Firefighter Exposures to Airborne Contaminants during Extinguishment of Simulated Residential Room Fires

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Abstract

At CBRN incidents there is significant potential for fire. A fire generates a complex mixture of airborne contaminants and smoke. The distribution and concentration of these contaminants is affected by many factors including temperature, ventilation and the fuel. The contaminants comprise a complex mixture of both particles and gaseous substances including particulate matter, polycyclic aromatic hydrocarbons (PAH), acid gases (e.g. hydrogen chloride), carbon monoxide (CO), and volatile organic materials (VOCs).

There is a large body of work reported concerning combustion products generated from burning materials, but data about the exposure of emergency responders is less common. Moreover, there is much debate within the literature about the long term health impacts on firefighters and other emergency responders of such exposures.

A fire within a structure is deemed to be an Immediately Dangerous to Life and Health (IDLH) environment. Firefighters don self contained breathing apparatus, and protective clothing incorporating jackets, overtrousers, gloves, boots and flash-hoods for entry. The primary route of entry or pathway for airborne contaminants into the human body is usually inhalation, however if a firefighter adopts respiratory protection then the skin becomes the primary route of entry. Whilst the protective clothing provides dermal protection against heat and flame the protection afforded, if any, against contaminants generated within the fire has not been widely reported or established.

A variety of fire products were characterised during simulated residential room fires and the values obtained compared to other workplace exposures and established workplace exposure standards. These standards were adopted as the levels of concern (LOC). The fire products characterised included:

- Polycyclic aromatic hydrocarbons (PAH);
- Volatile organic compounds (VOC) such as benzene and formaldehyde; and
- Simple inorganic compounds like cyanide.

The study focused on characterising the exposure of firefighters to various contaminants during extinguishment of simulated room fires. The locations sampled included:

- Outside the protective clothing;
- Inside the protective clothing;
- Deposition of PAHs onto the outer surface of firefighting protective clothing; and
- Deposition of PAHs onto skin simulant patches attached to the firefighter.

The results showed the firefighter was exposed to a variety of airborne contaminants outside their protective clothing. The contaminant distribution was similar across the simulated residential room fires. They included aromatic hydrocarbons like benzene,

oxygenated hydrocarbons like formaldehyde and polycyclic aromatic hydrocarbons such as naphthalene.

The concentrations of airborne contaminants inside the protective clothing were typically 50% to more than 99% lower than the external concentrations. Naphthalene accounted for the majority of PAHs inside the clothing. The results clearly demonstrated the protective clothing affords protection against the ingress of airborne contaminants during extinguishment. Other factors such as the influence of the extinguishing medium and the adopted tactics also likely contributed to the observed exposures.

Deposition of PAHs also occurred onto the swatches attached to the protective clothing. The concentration and distribution of the adsorbed PAHs were similar to the PAH concentration and distribution measured outside the protective clothing excepting naphthalene and acenaphthylene. Benzo[a]pyrene, a known carcinogen, was detected on the swatches. The results suggest the PAHs within the air are readily deposited onto protective clothing during extinguishment.

The studies also demonstrated that direct deposition of PAHs onto the skin from the airborne contaminants occurred at low concentrations. Three PAHs were identified, namely naphthalene, phenanthrene and pyrene. The values varied significantly across the simulated residential room fires and deposition was not observed in all instances. The results show the skin is a route of entry that cannot be discounted.

A series of recommendations have been provided to reduce the opportunities for exposure and hence reduce the cumulative dose of a firefighter. The recommendations include:

- Avoid / minimise the exposure to smoke;
- Adopt Self Contained Breathing Apparatus to prevent exposure to the smoke;
- Where possible remain below the neutral plane and behind the active water spray whilst extinguishing the fire;
- The firefighter should shower as soon as reasonably practical after they have extinguished the fire to reduce the opportunities for any deposited PAHs to enter the skin; and
- Communicate the findings of this study to operational firefighters.

The study has shown firefighters are exposed to airborne contaminants whilst extinguishing simulated residential room fires and the protective clothing affords some protection against penetration of these contaminants. Direct deposition of PAHs occurred onto the protective clothing. The study also showed despite the significantly lower concentration of airborne PAH within the protective clothing, deposition of PAH onto the skin swatches occurred. Hence the skin is an entry route for these materials.

CHAPTER ONE

COMBUSTION PRODUCTS OF RESIDENTIAL FIRES: LITERATURE REVIEW

Introduction

A fire is complex set of oxidation reactions that generate heat, light, and combustion products. The nature of the fire directly affects the types and distribution of combustion products generated (Michal, 1976; Michal et al., 1976; Ruokojärvi et al., 2000; Terrill et al., 1978; Wang et al., 2004). This variation can be considerable in magnitude, even when attempts are made to duplicate experimental conditions (Dills and Beaudreau, 2008). In the case of real structural fires, combustion conditions are known to vary considerably both within and between fires (DeHaan, 2002; Terrill et al., 1978). The combustion products generated reflect:

- Molecular structure of the material, including additives such as fire retardants;
- Type, quantity and mixture of materials;
- Storage, container and building construction;
- Temperature;
- Oxygen content;
- Decomposition pathways; and
- Fire type and evolution stage.

The variety of products generated during combustion is vast, and irrespective of the exact fire conditions at the time the general groups of combustion products generated (Rutkowski et al., 1986; Smith-Hansen, 1995; UK HSE, 2002; Andersson, 2003; Kirk, 2006) can be described and include:

- Carbon dioxide;
- Particulates such as carbon;
- Carbon monoxide;
- Undecomposed product, or monomers;
- Unsaturated hydrocarbons including aromatic hydrocarbons and polycyclic aromatic hydrocarbons;
- Saturated hydrocarbons;
- Partially oxygenated organics including organic acids, aldehydes and ketones such as acrolein;
- Partially nitrogenated and sulphurated organic compounds like propylnitrile;
- Partially halogenated organics like vinyl chloride;
- Simple inorganic molecules like nitrogen oxides, sulphur oxides and hydrogen cyanide; and
- Volatile metal/non metal oxides or other metal/non metal complexes such as arsine.

Very little specific information is available regarding the combustion products generated in typical residential fires in modern houses (Blomqvist et al., 2004, Blomqvist, 2005). The majority of scientific research into combustion products focuses on small-scale experiments of pure fuels which cannot be directly translated to the firefighting situation (Kirk, 2006). Those few studies that have considered actual firefighting environments tend to incorporate a large variety of fire types (residential, other structural and vehicle), and do not differentiate between these in presentation of results. In addition, the variation in residential fires internationally (due to differences in fuel loads, furnishing types, compartment size, layout and firefighting techniques) and over time (due to advancements in fire retardants, other additives and the development of new consumer products) brings into question the relevance of many of the early studies to modern firefighting approaches in both Australia and the United States.

This chapter will summarise the major factors influencing the exposure of firefighters to combustion products in residential fires, and present information on the physical and toxicological properties of the major combustion products. A brief outline of the existing literature on the formation of the major combustion products in residential fires is also provided. This information forms the basis of the experimental procedures developed for this study, as outlined in the next chapter.

Factors affecting exposure of firefighters to combustion products

A firefighter's actions impact significantly on the chemical composition of the combustion products to which they are exposed, through:

- whether they are engaged in extinguishment or overhaul activity;
- their selection of extinguishing agent;
- their method of applying the extinguishing agent; and
- the physical placement of firefighters within the compartment relative to the smoke plume.

Several other important factors that affect the generation of combustion products are discussed in greater detail below.

Fuel composition

Modern residences include a vast variety of natural and synthetic materials in the form of building materials, insulation, furniture, electronic goods, carpeting and decorative items. The burning of the complex array of modern building materials and modern furnishings causes the formation of large amounts of much more toxic chemicals than in fires involving traditional materials such as cellulose and wood (Stefanidou et al., 2008). The presence of additives such as fuel retardants can significantly increase the yield of some combustion products per gram of fuel consumed and the consequent smoke toxicity under fire conditions (Paulson and Moran, 1974, Kozlowski et al., 1999). However, the importance of other factors such as ventilation and the effect on yields and the product distribution cannot be discounted (Purser, 2001).

Ventilation

It is known from pyrolysis and flaming combustion studies of materials such as plastics and pesticides the fire ventilation conditions make a significant difference to the quantity and profile of combustion products generated (Michal et al., 1976; Andersson et al., 2003).

Purser (2001) categorises fires into three different types by ventilation: smouldering fires, ventilation-controlled flaming fires, and well-ventilated flaming fires. It is important to note a fire will most likely belong in more than one of these classifications over its lifetime (Drysdale, 1999; DeHaan, 2002). Smouldering or non-flaming fires tend to result in combustion products that are very rich in organic compounds (50% of the mass decomposed) and high levels of carbon monoxide, with slow release of inorganic acid gases if the appropriate anions are present in the fuel. By contrast, well-ventilated flaming fires are characterised by more efficient combustion, with the main products being carbon dioxide, water and heat. Initial yields of smoke and toxic products are low. If the fire later develops into a ventilation-controlled flaming fire, the restricted ventilation results in high yields of carbon monoxide, carbon dioxide, volatile organic compounds, particulates, hydrogen cyanide and other inorganic acid gases.

Temperature

The temperature at which combustion of materials such as wood and plastics occurs has a substantial impact on the relative quantities of combustion products formed (Westblad et al., 2002; Andersson et al., 2003; Font et al., 2003). It is difficult to effectively quantify the impact of temperature on the combustion products formed in fires outside the controlled laboratory environment, due to the complex temporal and spatial interactions as well as other factors which influence fire behaviour. Nonetheless as the temperature increases the generated combustion products favour simple molecular compounds like carbon dioxide.

Firefighting

The majority of reported studies of firefighter exposure to toxic combustion products in actual fires focussed on the aggregate exposure or dose accumulated from firefighting efforts overall (Gold et al., 1978; Treitman et al., 1980; Brandt-Rauf et al., 1988; Caux et al., 2002). This is also true for studies of firefighter exposure in training scenarios (Feunekes et al., 1997; Laitinen et al., 2010). Some studies have focussed on either the extinguishment/knockdown phase (in which the fire is brought under control) (Lowry et al., 1985; Austin et al., 2001) or the overhaul/damping down phase (in which fire suppression is complete, and firefighters are searching the structure for hidden fire) (Bolstad-Johnson et al., 2000, Burgess et al., 2001). The variability of actual fires (fuels, location etc) and the fire conditions makes it difficult to draw any conclusions about the relative concentrations of combustion products in extinguishment and overhaul phases of the firefighting from any of these studies.

Jankovic et al. (1991) took separate measurements during the extinguishment and overhaul phases of firefighting in 22 training and actual fires, including 15 residential fires. In general, many of the same air contaminants were present during both extinguishment and overhaul, but concentrations were lower during overhaul.

Extinguishing agent

Little research has been reported about the effect of extinguishing agent selection on the generation of combustion products (Dills and Beaudreau, 2008; Hietaniemi 1999). Dills and Beaudreau (2008) investigated the chemical composition of overhaul smoke after use of three different extinguishing agents: water; a protein-based water additive; and sulfonate detergent-based compressed air foam. They reported water extinguishment of experimental fires containing wood pallets and PVC resulted in a 6- to 10-fold higher level of aldehydes and a 5- to 11- fold increase in polycyclic aromatic hydrocarbons compared to extinguishment using a protein-based water additive. Extinguishment of low fuel-load fires with compressed air foam resulted in higher concentrations of carbon dioxide. Use of compressed air foam was also associated with an increase over time of less volatile VOCs (volatile organic compounds) as compared to extinguishment with water or protein-based water additives, an effect that was attributed either to a slower decrease in room temperature or pyrolysation of the foam itself.

Application of extinguishing agent

Water mist suppression systems studies have demonstrated factors such as spray characteristics (including water droplet size distribution, flux density and spray momentum), enclosure effects and dynamic mixing created by the discharge of water mist all affect the performance of a fire suppression system (Liu and Kim, 2000). Compared with automated systems, when extinguishment is conducted by firefighters additional variability is introduced by way of factors such as range, directionality, timing and volume of water flow. This variation impacts in multiple ways: on the quantity and combustion products being formed, smoke behaviour and movement, and on debris dispersion patterns (Queensland Fire and Rescue Service, 2009). In addition it would seem reasonable to expect a firefighter remaining behind a water curtain will be exposed to less smoke and airborne contaminants.

Smoke behaviour and firefighter placement

The behaviour of smoke in compartments is complex, and has been the subject of on-going research for many years. In general terms, smoke generated from a fire in a closed compartment will rise to the ceiling, forming a jet which spreads radially beneath the ceiling (Mowrer, 1999). When the jet reaches the wall boundaries, it is deflected downwards. The resulting smoke layer expands downwards to fill the compartment due to entrainment of fresh air into the fire plume and the expansion of heated gases. This expansion also forces gases to exit the compartment through available leakage paths. The presence of horizontal high-level barriers create impediments to smoke movement, while smoke flowing out of a compartment causes further entrainment of cooler air due to turbulence (Dennett, 2004).

The neutral plane is defined as the junction of the two pressure zones where the hot over-pressurised gases in the upper part of the compartment meet the cooler air being drawn into the lower part of the room. This is observed as a defined interface between the heated smoke layer in the upper part of the room and the comparatively cooler, cleaner air in the lower part of the room. Very little mixing occurs between the gas regions above and below the neutral plane, although it can occur at vents, shafts and at cooler walls of the compartment. Although the lower region is subject to heating and contamination with combustion products, it is to a substantially lesser degree than the gas region above the neutral plane (Quintiere, 1998).

The placement of firefighters within a compartment will have a considerable impact on the level of contaminant to which they are exposed. Variations due to the effects of turbulence are difficult to predict, however remaining beneath the neutral plane clearly offers advantages in reducing exposure to smoke and other airborne contaminants during extinguishment in addition to reducing their thermal exposure.

Exposure pathway

The turbulent nature of the atmosphere within the fire, heat generation and the resulting air movement causes the contaminants to be readily dispersed within the immediate environment and their concentrations to rapidly dissipate as they rise and are vented from the structure. The complexity of the fire interactions also impacts how the contaminants are transported.

The most obvious and significant exposure pathway is by air. A further exposure pathway is by contact with surfaces where the contaminants have been deposited or with fire debris during their extinguishment and overhaul activities.

Entry Routes

The possible routes of entry of airborne contaminants generated in a fire into the body include: inhalation; ingestion; dermal and injection. The most significant route of entry is through inhalation (Menzie et al, 1992). The contaminants (gases and particulates) can deposit or pass into the body through the lungs causing both acute and chronic adverse health effects. The human respiratory system is divided into two regions, namely the:

- Upper Respiratory Tract, where gases are inhaled into or exhaled out of the body, consisting of the
  - nose and nasal passages;
  - throat; and
  - pharynx.
- Lower Respiratory Tract, where exchanges of gases with blood stream occur, consisting of the:
  - respiratory airways;
  - trachea and bronchioles; and
  - lungs (respiratory bronchioles, alveolar ducts, alveolar sacs, and alveoli).

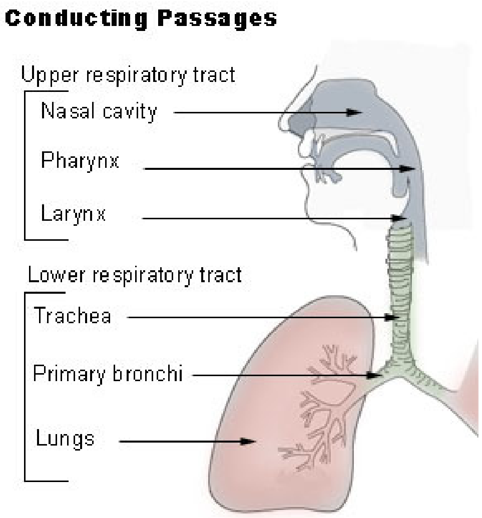

Figure 1.1 Conducting passages of lungs.
Source: http://en.wikipedia.org/wiki/Upper_respiratory_tract)

The inhalation and rate of inhalation of particulate matter, and subsequent entry into the human respiratory system is dependent on the nature and size of the particle. The rate of particulate inhalation decreases rapidly as a function of size. Only particulate matter present in the breathing zone and less than 10 micrometers (< 10 µm) will be inhaled into the body. Typically, respirable particulate matter greater than 5 micrometers (> 5 µm) does not pass the upper respiratory tract, but particulate matter <5 µm can pass into the lower respiratory tract and the lungs.

Ultrafine particles < 2.5 µm in diameter can also pass from the lungs and deposit in the alveolar region where gas exchange occurs during both inhalation and exhalation. These ultrafine particles can also be transported to the digestive tract, and potentially absorbed into the body. The combination of the small size, potential to penetrate deep in the respiratory system, and the amount of material that can be inhaled, is a basis for concern about adverse health effects.

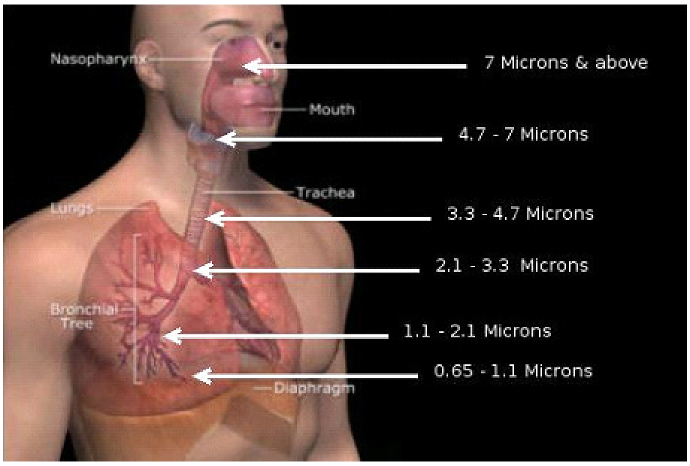

Figure 1.2 Particulate matter penetration into a typical human respiratory system.
Source: www.docep.wa.gov.au/ResourcesSafety

The behaviour of gases within the lungs is also complex and the absorption and distribution of the airborne contaminants is dependent on several factors including:

- airborne concentration of the contaminant;
- exposure duration;
- exertion;
- physico-chemical properties such as lipid solubility, aqueous solubility, and charge;
- concentration gradient across the alveolar air and plasma; and
- blood-gas partition coefficient.

These factors affect the ultimate diffusion rate. The contaminant may also induce biochemical, morphological or functional changes within the lung, which may be both short term and long term (Clayton and Clayton, 1978; Hill, 1980; Amdur et al., 1991; Salem and Katz 2006).

Despite the importance of this entry route, its significance within the firefighting environment should be considered in the context of firefighters' use of self contained breathing apparatus (SCBA) and their tactical methods. The IARC (International Agency Research Cancer) (IARC, 2010) reported fire fighting as an occupation is a possibly carcinogenic to humans (class 2B). A plausible mechanism for carcinogenesis is respiratory inflammatory effects, however it was acknowledged data was sparse.

Airborne contaminants (gases and particulates) generally will not be ingested as result of good hygiene practices and the use of SCBA. The importance of the skin as an entry route is less certain. Many contaminants will not penetrate the skin due to their size, chemical nature and time of exposure. However, it is well established polycyclic aromatic hydrocarbons, aromatic hydrocarbons and acid gases will be absorbed directly from the vapour phase and penetrate the skin. The penetration rate is dependent on many factors and the dose is also affected by the body's ability to de-toxify and excrete the contaminant. There is little evidence reported concerning the importance of the skin as an entry route in the context of firefighting. Given the extensive use of SCBA within the firefighting environment, it is likely the importance of the skin as an entry route has been underestimated.

LITERATURE REVIEW: MAJOR COMBUSTION PRODUCTS FROM RESIDENTIAL AND OTHER STRUCTURE FIRES

Background information

The following sections summarise some of the important physical and toxicological properties of major combustion products identified in the scientific literature published to date (Centres for Disease Control and Prevention, 2010; Chemwatch, 2010; Clayton and Clayton, 1978), and also review the scientific literature regarding previously measured concentrations of those combustion products in structural fires. To assist in interpretation of this information, the following definitions as applied in Australia should be noted:

> ***National Exposure Standard:*** The exposure standard means an airborne concentration of a particular substance in the worker's breathing zone, exposure to which, according to current knowledge, should not cause adverse health effects nor cause undue discomfort to nearly all workers. "Exposure standard – time weighted average (TWA)" means the average airborne concentration of a particular substance when calculated over a normal eight-hour working day, for a five day working week. "Exposure standard – peak" means a maximum or peak airborne concentration of a particular substance determined over the shortest analytically practicable period of time which does not exceed 15 minutes (National Occupational Health and Safety Commission, 1995).
>
> ***Immediately Dangerous to Life or Health (IDLH):*** "A situation that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate permanent adverse effects on health or prevent escape from such an environment" (Joint Technical Committee SF-010, Occupational Respiratory Protection, 2009).
>
> ***LC_{50}:*** "Median lethal concentration. A statistically derived concentration of a substance that can be expected to cause death during exposure or within a fixed time after exposure in 50% of animals exposed for a specified time" (National Occupational Health and Safety Commission, 2004).
>
> ***LC_{lo} (human):*** The lowest airborne concentration dose that is recorded to have caused mortality in humans after exposure to that particular chemical by inhalation. Time values in brackets represent the duration of exposure.

These descriptions of exposure guidelines and lethal concentrations are similar in the United States. Where concentration values have been specified in units of mg/m^3 (either in exposure standards or in scientific literature regarding measurements in fire environments) the measurement is presented in the original units, with a conversion to ppm (parts per million) based on conditions of standard temperature and pressure. It should be noted that this conversion is not necessarily accurate under fire conditions.

Carbon monoxide (CO)

Physical and toxicological properties

Molecular Weight	28.01
Vapour Pressure	101.08 kPa @ 20℃
Autoignition Temperature	608 – 700 ℃
Lower Flammability Limit	12.5 %
Upper Flammability Limit	74.2 %
National Exposure Standard (8 hour TWA)	30 ppm
Immediately Dangerous to Life or Health	1200 ppm
LC_{lo} (inhalation) (human)	4000 ppm (30 min)

Generation and concentration in structural fires

Virtually every fire generates carbon monoxide, as all carbon-based fuels produce CO as a result of incomplete combustion. As a major product of combustion, carbon monoxide is formed primarily in underventilated fires, fires where complete combustion is chemically inhibited, or fires where the initial products of combustion mix with colder gases thus halting the conversion of carbon monoxide to carbon dioxide. Fire suppression activities can also result in the development of elevated CO concentrations (National Fire Protection Association, 2001).

Carbon monoxide is repeatedly shown to be the predominant cause of fire-related deaths (Treitman et al., 1980). Gold et al. (1978) were among the first researchers to investigate the concentration of carbon monoxide in actual firefighting environments, which included but were not limited to residential fires. They found CO to be present at elevated levels at all fires in their sample, with a median concentration of 110 ppm and with 3% of fires having carbon monoxide concentrations over 1000 ppm. A further related study by Treitman et al. (1980) found carbon monoxide concentrations in a structural fire could approach 5000 ppm.

Jankovic et al. (1991) studied six training fires and 16 incidents, and separately considered the knockdown and overhaul phases of firefighting. They found that carbon monoxide concentrations during knockdown could reach 1900 ppm, with over 10% of the 22 fires studied having concentrations above 1500 ppm. During overhaul, the maximum observed carbon monoxide concentration was 82 ppm.

In a separate study focussing on overhaul at 25 fires in Phoenix, Bolstad-Johnson et al. (2000) found carbon monoxide exceeded 200 ppm in 5 fires, with an average concentration of 52.6 ppm and a maximum of 260 ppm. In the first ten minutes of readings, the maximum carbon monoxide concentration observed was 671 ppm.

Nitrogen dioxide (NO_2)

Physical and toxicological properties

Molecular Weight	46.01
Vapour Pressure	121 kPa at 25℃
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (8 hour TWA)	3 ppm
Immediately Dangerous to Life or Health	20 ppm
LC_{lo} (inhalation) (human)	200 ppm (1 min)

Generation and concentration in structural fires

The presence of nitrogen dioxide as a combustion product is expected through fixation of atmospheric nitrogen, and through the oxidation of nitrogenous materials such as silk, wool and polyurethane foam (Lees et al., 1995; National Fire Protection Association, 2001). Investigation of this chemical as a potential hazard to firefighters was included in early studies of fire-related toxic air contaminants, due to its toxicity and the observation that firefighters had at times suffered symptoms consistent with nitrogen dioxide inhalation (Gold et al., 1978). However, in their early study of actual firefighting environments (not specifically structural fires), Gold et al. (1978) found nitrogen dioxide to be present at only eight fires, with concentrations ranging from 0.02 to 0.89 ppm. Treitman et al. (1980) found concentrations of up to 8.3 ppm in predominantly structural fires, while Burgess et al. (1995) reported concentrations of up to 9.5 ppm in structural firefighting environments. In an investigation of contaminants present during overhaul, Bolstad-Johnson et al., (2000) found average NO_2 concentrations of 0.24 ppm, with a maximum concentration of 3.6 ppm.

These studies concluded that residential fires do not create conditions conducive to the formation of significant concentrations of nitrogen dioxide (Treitman et al., 1980), and more recent studies of air contaminants generated in structural fires have not included nitrogen dioxide as a chemical of interest.

Sulfur dioxide (SO_2)

Physical and toxicological properties

Molecular Weight	64.06
Vapour Pressure	380 kPa @ 25℃
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (8 hour TWA)	2 ppm
Immediately Dangerous to Life or Health	100 ppm
LC_{lo} (inhalation) (human)	1000 ppm / 10 min

Generation and concentration in structural fires

Sulfur dioxide is formed during the thermal decomposition of any sulfur-containing compounds (Wakefield, 2010). These may include materials such as wool, silk and rubber (Sumi and Tsuchiya., 1973; Holstege and Kirk., 2006, Blomqvist, 2005).

Brandt-Rauf et al. (1988) studied the exposure of firefighters to a limited range of combustion products during attendance at 26 fires. Within the limitations of the measurement processes used (colorimetric detector tubes), concentrations of sulfur dioxide were measured in this study to range between undetectable and 42 ppm. Bolstad-Johnson et al. (2000) found average concentrations of sulfur dioxide of 1.6 ppm and a maximum concentration of 8.69 ppm in their study of overhaul smoke in 25 structural fires. In a different investigation of overhaul smoke in structural fires, Burgess et al. (2001) found sulfur dioxide as a detectable component of overhaul smoke in all the residential fires investigated in their study conducted in two United States cities, with average concentrations of 0.4 and 1.5 ppm.

Hydrogen cyanide (HCN)

Physical and toxicological properties

Molecular Weight	27.03
Vapour Pressure	82.46 kPa @ 20°C
Autoignition Temperature	538 °C
Lower Flammability Limit	5.6%
Upper Flammability Limit	40 %
National Exposure Standard (Peak)	10 ppm
Immediately Dangerous to Life or Health	50 ppm
LC_{lo} (inhalation) (human)	200 ppm (5 min)

Generation in structural fires

Hydrogen cyanide is readily generated from the combustion of natural and synthetic materials such as wool, cotton, polyurethane, acrylonitriles, polyamides and nylon (Gold et al., 1978; Weiden et al., 2007). It has been suggested that hydrogen cyanide may be a contributing cause in fire deaths, although its role is difficult to determine (Baud et al., 1991; Alarie, 2002). Occupational exposure of firefighters to cyanide in structural fire environments has been reported (Levine and Radford, 1978; Varone et al., 2008), and the potential for dermal absorption of HCN has been demonstrated (Dugard, 1987).

Early studies of Boston firefighters found hydrogen cyanide in air samples collected at approximately 50% of all fires investigated (Gold et al., 1978) but only 10 % of fires sampled when predominantly structure fires were investigated (Treitman et al., 1980). In these studies, detected concentrations of HCN were generally less than 5 ppm, with mattress fires producing amongst the highest concentrations of hydrogen cyanide. Lowry et al. (1985) found detectable concentrations of HCN in only 12% of structural fires investigated in their study conducted in the Dallas area, with a maximum concentration of 40 ppm and average concentration of 3.7 ppm. Incidents in this study included office and chemical factory fires in addition to residential fires.

Considering knockdown and overhaul phases of fires separately, Jankovic et al. (1991) found concentrations of HCN of up to 23 ppm in a range of training scenarios and fire incidents. The corresponding maximum concentration of hydrogen cyanide during overhaul was 0.4 ppm. In a more recent study of exposure of firefighters to components of overhaul smoke in two cities in the United States, Burgess et al. (2001) found hydrogen cyanide was present at detectable levels in all of the residential fires investigated, with average concentrations of 0.8 and 0.9 ppm.

In their investigation into smoke present during overhaul operations in 16 structural fires in Phoenix, Bolstad-Johnson et al., (2000) found measurable concentrations of

HCN in only 4 fires, and all of these were at concentrations too low to quantify (<< 1 mg/m^3 (0.91 ppm)).

Hydrogen chloride (HCl)

Physical and toxicological properties

Molecular Weight	36.46
Vapour Pressure	7.68 kPa @ 120°C
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (Peak)	5 ppm
Immediately Dangerous to Life or Health	50 ppm
LC_{50} (inhalation) (rat)	1300 ppm (30 min)

Generation and concentration in structural fires

Hydrogen chloride is considered to be the most important halogen acid gas which may be evolved during combustion and is generated as a result of the chlorine content of many common materials such as polyvinyl chloride (Wakefield, 2010) and the use of fire retardant additives based on chlorine (Hartzell, 1996).

Gold et al. (1978) found hydrogen chloride in only five of the 90 fires investigated by their study. However, it is noteworthy both that all five incidents were reported as general involvement of a room, its contents and an assortment of rubbish, and that the maximum concentration of HCl recorded was 150 ppm.

Jankovic et al. (1991) found hydrogen chloride in concentrations up to 8.5 ppm in smoke generated during the knockdown phase of firefighting, but not in overhaul smoke. In the study of overhaul smoke by Bolstad-Johnson et al. (2000), hydrochloric acid was found at concentrations up to 3.96 mg/m^3 (2.66 ppm), with an average concentration of 0.99 mg/m^3 (0.66 ppm). Approximately one-third of samples collected contained detectable levels of HCl. Burgess et al. (2001) also found hydrogen chloride at detectable levels in over half of the residential fires investigated in their study of United States firefighter exposure to overhaul smoke, with average hydrogen chloride concentrations of 0.2 and 0.9 ppm.

Hydrogen fluoride (HF)

Physical and toxicological properties

Molecular Weight	20.01
Vapour Pressure	122 kPa @ 25°C
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (Peak)	3 ppm
Immediately Dangerous to Life or Health	30 ppm
LC_{lo} (inhalation) (human)	50 ppm (30 min)

Generation and concentration in structural fires

The major source of hydrogen fluoride as a combustion product is by the thermal decomposition of fluorine-containing polymers such as polytetrafluorethylene (PTFE, "Teflon") (Wakefield, 2010). Although HF has been noted among the most widely recognised of the potentially toxic combustion products (Hilado and Cumming, 1978), few studies of actual structural fires have attempted to measure it. Jankovic et al. (1991) found hydrogen fluoride in eight of the 22 fires considered in their study of six training scenarios and 16 incidents, all during the knockdown phase of firefighting. The maximum concentration detected was 6.4 mg/m^3 (7.8 ppm).

Hydrogen bromide (HBr)

Physical and toxicological properties

Molecular Weight	80.91
Vapour Pressure	2026.5 kPa @ 16.8°C
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (Peak)	3 ppm
Immediately Dangerous to Life or Health	30 ppm
LC_{50} (inhalation) (rat)	2858 ppm (1 hr)

Generation and concentration in structure fires

Fire retardant additives based on bromine are a main source of hydrogen bromide as a combustion product (Hartzell, 1996). Polymers containing these types of fire retardants include polystyrenes (foam and high-impact), polyurethanes and polycarbonates (Alaee et al., 2003). While laboratory studies have been conducted to measure the release of hydrogen bromide on combustion of retardant treated polymers (Benbow and Cullis, 1975; Barontini and Cozzani, 2006) this chemical has not typically been measured in studies of combustion products from actual structural fires. Recently, it has been reported (Blomqvist et al., 2004; Blomqvist, 2005) that low concentrations of hydrogen bromide were generated during simulated room burn fires.

Phosphoric acid (H_3PO_4)

Physical and toxicological properties

Molecular Weight	98
Vapour Pressure	0.75 kPa @ 20°C (75%)
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (8 hour TWA)	1 mg/m^3
Immediately Dangerous to Life or Health	1000 mg/m^3
LC_{50} (inhalation) (rat)	25.5 mg/m^3 (4 hr)

Generation and concentration in combustion processes

Phosphoric acid has been investigated as a combustion product from pesticides and a number of other chemical substances (Smith-Hansen and Jørgensen, 1994). It may be formed as a result of combustion of materials such as polyurethane foam or the casings or housings of electronic components treated with phosphorus-containing flame retardants (Gann et al., 2001; Wichman, 2003, Wakefield, 2010). Dills and Beaudreau (2008) tested for phosphoric acid as a combustion product in their study of overhaul smoke generated from the use of three different extinguishing agents, but did not find phosphoric acid in quantifiable concentrations. This chemical has not typically been investigated in studies of combustion products generated in actual structural fires.

Nitric acid (HNO_3)

Physical and toxicological properties

Molecular Weight	63.02
Vapour Pressure	8.26 kPa
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (8 hour TWA)	2 ppm
Immediately Dangerous to Life or Health	25 ppm
LC_{50} (inhalation) (rat)	130 mg/m^3 (50 ppm) (4 hr)

Generation and concentration in structural fires

Nitric acid is readily generated from nitrogen dioxide (see above) and it is also generated from combustion of nitrogenous based materials. Limited studies have investigated nitric acid as a combustion product. Jankovic et al. (1991) studied the concentration of nitric acid in a range of fire incidents and training scenarios. Concentrations of nitric acid ranged from not detectable to 1.8 mg/m^3 (0.7 ppm) during the knockdown phase of the fires, but were not detected during overhaul.

Sulfuric acid (H_2SO_4)

Physical and toxicological properties

Molecular Weight	98.07
Vapour Pressure	0.133 kPa @146°C
Autoignition Temperature	-
Lower Flammability Limit	-
Upper Flammability Limit	-
National Exposure Standard (8 hour TWA)	1 mg/m^3
Immediately Dangerous to Life or Health	15 mg/m^3
LC_{50} (inhalation) (rat)	510 mg/m^3 (2 hr)

Generation and concentration in structural fires

Sulfuric acid is readily generated from sulfur dioxide (see above) and it is also generated from combustion of sulfur based materials. Limited studies have investigated sulfuric acid as a combustion product. Jankovic et al. (1991) found concentrations of sulfuric acid in smoke generated during the knockdown phase of 22 fires (including training scenarios and actual incidents) to range from not detectable to 8.5 mg/m^3, and during the overhaul phase of fires from not detectable to 0.9 mg/m^3. In their study of combustion products present during overhaul, Burgess et al. (2001) found detectable levels of sulfuric acid at several of the residential fires investigated, with average concentrations of 1.21 ppm and 3.40 ppm (4.84 and 13.6 mg/m^3) in fires in Tucson and Phoenix respectively.

Volatile organic compounds (VOCs)

Physical and toxicological properties

	Benzene	**Toluene**	**Xylene**
Molecular Weight	78.12	92.14	106.18
Vapour Pressure	9.95 @ 20°C	2.93 @ 20°C	0.5 @ 15°C
Autoignition Temperature	562°C	529 – 536°C	495-516°C
Lower Flammability Limit	1.3%	1.3%	1.1%
Upper Flammability Limit	7.9%	7.0%	7.7%
National Exposure Standard (8 hour TWA)	1 ppm	50 ppm	80 ppm
Immediately Dangerous to Life or Health	500 ppm	500 ppm	900 ppm
LC_{lo} (inhalation) (human)	2000 ppm (5 min)	-	10 000 ppm (6 hr)
LC_{50} (inhalation) (rat)	>12600 ppm (4 hr)	4000 ppm (4 hr)	5000 ppm (4 hr)

The table above includes physical and toxicological data on three of the most common volatile organic compounds: benzene, toluene and xylene. Benzene, in particular, is of interest as it is a known carcinogen. The potential for dermal absorption of benzene in the occupational setting has been demonstrated (Colman and Coleman, 2006, United States Environmental Protection Agency, 1992), indicating that it poses more than just a respiratory hazard. For individuals unprotected against both inhalation and dermal exposure to vapours, estimates of dermal uptake are in the range of 1-2 percent of the uptake via inhalation (Riihimäki and Pfäffli, 1978; Brooke et al., 1998).

Generation and concentration in structural fires

Likely sources of benzene and other volatile organic compounds in fires include petroleum products and the thermal degradation of plastics (Treitman et al., 1980). The formation of aromatic hydrocarbons such as benzene tends to coincide with higher smoke production and higher temperatures (Fardell et al., 1986), while unsaturated and saturated hydrocarbons are likely to be derived from decomposition of the original fuel.

A study of structural firefighting in Boston (Treitman et al., 1980) found benzene concentrations could reach over 100 ppm, with over 50% of fires investigated having concentrations above 0.5 ppm. Jankovic et al. (1991) found benzene concentrations up to 22 ppm in the knockdown phase of the fire and up to 0.3 ppm in the overhaul phase during their study of combustion products generated during training and actual structural fires. In a study of nine structure fires of various types occurring in Canada, Austin et al (2001) found benzene (concentration range 0.12 to 10.76 ppm), xylene (concentration range of 0.06 – 9.19 ppm) and toluene (concentration range of 0.05 – 5.52 ppm) among the combustion products for all incidents.

Considering firefighter exposures during overhaul only, Bolstad-Johnson et al. (2000) found benzene concentrations in 53 of the 95 air samples collected at 25 structure fires. The average concentration of benzene in these samples was 0.383 ppm, with a maximum value of 1.99 ppm. Burgess et al. (2001) found no detectable levels of benzene in samples from fires in Tucson, but in approximately 50% of samples collected in fires in Phoenix, with an average concentration of 0.557 ppm.

Caux et al. (2002) found that 42% of Toronto firefighters who had participated in firefighting activities (primarily at structural fires) exhibited low but measurable levels of urinary t,t-muconic acid (a biomarker for benzene exposure). Among participants in this study, SCBA use was consistent during knockdown, but less consistent during overhaul. The observed levels of urinary t,t-muconic acid corresponded to atmospheric concentrations of benzene exceeding 1 ppm in 14% of cases. A more recent study conducted by Laitinen et al. (2010) in house and container simulators for firefighter training also found elevated levels of urinary muconic acid among trainers immediately after participation in training involving conifer plywood board as a fuel.

Aldehydes

Physical and toxicological properties

	Formaldehyde	**Acrolein**
Molecular Weight	30.0	56.07
Vapour Pressure	> 100 kPa	29.33 kPa @ 20°C
Autoignition Temperature	430°C	234°C
Lower Flammability Limit	7.0%	2.8%
Upper Flammability Limit	73%	31%
National Exposure Standard	1 ppm	0.1 ppm
Immediately Dangerous to Life or Health	20 ppm	2 ppm
LC_{50} (inhalation) (rat)	64 000 ppm (4hr)	8.3 ppm (4hr)
LC_{lo} (inhalation) (human)	-	5.5 ppm

Generation and concentration in structural fires

It has been suggested (Treitman et al., 1980) that aldehydes in general, and acrolein in particular, may play an important role in respiratory injury to fire victims. An experimental study of room burns of single fuels (Fardell et al., 1986) placed acrolein as the second most toxicologically significant compound investigated (after carbon monoxide), although the main hazard was determined to be irritancy, and the range of chemicals investigated in that study did not include acid gases.

The formation of acrolein at fires has been attributed to a wide range of materials, based on its high frequency of detection in studies of combustion products (Treitman et al., 1980). However, the main fuels implicated in the formation of acrolein are wood and other cellulosic products (National Fire Protection Association, 2001). Experiments involving wood have reported acrolein concentrations of up to 269 ppm in steady-state fires with low ventilation (Fardell et al., 1986)

Treitman et al. (1980) found that concentrations of acrolein in structural firefighting environments were above 0.3 ppm in 50% of fires studied, with 10% of fires having acrolein concentrations above 3 ppm. Jankovic et al. (1991) noted acrolein to be above the United States short-term exposure limit 0.3 ppm in approximately 50% of the air samples collected during extinguishment operations in 22 fires. Concentrations of acrolein and formaldehyde ranged from below detection limits to 3.2 ppm and 8 ppm respectively during knockdown in that study. Corresponding figures for overhaul activities were up to 0.2 ppm for acrolein, and up to 0.4 ppm for formaldehyde.

During overhaul at a total of 12 actual fires and four training fires in two cities in the United States, Burgess et al. (2001) found detectable levels of acrolein at only one incident (concentration 0.016 ppm). In comparison, formaldehyde concentrations were at quantifiable levels in all but one sample, with average values of 0.109 ppm and 0.257 ppm in the fires in Tucson and Phoenix respectively. Also considering combustion products present during overhaul, Bolstad-Johnson et al. (2000) found quantifiable formaldehyde and acrolein concentrations in 86 and 7 of 96 air samples collected at 25 structure fires respectively. The maximum measured concentration of acrolein was 0.3 ppm, while the maximum formaldehyde concentration was 1.18 ppm.

Polycyclic aromatic hydrocarbons (PAHs)

Toxicological properties

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals consisting of two or more aromatic rings. They are known to be generated by incomplete combustion and generally occur as complex mixtures rather than single compounds. There are more than 600 different polycyclic aromatic hydrocarbons (McKenzie, 2007 whilst others reported more than 100 (Nisbet and LaGoy, 1992; Agency for Toxic Substances and Disease Registry, 1995). Although there is evidence that a number of polycyclic aromatic hydrocarbons are probably or possibly carcinogenic to humans, the only one to date which has been definitively classified as carcinogenic by the International Agency for Research on Cancer is benzo[a]pyrene (IARC, 2006). The carcinogenic effect of other PAHs has been demonstrated to differ from that of benzo[a]pyrene in animal studies, resulting in a need to determine equivalency factors for risk assessments.

The United States Environmental Protection Agency (1993) has published interim recommendations on quantitative risk assessment of a selection of PAHs, choosing to label these factors as “estimated order of potential potency” due to not all of the guiding criteria being met for application of toxicity equivalency factors to a mixture. However, Nisbet and LaGoy (1992) separately developed a list of Toxic Equivalency Factors for polycyclic aromatic hydrocarbons that have been cited extensively in toxicology literature. The IARC Grouping and toxicity ratings of the polycyclic aromatic hydrocarbons measured in this study are summarised in the table below.

PAH	**IARC Grouping (2006)**	**Order of Potential Potencies (US EPA, 1993)**	**Toxic Equivalency Factor (Nisbet and La Goy, 1992)**
Benzo[a]pyrene	Group 1	1 (index compound)	
Dibenz[a,h]anthracene	Group 2A	1.0	5
Benz[a]anthracene	Group 2B	0.1	0.1
Benzo[b]fluoranthene	Group 2B	0.1	0.1
Benzo[k]fluoranthene	Group 2B	0.01	0.1
Chrysene	Group 2B	0.001	0.01
Indeno[1,2,3-cd]pyrene	Group 2B	0.1	0.1
Benzo[ghi]perylene	Group 3	-	0.01

Pyrene	Group 3	-	0.001
Fluoranthene	Group 3	-	0.001
Anthracene	Group 3	-	0.01
Phenanthrene	Group 3	-	0.001
Fluorene	Group 3	-	0.001
Acenaphthene	Group 3	-	0.001
Coronene	Group 3	-	-
Acenaphthylene	-	-	0.001
Naphthalene	-	-	0.001

IARC Grouping Scheme: Group 1 – carcinogenic to humans; Group 2A – probably carcinogenic to humans; Group 2B – possibly carcinogenic to humans; Group 3 – not classifiable as to carcinogenicity in humans.

Occupational exposure to polycyclic aromatic hydrocarbons has received significant attention in recent years in a number of occupational settings (McClean et al., 2004; Unwin et al., 2006). One major finding of studies of various occupational exposures is that even in situations where inhalational exposure protection measures are implemented; dermal exposure can form a major route of uptake for PAHs. Studies of coal liquefaction, coke-oven and creosote workers indicate that 50% to 90% of total body PAH dose is attributable to dermal uptake in environments where both inhalation and dermal exposure is possible (Van Rooij et al., 1993a,b; Quinlan et al., 1995).

Generation and concentration in structural fires

Despite the attention to occupational PAH exposure generally, levels of exposure during firefighting have been studied by only a few research groups. Jankovic et al., (1991) found 14 different polycyclic aromatic hydrocarbons during extinguishment operations at 22 fires of various types, with acenaphthene, and phenanthrene having the highest concentrations. However, fewer of the PAHs (fluoranthene, pyrene, benzo[e]pyrene, benz[a]anthracene and chrysene) were detectable during overhaul in the same study. Maximum total PAH concentrations were 0.5 mg/m^3 and 0.02 mg/m^3 during extinguishment and overhaul respectively, although naphthalene was only measured qualitatively and therefore not included in the total.

Wobst (1999) studied surface deposition of PAHs after two fires in private residences, finding total concentrations of between 34 µg/m^2 and 58 mg/m^2 depending on the incident and surface studied. In a study of seven simulated apartment fires by Ruokojärvi et al. (2000) total atmospheric concentrations of PAHs ranged from 6.4 to 470 mg/m^3, with the highest individual concentrations being of phenanthrene, fluoranthene and pyrene. Surface deposition (wipe) samples were also taken, with total PAH concentrations being in the range of 4.2 to 40 mg/m^2. The polycyclic aromatic hydrocarbons of greatest concentration in the wipe samples varied from sample to sample (fluoranthene, pyrene and benzo[ghi]perylene).

Bolstad-Johnson et al. (2000) measured 16 PAHs in their study of overhaul smoke from 25 structural fires, with acenaphthylene, naphthalene and fluoranthene being the PAHs recording the highest average concentrations in the samples collected. Considering naphthalene only, Austin et al (2001) found concentrations ranging from 0.01 to 2.14 ppm across nine structural fires.

A number of studies have been undertaken of firefighter exposure during training simulations. Feunekes et al. (1997) found average airborne concentrations to which firefighters were exposed ranged between 8.48 and 14.75 mg/m^3 during confined space oil fires, depending on the role of the study participant. The PAHs with the highest concentrations in that study were fluoranthene, phenanthrene and pyrene.

Laitinen et al. (2010) also investigated exposure of firefighting trainers during training activities, considering both house and container simulators. Atmospheric concentrations of PAHs, dermal exposures by handwashing and skin sampling, and uptake of PAHs via urinary 1-pyrenol excretions were all included in the study. Despite the use of respiratory protection, elevated levels of urinary 1-pyrenol were found post-exposure. The use of undergloves was found to reduce the amount of polycyclic aromatic hydrocarbons on trainers' hands by 80%.

Caux et al. (2002) investigated the exposure of firefighters during operational duties finding elevated levels of biomarkers for uptake of polycyclic aromatic hydrocarbons despite the wearing of respiratory protection. However, it was noted that for most firefighters in the study the exposure appeared low when compared to occupational exposures in other industries where PAH exposure has been quantified.

References

Agency for Toxic Substances and Disease Registry. (1995). Toxicological profile for polycyclic aromatic hydrocarbons. United States Department of Health and Human Services.

Alaee M, Arias P, Sjödin A, Bergman Á. (2003). An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environment International, 29, 683-689.

Alarie Y. (2002). Toxicity of fire smoke. Critical Reviews in Toxicology, 32, 259-289.

Amdur M, Doull J, Klassen C. (1991). Casarett and Doulls Toxicology the basic science of poisons. Pergamon Press. New York.

Andersson B, Markert F, Holmstedt G. (2003). Combustion products generated by hetero-organic fuels on four different fire test scales. Fire Safety Journal, 40, 439-465.

Austin CC, Wang D, Ecobichon DJ, Dussault, G. (2001). Characterization of volatile organic compounds in smoke at municipal structural fires. Journal of Toxicology and Environmental Health, Part A, 63, 437-458.

Barontini F, Cozzani V. (2006). Formation of hydrogen bromide and organobrominated compounds in the thermal degradation of electronic boards. Journal of Analytical and Applied Pyrolysis, 77, 41-55.

Baud FJ, Barriot P, Toffis V, Riou B, Vicaut E, Lecarpentier Y, Bourdon R, Astier A, Bismuth C. (1991). Elevated blood cyanide concentrations in victims of smoke inhalation. New England Journal of Medicine, 325, 1761-1766.

Benbow AW, Cullis CF. (1975). The formation of toxic products during the combustion of halogen-containing polymers. European Polymer Journal, 11, 723-727.

Blomqvist P. (2005). Emissions from fires consequences for human safety and the environment. Ph.D Thesis

Blomqvist P, Rosell, Simonsen M. (2004). Emissions from fires part II simulated room fires. Fire Technology 40, 59-73.

Bolstad-Johnson DM, Burgess JL, Crutchfield CD, Storment S, Gerkin R, Wilson JR. (2000). Characterization of firefighter exposures during overhaul. American Industrial Hygiene Association Journal, 61, 636-641.

Brandt-Rauf PW, Fallon LF, Tarantini T, Idema C, Andrews L. (1988). Health hazards of fire fighters: exposure assessment. British Journal of Industrial Medicine 45, 606-612.

Brooke I, Cocker J, Delic JI, Payne M, Jones K, Gregg NC, Dyne D. (1998). Dermal uptake of solvents from the vapour phase: an experimental study in humans. Annals of Occupational Hygiene, 42, 531-540.

Burgess JL, Nanson CJ, Bolstad-Johnson DM, Gerkin R, Hysong TA, Lantz RC, Sherrill DL, Crutchfield CD, Quan SF, Bernard AM, Witten ML. (2001). Adverse respiratory effects following overhaul in firefighters. Journal of Occupational and Environmental Medicine, 43, 467-473.

Caux C, O'Brien C, Viau C. (2002). Determination of firefighter exposure to polycyclic aromatic hydrocarbons and benzene during fire fighting using measurement of biological indicators. Applied Occupational and Environmental Hygiene, 17, 379-386.

Centers for Disease Control and Prevention. (2010). NIOSH Pocket Guide to Chemical Hazards. NIOSH Publication Number 2005-149.

Chemwatch. (2010). Chemgold II. Caulfield North, Victoria.

Clayton GD, Clayton FE. (1978). Patty's Industrial Hygiene and Toxicology. John Wiley and Sons. New York.

Colman R, Coleman A. (2006). Unexpected cause of raised benzene absorption in coke oven by-product workers. Occupational Medicine, 56, 269-271.

DeHaan JD. (2002). Kirk's Fire Investigation. Pearson Education, Upper Saddle River, NJ.

Dennett MF. (2004). Fire attack: an integrated strategy. Summerseat Publishing, Bury.

Dills RL, Beaudreau M. (2008). Chemical composition of overhaul smoke after use of three extinguishing agents. Fire Technology, 44, 419-437.

Drysdale DD. (1999). An introduction to fire dynamics. John Wiley and Sons, Chichester

Dugard PH. (1987). The absorption of cyanide through human skin in vitro from solutions of sodium cyanide and gaseous HCN. In: Ballantyne B, Marrs TC, eds. Clinical and experimental toxicology of cyanides. Wright, Bristol, IOP Publishing, pp. 127–137.

Fardell PJ, Murrell JM, Murrell JV. (1986). Chemical 'fingerprint' studies of fire atmospheres. Fire and Materials, 10, 21-28.

Feunekes FDJR, Jongeneelen FJ, vd Laan, H, Schoonhof FHG. (1997). Uptake of polycyclic aromatic hydrocarbons among trainers in a fire-fighting training facility. American Industrial Hygiene Association Journal, 58, 1, 23-28.

Font R, Aracil I, Fullana A, Martín-Gullón I, Conesa JA. (2003). Semivolatile compounds in pyrolysis of polyethylene. Journal of Analytical and Applied Pyrolysis, 68-69, 599-611.

Gann RG, Averill JD, Butler K, Jones WW, Mulholland GW, Neviaser JL, Ohlemiller TJ, Peacock RD, Reneke PA, Hall JR Jr, (2001). International Study of the Sublethal Effects of Fire Smoke on Survival and Health: Phase I Final Report, Technical Note 1439, National Institute of Standards and Technology, Gaithersburg, MD, 2001.

Gold A, Burgess WA, Clougherty EV. (1978). Exposure of firefighters to toxic air contaminants. American Industrial Hygiene Association Journal, 39, 534-539.

Hartzell GE. (1996). Overview of combustion toxicology. Toxicology, 115, 7-23.

Hietaniemi J, Kallonen R, Mikkola E. (1999). Burning characteristics of selected substances: influence of suppression of water. Fire and Materials 23, 149-169.

Hilado CJ, Cumming HJ. (1978). Short-term LC50 values: an update on available information. Fire Technology, 14, 46-50.

Hill D. (1980). Physics applied to Anesthesia. Butterworths, Boston.

Holstege CP, Kirk MA. (2006). Smoke inhalation. In: Flomenbaum NE, Goldfrank LR, Hoffman RS, Howland MA, Lewin NA, Nelson LS.. (eds) Goldfrank's toxicologic emergencies, eighth edition. McGraw-Hill.

International Agency for Research on Cancer. (2006). Polycyclic aromatic hydrocarbons. http://monographs.airc.fr/ENG/Meetings/92-pahs.pdf, accessed 21/07/2008.

International Agency for Research on Cancer. (2010) Shiftwork, Painting and Firefighting. IARC 98.

Jankovic J, Jones W, Burkhart J, Noonan G. (1991). Environmental study of firefighters. Annals of Occupational Hygiene, 35, 581-602.

Joint Technical Committee SF-010, Occupational Respiratory Protection (2009). Selection, use and maintenance of respiratory protective equipment. AS/NZS 1715:2009. Standards Australia.

Kirk KM. (2006). Air contaminants at residential fire investigation scenes. Thesis, Queensland University of Technology, Brisbane.

Kozlowski R, Wesolek D, Wladyka-Przybylak M. (1999). Combustibility and toxicity of board materials used for interior fittings and decorations. Polymer Degradation and Stability, 64, 595-600.

Laitinen J, Mäkelä M, Mikkola J, Huttu I. (2010). Fire fighting trainers' exposure to carcinogenic agents in smoke diving simulators. Toxicology Letters, 192, 61-65.

Lees, P. S. J. (1995) Combustion products and other firefighter exposures. Occupational Medicine: State of the Art Reviews 10, 691-706.

Levine MS, Radford EP (1978). Occupational exposures to cyanide in Baltimore firefighters. Journal of Occupational Medicine, 20, 53-56.

Liu Z, Kim AK. (2000). A review of water mist fire suppression systems – fundamental studies. National Research Council Canada, Report NRCC-41910.

Lowry WT, Juarez L, Petty CS, Roberts B. (1985). Studies of toxic gas production during actual structural fires in the Dallas area. Journal of Forensic Sciences, 30, 59-72.

McClean MD, Rinehart RD, Ngo L, Eisen EA, Kelsey KT, Herrick, RF. (2004). Inhalation and dermal exposure among asphalt paving workers. Annals of Occupational Hygiene, 48, 663-671.

McKenzie C. (2007). Chemical and physical characterisation of aerosols from exhaust emissions. Queensland University of Technology, Ph.D Thesis.

Menzie CA, Potocki BB, Santodonato J. (1992). Exposure to carcinogenic PAHs in the environment. Environmental Science and Technology, 26, 1278–1284.

Michal J. (1976). Toxicity of pyrolysis and combustion products of poly-(vinyl chloride). Fire and Materials, 1, 57-62.

Michal J, Mitera J, Tardon S. (1976). Toxicity of thermal degradation products of polyethylene and polypropylene. Fire and Materials, 1, 160-168.

Mowrer FW. (1999). Enclosure smoke filling revisited. Fire Safety Journal, 33, 93-114.

National Fire Protection Association. (2001). Guide for fire and explosion investigations, 2001 edition. NFPA International, Quincy, MA.

Nisbet ICT, LaGoy PK. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regulatory Toxicology and Pharmacology, 16, 290-300.

National Occupational Health and Safety Commission. (2004). Approved criteria for classifying hazardous substances. NOHSC:1008(2004). Australian Government.

National Occupational Health and Safety Commission. (1995). Adopted National Exposure Standards for atmospheric contaminants in the occupational environment. NOHSC:1003(1995). Australian Government.

Paulson DR, Moran GF. (1974). Analysis of some toxic combustion products of low-density flexible polyurethane-ether foams. Environmental Science and Technology, 8. 1116-1118.

Purser D. (2001). Toxicity of fire retardants in relation to life safety and environmental hazards. In: Horrocks AR, Price D. (eds) Fire retardant materials. Woodhead Publishing Ltd, Cambridge.

Queensland Fire and Rescue Service (2009). PUAFIR302B Practical firefighting. Queensland Government, Brisbane.

Quinlan R, Kowalczyk G, Gardiner K, Calvert IA, Hale K, Walton ST. (1995b). Polycyclic aromatic hydrocarbon exposure in coal liquefaction workers: the value of urinary 1-hydroxypyrene excretion in the development of occupational hygiene control strategies. Annals of Occupational Hygiene, 39, 329-346.

Quintiere JG. (1998). Principles of fire behaviour. Delmar Publishers, Albany New York.

Riihimäki V, Pfäffli P. (1978). Percutaneous absorption of solvent vapors in man. Scandinavian Journal of Work, Environment and Health, 4, 73-85.

Ruokojärvi P, Aatamila M, Ruuskanen J. (2000). Toxic chlorinated and polyaromatic hydrocarbons in simulated house fires. Chemosphere 41, 825-828.

Rutkowski J, Levin B. (1986). Acrylonitrile-butadiene-styrene copolymers (ABS): pyrolysis and combustion products and their toxicity - a review of the literature. Fire and Materials 10, 93.

Salem H, Katz S. (2006). Inhalation Toxicology. Taylor and Francis, New York.

Smith-Hansen L. (1995). Toxic hazards from pesticide warehouse fires. In: Mewis JJ, Pasman HJ, De Rademaeker EE (eds) Loss Prevention and Safety Promotion in the Process Industries. Vol I. Elsevier Science 265.

Smith-Hansen L, Jørgensen KH. (1994). Combustion products from pesticides and other chemical substances by use of DIN 53 436. Fire Safety Journal, 23, 51-66.

Stefanidou M, Athanaselis S, Spiliopoulou C. (2008). Health impacts of fire smoke inhalation. Inhalation Toxicology, 20, 761-766.

Sumi K, Tsuchiya Y. (1973). Combustion products of polymeric materials containing nitrogen in their chemical structure. Journal of Fire and Flammability, 4, 15-22.

Terrill JB, Montgomery RR, Reinhardt CF. (1978). Toxic gases from fires. Science 200, 1343-1347.

Tirey D, Dellinger B, Rubey W, Taylor P (1993), Thermal Degradation of environmentally sensitive pesticides. EPA/600/SR-93/102

Treitman RD, Burgess WA, Gold A. (1980). Air contaminants encountered by firefighters. American Industrial Hygiene Association Journal, 41, 796-802.

United Kingdom Health Safety Executive (2002) Safety Report Assessment Guidance for chemical warehouses.

United States Environmental Protection Agency (1993). Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. Washington.

United States Environmental Protection Agency (EPA). (1992). Dermal exposure assessment: principles and applications. Report EPA/600/8-91/011B, U.S. Washington.

Unwin J, Cocker J, Scobbie E, Chambers H. (2006). An assessment of occupational exposure to polycyclic aromatic hydrocarbons in the UK. Annals of Occupational Hygiene, 50, 395-403.

Van Rooij JG, Bodelier-Bade MM, Jongeneelen FJ. (1993a). Estimation of individual dermal and respiratory uptake of polycyclic aromatic hydrocarbons in 12 coke oven workers. British Journal of Industrial Medicine, 50, 623–632.

Van Rooij JG, Van Lieshout EM, Bodelier-Bade MM, Jongeneelen FJ. (1993b). Effect of the reduction of skin contamination on the internal dose of creosote workers exposed to polycyclic aromatic hydrocarbons. Scandinavian Journal of Work and Environmental Health. 19, 200-207.

Varone JC, Warren TN, Jutras K, Molis J, Dorsey J. (2008). Report of the investigation committee into the cyanide poisonings of Providence firefighters. New Solut, 18, 87-101.

Wakefield JC. (2010). A toxicological review of the products of combustion. HPA Chemical Hazards and Poisons Division, Health Protection Agency, Didcot.

Wang Z, Richter H, Howard JB, Jordan J, Carlson J, Levendis YA. (2004). Laboratory investigation of the products of the incomplete combustion of waste plastics and techniques for their minimization. Industrial Engineering and Chemical Research 43, 2873-2886.

Weiden MD, Banauch G, Kelly KJ, Prezant DJ. (2007). Firefighters' health and health effects of the World Trade Center Collapse. In: Environmental and occupational medicine, fourth edition. WN Rom, SB Markowitz (eds). Lippincott, Williams and Wilkins, Philadelphia.

Westblad C, Levendis YA, Richter H, Howard JB, Carson J. (2002). A study on toxic organic emissions from batch combustion of styrene. Chemosphere, 49, 395-412.

Wichman, IS. (2003). Material flammability, combustion, toxicity and fire hazard in transportation. Progress in Energy and Combustion Science, 29, 247-299.

Wobst M, Wichmann H, Bahadir M. (1999). Surface contamination with PASH, PAH and PCDD/F after fire accidents in private residences. Chemosphere, 38, 1685-1691.

CHAPTER TWO

EXPERIMENTAL DESIGN

Introduction

The Queensland Fire and Rescue Service School of Fire and Rescue Service Training uses an air pollution control shed to contain the emissions from many of its training scenarios, and consequently reduce the impact of its training operations on neighbouring facilities. Rooms purpose-built for fire training scenarios were constructed within the shed in metal shipping containers mounted on concrete bases. These rooms were of dimensions 2.4 metres wide by 2.8 metres deep by 2.6 metres high, with three walls, ceiling and floor. The front wall space was open to the environment of the air pollution control shed.

Room Set-up

The room was furnished with contents typical of a residence including a single bed with mattress, free-standing wardrobe, single-seat recliner, desk, chair and television. Wall and ceiling materials were gyprock sheeting, and carpet was used as a floor covering. Five rooms were constructed and the contents were placed in the same relative positions in each room.

Figure 2.1 Typical furnished room.

Ventilation systems within the shed were operated during the first test, but not during the subsequent four tests. Where consecutive room fire tests were conducted on the same day, ventilation systems inside the emissions shed were used to purge the air inside the air pollution control shed for a minimum of one hour between tests.

Firefighters

Three instructors from the Queensland Fire and Rescue Service School of Fire and Rescue Service Training participated in each room fire test. Two instructors formed the entry team, with the third instructor as a safety supervisor. Each firefighter donned standard Queensland Fire and Rescue Service firefighting protective clothing. The structural firefighting ensemble (jacket and overtrousers) was constructed of an outer shell of Nomex IIIA, a moisture barrier consisting of a breathable polyurethane membrane, and thermal barrier of Sontara E89. Additional personal protective clothing included firefighting gloves, boots and flashhood. Self-contained breathing apparatus was worn for the duration of the test by the entry team and safety supervisor, with an anticipated protection factor of 10 000 (Joint Technical Committee SF-010, Occupational Respiratory Protection. 2009).

Active and passive sampling media were attached to the firefighter. Sampling occurred outside and inside the firefighting protective clothing. In addition, a swatch was attached to the outside the protective clothing and skin surrogate patches were attached directly to the skin of the firefighter. Information about the sampling approaches is in the subsequent sections.

Figure 2.2 Firefighter with sampling media attached.

Where consecutive room combustion scenarios were conducted on the same day, different sets of structural firefighting ensemble were worn by participants for each scenario. In addition, personnel showered between scenarios and changed all clothing (including undergarments) worn under the structural firefighting ensemble.

Room Burn

A total of five room burns were conducted. Ignition was caused using a propane torch applied to the mattress at the head of the bed. The fire was allowed to build up to flashover, at which time standard firefighting tactics were applied by the participants to obtain near-extinguishment. The fire was allowed to build up again to flashover and then extinguished. The average duration of the test was 16 (± 4) minutes. Water was used as the extinguishing agent. During the room fire, the participants remained below the neutral plane as much as possible, except when extinguishing smouldering items at the conclusion of the test.

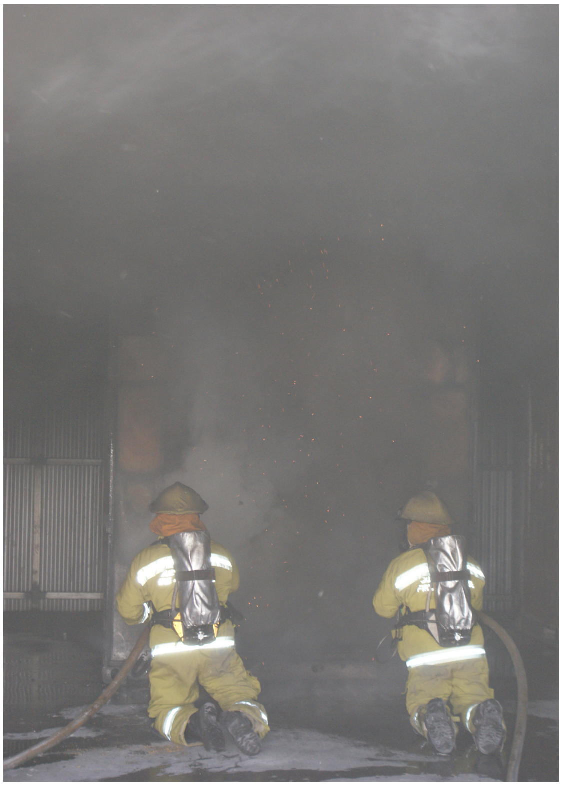

Figure 2.3 Example of approach adopted to extinguish the room burn.

Selection of sampling and analytical methods

Investigation of exposure of individuals to complex mixtures of gases, vapours and particulate matter is difficult, as the measurement of all components of mixtures is not possible for most mixtures of concern. Studies of health impacts of exposure to mixtures generally use a number of markers to represent exposure to the mixture as a whole. These may include chemical compounds, airborne particulates or metabolites in biological specimens. Ideal characteristics of markers for complex mixtures include being unique to the mixture's source, readily detectable at low concentrations, present in a consistent ratio to other components of the mixture, and measured easily and accurately at affordable cost (Leaderer et al., 1993).

In selecting the sampling and analytical methods used in this study, a number of factors were considered:

- ability of method to sample for one or more combustion products expected to be present in the room burn environment;
- prior use of sampling method in one or more studies of occupational exposure
- relevance of sampling method to firefighting environment or firefighter;
- existence of standard analytical method to quantify the sampled combustion product(s);
- local capability and accreditation to analyse samples using the standard analytical method;
- ability of the sampling media to sample concentrations of chemicals that are very high compared with normal environmental sampling levels;
- ability of the sampling media to be used for timeframes that are very short compared with normal environmental sampling timeframes;
- sensitivity and robustness of the analytical method to quantify the relevant combustion product(s) at expected concentration(s) (i.e. cope with very low or very high concentrations, as appropriate);
- resistance of the sampling media and ancillary equipment to the room burn environment (i.e. effect of heat and water on samples and equipment);
- potential for direct or indirect impact on the safety of study participants (e.g. by posing a hazard such as sharp glass edges, or by impeding action or movement);
- potential for influence on the actions or movements of study participants which may make their actions or movements differ from their normal actions or movements in a fire environment; and
- compatibility of sampling methods with other sampling methods (i.e. that one sample or sampling method does not block or otherwise impede another simultaneous sample or sampling method.

Since the purpose of this project was to quantify the exposures of firefighters to combustion products while undertaking a specific activity (individual room burn), sampling methods were restricted to air and surface sampling techniques. Biological sampling and analysis techniques (e.g. 1-hydroxypyrene in urine) were not used, as they are suited to measurement of occupational exposure during a full work day or longer work cycle (Jongeneelen et al., 1990). The sampling and analytical methods selected for this project are outlined in Sections 3.3 and 3.4 respectively. A full list of chemical compounds for which sampling was undertaken, by sampling method, appears in Appendix 1.

Sampling and Analytical methods

General information

Sampling of air contaminants and surface deposition was conducted on one of the two firefighters in each room fire. With the exception of the whole air samples (see below), sample collection began at donning of personal protective equipment in a fresh air environment, and ended at the instructors' return to the fresh air environment for doffing of personal protection equipment. After collection, all samples were refrigerated for transport to the laboratory for analysis, and transport blanks were included for all types of sample for all batches.

Active air sampling

Active air sampling during each room fire was conducted both inside and outside the structural firefighting ensemble of the firefighter. For active air sampling, air flow rates through the sampling tubes were measured before and after sample collection using a Dry Cal DC-Lite Primary Flow Meter (Bios International Corporation) to ensure consistency. All active air sampling using sampling tubes occurred with the tubes vertically oriented to prevent channelling effects.

In order to reduce the encumbrance associated with sampling equipment, sampling for volatile organic compounds, carbonyl compounds, acid gases and hydrogen cyanide was conducted using a single air sampling pump (SKC AirChek 2000) connected to a four-way manifold designed to hold four separate sampling tubes. Individual air flow rates for each sampling tube were obtained by adjustment of screw-type mechanisms at the base of the manifold. The sampling tube-manifold assembly was taped to a cardboard backing to prevent injury from sharp glass edges. The internal sampling tube was attached by clip to the shoulder braces of the ensemble overtrousers at chest height, while the external tube was attached to the harness of the self-contained breathing apparatus at chest height. Sampling pumps were carried in the pockets of the structural firefighting ensemble jacket, and attached to the sampling manifold by Tygon tubing. Care was taken to ensure that the outer set of sampling equipment did not impede flow of air through to the inner set of sampling equipment.

Volatile organic compounds

Tenax/Carboxen 569 tubes were supplied by Queensland Health Forensic Scientific Services Investigative Chemistry section for the purpose of sampling volatile organic compounds (VOC). These consist of a stainless steel tube containing 150 mg of Tenax followed by 100 mg of Carboxen 569. One µL of an internal standard consisting of six deuterated compounds (dichloroethane, benzene, toluene, styrene, dichlorobenzene and naphthalene) was used to pre-spike the Tenax/Carboxen 569 tubes. Air was drawn through the Tenax/Carboxen 569 tubes at a rate of approximately 200 mL/min. The VOC samples were analysed according to the established Queensland Health Forensic and Scientific Services Method using the principles of United States Environmental Protection Agency Compendium Method TO-17 (Center for Environmental Research Information, 1999). VOCs were thermally desorbed from the tubes and analysed by Gas Chromatography- Mass Spectrometry (GC-MS). The Limit of Reporting (LOR) for individual VOCs was typically 50 ng per tube.

Carbonyl compounds

Carbonyl compounds (aldehydes and ketones) were sampled using glass sorbent tubes packed with 2,4-dinitrophenylhydrazine-coated silica gel (SKC Inc). Sorbent in these tubes is in two separate sections (300 mg / 150 mg) to permit testing for breakthrough. The tubes also incorporate a built-in ozone scrubber (potassium chloride). Air flow rates through these tubes were set to approximately 500 mL/min. Samples were solvent-extracted from the tubes and analysed using High Performance Liquid Chromatography (HPLC) according to the established Queensland Health Forensic and Scientific Services Method using the principles of United States Environmental Protection Agency Compendium Method TO-11A (Center for Environmental Research Information, 1999). The LOR for individual carbonyl compounds ranged from 0.3 to 1 µg per tube.

Silica gel

Sampling for acid gases (fluoride, chloride, bromide, nitrate, phosphate and sulfate) was achieved using glass sorbent tubes packed with two sections of silica gel (400/200 mg) (SKC Inc). Air was drawn through the silica gel sorbent tubes at approximately 200 mL/min. Samples were analysed by Queensland Health Forensic and Scientific Services using the principles of NIOSH Method 7903 (National Institute for Occupational Safety and Health, 1994). The LOR were 0.5 µg/tube for fluorides, chlorides and nitrates, 1 µg/tube for bromides, and 2.5 µg/tube for phosphates and sulfates.

Hydrogen cyanide

Hydrogen cyanide was sampled using glass sorbent tubes packed with soda lime were also used to collect air samples. These tubes have two sections, packed with 600 mg and 200 mg of soda lime respectively (SKC Inc). Air flow rates for the soda lime sorbent tubes were set to approximately 150 mL/min. Samples were extracted into water and analysed by Queensland Health Forensic and Scientific Services using the principles of NIOSH Method 6010 (National Institute for Occupational Safety and Health, 1994). The limit of reporting was 0.5 µg/tube of hydrogen cyanide.

Polycyclic aromatic hydrocarbons (PAH)

Sampling of polycyclic aromatic hydrocarbons inside and outside the structural firefighting ensemble was achieved using glass tubes filled with 76 mm of polyurethane foam (PUF tubes) with glass fibre pre-filter (SKC Inc). As with the other active personal samples, sampling occurred both inside and outside the firefighting protective clothing. External sampling tubes were attached to the self-contained breathing apparatus harness at chest height (on the opposite side to the four-way manifold), while the internal sampling tubes were attached to the shoulder braces of the structural firefighting ensemble trousers, also at chest height. For both internal and external sampling tubes, a protective casing prevented damage to the sampling tube during the room burn but which did not impede the flow of air into the tube. Air was drawn into each of the sampling tubes at a rate of approximately 2 litres per minute using AirChek 2000 sampling pumps. Sampling pumps were carried in the pockets of the structural firefighting ensemble overtrousers, with Tygon tubing used to connect the pumps to the sampling tubes.

The PAH samples were analysed by Queensland Health Forensic and Scientific Services using the principles of the United States Environmental Protection Agency Compendium Method TO-13A (Center for Environmental Research Information, 1999). The glass fibre and PUF sections were extracted separately using Accelerated Solvent Extraction (ASE) on a Dionex ASE100 using cyclohexane as the extracting solvent. The ASE conditions were:

Cell size: 34mL
Temperature: 100°C
Static Time: 5 min
Flush Volume: 60%
Purge Time: 250 s
Static Cycles: 3

The extracting solvent was concentrated using Kuderna-Danish apparatus on a heated water bath. The final 1mL volume was analysed using GCMS. The limit of reporting for analysis was 50 ng/sample for individual PAHs in each of the vapour and particulate phases.

Whole air

Whole air samples were collected during each room fire using SilcoCans supplied by the Investigative Chemistry Section of Queensland Health Scientific Services. These canisters have 6 litre air capacity, a ¼ turn valve with locking pin to prevent accidental opening during transport, and a layer of fused silica as an inert lining to prevent reaction during storage between sample components and the sample container. A regulator was used to regulate the volume of air entering the canister per minute, so that the air sample was collected over the full duration of the room fire. Sample collection began just prior to ignition of the fire in the room, and ended on extinguishment as the instructors prepared to leave the room fire environment. For analysis, VOCs were collected in syringes from the canisters and analysed by GC-MS spectrometry. The VOC samples were analysed according to the established Queensland Health Forensic and Scientific Services Method using the principles of US EPA method TO-17. The limit of reporting for individual VOCs was typically 3-5 parts per billion (ppb).

Passive air sampling

In addition to active air sampling for volatile organic compounds and carbonyl compounds, passive sampling devices for these groups of chemicals were also fitted to the firefighter during the room fire tests. Volatile organic compounds were sampled passively using Supelco stainless steel tubes packed with Tenax. These were fitted with diffusion caps and attached to the same cardboard backing as the four-way manifold holding the other sorbent tubes. Passive sampling badges (UMEx 100, SKC Inc) were used to sample carbonyl compounds; badges were attached to the self-contained breathing apparatus harness in the breathing zone of the firefighter. Analysis of passive samples for VOCs and carbonyl compounds were conducted in the same manner as for the corresponding active samples.

Surface deposition

Swatches

Deposition of polycyclic aromatic hydrocarbons on the structural firefighting ensemble was sampled by attaching a 10cm x 10 cm swatch of Nomex IIIA fabric to the front of the ensemble. The swatch was pinned on the outside of the protective clothing on the opposite side of the torso to the PUF/glass fibre filter tube, at the same height. At the conclusion of each room fire, the swatches were removed by the attachment pins with minimal handling and placed in individual sealed polythene bags. The analytical method for these samples was identical to that used for the glass fibre/PUF tubes as described above.

Surrogate Skin Patches

Dermal patches for sampling skin deposition of polycyclic aromatic hydrocarbons were constructed using the method described by Jongeneelen et al. (1988). Polypropylene filter membranes of diameter 47 mm and pore size 0.1µm (Pall Corporation) were stapled to squares of double thickness aluminium foil (70 mm x 70 mm). These were attached to the skin of the instructor on the upper right outer forearm (avoiding the area covered by the firefighting glove cuff), centre chest and lower left outer thigh using adhesive tape applied around the perimeter of the aluminium foil. At the conclusion of each room fire, the patches were removed by the adhesive tape with minimal handling and folded inwards into quarters. They were then wrapped in aluminium foil and placed in individual sealed polythene bags.

The PAH samples were analysed by Queensland Health Forensic and Scientific Services using the principles of the United States Environmental Protection Agency Compendium Method TO-13A (Center for Environmental Research Information, 1999). Due to the lower expected concentration of PAHs on the dermal patches, analysis of these samples differed slightly from that used for the glass fibre/PUF tubes and swatches. Prior to extraction the samples were spiked with a deuterated PAH mixture (1 ng/µL) corresponding to the PAHs of interest. Final volume for GCMS analysis was 200 µL, and quantification was achieved using a ratio of d-PAH:PAH in an external calibration curve.

References

Center for Environmental Research Information. (1999). Compendium Method TO-11A: Determination of formaldehyde in ambient air using adsorbent cartridge followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]. In: Compendium of methods for the determination of toxic organic compounds in ambient air, Second Edition. United States Environmental Protection Agency, Cincinnati.

Center for Environmental Research Information. (1999). Compendium Method TO-13A: Determination of polycyclic aromatic hydrocarbons in ambient air using gas chromatography /mass spectrometry (GC/MS). In: Compendium of methods for the determination of toxic organic compounds in ambient air, Second Edition. United States Environmental Protection Agency, Cincinnati.

Center for Environmental Research Information. (1999). Compendium Method TO-17: Determination of Volatile Organic Compounds in ambient air using active sampling onto sorbent tubes. In: Compendium of methods for the determination of toxic organic compounds in ambient air, Second Edition. United States Environmental Protection Agency, Cincinnati.

Joint Technical Committee SF-010, Occupational Respiratory Protection. (2009). AS/NZS 1715:2009 Selection, use and maintenance of respiratory protective equipment. Standards Australia, Sydney.

Jongeneelen FJ, Scheepers PTJ, Groenendijk A, van Aerts LAGJM, Anzion RBM, Bos RP, Veenstra SJ. (1988). Airborne concentrations, skin contamination, and urinary metabolite excretion of polycyclic aromatic hydrocarbons among paving workers exposed to coal tar derived road tars. American Industrial Hygiene Association Journal, 49, 600–607.

Jongeneelen FJ, van Leeuwen FE, Oosterink S, Anzio RBM, van der Loop F, Bos RP, van Veen HG (1990). Ambient and biological monitoring of cokeoven workers: determinants of the internal dose of polycyclic aromatic hydrocarbons. British Journal of Industrial Medicine, 47, 454-461.

Leaderer BP, Lioy PJ, Spengler JD. (2003). Assessing exposures to inhaled complex mixtures. Environmental Health Perspectives Supplements, 101, 167-177.

National Institute for Occupational Safety and Health. (1994). NIOSH Manual of Analytical Methods (NMAM). Fourth Edition. http://www.cdc.gov/niosh/docs/2003-154/, accessed 11 February, 2010.

CHAPTER THREE

EXPOSURE OF FIREFIGHTERS TO AIRBORNE POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

The results described in this chapter address characterising the exposure of firefighters to a variety of airborne polycyclic aromatic hydrocarbon (PAH) contaminants generated during a fire. It is known there are 660 different PAHs (McKenzie, 2007) and the 18 PAHs listed by the US Environmental Protection Agency (United States Environmental Protection Agency, 1993) were considered in this study because of their toxicity. This chapter focuses on establishing the concentration and distribution of PAHs firefighters were exposed to outside and inside their protective clothing during extinguishment.

Outside Protective Clothing

The results describing the concentration and distribution of PAHs outside the protective clothing as a function of burn are shown in Table 3.1. The graph of the gas phase PAH distribution and concentration as a function of burn is shown in Figure 3.1.

Seven PAHs were identified in the gas phase during the burns. They were:

- naphthalene;
- acenaphthylene;
- phenanthrene;
- pyrene;
- fluorene;
- anthracene; and
- fluoranthene.

These PAHs are two, three and four aromatic ring molecules. Dills and Beaudreau (2008) reported two- and three-membered aromatic ring PAHs are common products during combustion of room furnishings, while four-membered aromatic ring PAHs were the favoured combustion products in overhaul smoke after extinguishing agents were applied.

Naphthalene was by far the PAH to which firefighters were exposed at the greatest concentrations. The average naphthalene concentration was 42,920 ng/m^3, much greater than the average concentration of any other PAH in the gas phase. The highest naphthalene concentration measured was below the established Australian National Exposure Standard (NES) (10 ppm) (Worksafe Australia, 1995), and less than the equivalent United States exposure standard. It was also less than the established odour threshold (0.038 ppm) (Nagata, 2010).

The firefighter exposure to naphthalene measured in this study and the few firefighter exposures reported in the literature (Aust et al., 2007; Jankovic et al., 1991; Feunekes et al., 1997) are significantly greater than the firefighter exposures reported during wildfires (Reh et al., 1994; Booze et al., 2004) and reflect the different operational environments and activities.

Table 3.1 Concentration of polycyclic aromatic hydrocarbons as a function of burn outside protective clothing

	External gas-phase (ng/m^3)					External particulate phase (ng/m^3)				
PAH	Burn One	Burn Two	Burn Three	Burn Four	Burn Five	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Naphthalene	**7600**	**26000**	**52000**	**40000**	**89000**	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthylene	**3700**	**9000**	**15000**	**9100**	**27000**	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Fluorene	**1600**	**3100**	**3600**	**2700**	**6900**	< LOR	< LOR	< LOR	< LOR	< LOR
Phenanthrene	**5500**	**8800**	**9500**	**9400**	**24000**	< LOR	< LOR	< LOR	< LOR	< LOR
Anthracene	< LOR	< LOR	**2000**	**2400**	**6200**	< LOR	< LOR	< LOR	< LOR	< LOR
Fluoranthene	**1900**	**3000**	**3300**	**5900**	**12000**	< LOR	< LOR	< LOR	< LOR	**1600**
Pyrene	**2400**	**3700**	**3900**	**5600**	**13000**	< LOR	< LOR	< LOR	< LOR	**2200**
Benz[a]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**4300**
Chrysene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**2100**	**4100**
Benzo[b+k]fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**3000**	**7300**
Perylene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[a]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**2500**	**5900**
Benzo[e]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**3000**
Indeno[1,2,3-cd]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**3000**
Dibenz[a,h]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[ghi]perylene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**3400**
Coronene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR

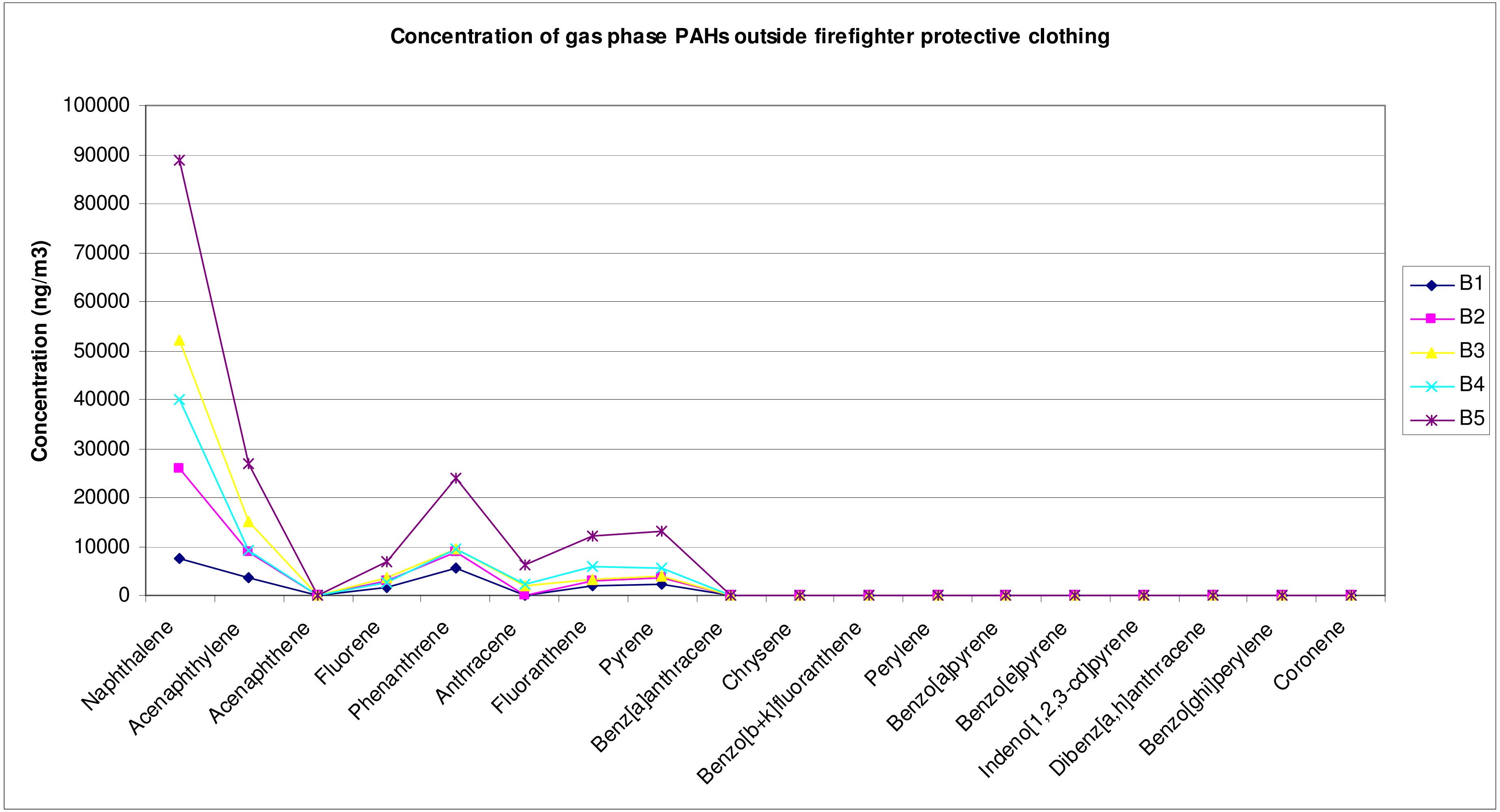

Figure 3.1 Type of PAH and gas phase concentration outside firefighter protective clothing for each burn.

The firefighter exposure to naphthalene measured in this study and the few firefighter exposures reported in the literature (Aust et al., 2007; Jankovic et al., 1991; Feunekes et al., 1997) are significantly greater than the firefighter exposures reported during wildfires (Reh et al., 1994; Booze et al., 2004) and reflect the different operational environments and activities.

The average concentration of other individual PAHs measured ranged from 2,120 ng/m^3 to 12,700 ng/m^3 and individually there was much variance across the burns. These values are also within the range reported in the literature concerning firefighter exposure and PAH formation in smoke. However, they are less than the maximum concentrations reported (Aust et al., 2007; Laitinen et al,. 2010; Jankovic et al., 1991; Bolstad-Johnson et al., 2000; Dills and Beaudreau, 2008).

The graph describing the relative concentration of the PAHs is shown in Figure 3.2. The naphthalene proportion of the total gas phase PAH ranged from 33.5% to 58.6%. Similar PAH distributions have been reported in other published data (Blomqvist, 2004, 2005; Jankovic et al., 1991), although Feunekes et al. (1997) found these other PAHs were collectively at higher concentrations than naphthalene during their firefighter exposures studies at a training school. These results demonstrate the complex and often contradictory nature of fire smoke and firefighter exposure.

The dominance of naphthalene in the overall airborne PAH profile of exposed workers is not confined to firefighters. Unwin et al. (2006) reported naphthalene dominated the airborne PAH profile of all work sites where they investigated workers exposures in the United Kingdom. Typically, naphthalene accounted for 50 % to 90% of the total PAHs measured.

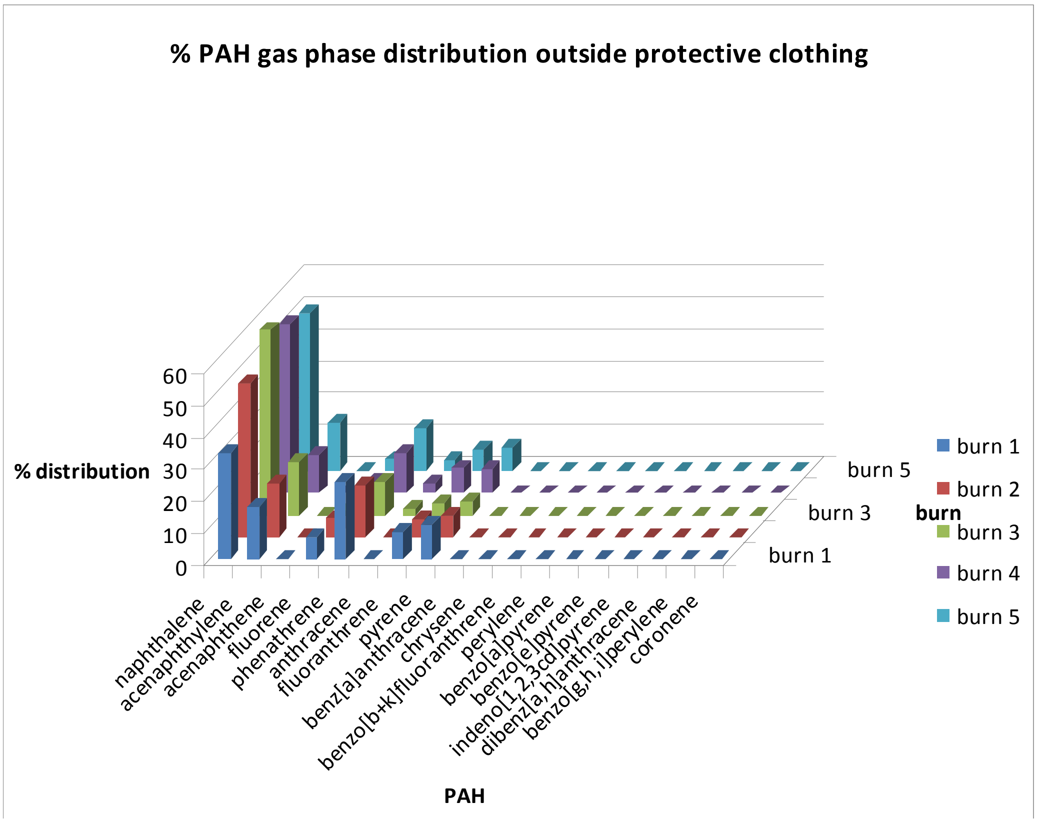

Figure 3.2 Percentage distribution of gas-phase PAH outside protective clothing as a function of burn

Airborne PAHs in the particulate phase were only identified in three out of the five burns, as shown in Table 3.1. The airborne particulate PAHs identified were:

- benzo[b+k]fluoranthene;
- benzo[a]pyrene;
- benz[a]anthracene;
- chrysene;
- benzo[e]pyrene;
- indeno[1,2,3cd]pyrene;
- pyrene; and
- fluoranthene

The graph describing the concentration of each of these as a function of PAH is shown in Figure 3.3. In general, the concentration of the majority of airborne particulate PAHs was less than the Limit of Reporting (LOR). The type and concentration of the PAHs detected varied between the two burns. The highest concentration and greatest variety of airborne particulate PAHs occurred when the highest PAH gas-phase concentration occurred.

Benzo[b+k]fluoranthrene was the PAH present in the greatest concentration in the particulate phase, with an average concentration of 2,060 ng/m^3. The average concentration of the individual PAHs measured ranged from 320 ng/m^3 to 1,680 ng/m^3. The average concentrations are much less than the average concentrations of the gas phase PAHs measured. These average values and peak values were also much less than the Australian NES values and the respective odour thresholds where they have been established (Worksafe Australia, 1995; Nagata, 2010).

It is noteworthy that benzo[a]pyrene was measured in the particulate phase and the gas phase. Other studies have reported benzo[a]pyrene is a common but minor combustion product. Feunekes et al (1997) suggested the firefighter benzo[a]pyrene exposures measured in their study were less than for workers in many other industries. Unwin et al. (2006) reported the median airborne benzo[a]pyrene exposure of workers in many UK workplaces was 10 ng/m^3 over 8 hours. They also reported more than 90% of workers were exposed to less than 750 ng/m^3. Clearly, the benzo[a]pyrene exposure varies significantly across industries, and the results in this study demonstrate the peak values obtained correspond to the most exposed worker groups reported by Unwin et al. and others. (Unwin et al., 2006; Deutsche Forschungsgemeinschaft, 2004; Jongeneelen et al, 1990; Van Rooij et al., 1993a, 1993b, 1994). The significance of this result from an exposures perspective is mitigated by the fact the firefighters don respiratory protection where the assigned SCBA protection factor is 10,000 (Occupational Safety and Health Administration, 2006) and operationally up to approximately 500,000 (Denhartog, 2009).

The pyrene/benzo[a]pyrene ratio has been used as a marker to illustrate worker exposure (Van Rooij et al., 1993a). In this study pyrene/benzo[a]pyrene ratio where it can be estimated varies from 2.4 to 2.6. However, other studies show in a firefighting context the pyrene/benzo[a]pyrene ratio varies significantly (Feunekes et al., 1997, Jankovic et al., 1991). Consequently, it is not clear the use of the ratio can be justified as a marker to illustrate firefighter exposure when the reported ratio in smoke varies so widely.

Coronene, dibenz[a,h]anthracene, and perylene were not detected and their concentrations were below the LOR in all burns. Several other PAHs typically identified in the gas phase in the burns were not detected in the particulate phase in any burn. These PAHs included:

- naphthalene;
- acenaphthylene;
- acenaphthene;
- phenanthrene;
- fluorene; and
- anthracene.

These PAHs are the lower molecular weight PAHs which are more likely to be found in the vapour phase (McKenzie, 2007). Jankovic et al. (1991) reported only acenaphthene, phenanthrene and anthracene were present both in the particle and vapour phase. As the PAH molecular weight exceeded 228 g/mol, more than 88% of the total PAH were particulates. Nonetheless, the contribution of the particulate PAHs to the total PAH concentration is significantly less than the contribution of gas-phase PAHs.

The data demonstrates that despite adopting similar approaches to set the burns and extinguish the simulated fires, firefighter exposure does vary. The firefighter exposure reflects the complex nature of the fire environment and consequently the variable gas-phase PAH product concentration and distribution. Similar observations about variability of product concentration and distribution were also reported in other published firefighter exposure and smoke investigations (Aust et al., 2007; Laitinen et al., 2010; Gold et al., 1978). The complex nature and behaviour of the fire combined with differences in the firefighting practices across the globe readily explains the observations reported in the literature.

Inside Protective Clothing

The results describing the concentration and distribution of PAHs inside the protective clothing as a function of burn are shown in Table 3.2. The graph showing the gas-phase PAH distribution and concentration inside the protective clothing for each burn is in Figure 3.4.

The results demonstrate clearly the concentration of the PAHs and the product distribution changed significantly on passing through the protective clothing. Individually, the results also exhibited significant variance between burns. Seven PAHs were measured outside the protective clothing, while only five PAHs were identified inside the protective clothing in the gas phase. They were:

- naphthalene;
- acenaphthylene;
- phenanthrene;
- pyrene; and
- fluoranthene.

These five PAHs were also the highest concentration of the airborne gas-phase PAHs measured outside the protective clothing. The most common PAH inside the protective clothing was naphthalene and reflects the fact it was the highest concentration PAH outside. The peak concentration was much lower than the peak outside concentration and the average value was less than 13% of the outside value.

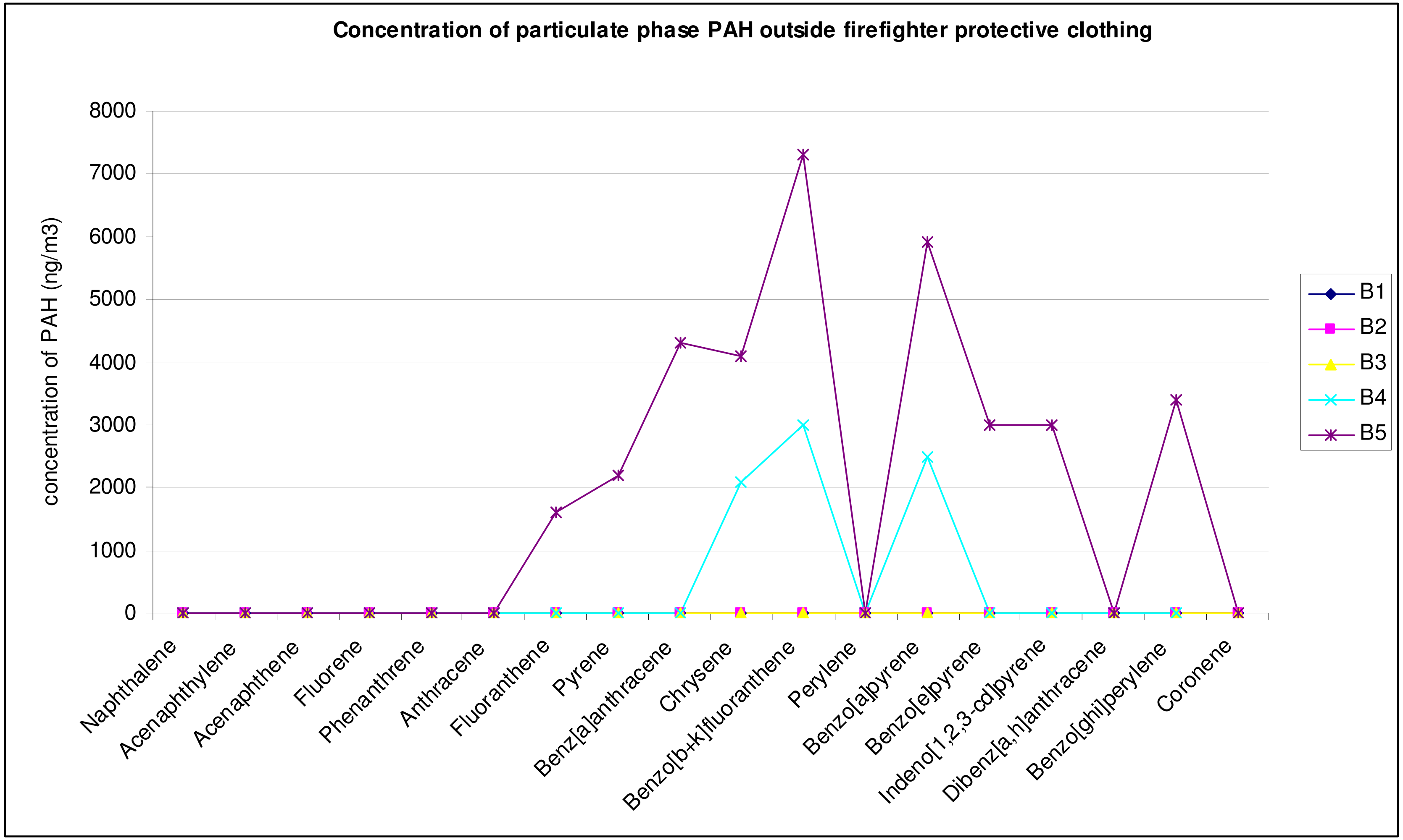

Figure 3.3 Concentration of particulate PAH in breathing zone outside firefighter protective clothing as a function of PAH.

The relative proportion of naphthalene inside ranged from 0 % to 100% of the PAHs. For the occasion where naphthalene was not detected, phenanthrene accounted for 100 % of the PAHs inside the protective clothing.

The peak concentration of the other PAHs was much lower than the peak outside concentrations. The average values were also much lower inside and ranged from 2% to 10 % of the average outside concentration.PAHs not measured in the gas phase outside the protective clothing were also not measured inside the protective clothing.

The concentration of particulate phase PAH as a function of burn inside the firefighter protective clothing is shown in Table 3.2. The graph of the particulate phase PAH results are shown in Figure 3.6.

The results demonstrate clearly the concentration of the PAHs and the product distribution changed significantly. Whilst eight PAHs were identified outside the protective clothing only two PAHs were identified inside the protective clothing in the particulate phase. They were:

- benzo[a]pyrene; and
- benzo[b+k]fluoranthrene.

More significantly, these two PAHs were detected only during a single burn. It is noteworthy benzo[a]pyrene was measured inside the protective clothing. These two PAHs were also the highest concentration particulate PAHs measured outside the protective clothing. For the burn for which these two PAHs were detected in the particulate phase inside the protective clothing (Burn 5), the benzo[a]pyrene and benzo[b+k]fluoranthene concentrations were respectively 66% and 74% lower than the corresponding outside concentrations. These trends were also observed with the gas phase PAHs inside the protective clothing.

In a workplace environment there is little data available concerning the penetration of naphthalene vapours and other PAHs into workers' clothing. Recently, Laitinen et al. (2010) reported PAH were deposited onto the skin of firefighters during simulated fire activities, but they did not report any information about the PAH concentrations inside the protective clothing. However, studies have been conducted addressing the penetration of other chemicals into workers' clothing (Stamper et al., 1989; Van Rooij et al., 1993a; Ness, 1994). Stamper et al. (1989) and Ness (1994) reported the concentration of airborne contaminants is often much less inside the workers' protective garments (35 %-99% reductions). Many of these studies focused on clothing such as Tyvek® coveralls, and working environments ranging from pesticide application to coke ovens (Ness, 1994; Van Rooij et al., 1993a).

Investigations into firefighter protective clothing have focused on the thermal performance of firefighter protective clothing (Zhiying et al., 2010; National Fire Protection Association, 2008; National Fire Protection Association, 2007; Lawson, 1996). The performance of protective clothing against water vapour has also been investigated (Barker 2006). There are two accepted firefighter protective clothing standards providing guidance about protection against chemicals. They are: European Standard EN 469 Protective clothing - Requirements for firefighters' protective clothing (European Committee For Standardization, 2006), and National Fire Protection Association Standard NFPA 1971 Standard on Protective Ensembles

Table 3.2 Concentration of polycyclic aromatic hydrocarbons (PAH) inside protective clothing as a function of burn

	Internal gas-phase (ng/m^3)					Internal particulate-phase (ng/m^3)				
PAH	Burn One	Burn Two	Burn Three	Burn Four	Burn Five	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Naphthalene	**3900**	< LOR	**5200**	**8000**	**10000**	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthylene	< LOR	< LOR	< LOR	< LOR	**1700**	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Fluorene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Phenanthrene	< LOR	**3100**	< LOR	< LOR	**2600**	< LOR	< LOR	< LOR	< LOR	< LOR
Anthracene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Fluoranthene	< LOR	< LOR	< LOR	< LOR	**2000**	< LOR	< LOR	< LOR	< LOR	< LOR
Pyrene	< LOR	< LOR	< LOR	< LOR	**2300**	< LOR	< LOR	< LOR	< LOR	< LOR
Benz[a]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Chrysene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[b+k]fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**1900**
Perylene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[a]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	**2000**
Benzo[e]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Indeno[1,2,3-cd]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Dibenz[a,h]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[ghi]perylene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Coronene	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR

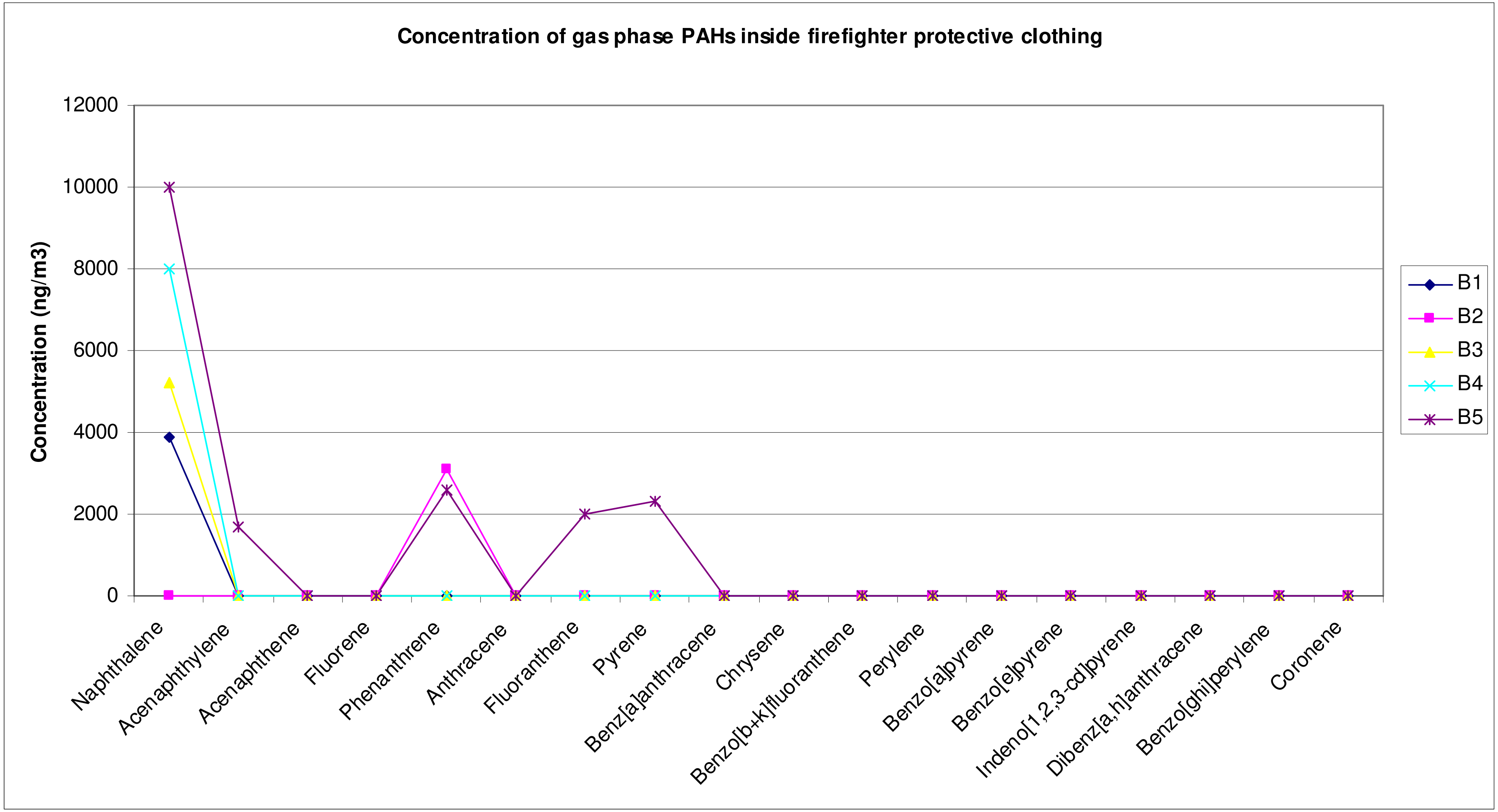

Figure 3.4 Concentration and distribution of airborne gas phase PAH inside firefighter protective clothing as a function of burn.

for Structural Fire Fighting and Proximity Fire Fighting (NFPA, 2007). They generally address protection against direct contact of four or five liquid chemicals. If the garment is “CBRN rated” within the US approach a further five liquids, chlorine and ammonia are tested. Importantly, there is no requirement to consider the penetration of PAHs or other airborne contaminants commonly found within smoke within these standards.

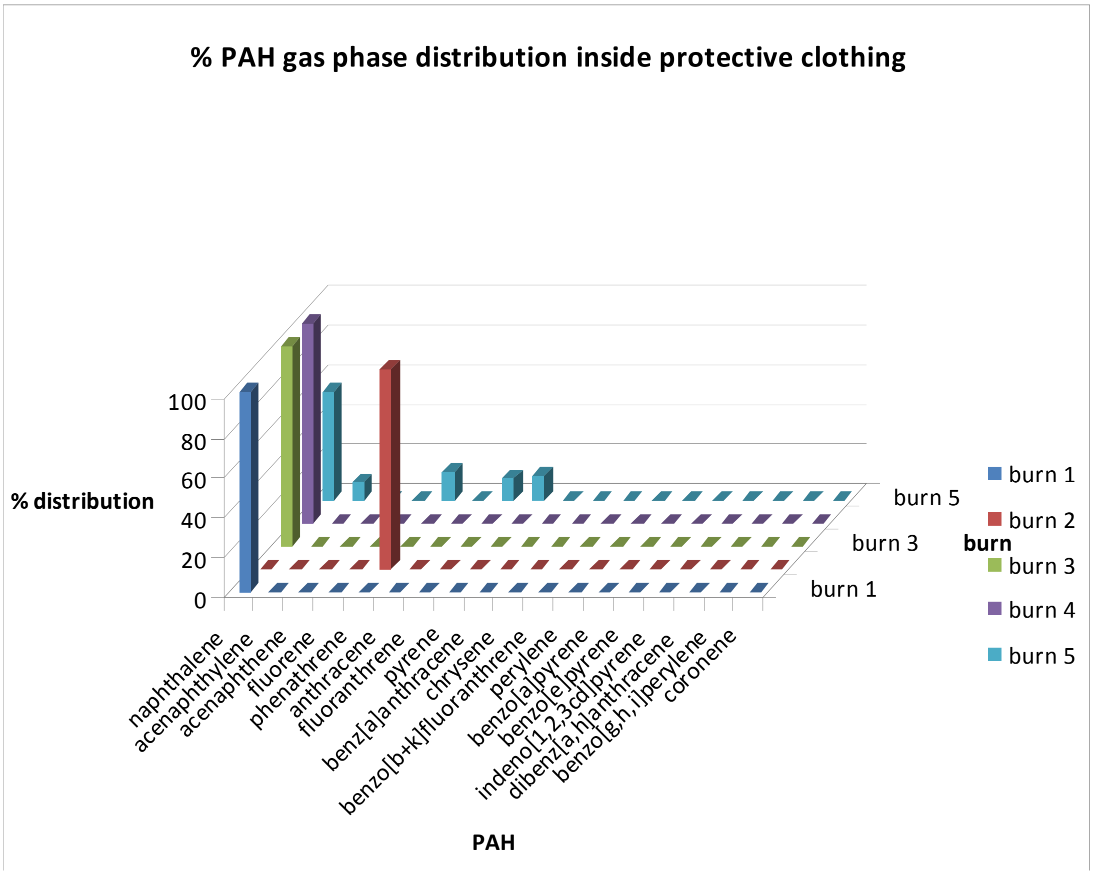

Figure 3.5 Relative distribution of gas phase PAH inside the protective clothing as a function of burn.

There are many alternative approaches to describing the results in terms of potential toxicity (EPA, 1984; Nisbet and LaGoy, 1992). Lin et al. (2008) suggested the approach reported by Nisbet and LaGoy (1992) best described the actual toxic potency of the individual PAH species. They equated the total PAH concentration to an equivalent benzo[a]pyrene concentration, called a Toxic Equivalency Factor (TEF).

The Toxic Equivalency Factors have been determined for these results using the method of Nisbet and LaGoy (1992). The value calculated for outside the protective clothing across the burns varies from 0.0243 to 7.6727 µg/m^3, with an average value of 2.155 µg/m^3. Only two values were greater than 1 µg/m^3. In contrast, the value obtained for inside the protective clothing across the burns varies from 0.0031 to 2.2086 µg/m^3, with an average value is 0.446 µg/m^3. Only one value obtained was greater than 1 µg/m^3. There was a 79% decrease between the average value obtained outside the protective clothing and the average value inside the protective clothing. The difference is similar to the values obtained when the total PAH concentrations are compared.

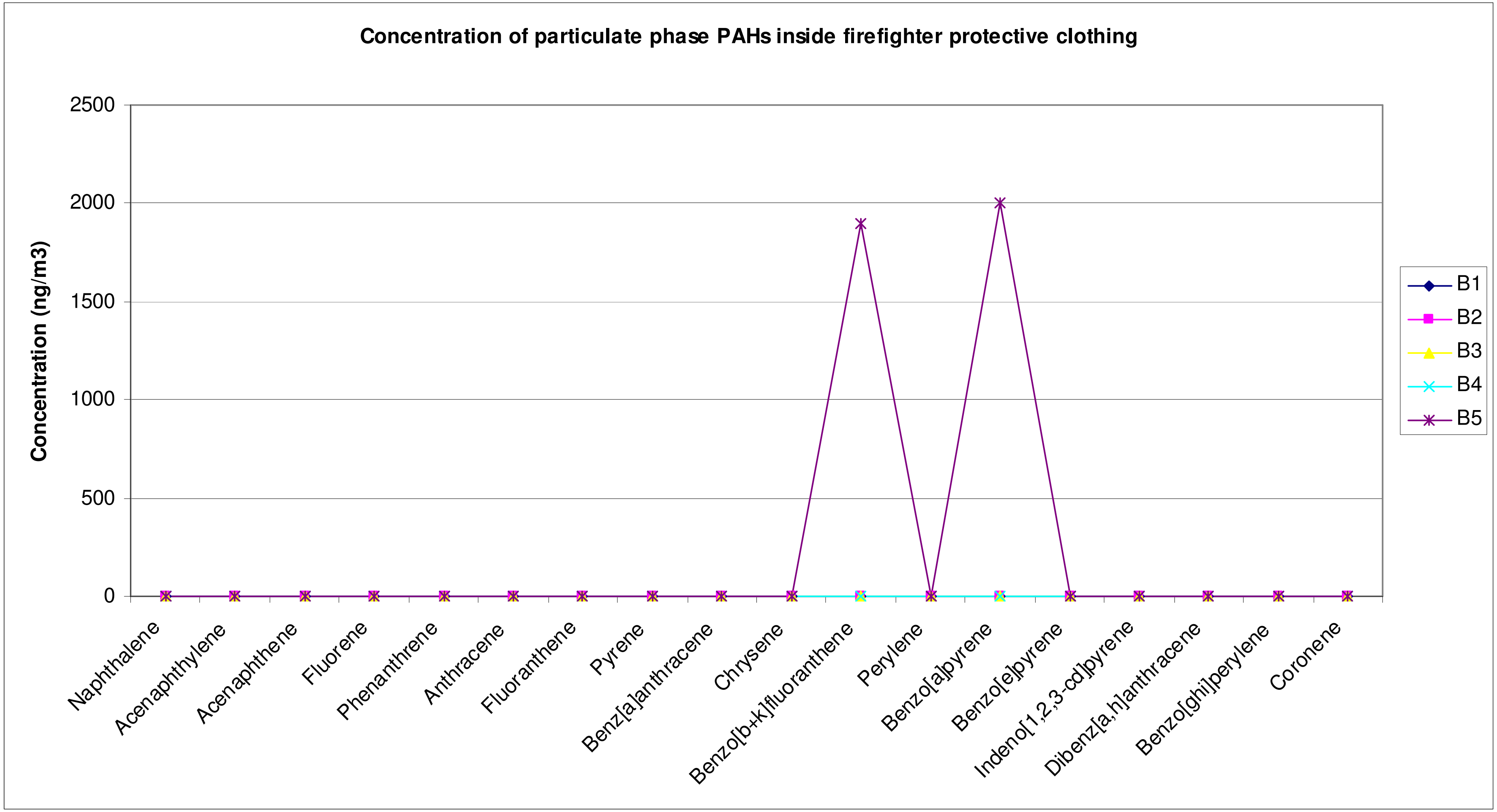

Figure 3.6 Concentration and distribution of airborne particulate PAH inside firefighter protective clothing as a function of burn.

The concentrations of total PAHs outside and inside the protective clothing as a function of burn are shown in Figure 3.7. The data in the graph shows the total PAH concentration outside the firefighters' protective clothing ranged from 22,700 ng/m^3 to 212,900 ng/m^3. The values obtained outside the protective clothing are significantly higher than reported by Lin and others for workers at a sinter plant and other similar industries with known exposures to airborne PAHs (Aries et al. 2008; Lin et al. 2008; Petry 1996; Tsai et al., 2001).

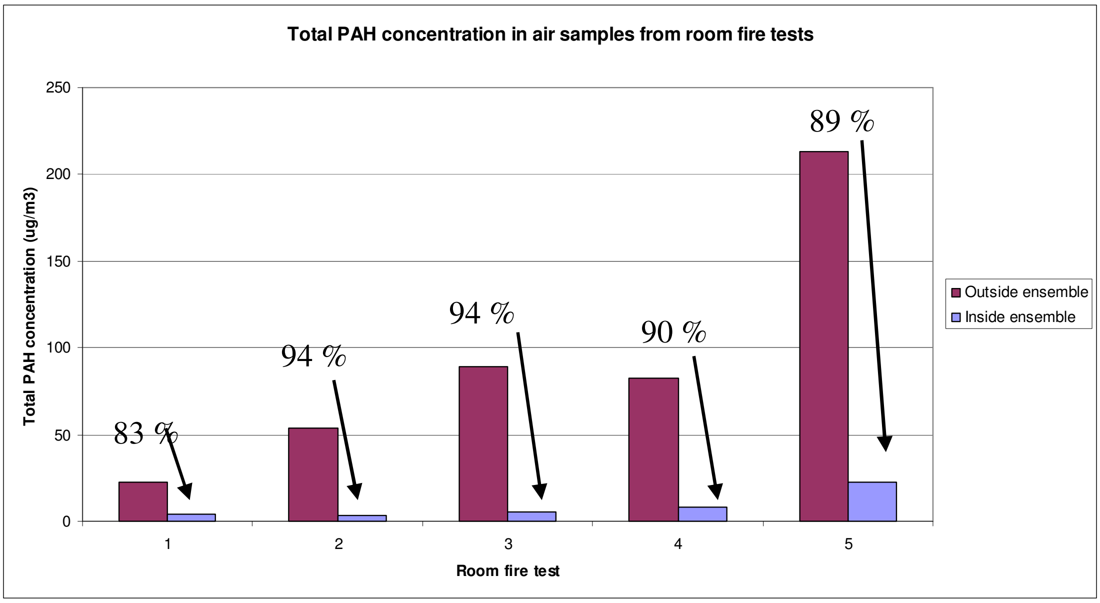

Figure 3.7 Concentration of total PAHs outside and inside the protective clothing as a function of burn, showing percentage reduction in concentration inside versus outside

Summary

The overall results show clearly the firefighters were exposed to PAHs outside their protective clothing. Individual PAH concentrations were much less than their respective exposure standards (NES) values where they have been established.

The results show significant variation between the burns, despite the similar fuels, fuel arrangements, and tactics applied to extinguish the fires. The observed variability illustrates the complexity of the interactions between the burning materials, fire behaviour, combustion product formation, temporal elements, firefighter activities and hence exposure. These striking variations are also reported in the literature concerning the PAH concentration in smoke, and measured firefighter exposures.

The results also demonstrate the firefighter PAH exposure is within the range of firefighter PAH exposures reported in the literature (Jankovic, 1991; Aust et al., 2007; Laitinen et al., 2010), which also exhibited significant variance. The results are also within the ranges reported by Unwin et al. (2006) for a variety of occupations. They found the total 8 hr PAH exposure varied from 80 ng/m^3 to 1,912,000 ng/m^3 and the geometric mean was 15,800 ng/m^3 across workers in a variety of UK work sites. However, the firefighter exposures were incurred in less than 20 minutes as opposed to an 8 hr day. After extrapolating the highest firefighter exposure to an equivalent 8 hr exposure it is clear their exposure is approximately 2.7 times higher than the highest exposure reported by Unwin et al. (2006).

Consequently, it is clear firefighters must manage and minimise their exposures to airborne PAHs during their activities. An obvious approach to reduce respiratory exposure is to ensure self contained breathing apparatus (SCBA) is donned.

The overall results also show clearly firefighters are exposed to PAHs inside their protective clothing. The individual PAH concentrations are much less than their respective NES values where they have been established. The data shows the total PAH concentration inside the protective clothing is 83% to 94% less than the outside PAH concentration. Similar differences have been observed in unpublished QFRS studies. Whilst individual PAH concentration deceases inside the protective clothing varied the observations applied equally to both gas-phase and particulate-phase PAHs.

The result is of great significance from two perspectives. Firstly; PAHs have been detected inside the protective clothing and secondly, the PAH concentration inside the protective clothing is significantly less than the outside concentration. Van Rooij et al. and others (van Rooij et al., 1993a, 1993b; Jongelneelen et al., 1990) have reported the skin is a significant entry route for workers exposed to airborne PAHs. The importance of this route varied but in some cases the proportion of the total dose was up to 95% for pyrenes (Van Rooij et al., 1993a). These conclusions are of great importance and can be considered to apply directly to firefighters. As discussed previously, the great majority of the studies determining firefighter exposures have considered only inhalation as the route of entry. As a result of the large protection factor assigned to SCBA and its use during fires, the skin is likely to be a more significant route of entry than previously considered and cannot be dismissed.

There are several explanations that collectively might account for the observed measurement of both gas-phase and particulate phase inside the firefighting protective clothing. There are several pathways by which airborne contaminants can be introduced into workers' clothing. Perhaps the two most well-known effects causing air flow within workers' clothing (and hence drawing in and distributing external airborne contaminants) are the "bellows effect" and the "chimney effect" (Castulik, 2009). The bellows effect occurs when a worker bends over, forcing the air within the clothing to be expelled. When they stand up, new air from outside the clothing is drawn in. The chimney effect occurs when a worker moves (e.g. walks) and there is natural movement of the clothing causing air to be introduced and expelled from the clothing.

The three other likely pathways are:

- direct penetration of the airborne contaminants through the clothing;
- direct entry through loose fittings such as collars; and
- direct entry as a result of specific activities such as hand movement.

There is little if any evidence in the literature about whether firefighters' clothing offers any protection against the ingress of airborne contaminants. The vast majority of work has focussed on clothing's heat and moisture performance (EN 2006; NFPA 2007). The recent United States Heroes project (NIOSH, 2009) focussed on designing new protective clothing to significantly reduce the opportunities for airborne contaminants such as chemical warfare agents to penetrate the firefighting clothing. Thus, the new generation fire protective clothing is "CBRN" resistant, and meets the established standard requirements for protection against fire and heat (NFPA, 2007). Information was not reported about the protection provided against common fire products.

It is not clear in the context of firefighting if any pathway is more significant than any other. However, information can be drawn from reports concerning the performance of protective clothing in other situations. Van Rooij et al. reported (1993a) Tyvek® coveralls reduced the skin deposition of pyrene by 35%. Similarly, Quinlan et al. (1995) found significant reductions of up to 50% were obtained after the clothing policy at a coal liquefaction plant was modified to include specific coveralls, undergarments and laundering. However, cross contamination of workers from their own clothing cannot be discounted as an explanation for a proportion of the dose. The results of these studies clearly demonstrate protective clothing does play a significant role to reduce the penetration of PAHs.

One of the more interesting and unresolved questions is whether the moisture barrier has any role preventing or reducing penetration of PAHs. The significance of any role given the barrier is intended to modify the movement of moisture was not investigated in this study. Consequently, the significance of the moisture barrier cannot be dismissed and warrants further investigation.

The most likely conclusion is that the clothing provides the most significant barrier to the entry of airborne PAHs for two simple reasons. Firstly, the construction of the garments and secondly, the fittings (including closures), since they are collectively intended to reduce air flow and ingress of hot combusted air inside the protective clothing.

References

Aries E, Anderson D, Fisher R. (2008). PCBs and PAHs at an electric arc furnace steelmaking plant in the UK. Annals Occupational Hygiene, 52, 213-225.

Aust N, Forssman B, Redfern N. (2007). Compartment Fire behaviour training exposure study. Heggies. Report 10-5289.

Barker R, Guerht-Schacher C, Grimes R, Hamouda H (2006). Effects of moisture on the thermal protective performance of firefighter protective clothing in low level radiative heat exposures. Textile Research Journal, 76, 27-31.

Blomqvist P. (2005). Emissions from fires consequences for human safety and the environment. Ph.D Thesis

Blomqvist P, Rosell L, Simonsen M. (2004). Emissions from fires part II simulated room fires. Fire Technology 40, 59-73.

Bolstad-Johnson DM, Burgess JL, Crutchfield CD, Storment S, Gerkin R, Wilson JR. (2000). Characterization of firefighter exposures during overhaul. American Industrial Hygiene Association Journal, 61, 636-641.

Booze T, Reinhardt T, Quiring S, Ottmar R. (2004). A screening label assessment of health risks of chronic smoke exposure of wildland firefighters. Journal of Occupational and Environmental Hygiene, 1, 296-305.

Castulik P. (2009). Novel testing methods for evaluation of personal chemical protective garments. Personal Protective Conference 2009. Ft Lauderdale Florida.

DenHartog E. (2009). Systemic approach to protection and ergonomics testing for personal protective equipment. Personal Protective Conference 2009. Ft Lauderdale Florida.

Deutsche Forschungsgemeinschaft. (2004). List of MAK and BAT values. Commission for the investigation of health hazards of chemical compounds in the work area, Report 40. Germany.

Dills RL, Beaudreau M. (2008). Chemical composition of overhaul smoke after use of three extinguishing agents. Fire Technology, 44, 419-437.

European Committee for Standardization. (2006). Protective clothing for firefighters – Performance requirements for protective clothing for firefighting - EN 469.

Feunekes FDJR, Jongeneelen FJ, vd Laan, H, Schoonhof FHG. (1997). Uptake of polycyclic aromatic hydrocarbons among trainers in a fire-fighting training facility. American Industrial Hygiene Association Journal, 58, 1, 23-28.

Gold A, Burgess WA, Clougherty EV. (1978). Exposure of firefighters to toxic air contaminants. American Industrial Hygiene Association Journal, 39, 534-539.

Jankovic J, Jones W, Burkhart J, Noonan G. (1991). Environmental study of firefighters. Annals of Occupational Hygiene, 35, 581-602.

Jongeneelen F, Van Leeuwen F, Oosterink S, Anizon R, Van der Lopp F, Bos R, Van Veen H. (1990). Ambient and biological monitoring of cokeoven workers:determinants of the internal dose of polycyclic aromatic hydrocarbons. British Journal of Industrial Medicine, 47, 454-461.

Laitinen J, Mäkelä M, Mikkola J, Huttu I. (2010). Fire fighting trainers' exposure to carcinogenic agents in smoke diving simulators. Toxicology Letters, 192, 61-65.

Lawson R. (1996). Firefighter protective clothing and thermal environments of structural firefighting. National Institute Standards and Technology, NISTR 5804.

Lin Y, Lee W, Chen S, Chang-Chien G, Tsai P. (2008). Characterisation of PAHs exposure in workplace atmospheres of a sinter plant and health-risk assessment for sintering workers. Journal of Hazardous Materials, 158, 636-643.

McKenzie C. (2007). Chemical and physical characterisation of aerosols from exhaust emissions. Queensland University of Technology Ph.D Thesis.

Nagata Y, (2010). Measurement of odor threshold by triangular odor bag method., http://www.env.go.jp/en/air/odor/. Accessed 2010.

National Fire Protection Association. (2007). Standard on protective ensembles for structural firefighting and proximity firefighting – NFPA 1971. National Fire Protection Association. USA.

National Fire Protection Association. (2008). Thermal capacity of firefighter protecting clothing. Fire Protection Research Foundation.

Ness S. (1994). Surface and Dermal Monitoring for Toxic Exposures. J.Wiley and Sons

Nisbet ICT, LaGoy PK. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regulatory Toxicology and Pharmacology, 16, 290-300.

Occupational Safety and Health Administration. (2006). Regulations (Standards – 29 CFR) Standard 1910.134 Respiratory Protection.

Petry T, Schmid P, Schlatter C. (1996). The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of PAHs. Chemosphere, 32, 639-648.

Quinlan R, Kowalczyk G, Gardiner K, Calvert IA, Hale K, Walton ST. (1995). Polycyclic aromatic hydrocarbon exposure in coal liquefaction workers: the value of urinary 1-hydroxypyrene excretion in the development of occupational hygiene control strategies. Annals of Occupational Hygiene, 39, 329-346.

Reh C, Letts D, Deitchman S. (1994). Health Hazard Evaluation report. United States Department of Interior National Park Services, Yosemite National Park, National Institute for Occupational Safety and Health.

Stamper J, Nigg H, Mahon W, Neilsen A, Royer M. (1989). Pesticide exposures to greenhouse handgunners. Archives of Environmental Contamination and Toxicology, 18, 515-529.

Tsai P. Shieh H, Lee W, Lai S. (2001). Health-risk assessment of workers exposed to polycyclic aromatic hydrocarbons in a carbon black manufacturing industry. The Science of The Total Environment. 278, 137-150.

United States Environmental Protection Agency (EPA). (1993). Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. Washington.

Unwin J, Cocker J, Scobbie E, Chambers H. (2006). An assessment of occupational exposure to polycyclic aromatic hydrocarbons in the UK. Annals of Occupational Hygiene, 50, 395-403.

Van Rooij JG, Bodelier-Bade MM, Jongeneelen FJ. (1993a). Estimation of individual dermal and respiratory uptake of polycyclic aromatic hydrocarbons in 12 coke oven workers. British Journal of Industrial Medicine, 50, 623–632.

Van Rooij JG, Van Lieshout EM, Bodelier-Bade MM, Jongeneelen FJ. (1993b). Effect of the reduction of skin contamination on the internal dose of creosote workers exposed to polycyclic aromatic hydrocarbons. Scandinavian Journal of Work and Environmental Health. 19, 200-207.

World Health Organisation. (1987). Air quality guideline for Europe. WHO European Series, WHO Regional Office for Europe. Copenhagen., 105-117.

Worksafe Australia. (1995). Adopted National Exposure Standards for Atmospheric Contaminants in the Occupational Environment [NOHSC:1003(1995)]. Australian Government Printing Service.

Zhiying C, Yanmin W, Weiyuan Z. (2010). Thermal protective performance and moisture transmission of firefighter protective clothing based on orthogonal design. Journal of Industrial Textiles, 39, 347-356.

CHAPTER FOUR

EXPOSURE OF FIREFIGHTERS TO VOLATILE ORGANIC COMPOUNDS AND ACID GASES

The study described in the previous chapter focussed on the characterisation of firefighter exposure to polycyclic aromatic hydrocarbon (PAH) airborne hazards. The results demonstrated firefighters were exposed to airborne PAHs like naphthalene.

The results described in this chapter address characterising the exposure of firefighters to a variety of airborne contaminants including:

- Acid gases;
- Volatile organic compounds - oxygenated hydrocarbons; and
- Volatile organic compounds - hydrocarbons.

This chapter focuses on establishing the concentration and distribution of these contaminants outside and inside firefighters' protective clothing during extinguishment.

Acid Gases (Excluding Hydrogen Cyanide)

Outside Protective Clothing

The airborne contaminants of interest include:

- hydrogen chloride;
- hydrogen fluoride;
- hydrogen cyanide;
- sulfuric acid;
- nitric acid; and
- phosphoric acid.

These chemicals are readily miscible or soluble in water (Chemwatch, 2010). The results describing the concentration and distribution of acid gases (as the anions) outside the protective clothing are shown in Table 4.1. The acid gas concentrations and distribution as a function of burn are shown in Figure 4.1. The acid gas distribution and concentration varied between burns. The concentration of all acid gases were less than the Limit of Reporting (LOR) except:

- sulfuric acid;
- nitric acid; and
- hydrochloric acid.

Sulfuric acid was the acid gas present in the highest concentrations, but was only detected in two burns. The measured sulfuric acid concentrations exceeded the established Australian National Exposure Standard (NES) for sulfuric acid (1 mg/m^3) and the highest value exceeded the Short Term Exposure Limit (STEL) value (3 mg/m^3). The peak nitric acid and hydrochloric acid values were less than their respective NES (Worksafe Australia, 1995).

These values are within the range reported in the literature concerning firefighter exposure and acid gas formation in smoke (Treitman et al., 1980; Brandt-Rauf et al., 1988; Bolstad-Johnson et al., 2000), but are much less than the maximum concentrations reported. The reported firefighter exposures vary significantly because of the complex nature of the fire behaviour and relative amount of these chemicals within the burning materials (Kirk, 2006).

Table 4.1 Concentration of acid gases (excluding cyanide) as a function of burn.

	Concentration ug/L				
Acid Gas	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Fluoride	< LOR	< LOR	< LOR	< LOR	< LOR
Chloride	< LOR	< LOR	< LOR	0.3	0.2
Bromide	< LOR	< LOR	< LOR	< LOR	< LOR
Nitrate	< LOR	< LOR	< LOR	0.2	< LOR
Phosphate	< LOR	< LOR	< LOR	< LOR	< LOR
Sulfate	< LOR	4.4	< LOR	< LOR	1.2

Not withstanding the complexity of the fire dynamics there are several explanations that readily explain the results including:

- low proportion of furnishings using the precursor anion based chemicals;
- the anions (acid gas) are readily soluble in water;
- fire conditions and ventilation; and
- at high temperatures acid gases readily react with many metals and other materials.

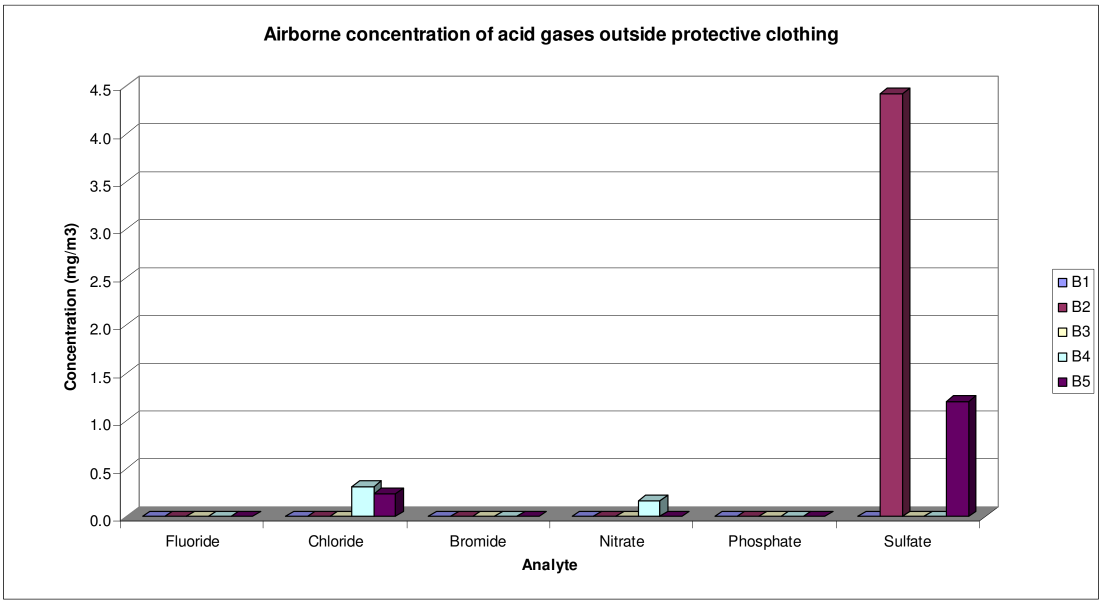

Figure 4.1 Concentration of acid gases outside the protective clothing.

Inside protective clothing

The results describing the concentration and distribution of acid gases inside the protective clothing are shown in Table 4.2. The graph showing the acid gas distribution and concentration inside the protective clothing for each burn is shown in Figure 4.2. Whilst three acid gases were measured outside the protective clothing only a single measurement was obtained inside the protective clothing during the burns, ie. sulfuric acid. The value is less than the Australian NES (Worksafe Australia, 1995) and the reported concentration at which skin irritation occurs (ChemKnowledge, 2010). The sparse and variable results obtained for the acid gases outside and inside the protective clothing preclude any inference being drawn about whether the protective clothing affords any protection.

Table 4.2 Concentration of acid gases inside the protective clothing as a function of burn

	Concentration ug/L				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Fluoride	< LOR	< LOR	< LOR	< LOR	< LOR
Chloride	< LOR	< LOR	< LOR	< LOR	< LOR
Bromide	< LOR	< LOR	< LOR	< LOR	< LOR
Nitrate	< LOR	< LOR	< LOR	< LOR	< LOR
Phosphate	< LOR	< LOR	< LOR	< LOR	< LOR
Sulfate	< LOR	< LOR	1.4	< LOR	< LOR

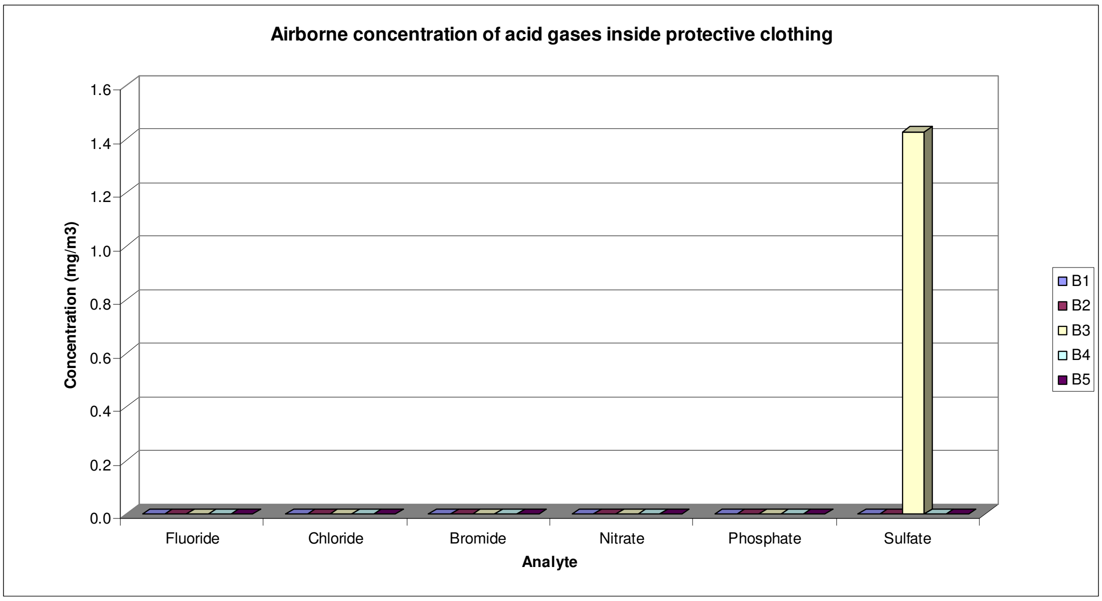

Figure 4.2 Concentration of airborne contaminants (excluding hydrogen cyanide) inside the protective clothing as a function of burn.

It is reasonable to conclude the low halogen/sulphur/phosphorus and nitrogenous (cyanide) content of the burning materials, ventilation, and fire conditions has a significant impact on their airborne concentration. The firefighter's exposure to acid gases is further reduced because of the approaches adopted during extinguishment (including operating behind a water spray combined with the high acid gas water solubility, even if the water spray is not continuous). However, firefighter exposure to acid aerosols (not measured by the current study protocol) cannot be discounted.

The current firefighter protective clothing standards do not require the clothing to be tested against the penetration of acid gases unless the clothing is intended to provide protection against chemical warfare agents. Based on the results in this study it is not clear testing of the clothing for protection against the acid gases is of value.

Hydrogen Cyanide

The results for airborne cyanide (as hydrogen cyanide) outside the firefighter's protective clothing as a function of burn are shown in Figure 4.3. These are reported separately from the acid gases, since the sampling method and LOR are substantially different.

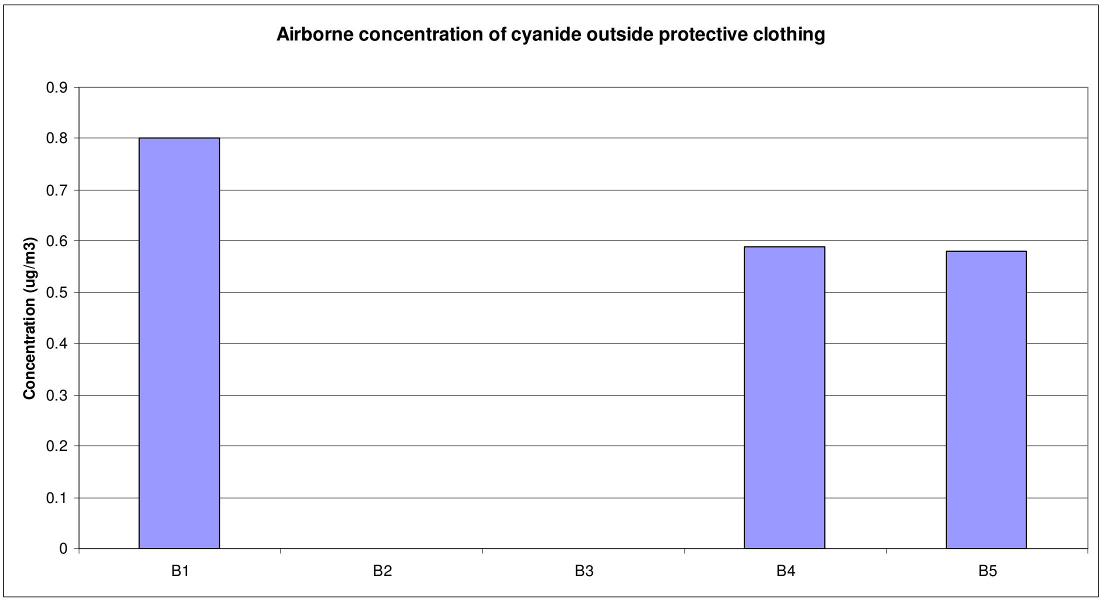

Figure 4.3 Concentration of hydrogen cyanide outside protective clothing as a function of burn.

The highest hydrogen cyanide (HCN) concentration obtained is significantly less than the established NES of 11 mg/m^3. The average concentration was 0.39 µg/m^3. The hydrogen cyanide concentration inside the protective clothing was less than the LOR in all burns.

There has been significant interest recently about the importance of firefighter exposure to hydrogen cyanide. Many studies have concluded the firefighter exposures have been significantly underestimated and they are exposed to high hydrogen cyanide concentrations (Walsh, 2006; Fortin et al., 2006; Walsh and Eckstein, 2004; Simonson et al., 2002), with some inferring the exposure was via the respiratory system (Simonson et al., 2002). Dugard et al. (1987) reported hydrogen cyanide can be absorbed directly through the skin and the rate is proportional to the airborne concentration. The toxic effect is enhanced by the presence of carbon monoxide (Norris et al., 1986). In the case of a firefighter using Self Contained Breathing Apparatus (SCBA) the influence of carbon monoxide and the importance of the respiratory system is significantly moderated. The skin becomes an important entry route.

The hydrogen cyanide concentration is significantly influenced by the proportion of nitrogenous materials burning, fire conditions and ventilation. Like the other acid gases, hydrogen cyanide is readily soluble in water and at high temperatures is very reactive. These factors likely explain the low observed HCN concentrations outside the clothing.

Volatile Organic Compounds - oxygenated hydrocarbons

Outside Protective Clothing

The results in this section focus on characterising the types and concentrations of oxygenated hydrocarbons to which firefighters were exposed whilst extinguishing the fires. The concentrations of volatile organic compounds (VOC - oxygenated hydrocarbons) outside the protective clothing as a function of burn are shown in Table 4.3. The graph describing the concentration of VOC - oxygenated hydrocarbons for each burn is shown in Figure 4.4.

Table 4.3 Concentration of VOC – oxygenated hydrocarbons outside the protective clothing as a function of burn

Aldehydes	Concentration (mg/m^3)				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Formaldehyde	0.14	< LOR	< LOR	0.26	< LOR
Acetaldehyde	0.10	0.56	0.75	0.45	0.84
Acrolein	< LOR	< LOR	< LOR	< LOR	< LOR
Acetone	< LOR	0.15	0.29	0.18	0.29
Propionaldehyde	< LOR	< LOR	< LOR	0.15	0.14
Crotonaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Methacrolein	< LOR	< LOR	< LOR	< LOR	< LOR
Methyl ethyl ketone	< LOR	< LOR	< LOR	< LOR	< LOR
Butyraldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Benzaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Valeraldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
p-Tolualdehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Hexaldehyde	< LOR	< LOR	0.12	0.13	0.17

The type and concentration of the oxygenated hydrocarbons varied between burns. Five oxygenated hydrocarbons were detected in the various burns. They were:

- formaldehyde;
- acetaldehyde;
- propionaldehyde;
- acetone; and
- hexaldehyde.

Acetaldehyde was the most common VOC - oxygenated hydrocarbon measured, with an average value was 0.54 mg/m^3. The highest VOC - oxygenated hydrocarbons concentrations were significantly less than the national exposure standards (Worksafe Australia, 1995) where they have been established. In contrast, when detected the concentrations of two of the oxygenated hydrocarbons (formaldehyde, acetaldehyde) were near or greater than their established odour thresholds (Nagata, 2010; Chemwatch, 2010).

These values are comparable with those reported in the literature concerning firefighter exposure and oxygenated hydrocarbon formation in smoke (Bolstad-Johnson et al., 2000; Dillsand Beaudreau, 2008; Brandt-Rauf et al., 1988; Kirk, 2006). However, they are less than the maximum concentrations reported.

The concentrations of many VOC - oxygenated hydrocarbons were below the LOR in all burns. They were:

- crotonaldehyde;
- methacrolein;
- butyraldehyde;
- methyl ethyl ketone;
- acrolein;
- p-tolualdehyde;
- benzaldehyde; and
- valeraldehyde.

It is of interest the concentration of the common irritant acrolein was less than the LOR.

Inside Protective Clothing

The concentration of VOC - oxygenated hydrocarbons inside the protective clothing as a function of burn are shown in Table 4.4. The graph describing the concentration of VOC - oxygenated hydrocarbons for each burn is shown in Figure 4.5.

Table 4.4 Concentration of VOC - oxygenated hydrocarbons inside the protective clothing as a function of burn.

Aldehyde	Concentration mg/m^3				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Formaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Acetaldehyde	0.30	0.76	< LOR	0.32	< LOR
Acrolein	< LOR	< LOR	< LOR	< LOR	< LOR
Acetone	< LOR	0.15	< LOR	0.23	< LOR
Propionaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Crotonaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Methacrolein	< LOR	< LOR	< LOR	< LOR	< LOR
Methyl ethyl ketone	< LOR	< LOR	< LOR	< LOR	< LOR
Butyraldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Benzaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Valeraldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
p-Tolualdehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Hexaldehyde	< LOR	< LOR	< LOR	0.09	< LOR

The results demonstrate the concentration of the oxygenated hydrocarbons and product distribution changed significantly. Whilst five oxygenated hydrocarbons were measured outside the protective clothing only three were detected inside the protective clothing. They were also detected less frequently. They included:

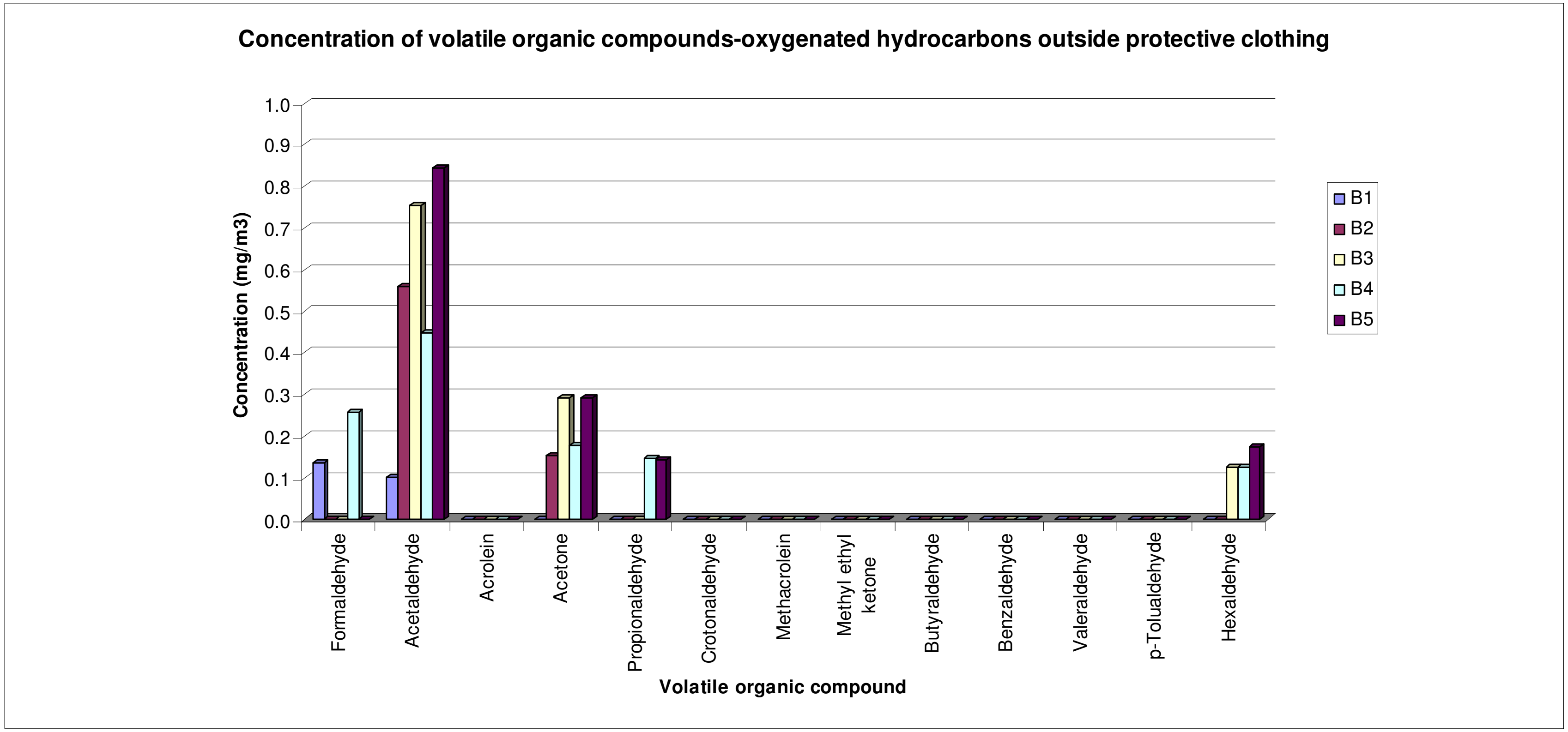

Figure 4.4 Concentration of VOC - oxygenated hydrocarbons outside the protective clothing as a function of burn.

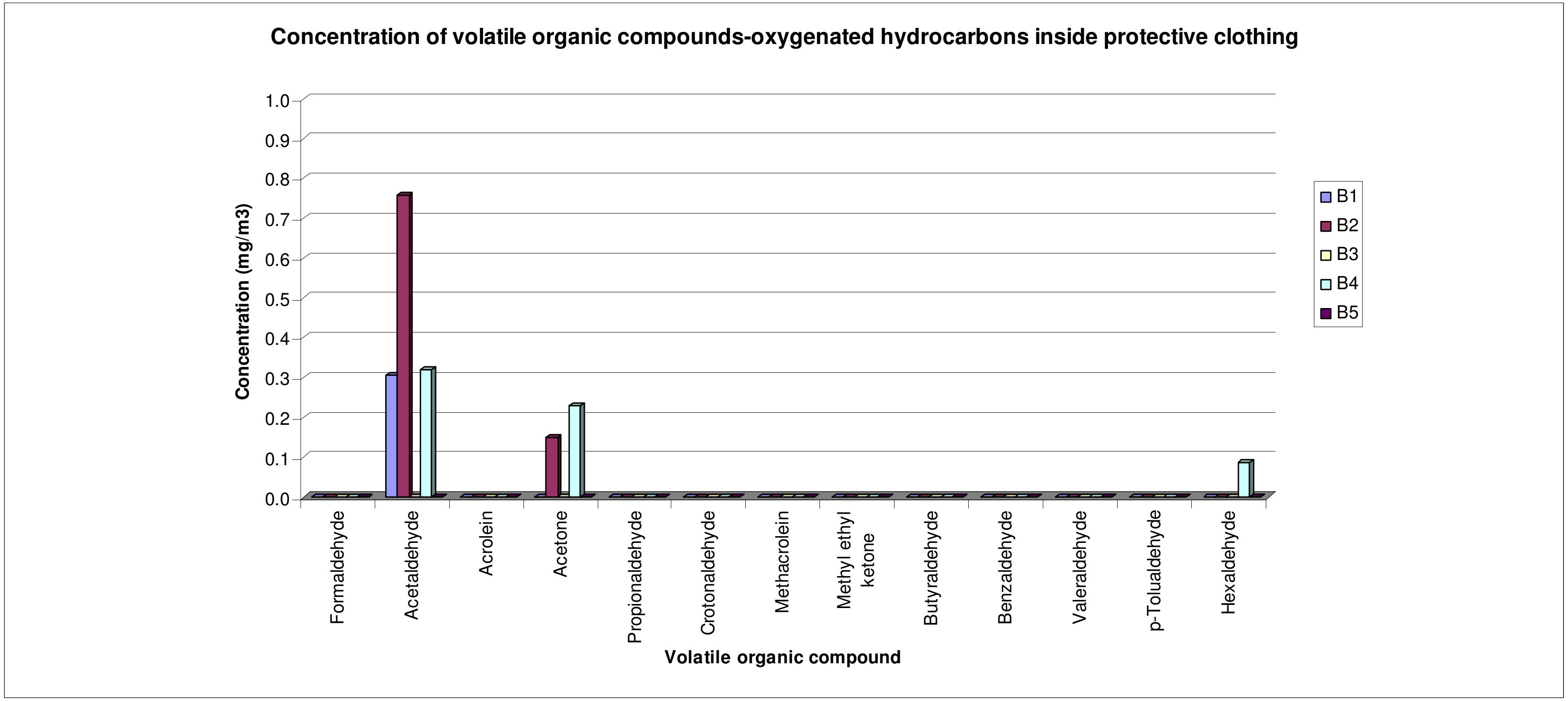

Figure 4.5 Concentration of VOC - oxygenated hydrocarbons inside the protective clothing as a function of burn.

- acetaldehyde;
- acetone; and
- hexaldehyde.

Acetaldehyde was the most common VOC - oxygenated hydrocarbon detected inside the protective clothing. The measurements varied and on two occasions were greater than the acetaldehyde concentration obtained outside the protective clothing. The average acetaldehyde value inside the protective clothing was approximately 48% less than outside. However, the detected concentrations were again above the odour threshold for this chemical (Chemwatch, 2010).

The average concentrations of the other oxygenated hydrocarbons were much lower inside the protective clothing, with a reduction of between 61% and > 99% from the corresponding outside concentrations.

The average concentration of VOC - oxygenated hydrocarbons outside and inside the protective clothing is shown in Figure 4.6. The oxygenated hydrocarbons where the average outside concentration was less than the Limit of Reporting (LOR) are not included. The data shows the average concentration inside was much less than the average outside concentration and the decreases ranged from 48 to > 99 %. These large differences between the outside and inside concentrations were also observed in the PAH results.

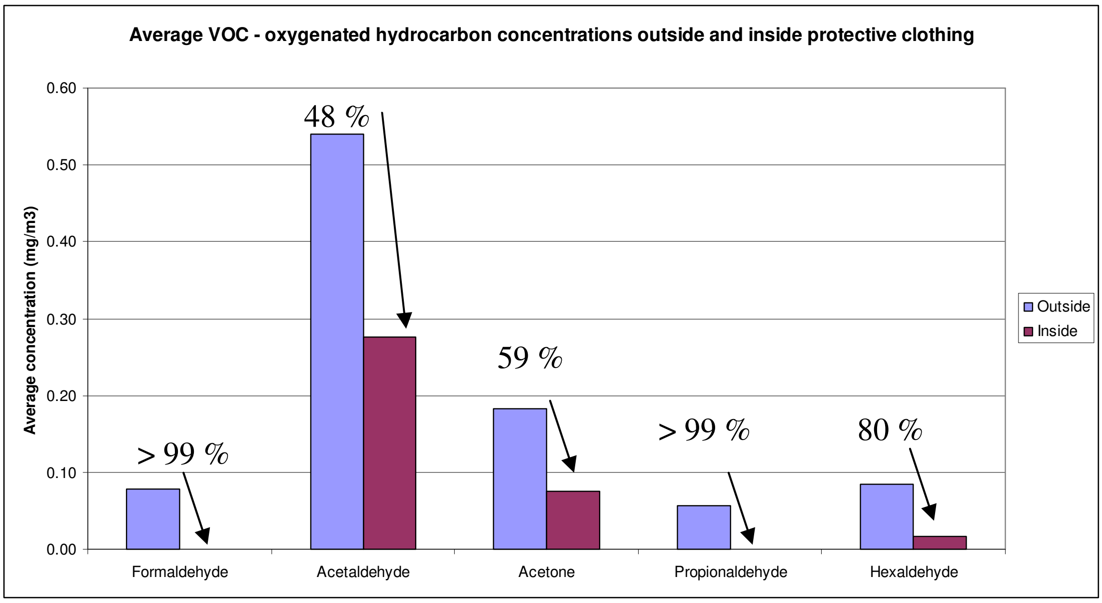

Figure 4.6 Average concentration of VOC – oxygenated hydrocarbons outside and inside protective clothing

Volatile organic compounds - hydrocarbons

Outside Protective Clothing

The results in this section focus on characterising the types and concentrations of volatile organic compounds - hydrocarbons (such as benzene and hexane) to which firefighters were exposed whilst extinguishing the fires. The concentration of VOC - hydrocarbons outside the protective clothing as a function of burn are shown in Table

4.5. The graph describing the concentration of VOC - hydrocarbons for each burn is shown in Figure 4.7.

Table 4.5 Concentration of VOC - hydrocarbons outside the protective clothing as a function of burn.

Volatile Organic Compounds	Concentration mg/m^3				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Benzene	0.08	0.16	0.24	0.21	0.36
Toluene	0.04	0.08	0.13	0.09	0.17
Ethyl benzene	< LOR	0.04	0.05	< LOR	0.04
Xylenes	0.06	0.21	0.27	0.12	0.12
Trimethyl benzenes	0.02	0.12	0.19	0.13	0.11
Methyl cyclohexane	< LOR	0.05	0.07	< LOR	0.05
n-Hexane	< LOR	< LOR	< LOR	< LOR	< LOR
n-Heptane	< LOR	< LOR	0.02	< LOR	< LOR
n-Octane	< LOR	0.02	0.05	< LOR	0.02
n-Nonane	< LOR	0.07	0.12	0.06	0.10
n-Decane	0.04	0.13	0.26	0.14	0.17
Dichloromethane	< LOR	< LOR	< LOR	< LOR	< LOR
Chloroform	< LOR	< LOR	< LOR	< LOR	< LOR
1,1,1-Trichloroethane	< LOR	< LOR	< LOR	< LOR	< LOR
Trichloroethene	< LOR	< LOR	< LOR	< LOR	< LOR
Tetrachloroethene	< LOR	< LOR	< LOR	0.12	< LOR
Methyl ethyl ketone	< LOR	< LOR	< LOR	< LOR	< LOR
Ethyl acetate	< LOR	< LOR	< LOR	< LOR	< LOR
Methyl isobutyl ketone	< LOR	< LOR	< LOR	< LOR	< LOR

A variety of volatile organic compounds - hydrocarbons were identified during the activities. The type and concentration of the hydrocarbons varied between burns. Eleven hydrocarbons were detected in the various burns. They were:

- benzene;
- toluene;
- ethyl benzene;
- xylene;
- trimethyl benzene;
- heptane;
- octane;
- decane;
- methyl cyclohexane;
- nonane; and
- tetrachloroethene.

Benzene was the hydrocarbon with the greatest average concentrations, with an average benzene value was 0.21 mg/m^3. In two instances the concentration of xylene was higher than the benzene concentration. The highest hydrocarbon concentrations were significantly less than the Australian National Exposure Standards (NES) (Worksafe Australia, 1995) and their odour thresholds (Nagata, 2010;

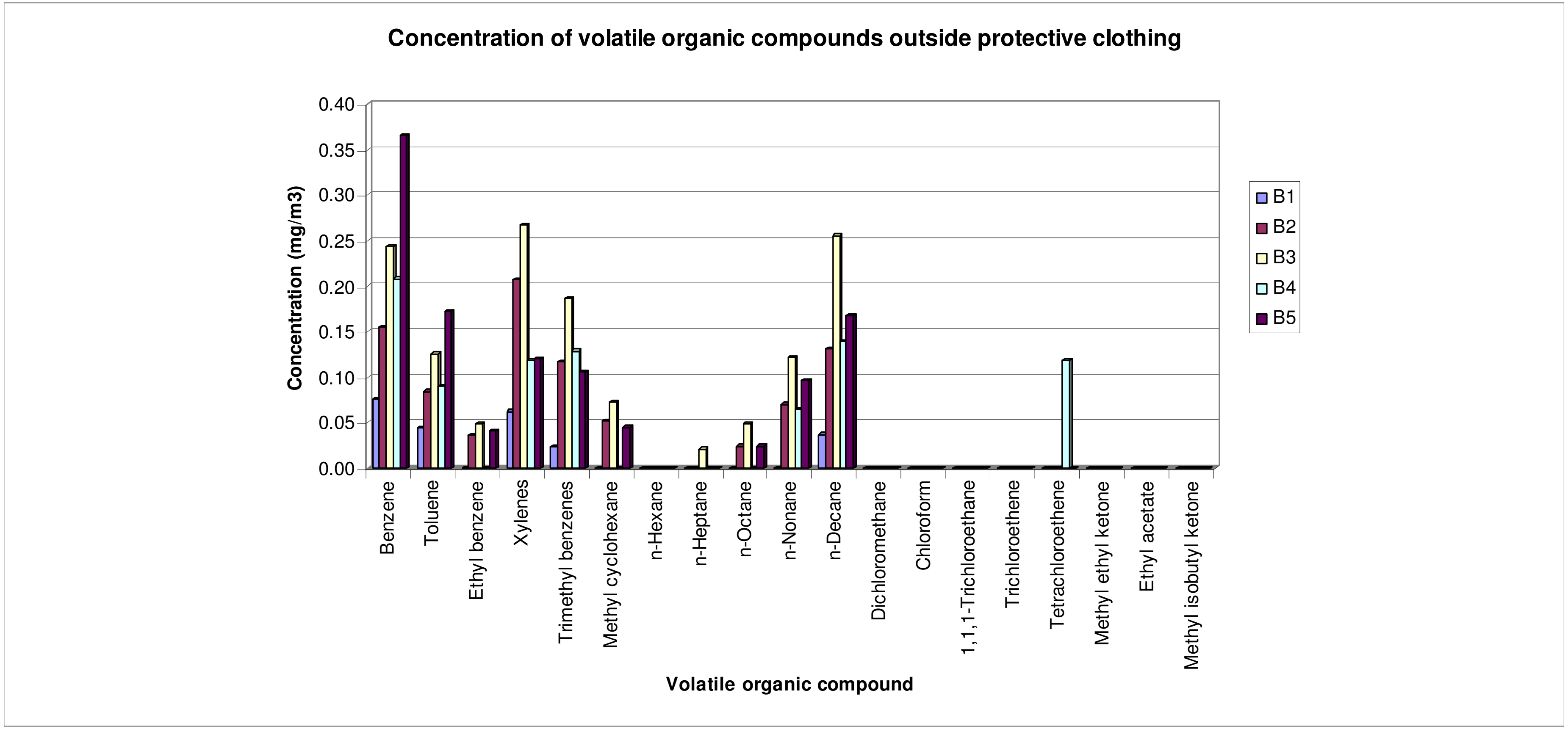

Figure 4.7 Concentration of VOC - hydrocarbons outside the protective clothing as a function of burn.

ChemKnowledge, 2010) where they have been established. These values are within the ranges reported in the literature concerning firefighter exposure and hydrocarbon formation in smoke (Bolstad-Johnson et al., 2000; Dills and Beaudreau, 2008; Brandt-Rauf et al., 1988; Kirk, 2006; Lees, 1995).

It is known the vast majority of worker exposure to these hydrocarbons occurs through inhalation (Gold et al., 1978; Figà-Talamanca et al., 2001) however, direct dermal permeation from the gas-phase also occurs (National Industrial Chemicals Notification and Assessment Scheme, 2001; Agency for Toxic Substances and Disease Registry, 2003). The relative importance of the skin as an entry route within workplace settings is not clear (Brooke et al.,1998; United States Environmental Protection Agency, 1992; National Industrial Chemicals Notification and Assessment Scheme, 2001; McDougal et al., 1986, 1987, 1990; Pierce et al., 1997). The use of respiratory protective equipment and other factors affect the relative importance of dermal absorption (United States Environmental Protection Agency, 1992; Riihimäki and Pfäffli, 1978). Riihimäki and Pfäffli (1978) reported volunteers exposed to low levels of xylene wearing respiratory protection absorbed xylene through the skin. It seems reasonable this observation holds true for benzene and toluene given their chemical similarity and similar fluxes. For example, McDougal et al. (1986, 1987, 1990) and Pierce et al. (1997) reported permeation of these hydrocarbons from the gas phase through rat skin.

The permeation and hence dose after one hour can be estimated. The relationship is assumed to be valid at low concentrations, assuming uniform flux and and a skin area of 1.8 m^2 (DuBois and DuBois, 1916). The calculated doses at the concentrations reported in this study are 0.012 μmoles, 0.025 μmoles and 0.031 μmoles for benzene, toluene and xylene respectively. In this example the estimated values of aromatic hydrocarbons absorbed through the skin are insignificant.

The relative concentration of the hydrocarbons outside the protective clothing referenced against the benzene concentration is shown in Figure 4.8. The figure shows benzene concentration is the highest except for xylene in two instances. The relative concentrations of the hydrocarbons and PAHs vary between the burns and consequently there is no definitive relationship between the relative concentration of naphthalene and any of the aromatic hydrocarbons generated.

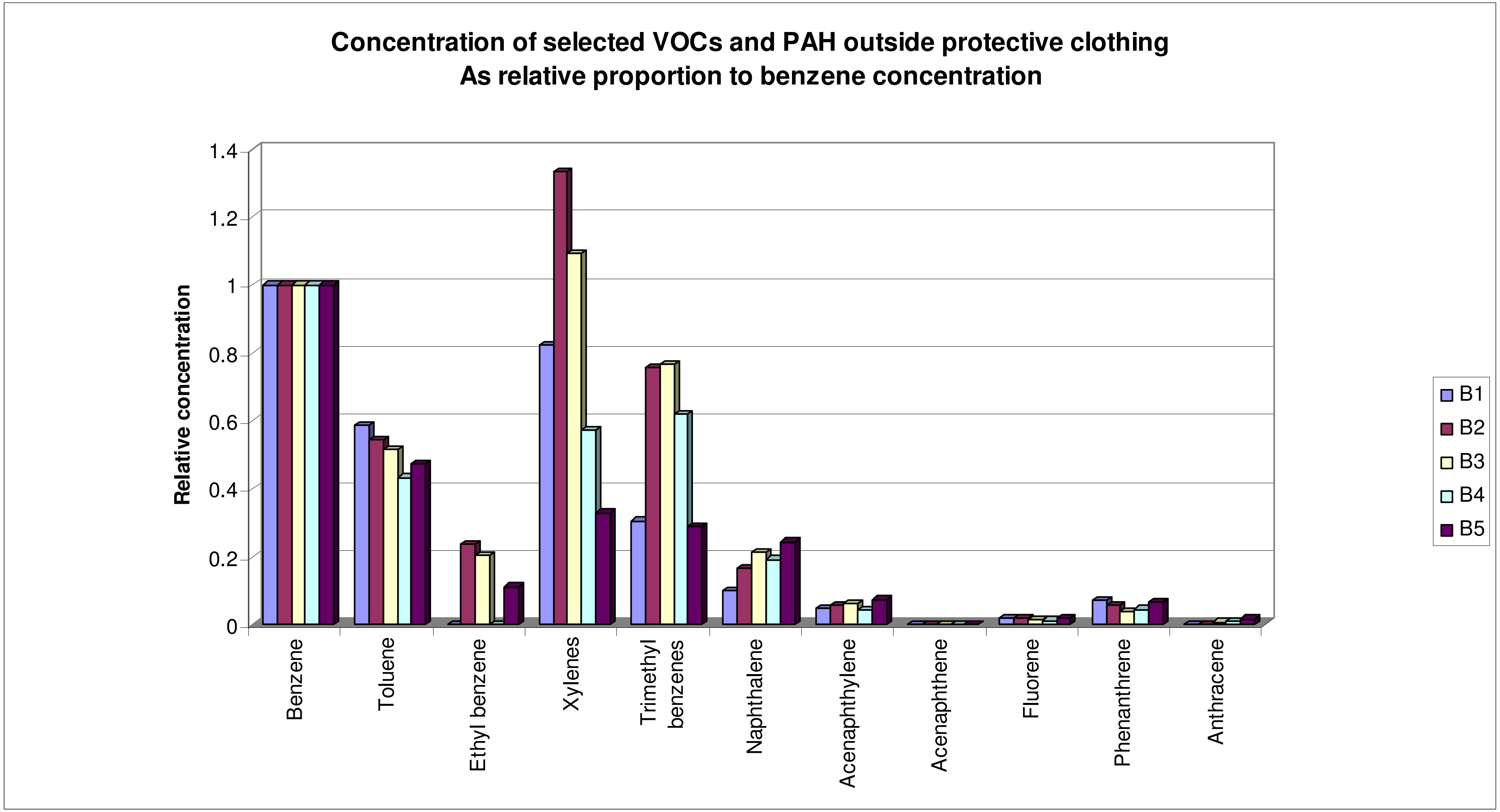

Figure 4.8 Relative concentrations of hydrocarbons (referenced to benzene) as a function of burn.

Inside Protective Clothing

The concentrations of VOC - hydrocarbons inside the protective clothing as a function of burn are shown in Table 4.6. The graph describing the concentration of VOC - hydrocarbons for each burn is shown in Figure 4.9.

Table 4.6 Concentration of VOC - hydrocarbons inside the protective clothing as a function of burn.

Volatile Organic Compounds	Concentration mg/m^3				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Benzene	< LOR	0.04	< LOR	0.11	< LOR
Toluene	0.03	0.05	< LOR	0.10	< LOR
Ethyl benzene	0.09	< LOR	< LOR	< LOR	< LOR
Xylenes	0.06	0.10	0.04	0.05	< LOR
Trimethyl benzenes	< LOR	< LOR	< LOR	0.05	0.04
Methyl cyclohexane	< LOR	< LOR	< LOR	< LOR	< LOR
n-Hexane	< LOR	< LOR	< LOR	< LOR	< LOR
n-Heptane	< LOR	< LOR	< LOR	< LOR	< LOR
n-Octane	< LOR	< LOR	< LOR	< LOR	< LOR
n-Nonane	< LOR	< LOR	< LOR	< LOR	< LOR
n-Decane	0.04	0.04	< LOR	0.05	< LOR
Dichloromethane	< LOR	< LOR	< LOR	< LOR	< LOR
Chloroform	< LOR	< LOR	< LOR	< LOR	< LOR
1,1,1-Trichloroethane	< LOR	< LOR	< LOR	< LOR	< LOR
Trichloroethene	< LOR	< LOR	< LOR	< LOR	< LOR
Tetrachloroethene	< LOR	< LOR	< LOR	< LOR	< LOR
Methyl ethyl ketone	< LOR	< LOR	< LOR	< LOR	< LOR
Ethyl acetate	< LOR	< LOR	< LOR	< LOR	< LOR
Methyl isobutyl ketone	< LOR	< LOR	< LOR	< LOR	< LOR

The results demonstrate the concentration of the VOC - hydrocarbons and product distribution changed significantly. Whilst eleven hydrocarbons were detected outside the protective clothing, only six were detected inside the protective clothing. They were also detected at lower concentrations when found to be present. These were:

- benzene;
- toluene;
- xylene;
- ethyl benzene
- trimethyl benzene; and
- decane.

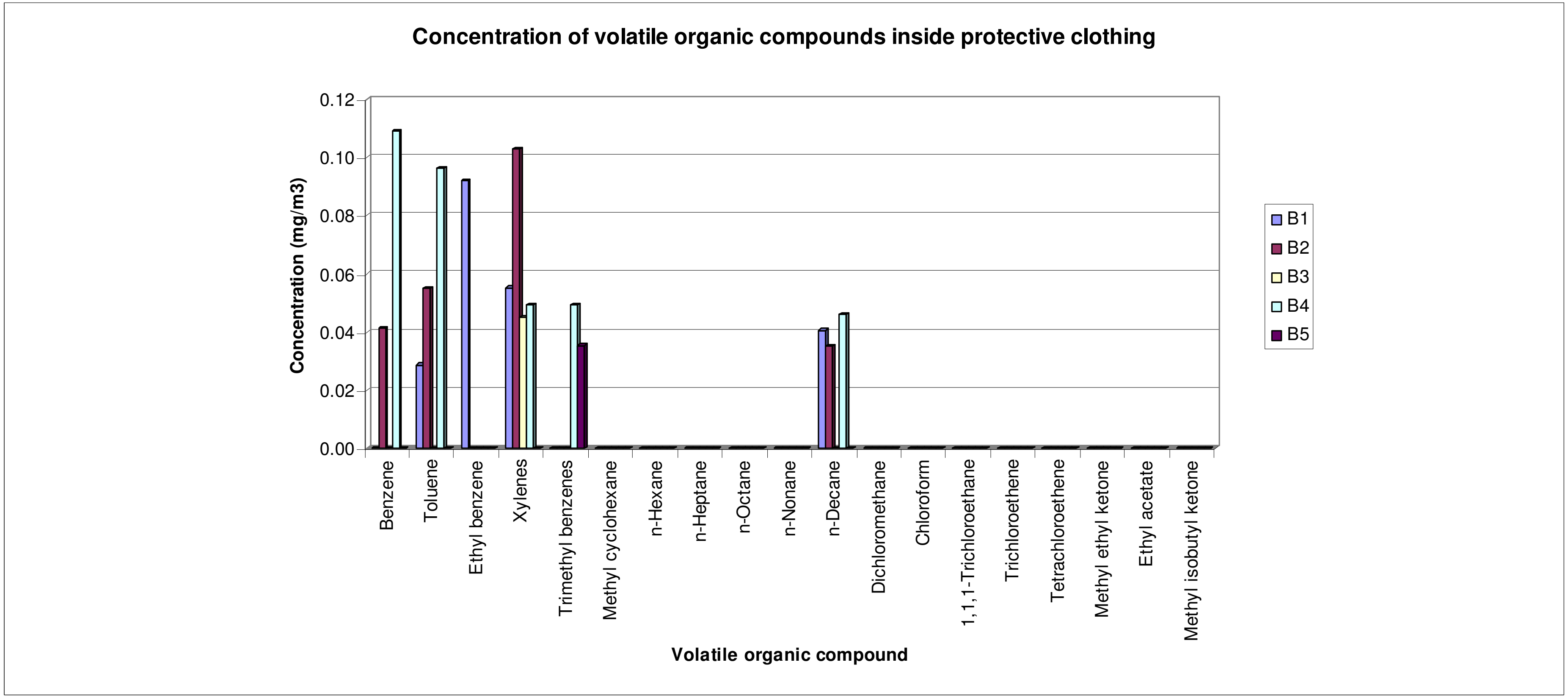

Figure 4.9 Concentration of VOC - hydrocarbons inside the protective clothing as a function of burn

Xylene was the most common hydrocarbon measured. The average xylene concentration inside the protective clothing was 68% less than outside. The average concentrations of the other hydrocarbons were much lower inside and ranged from 40 % to > 99 % less than the outside concentration. Other hydrocarbons which were not detected outside the protective clothing were also not detected inside the protective clothing. The average hydrocarbon concentration outside and inside the protective clothing is shown in Figure 4.10. The hydrocarbons where the average outside concentration was less than the LOR are not included, since their concentrations were also less than the LOR inside the protective clothing.

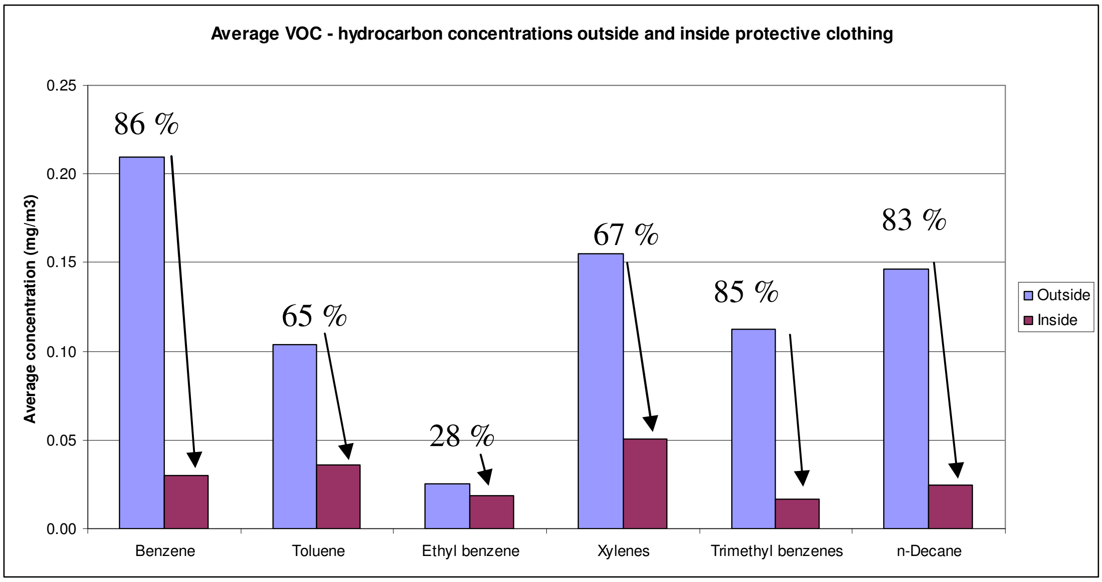

Figure 4.10 Average concentration of VOC - hydrocarbons outside and inside the protective clothing.

The significantly lower measured values inside the protective clothing show the estimated worst-case benzene, xylene and toluene skin permeation estimates obtained earlier (page 74) are likely to over-estimate the true skin dose. Hence, the risk is less.

Summary

The overall results show clearly the firefighters were exposed to VOC - oxygenated hydrocarbons and VOC – hydrocarbons outside and inside their protective clothing. The measured concentrations were much less than their respective NES values where they have been established (Worksafe Australia, 1995). However, the concentrations of some VOC – oxygenated hydrocarbons outside the protective clothing were greater than their respective odour thresholds. Significant decreases in concentrations of both VOC – oxygenated hydrocarbons and VOC – hydrocarbons were observed within the protective clothing as compared to the corresponding external concentrations.

The results show significant individual variance between the burns, despite the similar fuels, and tactics applied to extinguish the fires. The variability likely reflects the complex nature of the interactions between the burning materials, fire behaviour, firefighter activity and hence exposure (Dills and Beaudreau, 2008; Kirk, 2006).

The VOC – oxygenated hydrocarbons are of great interest since they are known respiratory irritants and many are also considered skin irritants particularly if direct contact with the liquid occurs (Chen et al., 2007; Kamath et al., 1985; Pausternbach et al., 2006; International Agency for Research on Cancer, 2006; World Health Organisation, 2010; National Industrial Chemicals Notification and Assessment Scheme, 2006; Department of Health Committee Medical Effects of Air Pollutants, 2000). However, there is little if any knowledge available about direct dermal absorption from the gas phase especially in the case of formaldehyde (National Industrial Chemicals Notification and Assessment Scheme, 2006). In this study, the results show the concentration of the oxygenated hydrocarbons within the protective clothing are significantly less than the concentrations at which skin irritation has been reported (Chemwatch, 2010; ChemKnowledge 2010).

There is little knowledge available about direct dermal absorption of VOC - hydrocarbons from the gas phase and a significant proportion of the studies reported have focused on the aromatic hydrocarbons namely benzene (United States Environmental Protection Agency, 1992 McDougal et al., 1986, 1987, 1990; McDougal and Boeniger, 2002). Based on the measurements the estimated absorption of the hydrocarbons through the skin directly from the gas phase is not significant in this case. However, the skin's relative importance as an entry route cannot be discounted for all combustion scenarios.

It is likely the pathways for penetration of contaminants into the protective clothing may include: air movement caused by the firefighter moving; direct penetration of airborne contaminants through the clothing (chimney and bellows effects); and direct entry through loose fittings. There is little if any information in the literature about the effectiveness of these pathways for the entry of chemicals such as VOC – oxygenated hydrocarbons into protective clothing (National Industrial Chemicals Notification and Assessment Scheme, 2006).

The restricted opportunities for air to enter the protective clothing in combination with the low outside concentrations readily explain the results. The significance if any of the moisture barrier within the protective clothing is not clear and warrants further investigation. However, the importance of other factors such as extinguishment tactics and the influence of water spray cannot be dismissed.

It is nonetheless clear firefighters must manage their exposures to the airborne hydrocarbons during their activities and donning Self Contained Breathing Apparatus is an obvious risk control measure.

References

Agency for Toxic Substances and Disease Registry. (2003). Toxicological profile for benzene and other volatile organic compounds. United States Department of Health and Human Services.

Bolstad-Johnson DM, Burgess JL, Crutchfield CD, Storment S, Gerkin R, Wilson JR. (2000). Characterization of firefighter exposures during overhaul. American Industrial Hygiene Association Journal, 61, 636-641.

Brandt-Rauf PW, Fallon LF, Tarantini T, Idema C, Andrews L. (1988). Health hazards of fire fighters: exposure assessment. British Journal of Industrial Medicine 45, 606-612.

Brooke I, Cocker J, Delic JI, Payne M, Jones K, Gregg NC, Dyne D. (1998). Dermal uptake of solvents from the vapour phase: an experimental study in humans. Annals of Occupational Hygiene, 42, 531-540.

ChemKnowledge. (2010). Thomson Micromedex. United States.

Chemwatch. (2010). Chemgold II. Caulfield North, Victoria.

Chen L, Lian G, Han L. (2007). Prediction of human skin permeablility using artificial neural network modelling. Acta Pharmacologica Sinica, 28, 591-600.

Colman R, Coleman A. (2006). Unexpected cause of raised benzene absorption in coke oven by-product workers. Occupational Medicine, 56, 269-271.

Department of Health Committee on the Medical Effects of Air Pollutants. (2000). Report on the Health Effects of Aldehydes in Ambient Air.

Dills RL, Beaudreau M. (2008). Chemical composition of overhaul smoke after use of three extinguishing agents. Fire Technology, 44, 419-437.

DuBois D, DuBois DF. (1916). A formula to estimate the approximate surface area if height and weight be known. Archives of Internal Medicine, 17, 863-71.

Dugard PH. (1987). The absorption of cyanide through human skin in vitro from solutions of sodium cyanide and gaseous HCN. In: Ballantyne B, Marrs TC, eds. Clinical and experimental toxicology of cyanides. Wright, Bristol, IOP Publishing, pp. 127–137.

Figà-Talamanca I, Salera E. (2001). Exposure to benzene among workers in a petroleum transport company. Journal of Occupational Health, 43, 53-55.

Fortin J, Waroux S, Arvis A, Giocanti J. (2006). Acute cyanide poisoning A Paris firefighter recovers from severe smoke inhalation. Fire Engineering, 159, s19-22.

Gold A, Burgess WA, Clougherty EV. (1978). Exposure of firefighters to toxic air contaminants. American Industrial Hygiene Association Journal, 39, 534-539.

International Agency for Research on Cancer. (2006). Formaldehyde, 2-butoxyethanol and 1-tert-butoxypropan-2-ol.

Kamath Y, Hornby S, Weignmann H. (1985). Irreversible chemisorption of formaldehyde on cotton cellulose. Textile Research Journal, 55, 663-666.

Kirk KM. (2006). Air contaminants at residential fire investigation scenes. Thesis, Queensland University of Technology, Brisbane.

Lees, P. S. J. (1995) Combustion products and other firefighter exposures. Occupational Medicine: State of the Art Reviews 10, 691-706.

McDougal, J.N.; Jepson, G.W.; Clewell, H.J., III; MacNaughton, M.G.; Andersen, M.E. (1986) A physiological pharmacokinetic model for dermal absorption of vapors in the rat. Toxicology. Appl. Pharmacol. 85(2):286-294.

McDougal, J.N.; Jepson, G.W.; Clewell, H.J., III; Andersen, M.E. (1987) Pharmacokinetics of organic vapor absorption. Pharmacol. Skin 1:245-251.

McDougal, J.N.; Jepson, G.W.; Clewell, H.J., III; Gargas, M.L.; Andersen, M.E. (1990) Dermal absorption of organic chemical vapors in rats and humans. Fundam. Appl. Toxicol. 14:299-308.

McDougal J, Boeniger M. (2002). Methods for assessing risks of dermal exposure in the workplace. Critical Reviews in Toxicology. 32, 291-327.

Nagata Y, (2010). Measurement of odor threshold by triangular odor bag method., http://www.env.go.jp/en/air/odor/. Accessed 2010.

National Industrial Chemicals Notification and Assessment Scheme. (2006). Priority existing chemical report – formaldehyde. Department of Health and Aging.

National Industrial Chemicals Notification and Assessment Scheme. (2001). Priority existing chemical report –benzene. Department of Health and Aging.

Norris J, Moore S, Hume A. (1986). Synergistic lethality induced by combination of carbon monoxide and cyanide. Toxicology, 40, 121-129.

Pausternbach D, Alarie Y, Kulle T, Schachter N, Smith R, Swenberg J, Hanspeter W, Horowitz S. (1997). A recommended occupational exposure limit for formaldehyde based on irritation. Journal of Toxicology and Environmental Health Part A, 50, 217-264.

Pierce C, Dills R, Lewandoskia T, Morgan M, Wessels M, Shen D, Kalman D. (1997). Estimation of background exposure to toluene using a physicologically –based kinetic model. Journal of Occupational Health, 39, 130-137.

Riihimäki V, Pfäffli P. (1978). Percutaneous absorption of solvent vapors in man. Scandinavian Journal of Work, Environment and Health, 4, 73-85.

Simonson M, Tuorinen H, Emanuelsson V. (2002). Formation of hydrogen cyanide in fires. SP Report 27.

Treitman RD, Burgess WA, Gold A. (1980). Air contaminants encountered by firefighters. American Industrial Hygiene Association Journal, 41, 796-802.

United States Environmental Protection Agency (EPA). (1992) Dermal exposure assessment: principles and applications. Report EPA/600/8-91/011B, U.S. Washington.

Walsh D (2006) Fire smoke an unrecognised threat to American firefighters. Fire Engineering, 159, S4 1-5.

Walsh D, Eckstein M.(2004). HCN in fire smoke: an underappreciated threat. Emergency Medical Services, October 160-163.

World Health Organisation Regional Office For Europe. (2010). Air Quality Guidelines for Europe.

Worksafe Australia. (1995). Adopted National Exposure Standards for Atmospheric Contaminants in the Occupational Environment [NOHSC:1003(1995)]. Australian Government Printing Service.

CHAPTER FIVE

DEPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) ONTO FIREFIGHTER PROTECTIVE CLOTHING

The deposition of airborne contaminants and surface sourced contaminants at fires onto firefighters' protective clothing has not received much attention in the literature. (Perry, 1999; Stull and Pinette, 1996). The vast majority of the literature has focused on establishing the performance of protective clothing including its design, performance and protection afforded against flame and radiant heat (National Fire Protection Association, 2007, 2008; European Committee for Standardization, 2006; Barker et al., 2002; Kutlu and Cireli, 2005; Song, 2007; Lawson, 1996, 2000). To a lesser extent, the literature has also focused on characterising physiological impacts on firefighters and establishing the extent of firefighter exposure to airborne contaminants through the respiratory system (Dreger et al., 2006; Bilzon et al., 2001; Rossi, 2003; Office of the Deputy Prime Minister, 2005a,b; Gold et al., 1978; Burgess et al., 2001; Brandt-Rauf et al., 1988; Bolstad-Johnson et al., 2000). In general, the most significant component of a worker's dose does not arise from penetration of the skin, but by inhalation. For example Hursh et al. (1989) investigated mercury absorption and found more than 95% of the dose occurred by inhalation. The skin as an exposure route often becomes significant in workplace settings where workers use respiratory protection (Van Rooij, 1993a,b) and where activities maximise the opportunities for the deposition of airborne contaminants or direct skin contact with contaminants (Nigg, 1986; Ness, 1994; United States Environmental Protection Agency, 1992; Wobst, 1999). This situation applies to firefighters where they must don Self Contained Breathing Apparatus (SCBA) to undertake firefighting activities within a structure and there are opportunities for direct contact with contaminants (Laitinen, 2010; Wobst, 1999). The importance and role of the skin as an entry route in workplace settings is further complicated by the use of protective clothing (Nigg, 1986; Van Rooij, 2007).

Much of the inferred knowledge about the likely deposition onto and movement of contaminants through fire fighting protective clothing are drawn from studies addressing the performance of clothing in other industries such as the pesticide industry (Ness, 1994). Perry (1999) reported five PAHs were detected on swatches attached to the fire fighting protective coats and phenanthrene was deposited in the greatest quantity. There was significant variance between swatch samples. More recently, Aust et al. (2007) reported naphthalene and acenaphthylene were deposited onto the clothing during compartment fire training. They also attempted to characterise the deposition of the Volatile organic compounds (VOCs) and reported they were less than the LOR.

Results

The study described in the previous chapters focussed on the characterisation of firefighter exposure to a variety of airborne hazards. The results demonstrated firefighters were exposed to airborne contaminants including polycyclic aromatic hydrocarbons (PAHs) like naphthalene and volatile organic compounds (VOC) like benzene. This chapter focuses on establishing whether PAHs are directly deposited onto a swatch attached to the outer layer of the protective clothing during extinguishment. The swatch was the same material as the outer shell of the protective clothing.

The study did not attempt to identify or quantify any VOCs such as benzene deposited onto a swatch because of their inherent physico-chemical properties and the concentrations of the airborne VOCs previously established. The influence of wetting of the garments' outer layers on the deposition of PAHs and other materials was also not investigated. As far as we are aware there is no evidence in the literature about whether the structural fire fighting protective clothing's sorptive capacities are affected by moisture, or other wetting agents.

After the extinguishment activity, the swatches often exhibited evidence of discolouration and gross contamination from the deposition of combustion products commonly described as soot.

Fourteen PAHs were found to have been deposited onto the swatches in measurable quantities. The four deposited at the highest concentrations were:

- phenanthrene;
- pyrene;
- fluoranthrene; and
- anthracene.

The data describing the concentration and distribution of PAHs deposited onto the swatches as a function of burn is shown in Table 5.1. The deposition distributions and concentrations of the PAHs as a function of burn are shown in Figure 5.1. The average phenanthrene concentration was ca. 12.4 ng/cm^2.

The known carcinogen benzo[a]pyrene was detected in all five burns, and the average concentration was approximately 2.1 ng/cm^2. This observation is significant and shows deposition of benzo[a]pyrene occurs directly from the fire "smoke". The airborne PAH results described in Chapter Four showed benzo[a]pyrene was present above the Limit of Reporting (LOR) only in the particulate phase.

The most striking differences between the PAH deposition distribution and the PAH airborne distribution is the concentration of absorbed naphthalene is less than the LOR. In contrast, naphthalene dominates the airborne PAH distribution. The concentration of absorbed acenaphthylene was also very low in comparison with the measured airborne concentration. Perry (1999) reported these two PAHs were not absorbed onto the protective clothing during their study. In contrast, Aust et al. (2007) reported naphthalene and acenaphthylene were deposited onto protective clothing during compartment fire training. However, the results are confusing since the units of measurement reported do not equate to a deposition concentration. It is not clear why naphthalene and acenaphthylene are absorbed poorly onto the swatch, but explanations such as the adopted analytical methodology or the nature of the chemical interaction with the protective clothing surface cannot be discounted.

Table 5.1 Concentration of polycyclic aromatic hydrocarbons (PAHs) deposited onto swatches as a function of burn.

PAH Deposition	Deposition concentration (ng/cm^2)				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Naphthalene	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthylene	**0.91**	**0.9**	**2.0**	< LOR	**2.6**
Acenaphthene	< LOR	< LOR	< LOR	< LOR	< LOR
Fluorene	**0.77**	**0.77**	**2.2**	< LOR	**1.3**
Phenanthrene	**6.4**	**9.3**	**29**	**3.1**	**14**
Anthracene	**1.6**	**2.4**	**8**	**0.59**	**3.4**
Fluoranthene	**3.6**	**6.9**	**21**	**3.1**	**13**
Pyrene	**3.8**	**7.4**	**22**	**3.1**	**14**
Benz[a]anthracene	**0.72**	**1.4**	**3.4**	**0.74**	**2.9**
Chrysene	**0.75**	**1.7**	**4.4**	< LOR	< LOR
Benzo[b]fluoranthene / benzo[k]fluoranthene	**1.6**	**2.2**	**6**	**1.2**	**4.2**
Perylene	< LOR	< LOR	**1**	< LOR	< LOR
Benzo[a]pyrene	**1.0**	**1.4**	**4.4**	**0.67**	**2.9**
Benzo[e]pyrene	**0.68**	**0.84**	**2.1**	< LOR	**1.6**
Indeno[1,2,3-cd]pyrene	< LOR	**0.66**	**2.1**	< LOR	< LOR
Benzo[ghi]perylene	< LOR	**0.75**	**2.1**	< LOR	**1.2**
Dibenz[a,h]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Coronene	< LOR	< LOR	< LOR	< LOR	< LOR

The PAH deposition concentrations exhibited differences across the burns. Van Rooij et al. and others (Van Rooij, 1995b) have suggested particular PAHs such as pyrene can be used as a marker for PAH exposure. In this study the PAH with the highest absorption (phenanthrene) was investigated to determine if it could be used as marker for PAH absorption onto the clothing. The ratio of deposited PAH concentration against the phenathrene deposition concentration is shown in Table 5.2.

Table 5.2 Absorbed PAH concentration relative to the absorbed concentration of phenanthrene as a function of burn.

PAH	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Anthracene	0.25	0.26	0.27	0.19	0.24
Fluoranthene	0.52	0.74	0.72	1	0.9
Pyrene	0.57	0.8	0.76	1	1
Benzo(a)pyrene	0.16	0.15	0.15	0.22	0.21

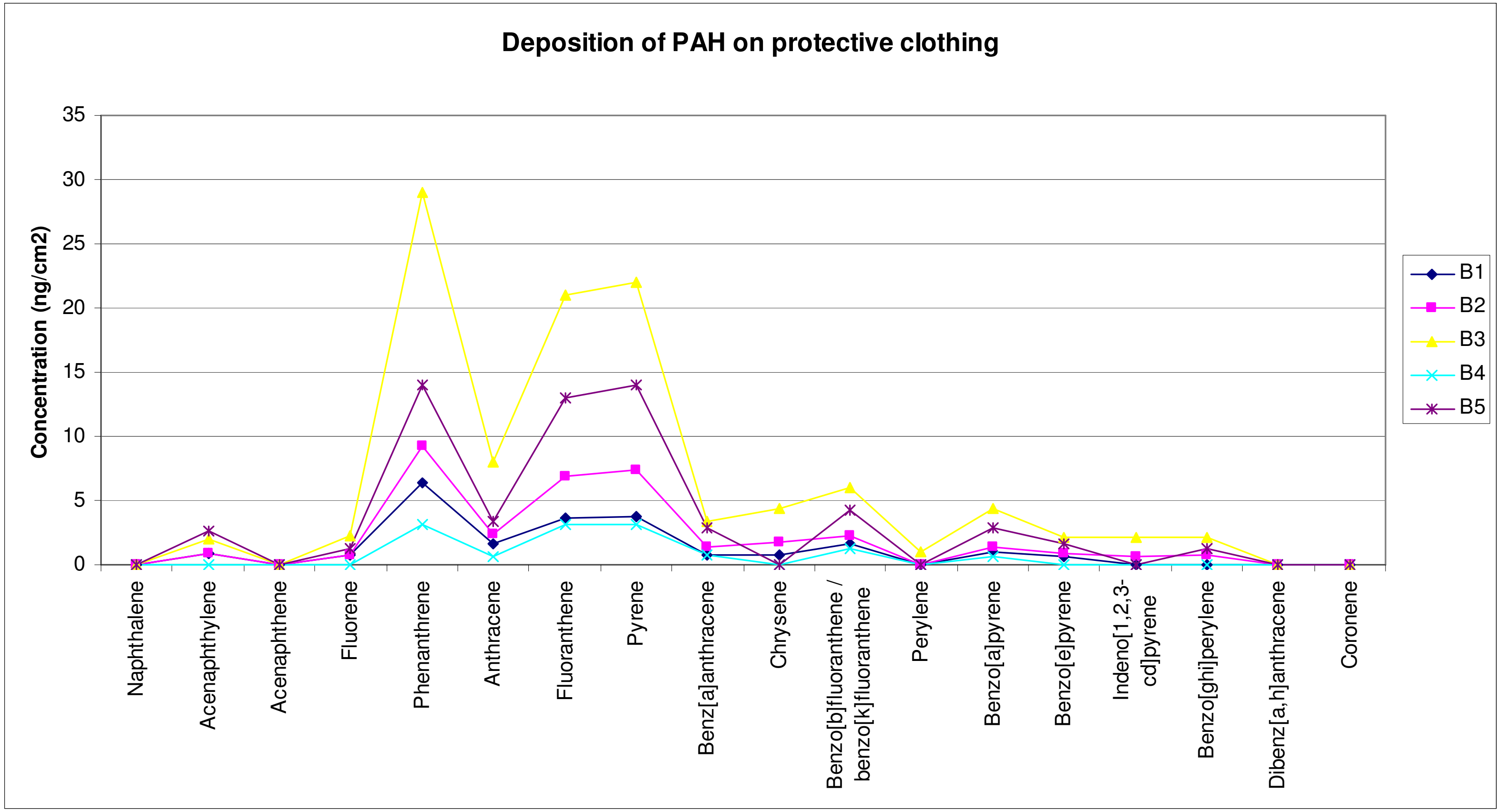

Figure 5.1 Absorbed PAH concentration distribution as a function of burn.

The data in Table 5.2 shows the deposition ratios of benzo[a]pyrene and anthracene are relatively consistent across the burns, whilst the pyrene and fluoranthene deposition ratios vary significantly. The corresponding airborne concentration ratios of benzo[a]pyrene and anthracene are also relatively consistent across the burns, but pyrene and fluoranthene exhibit significant variances. It is clear as a result of the varying ratios phenanthrene is not suitable to be used as a marker for determining the likely deposition of PAHs onto the clothing.

A key question of interest is whether there is any relationship between the PAH airborne concentration distribution and the PAH deposition distribution. The comparison of the PAH deposition distribution and the airborne PAH distribution as a function of burn is shown in Figure 5.2. In general, as the PAH airborne concentration decreases the PAH deposition concentration decreases. However, the highest PAH deposition concentration did not occur in the same burn as the highest measured PAH airborne concentration. There are many explanations to account for the observations including the inherent complexity of the fire environment (Jankovic et al., 1991; Drysdale, 1999; Aust et al., 2007)

The relative contribution of naphthalene and acenaphthylene obscures the data in Figure 5.2 so it is difficult to determine if any relationship exists. It is well known that three- and four-ring PAHs may exist in both the gas phase and particulate phase, whilst the higher molecular weight PAHs generally exist only in the particulate phase. It is therefore difficult to draw any inference for the higher molecular weight PAHs about whether a relationship exists between the airborne concentration distribution and the deposition pattern.

Figure 5.3 illustrates the data when the contributions of naphthalene and acenaphthylene have been excluded. It is clear there is an obvious similarity between the two profiles describing the distribution pattern of the airborne PAH and the PAH deposition onto the swatch. The highest airborne concentrations of PAHs correspond to the highest deposition concentrations of PAH on the swatch.

To further investigate whether a relationship can be defined, the relative airborne and deposited PAH concentration against phenanthrene are shown in Figure 5.4. There is an obvious relationship between the airborne concentration and the deposition concentration of these PAHs. The pyrene and fluoranthene ratios show the greatest variance between burns as previously demonstrated in Table 5.2 and this likely reflects the complex relationships within the fire and deposition pathways. The inference also extends to the higher molecular weight PAHs where they have been sufficiently detected.

There is little information available about the direct deposition of PAHs onto the clothing of workers exposed to PAHs in workplace settings. Thus it is difficult to determine whether the measured values are significant and whether the deposited PAH are available to be transported inside the protective clothing. Van Rooij et al. and others (Van Rooij, 1995b; Jongeneelen, 1989; Laitenen, 2010; Cho, 2000; Quinlan, 1995) reported protective clothing reduced the penetration of PAHs, and clean clothing reduced further the penetration of PAHs.

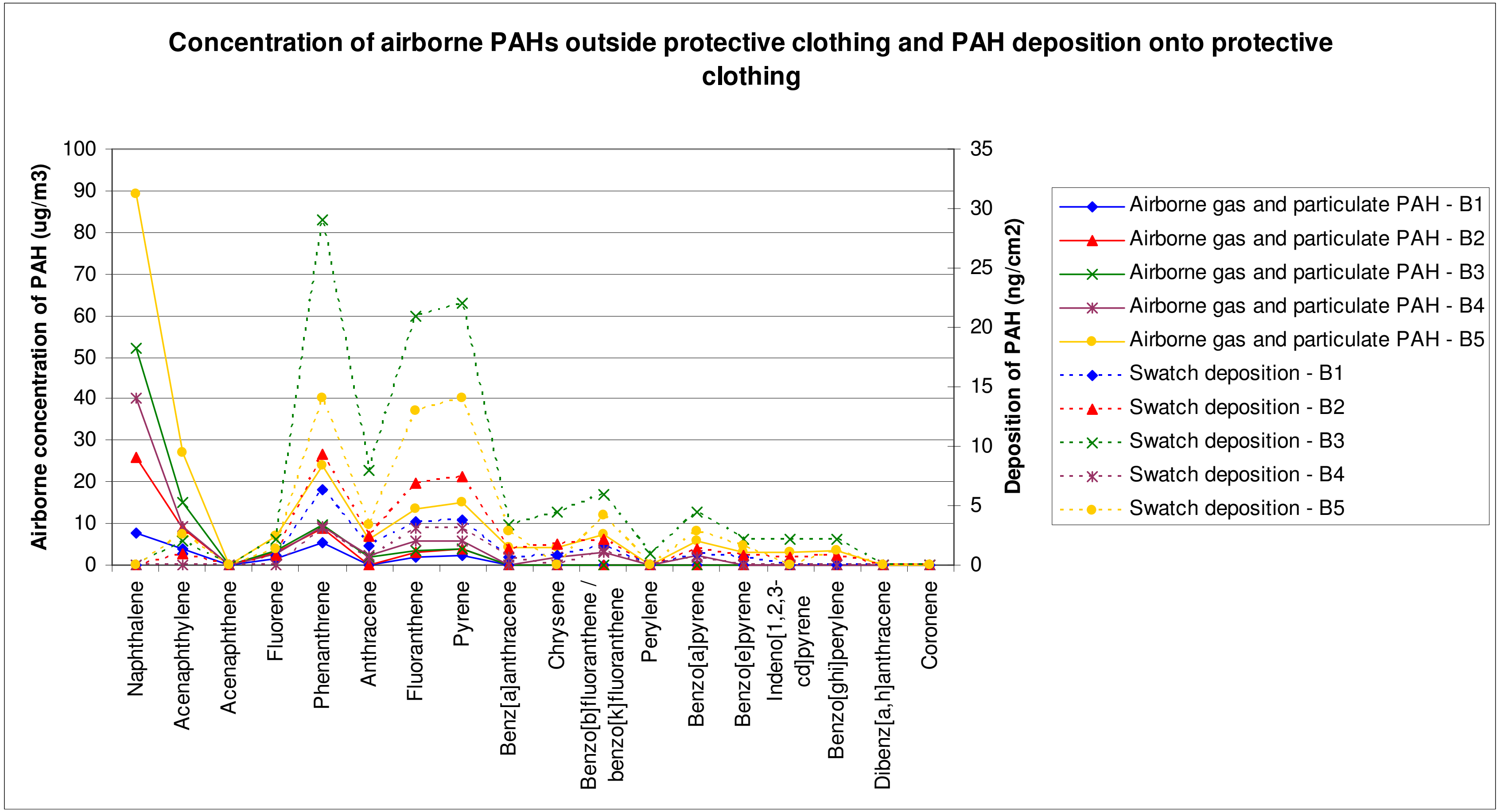

Figure 5.2 Concentration and distribution of airborne PAHs outside the protective clothing and the concentration of deposited PAHs as a function of burn.

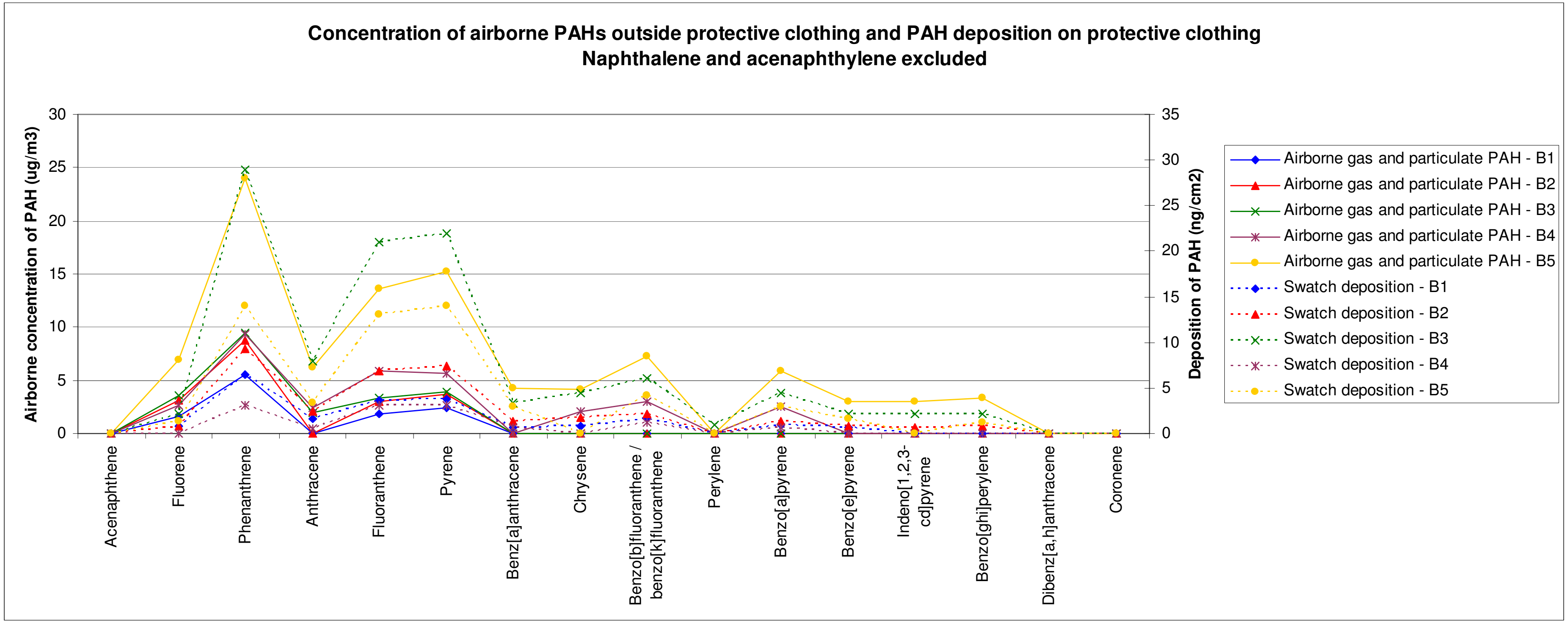

Figure 5.3 Concentration and distribution of airborne PAHs outside the protective clothing and the concentration of deposited PAHs as a function of burn (contributions of naphthalene and acenaphthylene have been omitted).

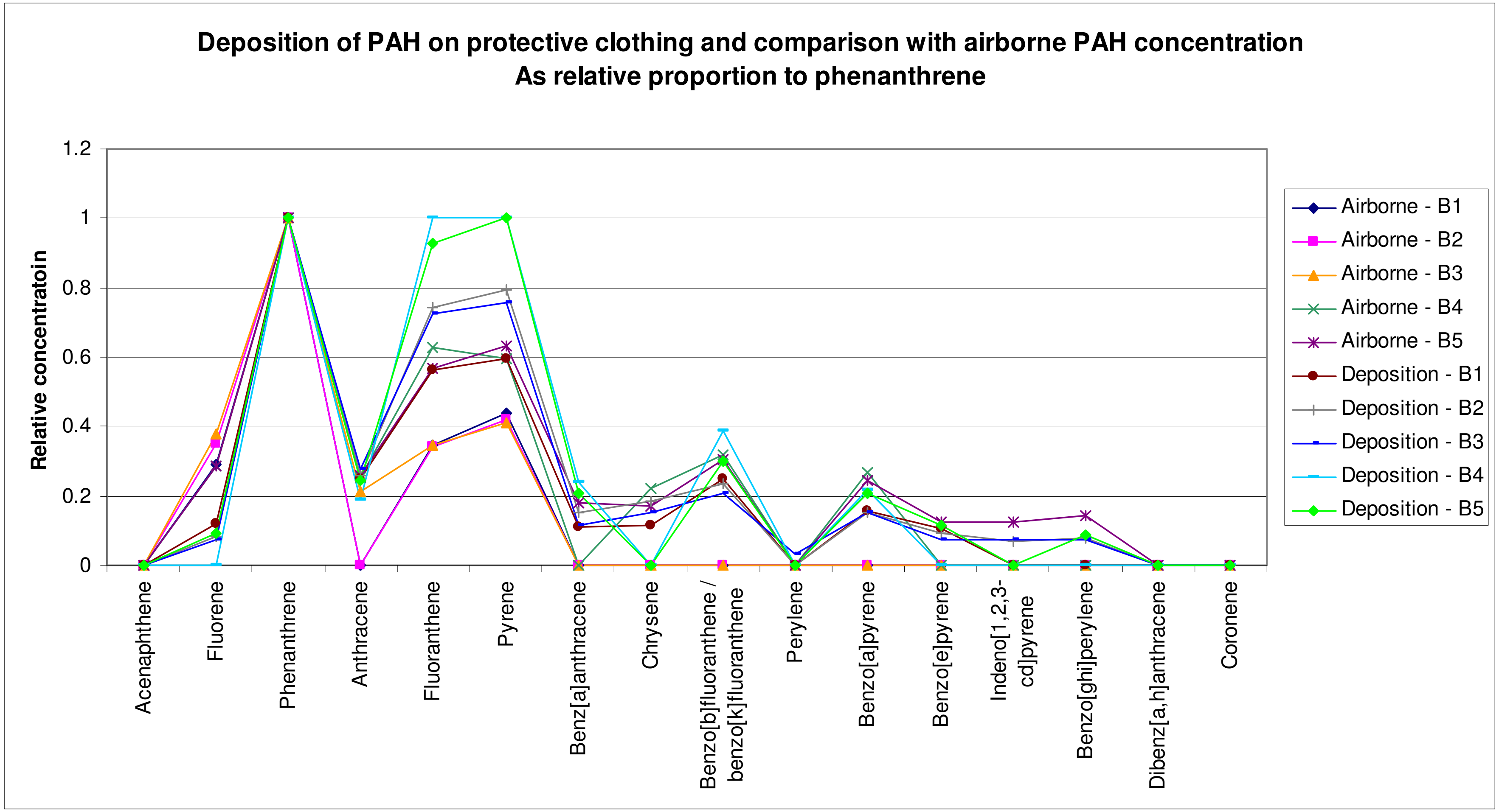

Figure 5.4 Ratio of PAH concentration against the phenanthrene concentration for airborne PAHs outside the protective clothing and deposited PAHs as a function of burn (naphthalene and acenaphthylene excluded).

Summary

The overall results show clearly the firefighter activities cause the direct deposition of PAHs onto the protective clothing. The results show individual variation between the burns and that deposition of benzo[a]pyrene, a known carcinogen, occurs. The PAH deposition pattern is similar to the airborne PAH pattern outside the protective clothing when the contributions of naphthalene and acenaphthylene are ignored. It is likely the greater the smoke concentration and time a firefighter is exposed to, the greater the deposition of PAHs on the protective clothing will be. Nonetheless, the PAH deposition concentration appears to be sensitive to the changes within the environment such fire conditions, tactical differences, firefighter positions and extinguishment.

The total PAH deposition concentration ranged from 12.5 ng/cm^2 to 109.7 ng/cm^2 and the average value was 48.4 ng/cm^2. The variation reflects the differing airborne PAH concentrations due to rapidly changing fire conditions during extinguishment in each activity.

If it is assumed the deposition is uniform and the protective clothing surface area is 4.45 m^2 then the average PAH loading is 2.15 mg. This study has not investigated whether there are distribution differences on the clothing, and the significance of the value is not clear. There is no recognised guidance in the context in firefighting about what constitutes an unsatisfactory amount of absorbed PAH on the protective clothing after a single entry, or multiple entries. The ultimate PAH loading onto the protective clothing is affected by many factors including:

- Fire conditions;
- Firefighter tactics and positioning;
- Smoke concentration;
- Temporal and spatial distribution of smoke; and
- Exposure time.

The complex interplay between these various factors likely contributes to the significant variation of amount of PAH absorbed on the protective clothing despite very similar nature of the activities.

Contaminant transport processes such as emission, resuspension, transfer and redistribution are likely to further complicate the makeup of the final loading (Vermeulen, 2000; Semple, 2004; Schneider, 1999; 2000; Thornburg, 2008). These processes will also affect the deposition concentration and distribution across the protective clothing and transfer to surfaces including within the clothing and hence the firefighter's skin.

As a firefighter is exposed directly to smoke at further fires using the same protective clothing, the PAH loading on the protective clothing is likely to increase. Other contaminants such as dioctyl phthalate, and metal oxides (Aust, 2007) can also be deposited onto the clothing. Whether loadings are affected by prior deposition of PAHs, or whether there is an upper limit to the possible PAH loading on protective clothing, has not been established.

The ready deposition of PAH onto the protective clothing clearly demonstrates that where possible firefighters should avoid direct exposure to smoke. This should be adopted in combination with other approaches to reduce the opportunities to contaminate their clothing such as using water curtains in front of the firefighter, avoiding or minimising contact with surfaces, and where possible remain below the neutral plane.

There is merit to further investigation of the deposition of PAHs and provide guidance about at what loading protective clothing is considered contaminated.

References

Aust N, Forssman B, Redfern N. (2007) Compartment Fire behaviour training exposure study. Heggies. Report 10-5289.

Barker R. Song G, Hamouda H, Thompson D, Kuznetsov A, Deaton AS, Chitrphiromsi P. (2002). Modeling thermal protection outfits for fire exposures. NTC Project S01-N02.

Bilzon J, Scarpello E, Smith C, Ravenhill N, Rayson M. (2001) Characterisation of the metabolic demands of simulated shipboard royal navy fire-fighting tasks. Ergonomics 44, 766-780.

Bolstad-Johnson DM, Burgess JL, Crutchfield CD, Storment S, Gerkin R, Wilson JR. (2000). Characterization of firefighter exposures during overhaul. American Industrial Hygiene Association Journal, 61, 636-641.

Brandt-Rauf PW, Fallon LF, Tarantini T, Idema C, Andrews L. (1988). Health hazards of fire fighters: exposure assessment. British Journal of Industrial Medicine 45, 606-612.

Burgess JL, Nanson CJ, Bolstad-Johnson DM, Gerkin R, Hysong TA, Lantz RC, Sherrill DL, Crutchfield CD, Quan SF, Bernard AM, Witten ML. (2001). Adverse respiratory effects following overhaul in firefighters. Journal of Occupational and Environmental Medicine, 43, 467-473.

Cho S, Kang D, Kand J, Ju Y, S ung C, Lee C, Lee S, Lee Y, Strickland P (2000). Use of urinary polyaromatic hydrocarbon metabolites to assess polyaromatic hydrocarbon exposure intervention among coke oven workers. Journal of Occupational Health, 42, 138-143.

Dreger R, Jones R, Petersen S. (2006). Effects of the self contained breathing apparatus and fire protective clothing on maximal oxygen uptake. Ergonomics, 49, 911-920.

Drysdale DD. (1999). An introduction to fire dynamics. John Wiley and Sons, Chichester.

European Committee for Standardization. (2006). Protective clothing for firefighters – Performance requirements for protective clothing for firefighting - EN 469.

Gold A, Burgess WA, Clougherty EV. (1978). Exposure of firefighters to toxic air contaminants. American Industrial Hygiene Association Journal, 39, 534-539.

Hursh J, Clarkson T, Miles E, Goldsmith L. (1989). Percutaneous absorption of mercury vapour by man. Archives of Environmental Health, 44, 120-127.

Jankovic J, Jones W, Burkhart J, Noonan G. (1991). Environmental study of firefighters. Annals of Occupational Hygiene, 35, 581-602.

Jongeneelen F, Van Leeuwen F, Oosterink S, Anizon R, Van der Lopp F, Bos R, Van Veen H. (1990) Ambient and biological monitoring of cokeoven workers:determinants of the internal dose of polycyclic aromatic hydrocarbons. British Journal of Industrial Medicine, 47, 454-461.

Kutlu B, Cireli A. (2005). Thermal analysis and performance of thermal protective clothing. Fibres and Textiles 13, 58-62.

Laitinen J, Mäkelä M, Mikkola J, Huttu I. (2010). Fire fighting trainers' exposure to carcinogenic agents in smoke diving simulators. Toxicology Letters, 192, 61-65.

Lawson J. (1996). Fire fighter's protective clothing and thermal environments of structural fire fighting. NISTR 5804, National Institute of Standards and Technology.

National Fire Protection Association. (2007). Standard on protective ensembles for structural firefighting and proximity firefighting – NFPA 1971. National Fire Protection Association. USA.

National Fire Protection Association. (2008). Thermal capacity of firefighter protecting clothing. Fire Protection Research Foundation.

Ness S. (1994). Surface and Dermal Monitoring for Toxic Exposures. J.Wiley and Sons

Nigg H, Stamper J, Mahon W. (1986). Dicofol exposure to Florida citrus applicators: effect of protective clothing. Archives of Environmental Contamination and Toxicology, 15, 121-134.

Office of the Deputy Prime Minister. (2005a). Operational physiological capabilities of firefighters: Literature review and research recommendations. Fire Research technical report 1/2005.

Office of the Deputy Prime Minister. (2005b). Physiological assessment of firefighting, search and rescue in the built environment. Fire Research technical report 2/2005.

Perry L. (1999). Chemical Contamination of firefighter turnout coats.Thesis. Queensland University of Technology.

Quinlan R, Kowalczyk G, Gardiner K, Calvert IA, Hale K, Walton ST. (1995b). Polycyclic aromatic hydrocarbon exposure in coal liquefaction workers: the value of urinary 1-hydroxypyrene excretion in the development of occupational hygiene control strategies. Annals of Occupational Hygiene, 39, 329-346.

Rossi R. (2003). Fire fighting and its influence on the body. Ergonomics, 46, 1017-1033.

Schneider T, Vermeulen R, Brouwer D, Cherie J, Kromhout H, Fogh C. (1999). Conceptual model of assessment of dermal exposure. Occupational and Environmental Medicine, 56, 765-773.

Schneider T, Vermeulen R, Cherie J, Kromhout H. (2000). Dermal Exposure Assessment. Annals Occupational Hygiene, 44, 493-499.

Semple S. (2004). Dermal exposure to chemicals in the workplace: just how important is skin absorption? Occupational Environmental Medicine, 61, 376-382.

Song G. (2007). Clothing air gap layers and thermal protective performance in single layer garment. Journal of Industrial Textiles, 36, 193-205.

Stull J, Pinette MF. (1990). Special considerations for conducting permeation testing of protective clothing materials with gases and chemical vapors. American Industrial Hygiene Association Journal, 51,291-296.

Thornburg J, Dart A, Seagraves J, Vanosdell D. (2008). Transfer of contaminant particles from skin or clothing to common household surface and implications to subsequent exposure. Epidemiology, 19, S138.

United States Environmental Protection Agency (EPA). (1992). Dermal exposure assessment: principles and applications. Report EPA/600/8-91/011B, U.S. Washington.

Van Rooij JG, Bodelier-Bade MM, Jongeneelen FJ. (1993a). Estimation of individual dermal and respiratory uptake of polycyclic aromatic hydrocarbons in 12 coke oven workers. British Journal of Industrial Medicine, 50, 623–632.

Van Rooij JG, Van Lieshout EM, Bodelier-Bade MM, Jongeneelen FJ. (1993b). Effect of the reduction of skin contamination on the internal dose of creosote workers exposed to polycyclic aromatic hydrocarbons. Scandinavian Journal of Work and Environmental Health. 19, 200-207.

Van Rooij J, Jongeneelen. (2007). Review of skin permeation hazard of bitumen fumes. Journal of Occupational and Environmental Hygiene, 4 (S1), 237-244.

Vermeulen R, Heideman J, Bos R, Kromhout H. (2000). Identification of dermal exposure pathways in the rubber manufacturing industry. Annals of Occupational Hygiene, 44, 533-541.

Wobst M, Wichmann H, Bahadir M. (1999). Surface contamination with PASH, PAH and PCDD/F after fire accidents in private residences. Chemosphere, 38, 1685-1691.

CHAPTER SIX

DEPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) ONTO THE SKIN

Over the past twenty years the interaction of chemicals with the skin has attracted much attention (United States Environmental Protection Agency, 1992; Bruijinzeel et al., 1995; European Centre for Ecotoxicology and Toxicology of Chemicals, 1993; Bieniek, 1998; Dankovic, 1989; Hardgraft, 2001; McDougal, 1990; Roy, 2007; Schneider et al., 1999; 2000; Scott, 1989; Semple, 2004; Van Rooij et al., 1993ab, 1994; 2007). However, there is little if any information about contaminants deposited onto firefighter skin during operational activities.

It is traditionally accepted that the most significant route of entry for airborne contaminants is the respiratory system. The protection factor assigned to the positive pressure self contained breathing apparatus (SCBA) exceeds 10,000 (Occupational Safety and Health Administration, 2006) and recent studies have reported the protection factor may exceed 400,000 (Denhartog, 2009). If the protected respiratory system is not the major route of entry then it is reasonable to suggest the most significant route of entry for these contaminants is the skin. Walter and Knecht (2007) reported more than 50% of a worker’s PAH dose was obtained by dermal absorption.

It is well established vapours, aerosols and liquids deposit onto the skin from the atmosphere (United States Environmental Protection Agency, 1992; McDougal, 1986; 1987; 1990; Hursh, 1989). If sufficient vapour is deposited, condensation may occur and a liquid-like phase formed. A proportion of these absorbed molecules also evaporate. The molecules will either physically interact (absorption) or chemically interact (adsorption) with the skin surface. The transport of chemicals through the skin (United States Environmental Protection Agency, 1992; Poet, 2001; Ho, 2002) is either active (mediated transport requiring energy) or passive (diffusion requiring no energy).

The penetration rate of gases is significantly less than that of liquids and hence the flux much less (United States Environmental Protection Agency, 1992). Molecules with molecular masses exceeding 350 are too large to pass through the strateum corneum unless there is a break (Ness, 1994). Given the sparse information available about contaminants deposited onto firefighter skin the importance and role of the skin as an entry route in a firefighting context is uncertain. However, there is a growing body of work describing the significance of skin as an entry route for PAHs in other contexts. For example, Walter and Knecht (2007) reported the dermal uptake of various PAHs of workers exposed to bitumen fume accounted for more than half the total dose. Importantly, the skin was shown to be a significant entry route for PAHs especially when respiratory protection was used (Van Rooij et al., 1993a; 1994).

Many studies have investigated the effect of chemical protective clothing as a barrier or sink for contaminants in occupational settings (Brouwer et al., 1999; Goyden and Schwope, 1992; Ness, 1994; Perkins, 1991; Smith and Burker, 1991; Tannahill, 1996; Van Rooij et al., 1993b, 1994). For example: Van Rooij et al. (1993b, 1994) reported the amount of polycyclic aromatic hydrocarbons (PAHs) on the skin decreased by more than 60% if coveralls were donned. They also reported significant inter-day variation and air movement within the coveralls affected the deposition of the PAHs. It was suggested contaminated coveralls were a significant source of skin contamination. There is little information available about the role of protective clothing in a firefighting context and any inferences concerning the potential for transfer of contaminants from the clothing onto the skin of firefighters has been drawn from these related studies.

The study described in the previous chapters focussed on characterising the exposure of firefighters to a variety of airborne contaminants. The results demonstrated firefighters were exposed to airborne contaminants such as polycyclic aromatic hydrocarbons (PAHs) and benzene. Deposition of PAHs onto the protective clothing was also shown. Of particular interest was the finding that a variety of PAH airborne contaminants were present inside the protective clothing immediately adjacent to the skin.

The results described in this chapter illustrate PAHs are directly deposited onto dermal patches (acting as skin surrogates) attached to the skin inside the protective clothing during extinguishment. This study did not attempt to identify or quantify the deposition of volatile organic compounds (VOC) such as benzene onto the skin because of their inherent physico-chemical properties, and the likely concentration of the VOCs inside the protective clothing.

Three dermal patches acting as skin surrogates were located at the chest, arm and inside leg of the firefighter. The PAH deposition distributions and concentrations on the arm, leg and chest dermal patches as a function of burn are shown in Figures 6.1, 6.2 and 6.3 respectively.

Three PAHs were identified once each on arm patches during different burns. They were: naphthalene; phenanthrene; and pyrene. Naphthalene exhibited the highest concentration of all the deposited PAHs. Importantly, the benzo[a]pyrene deposition concentration was less the Limit of Reporting (LOR) on all occasions. The three PAHs identified on the arm patches also exhibited the highest average airborne PAH concentration inside the protective clothing during the burns. The specific burns in which they were each detected did not correspond to the burn where the highest airborne concentration of each PAH was measured. Consequently, there is insufficient information to determine if any relationship between the airborne PAH concentration inside the protective clothing and the PAH deposition concentration onto the arm can be established.

Three PAHs were also identified once each on the leg patches during different burns. As for the arm patches, these were naphthalene, phenanthrene, pyrene. Naphthalene exhibited the highest concentration of all the PAHs deposited on leg patches. Importantly, the benzo[a]pyrene deposition concentration was less the LOR on all occasions. The naphthalene value was the highest value of all the PAH deposition concentration measured on any dermal patch in this study. The specific burns in which they were each detected did not correspond to the burn where the highest airborne concentration of each PAH was measured. Consequently, there is insufficient information to determine if any relationship between the airborne PAH concentration inside the protective clothing and the PAH deposition concentration onto the leg can be established.

The deposition concentrations for all PAHs on chest patches were below the LOR in all burns. The chest is considered the most protected area of the skin within the protective clothing and likely to exhibit the lowest deposition concentration. Results reported in the literature often show the deposition concentration of PAHs in workplace setting is much lower on the chest than measured at the extremities. Nonetheless, the results demonstrate there is insufficient information to determine

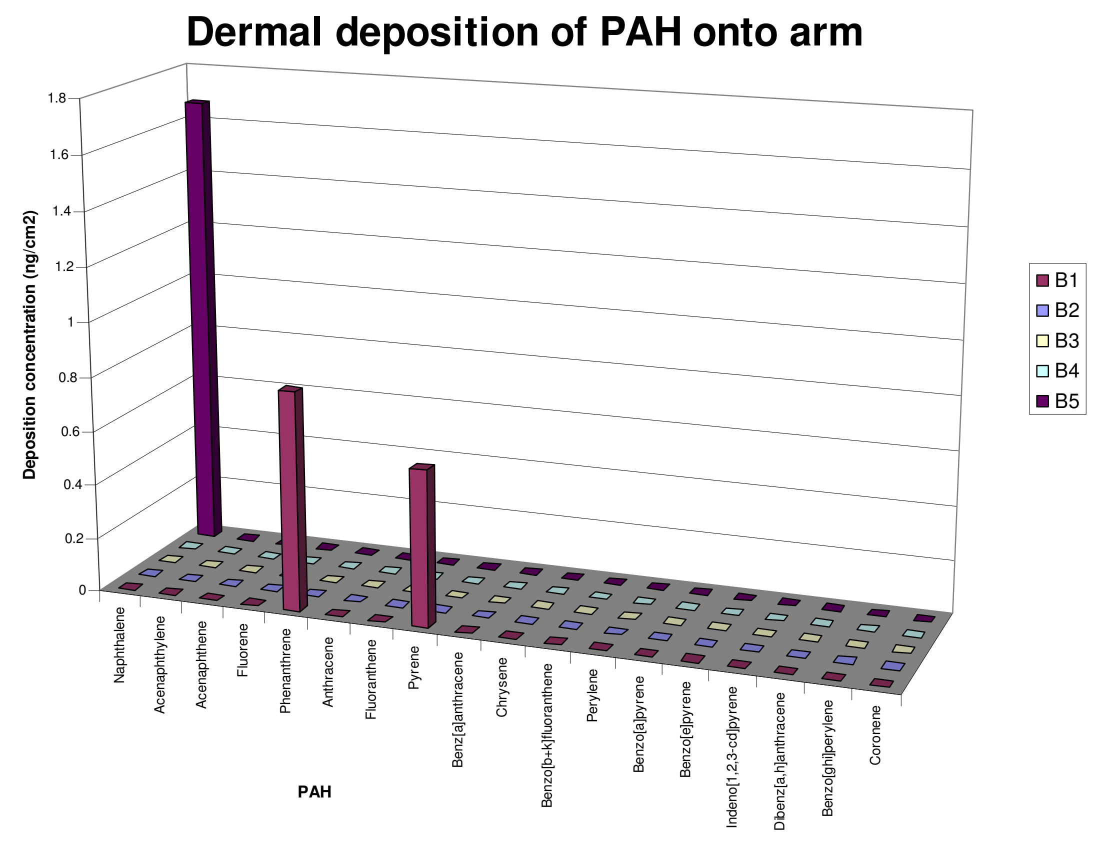

Figure 6.1 PAH deposition distribution and concentration on the arm dermal patch as a function of burn.

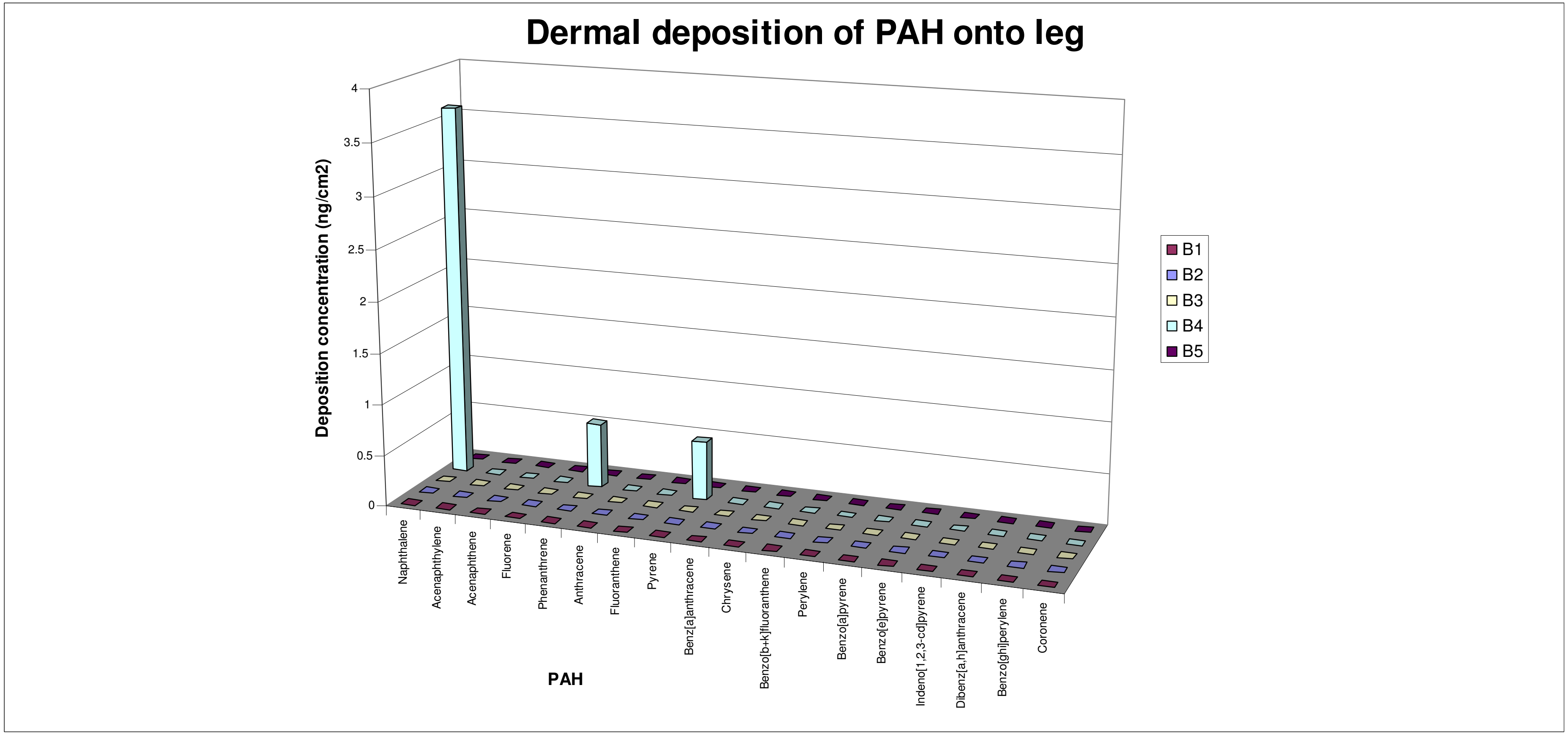

Figure 6.2 PAH deposition distribution and concentration on the leg dermal patch as a function of burn.

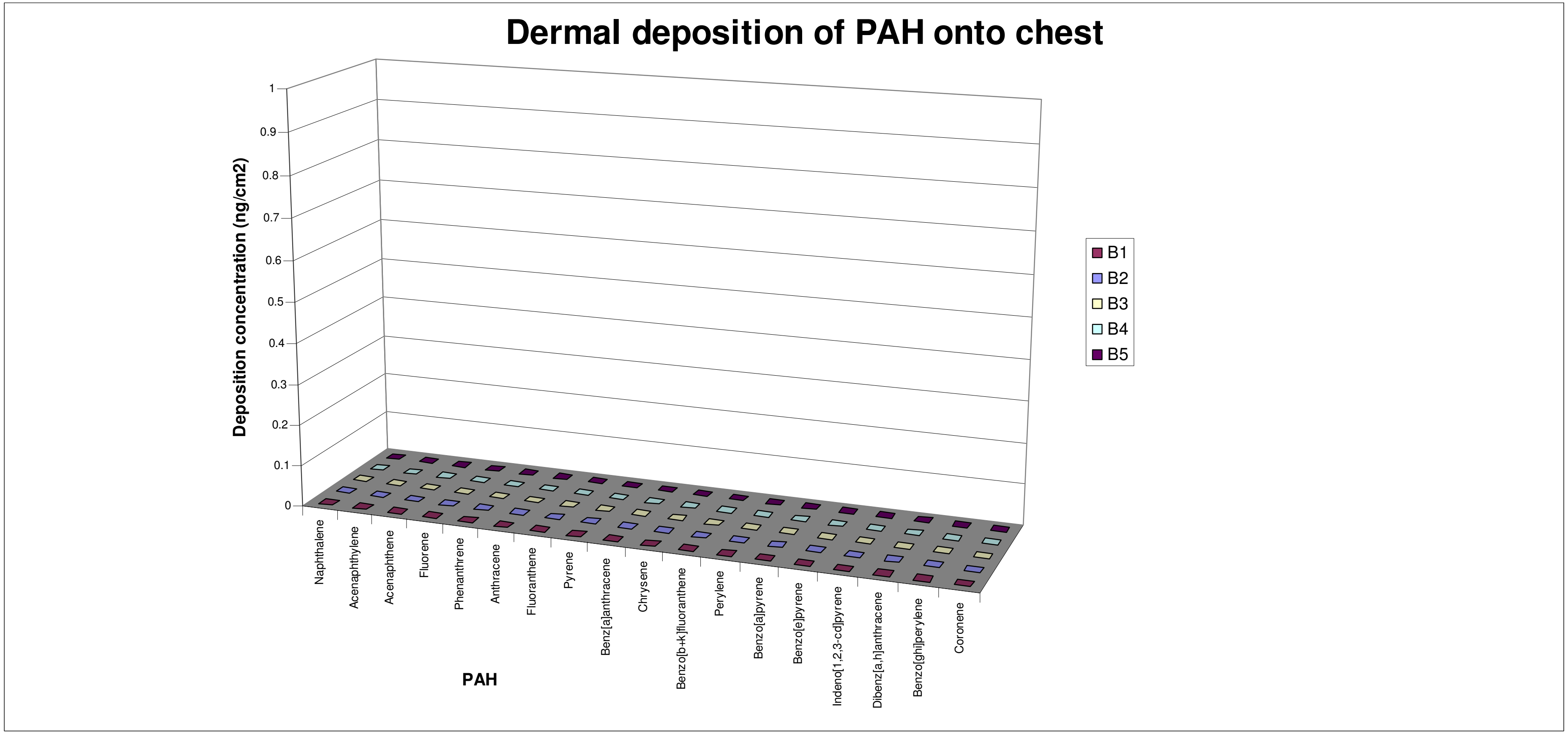

Figure 6.3 PAH deposition distributions and concentrations on the chest dermal patch as a function of burn.

whether any relationship between the airborne PAH concentration inside the protective clothing and the PAH deposition concentration onto the chest can be established.

Summary

The results show clearly the firefighter is exposed to PAHs within their protective clothing and PAH are deposited onto their skin. Significant individual variation is evident between burns, and PAHs were identified only on arm and leg patches. The dermal dose variability reflects the complexity of interactions between the materials, fire and activities. These variations are also commonly reported in studies where worker dermal exposure to PAHs in a variety of workplace setting and various industries has been assessed (Cirla, 2005; McClean et al., 2004, 2007; Väänänen et al., 2005, 2006; Zhou, 1997; Van Rooij et al., 1993a,b 1994, 2007). In general, other studies have reported the greatest PAH concentrations occurred on the hands and other exposed areas of the body.

Recently, Laitinen et al. (2010) reported the deposition of PAHs onto the skin of firefighter trainers during training activities. They found PAHs were readily deposited onto the firefighters, but reported only total skin doses. They suggested using simple risk control measures like cotton gloves reduced the hand PAH dose by up to 80%. Further unpublished work by the QFRS has also found PAHs were readily deposited onto firefighter skin often at much higher concentrations than reported in this study.

In this study the PAH concentration for the chest dermal patch was less than the LOR in all burns, and the average PAH concentrations for the leg and arm dermal patches were 0.98 ng/cm^2 and 0.61 ng/cm^2 respectively. Combining the deposition values gives an average total PAH value of 0.53 ng/cm^2. If it is assumed the skin surface area is approximately 1.8 m^2 (DuBois and DuBois, 1916) then the whole body dose rate is approximately 36,000 ng/hr.

In many published studies, pyrene was used as a marker of PAH dermal exposure (Cirla et al., 2005; McClean et al., 2004, 2007; Van Rooij et al., 1993a,b, 1994, 2007) and the reported dose varied considerably. For example McClean et al. (2007) found the pyrene dose of asphalt workers (over a work shift) varied from 2.4 to 221 ng/cm^2. The average pyrene dermal dose in this study when extrapolated to a whole body dose over an eight hour work day is 3.8 ng/cm^2 and corresponds to the lower end of the work pyrene dose ranges reported in the literature.

Similarly, the total PAH dermal exposure varies significantly across different workplace settings. For example Cirla et al. (2005) reported the median dermal deposition was 300 ng/hr for 9 PAHs and 2,905 ng/hr for asphalt workers.

Cirla et al. (2005) suggested the exposures reported in their study were lower than exposures in other industries, while Feunekes et al. (1997) reported the uptake of PAHs by instructors at a firefighting training facility were similar to the uptake of workers in a variety of other industries. Notwithstanding the restricted number of PAHs measured in the study by Cirla et al (2005), their reported values were much less than the average value calculated in this study.

Laitinen et al. (2010) estimated the dermal whole body exposure of instructors during fire simulations to be 13.5 ± 8.5 ng/cm^2-min for Bristol protective clothing and 14.4 ± 10.8 ng/cm^2-min for Brage protective clothing based on back and chest patches. It is understood the protective clothing investigated by Laitinen et al. complies with the recent European Standard (2006). The Brage protective clothing uses Nomex III and most closely resembles the clothing in this study, but no information was provided about whether it incorporated a moisture barrier. Despite the study limitations, they further reported the PAH doses ranged from 30 ng/cm^2 to 1200 ng/cm^2 depending on the fire simulation and the fuel. These values equate to equivalent whole body doses of 540,000 ng to 21,600,000 ng. These values are significantly higher than the values reported in this study and other unpublished measurements. The values reported by Laitinen et al. (2010) are higher than the highest worker exposures reported in the literature in other settings (Van Rooij et al., 1993a). Interestingly, they suggested the urinary 1-hydroxypyrene concentration (a measure of exposure to PAHs) was less than the recognised action level. This conclusion is of significance to this study and hence it is likely the exposures obtained in this study are much less than the recognised action level.

There are many pathways by which the PAHs can be deposited onto the firefighters' skin. Semple and others (Semple, 2004; Schneider, 1999, 2000) proposed a model to explain the movement of contaminants onto workers' skin. The model included several different pathways. It is clear the results described in the previous chapters show PAHs are present in the air within the protective clothing and are deposited directly onto the outside of the protective clothing. The firefighter actions lead to movement of the airborne contaminants within the protective clothing (the "bellows" and "chimney" effects described in Chapter Three). Subtle changes in the firefighter approaches may result in significant variation in deposition concentrations and patterns within the protective clothing.

The most obvious pathway is direct deposition of airborne PAHs onto the skin. Van Rooij et al. and others (Van Rooij et al., 1993; Cirla, 2005; Zhou, 2001; Laitinen et al., 2010) found the extremities of the workers receive the greatest doses as a result of the greatest and most direct exposure to airborne PAHs. It seems reasonable in this instance that this is also the pathway of greatest significance. Direct transfer of PAHs deposited on the protective clothing either from the external or internal surfaces cannot be dismissed, but this pathway is not likely to be significant since the firefighters removed their clothing immediately after use, and such direct transfer could result in firefighters' hands being the place of highest contamination. The other obvious route is direct transfer of PAHs from smoke- and debris-contaminated surfaces. Wobst et al. (1999) reported the PAH concentration on surfaces within residences after fire ranged from 34.3 μgcm^2 to 58,800 μg/cm^2. It is not likely that this route is significant for this study, since the firefighters minimised contact with surfaces during the fire.

Penetration and permeation of PAHs does occur through the skin and the rates are affected by many factors including skin anatomical features, skin damage and the chemical itself (United States Environmental Protection Agency, 1992; McDougal et al., 1986; 1987; 1990). Dankovic et al. (1989) measured the absorption of PAHs through mouse skin. They found the absorption half life (the time it takes for half the absorbed PAH to move through the skin) of eleven PAHs ranged from 5 hours to 8.8 hours and the half life of benzo[a]pyrene was 6.7 hours. If these PAHs were solvated then the absorption half life decreased significantly. The diagram in Figure 6.4 illustrates the percentage of PAH remaining on the skin as a function of time, using a half-life value of 5 hours. After one hour about 13 % of the PAH has been absorbed, but after 10 hours 75 % is absorbed.

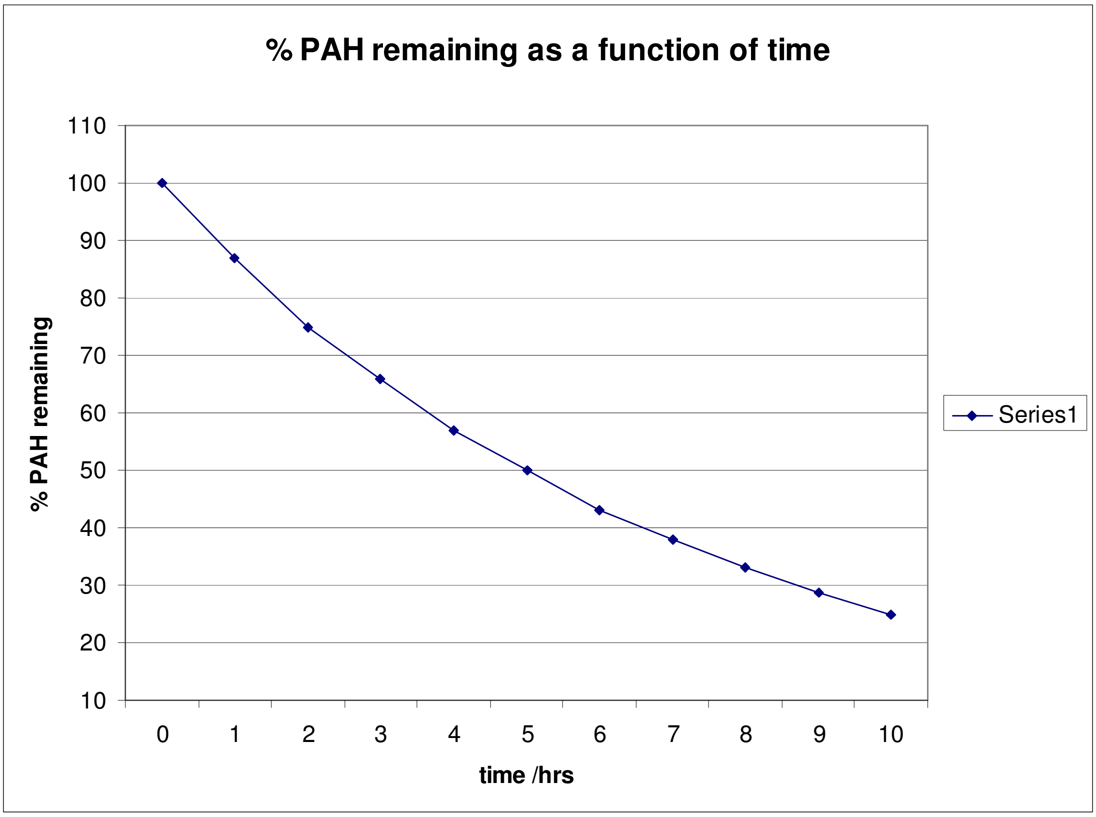

Figure 6.4 Percentage of PAH remaining on the skin as a function of time when the half life is five hours.

Previously reported studies (Caux et al., 2002; Feunekes et al., 1997; Steiner et al., 1997) clearly demonstrated PAH metabolites were in firefighter urine. Feunekes (1997) suggested the skin was a possible route and there was no significant correlation between the airborne PAH and urinary hydroxyl-pyrene. They also suggested the uptake was less than previously reported for workers in other industrial settings such as coke ovens. However there are significant exposure differences between typical firefighter exposures and exposures for workers in other industries (e.g exposure duration). A firefighter has the potential for multiple exposures in short time periods (i.e. attending many fires or multiple entries into a fire). The ultimate dose of PAH received is also affected by their use of respiratory protective equipment and the significant variability of the airborne PAH concentration. These environmental variabilities pose challenges to firefighters attempting to minimise their exposures.

The results provide a valuable insight into approaches that can be adopted to minimise the firefighter's exposure and hence their dose. Given the complexity of the smoke environment, temperature and other factors, the most obvious recommendation is to adopt respiratory protection whenever a task is likely to encounter smoke, or the environment has not been characterised. It should be removed only after the atmosphere has been characterised and the airborne concentrations measured are below the established levels of concern.

The other approaches to minimise the opportunity for PAH deposition onto clothing and the skin during firefighting operations are:

- For both exterior and interior operations, avoid contact with the smoke as much as possible;
- Adopt work methods that encourage the firefighter to stay low and below the smoke neutral plane;
- Stay behind the hose line (water curtain) if it is being used within the structure; and
- Minimise contact with internal surfaces in the structure.

Given that is practically impossible to avoid the deposition of PAH onto the protective clothing and the skin, other risk control measures should be adopted. The ease at which PAHs are deposited onto the protective clothing illustrates the necessity to ensure the protective clothing is regularly cleaned. Cho et al. (2000) illustrated the significance of direct transfer reporting the PAH dose was reduced by up to 50% when new PPE was provided at the start of each working shift. In addition, firefighters should consider using cotton gloves inside their firefighting gloves to further minimise the opportunities for direct transfer of any PAH contaminant from the protective clothing onto their hands, particularly during donning and doffing. The firefighter should also shower as soon as practical after they have undertaken activities within a burning structure. Van Rooij et al (1993b, 1994) suggested PAH doses were significantly reduced if practices such as regularly washing hands were adopted.

References

Bieniek G. (1998). Aromatic and polycyclic hydrocarbons in air and their urinary metabolites in coke plant workers. American Journal of Industrial Medicine, 34, 445-454.

Brouwer D, Kroese R, Van Hemmen J. (1999). Transfer of contaminants from surface to hands: experimental assessment of linearity of the exposure process, adherence to the skin and area exposed during fixed pressure and repeated contact with surfaces contaminated with a powder. Applied Occupational Environmental Hygiene, 14, 231-239.

Bruijinzeel L, Bodelierm M, Noordhoek J, Jongeneelen F. (1995). Dermal absorption of polycyclic aromatic hydrocarbons in the blood-perfused pig ear. Journal of Applied Toxicology, 15, 193-200.

Caux C, O'Brien C, Viau C. (2002). Determination of Firefighter Exposure to Polycyclic Aromatic Hydrocarbons and Benzene During Fire Fighting Using Measurement of Biological Indicators. Applied Occupational and Environmental Hygiene, 17, 379-386.

Cho S, Kang D, Kand J, Ju Y, S ung C, Lee C, Lee S, Lee Y, Strickland P (2000). Use of urinary polyaromatic hydrocarbon metabolites to assess polyaromatic hydrocarbon exposure intervention among coke oven workers. Journal of Occupational Health, 42, 138-143.

Cirla PE**,** Martinotti I, Buratti M, Fustinoni S, Campo L, Zito E**,.** Prandi E**,** Longhi O, Cavallo D, Foā V. (2005). Valutazione dell'esposizione a composti organici aromatici e IPA nelle opere di asfaltura : i resultati dello Studio PPTP-POPA. Giornale Italiano di Medicina Del lavoro ed Ergonomia, 27, 3003-307.

Dankovic D, Wright C, Zangar R, Springer D. (1989). Complex effects on dermal absorption of benzo(a) pyrene and other polycyclic aromatic hydrocarbons., Journal of Applied Toxicology, 9, 239-244.

Denhartog E. (2009). Systemic Approach to protection and ergonomics testing for personal protective equipment. Personal Protective Conference.

DuBois D, DuBois DF. (1916). A formula to estimate the approximate surface area if height and weight be known. Archives of Internal Medicine, 17:863-71.

European Centre for Ecotoxicology and Toxicology of Chemicals. (1993). Percutaneous absorption. Monograph 20, Brussels.

European Committee for Standardization. (2006). Protective clothing for firefighters – Performance requirements for protective clothing for firefighting- EN 469.

Feunekes FDJR, Jongeneelen FJ, vd Laan, H, Schoonhof FHG. (1997). Uptake of polycyclic aromatic hydrocarbons among trainers in a fire-fighting training facility. American Industrial Hygiene Association Journal, 58, 1, 23-28.

Goydon R, Schwope A. (1992). Should protective gloves be used? An analysis of the potential for residual permeation during repeated use. AIHA Conference Abstracts., Boston.

Hardgraft J. (2001). Skin the final frontier, International Journal of Pharmaceutics, 224, 1-18.

Ho C. (2002). A geoscience approach to modelling chemical transport through the skin., SAN, 3690.

Hursh J, Clarkson T, Miles E, Goldsmith L. (1989). Percutaneous absorption of mercury vapour by man. Archives of Environmental Health, 44, 120-127.

Laitinen J, Mäkelä M, Mikkola J, Huttu I. (2010). Fire fighting trainers' exposure to carcinogenic agents in smoke diving simulators. Toxicology Letters, 192, 61-65.

McClean MD, Rinehart RD, Ngo L, Eisen EA, Kelsey KT, Herrick, RF. (2004). Inhalation and dermal exposure among asphalt paving workers. Annals of Occupational Hygiene, 48, 663-671.

McClean M, Rinehart R, Sapkota A, Cavallari J, Herrick F. (2007). Dermal exposure and urinary 1-hydroxypyrene among asphalt roofing workers. Journal of Occupational Environmental Hygiene, 4(S1), 118-126.

McDougal, J.N, Jepson, G.W, Clewell, H.J III, MacNaughton, M.G, Andersen, M.E. (1986). A physiological pharmacokinetic model for dermal absorption of vapors in the rat. Toxicology Applied Pharmacology, 85(2), 286-294.

McDougal, J.N, Jepson, G.W, Clewell, H.J III, Andersen, M.E. (1987). Pharmacokinetics of organic vapor absorption. Pharmacology Skin, 1, 245-251.

McDougal, J.N, Jepson, G.W, Clewell, H.J III, Gargas, M.L, Andersen, M.E. (1990). Dermal absorption of organic chemical vapors in rats and humans. Fundamental Applied Toxicology, 14, 299-308.

Ness S. (1994). Surface and Dermal Monitoring for Toxic exposures. J.Wiley and Sons.

Occupational Safety and Health Administration. (2006). Regulations (Standards – 29 CFR) Standard 1910.134 Respiratory Protection.

Perkins J. (1991). Decontamination of protective clothing. Applied Occupational Environmental Hygiene, 6, 29-35.

Poet T, McDougal J. (2001). Skin absorption and human risk assessment. Chemical-biological interactions, 140, 19-34.

Roy T. (2007). Pecutaneous absorption of polyaromatic hydrocarbons from bitumen fume. Journal of Occupational Environmental Hygiene, 4(S1), 137-143.

Schneider T, Vermeulen R, Brouwer D, Cherie J, Kromhout H Fogh C. (1999). Conceptual model of assessment of dermal exposure. Occupational and Environmental Medicine, 56, 765-773.

Schneider T, Vermeulen R, Cherie J, Kromhout H. (2000). Dermal exposure assessment. Annals of Occupational Hygiene, 44, 493-499.

Scott R, Dugard P, (1989). The properties of skin as a diffusion barrier and route for absorption. In Pharmacology of the skin v2., Editors M.Greaves and S.Shuster., Springer Verlag, 93-114.

Semple S. (2004). Dermal Exposure to chemicals in the workplace: just how important is skin absorption? Occupational and Environmental Medicine, 61, 376-382.

Smith I, Burker K. (1991). Decontamination of protective suit materials in J.Perkins and J.Stull (editors) Chemical Protective Clothing. ASTM, 191-205.

Steiner M, Moen B. (1997). Assessment of exposure to polycyclic aromatic hydrocarbons during firefighting by measurement of urinary 1-hydroxypyrene. Journal of Occupational Environmental Medicine, 39, 515-519.

Tannahill S. (1996). Assessment of exposure to non agricultural pesticides and effectiveness of protective clothing. Institute of Occupational Medicine phase 1 report. HSE research project R3228/R46.60.

United States Environmental Protection Agency (EPA), (1992) Dermal exposure assessment: principals and applications. Report *EPA/600/8-91/011B*, U.S. Washington.

Väänänen V, Hämeilä M, Kalliokoski P et al. (2005). Dermal exposure to Polycyclic Aromatic Hydrocarbons among road pavers. Annals Occupational Hygiene, 49, 167-178.

Väänänen, Elovaara E, Nykyri E, Santonen T, Heikkilä P. (2006). Road pavers' occupational exposure to asphalt containing waste plastics and tall oil pitch. J Environmental Monitoring, 8, 89-99.

Van Rooij JG, Bodelier-Bade MM, Jongeneelen FJ (1993a). Estimation of individual dermal and respiratory uptake of polycyclic aromatic hydrocarbons in 12 coke oven workers. British Journal of Industrial Medicine, 50, 623–632.

Van Rooij JG, Van Lieshout EM, Bodelier-Bade MM, Jongeneelen FJ. (1993b). Effect of the reduction of skin contamination on the internal dose of creosote workers exposed to polycyclic aromatic hydrocarbons. Scandinavian Journal of Work and Environmental Health. 19, 200-207.

Van Rooij J, Maassen L, Bodelier-Bade M, Jongeneelen F. (1994). Determination of skin contamination with exposure pads among workers exposed to polycyclic aromatic hydrocarbons. Appl.Occup.Environ.Hyg, 9, 693-699.

Van Rooij J, Jongeneelen F. (2007). Review of skin permeation hazard of bitumen fumes. Journal of Occupational and Environmental Hygiene, 4 (S1) 237-244.

Walter D, Knecht U. (2007). Standardized investigation of percutaneous absorption of bitumen emission in humans. Journal of Occupational and Environmental Hygiene, 4 Suppl1, 144-153.

Walters K, Roberts M. (2008) Dermal Absorption and Toxicity Assessment. Informa.

Wobst M, Wichmann H, Bahadir M. (1999). Surface contamination with PASH, PAH and PCDD/F after fire accidents in private residences. Chemosphere, 38, 1685-1691.

Zhou Q. (1997). Biomonitoring workers exposed to polycyclic aromatic hydrocarbons in asphalt during road paving. Thesis, University of Cincinnati.

CHAPTER SEVEN

CONCLUSIONS

This study has focused on characterising the exposure of firefighters to various contaminants during extinguishment of simulated room fires. The major results from this study were as follows:

1. Firefighters were exposed to a variety of airborne contaminants outside their protective clothing, including hydrocarbons, oxygenated hydrocarbons, acid gases and polycyclic aromatic hydrocarbons.
2. Concentrations of air contaminants outside firefighters' protective clothing varied considerably between burns, despite the similar fuels, fuel arrangements, and tactics applied to extinguish the fires. This observed variability illustrates the complexity of the interactions between the burning materials, fire behaviour, combustion product formation, temporal elements, firefighter activities and hence exposure.
3. Concentrations of air contaminants outside firefighters' protective clothing were consistent with previously published scientific literature regarding air contaminants from structural fires and simulated structural fires.
4. Polcyclic aromatic hydrocarbons, including benzo[a]pyrene (a known carcinogen), are readily deposited onto protective clothing during extinguishment.
5. Protective clothing affords some protection against the ingress of airborne contaminants during extinguishment, the concentrations of airborne contaminants inside the protective clothing typically 50% to more than 99% lower than the external concentrations.
6. Direct deposition of polycyclic aromatic hydrocarbons onto the skin occurred at low concentrations, although it was not observed in all instances. The skin is a route of entry to the human body for toxic combustion products that therefore cannot be discounted.

A firefighter has the potential for multiple exposures in short time periods (i.e. attending many fires or multiple entries into a fire). The ultimate dose of toxic combustion products received is affected by firefighters' use of respiratory protective equipment and the significant variability of the airborne concentration. These environmental variabilities pose challenges to firefighters attempting to minimise their exposures. A series of recommendations have been provided to reduce the opportunities for exposure and hence reduce the cumulative dose of toxic combustion products to firefighters. These recommendations include:

- Avoid / minimise the exposure to smoke;
- Adopt Self Contained Breathing Apparatus to prevent exposure to the smoke;
- Where possible remain below the neutral plane and behind the active water spray whilst extinguishing the fire, for both exterior and interior operations;
- Minimise contact with internal surfaces of a structure;

- Shower as soon as reasonably practical after extinguishing the fire to reduce the opportunities for any deposited PAHs to enter the skin; and
- Communicate the findings of this study to operational firefighters.

Further research currently or soon to be conducted by QFRS Scientific Branch pertains to a number of related topics and areas that have been identified as requiring additional investigation. These include:

- Firefighter exposures to airborne contaminants during extinguishment of simulated office room fires, petrochemical fires and industrial fires;
- Deposition of PAHs on protective clothing, including at what loading should protective clothing be considered contaminated;
- Off-gassing from protective clothing after heavy use.

Also noted in this study as warranting further investigation is the effect on permeation of combustion products, if any, of the moisture barrier within the protective clothing. This remains outside the scope of studies currently being conducted by QFRS Scientific Branch.