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Flame Retardant Emissions from Spray Polyurethane Foam Insulation

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Abstract:

The desire to build more energy efficient homes in the United States has led to the expansion of the residential spray polyurethane foam (SPF) insulation industry. Upon application of SPF, reacting chemicals form expanding polyurethane foam that fills cracks and gaps, reducing infiltration and thermal conductivity of the building envelope. However, more information is being sought on chemical emissions from SPF to better understand occupant exposures and any potential impacts on health. The objective of this investigation was to investigate the emission of flame retardant tris (1-chloro-2-propyl) phosphate (TCPP) from SPF using both micro-chambers and a full scale residential test facility. Two high pressure, open cell foams and one high pressure, closed cell foam were tested using micro-chambers. After 100 hours, TCPP concentrations from the open cell samples were 100 times higher than TCPP concentrations from the closed cell SPF. TCPP emissions from open cell foam were found to correlate exponentially with temperature and vary with flow rate, indicating emission factors from SPF micro-chamber experiments may not directly predict TCPP concentrations in buildings without consideration of material mass transfer properties. Due to the use of TCPP in furniture, SPF has not previously been positively identified as a primary source of indoor TCPP concentrations in actual buildings. This research measured airborne TCPP concentrations in the furniture-free National Institute of Standards and Technology (NIST) Net Zero Energy Residential Test Facility (NZERTF) that contained 15 m² of exposed, two-year-old, open cell SPF. The measured NZERTF TCPP emission rates were not directly predicted by emission factors from the micro-chamber measurements, which suggests a mass transfer-based modelling approach is needed for predicting TCPP concentrations from open cell SPF. More research is needed to determine how data from micro-chamber studies can be used to predict exposures of residential occupants to emissions from SPF foam.

Keywords:

Spray Polyurethane Foam, TCPP, Flame Retardant, Emissions

ASTM Committee:

D.22.05 Indoor Air

Introduction

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. United States federal efforts towards creating more efficient buildings, such as tax incentives and programs like U.S. Environmental Protection Agency (EPA) Energy Star¹ and Design for the Environment² have increased SPF applications. In 2012 over 61 million kg of SPF were installed in residential applications in the United States³ and the industry expects to see significant growth in the use of their products over the next few years.⁴

SPF is produced on site via an exothermic reaction of two sets of chemicals. The A-side chemicals typically include methylene diphenyl diisocyanate. The B-side chemicals include polyols, amines, blowing agents, surfactants and flame retardants. Flame retardants are present in the reacted polyurethane foam at up to 12 % by mass.⁵ The reactions can be designed so the resulting foam is open (low density) or closed cell (medium density). SPF can be installed using high pressure systems by professional contractors or with low pressure do-it-yourself (DIY) kits. Whether the SPF is used to insulate a whole house by professionals or retrofits by homeowners, there is potential for the building occupants to be exposed to SPF associated emissions.

Several studies have investigated emissions of flame retardants from SPF.^{6,7} The most common identified flame retardant is tris (1-chloro-2-propyl) phosphate (TCPP). TCPP is not exclusive to SPF, and has also been used in mattresses, electronics, and upholstery.⁷ TCPP has been measured in homes at airborne concentrations ranging from 2.4 ng m⁻³ to 1,260 ng m⁻³,⁷⁻⁹ and found in similar concentrations in cars, offices and furniture stores.¹⁰ TCPP is persistent in the environment,¹¹ readily absorbed through skin, and breaks down rapidly into metabolites in the body.¹² Although there is limited data, TCPP is classified by the EPA Design for the Environment program as having a high hazard for reproductive and developmental effects.¹²

The Consumer Product Safety Commission (CPSC), along with the EPA, have received a number of complaints regarding health effects that are potentially associated with SPF applications. Residents have complained of health impacts including severe respiratory irritation, breathing difficulties, dizziness and nausea in the time frame of days to months after SPF installation in a home. In some cases, the effects are so severe that consumers report that they can no longer live in their homes.¹³ This time frame of health complaints is longer than the suspected time frame for the presence of isocyanates, suggesting that the emission of other chemicals (amines, blowing agents, surfactants, flame retardants or by-products of the reactions) from the SPF may be of concern. However, no direct connection between these health symptoms and SPF emissions have yet been established. In order to support such studies, 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.

This research was designed to contribute to the development and evaluation of voluntary standards for testing emissions from SPF. Specifically, the work was performed to support the ASTM Indoor Air Quality (D22.05) subcommittee efforts to standardize test methods and protocols relating to the measurement of emissions from SPF using micro-environmental test chambers. 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.

Methods

TCPP concentrations were measured in two environments: micro-chambers and in a residential test facility. The objective of the work was to quantify TCPP emissions from various SPF samples and to better understand these emissions based on the measurement results. The specific objectives were to 1) evaluate sampling times for TCPP in various SPF formulations using the micro-chamber method; 2) use micro-chamber data to assess if TCPP emissions are likely controlled by internal material diffusion or external mass transfer; and 3) compare TCPP emission rates from micro-chamber experiments to emission measurements in a full scale residential test facility.

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 to be representative of SPF then available in the marketplace. The formulations were created for research purposes only and were not optimized to meet the specifications of commercial producers and therefore may not reflect formulations currently available in the marketplace. Therefore, conclusions about how these foams would perform outside a laboratory setting are speculative. Foams Open 1 and Closed 1 were sprayed in factory settings under controlled conditions. The foams were packaged and shipped overnight to NIST in an insulated cooler in accordance with ASTM standard D7859.¹⁴ 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.

Open 2 was a high pressure, open cell, low density SPF that was applied during the construction of the National Institute of Standards and Technology (NIST) Net Zero Energy Residential Test Facility (NZERTF) in the summer of 2012. The 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.¹⁵ 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 (242 m² for occupied floors, 485 m² inside the building envelope 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 62.2-2010¹⁶ the HRV was sized to continuously deliver 137 m³ h⁻¹ of outdoor air. Special attention was paid to the design and construction of a highly insulated and airtight building envelope. Approximately 15 m² 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 and tested in micro-chambers. In July and August 2014 airborne TCPP concentrations were measured in the basement and first floor of the NZERTF.

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 D7859-13e1. 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,¹⁷ increase emissions to reduce problems associated with low detection limits, and capture the performance of foam in environments with elevated temperatures such as attics and exterior wall cavities. 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. The impact of flow was investigated by running samples of Open 1 at 50 mL min⁻¹, 100 mL min⁻¹ and 200 mL min⁻¹. The airflow contained an absolute humidity of 8.8 g m⁻³ (equivalent to a relative humidity of 38 % at 25 °C) for the Open 1 and Open 2 samples. The airflow contained zero humidity for the Closed 1 sample, based on discussions within 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 of sample) depending on the concentration of the flame retardant. For samples longer than 2 hours, a second Tenax tube was placed in series with the first tube and analyzed for breakthrough. For each foam, three micro-chambers were run concurrently. The 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 TALBOYS Standard Heatblock.

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. Temperature values shown in the 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 is 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).

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. 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 ($\approx 66\%$ based on GC/MS area response), bis(1-chloro-2-propyl) (2-chloropropyl) phosphate ($\approx 30\%$) and (1-chloro-2-propyl) bis(2-chloropropyl) phosphate ($\approx 4\%$). In this research only the first two isomers were consistently detected 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.¹⁸ The instrument TCPP detection limit was 8.65 ng and the method detection limit was $0.71 \mu\text{g m}^{-3}$ to $2.86 \mu\text{g m}^{-3}$ depending on the sample volume. Only values above the method detection limit for the corresponding sampling volume are shown below.

Tenax sorption tubes also captured amine catalysts, byproducts and other volatile organic compounds. 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.

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 tubes and TD-GC/MS analysis. 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 $2.0 \mu\text{g TCPP g}^{-1}$ material m^{-3} air to $6.3 \mu\text{g TCPP g}^{-1}$ material m^{-3} air).

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-741¹⁹ in July 2014. These rates reflect the combination of mechanical HRV ventilation associated with the HRV operation and infiltration due to building envelope leakage. Leakage rates were determined by subtracting the measured HRV flow from the total measured air change rate. An automated tracer gas system with sulfur hexafluoride injection and sampling at multiple locations (eight indoor and one outdoor) was employed. 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 %.

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:

$$V_{\text{chamber}} \frac{dC}{dt} = Q_{\text{in}} C_{\text{in}} - Q_{\text{out}} C + E_{f, \text{chamber}} A_{\text{chamber}} \quad (1)$$

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 ($\mu g m^{-3}$), C_{in} is the concentration in the inlet air ($\mu g m^{-3}$), $E_{f, chamber}$ is the area specific emission rate ($\mu g m^{-2} h^{-1}$) 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 included in the data analysis. The green data points (Open Cell 2) in Figure 2 show the TCPP concentration in the micro-chamber reaches a steady-state value of $\sim 300-400 \mu g/m^3$ by the four hour sample. This indicates that the exposed surface of the micro-chamber is in equilibrium with TCPP by four hours (sorption and desorption rates cancel each other). Hence, for the time scales of sampling (daily), steady state conditions can be assumed and Equation (1) simplifies to:

$$E_{f, chamber} = \frac{Q_{in}(C_{ss} - C_{in})}{A_{chamber}} \quad (2)$$

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 time frame it is likely that the building materials have reached an equilibrium with TCPP at ambient temperatures ($20-22^\circ C$) that the house was operated at for the two years prior the sampling. Hence, sorption and desorption rates will likely cancel each other. For this model basement air was exchanged with the 1st floor and outside air. TCPP concentrations were measured on the first floor and assumed to be constant:

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

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.

The airflow between the basement, the outdoors and the rest of the house is dominated by the 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 part 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 for foam in the NZERTF at steady state ($E_{f, NZERTF}$) can be calculated from Equation (3):

$$E_{f, NZERTF} = (C_{ss} - C_{1st}) \frac{Q_{1st in} V_{Basement}}{A_{SPF}} \quad (4)$$

Results and Discussion

All reported concentration and emission rates in this document only apply to the tested conditions and foams. The mass transfer processes in building systems may not be the same as those in a micro-chamber. Hence, emission rates in the two systems maybe different. TCPP was detected emitting from all tested foams.

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.

Influence of the foam. For the tested open cell foams (Open 1 and Open 2), concentrations of the flame retardant TCPP tended to be constant over time throughout the duration of the experiments (Figure 2). The two open cell foams TCPP concentrations were not statistically different ($p=0.06$), even though Open 1 was freshly sprayed and Open 2 was applied over 1.5 years prior to sampling. All statistical comparisons in this document use a one-way ANOVA, Tukey-Kramer analysis with $\alpha = 0.05$. The average TCPP concentration over more than 400 hours of sampling for Open 1 was $400 \mu\text{g m}^{-3}$ ($n=98$, standard error $23 \mu\text{g m}^{-3}$) and $314 \mu\text{g m}^{-3}$ ($n=78$, $23 \mu\text{g m}^{-3}$) for Open 2. The Open 2 results show that for this sample and for insulation temperatures of $40 \text{ }^\circ\text{C}$, flame retardants can be emitted at measurable concentrations for time frames greater than 18 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 $8 \mu\text{g}$ of TCPP was emitted from the roughly $300,000 \mu\text{g}$ of TCPP present initially in the 3.75 g SPF sample (TCPP was roughly 8% of the mass of ingredients used to make Closed 1⁵). One hypothesis to explain the decrease in emission rate is that the TCPP initially located near the surface emits over a short time frame and that long term emission from the bulk of the foam is limited by the diffusion of TCPP to the surface. The two different emission profiles for TCPP 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 prior to attempting to model the TCPP in full scale systems.

For both open and closed cell foams, it appears that the concentrations of TCPP did not appreciatively change after roughly 100 hours. For micro-chamber experiments, sampling prior to 100 hours should be sufficient to determine differences in TCPP emissions from different samples of SPF.

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. In addition, the emission profile may be different for different chemicals in a single foam. Figure 3 shows a decaying concentration for Bis (2-dimethylaminoethyl) ether (BDMAEE) and the steady emission profile for TCPP from the Open 1 sample. BDMAEE is a catalyst with an initial maximum concentration in this foam of less than 1 %, much smaller than the foam concentrations of TCPP.⁵ 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 1⁵). 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 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.²⁰ 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.

Influence of the micro-chamber flow rate.

TCPP has a wide range of reported values for vapor pressures.^{21,22} Depending on definitions and reported chemical properties, TCPP could be defined as either a volatile organic chemical (VOC) or a semi-volatile organic chemical (SVOC). The European Union Paints Directive (Directive 2004/42/EC)²³ defines a VOC as any chemical with a boiling point below 250 °C. TCPP has reported boiling points ranging from 235 °C²⁴ to >270 °C²¹. In general, the emissions of VOCs from materials are controlled by the diffusion of the VOC through the material matrix and are not highly chamber dependent. This can allow the direct use of VOC chamber emission factors to predict emissions in full scale buildings. In contrast the emission of SVOCs tends to be chamber dependent and controlled by the airflow above the material. Since the airflow above a material can be significantly different in a chamber and in a full scale building, SVOC chamber emission factors from micro-chamber studies should not be directly applied to full scale buildings. Emission parameters (mass transfer coefficient, initial concentration, partition coefficient, and diffusion coefficient) are needed to accurately predict the concentrations of SVOCs in buildings.

A series of experiments were conducted to determine if the flow rate (a surrogate for the mass transfer coefficient) influenced the emission rate ($\mu\text{g m}^{-2} \text{hr}^{-1}$) 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.²⁵ 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 5 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 will not be accurate. Therefore, building scale TCPP modeling must consider the mass transport parameters properties of the foam.

Influence of the micro-chamber temperature.

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 was present initially in the 1.2 g SPF sample (TCPP was roughly 12% of the mass of ingredients used to make Open 1). A separate test on a separate sample of Open 1 was conducted at 60 °C. Figure 6, shows the average emission rates for TCPP at the four temperatures for Open 1 foam. For comparison purposes, data from Ni et al.²⁵ 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 building temperature may have a relatively large impact on the TCPP concentration in the building.

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 foam was then tested at 0 % relative humidity over seven 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).

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.

Source of TCPP.

The NZERTF has approximately 15 m² of open cell SPF sprayed to seal the basement rim joists. The SPF is exposed to the basement air with no covering finish material. The basement ceiling is not finished and the basement has no internal dividing walls. 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 suggest that the source of the TCPP is 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 for micro-chamber data).

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 insulation materials from the walls, pipes and ductwork were tested at 40 °C in the micro-chamber and no TCPP was detected in any of the materials. Given the higher concentrations of TCPP in the basement and the fact no other sources of TCPP were found, it can be reasonably concluded that the TCPP measured in the upstairs living area was the result of emissions from the 15 m² of open cell SPF sprayed in the rim joists located in the basement.

TCPP emissions are temperature dependent. The temperature in the NZERTF was raised from 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).

Comparison of micro-chamber emission rates to NZERTF emission rates.

Emission rates were estimated for the SPF in the basement of the NZERTF using the assumptions described in the methods section. For the ambient temperature days (21.5 °C), the estimated TCPP emission rate was 6.7 µg m⁻² h⁻¹. A sensitivity analysis on the emission rate calculation, based on varying the estimated airflows by 50 %, results in a variation of emission rates from 3.3 µg m⁻² h⁻¹ to 10 µg 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 µg m⁻² h⁻¹, Figure 8). A previous study found TCPP emission rates in the range of 50 µg m⁻² h⁻¹ to 140 µg m⁻² h⁻¹ for one component foams tested in 0.02 m³ test chambers operated at 23 °C, 0.5 h⁻¹ air change rate and 50 % relative humidity.⁶ However, that SPF was not two years old prior to testing.

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 the foam. Since flow conditions in the micro-chamber and real building spaces are different, TCPP emission rates from micro-chamber 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.

Limitations and Implications

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. 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 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 of this work, several conclusions can be drawn from these results:

- TCPP emissions from SPF are temperature, flow, and foam dependent. Studies done at lower temperatures and flow rates may not quantify emissions of chemicals 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 yet 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.

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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Table 1. SPF samples tested. Open 2 sample was taken from the NZERTF.

Foam ID	Type	Density (Kg/m³)¹	Spray Date	Test Date
Open 1	Open Cell	12	2/26/2014	2/27/2014
Open 2	Open Cell	7	Summer 2012	1/28/2014
Closed 1	Closed Cell	30	11/4/2014	4/13/2105

¹Density determined by measured initial mass and approximate volume.

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

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



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

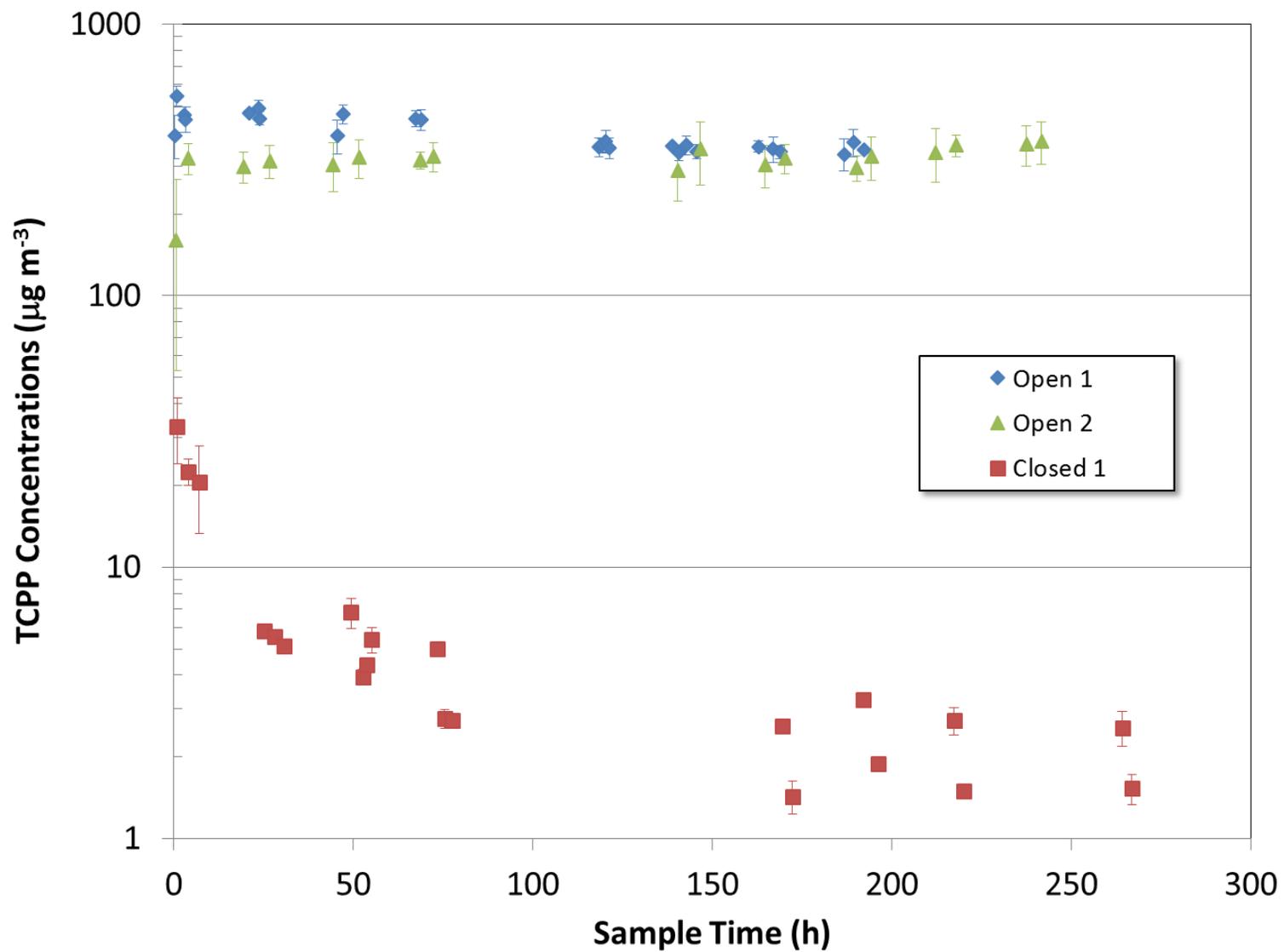


Figure 2. TCP concentrations from open and closed cell SPF tested in 40 °C micro-chambers. Error bars show standard error in triplicate data.

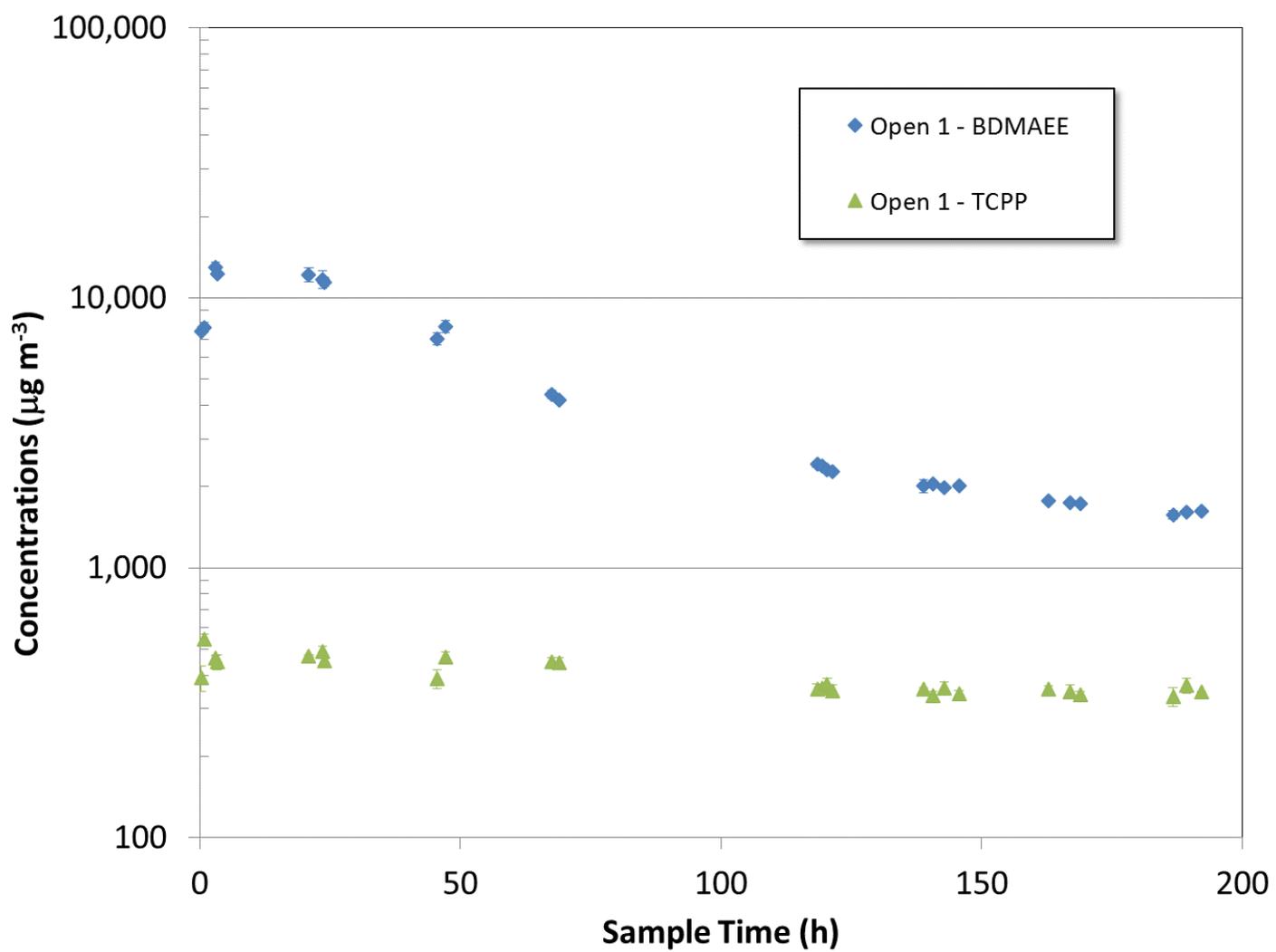


Figure 3. TCPP and BDMAEE concentrations from open cell SPF tested in 40 °C micro-chambers. Error bars show standard error in triplicate data.

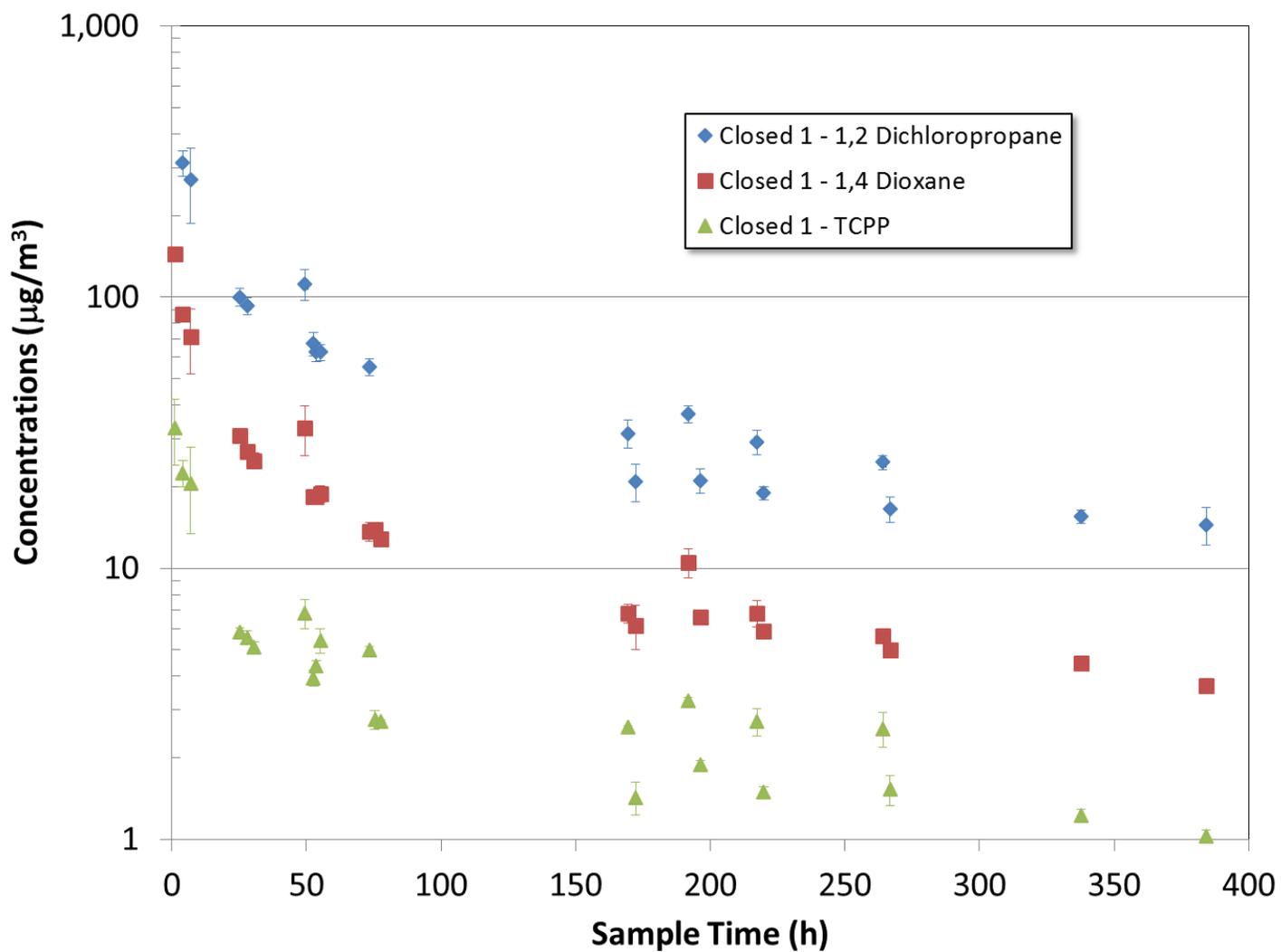


Figure 4. TCPP, 1,2 dichloropropane and 1,4 dioxane concentrations from closed cell SPF tested in 40 °C micro-chambers. Error bars show standard error in triplicate data.

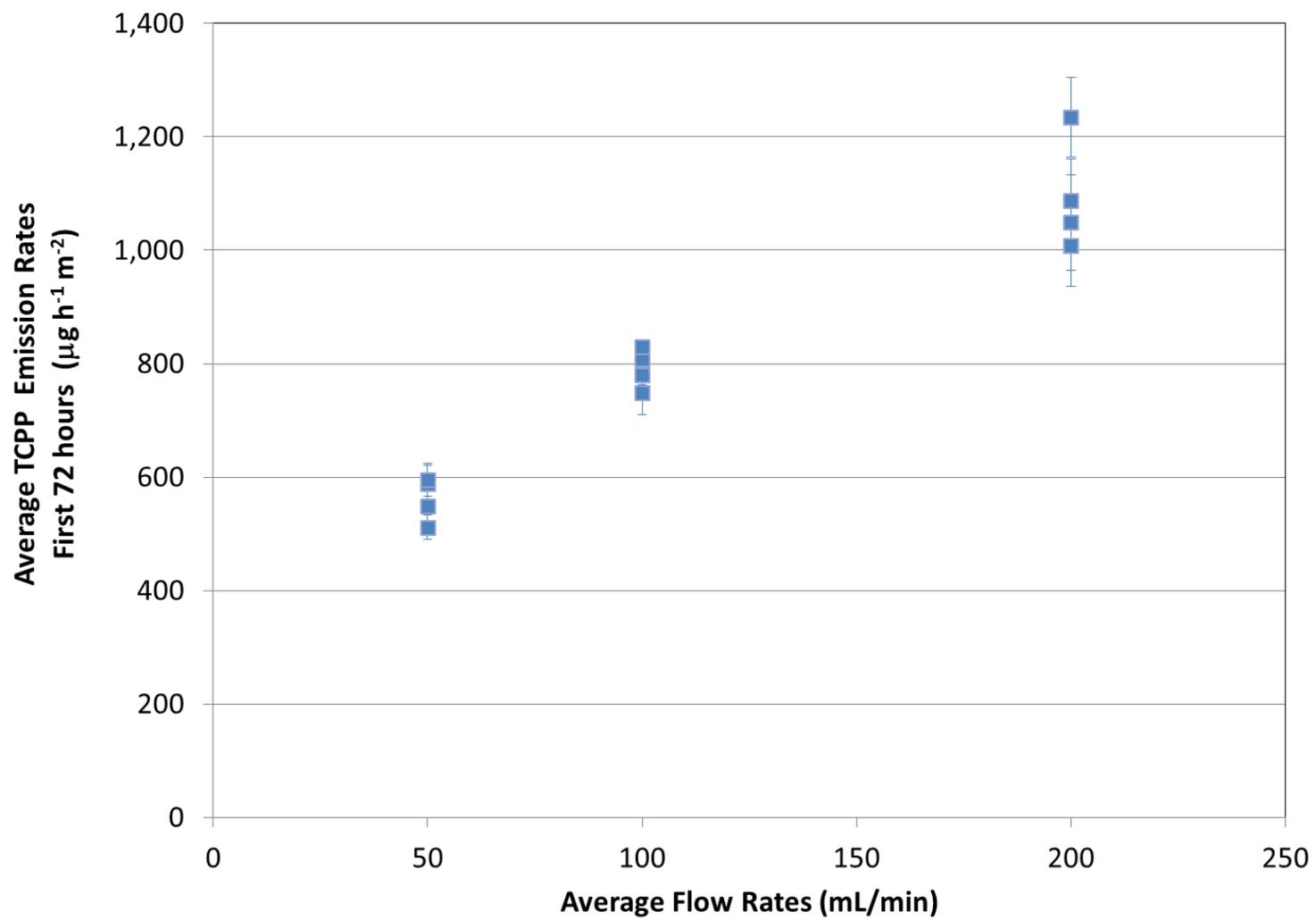


Figure 5: Average TCPP emission rates for experiments run at increasing flow rates. Error bars show standard error in triplicate data.

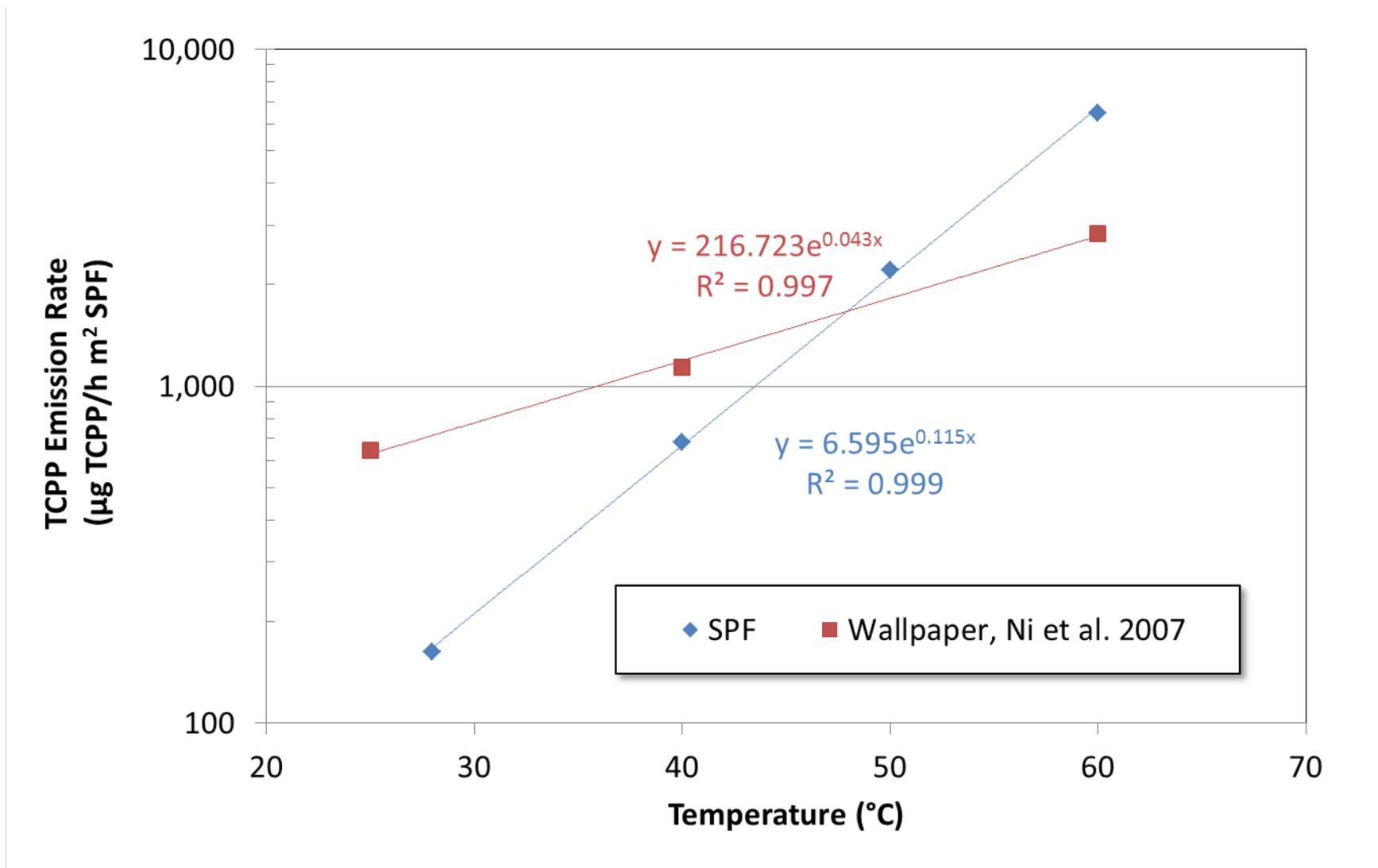


Figure 6: Average TCP emission rates for experiments run at increasing temperate.

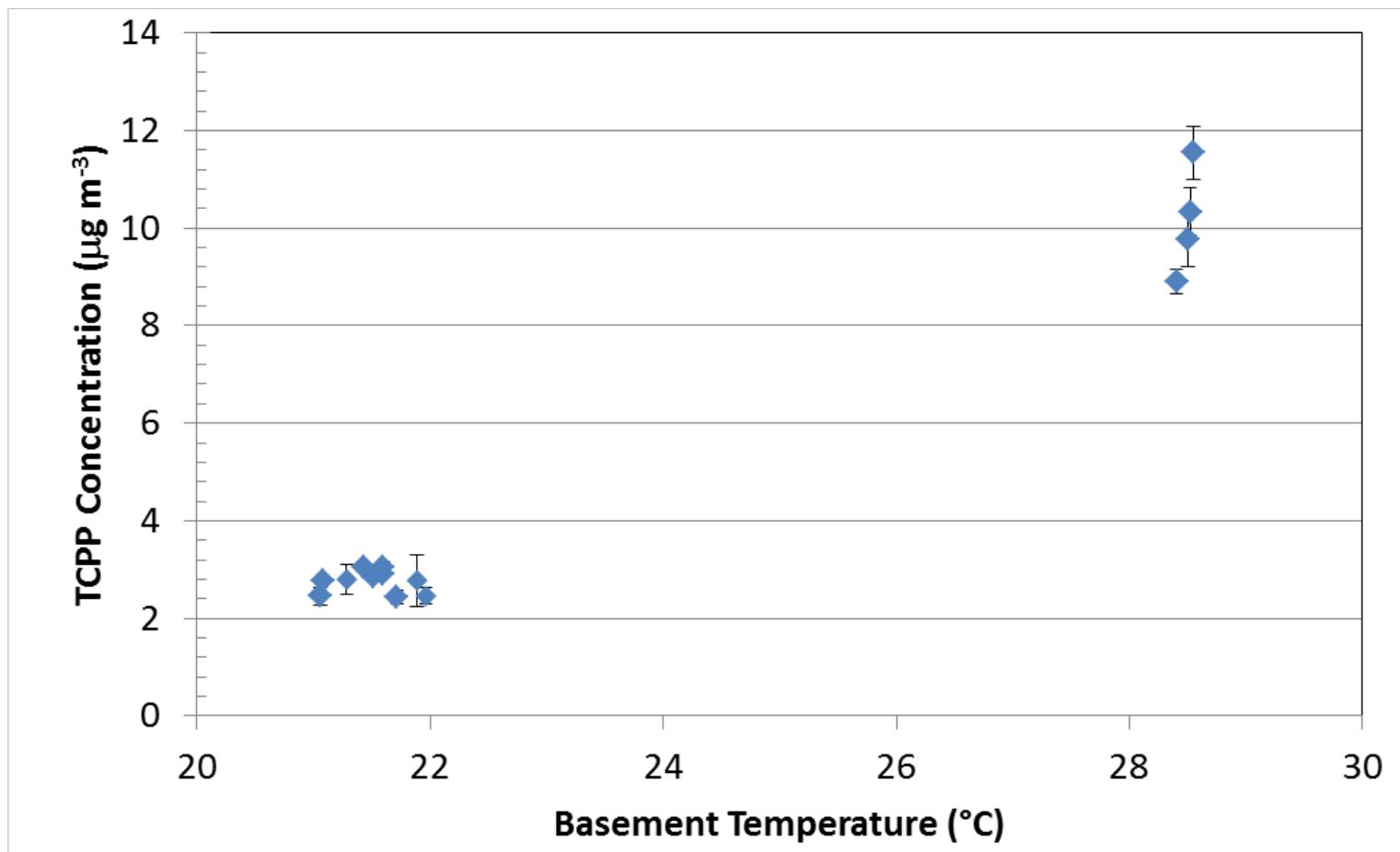


Figure 7: Average TCPP concentration in basement of the NZERTF at various temperatures. Error bars show standard error in triplicate data.

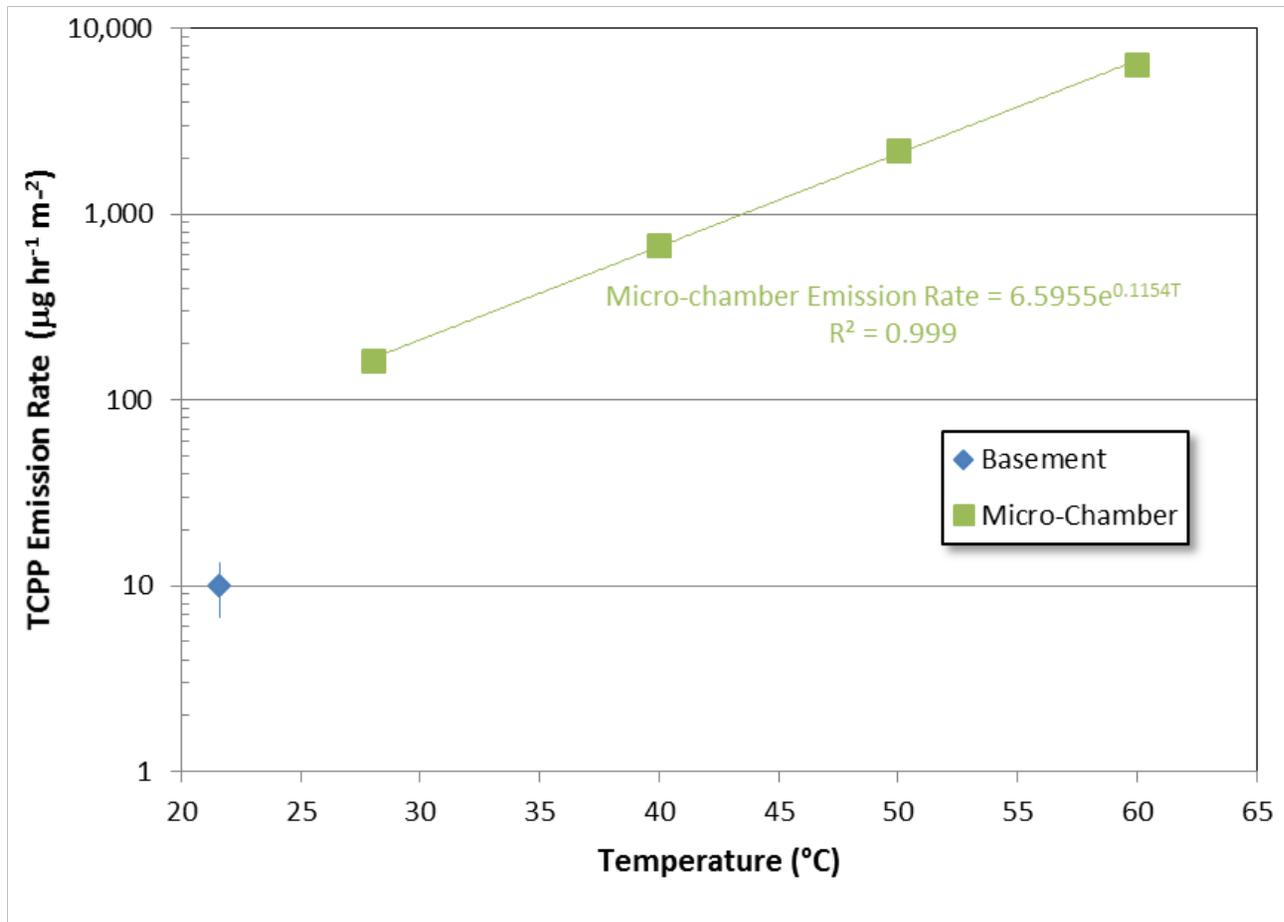


Figure 8: Comparison of TCPP emission rates in the basement of the NZERTF and micro-chambers. The error bars on the basement emission values show a 50% variation in interzone flow rates.

Supplementary Information

Table 4 and Table 5 document the settings used on the Markes Thermal Desorption System, the Agilent gas chromatogram/mass spectrometer (GC/MS)

Table 4. Thermal Desorption System Settings

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

Table 5. GC/MS Settings

Phase	Conditions	Value
<i>Helium Flow</i>	Pressure	10.2 psi
	Flow	1.3 mL min ⁻¹
	Mode	Constant Flow
	Average Velocity	41 cm s ⁻¹

<i>Temperature Profile</i>	Initial Time	2 minutes
	Initial Temperature	40 °C
	Ramp	15 °C mL min ⁻¹
	Final Time	3 minutes
	Final Temperature	315 °C
<i>Detector</i>	Temperature	250°C
	Mode	SCAN