Human Health in the Built Environment

A Study of Chemical Exposure Risk and Flammability of Upholstered Furniture and Consumer Electronics

Marilyn Black, PhD, Underwriters Laboratories Inc.
Aika Davis, PhD, Underwriters Laboratories Inc.
Debra Harris, PhD, RAD Consultants

In collaboration with University Research Partners:

P. Barry Ryan, PhD, Emory University, Rollins School of Public Health
Jordan R. Cohen, MPH, Emory University, Rollins School of Public Health

April 2019

Table of Contents

Table of Contents

Table of Figures

Table of Tables

Abstract

This study provided scientific insights on achieving chemical safe and fire safe residential furniture products. Upholstered furniture not only remains a significant fire hazard in consumer spaces, it also poses a potential human health risk from the exposure to flame retardants and other chemicals associated with its construction materials. This study focused on methodology development for studying pathways for human exposure to flame retardants and assessing exposure amounts during consumer use. It also evaluated the effectiveness of differing fire control strategies (with and without flame retardants and with a fire barrier material) on minimizing flammability hazards. Two flame retardants were evaluated - a standard organophosphorus flame retardant added to the resilient foam and a “reactive,” newer chemistry flame retardant that was chemically integrated in the foam. Open flame testing was performed on a series of upholstered chairs manufactured with or without flame retardants. Cigarette smoldering tests according to California Technical Bulletin 117-2013 (TB 117-2013) were also conducted on the chair materials. The same chairs were tested for flame retardant and volatile organic compound (VOC) consumer exposure levels prior to the open flame burn tests. During the burns, flame retardant and other chemical emissions in the fire effluents were also measured.

Results showed that volatile organic compounds (VOCs) inhalation exposure during consumer use was low for all types of chairs. The organophosphorus flame retardant used in this study was found in air, settled dust and dermal transfer samples resulting from use of the specific type of chair. Data showed the most significant human exposure pathway to be dermal transfer from skin contact followed by ingestion and inhalation. Dose determinations indicated that children would receive their highest dose from ingestion primarily resulting from frequent hand-to-mouth contact with settled dust. There was no indication of the “reactive” flame retardant in the environmental samples based on currently available measurement techniques.

Open flame testing showed that the chairs with a barrier material between the cover fabric and resilient foam (and no flame retardant) demonstrated significantly lower fire hazards (in peak heat release rates, carbon monoxide, volatile chemical and hydrogen cyanide emission levels, temperature, and smoke) when compared to the other chairs with and without flame retardants (and no barriers). There was no discernable difference in the open flame performance of chairs made with no flame retardant (and no barrier) and those made with flame retardants. All chairs failed the California Technical Bulletin 117-2013 (TB 117-2013) criteria, showing no correlation between the cigarette smoldering test and open flame performance of the chairs. Air emissions during the open flame burns showed elevated levels of numerous hazardous chemicals including the organophosphate flame retardant.

The base chair used in this study was available in the retail market at the time of the study, and the chair construction options presented in this study are available. Data from this study demonstrated that combined human health and flammability advantages may be achieved for upholstered chairs constructed with an effective fire barrier material and no flame retardants.

1. Executive Summary

1.1 Background

1.1.1 Safety Convergence

Current research, market awareness and policy updates continue to address the safety and human health impact of flame retardants in upholstered furniture and other consumer products. This has elevated the need to scientifically understand and manage the intersecting risks of product flammability and chemical exposure. With the public's increasing concern of hazardous chemicals in everyday products and the consumer expectation of safe products, there is a need to advance scientific understanding of processes for achieving fire safe and chemical safe products. This is a complex challenge, and we addressed this by bringing stakeholders together, providing forums for sharing of information and discussion, and conducting scientific research to bring data and new insights forward. Following stakeholder dialogue, a research plan was developed with the objectives of developing analytical methodologies and generating data on how consumer flame retardant exposure can occur from upholstered furniture, identifying the primary exposure routes, and correlating flammability characteristics of upholstered furniture with different types of flammability control technologies used in furniture construction. This research was designed to bring data forward to further understand the intersection or convergence of chemical exposure and fire protection and to encourage further actions in harmonizing consumer protection from fire and chemical exposure risks.

1.1.2 Flame Retardants

Flame retardants and other chemicals have been used for decades in the production of commercial and residential upholstered furniture and other consumer products. In general, the use of flame retardants is a method for achieving fire protection. The use of flame retardant chemicals in furniture filling, typically polyurethane foam (PUF), became customary in response to flammability regulations, such as the California flammability standard, Technical Bulletin 117 (TB 117) in 1975,[1] or the Furniture and Furnishings (Fire Safety) Regulations in the United Kingdom (U.K.) in 1988.[2] These regulations were established primarily to protect against home fires started by small open flames, such as candles, matches, and lighters.[3]

Prior to 2014 in the United States (U.S.), a variety of flame retardants were added to polyurethane foam (PUF) to meet the California Technical Bulletin 117 (TB 117) standard that required the foam to withstand an open flame test with minimal loss and no sustained ignition after the flame was removed. In response to the potential human harm associated with flame retardant exposures, California's Technical Bulletin 117 (TB 117) flammability regulation was replaced by California Technical Bulletin 117-2013 (TB 117-2013). Manufacturers are no longer required by the test protocol to make their products resistant to an open flame ignition source; they must only meet a cigarette smolder resistance test. California Technical Bulletin 117-2013 (TB 117-2013) allows manufacturers to pursue other methods of passing the flammability standard without the use of flame retardants. It does not, however, prohibit the use of flame retardants. Fires from open flame sources are still a threat, and there are concerns that furniture flammability evaluation only using smoldering cigarette ignition testing omits important aspects of how upholstered furniture contributes to real-world fire scenarios.

1.2 Research Objectives

The primary objectives for this research were to: 1) explore methodologies for studying pathways (and levels) for human exposure to flame retardants with typical upholstered furniture use, 2) evaluate the impact of furniture age on flame retardant exposure potentials and flammability performance, and 3) investigate differing fire control technologies (with and without flame retardants) for their management of open flame and chemical exposure risks. Secondary objectives provided by the study included: assessing volatile organic compound (VOC) and flame retardant exposure in the surrounding air during typical product use and furniture burns, comparing chemical emissions and product burn characteristics of upholstered furniture to other consumer electronics found in a typical indoor environment, and estimating the average daily dose (ADD) of the specific flame retardants originating from furniture designed for this study.

1.3 Test Samples

Upholstered chairs were constructed specifically for this study by a U.S.-based furniture company. The particular chair was already commercially available, and study chair construction followed the manufacturer's typical fabrication methods and materials, differing only in the flammability control technologies explored in this study. Of the 20 total chairs fabricated, five chairs each were constructed using one of four flame retardant technologies detailed below:

- No flame retardant added to the polyurethane foam (control) (NFR)
- Organophosphate chemical flame retardant added to the polyurethane foam (OPFR), identified as triphenyl phosphate (TPhP) and tertbutyl phenyl phosphates (TBPP mix)
- A proprietary reactive (polymer integrated) chemical flame retardant added to the polyurethane foam (RFR)
- No flame retardant added to the polyurethane foam, but a barrier material added between the polyurethane foam and textile cover (BNFR)

In addition, three individual chair cushions containing polyurethane foam (PUF) and flammability treatments became available and were tested for additional data. One cushion was fabricated without flame retardants; the second cushion had a commonly available flame retardant, identified as tris (1,3-dichloro-2-propyl) phosphate (TDCPP); and the third cushion was fabricated with a proprietary reactive flame retardant. All cushions were covered with a commercial grade 100% solution dyed nylon textile.

Finally, a 55-inch 4K light-emitting diode (LED) flat screen television and a 15.6-inch laptop computer, commonly available in the marketplace were tested to provide chemical emission and burn comparisons to the upholstered chairs.

1.4 Methodologies

Upholstered chairs, new and "aged," along with the electronic devices were tested for material composition identification, then placed in an environmental chamber for measurement of volatile organic compound (VOC) and aldehyde air emissions and flame retardants (in air, dust, and dermal transfer processes). A duplicate set of chairs was mechanically "aged" using American National Standards Institute (ANSI)/Business and Institutional Furniture Manufacturer's Association (BIFMA) X5.4 (3.2.1 Upholstered Chairs) to achieve a 10-year use period. A specialized robot was used to simulate a person using the chair during chemical sampling. Fire performance tests of the chairs and electronics included the California Technical Bulletin 117-2013 (TB 117-2013) smolder resistance test and full-scale open flame burn tests measuring heat and smoke release rates, total weight loss, gas emissions, smoke yield, and chemical and dust emissions. All measured data were used to determine exposure potentials.

1.5 Summary of Findings

1.5.1 Chemical Exposure: Consumer Use

- Emissions of volatile organic compounds (VOCs) and aldehydes from the four different chair types were low and would meet current indoor air guidelines.
- Total volatile organic compound (TVOC) levels of the chairs ranged from 68-160 microgram per cubic meter ($\mu g/m^3$) and were similar among new and aged chairs.
- Primary volatile organic compound (VOC) emissions of the chairs included alcohols, carboxylic acids, and aldehydes, as commonly associated with polyurethane foam.
- Chemicals of concern for chairs noted in the emissions at low levels included toluene, naphthalene, formaldehyde, and acetaldehyde, known carcinogens or reproductive toxins. These are likely associated with industrial solvent contamination or material composition.
- Volatile organic compound (VOC) emissions of the operating television were higher than the chairs with a total volatile organic compound (TVOC) value of 384 $\mu g/m^3$, and a complex mixture of siloxanes, alcohols, aromatics, acrylates, and phthalates measured. The laptop had low volatile organic compound (VOC) emissions, slightly above detectable levels.
- Chemicals of concern with the television included acetaldehyde, formaldehyde, naphthalene, toluene, ethyl benzene, and styrene, known carcinogens or reproductive hazards. These are likely associated with industrial solvents and product components.

1.5.2 Flame Retardant Exposure: Consumer Use

- Significant backgrounds of a variety of halogenated and nonhalogenated flame retardants were observed in the environmental chamber and measurement systems. This was an indication of the ubiquitous presence of flame retardants in our environments. Only those flame retardants that were specifically added to the products for this study were quantitatively reported.
- There were no measurable flame retardants observed, above variable backgrounds, from using the chairs constructed without flame retardants (NFR) or with the reactive flame retardants (RFR).
- Tris-isobutylated triphenyl phosphate (TBPP) and triphenyl phosphate (TPhP) were detected in the air, settled dust, and dermal transfer samples originating from use of the chair with added organophosphate flame retardant in the polyurethane foam (OPFR).
- Average daily doses (ADD) of triphenyl phosphate (TPhP) from the organophosphate flame retardant (OPFR) chair under assumed conditions, showed the most significant human pathway to be dermal transfer, followed by ingestion, and inhalation.
- Average daily dose (ADD) determinations showed that children would receive the highest exposure of triphenyl phosphate (TPhP) flame retardant through ingestion, due to the primary exposure route of frequent hand-to-mouth contact with settled dust.
- Operating electronics showed a range of halogenated and organophosphate flame retardants present in air and settled dust, but levels were not quantifiable.

1.5.3 Flammability: California Smoldering Technical Bulletin 117-2013 (TB 117-2013)

- All the chair types in this study, with and without flame retardants or with a barrier material, failed to meet the acceptable criteria of California Technical Bulletin 117-2013 (TB 117-2013). To pass, the cover textile, resilient filling materials, and decking material had to individually pass the smoldering test. If the cover textile failed, the barrier material had to pass, but it did not in this study.
- The upholstery cover textile, the barrier textile, and the resilient polyurethane foam (PUF) containing the organophosphate flame retardant (OPFR) failed to meet the smolder resistance requirements, and thus failed the test.
- The resilient foam with no flame retardant (NFR), the resilient foam with reactive flame retardant (RFR), the resilient loose fiber, and the decking textile passed the test for smolder resistance.

1.5.4 Flammability: Open Flame

- Heat release rates for the upholstered chairs were similar as measured from the Furniture Heat Release Calorimeter and the International Organization for Standardization (ISO) 9705 Test Room.
- Mechanical aging did not significantly affect the heat release rate or weight loss for all chair types. Peak carbon monoxide (CO) values, however, were lower after aging for the chairs without the fire barrier.
- The chairs with fire barriers (and no flame retardants) had significantly lower peak heat release rates with an average of 31 kilowatts (kW) as compared to an average of 1,400 kW for all other chairs without fire barriers.
- No significant differences were found when comparing the maximum heat release rate of the chairs with and without flame retardants and without the fire barrier. The chairs with no flame retardant (NFR), with the organophosphorus flame retardant (OPFR), and with the reactive flame retardant (RFR) all exceeded 1,000 kW of maximum heat release rates, with averages ranging between 1,294 and 1,336 kW for the Furniture Heat Release Calorimeter results and between 1,371 and 1,730 kW for the ISO 9705 Test Room results.
- The chairs with and without flame retardants and no barrier averaged a peak heat release rate of 1,400 kW which exceeded the 200 kW maximum heat release rate requirement for the flammability of mattresses. The chairs with barriers (and no flame retardants) with an average peak heat release of 31 kW and all electronics with an average peak heat release rate of 6 kW were below the 200 kW flammability requirement of mattresses.
- The fire barrier was found to significantly reduce the average weight loss of the chairs (6 pounds (lbs)) when compared to the nonbarrier chairs (37 lbs). The fire barrier also reduced the heat generation and resulted in lower transmitted fire hazards such as temperature, smoke, and carbon monoxide.
- Hydrogen cyanide (HCN) gas was not detected in the burn emissions for the chairs with the fire barrier.

- The home electronic items tested in this investigation had peak heat release rates of 10 kW or less. In comparison, all chairs without the fire barrier had peak heat release rates in excess of 1,000 kW, and the chairs with the fire barrier had an average peak heat release rate of 31 kW.

1.5.5 Flammability: Flame Retardant Exposure from Product Burns

- Tris-isobutylated triphenyl phosphate (TBPP) and triphenyl phosphate (TPhP) as used in the chair made with an organophosphate flame retardant (OPFR) were found in the burn emissions at significantly higher levels than found during typical consumer use.
- Mechanically aged chairs consistently measured less triphenyl phosphate (TPhP) than new chairs.

1.5.6 Flammability: Chemical Exposure from Product Burns

- Very complex mixtures of volatile organic compounds (VOCs) were released during the chair burns. More than 500 different volatile organic compounds (VOCs) were identified, but the reported air levels are considered semiquantitative at best, due to high contamination in the backgrounds and exploratory methodologies.
- Benzene, a known carcinogen was present in high levels during all chair burns, reaching an estimated level of greater than 25 milligrams per cubic meter (mg/m^3) and is significantly higher than the allowable occupational exposure limit.
- Other volatile organic compounds (VOCs) detected during the chair burns included aldehydes, nitriles, isocyanates, acrylates, phthalates, aromatics, carboxylic acids, and others. Many of these are carcinogens, reproductive and developmental toxins, irritants and odorants.
- Fewer volatile organic compounds (VOCs) were released from the electronic product burns. The television burn primarily released aromatics including benzene, styrene, toluene, phenanthrene and others; the laptop burn primarily released cyclic, branched and normal hydrocarbons.

1.6 Study Significance

This research has generated important scientific data to further understand the convergence of chemical exposure and fire protection relative to the use of flame retardants. The last stakeholder Summit acknowledged that fire risks of upholstered furniture are significant as home fires are more severe, given that modern homes burn faster and that upholstered furniture is a key fuel source of fire spread. This research allowed the study of a furniture product that currently exists in the marketplace with no added flame retardants and an option for a barrier material. This chair construction was simply modified to evaluate the impact of using common and innovative flame retardants currently available in the marketplace and being used in some cases. Chair constructions were realistic and constructed using the manufacturer's traditional processes and materials. The only variables were the barrier construction and different resilient foams, with and without flame retardants, that the manufacturer obtained from their supplier.

The data showed that if a traditional organophosphorus flame retardant (OPFR) was used in the polyurethane foam (PUF) of the chair, then exposure to that flame retardant could occur to a consumer through inhalation, ingestion (via settled dust) and dermal transfer from contact, with ingestion as the most significant exposure opportunity by hand-to-mouth transfer. The reactive flame retardant did not indicate any exposure based on currently available analytical methodologies. Data also showed that significantly higher inhalation exposure to the organophosphorus flame retardant (OPFR) occurred from the burn gases of the product. This may present a greater exposure for first responders or consumers on-site and potentially contaminate other materials with residual dust left in the burn environment.

Open flame fire data showed that the use of a barrier had a remarkable impact on the burn parameters of the upholstered chairs, whereas the use of flame retardants, as defined in this study, did not. Chairs with the fire barrier had lower peak release rates, an average of 31 kW, compared to all the chairs without a barrier, averaging 1,400 kW. Chairs with added flame retardants and without flame retardants and no barrier all presented similar heat release rates. The use of a fire barrier was found to reduce the weight loss of those specific chairs by a factor of 10 in comparison to the other chairs and reduce heat generation. Its use also resulted in lower fire hazards including carbon monoxide (CO), temperature, smoke optical density, and hydrogen cyanide (HCN).

Home electronics in return had small peak release rates equal to or less than 10 kW, less than the barrier containing chair.

Secondarily, it was found that certain volatile organic compounds (VOCs) were emitted from the various products, and these emissions became much more complex and hazardous in burn conditions.

This study was effective in developing active environmental chamber protocols for measuring human exposure to flame retardants via various pathways. It also demonstrated the difficulty in measuring low exposure amounts due to the ubiquitous use of flame retardants in everyday materials, equipment, and analytical systems. It demonstrated the important contributions that a barrier material has on the reduction of open flame fire hazards while showing that the use of flame retardants, as used in this study, did not reduce the fire hazards, but did present a human exposure potential for the organophosphorus flame retardant (OPFR). The study also showed the disconnect between California Technical Bulletin 117-2013 (TB 117-2013), designed to control smoldering and not open flame hazards. None of the chairs tested could meet California Technical Bulletin 117-2013 (TB 117-2013), but the chair made with a barrier showed remarkable reduction of open flame hazards. Most importantly is the fact that the chair with barrier option as tested in this study is already available in the retail marketplace. This chair with a barrier material and no flame retardants offers significant advancement to less fire and chemical exposure hazards.

2. Introduction

2.1 Background

Flame retardants and other chemicals have been used for decades in the production of commercial and residential upholstered furniture and other consumer products. In general, the use of flame retardants is a method for achieving fire protection objectives. Flame retardants disrupt the combustion stage of a fire cycle, including avoiding or delaying "flashover," insulating the available fuel source from the material source with a fire-resistant "char" layer, or reducing the flammable gases and oxygen concentrations in the flame formation zone by emitting water, nitrogen or other inert gases. The use of flame retardant chemicals in furniture filling, typically polyurethane foam (PUF), became customary in response to flammability regulations, such as the California flammability standard, Technical Bulletin 117 (TB 117) in 1975,[1] or the Furniture and Furnishings (Fire Safety) Regulations in the United Kingdom (U.K.) in 1988.[2] Even though the California Technical Bulletin 117 (TB 117) regulation was specific to California, manufacturers provided California Technical Bulletin (TB 117) compliant products across the U.S. as a de facto standard for fire safety. These regulations were established primarily to protect against home fires started by small open flames, such as candles, matches, and lighters.[3]

In the European Union (EU) and other countries outside of the U.S., flammability requirements vary. All nations regulate certain aspects of furniture and furnishings for health, safety, and environmental performance. Registration of the use of chemicals, including some high production flame retardants, is required by some countries. For residential use, the U.K. and Ireland have the strictest flammability standards. With concerns that more stringent fire regulations will lead to increased use of flame retardants, the EU furniture industries have suggested a harmonized testing method for upholstered furniture at a level where flame retardants are not needed. Other practical concerns of stricter fire regulation focus on economic impacts and other factors, such as production use, waste, and recycling. These concerns have led fire researchers from the Research Institutes of Sweden, for example, to investigate other options to produce fire-safe furniture, including barrier technologies, the use of fire-resistant wool in cover textiles, and the application of three-dimensional (3D) woven fabric combinations as a substitute for polyurethane foam (PUF).[4]

Prior to 2014 in the U.S., a variety of flame retardants were added to polyurethane foam (PUF) to meet the California Technical Bulletin 117 (TB 117) standard (1975) that required the foam to withstand an open flame test with minimal loss and no sustained ignition after the flame was removed.[3] Since the use of proprietary formulations of flame retardants was common along with the lack of labeling requirements or regulations, specific flame retardant identifications were not available. Research has indicated that prior to their 2004-2005 phase-out, polybrominated diphenyl ethers (PBDEs) were commonly used. Two commercial mixtures of polybrominated diphenyl ethers (PBDEs), PentaBDE and OctaBDE, were banned in California and the EU, and voluntarily withdrawn from production and use within the U.S. After their phase-out, other flame retardants found in residential furniture included tris (1,3- dichloro isopropyl) phosphate (TDCPP), Firemaster 550 (FM550) mixture components, and mixtures of nonhalogenated flame retardants, like triphenyl phosphate (TPhP) and tris-isobutylated triphenyl phosphate (TBPP).[5]

In general, public health professionals and consumers have become increasingly concerned with the human exposure to chemical flame retardants, specifically halogenated and organophosphate formulations that have been linked to serious health problems, including diabetes, neurobehavioral and developmental disorders, cancers, reproductive health effects, and alteration in thyroid function.[6] Early warnings of health risks from exposure to some flame retardants were not heeded, leading to decades of continued use, coinciding with increased presence in humans and adverse health effects.[6] Studies have found polybrominated diphenyl ethers (PBDEs) in house dust and within bodies of children and adults. They have also been found in breast milk and umbilical cord blood which carry chemicals across the placenta subjecting exposure to neonates in the womb.[7] Their presence in the outdoors has been measured, contributing to chemical loads in wastewater, rivers, and the natural environment.[8] Recent evidence supports the concern for adverse health effects and human exposure to more recently used nonhalogenated organophosphate components.[9]

During a fire, the inhalation of toxic gases produced from burning materials is a major cause of injury and death. According to death certificates dated between 1979 and 2007 in the U.K. for home fire deaths, there were eight smoke inhalation deaths for every one death from burns.[10] Common toxic gases in fire smoke include: carbon monoxide (CO), carbon dioxide (CO_2), hydrogen cyanide (HCN), hydrogen chloride (HCl), hydrogen bromide (HBr) and nitrogen oxide (NO).[11] The increased use of a variety of synthetic or petroleum-based materials in homes and buildings is believed to be the source of additional toxicants released during combustion. Homes, offices, and public buildings contain high concentrations of polybrominated diphenyl ethers (PBDEs) due to heavy usage of brominated flame retardants in furniture, electronics, and many other products as demonstrated in recent studies.[12] During combustion, these toxins are readily released resulting in exponentially higher levels in the environment. In a study that measured the serum of 12 California firefighters shortly after responding to a fire, researchers found levels of polybrominated diphenyl ethers (PBDEs) that were three times higher when compared to the general U.S. population. This suggested a significant occupational exposure.[13] In a meta-analysis of 32 studies looking at cancer rates in 110,000 firefighters, significant risk was found for multiple myeloma, prostate cancer, non-Hodgkin's lymphoma, and testicular cancer.[14] In another study of almost 30,000 U.S. firefighters followed from 1950 through 2009, researchers found excess cancer mortality and an increased incidence of digestive (esophageal and colorectal), respiratory, and urinary cancers.[15]

In response to the potential human harm associated with flame retardant exposures, and as of Jan. 1, 2014, California's Technical Bulletin 117 (TB 117) flammability regulation has been replaced by California Technical Bulletin 117-2013 (TB 117-2013).[1] The major change in the standard is that manufacturers are no longer required by the test protocol to make their products resistant to an open flame ignition source; they must only meet a cigarette smolder resistance test. California Technical Bulletin 117-2013 (TB 117-2013) allows manufacturers to pursue other methods of passing the flammability standard without the use of flame retardants. It does not, however, prohibit the use of flame retardants.

Fires from open flame sources are still a threat, according to the National Fire Protection Association (NFPA), and there are concerns that furniture flammability evaluation only using smoldering cigarette ignition testing omits important aspects of how upholstered furniture contributes to real-world fire scenarios. Estimates from National Fire Protection Association's (NFPA) Fire Department Experience Survey shows that since 1980; the number of reported home fires and fire deaths has been reduced by one-half.

Regardless of the downward trend of reported home fires, the number of home fire deaths has held steady between 2006 and 2016 with the death rate in 2016 surpassing the rate for the year 1980. U.S. fire departments responded to an estimated average of 358,500 home structure fires per year between 2011 and 2015.[3] These fires caused an average of 2,510 fire deaths, 12,300 fire injuries, and $6.7 billion in direct damage. During this time, home fires caused 93% of all structure fire deaths and 80% of all fire deaths. Home fires that started in the living room, family room, den, or bedroom caused 47% of all home fire deaths and 30% of all home fire injuries. While only 20% of reported home structure fires occurred between 11 p.m. and 7 a.m., these fires caused 52% of all home fire deaths. When compared to other age groups, older adults were more likely to be killed by a home fire.[3]

The two leading contributors home fire deaths remain upholstered furniture and mattresses or bedding when these items are the primary source contributing to fire spread.[3,16] For home fires where upholstered furniture is the item first ignited, 26% were started by smoking materials, 17% were started by electrical distribution or lighting equipment, and 11% were started by space heaters.[17] Deaths attributed to upholstered furniture fires included smoking materials at 52%, electrical distribution or lighting equipment at 14%, and space heaters at 12%. Since the 1980s, fire deaths from upholstered furniture have fallen 62% and mattress or bedding fires by 57%.

However, between 2011 and 2015, upholstered furniture was the item first ignited in an annual average of 5,500 home structure fires resulting in 460 fire deaths and 720 fire injuries. Only 2% of home structure fires began with upholstered furniture, however, these fires caused 18% of home fire deaths.[3] The flammability of upholstered furniture remains a significant fire safety hazard.

2.2 Purpose

Market demand for "consumer safe products" continues to increase. Chemicals are part of our daily life. All living matter and basic materials are made of chemicals, and virtually every manufactured product involves the use of chemicals. In fact, estimates indicate that more than 140,000 chemicals are used to make our everyday products on a global basis. Many chemicals when properly used, contribute to the improvement of our quality of life and well-being. However, some chemicals are considered hazardous and can negatively affect our health when improperly managed and become available for human exposure.

Chemical control has become a key focus across the globe with programs in place to eliminate or reduce exposure to hazardous chemicals and to educate the public. These include: the demand of public transparency of chemicals used to manufacture products, the listing of carcinogens and reproductive toxins by programs like California's Proposition 65,[18] and the public availability of third-party, certified low chemical emission building materials, electronics, and furnishings.[19] Health science is demonstrating that certain halogenated and organophosphate containing flame retardant chemicals have the potential for adverse human health impacts and that these chemicals are found prolifically in the environment as well as in public spaces and residential homes. In response, manufacturers, retailers, consumer advocacy groups, policymakers, regulatory bodies, and other stakeholders are discussing and evaluating potential ways of reducing flame retardant exposures through elimination in products, developing safer alternative chemicals, or changes in manufacturing processes to reduce exposure potentials.

The purpose of this research was to develop scientific data for better understanding of flame retardant and other chemical exposure risks and fire safety hazards related to consumer use of upholstered furniture. This study was designed to contribute data for quantifying flame retardant and chemical exposure levels during normal use of the products, to measure flammability characteristics of products during an open flame situation in relation to the use or nonuse of flame retardants, to measure chemical and other toxic hazards emitted during a fire event, and to evaluate the impact of product aging on both fire performance and chemical exposure of upholstered furniture. The research is an investigation of applying innovative fire safety strategies that can reduce fire growth potential and reduce chemical exposure.

Research Questions

1. How does human exposure to flame retardants from furniture typically occur?
2. What are the levels of human exposure to these chemicals, and how can risk be evaluated?
3. How does aging of the furniture affect human exposure to flame retardants and flammability performance?
4. Do chemical fire retardants and selected alternative solutions improve fire safety and reduce chemical health risks?
5. How is human exposure to chemicals affected by the availability of nonfurniture products found in a room or office that also contains flame retardants?
6. How can fire safety objectives be met while reducing the flame retardant chemical burden that is contributing to adverse health effects?

2.3 Preliminary Study

A preliminary furniture study was performed to evaluate methodologies for concurrently studying flammability performance and chemical exposure potentials. Two sets of marketplace upholstered furniture were obtained for the study of chemical emissions during normal use and for flammability performance during an open flame burning event. Differing protocols, equipment, and analytical measurements were explored for applicability during this process. One set of furniture was obtained from the U.K. where a national residential flammability requirement[2] exists; the other set of furniture was obtained from California in the U.S. where a residential furniture flammability standard exists.[1] The complete study results can be found in Appendix A.

Airborne volatile organic compound (VOC) emissions from each set of furniture were measured using environmental chamber protocols. Emissions of tris (chloroisopropyl) phosphate (TCPP), a commonly found organohalogen flame retardant, were detected from the U.K. furniture whereas none of the tested flame retardants were detected in the emissions of the U.S. furniture. After chemical emissions testing, the flammability of each furniture set was assessed in burn rooms that were furnished the same except for the studied furniture. The furniture sets were ignited with an open flame ignition source and flammability measures were tracked. The U.S. furniture room reached flashover in just two minutes and 45 seconds after ignition, whereas the U.K. room did not reach flashover until six minutes and 35 seconds. The preliminary study demonstrated that: 1) although the construction of the two sets of furniture was similar, the presence of flame retardants differed; 2) flame retardants and volatile organic compounds (VOCs) can be released into the environment and emission rates can be measured using environmental chamber technology and analytical measurement techniques; and 3) flame retardant technologies can affect fire behavior. This study served to demonstrate the feasibility of studying chemical exposure potentials and flammability expectations of upholstered furniture.

3. Experimental Design

3.1. Overview

Flammability performance and the potential for chemical exposure to flame retardants and other organic chemicals were evaluated for residential upholstered chairs manufactured with differing flammability control technologies. Two consumer electronic products were also studied to provide limited data to compare with the furniture for chemical exposure and fire performance. All products were evaluated through an experimental study shown in Figure 1. The chemical exposure potentials for humans were assessed through a series of exposure pathways, including air inhalation, dust inhalation and ingestion, and absorption through skin migration. After chemical testing, each product was burned using an open flame source, and fire performance and associated burn characteristics of each product were observed and measured. Test samples and chair construction are discussed in Section 3.2. Replicates of all test samples were prepared for quality assessments and retesting as necessary. In addition, one set of duplicate chairs was mechanically aged to simulate a 10-year use period. This allowed for a study comparison of new and aged chairs relative to chemical exposure and flammability potentials.

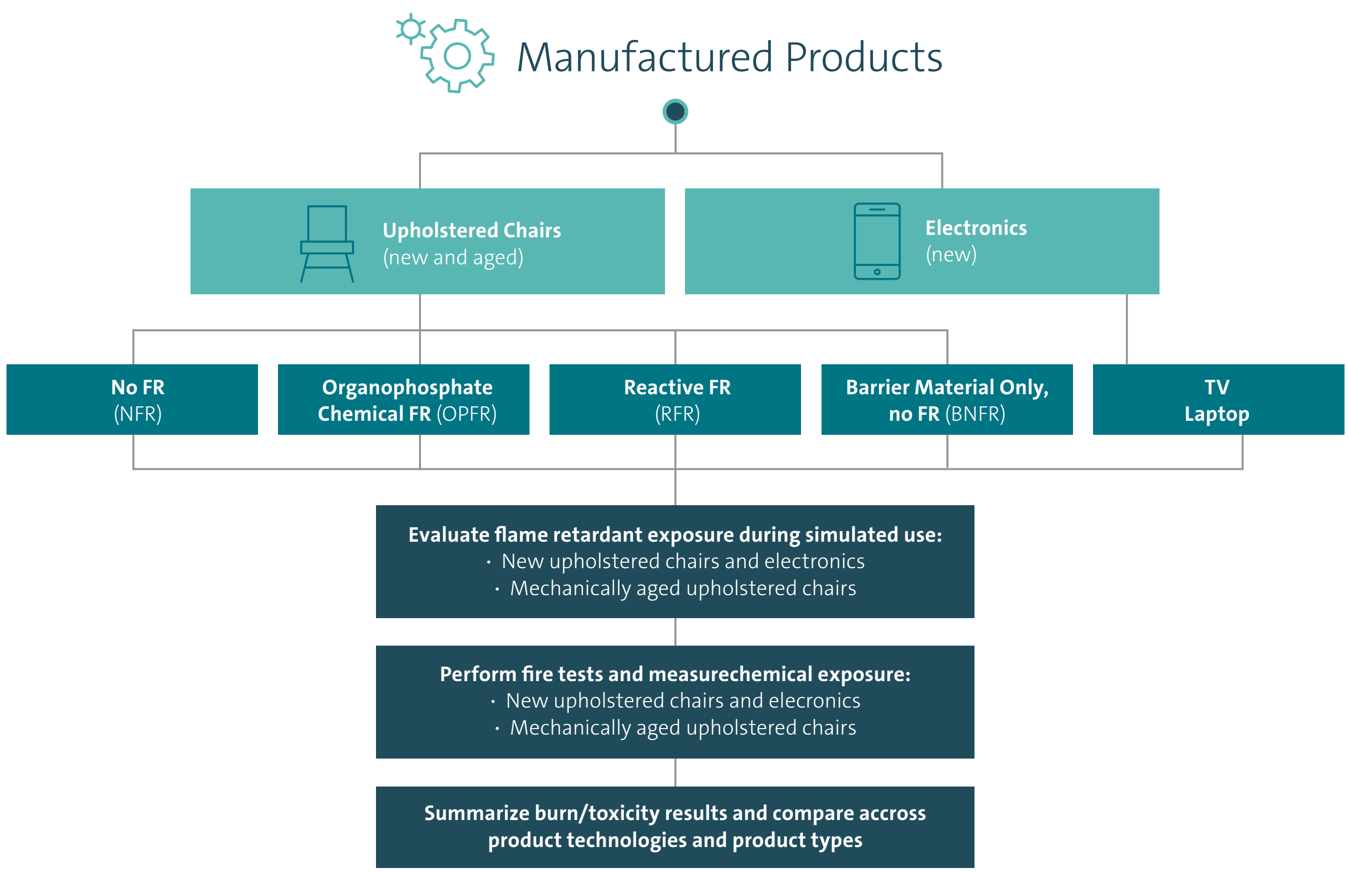


Figure 1: Framework for experimental design, including product selection, chemical exposure, and fire performance studies. FR stands for flame retardant.

3.2 Test Samples

3.2.1 Upholstered Chairs

The chair samples were manufactured by a furniture company in the U.S. The basic upholstered chair design selected for this study represented quality construction and materials with a life expectancy beyond 10 years. At about 10 years, it is expected that reupholstery with new cushioning on the existing frame may be warranted. The size of the chair is within common ergonomic standards for upholstered lounge chairs suitable for residential use. The fabrication utilized recycled and regenerated fibers, metals, and an engineered laminate frame with soy-based resins. The chair cushion foam material was a composition of polyurethane (70%) and soy-based (30%) foam. Other filling materials had recycled plastic content. Finish materials were specified for low volatile organic compound (VOC) content and low emissions. Available nonproprietary details of the chair construction and processes, as provided by the manufacturer, are provided in Appendix B.

A total of 20 chairs were constructed of the basic chair design, shown in Figure 2, based on the manufacturer's typical fabrication methods and materials, differing only in the flammability control technologies explored in this study. Of the 20 chairs, five chairs each were constructed using one of four flame retardant technologies below:

- No flame retardant added to the polyurethane foam (control) (NFR)
- Organophosphate chemical flame retardant added to the polyurethane foam (OPFR)
- Reactive (polymer integrated) chemical flame retardant added to the polyurethane foam (RFR)
- No flame retardant added to the polyurethane foam, but a barrier material wrapped around the polyurethane foam seat cushion, effectively creating a barrier between the polyurethane foam and the textile cover (BNFR)

Figure 2: Upholstered chair selected as test sample type, manufactured with four test conditions.

The chair fabricated with no flame retardant (NFR) represented the product as currently manufactured and sold by the furniture company. It is available through the retail marketplace, noted as meeting all requirements for fire safety including California's Technical Bulletin 117-2013 (TB 117-2013).[1] The polyurethane foams (PUFs) for the chair cushions containing standard flame retardants were prepared and provided by the furniture foam supplier using their standard formulation and preparation processes. The flame retardants, selected by the foam supplier to be representative of available and currently used flame retardants, were added to the foam at levels consistent with current standard practice. The specific flame retardants used in this study were not initially known to the study investigators.

Although it was not known to the investigators initially, the flame retardants in the polyurethane foam was independently identified through chemical analysis to be tris-isobutylated triphenyl phosphate (TBPP), a mixture of organophosphate-based flame retardants without any halogens. The chairs with a reactive flame retardant (RFR) represented the novel chemical flame retardant technology that chemically bonds to the polyurethane foam (PUF) during the polymerization process. This technology is expected to reduce leaching or migration of the flame retardant from the product into the environment. The formulation of this flame retardant was deemed to be proprietary from the supplier and was not provided to the investigators. An independent chemical analysis of this polyurethane foam (PUF) did not show any detection of a series of known flame retardants. This flame retardant was expected to be similar to the one that received the New Chemicals Program P2 Recognition Project Award in 2008,[20] which is a program under the Environmental Protection Agency's (EPA) Design for the Environment program. The award was given to a similar reactive flame retardant since it eliminates unwanted flame retardant emissions by bounding the flame retardants within the polymeric polyurethane foam (PUF) structure.

The fourth chair was fabricated without flame retardants, but a commercially available fiberglass textile barrier (BNRF) was used to wrap the polyurethane foam (PUF) and provide a barrier between the foam and cover textile.

Each of the four types of chairs used in this study represented currently available construction techniques in the marketplace. However, evidence supporting an understanding of potential chemical exposure and fire performance risks of the differing construction types is limited. This study provides data to evaluate human risks associated with flame retardants and other potential chemical exposures and to measure flammability performance; all of which is relevant to protecting the health and safety of consumers and fire safety professionals.

One hypothesis for this study was that as chairs are used over time, the risk of chemical exposure and reduced fire performance could increase when compared to new furniture. To test this hypothesis, one set of chairs with each construction type was mechanically aged to simulate a 10-year use age according to the American National Standards Institute (ANSI)/Business and Institutional Furniture Manufacturer's Association (BIFMA) X5.4 Seating Durability Test (Appendix I).[21] This aging only represented physical use and did not include environmental stressors, such as temperature, humidity, or light exposure. Comparative flammability and chemical exposure testing were performed on each chair construction type, new and aged.

3.2.2 Cushions

Three additional individual chair cushions containing polyurethane foam (PUF) and flammability treatments became available from another independent manufacturing source after the study was initiated. They were studied for chemical exposure potentials as were the previously described chairs. These three cushions were constructed as: 1) without a flame retardant, 2) with a commonly available flame retardant used in the industry, identified independently as tris (1,3-dichloro-2-propyl) phosphate (TDCPP), and 3) with a proprietary reactive flame retardant. Each foam cushion, 27 inches by 21 inches by 6 inches in size, was covered with a commercial grade 100% solution dyed nylon textile with a durability expectation for heavy use, or 350,000 double rubs. The chair cushions were evaluated for chemical exposure potential only, not fire performance. These cushions provided additional data on a different organophosphate flame retardant (OPFR) and reactive flame retardant (RFR) than those used in the manufactured study chairs. There was only one of each provided, so the data is limited, but it does provide some additional data relevant to the objectives of this study.

3.2.3 Electronics

Common electronics in a home include televisions and laptops. A television and a laptop were identified; multiples were sourced locally and purchased through a retail supplier. The items selected for this study provided a chemical source and burn comparison to the upholstered chairs. These are shown in Figure 3.

The television was a 55-inch 4K Ultra-high-definition light-emitting diode (LED) flat screen smart television with built-in Wi-Fi, weighing 35.7 pounds. The laptop computer with a 15.6-inch high definition screen, had a high-level processor, 4 gigabyte (GB) memory, 500 GB hard drive, and a Windows 10 Home operating system, weighing 5.3 pounds. Both electronics were commonly available in the marketplace. Little was known or acknowledged in the product materials about the component materials of each, so some limited material testing was conducted of the electronic components including the casings, printed circuit board laminates, and wire insulation.

Figure 3: Television (left) and laptop (right) selected as electronic test samples.

4. Laboratory Test Protocols

4.1 Overview

Laboratory testing consisted of four parts: 1) material composition evaluations, 2) environmental chamber measurements of chemical exposure, 3) open flame fire testing for flammability performance, and 4) smolder resistance testing of upholstered chair materials. A flow chart outlining the research process and associated methodologies is shown in Figure 4.

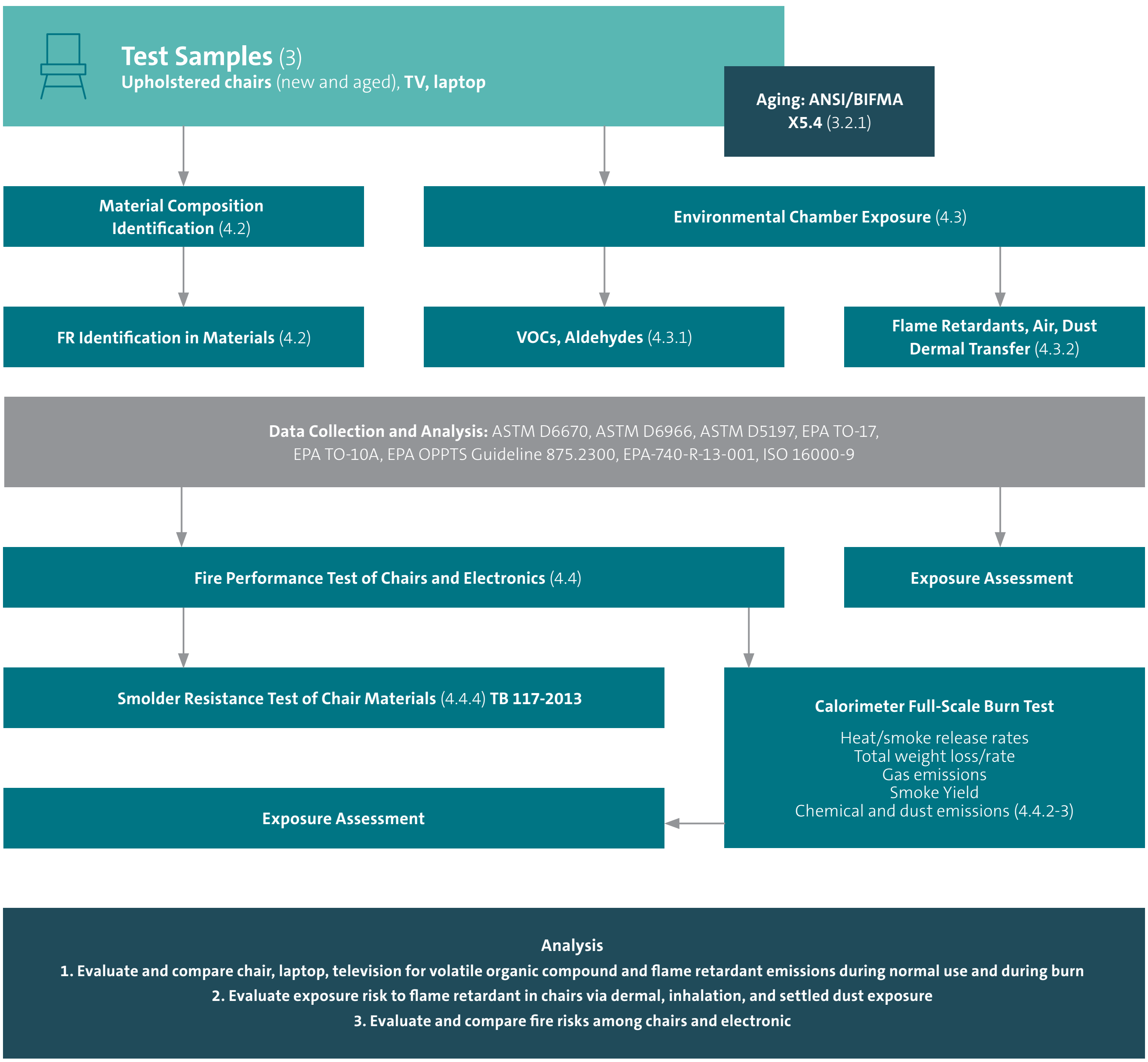


Figure 4: A flow chart describing the research process and methods. Numbers in parentheses represent relating sections in this report.

Test sample acquisition for the residential upholstered chairs and consumer electronics are described in Section 3. The upholstered chairs were manufactured by one specific furniture supplier, and each chair was packaged separately by product type to avoid cross-contamination. They were shipped directly to the laboratory where they were stored in an environmentally controlled space until environmental chamber exposure studies were performed. One set of chairs including each product type was mechanically aged (3.2.1 Upholstered Chairs), repackaged, and stored prior to testing. All other products were tested as new products and as originally received. When tested, each individual chair was removed from its packaging and placed in an environmental chamber for chemical exposure testing or a fire test room for flammability studies. Samples of the components used to manufacture the chairs were provided by the manufacturers. These materials were packaged and shipped to independent laboratories for material composition testing (4.2 Material Composition) or smoldering testing (4.4.2 Smoldering Flammability).

The new electronic products remained in their original packaging in an environmentally controlled space until they were removed for laboratory testing. One sample of each, television and laptop, was deconstructed to obtain components for material characterization. These components were individually packaged and sent to an independent laboratory for testing.

All newly manufactured and mechanically aged chairs and electronics were tested for volatile organic compound (VOC), flame retardant, and aldehyde chemical emissions inside a dynamic, environmentally controlled chamber (4.3 Environmental Chamber Exposure). The interior of the environmental chamber was constructed of stainless steel, providing a clean environment with a controlled ventilation system delivering filtered clean air free of chemical and particle contamination. Specific air, dust, and skin transfer samples were collected during simulated chair use and analyzed for the assessment of human exposure pathways including: air inhalation; particulate/dust inhalation, ingestion; and skin absorption.

Fire performance studies were conducted to determine the efficacy of the different upholstered chair fabrications in reducing fire hazards. Representative new and mechanically aged chair test samples were evaluated. A limited number of electronics were also tested for fire performance to allow for comparison to the furniture. Flammability testing (4.4 Flammability Testing) consisted of two parts: open-flame tests for fully assembled chairs and the electronics, and smoldering material evaluations for the chair materials. Open flame testing was performed under two different laboratory settings for the chairs: one in a Furniture Heat Release Calorimeter without limitation to supplied oxygen, and the second laboratory setting was inside an ISO 9705 Test Room[22] with one door open for air exchange. The electronics were tested only in the calorimeter setting. The smoldering tests, according to California Technical Bulletin 117-2013 (TB 117-2013), were conducted on individual components of the chair assembly, including cover fabrics, barrier materials, resilient filling materials, resilient foams, and decking materials.[1] This testing was conducted by the state of California's Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation (BEARHFTI) laboratory following their standard procedures.

4.2 Material Composition

Material content analysis was conducted by UL LLC's Materials Research and Development Laboratory on individual chair and electronic components to assist in identifying or confirming chemical composition. Energy dispersive X-ray spectroscopy (EDX) was used for elemental component analysis; evolved gas analysis (EGA) was performed for polymer identification; and pyrolysis/gas chromatography mass spectrometry (PY/GCMS) was used to identify composition polymers and flame retardants if present. The pictures of the materials tested are shown in Appendix I.

Additional testing was conducted by an independent laboratory on polyurethane foam (PUF) samples used in the chairs and cushion materials for flame retardant identification. Test samples were analyzed following published methodology by Stapleton et al.[5], where the polyurethane foam (PUF) samples are sonicated and extracts are analyzed by gas chromatography mass spectrometry (GC/MS). Mass spectrometric analyses could identify individual flame retardant chemicals, including polybrominated diphenyl ethers (PBDEs) such as PentaBDE; tris (1,3-dichloro-2-propyl) phosphate (TDCPP); tris (2-chloroethyl) phosphate (TCEP); triphenyl phosphate (TPhP); tris (1-chloro-2-propyl) phosphate (TCPP); tris (1,3-dibromopropyl) phosphate; tris-isobutylated triphenyl phosphate (TBPP); Firemaster® 550 (FM 550), a mixture of organophosphate and brominated flame retardants; a chlorinated organophosphate flame retardant mixture (V6); methylated phenyl phosphate as a mix (MPP); hexabromocyclododecane (HBCD or HBCDD); 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB or TBB); bis (2-ethylhexyl)-2,3,4,5-tetrabromophthalate (BEHTPH or TBPH); and numerous congeners associated with mixtures of the various flame retardants.

4.3 Environmental Chamber Exposure

Each chair, chair cushion, and electronic device was tested in an environmental chamber, 6 m^3 in volume, specially designed for quantifying emissions in a well-mixed clean environment as shown in Figure 5. Chamber operation and control measures used in this study complied with UL 2821,[19] ASTM D6670,[23] ISO 16000-9,[24] and European Computer Manufacturers Association (ECMA)-328.[25] The chamber was made of electropolished stainless steel interior surfaces to minimize contaminant adsorption. Airflow through the chamber entered and exited through an aerodynamically designed air distribution manifold also manufactured of stainless steel, operating at slightly positive pressure relative to the room to prevent the entrainment of room air. Supply air to the chamber was stripped of formaldehyde, volatile organic compounds (VOCs), and other contaminants including particles so that any contaminant backgrounds present in the empty chamber fell below strict levels (< 10 $\mu g/m^3$ total VOC (TVOC), < 1 $\mu g/m^3$ total particles, < 2 $\mu g/m^3$ formaldehyde, < 2 $\mu g/m^3$ for any individual volatile organic compound (VOC)). Air supply to the chamber was maintained at a temperature of 23 degrees Celsius ± 1 degrees Celsius and relative humidity (RH) at 50% ± 5%. The air exchange rate was 1 ± 0.05 air change/hour (ACH).

Specific products were placed in the environmental chamber and evaluated for flame retardant, volatile organic compound (VOC), and aldehyde emissions released in air and settled dust. Dermal transfer potentials were also evaluated for flame retardant exposure.

Electronic samples were placed in the chamber and energized during chemical sample collection. Both electronics were streaming videos during the duration of the sampling period.

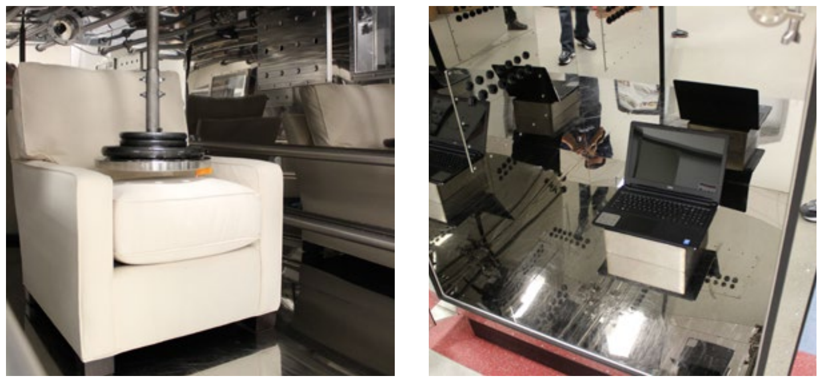


Figure 5: Chair (left) and electronic test products (laptop on right) in an environmental chamber.

A typical sampling timeline is shown in Figure 6. Each test product required a total of four days to collect the emissions of volatile organic compounds (VOCs), aldehydes, and flame retardants in air, settled dust, and dermal contact. The first phase of sampling was background contaminant sampling. The chair agitation mechanism was turned on in the empty chamber during the background sample collections. Immediately after the airborne sample collections were finished, the chamber door was opened, and the background dust wipe samples were collected. Then the test product was introduced inside the chamber and equilibrated overnight or for a minimum of four air changes before the sampling began. Airborne chemical and flame retardant samples were collected, followed by the collection of dust wipe samples. The flame retardant dermal transfer samples were collected from the product immediately after completion of air and dust sample collections. The test product was then removed from the chamber and repackaged in its original packaging material. The chamber was cleaned and purged overnight with clean air to prepare for the next background sampling.

Background Sample Collection	• Clean chamber and purge with clean air • Turn on chair agitation mechanism (for chair study only) • Collect empty chamber airborne background samples • Turn off chair agitation mechanism	• Collect background dust samples • Unpackage test product, load, and equilibrate in chamber
Air and Dust Sample Collection	• Turn on chair agitation mechanism (for chair study only) • Collect loaded chamber airborne (VOC, aldehyde, flame retardant) samples	• Turn off agitation mechanism • Collect flame retardant dust samples
Dermal Sample Collection	• Collect dermal flame retardant dermal samples • Remove test product and repackage for storage	

Figure 6: Environmental chamber sampling timeline.

The chairs were agitated during chemical sampling to simulate activity during personal use. Agitation was performed with a robot known as Robiesitz™, as shown in Figure 7. Robiesitz™, designed specifically for this project, provided a 3.6 centimeter (cm) (1.4 inch (in)) free fall onto the chair cushion using a pneumatic device with a weight of 56.7 kilograms (kg) (125 lb). This mimicked an average U.S. male's upper body sinking into the chair from a standing position. It was constructed of stainless steel and metal to avoid chemical contamination or the creation of a sink. The fall height, weight, weight diameter, and other specific parameters followed American National Standards Institute (ANSI)/Business and Institutional Furniture Manufacturer's Association (BIFMA) Standard X5.4.[21] Robiesitz™ operated at one sitting per minute; with the weight in air for 30 seconds, and the weight drop and rest on the chair for 30 seconds.

While agitation was occurring, air sampling was conducted for volatile organic compounds (VOCs), aldehydes, and flame retardants in gas and particle phases. Airborne flame retardant samples were collected overnight, and volatile organic compounds (VOCs) were collected at the beginning and at the end of the airborne flame retardant sampling period. Following air sampling, settled dust was collected from the floor of the environmental chamber using a predetermined area template and filter wipe. Samples were collected from the chair seat cushion for dermal/skin absorption.

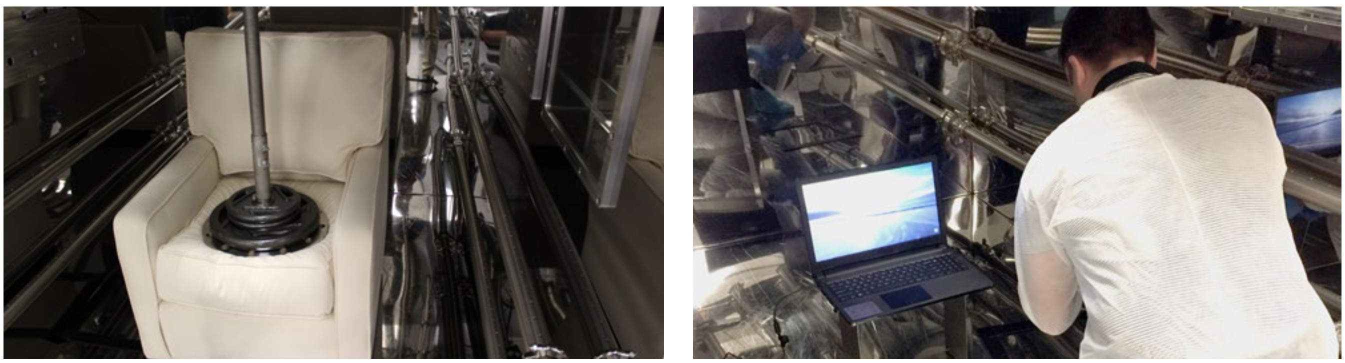


Figure 7: Environmental chamber exposure of chair with exposure agitation (left) device and operating electronic (right).

4.3.1 Volatile Organic Compound (VOC) and Aldehyde Measurements

The analytical methods for individual volatile organic compounds (VOCs) with the volatility range of n-pentane through n-heptadecane (C_5 - C_{17}) was based on ASTM D6196,[26] ASTM D7339,[27] and the U.S. Environmental Protection Agency (EPA) Methods TO-17[28] and TO-1.[29] Volatile organic compound (VOC) air samples were collected on a solid sorbent tube containing Tenax® (Figure 8) and subsequently analyzed using a capillary gas chromatograph mass spectrometer (GC/MS) with thermal desorption unit (GC/MS/TD). This method can separate, identify, and quantify individual volatile organic compounds (VOCs) using multipoint calibrations prepared using pure standards. The method provided sufficient sensitivity and accuracy to reliably quantify individual volatile organic compounds (VOCs) at concentrations of 2 $\mu g/m^3$ or less.

Individual volatile organic compounds (VOCs) were separated and detected by gas chromatograph mass spectrometer (GC/MS) and then identified using multipoint calibrations prepared using pure standards or from a specialized indoor air mass spectral database when available. Other compounds were identified with less certainty using a general mass spectral library available from the National Institute of Standards and Technology (NIST). This library contains mass spectral characteristics of more than 75,000 compounds as made available from National Institute of Standards and Technology (NIST), the United States (U.S.) Environmental Protection Agency (EPA), and the National Institutes of Health (NIH).

Authentic standard calibration was used for any volatile organic compound (VOC) present in the emissions and listed by various regulatory programs including California's Proposition 65,[18] California's Chronic and Acute Reference Exposure Levels,[30] United States (U.S.) Environmental Protection Agency's (EPA) Integrated Risk Information System (IRIS),[31] the Agency for Toxic Substances and Disease Registry's (ATSDR) minimum risk levels (MRL),[32] and the Occupational Safety and Health Administration's (OSHA) permissible exposure limits (PEL).[33] Other identified volatile organic compounds (VOCs) were calibrated using a relative response factor with toluene as a surrogate. The total volatile organic compound level (TVOC) was calculated by summing the total chromatographic response between for all measured volatile organic compounds (VOCs) in the analytical range of C_6 - C_{17}.
Air samples for formaldehyde, acetaldehyde and other low molecular weight aldehydes through butanal (C4 aldehyde)

Figure 8: Environmental exposure sampling media for air sampling: Tenax® tube (left) and 2,4-dinitrophenylhydrazine (DNPH) cartridge (right) for volatile organic compounds (VOCs) and aldehydes respectively.

Figure 9: Environmental exposure sampling media for airborne flame retardants.

were collected on 2,4-dinitrophenylhydrazine (DNPH) cartridges. The 2,4-dinitrophenylhydrazine (DNPH) cartridges were extracted and analyzed by high-performance liquid chromatography (HPLC) equipped with an ultraviolet (UV) detector and an analytical column providing full resolution of the hydrazone derivatives of reacted aldehydes. The analytical method was based on ASTM D5197.[34] Aldehydes analyzed by high-performance liquid chromatography (HPLC) were quantified based on multipoint calibrations prepared from hydrazone derivatives of the pure compounds.

4.3.2 Flame Retardant Measurements

Flame retardants were collected using four different sampling media following processes for inhalation, ingestion, and dermal exposures. These are described in the following sections and detailed protocols from Emory University are provided in Appendix C.

4.3.2.1 Airborne

Airborne flame retardants were sampled using a sampling train consisting of an air sampling pump and in-line quartz fiber filter designed to capture particulate phase (greater than 2.5 microns (µm) in aerodynamic diameter) of semi-volatile flame retardants followed by a polyurethane foam (PUF) cartridge capturing airborne semi-volatile flame retardants. The sampling media is shown in Figure 9. This sampling method is based on United States (U.S.) Environmental Protection Agency (EPA) Indoor Exposure Product Testing Protocols,[35] and United States (U.S.) Environmental Protection Agency (EPA) Method TO-10A.[36] More details are in Appendix C, F01.

4.3.2.2 Settled Dust

Flame retardants in settled dust around the test sample were evaluated using a wipe sample. A fixed surface area was sampled using a defined 1 ft^2 (0.093 m^2) template and sterile gauze impregnated with solvent (n-hexane). Dust collection is demonstrated in Figure 10. The method is based on EPA-740-R-13-001.[37] More details are in Appendix C, F03.

4.3.2.3 Dermal Transfer

Dermal transfer of flame retardants from the test product surface was sampled using a patch protocol. A filter paper patch impregnated with a 0.9% saline solution was placed on the seat of the test chair as demonstrated in Figure 11. A stationary weight was placed on top of the patch to mimic an average person sitting on top of a specific surface area. The dermal sampling method was developed based on United States (U.S.) Environmental Protection Agency (EPA) Indoor Exposure Product Testing Protocols,[35] Thomas et al.,[38] and United States (U.S.) Environmental Protection Agency (EPA) Guideline 875.2300.[39] More details are in Appendix C, F02.

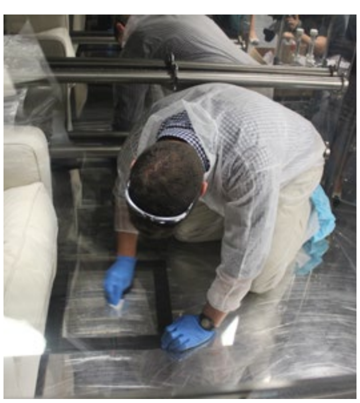
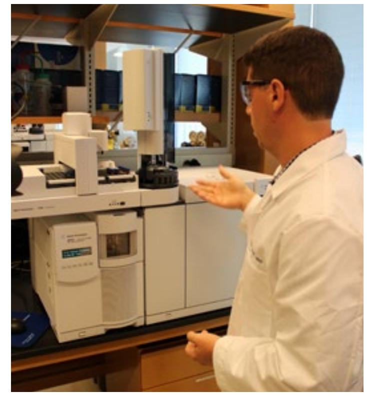


Figure 10: Settled dust collection from the chair for flame retardants analysis.

Figure 11: Dermal transfer sample collection from chair (left) shows the filter patch ready to be placed on a chair (right).

4.3.2.4 Flame Retardant Chemical Analysis

The chemical extraction method was based on protocols developed by van der Veen et al.[40] In this method, two separate extractions were utilized to assess the different flame retardants of interest. Once the two fractions were eluted by different solvents (n-hexane and ethyl acetate), they were evaporated and recontituted into a single solution in order to improve analyte throughput. The combined solution was analyzed using gas chromatography (GC) followed by electron impact ionization and mass spectrometry (MS) (Figure 12). This method identified selected polybrominated diphenyl ether (PBDE) congeners and organophosphorus flame retardants. Details on flame retardant sampling and analysis procedures are in Appendix C, L01 and L02.



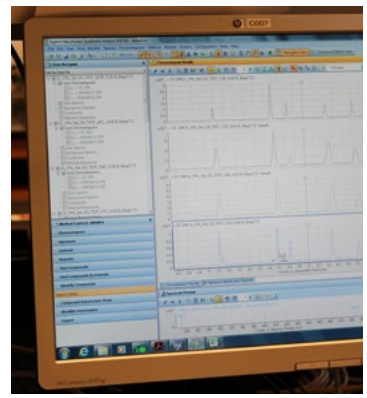


Figure 12: Instrumental analysis of flame retardants at Emory University, GC/MS (top) and a gas chromatogram (bottom).

4.3.3 Exposure Modeling

Human exposure levels of flame retardants through oral, dermal, and inhalation routes were calculated using experimentally measured concentration data combined with defined exposure models. The mathematical exposure models were based on the approach of Keil et al.,[41] and all model parameters were obtained from the United States (U.S.) Environmental Protection Agency (EPA) Exposure Factors Handbook[42] and other cited literature for the most realistic exposure scenarios. Exposure modeling was performed for three personal physiological models: adult, toddler (1 to 2 years old), and infant (3 to 6 months old).

4.3.3.1 Inhalation

The amount of flame retardant inhaled over the duration of a daily exposure was calculated using a predicted airborne concentration determined for a residential environment according to the California Department of Public Health Standard Method[43] and a similar inhalation exposure model designed for determining exposure concentrations from a mattress.[38] An emission factor from the source (chair and other tested products) was first calculated from the airborne sample concentration of a flame retardant ($C_{FR,I}$) obtained from environmental chamber exposure measurements and specific test parameters (Equation 1).

Equation 1

$$C_{FR,I} \times \frac{V_{chamber} \times N_{chamber}}{A_{chamber}} = EF_{FR,I}$$

$C_{FR,I}$: Concentration of a flame retardant (*FR*) detected from inhalation (*I*) sampling, from both quarts filter and polyurethane foam (PUF) cartridge (ng/m^3)
$V_{chamber}$: Volume of a chamber (6 m^3)
$N_{chamber}$: Air exchange rate inside the chamber (1 hr^{-1})
$A_{chamber}$: Product loading inside the chamber (1 unit of chair or other tested products)
$EF_{FR,I}$: Airborne emission factor of a flame retardant from a test product (ng/unit/hr)

To calculate an average daily dose via inhalation, the emission factors were converted to a predicted air concentration for a defined residential environment, multiplied by the amount of air inhaled and scaled by body weight (Equation 2).

Equation 2

$$EF_{FR,I} \times \frac{A_{model}}{V_{model} \times N_{model}} \times Q_{inhalation,i} \times \frac{t_{exposure,i}}{24\ \text{hours}} \times \frac{1}{BW_i} = ADD_{FR,I,i}$$

$EF_{FR,I}$: Airborne *(I)* emission factor of a flame retardant *(FR)* from a test product (ng/unit/hr)
A_{model}: Test product loading in a model room (1 unit of chair or other tested products)
V_{model}: Volume of an environment room (m^3)
N_{model}: Air exchange rate in a model room (hr^{-1})
i: Adult, toddler (1-2 years old), or infant (3-6 months old)
$Q_{inhalation,i}$: Inhalation rate by a person (*i*) (m^3/day)
$t_{exposure,i}$: Time of exposure for a person (*i*) (hr)
BW_i: Average body weight of a person (*i*) (kg)
$ADD_{FR,I,i}$: Average daily dose of a flame retardant (*FR*) from inhalation (*I*) for a person (*i*) (ng/kg/day)

The parameters used for inhalation exposure modeling are listed in Table 1. The default loading was one test product in an open floor residential setting combining living and dining areas. The single-family residence used was obtained from Appendix B of CDPH SM,[43] the 2008 United States (U.S.) Department of Energy (DOE) Buildings Energy Data Book,[44] and the residential model is presented in ANSI/CAN/UL 2904.[45] The average air exchange rate for a typical residential setting from American Society of Heating, Refrigeration, and Air-Conditioning Engineers (ASHRAE) 62.1[46] was used. Daily inhalation rate and average body weight are age specific and were obtained from the United States (U.S.) Environmental Protection Agency (EPA) Exposure Factor Handbook.[42] The exposure time is the time awake and present in residence for a specific age group per day. The time awake in residence is assumed to be the total time in residence (from the Exposure Factors Handbook[42] Table 16-1) minus the time in a bedroom (Exposure Factors Handbook[42] Table 16-15 and Table 16-16). For example, the average time an adult, 18 to 64 years old, spends indoors at a residence per day is 948 minutes, or 15.8 hours. The average time an adult spends in a bedroom is 533 minutes, or 8.9 hours, per day. Therefore, for an adult, the average time spent around the chair is assumed to be 415 minutes, or 6.9 hours.

Table 1: Adult, Toddler, and Infant Factors for Inhalation Exposure

Inhalation Exposure Factors	Adult	Toddler (1-2 years)	Infant (3-6 months)	Unit	Source
A_{model}	1	1	1	Chair	
V_{model} (Residential living/dining)	201	201	201	m^3	UL 2904
N_{model}	0.45	0.45	0.45	hr^{-1}	ASHRAE
$Q_{inhalation}$ (inhalation rate)	16	8.0	4.1	m^3/day	EFH T6-1
$t_{exposure}$	6.9	4.9	6.0	hr	EFH T16-1 and 16-15 and 16
BW	80	11	7.4	kg	EFH T8-1

EFH: EPA Exposure Factors Handbook[42] **ASHRAE: ASHRAE 62.1[46]** **UL 2904: ANSI/CAN/UL 2904[45]**

4.3.3.2 Oral

Saliva mediated oral exposure quantity was determined as the amount of flame retardant ingested during daily exposure, directly and indirectly. A combination of dust to hand-to-mouth contact (Equation 3), chair surface/fabric to hand-to-mouth contact (Equation 4), and chair surface to mouth contact (Equation 5) constitute the total amount of flame retardant ingested (Equation 6). The mathematical models for oral exposure were based on Keil et al.[41] and Babich.[47]

The average daily dose from dust to hand-to-mouth contact ($ADD_{FR,O1,i}$, Equation 3) was calculated from the dust sample concentration of a flame retardant ($C_{FR,O}$) measured in the environmental chamber study (4.3.2 Flame Retardant Measurements) multiplied by the fraction of dust transferred from ground to hands (f_{gh}), the total surface areas of one side of both hands ($SA_{h,i}$), the rate of hand-to-mouth contacts ($r_{contacts,i}$), time of exposure ($t_{exposure,i}$), scaled by the average body weight.

Equation 3

$$C_{FR,O} \times f_{gh} \times SA_{h,i} \times r_{contacts,i} \times t_{exposure,i} \times \frac{1}{BW_i} = ADD_{FR,01,i}$$

$C_{FR,O}$: Concentration of a flame retardant (*FR*) from dust ingestion sample collection (O) (pg/m^2)
f_{gh}: Fraction transferred from ground (floor) to hand (unitless)
i: Adult, toddler (1-2 years old), or infant (3-6 months old)
$SA_{h,i}$: Hand surface area for a person (*i*) (m^2)
$r_{contacts,i}$: Hand-to-mouth contact rate for a person (*i*) (# contacts/hr)
$t_{exposure,i}$: Time of exposure per day for a person (*i*) (hr/day)
BW_i: Average body weight for a person (*i*) (kg)
$ADD_{FR,01,i}$: Average daily dose of a flame retardant (*FR*) from dust to hand-to-mouth contact (*O1*) for a person (*i*) (pg/kg/day)

The factors used for dust to hand-to-mouth exposure are listed in Table 2. The fraction transferred from ground (floor) to hand was the moist fraction transferred for dust as in Babich[47] Table 8. The fraction transferred from ground to hand was the same for all ages; however, the hand-to-mouth contact frequency was different. The adult is assumed to have zero hand-to-mouth contacts following the United States (U.S.) Environmental Protection Agency (EPA) Exposure Factors Handbook.[42] Exposure time was the same from Inhalation section (Table 1).

Three months of chair use was mechanically mimicked inside the chamber through agitation before dust samples were collected.

Table 2: Adult, Toddler, and Infant Factors for Dust to Hand-to-Mouth Oral Exposure

Oral Exposure Factors	Adult	Toddler (1-2 years)	Infant (3-6 months)	Unit	Source
f_{gh}	0.05	0.05	0.05		Babich (2006) T8
SA_h	0.049	0.015	0.010	m^2	EFH T7-2
$r_{contacts}$ (hand-to-mouth contacts)	0	20	28	Contacts/hr	EFH T4-1
$t_{exposure}$	6.9	4.9	6.0	hr	EFH T16-1 and 16-15 and 16-16
BW	80	11	7.4	kg	EFH T8-1

EFH: EPA Exposure Factors Handbook[42] **Babich (2006)**[47]

The average daily dose from the chair surface to hand-to-mouth contact ($ADD_{FR,O2,i}$, Equation 4), was calculated by taking the measured dermal filter patch sample concentration ($C_{FR,D}$), normalizing this value for the exposure duration (age-specific exposure times ($t_{exposure,i}$)/ sampling time ($t_{sampling}$). Only a fraction of that concentration gets transferred from chair fabric to hand and hand-to-mouth using the following variables: the fraction transferred from fabric to hand (f_{fh}), surface area of hand ($S_{Ah,i}$), and hand-to-mouth factor (F_{hm}). This value was scaled by the average body weight (BW_i).

Equation 4

$$C_{FR,D} \times \frac{t_{exposure,i}}{t_{sampling}} \times (f_{fh} \times SA_{h,i} \times F_{hm}) \times \frac{1}{BW_i} = ADD_{FR,02,i}$$

$C_{FR,D}$: Concentration of a flame retardant (*FR*) from filter patch dermal sample collection (*D*) (pg/m^2)
$t_{sampling}$: Filter patch sample collection time (hr)
i: Adult, toddler (1-2 years old), or infant (3-6 months old)
$t_{exposure.i}$: Time of exposure per day for a person (*i*) (hr)
f_{fh}: Fraction transferred from fabric to hand
$SA_{h,i}$: Hand surface area for a person (*i*) (m^2)
F_{hm}: Hand-to-mouth transfer factor (day^{-1})
BW_i: Average body weight for a person (*i*) (kg)
$ADD_{FR,02,i}$: Average daily dose of a flame retardant (*FR*) from chair surface to hand-to-mouth contact (*O2*) for a person (*i*) (pg/kg/day)

The factors used for chair surface to hand-to-mouth exposure are listed in Table 3. The exposure times were the same from the Inhalation section (Table 1). Since the chair surface to hand-to-mouth exposure model was directly from Babich,[47] the parameters used in the reference were used in Equation 4. The fraction transferred from fabric to hand (f_{fh}) was the moist fraction transferred for tris (1,3-dichloro-2-propyl)phosphate (TDCPP or TRIS) in Babich[47] Table 8, assuming that other flame retardants in this study have a similar transfer factor as tris (1,3-dichloro-2-propyl) (TDCPP). Flame retardant specific transfer fractions from fabric to hand are not available for other flame retardants. The hand-to-mouth factor (F_{hm}) is independent of the number of individual mouthing events.

Table 3: Adult, Toddler, and Infant Factors for Chair Surface to Hand-to-Mouth Oral Exposure

Oral Exposure Factors	Adult	Toddler (1-2 years)	Infant (3-6 months)	Unit	Source
$t_{exposure}$	6.9	4.9	6.0	hr	EFH T16-1 and 16-15 and 16-16
$t_{sampling}$	6.0	6.0	6.0	hr	EFH T7-2
f_{fh}	0.06	0.06	0.06		Babich (2006) T8
SA_h	0.049	0.015	0.010	m^2	EFH T7-2
F_{hm}	0.43	0.43	0.43	/day	Babich (2006) T9 and Hatlelid (2003)
BW	80	11	7.4	kg	EFH T8-1

EFH: EPA Exposure Factors Handbook[42] **Babich (2006)**[47] **Hatlelid (2003)**[48]

The average daily dose from chair surface directly to mouth ($ADD_{FR,O3,i}$, Equation 5) was calculated by taking the measured filter patch sample concentration ($C_{FR,D}$), normalizing this value for the exposure duration (age specific exposure times ($t_{exposure,i}$)/ sampling time ($t_{sampling}$), and taking into account for the directly mouthed surface area ($SA_{m,i}$) and the fabric-to-mouth transfer factor (F_{fm}). This value was scaled by the average body weight (BW_i) to get to the average daily dose from chair surface to mouth exposure.

Equation 5

$$C_{FR,D} \times \frac{t_{exposure,i}}{t_{sampling}} \times (SA_{m,i} \times F_{fm}) \times \frac{1}{BW_i} = ADD_{FR,03,i}$$

$C_{FR,D}$: Concentration of a flame retardant (*FR*) from filter patch dermal sample collection (*D*) (pg/m^2)
$t_{sampling}$: Filter patch sample collection time (hr)
i: Adult, toddler (1-2 years old), or infant (3-6 months old)
$t_{exposure.i}$: Time of exposure per day for a person (*i*) (hr)
$SA_{m,i}$: Directly mouthed surface area for a person (*i*) (m^2)
F_{fm}: Fabric-to-mouth transfer factor (day^{-1})
BW_i: Average body weight for a person (*i*) (kg)
$ADD_{FR,03,i}$: Average daily dose of a flame retardant (*FR*) from chair surface directly to mouth contact (*O3*) for a person (*i*) (pg/kg/day)

The factors used for direct chair surface-to-mouth exposure are listed in Table 4. The exposure times were the same from Inhalation section (Table 1). Since the chair surface-to-mouth exposure model was directly from Babich,[47] the parameters used in the reference were used in Equation 5. Note that mouthing surface area for adults is zero. The fabric-to-mouth factor (F_{fm}) is independent of the number of individual mouthing events.

Table 4: The Adult, Toddler, and Infant Specific Parameters Used for Chair Surface to Mouth Oral Exposure Modeling

Oral Exposure Factors	Adult	Toddler (1-2 years)	Infant (3-6 months)	Unit	Source
$t_{exposure}$	6.9	4.9	6.0	hr	EFH T16-1 and 16-15 and 16-16
$t_{sampling}$	6.0	6.0	6.0	hr	
SA_m	0	0.001	0.001	m^2	Babich (2006) T9
F_{fm}	0.43	0.43	0.43	/day	Babich (2006) T9 and Hatlelid (2003)
BW	80	11	7.4	kg	EFH T8-1

EFH: EPA Exposure Factors Handbook[42] **Babich (2006)**[47] **Hatlelid (2003)**[48]

The total average daily dose from oral exposure ($ADD_{FR,O,i}$) was the sum of all the direct and indirect oral exposures calculated above (Equation 6).

Equation 6

$$(ADD_{FR,01,i} + ADD_{FR,02,i} + ADD_{FR,03,i}) \times \frac{1ng}{1000pg} = ADD_{FR,0,i}$$

$ADD_{FR,O,i}$: The total average daily dose from oral exposure (ng/kg/day)
i: Adult, toddler (1-2 years old), or infant (3-6 months old)
$ADD_{FR,O1,i}$: Average daily dose of a flame retardant (*FR*) from dust to hand-to-mouth contact (*O1*) for a person (*i*) (pg/kg/day)
$ADD_{FR,O2,i}$: Average daily dose of a flame retardant (*FR*) from chair surface to hand-to-mouth contact (*O2*) for a person (*i*) (pg/kg/day)
$ADD_{FR,O3,i}$: Average daily dose of a flame retardant (*FR*) from chair surface directly to mouth contact (*O3*) for a person (*i*) (pg/kg/day))

4.3.3.3 Dermal

Sweat mediated dermal exposure determinations were based on Keil et al.[41] and Thomas et al.[38] The experimentally measured level of flame retardant from filter patch sampling ($C_{FR,D}$) was normalized for the exposure duration (age specific exposure times ($t_{exposure,i}$)/ sampling time ($t_{sampling}$), and defined by the area of skin in contact with the chair ($SA_{contact,i}$) while in use and skin absorption rate (*ABS*). This amount was scaled by body weight to calculate the average daily dose via dermal exposure (Equation 7).

Equation 7

$$C_{FR,D} \times \frac{t_{exposure,i}}{t_{sampling}} \times SA_{contact,i} \times ABS \times \frac{1}{BW_i} \times \frac{1ng}{1000pg} = ADD_{FR,D,i}$$

$C_{FR,D}$: Concentration of a flame retardant (*FR*) from filter patch dermal sample collection (*D*) (pg/m^2)
i: Adult, toddler (1-2 years old), or infant (3-6 months old)
$t_{exposure,i}$: Time of exposure per day for a person (*i*) (hr/day)
$t_{sampling}$: Filter patch sample collection time (hr)
$SA_{contact,i}$: Surface area directly in contact with the surface of a chair for a person (*i*) (m^2)
ABS: Fraction of applied dose absorbed through the skin per event (unitless)
BW_i: Average body weight for a person (*i*) (kg)
$ADD_{FR,D,i}$: Average daily dose of a flame retardant (*FR*) from dermal exposure for a person (*i*) (ng/kg/day)

The factors used for dermal exposure are listed in Table 5. Exposure time was the same from Inhalation section (Table 1) in units of hours. The age-specific surface area in contact with a chair was calculated as one-third of each body part listed: trunk area, legs area, arms area, and hands area. One-third was used to account for the curvature of limbs. This is a conservative estimate since it assumes a person being shirtless; therefore, a discussion with the average daily dose decreasing linearly with a fraction exposed would be warranted. The fraction of applied dose absorbed through the skin per event (*ABS*) of 0.1 is the recommended value for semi-volatile organic compounds by the United States (U.S.) Environmental Protection Agency (EPA), but others recommend skin absorption rate (*ABS*) of 1.0 for worst case scenario according to Keil.[41] Dermal exposure was calculated assuming a conservative ABS of 1.0. This allows a discussion as to how exposure would be linearly related to the skin absorption rate (*ABS*) value, e.g., 0.1 would result on one-tenth the exposure.

Table 5: Adult Male and Female, Toddler, and Infant Factors for Dermal Exposure

Dermal exposure factors	Adult male	Adult female	Toddler (1-2 years)	Infant (3-6 months)	Unit	Source
$t_{exposure}$	6.9	6.9	4.9	6.0	hr	EFH T16-1 and 16-15 and 16-16
$t_{sampling}$	6.0	6.0	6.0	6.0	hr	
$SA_{contact}$	0.64	0.53	0.14	0.10	m^2	EFH T 7-2
ABS	0.1	0.1	0.1	0.1		EPA (2007)
ABS for worst case	1	1	1	1		Keil (2009)
BW	89	76	11	7.4	kg	EFH T8-1, 4 (male), 5 (female)

EFH: EPA Exposure Factors Handbook[42] **EPA (2007): Dermal Exposure Assessment**[49] **Keil (2009): Keil et al.**[41]

4.3.4 Fire Retardant Risk Assessment

Measured flame retardant exposure values were compared to available toxicity data. This allowed the daily dose of environmental exposure to be assessed for its hazard potential. The lowest no observed adverse effect level (*NOAEL*) found in available toxicity study literature was used to calculate a flame retardant's acceptable daily intake dose (*ADI*) using the equation below (Equation 8):

Equation 8

$$ADI = \frac{NOAEL \text{ or } LOAEL}{UF}$$

ADI: Acceptable daily intake (mg/kg/day)
NOAEL: No observed adverse effect level (mg/kg/day)
LOAEL: Lowest observed adverse effect level, used if NOAEL is not available (mg/kg/day)
UF: Uncertainty factor (unitless)

An uncertainty factor of 100 was used for this study including a factor of 10 for animal-to-human correlation uncertainty, and another 10 for human sensitivity variability.[50]

The acceptable daily intake (*ADI*) was then compared to the measured average daily dose (*ADD*) obtained from the chamber measurements to calculate a hazard index (HI) using the following equation (Equation 9), which is from Babich.[47]

Equation 9

$$HI = \frac{ADD}{ADI}$$

HI: Hazard index (unitless)
ADI: Acceptable daily intake (mg/kg/day)
ADD: Average daily dose (mg/kg/day)

When the hazard index is greater than one, the exposure scenario presents a potential hazard to consumers. The fractional effective dose (FED) equation is presented in Appendix I.

4.4 Flammability Testing

4.4.1 Open Flame

UL LLC Commercial and Industrial Research and Development staff conducted fire performance (open flame) tests on the upholstered furniture items and electronic devices. Two laboratory settings, the Furniture Heat Release Calorimeter (Figure 13) and the ISO 9705[22] Test Room equipped with a large scale heat release calorimeter (Figure 14) were utilized for fire performance testing. While the Furniture Heat Release Calorimeter measured heat release under well-ventilated conditions, studies in the ISO 9705 Test Room mimicked a realistic fire environment in a residential setting. An open Furniture Heat Release Calorimeter is typically used to assess fire hazards from a product, since heat release rate from a burning item is a driver for other hazards, i.e., temperature, smoke, and toxic gases, in a fire. Modeling and semi-empirical and empirical calculations may then be used to develop estimates of fire hazards. The ISO 9705 room test enables a more direct measurement of these hazards. Since airflow in the ISO 9705 Test Room is through a single doorway opening, available oxygen during the test can change with fire size. This can influence the combustion processes and hazards generated. Thus, the ISO 9705 Test Room enables measurement of the change in hazards relative to fire growth.

The open flame tests were performed using a calorimeter with a match equivalent 35 millimeter (mm) flame ignition source based upon the European Norm (EN) 1021-2 test

Figure 13: Furniture Heat Release Calorimeter open room setup with a chair (left) and a television (right) on the load cell assembly.

Figure 14: An ISO 9705 Test Room setup (left) with a chair on a corner load cell assembly (right).

standard.[2] Fire performance was measured by heat release rate, weight loss, and fire effluents. Smoke density was also measured at the doorway of the ISO room.

Active air samples for volatile organic compounds (VOCs), aldehydes, and flame retardants were collected during product burns using the same sampling media as in environmental chamber exposure sampling: Tenax® for volatile organic compounds (VOCs), 2,4-dinitrophenylhydrazine (DNPH) for aldehydes, and polyurethane foam (PUF) and quartz filter for airborne and particulate flame retardants.

Air samples for chemical analysis were collected directly from the exhaust system for the Furniture Heat Release Calorimeter and directly above the burning chair inside the ISO 9705 Test Room. Air samples were collected, sealed, and stored in a refrigerator immediately after sampling. At the end of the experiments, the air samples were shipped in a cooler to the analytical laboratories to be analyzed for volatile organic compounds (VOCs) by gas chromatography mass spectrometry (GC/MS) (4.3.1 Volatile Organic Compound (VOC) and Aldehyde Measurements), aldehydes by high-performance liquid chromatography (HPLC) (4.3.1 Volatile Organic Compound (VOC) and Aldehyde Measurements), and flame retardants by extraction and gas chromatography (GC) followed by electron impact ionization and mass spectrometry (MS) (4.3.2.4 Flame retardant chemical analysis).

4.4.2 Smoldering Flammability

California Technical Bulletin 117-2013 (TB 117-2013) tests[1] were conducted by the California Bureau of Electronic and Appliance Repair, Home Furnishings, and Thermal Insulation (BEARHFTI) for the smolder resistance of chair materials. Materials including upholstery textile (cover), barrier textile, resilient loose fiber, decking textile, and polyurethane (resilient) foam from the no flame retardant chair (NFR), organophosphate flame retardant chair (OPFR), and reactive chemical flame retardant chair (RFR) were sent to the laboratory for smolder resistance testing. The smoldering test was performed in triplicate to determine if the material passed or failed according to California Technical Bulletin 117-2013 (TB 117-2013) (Appendix D).

Figure 15: California Technical Bulletin 117-2013 (TB 117-2013) smolder resistance test (typical) showing testing of reactive flame retardant polyurethane foam.

This test method evaluated furniture component assemblies and was intended to estimate the performance of upholstered furniture when exposed to a smoldering cigarette. It was not intended to measure the performance of furniture under conditions of open flame exposure. Pass/fail criteria for the components were based on smoldering duration, the measured char length; and if the material mock-up transitions to flaming conditions. The material mock-up was constructed of consistent, standard materials except for the material being evaluated.

Figure 15 is a typical setup for testing material smoldering parameters under California Technical Bulletin 117-2013 (TB 117-2013) with three small scale mock-ups aligned side by side. For each specimen, a cigarette was placed on top of the mock-up scenario for the specific material being evaluated. Due to a lack of material, the resilient loose fiber was only tested twice.

5. Chemical Exposure Results

This multimethod study evaluated upholstered chairs and electronic products through material composition evaluations, environmental chamber and chemical exposure testing, bench-scale testing for fire smoldering hazards, and full-scale open flame testing for flammability performance. The results for material composition and chemical exposure are presented in this section. Flammability results are presented in Section 6.

5.1 Material Composition

Individual test samples of chair parts were tested at the Material Research and Development Materials Laboratory, UL LLC, for identification of key components. Common elements found in the chair materials included carbon (C) and oxygen (O) as shown in Table 6. A trace level of chlorine (Cl) at less than 1% was found in the fiberglass barrier and was associated with a trace of polyvinyl chloride (PVC). Analysis of the materials by pyrolysis gas chromatography/mass spectrometry (GC/MS) showed the presence of triphenyl phosphate flame retardant in the polyurethane foam (PUF) known to be manufactured with an organophosphate flame retardant (OPFR). There were no flame retardants detected in the other materials.

Table 6: Material Identification Analysis – Furniture Components

Material	EDX[1] Analysis	Polymer Type (EGA[2])
Cover textile	C, O	Cotton
Ticking textile	C, O	Cotton + PET[3]
Fiber filling	C, O	PET[3]
No flame retardant foam (NFR)	C, O	PU[4]
Organophosphate flame retardant foam (OPFR)	C, O	PU[4]
Reactive flame retardant foam (RFR)	C, O	PU[4]
Poly loose filling	C, O	PET[3]
Fiberglass barrier textile	C, O, Si, Ca, Al, Cl, Na, Ti	Glass fiber
Decking textile	C, O	Cotton + PET[3]

[1] **EDX: energy dispersive X-ray spectroscopy**
[2] **EGA: evolved gas analysis**
[3] **PET: polyethylene terephthalate**
[4] **PU: polyurethane**

Materials from the electronics were similarly tested for elemental analysis. There was no chemical or flame retardant information provided with the product packaging and materials list with the purchased products. Carbon (C) and oxygen (O) were again the primary elements. Other findings for the laptop included a trace of phosphorous in the plastic casing; 17% (by weight) of barium (Ba) in the solder; and 8% bromine (Br) in the printed circuit board laminate as shown in Figure 16. The television showed elevated levels of chlorine (Cl) in two wire insulations at 15% and 22% and bromine (Br) at 5% in the printed circuit board, as shown in Figure 17. The presence of halogens in the electronic materials could be associated with flame retardants. More material analysis data can be found in Appendix E.

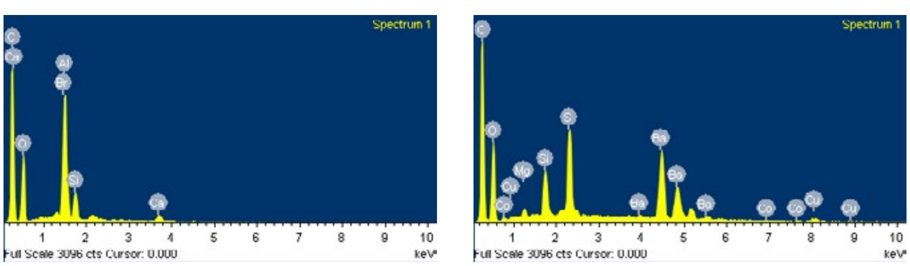


Figure 16: Elemental analysis of laptop solder (left) and laptop printed circuit board laminate (right).

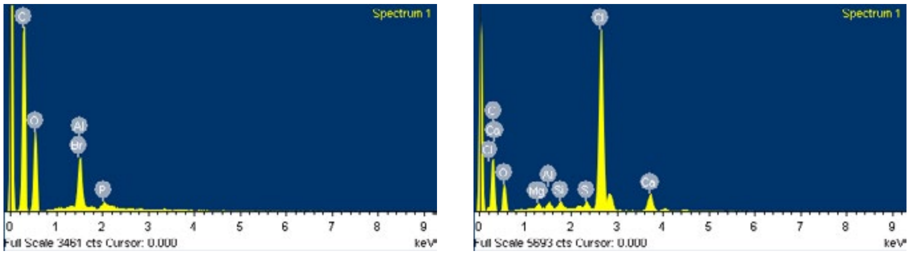


Figure 17: Elemental analysis of television wire insulation (left) and television printed circuit board (right).

5.2 Flame Retardant Identification

Polyurethane foam (PUF) used in chair samples were tested to validate flame retardant chemical content by a third-party independent laboratory, and the results are shown in Table 7. The no flame retardant (NFR) and reactive flame retardant (RFR) foams had no detectable levels of flame retardants. Some phthalates were found, but no flame retardants that were included in the screening methodology were detected. The organophosphate flame retardant (OPFR) foam was found to contain 2.9% by weight of tris-isobutylated triphenyl phosphate (TBPP), a mixture of organophosphate flame retardants that do not contain halogens, e.g. bromine or chlorine. This flame retardant mixture typically contains 58% by weight of (4-tert-butylphenyl) diphenyl phosphate (4tBPDPP), along with 30% by weight of triphenyl phosphate (TPhP), 11% by weight of (2,4-di-tert-butylphenyl) diphenyl phosphate (B4tBPPP), and 1% by weight of tris (4-tert-butylphenyl) phosphate (T4tBPP).

The individual chair cushion known to have a flame retardant was found to have 5.2% by weight of tris (1,3-dichloroisopropyl) phosphate (TDCPP). No flame retardants were detected in the chair cushion manufactured with no flame retardants.

Table 7: Flame Retardant Content Analysis of Flexible Polyurethane and Bio-Based Foam Used in Upholstered Chairs and Cushions

Sample Identification	Flame Retardant Detection
Chair, Bio based PUF[1], no flame retardant (NFR)	ND[2]
Chair, PUF[1], organophosphate flame retardant (OPFR)	TBPP[3], TPhP[4]
Chair, PUF[1], reactive flame retardant (RFR)	ND[2]
Cushion, PUF[1], No flame retardant	ND[2]
Cushion, PUF[1], Standard flame retardant	TDCPP[5]

[1] **PUF: polyurethane foam**
[2] **ND: not detected**
[3] **TPhP: triphenyl phosphate**
[4] **TBPP: tertbutyl phenyl diphenyl phosphates**
[5] **TDCPP: tris (1,3-dichloroisopropyl) phosphate**

5.2.1 Literature Review of Flame Retardant Chemicals

A limited hazard review of the two flame retardants used in this study is provided. Recent studies[51–54] and the U.S. Environmental Protection Agency (EPA)[55] have reported that tris-isobutylated triphenyl phosphate (TBPP) is a moderate hazard for reproductive and developmental toxicity.[55] There is a high potential for consumers to be exposed to tris-isobutylated triphenyl phosphate (TBPP) through household consumer products, including flexible foam products, particularly through dermal and inhalation routes of exposure. The United States (U.S.) Environmental Protection Agency (EPA) considered tris-isobutylated triphenyl phosphate (TBPP) to have a high potential for bioaccumulation and moderate persistence in the environment.[55]

Tris-isobutylated triphenyl phosphate (TBPP) commercial mixtures have been found to have neuro and developmental toxicity: disruption in *C. elegans* larval development; disruption in zebrafish embryonic development and its behavior; elevation in estradiol serum level; and alteration of reproductive cycles, cholesteryl lipidosis, and ovarian interstitial cells.[9] The tris-isobutylated triphenyl phosphate (TBPP) mix tends to have a large portion of triphenyl phosphate (TPhP) which has been found to have a high ecotoxicity, especially in the aquatic environment. According to Greenscreen® for Safer Chemicals, a chemical hazard assessment method by Clean Production Action,[56] triphenyl phosphate (TPhP) is known to have moderate concern over carcinogenicity, endocrine activity, organ toxicity, neurotoxicity, and eye irritation (Appendix F.5).

Tris (1,3-dichloroisopropyl) phosphate (TDCPP), a halogenated organophosphate flame retardant (OPFR), commonly replaced PentaBDE, a flame retardant mixture of brominated chemicals called polybrominated diphenyl ethers (PBDE).[54] Tris (1,3-dichloroisopropyl) phosphate (TDCPP) is most widely used in the U.S. (yearly estimates are 4,500-22,700 tons) as an additive flame retardant in resins, polymers, latexes, and foams[57] despite it being a probable carcinogen and a developmental neurotoxicant,[58] and an endocrine disruptor in fish.[59] Tris (1,3-dichloroisopropyl) phosphate (TDCPP) has high carcinogenicity and was included under California Proposition 65 in 2011. Since then, the use of tris (1,3-dichloroisopropyl) phosphate (TDCPP) in sofas and loveseats has declined however not completely eliminated.[51] Tris (1,3-dichloroisopropyl) phosphate (TDCPP) also has high ecotoxicity and is very persistent in the environment. It also has been shown to affect mutagenicity, endocrine activity, and reproductive, organ, and developmental toxicity (Appendix F.5).

5.3 Volatile Organic Compounds (VOCs) and Aldehydes: Consumer Use

5.3.1 Chairs

In general, the emissions of volatile organic compounds (VOCs) from the four different chair types were low. As shown in Table 8, the total volatile organic compound (VOC) values ranged from 68 µg/m^3 to 160 µg/m^3 and were similar between the new and mechanically aged chairs. A full listing of all identified chair volatile organic compounds (VOCs) can be found in Appendix G. Emissions consisted of mixtures of low-level volatile organic compounds (VOCs), which would result in low levels of exposure when used in a typical indoor environment. All chairs met current indoor air guidelines of GREENGUARD certification,[19] California Department of Public Health Standard Method,[43] and American Society of Heating, Refrigeration, and Air-Conditioning Engineers (ASHRAE) 189.1[60] allowable levels. The primary volatile organic compounds (VOCs) found to be emitting from each chair type are in Table 9. These volatile organic compounds (VOCs) included aldehydes, alcohols, and carboxylic acids that are common with polyurethane foam (PUF). There were traces of industrial solvents such as toluene and naphthalene that could be associated with material contamination or manufacturing processes. Individual chemicals of concern for each chair type are also listed in Appendix G.7. These are chemicals that fall on key regulatory or program lists and are evaluated for indoor use. Key chemicals of concern by product type are shown in Table 10. They primarily included known or suspected carcinogens and reproductive toxins, including formaldehyde, acetaldehyde, toluene, naphthalene, and xylenes. Although present, the levels of these chemicals of concern were low and would meet current standards or guidelines for indoor air. The specific volatile organic compounds (VOCs) and their levels were similar across the four different chair types, indicating that the flammability management process had little impact on these emissions when the chairs were used in typical consumer conditions.

Table 8: Comparison of Total Volatile Organic Compound (TVOC) Values (µg/m^3) Among Chair Types

	NFR[1]	OPFR[2]	RFR[3]	BNFR[4]
New	120	206	67.9	160
Aged	116	154	111	141

[1] **NFR: No flame retardant added to the polyurethane foam**
[2] **OPFR: Organophosphate chemical flame retardant added to the polyurethane foam**
[3] **RFR: Reactive (polymer integrated) chemical flame retardant added to the polyurethane foam**
[4] **BNFR: No flame retardant but a barrier material added between the polyurethane foam and textile cover**

Table 9: Primary Individual Volatile Organic Compounds (VOCs) Emitted Among Chair Types

NFR[1]	OPFR[2]	RFR[3]	BNFR[4]
Hexanal	Hexanal	Propanoic acid	Hexanal
1-Butanol (N-Butyl alcohol)	Propylene Carbonate	Hexanal	1-Butanol (N-Butyl alcohol)
Propanoic acid	Propanoic acid	Ethanol, 2-butoxy	Propanoic acid
Ethanol, 2-butoxy	Phenol	Formaldehyde	Pentanal
2-Ethylhexanoic acid	Pentanal	2-Ethylhexanoic acid	Hexanoic acid
1-Pentanol (N-Pentyl alcohol)	Propylene glycol monomethyl ether (2-Propanol, 1-methoxy-)	Hexanoic acid	2-Ethylhexanoic acid
1-Hexanol, 2-ethyl	2-Propanone, 1-hydroxy	Furfural (2-Furaldehyde)	Ethanol, 2-butoxy
Hexanoic acid	Propanal	Butanoic acid	1-Hexanol, 2-ethyl
Formaldehyde	Ethanol, 2-butoxy	Pentanal	Furfural (2-Furaldehyde)
Pentanal	Furfural (2-Furaldehyde)	2-Propanone, 1-hydroxy	1-Pentanol (N-Pentyl alcohol)

[1] **NFR: No flame retardant added to the polyurethane foam**
[2] **OPFR: Organophosphate chemical flame retardant added to the polyurethane foam**
[3] **RFR: Reactive (polymer integrated) chemical flame retardant added to the polyurethane foam**
[4] **BNFR: No flame retardant but a barrier material added between the polyurethane foam and textile cover**

Table 10: Primary Chemicals of Concern Among Chair Types

VOC Species	Regulation			
	Prop65[1]	TLV[2]	Chronic REL[3]	AgBB[4]
Acetaldehyde	X	X	X	X
Formaldehyde	X	X	X	X
Naphthalene	X	X	X	X
Toluene (Methylbenzene)	X	X	X	X

[1] **Prop65: California Proposition 65**[18]
[2] **TLV: American Conference of Governmental Industrial Hygienists' Threshold Limit Values**[61]
[3] **Chronic REL: The Office of Environmental Health Hazard Assessment in California's Chronic Reference Exposure Level**[30]
[4] **AgBB: Ausschuss zur gesundheitlichen Bewertung von Bauprodukten's Lowest Concentration of Interest**[62]

5.3.2 Cushions

The volatile organic compound (VOC) emissions of the individual cushions were also low. They were dominated by the emission of caprolactam, since the cover fabric was nylon. Primary emissions of the cushions are shown in Table 11.

Table 11: Total Volatile Organic Compound (TVOC) And Top 10 Volatile Organic Compound (VOC) Emissions (µg/m³) From Cushions

NO FR[1]		REACTIVE FR[2]		TDCPP FR[3]	
TVOC	58.7	TVOC	62.4	TVOC	90
î-Caprolactam (2H-Azepin-2-one, hexahydro)	40.9	î-Caprolactam (2H-Azepin-2-one, hexahydro)	43.8	î-Caprolactam (2H-Azepin-2-one, hexahydro)	40.5
2-Ethylhexanoic acid	9.1	Propylene Carbonate	6.2	Propane, 1,2,3-trichloro	32
Di-n-octyl phthalate	2.4	1-Hexanol, 2-ethyl	2.7	2-Ethylhexanoic acid	10.2
3-Heptene, 2,2,4,6,6-pentamethyl-	2.3	Phenol, 2,4-bis(1,1-dimethylethyl)-	2.2	2-Propanol, 1,1'-oxybis- (Dipropylene glycol)	4.7
2,4-Pentanediol, 2-methyl (Hexylene glycol)	2.2	2,4-Pentanediol, 2-methyl (Hexylene glycol)	2.1	1-Propanol, 2,2'-oxybis-	3.9
1-Tridecene	2.2	3-Heptene, 2,2,4,6,6-pentamethyl-	2.1	2,4-Pentanediol, 2-methyl (Hexylene glycol)	1.9
2-Ethylhexyl 2-ethylhexanoate	2.1	Cyclopentasiloxane, decamethyl	1.9	Phenol	1.9
Formaldehyde	2	Nonane, 2,2,4,4,6,8,8-heptamethyl	1.8	3-Heptene, 2,2,4,6,6-pentamethyl-	1.6
Benzaldehyde	1.7	Benzaldehyde	1.8	Phenol, 2,4-bis(1,1-dimethylethyl)-	1.6
1,4-Dioxane, 2,5-dimethyl	1.6	Formaldehyde	1.6	Cyclopentasiloxane, decamethyl	1.6

[1] **NO FR: Without a flame retardant**

[2] **REACTIVE FR: With a proprietary reactive flame retardant**

[3] **TDCPP FR: With a commonly available flame retardant used in the industry (identified independently as tris (1,3-dichloro-2-propyl) phosphate (TDCPP)**

5.3.3 Electronics

Emissions of the electronics were measured when the units were energized and operating. The operating television was a higher emitter than the laptop, and it was significantly higher in emissions than the upholstered chairs. The primary volatile organic compounds (VOCs) associated with each of the electronics are shown in Table 12. For the television, measurements showed a complex mixture of numerous volatile organic compounds (VOCs), with key emissions of siloxanes, phenol, and xylenes, as well as alcohols, aromatics, acrylates, benzenes, phthalates, and tetramethylsuccinonitrile. On the other hand, the laptop measured very low on the emissions scale, and the volatile organic compounds (VOCs) present included normal hydrocarbons, aldehydes, and alcohols. Chemicals of concern for the electronics can be found in Table 13 and a complete list can be found in Appendix G.7.

Table 12: Total Volatile Organic Compound (TVOC) and Primary Volatile Organic Compound (VOC) Emissions (µg/m³) from Electronics

TV		Laptop	
TVOC	384	TVOC	4.1
Cyclopentasiloxane, decamethyl	130	Benzaldehyde	1.7
Cyclohexasiloxane, dodecamethyl	75	Formaldehyde	1.4
Xylene (para and/or meta)	68		
Phenol	38		
1-Hexanol, 2-ethyl	32		
Hexasiloxane,1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-	27		
Tetramethylbutanedinitrile	18		
Tetradecane	16		
Pentasiloxane, dodecamethyl	12		
Ethanol, 2-butoxy	9		

Table 13: Chemicals of Concern from Electronics

VOC Species	Regulation			
	Prop65[1]	TLV[2]	Chronic REL[3]	AgBB[4]
Acetaldehyde	X	X	X	X
Formaldehyde	X	X	X	X
Naphthalene	X	X	X	X
Toluene (Methylbenzene)	X	X	X	X
Benzene, ethyl	X	X	X	X
Styrene	X	X	X	X

[1] **Prop65: California Proposition 65**[18]
[2] **TLV: American Conference of Governmental Industrial Hygienists' Threshold Limit Values**[61]
[3] **Chronic REL: The Office of Environmental Health Hazard Assessment in California's Chronic Reference Exposure Level**[30]
[4] **AgBB: Ausschuss zur gesundheitlichen Bewertung von Bauprodukten's Lowest Concentration of Interest**[62]

5.4 Flame Retardants – Consumer Use

Preliminary method development studies detected the presence of numerous flame retardant chemicals in the environmental chamber system and overall system backgrounds. These included polybrominated diphenyl ethers (PBDEs) and other chlorinated and brominated flame retardants as well as some organophosphate flame retardants (OPFR). There was variability in their presence during the method development processes. As a result, quantification limits were set higher than detection capabilities. The flame retardant backgrounds demonstrate the difficulty in conducting these types of studies when low levels of flame retardants are of concern. Specialized efforts are required due to: 1) ubiquitous existence of flame retardants from materials and the environment, 2) analytical contamination that cannot be minimized, which contributes to the flame retardant analysis being difficult to perform,[63] and 3) some flame retardants are known to be used as plasticizers and are unintentionally present. Only those flame retardants that were specifically used in this study are quantitated and reported, and only values above quantification limits are discussed in the following sections. All detailed flame retardant data are in Appendix F.

5.4.1 Upholstered Chairs

Measured flame retardants were only associated with the chairs manufactured with an organophosphate chemical flame retardant (OPFR). Triphenyl phosphate (TPhP) was detected in both volatile and airborne particle phases at levels below 1 ng/m^3. Triphenyl phosphate was the only flame retardant detected in volatile phase and in a new chair. In the particle phase, (4-tert-butylphenyl) diphenyl phosphate (4tBPDPP) was also detected at trace level in the new chair. Both (4-tert-butylphenyl) diphenyl phosphate (4tBPDPP) and triphenyl phosphate (TPhP) were consistently detected in settled dust from both new and aged organophosphate flame retardant (OPFR) chairs, with triphenyl phosphate (TPhP) levels (500-4,400 pg/ft^2 (5 ng/m^2 -47 ng/m^2)) at an order of magnitude higher than (4-tert-butylphenyl) diphenyl phosphate (4tBPDPP) concentrations (70-140 pg/ft^2 (0.75 ng/m^2 -1.5 ng/m^2)).Three out of four identified flame retardants in the organophosphate flame retardant (OPFR) chairs were measured in dermal transfer samples, listing from largest concentration: triphenyl phosphate (TPhP)(20-15,000 pg/in^2 (32 ng/m^2 -2,300 ng/m^2,)) 4-tert-butylphenyl) diphenyl phosphate (4tBPDPP) (60-120 pg/in^2 (92 ng/m^2 -185 ng/m^2)), then (2,4-ditert-butylphenyl) diphenyl phosphate (B4tBPPP) (20-30 pg/in^2 (31 ng/m^2 -46 ng/m^2)), (2,4-ditert-butylphenyl) diphenyl phosphate (B4tBPPP) was only detected for aged chairs. Tris (4-tert-butylphenyl) phosphate (T4tBPP) was never detected in the environmental chamber exposure samples of the study.

The flame retardant data among samples showed some variability, likely due to the trace levels being measured and analytical complexity. A consistent pattern began to emerge with the settled dust and dermal transfer samples where higher levels were being measured. The data generally showed that flame retardants in the polyurethane foam of the organophosphate chemical flame retardant (OPFR) chair did present for exposure in the air, settled dust, and dermal transfer.

5.4.2 Chair Cushions

Out of the three individual chair cushions tested, only the standard flame retardant chair cushion manufactured with tris (1,3-dichloroisopropyl) phosphate (TDCPP) released detectable levels of flame retardant. Tris (1,3-dichloroisopropyl) phosphate (TDCPP) was only detected in vapor (0.032 ng/m^3) but not in airborne particles. The tris (1,3-dichloroisopropyl) phosphate (TDCPP) level in settled dust from this chair cushion (70,000-80,000 pg/ft^2 (753 ng/m^2-861 ng/m^2)) was greater than the dust measurement for triphenyl phosphate (TPhP) from organophosphate flame retardant (OPFR) chairs. Tris (1,3-dichloroisopropyl) phosphate (TDCPP) concentrations from dermal transfer samples were also higher for the chair cushion (40,000-50,000 pg/in^2 (62,000 ng/m^2-77,500 ng/m^2)) compared to that measured for the organophosphate flame retardant (OPFR) chairs. There was consistency in the duplicate measurements made across the samples, indicating a higher quality of analytical measurement as a result of the higher concentrations. This data confirmed that flame retardant in the polyurethane foam (PUF) presents for exposure in air, settled dust, and dermal transfer.

The total masses of flame retardants in each test sample were estimated using polyurethane foam (PUF) density, volume of polyurethane foam (PUF), and flame retardant weight percentages provided or measured by a third-party laboratory. An organophosphate flame retardant (OPFR) chair contained 23.0 g of triphenyl phosphate (TPhP), 44.8 g of (4-tert-butylphenyl) diphenyl phosphate (4tBPDPP), 8.6 g of (2,4-ditert-butylphenyl) diphenyl phosphate (B4tBPPP), and 0.47 g of tris (4-tert-butylphenyl) phosphate (T4tBPP); total of 76.9 g of flame retardants. The standard flame retardant (TDCPP) chair cushion was smaller in volume and foam density than organophosphate flame retardant (OPFR) polyurethane foam but contained flame retardant at a higher weight percentage, which led to the seat cushion containing 82.7 g of tris (1,3-dichloroisopropyl) phosphate (TDCPP).

The environmental concentrations of tris (1,3-dichloroisopropyl) phosphate (TDCPP) from the chair cushion were compared to those measured from the triphenyl phosphate (TPhP) containing organophosphate flame retardant (OPFR) chair in Figure 18. This generally demonstrates that settled dust and dermal transfer may offer the most significant exposure opportunities. Since there are many variables including chemical and physical properties of the flame retardants, chair and cushion construction processes, and analytical complexities, these results should be considered qualitative as to exposure potential processes.

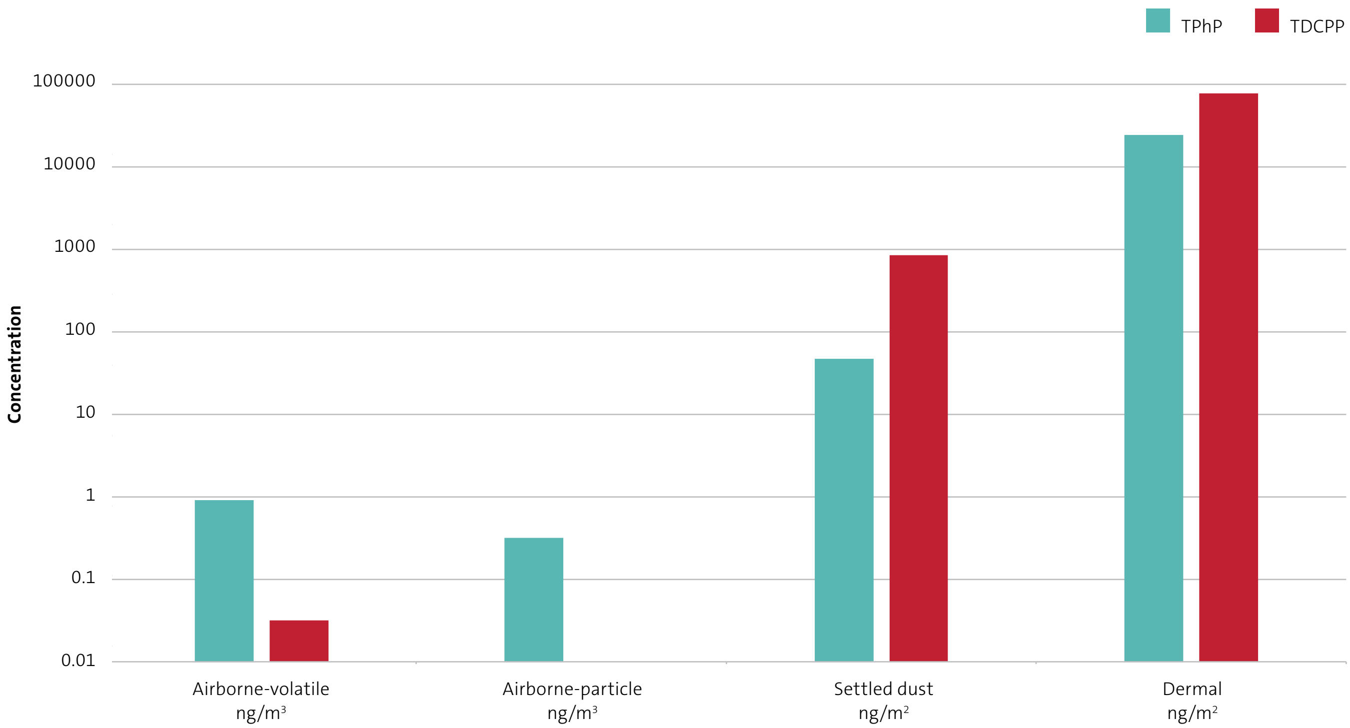


Figure 18: Highest concentrations measured of triphenyl phosphate (TPhP) from organophosphate flame retardant (OPFR) chair (blue) versus those of tris (1,3-dichloroisopropyl) phosphate (TDCPP) from standard flame retardant chair cushion (orange) for the four sampling methods listed across and their units shown below.

5.4.3 Electronics

Numerous flame retardants were observed in the environmental samples of the electronic products. Triphenyl phosphate (TPhP), tris (2-chloroethyl) phosphate (TCEP), 2,2',4,4,5-pentabromodiphenylether (PBDE 99), and 2, 2', 4, 4'-tetrabromodiphenyl ether (PBDE-47) were detected in some airborne and settled dust samples collected from the television operating for 24 hours. Tris (2-chloroethyl) phosphate (TCEP) in settled dust, and tris (1,3-dichloroisopropyl) phosphate (TDCPP), 2,2',4,4,5-pentabromodiphenylether (PBDE 99), and 2, 2', 4, 4'-tetrabromodiphenyl ether (PBDE-47) in coarse particles in air were detected from the laptop. Quantitation of these flame retardants was not possible due to their variable presence and levels in the background measurements. However, there was an indication of flame retardant presence that could lead to inhalation and settled dust exposure from the electronics.

5.5 Flame Retardant Exposure Modeling

5.5.1 Upholstered Chairs

Estimated personal flame retardant exposure levels were determined by applying defined exposure models with measured environmental chamber data. Analytical measurements of key flame retardants in this study are considered semi-quantitative because of methodology uncertainties; however, this exposure data provides an exploratory evaluation of exposure potentials by different exposure routes. It should not be used for risk assessments.

Average daily doses (ADDs) of flame retardants for adults, toddlers, and infants were calculated for the four human exposure pathways including dermal, ingestion, particle inhalation, and ultrafine particulates/volatile inhalation. The higher flame retardant values obtained from the two duplicate test samples were used to obtain the exposure levels. For dermal exposure, expected values (using a fraction of applied dose absorbed through the skin, skin absorption rate (ABS) of 0.1) and worse case values (using skin absorption rate (ABS) of 1) were calculated. For dermal exposure only, the adult values were separated for male and female. Data can be found in Appendix F.3.

For adults, regardless of male or female, the most significant flame retardant exposure pathway was dermal transfer, followed by ingestion and inhalation. This pattern was the same for all flame retardants identified for the organophosphate flame retardant (OPFR) chair. For toddlers and infants, ingestion and dermal exposures were in a similar range and much higher than inhalation exposure. Children's frequent hand-to-mouth contact from touching settled dust drove ingestion exposure for children to be much higher than that for adults.

Since triphenyl phosphate (TPhP) was measured as the most abundant flame retardant from the organophosphate flame retardant (OPFR) chair during chamber exposure testing, it is expected to present as the primary flame retardant for human exposure, followed by the two isomers of tris-isobutylated triphenyl phosphate (TBPP), (4-tert-butylphenyl) diphenyl phosphate (4tBPDPP) and (2,4-ditert-butylphenyl) diphenyl phosphate (B4tBPPP). The predicted triphenyl phosphate (TPhP) average daily doses (ADDs) from the organophosphate flame retardant (OPFR) chair were 0.6 ng/kg/day, 20 ng/kg/day, and 34 ng/kg/day for adults, toddlers, and infants, respectively. No significant differences in average daily dose (ADD) values were observed between new and mechanically aged chairs (differences were within a standard deviation). Tris (4-tert-butylphenyl) phosphate (T4tBPP) was not included in the assessment since it was not detected in the environmental chamber portion of the study.

The exposure modeling showed that young children, the most susceptible population, receive the highest flame retardant exposure (Figure 19). The total average daily dose (ADD) was higher for infants and toddlers than for adults; the mean of measurements from aged and new chairs ranged from 1.2 to 6.3 times higher. Ingestion exposure drove the average daily dose (ADD) to be higher for children, with infants having the largest average daily dose. The average daily dose for toddlers was about 33% lower than for infants.

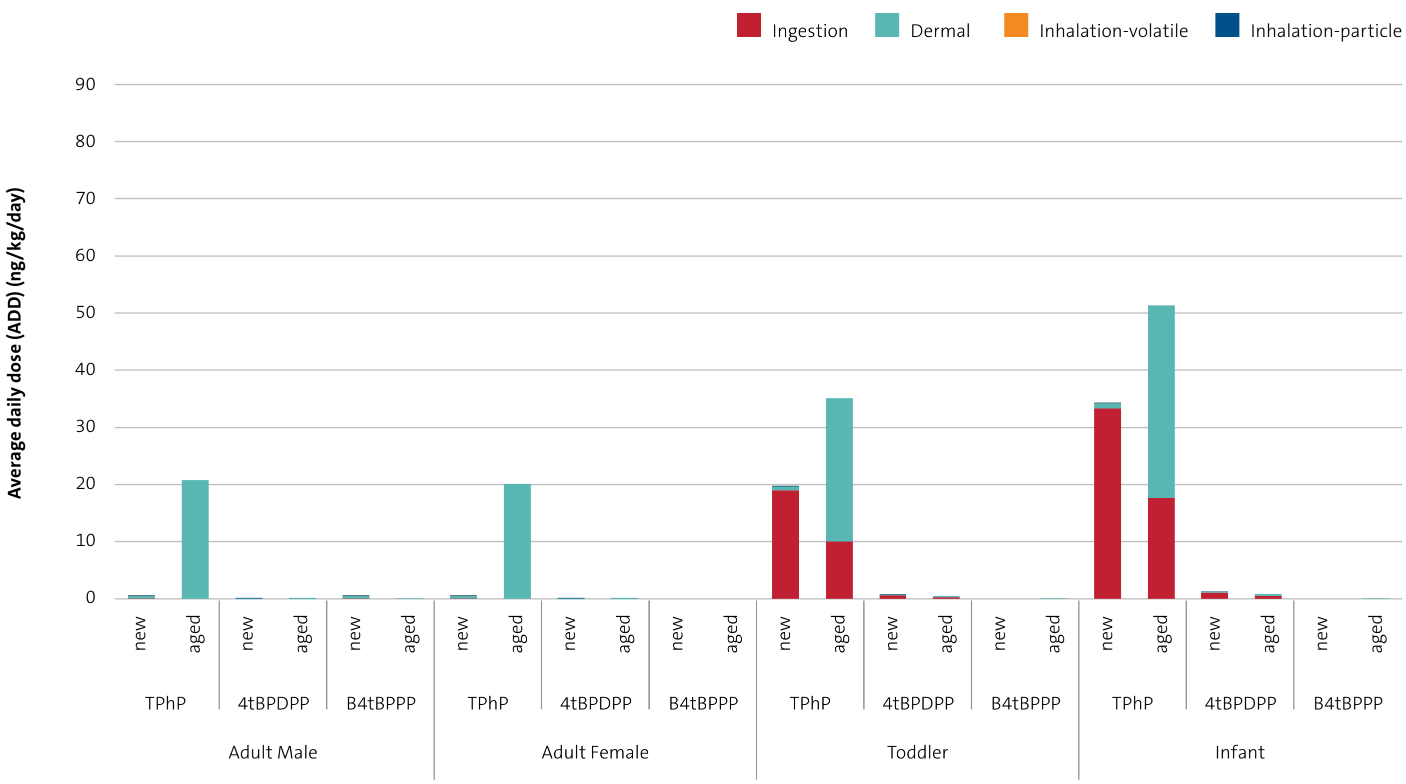


Figure 19: Comparison of adults' and children's average daily dose (ADD) of flame retardants predicted from emissions data from new and aged organophosphate flame retardant (OPFR) chairs. TPhP: triphenyl phosphate, 4tBPDPP: (4-tert-butylphenyl) diphenyl phosphate, B4tBPPP: (2,4-ditert-butylphenyl) diphenyl phosphate.

5.5.2 Chair Cushions

Tris (1,3-dichloroisopropyl) phosphate (TDCPP) exposure levels from the standard flame retardant chair cushion were also calculated (Figure 20). Similarly, infants had the highest average daily dose (ADD) (694 ng/kg/day, 10 times higher than adults), followed by toddlers (415 ng/kg/day, six times higher than adults), and then adults (68 and 66 ng/kg/day for male and female respectively). Adults had much higher exposure from dermal contact than ingestion and inhalation. Ingestion was the dominate exposure pathway for toddlers and infants, which raised the total tris (1,3-dichloroisopropyl) phosphate (TDCPP) average daily dose (ADD) to be much higher for children. The tris (1,3-dichloroisopropyl) phosphate (TDCPP) average daily dose (ADD) was much higher than the average daily doses (ADDs) of the various flame retardants found in the organophosphate flame retardant (OPFR) chair. This resulted from the higher chamber concentrations measured for tris (1,3-dichloroisopropyl) phosphate (TDCPP).

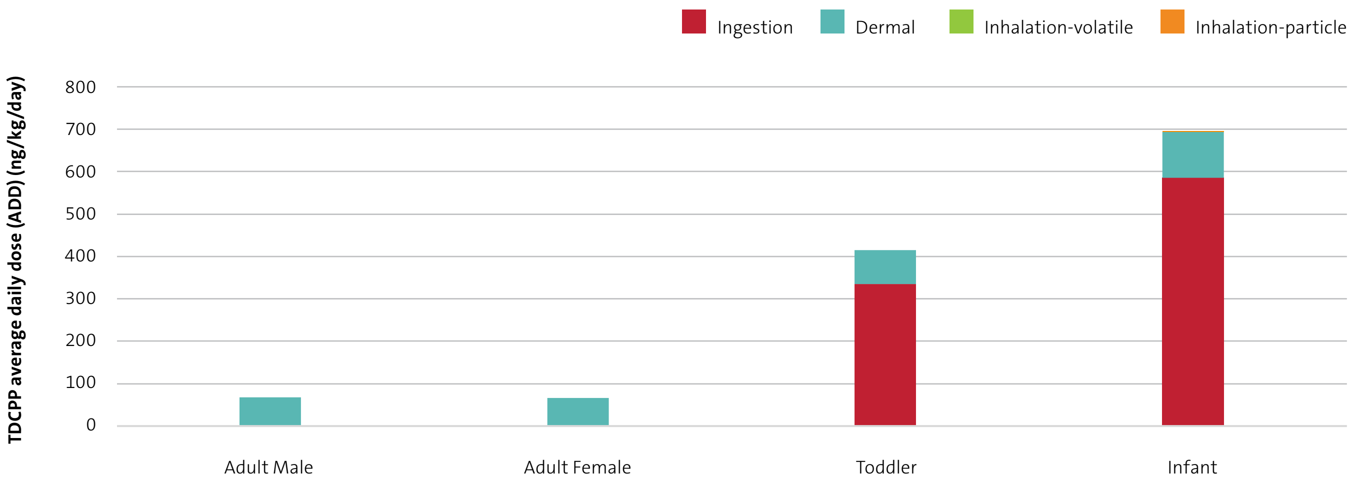


Figure 20: Comparison of adults' and children's average daily dose of tris (1,3-dichloroisopropyl) phosphate (TDCPP) predicted from standard flame retardant chair cushion emission data.

5.6 Dose Response/Toxicity Estimates

The lowest no observed effect level (NOEL) for triphenyl phosphate (TPhP) found in the literature was 161 mg/kg/day from a rat study by Sobotka et al.[64] Using an uncertainty factor of 100, the acceptable daily intake (ADI) was 1.61 mg/kg/day. This calculated acceptable daily intake for triphenyl phosphate (TPhP) was much higher than the measured triphenyl phosphate average daily dose (ADD) from the organophosphate flame retardant (OPFR) chair in this study.

The hazard index (HI) of triphenyl phosphate (TPhP) exposure from the organophosphate flame retardant (OPFR) chair was measured as 1.2×10^{-5}, 2.7×10^{-5}, 4.2×10^{-5} for adults, toddlers, and infants, respectively. These values are lower than one, which may be considered acceptable or not as hazardous by some guidelines. Similar to average daily dose (ADD) differences for infants to adults, hazard index (HI) values were 2.3 times higher for toddlers and 3.6 times higher for infants than adults.

The lowest no observed adverse effect level (NOAEL) for tris (1,3-dichloroisopropyl) phosphate (TDCPP) commonly cited was available from Kamata et al.,[65] which was a study on repeated exposure. This study reported a tris (1,3-dichloroisopropyl) phosphate (TDCPP) no observed adverse effect level (NOAEL) for female rats of 15.3 mg/kg/day.[65,66] Using this value, the acceptable daily intake (ADI) was calculated to be 0.153 mg/kg/day, using 100 as the uncertainty factor. Using the average daily dose (ADD) measured in this study, hazard index (HI) values were in the range of 4×10^{-4} to 4×10^{-3}, which are lower than a hazard index of one.

Another no observed adverse effect level (NOAEL) for tris (1,3-dichloroisopropyl) phosphate (TDCPP), as obtained from a reproductive toxicity study, was 5 mg/kg/day.[66,67] This was lower than the no observed adverse effect level (NOAEL) from Kamata et al. Based on this and an uncertainty factor of 100, the acceptable daily intake (ADI) was calculated as 0.05 mg/kg/day. This increased the hazard indices (HIs) to 1.3×10^{-3} to 1.4×10^{-2}, which were still lower than one.

6. Flammability Results

6.1 Smoldering Test Results: California Technical Bulletin (TB 117-2013)

This method consisted of a series of individual furniture component tests to evaluate their smoldering or cigarette ignition resistance. Components tested include the cover textile, barrier material, resilient filling materials, and decking material, all used in the manufacture of the upholstered chairs. Each test involved a small assembly consisting of the component material mounted on a plywood mock-up resembling a chair and back. The other materials used in the mock-up, other than the one being tested, was a standardized material.

The results of the smoldering tests for the component materials are shown in Table 14. A material failed if it continued to smolder after 45 minutes, if it exceeded a specific char length based on the material, or if it transitioned to open flaming. Failing one of these criteria was justification for an overall failure. If one or more of the triplicate test specimens failed, the material failed. As shown in Table 14, the upholstery cover textile, the barrier textile, and the resilient polyurethane foam (PUF) containing the organophosphate flame retardant (OPFR) all failed to meet the smolder resistance requirements. The resilient foam with no flame retardant, the resilient foam with reactive flame retardant, the resilient loose fiber, and the decking textile passed the test for smolder resistance. The cover and barrier textiles sustained smoldering for more than 45 minutes and were manually extinguished, whereas other tested materials independently self-extinguished within the 45 minutes test duration time.

In order to manufacture furniture that passes California Technical Bulletin 117-2013 (TB 117-2013), the following scenarios apply:

1. The cover textile, resilient filling materials, and decking material pass; or
2. If the cover textile fails, then a barrier material placed between the cover textile and resilient filling materials must pass; or
3. If the resilient filling materials fail, the barrier material placed between the cover textile and resilient filling materials must pass.

After extrapolating the test results, none of the four types of chairs with varying fire suppression technologies met the pass requirements of California Technical Bulletin 117-2013 (TB 117-2013).

Table 14: Smoldering Test Results: California TB 117-2013 For Upholstered Chair Test Samples

Material	Pass/Fail for 3 Tests	Overall	Extinguishing Method
Upholstery Textile (Cover)	Fail/Fail/Fail	**FAIL**	Manually Extinguished
Barrier Textile	Fail/Fail/Fail	**FAIL**	Manually Extinguished
No FR Resilient Foam (NFR)	Pass/Pass/Pass	**PASS**	Self-Extinguished
Organophosphate FR Resilient Foam (OPFR)	Fail/Pass/Pass	**FAIL**	Self-Extinguished
Reactive FR Resilient Foam (RFR)	Pass/Pass/Pass	**PASS**	Self-Extinguished
Resilient Loose Fiber (no FR)	Pass/Pass*	**PASS**	Self-Extinguished
Decking Textile (no FR)	Pass/Pass/Pass	**PASS**	Self-Extinguished

***Third test for resilient loose fiber was not conducted.**

6.2 Open Flame Studies

6.2.1 Overview

Two laboratory settings, the Furniture Heat Release Calorimeter and the ISO 9705[22] Room Test Laboratory were utilized for fire performance testing of upholstered chairs and electronic products. Typical burn remnants of upholstered chairs, laptop, and television in the Furniture Heat Release Calorimeter are shown in Figure 21.

Figure 21: Images (from left to right) of upholstered chair with an organophosphate flame retardant and no barrier (OPFR), upholstered chair with fire barrier, laptop, and television after burn tests.

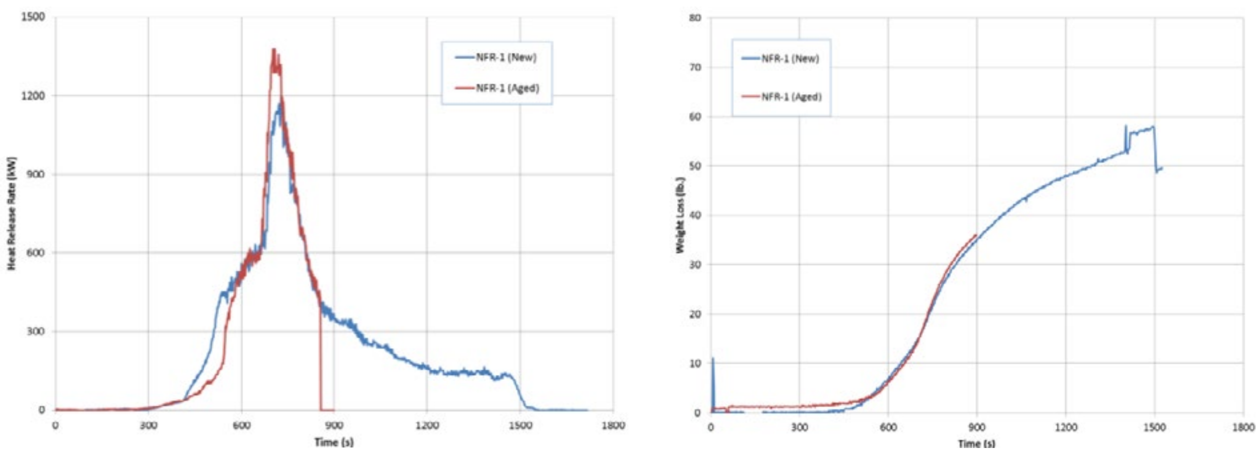


Figure 22: Time series heat release rate in kW (left) and weight loss in pounds (right) for no flame retardant (NFR) chairs (new chair shown in blue and aged chair shown in red).

Overall, the fire performance results for the chairs were similar between the two test settings, however, more variables were measured during the ISO 9705 room tests. Fire performance results for new and mechanically aged chairs of the four different construction types (no flame retardant (NFR), barrier and no flame retardant (BNFR), organophosphate flame retardant (OPFR), and reactive flame retardant (RFR)) and the electronics are presented in the following sections (6.2.2-6.2.3). Electronics were tested only in the Furniture Heat Release Calorimeter. The complete flammability report is provided in Appendix H. All data and figures in this report on open flame studies were taken from the complete flammability report as prepared by UL, LLC.

6.2.2 Furniture Heat Release Calorimeter

Time-series flammability characteristics data were obtained from the Furniture Heat Release Calorimeter. Examples of heat release rate and weight loss profiles are shown in Figure 22 for new and aged no flame retardant (NFR) chairs. The new no flame retardant (NFR) chair test was terminated when most of its mass was consumed. The aged chair was terminated when the heat release rate value dropped below 300 kW after reaching peak burning. In this test, most of the foam and fabric was consumed. As observed in Figure 22, weight loss increased substantially when the heat release rate was at its peak at 700 seconds. No significant differences were observed between new and aged chairs as the two data sets overlap one another in both heat release rate and weight loss plots.

The flammability characteristics as measured from the Furniture Heat Release Calorimeter indicated no significant flammability difference between chairs manufactured with no flame retardant (NFR); with an organophosphate flame retardant (OPFR); and with a reactive flame retardant (RFR). All three types of chairs lost 41-74% of their weight (Table 15). Maximum heat release rates ranged between approximately 1,200 and 1,400 kW, and the time to reach maximum release rate was about 12 minutes. It only took about eight minutes to reach 200 kW, which is the maximum heat release rate requirement for the flammability of mattresses.[68]

The chair with a barrier and no flame retardant (BNFR) showed significantly different flammability performance than the other chair types, with an average weight loss of 5.9 lbs (8.5%) compared to the other chair types that averaged 37.2 lbs (55%). When comparing the maximum heat release rates of the BNFR chair to the other chair types, the barrier no flame retardant (BNFR) chair averaged 32 kW (with time to maximum heat release rate of 34 minutes) while the other chairs averaged 1,305 kW (with time to maximum heat release rate of 12 minutes). The barrier no flame retardant (BNFR) chair produced a peak heat release rate of less than 100 kW, never reaching to the maximum heat release rate requirement for flammability of mattresses, while the other three types of chairs exhibited peak heat release rates greater than 1,000 kW. Despite the barrier material failing California Technical Bulletin 117-2013 (tb 117-2013) smoldering tests, it resulted in a significant reduction of flammability potential for the chair manufactured with the barrier and no flame retardant (BNFR), in comparison to the other chair types.

Table 15: Furniture Heat Release Calorimeter Summary

Chair Construction	Sample ID	New/ Aged	Test Duration[1] (min.)	Weight Loss (lb)	Weight Loss (%)	Max. Heat Release Rate (kw)	Time to Max. Heat Release Rate (min:sec)	Time to Reach 200 kW (min:sec)[2]
Non-FR Foam	NFR	New	23	49.9	74.1%	1,196	12:07	8:10
		Aged	15	34.7	50.7%	1,378	11:42	9:04
Standard OPFR Foam	OPFR	New	12	27.1	41.4%	1,200	11:16	7:46
		Aged	14	35.2	52.9%	1,373	12:26	9:00
Reactive FR Foam	RFR	New	15	39.7	59.4%	1,253	12:00	8:30
		Aged	15	36.3	52.0%	1,251	12:36	8:20
		Aged	15	38.9	55.7%	1,379	12:22	8:58
Non-FR Foam + Fire Barrier	BNFR	New	50	5.2	7.5%	17	30:51	NA[4]
		New	50	8.4	12.1%	63[3]	39:58	NA[4]
		Aged	50	4.1	6.0%	16	35:16	NA[4]

FR stands for flame retardant

[1] **Tests without fire barrier were terminated after they reached peak burning then heat release rate had reduced below 400 kW except for NFR new chair.**

[2] **Maximum heat release rate requirement (200 kW) for flammability of mattresses: Standard for the Flammability (Open Flame) of Mattress Sets - 16 CFR 1633**

[3] **Fire spread into the back cushion unlike other tests with fire barrier**

[4] **NA: not applicable since heat release rate never reached 200 kW**

Fourier transformation-infrared spectroscopy (FT-IR) gas analysis results did not detect any halogenated species in the effluent gases from the various burns. Gases detected included hydrocarbons, acetylene, and methanol at very low values, less than 10 parts per million (ppm) (see Appendix H). No significant differences were found when comparing new and mechanically aged chairs for all four types of chairs.

Fire performance tests for the electronic devices (flat screen television and laptop computer) were conducted in the Furniture Heat Release Calorimeter. Duplicates of each electronic were evaluated. The electronic devices never sustained fire independently, therefore the match-equivalent flame was in contact with the tested electronic for the duration of the experiment (50 minutes). The weight loss (1-2%) and maximum heat release rate (less than or equal to 10 kW) of these electronics were insignificant relative to the weight loss of the upholstered chairs (Table 16). The average of the maximum heat release rates for electronic devices was 5.75 kW, lower than that for upholstered chairs.

Table 16: Summary of Fire Performance of Home Electronics

Home Electronic Item	Test Specimen ID	Test Duration (min.)	Weight Loss (lb)	Weight Loss (%)	Max. Heat Release Rate (kw)	Time to Max. Heat Release Rate (min:sec)
Flat Screen TV	FS-1	50	0.8	1.8%	7	49:06
	FS-2	50	0.4	1.0%	5	19:30
Laptop	L-1	50	NA	NA[1]	1	16:50
	L-2	50	NA	NA[1]	10	10:16

[1] **NA – Below the resolution of load cell measurement (0.1 lb)**

6.2.3 ISO 9705 Test Room

Still frames of the four types of chairs burning inside ISO 9705 Test Room, where the intake oxygen by the fire was limited, are shown in Figure 23. All chairs were ignited similarly with match-equivalent fire on the inside of the arm rest for 1 minute. The three chairs without barrier textile, which are the no flame retardant (NFR) chair, the organophosphate flame retardant (OPFR) chair, and the reactive flame retardant (RFR) chair, self-sustained the fire as shown in the 7 minutes timepoints.

Figure 23: Still frames of the ISO 9705 Test Room burns for no flame retardant (NFR), organophosphate flame retardant (OPFR), reactive flame retardant (RFR), and no flame retardant with barrier textile (BNFR) chairs at 1, 7, 11, 14 minutes from ignition.

The charring on the surface of the barrier (BNFR) chair continued for the duration of the burn test; two still shots of BNFR chair past the 14 minute mark is shown in Figure 24. testing period.

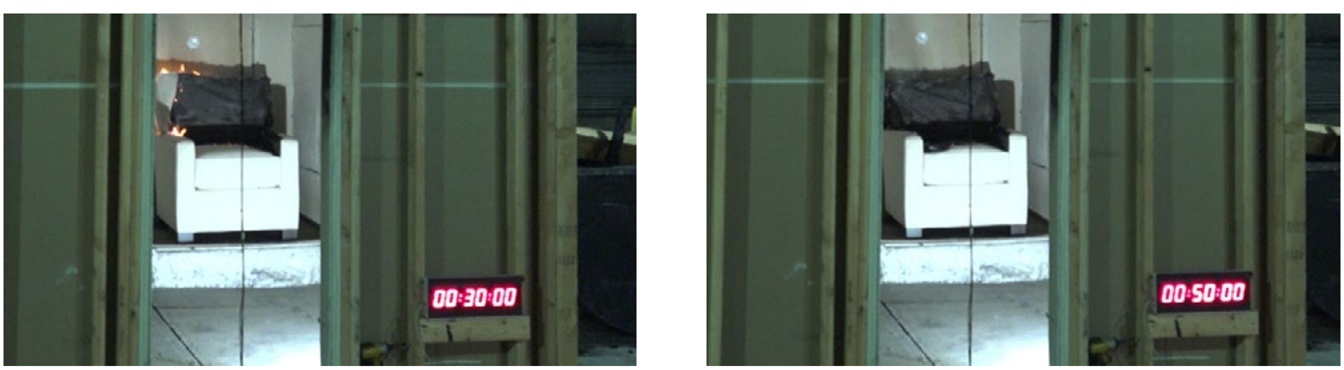


Figure 24: Still frames of the ISO 9705 Test Room burns for no flame retardant with barrier textile (BNFR) chair at 30 and 50 minutes from ignition.

The ISO 9705 Test Room allowed flammability evaluations of the four types of chairs by measuring weight loss; heat release rate; and doorway fire effluent gases, smoke density, and temperature. The measured doorway fire effluent gases included carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), hydrogen cyanide (HCN), and other combustion gases. Figure 25 shows examples of time series progressions of heat release rate, weight loss, carbon monoxide concentration, and effluent smoke optical density as determined from the no flame retardant chair (NFR). The peak heat release rate exceeded 1,400 kW for the new and aged chairs. In both tests, most of the chair upholstery materials were consumed. Heat release rate, weight loss, carbon monoxide (CO) concentration, and optical density all showed a relationship to one another; as heat release rate peaked, so did carbon monoxide (CO) concentrations and weight loss rates. The smoke optical density also increased indicating that visibility due to smoke is reduced when the burn is at its peak.

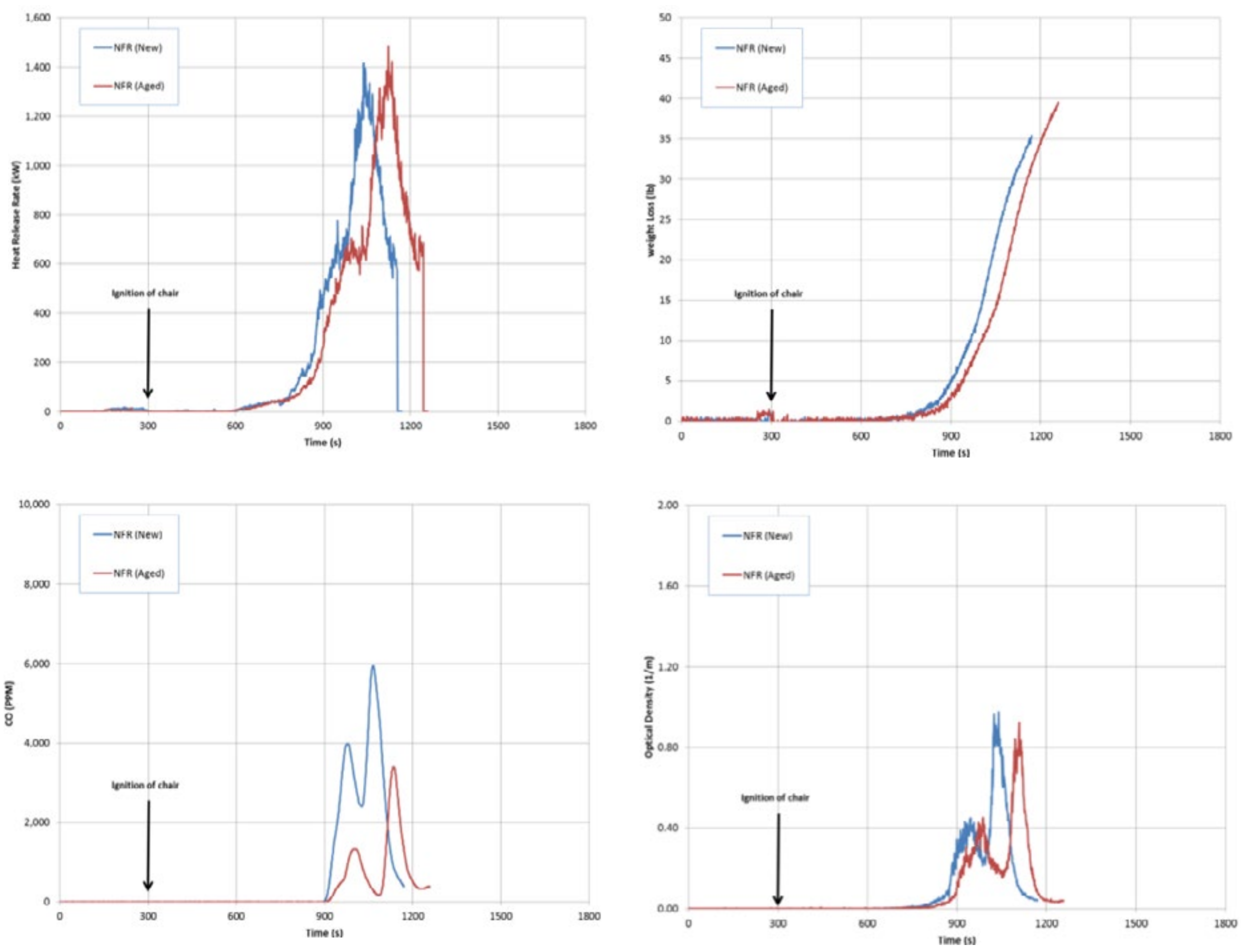


Figure 25: Heat release rate, weight loss, carbon monoxide concentration, and effluent smoke optical density for no flame retardant (NFR) chair (new chair in blue, aged in red).

Effluent gases identified by Fourier transformation-infrared spectroscopy (FT-IR) are listed in Table 17 by chair type. All gases detected by Fourier transformation-infrared spectroscopy (FT-IR) were the same for the three chairs without barrier technology, regardless of the chair being new or aged. Most gases identified were combustion products including hydrogen cyanide. No halogen species were detected by Fourier transformation-infrared spectroscopy (FT-IR). Minimal to no hydrogen cyanide (HCN) was detected from the barrier chairs (BNFR). The aged barrier (BNFR) chair was the only chair releasing formaldehyde at levels detectable by Fourier transformation-infrared spectroscopy (FT-IR).

Table 17: Summary of Gases Detected at the Doorway (ISO 9705 Room Tests)

Chair Construction	Sample ID	New/Aged	Fire Effluents From Doorway
Non-FR Foam	NFR	New	NA
		Aged	methanol, methane, propane, ethylene, acetylene, hydrogen cyanide
Standard OPFR Foam	OPFR	New	methanol, methane, propane, ethylene, acetylene, hydrogen cyanide
		Aged	methanol, methane, propane, ethylene, acetylene, hydrogen cyanide
Reactive FR Foam	RFR	New	methanol, methane, propane, ethylene, acetylene, hydrogen cyanide
		Aged	methanol, methane, propane, ethylene, acetylene, hydrogen cyanide
Non-FR Foam + Fire Barrier	BNFR	New	methanol, methane, propane, ethylene, acetylene
		Aged	formaldehyde, methanol, methane, propane, ethylene, acetylene

NA: instrumentation malfunction

Flammability characteristics are summarized in Table 18 by chair type. The results of flammability characteristics from the ISO 9705 Test Room indicated a significant difference between the barrier chair (BNFR) and the other three types of chairs, indicating that the barrier chair had significantly lower (by an order of magnitude) weight loss, heat release rate, doorway temperature, effluent gas concentrations, and optical density. No significant flammability difference between chair types with no flame retardant (NFR), organophosphate flame retardant (OPFR), and reactive flame retardant (RFR) was observed from the ISO 9705 Test Room experiments; all three types of chairs without a barrier lost 53-62% of their weight during the burn test; maximum heat release rates ranged between 1,330 to 2,030 kW; and maximum doorway temperature ranged from 530°C to 600°C. While the combustion smoke from the barrier chair did not affect visibility, the other three chairs showed the potential to reduce visibility down to 1 meter (3.3 ft).

Table 18: ISO 9705 Test Room Fire Hazard Summary

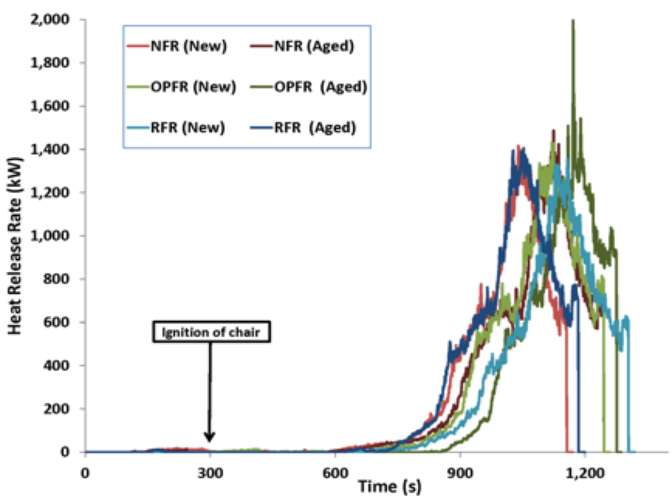
Chair Construction	Sample ID	New/ Aged	Weight Loss (lb)	% Weight Loss[1]	Max. Heat Release Rate (kW)	Max. Doorway Temperature (°C)	Max. CO Level (ppm)	Max. HCN Level (ppm)	Max. Smoke Optical Density (1/m)
Non-FR Foam	NFR	New	36.0	53.6%	1,416	530	5,950	NA	0.98
		Aged	39.7	58.3%	1,400	570	3,390	25	0.93
Standard OPFR Foam	OPFR	New	40.2	60.5%	1,432	594	1,613	43	1.00
		Aged	38.5	58.2%	2,028	601	1,137	47	1.10
Reactive FR Foam	RFR	New	41.9	61.8%	1,335	538	2,596	51	0.80
		Aged	40.0	59.4%	1,406	574	1,485	43	0.88
Non-FR Foam + Fire Barrier	BNFR	New	3.4	4.9%	8	59	266	T	0.01
		Aged	5.8	8.3%	51	69	821	T	0.03

Note: flame retardant (FR), carbon monoxide (CO), and hydrogen cyanide (HCN)

[1] The weight loss was influenced by early termination of the tests for chairs without barriers. It is anticipated that most of the combustible chair mass (i.e., wood and upholstery materials) would have been consumed if burning was allowed to continue further

NA – Malfunction in the FT-IR measurement

T – Trace amount



Flame retardants typically alter flammability in three different ways: 1) ignitability, 2) rate of fire growth, and 3) toxicity of the smoke.[70] For the chairs, ignitability did not change with or without chemical flame retardants, which was observed in both the Furniture Heat Release Calorimeter and the ISO 9705 Test Room experiments. Heat release rate progressions for the chairs without the fire barrier are shown in Figure 26. The minor differences between the chair types with and without flame retardants were within the testing variability; the rate of fire growth was not altered with the presence of fire retardants in the organophosphate flame retardant (OPFR) and reactive flame retardant (RFR) chairs.

Figure 26: Heat release rate for the three types of chairs without a fire barrier, new and aged. No flame retardant chair (NFR), organophosphate flame retardant chair (OPFR), and reactive flame retardant chair (RFR).

6.2.3.1 Smoke Toxicity

Toxicity analysis of the smoke from each chair type was conducted by comparing the chemical composition of the smoke measured by Fourier-transform infrared spectroscopy (FT-IR). Carbon monoxide (CO), a combustion byproduct, causes hypoxic stress which leads to reduced oxygen (O_2) carrying capacity of the blood. The no flame retardant (NFR) chairs had the highest maximum carbon monoxide (CO) concentrations (Table 18), producing concentrations to cause dizziness and nausea in five to 10 minutes, and death within 30 minutes.[69] If carbon monoxide (CO) concentrations sustain above 3,500 ppm for one minute, then the fractional effective dose (FED) of one is reached, representing that carbon monoxide (CO) would cause incapacitation or death to 50% of the exposed population.[70] According to the time series data from the no flame retardant (NFR) chairs (Figure 25), the fractional effective dose of one can be met simply from a single residential chair burning in a room. The carbon monoxide (CO) concentrations from the organophosphate flame retardant (OPFR) chairs and the reactive flame retardant (RFR) chairs were high enough to cause headache, tachycardia, dizziness, and nausea within 20 minutes and death within two hours. The concentration of emissions from the barrier (BNFR) chair was high enough to cause dizziness, nausea, and convulsions within 45 minutes.[69]

Hydrogen cyanide (HCN) is a combustion byproduct of polyurethane foam (PUF) pyrolysis.[70] Hydrogen cyanide (HCN) is also a systemic chemical asphyxiant that is rapidly fatal when exposed. The National Institute for Occupational Safety and Health (NIOSH) has a recommended short-term exposure limit (ST REL) of 4.7 ppm for hydrogen cyanide (HCN). The chairs with chemical flame retardants (OPFR and RFR) had the highest concentrations of hydrogen cyanide (HCN) in the smoke, average peaks of 45 ppm and 47 ppm respectively, at an order of magnitude higher than National Institute for Occupational Safety and Health's (NIOSH) exposure limit. Hydrogen cyanide (HCN) concentrations were below detection limit for the barrier (BNFR) chairs.

The risks associated with hot gas temperature, carbon monoxide (CO), and hydrogen cyanide (HCN) gases were significantly lower for the barrier (BNFR) chairs compared to those without barriers. The barrier (BNFR) chairs consistently showed the lowest mass loss, lowest heat release rate, and had the best visibility while burning. For more information, see Appendix H.

6.2.4 Chemical Air Exposure

Numerous volatile organic compounds (VOCs) were found emitting from the chairs and electronic products during the open flame burns. Air samples were collected for analysis during the open flame burns in the ISO 9705 Test Room and the Furniture Heat Release Calorimeter. While the samples in the Furniture Heat Release Calorimeter were collected directly in the room perimeter, samples in the ISO 9705 Test Room were collected via a sampling line inserted into the ISO 9705 Test Room and placed above the burning products. Overall more individual volatile organic compounds (VOCs) were measured in the Furniture Heat Release Calorimeter than in the ISO 9705 Test Room. It is suspected that volatile organic compounds (VOCs) were lost by deposition in the sampling lines of the ISO 9705 Test Room.

Volatile organic compound (VOC) data was compromised in the Furniture Heat Release Calorimeter Room in general due to high background contamination levels likely from previous burns. The data was more distinct but variable when obtained from the ISO 9705 Test Room. In general, sample collection volumes and recovery potentials for the volatile organic compounds (VOCs) being found were not optimized for either sampling system prior to analysis. As a result, the volatile organic compound (VOC) identifications are accurate, but the air levels measured should be considered exploratory and semi-quantitative at best. Full volatile organic compound (VOC) burn data for the furniture can be found in Appendix G, Tables 5-12. Some of the highest emitting volatile organic compounds (VOCs) can be found in the following Table 19 by chair type.

Table 19: Primary Volatile Organic Compounds (VOCs) Released During Burn of Upholstered Chairs

NFR Chair	OPFR Chair	RFR Chair	BNFR Chair
Hexanedioic acid, bis(2-ethylhexyl) ester	Benzene	Benzene	Acetaldehyde
Benzene	Nonane, 3-methyl-5-propyl	Nonanoic acid	Benzene
Octadecanamide	TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate)	Benzonitrile	Vinyl acetate (Acetic acid ethenyl ester)
Nonanoic acid	Octane, 2,6-dimethyl	Nonyl aldehyde (Nonanal)	Formaldehyde
Nonyl aldehyde (Nonanal)	Decanal	Hexadecanoic acid	D-Allose
Dodecanoic acid	Styrene	Toluene (Methylbenzene)	Furfural (2-Furaldehyde)
Formaldehyde	Benzonitrile	2-Propenoic acid, 2-methyl	1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan)
D-Allose	Formaldehyde	Naphthalene	2-Propanone, 1-hydroxy
9-Octadecenamide, (Z)-	Toluene (Methylbenzene)	Phenylethyne	Propanal
Toluene (Methylbenzene)	Hexane, 2,2,4-trimethyl	1,4-Pentadiene	1-Heptene, 2,4-dimethyl

Benzene, a Class 1 carcinogen, known to cause cancer, was present in high levels during the chair burns. It was the most dominant volatile organic compounds (VOC) present overall. The highest semi-quantitative value measured was 25 mg/m^3 that is about eight times higher than the allowable occupational exposure limit of 3.2 mg/m^3. Also present in the complex mixtures of volatile organic compounds (VOCs) measured during chair burns included aldehydes, nitriles, isocyanates, acrylates, phthalates, aromatics, carboxylic acids, and numerous others. Significant difference evaluations among chair types and new versus aged products were not feasible due to the exploratory data quality.

The television burn primarily produced numerous emissions of aromatic volatile organic compounds (VOCs) including benzene, styrene, toluene, phenanthrene, and others. The laptop burns produced emissions of normal and branched and cyclic hydrocarbons with some aromatics like styrene and xylenes. The polymer substrates were likely different chemicals between the laptop and television. Tables of all volatile organic compounds (VOCs) measured from the electronic burns can be found in Appendix G, Tables 16 and 17. Primary volatile organic compounds (VOC) emissions among the electronics are listed in Table 20.

Table 20: Primary Volatile Organic Compounds (VOCs) Released During Burn of Electronics

Television	Laptop
Styrene	Hexane
Hexane	Acetic acid
Benzene	Pentane, 3-methyl
Pentane, 3-methyl	Carbonic acid, dimethyl ester
Acetic acid	Acetaldehyde
Toluene (Methylbenzene)	Hexane, 2-methyl
Benzene, ethyl	Cyclopentane, methyl
Cyclopentane, methyl	Acetic acid, 1,1-dimethylethyl ester (tert-Butyl acetate)
Octane, 2,6-dimethyl	Hexane, 3-methyl
Cyclotrisiloxane, hexamethyl	Decanal

6.2.5 Flame Retardants in Air

Flame retardants were measured during the burning of the chairs constructed with the organophosphate flame retardant mix in the polyurethane foam (OPFR) chairs. Since this was the first application of this measurement technology, its results should be considered semiquantitative since recovery or accuracy verifications had not been made. The data presented were obtained from the ISO 9705 Test Room. The data from the Furniture Heat Release Calorimeter were compromised by the high background levels of multiple flame retardants, likely accumulations from past studies or materials in the room. Figure 27 shows the levels of each flame retardant isomer detected in the organophosphate flame retardant (OPFR) chair burns. Similar to the environmental chamber study of typical consumer use of the chair, triphenyl phosphate (TPhP) was most frequently found. The isomer (4-tert-butylphenyl) diphenyl phosphate (4tBPDPP) was detected at the second highest concentration. Similar concentrations of (2,4-ditert-butylphenyl) diphenyl phosphate (B4tBPPP) and tris (4-tert-butylphenyl) phosphate (T4tBPP) were released in the air during the combustion of organophosphate flame retardant (OPFR) chairs. The effect of mechanical aging can be seen in airborne flame retardant concentration during the burn (Figure 27). For all organophosphate flame retardant chairs, the aged chairs released less flame retardants than the newly manufactured chairs.

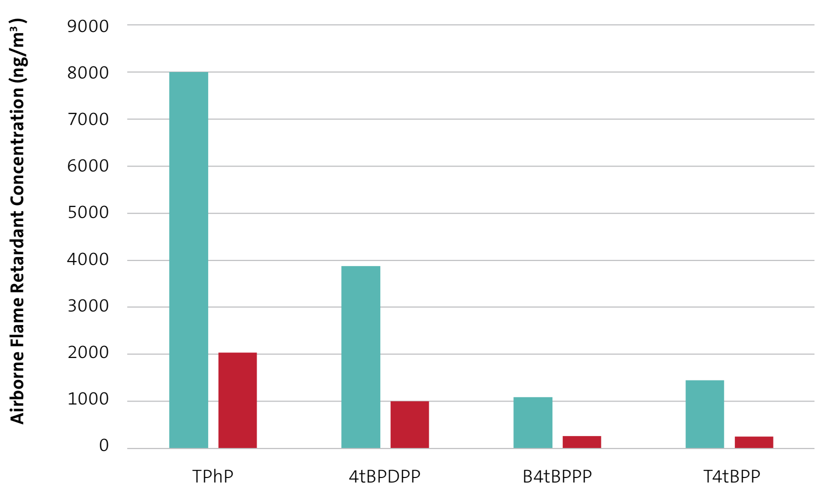


Figure 27: The average flame retardant concentrations detected in air during ignition of organophosphate flame retardant (OPFR) chairs (two new chairs and two mechanically aged chairs). TPhP: triphenyl phosphate; 4tBPDPP: (4-tert-butylphenyl) diphenyl phosphate; B4tBPPP: (2,4-ditert-butylphenyl) diphenyl phosphate; and T4tBPP: tris (4-tert-butylphenyl) phosphate.

The levels of the flame retardants from the organophosphate flame retardant (OPFR) chair detected in the environmental chamber testing (simulating consumer use) and in flammability testing are compared in Figure 28. Flame retardant concentrations from flammability testing were taken from the new chairs in the ISO 9705 Test Room experiments. The flame retardant concentrations were higher during combustion. Based on limited data and assumptions made, acute airborne flame retardant exposure during a fire is most likely to be much higher than typical environmental exposure during daily use.

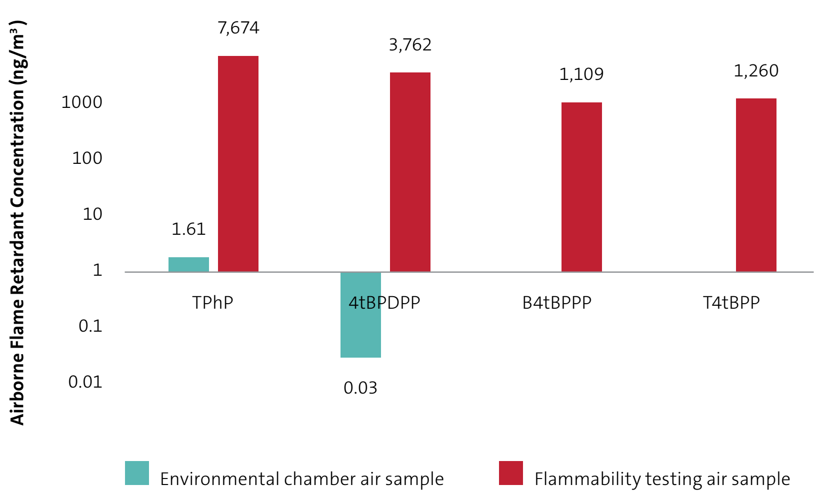


Figure 28: Airborne flame retardant concentrations of organophosphate flame retardant (OPFR) chairs detected in environmental chamber testing for exposure analysis and in flammability testing for fire characteristics. Airborne flame retardant concentrations from environmental chamber testing was a sum of gas phase and particle phase flame retardant concentrations. TPhP: triphenyl phosphate; 4tBPDPP: (4-tert-butylphenyl) diphenyl phosphate; B4tBPPP: (2,4-ditert-butylphenyl) diphenyl phosphate; and T4tBPP: tris (4-tert-butylphenyl) phosphate.

7. Acknowledgement

We would like to thank the esteemed members of the Human Health Flammability Steering Committee who provided guidance and shared their expertise in the open Summit meetings and research plan development. In addition, we are appreciative of the numerous professionals that attended the Summits and offered their knowledge and science data for discussion of this important topic and for development of our research initiatives. A full listing of these contributors can be found in the "Proceedings of the Furniture Flammability and Human Health Summit, May 20-22, 2014" and "Proceedings of the Furniture Flammability and Human Health Summit, Dec. 13-14, 2017."

We are grateful to Barry Ryan, PhD, and Jordan Cohen, MPH, at Emory University, Rollins School of Public Health for their expert contribution on sampling, analysis, and exposure studies of the flame retardants; Pravinray Gandhi, PhD, David Dubiel and research staff of Commercial and Industrial R&D, UL LLC, for conducting the open flame tests and analysis; Said Nurbakhsh, PhD, and research staff of the California Bureau of Electronic and Appliance Repair, Home Furnishings, and Thermal Insulation for conducting the California Technical Bulletin 117-2013 (TB 117-2013) furniture material tests; Stephen Kerber, MS, from UL Fire Science Research Institute for his fire expertise; Sunny Chi and Carl Wang, PhD, from Material Research and Development Laboratory, UL LLC, for material component analysis; and Heather Stapleton, PhD, from Duke University for analysis of material flame retardants and her flame retardant expertise. We also are appreciative of numerous furniture manufacturers, material suppliers, and chemical suppliers who contributed their expertise and commitment in development of our test products.

8. References

1. BEARHFTI. *Requirements, Test Procedure and Apparatus for Testing the Smolder Resistance of Materials Used in Upholstered Furniture;* Bureau of Electronic & Appliance Repair Home Furnishings & Thermal Insulation: Sacramento, CA, **2013.**
2. EN. *1021-2 Furniture - Assessment of the Ignitability of Upholstered Furniture - Part 2: Ignition Source Match Flame Equivalent;* European Standards: Czech Republic, **2014.**
3. Ahrens, M. Home Structure Fires. Retrieved from Quincy, Massachusetts. **2017.**
4. UL. *UL Furniture Flammability and Human Health Summit;* Underwriters Laboratories Inc.: Northbrook, IL, **2018.**
5. Stapleton, H. M.; Sharma, S.; Getzinger, G.; Ferguson, P. L.; Gabriel, M.; Webster, T. F.; Blum, A. Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out. **2012.**
6. Brown, P.; Cordner, A. Lessons Learned From Flame Retardant Use And Regulation Could Enhance Future Control Of Potentially Hazardous Chemicals. *Health Aff. (Millwood)* **2011,** *30* (5), 906–914.
7. Roosens, L.; D'Hollander, W.; Bervoets, L.; Reynders, H.; Van Campenhout, K.; Cornelis, C.; Van Den Heuvel, R.; Koppen, G.; Covaci, A. Brominated Flame Retardants and Perfluorinated Chemicals, Two Groups of Persistent Contaminants in Belgian Human Blood and Milk. *Environ. Pollut.* **2010,** *158* (8), 2546–2552.
8. Schreder, E. D.; La Guardia, M. J. Flame Retardant Transfers from US Households (Dust and Laundry Wastewater) to the Aquatic Environment. *Environ. Sci. Technol.* **2014,** *48* (19), 11575–11583.
9. Phillips, A. L.; Hammel, S. C.; Konstantinov, A.; Stapleton, H. M. Characterization of Individual Isopropylated and Tert-Butylated Triarylphosphate (ITP and TBPP) Isomers in Several Commercial Flame Retardant Mixtures and House Dust Standard Reference Material SRM 2585. *Environ. Sci. Technol.* **2017,** *51* (22), 13443–13449.
10. Hall, J. R. *Fatal Effects of Fire;* National Fire Protection Association. Fire Analysis and Research Division, **2011.**
11. Levin, B. C.; Kuligowski, E. D. Toxicology of Fire and Smoke. *Inhal. Toxicol.* **2005,** *2* (10), 205–228.
12. Shaw, S. Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? *Rev. Environ. Health.* **2010,** *25* (4), 261–306.
13. Shaw, S. D.; Berger, M. L.; Harris, J. H.; Yun, S. H.; Wu, Q.; Liao, C.; Blum, A.; Stefani, A.; Kannan, K. Persistent Organic Pollutants Including Polychlorinated and Polybrominated Dibenzo-p-Dioxins and Dibenzofurans in Firefighters from Northern California. *Chemosphere.* **2013,** *91* (10), 1386–1394.
14. LeMasters, G. K.; Genaidy, A. M.; Succop, P.; Deddens, J.; Sobeih, T.; Barriera-Viruet, H.; Dunning, K.; Lockey, J. Cancer Risk among Firefighters: A Review and Meta-Analysis of 32 Studies. J. *Occup. Environ. Med.* **2006,** *48* (11), 1189–1202.
15. Daniels, R. D.; Kubale, T. L.; Yiin, J. H.; Dahm, M. M.; Hales, T. R.; Baris, D.; Zahm, S. H.; Beaumont, J. J.; Waters, K. M.; Pinkerton, L. E. Mortality and Cancer Incidence in a Pooled Cohort of US Firefighters from San Francisco, Chicago and Philadelphia (1950–2009). *Occup Env. Med.* **2014,** *71* (6), 388–397.
16. Druso, F. *Hot Seat: A New Look at the Problem of Furniture Flammability and Home Fire Losses;* **2016.**
17. Babrauskas, V.; Blum, A.; Daley, R.; Birnbaum, L. Flame Retardants in Furniture Foam: Benefits and Risks. *Fire Saf. Sci.* **2011,** *10,* 265–278.
18. OEHHA. *PROPOSITION 65 SAFE HARBOR LEVELS: No Significant Risk Levels for Carcinogens and Maximum Allowable Dose Levels for Chemicals Causing Reproductive Toxicity;* Office of Environmental Health Hazard Assessment: Sacramento, CA, **2012.**
19. UL. *UL 2821 GREENGUARD Certification Program Method for Measuring and Evaluating Chemical Emissions from Building Materials, Finishes and Furnishings;* Underwriters Laboratories Inc.: Northbrook, IL, **2014.**
20. US EPA. P2 Recognition Project. May 19, **2017.**
21. ANSI; BIFMA. *ANSI/BIFMA X5.4-2012 Lounge and Public Seating - Tests: American National Standard for Office Furnishings;* ANSI: Washington DC, US, **2012.**
22. ISO. *ISO 9705-1993 Fire Tests - Full-Scale Room Test for Surface Products;* International Organization for Standardization: Geneva, Switzerland, **1993.**
23. ASTM. *ASTM D6670-13 Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials / Products;* ASTM International: West Conshohocken, PA, **2013.**

24. ISO. *ISO 16000-9 Indoor Air – Part 9: Determination of the Emission of Volatile Organic Compounds from Building Products and Furnishing – Emission Test Chamber Method;* International Organization for Standardization: Geneva, Switzerland, **2007.**

25. ECMA. *ECMA-328 Standard 7th Edition, Determination of Chemical Emission Rates from Electronic Equipment;* Ecma International: Geneva, Switzerland, **2015.**

26. ASTM. *ASTM D6196-15 Standard Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air;* ASTM International: West Conshohocken, PA, **2015.**

27. ASTM. *ASTM D7339-18 Standard Test Method for Determination of Volatile Organic Compounds Emitted from Carpet Using a Specific Sorbent Tube and Thermal;* ASTM International: West Conshohocken, PA, **2018.**

28. US EPA. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes;* U.S. Environmental Protection Agency: Cincinnati, OH, **1999.**

29. US EPA; National Risk Management Research Laboratory. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - TO-01 Second Edition;* U.S. Environmental Protection Agency: Cincinnati, OH, **1999.**

30. OEHHA. OEHHA Acute, 8-Hour and Chronic Reference Exposure Level (REL) Summary. June **2019.**

31. US EPA. Integrated Risk Information System. December 19, **2018.**

32. ATSDR. Minimal Risk Levels (MRLs) for Hazardous Substances. Agency for Toxic Substances & Disease Registry. August **2018.**

33. OSHA. OSHA Annotated Table Z-1. Occupational Safety and Health Administration. April 4, **2018.**

34. ASTM. *ASTM D5197-16 Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology);* ASTM International: West Conshohocken, PA, **2016.**

35. US EPA. *Indoor Exposure Product Testing Protocols;* U.S. Environmental Protection Agency: Cincinnati, OH, **2015.**

36. US EPA. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - TO-10A: Determination Of Pesticides And Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD);* U.S. Environmental Protection Agency: Cincinnati, OH, **1999.**

37. US EPA. *Model Certified Lead Dust Sampling Technician Refresher Training Course; EPA-740-R-13-001;* U.S. Environmental Protection Agency: Cincinnati, OH, **2013.**

38. Thomas, T.; Brundage, P. *Qualitative Assessment of Potential Health Effects From the Use of Fire Retardant Chemicals in Mattresses;* CPSC: Bethesda, MD, **2006.**

39. US EPA. *Indoor Surface Residue Dissipation (Guideline 875.2300);* B; U.S. Environmental Protection Agency: Cincinnati, OH; Vol. Chapter 6.

40. van der Veen, I.; de Boer, J. Phosphorus Flame Retardants: Properties, Production, Environmental Occurrence, Toxicity and Analysis. *Chemosphere.* **2012,** 88 (10), 1119–1153.

41. Keil, C. B.; Simmons, C. E.; Anthony, T. R. *Mathematical Models for Estimating Occupational Exposure to Chemicals,* 2nd ed.; AIHA Press: Fairfax, VA, **2009.**

42. US EPA. *Exposure Factors Handbook 2011 Edition;* U.S. Environmental Protection Agency: Cincinnati, OH, **2011.**

43. CDPH. Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources Using Environmental Chambers Version 1.2. California Department of Public Health. **2017.**

44. US DOE. *2011 Buildings Energy Data Book;* US Department of Energy, **2012.**

45. ANSI; Underwriters Laboratories Inc. *ANSI/CAN/UL 2904 Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers;* American National Standards Institute: Washington DC, US, **2019.**

46. ANSI; ASHRAE. *ANSI/ASHRAE Standard 62.1-2016 Ventilation for Acceptable Indoor Air Quality;* American National Standards Institute: Washington DC, US, **2016.**

47. Babich, M. A. *CPSC Staff Preliminary Risk Assessment of Flame Retardant (FR) Chemicals in Upholstered Furniture Foam;* US Consumer Product Safety Commission: Bethesda, MD, **2006;** pp 85–212.

48. Hatlelid, K. Cancer Risk Assessment for Arsenic Exposure from CCA-Treated Playground Structures. U.S. Consumer Product Safety Commission. **2003.**

49. USEPA. *Dermal Exposure Assessment: A Summary of EPA Approaches;* **2007.**

50. Lehman, A.; Fitzhugh, O. G. 100-Fold Margin of Safety. *Assoc Food Drug USQ Bull* **1954,** *18,* 33–35.

51. Cooper, E. M.; Kroeger, G.; Davis, K.; Clark, C. R.; Ferguson, P. L.; Stapleton, H. M. Results from Screening Polyurethane Foam Based Consumer Products for Flame Retardant Chemicals: Assessing Impacts on the Change in the Furniture Flammability Standards. *Environ. Sci. Technol.* **2016,** *50* (19), 10653–10660.

52. Ghislain, M.; Beigbeder, J.; Dumazert, L.; Lopez-Cuesta, J.-M.; Lounis, M.; Leconte, S.; Desauziers, V. Determination of the Volatile Fraction of Phosphorus Flame Retardants in Cushioning Foam of Upholstered Furniture: Towards Respiratory Exposure Assessment. *Environ. Monit. Assess.* **2016,** *188* (10), 576.

53. Keimowitz, A. R.; Strunsky, N.; Wovkulich, K. Organophosphate Flame Retardants in Household Dust before and after Introduction of New Furniture. *Chemosphere.* **2016,** *148,* 467–472.

54. Stapleton, H. M.; Klosterhaus, S.; Eagle, S.; Fuh, J.; Meeker, J. D.; Blum, A.; Webster, T. F. Detection of Organophosphate Flame Retardants in Furniture Foam and US House Dust. *Environ. Sci. Technol.* **2009,** *43* (19), 7490–7495.

55. US EPA. *Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update - Sections 1-6;* **2015.**

56. Clean Production Action. *GreenScreen® for Safer Chemicals;* **2018.**

57. Meeker, J. D.; Cooper, E. M.; Stapleton, H. M.; Hauser, R. Urinary Metabolites of Organophosphate Flame Retardants: Temporal Variability and Correlations with House Dust Concentrations. *Environ. Health Perspect.* **2013,** *121* (5), 580.

58. Dishaw, L. V.; Powers, C. M.; Ryde, I. T.; Roberts, S. C.; Seidler, F. J.; Slotkin, T. A.; Stapleton, H. M. Is the PentaBDE Replacement, Tris (1, 3-Dichloro-2-Propyl) Phosphate (TDCPP), a Developmental Neurotoxicant? Studies in PC12 Cells. *Toxicol. Appl. Pharmacol.* **2011,** *256* (3), 281–289.

59. Wang, Q.; Lam, J. C.; Han, J.; Wang, X.; Guo, Y.; Lam, P. K.; Zhou, B. Developmental Exposure to the Organophosphorus Flame Retardant Tris (1, 3-Dichloro-2-Propyl) Phosphate: Estrogenic Activity, Endocrine Disruption and Reproductive Effects on Zebrafish. *Aquat. Toxicol.* **2015,** *160,* 163–171.

60. ASHRAE. *ASHRAE 189.1 Standard for the Design of High-Performance Green Buildings Except Low-Rise Residential Buildings;* the American Society of Heating, Refrigerating and Air-Conditioning Engineers: Atlanta, GA, **2017.**

61. ACGIH. *BELs: Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices;* American Conference of Governmental Industrial Hygienists: Cincinnati, OH, **2004.**

62. AgBB. Health-Related Evaluation Procedure for Volatile Organic Compounds Emissions (VVOC, VOC and SVOC) from Building Products 1. **2015,** No. February, 1–26.

63. Stubbings, W. A.; Riddell, N.; Chittim, B.; Venier, M. Challenges in the Analyses of Organophosphate Esters. *Environ. Sci. Technol.* **2017.**

64. Sobotka, T. J.; Brodie, R. E.; Arnold, A.; West, G. L. Neuromotor Function in Rats during Subchronic Dietary Exposure to Triphenyl Phosphate. *Neurobehav. Toxicol. Teratol.* **1986,** *8* (1), 7–10.

65. Kamata, E.; Naito, K.; Nakaji, Y.; Ogawa, Y.; Suzuki, S.; Kaneko, T.; Takada, K.; Kurokawa, Y.; Tobe, M. Acute and Subacute Toxicity Studies of Tris (1, 3-Dichloro-2-Propyl) Phosphate on Mice. *Eisei Shikenjo Hokoku.* **1989,** No. 107, 36–43.

66. U.S. EPA. Furniture Flame Retardancy Partnership: Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam. U.S. Environmental Protection Agency: Washington DC, US **2005,** p.

67. Freudenthal, R. I.; Henrich, R. T. Chronic Toxicity and Carcinogenic Potential of Tris-(1,3,-Dichloro-2- Propyl) Phosphate in Sprague-Dawley Rat. *Int. J. Toxicol.* **2000,** *19* (2), 119–125.

68. United States Consumer Product Safety Commission. 16 CFR 1633: Standard for the Flammability (Open Flame) of Mattress Sets. *U. S. Consum. Prod. Saf. Comm. Lab. Test Man.* January **2008.**

69. Goldstein, M. Carbon Monoxide Poisoning. *J. Emerg. Nurs.* **2008,** *34* (6), 538–542.

70. McKenna, S. T.; Birtles, R.; Dickens, K.; Walker, R. G.; Spearpoint, M. J.; Stec, A. A.; Hull, T. R. Flame Retardants in UK Furniture Increase Smoke Toxicity More than They Reduce Fire Growth Rate. *Chemosphere.* **2018,** *196,* 429–439.

Underwriters Laboratories Inc.
2211 Newmarket Parkway, Suite 106, Marietta, GA 30067
UL.ChemicalSafety@ul.com
www.ulchemicalsafety.org

0419