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## Semi-Volatile Organic Compound (SVOC) Detection in Residential Furniture: A Comparison of Dermal, Oral, and Inhalation Exposure Routes in Children

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An abstract of A thesis submitted to the Faculty of the Rollins School of Public Health of Emory University in partial fulfillment of the requirements for the degree of Master of Public Health in Environmental Health 2017

## Abstract

Semi-Volatile Organic Compound (SVOC) Detection in Residential Furniture: A Comparison of Dermal, Oral, and Inhalation Exposure Routes in Children By Scott Laughlin

Semi-Volatile Organic Compounds (SVOC) are a group of organic compounds that include a variety of chemicals such as phthalates, pesticides, and flame retardants. SVOCs like flame retardants (FR) may be present in a residential environment due to their use in helping consumer products like furniture and electronics comply with safety regulations. In this project we investigated human exposure to volatile organic compounds (VOC) and SVOCs from residential furniture through inhalation, dermal, and oral exposure routes. Two types of FR chemicals, polybrominated diphenyl ethers (PBDE) and organophosphates (OP) were studied. A dataset of laboratory results, containing four types of sample media taken from 10 product samples and analyzed for the presence of FR chemicals, was reviewed. Oral, dermal, and inhalation risk assessment calculations for a 1-2 year old child were performed using parameters gathered from the US Environmental Protection Agency (US EPA) Exposure Factors Handbook, 2011. Results for calculated exposure were presented in nanograms per day (ng/day) in order to compare exposure routes. Calculated exposures ranged from less than 0.5 ng/day in some airborne samples to nearly 23,000 ng/day in one dermal sample. According to the calculations, the Filter Paper sample, as proxy for dermal exposure, consistently showed the highest exposure to SVOCs, and inhalation exposure samples were consistently a fraction of the calculated exposure totals of the oral or dermal samples. However, as absorption factors for chemicals encountered through inhalation, ingestion, and dermal absorption were not applied to these data, we would expect the dermal exposures to be lower in practice, proportionally altering the results of this study.

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# Table of Contents

| I.     | Introduction                         | . 1 |
|--------|--------------------------------------|-----|
|        | Background                           | . 1 |
| II.    | Methods                              | 4   |
|        | A. Sampling Conditions and Procedure | 4   |
|        | B. Exposure Calculations             | 5   |
| III.   | Results                              | . 9 |
| IV.    | Discussion                           | 11  |
| V.     | Conclusions and Recommendations      | 13  |
| Refere | ences                                | 14  |
| Figure | es and Tables                        | 15  |
| Appen  | ndices                               | 18  |

## I. Introduction

### Background

Semi-Volatile Organic Compounds, commonly abbreviated as SVOCs, are a family of organic compounds with a boiling point between 240°C and 400°C and a vapor pressure between 10<sup>-4</sup> and 10<sup>-14</sup> atmospheres.<sup>1,2</sup> SVOCs include chemicals like flame retardants (FR), phthalates, pesticides, and perfluoronated compounds (PFC).<sup>3</sup> SVOCs can exist in the indoor environment in both gaseous and solid phases, and studies have been conducted on individual routes of exposure.<sup>4,5,6</sup> Flame retardant chemicals are intended to delay the combustion of treated materials allowing more time to escape a fire. In order to comply with fire safety standards and regulations, flame retardant chemicals are often added to household furniture, textiles, and electronics. They are designed to be stable throughout the life of the product to which they are applied, and are therefore environmentally persistent.<sup>7</sup> Chronic exposure to these types of chemicals has been shown to cause respiratory irritation, skin sensitization, possible endocrine disruption and cancer.<sup>4,7</sup>

In this project we investigated human exposure to volatile organic compounds (VOC) and SVOCs from residential furniture through inhalation, dermal, and oral exposure routes. Two types of flame retardants, polybrominated diphenyl ethers (PBDE) and organophosphates (OP) were studied for this project. Before 2004, PBDEs were among the most common flame retardant blends used for furniture and electronics. However they were voluntarily phased out due to toxicity concerns in the early 2000s, which led to increased use of OP FRs in order to continue meeting flammability standards for polyurethane foam used in furniture.<sup>4,8</sup> More recent research suggests that OP FRs may also pose health risks. Flame retardant biomarkers of both PBDEs and OP FRs have been identified in human blood and urine, and have been associated with adverse health effects such as cancer, birth defects, endocrine disruption, and other adverse health outcomes in animals and humans.<sup>4</sup> A summary of these health risks for OP FRs is

included in tabular form, from Tables 2-1 and 2-2 of the US EPA report: Flame Retardants used in Flexible Polyurethane Foam: an Alternatives Assessment Update in Appendix A.<sup>7</sup>

The PBDE molecule consists of two phenyl rings connected by an oxygen atom. There are 10 positions on the molecule where bromine may take the position of a hydrogen atom. Theoretically, 209 different congeners could be formed by these structure combinations, but only a small subset of congeners have been detected in commercial products. They are formed by combining bromine with a diphenyl ether in the presence of an inorganic catalyst such as AlCl<sub>3</sub>.<sup>9</sup> PBDEs are mainly comprised of three formulations: pentaBDE, octaBDE, and decaBDE. The most dominant congeners in pentaBDE by percent weight are 2,2',4,4',5-penta-bromodiphenyl ether (BDE 99, 35-50%), 2,2',4,4'-tetra-bromodiphenyl ether (BDE 47, 25-37%), and 2,2',4,4',6-penta-bromodiphenyl ether (BDE 100, 6-10%).<sup>9</sup>

In 2010, the United States Environmental Protection Agency (US EPA) concluded that the largest source of US PBDE exposure was house dust, contributing 90% of estimated adult intakes, and that children aged 1-5 ingest about 5 times as much dust per day as adults.<sup>9</sup> Stapleton, et al., found in 2009 that levels of OP FRs are at least as high if not higher than PBDEs in house dust, concluding that children may be most at risk of exposure to FRs due to higher proportions of time on or near the floor crawling and doing other activities, and more hand to mouth contact than adults.<sup>8</sup> They estimated that a child's cumulative exposure to flame retardants chemicals was 1,600 nanograms per day (ng/day), compared to a calculated adult exposure of 325 ng/day.

The structures of the eight FR compounds included in the sampling and analysis conducted in this study are shown in Figure 1.

| and Chemical Structures  |
|--|
| $Br_{m} = \frac{3}{4} = \frac{2}{5} + \frac{1}{6} + \frac{2}{6} + \frac{2}{5} + \frac{3}{4} + \frac{3}{5} + \frac{3}{$ |
|  |
|  |
|  |
|  |
| O<br>O<br>Br<br>Br   |
|  |

Figure 1: Studied Flame Retardants and Chemical Structures

The aim of this project was to calculate SVOC exposure routes through interaction with products in a residential setting. Specifically, a child's (1 to <2 years old) inhalation, dermal, and oral exposures to these compounds via interaction with residential furniture.

## II. Methods

#### A. Sampling Conditions and Procedure

At the outset of this project, a dataset was reviewed containing values corresponding to mass of chemical per volume of extracted solvent. These data were collected from four types of sample media analyzed at Emory University's LEADER laboratory for the presence of FR chemicals. Sample media consisted of dust wipes (DW) to measure oral exposure, quartz filter (QF) and Polyurethane Foam plug (PUF) media to measure inhalation (airborne) exposures, and filter paper (FP) media to measure dermal exposures. Based on a review of current literature on FR exposure, we hypothesized that the bulk of a child's exposure to FR chemicals was through the ingestion route.

Environmental sampling was made of residential furniture samples under controlled laboratory conditions. The following FR chemicals were identified by the laboratory analysis: TCEP, TCPP, TDCPP, TPP, TBB, BDE-47, BDE-99, and BDE-100. TCEP, TCPP, and TDCPP are all halogenated organophosphates, sharing a similar structure with a central phosphorus bonded to oxygen atoms and chlorines. TPP is similar in structure to these, but features phenyl groups instead of chlorines bonded to the oxygen atoms. TBB is a brominated FR that has a structure unlike the other FRs reported. TBB is one of the four components of Firemaster 550, a leading FR chemical now in production (TPP is another component FR of Firemaster 550).<sup>7</sup>

Ten different samples were evaluated. Sampled products are numbered Sample #1 – Sample #10 in this report. A sample duplicate (Sample #1 – original, Sample #5-duplicate) and measurement duplicate (Sample #8 – original, Sample #10 – duplicate) were also conducted. Correlation analysis of sample and measurement duplicates is included in Section IV.

#### **Extraction Procedure**

The chemical extraction method used was based on that developed by Van den Eede et al.<sup>10</sup> The primary goal of the Emory LEADER laboratory in developing this method was the ability to examine the most compounds possible using a single method. In this method, two separate extractions were utilized to assess the different FRs of interest. Once the two fractions (shown as FRACTION 1 and FRACTION 2 in Appendix B) 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. Finally, the combined solution was analyzed using Gas Chromatography followed by Electron Impact Ionization and Mass Spectrometry (GC-EI-MS). This method was capable of collecting numerous PBDE congeners (BDE-47, 85, 99, 100, 153, and 154), OP FRs (TBPH, TBPP, TCEP, TCPP, TDCPP, TPP), and TBB.

### **B.** Exposure Calculations

Chemical concentration available for human exposure through the oral, dermal, and inhalation routes were calculated by taking values from the EPA Exposure Factors Handbook, 2011.<sup>11</sup> For each exposure route, a daily chemical exposure for a child between 1 and 2 years of age was calculated using the sample results and exposure factor parameters.

| Dermal :                   | Dermal Calculation<br>Parameters            | Number     | Unit           |
|----------------------------|---|------------|----------------|
| Filter patch SVOC          | Time tested                                 | 360        | min            |
| concentrations were        | Convert 1 in2 to m2                         | 0.00064516 | $m^2$          |
| reported in picograms (pg) | Surface area - child<br>(1 to <2 years old) | 0.17225    | m <sup>2</sup> |
|                            | Leisure time per day                        | 405        | min            |
| of chemical per microliter | Convert pg to ng                            | 1000       | pg/ng          |

 $(\mu L)$  of extracted solvent. This was converted to chemical mass exposure per day using the following formula:

| pg of chemical                          | total solvent volume          | average t     | time awake in residence * | * |
|---|-------------------------------|---------------|---------------------------|---|
| $\mu L$ of extracted solvent $^{\star}$ | surface area of filter patch  | ~             | day                       | - |
| dermal surface                          | area in contact with chair ** | 1 ng          | _ng of chemical           |   |
| *                                       | child                         | $^{1000  pg}$ | day                       |   |

\*Time awake in residence was derived from Exposure Factors Handbook by subtracting sleep time (Table 6-45 Chapter 6) from Total time in residence (Table ES-1 Chapter 16) (1065 min) – (660 min) = 405 min \*\*Dermal Surface area was derived by taking  $\frac{1}{2}$  mean total trunk area ( $0.188m^2$ ) +  $\frac{1}{2}$  mean total leg area  $(0.122m^2) + \frac{1}{4}$  mean total arm area  $(0.069m^2)$  for a child 1 to <2 years old from Exposure Factors Handbook Table ES-1 Chapter 7=  $0.094 m^2 + 0.061 m^2 + 0.01725 m^2 = 0.172 m^2$ 

#### Inhalation:

| Based on the provided          | Inhalation Calculation<br>Parameters           | Number | Unit                |  |  |  |  |
|--------------------------------|--|--------|---------------------|--|--|--|--|
| laboratory data, we measured   | Convert L to m <sup>3</sup>                    | 1000   | L/m <sup>3</sup>    |  |  |  |  |
| extracted concentration of the | Inhalation volume child<br>(1 to <2 years old) | 5.4    | m <sup>3</sup> /day |  |  |  |  |
|                                | Loading Factor for chamber                     |        |                     |  |  |  |  |
| individual SVOCs, derived      | Residential living/dining volume               | 252    | m <sup>3</sup>      |  |  |  |  |
| emission factors               | Convert pg to ng                               | 1000   | pg/ng               |  |  |  |  |
|                                | Air changes per hour (ACH)                     | 0.45   | ACH                 |  |  |  |  |
| (mass/unit*time), converted to | Time in room per day %<br>(405min/1440min)     | 28.125 | %                   |  |  |  |  |
| environmental concentration,   |  |        |                     |  |  |  |  |

and derived mass of inhalation per day (based on typical inhalation volume).

The emission rate data for the individual compounds identified during chamber testing was combined with expected use building parameters (room volume, product area, and room exchange rate) to determine a predicted exposure concentration. The assumption was made that the space within which the product is used is well-mixed. Furthermore, it assumes that the test chamber is a single compartment, well-mixed chamber at steady state. For each compound at any time point, the predicted exposure concentration can be calculated using the following equation:

$$C_p = EF\left(\frac{A}{V}\right)\left(\frac{1}{N}\right)$$

where,  $C_P$  = predicted exposure concentration (pg/m<sup>3</sup>)

 $EF = average \ emission \ factor \ at \ time \ since \ the \ beginning \ of \ sample \ (ng/m^2 \cdot hr \ or \ ng/g \cdot hr)$ 

 $A = product \ exposed \ in \ room \ (1 \ product)$  $V = room \ volume \ (m^3)$  $N = room \ air \ exchange \ rate \ (hr^{-1})$ 

## Inhalation: Particulate (SVOC) :

Step 1: calculate extracted concentration of chemical

(for the purpose of example, a starting value of  $\frac{1 \text{ pg of chemical}}{\mu L \text{ of extracted solvent}}$  is used.)

$$\frac{pg \ of \ chemical}{\mu L \ of \ extracted \ solvent} \times \frac{total \ solvent \ V \ (100 \mu L)}{Q \left(\frac{L}{min}\right) \times sampling \ time} \times \frac{1000 \ L}{1m^3} = C$$

$$\frac{1 \ pg \ of \ chemical}{\mu L \ of \ extracted \ solvent} \times \frac{\text{total solvent V } (100 \mu L)}{\frac{4L}{\min} \times 540 \ \min} \times \frac{1000 \ L}{1m^3} = \frac{100 \ pg}{2.16m^3}$$

Step 2: Derive Emission Factor

$$C\left(\frac{pg}{m^{3}}\right) \times \frac{N_{chamber} (hr^{-1})}{Loading \left(\frac{1 \ chair}{V_{chamber}}\right)} = EF\left(\frac{pg}{unit * hr}\right)$$

$$\frac{100 \ pg}{2.16m^3} \times \frac{N \ chamber \ (hr^{-1})}{Loading \ \left(\frac{1 \ chair}{6m^3}\right)} = \frac{277.78pg}{unit * hr}$$

Step 3: Calculate predicted concentration

$$EF\left(\frac{pg}{unit*hr}\right) \times \frac{1 \ chair}{V_{model\ room}} \times N_{model\ room} = C_P\left(\frac{pg}{m^3}\right)$$
$$\frac{277.78pg}{unit*hr} \times \frac{1 \ chair}{252 \ m^3} \times \frac{1}{0.45 \ hr^{-1}} = \frac{2.45 \ pg}{m^3}$$

Step 4: Calculate mass per day using breathing volume, time in residence, and conversion to

nanograms

$$C_{P}\left(\frac{pg}{m^{3}}\right) \times (V_{inhalation}) \times (\% time in room) \times \frac{1 ng}{1000 pg} = \frac{ng \ of \ chemical}{day}$$
$$\frac{2.45 \ pg}{m^{3}} \times \frac{5.4m^{3}}{day} \times (28.125\%) \times \frac{1 \ ng}{1000 \ pg} = \frac{0.003 \ ng}{day}$$

• 4L/min flow rate was used to approximate breathing volume

- Room Volume of 252 m<sup>3</sup> and ACH of 0.45 derived from UL 2818 GREENGUARD Standard Section 6.5.1 Living/Dining Area<sup>12</sup>
- Time in room derived by dividing total day (1,440 min) by time in residence (405 min) = 28.125% of the day

## **Oral (Ingestion) :**

| <b>Oral Calculation Parameters</b>          | Number   | Unit                            |
|---|----------|---------------------------------|
| Time tested                                 | 360      | min                             |
| Convert 1 ft <sup>2</sup> to m <sup>2</sup> | 0.092903 | m <sup>2</sup> /ft <sup>2</sup> |
| Hand to mouth contacts/hour                 | 20       | contacts                        |
| Surface area of child's hand                | 0.03     | m <sup>2</sup>                  |
| Leisure time per day                        | 405      | min                             |
| Convert pg to ng                            | 1000     | pg/ng                           |
| Convert hr to min                           | 60       | min/hr                          |

This calculation assumes that a child of 1 - <2 years old has 20 hand to mouth contacts per hour (derived from the Exposure Factors Handbook)

and ingests dust from the total surface areas (i.e. palm and back) of each hand.

| pg of chemical                      | total solvent V                             | Surface area of 1 child hand              |
|-------------------------------------|---|---|
| $\mu L of extracted solvent \times$ | surface area wiped ´                        | Contact                                   |
| , # of hand to mouth                | contacts 24 hrs                             | 1 ng <b>ng of chemical</b>                |
| x hour                              | $\times \frac{1}{1} day \times \frac{1}{1}$ | $\underline{1000 \ pg} = \frac{day}{day}$ |

## III. Results

In this study, our methods were capable of collecting numerous PBDE congeners (BDE-47, 85, 99, 100, 153, and 154). However, only BDE-47, 99, and 100 were detected. Further, we had the ability to collect several OP FRs (TBPH, TBPP, TCEP, TCPP, TDCPP, TPP) and TBB. However, only TBB, TCEP, TCPP, TDCPP, and TPP were detected. All results are presented in ng/day so that a comparison could be made across exposure routes.

### Comparing Routes of Exposure

After conducting the exposure calculations, it became apparent that dust wipe and filter paper media SVOC exposure route values were several times higher than those from the air sampling media. Therefore, to determine the highest exposure for each sample, we compared dust wipe and filter paper results only. Results are presented in Table 1. First, this analysis shows that all of the top 10 percent values seen were from Filter Paper samples. Secondly, of these samples, TPP was the FR type most often seen in the top 10%, followed by TBB, TCPP, and then TCEP. Also, the table shows that measurement of BDE 100 and 99 was more successful in the DW sample than in the FP sample. Finally, it was clear from this table that certain FRs were seen in one media type more than the other. For instance, TPP was seen in 10 FP samples, but only 5 DW samples. This table was also converted to a chart to show the maximum value for each FR reported in each sample. This is represented in Figure 2.

The next step was to perform color coded ranking on the DW and FP sections separately, in order to determine the highest exposures by FR and sample for each media type. These data are presented in Table 2. From this table, we found that TPP was in the top 10% in three samples for each media type, followed by TDCPP in the top 10% in two DW samples, and TCEP and TCPP both in the top 10% for one sample (Sample #10).

#### Comparison by Sample ID

Sample #1 and Sample #5 were listed as sample duplicates in the dataset. FP totals were highest among media types in Samples #1 and #5, totaling 1,436 ng/day and 556 ng/day, respectively. Sample #1 DW totaled about 245 ng/day, while there were no DW levels above the lab quantification limits in Sample #5.

Within Sample #2, FP media calculated to the highest FR load (14,179.79 ng/day), which was about 7 times the amount of FR seen in the DW media (1945.60 ng/day). Most of these totals came from TPP. Airborne exposures were calculated to be less than 0.5 ng/day.

Sample #3 was the only instance in which the dust wipe samples totaled higher than the FP samples (934.94 ng/day vs. 135.60 ng/day). The total ng/day coming from the QF and PUF samples were much lower than dust wipe and FP, both totaling less than 0.1 ng/day.

Sample #4 had lower than average total levels of calculated FR exposures, but TDCPP was seen at its highest levels in this sample for both FP and DW media types.

Sample #7 had the second highest overall totals of ng/day across all samples (only behind Sample #10). The FP sample totaled over 14,000 ng/day, and DW totals were about 2,000 ng/day. As seen in several other samples, airborne FR loads were less than 1 ng/day, and the dominant FR species present was TPP.

Sample #8 and Sample #10 were duplicates. In both instances, duplicate air samples were measured, and in Sample #8 duplicate dust wipe samples were collected. It was clear regardless of the duplicates that FP totals were much higher than the other sample types, totaling more than 12,200 ng/day in Sample #8. This total was approximately evenly distributed among TBB, TPP, TCPP, and TCEP FRs. DW samples totaled slightly over 30 ng/day, and the air samples (QF and PUF) were 0.32 and 0.23 ng/day, respectively. Sample #10 had the highest total seen for any sample in the FP media, totaling nearly 23,000 ng/day.

In Sample #9, the most common FR seen was TBB, followed by TPP and TCEP. As seen in other samples, FP was the highest exposure route seen. Calculated exposure charts for all 10 samples are included as Appendix

### IV. Discussion

This study sought to derive a comparison between three routes of exposure (dermal, inhalation, and ingestion) for children aged 1-<2 from residential furniture. Based on the data analyzed during this study, dermal exposures appear to deliver the highest quantities of SVOCs per day to a human subject. However, as there are not established methods for comparatively measuring and calculating these SVOC exposures, there is more work needed to create reliable and repeatable data sets.

Since further parameters of the samples was not provided in the dataset, it is difficult to determine possible causality for the differentiation in sample exposures modeled. Since the data were transformed equally (i.e. consistent calculations were performed for each media types across all samples) the results share the same trends as the original data. If samples were run through different protocols or had differing amounts of FR added, these factors could possibly be quantified. Non chemical flame retardant systems may also be in place, such as mechanical barriers. The bonding type of FR chemicals may also be a factor, as some FRs are chemically reacted with a substrate material, while others may be additive in nature.

TPP was the highest single FR measured overall (in the FP sample in Sample #7), and was also the highest calculated FR exposure seen in 5 different sample/media types: Sample #1 and #2 DW, Sample #1 and #7 FP, and Sample #8 FP. In the Sample #6 and #9 FP samples, TBB was the highest calculated FR exposure.

As with any risk assessment, there are limitations to the results discussed in Section III. True exposures were not measured during this study, and results of this study should not be considered

exact measurements of exposure. The EPA Exposure Factors Handbook represents summaries of known studies, each with differing statistical power and sample size. The risk assessment calculations assume a worst-case scenario, and may not always be representative of actual exposures. Therefore, altering any factors like room size, SVOC emissions, product construction and age, and test protocols could have profound effects on the results. Controlling for these factors would provide a more complete picture of their relative contributions.

While sample collection and analysis was conducted with trained field staff under controlled laboratory conditions, there were several points which should be further investigated. First, samples and duplicate measurements were somewhat inconsistent when stratified by SVOC type, but including data for all media types (Correlation of Measurement and Sample Duplicates are presented in Table 3 below). Further method development should be undertaken to minimize these variances. Second, some SVOCs may co-elute during the analysis phase, leading to some measurement error<sup>8</sup>. Several PBDE chemicals (BDE-85, 153, and 154), as well as TBPH were not seen above the limits of quantification in the analysis.



Table 3: Correlation of Measurement and Sample Duplicates

Finally, the exposure calculations assumed that 100% of the FR chemicals were absorbed through the skin (ie dermal absorption factor of 1), representing a worst case scenario. If dermal absorption factors were applied to these data, we would expect the dermal exposures to be lower, proportionally altering the results of this study. The FRs reported here also differ in size, structure, and water solubility, suggesting that they would be absorbed differentially through the skin. Exposure calculations could also be improved in the future by controlling for weight applied, time of test, and using an uncertainty factor for skin area covered by clothing.

## V. Conclusions and Recommendations

This study attempted to calculate a child's exposure to flame retardant chemicals through three different exposure routes: inhalation, oral ingestion, and dermal absorption. Calculated exposure totals varied from sample to sample. Overall, the outcome of the risk assessment calculations indicate that the Filter Paper sample, as proxy for dermal exposure, consistently showed the highest exposure to SVOCs. In every sample but one (Sample #3), FP calculated exposure levels were several times higher than Dust Wipe (Ingestion) and QF/PUF (Inhalation) samples. Inhalation exposure samples were consistently a fraction of the totals of the Oral or Dermal exposure samples. Based on the points raised in Sections III and IV, comparison of the samples stratified by exposure medium should provide a reasonable assessment of each type of furniture, but further development should be endeavored before accurate cross-medium comparisons are conducted.

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| Media Type                       | Sample ID  | TCEP     | TCPP     | TDCPP    | TPP       | твв      | BDE 47 | BDE 100 | BDE 99 |
|----------------------------------|------------|----------|----------|----------|-----------|----------|--------|---------|--------|
|                                  | Sample #1  | 12.39    | 41.80    | 94.58    |           | 56.50    | 5.72   | 7.65    | 26.31  |
|                                  | Sample #2  | 27.06    | 282.32   | 329.44   | 1,127.58  |          | 26.86  | 25.27   | 127.04 |
|                                  | Sample #3  | 5.06     | 169.39   | 245.83   | 371.92    |          | 22.88  | 19.84   | 100.01 |
|                                  | Sample #4  | 12.32    | 246.23   | 24.59    |           |          | 1.74   | 0.85    | 6.37   |
|                                  | Sample #4  | 11.31    | 62.57    | 2,989.24 | 57.78     |          | 7.97   | 4.48    | 50.29  |
| Dust Wipe - Oral                 | Sample #5  |          |          |          |           |          |        |         |        |
| Ingestion                        | Sample #6  | 10.43    |          | 15.76    |           | 61.86    |        | 2.12    | 6.03   |
|                                  | Sample #7  | 16.13    | 161.10   | 49.30    | 661.49    |          | 68.08  | 16.74   | 65.02  |
|                                  | Sample #8  |          |          |          |           | 57.85    |        |         |        |
|                                  | Sample #8  |          |          |          |           |          |        |         |        |
|                                  | Sample #9  | 1.00     | 186.67   | 5.14     |           |          | 4.86   | 0.66    | 5.10   |
|                                  | Sample #10 | 4.13     |          |          |           |          |        |         |        |
|                                  | Sample #1  |          |          | 162.57   | 67.96     |          | 25.29  |         |        |
|                                  | Sample #1  |          |          | 1,415.34 |           |          | 13.69  |         | 7.84   |
|                                  | Sample #2  |          |          | 23.20    | 14,142.03 |          | 14.56  |         |        |
|                                  | Sample #3  |          |          | 18.26    | 80.28     | 27.87    | 9.19   |         |        |
|                                  | Sample #4  |          |          | 2,343.62 | 46.14     |          | 7.25   |         | 5.40   |
| Filter Paper -<br>Dermal Contact | Sample #5  | 55.80    | 297.56   | 151.19   | 50.62     |          | 0.59   |         |        |
|                                  | Sample #6  | 1,877.75 | 3,513.68 | 68.88    | 2,377.17  | 5,676.55 | 7.78   |         |        |
|                                  | Sample #7  | 2,230.73 | 1,656.92 | 15.22    | 14,658.57 | 1,018.09 | 7.87   |         |        |
|                                  | Sample #8  | 68.70    | 1,554.39 | 274.17   | 6,086.97  | 4,255.69 | 11.15  |         |        |
|                                  | Sample #9  | 1,872.00 |          | 565.97   | 3,947.22  | 5,889.64 |        |         |        |
|                                  | Sample #10 | 9,611.37 | 7,392.91 | 587.17   | 2,271.02  | 3,013.09 | 0.08   |         |        |

Table 1: Comparison of Dust Wipe and Filter Paper results by sample and FR type with color coded rankings of calculated daily exposure, ng/day

| Media Type                       | Sample ID  | TCEP     | TCPP     | TDCPP    | TPP       | ТВВ      | BDE 47 | BDE 100 | BDE 99 |
|----------------------------------|------------|----------|----------|----------|-----------|----------|--------|---------|--------|
|                                  | Sample #1  | 12.39    | 41.80    | 94.58    |           | 56.50    | 5.72   | 7.65    | 26.31  |
|                                  | Sample #2  | 27.06    | 282.32   | 329.44   | 1,127.58  |          | 26.86  | 25.27   | 127.04 |
|                                  | Sample #3  | 5.06     | 169.39   | 245.83   | 371.92    |          | 22.88  | 19.84   | 100.01 |
|                                  | Sample #4  | 12.32    | 246.23   | 24.59    |           |          | 1.74   | 0.85    | 6.37   |
|                                  | Sample #4  | 11.31    | 62.57    | 2,989.24 | 57.78     |          | 7.97   | 4.48    | 50.29  |
| Dust Wipe - Oral                 | Sample #5  |          |          |          |           |          |        |         |        |
| Ingestion                        | Sample #6  | 10.43    |          | 15.76    |           | 61.86    |        | 2.12    | 6.03   |
|                                  | Sample #7  | 16.13    | 161.10   | 49.30    | 661.49    |          | 68.08  | 16.74   | 65.02  |
|                                  | Sample #8  |          |          |          |           | 57.85    |        |         |        |
|                                  | Sample #8  |          |          |          |           |          |        |         |        |
|                                  | Sample #9  | 1.00     | 186.67   | 5.14     |           |          | 4.86   | 0.66    | 5.10   |
|                                  | Sample #10 | 4.13     |          |          |           |          |        |         |        |
|                                  | Sample #1  |          |          | 162.57   | 67.96     |          | 25.29  |         |        |
|                                  | Sample #1  |          |          | 1,415.34 |           |          | 13.69  |         | 7.84   |
|                                  | Sample #2  |          |          | 23.20    | 14,142.03 |          | 14.56  |         |        |
|                                  | Sample #3  |          |          | 18.26    | 80.28     | 27.87    | 9.19   |         |        |
|                                  | Sample #4  |          |          | 2,343.62 | 46.14     |          | 7.25   |         | 5.40   |
| Filter Paper -<br>Dermal Contact | Sample #5  | 55.80    | 297.56   | 151.19   | 50.62     |          | 0.59   |         |        |
| 2 cm. contact                    | Sample #6  | 1,877.75 | 3,513.68 | 68.88    | 2,377.17  | 5,676.55 | 7.78   |         |        |
|                                  | Sample #7  | 2,230.73 | 1,656.92 | 15.22    | 14,658.57 | 1,018.09 | 7.87   |         |        |
|                                  | Sample #8  | 68.70    | 1,554.39 | 274.17   | 6,086.97  | 4,255.69 | 11.15  |         |        |
|                                  | Sample #9  | 1,872.00 |          | 565.97   | 3,947.22  | 5,889.64 |        |         |        |
|                                  | Sample #10 | 9,611.37 | 7,392.91 | 587.17   | 2,271.02  | 3,013.09 | 0.08   |         |        |

Table 2: Comparison of Dust Wipe and Filter Paper results by sample and FR type with color coded rankings of calculated daily exposure, stratified by media type, ng/day

Appendices

| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $  |
|--|
| VI. = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VH = Very High hazard       - Endpoints in colored a sasgued using values from predictive models a sasgued using values from predictive models a maximum subset upon the component with the highest hazard, whether it is an experimental or estimated value.         * Each hazard       Generative.       * and VER) were assigned using values from predictive models a sasgued using values for poorly soluble substant the highest hazard, whether it is an experimental or estimated value.       * and VER) were assigned using values for poorly soluble substant the highest hazard, whether it is an experimental or estimated value.         * Aquatic toxicity:       EPA/DE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substant trade names see the individual profiles in Section 7)       Human Health Effects       2         Halogenated       Fame Retarctant Alternatives       To is generative.       *       2         Firemaster® 500*       Mixture       L       M       M       M       M       M       M       M       L   |
| VI. = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VH = Very High hazard       — Endpoints in colored to assigned based one ompirical data. Endpoints in black tichles ( $TZ$ , $L$ , $M$ , $H$ , and $TB$ ) were assigned using values from predictive models at a sasigned lose or in other mixtures as an alternative.         * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. F and value profile is form predictive models and the mixtures as an alternative.       Human Health Effects       Application for predictive models and that may not be adequate for poorly soluble substan that may partition to sediment and particulates.       Human Health Effects       Application for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. F       Application for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. F         * Aquatic toxicity. EPADE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substan that may partition to sediment and particulates.       Human Health Effects       A         * for full chemical name and relevant trade names see the individual profile is n Section 7)       CASRN       A Care is poorly old uctive trade name segmentation on trade names see the individual trade names see the individual profile is set (TBPH)**       N Kutue       I       M       M       M       M       A         Firemaster 500°       Soft trade name sectin TDPH)**       2040-51-7  |
| VI. = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VH = Very High hazard       - Endpoints in colored te assigned using values from predictive models an * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. For poorly soluble substance value, For poorly soluble substance value, For poorly soluble substance value. For poorly soluble substance value, For poorly soluble substance value. For poorly soluble substance value, For poorly soluble substance value. For poorly soluble substance value, For poorly soluble substance value. For poorly soluble substance value, For poorly soluble substance value. For poorly soluble value pont is for poorly soluble value poorly soluble value |
| VI. = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VI = Very High hazard   |
| VI. = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored te assigned based on empirical data. Endpoints in black italics ( <i>VI</i> , <i>L</i> , <i>M</i> , <i>H</i> , and <i>VB</i> ) were assigned using values from predictive models anter a scale and restrict the component with the highest hazard, whether it is an experimental or estimated value. For no corresponding profile in Section 7.         * Fach hazard Chemical (for full chemical name and relevant trade names see the individual profiles in Section 7.       Human Health Effects       A         * Fach namester 550*       Exercise 1.2   |
| VI. = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VI = Very High hazard — Endpoints in colored to a signed using values from predictive models anter a signed using values from predictive models anter a maximum is based upon the component with the highest hazard, whether it is an experimental or estimated value. For no corresponding profile in Section 7.       This component is particulates.       Human Health Effects       Approximate of a maximum section of a maximum section of a maximum section and particulates.       Approximate and particulates.       Human Health Effects       Approximate of a maximum section of a maximum section of a substance trade name section 7.       Approximate and particulates.       Approximate   |
| VI. = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VH = Very High hazard       Endpoints in colored te assigned using values from predictive models an "Fach hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated wale. For poorly soluble substance in arge part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.       VIIII = Very High hazard - Endpoints in colored te as an alternative.         * Aquatic toxicity: EPA/DE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.       VIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII  |
| VL = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VH = Very High hazard — Endpoints in colored tea assigned based on empirical data. Endpoints in black italics ( <i>VL</i> , <i>L</i> , <i>M</i> , <i>H</i> , and <i>VH</i> ) were assigned using values from predictive models and * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. Fo no corresponding profile in Section 7.         ** Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. Fo adaptic toxicity: EPA/DE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.         ** Aquatic toxicity: EPA/DE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.       Human Health Effects       Active         * for full chemical name and relevant trade names see the individual profiles in Section 7)       CA SRN       Active in ooin oxicity is experimental or estimated value. Fo nod uctive is Sensitization in trade in trade in dividual profiles in Section 7)       Active is set is in trade in trade in trade is in trade in the individual is the indit is the individual is the indit is the in  |
| VL = Very Low hazard       L = Low hazard       M = Moderate hazard       H = High hazard       VH = Very High hazard — Endpoints in colored tex assigned based on empirical data. Endpoints in black italics ( <i>VL</i> , <i>L</i> , <i>M</i> , <i>H</i> , and <i>VH</i> ) were assigned using values from predictive models and * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. Fo no corresponding profile in Section 7.         * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. Fo no corresponding profile in Section 7.         * This component of Furemaster® 550 may be used alone or in other mixtures as an alternative.         * Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.         * Intermediate       Human Health Effects         * Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance trade names and relevant trade name and relevant         (for full chemical name and relevant trade names see the individual profiles in Section 7)       Human         AQ       G       R       D       N       R       Sign is siziation in tital in the profile is is respirit it in all in tital in the profile in Section 7.       AQ         Human Health Effects       L       C       G       R       D       N       R       Sign is iziation in  |
| VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored tex assigned based on empirical data. Endpoints in black italics ( <i>FL, L, M, H,</i> and <i>FH</i> ) were assigned using values from predictive models and * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. Fo no corresponding profile in Section 7.         * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. Fo no corresponding profile in Section 7.         * Aquatic toxicity: EPA/DEE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.         * Aquatic toxicity: EPA/DEE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.         * Chemical (for full chemical name and relevant trade names see the individual profiles in Section 7)       CASRN       A C G R D N R Paint L Ffects       AC         Acute       A C G R D N R S S R S E D Acute       A C G R D N R S S R S E D Acute       A C C C S R S E D Acute       A C C C C C C C C C C C C C C C C C C C  |
| VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored tex assigned based on empirical data. Endpoints in black italics ( <i>VL</i> , <i>L</i> , <i>M</i> , <i>H</i> , and <i>VH</i> ) were assigned using values from predictive models and * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. Fo no corresponding profile in Section 7.         This component of Firemaster® 550 may be used alone or in other mixtures as an alternative.         * Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substance that may partition to sediment and particulates.         Human Health Effects       Actional data may partition to sediment and particulates.   |
| VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored te assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models an * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. F no corresponding profile in Section 7.<br>This component of Firemaster® 550 may be used alone or in other mixtures as an alternative.<br>* Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures, which may not be adequate for poorly soluble substanc that may partition to sediment and particulates.   |
| $\overline{VL} = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored to assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models at * Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value.$  |
|  |

# Appendix A: EPA Screening Level Toxicity Hazard Summary

| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                   | Confidential A   | Fyroltm HF-5* | Confidential E | Confidential D | Confidential C | Emerald Innovation <sup>TM</sup> NH-1* |                                    | Oligomeric phosphonate polyol | Oligomeric ethyl ethylene phosphate | Diethyl bis(2-<br>hydroxyethyl)aminomethylphosphonate | Tris (p-t-butylphenyl) phosphate (TBPP) | Isopropylated triphenyl phosphate (IPTPP)^{\dagger} | Tricresyl phosphate (TCP) <sup>1</sup> | Triphenyl phosphate (TPP) |                        | Non-Halogenated Flame Retardant Alternatives continued | Chemical<br>(for full chemical name and relevant<br>trade names see the individual profiles<br>in Section 7) |          |                      | VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored te assigned based on empirical data. Endpoints in black italics ( <i>VL</i> , <i>L</i> , <i>M</i> , <i>H</i> , and <i>VH</i> ) were assigned using values from predictive models an <sup>5</sup> Based on analogy to experimental data for a structurally similar compound. <sup>d</sup> This hazard designation would be assigned MODERATE if >5% of the particles are in the respirable range as a result of dust forming operation <sup>d</sup> This component of Firemaster® 550 may be used alone or in other mixtures as an alternative. It can also be found in Table 2-1 of this report. <sup>‡</sup> The highest hazard designation of any of the oligomers with MW <1,000. *Each hazard designation for a mixture is based upon the component with the highest hazard, whether it is an experimental or estimated value. *Based on experimental test data for a residual impurity reported to be present in this substance at levels up to 5% by weight.   |
|---|------------------|---------------|----------------|----------------|----------------|--|------------------------------------|-------------------------------|-------------------------------------|---|---|---|--|---------------------------|------------------------|--|--|----------|----------------------|---|
| Confidential<br>r other methylate   | Confidential     | Proprietary   | Confidential   | Confidential   | Confidential   | Proprietary                            |                                    | 363626-50-0                   | 184538-58-7                         | 2781-11-5   | 78-33-1                                 | 68937-41-7  | 1330-78-5                              | 115-86-6                  |                        | tives continued  | CASRN  |          |                      | M = Moderate hazard<br>ts in black italics ( <i>PZ</i> , <i>I</i><br>structurally similar com,<br>MODERATE if >5% oft<br>used alone or in other m<br>oligomers with MW <1<br>ed upon the component v<br>al impurity reported to be  |
| L L   | L                | F             | F              | F              | H              | H                                      |                                    | ۲                             | F                                   | F   | F                                       | L   | Μ                                      | F                         |                        |  | Acute Toxicity   |          |                      | hazarı<br>s (VZ,<br>s cor<br>llar cor<br>>5% o<br>other<br>other<br>MW <<br>MW <  |
| M <sup>8</sup><br>henyl j   | L                | Ŋ             | M              | М              | М              | М                                      | .,                                 | М                             | T                                   | М   | M                                       | М   | L                                      | M                         |                        |  | Carcinogenicity  |          |                      | d H =<br>L, M,<br>f the p<br>f the p<br>mixtua<br>mixtua<br>mixtua<br>mixtua<br>f twith   |
| L<br>phospl   | М                | M             | ۲              | F              | L              | L                                      | lew-to                             | M                             | M                                   | M   | ۲                                       | L   | F                                      | ۲                         | 4                      |  | Genotoxicity   |          |                      | H = High hazard<br>, M, H, and VH) w<br>yound.<br>he particles are in the<br>ixtures as an alterna<br>000.<br>present in this sub-<br>present in this sub-  |
| L<br>late is  | Τ                | ۲             | F              | F              | М              | М                                      | -Mar                               | T                             | T                                   | ۲   | ×                                       | H   | Ħ                                      | F                         | Phos                   |  | Reproductive   |          |                      | hazan<br>hd <i>VH</i><br>s are i<br>an alte<br>an alte  |
| omers   | Γ                | ×             | ۲              | F              | VΓ             | F                                      | ket Pr                             | М                             | М                                   | F   | ۲                                       | Η   | Μ                                      | ۲                         | phate .                |  | Developmental  |          | H                    | rd V<br>) were<br>) were<br>n the r<br>rnativ<br>natard   |
| (phosl  | М                | M§            | Μ              | L              | Μ              | Μ                                      | opriet                             | М                             | M                                   | М   | ×                                       | Η   | Μ                                      | F                         | Phosphate Alternatives |  | Neurological   |          | nem                  | H = V<br>assigned as a signature of the second and |
| M<br>phoric aci   | $L^{\mathbf{a}}$ | Mq            | Μ              | Η              | L              | Η                                      | New-to-Market Proprietary Mixtures | Ι                             | Lª                                  | М   | Ħ                                       | Η   | H                                      | H                         | atives                 |  | Repeated Dose  |          | Human Health Effects | VH = Very High hazard-<br>ere assigned using values f<br>e respirable range as a resultive. It can also be found in<br>ive. It can also be found in<br>rd, whether it is an experim<br>rance at levels up to 5% by:   |
| L<br>d, bis(met   | Γ                | Ι             | Μ              | L              | Μ              | Μ                                      | ures                               | Γ                             | Γ                                   | М   | М                                       | L   | М                                      | F                         |                        |  | Skin<br>Sensitization  |          | Effecte              | hazard –<br>g values f<br>as a resul<br>found in<br>found in<br>1 experime<br>to 5% by 1  |
| thylpheny   |                  |               |                |                |                |  |                                    |                               |                                     |   |   |   |  |                           |                        |  | Respiratory<br>Sensitization   |          |                      | - Endpoi<br>rom pred<br>t of dust f<br>Table 2-1<br>Table 2-1<br>weight.  |
| 1) phen   | Μ                | ×             | VL             | F              | Μ              | M                                      |                                    | F                             | ×                                   | F   | F                                       | L   | F                                      | F                         |                        |  | Eye Irritation   |          |                      | ints in<br>lictive<br>orming<br>of this<br>stimate  |
| yl ester (C   | L                | F             | М              | VL             | Μ              | Μ                                      |                                    | VL                            | F                                   | ΥL  | M                                       | L   | L                                      | VL                        |                        |  | Dermal<br>Irritation   |          |                      | <ul> <li>Endpoints in colored text (VL, L, M, H, and VH) were<br/>om predictive models and/or professional judgment.</li> <li>of dust forming operations.</li> <li>(able 2-1 of this report.</li> <li>(able 2-1 of this report.)</li> </ul>   |
|   | Τ                | VΗ            | VH             | VH             | Η              | VΗ                                     |                                    | Ι                             | T                                   | М   | VΗ                                      | ΗΛ  | HΛ                                     | VΗ                        |                        |  | Acute  | Toxicity | Aquatic              | xt (VL, 1<br>d/or prof<br>s.  |
| <b>VH</b> <sup>∞</sup><br>6446-73-  | L                | ΗV            | vH_∞           | VΗ             | H              | VH                                     |                                    | М                             | T                                   | Τ   | VΗ                                      | ΗΛ  | Н                                      | VΗ                        |                        |  | Chronic  | city     | atic                 | L, M, H,<br>fessional   |
| M<br>1) and pho   | HΛ               | VH            | М              | L              | L              | М                                      |                                    | М                             | Η                                   | =   | ×                                       | Μ   | М                                      | F                         |                        |  | Persistence  |          | Envir                | xt (VL, L, M, H, and VH) w<br>d/or professional judgment.<br>s.   |
| VH         VH <sup>∞</sup> M         H <sup>∓</sup> ASRN 26446-73-1) and phosphoric acid, |                  | H‡            | Н              | М              | L              | Н                                      |                                    | Ι                             | Τ                                   | Ι   | H                                       | Н   | Η                                      | Μ                         |                        |  | Bioaccumulation  | Fate     | Environmental        | t.  |

From Table 2-1 and 2-2, Baker AK, Baker R, Baur W, et al. Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update. 2014:4121233-4121235. doi:10.1002/ejoc.201200111



## Appendix B: Emory LEADER Laboratory Chemical Extraction Procedure



Appendix C: Calculated Exposure Concentrations by Sample ID















Inhalation (QF)

Inhalation (PUF)

0

Oral (DW)

Dermal (FP)

