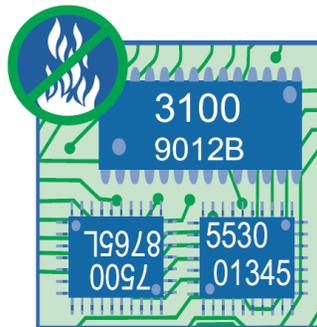


# FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS

## Chapter 6



### FINAL REPORT

August 2015

## 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<sup>th</sup> to 1/10<sup>th</sup> 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**

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

### 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 Dibenzop-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**

<b>Laminates Burned</b>	TBBPA laminate (BFR) Non-flame-retardant laminate (NFR) Phosphorus-based flame-retardant laminate (PFR1) Phosphorus-based flame-retardant laminate (PFR2)
<b>Laminate/Component Combinations Burned</b>	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)
<b>Scenarios (Heat Flux)</b>	Open Burn (50 kW/m <sup>2</sup> ) (Laminate abbreviation-50) Incineration (100 kW/m <sup>2</sup> ) (Laminate abbreviation-00)
<b>Analytes Tested</b>	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<sub>2</sub> 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<sub>2</sub> emissions varied depending on laminate type.

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

<b>Sample</b>	<b>PBDD/Fs</b>	<b>Quantity of PBDD/Fs detected (ng/g)</b>
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**

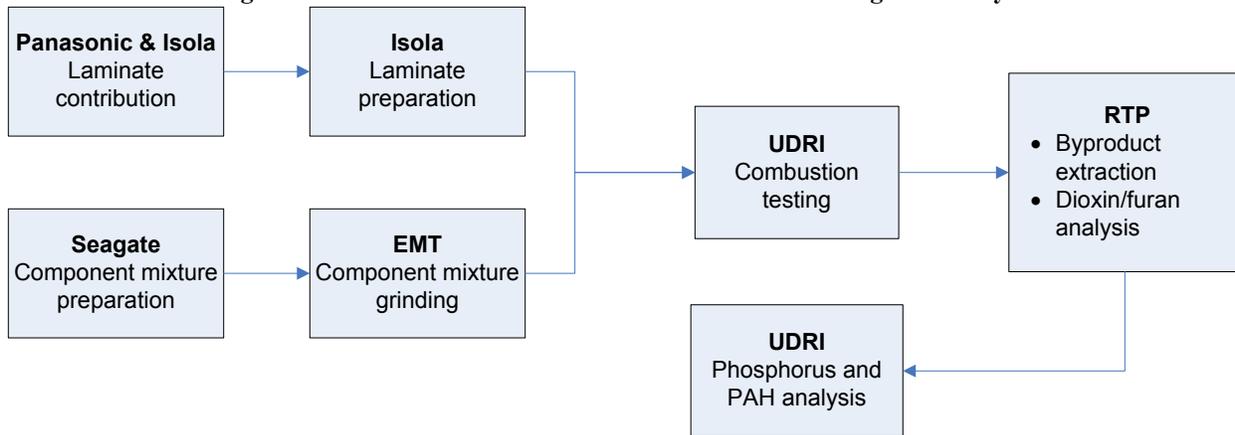
Sample	Quantity of PAHs detected (g/kg)
<b>Incineration (100 kW/m<sup>2</sup>)</b>	
BFR-100	5.08
PFR1-100	1.51
NFR-100	1.95
<b>Open burn (50 kW/m<sup>2</sup>)</b>	
BFR-50	5.22
PFR1-50*	1.74
PFR2-50	2.93
NFR-50*	0.624
<b>Open burn (50 kW/m<sup>2</sup>) with standard halogen components</b>	
BFR + SH-50	3.93
PFR1 + SH-50	2.04
PFR2 + SH-50	2.24
<b>Open burn (50 kW/m<sup>2</sup>) with low-halogen components</b>	
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<sub>2</sub>, 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 clean-up 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**



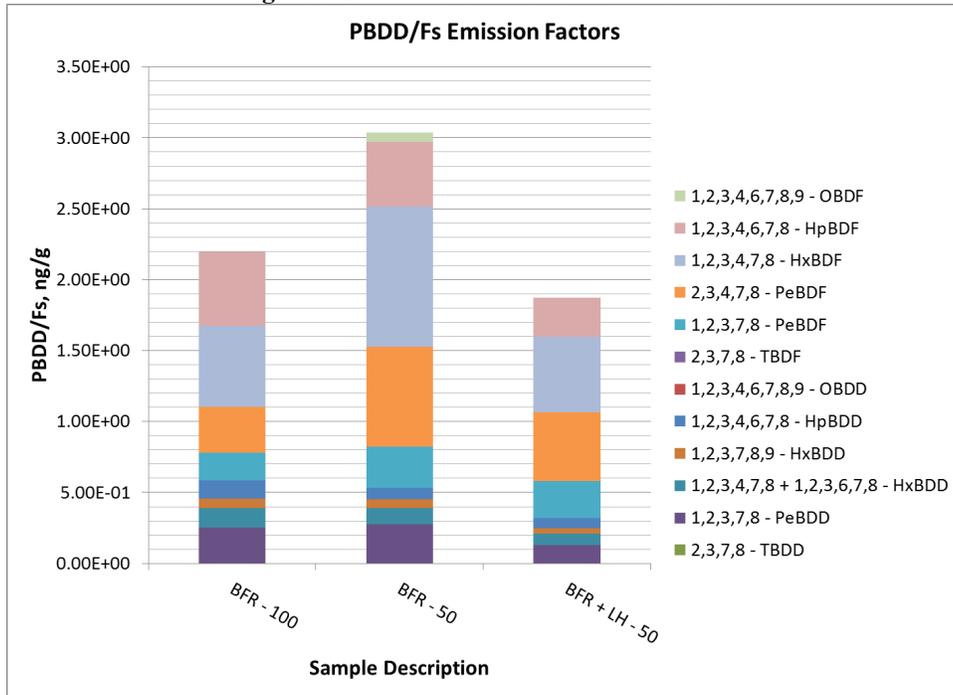
PBDD/Fs were detected and quantified in all six BFR samples (Figure 6-3); five of the six blanks had significantly lower levels of PBDD/Fs compared to the laminate samples. For example, the detection of 1,2,3,4,6,7,8 - HpBDF ranged from 4 to 9 ng/train for the six BFR laminate samples compared to not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

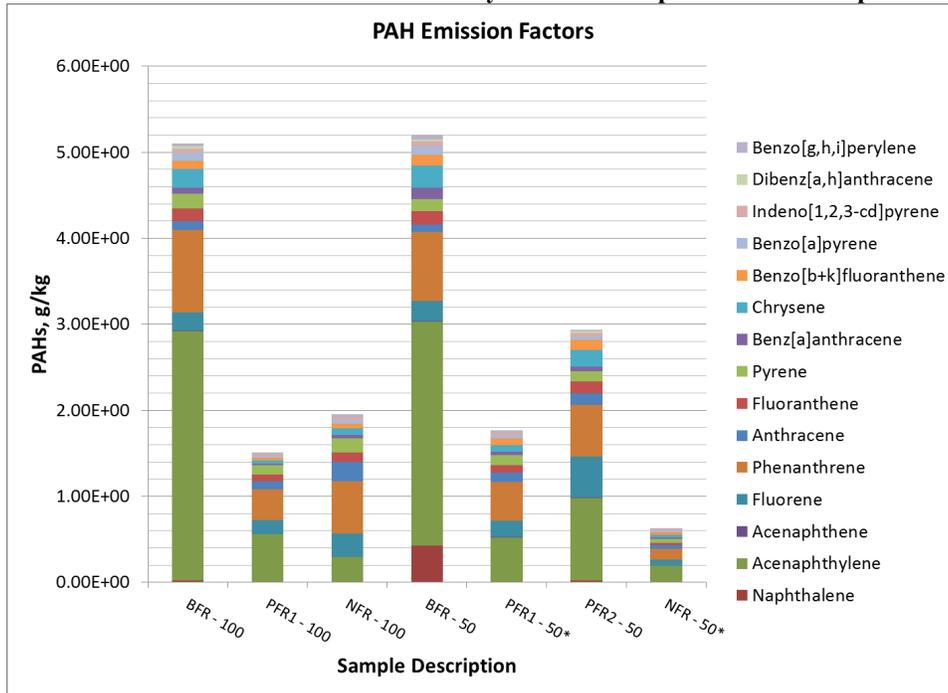
### Polyaromatic Hydrocarbon Analysis

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  $\leq 4$  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.

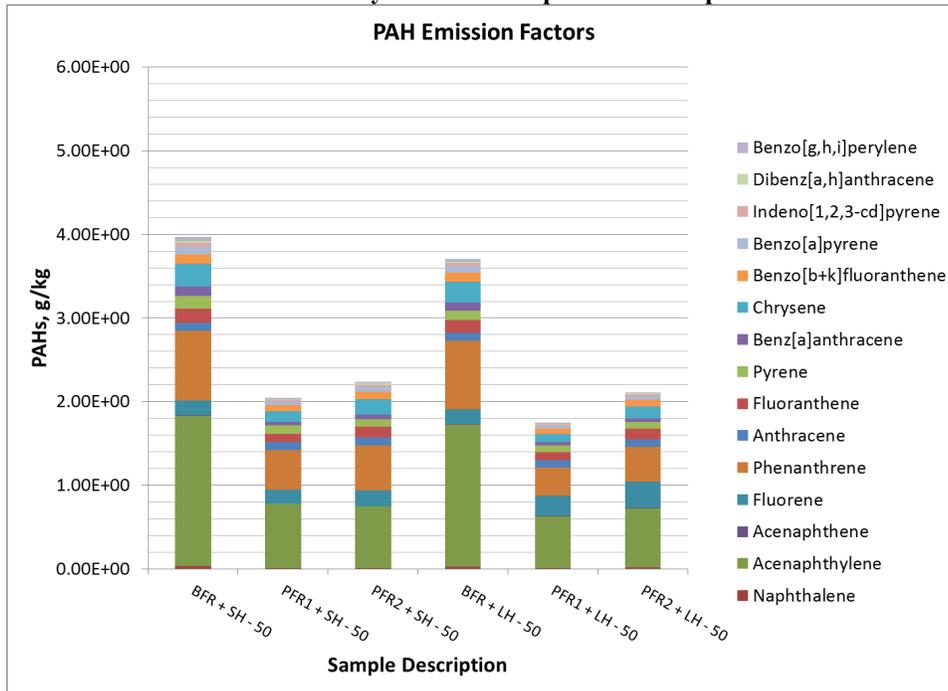
**Figure 6-4. PAH Emission Factors Plotted for Naphthalene and Higher Molecular Weight (MW) PAHs Detected from the EPA List of 16<sup>†</sup> Priority PAHs in Samples without Components**



<sup>†</sup>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<sup>†</sup> Priority PAHs in Samples with Components**

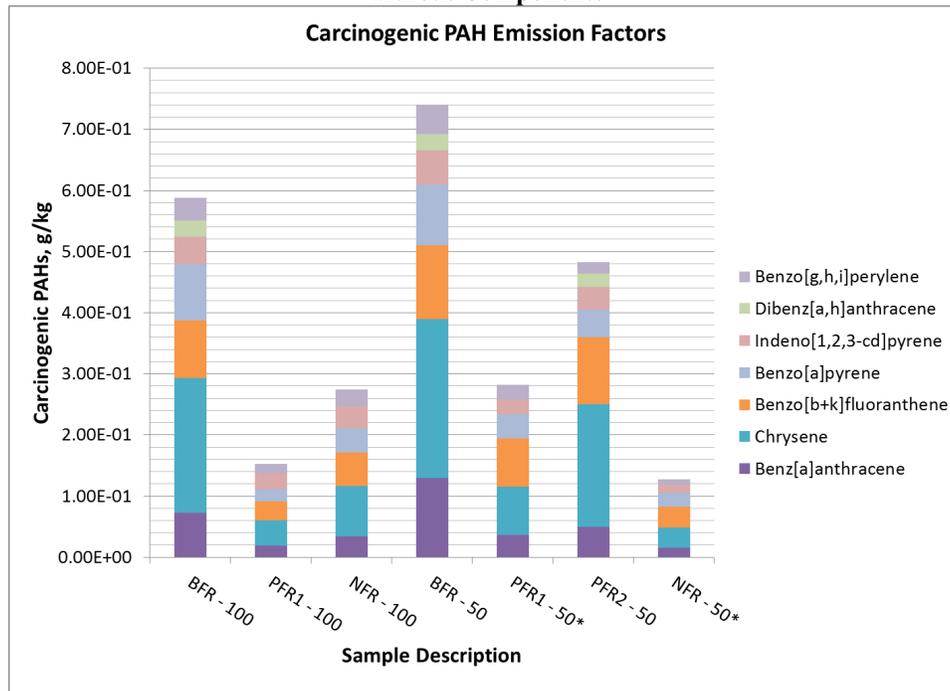


<sup>†</sup>Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

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.

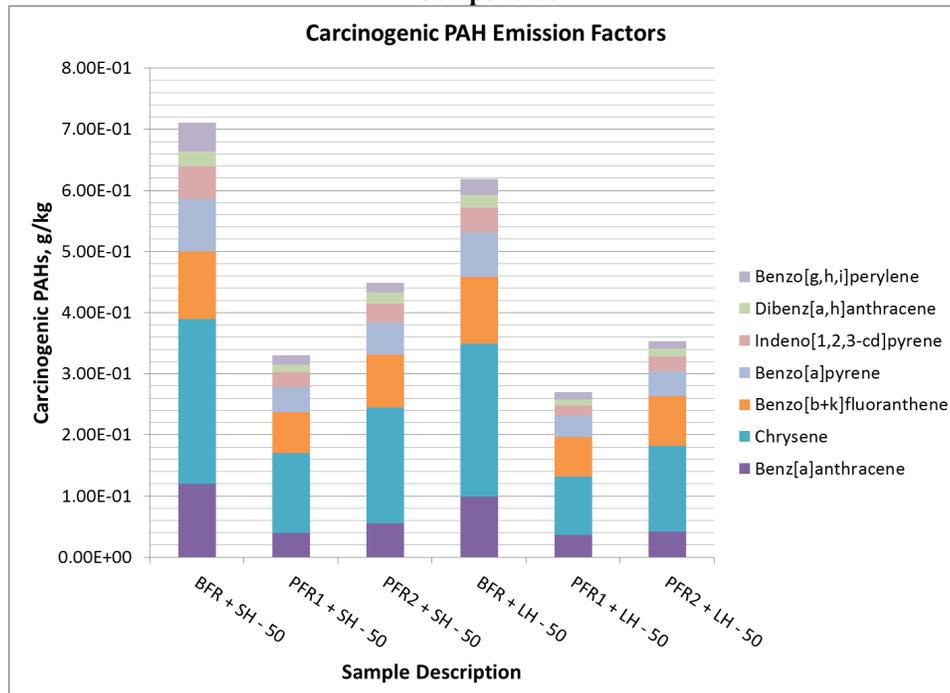
**Figure 6-6. Emission Factors of Carcinogenic PAHs from the EPA List of 16<sup>†</sup> Priority PAHs in Samples without Components**



<sup>†</sup>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**

<b>Laminate Description</b>	<b>Organophosphorus Compounds Detected</b>	<b>Area %</b>
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
BFR + SH -50	Phosphonic acid, methylenebis-, tetrakis(trimethylsilyl) ester	0.17
	O,O'-(2,2'-Biphenylene)thiophosphoric acid	0.38
BFR + SH -50	Bis(4-methoxyphenyl)phosphinic acid	0.10
PFR1 +SH-50	Phosphonic acid, phenyl-, diethyl ester	0.25
PFR2 + SH -50	Phosphorane, 11H-benzo[a]fluoren-1-ylidenetriphenyl-	0.43
	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.53
BFR + LH-50	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
	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

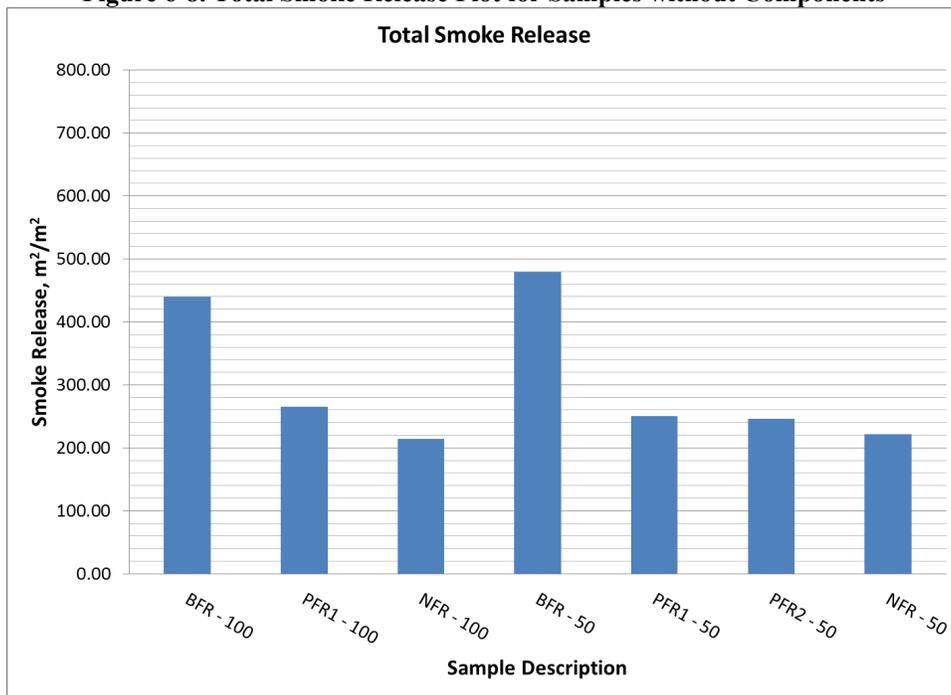
### Smoke Release Analysis

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

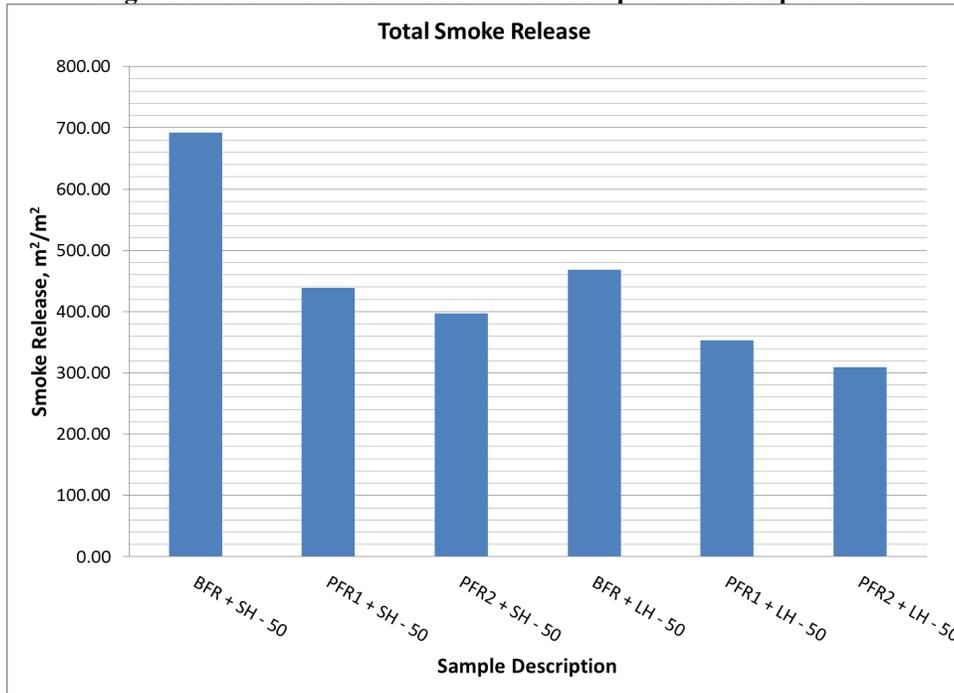
within the percent error of the smoke measurement device ( $\pm 10$  percent). The NFRs had the lowest total smoke release overall, but was within the percent error of PFR1 and PFR2.

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**

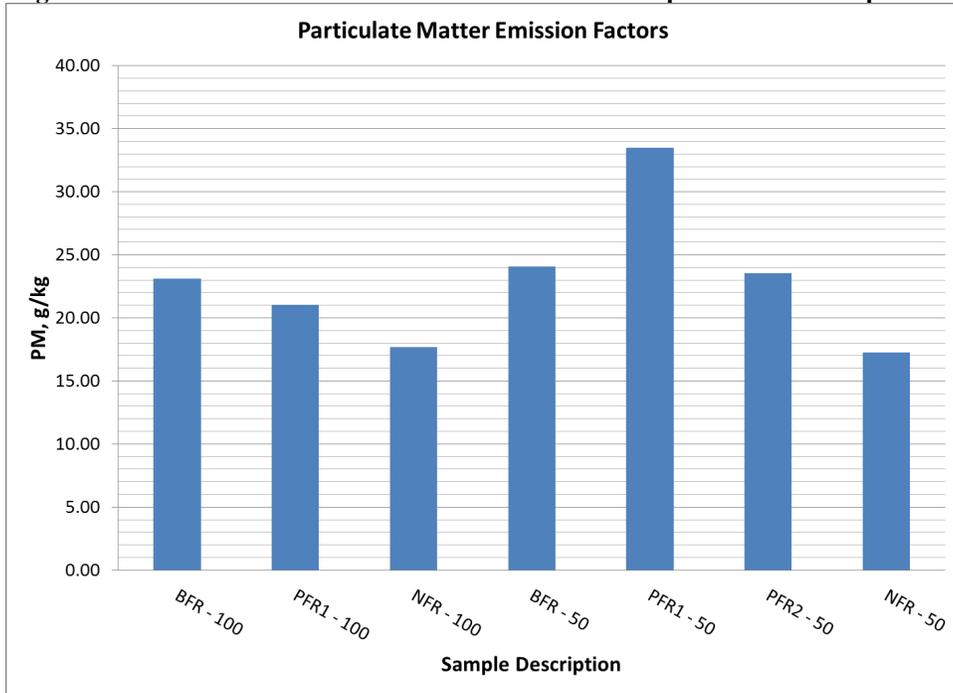


### **Particulate Matter Release Analysis**

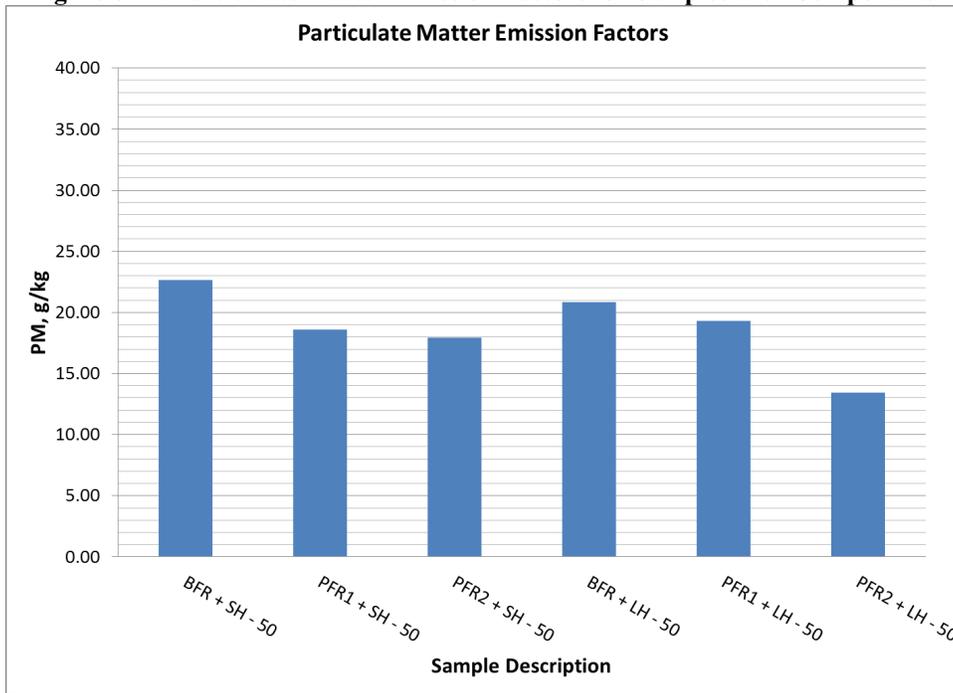
The particulate matter results do not directly correlate with smoke release. For example, total smoke release was greatest for the samples containing the BFRs, while particulate matter was not always highest for the samples containing the BFRs. Differences between smoke release and particulate matter 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<sub>2</sub> Release Analysis**

Figure 6-12 presents CO/CO<sub>2</sub> emissions for samples without components. In both combustion scenarios, BFRs without components had the lowest CO<sub>2</sub> emissions of all laminate types. CO<sub>2</sub>

emissions were also lowest for BFRs of the samples with components presented in Figure 6-13. The comparatively lower CO<sub>2</sub> emissions for the BFR laminates is likely due to the inhibition of total combustion by bromine, which prevents carbon from converting to CO<sub>2</sub>. However, a decrease in CO<sub>2</sub> 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<sub>2</sub> emissions. More CO<sub>2</sub> 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<sub>2</sub> yields. CO<sub>2</sub> 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<sub>2</sub> emissions are best explained by combustion chemistry, flame retardant type and the presence of components.

**Figure 6-12. CO/CO<sub>2</sub> Emission Factors Plot for Samples without Components**

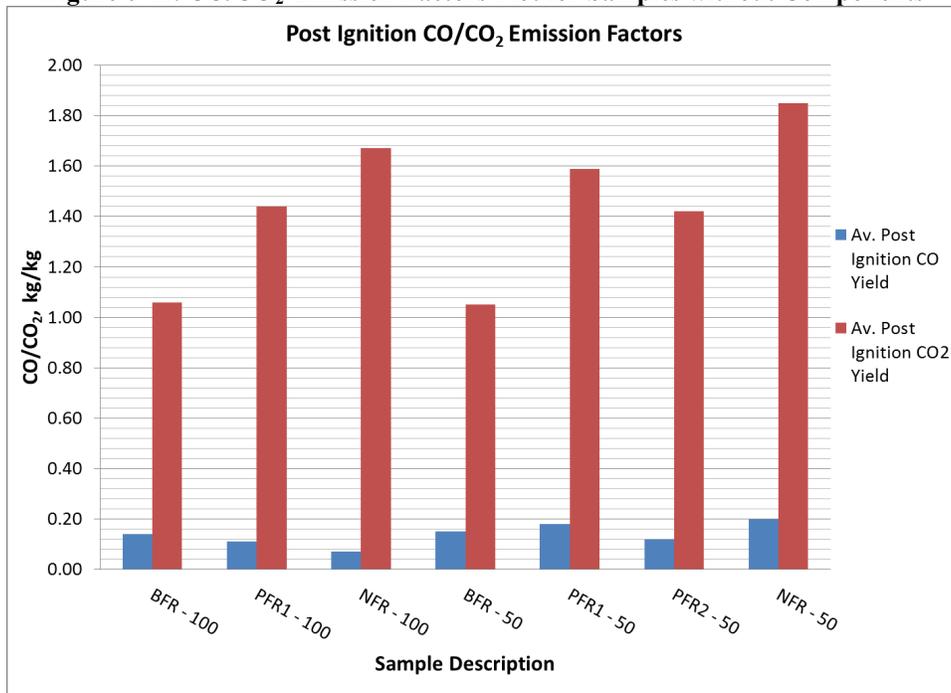
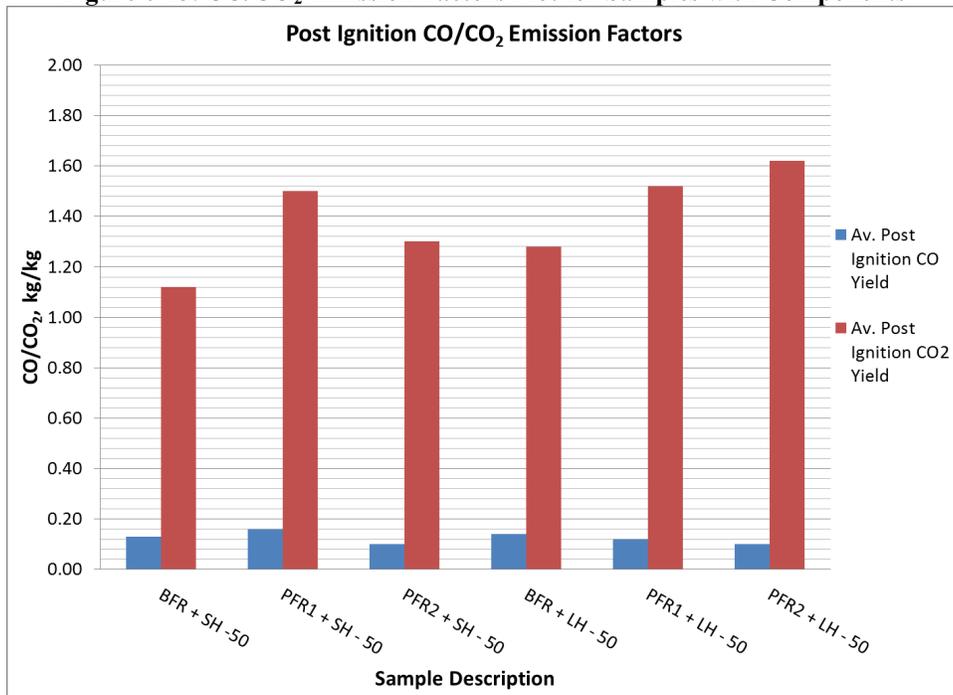


Figure 6-13. CO/CO<sub>2</sub> Emission Factors Plot for Samples with Components



## 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.