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MEASURING FLAME RETARDANT EMISSIONS FROM SPRAY POLYURETHANE FOAM IN A HOME

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SUMMARY

The use of spray polyurethane foam (SPF) insulation in the United States is increasing. The primary flame retardant used in SPF, Tris (1-chloro-2-propyl) phosphate (TCPP), has been detected in micro-chamber emission experiments investigating SPF. However, due to the use of TCPP in furniture, SPF has not previously been positively identified as a source of indoor TCPP concentrations. This research measured airborne TCPP concentrations in a furniture-free residential test facility that contained 15 m^2 of exposed, two-year-old, open cell SPF.

INTRODUCTION

Spray polyurethane foam (SPF) insulation is increasingly being used in both new construction and retrofits. SPF is a unique building product in two ways: 1) SPF reduces both convective and conductive heat loss through the building envelope, and 2) SPF is created on site through the reaction of two sets of chemicals. Chemicals used to make SPF include polyols, isocyanates, amines, surfactants, amine polyols, alkanolamines, blowing agents and flame retardants. SPF can contain more than 8 % flame retardant (Sebroski 2012). Recent research (Poppendieck et. al. 2015) has shown than when a sample of new open cell, high pressure SPF was tested in micro-chamber environments at 40 °C and 100 mL/min, the flame retardant Tris (1-chloro-2-propyl) phosphate (TCPP) was emitted at nearly a constant concentration (400 $\mu g/m^3$ to 500 $\mu g/m^3$). However, it is unclear how TCPP emissions emission factors from SPF micro-chamber experiments relate to TCPP sources and concentrations in buildings. TCPP is also used in products that contain polyurethane foam such as furniture, mattresses and sound insulation within consumer products. Hence, if TCPP is measured in air of an occupied house containing SPF, the TCPP source cannot be solely attributed to the insulation or the furniture.

The National Institute of Standards and Technology (NIST) built in 2012 a net-zero energy residential test facility (NZERTF) 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. (2014). The NZERTF is a two-story, detached home with an unfinished basement and attic within the building thermal envelope. The garage is not attached. The house is similar in size (242 m^2 for occupied floors, 485 m^2 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 heat recovery ventilator (HRV), and a 10.2 kW photovoltaic system. To comply with the outdoor air requirements in ASHRAE Standard 62.2-2010 (2010) the HRV was sized to deliver 137 m^3 h^{-1} of outdoor air. Special attention was paid to the design and construction of the highly insulated and airtight building envelope. Roughly 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 it can likely be attributed to the SPF. This work sought to measure airborne TCPP concentrations in the NZERTF.

METHODOLOGIES

The first floor and basement of the NZERTF were sampled for TCPP over a period of two months. 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. If TCPP breakthrough to the second tube was found, the data was not used. For each sampling event three sets of tubes were prepared.

Each tube set was sampled at 50 mL/min 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 of methanol). Blank tubes (with internal standard) were run between the samples to quantify any carryover between samples. Samples were analyzed using a thermal desorption-gas chromatography/mass spectrometer system (TD-GC/MS).

When used in field applications TCPP typically consists of three isomers: tris(1-chloro-2-propyl) phosphate (≈66%), bis(1-chloro-2-propyl) (2-chloropropyl) phosphate (≈30%) and (1-chloro-2-propyl) bis(2-chloropropyl) phosphate (≈4%). The relative response ratios of the three isomers on the tubes with TCPP and the subsequent blanks were summed to determine the total response ratio. The combined relative response ratio was then integrated using a five point standard curve (20 ng, 30 ng, 50 ng, 70 ng and 90 ng). Typically, only the first two isomers were detected and only the first two isomers were quantified.

The 13 standard curve R-square values averaged 0.98 for the first and second isomer. On days when a standard curve was not run, check standards were run. The instrument 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.

Samples were run over a period of two months in the summer of 2014. The initial thermostat set point (located on the first floor) was 23.9 °C, a setting that had been maintained for weeks prior to the analysis. The thermostat was raised to 32.2 °C and maintained at the temperature for a period of seven days. Temperatures in the basement were several degrees cooler than the thermostat set points. Temperature values shown in the following table and figure are 12-hour average readings from a thermocouple located in the center of the open basement.

To ensure that there we no sources of TCPP other than the SPF in the basement, small samples of a variety of materials 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 μg TCPP/g material m^3 air to 6.3 μg TCPP/g material m^3 air).

RESULTS AND DISCUSSION

Samples were taken in the basement and on the first floor with the HVAC (Heating, Ventilating, and Air Conditioning) operating under normal conditions (typical air change rates: 0.15 h^{-1} to 0.22 h^{-1}, Poppendieck et. al. 2015). Samples were also taken outdoors and no TCPP was detected. Table 1 shows that the average TCPP concentration for the basement samples was nearly twice that of the first floor samples. These data lends credence to the source of the TCPP being in the basement. As mentioned above, none of the other measured materials in the basement contained TCPP and there have never been other potential sources of TCPP, such as furniture or mattresses, in the NZERTF. This information indicates TCPP is being emitted from the SPF located in the basement, is transported to the living areas, and is measurable in the indoor air under normal operating conditions.

Table 1: Average TCPP concentrations measured in the NIST NZERTF.

Location	Average Temperature (°C)	Number of Samples (n)	Average Concentration (μg/m³)	Relative Standard Deviation
1st Floor	23.7	9	1.5*	7.0%
Basement	21.0	12	2.8	9.9%

*First floor samples ranged from 13 ng to 16 ng per sorbent tube. This is below the lowest standard, but above the instrument detection limit of 8.65 ng determined according to "Definition and procedure for the determination of the method detection limit – Revision 1.11" Pt. 136, App. B 40 CFR Ch. I (7–1–03 Edition).

Direct comparisons of measured concentrations (Table 1) to other residences is of limited use given the unique conditions of the NZERTF. First, SPF was not the primary insulation used in the house. SPF was only sprayed on 15 m^2 of the house exterior, a relatively small fraction of the greater than 600 m^2 of the building envelope. Other SPF application scenarios may involve a larger fraction of the building envelope. Second, the SPF was directly exposed to the basement air. In many SPF applications there are finishing products between the SPF and the occupied space. These products, such as drywall, can inhibit the transfer of TCPP to the occupied space. Third, there were no other sources of TCPP (furniture and mattresses) present in the house. Fourth, this work did not quantify the sorption and or re-emission of TCPP from dust or any other materials. Finally, the toxicological relevance of these concentrations is beyond the scope of this paper. There is limited data on chronic exposure to low TCPP concentrations (Farhat et. al. 2013). Current efforts to expand this knowledge are underway by other researchers.

Previous work (Poppendieck et. al. 2015) has shown a strong correlation between TCPP concentration and temperature when sampled in controlled micro-chamber experiments. To see if this relationship also held true in a full scale residence, the temperature of the NZERTF was raised for seven days (average basement temperate 28.5 °C). The results in Figure 1 illustrate the TCPP concentrations in the NZERTF are also strongly correlated to indoor temperature. There was minimal correlation with outdoor temperature (R square 0.03). The average outdoor temperature was 23 °C during both sets of indoor temperature experiments.

These data are consistent with the micro chamber data that demonstrate a relationship between temperature and emission rate of TCPP from SPF insulation. More research is needed to determine building envelope temperatures where SPF is applied and the fate and transport of TCPP through wall finishing materials.

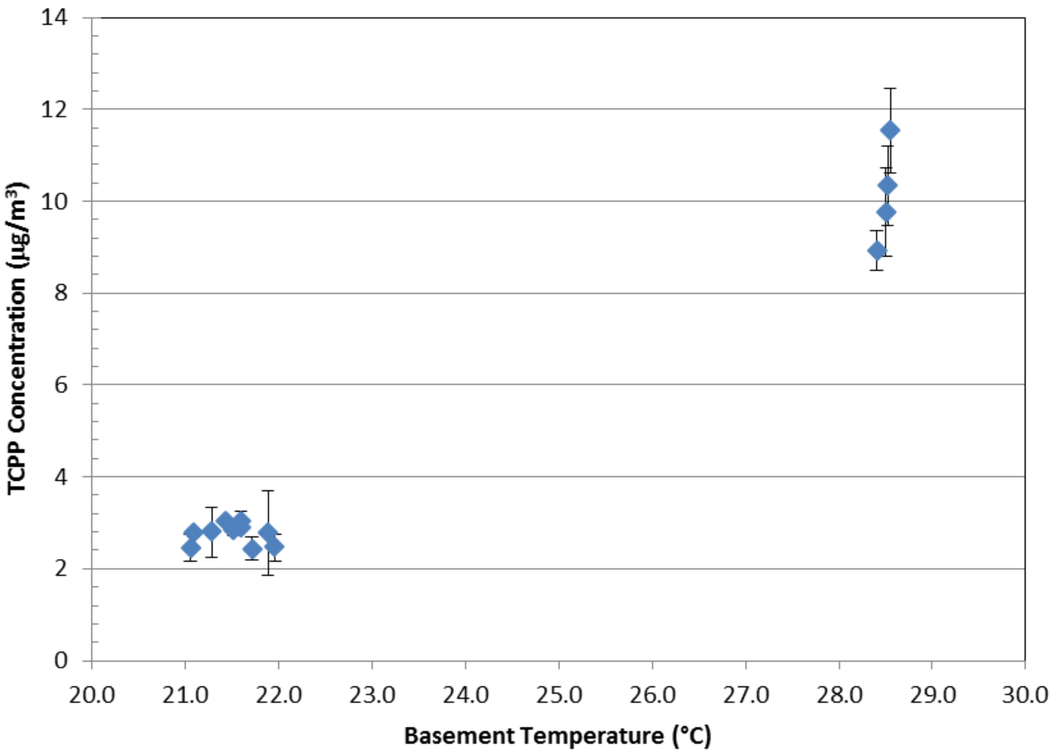

Figure 2: TCPP concentrations measured in the NIST NZERTF basement at various temperatures. Error bars show two standard deviations of triplicate sampling.

CONCLUSIONS

This research indicates that under the tested conditions, airborne TCPP concentrations can be measured in the NZERTF and the source of the TCPP is likely exposed, two-year-old, open-cell SPF.

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