

Characterization of Emissions from Spray Polyurethane Foam

Final Report to U.S. Consumer Product Safety Commission
Interagency Agreement CPSC-I-13-0016

Dustin Poppendieck
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NIST
**National Institute of
Standards and Technology**
U.S. Department of Commerce

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Dustin Poppendieck
Andrew Persily
Steve Nabinger
*Engineering Laboratory
Energy and Environment Division*

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U.S. Department of Commerce
Penny Pritzker, Secretary

National Institute of Standards and Technology
Willie May, Under Secretary of Commerce for Standards and Technology and Director

Objective

This report summarizes NIST activities under the FY2013 interagency agreement between the Consumer Product Safety Commission (CPSC) and the National Institute of Standards and Technology (NIST). The objective of that agreement is to develop testing and measurement protocols for determining the quantities and properties of compounds released from spray polyurethane foam (SPF) as it is applied in residential settings.

Background

Many homeowners and government programs are using insulating products at a growing rate, such as SPF, to increase the energy efficiency of their residences and other constructed buildings. Retrofitting or addition of foam insulation in new construction is also supported in the United States by Federal efforts, such as tax incentives, and programs like Environmental Protection Agency (EPA) Energy Star and Design for the Environment. Because of these programs and other drivers for more efficient buildings, the foam insulation industry expects to see significant growth in the use of their products over the next few years.^{1,2}

Homes can be insulated with SPF by a contractor hired by the homeowner or by using a do-it-yourself (DIY) kit. SPF is both an insulation and a sealant, which is formed 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. Having SPF installed professionally or through DIY, along with use in arts and craft projects, leads to the potential exposure of consumers to the chemicals found in the SPF.

In 2009, the EPA contacted CPSC, along with other federal agencies including the Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH), to establish a federal working group to address potential hazards from the chemicals in SPF during its use. EPA staff became aware of potential hazards from some of the compounds in SPF from a clinical report of a death that occurred from exposure and sensitization to isocyanates released during the application of a polyurethane paint to motor vehicles in an auto shop.³ Isocyanates are very reactive compounds; thus, exposure to isocyanates is believed to be of greatest concern during and immediately after the application or installation of products containing isocyanates, such as SPF, before they can polymerize or react with other compounds found in the indoor environment.

¹ http://www.businesswire.com/news/home/20130717005300/en/SPF-Insulation-Demand-Growth-Creating-Investment-Opportunities#.U2p6n_ldXzg

² <http://sprayfoamsupply.com/foam-insulation-to-gobble-up-market-share-by-2017/>

³ <http://www.cdc.gov/niosh/docs/2006-149/pdfs/2006-149.pdf>

CPSC staff, along with EPA and other federal agencies, has received a number of complaints regarding health effects resulting from the installation of SPF in homes.⁴ To better understand worker related health effects, NIOSH and EPA are developing action plans associated with SPF emissions, specifically a plan for measuring isocyanate emissions from SPF.^{5,6} Residents have also complained of a multitude of effects including severe respiratory irritation, breathing difficulties, dizziness and nausea. In some cases, the effects are so severe that consumers report that they can no longer live in their homes.⁷ These health effects occur several days to months following the SPF installation in the home. To determine what other compounds could be causing these health effects, CPSC contracted with Versar, Inc. to produce a toxicological profile of select amine catalysts found in SPF.⁸ Information from this report suggests that amine emissions may be one cause of these long term health effects. Also, anecdotal information suggests that aldehyde emissions may also add to these described health effects.

CPSC staff and its federal partners have met with members from the Center for the Polyurethanes Industry (CPI) of the American Chemistry Council (ACC), who provided exposure data on some high-pressure and low-pressure SPF systems. As a result of these exposure studies, the CPI recommends that homeowners leave the premises during SPF installation and not return until 24 hours after the installation of high pressure foam. Some low pressure systems recommend re-entry times of 1 hour. However, CPSC staff is not fully satisfied with the robustness of the data and question the sufficiency of the 24-hour re-entry time. CPSC, along with its federal partners, see a need to perform exposure studies that include measuring exposure levels (1) at different distances from the spray source, (2) on a time course, (3) under varied air change rates, and (4) from SPF that is not mixed correctly. Coupled with an understanding of the transport of emissions from foam to occupied areas the results of these studies will allow CPSC staff to make determinations of the potential health impacts of SPF insulation products and provide guidance to consumers on their safe use.

The results of these studies may also contribute to the development and evaluation of voluntary standards. There are work items under the ASTM Indoor Air Quality (D22.05) subcommittee to standardize test methods and protocols. A work item for spraying, sampling, and packaging SPF insulation products and to measure emissions from these products, was recently adopted as ASTM D 7859 -13 and is entitled: Standard Practice for Spraying, Sampling, Packaging, and Test Specimen Preparation of Spray Polyurethane Foam (SPF) Insulation for Testing of Emissions Using Environmental Chambers. Currently two work items (WK 40292 and 40293) are being combined to form a new standard for measuring the emissions of chemicals from SPF using micro-chamber apparatus. However, at present there are no standardized test methods that

⁴ <http://www.saferproducts.gov/Search/Result.aspx?dm=0&q=Spray+foam+insulation&srt=0>.

⁵ <http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/tdi.html>

⁶ http://www.epa.gov/dfe/pubs/projects/spf/spray_polyurethane_foam.html

⁷ <http://www.saferproducts.gov/Search/Result.aspx?dm=0&q=Spray+foam+insulation&srt=0>.

⁸ *Status Report: Staff Review of Five Amine Catalysts in Spray Polyurethane Foam. 09/19/2012. Melanie Biggs. Directorate for Health Sciences. Consumer Product Safety Commission.*

adequately address measuring the chemical emissions of SPF insulation products. These ASTM standards will help address that need.

Methods

A detailed Standard Operating Procedure was developed and reported in the April 2014 Letter Report from NIST to CPSC.⁹ This document provides a summary of the methods used by the NIST Indoor Air Quality and Ventilation Group to analyze amines and flame retardants using a Gas Chromatograph/Mass Spectrometer (GC/MS) and aldehydes with a Liquid Chromatograph/Ultraviolet Spectrometer (LC/UV).

A cutting tool was machined to precisely cut SPF to fit tightly within existing Markes 250 micro-chambers (Figure 1) according to ASTM D7859-e13. The chambers were operated at a temperature of 40 °C with a 100 mL/min airflow of ultra-high purity air. The airflow contained a humidity ratio that was equivalent to a relative humidity of 38 % at 25 °C. Emissions were captured on two types of sorption tubes. Tenax TA[®] sorption tubes were used to capture amine catalysts, flame retardants and other volatile organic compounds, and were subsequently analyzed by GC/MS. Aldehydes were sampled with 2,4-Dinitrophenylhydrazine (DNPH) cartridges and the extracted derivatives analyzed using LC/UV.



Figure 1. Sampling of foam (left). Sample in micro chamber (right).

Prior to sampling, the Tenax TA[®] tubes were cleaned with ultra high purity nitrogen for at least one hour at 320 °C with a Markes TC-20 tube cleaner. The tubes were spiked with 1.24 ng deuterated toluene as an internal standard using a liquid solution injection into a TALBOYS[®] Standard Heatblock. Tenax TA[®] tubes were attached to the effluent flow of each chamber for 2 min to 2 h (0.2 to 12 L of sample) depending on the concentration of the flame retardant. The Tenax TA[®] tubes were thermally desorbed using a Markes Unity thermal desorbing system. The setpoints used for the thermal desorption system are contained in the previous letter report to CPSC. A non-activated guard column was used in the transfer line to the GC/MS. An Rtx-5 Amine column (30.0m x 250 μ m x 0.50 μ m) was used for compound separation in the GC/MS.

⁹ *Characterization of Emissions from Spray Polyurethane Foam. Letter Report to U.S. Consumer Product Safety Commission. Interagency Agreement CPSC-I-13-0016. April 2014. Engineering Laboratory, National Institute of Standards and Technology*

DNPH tubes were attached to the microchamber outlets to capture aldehyde and ketones in 18 L to 100 L of the effluent gas, which correspond to 3 h to 18 h of sampling. DNPH tubes were extracted with acetonitrile. Verification of the presence of these chemicals was done using HPLC-UV retention time analysis.

Chemical standards (Table 1) were purchased for target compounds based on chemicals studied by previous researchers (e.g., John Sebroski, Bayer). Neat chemical standards were prepared by dilution in methanol. Standards were spiked onto Tenax TA[®] tubes along with the deuterated toluene internal standard. Chemicals were quantified using the response ratio for each chemical (area response for quantitation ion of the chemical divided by the area response for quantitation ion of the deuterated toluene). Linear standard curves were created for each chemical (average RSQ values for each linear curve are shown in Table 1) on a roughly weekly basis. Isocyanates were not analyzed as part of this research effort, as EPA and others are studying SPF isocyanate emissions. Instrument detection limits for amines and flame retardants 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 limits. Method detection limits were determined dividing the instrument detection limit by the average sample volume (0.554 L). Chambers were tested prior to the introduction of foam to ensure background concentrations of the chemicals of interest were zero.

Tested Foam

Three SPF foams were analyzed: 1) low pressure, closed cell SPF common, which is commonly applied by DIY applicators, 2) high pressure, open cell, low density SPF was applied to the NIST Net Zero Energy Residential Test Facility (NZERTF) in the summer of 2012, and, 3) high pressure, open cell, low density SPF freshly sprayed foam supplied by the Center for the Polyurethanes Industry (CPI). Foam 1 was sprayed two months prior to testing. The foam was stored in room temperature paint cans between the spray event and testing. Three ~3.0 g samples were tested. In January of 2014, three ~0.8 g samples were cored from overspray in the basement rafters of the NZERTF. Since the foam was in the basement, it is unlikely that the temperature of the foam ever exceeded 25 °C after application. Spray conditions of the foam is unknown.

The third foam was sprayed by Air Products on February 27th, 2014. The reported B side components are listed in Table 2. The foam was sprayed in a laboratory setting under standard conditions: ambient temperature of 21.6 °C, ambient relative humidity of 27.7%, 3.9 kPa, hose temperature of 48.9 °C, and nozzle pressure of 9,700 kPa to 10,300 kPa. The foam was packaged and shipped according to ASTM standard D7859. The foam was shipped overnight to NIST laboratories in an insulated cooler. The shipping temperature was not recorded. However, emissions from the foam were likely not impacted as the average outside temperature during shipping was -6 °C (20 °F), indicating that shipping vehicles were unlikely to experience extreme cargo temperatures.

Table 1. Chemicals with prepared standard curves

Chemical	Acronym	Average Linear RSQ	Instrument Detection Limit (ng)	Method Detection Limit ($\mu\text{g}/\text{m}^3$)
Tris-(1-chloro-2-propyl) phosphate	TCP	0.95	100 ¹	180
Bis (2-Dimethylaminoethyl) ether	BDMAEE	0.96	180 ¹	320
N,N,N-Trimethylaminoethylethanolamine	TMAEEA	0.97	2,600 ¹	4,700
Tetramethyliminobispropylamine	TMIBPA	0.94	ND ²	ND
Pentamethyldiethylene triamine	PMDTA	0.99	ND ²	ND
Bis (dimethylaminopropyl) methylamine	DAPA	0.93	ND ²	ND
Formaldehyde	-	0.99	2.4 ³	0.063
Acetaldehyde	-	0.99	1.8 ³	0.018
Benzaldehyde	-	0.99	2.8 ³	0.028
Butraldehyde	-	0.99	2.1 ³	0.021
Acrolein	-	0.99	1.1 ³	0.011
Crotonaldehyde	-	0.99	1.4 ³	0.014
Acetone	-	0.99	1.4 ³	0.014
Hexaldehyde	-	0.99	1.4 ³	0.014
Propionaldehyde	-	0.99	1.0 ³	0.010
Valeraldehyde	-	0.99	0.85 ³	0.009
Isovaleraldehyde	-	0.99	0.70 ³	0.007
m,o-Tolualdehyde	-	0.99	0.25 ³	0.002
p-Tolualdehyde	-	0.99	0.88 ³	0.009
2,5-Dimethylbenzaldehyde	-	0.99	0.61 ³	0.006

¹Determined using "Definition and procedure for the determination of the method detection limit – Revision 1.11" Pt. 136, App. B 40 CFR Ch. I (7–1–03 Edition).

²Chemical not above baseline noise in samples. Detection Limits not determined.

³Determined by multiplying 1.73 times standard error of calibration line.

Table 2. CPI foam reported B side components.

Chemical	Mass Percent
Polyether Polyol	34
NPE Polyether Polyol	11.9
Blow Agent	<4
Water	20
Silicone Surfactant	0.7 to 1.0
Tris-(1-chloro-2-propyl) phosphate (TCP)	25.2
Bis (2-Dimethylaminoethyl) ether (BDMAEE)	0.9
Tetramethyliminobispropylamine (TMIBPA)	2.0 to 3.0
N,N,N-Trimethylaminoethylethanolamine (TMAEEA)	4.0

Results

Both concentration and emission rates were determined from SPF foam exposed to 40 °C in a micro-chamber environment at a humidity ratio that was equivalent to a relative humidity of 38 % at 25 °C. Note that all concentration and emission rates in this document apply only to micro-chamber conditions and the tested foams. The mass transfer in building systems may not be similar to those experienced in a micro-chamber. Hence, this data should not be used to predict to full scale emissions until further testing has determined scaling parameters.

Micro-chamber Concentrations

Table 3 lists the average concentrations of the amines and flame retardant over at least 400 hours of sampling for the three experiments. Only chemicals that were detected above method detection limits and had standard curves are listed. Concentrations of the flame retardant tris (1-chloro-2-propyl) phosphate (TCPP) tended to be constant over time throughout the duration of the experiments (Figures 2 and 3) while the concentrations of the amines tended to peak in the first 24 to 48 hours and then decayed in a logarithmic manner (Figure 4).

Table 3. Average micro-chamber amine and flame retardant concentrations over 400 hours. The number following the symbol \pm is the numerical value of an expanded uncertainty $U = k u_c$, with U determined from a combination of the estimated standard deviation (u_c) and a coverage factor $k = 2$, with parameters assumed to be approximately normally distributed and the unknown value assumed to lie in the interval defined by U with a level of confidence of approximately 95 %.

	Foam 1 Average Concentration ($\mu\text{g}/\text{m}^3 \text{ g}$)	NZERTF Average Concentration ($\mu\text{g}/\text{m}^3 \text{ g}$)	CPI Average Concentration ($\mu\text{g}/\text{m}^3 \text{ g}$)
TCPP	770 \pm 140	400 \pm 270	330 \pm 210
BDMAEE	ND ¹	ND ¹	3,700 \pm 6,700
PMDTA	1,100 \pm 880	ND ¹	ND ¹
Number of data points	48	75	98

¹Not Detected

The flame retardant TCPP was emitted from all three samples, including the ~1.5 year old NZERTF samples. The two high-pressure, open cell foams emitted TCPP concentrations that were not statistically different. These results show that when wall temperatures are at temperatures of 40 °C, SPF flame retardants can be emitted into wall cavities and/or into air near applied foam at significant concentrations at time frames greater than 18 months after application.

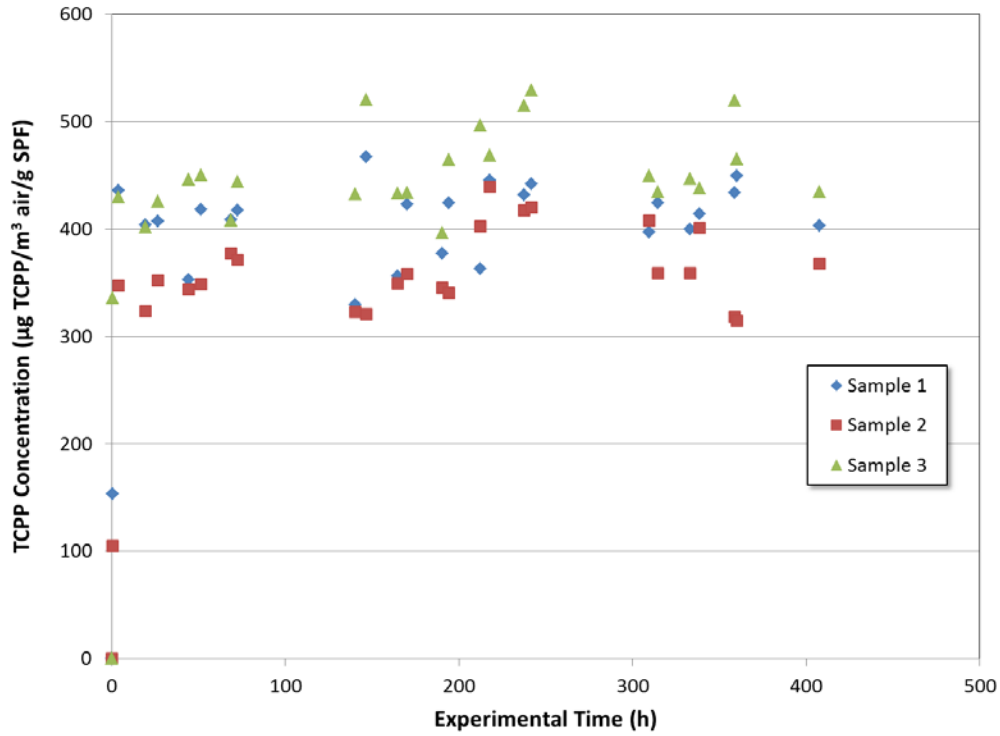


Figure 2. TCP Concentrations from 1.5 year old NZERTF SPF.

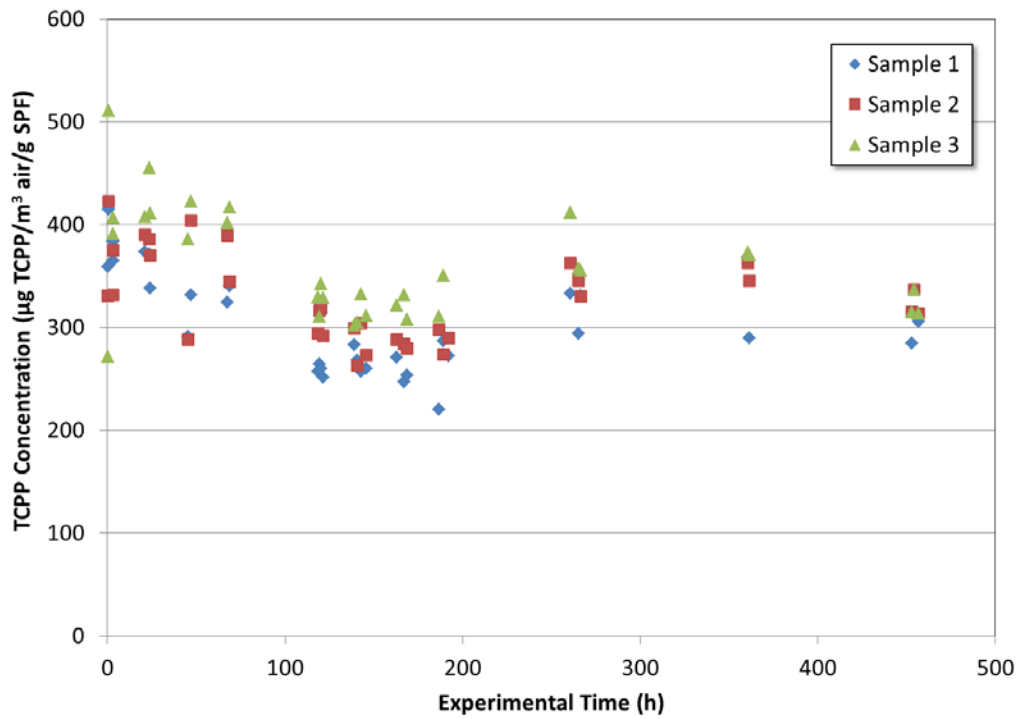


Figure 3. TCP Concentrations from new CPI SPF.

According to industry, the amine catalysts used in each SPF product are different. Some amine catalysts are designed to be reactive and are incorporated into the foam during the curing phase, while other catalysts are emitted after curing phase. PMDTA and BDMAEE (Figure 4) are examples of the later. The maximum BDMAEE micro-chamber concentration in the CPI sample was 12,000 $\mu\text{g}/\text{m}^3$ g occurred 3 hours after sampling began (note this is **NOT** three hours after the spray event). This delayed peak concentration is the result of the time required for the sample to heat to the experimental temperature and reach an local equilibrium with the exposed chamber surfaces. BDMAEE micro-chamber concentrations in the CPI foam remained above 2,000 $\mu\text{g}/\text{m}^3$ g for 120 hours. TMAEEA was detected as an emission in the CPI foam in the first 24 hours, but the concentration was just above the high detection limit of 4,700 $\mu\text{g}/\text{m}^3$. Although present in the foam (Table 2), TMIBPA was not measured above detection limits. Sample times could not be increased to lower detection limits of the amines as the high TCPF concentrations would result in saturation of the sorbent tube and analysis system. For the ~1.5 year old NZERTF sample, no amine catalysts were detected above the detection limits listed in Table 1. Amines may be present in the NZERTF sample below detection limits.

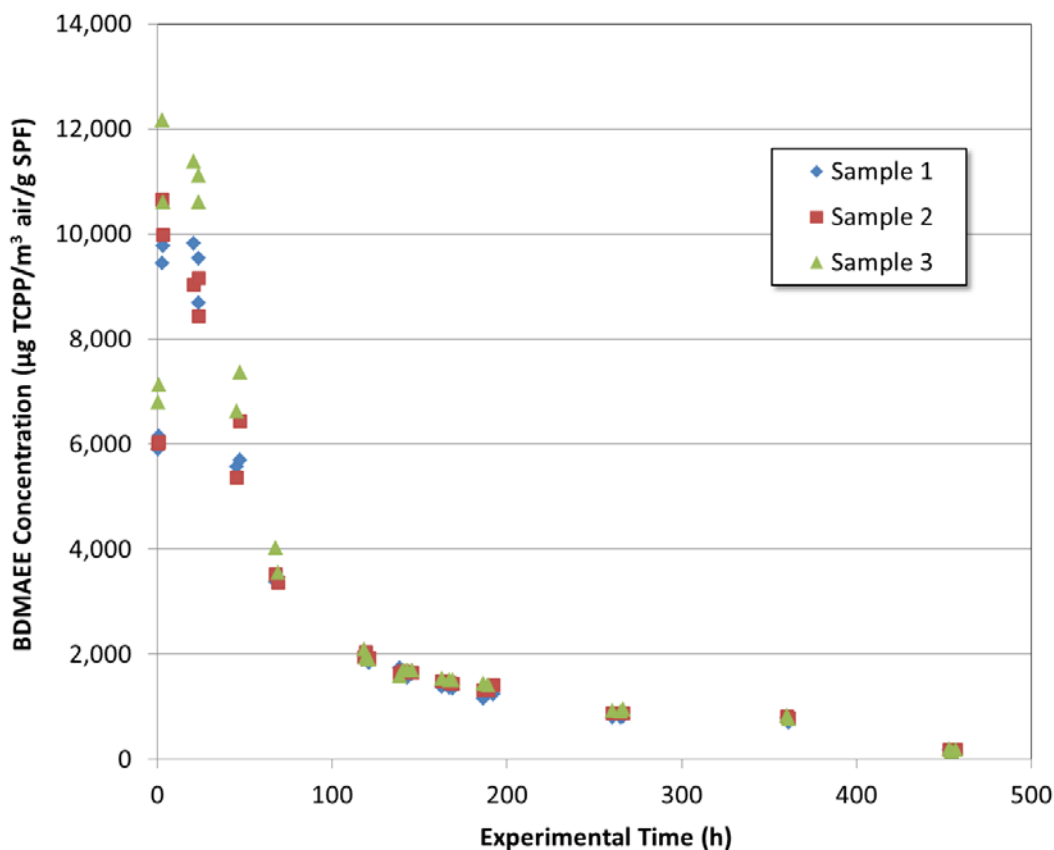


Figure 4. BDMAEE Concentrations from new CPI SPF.

Aldehydes concentrations were determined for both the NZERTF and CPI foams. A wide range of aldehydes (hexanal, heptanal, octanal, and nonanal) were detected from the NZERTF sample. However, given the fact the samples were aged in a house for 1.5 years, it is impossible to determine from these measurements alone whether the aldehydes were primary emissions or the desorption of

compounds that had been emitted by other building products and then sorbed to the SPF. The concentrations of these compounds have been measured in the indoor air of the house on a monthly basis since mid-2013, and emissions of these chemicals appear to be temperature dependent.

The CPI foam was prepared and shipped according to ASTM D7859 and then immediately placed in the micro-chamber. Hence, aldehydes sampled from the CPI micro-chambers can be attributed solely to the foam. Four aldehydes were consistently detected throughout the experiment: formaldehyde, acetaldehyde, benzaldehyde, and butraldehyde. Concentrations of the four aldehydes dropped for the first 50 hours and then stabilized (Figure 5).

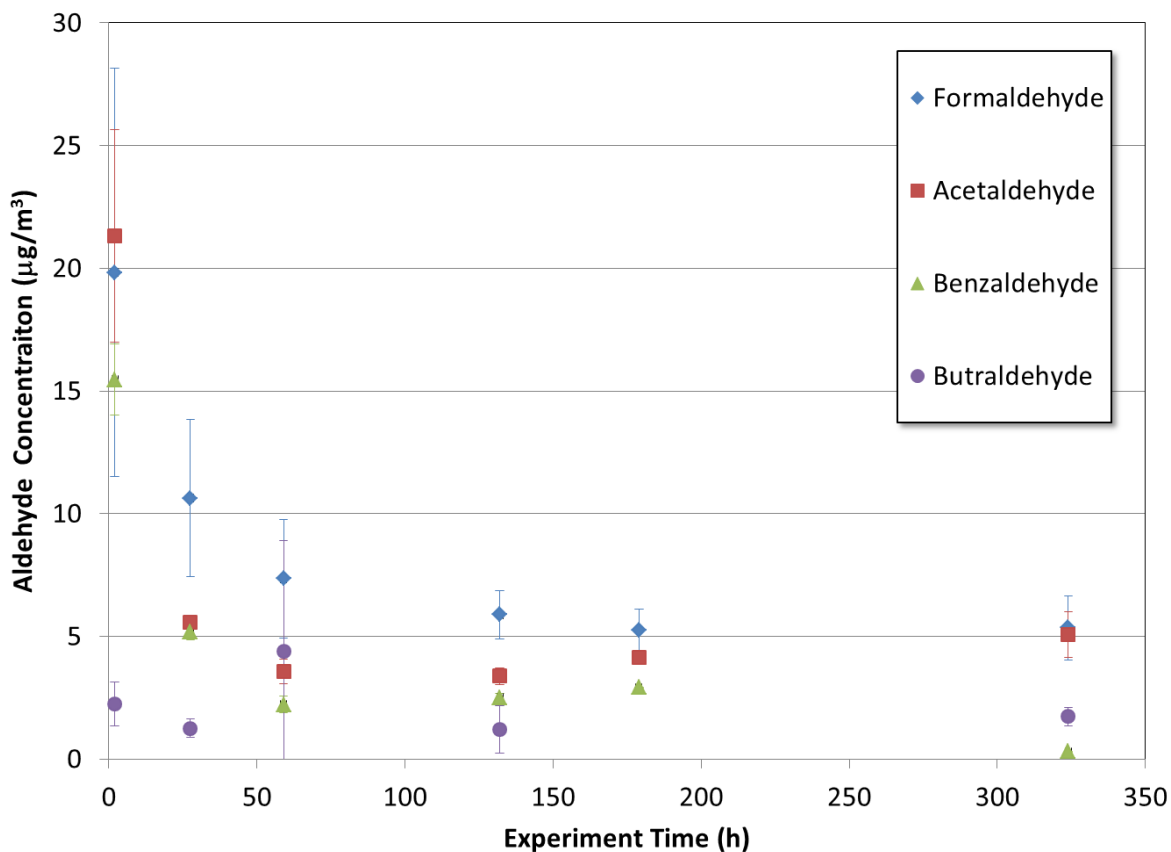


Figure 5. Aldehyde concentrations from new CPI SPF. Error bars show two standard deviations from triplicate samples run at 40°C.

In addition to the chemicals for which standard curves were prepared (Table 1), other chemicals were also identified in the emissions using the mass spectra database. Four chemicals were identified at a greater than 90 % spectral match and persisted for greater than 24 hours. The response area ratio relative to the internal standard (deuterated Toluene) chemicals are shown in Figure 6. The chemicals were not detected in samples past 48 hours.

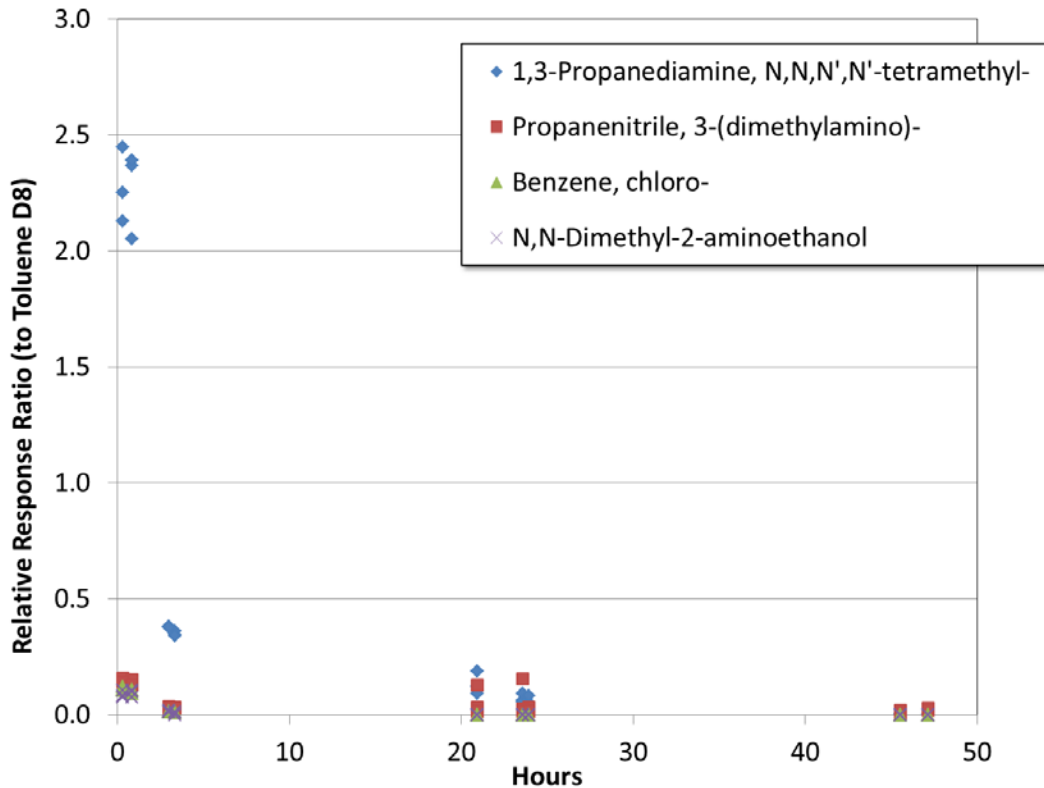


Figure 6. Relative response ratio of chemicals for which no standard curve was available from CPI SPF.

All previous data was collected at 40 °C, mimicking previous Canadian standards for SPF emission testing.¹⁰ However, the ASTM subcommittee 22.05 charged with setting up standard methods for SPF emission testing in micro-chambers is investigating a range of possible temperatures, including 23 °C. To address the role that temperature plays in SPF emissions the temperature of the micro-chambers was changed at the end of the CPI SPF experiment shown in Figures 3 through 6. The temperature was first reduced to 28 °C (adjacent equipment prevented the reduction to room temperature) for 48 hours. Six samples were taken at 28 °C (two from each chamber). The temperature was then raised to 50 °C for 96 hours. Twelve samples were taken at 50 °C. All samples were taken at least 24 hours after the temperature change. Both TCPP and BDMAEE concentrations showed an Arrhenius relationship (linear on a log scale). This indicates that the emission of these chemicals is highly temperature dependent. Any standard developed to quantify emissions into indoor air should take into account the temperatures that the foam experiences in real applications.

¹⁰ULC-S718 Site Quality Assurance Program for Spray Polyurethane Foam

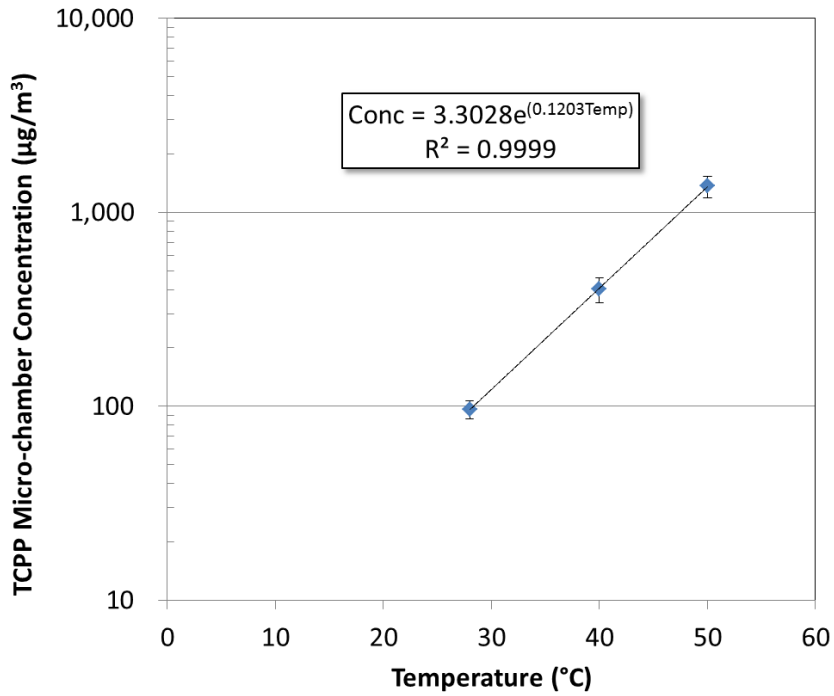


Figure 7. Average TCPP concentration from CPI SPF at various temperatures. Error bars show two standard deviations.

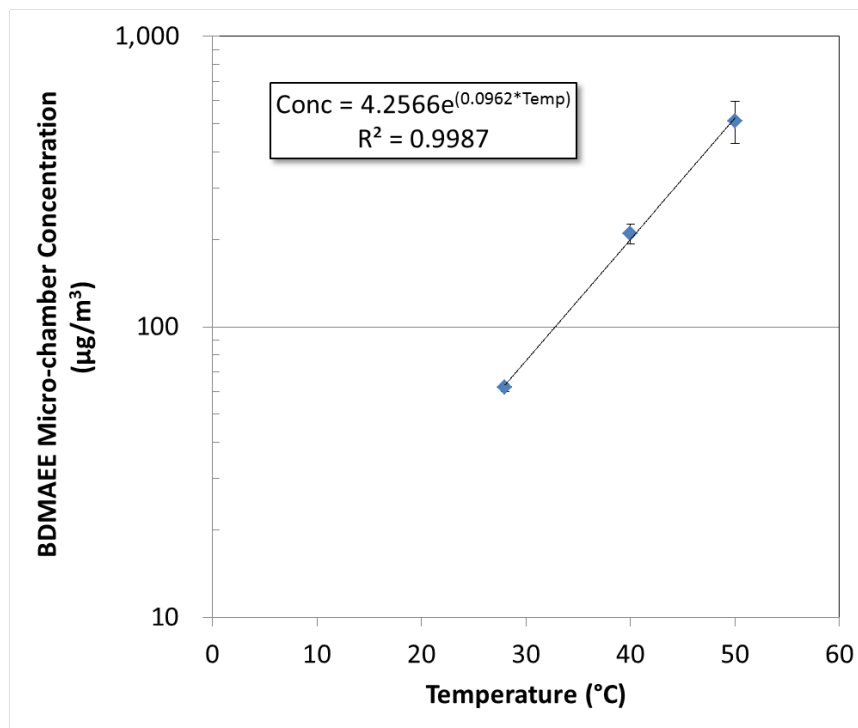


Figure 8. Average BDMAEE concentration from CPI SPF at various temperatures. Error bars show two standard deviations.

Micro-chamber Emission Rates

TCPP (Table 4) and aldehyde emission rates were determined for each experiment. Again, emission rates in this document apply only to micro-chamber conditions. This data should not be used to predict to full scale emissions until further testing has determined scaling parameters. The emission rates followed the same trends as seen with concentrations, including the temperature dependence (Figure 9).

Table 4. Average flame retardant emission rates over 500 hours. The number following the symbol ± is the numerical value of an expanded uncertainty $U = k uc$, with a coverage factor $k = 2$.

	Foam 1 Average Concentration ($\mu\text{g}/\text{m}^2 \text{ h}$)	NZERTF Average Concentration ($\mu\text{g}/\text{m}^2 \text{ h}$)	CPI Average Emission Rate ($\mu\text{g}/\text{m}^2 \text{ h}$)
TCPP	4,300 ± 1,600	540 ± 370	700 ± 210
Number of data points	48	72	98

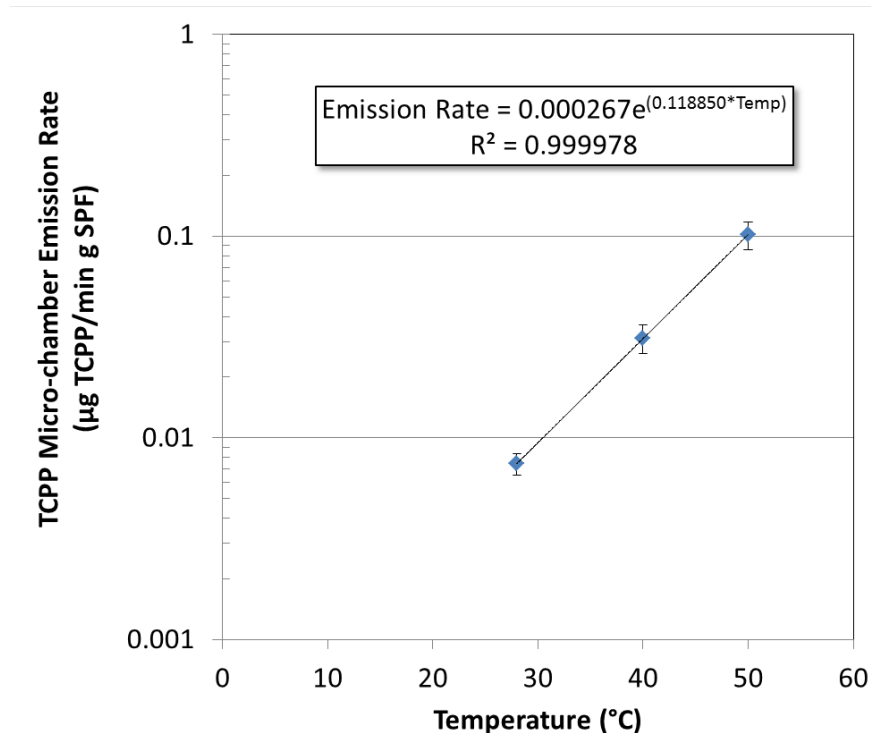


Figure 9. Average TCPP emission rates from CPI SPF at various temperatures. Error bars show two standard deviations.

The aldehyde emission rates of the CPI foam decreased over the first 100 hours of the experiment. For context, the Phase 2 CARB Equivalent Composite Wood Product Emission Rates for Formaldehyde is $62 \text{ mg}/\text{m}^2 \text{ h}$ to $137 \text{ mg}/\text{m}^2 \text{ h}$. However, these measured emission rates are not directly applicable as the CARB standards are for large and small chamber testing, not micro-

chamber testing. Further evaluation of the scaling of micro-chamber data is needed before making a direct comparison.

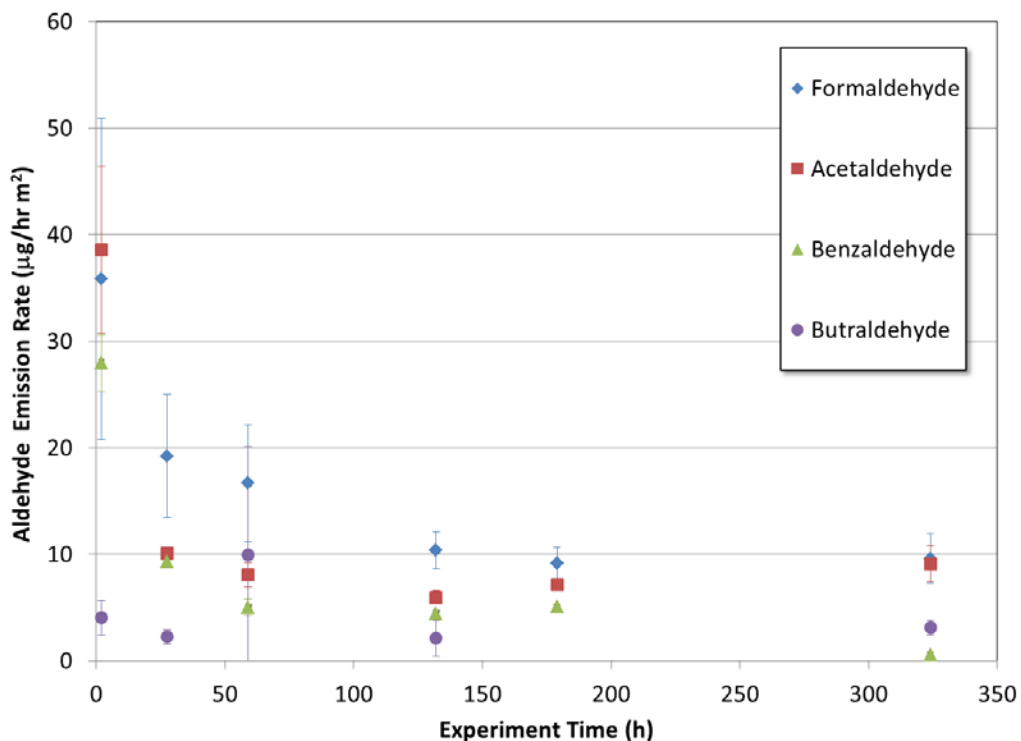


Figure 10. Aldehyde emission rates from new CPI SPF. Error bars show two standard deviations from triplicate samples.

Limitations of this work

The primary purpose of this effort was to collect information to support the development of protocols for using micro-chambers for evaluating emissions from SPF, including the development of ASTM standards. A key goal was to test the proposed methods to determine if the analytical techniques were adequate for the emitted chemicals, and to assess the role of temperature on emissions and the required sample time.

The work, however, was not intended to fully validate the proposed method. Such validation would require, among other efforts, a multi-lab study using standard gas generation sources to demonstrate the adequacy of the Tenax TA® sorbent tube - thermal desorption - GC/MS analytical approach. These particular studies are needed because this technique may not have adequate detection limits for characterization of the emissions from currently-used mixes of chemicals in commercially available SPF.

Emission factors from this work should not be used to predict emissions from other chambers or to predict real world exposures until scaling between micro-chambers and other systems has been

established for chemicals similar to those in this study. Finally, this work needs to be replicated at other labs to demonstrate the consistency of the methods employed.

Implications

Despite the above stated limitations of this work, several conclusions can be drawn from this initial data set:

- The flame retardant TCPP is emitted at near constant concentrations from SPF. Amines concentrations that are above detection limits tend to decay exponentially with time.
- These data are the first that examines emissions from SPF after prolonged curing (1.5 years). These results suggest that occupants may be exposed to measureable concentrations of the flame retardant TCPP at least 1.5 years after application.
- Although not a component of the foam, the newly sprayed SPF that was tested does emit aldehydes. However the aldehyde emission rates appear relatively low compared to other materials.
- Emissions from SPF are highly temperature dependent. Studies done at lower temperatures may not quantify emissions of lower concentration chemicals as detection limits may be an issue.

Note that these conclusions do not necessarily apply to all foams. High pressure, closed cell foam was not tested in this research. Field sprayed foam was also not tested. In addition, foam with different constituents or applied in a different manner may have different emission profiles.

Next Steps in Research Effort

Future research needs to support the development of testing protocols including the ASTM 22.05 proposed standards include:

- Verification of sampling volumes at higher chamber temperatures.
- Determine the impact of relative humidity on SPF emission rates.
- Recovery experiments for TCPP from micro-chambers at 40 °C.
- Replication of experiments for high pressure close-cell foam to determine if emission times and concentrations are consistent with open-cell foam.
- Replication of experiments for field sprayed foams.

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.