

Lessons Learned from Spray Polyurethane Foam Emission Testing using Micro-chambers

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ABSTRACT

Both governmental agencies and the SPF industry consortium have sought more information on potential chemical emissions from SPF to better understand any potential occupant exposures and health impacts. This research was designed to contribute to the development and evaluation of voluntary standards for testing emissions from SPF. Specifically, this work was performed to support the ASTM Indoor Air (D22.05) subcommittee consensus based efforts to develop a standard that can be used to compare emissions from SPF under uniform micro-chamber testing conditions. Although limitations in the current proposed method do not allow the generated data to be directly used in exposure modeling, it does allow conclusions to be drawn on how emissions between different types of SPF vary under the tested conditions. Micro-chamber SPF emission testing performed at NIST has demonstrated 1) a wide range of chemicals can emit from SPF under the tested conditions; 2) the same chemical may emit at concentrations that are an order magnitude different for open-cell versus closed-cell SPF, 3) the same chemical may emit at different concentrations from the same type of SPF (*i.e.* closed-cell SPF), 4) different chemicals may emit with different emission profiles (constant versus exponential decay) in the same foam, 5) emission rates from SPF are highly temperature dependent. This research establishes that emissions from SPF can be highly variable. In addition, micro-chamber testing can be used to demonstrate emission differences between SPF, whether the purpose is to compare new manufacturer formulations or to compare emissions from standard spray events and misapplications.

INTRODUCTION

Spray polyurethane foam (SPF) insulation is a unique building material as it 1) reduces both conductive and convective heat loss through the building envelope, and 2) is produced via a chemical reaction at the building site. The unique heat loss reducing properties of SPF and efforts towards creating more efficient buildings, such as tax incentives and programs like U.S. Environmental Protection Agency (EPA) Energy Star¹ and Design for the Environment² have increased the number of SPF applications in residences. This increase in SPF applications also means that chemical reactions are being conducted in a greater number of residential locations.

SPF is formed onsite via an exothermic chemical reaction between A-side and B-side chemicals. The A-side typically consists of monomeric or polymeric methylene diphenyl diisocyanate. Polyols are part of the B-side chemicals, which also include amine and/or metal catalysts, blowing agents, surfactants, and flame retardants. Amine and/or metal catalysts are used to promote the reaction between polyols and A-side chemicals, which help polyurethane foam cells develop sufficient strength to maintain their structure and resist collapsing. The reactions can be designed so the resulting foam is open (low density) or closed cell (medium density).

Flame retardants are present in reacted polyurethane foam at up to 12 % by mass.³ Several studies have investigated emissions of flame retardants from SPF.^{4,5} The most common identified flame retardant is tris (1-chloro-2-propyl)

phosphate (TCPP). TCPP is not exclusive to SPF, and has also been used in mattresses, electronics, and upholstery.⁵ TCPP has been measured in homes at airborne concentrations ranging from 2.4 ng m⁻³ to 1,260 ng m⁻³.⁵⁻⁷ and found in similar concentrations in cars, offices and furniture stores.⁸ TCPP is persistent in the environment,⁹ readily absorbed through skin, and breaks down rapidly into metabolites in the body.¹⁰ Although there is limited data, TCPP is classified by the EPA Design for the Environment program as having a high hazard for reproductive and developmental effects.¹⁰ Although not all chemicals that have been detected emitting from SPF have human health impacts, some chemicals that have been detected emitting from SPF likely have negative health impacts. For instance, 1,4 dioxane is commonly detected emitting from closed cell SPF and has been listed as likely to be carcinogenic to humans by the EPA Integrate Risk Information System (IRIS).¹¹

The Consumer Product Safety Commission (CPSC), along with the EPA, have received a number of complaints from residents regarding health effects that are potentially associated with SPF applications.¹² The time frame of health complaints is longer than the suspected time frame for the presence of isocyanates, suggesting that the emission of other chemicals (amines, blowing agents, surfactants, flame retardants or by-products of the reactions) from the SPF may be of concern. However, no direct connection between these health symptoms and SPF emissions have yet been established. In order scientifically investigate complaints associated with SPF applications, standardized measurement protocols are needed to determine emission rates of chemicals from SPF as well as methodologies to relate those emission rates to occupant exposure.

The ASTM Indoor Air Quality (D22.05) subcommittee develops standard test methods and protocols to determine the emissions rates from materials. Currently a new standard for measuring the emissions of chemicals from SPF using micro-chamber apparatus is being developed (WK 40293: Standard Test Method for Estimating Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation using Micro-Scale Environmental Test Chambers). This standard does not address emissions of isocyanates. NIST actively participates in the activities within D22.05 to develop consensus standards on the measurement of SPF emissions.

The objective of this paper is to summarize the major points that have been learned about SPF emissions from conducting research to support the development of WK40293.

EXPERIMENTAL METHODS

Four SPF samples were tested in micro-chamber experiments. Many of the experiments were performed to gain insight on experimental parameter values (temperature, flow, etc.) and conducted prior to determination of consensus values determined for WK40293.

Foams Tested

Four different foams were tested (Table 1). Samples Open 1 and Closed 1 were provided by the American Chemistry Council's Center for the Polyurethanes Industry (CPI). These research formulations were developed in 2011 to be representative of SPF then available in the marketplace. The formulations were created for research purposes only and were not optimized to meet the specifications of commercial producers and therefore may not reflect formulations currently available in the marketplace. Therefore, conclusions about how these foams would perform outside a laboratory setting are speculative. Foams Open 1 and Closed 1 were sprayed in factory settings under controlled conditions. The foams were packaged and shipped overnight to NIST in an insulated cooler in accordance with ASTM standard D7859.¹³ Emission testing on Open 1 was started within 24 hours of spraying. Emission testing on Closed 1 was delayed as noted in Table 1. Closed 1 was stored at room temperature (≈ 20 °C) during storage.

Table 1. SPF samples tested.

Foam ID	Type	Density (Kg/m ³) ¹	Spray Date	Test Date
Open 1	Open Cell	12	2/26/2014	2/27/2014
Open 2²	Open Cell	7	Summer 2012	1/28/2014
Closed 1	Closed Cell	30	11/4/2014	4/13/2105
Closed 2	Closed Cell	33.0 to 49.8 ¹	Summer 2015	3/14/2016

¹Density determined by measured initial mass and volume. Density of Closed 2 depended upon the sample location.

²Open 2 sample was taken from the NZERTF.

Open 2 was a high pressure, open cell, low density SPF that was applied during the construction of the National Institute of Standards and Technology (NIST) Net Zero Energy Residential Test Facility (NZERTF) in the summer of 2012. The design and construction of the NZERTF are described in Pettit et al.¹⁴ Closed 2 was closed cell, high pressure foam that was sprayed in a residential home in the summer of 2015.

Micro-chamber Experiments

A cutting tool was machined to precisely cut SPF to fit tightly within Markes 250 or Markes 125 micro-chambers (Figure 1) according to ASTM D7859-13e1. The top of the foam was not removed for Open 1, Open 2, and Closed 1. The top of the foam was removed for Closed 2. For Open 1, Open 2, and Closed 1, the 114 mL micro-chambers were operated at a temperature of 40 °C with a 100 mL min⁻¹ airflow of ultra-high purity air. For Closed 2, the 44 mL micro-chambers were operated at a temperature of 35 °C with a 24.1 mL min⁻¹ airflow of ultra-high purity air. The proposed consensus temperature in ASTM WK 40293 (Spring 2016 Ballot) is 35 °C. To investigate the impact of temperature on the TCPP emission rate, samples of Open 1 were also run at 28 °C, 50 °C and 60 °C.



Figure 1. Sampling of foam Open 1 for micro-chamber analysis (left). Sample installed in micro chamber (right).

The airflow contained an absolute humidity of 8.8 g m⁻³ (equivalent to a relative humidity of 38 % at 25 °C) for the Open 1 and Open 2 samples. The airflow contained zero humidity for the Closed 1 and Closed 2 sample. The proposed consensus humidity in ASTM WK 40293 is zero.

Tenax TA sorbent tubes were attached to the effluent flow of each micro-chamber for 2 min to 4 h (0.2 L to 24 L of sample) depending on the concentration of the flame retardant. For samples longer than 2 hours, a second Tenax tube was placed in series with the first tube and analyzed for breakthrough. For each foam, at least three micro-chambers were run concurrently. For the 114 mL experiments the fourth chamber was typically used as a control. Each foam was analyzed for at least 200 hours. Prior to sampling the tubes were spiked with an internal standard (1.0 µL of 1.25 mg Toluene D-8 mL⁻¹ of methanol) using a liquid methanol solution injected into a heatblock.

Tube Analysis

Samples were analyzed using a thermal desorption-gas chromatography/mass spectrometer system (TD-GC/MS). A non-activated guard column was used in the transfer line from the thermal desorption unit to the GC/MS. An Rtx-5 amine column (30.0 m x 250 µm x 0.50 µm) was used for compound separation in the GC/MS.

Instrument detection limits for TCPP were determined by multiplying three times the standard deviation of seven replicates at a concentration that was less than five times the determined method detection limit.¹⁵ The instrument TCPP detection limit was 8.65 ng and the method detection limit was 0.71 µg m⁻³ to 2.86 µg m⁻³ depending on the sample volume. Only values above the method detection limit for the corresponding

sampling volume are shown below. Tenax sorption tubes also captured amine catalysts, byproducts and other volatile organic compounds.

RESULTS and DISCUSSION

Chemicals were detected emitting to the air from each of the tested foams. The analysis of the four different SPF samples allowed conclusions to be drawn regarding the influence of the foam, the chemical, and the temperature.

Chemicals Detected

A wide range of chemicals can emit from SPF under the tested. TCPP was detected emitting from every SPF sample. Other chemicals were also present in each foam. As an example over 80 different chemicals were identified emitting from Closed 2. Of these chemicals, 17 were identified with the GC/MS (spectrum match with a quality score greater than 80) and had relatively large response areas (over 30,000). Six of these chemicals (Table 2) were positively identified and quantified for Closed 2 using standards. A large amine catalyst peak was also identified, but a standard was not available for positive identification.

Table 2. *Chemicals identified in preliminary sampling (ranked in order of largest GC/MS response area).*

Chemical	CAS Number	Average Linear RSQ
1,4-Dioxane	123-91-1	0.999
Propane, 1,2-dichloro-	78-87-5	0.992
Piperazine, 1,4-dimethyl	106-58-1	0.991
Tris-(1-chloro-2-propyl) phosphate (TCPP)	13674-84-5	0.989
Benzene, 1,2-dichloro	95-50-1	0.996
1,3-Dioxolane, 2-ethyl-4-methyl	126-39-6	0.993

Influence of Foam

The same chemicals emitted at different rates from different foams. For the tested open cell foams (Open 1 and Open 2), concentrations of the flame retardant TCPP tended to be constant over time throughout the duration of the experiments (Figure 2). The two open cell foams TCPP concentrations were not statistically different ($p=0.06$), even though Open 1 was freshly sprayed and Open 2 was applied over 1.5 years prior to sampling. All statistical comparisons in this document use a one-way ANOVA, Tukey-Kramer analysis with $\alpha = 0.05$. The average TCPP concentration over more than 400 hours of sampling for Open 1 was $400 \mu\text{g m}^{-3}$ ($n=98$, standard error $23 \mu\text{g m}^{-3}$) and $314 \mu\text{g m}^{-3}$ ($n=78$, $23 \mu\text{g m}^{-3}$) for Open 2. The Open 2 results show that for this sample and for insulation temperatures of 40°C , flame retardants can be emitted at measurable concentrations for time frames greater than 18 months after application.

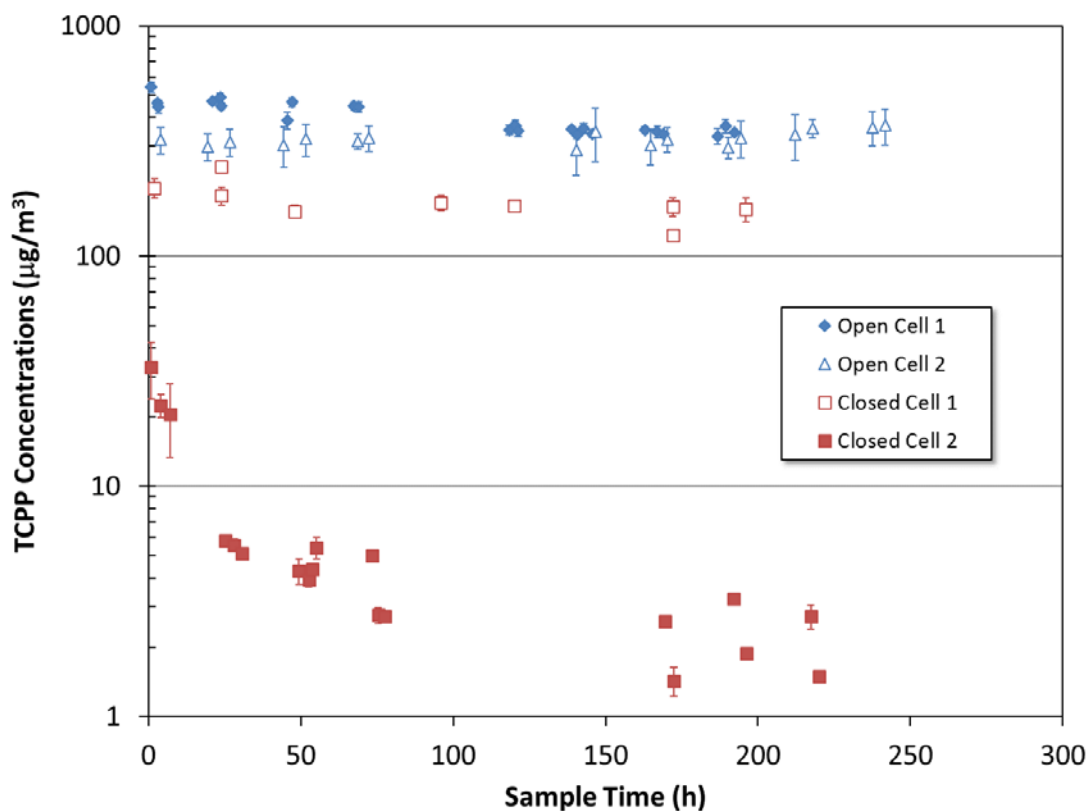


Figure 2. TCPP concentrations for different samples. Error bars show the standard error for each sampling time. Vertical axis is a logarithmic scale. Closed 1 tested at 35 °C, all other foam tested at 40 °C.

Unlike the tested open cell foams, the TCPP concentrations from Closed 1 decreased exponentially during the first 100 hours (**Error! Reference source not found.**) and was two orders of magnitude lower than Open 1 and Open 2. In contrast, Closed 2 followed a constant emission profile similar to Open 1 and Open 2. Despite the exponential decrease in TCPP concentration emitted from the Closed 1 sample, the total TCPP mass was not appreciably depleted. Over the course of the 400 hour experiment, less than 8 µg of TCPP was emitted from the roughly 300,000 µg of TCPP present initially in the 3.75 g SPF sample (TCPP was roughly 8% of the mass of ingredients used to make Closed 1³).

One hypothesis to explain the decrease in emission rate for Closed 1 is that the TCPP initially located near the surface emits over a short time frame and that long term emission from the bulk of the foam is limited by the diffusion of TCPP to the surface. The two different emission profiles for TCPP cell foams suggest that the limiting mass transport mechanism for TCPP is fundamentally different for the tested foams. It is possible that the emission of TCPP from open cell foam is controlled by the mass transfer coefficient of the airflow above the foam surface (flow dependent), while the emission from Closed 1 foam is controlled by the diffusion of TCPP through the closed cells.

This data highlights the importance of determining foam specific emission parameters (initial concentration, diffusion coefficient, partitioning coefficient and mass transfer coefficient) for each chemical prior to attempting to model the TCPP in full scale systems.

Influence of Chemicals

Different chemicals emit in the micro-chamber with different emission profiles (constant versus exponential decay) in the same foam. This held true for chemicals emitted from Open 1 and Closed 2. Figure 3 shows a decaying concentration for Bis (2-dimethylaminoethyl) ether (BDMAEE) and the steady

emission profile for TCPP from the Open 1 sample. BDMAEE is a catalyst with an initial maximum concentration in this foam of less than 1 %, much smaller than the initial foam concentrations of TCPP.³ Over the course of the 400 hour experiment, over 5,000 μg of BDMAEE was emitted from the roughly 7,200 μg of BDMAEE present initially in the 0.8 g SPF sample (BDMAEE was roughly 0.9% of the mass of ingredients used to make Open 1³). In contrast, roughly 500 μg of TCPP was emitted from the roughly 100,000 μg of TCPP initially present in Open 1.

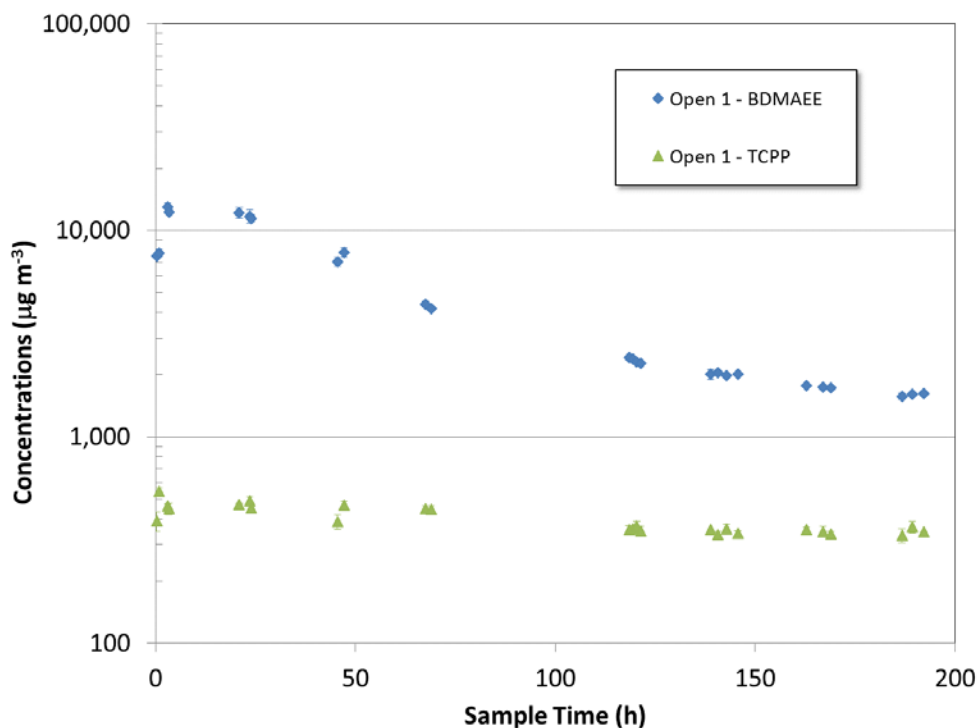


Figure 3. TCPP and BDMAEE concentrations from Open 1 tested in 40 °C micro-chambers. Error bars show standard error in triplicate data.

A similar trend was also seen for Closed 2. Figure 4 shows a steady emission profile for TCPP from the Closed 2 sample, while the concentrations for all other quantified chemicals drop exponentially. The initial concentration of these chemicals in Closed 2 is unknown.

This data highlights that emissions from SPF can be highly variable both from one foam to another and within the same foam sample. This indicates that foam and chemical specific data are needed prior to attempting to model exposure from SPF emissions.

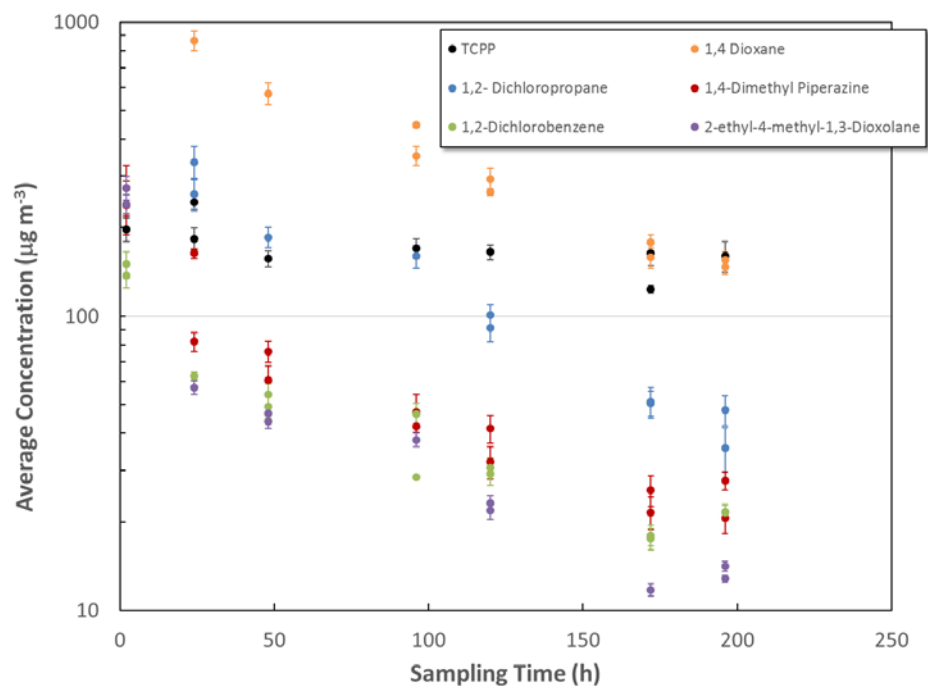


Figure 4. Concentrations of quantified chemicals emitted from Closed 2 tested in 35 °C micro-chambers. Error bars show the standard error for each sampling time. Vertical axis is a logarithmic scale.

Influence Temperature

Emission rates from SPF are highly temperature dependent. In field applications SPF experiences a range of temperatures. Hence, it is important to understand the temperature dependence of TCP emissions. A triplicate set of Open 1 SPF was analyzed at three temperatures (28 °C, 40 °C, and 50 °C) without removing the foam from the chambers. All samples were taken at least 24 hours after the temperature change. Over the course of the 550 hour experiment, less than 1,400 µg of TCP was emitted from the roughly 140,000 µg of TCP was present initially in the 1.2 g SPF sample (TCP was roughly 12% of the mass of ingredients used to make Open 1). A separate test on a separate sample of Open 1 was conducted at 60 °C. Figure 5, shows the average concentrations for TCP at the four temperatures for Open 1 foam. This data indicate that TCP emissions are exponentially dependent upon temperature for open cell foam. Hence, a small change in building temperature may have a relatively large impact on the TCP concentration in the building. A similar trend was seen for BDMAEE for the same Open 1.

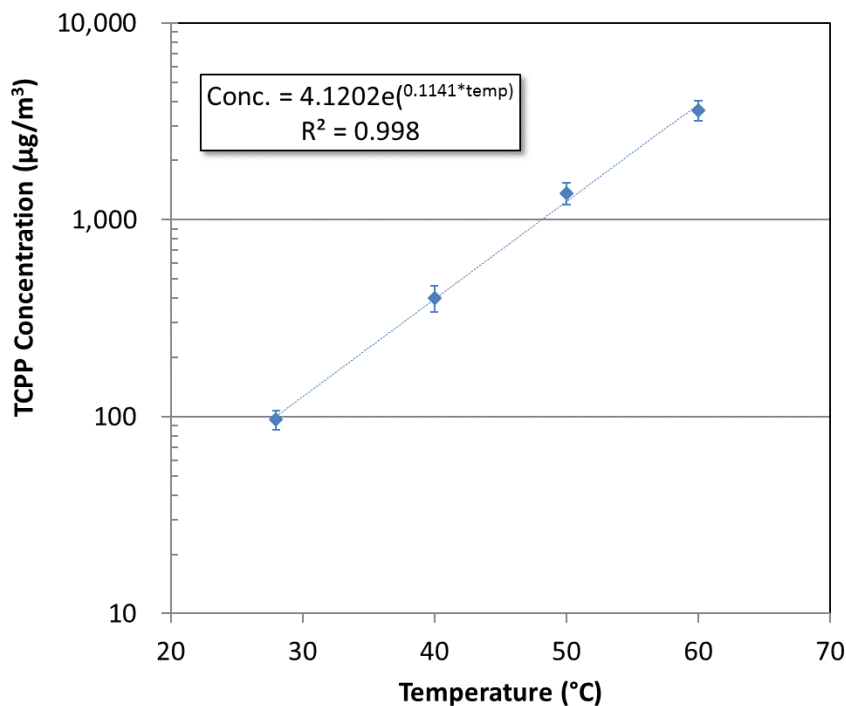


Figure 5: Average TCPP concentrations for experiments run at increasing temperature. Vertical axis is logarithmic.

Use of data

This data should not be used to calculate exposure in full scale scenarios. TCPP emissions highlight this issue. If emissions from TCPP are controlled by internal material diffusion scaling emission rates from micro-chambers to residences may be possible; however, if emissions are controlled by external mass transfer limitations then scaling of emission rates is unlikely to be successful. In general, the emissions of VOCs from materials are controlled by the diffusion of the VOC through the material matrix and are not highly chamber dependent. This can allow the direct use of VOC chamber emission factors to predict emissions in full scale buildings. In contrast the emission of SVOCs tends to be chamber dependent and controlled by the airflow above the material. Since the airflow above a material can be significantly different in a chamber and in a full scale building, SVOC chamber emission factors from micro-chamber studies should not be directly applied to full scale buildings. Emission parameters (mass transfer coefficient, initial concentration, partition coefficient, and diffusion coefficient) are needed to accurately predict the concentrations of SVOCs in buildings. Traditionally, VOCs and SVOC are defined based upon the vapor pressure or boiling point of the chemical. TCPP has a wide range of reported values for vapor pressures and boiling points, indicating it could behave as VOC or SVOC.^{16, 17} As a result, the data in this paper should not be used for full scale exposure estimates.

However, the micro-chamber emission testing method described in this document and refined in WK40293 can be used to demonstrate emission differences between SPF, whether the purpose is to compare new manufacturer formulations or to compare emissions from standard spray events and possible misapplications.

CONCLUSION

Emissions from SPF have been quantified from four samples using micro-chamber testing. A range of chemicals can be measured emitting from SPF under the tested conditions in time frames relevant to residential exposure.

Emission profiles from SPF are variable and dependent upon the:

- Foam type,

- Chemical properties,
- Temperature of the SPF.

The flame retardant TCPP emitted from all samples, even those that were sprayed 18 months prior to sampling. However, TCPP emitted at concentrations that differed by over an order of magnitude illustrating that emissions from one foam should not be used to predict emissions from all foam.

The data in this paper should not be used for full scale exposure estimates. However, the micro-chamber emission testing method in WK40293 can be used to demonstrate emission differences between SPF samples to compare emissions from standard spray events and possible misapplications.

DISCLAIMER

Certain trade names or company products are mentioned in the text to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment is the best available for the purpose.

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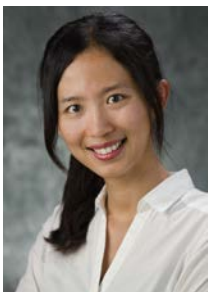
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BIOGRAPHIES



Dustin Poppendieck

Dustin earned his PhD in Environmental Engineering from the University of Texas at Austin. He was an assistant professor in environmental resources engineering at Humboldt State from 2004-2010. He has been at NIST since 2012 and has worked in the indoor air quality field for the past 15 years. He has investigated the deposition of disinfection agents used in anthrax remediation, desorption of a methamphetamine surrogate from wallboard, emissions from building materials used in net zero energy houses, methods for characterizing emissions from spray polyurethane foam, and characterized particle emissions from kerosene lamps used in developing countries.



Mengyan Gong

Mengyan Gong got her Ph.D. in Civil Engineering from Tsinghua University in 2015. She studied on assessment of dermal exposure to phthalates for her Ph.D. thesis, including developing model for predicting dermal absorption from gas phase chemicals, assessing phthalate dermal exposure by measuring its levels on different human body locations, examining the contribution of dermal absorption to total uptake, and investigating the influence of clothing on dermal exposure to phthalates. After her Ph.D., she started to work at NIST as a postdoctoral researcher. Her research topic at NIST is to characterize chemical emissions from spray polyurethane foam.



Lauren Lawson

Lauren is a student at the University of Louisville studying Chemical Engineering. She was a co-op at the National Institute of Standards and Technology in the Spring of 2016. Lauren has examined the chemical emissions of spray polyurethane foam, with a focus on volatile and semivolatile compounds using micro-chambers.

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