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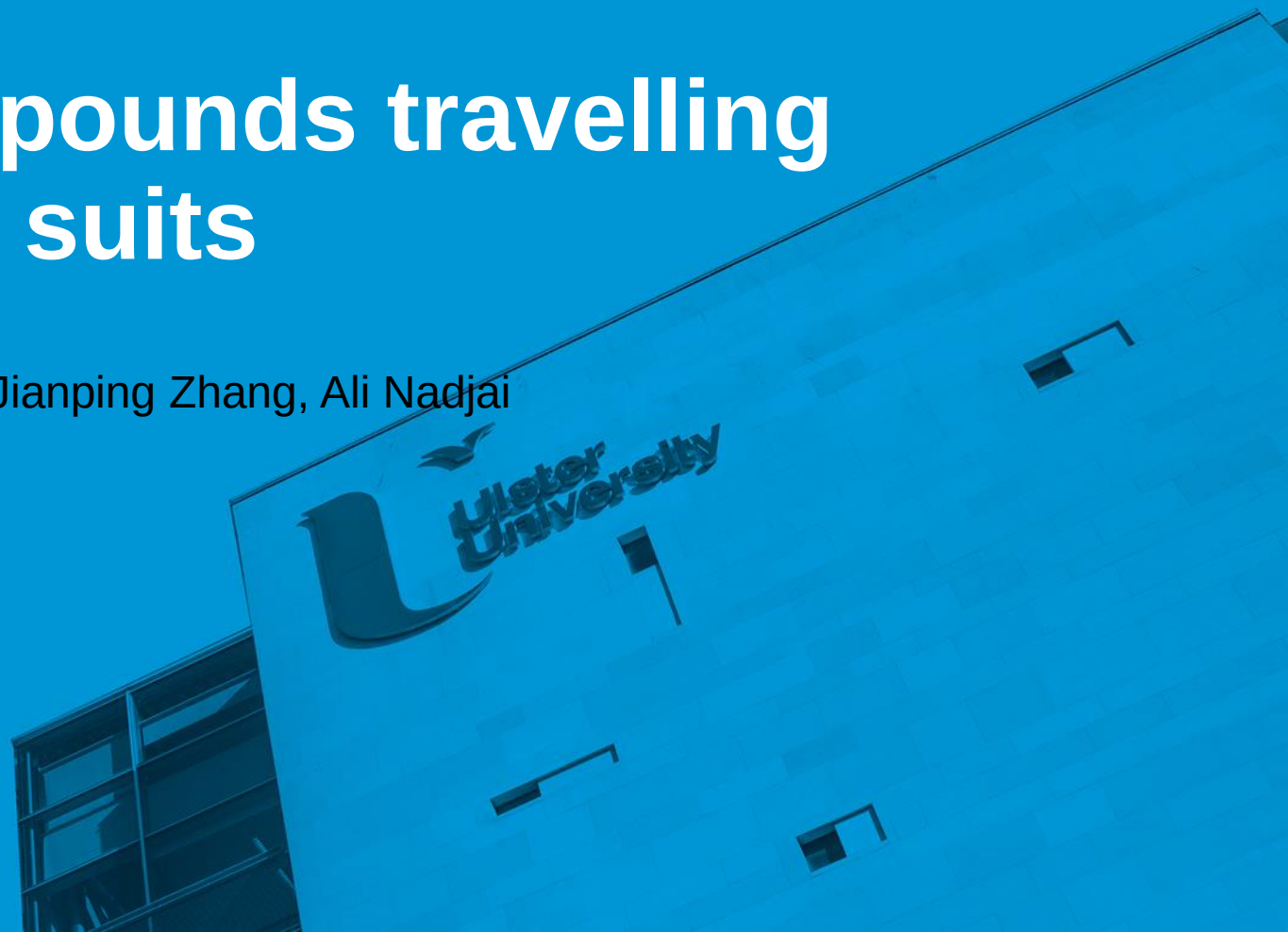
"Igniting Innovation – The Engineering Battle against Fire"

The fate of toxic compounds travelling through layers of fire suits

Svetlana Tretsiakova-McNally, Yong Kai Chen, Jianping Zhang, Ali Nadjai



Outline

- Research Background
- Toxic Compounds Formed in Fires
- Firefighters' PPE
- PFAS in Fire Suits
- InToxFire Project and Research Questions
- Experimental Set-Up and Methodology
- Preliminary Results
- Initial Findings and Recommendations

Research Background

- 15 million firefighters worldwide, among them about 1.5 million career firefighters.
- GB: 40,100 career firefighters, 19,000 part-time firefighters and 1,400 voluntary firefighters.
- Ireland: 2,012 career firefighters and 2,076 part-time firefighters.
- USA: 370,000 career firefighters and 745,000 voluntary firefighters [1].
- The most challenging and dangerous profession, regular exposure of workers to a cocktail of toxic agents, including **polycyclic aromatic hydrocarbons** (PAH), particulates, **per- and polyfluoroalkyl substances** (PFAS) and **volatile organic compounds** (VOC).
- **Increased mortality**, risk for **mesothelioma**, **multiple cancers** among firefighters globally.
- Plus, significantly higher mortality for acute ischaemic heart diseases, stroke, interstitial pulmonary diseases, renal failure and musculoskeletal system diseases.

Firefighting Exposure

International Agency for Research on Cancer

World Health Organization

IARC Group 1 – Known Carcinogens

Arsenic
Asbestos
Benzene
Benzo(α)pyrene
1,3-Butadiene
Cadmium
Chromium (IV)
1,2-Dichloropropane
Diesel exhaust
Ethylene oxide
Formaldehyde
Hepatitis B and C virus
Nickel
Perfluorooctanotic acid (PFOA)
2,3,4,7,8 - Pentachlorodibenzofuran
3,4,5,3',4'-Pentachlorobiphenyl (PCB-126)
Pentachlorophenol
Polychlorinated biphenyls (PCBs)
Radioactivity (α, β,γ)
Silica (crystalline)
Sulfuric acid
2,3,7,8-Tetrachlorodipenzo-*p*-dioxin (TCDD)
Trichloroethylene
UV radiation
Vinyl chloride
…

IARC Group 2A – Probable Carcinogens

Acrolein
Antimony (III)
Dibenz[a,h]anthracene
Dibenzo[a,l]pyrene
Dichloromethane
N,N-Dimethylformamide
Hydrazine
2-Nitroanisole
Lead (inorganic)
Polybrominated biphenyls (PBBs)
Styrene
Tetrabromobisphenol A
Tetrachloroethylene
1,1,1-Trichloroethane
Shiftwork (sleep disruption)

IARC Group 2B – Possible Carcinogens

38 chemicals

Research Importance

In 2022, the International Agency for Research on Cancer (IARC) re-categorized **firefighting occupational exposure** from **possibly carcinogenic** (Group 2B) to **carcinogenic** (Group 1) [2].

Along with the inhalation, **dermal** exposure to carcinogenic toxicants is highly likely, despite donning full personal protective equipment (PPE) [3-5].

The **nature**, **quantities** and **mechanisms** of **toxic chemicals movement through the PPE** are not fully understood → an area of our current research at FireSERT, UU.

The ability of toxicants to permeate through some layers of firefighters' protective clothing has not been investigated adequately.

Essential to inform the standards for firefighters' PPE and training/operational procedures to protect the over 15 million firefighters worldwide from dermal exposure to toxicants and hence reduce occurrence of cancers.

Toxic Compounds from Fires

Combustion products vary widely depending on a fuel composition, oxygen supply, combustion conditions, etc. [6].

The yield of toxic combustion products increases when fire transits from well- to under-ventilated conditions, e.g., PAHs amounts increased by over 1000 times [7].

[2], p.70

Table 1.3 Common fire effluents produced by different types of fire

Fire effluent(s)	Type of fire			
	Structure[a]	Wildland[b]	Waste[c]	Vehicle[d]
Acrolein	✓	✓		✓
Ammonia	✓	✓	✓	✓
Asbestos	✓			
Carbon monoxide	✓	✓	✓	✓
Formaldehyde	✓	✓	✓	✓
Hydrogen bromide	✓		✓	
Hydrogen chloride	✓		✓	✓
Hydrogen cyanide	✓	✓	✓	✓
Hydrogen fluoride	✓		✓	
Isocyanates	✓			✓
Metals	✓	✓	✓	✓
Nitrogen oxides	✓	✓	✓	✓
Particulate matter	✓	✓	✓	✓
Per-fluorinated chemicals	✓			✓
Polybrominated and polychlorinated dibenzo-*para*-dioxins and furans (PBCD/Fs and PCCD/Fs)	✓		✓	✓
Polychlorinated biphenyls (PCBs)	✓		✓	
Polybrominated diphenyl ethers (PBDEs)	✓		✓	
Polycyclic aromatic hydrocarbons (PAHs)	✓	✓	✓	✓
Semi- and volatile organic compounds (sVOCs and VOCs)	✓	✓	✓	✓
Sulfur dioxide	✓	✓	✓	✓
Synthetic vitreous fibres	✓			

[a] Brandt-Rauf et al. (1988); Persson & Simonson (1998); Lioy et al. (2002); Landrigan et al. (2004); Stec & Hull (2008); Organtini et al. (2015); Fent et al. (2018, 2020a); Stec et al. (2018); Alharbi et al. (2021).

[b] Urbanski et al. (2008); Hu et al. (2018).

Toxic Combustion Products

Live Fire Training

Wood-based products, which are permitted by NFPA 1403:2018 Standard on Live Fire Training Evolutions [8] guidelines, generated:

- PAHs
- Hydrogen bromide
- Hydrofluoric acid [6,9]

Presence of Known Carcinogens and Potential Carcinogens

Occupational hazards of firefighters include exposures to chemicals categorized by the IARC as:

- Carcinogens (Group 1), e.g., benzene, PCBs and 2,3,7,8-TCDD
- Probable carcinogens (Group 2A), e.g., 1,1,1-trichloroethane
- Possible carcinogens (Group 2B), e.g., naphthalene, furan, polychlorophenols and bromochloroacetic acid [2]

An urgent need to reduce exposure doses!

Firefighters' PPE

- Turnout gear (jacket and pants)
- Helmet
- Gloves
- Boots
- Flash hood
- Self-contained breathing apparatus (SCBA)

The turnout gear:

- Normally constitutes three main layers (outer shell, moisture barrier and thermal liner) [10]
- May contain per- and polyfluoroalkyl substances (PFAS) to repel water and oils

PFAS-based finishings have better oil repellency compared to those free from PFAS.

Standards for Turnout Gear

Design and performance provisions for turnout gears in existing standards cater only for chemical spill protection, but the diffusion of chemical vapours or condensate permeation not considered:

- NFPA 1971:2018 Standard on Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting [10]
- EN 469:2020 Protective Clothing for Firefighters – Performance Requirements for Protective Clothing for Firefighting Activities [11].

Main Layers of Turnout Gear [12]

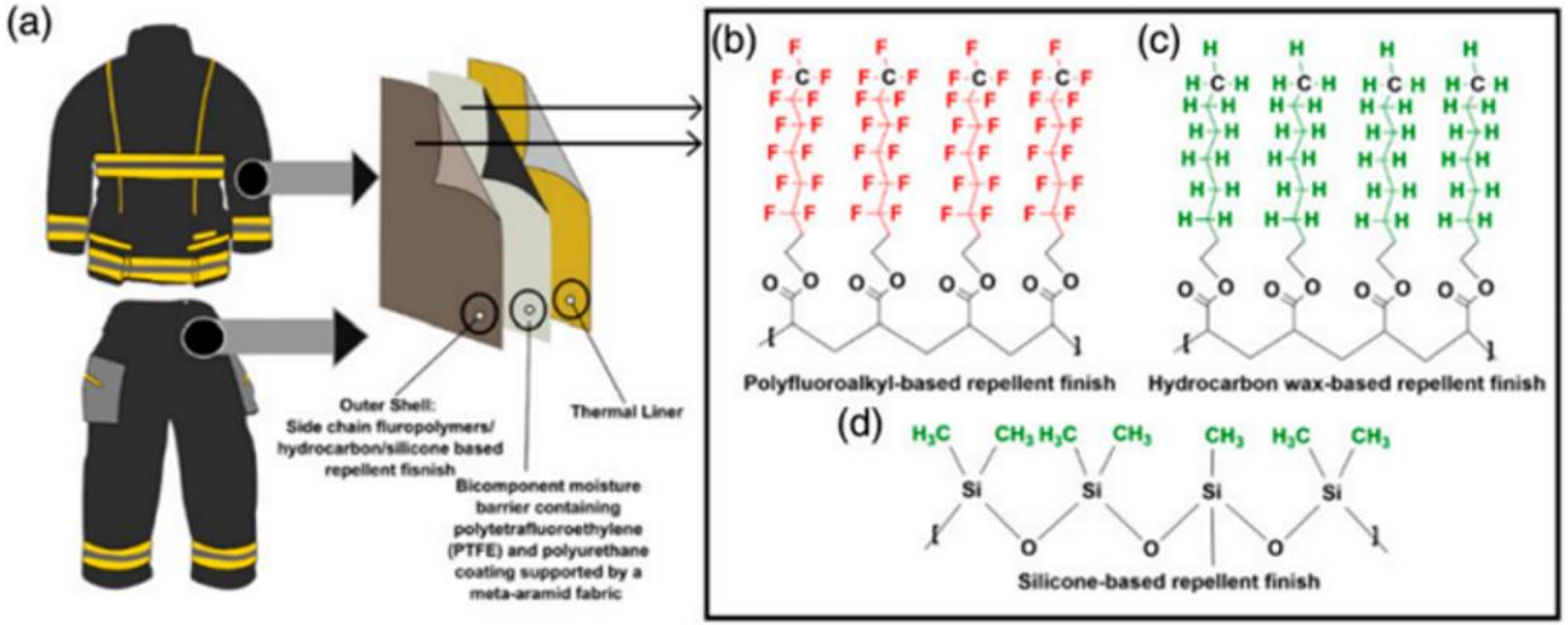
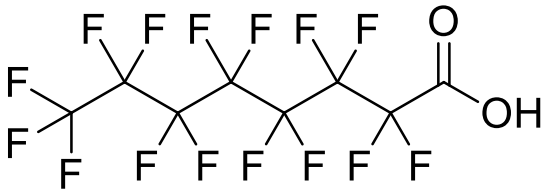


Figure 1. Examples of a structural turnout gear; (a) three layers of structural turnout gear (i.e., outer shell, moisture barrier, and thermal liner); commonly applied DWR chemistries on outer shell fabrics; (b) polyfluoroalkyl, (c) hydrocarbon, (d) silicone-based DWR chemistries.

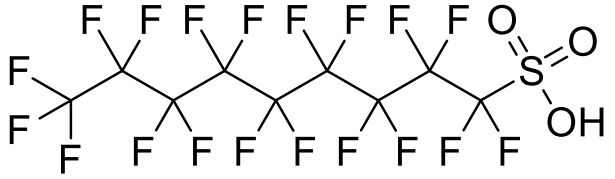
PFAS in Fire Suits

PFAS, “**forever chemicals**”, linked to health and environmental concerns.

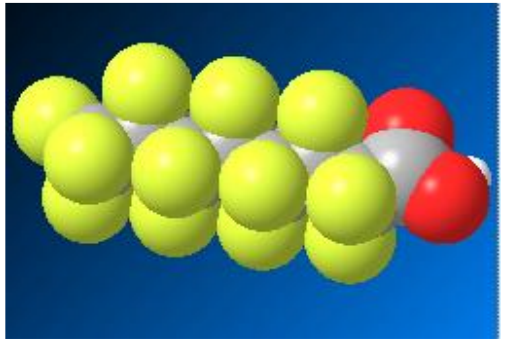
- Environmentally persistent, with high tendency to bioaccumulate [12,13].
- Discharge of perfluorooctanoic acid (PFOA), a known carcinogen (Group 1).
- PFAS can be emitted from new, used and washed PFAS-based fabrics [14,15].
- San Francisco is the first US city to ban PFAS in turnout gears [16].
- European Union began considering PFAS ban in Feb 2023 [17].

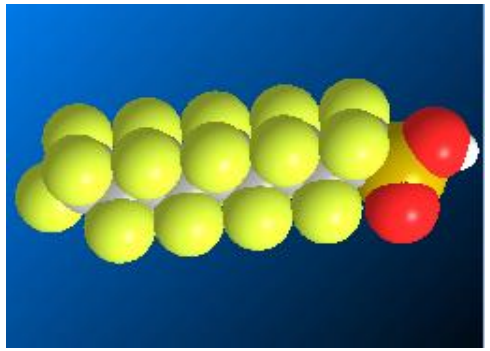


Perfluoro-Octanoic Acid (PFOA)



Perfluoro-OctaneSulphonic Acid (PFOS)





Dermal Exposure to Toxic Agents from Fires

Despite donning full PPE with SCBA, recent studies showed that some toxicants can be dermally absorbed:

- Breath benzene concentrations and urine PAH metabolite levels were the highest among firefighters who performed roles within the structure compared with other firefighters assigned to outside operations [3].
- Greater levels of volatile organic compound (VOC) metabolites in the urine of firefighters in both controlled-residential and training live fires [4].
- PFAS detected in blood and urine of first responders Maui Wildfire 2023 [18].

How Toxic Agents Get Transferred Through Layers of Fire Suits?

Some contradictory findings on PPE areas most prone to fire toxicants penetration

- ➢ Neck [19]
- ➢ Hands [20, 21]
- ➢ Similar at five different locations (fingers, back, forehead, neck and wrist) [22]

- The chemical vapour permeation study involving turnout gear fabric found was conducted by Corbally et al. (2021) [23], but it has limitations:
  - ➢ The use of a retired turnout gear
  - ➢ Burning of only 2 types of combustibles (vinyl siding and railroad tie)
  - ➢ Inappropriate experimental temperatures

UL Research Institutes | Discoveries in Safety Grants

Fire Safety Research Institute

Innovative Research Leading to the Reduction of Thermal and Chemical Fire Exposures to Firefighters

InToxFire Project

Project "**Investigation of Toxic Chemicals Transfer Through Clothing Layers of Fire Suits"**

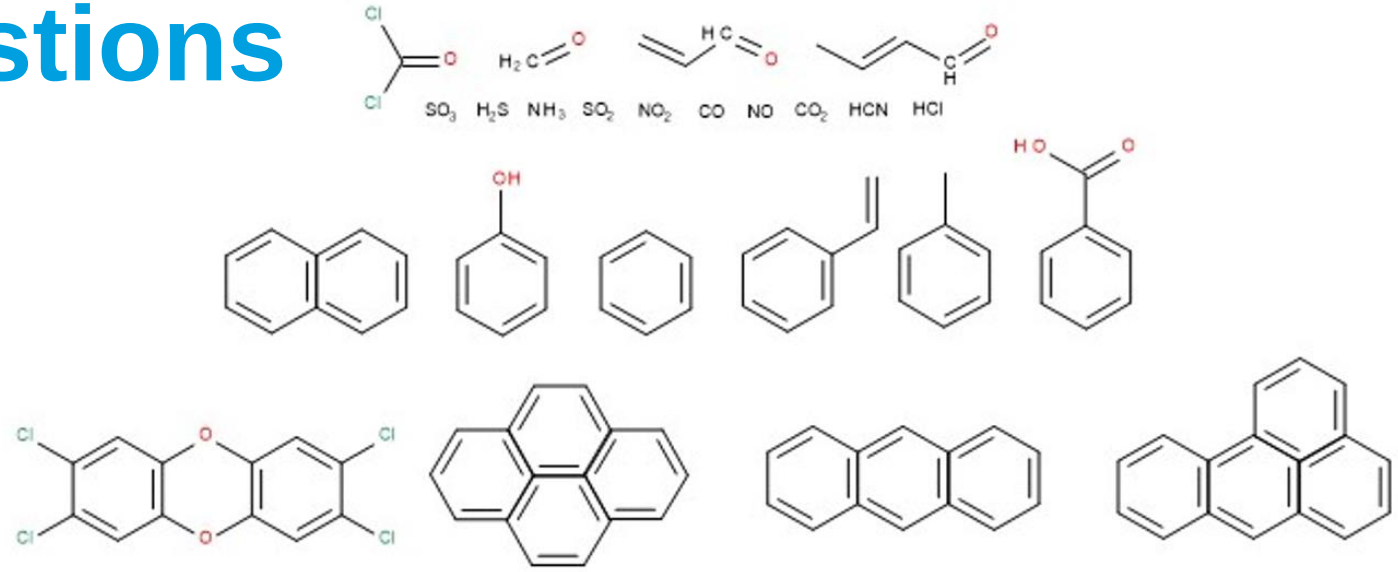
FireSERT, UU, commenced on 1st Sep 24, 36 months duration.

Project aims to:

- Investigate whether elements of firefighters' clothing allow the transport of toxic chemicals from the fire effluent towards the skin.
- Determine the nature and concentration levels of toxic chemicals using appropriate analytical techniques.
- Apply heat transfer and advanced computational models along with developed analytical methods to fully quantify the transfer of toxic chemicals through the layers of fire suits.

The first study on chemicals permeation through layers of functional turnout gear

Research Questions

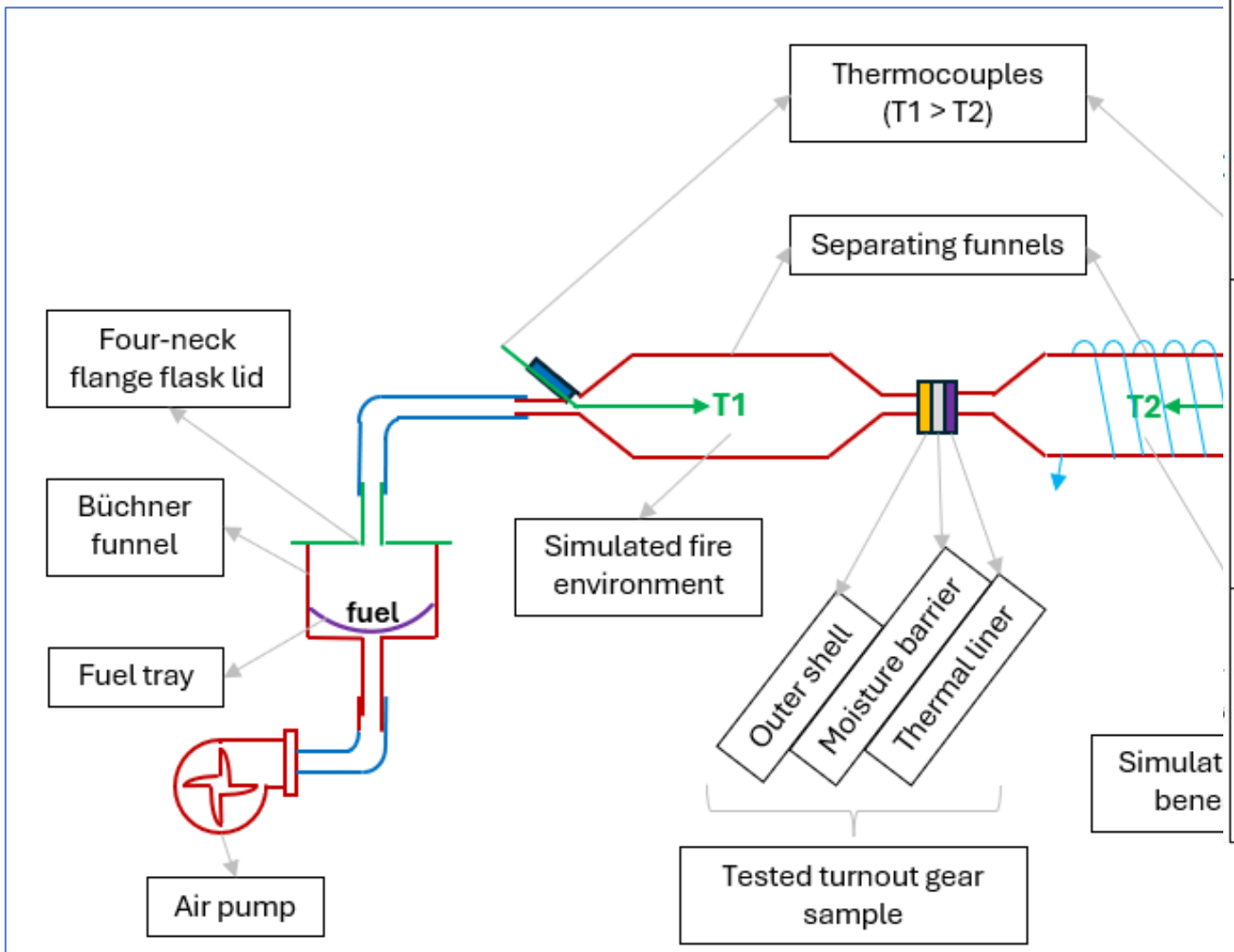


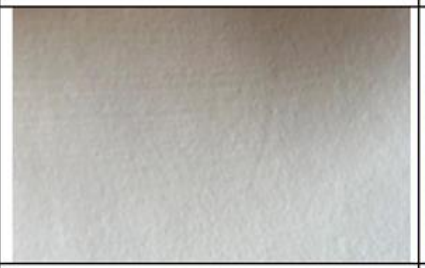
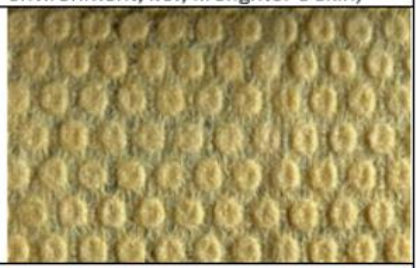
1. Toxic products of combustion/pyrolysis get trapped/adhered to/transferred through layers of fire suits, moving towards the skin of first responders during, or after, firefighting.

2. Understanding the nature of these toxicants and, most importantly, knowing their concentrations are of paramount importance for firefighters, manufacturers of PPE and clothing, regulators, health and safety specialists who are seeking robust and long term-solutions to the problems of repeated dermal or inhalation exposure.

3. Scenarios involving wildland fires, electric vehicle fires (LIBs) and photovoltaic installations, bring additional unexplored risks to firemen, which could further exacerbate risks to health.

Small-Scale Experimental Set-



Turnout Gear Type / Fabric Layer	Ensemble E1 (with PFAS content)	Ensemble E2 (without PFAS content)
Outer Shell (outermost layer facing the fire)	 a) PBI Gold®	 d) Aramid with an unknown coating (coated surface facing the inside environment, i.e., firefighter's skin)
Moisture Barrier (middle layer)	 b) PTFE laminated onto nonwoven fabric (PTFE surface facing the outside fire environment)	 e) Nonwoven fabric
Thermal Liner (innermost layer in direct contact with the skin)	 c) Flame-retardant lining	 f) Ripstop flame-retardant lining

Methodology & Analytical Techniques

After the experiment, liquid-liquid extraction was performed using dichloromethane (DCM) and distilled water → 8 samples of condensate were collected, sent for analysis to a forensics lab at King's College London.

Analytical techniques: Gas Chromatography-Mass Spectrometry (GC-MS).

High Performance Liquid Chromatography- High Resolution Mass Spectrometry (HPLC-MS).

Vial	Turnout Gear Sample Type	Separating Funnel	Condensate Sample
1	Ensemble E1 (with PFAS content)	Left side	Organic layer
2			Aqueous layer
3		Right side	Organic layer
4			Aqueous layer
5	Ensemble E2 (without PFAS content)	Left side	Organic layer
6			Aqueous layer
7		Right side	Organic layer
8			Aqueous layer

- GC-MS was used to establish the nature of the organic condensates
- HPLC-HRMS was used to establish the chemical nature of the water-soluble condensates

Chemical Nature of Toxic Agents in Condensate Detected by GC-MS: Initial Results

Table 4.4 Suspected non-polar chemical compounds present in the condensates

m/z Value	Suspected Chemical Compound	Number of Test Runs Compound was Detected			
		Ensemble E1 (with PFAS content)		Ensemble E2 (without PFAS content)	
		Fire Environment	Beneath Turnout Gear	Fire Environment	Beneath Turnout Gear
43.94327	3,5-dimethyloctane	2	0	0	0
83.93619	Dichloroacetaldehyde	0		3	
57.09686	4,4-dipropylheptane	3		0	
57.0955	Cyclohexane, 1,1'-[1,2-bis(1,1-dimethylethyl)-1,2-ethanediyl]bis-, (R*,R*)- (9CI)	1		2	
57.09647	Tetradecane	3		3	
158.9153	1,2-Diacetoxy-3-(2-methoxyphenoxy)propane	3		0	
44.10878	3-Cyclohexene-1-ethanol, α-ethenyl-α,3-dimethyl-6-(1-methylethylidene)-	3		0	
190.9674	2,4-Dit-butylphenyl 5-hydroxypentanoate	0		3	
57.09686	Pentadecane	3		0	
180.0046	Benzamide, 2-fluoro-N-ethyl-N-2-ethylhexyl-	3		0	
178.1222	Phenanthrene	3		3	
202.0554	Pyrene	0		3	
152.0626	Acenaphthylene	2		3	
178.07825	9-methylenefluorene/ Anthracene	3		3	
202.07825	Fluoranthene/ Pyrene	0		3	
166.07825	Fluorene	3		3	
57.20253	Methyl 2-methylbu	0		3	

PAHs

Chemical Nature of Toxic Agents in Condensate Detected by HPLC-HRMS: Initial Results

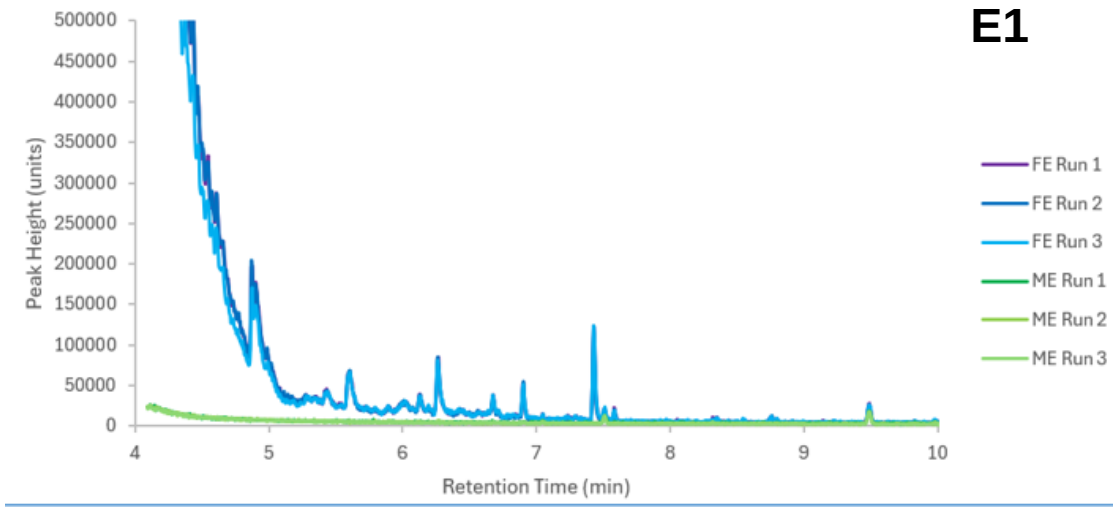
Presence of various compounds

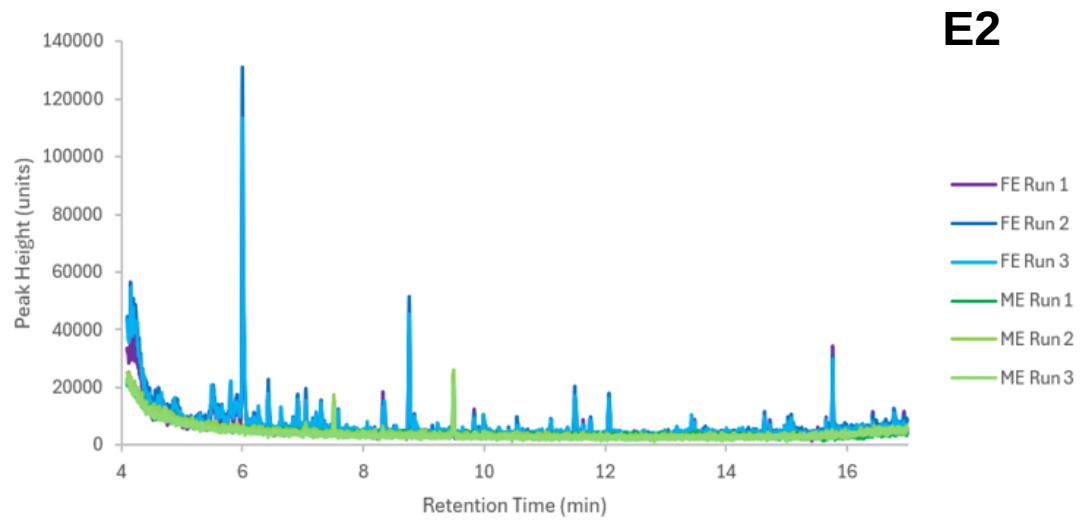
- Aromatic (e.g., C_7H_8O, $C_8H_{11}N$ and furan)
- Oxidized (e.g., $C_6H_{12}O_2$, $C_{16}H_{30}O$ and $C_{18}H_{38}O$)
- Isocyanate ($C_3Cl_3NO_2$)
- Nitrogen-containing (e.g., $C_8H_{17}N$, $C_9H_{17}N$ and $C_8H_{19}N$)
- Chlorine-containing (e.g., 1,1,1-trichloroethane, polychlorophenol ($C_6H_3Cl_3O$), PCB-126 ($C_{12}H_5Cl_5$), PCDDs (e.g., 2,3,7,8-TCDD) and PCDF)
- Bromine-containing (e.g., bromochloroacetic acid, PBDD and PBDFs)
- PFAS (CF_4 and $C_{12}F_{26}$)

Some products have been classified by the IARC as:

- **Carcinogens (Group 1)** – PCB-126 and 2,3,7,8-TCDD
- **Probable carcinogens (Group 2A)** – 1,1,1-trichloroethane
- **Possible carcinogens (Group 2B)** – furan, polychlorophenols and bromochloroacetic acid [2].

Retention of Toxicants Soluble in Organic Phase - Dichloromethane





A comparison of GC patterns of the condensates collected from fire effluent (FE) and micro-environment beneath the turnout gear (ME)

GC-MS Samples	Ensemble E1 (with PFAS content)		Ensemble E2 (without PFAS content)	
	Fire Environment	Beneath Turnout Gear	Fire Environment	Beneath Turnout Gear
No. of Peaks (after accounting for the control)	33-43	0	35-38	0

All compounds from fire effluent were stopped by both ensembles.

Retention of Toxicants Soluble in Aqueous Phase – Distilled Water

Sample and Environment / HPLC-HRMS Mode	No. of m/z signals (after accounting for the control)			
	Ensemble E1 (with PFAS)		Ensemble E2 (without PFAS)	
	Fire Environment	Beneath Turnout Gear	Fire Environment	Beneath Turnout Gear
Positive	39	0	18	1 passed through
Negative	68	5 passed through	12	5 passed through

The number of water-soluble compounds that were stopped by the turnout gear is above 80%

Compounds stopped include:

- **Carcinogens (Group 1)** – PCB-126 and 2,3,7,8-TCDD
- **Probable carcinogens (Group 2A)** – 1,1,1-trichloroethane
- **Possible carcinogens (Group 2B)** – furan, polychlorophenols and bromochloroacetic acid

Initial Findings

- All DCM-soluble and majority of water-soluble combustion compounds (including all carcinogens/potential carcinogens detected) in this preliminary study can be stopped by the turnout gear fabric layers.
- Both ensembles E1 and E2 (with and without PFAS layer) were equally effective against permeation of combustion products, particularly those soluble in DCM.
- As for water-soluble toxic compounds, the PFAS-containing ensemble prevented the permeation better than the ensemble without PFAS.
- Ensemble E1 (with PFAS layer) filtered out 95% of compounds, while the E2 filtered out 80% of compounds.
- The ensemble E1 blocked the diffusion of a polar compound with a formula $C_6H_{15}NO$ (possibly diethylaminoethanol or isomers [24]) as opposed to the ensemble E2.

Initial Recommendations

- Better PPE designs, with minimal gaps.
- Compatible PPE accessories and proper PPE donning.
- Updated and regular training.
- To reduce dermal exposure doses, skin wiping, hand washing and showering are recommended as soon as possible after firefighting [25].
- Repeated laundering of contaminated turnout gears to reduce off-gassing may degrade their protective performance [26, 27].
- For prolonged operations, crew rotation should be considered.

Contact Us

s.tretsiakova-mcnally@ulster.ac.uk

a.nadjai@ulster.ac.uk

j.zhang@ulster.ac.uk

Thank you! Any questions?

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Ulster University