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Systematic evaluation of 1,2-dichloropropane emissions from do-it-yourself spray foam insulation products

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Abstract

Previous studies found 1,2-dichloropropane (1,2-DCP) emitted from spray foam insulation (SPF) products and it was hypothesised that 1,2-DCP is emitted from cured SPF due to thermal degradation of flame retardants. This study experimentally tested this hypothesis using qualitative and quantitative gas-chromatography-mass-spectrometry (GC-MS) of 1,2-DCP in thirteen SPF products.

Multiple batches of each product were tested and 1,2-DCP was found in all samples: raw material (n=1), emitted during application and curing (n=12) and emitted from cured products (n=3). The flame retardants previously hypothesised as the source of 1,2-DCP were spiked onto Tenax-TA tubes and analysed, but no 1,2-DCP was detected. Our experimental data needs a new hypothesis to fully explain the presence of 1,2-DCP. We hypothesise that 1,2-DCP could be present in raw materials used in industrial processing or potentially enter as an impurity resulting from the production process of SPF materials.

Our results provide the first experimental evidence of 1,2-DCP emissions during application of do-it-yourself SPF products. 1,2-dichloropropane was classified as a Class 1 carcinogen in 2014, however most occupational exposure limits were developed prior to the re-classification. Further research focusing on health risks is recommended to evaluate optimal balance between energy conservation, chemical exposure, ventilation strategies and materials selection.

Keywords

Insulation, volatile organic compound, flame retardant, polyurethane, carcinogen

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Highlights

- 1,2-DCP detected during spraying and curing of DIY spray foams
- 1,2-DCP may be in raw products, but further data needed to prove hypothesis
- Although 1,2-DCP classified as carcinogen in 2014, few exposure limits have been revised since

1. Introduction

The polyurethane spray foam (SPF) industry is a large sector with a global value estimated to be \$70.67 billion in 2020¹. The use of polyurethane insulation materials is expected to increase further² considering the global drive for energy efficiency: the United Kingdom proposed a Future Homes and Buildings standard³, while all new European Union buildings must be nearly-zero energy from 2020⁴ and the United States of America proposed a federal building carbon emissions performance standard⁵. Considering polyurethane and polyisocyanurate insulation materials have the highest R-value compared to other insulation materials⁶, their potential for energy demand reduction and whole life carbon savings in buildings is significant⁷. However a potential unintended consequence of these measures may be the infiltration of volatile organic compounds (VOCs) into the indoor environment and their potential impact on indoor air⁸⁻¹⁰. For example, organophosphorus flame retardants are present in many indoor environments^{6,11} as they increase the flammability resistance of consumer and construction products¹². In order to design appropriate mitigation strategies for reducing human exposure to organic compounds present in indoor air, the source and scale of their emissions should be thoroughly investigated¹³.

Polyurethane and polyisocyanurate products are generally made by mixing raw liquid products, such as isocyanates, polyols, flame retardants, catalysts, blowing agents and other additives that react once exposed to atmospheric pressures and gases⁶. There is a historic evidence basis for isocyanate emissions during application, worker exposure to isocyanates and their health implications¹⁴⁻²⁰. However, research on other volatile organic compounds (VOCs) emitted from spray foam products, their concentrations in real environments and impact of individual VOCs on health is still limited²¹⁻²³. Small-scale exploratory studies indicate that 1,2-dichloropropane (1,2-DCP) emissions are found off-gassing from cured spray foam insulation products²⁴⁻²⁶; however the 1,2-DCP origin is unclear. It was hypothesised in 2003 that the likely source of the 1,2-DCP emissions is degradation from “side B” compounds, and in particular organophosphorus flame retardants²⁷. Salthammer et al.²⁷ reference a previous study from 1995²⁸, investigating thermal degradation of fire retardant polyurethane foams, as supporting evidence for the degradation pathway of organophosphorus flame retardants. However no further published studies were found supporting this origin hypothesis and in the meantime 1,2-DCP was re-classified as a Class 1 carcinogen²⁹. We therefore set out to experimentally test the origin hypothesis.

2. Objective

The objective of this work is to experimentally test whether 1,2-DCP emitted from polyurethane spray foams is a by-product from the degradation product process of organophosphate flame retardants, as previously hypothesized in 2003²⁷.

3. Methods

Testing procedure

A total of thirteen different spray foam polyurethane (SPF) products (two 2-component foams and eleven 1-component foams) were analysed over the course of two years in three separate experimental phases. The products were produced by four different parent companies manufacturing insulating foams.

First, quantitative analysis from three SPF products were assessed to determine whether 1,2-DCP was emitted from cured foam samples using solid-phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS). Second, the raw materials comprising one of the polyurethane products was quantitatively assessed for 1,2-DCP presence using thermal desorption gas chromatography mass spectrometry (TD-GC-MS). Finally, 1,2-DCP emissions of 12 products during application and curing were measured using TD-GC-MS. The one-component SPF products were applied in boxes with a volume of 1 L and the two-component foam in a box with a volume of 70 L. All boxes were placed outside in a shaded area with no direct sunlight exposure during spraying and curing. The spraying time ranged between 30-90 s for one component foams and 240 s for the two-component foam. The weight of each box was measured using a DYMO M2 scale before each test and 1 h after spraying had concluded to calculate the weight of each cured SPF sample. The cured one-component samples weighed between 21-135 g and the two-component foam weighed 679 g.

A blank tubes was analysed following each sample to confirm that no compounds were retained in the GC column or TD. Background samples in the location where the experiments were undertaken were collected for each experimental run. All products were tested in different areas and in sequential order to minimise the risk of cross contamination. The above precautions allowed us to discount contamination or chemical reaction between the storage materials, SPF and external air as possible sources of 1,2-DCP.

Products tested

Nearly all of the SPF products tested (n=12) were do-it-yourself products available for purchase and use by the general public. Their application requires no formal training or expertise and the products are supplied with a list of handling and application instructions. The majority (n=8) had a hazard statement H351 'Suspected of causing cancer' on their labels and almost all (n=11) had the H351 statement present on their safety data sheets (SDSs). All the tested products (n=13) contained polymeric isocyanates (pMDI, CAS no.: 9016-87-9), whilst nearly all (n=12) contained the flame retardant tris (1-chloro-2-propyl) phosphate (TCPP, CAS no.: 13674-84-5). Only 31% of the products (n=4) listed polyols in the safety data sheets. Some of the tested products had hydrofluorocarbon (HFC) blowing agents, however HFCs are expected to be phased out in the future due to the Kigali agreement³⁰. All the compounds present in more than one product and listed in the safety data sheets are illustrated in Figure 1.

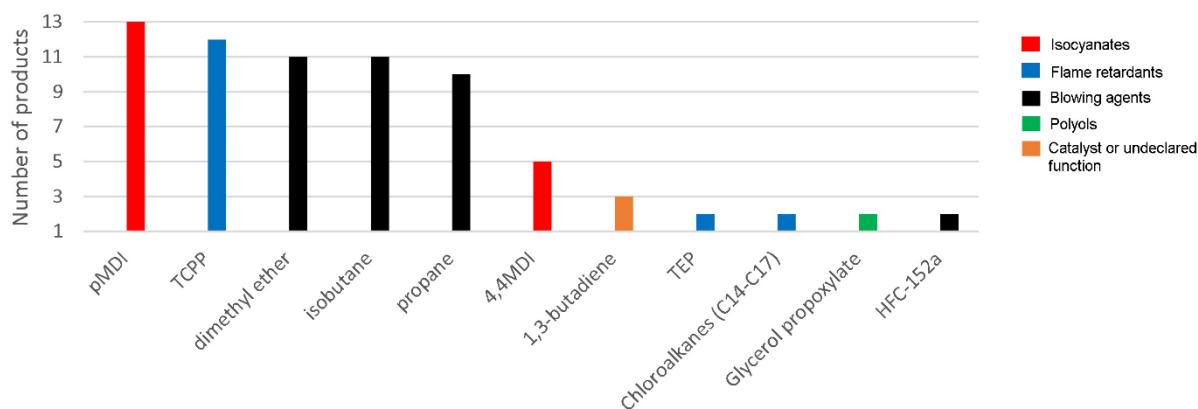


Figure 1. Frequency for compounds listed on the safety data sheets of the 13 tested spray foam products.

Analytical Parameters and Methods

A minimum of two batches of each individual product were tested to reduce sampling bias. Figure 2 outlines the experimental setup and analytical method used for each of the three phases.

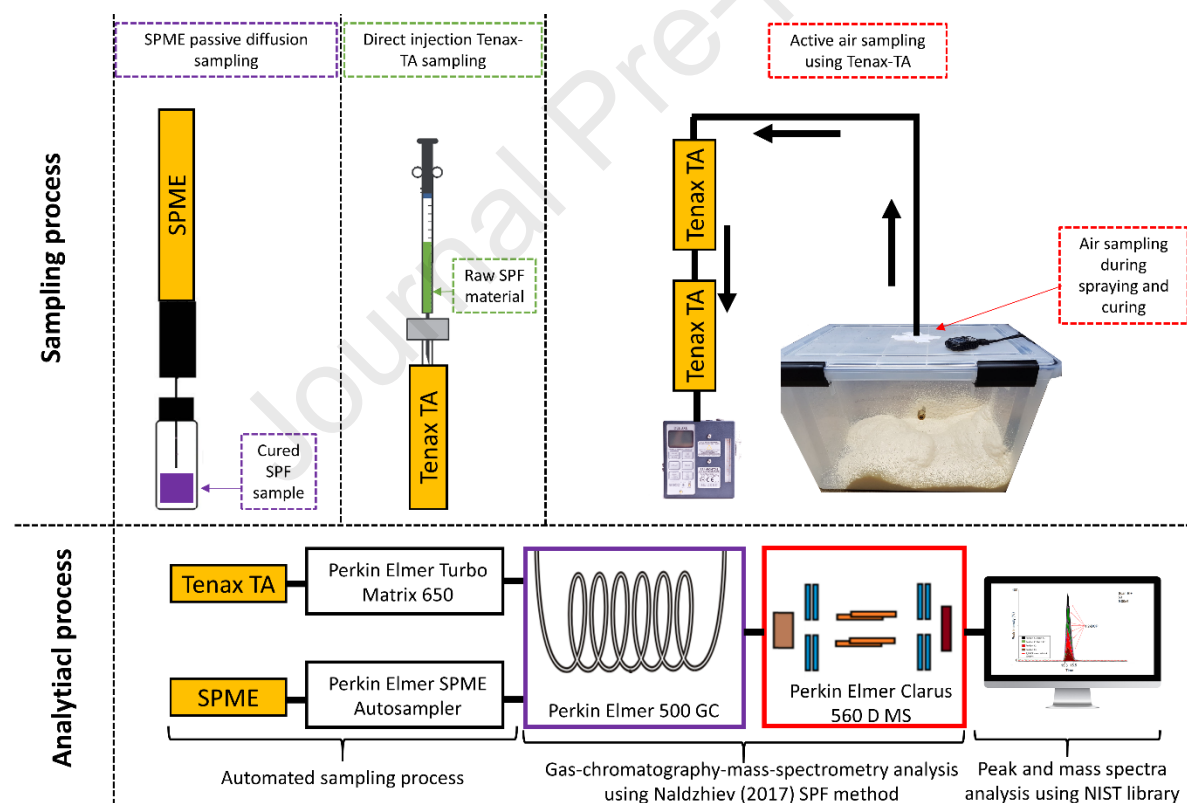


Figure 2. Sampling and analytical setup for the three experimental phases. Phase I (left): passive SPME sampling and 10mL glass vials with 1-3g cured SPF products were sampled (left). Phase II (middle): direct injection of raw materials and spiking onto Tenax-TA (middle) Phase III (right): active air sampling of emissions during spraying and curing using Tenax-TA and low flow pumps. All samples analysed using GCMS (bottom).

The qualitative SPME-GC-MS methodology alongside storage conditions and a broader assessment of VOCs emitted from cured spray foam using have been previously published³¹.

The quantitative analysis was undertaken using equipment and a TD-GC-MS method developed for measuring spray foam emissions³². Sigma Aldrich analytical grade 1,2-DCP (99%, Part #82270) was used to develop calibration curves. The analytical parameters for 1,2-DCP detection are outlined in Table 1.

Table 1. Analytical parameters for 1,2-DCP testing

Analytical Parameter	Calibration Results
Desorption efficiency	99% \pm 0.97%
Regression coefficient (R^2)	0.985
Calibration points	21
Calibration range (ng)	45-13,800
Limit of detection (ng) ³³	27.6 \pm 7.3

For the raw material analysis, two solutions were created using the raw liquid product diluted in hexane (50 μ L of raw material in 10 mL hexane and 500 μ L of raw material in 25 mL hexane). The first diluted solution was created within 6 h of procuring the raw materials, whereas the second diluted solution was created after the raw materials were stored in a cupboard for a period of 28 days. All samples were analysed using the TD-GC-MS method³². In addition, a small amount (5 μ L) of raw liquid material was spiked directly onto 6 Tenax-TA tubes and analysed using TD-GC-MS. This was conducted in order to discount the possibility of chemical reactions between the raw material and the solvent (hexane) as a possible origin route for 1,2-DCP occurrence.

The air samples were collected during spraying and curing. The pumps were turned on immediately before the spray foam was applied in the boxes and sample the air for 5-60 min during both spraying and curing. Low flow pumps (SKC 224-PCMTX8) with flow rates of 0.05-0.25 L min⁻¹ were used and the volumes extracted were generally 2-16 times lower the ASTM safe sampling volumes for 1,2-DCP³⁴. Plastic containers were used for air sampling experiments: one component foams were sprayed in 1 L plastic (PVC) containers, whilst two component foam was sprayed in a 70 L PVC container. Full details of the sampling conditions are available in the Supplementary Material. The containers and experimental data collection was undertaken at a well ventilated shaded external area, with no direct exposure to sun.

Conditions during application

The temperature and relative humidity during spraying and curing were recorded via HOBO UX100 data loggers. The sampling days were carefully selected in line with optimal ambient boundary conditions set by manufacturers as per Figure 3.

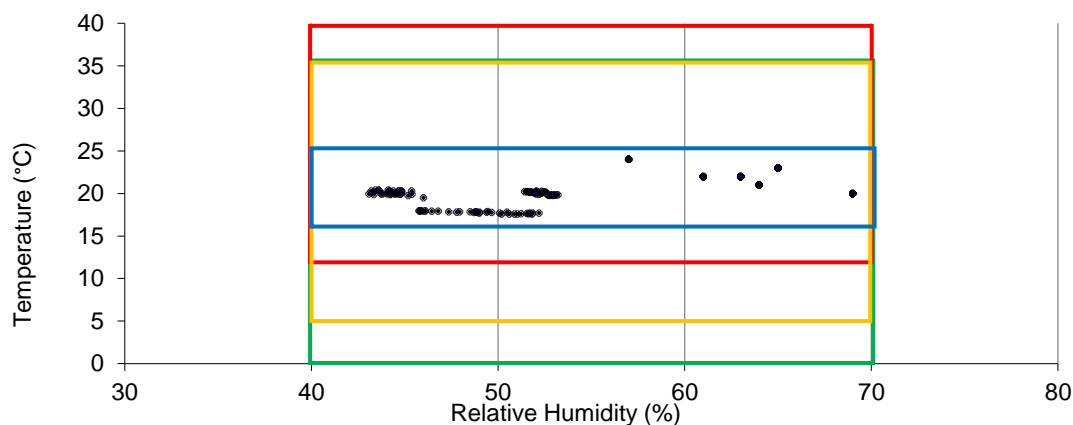


Figure 3. Ambient environmental conditions during spraying and sampling of the spray foam products. Blue, red, orange and green boxes outline recommended guidelines for optimal ambient conditions during application provided by manufacturers.

This experimental setup allowed for discounting misapplication of the products, due to inappropriate environmental conditions, as a reason for why 1,2-DCP could be emitted.

4. Results

The quantitative SPME-GC-MS analysis demonstrated that 1,2-DCP was emitted from all three cured spray foam samples that were tested. Figure 4 summarises the first phase results by overlapping chromatograms which demonstrate 1,2-DCP peaks clearly present in all samples.

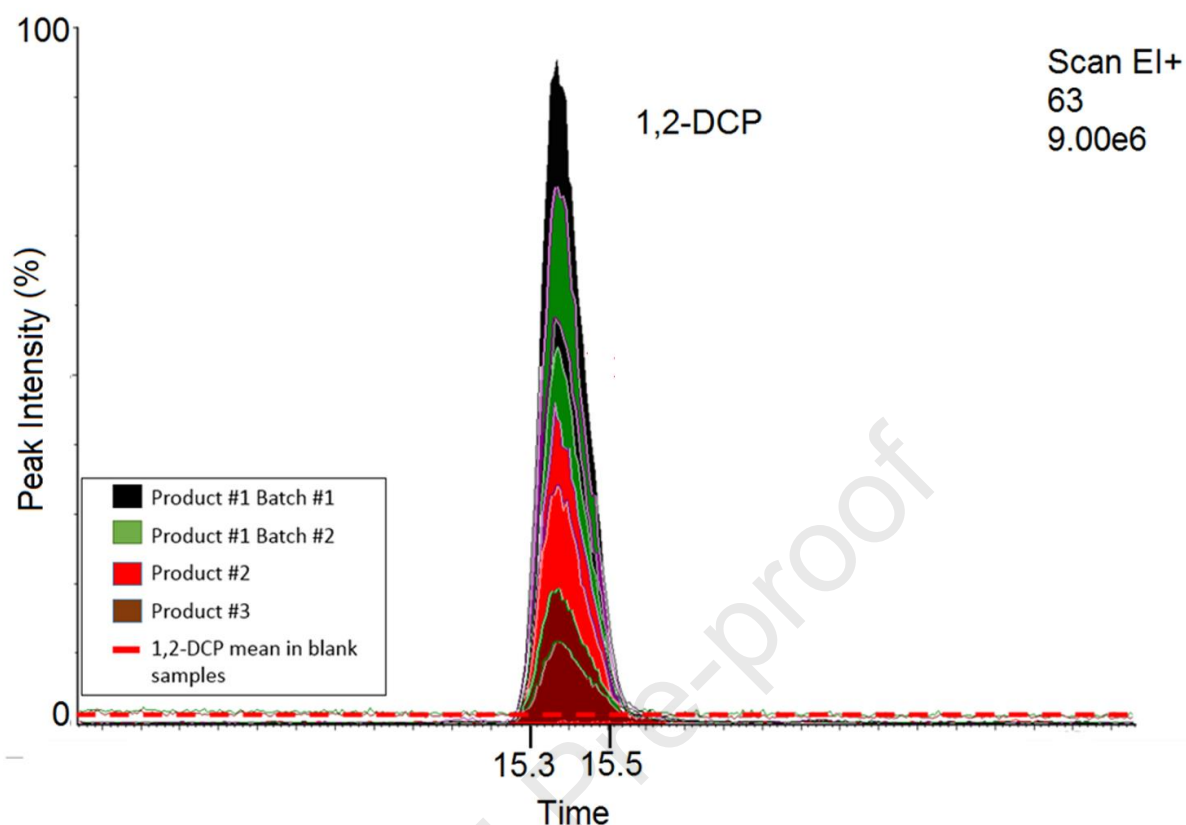


Figure 4. SPME-GC-MS results in SIM mode (m/z 63) of emissions from three cured spray foam products. Two samples from each product were analysed. Horizontal axis is the retention time (min) and the vertical axis is the abundance of the compound (peak intensity).

All results had a symmetrical Gaussian peak shape and no fronting or tailing occurred in any of the samples. The 1,2-DCP peak areas had a signal to noise ratio (S/N) of more than 10 for all of the chromatograms and no 1,2-DCP was found in any of the blanks. As 1,2-DCP was found to be emitted from all cured samples, further testing of raw materials were conducted.

Various volumes of the prepared solutions were spiked on Tenax-TA tubes and analysed using TD-GC-MS. Testing data demonstrated that 1,2-DCP was present in the raw material of the spray foam sample as presented in Table 2.

Table 2. Raw SPF material analysis for 1,2-DCP presence. Some samples exceeded the linearity limit (13,800 ng) of the analytical method.

Material tested	Spray foam raw material sample volume (μL)	1,2- DCP concentration/ Tenax-TA (ng)	1,2-DCP concentration/ SPF (ng/ μL)
Spray foam raw material	5	>13,800	> 2,760
	5	11,739 \pm 4,202	2348 \pm 840
	5	9,701 \pm 3,200	1940 \pm 640
	5	>13,800	> 2,760
	5	>13,800	> 2,760
	5	>13,800	> 2,760

Diluted solution #1	0.05	95 ± 29	$1,900 \pm 580$
	0.05	71 ± 27	$1,420 \pm 540$
	0.05	<MDL	-
Diluted solution #2	0.4	56 ± 26	140 ± 65
	0.4	54 ± 26	135 ± 65
	0.4	79 ± 28	198 ± 70
	3	351 ± 82	117 ± 27
	3	217 ± 42	72 ± 14
	3	450 ± 89	150 ± 30

In the majority of samples (67%) when the raw material was spiked directly onto the Tenax-TA tubes, the 1,2-DCP concentration exceeded the linear range of the calibration parameters. Salthammer et al. (2003) hypothesised that 1,2 DCP could occur as part of a degradation process of the flame retardant tris(1,3-dichloro-2-propyl)phosphate (TDCPP, CAS no.: 13674-87-8). Although TDCPP was not declared to be a constituent compound in any of the tested spray foam products we experimentally tested whether 1,2-DCP occurs during flame retardant degradation in the TD-GC-MS analytical process. We spiked triplicate Tenax-TA tubes with 12,500 ng of both TDCPP (Insight Biotechnology Ltd, Product #sc-229356, 98.5% purity) and triplicate Tenax-TA tubes with 12,500 ng of TCPP (Sigma Aldrich, Part # 119660, 97% purity) in two separate experiments and analysed them using the TD-GC-MS method. No 1,2-DCP was found in any of the chromatograms above the detection limit when spiking TDCPP or TCPP.

As 1,2-DCP was found in the raw material of one SPF product, a range of products were then quantitatively analysed for 1,2-DCP emissions during spraying and curing to explore whether 1,2-DCP could be detected in the air. The full dataset is found in the Supplementary Material. The calculated 1,2-DCP concentrations during application, based on the mass (ng) of 1,2-DCP in the primary tube, is plotted in Figure 5 for each product.

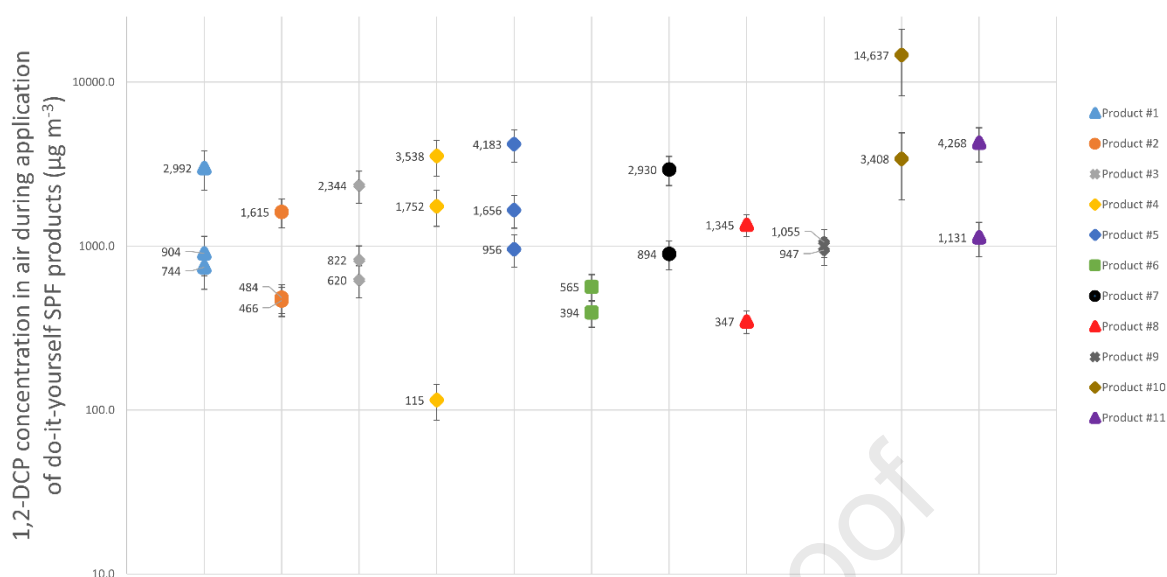


Figure 5. 1,2-DCP concentration in air during spraying and curing of eleven do-it-yourself spray foam insulation products. Each colour represents a different product and each point represents a different batch of the same product. Y-axis is logarithmic.

Although the application conditions were similar, as per Figure 3, there was variation in the 1,2-DCP concentration between different batches. As breakthrough occurred in the majority of tested batches, Figure 5 outlines the minimum concentration of 1,2-DCP in the air. This was calculated by dividing the concentration of 1,2-DCP in the primary Tenax-TA tube by the volume of extracted air. Breakthrough signifies that the concentration within the containers was too high or the flow rate of the pump was too high. This phenomenon occurred despite sampling rates and breakthrough volumes following ASTM recommendations³⁴ and the spray foam surface area covering 0.05-0.16 m², which is smaller than standard field application in refurbishment projects by a factor of 10-250,000³⁵. There was limited correlation between product weight and 1,2-DCP concentration in the air during application. We attempted to sample raw materials of one-component products, but were unsuccessful as an exothermic chemical reaction occurred as soon as the raw products exited the pressurised canisters. Therefore a mass balance calculation for individual compounds in the raw material was not achievable and no correlation was investigated between the individual compounds in the raw material and the recorded 1,2-DCP emissions. No 1,2-DCP was detected in any blank tube (between samples, air extracted from containers and external air where experiments were undertaken).

5. Discussion

Our study analysed raw SPF liquid, emissions during application and cured spray foam products. The data presented in this study demonstrated that 1,2-DCP was systematically present in thirteen different SPF products during spraying and curing. Whilst 1,2-DCP has been found to have impact on health^{36,37} the exposure values for both occupational and worker exposure vary by country and organisation. Table 3 outlines the exposure limits across different countries and the carcinogenic classification of 1,2-DCP.

Table 3. 1,2-DCP exposure limits and carcinogenic classification in different countries or by international organisations^{38,39,48–55,40–47}. Years on table denote when the classification or limit was established.

Country/Area	Agency	Year	Occupational Exposure Limit -OEL TWA ($\mu\text{g m}^{-3}$)	Short Term Exposure Limit STEL 15 min ($\mu\text{g m}^{-3}$)	IDLH- immediate danger ($\mu\text{g m}^{-3}$)	Carcinogenic Classification
-	IARC	2014	-	-	-	1 – carcinogenic to humans
EU	ECHA	2017	-	-	-	1B- presumed human carcinogen
Germany	DFG	2020	-	-	-	Carcinogenic to humans
U.S.	EPA	1994* (under review in 2021)	-	-	-	B2- probable human carcinogen (1994)
U.S.	ACGIH	2007	46,000 (10 ppm)	-	-	-
U.S.	OSHA	1999; 1994	347,000 (75 ppm)	508,000 (110 ppm)	-	-

U.S.	NIOSH	2014; 2016	-	-	1,848,000 (400 ppm)	Potential occupational carcinogen (2016)
Brazil	Inspeção do Trabalho - Governo Federal	2020	275,000 (59 ppm)			
Canada	Canada Labour Code	-	46,200 (10 ppm)	-	-	-
Australia	Safe Work Australia	2020* (proposed- consultation)	46,000 (10 ppm)	-	1,848,000 (400 ppm)	-
Belgium	Federal Public Service Employment, Work and Social Dialogue	2020	46,000 (10 ppm)	-	-	-
Canada	Government of Alberta	2021	46,000 (10 ppm)			
China	National Health Commission of People's Republic of China	2019	350,000 (76 ppm)	500,000 (100 ppm)		
Finland	Social- och hälsovårdsministeriet	2009	46,000 (10 ppm)	92,400 (20 ppm)	-	-
Germany	Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA)	2019	-	-	-	1B – presumed human carcinogen
Ireland	Health and Safety Authority	2021	46,000 (10 ppm)			
Japan	Japan Society for Occupational Health (JSOH)	2013	4,600 (1 ppm)			
New Zealand	WorkSafe New Zealand	2019	23,000 (5 ppm)	-		

Norway	The Norwegian Labour Inspection Authority - Arbeidstilsynet	2021	184,800 (40 ppm)	-	-	-
Poland	Minister of Family, Labour and Social Policy	2018	50,800 (11 ppm)	-	-	-
Singapore	Ministry of Manpower	2009	347,000 (75 ppm)	508,000 (110 ppm)		
Sweden	Swedish Work Environment Authority (Arbetsmiljöverket)	2018	-	-	-	-
United Kingdom	Health and Safety Executive	-	-	-	-	-

The comparison of occupational exposure limits (OELs) in Table 3 demonstrates that 1,2-DCP OELs in Europe are generally lower than those in Asia and America with China, Singapore and the United States having the highest OELs (75 ppm). European and Australasian countries have OELs ranging between 1-11 ppm, with the exception of Norway with a limit of 40 ppm. The absolute lowest exposure limits are found in Japan where associations between cancer and exposure to 1,2-dichloropropane among printing workers were reported in 2013-2014⁴². The EPA proposed 1,2-DCP as a high-priority substance for risk evaluation in 2019, however the evaluation has not been completed as of September 2021³⁷. A case of acute encephalopathy, dizziness, headache, and diplopia was recorded in a 41-year old worker in Korea after being exposed to 1,2-DCP levels (8-41 ppm) reportedly below many occupational limits presented in Table 3³⁶. It is a reasonable expectation that the current exposure limits will be revised in the future.

None of the spray foam products had a H350 hazard statement within their safety data sheets or labelling, however 1,2-DCP was found in air samples during spraying from all products in this study. No 1,2-DCP above the detection limit was found in any of the blank samples (empty boxes, external air or blank tubes between runs). Salthammer et al. (2003) hypothesised that 1,2 DCP could occur as part of a degradation process of the flame retardant Tris(1,3-dichloro-2-propyl)phosphate (TDCPP). None of the tested products as part of this study reported to contain TDCPP within the safety data sheets. The experimental data presented in this study provides evidence for an alternative hypothesis on the two plausible routes for 1,2-DCP formulation:

- 1,2-DCP was present in the raw materials of all thirteen different products

- A chemical reaction between the different chemical compounds leads to the formation of 1,2-DCP during the SPF application process or during the GC-MS analysis
- A combination of the above

We have only sampled the raw material of one product in this study, therefore the second and third plausible routes could not be excluded with certainty. The second hypothesis is however less likely as there were no two products with exactly the same formulation and none of the tested products reported to contain TDCPP as per the safety data sheets. The only compound that was declared to be present in all products was polymeric isocyanate (pMDI). As 1,2-DCP was historically used as a solvent in the production of toluene diisocyanate (TDI)⁵⁶, it is plausible that 1,2-DCP could have been used for the production of pMDI as well. However, the raw material (side B) tested in this study did not report to contain pMDI according to the safety data sheet. This finding supports the first hypothesis.

The results from this study demonstrate 1,2-DCP presence both within raw material, during application and curing of spray foam products. Data from previous studies provides evidence for 1,2-DCP emissions from cured spray foam products^{24,26,57,58}, from 6-10-month old SPF samples collected from insulated houses⁵⁹ and being present in the air in refurbished residential units²³. This collective evidence basis demonstrate systematic presence of 1,2-DCP across more than seventeen different one and two-component SPF products from different suppliers in multiple countries across the first year of the SPF product lifecycle (spraying, application, curing, use). To reduce exposure to volatile organic compounds in buildings, we require knowledge of the source of the emissions⁹ in order to design appropriate mitigation measures, such as ventilation.

Strategies for reducing human exposure to VOCs from spray foam products during application could be to wear personal protective equipment (PPE)⁶⁰ and to provide extract ventilation that negatively pressurises the spraying area⁶¹. It is reported that the main uses for 1,2-DCP are as a solvent, textile spot remover or formerly as soil pesticide⁴³ however it is unclear whether it could serve a functional service during spray foam production. If our alternative hypothesis is conclusively proven with further testing, a source control strategy following World Health Organisation⁶² and Public Health England⁶³ best practice would be optimal for reducing exposure to 1,2-DCP. Using the data from this study it is not possible to hypothesise how and where 1,2-DCP could have entered the spray foam raw materials during the production process.

Whilst the study assessed multiple products and batches from a number of manufacturers, a limitation is that the tested products may not be representative of the population of spray foam products available on the market. The testing procedure was undertaken in closed containers with small amounts of foam and limited ventilation, therefore the results may not be representative of field application practices and conditions. Due to the breakthrough during sampling, the presented results are not appropriate for calculating human exposure or comparison to exposure limits. Further international research is therefore recommended to develop a deeper understanding on the emissions from SPF products, their origin, levels of exposure and best-practice for application strategies.

6. Conclusion

Experimental analysis was conducted to test the hypothesis that 1,2-dichloropropane emissions from polyurethane spray foam (SPF) were the result of flame retardant degradation. Thirteen spray foam products were assessed for 1,2-dichloropropane emissions qualitatively (SPME-GC-MS) and quantitatively (TD-GC-MS). The study also assessed the raw material of one product for 1,2-DCP presence.

Our findings present systematic evidence for the presence of 1,2-DCP during application over a range of different do-it-yourself spray foam products and batches. The results indicate that 1,2-DCP is emitted in the air in measurable concentrations from all thirteen products during spraying and curing. We provide supporting data outlining 1,2-DCP presence in the raw material of one of the products. The experimental data supports an alternative hypothesis: that 1,2-DCP may either be used as a solvent during production of SPF or occur as a possible contaminant in the production process. The study found that some existing exposure values for 1,2-DCP were developed prior to it being classified as a Class 1 carcinogen by IARC and may need to be revised in the future. Taking into account the availability of SPF products for do-it-yourself purposes, a source control strategy following World Health Organisation best practice is considered optimal for reducing chemical exposure.

The study outlines the need for further sampling and analytical method optimisation as breakthrough occurred even when using a low sampling flow rate (0.050 l min^{-1}) and very small amounts of SPF (12-200 g). Further research focusing on human health is recommended to estimate optimal balance between volatile organic compounds exposure, energy conservation, ventilation strategies and materials selection.

Disclaimer:

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Supplementary Material

Test containers and experimental setup

Plastic containers with the following sizes were used for each experiment:

- 10x12x12cm 1 litre plastic (PVC) rectangular container
- 8x8x8cm 1 litre plastic (PVC) round container
- L 59 cm x W 39 cm x H 38 cm 70 litre plastic (PVC) rectangular container by Solent Plastic

Two holes were drilled in each box: one on top and one on the side. The top hole was used for spraying the polyurethane foams into the containers. The side hole was used for extracting air through thermal desorption tubes. The holes were drilled with a ¼ inch diameter, which was the external diameter of the Tenax-TA tubes. The ventilation rate of the box was not controlled and was driven by gaps and cracks in the containers, similar to an enclosed space within an existing house. The containers and experimental data collection was undertaken at a well ventilated shaded external area, with no direct sunlight or sun exposure. The setup is illustrated below in Figure 1.



Figure 1. For SPME-GC-MS analysis, glass vials with 88-102mg of cured SPF samples from Products #1-#3 were used (left), for TD-GC-MS 70l box for Product #2 (centre) and 1l container for Product #3-13 testing (right) were used.

For the samples analysed using SPME-GC-MS, the ASTM 7859-19 method was followed for the preparation and cutting of the samples⁶⁴. Small samples (2-5 mm) were cut out, with a different blade for each product, and placed in 20-ml glass vials. Once the samples were placed in vials, they were stored for 5 days before testing with SPME-GC-MS. The samples were then analysed using GC-MS method developed for detecting emissions from polyurethane products³². For the samples analysed using TD-GC-MS, the ASTM D8142-17 analytical setup, sampling volumes and principles were used to measure 1,2-DCP emissions. The days during which spraying occurred were carefully selected following the optimal procedures for ambient conditions by each

manufacture. The boxes were kept in a controlled laboratory environment of 20-25°C and taken outside just before the foam was applied in them. This ensured that their substrate surface temperature was within the optimal parameters recommended by foam manufacturers. All foams were applied within the boundary conditions recommended by the manufacturers in order to discount misapplication procedures as a possible source for the emissions. All manufacturers had instructions on ambient temperature during application, however only two manufacturers had guidance on relative humidity. We took a reserved approach by conducting tests at 40-70% relative humidity in order to ensure SPF reaction process and curing are representative of standard application conditions and follow optimal application procedures.

Table 1 below contains the complete dataset of 1,2-DCP results, which have been used to produce Figure 2.

Table 1. Complete dataset of 1,2-DCP results using quantitative TD-GC-MS analysis.

Product Number	Batch Number	Testing conditions	Sampling container (L)	Sampling flow rate (L min ⁻¹)	Sampling period (min)	Sample mass (g)	1,2- DCP concentration primary tube (µg m ⁻³)	1,2- DCP concentration backup tube (µg m ⁻³)
#2- Two component spray foam	1	During spraying [30-240 s] and curing	70	0.25	5	679	1,987 ± 440	1,669 ± 405
					10		917 ± 212	946 ± 215
					15		629 ± 143	679 ± 149
					30		284 ± 67	309 ± 71
					60		136 ± 33	112 ± 39
#3- One component spray foam	1		1	0.05	10	35	744 ± 166	313 ± 72
	2					30	904 ± 193	<MDL
	3					41	2,992 ± 1,107	1,698 ± 376
#4- One component spray foam	1		1	0.05	10	33	466 ± 87	132 ± 54
	2					31	484 ± 91	91 ± 29
	3					58	1,615 ± 367	788 ± 170
#5- One component spray foam	1		1	0.05	10	36	620 ± 158	166 ± 57
	2					35	822 ± 186	<MDL
	3					135	2,344 ± 433	2,068 ± 408
#6- One component spray foam	1		1	0.20	10	21	115 ± 22	81 ± 18
	2	55				1,752 ± 381	1,199 ± 199	
	3	51				3,538 ± 1197	1,918 ± 395	

#7- One component spray foam	1			0.05		43	1,656 ± 372	568 ± 154
	2			0.20		42	956 ± 197	<MDL
	3			0.05		62	4,183 ± 1014	2,958 ± 1102
#8- One component spray foam	1			0.05		89	394 ± 80	226 ± 63
	2			0.05		57	565 ± 97	231 ± 64
#9- One component spray foam	1			0.20		35	894 ± 301	415 ± 93
	2			0.05		62	2,930 ± 1097	1,552 ± 363
#10- One component spray foam	1			0.20		33	347 ± 53	182 ± 41
	2			0.05		21	1,345 ± 209	110 ± 19
#11- One component spray foam	1			0.05		18	948 ± 181	<MDL
	2			0.20		20	1,055 ± 206	202 ± 40
#12- One component spray foam	1			0.20		87	3,408 ± 1516	2,533 ± 651
	2			0.05		51	>13,800	8,795 ± 2549
#13- One component spray foam	1			0.20		33	1,131 ± 263	996 ± 248
	2			0.05		55	1,067 ± 256	719 ± 272

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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