Evaluating energy and indoor air quality potential impact of spray foam: a case study of robotic application

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A dissertation submitted in fulfilment

of the requirements for the degree of

Doctor of Philosophy

of

University College London

The Bartlett School of Environment, Energy and Resources

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October 2022

Declaration

I, Dzhordzhio Rosenov Naldzhiev, confirm that the work presented in this thesis is my own. When information has been derived from other sources, I confirm that this has been indicated in the thesis.

Dzhordzhio Naldzhiev

Abstract

Homes in the UK require transformational retrofit to meet Net Zero legislation. Selecting the right insulation balances multiple, often clashing, performance criteria: energy savings, capital cost, thermal comfort, installation disruption, heritage impact and indoor air quality. There is a lack of evidence in balancing trade-offs between energy, heritage and indoor air quality impact when comparing insulation products.

This thesis converged data from different disciplines and showed the retrofit potential, key barriers and enablers of insulating millions uninsulated floors in the UK. In underfloor voids with limited space polyurethane spray foam applied with robots offers better insulating potential compared to conventional products with the same thickness, however more scientific evidence was needed on off-gassing emissions.

To measure spray foam emissions, heritage science techniques were adopted to develop a novel method. The method could be applied in built environment case studies to measure volatile organic compounds (VOC) from polyurethane products. The VOC emissions during spraying were assessed for a majority of spray foam product available on the open market. The original data provided evidence for generating a new hypothesis for why 1,2-dichloropropane (1,2-DCP) was found in spray foams. The data suggests 1,2-DCP may have been part of some of the raw materials contrary to the existing hypothesis from 2003 suggesting it was a result of flame retardants degradation. This is relevant as 1,2-DCP was re-classified as Class 1 carcinogen in 2014.

Furthermore, ventilation strategies and their effectiveness as a mitigation measure for reducing VOCs were evaluated. Spray foam VOC concentrations were first measured in controlled conditions. Experimental data revealed that VOC concentrations are significantly lower next to sprayers when robots and robust ventilation are deployed.

The findings were validated in a case study where long-term VOC concentrations were measured for a period of up to 2 months after retrofit. The majority of VOC concentrations were not detected indoors post-installation with the exception of flame retardants.

Acknowledgements

The research was made possible by EPSRC funding for the Centre for Doctoral Training in Science and Engineering in Arts, Heritage and Archaeology (SEAHA), grant number EP/L016036/1.

First of all, contrary to conventional protocol, I would like to thank my wife Emilia for supporting me through the tsunami that is the venture into academia and science creation. It was unexpected, challenging, disruptive, life changing however fundamentally transformative in a way that I didn't think was possible before it hit. Thank you for being the load-bearing flood defence system for our physical, mental and overall wellbeing during this turbulent journey. I am forever grateful to my parents, Nadya and Rosen, for making my professional journey in the UK a possibility. Particular credit goes to my mother, Nadya, for shaping my values and without whom I would not be the man I am today. I thank my two young sisters, Dea-Maria and Angie, who will probably never read this thesis, but provided me with plenty of positive energy that were invaluable wellbeing reinforcement allowing me to be able to complete it. I also thank all my family and friends who received many, possibly unsolicited, spray foam chemistry lessons along the way and nevertheless supported me.

I would like to thank the supervisory team of Prof Dejan Mumovic and Prof Matija Strlic. Without their collective knowledge, wisdom and academic experience, this project would not have been possible nor impactful. I was motivated by their desire to achieve positive real-world impact whilst also delivering scientific excellence – I am forever grateful to both for shaping me as the scientists I am today.

I would like to thank Thomas Lipinski for his scientific curiosity, desire to learn from research and drive forward positive change in unconventional ways. I would like to thank Dr Mark Underhill, Dr Dustin Poppendieck , Dr Elizabeth Cooper, Dr Miriam Wright and Prof Katherine Curran for assisting with expert advice on exposure assessments, analytical chemistry and organic emissions. I would like to thank the UKIEG, CIBSE and ASTM committees for their knowledge and insight into the indoor air quality world. I would like to thank Dr Irena Kralj Cigić for her expertise and collaboration in chromatography analysis. I thank Robyn Parker, May Cassar, Josep Grau-Bove who masterfully managed SEAHA and facilitated us all in achieving our scientific objectives. Many others encouraged and

supported my work through discussions, debate and feedback: Dr Esfandiar Burman, Dr Hector Altamirano, Dr Marcella Ucci, Prof Mike Davies, Dr Sung-Min Hong, Dr Samuel Stamp, Prof Tim Dwyer, Dr Valentina Marincioni.

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Impact statement and list of publications

Contribution to knowledge

This thesis focused on further developing scientific knowledge within the built environment context by adopting a multidisciplinary approach. Its so called heritage origins were methods developed for measuring volatile organic compound (VOC) polyurethane emissions in museum and heritage environments. Through this thesis the knowledge from the heritage science field (combining heritage and analytical chemistry) was transferred to the built environment and environmental science field.

First, a method for measuring spray foam insulation emissions throughout their lifecycle was successfully developed. The method was utilised to measure emissions from the majority of the spray foam materials on the open market and provided original evidence in relation to short, mid and long-term concentrations. An alternative hypothesis was generated contrary to what was assumed as an established finding in the scientific literature – that the origin of a Class 1 carcinogen (1,2-dichloropropane) found in spray foam products was due to flame retardant degradation. This thesis offers empirical evidence in support of an alternative hypothesis that suggests some of the raw materials may have been partly, or fully, responsible for 1,2-dichloropropane (1,2-DCP) occurring during installation of spray foam materials.

Secondly, the use of robots to apply spray foam remotely from the operators and increased ventilation rates were experimentally proven to reduce VOC concentration near the spray both in controlled conditions and a case study. This is the first study assessing primary and secondary spray foam emissions and measuring their concentration through the full spray foam lifecycle: from raw materials up to post-installation in a building retrofitted with robots. The thesis provided novel evidence on the potential reduction of exposure to VOC in the inhalation zone during spraying, and curing, when using robots instead of conventional manual spraying.

Finally, a framework for both categorising and measuring spray foam emissions in-situ was developed. This would allow researchers to collect VOC data in a reproducible and repeatable manner and develop databases, which could be used to compare indoor concentration rates across the building stock.

Contribution to practice

The original evidence presented in this thesis had real-world implications. From a scientific perspective, it demonstrated the challenges and resource required to understand the origin source of some VOC emissions from construction products. The thesis provided evidence of 1,2-DCP possibly being present in raw spray foam materials. Even systematic testing of the majority of spray foam materials on the market made it difficult to hypothesise the origin of the VOC. Manufacturers of construction products may have multi-layered supply chains. Without regular testing of the chemical composition of these compounds, by-products or pollutants, may enter the system and eventually find their way into indoor air.

For built environment professionals, this thesis presents practical evidence on the importance of selecting the right material for retrofit. It demonstrates that polyurethane spray foams applied with robots offer better energy savings potential and less disruption for building occupiers during retrofits. However the total impact of these products on indoor

environmental quality must be considered in order to decide the optimal retrofit solution to avoid unintended consequences.

This project has the potential to justify a shift in the built environment field into undertaking more active VOC measurements of both materials and indoor air. Without testing emissions at their source, academics and practitioners are left to hypothesise or guess where the VOC emissions that they detected are coming from. As VOCs have varying thresholds for impacting health, some pollutants may have a much health burden on people at low concentration compared to others at high concentration.

Departmentally, this research reinforces UCL's reputation as a multidisciplinary indoor environment research hub and played a role in expanding its capacity and capability within this domain. The project partners gained valuable evidence that will help them improve their own practices and optimise procedures for achieving robust worker and occupant protection, whilst providing much needed energy and carbon savings via retrofitting homes. The project also helped raise the profile of all indoor pollutants and findings were shared at multiple workshops with industry partners educating designers on what evidence they should request from manufacturers.

Finally, the data in this thesis provides empirical evidence in support of more stringent VOC testing policy for construction products before they enter the market.

Academic outputs

This thesis has had academic, policy and industry impact.

Five peer reviewed papers were published based on the findings from the thesis:

[1] D. Naldzhiev, D. Mumovic, M. Strlič, Method development for measuring volatile organic compound (VOC) emission rates from spray foam insulation (SPF) and their interrelationship with indoor air quality (IAQ), human health and ventilation strategies, in: 38th AIVC Conf. "Ventilating Heal. Low-Energy Build. Proc., 2017.

[2] D. Naldzhiev, D. Mumovic, M. Strlič, An experimental study of spray foam insulation products- evidence of 1,2-dichloropropane and 1,4-dioxane emissions, in: IAQVEC 2019 Proc. - Int. Conf. Indoor Air Qual. Vent. Energy Conserv. Build. Sustain. Built Environ., 2019.

[3] D. Naldzhiev, M. Strlič, D. Mumovic, Robots can reduce the exposure of people to volatile organic compounds (VOCs) during application of spray foam insulation, in: Proc. Heal. Build. 2019, International Society of Indoor Air Quality and Climate (ISIAQ), Changsha, 2019.

[4] D. Naldzhiev, D. Mumovic, M. Strlic, Polyurethane insulation and household products – A systematic review of their impact on indoor environmental quality, Build.

Environ. 169 (2020) 106559. https://doi.org/https://doi.org/10.1016/j.buildenv.2019.106559

[5] D. Naldzhiev, D. Mumovic, M. Strlič, Systematic evaluation of 1,2-dichloropropane emissions from do-it-yourself spray foam insulation products, Build. Environ. 207 (2022) 108439. https://doi.org/https://doi.org/10.1016/j.buildenv.2021.108439

The results of the study were accepted as oral presentations at the following conferences:

- AIVC Conference 2017
- SEAHA Conference 2018
- Indoor Air Conference 2018
- UKIEG Conference 2018
- CIBSE Build2Perform 2019
- IAQVEC Conference 2019
- ISIAQ Healthy Buildings Conference 2019

In addition, the findings were shared at invited talks with the Department for Housing, Communities and Local Government (MHCLG) and the Department for Business, Energy and Industrial Strategy (BEIS) and provided evidence in relation to policy decisions covering building regulations, upholstered furniture and construction products regulations.

The findings from this study were covered in the Passivhaus Plus and CIBSE Journal magazines.

Last, but not least, the findings from this study informed a number of industry guidance documents including, but not limited to:

[6] CIBSE, CIBSE TM61-64: Operational performance of buildings (2020), 2020.

[7] D. Naldzhiev, E. Wealend, Breathe Easy -Volatile Organic Compounds, in: Indoor Air Qual. Knowl. Ser., CIBSE, 2019. https://doi.org/10.13140/RG.2.2.20938.31686.

1. Background

1.1. Polyurethane materials history

Polyurethane itself finds its origins in 1937 by Otto Bayer when aliphatic diisocyanate and diamine formed polyurea with polyester-polyisocyanate systems being commercially developed in the 1950s following the second World War (Sharmin and Zafar, 2012). During the 1950s-1970s, polyether polyols were gradually introduced to replace polyester ones and poly methylene diphenyl diisocyanate (MDI) products became available when production expanded to cover flexible PU foams (post 1960s) and rigid PU foams (post 1967) (Sharmin and Zafar, 2012). A detailed history of key events covering polyurethane development are outlined by the the European Diisocyanate and Polyol Producers Association (ISOPA, 2022) Whilst there has been a significant amount of material science innovation since the 1950s (Gama, Ferreira and Barros-Timmons, 2018), the primary components of polyurethanes remain the isocyanate and polyol forming a urethane linkage as per Figure 1.

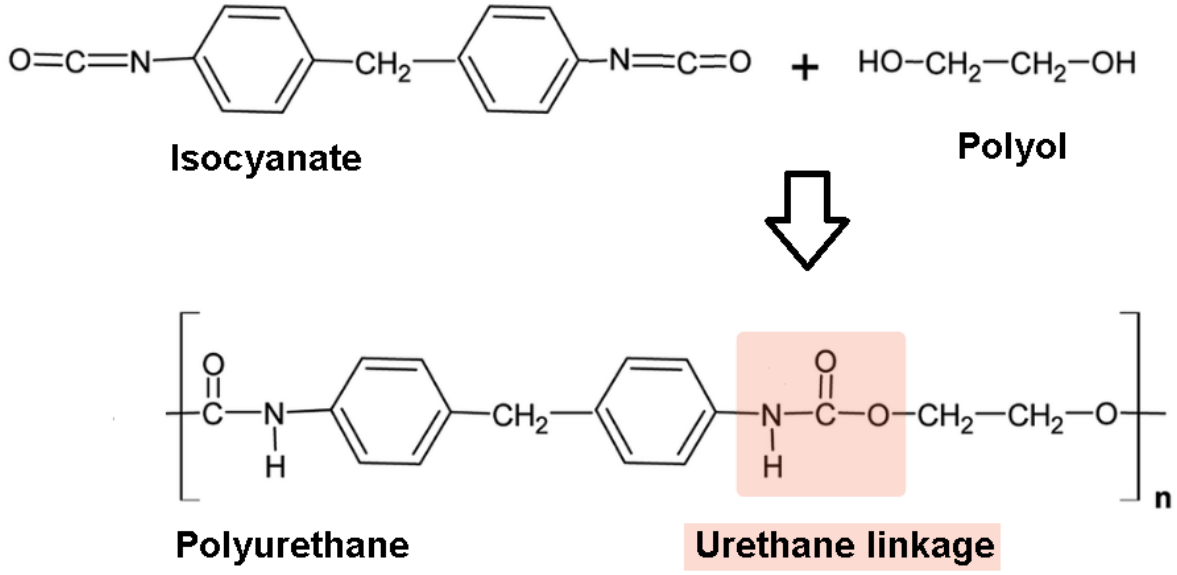


Figure 1. The polymerisation process during isocyanate and polyol mixing resulting in polyurethane production

In simple terms, modern day isocyanate based insulation products are typically produced by mixing two liquids: an A-side component consisted of isocyanates (Methylene diphenyl diisocyanate (MDI), polymeric-MDI (pMDI) or Toluene diisocyanate (TDI)) and a B-side component (polyol, fire retardant, catalyst, blowing agents and surfactants). The main chemical bond of the products is between the isocyanate and the polyol (urethane link) and therefore the isocyanate and polyol compounds often form the majority of the liquid raw materials. The other compounds are usually additives to enhance the reaction processes (catalyst, blowing agents) or foam properties (flame retardants). The A-side could be 90-100% isocyanate-based whereas the B-side is often >40% polyol (Mulkey, 2010) and a combination of other proprietary compounds.

Both the isocyanates and some of the polyol blends are chemically derived from processing petroleum sources (crude oil) and during the last decade, researchers and manufacturers have explored “bio-based” alternatives (Galhano dos Santos *et al.*, 2018). The composition of each specific product is proprietary information of the manufacturer. Modern polyurethane insulation materials are used for a variety of functions spanning across consumer upholstery, construction, automotive, textile, machinery, electronics and footwear products as per Figure 2.

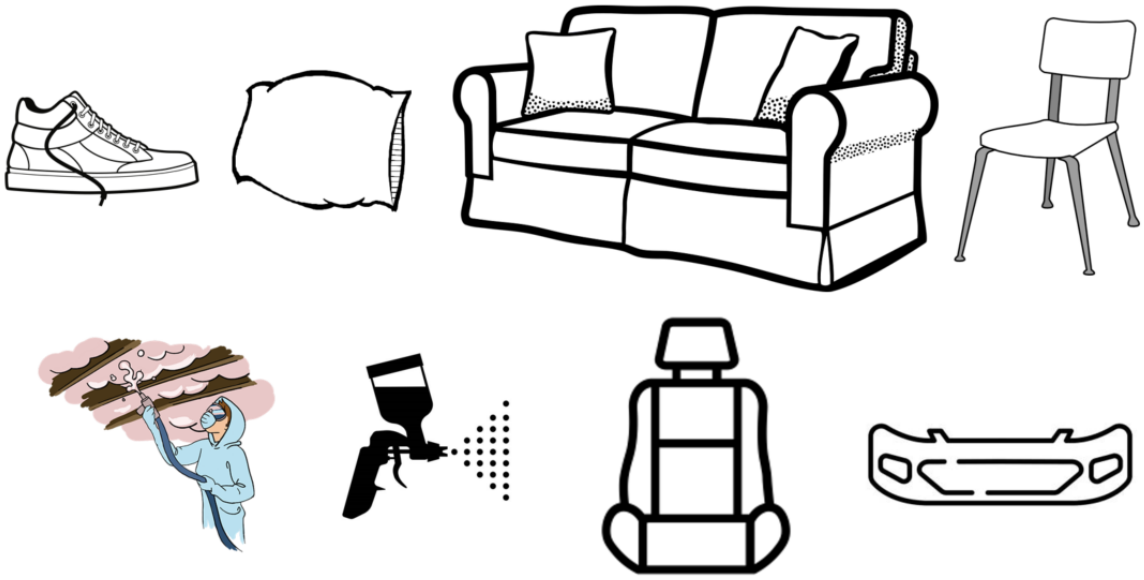


Figure 2. Product families where polyurethane products are used. Polyurethane spray foam image adapted from Float Tank Solutions.

Polyurethane products, product families, and product parts have become ubiquitous in all types of indoor environments since their emergence in the 1950s. The multifaceted properties of the materials made them suitable for usage for: construction and consumer products (Market Research Future, 2017) , aerospace engineering (Anderson, Walters and Glesner, 1970), analytical chemistry (Lemos *et al.*, 2007) and more recently even for cleaning oil spills (Qiu *et al.*, 2019) amongst other applications.

Whilst they are present ubiquitously however, each individual product and manufacturer select a specific combination of raw chemical compound ingredients based on the final functionality of the specific product. From a built environment perspective, their main functionality has historically been as insulation product for buildings (Gama, Ferreira and Barros-Timmons, 2018).

1.2. Polyurethanes and the built environment

Isocyanate based rigid board insulation (PUR/PIR) and spray polyurethane foam (SPF) insulation products topped the $1bn mark in sales in 2015 (Lucintel, 2017). The long term thermal benefits (Vanier, 2000) and energy efficiency improvement from SPF have been demonstrated for retrofits (Ascione, De Rossi and Vanoli, 2011). Polyurethane products have optimal thermal conductivity performance compared to other conventional insulation

products, such as mineral wool or polystyrene products during experimental testing (Cabeza *et al.*, 2010).

However as ageing occurs during the lifecycle of polyurethane insulation products, their properties change over time due to thermal degradation, oxidation and changed cell gas content processes due to diffusion of gases within the cell structure (Stovall, 2012; Persson, 2015). Their thermal performance has been examined in ageing experiments where a decreased performance of 4% of a retrofitted external wall was observed (D'Agostino *et al.*, 2022). Manufacturers advise that the "useable life" of the product is around 50 years and ageing is considered within the calculation methodology with the declared performance representative of an average value over the expected lifetime of a building – a minimum of 25 years (Federation of the European Rigid Polyurethane Foam Associations, 2016).

1.3. Where are polyurethane products used within the UK built environment?

Unfortunately, the simple answer is: we don't know *exactly*. There is not sufficiently granular data for accurate determination on a building stock level. The United Kingdom does not hold a central repository, or database, that could be examined on the exact product type installed in individual buildings. There are market research companies that provide estimations around the distribution of the market size of insulation products (AMA Research, 2021). The data outlines that polyurethane, and polyisocyanurate, building insulation products are market leading as per Figure 3 (AMA Research, 2021). However, as the authors outline, these are estimations.

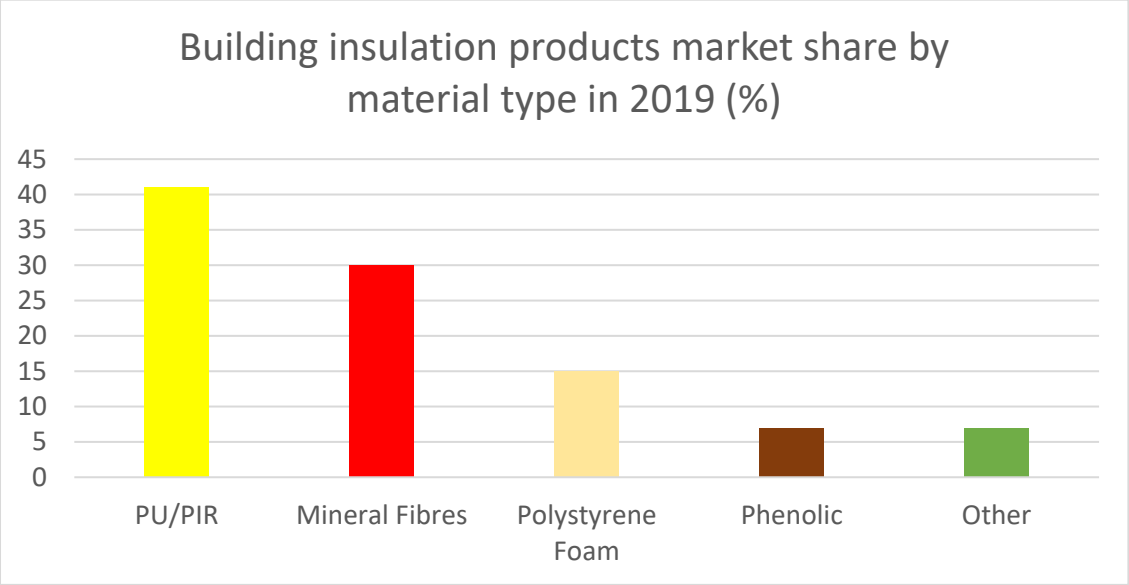


Figure 3. Market distribution estimates for building insulation products split by material type. Estimates extracted from AMA Research data (AMA Research, 2021)

A history of the built environment, its interlink with Building Regulations and building performance is presented in Appendix A. The built environment field has been perhaps dominated by energy efficiency for the last 50 years with researchers examining in depth case studies of buildings to determine the energy performance of both materials and buildings in-situ (Ionescu *et al.*, 2015). However in recent years, the subject of indoor air quality has grown in importance and built environment scholars have adopted various analytical chemistry techniques in order to measure indoor pollutants (Nielsen *et al.*, 2007;

Crump, Dengel and Swainson, 2009; Yu and Kim, 2010; Salthammer, 2014; Shrubsole *et al.*, 2019; Halios *et al.*, 2022).

1.4. Polyurethane insulation & analytical chemistry

Between the 1970s and the 1990s the analytical chemistry equipment saw further advances and it was applied on a wider scale measuring volatile organic compounds (VOCs) associated with different products (Bayer, Black and Galloway, 1988; Ross Highsmith, Zweidinger and Merrill, 1988; Tsuchiya, Clermont and Walkinshaw, 1988) and in various settings (Tsuchiya, 1988). The concepts of perceived air quality and odour were associated with VOCs (Hudnell *et al.*, 1990) and causal relationship between VOC exposure and health impact were demonstrated (Bayer and Black, 1989).

Since the 1990s the field has grown exponentially with the development of both active (Hodgson, Levin and Wolkoff, 1994) and passive sampling techniques (Brown, Crump and Gardiner, 1992). The precision and sensitivity of analytical chemistry tools and methodologies has drastically improved in the last 30 years allowing the measurement of many volatile organic compounds down to parts per billion (ppb) or even parts per trillion (ppt) levels (Watson, Davies and Wevill, 2011).

The term “volatile organic compound” has been used in many scientific fields: atmospheric chemistry (Mellouki, Wallington and Chen, 2015), toxicology (Dobrzyńska *et al.*, 2010), olfactory impact (Cometto-Muniz and Cain, 1995), heritage smells (Bembibre and Strlič, 2017) and building pathology (Yu and Kim, 2010) carrying different implications for the focus of researchers, practitioners and policy makers. The existing literature suggested there is potential for analytical chemistry methods developed for measuring emissions from heritage collections, that contain polyurethane, to be deployed in the built environment field.

Spray foam primary components, particularly B-side, has changed significantly in the last 30 years in reaction to environmental regulations and industry innovation in enhancing its overall performance so the product remains competitive compared to alternative insulation products. Measuring VOC emissions is important for spray foam products as not all insulation products have equal impact both on the energy and indoor environmental quality of buildings. Given that air permeability of buildings is continuously decreasing (Love *et al.*, 2017), the importance of understanding indoor emissions and their impact on people is therefore a subject that needs further exploration.

1.5. Polyurethane insulation & health

Spray foam materials are an unique subset of insulation products as their application is de-facto their ‘creation’. The health impacts from off-gassing have therefore been focused predominantly on occupational exposure emissions and the impact on health of workers (Woolrich, 1982; Sorahan and Nichols, 2002; Allport, Gilbert and Outterside, 2003b) and occupational asthma due to isocyanate exposure (Mapp *et al.*, 1988). Spray foam application occurs on-site rather than produced in a factory environment like mineral wool (Rockwool, Isover for example) or polyurethane and polyisocyanurate boards (Celotex and

Kingspan for example). In order to understand the implications of spray foam polyurethane insulation products on indoor air quality, one must consider each of the constituent compounds both in isolation and cumulatively and examine their interactions with indoor environments.

During the production, and lifecycle, of PU products various organic compounds can be released from the foams where they interact with the indoor environment in dynamic physicochemical processes. As industrial material science evolves at a rapid pace and product formulation may change on a yearly basis, it is plausible that this is one of the reasons why limited research has been undertaken in this area. Academic findings may become obsolete if the insulation material in question has a drastic change in formulation despite polyurethane products being ubiquitous in indoor environments.

A second explanation for the relative low amount of research compared to the size of the industry is that indoor air quality as a field is relatively novel compared to other more well established fields within the built environment sector. This theory is supported by scholars having previously focusing on findings ways to improve foam properties (Smits, 1994; Gama, Ferreira and Barros-Timmons, 2018) rather than understand their long-term impact on buildings or people.

Epidemiological evidence demonstrates that in isolation each VOC group that is present in spray foam could in theory have some impact on human health. As with all pollutants, some compounds carry higher risks compared to others and the concentration and cumulative exposure are critical factors for estimating risks (Bello *et al.*, 2004; Ali *et al.*, 2018).

Small-scale studies on spray foam insulation (SPF) emissions were undertaken in the 1980s and 1990s (Hosein and Farkas, 1981; Boomberg and Lstiburek, 1998), however are a scientifically niche research area given they fall between the fields of analytical chemistry, environmental exposure and human health. Often studies focus on a single compounds, property, or product (Poppendieck, Persily and Nabinger, 2014) and they often focus on spray foam material science development (Tsai, 2005; Kim and Yu, 2014; Gama, Ferreira and Barros-Timmons, 2018) rather than the impact on indoor air quality.

2. Literature review

This chapter reviews and critically analyses the holistic impact of polyurethane and spray foam products on indoor environments and people based on published literature findings.

The review is split into five conceptual themes: thermal and energy performance, volatile organic compound (VOC) emissions and analytical chemistry, health implications from spray foam emissions, perceived/olfactory indoor air quality impact and current industry practices. A systematic evidence review for each theme is presented in this chapter followed by a summary of the scientific evidence gap within the context of the built environment field.

2.1. Search strategy

The review is conducted using the rapid systematic review method (Ganann, Ciliska and Thomas, 2010). The reviewed literature consists predominantly of scientific journals and academic research outputs, but also includes industry guidelines and technical reports. Four conceptual themes are developed: thermal performance, health implications and IAQ, VOCs and SVOCs emissions and industry practices each using a variety of keywords and search terms (Table 1). Papers with the search terms included in any parts of the article are initially screened.

Table 1. Keywords used for gathering literature sources

Conceptual theme	N of search terms	Search term
Thermal conductivity and energy performance	7	Spray foam insulation, thermal conductivity, thermal performance, energy efficiency, natural material, polyurethane insulation, polyisocyanurate insulation
Emissions and analytical chemistry methods (VOCs and SVOCs)	20	Organic compound, Volatile organic compound, semi-volatile organic compound, exposure limit, chamber, case study, 4,4-MDI, TCPP, TCEP, TDCPP, isocyanate, polyol, blowing agent, flame retardant, exposure limit, concentration, emission rate, dichloropropane, benzene, formaldehyde
Health implications and IAQ	19	Indoor air quality, indoor environmental quality, sick building syndrome, health, epidemiology, toxicological, carcinogenicity, insulation, household product, mattress, isocyanate, polyol, blowing agent, flame retardant, exposure limit, dermal, symptom, asthma, irritation
Olfactory impact and perceived indoor air quality	7	Smell, Odour, perception, sense, olfactory, olfactometry, sensory analysis,

Industry practices	6	Re-occupancy, ventilation rate, misapplication, spraying, health and safety, procedures,

The following databases: Google Scholar, Science Direct, Scopus and Research Gate are utilised. Moreover, the Google search engine is used to search for publicly available documents, safety data sheets, industry reports, industry practices and government or international regulations. Following the initial screening process of keywords from Table 1 in any part of the report, a total of 956 reports are selected for initial screening.

2.2. Classification and quality assessment

The collected reports are subject to systematic evaluation following the flow diagram outlined in Figure 4.

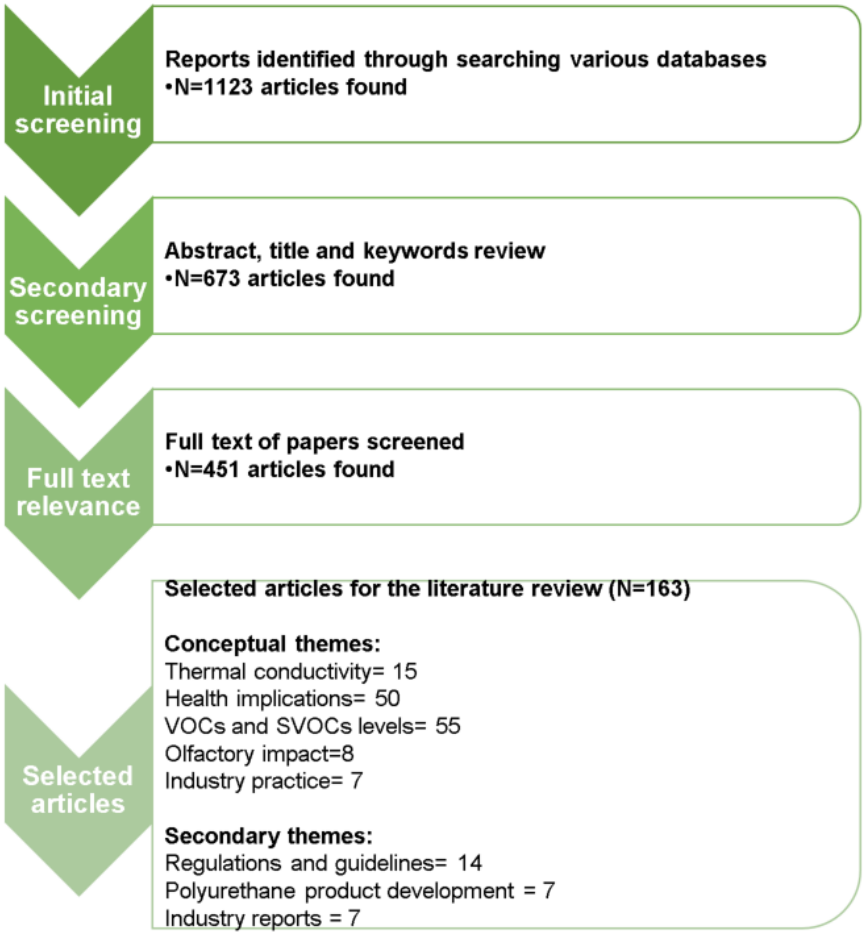


Figure 4. Flow diagram of screening process and paper selection

The 163 articles selected for the review are divided in five spreadsheets as per the conceptual themes of the review in Table 1. The classification of these topics enables me to systematically evaluate the existing literature sources, retrieve key findings and establish the gaps of knowledge using an analytical approach. For evaluating data from different studies, all measurements are converted to the same SI unit to present comparable values between different datasets.

2.3. Thermal conductivity and energy performance

In the UK, at least 19% of the total CO_2 emissions can be attributed to buildings (Committee on Climate Change, 2018), therefore the energy performance of buildings is a critical factor for reducing carbon emissions. The built environment is generally a fragmented industry and there are hundreds of decision-shapers and makers in designing, constructing and operating a single building. This is exemplified by the amount of factors that have to be considered when selecting a single product as part of the building design, insulation, as per Figure 5.

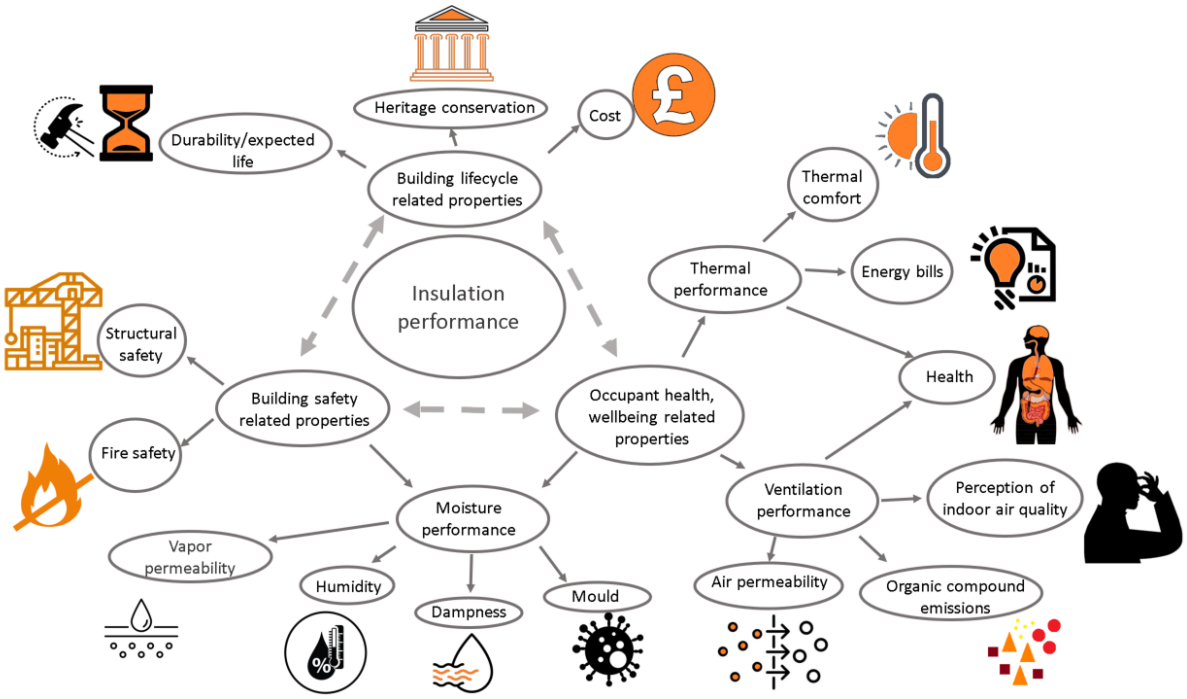


Figure 5. The complexity of decision making when selecting an appropriate insulation product for the design, construction and operation of built environment assets. Performance factors are indicative and not necessarily exhaustive.

Thermal conductivity and energy performance are a key factor in the decision making process.

A majority of buildings in the UK are de-facto prototypes due to the variation of both national and local planning requirements and unique conditions and requirements of each site. Whilst stock modelling has allowed the evaluation of the energy performance on a building stock level or a variety of building types (Mata, Sasic Kalagasidis and Johnsson, 2014; Steadman, P., Evans, S., Liddiard, R., Godoy-Shimizu, D., Ruyssevelt, P. and Humphrey, 2020; Schwartz *et al.*, 2021; Schwartz, Raslan and Mumovic, 2022), there is no central repository of what insulation materials are actually present in individual buildings. Whilst some market data, such as company market share distribution estimates exist, it is currently difficult to accurately split the market share by building type.

The UK holds multiple unique datasets, such as the Energy Performance Certificate database, ONS dataset, English Housing Survey and privately held datasets within the private sector that contain millions of datapoints with regards to the state of the building stock. However accurately linking specific products with individual buildings where they were used is a challenging task as highlighted by the Building Safety Programme data gathering programme (DLUHC, 2021) and its evaluation by the National Audit Office (NAO, 2020).

Despite the lack of accurate and precise building stock level data, there are numerous studies comparing insulation product performance on a building level.

Studies have shown that increasing or adding insulation within the thermal envelope of a building reduces the heating demand (Martínez-Molina *et al.*, 2016), energy bills (Webber, Gouldson and Kerr, 2015) and carbon footprint of the property (Jenkins, 2010), whilst also increasing thermal comfort (Hong *et al.*, 2009). Extensive modelling studies (Kerdan, Raslan and Ruyssevelt, 2016), experimental tests (Antonyová, Antony and Korjenic, 2016) and post-occupancy evaluations (Campbell *et al.*, 2017) have been conducted to quantify the impact of various insulation materials on energy use and thermal comfort. To understand the benefits of using PU insulation (both rigid boards and spray foam) for increasing thermal comfort, Figure 6 summarises the conductivity of common insulation materials with the full dataset included in Appendix B.

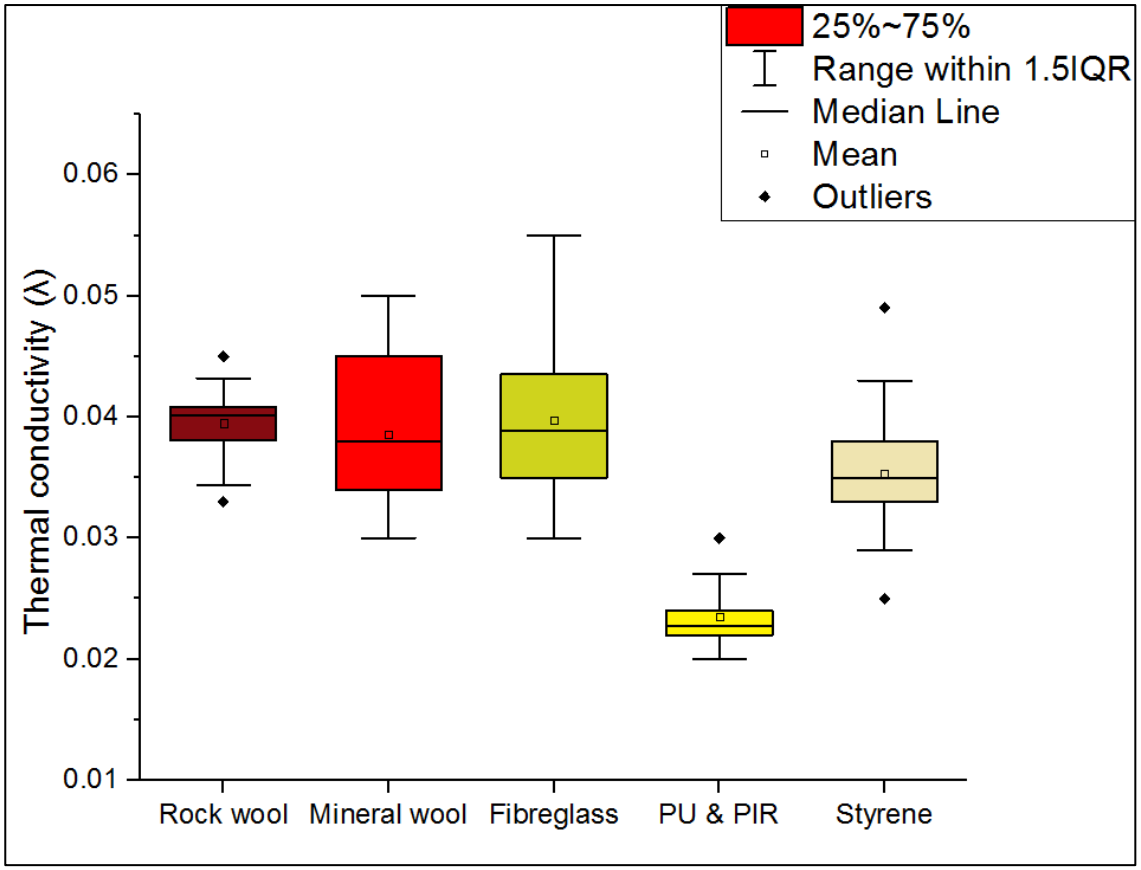


Figure 6. Comparative performance of insulation materials based on measured studies, design values and manufacturer declared data (Al-Ajlan 2006; Abdou & Budaiwi 2005; Al-Homoud 2005; Papadopoulos 2005; Budaiwi et al. 2002; Lakatos 2014; Berge & Johansson 2012; BS: EN ISO 10456:2007; Manufacturer declared data)*. Lower values are better insulators.*

Figure 6 illustrates the thermal conductivity ranges of insulation products based on four studies measuring conductivity, three literature reviews, BS 10456:2007 declared design values and manufacturer declared data. The literature suggests that PU insulations perform 39.1%-59.3% better compared to conventional insulation materials based on mean thermal conductivity. The data is supported by an analysis of 23,700 numerical measurements of conductivity for various insulation types, where PU insulation is shown to outperform all other common insulation materials (Domínguez-Muñoz *et al.*, 2010; Márquez *et al.*, 2017).

Experimental research has examined the potential of utilising a variety of insulation options specifically for the retrofit of suspended timber floors in the UK and their performance in-situ (Pelsmakers *et al.*, 2017).

For new buildings aiming at achieving zero carbon emissions and existing buildings aiming to alleviate fuel poverty, polyurethane offers higher potential for energy savings and thermal comfort (Kumar and Suman, 2013) compared to conventional materials. Development in modern application methods for polyurethane foam, such as the use of robots, offers a solution to the inconvenience and disruption factor of removing floor boards that building owners often cite as a barrier for retrofitting their suspended timber floors. In the UK, due to often limited crawlspace, lack of unheated basement or cellar and insufficient gap underneath the floor (Historic England, 2016; BEIS, 2020), there is a need to remove the floor boards and sometimes even saw them in order to place the insulation between and/or under the joists. Industry guidance (Wallace, 2019) outlines that usually the floorboards would need to be lifted, or removed, in order to install the insulation. Depending on their condition, the original floorboards might not be put back in place with the owners deciding to utilise more modern materials, which therefore impacts the heritage value of the building stock (Historic England, 2015). By utilising a robot that can apply insulation in spaces where it might not be feasible to undertake the installation manually, the heritage value of the floor in retrofitted buildings may therefore be preserved as well as reducing the disruption of having to remove, or lift, all floorboards for the installation process to be completed. Robots therefore offer potential reduction of the inconvenience factor for both installers and occupants as all the floorboards would not have to be removed during the process of installation.

2.4. Physicochemical and toxicological properties of spray foam (SPF) compounds

Whilst the impact of insulation on energy efficiency is quite clear, its impact on indoor air quality (IAQ) or indoor environmental performance (IEQ) (Taylor, Liu, et al., 2018) is a subject of recent research interest. In particular, the organic emissions from PU products throughout their lifecycle and their implications on indoor air quality and human health.

One study found a correlation between improper installation of SPF and association with various long term health related issues (Huang and Tsuang, 2014) even after the product has been removed from the property. There is however no national, or international, technical definition explicitly outlining what constitutes 'misapplication'. Improper installation or 'misapplication' is a term referring to when specified procedures by the SPF manufacturer for spraying "with respect to the depth of individual layers, timing between layer application, ratio of A:B side, temperature of liquid, and mixing of SPF components" are not followed (ASTM International, 2017c).

Potential health effects of SPF products have been reported mostly in the US with seven workers developing asthma whilst working for foam insulation companies, six office workers suffering occupational asthma after SPF retrofit, an additional list of 14 Consumer Product Safety Commission (CPSC) incident reports related to SPF applications (NRDC *et al.*, 2017). Furthermore, two people were reported to have developed cough and dyspnoea after their home was retrofitted with SPF (Tsuang and Huang, 2012).

Product safety data sheets disclose some of the chemicals that comprise the finished product, but they do not provide any data on primary, secondary or tertiary organic emissions associated with SPF throughout the lifecycle of the products. As SPF is applied in-situ where

a complex chemical reactions occur, the chemicals present in the MSDS may, or may not, be present in the finished product after the reaction during installation occurs on site. Furthermore, chemicals in the finished product may form as a result of reactions and may not be present in the MSDS. As spray foam products are usually formed by mixing two liquid parts (Side A and Side B), these are reviewed separately.

2.4.1. Side A- Isocyanates

Isocyanates are widely used for the production of polyurethane foams with methylene diphenyl diisocyanate (MDI) being the most popular choice in recent years (Gama, Ferreira and Barros-Timmons, 2018). MDI is an odourless solid with a boiling point of 314 °C (ATSDR, 2018).

At concentrations of 0.1-1 ppm, isocyanate are irritants to the mucous membrane and over 1 ppm are considered to have a toxic effect (Woolrich, 1982). The most common health effects include irritation to skin, eyes and respiratory tracts and can also induce asthma (IARC, 1999). Isocyanate induced asthma can be lethal as there have been cases of workers dying because of sensitisation (Carino *et al.*, 1997; Lee and Koh, 2008). Once sensitised, people could experience health issues years after the initial exposure (Pisati *et al.*, 2007) and even small concentrations (0.02-0.24ppb) can trigger a strong asthmatic reaction (Suojalehto *et al.*, 2011). Due to its impact on health, the California Department of Toxic Substances Control has labelled MDI as an initial priority product (Guo *et al.*, 2017). Air concentration of isocyanates is highest in the spray foam and coatings application industries compared to diisocyanate (raw materials) manufacturing, polyurethane manufacturing, foam manufacturing and adhesives industry (Rother and Schlüter, 2021). A recent death case report associated with MDI asthma, which occurred an aluminum parts foundry where MDI was introduced as a binding agent in the mold-making process, highlights the risks and hazards associated with MDI exposure (Wisnewski *et al.*, 2022).

Whilst isocyanates usually form 90-100% of the A-side of spray foam products, the B-side is comprised of many different combinations of compounds.

2.4.2. Side B- polyol, flame retardant, blowing agent and catalysts

The B-side is a blend of polyol and a mixture of additives that enhance foam properties and help the reaction process. The flame retardants reduce the risk of combustion and flammability of PU products. The blowing agents enhance the foam expansion. Different catalysts are added to enhance the reaction between the different chemicals and enhance the foam properties such as: dimensional stability, expansion time, compressive strength and permeability.

The polyol component usually forms the largest proportion of the B-side weight as it reacts with the isocyanate to form the urethane bonds in polyurethane

2.4.2.1. Polyols

Polyols are classed as odourless and are rarely mentioned in safety data sheets of PU materials. This suggests that their potential impact on perceived IAQ and health should be minimal, considering their content by weight forms 30-75% of the B-side (ASTM International, 2017c). In the last decade, the scientific research on spray foam has focused on the physical properties of polyols to increase the thermal, structural and fire resistance performance of foams (Francés and Bañón, 2014; Kurańska *et al.*, 2016; Madbouly *et al.*, 2016; Yuan *et al.*, 2016; Kairytė *et al.*, 2018). In order to provide ‘greener’ products, the

development of polyols has shifted from oil-based to bio-based, vegetable oil-based or using industrial residues as polyols (Gama, Ferreira and Barros-Timmons, 2018).

The main hazard associated with polyols used in PU production, according to the CPI, is that spillages can be very slippery (Center for Polyurethane Industry, 2013). Polypropylene glycols, which are used for PU polyol resin, have been deemed to have a very low risk to human health (Fowles, Banton and Pottenger, 2013), but the American Chemistry Council suggests that at high concentrations polyols might act as irritants towards the eyes, skin and respiratory tract especially during spray foam application (American Chemistry Council, 2016).

Unlike polyols, the impact of flame retardants on health has been a topic of great interest in recent years due to their use in a variety of both construction and consumer products.

2.4.2.2. Flame retardants

To enhance the fire resistant properties of PU and PIR products, flame retardants are added to spray foam materials with organophosphate (OFRs) growing in popularity in recent years (Xu *et al.*, 2019). Flame retardants form 15-60% of the B-side of the foam. The most widely used OFRs include: TCPP (Tris(2-chloroisopropyl)phosphate), TCEP (Tris(2-chloroethyl)phosphate), and TDCP (Tris (1,3-dichloroisopropyl) phosphate blend), which are known to have toxic effects (US EPA, 2016). Flame retardants are generally not chemically bound to the polyurethane matrix and may emit indefinitely (ECHA, 2018).

The group of OFRs (TCPP, TCEP and TDCP) are suspected carcinogens with observed effects on tumour growth in the kidney, liver, thyroid and brain (Wei *et al.*, 2015). TCPP and TDCP are found to irritate skin (Schramm, Leisewitz and Kruse, 2001). A report found strong correlation between TCEP ingestion (>2 ppm) from car seats and acute death in two dogs from seizure-inducing activities (Lehner, Samsing and Rumbeiha, 2010). TCEP has been reported as a known inducer of epileptic seizures, neurotoxic, reproductive toxicant and possible carcinogen based on animal testing (Lehner, Samsing and Rumbeiha, 2010). Men living in homes with high amounts of TDCPP are found to have a reduced sperm count and altered levels of hormones related to fertility (Meeker and Stapleton, 2010). Weak correlation was however found between median concentration of flame retardants and sick building syndrome in an analysis of 169 flats in Sweden (Bergh *et al.*, 2011). Some scholars argue that the added benefit of fire performance is perhaps not worth the risk of human health impact and materials should aim to meet flammability standards without added flame retardants (D Shaw *et al.*, 2010).

The European Chemical Agency has adopted a restriction on flame retardants (TCEP,TCPP and TDCP) (ECHA, 2018) in flexible polyurethane products (childcare articles and residential furniture) in Europe due to their implications on human health. The report highlights that out of the three, TCPP is the most widely used flame retardant whilst also being the least researched in terms of health impact (ECHA, 2018). The NTP is conducting toxicity and carcinogenicity studies for organophosphate flame retardants and some the results are published, whilst others are under review (National Toxicology Program, 2018). The critical effects to be considered in a review of risks to human health associated with TDCP is carcinogenicity, and in relation to TCPP, reproductive and developmental toxicity (Environment Canada, 2016).

Whilst emerging evidence exists about the impact on health from flame retardants, the other VOCs should also be considered in order to evaluate the spray foam products in their totality.

2.4.2.3. Blowing agents

Blowing agents have been the most rapidly evolving aspect of polyurethane insulation and spray foam production in the last 30-40 years, governed by international regulations (Figure 7).

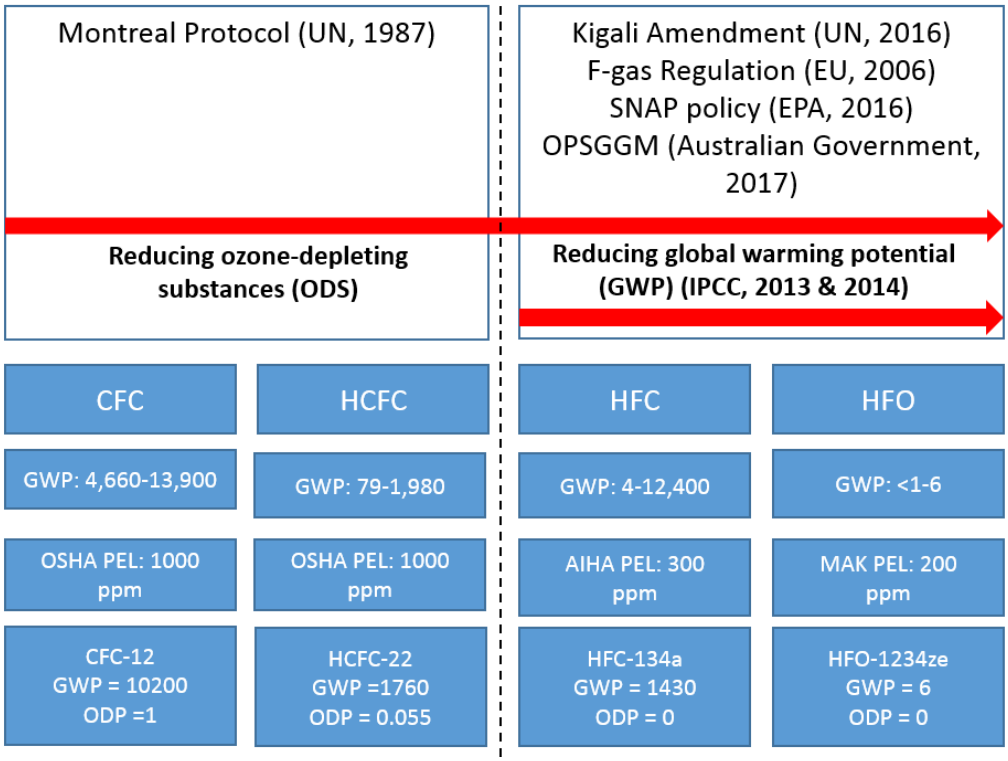


Figure 7. Blowing agents in polyurethane materials, phase-out regulations since 1980s and permissible exposure limits. Bottom row gives examples of blowing agents of each type used in PU production. Values derived from IPCC reports. (UN, 1987, 2016; IPCC, 2013, 2014; EU, 2014; EPA, 2016; Australian Government, 2017)

A study in 2010 suggested that chlorofuorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been effectively already phased out (Feldman, 2010) and no longer represent any real interest for further research. However, a report in 2018 (EIA, 2018) provided contrary evidence to this claim as 18 different companies were reported to illegally use CFC-11 in PU products.

A systematic literature review of hydrocarbon toxicity demonstrated that exposure to high levels could lead to significant negative health implications, including damage to the central nervous system, coughing, wheezing, pneumonitis, psychomotor speed, impaired learning memory, diarrhoea, pulmonary oedema, emotional lability and cardiotoxic effects (Tormoehlen, Tekulve and Nañagas, 2014) (NIOSH, 1989) (Borron, et al., 2007) (Harbison, et al., 2015). Over ten workers have died from cardiac arrhythmia, asphyxiation or inhalation when exposed to high quantities of CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) (NIOSH, 1989). The OSHA PEL for CFC-113 is 1,000 ppm and it has been recorded that at 2,500 ppm it impairs cognitive behaviour (Stopps & McLaughlin, 1967).

HFCs are generally considered to have a low or minimal impact on human health with exposure levels/limits of over 1,000 ppm according to the American Industrial Hygiene Association (Tsai, 2005). Animal studies of mice and rabbits have demonstrated that even in quantities of over 40,000 ppm HFC-245fa and HFC-134a would have limited adverse health effect, so their impact on people during spray foam retrofit would likely be insignificant (ECETOC, 2004).

Hydrofluoroolefins (HFOs) are the newest generation of blowing agents, whose potential effects according to EPA (2009) at low concentrations include dizziness and at high concentration could cause eye and skin irritation. Case studies of rats and mice exposed to 10,000 ppm of HFOs did not find any carcinogenic impacts (Schuster, 2009). Schuster (2009) also concluded that albeit 1,1,3-tetrafluoroepoxypropane, with potential toxic liver effect, and 3,3,3-trifluoropropionic acid were formed, no detrimental effect on animal health could be determined following the exposure to a blowing agent (HFO-1234ze).

The last constituent compound of spray foam, however also the most wide ranging ones, are catalysts.

2.4.2.4. Catalysts

The purpose of catalysts is to enhance the mixing, and expanding, synthesis of the foam for enhanced performance. As material science development focuses predominantly on product performance, there are hundreds of catalysts and this is the aspect of spray foam structure that sees both a lot of variation and development between different manufacturers. Each spray foam manufacturer could have a proprietary unique mix of catalysts with some of the more common amine catalysts including Bis(dimethylaminoethyl)ether (BDMAEE), diethanolamine, dimethylethanolamine, *N*-ethylmorpholine, *N*,*N*-dimethylaminopropylamine, triethanolamine, triethylamine, triethylenediamine and trimethylaminoethylethanolamine (TMAEE) (Sleasman, ASTM International 2017). Amines usually form a small percentage of the foam weight, usually between 1-5% of the B-side (ASTM International, 2017c).

A toxicology review of BDMAEE (Ballantyne, 2005) demonstrated that it is “acutely hazardous by swallowing (toxicity and corrosivity), skin contact (local inflammation and injury; systemic toxicity), eye contact (injury and corrosivity with the liquid; glaucopsia and irritation by vapor exposure) and moderately high vapor exposure (pulmonary injury)”. At 47 and 90 ppm it was lethal to rats and concentration of BDMAEE vapor is “related to relative humidity, the greater the moisture content in the air, the lower the BDMAEE concentration” (Ballantyne, 2005).

An EPA report on diethanolamine reported that short-term exposure may irritate skin, nose and throat, whilst animal studies based on chronic exposure reported effects on liver, kidney, blood and central nervous system (EPA, 2000). The US National Toxicology Program reported an increased incidence of liver and kidney tumors in mice from dermal exposure to diethanolamine (National Toxicology Program, 1999).

Apart from the constituent compounds, there are some by-products and residual products from spray foam that could also potentially impact human health.

2.4.2.5. By-products or residual products

A review of analytical techniques to understand emissions from spray foam (Sleasman, ASTM International 2017), concluded that 1,2-DCP (Class 1 carcinogen IARC), 1,4-dioxane (Class 2B carcinogen IARC), 1-chloro-2-propanol, chlorobenzene, isopropyl alcohol (Class 3 carcinogen IARC), methylpropanamine and phenoxyethanol have been found emitting from a range of spray foam insulation materials however the origin was unclear or uknown. 1-chloro-2-propanol and 1,2-DCP were hypothesised to be possible degradation products from flame retardants present in the foam (Salthammer, Fuhrmann and Uhde, 2003).

The above compounds could be released during standard operating conditions, however to assess the total impact of PU emissions extreme conditions are also considered.

Benzene (known carcinogenic), benzonitrile (eye irritation and respiratory difficulties) and phenol (eye irritation, rhinitis and respiratory difficulties) could be found during combustion of polyurethane foams (Reisen, Bhujel and Leonard, 2014). Liang & Ho (2007) and Reisen et al. (2014) used different methods of analysing the toxicity and health impact of spray foam combustion, however they reached a similar conclusion that fumes from polyurethane materials during fires are highly toxic for human health.

If flooding[MD1] occurs and PU comes in contact with water, the hydrolysis product of MDI could theoretically be MDA, as MDA is the result of hydrolysis of MDI. 4,4-MDA is on the ECHA candidate list of substances of very high concern (ECHA, 2008) and is listed as a potential occupational carcinogen by NIOSH (NIOSH, 1986). Acute (short term) oral or dermal 4,4-MDA exposure causes liver damage in humans and animals and also acts as an irritant (U.S. Environmental Protection Agency (EPA), 2010). A study in 2001 suggested that MDA concentrations formed in the environment following MDI reacting with water are however low (Sekizawa and Greenberg, 2001).

2.5. Exposure routes, reported concentrations and emission rates

2.5.1. Side A (isocyanates)

The MDI concentration in air from SPF application has been measured using predominantly liquid chromatography (LC) followed by ultraviolet and fluorescence detection (UV/FLU) (Occupational Safety & Health Administration, 2012), ultraviolet and electrochemical detection system (UV/EC) or coupled mass spectrometry (MS/MS) (Crespo and Galán, 1999a; Roberge, Gravel and Drolet, 2009). Figure 8 reports MDI concentration during spraying and the full results are reported in Appendix C. The reports measure MDI concentration in air near the sprayer.

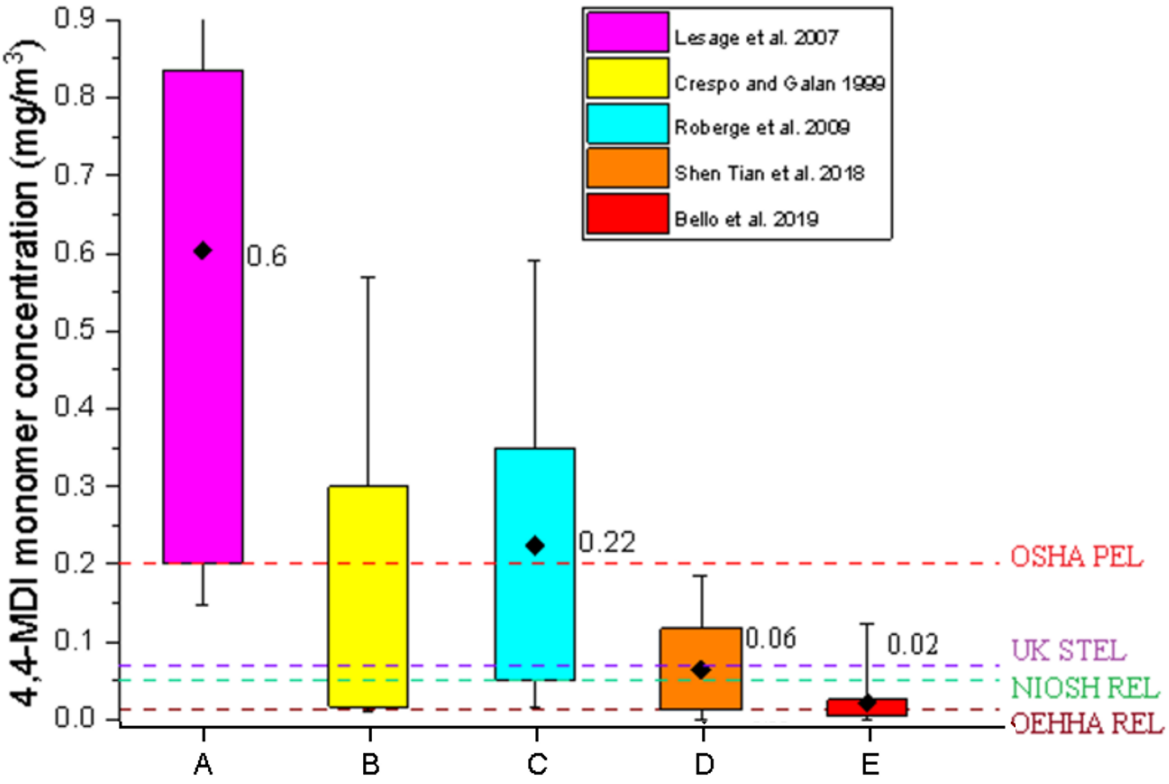


Figure 8. Measured exposure to MDI (mg/m^3) near a sprayer during installation of two-component polyurethane spray foams. Box plots show interquartile ranges. Shapes show mean concentrations and whiskers show min-max values. Crespo and Galan (1999) mean could not be calculated due to lack of a full data set. Dotted lines represent permissible, short-term and recommended exposure limits of different institutions and/ or countries.

The results measure exposure of MDI near the sprayer and are not necessarily representative of personal exposure if full health & safety equipment is used. The results highlight the risk of exposure if procedures are not put in place during installation. Almost all studies (A-D) in Figure 8 use a sampling rate of 1-1.1 l/s, apart from one which uses 15 l/s (E). The results from Figure 8 demonstrate that during application of SPF the MDI concentration in air could exceed the OSHA recommended threshold values by 3-8 times and UK short-term exposure limit (STEL) values by 9-22 times (Crespo and Galán, 1999a; Roberge, Gravel and Drolet, 2009).

The data from the limited existing studies suggest that that airborne MDI is reduced to levels below legal exposure thresholds after 120 min. Two studies (Won et al, Wood et al from ASTM) report that even during application MDI is below OSHA permissible exposure limits (PEL), but both studies were undertaken in rooms with extremely high and uncommon ventilation rates for the current UK building stock (ACH_{50} of 32.4 for Won and an extract rate of 10-598 ACH for Wood). A 598 ACH would be impossible/impractical to achieve in real buildings.

The Roberge (2009) study demonstrates that there is a significant difference in exposure of indoor application compared to outdoor application (Figure 13). Bello et. al (2019) measured breathing zone exposure of 24 sprayers during SPF spraying and reported that 4,4-MDI concentration exceeded NIOSH recommended exposure values (REL) for: 16% of personal air

samples and 35% of area samples near the vicinity of the workers. The results serve as evidence that mitigation measures must be put in place in order to reduce, and possibly eliminate, the risk of recurring spray foam incidents such as the ones recorded by NRDC in the US (NRDC *et al.*, 2017).

Figure 9 summarises MDI concentration further away from the source, exposure of helpers and concentration after spraying.

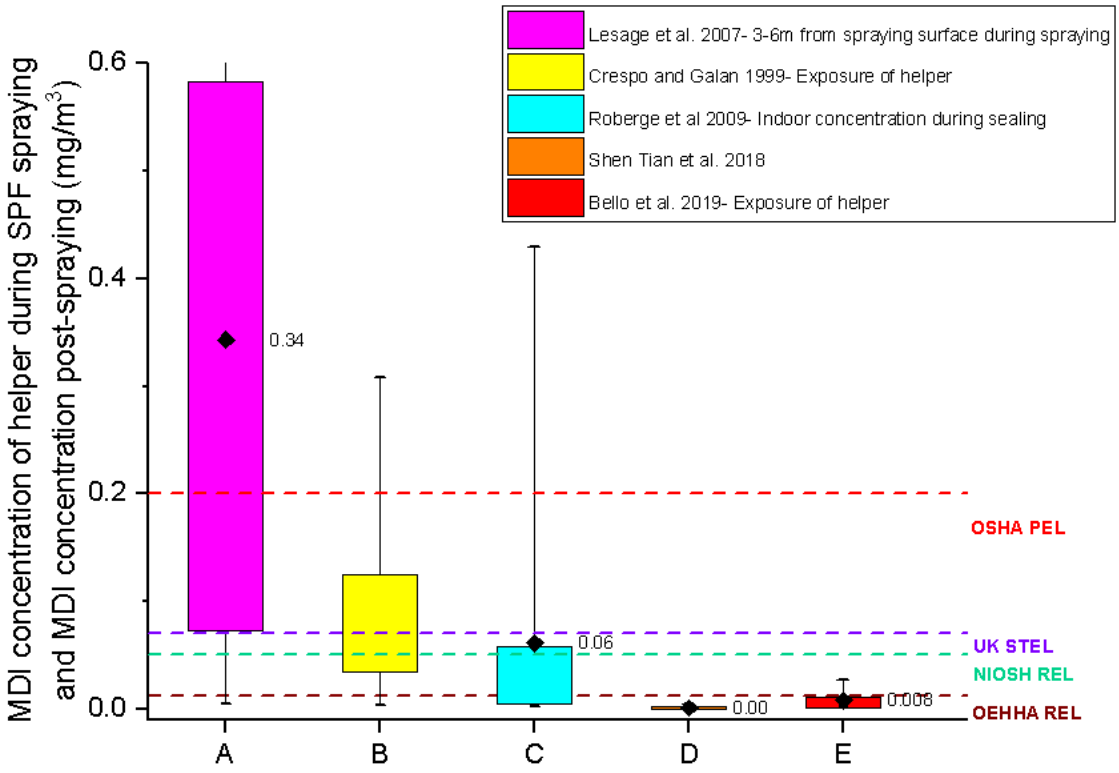


Figure 9. Measured exposure to MDI (mg/m^3) near helper during installation, exposure of sprayer during sealing and exposure post-application of two component polyurethane spray foam. Box plots show interquartile range. Points show mean concentrations and whiskers demonstrate min-max values. Crespo and Galan (1999) mean could not be calculated due to lack of the full data set. Dotted lines represent permissible and short-term exposure limits and recommended thresholds of different institutions and/ or countries.

Concentration of MDI decreases further away from the source of spraying as per Figure 9. Figure 8 and Figure 9 highlight that both the sprayer and the helper could be exposed to levels of isocyanate monomer above UK STEL values unless per and control procedures are used. Even when spraying outdoors, concentrations can still exceed the OEHHA recommended exposure limit. Bello et al. (2019) reported that helpers had a lower exposure (7.5 µg/m^3) compared to sprayers (19.6 µg/m^3).

Based on the existing studies, there is a short-term risk of exposure during spraying and curing of SPF. However as isocyanates are highly reactive compounds (Dahlin, 2007), the long term risk for isocyanate inhalation exposure of building occupants from polyurethane insulation, or polyurethane household products, under standard occupancy conditions is considered to be minimal. People suffering from asthma, or isocyanate sensitisation, may however be more vulnerable compared to the general population. Whilst in normal

operating conditions MDI long term exposure is low, based on existing data, during extreme cases (such as fires) it could be released back into the indoor environment.

2.5.2. Emissions during combustion and fires

Exposure to high levels of MDI from polyurethane boards and spray foam could possibly occur during fires, as pyrolysis-GC-MS analysis of polyurethane has shown that the urethane bond breaks at high temperatures (Ohtani *et al.*, 1987). A study on the thermal degradation of rigid polyurethane foams showed that polyols and isocyanates de-couple at 200 °C (Jiao *et al.*, 2013). This leads to MDI starting to emit at 200 °C and reaching its highest emission rate at temperatures between 350-450 °C, followed by a significant decrease at 850 °C (Garrido *et al.*, 2017),. Further studies from pyrolysis of SPF support this hypothesis (Hileman *et al.*, 1975; Hiltz, 2015). Temperatures between 200-600 °C usually occur during the first half hour of a fire (Lie, 1974), which theoretically suggests that when fires start and spread, there could be significant levels of MDI re-emitted into the indoor air from PU products in a short period of time. Pyrolysis data showed that PU foam mattresses release MDI at a rate of 0.0001-0.01 mg/g_{sample} (Garrido *et al.*, 2017).

Apart from MDI, large quantities of hydrogen cyanide, acrylonitrile, acetonitrile and carbon monoxide are released between 550-850 °C which coud have toxic effects (Garrido, Font and Conesa, 2016; McKenna and Hull, 2016).

A small-scale experiment demonstrated that isocyanates could also be released from a number of other common building products during fires such as glass wool (isocyanate acid and methyl isocyanate), particleboard, mineral wool (isocyanate acid and methyl isocyanate), PUR- both flexible and rigid foam (TDI and MDI) and PIR- rigid foam (TDI and MDI) (Blomqvist *et al.*, 2003). This highlights that not only polyurethane products, but also natural materials could contribute to releasing isocyanates during fires. Figure 10 represents the volume of product containing sufficient isocyanate (MDI) that would exceed the highest legal exposure limit of 0.2 mg/m^3 (OSHA PEL Ceiling Peak) if released back into the indoor air in a typical 50 m^3 bedroom.

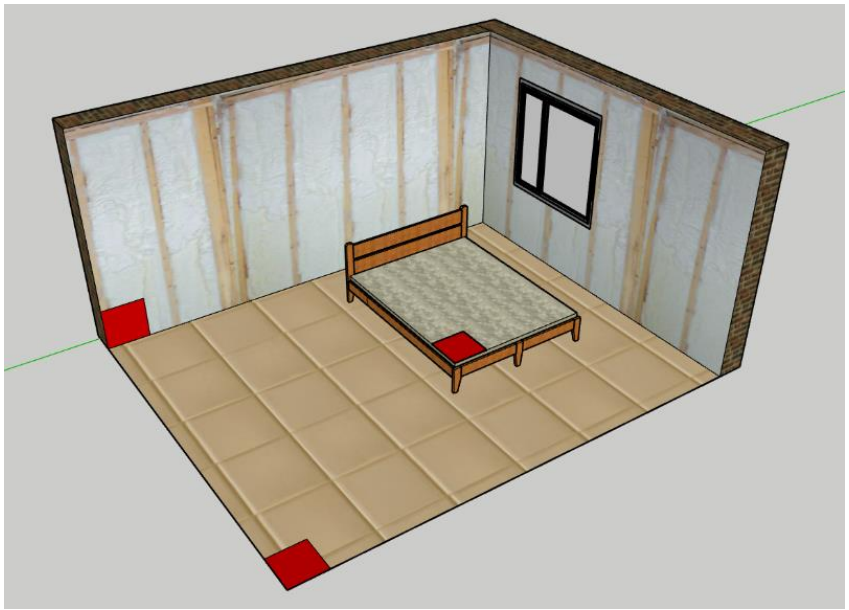


Figure 10. Area of various products (PU mattress, PU floor insulation and PU wall insulation) that contains sufficient isocyanate to exceed OSHA PEL if released into a typical 50 m^3

bedroom (5 m width, 4 m length, 2.5 m height). Thickness of 15cm assumed for all products. Density of 30 kg/m^3 assumed for all products.

In order to reduce the risk of fires, flame retardants are added to the liquid mixture of spray foams.

2.5.3. Side B - flame retardants

As flame retardants are not typically chemically bound to the polyurethane matrix (ECHA, 2018), they emit indefinitely. Exposure of people to flame retardants, in general, has been measured in numerous studies, summarised in Appendix D. Appendix D outlines indoor concentrations of TCPP, TCEP and TDCPP in indoor environments based on 20 studies and over 2000 samples from different cities and locations, covering homes, hotels, offices, schools, day-cares, gymnasiums, mosques, cars and outdoor environments (based in Brazil, Canada, China, Germany, New Zealand, Sweden, Saudi Arabia and the U.S.). All data is converted to the same SI unit in order to present comparable measurements between different datasets.

The mean concentrations of flame retardants in dust from 13 studies in 7 countries from indoor spaces (n=502) are plotted in Figure 11.

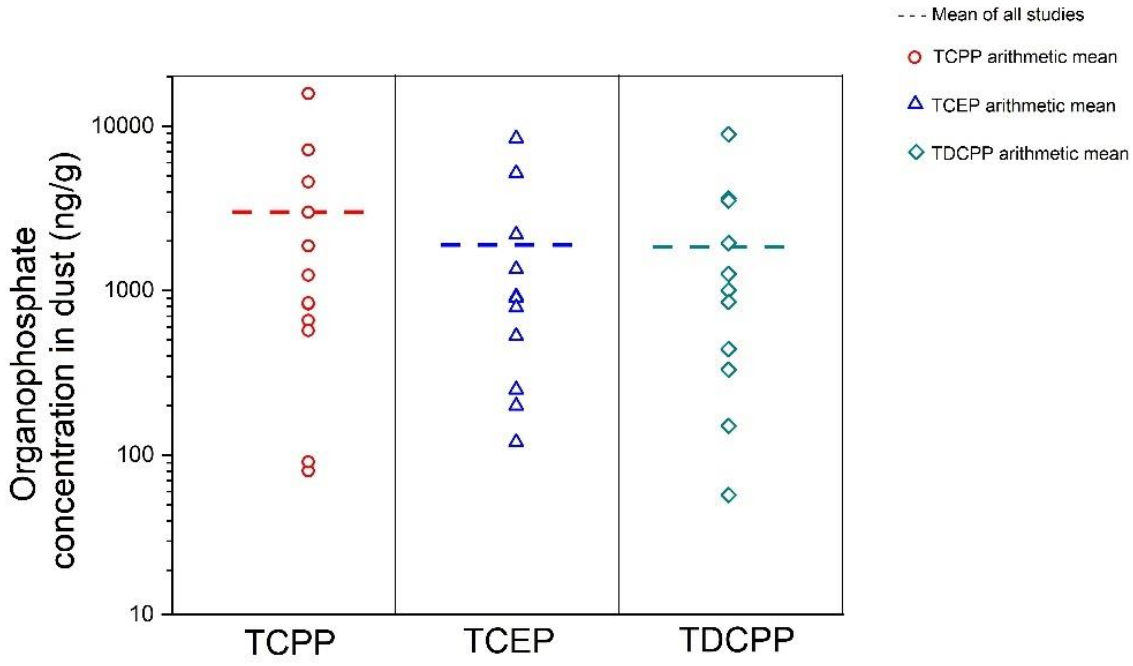


Figure 11. TCPP, TCEP and TDCPP arithmetic mean concentration in settled dust from 7 countries (n=502). Scale is logarithmic. Dotted lines represents arithmetic mean (AM) concentration of all studies. (Stapleton *et al.*, 2009; Ali *et al.*, 2012, 2018; Fromme *et al.*, 2014; He *et al.*, 2015; Hammel *et al.*, 2017; Tan *et al.*, 2017; Bi *et al.*, 2018; Deng *et al.*, 2018)

In Brazil, cumulative concentration of flame retardants in dust was found to be higher in schools, offices and cars compared to apartments and houses (Cristale *et al.*, 2018). The relationship between TCPP and TDCPP levels in dust and presence in polyurethane sofas and couches in one study were “not significant”, suggesting that other sources could be contributing to the flame retardant levels in dust (Hammel *et al.*, 2017). Bi et al. (2018)

measured flame retardant levels in settled dust and HVAC filter dust of 54 U.S. low-income homes and reported that median levels of TCPP in the U.S. was 3-180 times higher than reported levels in Belgium, Canada, China, Egypt, New Zealand, Saudi Arabia and Sweden, slightly higher than levels in Germany and Norway, but lower compared to studies in Japan.

Concentration of TDCPP in cars (Brommer *et al.*, 2012; Cristale *et al.*, 2018) was found to be 14-2,280 times higher than the concentration in buildings as per Appendix D.

Based on Figure 16 and Appendix D, the mean concentration in dust (ng/g) is 40-320 times higher than the mean concentration in air (ng/m^3). A literature review found that whilst the major exposure pathways differed between the various flame retardants, indoor dust seems to be the best proxy for internal exposure (Xu *et al.*, 2019). A weak correlation (R^2=0.06) of metabolites of flame retardants in human urine (n=229) with emissions from furniture suggests that dust ingestion from furniture is not the only exposure pathway (Ingle *et al.*, 2019).

The cumulative data suggests that all pathways (inhalation, ingestion and dermal) and all exposure locations (buildings, cars and other indoor environments) must be considered when calculating exposure of people to flame retardants.

A few pilot studies have looked at flame retardant emissions from spray foam insulation with the majority published as part of an ASTM compendium (ASTM International, 2017c). Micro-chamber tests demonstrated that flame retardant emission rates from open-cell SPF were up to 10 times higher at 40 °C and up to 100 times higher at 65 °C compared to 23 °C during the first few days after spraying, followed by a decrease in the emission rates until a quasi-steady-state condition was reached (Sebroski, ASTM International 2017). NIST micro-chamber analysis showed that after 100 h, flame retardant (TCPP) concentration of open-cell spray foam was 100 times higher compared to closed-cell spray foam (Poppendieck, ASTM International 2017). The studies concluded that flame retardant emissions in chambers will vary with flow rate, temperature and type of foam (ASTM International, 2017c). This means that in practice, flame retardant emissions in real case studies may be impacted by the foam, indoor temperature and ventilation strategy of the building.

NIST have undertaken long-term studies on TCPP emissions from SPF in micro-chambers, in-situ and by producing non-ideal foam samples and the main findings are:

- TCPP emissions from polyurethane and spray foam could be a long term issue, as micro-chamber emission rates were not statistically different between fresh sprayed open cell foam compared to two years after application (Poppendieck, Gong and Emmerich, 2017)
- Micro-chamber data could be used to compare TCPP between different products, but could not be extrapolated to full scale buildings as mass transfer-based modelling is needed to predict TCPP concentration (Poppendieck, Gong and Emmerich, 2017)
- Data from SPF in the NIST Net-Zero Energy Residential Test Facility (NZERTF) demonstrated that TCPP emissions are four times higher at 28 °C compared to 23 °C based on a study of one product (Poppendieck, Gong and Emmerich, 2017).

An assessment of personal exposure of workers to TCPP during SPF spraying reported that sprayer exposure (GM= 87.1 μg/m^3) was significantly higher than helper concentration (GM= 30.2 μg/m^3) (Estill et. al, 2019). The same study reported lower concentrations of TCPP personal exposure during SPF spraying (GM = 48.5 μg/m^3) compared to a previous study (GM = 295 μg/m^3) (Bello, 2018). This was contributed to Estill et. al (2019) measuring TCPP concentration for the workers' shift (177-640 min), whilst the Bello et al. (2018) reported concentration during different tasks (15-176 min). The application conditions are also an important factor that could influence the emission rates.

When foam is applied at an off-ratio between A and B-side, or applied at lower ambient temperatures (5 and 16 °C), the TCPP emissions are different compared to optimal application procedures (Won, ASTM International 2017). This suggests that misapplication, i.e. when spraying during ambient conditions outside the manufacturer recommendations, this may impact long-term emission rate of flame retardants in spray foam.

Whilst numerous studies have recorded flame retardant levels, there is limited data on blowing agent concentration from PU and SPF products.

2.5.4. Side B - Blowing agents

During a study of a single house, Tian and Sebroski (ASTM International, 2017c) found HFC-245fa seven days after SPF application at a range of 3.3-3.5 mg/m^3, which decreased to 1.6-1.75 mg/m^3 (0.3ppm) after 1 month. No other studies could be found that have measured blowing agent levels from spray foam. A possible explanation is that blowing agents are generally considered safe given that they have been used as refrigerants in many types of systems (fridges, air conditioning systems for buildings, cars, planes and other applications) since the 1990s (Tsai, 2005; Vollmer *et al.*, 2011).

Like blowing agents, there is also limited scientific evidence for catalyst emissions.

2.5.5. Side B - Catalysts

Microchamber tests of three products demonstrated that whilst amine emission rates ranged from 2,000 μg/m^3- 12,000 μg/m^3 for the first 120 h, they reduced significantly after 400 h and no amine catalyst above the detection limit was found emitting from a 1.5-year old spray foam sample (Poppendieck, Persily and Nabinger, 2014). A microchamber test of an open cell SPF product demonstrated that 70% of the initial amine (BDMAEE) concentration in the foam was depleted over the course of a 400-h experiment (Poppendieck, ASTM 2017).

Whilst amines are regularly disclosed in safety data sheets due to their implications on health, there is no requirement to list common by-products in safety data sheets. By-products, or residual, products are compounds that are the result of reaction between the material and the indoor air. As every indoor environment contains an almost unique mixture of hundreds of VOCs there may be many variations of by-products found indoors following the application of spray foam. Some of the more common ones found in the literature are reviewed.

2.5.6. By-products and residual products

The first by-products considered are ones associated with Side A (isocyanates). As hydrolysis of isocyanates may result in amines forming, these are considered. As the most common

isocyanate for spray foam production is MDI, therefore its potential by-product of MDA is considered.

Analysis during moulding of cured polyurethane foam panels demonstrated that although MDI concentration in the breathing zone was below detection limit in 64% of the samples (n=57) found detectable amounts of MDA (diaminodiphenylmethane) in 97% of the workers urine samples (Kaaria *et al.*, 2001). Monitoring of workers urine in 19 polyurethane industries reached similar conclusions that post-shift (post-working hours) MDA values were significantly higher than pre-shift values and a determinant of the exposure appeared to be the mixing operation of MDI and polyols (Robert *et al.*, 2007). Elevated levels of MDA in worker urine post-shifts were found of people working in polyurethane processing environments, such as car repair shops and welding district heating pipes (Rosenberg *et al.*, 2002).

However as MDA is the result of hydrolysis of MDI, it is possible that workers were actually exposed to MDI, which converted into MDA in their bodies. This theory is supported by findings that MDA is a suitable biomarker for MDI exposure (Robert *et al.*, 2007). However other emissions potentially associated with Side B reactions or a mixture of both sides are also considered.

In homes, a literature review of exposure to pollutants in sleeping microenvironments demonstrated that polyurethane bedding products emit a mixture of VOCs into the air including, but not limited to flame retardants, 1,4-dioxane and 1,2-dichloropropane (Boor *et al.*, 2017). These compounds have also been found emitting from polyurethane spray foam insulation (ASTM International, 2017).

2.6. Olfactory impact and perceived indoor air quality

It is crucial to determine the source and rate of all emissions from isocyanate based products indoors and analyse their total impact on the indoor environment and people. Albeit insulation materials are likely to represent the highest volume of polyurethane in households for example, the total concentration of VOCs could be underestimated if other indoor polyurethane sources are not taken into account.

Despite analytical chemistry and IAQ monitoring equipment sensitivity significantly developing and allowing compounds to be measured down to ppt levels, in real environments people often rely on their sense of smell in order to infer the level of pollutants indoors. Whilst there may be a correlation between perceived indoor air quality and indoor levels of organic pollutants (Wolkoff and Nielsen, 2001), it is extremely difficult to establish a causality between VOC levels and impact on human health. For this reason, Public Health England recommended exposure limits for organic pollutants on the basis of toxicological and epidemiological evidence with total volatile organic compounds (TVOC) being associated as an indicator for ventilation efficiency and indoor air quality, but not a health metric (Public Health England, 2019).

The strong association between smell and perceived indoor air quality has been demonstrated with how children experience indoor environments (Kim, Senick and Mainelis, 2019). In addition, odour perception was found to correlate with sick building syndrome. A study in Chinese residences found correlation between occupants reporting at

least one mucosal symptom (eye irritation, nose irritation, throat hoarseness and cough) and chemical or stuffy smell and also a correlation between elevated levels of some VOCs and self-reported mucosal or dermal health symptoms (Sun *et al.*, 2019). The odour, and odour threshold, for all SPF compounds groups are plotted in Table 2 to provide further insight on how it could impact perceived indoor air quality and people's perception of dwellings retrofitted with spray foam.

Table 2. Olfactory properties for polyurethane spray foam compounds

Polyurethane	Target compound	CAS-Number	Odour	Odour threshold	Short term exposure limit (15 min)
Side A	Diphenylmethane-4,4'-diisocyanate (MDI)	101-68-8	Odourless(Allport, Gilbert and Outterside, 2003a)	400ppm (Woolrich, 1982)	0.2 ppm (Health and Safety Executive, 2020)
	Toluene diisocyanate (TDI)	584-84-9	Sharp, pungent odour (Parod, 2014)	2.1ppm (Fazzalari, 1978)	
Side B	Dibutyltin dilaurate	77-58-7	Mild (Rhein Chemie Corporation, 2017)	No data available	
	Triethyl phosphate	78-40-0	Mild, pleasant (Lewis, 2001)		
	1,1,1,3,3-pentafluorobutane	406-58-6	Ethereal, faint, sweetish odor		
	N,N,N',N' – Tetramethyl-2,2'-oxybis(ethylamine)	3033-62-3	mild, amine/pungent-like (ECHA, 2021)		
	Tris(2-chloro-1-methylethyl)phosphate	13674-84-5	Mild odor (U.S. Environmental Protection Agency (EPA), 2015)		

	N,N-bis[3-(dimethylamino)propyl]-N'N'-dimethylpropane-1,3-diamine	33329-35-0	Low slight amine/pungent odour		
By-products	Trans-1,2-dichloroethylene	156-60-5	Slightly acrid, chloroform-like/sweet odor (NIOSH, 2019)		
	1, 2- dichloropropane	78-87-5	Sweet, chlofororm-like (Agency for Toxic Substances and Disease Registry (ATSDR), 2019)	15-23ppm	No data available
	1,4 – dioxane	123-91-1	Faint/mild and sweet (Agency for Toxic Substances and Disease Registry, 2012) ehhereal	No data available	
	Hexamethylcyclotrisiloxane	541-05-9	Sweet (Wang *et al.*, 2017)		
	2-ethyl-4-methyl-1,3-dioxolane	4359-46-0	Sweet (Schweitzer, Noblet and Suffet, 1999)		
	Chloro-benzene	108-90-7	Aromatic, almond-like (National Research Council, 2012)	0.2-1.8ppm (National Research Council, 2012)	3ppm (Health and Safety Executive, 2020)

From the available olfactory data in Table 2, it could be hypothesised that the only compounds which could have a negative impact on perceived indoor air quality are amines – either used as catalysts or by-products from the reaction between the spray foam and indoor environment. As the smell of amines has been associated to 'fishy' smell in olfactory research (Amoore and Forrester, 1976; Majid *et al.*, 2018), it is hypothesised that catalyst amines, or secondary amines formed by a reaction between the SPF and the indoor air were responsible for the "fishy" smell and negative impact on perceived IAQ found in field studies (Tsuang and Huang, 2012; Huang and Tsuang, 2014). All other known compounds in SPF formulation, and possible by-products, have either a sweet smell or are odourless as per Table 2.

It is clear that human receptors and olfactory perception are not however a good indicator for detecting potentially hazardous emissions from polyurethane products. As the data in Table 2 outlines, the odour threshold for some compounds exceeds the recommended exposure thresholds. Therefore people may be exposed to potentially harmful levels without realising, and in instances of compounds having a sweet smell – they could experience negative health impacts whilst experiencing a positive perceived/olfactory impact (i.e. sweet/pleasant smell). This outlines that people may be exposed to elevated levels of volatile organic compounds and not realise this, therefore not opening windows or increasing ventilation in their homes, which could have implications for their health. This is reinforced by recent research, which highlights that that indoor temperature was the most important influencing factor for window opening and closing behaviours and none of the studied air quality variables were found to have a large impact on people's operations of windows (Wang *et al.*, 2022).

After spray foam is installed, manufacturers and installers provide recommended guidelines for re-entry and re-occupancy of the dwelling (Center for Polyurethane Industry, 2012). Research using tracer gas techniques demonstrated that soil pollutants from basements/crawlspaces and underfloor can effectively reach living space and air infiltration from these areas makes a significant contribution to the whole house air infiltration rate (McGrath and McManus, 1996). Industry practice therefore becomes an important aspect for deciding the ventilation rate and re-occupancy strategy of the dwelling following the retrofit in order to reduce the short term and long-term exposure to organic pollutants.

2.7. Industry practice for spray foam application

2.7.1. Best practice guidance

The Centre for the Polyurethane Industry (CPI) has produced guidance on application of SPF (Center for Polyurethane Industry, 2012). It stipulates that PU insulation is "considered essentially inert and non-hazardous when properly installed and cured". It provides guidance that "adequate ventilation" is required during SPF installation, however no ventilation rate or time frame for re-occupancy is provided as this is considered a responsibility of the SPF manufacturers and/or sprayers.

In the UK specifically, the Health and Safety Executive (HSE) has set the rules and regulations with regards to chemical exposure in the Control of Substances Hazardous to Health Regulations (COSHH). The protocols within COSHH outline the responsibility of

companies/employers who need to protect workers from exposure to hazardous substances through undertaking risk assessments and setting out robust protocols in place to reduce exposure to carcinogens, mutagens and asthmagens in line with workplace exposure limits (Health and Safety Executive, 2020). There are a variety of guidance documents proided by the HSE for reducing risks when handling, spraying isocyanate (HSE, 2022a, 2022b), which include recommendations to use local exhaust ventilation (LEV) where possible however a specific ventilation rate or re-occupancy period is not prescribed and is the responsibility of the installer to define what "adequate ventilation", for example a specific ventilation rate, looks like during installation. As the HSE regulations focus on occupational exposure their primary function is to protect the health of workers working with spray foam during the spraying and curing process.

Manufacturers of the raw spray foam materials provide guidance and instructions to installers on how they should apply their products safely. The author was not able to find evidence for industry guidance of *specific* exhaust ventilation rate when applying spray foam. Presumably this could have occurred due to the lack of sufficient empirical evidence for such recommendations. As outlined in Sections 2.5, despite the wide use of spray foam globally, there is a low amount of empirical data outlining emissions rates and VOC concentrations during the lifecycle of these insulation products.

International industry standards for re-occupancy, in particular, are traditionally based on isocyanate (Side A) exposure and usually apply a 1-48 hr re-occupancy guideline with a majority of commercial appliers opting for a 24-hr re-occupancy period (Wood, 2017).

Emissions from the B-side in the context of re-occupancy have only been discussed since 2017 (ASTM International, 2017c). The EPA published a guide for ventilating SPF workspaces to minimise exposure to mist, vapour, particles and dust (U.S. Environmental Protection Agency (EPA), 2018) with the key aspects summarised by Poppendieck (Poppendieck *et al.*, 2019).

There are however no published datasets on ventilation strategies for building owners' post-application of SPF. A preliminary study on application conditions found that emission factors could be 1.2-2.3 times higher when A and B side were applied off-ratio and 1.1-15.4 times higher when SPF is applied at low temperatures (5 °C) (Won, ASTM International 2017). There is however no scientific data demonstrating whether emissions during optimal conditions, as per manufacturer guidelines, vary compared to "misapplied" products.

It is still however, widely unknown how ventilation conditions affect short and long emission rates of VOCs and semi-volatile organic compounds (SVOCs) from SPF products. The definitions for various organic compounds could be found in Appendix E. Whilst there is advice on best practice, that does not necessarily guarantee that it is being consistently followed or that the best practice protects workers and the general population from exposure to VOCs.

2.7.2. Examples of poor standards or insufficient worker protection

The risks associated with SPF spraying have been researched since the 1980s (Hosein and Farkas, 1981). Construction workers are often found not to wear gloves due to poor health and safety practices (Arcury *et al.*, 2012) and women have difficulty getting access to proper fitting PPE kit (Onyebeke *et al.*, 2016). Research comparing types of protective equipment

shows that MDI exposure could be reduced 10-100 fold by using different types of gloves (Mellette *et al.*, 2018).

Whilst respirators decrease exposure to volatile organic emissions, they have been found to interfere with many physiological and psychological aspects of task performance at levels from resting to maximum exertion (Johnson, 2016). A pilot study of flame retardant ingress in the human body during spray foam installation demonstrated that although best practice equipment was used, including air respirators, gloves and coveralls, post-shift urinary flame retardant biomarker was 26-35 times higher than that reported in general population (Bello *et al.*, 2018). Strong association was observed between dermal exposure and urinary flame retardant biomarkers (Bello *et al.*, 2018).

Figure 12 demonstrates the theoretical indoor concentration of VOCs during application, and post-installation, of spray foam insulation (SPF). The existing data suggest that emissions peak during spraying, however they are reduced when high extract ventilation is used.

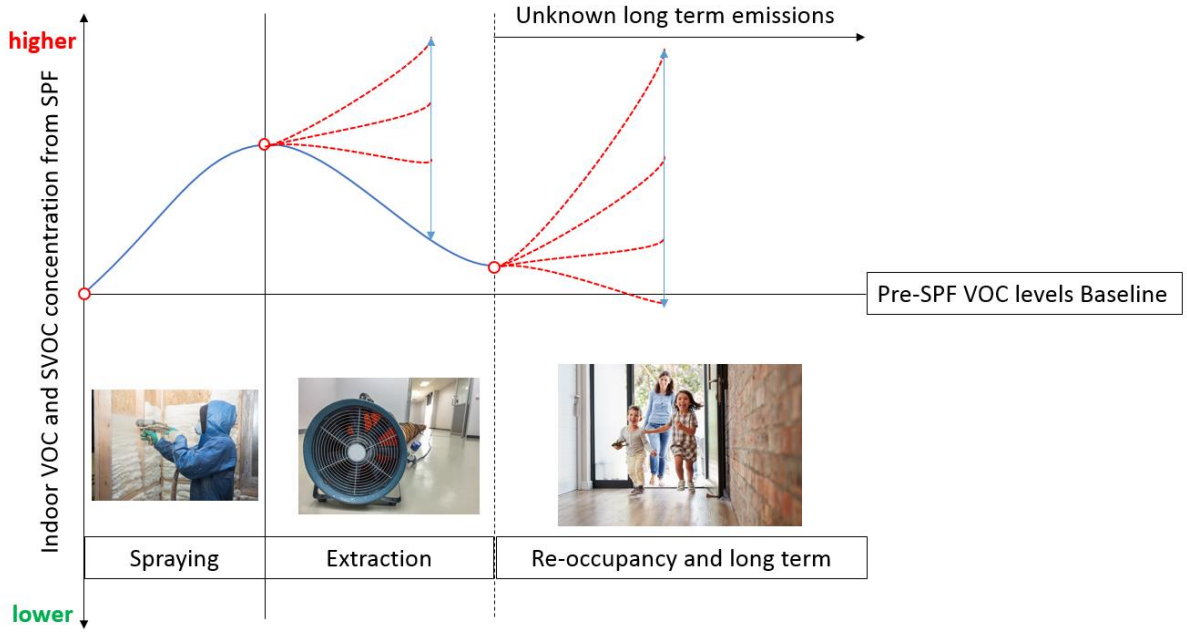


Figure 12. Schematically presented concentrations of VOCs and SVOCs in indoor air during and post SPF installation. Blue line represents data from chamber experiments and case studies. Red line represents area of uncertainty where further research required.

Existing data suggests that isocyanate emissions near the sprayer during application could exceed legal exposure limits and PPE must therefore be worn to protect workers, both sprayers and helpers. Using supplied air respirators, gloves and coveralls however might not be sufficient to reduce the risk of exposure to flame retardants during SPF application.

Existing literature has concluded that organophosphate flame retardants (OFRs) are found in abundance in indoor environments, even in buildings without PU insulation. There is evidence suggesting catalyst amines, or secondary amines formed in a reaction between SPF and oxidising components of indoor air, could be responsible for the “fishy” smell and negative impact on perceived IAQ reported in some cases.

All other constituent compounds, and known by-products, associated with PU materials either have a sweet smell or are odourless.

The critical missing aspect in the literature are the measurement of emissions from spray foam and the implications on indoor environmental quality tracking the process from laboratory conditions up to installation and verifying it with case study data. Long-term analysis (>1 month) of volatile organic emissions data from both A and B-sides following SPF retrofit exists in only one study, which is insufficient to draw definitive conclusions. The U.S. market for spray foam insulation is much bigger and well established compared to the UK one, where these products only represent a small proportion of retrofits and use in buildings (Market Research Future, 2021). In order to contextualise the importance of understanding these emissions, and their potential impact on human health, first the retrofit potential of this measure for the UK must be examined.

2.8. Summary

In summary, there is little empirical evidence of the impact of modern spray foam product on indoor environmental quality. A large proportion of the academic studies were undertaken more than 10 years ago and it is not clear whether the results are representative of modern day materials and relevant for the current building stock. Material science improvements driven by market competition has changed foam composition and significant changes have been adopted particularly to the B-side of foams, whereas the A-side has remained largely the same (isocyanates).

Based on a systematic review of the literature, the following knowledge gaps were identified:

1. Polyurethane materials offer higher energy savings compared to conventional insulation products. However there is no study assessing the potential for retrofitting the existing UK suspended timber floor building stock by applying spray foam insulation with robots.
2. There are multiple methods for measuring isocyanate emissions (side A), however there is no standardised method for measuring side B and by-product emissions of spray foam insulation products during the lifecycle of the product.
3. Most of the side-B and by-product volatile organic compounds (VOCs) may lead to health implications, however their impact is dependent on the exposure rates. There are pilot studies measuring some VOC emissions from spray foams, however there are no comprehensive studies measuring the full lifecycle (short, mid and long) term concentrations of modern polyurethane products.
4. Scientific, industry and non-governmental organisations have extensively assessed isocyanate exposure and mitigation measures to reduce risks for both sprayers and building occupants. There is however little empirical data on validating ventilation strategies for reducing B-side emissions and by-product emissions associated with spray foam application.

The next chapter outlines how these evidence gaps were filled and the overall research design.

3. Research Design

This chapter explains the design of the research, how it was structured and how each chapter addresses a particular research question. This chapter first explains the research rationale and context, where several decisions and developments in the wider scientific field defined the structure and shape of this thesis. The chapter then outlines the overall aims and four research questions followed by the specific objectives that were set for this PhD. The complete thesis design and structure is then presented outlining the connection between evidence gaps identified in the literature review, research questions and which chapter addresses each specific question. Lastly, this chapter concludes by outlining the contributions to knowledge and practice that this thesis has achieved.

3.1. Research Rationale and Context

First, the study applied the interdisciplinary structure proposed by Chynoweth (Chynoweth, 2009) and brought together different disciplines however grounding the thesis within the context of the built environment as per Figure 13.

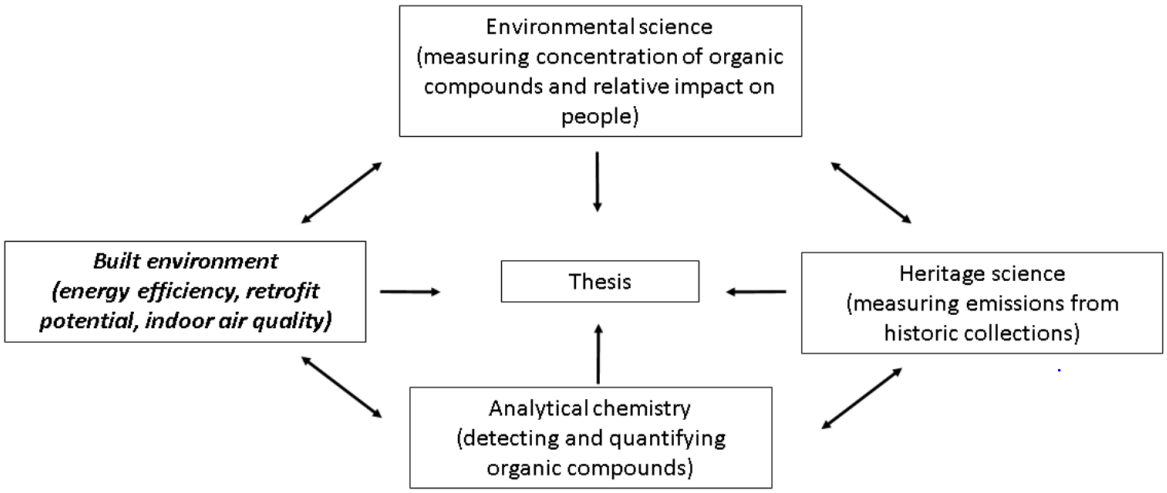


Figure 13. Contextualisation of this thesis and disciplines brought together for its development

Learnings from other fields (heritage science, analytical chemistry and exposure science) were integrated together forming an interdisciplinary thesis and providing novel scientific evidence in addressing the scholarly gaps as identified in Chapter 2.

Secondly, prior to the dissertation starting, Historic England had published guidelines for retrofitting suspended timber floors that advised that spray foam materials (polyisocyanurate or polyurethane) are "not usually appropriate for suspended timber floors" due to "their inability to absorb and release moisture may increase the risk of condensation" (Historic England, 2016). A review of existing guidance documents for retrofitting historic building walls showed that spray foam was only recommended in the U.S., but not Canada, England, Germany, Ireland or Scotland (Castele and Webb, 2019). In Scotland, there were a few case studies of spray foam being applied in historic buildings (Bennadji, 2013; Abdel-Wahab and Bennadji, 2015; Kishorn Insulations, 2023), however the Architectural Heritage Society in Scotland advised against spray foam being used in historic buildings in particular (The Architectural Heritage Society of Scotland, 2021). The author therefore decided that the PhD will focus on the entire building stock scope with potential to be retrofitted (an estimated 16%, or more, of existing UK building stock) rather than a narrow scope of "historic" buildings as per Historic England definitions (an estimated ~2% of the existing UK stock). The author also decided that moisture performance and risk of condensation was outside the scope of the PhD.

Thirdly, prior to starting this thesis, a proof-of-concept method for measuring B-side VOC emissions was developed to fulfil the purposes of an MRes dissertation (Naldzhiev, 2017). The MRes demonstrated that quantitative analysis of polyurethane emissions was theoretically possible, however the sensitivity of the analytical method was not sufficiently precise to allow measuring of emissions in field study environments as the calibration curves (R2) were not of sufficient quality to confidently report quantitative results (ASTM International, 2017c; Lemyre *et al.*, 2022). In the indoor air quality field, some spray foam pollutants have a legal long-term exposure (8-hr time weighted average) workplace

threshold limit of 1000ppb in the UK (Health and Safety Executive, 2020) whereas others have much lower international limits such as Bis(2-dimethylaminoethyl) ether which has a TWA of 50ppb (Sleasman, Hetfield and Biggs, 2017). As these guidelines had really low limits, down to 50ppb, for some spray foam pollutants, theMRes method was therefore considered insufficiently precise and further method development was needed to improve sensitivity. Preliminary analysis demonstrated that utilising heritage science techniques allowed for the detection of some of the spray foam emissions, but not all. Particularly, the side A emissions (isocyanates) could not be detected at all using the developed analytical method. In addition, not all of the side B and by-product emissions were detected therefore further method development as part of this thesis was required in order to deliver novel scientific findings suitable for peer-reviewed publication.

Finally, during the course of this PhD, an international method for measuring insulation emissions in microchambers was published by ASTM International (ASTM International, 2020). Chapter 5 of this thesis and part of the contribution to knowledge involved method development for measuring spray foam emissions as outlined above. The method developed as part of this thesis is suitable for measuring concentrations both during application of spray foam as well as microchambers and a comparison between the original work as part of this thesis and the ASTM method is presented in Chapter 5.

3.2. Aims and Research Questions

Before starting experimental work, given the significant resources associated with analytical chemistry method development, it was critical to understand the potential for insulating the UK building stock with spray foam applied with robots. If the energy savings potential was deemed insignificant, or limited building stock penetration was possible, then the emissions from spray foam products could have had limited relevance for the indoor air quality field in the UK context.

The first aim was therefore to assess existing datasets and understand the potential for retrofitting the suspended timber floors of the UK building stock. Focusing on existing data allowed the removal of uncertainty associated with building physics models, particularly the performance gap (Zou *et al.*, 2018b) and multiple assumptions and generalisations that have to be made when utilising building stock modelling (Mata, Sasic Kalagasidis and Johnsson, 2014; Jenkins, Simpson and Peacock, 2017).

R.Q1: What is the retrofit potential for insulating the UK building stock with polyurethane spray foam insulation applied with robots?

The analytical method development as part of this thesis acted as a original work of applied research rather than developing the analytical chemistry field itself. The PhD utilised a series of pre-existing techniques and 'borrowed' knowledge from two scientific domains (heritage science and analytical chemistry) applying them to develop built environment scientific gaps relevant to indoor air quality. For this reason, the second aim was to further develop a method that could be deployed in both controlled conditions and field studies.

R.Q2: Can volatile organic compound (VOC) emissions emitted from polyurethane products be measured using analytical chemistry developed for plastics and objects for museum collections?

As outlined in the literature review, very little empirical data exists on spray foam emissions during their lifecycle. The third aim was to experimentally measure VOC concentrations during the full lifecycle of modern spray foam insulation products (raw materials, during spraying, during curing and post-spraying).

R.Q3. What are the short, mid and long term concentrations of VOCs from spray foam materials in controlled conditions?

Lastly, in order to validate experimental findings and contextualise the thesis within the built environment field, the final aim was to assess whether ventilation could act as sufficient mitigation strategy for reducing VOC concentrations in-situ.

R.Q4: Based on experimental and laboratory work, can ventilation protocols to mitigate risks during the installation phase and building use be developed and validated in case studies?

3.3. Specific Objectives

The thesis had four specific objectives in order to achieve the aims and address the four research questions:

- To assess built environment, policy and social research datasets and converge findings evaluating the potential of retrofitting UK buildings with polyurethane spray foam materials applied with robots
- To test, develop and evaluate analytical chemistry methods allowing for quantitative analysis of VOC concentrations from spray foam pre, during and post-spraying
- To provide original experimental measurements of VOC concentrations emitted from a range of spray foam products available on the open market
- To validate a ventilation protocol designed to mitigate exposure risks from spray foam application in a case study

3.4. Study Design and Structure

The thesis structure is presented in Figure 14.

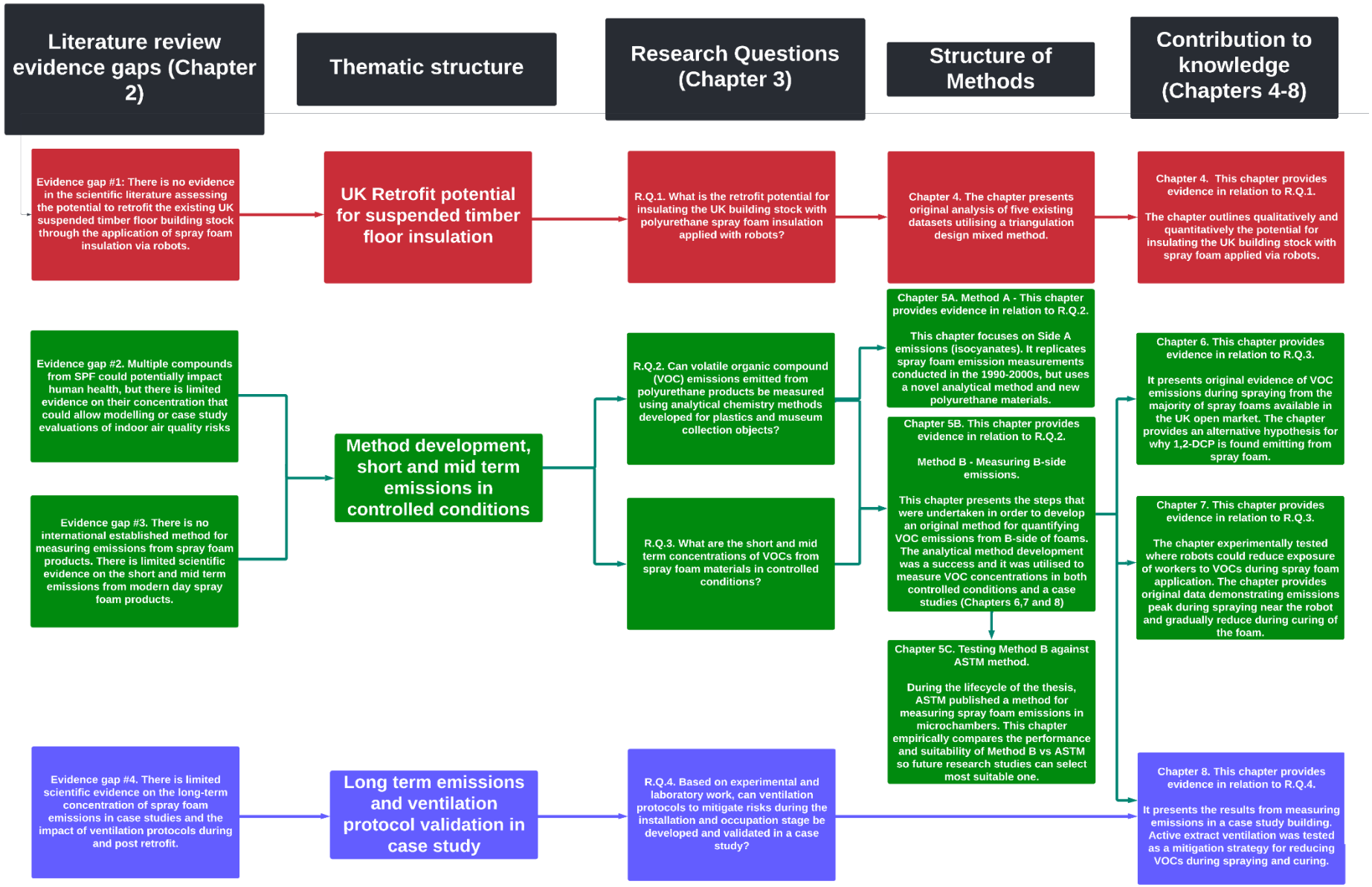


Figure 14. Study design and structure outlining the knowledge gaps, thematic structure and presents and outline of how the thesis addressed the research questions

3.5. Summary

This thesis identified four key evidence gaps and research questions.

R.Q.1 is addressed by presenting novel evidence in Chapter 4 through a triangulation design mixed research method that brings together findings from several existing datasets through novel analysis.

R.Q.2 is addressed through method development work (Chapter 5) demonstrating that it is possible to develop a highly sensitive method for measuring spray foam relevant emissions. Chapter 5 outlines that two methods were developed for measuring different VOC emissions from spray foam. In simple terms, Method A measures VOC emissions from Side A of spray foam (isocyanates) and Method B measures VOC emissions from side B (catalysts, blowing agents, flame retardants and by-products). Method A, albeit novel, was not carried forward for further work due to sufficient evidence in the literature in relation to isocyanate exposure. Method B was utilised for all experimental work in addressing the other research questions.

R.Q.3 is addressed through original work measuring VOC concentrations in controlled conditions (Chapter 7) near the sprayer operating the robot and near the spraying surface of a suspended timber floor.

R.Q.4 is addressed through original work validating ventilation strategies efficiency in a case study building (Chapter 8) presenting evidence of VOC concentrations pre, during and post-installation of spray foam for a period of up to two months after retrofit.

The findings from the chapters are brought together and contextualised within the wider literature in the discussion chapter where a spray foam risk matrix and novel VOCabulary for categorising VOCs are presented (Chapter 9). Chapter 10 presents the main conclusions of the thesis and Chapter 11 presents the limitations and suggestions for further research.

4. Review and Analysis of Driving Factors Affecting Potential of Underfloor Insulation Retrofit in the UK

The chapter addresses R.Q.1 and outlines qualitatively and quantitatively the potential for insulating the UK building stock with spray foam applied via robots.

The chapter presents original analysis of five existing datasets and triangulates the findings utilising a mixed mode research method. First, the reason why triangulation design was chosen as a mixed method is justified. This is followed by an outline of the method, description of each datasets and quality assurance process. Three themes are assessed in order to address the research question. The results of the analysis of each dataset are presented in separate sub-chapters.

Energy performance certificate (EPC) data of >20,000,000 dwellings are analysed demonstrating that >90% of suspended timber floors in dwellings are uninsulated. Whilst most of these >4,800,000 dwellings have other retrofit measures installed, estimations suggest annual carbon savings equivalent to nearly half of the NHS entire building stock could be made if the floors are insulated. It should be noted that EPC data is incomplete and doesn't cover the entire UK building stock therefore number of properties with uninsulated suspended timber floors is likely to be higher.

Current deployment levels of underfloor insulations are assessed via a combination of policy reviews, energy company obligation (ECO) data and social research data. The ECO data shows that underfloor insulations accounted for less than 1% of total retrofit measures installed between 2013-2018, however have gradually increased since 2019. Policy incentives exist to encourage wider market penetration and the introduction of PAS:2035 is expected to further drive forward demand.

Behavioural attitudes, Google Trend data and literature were assessed to understand retrofit attitudes. No observable causal link was established between underfloor installation, climate change concerns and energy prices. However, a statistically significant greater adoption and future intent to apply underfloor insulation to their homes has been found through analysis of survey data. This correlates well with ECO data outlining underfloor retrofits have increased in both private and ECO installations. Literature suggests that inconvenience, cost and heritage impact also play an important role on decision whether to retrofit suspended timber floors. The introduction of robots applying spray foam negates some of these factors as removal of floor boards is not necessarily required to undertake the retrofit.

Finally the findings from all individual analyses are converged in a synthesis matrix bringing together evidence from the data analysis that addresses the research question and a summary of the original work is presented.

4.1. Method

4.1.1. Method selection

The method applied for this chapter was selected based on a review of mixed method approaches specifically researching energy behaviour research (Zou *et al.*, 2018a). Table 3 outlines the possible methods that could have been adopted for this chapter.

Table 3. Overview of mixed research methods and examples for application in the built environment academic literature

Method	Overview	Example Applications
Triangulation design	Mixing of qualitative and quantitative data and/or methods so that diverse viewpoints or standpoints cast light upon a specific topic (Zou *et al.*, 2018a)	Perceptions of energy efficiency efforts among low-income housing residents in New York (Hernández and Phillips, 2015); Barriers to energy efficiency in shipping: investigating the principal agent problem (Rehmatulla and Smith, 2015)
Embedded design	Using one data set to provide supportive or a secondary role in a study primarily based on the other dataset. The primary could be either qualitative or quantitative data (Zou *et al.*, 2018a)	Integrating views and perceptions of UK energy professionals in future energy scenarios to inform policymakers (Parkes and Spataru, 2017)
Explanatory design	Using qualitative data to explain or further develop findings from quantitative results (Zou *et al.*, 2018a)	Monitoring ten Australian houses as Living Labs for a year monitoring both energy usage patterns and behaviour to better understand cooling and heating patterns in homes (Eon, Morrison and Byrne, 2018)
Exploratory design	Utilising qualitative research to develop or inform quantitative data gathering when no framework or theory is present (Zou *et al.*, 2018a)	Ethnographic study investigating design process of low-energy buildings (Zapata-Lancaster and Tweed, 2016)

Given that this chapter focuses on a retrospective analysis of existing UK datasets collected independently, but concurrently, a triangulation design is the most suitable method for addressing the research question. As outlined in Table 3, this method was successfully deployed to understand barriers to energy efficiency in shipping and for gathering insight into experiences of residents when undertaking energy efficiency retrofits.

4.1.2. Method and datasets overview

The triangulation method focused on bringing findings from several qualitative and quantitative datasets. The analysis was split into three themes for triangulation: deployment potential (i.e. how many homes could be retrofitted), current deployment level (i.e. what are the current conditions for retrofit) and barriers and incentives (i.e. what are blockers and levers for adoption of this particular measure). Figure 15 below outlines the themes for triangulation, datasets analysed and assessment factors for each dataset.

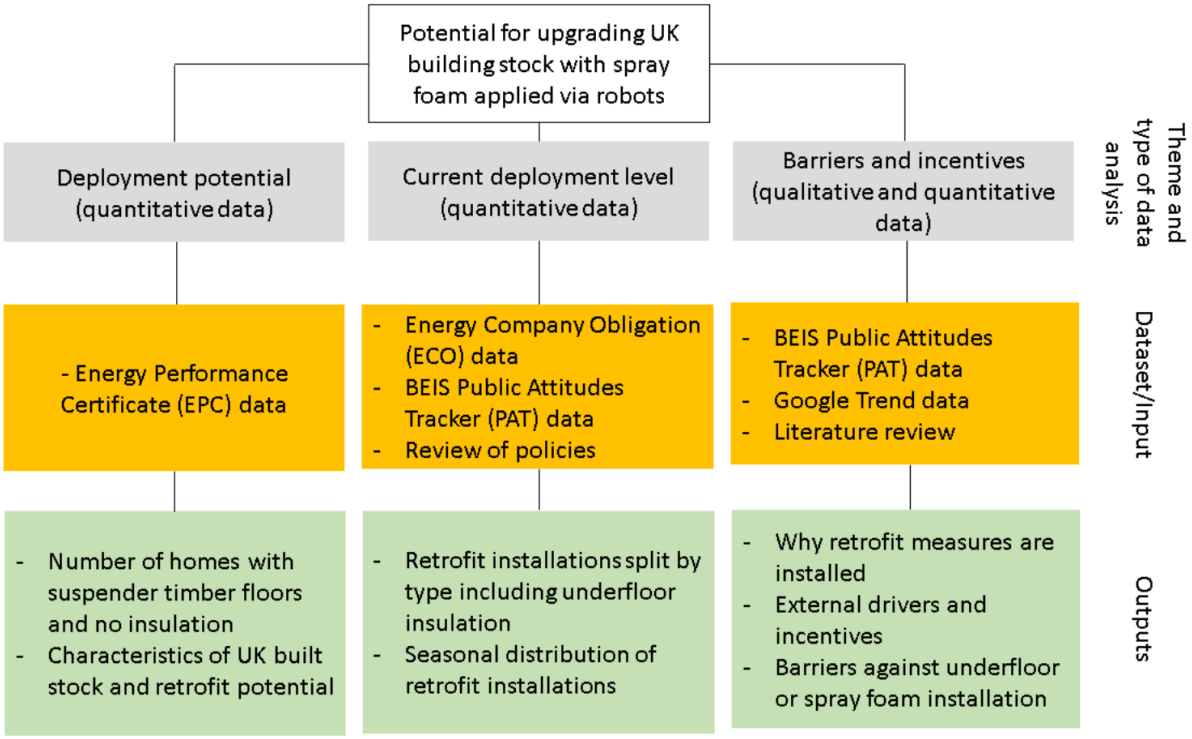


Figure 15. Method for addressing R.Q.1. aiming to understand the potential for retrofitting the UK building stock with no insulation in the suspended timber floors through the use of robots

4.1.3. Datasets description

There were four distinct datasets used for this original analysis. The datasets were split broadly into three groups: energy performance data, retrofit deployment statistics and social research data. The energy performance data analysis was undertaken on the Energy Performance Certificate (EPC) database. The EPC is the the energy "passport" of a home showing what energy efficiency measures the dwelling has and what can be improved. The EPC provides useful information about the property type (e.g., whether the walls have insulation and where improvements could be made).

The EPC database consists of two types of models: RdSAP (also known as simplified SAP) and a full SAP assessment. SAP stands for Standard Assessment Procedure and is the baseline energy model utilised for assessing compliance with Building Regulations in relation to energy efficiency matters of buildings.

RdSAP is the simplified assessment tool used for existing dwellings only in order to create an Energy Performance Certificate (EPC). The rdSAP database contains ~19.1 million datapoints for buildings generally built pre-2008, whilst full SAP database contains ~2.3 million datapoints for buildings generally built post-2008. Those datapoints are based on individual dwelling (flat or house), but could include duplications and voids.

RdSAP is largely done via survey and estimations of the property age, construction details and ventilation system therefore accuracy of construction details would vary between individual assessments. *RdSAP* requires the assessor to produce a sketch plan where full technical drawings are not available.

Full SAP requires for detailed drawings and as-built technical specifications to be recorded as EPC evidence. EPCs produced using *full SAP* methodology are more detailed and in theory should provide higher accuracy than *RdSAP*. For *full SAP* a site visit verifying whether specifications match the EPC model is not currently required albeit under consideration.

The Green Deal (GD) and Energy Company Obligation (ECO) statistics are National Statistics covering the deployment of retrofit measure covered by those policy schemes. The statistics utilise multiple data sources to collate the statistics, which are described in the Household Energy Efficiency Statistics: Background Quality Report (Department for Business Energy & Industrial Strategy, 2022).

The BEIS Public Attitudes Tracker is an Official Statistic developed via regular surveys measuring public awareness, attitudes and behaviours relating to energy and climate change policies. The tracker began in March 2012 and was run on a quarterly basis with 37 waves of data collection until 2021. Historically, the survey was conducted face to face until 2020 when due to the COVID-19 pandemic, it moved to an online omnibus.

Google Trend data reflects people's daily searches on Google by providing a data point for each month where the number of searches for a specific term are divided by the total searches within the geographic region. The subset is normalised by scaling on a range of 0-100 based on the topic's proportion to all searches on all topics. The limitations of the Google Trend index are that it is a crude measure for inferring opinions, only covers a sample of Google searches, and is based on a search algorithm rather than reflective of societal opinions. In simple terms, it demonstrates what people search for, not what they believe. However for temporal analysis, it adds useful context on how opinions shifted, what they searched for online and how this coincided with significant climate change events in recent history.

4.1.4. Quality assurance and data clearing

The BEIS Public Attitudes Tracker and ECO datasets are designated Official and National Statistics dataset respectively, which means they have undergone quality assurance and data clearing before publication. For this reason, these datasets were analysed without further data clearing and quality assurance.

The EPC register is based on assessor observations, and often quick visits to a dwelling. All excel raw data for each local authority were downloaded from the EPC register

(https://epc.opendatacommunities.org/). The files were then converted into two Excel data models combining all rdSAP EPCs (~19.1 million records). Analysis was undertaken using Origin Pro statistical software. Microsoft Power BI was used to visualise the results.

As the database is subject to human error, missing data and variability between individual assessments (Jenkins, Simpson and Peacock, 2017) a four step process for clearing[D2] the raw EPC datasets was adopted.

Step 1: Clearing duplications. All files within the raw data were arranged by postcode, following which by exact address. Where multiple EPCs were found for the same property, only the latest chronological version of the EPC were retained.

Steps 2-4: Assessing u-value records. Where u-values were inputted, unrealistic values with a value below 0.05 W/m²K, were removed from the model. This was undertaken as some Passivhaus dwellings have achieved calculated u-values of 0.067 W/m²K for roofs (Palmer and Clarke, 2014) and achieving a 0.05 W/m^{2}K or lower is theoretically possible, however unlikely. This step was applied for roofs (Step 2), walls (Step 3) and floors (Step 4) in consequential steps.

The final figure of EPCs within the database were 15,714,547 records. Figure 16 outlines the distribution of the UK building stock as per the domestic EPC database on the basis of the cleared dataset.

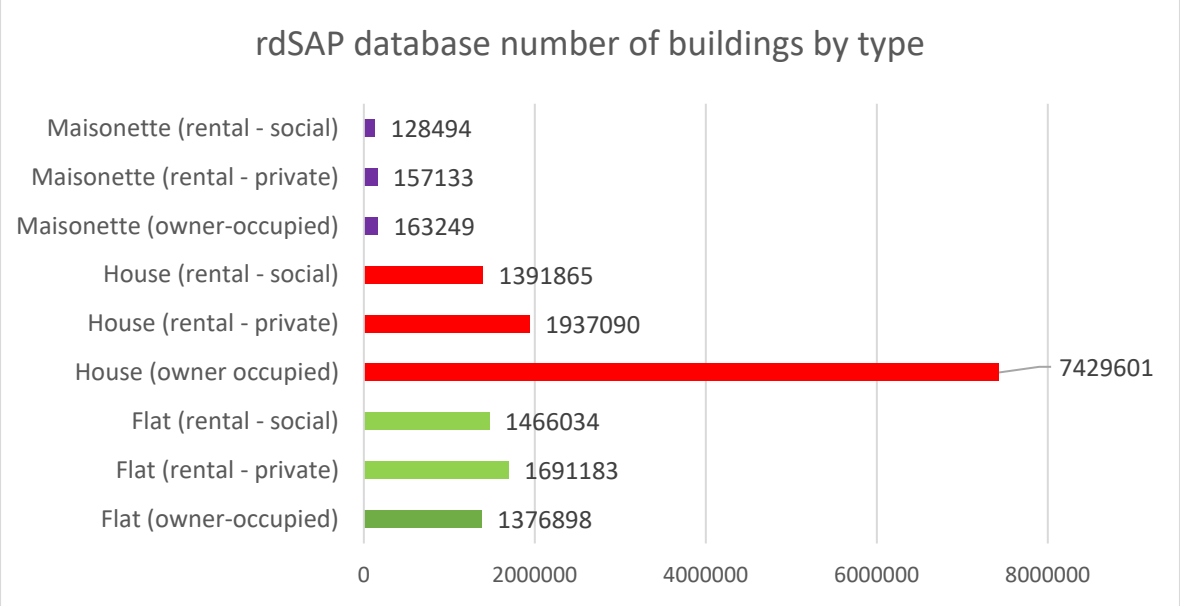


Figure 16. Distribution of UK housing stock according to the rdSAP database

As Figure 16 outlines, the majority of the properties in the UK are owner-occupied houses, followed by rented houses and flats.

4.2. Results

4.2.1. Deployment potential

4.2.1.1. Number of UK homes with uninsulated suspended timber floors

The UK built environment accounts for 66% of the UK electricity consumption and whilst the national grid has decarbonised at a significant rate, greenhouse gas emissions (GHG) from buildings are estimated to have decreased by only 1% between 2009-2016 (Committee on Climate Change, 2018).

Socially rented dwellings have a higher mean EPC rating (69) whereas owner-occupied dwellings have the lowest EPC rating on average (64) with more than 60% of them rated EPC band D and below (MHCLG, 2020). The energy performance (EPC) rating is a proxy for how energy efficient the dwelling is. This is an important factor for energy efficiency retrofit as a study has shown that owner-occupied dwellings are more likely to be retrofitted and in addition tenants would prefer under-floor insulation (Phillips, 2012).

According to the EPC database, there are 4,855,175 dwellings with suspended timber floors with no insulation. This represents 25.4% of the rdSAP building stock and is therefore a significant proportion of existing dwellings that could be retrofitted. Data from 2013 showed that the potential for retrofitting suspended timber floors in the UK is 4,896,737 dwellings (Element Energy, 2013). However the Elementa estimate is derived from English Housing Survey Data, which uses a different methodology for estimating dwellings with uninsulated timber floors. According to the English Housing Survey, in 2019 the distribution of privately owned, privately rented and social rented properties were 19%,20% and 51% respectively. However according to the EPC database from the same period the distribution was 24%,19%, and 57% respectively. This discrepancy between the overall figures is driven by the methodological differences between how the statistical samples are derived (Department for Business Energy & Industrial Strategy, 2020a). However even if taken as estimates, the findings from both datasets suggest >90% of dwellings with suspended timber floors are not insulated.

Additionally, there are projections that even new-built dwellings have to be retrofitted in the future with more insulation, or more energy efficient systems, in order to achieve the full decarbonisation of the building stock (Committee on Climate Change, 2019). To understand the potential for suspended timber floor insulation of current new-built dwellings, an analysis of the full SAP database is undertaken. Figure 17 plots the U-values of 534,820 records from the EPC database for new-built dwellings built between 2010-2017.

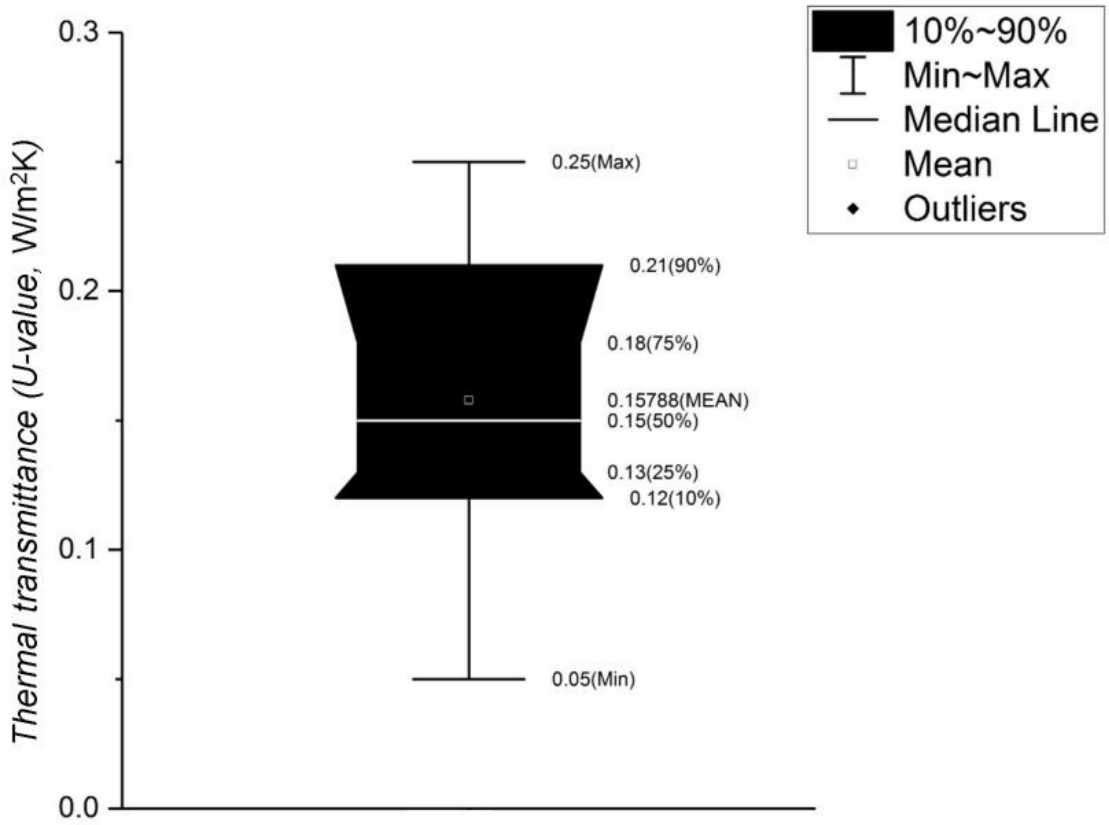


Figure 17.Thermal transmittance (U-value, W/m^{2}K*) distribution of floors in dwellings built between 2010-2017. Data from full SAP EPC register (n=534,820)*

Figure 17 outlines that both the median and mean values for newly built homes are within, or near, the limiting values for Passivhaus buildings (0.15 W/m^{2}K). From those dwellings, only a proportion would have suspended timber floors. Spray foam insulation is not often used in domestic new-builds in the UK, therefore the existing insulation may have to be removed prior to installation. These factors outline that there is limited market penetration, and potential, for homes built from 2010 onwards to be retrofitted with spray foam insulation.

4.2.1.2. Characteristics of UK building stock with uninsulated timber floors

To understand the characteristics of dwellings with uninsulated timber floors, Table 4 plots the total number of dwellings and proportions that have other retrofit measures.

Table 4. Dwellings with no insulation in the suspended timber and proportion that has other retrofit measures according to the rdSAP database

	Number	**%**
Total dwellings with uninsulated suspended timber floor	4,855,175	100
Double glazing (full or partial)	4,423,738	91.1
Some roof insulation	3,880,261	79.9

Some external wall insulation	3,644,636	75.1
No external wall insulation	1,210,539	24.9
No roof insulation	974,914	20.1
Single glazing (full)	299,210	6.2
Triple glazing (full or partial)	3,973	0.1

Table 4 data demonstrates that the majority of the dwellings with no insulation in the suspended timber floors have had some other retrofit improvements: notably double or triple glazing (91.2%), some roof insulation (79.9%) and some external wall insulation (75.1%).

This data supports the hypothesis that ‘deep’ or ‘whole-house’ retrofit has not been undertaken for millions of dwellings where the floors have been left uninsulated despite other retrofit measures being applied. However with the introduction of the PAS 2035:2019, it is expected that a ‘whole-house’ approach will be implemented in the future. Out of the 4.8 million dwellings, onlya tiny proportion of existing properties have not had any retrofit undertaken (<2%).

It is reasonable to assume that this also covers 'heritage' properties, such as Grade II listed buildings, for which retrofit may not be suitable or appropriate (Sustainable Traditional Buildings Alliance, 2015).

From a building physics perspective, the highest energy saving potential would be for buildings that have no other retrofit measures as those dwellings would be associated with the highest whole house heat loss coefficient (HTC) (Alzetto *et al.*, 2018). A modelling study suggests that for non-insulated detached Victorian dwellings, an insulated floor would only account for 11% decrease in the heating demand, compared to 69% for the external walls, if the whole dwelling was retrofitted (Ji, Lee and Swan, 2019). However sensitivity modelling and experimental data demonstrate that there is significant variability between different dwellings and an energy performance gap exists between modelled and measured data (Marshall *et al.*, 2017).

Research on suspended timber floors has demonstrated that models could significantly underestimate or overestimate the thermal conductivity of existing and retrofitted floors depending on where the measurement is taken from (Pelsmakers, Croxford and Elwell, 2019). In-situ measurements have shown a heat loss reduction of 65-92% through the floor could be achieved by fully filling the floor void with EPS beads and adding 100mm woodfibre insulation between the joists (Pelsmakers *et al.*, 2017). Additionally, in-situ measurement of total building heat loss pre and post-retrofit of a 1-bed bungalow in the UK demonstrated that a suspended timber floor could decrease the total building heat loss by 24% (Glew *et al.*, 2020). The case study building was retrofitted with 60mm insulation in the external walls, 200mm mineral wool in the roof and it was double glazed and still managed to achieve an additional 24% reduction via insulating the floor (Glew *et al.*, 2020).

In 2013, analysis commissioned by the Committee on Climate Change outlined that up to 1 $MtCO_2$ annual savings could be achieved by upgrading suspended timber floors (Element Energy, 2013). In comparative purposes, retrofitting all suspended timber floors in the UK could equate to the same carbon savings per annum as: the carbon dioxide emissions of the whole country of Barbados (The World Bank, 2020), or 2.3 million barrels of oil, or a 0.75 GW gas-fired power plant that could be closed down. The savings are equivalent to ~40% of the annual carbon emissions of the whole NHS building stock, which is ~2.5 $MtCO_2$ (NHS, 2022).

In summary, the analysis demonstrates that there are over 4,500,000 existing dwellings with uninsulated timber floors in the UK where heat loss savings of up to 24% total building heat loss could be achieved if they are retrofitted.

In the UK, and across the world, market-based instruments are still one of the primary ways of increasing energy efficiency of the existing building stock (Rosenow, Cowart and Thomas, 2019).

4.2.2. Current deployment level

4.2.2.1. Retrofit policies and installations split by type

The UK Government published an ambitious net-zero strategy outlining policies for decarbonisation pathways to net zero by 2050, including illustrative scenarios that include a range of energy efficiency policy proposals (Department for Business Energy & Industrial Strategy, 2021e). Historically, in the UK, one of the leading market incentive tools for encouraging building owners to retrofit their existing buildings are the Green Deal and the Energy Company Obligation (ECO) mechanisms. Both of those schemes aim to reduce carbon emissions and tackle fuel poverty. A history of the ECO scheme, details of how the policy evolved over time (ECO1, ECO2, ECO2t, ECO3) and its impact have been previously published (Hough, 207AD; BEIS, 2018, 2021a).

The ECO scheme focuses on fuel poverty and therefore is applicable for only a proportion of the building stock, which is estimated to be around 6.5 million dwellings (Department for Business Energy & Industrial Strategy, 2018). The current definition of a 'fuel poverty household' is if the owners are living in a property with a fuel poverty energy efficient rating of 'D' **and** when they spend the required amount to heat their home, they are left with a residual income below the official poverty line (Department for Business Energy & Industrial Strategy, 2021c). To outline the retrofit progress aimed at tackling fuel poverty, Figure 18 outlines the ECO measures installed by measure type distributed on a longitudinal basis during the period 2013-2020.

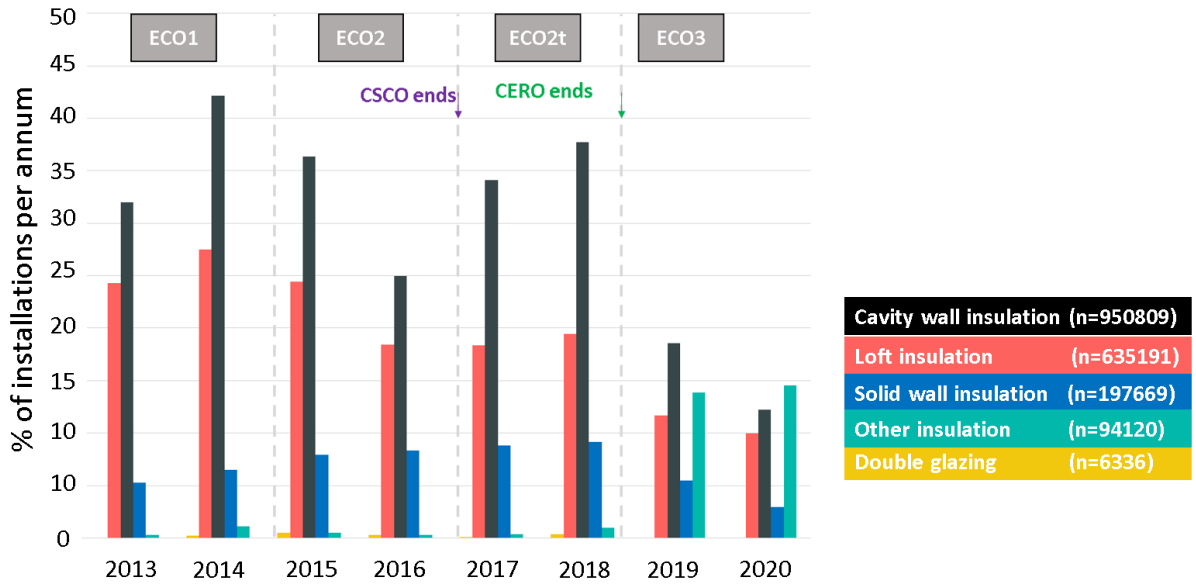


Figure 18. ECO measures installed by measure type between 2013-2020 in terms of proportion of installations per annum

Figure 18 outlines that "other" insulation measures, including suspender timber floor retrofit, were applied on a much lower relative rate in terms of proportions (~2% per annum) between the periods 2013-2018. The data demonstrates that until 2019, only a

small proportion of dwellings had their suspended timber floors retrofitted as part of the ECO scheme. Two limitation should however be noted with this dataset:

- The dataset does not include private installations without the use of ECO funding, however it is estimated that these account for a much smaller proportion of retrofits (Department for Business Energy & Industrial Strategy, 2021d).
- 'Other' measures includes all floor insulations, therefore suspended timber floor would only account for a proportion of these statistics.

Traditional methods for suspended timber floor insulation are considered intrusive and difficult as they require the removal of floorboards. The application of robots and spray foam insulation has made it possible to apply this retrofit measure with minimal disruption to the owners or occupiers where only an access hatch or a few floor boards would need to be removed for the robot to apply the insulation (Department for Business Energy & Industrial Strategy, 2020b). The application process requires a minimum void of 200mm where access via an access hatch, or by removing a few floorboards is possible. After an examination of the floor void's height, moisture level, layout, piping and condition of the floorboards, the installers can make an assessment on whether the property is suitable for installation via a robot as not all properties that have a suspended timber floor may be suitable. However as outlined previously, the ECO dataset only covers dwellings within the 'fuel poverty' category, which is linked to EPC ratings.

In the private rented sector (PRS), one of the other UK policy measures that aims to reduce fuel poverty is the Minimum Energy Efficiency Standard (MEES) (Department for Business Energy & Industrial Strategy, 2020a). MEES mandates that private rented properties must have a minimum EPC rating of 'E'. An impact assessment of MEES outlines that 73,845 instances were located where a private rented property with increased its EPC rating from a score of F or G (Department for Business Energy & Industrial Strategy, 2021b). The impact assessment highlights that it is not possible to establish a direct causal link between the regulation and retrofitting rates therefore it is not possible to undertake a breakdown of the distribution of retrofitting measures adopted because of MEES. Privately-rented sector carries a large proportion of fuel poor households (26.8%) and privately-rented properties carry an annual bill of ~£6 billion in energy bills per year (Department for Business Energy & Industrial Strategy, 2021b).

In order to understand the typology of buildings that MEES regulations might not cover, an assessment utilising SAP was undertaken of archetypal dwelling types (Mata, Sasic Kalagasidis and Johnsson, 2014). The characteristics for a flat and a house were applied on the basis of the UK building stock (Mata, Sasic Kalagasidis and Johnsson, 2014) followed by a search of representative sample EPCs from the Energy Performance of Buildings Data with no insulation, single glazing and an EPC rating of E or higher. Table 5 outlines that 'gaming' of EPCs to pass MEES requirements (currently EPC rating of 'E') is theoretically possible for flats and houses despite having poor thermal fabric and low-medium proportion of energy efficient lighting.

Table 5. Example EPCs based on archetypal dwellings that pass MEES standards

Property type	Mid-floor flat	Mid-floor flat	Mid-floor flat	Semi-detached house
Walls	Solid, no insulation	Solid, no insulation	Solid, no insulation	Solid, no insulation
Roof	-	-	-	Pitch, 100mm loft insulation
Floor	-	-	-	Solid, no insulation
Windows	Single glazed	Single glazed	Single glazed	Single glazed
Heating	Communal scheme	Boiler and radiators	Boiler and radiators	Boiler and radiators
Hot water	From main	From main	From main	From main
Lighting	50% low energy	29% low energy	25% low energy	30% low energy
Date issued	2017	2009	2017	2011
Floor area	45m^2	37m^2	65m^2	87m^2
Area	London	South East	South West	London
EPC rating	**C (75)**	**C (78)**	**D (58)**	**E (49)**
Median EPC rating for all UK dwellings of this type	**C (70)** **Existing flats** (Office for National Statistics, 2020)			**D (63)** **Existing houses**

MEES is considered to be an appropriate policy in order to attenuate fuel poverty within the private rented sector, however further improvements regarding the EPC methodology and assessor scrutiny are recommended (Organ, 2020). The Government has outlined ambitions to raise the MEES requirements to a 'C' EPC rating with a deadline of 2030, however in 2022 this has not been implemented into legislation.

In summary, current deployment levels of underfloor insulation are rising and market penetration of this retrofit measures has increased significantly in the last 3 years. There are a number of policy incentives that encourage adoption of retrofit measures and with the introduction of PAS 2035:2019, it is expected that adoption of underfloor insulation will continue to rise.

As building occupiers play a large role in the real term energy consumption of the UK building stock, it is important to understand their behaviours in relation to the drivers that underpin decisions to retrofit and operating buildings efficiently. In order to understand the penetration of suspended timber floor insulation for the wider market and triangulate the

EPC data, an analysis is undertaken on the BEIS Public Attitudes Tracker (PAT) historical data.

4.2.2.2. Distribution of what retrofit measures are installed

The BEIS PAT is a quarterly survey, which collects data on public awareness, behaviours and attitudes relating to the department's policy areas. It is sent to households and the aim is to have a consistent and reliable sample representative of the UK population, however sample size of the survey is typically 2000-4000 respondents. The answers are collected with a mixture of field collection and online responses, however with this type of sample, "the accuracy of estimates is conditional on the assumption that the combined effects of sampling, fieldwork protocols, quota application, and weighting have successfully eradicated biasing selection effects on the data" as outlined by BEIS (Department for Business Energy & Industrial Strategy, 2021a).

Nevertheless, the survey provides longitudinal results of a large sample size, which provides key insights on energy efficiency measures adaptation. This data supplements the EPC and ECO data well as it cuts across both datasets by capturing both fuel poverty dwellings and the rest of the building stock. Figure 19 below plots longitudinal data of energy efficiency measures adopted by household distributed by annum.

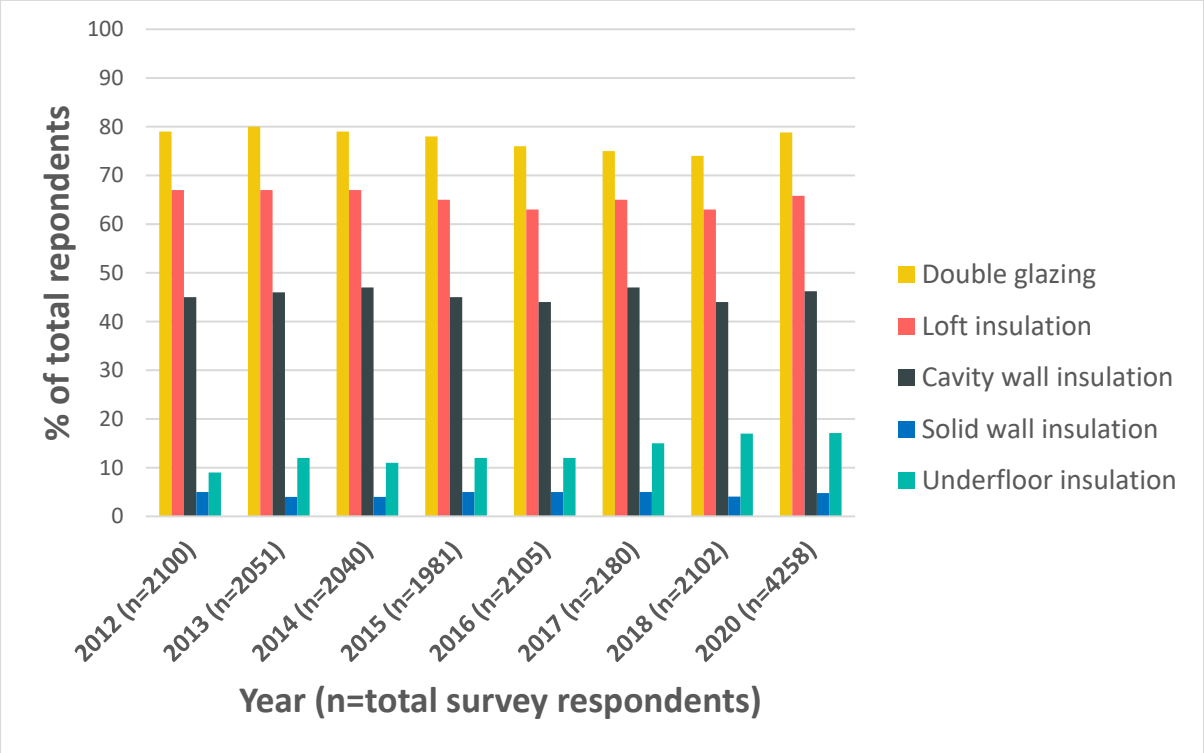


Figure 19. Distribution of energy efficiency retrofit measures already adopted by people as reported in the BEIS PAT

Figure 19 demonstrates that double glazing, loft insulation and cavity wall insulation are the most widely adopted measures across the general population (45-78%). Solid wall insulations and underfloor insulations are measures which are not adopted widely with only 5-17% of consumers reporting that they have undertaken these retrofit measures. The survey takes into account if the measure cannot be physically installed (e.g. cannot install loft insulation with a property with no loft, such as a flat). Figure 21 outlines that underfloor insulation had a consistent response rate of 9-12% between 2012-2016 with a gradual increase to 15-17% in 2017-2020. In addition, the sample size for 2020 was response was double that of previous years.

This analysis signifies that underfloor insulation is increasing its market penetration amongst all types of dwellings and across a representative range of consumers. Figure 23 previously outlined that floor insulation as part of the ECO scheme increased in the same period (2018-2020), which correlates well with this consumer data. As the PAT dataset covers dwellings outside the ECO scheme, both of these findings outline that there is a gradual increase in installation of suspended timber floor retrofits across both the social housing and private property building stock. In order to understand whether the increase in adoptions is a temporary phenomenon within this period, the future intentions of people to adopt this measure are plotted in Figure 20.

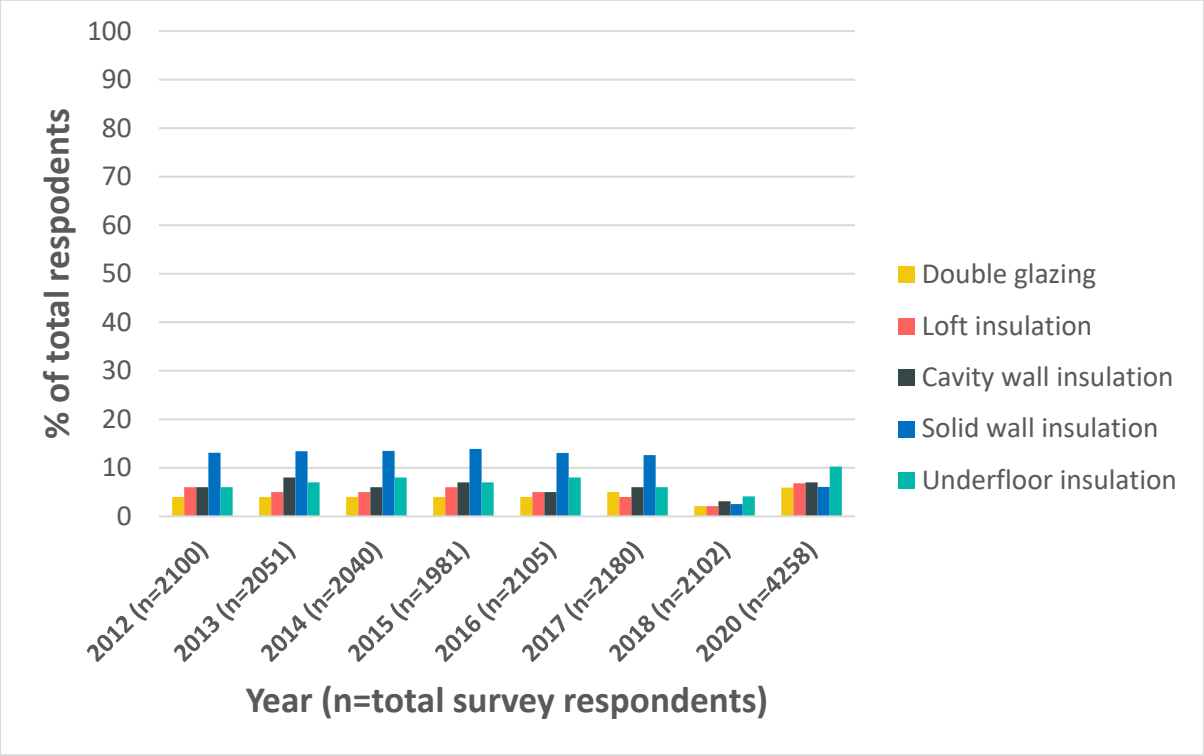


Figure 20. Distribution of peoples intention to adopt an energy efficiency retrofit measure as reported in the BEIS PAT.

Figure 20 demonstrates the intention of people to adopt various energy efficiency retrofit measures. Solid wall insulation and underfloor insulation are the measures, where people report to have the highest intent of adopting (6-14%) compared to double glazing, loft insulation and cavity wall insulation (2-8%). This finding makes logical sense and suggest

that people are most likely to adopt measures, which they have not yet. However a study has shown that homeowners may prioritise heritage and aesthetic values, especially if no incentives are available to support, or encourage, retrofit measures (Sunikka-Blank and Galvin, 2016). Studies show that policy incentives are often the driver for adopting retrofit measures (Trotta, 2018; Bobrova, Papachristos and Cooper, 2022).

The proportion of people responding to the survey intending to install underfloor insulation ranges between 6-8% during the period 2012-2017 with no statistically significant difference between different years. Whilst the absolute difference during that period may not be statistically significant, there is a statistically significant increase in the intent of people to install underfloor insulation between 2018 and 2020 (4 to 10% respectively). The BEIS PAT methodology stipulates that a statistically significant increase is based on a 95% confidence interval. In addition, the 2020 dataset has a sample size that is twice as large as previous years.

The intent of people to install underfloor insulation in their homes (Figure 20) correlates well with ECO data showing actual number of underfloor retrofits occurring in practice (Figure 18). Whilst ECO incentivises home owners in fuel poverty to retrofit their properties, there are other policy measures that also target properties which may not be covered by ECO. The traditional driver for insulating properties has been the reduction of energy for heating (Tovar, 2012). However global warming has meant that insulation for keeping cooler indoor temperatures during summer also have an important role for reducing impact on people and overheating (Taylor, Symonds, *et al.*, 2018).

4.2.3. Seasonal distribution of retrofit installations

The UK mean temperature in 2020 was 9.6°C, which is 0.8°C higher than the long-term average measured between 1981-2010 (Kendon *et al.*, 2021). Monthly mean temperatures varied between 4.3-7.7°C during the heating season (November-March) and 7.7-15.9°C during the non-heating season (Kendon *et al.*, 2021). An analysis of historic UK weather data demonstrated that heating degree days (HDDs) have decreased by 14.3% since pre-industrial levels, whilst cooling degree days (CDDs) increased by 144% as per Table 6.

Table 6. Average heating degree days and cooling degree days in the United Kingdom between 1961-2020 (Kendon *et al.*, 2021)

	Average HDDs				Average CDDs			
	1961-1990	1981-2010	2011-2020	2020	1961-1990	1981-2010	2011-2020	2020
UK	2739	2572	2419	2345	9	13	16	22
% difference to previous period	baseline	-6%	-6%	-3%	baseline	+44%	+23%	+38%

Ambient conditions are one of the variables that that may impact both the energy efficiency of buildings (CIBSE, 2020) and the choice of whether people decide to retrofit their homes (Tjørring and Gausset, 2019). According to a modelling study, whole-house retrofit could reduce regional domestic space heating energy use by 26% but could also increase summertime heat mortality 3–4% if overheating measures are not put in place (Taylor, Symonds, *et al.*, 2018). A temporal analysis of total installation under the ECO scheme between 2013-2018 demonstrates that there is a large amount of variability of retrofit installations per quarter as per Figure 21.

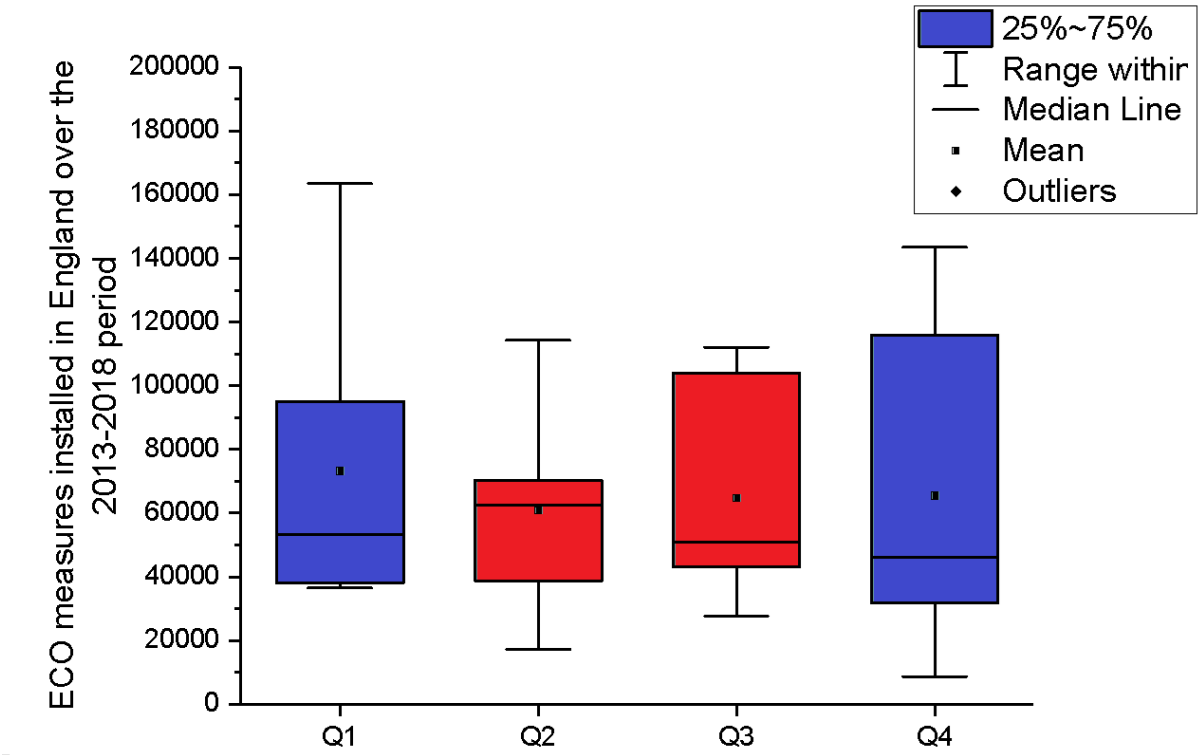


Figure 21. Temporal distribution of total installations under the Energy Company Obligations scheme between 2013-2018 split by quarter. Q1 (January-March), Q2 (April-June), Q3 (July-September), Q4 (October-December). Blue bars denote heating season and red bars denote non-heating season.

Figure 21 outlines that dwellings are most often retrofitted in the heating seasons, with particularly January-March having the highest mean. It is also evident from the data that a lower amount of installations generally occurred during the period between the heating and cooling season (April-June).

Figure 22 illustrates the number of retrofit installations tend to be higher during the heating season compared to the non-heating season.

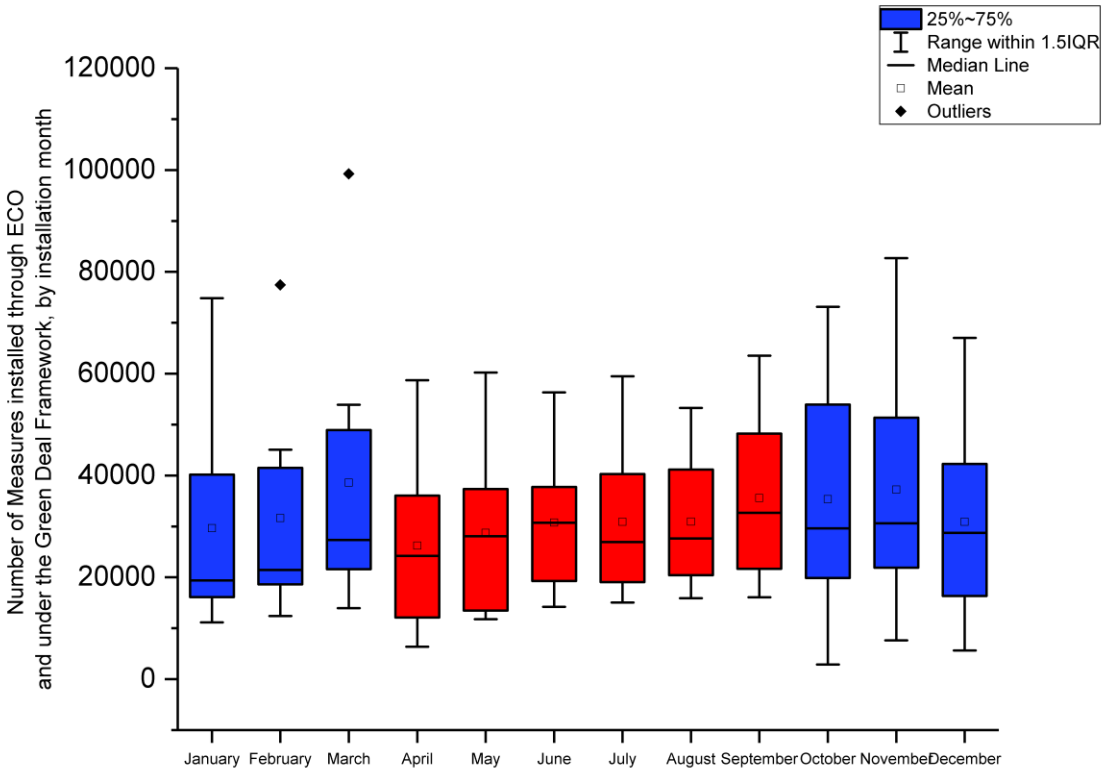


Figure 22. Number of measures installation through ECO and Green Deal Framework distributed by month during the 2013-2020 period. Blue bars represent heating season and red bars represent non-heating season.

The ambient environmental conditions could impact the long-term performance of spray foam insulation materials both during (Knowles, 2010; ASTM International, 2017c) and post-installation (Abdou and Budaiwi, 2013; Berardi and Naldi, 2017). For this reason, further analysis is undertaken focusing specifically on retrofitted floors under the ECO scheme in order to provide greater insight when the majority of installations occur. From a theoretical perspective, a logical hypothesis would be that as low-energy housing in the UK focus on financial savings (Rosenow and Eyre, 2016), most retrofits would occur in Q3 and Q4 in order to reduce winter bills. Figure 23 plots the distribution of floor insulation installations under the ECO scheme distributed by quarter.

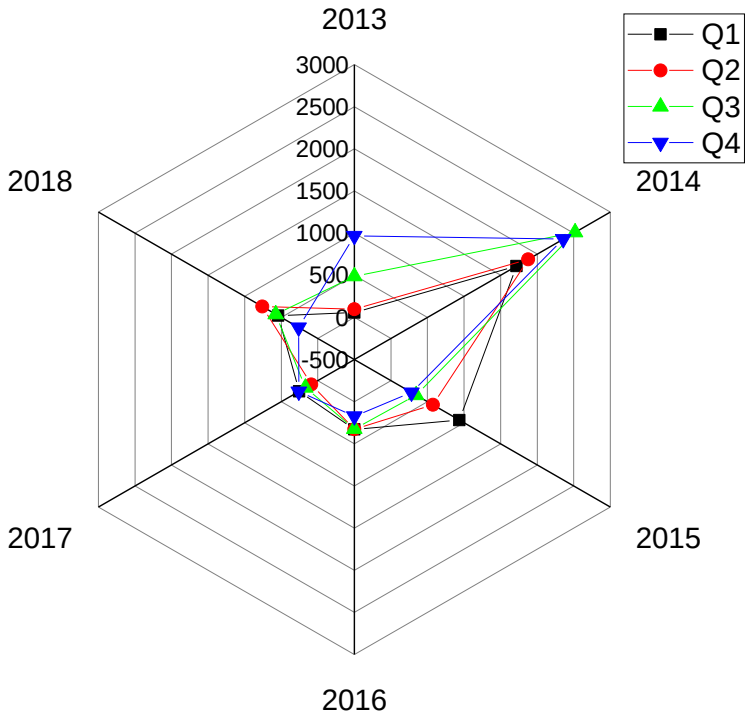


Figure 23. Distribution of floor insulation installations under the Energy Company Obligations scheme between 2013-2018 split by quarter

There is no clear pattern for installations during the heating or cooling season for underfloor insulation. This could be explained in practice by the intrusive nature of the retrofit measure and people may therefore opt to undertake it in the non-heating seasons as well. Ambient conditions have an implication on the curing process for polyurethane products and may impact their physicochemical properties (Dimier *et al.*, 2004). One of the primary reasons for the low levels of traditional suspended timber floor insulation (mineral wool, XPS, EPS) is that its installation is considered disruptive and inconvenient (Institute for Sustainability, 2011), which acts as a disincentive for energy efficiency improvements (Karvonen, 2013). As conventional methods cause disruption to the owners, or tenants, it is understandable that there are no peak installation periods and that it has not been implemented as a retrofit measure for the majority of buildings in the UK with suspended timber floors.

In summary, the survey data from the Public Attitudes Tracker correlated well with ECO data and EPC data. The analysis demonstrated that the market penetration, recent deployment levels and consumers interest in suspended timber floor insulation have significantly increased in the last 3 years.

Whilst climate change has had a large impact on retrofit policies, its direct impact on consumer adoption of energy efficiency measures is less clear. Only a proportion of retrofits are undertaken using government funding, therefore it is important to know not only when people insulate their homes, but why they do it as well.

4.2.4. Barriers and incentives

4.2.4.1. Why retrofit measures are installed

As global warming is likely to further increase cooling demands and decrease heating demands, it is important to consider whether climate change concerns play a big role on whether people want to insulate their homes in the first place. As decision-making on whether to retrofit in the first place and what materials to use are an important factor on the potential for suspended timber floor retrofit, consumer attitudes are further examined.

Figure 24 outlines public behaviours towards climate change and searches for ''climate change'' on Google during the period 2012-2019. Historic data from the BEIS Public Attitudes Tracker was extracted from (Q21 - How concerned, if at all, are you about current climate change, sometimes referred to as 'global warming'?) and the results are plotted as lines (BEIS, 2021b). The circles denote statistically significant changes between survey waves. The Google Trend Index for ''climate change'' searches during the period 2012-2019 is represented as grey columns and major events associated with climate change are also plotted.

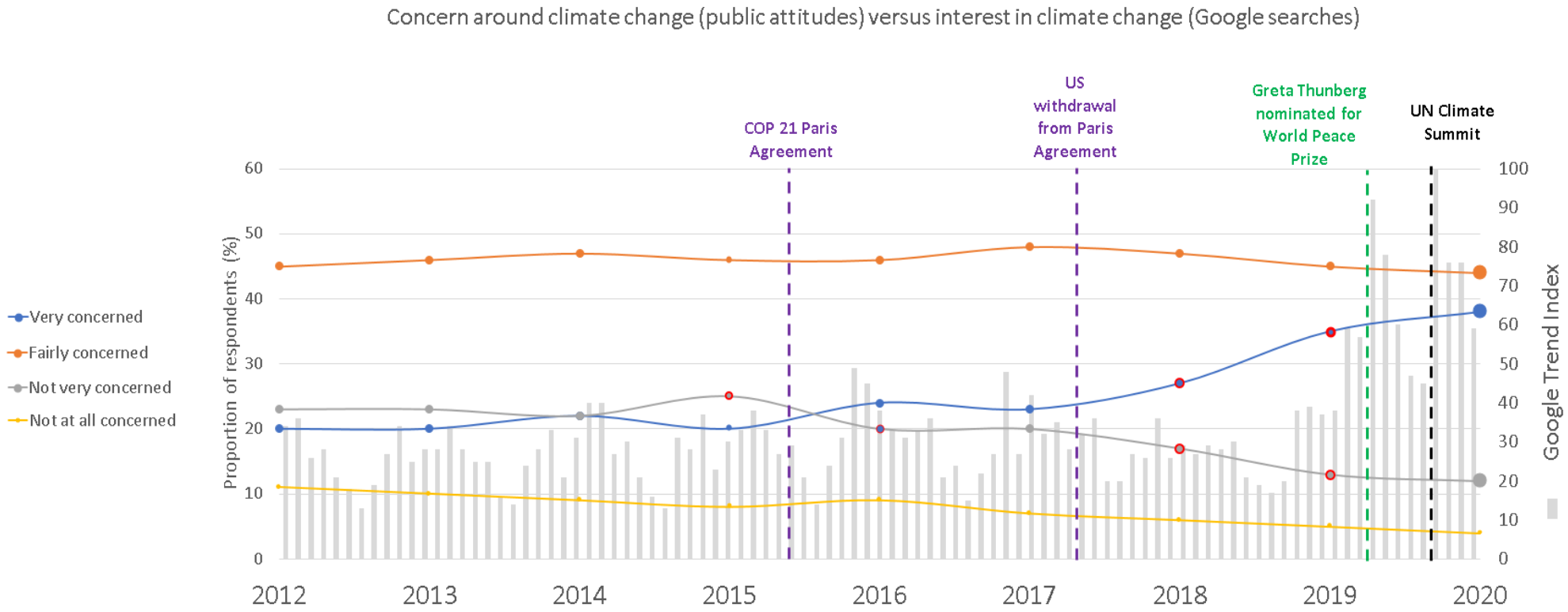


Figure 24. Level of concern of the general population towards climate change (lines) and Google Trend UK data for 'climate change' (columns). Survey data extracted from BEIS Public Attitudes Tracker. Circles highlighted in red denominate statistically significant change between survey waves on a 95% confidence interval. Size of circle markers denote survey sample size.

Figure 24 demonstrates that overall, the ''not at all concerned'' and 'fairly concerned'' populations have remained largely stable over time with little statistically significant difference between survey waves. It is however clear that since 2015, a pattern has emerged where the 'very concerned' proportion has grown over time with statistically significant rates. The comparison with Google Trend data as per Figure 31 demonstrates that overall levels of interest in climate change have been cyclical, and seasonal, between 2012-2018. An increase in searches is observed in the latter parts of 2018, followed by a continued period of increased interest- which could be associated with climate change activist movements (Extinction Rebellion) and global media interest. Nearly thirty years ago, in 1993, Kempton argued that even though environmental concern amongst consumers is high, this does not necessarily translate to action on global warming, and in particular energy efficiency (Kempton, 1993). This hypothesis is explored using more recent evidence.

4.2.4.2. Retrofit installation drivers

Socio-economic behavioural research demonstrates that energy efficiency retrofit investments are linked with age, income, dwelling type (Trotta, 2018; Liu, Teng and Han, 2020), lifestyle (Bobrova, Papachristos and Cooper, 2022) heritage values (Fouseki and Cassar, 2014; Sunikka-Blank and Galvin, 2016; Yarrow, 2016; Roberts and Henwood, 2019) however environmental conscientiousness, or attitudes towards climate change, are not a good predictor for likelihood of retrofit adoption (Maller, Horne and Dalton, 2012). This is due to the fact that whilst climate change may play a role in the initial decision of whether to adopt a retrofit measure, there are often trade-offs between pro-environmental variables and high-cost investments (Trotta, 2018). This is supported by the fact that adoption of energy efficient technologies varies strongly by income quartile and lowest income quartiles exhibit lower adoption propensity for all technologies (Schleich, 2019; Schleich, Faure and Meissner, 2021).

This suggests that whilst Figure 24 demonstrates concern about climate change in the general population has grown, it is not a good predictor of whether energy efficiency measures, such as insulation installation, may be adopted in practice. Whilst environmental concerns are not an appropriate factor, energy prices could have a bigger impact as they are directly associated with energy efficiency and cost of heating (Bottero, D'Alpaos and Dell'Anna, 2019). Therefore people's concern around energy prices is assessed as a separate factor.

Figure 25 below plots longitudinal data of actual energy prices (ONS index data) compared to people's concern about increasing energy prices (BEIS public attitudes tracker data) and people searching for "energy price" on Google (Google Trend data).

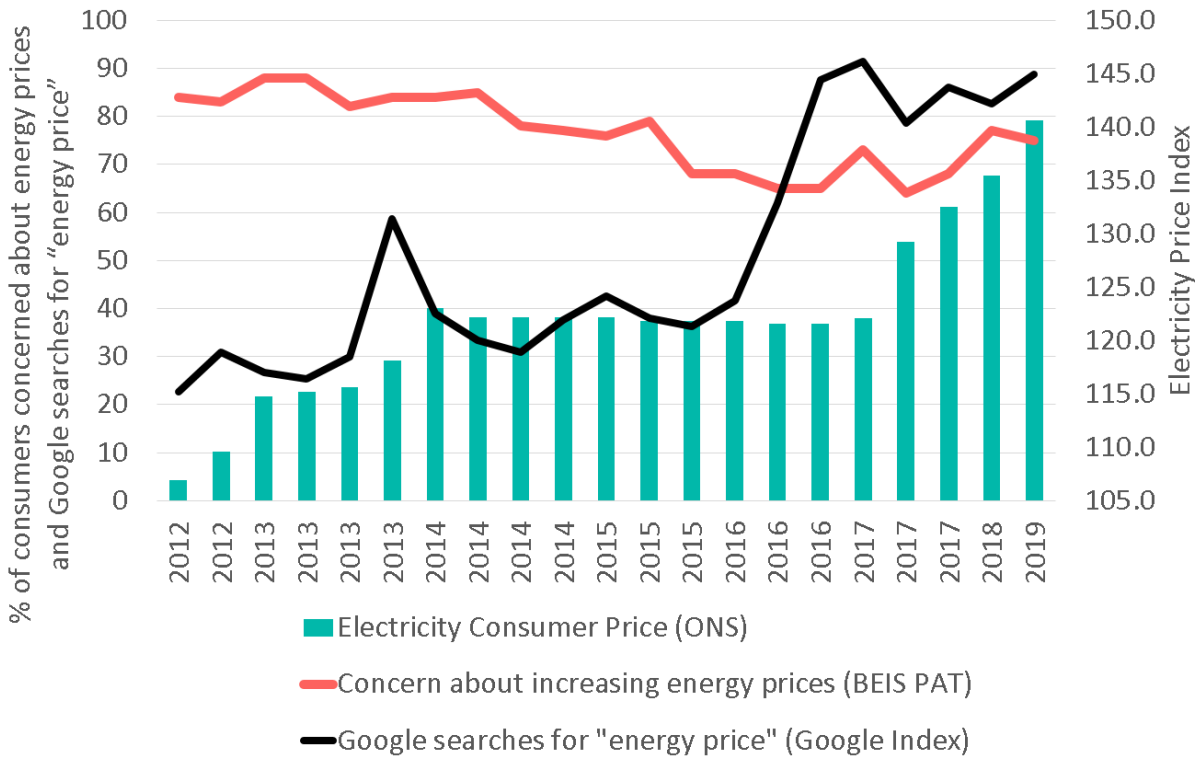


Figure 25. Comparison between electricity and gas prices for consumers versus people's concern about increasing energy prices and Google searches for "energy price"

Figure 25 outlines that there is a good observable correlation between how often people searched for ''energy price'' on Google and price increases on the market (ONS gas and electricity consumer price indices). However there is not a strong observable pattern linking people's concern around energy prices (BEIS PAT) and the actual searches on Google for energy prices. It could be inferred from the data that people were generally more concerned about energy prices following the Financial crisis in 2008, which slowly declined as the economy recovered (Office for National Statistics, 2018). Post 2013, the only observable correlation with people's concern around energy prices is between 2017-2018 when electricity prices increase by 16% in the course of a year. During the 2013-2017 period, over 1 million homes were retrofitted under the ECO scheme as per Figure 18.

Despite the lack of observable correlation between people's concerns around climate change, energy prices and deployment of energy efficiency measures, these factors could have an impact on the long-term adoption of underfloor insulation.

The Committee on Climate Change have outlined that without whole-house retrofit of the existing building stock, the UK would not be able to meet its climate objectives (Committee on Climate Change, 2019). Whilst climate change concerns may explain less well retrofit adoption, it is reasonably foreseeable that the energy price increase will increase demand for retrofit especially as analysis has suggested ~50% of energy currently used in UK housing could be saved (Rosenow *et al.*, 2018).

4.2.5. Evidence synthesis

The findings from the three themes are triangulated in a synthesis matrix presented in Table 7. These capture the key findings from the analysis of each individual dataset in order to triangulate the qualitative and quantitative data.

Table 7. Evidence synthesis matrix

Theme	Analysed parameter	Critical finding in addressing R.Q.1.
Deployment potential	Number of UK homes with uninsulated suspended timber floor insulation	According to EPC and English Housing Survey estimates analysis, >90% of the suspended timber floors in the UK are uninsulated. If retrofitted, equivalent carbon dioxide savings are close to half of the NHS building stock annual emissions.
	Characteristics of UK uninsulated timber floor stock	The majority of the dwellings with uninsulated timber floors have had one or more other retrofit measures installed (roof, windows, wall upgrade) with only <2% of the stock uninsulated.
Current deployment level	Installations by type	ECO data showed underfloor insulation accounted for less than 1% of installations when Government funding for retrofit was used between 2013-2018. There has been a gradual increase of installations since 2019.
	Retrofit policies and incentives	There are a number of policy measures that incentivise retrofits, however no specific for underfloor installations. Introduction of PAS2035 likely to encourage whole-house retrofit.
Retrofit attitudes	Seasonal distribution of installations	No observable pattern was observed suggesting underfloor installations are equally distributed through the year. This finding suggests economic savings may not be primary reason for installation, as this should have resulted in more installations before and during heating season.
	Why are measures installed	No observable relationship was observed between climate change concerns and underfloor insulation deployment levels. However a statistically significant rise in underfloor insulation and interest in this measure were observed based on BEIS PAT survey data. This finding correlates well with increase of installations from ECO data.
	Retrofit installation drivers	There is no observable causal relationship between energy price increases and underfloor insulation deployment. Literature suggests inconvenience, cost and heritage impact also play an important role on decision whether to retrofit suspended timber floors.

4.3. Summary

The collective evidence from this chapter suggests there is a significant potential for reducing energy bills and decreasing carbon emissions through the retrofit of millions of buildings with uninsulated timber floors. The overwhelming majority of dwellings have not had their floors retrofitted and in-situ data showed that floor thermal conductivity could be reduced by 65-92%, whereas total heat load of the dwelling could be reduced of up to 24%.

Social research data has demonstrated that there is growing market penetration of floor installations in addition to rising intent from people to adopt this retrofit measures. Existing barriers to uptake in the literature often relate to inconvenience, cost, heritage and aesthetic impact due to traditional floor retrofit measures requiring removal of floor boards. Spray foam installed via robots offer an alternative solution and emerging evidence suggests that it removes these barriers to market.

It is however unclear from the data whether climate change concerns and energy prices are expected to significantly increase market penetration and historic evidence suggests policy incentives are likely to remain important drivers for adoption of this measure.

The annual decarbonisation potential for retrofitting all UK suspended timber floors could be broadly equivalent to the total carbon emissions of the country of Barbados. This outlines the significant potential for this measure to be adopted in the UK and therefore the important question of the impact of these products on indoor environmental quality remains pertinent and valid.

In order to address this research gap, a robust quantitative method must be established that could allow measuring concentrations of the emissions associated with spray foam insulation throughout its lifecycle.

5. Method development

This chapter provides evidence in relation to R.Q.2. “Can volatile organic compound (VOC) emissions emitted from polyurethane products be measured using analytical chemistry methods developed for plastics and museum collection objects?”.

This chapter outlines the original method development work undertaken for the purposes of this thesis. It is split into three parts: Method A, Method B and comparison of Method B versus ASTM D8142-17.

Method A focuses on measuring isocyanates and their amine derivatives, which basically targets Side A emissions of spray foam. Method A sub-chapters demonstrates how I adapted a novel lab-based method for measuring raw isocyanate liquids and tested its performance for measuring spray foam isocyanate emissions. This also provided evidence of isocyanate emissions from modern insulation materials, as most spray foam data developed prior to this thesis, was undertaken >15 years ago.

Method B focuses on showcasing the steps I undertook to develop a precise, reliable and repeatable method for measuring VOCs from B-side of foams and also by-products. Prior to starting this thesis, I developed a proof-of-concept method for these VOCs by using knowledge from measuring emissions from polyurethane museum collections (Naldzhiev, Mumovic and Strlič, 2017). The proof-of-concept method was however not sufficiently precise and sensitive to accurately measure spray foam emissions in-situ. Method B sub-chapters outlines the original method development I undertook to make the method fit for purpose in order to accurately measure VOCs emitted from spray foams throughout their lifecycle. Method B was utilised for conducting all experimental work presented in Chapters 6-9.

During the later stages of the thesis, a method for measuring emissions from cured spray foam products was also published by ASTM International and I was part of the committee (ASTM International, 2020). The last sub-chapter therefore outlines a comparison between Method B versus ASTM D8142-17.

The evidence presented in this chapter allows both built environment and heritage practitioners to select which method would be most appropriate for their work depending on what compounds they want to measure.

5.1. Method A Context

5.1.1. Isocyanate exposure limits and health impact

Isocyanates (side A) are one of the primary chemical groups used for manufacturing polyurethane foams with Methylene Diphenyl Isocyanate (MDI) and polymeric-MDIs being primarily used for making construction products.

At low concentrations of 0.1-1ppm, isocyanates act as irritants to the mucous membrane and concentrations above 1ppm may have toxic effects (Woolrich, 1982). The National Institute for Occupational Safety and Health (NIOSH) therefore recommends an exposure value of 0.005ppm (0.05mg/m3) time weighted average (TWA) (Schlecht and Cassinelli, 1998) and HSE have set a value of 0.02 ppm for 8-hr TWA and 0.07ppm for a short-term exposure limit of 15 min (Health and Safety Executive, 2020). The most common health effects associated with isocyanate exposure include skin, eye and respiratory system irritation with prolonged exposure also able to lead to the development of asthma (IARC, 1999). The choice of analytical method is critical to accurately determine the total isocyanate presence in indoor air.

5.1.2. Methods for measuring isocyanate

The exposure rates of MDI from spray foam have been predominantly measured using high performance liquid chromatography (HPLC) coupled with ultraviolet and fluorescence detection (UV/FLU), ultraviolet and electrochemical detection system (UV/EC) or double mass spectrometry (MS/MS) (Crespo and Galán, 1999a; Bello *et al.*, 2004; Lesage *et al.*, 2007a; Kupczewska-Dobecka, Czerczak and Brzéznicki, 2012).

A method for testing MDI exposure limits has been developed by using a “CIP10M” air sample (Puscasu et al., 2015). The CIP10M is a commercially available personal aerosol sampler that has been validated for the collection of microbial spores into a liquid medium, which collects and stabilizes MDI aerosols (Puscasu et al., 2015). A different type of sampler developed for MDI detection (ASSET EZ4-NCO) has also been previously tested (Puscasu et al., 2014), however it was found to significantly underestimate MDI oligomers. It is important to consider not just MDI monomers, but oligomers as well, considering the UK workplace short-term exposure limit (STEL) is defined by the total amounts of airborne isocyanates, due to their toxicity. Table 8 outlines some of the studies and methods deployed for advancing knowledge in relation to, predominantly workplace, isocyanate exposure.

Table 8. Studies and methodologies for the determination of isocyanates measurements relevant to polyurethane and/or spray foam products

Study/Method	*OSHA 2012*	*Crespo and Galan 1999*	*Roberge et al. 2009*		*ISO 17734-1:2013*	*NIOSH 5525*
Purpose	Defining limiting exposure values that will not have adverse health impact	To obtain MDI exposure during indoor and outdoor SPF application	To obtain MDI exposure during indoor and outdoor SPF application and 30,60 and 120 post installation		General guidance for the sampling and analysis of airborne isocyanates in workplace air	
Number of objects/sites	Undisclosed	17 building sites. 1 office building, 2 sets of terraced houses, 14 flats. Indoor and outdoor measurement.	1 building site. Indoor and outdoor sampling.		N/A	N/A
Sampling media	Coated Glass Fiber Filter (37 mm open face) Coated with 1.0 mg 1-(2-	Impinger using a 2x10-4M solution of 1-(2-methoxyphenil) piperazine in	Impinger system containing a MOPIP solution	37 mm membrane impregnated with 9-(N-ethylaminomethyl) anthracene	Impinger followed by a 13mm glass fibre filter utilising a DBA solution	Impinger or impinger +filter or impregnated filter

	Pyridyl) piperazine	toluene as absorbent				
Analytical method	HPLC-UV/FLU	HPLC-UV/EC	HPLC-UV/FLU	HPLC and MS/MS	HPLC-MS or HPLC-CLND	HPLC-UV/FLU[SM3]
Flow rate	1 l/min					1-2 l/min
Method reference	OSHA Analytical Method	MTMA/MA-035/95	25/3 Organic Isocyanates in Air of the (HSE)	IRSST High Sensitivity	ISO 17334-1:2013	NIOSH 5525
Individual sample measurement (mg/m^3)	0.002[1]	0.001-0.57	-	-	0.000001 (detection limit) for 5l sample	0.0014-0.840 (useful detection limits for 15-l sample)
Mean average exposure (mg/m^3)	0.005-0.02[2]	0.004-0.057	0.01-0.15	0.13-0.29	n/a	n/a
Mean average exposure after 120 min (mg/m^3)	-	-	-	0.003-0.005	n/a	n/a

[1] OSHA Permissible Exposure Limit (PEL) - General Industry
[2] National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL)

The European Chemical Agency evaluated limit values for isocyanates the workplaces in 2019 (ECHA, 2019) and outlined that:

- It does not recommend a specific occupational exposure limit (OEL) and instead recommended that the most appropriate way to prevent asthma caused by diisocyanates would be to prevent its induction at source, and therefore prevent respiratory sensitisation altogether
- Instead of a specific OEL, it recommended that exposure-response is to be developed. Some workers may have, or develop, (di)isocyanate sensitisation during their working career and those with pre-existing asthma or other respiratory problems may have an increased risk to develop respiratory symptoms caused by diisocyanate-induced irritation

There are many international standards for measuring isocyanates such as: ISO 17734-1:2013, ISO 17735:2019, ISO 17736:2010, ISO 16702: 2007, MDHS 25/3, MDHS 25/4, NIOSH 5521 (1994), NIOSH 5522 (1998) and NIOSH 5525 (2003).

5.1.3. Isocyanate emissions from spray foam

Evidence has suggested that during conventional spray foam application airborne isocyanate concentration near the spraying surface could be up to 13 times higher than recommended exposure limits (Crespo and Galán, 1999b; Roberge, Gravel and Drolet, 2009; Bello *et al.*, 2017, 2019; ECHA, 2019). Whilst spray foam installations have increased significantly over the last 25 years, as Chapter 2 outlined, few scientific studies have repeated isocyanate exposure experiments.

As outlined in Chapter 2, material science has evolved particularly for the B-side of spray foam products due to legislation limiting ozone depletion potential of chemicals (UN, 2016). Simultaneously, the air-permeability of buildings has significantly decreased in the last decade due to buildings being retrofitted and is continued to decrease further in order to reach the UK decarbonisation targets (Sinnott and Dyer, 2012; Gillott *et al.*, 2016) The Crespo and Galan (1999) study for example was conducted more than 17 years ago. If the same study is carried out now, the exposure concentrations could in theory be higher due to reduced building ventilation rates. Almost all existing studies only include a single SPF product, contractor team and building site apart from the studies by Bello et al (Bello *et al.*, 2017, 2019; Mellette *et al.*, 2018) in the US, who have conducted multiple field studies exploring exposure assessments in relation spray foam.

In 2014, a novel analytical chemistry method (Ferreira *et al.*, 2014) was developed that could be used to measure both isocyanates and their derivative amines simultaneously in a laboratory using raw liquids. The Ferreira (2014) method offered excellent recovery rates in a laboratory, however had not been tested in the field to understand its applicability for measuring isocyanate concentrations during spray foam application. Whilst 4,4-MDI has been measured in several research experiments during spray foam installation, no previous studies were found measuring 4,4- Methylenedianiline (4,4-MDA) in the academic literature. 4,4-MDA is considered to be the reaction product of 4,4-MDI and water (Neuland *et al.*, 2021) and is also on the REACH list of substances of very high concern due to its toxicity.

Whilst 4,4-MDI has potential to convert to 4,4-MDA when hydrolysed (mixed with water), it is unclear whether during standard atmospheric conditions and a high relative humidity (>70%), this process could occur in practice during spray foam application.

5.1.4. Objective

It was previously hypothesised that once spray foam is cured, airborne isocyanate concentration would be minimal (Kim and Yu, 2014). Given polyurethane chemistry formulation has changed significantly in the last 20 years (Heath, 2017), a small isocyanate experiment was setup to test this finding for the purposes of the thesis. An experiment was developed with two specific objectives:

- Validate the Ferreira methodology and test whether it could be used for measuring spray foam Side A emissions
- Experimentally test what are the isocyanate (4,4-MDI) and amine (4,4-MDA) airborne concentrations during spraying of modern spray foam materials

5.1.5. Experimental setup

The target compounds for detection are outlined in Table 9.

Table 9. Target compounds for detection during application and curing of spray foam using Ferreira (2014) methodology

Isocyanate				
	Compound	Short name	Sigma no.	CAS no.
1	1-Naphthyl isocyanate	ISNI	170518	86-84-0
2	Toluene 2,4-diisocyanate	24TDI	33427	584-84-9
3	Toluene 2,6-diisocyanate	26TDI	33493	91-08-7
4	4,4'-Methylene Diphenyl Diisocyanate	44MDI	33428	101-68-8
Amine				
1	2,4-Diaminotoluene	24TDA	442311	95-80-7
2	2,6-Diaminotoluene	26TDA	148113	823-40-5
3	4,4'-Methylenedianiline	44MDA	31640	101-77-9

The following equipment was utilised for the experimental setup:

- 70l polypropylene box
- Low SKC Deluxe Pump (Part Number: 224-PCMTX8) calibrated to extract at 1L/min in line with previous studies
- Two component isocyanate-based commercial polyurethane foam purchased from the open market
- HOBO MX1101 temperature and humidity data logger
- 25 ml glass impinger

Two holes were drilled on two adjacent sides of the box: one for TD-GC-MS testing and the other for LC-MS/MS analysis. A third hole was drilled on top of the box so that the insulation could be sprayed inside in the closed boxes as per Figure 26.

Before the spraying started, a 30min blank sample of each was tested to ensure that no isocyanate was present prior to the experiment starting. A HOBO was placed inside the box and outside the immediate vicinity to measure the conditions during spraying and curing. The glass impinger was connected to a trap, which was connected to a pump. The pump extraction rate was 1L/min.

Figure 26. Experimental setup for isocyanate detection with the empty box (left) and the application of spray foam (right)

5.1.6. Sampling procedure

Following the Ferreira (2014) method, for each sample run a new bottle of acetonitrile was purchased. The stock sampling solution was created through mixing 19.72 mg 1-naphthyl isocyanate 98%, 40 mL of Nbenzylmethylamine injected in 1000 mL of dry acetonitrile. Once sampling finished, the solution was topped up with anhydrous acetonitrile. The bottle was opened in the fume hood and the rest of the chemicals were added within 2 minutes. The acetonitrile was open and 19.72mg of 1-napthyl isocyanate was measured on a scale. 10ml of acetonitrile was added to the flask of isocyanate and it was all then put into the 1L bottle of acetonitrile. 40mL of amine was then added to the 1L bottle of acetonitrile. The bottle was then closed. During testing the bottle was only opened during injecting reactive solution in the impinge. For each sampling run using the impinger, 20mL of the stock solution was used.

All measurements were undertaken outside in a well ventilated area. The experiment was undertaken three times

- Experiment 1: Box remained open throughout the duration of the experiment.
- Experiments 2 & 3: Box was closed during both spraying and curing

This setup was selected in order to understand the difference between applying spray foam in an environment with good ventilation (open box) and an environment with poor ventilation (closed box). In theory, the open box could be considered conceptually representative of external environments, such as external flat roofs (American Chemistry

Council, 2018). The closed box could be conceptually considered representative of a suspended timber floor application in an existing dwelling with limited ventilation. It was important to consider both conditions as research has shown that air infiltration from underfloor areas/crawlspaces makes a significant contribution to the whole house air infiltration rate and contaminated soil gases may be transported into the living space (McGrath and McManus, 1996).

5.1.7. Closed box sampling protocol

There were several samples taken for isocyanates. For the isocyanate, the glass impinger was connected to a trap, which was connected to a pump. The pump extraction rate was 1L/min. Once each sample was finished, the liquid was measured and then topped up with fresh acetonitrile up to 20mL. After that 2 x 2ml aliquots were taken for HPLC sampling from each sampling run. This ensured that we have duplicate samples for each testing point. The rest of the solution was thrown away and the empty impinger was rinsed with 10-15ml of acetonitrile between each run to clean any potential residue. The 'cleaning' acetonitrile was then thrown away. After that the clean impinger was again filled up with 20ml of reactive solution for the next run. This protocol was used for both closed box experiments as per Table 10.

Table 10. Protocol for sampling 4,4-MDI and 4,4-MDA emissions from spray foam insulation in a closed box experiment

	Sampling Time	Actual sampling rate	Date	Impinger sample	Liquid left before top up (mL)
1. Blank air sample (30min) box closed	16:45-17:15	1 L/min	08.06.18	Yes	17
2. 5 min air sample	17:25-17:30	1 L/min	08.06.18	Yes	19.5-20
3. 10 min air sample	17:37-17:47	1 L/min	08.06.18	Yes	19.5-20
4. 15 min air sample	17:53-18:08	1 L/min	08.06.18	Yes	19.5-20
5. 30 min air sample	18:28-19:00	1 L/min	08.06.18	Yes	17
6. Blank air sample (15min) outside of box	19:05-19:20	1 L/min	08.06.18	Yes	15

5.1.8. Open box sampling protocol

There were several samples taken for isocyanates. For the isocyanate, the glass impinger was connected to a trap, which was connected to a pump. The same procedure was used for the open box protocol as for the closed box protocol with detailed timings set out below in Table 11.

Table 11. Protocol for sampling 4,4-MDI and 4,4-MDA emissions from spray foam insulation in an open box expriment

	Time	Sampling rate	Date	Impinger sample	Liquid left
7. Blank air sample (15min) box open	19:40-19:55	1 L/min	08.06.18	Yes	16.5
8. 5 min air sample	20:08-20:13	1 L/min	08.06.18	Yes	19
9. 11 min air sample	20:18-20:29	1 L/min	08.06.18	Yes	18
10. 17 min air sample	20:33-20:51	1 L/min	08.06.18	Yes	17
11. 30 min air sample	21:01-21:31	1 L/min	08.06.18	Yes	15
12. Blank air sample (16min) outside of box	21:36-22:02	1 L/min	08.06.18	Yes	16.5

For each sample, 4ml out of the 20ml vials was then extracted and injected in two sets of 2 ml plastic vials. The plastic vials were shipped to the University of Ljubljana and analysed within a period of 72-128 h for each sample. Analysis was undertaken using a 3200 QTRAP LC-MS/MS system. The analytical sampling system and samples are shown in Figure 27.

Figure 27. LC-MS/MS analytical sampling kit for measuring monomeric isocyanate and Methylenedianiline emitted from spray foam products

5.1.9. Environmental conditions

During the experiment, the temperature and relative humidity were recorded. The position of the HOBO inside the box could be seen in Figure 30. The outside HOBO was placed 3 metres away from the spraying area in a shaded environment. All the experiments were conducted in a location where there was no direct sunlight. Figure 28 plots the environmental conditions recorded.

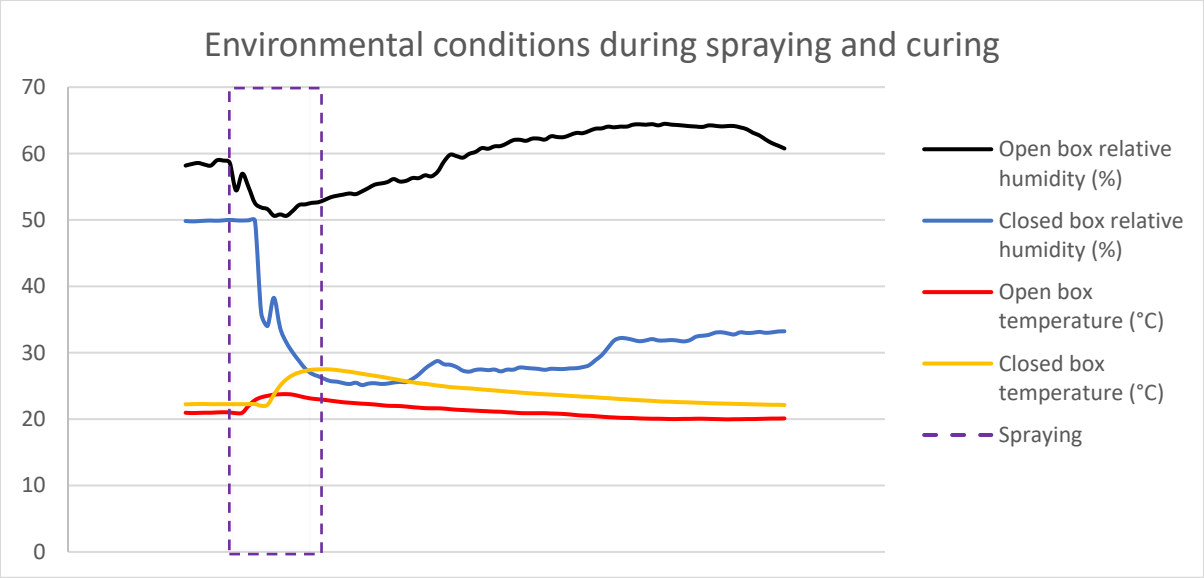


Figure 28. Environmental conditions (T,RH) during spraying and curing of two-component spray foam.

The environmental condition reveal how the spray foam reacts with the external environment. Both during the open box and closed box experiments, the temperature increased slightly during spraying: by ~5°C when the box was closed and by ~3°C when the box was open. However the relative humidity reduced drastically when the box was closed (50% to 25%) compared to when the box was open (59% to 51%) when it quickly equilibrated to outdoor levels. This demonstrates the exothermic chemical reaction that occurs when spray foam is applied – the raw chemical compounds react with each other and the external environment simultaneously.

5.2. Method A Results

5.2.1. Isocyanates

The 4,4-MDI concentrations for all three experiments are plotted in Figure 29 and compared with HSE workplace exposure limits.

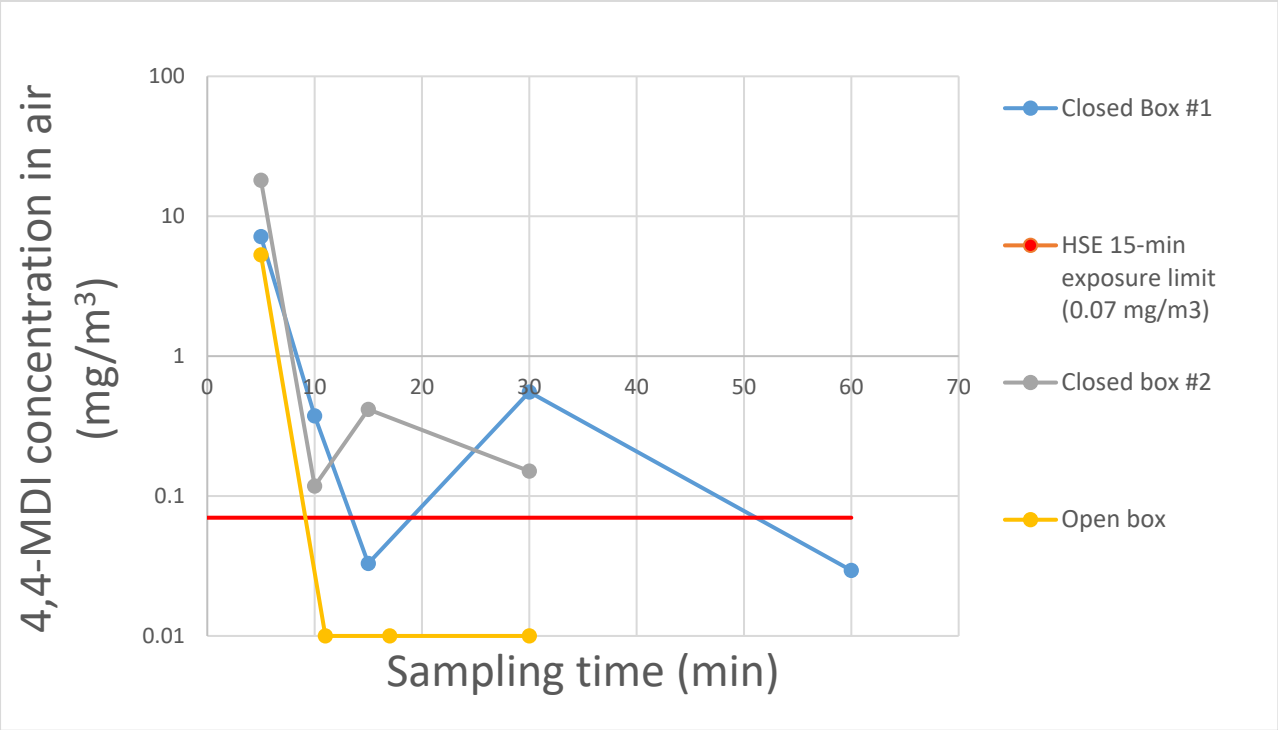


Figure 29. 4,4-MDI concentration recorded during spraying and curing of two-component spray foam in an open and closed box experiment.

Albeit the samples were taken continuously (5,10,15,30 and 60 min), Figure 29 only plots data where the detected amount in the air exceeded both the limit of detection (LOD) and limit of quantification (LOQ).

The data in Figure 29 clearly demonstrates a pattern where the peak emissions occur during spraying with a slight peak observable during curing for the first 30 min. The airborne isocyanate emissions decreased below the exposure thresholds after 30 min. The data highlights that when there is ventilation provided (open box), the airborne isocyanate concentration reduces much quicker after spraying occurs.

The data is consistent with the existing literature, outlined in Chapter 2, that isocyanate is very reactive and does not remain in monomeric form for a long period of time. This data supports the hypothesis that in well-ventilated areas the risk of exposure to airborne isocyanate is lower compared to poorly ventilated areas, such as crawlspaces/underfloor voids with blocked or no airbricks (Pelsmakers *et al.*, 2019). The measured monomeric isocyanate concentrations are similar to previously published field study results where the mean average exposure levels varied between 0.004-0.29 mg/m^3 (Crespo and Galán, 1999a; Roberge, Gravel and Drolet, 2009) as plotted in Figure 30.

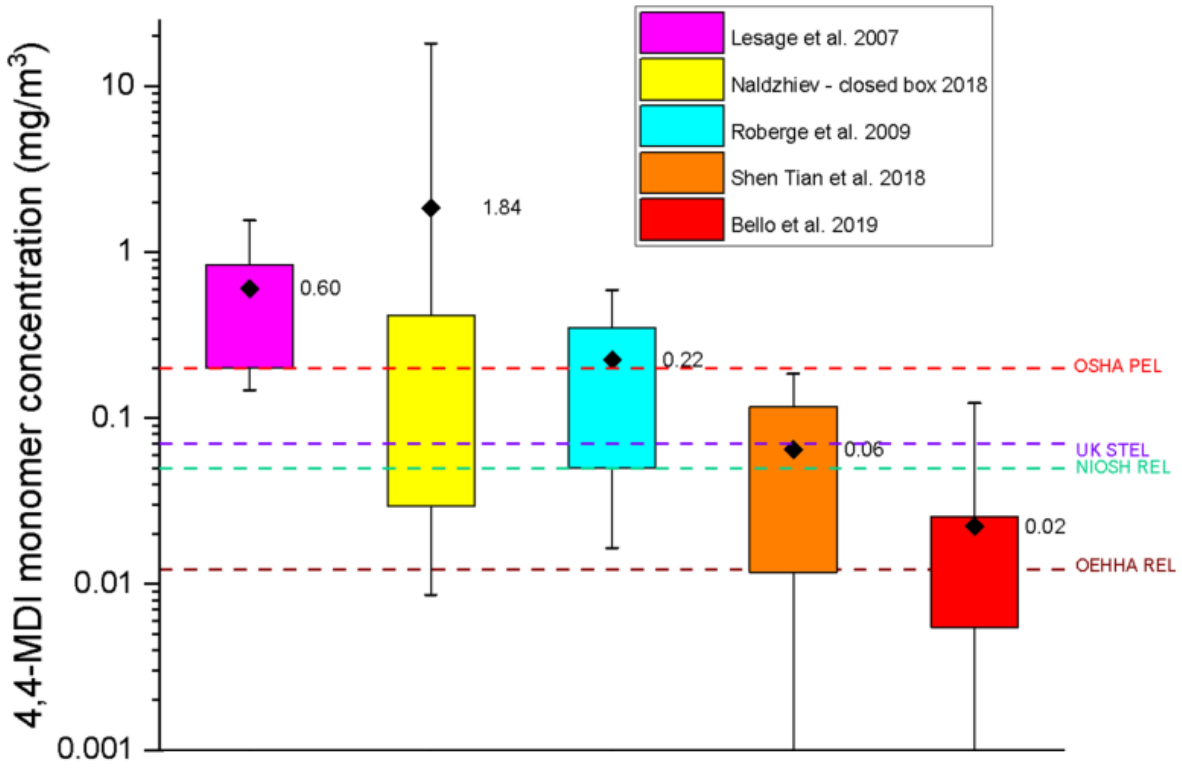


Figure 30. Measured exposure to MDI (mg/m^3) near a sprayer during installation of two-component polyurethane spray foams. Box plots show interquartile ranges. Mean concentrations are shown and whiskers outline min-max values. Crespo and Galan (1999) mean could not be calculated due to lack of a full data set. Dotted lines represent permissible, short-term and recommended exposure limits of different institutions and/ or countries. Scale is logarithmic.

As Figure 30 outlines, apart from the initial observable peak during both the spraying events (7.15mg/m^3 and 18.06 mg/m^3 respectively), the other results are comparable to what has been found in the literature. It should be noted that other studies recorded concentrations over prolonged periods of spraying whole roofs or buildings, whereas for this experiment the spraying area was really small (0.25m^2).

Bello et al (2019) found that sprayers and helpers were exposed to up to 123mg/m^3 and 42.2mg/m^3 respectively as the maximum 4,4-MDI concentration during spraying (Bello *et al.*, 2019). The collective data, as per Figure 32, outlines that without necessary protective equipment and when applying spray foam manually, it is possible for people to be exposed

to isocyanate concentrations exceeding both recommended and legal workplace limits - particularly if applied in areas with poor ventilation.

The small scale results, as per Figure 34, demonstrate ventilation could theoretically reduce airborne exposure, however it has limited impact on concentrations near the spraying zone (within 15-30cm of the spraying nozzle) during spraying. Albeit this experiment was limited in scope and breadth, this finding further reinforces the importance of utilising personal protective equipment and benefits of supplementing with robotic application when applying isocyanate based spray foam product due to their potential health impact as outlined in Chapter 2.

5.2.2. Amines

No 4,4-MDA was detected in any of the samples. This finding supports the theory that in normal atmospheric conditions and during spray foam application, it is not expected that 4,4-MDI will undergo hydrolysis and convert into 4,4-MDA when reacting with moisture from the ambient air. Using a similar analytical method, 4,4-MDA emissions were measured from heritage collections containing polyurethane products and no 4,4-MDA was found after 'accelerated aerobic tests' supporting the findings of this study (Tillotson *et al.*, 2019).

5.3. Method A Summary

The three experiments outlined that the method developed by Ferreira (2014) could be successfully applied for measuring airborne isocyanate emissions from spray foam materials. However its variability and performance compared to other analytical methodologies (Lesage *et al.*, 2007a; Bello *et al.*, 2019) and the ISO 17736:2010 has not been examined or validated within this thesis.

The experimental results from the box experiments reaffirmed existing literature findings that isocyanate emissions are a significant risk factor for workers if improper health and safety procedures are not put in place during spraying foam insulation.

5.4. Reasons for not using Method A in other experimental work as part of this thesis

Analysis via web of science searching for "isocyanate" in combination with "exposure" as keywords returns 856 scientific publications in different fields. Searching for "spray foam" and "exposure" returns 9, when excluding the papers published as a result of this thesis.

Based on experimental results within this chapter, and scientific literature within the domain of isocyanate exposure, airborne isocyanate monomers or polymers are not expected to be emitted from spray foam insulation in the long-term during normal operating conditions. For this reason, further examination of isocyanate exposure during application of spray foam was considered to have limited scientific value. This method was therefore not used in any of the other experiments as part of this thesis.

On the other hand, little scientific knowledge exists within the domain of B-side emissions and by-products found in indoor environments during and post-application of polyurethane spray foam. Chapter 3 outlined that VOCs could theoretically be released into indoor

environments throughout the lifecycle of the insulation. In order to accurately quantify emissions, a highly sensitive and precise analytical chemistry method had to be developed in order to address R.Q.2, R.Q.3 and R.Q.4. Chapter 5.5 outlines the method development (Method B) that was crucial for the delivery of the thesis as it was utilised for all the subsequent experimental work.

During the lifecycle of this thesis, a method for quantifying B-side and by-product emissions from spray foams was published (ASTM International, 2020), however that was specifically for micro-chambers sampling of cured polyurethane products. For this reason, Chapter 5.7 compares the performance of Method B against the ASTM methodology.

5.5. Method B Context

5.5.1. Prior work

A proof-of-concept for a novel method for measuring Side B (polyol, catalysts, flame retardants, additives) and by-product VOCs from spray foam was developed for an MRes thesis awarded in 2017.

The published dissertation demonstrated the potential for qualitatively detecting volatile organic compounds from the B side of spray foam products utilising SPME and TD-GC-MS. This meant that VOCs could be detected in indoor air, however could not be accurately quantified with sufficient precision and sensitivity. Whilst the MRes provided promising proof-of-concept results, the calibration curves for calculating airborne concentration of VOCs were not of sufficient scientific quality for undertaking reproducible and repeatable experiments. Further method development was required in order for high-quality reproducible and repeatable chromatography results to be obtained. In simple words, further original method development was required so that VOCs could be measured in both controlled conditions and field studies.

5.5.2. Objective

The objective of the method development was two-fold:

- Develop a high-precision analytical methodology which could be used for quantitative analysis of spray foam emissions using TD-GC-MS
- Assess which chemical compounds could be assessed quantitatively using SPME-GC-MS

The secondary objective was undertaken for several reasons. First, SPME-GC-MS is a an analytical technique applied in a variety of fields and matrices such as air, water, soil and sediment samples in on-site and off-site analysis and recently established itself as a tool utilised by heritage scientists (Ou and Whang, 2006; Prosen *et al.*, 2007; Merkle, Kleeberg and Fritsche, 2015; Curran *et al.*, 2016; Ceballos *et al.*, 2017; La Nasa *et al.*, 2019; Sekar, Varghese and Ravi Varma, 2019). Second, built environment researchers have not used SPME-GC-MS extensively therefore if interdisciplinary collaborations are formed, if proven successful this methodology may offer a route for quick, reliable and precise quantitative assessment of volatile organic compounds in indoor environments. Thirdly, SPME is a simple, sensitive,

rapid, solvent-free and relatively low cost sampling technique for the extraction of analytes from different samples therefore offers an alternative option for laboratories with no thermal desorption capability (Merkle, Kleeberg and Fritsche, 2015).

Multiple parameters were changed on the TD-GC-MS analytical setup until calibration curves with a high analytical precision ($R^2 \geq 0.98$) were developed. The equipment used is presented below.

5.5.3. Experimental setup

5.5.3.1. Equipment used

The lab equipment that was used is as follows:

- SKC Deluxe 224-PCMTX8 Universal Air Sampling Pump
- Aalborg Mass Flow Controller GFC 17 (range of 0-1000 mL/min)
- Perkin Elmer TurboMatrix 650
- Automated Thermal Desorber (ATD) connected to Perkin Elmer 500 Gas Chromatograph (GC) and Perkin Elmer Clarus 560D Mass Chromatograph (MS)
- 60m x 0.25mm x 1.5 µm VOCOL fused silica capillary column

For the purposes of method development, three types of tubes were used to test which was best suited to measure spray foam emissions:

- Carbopack B (analyte volatility range is n-C5 to n-C12)
- Tenax TA tubes
- Spray foam specific tubes as per ASTM D8142 (ASTM International, 2020)

5.5.3.2. Chemical compounds used

The chemical compounds selected for this study was collated via evidence in the published literature and proof-of-concept work by Naldzhiev (2017) outlined in the previous chapter. Table 12 outlines all the chemical compounds that were purchased for method development.

Table 12. Exhaustive list of chemical compounds of interest selected for the purposes of method development

Chemical compound	CAS Number	Ref/part number and distributor
1,2 dichloropropane	78-87-5	Ref. number - 02577 1ml pure. Sigma Aldrich
1,4 dioxane	123-91-1	Ref. number 76887- 5 ml. Sigma Aldrich
Chloro-benzene	108-90-7	Ref. number 08650 – Pure 5 ml. Sigma Aldrich
Dibutyltin dilaurate	77-58-7	Ref. number 291234 Pure 5g. Sigma Aldrich
Triethyl phosphate	78-40-0	Ref. number 538728 – 100 ml. Sigma Aldrich

1,1,1,3,3-pentafluorobutane	406-58-6	
N,N,N',N' – Tetramethyl-2,2'-oxybis(ethylamine)	3033-62-3	Ref. number 667609 Pure 100 ml. Sigma Aldrich
N,N-bis(3-(dimethylamino)propyl)-N',N'-dimethyl	33329-35-0	Ref. number: APOH6F3D0484-250MG. Sigma Aldrich
TCPP	13674-84-5	Ref. number: 32952-100MG. Merck Life Sciences
TDCPP	13674-87-8	Ref. number: sc-229356. Insight Biotechnology Ltd
1,3-butadiene	106-99-0	Ref. number: 12962994. Fisher Scientific
1,4-dichlorobenzene	106-46-7	Ref. number: D56829-25G. Merck Life Sciences
Trans-1,2-dichloroethylene	156-60-5	Ref. number: 36969-1G. Merck Life Sciences
Hexane	110-54-3	Ref. number: 296090. Sigma Aldrich

5.5.3.3. MRes thesis method

The proof-of-concept method parameters are outlined in Table 13.

Table 13. TD-GC-MS analytical method parameters as per 2017 MRes thesis

ATD	Air sampling	Tube spiking
Purge		
Prepurge time	1 min	1 min
Trap in line	No	No
Split	On	On
Flow rate	25 mL min^{-1}	25 mL min^{-1}
Tube desorption		
Time	8 min	8 min
Temperature	300 °C	300 °C
Split	Off	Off
Trap desorption		
Trap low temperature	-10 °C	-10 °C
Trap high temperature	330 °C	330 °C

Trap hold time	5 min	5 min
Split	On	On
Trap heating rate	40 °C sec^{-1}	40 °C sec^{-1}
Split flow rate	25 mL/min	35 mL/min
Split ratios		
Inlet	32.5:1	No split
Outlet	26.3:1	26.3:1
Total	58.8:1	26.3:1
Other		
Flow path temperature	250 °C	250 °C
GC cycle time	60 min	120 min
GC		
Helium Flow	1mL min^{-1}	1mL min^{-1}
Temperature Profile		
Initial Temperature	35 °C (hold 5 min)	50 °C (hold 5 min)
Ramp	10 °C min^{-1}	10 °C min^{-1}
Second Temperature	200 °C (hold 10 min)	100 °C (hold 0 min)
Ramp		7 °C min^{-1}
Third Temperature		200 °C (hold 0 min)
Ramp		2 °C min^{-1}
Final temperature		220 °C (hold 25.7 min)
Total run time	31.5 min	60 min
MS		
MS Ionization Mode	E+	E+
MS Inlet Temperature	200 °C	200 °C
MS Source Temperature	180 °C	180 °C
Mode	Scan	Scan

Mass Scan Range	45-300	45-550

5.5.3.4. Statistical analysis used for calculating concentrations

The peak area for each individual injected quantity for all samples were calculated following post-processing with single-ion monitoring. Each peak was assessed using the NIST library. This was deployed to reduce baseline noise and variability (Hübschmann, 2015).

All the raw datapoints were extracted in raw Excel files and a correction factor was applied by validating the GC performance with a standard stock solution (Hübschmann, 2015). As each calibration curve point was developed using triplicate spiking, the mean of the three corrected peak area were calculated for each injected quantity. The mean peak area and injected quantity were assessed using statistical analysis by means of OriginPro 2017 developing a Pearson's linear regression (R^2) model for each individual organic compounds. Linear fit with x-error and t-tests were used to develop calibration curves.

5.5.3.5. Method development overview

Multiple rounds of experimental work were conducted over a period of 2 years including: active air sampling of VOC emissions, injecting spray foam VOCs and spray foam known by-products (in liquid form) onto thermal desorption tubes and testing method performance.

In order to develop precise calibration curves, a known concentration of all chemical compounds of interest was injected into thermal desorption tubes and the results were assessed in an iterative process. As part of the original method development, an assessment of the linearity, precision, accuracy, sensitivity and other parameters were studied. Several variations of solutions consisted of compounds associated with spray foam were developed and experimentally tested.

5.6. Method B Results

5.6.1. MRes results and context

The main complexity of assessing volatile organic compounds is the complexity of behaviour of organic compounds depending on their functional group. Spray foam B-side raw materials, and by-products, cover a wide range of chemical compound groups. For this reason, the method had to be developed in a way that would allow the quantification of a maximum number of VOCs ideally using a specific thermal desorption tube ('Gas Chromatography Problem Solving and Troubleshooting', 1996).

The selection of the sorbent material for packing the thermal desorption tubes is critical as it not only influences the cost for identification, but also has a great impact on the linearity, limit of detection and quantification (Aparicio-Ruiz *et al.*, 2018). The starting point of the methodological development for this thesis was the proof-of-concept method development results as per Figure 31.

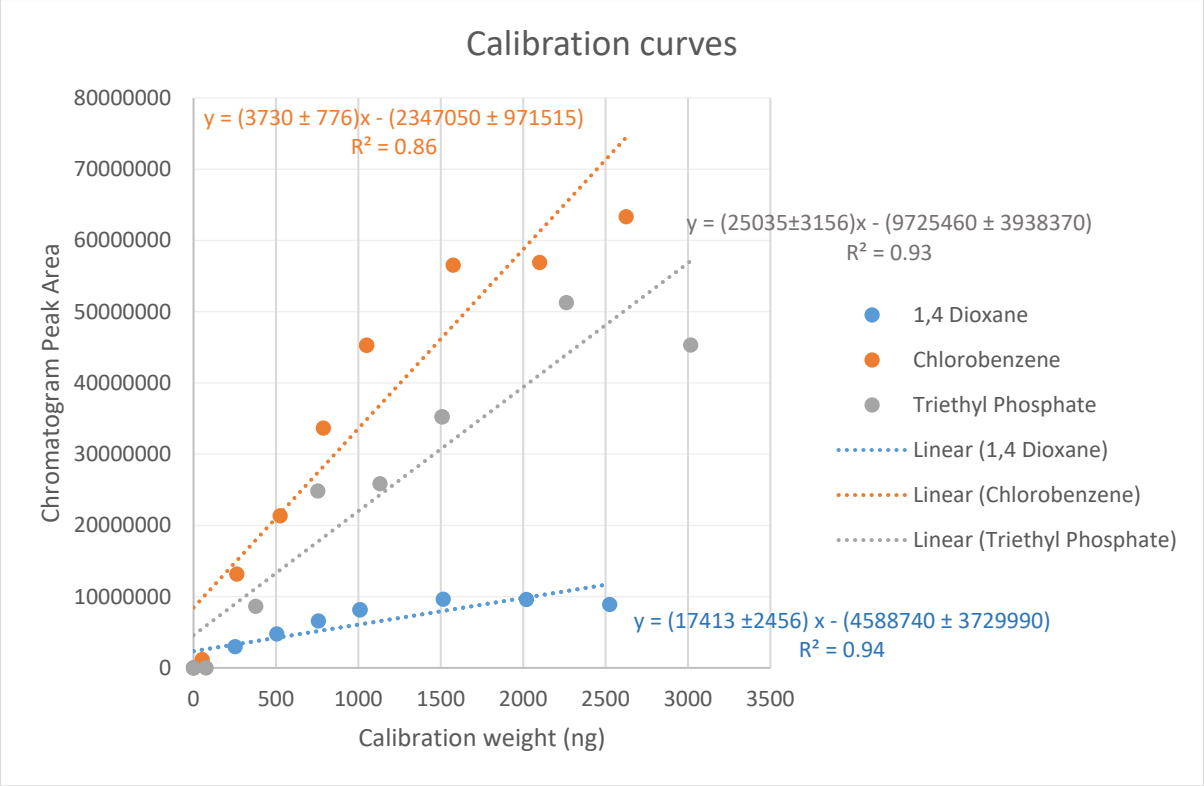


Figure 31. Calibration curves for 1,4-dioxane, chlorobenzene and triethyl phosphate adapted from Naldzhiev (2017) including total range of experimental results. Each point outlines the mean of triplicate direct injections.

The linearity limit is considered the point above which the analytical response (peak area) no longer linearly corresponds to the injected amount.

As Figure 31 demonstrates, for 1,4-dioxane, the peak area above 1010 ng remains broadly flat whereas the injected amount is increased more than two-fold. As it is unknown where the linearity limit using a specific technique is, a repeatable number of experiments are undertaken where the injected amount is gradually increased. The linearity limit is therefore found experimentally followed by statistical analysis of the data. The process of obtaining analytical response (peak areas) proportionate to the amount of analyte injected in a sample is what defines linearity of TD-GC-MS analysis (Aparicio, Conte and Fiebig, 2013). The higher the linear response, the lower the uncertainty interval in calculating concentrations of chemical compounds from airborne collected samples.

It is therefore critical that the methodology developed is highly sensitive and precise, otherwise the concentration results effectively become qualitative rather than quantitative due to the huge uncertainty intervals. This is an important consideration in order to develop a repeatable, reproducible method allowing comparison between different materials and to allow meaningful interrogation of ventilation strategies during spraying, curing and occupation when using spray foam.

Figure 31 show the full range of results obtained during testing of several analytical compounds. Figure 32 only includes calibration curve ranges below the linearity limit.

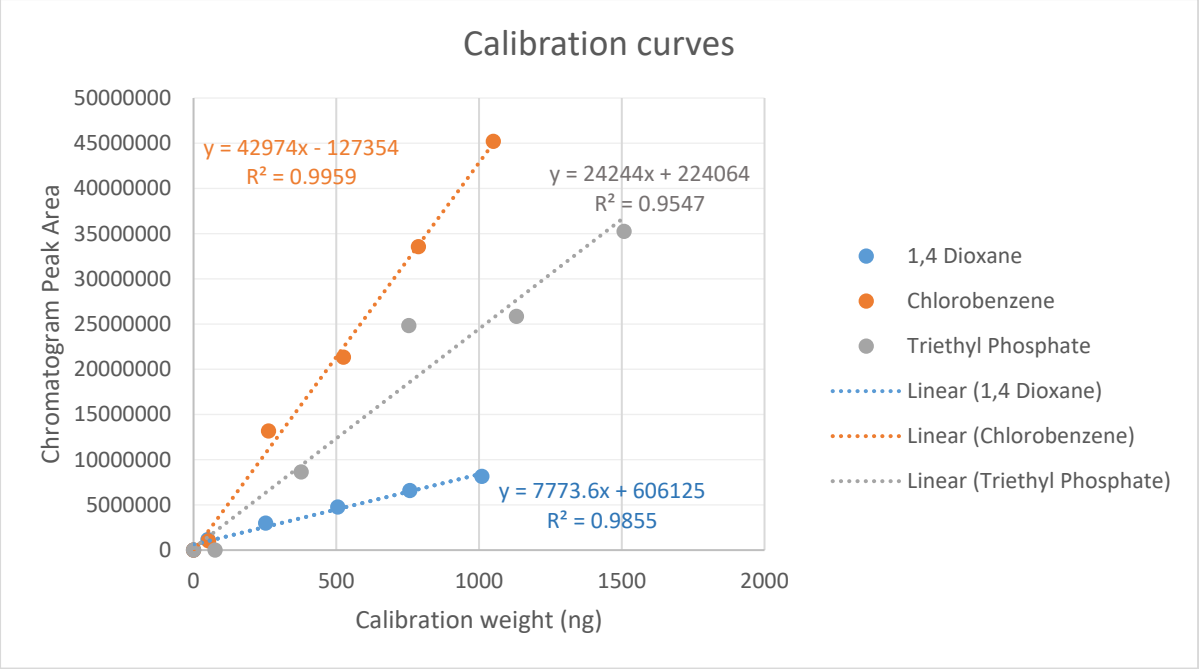


Figure 32 Calibration curves for 1,4-dioxane, chlorobenzene and triethyl phosphate adapted from Naldzhiev (2017) including only the range for experimental results below the linearity limit. Each point outlines the mean of triplicate direct injections.

5.6.2. Method development

ASTM protocols were followed for spraying, storing, cutting and sample preparation (ASTM International, 2017a). To further develop the method, this thesis implemented a three step protocol in order to produce a reliable protocol for quantifying SPF emissions:

- Step 1. Experimentally test emissions from at least 5 SPF products (one and two-component foams) with at least two batches of each product utilising SPME-GC-MS
- Step 2. Experimentally test Tenax-TA as a sorbent medium utilising TD-GC-MS method to assess linearity, limit of detection (LOD) and limit of quantification (LOQ) compared to proof-of-concept method for four chemical compounds
- Step 3. If Step 2 is successful, optimise TD-GC-MS analytical settings for highest linearity limit, lowest LOD and LOQ and develop calibration curves

5.6.2.1. Step 1 Results

The purpose of these experiments was to obtain qualitative results and establish calibration curves in order to deliver quantitative results in future research. Each peak was assessed using the NIST library. Each result was evaluated against the top five highest likelihood

peaks (%) and through manual sifting comparing mass spectra responses on the basis of the expected VOCs outlined in the previous chapter.

An example chromatogram from the study is presented in Figure 33.

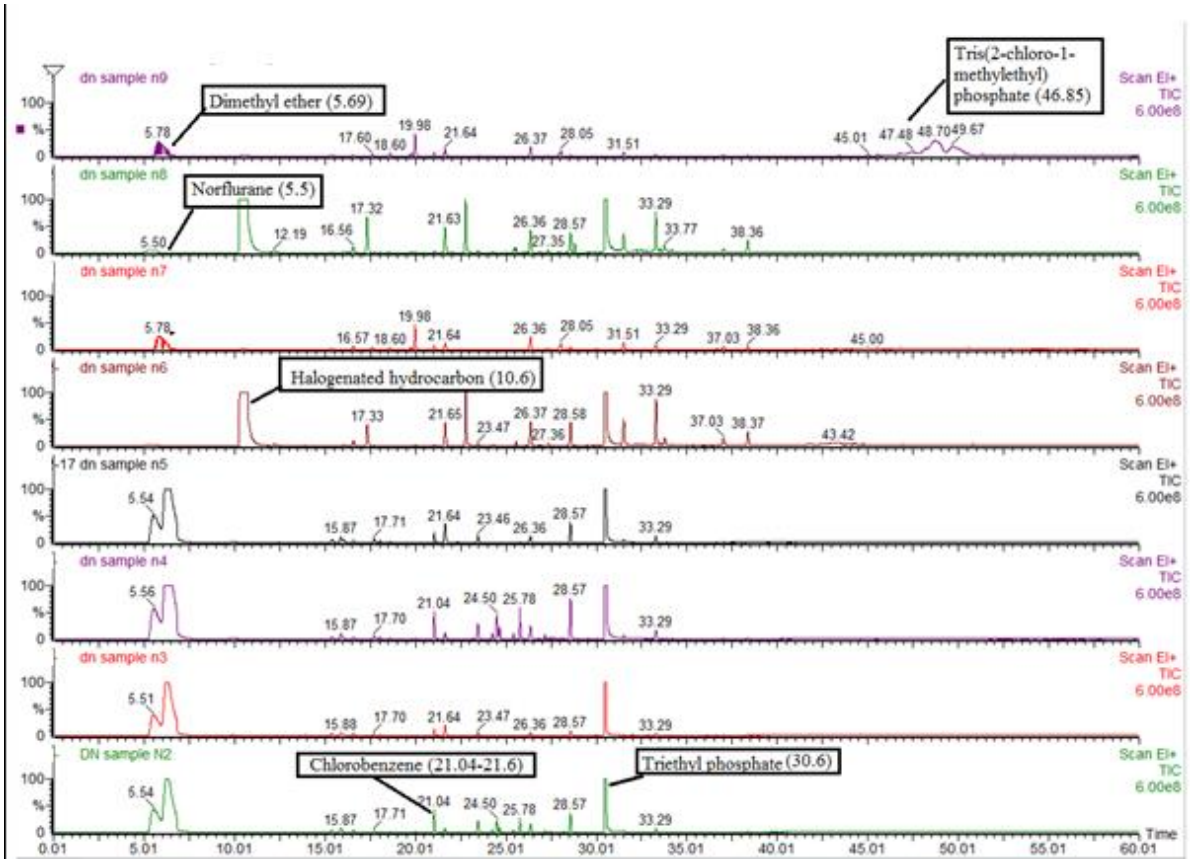
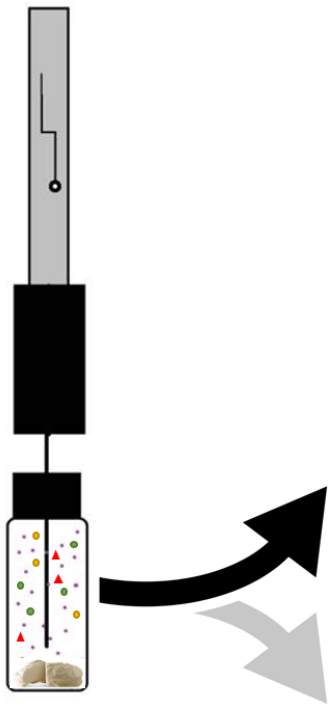


Figure 33. Example chromatogram of SPME-GC-MS analysis of headspace emissions in 20ml vial from one and two-component cured SPF samples

The results from the SPME analysis of multiple one and two-component foam samples are presented in Figure 34.



Compounds found (listed on material safety data sheet)	CAS	Bp (°C)
4,4-MDI	101-68-8	314
Polymeric MDI (pMDI)	9016-87-9	392
Dibutyltin dilaurate (DBTDL)	77-58-7	204
Tris(chloropropyl)phosphate (TCPP)	13674-84-5	235-248
BDMAEE	3033-62-3	189
N,*N*-bis[3-(dimethylamino)propyl]-*N*',*N*'-dimethylpropane-1,3-	33329-35-0	298
Isobutane	75-28-5	-12
Propane	74-98-6	-42
Halogenated aliphatic polyether polyol	68441-62-3	238
Dimethylbis[(1-oxoneodecl)oxy]stannane	68928-76-7	266
Alkanes, C14-17, chloro	85535-85-9	>200
Triethyl phosphate (TEP)	78-40-0	216
HFC-365mfc	406-58-6	40
Norflurane (HFC-134a)	811-97-2	-26
trans-1,2-dichloroethylene	156-60-5	48-60
Dimethyl ether	115-10-6	-25

Additional compounds found (not listed on material safety data sheets)	CAS	Bp (°C)	Product
1,2-DCP	78-87-5	95.5	1,2 and 3
1,4-dioxane	123-91-1	101	1
Chlorobenzene	108-90-7	132	1,2 and 3
Dimethyl methylphosphonate	756-79-6	181	3

Figure 34. Step 1 results and compound properties (CAS number and boiling point). Compounds highlighted in red could not be detected in NIST library at the time of analysis (2018). The compounds in yellow could not be detected using the SPME technique. The compounds in green were qualitatively detected utilising the SPME technique.

The compounds highlighted in red could not be detected in the NIST library at the time of analysis (2018). The result in yellow were found in the NIST library, but could not be found detected utilising the SPME technique. The compounds in green are the detected compounds, which were successfully quantitatively analysed.

The only exception is a blowing agent (HFC-365mfc), which was detected, but was not available in the NIST library at the time of the experiment. A compound was detected at a retention time (RT) of 6.5 min with the highest peak area of all compounds detected. During the sample preparation, the foam was cut up into small samples, therefore it was expected that some of the blowing agent (HFC-365mfc) was going to escape the closed cell structure of the foam. I calculated the theoretical breakdown of the mass spectra of that compound manually and my calculations were quality assured by the senior chromatography technician. It matched the exact structure of the HFC-365mfc. Given the low volatility of the chemical compound it was expected that it would elute before other compounds, such as 1,2-dichloropropane (RT=15.86), 1,4-dioxane (RT=16.20) and chlorobenzene (RT=19.8). The blowing agents (HFC-365mfc and HFC-134a) have not been previously detected using SPME-GC-MS.

If the SPME-GC-MS method is further validated, this could mean that blowing agent emissions could be detected using a non-invasive methodology. Within the built environment field, SPME-GC-MS could therefore offer a high-precision non-invasive methodology for detecting leakages in HVAC systems given that HFC blowing agents are also used in air conditioning units (Tsai, 2005). In practice, this therefore may be a useful method for qualitative assessment of emissions from both construction or consumer products (Johnson, 2004) and even outdoor detection given the significant impact of refrigerants on the ozone layer (Vollmer *et al.*, 2011). This might be particularly relevant for regulatory purposes given that some blowing agents/refrigerants, as they are the same compound used for different purposes, were phased out/banned by the Kigali agreement (UN, 2016)

5.6.2.2. Step 2 Results

When using Carbopack-B tubes, 1,2-DCP was recorded as the second largest peak, following triethyl phosphate. Single ion monitoring (SIM) was used for each compound to isolate the chromatogram peaks associated with the highest m/z ions for each of the compounds: 63 for 1,2-DCP and 88 for 1,4-dioxane. Figure 35 demonstrates the 1,2-DCP and 1,4-dioxane found in Product 1 using both SPME and TD.

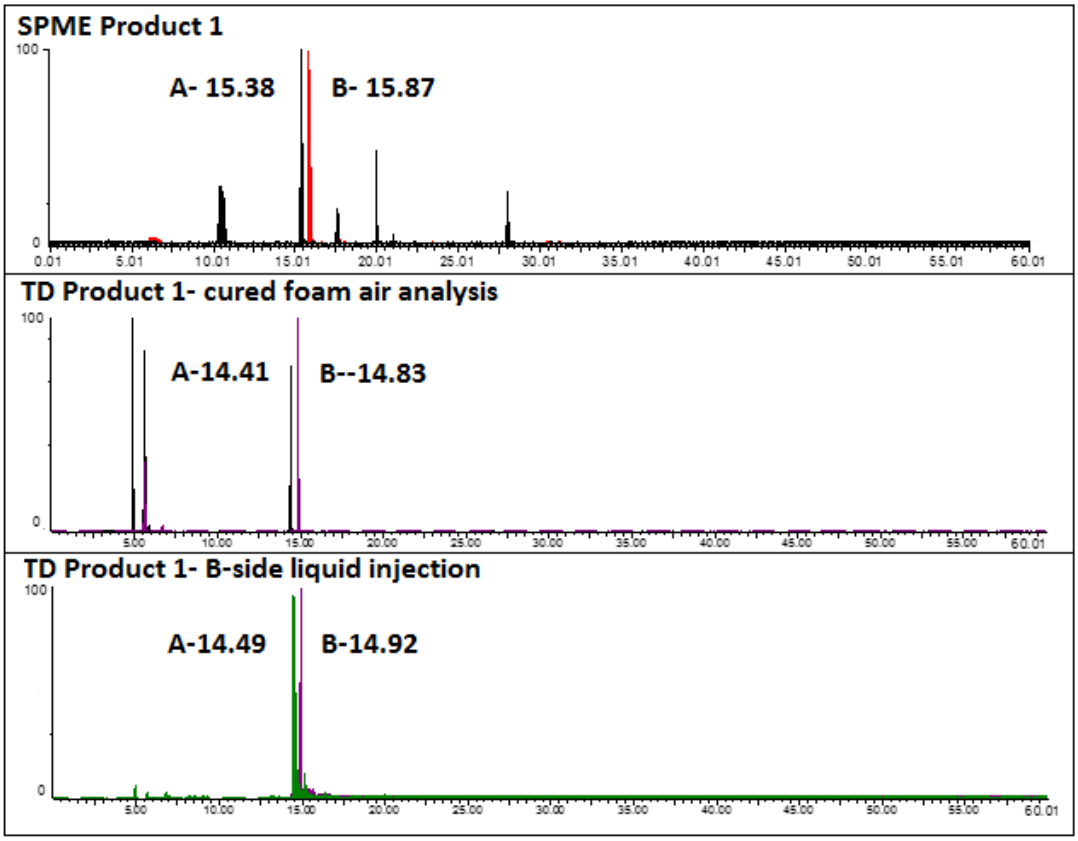


Figure 35. Quantitative detection of 1,2DCP (RT=14.41-15.38) and 1,4-dioxane (RT=14.83-15.87) utilising SPME-GC-MS and TD-GC-MS headspace analysis of cured spray foam sample and direct injection of raw material sample of a two-component foam.

The successful quantitative detection of these compounds in the SPME experimental work demonstrated the analytical technique potential and proved it is repeatable in detecting SPF related chemical compounds.

Multiple siloxane elements were detected in both the SPME and TD work, which were also present in blank samples. Siloxanes are associated with column bleed, which is expected during normal GC-MS operation and interferences with analytes could be avoided through regular maintenance and replacement of columns where problems during troubleshooting are identified.

The isocyanates (MDI) were not detected wither neither SPME nor TD. This was expected as isocyanates are semi-volatile organic compounds, they observe a high sink effect and a high boiling point. In addition, as outlined in Chapters 2 and 5.1, they are usually released in higher concentrations only during spraying and are likely to be easily adsorbed onto surfaces therefore making them difficult to detect (Crespo and Galán, 1999a; Lesage *et al.*, 2007a; Kupczewska-Dobecka, Czerczak and Brzéznicki, 2012; Puscasu *et al.*, 2015). For this reason, HPLC methodologies with impinge samples are a more appropriate methodology for isocyanate analysis compared to SPME/TD-GC-MS.

For Step 3, the objective was to develop highly-precise calibration curves were in order to be able to measure spray foam B-side emissions, as well as possible by-products.

5.6.2.3. Step 3 method improvements and results

5.6.2.3.1. Method improvements

When using Carbopack-B tubes, 1,2-DCP was recorded as the second largest peak, following triethyl phosphate.

Tenax-TA was therefore selected for the packing material of choice for Step 3 for several reasons. First, previous experimental work suggested it showed less breakthrough and higher breakthrough volume compared to Carbopack-B (Szulejko *et al.*, 2014). Second, it was successfully applied to measure emissions from polyurethane products in indoor dust samples (Sonnette *et al.*, 2017). Thirdly, it is used in international methods for measuring indoor air emissions as part of the ISO 16000 series.

In addition to changing the adsorption material, adjustments were made in the TD-GC-MS settings on the basis of SPF methodological findings being published as per Table 14 (ASTM International, 2017b; Poppendieck, Gong and Emmerich, 2017).

Table 14. Improved GC-MS settings for Method B

ATD	Air sampling	Tube spiking
Purge		
Prepurge time	1 min	1 min
Trap in line	No	No

Split	On	On
Flow rate	25 mL min^{-1}	25 mL min^{-1}
Tube desorption		
Time	8 min	8 min
Temperature	300 °C	300 °C
Split	Off	Off
Trap desorption		
Trap low temperature	-10 °C	-10 °C
Trap high temperature	330 °C	330 °C
Trap hold time	5 min	5 min
Split	On	On
Trap heating rate	40 °C sec^{-1}	40 °C sec^{-1}
Split flow rate	25 mL/min	35 mL/min
Split ratios		
Inlet	32.5:1	No split
Outlet	26.3:1	26.3:1
Total	58.8:1	26.3:1
Other		
Flow path temperature	250 °C	250 °C
GC cycle time	60 min	120 min
GC		
Helium Flow	1mL min^{-1}	1mL min^{-1}
Temperature Profile		
Initial Temperature	35 °C (hold 5 min)	50 °C (hold 5 min)
Ramp	10 °C min^{-1}	10 °C min^{-1}
Second Temperature	200 °C (hold 10 min)	100 °C (hold 0 min)
		7 °C min^{-1}

Ramp Third Temperature Ramp Final temperature Total run time	31.5 min	200 °C (hold 0 min) 2 °C min^{-1} 220 °C (hold 25.7 min) 60 min
MS		
MS Ionization Mode MS Inlet Temperature MS Source Temperature Mode Mass Scan Range	E+ 200 °C 180 °C Scan 45-300	E+ 200 °C 180 °C Scan 45-550

5.6.2.3.2. Results

The same concentrations as per the proof-of-concept method were therefore injected onto Tenax-TA tubes. The results are presented in Figure 36.

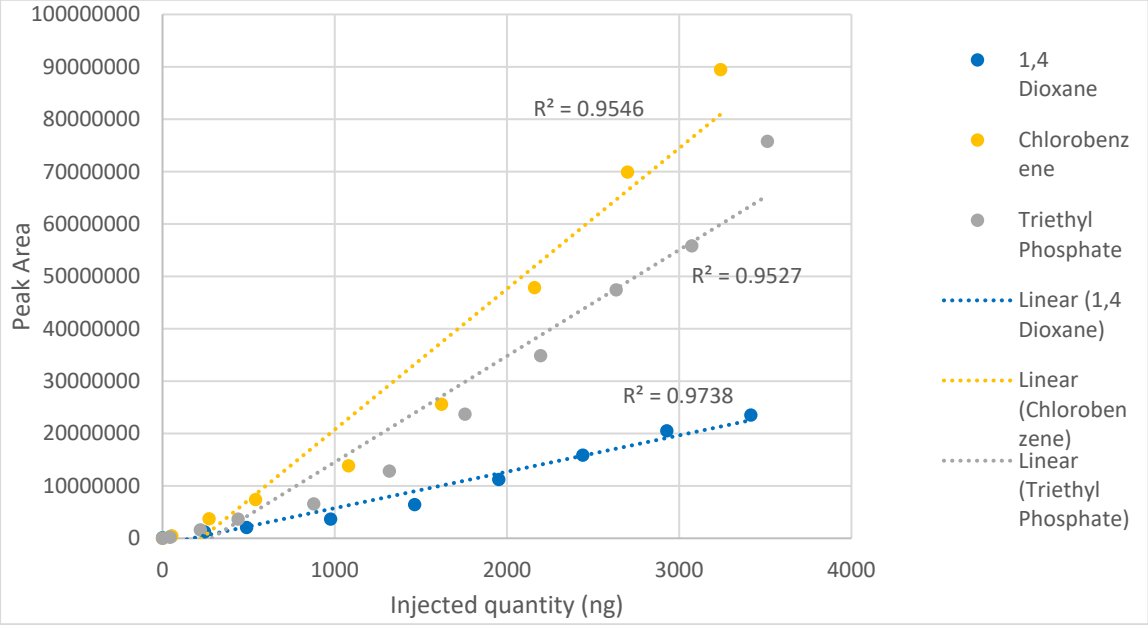


Figure 36. Calibration curves for 1,4-dioxane, chlorobenzene and triethyl phosphate adopting Naldzhiev (2017) method and Tenax-TA tubes

As it can be seen in Figure 36, the linearity limit was not exceeded utilising Tenax-TA tubes at concentrations of 3240-3512ng. For comparison, using Carbopack-B tubes, the linearity limit was reached at concentrations several times lower (1010-1580ng).

In practice, these results meant that utilising Tenax-TA instead of a Carbopack-B tube would allow the detection of higher levels of VOC concentrations and could in theory have a higher breakthrough and safe sampling volume (ASTM International, 2020).

For the purposes of this thesis, it was deemed that Step 3 was successful and Tenax-TA was selected as the adsorbent of choice. The next step of the method was to find the linearity limit for each compound.

Figures 37-40 plot the calibration curves developed using Tenax-TA tubes. They demonstrate calibration curves calculated for a different linearity limit in order to ensure that the most precise and sensitive curve is used for calculating emissions in-situ.

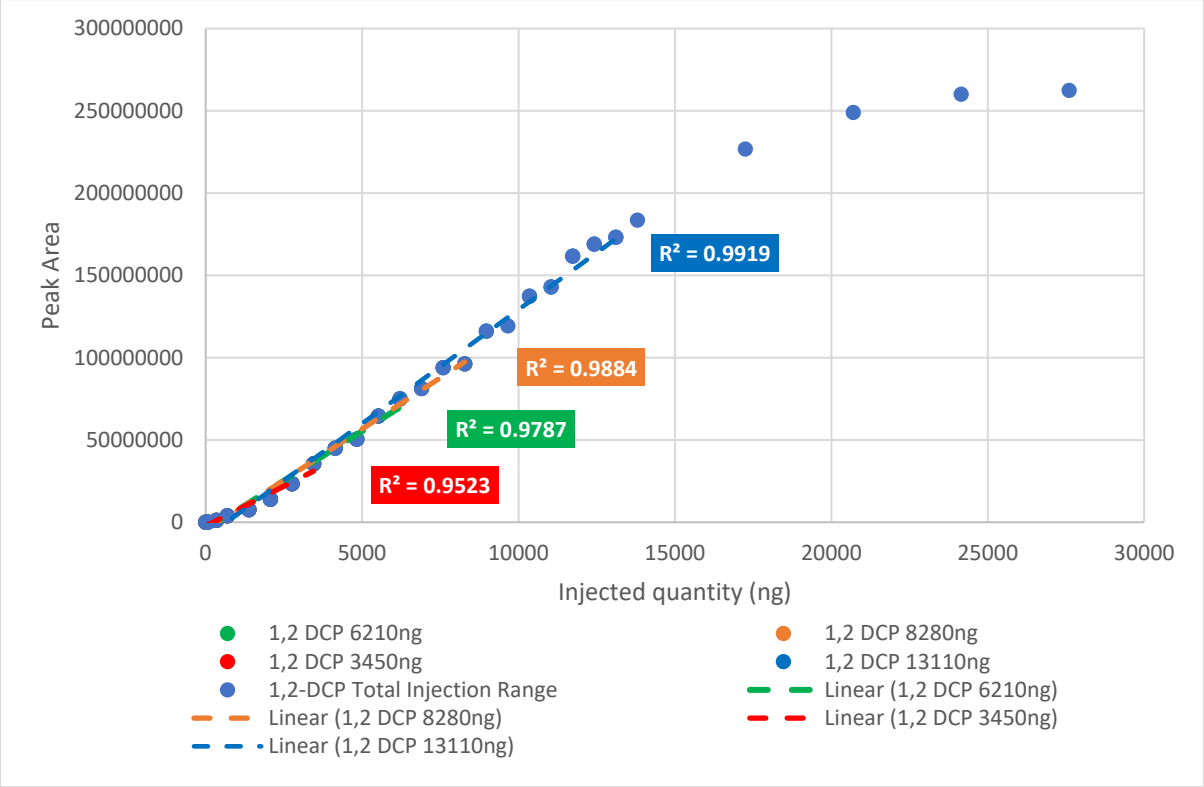


Figure 37. Calibration curves results for 1,2-dichloropropane (1,2-DCP). Each point on the graph is the result of the calculated mean of triplicate spiking.

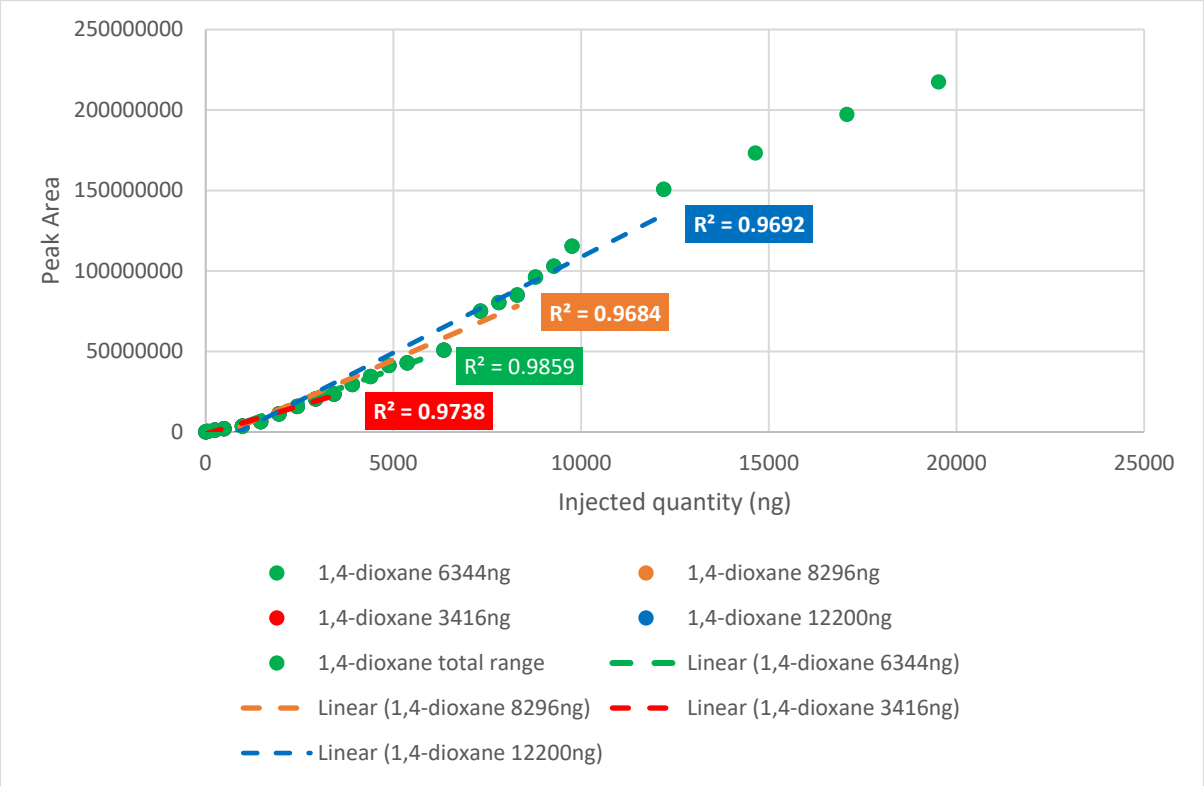


Figure 38. Calibration curves results for 1,4-dioxane. Each point on the graph is the result of the calculated mean of triplicate spiking.

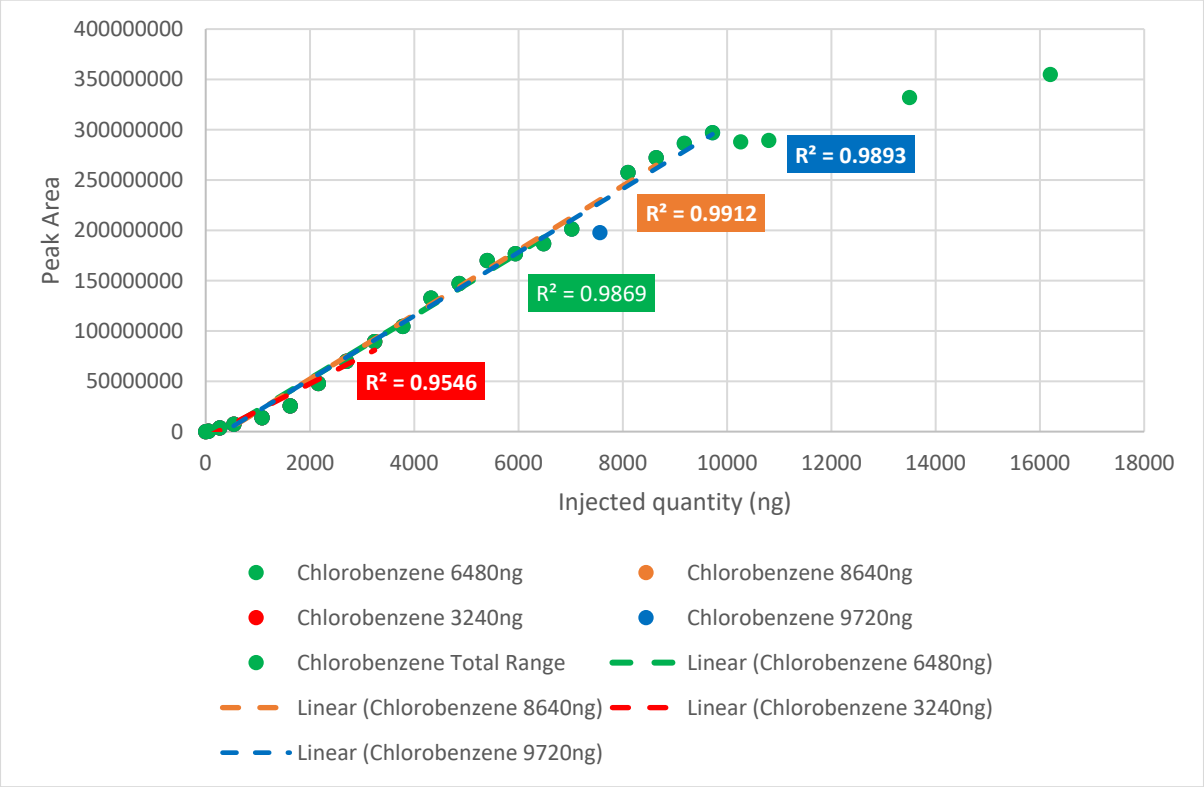


Figure 39. Calibration curves results for chlorobenzene. Each point on the graph is the result of the calculated mean of triplicate spiking.

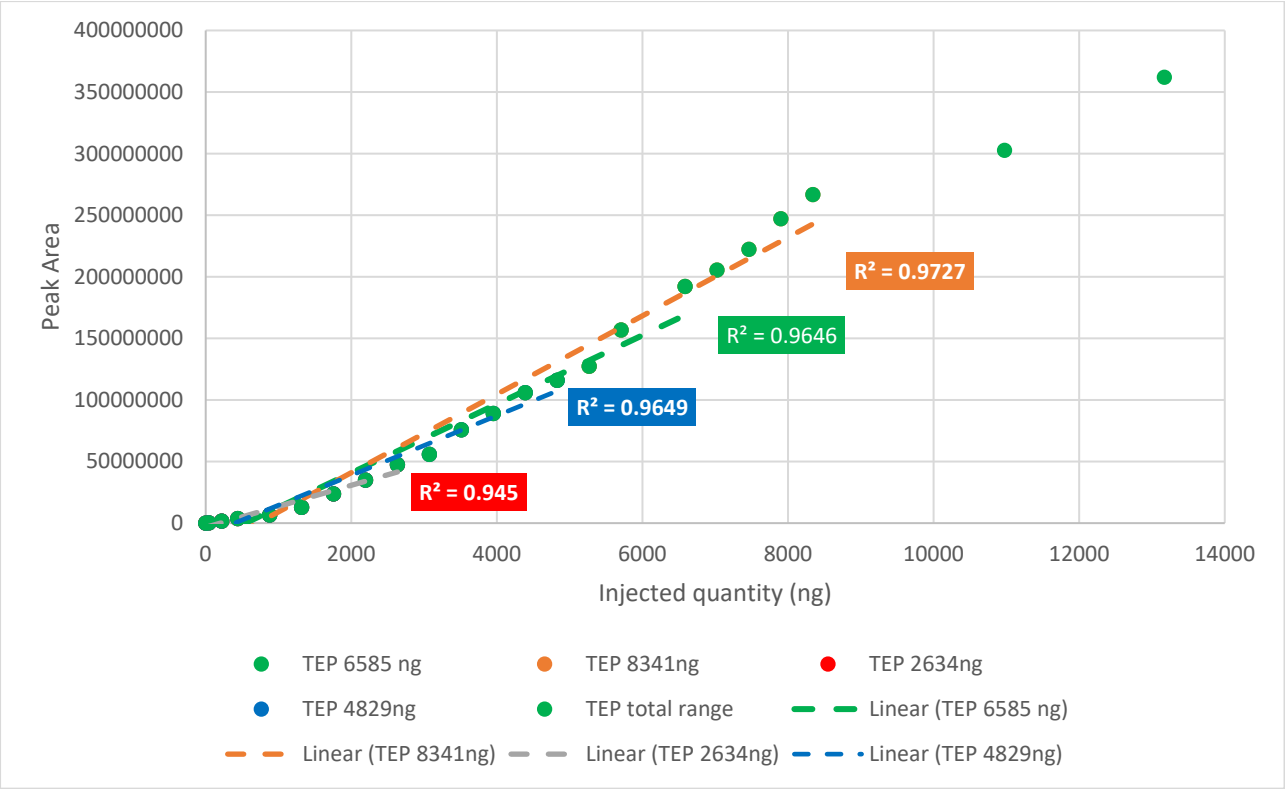


Figure 40. Calibration curves results for triethyl phosphate (TEP) spiking. Each point on the graph is the result of the calculated mean of triplicate spiking.

There were siloxane elements detected in all tests, which are most likely released from the column as they are also consistently present in the blank samples in very small quantities. It should be noted that some of the other compounds from SPF products have been successfully quantified through the use of Tenax-TA tubes, emission chambers and ATD-GC-MS such as tris(1-chloro-2-propyl)phosphate (TCPP) (Poppendieck *et al.*, 2016), therefore reinforcing the case for the analytical methodology as proposed here.

5.7. Method B versus ASTM D8142-17 Results

Calibration curves were developed utilising the ASTMD8142-17 methodology and the results are plotted in Figure 41.

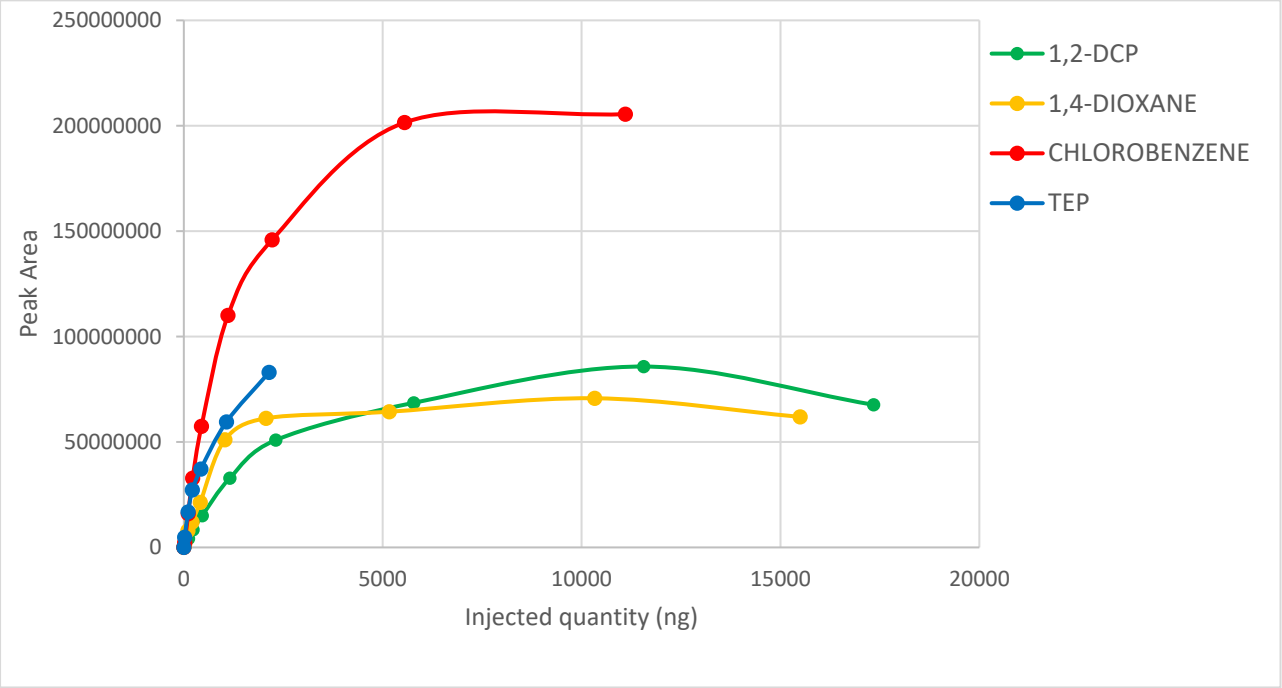


Figure 41. Calibration curves and range of linearity for selected organic compounds using SPF specific desorption tubes and ASTM D8142-17 method

As it can be seen from Figure 41 above, using the ASTM D8142-17, the linearity limit for the compounds is reached in or around 2000 ng (ASTM International, 2017b). This is much lower compared to Method B where it was reached at well over 13000 ng for some compounds.

This was perhaps expected as the primary aim of the ASTM method was to measure emissions in micro chambers from cured spray foam products. This means that very low VOC concentrations are expected and high-precision in the 0-1000 ng range is therefore required.

5.8. Summary

This chapter provides evidence in relation to R.Q.2. “Can volatile organic compound (VOC) emissions emitted from polyurethane products be measured using analytical chemistry methods developed for plastics and museum collection objects?”.

This chapter outlined the original method development work and was split into three parts: measuring A-side emissions (Method A), measuring B-side emissions (Method B) and comparing to an international method developed during the lifecycle of the thesis (ASTM vs method B performance).

The Method A results demonstrated empirically that the analytical method developed by Ferreira (2014) coupled with the sampling methodology deployed as part of this thesis could be utilised to measure airborne isocyanates. The open box and closed box experiments demonstrated that isocyanate concentrations observed during spray foam application of modern materials are consistent with the existent literature findings. Given the range of studies in the literature examining isocyanate emissions and strict national regulations minimising their exposure, it was deemed that further A-side explorations would not result in scientifically novel findings. On the other hand, very little empirical evidence existed in relation to B-side emissions.

Results from Method B demonstrated that it was possible to develop a highly precise analytical method to measure VOCs from spray foam materials down to ppb levels. The comparison of Method B versus ASTM D8142-17 demonstrated that Method B is better suited for measuring VOCs during spraying due to its higher analytical measurement limit.

The evidence presented in this chapter allows both built environment and heritage practitioners to select which method would be most appropriate for their work depending on what compounds they want to measure. Due to the successful development of Method B for measuring VOC emissions, it was therefore used for undertaking the experimental work for all the following chapters presenting original evidence (Chapter 6-9).

6. Systematic analysis of VOC emissions during spraying

This chapter provides evidence in relation to R.Q.3. "What are the short and mid-term concentrations of VOCs from spray foam materials in controlled conditions?". For the purposes of this thesis, short and long term refers to the time period during which emissions are released from the product. Specifically, the chapter provides original evidence of concentration of 1,2-dichloropropane (1,2-DCP) and a novel hypothesis with regards to its origin from spray foam products.

The chapter first outlines why the focus of the experimental work was on one specific VOC and provides a justification for the hypothesis being experimentally tested. This is followed by a review of international guidelines for exposure of 1,2-DCP. These demonstrate the variability between countries in terms of exposure limits, which offer an important reference point for the measured quantities. An outline of the method utilised for this particular experiment is then described. Finally, the original results are presented for all 13 spray foam products. The chapter presents 1,2-DCP concentrations data recorded during spraying from multiple batches of 13 spray foam products available. These products represented the majority of spray foams available for consumers to purchase in the UK at the time of testing.

Previous research suggested 1,2-DCP was found emitted from spray foam due to being a degradation product of flame retardants. Based on the original data, I provide experimental evidence in support of an alternative hypothesis. Namely, that 1,2-DCP could have possibly entered all spray foam products via contamination, or processing, and is actually present in the raw products before spray foam is applied in-situ.

6.1. Context

6.1.1. Origin hypothesis for 1,2-DCP emissions from spray foam

The reason 1,2-DCP was chosen as the compound of interest for this chapter was three-fold.

First, it was re-classified as a Class 1 carcinogen in 2014 (International Agency for Research on Cancer, 2014) and as such I deemed it a priority compound. Second, small-scale exploratory studies indicated that 1,2-dichloropropane (1,2-DCP) emissions were found off-gassing from cured spray foam insulation products however the origin was unclear and it was listed as a by-product (Nie, Kleine-Benne and Thaxton, 2017; Poppendieck *et al.*, 2017; Sleasman, Hetfield and Biggs, 2017); Thirdly, I tracked the literature to the original source and found that it was hypothesised in 2003 that the likely source of the 1,2-DCP emissions is degradation from "side B" compounds, namely flame retardants (Salthammer, Fuhrmann and Uhde, 2003). The experimental study (Salthammer, Fuhrmann and Uhde, 2003) referenced an even earlier study from 1995 (Matuschek, 1995), that investigated thermal degradation of fire retardant polyurethane foams, as supporting evidence for 1,2-DCP being the degradation product of flame retardants.

It was deemed important to experimentally test this hypothesis as flame retardants are present ubiquitously in indoor environments and are found in many consumer and construction products as the literature review revealed. This means that if polyurethane product with flame retardants thermally degrade, 1,2-DCP emissions could theoretically be

found indoors potentially posing risks to human health given the re-classification of the compound as a carcinogen. Like any VOC, the potential impacts on health are directly linked to the exposure concentration and duration of exposure. For this reason, some of the international guidelines for 1,2-DCP exposure are reviewed.

6.1.2. International guidelines for 1,2-DCP

Whilst 1,2-DCP has been found to have impact on health (Kwak *et al.*, 2018; U.S. Environmental Protection Agency (EPA), 2019) the exposure values for both occupational and worker exposure vary widely by country and organisation. Table 15 outlines the exposure limits across different countries and the carcinogenic classification of 1,2-DCP.

Table 15. 1,2-DCP exposure limits and carcinogenic classification in different countries or by international organisations (Pohanish, 2011; Benbrahim-Tallaa *et al.*, 2014; Kawai, Mitsuyoshi and Ikeda, 2015; THE EUROPEAN COMMISSION, 2017; IARC, 2017; MINISTRA Rodziny PRACY I POLITYKI SPOŁECZNEJ, 2018; Agency for Toxic Substances and Disease Registry (ATSDR), 2019; National Health Commission of the People's Republic of China, 2019; Ministério do Trabalho e Previdência, 2020; Social- och hälsovårdsministeriet, 2020; The Japan Society for Occupational Health, 2020; WorkSafe, 2020; Arbetsmiljöverkets, 2020; DFG, 2020; FEDERALE OVERHEIDSDIENST WERKGELEGENHEID, 2020; Government of Alberta, 2020; Arbeids- og sosialdepartementet, 2021; Health and Safety Authority, 2021) . *Years on table denote when the classification or limit was established.*

Country/Area	**Agency**	**Year**	**Occupational Exposure Limit -OEL TWA (µg m^{-3})**	**Short Term Exposure Limit STEL 15 min (µg m^{-3})**	**IDLH-immediate danger (µg 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 15 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 2013-2014 (Benbrahim-Tallaa *et al.*, 2014) and this study played a role in the re-classification of the compound as a Class 1 carcinogen by IARC.

The US Environmental Protection Agency (EPA) proposed 1,2-DCP as a high-priority substance for risk evaluation in 2019, however the evaluation had not been completed as of September 2021(U.S. Environmental Protection Agency (EPA), 2019).

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 13 (Kwak *et al.*, 2018). It is a reasonable expectation that the current exposure limits will be revised in the future. These concentrations often form the bedrock of occupational limits as they allow retrospective cohort evaluation where analysis of the workplace population are assessed in order to detect patterns of exposure and causal links between compound and health impacts. In the meantime, it is however important to understand workplace exposure concentrations and 1,2-DCP emissions from products. For this reason, multiple batches of the majority of spray foam products available for purchasing by consumers in the UK were undertaken to experimentally test whether the origin hypothesis for 1,2-DCP emissions from spray foam was valid for modern products.

6.2. Method

6.2.1. Method overview

The experiments were split in three stages.

First, the 1,2-DCP emissions of three SPF products were assessed qualitatively to determine whether 1,2-DCP was emitted from cured foam samples. This was undertaken 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.

Blank thermal desorption tubes were 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 me to discount contamination or chemical reaction between the storage materials, SPF and external air as possible sources of 1,2-DCP.

6.2.2. Products tested

A total of thirteen different spray foam polyurethane (SPF) products (two 2-component foams and eleven 1-component foams) were assessed. The products were produced by four different parent companies manufacturing insulating foams.

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). 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 agreement (UN, 2016).

All the compounds present in more than one product and listed in the safety data sheets are illustrated in Figure 42.

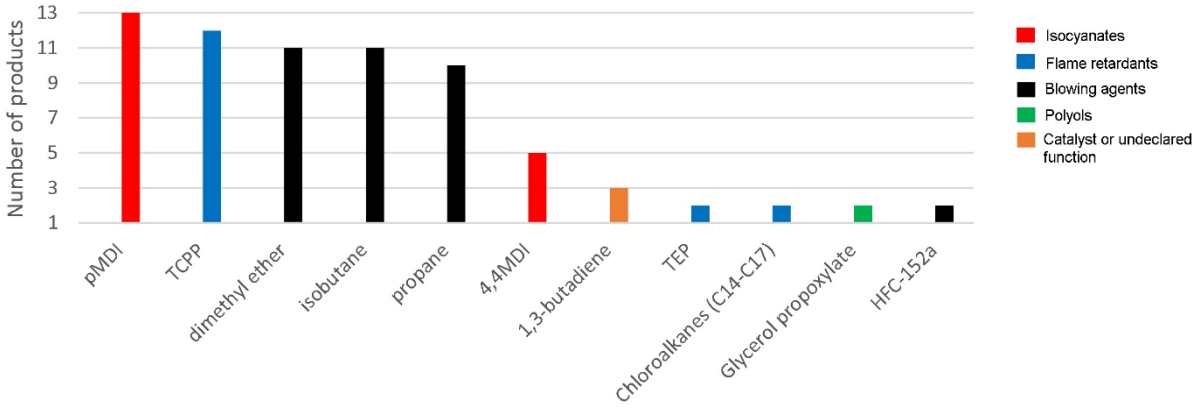


Figure 42. Frequency for compounds listed on the safety data sheets of the 13 tested spray foam products.

6.2.3. Analytical and sampling setup

A minimum of two batches of each individual product were tested to reduce sampling bias. Figure 43 outlines the experimental setup and analytical method used for each of the three experiments.

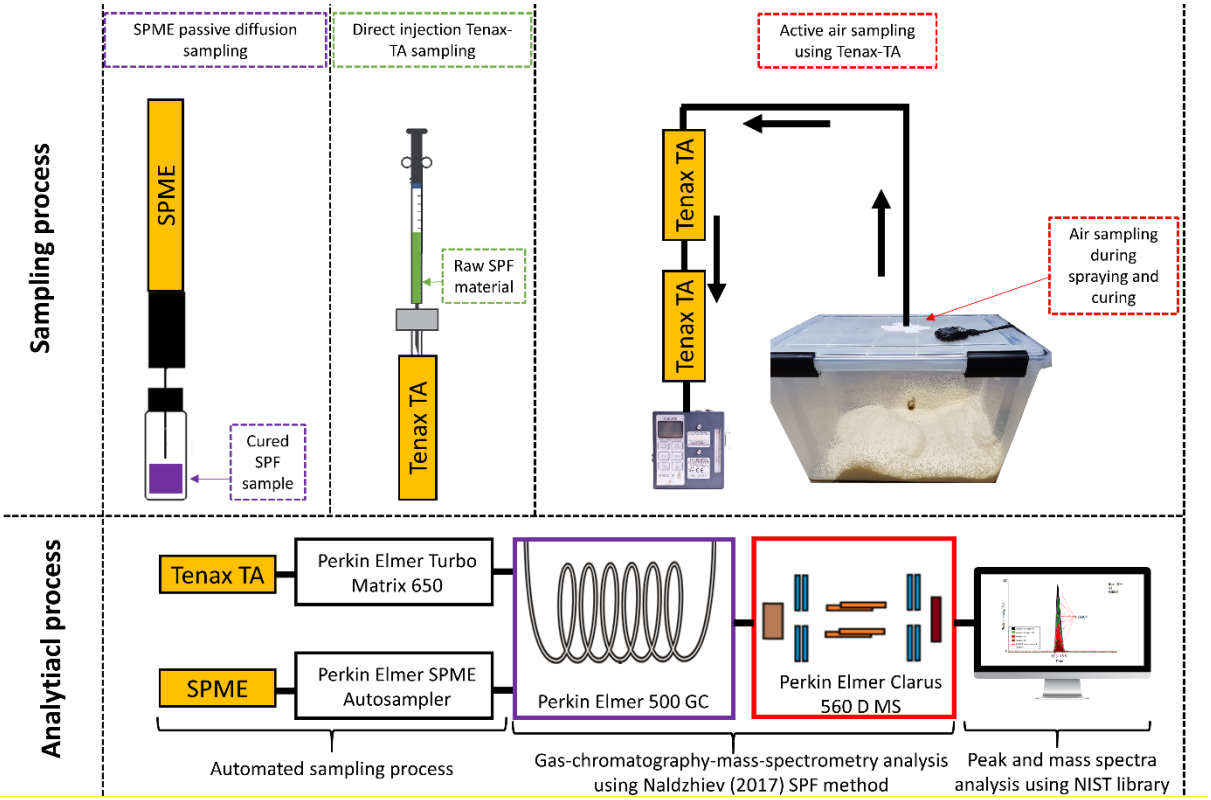


Figure 43. Sampling and analytical setup for the three experimental phases. Phase I (left): passive SPME sampling and 10mL glass vials with 1-3g cured SPF products were sampled (left). Phase II (middle): direct injection of raw materials and spiking onto Tenax-TA (middle) Phase III (right): active air sampling of emissions during spraying and curing using Tenax-TA and low flow pumps. All samples analysed using GCMS (bottom).

The quantitative analysis was undertaken using equipment and the Method B.

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 16.

Table 16. Analytical parameters for 1,2-DCP testing

Analytical Parameter	Calibration Results
Desorption efficiency	99% ± 0.97%
Regression coefficient (R^2)	0.985
Calibration points	21
Calibration range (ng)	45-13,800
Limit of detection (ng)(Federal Government of the United States, 2017)	27.6 ± 7.3

For the raw material analysis, two solutions were created using the raw liquid product diluted in hexane (50 µL of raw material in 10 mL hexane and 500 µL 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. In addition, a small amount (5 µL) 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 the air was sampled 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 than the ASTM safe sampling volumes for 1,2-DCP (ASTM International, 2017b).

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. The containers and experimental data collection was undertaken at a well ventilated shaded external area, with no direct exposure to sun.

6.2.4. Environmental conditions

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 44.

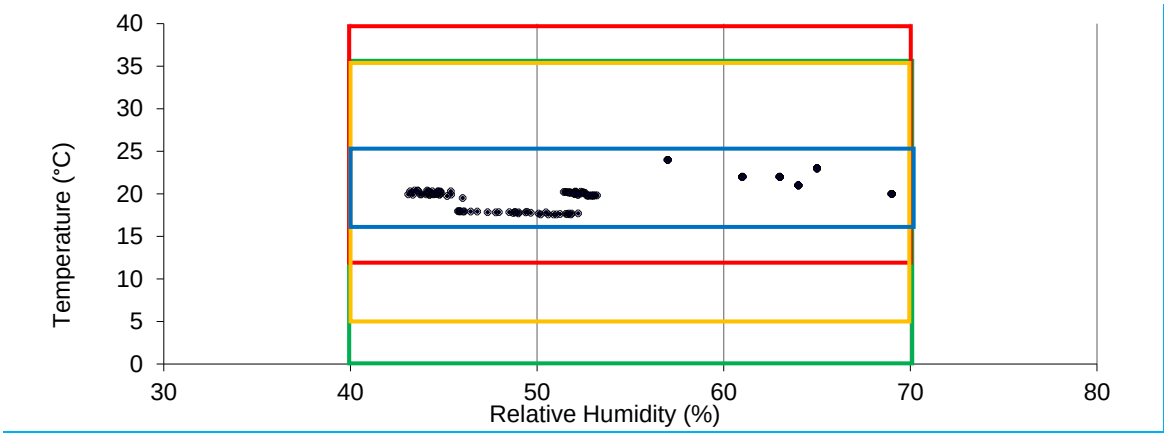


Figure 44. Ambient environmental conditions during spraying and sampling of the spray foam products. Blue, red, orange and green boxes outline recommended guidelines for optimal ambient conditions during application provided by manufacturers. Black dots outline temperature and relative humidity during all experiments.

As Figure 44 demonstrates, the ambient conditions were all within the optimal ranges as recommended by the various spray foam manufacturers. This careful selection of timing when to spray the foams allowed for discounting misapplication of the products, due to inappropriate environmental conditions, as a reason for why 1,2-DCP could be emitted.

6.3. Results

6.3.1. Qualitative analysis (SPME-GC-MS)

The qualitative 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 as per Figure 45.

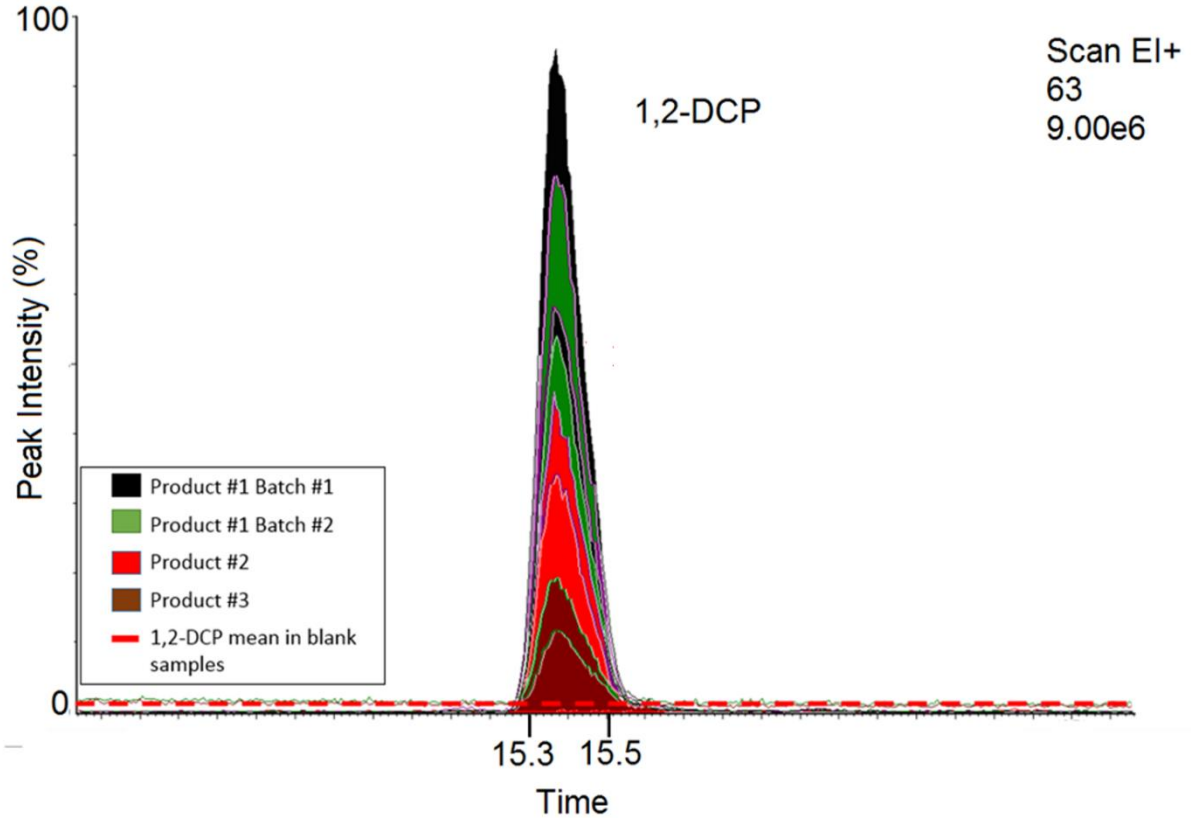


Figure 45. SPME-GC-MS results in SIM mode (m/z 63) of emissions from three cured spray foam products. Two samples from each product were analysed. Horizontal axis is the retention time (min) and the vertical axis is the abundance of the compound (peak intensity).

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.

6.3.2. Raw materials analysis (TD-GC-MS)

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 17.

Table 17. 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 ± 4,202	2348 ± 840
	5	9,701 ± 3,200	1940 ± 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 ± 580
	0.05	71 ± 27	1,420 ± 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 linearity range of the calibration parameters. This signified that 1,2-DCP concentration was measured in quantities exceeding what could be measured with the analytical method. This means that where “>13,800” is seen in Table 17, the actual 1,2-DCP quantity was even higher, but the exact amount could not be calculated.

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, I experimentally tested whether 1,2-DCP occurs during flame retardant degradation in the TD-GC-MS analytical process.

I 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 Method B. No 1,2-DCP was found in any of the chromatograms above the detection limit when spiking TDCPP or TCPP.

This novel finding suggested that an alternative hypothesis is required to explain the presence of 1,2-DCP in the spray foam products. As 1,2-DCP was historically used as a solvent in the production of toluene diisocyanate (TDI) (Agency for Toxic Substances and Disease Registry, 1999), it is plausible that 1,2-DCP could have been used for the production of other isocyanates as well. Given that isocyanates are present in all spray foam products on the open market, an alternative origin hypothesis of 1,2-DCP was formed - that it was present in the raw spray foam products rather than being a by-product.

To test the hypothesis experimentally, twelve products I then tested twelve products for 1,2-DCP emissions during spraying and curing.

6.3.3. Concentrations of 1,2-DCP during spraying and curing of twelve spray foam products

The first material sampled was Product #2 within a 70-L container at a 0.25 L min-1 extraction rate. Air was extracted continuously for a total period of 120 min during which five consecutive air samples taken. There was a period of 1 min while the sets of tubes were replaced.

The 1,2-DCP mass in the Tenax-TA tubes have been plotted in Figure 46.

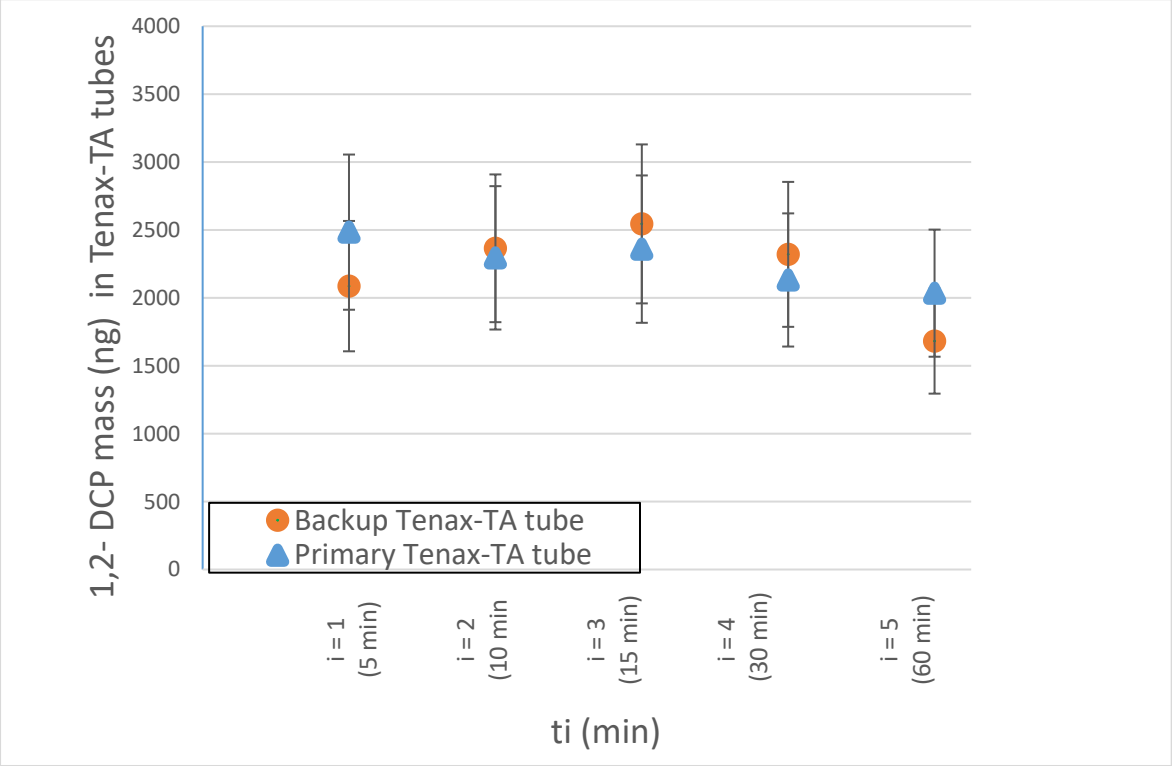


Figure 46. Sampling of 1,2-DCP during Product #2 spraying and curing. Error bars show standard error for sampling. The data show 1,2-DCP mass (ng) on Tenax-TA tubes. Sampling was undertaken for a total continuous period of 120 min at 5 different sampling intervals (5, 10, 15, 30 and 60 min).

Breakthrough occurred in all sampling tubes. The data illustrates that the concentration within the 70-L plastic box was too high or the flow rate of the pump was too high. The surface area that was covered was 0.16 m^2, which is many times smaller than standard application in refurbishment projects by a factor of 10-250,000 (American Chemistry Council, 2014) where roofs , walls and floors are covered with SPF. From the data in Figure 51, it could be concluded that 1,2-DCP concentration saturated all tubes and only the minimum concentration could be calculated.

The actual concentration during the application process could not be determined because of the breakthrough, however a minimum concentration of 1,987 µg m^{-3} was recorded during the spraying. This was calculated by dividing the concentration of 1,2-DCP in the primary tube by the volume of extracted air. It is clear however that 1,2-DCP was present for up to 2 h after application in a large container with limited ventilation.

The calculated 1,2-DCP concentrations during application of the other eleven products, based on the mass (ng) of 1,2-DCP in the primary tube, is plotted in Figure 47.

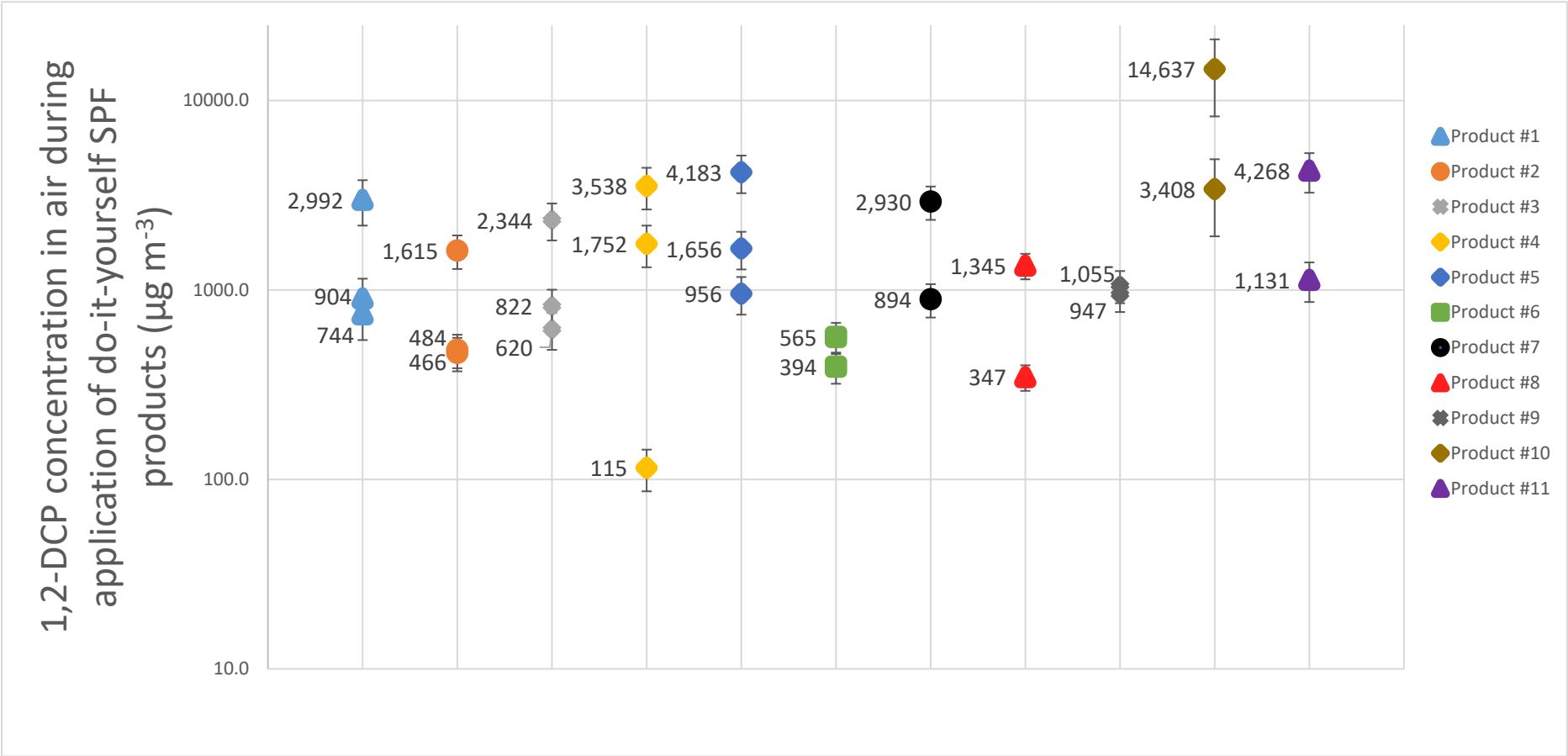


Figure 47. 1,2-DCP concentration in air during spraying and curing of eleven do-it-yourself spray foam insulation products. Each colour represents a different product and each point represents a different batch of the same product. Y-axis is logarithmic.

Although the application conditions were similar there was variation in the 1,2-DCP concentration between different batches. As breakthrough occurred some of the tested batches, Figure 47 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 recommendations (ASTM International, 2017b) and the spray foam surface area covering 0.05-0.16 m^2, which is smaller than standard field application in refurbishment projects by a factor of 10-250,000 (American Chemistry Council, 2014).

There was limited correlation between product weight and 1,2-DCP concentration in the air during application. I attempted to sample raw materials of one-component products, but was unsuccessful as an exothermic chemical reaction occurred as soon as the raw products exited the pressurised canisters. In simple terms, the liquid started expanding as soon as it exited the pressurised can and I could not obtain a liquid sample of the one-component foams.

Therefore a mass balance calculation for individual compounds in the raw material was not achievable and no correlation was investigated between the individual compounds, such as isocyanates, in the raw material and the recorded 1,2-DCP emissions.

No 1,2-DCP was detected in any blank tubes between samples, air extracted from containers before spraying and outdoor air where experiments were undertaken.

6.4. Summary

This chapter analysed raw SPF liquid, emissions during application and cured spray foam products. The data presented demonstrated that 1,2-DCP was systematically present in thirteen different SPF products during spraying and curing. This experimental data provided evidence in support of an alternative hypothesis of the origin of 1,2-DCP contrary to previous theory that it occurs as a result of thermal degradation of flame retardants. The original work presented in this chapter support the alternative hypothesis that 1,2-DCP was present in the raw ingredients of the spray foam products before they were applied. Whilst it is theoretically plausible that 1,2-DCP was present in isocyanate mixtures given it was previously used as a solvent in the processes for making isocyanates, the origin of the 1,2-DCP could not be confirmed through this experimental work.

These findings however raised an important question. If 1,2-DCP was present in the raw ingredients, what are the concentrations recorded during spraying in controlled conditions when a whole floor is retrofitted. The next chapter outlined empirical evidence in relation to this research question.

7. Workplace exposure to PU emissions in controlled conditions

This chapter provides evidence in relation to R.Q.3. “What are the short and mid-term concentrations of VOCs from spray foam materials in controlled conditions?”. Specifically, the chapter tested whether robots could reduce exposure of workers to volatile organic compounds during spray foam application when compared to manual application

In theory, this seems logical given that the literature review outlined that the highest concentration of VOCs occur near the spraying surface during spraying. However no empirical evidence in the literature existed comparing manual application versus application with robots.

For the experiments presented in this chapter, a testing facility was setup in a room with mechanically controlled ventilation. The facility mimicked a real life application environment with a suspended timber floor constructed and retrofitted with spray foam. During the spraying and curing of the foam, the VOC concentrations were measured both near the spraying surface (next to the robot) and near the sprayer (operating the robot). The sprayer was standing outside the testing facility. Four VOCs of interest were measured and the experiment was repeated four times in order to provide statistically significant results. All VOCs were successfully measured with original empirical data found in support of the hypothesis.

7.1. Method

7.1.1. Method overview

To measure VOC concentration, active sampling using thermal desorption tubes was used as per the method in Chapter 5B (Method B).

Four VOCs emitted were selected for this experiment: 1,2-dichloropropane (1,2-DCP), 1,4-dioxane, chlorobenzene and triethyl phosphate (TEP). Air was extracted in a room where the ventilation rate was controlled and temperature and relative humidity were monitored during the experimental period. The experiment was repeated four times with a different timber floor being constructed and sprayed each time.

7.1.2. Testing facility information and insulation material used

A two component closed cell SPF was sprayed to the interior of a wooden box with a suspended timber floor. The box was placed within a room with a total volume of 39.4m^3 and dimensions of 4m by 4m and height of 2.2-2.4m as per Figure 48.

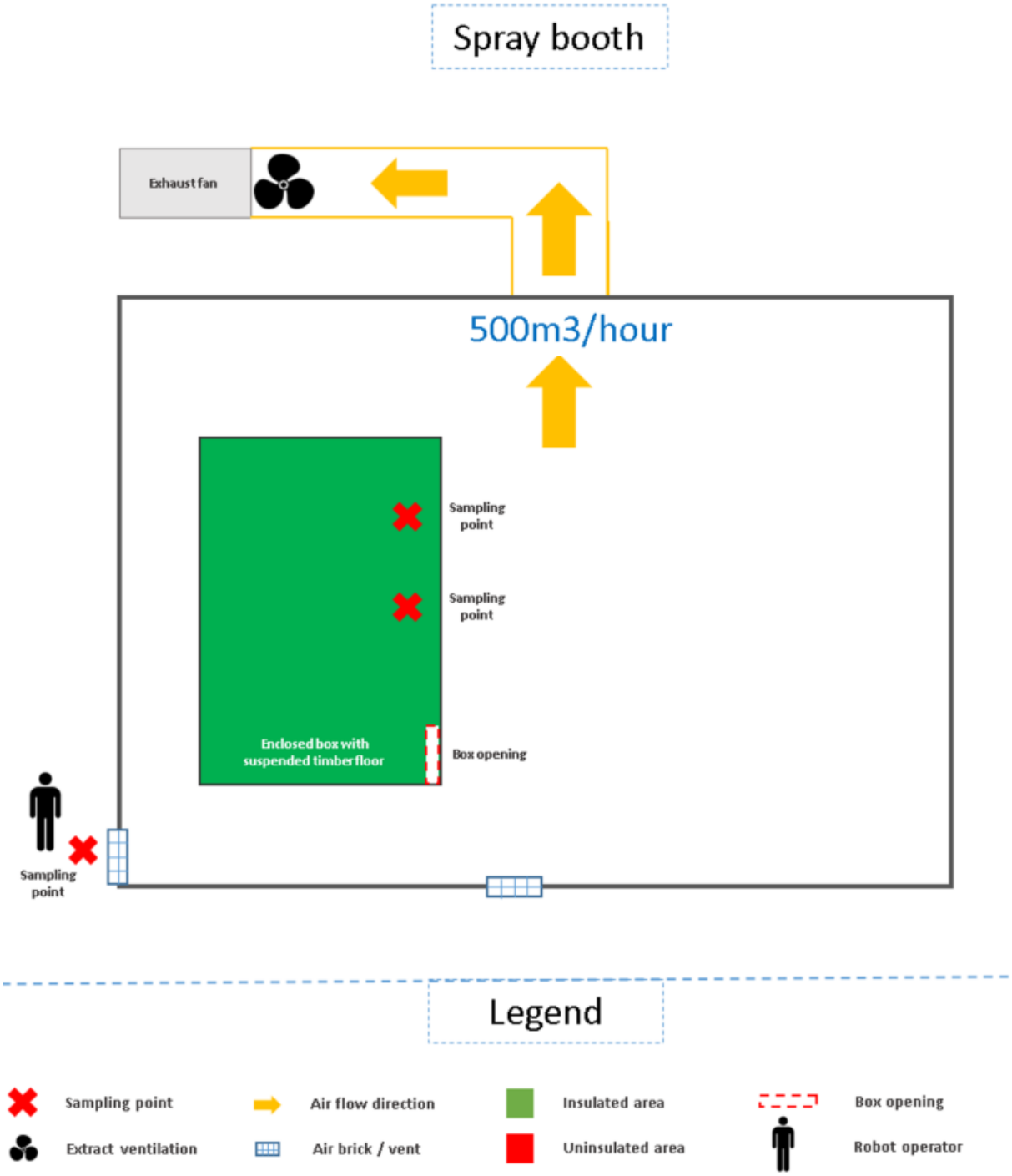


Figure 48. Setup for assessing volatile organic compound emissions levels during SPF spraying in a controlled environment

Samples were collected from inside the box and near the sprayer operating the robot as per Figure 48.

The facility had a radiant heater, however it was turned off during the duration of the experimental work. The room was unheated however the ventilation was controlled. The ventilation rate of the room was controlled through an extract fan located on top of the room, as per Figure 49, that generated negative pressure within the controlled environment.


Figure 49. Setup of controlled room environment (left) and position of measurement for emissions near sprayer (right)

The ventilation rate used for the experiment was 550m^3/h (153 l/s) as per best practice procedures for spraying (Center for Polyurethane Industry, 2012; Poppendieck *et al.*, 2019) and was measured with a Testo 417 anemometer attached to a funnel. This provided an effective air change rate of ~9 ACH during spraying. The ventilation was left running for 48-168h at a rate of 126m^3/h (37 l/s) between experiments to flush out VOCs generated during the spraying and curing of the foam products providing an air change of ~2 ACH between spraying events.

Between each experiment, the timber floor and aluminium foil from the box were replaced with new ones in order to remove organic compounds that deposited on the internal surfaces of the box as per Figure 50. Room air 'flushing' (running the mechanical ventilation for at least 24h) between experiments was also undertaken.


Figure 50.Chamber for measuring emissions during spraying showing the suspended timber floor setup (left) and picture of Inside the chamber (right)

The experimental setup simulates a best practice field study environment:

- an extractor fan is used during the spraying process in order to flush VOC emissions to the outside during the spraying process by creating a negative pressure near the application area (Poppendieck *et al.*, 2019)
- a worker is applying the spray foam remotely through the use of a robot

7.1.3. Product description and target VOCs overview

The SPF used was a two component closed cell spray foam, which contained polymeric methylene diphenyl diisocyanate (pMDI) (side A) and a mixture of polyol and additives (side B). Side B contained a polyol, flame retardants, catalyst and blowing agent. During the application, the two components were heated and mixed using a Graco E-20 hydraulic foam equipment and sprayed through a nozzle attached on a robot. The foam was applied to the underside of the timber floor structure at a thickness of 150mm also covering the floor joists.

The compounds chosen for evaluation and their respective emission criteria are listed in Table 18.

Table 18. Criteria values for chemicals evaluated in this study (all units are µg/m^3)

Chemical	Carcinogenicity (IARC)	CAS Number	EU-LCI	California OEHHA CREL	UK HSE STEL (15-min)	NIOSH REL (30-min)	New Zealand WES (8-hour)	EPA AEGL (10 min)
1,2-DCP	Class 1	78-87-5	n/a	n/a	n/a	n/a	23,100	n/a
1,4-dioxane	Class 2B	123-91-1	400	3000	n/a	3600	n/a	61,000*
Chlorobenzene	n/a	108-90-7	n/a	1000	14,000	n/a	n/a	46,000
Triethyl phosphate	n/a	78-40-0	n/a	n/a	n/a	n/a	n/a	n/a

7.1.4. Analytical method and sampling protocol

All sampling was undertaken using Tenax-TA thermal desorption tubes and low flow SKS 224-PCMTX8 pumps. The concentration of VOCs during spraying (15 min) and curing (10 min) were measured using TD-GC-MS. The short sampling time was selected due to the high amount of VOCs during spraying and to avoid saturation of the sampling tubes. The locations of the pumps were selected to quantify the difference in exposure of the sprayer during manual application compared to when using a robot. The flow rate of a published field study measuring spray foam VOCs was selected (Tian *et al.*, 2018). A flow rate of 0.05 L/min was used to quantify the concentration in the box and 0.2 L/min was used for the worker exposure and background samples. The pumps were calibrated using two clean desorption tubes before each sample was taken. The sampling parameters are shown in Table 19.

Table 19. Sampling and analytical chemistry procedure

Unit	Location	Sampling rate (l/min)	Sampling period (min)			Sampling media
			Background	Spraying	Curing	
Pump #1	Inside box	0.05	30	15	10	Tenax-TA tube
Pump #2	Inside box	0.05		15	10	
Pump #3	Near worker	0.20	30	30		

Background samples of the empty box and the working area of the sprayer were taken between each test. Blank tubes were used between each sample and all consumables were brand new. The pump and tubes near the worker were left running for 30 minutes during the spraying and curing of the SPF occurred. The tubes in the box were replaced by new ones after spraying had finished to measure the concentration of VOCs during curing. After each sampling process, the tubes were closed with long-term storage brass caps (Perkin Elmer Part Number M0413624). The experiment dates and duration are outlined in Table 20.

Table 20. Experiments undertaken during the sample study

Experiment Number	Date	Duration
Experiment #1	31^{sh} October	3 hours
Experiment #2	6th November	2 hours
Experiment #3	9th November	2 hours
Experiment #4	30th November	2 hours

All samples were analysed within 12 hours using the GC-MS. The analytical conditions of as per the methodological chapter (Chapter 5) were used for all analytical runs.

Between each set of sampling tubes (primary and backup), a blank tube was analysed to ensure no contaminants were transferred between samples and the column and TD lines were flushed. Each tube was conditioned at 350 °C at a 150ml/min nitrogen flow for 15 minutes before, and between, each use. All brass storage caps were placed in oven at 150 °C for 24h between experiments. PTFE ferrules inside brass caps were submerged in methanol and cleaned with ultrasonic bath for 15 minutes and placed inside oven at 150 °C for 5 minutes to dry between experiments.

The analytical calibration parameters for each VOC are summarised in Table 3. For each individual VOC, the mass-spectra was retrieved using single-ion-monitoring (SIM). Regression analysis using the calibration curves was used to calculate the concentrations of each VOC in the samples. A Pearson's linear regression (r^2) model for each VOC was developed using OriginPro2017. Linear fit with x-error and Pearson's linear regression (r^2) was used for the calibration points as per Table 21 to calculate the concentration of each VOC in the samples.

Table 21. Analytical calibration parameters for VOCs in TD-GC-MS process

Chemical	1,2-DCP	1,4-dioxane	Chlorobenzene	TEP
Desorption efficiency	99% ± 0.97%	99% ± 1.67%	99% ± 1.23%	100% ± 1.82%
Linear regression (r^2)	0.985	0.986	0.989	0.991
Calibration points	21	21	21	21
Calibration range (ng)	45-13800	49-9272	54-9720	44-8341
Limit of detection [3](ng)	28	42	17	119

[3] Code of Federal Regulations, Definition and procedure for the determination of the method detection limit – Revision 1.11. In 2003; Vol. CFR 40, Ch. 1, Pt. 136

7.1.5. Environmental conditions

The temperature and relative humidity in the testing room were recorded using a HOBO data logger with a reporting resolution of 1 minute. The logger was calibrated by the manufacturer before use and had a declared accuracy of ±0.21°C (temperature) and ±2.5% (RH). Figure 51 shows the ambient conditions during all studies, which were within the recommended ranges as per spray foam best practice application.

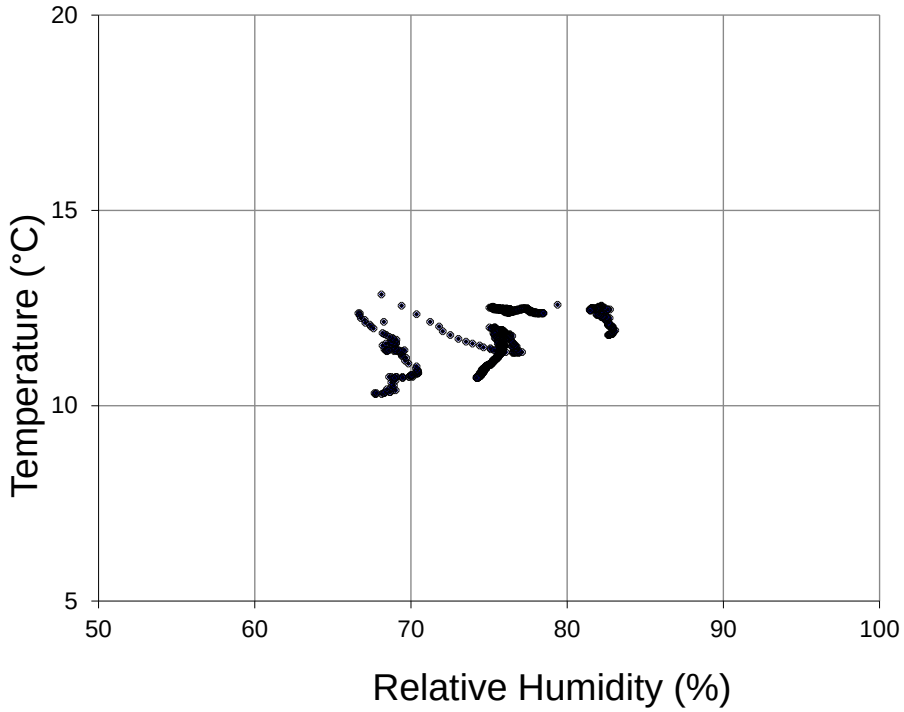


Figure 51. Ambient application conditions during sampling

7.2. Results

No breakthrough over the detection limits occurred during the sampling process meaning all results were quantifiable.

All concentrations in the background samples (box and sprayer area) and the worker area were below the detection limits for all experiments.

Figures 52-55 show the concentration of the four VOCs in the spray box during spraying and curing.

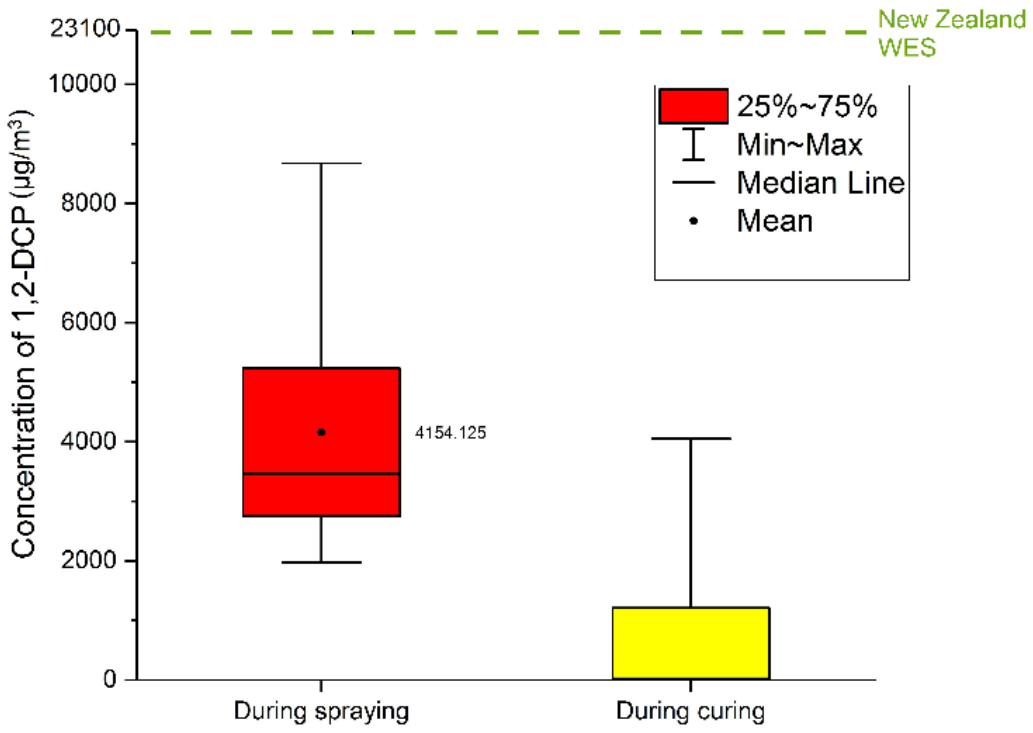


Figure 52. Concentration of 1,2-DCP (µg/m³) in air in the control box during spraying and curing. During curing 62.5% of the samples (n=5) were below detection limits therefore mean was not calculated.

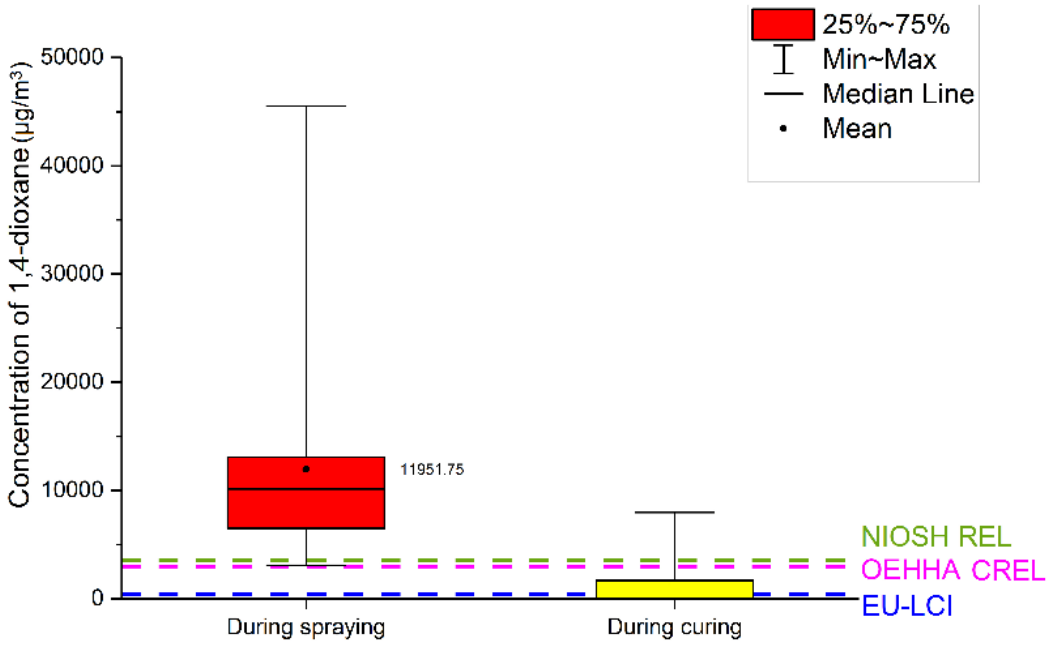


Figure 53. Concentration of 1,4-dioxane (µg/m³) in air in the control box during spraying and curing. During curing 75% of the samples (n=6) were below detection limits therefore mean was not calculated.

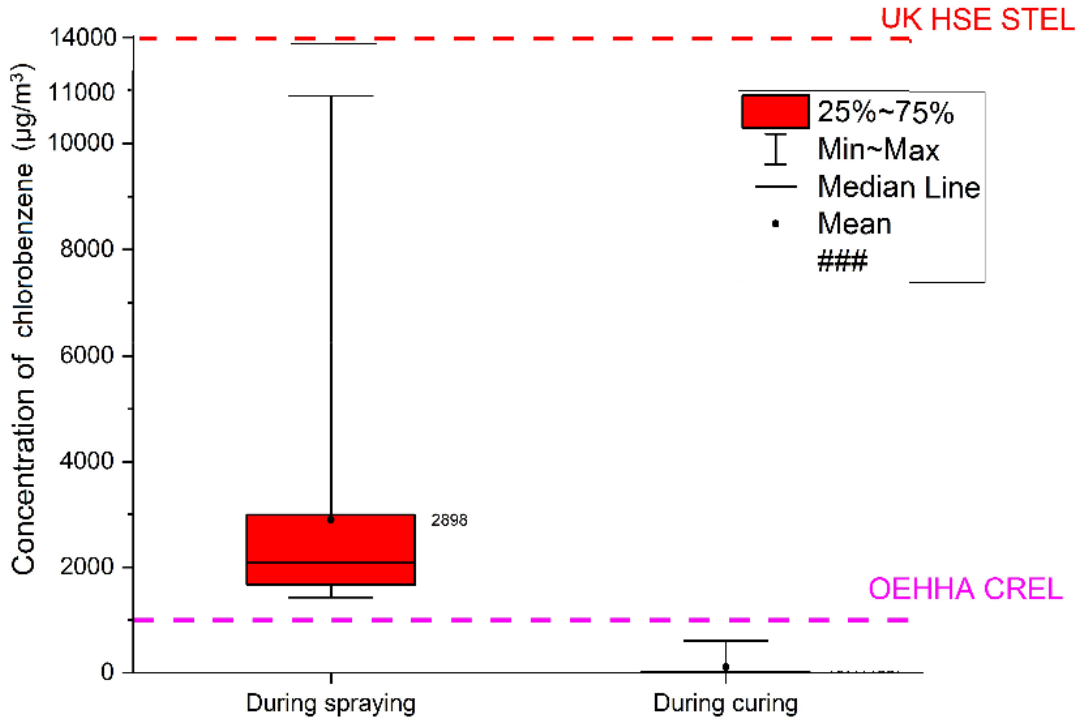


Figure 54. Concentration of chlorobenzene (µg/m^3) in air in the control box during spraying and curing. During curing 75% of the samples (n=6) were below detection limits therefore mean was not calculated.

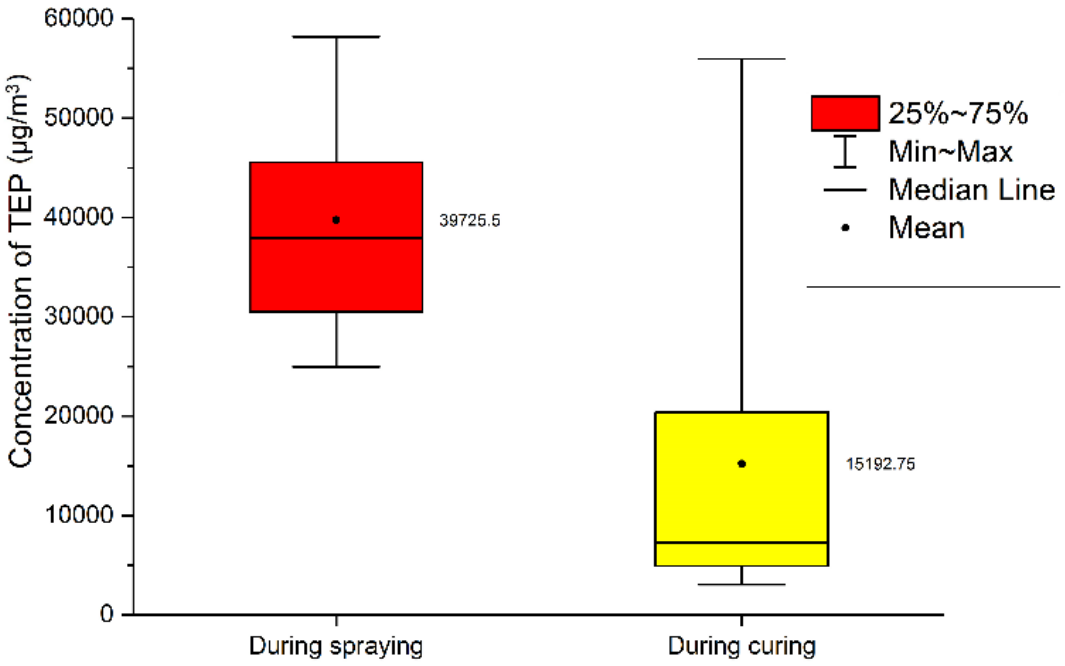


Figure 55. Concentration of TEP (µg/m^3) in air in the control box during spraying and curing. All concentrations were above detection limits

The concentration of the three compounds that were not present in the safety data sheets (1,2-DCP, 1,4-dioxane and chlorobenzene) decreased exponentially after spraying stopped in the spray box (Figures 60-63).

The 1,2-dichloropropane concentration in the box did not exceed the New Zealand workplace exposure standards (WES) value during spraying (Figure 54).

The 1,4-dioxane concentration exceeded the NIOSH REL, OEHHA CREL and EU-LCI values, whilst the chlorobenzene concentrations exceeded the OEHHA CREL values during spraying (Figure 55 and 56).

The flame retardant (TEP) concentration decayed after spraying had finished, however was still present in measurable concentrations during the curing process as per Figure 57.
All four VOCs within the spraying area were below the recommended maximum exposure values during the curing process.

These results outlined the potential for utilising robots in reducing people's exposure to SPF emissions during spraying. However to validate the results, a case study was required to understand whether the results in a controlled environment were representative of a real environment.

7.3. Summary

This chapter provided evidence in relation to R.Q.3. "What are the short and mid-term concentrations of VOCs from spray foam materials in controlled conditions?". Specifically, the chapter presented evidence how using robots could reduce exposure of workers to volatile organic compounds during spray foam application.

A facility mimicking real life application environment with a suspended timber floor was constructed and retrofitted with spray foam. The ventilation rate of the room was controlled providing 9 ACH during spraying events and 2 ACH post-spraying events. Four VOCs of interest were measured and the experiment was repeated four times in order to provide statistically significant results.

During the spraying and curing of the foam, the VOC concentrations for the four compounds near the spraying surface (next to the robot) varied between 2000-59000 $\mu g/m^3$. During curing, the ranges next to the robot were much lower between 44-9900 $\mu g/m^3$ with the exception of the flame retardant. The flame retardant emissions decreased during curing, however the maximum levels recorded in some tubes were comparable to levels during curing.

The findings demonstrated that in a controlled environment, a reduction in VOCs is observed. However to validate the efficiency of ventilation as a mitigation in a real environment, a case study building was tested longitudinally.

8. Occupational exposure to PU emissions (field case study)

This chapter presents the analysis and results from a field study where ventilation was tested as a mitigation strategy for reducing VOCs during spraying and curing.

Long-term VOC concentration measurements were undertaken in an occupied house in London. The measurements covered pre-installation, during installation and post-installation concentrations for up to 2 months after the house was retrofitted. The chapter outlines the method, sampling procedure and spraying log. Then the results for the four VOC compounds that were measured in the controlled facility, as presented in the previous chapter, are presented. Where the VOCs were found in measurable concentration, they are compared to the controlled facility concentrations providing original evidence of emissions occurring in-situ in real environments.

A second case study was also tested with measurements in an occupied house several months after the foam was installed. However due to problems with the analytical chemistry software, the results could not be used for the purposes of this thesis as described in the chapter. This problem is described in the end of the chapter.

8.1. Method

8.1.1. Method overview

For both case studies, the same analytical procedure (TD-GC-MS) as per Chapter 5 was used to analyse the volatile organic compounds. Both Tenax-TA and spray foam specific TD tubes (ASTM International, 2017b) were used in order to measure emissions in-situ during and post-application of the spray foam.

8.1.2. Case study overview

The case study was a two-storey terraced house in London. The front part of the house (living room and corridor) had a suspended timber floor and was insulated. The crawlspace had a full ceiling height underneath the staircase, however underneath the living room the crawlspace height was less than 1 meter. Figure 56 outlines the setup of the field study.

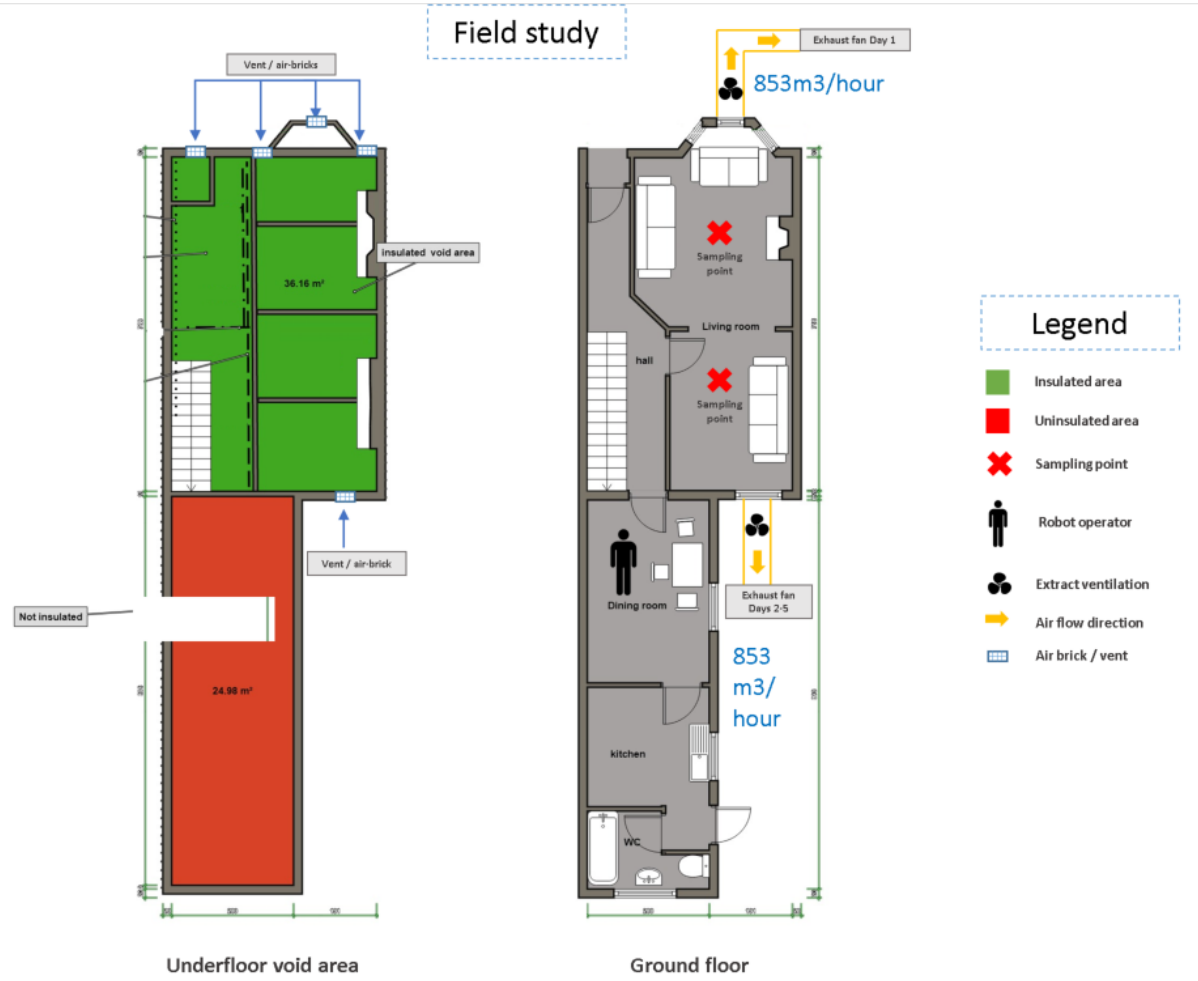


Figure 56. Outline of the experimental protocol for the long-term case study

8.1.3. Sampling procedure

All tubes used were brand new purchased from Markes International: Tenax TA (part number: C1-AAXA-5003) and spray foam specific desorption tubes - Tube A and Tube B (ASTM International, 2020).

Brand new plastic tubing connecting the analytical and backup desorption tubes were used for every pair of sampling tubes. After collection was finished, the long-term brass caps were tightened with wrenches and each set of 2 tubes were labelled and individually wrapped in aluminium foil. At the end of the sampling period, all tubes were placed in a freezer at 4 °C for a maximum period of 9 days before analysis with the GC-MS. Once tubes were taken out of freezer, they were immediately placed on the TD carrousel and analysed using Method B. A spiking experiment using SPF standard solution was done to compare whether any degradation occurs when keeping tubes in freezer and in long-term storage caps. Through experimental testing, it was found that no degradation was found when keeping the sample for a period of up to 3 weeks in the freezer. This meant that even when the samples were analysed in the GC-MS 9 days after collection, the VOC amount in the tubes did not decrease due to escaping from the TD tubes.

Extraction tubes were placed at a height of ~75 cm as per Figure 57.

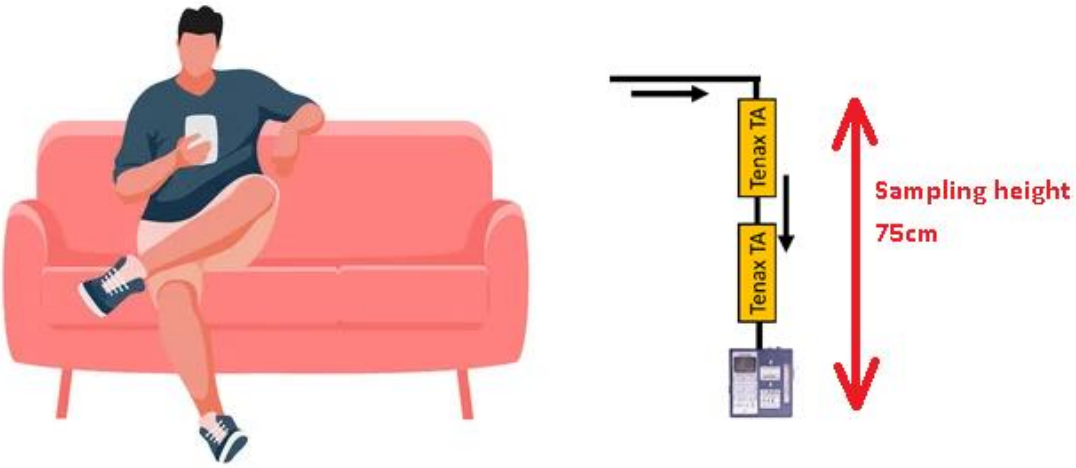


Figure 57. Sampling procedure for active VOC extraction in the field study.

This height is considered to be representative of the breathing height for people sitting on couches in their living room. This height was selected to mimic the inhalation exposure of people to VOCs.

Two locations were selected in the living room to check whether there was spatial distribution of VOCs within the room . One sampler was placed closer to the window and above the carpet. The other was placed in the middle of the living room where there was no carpet. The extraction rate was 0.1L/min and all pumps were calibrated prior to each site visit.

Spray foam was installed under the whole floor via robotic installation. The house had a small attic underneath the corridor providing access to the underfloor void underneath the living room. Manual application of spray foam would have been impractical due to the small void area underneath the living area. Without the use of a robot, it may have been necessary to remove the floorboards in order to retrofit the suspended timber floor. Duplicate tubes were used for measuring difference in spatial distribution. This was considered important as carpets are known sinks for volatile organic compound emissions and it was expected they would therefore adsorb VOCs (Elkilani *et al.*, 2003). The sampling log is outlined in Table 22 below.

Table 22. VOC collection log for long-term case study.

Tube #	Location	Sampling medium	Sampling period
1. Background Analysis	Front space of living room	Tenax-TA	60 min
2. Background Backup	Front space of living room	Tenax-TA	60 min
3. Background Analysis #2	Middle of living room	Tenax-TA	60 min
4. Background Backup #2	Middle of living room	Tenax-TA	60 min

5. During spraying analysis	Front space of living room	Tenax-TA	60 min
6. During spraying backup	Front space of living room	Tenax-TA	60 min
7. During spraying analysis	Middle of living room	Tenax-TA	60 min
8. During spraying backup	Middle of living room	Tenax-TA	60 min
9. During spraying afternoon analysis	Front space of living room	Tenax-TA	60 min
10. During spraying afternoon backup	Front space of living room	Tenax-TA	60 min
11. During spraying afternoon backup	Middle of living room	Tenax-TA	60 min
12. During spraying afternoon backup	Middle of living room	Tenax-TA	60 min
13. 18hr after spraying stopped	Front space of living room	Tenax-TA	60 min
14. 18hr after spraying stopped	Front space of living room	Multi-sorbent ASTM	60 min
15. 18hr after spraying stopped	Middle of living room	Multi-sorbent ASTM	60 min
16. 18hr after spraying stopped	Middle of living room	Tenax-TA	60 min
17. During spraying day 2	Front space of living room	Tenax-TA	65 min
18. During spraying day 2	Front space of living room	Tenax-TA	65 min
19. During spraying day 2	Middle of living room	Tenax-TA	65 min
20. During spraying day 2	Middle of living room	Tenax-TA	65 min
21. 1hr after spraying of day 3 completed	Front space of living room	Multi-sorbent ASTM	60 min
22. 1hr after spraying of day 3 completed	Front space of living room	Tenax-TA	60 min
23. 1hr after spraying of day 3 completed	Middle of living room	Multi-sorbent ASTM	60 min

24. 1hr after spraying of day 3 completed	Middle of living room	Multi-sorbent ASTM	60 min
25. 24hr after spraying of day 3 completed	Front space of living room	Multi-sorbent ASTM	63 min
26. 24hr after spraying of day 3 completed	Front space of living room	Multi-sorbent ASTM	63 min
27. 24hr after spraying of day 3 completed	Middle of living room	Multi-sorbent ASTM	63 min
28. 24hr after spraying of day 3 completed	Middle of living room	Multi-sorbent ASTM	63 min
29. 48 hr after spraying of day 3 completed	Front space of living room	Tenax-TA	60 min
30. 48 hr after spraying of day 3 completed	Front space of living room	Tenax-TA	60 min
31. 48 hr after spraying of day 3 completed	Middle of living room	Tenax-TA	60 min
32. 48 hr after spraying of day 3 completed	Middle of living room	Tenax-TA	60 min
33. 72h after spraying completed	Front space of living room	Multi-sorbent ASTM	60 min
34. 72h after spraying completed	Front space of living room	Tenax-TA	60 min
35. 72h after spraying completed	Middle of living room	Tenax-TA	60 min
36. 72h after spraying completed	Middle of living room	Tenax-TA	60 min
37. 1 week after spraying completed	Front space of living room	Multi-sorbent ASTM	55 min
38. 1 week after spraying completed	Front space of living room	Tenax-TA	55 min

39. 1 week after spraying completed	Middle of living room	Tenax-TA	55 min
40. 1 week after spraying completed	Middle of living room	Tenax-TA	55 min
41. 2 weeks after spraying completed	Front space of living room	Multi-sorbent ASTM	60 min
42. 2 weeks after spraying completed	Front space of living room	Tenax-TA	60 min
43. 2 weeks after spraying completed	Middle of living room	Tenax-TA	60 min
44. 2 weeks after spraying completed	Middle of living room	Tenax-TA	60 min
45. 1 month after spraying completed	Front space of living room	Tenax-TA	64 min
46. 1 month after spraying completed	Front space of living room	Multi-sorbent ASTM	64 min
47. 1 month after spraying completed	Middle of living room	Tenax-TA	64 min
48. 1 month after spraying completed	Middle of living room	Tenax-TA	64 min
49. 2 months after spraying	Front space of living room	Multi-sorbent ASTM	60 min
50. 2 months after spraying	Front space of living room	Multi-sorbent ASTM	60 min
51. 2 months after spraying	Middle of living room	Multi-sorbent ASTM	60 min
52. 2 months after spraying	Middle of living room	Multi-sorbent ASTM	60 min

The spraying equipment (computer) was located in the middle of the kitchen and one person was sporadically sitting in the living room during the duration of the spraying to observe the spraying process. To warm the spray foam a diesel generator was used on-site, however this was placed outside the dwelling.

The extract fan, used during spraying and curing, was connected to the front air brick and the extract ventilation was set at a rate of 1700 m^3/hr. There was a G4 filter fitted in the extractor fan following which the emissions were dispersed on the street. The measured extraction speed in-situ behind the air-bricks was 6.34 m/s using a Testo 417 flow meter. Accounting for the size of the air brick, the actual extraction flow rate occurring was calculated to be around 853 m^3/hr (CIBSE, 2016), however this could vary depending on how well the extractor was fitting to the wall at any given stage. It was observed that on occasion the extractor would slightly tilt away from the air brick and therefore the airflow was reduced.

8.1.4. Environmental conditions

The temperature and relative humidity were recorded using a range of data loggers with a reporting resolution of 15 minutes. The logger data recorded the temperature of various locations in the case study for a period of 1 year up the point of retrofit. Figure 58 shows the ambient conditions before spraying outlining the overall difference in temperature in the various locations of the house.

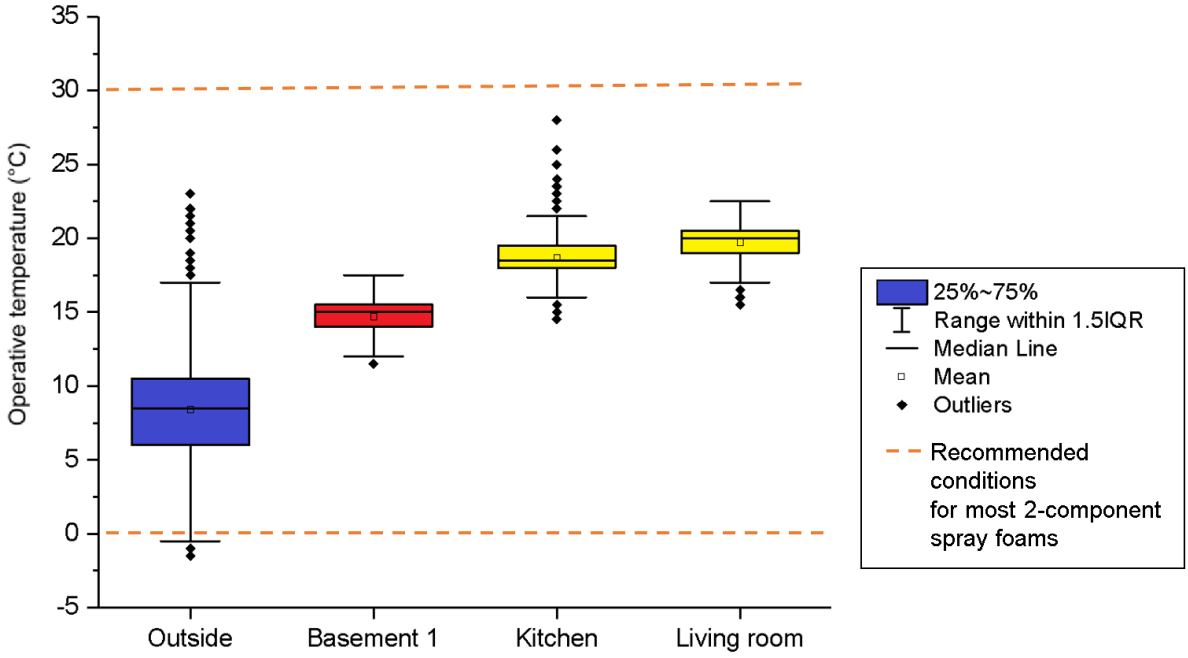


Figure 58. Temperature in the case study prior to insulation being installed. Boxplots based on monitoring of temperature for a period of 12 months with a reporting resolution of 15 minutes.

Logger data was not retrieved post-installation and analysed as part of this thesis. However as Figure 58 outlines both prior, and immediately during the installation, the temperature was well within the recommended range of manufacturers recommendations.

8.1.5. Spraying log

Day 1

Spraying started at 13:30 and stopped at 15:15. Extraction fan was started at 13:00 and stopped at 15:30 and placed on front air vent with dimensions (W22cm x H17cm). The front door was open from 09:00 to 16:30-17:00, following which was closed from 17:00 (25.02.19) - 08:30 (26.02.19). All windows were closed during spraying and curing. Apart from airbricks, no other ventilation was provided. Half of the floor was insulated during day 1 (25.02.2019): the front half of the living room facing the street up until where Pump #2 was located. Tubes #1-#12 were closed with long-term storage brass caps and individually wrapped in aluminium foil. The twelve tubes were then wrapped in parafilm and placed in a freezer at 4 °C at 18:00 (2-4 hours after collection). Carpet and furniture were not removed during spraying, however all furniture in the living room was wrapped in plastic sheets including placing covers on the floor areas that were being sprayed from underneath.

Day 2

The extraction fan started at 10:15 and stopped at 16:00 (extractor had slipped of the vents, so actual extraction rate could have been lower during that period. The extractor was then placed on rear air vent with dimensions (W22cm x H17cm), which was closer to the area being sprayed. Spraying started at 11:30 and stopped at 15:10. The front door was open from 08:30-17:00 and the living room door was closed during spraying. The extraction fan had slightly fallen off from the wall between 12:00 and 13:00 and it was later connected back to the air brick.

Day 3

The extraction fan started at 10:00 and stopped at 14:10. It was placed on the rear air vent. Spraying started at 10:45 and stopped at 13:10. The front door was open from 08:30-17:00. Spraying finishing touches were done mostly manually. The floor was completed as well as the wall of the basement beneath the stairs. The living room door was open during the day and closed during the night.

Day 4

No “fishy” smell was detected by the researchers, sprayers or occupiers during or after spraying. The living room door was closed during the day and night for most of the time as reported by the occupiers.

8.2. Results

First, the results during spraying are presented.

8.2.1. Concentrations during spraying

For each compound, they are plotted against concentrations found in the controlled conditions (near the spraying area) as outlined in Chapter 7. This allows a comparison of the concentration near the spraying surface and inside the case study during installation.

In the case of 1,2-DCP, 1,4-dioxane and chlorobenzene, no results are provided as for the case study no concentrations above the LOQ or LOD were detected. The implications of this finding are further explored in the discussion.

Triethyl phosphate, which acts as a flame retardant, was detected in the air samples. All 6 samples recorded a concentration above the limit of detection for triethyl phosphate, however the results were below the limit of quantification. There is an international consensus on the definition of "lower limit of quantification", however there is not an agreed international method to calculate quantification limit (Hempel, 2020). If a different methodology was used to calculate the LOQ for this methodology, then the same results could have been deemed "quantifiable". For this reason they are reported in Figure 59.

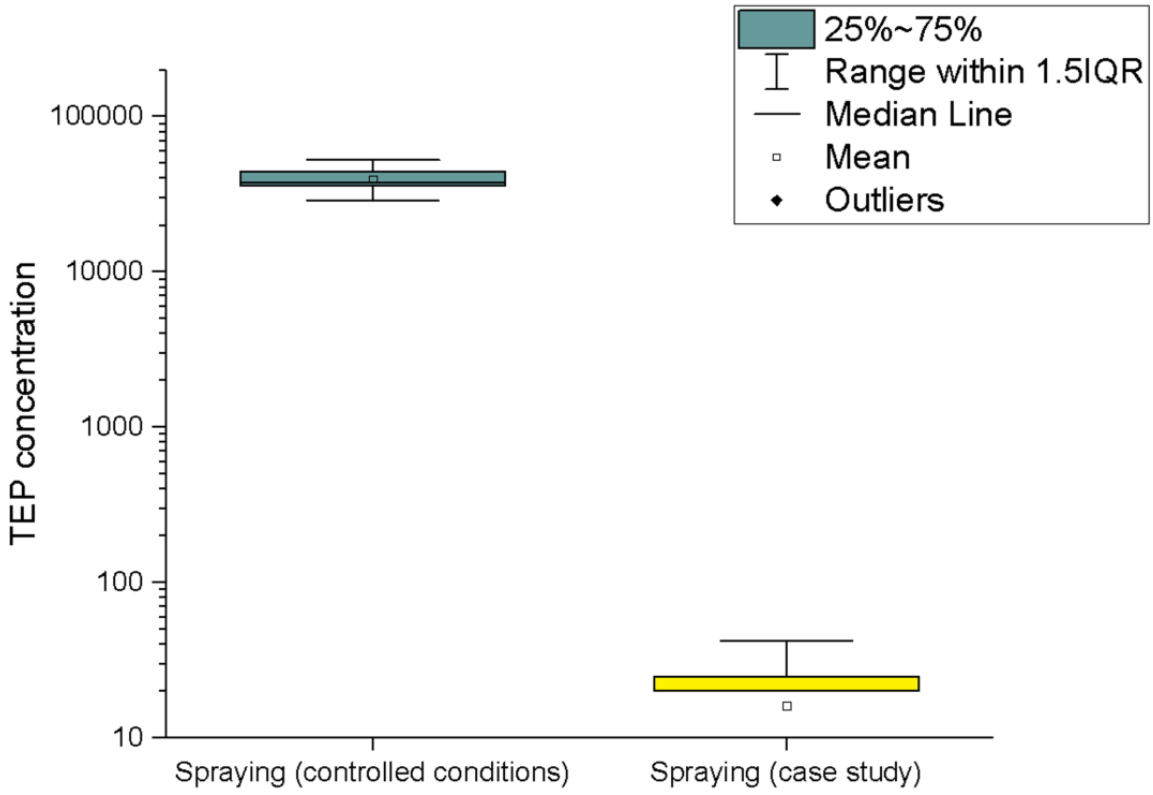


Figure 59. TEP concentration (µg/m^3) during spraying – comparison between concentration near spraying equipment (controlled conditions) and a living room (case study). Scale is logarithmic.

Second, the results during curing are presented.

8.2.2. Concentrations during curing

Whilst curing times vary, in this case the curing period was considered up to 24 hours after the final spraying (day 3) had concluded. It should be noted that for two out of the four samples in the case study (#23,#27) breakthrough occurred into the backup tube. Figure 60 plots the 1,4-dioxane concentration during curing comparing the experimental results in controlled conditions from Chapter 8 and the field study data.

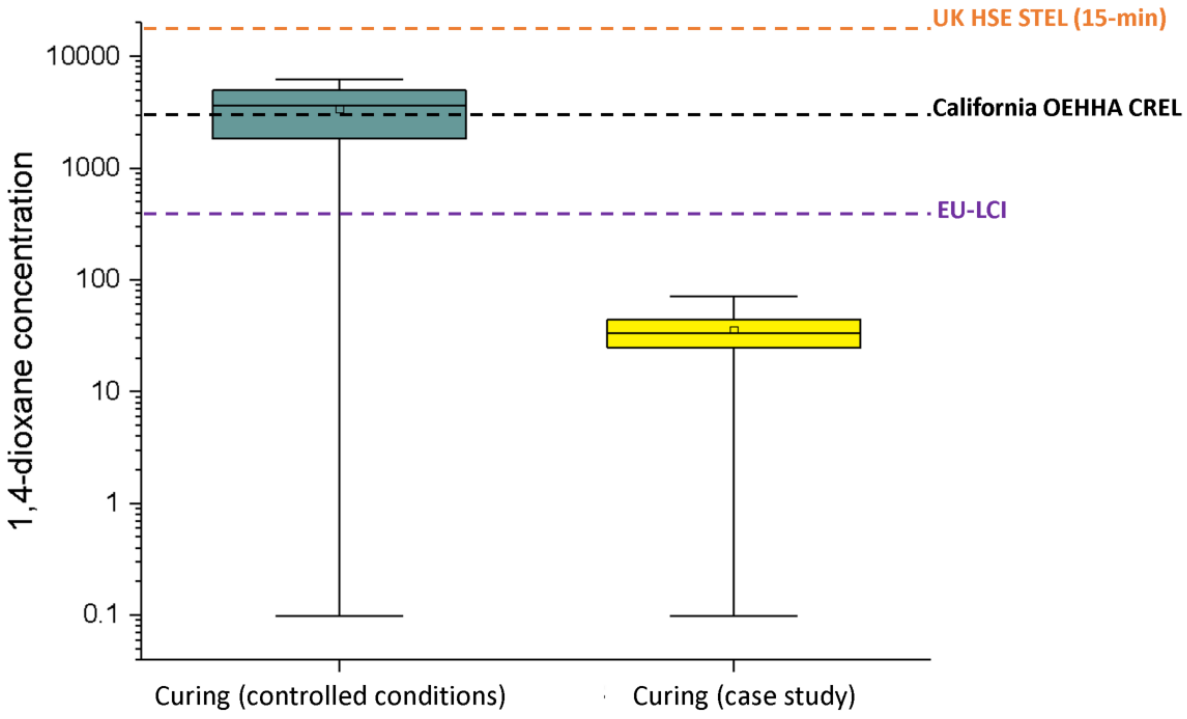


Figure 60. 1,4-dioxane concentration (µg/m³) during curing – comparison between concentration near spraying equipment (controlled conditions) and a living room (case study at 1 and 24 hours). Scale is logarithmic.

Thirdly, the results post-installation are presented.

8.2.1. Concentrations during occupation

In the case of 1,2-DCP, 1,4-dioxane and chlorobenzene, no results are provided as for the case study no concentrations above the LOQ or LOD were detected. For triethyl phosphate the results are plotted in Figure 61.

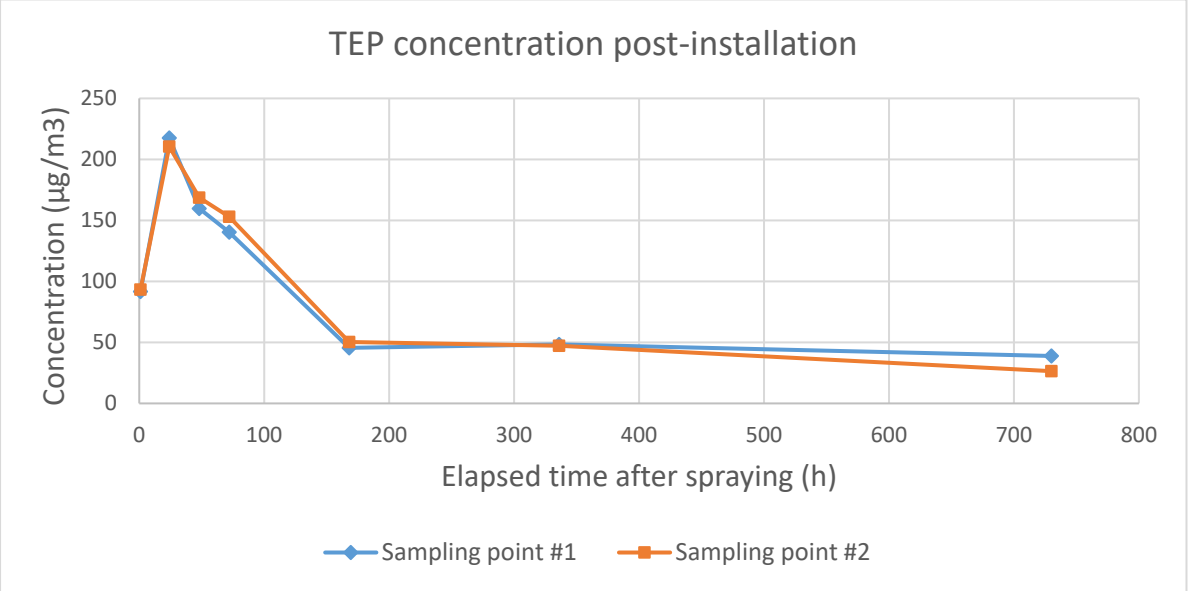


Figure 61. TEP concentration (µg/m^3) in retrofitted room during occupation

8.2.2. Troubleshooting and error messages

Due to a GC-MS software error, the data beyond month 2 after installation and second case study data could not be accurately assessed quantitatively or qualitatively. When assessing mass spectra utilising the NIST library, all the detected peaks were consistently appearing however all detected ions were appearing wrongly. The error appeared systematic as for all scanned peaks the result occurred with an error of 1 ion. Instead of the highest peak of a compound being 63 for example, the system was showing 62 instead.

Software reinstalling, column cleaning, tube cleaning, GC-MS settings reset and other troubleshooting method as per the TD-GC-MS handbooks were trialled. The problem was not resolved and at that stage of the experimental process, a new TD-GC-MS system was commissioned for undertaking further experiments. The two raw datasets, with data from 2 months after installation of the first case study and the second case study, could therefore not be used for the purposes of this thesis. The reason why they were not used as mass spectra is used for both quantification and detection of compounds in the NIST library. Without the system operating as expected, the results were unfortunately unusable.

8.3. Summary

This chapter presented results from a field study where ventilation was tested as a mitigation strategy for reducing VOCs during spraying and curing.

Long-term VOC concentration measurements were undertaken covering pre-installation, during installation and post-installation concentrations for up to 2 months after the house was retrofitted. Out of the four VOCs measured, only the flame retardant was detectable in the air longer than 24 hours after the retrofit was completed. The flame retardants were detected throughout the observation period with the concentration gradually decreasing over time with a steady state observed after 168 hours.

From the other three VOCs (1,4-dioxane, 1,2-DCP and chlorobenzene), only 1,4-dioxane was experimentally observed in the dwelling in some of the sampling tubes. However the concentration in the field study was a magnitude lower compared to the concentration during curing in the controlled experiment. Chlorobenzene and 1,2-DCP were not observed experimentally during spraying or curing in the field study.

This chapter provided experimental evidence of B-side and by-product emissions in a real environment where ventilation was deployed as a mitigation strategy for reducing VOC concentrations during spraying. To bring together the original work in this thesis, the next chapter outlines the significance of the results within the context of the existing literature.

9. Discussion

9.1. Retrofit potential

The collective evidence from this chapter addressed the research question and provided original evidence outlining there are millions of buildings with no insulation in their floor in the UK. Chapter 4 combined energy data, social research data and policy data analysis critically outlining the growing market penetration of floor installations and intent from people to adopt this retrofit measures. Modelling data shows that energy usage of a dwelling could be reduced by 12% when insulating the floor (Ji, Lee and Swan, 2019), however in this study the floor insulation was applied sequentially after other retrofit measures. However in-situ measurements demonstrate heat loss of floors could be reduced by up to 92% and whole house heating demand by up to 24% (Pelsmakers, Croxford and Elwell, 2019; Glew et al., 2020). The original analysis presented in Chapter 4 coupled with modelling and field study data demonstrate the potential for this measure in improving the existing UK building stock. Previous analysis estimated that by insulating all suspended timber floors in the UK, the carbon savings equivalent to the annual emissions of nearly half the NHS building stock (Element Energy, 2013; NHS, 2022). Energy and carbon savings estimations on a building stock level should be however critically examined as they are subject to large degree of uncertainty due to the underlying assumptions: thermal envelope data, variability in performance in-situ and difference on people's building usage behaviour (Domínguez-Muñoz *et al.*, 2010; Azar and Menassa, 2012; Loucari *et al.*, 2016; Imam, Coley and Walker, 2017; Jenkins, Simpson and Peacock, 2017; Marshall *et al.*, 2017; Taylor, Symonds, *et al.*, 2018).

Underfloor installations are often not taken up by consumers due to a combination of inconvenience, impact on heritage, cost and disruption to their activities (Mallaband, Haines and Mitchell, 2013; Sunikka-Blank and Galvin, 2016; Bobrova, Papachristos and Cooper, 2022). However, the use of robots and spray foam overcomes a lot of these consumer barriers (Historic England, 2016; Sunikka-Blank and Galvin, 2016; Department for Business Energy & Industrial Strategy, 2020b). Chapter 4 outlines a recent increase in underfloor installations, which correlates well with the emergence of robots as a retrofit tool.

Whilst no causal relationship was observed between rising energy prices, climate change attitudes and underfloor insulation retrofits, these factors are expected to further increase adoption of this retrofit measures (Ascione, De Rossi and Vanoli, 2011; Webber, Gouldson and Kerr, 2015; Trotta, 2018; Schleich, 2019).

Chapter 4 outlined the significant energy efficiency potential of suspended timber floor insulation applied via robots. Millions of UK homes have uninsulated floors and there are measurable savings that could be achieved on a building stock level. Application via robots may reduce one of the main barriers for occupiers retrofitting their floors – disruption. Due to the innovative nature of the technology, there is however limited evidence on cost comparison, and market adoption, between traditional and innovative floor retrofits. This is

also understandable as Chapter 4 outlined that whilst millions of homes have suspended timber floors, the overwhelming majority of those have not been insulated so far. The potential of robots to solve the inconvenience and disruption barrier by applying spray foam raised the importance of exploring VOC emissions as previous research has suggested retrofits could have unintended consequences on indoor air quality (Shrubsole *et al.*, 2014).

9.2. Method development

This thesis presented original evidence in relation to method development for analysing VOCs emitted from spray foams. Two methods were presented in Chapter 4: Method A focusing on Side A emissions (isocyanates and their derivatives) and Method B focusing on Side B emissions and by-products.

Method A evidence demonstrated that a novel laboratory method for analysing isocyanates (Ferreira *et al.*, 2014) could be successfully applied for measuring emissions from spray foam materials. The experimental results of Method A correlated well with previous literature findings that isocyanates rapidly transform and form polyurethane links, however due to the elevated airborne isocyanate levels short-term exposure risks exist for sprayers and workers (Crespo and Galán, 1999a; IARC, 1999; Rosenberg *et al.*, 2002; Bello *et al.*, 2004, 2017, 2018; Lesage *et al.*, 2007b; Mellette *et al.*, 2018). The experimental results from the box experiments reaffirmed existing literature findings (Crespo and Galán, 1999a; Bello *et al.*, 2004, 2019; Lesage *et al.*, 2007b) that isocyanate emissions are a significant risk factor for workers during spraying spray foam products. If improper health and safety procedures are not put in place during spraying foam insulation, workers could be 'sensitised' and develop 'isocyanate-asthma' and there has been an instance in the medical literature of overexposure to isocyanate leading to an asthma attack and resulting in the death of a foundry worker (Wisnewski *et al.*, 2022). Robots offer a great opportunity to reduce isocyanate related exposure during spraying, however they do not completely remove the need for personal protective equipment and it remains important during the operational cycle of handling, spraying and working with chemicals such as isocyanate.

Whilst Method A offered promising scientific results, its performance was not compared to well-established methods such as the ISO 17736:2010. The difference with existing methods was that the Ferreira (2014) method allowed for both 4,4-MDI and 4,4-MDA to be measured simultaneously. As 4,4-MDA is the result of hydrolysis of 4,4-MDI, the Method A results experimentally tested whether 4,4-MDA occurs when spray foam isocyanates reacts with moisture in the air during spraying. No 4,4-MDA was recorded during spraying, which correlates well with previous hypothesis that 4,4-MDA is not expected to be formed under typical environmental conditions found indoors (Neuland *et al.*, 2021). For this reason, this thesis did not explore long-term 4,4-MDA emissions as they are not typically expected during the lifecycle of spray foam in indoor dwelling environments (Dahlin, 2007; Neuland *et al.*, 2021; Schupp and Plehiers, 2022).

As presented in Chapter 2, the literature clearly outlined that whereas there were hundreds of scientific publication related to Side A (isocyanates) exposure, there were only a handful

of peer-reviewed articles in relation to spray foam B-side and by-product emissions. A compendium of 13 studies in support of the development of an ASTM standard for measuring emissions in microchambers almost exhaustively summarised the scientific knowledge in relation to spray foam B-side and by-product emissions (ASTM International, 2017c). The ASTM method, under development in 2017-2020, focused on micro-chamber emissions from cured products and therefore very low concentrations. For the purposes of this thesis a novel method (Method B) was developed that could be applied for measuring emissions from spray foam during the whole lifecycle of the product (spraying, curing and in-situ after installation).

Method B found its origins, and principles, in the heritage science field where practitioners measured emissions from museum polyurethane objects. For Method B four organic compounds were prioritised, which represented <12.5 of the weight of the raw products. The reason for selecting these particular organic compounds were two-fold and explained in detail in Chapter 2: by-products (1,2-DCP, chlorobenzene,1,4-dioxane) were prioritised due to their impact on health and flame retardants due to their growing scientific importance.

Flame retardants are currently a widely debated area within the scholarly, policy and industry fields. They are ubiquitous in indoor environments emitted from a variety of consumer and construction products, however there are on-going debates whether the fire safety prevention benefits outweigh the chemical exposure risks and long-term impact on health (D Shaw *et al.*, 2010; McKenna and Hull, 2016; Boor *et al.*, 2017; Sugeng *et al.*, 2018). The built environment domain has focused on indoor air quality as a priority area in recent years with its growing importance particularly prominent during the COVID-19 pandemic (Cakmak *et al.*, 2014; Shrubsole *et al.*, 2014; Taylor, Liu, *et al.*, 2018; Domínguez-Amarillo *et al.*, 2020; Morawska *et al.*, 2020). The original work leading to the development of Method B provides a repeatable, reproducible method that could be deployed for calculating VOC concentrations in raw materials, during spraying, curing and post-application in case studies. Method B allows quantification of some of the VOCs down to 45 ng. In practice, this means that in 1L of extracted air, the lowest detectable quantity of those VOCs was down to 0.045 ppb. This level of sensitivity and precision is important when measuring pollutants for which there may be no “safe” exposure limits. The final part of Chapter 5 presented the performance between the published ASTM method and Method B. It outlined experimentally why Method B is more suitable for field study measurements given its higher limits of quantification, which allow longer sampling times in-situ.

Given the success of the method development, it was therefore possible do use Method B for measuring emissions in both controlled conditions and in-situ.

9.3. Short term VOC concentrations in raw materials and during spraying

Thirteen foams were tested in controlled conditions during spraying as presented in Chapter 6. These represented the majority of spray foam products available to consumers at the time of testing. 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, which has been re-designated as a Class 1 carcinogen in

2014. 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 in Chapter 6 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

I only sampled the raw material of one product in this study, therefore the second and third plausible routes could not be excluded with definitive 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) (Agency for Toxic Substances and Disease Registry, 1999), it is plausible that 1,2-DCP could have been used for the production of other isocyanates as well – such as the ones used in spray foams (pMDI). However, the raw material (side B) tested in this study did not report to contain pMDI according to the safety data sheet and experimental data in this study presents that 1,2-DCP was present. This experimental 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 some evidence for 1,2-DCP emissions from cured spray foam products (Sebroski *et al.*, 2012; Poppendieck *et al.*, 2016; Nie, Kleine-Benne and Thaxton, 2017; Sleasman, Hetfield and Biggs, 2017) , from 6-10-month old SPF samples collected from insulated houses (Huang and Tsuang, 2014) and separately being present in the air in refurbished residential units (Liang, 2020). The collective evidence demonstrates 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 spray foam product lifecycle (spraying, application, curing, use). It is reported that the main uses for 1,2-DCP are as a solvent, textile spot remover or formerly as soil pesticide (Agency for Toxic Substances and Disease Registry (ATSDR), 2019) however it is unclear whether it could serve a functional service during spray foam production.

Strategies for reducing human exposure to VOCs from spray foam products during application could be to: wear personal protective equipment (PPE) (Bello *et al.*, 2018) and to provide extract ventilation that negatively pressurises the spraying area (Poppendieck *et al.*, 2019). If my alternative hypothesis is conclusively proven with further testing, removing the 1,2-DCP at the source would be the optimal strategy following World Health Organisation (WHO, 2010) and Public Health England (Public Health England, 2019). With the data from

Chapter 5, 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 thesis 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 entire global 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. To provide a deeper understanding on the emissions from spray foam products and levels of exposure, an experiment in a testing facility was undertaken.

9.4. Short and mid-term concentrations during spraying and curing

Chapter 8 presented original evidence in relation to the different concentrations of VOCs near the spraying surface and near the sprayer when a robot is used to apply the foam instead of it manually being applied by a worker.

The results from Chapter 8 demonstrated that during spraying high concentrations of VOCs were recorded near the spraying surface (inside the spraying box with the suspended timber floor). The mean 1,4-dioxane concentration exceeded NIOSH recommended exposure limits (REL) by a factor of 10 with the maximum level recorded exceeding NIOSH REL by a factor of 34. The measurements indicated that most VOC concentrations reduce drastically during curing and fall below recommended exposure limits. The only exception was the flame retardant emissions (TEP).

There are currently no existing occupational guidelines or recommended exposure levels for TEP that could be found in the literature. Whilst the mean and median TEP emissions during curing were lower than during spraying, the maximum ranges were comparable during both periods. This could be explained by literature findings suggesting other spray foam flame retardants have been found to have constant emission rates in laboratory micro-chamber tests, mainly impacted by temperature and airflow (Poppendieck *et al.*, 2017).

My findings confirm even if best practice for extract ventilation is used providing ~9 ACH during spraying, high concentrations of VOCs not outlined in manufacturer safety data sheets, will be released near the spraying surface. This finding reinforces the need for appropriate PPE equipment to be utilised when applying any type of spray foam especially when manual installation is applied. Literature suggests workers in the spray foam industry were found to not always wear the full PPE kit, with helpers particularly vulnerable to exposure of chemical emissions (Estill *et al.*, 2019). Even when full PPE kit is used, including respirators, coveralls and gloves, workers in the spray foam industry could still be exposed to measurable concentrations of chemical compounds, such as flame retardants (Bello *et al.*, 2018).

My findings suggest that emissions of chemicals not listed in safety data sheets (1,2-DCP, 1,4-dioxane and chlorobenzene) decrease exponentially after spraying had stopped when a

robust ventilation protocol is implemented near and within the spraying area. These compounds have however been found emitting from cured, and up to 2 year old, SPF products (ASTM International, 2017c; Poppendieck, Gong and Emmerich, 2017). VOC concentration near the worker, when a robot was used, were all below detection limits in the controlled experiment results presented in Chapter 8. Although these measurements were undertaken in semi-controlled conditions, they demonstrate the potential of using robots to minimise exposure of workers to chemical emissions when applying spray foam insulation.

The results in Chapter 8 could be utilised for calculating exposure during spraying, however they do not translate to personal exposure. Workers may also undertake manual spraying for finishing touches as well as transport and carry the barrels with the raw chemical compounds. Their cumulative exposure during their entire shift will also be impacted by whether they are using appropriate fit tested PPE kit. For this reason, existing studies deploy multiple techniques to measure holistic exposure simultaneously such as: personal exposure collector, urine samples pre and post-shift, as well as environmental measurements in the workplaces (Bello *et al.*, 2017, 2018, 2019; Mellette *et al.*, 2018). As discussed in Chapter 2, the focus in the scientific field with regards to spray foam emissions has historically been focused predominantly on isocyanates with flame retardants growing in relevance in the last decade. Chapter 8 is the first experimental study focusing comprehensively on B-side emissions and by-products throughout the lifecycle of SPF products. As Chapter 2 outlined, some of these VOCs can negatively impact health and are even known carcinogens. The empirical data presented in this study could be used by epidemiologists and toxicologists to undertake assessments of what health implications are possible under the concentrations recorded during and after spraying. As this thesis is not grounded in the health literature, it only presents empirical observations on concentrations and is not able to offer a scientific view on the implications for human health occurring at these concentrations. From an occupant exposure perspective and re-occupancy, only flame retardants were measured in my case study post-application. This would suggest that with robust ventilation deployment (negative pressure within crawlspace via extract fan), re-occupancy within 24-48h may be suitable for B-side emissions as well as A-side emissions. It should be noted however that further cases studies and an even wider coverage of emissions is recommended to validate this finding as it is limited to a single UK case study.

In addition, only one SPF product with several batches was tested, therefore the results may not be representative of all other products available on the market. The experiments were undertaken in a semi-controlled environment with limited external air infiltration, therefore the ventilation of the room was driven by the mechanical ventilation. Although the experimental facility was designed to mimic a real environment, further investigation had to be undertaken to determine concentrations in-situ.

9.5. Long-term VOC concentrations in a case study

Chapter 9 presented empirical evidence of VOC concentrations in-situ during spraying and post-spraying for a period of 8 weeks. A terraced house in London was retrofitted with spray

foam over the course of 3 days where VOC concentrations were recorded in multiple locations.

The Chapter 9 results demonstrate comparable patterns of VOC decay found in chamber experiments (Poppendieck, Gong and Emmerich, 2017) and case studies (ASTM International, 2017c; Tian *et al.*, 2018). The original experimental data in this thesis show VOC emissions peak during spraying following which a gradual decay pattern is observed. The findings from Chapters 2,6,7 and 8 together outline that when ventilation is applied as a mitigation measure for extracting air during spraying, airborne VOC concentrations were significantly lower in the retrofitted room in comparison to the spraying surface (i.e. next to the robot).

The three compounds with known potential health impact (1,4-dioxane, 1,2-dichloropropane and chlorobenzene) were only detected either during spraying and/or curing and the concentrations recorded in the case study below recommended exposure threshold limits. Apart from triethyl phosphate, which was a known constituent of the SPF formulation, none of the other three compounds of interest were detected in measurable quantities beyond 24 hours after spraying had concluded. This finding neither confirms nor excludes the possibility of all three potentially being part of the raw materials, however supports some industry guidelines that re-occupation should occur at least 24 hours after spraying had completed and the house was well-ventilated (American Chemistry Council, 2021). The fact that the three compounds (1,4-dioxane, 1,2-dichloropropane and chlorobenzene) were not recorded in the air during the sample study would suggest that these emissions do not emit in the long-term following spray foam application. However the flame retardant (TEP) was detected in measurable concentrations in the air even two months post-application. As TEP was not recorded in measurable background levels before spraying occurred, it could be reasonably attributed to emissions from the spray foam insulation. This finding suggests semi-volatile organic compounds, like flame retardants, may accumulate in the indoor environment and other mitigation measures are needed to reduce human exposure beyond ventilation. This correlates well with literature findings presented in Chapter 2 that outline flame retardant are ubiquitously present in indoor dust, surfaces and air in most indoor environments we occupy such as offices, homes, schools, cars and more.

Previous studies have found some of the B-side and by-product VOCs could be emitted from aged insulation foams over a year old (ASTM International, 2017c). Further large scale investigations are required including multiple types and brands of insulation to reaffirm the findings in this experiment. More long-term case studies are also needed to definitively rule out long-term exposure to these VOCs. Method B, developed as part of this thesis (Appendix F), could be deployed to develop reproducible datasets.

9.6. Spray foam risk matrix

Whilst PU insulation have SDS/MSDS publicly available due to their application on-site, regular household products do not have to present safety data sheets. The risk matrix presents the risks of exposure to specific types of VOCs throughout the lifecycle of spray

foams. As more experimental data of spray foam emissions is developed in the future, the risk matrix could be revised and specific ventilation strategies for each period (spraying, curing and occupation) could be deployed depending on the specific VOCs expected from the foam. In order to provide practitioners from the built environment and heritage fields with a tool to estimate the risks associated with SPF application, the findings from this thesis have been translated into a risk matrix in Table 23. The supplementary information for developing Table 23 is presented in Appendix G.

Table 23. Weighted risk profile of VOCs and SVOCs during SPF installation, during the first month after retrofit and long term (> 1 month) at standard operating conditions. The detailed assessment is provided in Appendix G. Highlighted areas in red indicate high risk based on known health hazards, exposure risk and level of uncertainty in the scientific evidence. Yellow indicates moderate risk with more research is required to validate results. Green indicates low weighted risk based on existing data.

SPF chemical compound family ↓	During installation		<1 month	>1 month
Isocyanates	High [Manual application]	Low* [Robot]	Low	Low
Polyol	Low		Low	Low
Flame retardants	High [Manual application]	Low* [Robot]	Moderate	Moderate
Blowing agents	Moderate		Low	Low
Catalysts	High [Manual application]	Low* [Robot]	Moderate	Moderate
By-products, non-disclosed VOCs and tertiary emissions	High [Manual application]	Low [Robot]	Moderate	Moderate

As SPF structure and properties could vary in different countries, depending on local regulations, a database of VOCs for each product would be key to determining exposure from PU materials. An appropriate database for modelling purposes would contain data from multiple chamber sizes as emission factors vary between micro and small chambers (ASTM International, 2017c). The database will also include a range of temperature dependent testing conditions. A proposed sampling protocol methodology for measuring airborne VOCs from spray foam in order to determine efficiency of ventilation strategies and mitigation measures is presented in Appendix F.

The active measurements in a case study could be changed from weekly to monthly after month 3 when it is expected that some of the emissions would have reached their peak (Tian *et al.*, 2018; Poppendieck *et al.*, 2019). Utilising Method B and Appendix F, emissions from building products, and their impact on retrofitted buildings can therefore be measured.

To provide a detailed scientific knowledge the dynamic indoor chemistry interactions, the air samples should be supplemented by assessing dust, surface and product material samples for VOC concentrations as well (Ceballos, 2007; Luongo and Östman, 2016; ASTM, 2019; Wang *et al.*, 2019; Xu *et al.*, 2019; Yang *et al.*, 2019; ASTM International, 2020). A comprehensive evaluation approach is also required for policy-making.

9.7. Policy recommendations

The optimal approach for indoor air quality is to limit pollutants at the source. It should however be noted that existing building regulations and optional guidelines do not have specific values for exposure to flame retardants indoors for example.

Figure 62 below outlines some of the relevant mandatory regulations for indoor environments as well as optional building specific guidelines.

Figure 62. Regulatory, and optional, frameworks for IAQ design in the UK

Limits for VOCs applicable to all building types exist in the UK Building Regulations and multiple optional guidelines, such as WHO Guideline, CIBSE TM40, CIBSE TM61-64, IAQM indoor air quality guidance, BREEAM, WELL and other technical documents. However these are guidance documents, therefore there is no legal basis for their adoption and most could

be considered best practice. Figure 63 shows how individual policies and regulators may focus on assessing risks, and compliance, from a product perspective or building perspective.

*Figure 63. Compliance assessment for different parts of the building system. Construction Products Regulation would require a product risk assessment. COSHH requires a workplace risk assessment. General Product Safety Regulation requires a consumer product risk assessment. BSA requires a building risk assessment. Ventilation provision (Part F) does not require a risk assessment, but assesses compliance and whether theoretically the building could remove pollutants down to prescribed levels when in operation. ** denotes acts or policies still under development.*

However as Figure 63 outlines, there is currently no overarching cumulative risk assessment that for example would look at a specific organic pollutant and outline how to most effectively reduce human exposure. For example, consumer and construction products may emit Compound A below the legislative requirement values for each product, however the cumulative exposure of all of the products in combination with a poorly ventilated building with vulnerable consumers is where the health risk is potentially the greatest.

The Construction Product Regulations in Great Britain have >440 standards, some of which may have limiting values with regards to VOC emissions, however the majority of standards do not have specific requirements. For example BS EN 14315-1:2013 and BS EN 14320-

1:2013 both standards cover spray foam products, however have no designated test method for measuring VOC emissions (Table 5 an Table 7) respectively.

- On the basis of the findings of this thesis, I therefore propose that regulators and policy-makers should consider adopting EU-LCI values for construction products – both in terms of risk assessment and as limiting values within standards.

That alone however would not solve the cumulative exposure conundrum. Currently, hazardous substances which could harm the health of employees in workplaces in the UK are defined in COSHH E40/2005 (HSE, 2018). These limits are the statutory legal requirements for over 400 organic and non-organic pollutants which employers must limit to minimise the impact on workers occupational health. These limits are however designed for industrial activities and the exposure levels are focused on *reducing risks*, not optimizing human performance and wellbeing. How much people are actually exposed to VOCs is a function of the products, ventilation capacity of the building (Building Regulations) its overall safety (Building Safety Act) and the dynamic complex indoor chemistry influenced by the behaviour of occupants (Heeley-Hill *et al.*, 2021). Therefore to protect consumers health, a holistic approach where each policy complements each other and they work together cohesively is required.

Regulating indoor air from a practical perspective is an extremely challenging matter. As outlined in this thesis, even measuring less than 10 VOCs accurately requires analytical chemistry methodology that requires a high degree of expertise, resources and is cost intensive. An important finding from this thesis is the difficulty, and limitations, of measuring emissions post installation. Without testing the raw products, the evidence provided in this thesis in support of 1,2-DCP being a constituent product would not have been possible. A particular scientific lesson is therefore requiring more transparency on the constituent raw materials for each products in order to determine its impact on indoor environments, materials and most importantly – people.

- The second policy recommendation is that the regulatory risk assessments for consumer and construction products should contain the full list of constituent chemicals, regardless of weight or volume, and that the HSE duty-holder principle of ‘as low as reasonably practicable’ (ALARP) is considered for limiting VOC emissions at source.

Flame retardants are a particular class of compounds that have attracted many recent scholarly, industry and policy debates covering a variety of indoor related products such as insulation, furniture products, electrical products and more (Schramm, Leisewitz and Kruse, 2001; D Shaw *et al.*, 2010; McKenna and Hull, 2016; Sugeng *et al.*, 2018).

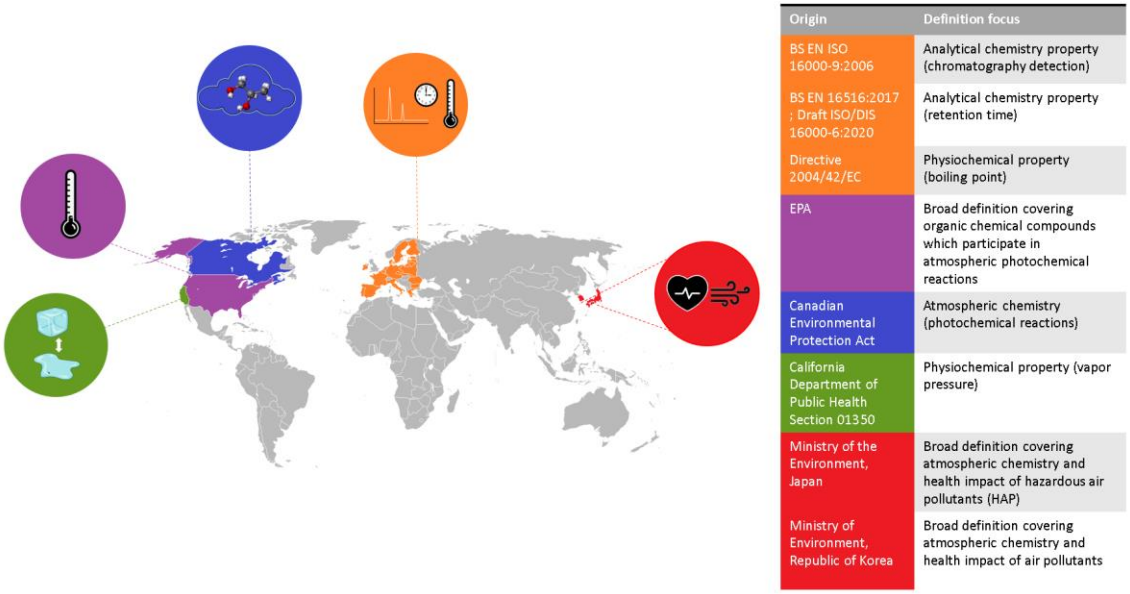
- It is recommended that manufacturers consider chemically bounded flame retardants to reduce long-term exposure given the findings from this thesis and the wider research literature

Despite analytical chemistry development and researchers calling for international definition for volatile organic compound since the 1990s (Mølhave and Nielsen, 1992;

Brown *et al.*, 1994), there is still ambiguity around the VOC terminology and its use within the built environment sector. For this reason, I recommend a "VOCabulary" data framework so that cross-disciplinary policy and research could merge findings from different fields for a comprehensive health-based approach for risk assessing products, buildings and environments.

9.8. VOCabulary

Nasa et al. (La Nasa *et al.*, 2019) suggested a VOC-abulary for comic book smells. A review of perception of odour in relation to chemical exposure however concluded human perception is not a reliable indicator for chemical exposure and is subject to individual biases in perception (Greenberg, Curtis and Vearrier, 2013). Figure 63 and Appendix E outlines all the different definitions for 'volatile organic compounds' according to different institutions.



Origin	Definition focus
BS EN ISO 16000-9:2006	Analytical chemistry property (chromatography detection)
BS EN 16516:2017 ; Draft ISO/DIS 16000-6:2020	Analytical chemistry property (retention time)
Directive 2004/42/EC	Physiochemical property (boiling point)
EPA	Broad definition covering organic chemical compounds which participate in atmospheric photochemical reactions
Canadian Environmental Protection Act	Atmospheric chemistry (photochemical reactions)
California Department of Public Health Section 01350	Physiochemical property (vapor pressure)
Ministry of the Environment, Japan	Broad definition covering atmospheric chemistry and health impact of hazardous air pollutants (HAP)
Ministry of Environment, Republic of Korea	Broad definition covering atmospheric chemistry and health impact of air pollutants

Figure 64. Definition and focus of VOC terminology across public and private institutions

Chapter 4 of this thesis demonstrated that there is an incredible amount of variability between the olfactory response at which people can detect SPF pollutants and levels at which health related implications could be observed. Pollutants such as benzene have an olfactory detection threshold (ODT)(NIOSH, 2011) that is 40-6000 times higher than levels found in buildings (Hazrati *et al.*, 2016)(Stamp *et al.*, 2020). According to Public Health England, there is no safe level of benzene indoors (Public Health England, 2019).

Based on the empirical findings from the thesis, I therefore propose a practical "VOCabulary" data framework for organic chemical compounds. I recommend that the relevant UK Government departments, regulators and executive agencies consider adopting the EU 'one substance, one assessment' approach to harmonise efficiency, effectiveness,

coherence and transparency of the delivery of safety assessments of chemicals across all relevant legislation[4].

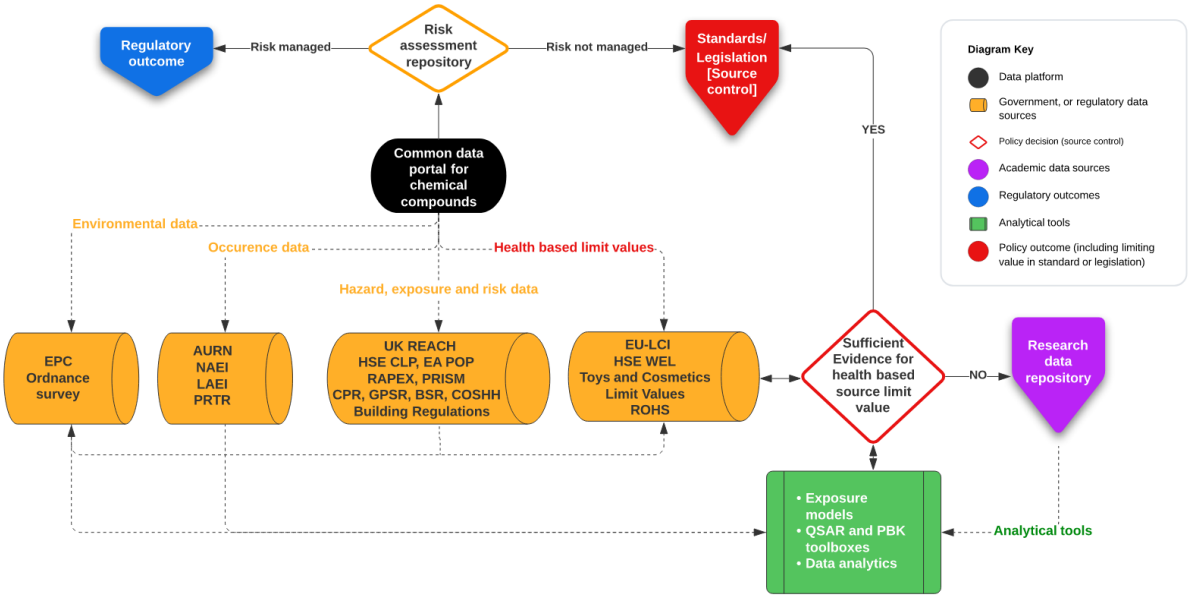


Figure 65. Theoretical minimum viable product for a common data portal in support of adopting "1 substance 1 assessment approach" in the United Kingdom. EPC = Energy Performance Certificates database. Ordnance survey data allows mapping regions between different data platforms as a common geographic information system backbone. AURN = Automatic Urban and Rural Network where outdoor air quality data could be extracted. NAEI = National Atmospheric Emissions Inventor from which outdoor emission data could be extracted. HSE CLP = Health & Safety Executive classification, labelling and packaging regulation for chemical classification, so the hazards could be classified according to a unified system. EA POP = Environment Agency Persistent Organic Pollutants. RAPEX = EU rapid alert system for unsafe consumer and construction products. PRISM = Product Safety Risk Assessment Methodology. CPR = Construction Product Regulations. GPSR = General Product Safety Regulation. BSR = Building Safety Regulator. COSHH = Control of Substances Hazardous to Health. EU-LCI = EU Lowest Concentration of Interest. HSE WEL = Health & Safety Executive Workplace Exposure Limits. Toys and Cosmetics = The Toys and Cosmetic Products (Restriction of Chemical Substances) Regulations 2022. ROHS = Restriction of Hazardous Substances regulations. QSAR = Quantitative structure-activity relationship. PBK = Physiologically Based Kinetic model.

The methodological concept in Figure 64 is grounded on the empirical evidence developed by Levin and Hodgson (Hodgson and Levin, 2003) and adapts the minimum viable product of the EU Common Data Platform on Chemicals (Kobe, 2022) but applied within a UK context.

As Figure 63 outlines, there is an enormous variability in how volatile organic compounds are classified, which impacts the way they are measured and evaluated. Salthammer (Salthammer, 2022) published a comprehensive overview of TVOC metrics and supported

[4] https://environment.ec.europa.eu/events/information-session-one-substance-one-assessment-stakeholders-and-citizens-2022-06-01_en#:~:text=The%20Chemicals%20Strategy%20for%20Sustainability,chemicals%20across%20all%20relevant%20legislation.

the Shrubsole et al (Shrubsole *et al.*, 2019) conclusion that the TVOC metric, even when derived via analytical chemistry methodologies, is not a suitable health based metric.

- I recommend that the UK cross-Government indoor air quality group considers the 'one substance, one assessment' principle and a digital pilot is funded exploring the minimum viable UK "VOCabulary" data framework

Without a comprehensive *data sharing platform* policy-makers, regulators, scientists and industry professionals may continue to talk in different languages when discussing volatile organic compounds without a common version of the truth – i.e. a shared "VOCabulary". With the introduction of a risk assessment for construction products, there will be multiple actors in the construction space providing individual risk assessments for protecting both workers and the general population. The digitally enabled "VOCabulary" could inform guidance for practitioners on managing indoor air quality in addition to regulatory requirements for indoor air concentrations of pollutants (Approved Document (AD) F of the UK Building Regulations).

CIBSE TM40 suggests that WHO guidelines (WHO, 2010) for pollutants should be adopted for indoor environments and there are now a range of voluntary guides for limiting VOC exposure in buildings – the Public Health England Indoor Air Quality Guideline for selected VOCs (Public Health England, 2019) and the IAQM indoor air quality guidance (Institute of Indoor Air Quality Management, 2021). The "VOCabulary" could serve as a one stop shop that brings together both legislative requirements and optional guidelines for best practice design and operation. The reason why a VOC shared language system is important is equal parts terminological and practical. It can, and should, bring academics, policy-makers and industry professionals to agree on what "good" or "healthy" indoor air quality actually looks like in practice from an organic compound perspective.

10. Conclusions

There are several conclusions, which could be drawn from the novel experimental scientific evidence presented in this thesis.

10.1. RQ1: What is the retrofit potential for insulating the UK building stock with polyurethane spray foam insulation?

This thesis presents original analysis of several databases. Chapter four demonstrates that >90% of existing dwellings with suspended timber floors have uninsulated floors. The EPC database analysis demonstrates that the majority of these dwellings have had some retrofit measures installed. Estimations demonstrate if all floors are retrofitted, the total carbon emissions equivalent to nearly half of the NHS building stock annual emissions per annum. There are existing policy tools, in terms of both incentives and regulations, that are expected to drive further the installation of underfloor insulation across both the social and private building stock. There may not exist a causal relationship between rising energy prices, climate change attitudes and underfloor insulation retrofits, however these factors are expected to further increase the adoption of this retrofit measures.

Social research data and literature findings suggest some of the reason for low uptake in suspended timber floor retrofits are: concerns that traditional methods are considered intrusive, time intensive and difficult as they often require the removal of floorboards. Consumers are therefore less likely to have either taken this retrofit measures previously, or to undertake it in the future, without also undertaking a whole house retrofit approach which also requires capital investment. The use of robots and spray foam reduce these 'inconvenience' factors. There is a correlation between increased public interest in this measure and the introduction of robots as an installation measure.

10.2. RQ2: Can VOCs emitted from polyurethane products be measured under controlled conditions and field studies?

Chapter 5 results outlined that the novel method for derivatizing isocyanates developed by Ferreira could be applied in spray foam isocyanate detection. The findings reaffirmed previous academic hypothesis that isocyanates are airborne during installation and up to a few hours post-installation, following which a decrease below detectable levels is observed due to their high reactivity. The work also reaffirmed the hypothesis that amines such as 4,4-MDA are not detected during spray foam installation despite clear evidence that the isocyanate was reacting with the moisture from the air.

Chapter 5 presented a novel method for successfully measuring B-side spray foam emissions. The four compounds that were measured are: 1,4-dioxane, chlorobenzene, 1,2-dichloropropane and triethyl phosphate. The method allows for both practitioners and scholars to apply a reproducible, repeatable method in order to develop large-scale data for concentrations from spray foam products.

During the lifecycle of this thesis, a methodology for measuring SPF organic emissions in microchambers was accepted and published by ASTM. Results in Chapter 5 outline that the

method developed as part of this thesis is better suited for field studies compared to the ASTM method.

10.3. RQ3: What are the short, mid and long term impacts of VOCs from spray foam materials in relation to health and exposure thresholds in dwellings?

Chapter 2 showed that the four VOCs (1,2-DCP, 1,4-dioxane, chlorobenzene and triethyl phosphate) could all *potentially* have indoor air quality implications at elevated concentrations and prolonged exposure. Occupational workplace exposure limits exist for 1,2-DCP, chlorobenzene and 1,4-dioxane, but no exposure limits were found for triethyl phosphate.

Chapter 6 presents novel experimental evidence contradicting the existing hypothesis that 1,2-dichloropropane is a by-product as a result of flame retardant (TCPP) degradation. This is an important finding as flame retardants, such as TCPP, are present ubiquitously in indoor environments as outlined in Chapter 2. The experimental evidence in this thesis provide an alternative hypothesis that the 1,2-DCP may have been a constituent product of the raw chemicals that are used during the production of SPF products, however it was not possible to conclusively define its origin. Whilst the evidence is empirically robust, it is considered that further experiments are required to refute the Salthammer hypothesis given that only one raw product was tested for the purposes of this thesis.

Chapters 6 and 7 present original evidence showing concentrations of the four VOCs are significant near the spraying surface, however are below detection limits near the sprayer when robots and robust ventilation are used. This novel finding empirically validates the hypothesis that robots offer potential for reducing exposure to spray foam emissions compared to manual spraying, which has been known to have impacted workers health in the past. This finding however does not preclude workers from wearing personal protective equipment as the study focused on key periods (raw materials and application) however did not measure the total exposure of workers using personalised samples attached to their clothes.

10.4. RQ4: Based on experimental and laboratory work, can protocols to mitigate risks during the installation phase and building use be developed and validated in case studies?

Chapter 9 presents original evidence of ventilation protocols utilised as a measure to reduce VOC exposure during underfloor retrofits with spray foam. The case study data demonstrated that in the field, 1,2-dichloropropane, 1,4-dioxane and chlorobenzene were not detected longer than several hours after application. Passive sampling was not deployed as part of this project, but could be utilised in further studies to experimentally test the prolonged "exposure" to spray foam emissions. The data from the case study, which measured concentrations at regular intervals, up to two months after installation, demonstrated that only triethyl phosphate was present in measurable concentrations post the 24 hours usually recommended by practitioners as a re-occupancy period. The study demonstrated that when extraction ventilation is used during application, the observable airborne concentrations in field studies are much lower even when measuring near the spraying surface in the living room of the house.

This finding is consistent with the existing literature that flame retardants are not bound to the polyurethane matrix and could be released throughout the lifecycle of the foam itself. The

data highlighted that airborne concentration was elevated during spraying and then decreased to low observable levels, close to the detection limit of the methodological protocol.

The whole thesis findings paint a holistic picture that airborne is only one pathway for exposure, whereas surface deposition and ingestion via dust or larger particles may also play an important role in total exposure to all VOCs generated as a result of the retrofit.

11. Research Limitations & recommended research

11.1. Research limitations

11.1.1 Number of VOCs measured

Apart from triethyl phosphate (TEP), none of the other detected compounds were listed as constituent chemicals as part of the raw ingredients. In practice, it could be theorised that the VOCs measured as part of this thesis only represented <12.5% of the volume of the raw products. A decision was made to focus on the measurable compounds, which were found to carry the highest health burden risks in the relevant medical literature. Whilst the study only covered a limited number of compounds, their overall concentrations could in theory be representative of some of the chemical compounds within the same class (VOCs or SVOCs). This means that the findings in this thesis were not necessarily representative of all emissions from spray foam products in-situ. Whilst volatile organic compounds of similar volatility, vapor pressure or molecular weight may experience a similar decay profile, this finding would need to be experimentally proven. In simple terms, other VOCs from spray foam may show similar patterns of decay as TEP, however further data is required to validate this hypothesis.

11.1.2 Alternative hypothesis for 1,2-DCP

The thesis presents evidence that 1,2-DCP may have been part of the raw ingredients, however the experimental results cannot with certainty claim that it was not a result of chemical reactions between the foam and organic compounds in the air. Albeit this is a less likely hypothesis, to refute the Salthammer hypothesis completely, larger scale experimental data of raw ingredients is therefore required.

11.1.3 Ventilation in real environments

The case study investigation was limited by the fact that interzonal airflow and concentrations of VOCs were not monitored throughout the whole dwelling. The concentrations recorded may not necessarily be representative of the cumulative VOC exposure of occupiers due to the active sampling methodology where concentrations are recorded for a specific point in time, rather than continuously.

For both the controlled conditions and case study, appropriate and robust ventilation rates were deployed in order to reduce VOC emissions following EPA best practice guidelines (U.S. Environmental Protection Agency (EPA), 2018). In real life, there may be low-ventilated environments where extract ventilation is not utilised during spraying. In these environments, the emission rates and indoor airborne concentration of organic compounds may be higher.

11.1.4 Misapplication of spray foam and wider SPF products

Misapplication of spray foam is proven to have an impact on emissions (ASTM International, 2017c), however was not explored as part of this thesis as SPF manufacturer guidelines were observed for all spraying events. Separately, the results from this thesis may not hold for other proprietary SPF products, non-analysed compounds and higher spraying rates - for example where both the floor and roof are retrofitted.

11.1.5 Other routes of exposure

Studies have demonstrated the importance of dermal and ingestion exposure to VOCs (Arnold *et al.*, 2012; Boor *et al.*, 2017; Bello *et al.*, 2019; Brandsma *et al.*, 2021). This is particularly relevant for semi-volatile organic compounds, such as flame retardants, where dust and surface concentrations may exceed airborne ones by a significant amount (Ali *et al.*, 2012; Brommer *et al.*, 2012; La Guardia and Hale, 2015; Luongo and Östman, 2016).

The focus of the thesis was particularly airborne concentration and no measurements of concentrations in dust and surfaces were recorded. Therefore the total amount of VOCs accumulated in the indoor environment could have been higher than the results presented in this thesis.

11.1.6 Applying findings to building stock

Whilst the controlled conditions and case study data provided original evidence on SPF concentrations in-situ, the findings could not be generalised to the entire building stock. As this research has demonstrated empirically, there is variability in emissions from the same polyurethane products despite being applied under similar environmental conditions. In addition, there are multiple possible 'misapplication' errors that can cause variability between houses: improper mixing of materials, improper application on site, improper environmental conditions during application, improper health & safety precautions and improper ventilation measures during and post-application.

Whilst this study provided new scientific knowledge within the context of the built environment, it raised even more questions in relation to the total performance of retrofitted buildings and the balance that has to be made when selecting appropriate materials with relation to retrofitted buildings and heritage impact. A series of recommendations for further work on how to bring together interdisciplinary findings are presented for consideration by the academic, policy and industry sectors.

11.2. Further work

11.2.1 Overcoming VOC measurement limitations

One of the limitations outlined was that only airborne exposure was measured as a 'spot check' as a point in time. This limitation could be overcome with multiple pumps continuously running in series, however due to the low breakthrough volume of the tubes, it will be impractical as tubes would need to be changed every 1-3 hours continuously. Passive sampling (Poulhet *et al.*, 2015; Schlink *et al.*, 2016) in combination with active sampling may offer a complementary approach to overcome this practical methodological limitation. It is therefore recommended that future case studies expand to cover a combination of active and passive measurements to capture both peak concentrations and long-term exposure rates.

11.2.2 Developing VOC database

The use of standard protocols, such as the ASTM D8142-17, would be beneficial to determine repeatable and comparable emission rates. To tackle the gaps in knowledge

associated with spray foam emissions in-situ, a framework is proposed to assess these scientific issues in a holistic manner as per Figure 66.

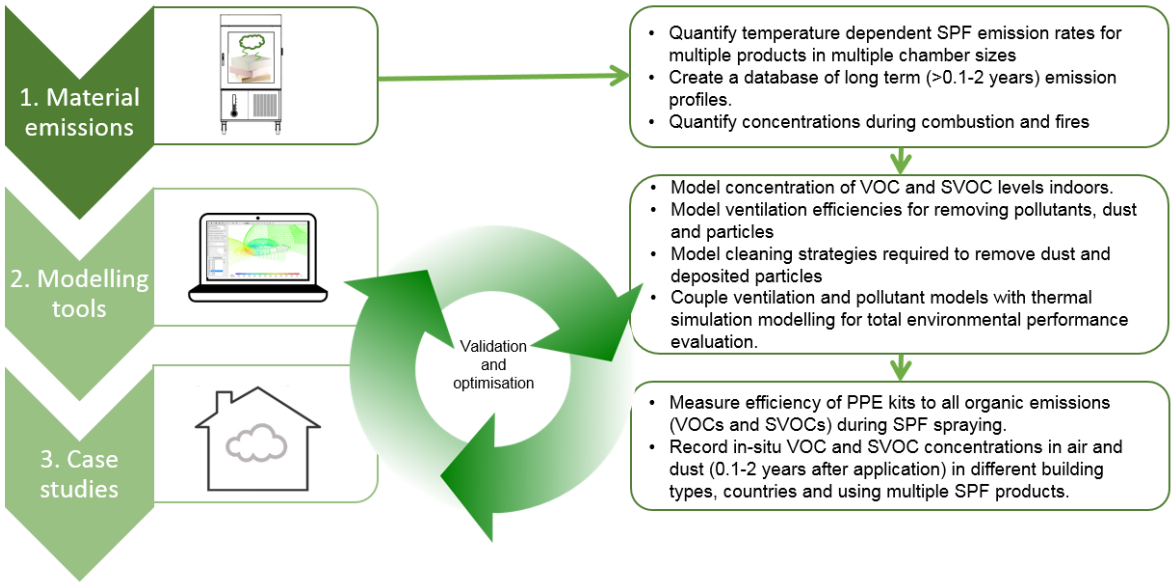


Figure 66. Framework for further research identified from the literature review

The first step is to develop a database of emission rates replicated by interlaboratory teams to draw statistically representative conclusions. The next two steps are to correlate laboratory experiments with modelling tools and validate with case study data. The framework could establish better worker protection protocols for a healthier and more productive workforce. In order to measure emissions in a repeatable and reproducible manner, a protocol was developed as part of the evidence gathered in this thesis. The long-term sampling protocol allows the quantification of VOC concentrations emitted from spray foam in retrofitted properties. If applied consistently across a range of retrofitted dwellings, this sampling protocol would also allow the evaluation of various mitigation measures and ventilation strategies for reducing human exposure to VOCs. The gap between predicted and actual IAQ can result from error associated with both the modelling and measurement uncertainties.

One area of uncertainty in IAQ modelling is the emission characteristics from indoor sources, such as building materials. Evidence on emission and deposition rates for pollutant/source combinations and at different environmental conditions is sparse and there are few existing databases, such as the National Research Council database (Ye, Won and Zhang, 2014). Although the database is one of the most comprehensive ones in terms of the range of materials, it still has several limitations. Those include measuring pollutants only at 23 °C, which is not representative of summer indoor conditions. They were also measured for a short period of time and only in one chamber size. The products sourced in Canada will not necessarily be representative of UK based materials caused by different regulations and manufacturing requirements.

This data highlights the lack of knowledge in this area, which calls for further evidence of national databases to be developed for better understanding of emission rates from a range

of materials. Modelling exposure through desktop studies is possible when a robust database is developed and results are validated through case study measurements. For accurate modelling results, the input parameters must be reflective of the building in use.

11.2.3 Indoor air quality metrics and selection of proxies

A truly comprehensive IAQ assessment would include evaluation of concentrations of all indoor air pollutants. Selecting suitable pollutants using the "VOCabulary" is based on identification of the sources, relevant to the specific building. This presents consistency and comparability issues between buildings. It can be challenging because of uncertainties around maximum acceptable limits for individual pollutants (e.g. VOCs) and impractical, however it is the only way of defining a representable IAQ evaluation.

The suitability of the selection of pollutants as proxies of IAQ in prediction (modelling) and monitoring is a key cause of IAQ performance gap and a source of difficulty in its quantification. The use of proxies is often unavoidable, but has been proven as an effective tool when used to control ventilation systems, rather than as a single metric of IAQ. As exposure values of organic pollutants could vary between 0.001-2,000ppm, knowing what the indoor pollutants are is the first step for understanding their potential impact on health. Given the findings of this thesis in terms of VOC concentration variability and the comprehensive work of Salthammer (Salthammer, 2022) and Shrubsole et al (Shrubsole *et al.*, 2019) in reviewing TVOC guidelines, it is recommended that the TVOC metric is not utilised for health related evaluations of products.

11.2.4 Indoor air quality academic field

Where source control is not adopted as a preferred option for controlling product emissions, ventilation strategies have to be developed to ensure occupants health and wellbeing. Indoor air quality is however only one design criteria out of many that both designers and users of buildings have to balance throughout the lifecycle of built environment assets. Whilst there is growing broader academic, industry and societal interest in indoor air quality related issues in general spurred by the COVID-19 pandemic (Morawska *et al.*, 2021), as an academic discipline it is scarcely developed compared to other fields such as energy. Building owners (residential and non-domestic), indoor air quality is not a prominent decision-making factor when the decision has to be made whether and how to retrofit a building (Salthammer, 2014; Murgul and Pukhkal, 2015; Wells *et al.*, 2015; Trotta, 2018; Schleich, 2019).

This thesis provides further evidence on why indoor air quality, health sciences (epidemiology and toxicology)energy efficiency are interdependent and the artificial separation of the fields is a limitation in terms of existing built environment research. Knowing the impact of materials selection on indoor air quality and human health should go hand in hand with capital cost, energy efficiency savings and heritage impact. Multidisciplinary research converging findings from different fields in a coherent framework, such as the "VOCabulary", could perhaps allow for better estimations of VOC impact on human health on a population level. What is a glaring evidence gap in the literature is the cumulative combined impact of multiple VOCs, at lower concentrations, and causality with

health impacts. In addition, epidemiological evidence relies on monitoring and measuring emissions that happen in the past. The indoor air quality scientific field remains relatively small compared to other disciplines. We are exposed to thousands of VOC emissions for ~95% of our lives, on average, and their cumulative impact remains difficult to estimate, especially compared to outdoor pollutants for example. Scientific, policy and industry gaps need to be addressed in order to ensure that the buildings of today are fit for the climate of tomorrow, whilst ensuring they not only reduce the health burden, but actively provide indoor conditions improving our overall health and wellbeing.

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Appendix A - History of energy and indoor environmental quality development within the context of the UK built environment academic, industry and policy fields

Industry fragmentation

In the case of construction products, the delivery of buildings involves a tiered layer system where it is not uncommon to have 50-70 suppliers and sub-contractors (BIS, 2013). Because of the multi-layered system, it is also possible that some sub-contractors (specialists in design, purchasing, installation or procurement) may not necessary communicate directly and there are multiple intermediaries. The results of the BIS commissioned analysis revealed that material producers, plant hire businesses and builders merchants play an important role within the supply chains ecosystem to facilitate the ready availability of construction products. Given tight margins and deadlines within the construction industry, material substitution occurs during the design (Stopps *et al.*, 2021) and also operation buildings (Sobotka, Linczowski and Radziejowska, 2021).

There are therefore billions of construction products being installed yearly and millions of square metres of insulation. To provide a sense of scale the UK construction industry output in February 2021 alone was £13.32 billion split in £8.34 billion covering total all new work and £4.98 billion covering repair and maintenance (ONS, 2021). For this reason in the absence of data, whilst some estimations are possible, it is often difficult to track specific products and where they have been installed given the complexity of the supply chain and lifecycle of insulation products. Figure 70 outlines the various types of construction projects, for the majority of which polyurethane insulation products could be utilised to enhance their performance or meet regulations.

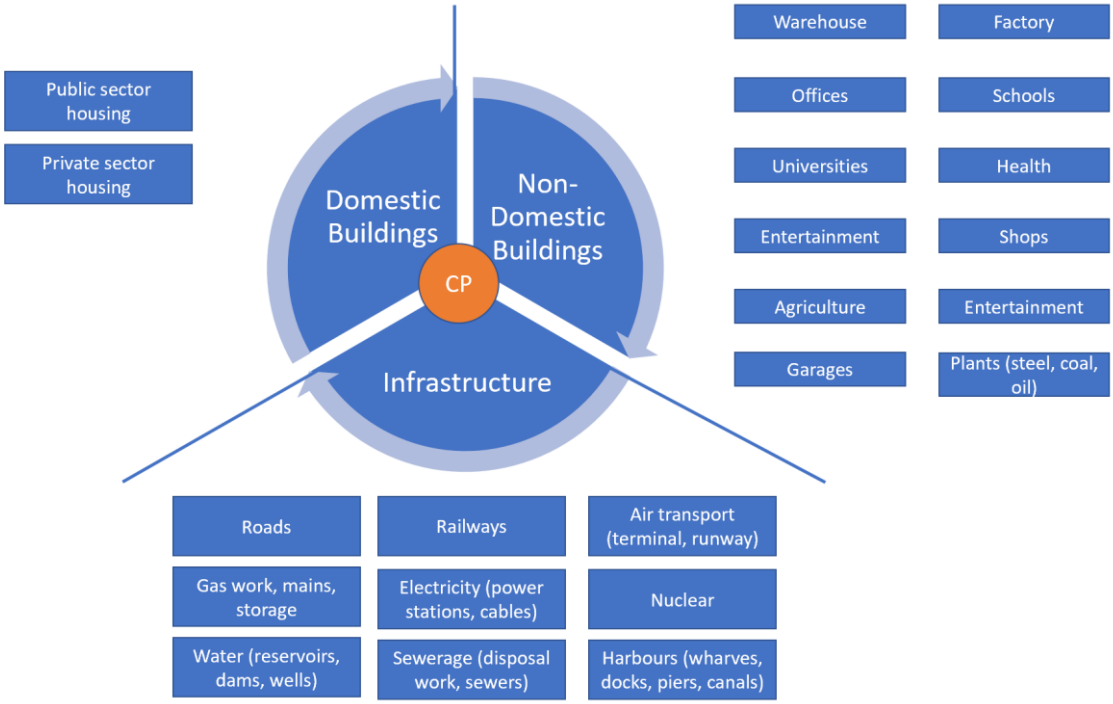

Figure 67. Types of construction projects distributed by sector.

Given the variety of construction projects and absence of comprehensive granular datasets for insulation products, a reasonable hypothesis would be that via analysis of supply chains, one would be able to determine where certain products have been installed. The supply chain is the interconnected system of supply contracts necessary to procure a built asset (Le *et al.*, 2020).

Most construction project types have a unique supply chain including multi-tiered contractors depending on the scale and size of the project (Le *et al.*, 2020). Procurement routes are particularly pertinent for domestic and non-domestic buildings delivery. According to the Joint Contracts Tribunal (JCT) there are 40-50 types of contracts reflecting the different contractual arrangements between suppliers and providers of goods and services (RIBA, 2018).

The most common procurement frameworks for buildings are: traditional, design and build, management contracts and public finance initiative (PFI)/ public private partnership (PPP). This is an important factor as design and build incentivises meeting a specific outcome/performance, where product substitution could play a bigger role compared to traditional contracts. In 2000, Vriejhoef and Koskela found that clients were often perceived as the ultimate source of changes in specifications in make-to-order production, however their study presented evidence of how installation co-ordination was crucial and make-to-order logistics networks contained vast potential for improvements by managing delivery (Vrijhoef and Koskela, 2000).

Ten years later, the Chartered Institute of Building undertook qualitative research assessing survey responses from 525 construction industry professionals on the different procurement routes topical areas such as: restructuring needs, problem areas, exceeding budgets, exceeding timelines, transparency and EU regulation, bidding, partnerships and procurement problem areas (CIOB, 2010). Some of the key issues identified were over: responsibility, lack of communication, alterations to clients requirements, design team problems, design faults and supply chain issues (CIOB, 2010). In 2020, Killip et al, found that whilst supply chains have become more complex, similar issues were persisting along the themes of industry practices, skills and knowledge, roles and responsibilities, innovation, engagement with installers and policy (Killip, Owen and Topouzi, 2020). In addition, more recent events, such as the Grenfell tragedy and COVID-19 have both further exacerbated and made more visible the importance of building products supply chain ecosystems (Hackitt, 2018; Jallow, Renukappa and Suresh, 2021).

A recent long-term study (Alshamsi, 2020) found that some of the major drivers for construction supplier selection in the UK are ranked as follows (1- most important for purchaser, 8 – least important):

1. Supplier financial position (financial stability, price and quantity discount)
2. Supplier quality management (quality of system, support service; meeting regulation requirements, reliability)
3. Supplier experience (expertise, marketing position, reputation, innovation)
4. Cooperate social responsibility (environmental, economical, social, sustainability)

5. Green practice (green technology, certification and waste disposal)
6. Supplier logistics performance (location, distance, packaging)
7. Supplier process performance (process capability, manufacturing capability, bidding procedure)
8. Communication and responsiveness

The findings of the Alshamsi study, that logistics, process performance and communication were found to be the least important factors for supplier selection, are seemingly in contrast with existing literature. The collective evidence from other studies suggested that these factors are the most common issues that actors across the construction supply chain experience when dealing with each other (Vrijhoef and Koskela, 2000; CIOB, 2010; Khalfan *et al.*, 2010; Arthur, 2016; Killip, Owen and Topouzi, 2020).

There are two plausible explanation for this seemingly contradictory evidence – one is that *because* actors within the supply chain do not prioritise logistics, process and communication performance, this is why these problems persist. The other plausible explanation is that both observations are equally valid and the construction supply chain is so vast, that it is difficult to draw meaningful conclusions even with large scale quantitative and qualitative interviews as there is a likelihood that the findings may represent outliers.

Unlike the automotive or consumer products industry, the construction industry has an ecosystem where depending on the sector, or type or procurement route, each project may be developed by a unique team of suppliers, consultants, contractors, engineers, building control and other actors that may have never worked together before as a team, may not work together again in the exact same setup and are effectively developing a building-prototype to meet the client demands, whilst balancing the local site conditions, requirements and national and local legislation. For this reason, without gathering new evidence, it is difficult to triangulate existing data source and accurately produce reliable statistics for the market distribution of insulation materials by project type, sector or archetypal/stock level.

Whilst evidence is presented that clearly outlines the fragmentation of the industry, a way to understand why it has reached this position is to review the development of UK Building Regulations, which are the core driver of how buildings should be designed, built and to some extent operated.

Building Regulations evolution

An OECD review outlines the history of regulatory development where change was initially episodic in nature and led to ambitions for one-off set of interventions to solve a specific problem, which was followed by a cycle of: eliminating regulation and gave way to more systemic regulatory reform, involving a mixture of de-regulation, re-regulation and improving the effectiveness of regulations (Malyshev, 2006). These cycles more or less describe how Building Regulations evolved in the UK between the 1700s until modern times. The Great Fire of London in 1666, when over 13,000 buildings or nearly 80% of the building stock was destroyed, led to the London Building Act of 1667. Whilst this was only a local policy for London, it paved the way by prescribing that all new buildings had to be constructed of brick or stone against the future perils of fire and imposed a maximum number of storeys per house for a fixed number of abodes to eliminate overcrowding (UK Parliament, 1667).

Several addition were made later on with the Building Acts of 1707 and 1709 with a broader policy being adopted in 1774 called the Fires Prevention (Metropolis) Act (UK Parliament, 1774). It's focus was predominantly fire performance by conditioning buildings in London to be built of non-combustible materials, namely stone, alongside effectively introducing building insurance for non-accidental fires, which still carries implications in modern court cases (Herbert Smith Freehills LLP, 2012).

Between 1774 and 1963, there were hundreds of local "improvement" Acts, which effectively introduced a whole series of local building regulations (Gaskell, 1983). The Public Health Act in 1961 was the statutory instrument, which allowed national building regulations to be established and replace local regulations (Ley, no date).

Since the 1960s, Building Regulations have evolved alongside local planning regulations where both building regulation approval and local planning permission and requirements operate in parallel effectively defining the *outcome* of how buildings should be designed and built. Particularly in the context of energy efficiency, whilst the 1962 provisions impacted energy use, their primary function was the control of condensation of buildings.

In 1972 and 1974 conservation of fuel and power provisions for dwellings and non-dwellings were respectively introduced demanding buildings to achieve certain performance in terms of fabric elements. As Table 24 outlines until 1985, UK homes were not legally required to have any insulation in the walls or floors in order to comply with Building Regulations.

Table 24. UK Building regulations minimum requirements for thermal envelope performance

Year	U-values (W/m²K)			
	Wall	Roof	Floor	Windows
1965	1.7	1.42	-	5.7
1974	1.0	0.60	-	5.7
1981	0.6	0.35	-	5.7
1990	0.45	0.25	0.45	5.7
1995	0.45[1]	0.25[1]	0.45[1]	3.3

Since the 1990s up until now, with the introduction of the Energy Performance of Buildings Directive, energy efficiency regulations were interlinked with carbon emissions and increasingly more onerous requirements were gradually introduced on a national level.

The Standard Assessment Procedure (SAP) was introduced in 1995, which has undergone multiple revisions. It has however remained the primary methodological tool for assessing compliance with Building Regulations in relation to conservation of fuel and power and has had an enormous impact on building specifications both in terms of materials and heating, ventilation and hot water systems. The target carbon dioxide (CO_2) emission rate associated with the "regulated" electricity usage by SAP is calculated using the notional building requirements as per Approved Document L (CIBSE, 2020).

To achieve those targets, various classification schemes were therefore established in order to represent a building's relative energy performance and respective carbon emissions (Wang, Yan and Xiao, 2012). In the UK, these schemes cover the design stage [Part L calculations and Energy Performance Certificates (EPC)] and in-use operational stage [Display Energy Certificates (DEC)]. The inputs for all schemes are related to the energy consumption of buildings, however the final output represents the CO_2 emissions equivalent to the consumed regulated energy.

The energy performance of the building stock is critical as the built environment is responsible for 66% of the UK electricity consumption, however greenhouse gas emissions (GHG) from buildings have only decreased by 1% between 2009-2016 (Committee on Climate Change, 2018). Up until 2016, local authorities in England were allowed to specify a percentage reduction against that target beyond Building Regulations, which had implications for how the building was designed and what energy efficiency measures were adopted, including type and thickness of the insulation. In 2016, the Deregulation Act was adopted effectively restricting local authorities from being able to demand a percentage reduction above 19% (Code for Sustainable Homes Level 4) in order to provide a level playing field across the country.

According to previous policy trajectories, a net-zero national target of 100% reduction of CO_2 emissions against the SAP notional emissions was due to come into force post-2016 (Forde, Osmani and Morton, 2021). The accredited assessment tools for producing EPCs and DECs range from steady-state calculations to dynamic simulation models and are used to compare the energy and carbon performance of a building compared to a pre-defined baseline (notional building). It should be noted that whilst national building energy use targets are defined via Building Regulations, there are multiple voluntary certification systems such as BREEAM (Building Research Establishment Environmental Assessment Method) and LEED (Leadership in Energy and Environmental Design). Local authority planning regulations in the UK have also required some new developments to exceed national standards and adopt these voluntary certification system, such as BREEAM "Excellent".

As compliance modelling contains many standardisations and does not take into account unregulated loads or occupational variabilities, scholars argue that it is a more robust strategy to use performance modelling instead. For commercial buildings, this transition may be a straightforward process as there are many existing industry guidance protocols for achieving this: Level 5 (DSM) compliance modelling, CIBSE TM52, CIBSE TM54 and CIBSE TM63. For domestic buildings, a longer transition may be reasonably expected as dynamic simulations are slowly entering the domestic market and policy development within this area is entering research and pre-implementation stage (Oreszczyn *et al.*, 2021). It could be reasonably assumed that dynamic modelling of the domestic building stock may not be perceived as cost-effective from an industry perspective, therefore it could take time for full market penetration even if the non-domestic simulation tools could be re-deployed for smaller scale residential buildings. However the integration of dynamic modelling throughout the built environment lifecycle should assist in reducing the performance gap

and possibly expanding models to include overheating, ventilation, air quality and other multi-parametric built environment performance criteria.

In 2022, Building Regulations were revised, Approved Document L achieved an uplift in national energy efficiency requirements and trajectory for developing a "Future Homes Standard" was published (MHCLG, 2021a). The Future Homes standard is designed to achieve a CO_2 reduction of 75% lower than 2016 national standards to ensure all new homes are designed to be net zero to provide an urgent response to climate change (MHCLG, 2021b). However in the current regulatory framework, Building Regulations are focused around whether the building achieves its design specifications and is signed-off by Building Control in order to comply with the law. It is then up to occupiers, facilities management and building users to actually ensure that it operates as per the indented design.

Scholars have long argued and supported with empirical evidence that even when a building complies with regulations, its performance in-use varies significantly compared to designed estimations, which is often referred to as the 'performance gap' (Bordass, Cohen and Standeven, 2001; Leaman, Stevenson and Bordass, 2010; Menezes *et al.*, 2012; Austin, 2013; de Wilde, 2014; Cohen and Bordass, 2015; van Dronkelaar *et al.*, 2016; CIBSE, 2020; Forde, Osmani and Morton, 2021). Innovate UKs Building Performance Evaluation (BPE) studies found that, on average, buildings were using 3.6 times as much energy as what the Building Regulations compliance calculations project (Innovate UK, 2016). The building performance evaluations carried out after implementation of the Energy Performance of Buildings Directive (EBPD) in the EU demonstrates the challenges of meeting increasingly stringent energy regulations in practice (Palmer *et al.*, 2016). The energy use from compliance tools has been shown to demonstrate a significant discrepancy compared to the actual use of a building in-use.

This phenomenon has been described as 'the performance gap' (Carbon Trust, 2011; Menezes *et al.*, 2012; de Wilde, 2014; Cohen and Bordass, 2015). Due to the complexity of the built environment, a margin of error between the predicted and actual energy use is unavoidable due to the uncertainties during the four stages of the building lifecycle (design, construction, handover and commissioning, operation). In a way, what energy efficiency scholars have found is not too dissimilar to what fire safety scholars have found. Trying to use simulations, single-performance test in labs and even systems tests to predict what could happen in real buildings is an incredibly complex process of many phenomena occurring simultaneously whereas a single parameter could have enormous impact (Rein *et al.*, 2009; Law, 2016; Crewe *et al.*, 2018; Bonner *et al.*, 2020).

For this universal academic problem, it is crucial to understand the limitations of the measurement tools, appreciate their magnitude and analyse the underlying causes for the 'performance gap'. This will reduce and optimise energy use in the building stock in line with the UK and global ambitions of a zero-energy (or carbon neutral) building stock. Historically the regulatory performance gap has been extensively examined and discussed, including its limitations and drawbacks (van Dronkelaar *et al.*, 2016). There are multiple scientific

domains, which have been developing since the 1970s that have been devoted to exploring why this gap occurs and how it could be reduced. In addition, transdisciplinary fields have also emerged, which focuses on the total performance of buildings showcasing the complexity of what we expect modern day buildings to achieve (Hartkopf, Loftness and Mill, 1986; Taylor, Liu, *et al.*, 2018). However whilst academic research drives forward construction industry and policy learning and innovation, it itself is not immune to experiencing systematic problems in silo-mentality and dichotomies (Sovacool and Geels, 2016). Scientific dichotomies have been made publicly, and globally, apparent during the COVID-19 pandemic where “aerosols” and “droplets” terminologies have had an enormous impact on mitigation measures across the world potentially costing lives (Drossinos, Weber and Stilianakis, 2021; Escandón *et al.*, 2021; Randall *et al.*, 2021).

Appendix B - Thermal performance of common insulation materials based on their thermal conductivity (λ) W/mK

Study →	(Al-Ajlan, 2006)	(Abdou and Budaiwi, 2005)	(Al-Homoud, 2005)	(Papadopoulos, 2005)	(Budaiwi, Abdou and Al-Homoud, 2002)	(Lakatos, 2014)	(Berge and Johansson, 2012)	BS: EN ISO 10456:2007	Manufacturer declared data	
Type of study →	Measured conductivity	Measured conductivity	Literature review	Literature review	Measured conductivity	Measured conductivity	Literature review	Design values	Industry published data	
Material ↓	Thermal conductivity (λ) W/mK									
Polystyrene	0.036	0.039	0.03	0.025		0.049	0.036	0.032	0.034 - 0.038	[Product #1]
	0.034	0.040	0.032	0.035		0.037	0.034	0.035	0.033	[Product #2]
	0.033	0.040	0.038	0.029		0.036	0.031	0.04	0.038	[Product #3]
	0.032	0.035	0.037	0.041		0.035		0.043	0.035	[Product #4]
	0.031	0.037				0.039		0.032	0.038	[Product #5]
	0.034	0.035						0.035	0.037	[Product #6]
	0.033	0.034						0.040	0.032	[Product #7]
		0.034						0.032	0.034 - 0.036	[Product #8]

		0.034						0.035		
		0.030						0.040		
PU/PIR board	0.024	0.023	0.023	0.020			0.024	0.022	0.022	[Products #9-#16]
	0.022			0.027			0.022	0.025		
								0.030	0.022	[Product #17]
Glass fiber	0.042	0.050	0.033	0.030	0.039			0.035		
	0.038	0.037	0.040	0.045	0.038			0.040		
	0.034	0.032	0.032		0.040			0.045		
	0.046		0.035		0.039			0.050		
					0.039			0.055		
					0.041			0.035		
Mineral wool		0.037		0.030		0.039		0.032	0.044	[Product #18]
				0.045				0.034	0.036	[Product #19]
								0.035	0.044	[Product #20]
								0.038	0.044	[Product #21]
								0.040	0.032	[Product #22]
								0.045	0.040	[Product #23]

								0.050		
Rock wool	0.042	0.038	0.037	0.033	0.040				0.035	[Product #24]
	0.040	0.040	0.040	0.045	0.039				0.034	[Product #25]
		0.040			0.041					
		0.041			0.041					
		0.036			0.040					
		0.034			0.043					

Appendix C - MDI Exposure limits and values obtained during and post SPF insulation application

Study	*Sleasman et al. 2017*	*Lesage et al. 2007*	*Crespo and Galan 1999*	*Bello et al 2019*	*Roberge et al. 2009*	*Shen Tian et al. 2018*	*ASTM International, 2017*	
							Won et al. 2017	*Wood et al. 2017*
Purpose	Defining limiting exposure values that will not have adverse health impact for MDI	Measuring airborne MDI concentration during SPF application in residential construction	To obtain MDI exposure during indoor and outdoor SPF application	Assessing pMDI during spray foam applications	To obtain MDI exposure during indoor and outdoor SPF application and 30,60 and 120 post installation	Air quality evaluation in a residential project using SPF	To measure MDI concentration from one component join sealant	Estimating re-entry time for workers following SPF application
Number of objects/sites	n/a	5 single-family houses in the U.S. and Canada. Breathing zone samples and indoor concentrations near spray area were collected.	17 building sites. 1 office building, 2 sets of terraced houses, 14 flats. Indoor and outdoor measurement.	14 trips at 12 distinct SPF insulation sites A total of 54 study participants, 41 of whom were sprayers, 9 helpers, and 4 bystanders.	1 building site. Indoor and outdoor sampling.	1 building site. Indoor sampling only.	3 products (10 grams of each) sprayed in petrie dish and emissions measured in glass chamber	Three SPF products applied in spray room at three different ventilation rates (10,233 and 598 air changes per hour)

Sampling media	Coated Glass Fiber Filter (37 mm open face) Coated with 1.0 mg 1-(2-Pyridyl) piperazine	Several methods were used including both impinger and filters.	Impinger using a 2x10-4M solution of 1-(2-methoxyphenil) piperazine in toluene as absorbent	CIP10 MI personal sampler filled with 2 mL of 1 mM MAP in butyl benzoate	Impingers with 15 mL of 0.1 mM MAP in butyl benzoate followed by a 13-mm MAP-impregnated glass fiber filter (500 µg MAP/filter)	Impinger system containing a MOPIP solution	37 mm membrane impregnated with 9-(N-ethylaminomethyl) anthracene	90mm filter with 1-(2-pyridyl piperazine)	37 mm membrane glass filter coated with 9-methylaminomethyl anthracene (MAMA)	13-mm glass fiber filter coated with 1mg 1-(2-pyridyl) piperazine (1-2PP)
Analytical method	HPLC-UV/FLU	GC-FID	HPLC-UV/EC	LC-ESI-MS/MS		HPLC-UV/FLU	HPLC and MS/MS	LC-MS	LC-MS	HPLC-UV

Method reference	OSHA Analytical Method	NIOSH 5521	MTMA/MA-035/95 (NIOSH-Spain)		25/3 Organic Isocyanates in Air of the (HSE)	IRSST High Sensitivity	Modified OSHA 47 & USEPA CTM 036		Modified OSHA 47
Individual sample measurement (mg/m³)	0.00008[5] -0.2[6]	0.005-1.55	0.001-0.57	0.009-0.123	-	-	0.0023-0.185	0.0001-0.0042	<0.00143-0.00154
Mean average exposure (mg/m³)	0.005[7]	0.122-0.603	0.004-0.057	0.0196	0.01-0.15	0.13-0.29			Below detection limit
Mean average exposure after 120 min (mg/m³)	-	Below detection limits	-	0.04	-	0.003-0.005	0.000002-.000068		

[5] California Office of Environmental Health and Hazard Assessment (OEHHA) chronic reference exposure limit (REL)- 0.00008 mg/m³, OEHHA acute REL- 0.012 mg/m³. Germany, Sweden STEL- 0.05 mg/m³. United Kingdom STEL- 0.07 mg/m³. Austria and China STEL-0.1 mg/m³, Poland STEL- 0.2 mg/m³

[6] OSHA Permissible Exposure Limit (PEL) - General Industry

[7] National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL)

Appendix D - Organophosphate flame retardant concentration and exposure in indoor environments

The table summarises flame retardant levels in total daily intake (ng/kgbw/day), urine (ng/l), indoor air (ng/m3) and dust (ng/g) as determined in different international studies (P=Percentile, 50-P= Median, 95-P=95 percentile, GM- Geometric Mean, AM- Arithmetic Mean) on the basis of region.

Country	Description	Location and samples	Sample type	C_{indoor} TCPP (CAS: 13674-84-5)	C_{indoor} TCEP (CAS: 115-96-8)	C_{indoor} TDCP/ TDCPP (CAS: 13674-87-8)	Reference
China	Testing urinary metabolites in China to measure total daily intake (TDI) of organophosphate flame retardants	13 cities 323 samples	Total daily intake (TD)		607 ng/kgbw/day (AM) 52.2-25,200 ng/kgbw/day (range)		(Zhang *et al.*, 2018)
U.S.	Testing urinary metabolites in U.S. infants to estimate total daily intake (TDI) of TDCP	Durham (NC) 43 samples	Total daily intake (TD)			10-15,300 ng/kgbw/day (range)	(Hoffman *et al.*, 2017)
Germany	Flame retardants in air, dust and biomonitoring in Germany day-care centers	Bavaria and North Rhine-Westphalia 63 day-cares	Concentration in urine	21% DF 200 ng/l (AM) <200-8,400 ng/l (range)	65% DF 400 ng/l (AM) <100-13,100 ng/l (range)		(Fromme *et al.*, 2014)
			Concentration in dust	59% DF 4,650 ng/g (AM)	63% DF 1,350 ng/g (AM)	4% DF	

				710- 47,000 ng/g (range)	100-8,300 ng/g (range)		
			Concentration in air	43% DF 4.1 ng/m^3 (AM) <2-45 ng/m^3 (range)	43% DF 2.2 ng/m^3 (AM) <2-33 ng/m^3 (range)		
Sweden	Orghanophosphate in settled dust from apartment buildings in Stockholm	Stockholm, 62 samples from 19 buildings	Concentration in dust	100% DF 11,000 ng/g (50-P) 1,210- 98,000 ng/g (range)	97% DF 4,000 ng/g (50-P) n.d.- 9,800 ng/g (range)	81% DF 2,000 ng/g (50-P) n.d.-12,000 ng/g (range)	(Luongo and Östman, 2016)
			Concentration in air	100% DF 19 ng/m^3 (50-P) 1.3- 1,179 ng/m^3 (range)	65% DF 3.9 ng/m^3 (50-P) n.d.-233 ng/m^3 (range)		
Sweden	Organophosphate and phthalate esters in indoor air: a comparison between multi-storey buildings with high and low prevalence of sick building symptoms	Stockholm 169 apartments; 1 building	Concentration in air	59 ng/m^3 (AM) 14 ng/m^3 (50-P) <0.5-1,200 ng/m^3 (range)	10 ng/m^3 (AM) 4 ng/m^3 (50-P) n.d.-230 ng/m^3 (range)		(Bergh *et al.*, 2011)

Germany	Concentrations of organophosphate esters and brominated flame retardants in German indoor dust samples	Germany, 12 cars, 6 homes, 10 offices	Concentration in dust (n=12) in cars	3,100 ng/g (AM) 1,400-4,300 ng/g (range)	950 ng/g (AM) <80-5800 ng/g (range)	130,000 ng/g (AM) <80-620,000 ng/g (range)	(Brommer *et al.*, 2012)
			Concentration in dust (n=6) in homes	740 ng/g (AM) 370-960 ng/g (range)	200 ng/g (AM) 140-280 ng/g (range)	<80 ng/g (AM) <80- 110 ng/g (range)	
			Concentration in dust (n=10) in offices	3,000 ng/g (AM) 180- 9,400 ng/g (range)	120 ng/g (AM) <80-170 ng/g (range)	150 ng/g (AM) <80-290 ng/g (range)	
Germany	Flame retardants in indoor and outdoor air in the Rhine/ Main area (7 homes, 5 cars, 12 schools, 11 offices, 6 day care centers, 9 building material markets, 6 carpet stores)	Rhine/Main area 56 indoor samples	Concentration in air	100% DF 39 ng/m^3 (AM) 1.2- 496.9 ng/m^3 (range)	36% DF 1 ng/m^3 (AM) <MDL- 9.24 ng/m^3 (range)	52% DF 2.6 ng/m^3 (AM) <MDL- 29.9 ng/m^3 (range)	(Zhou *et al.*, 2017)
		9 outdoor samples		78% DF 2.7 ng/m^3 (AM) <MDL- 11.1 ng/m^3 (range)	0% DF	44% DF 1.1 ng/m^3 (AM) <MDL- 7.1 ng/m^3 (range)	
U.S.	Detection of organophosphate flame retardants in furniture foam and U.S. house dust	Boston (MA) 50 houses	Concentration in dust	24% DF 572 ng/g (GM) 140-5,490 ng/g (range)		96% DF 1,890 ng/g (GM) <90-56,090 ng/g (range)	(Stapleton *et al.*, 2009)

Canada	Passive air sampling of flame retardants in Canadian homes	Toronto (CA) 32 homes Ottawa (CA) 19 homes	Concentration in air	93% DF 20 ng/m^3 (AM) <MDL- 270 ng/m^3 (range)	87% DF 11 ng/m^3 (AM) <MDL- 230 ng/m^3 (range)	99% DF 0.23 ng/m^3 (AM) 0.03- 1.6 ng/m^3 (range)	(Okeme *et al.*, 2018)
Canada	Determining whether cell phones are a good indicator of personal exposure to organophosphate flame retardants	Ontario (CA) 51 houses	Concentration in air-bedrooms	2.6 ng/m^3 (GM) 71.5 ng/m^3 (95-P)	1.6ng/m^3 (GM) 13.9 ng/m^3 (95-P)		(Yang *et al.*, 2019)
			Concentration in air- most usable room	7.4 ng/m^3 (GM) 55 ng/m3 (95-P)	2.9ng/m^3 (GM) 40ng/m3 (95-P)		
			Concentration in dust-bedrooms	934 ng/g (GM) 9,420 ng/g (95-P)	466 ng/g (GM) 1,630 ng/g (95-P)		
			Concentration in dust-most usable rooms	1,330 ng/g (GM) 10,840 ng/g (95-P)	642 ng/g (GM) 2,270 ng/g (95-P)		
U.S.	Human indoor exposure to airborne flame retardants inhalable fractions	Seattle (WA) 10 offices	Inhalable concentration	100% DF 371 ng/m^3 (AM) 16-1,180 ng/m^3 (range)	89% DF 19.1 ng/m^3 (AM) N.d.-77.8 ng/m^3 (range)	33% DF 19.1 ng/m^3 (AM) N.d.-82.2 ng/m^3 (range)	(La Guardia *et al.*, 2017)
		4 coaches offices		100% DF 536 ng/m^3 (AM)	0% DF	100% DF 50.1 ng/m^3 (AM)	

				209-1,360 ng/m^3 (range)		32-69.2 ng/m^3 (range)	
		4 gymnasiums		100% DF 266 ng/m^3 (AM) 136-525 ng/m^3 (range)	0% DF	100% DF 244 ng/m^3 (AM) 125-397 ng/m^3 (range)	
China	Concentration of Halogenated Flame Retardants in the Atmospheric Fine Particles in Chinese Cities	10 cities Beijing, Shanghai, Guangzhou, Nanjing, Wuhan, Taiyuan, Chengdu, Lanzhou, Guiyang, and Xinxiang)	Concentration in air on rooftops (15-20m above ground)	0.01-7 ng/m^3 (range)	0.01-4.7 ng/m^3 (range)	0.001- 0.28 ng/m^3 (range)	(Liu *et al.*, 2016)
U.S.	Organophosphates in settled dust and HVAC filter dust in U.S. low-income homes	Texas 54 homes	Concentration in dust in HVAC filters	91% DF 150,000 ng/g (AM) <MDL- 4,090,000 ng/g (range)		11% DF 3,100 ng/g (AM) <MDL- 47,700 ng/g (range)	(Bi *et al.*, 2018)
			Concentration in settled dust	77% DF 15,800 ng/g (AM) <MDL- 418,000 ng/g		37% DF 8,890 ng/g (AM) <MDL- 122,000 ng/g (range)	

				(range)			
Brazil	Occurrence and human exposure to brominated and organophosphorus flame retardants via indoor dust in a Brazilian city	Araraquara city, Sao Paulo State, Brazil 10 houses, 10 apartments, 5 schools, 5 offices, 16 cars,	Apartments Concentration in dust	100% DF 1,870 ng/g (50-P) 820- 6,420 ng/g (range)	90% DF 237 ng/g (50-P) 136- 826 ng/g (range)	90% DF 2,250 ng/g (50-P) 600-61,200 ng/g (range)	(Cristale *et al.*, 2018)
			Houses Concentration in dust	100% DF 771 ng/g (50-P) 442- 2,280 ng/g (range)	60% DF 230 ng/g (50-P) 153-421 ng/g (range)	100% DF 1,370 ng/g (50-P) 369- 28,600 ng/g (range)	
			Schools Concentration in dust	100% DF 385 ng/g (50-P) 109-69,200 ng/g (range)	40% DF 4,740 ng/g (50-P) 547- 8,930 ng/g (range)	20% DF 397 ng/g (50-P)	
			Offices Concentration in dust	100% DF 1,820 ng/g (50-P) 763-2,510 ng/g (range)	80% DF 237 ng/g (50-P) 145-681 ng/g (range)	80% DF 4,480 ng/g (50-P) 249-10,500 ng/g (range)	
			Cars Concentration in dust	100% DF 2,420 ng/g (50-P)	69% DF 4,200 ng/g (50-P)	100% DF 506,000 ng/g (50-P)	

				315-9,220 ng/g (range)	138- 40,400 ng/g (range)	1,050- 1,600,000 ng/g (range)	
Saudi Arabia	Flame retardants in settled dust of masjids and hotels	Mosques in Jeddah. Hotels in Makkah and Medina. 30 buildings in total	Mosques Concentration in dust	100% DF 2,420 ng/g (GM) 1,570- 4,820 ng/g (range)	100% DF 600 ng/g (GM) 270- 3,470 ng/g (range)	100% DF 2,960 ng/g (GM) 970- 6,945 ng/g (range)	(Ali *et al.*, 2018)
			Hotels Concentration in dust	4,585 ng/g (AM) 375- 12,620 ng/g (range)	920 ng/g (AM) 250- 1,750 ng/g (range)	3,625 ng/g (AM) 1,150- 9,050 ng/g (range)	
Hong Kong	Phosphorus flame retardants in indoor dust in kindergartens and primary schools in Hong Kong	Hong Kong 9 kindergartens	Concentration in indoor $PM_{2.5}$	100% DF 9.1 ng/m^3 (AM) 3.5-19 ng/m^3 (range)	100% DF 20 ng/m^3 (AM) 4.7-49 ng/m^3 (range)	100% DF 15 ng/m^3 (AM) 1.5-38 ng/m^3 (range)	(Deng *et al.*, 2018)
		Hong Kong 2 primary schools	Concentration in dust	80 ng/g (AM) 21- 190 ng/g (range)	250 ng/g (AM) 26- 840 ng/g (range)	1,000 ng/g (AM) 53- 3000 ng/g (range)	
South China	Flame retardants in house dust	Guangzhou 20 homes	Concentration in dust	100% DF 1,240 ng/g (AM) 110- 4,590 ng/g (range)	100% DF 530 ng/g (AM) 50- 3,130 ng/g (range)	100% DF 3,510 ng/g (AM) 420- 10,190 ng/g (range)	(Tan *et al.*, 2017)
South China	Flame retardants in house dust in multiple urban and	Guangzhou 11 urban homes	Concentration in dust	830 ng/g (AM) 160- 2,930 ng/g (range)	5,180 ng/g (AM) 1,550-9,770 ng/g (range)	1,260 ng/g (AM) <MDL- 9,630 ng/g (range)	(He *et al.*, 2015)

	rural locations in south China	Guangzhou 15 urban college dormitories		660 ng/g (AM) 60- 2,300 ng/g (range)	8,420 ng/g (AM) 2,780-20,800 ng/g (range)	440 ng/g (AM) 60- 3,710 ng/g (range)	
		Qingyan 17 rural e-waste recycling workshop		7,180 ng/g (AM) 110-22,300 ng/g (range)	900 ng/g (AM) 180-1,560 ng/g (range)	850 ng/g (AM) 110- 7,020 ng/g (range)	
		Qingyuan 25 rural homes		1,870 ng/g (AM) 240- 10,700 ng/g (range)	2,190 ng/g (AM) 50-9,360 ng/g (range)	330 ng/g (AM) <MDL- 2,770 ng/g (range)	
U.S.	Associations between flame retardant applications in furniture foam, house dust levels, and residents' serum levels	153 homes	Concentration in dust	94% DF 90.9 ng/g (AM) 2,141 ng/g (GM) 6,350 ng/g (75-P)		92% DF 57 ng/g (AM) 1,384 ng/g (GM) 3,269 ng/g (75-P)	(Hammel *et al.*, 2017)
New Zealand	Occurrence of alternative flame retardants in indoor dust from New Zealand	Wellington, Wairarapa, Christchurch, and North Canterbury (NZ)	Concentration in dust from living room floors (n=34) and mattresses (n=16)	100% DF 840 ng/g (AM)	100% DF 788 ng/g (AM)	100% DF 1,936 ng/g (AM)	(Ali *et al.*, 2012)

		50 homes					

Appendix E - VOC definitions

Origin	VVOC definition	VOC definition	SVOC definition	Products covered	Definition focus	Olfactory-impact	Health-related
BS EN ISO 16000-9:2006		Organic compound that is emitted from the test specimen and all those detected in the chamber outlet air		Building products or furnishing	Analytical chemistry property (chromatography detection)	No	no
BS EN 16516:2017 ; Draft ISO/DIS 16000-6:2020	Organic compound eluting before n-hexane on a gas chromatographic column specified as 5% phenyl 95% mehtyl polysiloxnae capillary column.	Organic compound eluting between and including n-hexane and n-hexadecane on a gas chromatographic column specified as a 5% phenyl 95% methyl polysiloxane capillary column	Organic compound eluting after n-hexadecane and up to and including n-C30 on a gas chromatographic column specified as a 5% phenyl 95% emthyl polysiloxane capillary column.	Construction products. Products or materials used in indoor environments	Analytical chemistry property (retention time)	No	no
Directive 2004/42/EC		Volatile organic compound (VOC)' means any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101,3 kPa;		Paints, varnishes and vehicle products	Physicochemical property (boiling point)	No	no
EPA	When discussing indoor environments, all organic chemical compounds that can volatize under normal indoor atmospheric conditions of temperature and pressure are VOCs. While the demarcation line between the Very Volatile Organic Compound (VVOC), Volatile Organic Compound					No	~

	(VOC) and Semivolatile Organic Compound (SVOC) classifications (see table above) is somewhat arbitrary, it does show the wide range of volatility among organic compounds. The three classifications are all important to indoor air, and are all considered to fall within the broad definition of indoor volatile organic compounds.						
Japan (ref)		Organic compounds in gas condition when they are exhausted in the atmosphere. Hazardous air pollutant: any substance that is likely to harm human health if ingested continuously and that is a source of air pollution.				No	yes
Korea (ref)		Air pollutants that are feared to directly or indirectly inflict any harm or injury on the health and property of humans or on the birth and breeding of animal and plants				No	yes
Canada (ref1, Ref 2, ref 3)		Volatile organic compounds (VOCs) are organic compounds containing one or more carbon atoms that evaporate readily into the atmosphere excluding a list of 48 substances.			Atmospheric chemistry	No	no

California Department of Public Health (ref)		Carbon-containing compounds (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides and carbonates and ammonium carbonate) with vapor pressures at standard conditions approximately ranging between those for n-pentane through n-heptadecane. For the purposes of this method, formaldehyde and acetaldehyde are considered to be VOCs.			Physicochemical property (vapor pressure)	No	no
Finland (ref)		Volatile organic compounds mean organic compounds with a boiling point between 50–260 degrees Celsius			Physicochemical property (boiling point)	no	yes

Appendix F - Method for measuring airborne VOCs from spray foam in-situ to determine efficiency of ventilation strategies as a mitigation measure for reducing VOC exposure

Sample collection

Sample collection to be undertaken both passively and actively. A minimum of 40-60 tubes to be used in for each case study with the minimum number of samples as per the protocol in Table XX. The kit necessary for sampling:

4 x low flow pumps (calibrated the morning before the tests are carried out)

40-60 x thermal desorption tubes

60 x long-storage brass caps

40-60 x analytical tubes (Tenax-TA or SPF specific tubes)

	Sampling duration	**Location of extraction**	**Pump flow**	**Foam Stage (approximate)**
1. Blank air sample from house	2 hours	Living room	50-100ml/min	Before spraying
2. Blank air sample from house	2 hours	Bedroom	50-100ml/min	Before spraying
3. Blank air sample from outside house	2 hours	Outside	50-100ml/min	Before spraying
4. Laboratory standard	Used for GC-MS quality assurance and calibration curves			
5. Laboratory standard				
6. Laboratory standard				
7. Blank sample in laboratory	n/a	n/a	n/a	n/a
8. Air sample #1 (analysis tube)	30 mins	Living room	50-100ml/min	During spraying (as soon as it starts)
9. Air sample #2 (backup tube)	30 mins	Living room	50-100ml/min	During spraying (as soon as it starts)
10. Air sample #3 (analysis tube)	30 mins	Living room	50-100ml/min	During spraying (as soon as it starts)
11. Air sample #4 (backup tube)	30 mins	Living room	50-100ml/min	During spraying (as soon as it starts)
12. Blank from laboratory	Used to check whether no VOCs are left in the column of the analytical instrument (GCMS)			

13. Air sample #5 (analysis tube)	1 hour	Living room	50-100ml/min	During spray (45 minutes after it has started)
14. Air sample #6 (backup tube)	1 hour	Living room	50-100ml/min	During spray (45 minutes after it has started)
15. Air sample #7 (analysis tube)	1 hour	Bedroom	50-100ml/min	During spray (45 minutes after it has started)
16. Air sample #8 (backup tube)	1 hour	Living room	50-100ml/min	During spray (45 minutes after it has started)
17. Blank from laboratory	Used to check whether no VOCs are left in the column of the analytical instrument (GCMS)			
18. Air sample #9 (analytical tube)	2 hours	Living room	50-100ml/min	After spray has completed, but extract fan is still working
19. Air sample #10 (backup tube)	2 hours	Living room	50-100ml/min	After spray has completed, but extract fan is still working
20. Air sample #11 (analytical tube)	2 hours	Living room	50-100ml/min	After spray has completed, but extract fan is still working
21. Air sample #12 (backup tube)	2 hours	Living room	50-100ml/min	After spray has completed, but extract fan is still working
22. Blank laboratory	Used to check whether no VOCs are left in the column of the analytical instrument (GCMS)			
23. Air sample #13 (analytical tube)	1-2 hours	Living room	50-100ml/min	2 hours after fan has stopped
24. Air sample #14 (backup tube)	1-2 hours	Living room	50-100ml/min	2 hours after fan has stopped
25. Air sample #15 (analytical tube)	1-2 hours	Bedroom	50-100ml/min	2 hours after fan has stopped
26. Air sample #16 (backup tube)	1-2 hours	Living room	50-100ml/min	2 hours after fan has stopped
27. Blank laboratory	Used to check whether no VOCs are left in the column of the analytical instrument (GCMS)			
28. Air sample #17 (analytical tube)	1-2 hours	Living room	50-100ml/min	4 hours after fan has stopped

29. Air sample #18 (backup tube)	1-2 hours	Living room	50-100ml/min	4 hours after fan has stopped
30. Air sample #19 (analytical tube)	1-2 hours	Bedroom	50-100ml/min	4 hours after fan has stopped
31. Air sample #20 (backup tube)	1-2 hours	Living room	50-100ml/min	4 hours after fan has stopped
32. Blank laboratory	Used to check whether no VOCs are left in the column of the analytical instrument (GCMS)			
33. Passive sampling #1	1 week	Living room	n/a	Left there 2 hours before application
34. Passive sampling #2	1 week	Living room	n/a	Left there 2 hours before application
35. Passive sampling #3	1 week	Living room	n/a	Left there after extraction fan has stopped
36. Passive sampling #4	1 week	Living room	n/a	Left there after extraction fan has stopped
37. Passive sampling #5	1 week	Bedroom	n/a	Left there after extraction fan has stopped
38. Passive sampling #6	2 weeks	Living room	n/a	Left there 24 hours after application
39. Passive sampling #7	2 weeks	Living room	n/a	Left there 24 hours after application
40. Passive sampling #8	2 weeks	Bedroom	n/a	Left there 24 hours after application

Analytical sampling

All tubes should be conditioned prior to each experiment by purging them with nitrogen at 100 mL/min for 30 min at 300 °C. After the samples are collected, they will be brought straight to the lab where they will be loaded for analysis.

	Sampling duration	**Location of extraction**	**Pump flow**	**Foam Stage (approximate)**
41. Air sample #21 (analysis)	2 hours	Living room	50-100ml/min	24 hours after spraying
42. Air sample #22 (backup)	2 hours	Living room	50-100ml/min	24 hours after spraying
43. Air sample #23 (analysis)	2 hours	Living room	50-100ml/min	24 hours after spraying
44. Air sample #24 (backup)	2 hours	Living room	50-100ml/min	24 hours after spraying
45. Air sample #25 (analysis)	2 hours	Living room	50-100ml/min	24 hours after spraying
46. Air sample #26 (backup tube)	2 hours	Living room	50-100ml/min	24 hours after spraying
47. Air sample #27 (analysis tube)	2 hours	Bedroom	50-100ml/min	24 hours after spraying
48. Air sample #28 (backup)	2 hours	Bedroom	50-100ml/min	24 hours after spraying
49. Air sample #29 (analysis)	2 hours	Living room	50-100ml/min	72 hours after spraying
50. Air sample #30 (backup)	2 hours	Living room	50-100ml/min	72 hours after spraying
51. Air sample #31 (analysis)	2 hours	Living room	50-100ml/min	72 hours after spraying
52. Air sample #32 (backup)	2 hours	Living room	50-100ml/min	72 hours after spraying
53. Air sample #33 (analysis)	2 hours	Living room	50-100ml/min	72 hours after spraying
54. Air sample #34 (backup tube)	2 hours	Living room	50-100ml/min	72 hours after spraying
55. Air sample #35 (analysis tube)	2 hours	Bedroom	50-100ml/min	72 hours after spraying
56. Air sample #36 (backup)	2 hours	Bedroom	50-100ml/min	72 hours after spraying

Repeat protocol as per above for Week 1 results.

	Sampling duration	Location of extraction	Pump flow	Foam Stage (approximate)
57. Air sample #37 (analysis)	2 hours	Living room	50-100ml/min	96 hours after spraying
58. Air sample #38 (backup)	2 hours	Living room	50-100ml/min	96 hours after spraying
59. Air sample #39 (analysis)	2 hours	Living room	50-100ml/min	96 hours after spraying
60. Air sample #40 (backup)	2 hours	Living room	50-100ml/min	96 hours after spraying
61. Air sample #41 (analysis)	2 hours	Living room	50-100ml/min	96 hours after spraying
62. Air sample #42 (backup tube)	2 hours	Living room	50-100ml/min	96 hours after spraying
63. Air sample #43 (analysis tube)	2 hours	Bedroom	50-100ml/min	96 hours after spraying
64. Air sample #44 (backup)	2 hours	Bedroom	50-100ml/min	96 hours after spraying

Repeat protocol as per above for analysing TD tubes, conditioning them and returning them to the property for further measurements.

	Sampling duration	Location of extraction	Pump flow	Foam Stage (approximate)
65. Air sample #45 (analysis)	2 hours	Living room	50-100ml/min	120 hours after spraying
66. Air sample #46 (backup)	2 hours	Living room	50-100ml/min	120 hours after spraying
67. Air sample #47 (analysis)	2 hours	Living room	50-100ml/min	120 hours after spraying
68. Air sample #48 (backup)	2 hours	Living room	50-100ml/min	120 hours after spraying
69. Air sample #49 (analysis)	2 hours	Living room	50-100ml/min	120 hours after spraying
70. Air sample #50 (backup tube)	2 hours	Living room	50-100ml/min	120 hours after spraying
71. Air sample #51 (analysis tube)	2 hours	Bedroom	50-100ml/min	120 hours after spraying
72. Air sample #52 (backup)	2 hours	Bedroom	50-100ml/min	120 hours after spraying

Repeat protocol as per above for analysing TD tubes, conditioning them and returning them to the property for further measurements.

	Sampling duration	Location of extraction	Pump flow	Foam Stage (approximate)
73. Air sample #53 (analysis)	2 hours	Living room	50-100ml/min	144 hours after spraying
74. Air sample #54 (backup)	2 hours	Living room	50-100ml/min	144 hours after spraying
75. Air sample #55 (analysis)	2 hours	Living room	50-100ml/min	144 hours after spraying
76. Air sample #56 (backup)	2 hours	Living room	50-100ml/min	144 hours after spraying
77. Air sample #57 (analysis)	2 hours	Living room	50-100ml/min	144 hours after spraying
78. Air sample #58 (backup tube)	2 hours	Living room	50-100ml/min	144 hours after spraying
79. Air sample #59 (analysis tube)	2 hours	Bedroom	50-100ml/min	144 hours after spraying
80. Air sample #60 (backup)	2 hours	Bedroom	50-100ml/min	144 hours after spraying

Repeat protocol as per above for analysing TD tubes, conditioning them and returning them to the property for further measurements.

	Sampling duration	Location of extraction	Pump flow	Foam Stage (approximate)
81. Air sample #61 (analysis)	2 hours	Living room	50-100ml/min	168 hours after spraying
82. Air sample #62 (backup)	2 hours	Living room	50-100ml/min	168 hours after spraying
83. Air sample #63 (analysis)	2 hours	Living room	50-100ml/min	168 hours after spraying
84. Air sample #64 (backup)	2 hours	Living room	50-100ml/min	168 hours after spraying
85. Air sample #65 (analysis)	2 hours	Living room	50-100ml/min	168 hours after spraying
86. Air sample #66 (backup tube)	2 hours	Living room	50-100ml/min	168 hours after spraying
87. Air sample #67 (analysis tube)	2 hours	Bedroom	50-100ml/min	168 hours after spraying
88. Air sample #68 (backup)	2 hours	Bedroom	50-100ml/min	168 hours after spraying

Repeat protocol as per above for analysing TD tubes, conditioning them and returning them to the property for further measurements. After 168 hours, airborne emissions are expected to reach near steady state with theoretical decay over time. Samples could be taken with less frequency over time.

Sampling period	Frequency of active airborne sampling
Week 1	As per above
Week 2-4	Daily or a minimum of three times per week
Week 4-12	A minimum of twice per week
Week 12-24 and beyond	A minimum of once per week

The ventilation protocol prior to sampling should be recorded via building occupier questionnaires. For example, if the occupiers had opened the windows to ventilate shortly before the sampling, this should be recorded. Ideally, the windows should remain closed shortly prior (4 hours) and during the sampling. Further experiments could be undertaken with the windows being open, or with air cleaners introduced for a short period of time, to test air 'flushing' as a measure of reducing VOC concentrations indoors. The data could be utilised to advise occupants on how often, and for how long, they should open windows to reduce airborne VOC levels. Dust and surface samples should ideally be collected as well in order to understand total exposure to VOCs from all exposure routes.

Appendix G – Glossary and common terms within the thesis explained

SPF Chemical class	Characteristic	Assessment based on literature review and empirical data from thesis		
	Spray foam lifecycle period	**During installation**	**<1 month**	**>1 month**
Isocyanates	Hazard/ Health impact	**High** Over 1 ppm could have toxic effects. Could cause isocyanate asthma. High risk of sensitisation even at low concentrations.		
	Exposure risk	**High** Data from this thesis and existing literature demonstrate that exposure above HSE legal limits could occur near spraying equipment during manual installation.	**Low** Isocyanate reacts quickly, and data suggests no significant risk after foam has cured.	**Low** Free monomer isocyanates are not expected to be found indoors in the long-term.
	Level of uncertainty	**Low** Extensive literature findings on both health hazards and exposure risk.		
Polyol	Hazard/ Health impact	**Moderate** No significant health risk found in literature, apart that very high levels could act as irritant.		
	Exposure risk	**Low**		

		Data from this thesis and existing literature demonstrate that polyol reacts with isocyanate and emissions have not been detected above recommended guidelines.	
	Level of uncertainty	**Low**	
Flame retardants	Hazard/ Health impact	**High** Health risks include: irritation, suspected carcinogens, suspected to induce seizures.	
	Exposure risk	**High** Oral, dermal exposure possible even with H&S equipment.	**Moderate** Literature and thesis data suggests flame retardants continue off-gassing indefinitely. Emission rates and exposure dependent on multiple variables (temperature, ventilation, occupancy profile). Flame retardants are present in abundance emitted from multiple sources, not just insulation. Possible de-escalation to 'low' theoretically possible if reactive flame retardants are used that bond to the polyurethane matrix and evidence is provided that they do not emit into the indoor environment.
	Level of uncertainty	**Moderate** Few studies and this thesis examined spray foam have demonstrated human exposure empirically.	**High** Very limited case study data available. No case studies data were found at the point of completing this thesis where bonded flame retardants have been used and emission concentrations measured in situ. Novel flame retardants lack empirical evidence in relation to health hazards (TCPP versus TCEP for example).
Blowing agent	Hazard/Health impact	**Low**	

		No significant risk found in the literature for HFOs apart from data that very high could act as irritant.	
	Exposure risk	**Low** Recorded amount is lower than recommended exposure thresholds by a statistically significant factor in existing studies.	
	Level of uncertainty	**Moderate** Limited case study data is available on blowing agent emissions.	
Catalyst	Hazard/ Health impact	**Moderate-High** Oral, dermal exposure possible if proper H&S equipment is not used. Could cause irritation. Chronic exposure reported effects on liver, kidney, blood and central nervous system.	
	Exposure risk	**High** Emissions are found to deplete within one week after PU installation.	**Low-Moderate** Emissions expected to deplete within the first year based on experimental foam testing in chambers. . Possible de-escalation to 'green' status would be possible if further chamber and case study data is provides empirical evidence that in-situ concentrations are below risk tolerability limits or catalysts are replaced with
	Level of uncertainty	**Low-Moderate** Limited data available from case studies whether re-occupancy strategy or ventilation protocol post-installation is sufficient to reduce risks.	**High** There is limited case study data with regards to amine catalyst emissions from spray foam products in situ.

Non-disclosed constituent compounds, by-products and tertiary emissions	Health impact	**High** Some compounds listed as Class 1 and Class 2B carcinogens by IARC.	Secondary or tertiary VOCs and SVOCs could impact IAQ.
	Exposure risk	**High** Data in Chapters 6-8 demonstrate that emission concentrations could exceed exposure recommended values (in particular 1,4-dioxane exceeding NIOSH REL and OEHHA CREL during spraying)	**Low-Moderate** Data from this study, particularly Chapter 8, suggests limited risk however one case study was not sufficiently exhaustive to rule out long-term exposure risks. More research is recommended.
	Level of uncertainty	**Moderate** This thesis filled partially the evidence gaps, however more research is recommended in relation to this family of VOCs and SVOCs.	**High** There is limited evidence with regards to and non-disclosed constituent compounds, by-product and tertiary emissions from spray foam products.

Appendix H – Glossary and common terms within the thesis explained

ACGIH	American Conference of Governmental Industrial Hygienists
COSHH	Control of Substances Hazardous to Health
CPI	Centre for Polyurethane Industry
GM	Geometric Mean
GWP	Global Warming Potential
IAQ	Indoor Air Quality
IDLH	Immediately Dangerous to Life or Health
IPCC	Intergovernmental Panel on Climate Change
MDA	Methylenediphenyl Diamine
MDI	Methylene Diphenyl Diisocyanate
Ng/kgbw/day	Nanograms per kilogram of body weight per day
ODP	Ozone Depletion Potential
OFR	Organophosphate Flame Retardant
PEL	Permissible Exposure Limit
PIR	Polyisocyanurate
PU	Polyurethane
REL	Recommended Exposure Limit
RH	Relative Humidity
SPF	Spray Foam Insulation
STEL	Short Term Exposure Limit
T	Temperature
TCPP	Tris (1-chloro-2-propyl) phosphate
TERA	Toxicology Excellence for Risk Assessment
TWA	Time Weighted Average