Polyurethane insulation and household products – a systematic review of their impact on indoor environmental quality

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Abstract

We systematically review the impact of polyurethane insulation and polyurethane household products on the indoor environmental quality of buildings. The review breaks down polyurethane products into constituent compounds (isocyanate, polyol, flame retardant, blowing agent and catalyst) as well as secondary emissions, and discusses their implications on human health. Concentrations of compounds emitted from insulation, and household materials, measured in laboratory experiments and case studies are presented in the context of the built environment.

We outline that isocyanate exposure over the current legal limits could take place during spray foam insulation application in the absence of personal protection equipment. The study reports that flame retardants are not chemically bound to polyurethane products and they are found in measurable concentrations in indoor environments. Additionally, we provide evidence that catalysts are responsible for at least some negative impact on perceived indoor air quality. More data is required to determine the long-term emissions from spray foam products and the ventilation strategies required to balance energy savings, thermal comfort and good indoor air quality. However, it is not yet possible to determine whether potential health impacts could result from exposure to a single compound or a combination of compounds from spray foam products. We present a risk matrix for polyurethane compounds and propose that flame retardants, by-products, and residual compounds are particularly important for indoor air quality. We conclude by suggesting a framework for further research.

Highlights:

- Organic emissions from PU materials in the context of human health and exposure are investigated
- Reported VOC and SVOC concentrations from PU insulation and household materials are reviewed
- OFRs are emitted in the long term and are found abundantly indoors even in buildings with no PU insulation
- Amines impact perceived IAQ, but it’s unclear which PU compound/s impact health individually or cumulatively
- A risk matrix is proposed based on implications on IAQ and further research needs

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Table of Contents:

List of Figures:

List of Tables:

List of Appendices:

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

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

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

Glossary

ACGIH	American Conference of Governmental Industrial Hygienists
BDMAEE	Bis-(2-dimethylaminoethyl)ether
COSHH	Control of Substances Hazardous to Health
CPI	Centre for Polyurethane Industry
GM	Geometric Mean
DBTDL	Dibutyltin dilaurate
GWP	Global Warming Potential
IAQ	Indoor Air Quality
IEQ	Indoor Environmental Quality
IDLH	Immediately Dangerous to Life or Health
IPCC	Intergovernmental Panel on Climate Change
MDA	Methylenediphenyl Diamine
MDI	Methylene Diphenyl Diisocyanate
MSDS	Material Safety Data Sheet
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 rigid board
pMDI	Polymeric Methylene Diphenyl Diisocyanate
PU	Polyurethane
PUR	Polyurethane rigid board
REL	Recommended Exposure Limit

RH	Relative Humidity
SDS	Safety Data Sheet
SPF	Spray Foam Insulation
STEL	Short Term Exposure Limit
SVOC	Semi-Volatile Organic Compound
T	Temperature
TCPP	Tris (1-chloro-2-propyl) phosphate
TCEP	Tris(2-chloroethyl)phosphate
TCDP/TCDPP	Tris (1,3-dichloroisopropyl) phosphate
TERA	Toxicology Excellence for Risk Assessment
TMAEEA	N,N,N-trimethylaminoethylethanolamine
TWA	Time Weighted Average
VOC	Volatile Organic Compound

1. Introduction

In the UK, 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. Studies have shown that increasing or adding insulation within the thermal envelope of a building reduces the heating demand of the property by 20-60% (Martínez-Molina *et al.*, 2016), while also increasing thermal comfort (Hong *et al.*, 2009).

Isocyanate based rigid board insulation (PUR/PIR) and spray polyurethane foam (SPF) insulation products have 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), and in comparison to conventional insulation products (Cabeza *et al.*, 2010). Meanwhile, the total environmental quality of buildings is still a subject of continuing research (Taylor *et al.*, 2018). While polyurethane (PU) materials are commonly found indoors in clothing, appliances (fridges and freezers), composite wood, floorings, furnishing, car seats, insulation and packaging materials (American Chemistry Council, 2018), there is little information on their impact on indoor air quality. In an effort to address the impact of the building sector on CO_2 emissions, “green buildings” with lower air-permeability for improved energy performance, grow in popularity. The issue of indoor air quality to promote better health and well-being for building occupants (Steinemann, Wargocki and Rismanchi, 2017) must, however, be considered alongside energy efficiency.

Isocyanate based insulation products are typically produced by mixing two liquids: an A-side component (isocyanate: MDI, pMDI or TDI) and a B-side component (polyol, fire retardant, catalyst, blowing agents and surfactants). These insulating materials could either be produced in factories (PUR/PIR rigid boards/sheets/panels) or applied in-situ (SPF insulation). To understand the implications of these products on indoor air quality, each of their constituent compounds should be considered. The main chemical bond of the insulation is between the isocyanate and the polyol, which form the urethane link, whilst other compounds enhance the reaction process (catalyst, blowing agents) or foam properties (flame retardants). Existing studies usually focus on only one group of compounds and evaluate their implications on health, IAQ or future development (Tsai, 2005; Kim and Yu, 2014; Gama, Ferreira and Barros-Timmons, 2018). Research demonstrates that in isolation each group could impact human health, with some carrying higher risks compared to others (Bello *et al.*, 2004; Ali *et al.*, 2018).

During the production, and lifecycle, of PU products various organic compounds can be released from the foams into the indoor environment. Scarce data is available covering these emissions and to address the knowledge gap, a compilation of small studies was published by ASTM to provide further insight (ASTM International, 2017), followed by the ASTM D8142 - 17 standard for measuring the chemical emissions (2018). This collection of reports provides data in relation to SPF emissions and their implications on indoor environmental quality (IEQ). Polyurethane products are found abundantly in modern indoor environments (American Chemistry Council, 2018), however their cumulative volatile and semi-volatile organic (VOCs, SVOCs) long-term emissions and implications on human health are still largely unknown.

To fill this gap, this review presents novel data on the impact of PU materials specifically on indoor environmental quality. We present a risk matrix, based on the main findings, which aims to establish the hazards related to human exposure to organic emissions during the PU products lifecycle. This study is the first to systematically evaluate PU and SPF emissions throughout their lifecycle in the context of health and reported long-term concentrations. We provide a systematic assessment of the impact of these products on the indoor environmental quality. The review concludes by suggesting a framework for further research, which may serve as a basis for further evaluation of the balance between energy efficiency and healthy IAQ.

2. Method

The study reviews and critically analyses the holistic impact of PU and SPF products on indoor environments and people. The objectives of the study are to:

- quantify the energy efficiency and thermal comfort benefits of polyurethane products compared to conventional insulation materials
- review the impact of emissions from isocyanate-based products, present in indoor environments, on health
- review the measured VOCs and SVOCs during a product's lifecycle, with a focus on insulation materials
- review current SPF application practices in the context of worker protection and IAQ
- develop a risk matrix for SPF emissions and suggest further areas of research

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.

Search strategy

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 performance	7	Spray foam insulation, thermal conductivity, thermal performance, energy efficiency, natural material, polyurethane insulation, polyisocyanurate insulation
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
VOCs and SVOCs emissions	16	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
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.

Classification and quality assessment

The collected reports are subject to systematic evaluation following the flow diagram outlined in Figure 1.

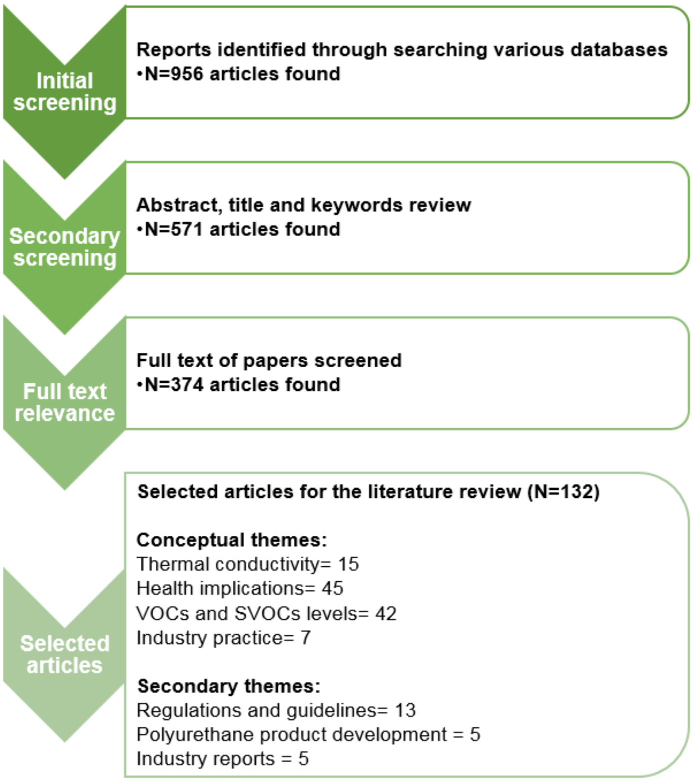

Figure 1. Flow diagram of screening process and paper selection

The 132 articles selected for the review are divided in four spreadsheets as per the conceptual themes of the review in Table 1. The classification of these topics enables the authors 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.

3. Thermal performance

Using insulation materials in buildings increases the thermal comfort of residents (Hong *et al.*, 2009), reduces their energy bills (Webber, Gouldson and Kerr, 2015) and carbon footprint (Jenkins, 2010). 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 IEQ (thermal comfort). To understand the benefits of using PU insulation (both PUR/PIR rigid boards and SPF) for increasing thermal comfort, Figure 2 summarises the conductivity of common insulation materials with the full dataset included in Appendix A.

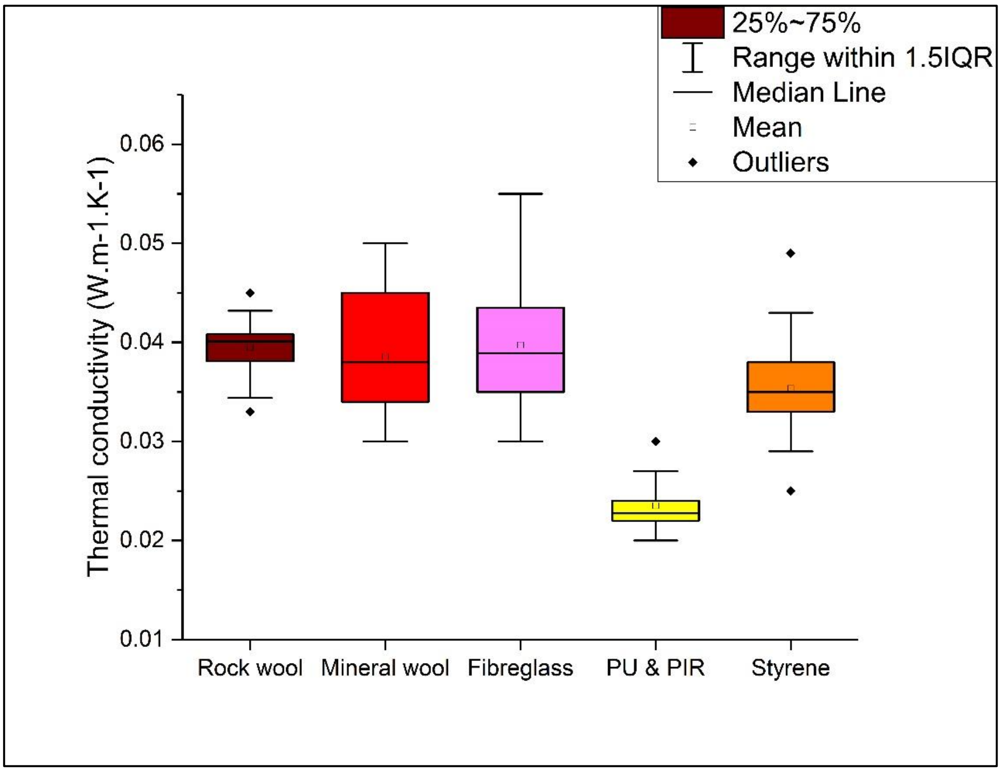

Figure 2. Comparative performance of insulation materials based on measured studies, design values and manufacturer declared data (Al-Ajlan 2006; Abdou & Budaiwi 2005; Al-Homoud 2005; Papadopoulos 2005; Budaiwi et al. 2002; Lakatos 2014; Berge & Johansson 2012; BS: EN ISO 10456:2007; Manufacturer declared data). *Lower values are better insulators.*

Figure 2 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). 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. However the impact of PU on the total environmental performance (IEQ) of the built environment (Taylor *et al.*, 2018) is a subject of further research. In particular, the organic emissions from PU products throughout their lifecycle and their implications on indoor air quality and human health.

4. Impact on health and IAQ

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 a property. 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, 2017). There is however no national, or international, technical definition explicitly outlining what constitutes ‘misapplication’. There have been several lawsuits in the United States against companies that have reportedly ‘misapplied’ spray foam insulation or in relation to failure to report risks associated with SPF constituents:

Renzi v Demilec Southern District of Florida case# 12 cv 80516

Albanese v Demilec District of Connecticut case # 12 cv 01053

Heckler v Demilec Western District of Wisconsin #12 cv 00682

Markey v Lapolla Industries Eastern District of New York # 12 cv 04622

Schraeder v Demilec District Court of New Jersey case # 12-cv 06074

Beyer v Anchor Insulation CO. Civil No. 3:13-cv-1576 (JBA)

In one of the cases, the court ruled that although material safety data sheets (MSDS) admit inhalation of vapours emitted ‘can’ or ‘may cause’ health issues (irritation to the upper respiratory tract, fatigue, weakness, drowsiness, and headache), the jury was unable to speculate on scientific issues with the finished product.

This legal decision highlights how critical it is for more scientific data to be made available to determine whether SPF products represent any long-term risks for human health. Potential health effects of these products have been reported: evidence of seven workers developing asthma whilst working for foam insulation companies, six office workers suffering occupational asthma after SPF retrofit, an additional list of 14 CPSC incident reports related to SPF applications (NRDC *et al.*, 2017) and two people have developed cough and dyspnoea after their home was retrofitted with SPF (Tsuang and Huang, 2012). There is a clear gap in knowledge as safety data sheets disclose some of the chemicals that comprise the finished product, but it does 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. Likewise, chemicals in the finished product may form as a result of reactions and may not be present in the MSDS. The above cases clearly indicate that the potential health impacts of the PU products requires further investigation of all organic emissions.

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

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 to provide better foam stability, expansion time and physical properties. The polyol reacts with the isocyanate to form the urethane bonds in polyurethane.

Polyols

In the last decade, the scientific research on SPF 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).

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, 2017). 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 SPF spraying (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 products.

Flame retardants

To enhance the fire resistant properties of PU and PIR products, fire retardants are added to spray foam materials with organophosphate (OFRs) growing in popularity in recent years (Xu *et al.*, 2019). The most widely used OFRs include: TCPP (Tris(2-chloroisopropyl)phosphate), TCEP (Tris(2-chloroethyl)phosphate), and TDCP/TDCPP (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). Flame retardants form 15-60% of the B-side of the foam.

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). TCPP and TDCP are however associated with a slightly sweet odour (Environment Canada, 2016) and may not have an adverse impact on perceived IAQ.

Whilst OFRs are classed as SVOCs and generally associated with long-term health impacts, other emissions from PU materials are VOCs which are also important to consider.

Blowing agents

Blowing agents have been the most rapidly evolving aspect of PU insulation and SPF production in the last 30-40 years, governed by international regulations (Figure 3). A study in 2010 suggested that chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been effectively already phased out (Feldman, 2010) and no longer represent any real interest for further research. However, a recent report (EIA, 2018) provided contrary evidence as 18 different companies were found 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).

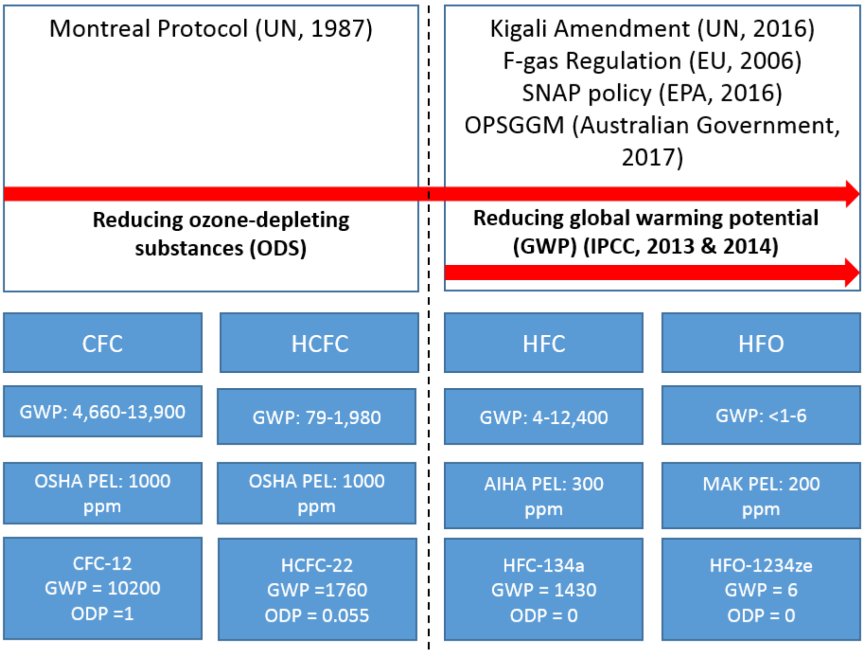

Figure 3. Blowing agents in polyurethane materials, phase-out regulations since 1980s and permissible exposure limits. Bottom row gives examples of blowing agents of each type used in PU production. Values derived from IPCC reports. (UN, 1987, 2016; IPCC, 2013, 2014; EU, 2014; EPA, 2016; Australian Government, 2017)

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 SPF retrofit would likely be insignificant (ECETOC, 2004).

Hydrofluoroolefins (HFOs) are the new-generation of blowing agents, whose potential effects at low concentrations include dizziness and at high concentration could cause eye and skin irritation according to EPA (2009). 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 HFO-1234ze.

As most blowing agents are odourless, or have a faint sweet smell, they appear to have little impact on perceived indoor air quality. Unlike blowing agents, amine catalysts could impact the perceived IAQ as they have a “fishy” odour (Amoore and Forrester, 1976).

Catalysts

The purpose of catalysts is to enhance the mixing, and expanding, synthesis of the foam for enhanced performance. Each SPF manufacturer could have a proprietary unique mix of catalysts with some of the common being amine catalysts: bis-(2-dimethylaminoethyl)ether (BDMAEE), diethanolamine, dimethylethanolamine, *N*-ethylmorpholine, *N*,*N*-dimethylaminopropylamine, triethanolamine, triethylamine, triethylenediamine and trimethylaminoethylethanolamine (TMAEEA) (Sleasman, ASTM International 2017). Amines usually form a small percentage of the foam weight, usually between 1-5% of the B-side (ASTM International, 2017).

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). NTP reported an increased incidence of liver and kidney tumours in mice from dermal exposure to diethanolamine (National Toxicology Program, 1999). Amine catalysts, secondary amines or tertiary amines created during SPF production could also impact perceived IAQ and therefore occupant wellbeing. Amines have a “fishy” odour, which is often associated with “misapplied” spray foam insulation (Light, ASTM International, 2017).

Tin-based catalysts, such as dibutyltin dilaurate (DBTDL), are also used for the production of some polyurethane products however are less common and usually form less than 0.15% of the B-side weight in two component foams. Metal-based catalyst used in polyurethane production could irritate the eyes, skin and respiratory tract and prolonged skin contact can cause dermatitis. When rats were administered with 5-40 mg/kg of DBTDL, neurotoxic damage to the brain and aggravated poisoning symptom were recorded (Jin et al., 2012).

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

By-products or residual products

A review of analytical techniques to understand emissions from SPF (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 SPF insulation materials with an unknown origin. 1-chloro-2-propanol has been hypothesised to be a degradation product of TCPP-2 and 1,2-DCP a possible degradation product of TDCPP (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 SPF combustion, however they reached a similar conclusion that fumes from SPF materials during fires are highly toxic for human health.

If flooding occurs and PU comes in contact with water, the hydrolysis product of MDI is MDA. 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 suggested that MDA concentrations formed in the environment of MDI reacting with water are however low (Sekizawa and Greenberg, 2001). Studies of workers have identified MDA in urine and blood suggesting that it may be a used as a marker of long-term exposure to MDI (Sekizawa and Greenberg, 2001).

Whilst it is evident that multiple compounds from SPF could potentially impact human health, the concentration, duration and type of exposure of each compound are critical factors in evaluating the risks for IAQ and people.

5. Exposure routes, concentration and emission rates

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, 1999; Roberge, Gravel and Drolet, 2009). Figure 4 reports MDI concentration during spraying with the full dataset of numerical findings is in Appendix B. The reports measure MDI concentration in air near the sprayer from two component closed cell spray foams.

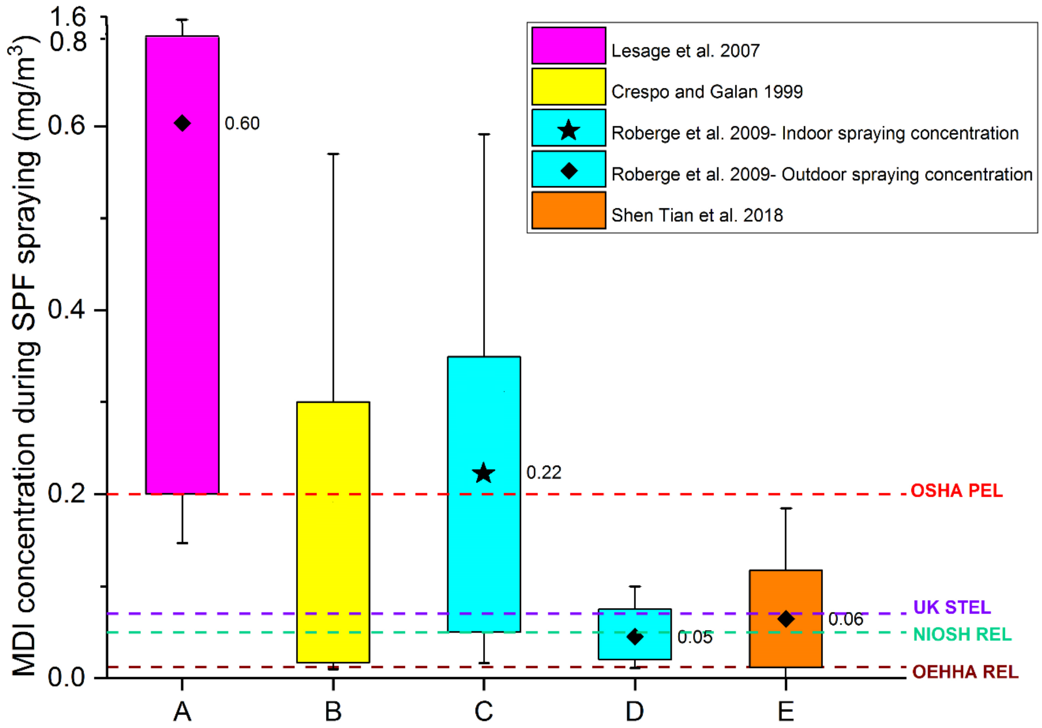

Figure 4. Measured exposure to MDI (mg/m^3) near a sprayer during installation of two-component polyurethane spray foams. Box plots show interquartile ranges. Shapes show mean concentrations and whiskers show min-max values. Crespo and Galan (1999) mean could not be calculated due to lack of a full data set. Dotted lines represent permissible, short-term and recommended exposure limits of different institutions and/ or countries.

Almost all studies (A-D) in Figure 4 use a sampling rate of 1-1.1 l/s, apart from one which uses 15 l/s (E). The results from Figure 4, and Appendix B, demonstrate that during application of SPF the MDI concentration in air could exceed the OSHA recommended threshold values by 3-8 times and UK STEL values by 9-22 times (Crespo and Galán, 1999; Roberge, Gravel and Drolet, 2009). 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. The data from the limited existing studies (Appendix B) 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 PEL, but both studies were undertaken in rooms with high ventilation rates (ACH_{50} of 32.4 for Won and an extract rate of 10-598 ACH for Wood). A 598 ACH would be nearly impossible 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 4). Bello et. al (2019) measured breathing zone exposure of 24 sprayers during SPF spraying and reported that 4,4-MDI concentration exceeded NIOSH REL values for: 16% of personal air samples and 35% of area samples near the vicinity of the workers. The results serve as evidence that regulations must be put in place in order to reduce, and possibly eliminate, the risk of recurring incidents such as the ones recorded by NRDC covered in Section 4 (NRDC *et al.*, 2017).

Figure 5 summarises MDI concentration further away from the source, exposure of helpers and concentration after spraying two component closed cell spray foams

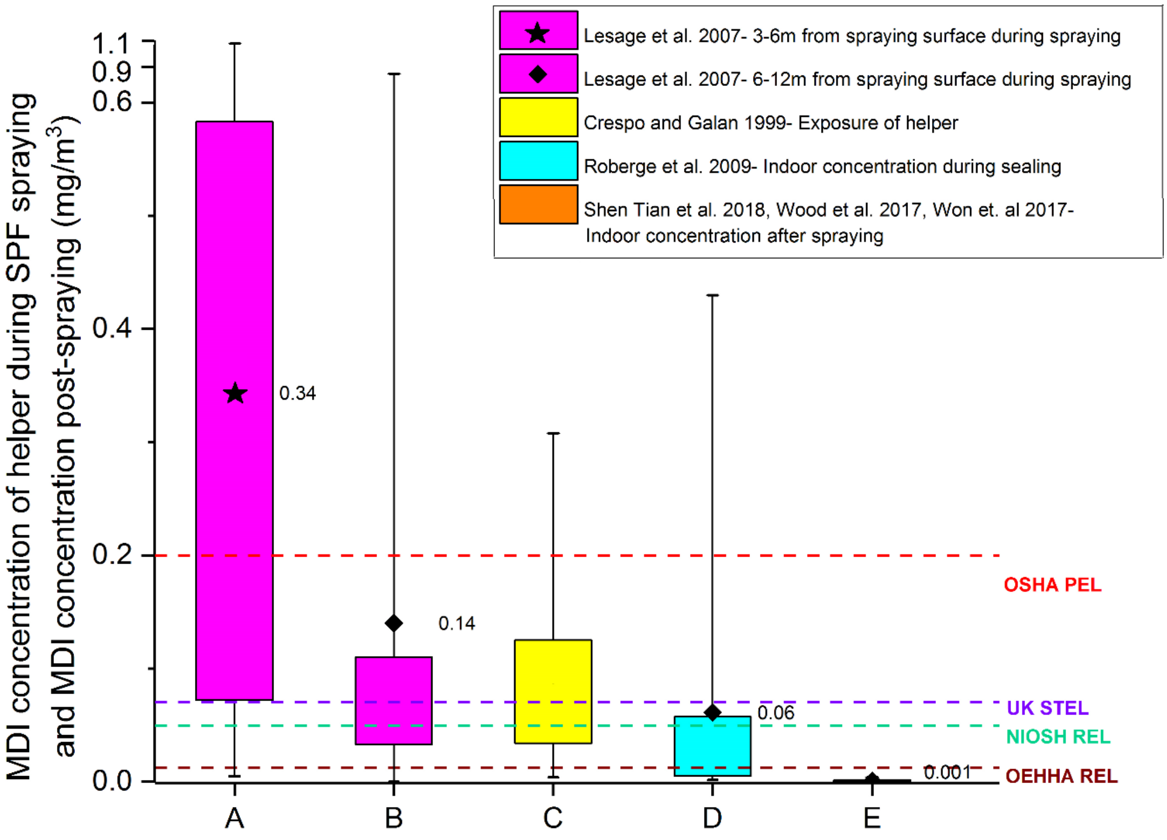

Figure 5. Measured exposure to MDI (mg/m^3) near helper during installation, exposure of sprayer during sealing and exposure post-application of two component polyurethane spray foam. Box plots show interquartile range. Points show mean concentrations and whiskers demonstrate min-max values. Crespo and 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 5. Figure 4 and Figure 5 highlight that both the sprayer and the helper could be exposed to levels of isocyanate monomer above UK STEL values unless PPE and control procedures are used. Bello et al. (2019) reported that sprayers had a lower exposure (7.5 µg/m^3) compared to sprayers (19.6 µg/m^3). Even when spraying outdoors, concentrations can still exceed the OEHHA recommended exposure limit.

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 PU insulation, or PU household products, post-installation under standard occupancy conditions is considered to be minimal. People suffering from asthma, or isocyanate sensitisation, may be more vulnerable compared to the general population.

Importance of sampling method

A method for testing MDI exposure limits has been developed by using a CIP10M approach (Puscasu *et al.*, 2015). The CIP10M method 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 sampler developed for MDI detection (ASSET EZ4-NCO) was also 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 STEL reference value (HSE) is reflective of all of the isocyanate functions based on the scientific data of their toxicity. The oligomerisation degree of the MDI could potentially impact the isocyanate emissions during application, however there is no reliable data in existing literature demonstrating those impacts. Different isocyanate mixtures consisted of various splits of 2,2-MDI, 2,4-MDI, 4,4-MDI and pMDI may impact isocyanate emissions and this should be looked at in the future. The choice of analytical method is critical to accurately determine the total isocyanate presence in indoor air. 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.

Emissions during combustion and fires

Exposure to high levels of MDI from PU boards and SPF could possibly occur during fires, as pyrolysis-GC-MS analysis of PU has shown that the urethane bond breaks at high temperatures (Ohtani *et al.*, 1987). A study on the thermal degradation of rigid PU 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$_{\text{sample}}$ (Garrido *et al.*, 2017).

Apart from MDI, large quantities of hydrogen cyanide, acrylonitrile, acetonitrile and carbon monoxide are released between 550-850 °C, as per Table 2, which could have toxic effects (Garrido, Font and Conesa, 2016). Although the study is limited to a single product, it does highlight the potential risks during fires.

Table 2. Emissions from polyurethane mattress after pyrolysis (Garrido, Font and Conesa, 2016)

Compound	Emissions from polyurethane mattress during pyrolysis (mg/kg$_{\text{sample}}$)	Fatal or immediately dangerous to health (IDLH) exposure levels (mg/m^3)
Hydrogen cyanide	1,445-54,330	199-603 (fatal) (ATSDR, 2006)
Acrylonitrile	2,490-12,206	184 (IDLH) (NIOSH, 1994b)
Acetonitrile	1,337-11,764	839 (IDLH) (NIOSH, 1994a)
Carbon monoxide	26,764-134,060	1,374 (IDLH) (NIOSH, 1994c)

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 PU products, but also natural materials could contribute to releasing isocyanates during fires. Figure 6 represents the volume of product containing sufficient isocyanate (MDI) that would exceed the highest legal exposure limit (OSHA PEL) if released back into the indoor air in a typical 50 m^3 bedroom.

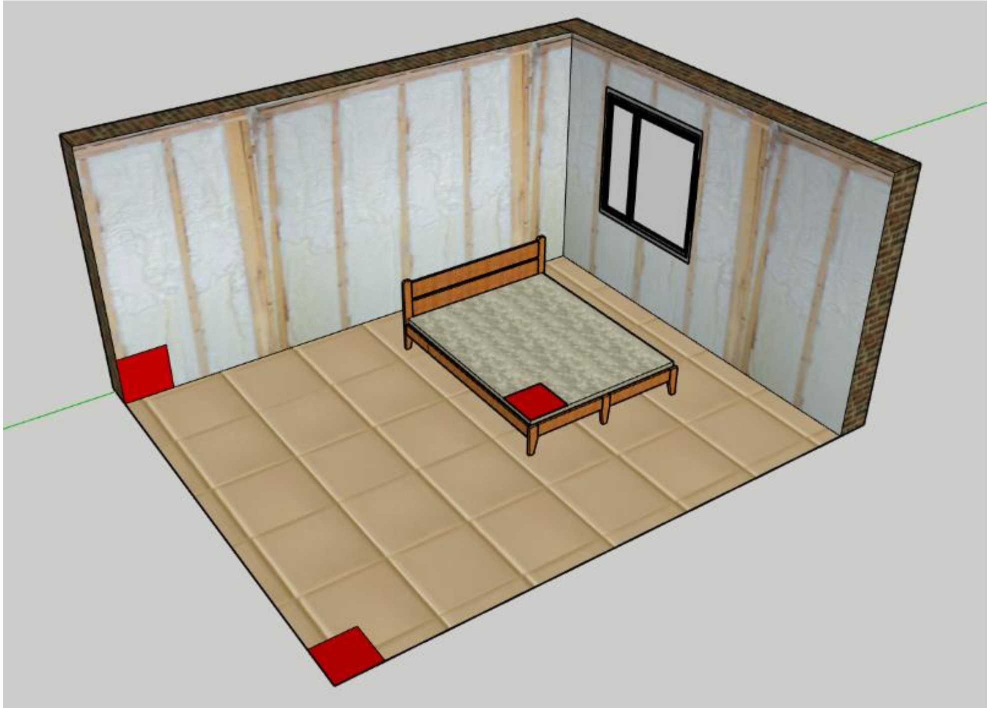

Figure 6. Area of various products (PU mattress, PU floor insulation and PU wall insulation) that contains sufficient isocyanate to exceed OSHA PEL if released into a typical 50 m^3 bedroom (5 m width, 4 m length, 2.5 m height). Thickness of 15cm assumed for all products. Density of 30 kg/m^3 assumed for all products.

Whilst flame retardants reduce the risks of combustions and fire, it has been questioned whether this benefit outweighs their potential long-term impact on health (D Shaw *et al.*, 2010).

Flame retardants

As OFRs are not typically chemically bound to the polyurethane matrix (ECHA, 2018), they emit indefinitely. Exposure of people to flame retardants has been measured in numerous studies, summarised in Appendix C. Appendix C 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 to present comparable measurements between different datasets.

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 PU sofas and couches in one study were "not significant", suggesting that other sources could be contributing to the OFR levels in dust (Hammel *et al.*, 2017). Bi et al. (2018) measured OFR 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. The authors theorised that the high levels of TCPP in the U.S. could be caused by PU insulation used in roof and wall insulation as TCPP is predominantly used in construction products (Bi *et al.*, 2018). The rationale is robust however TCPP has also been found in homes where no PU insulation is present therefore further research is required to establish a conclusive relationship.

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

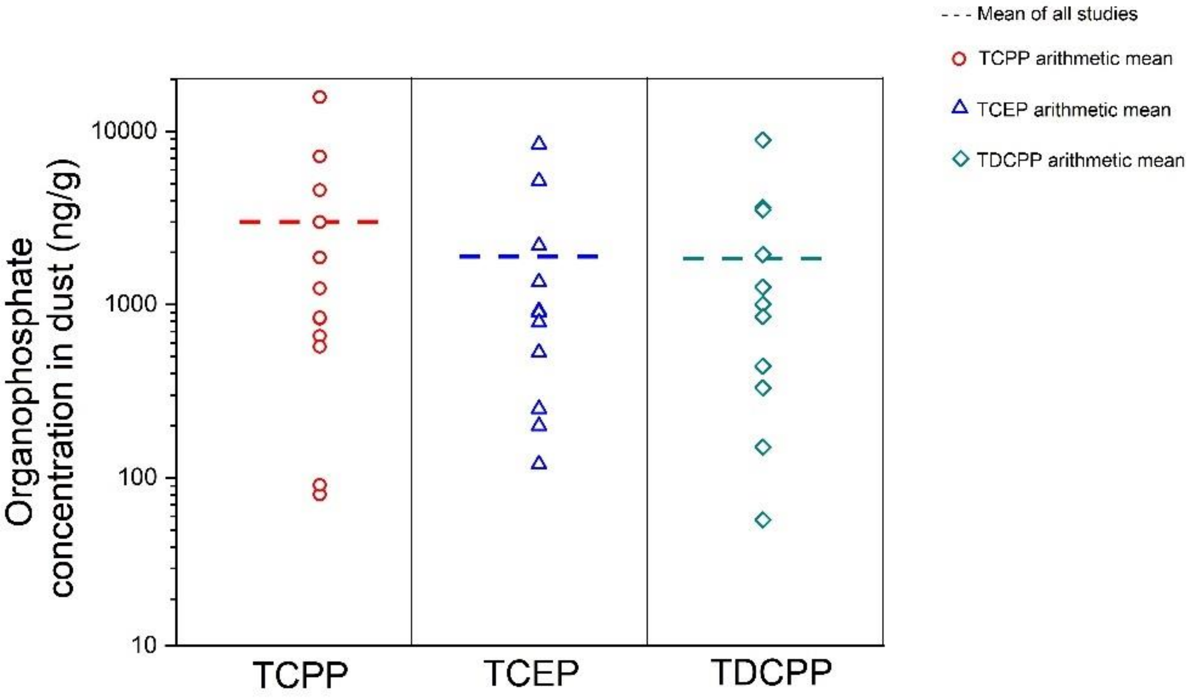

Figure 7. TCPP, TCEP and TDCPP arithmetic mean concentration in settled dust from 7 countries (n=502). Scale is logarithmic. Dotted lines represents arithmetic mean (AM) concentration of all studies. (Stapleton *et al.*, 2009; Ali *et al.*, 2012, 2018; Fromme *et al.*, 2014; He *et al.*, 2015; Hammel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

Figure 7 shows that the mean concentration of TCPP in settled dust is 3010 ng/g, of TCEP is 1895 ng/g and of TDCPP is 1844 ng/g based on 502 indoor samples from four continents. Based on Figure 7 and Appendix C, 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 OFRs, 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 OFRs 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 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 studies have looked at TCPP emissions from PU and spray foam insulation with the majority published as part of an ASTM study (ASTM International, 2017). Micro-chamber tests demonstrated that TCPP 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, 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 TCPP emissions in chambers vary with flow rate, temperature and type of foam (ASTM International, 2017).

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 PU and SPF 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).
- Do-it-yourself (DIY) SPF insulation was used in a basement and a blower door fan operating at 5000 m^3/h was used to negatively pressurise the space to −117 Pa compared to rest of the building. Statistically significant airborne TCPP concentrations only during the first eight hours was recorded followed to a reduction to background levels (Poppendieck *et al.*, 2019)

An assessment of personal exposure of workers to TCPP during two component closed cell 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). Whilst numerous studies have recorded flame retardant levels, there is limited data on blowing agent concentration from PU and SPF products.

Blowing agents

During a study of a single house, Tian and Sebroski (ASTM International, 2017) found HFC-245fa seven days after two component closed cell 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. All blowing agents are either odourless or have a faint ‘sweet’ smell at high concentrations, unlike the amine catalysts.

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 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). From the 14 Consumer Product Safety Commission (CPSC) incident reports that reported health impacts from SPF retrofit, 64% (n=9) reported a “chemical”, “unpleasant” or “ammonia-lie” smell (NRDC *et al.*, 2017). As the other constituent chemicals have either a “sweet” or “neutral” smell, the most likely hypothesis is that this was caused by the amine catalyst, secondary amines or tertiary amines created during the spraying and curing of the foams. A prolonged unpleasant smell could be associated with misapplication (Light, ASTM International, 2017).

There are no reported studies that have measured tin-based catalyst emissions, such as DBTDL, from polyurethane foam materials. Considering their potential health impact, this could be explained by the low amount commonly used in polyurethane production (<0.15% weight of B-side in two component foams) (American Chemistry Council, 2016).

Whilst amines are regularly disclosed in SDSs due to their implications on health, by-products are not mentioned in SDSs.

By-products and residual products

Analysis during moulding of cured PU foam panels demonstrated that although MDI concentration in the breathing zone was below detection limit in 64% of the samples (n=57), detectable amounts of MDA (diaminodiphenylmethane) were found 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). Workers could also be exposed to MDA when handling one-component MDI-containing raw materials (Henriks-Eckerman *et al.*, 2015). The MDA exposure which could occur during application of products (Henriks-Eckerman *et al.*, 2015), thermal degradation of cured PU products at ambient temperature (Kaaria *et al.*, 2001) and during high temperatures (welding or grinding) (Robert *et al.*, 2007) reviews workplace conditions.

In homes, a literature review of exposure to pollutants in sleeping microenvironments demonstrated that PU bedding products emit a mixture of VOCs and SVOCs into the air including, but not limited to OFRs, 1,4-dioxane and 1,2-dichloropropane (Boor *et al.*, 2017), which have also been found emitting from SPF insulation (ASTM International, 2017). Based on the reviewed literature, it is critical to consider total emissions from all PU sources to determine the long-term risk to indoor air quality and people.

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. Based on Section 3 and Section 4, the main risks and areas of further research highlighted by the literature review have been summarised in Table 3.

Table 3. Summary of exposure of VOCs and SVOCs during SPF installation, during the first month after retrofit and long term (> 1 month) at standard operating conditions. Highlighted areas in red indicate high risk based on known health impacts and evaluated exposures. Orange indicates medium risk based on existing literature, but more research is required to validate results. Green indicates that existing literature suggests there is low risk of impact on health.

	Risk of exposure based on health impacts and reported concentrations		
SPF emissions	During installation	<1 month	>1 month
Isocyanate	Over 1 ppm -toxic effect. Could cause isocyanate asthma. High risk of sensitisation	Isocyanate reacts quickly, and data suggests no significant risk after foam has cured. Further research is needed on ventilation requirements post-installation.	Free monomer isocyanates are expected to have reacted with the environment
Polyol	No significant health risk found in literature, apart that elevated levels could act as irritant.	No significant risks could be found in the literature as polyol reacts with isocyanate to form polyurethane links.	
Flame retardant	Oral, dermal exposure possible even with H&S equipment. Health risks include: irritation, suspected carcinogens, suspected to induce seizures.	Data suggests OFRs continue off-gassing indefinitely. Emission rate dependant on multiple variables. OFRs are present in abundance in indoor environment, emitted from multiple sources.	
Blowing agent	No significant risk found in the literature for HFOs apart from data that elevated levels could act as irritant.	Amount is lower than recommended exposure thresholds by a statistically significant factor in existing studies. More long-term case study data is required to confirm these findings.	
Catalyst	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.	Emissions are found to deplete within one week after PU installation. More data is needed to validate findings.	Emissions are expected to deplete and long-term foam tests suggest long-term risk of exposure is low.

By-products, secondary emissions and non-disclosed VOCs	Oral, dermal exposure possible without H&S equipment. Some chemicals listed as Class 1 and Class 2B carcinogens by IARC.	Secondary or tertiary VOCs and SVOCs could impact IAQ. Long-term risks could not be determined based on existing data and more research is required.

To place the risk matrix in the context of the built environment sector, existing industry practices for SPF installation are reviewed in the next chapter.

6. Industry practice

Best practice & protocols

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. Current industry standards for re-occupancy are based on isocyanate 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 recently been discussed (ASTM International, 2017). 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 (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). It is still however, widely unknown how application conditions affect short and long emission rates of VOCs and SVOCs from SPF products. Whilst there is advice on best practice, that does not guarantee that it is being consistently followed or that the best practice protects workers and the general population from exposure.

Examples of poor standards of practice

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 different types of gloves shows that MDI exposure could be reduced 10-100 fold by using different types of gloves (Mellette *et al.*, 2018). Respirators 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 on TCPP ingress in the human body during both open and closed cell SPF installation demonstrated that although best practice equipment was used, including air respirators, gloves and coveralls, post-shift urinary TCPP 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 TCPP biomarkers (Bello *et al.*, 2018). All exposure pathways (inhalation, ingestion and skin absorption) must be considered for a comprehensive evaluation. In the case of DIY applications, the statutory warning on products could be insufficient to protect the general population from the risks of exposure.

7. Discussion and conclusion

Existing studies demonstrate the benefits of using polyurethane products compared to conventional insulation materials in terms of energy savings and increasing thermal comfort. There is however, insufficient research to determine the implications on total IEQ, specifically indoor air quality and ventilation required to minimise VOCs and SVOCs from PU products.

The data presented in this paper demonstrates that individual PU and SPF compounds (isocyanates, polyols, blowing agents, flame retardants, catalysts and by-products) could cause dizziness, eye irritation, skin irritation and pulmonary irritation at high concentrations. It could not be concluded whether a single compound, or a cumulative effect of multiple pollutants, was the possible cause of negative health effects reported post-SPF installation in retrofitted homes (Huang and Tsuang, 2014; Guo *et al.*, 2017). There is little data demonstrating whether emissions during optimal conditions, as per manufacturer guidelines, vary compared to "misapplied" products. An unpleasant, "fishy" or "chemicals smell is associated with misapplication, however the development of low odour catalysts might lead to the reduction of odours and this association. A technical definition of "misapplication" would therefore need to be formally developed.

Figure 9 demonstrates the theoretical indoor concentration of VOCs and SVOCs during application, and post-installation, of PU foam insulation (SPF). The existing data suggest that emissions peak during spraying, however they are reduced when high extract ventilation is used. The indoor concentrations in Figure 9 are based on chamber and case study data presented in chapter 4.

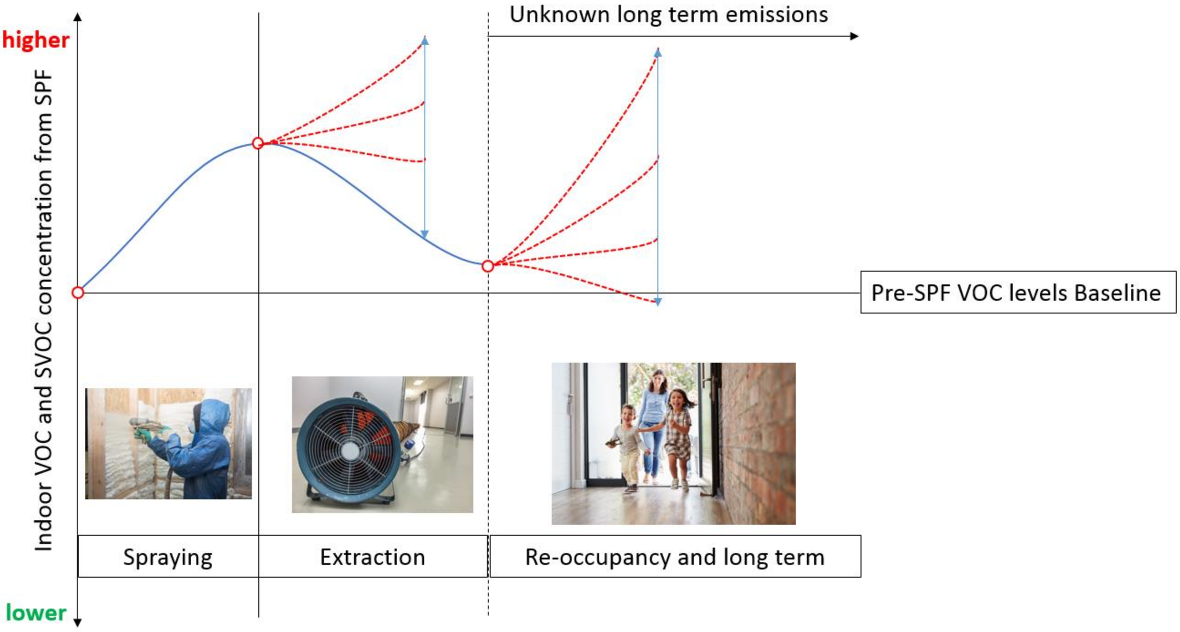

Figure 8. Schematically presented concentrations of VOCs and SVOCs in indoor air during and post SPF installation. Blue line represents data from chamber experiments and case studies. Red line represents area of uncertainty where further research required.

Existing data suggests that isocyanate emissions near the sprayer during application could exceed legal guidelines and PPE must be worn to protect workers, both sprayers and helpers. Future research should validate the hypothesis that the risk of isocyanate exposure is restricted to several hours after application and could be avoided through high extract ventilation, appropriate equipment and optimal application procedures. Using supplied air respirators, gloves and coveralls however might not be sufficient to reduce the risk of exposure to flame retardants during SPF application. Further evaluation of PPE efficacy and user compliance on worker exposures to all organic emissions from SPF is needed.

Existing literature has concluded that organophosphate flame retardants (OFRs) are found in abundance in indoor environments, even in buildings without PU insulation. It could also be concluded that catalyst amines, or secondary amines formed in a reaction between SPF and oxidising components of indoor air, are 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. Further research is required to establish a causal relationship between a specific VOC, SVOC or cumulative effect of multiple organic pollutants from PU products and health impacts. The long-term risks associated with SPF and indoor air quality are summarised in Table 3, however further research is required to validate the risk matrix.

This literature review demonstrates that the research on PU insulation and household products and their implications on indoor environmental quality requires further investigation. A long-term analysis of organic emissions data from both A and B-sides following SPF retrofit exists in only one study, which is insufficient to draw conclusions. 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 (Sebroski, ASTM International, 2017). The database will also include a range of temperature dependent testing conditions. 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 highlighted in this review, a framework is proposed to assess these scientific issues in a holistic manner as per Figure 10.

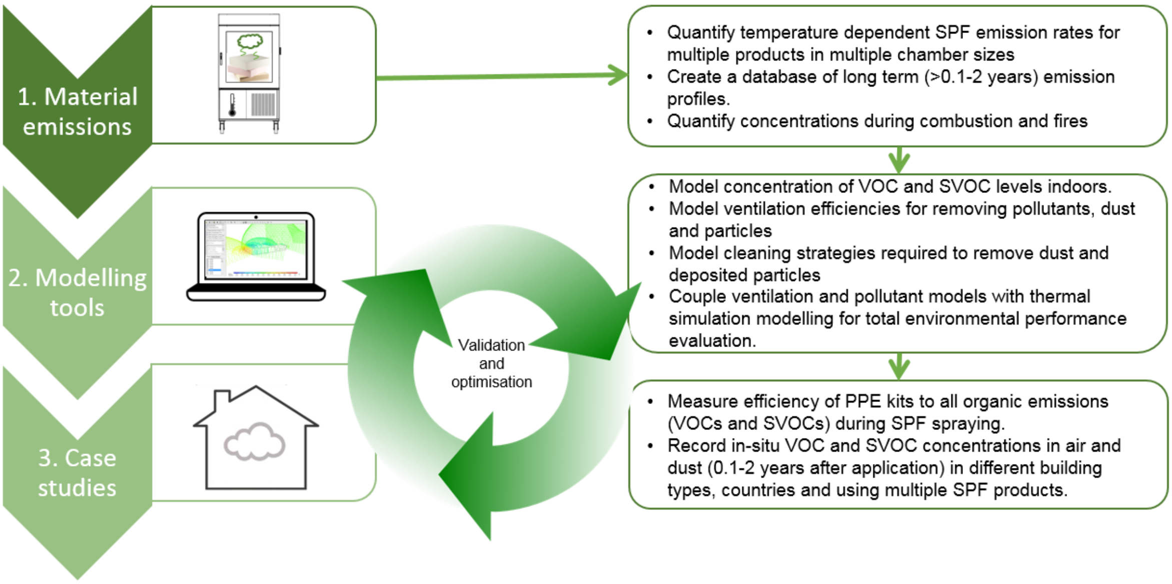

Figure 9. Framework for further research identified from the literature review

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. It could also lead to more efficient building operational strategies that reduce the carbon emissions of the built environment, whilst providing a healthy indoor air quality.

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Appendix A- 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 B- 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*	*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	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.	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	Several methods were used including both impinger and filters.	Impinger using a 2x10-4M solution of 1-(2-methoxyphenil) piperazine in toluene as absorbent	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)

	mg 1-(2-Pyridyl) piperazine							
Analytical method	HPLC-UV/FLU	GC-FID	HPLC-UV/EC	HPLC-UV/FLU	HPLC and MS/MS	LC-MS	LC-MS	HPLC-UV
Flow rate	1l/min					15l/ min	1.1 l/min	1l/ min
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/m^3)	0.00008[1]-0.2[2]	0.005-1.55	0.001-0.57	-	-	0.0023-0.185	0.0001-0.0042	<0.00143-0.00154
Mean average exposure (mg/m^3)	0.005[3]	0.122-0.603	0.004-0.057	0.01-0.15	0.13-0.29			Below detection limit
Mean average exposure after 120 min (mg/m^3)	-	Below detection limits	-	-	0.003-0.005	0.000002-.000068		

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[1] California Office of Environmental Health and Hazard Assessment (OEHHA) chronic reference exposure limit (REL)- 0.00008 mg/m^3, OEHHA acute REL- 0.012 mg/m^3. Germany, Sweden STEL- 0.05 mg/m^3. United Kingdom STEL- 0.07 mg/m^3. Austria and China STEL-0.1 mg/m^3, Poland STEL- 0.2 mg/m^3

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

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

Appendix C- 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) 710- 47,000 ng/g (range)	63% DF 1,350 ng/g (AM) 100-8,300 ng/g (range)	4% DF	
			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	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)

	day care centers, 9 building material markets, 6 carpet stores)	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) 209-1,360 ng/m^3 (range)	0% DF	100% DF 50.1 ng/m^3 (AM) 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 (range)		37% DF 8,890 ng/g (AM) <MDL- 122,000 ng/g (range)	
Brazil	Occurrence and human exposure to brominated and organophosphorus flame retardants via	Araraquara city, Sao Paulo State, Brazil	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)

	indoor dust in a Brazilian city	10 houses, 10 apartments, 5 schools, 5 offices, 16 cars,	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) 315-9,220 ng/g (range)	69% DF 4,200 ng/g (50-P) 138- 40,400 ng/g (range)	100% DF 506,000 ng/g (50-P) 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	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)

	and primary schools in Hong Kong	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 rural locations in south China	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)
		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) 50 homes	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)