6 plies, run 2	3.2	190	134	326	136	72	64.3	14.9	23.2	30.0	1336	20.13	59	0.41
Non Hal FR Epoxy Laminate, 6 plies, run 3	3.2	206	222	230	24	74	64.5	13.8	21.4	28.0	1209	20.33	59	0.96
Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4	0.5	17	104	29	12	46	12.6	2.2	17.4	4.9	283	22.22	41	3.58
Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5	0.5	15	231	29	14	62	11.0	2.8	25.5	4.5	276	15.47	63	7.96

Along with the heat release data in Table 11, the heat release rate curves are plotted in Figures 8-10. Each of the laminates had their own fire behavior which is described separately below.

Brominated FR Epoxy Laminate Fire Behavior

For the 6-ply laminate stacks, the only reproducible part of the heat release phenomena was the initial ignition and the detection of the 1st HRR peak, given the observed fire behavior of these samples this correlates nicely. Each of the 6 ply laminate stacks, upon exposure to the cone heater, began to smoke within 10 seconds of heat exposure, and then the samples quickly foamed up as a large bubble and ignited. This rapid ignition flashed off quickly and then died back with some edge burning on the top ply, followed by a decrease in heat release. Then the underlying material began to ignite which led to a 2nd HRR peak. These flames continued to grow until all of the remaining plies foamed up and flames began to come out from the sides of the sample. This rapid flare up led to the final HRR peak between 150 and 250 seconds as shown in Figure 8. After this rapid flare up the flames began to die down and eventually the sample extinguished. One sample (HRR-3) actually self extinguished after the 1st HRR peak and reignited after a brief delay (Figure 8 left), again attesting to the physical effects of burning laminate stacks which led to irreproducibility in the HRR curves. Final chars were primarily glass laminate with blackened metal strips. Some soot/char was present on the lower laminates, but the top laminate was a light grey in color and had very little soot/char carbon present. Due to the sample foaming late in the fire, the shutters of the cone calorimeter could not be closed at the end of the test – otherwise the shutters would have crushed the sample residue which would have

led to a false load cell (weight loss) result which would have affected many other cone calorimeter measurements. So, after the last flame went out, the sample was allowed to stay under the cone heater for another 60 seconds to collect good baseline data. This change in procedure is noteworthy since it may have burned off the residual carbon on the top ply of the burned laminates since for the single ply laminates, carbon char was found after the sample extinguished. Another thing to note for these samples is that, after ignition and once the flames had grown sufficiently, wherever the sample was burning next to copper, the flames were a bright blue in color, typical for burning of copper salts. The flame color was yellow to orange where there was no copper.

For the single ply laminates (Figure 9 left) the observed behavior of burning was different than that observed with the 6 ply laminate stacks. Upon exposure to the cone heater, the sample rapidly began to smoke, and then quickly foamed up and ignited. The flames grew quickly in intensity and then rapidly extinguished as the epoxy in this thin sample burned away. Final chars were black with carbon/soot noted along with blackened Cu metal strips. There does appear to be some slight difference in HRR behavior for the single and 2 Cu metal strip laminates in that the single Cu strip sample has two peaks of HRR while the double Cu strip sample has only 1 peak of HRR. As described above, blue flames were seen where the sample was burning next to the Cu metal strips.

No Flame Retardant Epoxy Laminate Fire Behavior

The fire behavior of laminates with no flame retardant (control) in the cone calorimeter was very different than that observed for the brominated flame retardant samples. First of all,

none of the laminates (either 6 ply or single ply) foamed up upon exposure to the cone heater. Instead, the laminates had a strong tendency to warp and bend up towards the cone heater with snapping and popping heard right before ignition. This behavior was so pronounced for the 6-ply laminates that the cone calorimeter shutters could not be closed when the sample extinguished as the laminate plies had curled up into the space where the shutters would normally close.

Fire behavior of the 6-ply laminates with the non-flame retardant epoxy began with smoke being released shortly after exposure to the heat source (about 12 seconds after start of test) followed shortly thereafter by ignition of the sample. Some blue flames (of lesser blue color intensity than that seen with the brominated FR epoxy laminates) were observed, but for the most part the color of the flames were orange-yellow with some smoke/soot observed at all times. As with the brominated 6-ply stacks, the 6-ply stacks of non-FR epoxy showed irreproducible fire behavior as the top ply would ignite, settle down in heat release/flame intensity, and then the second ply underneath would ignite. Sometimes the top ply would provide sufficient insulation to delay ignition of the underlying plies (see HRR-2 and HRR-3 in Figure 8 right) and in other cases the top ply would deform so much that most of the underlying 2^{nd} ply would be exposed to the cone heater. With all these physical effects of burning, the HRR data for this sample showed a lot more scatter different HRR curve shape, as can be seen in Figure 9 (right). The HRR peak occurred when the bottom 4 plies would finally all ignite at once, leading to a slow rise in heat release followed by a slow steady decrease in HRR whereupon the sample finally extinguished. The final chars from these 6-ply laminates showed very little carbon char; just some soot and the blackened/oxidized copper metal strips.

For the single ply no FR epoxy laminates (Figure 9, right), the samples smoked, began to pop and deform (as seen with the 6 ply laminates) and then rapidly ignited and burned out. No blue flames were observed for these samples when they were burning. As with the 6 ply laminates, the shutters could not be closed at the end of the test due to laminate deformation. The final chars were the same as those observed with the 6-ply laminate stacks, with only fiberglass and blackened metal remaining. Unlike with the single ply brominated FR epoxy laminate HRR data, there is a lot more difference in HRR behavior of 1 Cu metal strip and 2 Cu metal strip HRR data for the non-halogenated FR epoxy laminates (Figure 9 right), but the reason for this major difference is not clear since the observed fire behavior was very similar for both samples. A likely explanation though is that the amount of Cu metal on the surface affected the amount of surface available for burning and pyrolysis.

Non-Halogenated Flame Retardant Epoxy Laminate Fire Behavior

Fire behavior for the non-halogenated flame retardant epoxy laminates (assumed to be phosphorus-based flame retardant) was different than the other two types of epoxy laminates. Phosphorus-based flame retardants in epoxies tend to be condensed phase char formation systems, so that when they burn they convert the carbon-based epoxy "fuel" into graphitic-type protective chars which slow down the rate of mass loss and heat release. Indeed, this type of behavior was observed for the 6-ply laminate stacks, as the samples did ignite rapidly after exposure to the cone heater, but they then extinguished and did not re-ignite for another 150 seconds after the 1st initial ignition (see Figure 10 left). When these laminate stacks were exposed to the cone heater, they smoked and made crackling/popping sounds (caused by

delamination) within 10 seconds of exposure to the cone heater. Shortly after that, they ignited, but then the flames died down quickly and the flame went out. The spark igniter was reinserted and eventually the sample reignited. The sample deformed and curled up towards the cone heater towards the end of the test such that the shutters could not be closed at the end of the test. During the burning of the sample, no blue flames were observed, only yellow/orange flames with smoke were seen. At the edges of the sample and towards the end of the test some white colors could be seen at the bottom of the flame, which confirms the presence of phosphorus-based flame retardants. The final chars were black, but the fiberglass could be seen through this black char, which was more than just soot. The copper metal strips were completely blackened. As with the other 6-ply laminate stack data, due to the physical effects during burning, the HRR curve shapes were not very reproducible, but the times to ignition and flameout were reproducible within the cone calorimeter test % error of about 10%.

For the single ply laminates, the effect of the copper strips was more pronounced than that seen with the other samples. The sample with only one copper strip rapidly burned off while the sample with two copper strips did not burn as intensely and took a little longer to burn. Otherwise the fire behavior of this sample was very similar to that of the 6 ply laminate stacks, with the sample smoking and cracking right before ignition, and the laminate curling up towards the cone heater by the end of the test [1].

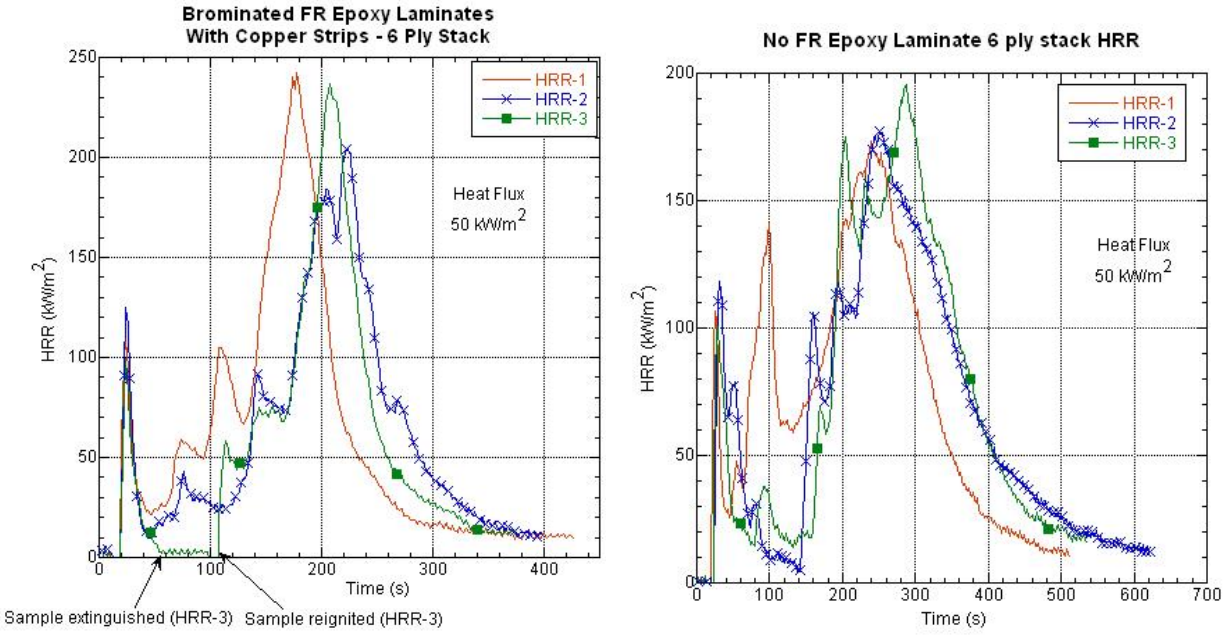


Figure 8. HRR for 6 ply Br Flame Retardant Epoxy Laminate Stacks (left) and No Flame Retardant Epoxy Laminate Stacks (right).

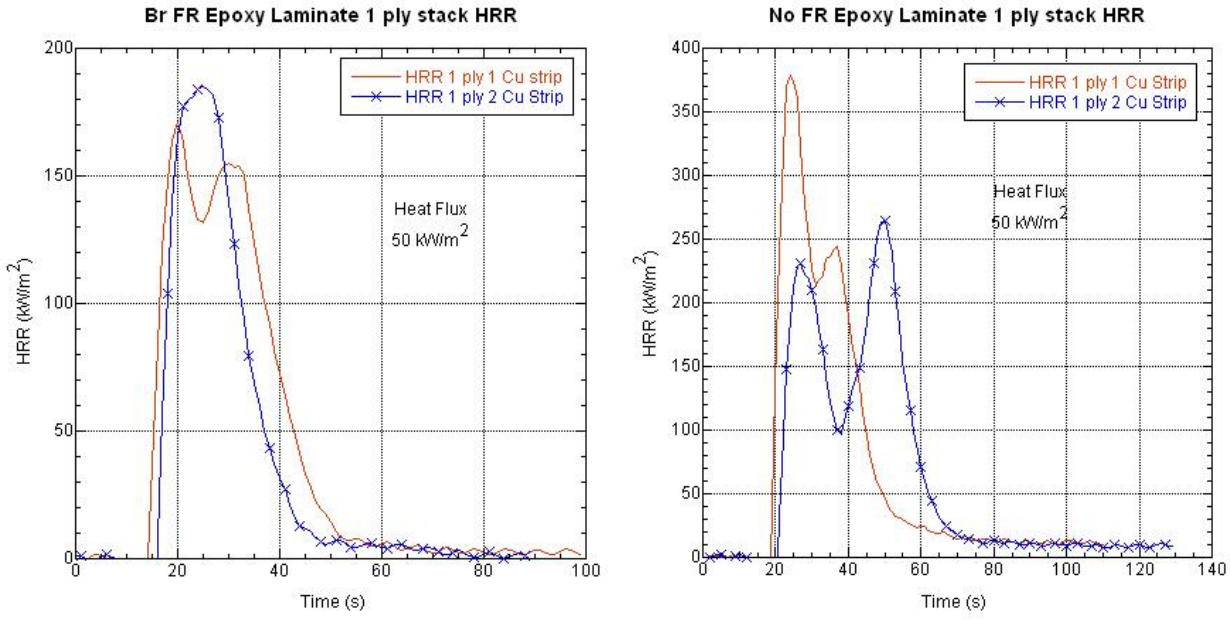


Figure 9. HRR for 1 ply Br Flame Retardant Epoxy Laminates (left) and 1 ply No Flame Retardant Epoxy Laminates (right).

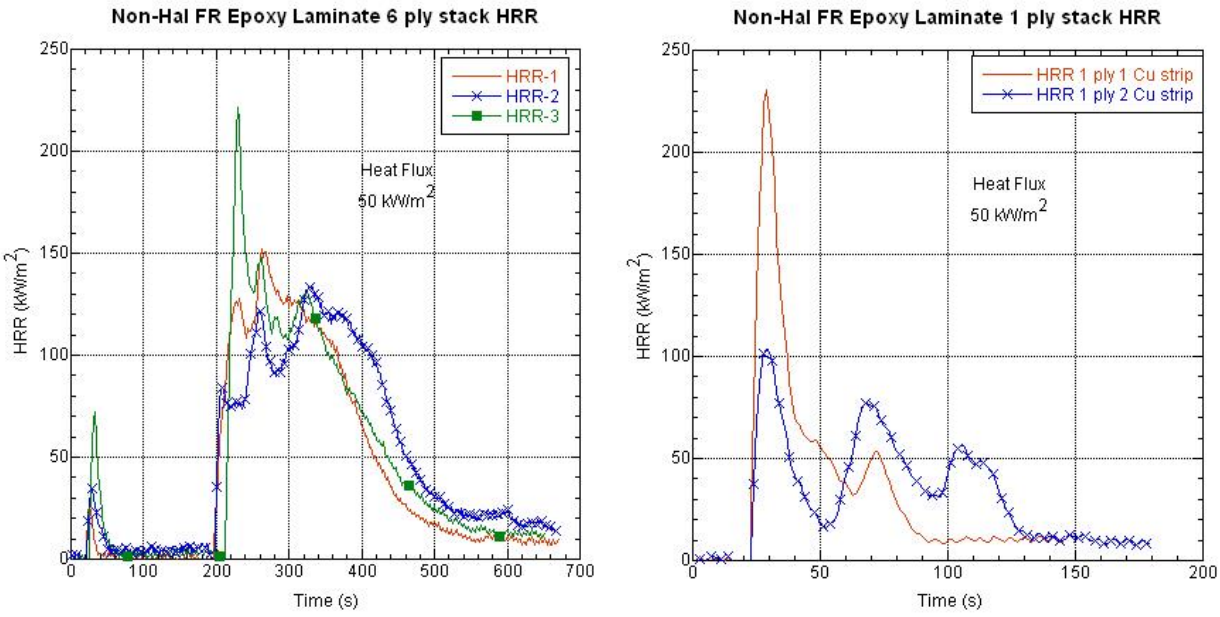


Figure 10. HRR for 6 ply Phosphorous based Flame Retardant Epoxy Laminate Stacks (left) and HRR for 1 ply Phosphorous based Flame Retardant Epoxy Laminates (right).

Conclusion

Laminates' Fire Behavior and Heat Release Data

There are four major conclusions that can be made about these samples from the observed physical fire behavior and from the recorded heat release/smoke release measurements:

1) The 6 ply laminate samples showed erratic HRR behavior due to the physical effects of laminates igniting and curling/foaming/charring at different rates from stack to stack, even with the same material. This type of behavior would be normal for a non-coherent stack of

laminates which would have nothing adhering them together and instead would have air gaps between each ply to allow for additional heat release and secondary fire events to occur.

2) 6-ply laminates showed lower peak HRR compared to single ply laminates. The likely reason for this is that the underlying laminates pull some heat away from the top laminate which makes the 6 ply stack act a little bit more like a thermally thick sample than a thermally thin sample like the single ply laminates. However, it is well known that for the cone calorimeter that sample thickness affects heat release results, and therefore it is not surprising that the peak HRR is higher for the single ply laminates when compared to the 6-ply laminate stacks.

3) The amount of Cu metal on the surface appears to have a slight effect on time to ignition. The more Cu metal present, the more likely that time to ignition will be delayed by a few seconds. This makes sense as the Cu metal can reflect some heat energy back, and, can conduct some of the heat energy out and away from the epoxy laminate. However, the 2-3 second delay in time to ignition, while seen in all of the samples, isn't significant in regards to overall fire behavior of these materials. Once the single ply laminates ignite, they rapidly go to peak HRR and then extinguish as the fuel is rapidly burned off.

4) Since peak HRR and moment specific data is difficult to compare between samples due to physical effects of burning, it is better to look at total HR and total smoke when comparing between samples. By doing this the following trends appear: Brominated FR epoxy has highest smoke release and lowest total heat release. The non-FR epoxy control has the highest heat release and middle-level smoke release. The non-halogenated FR epoxy has the lowest smoke release (although similar to the non-FR epoxy) and middle level total heat release.

Since the purpose of these experiments was to generate a total amount of material to burn for emissions testing, the total smoke and total heat release data indicate that the experiments were in general a success and that all experiments done did yield a controlled amount of burning material. So while individual specimens tested may not correlate exactly in regards to specific moments of heat release, the total amount of fuel burned/smoke released from specimen to specimen did correlate well, indicating that the cone calorimeter did provide controlled burning specimens over a total amount of sampling time. This is important for the emissions testing since the sampling is done over the total amount of sample burned rather than a specific moment in time of burning [1].

PCDD/Fs and PBDD/Fs emission data

No significant concentrations of PCDD/Fs were found after sampling and analysis of emissions from the combustion of BrFR laminates containing brominated flame retardant, PFR laminates containing non-halogen flame retardant (Phosphorous- based), and NFR laminates containing no-flame retardant. Most targets pollutants were found to be below the limit of detection of the analysis. The targets that were detected appeared to be a carry over from a standard. The results obtained from the analysis of emissions for PBDD/Fs concentrations in the extracts confirmed the presence of pollutants for the combustion of BrFR laminates containing brominated flame retardant. The laminates contained copper strips which could have promoted the formation of dioxins in the emissions. No published data on PBDD/Fs concentrations in ng per kg of combustible material burned was found to compare the results of this study. For the PFR laminates and NFR laminates, no PBDD/F congener was detected.

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APPENDIX I: SAMPLING DATA

Table 1.

Note: All masses are in grams	BFR	NFR	PFR	BFR (repeat)
Mass of cap+container	209.44	209.87	207.68	209.53
Mass of cap+container+water (pre-sampling)	309.78	311.95	308.24	282.99
Mass of cap+container+water (post-sampling)	309.11	310.3	307.36	282.06
(pre-sampling water) - (post-sampling water)	0.67	1.65	0.88	0.93
Mass of cap+container	68.15	68.17	68.15	68.15
Mass of cap+container+silica gel (pre-sampling)	269.06	268.16	268.04	268.35
Mass of cap+container+silica gel (post-sampling)	271.06	270.75	270.93	270.18
Mass of water absorbed in silica gel	**2**	**2.59**	**2.89**	**1.83**
Mass of cap+container	207.9	209.02	208.61	209.05
Mass of cap+container+XAD	247.99	249.09	248.95	249.05
Mass of XAD (pre-sampling)	40.09	40.07	40.34	40
Petri dish	68.24	68.23	68.23	68.23
Petri dish+filter (pre-sampling)	68.66	68.65	68.64	68.65
Mass of filter (pre-sampling)	0.42	0.42	0.41	0.42
Mass of container+cap	209.88	209.13	207.49	208.61
Mass of container+cap+filter (post-sampling)	210.38	209.62	207.99	NA
Mass of filter (post-sampling)	0.5	0.49	0.5	NA
Mass of soot	**0.08**	**0.07**	**0.09**	**NA**

Table 2.

	BFR	NFR	PFR	BFR (repeat)
Soot formed (g)	0.08	0.07	0.09	NA
Mass burned (g)	10.1	12.4	13.9	10.5
soot formed/mass burned (g/g)	0.00792	0.00565	0.00647	NA

Table 3.

	BFR REPEAT				PFR			
	Time (h:m:s)	Inside Wall temperature (°C)	Mass (g)	Comments	Time (h:m:s)	Inside Wall temperature (°C)	Mass (g)	Comments
Run 1	0:00:00	95	61.3		0:00:00	96	63.2	
	0:01:44	104	57.4	ignition	0:03:00	95	61.9	
	0:02:44	124	52.1		0:05:00	108	60.3	
	0:03:36	134	44.6	max temp	0:06:00	128	55.3	
	0:04:30	122	43		0:07:15	130	50.5	max temp
	0:05:20	116	42.5		0:08:30	121	48	
	0:06:09	110	42.2	removed	0:09:15	115	47.6	
					0:10:15	110	47	
					0:11:45	106	46.6	
					0:13:40	105	46	removed
Run 2	0:09:34	103	59.8		0:16:35	102	63.8	
	0:09:44	107	58.4	ignition	0:17:37	101	63.1	ignition
	0:10:44	111	56.2		0:19:10	100	62.1	
	0:11:44	127	49.3		0:20:10	117	59.4	re-ignited
	0:12:36	133	43.4	max temp	0:21:10	123	57.3	
	0:13:45	121	41.8		0:22:25	130	52.5	max temp
	0:14:46	116	41.3	removed	0:23:36	128	48.9	
					0:24:36	119	47.9	
					0:25:36	113	47.3	
					0:27:03	109	46.7	
					0:28:31	107	46.4	
					0:30:56	105	45.8	removed
Run 3	0:17:17	107	61		0:33:45	102	64.2	
	0:17:46	109	59.8	ignition	0:34:57	104	63.2	ignition
	0:18:16	109	59.2	re-ignited	0:36:36	102	62	
	0:19:16	119	54.7		0:37:25	107	60.6	re-ignited
	0:20:18	131	46.8	max temp	0:39:03	130	53.1	max temp
	0:21:32	126	42.8		0:40:23	127	49.4	
	0:22:30	118	42.3	removed	0:41:45	118	48.3	
					0:42:50	112	47.9	
					0:44:35	109	47.4	
					0:46:32	107	46.8	removed
Run 4	0:26:40	108	10.4		0:49:12	104	10.6	
	0:27:01	111	9.9	ignition	0:49:42	114	8.4	
	0:27:23	114	7.8	max temp	0:50:20	114	7.7	no flame
	0:27:57	113	9.1	removed	0:52:49	109	7.2	removed
Run	0:31:07	107	11.9		0:55:30	105	12.5	

5								
	0:31:20	110	10.6		0:57:00	113	9.7	
	0:31:42	114	8.5	max temp	0:57:39	113	10.1	no flame
	0:32:00	113	8.5	removed	0:58:29	110	10	removed

NFR			
Time (h:min:sec)	Inside Wall temperature (°C)	Mass (g)	Comments
0:05:31	118	61.1	
0:07:00	127	50.5	
0:08:23	132	46.5	max temp
0:10:00	122	45.1	
0:10:55	117	44.7	
0:11:47	114	44.3	
0:12:51	112	43.8	removed
0:16:09	107	64.2	
0:18:09	113	61.7	
0:19:19	120	58.6	
0:20:32	129	54.3	
0:21:30	131	50.3	max temp
0:22:55	125	47.8	
0:23:58	120	47.1	
0:25:09	116	48.4	
0:26:18	113	47.4	no flame
0:27:44	111	46.2	removed
0:30:46	107	63.6	
0:31:46	111	62	
0:32:45	111	61.2	
0:34:06	126	58.5	
0:35:06	131	54.4	max temp
0:36:41	134	50.6	
0:37:30	128	46.1	
0:38:44	121	45.7	no flame
0:40:08	116	44.8	removed
0:43:39	109	10.8	
0:44:00	121	8	
0:44:22	124	7.1	max temp
0:44:58	120	6.9	
0:45:52	116	6.8	removed
0:49:16	111	12.1	
0:49:32	112	11	
0:50:06	123	8.5	max temp
0:51:00	117	8.6	
0:51:48	114	8.3	removed

Additional Comments

NFR: Stack conditions after experiment:
Outside Wall temperature: 167°C
Inside Wall temperature: 112°C

PFR: Stack conditions after experiment:
Outside Wall temperature: 155°C and 162°C (2 thermocouples on outside wall)
Inside Wall temperature: 74°C

BFR REPEAT : Stack conditions after experiment:
Outside Wall temperature: 158°C and 164°C (2 thermocouples on outside wall)
Inside Wall temperature: 96°C

APPENDIX 2: ANALYSIS DATA

PCDD/Fs:

Pre-extraction surrogate recovery limits:

	Surrogate Recovery limits (range in %)	
13C12-2 MCDF	25.0	130
13C12-2 MCDD	25.0	130
13C12-2,4 DCDF	25.0	130
13C12-2,7 DCDD	25.0	130
13C12-2,4,8 TrCDF	25.0	130
13C12-2,3,7,8 TeCDF	25.0	130
13C12-2,3,7,8 TeCDD	25.0	130
13C12-1,2,3,7,8 PCDF	40.0	130
13C12-1,2,3,7,8 PCDD	40.0	130
13C12-1,2,3,6,7,8 HxCDF	40.0	130
13C12-1,2,3,6,7,8 HxCDD	40.0	130
13C12-1,2,3,4,6,7,8 HpCDF	40.0	130
13C12-1,2,3,4,6,7,8 HpCDD	40.0	130
13C12-1,2,3,4,6,7,8,9 OCDD	25.0	130

Pre- sampling surrogate recovery limits:

	Pre Spike Recovery Limits (range in %)	
13C12-2,8-DCDF	70.0	130
13C12-2,3-DCDD	70.0	130
13C12-2,3,7-TrCDD	70.0	130
37Cl4-2,3,7,8-TeCDD	70.0	130
13C12-2,3,4,7,8-PCDF	70.0	130
13C12-1,2,3,4,7,8-HxCDF	70.0	130
13C12-1,2,3,4,7,8-HxCDD	70.0	130
13C12-1,2,3,4,7,8,9-HpCDF	70.0	130

BR FR Epoxy Laminate:

Sampled: 6/05/08
Extracted: 7/15/08
Acquired: 01/27/09
Sample description/Narrative: Sample Rerun; Elevated Standard Recoveries are due to a large interferent peak causing reduced signal on the TeCDD Recovery Standard.

Pre Extraction Surrogates	**% Recovery**	**Pass or Fail recovery limits**
13C12-2,3,7,8 TeCDF	135.0	F
13C12-2,3,7,8 TeCDD	125.9	P
13C12-1,2,3,7,8 PCDF	108.6	P
13C12-1,2,3,7,8 PCDD	93.4	P
13C12-1,2,3,6,7,8 HxCDF	68.7	P
13C12-1,2,3,6,7,8 HxCDD	65.3	P
13C12-1,2,3,4,6,7,8 HpCDF	59.6	P
13C12-1,2,3,4,6,7,8 HpCDD	78.6	P
13C12-1,2,3,4,6,7,8,9 OCDD	67.3	P

Pre-Sampling Surrogates	% Recovery	Pass or Fail recovery limits
37Cl4-2,3,7,8-TeCDD	91.3	P
13C12-2,3,4,7,8-PCDF	91.8	P
13C12-1,2,3,4,7,8-HxCDF	108.1	P
13C12-1,2,3,4,7,8-HxCDD	112.9	P
13C12-1,2,3,4,7,8,9-HpCDF	112.7	P

Isomer.	ng/train		2005 WHO (Mammal/Humans) Toxicity Equiv. Factor	TEQ ng/train
2,3,7,8 - TeCDD	0.029	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.095	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.113	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.103	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.113	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.196	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDD	0.231	LOD	0.0003	0.00000
2,3,7,8 - TeCDF	0.03	LOD	0.1	0.00000
1,2,3,7,8 - PCDF	0.064	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.064	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.032	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.029	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.036	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.04	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.084		0.01	0.00084
1,2,3,4,7,8,9 - HpCDF	0.064	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.131	LOD	0.0003	0.00000

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection

Total TEQ ng/train **0.0008**

NFR Epoxy Laminate:

Sampled: 6/16/08
Extracted: 7/15/08
Acquired: 12/15/08
Sample description/Narrative: All detected targets appear to be carry over from a Standard.

Pre Extraction Surrogates	**% Recovery**	**Pass or Fail recovery limits**
13C12-2,3,7,8 TeCDF	88.1	P
13C12-2,3,7,8 TeCDD	88.0	P
13C12-1,2,3,7,8 PCDF	97.4	P
13C12-1,2,3,7,8 PCDD	101.8	P
13C12-1,2,3,6,7,8 HxCDF	75.9	P
13C12-1,2,3,6,7,8 HxCDD	73.6	P
13C12-1,2,3,4,6,7,8 HpCDF	67.9	P
13C12-1,2,3,4,6,7,8 HpCDD	85.1	P
13C12-1,2,3,4,6,7,8,9 OCDD	72.4	P

Pre-Sampling Surrogates	**% Recovery**	
37Cl4-2,3,7,8-TeCDD	90.0	P
13C12-2,3,4,7,8-PCDF	100.9	P
13C12-1,2,3,4,7,8-HxCDF	104.2	P
13C12-1,2,3,4,7,8-HxCDD	111.1	P
13C12-1,2,3,4,7,8,9-HpCDF	115.5	P

Isomer.	ng/train		2005 WHO (Mammals/Humans) Toxicity Equiv. Factor	TEQ ng/train
2,3,7,8 - TeCDD	0.013	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.015	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.024	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.022	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.024	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.06		0.01	0.00060
1,2,3,4,6,7,8,9 - OCDD	0.096		0.0003	0.00003
2,3,7,8 - TeCDF	0.036		0.1	0.00360
1,2,3,7,8 - PCDF	0.014	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.014	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.018	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.016	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.02	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.022	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.028		0.01	0.00028
1,2,3,4,7,8,9 - HpCDF	0.025	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.063	LOD	0.0003	0.00000
ND = not detected	EMPC=Est. Max. Possible Concentration		**Total TEQ**	
NS= not spiked	LOD=Limit of Detection		**ng/train**	**0.0045**

PFR Epoxy Laminate:

Sampled: 06/17/08
Extracted: 07/15/08
Date Acquired: 12/15/08
Sampled description/ Narrative: All detected targets appear to be carry over from a Standard.

Pre Extraction Surrogates	% Recovery	Pass or Fail recovery limits
13C12-2,3,7,8 TeCDF	90.0	P
13C12-2,3,7,8 TeCDD	89.4	P
13C12-1,2,3,7,8 PCDF	109.9	P
13C12-1,2,3,7,8 PCDD	110.9	P
13C12-1,2,3,6,7,8 HxCDF	70.4	P
13C12-1,2,3,6,7,8 HxCDD	69.2	P
13C12-1,2,3,4,6,7,8 HpCDF	64.4	P
13C12-1,2,3,4,6,7,8 HpCDD	80.2	P
13C12-1,2,3,4,6,7,8,9 OCDD	72.5	P

Pre-Sampling Surrogates	% Recovery	Pass or Fail recovery limits
37Cl4-2,3,7,8-TeCDD	105.3	P
13C12-2,3,4,7,8-PCDF	115.5	P
13C12-1,2,3,4,7,8-HxCDF	119.9	P
13C12-1,2,3,4,7,8-HxCDD	128.5	P
13C12-1,2,3,4,7,8,9-HpCDF	135.2	F

Isomer.	ng/train		2005 WHO (Mammals/Humans) Toxicity Equiv. Factor	TEQ ng/train
2,3,7,8 - TeCDD	0.012	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.015	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.025	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.023	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.025	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.036	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDD	0.047	LOD	0.0003	0.00000
2,3,7,8 - TeCDF	0.024	EMPC	0.1	0.00240
1,2,3,7,8 - PCDF	0.013	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.013	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.014	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.013	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.016	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.018	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.015	LOD	0.01	0.00000
1,2,3,4,7,8,9 - HpCDF	0.02	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.047	LOD	0.0003	0.00000
ND = not detected	EMPC=Est. Max. Possible Concentration		**Total TEQ**	
NS= not spiked	LOD=Limit of Detection		**ng/train**	**0.0024**

BR FR Epoxy Laminate repeat run:

Sampled: 06/18/08
Extracted: 07/15/08
Acquired: 12/09/08
Sampled description/ Narrative: All detected targets appear to be carry over from a Standard.

Pre Extraction Surrogates	% Recovery	Pass or Fail recovery limits
13C12-2,3,7,8 TeCDF	109.5	P
13C12-2,3,7,8 TeCDD	114.9	P
13C12-1,2,3,7,8 PCDF	112.3	P
13C12-1,2,3,7,8 PCDD	110.2	P
13C12-1,2,3,6,7,8 HxCDF	52.2	P
13C12-1,2,3,6,7,8 HxCDD	56.6	P
13C12-1,2,3,4,6,7,8 HpCDF	47.9	P
13C12-1,2,3,4,6,7,8 HpCDD	55.4	P
13C12-1,2,3,4,6,7,8,9 OCDD	49.2	P

Pre-Sampling Surrogates	% Recovery	Pass or Fail recovery limits
37Cl4-2,3,7,8-TeCDD	96.4	P
13C12-2,3,4,7,8-PCDF	100.9	P
13C12-1,2,3,4,7,8-HxCDF	120.5	P
13C12-1,2,3,4,7,8-HxCDD	126.4	P
13C12-1,2,3,4,7,8,9-HpCDF	127.2	P

Isomer.	ng/train		2005 WHO (Mammals/Humans) Toxicity Equiv. Factor	TEQ ng/train
2,3,7,8 - TeCDD	0.036	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.036		1	0.03600
1,2,3,4,7,8 - HxCDD, co-elution	0.052		0.1	0.00520
1,2,3,6,7,8 - HxCDD	0.036		0.1	0.00360
1,2,3,7,8,9 - HxCDD	0.056		0.1	0.00560
1,2,3,4,6,7,8 - HpCDD	0.092		0.01	0.00092
1,2,3,4,6,7,8,9 - OCDD	0.172		0.0003	0.00005
2,3,7,8 - TeCDF	0.072		0.1	0.00720
1,2,3,7,8 - PCDF	0.06		0.03	0.00180
2,3,4,7,8 - PCDF	0.06		0.3	0.01800
1,2,3,4,7,8 - HxCDF	0.084		0.1	0.00840
1,2,3,6,7,8 - HxCDF	0.076		0.1	0.00760
2,3,4,6,7,8 - HxCDF	0.1		0.1	0.01000
1,2,3,7,8,9 - HxCDF	0.116		0.1	0.01160
1,2,3,4,6,7,8 - HpCDF	0.14		0.01	0.00140
1,2,3,4,7,8,9 - HpCDF	0.132		0.01	0.00132
1,2,3,4,6,7,8,9 - OCDF	0.22		0.0003	0.00007
ND = not detected	EMPC=Est. Max. Possible Concentration		**Total TEQ**	
NS= not spiked	LOD=Limit of Detection		**ng/train**	**0.1188**

Blank run:

Sampled: 05/29/08
Extracted: 07/15/08
Acquired: 01/27/09
Sample Description/ Narrative: sample rerun.

Pre Extraction Surrogates	% Recovery	Pass or Fail recovery limits
13C12-2,3,7,8 TeCDF	90.6	P
13C12-2,3,7,8 TeCDD	86.3	P
13C12-1,2,3,7,8 PCDF	78.5	P
13C12-1,2,3,7,8 PCDD	79.8	P
13C12-1,2,3,6,7,8 HxCDF	73.6	P
13C12-1,2,3,6,7,8 HxCDD	72.2	P
13C12-1,2,3,4,6,7,8 HpCDF	66.1	P
13C12-1,2,3,4,6,7,8 HpCDD	86.0	P
13C12-1,2,3,4,6,7,8,9 OCDD	77.1	P

Pre-Sampling Surrogates	% Recovery	Pass or Fail recovery limits
37Cl4-2,3,7,8-TeCDD	100.9	P
13C12-2,3,4,7,8-PCDF	112.8	P
13C12-1,2,3,4,7,8-HxCDF	118.4	P
13C12-1,2,3,4,7,8-HxCDD	122.2	P
13C12-1,2,3,4,7,8,9-HpCDF	109.2	P

Isomer.	ng/train		2005 WHO (Mammals/Humans) Toxicity Equiv. Factor	TEQ ng/train
2,3,7,8 - TeCDD	0.026	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.043	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.061	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.056	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.061	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.129	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDD	0.152	LOD	0.0003	0.00000
2,3,7,8 - TeCDF	0.029	LOD	0.1	0.00000
1,2,3,7,8 - PCDF	0.033	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.033	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.033	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.03	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.036	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.041	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.036	LOD	0.01	0.00000
1,2,3,4,7,8,9 - HpCDF	0.048	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.113	LOD	0.0003	0.00000
ND = not detected	EMPC=Est. Max. Possible Concentration		**Total TEQ**	
NS= not spiked	LOD=Limit of Detection		**ng/train**	**ND**

PBDD/Fs:

BR FR Epoxy Laminate:

Sampled: 6/05/08
Extracted: 7/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	% Recovery
13C 237 TrBDD (IS)	87.0
13C 2378 TeBDD (IS)	56.4
13C 123678 HxBDD (IS)	115.1
13C 123789 HxBDD (IS)	96.3
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	123.7
13C 12378 PeBDD (DSSP)	127.9

Isomer	ng/train
237 TrBDD*	0.08
237 TrBDF*	ND
2378 TeBDD	0.37
2468 TeBDF	0.56
2378 TeBDF	2.80
12378 PeBDD	ND
12378 PeBDF	1.06
23478 PeBDF	0.54
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	0.35
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	4.76
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

NFR Epoxy Laminate:

Sampled: 6/16/08
Extracted: 7/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	% Recovery
13C 237 TrBDD (IS)	108.9
13C 2378 TeBDD (IS)	89.7
13C 123678 HxBDD (IS)	132.8
13C 123789 HxBDD (IS)	102.4
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	103.7
13C 12378 PeBDD (DSSP)	113

Isomer	ng/train
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	ND
2468 TeBDF	ND
2378 TeBDF	ND
12378 PeBDD	ND
12378 PeBDF	ND
23478 PeBDF	ND
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	ND
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	ND
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

PFR Epoxy Laminate:

Sampled: 06/17/08
Extracted: 07/15/08
Date Acquired: 12/15/08

Pre Extraction Surrogates	% Recovery
13C 237 TrBDD (IS)	79.6
13C 2378 TeBDD (IS)	61.1
13C 123678 HxBDD (IS)	122.6
13C 123789 HxBDD (IS)	116.1
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	117.6
13C 12378 PeBDD (DSSP)	139.1

Isomer	ng/train
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	ND
2468 TeBDF	ND
2378 TeBDF	ND
12378 PeBDD	ND
12378 PeBDF	ND
23478 PeBDF	ND
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	ND
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	ND
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*
congeners; quantified based on concentration of the congeners of the same bromination level present in the standard
*** assignment based on the elution order of HpCDD congeners on the DB5 column*
ND = not detected
NS= not spiked
EMPC=Est. Max. Possible Concentration
LOD=Limit of Detection (S/N=3)
NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

BR FR Epoxy Laminate repeat run:

Sampled: 06/18/08
Extracted: 07/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	% Recovery
13C 237 TrBDD (IS)	77.2
13C 2378 TeBDD (IS)	57.1
13C 123678 HxBDD (IS)	112.5
13C 123789 HxBDD (IS)	120.9
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	110.5
13C 12378 PeBDD (DSSP)	139.6

Isomer	ng/train
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	0.24
2468 TeBDF	0.47
2378 TeBDF	1.45
12378 PeBDD	ND
12378 PeBDF	0.81
23478 PeBDF	0.30
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	0.26
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	5.64
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

Blank run:

Sampled: 07/15/08
Extracted: 07/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	% Recovery
13C 237 TrBDD (IS)	117.3
13C 2378 TeBDD (IS)	93.5
13C 123678 HxBDD (IS)	118.1
13C 123789 HxBDD (IS)	106.0
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	105.3
13C 12378 PeBDD (DSSP)	112.1

Isomer	ng/train
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	ND
2468 TeBDF	ND
2378 TeBDF	ND
12378 PeBDD	ND
12378 PeBDF	ND
23478 PeBDF	ND
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	ND
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	ND
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*
congeners; quantified based on concentration of the congeners of the same bromination level present in the standard
*** assignment based on the elution order of HpCDD congeners on the DB5 column*
ND = not detected
NS= not spiked
EMPC=Est. Max. Possible Concentration
LOD=Limit of Detection (S/N=3)
NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX C

U.S. EPA. Analysis of Circuit Board Samples by XRF. Original Report - July 28, 2008. Revised Report - March 23, 2009. Prepared by Arcadis.

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Analysis of Circuit Board Samples by XRF

Report

Original Report - July 28, 2008
Revised Report - March 23, 2009

DISCLAIMER: The USEPA Design for the Environment Program has provided additional information in Appendix B and Appendix C to further explain methods and results. This information is critical for interpreting the main report, especially in regards to chorine measurements. Results found in the main report are not complete without the information in the appendices, and cannot be correctly understood or interpreted without their aid.

ARCADIS

Analysis of Circuit Board Samples by XRF

Report

Prepared for:
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Tables

Figures

Appendices

1. Statement of Work

The following report is in response to a task under Work Assignment (WA) No. 3-37, that consisted of an elemental analysis of two sets of circuit boards samples by X-ray Fluorescence (XRF) Spectrometry. This report describes the results of those analyses and provides discussions of several questions that have arisen from these analyses.

2. Introduction

Under two separate events, described as “Phase 1” and “Phase 2,” circuit board samples were received for analyses. Table 1 presents this information.

Table 1: Samples Received

Laminate #	**Phase**	Laminate type
1	1	NFR
2	1	BFR
3	1	PFR
4	2	HF
5	2	HF
6	2	HF
7	2	HF

NFR : Non-flame Retardant ; BFR: Bromine Flame Retardant ; PFR: Phosphorous Flame Retardant ; HF: Halogen-free

Each board was received “mostly” free of copper plating. Phase 2 samples were accompanied by a letter that indicated 12” by 12” samples of “halogen-free laminates.” Inspection of each showed a rectangular area of plated copper in one corner of each sample that was used to identify each sample. Further inspection showed that some samples had additional small, random areas of elemental copper. This was also true of the phase 1 samples.

3. Experimental

3.1 Sample preparation

3.1.1 Phase 1

As directed, phase 1 samples were cored in the shop at random locations. These circuit board disks were sized to be a slip fit to our standard sample cups. Separate disks were cut for each individual analysis.

3.1.2 Phase 2

As agreed prior to sample receipt, samples were homogenized, powdered, pelletized, and analyzed by XRF. One sample was prepared and analyzed in duplicate. One spiked sample was prepared and analyzed.

3.1.2.1 Sub-sampling

To minimize the errors of heterogeneity, each board was sub-sampled from several locations. One board was weighed at ~ 79 g. per square foot. To ensure that any one sample was of sufficient size to provide sufficient material for sample, replicate, and spike, it was decided to sample 21-1” diameter locations in a representative manner. Boards were delivered to the shop, which laid out a 9 by 7 grid. With directions to avoid potential elemental copper, all edge areas were not sampled. 21 of the remaining 35 positions were sampled by coring.

3.1.2.2 Milling

The 21 disks from each sample were homogenized by milling. A Spex Certiprep model 6850 Freezer/Mill was used for this step. This instrument is basically a hammer mill operating at liquid nitrogen temperatures. All 21 disks were added to a sample tube along with the stainless steel, SS, hammer. This instrument has the capacity to handle a single sample of this size. Table 2 provides the operating parameters for the first milling operation.

Table 2: Milling parameters

Operation	Value
Pre-cool time	15 min.
# of cycles	4
Milling time	3 min.
Re-cool time	10 min.

After samples had warmed back to room temperature, they were opened and examined. The milling was considered generally acceptable, with a large fraction of the sample present as powder. A fraction of each sample, however, was present as large flakes. Figure 1 shows one sample after size classification.

Figure 1 . Sieved Circuit Board

It was unclear whether this coarse flake fraction (left) represented a surface treatment coating or was merely incomplete milling of a homogeneous sample. After discussions it was decided to sieve, re-mill the coarse fraction, and combine. A W.S. Tyler Number 18 sieve, Tyler Equivalent 16 mesh, was used for the fractionation. The fine fraction was transferred to a pre-cleaned 40 mL sample vial while the coarse fraction was returned to the cryo-mill for further milling. Table 3 provides the operating parameters for this second milling operation.

Table 3. Coarse fraction Milling Parameters

Operation	Value
Pre-cool time	10 min.
# of cycles	4
Milling time	2 min.
Re-cool time	5 min.

Less stringent conditions were used since the coarse fraction represented a smaller sample. Coarse fractions were found to range between ~ 1 g and 3 g. This second milling operation was successful and the sample fractions were combined.

3.1.2.3 Homogenization and sub-sampling

Sample homogenization began with the coring of multiple discs spanning the area of each sample. It continued with the cryo-milling operation described in the previous section. It was finalized just prior to sample weighing by sample riffling. A Humboldt Mfg. Co. Model H-3971C archeological grade riffler was used for this purpose. This model was designed for samples in the several gram range. A riffler has the purpose of sub-sampling a larger powdered sample in a statistically equivalent manner that is particle-size and density independent. It achieves this by fractionating the total sample through multiple, equivalently sized paths leading to two or more sample buckets. No assumptions, however, can be made that the sub-samples will remain equivalent if time is allowed to pass. Riffling must be done immediately prior to sample use.

This riffler is manufactured of SS (stainless steel). It consists of a hopper, a gate, multiple equivalent alternating vertically angled slots, and two buckets. It may be used for both homogenization and sub-sampling and was used for both purposes in this project. The entire sample was passed through the riffler twice. After the second pass, sample material in one bucket was returned to the sample vial. The sub-sample in the second bucket represented ~ 4 g at this point. This fraction was passed through the riffler one more time. Each bucket contained about 2 g, which was the correct size for preparing a single XRF pellet.

3.1.2.4 Pellet Preparation

Pellets were prepared by pressing a mixture of powdered sample with a polymeric binder. 2 grams of sample were weighed and transferred to a boron carbide mortar and

pestle. The sample was ground for a period, though little grinding took place at this stage for these samples. 2 mL of Spex Liquid Binder, equivalent to 200 mg of binder in a dichloromethane carrier, were added using a Gilson Microman positive displacement pipettor. Sample was mixed until the sample returned to a free-flowing state. Sample was transferred to 32 mm dies with vacuum port. Pellet was pressed under vacuum in a Spex 3630 X-press programmable hydraulic press. Table 4 presents the pelletizing parameters.

Table 4. Pellet Press Parameters

Operation	Value
Applied pressure	20 tons
Hold time	1.1 min.
Release time	1.0 min.

Formed pellets were transferred to Millipore 47 mm Petrislides for identification and stored in a silica gel controlled desiccator until ready for analysis.

As agreed, one sample was prepared in duplicate. As agreed, one sample was spiked with known masses during the pellet preparation stage. After discussions with the work assignment manager and the industry committee, spiking materials and elements were selected as described in the next section. Based upon data from the first set of circuit boards; spikes were prepared for aluminum, calcium, and copper.

3.1.2.5 Preparation of Spiked Sample

As directed, one sample was prepared by spiking with known masses of certain analytes to provide data on recovery. Sample 7 was chosen since that sample represents the most complete data set. In other words, sample 7 was prepared in duplicate and analyzed in replicate. This sample had the most data available for comparison to the spiked sample.

Based upon data from the Phase 1 circuit boards; spikes were prepared for aluminum, calcium, and copper using reagent grades of Al_2O_3, $CaCO_3$, and $CuSO_4$, respectively. This gave us data on a fourth element; S. Table 5 provides data on the preparation of the spiked sample.

Table 5. Composition of Spiked Sample 7

Material	Mass, g
Sample 7	1.761
Al_2O_3	0.0383
$CaCO_3$	0.1504
$CuSO_4$	0.0505
Total	2.0002

The four materials listed in Table 5 were weighed in the amounts described in Table 5 and mixed manually using mortar and pestle. A pellet was prepared from this mix as described in the previous section.

3.2 Analysis

Pressed sample pellets were analyzed on a Panalytical model PW2404 wavelength dispersive X-Ray Fluorescence Spectrometer equipped with the PW2540 sample changer. The instrument is equipped with both flow and scintillation detectors plus five crystals. The instrument is controlled and acquires data using the manufacturer's software, ***SuperQ***. The entire spectrum is acquired as 10 sub-scans using variations in applied power, crystal, detector, filter material, and goniometer setting.

Data were acquired using the application, ***IQ+Metalloids***. ***IQ+Metalloids*** is a variation of the manufacturer supplied application, ***ZIQ+***. ***IQ+Metalloids*** adds 4 channels to provide increased sensitivity for the elements: arsenic, selenium, mercury, and lead. The increased sensitivity comes from increased counting times while the goniometer sits at the peak maxima. ***ZIQ+*** is a full scan application, which optimizes sample throughput.

3.3 Quantification

Data acquired as above are quantified using the manufacturer supplied software, ***IQ+***. ***IQ+*** is a matrix independent, fundamental parameters based quantification program.

4. Data

4.1 Phase 1

Table 6 presents the data for the three Phase 1 samples. Each was analyzed in duplicate; where each analysis also represents a replicate sample preparation (cores from different locations on the board). To be explicit, due to sample decomposition within the instrument, each sample core was analyzed once. During analysis, the whole-board cores charred. Replicate analysis on charred samples seemed neither good chemistry nor good for the instrument.

Table 6. Results for Phase 1 Samples

Sample	1-NFR		2-BFR		3-PFR	
Element	Mean, %	% RSD	Mean, %	% RSD	Mean, %	% RSD
Na	0.109	1.76	0.01		0.114	67.47
Mg	0.008	5.38			0.0070	
Al	0.083	31.94	1.042		0.773	5.50
Si	0.398	37.02	0.145	2.34	0.201	8.84
P	0.0016	16.26	0.0017	23.03	4.19	1.75
S	0.010	14.89	0.0081	60.67	0.013	8.03
Cl	0.878	9.91	0.591	42.27	0.517	11.30
K	0.0078	27.70	0.0043		0.0070	49.55
Ca	2.62	10.04	1.29	33.60	2.49	4.67
Ti	0.061	9.09	0.038	25.42	0.060	4.20
Cr	0.0039				0.0044	
Fe	0.036	9.69	0.033	28.74	0.038	2.30
Cu	0.054	1.03	1.81	137.65	3.59	13.93
As	0.0008	17.32	0.056	27.16	0.0011	
Br			6.13	22.53	0.0047	12.49
Sr	0.064	4.72	0.064	28.89	0.083	1.08
Pb	0.0007	30.44			0.0007	
Zr			0.0088			

NFR : Non-flame Retardant ; BFR: Bromine Flame Retardant ; PFR: Phosphorous Flame Retardant ; HF: Halogen-free

Results above are the average of duplicate samples; reproducibility is also presented as % relative standard deviation, % RSD. In Table 6, an empty cell under a Mean column heading indicates that this element was not detected in either replicate of this sample. An empty cell under % RSD indicates that the element was only observed in one of the replicates of that sample.

In examining Table 6, the most striking feature is the very large % RSDs found for several results. This is true for all three samples. This is attributed to circuit board heterogeneity.

4.2 Phase 2

Table 7 presents the data acquired under this task. Colored cells represent not detected elements for the respective samples.

The first pellet (sample 7) was analyzed three times within a 1 hour period to provide data on short term reproducibility. These data are provided in Table 8.

As directed, one sample was selected for replicate sample preparation and analyses. These data may be found in Table 9. Here, both “Replicate 1” and “Replicate 2” represent the mean determinations of triplicate data collections on a single pellet.

The results for sample 7 spiked as described in Table 5 are provided in Table 10. For comparison the results from replicate preparations of sample 7 are repeated from Table 9.

Table 7. Elemental Concentrations, weight %

Element	4	5	6	7
F				0.054
Na	0.135	0.143	0.121	0.151
Mg	0.663	0.085	0.410	0.375
Al	2.76	5.65	6.35	5.30
Si	15.65	9.23	7.77	10.07
P	1.42	0.84	0.74	0.68
S	0.0104	0.0050	0.0049	0.0098
Cl	0.449	0.427	0.488	1.044
K	0.0161	0.0126	0.0087	0.0123

Element	4	5	6	7
Ca	5.39	4.58	4.47	5.64
Ti	0.107	0.096	0.093	0.117
Cr	0.0184	0.0045	0.0058	0.0065
Fe	0.135	0.067	0.064	0.088
Ni	0.0044			
Cu	0.051	0.041	0.047	0.056
Zn	0.0050	0.0031	0.0044	0.0043
Br		0.0012		0.0012
As			0.00071	0.00116
Sr	0.0616	0.0627	0.0581	0.0722
Zr	0.0038			
Ba			0.0168	
Pb	0.00084			0.00087

Table 8. Sample 7, Short Term Reproducibility, weight %

Element	Rep 1	Rep 2	Rep 3	Mean	% RSD
F			0.05028	0.05028	
Na	0.148	0.1447	0.1473	0.146667	1.19
Mg	0.3678	0.3776	0.3834	0.376267	2.10
Al	5.305	5.253	5.325	5.294333	0.70
Si	9.97	9.972	10.04	9.994	0.40
P	0.6837	0.6793	0.6879	0.683633	0.63
S	0.0122	0.008915	0.00974	0.010285	16.62
Cl	0.9215	0.8356	0.813	0.8567	6.68
K	0.01335	0.01237	0.01404	0.013253	6.33
Ca	5.659	5.674	5.614	5.649	0.55
Ti	0.1199	0.1182	0.114	0.117367	2.59
Cr	0.006383	0.007127	0.006177	0.006562	7.62
Fe	0.09025	0.09096	0.09163	0.090947	0.76
Ni					
Cu	0.059	0.05484	0.05479	0.05621	4.30
Zn	0.00449	0.003899	0.00459	0.004326	8.63
Br	0.001292	0.001128	0.001084	0.001168	9.39
As					
Sr	0.072	0.07354	0.07197	0.072503	1.24
Zr					
Ba					
Pb	0.000619	0.000709	0.001066	0.000798	29.65

Table 9. Sample Preparation Reproducibility, Sample 7

Element	Replicate 1	Replicate 2	Mean	% RSD
F	0.0503	0.0570	0.0537	8.91
Na	0.1467	0.1558	0.1513	4.29
Mg	0.3763	0.3731	0.3747	0.60
Al	5.294	5.302	5.298	0.10
Si	9.994	10.143	10.069	1.05
P	0.6836	0.6713	0.6774	1.29
S	0.01029	0.00934	0.00981	6.84
Cl	0.86	1.23	1.04	25.36
K	0.0133	0.0113	0.0123	11.40
Ca	5.649	5.625	5.637	0.30
Ti	0.11737	0.11597	0.11667	0.85
Cr	0.00656	0.00653	0.00655	0.32
Fe	0.09095	0.08504	0.08799	4.75
Ni				
Cu	0.05621	0.05573	0.05597	0.61
Zn	0.00433	0.00428	0.00430	0.74
Br	0.0012	0.0012	0.0012	0.00
As		0.0012	0.0012	
Sr	0.07250	0.07199	0.07225	0.50
Zr				
Ba				
Pb	0.00080	0.00095	0.00087	12.38

Table 10. Recovery of Spikes, Sample 7, weight %

Element	Sample 7 Mean (Table 9)	Sample 7 Spike	Mean % Recovery	Recovery % RSD
Al	5.298	5.193333	91	0.5
Ca	5.637	8.201	103	0.9
Cu	0.05597	1.019333	97	1.3
S	0.00981	0.614233	119	2
F	0.0537			
Na	0.1513	0.147767	111	4
Mg	0.3747	0.293467	89	0.4
Si	10.069	8.333	94	0.5
P	0.6774	0.5176	87	0.5
Cl	1.04	0.846133	92	8
K	0.0123	0.010305	95	2
Ti	0.11667	0.100767	98	2
Cr	0.00655	0.006422	111	15
Fe	0.08799	0.072413	93	2
Ni				
Zn	0.00430	0.004176	110	5
Br	0.0012	0.001184	115	0
As	0.0012	0.00118	115	23
Sr	0.07225	0.066293	104	1.2
Zr				
Ba				
Pb	0.00087	0.000601	78	15

The spiking of a non-blank material provides results that are slightly difficult to interpret. The spiked material acts as a diluent for all elemental results that are not added as part of the spiking process. Iron and magnesium in Table 10 are an example of this.

The proper calculation is described by equations 1 and 2.

$$\%Theoretical\,\mathrm{Recovery}_i = 100 * \frac{\frac{\%analyte_i * Sample7}{100} + \sum GRAV_{ij} * Spike_j}{Sample7 + \sum Spike_j} \qquad \text{Equation 1}$$

$$\%Spike\,\mathrm{Recovery} = 100 * \frac{\%SpikedSample_i}{\%Theoretical\,\mathrm{Recovery}_i} \qquad \text{Equation 2}$$

Where sample 7 and $Spike_j$ refer to the values found in Table 5, %analyte values are found in the first column of Table 9. $GRAV_{ij}$ refers to the gravimetric factor for analyte i in spike material j.

To be more explicit, one example of $Spike_j$ from Table 5 would be Al_2O_3. The only $analyte_i$ in alumina would be aluminum. Therefore, $GRAV_{ij}$ in this case would be the gravimetric factor for aluminum in alumina. The gravimetric factor is a well established concept in quantitative chemistry and is defined as the molecular weight of the analyte, Al, divided by the molecular weight of the form it is in, alumina.

$$\frac{2 * MW\_of\_Al}{(2 * MW\_of\_Al + 3 * MW\_of\_O)} = 0.529527$$

Table 10 presents these spike recovery data. Spike recovery data are presented in the final two columns to represent the mean spike recovery and the % variance (based upon 1 σ of triplicate analyses performed on the spiked sample pellet) about that mean. Fluorine was not observed in the spiked sample despite having been reported in Tables 7, 8, and 9. As Table 8 demonstrates, fluorine is not dependably quantified at this level. The values in blue represent those analytes for which spikes were introduced into the sample. Black values are strictly based upon the dilution effect mentioned above.

5. Conclusions

Several conclusions may be observed from the data presented here.

- The Phase 1 sample preparation of cored boards did not provide quality data. This likely had to do with two aspects. First, these boards are heterogeneous. This can be seen in the data variability associated with "replicate" samples cored from different locations on the boards. The second is that the cored boards charred during analysis. Due to this, we were unwilling to perform replicate analyses on any of these Phase 1 samples.

- The Phase 2 efforts to achieve homogeneous samples were successful. Sampling of several aliquots across the circuit boards followed by milling and riffling has achieved reproducible results. This is observed, in particular, in Table 7 where replicate samples were prepared.

- From this it may be inferred that the circuit boards are heterogeneous. The analysis of cored single disks, while the cheaper approach, does not provide dependable data. This was seen in the phase 1 analyses.

- Pellets prepared from these powdered samples are robust and may be used for multiple analyses without significant deterioration.

- The cryo-mill is an appropriate approach to powdering this type of sample. Other mills, hammer and ball mills may also work.

- It is unclear whether the flaked material found after the first milling represents the effect of surface coating or not. It is also possible that it is the result of samples larger than desirable for that size sample container on the cryo-mill

- The pellets prepared by the methods described in this memo were of good quality. However, separation by sieving could have been carried out more extensively and would have ultimately resulted in pellets that were stronger and more homogeneous than those achieved during this work.

- Table 8 describes the short term reproducibility achieved for multiple analyses of a single pellet. The standard deviations described in this table provide one approach to detection limits by this method.

- Table 10 described the recovery of spiked materials. Four elements were deliberately spiked during these experiments. Recovery for these spikes is very good. Copper and calcium, in particular, are excellent at 97 and 103 % recovery. Aluminum and sulfur at 91 and 121 % are also very good recovery. The low recoveries for lead are not considered significant since this element was not spiked and because this element is very close to detection limits. This is seen in Table 8 where %RSD for lead is 30% and the individual analyses are only 6-10ppm.

- The results for chlorine are somewhat unclear. Data for this element shows somewhat more variance than is seen for most other elements. It must be considered possible that some or all of the chlorine represents contamination from the Liquid Binder carrier material, dichloromethane. Two steps, mixing the sample plus binder till it returns to a free flowing state, and operation of the pellet dies under vacuum, were specifically included as quality assurance steps to minimize dichloromethane retention. No proof is available either way. This could be investigated in future work by preparing pellets with both liquid binder and binder pellets. The latter are solvent free.
  However, the Phase 1 chlorine results are also high and variable. No dichloromethane was used in the preparation of these Phase 1 samples.

- When certified standard reference materials are not available for the sample matrix, spiked samples become the best alternative available. This approach is highly dependent upon operator experience and attention to detail. Additional replicates, spiking with other elements would be appropriate for the future.

- The submittal letter described these samples as “halogen free laminates”. This data found one or more halogen in each sample. Chlorine was found in all samples, though the source of that chlorine remains an open question. Separate from chlorine, however, fluorine was found in 1of 7 samples and bromine in 4 of 7 samples. Laboratory contamination does not appear to be a source for either of these elements.

- During the quantification process, matrix of these boards was described as an organic polymeric material. This was used as a “balance compound” during quantification. This was an assumption in the absence of better information. The data can be re-calculated should this be an invalid assumption.

- We have investigated interactions between bromine and arsenic as a result of questions from the committee. As described in a separate section, it is likely that

the majority of the arsenic response in the high bromine Phase 1 sample is due to a bromine interference. As described, two corrective approaches are available that could be investigated and implemented in future work.

Appendix A: Responses to Questions

A1. Comments from Draft Version

SS = stainless steel

Yes. The appropriate section has been edited.

Homogenization and Sub-sampling section. Does "several gram range" refer to 2 to 10 grams?

Yes, though it is not that specific. The actual capacity is restricted by the mass that can be held in the 2 buckets. That varies with the density of the material.

What is the composition of this binder? Would it have any influence of the results?

As described in that section, this binder is composed of a polymer dissolved in dichloromethane at a concentration of 100 mg of polymer per 1 mL of solution. The exact composition of the polymer is not provided by the manufacturer, of course; its elemental composition is based upon carbon, hydrogen, oxygen, and nitrogen (per the retailer's literature).

As an organic structure, the polymer does not have any specific response by XRF; though it may contribute in some small fashion to the baseline. We have found no evidence of elemental contamination from this liquid binder material and it has been used in this laboratory for many years. As described in previous communications, the solvent, dichloromethane, **could** contribute to the chlorine response…if it remained in the pellet until analysis. Our pellet preparation procedures are designed to prevent residual dichloromethane in the prepared pellets.

Are there quality controls associated with this (ZIQ+) analysis? Can you briefly mention what they are?

On a monthly basis, drift is measured and a correction factor is calculated and stored. This is based upon the analysis of a manufacturer-supplied drift standard.

On a monthly basis, control charts are maintained based upon the analyses of 4 historical standards. These control charts are used to alert personnel to instrumental problems.

For each analysis by this program identification is based upon a manufacturer's supplied library of peaks.

Additional quality control is based upon what the customer specifies. This can include replicate analyses of each pellet or other sample form, analyses of replicate pellets, homogenization procedures, analyses of standard reference materials, when available, and preparation and analysis of spiked samples. For the Phase 2 samples, all of these except standard reference materials were implemented.

Could you express variability as percent coefficient of variation?

This has been done in the pertinent tables.

Could you provide all the raw data for the replicates in an appendix? Printouts of raw data from the computer would be fine. Since the final mean value is a mean of two means, would you agree that expressing the standard deviation or standard error with the means for replicates 1 and 2 would be appropriate?

This raw data will follow separately.

How was the spiking done? Can you add that to the methods section?

A separate experimental section was implemented for this version of the report. The description of the spiking process may be found there.

Why did the wt% of Al not increase with spiking? Ca, S and Cu all increased markedly.

Each additional spiking compound acts as a diluent on the others. As such it is quite possible for a spiked element to be lower on a concentration basis and yet be correct.

Could you provide the gravimetric factors for the analytes so that myself and the partners can understand the calculations? Refers to equation 1

An expanded description of gravimetric factors has been added above. They may also be found in reference books, such as ***Lange's Handbook of Chemistry***.

Should the %analyte$_i$ be expressed as a percent or as a decimal in this equation? Refers to equation 1

%analyte should be used in the percent form. This is why there is a factor of 100 in the equation.

Why is spike$_j$ in the denominator, preceded by a sum sign? I see only one value in Table 8 (Now table 5). Refers to equation 1

The equation includes a Σ because there are 3 spiking compounds added to the sample. J is the counting integer for the multiple spiking compounds and varies from 1-3. The summation is correct. Sample 7+Σ = 2.002, as the final row of Table 5 indicates.

Why is this so high? (Refers to sulfur) I understand variability around 100% but does 119% suggest a measurement problem? Similar for Br and As – 115%

While sulfur is an element we are "watching," we are not prepared at this time to declare that there is a problem needing resolution with this element. Consider equation 2, where the numerator is based upon experimentally acquired data from the XRF. Similarly, the denominator of 2 comes from equation 1 and also includes experimentally acquired data; both XRF and balance. There is variability in both the numerator and denominator of equation 2 and we would need additional data to be certain biases existed here.

Bromine and arsenic are present at 12 ppm in the unspiked sample. For arsenic, in particular, this must be considered at the detection limit since it was observed in only 1 of 2 replicate samples. At this level for these elements, noise becomes more important and the difference between 100 % and 115 % cannot be considered significant for a single sample.

Conclusions: Could you explain this sentence? The standard deviation describes the detection limits? Doesn't it describe the variability around the mean?

One definition of detection limit is nσ; where n is an integer selected based upon the desired confidence level. To be done properly, detection limits are measured using dilute samples. In many cases that is shortcut by using the nσ calculation.

Conclusions: Where appropriate, could you provide the detection limits, e.g. for lead?

As described in the previous response, this depends upon the confidence level desired. N = 3 is generally considered a reasonably conservative approach. Referring to Table 6, short term reproducibility, of the draft report, we can use σ = 0.000237 weight %. 3σ then becomes 0.0007 weight % for lead. This is strictly an estimate that would need to be confirmed experimentally.

Conclusions: Brian et al, could you elaborate your conclusions here … e.g. Brian commented that based on the phase I XRF data, these high chlorine levels may be accurate. Dennis commented that he saw decreasing Cl concentrations as he made replicate measurements

Simply put, both the range of concentrations and variability are similar between phase 1 and phase 2 samples. Chlorine in phase 1 samples ranged from 0.5 to 0.9 % and had % RSDs ranging from 10 to 40. Similarly, phase 2 samples ranged from 0.4 to 1 % while the % RSD of replicate sample preparations was 25 % for sample 7. And, since no binder was used for the phase 1 samples, there is every indication that the chlorine concentrations observed during phase 1 are real.

Dennis may be referring to the chlorine data where the replicates could be exhibiting a decreasing trend with time. This is, however, a small trend, from 0.92 to 0.81 % across triplicate analysis.

All phase 2 samples exceed the "halogen free" definition for chlorine. Sample 7 is simply consistently high across several sample preparations and analyses.

Conclusions: Yes this is correct – can you explain what a "balance compound" is and how it is used?

In the absence of information about the organic mass present, the material that is not observed by XRF, the quantification program will assign the full sample mass to the analytes observed. This will usually result in unacceptably high, and wrong, results. Informing the program that there is a balance compound present avoids this.

Bromine-Arsenic Question

In an e-mail dated July 15, 2008, [redacted] transmitted a communication from [redacted] regarding a potential interference between bromine and arsenic by XRF. The following figure was prepared by [redacted] from the phase 1 analytical results and was attached to these messages.

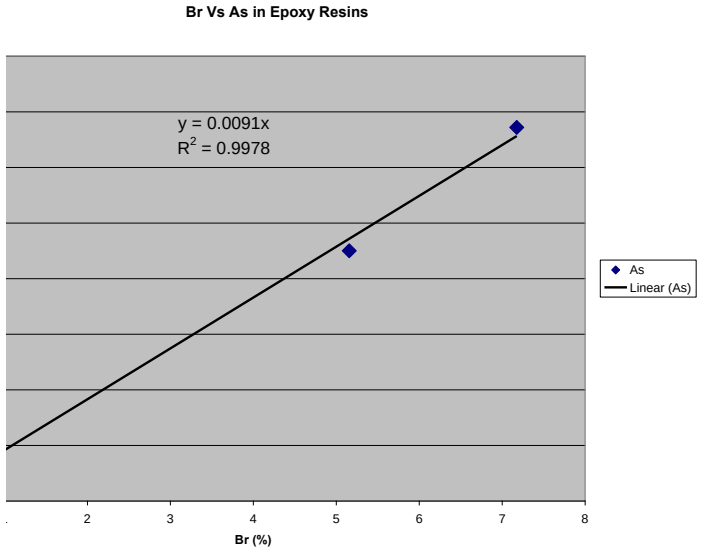


Figure A-1. Bromine vs. Arsenic in Phase 1 samples

This graph clearly shows a direct relationship between the Phase 1 bromine and arsenic results. While there are more than one possible explanation for such a causal

relationship, [redacted] warns of a spectral interference leading to arsenic false positives. After investigating the data, there is every indication that he is correct.

The instrument is currently not operational while it awaits the arrival and installation of a new chiller. If the instrument were up, running several known standards would have been the most appropriate approach to investigating this potential interference. Since we do not have that option at the moment, the following several paragraphs consider the question.

Tables A-1 and A-2 provide information on instrumental operational parameters for the several sub-scans and channels that were used for these analyses. “LOCorr” is the acronym for line overlap correction; it is marked yes for the all sub-scans and channels. While the several acronyms used in these tables are not important; what is important is that:

- Channel 2 defines the conditions under which the arsenic data was collected
- Sub-scan 3 defines the conditions under which bromine data was collected
- Channel 2 instrumental conditions match those used under sub-scan 3

Table A-1. Arsenic and Bromine Scans

Analyte	Line	Scan or channel	Use LOCorr	Measured (kcps)	LO Corrected (kcps)	Used (kcps)	Calculated (kcps)	Difference (kcps)
As	KB	Ch 2	Yes	5.539	5.539	5.532	5.532	0
Br	KB1,3	Sc 3	Yes	542.153	542.153	541.46	541.475	-0.016

Table A-2. Line Selection Parameters

Scan or channel	X-tal	Detector	Collimator (µm)	Tube Filter material / µm	kV	mA	Start (°)	End (°)	Step (°)
Sc 1	LiF220	Scint	150	Brass / 100	60	66	14.02	18.58	0.04
Sc 2	LiF200	Scint	150	Brass / 300	60	66	12.02	20.99	0.03
Sc 3	LiF220	Scint	150	None	60	66	26.63	44.98	0.05
Sc 4	LiF220	Scint	150	Al / 200	60	66	42.03	61.98	0.05
Sc 5	LiF220	Duplex	150	None	50	80	61.03	126	0.05
Sc 6	LiF200	Flow	150	None	32	125	76.04	146	0.08
Sc 7	Ge	Flow	300	None	32	125	91.05	146	0.1
Sc 8	PE	Flow	300	None	32	125	100.1	114.9	0.12
Sc 9	PE	Flow	300	None	32	125	130.1	147	0.12
Sc 10	PX1	Flow	300	None	32	125	20.08	59.98	0.15
Ch 1	LiF220	Scint	150	None	60	66	40.35	40.35	0
Ch 2	LiF220	Scint	150	None	60	66	43.58	43.58	0
Ch 3	LiF220	Scint	150	Al / 200	60	66	45.64	45.64	0
Ch 4	LiF220	Scint	150	Al / 200	60	66	51.65	51.65	0

It is, therefore reasonable to examine the sub-scan 3 data for evidence of spectral interference. Figure A-2 provides an expanded view of sub-scan 3 in the vicinity of the arsenic Kβ lines. In Figure A-2, we can observe that the bromine Kα1,2 doublet is in the vicinity of the arsenic Kβ lines. The horizontal colored line below the doublet represents the calculated baseline. The green vertical hashmarks to the right of the doublet represent predicted arsenic peak locations. As can be seen from the cells at lower left, the graphic crosshairs are at the arsenic Kβ3 line and it can be seen that the tail of the bromine doublet contributes a non-zero response at this 2θ angle. Figure A-3 expands the bromine tail region of this spectrum.

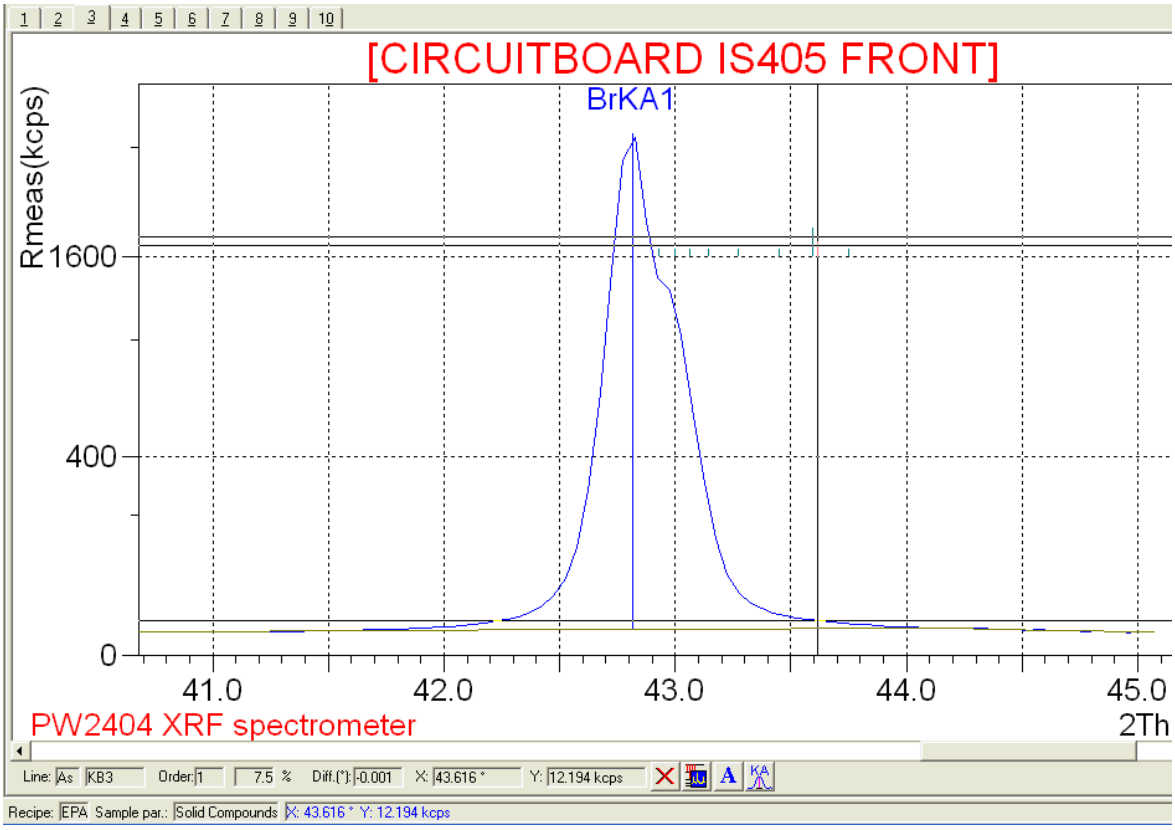


Figure A-2. Sub-scan 3, Bromine doublet

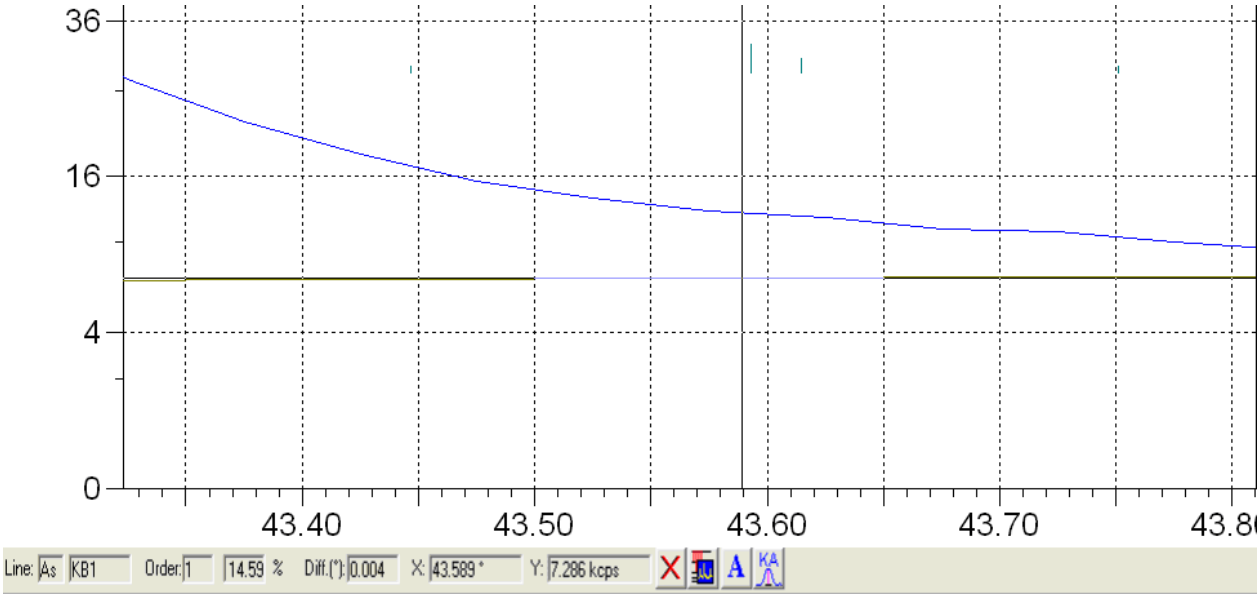


Figure A-3. Bromine Tail in Arsenic Region

Having said that there is spectral overlap of bromine on arsenic, just as [redacted] noted, we must also note that Table A-2 says that line overlap correction is used. Having said **that**, we must also note that the arsenic response in the LO Corr cell is identical to the measured value, which would seem to contradict that.

Examining Figure A-3 it looks a lot as if the 5.539 kcps measured value in Table A-2 comes from the difference between the calculated background at the crosshair and the bromine tail response. The question remains as to whether or not corrective procedures have been implemented. The ***Panalytical*** software provides 2 approaches to corrective action that are applicable to interferences. One is the already mentioned line overlap correction. The other is a line specific, as opposed to sub-scan specific, background correction procedure. Details on these procedures are not available to the operator within the ***IQ+*** quantification program.

While the details of such applications as ***IQ+Metalloids*** are not available through the ***IQ+*** program, they can be found via the ***Setup*** program. Here we can find that channel 2, arsenic, was set up without any background points. Four are available to provide from 0^{th} to 4^{th} order regressions of curved backgrounds in the vicinity of an analytical

channel. By using the channel set button on the bottom of the application specific page, one arrives at a graphic representation of the appropriate standard. On this page, there is a box for defining line overlap interferences. For arsenic in the ***IQ+Metalloids*** application no line overlaps are defined.

In summary, the above suggests there is a strong probability that an uncorrected bromine interference on arsenic exists in this application. Once the instrument is back up, the new chiller is installed, running of standards while modifying the application; followed by re-running certain samples would be appropriate.

There are two comments to be made on this subject

- The applications that are currently on this instrument were set up by the manufacturer's representative during installation of the software

- As noted in the last few paragraphs, the operator does not have easy access to such details as background correction and line overlap correction.

Appendix B: Laminate Etching and Chlorine Measurements

Both phase 1 and phase 2 samples were sent directly from each manufacturer to David Bedner at ISOLA. Mr. Bedner prepared the laminates for the experiments by etching a portion of the copper from the laminate using standard methods and procedures.

To prepare the copper clad laminates for etching, 33% of the copper was masked with an acrylic tape and 66% of the copper was left exposed. Standard Cupric Chloride solution (2.5% Normal, 130°F) was then applied to the laminate using a Chemcut Etcher model GSK-168 with a line speed of 1.5 feet per minute. Thirty-three percent of each sample's copper surface remained intact after etching. Once etching was complete, the samples were sent to the appropriate laboratory for combustion testing and XRF analysis.

Laminate suppliers certified that the supplied pre-preg samples met the IPC's halogen free definition of less than 900 ppm chlorine (Table B-1). However, the etching process described above caused residual chlorine to be left on the laminates, as demonstrated by a subsequent experiment conducted by ISOLA (Appendix C). As a result, the measured chlorine levels noted in Tables 6 and 7 of the report should be considered in the context of the procedures used to etch the laminates. Furthermore, elemental composition was measured using XRF analysis, which some partners view as less quantitative than other methods. In addition, phase 1 samples were not homogenized prior to analysis, whereas phase 2 samples were homogenized. Dichloromethane was used during homogenization, but specific steps were taken to prevent the samples from retaining any dichloromethane.

Table B-1. Laminate suppliers' independent chlorine analyses

Sample Number	Chlorine concentration in the laminate based upon suppliers analysis by an independent third party
4	**Not provided**
5	**317 ppm** Method : IC
6	**290 ppm** Method: IC
7	**265 ppm** Method: IC

Due to this information, which was discovered after original preparation of the report, DfE would like to alter the tenth conclusion bullet in the report as following (page 15, second bullet):

"The results for chlorine are higher than predicted based on halogen free definitions (<900 ppm chlorine) and are likely due to contamination with chlorine during the etching process when the laminates were prepared. Data for this element also shows somewhat more variance than is seen for most other elements. A second possibility of chlorine contamination was the Liquid Binder carrier material, dichloromethane used for phase 2 sample preparation. Two steps, mixing the sample plus binder till it returns to a free flowing state, and operation of the pellet dies under vacuum, were specifically included as quality assurance steps to minimize dichloromethane retention. Chlorine results for Phase 1 laminates, where no homogenization was done and therefore no dichloromethane was used, are also high and variable. Therefore, chlorine contamination likely came from the etching process. To demonstrate this Mr. Bedner did an experiment comparing chlorine levels of laminates prepared in three different ways. Results are shown in Appendix C."

Appendix C: ISOLA Experiment Demonstrating the Impact of the Etching Process on Chlorine Measurements

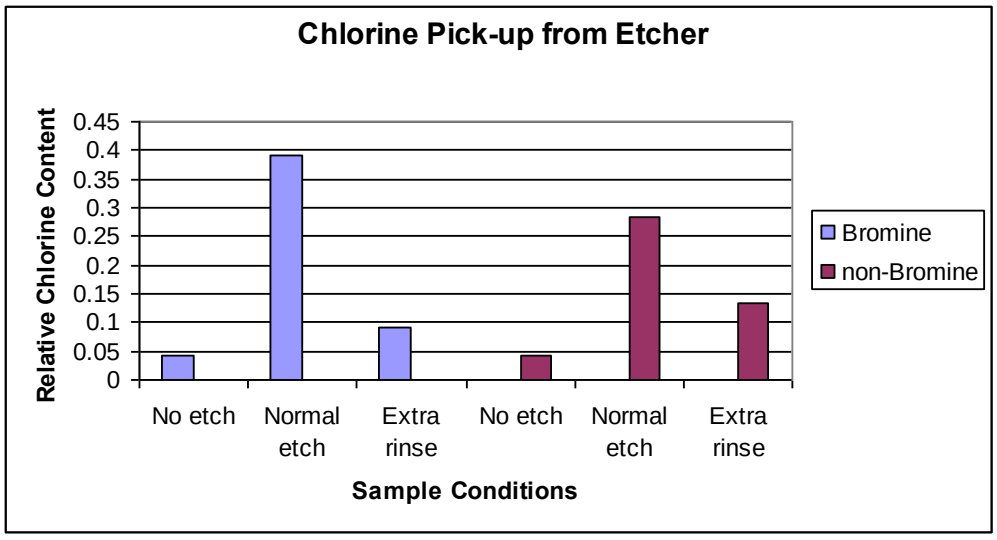
Samples of two laminates, one with a brominated flame retardant and one with a flame retardant that was not brominated, were each prepared one of three ways: 1) copper was peeled from the laminate, i.e. no etching, 2) copper was etched from the laminate using the standard method described in Appendix B or 3) copper was etched from the laminate using the standard method described in Appendix B, followed by an additional de-ionized water rinse before analysis. Chlorine content was analyzed using XRF and results were reported as relative chlorine content compared to known quantity of bromine or another element (proprietary). The results are shown in the Tables and Figures below. Standard etching resulted in 7-9 times more chlorine compared to un-etched laminate whereas additional water rinsing yielded only 2-3 times more chlorine than the un-etched laminate.

Laminate manufacturers typically measure elemental concentrations by IC and believe this is the most accurate method for determining element levels. XRF was chosen for this experiment for the objective of determining general differences in composition between laminate samples, to aid in choosing a diverse set of laminates for Phase II experiments.

XRF measurement

	Br	Cl	X
16533-1	96.85	3.15	
BrFR No Etch	95.98	4.02	
	94.69	5.31	
Average	95.84	4.16	
16533-2	75.20	24.80	
BrFR Normal Etch	71.05	28.95	
	69.30	30.70	
Average	71.85	28.15	
16533-3	95.47	4.53	
BfFR Extra Rinse	89.25	10.75	
	90.31	9.69	
Average	91.68	8.32	
16533-4		2.27	72.57
PFR No Etch		4.63	68.57
		2.13	72.41
Average		3.01	71.18

	Br	Cl	X
16533-5		21.41	56.73
PFR Normal Etch		16.55	61.49
		13.07	62.12
Average		17.01	60.11
16533-6		7.54	59.80
PFR Extra Rinse		7.23	58.63
		8.81	58.51
		7.86	58.98



	Cl pick "normal"	Cl pick up X-Rinse
Bromine Samples	9x	2x
non-Bromine Samples	7x	3x

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX D

U.S. EPA. Flame Retardant in Printed Circuit Boards Partnership: Short Summary of Elemental Analyses. DRAFT. December 9, 2009.

***This Short Summary is based on the work presented in the following three documents, which are also included in Appendix D:**

ICL Industrial. JR 22 – Br and Cl Analysis in Copper Clad Laminates – part II. February 12, 2009. ***(See page A-150)***

ICL-IP Analysis of Laminate Boards. Memo from Stephen Salmon. November 16, 2009. ***(See page A-152)***

Dow. Analysis of Chlorine and Bromine. November 2, 2009. ***(See page A-156)***

Flame Retardant in Printed Circuit Board Partnership

Short Summary of Elemental Analyses

December 9, 2009

Dow and ICL-IP tested the seven laminate samples for elemental composition. Dow tested for bromine and chlorine using neutron activation (NA). ICL-IP tested for aluminum, calcium, magnesium, and phosphorus using ICP, bromine using titration, and chlorine using ion chromatography. Results from Dow and ICL-IP are shown alongside prior XRF results.

Aluminum, Calcium, and Magnesium

The partnership had previously decided to analyze levels of aluminum, calcium, and magnesium to determine whether any of these elements were present as a flame retardant filler, such as $Al(OH)_3$, $Mg(OH)_2$ or $CaCO_3$. As is shown in ICL's report, results for Al, Ca, and Mg were not repeatable. In addition, results were low and further testing showed that Al, Ca, and Mg were not completely digested in the initial procedure. This led ICL to conclude that the Al, Ca, and Mg were most likely from glass fiber or glass treatment, and not from a flame retardant filler (personal communication with ICL, Dec 2009). For these reasons, we do not summarize results for Al, Ca, and Mg here, but instead focus on phosphorus, bromine, and chlorine.

Phosphorus

As is shown in Table 1 and Figure 1, phosphorus levels are highest in laminate 3. There is some discrepancy between XRF and ICP results, but both test methods agree that laminate 3 has the highest level of phosphorus.

Table 1. Phosphorus

	Test Method			
	ICP		XRF	
Laminate	wt%	±[1]	wt%	±[1]
1	0.011	0.0068	0.0016	0.00036
2	0.012	0.0013	0.0017	0.00054
3	1.7	0.020	4.2	0.10
4	1.1	0.054	1.4	n/a
5	0.80	0.0065	0.84	n/a
6	0.69	0.0065	0.74	n/a
7	0.52	0	0.68	0.0049

1: Confidence intervals are based on variance among reported values. It is not possible to determine the extent to which these intervals account for measurement uncertainty.

n/a: not applicable (not enough data to determine confidence bounds)

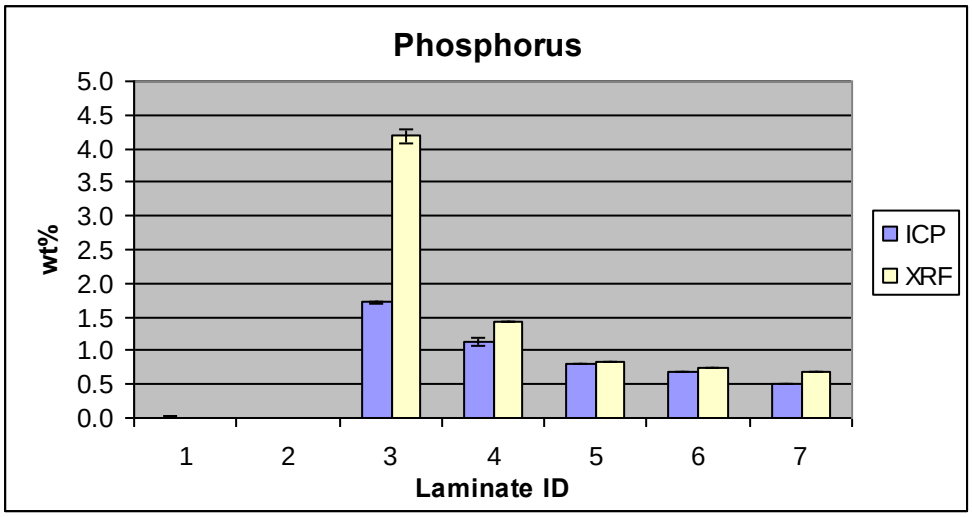


Figure 1. Phosphorus levels measured by ICP and XRF

Bromine

As is shown in Table 2 and Figure 2, bromine levels are highest in laminate 2. There is some discrepancy in results for laminate 1 (titration results are an order of magnitude higher than neutron activation results), but keep in mind that prior testing did not show noticeable levels of brominated dioxins or furans for laminate 1. Laminates 3 through 7 appear to have negligible amounts of bromine (two to three orders of magnitude lower than for laminate 2).

Table 2. Bromine

	Test Method					
	Titration		Neutron Activation		XRF	
Laminate	wt%	±[1]	wt%	±[1]	wt%	±[1]
1	0.7	n/a	0.0017	0.00093	n.d.	n/a
2	8.1	n/a	7.2	0.30	6.1	1.9
3	<0.04	n/a	0.0038	0.000063	0.0047	0.00015
4	<0.04	n/a	0.00054	0.00012	n.d.	n/a
5	<0.04	n/a	0.0026	0.0011	0.0012	n/a
6	<0.04	n/a	0.00011	0.0000098	n.d.	n/a
7	<0.04	n/a	0.0014	0.000079	0.0012	0.00012

1: Confidence intervals are based on variance among reported values. It is not possible to determine the extent to which these intervals account for measurement uncertainty.

n/a: not applicable (not enough data to determine confidence bounds)

n.d.: not detected

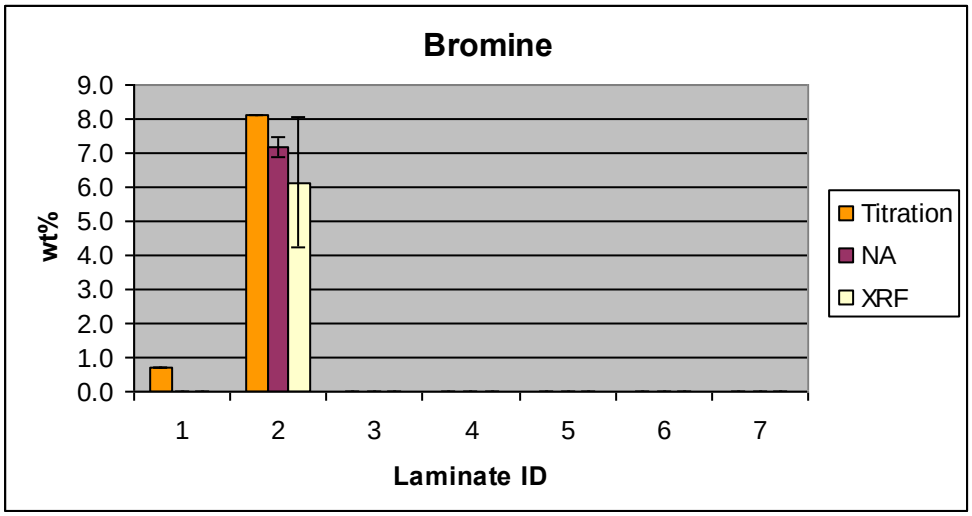


Figure 2. Bromine levels measured by titration, neutron activation (NA), and XRF

Chlorine

Table 3 and Figure 3 show noticeably lower chlorine results with neutron activation and ion chromatography than with XRF (order of magnitude difference), which is as expected under the revised washing protocols. Despite potential discrepancies between test methods, the results show that chlorine levels are similar between laminates, and along the order of 1/100th to 1/10th of a percent by weight.

Table 3. Chlorine

	Test Method					
	Ion Chromatography		Neutron Activation		XRF	
Laminate	wt%	±	wt%	±[1]	wt%	±[1]
1	0.06	n/a	0.075	0.0013	0.88	0.12
2	0.02	n/a	0.073	0.018	0.59	0.35
3	0.02	n/a	0.062	0.0013	0.52	0.081
4	<0.02	n/a	0.063	0.00065	0.45	n/a
5	0.02	n/a	0.060	0.0023	0.43	n/a
6	0.04	n/a	0.046	0.0033	0.49	n/a
7	<0.02	n/a	0.030	0.0020	1.0	0.065

1: Confidence intervals are based on variance among reported values. It is not possible to determine the extent to which these intervals account for measurement uncertainty.

n/a: not applicable (not enough data to determine confidence bounds)

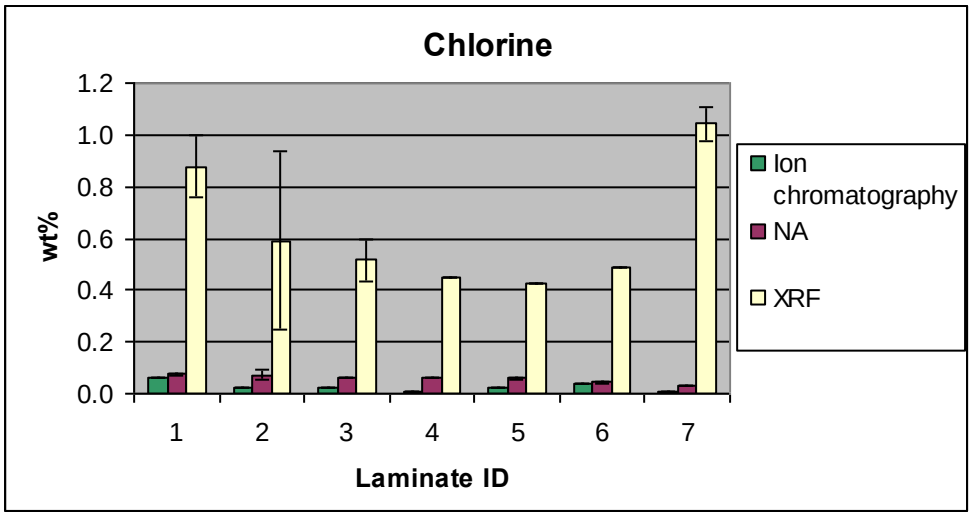


Figure 3. Chlorine levels measured by ion chromatography, neutron activation (NA), and XRF
Note: Ion chromatography results for laminate 4 and 7 were below detection limits, and are shown in Figure 3 as one-half the detection limit.

ICL Industrial
PRODUCTS

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Iris Ben-David, Ph.D.

02/12/2009

To: Pierre Georlette

From: Dr. Iris Ben David

Re: JR 2293 – Br and Cl Analysis in Copper Clad Laminates – part II

Following our previous report on the analysis of bromine and chlorine in Copper Clad laminates (see **Appendix-1**) we received a request for analyzing the halides in these samples at levels under 0.5 %. We analyzed the samples using ion chromatography, with detection limit of 0.02 % for chlorine and 0.04 % for bromine.

The results are summarized in the table.

Sample ID	Br Content (%)	Cl Content (%)
EPA-1	0.7 [1]	0.06
EPA-2	8.1 [1]	0.02
EPA-3	< LOD	0.02
EPA-4	< LOD	< LOD
EPA-5	< LOD	0.02
EPA-6	< LOD	0.04
EPA-7	< LOD	< LOD

Notes:

1) Determined by titration – see **Appendix-1**.

Please let us know if you need any additional analyses for these samples.

With Best Regards,

Iris Ben David

Appendix-1: Our report from November 11, 2009 – JR 2283.

11/11/2009

To: Pierre Georlette

From: Dr. Iris Ben David

Re: JR 2283 – Br & Cl Analysis in Copper Clad Laminates

We received seven samples of Copper Clad laminates (marked EPA-1 to EPA-7). We analyzed the samples for their bromine and chlorine contents. Two of the samples had metal strips on them; we examined only the metal free section, in comparison with the other samples.

The Br/Cl contents are given below:

Sample ID	Br Content	Cl Content
EPA-1	0.7 % (± 0.4 %)[1]	n.d.[2]
EPA-2	8.1 %[3] (± 0.2 %)[4]	n.d.
EPA-3	n.d.	< 0.5 %[4]
EPA-4	n.d.	< 0.5 %
EPA-5	n.d.	< 0.5 %
EPA-6	n.d.	< 0.5 %
EPA-7	n.d.	< 0.5 %

Notes:

2) The uncertainty at 1 % level is 5 %.
3) n.d. = Not detected.
4) Average of 5 specimens (including the second set of samples EPA 2).
5) The uncertainty at 10 % level is 2 %.

The analytical method used has a limit of quantification of 0.5 %. At levels under 0.5 % the uncertainty is >50%. If the accuracy at lower levels of halides is important and should be determined, we can use a different analytical method. Upon request, the analytical results will be available within a month.

With Best Regards,

Date: November 16, 2009

Subject: Analysis of Laminate Boards.

From: Stephen Salmon, ICL-IP

Determination of P, Al, Ca, Mg

Analyses were completed on seven laminate boards. The results show repeatability was very good for P, but very poor for Al, Ca, and to a lesser extent Mg. The nature of the sample matrix appears to be the problem. Details are given below.

The laminate boards were sampled by taking very thin slices across areas that did not contain any of the copper cladding. The slivers were cross cut to produce very small pieces. This material was mixed and sub-sampled for acid digestion to get a representative sample across the board. It was noted that this cutting procedure produced some very fine glass dust from the edges of the pieces. Some of this dust was included in the sub-samples.

The samples were digested with sulfuric acid using nitric acid and 30% hydrogen peroxide as needed to destroy the organic matrix. The resulting solution contained the insoluble fiberglass. The digested samples were filtered through 0.45 um polypropylene syringe filters into 100-mL volumetric flasks and made to volume at 4% sulfuric acid. The samples prepared in triplicate were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using calibration standards matched to the 4% sulfuric acid of the samples.

Results for triplicate analyses of the seven laminate boards are shown in Table 1.

Table 1
ICP Analysis of slivered laminate boards

Sample ID	wt% Al	wt% Ca	wt % P	wt% Mg
EPA-1 A	0.21	0.54	0.017	<0.01
EPA-1 B	0.26	0.62	<0.01	0.010
EPA-1 C	0.19	0.45	0.010	<0.01
EPA-2 A	0.31	0.78	0.011	0.013
EPA-2 B	0.32	0.79	0.011	0.013
EPA-2 C	0.39	0.93	0.013	0.016
EPA-3 A	0.21	0.50	1.71	<0.01
EPA-3 B	0.40	0.32	1.71	<0.01
EPA-3 C	0.48	0.78	1.74	<0.01
EPA-4 A	0.35	0.68	1.14	0.080
EPA-4 B	1.60	3.34	1.07	0.14
EPA-4 C	0.27	0.74	1.16	0.070
EPA-5 A	1.09	0.69	0.80	0.014
EPA-5 B	2.34	0.51	0.81	0.013
EPA-5 C	0.34	0.26	0.80	<0.01
EPA-6 A	2.67	1.63	0.68	0.056
EPA-6 B	2.96	1.37	0.69	0.046
EPA-6 C	2.21	0.72	0.69	0.040
EPA-7 A	2.86	1.74	0.52	0.085
EPA-7 B	3.09	2.14	0.52	0.10
EPA-7 C	1.81	0.96	0.52	0.059

The results show that only P determination was repeatable. To check if the fine glass dust that was included at various levels in the acid digested samples skewed the results four of the laminate boards were prepared again in triplicate. This time a single chip of sample of the desired weight was cut out of three sections of the laminate board. The acid digestion and ICP-OES analyses were repeated.

The results of this evaluation are shown in Table 2.

Table 2
Repeat Digestions on single laminate board chips.

Sample ID	wt% Al	wt% Ca	wt % P	wt% Mg
EPA-4 A chip	0.31	0.66	1.18	0.070
EPA-4 B chip	0.22	0.72	1.23	0.068
EPA-4 C chip	0.23	0.73	1.23	0.073
EPA-5 A chip	0.38	0.25	0.81	0.004
EPA-5 B chip	0.80	0.67	0.83	0.010
EPA-5 C chip	0.85	0.57	0.83	0.011
EPA-6 A chip	2.91	1.35	0.63	0.043
EPA-6 B chip	0.77	0.85	0.70	0.018
EPA-6 C chip	1.87	1.29	0.69	0.024
EPA-7 A chip	0.49	0.24	0.50	0.017
EPA-7 B chip	0.39	0.34	0.51	0.016
EPA-7 C chip	0.43	0.35	0.51	0.012

The results show that P again was very repeatable and matched the values from digestion of the small pieces. Al and Ca, and to a lesser extent Mg, again showed very poor repeatability.

The acid digestion of the single chip samples resulted in four small sheets of fiberglass from each sample. These were recovered from the filtration step and the washed fiberglass was dried and weighed. The fiberglass was subjected to the acid digestion procedure again and an ICP-OES analysis showed significant and variable amounts of Al and Ca had not been recovered by the first digestion. Mg showed the same to a lesser extent, but P was not detected indicating quantitative recovery in the original digestion.

Table 3 shows the results of this evaluation.

Table 3
Redigestion of fiberglass recovered from digestion of single chips.

Sample ID	wt% Al	wt% Ca	wt % P	wt% Mg
EPA-6 A chip 2nd	0.45	0.50	nd	0.016
EPA-6 B chip 2nd	0.64	1.30	nd	0.030
EPA 6 C chip 2nd	0.41	0.086	nd	0.011

The conclusion is that Al and Ca are in the fiberglass or can not be separated from the sample matrix quantitatively. This is also the case for Mg, but to a lesser extent. P,

however, is quantitatively recovered from the laminate board matrix by the procedure used.

Determination of Br and Cl

An analysis of slivered laminate board for halogens was attempted by metallic sodium reflux in isopropanol with silver nitrate titration for Br and Cl. Unfortunately, the laminate board matrix proved to be impervious to extraction by the reagent and this approach had to be abandoned.

Samples of the seven laminate boards were sent to ICL in Israel for sample preparation by sodium peroxide bomb. Preliminary results are shown below. Other results are pending and will be sent when available.

Date: 11/11/2009
To: Pierre Georlette
From: Dr. Iris Ben David

Re: JR 2283 – Br & Cl Analysis in Copper Clad Laminates

We received seven samples of Copper Clad laminates (marked EPA-1 to EPA-7). We analyzed the samples for their bromine and chlorine contents. Two of the samples had metal strips on them; we examined only the metal free section, in comparison with the other samples.
The Br/Cl contents are given below:

Sample ID	Br Content	Cl Content
EPA-1	0.7 % (± 0.4 %)[1]	n.d[2]
EPA-2	8.1 %[3] (± 0.2 %)[4]	n.d.
EPA-3	n.d.	< 0.5 %[4]
EPA-4	n.d.	< 0.5 %
EPA-5	n.d.	< 0.5 %
EPA-6	n.d.	< 0.5 %
EPA-7	n.d.	< 0.5 %

Notes:
1) The uncertainty at 1 % level is 5 %.
2) n.d. = Not detected.
3) Average of 5 specimens (including the second set of samples EPA 2)
4) The uncertainty at 10 % level is 2 %.

The analytical method used has a limit of quantification of 0.5 %. At levels under 0.5 % the uncertainty is >50%. A different analytical method will be used to get more precise Cl results. The analytical results will be available within two weeks.

Triplicate samples were prepared by transferring 0.3 grams respectively into pre-cleaned 0.25-dram polyethylene vials. Samples were measured for thickness and cleaned with isopropanol prior to placing into the vials. Areas with copper were not sampled. Standards of chlorine, bromine were prepared from standard solutions and placed into pre-cleaned 0.25 dram vials. The standards were diluted to the same volume as the samples and the vials heat-sealed. The samples, standards and blanks were irradiated and counted in four batches. Triplicate samples of EPA -2 were irradiated separately using 0.01grams. The higher concentration of bromine identified interferes with the detection of chlorine. Thickness was measured in triplicate using a micrometer.

Sample ID	20 min @ 250 kW		10 min @250 kW		10 min @30 kW 10 min decay	
	Cl (ppm) t_d =1 h = 1 h	Br (ppm) t_d =1 h t_c = 1 h	Cl (ppm) t_d =1 h t_c = 1 h	Br (ppm) t_d =1 h t_c = 1 h	Cl (ppm) t_d =1 h t_c = 1 h	Br (ppm)
EPA 1	760±40	15.5±0.8	740±40	9.7±0.5	740±40	25.9±1.3
EPA 3	630±30	38.2±1.9	630±30	37.8±1.9	610±30	37.1±1.9
EPA 4	640±30	4.5±0.2	630±30	5.2±0.3	630±30	6.5±0.3
EPA 5	600±30	20.6±1.0	580±30	37.8±1.9	620±30	20.1±1.0
EPA 6	440±20	1.0±0.1	440±20	1.1±0.1	490±20	ND@2ppm
EPA 7	290±10	13.3±0.7	320±20	14.7±0.7	290±10	14.0±0.7

10 min@5kw: Cl t_d =10 min, t_c = 7 min; Br t_d = 5 hour, t_c = 1.5 hour						
Sample ID	Cl (ppm)	Br (wt%)	Cl (ppm)	Br (wt%)	Cl (ppm)	Br (wt%)
EPA 2	650±130	6.9±0.3	920±180	7.4 ±0.4	630±130	7.3±0.4

Thickness	Inch	Inch	Inch	Average± Stdev
EPA 1	0.018	0.021	0.019	0.019±0.002
EPA 2	0.016	0.018	0.018	0.018±0.001
EPA 3	0.019	0.019	0.02	0.020±0.001
EPA 4	0.018	0.017	0.02	0.019±0.001
EPA 5	0.018	0.018	0.018	0.018±0.001
EPA 6	0.017	0.017	0.017	0.017±0.001
EPA 7	0.018	0.018	0.018	0.018±0.001

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX E

University of Dayton Research Institute. Use of Cone Calorimeter to Identify Selected Polyhalogenated Dibenzo-P-Dioxins/Furans and Polyaromatic Hydrocarbon Emissions from the Combustion of Circuit Board Laminates. October 22, 2013.

USE OF CONE CALORIMETER TO IDENTIFY SELECTED POLYHALOGENATED DIBENZO-P-DIOXINS/FURANS AND POLYAROMATIC HYDROCARBON EMISSIONS FROM THE COMBUSTION OF CIRCUIT BOARD LAMINATES

Final Report
Prepared for the U.S. Environmental Protection Agency

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Office of Research and Development
Research Triangle Park, NC 27711

October 22, 2013

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LIST OF ACRONYMS

1556 HFR	1556 halogen-free flame retardant
ASTM	American Society for Testing and Materials
Avg HRR	Average heat release rate
BFR	Brominated flame retardant
CIL	Cambridge Isotope Laboratories
CO/CO_2	Carbon monoxide/carbon dioxide
DfE	Design for the Environment Program
DQI	Data quantity indicator
DQO	Data quantity objective
EMPC	Estimated maximum possible concentration
EMT	Environmental Monitoring Technologies Inc
EPA	U.S. Environmental Protection Agency
E-waste	Electronic waste
FIGRA	Fire growth rate
FMS	Fluid Management Systems Inc
FTT	Fire testing technology
GC/MS	Gas chromatography/mass spectrometry
HFR	Halogen-free flame retardant
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry
HRR	Heat release rate
ISO	International Organization for Standardization
KOH	Potassium hydroxide
LRMS	Low resolution mass spectrometry
MARHE	Maximum average rate of heat emission
NFR	No flame retardant
NGO	Non-governmental organization
NRMRL	National Risk Management Research Laboratory
OSL	EPA Organic Support Laboratory
P	Populated by halogen components
PAHs	Polyaromatic hydrocarbons
PBDD/Fs	Polybrominated dibenzo-p-dioxins/furans
PCB	Printed circuit board
PCDD/Fs	Polychlorinated dibenzo-p-dioxins/furans
Peak HRR	Peak heat release rate
PFK	Perfluorokerosene
PHF	Populated by low-halogen components
PM	Particulate matter
PUF	Polyurethane foam
R&D	Research and development
RoHS	Restriction of Hazardous Substances
RTP	EPA Research Triangle Park
TBBPA	Tetrabromobisphenol A
TEF	Toxic equivalent factor
TEQ	Toxic equivalent quantity

THR	Total heat release
Tig	Time to ignition
UDRI	University of Dayton Research Institute
UL	Underwriters Laboratories
UV	Ultraviolet
WEEE	Waste Electrical and Electronic Equipment

1 Executive Summary

The U.S. Environmental Protection Agency (EPA) Design for the Environment (DfE) program convened a partnership to conduct an alternatives assessment for TBBPA in printed circuit boards. The partnership determined that combustion testing of sample laminates using the alternatives would strengthen the assessment and industry decision-making on use of alternatives. This report explains the outcome of that testing.

The purpose of this study was to understand the potential emissions of halogenated dioxins or furans and polyaromatic hydrocarbons (PAHs) from burning circuit board laminates. The methods of this study mimic two types of fire events: open burn and incineration of electronic waste (e-waste), both of which are used for precious metal recovery. While difficult to model these two complex fire scenarios exactly, the University of Dayton Research Institute (UDRI) utilized a cone calorimeter, a fire safety engineering instrument capable of simulating these scenarios and measuring combustion efficiency.

Combustion conditions, as well as model samples for burning, were selected with input from a group of stakeholders "Partnership" assembled by DfE. These stakeholders included circuit board laminate manufacturers, flame retardant producers, government regulators, and non-governmental organizations (NGOs) with vested interests in the potential emissions from these burning items. Some stakeholders funded the UDRI experiments while EPA funded the sample extractions and dioxin/furan analyses.

The results of this study show that when these materials are burned, even at high heat flux that would attempt to mimic an incinerator, various pollutants are released. Further, flame retarded materials release more PAHs and other pollutants when burning compared to materials that are not flame retarded, but this is expected and indicates that the flame retardants are working as designed. Specifically, the retardation of flame and combustion will result in more incomplete combustion products.

The combined dioxin/furan and PAH emission studies suggest that circuit board polymers cannot be analyzed in isolation when determining emissions; the entire populated board must be considered. While certain pollutants were found in both flame retardant and non-flame retardant circuit boards, toxicity studies were not conducted. Therefore the relative toxicity of the combustion by-products from the different laminate formulations can only be partially calculated.

While the exact flame retardants used in this study were not identified to the Partnership, the flame retardant chemistry of these materials behaved as expected. Brominated flame retardants inhibited combustion and produced brominated phenols (detected, but not quantified), dioxins, furans, and other aromatics during burning. Non-halogenated flame retardants (presumed to be phosphorus-based) slowed down burning through char formation. This generated more PAHs than the non-flame retardant circuit boards in certain circumstances (lower heat flux) but less PAHs when compared to BFRs.

In general, these emissions fit the known combustion chemistry of these flame retardants classes. Therefore, this study contributes data supporting the approach that, to achieve both fire safety

and lower emissions, disposal must be done properly with full incineration and appropriate air pollution control devices in place.

Despite this confirmation of open burning pollution, the study does also leave some questions unanswered. The results from this study are not definitive regarding which specific pollutants were released since chemical identification was limited. Further, the results do not show which chemistries and circuit board components may lead to lower emissions, even under simulated incineration conditions. A cone calorimeter may not achieve temperatures as high as those of real-world incinerators. The high heat flux results may not be fully indicative of real-world emissions should printed circuit boards be put into an incinerator. Because some flame retardants (including those in this report) inhibit combustion even at very high heat fluxes, additional research is needed to identify circuit board flame retardant chemistry with lower environmental and human health impact emissions. Incinerator conditions are likely to reduce the emissions, but additional emission controls (baghouses, filters) may be needed to prevent all emissions of concerns as the efficiency of an incinerator is a function of its design and actual operation temperatures.

Finally, this study demonstrated that the technique of using the cone calorimeter (ASTM E1354) for emission studies in combination with a custom-built emissions capture sampling train was successful with small samples. Specifically, the cone calorimeter can be used to collect emissions from circuit board materials without having to conduct actual open burns. However this proved to be a labor intensive analytical technique needing refinement of procedures. To summarize the findings of this study:

50 kW/m^2 heat flux:
- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at higher levels than NFR sample.
- NFR: PAHs emitted at lowest levels compared to other samples.

100 kW/m^2 heat flux:
- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at lowest levels compared to other samples.
- NFR: PAHs emitted at a level slightly lower than the BFR sample.

Effect of components on emissions:
- PBDD/Fs: PBDD/Fs were similar or lower than sample without components.
- PAHs: In general, presence of components reduced PAH emissions for BFR, were similar or slightly higher for HFR and were lower for 1556 HFR. The size of these differences varied depending on how PAHs were defined (see section 4.6).

Smoke, PM, CO and CO_2 release:
- Smoke release was higher for BFR than HFR laminates. Smoke release was higher with components due to greater amount of material. PM generally had small differences between samples. There were negligible differences in CO release between samples. CO_2 release was lowest for BFR but with small differences between samples. Results are complex and smoke/PM results do not always correlate.

2 Introduction

2.1 Electronic Waste

According to statistics gathered by the Electronics TakeBack Coalition, which were derived from EPA statistics, 2.4 million tons of e-waste were generated in 2010, only 27% of which was recycled (see Table 2-1).[1] However, with the price of precious metals and rare earths increasing due to demand and geopolitical issues, there is increased demand to recycle electronics in order to recover the metals and rare earths. One of the more popular and cost-effective techniques for this type of metal/rare earth recovery is incineration, which burns off the polymeric components of the e-waste and leaves behind inorganic ash. This ash can be further smelted down and refined to isolate the precious metals and rare earths. When incineration is not conducted properly, the combustion of polymeric components creates toxic by-products that can be released into the environment. Improper incineration of electronics in developing countries, as seen in popular magazines like National Geographic[2], has led to concerns about the improper disposal of these products and has influenced the research in this report. Improper disposal of waste that leads to widespread environmental damage and under-ventilated toxic by-product release is highly undesirable and illegal in many countries. This issue may be attributable to companies sending e-waste to countries with looser regulations for improper incineration instead of following incineration regulatory standards in place in many developed countries. The drivers for improper waste disposal are numerous, but ultimately financial, and the drive to recover precious metals is causing more developed countries to keep the wastes inside borders to recycle materials via internal infrastructure. However, even for operations that will utilize clean burning incinerators and afterburner/scrubber technology, there still needs to be some knowledge of what is being released from burning this waste so incinerators can be designed and engineered correctly.

Table 2-1. E-Waste by Category in 2010

E-Waste by Ton in 2010				
Products	**Total disposed** (tons)**	**Trashed (tons)**	**Recycled (tons)**	**Recycling Rate (%)**
Computers	423,000	255,000	168,000	40%
Monitors	595,000	401,000	194,000	33%
Hard copy devices	290,000	193,000	97,000	33%
Keyboards and Mice	67,800	61,400	6,460	10%
Televisions	1,040	864,000	181,000	17%
Mobile devices	19,500	17,200	2,240	11%
TV peripherals*	Not included	Not included	Not included	Not included
Total (tons)	2,440,000	1,790,000	649,000	27%
E-Waste by Unit in 2010				
Products	**Total disposed** (units)**	**Trashed (units)**	**Recycled (units)**	**Recycling Rate (%)**
Computers	51,900,000	31,300,000	20,600,000	40%
Monitors	35,800,000	24,100,000	11,700,000	33%
Hard copy devices	33,600,000	22,400,000	11,200,000	33%
Keyboards and Mice	82,200,000	74,400,000	7,830,000	10%
Televisions	28,500,000	23,600,000	4,940,000	17%
Mobile devices	152,000,000	135,000,000	17,400,000	11%
TV peripherals*	Not included	Not included	Not included	Not included
Total (units)	384,000,000	310,000,000	73,700,000	19%

Computer products include CPUs, desktops, and portables.
Hard copy devices are printers, digital copiers, multi-functions and faxes.
Mobile devices are cell phones, personal digital assistants (PDAs), smartphones, and pagers.
*Study did not include a large category or e-waste: TV peripherals, such as VCRs, DVD players, DVRs, cable/satellite receivers, converter boxes, game consoles.
**"Disposed" means going into trash or recycling. There totals don't include products that are no longer used, but which are still stored in homes and offices.

[1] Table adapted from "Facts and Figure on E-Waste and Recycling", Electronics TakeBack Coalition, 2012. Statistics from "Electronics Waste Management in the United States Through 2009", U.S. EPA, 2011.

2.2 Performance Requirements for Printed Circuit Boards

The materials in printed circuit boards are influenced by performance and regulatory requirements that must be met by manufacturers. These selections ultimately influence the emissions from these components when they burn. For electronic products produced today, numerous environmental requirements must be met. Environmental regulations in the European Union, namely the Restriction of Hazardous Substances (RoHS)[3] and Waste Electrical and Electronic Equipment (WEEE)[4] directives have been driving the elimination of specific metals and organic compounds of environmental concern so that incineration and recycling are easier, and in the event of improper disposal, environmental damage is limited. Regulations from one nation automatically affect other nations as most electronics manufacturers prefer to produce for a global market rather than tailor specific products for specific markets that would result in higher manufacturing and research and development (R&D) costs.

Flame retardants are added to consumer products, including printed circuit boards, to protect highly flammable polymers against potential fire/ignition risks. The primary fire risk that flame retardants are protecting against in circuit boards is that of an electrical fault or short circuit ignition source that can cause the polymer (typically an epoxy) to thermally decompose and ignite. This ignition site can lead to flame spread across the board and can cause the electronic casing (also typically made out of flammable polymer) to also ignite, which may lead to flame spread out of the electronic device into a larger compartment such as a home, a vehicle, or a

mass transport structure (e.g., subway, train, bus), which may contain other flammable products that can cause the initial fire to further propagate. If a fire gets out of control, one might hypothesize that because flame retardants may prevent a product from being fully consumed in an accidental fire event, there is less total emissions when compared to a non-flame retardant product that fully ignites. This is especially true if the non-flame retardant product is composed of a high heat release material which in turn causes other nearby objects to burn and lead to a large fire event (flashover). It should be pointed out though that this toxic emission reduction enabled by flame retardant products in the event of accidental fires is only realized in life cycle models if that product is disposed of properly at the end of its lifetime.[5,6,7] If products are not disposed of properly then flame retardants have some potential to leach into the environment and lead to measureable levels of pollution. The flame retardant technology in use today for most circuit boards typically consists of brominated bisphenol A epoxies that are co-polymerized into the circuit board, or are reactive phosphorus-based flame retardants that are also co-polymerized into the circuit board.[8,9,10] These technologies have been in use for decades because they are cost-effective and reliable while not compromising other essential epoxy circuit board properties (e.g., electrical insulation properties, mechanical). These systems in place today served as the baseline for the DfE project initially conducted in 2008-09 to study the emissions of circuit boards using brominated and phosphorus-based flame retardants.[11]

2.3 Project Goal

The goal of this project was to understand the potential emissions of halogenated dioxins, halogenated furans, and PAHs and fire characteristics of a standard tetrabromobisphenol A (TBBPA) laminate compared to different halogen-free laminates in various scenarios with and without typical circuit board components. The methods of this study mimic two types of fire events used for precious metal recovery: open burning and proper incineration. Definitions of open burning and proper incineration are needed here:

- Open burning means that combustion is done in a crude vessel, open to the environment, where there are no good engineering measures in place to capture emissions or drive the combustion process to completion.

- Proper incineration means that combustion is carried out in a system designed and engineered to fully combust a material can capture its emissions through the use of afterburner and baghouse-type emissions capture systems.

The results will provide scientific information to aid electronics and electrical manufacturers in their decision-making processes to design and choose sustainable and environmentally-friendly materials for their products.

3 Experimental Methods

A series of circuit boards were selected based on Phase I of this project to be tested under various conditions mimicking open burning and incineration operations. The components used on circuit boards were ground up and combusted along with the copper-clad circuit board laminate to simulate the potential emissions from printed circuit board e-waste. An overview of the testing methodology for Phase II of this project is provided in Table 3-1.

Table 3-1. Overview of Phase II Testing Methodology

Laminates Burned (Acronym)	TBBPA laminate (BFR) Non-flame retardant laminate (NFR) Halogen-free flame retardant laminate (HFR) Halogen-free flame retardant laminate (1556-HFR)
Components Burned	Standard halogen components (P) Low-halogen components (PHF)
Laminate/Component Combinations Burned	BFR + standard halogen components (BFR +P) BFR + low-halogen components (BFR + PHF) HFR + standard halogen components (HFR + P) HFR + low-halogen components (HFR + PHF) 1556-HFR + standard halogen components (1556HFR + P) 1556-HFR + low-halogen components (1556HFR + PHF)
Scenarios (Heat Flux)	Open Burn (50 kW/m^2) (Laminate Name -50) Incineration (100 kW/m^2) (Laminate Name – 100)
Analytes Tested	Polybrominated dibenzo-p-dioxins/furans (PBDD/Fs) Polyaromatic hydrocarbons (PAHs)

Multiple entities were responsible for conducting different parts of Phase II's combustion testing experiment. Figure 3-1 depicts the workflow throughout the project. DfE facilitated and oversaw the workflow by communicating directly with Isola, Seagate, UDRI, and EPA Research Triangle Park (RTP).

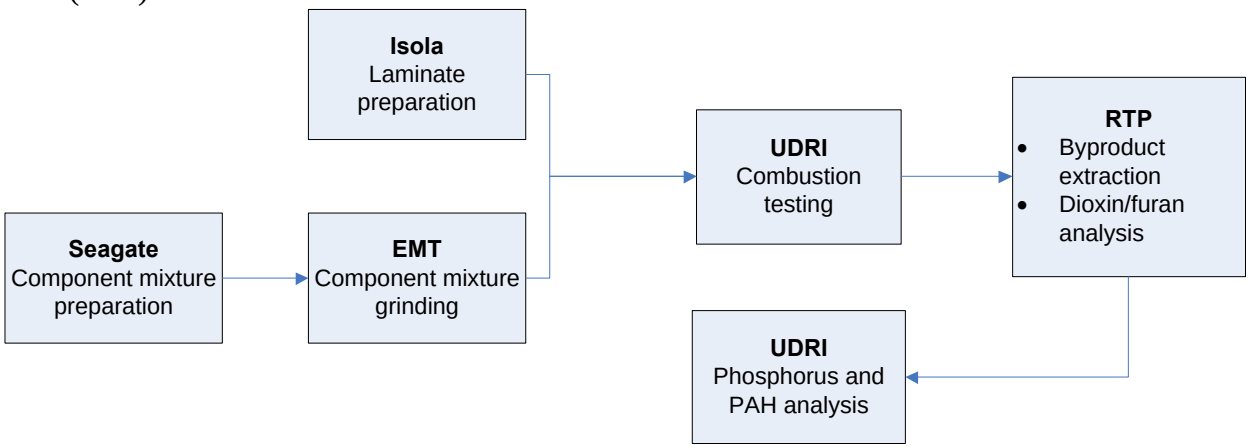

Figure 3-1. Overview of Workflow for Combustion Testing and Analysis

The circuit board laminates selected and the conditions used to burn the components and circuit board combinations are shown in Table 3-2. This experimental plan was created with input from the DfE stakeholders participating in this project including government officials, NGOs, circuit board laminate manufacturers, electronics producers, and flame retardant producers. The instrument and method selected to mimic open burning and incineration was the cone calorimeter, which is a standard fire science measurement tool (ASTM E1354, ISO 5660) used to quantify heat release, smoke release, and CO/CO_2 emissions from burning objects in a variety of fire scenarios. This tool was chosen based on UDRI hypothesis that it could mimic burning conditions of interest to the program while providing quantitative emissions on complex

heterogeneous circuit board samples. More specifically, the cone calorimeter provided a dynamic model in that it could burn a realistic amount of material (an actual circuit board laminate with components or component mimics) and be instrumented in such a way to capture all of the emissions from that burning event.

UDRI and EPA conducted the experiments in Table 3-2 in 2011. The original experiment plan included a third combustion scenario for low-oxygen combustion. These low-oxygen experiments were not carried out because the low-oxygen attachment for the cone calorimeter was unable to yield dependable results for simulated smelting conditions at 100 kW/m^2 heat flux at 10% O_2. The investigators discovered that when a sample was initially pyrolyzed/burned under these conditions, combustion gases escaped from the top of the unit where they could potentially be exposed to more oxygen. This event could lead to a more complete combustion and thus generate inaccurate results. For reasons of integrity and efficiency, UDRI and the partnership collectively decided to exclude the 100 kW/m^2 heat flux at 10% O_2 test condition from the study.

Table 3-2. Emission/Combustion Tests for Phase II DfE Work

Heat flux	Combustion atmosphere	Sample description	# of blank runs[1]	# of laminate burns	PBDD/Fs	Test Blanks for PBDD/Fs	PAHs	Phosphorus
50 kW/m^2	Air (Open-burn)	BFR	2	2	x	x	X	x
		BFR + P	2	2			X	x
		BFR + PHF	2	2	x	x	X	x
		HFR	1	2			X	x
		HFR + P	1	2		x	X	x
		HFR + PHF	1	2			X	x
		1556 HFR	1	2			X	x
		1556 HFR + P	1	2		x	X	x
		1556 HFR + PHF	1	2			X	x
		NFR	1	2			X	x
100 kW/m^2	Air (Incineration)	NFR	1	2		x	X	x
		BFR	1	2	x	x	X	x
		HFR	1	2			X	x
Subtotal			***16***	***26***				
Total (blanks + laminates)			***42***					

[1] Blanks between burns of the same laminate for the first several burns that could produce PBDD/Fs were analyzed for PBDD/Fs carry-over. The blanks were clean; therefore the number of blanks in subsequent sets of samples was reduced.

3.1 Laminate Preparation

The laminate manufacturer Isola was responsible for laminate preparation. Each laminate was 61cm x 46cm (2,806cm^2) and had a 4-ply 2116 Taiwan glass S409 finish. These samples were prepared by pressing each side of the laminates with 1oz of shiny copper from Nan Ya and

etching a portion of the copper from the laminate using standard methods and procedures, just as was done during Phase I testing (see Phase 1 Report)[12], followed by a rinse with dilute KOH. To prepare the copper clad laminates for etching, a portion of the copper was masked with an acrylic tape and the rest of the copper was left exposed. Standard cupric chloride solution (2.5% normal, 266°C) was then applied to the laminate using a chemical etching machine. Etched laminates were then washed with KOH (2.5% normal) to remove residual chlorine. During preliminary testing, laminates were washed only with water and not with KOH. However, it is standard practice in industry to wash laminates with dilute KOH after etching, so the partnership decided to replicate this approach to reflect real-world conditions.

Due to a miscommunication, Isola initially etched off 25% of the copper, leaving 75% of the surface area covered by copper. However, the partnership agreed that a copper surface area of approximately 33% would be more representative of real-world conditions. The copper was distributed evenly over the surface in a way that allowed UDRI to cut the laminate into 100mm x 100mm squares for combustion testing, each containing an equal amount of copper. In order to achieve a surface area as close as possible to 33% and also obtain an even distribution of copper, Isola etched the copper so that 25% remained on one side, and 37.5% on the other side. This resulted in total surface area coverage of 31%. The total amount of copper present in the actual samples is shown in Table 3-3. Pictures of representative samples of the four different copper clad sample types are provided in Figure 3-2 through Figure 3-5.

Table 3-3. Copper Area of Circuit Board Laminates

Sample Description-Heat Flux (kW/m^2)	Copper area content (%)
BFR - 50	32.01
BFR - 50	32.56
BFR - 100	32.95
BFR - 100	32.85
BFR + P - 50	33.86
BFR + P - 50	33.50
BFR + PHF - 50	32.85
BFR + PHF - 50	32.76
HFR - 50	32.66
HFR - 50	32.78
HFR - 100	32.72
HFR - 100	32.68
HFR + P - 50	32.98
HFR + P - 50	32.65
HFR + PHF - 50	32.96
HFR + PHF - 50	31.90
1556 HFR - 50	32.92
1556 HFR - 50	32.86
1556 HFR + P - 50	33.12
1556 HFR + P - 50	33.10
1556 HFR + PHF - 50	32.87
1556 HFR + PHF - 50	32.68
NFR - 50	32.75

Sample Description-Heat Flux (kW/m^2)	Copper area content (%)
NFR - 50	32.80
NFR - 100	32.22
NFR - 100	32.25

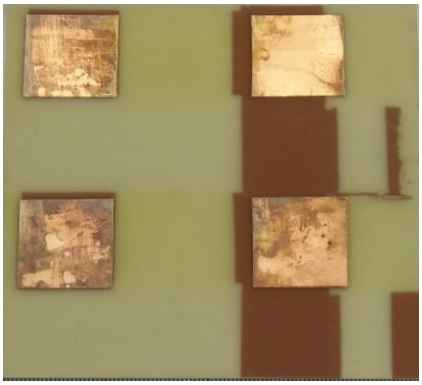

Figure 3-2. NFR Sample

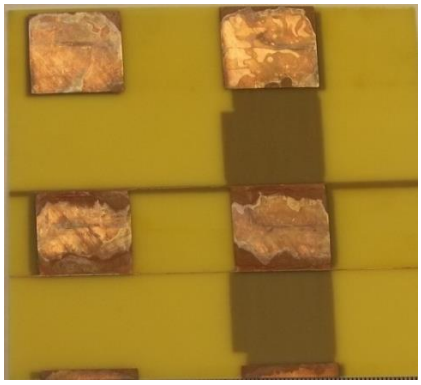

Figure 3-3. BFR Sample

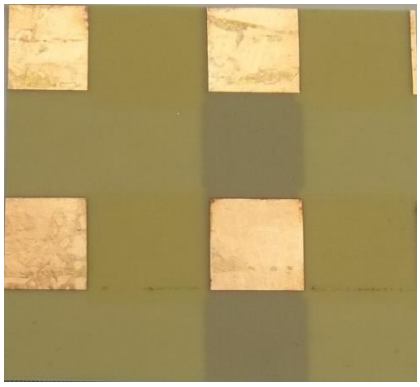

Figure 3-4. HFR Sample

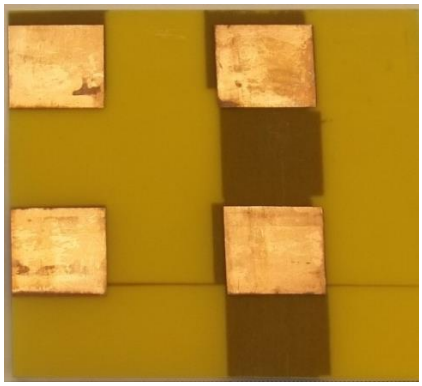

Figure 3-5. 1556-HFR Sample

3.2 Component Mixture Preparation and Component Mixture Grinding

Seagate prepared a standard mixture of components, which Environmental Monitoring Technologies, Inc. (EMT) ground up and sent to UDRI for combustion testing. The mixture was combusted with selected laminate samples to simulate populated circuit boards. Both a low-halogen mixture and a standard halogen mixture were prepared and were added to the laminates. To the extent possible, the types of components in the low-halogen and standard halogen mixtures were made identical. Seagate formulated and supplied the mixtures based on the electronic components found on standard disk drive boards. Seagate provided as much detail as possible about the composition of the ground-up mixtures and calculated the amount to add to each laminate sample. The mixtures included integrated circuits, resistors, capacitors, connectors (main source of plastic housing), shock sensors, and accelerometers. The partnership decided to grind up components into a mixture prior to combustion testing. The blend of components that was ground up to mimic circuit board components is shown in Table 3-4. Since the chemical

composition of the component mixtures will determine emissions, Seagate provided information on the chemicals present in the component mixtures, which is shown in Appendix C: Elemental Analyses of Component Mixtures.

There are a few advantages to using ground-up components instead of whole components:

- More reliable results: Combustion results are consistent for ground-up components, but are not consistent for whole components. This is because small changes in the placement of whole components on the boards can affect the amount and type of materials that come into contact with each other during combustion, which affects the formation of combustion by-products.
- Better estimate of worst-case-scenario: Using ground-up components ensures maximum contact between component materials and would give a higher probability of producing combustion by-products.
- More inclusive sample: Capacitors can be included in the mixture of ground-up components, as they are not an explosion hazard when ground-up.
- Less variability in sample preparation: Components do not have to be attached to the laminate, which removes potential sources of variability (e.g., human error that might occur while fixing components to the laminate and increased probability of introducing contaminants).

Table 3-4. Blend of Components to Mimic Circuit Board Components

Component	Amount (g)	
	Typical PCB[1]	Component Mix
Resistor (fixed)	0.07	30.77
Capacitor	1.59	694.51
Shock Sensor	0.03	10.94
Xstr (thermistor, bipolar transistor, FET)	0.08	33.19
Frequency Drive	0.06	25.38
EMIRFI Filter	0.02	6.57
Inductor	0.53	229.82
Integrated Circuit (custom drive specific, linear, memory)	1.64	718.82
Connector	3.05	1335.17
Total	7.05	3085.17

[1]Typical circuit board component mass/surface area of board is 0.128 g/cm^2. The component mixture loading used for experiments was 0.1 g/cm^2 (10±0.05 g/100 cm^2 of laminate burned).

3.3 Combustion Testing

3.3.1 Cone Calorimeter Apparatus Description

A cone calorimeter (FTT, United Kingdom) housed at UDRI was modified and used to characterize emissions from combustion of various printed circuit board laminate samples. The cone calorimeter is a fire testing instrument which quantitatively measures the inherent flammability of material through the use of oxygen consumption calorimetry, and is a standard technique[14] under ASTM E-1354/ISO 5660. This instrument was designed primarily as a fire safety engineering tool, but has found great utility as a scientific tool for understanding fire

performance in relation to regulatory pass/fail tests as will be referred to in the next paragraph. In effect, it mimics a well-ventilated forced combustion scenario of an object being exposed to a constant heat source and constant ventilation (Figure 3-6). This scenario represents many real world fires where an object or material is aflame and radiates heat to other objects that also catch fire as a result. The cone calorimeter serves as a very useful fire safety engineering tool by looking at the heat release rates of a material under these forced conditions.

By studying the various parameters measured by the cone calorimeter, one can correlate the cone calorimeter measurements to other tests, or, bring understanding of how a material behaves when a flame is exposed to various fire scenarios. Work on comparing cone calorimeter to other tests has included full scale flammability tests,[15] bench scale tests like UL-94 or limiting oxygen index,[16-20] automotive material flame spread tests,[21] wire and cable flame spread tests,[22] and other types of fire tests/scenarios[23-26]. A schematic of the cone calorimeter basic setup is shown in Figure 3-6.

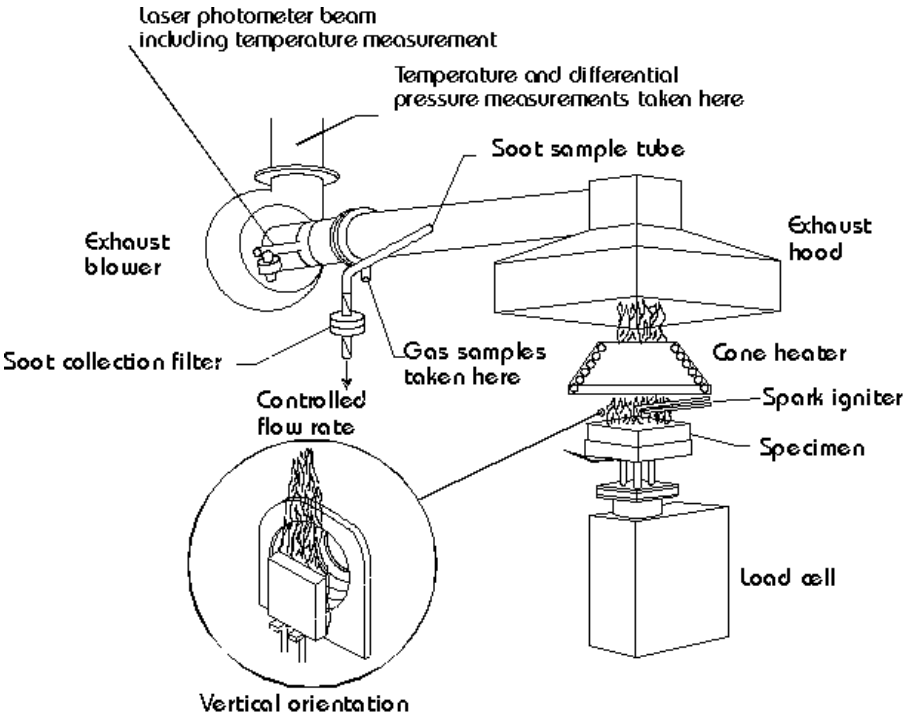

Figure 3-6. Cone Calorimeter Schematic

Several measurements can be obtained from the cone calorimeter. The cone calorimeter at UDRI is equipped with a laser for smoke measurements (laser photometer beam in Figure 3-6), oxygen sensor (paramagnetic) for measuring oxygen consumption, and load cell for measuring mass loss as the sample pyrolyzes during heat exposure. The instrument at UDRI also has a CO/CO_2 (infrared-based) detection system, allowing for the measurement of CO/CO_2 production as a function of time during sample combustion. From these parts of the instrument, various measurements are collected during each test which can reveal scientific information about material flammability performance. These include:

- Time to ignition (Tig): Measured in seconds, this is the time to sustained ignition of the sample. Interpretation of this measurement assumes that earlier times to ignition mean that the sample is easier to ignite under a particular heat flux.
- Heat Release Rate (HRR): The rate of heat release, in units of kW/m^2, as measured by oxygen consumption calorimetry.
- Peak Heat Release Rate (Peak HRR): The maximum value of the heat release rate during the combustion of the sample. The higher the peak HRR, the more likely that flame will self-propagate on the sample in the absence of an external flame or ignition source. Also, the higher the peak HRR, the more likely that the burning object can cause nearby objects to ignite.
- Time to Peak HRR: The time to maximum heat release rate. This value roughly correlates the time it takes for a material to reach its peak heat output, which would in turn sustain flame propagation or lead to additional flame spread. Delays in time to peak HRR are inferred to mean that flame spread will be slower in that particular sample, and earlier time to peak HRR is inferred to mean that the flame spread will be rapid across the sample surface once it has ignited.
- Time to Peak HRR – Time to Ignition (Time to Peak HRR – Tig): This is the time in seconds that it takes for the peak HRR to occur after ignition rather than at the start of the test (the previous measurement). This can be meaningful in understanding how fast the sample reaches its maximum energy release after ignition, which can suggest how fast the fire grows if the sample itself catches fire.
- Average Heat Release Rate (Avg HRR): The average value of heat release rate over the entire heat release rate curve for the material during combustion of the sample.
- Starting Mass, Total Mass Lost, Weight % Lost: These measurements are taken from the load cell of the cone calorimeter at the beginning and end of the experiment to see how much total material from the sample was pyrolyzed/burned away during the experiment.
- Total Heat Release (THR): This is measured in units of MJ/m^2 and is the area under the heat release rate curve, from time to ignition to time to flameout, representing the total heat released from the sample during burning. The higher the THR, the higher the energy content of the tested sample. THR can be correlated roughly to the fuel load of a material in a fire, and is often affected by polymer chemical structure.
- Total Smoke Release: This is the total amount of smoke generated by the sample during burning in the cone calorimeter from time to ignition to time to flameout. The higher the value, the more smoke generated either due to incomplete combustion of the sample, or due to polymer chemical structure. Note that this is a light obscuration measurement, and the smoke measurement does not discriminate between particulate matter (PM) which obscures light and organic vapors/pyrolyzed molecules which also may obscure light.
- Maximum Average Rate of Heat Emission (MARHE): This is a fire safety engineering parameter,[27] and is the maximum value of the average rate of heat emission, which is defined as the cumulative heat release (THR) from time t=0 to t divided by time t. The MARHE can best be thought of as an ignition modified rate of heat emission parameter, which can be useful to rank materials in terms of ability to support flame spread to other objects.
- Fire Growth Rate (FIGRA): This is another fire safety engineering parameter, determined by dividing the peak HRR by the time to peak HRR, giving units of kW/m^2 per second. The FIGRA represents the rate of fire growth for a material once exposed to heat, and higher FIGRA suggest faster flame spread and possible ignition of nearby objects.

- CO/CO_2 Yields: This is the total measured amounts of CO/CO_2 measured during testing, pre-ignition and post-ignition. The yields are in units of kg gas (CO, CO_2) per kg sample.

3.3.2 Cone Calorimeter Testing Methods

Circuit board samples were provided as very thin (0.4mm to 0.6mm thick) epoxy + e-glass laminates. These laminates contained copper plating in squares on both sides of the laminates and were cut in such a way that each sample had the same amount of copper metal present in the same configuration. Since the laminates provided were too large to be tested as is in the cone calorimeter, the samples were cut into 100 cm^2 square ($\pm 0.1 cm^2$) pieces for cone calorimeter testing. Samples were not conditioned in any way prior to testing. All of the samples were tested as single ply laminates, with some of the laminates also having ground component powder put upon them in 10g batches prior to testing in the cone. Any powder used was weighed out right before the cone experiment and spread evenly across the sample surface. The powder was not conditioned before use but was always kept in a sealed jar and was weighed out with a typical benchtop digital scale (accurate to +/- 10mg).

Samples tested included epoxy with brominated flame retardant (BFR), epoxy with non-flame retardant (NFR), and two epoxies each with different halogen-free flame retardant additives (HFR). Powders put on the board samples include standard halogen-containing component powder (P) and low halogen-containing component powder (PHF).

Cone calorimeter experiments were conducted on a FTT Dual Cone Calorimeter as per the ASTM E-1354-07 method at two heat fluxes (50 kW/m^2 and 100 kW/m^2). Samples were tested in triplicate without frame and grid, with the back side of each sample wrapped in aluminum foil. The only deviation from the ASTM method was that an exhaust flow of 15 L/s was used instead of the standard 24 L/s exhaust flow rate. The lower flow rate was used to better mimic the "open burning" fire scenario as the normal 24 L/s flow rate would give more oxygen to the fire than is typically seen in a "open burning" flaming combustion scenario. Heat release rate data from cone calorimeter can be found in Appendix A: Circuit Board Flammability Data.

3.3.3 Sampling Train

The total sampling train was designed and constructed specifically for these experiments to collect the total exhaust gas emitted from the combustion of samples in a standard cone calorimeter (Figure 3-7 and Figure 3-8). Sampling the total exhaust reduces the amount of sample that has to be burned to characterize and quantify emissions. The exhaust duct on the FTT Dual Cone Calorimeter from Fire Testing Technology Limited, UK, was modified to enable connecting of the total sampling train. The exhaust hood above the combustion zone was connected to the sampling exhaust duct (110mm in diameter) with a cooling jacket (not used for these experiments). The sampling exhaust duct was connected to a stainless steel filter holder 61cm x 25.5cm x 2.5cm. The filter holder holds three 20.5cm x 25.5cm filters. The filter holder was connected to an amber-glass coiled-condenser to cool the hot gas flowing before it entered an amber-glass cartridge containing four polyurethane foam (PUF) cartridges of 10cm x 5cm meant to capture semi-volatile organic compounds. Amber glass is important to note here since many of the chemical species of interest in this study can be UV light sensitive. The PUFs were retained by a fritted Teflon disk inside the cartridge. The gas exiting the PUFs was passed

through an impinger which was connected to a vacuum pump and the gas exiting the pump was directed to the cone calorimeter exhaust system through a wire reinforced vacuum tube.

At the beginning of each sampling period after assembling the sampling train, the system was checked for leaks. Once any leaks were fixed, the air flow was set to 15 L/s by turning the vacuum pump on and using a gate valve to control the air flow. All the circuit board laminate samples tested were exposed to a heat flux of 50 kW/m^2 or 100 kW/m^2. For additional details on the cone heater temperature (which is not the temperature that the samples encountered during burning), see Appendix B: Experimental Conditions. Once the cone reached its set temperature, the cone calorimeter ignition was turned on and samples were placed in the sample holder at the center of the cone heater and ignited. Once the samples ignited, they were allowed to burn until no flame and smoke were detectable. During sampling, the gas temperature inside the sampling train was constantly monitored at eight different positions. The first two thermocouples (T1 and T2) were placed inside the stainless steel duct at 5cm and 25.5cm from the exhaust hood above the cone to monitor the gas temperature entering the duct (T1) and entering the filter holder (T2). The third thermocouple (T3) was placed at the outlet of the filter holder (or entrance of condenser). The fourth thermocouple (T4) was positioned at the inlet of the PUF cartridge and the fifth thermocouple (T5) was placed to monitor the gas temperature exiting the PUF cartridge. The cold bath temperatures are adjusted to maintain the PUF cartridge exit gas temperatures (T5) to ~20-25°C. However, the average gas temperatures exiting the PUFs were ~30°C for all experiments. The other thermocouples were used to monitor the water bath temperatures for the stainless steel duct water jacket, the condenser, and the glass cartridge water jacket. All thermocouples used were 3mm sheath diameter, grounded, type K thermocouple probes from Omega Engineering, Stamford, Connecticut. During sampling, the pressure dropped inside the sampling train and the flow through the sampling train was constantly monitored by a digital gauge manometer placed at the pump inlet and by a differential flow meter on the cone calorimeter exhaust system, respectively. When the soot particles started to build up on the glass filter and decreased the gas flowing through it, the flow was adjusted by opening the gate valve situated at the inlet of the pump.

Post-sampling, the sampling train was disassembled; the condensate from the condenser was recovered to a pre-cleaned container for analysis, the various components of the train were covered with hexane-rinsed aluminum foil and transported to the recovery lab. In the recovery lab, the filters and PUFs were removed, the filters were weighed to determine their PM loading and the entire sampling train (from the hood and duct work above the cone/combustion zone) up to the inlet of the impinger was rinsed with three solvents (methanol, methylene chloride and toluene, respectively) to recover condensed material for analysis. All solvent rinses, condensate, PUFs and filters were stored in pre-cleaned amber glass containers with Teflon lined caps; the solvent levels were marked with the appropriate labels; and were refrigerated till they were either shipped to the analytical lab or were analyzed at UDRI using GC/MS. The glass fiber filter and PUF adsorbents were shipped to the Organic Support Laboratory (OSL) of EPA at RTP where they were combined together, extracted, and analyzed for PxDD/Fs. After extraction, the OSL of EPA at RTP shipped back a part of the PUF and Filter extract to UDRI to analyze for PAHs and phosphorous-containing compounds. The analytical methods used to quantify involved isotope dilution and internal standard procedures that are described later in Sections 3.6 through 3.8. After the final solvent rinse (i.e., toluene), the metal duct and filter holder were rinsed with

methylene chloride and covered with hexane-rinsed aluminum foil until the next experiment; the glassware was rinsed with Sparkleen soap solution/deionized water and baked at 475°C for 8 hours in a Barnstead Thermolyne Pyro-clean Trace oven for baking glassware. After baking, the glassware was rinsed with methylene chloride and covered with hexane-rinsed aluminum foil. A field blank was performed to check for carry over and memory effects.

All fluorescent lights in the laboratory, as well as in the fume hood, were covered with clear UV-absorbing filters supplied by UV Process Supply, Chicago, Illinois. This was done to minimize/eliminate decomposition of UV light sensitive compounds from the pre-sampling surrogates and samples recovered from the experiments. The three solvents used were toluene (Envisolv, 34413) and Methanol (Pestanal, 34485) purchased from Sigma-Aldrich, Milwaukee, Wisconsin and Methylene Chloride (Pestisolv, PS 724) purchased from Spectrum Chemicals, New Brunswick, New Jersey at purity levels required as per EPA method 23 for analysis of dioxins and furans. The 150 mm glass-microfiber filters (TE-EPM2000) without binder were purchased from Whatman, USA. The PUFs were purchased from Tisch Environmental. The PUFs and the filters were cleaned by the OSL at EPA, RTP by Soxhlet extraction with methylene chloride for 16 hours and wrapped in aluminum foil, labeled, and shipped to UDRI in airtight cans to use for sampling.

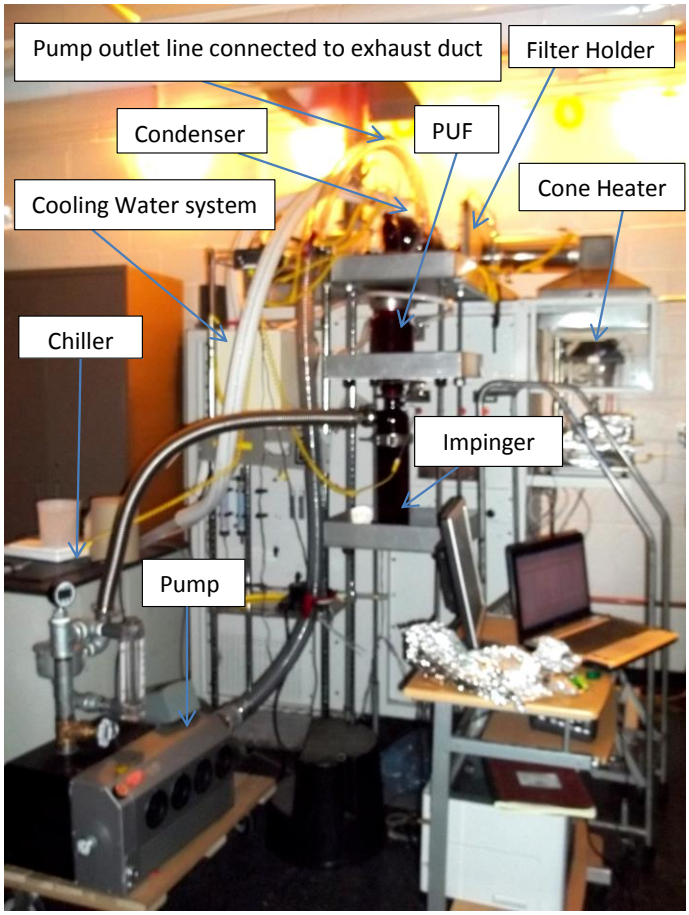

Figure 3-7. Total Sampling Train Coupled with UDRI Cone Calorimeter

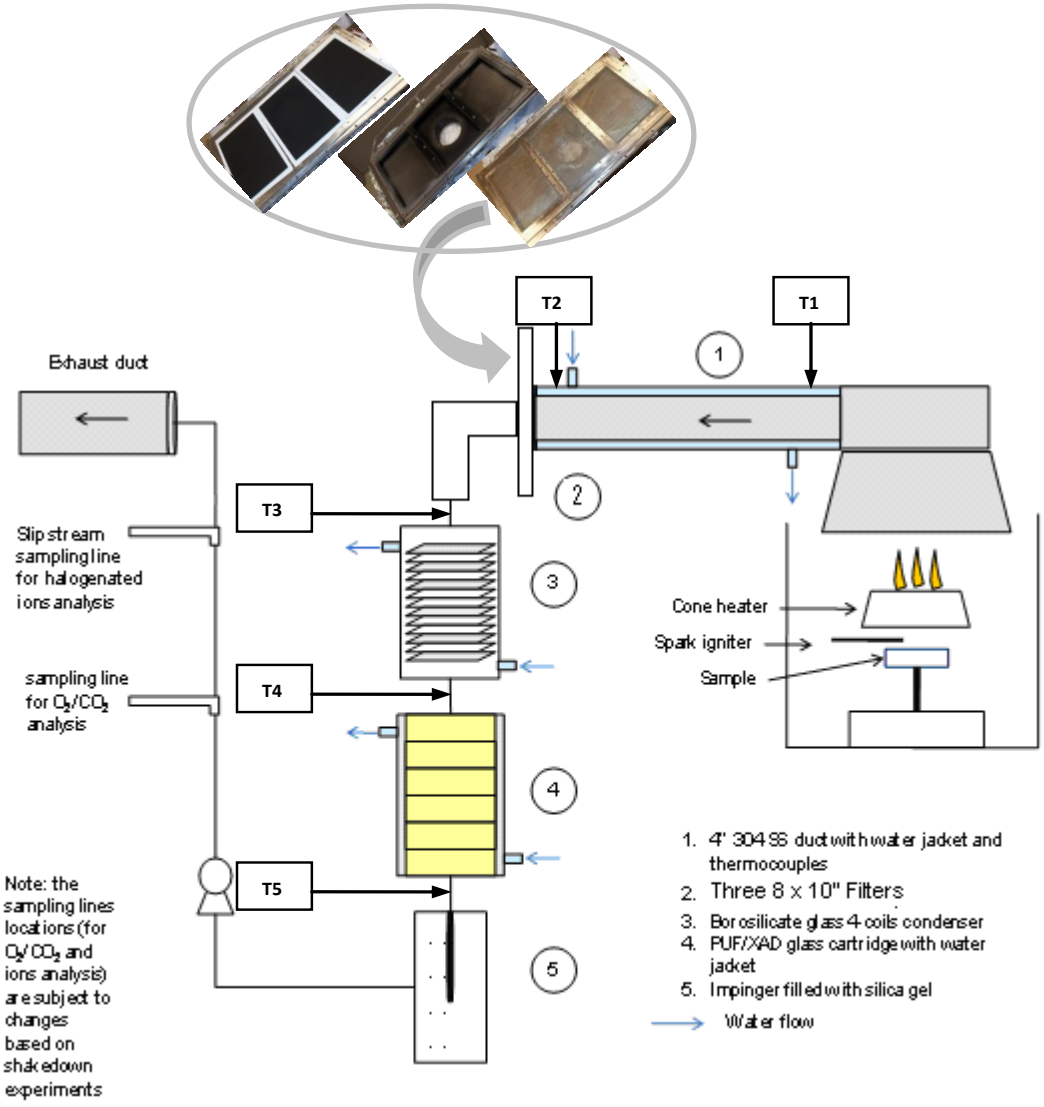

Figure 3-8. Schematic of Total Sampling Train

Prior to taking the sampling train from the sample prep/recovery lab to the cone test facility, the cleaned PUFs were placed in the glass cartridge and spiked with the necessary pre-sampling surrogates, the filters were weighed and placed in the filter holder and the glass cartridge and filter holder were sealed with hexane-rinsed aluminum foil and transported to the cone calorimeter laboratory with all other glassware and components also wrapped in hexane-rinsed aluminum foil. The printed circuit board laminate samples to be tested were also weighed and placed in a hexane-rinsed aluminum foil sample holder and were covered with hexane-rinsed aluminum foil.

3.3.4 Samples Tested

To ensure that enough material could be detected, especially in the case of small quantity compounds of interest (specific dioxins and PAHs), minimum levels of laminate and components

had to be tested; they were cut into 100cm^2 square pieces. Four types of laminates were tested for Phase II: laminate without flame retardant (NFR), laminate containing brominated flame retardant (BFR), laminate containing halogen-free flame retardant (HFR), and laminate containing halogen-free flame retardant (1556-HFR). The printed circuit board laminate samples were tested at two different heat fluxes to mimic different combustion scenarios. The lower heat flux (50 kW/m^2) was used to mimic an "open burn" type of event and the higher heat flux (100 kW/m^2) was used to mimic an incinerator furnace condition that would be encountered during incineration of the boards.

3.4 Sample Handling and Custody

3.4.1 Shipping Custody

Samples were collected at UDRI, packaged, and shipped by UPS to RTP. In RTP, the samples were received and brought to the laboratory and then opened by the laboratory custodian. The samples were stored in laboratory refrigerators until extraction. The sample custody form was included in the shipping cooler, and the UPS records are the custody records for the transfer from UDRI to RTP. The boxes and coolers were sealed with tape and the tape was removed in the laboratory.

3.4.2 Sample Identification and Log

Each sample was given an identifying laboratory code number and name (laboratory ID). The laboratory ID was assigned to the samples upon receiving and samples were logged in the sample ID log book along with the sample name and project description. The code sequence was explained to the laboratory personnel to prevent sample mislabeling. Proper application of the code simplified sample tracking throughout the handling, analysis, and reporting processes. Table 3-5 shows the laboratory ID coding that was used in this study. PUF and Filters were not given separate numbers.

Table 3-5 Laboratory ID Coding System

YYMMXX		
	Laboratory ID Code	**Sample Type**
	YYMM	Year and month of the sample logging in the laboratory system
	XX	Consecutive sample number of the given year (YY) and month (MM)

3.5 By-product Extraction

After the samples were collected and shipped back to RTP, the EPA OSL performed extraction, cleanup, and fractionation of samples provided by UDRI. The extracts were analyzed using High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) for target PCDD/Fs and PBDD/Fs (Table 3-6). The results were reported in a spreadsheet to UDRI for inclusion in the final report (results were reported as amounts per sampling train). In very early samples, less than ten percent of the dioxins and furans were found in the sampler rinses and the rinses would cause very high shipping costs, so only the PUF and filters from each sample were sent to RTP for extraction and analysis.

3.5.1 Organic Compound Target List

Chlorinated and brominated dioxins and furans (PCDD/Fs and PBDD/Fs, respectively) were targeted in this project. Analysis concerned 2,3,7,8-substituted congeners of PCDD/Fs (17 congeners) and their brominated counterparts (only 13 2,3,7,8 PBDD/Fs congeners were reported due to limited availability of commercial standards). Table 3-6 presents the congener-specific list of PCDD/Fs and PBDD/Fs target analytes.

Table 3-6. PCDD/Fs and PBDD/Fs Target Analytes

Congener Pattern	PCDD/Fs targets	PBDD/Fs targets
2,3,7,8	TeCDD	TeBDD
1,2,3,7,8	PCDD*	PBDD
1,2,3,4,7,8	HxCDD	HxBDD
1,2,3,6,7,8	HxCDD	HxBDD
1,2,3,7,8,9	HxCDD	HxBDD
1,2,3,4,6,7,8	HpCDD	HpBDD
1,2,3,4,6,7,8,9	OCDD	OBDD
2,3,7,8	TeCDF	TeBDF
2,4,6,8	***	TeBDF**
1,2,3,7,8	PCDF	PBDF
2,3,4,7,8	PCDF	PBDF
1,2,3,4,7,8	HxCDF	HxBDF
1,2,3,6,7,8	HxCDF	***
1,2,3,7,8,9	HxCDF*	***
2,3,4,6,7,8	HxCDF*	***
1,2,3,4,6,7,8	HpCDF	HpBDF
1,2,3,4,7,8,9	HpCDF	***
1,2,3,4,6,7,8,9	OCDF	OBDF

* Were reported as co-elution.
** FromTeBDF homolog group 2,4,6,8 -TeBDF can be reported because it was present in the calibration solution and therefore has an accurate retention time.
*** In the various calibration solutions, 18 different congener patterns were included, e.g. 2,3,7,8. Of the 18 individual congener patterns that were looked for, five were only in one of the solutions (either bromo or chloro).

3.5.2 EPA-RTP Experimental Strategy

Figure 3-9 presents the original experimental strategy for RTP's part of the project. The first phase of this project was extraction, cleanup and fractionation (described in detail in Section 3.5.3 and Section 3.5.4 of this report) of samples provided by UDRI for HRGC/HRMS instrumental analysis of PCDD/Fs and PBDD/Fs. The second phase described in detail in Section 3.6.2 was the instrumental analysis. The third phase of the analysis was data processing and reporting (see Section 3.6.3 for details).

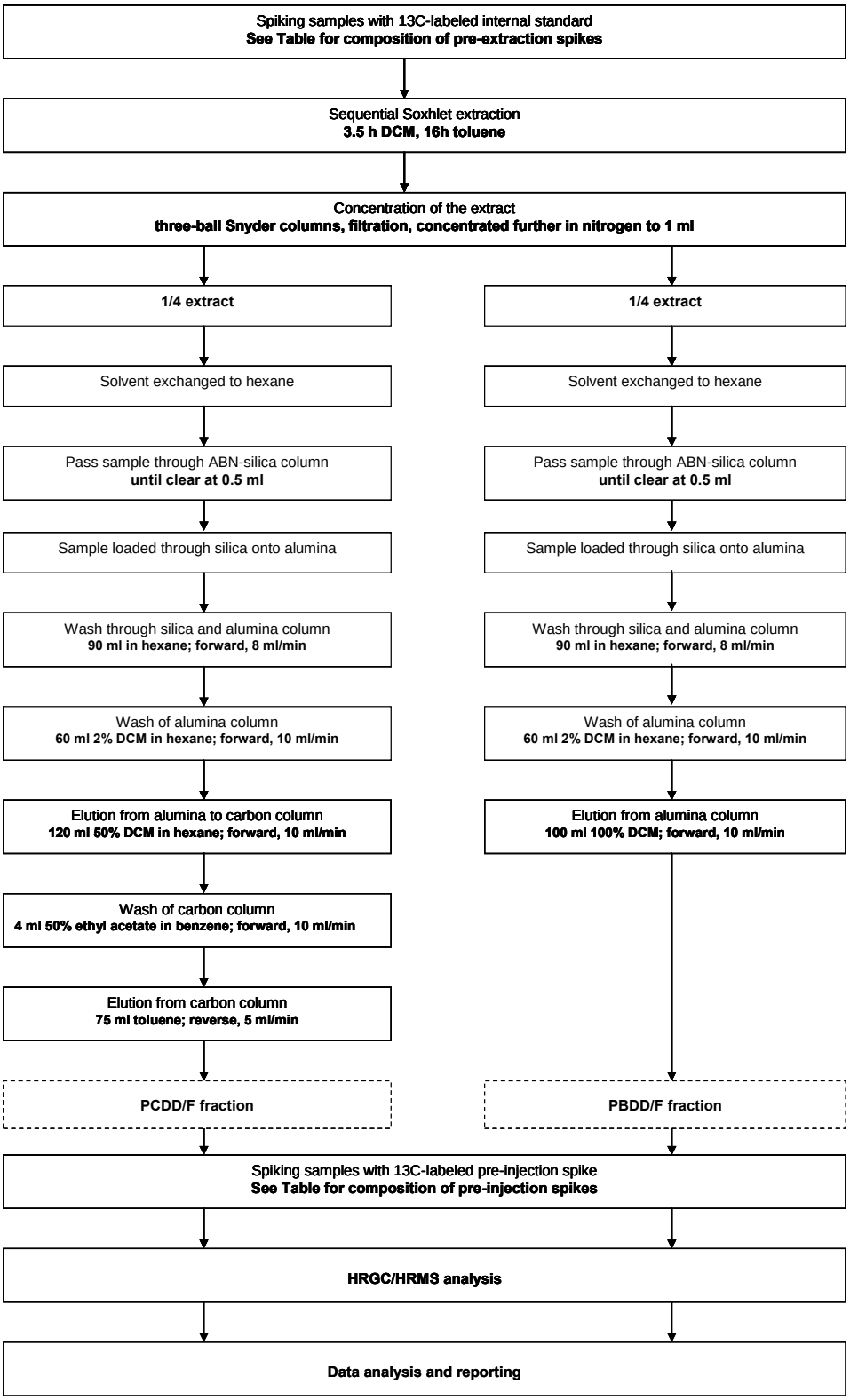

Figure 3-9. Original RTP Experimental Strategy.
The actual work added a step to the PCDD/Fs cleanup and dropped the PBDD/Fs cleanup.

3.5.3 Same-Sample Extraction of PCDD/Fs and PBDD/Fs

Extraction of sampling trains for PBDD/Fs and PCDD/Fs measurements was performed by sequential Soxhlet extraction: overnight (16 hours) with methylene chloride, followed by overnight (16 hours) extraction with toluene. This project had such a large sample volume that the regular 3.5 hours methylene chloride extraction did not give enough cycles for the extraction. Before extraction, samples were spiked with the internal standard mixtures. Pre-extraction spikes were purchased from Cambridge Isotope Laboratories Inc., Andover, Massachusetts (EDF-5408, EDF-4137A). The composition of ^{13}C-labeled PCDD/Fs and PBDD/Fs pre-extraction internal standard mixes is given in Table 3-7 and Table 3-8. All solvents were HPLC/GC/spectrophotometry grade ACS/HPLC certified (Burdick and Jackson, Honeywell, Muskegon, Michigan).

3.5.4 Cleanup and Fractionation of PCDD/Fs and PBDD/Fs

For determination of PBDD/Fs and PCDD/Fs, one-quarter of the extract was cleaned and fractionated using an automated liquid chromatography multicolumn Power Prep/Dioxin System (FMS Fluid Management Systems, Inc., Watertown, Massachusetts). One-twentieth of the extract was sent to UDRI for further analysis of other target compounds. The remainder of the extract was archived. Prior to the automated cleanup process, extracts were concentrated and then diluted in hexane, causing precipitation of non-dioxin-like compounds that could have caused interferences in the analysis. This step was repeated until no more precipitate formed and the extract was less than ten percent toluene. The extracts were then loaded and pumped sequentially through individual sets of FMS proprietary columns. Acidic and multilayer silica, carbon, and alumina columns were pre-packed, disposable cartridges available from FMS Fluid Management Systems, Inc., U.S.A. The previous experiments on HRGC/HRMS analysis of some combustion-related matrices showed interferences from other compounds that interfere with quantitative determination of the target compounds (PCDD/Fs and PCBs)[1]. This interference necessitates the introduction of an additional cleanup step, prior to the usual[2] automated PowerPrep liquid chromatography cleanup used in the OSL for same-sample determination of PBDD/Fs and PCDD/Fs from combustion flue gas. The additional step involved passing the extract through a large acidic silica gel column for the cleanup of the raw extract and concentration of the eluate to 0.5ml. This additional cleanup step was repeatedly performed until the extract was clear at 0.5ml volume. If the extract was not clear the eluate was diluted to 12ml with hexane and processed again. This clear 0.5ml of extract was then diluted to 12ml in hexane and processed through multilayer silica (4g acid, 2g base, and 1.5g neutral) column, followed by a basic alumina (11g) column and also a carbon column (0.34g). Composition of elution solutions and elution volumes are presented in Figure 3-9 of this report. To quantitate the PBDD from a single aliquot of extract, an additional step was added after the toluene elution of the carbon column, in which the alumina column was washed with 100ml of methylene chloride and that eluate was concentrated and exchanged into decane. In the later samples this portion was analyzed separately. It has been determined since the 2009 publication[2] that a separate FMS cleanup for the PBDD/Fs was not necessary, just this additional alumina

[1] Data not published, information archived and available from OSL.

[2] Tabor D., Gullett B.K., Same-Sample Determination of Ultratrace Levels of Polybromodiphenylethers, Polybromodibenzo-p-dioxins/Furans, and Polychlorodibenzo-p-dioxins/Furans from Combustion Flue Gas. Anal. Chem. 2009, 81, 4334–4342

column wash. Also, the removal of the carbon column step completely (as was done previously) was considered insufficient cleanup for most samples. The final eluates were then spiked with pre-analysis compounds, and then decane was concentrated to a final volume of about 25µl.

3.6 Dioxin/Furan Analysis

3.6.1 HRGC/HRMS Calibration and Maintenance

EPA methods require that a laboratory record be maintained of all calibrations, including daily calibration checks. These daily checks ensure continued reliable operation and provide the operator warnings of abnormal operation.
The following calibration activities were conducted:

- Daily optimization of the HRMS instrument was carried out using a perfluorokerosene (PFK) calibration standard; static resolving power checks were performed before and after data acquisition to demonstrate the required resolution of 10 000 (5% valley).
- Bromodioxin/furan and chlorodioxin/furan calibration standard solutions (please see Section 3.5.1. for details) were used for the initial calibration of the HRGC/HRMS. The medium concentration standard was used for calibration verification according to requirements of U.S. EPA M-23.[3]
- The daily calibration was acceptable if the concentration of each labeled and unlabeled compound is within the calibration verification limit of 25-30%. If all compounds met the acceptance criteria, calibration was verified and analysis of standards and sample extracts proceeded. When any compound failed its respective limit, recalibration for all congeners was performed. In addition, the ion abundance ratios were within the allowable control limits of 15%.

Instrument maintenance was conducted as recommended by the manufacturer and on an as-needed basis. Replacement parts, including columns and filaments, were maintained in the laboratory to minimize downtime. Service engineers' visits were utilized in major failure situations and for annual preventive maintenance.

3.6.2 HRGC/HRMS Analysis

For analysis of tetra- through octa-BDD/Fs, the GC was equipped with 15m DB-5 (0.25µm film thickness × 0.25mm i.d.) column (J&W Scientific, Folsom, California). For analysis of tetra- through octa-CDD/Fs, a 60m RTX-Dioxin-2 (Restek, Bellefonte, Pennsylvania) column was used (0.25µm film thickness × 0.25 mm i.d.).

The GC oven temperature for PBDD/Fs analysis was programmed from 130°C to 320°C at 10°C/min (21 minute hold). The temperature program for PCDD/Fs went from an initial temperature of 150°C to 260°C at 10°C/min with a final hold time of 55 minutes. The carrier gas (helium) flow rates were 1 and 1.2ml/min for PBDD/Fs and PCDD/Fs, respectively. The PCDD/Fs flow was ramped to 1.5ml/min after 15 minutes. Two microliters (2µL) of the extract

[3] U.S. EPA Test Method 23. Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors; Office of Solid Waste and Emergency Response, Environmental Protection Agency: Washington, DC, 1996.

was injected under splitless mode (injection port temperature set as 300°C and 270°C for brominated and chlorinated targets, respectively).

The HRMS was operated in an electron ionization (35 eV and 650 μA current) selective ion recording (SIR) mode at resolution R > 10 000 (5% valley). The temperature of the ion source was 280°C for the PBDD/Fs analyses, whereas for PCDD/Fs, the ion source was kept at 250°C. The two strongest ions in the molecular cluster were monitored in every retention time window for each native and labeled PBDD/Fs and PCDD/Fs based on mass spectroscopy libraries and literature data, unless interferences are present. Peak responses for each of the two selected molecular ion clusters must be at least 2.5 times the noise level (S/N > 2.5), otherwise the compound was considered below the limit of detection. The bromine/chlorine isotope ratio for the two molecular ion clusters was within ±15% of the correct isotope ratio, if not they were flagged EMPC (Estimated Maximum Possible Concentration).

The standards used for PBDD/Fs identification and quantification were a commercially available set of calibration standards that contained native target tetra- through octabromodioxins and/or furans at concentrations from 0.4 to 4.0 (CS-2) through 50-500 (CS-5) ng/ml depending on the degree of bromination (EDF-5407, CIL Cambridge Isotope Laboratories Inc., U.S.A.). The standards used for chlorinated dioxin/furan identification and quantification were a mixture of standards containing tetra- to octa-PCDD/Fs native and ^{13}C-labeled congeners designed for modified U.S. EPA Method 23 (ED-2521, EDF-4137A, EDF-4136A, EF-4134, ED-4135, CIL Cambridge Isotope Laboratories Inc., U.S.A.). The PCDD/Fs calibration solutions were prepared in house and contain native PCDD/Fs congeners at concentration from 1 (ICAL-2)-20 (ICAL-6) ng/ml.

3.6.3 Data Processing and Reporting

For the data collection, Mass Lynx software (Waters, Milford, Massachusetts), version 4.1 was used (including Target Lynx 4.1. for processing and quantitation). Data processing included not only the determination of PCDD/Fs and PBDD/Fs concentrations, but also the determination of the method detection and quantitation limits (LOD and LOQ, respectively). Every set of data was reported as ng per train. For PCDD/Fs analysis, data would have been reported as ng-TEQ per train, if the analyses were accepted (pre-sampling surrogate problems will be detailed later).

3.6.4 Quality Assurance/Quality Control

The data quality objectives (DQOs) define the critical measurements needed to address the objectives of the test program, and specify tolerable levels of potential errors associated with data collection as well as the limitations of the use of the data. The data quality indicators (DQIs) are specific criteria used to quantify how well the collected data meet the DQOs. The DQI goals for the critical measurements correspond to and are consistent with the standards set forth in each respective referenced EPA Method. DQI goals will correspond to recovery criteria of the labeled standards in the respective reference methods. The DQI goals specified for the respective sampling method used by UDRI sampling team, such as pre-sampling surrogates recoveries are not included in the DQOs, but were reported to UDRI, along with quality criteria guidelines.

Composition of labeled pre-sampling (surrogate standards), pre-extraction (internal standards) and pre-injection (recovery standards) spiking solutions are given in Table 3-7 and Table 3-8.

Table 3-7. Composition of the PCDD/Fs Sample Spiking Solution

Spiking Solution	Analytes	Concentration (µg/ml)	Special Notes
Surrogate standards (Field spikes) EDF-4136A*	$^{37}Cl_4$-2,3,7,8-TCDD	1.25	Added to the sample prior to sampling
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	
	$^{13}C_{12}$-2,3,4,7,8-PeCDD	2.5	
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	
Internal standards EDF-4137A*	$^{13}C_{12}$-2,3,7,8-TCDD	1.25	Added to the sample prior to extraction
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	2.5	
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	2.5	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	2.5	
	$^{13}C_{12}$-OCDD	5	
	$^{13}C_{12}$-2,3,7,8-TCDF	1.25	
	$^{13}C_{12}$-1,2,3,7,8-PeCDF	2.5	
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	2.5	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	2.5	
Recovery Standards ED-2521*	$^{13}C_{12}$-1,2,3,4-TCDD	5	Added to extracts prior to analysis
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	5	

*Commercially available from CIL Cambridge Isotope Laboratories Inc., U.S.A.

Table 3-8. Composition of the PBDD/Fs Sample Spiking Solution

Spiking Solution	Analytes	Concentration (ng/ml)	Special Notes
Surrogate standard (Field spikes) EF-5410*	$^{13}C_{12}$-1,2,3,4,7,8-TeBDF	100	Added to the sample prior to sampling
Internal standards EDF-5408*	$^{13}C_{12}$-2,3,7,8-TBDD	100	Added to the sample prior to extraction
	$^{13}C_{12}$-1,2,3,7,8-PeBDD	100	
	$^{13}C_{12}$-1,2,3,4,7,8-HxBDD	250	
	$^{13}C_{12}$-1,2,3,6,7,8-HxBDD	250	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDD	500	
	$^{13}C_{12}$-OBDD	750	
	$^{13}C_{12}$-2,3,7,8-TBDF	100	
	$^{13}C_{12}$-2,3,4,7,8-PeBDF	100	
	$^{13}C_{12}$-1,2,3,4,7,8-HxBDF	250	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDF	500	
	$^{13}C_{12}$-OBDF	750	
Recovery Standards EDF-5409*	$^{13}C_{12}$-1,2,3,7,8-PeBDF $^{13}C_{12}$-1,2,3,7,8,9-HxBDD	100 250	Added to extracts prior to analysis

*Commercially available from CIL Cambridge Isotope Laboratories Inc., U.S.A.

3.6.5 Pre-Sampling Spikes Quality Criteria and Performance

A group of carbon-labeled PBDD/Fs and PCDD/Fs congeners (Table 3-7. and Table 3-8) were added to the PUF sorbent before the sample was collected in UDRI. The surrogate recoveries were measured as relative to the internal standards and were a measure of the sampling train collection efficiency.

OSL provided results of pre-sampling spikes recovery to UDRI, using the acceptance criteria outlined in Table 3-9.

Table 3-9. Pre-Sampling Spike Recovery Limits [%]

Pre-sampling spike	Minimum	Maximum
PCDD/Fs	%	%
$^{37}Cl_4$-2,3,7,8-TeCDD	70.0	130
$^{13}C_{12}$-2,3,4,7,8-PCDF	70.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	70.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	70.0	130
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	70.0	130
PBDD/Fs	%	%
$^{13}C_{12}$-1,2,3,4,7,8-TeBDF	70.0	130

The pre-sampling surrogates recovery acceptance criteria were as recommended by U.S. EPA Method 23 for chlorinated dioxins.[4] There is no standard method guidance for PBDD/Fs pre-sampling surrogates recovery; hence Method 23 acceptance criteria were used for brominated targets.

Upon analysis of the PCDD/Fs samples, the pre-sampling surrogates were found to be absent from seven of the ten samples requested for PCDD/Fs analysis. Because this constituted a large majority of the PCDD/Fs samples and that there were no PCDD/Fs detected in the first phase of this project, the investigators decided not to report PCDD/Fs data. In the samples that were analyzed, there were virtually no PCDD/Fs detected consistent with the first phase of the project but it would be consistent with complete loss of target compounds which is highly unlikely given the PBDD/Fs data. Given both of these possibilities, not reporting the data was of the most objective action.

There was significant brominated interference in 6 of 18 tests. The six tests with bromine interference were all the samples that had standard halogen-containing ground components added. This reduced the number of measured experimental samples to 12. In the PBDD/Fs samples there was also a brominated pre-sampling surrogate. The recoveries for the 12 samples ranged from 0.8% recovery to 234% recovery. Four samples appear to have been double-spiked with recoveries near 200% and the sample near 0% recovery was probably not spiked. Five of the remaining samples were between 90 and 110% recovery. The other two samples had low recovery which was not likely due to spiking problems.

3.6.6 Pre-Extraction Spikes Quality Criteria

A group of 11 PBDD/Fs and 9 PCDD/Fs ^{13}C-labeled internal standards (see Table 3-7. and Table 3-8), representing the tetra- through octa-halogenated homologs, were added to every sample

[4] U.S. EPA Test Method 23. Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors; Office of Solid Waste and Emergency Response, Environmental Protection Agency: Washington, DC, 1996.

prior to extraction. The role of the internal standards is to allow quantification (via the isotope dilution internal standard methodology) of the native targets in the sample as well as to determine the overall method efficiency.

Recovery criteria for the internal standards of PBDD/Fs and PCDD/Fs are given in Table 3-10.

Table 3-10. Pre-Extraction Spike Recovery Limits [%]

Pre-extraction spike	Minimum	Maximum
PCDD/Fs	%	%
$^{13}C_{12}$-2,3,7,8 TeCDF	40.0	130
$^{13}C_{12}$-2,3,7,8 TeCDD	40.0	130
$^{13}C_{12}$-1,2,3,7,8 PCDF	40.0	130
$^{13}C_{12}$-1,2,3,7,8 PCDD	40.0	130
$^{13}C_{12}$-1,2,3,6,7,8 HxCDF	40.0	130
$^{13}C_{12}$-1,2,3,6,7,8 HxCDD	40.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8 HpCDF	25.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8 HpCDD	25.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8,9 OCDD	25.0	130
PBDD/Fs	%	%
$^{13}C_{12}$-2,3,7,8-TBDF	40.0	130
$^{13}C_{12}$-2,3,7,8-TBDD	40.0	130
$^{13}C_{12}$-2,3,4,7,8-PeBDF	40.0	130
$^{13}C_{12}$-1,2,3,7,8-PeBDD	40.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxBDF	40.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxBDD	40.0	130
$^{13}C_{12}$-1,2,3,6,7,8-HxBDD	40.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDF	25.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDD	25.0	130
$^{13}C_{12}$-OBDD	25.0	130
$^{13}C_{12}$-OBDF	25.0	130

The pre-extraction internal standard recovery acceptance criteria were as recommended by U.S. EPA Method 23 for chlorinated dioxins.[5] There is no standard method guidance for PBDD/Fs pre-extraction internal standards recovery; U.S. EPA Method 23 criteria were therefore used for brominated targets.

[5] U.S. EPA Test Method 23. Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors; Office of Solid Waste and Emergency Response, Environmental Protection Agency: Washington, DC, 1996.

As was mentioned before, the PCDD/Fs results were considered not reportable and the pre-extraction results are not reported as well.

The brominated pre-extraction spikes mostly passed the PCDD/Fs criteria up to the hexa congeners but the hepta and octa congeners were frequently below the PCDD/Fs criteria although detectable. In the original QAPP, the table for the PBDD/Fs pre-extraction spike criteria was not the table of criteria specified in the Method 23 for PCDD/Fs pre-extraction spikes (Table 3-10).

3.7 Polyaromatic Hydrocarbon Analysis

Combustion by-products were collected into PUF and filter and Soxhlet extracted using both methylene chloride and toluene, yielding two separate samples for analysis. The sampling train was also rinsed sequentially with methanol, methylene chloride, and toluene following each experiment to collect any by-products that may not have been collected by the PUF or filter. The methanol rinse was solvent extracted with the methylene chloride rinse (liquid-liquid extraction) and separated, yielding two separate samples from the three rinses. Therefore, UDRI tested four different sample media for the presence of PAHs: (1) methylene chloride from methanol and methylene chloride rinses, (2) toluene rinse, (3) methylene chloride Soxhlet extraction of PUF and filter, and (4) toluene Soxhlet extraction of PUF and filter. Using samples from brominated laminate tests, the PAH content of the rinses were compared to the PAH content of the PUF/filter extracts. Methylene chloride and toluene rinses from experiments with BFR + P - 50 (E6), BFR - 100 (E15), and BFR + PHF - 50 (E30) were analyzed (for Experiment # see Appendix B: Experimental Conditions). Experiment BFR - 100 (E15) was used to analyze the toluene rinse and was compared to the extract. For methylene chloride, most of the PAHs (EPA list of priority PAHs) in the rinse were estimated to be <10% of the magnitude of the PAHs from the extract. This excludes naphthalene and compounds lighter than fluorine where breakthrough was likely. The naphthalene and lighter compounds were less than 1% in the rinses when compared to the PUF/filter extracts. Even in the extract, the naphthalene signal was significantly smaller than the other PAHs detected probably due to breakthrough through the PUF. UDRI found ~90% of the PAHs to be in the methylene chloride extracts compared to <10% in the methylene chloride rinses. The level of PAHs detected in the toluene extract was <1% and in the toluene rinse was <0.1%. These findings and budgetary constraints led the researchers to decide to only analyze the methylene chloride extracts. PAHs were thus only measured for the methylene chloride extraction samples for the remainder of the project.

3.8 Organophosphorus and Chlorinated Benzene/Phenol Analysis

The chromatograms from PAH analysis were used to generate library search reports to determine the presence of organophosphorous compounds. In addition, since no attempt was made to analyze for chlorinated dioxins and furans due to reasons explained in Section 3.6.5, an attempt was made to determine the presence of chlorinated benzenes and phenols known to be precursors for the formation of halogenated dioxins and furans. The following integration events were used when generating the library search reports: initial area reject at 1%; initial peak width of 0.02; shoulder detection off; initial threshold of 16. The compound with the highest match quality is reported for the compounds detected.

4 Results and Discussion

The purpose of this study as part of the U.S Environmental Protection Agency (EPA) Design for the Environment (DfE) program was to understand the potential emissions of halogenated dioxins or furans, and polyaromatic hydrocarbons (PAHs) from burning circuit board laminates. This objective was achieved by using the cone calorimeter to expose circuit board laminates to simulated combustion scenarios under ventilated fire conditions (15 L/s) at two heat fluxes (50 kW/m^2 and 100 kW/m^2). The 50 kW/m^2 heat flux was chosen to mimic open burn conditions when circuit boards are improperly burned for precious metal recovery. The higher heat flux, 100 kW/m^2, was chosen to mimic incineration conditions that would be used to recover/smelt away precious metals and properly dispose of e-waste. Since the sampling train for this study prevented the normal collection of oxygen consumption calorimetry data (Sections 3.3.1 to 3.3.3), experiments were done using the normal cone calorimeter exhaust system to collect data for heat release (see Appendix A: Circuit Board Flammability Data), smoke yield, fire safety information, oxygen consumption rates, CO/CO_2 production rates, and effective heats of combustion needed to attempt to correlate back to observed emission products. The emphasis of this section of the report is on the emissions observed from the cone calorimeter (smoke, CO/CO_2) which will then be later compared to the emissions data collected from the sampling train.

4.1 Total Mass Burned

The total mass of each type of printed circuit board laminate sample burned for the cone calorimeter total sampling train experiments is given in Table 4-1. Total mass is important for determining emissions factors; the amount of flammable mass burned will determine how much total emissions are obtained.

Table 4-1. Total Mass Burned Per Sample

Sample Description-Heat Flux (kW/m^2)	Total Mass Burned per Sample (g)
BFR - 50	11.8
BFR - 50	13.6
BFR - 100	14.3
BFR - 100	15
BFR + P - 50	20
BFR + P - 50	20.4
BFR + PHF - 50	18.2
BFR + PHF - 50	17.3
HFR - 50	8.9
HFR - 50	8.1
HFR - 100	13.3
HFR - 100	13.3
HFR + P - 50	18.1
HFR + P - 50	19.8
HFR + PHF - 50	19.6
HFR + PHF - 50	18.6
1556 HFR - 50	9.3
1556 HFR - 50	9.7
1556 HFR + P - 50	17.9
1556 HFR + P - 50	17.8
1556 HFR + PHF - 50	16.4
1556 HFR + PHF - 50	15.9
NFR - 50	16.5
NFR - 50	15.6
NFR - 100	7.9
NFR - 100	8.8

4.2 Smoke

Smoke data obtained using the standard cone calorimeter (without the total sampling train) for all of the printed circuit board samples are shown in Table 4-2. Total smoke release was affected by both component blend and flame retardant chemistry, with flame retardant chemistries always having higher smoke release than the non-flame retardant samples. It should be noted that smoke release in the cone calorimeter is a simple light obscuration measurement and may be composed of many different components. While smoke is a good indication of incomplete combustion, its presence cannot be directly correlated to emissions of concern (PM, PAH, dioxins, etc.). Instead, smoke provides some insight into likely emissions trends from the different flame retardant chemistries.

Table 4-2. Smoke Release Data

Sample Description-Heat Flux (kW/m^2)	Average smoke release. N=3 per sample* (m^2/m^2)
NFR - 50	222.03
BFR - 50	479.10
HFR - 50	250.80
1556 HFR - 50	246.33
NFR - 100	214.73
BFR - 100	439.77
HFR - 100	264.83
BFR + P - 50	691.80
HFR + P - 50	438.53
1556 HFR + P - 50	397.43
BFR + PHF - 50	468.13
HFR + PHF - 50	353.43
1556 HFR + PHF - 50	309.23

* Raw data listed in appendix

The smoke release information is also presented in Figure 4-1 and the following conclusions can be made.

Brominated Flame retardant (BFR) – When compared to the other chemistries, BFR smoke release was more than 50 to 90% greater than HFR samples. This is expected due to the flame retardant mechanism of BFR which inhibits vapor phase combustion and in turn creates more smoke. As heat in the flame increases due to higher heat flux, more of the smoke should burn away and total smoke should decrease; this is observed in Figure 4-1.

Halogen-Free Flame retardant (HFR) **and** ***1556 Halogen-Free Flame retardant (1556 HFR)*** – Due to the mechanism of flame retardancy, which should be condensed phase char formation assuming that the halogen-free flame retardants are phosphorus-based, lower smoke release is observed compared to the BFR laminates. Unlike the BFR laminates, as heat flux is increased for HFR, a slight increase (5.6 %) in total smoke was observed compared to NFR(-4.6%). This may be due to the fact that the higher heat flux of burning is causing more of the PAHs in the char of the samples to become pyrolyzed and form soot and condensed phase soot precursors. However, this difference between NFR and HFR samples is within the percentage error of the cone calorimeter smoke measurement device (± 10%). The difference should be considered with caution even though the trend was reproducible with the triplicate cone calorimeter experiments conducted.

No Flame retardant (NFR) – These materials show the lowest smoke release as expected since they have no flame retardants present. However, the difference compared to HFR is within the margin of error of the measurement device as described above.

Halogenated and Low-Halogen Components – The addition of powdered components produced variable smoke release results (-2.2 to 74.6 %) compared to the laminates alone. For example, the addition of halogen containing components to BFR increased smoke by 44.2%, but when low-halogen component powders were present, total smoke was reduced by 2.2%. The addition of halogen containing components to halogen-free laminates provided the highest increases in smoke release 74.6% and 61.3% for HFR and 1556 HFR laminates respectively. Halogen-free component powders yielded a smaller increase in smoke compared to the halogen-containing component powders, with a reduction in total smoke (2.2%) seen with BFR laminates, and only a 40.9% and 25.6% increase for HFR and 1556 HFR laminates respectively. The extra flammable mass in both powders contributes to some smoke from burning, but the presence of halogen increased smoke release even more.

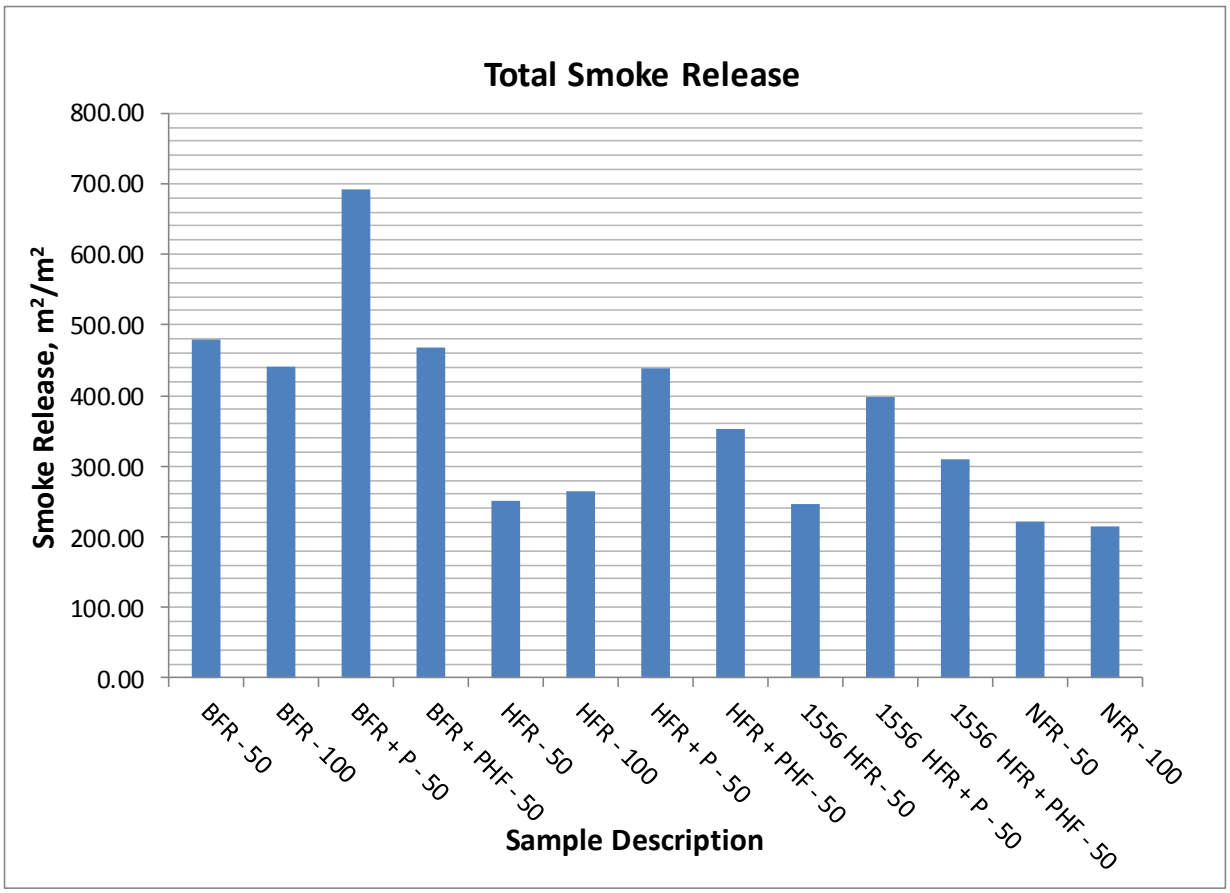

Figure 4-1. Smoke Release Plot

4.3 CO/CO_2 Emissions

The brominated FR laminates, with or without components, show lower emissions of CO_2 than the other sample types (1.05 to 1.28 kg/kg compared to 1.3 to 1.62 kg/kg for HFR and 1.85 and 1.67 kg/kg for NFR) (Table 4-3 and Figure 4-2). Less total CO_2 is observed because bromine inhibits full combustion of carbon to CO_2. However, a significant increase in CO is not always observed with the samples tested in this study when CO_2 emissions decrease. Therefore, the data only support the idea that the brominated FR compounds reduce total CO_2 emissions when

combusted under open burn (50 kW/m^2 heat flux) or incinerator (100 kW/m^2 heat flux) conditions. The mass balance of emissions must lie in other gases and compounds if the CO_2 emissions are lower. The non-halogenated FR laminates have similar CO yields when compared to the BFR compounds, but higher CO_2 yields. This makes sense in that the flame retardants are causing more char formation, which would lower the total amount of carbon that is combusted. Since the non-halogenated laminates do not contain halogens that can affect combustion chemistry, CO_2 yields should be higher. The non-flame retardant samples burn with the highest CO_2 yields but have CO emissions roughly equal to or higher than the other flame retardant systems when burned at low heat flux (50 kW/m^2). This is because in the flame retardant systems, potential carbon is present as PAHs and soot rather than being partly oxidized. Total mass burned (total potential carbon that could convert to CO or CO_2; see **Table 4-1**) does not seem to correlate well to average CO and CO_2 emissions, allowing combustion chemistry of the boards, flame retardants, and components to explain to CO/CO_2 emissions factors.

Table 4-3. CO/CO_2 Emission Factors

	Av Post Ignition	
	CO Yield	CO_2 Yield
Sample Description-Heat Flux (kW/m^2)	(kg/kg)	
BFR - 50	0.15	1.05
BFR - 100	0.14	1.06
BFR + P -50	0.13	1.12
BFR + PHF - 50	0.14	1.28
HFR - 50	0.18	1.59
HFR - 100	0.11	1.44
HFR + P - 50	0.16	1.50
HFR + PHF - 50	0.12	1.52
1556 HFR - 50	0.12	1.42
1556 HFR + P - 50	0.10	1.30
1556 HFR + PHF - 50	0.10	1.62
NFR - 50	0.20	1.85
NFR - 100	0.07	1.67

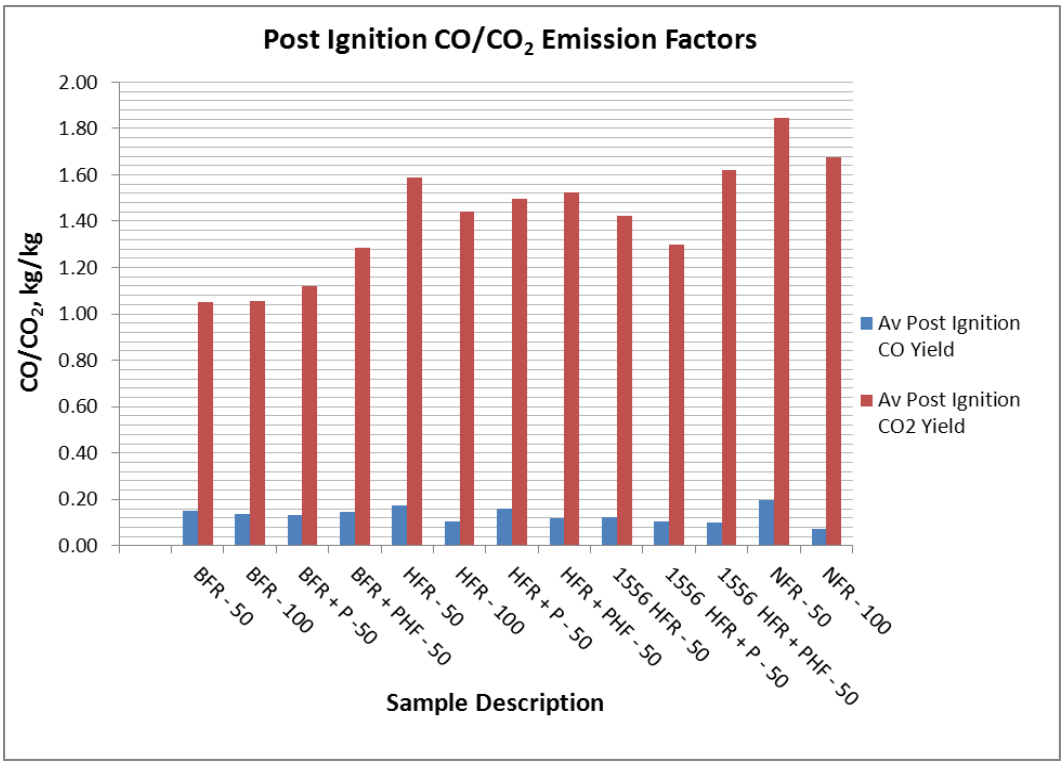

Figure 4-2. CO/CO_2 Emission Factors Plot

4.4 Particulate Matter Emissions

The cone calorimeter data (Table 4-4 and Figure 4-3) demonstrates that most of the samples have similar PM emissions when components are present, but can vary depending on base resins. The halogen-free flame retardant (HFR) at 50 kW/m^2 has the highest level (40% higher than BFR 50 kW) of PM emitted during burning. This relates to the condensed phase mechanism of action, where the phosphorous flame retardant reacts with the polymer and is involved in its charring. These charred and cross-linked polymer components will have chemical structures similar to soot precursors, and as those molecules pyrolyze off the surface of the burning circuit board, higher amounts of PM may be seen. The BFR compounds do show some higher PM emissions when compared to the NFR and HFR + component blends. While smoke yields were higher for BFR compounds compared to other sample types (Table 4-2 and Figure 4-1), PM was not always higher for BFR. This may simply indicate that the smoke produced by burning BFR materials is not captured by the PM filters in our experiments or that the smoke measured by the cone calorimeter system was not a particulate but was instead organic vapors which obscured light.

Table 4-4. PM Emission Factors

Sample Description-Heat Flux (kW/m^2)	PM, g/kg fuel in
BFR - 50	24.05
BFR - 100	23.11
BFR + P - 50	22.66
BFR + PHF - 50	20.85
HFR - 50	33.48

Sample Description-Heat Flux (kW/m^2)	PM, g/kg fuel in
HFR - 100	21.02
HFR + P - 50	18.59
HFR + PHF - 50	19.32
1556 HFR - 50	23.54
1556 HFR + P - 50	17.93
1556 HFR + PHF - 50	13.42
NFR - 50	17.28
NFR - 100	17.70

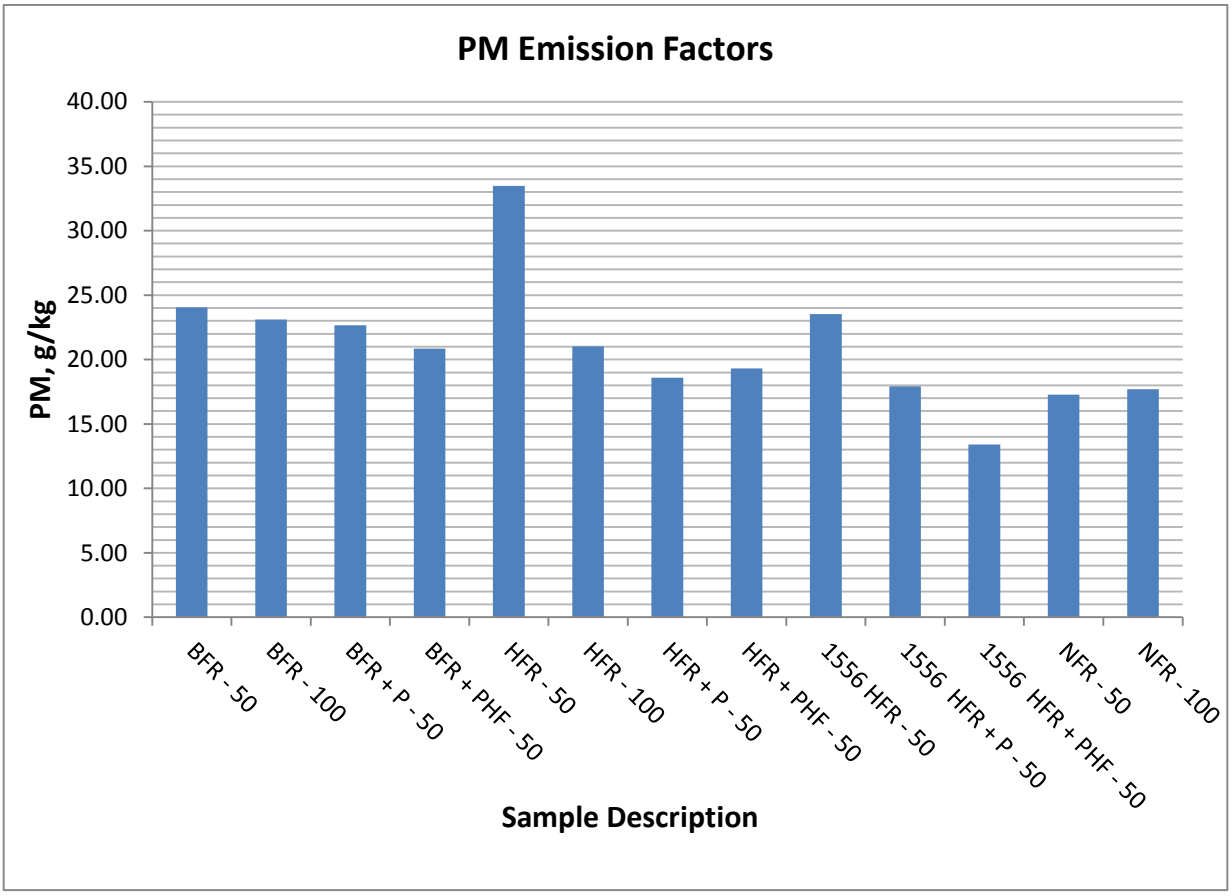

Figure 4-3. Particular Matter (PM) Emission Factors

4.5 PBDD/Fs and PCDD/Fs Emission Factors

Printed circuit board combustion at UDRI generated 42 samples for analysis. Not all samples were analyzed for PCDD/Fs and PBDD/Fs due to resource limitations; instead a relevant subset of samples was selected for analysis. The laminate samples containing brominated flame retardant tested at 50 kW/ m^2 alone and with halogenated components or with low halogen components, and at 100 kW/m^2 alone, and the necessary blanks were analyzed for PCDD/Fs and PBDD/Fs. This approach resulted in nine samples being selected for PCDD/Fs analysis, and 14

samples selected for PBDD/Fs analysis at EPA. Due to problems with the pre-sampling spike, the PCDD/Fs analysis was not quantitated. In the PBDD/Fs analysis, four blanks were added to the fourteen samples selected, yielding 18 samples. Of the 18 total samples, 12 were able to be quantitated. The six samples that could not be quantitated were of brominated flame retardant with halogenated components. The quantitation could not be done due to significant interference that caused the internal standards to not be useable for quantitation. Analysis of one sample on a LRMS in full scan resulted in insufficient sensitivity to identify the compound emissions.

PBDD/Fs compounds were quantitated in 12 samples. Six of these samples were BFR laminates and six were combustion blanks. Five of the six blanks had significantly lower levels of PBDD/Fs compared to the laminate samples. For the higher concentrated PBDD/Fs detected, the difference in detection level between the combustion blanks and the BFR laminates was as large as a factor of 100. For example, the detection of 1,2,3,4,6,7,8 - HpBDF in all but the first blank ranged from not detected to 0.3 ng/train compared to 4 to 9 ng/train for the six BFR laminate samples. In a system that is as complex as the calorimeter and has as many reused parts very low levels in the actual heated calorimeter blanks are not surprising.

The chromatographic peaks for the 2,3,7,8 congeners were small compared to the non-2,3,7,8 congeners based on visual confirmation. This finding was confirmed by quantification of a single non-2,3,7,8 congener. 2,4,6,8-TeBDF congener was a factor of four higher than the highest of the 2,3,7,8-Br-substituted toxic congeners in the samples. Other visible brominated compounds in the chromatograms were of similar concentrations.

The total PBDD/Fs emission from the cone calorimeter experiments shown in Table 4-5 and Figure 4-4 indicate that brominated flame retardant (BFR) laminates have higher total PBDD/Fs emission factors than brominated flame retardant laminates with halogen-free components. For all six brominated samples, PBDD/Fs were released in the range of 1.89 to 4.14 ng/g (Table 4-5) with variability that suggests there is no large difference between each sample based on only N=2. Figure 4-4 is based on the average emission factors and suggest differences in the samples that cannot be conclusive without larger sample sizes.

Brominated dioxins and furans were not analyzed in the NFR and HFR systems since these systems were free of brominated FR structures (TBBPA) that could have formed PBDD/Fs compounds.

Interestingly, the addition of components did not appear to increase PBDD/Fs emissions. This may due to (1) a chemical interaction between the halogen-free component powder and PBDD/Fs, (2) a dilution effect from the additional non-halogenated mass burned contributing to the total mass lost used in the emission factor calculation, or (3) a combination of both. At this time, it is not be possible to clearly discern given the data scatter between the replicates shown in Table 4-5.

Based on the available data, the conclusion is that PBDD/Fs are detected in the emissions of these brominated samples.

Table 4-5. PBDD/Fs Emission Factors

Analyte	Sample Description - Heat flux (kW/m^2)					
	BFR - 50	BFR - 50	BFR - 100	BFR - 100	BFR + PHF-50	BFR + PHF-50
ND=0,EMPC=EMPC	ng/g					
2,3,7,8 - TBDD	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1,2,3,7,8 - PeBDD	3.72E-01	1.79E-01	1.85E-01	3.25E-01	1.20E-01	1.42E-01
1,2,3,4,7,8 + 1,2,3,6,7,8 - HxBDD	1.38E-01	9.57E-02	1.25E-01	1.49E-01	8.79E-02	6.94E-02
1,2,3,7,8,9 - HxBDD	6.97E-02	4.68E-02	5.45E-02	7.65E-02	4.49E-02	3.16E-02
1,2,3,4,6,7,8 - HpBDD	8.76E-02	7.73E-02	1.42E-01	1.18E-01	7.36E-02	7.18E-02
1,2,3,4,6,7,8,9 - OBDD	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2,3,7,8 - TBDF	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1,2,3,7,8 - PeBDF	5.81E-01	0.00E+00	1.59E-01	2.24E-01	2.42E-01	2.79E-01
2,3,4,7,8 - PeBDF	8.90E-01	5.14E-01	2.47E-01	4.06E-01	3.60E-01	6.11E-01
1,2,3,4,7,8 - HxBDF	1.32E+00	6.60E-01	2.29E-01	9.04E-01	4.86E-01	5.72E-01
1,2,3,4,6,7,8 - HpBDF	5.68E-01	3.45E-01	4.21E-01	6.25E-01	2.48E-01	3.11E-01
1,2,3,4,6,7,8,9 - OBDF	7.35E-02	5.57E-02	-	0.00E+00	0.00E+00	0.00E+00
Total PBDD/Fs (ND=0; EMPC= 0)	3.21E+00	1.97E+00	1.56E+00	2.83E+00	1.66E+00	2.06E+00
Total PBDD/Fs (ND=0; EMPC= EMPC)	4.10E+00	1.97E+00	1.56E+00	2.83E+00	1.66E+00	2.09E+00
Total PBDD/Fs (ND=DL; EMPC= EMPC)	4.14E+00	2.05E+00	1.89E+00	3.07E+00	2.09E+00	2.63E+00

The laminate samples with halogenated components (BFR-P) could not be quantitated due to significant halogenated interference.

"EMPC" indicates that the bromine isotope ratio for the two molecular ion clusters was not within ±15% of the correct isotope ratio. When the two molecular ions are not within the correct isotope ratio, the two molecular ions are quantitated separately and the smaller quantitation is denoted EMPC. The EMPC notation identifies that the presence of an additional molecule may be influencing the detection level of the compounds of interest.

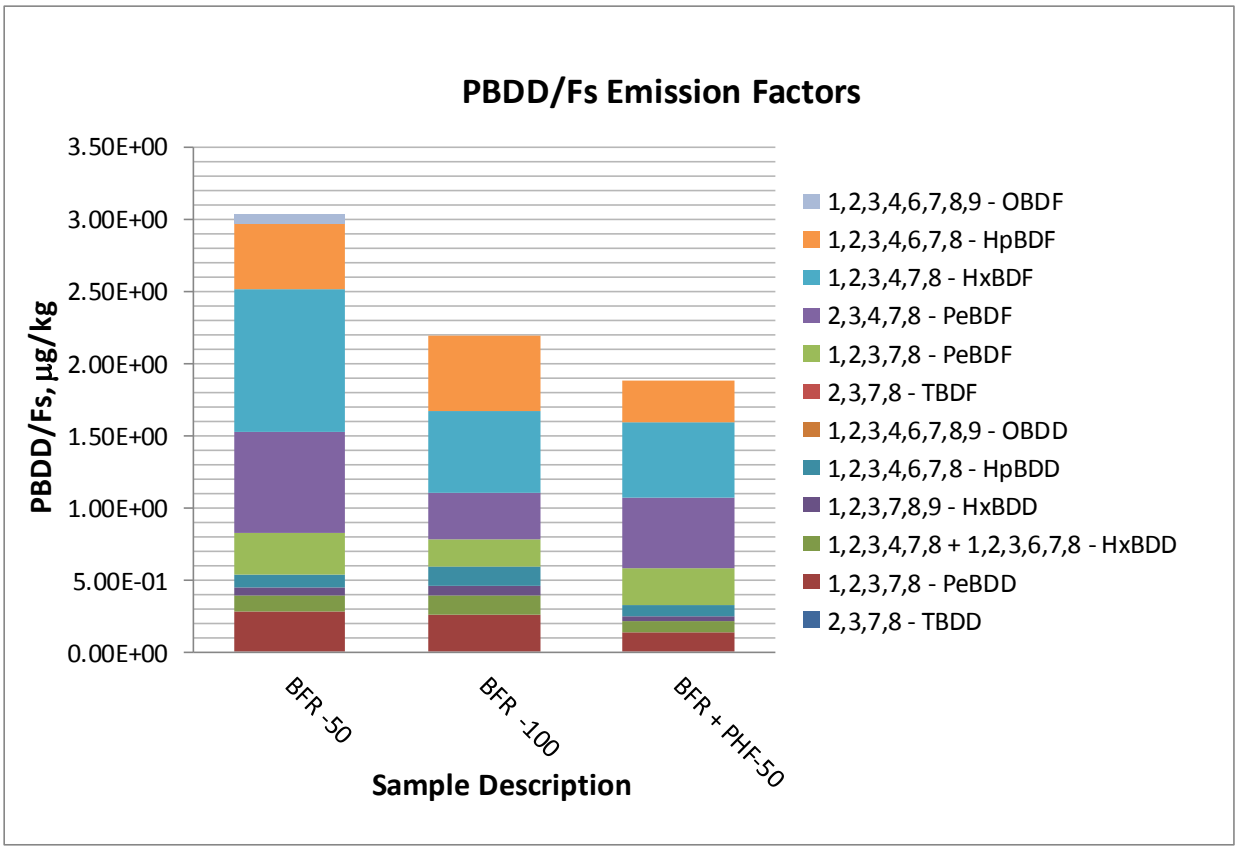

Figure 4-4. PBDD/Fs Emission Factors Plot for ND=0 and EMPC=EMPC
The laminate samples with halogenated components (BFR + P) could not be quantitated due to significant interference.

4.6 PAH Emissions

Table 4-6, Table 4-7 and Figure 4-5 show the total PAH emission factors for the 16 EPA priority PAHs quantified for the different printed circuit board laminates tested using the cone calorimeter. Brominated flame retardant (BFR) laminates burned at 50 kW/m^2 heat flux had the highest total PAH emissions and no flame retardant (NFR) laminates burned at 50 kW/m^2 heat flux had the least. At a higher heat flux (100 kW/m^2), the NFR sample showed 29% higher PAH emissions than the halogen-free (HFR) sample at the same heat flux. Emissions for the BFR were similar at both heat flux levels.

The observed trends of PAH emissions make sense in light of both the known and assumed flame retardant mechanisms for the two types of flame retardant systems. Since the BFR is a vapor phase flame retardant, any combustion of that flame retardant with decomposing epoxy structures should generate more incomplete combustion products. In the case of the HFR system, it is assumed a phosphorus-based flame retardant is present, which has more of a condensed phase (char formation) mechanism and binds up most of the possible PAH structures on the burned sample residue rather than created in the flame front as seen with BFRs. The results presented in Figure 4-5 support this general trend with a wide range of PAH products detected. The presence of component powders affected PAH emissions for both BFR and HFR systems. PAH emissions were reduced for the 1556 HFR samples that had components compared to the

other HFR samples. In some cases, a slight increase in PAH emissions was noted for the other HFR laminates when components were present. For the BFR systems, the presence of components slightly lowered total PAH emissions.

Since PAHs are known to be the nascent precursors of soot, a higher presence of PAHs should lead to higher PM yields from combustion. In this study, the PM yields (Table 4-4 and Figure 4-3) and the PAH emissions (Table 4-6 and Figure 4-5) did not always have this positive correlation. Typically, naphthalene yields should have been higher than the other PAHs detected. Analysis of our methods to determine breakthrough of PAHs during sampling at these high velocities has shown that fluorene and heavier compounds are captured using 4 PUFs in the glass cartridge that holds the PUFs and that acenaphthylene breakthrough was almost 50%. However, since the carcinogenic PAHs are of interest and the extraction of eight PUFs is complex, no attempt was made to prevent breakthrough of compounds lighter than fluorene by increasing the number of PUFs. Figure 4-6 displays the PAH emissions data excluding compounds with a lower molecular weight than fluorene likely to have had breakthrough. The same emission trends were observed when naphthalene, acenapthylene, and acenapthene were excluded, suggesting that no crucial information was lost by not sampling compounds requiring eight sampling PUFs.

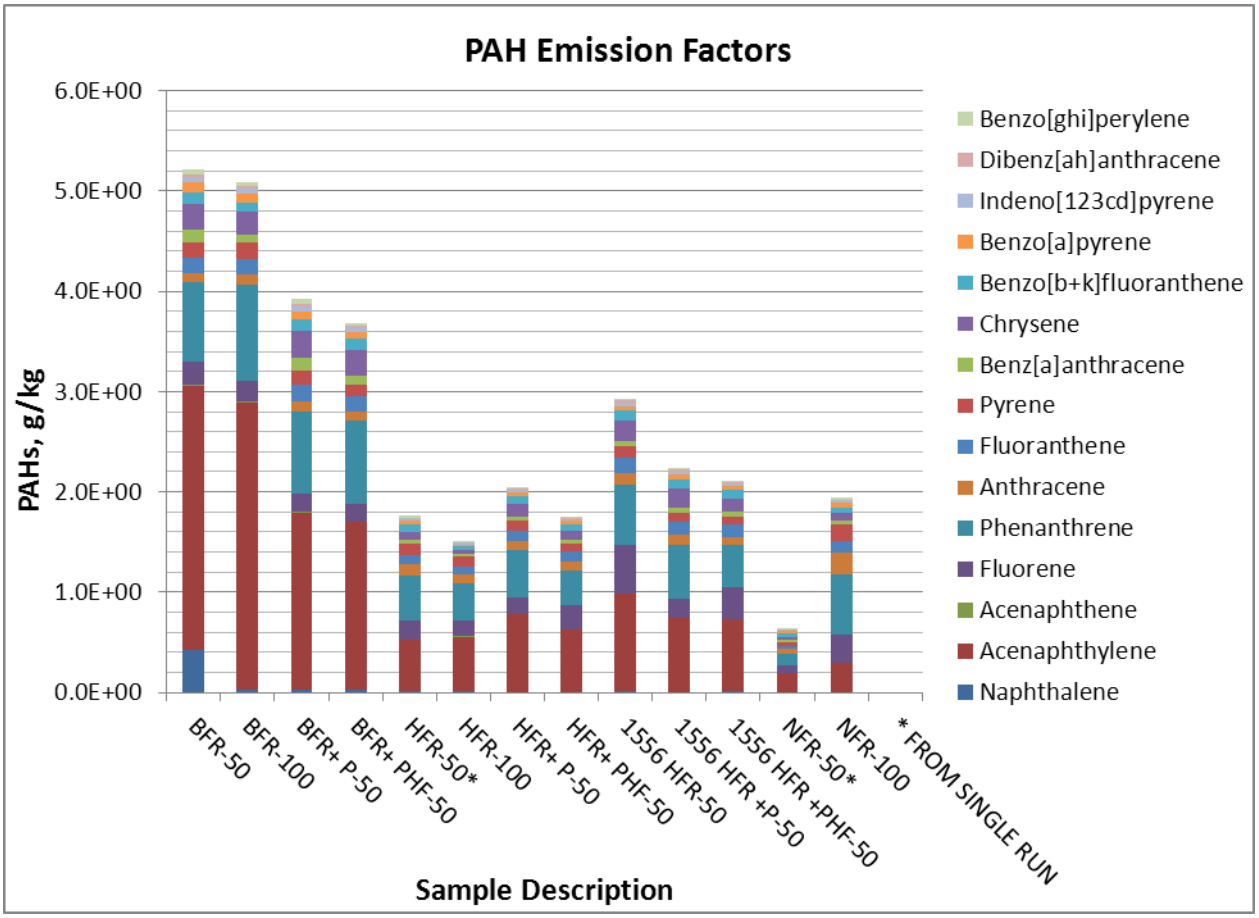

Figure 4-5. PAH Emission Factors Plotted for Naphthalene and Higher Molecular Weight PAHs Detected from the EPA List of 16‡ Priority PAHs

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

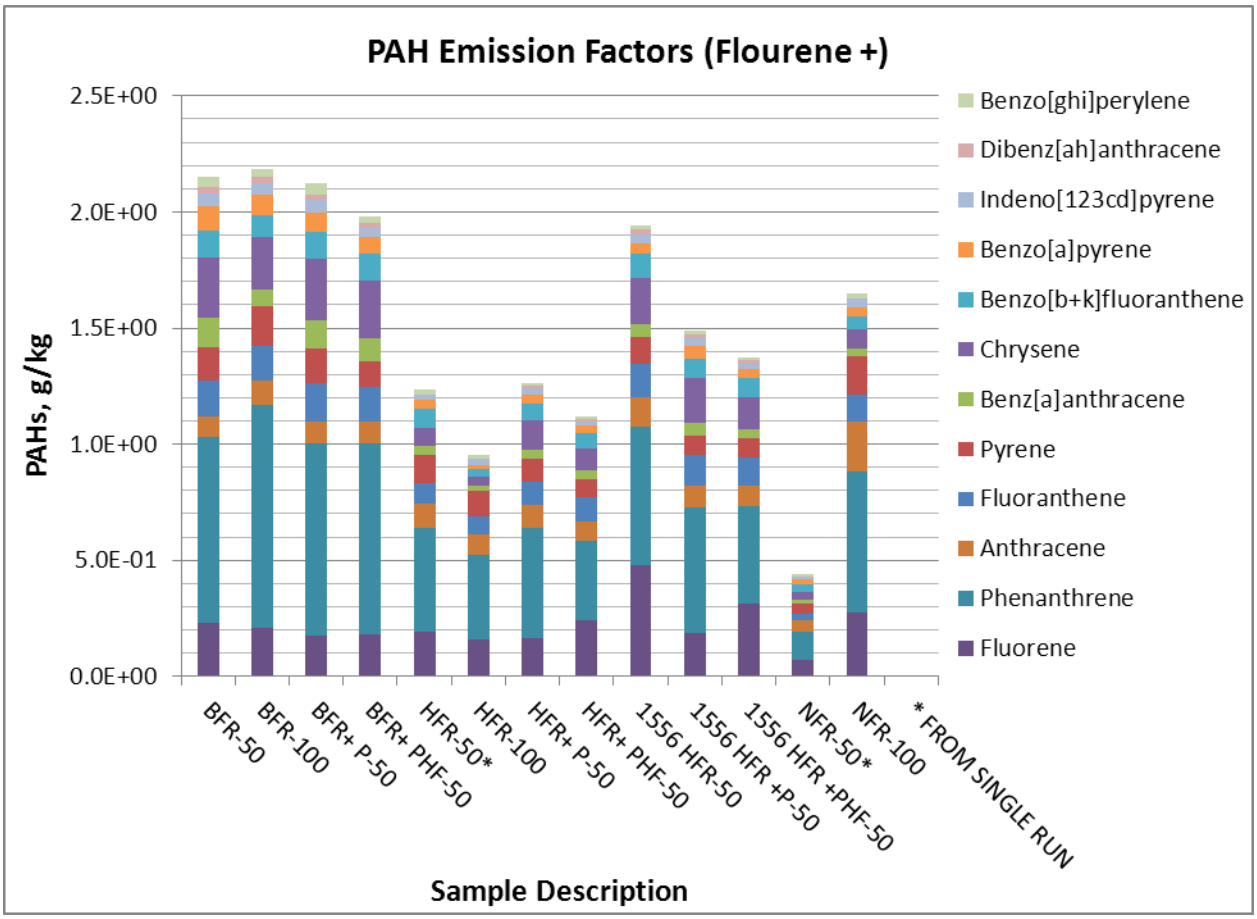

Figure 4-6. PAH Emission Factors for Fluorene and Higher Molecular Weight PAHs Detected from the EPA List of 16‡ Priority PAHs

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

When looking solely at the release of known carcinogenic PAHs (Figure 4-7), trends similar to those in Figure 4-5 and Figure 4-6 are observed. BFR systems produce more of the carcinogenic PAHs than the HFR or NFR systems. The addition of components does not appear to drastically affect the yields of carcinogenic PAHs. The presence of components decreases the yields in some cases probably due to a dilution effect from the added mass when calculating emission factors. The high heat flux can cause the NFR system to give off just as much carcinogenic PAHs as a flame retardant + component system from a lower heat flux. When looking at only the toxic equivalent emission factors of carcinogenic PAH values (Figure 4-8), it is again observed that BFR has the highest value followed by the HFR systems and then the NFR system.

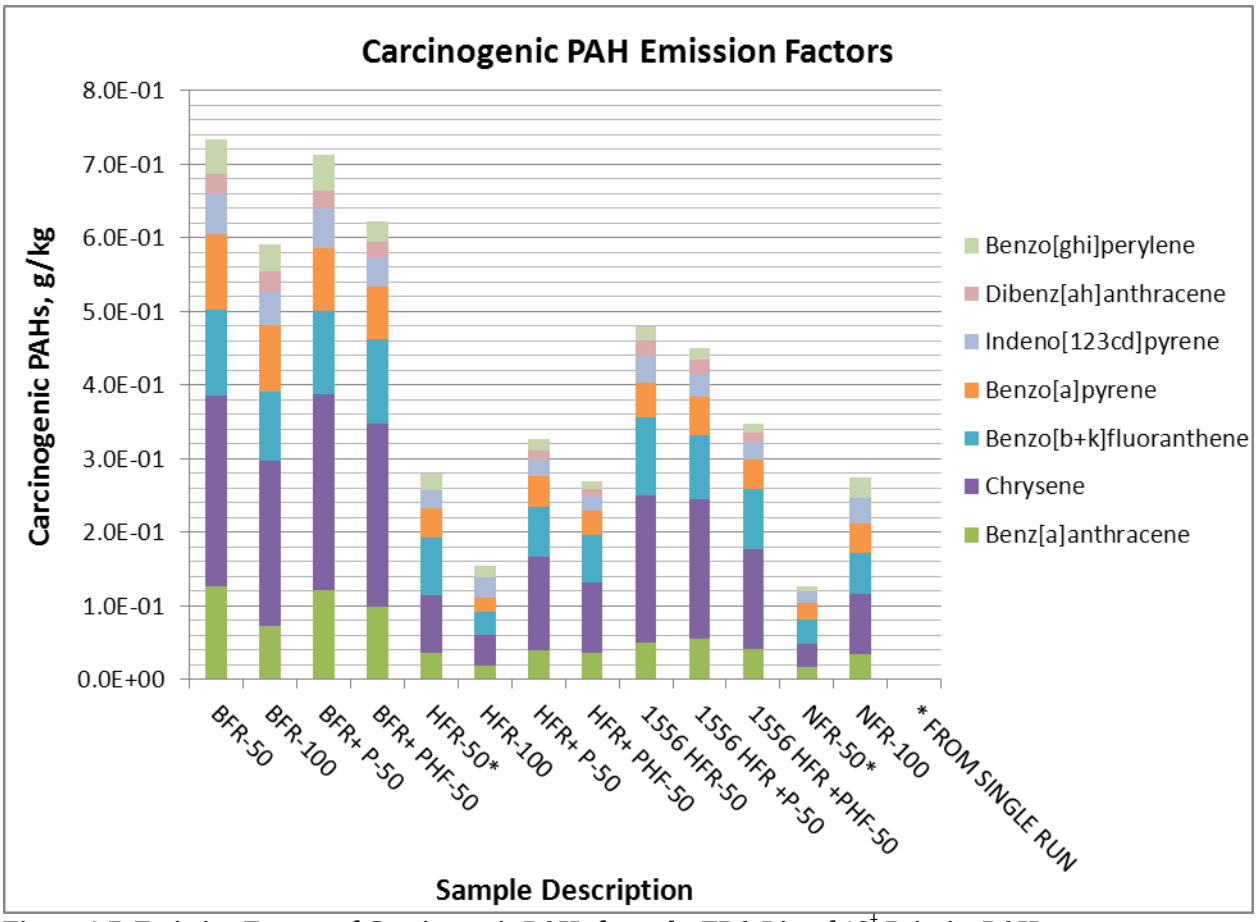

Figure 4-7. Emission Factors of Carcinogenic PAHs from the EPA List of 16‡ Priority PAHs

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

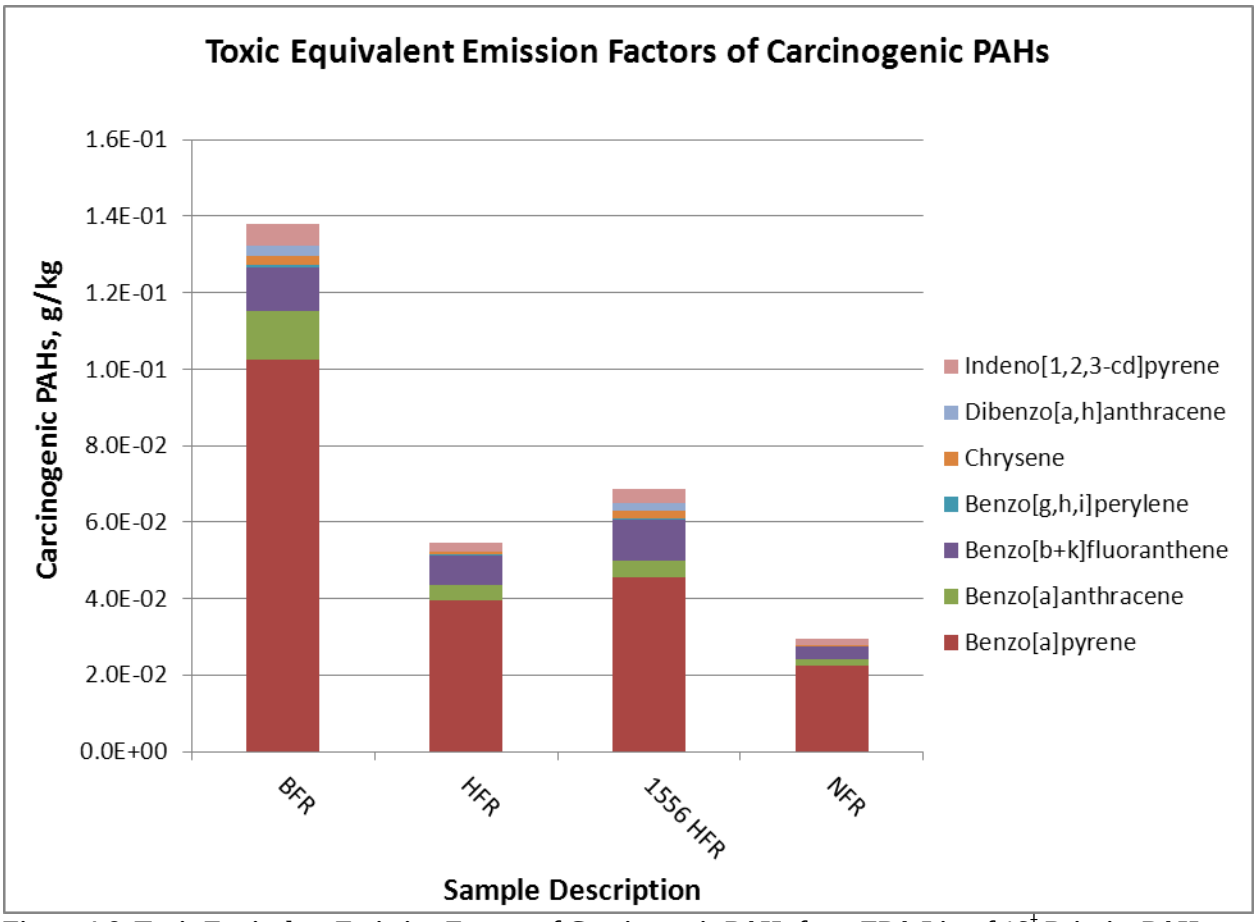

Figure 4-8. Toxic Equivalent Emission Factors of Carcinogenic PAHs from EPA List of 16‡ Priority PAHs Compared at 50 kW/m^2 Conditions

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

Table 4-6. PAH Emission Factors from EPA List of 16‡ Priority PAHs for BFR and NFR at 50 and 100 kW/m^2

Analyte	Sample Description - Heat flux (kW/m^2)					
	BFR - 50	BFR - 100	BFR + P - 50	BFR + PHF - 50	NFR - 50*	NFR - 100
	Emission Factors, g/kg					
Naphthalene	4.3E-01	2.1E-02	3.1E-02	2.5E-02	4.1E-03	7.7E-03
Acenaphthylene	2.6E+00	2.9E+00	1.8E+00	1.7E+00	1.9E-01	2.9E-01
Acenaphthene	1.1E-02	5.4E-03	6.3E-03	5.4E-03	0.0E+00	0.0E+00
Fluorene	2.3E-01	2.1E-01	1.8E-01	1.8E-01	7.2E-02	2.7E-01
Phenanthrene	8.0E-01	9.6E-01	8.3E-01	8.2E-01	1.2E-01	6.1E-01
Anthracene	8.7E-02	1.0E-01	9.3E-02	9.4E-02	4.9E-02	2.2E-01
Fluoranthene	1.6E-01	1.5E-01	1.7E-01	1.5E-01	2.7E-02	1.1E-01
Pyrene	1.4E-01	1.7E-01	1.5E-01	1.1E-01	4.3E-02	1.7E-01
Benz[*a*]anthracene	1.3E-01	7.3E-02	1.2E-01	9.9E-02	1.6E-02	3.4E-02
Chrysene	2.6E-01	2.2E-01	2.7E-01	2.5E-01	3.3E-02	8.2E-02
Benzo[*b+k*]fluoranthene	1.2E-01	9.4E-02	1.1E-01	1.1E-01	3.3E-02	5.5E-02
Benzo[*a*]pyrene	1.0E-01	9.2E-02	8.6E-02	7.2E-02	2.3E-02	4.0E-02
Indeno[*1,2,3-cd*]pyrene	5.6E-02	4.5E-02	5.3E-02	4.0E-02	1.4E-02	3.6E-02

Analyte	Sample Description - Heat flux (kW/m^2)					
	BFR - 50	BFR - 100	BFR + P - 50	BFR + PHF - 50	NFR - 50*	NFR - 100
	Emission Factors, g/kg					
Dibenz[*a,h*]anthracene	2.6E-02	2.7E-02	2.5E-02	2.1E-02	0.0E+00	0.0E+00
Benzo[*g,h,i*]perylene	4.8E-02	3.7E-02	4.7E-02	2.7E-02	8.2E-03	2.7E-02
Total 16 EPA PAHs	**5.22E+00**	**5.08E+00**	**3.93E+00**	**3.69E+00**	**6.24E-01**	**1.95E+00**

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together
*From a single run

Table 4-7. PAH Emission Factors from EPA List of 16‡ Priority PAHs for HFR and 1556 HFR at 50 and 100 kW/m^2

Analyte	Sample Description - Heat flux (kW/m^2)						
	HFR - 50*	HFR - 100	HFR + P - 50	HFR + PHF - 50	1556 HFR - 50	1556 HFR + P - 50	1556 HFR + PHF - 50
	Emission Factors, g/kg						
Naphthalene	7.9E-03	8.4E-03	6.7E-03	6.7E-03	1.9E-02	6.3E-03	1.6E-02
Acenaphthylene	5.1E-01	5.5E-01	7.7E-01	6.2E-01	9.6E-01	7.4E-01	7.1E-01
Acenaphthene	7.9E-03	3.6E-03	1.8E-03	6.7E-03	6.7E-03	0.0E+00	6.9E-03
Fluorene	1.9E-01	1.6E-01	1.7E-01	2.4E-01	4.8E-01	1.9E-01	3.1E-01
Phenanthrene	4.5E-01	3.6E-01	4.7E-01	3.4E-01	6.0E-01	5.4E-01	4.2E-01
Anthracene	1.1E-01	9.3E-02	9.8E-02	8.6E-02	1.3E-01	9.7E-02	8.7E-02
Fluoranthene	8.7E-02	7.5E-02	1.0E-01	1.0E-01	1.4E-01	1.3E-01	1.3E-01
Pyrene	1.2E-01	1.1E-01	1.0E-01	7.8E-02	1.2E-01	8.3E-02	7.9E-02
Benz[*a*]anthracene	3.6E-02	1.9E-02	4.0E-02	3.6E-02	5.0E-02	5.5E-02	4.2E-02
Chrysene	7.9E-02	4.1E-02	1.3E-01	9.6E-02	2.0E-01	1.9E-01	1.4E-01
Benzo[*b+k*]fluoranthene	7.9E-02	3.1E-02	6.7E-02	6.4E-02	1.1E-01	8.6E-02	8.1E-02
Benzo[*a*]pyrene	4.0E-02	2.0E-02	4.2E-02	3.4E-02	4.5E-02	5.3E-02	4.1E-02
Indeno[*1,2,3-cd*]pyrene	2.4E-02	2.6E-02	2.4E-02	1.8E-02	3.7E-02	3.1E-02	2.4E-02
Dibenz[*a,h*]anthracene	0.0E+00	0.0E+00	1.2E-02	1.0E-02	2.2E-02	1.8E-02	1.3E-02
Benzo[*g,h,i*]perylene	2.4E-02	1.6E-02	1.5E-02	1.2E-02	1.9E-02	1.6E-02	1.2E-02
Total 16 EPA PAHs	**1.74E+00**	**1.51E+00**	**2.04E+00**	**1.75E+00**	**2.93E+00**	**2.24E+00**	**2.11E+00**

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together
*From a single run

Table 4-8. Toxic Equivalent Emission Factors of Carcinogenic PAHs from EPA List of 16‡ Priority PAHs

Carcinogenic -PAHs	Toxic Equivalency Factor (TEF)	Toxic Equivalent Emission Factors of Carcinogenic PAHs (g/kg)			
		BFR	HFR	1556 HFR	NFR
Benzo[*a*]pyrene	1	1.0E-01	4.0E-02	4.5E-02	2.3E-02
Benzo[*a*]anthracene	0.1	1.3E-02	4.0E-03	4.5E-03	1.6E-03
Benzo[*b+k*]fluoranthene	0.1	1.2E-02	7.9E-03	1.1E-02	3.3E-03
Benzo[*g,h,i*]perylene	0.01	4.8E-04	2.4E-04	1.9E-04	8.2E-05
Chrysene	0.01	2.6E-03	7.9E-04	2.0E-03	3.3E-04
Dibenzo[*a,h*]anthracene	0.1	2.6E-03	0.0E+00	2.2E-03	0.0E+00
Indeno[*1,2,3-cd*]pyrene	0.1	5.6E-03	2.4E-03	3.7E-03	1.4E-03

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

Although attempts were also made to determine presence of other chlorinated benzenes/phenols known to be PCDD/Fs precursors, none were detected at the sample concentrations analyzed for PAHs. No significant presence of chlorobenzenes and phenols detected in the laminate burns is a likely indicator of a negligible presence of chlorinated dioxins under the conditions explored in this study. However, the absence of PCDD/Fs cannot be conclusively stated without further analysis of more concentrated samples or attempts to analyze extracts for PCDD/Fs disregarding the previously discussed issues related to the absence of the chlorinated pre-sampling surrogates.

Scanning for organophosphorus was also done because it was believed that the non-halogenated flame retardants present in the samples were phosphorus-based. The detection of organophosphorus emissions would indicate the presence of a vapor phase flame retardant while the detection of no organophosphorus emissions would indicate the presence of a condensed phase flame retardant. The organophosphorous compounds detected in this study are given in Table 4-9. As Table 4-9 shows, different compounds were detected from the repeat burn of the same laminate. The environmental and health effects of the compounds detected are not evaluated in this report to explain their impact. From a flame retardant perspective, some of the compounds fit with known flame retardant chemistry while others are likely post-combustion reaction products or reactions between the phosphorus flame retardant and parts of the circuit board. For example, the phosphorous compounds with silicon in their chemical structure are likely present due to reactions between organophosphorus and e-glass during burning. The presence of any halogen-phosphorus compounds is likely due to reaction between halogen and organophosphorus during burning. Other organophosphorus compounds present that contain phosphonic or phosphinic acids are decomposition products of known phosphorus flame retardants, especially compounds containing phenyl groups. However, it should be recognized that the exact phosphorus flame retardant used in these systems was not reported to UDRI, leaving the interpretation of the data based upon information in open literature for phosphorus flame retardants. Combustion chemistry is complex, especially when many components are present, and the list of compounds detected is not surprising.

Table 4-9. Organophosphorous Compounds Detected

Laminate Description	Organophosphorous Compounds Detected	Area %
BFR -50	1-Ethyl-1-hydridotetrachlorocyclotriphosphazene	0.04
BFR -50	Silanol, trimethyl-, pyrophosphate	0.51
	Phosphonic acid, methylenebis-, tetrakis(trimethylsilyl) ester	0.17
BFR + P -50	O,O'-(2,2'-Biphenylylene)thiophosphoric acid	0.38
BFR + P -50	Bis(4-methoxyphenyl)phosphinic acid	0.1
	Silanol, trimethyl-, pyrophosphate(4:1)	0.08
	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.61
	4-Phosphaspiro[2.4]hept-5-ene, 4-methyl-5,6-diphenyl-	0.15
BFR + PHF-50	Bis(4-methoxyphenyl)phosphinic acid	0.15
BFR + PHF-50	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.23
BFR -100	Ethylphosphonic acid, bis(tert-butyldimethylsilyl) ester	8.33
BFR -100	Methylenebis(phosphonic acid), tetrakis(3-hexenyl) ester	0.29
HFR +P-50	Phosphonic acid, phenyl-, diethyl ester	0.25
HFR + PHF-50	(2-Bromo-3-methylphenyl) diphenylphosphine	0.34
HFR + PHF-50	Phosphine imide, P,P,P-triphenyl-	0.3
	Phosphorane, 11H-benzo[a]fluoren-1-ylidenetriphenyl-	0.43
1556 + P -50	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.53
1556 + PHF-50	Phosphine imide, P,P,P-triphenyl-	0.21

4.7 Heat Release (Flammability) Results

The flammability data for the laminate samples and laminates + component powders are shown in Appendix A. Since material flammability/fire safety was not the primary focus of this study, it is not a primary focus of the Results and Discussion section. Instead, suggestions are provided on how the heat release results should and should not be interpreted and used.

The circuit board samples in this report are likely formulated to pass a small flame test, such as UL-94 V-0/-1/-2 (ASTM D3801), or a glow wire test (ASTM D6194) that mimics a short circuit ignition scenario. The cone calorimeter used in this report represents a well-ventilated fire scenario when it is run at a flow of 24 L/s as per the ASTM E1354 method. It better represents a larger fire source and not the small ignition source typically seen in electronic circuit boards. In this report, the cone calorimeter experiments were run at a lower flow rate of 15 L/s, which would roughly simulate open burn type conditions, not an intense well ventilated fire. Further, where ASTM D3801 uses a small flame source, the cone calorimeter uses a radiant heater, which in this case was set to heat fluxes of 50 and 100 kW/m^2 and represent a medium sized and a very large scale fire, respectively. The measurement of heat release from materials that were not designed to protect against robust heat sources like that of the cone calorimeter is a limitation of this study. It should not be used to infer the fire safety of the products in their respective scenarios. Each fire test used for regulating flame retardant materials is tailored for a specific fire risk scenario; the standards are not interchangeable. Therefore, the cone calorimeter data in this

study is best used to understand how much heat an object gives off when burned in a situation where it is well ventilated and a robust heat source is present. With this in mind, heat release rate and smoke data from the cone calorimeter testing of circuit boards can be used to better understand:

- Heat output from the burning material when properly disposed of (100 kW/m^2 heat flux conditions) to know if the laminate gives off enough heat to run the incinerator cleanly.
- Heat output if e-waste was to be used for waste-to-energy processes (how much energy would be generated by the burning of e-waste).
- Relative rankings on flame retardant performance *outside* the regulatory test scenario for which it was designed. Specifically, cone calorimeter measures can inform how the materials would contribute to a larger fire event (server room fire, house fire) when set afire by another object in the same room. The lower the heat release of the material, the less likely it will contribute negatively to a large fire event, or, spread fire should it be exposed to heat and flame.

While the cone calorimeter data can be useful, care should be taken when using it for the selection of fire safe materials, or in the case of this report, figuring out which flame retardant chemistry (brominated or non-halogenated) is appropriate for a particular need. Cone calorimeter data can guide selections, but each material scientist and engineer will need to look closely at the fire standards to decide what aspect of fire performance certain materials must meet.

Although cone calorimeter measurements can give insight into heat output and comparative flame retardant performance, there are conclusions that cannot be made with the flammability/heat release data in this report:

- The measured heat release of each of the system does not infer that any one material is safer than another from a fire safety perspective. Since the cone calorimeter measures flammability in a different way than other regulatory tests, a low heat release in the cone calorimeter does not ensure a "pass" result in a regulatory test. A lower peak HRR would mean that the burning laminate would be less likely to ignite other nearby objects though. A lower total HR would indicate that if the burning laminate was fully burned, it would contribute less total heat (fuel) to the overall fire.
- Smoke release in the cone calorimeter is very much a function of the combustion conditions used in the test. Smoke release may be more intense or less intense under different ventilation conditions and the results cannot be used to infer that a particular material will be better or worse than another in a different flaming combustion configuration/scenario. Smoke release in the cone calorimeter is very different than smoke release from a full high heat flux fire and is also very different than smoke release from a small flame ignition source.
- Cone calorimeter data has a known % error of ±10%.

With the above caveats in mind, the following trends are observed in Table 4-10 and Table 4-11:

- At a heat flux of 50 kW/m^2, the flame retardant systems show lower peak heat release when compared to the non-flame retardant systems. The non-halogenated "1556 HFR" sample shows the lowest flammability overall but also has a lower amount of total mass lost, suggesting that it either has more non-combustible mass present or is a more robust char forming flame retardant system.

- The addition of component powders generally increased total heat release and had mixed effects on peak HRR.
- At a heat flux of 100 kW/m^2, only the brominated flame retardant continues to lower heat release (peak HRR and total HR) versus the non-flame retardant control. The non-halogenated system gives heat release roughly equal to, or slightly higher, than the non-flame retardant system.

Table 4-10. Heat Release Summary for Laminates and Laminates + Component Powders Tested at 50 kW/m^2

Sample Description - Heat Flux (50 kW/m^2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m^2)	Average HRR (kW/m^2)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	MARHE (kW/m^2)
BFR -1	0.49	11	279.0	65.31	37.2	4.4	485.2	115.6
BFR -2	0.49	10	272.4	64.23	39.8	4.8	496.9	114.2
BFR -3	0.50	10	296.5	91.31	37.5	4.8	455.2	146.8
BFR + P -1	0.49	9	280.2	81.29	29.3	6.9	719.9	127.7
BFR + P -2	0.48	8	265.0	79.41	28.8	6.9	698.5	116.3
BFR + P -3	0.49	14	255.7	79.94	27.9	6.6	657.0	105.9
BFR + PHF -1	0.48	12	279.3	83.44	25.2	6.8	467.1	111.7
BFR + PHF -2	0.48	18	331.4	88.70	25.1	6.9	446.5	107.5
BFR + PHF -3	0.48	14	266.8	81.37	24.9	6.9	490.8	108.4
NFR -1	0.43	11	406.1	77.77	32.3	5.8	228.3	130.0
NFR -2	0.41	11	391.6	87.52	28.4	6.1	199.0	139.4
NFR -3	0.44	12	445.9	88.69	34.9	6.5	238.8	140.8
HFR -1	0.57	12	406.7	98.15	35.8	7.8	240.2	141.4
HFR -2	0.56	15	292.1	84.51	32.3	6.7	237.5	106.9
HFR -3	0.58	17	368.5	94.59	34.2	7.3	274.7	124.7
HFR + P -1	0.56	10	267.4	88.64	25.0	8.2	451.2	116.1
HFR + P -2	0.58	8	278.9	102.55	25.9	9.6	461.4	139.8
HFR + P- 3	0.58	14	303.5	102.61	25.6	9.2	403.0	128.4
HFR+ PHF -1	0.58	21	343.0	111.98	25.1	9.8	330.9	128.4
HFR + PHF -2	0.57	31	294.0	96.43	21.5	7.8	372.5	92.4
HFR + PHF -3	0.56	26	271.1	86.55	22.5	8.0	356.9	98.5
1556 HFR -1	0.46	14	181.2	55.56	27.2	4.2	270.5	76.0
1556 HFR -2	0.45	24	205.9	50.88	23.0	3.6	232.1	60.7
1556 HFR -3	0.46	16	230.9	63.06	25.3	4.6	236.4	84.1
1556 HFR + P -1	0.46	12	165.7	73.22	23.3	6.6	400.4	93.1
1556 HFR + P-2	0.46	9	185.9	68.54	20.9	6.1	382.6	92.3
1556 HFR + P-3	0.45	9	165.8	71.18	22.8	6.6	409.3	92.2
1556 HFR +PHF -1	0.45	18	196.7	76.26	20.0	6.4	293.6	88.3
1556 HFR + PHF-2	0.46	22	209.4	83.15	20.4	7.1	324.0	88.6
1556 HFR +PHF -3	0.46	22	220.6	81.50	20.5	6.5	310.1	84.4

Table 4-11. Heat Release Summary for Laminates and Laminates + Component Powders Tested at 100 kW/m^2

Sample Description - Heat Flux (100 kW/m2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m^2)	Average HRR (kW/m^2)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	MARHE (kW/m^2)
BFR -1	0.41	3	226.7	55.5	41.1	4.5	475.6	128.5
BFR -2	0.42	5	390.6	80.4	45.8	5.7	451.0	180.2
BFR -3	0.40	3	356.8	77.0	45.3	5.4	392.7	189.4
NFR -1	0.32	3	356.4	79.7	36.5	5.3	194.6	188.4
NFR -2	0.35	4	490.5	94.5	38.9	6.6	230.1	201.3
NFR -3	0.34	4	387.5	70.8	37.5	5.0	219.5	152.5
HFR -1	0.49	6	494.7	104.0	38.6	7.4	231.4	205.4
HFR -2	0.48	6	495.2	104.9	35.8	7.5	237.5	215.9
HFR -3	0.49	5	367.1	120.0	40.5	10.2	325.6	200.5

5 Conclusions

While the cone calorimeter is a useful instrument for measuring flammability from a fire safety perspective, the use of the cone calorimeter in this study was as a combustion science tool. Heat fluxes plus a lower flow rate were chosen to represent potential open burn (50 kW/m^2) and incineration for metal recovery (100 kW/m^2). The following general trends were observed:

50 kW/m^2 heat flux:

- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at higher levels than NFR sample.
- NFR: PAHs emitted at lowest levels compared to other samples.

100 kW/m^2 heat flux:

- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at lowest levels compared to other samples.
- NFR: PAHs emitted at a level slightly lower than the BFR sample.

Effect of components on emissions:

- PBDD/Fs: PBDD/Fs were similar or lower than sample without components.
- PAHs: In general, presence of components reduced PAH emissions for BFR, were similar or slightly highly for HFR and were lower for 1556 HFR. The size of these differences varied depending on which PAHs were summarized (see section 4.6).
- PAH emissions and smoke release of laminates with low halogen components were slightly lower than standard components across all three difference laminates.

Smoke, PM, CO and CO_2 release:

- Smoke release was higher for BFR than HFR laminates. Smoke release was higher with components due to greater amount of material. PM generally had small differences between samples. There were negligible differences in CO release between samples. CO_2 release was

lowest for BFR but with small differences between samples. Results are complex and smoke/PM results do not always correlate.

The results of this report do not suggest that any one material is safer than another in regards to fire safety. The results do show that the flame retardants lower heat release under flaming combustion even at high heat fluxes.

Overall, the results clearly show that all of the samples generated combustion by-products other than CO_2 and water. The flame retardant samples in some cases generated more pollutants than the NFR samples, as one would expect since the flame retardants are inhibiting combustion. Any system that slows down flaming combustion will generate higher levels of smoke, CO, PM, and other incomplete combustion products. A flame retardant with a vapor phase mechanism (such as BFR) will generate more species than a flame retardant that uses a condensed phase mechanism (assumed to be the case of the phosphorus-based HFR system). It is important to look at flame retardant chemistry, flame retardant mechanism, polymer decomposition chemistry, and fire scenario (heat, ventilation) to determine what sorts of species may be formed during accidental fires (where flame retardants serve as passive protection) or intentional ones (proper and improper incineration).

The other major finding of this report is that the cone calorimeter was able to obtain a diverse amount of information about emissions from circuit boards. For the brominated laminate with halogenated components, the complexity of the emissions made them difficult to separate and identify but the results show that pollutants exist. Further work and separation science would be needed to achieve that higher level of data resolution with these particular samples.

Based upon the results in this report, users of flame retardants for circuit boards should realize that if PCBs or other e-waste is to be incinerated for precious metal recovery, it should be done properly with good incinerator control to address the pollutant emissions that will occur. Even non-flame retardant boards when incinerated improperly will release pollutants of concern, as was seen from the data in this report. Emissions may have been lower, but they were still present. The use of flame retardants is a technology compromise: it provides fire safety performance (thus lowering risk of short circuit ignitions in daily use) but will generate higher pollutants when incinerated improperly. Other environmental concerns may drive the selection of different flame retardant chemistry, but from emissions alone, such a decision cannot be made. With careful attention to polymer thermal decomposition chemistry and combustion science, it may be possible to generate a flame retardant in the future which provides fire protection *and* minimizes emissions/pollutants of concern during burning. If there is a desire to develop clean burning flame retardant materials, entirely different flame retardant chemistries must be developed. Otherwise, the safest solution to this problem is to recover precious metals via well controlled incineration with regulatory emissions controls in place as well as cost-effective methods of e-waste collection and disposal.

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7 Appendix A: Circuit Board Flammability Data

Along with emissions data, heat release information as per ASTM E1354 was also collected. This data is reported in below as a function of heat flux and samples tested. Observed fire behavior, final chars, and heat release rate curves are given. The data is presented for the purposes of completeness in this report. It does not infer any particular level of fire safety about the samples tested. Merely it shows what the measured heat release information was from these samples when tested at 15 L/sec exhaust flow in triplicate as per the ASTM methodology.

In the section below, BFR indicates a brominated flame retardant system being tested, while HF indicates halogen-free flame retardant and NFR indicates that the sample had no flame retardant present. Component blends are identified as "Comp", meaning a component blend where halogen was present in the component blend powder, and as "HF Comp" meaning the mostly halogen-free component blend was used.

Heat Release Rate-50 kW/m^2

Table 7-1. Heat Release Rate Data (50 kW/m^2)

Sample Description - Heat Flux (50 kW/m^2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m^2)	Time to Peak HRR (s)	Average HRR (kW/m^2)	Starting Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m^2)	FIGRA
BFR -1	0.5	11	279	20	65	10.5	3.9	37.2	4.4	485	15.14	116	13.95
BFR -2	0.5	10	272	20	64	10.8	4.3	39.8	4.8	497	11.21	114	13.62
BFR -3	0.5	10	296	25	91	10.4	3.9	37.5	4.8	455	17.58	147	11.86
BFR + P -1	0.5	9	280	30	81	20.5	6.0	29.3	6.9	720	11.92	128	9.34
BFR + P -2	0.5	8	265	35	79	20.5	5.9	28.8	6.9	699	11.71	116	7.57
BFR + P -3	0.5	14	256	34	80	20.4	5.7	27.9	6.6	657	11.50	106	7.52
BFR + PHF -1	0.5	12	279	33	83	20.3	5.1	25.2	6.8	467	13.09	112	8.46
BFR + PHF -2	0.5	18	331	37	89	20.3	5.1	25.1	6.9	447	13.39	108	8.96
BFR + PHF -3	0.5	14	267	32	81	20.5	5.1	24.9	6.9	491	13.14	108	8.34
NFR -1	0.4	11	406	28	78	9.3	3.0	32.3	5.8	228	18.66	130	14.50
NFR -2	0.4	11	392	26	88	9.1	2.6	28.4	6.1	199	22.87	139	15.06
NFR -3	0.4	12	446	29	89	9.5	3.3	34.9	6.5	239	19.36	141	15.37
HFR -1	0.6	12	407	31	98	11.4	4.1	35.8	7.8	240	19.00	141	13.12
HFR -2	0.6	15	292	39	85	11.5	3.7	32.3	6.7	238	17.75	107	7.49
HFR -3	0.6	17	368	36	95	11.4	3.9	34.2	7.3	275	18.44	125	10.24
HFR + P -1	0.6	10	267	45	89	21.2	5.3	25.0	8.2	451	15.36	116	5.94
HFR + P -2	0.6	8	279	39	103	21.6	5.6	25.9	9.6	461	17.01	140	7.15
HFR + P- 3	0.6	14	304	41	103	21.5	5.5	25.6	9.2	403	16.50	128	7.40
HFR+ PHF -1	0.6	21	343	49	112	21.5	5.4	25.1	9.8	331	17.90	128	7.00
HFR + PHF -2	0.6	31	294	47	96	21.4	4.6	21.5	7.8	373	16.67	92	6.26
HFR + PHF -3	0.6	26	271	43	87	21.3	4.8	22.5	8.0	357	16.38	99	6.30
1556 HFR -1	0.5	14	181	32	56	10.7	2.9	27.2	4.2	271	14.16	76	5.66
1556 HFR -2	0.5	24	206	38	51	10.5	2.4	23.0	3.6	232	14.61	61	5.42
1556 HFR -3	0.5	16	231	30	63	10.7	2.7	25.3	4.6	236	16.38	84	7.70

Sample Description - Heat Flux (50 kW/m^2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m^2)	Time to Peak HRR (s)	Average HRR (kW/m^2)	Starting Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m^2)	FIGRA
1556 HFR + P -1	0.5	12	166	49	73	20.6	4.8	23.3	6.6	400	13.56	93	3.38
1556 HFR + P-2	0.5	9	186	34	69	20.6	4.3	20.9	6.1	383	13.99	92	5.47
1556 HFR + P-3	0.5	9	166	45	71	20.6	4.7	22.8	6.6	409	13.86	92	3.69
1556 HFR +PHF -1	0.5	18	197	34	76	20.0	4.0	20.0	6.4	294	15.73	88	5.79
1556 HFR + PHF-2	0.5	22	209	39	83	20.6	4.2	20.4	7.1	324	16.49	89	5.37
1556 HFR +PHF -3	0.5	22	221	44	82	20.5	4.2	20.5	6.5	310	15.31	84	5.01

BFR Fire Behavior

Upon exposure to the cone heater, the sample began to smoke and make crackling sounds very quickly. It then burst into flame with orange, blue, and purple colors noted. The sample was noted to curl up some during burning with the 2nd sample curling and delaminating to a severe degree such that the cone heater shutters could not close at the end of the experiments. Heat release was reproducible (Figure 7-1) and the final chars (Figure 7-2) were blackened with copper plates noted. The sample where the shutters could not be closed is shown on the far left of Figure 7-2 where the surface char has be slowly burned away leaving behind just copper and fiberglass. So with sufficient heat and oxygen, eventually most of the carbon can be burned away/ consumed.

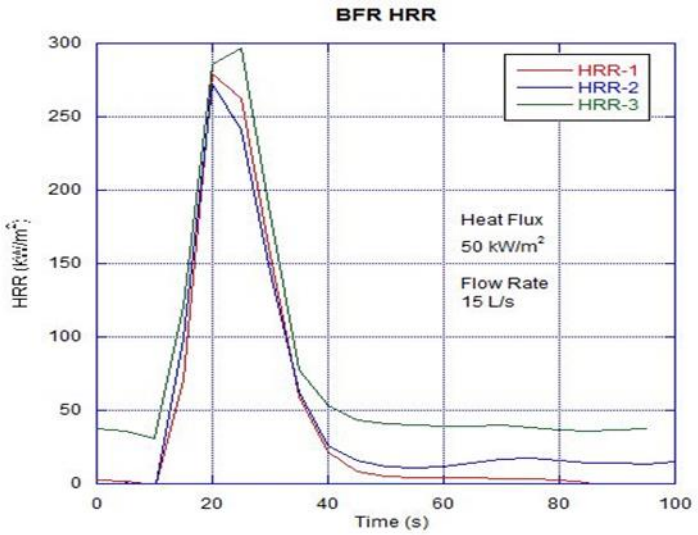

Figure 7-1. HRR for BFR Sample

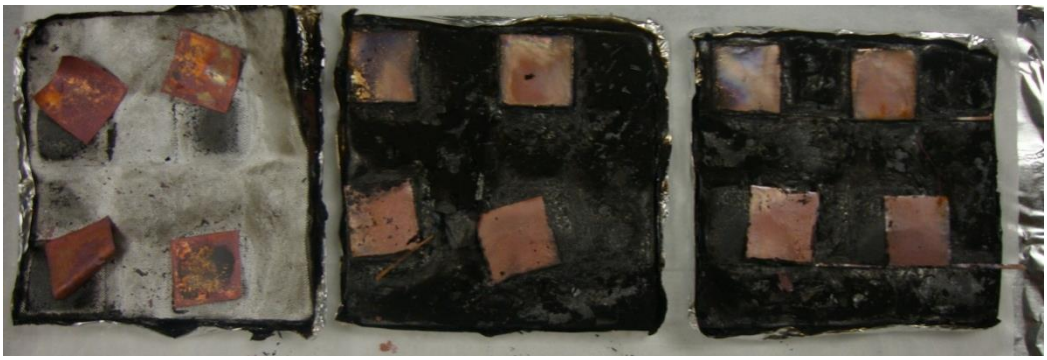

Figure 7-2. Final Chars for BFR Sample

BFR + P (populated halogen components)Fire Behavior

Fire behavior of this sample was the same as the BFR sample, but the flame colors were more muted. The component powder was also noted to spit and pop a bit, with occasional pieces of the powder leaving the aluminum foil holder. Heat release rates (Figure 7-3) were reproducible indicating that the powder did not inhibit burning behavior. Final chars (Figure 7-4) were black with yellowish-black powder on top.

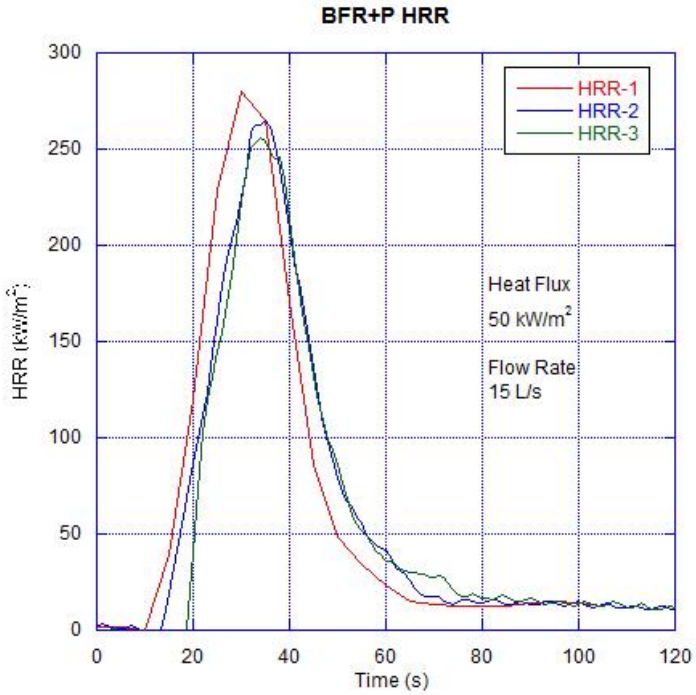

Figure 7-3. HRR for BFR + P Sample

Figure 7-4. Final Chars for BFR + P Sample

BFR + PHF(Populated halogen-free components)Fire Behavior

Upon exposure to the heater, the sample smoked and crackled, and then ignited on one side of the sample with the flames sweeping across the surface quickly. Flames were noted to be blue and purple in color, and the component powder had a tendency to crackle and bubble, suggesting the presence of thermoplastic material in the HF powder. HRR was fairly reproducible (Figure 7-5) although the 2nd sample (HRR-2) has a higher peak HRR and delayed time to ignition when compared to the other two samples. Final chars (Figure 7-5) were black with copper squares noted. From this observation the halogen-containing component powder does not flow (Figure 7-4) and may contain less thermoplastic material as opposed to the halogen-free component powder which appears to burn up more completely and leave less of a powdery residue.

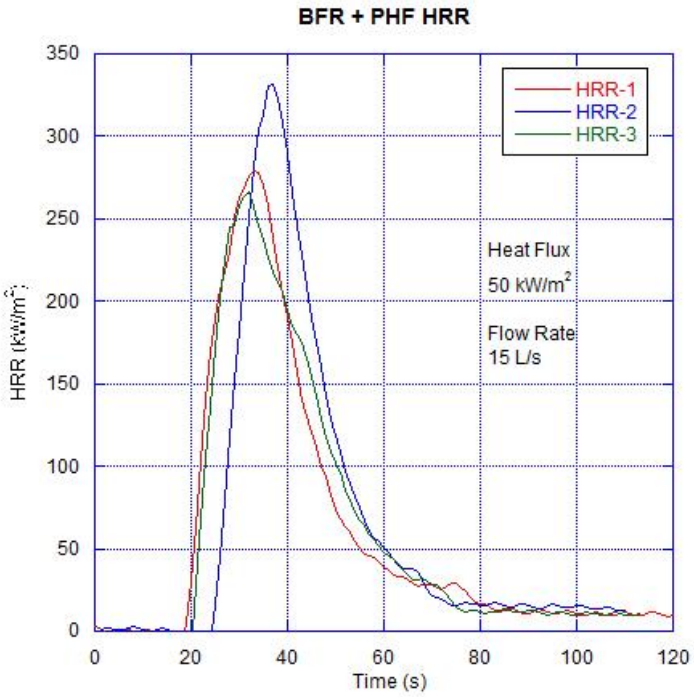

Figure 7-5. HRR for BFR + PHF Sample

Figure 7-6. Final Chars for BFR + PHF Sample

NFR Fire Behavior

Upon exposure the cone heater, the sample made a lot of crackling noises, and then began to smoke before quickly igniting. The sample curled quite a bit during burning such that the shutters could not be closed at the end of the experiment. Heat release (Figure 7-7) was very reproducible and the final chars (Figure 7-8) show just the copper and fiberglass as most of the residual carbon was burned away since the shutters would not close. Therefore any char which had self-extinguished during the test was slowly pyrolyzed away until the sample could be removed from the cone calorimeter.

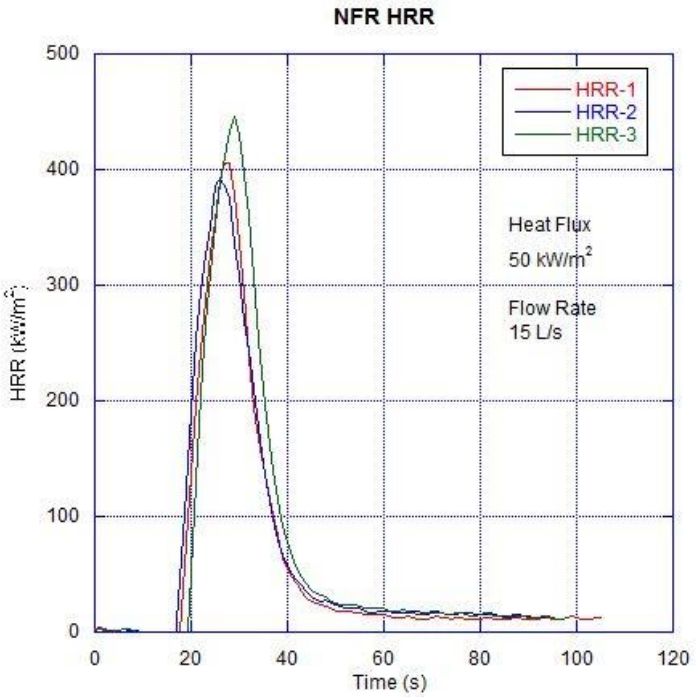

Figure 7-7. HRR for NFR Sample

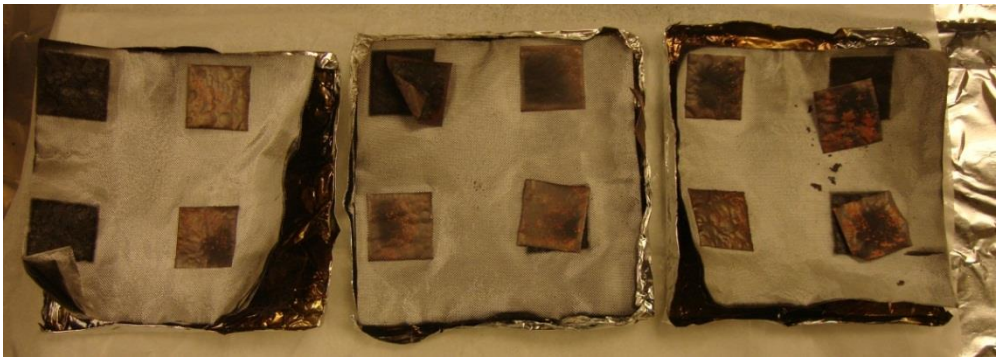

Figure 7-8. Final Chars for NFR Sample

HFR Fire Behavior

Upon exposure to the cone heater, the sample began to crackle and then smoke, followed by ignition. The sample burned with some white colors, suggesting the presence of a phosphorus-based flame retardant. The first sample curled during the test and the shutters could not be closed. Some scatter in the HRR was noted (Figure 7-9), especially in the peak HRR values. Final chars (Figure 7-10) in general show black-grey chars on the surface of the fiberglass, but some char is noted on the copper squares as well.

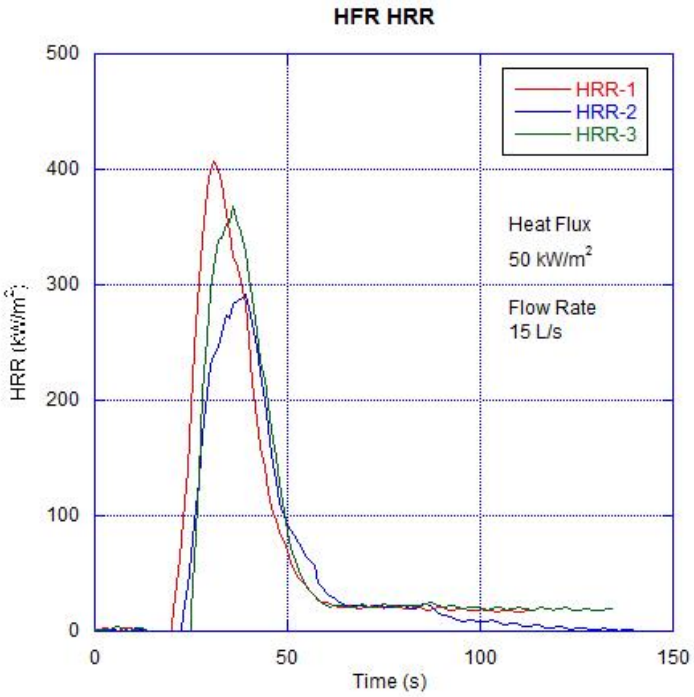

Figure 7-9. HRR for HFR Sample

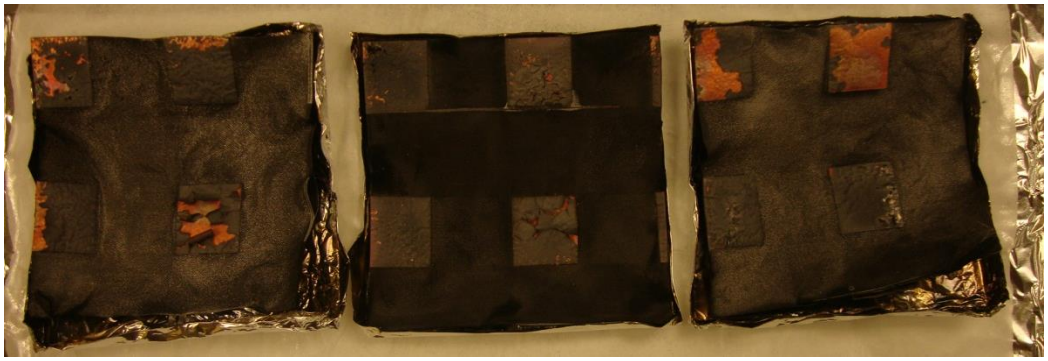

Figure 7-10. Final Chars for HFR Sample

HFR+ P (Comp) Fire Behavior

Upon exposure to the cone heater, the sample began to smoke right away, followed an ignition and some loud crackling noises. Some parts of the powder also spat out of sample surface during this burning behavior with some flames going out sideways from under the powder. Some blue flames were noted at the beginning and end of the test. The third sample tested had some curling and the shutters could not be closed at the end of the test. Heat release (Figure 7-11) showed some scatter in the peak HRR values, but the scatter was not severe. Final chars (Figure 7-12) were completely black and the powder is of a similar color, unlike the BFR sample above which had the same component powder but the powder char was of a different color at the end of the test (Figure 7-4). The curling observed for the 3rd sample can be seen in the middle of Figure 7-12.

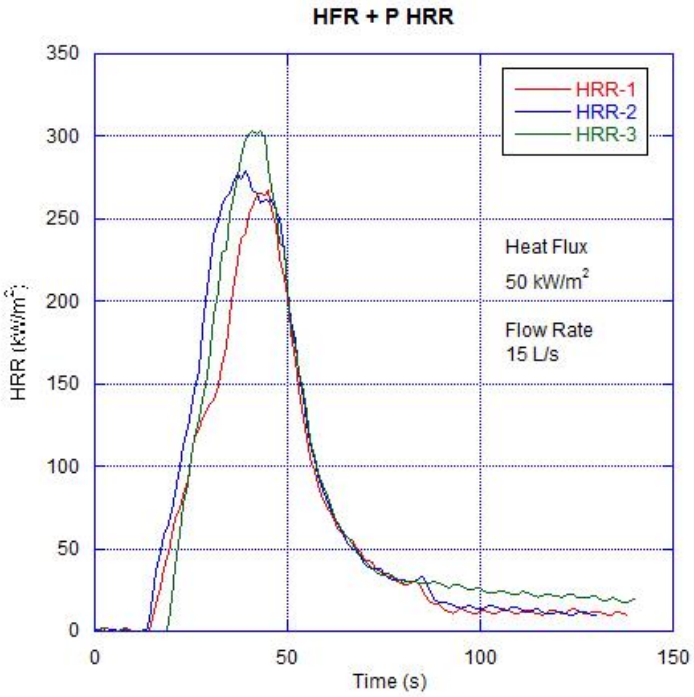

Figure 7-11. HRR for HFR + P Sample

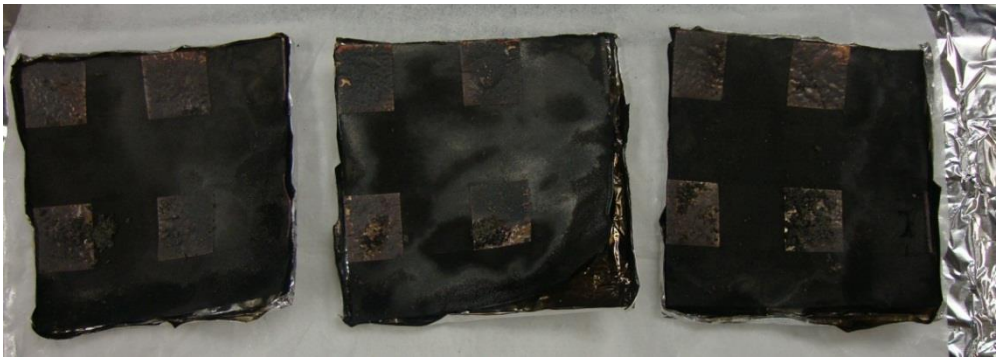

Figure 7-12. Final Chars for HFR + P Sample

HFR + PHF Fire Behavior

Fire behavior for this sample was similar to that of the sample above, except no blue colors were noted. All of the samples had a tendency to curl such that it was difficult to close the shutters at the end of the test. Loud crackling and popping was heard, but no bubbling seen this time as was observed for the BFR + PHF sample. HRR showed some scatter in the time to ignition and peak HRR values (Figure 7-13). Final chars (Figure 7-14) showed intact charred powder, but with more residual color noted. Some of the copper squares can be seen under the charred component powder.

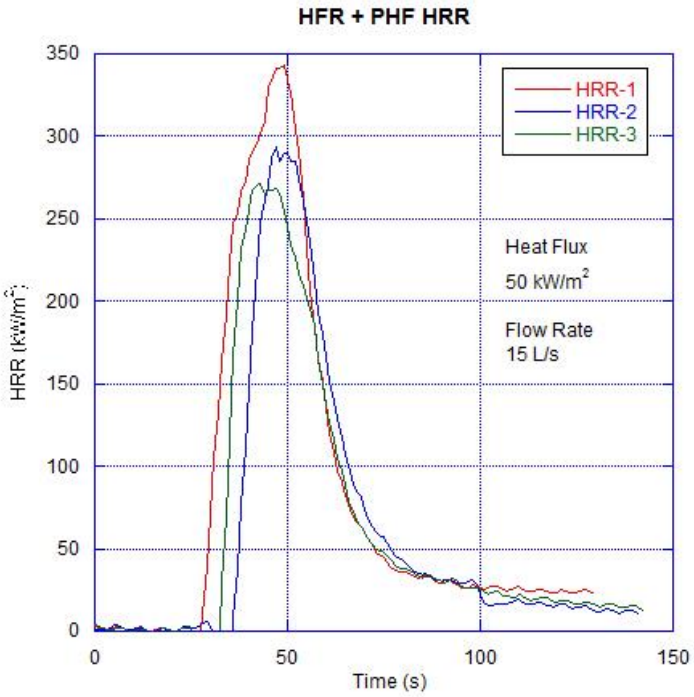

Figure 7-13. HRR for HFR + PHF Sample

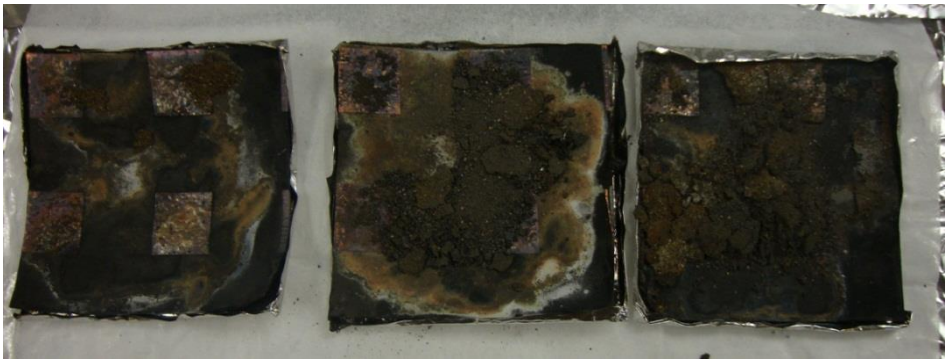

Figure 7-14. Final Chars for HFR + PHF Sample

1556 HFR Fire Behavior

Upon exposure to the cone heater, the sample was heard to crackle and pop, then smoke, then ignite. The sample had small flames which were not as sooty as those seen in previous samples. The sample also curled during burning, but flaked apart as it burned, suggesting the presence of a phenolic resin, or some sort of charring polymer. HRR (Figure 7-15) was not very reproducible for this sample, with notable variability in the peak HRR and time to peak HRR behavior. Final chars (Figure 7-16) are black and grey with regions of soot on the surface. Some of the copper squares have moved suggested they debonded from the surface during burning.

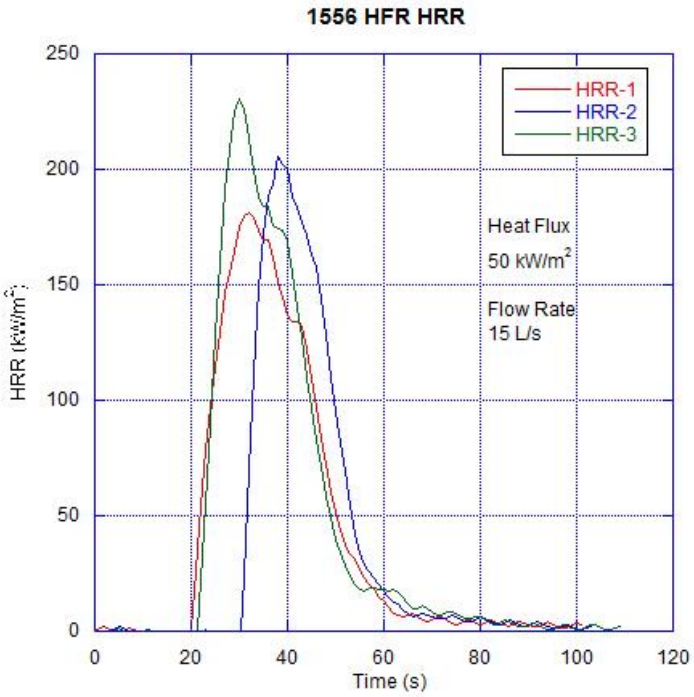

Figure 7-15. HRR for 1556 HFR Sample

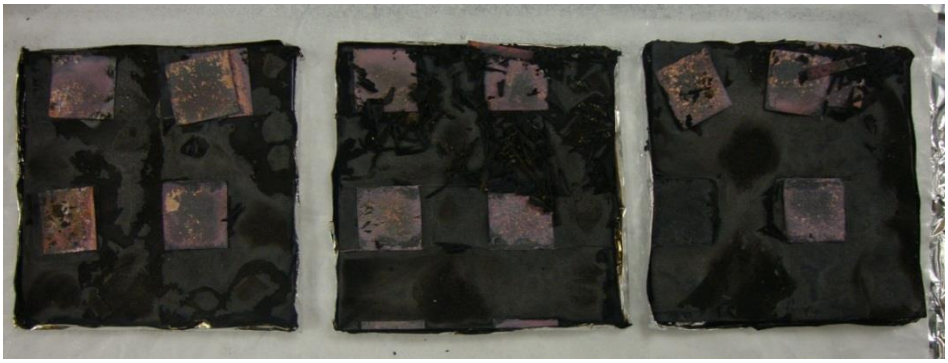

Figure 7-16. Final Chars for 1556 HFR Sample

1556 HFR+ P Fire Behavior

Fire behavior for this sample was similar to that of sample 1556 HFR, but some blue flames were noted as well. No real curling of the sample occurred when the powder was present, but some spitting of the component powder out of the sample holder was noted. HRR (Figure 7-16) was fairly reproducible, with only the 2nd sample (HRR-2) showing variability in the peak HRR and time to peak HRR. Final chars (Figure 7-17) were black underneath with copper squares and the powder was a dark yellow-green in color.

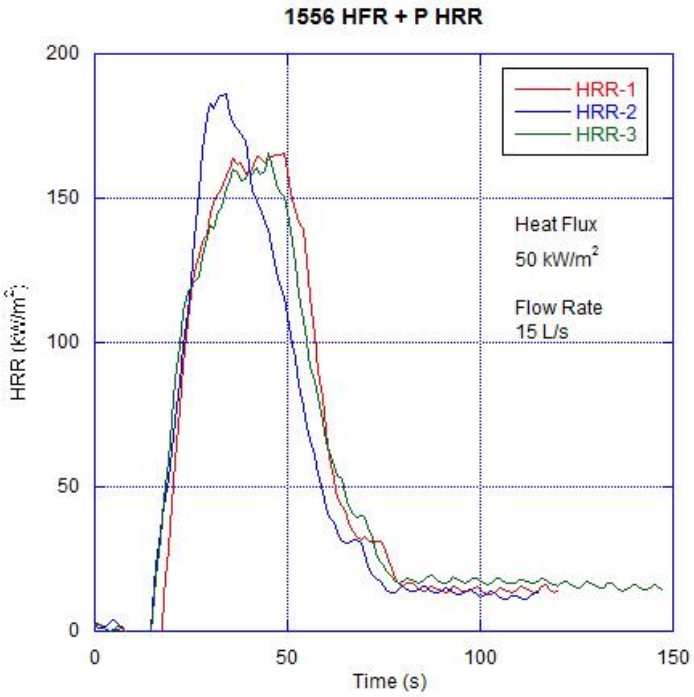

Figure 7-17. HRR for 1556 HFR + P Sample

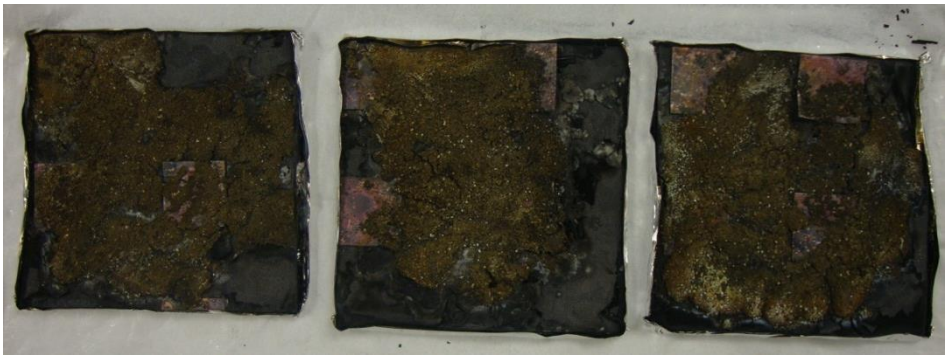

Figure 7-18. Final Char for 1556 HFR + P Sample

1556 HFR+ PHF Fire Behavior

Fire behavior for this sample was also similar to that of sample 1556 HFR, that some colors were seen in the flames toward the end of the test with some blue and blue/green colors noted. HRR (Figure 7-19) was reproducible and the final chars (Figure 7-20) were black and grey with the powder being mostly intact.

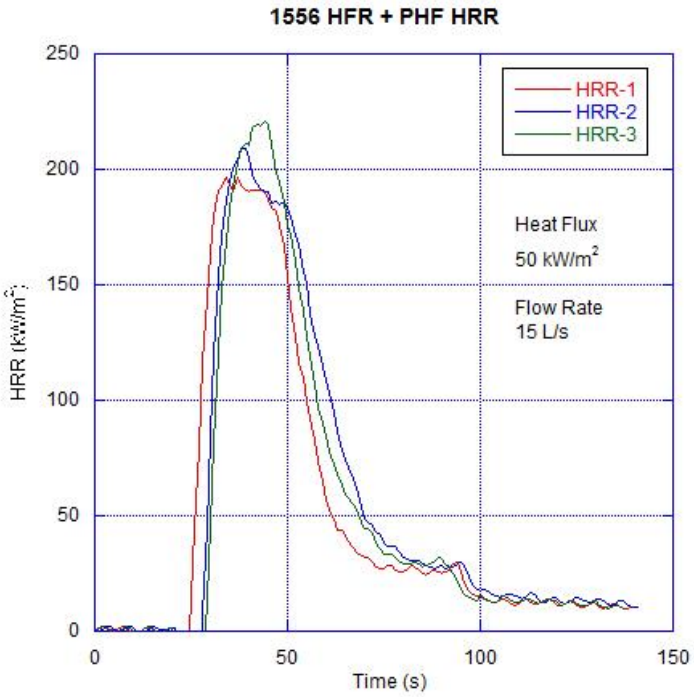

Figure 7-19. HRR for 1556 HFR + PHF Sample

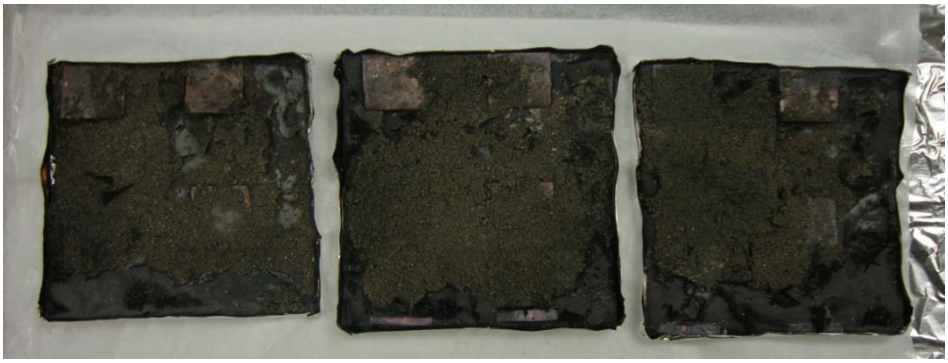

Figure 7-20. Final Chars for 1556 HFR + PHF Sample

Heat Flux-100 kW/m^2

Table 7-2. Heat Release Data (100 kW/m^2)

Sample Description - Heat Flux (50 kW/m^2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m$^{2)}$	Time to Peak HRR (s)	Average HRR (kW/m^2)	Starting Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m^2)	FIGRA
BFR -1	0.4	3	227	15	56	10.2	4.2	41.1	4.5	476	11.05	129	15.11
BFR -2	0.4	5	391	15	80	10.7	4.9	45.8	5.7	451	11.58	180	26.04
BFR -3	0.4	3	357	15	77	10.4	4.7	45.3	5.4	393	11.72	189	23.79
NFR -1	0.3	3	356	15	80	8.8	3.2	36.5	5.3	195	17.75	188	23.76
NFR -2	0.4	4	490	15	94	9.5	3.7	38.9	6.6	230	18.37	201	32.70
NFR -3	0.3	4	387	15	71	8.8	3.3	37.5	5.0	220	15.91	153	25.83
HFR -1	0.5	6	495	20	104	10.9	4.2	38.6	7.4	231	18.49	205	24.74
HFR -2	0.5	6	495	20	105	11.2	4.0	35.8	7.5	238	20.75	216	24.76
HFR -3	0.5	5	367	25	120	14.1	5.7	40.5	10.2	326	17.95	201	14.68

BFR Fire Behavior

Upon exposure to the cone heater, the sample quickly began to smoke and crackle, and then ignited quickly. The flames were noted to be orange and blue in color. With some of the samples, smoke would shoot out the sides of the sample and escape the cone calorimeter exhaust ducting. Some of the samples also curled/deformed during testing. Heat release (Figure 7-21) showed some notable scatter in the peak HRR value for the 1st sample (HRR-1). The reasons for this scatter with the 1st sample are not clear at this time, but perhaps this sample had slightly less flammable epoxy mass than the other two samples tested. Final chars (Figure 7-22) were dark grey with exposed glass fiber and burned/damaged copper metal squares.

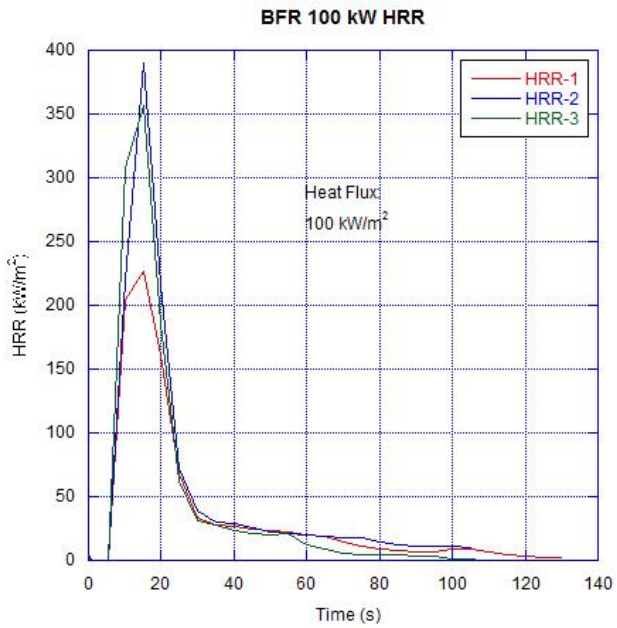

Figure 7-21. HRR for BFR Sample

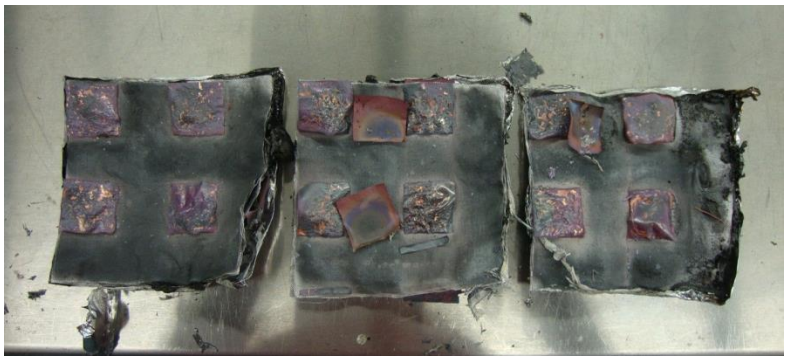

Figure 7-22. Final Chars for BFR Sample

NFR Fire Behavior

Fire behavior was identical to that of the BFR sample, except no blue colors in the flames were noted, the appeared to be more charring and soot generated during burning, and more curling/deformation was noted during burning. HRR was fairly reproducible (Figure 7-23) and the final chars (Figure 7-24) were blackened over most of the surface, including the copper metal squares.

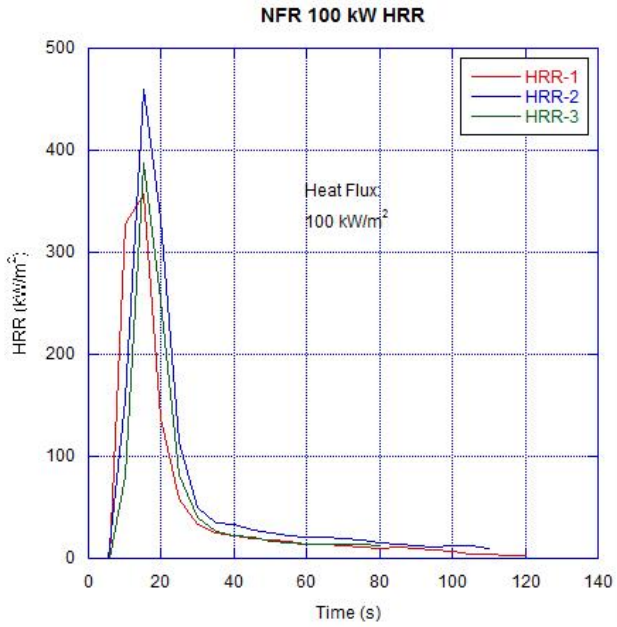

Figure 7-23. HRR for NFR Sample

Figure 7-24. Final Chars for NFR Sample

HFR Fire Behavior

Upon exposure to the heater, the sample began to smoke and crackle, with more of a whiter smoke noted prior to ignition. Some deformation during burning was noted, and the sample was noted to have a distinct smell to it when removed from the cone heater. HRR was reproducible for the 1st two samples (HRR-1, HRR-2), but the third sample (HRR-3) shows a lower peak HRR and a bit of delay in time to peak HRR (Figure 7-25). Again, reasons for this difference are unclear at this time. Since some of the samples deformed greatly during testing, it was not possible to close the cone heater shutters at the end of the test and so the samples were exposed to additional heat at the end of the test after extinguishment which burned off additional surface char, yielding light grey specimens of bare glass fiber (Figure 7-26). One of the samples

did not deform as much and the shutters could be closed, giving a specimen with more surface char (middle of Figure 7-26).

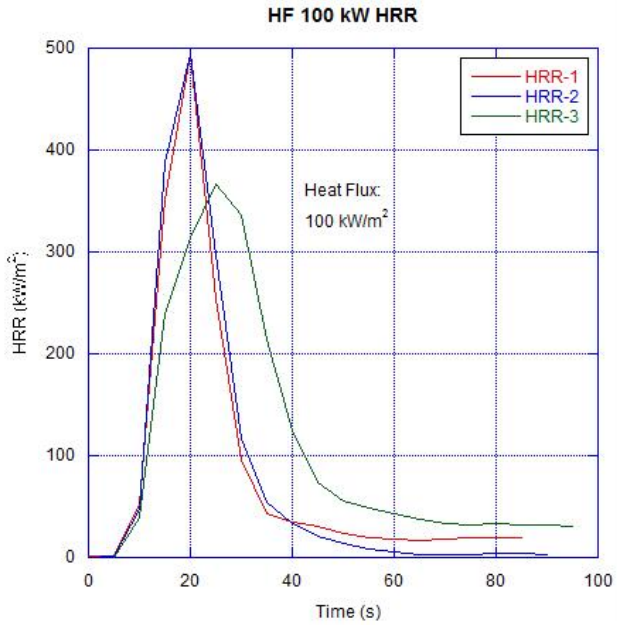

Figure 7-25. HRR for HFR Sample

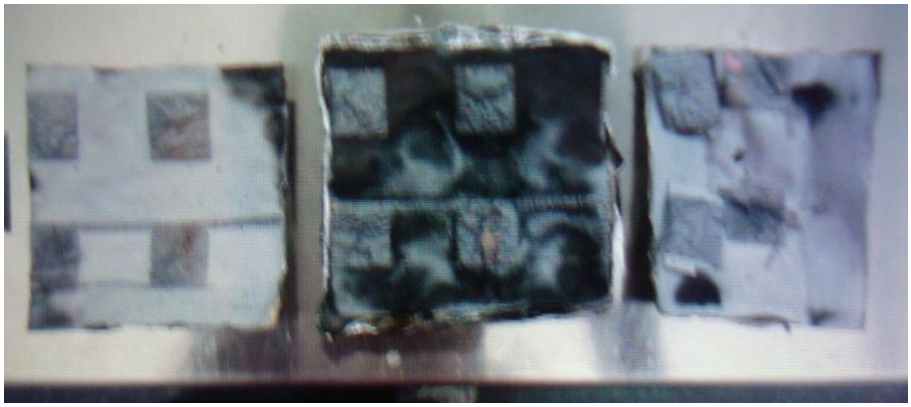

Figure 7-26. Final Chars for HFR Sample

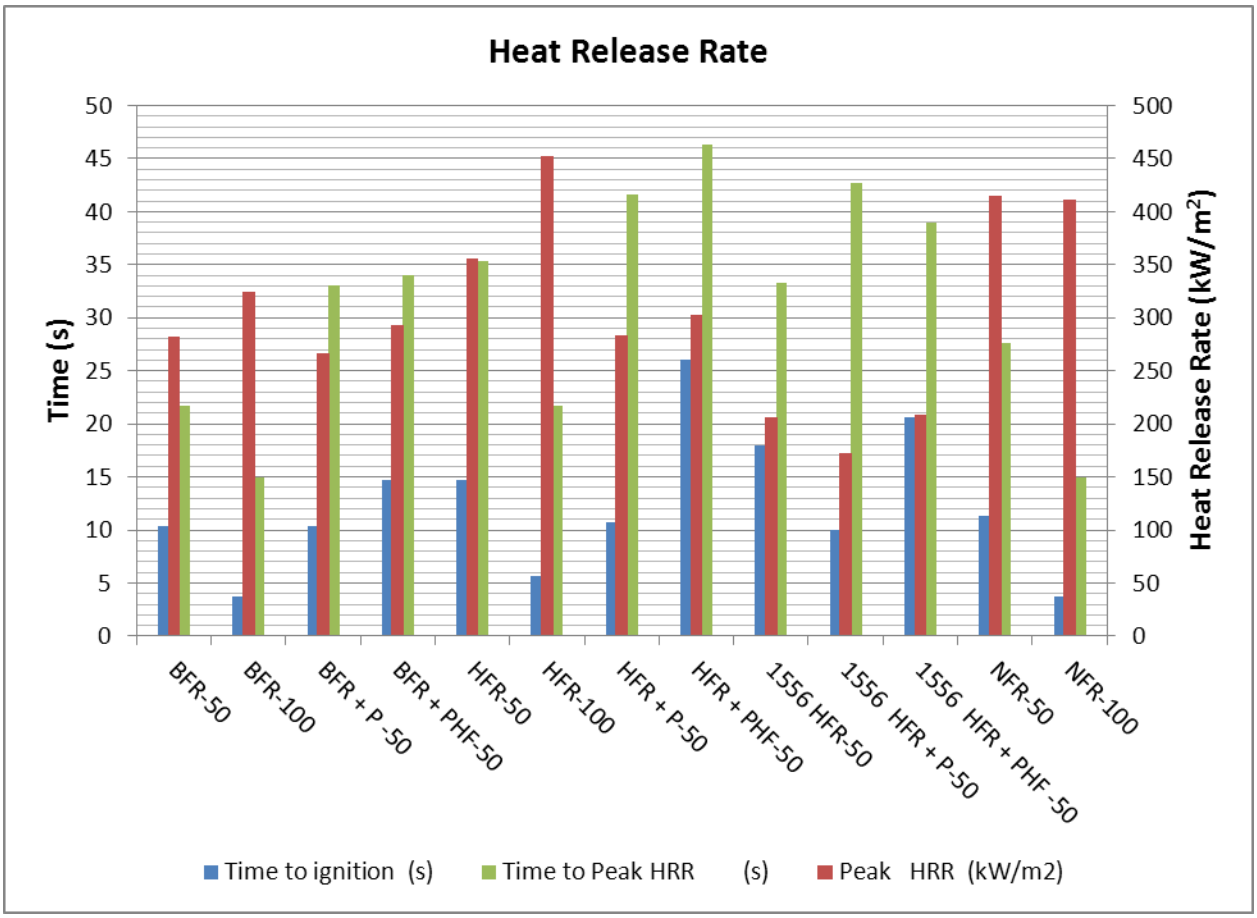

Figure 7-27. Heat Release Rate Plot

Overall Remarks on 50 kW/m^2 Heat Flux Sample Burning Behavior:

There are notable interactions between the component powder and the polymer decomposition chemistry going on as these samples burn. Brominated FR epoxy reacts differently with halogen-containing and halogen-free component powder, as does the halogen-free epoxy. The 1556 HFR sample also shows some differences when exposed to the two different powders, but not to as great a degree seen with the BFR and HF epoxy samples. The behavior of the HF comp powder is worth noting on here since in one case it showed bubbling but not in others. This may be due to a unique flame retardant reaction in the presence of brominated epoxy, but no obvious reason for this behavior can be given at this time.

The BFR samples, as expected, gave off lots of smoke and pyrolyzed some of the copper away in the form of copper halides, which were seen in the flames as blue colors. The HF samples showed some white colors indicating phosphorus release, but no blues until halogen-containing component powder was added, suggesting that less copper was pyrolyzed during burning. The 1556 HFR samples showed color in the presence of the halogenated powder, and surprisingly in the presence of the HF component powder as well, indicating the components again have an effect on metal pyrolysis/thermal reaction behavior.

Overall Remarks on Burning Behavior – 100 kW/m^2 Heat Flux:

At 100 kW/m^2 heat flux, the differences in fire behavior between the samples tested were minimal, but there were some differences noted in physical burning behavior which correlate to

the fire behavior noted at 50 kW/m^2 heat flux. The brominated FR epoxy does give off more smoke and does inhibit combustion as expected, and the blue colors noted during burning are visual evidence of bromine reacting with copper under burning/pyrolysis conditions. The non-FR sample burns quickly and rapidly (as a sample with no flame retardant should), and the non-halogenated FR sample also shows physical fire behavior similar to that of the non-FR sample. The non-halogenated FR has an equally high effective heat of combustion to that of the non-FR sample which may just suggest that the flame retardant mechanism for this material has little effect at very high heat fluxes, or at least does not inhibit combustion as much at very high heat fluxes. Smoke release is slightly higher though, and so the non-halogenated FR sample is having some effect on combustion products even if no change in measured heat of combustion is observed.

8 Appendix B: Experimental Conditions

Table 8-1. Ambient Conditions during Cone Testing

Experiment #	Laminate Description-Heat Flux-kW/m^2	Ambient Conditions			
		Temperature °C	Relative Humidity %	Pressure mbar	Cone Set Temperature °C
E2	BFR - 50	24	22	998	731
E4	BFR - 50	22.5	46	974	721
E6	BFR + P - 50	22.5	32	969	721
E8	BFR + P - 50	23	36	980	721
E10	BFR + PHF - 50	23	43	980	721
E30	BFR + PHF- 50	22.5	37	978	725
E12	NFR -100	22.5	45	981	978
E13	NFR -100	24	47	982	978
E15	BFR -100	23	43	975	937
E16	BFR -100	22.5	38	987	927
E18	HFR -100	22.5	44	986	924
E19	HFR -100	22.5	42	986	922
E21	NFR - 50	22.5	38	987	740
E22	NFR - 50	22.5	41	982	736
E24	HFR - 50	23	37	985	736
E25	HFR - 50	23	27	996	736
E27	1556 HFR - 50	22	37	986	727
E28	1556 HFR - 50	22	40	980	725
E32	HFR + P - 50	22	35	995	722
E33	HFR + P - 50	21.5	28	991	722
E35	HFR + PHF - 50	21.5	26	981	721
E36	HFR + PHF - 50	21.5	32	992	721
E38	1556 HFR + P - 50	22	32	981	721
E39	1556 HFR + P - 50	21.5	33	981	721
E41	1556 HFR + PHF - 50	21.5	24	998	719
E42	1556 HFR + PHF - 50	20.5	35	990	719

9 Appendix C: Elemental Analyses of Component Mixtures

Table 9-1. Elemental Analyses of Component Mixtures

Substance	Low Halogen: Total Mass (g) per 3052.25 g of mixture	Non-Low Halogen: Total Mass (g) per 3052.25 g of mixture
1,4-BENZENEDICARBOXYLIC ACID, POLYMER WITH [1,1'-BIPHENYL]-4,4'-DIOL,	845.140	0.000
4-HYDROXYBENZOIC ACID, 6-HYDROXY-2-NAPHTHALENECARBOXYLIC ACID AND N-(4-HYDROXYPHENYL)ACETAMIDE (9CI)	845.140	0.000
1,4-BIS(2,3-EPOXYPROPOXY)BUTANE	0.002	0.002
ACRYLIC RESIN	0.135	0.135
AG (Silver)	8.208	8.208
AL (Aluminum)	0.004	0.004
AL2O3 (Aluminum oxide)	41.150	41.150
ANTIMONY TRIOXIDE	0.000	0.000
ARALDITE GY 250	1.721	1.721
AU (Gold)	7.065	7.065
B (Boron)	0.000	0.000
BARIUM TITANATE(IV)	453.479	453.479
BASIC DUROMER: POLYURETHANE RESIN (COMPOUND OF A POLYMERIC NETWORK)	1.082	1.082
BERYLLIUM	0.000	0.000
BROMINE	0.086	0.085
C.I. PIGMENT BLACK 28	0.281	0.281
CALCIUM	0.000	0.000
CALCIUM MONOXIDE	0.157	0.157
CALCIUM-CARBONATE	1.866	1.866
CARBON BLACK	12.662	1.318
CHLORINE	0.086	5.757
CHROMIUM	0.001	0.001
CHROMIUM(III)OXIDE	0.355	0.355
COBALT, ELEMENTAL	0.615	0.615
COPPER (METALLIC)	425.069	425.069
COPPER OXIDE (CUO)	9.852	9.852
CRISTOBALITE	1.174	1.174
DIIRON-TRIOXIDE	121.742	121.742
DODECANE	0.014	0.014
DUMMY SUBSTANCE	0.002	0.002
Epoxy Resin	33.936	33.936
FE (Iron)	8.160	8.160
FIBROUS-GLASS-WOOL	277.933	453.768
FLOWERS OF ZINC (Zinc Oxide)	29.989	29.989
FORMALDEHYDE, OLIGOMERIC REACTION PRODUCTS WITH 1-CHLORO-2,3-EPOXYPROPANE AND PHENOL	1.906	1.906
FRITS, CHEMICALS	0.280	0.280
FUSED SILICA	374.758	374.758
IN (Indium)	0.000	0.000
LEAD	0.170	0.170
LEAD (II) OXIDE	0.062	0.062
LEAD (II) TITANATE	0.767	0.767
MAGNESIUM TITANIUM OXIDE (MGTIO3)	9.767	9.767
MAGNESIUM-OXIDE	0.131	0.131
MANGANESE	0.031	0.031
MO (Molybdenum)	0.355	0.355
NICKEL	101.263	101.263
NICKEL OXIDE	26.977	26.977
P (Phosphorous)	0.036	0.036
PALLADIUM	0.451	0.451
P-F-R-2	25.913	25.913
Polyphenylene Sulfide		674.980
SI (Silica)	14.265	14.265
SILICA	0.761	0.761
SILICONE	2.555	2.555
SN (Stannum/Tin)	7.623	7.623
SOLVENT NAPHTHA (PETROLEUM), HEAVY AROM.	0.018	0.018
STABILIZATION UV, LIGHT, HEAT	2.094	2.094
TUNGSTEN (W)	0.780	0.780
ZINC POWDER - ZINC DUST (NOT STABILIZED)	199.323	199.323

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