Chemical emissions from spray polyurethane foam (SPF) insulation in residences

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SUMMARY
Spray polyurethane foam insulation (SPF) is a two-component spray foam and an alternative to traditional building insulation such as fiberglass batt insulation. SPF has the advantage of also being an effective air barrier. Two components, A (isocyanates) and B (polyol resin and additives, including fire retardants), are mixed together on-site and sprayed from an application gun onto surfaces such as the underside of roof decks and the cavity side of exterior walls. In some instances following the application of SPF, occupants experience odors and respiratory and sensory irritation that persists for many months. The results from this study indicate that for some installations of SPF, the chemical emissions can result in elevated indoor concentrations long after SPF application. A hydrolysis chemical reaction is hypothesized, where tris(1-chloro-2-propyl) phosphate (TCPP), a fire retardant found in SPF formulations yields 1-chloro-2-propanol, which in the presence of a metal catalyst yields allyl chloride.

KEYWORDS
allyl chloride, bis(2-(dimethylamino)ethyl)ether, 1-chloro-2-propanol, tris(1-chloro-2-propyl) phosphate, volatile organic compounds.

1 INTRODUCTION
Spray polyurethane foam insulation (SPF) is a two-component spray foam and an alternative to traditional building insulation such as fiberglass batt insulation. SPF has the advantage of also being an effective air barrier. Two components, A (isocyanates) and B (polyol resin and additives, including fire retardants), are mixed together on-site and sprayed from an application gun onto surfaces such as the underside of roof decks and the cavity side of exterior walls. In some instances following application of SPF, occupants experience odors and respiratory and sensory irritation that persist for many months.

2 MATERIALS/METHODS
We investigated five single-family detached homes where following the application of SPF insulation, the occupants experienced odors, respiratory irritation, and eye irritation, which persisted for many months. Three different brands of SPF were installed in the five homes, consisting of two open-cell foams (SPF-1 and SPF-2) and one closed-cell foam (SPF-3). The chemicals reported by the SPF manufacturer's Safety Data Sheets – Section 3 Composition, are summarized in Table 1.

The SPF A-Components were all isocyanates. The SPF B-Components contained the resin components, including additives such as fire retardants, many of which were undisclosed as trade secrets. The SPF was applied to the underside of the roof deck in the Attics in all five homes, and in two of these five homes SPF was also applied to exterior wall cavities. The attic application for one home is shown in Figure 1.

Table 1. Spray polyurethane foam (SPF) chemical composition as reported in the SPF manufacturer's Safety Data Sheets.

SPF ID open/closed	A - Components	B- Components
SPF-1 open cell	- Polymethylene polyphenyl isocyanate (CAS# 9016-87-9), 30-70% W/W	- Chlorinated phosphate ester (Trade Secret)[a], 20-25% W/W
	- 4,4'-Methylenediphenyl diisocyanate (CAS# 101-68-8), 30-70% W/W	- Proprietary amines (Trade Secret)[b], 3-15% W/W
		- Surfactant (Trade Secret), 1-5% W/W
		- Polyol resin (Trade Secret), < 40% W/W
		- Proprietary silicone polymer (Trade Secret), < 2% W/W
		- Water (CAS# 7732-18-5), < 30% W/W
SPF-2 open cell	- 4,4'-Methylenediphenyl diisocyanate (CAS# 101-68-8), 30-60% W/W	- Halogenated Phosphate (CAS# NA), 30-50% W/W
	- MDI, mixed isomers (CAS# NA), 30-60% W/W	- Non-Emissive Amine Catalyst (CAS# NA), 5-10% W/W
		- Proprietary Amine (CAS# NA), 0-10% W/W
SPF-3 closed cell	- Polymethylene polyphenyl isocyanate (CAS# 9016-87-9), 30-70% W/W	- Proprietary polyols (Trade Secret) 5-20% W/W
	- 4,4'-Methylenediphenyl diisocyanate (CAS# 101-68-8), 30-70% W/W	- Surfactant (Trade Secret), 1-5% W/W
		- Ethylene Glycol (CAS# 107-21-1), 1-5% W/W

a.) disclosed as Tris(1-chloro-2-propyl) phosphate (TCPP) CAS# 13674-84-5
b.) disclosed as Bis(2-(dimethylamino)ethyl)ether (BDMAEE) CAS# 3033-62-3

Figure 1. Photograph of the SPF applied to the underside of the roof deck in the Attic of home GA-2.

For each home investigated we requested that all windows be closed and that any temporary ventilation fans installed in the Attics turned off from the night before the test, and that the HVAC systems, which were all located in the Attic, be operated in their normal mode.

In each home we collected air samples for the analysis of volatile organic compounds (VOCs) in the Attic, the living space below the Attic, and the outdoor air. Air samples with a volume of 6-8 L were collected over an approximate 90 minute period on multi-sorbent tubes containing Tenax-TA as the primary sorbent backed by a carbonaceous sorbent. Air samples were analyzed for individual VOCs by thermal desorption GC/MS following U.S. EPA Compendium Method TO-17 (EPA, 1999) by an ISO/IEC 17025 accredited laboratory (Berkeley Analytical, Richmond, CA, USA). Following the collection of the air samples, a sample of the installed SPF was collected from the Attic, leaving the air-side surface intact, and then wrapped in two layers of heavy-duty aluminum foil. VOC emission rates from the SPF samples were measured by the laboratory following ASTM D7706 (ASTM, 2017a). A sample of the SPF with an exposed surface area of 31.2 cm^2, was placed into the micro-scale stainless test chamber which was operated at 35 ^oC with a 50 ± 3 cm^3/min of dry ultra-high purity air, as described in ASTM D8142 (ASTM, 2017b). The air-side surface of the sample was untrimmed and as it was installed in the home.

3 RESULTS

Four chemicals dominated the SPF chemical emission rates and the indoor air concentrations; allyl chloride, bis(2-(dimethylamino)ethyl)ether (BDMAEE), 1-chloro-2-propanol, and tris(1-chloro-2-propyl)phosphate (TCPP). The SPF chemical emission rates and air concentrations for these four chemicals are summarized in Tables 2 and 3. Also indicated are the type of SPF, the application location, the time (months) since application, and the average outdoor air temperature on the day of the air sampling for each home.

For exposure guidelines we selected 1% of Cal/OSHA Occupational 8-hour Permissible Exposure Level as being appropriate for residential exposure for allyl chloride (30 $\mu g/m^3$) and bis(2-(dimethylamino)ethyl)ether (BDMAEE, 3.3 $\mu g/m^3$). No exposure guidelines were identified for 1-chloro-2-propanol or TCPP. Hazard Quotients (HQs) were calculated as the ratio of the measured concentration to the exposure guideline, with HQ ≥ 1 indicating exceedance.

3.1 SPF-1 Test Results

The ranges of the chemical emission rates of the SPF-1 open cell samples in three homes, GA-1, GA-2, and AZ-1 (Table 2), were in descending order of magnitude; BDMAEE (330 - > 552 $\mu g/m^2$-h), TCPP (46.2 – 131 $\mu g/m^2$-h), and allyl chloride (<9.6 – 35.2 $\mu g/m^2$-h). The chemical emissions of 1-chloro-2-propanol were all below the detection limit of 9.6 $\mu g/m^2$-h.

Home GA-2 was tested twice, once during cooler weather (i.e., outdoor air temperature 20.3 ^oC) and a second time 8.2 months later during warmer weather (i.e., outdoor air temperature 32.5 ^oC).

The indoor air concentrations of all four VOCs were observed to be elevated over the outdoor concentrations in the Attics of the three homes with SPF-1. In the Living Spaces elevated concentrations were observed in all three homes for 1-chloro-2-propanol, in two of the three homes for allyl chloride, and in one of the three homes for TCPP. BDMAEE exceeded the exposure guideline in the Attic for all three homes, with the concentrations in home GA-2, exceeded during both tests (cooler, GA-2a, and warmer weather, GA-2b). In the Living Space

Table 2. Spray polyurethane foam (SPF) chemical emission rates and indoor concentrations; Homes GA-1, and GA-2.

Home ID State-# (HVAC Location)	SPF Type (months)[a] Location	Chemical CAS#	Emission Rate (µg/m²-h)	Concentrations (µg/m3)			
				Attic	Living Space	Outdoors (Temp °C)	Exposure [c] Guideline
GA-1 (Attic with outdoor air)	SPF-1 open cell (8.8) Attic	Allyl chloride 107-05-1	35.2	**104** [b]	**65.4**	< 2 (30.6)	30
		BDMAEE 3033-62-3	> 511	**37.9**	< 2	< 2	3.3
		1-Chloro-2-propanol 127-00-4	< 9.6	15.7	8.3	< 2	NA
		TCPP 13674-84-5	52	14.5	< 2	< 2	NA
GA-2a (Attic) Test 1	SPF-1 open cell (4.3) Attic	Allyl chloride 107-05-1	25.7	13.2	< 2	< 2 (20.3)	30
		BDMAEE 3033-62-3	> 552	**24.5**	< 2	< 2	3.3
		1-Chloro-2-propanol 127-00-4	< 9.6	6.0	2.4	< 2	NA
		TCPP 13674-84-5	46.2	6.6	< 2	< 2	NA
GA-2b (Attic) Test 2	SPF-1 (12.5) open cell Attic	Allyl chloride 107-05-1	NA	**67.3**	**44.8**	< 2 (32.5)	30
		BDMAEE 3033-62-3	NA	**14.5**	< 2	< 2	3.3
		1-Chloro-2-propanol 127-00-4	NA	43.3	29.2	< 2	NA
		TCPP 13674-84-5	NA	95.8	6.8	2.3	NA
AZ-1 (Attic with HRV)	SPF-1 (14.3) open cell Attic and walls	Ally chloride 107-05-1	< 9.6	**43.7**	7.1	< 2 (27.8)	30
		BDMAEE 3033-62-3	330	**>107**	< 2	< 2	3.3
		1-Chloro-2-propanol 127-00-4	< 9.6	26.1	< 2	< 2	NA
		TCPP 13674-84-5	131	73.1	< 2	< 2	NA

a.) age: months since installation
b.) concentrations **bolded** exceed exposure guideline
c.) 1% of Cal/OSHA 8-hour PEL

below the Attic, the BDMAEE air concentrations exceeded the exposure guideline for two of the three homes, GA-1 and GA-2 (only during the re-test with the warmer weather, GA-2b).

The Hazard Quotient (HQ) for BDMAEE ranged from 4.4 to 100 in the Attics, and < 0.6 (concentrations below detection limit) in the Living Spaces.

Table 3. Spray polyurethane foam (SPF) chemical emission rates and indoor concentrations; Homes CT-1 and CT-2.

Home ID State-# (HVAC Location)	SPF Type (months)[a] Location	Chemical CAS#	Emission Rate (μg/m^2-h)	Concentrations (μg/m3)			
				Attic	Living Space	Outdoors (Temp ^{o}C)	Exposure Guideline [c]
CT-1 (Attic)	SPF-2 open cell (8.3) Attic	Allyl chloride 107-05-1	1,070	**461**	5.9	< 2 (31.1)	30
		BDMAEE 3033-62-3	< 3.2	< 2	< 2	< 2	3.3
		1-Chloro-2-propanol 127-00-4	3.3	48.2	< 2	< 2	NA
		TCPP 13674-84-5	450	> 266	11.7	6.1 *	NA
CT-2 (Attic with HRV)	SPF-3 (10.7) closed cell Attic and walls	Allyl chloride 107-05-1	100	< 2	< 2	< 2 (7.8)	30
		BDMAEE 3033-62-3	< 3.2	< 2	< 2	< 2	3.3
		1-Chloro-2-propanol 127-00-4	< 3.2	< 2	< 2	< 2	NA
		TCPP 13674-84-5	< 3.2	< 2	< 2	< 2	NA

a.) age: months since installation
b.) concentrations **bolded** exceed exposure guideline
c.) 1% of Cal/OSHA 8-hour PEL
* Outdoor air sample analysed following Attic sample and may have experienced carry over of some TCPP.

The indoor air concentrations for allyl chloride exceeded the exposure guideline in the Attic for all three homes, with the concentrations in home GA-2, exceeded only during the re-test (GA-2b) conducted during warmer weather. In the Living Space below the Attic, the allyl chloride concentrations exceeded the exposure guideline for two of the three homes, GA-1 and GA-2 during the re-test (GA-2b) with the warmer weather. The HQ for allyl chloride ranged from 0.4 to 3.5 in the Attics and 0.2 to 2.1 in the Living Spaces.

3.2 SPF-2 Test Results

The chemical emission rates of the SPF-2 open cell sample in home CT-1 (Table 3) were in descending order of magnitude; allyl chloride (1,070 μg/m^2-h), TCPP (450 μg/m^2-h), and 1-chloro-2-propanol (3.3 μg/m^2-h). The chemical emission rate of BDMAEE was below the detection limits of 3.2 μg/m^2-h. The indoor air concentrations of all allyl chloride, 1-chloro-2-propanol, and TCPP were observed to be elevated over the outdoor concentrations in the Attic of CT-1, and allyl chloride and TCPP were also observed to be elevated in the Living Space of CT-1. Only allyl chloride in the Attic was observed to be exceed the exposure guideline, with an HQ of 15.4.

3.3 SPF-3 Test Results
The chemical emission rates of the SPF-3 closed cell sample in CT-2 (Table 3) consisted only of allyl chloride (100 µg/m^2-h). The chemical emission rates of BDMAEE, 1-chloro-2-propanol, and TCPP were all below the detection limits of 3.2 µg/m^2-h. The indoor air concentrations of all four chemicals were observed to be below detection limits in the Attic and Living Space of CT-2, with HQs of less than 0.07 for allyl chloride and less than 0.6 for BDMAEE.

4 DISCUSSION
In home GA-2, the indoor concentrations of SPF chemicals were observed to significantly increase for the re-test during warmer months, 8.2 months later. With an increase in the outdoor air temperature of 1.6 (20.3 ^oC during the initial test, GA-2a, and 32.5 ^oC during the re-test, GA-2b), the indoor concentrations in the Attic increased by factors of 5.1 for allyl chloride, 7.2 for 1-chloro-2-propanol, and 14.5 for TCPP, while the concentration of BDMAEE decreased by a factor 0.6. The indoor concentrations in the Living Space below the Attic also increased during the re-test for allyl chloride, 1-chloro-2-propanol, and TCPP.

In home CT-2 with the closed cell foam, SPF-3, only chemical emissions of allyl chloride (100 mg/m^2-h) were observed. The indoor concentrations of all four SPF chemicals measured were below detection limits (i.e., 2 µg/m^3) in both the Attic and the Living Space. The absence of detectable indoor concentrations of allyl chloride in the Attic and the Living Space despite the observed chemical emissions of allyl chloride from the SPF sample is attributed to the cold weather (i.e., 7.8 ^oC outdoor air temperature) during the collection of the air samples and the higher air temperatures utilized for the micro-chamber chemical emission rate tests (i.e., 35 ^oC).

While the chemical emissions of BDMAEE and TCPP from the SPF samples in this study is understood since manufacturer's SDS indicates or suggests that their SPF products do contain these chemicals, the chemical emissions, and the ensuing indoor concentrations, of allyl chloride and 1-chloro-2-propanol is not well understood, as these chemicals are not identified as chemicals in the manufacturer's SDS.

The following hydrolysis chemical reaction in Figure 2 is hypothesized, where TCPP and water form 1-chloro-2-propanol.

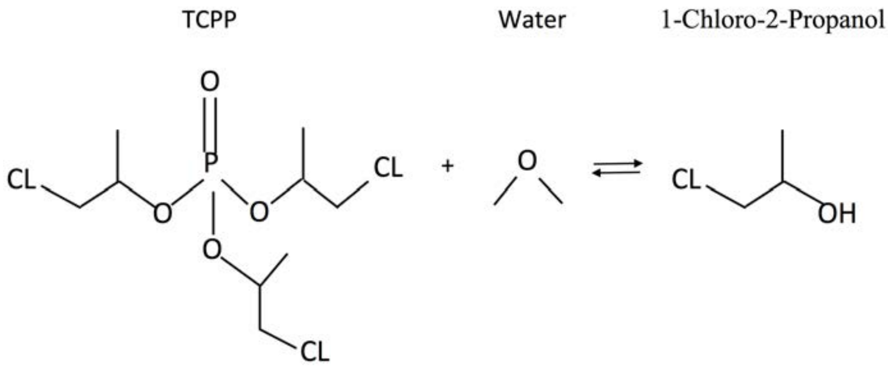

Figure 2. Hypothesized hydrolysis reaction of TCPP with water to create 1-chloro-2-propanol.

This hypothesized hydrolysis reaction is consistent with the chemical emission rate measurements, which are conducted with dry ultra-high purity air, where the emissions of 1-chloro-2-propanol from SPF containing TCPP were observed to be at or below the detection limit despite the observation of elevated indoor air concentrations.

The following metal catalyst chemical reaction in Figure 3 is hypothesized, where 1-chloro-2-propanol in the presence of a metal catalysts forms allyl chloride.

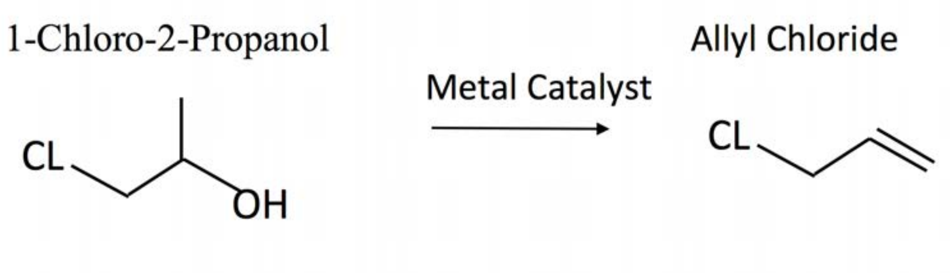

Figure 3. Hypothesized metal catalyst reaction of 1-chloro-2-propanol forming allyl chloride.

With respect to the persistence of the SPF chemical emissions, we note the emission rates of the four chemicals considered in this paper were observed to persist for many months following the SPF application (e.g., chemical emission rates were observed from each of the SPF samples at the time of the sample collection, which ranged from 4.3 to 14.3 months, despite efforts to reduce the emission rates by installing temporary ventilation fans in the Attics).

Considering the mass of TCPP and BDMAEE in the SPF samples in this study, and the observed chemical emission rates of these chemicals, the emissions are expected to persist for decades.

5 CONCLUSIONS

The results from this study indicate that for some installations of SPF, the chemical emissions result in elevated indoor concentrations that are observed to persist for many months and are expected to persist for decades. In addition, the SPF chemical emissions and ensuing elevated indoor concentrations were observed to significantly increase during periods of warmer outdoor air temperatures. Emissions of ally chloride, a potent sensory irritant, were observed from the SPF samples collected in four of the five homes. The respiratory and sensory irritation reported by the occupants is consistent with exposure to allyl chloride. A hydrolysis chemical reaction is hypothesized, where TCPP, a common fire retardant found in SPF formulations, and water yields 1-chloro-2-propanol, and 1-chloro-2-propanol in the presence of a metal catalyst yields allyl chloride. Further research is needed to understand the potential chemical reactions of TCPP and the suitability of this chemical as a fire retardant in SPF insulation.

ACKNOWLEDGEMENT

The chemical reactions for the formation of 1-chloro-2-propanol and allyl chloride from TCPP were proposed to me by the late Bernard Bloom, whom I greatly appreciated his insights.

6 REFERENCES

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