NIST Technical Note 1921

Characterization of Emissions from Spray Polyurethane Foam

Final Report to U.S. Consumer Product Safety Commission

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Wilbur L. Ross, Jr., Secretary

National Institute of Standards and Technology
Kent Rochford, Acting NIST Director and Under Secretary of Commerce for Standards and Technology

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Abstract

Spray polyurethane foam (SPF) insulation increases building energy efficiency by reducing conductive and convective heat losses through the building envelope and is used in both new construction and retrofit applications. Health complaints relating to emissions from SPF installations have spurred a joint industry and federal effort to develop standard methods to quantify airborne emissions from SPF. As part of this effort, the Consumer Product Safety Commission (CPSC) tasked the National Institute of Standards and Technology (NIST) with developing testing and measurement protocols to determine the quantities and properties of compounds released from SPF, such as amine catalysts and aldehydes, as it is applied in residential settings. Specifically, this effort examined if micro-chamber emission results can be used to determine concentrations in indoor environments and to quantify the emissions from a SPF sample that was applied in a potentially non-ideal manner. The data demonstrate that emissions from SPF are chemical, temperature, flow, and foam type dependent. Micro-chamber data can be used to compare chemical emission profiles from various foams, but micro-chamber emission rates for flame retardants cannot be directly applied to full scale emissions in a building. The results from examining SPF in a residential test home suggest that occupants may be exposed to measureable concentrations of the flame retardant tris (1-chloro-2-propyl) phosphate (TCPP) two years after application of open cell foam. CPSC submitted a SPF sample suggestive of being applied in a non-ideal manner. When the submitted SPF was tested in the micro-chamber, over 17 different chemicals were identified with a spectrum match, seven of which had not been previously identified in literature emitting from other foams. Of the chemicals for which concentrations were quantified in the micro-chamber experiments, triethylenediamine concentrations were the highest. The emission rates of six chemicals were quantified from the SPF. The emission rates of all chemicals except for TCPP decreased in a negative exponential manner. More information on chemicals emitted from SPF in buildings are needed to determine if the tested foam is indeed a misapplied foam. Emission rates in this document apply only to micro-chamber conditions. This data should not be used to predict full-scale emissions until further testing has determined mass transfer parameters.

Keywords: Spray Polyurethane Foam, Emissions, Flame Retardant, TCPP, SVOC

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1. Objective

This report summarizes activities under the FY2013 and FY2014 interagency agreements between the United States Consumer Product Safety Commission (CPSC) and the National Institute of Standards and Technology (NIST). The objective of these agreements was to characterize and quantify compounds, such as amine catalysts, flame retardants and aldehydes, that may be released from spray polyurethane foam (SPF) after application. NIST met this objective by aiding in the development of testing and measurement protocols for determining the quantities and properties of compounds released from SPF.

2. Background

SPF insulation increases building energy efficiency by reducing conductive and convective heat losses through the building envelope and is used in both new construction and retrofit applications. In 2012, over 61 million kg of SPF were installed in residential applications in the United States,[1] and the industry expects to see continued growth in the use of their products.[2]

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 cell (low density) or closed cell (medium density).

Flame retardants are present in the 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 use is not exclusive to SPF, and it 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 United States Environmental Protection Agency (EPA) Design for the Environment program as having a high hazard for reproductive and developmental effects.[10]

The CPSC, along with the EPA, have received a number of health complaints that are potentially associated with SPF applications.[11] Residents have complained of health impacts including severe respiratory irritation, breathing difficulties, dizziness and nausea in the timeframe of days to months after SPF installation in a home. In some cases, consumers report that they can no longer live in their homes.[11] This timeframe 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.[12] However, direct connection between these health symptoms and SPF emissions has yet to be established. In order to support studies investigating SPF emissions, 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.

CPSC tasked NIST with performing research to characterize SPF emissions to assist CPSC staff in determining what compounds in SPF insulation have the potential to impact the health of consumers with SPF installed in their homes.

2.1. Tasks

There have been two interagency agreements between CPSC and NIST. A summary of the tasks (A-F) of the first interagency agreement (CPSC-I-13-2016) is provided here:

A. **Develop Testing Plan**. The ASTM Indoor Air Quality (D22.05) subcommittee develops standard test methods and protocols to determine 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). A testing plan was developed based upon WK40293 to use micro-chambers to measure aldehyde, amine, and flame retardant emissions from SPF samples.

B. **Experimental Testing – Phase 1**. The experimental protocol was used to measure amine and flame retardant emissions from three SPF foams: 1) low pressure, closed cell SPF, which is commonly applied by do-it-yourself applicators, 2) high pressure, open cell, low density SPF which 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). Aldehyde emissions were measured from the CPI SPF sample.

C. **Letter Report on Phase I.** A September 2013 letter report from NIST to CPSC provided a summary of the proposed micro-chamber methods to analyze amines and flame retardants using a Gas Chromatograph/Mass Spectrometer (GC/MS) and aldehydes using a Liquid Chromatograph/Ultraviolet Spectrometer (LC/UV).

D. **Experimental Testing – Phase II.** This effort examined the impact of flow rate on the emission of chemicals from SPF samples in micro-chambers. This data was used to assist in setting proposed ASTM WK40293 consensus values for these parameters.

E. **Standards Development.** NIST actively participated in activities within D22.05 related to consensus standards for the measurement of SPF emissions. NIST participated in semi-annual D22.05 subcommittee meetings (4/14/13, 10/22/13, 4/7/14) and D22.05 conference calls (3/25/14) related to the topic.

F. **Final Report.** A final report covering the data in the first interagency agreement was submitted to CPSC in June 2014. The conclusions of this report include:

    - The flame retardant TCPP was emitted at near constant concentrations from SPF. Amines concentrations above detection limits tend to decay exponentially with time.
    - TCPP emissions were detected in micro-chamber studies over 1.5 years after application.

- Although not a component of the foam, newly sprayed tested SPF emitted aldehydes. However, the aldehyde emission rates from SPF appeared to be relatively low compared to aldehyde emission rates from other materials.
- Emissions from SPF are temperature dependent. Studies done at lower temperatures may not quantify emissions of lower concentration chemicals as detection limits may be an issue.

Note that the conclusions of this report do not necessarily apply to all foams. High pressure, closed cell foam was not tested in this phase. Field sprayed foam was also not tested.

More detail about the first interagency agreement (CPSC-I-13-2016) can be found in the final report.[13] The work for the second interagency agreement (CPSC-I-14-0023) had six major tasks that are the focus of this report:

G. **Indoor concentration estimation from micro-chamber emission results**. NIST determined SPF emission rates in micro-chambers and measured indoor concentrations in the NIST Net Zero Energy Residential Test Facility (NZERTF). The purpose of the analysis was to determine if the micro-chamber data could be used to estimate indoor concentrations in an actual residential facility.

H. **Experimental Testing – closed cell foam.** Previous work investigated emissions from open cell foam. In order to determine appropriate closed cell foam sampling times for ASTM standards under development, NIST conducted micro-chamber testing of a closed cell, high pressure SPF sample.

I. **Experimental Testing – Non-ideal foam**. One hypothesis to explain consumer complaints related to SPF is that they are the result of applying SPF in a non-ideal manner. Non-ideal conditions include off-ratio (A-side to B-side) application, low substrate temperature application, and incorrect nozzle pressure and temperature. To date, there is minimal data on emissions from non-ideal foam. This task involved the analysis of two SPF samples from a residential building in which the occupants complained about SPF emissions and health effects. This foam will be described in this report as non-ideal foam. However, no details are available about the preparation and application of this specific foam.

J. **Standards Development.** NIST actively participated in activities within D22.05 related to consensus standards for the measurement of SPF emissions. NIST presented data at the ASTM D22.05 SPF symposium in Anaheim, California in April 2015, submitted an article to the ASTM Selected Technical Papers (STP)[14] resulting from that symposium, and participated in semi-annual D22.05 subcommittee meetings (10/6/14, 4/27/15, 10/22/15, 4/12/16) and D22.05 conference calls (6/12/14, 11/12/14, 12/18/15, 8/18/15, 10/22,15, 3/15/16) related to the topic.

K. **Experimental Testing – Standard Support Tests**. In order to help validate ASTM standards related to SPF emissions currently under development, NIST conducted experiments to determine the impact of temperature and humidity on SPF emissions in micro-chamber testing.

L. **Final Report**. This document serves as the final report for this interagency agreement.

Tasks G and I are described in detail in Sections 3 and 4 respectively of this report. Task H and K are described within the description of Task G (Sections 3.2.1.1, 3.2.1.4 and 3.2.1.5).

2.2. Data Use

This research was designed to aid CPSC in assessing chemical emissions from SPF. This work also contributed to the development and evaluation of voluntary standards for testing emissions from SPF. Specifically, the work supported the ASTM Indoor Air Quality (D22.05) subcommittee efforts to standardize test methods and protocols relating to WK40293. Some of the measurement parameters in this study varied from the values that the subcommittee is considering. Thus, comparisons to other data should note the specific experimental parameters employed.

3. Indoor Concentration Estimation from Micro-chamber Emission Results

This effort focused on the flame retardant TCPP. TCPP was the only chemical emitted from SPF that could be both measured as being emitted from SPF samples and likely did not have other sources in a full-scale residential test facility. TCPP concentrations were measured in two environments: micro-chambers and in a residential test facility. The specific objectives were to 1) use micro-chamber data to asses if TCPP emissions are controlled by internal material diffusion or external mass transfer; and 2) compare TCPP emission rates from micro-chamber experiments to emission measurements in the full-scale residential test facility.

If emissions from TCPP are controlled by internal material diffusion, direct scaling of emission rates from micro-chambers to residences may be possible; however, if emissions are controlled by external mass transfer limitations then direct scaling of emission rates is unlikely to be successful. In general, the emissions of volatile organic chemicals (VOCs) from materials are controlled by the diffusion of the VOC through the material matrix and are not highly dependent on indoor environmental conditions. This can allow the direct use of VOC chamber emission factors to predict emissions in full scale buildings. In contrast, the emissions of semi-volatile organic chemicals (SVOCs) tend to be environment dependent and controlled by the airflow above the material.[15] 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.[15]

Traditionally, VOCs and SVOCs are defined based upon their vapor pressures or boiling points. TCPP has a wide range of reported values for vapor pressures.[16, 17] Depending on definitions and reported chemical properties, TCPP could be defined as either a VOC or a SVOC. The European Union Paints Directive (Directive 2004/42/EC)[18] defines a VOC as any chemical with a boiling point below 250 °C. TCPP has reported boiling points ranging from 235 °C[19] to >270 °C[16]. Hence, TCPP could be behaving either as a VOC or SVOC when emitting from SPF. As a result, it is important to determine the mass transfer limitations for TCPP emitting from SPF.

3.1. Methods

Different types of SPF were tested in micro-chamber experiments to examine TCPP mass transfer limitations. In addition, TCPP concentrations and air change rates were determined in a residential test facility.

3.1.1. Foams Tested

Three 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 for the ASTM D22.05 SPF working group 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 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.[20] 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. Closed 1 was evaluated in part to address the Task H objective.

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 2[2]	Open Cell	7	Summer 2012	1/28/2014
Closed 1	Closed Cell	30	11/4/2014	4/13/2105

[1] Density determined by measured initial mass and approximate volume.
[2] Open 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 NIST NZERTF in the summer of 2012. The NZERTF was built to support the development and adoption of cost-effective net-zero energy designs and technologies, construction methods, and building codes. The design and construction of the NZERTF are described in Pettit et al.[21] The NZERTF is a two-story, detached house with an unfinished basement and attic within the building thermal envelope. The garage is not attached. The house is similar in size (occupied floor area of 242 m^2, 485 m^2 including the attic and basement) and aesthetics to homes in the surrounding communities. To achieve the net-zero energy goals, several technologies are employed, including a high efficiency heat pump, a solar hot water system, a 10.2 kW photovoltaic system, and a heat recovery ventilator (HRV). To comply with the outdoor air requirements in ASHRAE Standard 62.2-2010[22] the HRV was sized to continuously deliver 137 m^3 h^{-1} of outdoor air. Special attention was paid to the design and construction of a highly insulated and tight building envelope. Approximately 15 m^2 of high pressure, open cell SPF was used to insulate the basement rim joists. The basement is unfinished, and the SPF is not covered by any finishing material. The house has no carpet and is not furnished other than permanently installed cabinetry. Hence, if TCPP is present in the indoor air of the house and not measured in the outdoor air, then it can likely be attributed to the SPF.

This work included measurements of airborne TCPP concentrations both in the NZERTF and in a micro-chamber for the same foam. In January of 2014, three roughly 0.8 g samples were cored from SPF in the basement rim joists of the NZERTF (sample Open 2) and tested in micro-chambers. In July and August 2014, airborne TCPP concentrations were measured in the basement and first floor of the NZERTF.

3.1.2. Micro-chamber Experiments

A cutting tool was machined to precisely cut SPF to fit tightly within Markes 250 micro-chambers (Figure 1) according to ASTM D7859. The top of the foam was not removed. Unless otherwise noted, the chambers were operated at a temperature of 40 °C with a 100 mL min^{-1} airflow of ultra-high purity air. The temperature of 40 °C was chosen to be consistent with other standards,[23] to increase emissions to reduce problems associated with low detection limits, and to capture the performance of foam in environments with elevated temperatures, such as attics and exterior wall cavities. The proposed consensus temperature in ASTM WK 40293 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 impact of airflow was investigated by running samples of Open 1 at 50 mL min^{-1}, 100 mL min^{-1} and 200 mL min^{-1}. The airflow was at 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. Open 1 was also tested at zero humidity for comparison purposes. The airflow contained zero humidity for the Closed 1 sample, based on discussions within the ASTM subcommittee D22.05 on humidity values for a proposed standard.

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 sample volume) 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, three micro-chambers were run concurrently. An empty fourth chamber was typically used as a control. Each foam was analyzed for at least 300 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.

3.1.3. NZERTF Air Sampling

The indoor air was sampled from the first floor and basement of the NZERTF for TCPP over a period of two months in the summer of 2014. Air temperatures shown in the following tables and figures are 12-hour average readings from a thermocouple located in the center of the open basement or in the open floor plan area of the first floor.

The NZERTF TCPP sampling involved two Tenax sorbent tubes in series. The first tube was used to quantify the TCPP concentration and the second to evaluate if there was breakthrough through the first tube. If TCPP breakthrough to the second tube was found, the data were not used. For each sampling event three sets of tubes were prepared. Each tube set was sampled at 50 mL min^{-1} using a mass flow controller sampling system. Sampling times varied from 52 min to 216 min (average 155 min). The tubes were separated and spiked with internal standard (1.0 µL of 1.25 mg Toluene D-8 mL^{-1} of methanol).

3.1.4. 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. Operational parameters for the thermal desorption system and GC/MS can be found in the supplementary information (Section 9 of this report). For all open cell samples, each sample tube was followed by a blank tube to check for carryover between samples.

In the tested foams, TCPP typically consisted of three isomers: tris (1-chloro-2-propyl) phosphate (≈66 % based on GC/MS area response), bis(1-chloro-2-propyl) (2-chloropropyl) phosphate (≈30 %) and (1-chloro-2-propyl) bis(2-chloropropyl) phosphate (≈4 %). In this research, only the first two isomers were consistently detected in the air above quantification limits. The response ratios of the three isomers on the tubes with TCPP and any carryover on subsequent blanks were summed. The response ratio for each isomer was integrated using a five-point standard curve. The total reported TCPP concentration was determined as the sum of the isomer concentrations.

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.[24] 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 VOCs. These other chemicals were analyzed in similar manners to those described for TCPP above and some are presented in the discussion to illustrate additional concepts and trends.

3.1.5. Other TCPP Analyses

To ensure that there were no sources of TCPP other than the SPF in the NZERTF basement, small samples of a variety of materials from the NZERTF basement with foam components were placed in a micro-chamber at 40 °C and sampled for TCPP using the same Tenax sorbent tube and TD-GC/MS analysis methods. The sampled materials include rigid expanded polystyrene insulation, duct insulation, and two varieties of pipe insulation. No TCPP was detected from any of these materials (method detection limit 2.0 μg TCPP g^{-1} material m^{-3} air to 6.3 μg TCPP g^{-1} material m^{-3} air).

3.1.6. Tracer Gas Measurements of Air Change Rates

Air change rates in the NZERTF were measured by tracer gas decay (using sulfur hexafluoride, SF_6) following ASTM E-741 in July 2014.[25] These rates reflect the combination of mechanical HRV ventilation associated with the HRV operation and infiltration due to building envelope leakage. An automated tracer gas system with sulfur hexafluoride injection and sampling at multiple locations (eight indoor and one outdoor) was employed. Concentration measurements were made at each location once every 27 minutes following a one-hour mixing period. The estimated uncertainty in the measured air change rates is 10 %.

3.1.7. Emission Rate Calculations

TCPP emission rates were calculated from both the micro-chamber and NZERTF experiments. For the micro-chamber, a single zone mass balance model was used to determine emission rates:

$$V_{chamber}\frac{dC}{dt} = Q_{in}C_{in} - Q_{in}C + E_{f,chamber}A_{chamber} \tag{1}$$

where Q_{in} is the airflow rate into the chamber ($m^3\ h^{-1}$), $V_{chamber}$ is the total chamber volume (m^3), C is the average chamber concentration (micro-chamber exhaust, μg m^{-3}), C_{in} is the concentration in the inlet air (μg m^{-3}), $E_{f,\ chamber}$ is the area specific emission rate (μg $m^{-2}\ h^{-1}$) and $A_{chamber}$ is the surface area of the SPF sample (m^2). Sorption and desorption of TCPP to the exposed micro-chamber walls was assumed to be in equilibrium at the time scales of sampling and are not considered in the data analysis. The green data points (Open Cell 2) in Figure 2 show the TCPP concentration in the micro-chamber reaching a steady-state value of ≈300 μg/m^3 to 400 μg/m^3 after about four-hours. This result indicates that the exposed surface of the micro-chamber is in equilibrium with TCPP within four hours (sorption and desorption rates are approximately equal). Hence, for the time scales of sampling (daily), steady state conditions can be assumed and Equation (1) simplifies to:

$$E_{f\ chamber} = \frac{Q_{in}\left(C_{ss} - C_{in}\right)}{A_{chamber}} \tag{2}$$

The NZERTF basement was modeled using a single zone mass balance with no net sorption or reaction losses. The exposed SPF in the NZERTF was sprayed at least two years prior to sampling. In this timeframe, it is likely that the building materials have reached an equilibrium with TCPP at the ambient temperatures (20 °C to 22°C) the house was operated at for the two years prior to the sampling. Hence, sorption and desorption rates are likely to be approximately equal. For this model, basement air was exchanged with the 1st floor and the outside. TCPP concentrations were measured on the first floor and assumed to be constant:

$$V_{Basement}\frac{dC}{dt} = Q_{1st\ in}C_{1st} + Q_{outside\ in}C_{out} - Q_{1st\ out}C - Q_{outside\ out}C + E_{f\ NZERTF}A_{SPF} \tag{3}$$

where $Q_{1st\ in}$ is the airflow rate from the 1st floor to the basement ($m^3\ h^{-1}$), $Q_{1st\ out}$ is the airflow rate from the basement to the 1st floor ($m^3\ h^{-1}$), $Q_{outside\ in}$ is the airflow rate from the outside to the basement ($m^3\ h^{-1}$), $Q_{outside\ out}$ is the airflow rate from the basement to the outside ($m^3\ h^{-1}$), $V_{Basement}$ is the basement volume (m^3), C is the average indoor basement concentration ($\mu g\ m^{-3}$), C_{1st} is the TCPP concentration measured on the 1st floor ($\mu g\ m^{-3}$), C_{out} is the outdoor TCPP concentration ($\mu g\ m^{-3}$), $E_{f,\ NZERTF}$ is the NZERTF area specific emission rate ($\mu g\ m^{-2}\ h^{-1}$) and A_{SPF} is the surface area of the SPF in the basement of the NZERTF (m^2). The outdoor TCPP concentration (C_{out}) was below detection limits and is assumed to be zero in the analysis.

The airflow between the basement, the outdoors and the rest of the house is dominated by the heating, ventilation, and air conditioning (HVAC) system. The HVAC total supply airflow rate into the basement, based on airflow rate measurements in the system, was 103 $m^3\ h^{-1}$. All the return vents for the HVAC system are located in the 1st and 2nd floors. The infiltration rate for the entire house measured by SF_6 tracer decay was roughly 30 $m^3\ h^{-1}$, with some dependence on outdoor weather conditions. Given the ratio of the external surface area of the basement to the entire house and that $Q_{outside\ in}$ is a portion of the infiltration rate for the entire house, $Q_{outside\ in}$ is at least an order of magnitude smaller than the total supply airflow rate to the basement. As a result, for the purpose of emission calculations, $Q_{outside\ out}$ and $Q_{outside\ in}$ were assumed to be zero. Given that there are no HVAC return vents in the basement, $Q_{1st\ out}$ can be assumed to equal the airflow from the HVAC supply. Hence, $Q_{1st\ in}$ and $Q_{1st\ out}$ were set equal to the total supply airflow rate to the basement, adjusted for the system operating fraction during the TCPP sampling period. Based on these assumptions, the area specific emission rate ($E_{f,\ NZERTF}$) for foam in the NZERTF at steady state ($C = C_{ss}$) can be calculated from Equation (3):

$$E_{f,NZERTF} = \left(C_{ss} - C_{1st}\right)\frac{Q_{1st\ in}}{A_{SPF}} \tag{4}$$

3.2. Results and Discussion

As stated above, the objectives of this work were to 1) use micro-chamber data to asses if TCPP emissions are likely controlled by internal material diffusion or external mass transfer; and 2) compare TCPP emission rates from micro-chamber experiments to emission measurements in a full scale residential test facility. To address the first objective, a series of experiments were performed in micro-chambers. This data was then compared to measurements made in the NZERTF. All reported concentration and emission rates in this document only apply to the tested conditions and foams.

3.2.1. Micro-chamber Experiments

A series of micro-chamber experiments were conducted to determine the impact of foam type, chemical type, flow rate, temperature and humidity on TCPP emissions.

3.2.1.1. Influence of the Foam.

TCPP emitted from all tested 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, which was greater than 400 hours of sampling (Figure 2). The two open cell foam TCPP concentrations were not statistically different (p=0.06), even though Open 1 was freshly sprayed and Open 2 was applied over 2 years prior to sampling. All statistical comparisons in this section (3.2.1.1) use a one-way ANOVA, Tukey-Kramer analysis with $\alpha = 0.05$. The average TCPP concentration over 400 hours of sampling for Open 1 was 400 μg m^{-3} (n=98, standard error 23 μg m^{-3}) and 314 μg m^{-3} (n=78, 23 μg m^{-3}) for Open 2. The Open 2 results show that, for this sample and insulation temperatures of 40 °C, flame retardants can be emitted at measurable concentrations more than 24 months after application.

Unlike the tested open cell foams, the TCPP concentrations from the closed cell sample (Closed 1) decreased exponentially during the first 100 hours (Figure 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 1[3]). One hypothesis to explain the decrease in emission rate is that the TCPP is initially located near the surface and 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 from the open and closed cell foams suggest that the limiting mass transport mechanism for TCPP is fundamentally different for the two types of 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 the closed cell 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 in order to model TCPP in full scale systems.

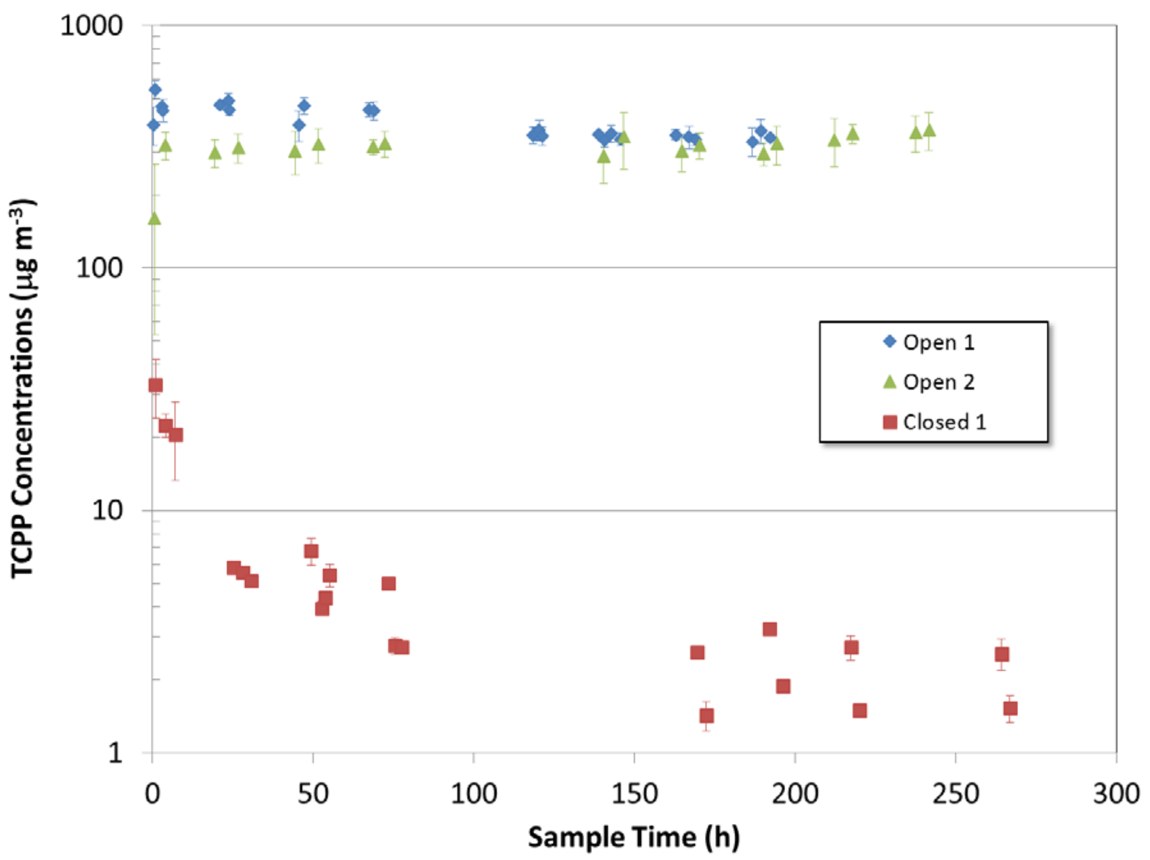

Figure 2. TCPP concentrations from open and closed cell SPF tested in 40 °C micro-chambers. Error bars show standard error in triplicate data.

For both open and closed cell foams, it appears that the concentrations of TCPP did not appreciatively change after roughly 150 hours. For micro-chamber experiments, sampling at approximately 150 hours should be sufficient to determine differences in steady state TCPP emissions from different samples of SPF.

3.2.1.2. Influence of the Chemical.

Figure 2 illustrated that the type of foam will influence the emission profile and likely the controlling mass transfer mechanism of a given chemical from SPF. Examining how other chemicals emit from foam can give insights into the mechanisms controlling emissions. For example, the emission profile may be different for different chemicals in a single foam. Figure 3 shows a decaying concentration for the amine catalyst bis (2-dimethylaminoethyl) ether (BDMAEE) and the steady emission profile for TCPP from the Open 1 sample. BDMAEE has 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 1[3]). Hence, the depletion of BDMAEE may be dominating the emission profile, while the large source of TCPP results in no reduction in the TCPP concentration.

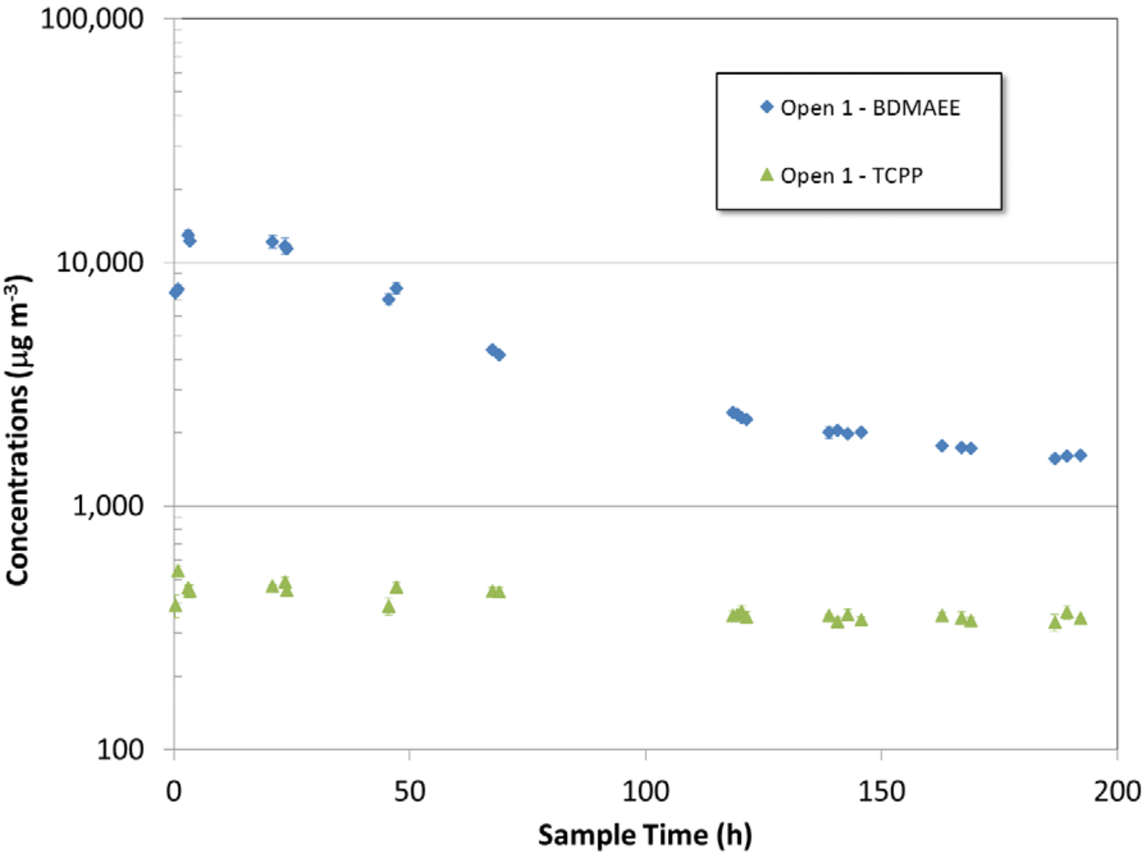

Figure 3. TCPP and BDMAEE concentrations from open cell SPF tested in 40 °C micro-chambers. Error bars show standard error in triplicate data.

Figure 4 illustrates emissions from the Closed 1 sample. The 1,4 dioxane, 1,2 dichloropropane and TCPP concentrations all decayed rapidly in the first 100 hours before decreasing at a slower rate. Whether this decay for 1,4 dioxane and 1,2 dichloropropane illustrates source depletion or diffusion limitation is unknown since determining the initial concentrations in the foam was beyond the scope of this research. Salthammer, et al. [26] identified 1,2 dichloropropane as a degradation product of TCPP in soft polyurethane foam. Regardless of the exact mechanisms, Figure 3 and Figure 4 illustrate that the emissions of chemicals from a specific foam can be controlled by a range of mechanisms and should not be assumed to be consistent across the range of chemicals present in the foam.

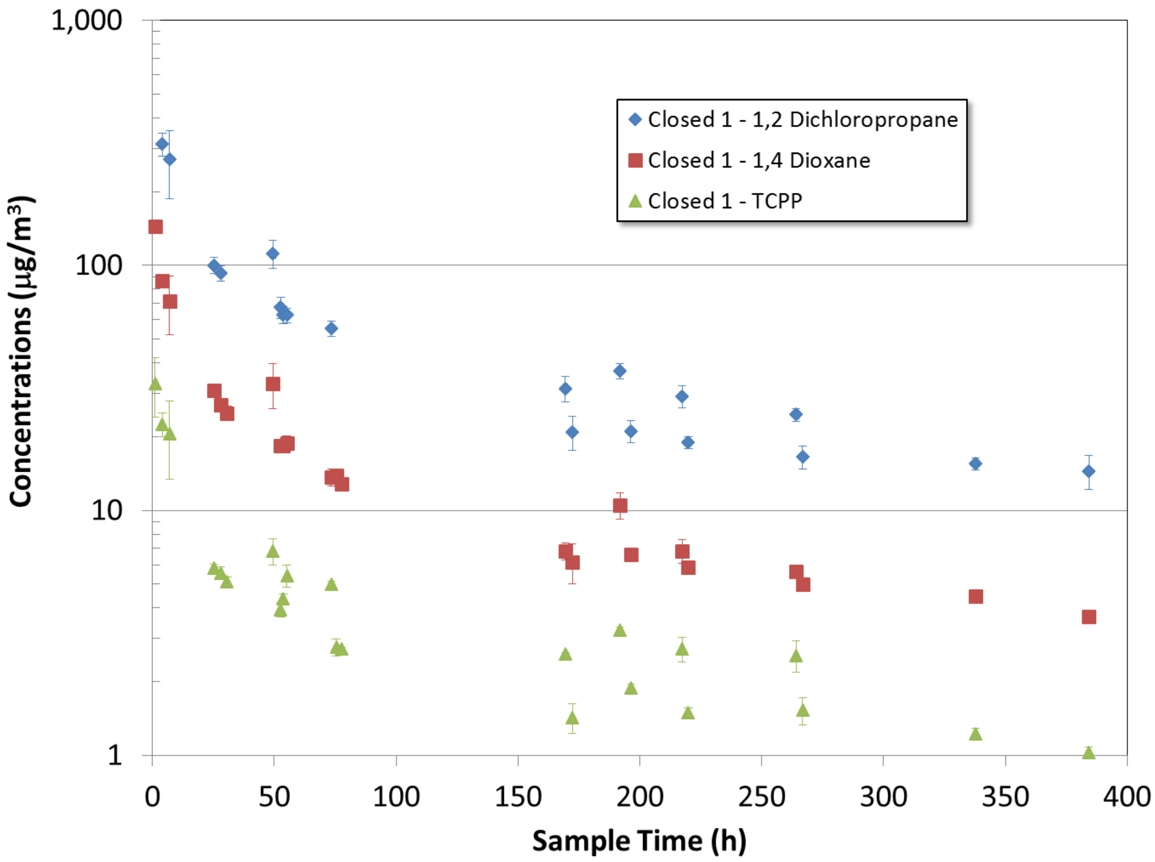

Figure 4. TCPP, 1,2 dichloropropane and 1,4 dioxane concentrations from closed cell SPF tested in 40 °C micro-chambers. Error bars show standard error in triplicate data.

3.2.1.3. Influence of the Micro-chamber Flow Rate.

A series of experiments were conducted to determine if the flow rate (a surrogate for the mass transfer coefficient) influenced the emission rate (µg m^{-2} hr^{-1}) of TCPP from open cell foam. Samples of Open 1 foam were run at 50 mL min^{-1}, 100 mL min^{-1}, and 200 mL min^{-1}. Figure 5 shows the TCPP concentrations at the three flow rates. There was a significant difference between the emission rate for TCPP concentrations at 50 mL min^{-1} compared to 200 mL min^{-1} (p=0.0001) and 100 mL min^{-1} compared to 200 mL min^{-1} (p=0.0033). Ni et al.[27] used a passive sampler to demonstrate that the emission rate of TCPP from wallpaper depended upon the diffusion length to the passive sampler. This indicates that the TCPP emission rate from the wallpaper depended primarily on external mass transfer limitations, and not internal diffusion within the wallpaper, which suggests that the flow field around the SPF may impact the TCPP concentration measured. Combined with the data in Figure 2, this suggests that TCPP is likely behaving as an SVOC in open cell foam and direct predictions of building scale TCPP concentrations using micro-chamber emission factors alone will not be accurate. Therefore, building scale TCPP emission modeling from open cell SPF must consider the mass transport properties of the foam.

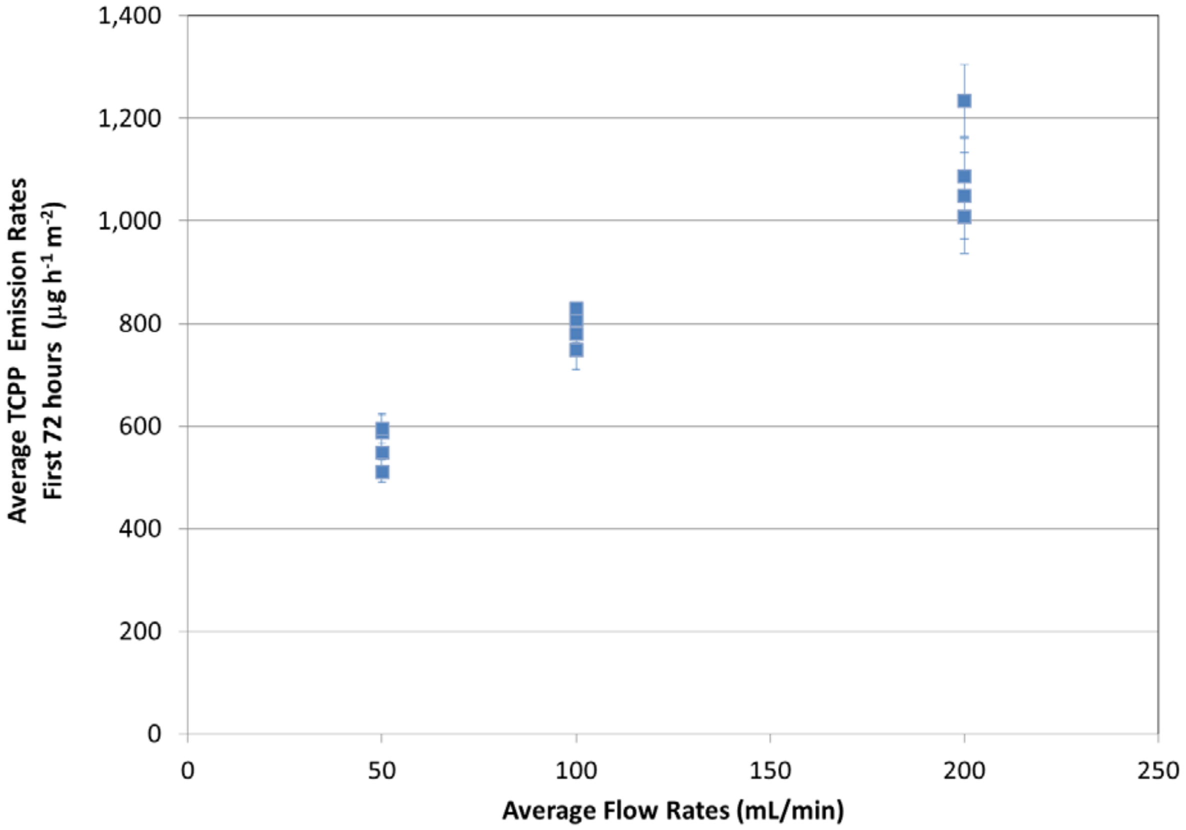

Figure 5: Average TCPP emission rates for experiments run at increasing flow rates. Error bars show standard error in triplicate data.

3.2.1.4. Influence of the Micro-chamber Temperature.

In order to help support the development of ASTM standards related to SPF emissions, NIST conducted experiments to determine the impact of temperature and humidity on SPF emissions in micro-chamber testing. The influence of humidity and temperature were not part of Task G, but rather Task K. However, the methods used were the same as Task G, so the data is presented here.

In field applications SPF experiences a range of temperatures. Hence, it is important to understand the temperature dependence of TCPP 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. Temperatures typically reached steady state values within one hour of the change. Over the course of the 550 hour experiment, less than 1,400 µg of TCPP was emitted from the roughly 140,000 µg of TCPP present initially in the 1.2 g SPF sample (TCPP was roughly 12 % of the mass of ingredients used to make Open 1[3]). A separate test on a separate sample of Open 1 was conducted at 60 °C. Figure 6, shows the average emission rates for TCPP at the four temperatures for Open 1 foam. For comparison purposes, data from Ni et al.[27] of measured TCPP emission rates from wallpaper at various temperatures using a passive sampling system are also shown. This data indicate that TCPP emissions are exponentially dependent upon temperature for open cell foam. Hence, a small change in the SPF temperature may have a relatively large impact on the TCPP concentration in the building.

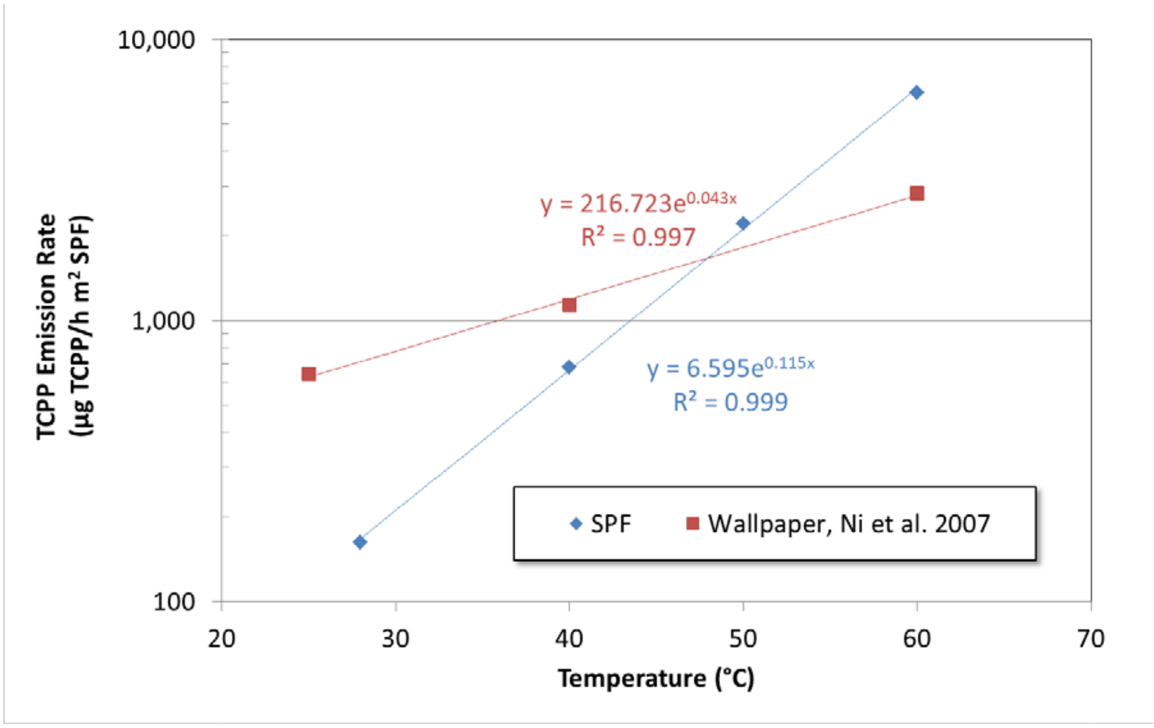

Figure 6: Average TCPP emission rates for experiments run at increasing temperate.

3.2.1.5. Influence of the Micro-chamber Humidity.

A sample of Open 1 was tested at 40 °C and 60 °C with and without water vapor present. The foam was sampled seven times over six days in triplicate with 0 % relative humidity. The same foam was also sampled four times over three days with an absolute humidity of 9.4 g m^{-3} (standard error 0.1 g m^{-3}, equal to a relative humidity of 40.6 % at 25 °C). The foam was then raised to 60 °C with an absolute humidity of 8.9 g m^{-3} (standard error 0.1 g m^{-3}, 38.4 % relative humidity at 25 °C) and sampled over five days. The average TCPP concentration with humidity present was higher than without humidity (Table 2). The difference was not statistically significant at 40 °C, but was significant at 60 °C (p=0.009). Overall, the impact of humidity on the emission of TCPP was not as large as the impact of temperature.

Table 2. Impact of humidity on average TCPP concentration in micro-chambers.

Temperature (°C)	Absolute Humidity (g m^{-3})	Standard Error (g m^{-3})	Average TCPP Concentration (µg m^{-3})	Standard Error (µg m^{-3})	Number of Samples (n)
40	0	NA	308	16	21
40	9.4	0.1	355	16	12
60	0	NA	2,630	96	25
60	8.9	0.1	3,500	156	21

3.2.2. NZERTF Measurements

A series of measurements were conducted in the NZERTF to determine the source of the TCPP and if micro-chamber emission rates can be directly used to predict TCPP concentrations in building scale environments.

3.2.2.1. Source of TCPP.

The NZERTF has approximately 15 m^2 of open cell SPF sprayed to insulate and seal the basement rim joists. The SPF is exposed to the basement air with no covering finish material. In some places the SPF is greater than 10 cm deep. The basement ceiling is not finished, and the basement has no internal dividing walls other than the stairwell. SPF concentrations were measured over a period of 43 days in the summer of 2014, two years after the foam was installed. TCPP concentrations were measured in both the first floor and the basement (Table 3). Average TCPP concentrations were significantly higher in the basement than the first floor (p=0.008), despite the fact the temperature was higher in the first floor. These results support the source of the TCPP being located in the basement of the NZERTF. If the TCPP source was uniformly distributed throughout the NZERTF, one would expect higher TCPP concentrations in the first floor associated with the higher temperatures (as seen in Figure 6 of the micro-chamber data).

Table 3. Average TCPP concentrations measured in the NZERTF.

Location	Average Temperature (°C)	Number of Samples	Average TCPP Concentration (µg m^{-3})	Standard Error (µg m^{-3})
1st Floor	23.7	9	**1.5**	0.1
Basement	21.0	12	**2.8**	0.1

TCPP can often be found as a flame retardant in furniture and insulation materials. However, as noted earlier, there is no furniture in the NZERTF. Five samples of other insulation materials from the basement walls, pipes and ductwork were tested at 40 °C in the micro-chamber, and no TCPP was detected emitting from any of the materials. Given the higher concentrations of TCPP in the basement and the fact no other sources of TCPP were found in the basement, it can be reasonably concluded that the TCPP measured in the upstairs living area was the result of emissions from the 15 m^2 of open cell SPF sprayed in the rim joists located in the basement.

Given that TCPP emissions are temperature dependent, the temperature in the NZERTF was raised for four days. The average TCPP concentration at the elevated temperature (28.5 °C) was 3.4 times higher than the average TCPP concentration at typical basement temperatures (21.5 °C, Figure 7).

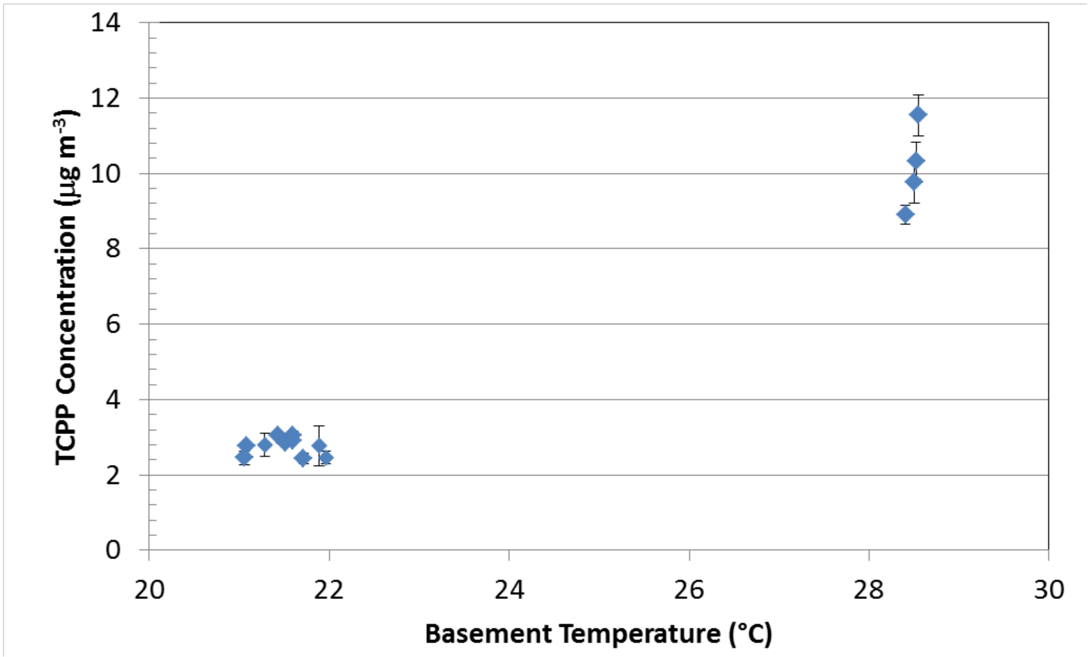

Figure 7: Average TCPP concentration in basement of the NZERTF at various temperatures. Error bars show standard error in triplicate data.

3.2.2.2. Comparison of Micro-chamber Emission Rates to NZERTF Emission Rates.

Emission rates were estimated for the open cell SPF in the basement of the NZERTF using the assumptions described in section 3.1.7. For the typical temperature days (21.5 °C), the estimated TCPP emission rate was 6.7 $\mu g\ m^{-2}\ h^{-1}$. A sensitivity analysis on the emission rate calculation, based on varying the estimated airflows by 50 %, results in emission rates of 3.3 $\mu g\ m^{-2}\ h^{-1}$ to 10 $\mu g\ m^{-2}\ h^{-1}$. These NZERTF emission rates are 4 % to 12 % of the emission rates predicted in the micro-chamber at 21.6 °C (80 $\mu g\ m^{-2}\ h^{-1}$, Figure 8). A previous study found TCPP emission rates in the range of 50 $\mu g\ m^{-2}\ h^{-1}$ to 140 $\mu g\ m^{-2}\ h^{-1}$ for one component foams tested in 0.02 m^3 test chambers operated at 23 °C, 0.5 h^{-1} air change rate and 50 % relative humidity.[4]

Taken together, the data in Figure 5 and Figure 8 illustrate that the emission rates for TCPP from SPF are a function of airflow conditions, which indicates that gas phase mass transfer limitations are likely controlling the release of TCPP from open cell foam. Since airflow conditions in the micro-chamber and real building spaces are different, TCPP emission rates from micro-chamber studies should not be used to directly predict concentrations in real world environments. TCPP emission rates from SPF will likely be more accurately predicted using mass transfer-based approaches that include foam specific measurements of mass transfer parameters.

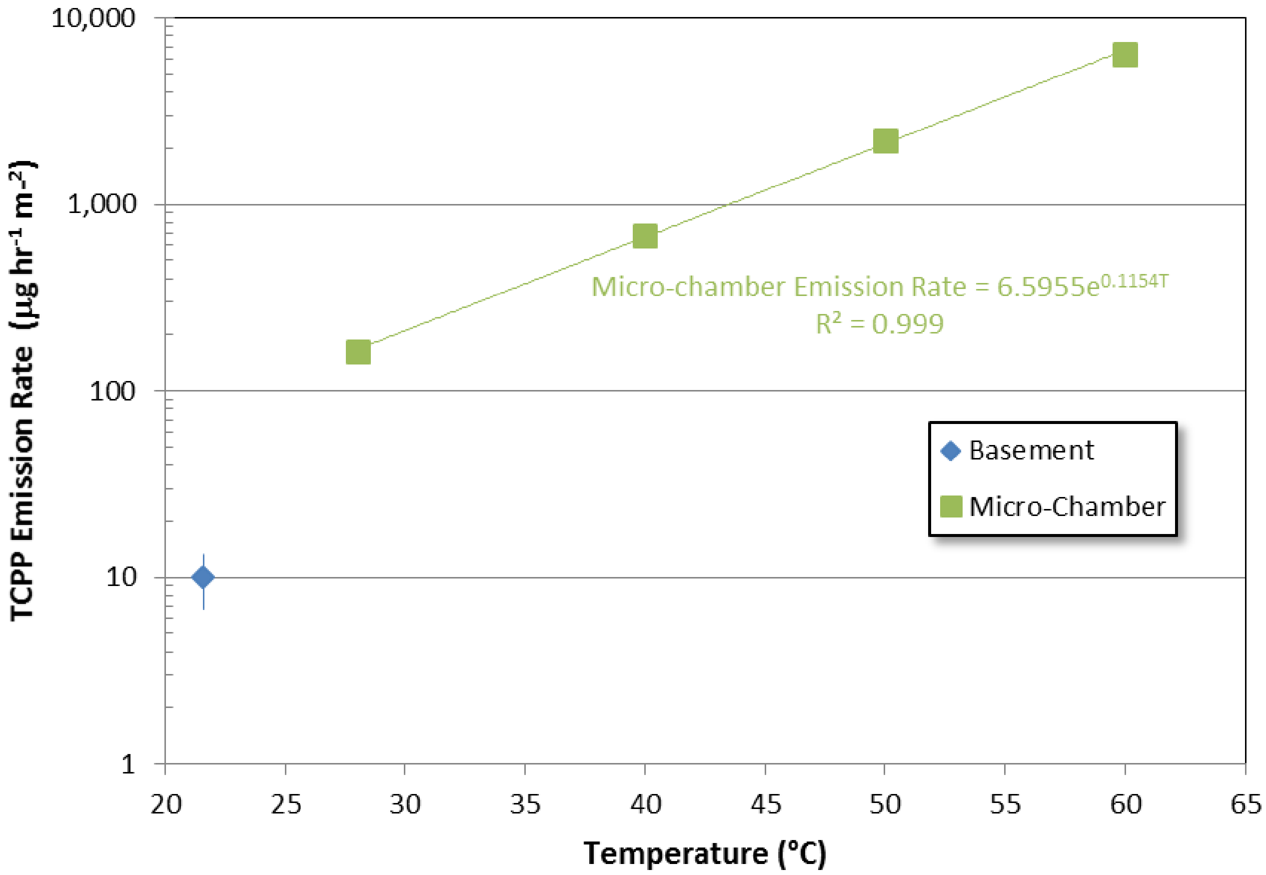

Figure 8: Comparison of TCPP emission rates in the basement of the NZERTF and in micro-chambers. The error bars on the basement emission values show a 50 % variation in interzone flow rates.

3.2.3. Limitations and Implications

The data from this work only applies to the tested foams. Foam with different constituents or applied in a different manner may have different emission profiles. Each foam should be tested in micro-chambers prior to drawing conclusions about its emissions. Emission factors from this work also 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 should be replicated at other laboratories to demonstrate the consistency of the methods employed.

Despite the above stated limitations, several conclusions can be drawn from these results:

- TCPP and BDMAEE emissions from SPF are temperature, flow, and foam type dependent. Studies performed at lower temperatures and flow rates may not quantify chemical emissions for which the concentrations are below or close to the detection limits.

- Micro-chamber data can be used to compare emission profiles from various foams, but TCPP micro-chamber emission rates cannot be directly applied to full scale emissions in a building.
- The results suggest that occupants may be exposed to measureable concentrations of TCPP two years after application of open cell foam.

4. Evaluation of Non-Ideal Foam

To date there is minimal published data on emissions from non-ideal foam. Non-ideal conditions may include off-ratio (A-side to B-side) application, low substrate temperature application, and wrong nozzle pressure and temperature. This report provides emission data on two SPF samples from a residential building in which the occupants have reported health affects after SPF installation. This section of the report addresses Task I in the interagency agreement. As per the NIST/CPSC agreement, this foam is described in this report as non-ideal foam. However, no details are available about the preparation and application of this specific foam.

4.1. Non-Ideal Foam: Methods

Two samples of closed cell foam from the same spraying event, but applied at two different locations in the house, were delivered to NIST on February 22, 2016. The foam was stored in room temperature coolers between delivery and testing. Preliminary testing was conducted on February 24, 2016 to determine the chemicals present in the foam and the required sampling times. After preliminary sampling, newly identified chemicals were acquired and standards were made. Quantification testing began on March 14, 2016. The foam was analyzed in a similar manner as that described in Section 3.1.

4.1.1. Foam Preparation

Density of the foam was determined by cutting 3.0 cm (±0.1 cm) cubes from the 15 cm x 33 cm x 45 cm sample. Triplicate cubes were randomly taken from the sample. Each cube was weighed to the nearest mg. A machined cutting tool was used to cut six SPF samples to fit tightly within Markes 125 small micro-chambers (44 mL chambers) according to ASTM D7859. Three chambers were filled with SPF from location 1, and three chambers were filled with SPF from location 2. The top of each sample was removed to make the samples uniformly flat. Samples were cut to a depth of 24 mm, leaving a 6 mm headspace.

4.1.2. Micro-chamber Experiments

The micro-chambers were operated at the parameters that were in the ASTM WK40293 Spring 2016 ballot. That is, the 44 mL chambers were operated for 200 hours at a temperature of 35.2 °C (standard deviation 0.4 °C) with a 24.1 mL/min (standard deviation 1 mL/min) airflow of ultra-high purity air. No moisture was added to the high purity air, resulting in a relative humidity of zero.

Emissions were captured on sorption tubes. Tenax TA sorption tubes were used to capture amine catalysts, flame retardants and other VOCs, and were subsequently analyzed by gas chromatography/mass spectrometry (GC/MS).

Prior to sampling, the Tenax TA tubes were cleaned with ultra-high purity helium for one hour at 315 °C with a tube cleaner. The tubes were attached to the effluent flow of each chamber for 5 min to 1 h depending on the estimated concentrations of the target chemicals determined from the preliminary experiments. Samples were taken 2 h, 24 h, 48 h, 96 h, 120 h, 172 h, and 196 h after samples were placed in the chambers. At each sampling time two sorbent tubes were collected to ensure each chemical sampled was within the standard curve.

4.1.3. Tube Analysis

Following sample collection, the Tenax TA tubes were spiked with 1 µg deuterated toluene as an internal standard by injecting liquid solution into a heatblock. The Tenax TA tubes were thermally desorbed using a thermal desorbing system. Although the GC/MS was the same as in the Section 3 experiments, the thermal desorption injection system was different. The set points used for the thermal desorption system and GC/MS are summarized in the Supplementary Information (Section 9 of this report). A Rtx-5 Amine column (30.0 m x 250 µm x 0.50 µm) was used for compound separation in the GC/MS.

4.1.4. Targeted Chemicals

Preliminary work identified the presence of over 80 different chemicals after heating the non-ideal SPF samples to 35 °C for 24 h and sampling for 20 min. 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). These chemicals are listed in Table 4 ranked in order of GC/MS response area.

The first seven chemicals in Table 4 were targeted for the quantification experiments, since they had the largest response areas (over 100 000) in the preliminary testing. Chemical standards were purchased for target compounds. Neat chemical standards were prepared by dilution in methanol. Neat triethylenediamine was purchased but was not received in time for the quantification experiment. Nevertheless, this chemical's relative response ratio (area response for quantitation ion of the chemical divided by the area response for quantitation ion of the deuterated toluene) is reported.

Standards were spiked onto Tenax TA tubes along with the deuterated toluene internal standard. Chemicals were quantified using the response ratio between target chemical and internal standard for each chemical. Linear standard curves (injected mass versus relative response ratio) were created for each chemical (average RSQ values for each linear curve are shown in Table 1) on a daily basis. The chambers were tested prior to the introduction of the foam samples to ensure background concentrations of the chemicals of interest were below detection limits. Blank Tenax TA tubes were run at least every seven tubes to demonstrate the absence of carryover between samples.

Table 4. Chemicals identified in preliminary sampling (ranked in order of largest GC/MS response area).

Chemical	CAS Number	Acronym	Average R Squared Value of Linear Calibration
Triethylenediamine	280-57-9	TEDA	N/A
1,4-Dioxane	123-91-1	D	0.999
Propane, 1,2-dichloro-	78-87-5	DCP	0.992
Piperazine, 1,4-dimethyl	106-58-1	DMP	0.991
Tris-(1-chloro-2-propyl) phosphate	13674-84-5	TCPP	0.989
Benzene, 1,2-dichloro	95-50-1	DCB	0.996
1,3-Dioxolane, 2-ethyl-4-methyl	126-39-6	DEM	0.993
Cyclotetrasiloxane, octamethyl-	556-67-2		N/A
1,4-Dioxane, 2,5-dimethyl-	15176-21-3		N/A
Octane	111-65-9		N/A
1-Propanol, 2-chloro-	19210-21-0		N/A
Piperazine, 1,2,4-trimethyl-	120-85-4		N/A
Azulene	275-51-4		N/A
Benzaldehyde	100-52-7		N/A
1,4-Dioxin, 2,3-dihydro-	493-09-4		N/A
2-Butenal, 2-methyl-, (E)-	497-03-0		N/A
Benzene	71-43-2		N/A

Emission rates were calculated in the same manner as described in Section 3.1.7.

4.2. Non-Ideal Foam: Results and Discussion

Both concentrations and emission rates were determined for the non-ideal SPF samples, all of which apply only to micro-chamber conditions. As demonstrated in Section 3.2, the mass transfer conditions or rates 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 research has determined scaling parameters.

4.2.1. Density:

The foam densities are listed in Table 5. SPF from location 1 had a density that was roughly 1.7 times greater than typical closed-cell SPF. SPF from location 2 had a density that was roughly 1.2 times greater than typical closed-cell SPF. The non-ideal foam samples also had higher densities than measured densities of comparative SPF provided by CPI (Open 1 and Closed 1, Table 1).

Table 5. Average Density of Tested Samples. Typical values come from ASTM WK40293.

Foam	Average Density (kg m^{-3})	Number of Samples	Standard Error (kg m^{-3})
Location 1	49.8	3	2.6
Location 2	33.0	3	2.6
Typical Closed	24-32	N/A	N/A
Typical Open	6.4-9.6	N/A	N/A

4.2.2. Pore Structure

Characterizing the pore structure of the SPF was beyond the scope of this research. However, a visible inspection of the pores after cutting the non-ideal SPF showed pores present that were greater than 10 mm across (Figure 9a). In contrast, the visible pores of cut Closed 1 SPF were smaller than 1 mm (Figure 9b). These differences could impact the emission of chemicals if the chemical release is limited by diffusion through the SPF.

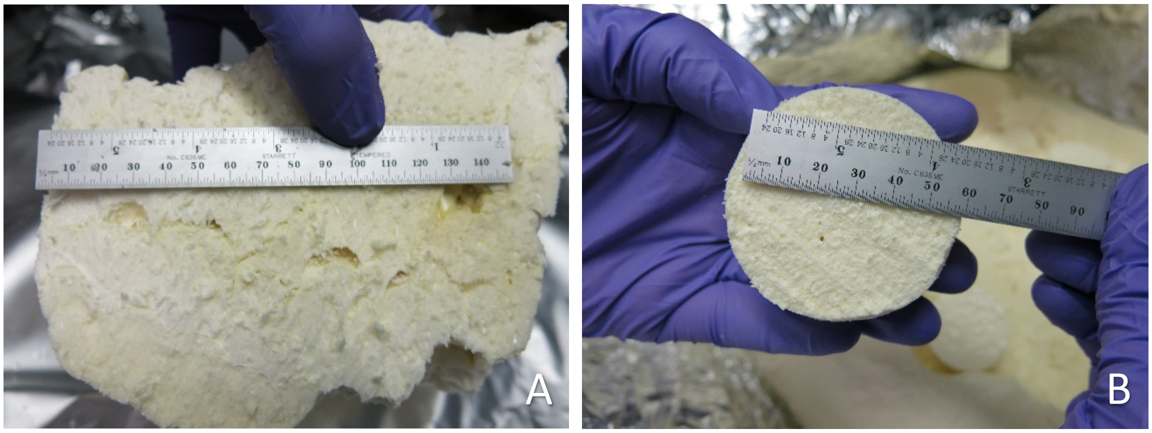

Figure 9: Comparison of pore size for non-ideal SPF (left) and CPI closed-cell foam (Closed 1).

4.2.3. Chemicals Present

In general, the non-ideal foam had a greater number of chemicals present (number of peaks) at greater concentrations (peak height) than the CPI closed-cell foam (Closed 1) (Figure 10). Comparison of this data to unpublished data from four institutions[28] showed that seven of the chemicals in Table 4 had not been previously identified in other foams: 1,2-dichlorobenzene, triethylenediamine, 1,2-chloropropanol, 1,2,4-trimethylpiperazine, azulene, 2,3-dihydro 1,4-dioxin, and 2-methyl 2-butenal. Their presence may be specific to the non-ideal foam or reflect the fact that the published surveys of chemicals emitting from SPF are limited. Of the seven new chemicals, 1,2-dichlorobenzene and triethylenediamine were chosen for quantification due to their large response areas.

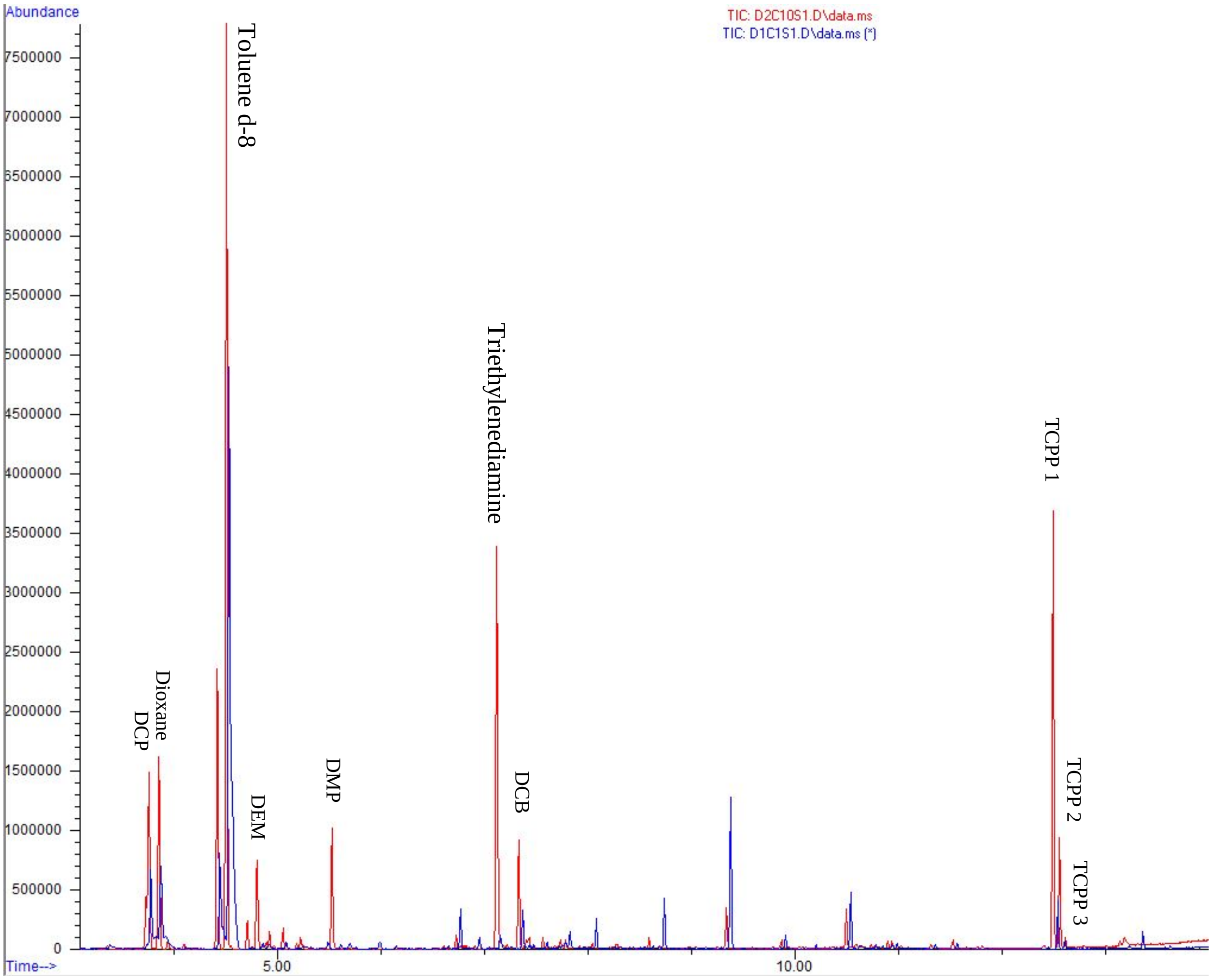

Figure 10 GC/MS comparison of chromatograms from samples at 24 hours from non-ideal foam (red, sampled for 45 minutes) and Closed 1 (blue, sampled for 90 minutes). Due to slightly different GC/MS parameters the peaks do not perfectly line up for the same chemicals. The horizontal axis is time (min), the vertical axis is abundance of the chemical.

4.2.4. Location Comparison

In general, the samples from the two locations of the same spray event had similar emission profiles (Figure 11). Peaks present in one sample were present in the second sample. For the quantified peaks, the concentrations were typically similar for both samples. Figure 12 shows a typical example of this trend (1,4 dioxane). However, TCPP concentrations for foam from location 1 were higher for most of the samples (Figure 13). For the remainder of this document, the concentrations and emission rates are presented as an average value from all six chamber measurements, regardless of SPF sample location.

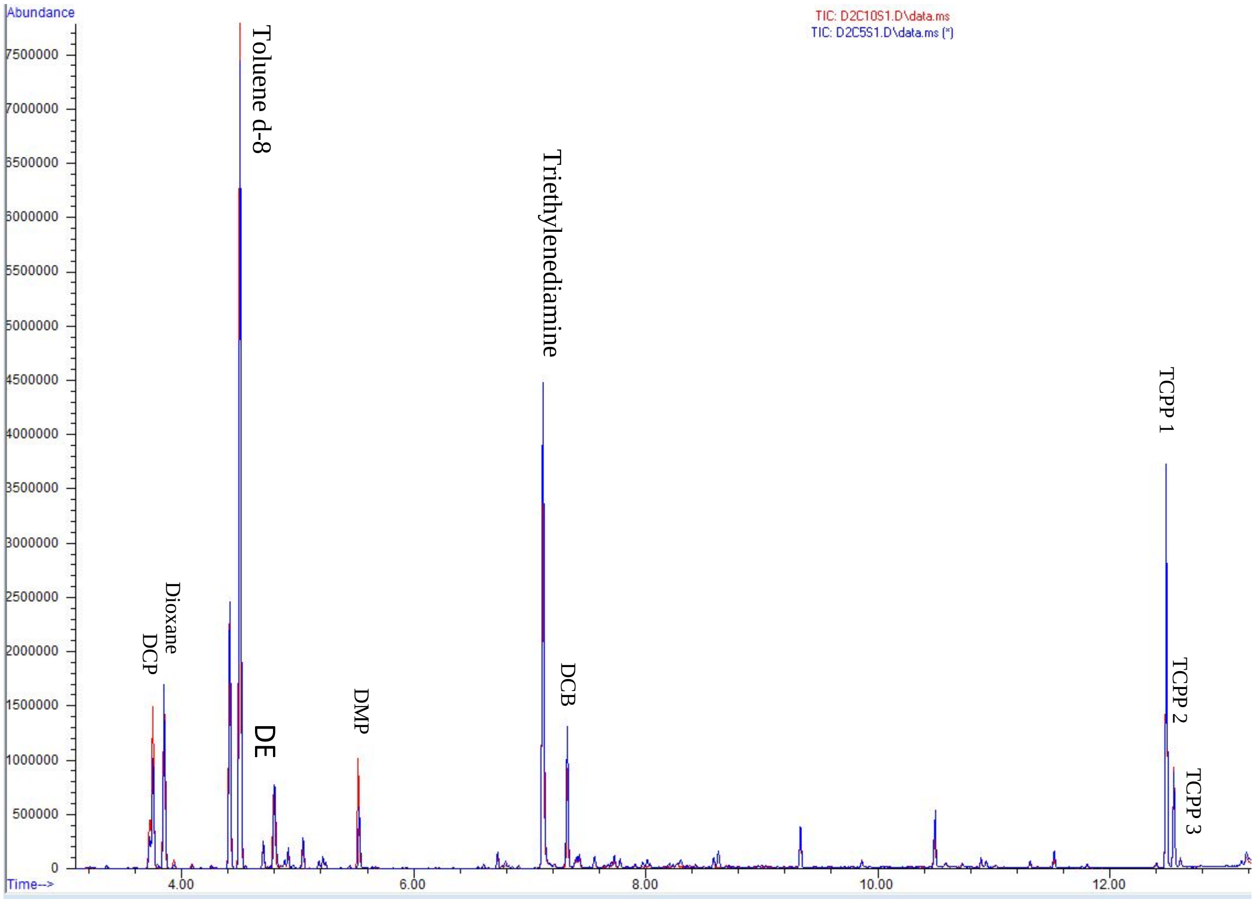

Figure 11. GC/MS comparison of chromatograms from the two locations of non-ideal SPF. Blue line is from location 1 and red line is from location 2. The horizontal axis is time (min), the vertical axis is abundance of the chemical.

4.2.5. Micro-Chamber Concentrations

Concentrations of the flame retardant TCPP remained relatively constant for samples taken after 48 hours (Figure 13), while concentrations of 5 other quantified chemicals decreased in a negative exponential manner over time (Figure 14).

The response ratio for triethylenediamine also decreased in a negative exponential manner (Figure 15). Triethylenediamine was not quantified due to shipping delays of the standard. The decreasing triethylenediamine concentrations for the response ratios shown in Figure 15 are estimated to be between 2 500 µg m^{-3} to 100 µg m^{-3}. The maximum value maybe lower and the minimum value maybe higher. These values should only be used as estimates of the micro-chamber concentrations as they are derived from a liquid injection of triethylenediamine into the GC\MS (rather than thermal desorption) months after original analysis.

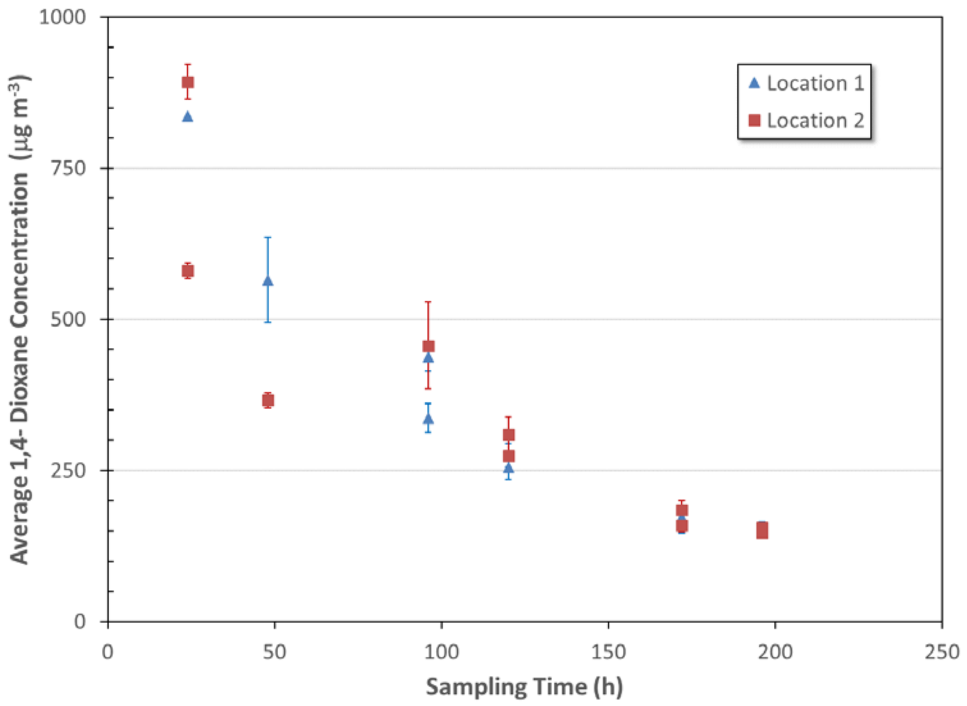

Figure 12. 1,4 Dioxane concentrations over seven sampling periods. Uncertainty bars show the standard error for each sampling time.

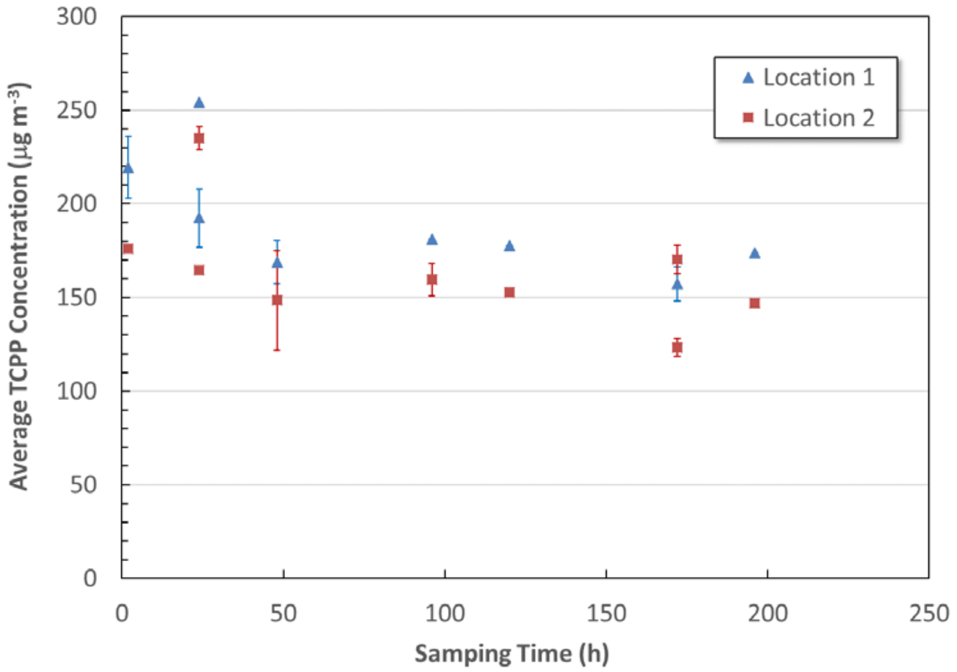

Figure 13. TCPP concentrations over seven sampling periods. Uncertainty bars show the standard error for each sampling time.

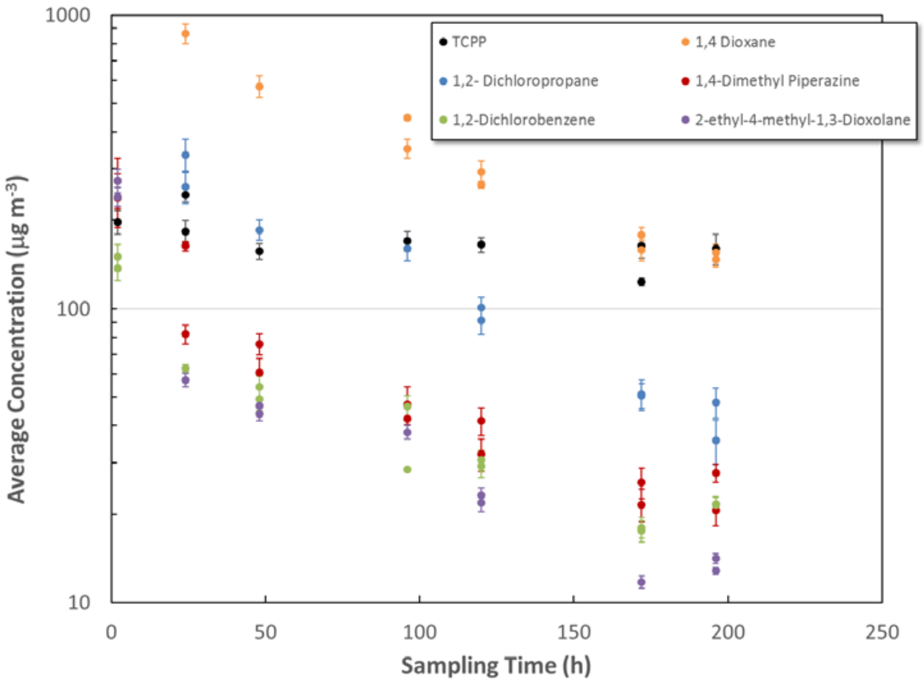

Figure 14. Concentrations of all quantified chemicals over seven sampling periods. Uncertainty bars show the standard error for each sampling time. Vertical axis is a logarithmic scale.

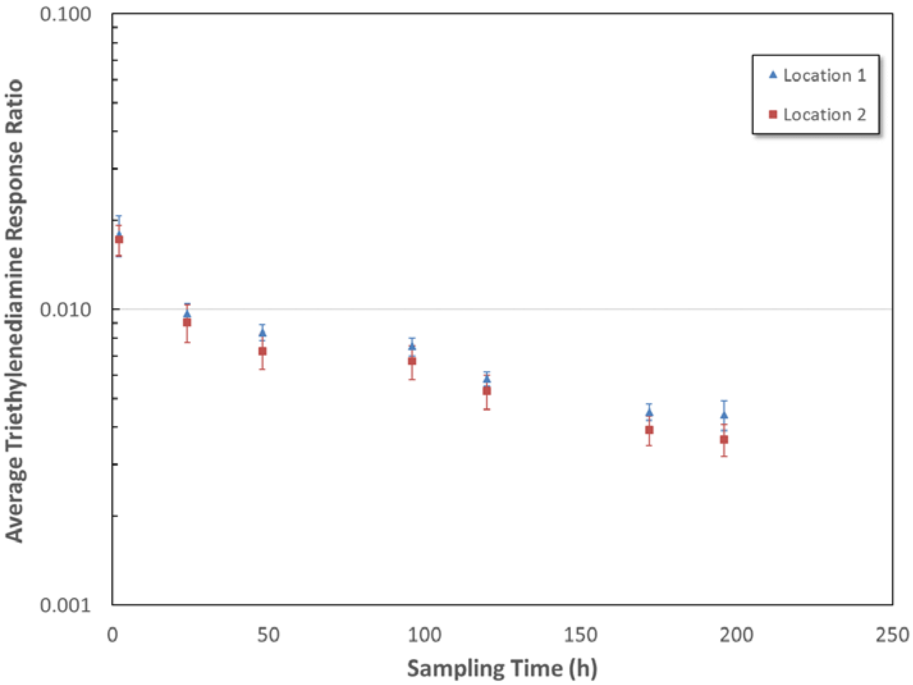

Figure 15. Relative response ratio between triethylenediamine and internal standard. Uncertainty bars show the standard error for each sampling time. Vertical axis is a logarithmic scale.

4.2.6. Micro-Chamber Emission Rates

The emission rates followed the same trends as the concentrations. The emission rate of all chemicals other than TCPP decreased in a negative exponential manner with time (Figure 16).

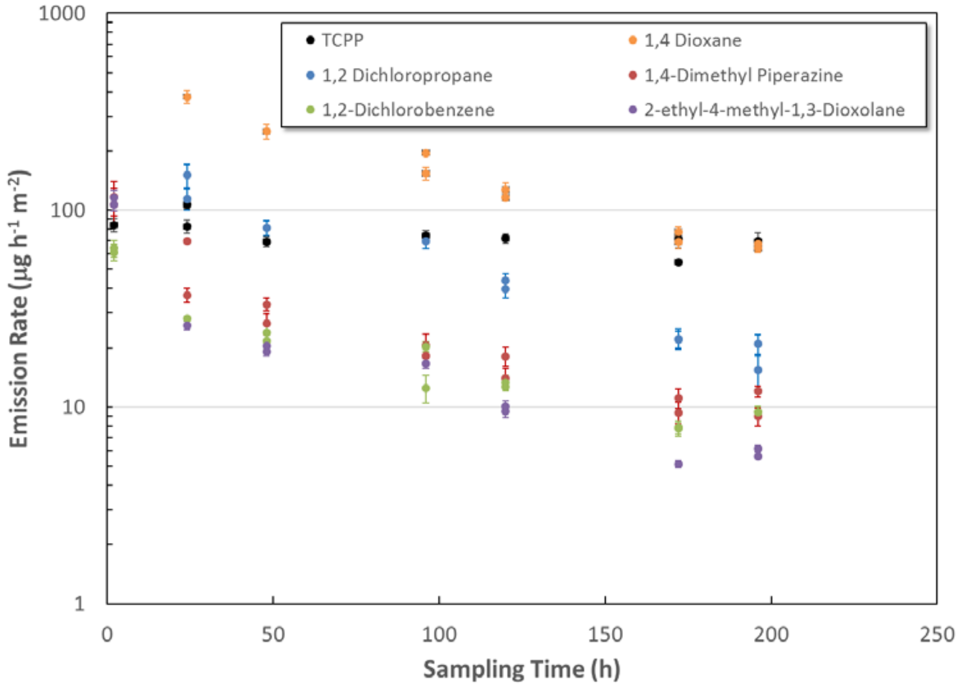

Figure 16. Emission rates for all quantified chemicals. Uncertainty bars show the standard error for each sampling time. Vertical axis is a logarithmic scale.

The TCPP emission rates from the closed cell non-ideal foam followed similar trends compared to previously tested Open 1 and Open 2 but were different from previously tested Closed 1 (red open square values in Figure 17). The emission data from the non-ideal foam were collected in 44 mL micro-chambers (flow rate of 25 mL/min), while the other emission rates were collected in 114 mL micro-chambers (flow rate 50 mL/min). In addition, the previously collected data was sampled at a slightly higher temperature (35 °C versus 40 °C). The differing flow rates and temperatures are not expected to change the shape of the TCPP emission profile to the degree seen in Figure 17. This differing TCPP emission rate profile may be a function of the SPF being non-ideal or reflect the fact that published surveys of chemical emission rates from SPF are limited.

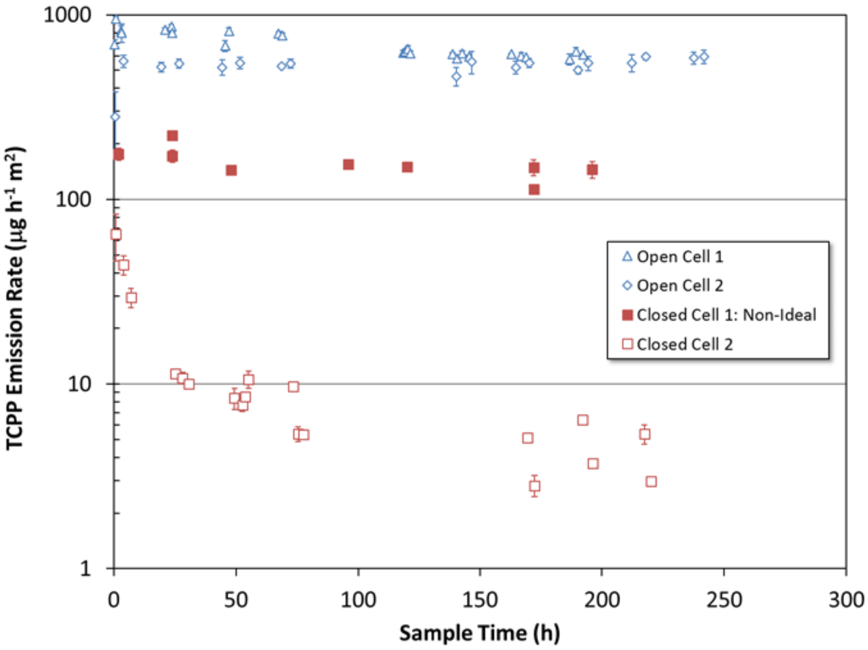

Figure 17. TCPP emission rates for different samples. Error bars show the standard error for each sampling time. Vertical axis is a logarithmic scale. Non ideal foam tested at 35 °C, all other foam tested at 40 °C.

Both 1,4 dioxane and 1,2 dichloropropane were also quantified as emitting from Closed 1. The emission rates for 1,2 dichloropropane were similar for the non-ideal and Closed 1 foams over the duration of the experiments (Figure 18). However, the emission rates of 1,4 dioxane were approximately an order of magnitude higher for the non-ideal foam compared to Closed 1.

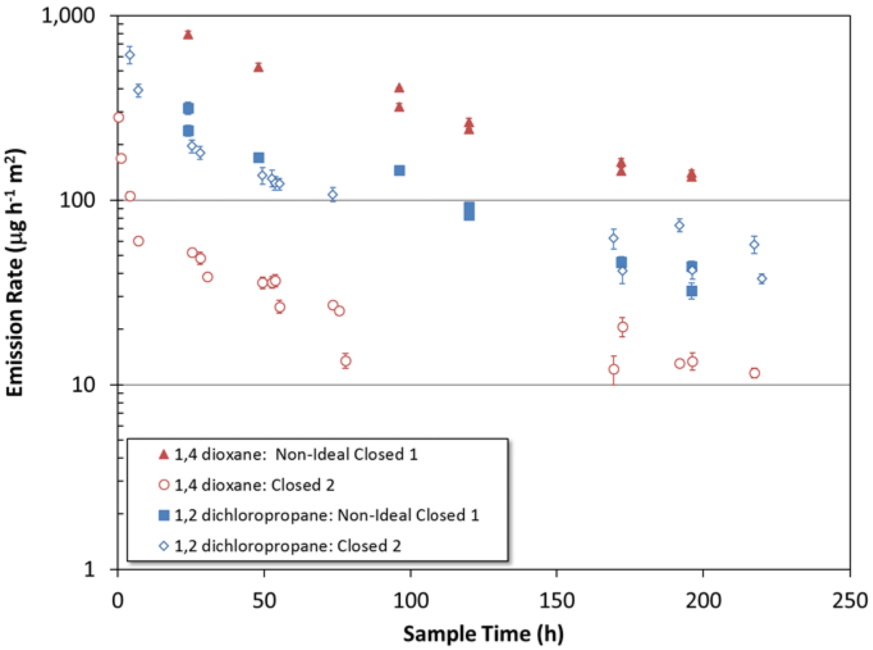

Figure 18. Emission Rates for 1,4 dioxane and 1,2 dichloropropane for tested non-ideal foam (Closed 1) compared to CPI closed-cell foam (Closed 2). Error bars show the standard error for each sampling time. Vertical axis is a logarithmic scale. Non ideal foam tested at 35 ^{o}C, all other foam tested at 40 ^{o}C.

4.3. Non-Ideal Foam: Summary and Implications

There is limited published data on emissions from SPF. This study expands the known data by analysing a non-ideal foam sample. This foam had the following features:

1. SPF from location 1 had a density that was roughly 1.7 times greater than typical closed-cell SPF. SPF from location 2 had a density that was roughly 1.2 times greater than typical closed-cell SPF.
2. The non-ideal SPF had some pore spaces that were an order of magnitude greater than previously analyzed closed cell SPF.
3. Over 80 peaks representing different chemicals were recognized as emitting from the tested non-ideal SPF. A total of 17 chemicals were relatively substantial in size and identified with a spectrum match. Seven of those chemicals have not been identified in other SPF emission studies using similar test methods.
4. The concentrations of chemicals emitted from both location 1 and location 2 were similar.
5. The emission rates of six chemicals were quantified. The emission rates of all chemicals except for TCPP decreased in a negative exponential manner.
6. The emission rate of TCPP was relatively constant after 48 hours. This is in contrast to TCPP emission rates from the other tested closed-cell foam.

The above conclusions on the differences between tested non-ideal SPF samples in the present study and previous CPI foam indicate that the tested non-ideal SPF may have been misapplied. However, the results may simply reflect the fact that the tested SPF samples are different from CPI foam.

To conclusively determine that a foam is misapplied, the suspect foam should be tested in micro-chambers at the same time correctly applied foam with the same formulation (preferably from the same systems house) is tested. The presence of a chemical in the emissions of suspect foam but not in the correctly applied foam would indicate that the suspect foam was misapplied. If enough correctly applied foams were tested using micro-chambers, then a database of expected chemical emissions from correctly applied foams could be created for comparison. However, formulations are different for different systems houses, and change over time. Hence, a database comparison is unlikely to be as conclusive as testing suspect and correctly applied foam at the same time.

5. Conclusions

This research demonstrated that chemicals are emitted from SPF both in laboratory and residential settings. Specifically:

- Emissions from the tested SPF are chemical, flow, temperature and foam type dependent.
- A wide range of chemicals were emitted and quantified using the micro-chamber protocol. These include SPF constituents such as flame retardants (TCPP) and amines (BDMAEE) and byproducts or contaminates such as aldehydes, chlorinated alkanes, chlorinated aromatics and other chemicals (Table 4).
- Aldehyde emissions from SPF can be measured using micro-chamber experiments. However, unless the SPF is sampled immediately after a spray event micro-chamber experiments cannot provide evidence that the detected aldehydes are primary emissions from sampled SPF and not secondary emissions (desorbing during the experiment after absorption to the SPF from another source in the building)
- Quantification of the amine BDMAEE using thermal desorption analysis methods was successful. However, quantitation of other detected amines using thermal desorption did not meet quality control/quality assurance criteria.
- Exposure to TCPP could be a long term problem as micro-chamber emission rates of TCPP were not statistically different for fresh sprayed open cell SPF and SPF tested two years after application.
- Micro-chamber data can be used to compare emission profiles from various foams. However, TCPP micro-chamber emission rates cannot be directly applied to full scale emissions in a building. Micro-chamber emission comparisons between suspect non-ideal SPF applications and correctly applied SPF from the same systems house can be used to confirm if the suspect foam is non-ideal.
- The tested non-ideal foam emitted chemicals that had not previously been detected. However, due to lack of data on emissions from SPF, it is not known whether these results reflect misapplication.

The conclusions from this work only apply to the tested foams. Foam with different constituents or applied in a different manner may have different emission profiles. Each foam should be tested in micro-chambers prior to drawing conclusions about its emissions. 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.

6. 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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9. Supplementary Information

Table 6 and Table 7 document the settings used on the Markes Thermal Desorption System, the Agilent gas chromatogram/mass spectrometer (GC/MS) for the data presented in Section 3.

Table 6. Thermal Desorption System Settings for Section 3.

Phase	Conditions	Value
Purge	Pre-purge Time Trap In Line Split Flow Rate	1 minute No On 20 mL min^{-1}
Tube Desorption	Time Temperature Split	8 minutes 300 °C Off
Trap Desorption	Trap Low Temperature Trap High Temperature Trap Hold Time Split Trap Heating Rate Split Flow Rate	-10 °C 330 °C 3 minutes On Maximum (°C s^{-1}) 50 mL min^{-1}
Split Ratios	Inlet Outlet Total	No Split 27.3 : 1 27.3 : 1
Other	Flow Path Temperature GC Cycle Time	200°C 20 minutes

Table 7. GC/MS Settings for Section 3.

Phase	Conditions	Value
Helium Flow	Pressure Flow Mode Average Velocity	10.2 psi 1.3 mL min^{-1} Constant Flow 41 cm s^{-1}
Temperature Profile	Initial Time Initial Temperature Ramp Final Time Final Temperature	2 minutes 40 °C 15 °C mL min^{-1} 3 minutes 315 °C
Detector	Temperature Mode	250°C SCAN

Table 8 documents the settings used on the Gerstel Thermal Desorption System, the Agilent gas chromatogram/mass spectrometer (GC/MS) for the data presented in Section 4.

Table 8. Summary of thermal desorption and GC/MS parameters for non-ideal foam for Section 4.

Parameter	Setting
Thermal Desorption Unit (TDU)	
Hold	30˚C for 0.5 min
Ramp	360˚C min^{-1}
Final	300˚C for 8 min
Cooled Injection System (CIS)	
Hold	-120˚C
Ramp	12˚C sec^{-1}
Final	275˚C for 8 min
Oven	
Flow	1 mL min^{-1}
Hold	40˚C for 2 min
Ramp	20˚C min^{-1}
Final	300˚C for 2min