THE UNIVERSITY OF QUEENSLAND
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# Firefighter Exposure Risks and Subsequent Reproductive Effects

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School of Pharmacy

**Abstract**

Firefighter is an occupation that include exposure to hazardous environments. Much of the research surrounding firefighter exposure has been based around potential cancer, cardiovascular and respiratory illness risks, with comparatively minimal focus surrounding risks to reproduction.
As such, this PhD research study was designed to investigate firefighter exposure and risks to reproduction via the following aims: 1) to clearly identify what occupational exposure to chemicals firefighters face by means of a systematic review of biomonitoring studies, 2) to determine potential indirect mechanisms of exposure, 3) to assess Australian firefighters for chemical exposure via a targeted biomonitoring study incorporating blood, urine, semen and breast milk samples, and 4) to examine the relationship between such exposures and firefighters' reproductive effects. These questions were answered through a series of sub-studies hereafter identified as chapters.
Chapter 1 provides an overview of firefighter exposure including direct and indirect routes (inhalation, ingestion and dermal absorption), and potential reproductive effects due to chemicals identified in fire smoke. Chapter 2 expands on this to present a systematic review of occupationally specific chemicals biomonitored in firefighters by means of pre and post exposure comparisons, and comparisons with general populations. Firefighters were found to have increased concentrations in blood and urine of chemicals including semi-volatile organic compounds (SVOCs), volatile organic compounds (VOCs), and metals. These results provided scope for the selection of chemicals analysed for indirect exposure in subsequent sub-studies, as well as supported the shape and scope of the targeted biomonitoring study.

Chapter 3 investigated indirect exposure to SVOCs, VOCs, and metals at Australian fire stations compared to Australian homes and offices through the analysis of air and dust samples. Metals were detected most frequently in dust with ranges including: chromium (39-490μg/m$^2$), lead (47-620μg/m$^2$), copper (590-3400μg/m$^2$), zinc (11000-21000μg/m$^2$), nickel (29-2400μg/m$^2$) and manganese (73-1000 μg/m$^2$). These concentrations were, in most instances, orders of magnitude higher when compared to homes and offices. Risk quotient analysis suggested fire stations presented a risk of adverse health effects, in line with prior international research.

Chapter 4 further investigated indirect exposure, identifying the potential for toxic smoke to contaminate undergarments that sit over highly permeable skin and reproductive organs. The investigation found polycyclic aromatic hydrocarbon (PAH) contamination on socks, underwear, and crop tops post fire incident exposure, and that those items, when laundered, can cross contaminate. Post-burn $\Sigma_{13}$PAHs average concentrations (range) were: socks, 2600ng/g (570-12,000ng/g); briefs, 1200ng/g (45-7600ng/g); and crop tops, 470ng/g (69-1400 ng/g). Laundering

resulted in an average $\Sigma_{13}$PAHs concentration reduction of 36% on socks, 9% on briefs and a 160% increase in crop tops. This study provided novel data confirming the ability of fire smoke to contaminate personal items of clothing worn under personal protective clothing, presenting a potential route of indirect exposure.

Chapter 5 provided a global first exploratory investigation into male firefighter fertility through semen analysis. Results showed firefighter semen parameters were below World Health Organisation reference values for male fertility. Men <45y had a higher incidence of abnormal semen parameters (42%) than those ≥45y (9%). An increased frequency of fire exposure showed a reduction in normal forms, volume, sperm concentration and total sperm count suggesting the potential that occupational exposure may be affecting male fertility.

Chapter 6 furthered investigations into male fertility by considering chemical concentrations in blood and urine, investigated female reproduction through chemical exposure risks, and assessed a range of chemical concentrations in firefighter breast milk. Chapter 6 considered demographic, occupational, and reproductive data from a comprehensive survey in line with biomonitored data. This chapter presents the results of 774 firefighters who completed an online survey, and 97 firefighters who produced 125 urine, 113 plasma, 46 breast milk and 23 semen samples. Results of self-reported rates of miscarriage were found to be higher than the general population (22% vs 2-15%), in line with prior studies. Chemical concentrations in firefighter blood and urine were, in some instances, above what has been found to affect semen quality in other cohorts of men. Estimated daily intake for infants was above reference values for multiple chemicals in breast milk. More frequent fire incident exposure (more than once per fortnight), longer duration of employment (≥15yrs), or not always using breathing apparatus demonstrated significantly higher concentrations across a range of investigated chemicals. Overall, this chapter further supported the potential that firefighting may adversely affect reproduction.

This research study has shown that firefighters experience a broad spectrum of exposure profiles which may depend upon a range of occupational variables (for example, frequency and type of fire exposure, occupational and person hygiene). This study has demonstrated the potential for those exposures to affect reproduction. Results of this study also suggest that firefighters may reduce exposure through increased use of breathing apparatus, thorough decontamination at the incident, and showering and laundering contaminated items. More research is urgently required to further understanding surrounding firefighter exposure and reproduction.

## Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of the Graduate School.

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**Publications included in this thesis**

1. Engelsman, M., L.-M. L. Toms, A. P. W. Banks, X. Wang and J. F. Mueller (2020). "Biomonitoring in firefighters for volatile organic compounds, semivolatile organic compounds, persistent organic pollutants, and metals: A systematic review." Environmental research 188. doi:10.1016/j.envres.2020.109562
2. Engelsman, M., M. F. Snoek, A. P. W. Banks, P. Cantrell, X. Wang, L. M. Toms and D. J. Koppel (2019). "Exposure to metals and semivolatile organic compounds in Australian fire stations." Environmental Research 179. doi:10.1016/j.envres.2019.108745
3. Engelsman, M., Toms, L.-M. L., Wang, X., Banks, A. P. W. (2023) Firefighter undergarments: Assessing contamination and laundering efficacy. Environmental Research, 216. doi:10.1016/j.envres.2022.114344
4. Engelsman, M., L.-M. L. Toms, X. Wang, A. P. W. Banks and D. Blake (2021). "Effects of firefighting on semen parameters: an exploratory study." Reproduction and Fertility 2(1): L13-L15. doi:10.1530/RAF-20-0070
5. Engelsman, M., A. P. W. Banks, C. He, S. Nilsson, D. Blake, A. Jayarthne, Z. Ishaq, L.-M. L. Toms and X. Wang (2023). "An Exploratory Analysis of Firefighter Reproduction through Survey Data and Biomonitoring." International Journal of Environmental Research and Public Health **20**(8): 5472

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2. Banks, A. P. W., P. Thai, M. Engelsman, X. Wang, A. F. Osorio and J. F. Mueller (2021). "Characterising the exposure of Australian firefighters to polycyclic aromatic hydrocarbons generated in simulated compartment fires." Int J Hyg Environ Health 231: 113637. doi: 10.1016/j.ijheh.2020
3. Banks, A. P. W., X. Wang, M. Engelsman, C. He, A. F. Osorio and J. F. Mueller (2021). "Assessing decontamination and laundering processes for the removal of polycyclic aromatic hydrocarbons and flame retardants from firefighting uniforms." Environ Res 194: 110616. doi: 10.1016/j.envres.2020.110616

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- The Occurrence of PAHs, Flame Retardants and Metals in Air and Dust from Australian Fire Stations, Australasian Fire and Emergency Service Authorities Council Conference, Oral Presentation – 2021
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Magazine Articles:

1. Engelsman, M., & Banks, A. P. W. (2020). Chemicals in Air and Dust at Australian Fire Stations. Asia Pacific Fire, (72), 42-44.

**<u>Contributions by others to the thesis</u>**

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Numerous participants provided samples and completed surveys for this project.

## **Statement of parts of the thesis submitted to qualify for the award of another degree**

No works submitted towards another degree have been included in this thesis.

## **Research Involving Human or Animal Subjects**

University of Queensland Ethics Approval #2017000255

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This study began when I questioned my newborn's potential exposure risks if I were to return to active-duty firefighting while breast feeding. My then Manager at Fire Investigation and Research Unit (FIRU), Superintendent Jeremy Fewtrell (now Deputy Commissioner) understood my concerns and supported my desire to research lactating firefighters. The (now retired) Assistant Commissioner Community Safety, Mark Whybro, possibly my greatest support within Fire and Rescue NSW, was steadfast in his support of me expanding my study into a PhD, and to include reproduction as a whole.

Superintendent Graham Kingsland (now Chief Superintendent) took over my FRNSW research supervision, subsequent to Mr Fewtrell's promotion, and has tirelessly supported my every endeavour in this study. Commissioner Paul Baxter provided me the opportunity to present to the Executive Leadership Team and followed my presentation with his important words of support. To each of these supportive gentlemen, I offer my thanks.

When I started investigating firefighter exposure I had yet to transition this study into a higher degree. I began as a research officer within FIRU and requested help and expertise from the FRNSW librarian, Julie Wyner. She trawled through databases for me to support me in my early research, and I'm grateful for her support.

A few months after beginning investigating firefighter exposure and reproduction, I began seeking a supervisor to undertake a PhD to ensure the study would be both independent and of high quality. When I first approached Professor Jochen Mueller at the University of Queensland I had a plan of what I hoped to do for the research study already formulated. He was gracious and supportive and took me on as a PhD Candidate though I was relatively unyielding in study direction. His expert guidance and supervision supported me to maintain the structure, quality, and integrity in this work. He assisted me to transform my style of writing to a higher level and guided me through my journey of understanding higher level research studies. Thank you Jochen.

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**Keywords**

reproduction, firefighting, fire fighter, biomonitoring, semen, breast milk, blood, urine, fire station, estimated daily intake

**Australian and New Zealand Standard Research Classifications (ANZSRC)**

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Dedication:

This work is dedicated to my beloved wife and children, who have offered me unwavering support over the many years required to complete this work.

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List of Abbreviations

12346789-octachlorodibenzo-p-dioxin (OCDD)

1234678-heptachlorodibenzofuran (1234678-HpCDF)

1234678-heptachlorodibenzo-p-dioxin (1234678-HpCDD)

1234789- heptachlorodibenzofuran (1234789-HpCDF)

123478-hexachlorodibenzofuran (123478-HxCDF)

123478-hexachlorodibenzo-p-dioxin (123478-HxCDD)

123678-hexachlorodibenzofuran, (123678-HxCDF)

123678-hexachlorodibenzo-p-dioxin (123678-HxCDD)

123789-hexachlorodibenzofuran (123789-HxCDF)

123789-hexachlorodibenzo-p-dioxin (123789-HxCDD)

12378-pentabromodibenzofuran (12378-PeBDF)

12378-pentachlorodibenzo-p-dioxin (12378-PeCDD)

12378-pntachlorodibenzofuran (12378-PeCDF)

1-Hydroxy-2-propyl bis(1-chloro-2-propyl) phosphate (BCIPHIPP)

22’33’44’566’-nonabromodiphenyl ether (PBDE-207)

22’33’44’66’-octabromodiphenyl ether (PBDE-197)

22'44'55'-hexabromodiphenl ether (PBDE-153)

22'44'5-pentabromodiphenyl ether (PBDE-99)

22'44'6-pentabromodiphenyl ether (PBDE-100)

22'44'-tetrabromodiphenyl ether (PBDE-47)

234678-hexachlorodibenzofuran (234678-HxCDF)

23478-pentabromodibenzofuran (23478-PeBDF)

23478-pentachlorodibenzofuran (23478-PeCDF)

2378-petrabromodibenzo-p-dioxin (2378-TBDD)

2378-tetrabromodibenzofuran (2378-TBDF)

2378-tetrachlorodibenzodioxin (2378-TCDD)

2378-tetrachlorodibenzofuran (2378-TCDF)

244'-tribromodiphenyl ether (PBDE-28)

2-Ethylhexyl diphenyl phosphate (EHDPP)

aluminium (Al)

Anthracene (Ant)

antimony (Sb)

arsenic (As)

arsenic (As)

barium (Ba)

Benz[a]anthracene (BaA)

benzene, toluene, ethyl benzene, and xylene chemicals (BTEX chemicals)

Benzo[a]pyrene (BaP)

Benzo[b]fluoranthene (BbF)

Benzo[e]pyrene (BeP)

Benzo[ghi]perylene (BghiP)

Benzo[k]fluoranthene (BkF)

benzophenone-3 (BP-3)

Bis(1,3-dichloroisopropyl) phosphate (BDCIPP)

Bis(1-chloroisopropyl) phosphate (BCIPP)

Bis(2-butoxyethyl) 3-hydroxyl-2-butoxyethyl phosphate (3OH-TBOEP)

Bis(2-butoxyethyl) hydroxyethyl phosphate (BBOEHEP)

Bis(2-butoxyethyl) phosphate (BBOEP)

Bis(2-chloroethyl) phosphate (BCEP)

Bis(2-ethylhexyl) phosphate (BEHP)

Bis(methylphenyl) phosphate (BMPP)

bismuth (Bi)

Bisphenol-A (BPA)

bromine (Br)

butyl paraben (BP)

cadmium (Cd)
caesium (Cs)
calcium (Ca)
carbon monoxide (CO)
carboxyhaemoglobin (COHb)
chromium (Cr)
Chrysene (Chr)
cobalt (Co)
compartment fire behavioral training (CFBT)
copper (Cu)
Critical Appraisal Skills Program (CASP)
decabromodiphenyl ether (PBDE-209)
Dibenzo[a,h]anthracene DahA
Dibutyl phosphate (DBP)
dichlorodiphenyldichloroethylene (DDE)
dichlorodiphenyltrichloroethane (DDT)
Diphenyl phosphate (DPhP)
endocrine disrupting chemicals (EDCs)
environmental phenols (EPs)
estimated daily intake (EDI)
ethyl paraben (EP)
Firefighter Occupational Exposures Project (FOX)
Fluoranthene (Flu)
Fluorooctane sulfonamide (FOSA)
gallium (Ga)
germanium (Ge)
gold (Au)
hafnium (Hf)
hexachlorobenzene (HCB)
hydroxyacenaphthene (OH-ACE)
hydroxybenzo[a]anthracene (OH-BaA)
hydroxybenzo[a]pyrene (OH-BaP)
hydroxychrysene (OH-CHR)
hydroxyfluoranthene (OH-FLU)
hydroxyfluorene (OH-FLO)

Hydroxynaphthalene (OH-NAP)

hydroxyphenanthrene (OH-PHE)

hydroxypyrene (OH-PYR)

Indeno[1,2,3-c,d]pyrene (I123cdP)

indium (In)

International Agency for Research on Cancer (IARC)

iodine (I)

iridium (Ir)

iron (Fe)

lead (Pb)

lead (Pb)

limit of detection (LOD)

limit of quantitation (LOQ)

linear and branched isomers (Total PFOS)

magnesium (Mg)

manganese (Mn)

manganese (Mn)

Mercury (Hg)

mercury (Hg)

methyl paraben (MP)

mono(2-ethyl-5-carboxypentyl) phthalate (MECPP)

mono(2-ethyl-5-hydroxyhexyl) phthalate (MEHHP)

mono(2-ethyl-5-oxohexyl) phthalate (MEOHP)

mono(2-ethylhexyl) phthalate (MEHP)

mono(3-carboxypropyl) phthalate (MCPP)

monobenzyl phthalate (MBzP)

mono-butyl phthalate (MnBP)

monocyclohexyl phthalate (MCHP)

monoethyl phthalate (MEP)

mono-isobutyl phthalate (MiBP)

monomethyl phthalate (MMP)

mono-n-octyl phthalate (MnOP)

National Health and Nutrition Examination Survey (NHANES)

National Institute for Occupational Safety and Health (NIOSH)

N-Ethyl-perfluorooctane sulfonamido acetic acid (NEtFOSAA) nickel (Ni)

niobium (Nb)

N-Methyl-perfluorooctane sulfonamido acetic acid (NMeFOSAA)

n-propyl paraben (PP)

octabromodibenzofuran (OBDF)

octachlorodibenzofuran (OCDF)

organophosphate esters (OPEs)

oriental strand board (OSB)

p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE)

palladium (Pd)

per- and polyfluoroalkyl substances (PFAS)

perfluordecanesulphonate (PFDS)

Perfluorobutane sulphonic acid (PFBS)

perfluorobutanesulfonic acid (PFBS)

Perfluorobutanoic acid (PFBA)

perfluorodecane sulfonate (PFDS)

Perfluorodecanoic acid (PFDA)

Perfluorododecanoic acid (PFDoA)

Perfluorododecanoic acid (PFDoDA)

perfluoroheptanesulfonate (PFHpS)

perfluoroheptanesulfonic acid (PFHpS)

Perfluoroheptanoic acid (PFHpA)

perfluoroheptonic acid (PFHpA)

Perfluorohexane sulfonate (PFHxS)

Perfluorohexane sulphonic acid (PFHxS)

perfluorohexanoic acid (PFHxA)

perfluorononanesulfonate (PFNS)

perfluorononanesulfonic acid (PENS)

Perfluorononanoic acid (PFNA)

perfluorooctane sulfonamide acetic acid (FOSAA)

perfluorooctane sulfonate (PFOS)

Perfluorooctane sulphonic acid (PFOS)

Perfluorooctanoic acid (PFOA)

perfluoropentane sulphonate (PFPeS)

perfluoropentanesulfonic acid (PFPeS)

Perfluoropentanoic acid (PFPeA)
perfluorotetradecanoic acid (PFTeA)
perfluorotridecanoic acid (PFTrDA)
perfluoroundecanoic acid (PFUnDA)
Perfluoroundecanoic acid (PFUnDA)
persistent organic pollutants (POPs)
personal protective clothing (PPC)
personal protective equipment (PPE)
Phenanthrene (Phe)
phosphorus (P)
platinum (Pt)
polybrominated diphenyl ethers (PBDEs)
polychlorinated biphenyl (PCBs)
polychlorinated dibenzodioxins (PCDDs)
polychlorinated dibenzofurans (PCDFs)
polycyclic aromatic hydrocarbons (PAHs)
potassium (K)
Pyrene (Pyr)
Queensland Alliance for Environmental and Health Sciences (QAEHS)
reference doses (RfD)
rhodium (Rh)
Risk Quotient (RQ)
rubidium (Rb)
selenium (Se)
self-contained breathing apparatus (SCBA)
semivolatile organic compounds (SVOCs)
short term exposure limits (STEL)
silicon (Si)
silver (Ag)
sodium (Na)
strontium (Sr)
sulfur (S)
Supplementary Information (SI)
tantalum (Ta)
tellurium (Te)

tellurium (Tl)

time to pregnancy (TTP)

Time Weighted Average (TWA)

tin (Sn)

titanium (Ti)

Toxic equivalency (TEQ)

Tributyl phosphate (TBP)

Triphenyl phosphate (TPhP)

tris(1,3-dichloroiospropyl) phosphate (TDCPP)

Tris(2-butoxyethyl) phosphate (TBOEP)

Tris(2-chloroethyl) phosphate (TCEP)

Tris(2-chloroisopropyl) phosphate (TCIPP)

Tris(2-ethylhexyl) phosphate (TEHP)

Tris(methylphenyl) phosphate (TMPP)

tungsten (W)

uranium (U)

vanadium (V)

volatile organic compounds (VOCs)

World Health Organisation (WHO)

yittrium (Y)

zinc (Zn)

zirconium (Zr)

β-Hexachlorocyclohexane (β-BHC)

# Chapter 1

This chapter provides a general overview of the occupational exposures firefighters face, presents routes of those exposures, and provides an introductory look at firefighting and potential reproductive risks.

## Chapter 1: Introduction

Firefighting is an occupation that experiences a diverse range of health risks including (but not limited to): chemical, thermal, noise and physical exertion exposures; though limited investigations exists in relation to reproduction (Agnew et al., 1991; Jahnke et al., 2018; McDiarmid, Lees, et al., 1991). Although the range of firefighter responsibilities and duties extends far beyond fire suppression activities, this thesis will focus on exposure due to combustion products.

During fires, tens of thousands of chemicals are produced due to the combustion of vehicles, furnishings, building materials, industrial sites, waste sites, and bushlands (Austin et al., 2001; Fent & Evans, 2011). The composition and physical state of combustion products varies between fires due to the influential effects of fuel composition, ventilation profile, temperature and extinguishing agents of any individual fire environments (Kirk & Logan, 2015; NFPA, 2012). Furthermore, an individual fire will experience spatial and temporal variability leading to varying exposure profiles within a single fire environment (National Fire Protection & Society of Fire Protection, 2002). Firefighters are exposed to these combustion products as chemicals in vapour state and particulate phase, through dermal exposure, inhalation, and ingestion (Easter et al., 2016; Evans & Fent, 2015; Fent & Evans, 2011). Due to these exposures, firefighting as an occupation was elevated to “Group 1 – carcinogenic to humans” under the International Agency for Research on Cancer (IARC) Monographs in 2022 following considerable research into the occupation and health related data (Demers et al., 2022).

### 1.1 Routes of Firefighter Exposure

Firefighters can be exposed to the various combustion products by several pathways including inhalation, ingestion and dermal exposure. These routes of exposure can be present even when fully attired in designated and appropriate personal protective clothing (PPC) and personal protective equipment (PPE) including self-contained breathing apparatus (SCBA). Due to combustion products being tracked back to stations post fire suppression incidents, these risks are present through indirect exposures at fire stations, in vehicles, and due to contaminated PPC and PPE (Brown et al., 2014). Each of these exposure pathways will be discussed in turn.

### 1.1.1 Inhalation

Research has shown that the burning of synthetic materials (ever present in modern households) produce greater smoke release rates than the equivalent burning of natural materials (Fabian et al., 2014). Furthermore, many of these combustion products are chemically reactive and may continue to form more and/or different chemical toxins upon release including post fire suppression and during overhaul (Stefanidou et al., 2008). The positive mitigating effects of SCBA on inhalation risks are well known, as shown in biomonitoring studies assessing exposure to brominated flame retardants and volatile organic chemicals (Park et al., 2015; Pleil et al., 2014). For example, biomonitoring studies on firefighters have shown lower levels of polybrominated diphenyl ethers (PBDEs) in serum samples of firefighters who consistently used SCBA whilst undertaking ventilation (17% lower), exterior fire suppression (15% lower) and during overhaul (7% lower) (Park et al., 2015).

It has been found that many combustion products are present at hazardous levels during both extinguishment and overhaul (Fabian et al., 2010). During these phases of fire incidents 99+% of smoke particles are less than 1 micron in diameter, 97+% of which are too small for the naked eye to see suggesting a clean air environment when in fact the air remains contaminated (Fabian et al., 2010). These ultrafine micro particles present major health risks if inhaled due to their high efficiency in depositing deep in the lung tissue and potentially resulting in subsequent transfer to the liver, cardiovascular and nervous systems, and other body tissue. Furthermore, airborne toxins including heavy metals and polycyclic aromatic hydrocarbons (PAHs) can be carried by these particles (Fabian et al., 2010). Furthermore, VOCs and SVOCs that are produced during the combustion processes may release into the air and present in the gaseous phase which may be inhaled by firefighters.

The process by which chemicals enter the human system by means of inhalation is shown in Figure 1.1 (Falcón-Rodríguez et al., 2016).

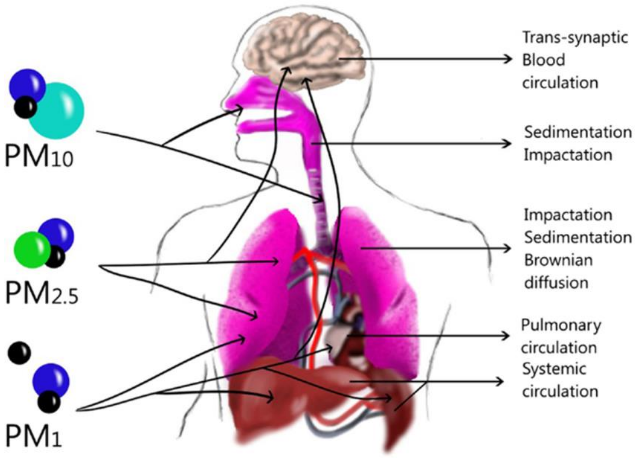


**Figure 1.1: Particle Size and Lung Deposits (Falcón-Rodríguez et al., 2016)**

Research has shown that firefighters may remove respiratory protection in the absence of visible smoke, leaving them at immediate risk of inhaling micro-particulates and associated chemicals that have the potential to negatively affect health (Chernyak et al., 2012). Furthermore, firefighter reliance on basic gas monitors to determine when it is safe to remove breathing apparatus is not fool-proof as short term exposure limits (STEL) to chemicals such as arsenic were exceeded in fire testing, and many gas monitors would not provide warning for such an exposure (Fabian et al., 2010).

Firefighters have reported not wearing respiratory protection during vehicle fires (Fent & Evans, 2011). Vehicle fires contain a large number of chemicals known to be carcinogenic including volatile organic compounds (VOCs), PAHs, aldehydes, dioxins and furans, among others (Lönnermark & Blomqvist, 2006). A recent study of 75 VOCs resulting from engine and cabin vehicle fires confirmed that vehicle fires present hazardous conditions with numerous chemicals and known carcinogens present in the atmosphere (Fent & Evans, 2011). Given these findings, firefighters not wearing SCBA face substantial risks to their long term health, and risk short term exposure to the respiratory tract and eyes at greater than nine times the calculated acceptable risk level (Fent & Evans, 2011).

Wildfire environments present exposures with regard to many potentially hazardous chemicals in a complex mixture of gases and particles, including: VOCs, PAHs, persistent organic pollutants (POPs) such as dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), various flame retardants and other chemicals with the potential for damaging health effects (De Vos et al., 2009; Reisen et al., 2011). Research undertaken for the National Dioxins Program demonstrated that burning biomass and soil unequivocally releases substantial levels of

PCDDs, PCDFs and PCBs, which are persistent and known to be adversely associated with human health (Meyer, 2009). Further compounding the risk of exposure, survey results have shown that firefighters may not wear any respiratory protection during wildfire suppression (Neitzel et al., 2009).

Firefighters have been found to be at risk of chemical inhalation due to off-gassing PPC and the degradation of soot (termed off-dusting hereafter) containing highly toxic and carcinogenic micro particles. One research study on VOCs demonstrated a greater than fivefold increase in mean off-gas concentration compared to background levels, and research has suggested that fire station contamination is due to contamination tracked back on items of PPC and PPE (Fent et al., 2014; Fent et al., 2015; Park et al., 2015).

### 1.1.2 Ingestion

Flame retardants including polybrominated diphenyl ethers (PBDEs) and organophosphate esters (OPEs) have been analysed in dust samples in fire stations and households in both Australia and USA with the result showing that fire stations have increased levels of both chemical groups (Banks et al., 2020; Brown et al., 2014; Park et al., 2015). Global research studies have correlated PBDE concentrations in household dust and subsequent levels in human serum and milk samples suggesting that dust ingestion is a major potential exposure pathway (Brown et al., 2014; Sjodin et al., 2004; Wilford et al., 2005).

This heightened presence of flame retardant in dust is most likely due to the contamination of firefighting gear by flame retardant ash post fire incidents (Brown et al., 2014). Residual PBDEs are likely to be present on contaminated hoses, ladders, SCBA, turn out gear, etc, and unless cleaned prior to returning to the station, the residual soot can result in contaminated dust being spread (Park et al., 2015). Turnout gear itself may be a source of flame retardant, per- and polyfluoroalkyl substances (PFAS), and phthalate diester exposure for firefighters due to the intricate requirements for the clothing to keep firefighters safe (Alexander & Baxter, 2014; Park et al., 2015; Young et al., 2021).

Park et al. 2015 showed firefighters who reported cleaning their PPC outside at the fire station (compared to inside) had a 25% lower sum of five PBDEs, potentially due to adhering contamination post fire suppression being cleaned and left outside, rather than becoming part of the fire station dust profile. Californian firefighters who reported regular hand washing returned lower levels of cadmium and certain PBDEs in their blood samples than those who washed their hands less frequently (Dobraca et al., 2015; Park et al., 2015). Ingestion exposure may occur after removing PPC, during station maintenance/cleaning, or when undertaking PPE maintenance or cleaning if equipment is not fully decontaminated and hands are not washed following such activities.

### 1.1.3 Dermal

Recent research has investigated the ability of fire smoke to permeate or penetrate firefighter structure PPC and contaminating skin underneath. Specifically placed monitoring equipment has demonstrated the inability of PPC to prevent exposure to human skin (Fent et al., 2017; Kirk & Logan, 2015; Poutasse et al., 2020). Modern PPC with moisture barriers mitigates the exposure by retarding the permeation and penetration of hazardous chemicals. However, movement of air is required in modern firefighting ensembles in order for firefighters to cool themselves and avoid major heat-related illnesses that would arise from a fully insulated outfit (McQuerry, 2016). This therefore allows for the movement of smoke to reach firefighter skin.

Figure 1.2 explains permeation and penetration with respect to liquid, vapour and particulates (labelled molecules in the following description).

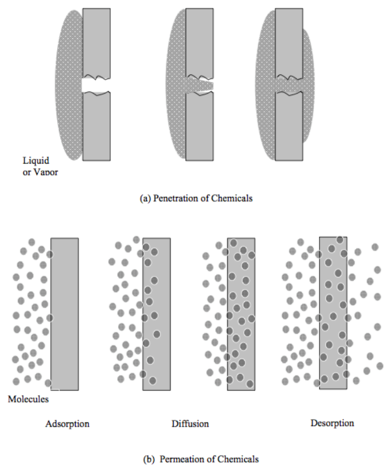


Figure 1.2: Chemical Interactions with Clothing/Equipment Materials (Stull & Stull, 1999)

Figures 1.3 (a-e) are from a Fluorescent Aerosol Screening Test for International Personal Protection, Inc., and demonstrate the potential for firefighter skin and under clothing to become contaminated when wearing shorts and t-shirts under structural firefighter ensemble (Hill, 2015). Highlighted areas post exposure show areas on the head and neck (Figure 1.3c) where the fluorescent particles have penetrated the hood, highlighted areas on the legs, arms and torso (Figures 1.3d&e) are due to overlapping layers, seams, or the general movement of air due to the bellows and chimney effects.

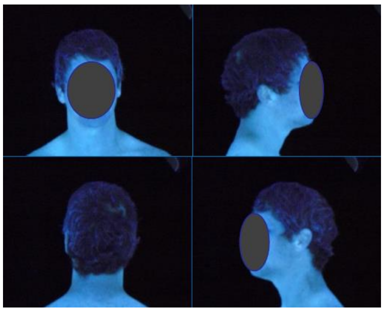

Figure 1.3a: Black lit face pre-exposure

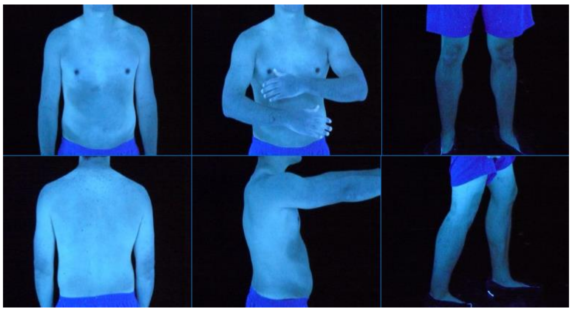

Figure 1.3b: Black lit body pre-exposure

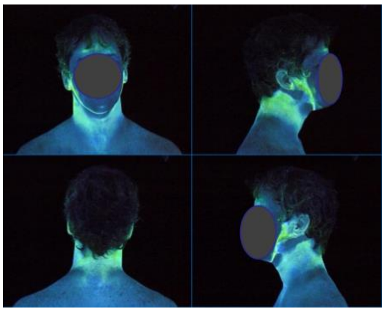

Figure 1.3c: Black lit face post exposure

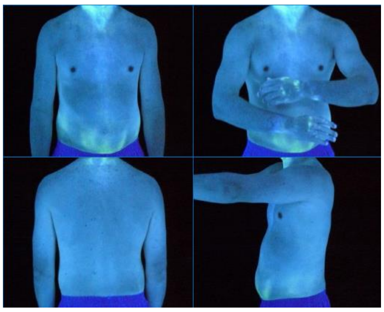

Figure 1.3d: Black lit torso post exposure

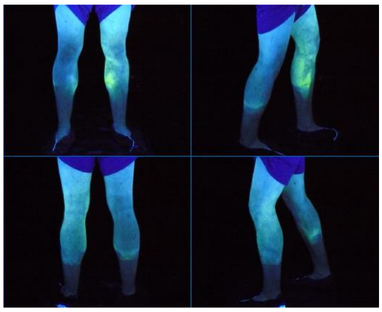

Figure 1.3e: Black lit legs post exposure

Figure 1.3: Demonstrating the Ability for Particulates to Reach Under Firefighting Personal Protective Clothing (Hill, 2015)

The permeation or penetration of combustion products has been detected through flash hoods (Fent et al., 2017; Fent et al., 2014). With high skin permeability of the jaw line, scalp, and forehead (Kapitány et al., 2021), flash hood contamination has the potential to continue to expose a firefighter whenever worn if it has not been fully decontaminated. Endocrine disrupting chemicals have been found on PPC post fire suppression activities and found to accumulate on contaminated PPC and PPE over time if not cleaned (Alexander & Baxter, 2014; Demers et al., 2022; Stevenson et al., 2015).

Processes for decontamination vary across fire services, and even within fire stations. Prior studies have identified differenced in the contamination of PPC within fire stations based on firefighters decontaminating their PPC inside or outside (hand washing), and other studied have identified the use of professional laundering services and in station washing machine facilities (Calvillo et al., 2019; Fent et al., 2017; Keir et al., 2020; Park et al., 2015).

Phthalate diesters have been found not only on the external layers of soiled firefighter PPC, but also on inner layers next to the skin. Given the lipophilic nature of phthalates (Serrano et al., 2014), dermal absorption presents a route of exposure in firefighters (Alexander & Baxter, 2014). Dioxins and PCBs have been found on helmets, face guards, gloves, and firefighting coats following fire suppression activities risking secondary ingestion and/or dermal exposures (Chernyak et al., 2012).

### 1.2. Biomonitoring Firefighters

Of the multitude of chemicals present in fire environments only a fraction have been studied and chemically determined, with less biomonitored in firefighters leading to a risk of under-representation of the occupational exposures firefighters may face (Laitinen et al., 2012). Many within this myriad of chemicals are known carcinogens which may be responsible for the increases in firefighter incidence of cancer (Demers et al., 2022; Glass et al., 2014).

Biomonitoring studies include the biological monitoring of chemicals in human systems. This has been defined as, "the method for assessing human exposure to chemicals or their effects by measuring these chemicals, their metabolites or reaction products in human specimens" (Control & Prevention, 2005). In brief, chemical absorptions and excretion processes are shown in Figure 1.4. With the metabolic process shown in Figure 1.5 (Hays et al., 2007).

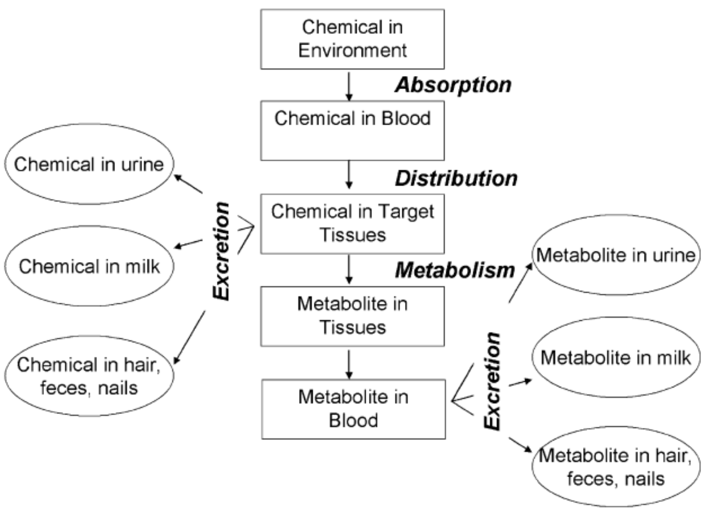


Figure 1.4: Chemical Absorption and Excretion Process (Hays et al., 2007)

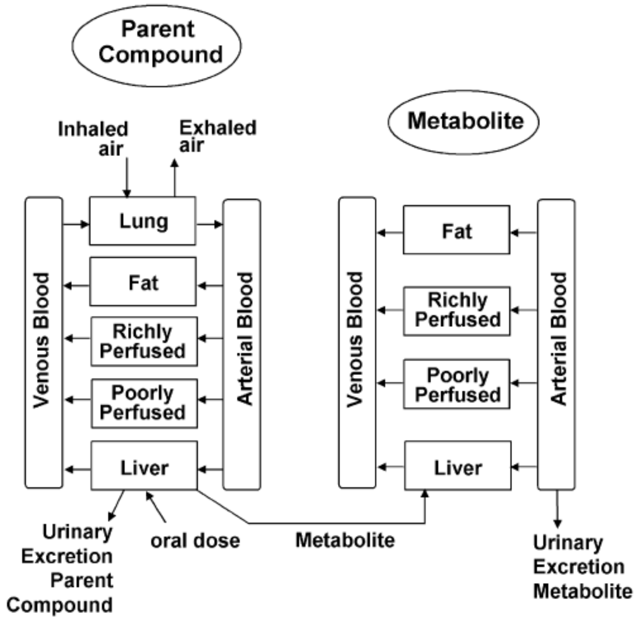


**Figure 1.5: Parent Compound and Metabolite Processes (Hays et al., 2007)**

Multiple types of biosamples are utilised in biomonitoring; including, but not limited to, nails, hair, tissue, blood, urine, semen, breast milk and breath (WHO, 2015). The most easily collected sample types with reduced risk of environmental contamination include blood, urine, semen and breast milk. Considering these pathways, the correct selection of target chemicals and related matrices with consideration around time since, or duration of, exposure is important.

## 1.3. Firefighting and Reproduction

Although much research has been undertaken to determine the short term and long term general health effects of firefighting, less has assessed the potential for reproductive insult. This is true across workplaces and industries due to the high cost of toxicological assessment and the traditional focus on acute or lethal exposure levels, rather than hazards associated with chronic exposure such as reproductive insult (McDiarmid, Lees, et al., 1991).

Unlike most physiological functions, reproduction is an intermittently expressed human function. As such, the potential for insult to human reproduction and offspring depends on the timing and extent of exposure, and how that directly relates to the stage of reproductive function (McDiarmid & Agnew, 1995). For example, if the exposure is of sufficient toxicity during a vulnerable period of sperm, oocyte, foetal development, or during lactation, adverse outcomes may be the result (McDiarmid & Agnew, 1995). Most chemicals that have been tested historically with regard to reproduction have been found to affect the reproductive systems of both genders (McDiarmid & Agnew, 1995).

### 1.3.1. Firefighter Exposure and Male Reproduction

Although firefighting can trace its history to the 17th century and has been a predominately male occupation, relatively minimal research has considered the potential exposure effects of firefighting on male reproduction. Although, as mentioned, some studies were undertaken in the 1980s and 1990s, there remains a significant lack of detail surrounding the potential for reproductive disruption, especially in the context of modern homes and furnishings.

A literature review of epidemiological studies on paternal occupations and birth defects was undertaken in 2002 (Chia et al., 2002). This review compared both large and small population-based studies, population registry-based case-control studies, and matched case-control studies. The results showed a repeated association between occupational firefighters and congenital heart defects among offspring. Other reported birth defects linked to firefighting as an occupation included ventricular septal defects, atrial septal defects, other cardiac congenital anomalies, cleft lip, hypospadios, and club foot (Chia et al., 2002; Olshan et al., 1990). Postulated mechanisms for these birth defects included mutagenesis of germ cells prior to conception, maternal contamination due to toxins in seminal fluids, and home contamination through work clothes and equipment leading to maternal exposure (Chia et al., 2002).

More findings of reduced fertility come from a cohort of Danish male firefighters. These men were found to have reduced fertility in comparison to the general population when considered via registry studies from IVF clinics with specific focus on employment (Petersen et al., 2019).

Male germ cell mutagenesis can increase the chances of spontaneous abortions, physical malformations, behavioural alterations, and increase the incidence of certain diseases including cancer (Robaire & Hales, 1993). Other mechanisms of reproductive insult following paternal exposure could be a direct effect on the ovulated egg, the process of fertilisation, or embryonic development (Robaire & Hales, 1993). Male spermatogenesis is a complicated biological process that requires approximately 72-74 days to produce mature sperm (Paul & Himmelstein, 1988). As such, provided that reproductive insult spares the primitive stem cell pool, any damage is likely to be reversible (Paul & Himmelstein, 1988).

Many of the chemicals firefighters are exposed to can lead to changes in sperm morphology and reduced semen parameters, thereby potentially reducing reproductive success (Jeng et al., 2018; Wang et al., 2015). Much of the research in this area has been conducted in animal studies, with some human study research available (Mima et al., 2018).

Human paternal occupational exposure prior to conception has been linked to increased risk of brain tumours in children, and increased potential for sperm damage (Cordier et al., 2004). Metals, including lead and cadmium, can affect male fertility with increases in abnormal spermatozoa in lead intoxicated workers, and marked testicular degeneration due to a single acute dose of cadmium to rodents (McDiarmid & Agnew, 1995; Paul & Himmelstein, 1988). Humans, if in a chronic exposure environment, have proven more resistant to testicular degeneration due to the binding of cadmium to a testicular protein; however, studies have shown the potential of the exposure to imply a germ cell hazard (Paul & Himmelstein, 1988).

Many of the products of combustion have been shown to be endocrine disrupting chemicals (EDCs). These chemicals can mimic or disrupt oestrogenic and other hormone activities, potentially decreasing fertility (Stevenson et al., 2015). Chemicals designated as EDCs that fit within firefighter exposure profiles include: phthalate diesters, VOCs, PFAS, PAHs (including benzo[a]pyrene), PCDD/Fs, PBDD/Fs, and environmental phenols. Chemicals from each of these groups are found in nearly every fire environment, and phthalates have been found deposited on every sample of used firefighter clothing at rates of 52 to 875 times higher than PAHs (Alexander & Baxter, 2014). The prolonged exposure of these chemicals is unknown, but may present an increased risk of hormone disruption in exposed firefighters (Stevenson et al., 2015).

Other chemicals that have been listed as affecting male fertility include methylene chloride, sulphur dioxide, toluene, trichloroethylene and chloroform. All of which are present in fire environments (Austin et al., 2001).

### 1.3.2. Firefighter Exposure and Female Reproduction

Compared with male fertility, female fertility and reproduction is far less understood, with very little research available specifically to firefighting (Jahnke et al., 2012). This is in part due to the fact that minimal scientific literature exists surrounding female firefighters due to smaller numbers of female firefighters. Jahnke et al., 2012 presented that although large scale scientific studies exist surrounding the biomonitoring of firefighters for occupational exposure, many do not focus on women's health, and some have eliminated women due to small sample size and therefore reduced confidence in results. The number of studies on women is; however, beginning to grow.

A research study on female firefighters in Korea comparing hospital admissions around pregnancy, childbirth and puerperium outcomes (Park et al., 2020). Results indicated that female firefighters showed high standardised admission rate to hospitals across categories analysed when compared to the general population. These categories included standardised admission rates for pregnancy, childbirth, and puerperium outcomes (Park et al., 2020). The authors suggested the need for policy-based support for female firefighters reproductive health, and that further studies may be necessary.

A recent survey-based study on female firefighters in the USA found firefighters to have an incidence of spontaneous abortion (miscarriage and still birth) of 27%, notably higher than the general population (13.5%) (Jahnke et al., 2018). The rates of miscarriage increased as women had subsequent births, with the rates of miscarriage increasing from first to fourth pregnancies from 22.6% to 31.7%. Of those included in the study, only 14.8% were not actively running emergency calls whilst pregnant.

Many chemicals that firefighters are occupationally exposed to may affect female hormones due to the estrogenic and/or anti-estrogenic activity, which may inhibit implantation. Heavy metals, including lead and cadmium, can interfere with the binding of oestradiol to human endometrial and myometrial cytosols, with the result being a decreased likelihood of embryonic implantation and reduced fertility (Evanoff & Rosenstock, 1986; Paul & Himmelstein, 1988). Positive associations have been found through the National Birth Defects Prevention Study that maximum pollutant exposure levels of carbon monoxide, nitrogen dioxide, ozone sulphur dioxide and particulate matter during weeks 2-8 of pregnancy can negatively impact upon foetal heart development. (Stingone et al., 2014). International research on pregnant female firefighters has identified that this is a period of time wherein female firefighter may still face such exposures due to fire incidents (Jahnke et al., 2018).

Furthermore, recent research identifying the presence of POPs in follicular fluid has suggested that increasing age contributes to the increasing rate of transfer of POPs form blood to follicular fluid, and that exposure to POPs can affect outcomes of assisted reproductive technology (Björvang et al., 2022).

Direct toxicity to the oocyte can cause reproductive insult by means of genotoxic damage, which in turn can lead to pregnancy loss, decreased fertility, or birth defects (Paul & Himmelstein, 1988). Furthermore, reproductive insult can affect parturition, offspring fertility, or ongoing offspring growth and development post birth (Costa & Giordano, 2007; McDiarmid & Agnew, 1995).

Firefighters are regularly exposed to environments containing high levels of carbon monoxide (CO). Acute, non-lethal maternal exposure to CO has been associated with foetal loss and adverse neurological changes (McDiarmid, Agnew, et al., 1991). The physiological responses of an unborn baby result in increased levels of carboxyhaemoglobin (COHb) concentrations when compared with maternal blood levels, at a rate of 10-15% higher (McDiarmid, Agnew, et al., 1991).

Elemental carbon (also known as black carbon or soot) from ambient exposure has been found to cross the placenta during pregnancy, with findings of elemental carbon particles in foetal liver, lung and brain tissues of 2$^{nd}$ trimester foetesus (Bongaerts et al., 2022; Bové et al., 2019).

Other VOCs known to affect reproduction and present within fire environments were assessed via two USA based studies examined the prevalence of birth defects (congenital heart defects and neural tube defects) due to maternal exposure to air pollutants. One study focused around BTEX chemicals (benzene, toluene, ethyl benzene, and xylene) and determined an association between benzene and spina bifida (Lupo et al., 2011). Benzene was measured in cord blood at equal or higher levels than maternal blood. The assessment was based on chronic exposure due to ambient air pollution levels of BTEX, with the findings that pregnant women living in census tracts of ≥3mg/m3 (≥94ppm[1]) benzene were at more than double the risk of giving birth to a child with neural tube defects. The exposure of firefighters to benzene has been confirmed by a study assessing breath concentrations of benzene following simulated routine fire suppression activities, with the results being comparable to levels of benzene in non-smoking automobile mechanics following four hours of work (Fent et al., 2014).

In-utero exposure to PFAS has been shown to affect delayed onset of menstruation in daughters that were exposed to higher levels of PFOA, and increased prevalence of obesity and high waist circumference in daughters exposed to low levels of PFOA in-utero (Halldorsson et al., 2012). PFHxS and PFUnDA have been linked with decreased and increased birth weight, respectively (Callan et al., 2016).

## 1.3.3. Lactating Firefighters

POPs have been found present in breast milk biomonitoring studies around the world. Specific POPs bioaccumulate in adipose tissue, and those that are lipophilic (tending to combine or dissolve in lipids or fats) are able to pass through from serum to breast milk. These chemicals are found in household dust, in drinking water, in food, in household items, building materials, automobiles; etc. Even though certain chemicals have been banned by means of the Stockholm Convention (UNEP, 2001), or by the Australian government, they continue to exist in both the global and local environment, contaminating the population.

Breast milk is a known conduit for many environmental contaminants including, but not limited to: PCDD/Fs, PBDEs, OCPs (including DDT, DDE and HCB), PCBs, PFAS, PAHs, and certain metals, with some chemicals passing through more readily than others (LaKind et al., 2009; Lehmann et al., 2018; Mueller et al., 2008).

With the potential of occupational exposure to these chemicals due to combustion that are known to be able to pass into breast milk, it becomes important to consider what toxins may be elevated in firefighter breast milk. As previously mentioned, prior to the current study only a single research study has been published surrounding lactating firefighters. This study considered the excretion of PBDEs and AhR activation in breast milk from firefighters pre exposure, post exposure (up to 72hrs) and in comparison to office workers (Jung et al., 2023). The study did not find any significant differences post exposure, but suggested more research was required to understand the risks lactating firefighters may face.

The World Health Organisation (WHO) recommends exclusive breastfeeding for six months (WHO, 2023a). It further suggests continued breastfeeding for two years and beyond in all but the most extreme situations of contamination as an important stage in the reproductive process for mothers, and due to the significant positive health qualities it provides to the infant (WHO, 2023b),

The well documented health benefits of breast milk further include the reduced risks of infection and chronic diseases such as allergies, asthma, arthritis, diabetes, obesity, cardiovascular disease, and various cancers (both in childhood and adulthood) (Landrigan et al., 2002; Mead, 2008). As such, in the interest of the health of the child, the focus becomes on mitigating potential maternal re-exposures during lactation to ensure chemical burden does not increase unnecessarily over the duration of breast feeding.

Infancy is unique in its heightened exposure pathways for lipophilic pollutants as an infant's nutritional intake includes a higher lipid ratio than at other stages of life (Chen et al., 2015). It also marks a critical stage in development, with increasing evidence suggesting that early life exposure is an important determinant of long-term health risk (Landrigan et al., 2002). The challenge with any assessment of exposure; however, is due to lack of information accurately outlining what levels, if any, are safe for the uniquely susceptible infant.

## 1.4. Thesis Structure

To investigate how these international findings might apply specifically to firefighters in an Australian context, the following plan was adopted as an outline listed in conjunction with aims addressed (following this Chapter, the introduction):

Chapter 2: Aim 1, a systematic review relative to the biomonitoring of firefighters globally to determine specific chemical exposures can that feasibly be studied as part of this thesis;

Chapter 3: Aim 2, Investigations into the exposures at Australian fire stations in comparison to Australian homes and offices;

Chapter 4: Aim 2, Investigation into the ability of fire related chemicals to extend beyond external personal protective clothing to undergarments and socks, items washed at home and worn over highly permeable skin;

Chapter 5: Aims 3&4, Providing an introduction to firefighter reproduction through an analysis of semen for quality;

Chapter 6: Aims 3&4, Delving further into male fertility through an assessment of chemical exposure via blood and urine, and introducing female firefighter reproduction and exposure by means of blood, urine and breast milk chemical concentrations; and,

Chapter 7: Conclusions drawn from the research and future perspectives.

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Engelsman, M., Toms, L.-M. L., Banks, A. P. W., Wang, X., & Mueller, J. F. (2020). Biomonitoring in firefighters for volatile organic compounds, semivolatile organic compounds, persistent organic pollutants, and metals: A systematic review. *Environmental Research*, *188*. https://doi.org/10.1016/j.envres.2020.109562

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# Chapter 2

A range of biomonitoring studies on firefighters have presented routes of exposure and liklihood of fire being the cause of elevated concentrations of specific chemicals. However, no systematic review exists to comprehensively evaluate the results of these studies. Furthermore, there was no studies to collate and present results of firefighter biomonitoring studies across a range of chemcials in a single place potentially limiting awareness of the bredth of exposure faced by this occupation. This systematic review served to not only identify and confirm the range of chemical exposures of firefighters due to fire incidents, but also provide shape and scope for the remainder of the PhD project with regards to potential indirect exposurers, and targeted chemicals for the biomonitoring aspect of this study. This chapter presents a broad range of chemical exposures identified in firefighters through biomontioring, assessing specific cohorts of firefighters (aviation, wildland, urban, fire trainers and fire investigators) around chemical concentrations and findings of occupational exposure. The following publication has been incorporated as Chapter 2.

**Biomonitoring in Firefighters for Volatile Organic Compounds, Semivolatile Organic Compounds, Persistent Organic Pollutants, and Metals: A Systematic Review**

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**Abstract**

Firefighters are exposed to a wide range of toxic chemicals due to combustion, with numerous biomonitoring studies completed that have assessed exposure. Many of these studies focus on individual classes of chemicals, with a few considering a broad range of systemic exposures. As yet, no review process has been undertaken to comprehensively examine these studies. The aims of this are to: (1) ascertain whether biomonitoring studies pertaining to firefighters demonstrate occupational exposure to volatile organic compounds, semivolatile organic compounds, and metals; (2) determine and present results of biomonitoring studies; (3) provide any recommendations presented from the literature that may support exposure mitigation; and (4) suggest future study parameters that may assist in providing a greater understanding surrounding the occupational exposure of firefighters. A systematic review was undertaken with regards to firefighters and biomonitoring studies utilising the matrices of blood, urine, semen and breast milk. This yielded 5690 results. Following duplicate removal, inclusion and exclusion criteria screening and full text screening, 34 studies remained for review. Results of over 80% of studies analysed determined firefighters to experience occupational exposure. Results also show firefighters to be exposed to a wide range of toxic chemicals due to fire smoke; potentially exceeding the range of exposure of other occupations. As firefighters may face increased risk of health effects due to the additive, synergistic, and/ or antagonistic effects of chemical exposure, all care must be taken to reduce exposure. This may be achieved by considering tactical decisions, increased personal hygiene, and thorough decontamination procedures. Future biomonitoring studies recognising and assessing the range of chemical exposure firefighters face would be beneficial.

## 2.1. Introduction

Firefighting is an occupation facing exposure by means of inhalation, ingestion or dermal absorption, to a wide range of chemicals due to combustion. Every fire is unique due to ventilation profile and materials burned, yet all fires produce many chemicals including known human carcinogens and endocrine disruptors in a complex mixture of gases and particulates (De Vos et al., 2009; Evans & Fent, 2015; Fent & Evans, 2011; Kirk & Logan, 2015; Lönnermark & Blomqvist, 2006; Neitzel et al., 2009; Reisen & Brown, 2009; Reisen et al., 2011). Firefighters are exposed to these chemicals during fire suppression operations, and more passively due to air and dust exposure both in the fire truck or at the station (Banks et al., 2020; Engelsman et al., 2019; Oliveira et al., 2017a). Secondary exposure may also occur when firefighters work with or maintain equipment or clothing that has not been thoroughly decontaminated (Alexander & Baxter, 2014; Banks et al., 2020; Chernyak et al., 2012; Easter et al., 2016; Engelsman et al., 2019; Fabian et al., 2014; Park et al., 2015; Stevenson et al., 2015).

Elevated levels of chemicals have been detected in a firefighters' blood, urine and breath despite the high level of protection afforded to them by their personal protective clothing and equipment, potentially contributing to an increased risk of certain cancers and other health conditions (Chernyak et al., 2012; Dobraca et al., 2015; Fent & Evans, 2011; Hsu et al., 2011; LeMasters et al., 2006). Consideration has been given to the possibility that long-term, repeated exposure may accelerate and/or exacerbate adverse health effects such as thyroid functioning, cardiovascular disease, and cancer (Fabian et al., 2010; Laitinen et al., 2014).

Much research has focused on the environmental monitoring of chemicals within the smoke plume or deposited on firefighter ensemble, skin, and elsewhere. This research, which determines the emissions from analysed fires to be highly toxic, carcinogenic, and to deposit on firefighter ensemble, provides important data surrounding the exposures present at a fire incident (Austin et al., 2001; Easter et al., 2016; Fent & Evans, 2011; Lönnermark & Blomqvist, 2006; Stevenson et al., 2015). Such external data does not outline whether the fire environment increases a firefighters' risk of exposure, given the high levels of personal protective clothing and equipment worn during fire suppression, with studies suggesting urinary metabolites of analystes found in the smoke be analysed as markers for fire exposure (Austin et al., 2001). As such, an increasing number of studies are utilising biomonitoring to assess firefighters' integrated exposure. Biomonitoring is a method of assessing human exposure by using a specific matrix e.g. blood serum and urine. Systematic sampling and analysis of body fluids for specific exposure biomarkers (either the chemical a person is exposed to or a metabolite of the chemicals) is used as a tool for assessing exposure of the individual to the chemical. Human biomonitoring by means of blood, urine, semen and breast milk occur globally in order to ascertain exposure to environmental chemicals (WHO, 2015).

At present, no review of firefighter biomonitoring studies exists that provides a clear presentation of whether or not firefighters experience elevated levels of chemicals in their systems due to occupation, be that due to fire suppression activities or subsequent exposures from contaminated gear. As such, a systematic review process was undertaken to (1) ascertain whether biomonitoring studies pertaining to firefighters demonstrate occupational exposure to volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and metals; (2) determine and present results of biomonitoring studies; (3) provide any recommendations presented from the literature that may support exposure mitigation; and (4) suggest future study parameters that may assist in providing a greater understanding surrounding the occupational exposure of firefighters to smoke.

## 2.2. Method

A systematic review was undertaken to identify scientific papers related to blood, urine, semen and breast milk biomonitoring of firefighters across a variety of databases including Web of Science, Embase, Pubmed, CINAHL, International Pharmaceuticals Abstracts and SciFinder Scholar. Search criteria was applied for all years up to September 2019 and included the key words firefighter(s) and exposure. Each database required entry of terms in a slightly different fashion. Exact phrasing and information can be found in the Appendix 1.

Studies that analysed specific chemicals (or groups of chemicals) in body fluids (blood, urine, semen, and breast milk) attributed to fire smoke exposure were included as these fluids can be readily made available by consenting participants and can provide information on a wide range of chemicals (WHO, 2015). Although beneficial to understanding firefighter occupational exposure to products of combustion, hair, fingernail, saliva and expelled breath studies were not included due to the potential confounding factor of environmental contamination, or lack of sensitivity in analysis (WHO, 2015).

Any studies surrounding wildfire or simulation burns were included, as were general firefighter studies. A profile of firefighters in general was sought, and as such unique and/or catastrophic events (World Trade Centre, Shelekov firefighter studies, Amsterdam Air Disaster, etc) were excluded. Studies focusing on carbon monoxide, asbestos, levoglucosan, and other chemical contaminants were not included as the focus of this review was metals, VOCs, and SVOCs.

The database search yielded 5690 results. After screening for duplicates, 1746 articles remained to be screened by title, with conference proceedings and foreign language titles removed. The screening process resulted in 36 cohort studies. All were accepted, and the 36 studies were retrieved. Following full text screening, two were discarded due to the studies being based on the same firefighter cohort, assessing the same chemicals, and assessing them against the same comparison control as parallel and included studies.

The remaining 34 articles were assessed for quality using the Critical Appraisal Skills Program (CASP) checklist for cohort studies (CASP-UK, https://casp-uk.net/casp-tools-checklists/). The checklist was moderately altered to enable table layout and was then applied across the 34 articles. No articles were excluded based on the CASP Cohort Study Checklist findings. Results are presented in Table S2.1.

A visual representation of the review process produced using the PRISMA Flow Diagram Generator resulting in a final 34 studies retrieved is presented in Figure 2.1.

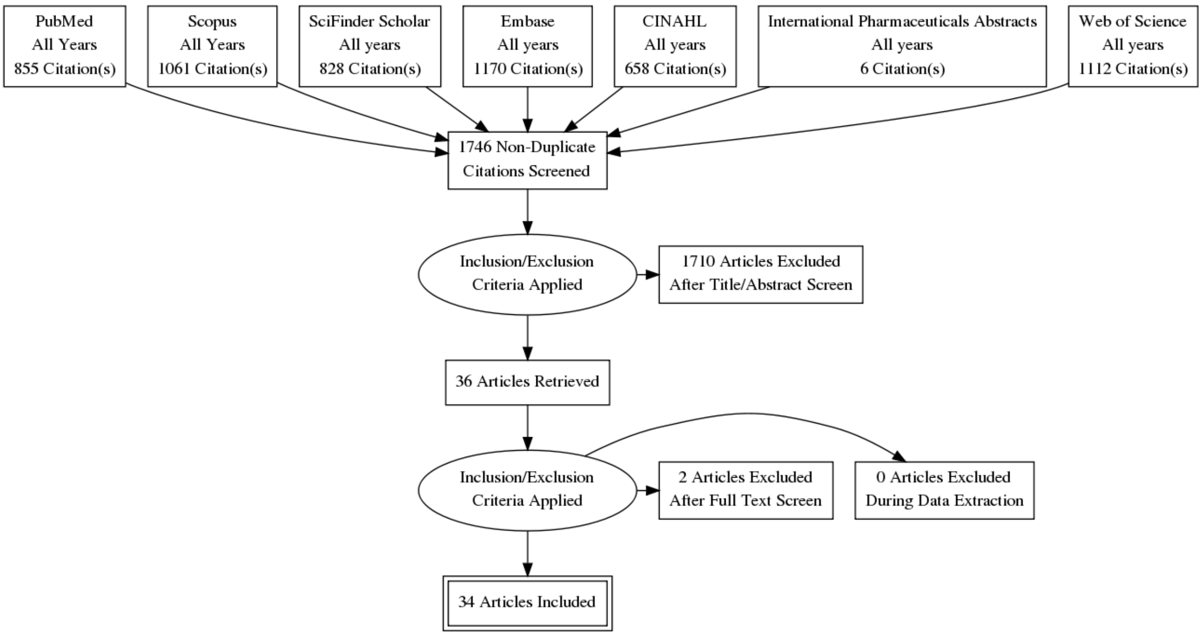


Figure 2.1: Systematic Review Process

Data were extracted, including cohort, matrix, chemicals analysed, study design, confounders and results from the 34 studies, with these dual reviewed to ensure accuracy.

Many of the included studies assessed occupational exposure using additional tests in conjunction with biomonitoring. For example, some studies also included wipe or personal air sampling to support investigations into routes of exposure, and to ascertain if environmental contamination was reflected in firefighter biomonitoring samples. Other studies supplemented blood or urine analysis with expelled breath chemical analysis, and several studies included surveys or questionnaires to better understand cohort demographics, exposure history and lifestyle. The wipe, personal air sampling, survey, questionnaire and expelled breath results were not extracted in full, though if results supported discussion of occupational exposure, that information was considered.

Extracted data were reviewed and considered based on the author's interpretation of the results of each reported study, and overarching themes were considered in a similar vein. The focus of this review was not to compare or contrast study findings due to the wide range of variables within each (including variation in duration and type of exposure, personal protective clothing and equipment worn, timing of sampling, comparison cohort, etc); rather to present results and evaluate the likelihood of firefighters experiencing occupational exposure based on the included studies. As such, all data related to biomonitoring within scope of this study were included in tables without specific effort to clearly compare data on individual metabolites, for example. Where possible, units were converted to support consistency in the presentation of results; however, this was not always possible.

### 2.3. Selected Studies

No studies were found at the time of this review that presented on semen or breast milk biomonitoring specific to firefighters. Of the 34 studies selected, 22 utilised urine for biomonitoring, ten utilised blood, and two utilised both urine and blood (Table S2.2).

Five different classifications of firefighters were presented within the extracted studies: wildland firefighters (those participating primarily in wildfire suppression), urban firefighters (those participating across the range of fires, including wildfire within an urban environment, structure and vehicle fire, etc), aviation firefighters (those participating in fire suppression activities at airports), fire trainers (those leading fire training as their primary role), and fire investigators (those who examine fire scenes post fire suppression activities). Some studies included multiple classifications of firefighters and identified them as such. Given the different exposures faced by each classification of firefighter, it is reasonable to consider them to represent different cohorts studied, even if presented within the same study. Applying this consideration lead to greater than 34 cohorts of firefighters being studied and having results presented on. Nineteen studies presented data on urban firefighters, four on wildland, three on aviation, five on fire trainers, one on investigators, and a single study did not identify the firefighter cohort in any way; however, it is assumed based on the geographic location and general description that firefighters in the study were urban firefighters. The data from each of these studies will be presented as grouped data by firefighter classification.

Table 2.1 presents the findings of reviewed studies by cohort and chemical group, thereby providing total cohort/chemical group information. The data presented excludes a single incident of cohort/chemical group that presented on firefighter blood serum levels but provided no comparative control against which to assess chemical exposure. The results of the included studies were separated out to consider the exposure of each classification or cohort of firefighter included in the study. Furthermore, several studies included multiple chemical groups. These were also separated out to be able to cross analyse results across chemicals and associated firefighter cohorts. This resulted in 50 sets of data across the cohorts and chemical groups providing information as to whether or not firefighters face occupational exposure. References have not been included in this table for ease of reading as they are included in subsequent tables separated by firefighter cohort.

Table 2.1: Occupational Exposure by Firefighter Cohort and Chemical Group Analysed

| Firefighter Classification | Chemical Group | Studies Demonstrating Occupational Exposure | Studies Demonstrating No Occupational Exposure | Total Studies Per Cohort, Per Chemical Group |
|---|---|---|---|---|
| Urban Firefighters | OH-PAHs | 11 | 0 | 11 |
| Wildland Firefighters | | 4 | 1 | 5 |
| Fire Trainers | | 4 | 0 | 4 |
| Urban Firefighters | VOC metabolites | 1 | 0 | 1 |
| Fire Trainers | | 1 | 1 | 2 |
| Urban Firefighters | Environmental Phenols | 3 | 0 | 3 |
| Wildland Firefighters | | 1 | 0 | 1 |
| Urban Firefighters | PFAS | 3 | 0 | 3 |
| Aviation Firefighters | | 3 | 0 | 3 |
| Urban Firefighters | PCDD/Fs | 1 | 1 | 2 |
| Fire Investigators | | 1 | 0 | 1 |
| Urban Firefighters | Metals | 2 | 1 | 3 |
| Wildland Firefighters | | 0 | 1 | 1 |
| Fire Trainers | | 1 | 0 | 1 |
| Urban Firefighters | Flame Retardants | 4 | 0 | 4 |
| Urban Firefighters | PCBs | 0 | 2 | 2 |
| Urban Firefighters | Pesticides and Insecticides | 2 | 1 | 3 |
| | | | Total Cohort Across Total Chemical Group Studies | 50 |

## 2.4. Chemicals Assessed

There were ten overall chemical groups analysed in the 34 studies assessed in this systematic review, including hydroxyl polycyclic aromatic hydrocarbons (OH-PAHs), polychlorinated biphenyls (PCBs), volatile organic compound (VOCs) metabolites, environmental phenols (EPs), per- and polyfluoroalkyl substances (PFAS), dioxins and furans, metals, flame retardants and pesticides. Table 2.2 details the chemicals assessed within each group.

**Table 2.2: Chemical Groups and Chemicals Assessed Across Selected Firefighter Studies**

| Chemical Group | Analytes Studied | Approximate Half-Life |
|---|---|---|
| OH-PAHs | Hydroxynaphthalene (OH-NAP), hydroxyfluorene (OH-FLO), hydroxyphenanthrene (OH-PHE), hydroxypyrene (OH-PYR), hydroxybenzo[a]anthracene (OH-BaA), hydroxychrysene (OH-CHR), hydroxybenzo[a]pyrene (OH-BaP), hydroxyfluoranthene (OH-FLU), and hydroxyacenaphthene (OH-ACE) | Hours[1] |
| PCBs | PCB-16 through to -209 | Months to Years[2] |
| VOC metabolites | t-t- muconic acid (a metabolite of benzene) | Hours[3] |
| EPs | Bisphenol-A (BPA), triclosan, methyl paraben (MP), ethyl paraben (EP), butyl paraben (BP), *n*-propyl paraben (PP), benzophenone-3 (BP-3), methylsyringol, ethylsyringol, propylsyringol | Hours[4] |
| PFAS | Perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS), perfluoroheptonic acid (PFHpA), perfluorooctanioic acid (PFOA), perfluoroonanioc acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorohexanoic acid (PFHxA), Perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeA), perfluoroheptanesulfonate (PFHpS), perfluorobutanesulfonic acid (PFBS), perfluoropentanesulfonic acid (PFPeS), perfluorononanesulfonic acid (PENS), and unknown sulfonic acids (Cl-PFOS, ketone-PFOS, ether-PFHxS and Cl-PFHxS) | Months to Years[5] |
| Dioxins and furans | 2378-tetrachlorodibenzofuran (2378-TCDF), 12378-pntachlorodibenzofuran (12378-PeCDF), 23478-pentachlorodibenzofuran (23478-PeCDF), 123478-hexachlorodibenzofuran (123478-HxCDF), 123678-hexachlorodibenzofuran, (123678-HxCDF), 234678-hexachlorodibenzofuran (234678-HxCDF), 123789-hexachlorodibenzofuran (123789-HxCDF), 1234678-heptachlorodibenzofuran (1234678-HpCDF), 1234789- heptachlorodibenzofuran (1234789-HpCDF), octachlorodibenzofuran (OCDF), 2378-tetrachlorodibenzodioxin (2378-TCDD), 12378-pentachlorodibenzo-p-dioxin (12378-PeCDD), 123478-hexachlorodibenzo-p-dioxin (123478-HxCDD), 123678-hexachlorodibenzo-p-dioxin (123678-HxCDD), 123789-hexachlorodibenzo-p-dioxin (123789-HxCDD), 1234678-heptachlorodibenzo-p-dioxin (1234678-HpCDD) and 12346789-octachlorodibenzo-p-dioxin (OCDD), 2378-petrabromodibenzo-p-dioxin (2378-TBDD), 2378-tetrabromodibenzofuran (2378-TBDF), 12378-pentabromodibenzofuran (12378-PeBDF), 23478-pentabromodibenzofuran (23478-PeBDF), and octabromodibenzofuran (OBDF) | Years[6] |

| | | |
|---|---|---|
| Metals | Mercury (Hg), arsenic (As), cadmium (Cd), manganese (Mn) and lead (Pb) | Hours to Years[7] |
| Flame Retardants | 244'-tribromodiphenyl ether (PBDE-28), 22'44'-tetrabromodiphenyl ether (PBDE-47), 22'44'5-pentabromodiphenyl ether (PBDE-99), 22'44'6-pentabromodiphenyl ether (PBDE-100), 22'44'55'-hexabromodiphenl ether (PBDE-153), 22’33’44’66’-octabromodiphenyl ether (PBDE-197), 22’33’44’566’-nonabromodiphenyl ether (PBDE-207), and decabromodiphenyl ether (PBDE-209) | Weeks to Years[8] |
| Pesticides | β-Hexachlorocyclohexane (β-BHC), *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE), hexachlorobenzene (HCB) | Hours to Years[9] |

Note: references associated with superscript notation in the Approximate Half-Life column serve as examples and are not inclusive of all chemicals listed due to the impracticality of such an undertaking in this situation. 1 - (Li et al., 2012), 2 - (Gao et al., 2019), 3 - (Qu et al., 2000), 4 - (Sandborgh-Englund et al., 2006), 5 - (Zhang et al., 2013), 6 - (Aylward et al., 2005), 7 - (Pierrehumbert et al., 2002), 8 - (Krishnan et al., 2011; Thuresson et al., 2006), 9 - (Longnecker, 2005).

## 2.5. Results

### 2.5.1. Urban Firefighters

Urban firefighters were represented in 21 (62%) studies with eight chemical groups analysed (OH-PAHs, VOC metabolites, EPs, PCBs, dioxins and furans, metals, flame retardants, PFAS, and pesticides).

#### 2.5.1.1 Urban Firefighters: Polycyclic Aromatic Hydrocarbons

Exposure to PAHs was analysed though OH-PAHs metabolites in urban firefighters across eleven studies, all of which identified occupational exposure. Studies considered exposure by different means, for example, pre and post exposure, results compared against the general population, select populations without occupational exposure, other firefighter studies, or results against other industries with known exposure (for example road pavers). Table 2.3 presents information pertaining to location, sample size and basic results of chemical analysis.

**Table 2.3: Urban Firefighter Exposure to Polycyclic Aromatic Hydrocarbons**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Caux et al., 2002) | Toronto, Canada | n=43 | Urine. 1-OH-PYR median and range concentrations µmol/mol creatinine post firefighting: 0h (0.11, BDL-1.08), 0-4h (0.22, 0.049-1.01), 4-8h (0.15, 0.032-3.63) 8-12h (0.10, BDL-3.05) 12-16hr (0.14, BDL-0.52), 16-20hr (0.22, BDL-1.15). |
| (Fernando et al., 2016) Table S2.3, SI | Ontario, Canada | n=28, 24 males, 4 females | Urine. Median pre and 24h post exposure (µg/g creatinine): ΣOH-PAHs 1.73 (0.20-11.21), 3.33 (0.93-28.43) |

| | | | |
|---|---|---|---|
| (Andersen et al., 2017) Table S2.5, SI. | Denmark | n=43, 32 males, 11 females | Urine. Mean pre, at exposure, morning after (µmol/mol creatinine): 1-OH-PYR 0.35 ± 0.3, 0.79 ± 0.5, 0.44 ± 0.3 |
| (Wingfors et al., 2018) | Sandö, Sweden | n=20 | Urine. Median preexposure, 6hr, and 20hr (µmol/mol creatinine): 1-OH-NAP: 0.31, 1.59, 0.55, 2-OH-NAP: 1.42, 2.61, 1.55, 1-OH-ACE: 0.01, 0.02, 0.01, 9-OH-FLO: 0.16, 0.60, 0.14, 2-OH-FLO: 0.55, 0.87, 0.58, 9-OH-PHE: 0.03, 0.07, 0.07, 1-OH-PYR: 0.14, 1.07, 0.52. |
| (Oliveira et al., 2017a) | District of Bragança, Portugal | n=75, 63 males, 12 females | ΣOH-PAH median(min, max) firefighters per abbreviated location (µmol/mol creatinine): MRD 1.61(0.889–1.88), TDC 0.259(0.133–1.56), SDM 1.52(0.780–2.28), MDL 1.29(0.979–2.62), TMC 0.786(0.281–5.42), VNC 1.79(0.198–8.13), BRG 0.879(0.737-2.20), FEC 3.71(3.37-4.27) |
| (Keir et al., 2017) | Ottawa, Canada | n=27 males | Urine. Geometric mean and range pre and post firefighting (µmol/mol creatinine) 1-OH-PYR: 0.05 (0.01-0.17), 0.14 (0.03-0.94), ΣOH-PHE 0.20 (0.05-0.57), 0.52 (0.12-3.82), ΣOH-FLO 0.30 (0.07-0.73), 0.81 (0.20-4.40), ΣOH-NAP 4.39 (1.52-10.44), 9.82 (2.22-59.47). Other OH-PAHs below limit of detection. |
| (Andersen et al., 2018a) | Denmark | n=53, 41 males, 12 females | Urine. 1-OH-PYR Median (25%-75% quartiles) and mean (SD) (µmol/mol creatinine) pre exposure: 0.27 (0.19-0.43), 0.41 (0.40), post exposure: 0.51 (0.28-0.98), 0.68 (0.53), 2 weeks later: 0.41(0.23-0.60), 0.48 (0.23) |
| (Andersen et al., 2018b) | Denmark | n=22 males | Urine. 1-OH-PYR Mean (µmol/mol creatinine) pre, post shift samples: Fire exposure reported: 0.66 ± 0.59, 0.67 ± 0.57. No fire exposure: 0.29 ± 0.18, 0.36 ± 0.42. Overall 0.52 ± 0.51, 0.56 ± 0.53. |
| (Cherry et al., 2019) | Alberta, Canada | n=172, 162 males, 10 females | Urine. 1-OH-PYR mean (SD) each fire service (µmol/mol creatinine): A – 0.03 (0.03), B – 0.05 (0.03), C – 0.03 (0.02), Overall 0.03 (0.03). |
| (Fent et al., 2019a) | Illinois, USA | n=24, 22 males, 2 females | Urine. Median 3 hr post concentrations (simulation smoke, pallet and straw, alpha OSB, bravo OSB) in (µmol/mol creatinine): 1-OH-NAP (1.7, 2.8, 6.7, 16), 2-OH-Nap (6.6, 5.9, 9.4, 16), 1-OH-PHE (0.13, 0.22, 0.29, 0.76), 2,3-OH-PHE (0.19, 0.32, 0.54, 1.3), 1-OH-PYR (0.08, 0.13, 0.17, 0.40), 2-OH-FLO (0.28, 0.34, 0.60, 0.93), 3-OH-FLO (0.11, 0.12, 0.18, 0.28) |
| (Fent et al., 2019b) | Illinois, USA | n=36 | Urine. (µmol/mol creatinine). (Pre-exposure, 3h, 6h, 12h, 23h). ΣOH-NAP: Attack / search (3.8, 25, 13, 6.3, 5.0), Outside Vent (4.2, 11, 6.9, 5.0, 4.2), Backup / Overhaul (2.9, 7.3, 4.9, 3.9, 3.3). ΣOH-PHE: Attack / search (0.15, 1.8, 1.3, 0.58, 0.39), Outside Vent (0.16, 0.76, 0.48, 0.30, 0.22), Backup / Overhaul (0.21, 0.64, 0.43, 0.28, 0.24). 1-OH-PYR: Attack / search (0.06, 0.29, 0.42, 0.38, 0.25), Outside Vent (0.07, 0.23, 0.17, 0.13, 0.12), Backup / Overhaul (0.06, 0.24, 0.15, 0.12, 0.11). ΣOH-FLO: Attack / search (0.21, 0.68, 0.38, 0.27, 0.22), Outside Vent (0.22, 0.46, 0.33, 0.25, 0.21), Backup / Overhaul (0.20, 0.42, 0.27, 0.24, 0.20). |

Oliveira et al (2017a) focused on the exposures firefighters may face due to contaminated fire station air. The authors determined a significant correlation between the concentrations of ΣPAHs in fire station air and concentrations of ΣOH-PAHs in firefighters' urine at four of the fire stations ($r \geq 0.733$, $p \leq 0.025$), suggesting fire station air could be a major source of PAH exposure. Caux et al. (2002) demonstrated clear evidence that even when wearing PPC, firefighting was associated with exposure to PAHs above background levels. Firefighters demonstrated higher mean and maximum urinary excretion values of 1-OH-PYR post-fire ($p<0.0001$).

Fent et al. (2019a) assessed emissions from burning different materials in simulation fire experiments and their effect on urban firefighter and fire trainer contamination. Only urban firefighters will be discussed in this section. The authors found the burning of oriental strand board (OSB) to produce the highest median increases in urinary hydroxy PAHs compared to simulation smoke or burning pallet and straw. OSB is an engineered wood formed through adhesive addition and lay compression of wood strands in specific orientations. Results found urine levels of OH-PAHs post exposure to OSB and pallet and straw to be greater than respective 95th percentiles of these OH-PAHs in data obtained from the general population. Anderson et al (2018a) determined simulation burns using only wood pallets to be associated with higher 1-OH-PYR concentrations ($p<0.001$) than those supplemented with electrical cords and mattresses. The authors concluded that live-fire training may expose firefighters to hazardous chemicals, with the dose of exposure quite dependant on the number of training fires and the selection of fuel package for the simulation fire.

Studies found that firefighters not wearing full respiratory protection (Cherry et al., 2019), full bunker gear (Keir et al., 2017) or who wore reduced layers of personal protective clothing demonstrated a greater increase in the OH-PAH concentrations in urine (Wingfors et al., 2018). Role during firefighter operations was identified as affecting exposure profiles, with the highest exposures per study being reported by firefighters involved in vertical ventilation (Keir et al., 2017) interior attack, and attack and search operations (Fent et al., 2019b). Mitigation suggestions for elevated exposure included: the full utilisation of bunker gear and self-contained breathing apparatus (SCBA); the use of additional thick cotton layers under bunker gear; and (if operationally suitable) assigning firefighters to transitional attack as a first step in fire attack (Fent et al., 2019b; Keir et al., 2017; Wingfors et al., 2018).

The study by Andersen et al. (2018b) considered firefighter exposure over 24-hour shift cycles. Urine samples were collected before and after shift cycles, with data collected surrounding fire exposure during the shift. Twenty-two male firefighters were involved, with fourteen experiencing fire smoke exposure while on shift, and the remaining eight experiencing no fire smoke exposure. Mean increases in the 1-OH-PYR concentration were presented (in µmol/mol creatinine) for fire exposed $0.66 \pm 0.59$ to $0.67 \pm 0.57$, for non-exposed $0.29 \pm 0.18$ to $0.36 \pm 0.42$ and overall $0.52 \pm 0.51$ to $0.56 \pm 0.53$; however, the increases were not linked to direct fire exposure. Grilled foods and smoking were confounders considered in this study. The study identified that Danish firefighters exhibited higher levels of OH-PAHs when compared with non-smoking Danish mail carriers, suggesting occupational exposure. It is possible, therefore, that mean increase in 1-OH-PYR was due to residing in the fire station for 24 hours, which has been determined to be a route of exposure to PAHs for firefighters not exposed to fires (Oliveira et al., 2017a).

### 2.5.1.2 Urban Firefighters: Benzene

A single study examined benzene exposure by measuring one of its metabolites *t,t*-muconic acid in urine (Caux et al., 2002). Caux et al (2002) found Canadian firefighters to experience increased levels of *t,t*-muconic acid in their urine after fire suppression activities. None of the controls measured in this study had *t,t*-muconic acid concentrations above the limit of detection; however, seventeen of forty-three firefighters had measurable excretions post fire suppression activities with six exceeding 1.1mmol/mol creatinine. Firefighter benzene exposure in this study was described as low when compared to other industries with known exposure.

### 2.5.1.3 Urban Firefighters: Environmental Phenols

Three studies assessed environmental phenols in firefighters, one through blood (Shaw et al., 2013), and two through urine (Fernando et al., 2016; Waldman et al., 2016). Fernando et al. 2015 and Waldman et al. 2016 both demonstrated occupational exposure to phenols monitored in their studies. Table 2.4 provides results of the three studies.

**Table 2.4: Urban Firefighters and Occupational Exposure to Environmental Phenols**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Shaw et al., 2013) | San Francisco, CA, USA | n=12, 11 males, 1 female | Serum. BPA (ng/ml wet weight): mean 0.4, median 0.2, range (0.03-1.2). |
| (Fernando et al., 2016) | Ontario, Canada | n=28, 24 males, 4 females | Urine. Median pre and 24h post exposure (µg/g creatinine): Methoxyphenols (0.47 (0.00-15.93), 2.16 (0.14-44.23) |
| (Waldman et al., 2016) | FOX Study, Southern California | n=101, 99 males, 2 females | Urine. Those greater than 60%>LOD (µg/g creatinine) BPA 1.40, BP-3 69.8, triclosan 18.0, methyl paraben 41.7, *n*-propyl paraben 4.08 |

Shaw et al. (2013) presented that the concentrations of BPA in firefighter serum were relatively low compared to populations studied globally (general populations and those of women specifically), with only two of twelve comparative population reporting lower concentrations.

As was found with exposure to PAHs, Fernando et al (2016) determined firefighter role to affect levels of methoxyphenol exposure. The authors found firefighters conducting search and rescue activities had increased excretion of metabolites, particularly methylsyringol (p=0.00023) and propylsyringol (p=0.013). Overall results showed significant elevation (p<0.05) at 24 hours post exposure for firefighters involved in the study, regardless of role in fire suppression activities.

Waldman et al (2016) found levels of BPA, benzophenone-3 (BP-3), triclosan and methyl paraben to be present in high percentages of all studied firefighters (94%, 100%, 99%, 98% respectively), similar to the comparable National Health and Nutrition Examination Survey (NHANES) group (2009–2010, males, 25 years and older). NHANES is a survey of the general population in the United States. Geometric mean point estimates for *n*-propyl paraben, methyl paraben and triclosan were elevated compared to NHANES; however, BP-3 was found to be elevated (both unadjusted and creatinine adjusted) by approximately five times. The authors suggested that exposure could be due to plastic components of personal protective equipment used by firefighters (containing BP-3 as an ultraviolet stabiliser), or personal protective clothing treated with ultraviolet-resistant chemicals. Sunscreen was considered an unlikely source of exposure due to sample collection occurring during the colder months.

#### 2.5.1.4 Urban Firefighters: Per- and Poly- Fluoroalkyl Chemicals (PFAS)

PFAS were analysed in three separate studies. One study utilised the C8 Health Project, a court-directed study resulting from the discovery of PFOA contaminated water in the mid-Ohio Valley, USA. (Jin et al., 2011) Data collected on 8826 males included 36 currently employed firefighters. Two other studies utilised a convenience sample of firefighters to assess exposure to PFAS (Dobraca et al., 2015; Shaw et al., 2013). Table 2.5 presents PFAS results in firefighters.

**Table 2.5: Urban Firefighters and Occupational Exposure to Per- and Poly- Fluoroalkyl Chemicals**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Jin et al., 2011) | mid-Ohio Valley | n=36 males | Serum. Median and range values detected (ng/mL): PFHxS (4.6, 0.25-14.60), PFOA (31.50, 0.25-7534.60), PFOS (27.85, 0.25-67.50) PFNA (1.60, 0.25-4.40), |
| (Shaw et al., 2013) | San Francisco, CA, USA | n=12, 11 males, 1 female | Serum. Median and range values detected (ng/mL wet weight): PFHxS (1, 0.3-2), PFOA (6, 2-12), PFOS (9, 3-59), PFNA (2, 1-4), PFDS (0, nd-0.1), PFHpA (0.3, 0.1-1), PFDA (1, 0.2-1), PFUnDA (0.2, 0.1-1) |
| (Dobraca et al., 2015) | Fox Study, Southern California | n=101, 99 males, 2 females | Serum. 50th Percentile and maximum values detected (ng/mL): PFHxS (2.27, 13.20), PFOA (3.86, 18.10), PFOS (12.70, 46.60), PFNA (1.13, 4.23), PFHpA (0.12, 0.98), PFDeA (0.72, 4.60), PFOSA (0.029, 0.396), N-MeFOSAA (0.14, 1.86), N-EtFOSAA (0.016, 0.464), PFUA (0.26, 0.73), PFDoA (<LOD, <LOD), PFBuS (<LOD, 0.04) |

Occupational exposure to PFHxS was demonstrated in the mid-Ohio Valley firefighter cohort, statistically higher both before (p=0.01) and after adjustments (p=0.05) for firefighters over other employment categories or no employment. PFOS and PFNA concentrations were also higher before and after adjustment for age, district and income, but were not significant. PFOA result was found to not to be significant, but that could be due to members of the comparison group having exposure due to PFOA contaminated drinking-water systems. Jin et al. (2011) suggested that the likely source of firefighter exposure to PFAS is firefighting foams coupled with fires in households with stain-resistant applications to carpets.

Shaw et al. (2013) determined firefighter PFOS and PFHxS concentrations to be approximately two-fold lower, and PFOA and PFNA approximately two-fold higher in firefighters compared to the general US population. It is worth noting that firefighter samples were collected in 2009, but were compared with a US general population study from 2003/2004. Since levels have decreased over time, this comparison may not be appropriate and may incorrectly represent firefighter data.

Dobraca et al. (2015) found PFOS concentrations to be the highest (µg/L) of the PFAS measured in the Firefighter Occupational Exposures (FOX) Project cohort, presenting similar results to National Health and Nutrition Examination Survey (NHANES, 2009-2010, males aged 20 years or older). PFDeA was found to be approximately three times higher in firefighters compared to NHANES. PFOSA was higher in firefighters 50 years or older. Monthly or more frequent response to commercial fires was associated with elevated PFHpA concentrations. PFNA and PFOA were significantly higher in firefighters who had not professionally decontaminated their structural firefighting jacket and pants within the last year. Firefighters who reported using fire suppression foams presented significantly higher PFHpA. PFHxS concentrations were found to not be significantly different to NHANES results.

All three studies demonstrated occupational exposure to PFAS; however, the studies were inconsistent in their findings of which PFAS chemicals were elevated in firefighters. This could be due to the variation in control populations, and time lag between the sampled control population and the sampling of firefighters.

#### 2.5.1.5. Urban Firefighters: Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

Two studies assessed PCDD/Fs in firefighters, with fire investigators also included in one. Due to this being the only study on fire investigators, it is included in this section. The results of the chemical analysis are presented in Table 2.6.

**Table 2.6: Urban Firefighters, Fire Investigators and Occupational Exposure to Polychlorinated and Polybrominated Dibenzo-p-dioxins and Dibenzofurans**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Hsu et al., 2011) | Tainan Country, Taiwan | n=20, 16 firefighters, 4 fire investigators | Serum. Median and range values detected in firefighters and investigators (pg/g lipid weight): 2378-TCDD (1.4, 0.84-2.6), 12378-PeCDD (5.2, 2.3-11), 123478-HxCDD (1.6, 0.41-3.4), 123678-HxCDD (7.3, 2.3-21), 123789-HxCDD (1.8, 0.29-4.2), 1234678-HpCDD (12, 5.5-36), OCDD (210 (100-710), 2378-TCDF (0.93, 0.47-1.5), 12378-PeCDF (0.83, 0.29-1.5), 23478-PeCDF (8.0, 4.4-13), 123478-HxCDF (2.7, 1.3-4.8), 123678-HxCDF (3.1, 1.5-5.7), 234678-HxCDF (1.1, 0.35-2.3), 123789-HxCDF (0.35, 0.067-1.4), 1234678-HpCDF (5.1, 2.9-18), 1234789-HpCDF (0.59, 0.13-1.5), OCDF (1.3, 0.31-4.9). $\Sigma_{17}$PCDD/F (270, 150-810). TEQ PCDD/F (12, 6.3-18). Firefighter TEQ 12pg/g lipid, Investigator TEQ 15pg/g lipid. |
| (Shaw et al., 2013) | San Francisco, CA, USA | n=12, 11 males, 1 female | Serum. Median and range values detected in firefighters (pg/g lipid weight): 123678-HxCDD (28, 8-101), 124678-HpCDD (77, 26-184), OCDD (194, 42-674), 1234678-HpCDF (0, nd-342), 2378-TBDD (0, nd-356), 2378-TBDF (0, nd-504), 12378-PeBDF (0, nd-922), 23478-PeBDF (0, nd-996), OBDF (2087, 1350-5640). ΣPCDD/Fs (310, 183-856), TEQ PCDD/Fs (5, 1-11), ΣPBDD/Fs (2490, 1350-7200), TEQ PBDD/Fs (1, 0.2-734) |

Both studies demonstrated occupational exposure to their total study cohort, with Hsu et al (2011) identifying reduced protective clothing and respiratory protection to be the cause of any heightened exposure. Congener profile for firefighters and fire investigators were not the same as the controls, suggesting different exposures sources. Toxic equivalency (TEQ), a single figure resulting from the product of concentration of toxic equivalency factors of each individual congener analysed, was utilised in order to describe the exposure of firefighters and the general population to dioxins and furans. Median firefighters TEQs suggest firefighters were not occupationally exposed compared to general Taiwanese population (9.4pg WHO2005-TEQ/g lipid, Mann-Whitney U test, p:0.12); however, given the congener profiles from firefighters matched wipe samples from gear exposed to fire smoke, firefighting may be an exposure route. Firefighters who did not report wearing thermal PPC while undertaking fire suppression activities had higher PCDD/F serum levels than those who did. Median results for fire investigators (n=4) were found to be significantly different to controls (Mann-Whitney U test, $p<0.01$); however, this part of the study was limited by sample size. Not wearing thermal protective equipment (including helmet with face guard, thermal protective overcoat, thermal protective over pants and SCBA) resulted in higher serum PCDD/F levels (Mann-Whitney U test, $p=0.01$). Firefighters who wore full personal protective clothing and SCBA did not demonstrate occupational exposure by means of higher PCDD/F TEQs; however, the pattern of congeners in firefighters was closely aligned with congener profiles found on helmet wipe samples suggesting occupational exposure. The data from this study suggests that fire scene investigators may be occupationally exposed to large amounts of PCDD/Fs due to poor personal protection. This study highlights the importance of vigilant use of personal protective clothing and equipment to reduce exposure.

Shaw et al (2013) found ΣPCDD/F concentration slightly lower than reported in the US population (sampled in 2003/2004). Relatively high 1234678-HpCDD exceeded the median concentration measured in the US population (28.4 pg/g lw). OCDD was found to be the dominant congener in firefighter serum (55%). 1234678-HpCDF measured at an order of magnitude higher than US population (pooled sample 3.9 pg/g lw). ΣPBDD/F concentrations were found to be relatively high with the congener OBDF accounting for 92%. The authors suggest that the distinctive patterns of PBDD/F congeners suggest occupational exposure. Although limited by a small sample size, the authors suggest that calculated TEQs for PBDD/Fs indicate they may contribute substantially to firefighter toxicity, and that halogenated contaminants should be monitored in firefighters.

A study that was not included in this systematic review due to its focus on a single fire (and therefore not representative of firefighters in general) was that of the 1992 Shelekov fire (Chernyak et al., 2012). It deserves a mention for the purpose of recognising that firefighters can face exposure to PCDD/Fs and PCBs, particularly given few biomonitoring studies have considered these classes of chemicals. Firefighters involved in the fire demonstrated significantly higher levels of PCDFs when compared with non-firefighters ($p<0.05$). The study determined that firefighting is a source of exposure to dioxins.

#### 2.5.1.6. Urban Firefighters: Metals

Three studies have assessed metals in firefighters, in three countries across a 35-year time period. Table 2.7 presents results of metals in urban firefighters.

**Table 2.7: Urban Firefighters and Occupational Exposure to Metals**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Phoon & Ong, 1982) | Singapore | n=30 males | Whole blood. Mean and standard deviation: Pb 21.10±5.2µg/dL |
| (Dobraca et al., 2015) | FOX Study, Southern California | n=101, 99 males, 2 females | Whole blood. 50th Percentile and maximum values: Pb (0.95, 5.92) µg/dL, Cd (0.20, 0.77) µg/L, Hg (2.90, 13.42) µg/L, Mn (7.70, 15.81) µg/L. |
| | | | Urine*. 50th Percentile: As 10.4µg/L, Cd 0.138µg/g creatinine, Hg 0.447µg/L, Mn <LOD |
| (Salama & Bashawri, 2017) | Dammam and Khobar, Saudi Arabia | n=100, 100 males, from Dammam (50), Khobar (50) | Serum. Mean and standard deviation (µg/dL): Pb Dammam 3.03±1.09, Khobar 3.9±0.8, Cd Dammam 0.24±0.04, Khobar 0.17±0.05, Hg Dammam 0.41±0.67, Khobar 0.24±0.17, Sb Dammam 0.006±0.002, Khobar 0.0015±0.003 |

Note: lead (Pb), cadmium (Cd), mercury (Hg), manganese (Mn), antimony (Sb) urine samples found on Biomonitoring California Firefighter Occupational Exposures (FOX) Project website. Data was not specified in the publication but is included in this review as urinary metals were referred to by Dobraca et al. (2015).
*

Phoon and Ong (1982) presented that at the time of study, lead exposure was widespread in Singapore due to the commonplace use and manufacturing of lead-containing materials. Out of a list of occupations selected with presumed exposure to lead, firefighters were ranked 11th out of 14 organisations, ahead of wire splicers, automobile manufacturers and medical/auxiliaries.

The FOX study found blood Pb and Cd concentrations below the Centers for Disease Control and Prevention (CDC) early reporting thresholds, levels established for NHANES requiring notification if an individual’s results exceeded these values. Six male firefighters had total blood mercury (rounded to whole number) that equalled or exceeded early reporting thresholds, with associated urine metals analysis finding low inorganic mercury. This indicated that the modestly elevated blood concentrations (2.79µg/L vs 1.09µg/L for NHANES) were predominantly organic mercury, likely related to fish consumption. Blood Mn was found to be within usual ranges as compared with NHANES (2009-2010, males aged 20 years or older). Firefighters who washed their hands less frequently reported significantly higher blood Cd, and a significant elevation in Mn was found in firefighters who had responded to commercial fire incidents at least once in the last year. Significantly elevated Mn was also noted in firefighters assigned to fire stations built after 2000. Firefighters who had responded to wildfires at least once in the last year reported significantly higher mercury compared to those who had not.

No significant difference was found between serum metal levels of the Dammam or Khobar firefighters, or between firefighters and the control group of men from the same cities (Salama & Bashawri, 2017). This suggests that occupational exposure did not result in exposure that is in excess of what is observed in the general population.

### 2.5.1.7. Urban Firefighters: Flame Retardants

Four studies assessed urban firefighter exposure to polybrominated flame retardants as well as chlorinated and non-chlorinated organophosphate flame retardants. These results are presented in Table 2.8.

**Table 2.8: Urban Firefighters and Occupational Exposure to Flame Retardants**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Shaw et al., 2013) | San Francisco, CA, USA | n=12, 11 males, 1 female | Serum. Median and range values (ng/g lipid weight): 244'-tribromodiphenyl ether PBDE-28 (1, 0.1-10), 22'44'-tetrabromodiphenyl ether PBDE-47 (25, 5-253), 22'44'5-pentabromodiphenyl ether PBDE-99 (6, 1-41), 22'44'6-pentabromodiphenyl ether PBDE-100 (5, 2-56), 22'44'55'-hexabromodiphenl ether PBDE-153 (20, 5-98), decabromodiphenyl ether PBDE-209 (24, 4-88). ΣPBDEs (99, 48-442) |
| (Park et al., 2015) | FOX Study, Southern California | n=101, 99 males, 2 females | Serum. 50th Percentile and Geomean (ng/g lipid): PBDE-28 (1.63, 1.70), PBDE-47 (29.9, 32.3), PBDE-99 (5.79, 6.19), PBDE-100 (5.14, 5.68), PBDE-153 (12.9, 15.4), PBDE-197 (1.25, 1.35), PBDE-207 (1.31, 1.44), ΣPBDE 28,47,99,100,153 (59.1, 66.2) |
| (Jayatilaka et al., 2017) | NIOSH firefighters | n=146 | Urine. Median and range (ng/mL). bis(2-chloroethyl) phosphate (BCEtP) (0.86, <LOD-10), bis(1-chloro-2-propyl) phosphate (BCPP) (0.24, <LOD-2.9), bis-(1,3-dichloro-2-propyl) phosphate (BDCPP) (3.4, 0.30-44), di-n-butyl phosphate (DBuP) (0.18, <LOD-2.4), diphenyl phosphate (DPhP) (2.9, 0.24-28), di-p-cresylphosphate (DpCP) (<LOD, <LOD-0.31) 2345-tetrabromobenzoic acid (TBBA) (<LOD, <LOD-0.21) |
| (Jayatilaka et al., 2019) | NIOSH firefighters | n=145 | Urine. Median and range (ng/mL). bis(2-chloroethyl) phosphate (BCEtP) (0.84, <LOD-9.8), bis(1-chloro-2-propyl) phosphate (BCPP) (0.24, <LOD-3.0), bis(1,3-dichloro-2-propyl) phosphate (BDCPP) (3.3, <LOD-42), di-n-butyl phosphate (DBuP) (0.12, <LOD-2.9), diphenyl phosphate (DPhP) (4.0, 0.14-32), 2345-tetrabromobenzoic acid (TBBA) (0.10, <LOD-0.13), 2-((isopropyl) phenyl) phenyl phosphate (iPPPP) (0.11, <LOD-0.49), 4-((tert-butyl) phenyl) phenyl phosphate (tBPPP) (0.17, <LOD-1.1), dimethylphosphate (DMP) (9.9, <LOD-190), dimethylthiophosphate (DMTP) (15, <LOD-300), dimethyldithiophosphate (DMDTP) (1.2, <LOD-11), diethylphosphate (DEP) (4.2, <LOD-60), diethylthiophosphate (DETP) (0.74, <LOD-5.0), diethyldithiophosphate (DEDTP) (0.22, <LOD-0.35). |

Shaw et al (2013) found firefighter concentrations of tri- through deca-BDE ranged from 48ng/g lw to 442ng/g lw (median 99ng/g lw). PBDE-47 and -209 and -153 were found to be the dominant congeners (in order) with regards to total PBDE concentration; however, with the exclusion of an outlier value for PBDE-47, PBDE-209 became the dominant congener. ΣPBDE concentrations were found to be lower in firefighters than in carpet layers and foam recyclers from California and Maryland (median 178ng/g lw and 160ng/g lw respectively); however, threefold greater than the general US population (mean range 38.6-61.8 ng/g lw). Elevated concentrations of ΣPBDEs and a unique congener profile suggest occupational exposure to all three PBDE formulations. Relatively high presence of PBDE-209 (deca-BDE), a congener with an approximately 15-day half-life in serum suggests continuous exposure (Thuresson et al., 2006).

PBDE levels in the FOX study (collected 2010-2011) exceeded NHANES values (2003-2004, males aged 20 years or older) (Park et al., 2015). Further findings included that geometric means were higher than NHANES for PBDE-47 (60%), PBDE-153 (136%), with other major PBDEs elevated to a lesser extent. This study went further to ascertain what factors may be associated with elevated PBDEs, and considered hygiene, fire suppression tactics, and use of protective equipment.

Results adjusted by means of a multi-stage modelling process showed that firefighters who cleaned their structural firefighting personal protective clothing outside had a statistically significant 30% reduction in $\Sigma_5$PBDEs (-28, -47, -99, -100, -153) compared with those who did not clean it. Storing structural firefighting personal protective clothing in an open room (verses a personal locker) resulted in statistically significant reductions of 60-80% on PBDE levels. Firefighters who reported cleaning their gear at the site of the fire incident presented elevated levels of PBDE-99. Internal fire attack, when firefighters enter the structure in order to undertake fire suppression activities, resulted in a statistically significant 30-40% increase in PBDE-47 and PBDE-100.

Unadjusted results (results not adjusted by a multi-stage modelling process) show that firefighters who reported always using SCBA during ventilation had a 17% lower $\Sigma_5$PBDEs (-28, -47, -99, -100, -153), and those who always wore SCBA during exterior fire suppression activities resulted in a 15% reduction in the same. Firefighters who removed their SCBA during salvage and overhaul presented a 7% increased level of $\Sigma_5$PBDEs. Unadjusted results also demonstrated PBDE levels to have a slight inverse association with several fire types, and that working at an older fire station resulted in increased levels of all PBDE congeners (Park et al., 2015).

The median $\Sigma_5$PBDEs (59.1ng/g lipid) calculated for firefighters were found to be among the highest found in any US population during the study period (2010-2012). Authors suggested that PBDEs were being transported back to fire stations on equipment and clothing post fire suppression activities. Park et al (2015) suggested that decontamination of personal protective clothing at the response site may seem prudent; however, they suggested this was not adequate to remove all the PBDE contamination due to fire incident exposure.

Jayatilaka et al (2017) found median concentrations of BDCPP and DPhP in the firefighters' samples to be approximately five and three times higher, respectively, than the selected comparison controls, suggesting occupational exposures may be higher than background exposures. Jayatilaka et al (2019) compared the sample of firefighters with a different comparison control to the 2017 study. In the 2019 study BCPP to be two times higher in firefighters than comparison controls (0.24 vs 0.11ng/mL) and DMTP to be 37 times the concentrations of non-occupationally exposed comparison control (15 vs 0.39ng/mL).

### 2.5.1.8 Urban Firefighters: Other POPs (Polychlorinated Biphenyls and Pesticides)

Two studies in the US assessed urban firefighters for PCB and pesticide exposure. The results of the studies are presented in Table 2.9.

**Table 2.9: Urban Firefighters and Occupational Exposure to Other POPs (Polychlorinated Biphenyls and Pesticides)**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Shaw et al., 2013) | San Francisco, CA, USA | n=12, 11 males, 1 female | Serum. Median and range values (ng/g lipid weight): *p,p'*-DDE (249, 128-662), HCB (21, 8-46), PCB-16 (0, nd-2), PCB-41 (0, nd-5), PCB-44 (0, nd-6), PCB-49 (0, nd-2), PCB-18 (0, nd-8), PCB-60 (0, nd-3), PCB-66 (0, nd-2), PCB-70 (0, nd-8), PCB-74 (0, nd-7), PCB-87 (0, nd-7), PCB-93 (0, nd-13), PCB-97 (0, nd-4), PCB-99 (0, nd-7), PCB-101 (0, nd-13), PCB-105 (0, nd-5), PCB-110 (0, nd-17), PCB-118 (0, nd-19), PCB-136 (0, nd-3), PCB-138 (14, 5-34), PCB-146 (0, nd-10), PCB-149 (0, nd-16), PCB-151 (0, nd-4), PCB-153 (23, 11-52), PCB-156 (4, 1-12), PCB-170 (6, 1-17), PCB-172 (0, nd-3) PCB-177 (1, 0.2-3), PCB-178 (0, nd-3), PCB-180 (24, 10-59) , PCB-183 (1, 0.2-5), PCB-187 (5, 1-15), PCB-194 (4, 0.01-14), PCB-195 (0, nd-2), PCB-196 (3, 1-9), PCB-199 (3, 1-10), PCB-202 (1, 0.2-4), PCB-206 (1, 0.2-9), PCB-209 (0, nd-2), ΣPCBs (126, 36-317) |
| (Park et al., 2015) | Fox Study, Southern California | n=101, 99 males, 2 females | Serum. 50th Percentile and geomean (ng/g of lipid): β-BHC (2.23, 2.19), 4,4'-DDT (1.43, 1.34), 4,4'-DDE (182, 177), HCB (11.7, 11.8), trans-nonachlor (7.32, 7.32), oxychlordane (4.31, 4.08), PCB-66 (1.19, 1.17), PCB-74 (1.73, 1.77), PCB-99 (1.74, 1.76) , PCB-118 (2.75, 2.66), PCB-138 (5.54, 5.53), PCB-153 (12.9, 12.2), PCB-156 (1.88, 1.84), PCB-170 (3.85, 3.64), PCB-180 (14.7, 13.4), PCB-183 (1.04, 1.03), PCB-187 (2.94, 2.99), PCB-194 (3.38, 3.37), PCB-203 (3.83, 3.37) |

Shaw et al. (2013) found the ΣPCB concentration for firefighters to be lower than median US control population concentrations (154ng/g lw), and concentrations of both *p,p'*-DDE and HCB to be higher in firefighters.

Park et al (2015) did not find firefighting to be a significant source of exposure to PCBs and OCPs. It is worth noting; however, that this conclusion was based on a comparison to results from a general population sample set that was analysed 6-7 years earlier, and PCBs and OCPs are known to be decreasing in concentration in human systems. All major PCBs and organochlorine pesticides (OCPs) were detected in participants at levels below NHANES (2003-2004, males aged 20 years or older). Through multivariate analysis the authors determined that levels of PCBs and OCPs were lower among firefighters whose turnout gear professionally decontaminated in past year, and that personal hygiene also played a role, with PCB-138 concentrations 30% lower in firefighters who washed their hands more frequently (p=0.08). These results suggest occupational exposure, even if it is not significant when compared with NHANES (2003-2004).

### 2.5.2. Wildland Firefighters

Biomonitoring studies pertaining to wildland firefighters were not as prevalent, with only seven studies meeting the inclusion criteria. One study assessing urinary metals in wildland firefighters was excluded from the study after full text screen as part of the wildfire burned on Los Alamos National Laboratory administered land, a United States Department of Energy facility working with radioactive materials (Wolfe et al 2004). That study concluded that smoke exposure resulted in spot urine metal concentrations above national reference values, but results may not be representative of wildfires in general. The six studies that met the criteria were deemed to be representative with regards to wildland firefighters.

#### 2.5.2.1 Wildland Firefighters: Polycyclic Aromatic Hydrocarbons, Methoxyphenols, and Metals

Table 2.10 outlines the results of the seven studies pertaining to wildland firefighters.

**Table 2.10: Wildland Firefighters and Occupational Exposure to Polycyclic Aromatic Hydrocarbons, Methoxyphenols, and Metals**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Robinson et al., 2008) | Arizona, USA | n=21, 18 males, 3 females | Urine. 1-OH-PYR mean and range values (µg/L): Baseline (0.14, <0.01-0.56), End-of-shift (0.09, <0.01-0.50), Next-Am (0.05, <0.01-0.53). |
| (Neitzel et al., 2009) | South Eastern USA | n=13, 11 males, 1 female | Methoxyphenols, mean preshift (min, max)/post shift (min, max) (µg methoxyphenol/mg creatinine): Guaiacol 0.343 (0.138, 1.295) / 0.862 (0.071, 1.996), Methylguaiacol 0.051 (0.009, 0.291) / 0.427 (0.016, 1.757), 23DMP 0.034 (0.001, 0.347) / 0.031 (0.001, 0.193), Ethylguaiacol 0.034 (0.002, 0.434) / 0.096 (0.006, 0.359), Syringol 0.030 (0.007, 0.112) / 0.176 (0.021, 0.937), Syringola 0.029 (0.007, 0.112) / 0.140 (0.021, 0.627), Eugenol 0.282 (0.018, 2.123) / 0.313 (0.013, 1.258), Propylguaiacol 0.003 (0.000, 0.009) / 0.012 (0.001, 0.037), Vanillin 0.041 (0.016, 0.098) / 0.061 (0.027, 0.106), cis-Isoeugenol 0.025 (0.012, 0.048) / 0.117 (0.023, 0.382), Methylsyringol 0.015 (0.002, 0.055) / 0.090 (0.011, 0.660), Methylsyringola 0.014 (0.003, 0.055) / 0.060 (0.011, 0.353), trans-Isoeugenol 0.027 (0.004, 0.066) / 0.066 (0.017, 0.179), Acetovanillone 0.112 (0.028, 0.350) / 0.249 (0.073, 1.296), Ethylsyringol 0.012 (0.000, 0.047) / 0.044 (0.001, 0.323), Ethylsyringola 0.013 (0.000, 0.047) / 0.031 (0.001, 0.136), Guaiacylacetone 0.012 (0.002, 0.036) / 0.052 (0.015, 0.118), Allylsyringol 0.027 (0.003, 0.249) / 0.068 (0.003, 0.390), Propylsyringol 0.011 (0.004, 0.019) / 0.015 (0.001, 0.063), Syringaldehyde 0.187 (0.003, 1.077) / 0.122 (0.001, 1.243), Acetosyringone 0.017 (0.002, 0.074) / 0.032 (0.004, 0.079), |

| | | | |
|---|---|---|---|
| | | | Coniferylaldehyde 0.008 (0.004, 0.013) / 0.014 (0.014, 0.014), Propionylsyringone 0.009 (0.002, 0.025) / 0.014 (0.004, 0.029), Butyrylsyringone 0.005 (0.005, 0.005) / 0.006 (0.002, 0.014), Sinapylaldehyde 0.014 (0.012, 0.017) / 0.005 (0.004, 0.007) |
| (Oliveira et al., 2016) | Bragança district, Portugal | n=153, 120 males, 33 females | Urine. ΣOH-PAH median(min, max) non-exposed/exposed firefighters per abbreviated location (µmol/mol creatinine): MGD 1.54(0.438–2.24)/2.40(0.818–4.33), TDC 0.249(0.252–1.55)/8.75(5.99–9.06), MRD 0.808(0.240–2.39)/7.67(6.82–8.90), VNH 1.57(1.11–2.57)/7.86(1.93–121), BRG 0.446(0.208–2.20)/0.973(0.402–4.39), MDL 1.14(0.804–2.08)/1.97(1.31–2.62) |
| (Adetona et al., 2017) | South Carolina, USA | n=19, 17 males, 2 females | Urine. Geometric mean (95% Confidence Intervals) (µmol/mol creatinine) Pre and Post shift: 1-OH-NAP Pre 1.6 (1.0, 2.6) Post 6.9 (4.3, 11), 2-OH-NAP Pre 3.1 (2.4, 4.2) Post 9.5 (7.2, 12), 2-OH-FLO Pre 0.31 (0.23, 0.41) Post 0.93 (0.69, 1.2), 3-OH-FLO Pre 0.12 (0.09, 0.16) Post 0.26 (0.20, 0.35), 1-OH-PHE Pre 0.14 (0.11, 0.19) Post 0.32 (0.24, 0.44), 2-OH-PHE Pre 0.07 (0.05, 0.09) Post 0.20 (0.15, 0.27), 3-OH-PHE Pre 0.12 (0.09, 0.15) Post 0.41 (0.31, 0.54), 4-OH-PHE Pre 0.02 (0.01, 0.03) Post 0.07 (0.05, 0.09), 1-OH-PYR Pre 0.16 (0.11, 0.24) 0.30 (0.20, 0.44) |
| (Oliveira et al., 2017b) | Bragança district, Portugal | n=108 | Urine. ΣOH-PAH median(min, max) non-smoking non-exposed/smoking non-exposed/smoking exposed firefighters per abbreviated location (µmol/mol creatinine): VNH 0.16(0.12–1.12)/0.82(0.05–1.67)/5.34(2.20–8.59), MDL 0.82(0.56–1.24)/2.06(0.59–3.59)/5.71(5.44–5.94), BRG 0.42(0.05–0.47)/0.74(0.49–1.02)/1.91(0.09–52.4) |
| (Adetona et al., 2019) | South Carolina, USA | n=12, 9 males, 3 females | Urine. Geometric mean (95% Confidence Intervals) 1-OH-PYR (µmol/mol creatinine): Burn day: Pre-work shift 0.08 (0.06, 0.10), Post-work shift 0.12 (0.09, 0.16), Morning-after work shift 0.10 (0.08, 0.13). Non-burn day: Pre-work shift 0.09 (0.07, 0.12), Post-work shift 0.08 (0.06, 0.10), Morning-after work shift 0.07 (0.05, 0.11). |
| (Smith et al., 2013) | Western United States | n=66, 62 males, 4 females | Whole blood. Hg levels pre and post exposure ranges for each year (µg/L): 2007 (<LOD-5, <LOD-8), 2008 (<LOD-9, <LOD-8), 2009 (<LOD-<LOD, <LOD-16) |

Neither Robinson et al (2008) or Smith et al (2013) determined fire smoke to be a significant source of occupational exposure for wildland firefighters. Robinson et al (2008) measured a non-significant elevation in baseline urinary 1-OH-PRY as compared with next-AM post-exposure. The elevation was deemed unlikely to be toxicologically relevant, as dietary factors not fully accounted for may be influencing the results. Smith et al (2013) found no statistically significant elevations in Hg during three consecutive summers, though the authors discussed the study limitations with regards to sample size and the ability to obtain blood samples before and after exposure.

In the wildland pilot study by Neitzel et al (2009), twenty of the twenty-two analysed methoxyphenols (MPs) in wildland firefighter urine demonstrated cross-shift increases (pre to post shift). Of these, fourteen demonstrated significant increases. The study also found correlations between select MPs and carbon monoxide, correlations with levoglucosan, but not with particulate matter.

Both Adetona et al studies presented in Table 2.10 demonstrated occupational exposure to PAHs. Adetona et al (2017) observed post shift geometric mean concentrations for urinary OH-PAHs to be significantly elevated compared to pre-shift ($p<0.0001$), ranging from 1.83-4.23-fold. The authors suggest that 1-OH-PYR may not be the most representative marker for exposure, as it presented the least increase (83%) compared to 1-OH-NAP which presented the greatest increase (323%) pre to post shift. The study showed wildland firefighters during burn season to have median post-shift concentrations exceeding the 90th percentile of the general population. Median pre-shift concentrations for some OH-PAHs were elevated compared to the general population likely demonstrating ongoing exposure during the burn season. Adetona et al (2019) observed a significant correlation between adjusted cross-work shift (pre to post) changes in creatinine-adjusted urinary mutagenicity and 1-OH-PYR exposure ($p=0.0001$); however, levels were not as high as in the previous study.

Both Oliviera studies demonstrate consistency in the evidence that exposure to PAHs in firefighters that attend wildfires is on average elevated compared to those who do not. Oliviera et al (2016) found that across the six studied wildland fire corporations (abbreviations provided, please visit the full article for full location names), with the exception of MGD fire station, exposed firefighters had significantly higher levels of urinary ΣOH-PAHs ($p < 0.05$); nonparametric Mann–Whitney U test), ranging from 1.7-35 times higher than non-exposed firefighters. These results suggest occupational exposure, with 1-OH-NAP representing 63-98%, 2-OH-FLO 1-17%, 1-OH-PHEN 1-13% and 1-OH-PYR 0.3-10% of the total ΣOH-PAH. These findings were important given the 1-OH-PYR levels (often considered as a biomarker for PAH exposure) were within the safe levels proposed by the American Conference of Governmental Hygienists (0.5 µmol/mol creatinine); however, represented only 0.3-10% of the total measured exposure. The authors suggest that including other metabolites may provide a better estimate of exposure.

In their 2017 study, the authors found that of the six OH-PAHs measured in urine, 1-OH-NAP + 1-OH-ACE were dominant (66-91%), followed by 2-OH-FLO (2.8-28%), 1-OH-PHE (1.3-7%) and 1-OH-PYR (1.4-6%). 3OHB[a]P was not detected. These results were in keeping with Oliviera et al. (2016). This study further considered exposures and their effects on OH-PAH levels, finding that fire combat activities led to a 158-551% increase in urinary ΣOH-PAH concentrations, and the regular consumption of tobacco increase ΣOH-PAHs by 76-412%. Of note was that 2-OH-FLO was most affected by firefighting activities (111-1068% increase) with 1-OH-NAP + 1-OH-ACE being most affected by tobacco use (22-339%). 1-OH-PHE and 1-OH-PYR, the regularly used biomarker, were least affected by either fire smoke exposure or tobacco use.

### 2.5.3. Aviation Firefighters

Three studies focused on aviation firefighters with results presented in Table 2.11.

**Table 2.11: Aviation Firefighters and Occupational Exposure to per- and polyfluoroalkyl substances (PFAS)**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Laitinen et al., 2014) | Oulu, Finland | n=8 males | Serum, urine. Median and range (ng/mL): PFOS (11.1, 2.79-35.9), PFHxS (2.19, 1.05-4.30), PFOA (2.94, 1.61-4.85), PFNA (1.22, 0.43-6.69), Total PFASs (18.4, 6.54-51.2). 2-BAA (mmol/mol creatinine) pre exposure (<0.5, <0.5) post exposure (<0.5, <0.5-2.7). |
| (Rotander, Toms, et al., 2015) | Qld, Aus | n=149 144 males, 5 females | Serum. Median and range (ng/mL): PFOS (66, 3.4-391) PFHxS (25, 0.7-277), PFOA (4.2, 0.3-18), PFNA (0.69, 0.09-2.4), PFHpA (0.07, <0.03-0.38), PFDA (0.27, <0.04-0.99), PFUnDA (0.14, <0.06-0.58), PFDoDA (<0.05, <0.05-0.12), PFTrDA (<0.06, <0.06-0.10), PFBS (<0.02, <0.02-0.09), PFDS (<0.03, <0.03-0.07). |
| (Rotander, Karrman, et al., 2015) | Brisbane, Qld, Aus | n=20 | Serum. PFHxS, PFOS, PFPeS, PFHpS, Cl-PFOS, ketone-PFOS, Cl-PFHxS higher in firefighters, PFNS and ether-PFHxS exclusively detected in firefighters (concentration not provided). |

Finnish firefighters participated in three consecutive training burns over a three-month period. They measured a 2-BAA average post exposure concentration of 1.4mmol/mol creatinine (Laitinen et al., 2014). This represented 1.3-2.3% of the biological action limit. Relative concentrations of PFASs were higher after the entire training period, with the highest increases of 17% and 10% observed with PFHxS and PFNA respectively. As these PFASs were both low in the firefighting foam the authors suggested that PFHxS exposure could be due to thermal decomposition of longer chain fluorotelomers in jet propulsion fuel fire. Results seemed to indicate dermal exposure given the use of protective respiratory equipment. Only limited analysis was possible due to the small sample size.

In an Australian study with 149 aviation firefighters, participants who had 10 years or less of work experience as a firefighter had levels of PFOS similar to or only slightly above levels reported in the general population (Rotander, Toms, et al., 2015). PFOS concentrations appeared to plateau with 20 years or more use of aqueous film forming foams (AFFF), fire suppression forms utilised by fire services for many years that contained high concentrations of PFOS and PFOA. Past employment with exposure to AFFF was associated with significantly elevated PFOS and PFHxS. Ten years after the phase out of AFFF, PFOS remained above 100ng/mL and 200ng/mL in 27% and 3% of participating firefighters. Levels of PFOS, PFHxS and PFOA were found to be negatively associated with blood donation, and female levels were found to be statistically significantly lower compared to males for PFOS (p=0.029), PFHxS (p=0.041) and PFOA (p=0.038). The authors suggested aerosolised foam or dermal absorption to be the likely routes of exposure.

A subsequent investigative PFAS study that included a sub-group of the previously assessed aviation firefighters as a cohort had a primary aim of analysing fluorinated surfactants in the serum of firefighters with AFFF exposure and discovered previously unidentified persistent PFAS (Rotander, Karrman, et al., 2015). Although this study utilised a subgroup of a study already included in the review, it was included also as different chemicals were assessed, comparative to a different control group. PFOS levels were one order of magnitude higher in firefighters compared with controls and those of the same age group in the Australian general population.

### 2.5.4. Fire Trainers

Five studies focused on or included fire trainers in their cohort of firefighters studied. Table 2.12 presents the results of these five studies.

**Table 2.12: Fire Trainers and Occupational Exposure to Polycyclic Aromatic Hydrocarbons, Volatile Organic Compounds, and Metals**

| Reference | Location | Population Descriptive | Result of Chemical Analysis |
|---|---|---|---|
| (Phoon & Ong, 1982) | Singapore | n=42, males | Whole blood. Mean and standard deviation: blood Pb 40.80+-9.8µg/dL |
| (Feunekes et al., 1997) | The Netherlands | n=33 | Urine. 1-OH-PYR median pre and post exposure for smokers/non-smokers (µmol/mol creatinine): Pre: (0.47/0.15), Post Group A: (0.65/0.60), Post Group B: (1.01/0.51) |
| (Laitinen et al., 2010) | Kuopio Finland, Paris, France | n=4, males | Urine. Muconic acid mean (before, after) exposure (µmol/L): conifer plywood board (0.6, 1.5), pure spruce and pine wood (1.0, 1.0), gas simulator (0.7, 0.8). 1-OH-PYR means (nmol/L) (before, immediately after, 6hr post, next am): chipboard (1.7, 4.4, 4.3, 2.1), conifer plywood board (0.8, 5.1, 9.2, 7.3), pure spruce and pine wood (0.6, 0.8, 1.5, 1.2), gas simulator (0.6, 0.9, 1.2, 1). 1-OH-NAP means (nmol/L) (before, immediately after, 6hr post, next am): pure spruce and pine wood (43, 135, 135, 48), gas simulator (30, 45, 65, 40). |
| (Fent et al., 2014) | Chicago, USA | n=15 each round, males | Urine. Median (range) PAH metabolite levels 3hr post exposure: 62µg/g, (29-140µg/g). All post s-PMA urine concentrations <LOD (5µg/L). |
| (Fent et al., 2019a) | Illinois, USA | n=10, 9 males, 1 female | Urine. Median 3 hr post concentrations (simulation smoke, pallet and straw, alpha OSB, bravo OSB) (µmol/mol creatinine): 1-OH-NAP (2.6, 5.3, 13, 17), 2-OH-NAP (10, 11, 14, 13), 1-OH-PHE (0.19, 0.42, 0.82, 0.87), 2,3-OH-PHE (0.39, 0.70, 1.3, 1.7), 1-OH-PYR (0.14, 0.43, 0.78, 1.8), 2-OH-FLO (0.55, 0.81, 0.93, 1.4), 3-OH-FLO (0.13, 0.36, 0.42, 0.57). |

The fire trainers presented across these five studies appear to be from both urban and aviation fire services; however, fire trainers may fill a similar role across the various classifications of firefighters. Therefore, these are assumed to be representative of fire trainers in general participating in indoor simulation burns.

Lead in fire trainers was found to exceed the levels in firefighters, with 8% of fire trainers exceeding 60µg/dL (Phoon & Ong, 1982). Fire trainers equal 6th for lead exposure out of fourteen industries, ahead of secondary lead smelting, ship repairing, PVC industry and firefighters.

Firefighters in the Feunekes et al. (1997) study were divided into two groups (A and B) for the purpose of scheduling and undertaking test burns. Group A showed a non-significant increase in 1-OH-PYR. Group B showed significant increases of 1-OH-PYR in urine, equally important with smoking. The difference was explained due to urine samples from Group B being retrieved soon after a long duration of smoke exposure, with Group A having fewer trainers working shortly before contributing a sample. This study provided evidence of exposure and uptake of PAH among fire-fighting instructors despite the short period of exposure and use of protective respirators.

Laitinen et al. (2010) also determined fire trainers to experience uptake of PAHs due to fire exposure. The study was designed to determine if the burning of different materials affected fire trainer exposure. 1-OH-PYR was found to be elevated in urine collected immediately after, 6h post, and in the next morning void in all instances of materials burned. 1-OH-NAP was elevated immediately after, 6h and next morning; however, the excretions due to gas simulator (propane) exposure was 50% of the levels when pure spruce and pine were burned. Muconic acid levels were elevated post the burning of conifer plywood board, gas simulator, pure spruce and pine wood. The burning of conifer plywood resulted in elevated levels compared to pure spruce and pine wood or the gas simulator. Exposure was measurable despite fire trainers wearing full bunker gear and SCBA. The authors concluded that the type of simulator used affected the trainers' exposure to PAHs and VOCs.

Although Fent et al. (2014) utilised fire trainers as their cohort, the study was designed with one burn per day, more similar to the experience of a firefighter; however, as fire trainers were the selected cohort and their exposure profile long term may differ to that of firefighters, the study was positioned within this review based on cohort rather than study design. The study determined that the total dose of benzene over the short exposure period ≤30 min was not enough to increase urinary excretion of biomarkers for benzene above exposure criteria. Measured breath was found to be statistically elevated post exposure by 1-2 orders of magnitude. Urinary PAHs were not statistically different pre-exposure to 3 hours; however, significant correlations with change in urinary PAH metabolite levels

(3 hours vs pre) and personal air concentrations were noted ($p<0.01$). The authors determined that fire trainers experience systemic exposure to PAHs and other aromatic hydrocarbons even when wearing full bunker gear and SCBA. Fent et al. (2014) suggested this was most likely due to skin absorption in the neck region due to lower level of dermal protection afforded by hoods.

In a subsequent study, Fent et al. (2019a) included both urban firefighters and fire trainers, and all participants used skin cleansing wipes to decontaminate skin immediately following exposure. As urban firefighter results have previously been discussed (Section 5.1.1), this discussion will focus on fire trainers and any comparison results between the two. The study found statistically significant differences between firefighters and fire trainers from pre to end of days exposure suggesting a cumulative exposure to PAHs in the instructors due overseeing multiple training exercises in a day. Oriental strand board simulation fires resulted in pre to end of shift median percentage increase in 1-OH-PYR of 2860% and OH-NAP increases of 34.3ug/g. Fire trainers were found to have statistically significant differences in their pre to end of total day exposure when compared with firefighters. 1-OH-PYR was elevated by 103% in firefighters, and 397% in fire trainers ($p<0.001$). OH-PHE were increased by 234% in firefighters and 480% in instructors ($p=0.046$).

## 2.6. Discussion

As Table 2.1 demonstrated, when cohorts of firefighters are separated by class of chemical across the 34 studies, the result is 50 cohorts of firefighters studied. The results of 42 (84%) of these groups found firefighters to face occupational exposure. This is particularly of note given the wide range of exposures firefighters may face within a single fire due to the special and temporal variations in smoke profiles caused by burn material, ventilation profile, and temperature (Caux et al., 2002; Fabian et al., 2010)

Wildland firefighters were slightly less likely to have statistically significant elevation in chemical concentrations in blood and urine, with 71% of the studied documenting occupational exposure. When assessing this it is important to note that only six studies were included in this systematic review, and of those not determining occupational exposure, one noted non-significant elevations in 1-OH-PYR, and the other stated it was limited by sample size and ability to collect samples both pre and post exposure. Four of the five studies examining PAH exposure documented occupational exposure.

All other classifications of firefighters exceeded 80% of studies determining occupational exposure. This is particularly of interest when considering urban firefighters, as they were found to be occupationally exposed to PAHs (100% of 11 studies), benzene (100% of 1 study), PFASs (100% of

3 studies), PCDD/Fs (50% of 2 studies), metals (67% of 3 studies), flame retardants (100% of four studies), and pesticides (67% of 3 studies). Occupational exposure to PCBs was not apparent since serum concentrations were not found elevated compared to the general population (Park et al., 2015) however, when considering Chernyak et al. (2012), this may be due to the time difference in analysis of samples between firefighters and control groups (i.e. NHANES).

Studies demonstrated that increased respiratory protection and the use of personal protective clothing reduced the level of exposure (Keir et al., 2017), and that additional layers of protective clothing were beneficial to reducing the deposition of chemical on skin and subsequent systemic uptake (Laitinen et al., 2010; Wingfors et al., 2018). Furthermore, studies suggest that considerations should be taken into account by incident controllers to limit exposure, for example, selecting transitional attack (exterior followed by interior attack) over immediate interior attack or search and rescue, if fire ground conditions permit (Fent et al., 2019b). Also, consideration should be given to the material burned in simulation burns as well as the frequency and duration of exposure of fire trainers (Fent et al., 2019a; Feunekes et al., 1997; Laitinen et al., 2010). Fire services and firefighters incorporating all of these suggestions may reduce the level of exposure experienced by firefighters due to fire suppression activities.

Although results are elevated across the studies for a range of chemicals, the authors present that the levels often still fall within what are considered to be safe levels. Oliviera et al. (2016) and (2017b), two studies assessing wildland firefighters' exposure to fire smoke via urinary analysis of PAH metabolites, suggested that the current biomarker for fire smoke exposure is likely insufficient in describing full exposure to PAHs. The biomarker often used, 1-OH-PYR, represented 10% or less of the total PAHs measured in firefighter urine, and was only minimally affected by fire smoke exposure compared to other metabolites. As such, although firefighter exposure to 1-OH-PYR has been considered in line with road pavers (Fent et al., 2019b; Feunekes et al., 1997), this may not be a holistic description of exposure.

Firefighter exposure to PBDD was found to be equivalent to occupationally exposed extruder workers (Shaw et al., 2013). ΣPBDE levels were found to be much higher than the US general population, yet lower compared with occupationally exposed e-waste and foam recyclers or carpet layers. (Shaw et al., 2013). The primary difference with firefighters appears to be the breadth of exposures verses other occupations with researchers suggesting that risk assessments derived from the results of exposure analysis to one or two groups of chemicals may underestimate the actual hazard associated with fire suppression activities (Fent et al., 2019b). Firefighters may uniquely be exposed to a wide range of chemicals, and the snapshot of a single or few chemicals assessed may prove a dangerous underrepresentation of the true exposure.

The possible additive, synergistic or antagonistic effect of the systemic exposure of multiple classes of chemicals has been considered, for example the possible effect on human endocrine systems, reproductive function and/or neurodevelopment (Laitinen et al., 2012; Laitinen et al., 2014; Park et al., 2015). The range of chemical exposures firefighters face has been postulated to be the cause of increased mortality and morbidity rates. One study utilised the MIXIE program developed in Canada to determine combined health effects due to smoke (Laitinen et al., 2012). This study presented that chemicals entered into the MIXIE program outlined additive effects related to cancer, respiratory, nervous system disorders, and others; however, at this stage the program relates to exposure guidelines via inhalation and not those relative to biomonitoring.

Specific to metabolites with shorter half-lives, no ideal timing of sample collection appears to exist for fire smoke exposure, with studies finding timing can depend on the route of exposure (inhaled, ingested or dermally absorbed) (Fent et al., 2014). Furthermore, 8 of 11 PAH studies assessed 1-OH-PYR in isolation, with other studies finding that to be a likely incomplete indicator of exposure (Andersen et al., 2018b; Andersen et al., 2017; Oliveira et al., 2017a; Wingfors et al., 2018). Given this, it is likely that more research is required to determine a more accurate biomarker for occupational exposure, the most accurate timing for sample collection considering likely exposure routes.

Strengths and limitations exist across the studies presented in this systematic review. The selection of comparison controls may have affected determination of occupational exposure, particularly when considering POPs that are decreasing over time, yet the comparison control was sampled 6-7 years prior to the firefighter cohort being sampled. Cohort size is another factor that can increase strength within a study. Two cohorts of firefighters were assessed for a wide range of chemical exposures, one including results from 12 firefighters (Shaw et al., 2013), the other assessing a cohort of 101 firefighters (Dobraca et al., 2015; Park et al., 2015; Waldman et al., 2016). Although providing important insight, a study on 12 firefighters is more constrained in its ability to apply data to an entire population due to sample size.

This systematic review included studies that spanned decades over which time the materials used in building and furnishing structures and vehicles has changed, as has personal protective clothing and the use of breathing apparatus. The focus remains therefore on the identification of occupational exposure more so than the specific comparison of exposure levels between studies.

Determining appropriate comparison controls is another challenge with this cohort as pre and post exposure assessment may not be appropriate for chemicals with long duration half-lives. This may be why many researchers select PAHs or other groups of chemicals with shorter elimination time frames. To circumvent this issue, participants with extended duration breaks from firefighting before contributing pre-exposure samples could be contributed, as was done by Feunekes et al. (1997). Alternately, firefighters could be sampled while attending the training academy (pre any fire exposure) and then again in years following. Aside from capturing such an unexposed population that subsequently becomes fire exposed through employment, any study will rely on self-evaluation of exposure.

Firefighters may present as their own best control group, comparing an individual to themselves pre to post exposure to see if there is a difference. This may be difficult to undertake for chemicals with longer half-life durations, and it may prove difficult to capture a random sample. As such, data from the general population may be appropriate, if available, for comparison. It is important to note that for persistent organic pollutants (POPs), comparison should occur, ideally, with a general population from the same country and at the same time, as levels of POPs vary between countries and over time. (Gyalpo et al., 2015).

Firefighters, although consistently demonstrating exposure, showed variation in the levels of chemicals present in their system even for chemicals with short half-lives. This appeared to depend on location of study, timing of testing, whether samples were taken post fire exposure or at a more generic time, or if they were specifically centred around fire training operations. This demonstrates that capturing data from firefighters in a range of different scenarios and settings provides valuable data on the overall exposure firefighters face; for example, the exposure from being present at a fire station, from attending a fire call, from fire training, or at a time of convenience (for example when firefighters undergo routine medical testing).

To build on the strengths evaluated in this review, and reduce limitations, future studies might be developed where recruitment to studies occurs particularly with the recruitment of new firefighters, collecting specimen samples (blood, urine, and potentially others) to be archived for future use. If possible, ideally, such a study would become part of an ongoing health survey with similar longitudinal studies carried out in other professions presenting a vehicle to study exposure and link such exposure to health outcomes. Such studies would ideally evaluate firefighters across a range of chemicals, consider individual fire attendance exposure histories, consider fire station exposures, as well as alternate sources of chemical exposure. Given that many of these chemicals are known carcinogens, endocrine disruptors and/or known reproductive toxins, the potential for unwanted health effects is likely present. Further research into the breadth of exposures, as well as increased consideration surrounding the potential additive, synergistic or antagonistic effects is warranted.

### 2.7. Conclusion

Overall, the results of the studies in the systematic review indicate that firefighters consistently show low level systemic exposure to a range of chemicals, and that further research is required in order to comprehensively understand this unique and occupationally exposed cohort.

With 84% of 50 cohort studies including over 1500 total firefighters within this systematic review demonstrating occupational exposure, the question becomes less whether firefighters face occupational exposure, and more to consider how to accurately measure the exposure in a complete and meaningful way that captures the range, breadth and depth of exposure. As many studies were limited to one or two classes of chemicals, some to a single metabolite analysed, many firefighter studies may be limited in their ability to fully describe occupational exposure to firefighters. These results are important and add to the body of knowledge required to understand the exposures firefighters may face and have likely been structured as such due to the high costs of biomonitoring. Even so, a greater range of chemicals needs to be considered in order to accurately assess the exposures of this occupation. Furthermore, studies including exposure limiting practices, tactics, clothing or personal hygiene methods are needed to move beyond recognising exposure to determining clear methods to reduce exposure. The front-line service of firefighting will be required long into the future. The topic is particularly poignant in Australia with vast quantities of Australian bushland and surrounding infrastructure burning due to wildfires annually, with countless firefighters undertaking long duration fire suppression activities on a regular basis.

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# Chapter 3

Routes of exposure were presented in Chapter 1, and occupational exposure to chemicals was reviewed in Chapter 2. Both of these chapters raised the potential for indirect exposures to be contributing to overall firefighter exposure. Prior resarch findings of indirect exposure when at fire stations and/or when handling contaminated personal protective clothing and equipment led to the development of this next chapter, an assessment of exposure within Australian fire stations when compared to Australian homes and offices. This study was designed to consider indirect exposure, given such exposure may be avoidable, and may present a route for firefighters to reduce exposure. Prior to this study, metal contamination in fire stations had not been reported. Therefore, this chapter incorporated metals as well as semivolatile organic compounds and volatile organic compounds to understand whether environmental matrices in Australian fire stations have elevated concentrations of these groups of chemicals compared to homes and offices. This chapter considers routes by which fire station contamination may have occurred and provides an assessment of potential health risk by risk quotient. The following publication has been incorporated as Chapter 3.

**Exposure to Metals and Semivolatile Organic Compounds in Australian Fire Stations**

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Abstract: Firefighting is an occupation with exposure to a wide range of chemicals by means of inhalation, ingestion or dermal contact. Although advancements in personal protective clothing and equipment have reduced the risks for acute exposure during fire suppression operations, chronic exposure may still be present at elevated levels in fire stations. The aim of this study was to assess chemicals in air and on surfaces in fire stations, compare this with other indoor environments, and use this data to estimate firefighter exposure within the fire station. Fifteen Australian fire stations were selected for chemical exposure assessment by means of 135 active air monitors, 60 passive air monitors, and 918 wipe samples. These samples were collected from the interior and exterior of fire stations, from personal protective clothing and equipment, and from within the cabins of vehicles. Chemicals analysed included polycyclic aromatic hydrocarbons, volatile organic compounds, metals, and diesel particulate matter. Specific chemicals were detected from within each class of chemicals, with metals being most frequently detected. Statistical analysis by means of Pearson's Correlations and threshold tests were used to consider the source of exposure, and a collective addition risk quotient calculation was used to determine firefighter exposure. The presence of metals in fire stations was compared with findings from global indoor dust measurements. Concentrations across firefighter ensemble, inside vehicle cabins, and within fire stations for chromium (39.5-493 $\mu g/m^2$), lead (46.7-619 $\mu g/m^2$), copper (594-3440 $\mu g/m^2$), zinc (11100-20900 $\mu g/m^2$), nickel (28.6-2469 $\mu g/m^2$) and manganese (73.0-997 $\mu g/m^2$) were in most instances orders of magnitude higher when compared with concentrations measured in homes and offices. Our study suggests that the elevated concentrations are associated with the transfer of chemicals from fire suppression operations. Due to this elevated concentration of chemicals, firefighters may face increased exposure, and in turn increased risk of adverse health effects. Data suggest that exposure may be mitigated by means of increased laundering frequency and increased decontamination at the scene of the fire.

## 3.1. Introduction

Firefighters have been found to have an increased risk of certain cancers and other health conditions (Daniels et al., 2014; Lemasters et al., 2006). They are exposed to a myriad of combustion products as chemicals in the vapour state and particulate phase, through dermal exposure, inhalation, and ingestion (Fabian et al., 2014; Kirk et al., 2011; Stevenson et al., 2015). The exposures firefighters face on a regular basis may present a contributing factor to adverse health effects (Chernyak et al., 2004; Dobraca et al., 2015; Evans & Fent, 2015; Fent et al., 2012; Fent et al., 2014; Hsu et al., 2011).

When materials burn they produce a wide range of toxic and carcinogenic chemicals. Polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and metals have been found on personal protective clothing (PPC) and equipment (PPE) through wipe sampling, in fire stations by means of air and dust monitoring, and through human blood, urine and breath samples (Banks et al., 2019; Baxter et al., 2014; Brown et al., 2014; Caux et al., 2002; Dobraca et al., 2015; Fent et al., 2014; Oliveira, Slezakova, Alves, et al., 2017; Park et al., 2015; Shaw et al., 2013; Wolfe et al., 2004).

Much research has contributed to the understanding of acute exposures firefighters face at fire incidents, but less is available with respect to exposures at fire stations and from firefighting clothing and equipment. The storage location of PPC in fire stations, and the level of post fire decontamination or laundering may both affect the chemical load of firefighters, and the chemical contamination of fire stations (Banks et al., 2019; Kirk et al., 2011; Oliveira, Slezakova, Fernandes, et al., 2017; Park et al., 2015; Pleil et al., 2014). It is possible that the contamination of PPC and PPE at the scene of the fire is leading to the subsequent contamination of fire stations, and contributing to firefighter exposure; however, further information is needed to confirm this assertation (Banks et al., 2019; Brown et al., 2014; Park et al., 2015).

Additional to contaminant exposure at fire incidents and carryover on PPC and PPE, diesel engine exhaust from fire appliances may present a potential risk. Diesel exhaust was classified by the International Agency for Research on Cancer as carcinogenic to humans (Group 1) in June 2012 (IARC, 2012). Recent studies have found diesel exhaust to be a contributing factor to fire station contamination (Bott et al., 2017; Sparer & Burke, 2018).

The aim of this study was to assess chemicals in air and on surfaces in fire stations, compare this with other indoor environments, and use this data to estimate firefighter exposure within the fire station by means of a risk quotient. To apply meaning to these results guidance was sought from Australian and international regulatory authorities. When considering exposure standards, it is important to note that these are legally enforceable maximum exposure limits that must not be exceeded. These standards do not provide guidance on acceptable working levels, merely levels that cannot be exceeded. The standards do not specify a delineation between healthy and unhealthy working environments, as it is possible for individuals to experience adverse effects below the defined health standard or legal limit (SafeWork, 2019). Given this, and the fact that firefighters are exposed to a wide range of potentially toxic chemicals which may present additive, synergistic or antagonistic effects, the lowest designated safe levels will be utilised, where possible, to assess safe working environments in fire stations. At present, there are no Australian standards for surface contamination from metals or absorbed organic chemicals.

Reference is made in this paper to NIOSH (the National Institute for Occupational Safety and Health) which is the federal agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness in the United States. These levels are generally more expansive and up to date than the current Safe Work Australia levels.

## 3.2. Methods

### 3.2.1. Station Selection and Planning

Fifteen metropolitan fire stations from within a single fire service were selected for assessment at locations accessible to a contracted Senior Hygienist. These stations were selected based on a range of fire station attributes, including: average number of fire calls per annum (actual fires, not including false alarm fire calls), age of building, station layout, engine bay design, and the storage location of PPC. The stations included 10 stations staffed 24 hours a day, three stations staffed in a part time capacity, and two stations with mixed 24 hour a day and part time staffing. Each participating fire station had an identically prescribed cleaning protocol designated by the Fire Service for both within the fire station and for the vehicle; as such, it was assumed this was adhered to.

The above listed station details were garnered through access to internal database systems and fire station design maps, both provided by the related fire service. Each station was visited prior to commencing analysis, with station details cross checked. Ethical approval was not sought following a discussion with a Human Ethics Officer at the University of Queensland outlining that it was not required given the nature of the study.

Limitations exist when comparing fire stations. Every fire station design is different due to date of build, footprint of land, internal ventilation profile, and variation in human activity. Furthermore, fire suppression activities vary between fires, as do overhaul activities, due to the unique nature of each individual fire (Fabian et al., 2010), and the wide range of possible ways to undertaken fire suppression activities. This study represents a snapshot in time of station contamination, with recognition that some level of fluctuation may occur depending on activities and fire scene attendance of firefighting crews on any given day.

### 3.2.2. Air Monitoring

Air monitoring included 13 overall samples: four for PAHs, four for VOCs, three for metals, and two for diesel particulate matter. Exact placement of the samplers varied between stations due to the wide variety of station designs (Table 3.1).

Table 3.1 Active & Passive Air Monitoring Locations

| Position | Pos A | Pos B | Pos C | Pos DS | Pos DE | Pos E |
|---|---|---|---|---|---|---|
| Location | Living Quarters | Living Quarters | PPC Store Location | Living Quarters | Engine Bay | Outside of Fire Station (background monitoring) |
| Chemicals tested for | PAHs, Metals, VOCs | PAHs, Metals, VOCs | PAHs, Metals, VOCs | Diesel Particulate Matter | Diesel Particulate Matter | PAHs, VOCs |

Active air samples were taken using SKC Airchek Universal Sample Pumps at a rate of 2 L/min, model 224-PCXR4, with PTFE filters and XAD-2 tubes. Isopropyl alcohol wipes were used to remove any possible contaminants from XAD-2 attachment sites prior to connection. PAHs were monitored using sampling pumps running at 2 L/min for approximately 500 minutes drawing air through a 37 mm 2 µm PTFE laminated membrane filter backed by a cellulose support pad mounted into a 2-piece cassette. In series with this was an XAD-2 tube (SKC 226-30-04). The filter collected the particulate PAHs and the sorbent tube collected vapour phase PAHs. After sampling, the filter cassette and sorbent tube were wrapped in foil to prevent sample from photo-degradation. Samples were then transported to SafeWork NSW Chemical Analysis Branch, TestSafe Laboratory, for analysis of 16 PAHs according to in-house method WCA.178 which is based on the modified NIOSH Method 5515, Polynuclear Aromatic Hydrocarbons by GC-MS (NSW). The limit of detection, as reported by the laboratory, was 0.1 µg/sample for all analytes.

Atmospheric monitoring for metals was done using a Caselle Seven Hole Head (7HH) sampler. The flow setting for this sampling head was 2 L/min and uses a 25 mm PVC membrane. 50 elements were analysed from the 25 mm PVC filters at the TestSafe Laboratories using TestSafe method WCA/113 modified (NSW). This involved the direct determination of elements in filter samples by x-ray fluorescence spectrometry and UniQuant. All elements reported were stripped of oxygen. The limit of detection (LOD) per sample taken, irrespective of sample size, defined by the laboratory ranged between 1-8 μg, depending on element analysed. Specific LODs for metals can be found in Appendix 2 (Limits of Detection for Metals Analysed).

Diesel particulate monitors were made up using 25 mm quartz filters held in a two-piece cassette and wrapped in aluminium foil to prevent any possible degradation of the collected filter particulate. These monitors were run at 2 L/min for a period up to 500 minutes. The 25 mm quartz filters were analysed at Coal Services in North Wollongong. Thermal optical organic carbon and elemental carbon were measured using the principles of NIOSH Method 5040 and TMDPM01. Measurements uncertainty was +/- 6%, confidence levels, 95%, with a coverage factor of 2. The limit of detection was 1 µg/cm$^2$.

Passive air monitoring badges (SKC, VOC 575 type) were used to monitor for VOCs. Analysis for 73 quantified VOCs trapped in the passive monitor was undertaken at TestSafe laboratories. Samplers were desorbed in the laboratory with $CS_2$, and an aliquot of the desorbant was analysed by capillary gas chromatography with mass spectrometry detection. TestSafe Method WCA.207 (NSW) was used, with a resulting limit of quantitation of 5 µg/section.

All samples were stored at 4 °C temperature in the laboratory prior to chemical analysis.

### 3.2.3. Wipe Sampling

918 wipe samples were taken across the same 15 stations from personal protective clothing, equipment, inside the vehicle cabin, and from internal station locations. One set of 459 samples were taken using a water based 'ghost wipe' to collect metals, while the remaining 459 samples were taken using isopropyl alcohol wipes to collect PAHs. Each sample was taken over an area of approximately 100 cm$^2$, utilising both sides of the wipe. Samples taken from firefighter jackets and pants were from the cuff region, gloves were sampled from the palm, boots from the toe region, and helmets from the top and interior strapping. Steering wheel samples were taken from the wheel ring, seat belts from the chest strap of the two window seats in the rear of the cabin, the external side (cylinder side) of breathing apparatus back plates, and the handle of the thermal imaging camera. The handle of the food fridge and engine bay door were wiped, the keys across the keyboard used by firefighters for data entry, and the taps and surrounding region of the breathing apparatus wash sink.

All wipes were stored in sealed sample jars, PAHs in brown glass, and stored at 4 °C temperature in the laboratory prior to analysis. Isopropyl alcohol wipes used for PAH determinations were desorbed in the laboratory with cyclohexane and the extracts were analysed by gas chromatography / mass spectrometry (GC/MS) in SIM mode with an isotopically labelled isotope. The detection limit was approximately ~0.1 µg/sample for all analytes. The method used by the TestSafe laboratories was WCA.178 (NSW).

'Ghost wipes' used for heavy metal detection were digested with concentrated nitric acid and hydrochloric acid. Analyses was carried out using an inductively coupled plasma mass spectrometer. Limits of quantitation were 5 µg/sample for all elements excluding Be, which was 1 µg/sample. The analysis was carried out by the TestSafe laboratories using the method WCA.219 (NSW).

The unique code associated with firefighting jackets and pants was noted for each item wiped, and the item's service history was determined. The alternate sets of associated items per firefighter were also identified. Most firefighters appeared to be assigned two jackets and two trousers, and laundry history suggested an implemented system of swapping between pairs, meaning these were rotated through laundry whenever the firefighter deemed that their jacket and trousers needed to be washed. As such, to measure the amount of time the wiped items had been in use, the date the alternate set was sent into laundry was taken as the date the wiped set began use. This was based on the assumption that the same gear was utilised at all fires attended between the last recorded laundry date and the sample date. This date was then overlaid with firefighter fire attendance histories through another fire service database to determine the number and type of fires that firefighter, and therefore that jacket and pants set, had been exposed to. This information was overlaid with the chemical findings on the wipe samples.

## 3.3. Statistical Analysis and Calculations

### 3.3.1. General Statistical Analysis

The wipe sample data were checked for completeness, consistency, accuracy and validity. Invalid or uncertain data found in the laundry data were removed, for example if the laundry history for an item wiped was irregular, that item was removed due to the impossibility of applying the aforementioned assumption. No further data exclusions were required.

Data were analysed using IBM SPSS Statistics Version 25 and Microsoft Excel 2016. Descriptive statistics of the contamination levels were performed to summarise the data. Pearson's correlations (1-tailed) were used to investigate the relationship between contamination levels and sample characteristics. Mann-Whitney U tests were used to assess the differences in contamination levels in the new and used gear samples. Binomial tests were used to compare the incidence of contamination when specific metals were not detected in all samples.

Sub-groups were systematically split to determine whether there were threshold values (1-tailed) where the two sub-groups became significantly different to the sample mean. 1-tailed statistical analysis was undertaken given data suggested that differences in contamination occurred in one direction only. These findings were supported by prior research showing PPC retains contamination even post decontamination/laundering. Utilising a 1-tailed statistical analysis allowed for tighter analysis.

### 3.3.2. Housekeeping Limits for Wipe Sampling

Housekeeping limits for surface contamination were calculated by a method outlined by NIOSH standards (Labor, 2012). The NIOSH guideline maximum allowable dose (based on the chemical's airborne exposure limit in units of $\mu g/m^3$) was multiplied by $10\ m^3$ for the approximate volume of air inhaled in 8 hours, divided by approximate area of a worker's hand ($100cm^2$).

### 3.3.3. Risk Quotient Calculations

As firefighters are exposed to a range of metals the risk of exposure to mixtures of contaminants was calculated as a risk quotient to quantify exposure to firefighters. This was determined based on a concentration addition approach to measuring mixture toxicity (Berenbaum, 1985). The formula applied is found in Equation 3.1, where the concentration (x) of each contaminant (i) are divided by any consistent measure of their toxicity or risk (the guideline limit), and subsequently added together.

Equation 3.1 Risk Quotient (RQ) calculation from individual contaminants and their respective guideline limits

$$RQ = \sum_{i=1}^{n} \frac{x_i}{guideline\ limit_i}$$

This calculation was utilised to determine if the sum of the ‘risk quotients’ (RQ) was >1, suggesting the sum of the exposure may cause a possible risk (Backhaus et al., 2013; Gustavsson et al., 2017; Koppel et al., 2019; Nys et al., 2017).

## 3.4. Results and Discussion

### 3.4.1. Chemicals in Air

For metals, the detection frequency was generally low and the most frequently detected was Fe (11 out of 15) with the highest concentration of 1.6 $\mu g/m^3$. Si (three instances) and Na (one instance) were highest at 5.3 $\mu g/m^3$ and 4.6 $\mu g/m^3$ respectively, and Pb (three instances) was highest at 2.7 $\mu g/m^3$.

Amongst PAHs, only naphthalene (nap) was detected in 10 out of the 15 stations, across three locations, with a concentration ranging from <0.1- 0.4 $\mu g/m^3$. No other PAHs presented concentrations above the limit of detection in any sample.

Six VOCs were reported above limit of detection including 2-methylbutane, toluene, styrene, n-pentane, 2-methylpentane, and isopropyl alcohol. The sum of these from each sample was slightly below the total VOC count, suggesting others may present but below the limit of detection. The levels of 2-methylbutane and toluene were not statistically above background levels. In two fire stations styrene was recorded at low levels (0.1 ppm and 0.08 ppm) in the living quarters and not present within background monitoring. n-pentane was recorded in a single fire station in the PPC store location, and 2-methylpentane was recorded in a single station at 0.25ppm. It is likely that the presence of isopropyl alcohol is due to the proximity of sample wipes.

The low presence and range of PAHs and VOCs detected in air samples across the 15 fire stations is likely due to the high limits of detection achieved in the laboratory which focuses on occupational limits, compared to other studies successfully detecting ranges of PAHs and VOCs through analysing in the environmental ranges (Kirk & Logan, 2015; Oliveira, Slezakova, Alves, et al., 2017). As such, further discussion surrounding the source and presence of PAHs and VOCs in air in this study is limited.

No PAH, VOC, or metal concentrations were detected in air above NIOSH or Safe Work Australia guidelines. Of those chemicals detected, naphthalene was calculated to be at a minimum of 125 times less than the NIOSH and Safe Work Australia level of 50 $mg/m^3$. Levels of toluene and 2-methylbutane were below the NIOSH TWA and the Safe Work Australia (SWA) ES-TWA limit of 50 ppm. n-pentane was below the NIOSH TWA of 120 ppm, and 2-methylpentane was below the NIOSH TWA of 100 ppm. Si and Fe were both 1000x under the exposure limit. No limit was available for Na. Pb was found to be 20-25 times under the limit.

The levels of elemental carbon found on the quartz filters ranged from between 0.001 $mg/m^3$ to 0.02 $mg/m^3$ in the station, and <0.001$mg/m^3$ to 0.02 $mg/m^3$ in the engine bay. The average for the station living quarters was 0.003 $mg/m^3$, with 0.004 $mg/m^3$ as the average for the engine bay. Across the 15 stations there was an average of 3 engine ignitions during the monitoring period. These levels of elemental carbon ranged from 5-100x lower than the New South Wales (NSW) and Western Australia (WA) Government stipulations of 0.1 $mg/m^3$ (8-hour time weighted average).

Three fire stations presented statistically higher levels of elemental carbon in the living quarters than in the engine bay. Of these three stations, two presented permanent and sizable gaps between the engine bay and the living quarters room in which the monitoring was undertaken (1 cm gaps around the window or door). The third had limited ventilation in the engine bay and minor gaps surrounding the door that separated the engine bay and living quarters. It is possible that station design elements such as reverse in vs. driver through, or engine bay ventilation profile affected the results; however, results do not suggest either of these played a pivotal role. The three stations represent 3 of 10 stations with manually operated or no ventilation present within the engine bay. Drive through engine bays were present in 2 of the 3 (overall 9 or 15 had this design), and one is reverse in only (total 6 of 15 were reverse in only).

As elemental carbon is formed during fires (Fernandes et al., 2003; Samsonov et al., 2012), it is impossible to determine whether the elemental carbon found on the quartz filter was due entirely to diesel engine exhaust, or residual in the air due to firefighting; however, diesel exhaust monitoring occurred in living quarters rooms that did not include any personal protective clothing or equipment, and two of the stations recording significantly higher levels of elemental carbon in the living quarters do not store any PPC or PPE within the living quarters.

These findings suggest that diesel exhaust may be flowing into fire stations, and that improvement to air seals between engine bay and station living quarters may assist in containing diesel exhaust to the engine bay. The findings are in line with international findings showing diesel to be an exposure risk for firefighters (Bott et al., 2017; Sparer & Burke, 2018).

### 3.4.2. Chemicals on Wipes

For PAHs, the highest detection frequency was observed for phenanthrene (1% of samples). In total ten PAHs were recorded above LOD (0.1-0.7 $\mu g/100cm^2$). These included acenaphthylene, acenaphthene, phenanthrene, fluoranthene, pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene. Table S3.1 in Appendix 2.

Metals were detected across wipe samples in the following order of frequency: Te (0.22%), V (0.87%), As (1.1%), Sn (2.2%), Ni (9.1%), Sr (11%), Sb (14%), Pb (18%), Cr (20%), Mn (22%), Cu (50%), Zn (100%), Fe (100%). Ten metals, including Be, Se, Co, Cd, In, Pt, Hg, Tl, Bi and U were not detected across any samples. Detection frequency per item wiped for the remaining 13 metals are provided in Table S3.2.

Given the limited frequency of detection of PAHs, the following discussion will focus on metals. Data from firefighter PPC, the vehicle cabins, and the fire stations were separated by employment status (full time, part time), and by groups of items wiped to garner information on exposure.

The number of items on which each metal was detected was separated into four sampling groups: firefighter ensemble (15.2%), vehicle cabin (13.2%), fire station including the breathing apparatus wash sink (18.7%), and fire station not including the breathing apparatus wash sink (13.8%). The reason to consider the fire station both with and without the breathing apparatus sink was due to its location. The sink was present within the living quarters in some stations, and external in others.

#### 3.4.2.1. Fire Station vs Global Homes/Offices

Fire stations are not only workplaces but also act as a home for firefighters while they are on shift. As such, results from this study have been compared with levels in global homes (Barrio-Parra et al 2018) rather than occupational settings, with a primary focus on Sydney as the sampled fire stations were within the greater Sydney area. Table 3.2 outlines this study relative to Sydney homes. Table S3.3 outlines global homes vs fire stations in this study.

Table 3.2 Metal concentrations ($\mu g/m^2$) from wipe sampling in fire stations compared to homes in Sydney, Australia.

| Averages $\mu g/m^2$ | Reference | Cd | Cr | Pb | Cu | Zn | Ni | Mn | # samples |
|---|---|---|---|---|---|---|---|---|---|
| Ensemble All | This study | <5 | 405 | 456 | 619 | 18300 | 35.9 | 784 | 270 |
| Vehicle All | This study | <5 | 39.5 | 130 | 690 | 12600 | 49.6 | 166 | 129 |
| Fire Station, no BA Wash Sink | This Study | <5 | 40.0 | 46.7 | 596 | 11800 | 2470 | 73.0 | 45 |
| Fire Station, including BA Wash Sink | This Study | <5 | 493 | 480 | 3440 | 15700 | 2170 | 638 | 60 |
| Ensemble Part Time Firefighters | This study | <5 | 459 | 67.8 | 610 | 11100 | 47.8 | 259 | 81 |
| Ensemble Full Time Firefighters | This study | <5 | 360 | 619 | 594 | 20900 | 28.6 | 997 | 189 |
| Sydney, Australia | (Chattopadhyay et al., 2003) | 0.34 | 6.5 | 30 | 11 | 51 | 2.1 | 5.9 | 82 |

Although the comparison of fire stations with Sydney homes has demonstrated that fire stations exhibit concentrations of metals, particularly Cr, Cu, Zn, Ni and Mn at orders of magnitude higher than households in a similar geographic region, direct comparison is limited due to the wide range of variables presented in 3.2.1. Station Selection and Planning.

This comparison demonstrates that fire stations exhibit orders of magnitude higher concentrations of metals, particularly of Cr, Cu, Zn, Ni and Mn than households in a similar geographic region. It is important to note that fire station data do not include floor wipes. If included the results may be relatively higher due to the comparatively high levels of Cr, Pb, Cu, Zn, Ni and Mn on ensemble, and studies suggesting that metals were tracked back in on boots and clothing (Barrio-Parra et al., 2018).

#### 3.4.2.2. Fire Attendance and Chemical Contamination Correlations

Correlations between heavy metal presence, years in service, likely days since laundering, and fire attendance were investigated for firefighter jackets and pants. These were run as 1-tailed, and those significant to $p<0.05$ are shown in Table S3.4. A summary of metals reporting significant correlations is found in Table 3.3 by employment demographic.

Table 3.3: Metals with significant correlations of exposure to full and part time firefighters by fire exposure, laundry history, and employment demographic.

| Significant metal correlation ($p<0.05$) | Years in Service | Likely Days Since Laundering | Total Fires | Structure Fires | Outside/ Storage Fires | Vehicle/ Transport Fires | Wild Fires | Rubbish Fires | Explosion Fires |
|---|---|---|---|---|---|---|---|---|---|
| Part Time Firefighters (n=18) | Cr, Sr | Cu, Mn, Sb | Cu, Mn, Sb | Cu, Mn, Sb | Cu, Mn, Sb | Cu, Mn, Sb | Cu, Mn, Sb | Cu, Mn, Sb | Not Found |
| Full Time Firefighters (n=37) | Not Found | Sr, Sb, Pb | Mn, Zn, Sr, Sb, Pb, | Mn, Zn, Sr, Sb, Pb | Sn | Mn, Zn, Sr, Sb, Pb, Cr | Cr, Mn, Zn, Pb, Cu | Cr, Mn, Zn, Sr, Sb, Pb, Cu | Mn, Zn, Sr, Sb, Pb |

The profiles of metal correlations were different for full and part time firefighters. Metals were found above levels of detection on both internal and external wipe samples for full-time firefighter jackets and pants. These were correlated with days since laundering, and across both the total and the ranges of fire types attended. Correlation data for full-time firefighters is found in Table S3.5. Part-time firefighters show internal Cu and external Mn and Sb showing up across the range of fires. This could be due to a smaller sample size, smaller variability in number of fires attended, or due to unidentified reasons. Two notable correlations were found with part-time firefighters only, external Cr and Sr correlated with years in service (Table S3.6).

Antimony was found as a moderate significant correlation on external wipe samples for all types of fires, as well as likely days since laundering. Prior studies have recognised antimony as present within firefighter ensemble (de et al., 2010); however, it was not found on wipe samples of new gear in this study and as such, it is most likely due to fire contamination (Edelman et al., 2003). Total fires showed weak significant correlations for Mn, Zn, Sr and Sb on internal sample wipes, and Pb on external wipe samples. Explosion fires demonstrated similar significant results to total fires, excluding internal Zn.

These correlations indicate that metals are accumulating on firefighter ensemble, both internally and externally, due to fire attendance, and there is a positive relationship between increasing time since laundering and increasing levels of metals detected. These findings are in line with other studies showing chemicals, including metals, to adhere to firefighter ensemble post fire suppression activities (Easter et al., 2016; Fabian et al., 2010; Fabian et al., 2014; Kirk & Logan, 2015).

#### 3.4.2.3. New vs Used Gear

Items of new, unused firefighter ensemble were sampled for comparison with used ensemble to determine background presence of metals. The Mann-Whitney U test indicated that the mean concentration of Cu was greater on used gear (M = 6.19) when compared to new gear (M = 0.39) (U = 765, p = 0.035), and that the mean concentration of Fe on used gear (M = 176) was greater than new gear (M = 15.8) (U = 118, p = 0.000). A binomial test indicated that the proportion of Pb in the used gear (18%) is statistically different to the proportion of Pb in new gear (6%) ($p<0.001$), and that the proportion of Cu in used gear (43%) is statistically higher to the proportion of Cu in new gear (6%)($p<0.001$). Average and maximum levels for the five metals found on new gear were compared with used gear and found to be notably lower (Table S3.7).

Boots and gloves appear to have Cr in the material used, given their similar concentrations in new and used gear. From the binomial tests, only Pb and Cu were found to be statistically different; however, a greater difference becomes apparent when maximum values (averages) of used gear (71.6 µg/100cm$^2$ for Pb and 56.6 µg/100cm$^2$ for Cu) versus new gear (0.70 µg/100cm$^2$ for Pb and 0.8 µg/100cm$^2$ for Cu) are considered. Similar findings were observed for Zn and Fe (683 µg/100cm$^2$ and 1060 µg/100cm$^2$ for used gear respectively and 108 µg/100cm$^2$ and 18.0 µg/100cm$^2$ for new gear respectively). The maximum level found on used gear for Cr was six times that of new gear (130 µg/100cm$^2$ and 23 µg/100cm$^2$ respectively).

#### 3.4.2.4. Thresholds for Chemical Contamination

To understand whether specific types of fires or laundering period were important contributors to the exposure risk from metals on firefighting jackets and pants, a threshold test was performed. This was run for full-time firefighters (n=37) only due to sample numbers and the increased possibility that part-time firefighter (n=18) results could be skewed by individual items. The threshold test was run by comparing the count of items with a select metal present on items under the designated threshold, compared with the count of items with a select metal present above the designated threshold. No threshold was obtained for years in service; however, all other tests resulted in threshold findings for multiple metals.

Days since laundering resulted in a threshold of 36 days (Sb). Fire threshold tests resulted in the following findings: 9 total fires (Cu), 1 vehicle fire (Mn, Cu, with Pb close to threshold), 5 structure fires (Cu, Pb), four wildfires (Mn, Cu, Cr, Pb), and one rubbish fire (Pb). These results are outlined in Table S3.8. The findings that chemical contamination of firefighter ensemble increases with use are in line with prior studies (Easter et al., 2016; Kirk & Logan, 2015).

Averages were determined for days since laundering, and fires since laundering to assess if jackets and pants are being laundered in line with threshold levels. Averages for laundering were 2-4x higher in value than the threshold levels, suggesting that more frequent laundering may be beneficial to reducing exposure risk related to firefighting jacks and pants (Table 3.4). In contrast, the age of jackets and pants did not appear to contribute to exposure risk.

Table 3.4 Thresholds for the metal-exposure risk from firefighting jackets and pants related to types of fires and days since laundering compared to firefighting averages.

| | Firefighter Average | Statistically Significant Threshold Level |
|---|---|---|
| Years In Service | 4.22 | Not Found |
| Days Since Laundering | 158 | 36 |
| Total Fires Since Laundering | 28 | 9 |
| Vehicle Fires Since Laundering | 3 | 1 |
| Structure Fires Since Laundering | 11 | 5 |
| Rubbish Fires Since Laundering | 4 | 1 |
| Wild Fires Since Laundering | 10 | 4 |

It is important to note that each of these numbers is potentially higher than the actual threshold due to firefighters serving multiple roles at a fire incident. Information surrounding a firefighter’s role at each fire incident was not obtainable, meaning it was possible for the firefighter to not be involved in fire suppression activities at all (waiting in reserve, for example), yet still noted as having attended the fire.

#### 3.4.2.5. Housekeeping Limits

Of the 23 metals analysed for, NIOSH provided limits for 20, Occupational Health and Safety Administration (OSHA) for 19, Safe Work Australia for 14 and Brookhaven National Laboratories for 4. Brookhaven National Laboratories, a United States Department of Energy Laboratory, was the only one to provide actual wipe sample housekeeping limits (Energy, 2019). It was also the only to list varying levels acceptable depending on location of sampling for lead, ranging from operational floors and surfaces to food preparation areas. `

Utilising these figures to assess housekeeping limits to determine if any metals exceeded safe levels, 19 were found to exceed safe levels. The metals exceeding safe levels included Ni in 1 instance, As in 5 instances, and Pb in 13 instances. All other wipe samples were found to be within permissible limits, even when utilising the lowest safe defined limit.

Table S3.9 outlines the safety levels utilised for assessment in this study (from Brookhaven National Laboratories and/or calculated from NIOSH) for each metal and includes International Agency for Research on Cancer classifications. No safe limit for exposure was found for Sr or Bi.

Limitations in this analysis were due to the existence of mainly only occupational area safe limits, the NIOSH handbook only listing oxidised forms for the chemicals, Zn, Fe and V, and TestSafe laboratory only providing information on the total metal, which may include oxidised or other species. As such, metals with toxicities dependent on their chemical speciation, such as the more toxic $Cr^{6+}$ compared to $Cr^{3+}$ or $Cr^{0}$, are presented simply as total metals.

#### 3.4.2.6. Risk from Exposure to Multiple Contaminants

The risk of exposure to multiple contaminants was investigated using a risk quotient (RQ, Section 3.0). A RQ >1 suggests that the sum of the exposure may cause a possible risk. Utilising the lowest ascertainable safety standards for detected metals, and applying Equation 3.1, the sum of the risk quotients was calculated for each item wiped. The results were separated as total metals detected, and carcinogenic metals only. The risk quotient ranged from 0.0 to 52.8, averaging 6.4 overall across the two employment demographics.

Full time firefighters demonstrated the highest percentage of PPC items with a risk quotient above 1 (6.3%). Given the correlations demonstrated a wider range of metals present across the fire types, this seems understandable. Differences were seen between full time firefighters and part time firefighters. For example, the average total risk quotient was 0.6 for full time, 0.5 for part time. The average exposure for risk quotients above 1 was 8.4 for full time and 11.5 for part time. Maximum risk quotients calculated were 52.8 for full time and 16.0 for part time. The count of those above one was 12 for full time firefighters, and 3 for part time firefighters. (Table 3.5).

Table 3.5 Average, Min, Max and Count of Risk Quotient Exposure, PPC by Employment Demographic

| | Average Total Risk Quotient | Average Exposure for Risk Quotient ≥1 | Maximum Risk Quotient | Minimum Risk Quotient | Count of Risk Quotient ≥1 |
|---|---|---|---|---|---|
| Full Time PPC (n=37) | 0.6 | 8.4 | 52.8 | 0.0 | 12.0 |
| Part Time PPC (n=18) | 0.5 | 11.5 | 16.0 | 0.0 | 3.0 |

The two groups that returned the highest percentage of wipes that exceeded a risk quotient of 1 were firefighter PPC (5.6% all metals and carcinogenic metals only) and the fire station (12% all metals, 10% carcinogenic metals only). Removing the breathing apparatus sink from the fire station group resulted in a decreased percentage of wipes exceeding 1 (2.2% all metals and carcinogenic metals only).

Vehicle cabin wipes did not record the same presence of contamination, and it is possible this was due to the locations wiped. Alternate sample locations within the vehicle cabin, such as footwells and/or door handles/armrests may provide better indicative data on the hygiene of the cabin than seatbelts, for example. Fire station contamination due to firefighters bringing fire chemicals back with them post fire suppression activities have been reported previously (Brown et al., 2014; Park et al., 2015), suggesting that the vehicle cabin should contain some level of contamination also. Tables S3.10-S3.12 present the percentage of all metals and carcinogenic metals per grouping of items wiped that have a risk quotient of greater than one.

Pb was a major contributing metal to the risk quotient, with As, Ni and Zn also providing meaningful contributions on one or more items across the range or samples. This is unsurprising given Pb was one of the few metals to have a non-occupational exposure level, considerably lower than occupational exposure limits. Arsenic presented a low limit also, following NIOSH’s recent changes to reduce the limit for carcinogenic substances.

Pb and As have been found to be present in measurable concentrations on firefighter ensemble post fire suppression activities, with the suggestion that human behaviours such face wiping or touching garments with bare skin could result in subsequent contamination (Fabian et al., 2010).

It is possible that true figures may exceed those listed in Table 3.5 due to the limitations discussed with regards to housekeeping limits.

## 3.5. Conclusion

The results of this study demonstrate that there were detectable concentrations across the analysed chemical groups in fire stations. Concentrations of metals on surface wipes were found to be higher than in homes, and the source of these metals is likely fires. When considering this result, it is important to note that the PPC, the vehicles and fire stations are all assumed to be in a clean and ready state, thereby not increasing firefighter overall exposure when away from fire incidents. It is also important to note that these exposures are being measured in the home-style environment of the fire station where firefighters eat, sleep and exercise, far removed from operational fire suppression locations. Firefighting PPC is worn during training exercises and in non-fire operations, during school visits and other public exercises, potentially providing a source of contamination.

Firefighters could also face increased risk of adverse health effects through exposure to contaminant mixtures, with 6.3% of full-time firefighter PPC containing mixtures of carcinogenic metals at concentrations that combined to exceed guideline concentrations. This is also likely an underestimation as only metal wipe data were included. Should other contaminants like PAHs be included it is possible that firefighters may face higher potential health risks.

Threshold tests show that full time firefighters are not laundering their jackets and pants at a frequency in line with calculated metal threshold levels for fires attended, and that increased exposure increases chemical contamination. As such, it is possible that these exposure risks can be reduced by increased laundering. Data showing increased chemical contamination due to fire exposure also suggests increased decontamination at the scene of the fire may support the reduction in transfer of chemicals from PPC and equipment to the fire station.

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The following publication is incorporated as Chapter 4:

Engelsman, M., Toms, L.-M. L., Wang, X., & Banks, A. P. W. (2023). Firefighter undergarments: Assessing contamination and laundering efficacy. *Environmental Research*, *216*, 114344. doi.org/10.1016/j.envres.2022.114344

Utilising a simplified version of the Credit Authorship Statement:

Conceptualization: Michelle Engelsman, Andrew Banks; Data curation: Andrew Banks; Formal analysis: Michelle Engelsman, Andrew Banks; Funding acquisition: Michelle Engelsman; Investigation: Michelle Engelsman, Andrew Banks; Methodology: Michelle Engelsman, Andrew Banks, Leisa-Maree Toms, Xianyu Wang; Project administration: Michelle Engelsman, Andrew Banks, Leisa-Maree Toms, Xianyu Wang; Resources: Michelle Engelsman, Andrew Banks; Validation: Michelle Engelsman, Leisa-Maree Toms, Xianyu Wang, Andrew Banks; Visualization: Michelle Engelsman, Leisa-Maree Toms, Xianyu Wang, Andrew Banks; Writing original draft: Michelle Engelsman; Writing review & editing: Michelle Engelsman, Leisa-Maree Toms, Andrew Banks, Xianyu Wang.

# Chapter 4

Chapter 3 identified that the level of contamination within fire stations presented a potential health risks by means of indirect exposure. This raised the question of what other potential indirect exposures could be present that are currently unknown. With an awareness from prior research that smoke can contaminate shorts and t-shirts worn under structure firefighting ensemble, this raised the question of whether smoke can penetrate or permeate through to smaller, more personal items such as socks, underwear and crop tops, providing a potential route for indirect exposure to the firefighters. These items are regularly taken home and laundered, raising the question as to whether they present secondary contamination risks to homes. Furthermore, these items are worn over highly permeable skin and reproductive organs presenting the potential for dermal exposure. This chapter presents an investigation into the ability of the most ubiquitous chemical group in fire smoke, polycyclic aromatic hydrocarbons (as identified via systematic review in Chapter 2), to extend beyond external PPC to undergarments and socks. Findings demonstrated that these items could become contaminated and retain contamination following home washing machine laundering cycles. The following publication has been incorporated as Chapter 4.

**Firefighter Undergarments: Assessing Contamination and Laundering Efficacy**

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Abstract: Firefighters are exposed to toxic chemicals including polycyclic aromatic hydrocarbons (PAHs) during fire suppression activities. This exposure can result in the contamination of personal protective clothing and seemingly protected skin underneath. This study is the first of its kind to determine the potential contamination of firefighters' undergarments: notably socks, crop tops and briefs. This study was designed with the following aims: 1) to understand if PAHs from fire smoke can contaminate socks and undergarments, 2) to determine the effectiveness of laundry detergent in removing these PAHs, 3) to assess how different fabrics affect the retention of PAHs during laundering, 4) to determine if there is any risk of intra and inter load cross contamination during the laundering process. To investigate, 10 firefighters undertook a range of tasks to mimic real fire scenarios during three simulated 20-minute compartment fires. New socks, briefs and crop tops were worn by each firefighter for each evolution and removed immediately following its completion. These items were sampled post-burn and post-laundering, with clean fabric included in each load to test for cross contamination. Laundering resulted in an average $\sum_{13}$ PAHs concentration reduction of 36% on socks, 9% on briefs and a 160% increase in crop tops. The concentration changes did not appear to differ between laundry detergents (n=5) used. Swatches of clean fabric included within laundry loads identified cross contamination. This study suggests the potential for the secondary contamination of items washed in a domestic washing machine with undergarments that have been worn at a fire scene. Findings demonstrate that fire smoke can contaminate firefighter's undergarments with the potential

for secondary exposure by means of dermal absorption and the cross-contamination of other items during laundering. This study provides novel findings for firefighters and fire services suggesting the separate laundering of such items post fire incident exposure.

## 4.1. Introduction

Firefighting is an occupation with known exposure to a wide range of carcinogenic and endocrine disrupting chemicals, including polycyclic aromatic hydrocarbons (PAHs). PAHs are ubiquitous in fire incidents and have been detected in urine and on skin wipe samples (ie. hands, neck) of firefighters wearing self-contained breathing apparatus and personal protective clothing (PPC) (Baxter et al., 2014; Cherry et al., 2019; Ekpe et al., 2021; Engelsman et al., 2020; Fent et al., 2014; Fent et al., 2019a; Fent et al., 2019b). Chemicals due to fire exposure have been found on the exterior and interior of PPC, as well as on items of clothing worn underneath (Banks, Wang, Engelsman, et al., 2021; Fent et al., 2017; Kirk & Logan, 2015; Mayer et al., 2019). Although studies have determined that wearing additional layers (including thick cotton underlayers) reduces the deposition of PAHs on skin (Wingfors et al., 2018), no prior studies have examined whether PAHs can contaminate socks and undergarments (underwear and crop tops).

Research has demonstrated that if PPC is not effectively laundered post exposure, secondary exposure may occur (Banks, Wang, He, et al., 2021; Easter et al., 2016; Fent et al., 2017; Mayer et al., 2019; Wingfors et al., 2018). Furthermore, studies have shown that the laundering of these items is ineffective with items retaining contaminants above pre-exposure levels, and that post-exposure contaminants may cause inter and intra load cross contamination (Banks, Wang, Engelsman, et al., 2021; Fent et al., 2017; Kirk & Logan, 2015; Mayer et al., 2019). No prior studies have determined the risk of cross contamination in a domestic laundry setting.

Studies of health outcomes in firefighters have found numerous adverse health effects, some linked to occupational exposure to chemicals including PAHs. In general, the observed adverse health effects include multiple cancers (including breast and testicular), cardiovascular impairments, and reduced fertility (Andersen et al., 2017; Engelsman et al., 2021; Glass et al., 2019; LeMasters et al., 2006; Petersen et al., 2019). Considering the dermal absorption of PAHs and the fact that apocrine gland-rich (groin, armpits and nipples) regions exhibit higher rates of permeability (Kapitány et al., 2021), this study was designed around items worn over those regions with the following aims: 1) to understand if PAHs from fire smoke can contaminate socks and undergarments, 2) to determine the effectiveness of laundry detergent in removing these PAHs, 3) to assess how different fabrics affect the retention of PAHs during laundering, 4) to determine if there is any risk of intra and inter load cross contamination during the laundering process.

## 4.2. Methods

### 4.2.1 Sample Collection

Sampling for this study took place over three simulated compartment fires consisting of particleboard fires in shipping containers with a low neutral plane (smoke level) representative of a fire burning within a structure requiring the use of a 38mm firefighting hose for fire suppression. 10 firefighters were present within each of the three compartment fires for 20 minutes. At each of the three burns, firefighters wore new undergarments (socks, briefs and crop tops) composed of different fabric types (see Table 4.1). During each evolution firefighters performed a prescribed set of activities that included 50 bodyweight squats and crawling along a circular track for the duration of the burn. This movement was designed to simulate the bellows and chimney effect inside firefighting ensemble while performing firefighting activities and support relatively even fire exposure within the compartment.

Upon completion of each burn, firefighters removed their external PPC including firefighter helmets, hoods, tunics, trousers and boots while wearing nitrile gloves. After removing their nitrile glove the firefighters progressed to the changerooms, at which time their undergarments were removed and placed individually in an aluminium foil packet and placed into a zip lock bag. Samples were shipped overnight to QAEHS and stored at -20°C prior to laundering to reduce any changes in concentration of PAHs due to off-gassing or sample degradation.

Table 4.1: Fabric Type of Items Worn by Burn

| | Fabric Type | | | Firefighters' Sample Codes |
|---|---|---|---|---|
| | Briefs | Crop tops | Fabric Socks | |
| Burn 1 | Cotton 95%<br>Elastane 5% | Cotton 95%<br>Spandex 5% | Cotton 95%<br>Other Fibres 5% | 1,2,3,4,5,6,7,8,9,10 |
| Burn 2 | Polyester 92%<br>Elastane 8% | Nylon 92%<br>Elastane 8% | Cotton 95%<br>Other Fibres 5% | 11,12,13,14,15,16,17,18,19,20 |
| Burn 3 | Cotton/Elastane | Cotton/Elastane | Cotton 95%<br>Other Fibres 5% | 21,22,23,24,25,26,27,28,29,30 |

4.2.2. Laundering

Post-burn a swatch was cut from each item and packaged in a zip lock bag. Swatches were taken from the cuffs of socks and the from the front of briefs and crop tops. Five loads of laundering were undertaken in a domestic style front-loading washing machine at 60ºC using four domestic laundry detergents available in Australia: a premium, mid-range, economy, and environmentally friendly brand. Each wash cycle was run with 25L per load, 1 rinse cycle, 600 rpm spin cycle, 60 minutes in total. These four domestic laundry detergents were all used as per the instructions from each brand. In addition to this the premium brand (containing sodium dodecyl sulfate) was combined with Triton X 305 to assess if this combination (previously shown to enhance the solubility of PAHs (Zhu & Feng, 2003) increased laundering efficiency. Post-laundering the undergarments were air dried and resampled. The samples laundered in each washing load are presented in Table 4.2. A list of ingredients of each laundry powder type is listed in the supplementary information. The washing machine was run empty between loads.

Table 4.2: Laundry Power by Washing Load

| Washing Load | Laundry Powder Type | Weight of laundry powder | Samples in washing load |
|---|---|---|---|
| 1 | Premium | 53g | 1,6,11,16,21,26 |
| 2 | Mid-range | 52g | 2,7,12,17,22,27 |
| 3 | Economy | 75g | 3,8,13,18,23,28 |
| 4 | Environmentally Friendly | 53g | 4,9,14,19,23,29 |
| 5 | Premium + Triton X 305 | 53g + 38g | 5,10,15,20,25,30 |

4.2.2.1. Intra-load Contamination

To assess intra-load contamination, unworn fabric swatches were laundered with contaminated firefighting undergarments in each load of the five loads of washing. These fabrics swatches consisted of the four different fabric types in this study (cotton/elastane, cotton 95% elastane 5%, polyester 92% elastane 8% and nylon 92% elastane 8%) to assess the role fabric type plays in cross-contamination in laundering.

4.2.2.2. Washing Machine Contamination

Surface wipe samples were collected from the inside of the washing machine prior to each washing load and after each cycle. Surface wipes were taken from a 10cm x 10cm area of the washing machine drum using a 70% isopropanol wipe, ensuring no sampling from within the annulus of the drum.

4.2.3 Sample Extraction and Analysis

The extraction and analysis methods used for the analysis of PAHs have previously been described in-depth by Banks et al. (Banks, Wang, He, et al., 2021). In summary, samples were spiked with internal standards (500 ng D10- Phe, 200 ng D10-Flu, 50 ng each of D12-Chr, D12-BbF, D12-BaP, D12-I123cdP and D12-BghiP). The sample was extracted using 20 mL of 1:1 acetone:n-hexane solution in an ultra-sonic bath for 15 minutes. The solvent was removed and this was repeated with a further 20 mL of 1:1 acetone:n-hexane. These solvent extracts were combined, taken to near-dryness and made up in 1 mL of DCM before being filtered through a 0.2 m PTFE filter. The extract in DCM were then cleaned up by gel permeation chromatography (GPC), using a Shimadzu LC-20AC system coupled with an EnvirogelTM GPC Guard Column 4.6x30mm (Waters), an EnvirogelTM GPC Cleanup Column 19x300mm (Waters), and a Shimadzu FRC-10A fraction collector. The mobile phase solvent was DCM, pumped at a flow rate of 5 mL $min^{-1}$. 500 µL of the filtered DCM extract was injected onto the column. The sample was collected from 8.33 until 16.32 minutes. The collected fraction was then blown down to near-dryness and reconstituted in 50 µL of recovery standard (10 ng 13C12-BDE 77) in isooctane.

Extracts were analysed using a TRACE GC Ultra, coupled with a TSQ Quantum XLS triple quadrupole mass spectrometer that is equipped with a TriPlus Autosampler. A DB-5MS column (30 m×0.25 mm i.d.; 0.25 µm film thickness, J&W Scientific) was used for separation. The total run time was 25 minutes at constant flow rate of 1.0 mL $min^{-1}$. The volume injected was 1.0 µL, in splitless mode. The QqQ mass spectrometer was operated in electron ionization (EI) mode using the multiple reactions monitoring (MRM) mode with an emission current set at 20 µA.

Table 4.3: List of Targeted PAHs

| PAHs | Abbreviation | CAS number |
|---|---|---|
| Phenanthrene | Phe | 85-01-8 |
| Anthracene | Ant | 120-12-7 |
| Fluoranthene | Flu | 86-73-7 |
| *Pyrene* | Pyr | 129-00-0 |
| Chrysene | Chr | 218-01-9 |
| Benz[a]anthracene | BaA | 56-55-3 |
| Benzo[b]fluoranthene | BbF | 205-99-2 |
| Benzo[k]fluoranthene | BkF | 207-08-9 |
| Benzo[e]pyrene | BeP | 192-97-2 |
| Benzo[a]pyrene | BaP | 50-32-8 |
| Indeno[1,2,3-c,d]pyrene | I123cdP | 193-39-5 |
| Dibenzo[a,h]anthracene | DahA | 200-181-8 |
| Benzo[ghi]perylene | BghiP | 191-24-2 |

### 4.2.4 Quality Assurance and Quality Control

Unworn samples of each fabric type (n=5 for each fabric type) were prepared and analysed alongside laundering samples. The unworn samples were extracted and analysed in each batch of samples. These unworn samples were treated as travel blanks to ensure that the baseline contamination between fabric types would not affect interpretation of results. Method detection limits (MDL) were defined as the average blank concentrations plus three times their standard deviations (SDs). MDLs are presented in Tables S4.1 & S4.2. Duplicates of worn undergarments (n = 5) and duplicate samples fortified 100 μg with native standards (n = 5) were included in the analysis to assess the reproducibility of the analytical method. The average relative standard deviation (RSD) was calculated from duplicate samples and accuracy was calculated from native-fortified samples. The quality assurance and quality control results of are presented in SI.

### 4.2.5 Statistical Analysis

Statistical analysis was performed using XLSTAT (version 2019.3.2, Addinsoft, Paris, France) and GraphPad Prism (version 7.00, GraphPad Software Inc., La Jolla, CA). Paired two-tailed t-tests were used to assess the differences between pre- and post-laundering data. Statistical significance was set at $p < 0.05$. When concentrations of chemicals in datasets were < MDLs, half the method detection limit (MDL/2) was used.

## 4.3. Results and Discussion

The concentrations of PAHs measured in this study are summarised in Figures 4.1 – 4.3 as well as in the SI (Tables S4.3 – S4.23). Detection frequencies and ranges [%DF (min, max)] of individuals PAHs found across all post-burn items ($ng.g^{-1}$) were: Phe 88% (<MDL, 3600), Ant 64% (<MDL, 730), Flu 81% (<MDL, 2700), Pyr 81% (<MDL, 4000), BaA+Chr 59% (<MDL, 950), BbF+BkF 86% (<MDL, 900), BeP 79% (<MDL, 680), BaP 86% (<MDL, 1600), I123cdP 92% (<MDL, 210), DahA 70% (<MDL, 59), BghiP 82% (<MDL, 530). Results are presented as $ng.g^{-1}$ in relation to PAH(s) per garment material. For consistency and ease of interpretation, results have been presented as $\sum_{13}$ PAHs.

### 4.3.1 Contamination and Laundering Efficiency

Post-burn socks, briefs and crop tops had average concentrations for $\sum_{13}$ PAHs of 2600, 1200 and 470 $ng.g^{-1}$, respectively. Post-burn, socks ranged from $\sum_{13}$ PAHs of 570 $ng.g^{-1}$ to 12000 $ng.g^{-1}$, briefs from $\sum_{13}$ PAHs of 45 $ng.g^{-1}$ to 7600 $ng.g^{-1}$, and crop tops $\sum_{13}$ PAHs of 69 $ng.g^{-1}$ to 1400 $ng.g^{-1}$. These results are within ranges of concentrations previously measured (63 to 43000 $ng.g^{-1}$) in separate fire scenarios measuring the $\sum_{13}$ PAHs contamination of firefighter PPC (including shorts and t-shirts worn underneath) and the laundering efficiency of all items (Banks, Wang, Engelsman, et al., 2021).

Briefs and crop tops with fabrics consisting of predominantly cotton (Table 4.1) presented lower levels of post-burn contamination compared to garments made of entirely synthetic fabrics (polyester elastane briefs and nylon elastane crop tops). Post-laundering, the average concentration of $\sum_{13}$ PAHs on socks was significantly different ($p<0.05$) lowering from 2600 to 1700 $ng.g^{-1}$ (range $\sum_{13}$ PAHs of 410 $ng.g^{-1}$ to 7400 $ng.g^{-1}$) The concentration change of $\sum_{13}$ PAHs on briefs reduced from an average of 1200 to 1100 $ng.g^{-1}$ (range $\sum_{13}$ PAHs of 340 $ng.g^{-1}$ to 2600 $ng.g^{-1}$), which was not significantly different ($p<0.05$). The average concentration $\sum_{13}$ PAHs on crop tops after laundering was significantly different ($p<0.05$), increasing from 470 to 1200 $ng.g^{-1}$ (range $\sum_{13}$ PAHs of 320 $ng.g^{-1}$ to 3100 $ng.g^{-1}$) and equating to an average 160% increase in concentration. Prior research surrounding fire exposed firefighter hoods has demonstrated significant reduction in PAH contamination post laundering, with some evidence of cross contamination present within the laundering cycle that the authors determined did not present a meaningful risk of exposure (Mayer et al., 2019).

A significant decrease (paired t-test) in concentrations of $\sum_{13}$ PAHs ($p<0.05$) was measured across socks from all laundry loads, as well as individually in washing load 1. Crop tops, collectively, presented a significant increase ($p<0.05$) in the concentrations of $\sum_{13}$ PAHs (paired t-test) post-laundering, as well as individually in washing load 1, 2, 3 and 5. The average concentrations of $\sum_{13}$ PAHs on briefs made of cotton/elastane and crop tops made of nylon (92%) elastane (8%) both slightly increased post-laundering. Crop tops made of Cotton 95% Spandex 5% and a Cotton Elastane blend had significant ($p<0.05$) increases in the concentrations of $\sum_{13}$ PAHs post-laundering. Figure 4.1 presents the concentrations of ∑13 PAHs in firefighters' undergarments (ng.g$^{-1}$), wherein bars represent the average, whiskers represent the standard deviation of the results.

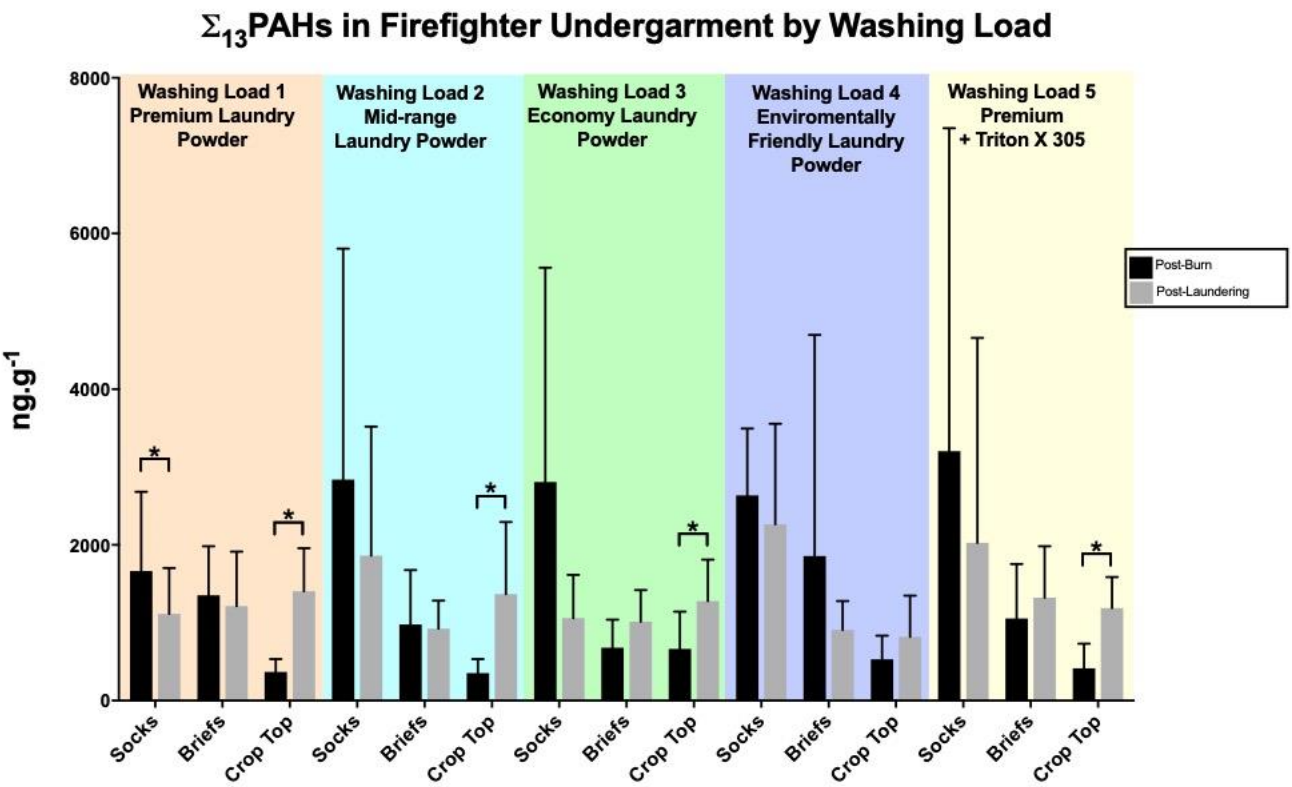


Figure 4.1: $\sum_{13}$ PAHs (ng/g) in Firefighters' Undergarments (socks, briefs and crop tops) worn during simulated burns by washing load using different detergents (1-5)

* denotes a significant difference between post-burn and post-laundering sample.

The significant ($p<0.05$) post-laundering decrease in ∑13 PAHs concentration in socks not observed in underwear and crop tops suggest the possibility of PAHs being re-distributed (cross-contaminated) during the laundering process. This appears particularly apparent in crop tops given their relatively lower post-burn contamination and significant ($p<0.05$) increase in $\sum 13$ PAHs post-laundering. These findings are in line with prior studies (Banks, Wang, Engelsman, et al., 2021) . Figure 4.2 presents the concentrations of $\sum 13$ PAHs in firefighters' undergarments grouped by fabric type ($ng.g^{-1}$), wherein bars represent the average, whiskers represent the standard deviation of the results.

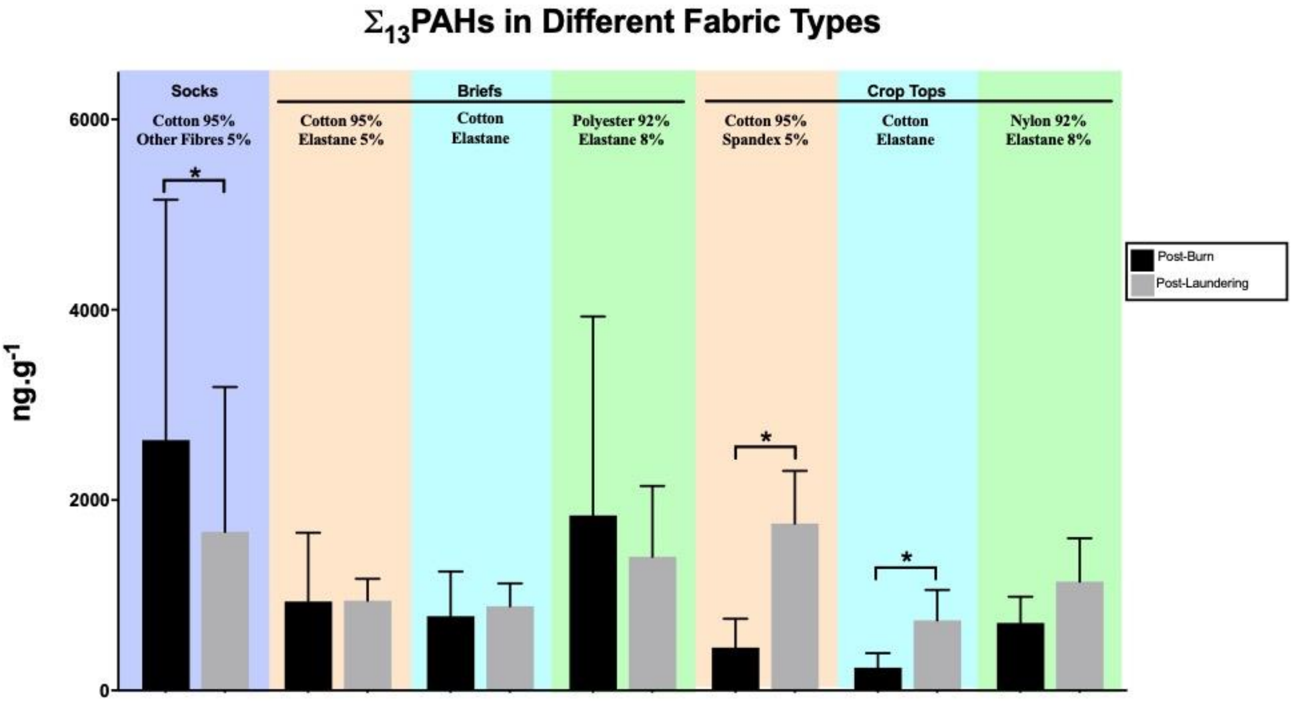


Figure 4.2: $\sum_{13}$ PAHs ($ng.g^{-1}$) by fabric type for socks, briefs and crop tops

* denotes a significant difference between post-burn and post-laundering sample.

Washing load 5 was washed with a mix of Premium and Triton X 305, which is noted as an unfeasible practice in home laundering. Overall, there did not appear to be a difference in the efficiency of detergents removing PAHs between the five laundering detergents trialled.

4.3.2 Cross-contamination during laundering

Fabric swatches were taken from the travel blanks used in this study and washed with the loads of laundering. All fabric swatches utilised for cross-contamination analysis demonstrated a significant post-laundering increase in the concentration of $\sum_{13}$ PAHs, with the exception to this were swatches of Nylon (92%) Elastane (8%) which had a much higher MDL and thus a low detection frequency. The magnitude of increase appears to be similar between fabric types. In line with our prior research (Banks et al. 2021), the swatches from the other three fabric types showed significant ($p<0.05$) post-laundering increases in the concentration of $\sum_{13}$ PAHs from <MDL to an average of 500 $ng.g^{-1}$. The increase in PAH concentration of these swatch was very similar to the increase in concentration of crop tops where the post-burn and post-laundering concentrations of $\sum_{13}$ PAHs were 470 and 1200 $ng.g^{-1}$ respectively.

Figure 4.3 provides a visual representation of the concentrations of $\sum_{13}$ PAHs in the swatches of unworn undergarments post laundering, presented by fabric type and laundry load, wherein bars represent the average, whiskers represent the standard deviation of the results..

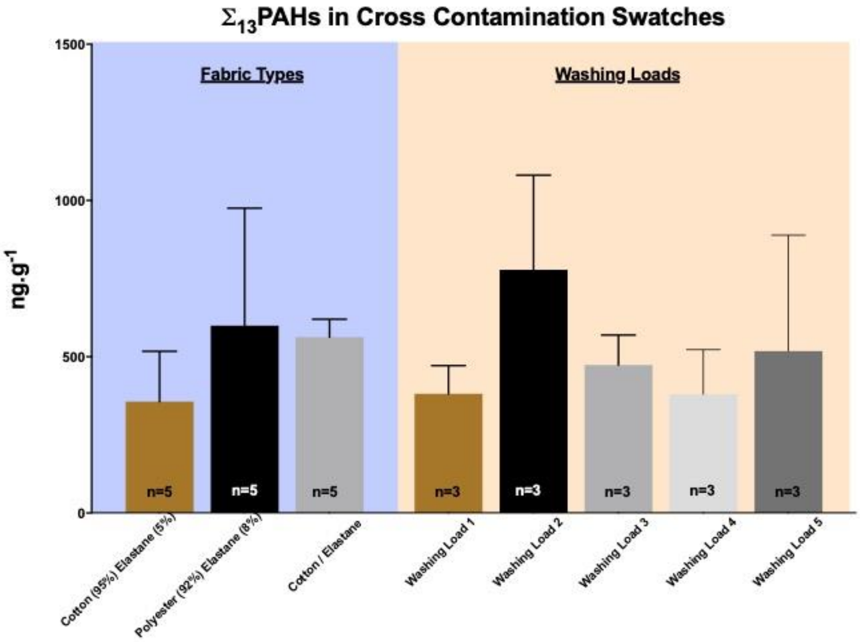


Figure 4.3: Concentrations of $\sum_{13}$ PAHs in the Swatches of Unworn Undergarments Post Laundering that were Utilised for the Assessment of Cross Contamination, Presented by Fabric Type and Laundry Load ($ng.g^{-1}$).

This data, when considered collectively across garments and fabric types, suggest that garments made of predominantly cotton (95% cotton or a cotton blend) may become less contaminated during fire suppression activities}. Post-laundering, the garments that were entirely synthetic (see Table 4.1) resulted in a higher average $\sum_{13}$ PAHs than cotton garments presented post-burn. This finding suggests firefighters may be better protected wearing undergarments of cotton than those of entirely synthetic materials, though more research specific to the fabrics would be required to confirm this suggestion (Brnada et al., 2022).

The results of this study suggest that cotton is more capable of being cleaned of PAHs, as shown in the significant ($p<0.05$) reduction on contamination of socks post-laundering. This; however, must be considered in line with what items are included in a laundry cycle. Post-burn the socks contained higher concentrations than other items. If highly contaminated post-burn items such as socks are washed with less contaminated post-burn undergarments, or with items not worn in a burn, there is the potential for cross contamination within the load of laundry. This may reduce the PAH concentration on a single item but re-distribute that concentration through the laundry load onto other items. This is likely how the increase in concentration of crop tops occurred, and these findings are in line with our prior research (Banks, Wang, Engelsman, et al., 2021).

The concentrations of PAHs measured in the wipe samples collected from the inside of a washing machine before and after loads of laundering were below the MDLs and have not been presented. This suggests that the drum washing machine itself did not become contaminated and may not be a source of contamination in subsequent loads of laundry.

### 4.3.3 Limitations and Considerations

We acknowledge there are limitations of this study. Firstly, the material burnt to simulate a compartment fire and the activities firefighters undertook during the fires may not be representative of real-world firefighting. Fabric type determination was limited to the manufacture label. Specific fabric construction has been found to impact the ability of contaminants to sorb and desorb from the fabric (Brnada et al., 2022), but determining such was outside the scope of this study. Cross-contamination was measured in the loads of laundering, although the types of fabric used in this study may not be representative of all fabric types with other fabrics potentially enhancing or reducing the amount of cross-contamination during laundering. In this study each item was only worn once, exposed to a single fire, thus does not determine the possibility of whether contamination may accumulate over multiple exposures, or whether the saturation point of PAHs on these undergarments was reached. Laundering each item once means it is unable to be determined if items would continue to change in PAH concentrations over subsequent laundering cycles and thus potentially continue to cross contaminate other items laundered with them. The bioavailability of PAHs on fabric remains unknown, as well as the role sweat and other factors may play in the dermal absorption of PAHs from undergarment. Due to this, the authors are unable to estimate what exposure firefighters may face though the dermal adsorption of PAHs from undergarments or at what concentration PAHs in undergarments begin to pose a health risk for firefighters. Given the health findings related to firefighters, further research is required in this area.

## 4.4. Conclusion

This study shows that PAHs can contaminate firefighters' undergarments including socks, briefs and crop tops when attending fire scenes. This study demonstrates that the home laundering of undergarments is not effective at removing PAHs. Furthermore, laundering can lead to a redistribution of PAHs from contaminated items to less or uncontaminated items during the laundry cycle. This study suggests the potential for the secondary contamination of items washed in a domestic washing machine with undergarments that have been worn at a fire scene. These findings suggest that higher contaminated items should be laundered individually, away from other items. The bioavailability of fabric-bound PAHs remains unknown; however, given the proximity of briefs and crop tops to high permeability regions of skin warrants further investigations. This study demonstrates that fire smoke can contaminate firefighter's undergarments and has the potential for secondary exposure by means of dermal absorption and the cross-contamination of other items during laundering. This study provides novel findings for firefighters and fire services suggesting the wearing of natural fibre undergarments and socks to reduce contamination, and the separate laundering of such items post fire incident exposure.

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The following publication is incorporated as Chapter 5:

Engelsman, M., Toms, L.-M. L., Wang, X., Banks, A. P. W., & Blake, D. (2021). Effects of firefighting on semen parameters: an exploratory study. *Reproduction and Fertility*, *2*(1), L13-L15. doi.org/10.1530/raf-20-0070

Utilising a simplified version of the Credit Authorship Statement:

Conceptualization: Michelle Engelsman, Xianyu Wang, Leisa-Maree Toms, Andrew Banks; Data curation: Michelle Engelsman; Formal analysis: Michelle Engelsman, Xianyu Wang, Leisa-Maree Toms, Andrew Banks, Debbie Blake; Funding acquisition: Michelle Engelsman; Investigation: Michelle Engelsman; Methodology: Michelle Engelsman, Leisa-Maree Toms; Project administration: Michelle Engelsman, Xianyu Wang, Leisa-Maree Toms, Andrew Banks, Debbie Blake; Resources: Michelle Engelsman; Validation: Michelle Engelsman, Xianyu Wang, Leisa-Maree Toms, Andrew Banks, Debbie Blake; Visualization: Michelle Engelsman, Debbie Blake; Writing original draft: Michelle Engelsman; Writing review & editing: Michelle Engelsman, Xianyu Wang, Leisa-Maree Toms, Andrew Banks, Debbie Blake.

# Chapter 5

Chapters 2-4 identified that firefighters face exposures both at fire stations, within fire appliances (vehicles), from personal protective clothing and equipment, and on items of clothing worn over highly permeable skin. As chapter 1 presented, a multitude of chemicals present within firefighting environments are able to potentially affect male fertility, and prior registry studies on male firefighters have demonstrated reduced fertility. Considering that, this chapter examines firefighter semen quality and whether firefighting as an occupation may be affecting firefighter fertility. This exploratory study presents a global first analysis of male firefighter fertility through biomonitoring, and demonstrated the reduced semen quality and fertility of the cohort of firefighters included. This data is then considered in line with survey results around reproductive history, rank, and exposure. Although no associations between firefighting and fertility are directly drawn from this limited exploratory study at firefighters' semen, it suggests that more research in this area is required, and provides important and previously unkonwn insight into the understanding of male firefighters, exposure and fertilty. The following publication has been incorporated as Chapter 5.

**Effects of Firefighting on Semen Parameters: An Exploratory Study**

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5.1. Research Letter:

Firefighters are occupationally exposed to heat intensities and chemical concentrations that are known to affect fertility. As part of a wider study on firefighter exposure and reproduction, firefighters were recruited to contribute a semen sample to (1) evaluate semen parameters against fertility standards and other cohorts (2) assess demographic, exposure and reproductive history against semen analysis results, and (3) consider how occupational exposures may affect semen parameters. Of the 185 firefighters that consented via an online survey, 20 firefighters contributed 23 semen samples at specified pathology centres. Analysis of the semen samples included assessment of viscosity, liquefaction, agglutination, volume, sperm concentration, progressive motile, total motile, immotile, and normal forms.

Sample data were checked for completeness, consistency, accuracy and validity. Descriptive statistics were performed to summarise the data. Pearson's correlations (2-tailed) were used to investigate the relationship between firefighter survey results and sample characteristics. Demographic data for participants in the semen exploratory study are presented in Table 5.1.

**Table 5.1: Characteristics of Participants in Semen Exploratory Study**

| Characteristic | *n* |
|---|---|
| Total Participants | 20 |
| Age Mean* ± standard deviation | 45±10 |
| Age <45 | 11 |
| Age ≥45 | 9 |
| Active Duty (Current Fire Exposure) | 18 |
| Rank Firefighter | 18 |
| Rank Station Officer/Captain | 2 |
| Full-time Firefighter | 16 |
| Part-Time Firefighter | 4 |
| Years in Job Mean* ± standard devation | 20±10 |
| Tobacco Smoker | 0 |
| Successfully conceived at least one child | 15 |
| Unable to conceive in one or more attempts | 1 |
| Difficulty conceiving: | 6 |
| Unknown cause | 4 |
| Abnormal semen parameters | 1 |
| Hormone imbalance | 1 |
| Underwent IVF in any instance | 4 |
| Reported time to pregnancy (TTP) | 7 |
| ≤12 months | 5 |
| >12 months | 2 |
| Experienced miscarriage(s) | 3 |
| Negative pregnancy or birth outcomes including: miscarriage, still birth, pre-term birth, low birth weight, astigmatisms, attention deficit hyperactivity disorder (ADHD), club foot, dyspraxia, and asthma. | 7 |

* Age and duration of employment data was collected in 5-year increments (employment had one option of <1 year). To calculate the crude mean the midpoint of each bracket was utilised.
** This data is from firefighters self-reporting via the Stage 1 survey

Data were stratified by age (<45 and ≥45 years of age) based around research demonstrating statistically significant reductions in semen and sperm parameters for men in increasing age brackets above 45 years of age (Hellstrom et al., 2006; Stone et al., 2013). Younger participants (<45y) presented non-significant mean decreases in total motility (50% vs 61%), rapid progression (40% vs 53%) and morphology (8.7% vs 12%) when compared with those ≥45y. Frequency of exposure (≤weekly vs >weekly) was associated with non-significant mean decreases in morphology (7.8% vs 12%), volume (2.2 mL vs 2.8 mL), sperm concentration (80 M/mL vs 87 M/mL) and total sperm count (150 M/ejaculate vs 220 M/ejaculate). Age stratified data, including World Health Organisation (WHO) reference values for fertility has been included in Table 5.2.

**Table 5.2: Firefighter Semen Parameters ($5^{th}$-$50^{th}$-$95^{th}$ Percentile) Stratified by Age**

| Cohort | Total Motility (%) | Progressive Motility (%) | Normal Forms (%) |
|---|---|---|---|
| Firefighters <45 | 32, 49, 69 | 14, 43, 62 | 2.7, 8.5, 17 |
| Firefighters ≥45 | 46, 57, 86 | 36, 48, 79 | 3.5, 11, 28 |
| All Firefighters | 34, 55, 73 | 16, 46, 72 | 3.1, 9.5, 21 |
| (WHO, 2010) | 40, 61, 78 | 32, 55, 72 | 4, 15, 44 |

Overall, firefighter semen parameters were below the upper medium and low WHO reference values for fertile men, in numerous categories, with more pronounced differences present in the <45y age cohort. Positive correlations ($p<0.05$) in semen quality were found across semen parameters with increased rank, occupational and personal hygiene. Negative associations were detected for normal forms, volume, sperm concentration and total sperm count with increasing frequency of fire exposure. Sperm agglutination was >10% in 26% of samples.

This is the first investigation to be published on Australian Firefighter sperm quality. Internationally, studies exist on firefighter reproductive history, with suggested links to toxic work (Petersen et al., 2019). There is however a scarcity of data on firefighter semen parameters. This highlights the practical difficulties in obtaining semen samples for altruistic research purposes, due to a variety of factors including embarrassment, inconvenience and lack of motivation, especially where feedback about the results are not permitted. The attrition from 189 interested participants down to 20 participants is testament to the inherent challenges that investigators face in such studies. This exploratory study provides novel data that supports the hypothesis that there is indeed an association between semen quality and firefighter's occupational exposure to toxic environments. These results will add value to the design of a well powered and targeted investigation aimed at maintaining and improving the health and well-being of firefighters, their families and offspring.

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The following submitted publication is incorporated as Chapter 6:

Engelsman, M., A. P. W. Banks, C. He, S. Nilsson, D. Blake, A. Jayarthne, Z. Ishaq, L.-M. L. Toms and X. Wang (2023). "An Exploratory Analysis of Firefighter Reproduction through Survey Data and Biomonitoring." International Journal of Environmental Research and Public Health **20**(8): 5472

Utilising a simplified version of the Credit Authorship Statement:
Conceptualization: Michelle Engelsman, Xianyu Wang, Leisa-Maree Toms, Andrew Banks; Data curation: Michelle Engelsman, Andrew Banks, Chang He, Ayomi Jayarathne, Sandra, Nilsson, Debbie Blake, Leisa-Maree Toms, Xianyu Wang; Formal analysis: Michelle Engelsman, Andrew Banks, Chang He; Funding acquisition: Michelle Engelsman; Investigation: Michelle Engelsman, Andrew Banks, Chang He, Ayomi Jayarathne, Sandra, Nilsson, Debbie Blake, Leisa-Maree Toms, Xianyu Wang; Methodology: Michelle Engelsman, Leisa-Maree Toms, Xianyu Wang; Project administration: Michelle Engelsman, Leisa-Maree Toms, Xianyu Wang, Andrew Banks; Resources: Michelle Engelsman, Andrew Banks, Chang He, Ayomi Jayarathne, Sandra, Nilsson, Debbie Blake, Leisa-Maree Toms, Xianyu Wang; Software: N/A; Supervision: Xianyu Toms, Leisa-Maree Toms; Validation: Michelle Engelsman, Andrew Banks, Chang He, Ayomi Jayarathne, Sandra, Nilsson, Debbie Blake, Leisa-Maree Toms, Xianyu Wang; Visualization: Michelle Engelsman; Writing original draft: Michelle Engelsman; Writing review & editing: Michelle Engelsman, Andrew Banks, Chang He, Ayomi Jayarathne, Sandra, Nilsson, Debbie Blake, Leisa-Maree Toms, Xianyu Wang.

# Chapter 6

All chapters thus far in this overall investigation supported the initial assertion of occupational exposurers due to firefighting. Chapters 1&2 identified routes of exposure as well as the broad range of chemicals biomonitored in firefighters and considered due to occupational exposure. Chapters 3&4 determined routes of indirect exposure for firefighters, including at fire stations as well as on personal items worn under firefighter personal protective clothing. Chapter 5 presented that the cohort of firefighters in the exploratory study encompassing semen analysis had parameters below World Health Organsation fertility standards, in line with prior registry studies on male firefighter denoting reduced fertility likely due to occupation.

Chapter 6 further examines semen quality findings associated with chemical concentrations measured in biological samples (i.e. blood and urine) and ties this data together through a literature review surrounding male repoductive health and chemical exposure. It then expands risks around occupational exposure to encompass female firefighter exposure and reproductive health through analysis of chemical concentrations in blood and urine, and through the introduction of chemical concentrations within breast milk – an integral stage in female reprodcutive with implications related to the health of the mother (WHO 2023).

With research on firefighters often excluding females due to limited participants, this study presents important data on female firefighter results in blood, urine and breast milk, linking to survey data on reproductive history. This chapter is the culmination of work surrounding the investigation of firefighter exposure and the potential effects on reproduction, and demonstrates that there exists a potential for firefighting to affect reproduction. Chapter 6 also presents means by which firefighters may reduce their exposure. The following publication is incorporated as Chapter 6

An Exploratory Analysis of Firefighter Reproduction through Survey Data and Biomonitoring

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**Abstract:** Firefighters are occupationally exposed to chemicals that may affect fertility. To investigate, firefighters were recruited to contribute blood, urine, breast milk or semen samples to: (1) evaluate chemical concentrations and semen parameters against fertility standards and the general population, (2) assess correlations between chemical concentrations and demographics, fire exposure and reproductive history, (3) consider how occupational exposures may affect reproduction. 774 firefighters completed the online survey, 97 firefighters produced 125 urine, 113 plasma, 46 breast milk and 23 semen samples. Blood, urine, and breast milk samples were analysed for chemical concentrations (semivolatile organic compounds, volatile organic compounds, metals). Semen samples were analysed for quality (volume, count, motility, morphology). Firefighter semen parameters were below WHO reference values across multiple parameters. Self-reported rates of miscarriage were higher than the general population (22% vs 12-15%) and in line with prior firefighter studies. Estimated daily intake for infants was above reference values for multiple chemicals in breast milk. More frequent fire incident exposure (more than once per fortnight), longer duration of employment (≥15yrs), or not always using breathing apparatus demonstrated significantly higher concentrations across a range of investigated chemicals. Findings of this study warrant further research surrounding the risk occupational exposure has on reproduction.

## 6.1. Introduction

Firefighters are occupationally exposed to chemical hazards at fire incidents, within vehicles and fire stations, and through use of contaminated equipment. Even with high levels of personal protective clothing and equipment, chemical exposure still occurs through dermal absorption, inhalation due to off-gassing equipment post fire exposure, inhalation when reduced levels of breathing protection are employed during fire suppression, and subsequent exposure through various routes due to cross contamination (Alexander and Baxter 2016, Easter, Lander et al. 2016, Engelsman, Snoek et al. 2019, Banks, Engelsman et al. 2020, Engelsman, Toms et al. 2020). A recent review has investigated the potential exposures and health effects of a range of chemicals, including some reproductive and developmental effects (Barros, Oliveira et al. 2023). Reproductive toxins and endocrine disrupting chemicals (EDCs) firefighters face occupationally include metals and semivolatile organic compounds (SVOCs) such as polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organophosphate esters (OPEs), volatile organic compounds (VOCs), per- and polyfluoroalkyl substances (PFAS), phthalates and organochlorine pesticides (OCPs) (Annamalai and Namasivayam 2015, Ponsonby, Symeonides et al. 2016).

In men, such chemicals have been found to impair spermatogenesis, reduce semen quality, induce sperm DNA damage, affect endocrine levels in exposed men, and increase the risk of offspring childhood brain and astroglial tumours (Cordier, Monfort et al. 2004, Jurewicz, Radwan et al. 2013, Albert, Huang et al. 2018, Mima, Greenwald et al. 2018). For females, SVOCs have presented negative associations with fertility, timing of partition, preterm birth, birth weight and size, and increased pregnancy loss (Padula, Noth et al. 2014, Valvi, Oulhote et al. 2017). They have also been found to affect the endocrine markers of ovarian function, increase the risk of premature ovarian dysfunction and lead to early onset menopause, (Lefevre, Wade et al. 2016, Peng, Ji et al. 2016, Ruark, Song et al. 2017). SVOCs and metals are known to pass through the placenta and breast milk, though there remains limited data related to developmental effects (Nickerson 2006, Al-Saleh, Alsabbahen et al. 2013, Oliveira, Duarte et al. 2020, Bhardwaj, Paliwal et al. 2021, Liu, Xie et al. 2022).

Data is limited with regards to the potential for additive, synergistic or antagonistic effects of multiple chemical exposures on reproduction. Researchers have subsequently called for additional work to be done in this area to better understand the health impacts, particularly with regards to long term health of developing foetuses (Wilkinson, Christoph et al. 2000, Mori 2003, Koppe, Bartonova et al. 2006, Hernández, Gil et al. 2014, Govarts, Remy et al. 2016).

Although increasingly research has focused on firefighter exposure through human biomonitoring (health related monitoring through body fluids such as blood, urine, breath and hair to determine levels of exposure to environmental pollutants), to our best knowledge only two previous studies have utilised biomonitoring to assess aspects of firefighter reproduction (Engelsman, Toms et al. 2021, Jung, Beitel et al. 2023). Studies examining the potential for firefighter reproductive dysfunction due to occupation have predominantly been by means of survey or through assessing occupation and fertility registries for individuals involved, with no epidemiological studies having been undertaken (Aronson, Dodds et al. 1996, Chia, Shi et al. 2002, Jahnke, Poston et al. 2018, Petersen, Hansen et al. 2019, Siegel, Rocheleau et al. 2022).

This biomonitoring and reproduction study sits within a greater study considering firefighter exposure. The aims of the current study are to: (1) evaluate chemical concentrations and semen parameters against fertility standards and the general population, (2) assess correlations between chemical concentrations and demographics, fire exposure and reproductive history, (3) consider how occupational exposures may affect reproduction. Much of the literature surrounding firefighter exposure has pertained to male firefighters due to limited access to female firefighters, or women representing a small fraction of the cohort studied and therefore excluded (Jahnke, Poston et al. 2018, Barros, Oliveira et al. 2023). The current study has been shaped around increasing inclusion opportunities for women to ensure a more balanced presentation of male and female firefighters in health studies.

## 6.2. Materials and Methods

### 6.2.1 Survey

Ethics approval was granted through The University of Queensland (#2017000255). To engage in the study, firefighters completed an online consent form and subsequent detailed survey capturing information relating to demographics, exposure, employment, and reproduction. Firefighters were invited to contribute biological samples (blood & urine, breast milk or semen), and those who did were instructed to complete a further post contribution study surrounding their most recent fire exposure(s) (i.e. what type of fire incident was attended prior to the sample collection). Participants who elected to provide a biological sample were provided with code names to protect their identity from that point forward. Participants were requested to provide a single sample although some offered to contribute multiple samples within the study period. Further details are available in Appendix 4.

### 6.2.2 Sample Collection

A group of pathology companies with collection centres in urban, regional, and outer regional locations were engaged to collect samples due to the group's flexibility in coordinating and supporting a geographically broad anonymous study. 97 Firefighters contributed blood (n=113), urine (n=125) and semen (n=23) samples via the pathology centres, and breast milk (n=46) samples at home. Firefighters were not required to provide samples in combination, though paired sample contributions were requested (primarily blood and urine, though semen and breast milk contributions were requested to be paired with blood and urine where possible). All blood contribution were provided with a paired urine sample, 12 urine samples were provided in isolation by six firefighters. Nineteen of the 20 men who provided semen samples also provided blood and urine samples, one provided semen in isolation. Twenty-seven breast milk samples were provided in isolation, with 17 paired with blood and urine. Four breast milk samples were collected in 2016 as a pilot study analysis, and all other samples were collected between March 2018 and July 2021 (blood, urine, semen and breast milk). Further detailed information surrounding the collection of samples is provided in Appendix 4.

### 6.2.3 Chemical Analysis

This paper reports on the results of 1-hydroxypyrene (1-OH-PYR), metals and VOCs analysed at the SafeWork NSW Chemical Analysis Branch TestSafe Laboratory (TestSafe) and 1-, 2- hydroxynaphthalene (1-, 2-, OH-NAP), 2-, 3-, hydroxyflourene (2-, 3- OH-FLU), 1-, 2-, 4-, 9- hydroxyphenanthrene (1-, 2-, 4-, 9- OH-PHEN), OPEs, phthalates, PBDEs and PFAS analysed at the Queensland Alliance for Environmental and Health Sciences (QAEHS) at the University of Queensland. Details surrounding analytical methods utilised (links to methods published elsewhere), limits of detection, matrix, and the list of individual target analytes can be found in Table S6.1 in Appendix 4.

### 6.2.4 Statistical Analysis

Data were analysed using IBM SPSS Statistics Version 27, Microsoft Excel 2016, GraphPad Prism 9, and Statistics Kingdom 2017. Sample data were checked for completeness, consistency, accuracy, and validity. Exclusions were made for selected analyses if data sets were missing or uncertain. Descriptive statistics were performed to summarise the data. Pearson's correlations (2-tailed) were used to investigate relationships in normally distributed survey data. Correlations with p-values lower than 5% ($p<0.05$) were designated statistically significant. Due to non-normal distributions in biomonitored data, Mann-Whitney U tests were used when comparing biomonitored results from groups between firefighters within the study separated by characteristics such as gender, frequency of exposure, type of fire exposure (structure, vehicle, rubbish, wildfire, etc), duration of employment, and others as normal distribution was not observed. During statistical analysis, analytes below the limit of detection (LOD) and limit of quantitation (LOQ) were estimated as the LOD or LOQ divided by two. LOQs were provided by TestSafe NSW, LODs by QAEHS. Rather than reduce sensitivity in analysis by utilizing LOQ from QAEHS (as LOD from TestSafe was not available), the use of LOQ or LOD was determined appropriate depending on laboratory preforming analysis. Only chemicals with a detection frequency of >50% were included in statistical analyses. When comparing this study with average results from other studies reporting on pooled sample results (without the inclusion of creatinine concentrations), the creatinine concentration of $1.304 g.L^{-1}$ was utilised (Barr, Wilder et al. 2005). This provided only an estimate and did not allow for the variability of creatinine, so caution must be applied when considering results.

## 6.3. Results & Discussion

### 6.3.1 Characteristics of Participants

A total of 774 firefighters completed the online survey collecting data surrounding demographic, employment, exposure, and reproductive history. 97 contributed biosamples resulting in 125 urine, 113 blood, 46 breast milk and 23 semen samples. Of those who contributed biosamples, 59 provided reproductive history data including pregnancy and birth outcomes. Of those who completed the survey only, 382 provided reproductive history data. Reproductive history was only sought from those who selected that they had attempted to have children since becoming firefighters.

There were no statistically significant differences between firefighters in the “contributed a biosample” group vs “survey only” with regards to frequency of exposure or use of self-contained breathing apparatus (SCBA) in any of the following: working structure fires (internal); external fire suppression; overhaul; and vehicle fires. The survey only group presented non-significant lower percentages (range 2-5%) with regards to always wearing SCBA across fire types than the group who contributed. As such, the 97 participants who contributed biosamples were used to represent the characteristics of firefighters involved in this study.

#### 6.3.1.1 Surveyed Firefighter Reproductive History

Characteristics and self-reported reproductive history of those who had or attempted to have children since becoming a firefighter are presented in Table 6.1.

Table 6.1: Firefighter Fertility Experiences Reported via Online Survey

| | Contributed a Biosample | | Survey Only | |
|---|---|---|---|---|
| Characteristic | n | % | n | % |
| Total Participants | 97 | | 677 | |
| Male | 64 | | 546 | |
| Female | 33 | | 131 | |
| Age Mean* ± Standard Deviation | 44±11 | | 43±11 | |
| Active Duty (Current Fire Exposure) | 91 (94%) | | 546 (81%) | |
| Years served Mean* ± Standard Deviation | 25±8.5 | | 17±11 | |
| Tobacco Smoker** | 3 (3.1%) | | 48 (7.1%) | |
| Reported on fertility (% of total surveys in group) | 59 | 61% | 382 | 56% |
| Naturally conceived at least one child | 53 | 90% | 325 | 85% |
| Unsuccessful at conceiving | 4 | 7% | 36 | 9% |
| Unknown cause | 11 | 19% | 29 | 8% |
| low sperm count | 1 | 2% | 20 | 5% |
| abnormal sperm | 0 | 0% | 7 | 2% |
| didn't ovulate | 1 | 2% | 8 | 2% |
| didn't menstruate | 0 | 0% | 1 | 0% |
| hormone imbalance*** | 1 | 2% | 3 | 1% |
| other | 0 | 0% | 6 | 2% |
| Miscarriage**** | 14 | 24% | 91 | 24% |
| Still Birth | 0 | 0% | 5 | 1% |
| preterm birth | 3 | 5% | 25 | 7% |
| gestational diabetes | 3 | 5% | 10 | 3% |
| low birth weight | 3 | 5% | 12 | 3% |
| high birth weight | 1 | 2% | 4 | 1% |
| spina bifida | 1 | 2% | 2 | 1% |
| congenital heart abnormalities | 0 | 0% | 4 | 1% |
| club foot | 1 | 2% | 2 | 1% |
| hydrocephalus, Duane Syndrome, autism spectrum disorder, other neural tube defects | 0 | 0% | 2 | 1% |
| other physical disabilities | 1 | 2% | 6 | 2% |
| other | 5 | 8% | 31 | 8% |
| No, none of these | 31 | 53% | 252 | 66% |

Other negative birth outcomes reported included (maximum of one firefighter per group, but could involve multiple children by that individual): cleft pallet, gastroschisis, astigmatisms, attention deficit disorder, hyperactivity disorder, dyspraxia, craniosynostosis, childhood cancer, hyper twisted umbilical cord, dyslexia, encephalocele, cerebral palsy, down syndrome, Trisomy 13, diabetes, oculocutaneous albinism, migraines, tongue tied and jaundice

* Age and duration of employment data was collected in 5-year increments (employment had one option of <1 year). To calculate the crude mean the midpoint of each bracket was utilised.

** The data of three tobacco smokers excluded in all chemical analysis of biosamples to ensure consistency across analysis and remove potential for confounding factors

*** hormone imbalance was reported in both male and female responses.

**** Miscarriage and multiple miscarriage were two survey options, and some firefighters selected both. To calculate estimated total rate of miscarriage the number of reported miscarriages was added to the number of reported multiple miscarriages, and only one instance was included if both were selected.

This study was not specifically designed to compare fertility rates or the overall fecundity of firefighters with the general population (Smarr, Sapra et al. 2017). However, we can report that all respondents who provided details of their fertility in Table 2, 441 had attempted a pregnancy of which 86% (n=378) conceived at least one live birth and 9.0% (n=40) were unsuccessful in conceiving. More detailed data would be required to determine how the fertility rates of this occupational cohort compares with the general Australian population. For example, to obtain such data, this survey would have required questions such as time to pregnancy (TTP) and data relating to their partner's or fertility treatment, which was outside the scope of this study. The Fertility Society of Australia and New Zealand report that approximately 17% of Australian couples are likely to experience infertility, which is defined as unable to achieve a pregnancy within 1 year of unprotected intercourse; however, for many of those infertility can be treated through intervention (FSANZ).

The rates of miscarriage across all pregnancies reported was 24%, taken from survey answers from both female and male firefighters. Rate of miscarriage by gender warrants consideration as there is a well-established association of pregnancy loss in men with elevated sperm DNA fragmentation as a consequence of several known factors, one of which is exposure to environmental factors (Robinson, Gallos et al. 2012). Male firefighters reported a miscarriage rate of 24% and female firefighters reported a miscarriage rate of 22%. These values exceed the estimated rate of miscarriage for women (12-15%) in the general population, with no known comparable value for men (Jeve and Davies 2014). These results are in line with rates of miscarriage noted by female firefighters in the United States (Jahnke, Poston et al. 2018).

The remaining 333 survey respondents consisted of those of unknown fertility status, having not intentionally planned a conception since employment as a firefighter. It is relevant to note that while the mean age of respondents is 43y, this dataset may encompass firefighters who have yet to plan a pregnancy, and those who have definitively chosen not to.

### 6.3.2. Exploratory Analysis into Firefighter Semen

Between 2018-2021, twenty men contributed 23 semen samples and 21 blood and urine samples within 2 weeks of the associated semen samples (16 of which were provided on the same day). This section is an extension of findings previously published in a brief research letter related to the current study (Engelsman, Toms et al. 2021).

Semen data were stratified by age (<45 and ≥45 years of age) based around research demonstrating statistically significant reductions in semen and sperm parameters for men in increasing age brackets above 45 years of age (Hellstrom, Overstreet et al. 2006). In this study, younger participants (<45y) presented non-significant lower mean motility (50% vs 61%), lower rapid progression (40% vs 53%) and reduced normal morphology (8.7% vs 12%) when compared with those ≥45y. Increased frequency of exposure to fire (at least one fire each week verses frequency of fire exposure being greater than each week) was associated with non-significant mean decreases in morphology (7.8% vs 12%), volume (2.2 mL vs 2.8 mL), sperm concentration (80 M/mL vs 87 M/mL) and total sperm count (150 M/ejaculate vs 220 M/ejaculate).

Pearson's correlations demonstrated significant positive correlations ($p<0.05$) between semen quality and age, rank (firefighter vs Officer), and occupational hygiene (including use of breathing apparatus, frequency of handwashing, showering post-fire, and laundering of personal protective equipment). Increased frequency of laundering, the wearing of breathing apparatus during fire suppression and overhaul and showering post incident were all found to have positive effects on semen quality ($p<0.05$). Three firefighters contributed more than one semen sample. These men experienced 10%-88% differences in their own semen parameters. Existing literature has reported an elevated risk of male infertility in firefighters compared with references group (Petersen, Hansen et al. 2019). Although the assessment in this study cannot determine any causal relationships between semen quality and occupational factors, our findings warrant further research.

Twenty six percent of semen samples had sperm concentration, motility and/or morphology value(s) below WHO reference values. This value increased to 42% for those under 45 years of age and decreased to 9% for semen samples from firefighters ≥45 years of age. Findings related to percentage of firefighters with one or more parameter (sperm concentration, motility and/or normal forms) falling below WHO Reference values, with age stratification, are presented in Figure 6.1.


Figure 6.1: Semen Samples with Combined Parameters Below WHO Reference Values for Fertile Men

The prevalence of sperm agglutination, an occurrence wherein motile sperm adhere to each other, was found to be higher in the current study than other published cohorts as shown in Table 6.2. The rate of sperm agglutination was higher in the younger firefighter cohort.

Table 6.2: Presence of Sperm Agglutination

| Study | Cohort | *N* | Rate of Agglutination: |
|---|---|---|---|
| This Study | Total Firefighters | 23 | 26% |
| This Study | Age <45 Years | 12 | 33% |
| This Study | Age ≥45 Years | 11 | 18% |
| (Arora, Sudhan et al. 1999) | Infertile men age 20-50 | 100 | 18% |
| (Berger, Smith-Harrison et al. 2019) | All men via reproductive centre, age not defined | 1095 | 12% |

Seminal volume is known to reduce with age so it was not unexpected to see that the ≥45y group lower than the WHO standards, however it was unexpectedly low in the younger cohort (Sengupta 2015). In contrast to well established paradigms regarding semen quality and aging (Hellstrom, Overstreet et al. 2006, Stone, Alex et al. 2013), this study shows a trend towards higher sperm quality in older participants. This may be associated with older firefighters within this study self-reporting as having an overall lower frequency of fire exposure.

No significant correlations were found between semen parameters and individual chemical concentrations in blood and urine. This may be due to the potential additive and/or interactive effects of the mixture of chemicals firefighters are exposed to, confounding interpretation when considering relationships between seminal parameters and single chemicals (Sharpe 2010).

When blood and urine chemical concentrations for firefighters who contributed semen were compared with men who did not contribute semen, very few significant differences ($p<0.05$) were found across the nearly 100 individual chemicals monitored. The few that were found were in urine and include: 1-hydroxy-2-propyl bis(1-chloro-2-propyl) phosphate (BCIPHIPP) (semen median 1.9 µg/g creatinine vs non-semen 1.2 µg/g creatinine); copper (Cu) (semen median 4.3 µg/g creatinine vs non-semen 2.0 µg/g creatinine); dimethyl arsinic acid (DMA) (semen median 2.0 µg/g creatinine vs non-semen 0.72 µg/g creatinine); arsenobetaine (semen median 48 µg/g creatinine vs non-semen 71 µg/g creatinine). Some other differences in medians were noted; however, statistical analysis was not run as one groups or both was below 50% detection frequency. Male firefighters contributing semen were therefore considered statistically similar to male firefighters, and reproductive effects of chemical concentrations is grouped as male and covered in 3.4 Blood & Urine Analysis.

### 6.3.3. Exploratory Analysis into Firefighter Breast Milk

46 samples were produced from 15 lactating firefighters. Six women contributed at least two samples, five of which contributed samples after fire incident exposure. An initial analysis was done on four firefighter breast milk samples contributed in 2016, the other samples were contributed between 2018 and 2020 and analysed in 2022. Between the two analysed sets of samples there were different limits of detection due to changes in instrumental procedures, and as such year of analysis will be noted where relevant.

#### 6.3.3.1 Exploratory Analysis of Chemicals in Breast Milk

When compared with other Australian data reporting on medians concentration in breast milk (Chen, Wang et al. 2015), median firefighter concentrations were higher with regards to the following: 22’44’5-Pentabromodiphenyl ether (BDE-99) (1.1 ng/g lipid, 0.33 ng/g lipid), 22’44’6-Pentabromodiphenyl ether (BDE-100) (0.64 ng/g lipid, 0.57 ng/g lipid), mirex (0.23 ng/g lipid, 0.12 ng/g lipid), (Table S2 for breast milk results). Median and 95th % levels of tributyl phosphate (TnBP), Tris(2-chloroethyl) phosphate (TCEP), Tris(2-chloroisopropyl) phosphate (TCIPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) in breast milk far exceeded levels found in 105 women in Beijing (Chen, Zhao et al. 2021). For a full list of chemicals analysed in breast milk, see Table S2, Appendix 4.

22’44’-Tetrabromodiphenyl ether (BDE-47) was the dominant congener in both plasma and breast milk. Significant differences were noted with regards to frequency of exposure, with more frequent exposure presenting elevated concentrations of BDE-47, pp-DDE and PCB153 compared with less frequent exposure (see Appendix 4, section S6.4 Breast Milk).

Five firefighters provided breast milk samples following two separate fire exposures each, with varying concentrations of chemicals in breast milk suggesting fire exposure may be affecting depuration. For samples provided at 24hr intervals post fire exposure, a short period of intense fluctuation appeared to follow fire exposure for BDE-47, 22’44’55’-Hexabromodiphenyl ether (BDE-153), TiBP, TCIPP, 2,2’,4,4’,5,5’-hexachlorobiphenyl (PCB153), 2,3,3’,4,4’,5-hexachloro-1,1’-biphenyl (PCB156), and 2,2’,3,4,4’,5,5’-heptachlorobiphenyl (PCB180). This could be denoting a short period of intense depuration, it could be related to contamination during sample collection although all procedures possible to prevent such contamination were carried out, or it could be due to uncertainties around the analysis of these compounds from complex matrices such as breast milk. This pattern was not observed for other analysed groups recording levels above LOD including TCEP, or OCPs. Graphical representation for fluctuations in breast milk for BDE-47, BDE-153, PCBD153 and PCB156 are included in Figures S1-S4.

While some studies have found that not all breastfeeding women demonstrate decreases in chemicals (Hooper, She et al. 2007, LaKind, Berlin et al. 2009), with other studies demonstrate the stability or general depuration over time for many POPs (Thomsen, Haug et al. 2010, Bramwell, Fernandes et al. 2014, Harrad and Abdallah 2015). A single prior research study on lactating firefighters in the United States monitoring PBDE concentration and aryl hydrocarbon receptor (AhR) activation found individual variation without consistent pattern, and no significant difference among firefighters following fire exposure (Jung, Beitel et al. 2023). Outside of the current study, no prior studies have monitored lactating women experiencing sporadic, acute exposure over an extended period including multiple exposures, which may be particularly of note given the intensity and duration of exposure is likely playing a role in contamination levels.

Although it was outside of capacity to test collected breast milk for PAHs, given the elevated levels across the PAHs in firefighters it is worth noting potential risks. Urinary 1-hydroxynaphthalene (1-OH-NAP) has been associated with breastmilk, with a 10% increase in 1-naphthol associated with a 1.6% increase in naphthalene in breast milk (Wheeler, Dobbin et al. 2014). Both metabolized and unmetabolized PAHs have been found in the breastmilk of lactating Portuguese women, with phenanthrene and naphthalene (and their metabolites) being amongst the major compounds (Oliveira, Duarte et al. 2020). PAHs are included in the international list of endocrine-disrupting substances (WHO 2015), so care should be taken to reduce exposure, where possible.

6.3.3.2. Exploratory Analysis of Child Health Effects

To understand the contamination of breastmilk in relation to potential child health effects an assessment of the potentially daily intake for an infant (0-6 months) is conducted. This age bracket was selected based around the higher potential for exclusive breast feeding. The calculation of estimated daily intake (EDI) utilized is shown in Equation 6.1 Estimated Daily Intake Calculations:

$$EDI = (C_{BM} \times V_{BM}) / BW$$

where $C_{BM}$ is the concentration for the selected chemical in breast milk, $V_{BM}$ is the average infant daily intake of breast milk, and BW is the average body weight for an infant 0-6 months. For comparison with reference doses (RfD), estimated daily intake (EDI) (ng/kg/day) was calculated using average values of 925mL of milk per day, and an average infant weight of 5.8kg (WHO 2006, Marks 2015).

Several EDI’s were found to be above RfD (see Table 3): BDE-47 (median & 95$^{th}$ %), BDE-99 (median & 95$^{th}$ %) BDE-153 (95$^{th}$ %), TCEP (95$^{th}$ %), TCIPP (median, 95$^{th}$ %), Tris(2-butoxyethyl) phosphate (TBOEP) (median, 95th %) and Tris(2-ethylhexyl) phosphate (TEHP) (median, 95th %). Reference values were unavailable for other chemicals, and even those mentioned may underestimate the risks facing a developing infant (Van den Eede, Dirtu et al. 2011, Lyche, Rosseland et al. 2015, Ma, Zhu et al. 2019). EDI calculations for chemicals without a known RfD are included in Table S3.

Table 6.3: Estimated Daily Intake (EDI) Values Through Firefighter Breast Milk

| Analyte | RfD | EDI Med (ng/kg/day) | EDI 95th % (ng/kg/day) | Detection Frequency |
|---|---|---|---|---|
| BDE-47 | 100 | 220 | 630 | 68% |
| BDE-99 | 100 | 170 | 220 | 100% |
| BDE-153 | 200 | 170 | 630 | 68% |
| TCIPP | 3600 | 72000 | 420000 | 50% |
| TCEP | 2200 | * | 5200 | 15% |
| TBOEP | 1500 | 10000 | 14000 | 100% |

RfD; Reference dose

* These chemicals had detection frequencies below 50% and as such median values were not calculated.

EDI was calculated by dividing the daily intake of breast milk (925 mL) times the concentration of contaminant in breast milk by body weight (5.8 kg).

Most toxicological research focuses on exposure to a single agent or analyte; very little research has been undertaken to consider mixed exposures such as those that firefighters and their breast-fed infants may face (Laitinen, Makela et al. 2012, Lyche, Rosseland et al. 2015). Furthermore, there exists a lack of information accurately outlining what levels, if any, are specifically safe for infants given their unique susceptibilities.

Infancy is unique in its heightened exposure pathways for lipophilic pollutants as an infant's nutritional intake includes a higher lipid ratio than at other stages of life (Chen, Wang et al. 2015). Although risks of exposure exist and are potentially at its highest in the early weeks of breast feeding due to high infant intake (g/kg body weight), long-term breastfeeding has been proven beneficial to neurodevelopment with the strong suggestion that the benefits counterbalance the impact of exposure (Ribas-Fitó, Cardo et al. 2003, Nickerson 2006). It is important to recognise that if an infant is at risk of exposure through breast milk, it is likely that some exposure has occurred through placental transfer, and therefore the detoxifying and neurological development aspects of breast milk become more important in ensuring the long term health of the child (Mead 2008).

Despite the potential of environmental contaminants in breast milk, it is still the recommended infant feeding method due to its nutritional balance, biologically appropriate composition, promotion of protection against infections, support of immune and neurologic system development, and facilitation of maternal-infant attachment (Nickerson 2006).

### 6.3.4. Blood and Urine Analysis

Results of the blood and urine analysis are presented by gender and by matrix in Appendix 4 (Tables S6.4-S6.7). For statistical analysis data was grouped (where appropriate) by gender, time since exposure, frequency of exposure, duration of employment, rank (firefighter vs Officer), brigade classification, use of breathing apparatus, biosamples contributed, and type of exposure. Correlation between each group and chemical concentration was assessed separately, thus potential confounding was not considered. Thus, the findings should be interpreted with caution. Statistically significant differences (Mann Whitney U Test results) are noted in Appendix 4 to avoid congestion of reporting within the following results and discussion. The presence of statistically significant differences is noted within each following chemical sub-section. Due to the analysis results suggesting occupational exposure, both median and $95^{th}$% concentrations for chemicals biomonitored in blood and urine are reported on, as the exposure that firefighters face when attending incidents varies considerably based around material burnt, duration of exposure, role at the incident, and density of smoke (Fabian, Borgerson et al. 2014). Given the non-normal, right skewed distribution of chemical concentrations found in firefighter blood and urine, presenting only median without mention of $95^{th}$% risks underestimating the risks.

Twenty four of the 125 urine samples provided were outside of WHO confidence ranges with regard to creatinine levels (too dilute) (WHO 1996). Even so, given the sensitivity of modern analytical equipment, all samples have been included in the data analysis. Both corrected and uncorrected results have been included in the Appendix 4 (Tables S6.4-S6.7).

6.3.4.1. Polycyclic Aromatic Hydrocarbons (Urine)

Sum Hydroxy-naphthalene (∑OH-NAP) and sum hydroxy-fluorene (∑OH-FLU) were detected across most groups at frequencies ≥50% and were thus used for statistical comparisons. No statistically significant differences on concentrations of ΣOH-NAP (sum of 1- and 2- hydroxynaphthalene) or ΣOH-FLU (sum of 2- and 3- hydroxyflourene) were noted between types of real fire scenario exposures, possibly due to multiple types of real fires selected by participants for many of the samples, and the ubiquitous nature of PAHs. Real fire scenario median results for ΣOH-NAP (median 5.9 µg/g creatinine, $95^{th}$% 19 µg/g creatinine) and ΣOH-FLU (median 0.38 µg/g creatinine, $95^{th}$% 1.3 µg/g creatinine) do not appear to exceed concentrations observed in general population studies from Australia (24 µg/g creatinine and 0.51 µg/g creatinine respectively) (Thai, Banks et al. 2020). Based on survey responses less than half of the firefighters who contributed urine for this study did so within 24hrs of fire exposure. PAHs can be eliminated from the human system within hours of exposure which may have limited the potential of finding quantifiable levels (Li, Romanoff et al. 2012).

Statistically significant elevations were noted across the urinary PAH results for those exposed to compartment fire behavioral training (CFBT) fires compared with all other fire exposed groups. CFBT is a method of training to "…ensure that firefighters are adequately trained and equipped to perform their roles effectively and safely, …to recognise the behaviour of fires, assess conditions in a compartment and make decisions on whether to undertake firefighting in a compartment, and respond appropriately" (NDFEM 2010).

Median and $95^{th}$% results for firefighters exposed to CFBT in the previous 24hrs for ΣOH-NAP (70 µg/g creatinine, 322 µg/g creatinine) and ΣOH-FLU (4.3 µg/g creatinine, 21 µg/g creatinine) exceeded levels of the same who attended real fire scenarios in the previous 24hrs (see above). The CFBT group was the only one to present 1-OH-PYR detection frequencies above 50% (median 0.70 µg/g creatinine, $95^{th}$% 1.6 µg/g creatinine). The Biological Occupational Exposure Limit (BOEL) for 1-OH-PYR of 1µg/L (0.77 µg/g creatinine) (WCNSW 2010) was exceeded by 50% of CFBT results within 24hrs. These results represent high exposure to PAHs that are not necessarily achieved regularly outside of a contrived environment of specific smoke density and duration.

These differences noted between CFBT exposure samples and others were potentially because CFBT exposure was selected in isolation on each occasion (no overlapping other fire exposures) and further likely as four firefighters provided samples following two closely spaced CFBT fires within a 24hr prior (see section S6.5.1.1 PAHs in Appendix 4). Findings of fire trainers and firefighters experiencing fire training having higher concentrations of PAHs in urine are not unique to this study (Fent, Toennis et al. 2019a).

Overall, median male firefighter PAHs in urine were lower than those of the cohort in China with median 1-hydroxypyrene (1-OH-PYR) (<0.38 µg/g creatinine v 0.8 µg/g creatinine), firefighter ΣOH-NAP results lower (3.8 µg/g creatinine v 6.2 µg/g creatinine), ΣOH-FLU results relatively equivalent (0.30 µg/g creatinine v 4.3 µg/g creatinine) and ΣOH-PHE results lower in firefighters (0.91 µg/g creatinine v 5.2 µg/g creatinine) (Yang, Wang et al. 2017). Firefighters presented with higher concentration (73 million/mL v 43 million/mL) and total motility (56% v 42%) than the Chinese cohort but were lower for progressive motility (46% v 42%), volume (2.0mL v 3.0mL), and normal forms (9.0% vs 21%). When CFBT results are considered, firefighters are ~11x higher for median ΣOH-NAP, and equivalent for ΣOH-FLU.

Heavier PAHs have been shown to reduce semen quality and increased 1-OH-PYR has been positively associated with sperm neck abnormalities, decreased volume and motility (Jeng, Pan et al. 2013, Jurewicz, Radwan et al. 2013, Jeng, Lin et al. 2018). Prior reproductive studies have found levels of 1-OH-PYR (0.33±0.31 µg/L) to be associated with reduced semen parameters (Jurewicz, Radwan et al. 2013), which are lower than what has previously been considered safe (0.5 µg/L) (Wilhelm, Hardt et al. 2008). With an LOQ of 0.5µg/L, analysis in the current study was limited.

Urinary PAH concentrations approximately equal to those of female firefighters (see Table S6.6 in Appendix 4) in the current study have been found to be associated with changes to endocrine markers of ovarian function in women, with other studies supporting similar associations through serum assessment of PAH exposure (Luderer, Christensen et al. 2017, Yin, Tang et al. 2017, Ye, Pan et al. 2020).

6.3.4.2. Metals (Whole Blood & Urine)

Higher detection frequency, median and 95th% values for blood lead (Pb) and mercury (Hg) were reported for those not always wearing SCBA (Pb: 43%, <LOD, 24.9 µg/L and Hg: 50%, 0.75 µg/L, 8.9 µg/L) compared with those always wearing SCBA (Pb: 9.0%, <LOD, 14 µg/L and Hg:33%, <LOD, 2.5 µg/L), suggesting the importance of occupational hygiene. Statistically significant differences were noted for urinary Cu, selenium (Se), and inorganic arsenic (As) with regard to type of fire exposure, and inorganic As for gender (see section S6.5.1.2 Metals in Appendix 4).

Firefighters in this study presented with maximum urinary cobalt (Co) levels above what was found to lead to below reference sperm concentrations (Zeng, Feng et al. 2015). The cross-sectional study on Chinese males by Zeng et al. found significant trends for below reference sperm count with increasing Se interquartiles (IQs), and it is of note that the Chinese males had much lower Se levels than Australian firefighters (approximately 1/3). Increasing Se supported a decrease in abnormal sperm head morphology and increasing nickel (Ni) was associated with increasing trend for abnormal sperm head morphology. Firefighter Ni concentrations in urine were approximately ½ of Chinese males. Overall, the Chinese males presented with better semen quality than Australian firefighters.

Research has found blood Pb to be related to a moderate alteration in seminal parameters. Although Pb was found present in whole blood in Australian firefighters, its concentration was much lower when compared to results from the literature related to Spanish men (Mendiola, Moreno et al. 2011). Another Chinese study related to metals in urine showed associations between heavy metals and total sperm motility, progressive motility, or the proportion of normal sperm morphology. Firefighters presented lower median levels of urinary metals to this population for As (6.0 µg/g creatinine v 26 µg/g creatinine) and Pb (<LOD v 0.68 µg/g creatinine). Firefighter semen (median results) was found to be slightly elevated for motility (56% v 49%) and progressive motility (46% v 42%), yet considerably lower normal morphology (9% v 21%) (He, Zou et al. 2020). These findings were further supported by Wang et al. 2017 (Wang, Wang et al. 2017).

In a study conducted on 815 pregnant women in Puerto Rico, multiple blood metals were found to act as endocrine disruptors (maternal and fetal), including As, Co, manganese (Mn), nickel (Ni) and Pb (Rivera-Núñez, Ashrap et al. 2021). 95th% results for blood Pb in firefighters in the current study (15 µg/L) were more than double those of the Puerto Rican women (6.4 µg/L), though firefighter median levels were lower than Puerto Rican women (<LOD v 3.3 µg/L).

6.3.4.3. Phthalates (Urine)

Within the current study, firefighters with exposure occurring less than 24hrs ago presented with significantly lower urinary levels than those with exposure >24hrs ago for mono(2-ethylhexyl) phthalate (MEHP) (1.4 vs 2.0 µg/g creatinine), mono(2-ethyl-5-oxohexyl) phthalate (MEOHP) (1.4 vs 3.7 µg/g creatinine), and mono(2-ethyl-5-carboxypentyl) phthalate (MECPP) (3.5 vs 6.8 µg/g creatinine) ($p<0.05$ for all). Further significant differences were noted within the current study for MEOHP, MEHP and MECPP with regards to type of fire exposure (see section S6.5.1.3 Phthalates in the Appendix 4).

Phthalates have been found to be associated with reduced sperm concentration, straight line velocity, motility, sperm DNA damage, sperm aneuploidy, and increased comet extent even when exposure is below prescribed reference doses (Jurewicz, Radwan et al. 2013, Cai, Zheng et al. 2015, Chen, Yang et al. 2017). Firefighter levels reported for IQ3&4 for monoethyl phthalate (MEP) (µg/L) exceeded levels reporting significant reductions in sperm concentration and progressive motility, and firefighter maximum levels for mono(3-carboxypropyl) phthalate (MCPP), which is associated with reduction in sperm motility, exceeded levels in the Chinese population (Chen, Yang et al. 2017).

Median MEP levels in male firefighters (12 µg/g creatinine) exceeded fertile male partners (11 µg/g creatinine) in a Taiwanese study correlated MEP in urine to that in semen, with a resultant decrease in insulin-like factor3 (Chang, Wu et al. 2017). Median female firefighter concentrations for mono-isobutyl phthalate (MiBP) (5.5 µg/g creatinine) exceeded the levels of women found to be experiencing recurrent, unexplained miscarriage (4.2 µg/g creatinine) in a Chinese study (Peng, Ji et al. 2016). The Ma'anshan Birth Cohort study in China demonstrated that increasing MEP has been associated with a lower concentration of maternal total thyroxine, and when compared with this study female firefighters presented higher median MEP (11 v 7.8 ug/g creatinine) (Yao, Han et al. 2016).

6.3.4.4. VOCs (Urine)

Only hippuric acid and mandelic acid (styrene) were detected at a rate of >50%, with 100% of urine samples assessed for styrene returning a positive result. Only the final 10 samples submitted during the study period were analysed for styrene exposure by means of mandelic acid, all prior samples were analysed for ethylbenzene exposure by the same. Statistically significant differences were noted for type of fire exposure as well as gender (see section S6.5.1.4 VOCs in Appendix 4). Hippuric acid exposure could be due to diets rich in fruits and others (Villanueva, Jonai et al. 1994); however, 3 firefighters had levels exceeding 1600 mg/g creatinine (ACGIH 2014), all having contributed samples post fire exposure.

Levels in exposed workers at a steel furniture manufacturing company presented with a median level of 800mg/g creatinine hippuric acid, with unexposed controls presenting 200mg/g creatinine. Although median concentrations in firefighters (male and female) were in line with unexposed controls, maximum firefighter concentrations were essentially equivalent with those most exposed in the steel furniture manufacturing worker group (Decharat 2014).

Limited data exists around toluene exposure and reproduction, with uncertainty surrounding the possibility of lower-level exposure being associated with miscarriage (Bukowski 2001). Styrene exposure has been found to cause DNA fragmentation in germ cells of Italian male workers facing occupational exposure. The firefighters in this study had considerably lower mandelic acid levels than those in the Italian study, and at this stage it is unknown whether firefighter concentrations could affect fertility (Migliore, Naccarati et al. 2002).

6.3.4.5. OPEs (Urine)

When compared to pooled data from the Australian population, concentrations from firefighters are considerably higher both in detection frequency and concentration for bis(2-butoxyethyl) phosphate (BBOEP) (0.87 µg/g creatinine, <LOD of 0.27 µg/g creatinine). The Australian population was higher than firefighters in bis(1,3-dichloroisopropyl) phosphate (BDCIPP) (0.33 µg/g creatinine, 0.17 µg/g creatinine), diphenyl phosphate (DPhP) (34 µg/g creatinine, 0.32 µg/g creatinine) and dibutyl phosphate (DBP) (0.23 µg/g creatinine, 0.08 µg/g creatinine) (Van den Eede, Heffernan et al. 2015). OPEs have been previously shown to be an occupational exposure for firefighters in the United States, with female firefighters showing specific OPEs to be up to 5x higher than in the comparison group of female office workers supporting the risks of occupational exposure to OPEs (Trowbridge, Gerona et al. 2022).

In the current study, statistically significant differences were measured in urine across groups with regards to: bis(methylphenyl) phosphate (BMPP), bis(2-chloroethyl) phosphate (BCEP), BCIPHIPP, DBP, BDCIPP, bis(1-chloroisopropyl) phosphate (BCIPP), DPhP (see Appendix 4, S6.5.1.5). Other OPEs were not found to present statistically significant difference.

Although research has found OPEs to be associated with reduced male fertility, firefighter urinary levels were below those found to cause adverse effects (Carignan, Mínguez-Alarcón et al. 2018, Hales and Robaire 2020). Limited studies suggest OPEs may interfere with endocrine systems, and that exposure has been associated with fertility and pregnancy loss, timing of parturition and preterm birth (Doherty, Hammel et al. 2019, Wang, Hales et al. 2021). Overall, reproductive data is lacking for human exposure to OPEs.

6.3.4.6. PFAS (Plasma)

Within the current study, statistical differences were noted by gender with females presenting significantly higher plasma concentrations of perfluoropentanoic acid (PFPeA) and perfluoropentane sulphonate (PFPeS), yet males being significantly higher in perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexane sulphonic acid (PFHxS), (PFHpS), and perfluorooctane sulphonic acid (PFOS). Overall, these findings were reasonable given females have been found to have reduced concentrations of PFAS in general due to menstruation and lactation [98]. Significantly elevated concentrations were noted for frequency of exposure (PFOS) and longer duration of employment (PFOA, PFOS, PFNA, PFHxS, PFHpS). Those not always wearing SBCA during smoke diving were statistically elevated for (PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), PFHxS, PFHpS, and PFOS) than those who reported always wearing SCBA. Statistical findings are reported in section S6.5.1.6 PFAS of Appendix 4.

Elevations mean plasma concentrations became particularly noticable with increasing duration of employment wherein PFHxS increased from 2.7±3.3μg/L to 5.7±4.8μg/L for those employed >15 years. The same was observed for total PFOS where an increase from 4.8±3.4μg/L to 13.2±14μg/L was observed those employed >15 years vs ≤15 years. Given aqueous film forming foams (AFFF) containing PFAS were phased out in the early 2000s from many fire services in Australia, these results are unsurprising (Rotander, Toms et al. 2015). Furthermore, this finding could be influenced by firefighter age as those employed for >15 years had mean±SD age of 53±6.0 years vs 38±8.4 years for those employed for a shorter duration. A positive association between PFAS concentration and age is also generally observed in the general population (Toms, Bräunig et al. 2019).

Firefighters were found to have elevated mean plasma concentrations of PFHpA, PFUnDA, , perfluorododecanoic acid (PFDoDA), PFPeS, PFHxS, PFHpS, and PFOS when compared with the

Australian general population, estimated from pooled serum samples collected from the general population in 2016-2017. On the other hand, mean concentrations of PFOA and PFNA were found to be lower than the general population (Toms, Bräunig et al. 2019). Firefighter samples were collected between 2018-2020 and are therefore not strictly comparable given temporal decreases of the general australian population, resulting in the magnitude of the elevation potentially being underestimated.

PFAS have been studied with regards to seminal parameters, with mixed findings. Two PFAS systematic reviews considering male infertility found a lack of consistent results to confirm an association; however, subtle associations between PFOS and lower testosterone or abnormal morphology could not be excluded (Bach, Vested et al. 2016, Kirk, Smurthwaite et al. 2018).

PFOA has been correlated with longer menstrual cycles, reduced birth size, and reduced weight and height (Chen, Ng et al. 2017, Minatoya, Itoh et al. 2017, Valvi, Oulhote et al. 2017). PFAS have been found to transfer from maternal blood to the placenta (Chen, Yin et al. 2017, McCoy, Bangma et al. 2017). PFAS in follicular fluid has been linked to increased risk of some fertility factors (Kim, White et al. 2020). PFHxS has been found to negatively correlate with basline follicle counts, and upper quartile levels of PFOA and PFOS from NHANES population studies have been found to associated with earlier onset of menopause (Ruark, Song et al. 2017). Studies have found that exposure during developmental windows (pregnancy, pre-puberty) can be key influencers on reproductive outcomes (Tarapore and Ouyang 2021). Firefighters in this study presented with PFAS levels below what has been suggested to affect reproduction.

6.3.4.7. PBDEs (Plasma)

Within this study, occupational exposure was noted with significant differences between groups with regards to gender, duration of employment, and wearing of SCBA. Males presented notably higher detection frequency and concentration across all congeners measured in plasma (excluding BDE-99). Female only demonstrated a detection frequency >50% for BDE-47, limiting the ability to undertake statistical comparison between genders.

When comparing duration of employment, only BDE-47 was detected above 50% in those employed for ≤15yrs. >15yrs employed (median, 95$^{th}$%: 3.4, 18 ng/g lipid) was statistically significantly greater compared to ≤15yrs (median, 9:5$^{th}$% 1.4, 4.0 ng/g lipid). When comparing groups who reported always wearing SCBA at fire incidents (vehicle, structure fires and overhaul) to those who reported not always wearing BA, the not always group demonstrated notably higher detection frequencies and concentrations across the interquartile ranges. Always wearing SCBA was below 50% detection frequency for all congeners. Further statistical findings are reported in section S6.5.1.7 PBDEs of Appendix 4.

Conflicting evidence exists surrounding the effects of PBDE exposure on semen quality (Toft, Lenters et al. 2014, Albert, Huang et al. 2018, Yu, Lin et al. 2018). Although studies have demonstrated that elevated levels of BDE-47 in plasma (≥4.4 ng/mL) significantly increase the odds of both indicated and spontaneous preterm birth, female firefighters within this study were below that threshold (Peltier, Fassett et al. 2021).

### 6.3.5. Study Strength and Limitations

This study captures a broad spectrum look at firefighters in real fire scenario situations, thereby providing a snapshot of firefighter exposure outside of prescribed events. However, this presents a wide range of variables surrounding attendance and exposure at real fire scenarios provides for levels of uncertainty that cannot be avoided. It does; however, present a more realistic perspective on the average firefighter, even if the current cohort who contributed samples are likely more conscientious than the greater population of firefighters based around survey responses. A strength of this study is the demonstration that firefighters are exposed to many different chemicals. Most studies assessing the health and chemical exposure of firefighters are often just assessing relationships between one compound or group of compounds.

The semen and breast milk segments of this study are presented as exploratory investigation given the limited number of participants and samples. Other lifestyle factors, such as diet, cannot be ruled out as contributing to study findings.

The reproductive element of this study focused only on chemical exposure, with other elements known to cause reproductive distress such as noise, heat, sleep deprivation, physical challenges and psychological traumas being outside of the scope (Jahnke, Poston et al. 2018). Furthermore, in this study only relationships between two variables are assessed (characteristic and chemical concentration) without more detailed assessment of the effect of other variables that may explain the results. For example, when comparing the differences between two groups, ages/gender/diet/health characteristics that may differ in the groups are not directly considered.

This research study did not seek to identify the effects of multiple chemical exposures in firefighters, but rather present that multiple exposures exist within the cohort studied and how such exposures may affect firefighter reproduction.

Limits of quantitation and detection were higher for some chemicals than others, at times above levels found to affect semen parameters in other cohorts or above levels of POPs found in the general population. These factors may contribute to a reduced ability to find statistically significant differences surrounding firefighter exposure across the range of variables imposed and may underrepresent the risks. Furthermore, with only LOQ available from TestSafe, the sensitivity of analysis was reduced. The combination of LOQ from TestSafe with LOD from QAEHS provided a limitation, but was deemed appropriate to support more sensitive analysis, where possible.

Finally, to engage participants for the survey, information relating to the survey and the survey link was disseminated by gatekeeper organisations such as fire services, unions, and fire related organisations. No data is known surrounding active contact lists for those gatekeeper organisations, and no data was supplied around how many individuals received and acted on information disseminated limiting understanding as to the reach of this study.

## 6.4. Conclusion

In this study we show that firefighters are experiencing a broad range of chemical exposures. This research study presents novel data showing firefighters within this study had reduced quality of semen in comparison to WHO fertility standards highlighting the need for further research. This study built on prior research to provide a more expanded and novel look at lactating firefighters, investigating a range of chemicals passing through breast milk, calculating estimated daily intake concentrations for breast fed infants, and applying reference doses to provide meaning to those concentrations. This study provides insight into the possible reproductive effects of a range of chemicals biomonitored within firefighter systems and provides important information surrounding the self-reported reproductive history of firefighters. The results highlight the potential for firefighting to negatively affect reproduction for both males and females, as well as the ability for fire related chemicals to pass through to a breast fed infant. Our study highlights the broad spectrum in exposure profiles experience by individual firefighters which may depend on their occupational and personal hygiene, frequency of exposure, duration of employment, and types of fires attended.

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# Chapter 7

## 7.1 Key Findings

The results of this PhD research study have identified that a) firefighters are vulnerable to occupational exposure to a wide range of chemicals; b) there are multiple routes for this exposure including direct and indirect ones, likely through inhalation, dermal absorption and ingestion; c) fire smoke can reach under personal protective clothing to personal clothing items including socks, underwear and crop tops; and d) firefighters may experience reduced reproductive health due to their occupational exposures to hazardous chemicals.

This study further identified that firefighters experience a broad spectrum of exposure profiles associated with factors such as occupational and personal hygiene, frequency of exposure, duration of employment, and types of fires attended. Fire station analysis in Ch 3 demonstrated a range of contamination risks depending on personal experience; which was supportive of findings from Ch 2 where different concentrations of biomonitored chemicals were reported based around classification of firefighters. This was further exemplified within Ch 4's finding that within a single fire there exists a considerable range in level of contamination that reaches underwear and crop tops; suggesting that exposure profiles from firefighting within any single fire may differ. Ch 6 presented significantly different levels of concentrations in firefighters associated with duration of employment, use of breathing apparatus, and types of fires attended. Ch 6 also considered concentrations of chemicals found in firefighter blood, urine and breast milk. These findings, aligned with results from Ch 5, suggest that occupational exposures to hazardous chemicals may contribute to reduced reproductive health in both male and female firefighters.

The finding that firefighting may be affecting the reproductive health of both male and female firefighters aligns with prior data (Chia et al., 2002; Jahnke et al., 2018; Park et al., 2020; Petersen et al., 2019). This data contributes to the overall understanding of occupational exposures, their potential risks, and supports the call from prior studies for increased research into firefighter reproductive health (Jahnke et al., 2018; Jung et al., 2023; Pedersen et al., 2019).

## 7.2. Chapter Review

Ch 1 of this thesis reviewed the risks of exposure and reproduction that firefighters may face. This chapter provided the background information to support the subsequent chapters.

In Ch 2 the occupational exposure of firefighters to chemicals due to fire incidents was confirmed via systematic review, ensuring aim 1 of this study was met. Some variation in chemical concentration and even specific groups of chemicals was found depending on variables such as classification of firefighter (aviation, rural, urban, fire investigator, fire trainer), as well as surrounding types of fires attended. These findings through the systematic review of biomonitoring in firefighters highlighted the diverse exposure profiles, and the difficulty in investigating exposure risks for this occupation.

Risks of potential indirect, secondary exposure were demonstrated in Ch 3 & 4, as required by the second aim of this research study. Ch 3 presented secondary exposure occurring due to the contamination of air and dust in vehicle cabins, within fire stations, on personal protective clothing and equipment. This study examined, by risks quotient, the potential for health risks to metals at fire stations and found that there were potentially avoidable indirect exposure risks being experienced by firefighters. Ch 4 demonstrated the contamination of undergarments and the potential for the contamination to spread to other home items through home laundering. The persistent nature of the contamination was identified, with socks, underwear and crop tops retaining (or increasing in the case of crop tops) some levels of polycyclic aromatic hydrocarbon contamination. Although international research (Banks et al., 2020; Brown et al., 2014) had previously demonstrated that fire stations and clothing worn under firefighter ensemble can be contaminated, this research study was the first to investigate metals in fire stations and provided novel data regarding the contamination of personal undergarments. Furthermore, these chapters confirmed that the experience of Australian firefighters is in line with international firefighters.

Ch 5 & 6 presented the findings of the biomonitoring aspects of this study, supporting aims 3&4 related to assessing Australian firefighters by means of biomonitoring and identifying if firefighting may be affecting reproduction. Ch 5 presented a unique exploratory investigation into male firefighter fertility, progressing beyond survey and registry based data and including semen analysis (Petersen et al., 2019). Findings of reduced semen parameters compared to World Health Organisation (WHO, 2010) standards, as well as younger men reporting lower quality semen samples than older males suggest that something is affecting fertility of these men. Ch 6 further expanded on these findings to include semen results analysed in combination with blood urine results, and included a deeper look at overall reproductive success of firefighting males finding that occupational exposure to hazardous chemicals could be contributing to reduced semen parameters.

Ch 6 also included a biomonitoring and survey based examination of female firefighter exposure and reproduction, providing a set of data previously unavailable for this subset of firefighters. This chapter delved into the reproductive success of female firefighting, finding miscarriage rates of this cohort in line with previous results from firefighters in the United States of America (Jahnke et al., 2018). Biomonitored data from female firefighters including blood, urine and breast milk was also included, with investigations into concentrations of chemicals and their potential to affect reproduction. Lactating firefighters were investigated in an exploratory fashion to identify a range of chemical groups that can pass through breast milk, with findings that several were above reference dose for breast fed infants. Prior to this study only a single publication existed chemically analysing firefighters' breast milk, which resulted in inconclusive findings and the suggestion that further research was required (Jung et al., 2023).

Overall, results from this study suggest the potential for firefighting to negatively affect reproduction for both males and females.

## 7.3 A Novel Approach

This study was novel in requesting firefighters to provide samples after fire exposure in the real world as a method of exposure, not through prescribed burns (though a few firefighters gave samples after training burns). This method perhaps captured more accurately the reality of the broad range of exposures firefighters face within a single study, but also invited challenges with regards to capturing information. Inviting firefighters to give samples after real fire scenarios that may occur at any hour of the 24hr cycle of day, with only subjective information available around intensity of the fire comes with a range of other challenges. Regardless, the important feature of this study of assessing a broad range of chemicals from real world fire exposure to further understanding of the exposures that members of this occupation may face on any given day.

## 7.4 Study Limitations

An unavoidable challenge when attempting to assess exposure risk for this occupation is that many of the chemicals present in firefighting environments have no officially established safe or toxic threshold, and many have yet to identify half-lives (Barros et al., 2023).

Shaping a study on firefighters contributing samples post fire incident exposure, rather than at set times, created challenges. As it were, only some 25% of those who opted to contribute samples actually did, with anecdotal feedback from participants surrounding issues like forgetting forms or not having time post exposure and other life commitments. No doubt a multitude of reasons played into the drop off in contribution, but the study design supported attrition in a way that convenience samples might not.

Results demonstrated the ability for fire related chemicals to pass through to a breast fed infant. The study was limited in assessing whether findings of chemicals passing through above designated reference dose were due directly to fire incidents, affected by secondary contamination at fire stations and through PPC&E, or due to lifestyle factors. Further research is required following a group of lactating women over the duration of their lactation period, recording any fire incident exposure as well as time on maternity leave and active-duty work.

This study was limited by participant numbers with regards to semen and breast milk contributions. Fire station analysis was limited to NSW, and assessment of intensity of exposure was limited to subjective responses in the survey.

Another limitation lies on not being able to identify whether lifestyle factors could also be playing a role; and as such future well powered studies would ideally follow (and biomonitor) firefighters from their acceptance at recruit college through years following, actively capturing potential confounding information over that time also.

## 7.5. Study Strengths

This was the first study to actively request and collect blood, urine, semen, and breast milk samples following exposure to real world fires. Many other studies have successfully utilised prescribed burns to assess exposure (Adetona et al., 2017; Fent et al., 2019a; Laitinen et al., 2010; Wingfors et al., 2018), with others using convenience samples (Dobraca et al., 2015; Ekpe et al., 2021). Other studies have analysed a group of firefighters following real world fires; however, all attending the same type of fire (Oliveira et al., 2016), providing vital information into exposure to wildland fires. The strength of this study was to highlight the wide variety of exposures firefighters can face in their call of duty, and the variety of exposures that can be faced when attending a similar style of incident.

Studying the occupational exposure of firefighting presents a multitude of variables, not just what chemicals to assess, but also what types of fire, types of firefighters (wildland, urban, aviation, fire investigator, fire trainer), and all the variables around availability and use of personal protective clothing and equipment. This study highlighted the broad range of firefighters, their exposures, their use of personal protective clothing and equipment, and that duration of employment and frequency of being exposed to fires can play roles in the overall exposure. This study collected data across a broad range of chemicals, highlighting the need to cast a wide net in order to fully examine occupational risks, as focusing on a single chemical group may limit assessment.

This study was also the first to broadly delve into reproduction through biomonitoring for firefighters, providing the first look at the quality of firefighter semen, and identifying a range of chemicals within breast milk, some of which may present above reference dose for breastfed infants. Through a literature review related to chemical exposure and reproductive health of both males and females, this study considered what reproductive risks may be present based on investigations into firefighter blood, urine and breast milk. The data presented adds to the understanding of occupational exposure and risks, though far more work is required in this area.

This study was the first to investigate fire stations for metal contamination, and to determine the risks of contamination to firefighters' socks, underwear, and crop tops. Through this novel data firefighters and fire services may find ways to reduce exposure.

## 7.6 Future Studies

Ideally future studies would follow a group of male and female firefighters from pre-fire exposure over an extended period of time. The study would encapsulate assessing multiple biosample matrices for a broad range of chemicals including potentially suspect/non-target screening approaches. Having a larger number of firefighters to follow and assess for quality and chemicals in semen and breast milk would provide valuable insight into the potential for occupational insult in these areas of reproduction. Both broad sweep and targeted studies are required to drill further into this uniquely exposed occupational group, broad studies to further identify specific risks, and targeted studies to unpack those risks more thoroughly.

## 7.7. A Personal Note

Since beginning this study as a lactating firefighter wondering what potential exposures my child might face were I to return to active-duty firefighting, I have seen big changes; locally related to firefighter understanding of the risks, and within fire service action on safety. When I first began, aside from a few committed supporters, I experienced some who actively presented roadblocks, and others who simply dismissed the work I was undertaking as unnecessary. The focus around exposure (locally) was almost entirely on diesel exhaust, with limited consideration amongst firefighters, fire services and others (anecdotally) for fire contaminants.

Over the years through which I have been undertaking this research into firefighter exposure and reproduction, change surrounding firefighter awareness and safety has blossomed in Australia. I by no means attribute this change specifically to this overall research study, though I am confident that it has supported the multiple pieces of the puzzle to come together in unison, with all parts supporting the whole. Presumptive legislation for cancer, changes in the upper echelons of fire services, recent escalations of categorisation of firefighting as an occupation by the IARC (Demers et al., 2022) and increasing pressure from Unions came at the same time as this research study, all uniting to increase firefighter safety and awareness. My role has been in furthering this research, aligning with other researchers, presenting at multiple fire related conferences in Australia, working with organisations such as Women and Firefighting Australasia, and feeding my data through my place of employment and beyond.

There remains much work to be done around education and awareness across the fire services in Australia, but I am honoured to have feel that I have played a role in supporting the current catapult Australian firefighting is experiencing towards cleaner firefighters.

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Appendix 1

Supplementary Information: Biomonitoring in Firefighters for Volatile Organic Compounds, Semivolatile Organic Compounds, Persistent Organic Pollutants, and Metals: A Systematic Review

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Database Search Terms – 09/09/2019

- PubMed: n=855: ((exposure) AND ((((firefighter*[Title/Abstract] OR "fire fighter"[Title/Abstract] OR "fire fighters"[Title/Abstract] OR firefighting[Title/Abstract] OR "fire fighting"[Title/Abstract]))) OR "Firefighters"[Mesh]))

- Scopus: n=1061: TITLE-ABS-KEY ( ( ( *'fire* AND *fighter'* OR *'firefighter'* OR *'firefighting'* OR *'fire* AND *fighting'* OR *'fire* AND *fighters'* OR *'firefighters'* ) AND *exposure* ) ) AND ( LIMIT-TO ( DOCTYPE , *"ar"* ) OR LIMIT-TO ( DOCTYPE , *"re"* ) OR LIMIT-TO ( DOCTYPE , *"le"* ) OR LIMIT-TO ( DOCTYPE , *"ed"* ) )

- Web of Science n=1112: You searched for: ALL FIELDS:(((‘fire fighter’ OR ‘firefighter’ OR ‘firefighting’ OR ‘fire fighting’ OR ‘fire fighters’ OR ‘firefighters’) AND exposure)) Refined by: DOCUMENT TYPES: (ARTICLE OR REVIEW) Timespan: All years. Indexes: SCI-EXPANDED, SSCI, A&HCI, CPCI-S, CPCI-SSH, BKCI-S, BKCI-SSH, ESCI, CCR-EXPANDED, IC.

- Embase: n=1170 : ('fire fighter'/exp OR 'fire fighter' OR 'firefighter' OR 'firefighting' OR 'fire fighting' OR 'fire fighters' OR 'firefighters') AND ('exposure'/exp OR exposure)
- Scifinder Scholar: 828 : (firefighter* OR firefighting OR "fire fighter*" OR "fire fighting") AND exposure

- CINAHL: n=658: (AB firefighter* OR AB firefighting OR AB "fire fighter*" OR AB "fire fighting" AND AB exposure)  Search modes - Boolean/Phrase limit to academic journals, dissertations, CEUs

- International Pharmaceuticals Abstracts: n=6: AB firefighter* OR AB firefighting OR AB "fire fighter*" OR AB "fire fighting" AND AB exposure - Search modes - Boolean/Phrase

Table S2.1: CASP Cohort Study Checklist findings

| Research Study | Did the study address a clearly focused issue? | Was the cohort recruited in an acceptable way? | Was the exposure accurately measured to minimise bias? | Was the outcome accurately measured to minimise bias? | Have the authors identified all important confounding factors? | Have they taken account of confounding factors in the design and/or analysis? | Was the follow up of subjects complete enough? | Was the follow up of subjects long enough? | Are the results of this study clearly reported with presentation of comparison between exposed/unexposed? | Are the results precise? | Are the results believable? | Can the results be applied to the local population? | Do the results of this study fit with other available evidence? | Does this study present evidence of significant occupational exposure? | Retain study in the Systematic Review? |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Adetona et al 2017 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Adetona et al 2019 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Andersen et al 2017 | Y | Y | Y | Y | N | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Anderson et al 2018a | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Anderson et al 2018b | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | N | Y |
| Caux et al 2002 | Y | Y | Y | Y | C | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Cherry et al 2019 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Dobraca et al 2015 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Fent et al 2014 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Fent et al 2019a | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Fent et al 2019b | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Fernando et al 2015 | Y | Y | Y | Y | C | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Feunekes et al 1997 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Hsu et al 2011 | Y | Y | Y | Y | C | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Jayatilaka et al 2017 | Y | Y | Y | Y | C | C | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Jayatilaka et al 2019 | Y | Y | Y | Y | C | C | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Jin et al 2011 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Keir et al 2017 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Laitinen et al 2010 | Y | Y | Y | Y | N | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Laitinen et al 2014 | Y | Y | Y | Y | C | C | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Neitzel et al 2009 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Oliveira et al 2016 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Oliveira et al 2017a | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Oliveira et al 2017b | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Park et al 2014 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Phoon & Ong 1982 | Y | Y | Y | Y | C | C | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Robinson et al 2008 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | N | Y |
| Rotander, Toms et al 2015 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Rotander, Karrman et al 2015 | Y | Y | Y | Y | C | C | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Salama et al 2017 | Y | Y | Y | Y | C | Y | Y | Y | Y | Y | Y | Y | Y | N | Y |
| Shaw et al 2013 | Y | Y | Y | Y | C | C | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Smith et al 2013 | Y | Y | Y | Y | C | C | Y | Y | Y | Y | Y | Y | Y | N | Y |
| Waldman et al 2016 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Wingfors et al 2017 | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |

Table S2.2: Selected Studies – Matrix Utilised

| Research Study | Matrix: Urine | Matrix: Blood | Matrix: Urine & Blood |
|---|---|---|---|
| Adetona et al 2017 | 1 | | |
| Adetona et al 2019 | 1 | | |
| Andersen et al 2017 | 1 | | |
| Anderson et al 2018a | 1 | | |
| Anderson et al 2018b | 1 | | |
| Caux et al 2002 | 1 | | |
| Cherry et al 2019 | 1 | | |
| Dobraca et al 2015 | | | 1 |
| Fent et al 2014 | 1 | | |
| Fent et al 2019a | 1 | | |
| Fent et al 2019b | 1 | | |
| Fernando et al 2015 | 1 | | |
| Feunekes et al 1997 | 1 | | |
| Hsu et al 2011 | | 1 | |
| Jayatilaka et al 2017 | 1 | | |
| Jayatilaka et al 2019 | 1 | | |
| Jin et al 2011 | | 1 | |
| Keir et al 2017 | 1 | | |
| Laitinen et al 2010 | | 1 | |
| Laitinen et al 2014 | | | 1 |
| Neitzel et al 2009 | 1 | | |
| Oliveira et al 2016 | 1 | | |
| Oliveira et al 2017a | 1 | | |
| Oliveira et al 2017b | 1 | | |
| Park et al 2014 | | 1 | |
| Phoon & Ong 1982 | | 1 | |
| Robinson et al 2008 | 1 | | |
| Rotander, Toms et al 2015 | | 1 | |
| Rotander, Karrman et al 2015 | | 1 | |
| Salama et al 2017 | | 1 | |
| Shaw et al 2013 | | 1 | |
| Smith et al 2013 | | 1 | |
| Waldman et al 2016 | 1 | | |
| Wingfors et al 2017 | 1 | | |
| | 22 | 10 | 2 |

Appendix 2

# Supplementary Information: Exposure to Metals and Semivolatile Organic Compounds in Australian Fire Stations

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**Limits of Detection for Metals Analysed:**

Limits of detection as presented by the laboratory were 1 μg for titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), lead (Pb), tungsten (W), 2 μg for tin (Sn), cadmium (Cd), 4 μg for sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulfur (S), potassium (K), calcium (Ca), 3 μg for gallium (Ga), germanium (Ge), bromine (Br), rubidium (Rb), strontium (Sr), yittrium (Y), zirconium (Zr), niobium (Nb), rhodium (Rh), palladium (Pd), silver (Ag), indium (In), antimony (Sb), tellurium (Te), iodine (I), hafnium (Hf), tantalum (Ta), iridium (Ir), platinum (Pt), gold (Au), mercury (Hg), tellurium (Tl), bismuth (Bi) and uranium (U), and 8 μg for barium (Ba), and 5 μg for caesium (Cs).

**Table S3.1 Detected PAHs on Wipe Samples (μg/100cm$^2$)**

| Station Number | 3 | 6 | 6 | 6 | 6 | 10 | 13 | 14 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|
| Item Sampled (μg/100cm$^2$) | Therma l Imaging Camera | Therma l Imaging Camera | jacket internal | helmet external | helmet internal | Steering Wheel | BA Cleaning Station | Engine bay door handle internal | helmet internal | helmet internal |
| Acenaphthylene | <0.1μg | <0.1μg | 0.2 | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg |
| Acenaphthene | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | 0.1 | <0.1μg | <0.1μg | <0.1μg | <0.1μg |
| Fluorene | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg |
| Phenanthrene | <0.1μg | <0.1μg | <0.1μg | 0.1 | <0.1μg | <0.1μg | 0.1 | 0.1 | <0.1μg | <0.1μg |
| Anthracene | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg |
| Fluoranthene | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | 0.2 | 0.1 | <0.1μg | <0.1μg |
| Pyrene | 0.1 | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | 0.2 | <0.1μg | <0.1μg | <0.1μg |
| Benzo[b]fluoranthene | <0.1μg | <0.1μg | <0.1μg | <0.1μg | 2.1 | <0.1μg | <0.1μg | <0.1μg | 0.7 | <0.1μg |
| Benzo[k]fluoranthene | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | 0.1 | 0.6 |
| Benzo[a]pyrene | 0.2 | 0.1 | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg |
| Indeno[1,.2.3-cd]pyrene | 0.1 | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg |
| Benzo[ghi]perylene | 0.1 | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg | <0.1μg |

## Table S3.2 Detection Rates Heavy Metals Across Wipe Samples

| Heavy Metal | V | Cr | Mn | Fe | Ni | Cu | Zn | As | Sr | Sn | Sb | Tl | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| # Detected | | | | | | | | | | | | | |
| Boots 1 | 1 | 24 | 16 | 30 | 2 | 22 | 28 | 2 | 8 | 0 | 9 | 0 | 8 |
| Glove Internal | 0 | 4 | 2 | 30 | 0 | 7 | 30 | 0 | 1 | 1 | 0 | 0 | 1 |
| Glove External | 0 | 28 | 11 | 30 | 5 | 20 | 30 | 2 | 13 | 2 | 7 | 0 | 15 |
| Helmet Internal | 0 | 0 | 4 | 30 | 2 | 14 | 30 | 0 | 0 | 0 | 1 | 0 | 2 |
| Helmet External | 0 | 0 | 2 | 30 | 2 | 7 | 30 | 0 | 1 | 0 | 1 | 0 | 4 |
| Pants Internal | 0 | 1 | 8 | 30 | 0 | 10 | 30 | 0 | 0 | 1 | 0 | 0 | 1 |
| Pants External | 0 | 3 | 11 | 30 | 0 | 17 | 30 | 0 | 8 | 1 | 18 | 0 | 7 |
| Jacket Internal | 0 | 1 | 3 | 30 | 0 | 4 | 30 | 0 | 1 | 0 | 1 | 0 | 2 |
| Jacket External | 1 | 7 | 10 | 30 | 0 | 16 | 30 | 1 | 7 | 0 | 6 | 0 | 8 |
| Steering Wheel | 0 | 4 | 4 | 17 | 3 | 16 | 17 | 0 | 0 | 0 | 5 | 0 | 1 |
| BA Backplate | 0 | 3 | 4 | 34 | 5 | 33 | 34 | 0 | 1 | 0 | 3 | 0 | 16 |
| Seat Belt | 0 | 0 | 2 | 34 | 0 | 7 | 34 | 0 | 0 | 0 | 0 | 0 | 0 |
| Portable Radio | 0 | 0 | 3 | 34 | 0 | 9 | 34 | 0 | 0 | 0 | 0 | 0 | 0 |
| Thermal Imaging Camera | 0 | 0 | 1 | 10 | 0 | 6 | 10 | 0 | 1 | 0 | 3 | 0 | 4 |
| Firefighter data entry computer | 0 | 0 | 4 | 15 | 1 | 14 | 15 | 0 | 0 | 0 | 6 | 0 | 2 |
| Engine Bay Door Handle Internal | 0 | 2 | 1 | 15 | 10 | 9 | 15 | 0 | 0 | 0 | 0 | 0 | 0 |
| Food Fridge Door Handle | 0 | 0 | 0 | 15 | 1 | 2 | 15 | 0 | 0 | 0 | 0 | 1 | 0 |
| BA Cleaning Station | 2 | 13 | 14 | 15 | 11 | 15 | 15 | 0 | 9 | 5 | 6 | 0 | 10 |

## Table S3.3 Metals in Fire Stations vs Global Homes and Offices (μg/m$^2$)

| Averages μg/m$^2$ | Reference | Cd | Cr | Pb | Cu | Zn | Ni | Mn | # samples |
|---|---|---|---|---|---|---|---|---|---|
| Ensemble All | This study | <5μg | 405 | 456 | 619 | 18300 | 35.9 | 784 | 270 |
| Vehicle All | This study | <5μg | 39.5 | 130 | 690 | 12600 | 49.6 | 166 | 129 |
| Fire Station, no BA Wash Sink | This Study | <5μg | 40.0 | 46.7 | 596 | 11800 | 2470 | 73.0 | 45 |
| Fire Station, including BA Wash Sink | This Study | <5μg | 493 | 480 | 3440 | 15700 | 2170 | 638 | 60 |
| Ensemble Part Time Firefighters | This study | <5μg | 459 | 67.8 | 610 | 11100 | 47.8 | 259 | 81 |
| Ensemble Full Time Firefighters | This study | <5μg | 360 | 619 | 594 | 20900 | 28.6 | 997 | 189 |
| Madrid, Spain | (Barrio-Parra, Miguel et al. 2018) | 0.05 | 2.10 | 5.5 | 64 | 142 | 2.9 | 8.3 | 40 |
| Giza, Egypt | (Khoder, Hassan et al. 2010) | 55 | N/A | 533 | N.A | N/A | 88 | N/A | 8 |
| Canada | (Rasmussen, Levesque et al. 2013) | 0.8 | 15 | 21 | 35 | 122 | 18 | n/a | 1025 |
| Istanbul, Turkey | (Kurt-Karakus 2012) | 0.06 | 4.3 | 2.2 | 12 | 65 | 20 | 11 | 31 |
| Sydney, Australia | (Chattopadhyay, Lin et al. 2003) | 0.34 | 6.5 | 30 | 11 | 51 | 2.1 | 5.9 | 82 |
| Kwun Tong, China | (Tong and Lam 2000) | 3.0 | n/a | 24 | 63 | 164 | n/a | 2.6 | 151 |
| Dharan, S. Arabia | (Turner and Hefzi 2010) | 0.11 | 2.4 | 2.0 | 5.8 | 27 | 1.5 | 7.7 | 32 |
| Warsaw, Poland | (Lisiewicz, Heimburger et al. 2000) | n/a | 7.3 | 12 | 9.9 | 89 | 3.2 | n/a | 27 |
| Amman, Jordan | (Al-Momani 2007) | 0.22 | 5.1 | 13 | 10 | 153 | 2.4 | 22 | 20 |
| Plymouth, UK | (Turner and Ip 2007) | 0.12 | 4.9 | 8.5 | 13 | 44 | 3.5 | 31 | 7 |

Note to Table S.3: excluding data presented from the study in Madrid, Spain (Barrio-Parra, Miguel et al. 2018), wherein samples were collected using 'ghost wipes', samples were obtained using other techniques such as vacuum sampling, dust from dust plates, etc. Data from these studies was converted into µg/m$^2$ for comparison by Barrio-Parra et al. As such, all global study figures listed in Table S.3 are taken from Table 3 in Barrio-Parra et al. 2018 for ease of a direct comparison with µg/m$^2$ data in this study. Individual study references are provided in Table S.3.

**Table S3.4 Laundering and Fire Correlations with Heavy Metals, All Employment Demographics**

| All Correlations 1 tailed | | | | | | | |
|---|---|---|---|---|---|---|---|
| n=55 | | Int. Mn | Int. Zn | Int. Sr | Int. Sb | Ext. Sb | Ext. Pb |
| Likely Days Since Laundering | Pearson Correlation | | | | | .494 | |
| | Sig. (1-tailed) | | | | | 0.000 | |
| Total Fires | Pearson Correlation | | | | | .523 | |
| | Sig. (1-tailed) | | | | | 0.000 | |
| Structure Fires | Pearson Correlation | .257 | .229 | .398 | .398 | .544 | .338 |
| | Sig. (1-tailed) | 0.029 | 0.046 | 0.001 | 0.001 | 0.000 | 0.006 |
| Outside/Storage Fires | Pearson Correlation | | | | | .429 | |
| | Sig. (1-tailed) | | | | | 0.001 | |
| Vehicle/Transport Fires | Pearson Correlation | | | | | .483 | |
| | Sig. (1-tailed) | | | | | 0.000 | |
| Wild Fires | Pearson Correlation | | | | | .450 | |
| | Sig. (1-tailed) | | | | | 0.000 | |
| Rubbish Fires | Pearson Correlation | | | | | .528 | |
| | Sig. (1-tailed) | | | | | 0.000 | |
| Explosion Fires | Pearson Correlation | .282 | | .486 | .486 | .517 | .362 |
| | Sig. (1-tailed) | 0.018 | | 0.000 | 0.000 | 0.000 | 0.003 |

## Table S3.5 Laundering and Fire Correlations with Heavy Metals, Full Time Firefighters

| Full Time Correlations 1 tailed | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| n=37 | | Int Cr | Int. Mn | Int. Zn | Int. Sr | Int Sn | Int Sb | Int. Pb | Ext. Cr | Ext Mn | Ext Cu | Ext Zn | Ext Sb | Ext Pb |
| Likely Days Since Laundering | Pearson Correlation | | | | .347 | | .347 | | | | | | .303 | .298 |
| | Sig. (1-tailed) | | | | 0.018 | | 0.018 | | | | | | 0.034 | 0.037 |
| Total Fires | Pearson Correlation | | .439 | .438 | .575 | | .575 | .284 | .333 | | .286 | .305 | .403 | .557 |
| | Sig. (1-tailed) | | 0.003 | 0.003 | 0.000 | | 0.000 | 0.044 | 0.022 | | 0.043 | 0.033 | 0.007 | 0.000 |
| Structure Fires | Pearson Correlation | | .441 | .419 | .631 | | .631 | | | | | .297 | .384 | .571 |
| | Sig. (1-tailed) | | 0.003 | 0.005 | 0.000 | | 0.000 | | | | | 0.037 | 0.010 | 0.000 |
| Outside/Storage Fires | Pearson Correlation | | | | | .285 | | | | | | | | |
| | Sig. (1-tailed) | | | | | 0.044 | | | | | | | | |
| Vehicle/Transport Fires | Pearson Correlation | | .406 | .504 | .535 | | .535 | .386 | .306 | | | .341 | .315 | .522 |
| | Sig. (1-tailed) | | 0.006 | 0.001 | 0.000 | | 0.000 | 0.009 | 0.033 | | | 0.020 | 0.029 | 0.000 |
| Wild Fires | Pearson Correlation | .281 | .277 | .392 | | | | .316 | .347 | | .292 | .299 | | .283 |
| | Sig. (1-tailed) | 0.046 | 0.048 | 0.008 | | | | 0.028 | 0.018 | | 0.040 | 0.036 | | 0.045 |
| Rubbish Fires | Pearson Correlation | .297 | .424 | .333 | .494 | | .494 | .411 | .440 | .289 | .334 | | .424 | .531 |
| | Sig. (1-tailed) | 0.037 | 0.004 | 0.022 | 0.001 | | 0.001 | 0.006 | 0.003 | 0.041 | 0.022 | | 0.004 | 0.000 |
| Explosion Fires | Pearson Correlation | | .451 | .299 | .697 | | .697 | | | | | | .347 | .561 |
| | Sig. (1-tailed) | | 0.003 | 0.036 | 0.000 | | 0.000 | | | | | | 0.018 | 0.000 |

## Table S3.6 Laundering and Fire Correlations with Heavy Metals, Part Time Firefighters

| Part Time Correlations 1 tailed | | | | | | | |
|---|---|---|---|---|---|---|---|
| n=18 | | Int Cu | Ext Cr | Ext Mn | Ext Cu | Ext Sr | Ext Sb |
| Years in Service | Pearson Correlation | | .476 | | | .430 | |
| | Sig. (1-tailed) | | 0.023 | | | 0.037 | |
| Likely Days Since Laundering | Pearson Correlation | .680 | | .594 | .448 | | .714 |
| | Sig. (1-tailed) | 0.001 | | 0.005 | 0.031 | | 0.000 |
| Total Fires | Pearson Correlation | .675 | | .642 | .500 | | .708 |
| | Sig. (1-tailed) | 0.001 | | 0.002 | 0.017 | | 0.001 |
| Structure Fires | Pearson Correlation | .680 | | .632 | .481 | | .714 |
| | Sig. (1-tailed) | 0.001 | | 0.002 | 0.022 | | 0.000 |
| Outside/Storage Fires | Pearson Correlation | .597 | | .525 | | | .622 |
| | Sig. (1-tailed) | 0.004 | | 0.013 | | | 0.003 |
| Vehicle/Transport Fires | Pearson Correlation | .666 | | .580 | .447 | | .678 |
| | Sig. (1-tailed) | 0.001 | | 0.006 | 0.032 | | 0.001 |
| Wild Fires | Pearson Correlation | .664 | | .654 | .519 | | .700 |
| | Sig. (1-tailed) | 0.001 | | 0.002 | 0.014 | | 0.001 |
| Rubbish Fires | Pearson Correlation | .663 | | .606 | .452 | | .673 |
| | Sig. (1-tailed) | 0.001 | | 0.004 | 0.030 | | 0.001 |

## Table S3.7 New Vs Used Gear Statistical Tests

| Metal | Mean (Min-Max) (µg/100cm$^2$) | | p value* | Proportion of samples | | p value** |
|---|---|---|---|---|---|---|
| | New | Used | | New | Used | |
| Antimony | 0 (0-0) | 1.39 (0-52) | 0.196 | 0% | 16% | N/A |
| Arsenic | 0 (0-0) | 0.22 (0-33) | 0.681 | 0% | 2% | N/A |
| Chromium | 3.83 (0-23) | 4.05 (0-130) | 0.947 | 22% | 25% | 0.121 |
| Copper | 0.39 (0-3.5) | 6.193 (0-176) | 0.035 | 6% | 42% | 0.000 |
| Iron | 15.78 (9-36.5) | 175.89 (9-2610) | 0.000 | 100% | 100% | N/A |
| Lead | 0.33 (0-3) | 4.56 (0-345) | 0.506 | 6% | 18% | 0.000 |
| Manganese | 0 (0-0) | 7.84 (0-302) | 0.091 | 0% | 25% | N/A |
| Nickel | 0 (0-0) | 0.36 (0-25) | 0.538 | 0% | 4% | N/A |
| Strontium | 0 (0-0) | 2.83 (0-222) | 0.221 | 0% | 14% | N/A |
| Tin | 0 (0-0) | 0.21 (0-24) | 0.681 | 0% | 2% | N/A |
| Vanadium | 0 (0-0) | 0.04 (0-7) | 0.796 | 0% | 1% | N/A |
| Zinc | 103.83 (97-114.5) | 183.27 (0-14400) | 0.080 | 100% | 99% | N/A |
| | | | | | | |
| * Mann-Whitney U test | | | | | | |
| ** Binomial test (cannot be performed when the test proportion is 0 or 1) | | | | | | |

## Table S3.8 Threshold Tests by Item History

| | | | |
|---|---|---|---|
| Years in Service | <2 v >=2 | years | all accept |
| | <3 v >=3 | years | all accept |
| | <4 v >=4 | years | all accept |
| Days Since Laundering | <=14 v >14 | days | all accept |
| | <=19 v >19 | days | all accept |
| | <30 v >=30 | days | all accept |
| | <=36 v >36 | days | e Sb rej |
| | <=48 v >48 | days | e Sb rej |
| | <=60 v >60 | days | e Cu rej |
| Total Fires Since Laundering | =0 v >0 | fires | all accept |
| | <=5 v >5 | fires | all accept |
| | <=7 v >7 | fires | all accept |
| | <=8 v >8 | fires | all accept |
| | <=9 v >9 | fires | eCu rej |
| | <=11 v >11 | fires | eMn, eCu rej |
| | <=13 v >13 | fires | iCu, eMn, eCu, ePb rej |
| Vehicle Fires since Laundering | =0 v >0 | veh fires | eMn eCu rej, ePb close |
| | <=1 v >1 | veh fires | iPb,eMn,eCu,ePb rej |
| | <=2 v >2 | veh fires | iPb>2rej |
| Structure Fires since Laundering | =0 v >0 | structure fires | all accept |
| | <=1 v >1 | structure fires | all accept |
| | <5 v >=5 | structure fires | all accept |
| | <=5 v >5 | structure fires | iCu, eCu, ePB rej |
| Wild Fires since Laundering | =0 v >0 | Wildfire | all accept |
| | <=1 v >1 | Wildfire | all accept |
| | <=2 v >2 | Wildfire | all accept |
| | <=3 v >3 | Wildfire | eMn reject |
| | <=4 v >4 | Wildfire | iMn,iCu,eCr,eMn,eCu,ePb rej |
| Rubbish Fires since Laundering | =0 v >0 | rubbish fires | all accept |
| | <=1 v >1 | rubbish fires | ePb rej |
| | <=2 v >2 | rubbish fires | iCu eCu rej |
| | <=3 v >3 | rubbish fires | iCu, eCr rej, eCu rej |
| | <=5 v >5 | rubbish fires | iCu, eCr, eSb rej |

Note to Table S.8: e = external wipe sample location, i = internal wipe sample location.

## Table S3.9 Heavy Metal and Exposure Limits

| Metal | CAS Number | IARC Classification | Exceed Brookhaven Housekeeping based on individual items | Exceed NIOSH Housekeeping based on individual items | Exceeding safe levels - lowest values utilised | Wipe Criteria, lowest/safest levels utilised | |
|---|---|---|---|---|---|---|---|
| Beryllium | 7440-41-7 | Group 1: carcinogenic to humans | 0 | 0 | 0 | 0.2 | μg/100cm$^2$ |
| Vanadium | 1314-62-1 | Group 2B: possibly carcinogenic to humans | | 0 | 0 | 500 | μg/100cm$^2$ |
| Chromium | 7440-47-3 | Group 3: Not classifiable as to carcinogenicity to humans | | 0 | 0 | 5000 | μg/100cm$^2$ |
| Manganese | 7439-96-5 | | | 0 | 0 | 10000 | μg/100cm$^2$ |
| Iron | 1309-37-1 | Group 3: Not classifiable as to carcinogenicity to humans | | 0 | 0 | 50000 | μg/100cm$^2$ |
| Cobalt | 7440-48-4 | Group 2B: possibly carcinogenic to humans | | 0 | 0 | 500 | μg/100cm$^2$ |
| Nickel | 7440-02-0 | Group 2B: possibly carcinogenic to humans | | 1 | 1 | 150 | μg/100cm$^2$ |
| Copper | 7440-50-8 | | | 0 | 0 | 10000 | μg/100cm$^2$ |
| Zinc | 1314-13-2 | | | 0 | 0 | 50000 | μg/100cm$^2$ |
| Arsenic | 7440-38-2 | Group 1: carcinogenic to humans | 2 | 5 | 5 | 0.625 | μg/100cm$^2$ |
| Selenium | 7782-49-2 | Group 3: Not classifiable as to carcinogenicity to humans | | 0 | 0 | 2000 | μg/100cm$^2$ |
| Strontium | 7440-24-6 | | | | | | |
| Cadmium | 7440-43-9 | | 0 | 0 | 0 | 3.3 | μg/100cm$^2$ |
| Indium | 7440-74-6 | | | 0 | 0 | 1000 | μg/100cm$^2$ |
| Tin | 7440-31-5 | | | 0 | 0 | 20000 | μg/100cm$^2$ |
| Antimony | 7440-36-0 | | | 0 | 0 | 5000 | μg/100cm$^2$ |
| Tellurium | 13494-80-9 | | | 0 | 0 | 1000 | μg/100cm$^2$ |
| Platinum | 7440-06-4 | | | 0 | 0 | 10000 | μg/100cm$^2$ |
| Mercury | 7439-97-6 | Group 3: Not classifiable as to carcinogenicity to humans | | 0 | 0 | 1000 | μg/100cm$^2$ |
| Thallium | 7440-28-0 | | | 0 | 0 | 1000 | μg/100cm$^2$ |
| Lead | 7439-92-1 | Group 2A: probably carcinogenic to humans | 13 | 0 | 13 | 22 | μg/100cm$^2$ |
| Bismuth | | | | | | | |
| Uranium | 7440-61-1 | | | 0 | 0 | 62.500 | μg/100cm$^2$ |

## Table S3.10 Percentages of Metal and Carcinogenic Metal Groups for all Items Wiped

| Percentage of All Metals and Carcinogenic Metals per Grouping of Items Wiped | | | | |
|---|---|---|---|---|
| | PPC | Vehicle | Station BA Wash | Station No BA Wash |
| Number of Items | 270 | 129 | 60 | 45 |
| % All | 5.6% | 0.0% | 11.7% | 2.2% |
| % Carcinogens Only | 5.6% | 0.0% | 10.0% | 2.2% |

**Table S3.11 Percentages of Metals and Carcinogenic Metals Groups for Part Time Firefighter Items**

| Percentage of All Metals and Carcinogenic Metals per Grouping of Items Wiped, Part Time Fire Stations | | | | |
|---|---|---|---|---|
| | PPC | Vehicle | Station BA Wash | Station No BA Wash |
| Number of Items | 81 | 36 | 12 | 9 |
| % All | 3.7% | 0.0% | 8.3% | 0.0% |
| % Carcinogens Only | 3.7% | 0.0% | 8.3% | 0.0% |

**Table S3.12 Percentages of Metals and Carcinogenic Metals Groups for Full Time Firefighter Items**

| Percentage of All Metals and Carcinogenic Metals per Grouping of Items Wiped, Full Time Fire Station | | | | |
|---|---|---|---|---|
| | PPC | Vehicle | Station BA Wash | Station No BA Wash |
| Number of Items | 189 | 81 | 40 | 30 |
| % All | 6.3% | 0.0% | 15.0% | 3.3% |
| % Carcinogens Only | 6.3% | 0.0% | 12.5% | 3.3% |

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Appendix 3:

Supplementary Information: Firefighter Undergarments: Assessing Contamination and Laundering Efficacy

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<u>Ingredient List</u>
Premium:
Sodium Sulfate, Sodium Carbonate, Sodium Dodecylbenzene Sulfonate, Sodium Silicate, Sodium Carbonate Peroxide, Zeolite, Sodium Acrylic Acid/Ma Copolymer, C12-15 Pareth-7, Tetraacetyl Ethylene Diamine, Perfume, Disodium Anilinomorpholinotriazinylaminostilbenesulfonate, , Disodium Distyrylbiphenyl Disulfonate, Cellulose Gum, Calcium Sodium Edtmp, Phenylpropyl Ethyl Methicone, Protease, Amylase, Mannanase, Lipase, Water, Ci 74160.
Mid-Range:
Sodium Carbonate, Sodium Sulphate, Sodium Linear Alkyl Benzene Sulfonate, Radiant brilliant whites sharper colours laundry powderSodium Silicate, Zeolite, C12-15 Pareth-8, Sodium Diethylenetriamine Pentamethylene Phosphonate, Cellulose Gum, Water, Fragrance, Polyvinyl Pyridine, Protease, Disodium Distyrylbiphenyl Disulfonate, Cellulase, Lipase, Amylase, Silicone Emulsion, Dye.
Economy:
Sodium Carbonate, alcohols C12-14 ethoxylated, sodium percarbonate, sodium dodecylbenzenesulfonate, sodium metasilicate, citric acid, other ingredients determined not to be hazardous.

Environmentally Friendly:

Sodium Carbonate, Sodium Sulfate, Sodium Citrate, Sodium Bicarbonate, Zeolite, Sodium Methyl Ester Sulfonate, Bentonite, Oleic Acid, Cellulose Gum, Fragrance

Table S4.1: Method Detection Limits for the Different Fabric Types Used in this Study (ng.g$^{-1}$)

| | Socks | Briefs | | | Crop Tops | | |
|---|---|---|---|---|---|---|---|
| | Cotton (95% ) Other Fibres (5%) | Cotton (95%) Elastane (5%) | Polyester (92%) Elastane (8%) | Cotton/Elastane | Cotton (95%) Spandex (5%) | Nylon (92%) Elastane (8%) | Cotton/Elastane |
| Phe | 30 | 15 | 170 | 33 | 16 | 250 | 44 |
| Ant | 7.0 | 2.1 | 45 | 7.0 | 3.1 | 32 | 6.9 |
| Flu | 20 | 13 | 71 | 20 | 3.9 | 89 | 19 |
| Pyr | 24 | 13 | 280 | 55 | 5.1 | 44 | 24 |
| BaA+Chr | 8.3 | 2.1 | 13 | 10 | 11 | 180 | 3.6 |
| BbF+BkF | 5.1 | 1.4 | 41 | 3.4 | 5.1 | 64 | 5.1 |
| BeP | 1.5 | 1.4 | 15 | 1.7 | 5.8 | 220 | 4.9 |
| BaP | 2.6 | 1.5 | 28 | 1.4 | 2.0 | 31 | 1.2 |
| I123cdP | 1.5 | 0.97 | 7.5 | 0.63 | 0.91 | 5.4 | 1.2 |
| DahA | 3.1 | 0.14 | 0.83 | 0.37 | 1.1 | 14 | 0.17 |
| BghiP | 2.0 | 1.6 | 8.7 | 1.5 | 2.1 | 44 | 2.2 |

Table S4.2: Method Detection Limits for Washing Machine Wipes (ng.sample$^{-1}$)

| | Washing Machine Wipe |
|---|---|
| Phe | 23 |
| Ant | 4.0 |
| Flu | 5.0 |
| Pyr | 0.63 |
| BaA+Chr | 0.94 |
| BbF+BkF | 0.71 |
| BeP | 0.291 |
| BaP | 0.56 |
| I123cdP | 0.69 |
| DahA | 0.13 |
| BghiP | 0.34 |

**Table S4.3:** Laundering Load 1 – Premium Laundry Powder: Concentrations of PAHs on Socks Pre- and Post-Laundering.

| | Socks (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Pre-Laundering (ng.g$^{-1}$)** | | | | | **Post-Laundering (ng.g$^{-1}$)** | | | | | **Significantly Different (paired t-test)** |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 690 | ± | 320 | 310 | 1100 | 610 | ± | 290 | 250 | 1000 | No |
| Ant | 160 | ± | 100 | 75 | 310 | 110 | ± | 85 | 3.5 | 250 | No |
| Flu | 250 | ± | 190 | 64 | 580 | 140 | ± | 84 | 59 | 300 | No |
| Pyr | 250 | ± | 170 | 100 | 550 | 140 | ± | 93 | 12 | 290 | Yes↓ |
| BaA+Chr | 88 | ± | 92 | 4.2 | 260 | 25 | ± | 27 | 4.2 | 72 | No |
| BbF+BkF | 43 | ± | 42 | 6.6 | 120 | 19 | ± | 14 | 2.6 | 37 | No |
| BeP | 31 | ± | 29 | 4 | 72 | 16 | ± | 9.9 | 5.4 | 32 | No |
| BaP | 62 | ± | 53 | 11 | 150 | 26 | ± | 18 | 7.2 | 54 | No |
| I123cdP | 35 | ± | 33 | 7.2 | 88 | 12 | ± | 7.4 | 4.8 | 22 | No |
| DahA | 5.9 | ± | 5.1 | 1.6 | 15 | 2.5 | ± | 1.4 | 1.6 | 4.5 | No |
| BghiP | 42 | ± | 37 | 7.7 | 110 | 13 | ± | 7.5 | 2.5 | 24 | No |
| $\sum_{13}$ PAHs | 1700 | ± | 1000 | 590 | 3300 | 1100 | ± | 590 | 400 | 2100 | Yes↓ |

**Table S4.4:** Laundering Load 1 – Premium Laundry Powder: Concentrations of PAHs on Briefs Pre- and Post-Laundering.

| | Briefs (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 410 | ± | 150 | 190 | 580 | 330 | ± | 130 | 150 | 510 | No |
| Ant | 58 | ± | 31 | 23 | 93 | 140 | ± | 220 | 23 | 590 | No |
| Flu | 250 | ± | 160 | 36 | 470 | 250 | ± | 130 | 110 | 490 | No |
| Pyr | 340 | ± | 160 | 160 | 580 | 300 | ± | 150 | 160 | 570 | No |
| BaA+Chr | 54 | ± | 55 | 6.5 | 150 | 33 | ± | 24 | 6.5 | 61 | No |
| BbF+BkF | 48 | ± | 34 | 21 | 98 | 33 | ± | 29 | 18 | 91 | No |
| BeP | 38 | ± | 33 | 7.5 | 85 | 28 | ± | 19 | 16 | 66 | No |
| BaP | 75 | ± | 59 | 29 | 150 | 49 | ± | 40 | 25 | 130 | No |
| I123cdP | 37 | ± | 30 | 13 | 77 | 22 | ± | 20 | 7.2 | 60 | No |
| DahA | 6 | ± | 5 | 2.2 | 14 | 3.7 | ± | 3.4 | 1.1 | 10 | No |
| BghiP | 48 | ± | 39 | 17 | 110 | 25 | ± | 19 | 9.4 | 61 | No |
| $\sum_{13}$ PAHs | 1400 | ± | 630 | 680 | 2200 | 1200 | ± | 700 | 550 | 2600 | No |

**Table S4.5:** Laundering Load 1 – Premium Laundry Powder: Concentrations of PAHs on Crop Tops Pre- and Post-Laundering.

| | Crop Tops (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 140 | ± | 48 | 57 | 200 | 260 | ± | 120 | 130 | 430 | Yes↑ |
| Ant | 13 | ± | 13 | 1.6 | 35 | 58 | ± | 36 | 16 | 99 | No |
| Flu | 40 | ± | 29 | 2 | 73 | 360 | ± | 310 | 45 | 880 | No |
| Pyr | 35 | ± | 33 | 2.6 | 80 | 360 | ± | 310 | 22 | 900 | No |
| BaA+Chr | 40 | ± | 41 | 1.8 | 90 | 130 | ± | 68 | 61 | 240 | No |
| BbF+BkF | 26 | ± | 11 | 9.4 | 40 | 98 | ± | 78 | 22 | 210 | No |
| BeP | 44 | ± | 52 | 2.5 | 110 | 67 | ± | 42 | 13 | 110 | No |
| BaP | 14 | ± | 5.3 | 9.2 | 24 | 32 | ± | 16 | 16 | 53 | Yes↑ |
| I123cdP | 4.4 | ± | 3.5 | 2.2 | 11 | 14 | ± | 14 | 2.7 | 41 | No |
| DahA | 3.4 | ± | 3 | 0.46 | 7 | 6.2 | ± | 5.4 | 1.1 | 16 | No |
| BghiP | 13 | ± | 7.9 | 3.8 | 22 | 22 | ± | 8.1 | 12 | 32 | No |
| $\sum_{13}$ PAHs | 370 | ± | 170 | 110 | 490 | 1400 | ± | 550 | 630 | 2000 | Yes↑ |

**Table S4.6:** Laundering Load 2 – Midrange Laundry Powder: Concentrations of PAHs on Socks Pre- and Post-Laundering.

| | Socks (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 1100 | ± | 860 | 380 | 2600 | 1100 | ± | 1000 | 430 | 3200 | No |
| Ant | 250 | ± | 240 | 85 | 730 | 230 | ± | 210 | 110 | 650 | No |
| Flu | 460 | ± | 590 | 91 | 1600 | 210 | ± | 160 | 120 | 540 | No |
| Pyr | 520 | ± | 660 | 85 | 1800 | 200 | ± | 140 | 110 | 490 | No |
| BaA+Chr | 140 | ± | 180 | 4.2 | 470 | 54 | ± | 36 | 31 | 130 | No |
| BbF+BkF | 76 | ± | 97 | 6 | 260 | 22 | ± | 14 | 13 | 51 | No |
| BeP | 52 | ± | 56 | 5.3 | 150 | 18 | ± | 13 | 9.4 | 44 | No |
| BaP | 120 | ± | 140 | 16 | 370 | 33 | ± | 22 | 20 | 77 | No |
| I123cdP | 61 | ± | 80 | 4.7 | 210 | 17 | ± | 10 | 7.9 | 36 | No |
| DahA | 9.5 | ± | 18 | 1.6 | 46 | 2.6 | ± | 1.9 | 1.6 | 6.3 | No |
| BghiP | 61 | ± | 67 | 11 | 160 | 20 | ± | 13 | 13 | 46 | No |
| $\sum_{13}$ PAHs | 2800 | ± | 3000 | 700 | 8400 | 1900 | ± | 1700 | 950 | 5200 | No |

**Table S4.7:** Laundering Load 2 - Midrange Laundry Powder: Concentrations of PAHs on Briefs Pre- and Post-Laundering.

| | Briefs (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 270 | ± | 150 | 62 | 430 | 310 | ± | 140 | 85 | 460 | No |
| Ant | 32 | ± | 31 | 1.1 | 72 | 47 | ± | 26 | 23 | 87 | No |
| Flu | 190 | ± | 140 | 41 | 420 | 180 | ± | 84 | 36 | 260 | No |
| Pyr | 260 | ± | 200 | 58 | 540 | 240 | ± | 86 | 140 | 370 | No |
| BaA+Chr | 35 | ± | 58 | 1.1 | 150 | 35 | ± | 24 | 6.5 | 65 | No |
| BbF+BkF | 34 | ± | 31 | 9.5 | 93 | 24 | ± | 10 | 12 | 41 | No |
| BeP | 30 | ± | 25 | 7 | 78 | 19 | ± | 8.8 | 7.5 | 34 | No |
| BaP | 59 | ± | 54 | 12 | 160 | 36 | ± | 18 | 14 | 66 | No |
| I123cdP | 26 | ± | 22 | 6.3 | 66 | 13 | ± | 7.7 | 3.8 | 27 | No |
| DahA | 4.4 | ± | 3.3 | 1.1 | 9 | 1.9 | ± | 1.5 | 0.27 | 4.1 | No |
| BghiP | 36 | ± | 33 | 8.7 | 96 | 16 | ± | 9.6 | 4.4 | 33 | No |
| $\sum_{13}$ PAHs | 980 | ± | 700 | 230 | 2100 | 920 | ± | 360 | 340 | 1300 | No |

**Table S4.8:** Laundering Load 2 - Midrange Laundry Powder: Concentrations of PAHs on Crop Tops Pre- and Post-Laundering.

| | Crop Tops (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 110 | ± | 36 | 47 | 140 | 330 | ± | 97 | 250 | 510 | Yes↑ |
| Ant | 14 | ± | 17 | 1.6 | 46 | 53 | ± | 35 | 16 | 110 | Yes↑ |
| Flu | 42 | ± | 23 | 9.5 | 75 | 260 | ± | 250 | 45 | 710 | No |
| Pyr | 29 | ± | 23 | 2.6 | 58 | 340 | ± | 500 | 22 | 1300 | No |
| BaA+Chr | 48 | ± | 37 | 1.8 | 90 | 88 | ± | 68 | 1.8 | 210 | No |
| BbF+BkF | 42 | ± | 28 | 9.4 | 74 | 150 | ± | 81 | 51 | 230 | Yes↑ |
| BeP | 41 | ± | 54 | 2.5 | 110 | 56 | ± | 43 | 12 | 110 | No |
| BaP | 13 | ± | 7.1 | 3 | 22 | 42 | ± | 40 | 16 | 120 | No |
| I123cdP | 5.4 | ± | 3.2 | 1.8 | 10 | 17 | ± | 18 | 2.7 | 50 | No |
| DahA | 2.9 | ± | 3.2 | 0.32 | 7 | 8.7 | ± | 7.8 | 1.3 | 22 | No |
| BghiP | 10 | ± | 10 | 1.1 | 22 | 15 | ± | 11 | 1.1 | 26 | No |
| $\sum_{13}$ PAHs | 350 | ± | 180 | 92 | 540 | 1400 | ± | 920 | 640 | 3000 | Yes↑ |

**Table S4.9:** Laundering Load 3 – Economy Laundry Powder: Concentrations of PAHs on Socks Pre- and Post-Laundering.

| | Socks (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 1300 | ± | 1100 | 270 | 2800 | 600 | ± | 330 | 240 | 1100 | No |
| Ant | 260 | ± | 260 | 68 | 710 | 120 | ± | 70 | 41 | 210 | No |
| Flu | 410 | ± | 460 | 66 | 1200 | 130 | ± | 63 | 69 | 220 | No |
| Pyr | 420 | ± | 440 | 63 | 1200 | 130 | ± | 53 | 67 | 200 | No |
| BaA+Chr | 140 | ± | 170 | 4.2 | 440 | 19 | ± | 23 | 4.2 | 49 | No |
| BbF+BkF | 60 | ± | 75 | 2.6 | 190 | 15 | ± | 6 | 8.1 | 23 | No |
| BeP | 46 | ± | 57 | 7.2 | 150 | 12 | ± | 6.4 | 5.7 | 23 | No |
| BaP | 98 | ± | 130 | 4.9 | 330 | 20 | ± | 9.7 | 11 | 34 | No |
| I123cdP | 49 | ± | 61 | 3.2 | 160 | 11 | ± | 3.8 | 3.9 | 14 | No |
| DahA | 4.6 | ± | 4.2 | 1.6 | 12 | 1.6 | ± | | 1.6 | 1.6 | No |
| BghiP | 74 | ± | 93 | 9.8 | 240 | 15 | ± | 5.6 | 9.1 | 22 | No |
| $\sum_{13}$ PAHs | 2800 | ± | 2800 | 570 | 7200 | 1100 | ± | 550 | 460 | 1900 | No |

**Table S4.10:** Laundering Load 3 - Economy Laundry Powder: Concentrations of PAHs on Briefs Pre- and Post-Laundering.

| | Briefs (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 230 | ± | 130 | 110 | 470 | 360 | ± | 130 | 200 | 520 | Yes↑ |
| Ant | 24 | ± | 14 | 3.5 | 43 | 44 | ± | 22 | 23 | 71 | Yes↑ |
| Flu | 120 | ± | 83 | 36 | 270 | 200 | ± | 93 | 81 | 320 | No |
| Pyr | 170 | ± | 130 | 63 | 420 | 270 | ± | 140 | 100 | 440 | No |
| BaA+Chr | 17 | ± | 18 | 5 | 46 | 21 | ± | 17 | 5 | 41 | No |
| BbF+BkF | 21 | ± | 8.4 | 9.5 | 31 | 23 | ± | 11 | 12 | 44 | No |
| BeP | 20 | ± | 7.6 | 8.5 | 28 | 21 | ± | 11 | 10 | 38 | No |
| BaP | 36 | ± | 16 | 13 | 53 | 38 | ± | 21 | 15 | 68 | No |
| I123cdP | 17 | ± | 7.4 | 6.9 | 24 | 16 | ± | 9.5 | 5.9 | 29 | No |
| DahA | 2.6 | ± | 1.4 | 1 | 4.5 | 2.2 | ± | 1.4 | 1.2 | 5 | No |
| BghiP | 23 | ± | 9.3 | 10 | 33 | 21 | ± | 13 | 9.5 | 41 | No |
| $\sum_{13}$ PAHs | 680 | ± | 360 | 290 | 1400 | 1000 | ± | 400 | 480 | 1500 | No |

**Table S4.11:** Laundering Load 3 - Economy Laundry Powder: Concentrations of PAHs on Crop Tops Pre- and Post-Laundering.

| | Crop Top (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 130 | ± | 63 | 53 | 210 | 370 | ± | 170 | 160 | 600 | Yes↑ |
| Ant | 22 | ± | 22 | 1.6 | 57 | 61 | ± | 49 | 16 | 150 | No |
| Flu | 120 | ± | 120 | 9.5 | 270 | 170 | ± | 140 | 45 | 420 | No |
| Pyr | 110 | ± | 160 | 12 | 430 | 270 | ± | 170 | 80 | 500 | Yes↑ |
| BaA+Chr | 93 | ± | 120 | 1.8 | 330 | 90 | ± | 52 | 5.5 | 170 | No |
| BbF+BkF | 83 | ± | 87 | 14 | 210 | 180 | ± | 140 | 51 | 400 | Yes↑ |
| BeP | 47 | ± | 49 | 6 | 110 | 61 | ± | 39 | 26 | 110 | No |
| BaP | 20 | ± | 17 | 5.8 | 54 | 32 | ± | 26 | 16 | 83 | No |
| I123cdP | 13 | ± | 10 | 1.6 | 27 | 17 | ± | 12 | 2.7 | 33 | No |
| DahA | 14 | ± | 16 | 0.36 | 36 | 6.4 | ± | 5.1 | 1.7 | 16 | No |
| BghiP | 17 | ± | 16 | 1.1 | 44 | 20 | ± | 2.9 | 16 | 24 | No |
| $\sum_{13}$ PAHs | 670 | ± | 480 | 120 | 1400 | 1300 | ± | 530 | 590 | 2000 | Yes↑ |

**Table S4.12:** Laundering Load 4 – Environmentally Friendly Laundry Powder: Concentrations of PAHs on Socks Pre- and Post-Laundering.

| | Socks (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 1200 | ± | 340 | 790 | 1700 | 1100 | ± | 750 | 460 | 2300 | No |
| Ant | 280 | ± | 77 | 200 | 400 | 230 | ± | 200 | 50 | 590 | No |
| Flu | 260 | ± | 110 | 140 | 430 | 190 | ± | 92 | 95 | 300 | No |
| Pyr | 330 | ± | 100 | 180 | 490 | 450 | ± | 270 | 180 | 830 | No |
| BaA+Chr | 150 | ± | 130 | 4.2 | 370 | 61 | ± | 45 | 4.2 | 130 | No |
| BbF+BkF | 170 | ± | 94 | 68 | 330 | 120 | ± | 66 | 34 | 210 | No |
| BeP | 43 | ± | 34 | 0.75 | 78 | 9.3 | ± | 8.5 | 0.75 | 23 | No |
| BaP | 120 | ± | 100 | 30 | 290 | 51 | ± | 16 | 25 | 67 | No |
| I123cdP | 69 | ± | 49 | 24 | 140 | 30 | ± | 27 | 5.9 | 79 | Yes↓ |
| DahA | 12 | ± | 14 | 1.6 | 37 | 8.6 | ± | 9.6 | 1.6 | 26 | No |
| BghiP | 37 | ± | 39 | 2 | 110 | 53 | ± | 89 | 5 | 230 | No |
| $\sum_{13}$ PAHs | 2600 | ± | 860 | 1500 | 4200 | 2300 | ± | 1300 | 1100 | 4100 | No |

**Table S4.13:** Laundering Load 4 – Environmentally Friendly Laundry Powder: Concentrations of PAHs on Briefs Pre- and Post-Laundering.

| | Briefs (n=6) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 170 | ± | 100 | 7.5 | 270 | 310 | ± | 150 | 85 | 500 | No |
| Ant | 40 | ± | 45 | 1.1 | 110 | 58 | ± | 45 | 23 | 130 | No |
| Flu | 520 | ± | 1100 | 6.5 | 2700 | 150 | ± | 94 | 36 | 280 | No |
| Pyr | 760 | ± | 1600 | 6.5 | 4000 | 240 | ± | 93 | 140 | 390 | No |
| BaA+Chr | 220 | ± | 370 | 1.1 | 950 | 40 | ± | 32 | 6.5 | 77 | No |
| BbF+BkF | 75 | ± | 56 | 11 | 170 | 43 | ± | 22 | 21 | 81 | No |
| BeP | 17 | ± | 16 | 0.7 | 45 | 13 | ± | 6.5 | 7.5 | 23 | No |
| BaP | 31 | ± | 27 | 2.2 | 74 | 29 | ± | 17 | 14 | 62 | No |
| I123cdP | 14 | ± | 11 | 1.8 | 33 | 8.8 | ± | 3 | 3.8 | 12 | No |
| DahA | 2.1 | ± | 2.1 | 0.19 | 4.9 | 1.5 | ± | 1.2 | 0.42 | 3.8 | No |
| BghiP | 17 | ± | 8.9 | 6.9 | 27 | 13 | ± | 7.3 | 4.4 | 25 | No |
| $\sum_{13}$ PAHs | 1900 | ± | 2800 | 46 | 7500 | 910 | ± | 370 | 340 | 1300 | No |

**Table S4.14:** Laundering Load 4 – Environmentally Friendly Laundry Powder: Concentrations of PAHs on Crop Tops Pre- and Post-Laundering.

| | Crop Tops (n=6) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 120 | ± | 48 | 72 | 200 | 160 | ± | 37 | 130 | 200 | No |
| Ant | 14 | ± | 17 | 1.6 | 46 | 43 | ± | 38 | 3.5 | 98 | No |
| Flu | 50 | ± | 35 | 9.5 | 94 | 120 | ± | 80 | 45 | 230 | No |
| Pyr | 130 | ± | 150 | 12 | 430 | 250 | ± | 370 | 12 | 950 | No |
| BaA+Chr | 51 | ± | 48 | 1.8 | 100 | 62 | ± | 37 | 1.8 | 90 | No |
| BbF+BkF | 58 | ± | 58 | 31 | 180 | 68 | ± | 37 | 32 | 120 | No |
| BeP | 50 | ± | 48 | 2.9 | 110 | 51 | ± | 46 | 12 | 110 | No |
| BaP | 17 | ± | 12 | 4.1 | 40 | 33 | ± | 32 | 15 | 95 | No |
| I123cdP | 8.5 | ± | 8.1 | 2.7 | 24 | 11 | ± | 9 | 2.7 | 25 | No |
| DahA | 12 | ± | 23 | 0.36 | 59 | 5.4 | ± | 2.9 | 1.2 | 7.7 | No |
| BghiP | 16 | ± | 8.7 | 6.3 | 26 | 15 | ± | 5.6 | 7.4 | 22 | No |
| $\sum_{13}$ PAHs | 530 | ± | 310 | 180 | 890 | 820 | ± | 530 | 310 | 1700 | No |

**Table S4.15:** Laundering Load 5 – Premium Laundry Powder+ Triton X 305: Concentrations of PAHs on Socks Pre- and Post-Laundering.

| | Socks (n=6) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 1100 | ± | 1200 | 250 | 3600 | 600 | ± | 590 | 140 | 1800 | No |
| Ant | 270 | ± | 210 | 85 | 640 | 120 | ± | 75 | 56 | 220 | No |
| Flu | 340 | ± | 360 | 130 | 1100 | 320 | ± | 510 | 68 | 1400 | No |
| Pyr | 510 | ± | 610 | 170 | 1700 | 720 | ± | 1200 | 130 | 3200 | No |
| BaA+Chr | 150 | ± | 230 | 4.2 | 610 | 75 | ± | 66 | 4.2 | 170 | No |
| BbF+BkF | 200 | ± | 340 | 23 | 900 | 100 | ± | 130 | 19 | 350 | No |
| BeP | 130 | ± | 270 | 0.75 | 680 | 21 | ± | 22 | 5.5 | 64 | No |
| BaP | 320 | ± | 650 | 16 | 1600 | 43 | ± | 61 | 1.3 | 160 | No |
| I123cdP | 35 | ± | 60 | 2.8 | 160 | 24 | ± | 33 | 0.75 | 88 | No |
| DahA | 6.3 | ± | 7.4 | 1.6 | 20 | 4.4 | ± | 3.1 | 1.6 | 9.7 | No |
| BghiP | 120 | ± | 210 | 3.4 | 530 | 2.3 | ± | 1.5 | 1 | 4.3 | No |
| $\sum_{13}$ PAHs | 3200 | ± | 4100 | 790 | 12000 | 2000 | ± | 2600 | 670 | 7400 | No |

**Table S4.16:** Laundering Load 5 – Premium Laundry Powder+ Triton X 305: Concentrations of PAHs on Briefs Pre- and Post-Laundering.

| | Briefs (n=6) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 280 | ± | 170 | 83 | 530 | 330 | ± | 120 | 150 | 500 | No |
| Ant | 19 | ± | 23 | 1.1 | 62 | 71 | ± | 46 | 23 | 130 | No |
| Flu | 180 | ± | 110 | 37 | 280 | 230 | ± | 130 | 120 | 470 | No |
| Pyr | 290 | ± | 390 | 28 | 1100 | 350 | ± | 310 | 120 | 920 | No |
| BaA+Chr | 72 | ± | 99 | 5 | 230 | 150 | ± | 140 | 56 | 410 | No |
| BbF+BkF | 87 | ± | 43 | 23 | 140 | 73 | ± | 30 | 44 | 130 | No |
| BeP | 19 | ± | 10 | 7.5 | 30 | 21 | ± | 11 | 11 | 41 | No |
| BaP | 62 | ± | 42 | 16 | 120 | 47 | ± | 26 | 22 | 83 | No |
| I123cdP | 19 | ± | 13 | 5 | 39 | 17 | ± | 12 | 7.3 | 40 | No |
| DahA | 2.7 | ± | 1.3 | 0.42 | 4 | 3.3 | ± | 4 | 1 | 11 | No |
| BghiP | 23 | ± | 12 | 8.8 | 37 | 25 | ± | 14 | 16 | 51 | No |
| $\sum_{13}$ PAHs | 1100 | ± | 700 | 310 | 2200 | 1300 | ± | 660 | 650 | 2200 | No |

**Table S4.17:** Laundering Load 5 – Premium Laundry Powder+ Triton X 305: Concentrations of PAHs on Crop Tops Pre- and Post-Laundering.

| | Crop Tops | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) (n=6) | | | | | Post-Laundering (ng.g$^{-1}$) (n=5) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 160 | ± | 140 | 22 | 410 | 230 | ± | 110 | 130 | 400 | Yes↑ |
| Ant | 19 | ± | 17 | 3.5 | 48 | 37 | ± | 24 | 16 | 67 | Yes↑ |
| Flu | 28 | ± | 16 | 9.5 | 45 | 160 | ± | 210 | 45 | 580 | No |
| Pyr | 62 | ± | 110 | 12 | 280 | 300 | ± | 320 | 22 | 730 | No |
| BaA+Chr | 39 | ± | 41 | 1.8 | 90 | 120 | ± | 90 | 34 | 280 | Yes↑ |
| BbF+BkF | 22 | ± | 12 | 6.1 | 32 | 85 | ± | 63 | 32 | 190 | Yes↑ |
| BeP | 41 | ± | 54 | 2.5 | 110 | 66 | ± | 51 | 2.9 | 110 | No |
| BaP | 15 | ± | 12 | 3.1 | 37 | 25 | ± | 12 | 16 | 43 | No |
| I123cdP | 9.7 | ± | 13 | 1.6 | 36 | 16 | ± | 9.4 | 2.7 | 29 | No |
| DahA | 3 | ± | 3.2 | 0.35 | 7 | 6.5 | ± | 3.6 | 2.4 | 13 | No |
| BghiP | 13 | ± | 8.9 | 2.5 | 22 | 22 | ± | 0.62 | 21 | 22 | No |
| $\sum_{13}$ PAHs | 410 | ± | 320 | 69 | 800 | 1100 | ± | 460 | 490 | 1800 | Yes↑ |

**Table S4.18:** Laundering Loads 1- 5: Concentrations of PAHs on Socks Pre- and Post-Laundering.

| | Socks (n=30) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | Mean | ± | SD | Min | Max | Mean | ± | SD | Min | Max | |
| Phe | 1100 | ± | 820 | 250 | 3600 | 790 | ± | 650 | 140 | 3200 | Yes↓ |
| Ant | 240 | ± | 190 | 68 | 730 | 160 | ± | 140 | 3.5 | 650 | Yes↓ |
| Flu | 350 | ± | 370 | 64 | 1600 | 200 | ± | 240 | 59 | 1400 | Yes↓ |
| Pyr | 410 | ± | 440 | 63 | 1800 | 330 | ± | 570 | 12 | 3200 | No |
| BaA+Chr | 130 | ± | 160 | 4.2 | 610 | 47 | ± | 45 | 4.2 | 170 | Yes↓ |
| BbF+BkF | 110 | ± | 170 | 2.6 | 900 | 55 | ± | 76 | 2.6 | 350 | Yes↓ |
| BeP | 61 | ± | 120 | 0.75 | 680 | 15 | ± | 13 | 0.75 | 64 | Yes↓ |
| BaP | 140 | ± | 300 | 4.9 | 1600 | 35 | ± | 31 | 1.3 | 160 | Yes↓ |
| I123cdP | 50 | ± | 56 | 2.8 | 210 | 19 | ± | 20 | 0.75 | 88 | Yes↓ |
| DahA | 7.7 | ± | 11 | 1.6 | 46 | 3.9 | ± | 5 | 1.6 | 26 | No |
| BghiP | 66 | ± | 100 | 2 | 530 | 21 | ± | 41 | 1 | 230 | Yes↓ |
| $\sum_{13}$ PAHs | 2600 | ± | 2500 | 570 | 12000 | 1700 | ± | 1500 | 400 | 7400 | Yes↓ |

**Table S4.19:** Laundering Loads 1- 5: Concentrations of PAHs on Briefs Pre- and Post-Laundering.

| | Briefs (n=30) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) | | | | | Post-Laundering (ng.g$^{-1}$) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 270 | ± | 160 | 7.5 | 580 | 330 | ± | 130 | 85 | 520 | No |
| Ant | 34 | ± | 32 | 1.1 | 110 | 71 | ± | 100 | 23 | 590 | No |
| Flu | 250 | ± | 470 | 6.5 | 2700 | 200 | ± | 110 | 36 | 490 | No |
| Pyr | 360 | ± | 720 | 6.5 | 4000 | 280 | ± | 170 | 100 | 920 | No |
| BaA+Chr | 79 | ± | 180 | 1.1 | 950 | 57 | ± | 80 | 5 | 410 | No |
| BbF+BkF | 53 | ± | 43 | 9.5 | 170 | 39 | ± | 28 | 12 | 130 | No |
| BeP | 25 | ± | 21 | 0.7 | 85 | 21 | ± | 12 | 7.5 | 66 | No |
| BaP | 53 | ± | 43 | 2.2 | 160 | 40 | ± | 25 | 14 | 130 | No |
| I123cdP | 23 | ± | 19 | 1.8 | 77 | 15 | ± | 12 | 3.8 | 60 | Yes↓ |
| DahA | 3.6 | ± | 3.1 | 0.19 | 14 | 2.5 | ± | 2.5 | 0.27 | 11 | No |
| BghiP | 30 | ± | 25 | 6.9 | 110 | 20 | ± | 13 | 4.4 | 61 | Yes↓ |
| $\sum_{13}$ PAHs | 1200 | ± | 1300 | 46 | 7500 | 1100 | ± | 510 | 340 | 2600 | No |

**Table S4.20:** Laundering Loads 1- 5: Concentrations of PAHs on Crop Tops Pre- and Post-Laundering.

| | Crop Tops | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pre-Laundering (ng.g$^{-1}$) (n=30) | | | | | Post-Laundering (ng.g$^{-1}$) (n=29) | | | | | Significantly Different (paired t-test) |
| | **Mean** | **±** | **SD** | **Min** | **Max** | **Mean** | **±** | **SD** | **Min** | **Max** | |
| Phe | 130 | ± | 74 | 22 | 410 | 270 | ± | 130 | 130 | 600 | Yes↑ |
| Ant | 17 | ± | 16 | 1.6 | 57 | 52 | ± | 36 | 3.5 | 150 | Yes↑ |
| Flu | 56 | ± | 62 | 2 | 270 | 220 | ± | 220 | 45 | 880 | Yes↑ |
| Pyr | 73 | ± | 110 | 2.6 | 430 | 310 | ± | 330 | 12 | 1300 | Yes↑ |
| BaA+Chr | 54 | ± | 64 | 1.8 | 330 | 98 | ± | 67 | 1.8 | 280 | Yes↑ |
| BbF+BkF | 46 | ± | 51 | 6.1 | 210 | 120 | ± | 92 | 22 | 400 | Yes↑ |
| BeP | 44 | ± | 48 | 2.5 | 110 | 58 | ± | 41 | 2.9 | 110 | Yes↑ |
| BaP | 16 | ± | 11 | 3 | 54 | 34 | ± | 26 | 15 | 120 | Yes↑ |
| I123cdP | 8.2 | ± | 8.7 | 1.6 | 36 | 16 | ± | 12 | 2.7 | 50 | Yes↑ |
| DahA | 7.2 | ± | 13 | 0.32 | 59 | 6.6 | ± | 5.1 | 1.1 | 22 | No |
| BghiP | 14 | ± | 10 | 1.1 | 44 | 19 | ± | 7.1 | 1.1 | 32 | Yes↑ |
| $\sum_{13}$ PAHs | 470 | ± | 310 | 69 | 1400 | 1200 | ± | 610 | 310 | 3000 | Yes↑ |

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**Table S4.21: Cross Contamination Swatches: Cotton (95%) Elastane (5%)**

| | Post-Laundering (ng.g$^{-1}$) (n=5) | | | | |
|---|---|---|---|---|---|
| | **Mean** | **±** | **SD** | **Min** | **Max** |
| Phe | 150 | ± | 57 | 97 | 210 |
| Ant | 37 | ± | 15 | 17 | 54 |
| Flu | 82 | ± | 37 | 49 | 140 |
| Pyr | 86 | ± | 46 | 40 | 160 |
| BaA+Chr | 55 | ± | 31 | 21 | 100 |
| BbF+BkF | 31 | ± | 16 | 16 | 56 |
| BeP | 15 | ± | 10 | 7.5 | 33 |
| BaP | 27 | ± | 13 | 13 | 49 |
| I123cdP | 9.6 | ± | 6.7 | 3.5 | 21 |
| DahA | 3.2 | ± | 1.9 | 1.5 | 6.1 |
| BghiP | 12 | ± | 9.4 | 0.8 | 27 |
| $\sum_{13}$ PAHs | 500 | ± | 220 | 320 | 860 |

**Table S4.22: Cross Contamination Swatches: Polyester (92%) Elastane (8%)**

| | Post-Laundering (ng.g$^{-1}$) (n=5) | | | | |
|---|---|---|---|---|---|
| | Mean | ± | SD | Min | Max |
| Phe | 240 | ± | 100 | 85 | 340 |
| Ant | <MDL | | | <MDL | <MDL |
| Flu | <MDL | | | <MDL | 210 |
| Pyr | <MDL | | | <MDL | 410 |
| BaA+Chr | <MDL | | | <MDL | <MDL |
| BbF+BkF | <MDL | | | <MDL | 63 |
| BeP | 18 | ± | 6.5 | 7.5 | 23 |
| BaP | 27 | ± | 12 | 14 | 38 |
| I123cdP | 11 | ± | 3.2 | 7.7 | 15 |
| DahA | 2.2 | ± | 1.1 | 1.1 | 3.4 |
| BghiP | 13 | ± | 3.3 | 10 | 17 |
| $\sum_{13}$ PAHs | 450 | ± | 390 | 130 | 1100 |

**Table S4.23: Cross Contamination Swatches: Cotton/Elastane**

| | Post-Laundering (ng.g$^{-1}$) (n=5) | | | | |
|---|---|---|---|---|---|
| | Mean | ± | SD | Min | Max |
| Phe | 150 | ± | 43 | 94 | 200 |
| Ant | 78 | ± | 44 | 41 | 150 |
| Flu | 91 | ± | 13 | 77 | 110 |
| Pyr | 150 | ± | 75 | 59 | 240 |
| BaA+Chr | 29 | ± | 23 | 5 | 51 |
| BbF+BkF | 25 | ± | 8.5 | 17 | 38 |
| BeP | 11 | ± | 5.7 | 3.1 | 19 |
| BaP | 17 | ± | 7.4 | 7.8 | 25 |
| I123cdP | 4.8 | ± | 1.4 | 3.1 | 6.3 |
| DahA | 0.75 | ± | 0.37 | 0.41 | 1.4 |
| BghiP | 6.9 | ± | 0.97 | 5.7 | 8.4 |
| $\sum_{13}$ PAHs | 560 | ± | 57 | 480 | 640 |

**Table S4.24: Cross Contamination Swatches: Nylon (92%) Elastane (8%)**

| | Post-Laundering (ng.g$^{-1}$) (n=5) | | | | |
|---|---|---|---|---|---|
| | Mean | ± | SD | Min | Max |
| Phe | <MDL | | | <MDL | <MDL |
| Ant | <MDL | | | <MDL | <MDL |
| Flu | <MDL | | | <MDL | <MDL |
| Pyr | <MDL | | | <MDL | <MDL |
| BaA+Chr | <MDL | | | <MDL | <MDL |
| BbF+BkF | <MDL | | | <MDL | <MDL |
| BeP | <MDL | | | <MDL | <MDL |
| BaP | <MDL | | | <MDL | <MDL |
| I123cdP | <MDL | | | <MDL | <MDL |
| DahA | <MDL | | | <MDL | <MDL |
| BghiP | <MDL | | | <MDL | <MDL |
| $\sum_{13}$ PAHs | <MDL | | | <MDL | <MDL |

**Table S4.25: Cross Contamination Swatches: Cotton (95%) Elastane (5%), Cotton/Elastane and Cotton/Elastane in different loads of laundry**

| | Post-Laundering (ng.g$^{-1}$) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Load 1 (n=3) | | | Load 2 (n=3) | | | Load 3 (n=3) | | | Load 4 (n=3) | | | Load 5 (n=3) | | |
| | Mean | ± | SD | Mean | ± | SD | Mean | ± | SD | Mean | ± | SD | Mean | ± | SD |
| Phe | 140 | ± | 73 | 250 | ± | 81 | 200 | ± | 120 | 160 | ± | 59 | 140 | ± | 65 |
| Ant | 67 | ± | 72 | 52 | ± | 36 | 27 | ± | 13 | 38 | ± | 14 | 47 | ± | 21 |
| Flu | 54 | ± | 21 | 140 | ± | 68 | 70 | ± | 32 | 56 | ± | 22 | 91 | ± | 54 |
| Pyr | 85 | ± | 47 | 200 | ± | 190 | 120 | ± | 23 | 130 | ± | 87 | 180 | ± | 51 |
| BaA+Chr | 26 | ± | 17 | 42 | ± | 32 | 35 | ± | 25 | 11 | ± | 8.8 | 38 | ± | 55 |
| BbF+BkF | 20 | ± | 4.2 | 41 | ± | 19 | 29 | ± | 8.8 | 20 | ± | 1.9 | 31 | ± | 22 |
| BeP | 15 | ± | 6.9 | 18 | ± | 5.7 | 15 | ± | 5.3 | 11 | ± | 4.7 | 15 | ± | 16 |
| BaP | 25 | ± | 6.1 | 29 | ± | 6.8 | 28 | ± | 9.2 | 13 | ± | 1.3 | 24 | ± | 22 |
| I123cdP | 8.8 | ± | 3.3 | 10 | ± | 4.7 | 7.6 | ± | 2.8 | 4.9 | ± | 2.7 | 11 | ± | 9.1 |
| DahA | 2.7 | ± | 1.7 | 2.4 | ± | 1 | 1.5 | ± | 0.74 | 1 | ± | 0.49 | 2.7 | ± | 3 |
| BghiP | 12 | ± | 5 | 12 | ± | 4.9 | 9.7 | ± | 2.1 | 5.7 | ± | 4.9 | 14 | ± | 11 |
| $\sum_{13}$ PAHs | 460 | ± | 95 | 790 | ± | 320 | 550 | ± | 120 | 450 | ± | 120 | 590 | ± | 260 |

**Appendix 4**

**Supplementary Information: An Exploratory Analysis of Firefighter Reproduction through Survey Data and Biomonitoring**

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S6.1. Survey:

The recruitment of firefighters commenced by means of information dissemination through multiple gatekeeper organisations. The study was anonymous to support firefighters providing accurate information surrounding personal, reproductive, and occupational hygiene. Stage 1 of the study involved the completion of the survey, which was available to Australian firefighters, aged 18 and over. Stage 2 of the study involved asking participants to contribute human samples. These participants provided an email address by which to be contacted to receive pathology forms, breast milk collection kits, and other study specific information.

Demographic and occupational: 20 questions
Fire exposure, post fire actions, fire station design & hygiene: 27 questions
Reproduction: 8 questions
Breast milk initial survey question: 19 questions

S6.2. Sample Collection:

Firefighters who opted to produce a sample (blood, urine, or semen) for the study were sent deidentified pathology forms. Separate pathology forms were created for blood, urine, and semen contributions outlining what was required from the contribution in each matrix. Firefighters had the option to select from the following: blood & urine, semen, breast milk, or a combination of the three options. Firefighters were told to provide the pathology forms at their choice pathology centre, with all requirements for the phlebotomist outlined on the form. Each firefighter contributing a sample was assigned a unique code name, which was applied to any pathology forms provided to that firefighter. All pathology form were given the same birth date (01/01/1980) to support anonymity, with age range data collected by means of the survey. Breast milk samples were not collected via pathology centre. That breast milk collection method is outlined following the presentation of the blood, urine, and semen collection method.

Firefighters were requested to contribute a total of 40ml of whole blood, 100ml of urine, a minimum of 100ml of breast milk, or an entire semen sample by means of masturbation 3-5 days after last ejaculation, ensuring no condoms, artificial lubricants, or talcs were utilised. Firefighters who contributed blood and urine samples provided 2x20mL of whole blood and 2x50mL of urine as two separate laboratories were engaged in the analysis of the samples. For the blood and urine sent to the Queensland Alliance for Environmental Health Services (QAEHS), 2x10ml lithium heparin tubes of blood were collected, spun and separated into 2x aliquots. They and the urine (50ml container) were then frozen and shipped to the laboratory. For the blood and urine sent to the SafeWork NSW Chemical Analysis Branch, TestSafe Laboraty (TestSafe), 2x10ml lithium heparin whole blood was collected and refrigerated alongside the contributed urine (50ml container) and sent to TestSafe. Blood samples were collected by a trained phlebotomist, urine samples were collected by the firefighter in private.

Firefighters who contributed semen were provided with a sterile, semen specific container for collection by the pathology centre. Firefighters were advised that the sample needed to reach the testing laboratory for analysis within 60 minutes of collection, keeping the sample at body temperature until delivered. Upon receipt at the pathology centre, samples were maintained at room temperature (20-37°C) until analysis occurred. Analysis occurred in line with Australian National Association of Testing Authorities (NATA) requirements, and via methodology developed based on the World Health Organisation’s (WHO) Laboratory Manual for the Examination and Processing of Human Semen, Fifth Edition. Due to the location of participants, 19 samples analysed in New South Wales (NSW) by an automated analyser (SQA-V Gold) and 2 samples were manually analysed in Queensland (QLD).

Analysis of the samples included assessment of viscosity, liquefaction, agglutination, volume, sperm concentration, progressive motile, total motile, immotile, and normal forms. The QLD samples included pH, leukocyte count and immature germ cells.

Firefighters contributing breast milk samples were mailed a collection kit including a sterile jar with markers for volume (a minimum of 100ml requested), a freezer brick, a small esky, and return courier forms for overnight delivery. Firefighters were requested to thoroughly wash hands and any pumps utilised in the collection of expressed milk.

## S6.3. Chemicals

Table S6.1: List of Chemicals Analysed by Matrix including LOD/LOQ and Methods, with Abbreviations Included

| Matrix | Chemical(s) | LOD/LOQ | Analytes | Method |
|---|---|---|---|---|
| Urine | PAHs | 0.05µg/L | 1-hydroxypyrene (1-OH-PYR) | WCA.158* |
| | | <0.42 µg/L | 1-hydroxynaphthalene (1-OH-NAP), 2-hydroxynaphthalene (2-OH-NAP), 2-hydroxyflourene (2-OH-FLU), 3-hydroxyflourene (3-OH-FLU), 1-hydroxyphenanthrene (1-OH-PHEN), 2-hydroxyphenanthrene (2-OH-PHEN), 4- hydroxyphenanthrene (4-OH-PHEN), 9- hydroxyphenanthrene (9-OH-PHEN) | https://doi.org/10.1016/j.envres.2019.109048 |
| | Benzene | 0.5 µg/L | s-Phenylmercapturic acid | WCA.211* |
| | Ethylbenzene & Styrene | 0.3 mmol/L | Mandelic Acid | WCA.125* |
| | Toluene | 0.5 mmol/L | Hippuric Acid | WCA.131* |
| | Xylene | 0.5 mmol/L | Toluric Acid | WCA.131* |
| | Metals | Varying: 0.01 – 40 µmol/L | Antimony (Sb), Beryllium (Be), Bismuth (Bi), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), Selenium (Se), Tellurium (Te), Thallium (Tl), Uranium (U), Vanadium (V) | WCA.215* |
| | Arsenic | 0.02 µmol/L | Monomethyl arsonic acid (MMA), Dimethyl arsinic acid (DMA), Arsenic (III) ($As^{III}$), Arsenic (V) ($As^{V}$), Total inorganic arsenic, Arsenobetaine | WCA.218* |
| | OPEs | <1.360 µg/L | Dibutyl phosphate (DBP), Bis(2-chloroethyl) phosphate (BCEP), Bis(1-chloroisopropyl) phosphate (BCIPP), Bis(methylphenyl) phosphate (BMPP), Bis(2-ethylhexyl) phosphate (BEHP), Diphenyl phosphate (DPhP), Bis(1,3-dichloroisopropyl) phosphate | https://doi.org/10.1016/j.envint.2017.11.019 |

| | | | | |
|---|---|---|---|---|
| | | | (BDCIPP), Bis(2-butoxyethyl) phosphate (BBOEP), Triphenyl phosphate (TPhP), 2-Ethylhexyl diphenyl phosphate (EHDPP), Tributyl phosphate (TBP), Tris(2-chloroethyl) phosphate (TCEP), Tris(2-chloroisopropyl) phosphate (TCIPP), Tris(methylphenyl) phosphate (TMPP), tris(1,3-dichloroiospropyl) phosphate (TDCPP), 1-Hydroxy-2-propyl bis(1-chloro-2-propyl) phosphate (BCIPHIPP), Tris(2-butoxyethyl) phosphate (TBOEP), Bis(2-butoxyethyl) 3-hydroxyl-2-butoxyethyl phosphate (3OH-TBOEP), Bis(2-butoxyethyl) hydroxyethyl phosphate (BBOEHEP), Tris(2-ethylhexyl) phosphate (TEHP) | |
| | Phthalates | <0.71 µg/L | monomethyl phthalate (MMP), monoethyl phthalate (MEP), mono-isobutyl phthalate (MiBP), mono-butyl phthalate (MnBP), mono(3-carboxypropyl) phthalate (MCPP), monobenzyl phthalate (MBzP), mono(2-ethylhexyl) phthalate (MEHP), mono(2-ethyl-5-oxohexyl) phthalate (MEOHP), mono(2-ethyl-5-hydroxyhexyl) phthalate (MEHHP), mono(2-ethyl-5-carboxypentyl) phthalate (MECPP), monocyclohexyl phthalate (MCHP), mono-n-octyl phthalate (MnOP) | https://doi.org/10.1016/j.envint.2020.105534 |
| Whole Blood | Metals | <0.1µmol/L | Cadmium (Cd), Cobalt (Co), Lead (Pb), Manganese (Mn), Mercury (Hg) | WCA.214* |
| Plasma | PFAS | <0.0891 µg/L | Perfluorobutanoic acid (PFBA), Perfluoropentanoic acid (PFPeA), Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluoroundecanoic acid (PFUnDA), Perfluorododecanoic acid (PFDoDA), Perfluorobutane sulphonic acid (PFBS), perfluoropentane sulphonate (PFPeS), Perfluorohexane sulphonic acid (PFHxS), perfluoroheptanesulfonic acid (PFHpS), Perfluorooctane sulphonic acid (PFOS), linear and branched isomers (Total PFOS), N-Methyl-perfluorooctane sulfonamido acetic acid (NMeFOSAA), perfluorohexanoic acid (PFHxA), perfluorononanesulfonate (PFNS), perfluordecanesulphonate (PFDS), Fluorooctane sulfonamide (FOSA), perfluorooctane sulfonamide acetic acid (FOSAA), N-Ethyl-perfluorooctane sulfonamido acetic acid (NEtFOSAA) | https://doi.org/10.1016/j.ijheh.2019.03.004 |

| | | | | |
|---|---|---|---|---|
| Plasma | PBDEs | <0.0078 µg/L | 244’-Tribromodiphenyl ether (BDE28), 22’44’-Tetrabromodiphenyl ether (BDE47), 22’44’5-Pentabromodiphenyl ether (BDE99), 22’44’6-Pentabromodiphenyl ether (BDE100), 22’44’55’-Hexabromodiphenyl ether (BDE153) | https://doi.org/10.1016/j.envint.2018.09.014 |

*Further Workcover details can be found by accessing the Chemical Analysis Branch Handbook via: www.nsw.gov.au/sites/default/files/2022-02/TestSafe-Chemical-Analysis-Branch-Handbook-9th-edition-TS033.pdf

## S6.4. Breast Milk

When comparing exposure history within the breast milk group more frequent exposure (≤fortnightly) was significantly higher for the following analytes compared to less frequent exposure (>fortnightly), BDE-47: (U=140, p=0.03677), pp-DDE (U=130, p=0.002857), and PCB153 (U=149, p=0.01363).

Table S6.2: Results of Chemicals Analysed in Breast Milk, Including LODs and Detection Frequencies

| Congener or analyte ng/g lipid | LOD | n | % Detect | Mean ± SD | Min | Max | 25th % | 50th % | 75th % | 95th % |
|---|---|---|---|---|---|---|---|---|---|---|
| BDE-28 (2022) | 0.57 | 30 | 10% | * | <LOD | 4.06 | <LOD | <LOD | <LOD | 1.41 |
| BDE-28 (2016) | 0.21 | 4 | 25% | * | <LOD | 0.76 | <LOD | <LOD | <LOD | 0.65 |
| BDE-47 (2022) | 0.84 | 30 | 63% | 1.66 ± | <LOD | 6.33 | <LOD | 1.22 | 2.65 | 4.07 |
| BDE-47 (2016) | 0.21 | 4 | 100% | 3.83 ± | 2.68 | 4.90 | 3.51 | 3.87 | 4.19 | 4.76 |
| BDE-99 (2022) | 0.05 | 4 | 100% | 1.13 ± | 0.91 | 1.43 | 1.04 | 1.09 | 1.17 | 1.38 |
| BDE-100 (2022) | 0.07 | 4 | 100% | 0.72 ± | 0.56 | 1.06 | 0.56 | 0.64 | 0.81 | 1.01 |
| BDE-153 (2022) | 0.16 | 30 | 63% | 1.4 ± 1.49 | <LOD | 5.59 | <LOD | 1.12 | 2.16 | 4.16 |
| BDE-153 (2016) | 0.42 | 4 | 100% | 1.99 ± | 0.53 | 3.04 | 1.41 | 2.19 | 2.77 | 2.99 |
| BDE-154 (2022) | 1.07 | 30 | 3% | * | <LOD | 3.75 | <LOD | <LOD | <LOD | <LOD |
| HCB (2022) | 0.36 | 9 | 67% | 3.29 ± | <LOD | 6.70 | <LOD | 3.07 | 5.64 | 6.30 |
| HCB (2016) | 0.10 | 3 | 100% | 4.31 ± | 2.30 | 6.70 | 3.11 | 3.92 | 5.31 | 6.42 |
| pp-DDE (2022) | 0.55 | 26 | 100% | 29.98 ± | 6.57 | 78.04 | 22.57 | 26.44 | 32.41 | 60.39 |
| pp-DDE (2016) | 0.83 | 4 | 100% | 28.29 ± | 10.24 | 41.54 | 23.81 | 30.69 | 35.17 | 40.27 |
| pp-DDT (2022) | 1.67 | 26 | 8% | * | <LOD | 5.33 | <LOD | <LOD | <LOD | 1.99 |
| pp-DDT (2016) | 0.21 | 4 | 100% | 2.88 ± | 1.00 | 6.80 | 1.38 | 1.85 | 3.35 | 6.11 |
| mirex (2016) | 0.10 | 4 | 100% | 0.29 ± | 0.14 | 0.54 | 0.17 | 0.23 | 0.35 | 0.50 |
| trans-chlordane | 0.41 | 30 | 13% | * | <LOD | 1.93 | <LOD | <LOD | <LOD | 1.30 |
| β-HCH (2016) | 0.21 | 3 | 100% | 2.18 ± | 0.61 | 3.83 | 1.36 | 2.12 | 2.97 | 3.66 |
| PCB28 (2022) | 0.25 | 4 | 75% | 0.5 ± 0.33 | <LOD | 0.92 | 0.34 | 0.48 | 0.63 | 0.86 |
| PCB52 (2022) | 0.10 | 4 | 50% | 0.12 ± | <LOD | 0.21 | <LOD | 0.12 | 0.19 | 0.21 |
| PCB101 (2022) | 0.56 | 30 | 10% | * | <LOD | 0.88 | <LOD | <LOD | <LOD | 0.55 |
| PCB101 (2016) | 0.10 | 4 | 100% | 0.18 ± | 0.12 | 0.23 | 0.16 | 0.18 | 0.20 | 0.22 |
| PCB105 (2022) | 0.42 | 30 | 3% | * | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| PCB105 (2016) | 0.04 | 4 | 100% | 0.27 ± | 0.12 | 0.38 | 0.19 | 0.30 | 0.38 | 0.38 |
| PCB114 (2022) | 0.04 | 4 | 100% | 0.08 ± | <LOD | 0.20 | 0.04 | 0.06 | 0.10 | 0.18 |
| PCB118 (2022) | 1.08 | 30 | 17% | * | <LOD | 2.1 | <LOD | <LOD | <LOD | 1.76 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| PCB118 (2016) | 0.10 | 4 | 100% | 1.46 ± | 0.42 | 2.7 | 0.94 | 1.38 | 1.9 | 2.5 |
| PCB138 (2022) | 0.90 | 30 | 43% | * | <LOD | 6.4 | <LOD | <LOD | 1.3 | 2.9 |
| PCB138 (2016) | 0.06 | 4 | 100% | 2.74 ± | 0.76 | 6.6 | 1.30 | 1.79 | 3.2 | 5.9 |
| PCB153 (2022) | 0.65 | 30 | 73% | 3.2 ± 6.51 | <LOD | 36 | <LOD | 1.93 | 3.0 | 7.9 |
| PCB152 (2016) | 0.03 | 4 | 100% | 4.05 ± | 1.04 | 10 | 1.98 | 2.51 | 4.6 | 9.0 |
| PCB156 (2022) | 0.03 | 30 | 67% | 0.32 ± | <LOD | 1.6 | <LOD | 0.17 | 0.34 | 1.2 |
| PCB156 (2016) | 0.04 | 4 | 100% | 0.36 ± | 0.07 | 0.92 | 0.15 | 0.22 | 0.43 | 0.82 |
| PCB157 (2022) | 0.05 | 30 | 23% | * | <LOD | 0.25 | <LOD | <LOD | <LOD | 0.16 |
| PCB157 (2016) | 0.04 | 4 | 75% | 0.11 ± | <LOD | 0.23 | 0.07 | 0.10 | 0.14 | 0.21 |
| PCB167 (2022) | 0.32 | 30 | 3% | * | <LOD | 0.20 | <LOD | <LOD | <LOD | <LOD |
| PCB167 (2016) | 0.05 | 4 | 50% | 0.08 ± | <LOD | 0.19 | <LOD | 0.05 | 0.11 | 0.18 |
| PCB180 (2022) | 1.61 | 30 | 37% | * | <LOD | 8.2 | <LOD | <LOD | 1.7 | 3.1 |
| PCB180 (2016) | 0.10 | 4 | 100% | 2.27 ± 2.5 | 0.59 | 6.0 | 1.1 | 1.2 | 2.4 | 5.3 |
| PCB189 (2022) | 0.16 | 34 | 18% | * | <LOD | 0.20 | <LOD | <LOD | <LOD | <LOD |
| TPhP (2016) | 6.20 | 4 | 100% | 12.58 ± | 7.70 | 22 | 8 | 10.30 | 15 | 21 |
| TBP (2016) | 0.94 | 4 | 100% | 26.5 ± 8.7 | 16.00 | 35 | 21 | 27.50 | 33 | 35 |
| TiBP (2022) | 1207 | 16 | 25% | * | <LOD | 2794 | <LOD | <LOD | 826 | 2021 |
| TnBP (2022) | 71.91 | 16 | 6% | * | <LOD | 101.86 | <LOD | <LOD | <LOD | 52.43 |
| TCEP (2022) | 15.35 | 16 | 19% | * | <LOD | 33.55 | <LOD | <LOD | <LOD | 32.71 |
| TCP (2016) | 1.10 | 4 | 100% | 6.25 ± | 5.00 | 8.20 | 5.30 | 5.90 | 6.85 | 7.93 |
| TCIPP (2022) | 909 | 16 | 63% | 964 ± 831 | <LOD | 2676 | <LOD | <LOD | 1176 | 2666 |
| TCIPP (2016) | 78.00 | 4 | 100% | 190 ± | 150 | 220 | 180 | 195 | 205 | 217 |
| TDCIPP (2016) | 1.70 | 4 | 75% | 5.24 ± | <LOD | 13.00 | 2.46 | 3.55 | 6.33 | 11.67 |
| TBOEP (2016) | 3.90 | 4 | 100% | 68.25 ± | 56.00 | 88.00 | 58.25 | 64.50 | 74.50 | 85.30 |
| TEHP (2016) | 21.00 | 4 | 75% | 57.38 ± | <LOD | 86.00 | 51.38 | 66.50 | 72.50 | 83.30 |
| PFOA | 0.01 | 4 | 100% | 0.06 ± | 0.05 | 0.07 | 0.06 | 0.07 | 0.07 | 0.07 |
| PFNA | 0.02 | 4 | 50% | 0.02 ± | <LOD | 0.03 | <LOD | 0.02 | 0.03 | 0.03 |
| PFUnDA | 0.02 | 4 | 100% | 0.1 ± 0.04 | 0.06 | 0.14 | 0.08 | 0.09 | 0.10 | 0.14 |
| PFDoDA | 0.03 | 4 | 25% | * | <LOD | 0.05 | <LOD | <LOD | <LOD | 0.04 |
| PFTriDA | 0.02 | 4 | 25% | * | <LOD | 0.28 | <LOD | <LOD | 0.08 | 0.24 |
| PFTeDA | 0.08 | 4 | 25% | * | <LOD | 0.17 | <LOD | <LOD | 0.07 | 0.15 |
| PFHxS | 0.00 | 4 | 75% | 0.03 ± | <LOD | 0.06 | 0.01 | 0.03 | 0.04 | 0.06 |
| PFOS (linear) | 0.02 | 4 | 100% | 0.2 ± 0.05 | 0.13 | 0.26 | 0.19 | 0.21 | 0.23 | 0.26 |
| PFOS (branched, semi-quantification) | 0.02 | 4 | 100% | 0.14 ± 0.11 | 0.07 | 0.31 | 0.08 | 0.10 | 0.15 | 0.28 |

Figures S6.1-S6.4 present graphical representations of the results from these 5 women, providing concentrations of contaminants measured in breast milk relative to time post birth for samples provided within five days following fire exposure. Where more than one sample was provided within the 5-day period, error bars have been included for Mean±SD.

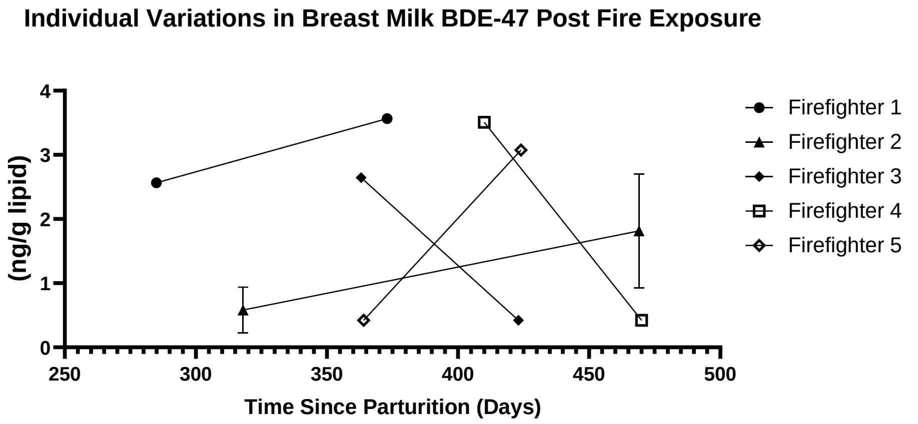


Figure S6.1: Individual Variations in Breast Milk BDE-47 Post Fire Exposure

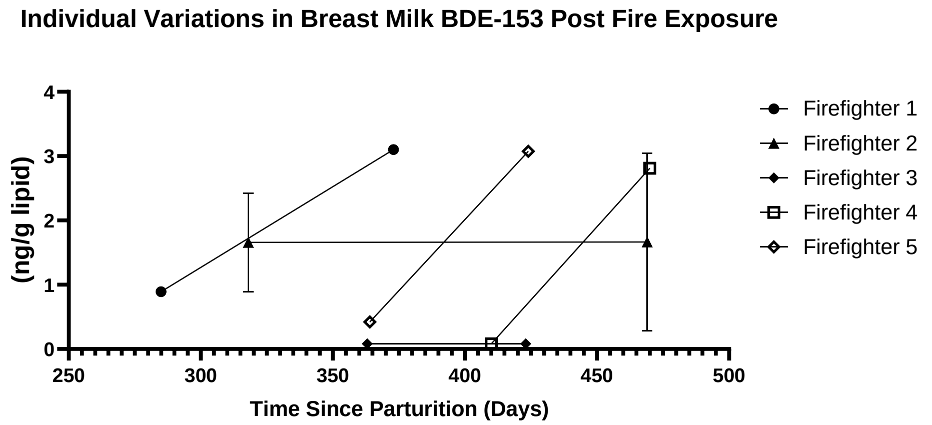


Figure S6.2: Individual Variations in Breast Milk BDE-153 Post Fire Exposure

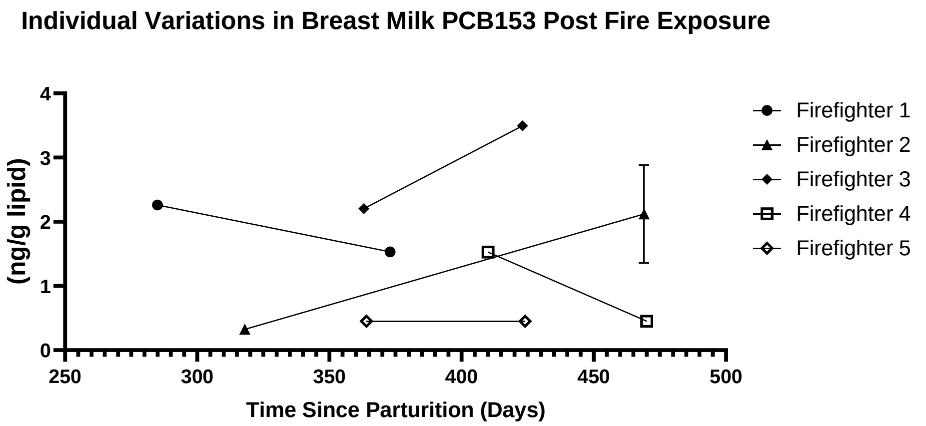


Figure S6.3: Individual Variations in Breast Milk PCB153 Post Fire Exposure

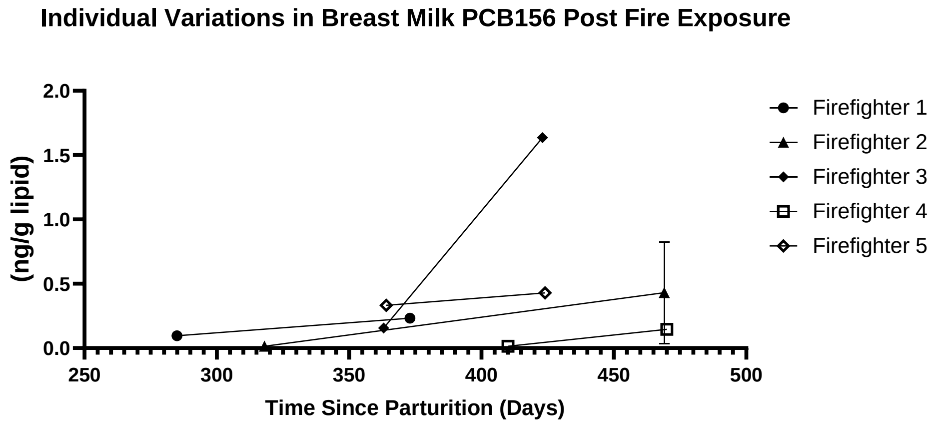


Figure S6.4: Individual Variations in Breast Milk PCB156 Post Fire Exposure

## S6.5. Breast Milk EDIs

Table S6.3: Calculated Estimated Daily Intake for Breast Fed Infants Based on Chemical Concentrations Found in Breast Milk

| Analyte | n | RfD* | $C_{BM}$ median ng/mL | $C_{BM}$ 95th% ng/mL | EDI Med | EDI 95th% | Detection Frequency |
|---|---|---|---|---|---|---|---|
| BDE-28 | 34 | | * | 1.17 | * | 186 | 12% |
| BDE-47 | 34 | 100 | 1.39 | 3.96 | 222 | 631 | 68% |
| BDE-99 | 4 | 100 | 1.09 | 1.38 | 173 | 220 | 100% |
| BDE-100 | 4 | | 0.64 | 1.01 | 102 | 160 | 100% |
| BDE-153 | 34 | 200 | 1.08 | 3.96 | 171 | 631 | 68% |
| BDE-154 | 34 | | * | 0.53 | * | 85 | 3% |
| HCB | 13 | | 2.82 | 6.11 | 450 | 974 | 77% |
| pp-DDE | 30 | | 26.56 | 56.76 | 4236 | 9052 | 100% |
| pp-DDT | 30 | | * | 4.00 | * | 638 | 20% |
| trans-chlordane | 34 | | * | 1.59 | * | 254 | 15% |
| PCB28 | 4 | | 0.48 | 0.86 | 76 | 137 | 75% |
| PCB52 | 4 | | 0.12 | 0.21 | 19 | 33 | 50% |
| PCB101 | 34 | | * | 0.49 | * | 78 | 9% |
| PCB105 | 34 | | * | 0.24 | * | 39 | 12% |
| PCB114 | 4 | | 0.06 | 0.18 | 9.1 | 28 | 100% |
| PCB118 | 34 | | * | 1.71 | * | 273 | 24% |
| PCB138 | 34 | | 0.53 | 3.85 | 84 | 615 | 50% |
| PCB153 | 34 | | 1.93 | 8.69 | 308 | 1386 | 76% |
| PCB156 | 34 | | 0.17 | 1.22 | 27 | 194 | 71% |
| PCB157 | 34 | | * | 0.16 | * | 26 | 29% |
| PCB167 | 34 | | * | 0.16 | * | 26 | 6% |
| PCB180 | 34 | | * | 3.37 | * | 537 | 41% |
| PCB189 | 34 | | * | 0.10 | * | 16 | 18% |
| TCEP | 20 | 2200 | * | 32.48 | * | 5181 | 15% |
| TCIPP | 20 | 3600 | 454.42 | 2662.90 | 72472 | 424686 | 50% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| TPhP | 4 | 7000 | 10.30 | 20.50 | 1643 | 3269 | 100% |
| TBP | 4 | | 27.50 | 34.55 | 4386 | 5510 | 100% |
| TCP | 4 | 1300 | 5.90 | 7.93 | 941 | 1265 | 100% |
| TDCIPP | 4 | | 3.55 | 11.67 | 566 | 1860 | 75% |
| TBOEP | 4 | 1500 | 64.50 | 85.30 | 10287 | 13604 | 100% |
| TEHP | 4 | 35000 | 66.50 | 83.30 | 10606 | 13285 | 75% |
| PFOA | 4 | | 0.07 | 0.07 | 10 | 11 | 100% |
| PFNA | 4 | | 0.02 | 0.03 | 2.8 | 4.3 | 50% |
| PFUnDA | 4 | | 0.09 | 0.14 | 14 | 22 | 100% |
| PFDoDA | 4 | | * | 0.04 | * | 6.6 | 25% |
| PFTriDA | 4 | | * | 0.24 | * | 38 | 25% |
| PFTeDA | 4 | | 0.04 | 0.15 | 6.6 | 24 | 25% |
| PFHxS | 4 | | 0.03 | 0.06 | 4.5 | 8.9 | 75% |
| PFOS (linear) | 4 | | 0.21 | 0.26 | 34 | 41 | 100% |
| PFOS (branched, semi-quantification) | 4 | | 0.10 | 0.28 | 15 | 44 | 100% |

## 6.1.Blood & Urine Analysis

### Table S6.4: List of Female Firefighter Blood Results, Including LODs and Detection Frequencies

| Congener or analyte | LOD ug/L | N | % Detect | Unit | Min | 25th % | 50th % | 75th % | Max |
|---|---|---|---|---|---|---|---|---|---|
| ∑PBDE | 0.0497* | 32 | 6% | ng/g lipid | <LOD | <LOD | <LOD | <LOD | 33.00 |
| BDE28 | 0.001 | 32 | 16% | ng/g lipid | <LOD | <LOD | <LOD | <LOD | 0.92 |
| BDE47 | 0.00076 | 32 | 56% | ng/g lipid | <LOD | <LOD | 0.86 | 2.23 | 16.69 |
| BDE99 | 0.0027 | 32 | 13% | ng/g lipid | <LOD | <LOD | <LOD | <LOD | 8.67 |
| BDE100 | 0.0016 | 32 | 16% | ng/g lipid | <LOD | <LOD | <LOD | <LOD | 3.42 |
| BDE153 | 0.0078 | 32 | 6% | ng/g lipid | <LOD | <LOD | <LOD | <LOD | 3.91 |
| PFBA | 0.0162 | 33 | 79% | ng/mL | <LOD | 0.03 | 0.06 | 0.10 | 0.42 |
| PFPeA | 0.0414 | 33 | 79% | ng/mL | <LOD | 0.18 | 0.45 | 0.61 | 1.09 |
| PFHpA | 0.0412 | 33 | 15% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.10 |
| PFOA | 0.0307 | 33 | 100% | ng/mL | 0.24 | 0.40 | 0.88 | 1.32 | 5.66 |
| PFNA | 0.0318 | 33 | 97% | ng/mL | <LOD | 0.13 | 0.26 | 0.33 | 1.71 |
| PFDA | 0.0387 | 33 | 97% | ng/mL | <LOD | 0.11 | 0.15 | 0.23 | 0.87 |
| PFUnDA | 0.0286 | 33 | 97% | ng/mL | <LOD | 0.08 | 0.10 | 0.14 | 0.36 |
| PFDoDA | 0.0336 | 33 | 6% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.14 |
| PFBS | 0.0131 | 33 | 48% | ng/mL | <LOD | <LOD | <LOD | 0.06 | 0.16 |
| PFPeS | 0.0414 | 33 | 79% | ng/mL | <LOD | 0.18 | 0.45 | 0.61 | 1.09 |
| PFHxS | 0.0236 | 33 | 100% | ng/mL | 0.40 | 0.64 | 0.94 | 1.84 | 6.08 |
| PFHpS | 0.0170 | 33 | 67% | ng/mL | <LOD | <LOD | 0.06 | 0.11 | 0.43 |
| PFOS | 0.0891 | 33 | 100% | ng/mL | 0.69 | 1.29 | 2.34 | 3.42 | 7.30 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Total PFOS* | 0.0595 | 33 | 100% | ng/mL | 1.28 | 1.70 | 2.89 | 4.26 | 10.23 |
| NMeFOSAA | 0.0426 | 33 | 12% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.26 |
| Co | 0.59 | 34 | 12% | µg/L | <LOD | <LOD | <LOD | <LOD | 1.00 |
| Pb | 20.72 | 34 | 3% | µg/L | <LOD | <LOD | <LOD | <LOD | 22.79 |
| Mn | 5.49 | 34 | 94% | µg/L | <LOD | 8.38 | 9.34 | 11.95 | 19.78 |
| Hg | 1.00 | 35 | 34% | µg/L | <LOD | <LOD | <LOD | 1.20 | 6.22 |
| BDE154 | 0.0250 | 32 | 0% | | | | | | |
| BDE183 | 0.0110 | 32 | 0% | | | | | | |
| PFHxA | 0.0236 | 33 | 0% | | | | | | |
| PFNS | 0.0291 | 33 | 0% | | | | | | |
| PFDS | 0.0205 | 33 | 0% | | | | | | |
| FOSA | 0.0166 | 33 | 0% | | | | | | |
| FOSAA | 0.0671 | 33 | 0% | | | | | | |
| NEtFOSAA | 0.0409 | 33 | 0% | | | | | | |
| 8:2 FTS | 0.0437 | 33 | 0% | | | | | | |
| 6:2 FTS | 0.0390 | 33 | 0% | | | | | | |
| 4:2 FTS | 0.0301 | 33 | 0% | | | | | | |
| PFECHS | 0.2258 | 33 | 0% | | | | | | |

Table S6.5: List of Male Firefighter Blood Results, Including LODs and Detection Frequencies

| Congener or analyte | LOD ug/L | N | % Detect | Unit | Min | 25th % | 50th % | 75th % | Max |
|---|---|---|---|---|---|---|---|---|---|
| ∑PBDE | 0.0497* | 59 | 46% | ng/g lipid | <LOD | <LOD | <LOD | 23.28 | 64.56 |
| BDE28 | 0.001 | 59 | 29% | ng/g lipid | <LOD | <LOD | <LOD | 0.31 | 1.76 |
| BDE47 | 0.00076 | 59 | 78% | ng/g lipid | <LOD | 0.73 | 2.62 | 4.44 | 23.22 |
| BDE99 | 0.0027 | 59 | 15% | ng/g lipid | <LOD | <LOD | <LOD | <LOD | 3.53 |
| BDE100 | 0.0016 | 59 | 54% | ng/g lipid | <LOD | <LOD | 0.72 | 1.64 | 7.87 |
| BDE153 | 0.0078 | 59 | 39% | ng/g lipid | <LOD | <LOD | <LOD | 12.80 | 44.39 |
| PFBA | 0.0162 | 62 | 76% | ng/mL | <LOD | 0.03 | 0.07 | 0.15 | 9.00 |
| PFPeA | 0.0414 | 62 | 55% | ng/mL | <LOD | <LOD | 0.21 | 0.49 | 1.37 |
| PFHxA | 0.0236 | 62 | 2% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.18 |
| PFHpA | 0.0412 | 62 | 8% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.15 |
| PFOA | 0.0307 | 62 | 100% | ng/mL | 0.42 | 1.22 | 1.64 | 2.48 | 3.86 |
| PFNA | 0.0318 | 62 | 100% | ng/mL | 0.13 | 0.29 | 0.39 | 0.57 | 2.21 |
| PFDA | 0.0387 | 62 | 95% | ng/mL | <LOD | 0.13 | 0.19 | 0.24 | 0.64 |
| PFUnDA | 0.0286 | 62 | 89% | ng/mL | <LOD | 0.08 | 0.11 | 0.19 | 0.57 |
| PFDoDA | 0.0336 | 62 | 2% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.05 |
| PFBS | 0.0131 | 62 | 48% | ng/mL | <LOD | <LOD | <LOD | 0.06 | 0.23 |
| PFPeS | 0.0414 | 62 | 58% | ng/mL | <LOD | <LOD | 0.21 | 0.49 | 1.37 |
| PFHxS | 0.0236 | 62 | 100% | ng/mL | 0.34 | 2.68 | 3.97 | 6.14 | 27.01 |
| PFHpS | 0.0170 | 62 | 98% | ng/mL | <LOD | 0.21 | 0.35 | 0.45 | 1.86 |
| PFOS | 0.0891 | 62 | 100% | ng/mL | 0.84 | 3.81 | 5.34 | 9.44 | 73.06 |
| Total PFOS* | 0.0595 | 62 | 100% | ng/mL | 0.95 | 5.14 | 7.29 | 12.37 | 83.32 |
| PFNS | 0.0291 | 62 | 3% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.39 |
| NMeFOSAA | 0.0426 | 62 | 10% | ng/mL | <LOD | <LOD | <LOD | <LOD | 0.16 |
| Co | 0.59 | 62 | 8% | µg/L | <LOD | <LOD | <LOD | <LOD | 1.06 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Pb | 20.72 | 62 | 42% | µg/L | <LOD | <LOD | <LOD | 16.58 | 80.81 |
| Mn | 5.49 | 62 | 95% | µg/L | 2.75 | 6.73 | 8.79 | 10.99 | 65.93 |
| Hg | 1.00 | 64 | 41% | µg/L | 0.50 | 0.50 | 0.50 | 2.46 | 17.85 |
| BDE154ng/glipid | 0.0250 | 32 | 0% | | | | | | |
| BDE183ng/glipid | 0.0110 | 32 | 0% | | | | | | |
| PFDS | 0.0205 | 62 | 0% | | | | | | |
| FOSA | 0.0166 | 62 | 0% | | | | | | |
| FOSAA | 0.0671 | 62 | 0% | | | | | | |
| NEtFOSAA | 0.0409 | 62 | 0% | | | | | | |
| 8:2 FTS | 0.0437 | 62 | 0% | | | | | | |
| 6:2 FTS | 0.0390 | 62 | 0% | | | | | | |
| 4:2 FTS | 0.0301 | 62 | 0% | | | | | | |
| PFECHS | 0.2258 | 62 | 0% | | | | | | |

## Table S6.6: List of Female Firefighter Urinary Results, Including LODs and Detection Frequencies

| Urinary congener or analyte | LOD ug/L | N | % Detect | Unit | Min | 25th % | 50th % | 75th % | Max |
|---|---|---|---|---|---|---|---|---|---|
| 1-OH-PYR | 0.5 | 40 | 10% | µg/L | <LOD | <LOD | <LOD | <LOD | 3.19 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 2.46 |
| ΣNAP | 0.51 | 41 | 98% | µg/L | <LOD | 1.47 | 4.05 | 8.05 | 98.71 |
| | | | | µg/g creatinine | <LOD | 3.82 | 6.63 | 9.43 | 56.12 |
| 23-OH-FLU | 0.16 | 41 | 66% | µg/L | <LOD | <LOD | 0.26 | 0.62 | 9.87 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.43 | 0.89 | 4.59 |
| ΣPHE | 1.06 | 41 | 15% | µg/L | <LOD | <LOD | <LOD | <LOD | 5.25 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 5.19 |
| MMP | 0.21 | 23 | 70% | µg/L | <LOD | <LOD | 1.36 | 2.13 | 14.37 |
| | | | | µg/g creatinine | <LOD | <LOD | 1.65 | 2.08 | 10.16 |
| MEP | 0.13 | 23 | 91% | µg/L | <LOD | 5.00 | 9.75 | 23.59 | 194.29 |
| | | | | µg/g creatinine | <LOD | 6.03 | 11.20 | 27.70 | 341.96 |
| MiBP | 0.71 | 23 | 96% | µg/L | <LOD | 2.34 | 4.00 | 8.43 | 26.41 |
| | | | | µg/g creatinine | <LOD | 3.20 | 5.52 | 7.87 | 30.16 |
| MnBP | 0.54 | 23 | 96% | µg/L | <LOD | 3.62 | 9.12 | 14.22 | 38.02 |
| | | | | µg/g creatinine | <LOD | 6.02 | 8.88 | 12.87 | 55.09 |
| MCPP | 0.01 | 23 | 9% | µg/L | <LOD | <LOD | <LOD | <LOD | 6.40 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 5.77 |
| MbzP | 0.46 | 23 | 87% | µg/L | <LOD | 0.63 | 1.09 | 1.53 | 12.00 |
| | | | | µg/g creatinine | <LOD | 0.91 | 1.18 | 1.67 | 5.58 |
| MEHP | 0.35 | 23 | 100% | µg/L | 0.46 | 0.88 | 1.64 | 2.80 | 13.97 |
| | | | | µg/g creatinine | 0.64 | 1.24 | 2.10 | 3.36 | 12.60 |
| MEOHP | 0.11 | 23 | 78% | µg/L | <LOD | 0.57 | 2.42 | 4.51 | 13.08 |
| | | | | µg/g creatinine | <LOD | 0.76 | 2.77 | 4.70 | 11.79 |
| MEHHP | 0.19 | 23 | 96% | µg/L | <LOD | 1.18 | 3.68 | 7.53 | 30.17 |
| | | | | µg/g creatinine | <LOD | 1.81 | 5.17 | 7.86 | 27.21 |
| MECPP | 0.02 | 23 | 100% | µg/L | 0.03 | 1.48 | 3.61 | 6.84 | 16.57 |
| | | | | µg/g creatinine | 0.06 | 1.87 | 4.54 | 7.13 | 18.46 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| DBP | 0.026 | 33 | 97% | µg/L | <LOD | 0.04 | 0.05 | 0.09 | 0.27 |
| | | | | µg/g creatinine | <LOD | 0.06 | 0.10 | 0.15 | 0.42 |
| BCEP | 0.041 | 33 | 82% | µg/L | <LOD | 0.05 | 0.10 | 0.19 | 0.72 |
| | | | | µg/g creatinine | <LOD | 0.11 | 0.17 | 0.33 | 0.97 |
| BCIPP | 0.474 | 33 | 73% | µg/L | <LOD | <LOD | 0.83 | 1.76 | 186.09 |
| | | | | µg/g creatinine | <LOD | <LOD | 1.83 | 2.48 | 150.93 |
| BMPP | 0.001 | 33 | 85% | µg/L | <LOD | 0.00 | 0.01 | 0.02 | 0.15 |
| | | | | µg/g creatinine | <LOD | 0.01 | 0.02 | 0.04 | 0.16 |
| BEHP | 0.129 | 33 | 3% | µg/L | <LOD | <LOD | <LOD | <LOD | 0.22 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 0.63 |
| DPhP | 0.059 | 33 | 61% | µg/L | <LOD | <LOD | 0.21 | 0.42 | 2.75 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.26 | 0.62 | 3.04 |
| BDCIPP | 0.041 | 33 | 52% | µg/L | <LOD | <LOD | 0.06 | 0.38 | 2.44 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.13 | 0.34 | 3.50 |
| BBOEP | 0.307 | 33 | 42% | µg/L | <LOD | <LOD | <LOD | 0.92 | 13.30 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 1.13 | 5.57 |
| TPhP | 0.057 | 33 | 42% | µg/L | <LOD | <LOD | <LOD | 0.10 | 22.16 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 0.41 | 30.14 |
| EHDPP | 0.013 | 33 | 52% | µg/L | <LOD | <LOD | 0.05 | 0.13 | 15.50 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.03 | 0.46 | 21.07 |
| TBP | 1.360 | 33 | 21% | µg/L | <LOD | <LOD | <LOD | <LOD | 2533.16 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 3445.17 |
| TCEP | 0.059 | 33 | 48% | µg/L | <LOD | <LOD | <LOD | 2.14 | 35.50 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 2.98 | 348.67 |
| TCIPP | 1.037 | 33 | 27% | µg/L | <LOD | <LOD | <LOD | 2.02 | 5231.80 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 3.31 | 7115.38 |
| TDCPP | 0.101 | 33 | 6% | µg/L | <LOD | <LOD | <LOD | <LOD | 307.39 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 418.06 |
| BCIPHIPP | 0.166 | 33 | 82% | µg/L | <LOD | 0.70 | 2.05 | 5.06 | 194.64 |
| | | | | µg/g creatinine | <LOD | 0.84 | 2.23 | 7.86 | 955.91 |
| TBOEP | 0.030 | 33 | 3% | µg/L | <LOD | <LOD | <LOD | <LOD | 7.63 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 10.37 |
| 3OH-TBOEP | 0.005 | 33 | 73% | µg/L | <LOD | <LOD | 0.11 | 0.27 | 86.76 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.17 | 0.54 | 118.00 |
| BBOEHEP | 0.001 | 33 | 58% | µg/L | <LOD | <LOD | 0.02 | 0.07 | 94.23 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.02 | 0.27 | 128.16 |
| TEHP | 0.593 | 33 | 6% | µg/L | <LOD | <LOD | <LOD | <LOD | 8.88 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 12.08 |
| Chromium | 1.04 | 34 | 9% | µg/L | <LOD | <LOD | <LOD | <LOD | 1.45 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 5.11 |
| Copper | 1.27 | 34 | 44% | µg/L | <LOD | <LOD | <LOD | 5.53 | 15.89 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 7.40 | 117.03 |
| Ni | 1.17 | 34 | 15% | µg/L | <LOD | <LOD | <LOD | <LOD | 4.67 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 7.69 |
| Se | 31.58 | 34 | 35% | µg/L | <LOD | <LOD | <LOD | 38.36 | 209.92 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 72.56 | 201.71 |
| Vanadium | 2.55 | 34 | 15% | µg/L | <LOD | <LOD | <LOD | <LOD | 2.04 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 13.86 |
| DMA | 1.50 | 33 | 55% | µg/L | <LOD | <LOD | 2.25 | 3.75 | 11.99 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | µg/g creatinine | <LOD | <LOD | 3.31 | 4.45 | 28.15 |
| Arsenic (V) | 1.50 | 33 | 3% | µg/L | <LOD | <LOD | <LOD | <LOD | 1.87 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 7.36 |
| Arsenobetaine | 1.50 | 33 | 58% | µg/L | <LOD | <LOD | 2.55 | 5.32 | 13.49 |
| | | | | µg/g creatinine | <LOD | <LOD | 3.57 | 7.36 | 103.03 |
| Mandelic Acid | 45.65 | 36 | 3% | µg/L | <LOD | <LOD | <LOD | <LOD | 224.17 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 64.63 |
| Hippuric Acid | 89.59 | 36 | 58% | µg/L | <LOD | <LOD | 225.62 | 310.94 | 698.78 |
| | | | | µg/g creatinine | <LOD | <LOD | 120.98 | 170.61 | 497.02 |
| MMA | 1.50 | 33 | 0% | | | | | | |
| Arsenic (III) | 1.50 | 33 | 0% | | | | | | |
| Tellurium | 10.21 | 34 | 0% | | | | | | |
| Thallium | 0.82 | 34 | 0% | | | | | | |
| Cobalt | 1.18 | 34 | 0% | | | | | | |
| Lead | 4.14 | 34 | 0% | | | | | | |
| Mn | 1.10 | 34 | 0% | | | | | | |
| Hg | 4.01 | 35 | 0% | | | | | | |
| MCHP | 0.12 | 23 | 0% | | | | | | |
| MnOP | 0.17 | 23 | 0% | | | | | | |
| Toluric Acid | 89.59 | | 0% | | | | | | |
| s-Phenylmercapturic acid | | | 0% | | | | | | |

Table S6.7 List of Male Firefighter Urinary Results, Including LODs and Detection Frequencies

| Urinary congener or analyte | LOD ug/L | N | % Detect | Unit | Min | 25th % | 50th % | 75th % | Max |
|---|---|---|---|---|---|---|---|---|---|
| 1-OH-PYR | 0.5 | 79 | 9% | µg/L | <LOD | <LOD | <LOD | <LOD | 3.72 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 2.21 |
| ΣNAP | 0.51 | 77 | 96% | µg/L | <LOD | 1.65 | 3.00 | 6.68 | 837.32 |
| | | | | µg/g creatinine | <LOD | 2.27 | 4.27 | 11.31 | 366.44 |
| 23-OH-FLU | 0.16 | 77 | 68% | µg/L | <LOD | <LOD | 0.29 | 0.65 | 55.30 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.31 | 0.71 | 21.74 |
| ΣPHE | 1.06 | 77 | 21% | µg/L | <LOD | <LOD | <LOD | <LOD | 37.04 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 16.21 |
| MMP | 0.21 | 58 | 29% | µg/L | <LOD | <LOD | <LOD | 1.42 | 17.58 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 1.22 | 12.42 |
| MEP | 0.13 | 58 | 95% | µg/L | <LOD | 5.63 | 19.36 | 46.00 | 871.39 |
| | | | | µg/g creatinine | <LOD | 6.83 | 12.16 | 35.18 | 1100.46 |
| MiBP | 0.71 | 58 | 100% | µg/L | 1.20 | 3.12 | 6.90 | 14.85 | 125.05 |
| | | | | µg/g creatinine | 1.19 | 3.22 | 5.84 | 9.09 | 82.41 |
| MnBP | 0.54 | 58 | 100% | µg/L | 0.90 | 4.67 | 10.46 | 23.35 | 51.22 |
| | | | | µg/g creatinine | 1.38 | 5.47 | 8.11 | 15.11 | 27.91 |
| MCPP | 0.01 | 58 | 14% | µg/L | <LOD | <LOD | <LOD | <LOD | 14.88 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 17.67 |
| MbzP | 0.46 | 58 | 81% | µg/L | <LOD | 0.53 | 1.28 | 3.97 | 17.93 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | µg/g creatinine | <LOD | 0.48 | 1.12 | 2.54 | 10.73 |
| MEHP | 0.35 | 58 | 100% | µg/L | 0.39 | 1.09 | 1.82 | 3.10 | 8.89 |
| | | | | µg/g creatinine | 0.22 | 1.10 | 1.56 | 2.29 | 4.58 |
| MEOHP | 0.11 | 58 | 76% | µg/L | <LOD | 0.73 | 3.15 | 5.82 | 18.61 |
| | | | | µg/g creatinine | <LOD | 0.68 | 2.63 | 3.95 | 8.75 |
| MEHHP | 0.19 | 58 | 100% | µg/L | 0.78 | 3.17 | 4.53 | 8.59 | 41.02 |
| | | | | µg/g creatinine | 0.71 | 2.63 | 4.03 | 6.31 | 19.09 |
| MECPP | 0.02 | 58 | 100% | µg/L | 0.66 | 2.81 | 4.85 | 8.97 | 29.00 |
| | | | | µg/g creatinine | 0.75 | 2.63 | 4.18 | 6.83 | 14.81 |
| DBP | 0.026 | 70 | 93% | µg/L | <LOD | 0.04 | 0.06 | 0.09 | 0.47 |
| | | | | µg/g creatinine | <LOD | 0.05 | 0.08 | 0.11 | 0.71 |
| BCEP | 0.041 | 70 | 81% | µg/L | <LOD | 0.06 | 0.11 | 0.25 | 0.69 |
| | | | | µg/g creatinine | <LOD | 0.09 | 0.15 | 0.28 | 0.76 |
| BCIPP | 0.474 | 70 | 83% | µg/L | <LOD | 0.63 | 1.51 | 3.19 | 71.88 |
| | | | | µg/g creatinine | <LOD | 0.92 | 1.70 | 3.71 | 33.27 |
| BMPP | 0.001 | 70 | 96% | µg/L | <LOD | <LOD | 0.03 | 0.05 | 0.19 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.03 | 0.05 | 0.23 |
| BEHP | 0.129 | 70 | 7% | µg/L | <LOD | <LOD | <LOD | <LOD | 1.92 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 0.89 |
| DPhP | 0.059 | 70 | 81% | µg/L | <LOD | 0.10 | 0.31 | 0.84 | 6.73 |
| | | | | µg/g creatinine | <LOD | 0.15 | 0.35 | 0.81 | 2.95 |
| BDCIPP | 0.041 | 70 | 66% | µg/L | <LOD | <LOD | 0.22 | 0.67 | 5.02 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.18 | 0.64 | 4.49 |
| BBOEP | 0.307 | 70 | 63% | µg/L | <LOD | <LOD | 0.94 | 2.82 | 10.46 |
| | | | | µg/g creatinine | <LOD | <LOD | 0.91 | 2.05 | 15.92 |
| TPhP | 0.057 | 70 | 20% | µg/L | <LOD | <LOD | <LOD | <LOD | 0.43 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 1.35 |
| EHDPP | 0.013 | 70 | 29% | µg/L | <LOD | <LOD | <LOD | 0.05 | 0.33 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 0.04 | 1.14 |
| TBP | 1.360 | 70 | 6% | µg/L | <LOD | <LOD | <LOD | <LOD | 123.96 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 405.85 |
| TCEP | 0.059 | 70 | 34% | µg/L | <LOD | <LOD | <LOD | 0.13 | 61.54 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 0.15 | 320.00 |
| TCIPP | 1.037 | 70 | 10% | µg/L | <LOD | <LOD | <LOD | <LOD | 124.93 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 204.53 |
| TDCPP | 0.101 | 70 | 11% | µg/L | <LOD | <LOD | <LOD | <LOD | 4.74 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 14.97 |
| BCIPHIPP | 0.166 | 70 | 83% | µg/L | <LOD | 0.53 | 1.21 | 2.31 | 7.13 |
| | | | | µg/g creatinine | <LOD | 0.57 | 1.37 | 2.25 | 7.95 |
| TBOEP | 0.030 | 70 | 4% | µg/L | <LOD | <LOD | <LOD | <LOD | 0.14 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 0.13 |
| 3OH-TBOEP | 0.005 | 70 | 47% | µg/L | <LOD | <LOD | <LOD | 0.22 | 3.86 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 0.21 | 2.71 |
| BBOEHEP | 0.001 | 70 | 49% | µg/L | <LOD | <LOD | <LOD | 0.03 | 2.20 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 0.06 | 1.17 |
| TEHP | 0.593 | 70 | 0% | µg/L | <LOD | <LOD | <LOD | <LOD | <LOD |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | <LOD |
| Chromium | 1.04 | 73 | 8% | µg/L | <LOD | <LOD | <LOD | <LOD | 5.28 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 8.11 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Cobalt | 1.18 | 73 | 3% | µg/L | <LOD | <LOD | <LOD | <LOD | 2.77 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 5.21 |
| Copper | 1.27 | 73 | 59% | µg/L | <LOD | <LOD | 4.64 | 8.39 | 22.80 |
| | | | | µg/g creatinine | <LOD | <LOD | 3.75 | 6.74 | 49.57 |
| Lead | 4.14 | 73 | 4% | µg/L | <LOD | <LOD | <LOD | <LOD | 12.43 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 18.32 |
| Mn | 1.10 | 73 | 1% | µg/L | <LOD | <LOD | <LOD | <LOD | 1.26 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 4.86 |
| Ni | 1.17 | 73 | 27% | µg/L | <LOD | <LOD | <LOD | 2.49 | 65.00 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | 2.75 | 36.84 |
| Se | 31.58 | 73 | 59% | µg/L | <LOD | <LOD | 38.10 | 58.36 | 157.89 |
| | | | | µg/g creatinine | <LOD | <LOD | 37.76 | 50.95 | 139.60 |
| Thallium | 0.82 | 73 | 3% | µg/L | <LOD | <LOD | <LOD | <LOD | 1.11 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 3.61 |
| Vanadium | 2.55 | 73 | 25% | µg/L | <LOD | <LOD | <LOD | <LOD | 2.55 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 11.26 |
| Hg | 4.01 | 63 | 5% | µg/L | <LOD | <LOD | <LOD | <LOD | 6.13 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 17.73 |
| MMA | 1.50 | 74 | 1% | µg/L | <LOD | <LOD | <LOD | <LOD | 2.25 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 6.62 |
| DMA | 1.50 | 74 | 76% | µg/L | <LOD | 1.50 | 3.03 | 4.48 | 14.38 |
| | | | | µg/g creatinine | <LOD | 2.14 | 2.99 | 4.50 | 21.53 |
| Arsenic (III) | 1.50 | 74 | 1% | µg/L | <LOD | <LOD | <LOD | <LOD | 4.50 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 6.62 |
| Arsenic (V) | 1.50 | 74 | 1% | µg/L | <LOD | <LOD | <LOD | <LOD | 8.32 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 11.31 |
| Arsenobetaine | 1.50 | 74 | 66% | µg/L | <LOD | <LOD | 2.92 | 9.66 | 533.14 |
| | | | | µg/g creatinine | <LOD | <LOD | 3.93 | 8.24 | 462.07 |
| Mandelic Acid (ethylbenzene) | 45.65 | 62 | 11% | µg/L | <LOD | <LOD | <LOD | <LOD | 275.73 |
| | | | | µg/g creatinine | <LOD | <LOD | <LOD | <LOD | 162.86 |
| Mandelic Acid (Styrene) | 45.65 | 10 | 100% | µg/L | 37.79 | 47.65 | 55.89 | 83.76 | 139.88 |
| | | | | µg/g creatinine | 65.41 | 95.78 | 103.43 | 162.56 | 368.68 |
| Hippuric Acid | 89.59 | 73 | 73% | µg/L | <LOD | <LOD | 232.93 | 403.89 | 1615.57 |
| | | | | µg/g creatinine | <LOD | <LOD | 206.94 | 493.43 | 2507.93 |
| Tellurium | 10.21 | 73 | 0% | | | | | | |
| Toluric Acid (xylene) | 89.59 | | 0% | | | | | | |
| s-Phenylmercapturic acid (Benzene) | 2.0 | | 0% | | | | | | |

### 6.5.1. Statistical significance by Chemical Group

#### 6.5.1.1. PAHs (Urine)

Significant differences in ΣOH-NAP (U=3, $p<0.01$) and ΣOH-FLU (U=3, $p<0.01$) were found between <24hrs real fire scenarios and <24hrs CFBT wherein the level of exposure due to CFBT fire was statistically higher. Measurable increases were noted in detection frequency and analyte concentration across PAHs in <24hrs CFBT compared with real fire scenarios, in some instances by orders of magnitude with regards to median and max.

S6.5.1.2. Metals

When considering metals in whole blood, only manganese (Mn) appeared above 50% across the groups. As such only Mn is used for statistically significant comparisons, of which none were found. It was of note that lead (Pb) and mercury (Hg) increased in detection frequency in men vs women (42v3% and 41v34%). Pb was found to increase in detection frequency in the more exposed group (39% for ≥fortnightly exposure vs 17% for ≥monthly exposure). The detection frequencies of both Pb and Hg increased in the >15 years service group vs the <15 years service (45v20% and 43%v35% respectively) with descriptive statistics showing longer duration employment led to elevated levels of these metals.

Regarding urinary metal results, those exposed to CFBT fires had statistically significant elevations in uncorrected urine for copper (Cu): <72hrs since exposure vs <72hr since CFBT exposure (U=215, $p<0.05$); and selenium (Se): <72hrs since structure fire vs <72hr since CFBT exposure (U=67.5, $p<0.01$). Similiar results were noted when comparing CFBT firefighters with all other firefighters exposed within the prior 24hrs. These differences were no longer apparent when urine was creatinine corrected. CFBT (median 6.4µg/L, maximum 16µg/L) were statistically significant greater for inorganic As compared to structure fires (4.4µg/L, maximum 12µg/L) (U=268, $p<0.05$); however, the reverse was noted for µg/g creatinine wherein structure fires were higher than CFBT (U=308, $p<0.01$).

Males had statistically significant greater concentrations of inorganic As in µg/L (U=1528, $p<0.05$); however, the reverse was noted for µg/g creatinine wherein female had higher concentrations than males (U=908.5, $p<0.05$). As(V) was detected in 29% of samples reporting recent vehicle fire exposure, compared with 0-3% for other fire types. Other metals were below 50% across all groups so no statistical comparisons were run.

S6.5.1.3 Phthalates

Within the current study, statistically significant differences were noted across groups with regards to the following metabolites: MEOHP, MEHP and MECPP (both ng/L and creatinine corrected). Firefighters exposed to CFBT within the past 24hrs presented with significantly elevated levels of MEOHP ng/L (median 4.4 vs 0.06ng/L) ($p<0.05$, U=58.5). The same did not hold when creatinine corrected. Firefighters with exposure occurring less than 24hrs ago presented with significantly lower median creatinine corrected (ng/g creatinine) urinary levels of MEHP (1.5 vs 2.0), MEOHP (1.5 vs 5.2), and MECPP (3.7 vs 6.8) than those with exposure >24hrs ago (U=213, $p<0.01$, U=185, $p<0.01$, U=226 , $p<0.05$, respectively). No statistically significant differences were seen between <72hr and >72hrs since exposure, exposure frequency (weekly/fortnightly vs greater than), gender or by specific type of fire.

S6.5.1.4. VOCs

In this study statistically significant differences noted in uncorrected urine samples were not seen in creatinine corrected samples, and visa versa. For example, <24hr CFBT presented higher Hippuric Acid (mg/L) compared to real fire scenario exposure <24hrs (U=310, $p<0.01$), yet the finding did not stand when creatinine corrected. Males were elevated in hippuric acid (mg/L) compared to females (U=670, $p<0.01$), but not when creatinine corrected. Hippuric Acid was greater in <24hrs since exposure than >24hrs since exposure (active duty) for creatinine corrected samples (median 290 vs 200 mg/g creatinine) (U=1760.5, $p<0.05$).

S6.5.1.5. OPFRs

Structure Fires (<72hrs) were significantly elevated compared with CFBT (<72hrs) for BCEP (median 0.10 vs 0.06µg/g creatine respectively) (U=250.5, $p<0.01$) and BCIPHIPP (median 1.6 and 0.81µg/g creatinine respectively) (U=216, $p<0.05$). CFBT (<24hrs) were significantly higher than structure fires (<24hrs) for DBP (median 0.10 vs 0.05ng/mL respectively) (U=85, $p<0.05$), BCIPP (median 3.1 and 2.3ng/mL) (U=76, $p<0.05$), BMPP (median 0.04 vs 0.02ng/mL) (U=75, $p<0.05$) and DPhP (median 1.7 vs 0.29ng/mL) (U=69.5, $p<0.05$).

Concentrations in firefighters who attended rubbish fires were significantly elevated compared with structure fires for DBP (median 0.09 vs 0.05ng/mL) (U=28, $p<0.05$) and structure fires significantly greater than wildland fires for BDCIPP (median 0.34 vs 0.14µg/g cr) (U=196, $p<0.05$). With regards to gender, females were significantly higher than males for BCIPHIPP (2.2 vs 1.4µg/g creatinine and 2.0 vs 1.2ng/mL) (U=1546, $p<0.01$ and U=1454, $p<0.05$), yet males were significantly higher than females for BMPP (0.03 vs

0.01ng/mL) (U=715.5, $p<0.01$). Concentrations for firefighters with increased frequency of exposure (<fortnightly, median 0.06µg/L) were significantly greater than for those with less frequent exposure (≥fortnightly, median 0.05µg/L) for DBP (U=1629, $p<0.05$).

S6.5.1.6. PFAS

Within the current study, statistical differences were noted by gender with females presenting significantly higher plasma concentrations of PFPeA (U=1296, p<005) and PFPeS (U=1289, $p<0.05$), yet males being significantly higher in PFOA (U=428, p=0.000003371), PFNA (U=488, $p<0.01$), PFHxS (U=256, $p<0.01$), PFHpS (U=180.5, $p<0.01$), and PFOS (U=322, $p<0.01$).

Statistical differences were noted across frequency of exposure with more frequent exposure (≤fortnightly vs >fortnightly) being significantly higher for PFOS (U=1385, $p<0.05$). Duration of employment also presented significant differences wherein those employed for more than 15 years were significantly elevated for a number of PFAS compared to those with shorter employment timeframes: PFOA (U=675, $p<0.01$), PFNA (U=664, $p<0.01$), PFHxS (U=421, $p<0.01$), PFHpS (U=254.5, $p<0.01$), PFOS (U=337, p0.01).

Statistical differences were noted with regards to wearing SCBA. Those not always wearing a breathing apparatus during smoke diving were found to have statistically significant higher plasma concentrations of several PFAS when compared to those who stated that they were always wearing SCBA: PFOA (U=67, $p<0.01$), PFNA (U=67, $p<0.01$), PFDA (U=71, $p<0.01$), PFUnDA (U=80, $p<0.01$), PFHxS (U=81, $p<0.01$), PFHpS (U=77, $p<0.01$), PFOS (U=93, $p<0.01$).

S6.5.1.7 PBDEs

For BDE-47, males were statistically significantly higher than females (median, max 2.6, 23 vs median, max 0.86, 17 ng/g lipid respectively) (U-617, $p<0.01$). When comparing duration of employment, only BDE-47 >15yrs employed was statistically significantly greater compared to ≤15yrs (U=534, $p<0.01$).

THE UNIVERSITY OF QUEENSLAND

# Institutional Human Research Ethics Approval

| | |
|---|---|
| **Project Title:** | Firefighter Exposure Risks and Subsequent Reproductive Effects |
| **Chief Investigator:** | Ms Michelle Engelsman |
| **Supervisor:** | Prof Jochen Mueller, Prof Jose Torero |
| **Co-Investigator(s):** | None |
| **School(s):** | School of Pharmacy |
| **Approval Number:** | 2017000255 |
| **Granting Agency/Degree:** | TestSafe Laboratories; Fire & Rescue NSW |
| **Duration:** | 31st October 2022 |

**Comments/Conditions:**

- HREA Application Form, 04/05/2017
- Project Description, 04/05/2017
- Main Survey, 22/05/2017
- Consent and Survey – Blood and Urine, 22/05/2017
- Consent and Survey – Breast Milk Survey, 15/06/2017
- Consent and Survey – Semen, 22/05/2017
- UQ Deed, 27/03/2017
- FRNSW Gatekeeper approval, 06/04/2017
- NSWRFS Gatekeeper approval, 21/02/2017

Note: if this approval is for amendments to an already approved protocol for which a UQ Clinical Trials Protection/Insurance Form was originally submitted, then the researchers must directly notify the UQ Insurance Office of any changes to that Form and Participant Information Sheets & Consent Forms as a result of the amendments, before action.

**Name of responsible Committee:**
**University of Queensland Human Research Ethics Committee B**
This project complies with the provisions contained in the *National Statement on Ethical Conduct in Human Research* and complies with the regulations governing experimentation on humans.

**Name of Ethics Committee representative:**
**Dr. Frederick Khafagi**
**Chairperson**
**University of Queensland Human Research Ethics Committee**
**Registration: EC00457**

Signature ______________________ Date 15/06/2017