



**Firefighter Exposures to Airborne  
Contaminants during Extinguishment of  
Simulated Liquefied Petroleum Gas (LPG) Fires**

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## CHAPTER ONE

# COMBUSTION PRODUCTS OF LIQUEFIED PETROLEUM GAS (LPG) FED FIRES: LITERATURE

### 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). Liquefied Petroleum Gas (LPG) is a mixture of hydrocarbons. The major constituent is propane; typically the proportion is above 85%. The composition of the minor products depends on several factors including the source of the LPG and may include:

- Butane;
- Isobutane;
- Propylene; and
- Butenes.

LPG finds great use as a household and industrial fuel. It is also a common precursor chemical in the chemical manufacturing industry. Consequently, there is a vast literature concerning the chemistry of LPG during thermolysis, oxidation and pyrolysis over various materials under a vast array of experimental conditions (Arbake and Susu, 1988; Warnatz, 1985; Santos and Delichatsios, 1984; Harris and Egerton, 1948; Volkan and April, 1977; Lifshitz and Frenklach, 1975; Nabavi et al., 2007; Oehlschlaeger et al, 2005; Landi et al., 2004; Caeiro et al, 2006, Kumar and Sarkar, 1984; Hilde et al., 2005). The combustion products generated reflect:

- Chemical constituents of LPG and quantity;
- 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 (Hautmann et al., 1981, Knox and Kinnear, 1971; Yokley and Ferguson, 1958; Cooke and Williams, 1975; Jachimowski, 1984; Harris et al., 1988a,b; Horning, 2000; DiNenno et al., 2002; Karlsson and Quintiere, 1999; Turns, 1996) can be described and include:

- Carbon dioxide;
- Particulates such as carbon;
- Carbon monoxide;
- Undecomposed product;
- Unsaturated hydrocarbons including aromatic hydrocarbons and polycyclic aromatic hydrocarbons;
- Saturated hydrocarbons; and
- Partially oxygenated organics including organic acids, aldehydes and ketones such as acrolein.

Very little specific information regarding the combustion products generated in typical industrial fires involving LPG has been reported (Cowley and Pritchard, 1990; Wighus, 1994; Hirst 1984; Tam and Cowley, 1988; Mannan, 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 (Karlsson and Quintiere, 1999; Turns, 1996; Gray, 1974; Volkan and April, 1977). Those few studies that have considered actual firefighting environments tend to focus on the consequences of BLEVEs and other explosions or fires on on-shore and off-shores facilities (Park et al., 2006, Moodie, 1988; Cowley and Pritchard, 1990; Hirst, 1984; Birk, 1995; Birk et al., 2007; DiNenno et al., 2002)

This chapter will summarise the major factors influencing the exposure of firefighters to combustion products in LPG-fed 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 LPG-fed 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 their selection of:

- their selection of extinguishing agent;
- their method of applying the extinguishing agent; and
- the physical placement of firefighters with respect to the direction of the emitted radiant heat and smoke plume.

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

### ***Fuel composition***

Unlike modern residences where a plethora of materials ranging from fuels, plastics to wood are present (Stefanidou et al., 2008), LPG-fed fires are distinguished by the relative homogeneity of the fuel. (Volkan and April, 1977). The presence of additives and higher molecular weight hydrocarbons can significantly alter the yield of some combustion products per gram of fuel consumed and the consequent smoke toxicity under fire conditions (Lowesmith et al., 2007; Paulson and Moran, 1974, Kozlowski et al., 1999).

### ***Ventilation***

It is known from pyrolysis and flaming combustion studies of LPG the fire ventilation conditions make a significant difference to the quantity and profile of combustion products and the radiant heat generated (Volkan and April, 1977; Berl and Halpin, 1979; Wong et al. 2006; Yokley and Ferguson, 1958; Werle et al., 2010; Layokun 1979). From an industrial perspective much work concerning the combustion or oxidation of LPG has focussed on optimising the operating conditions particularly as an industrial feedstock.

### ***Firefighting***

The majority of reported studies of firefighter exposure to toxic combustion products in actual fires focussed on exposures obtained at residential fires or within training facilities (Gold et al., 1978; Treitman et al., 1980; Brandt-Rauf et al., 1988; Caux et al., 2002, Feunekes et al., 1997; Laitinen et al., 2010). The authors are not aware of any specific studies investigating firefighter exposures to combustion products generated during LPG fires with the exception

of Laitinen et al, who reported some data about firefighter exposures obtained in training scenarios. They found the exposures incurred when LPG was the fuel were less than those incurred when other materials were burnt.

### ***Smoke behaviour and firefighter placement***

The behaviour of smoke generated during LPG fires is complex and complicated by the fact these fires tend to be external. In addition they are influenced by the enormous amount of radiant heat generated and often the direction of the jet emanating from the pipe break. The smoke quickly rises and is dispersed by cooling sprays applied by firefighters.

The placement of firefighters has a considerable impact on the level of contaminant to which they are exposed. Variations are difficult to predict due to the effects of turbulence and the effect of the water curtains applied to disperse and reduce the effect of the radiant heat. However remaining behind the water curtains clearly offers advantages in reducing exposure to smoke and other airborne contaminants during extinguishment in addition to reducing thermal exposure.

### **Exposure pathway**

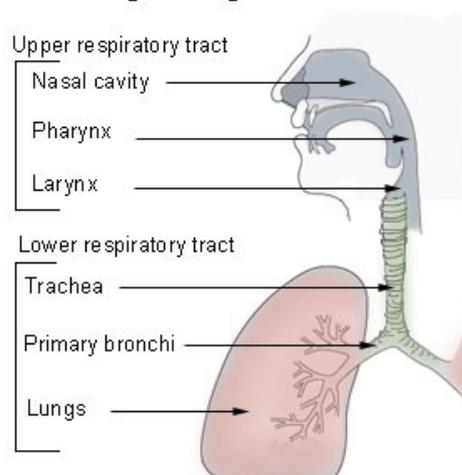
The turbulent nature of the atmosphere within the fire, heat generation and the resulting air movement causes the contaminants to be readily dispersed within the immediate environment and their concentrations to rapidly dissipate as they rise and are vented from the structure. The complexity of the fire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

### ***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,
  
- the Lower Respiratory Tract, where exchanges of gases with blood stream occur, consisting of the:
  - respiratory airways;
  - trachea and bronchioles;
  - lungs – respiratory bronchioles, alveolar ducts, alveolar sacs and alveoli.

### Conducting Passages

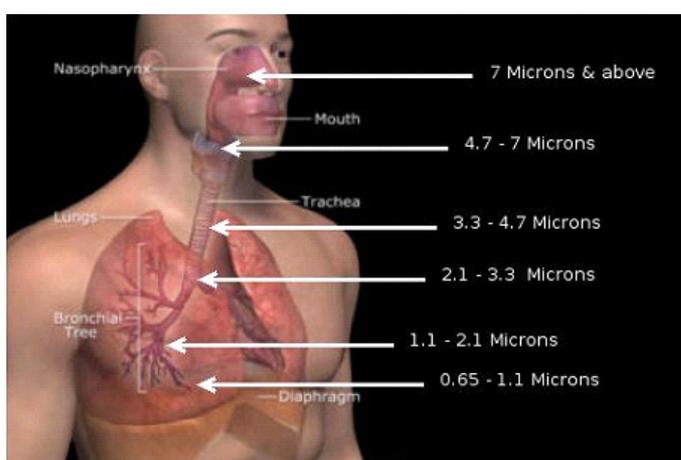


**Figure 1.1** Conducting passages of lungs.

Source: [http://en.wikipedia.org/wiki/Upper\\_respiratory\\_tract](http://en.wikipedia.org/wiki/Upper_respiratory_tract))

The inhalation of and rate of inhalation of particulate matter, and 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 micrometres ( $< 10 \mu\text{m}$ ) in diameter will be inhaled into the body. Typically, respirable particulate matter greater than 5 micrometres ( $> 5 \mu\text{m}$ ) in diameter does not pass the upper respiratory tract, but particulate matter  $< 5 \mu\text{m}$  can pass into the lower respiratory tract and the lungs.

Ultrafine particles less than 2.5 micrometres 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](http://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 and the contaminant may also induce biochemical, morphological or functional changes within the lung. These effects may be both short term and long term (Clayton and Clayton, 1978; Hill, 1980; Amdur et al., 1991; Salem and Katz, 2006).

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. There is little evidence reported concerning the importance of the skin as an entry route in the context of firefighting. 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 detoxify and excrete the contaminant.

## **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, and also review the scientific literature regarding previously measured concentrations of those combustion products in fires involving liquefied petroleum gas. 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<sub>50</sub>:** "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<sub>10</sub> (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<sup>3</sup> (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°C
Autoignition Temperature	608 – 700 °C
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 <sub>10</sub> (inhalation) (human)	4000 ppm (30 min)

### *Generation and concentration in LPG-fed fires*

Virtually every fire generates carbon monoxide, as all carbon-based fuels produce CO as a result of incomplete combustion. In the case of LPG much work has been undertaken to characterise the generation of CO. As a major product of combustion, carbon monoxide is formed primarily in underventilated fires. However, Santos and Delichatsios (1984) suggested CO production from burning LPG pool fires was not significantly affected by ventilation.

## Volatile organic compounds (VOCs)

### *Physical and toxicological properties*

	<b>Benzene</b>	<b>Toluene</b>	<b>Xylene</b>
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 <sub>10</sub> (inhalation) (human)	2000 ppm (5 min)	-	10 000 ppm (6 hr)
LC <sub>50</sub> (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 LPG fires***

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. LPG generates little smoke, but it has been reported that low concentrations of compounds such as benzene, toluene, xylene and styrene are generated during the combustion of propane and n-butane (Mukai et al., 1965; Marinov et al., 1998). The formation of other VOCs such as ethane, ethylene and propylene during the combustion of propane have been described in studies by Layokun (1979) and Jachimowski (1984).

## Aldehydes

### *Physical and toxicological properties*

	<b>Formaldehyde</b>	<b>Acrolein</b>
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 <sub>50</sub> (inhalation) (rat)	64 000 ppm (4hr)	8.3 ppm (4hr)
LC <sub>10</sub> (inhalation) (human)	-	5.5 ppm

### *Generation and concentration in LPG 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 minor quantities of methanol, ethanol, formaldehyde and organic acids have been reported during the combustion of LPG, propane and butane. Many of these products have been detected in cool flame oxidation and in some instances organic peroxides were also generated. However, they are usually short lived and their concentration is dependent on the distance from the burner, and air/fuel equivalence ratio. The most favoured products appear to be methanol, formaldehyde and formic acid (Zervas, 2005).

## 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 (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 (McClellan 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., 1993 a,b; Quinlan et al., 1995).

### ***Generation and concentration in LPG fires***

Despite the attention to occupational PAH exposure generally, there have been very few published studies about PAH formation in LPG, propane, or butane flames. Marinov et al (1998) reported cyclopentadiene was a key intermediate during the formation of PAHs and benzene also contributed to the production of higher order PAHs. Modelling of propane and similar simple alkane combustion suggests an array of PAHs at low concentrations are generated within the flames eg. phenanthrene (< 4 ppm).

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## CHAPTER TWO

# EXPERIMENTAL DESIGN

### Introduction

The Queensland Fire and Rescue Service School of Fire and Rescue Service Training uses a variety of open-air facilities to assist with delivery of petrochemical firefighting training, including a large multi-level process plant and a petrochemical valve/flange/split pipe training area.

### Petrochemical training scenarios

Measurements were conducted during a total of five petrochemical training scenarios. All tests were conducted on the multi-level process plant (Figure 2.1), and involved a team of two firefighters advancing on a jet fire using a single hose line (water curtain spray configuration) as protection (Figure 2.2). Tests were conducted under the supervision of a safety supervisor, with gas flow controlled by site personnel from a remote control point.



**Figure 2.1** School of Fire and Rescue Service Training - Multi-level process plant

### Firefighters

Personnel from the Queensland Fire and Rescue Service School of Fire and Rescue Service Training participated in each petrochemical fire test. 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



**Figure 2.2** Firefighters (white helmets) advancing on jet fire under supervision of safety supervisor (yellow helmet).

IIIA, a moisture barrier consisting of a breathable polyurethane membrane, and thermal barrier of Sontara E89. Additional personal protective clothing included firefighting gloves, boots, flash hood and helmet. Respiratory protection was not worn for the tests, in accordance with existing standard procedures for instructors and trainees at the School of Fire and Rescue Service Training.

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.

Active and passive sampling media were attached to the lead firefighter in the team. 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.

### **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 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 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 (petrochemical training scenario), 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 below.

## **Sampling and Analytical methods**

### ***General information***

Sampling of air contaminants and surface deposition was conducted on one of the two firefighters in each training scenario. Sample collection began at donning of personal protective equipment in a fresh air environment, and ended at the firefighters' return to the fresh air environment for doffing of personal protection equipment. After collection, all samples (except whole air samples) were refrigerated for transport to the laboratory for analysis, accompanied by transport blanks.

### ***Active air sampling***

Active air sampling during each training scenario was conducted both inside and outside the structural firefighting ensemble of the firefighter. To ensure consistency during active air sampling, air flow rates through the sampling tubes were measured before and after sample collection using a Defender 510 Primary Flow Meter (Bios International Corporation) for samples collected with a nominal air flow rate at or above 400 mL/min, or a Dry Cal DC-Lite

Primary Flow Meter (Bios International Corporation) for samples collected with a nominal flow rate below 400 mL/min. 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.

Prior to the first training scenario, sampling was conducted for volatile organic compounds, carbonyl compounds, acid gases, hydrogen cyanide and polycyclic aromatic hydrocarbons in order to establish the ambient atmospheric concentrations of these materials at the site. Reported concentrations of atmospheric contaminants reported in this study have been adjusted for these background levels, and represent the contaminants generated by the training scenarios only.

### ***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  $\mu\text{L}$  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 100 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, 1999a). 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 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, 1999b). The LOR for individual carbonyl compounds ranged from 0.3 to 1  $\mu\text{g}$  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 0.2 µg/tube for bromides, 0.5 µg/tube for fluorides, chlorides and nitrates, 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 2000 mL/min 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, 1999c). The glass fibre and PUF sections were extracted separately using Accelerated Solvent Extraction (ASE) with cyclohexane, concentrated, and the final 1mL volume analysed using GC-MS. The limit of reporting for analysis was 50 ng/sample for individual PAHs in each of the vapour and particulate phases (except coronene, for which the LOR was 500 ng/sample).

### ***Whole air***

Whole air samples were collected during each training scenario using Silonite® MiniCans™ (Entech Instruments, Inc). These canisters have 1 litre air capacity, and a layer of fused silica as an inert lining to prevent reaction during storage between sample components and the sample container. A restrictor was used to control the volume of air entering the canister per minute, so that the air sample was collected over the full duration of the training scenario. 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 United States Environmental Protection Agency Compendium Method TO-17 (Center for Environmental Research Information, 1999a). The limit of reporting for individual VOCs was 0.5 parts per billion (ppb).

## **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 similar to that used for the glass fibre/PUF tubes as described above. However, the limit of reporting for this analysis was 10 ng per swatch.

### **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 0.1 $\mu$ m (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 analytical method for these samples was similar to that used for the glass fibre/PUF tubes as described above. However, the LOR for each individual PAH in this analysis was 10 ng per patch (except for coronene, for which the LOR was 20 ng/patch).

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## CHAPTER THREE

# EXPOSURE OF FIREFIGHTERS TO 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), although this study focussed on the 18 PAHs listed by the United States Environmental Protection Agency (1993) because of their toxicity. This chapter focuses on establishing the concentration and distribution of PAHs to which firefighters were exposed outside and inside their protective clothing during extinguishment.

The tactical method adopted by the firefighters incorporated approaches to minimise their exposure and any opportunities for contamination. These approaches to extinguishing the outside burning liquefied petroleum gas (LPG) industrial plant where possible included:

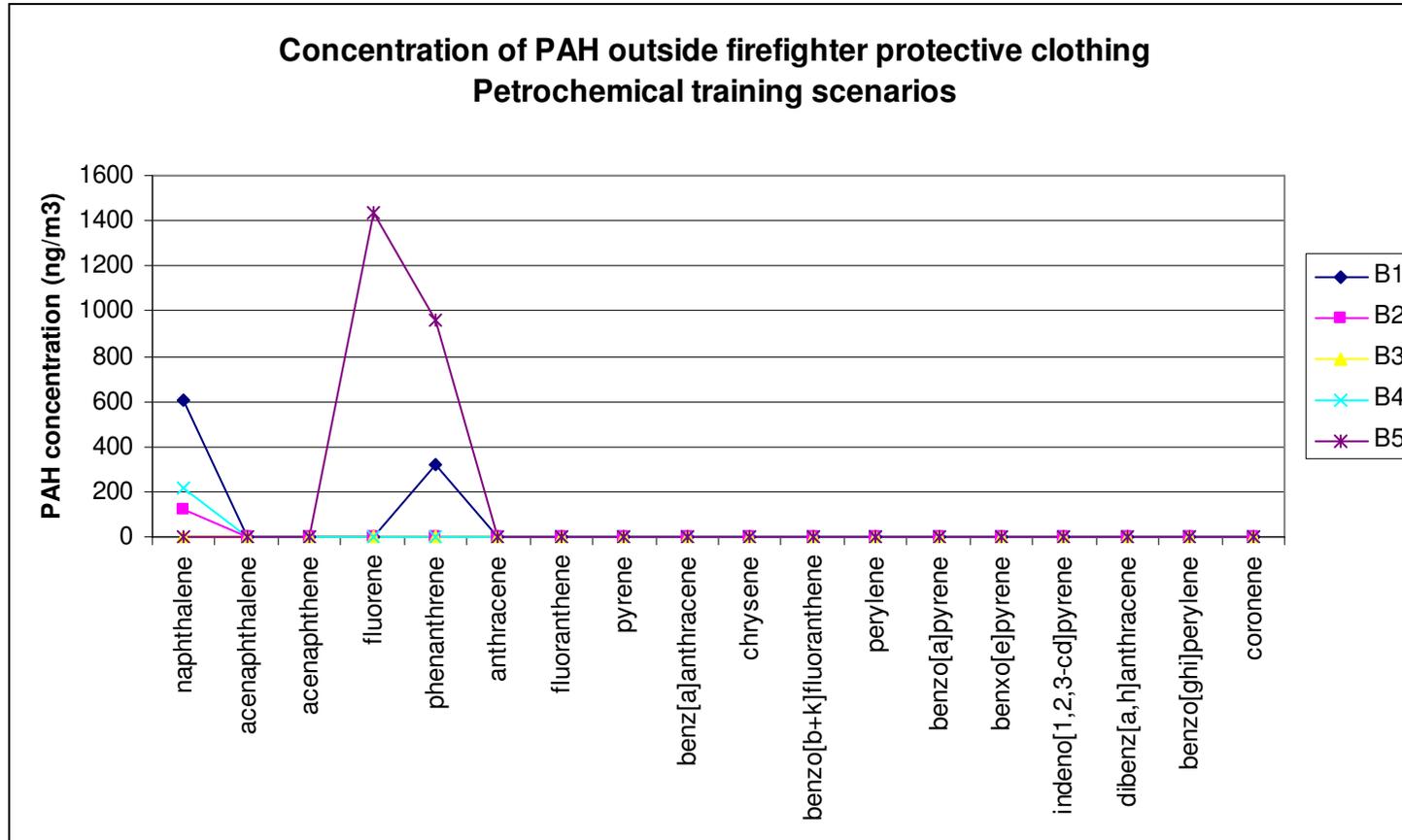
- Avoiding contact with smoke;
- Remaining upwind where possible; and
- Remaining behind the water spray whilst cooling the fire/structure and extinguishing the fire

### Outside Protective Clothing

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

The type and concentration of the PAHs identified varied between burns. Three PAHs were identified: naphthalene, fluorene and phenanthrene. These PAHs are two- and three-aromatic ring molecules. Naphthalene was detected in all training scenarios, but was present at concentrations above existing background levels during only three training scenarios. The average naphthalene concentration measured outside the firefighters' protective clothing was 2,500 ng/m<sup>3</sup>, however the average contribution from the LPG combustion was only 190 ng/m<sup>3</sup>, with the remainder coming from ambient sources. The highest naphthalene concentration measured (even including ambient sources) is below the established Australian National Exposure Standard (NES) of 10 ppm (52.4 mg/m<sup>3</sup>) (Worksafe Australia, 1995) and the equivalent United States exposure standard (National Institute for Occupational Safety and Health, 2007). It is also less than the established odour threshold of 0.038 ppm (Chemwatch, 2010).

The total PAH exposure of the firefighters was higher than the typical PAH exposures reported within urban environments. Unwin et al. (2006) reported worker exposures to airborne PAH in the United Kingdom. They also reported the PAH exposures varied from 0.08 µg/m<sup>3</sup> to 1912 µg/m<sup>3</sup> and the mean was 93.62 µg/m<sup>3</sup>. The values obtained in this study were less than the mean worker PAH exposures reported by Unwin et al. (2006). Firefighter total PAH exposures were also significantly less than the range of firefighter PAH exposures reported in the literature (Jankovic, 1991; Aust et al., 2007; Laitinen et al., 2010).



**Figure 3.1** Type of PAH and concentration outside firefighter protective clothing for each training scenario.

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

PAH	External concentration (ng/m <sup>3</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Naphthalene	<b>600</b>	<b>100</b>	< LOR	<b>200</b>	< LOR
Acenaphthylene	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthene	< LOR	< LOR	< LOR	< LOR	< LOR
Fluorene	< LOR	< LOR	< LOR	< LOR	<b>1400</b>
Phenanthrene	<b>300</b>	< LOR	< LOR	< LOR	<b>1000</b>
Anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR
Pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Benz[a]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Chrysene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[b+k]fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR
Perylene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[a]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[e]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Indeno[1,2,3-cd]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Dibenz[a,h]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[ghi]perylene	< LOR	< LOR	< LOR	< LOR	< LOR
Coronene	< LOR	< LOR	< LOR	< LOR	< LOR

Average naphthalene and total PAH values measured outside the firefighters' protective clothing are significantly less than the corresponding average values obtained during the simulated residence and office fires. These differences arise from a combination of differences between the environments. The fuel for the fire is one significant consideration. Polycyclic aromatic hydrocarbons are generated during the combustion of LPG, however, they are not favoured minor products. Industrial fires involving LPG usually involve steel structures and generate significant radiant heat and little smoke, unless higher molecular weight hydrocarbons and other materials are involved (Dills and Beaudreau, 2008). However, other factors such as external versus internal operations, different firefighter posture and different extinguishment tactics may also have played a role, since the firefighter PAH exposures in this study were significantly less than the PAH exposures obtained by firefighters extinguishing LPG-fed fires within an internal structure as reported by Laitinen (2010).

### 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 airborne PAH distribution and concentration inside the protective clothing for each burn is in Figure 3.2.

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

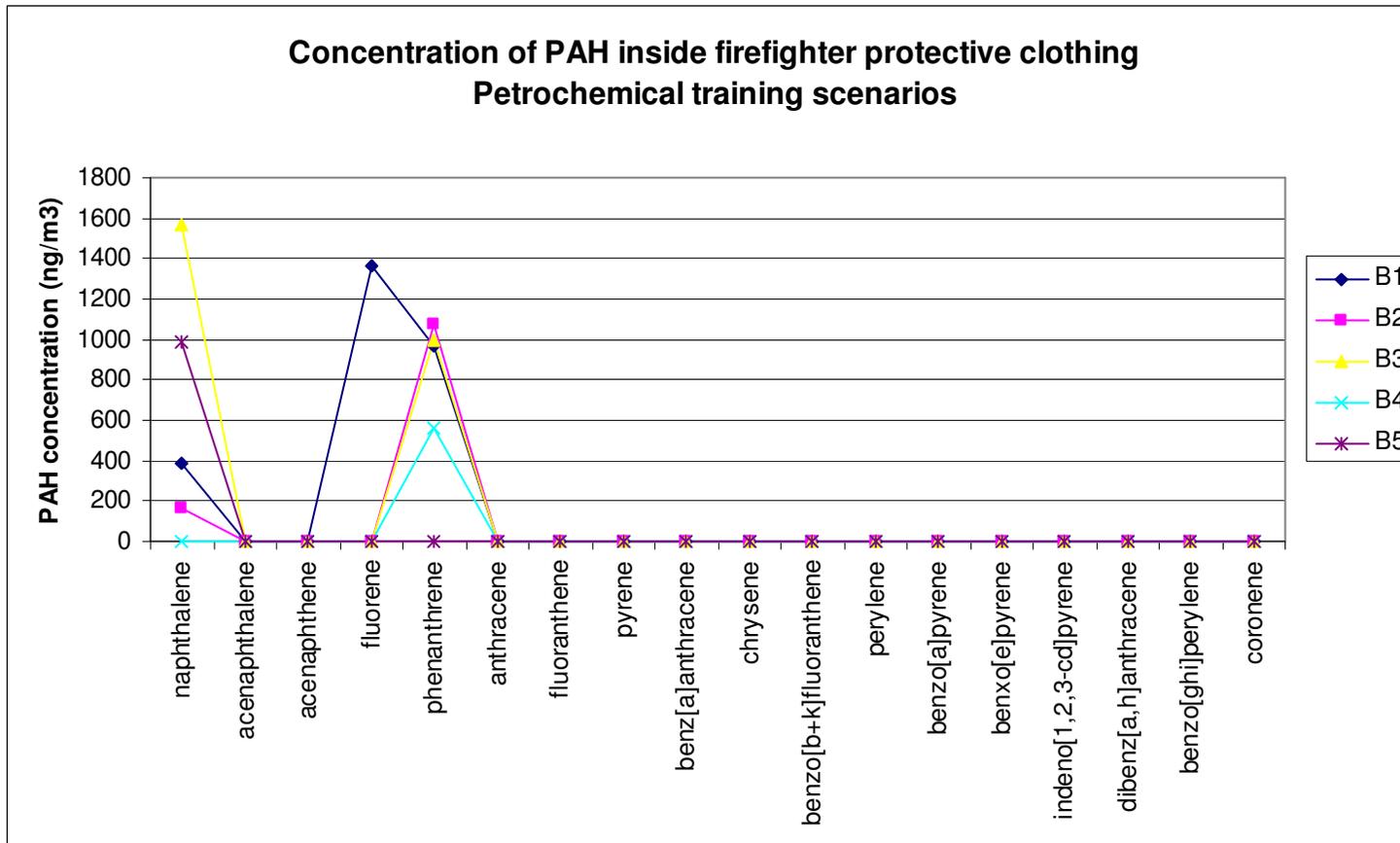
PAH	Internal concentration (ng/m <sup>3</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Naphthalene	<b>400</b>	<b>200</b>	<b>1600</b>	< LOR	<b>1000</b>
Acenaphthylene	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthene	< LOR	< LOR	< LOR	< LOR	< LOR
Fluorene	<b>1400</b>	< LOR	< LOR	< LOR	< LOR
Phenanthrene	<b>1000</b>	<b>1000</b>	<b>1000</b>	<b>600</b>	< LOR
Anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR
Pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Benz[a]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Chrysene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[b+k]fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR
Perylene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[a]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[e]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Indeno[1,2,3-cd]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Dibenz[a,h]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[ghi]perylene	< LOR	< LOR	< LOR	< LOR	< LOR
Coronene	< LOR	< LOR	< LOR	< LOR	< LOR

Results obtained inside the protective clothing exhibited substantial variance between the burns. Naphthalene and phenanthrene were the most common PAHs to which firefighters were exposed, with average concentrations of 600 ng/m<sup>3</sup> and 700 ng/m<sup>3</sup> respectively. The same three PAHs measured outside the protective clothing (Table 3.1) were identified inside the protective clothing, however many of the concentrations were observed to be higher inside the protective clothing than for the corresponding exterior measurements (Figure 3.3).

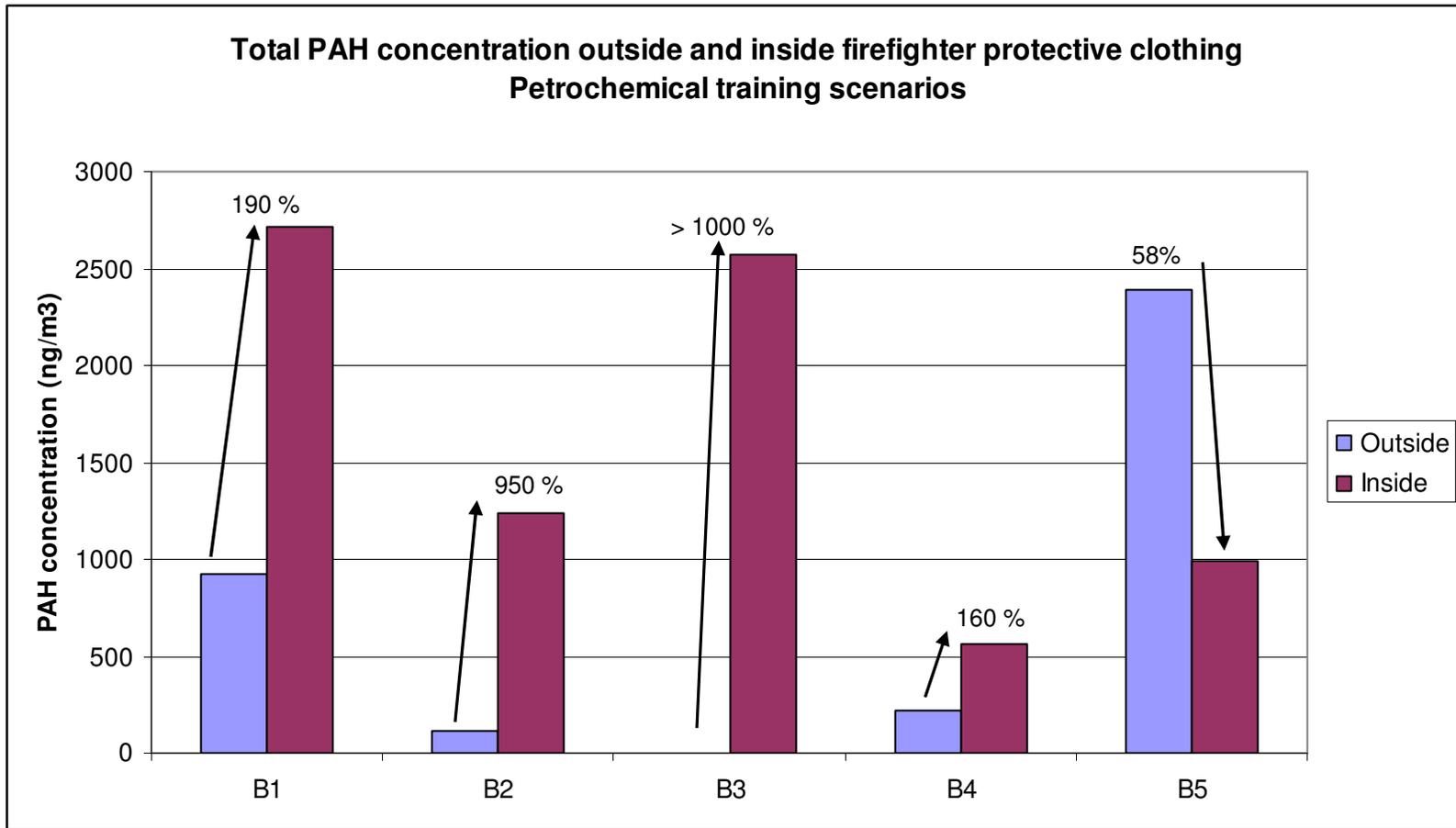
These results are very different from the observations obtained for the simulated residence and office burns (Figure 3.4). In the simulated bedroom fire and office fire scenarios, the concentrations of PAHs inside the protective clothing were generally reduced compared with the exterior concentrations, whereas in the LPG fires the concentrations inside are generally higher. However, it should be noted from Figure 3.4 that even within the protective clothing the levels of PAH contamination are far less than those observed during extinguishment of the simulated residence and office fires.

There are many alternative approaches to describing the PAH exposure results in terms of potential PAH toxicity with respect to benzo[a]pyrene and other PAHs (United States Environmental Protection Agency, 1984; Nisbet and LaGoy, 1992). Lin et al. (2008) suggested the approach reported by Nisbet and LaGoy best described the actual toxic potency of the individual PAH species and they equated the total PAH concentration to an equivalent benzo[a]pyrene concentration.

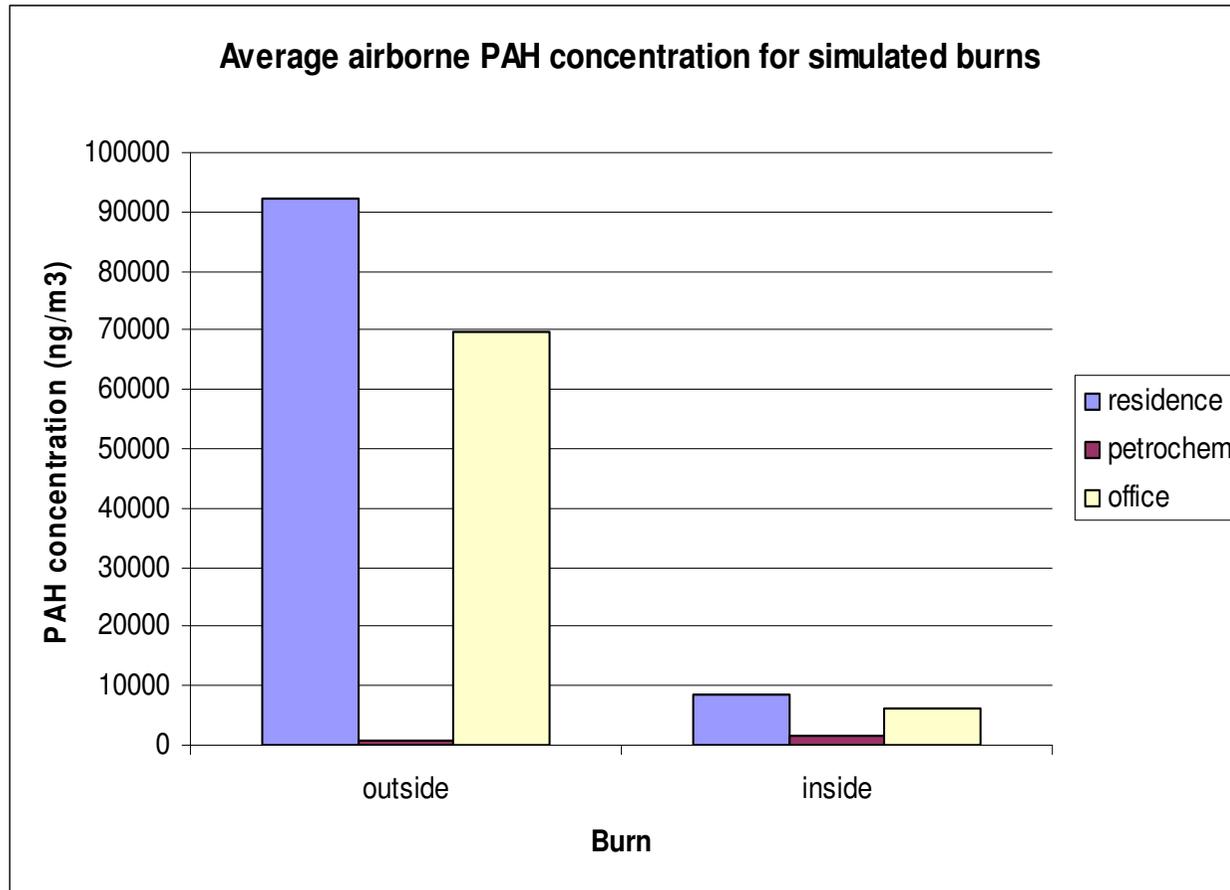
Using the approach described by Nisbet and LaGoy (1992), the total PAH value as a benzo[a]pyrene equivalency outside the protective clothing varies across the burns from 0.0 to 2.3 ng/m<sup>3</sup>, with an average value of 0.76 ng/m<sup>3</sup>. Only two values were



**Figure 3.2** Type of PAH and concentration inside firefighter protective clothing for each training scenario



**Figure 3.3** Comparison of total PAH concentrations outside and inside the protective clothing for each training scenario. Arrows show the relative increase or decrease in concentration from outside to inside.



**Figure 3.4** Comparison of the average airborne PAH values outside and inside the firefighter protective clothing as a function of simulated burn type

greater than  $1 \text{ ng/m}^3$ . These average values are at least 1000 times less than the average value of the simulated residence burns and approximately 115 times less than the average value of the office burns. The differences reflect the absence of benzo[a]pyrene in LPG emissions, which is rated as comparatively more toxic than the three PAHs detected in these samples. However, the benzo[a]pyrene equivalency values obtained outside the protective clothing are higher than those 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).

The values obtained for inside the protective clothing across the burns vary from 0.4 to  $2.6 \text{ ng/m}^3$ , with an average value of  $1.48 \text{ ng/m}^3$ . These low values reflect the nature of the PAH emissions from the LPG and the ingress of PAH into the firefighter protective clothing. There are several pathways by which airborne contaminants can be pass into workers' clothing. Perhaps the two most well-known effects causing air flow within workers' clothing (hence drawing in and distributing external airborne contaminants) are the "bellows effect" and the "chimney effect" (Castulik, 2009). Three other 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.

It is clear the exposures incurred in this simulation are significantly less than those incurred by firefighters during the extinguishment of the simulated residence and office fires (approximately 300 times and 7 times lower, respectively). The lower exposures combined with the variable outside environment (e.g wind gusts and radiant heat-induced air movement) may affect the exchange rate between the micro-climate within the protective clothing and outside. The posture adopted by the firefighter compared with that posture adopted inside structures may also influence the exchange rate. However, other plausible explanations cannot be discounted.

## Summary

The overall results show the firefighters were exposed to PAHs outside their protective clothing. The individual PAH concentrations were much less than their respective exposure standards (NES) values where they have been established. Their PAH exposures are greater than PAH exposures typical in urban environments. However, the firefighter PAH exposures are lower than the mean PAH exposures reported for workplaces and significantly less than the exposures obtained during the simulated residence and office burns.

The results show individual variation between the burns, despite the similar fuels, and tactics applied to extinguish the fires. The observed variability illustrates the complexity of the fire behaviour, combustion product formation, temporal elements, firefighter activities including the outside location and the environmental conditions such as the wind speed and atmospheric stability.

There are many plausible explanations to account for the observations including the basic fact the LPG fire was an outside fire whereas the simulated residence and office fires were internal building fires. Obviously, the external environment is much more variable because of the atmospheric conditions, radiant heat and water spray than the flame- and smoke-laden internal environments. It should be noted that in

addition to their influence on the overall training environment, these differences may also affect the micro environment within the protective clothing.

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## CHAPTER FOUR

# EXPOSURE OF FIREFIGHTERS TO VOLATILE ORGANIC COMPOUNDS AND ACID GASES

The previous chapter focussed on the characterisation of firefighter exposures to polycyclic aromatic hydrocarbon (PAH) airborne hazards such as naphthalene. This chapter addresses characterising the exposure of firefighters to a variety of other airborne contaminants including:

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

In particular, this chapter focuses on establishing the concentrations and distributions of contaminants to which firefighters were exposed outside and inside their protective clothing during extinguishment.

### Acid Gases

#### *Outside Protective Clothing*

The acid gases of interest include:

- Hydrogen chloride;
- Hydrogen fluoride;
- Hydrogen cyanide;
- Sulphuric 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 concentration and distribution as a function of burn is shown in Figure 4.1. Results obtained in burn one for acid gases other than hydrogen cyanide were not useable, due to internal obstruction of the sampling tube during sampling.

The concentration of all acid gases including hydrogen cyanide were less than the Limit of Reporting (LOR), except sulfuric acid and hydrochloric acid in burn five. The measured sulfuric acid concentration exceeded the established Australian National Exposure Standard (NES) for sulfuric acid ( $1 \text{ mg/m}^3$ ) but was less than the Short Term Exposure Limit (STEL) value ( $3 \text{ mg/m}^3$ ). The hydrochloric acid value was less than the NES ( $7.5 \text{ mg/m}^3$ ) (Worksafe Australia, 1995).

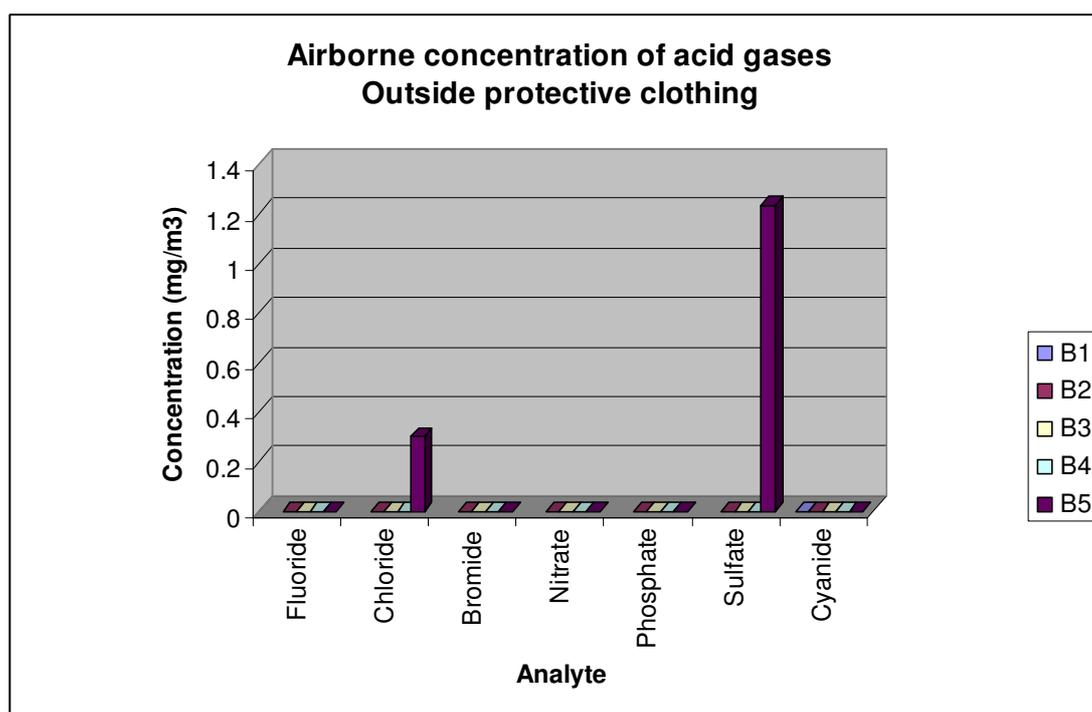
The results in Table 4.1 are readily explained when the following factors are considered:

- LPG contains only trace levels of inorganic contaminants;
- these anions are soluble in water; and
- fire conditions.

Thus, it is not expected significant quantities of inorganic acid gases will be emitted when LPG is combusted. Moreover, those products generated are readily dispersed, or dissolved into the applied water stream before reaching the firefighter. These values are within the ranges reported in the literature concerning firefighter exposure and acid gas formation in smoke. However, they are much less than the maximum concentrations reported (Treitman et al., 1980; Brandt-Rauf et al., 1988; Bolstad-Johnson et al., 2000).

**Table 4.1** Concentration of acid gases as a function of burn

Acid Gas	Concentration (mg/m <sup>3</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Fluoride	-	< LOR	< LOR	< LOR	< LOR
Chloride	-	< LOR	< LOR	< LOR	0.3
Bromide	-	< LOR	< LOR	< LOR	< LOR
Nitrate	-	< LOR	< LOR	< LOR	< LOR
Phosphate	-	< LOR	< LOR	< LOR	< LOR
Sulfate	-	< LOR	< LOR	< LOR	1.2
Cyanide	< LOR	< LOR	< LOR	< LOR	< LOR



**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. In all cases the concentration of the acid gases was less than the limit of reporting (LOR). The sparse results obtained for the acid gases outside and inside the protective clothing precludes any inference being drawn about whether the protective clothing affords any protection against acid gases.

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

	Concentration (mg/m <sup>3</sup> )				
	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	< LOR	< LOR	< LOR

## 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 LPG fires. The concentration of all volatile organic compounds (VOC – oxygenated hydrocarbons) outside the protective clothing (as measured using glass sorbent tubes packed with 2,4-dinitrophenylhydrazine-coated silica gel) were less than the limit of reporting (LOR) for all burns, as shown in Table 4.3.

**Table 4.3** Concentration of VOC – oxygenated hydrocarbons outside the protective clothing as a function of burn (silica gel sorbent tube method)

<b>Aldehydes</b>	Concentration (mg/m <sup>3</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Formaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Acetaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Acrolein	< LOR	< LOR	< LOR	< LOR	< LOR
Acetone	< LOR	< LOR	< LOR	< LOR	< 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	< LOR	< LOR

Several oxygenated hydrocarbons were also measured using an evacuated canister attached to the outside of the firefighter (see Figure 4.3). Using this more sensitive method, a number of oxygenated hydrocarbons were detected as shown in Table 4.4.

**Table 4.4** Concentration of VOC – oxygenated hydrocarbons outside the protective clothing as a function of burn (evacuated canister method)

Aldehydes	Concentration (ppb)				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Ethanol	9.1	6.4	7.2	11	9.9
Acrolein	0.9	1.2	1	1.1	0.7
Acetone	5.5	6.9	4.6	5.7	5.3
Isopropyl alcohol	5.5	5	1.9	4.6	1.1
Methyl ethyl ketone	0.6	0.6	< LOR	0.5	< LOR

Ethanol exhibited the highest average concentration (8.7 parts per billion (ppb)), whilst the average values of methyl ethyl ketone and acrolein were less than 1 ppb. These values are low and are similar to average urban airshed concentrations reported (World Health Organisation, 1991; Grosjean, 1997; Department of Environment and Resource Management, 2010). Moreover the products and their distribution is similar to those reported by Yokely and Ferguson (1958) and Harris and Egerton (1948), who reported low concentrations of oxygenated hydrocarbons were generated during combustion of propane under various combustion conditions. In particular, they found methanol and ethanol were favoured products.

### ***Inside Protective Clothing***

The results describing the concentration and distribution of VOC – oxygenated hydrocarbons inside the protective clothing are shown in Table 4.5. In all burns the concentration of all VOC – oxygenated hydrocarbons was less than the limit of reporting (LOR). The sparse results obtained for the VOC – oxygenated hydrocarbons outside and inside the protective clothing precludes any inference being drawn about whether the protective clothing affords any protection against these chemicals.

**Table 4.5** Concentration of VOC – oxygenated hydrocarbons inside the protective clothing as a function of burn

Aldehydes	Concentration (mg/m <sup>3</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Formaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Acetaldehyde	< LOR	< LOR	< LOR	< LOR	< LOR
Acrolein	< LOR	< LOR	< LOR	< LOR	< LOR
Acetone	< LOR	< LOR	< LOR	< LOR	< 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	< LOR	< LOR

## Volatile organic compounds – hydrocarbons

### Outside Protective Clothing

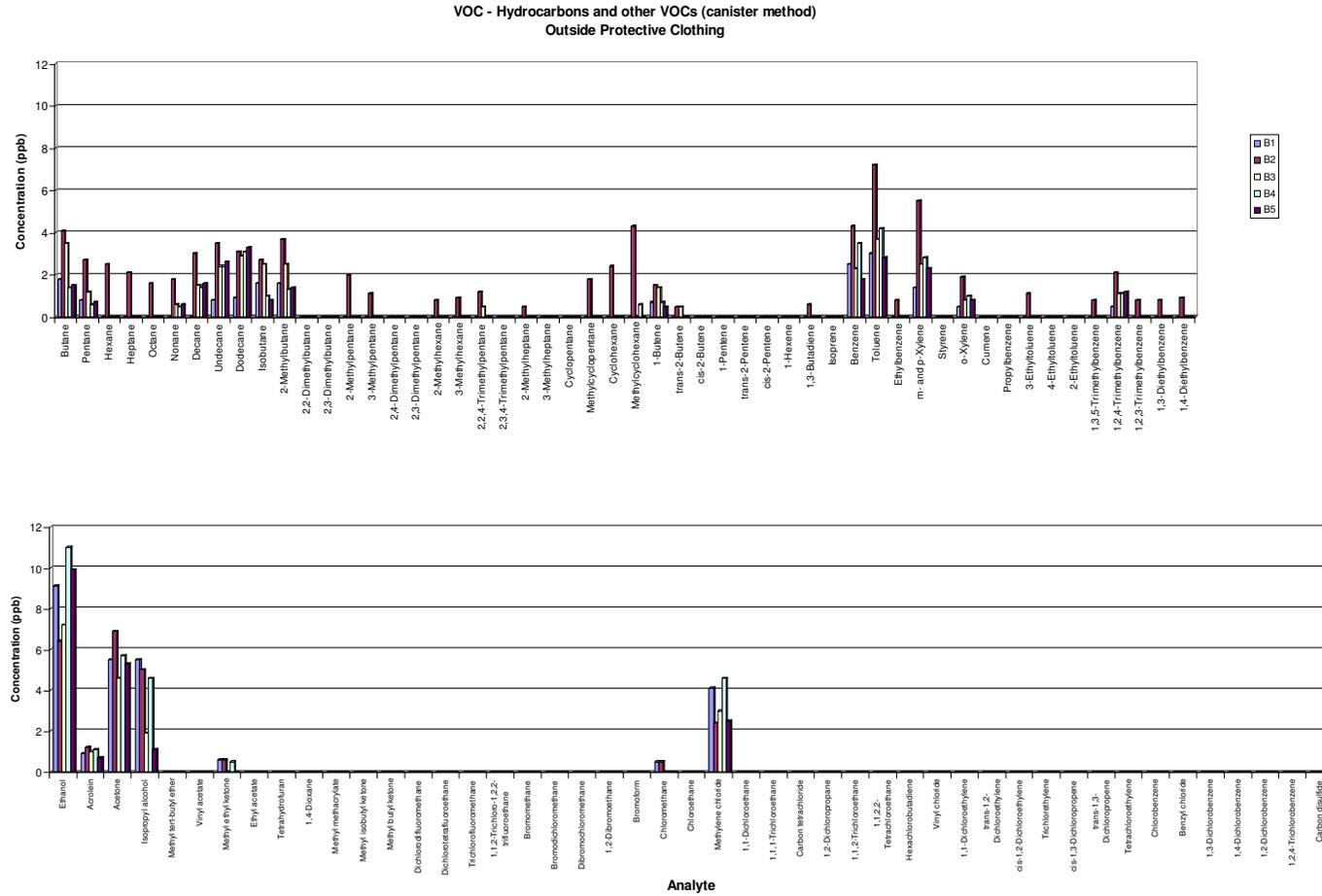
The results in this section focus on characterising the types and concentrations of volatile organic compounds – hydrocarbons (such as benzene and hexane) to which firefighters were exposed whilst extinguishing the fires. The concentration of VOC – hydrocarbons outside the protective clothing as a function of burn collected using sorbent tubes filled with Tenax/Carboxen 569 in series are shown in Table 4.6.

**Table 4.6** Concentration of VOC hydrocarbons outside the protective clothing as a function of burn (sorbent tube method)

Volatile Organic Compounds	Concentration (mg/m <sup>3</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Benzene	<b>0.030</b>	< LOR	< LOR	< LOR	< LOR
Toluene	< LOR	< LOR	< LOR	< LOR	< LOR
Ethyl benzene	< LOR	< LOR	< LOR	< LOR	< LOR
Styrene	< LOR	< LOR	< LOR	< LOR	< LOR
Xylenes	< LOR	< LOR	< LOR	< LOR	< LOR
Trimethyl benzenes	< LOR	< LOR	< LOR	< LOR	< LOR
Methyl cyclohexane	< LOR	<b>0.028</b>	< 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	< LOR	< LOR	< LOR	< LOR	< 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

Only two volatile organic compounds – hydrocarbons were identified during the activities: benzene and methyl cyclohexane. The measured values are low compared with the established NES (Worksafe Australia, 1995) and 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).

In contrast, the results describing VOC - hydrocarbons obtained from the evacuated canister are shown in Figure 4.2. A range of hydrocarbons were identified via this more sensitive method, along with other compounds such as chlorinated hydrocarbons. Whilst the results show firefighters are exposed to a range of volatile organic compounds (VOC) hydrocarbons, the concentrations were in the low parts



**Figure 4.2** Concentration of VOC hydrocarbons outside the protective clothing as a function of burn obtained in the canisters.

per billion (ppb) range. The values measured are similar to values typically found in the urban environment and are significantly less than the established NES (Worksafe Australia, 1995). Moreover, they are significantly lower than results reported in the literature concerning firefighter exposure during the extinguishment of residential and other urban fires. The results are also significantly less than the results obtained from the simulated office and residence burns.

### ***Inside Protective Clothing***

The concentrations of VOC - hydrocarbons measured inside the protective clothing as a function of burn are shown in Table 4.7.

**Table 4.7** Concentration of VOC hydrocarbons inside the protective clothing as a function of burn

Volatile Organic Compounds	Concentration (mg/m <sup>3</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Benzene	< LOR	< LOR	< LOR	< LOR	< LOR
Toluene	< LOR	< LOR	< LOR	< LOR	< LOR
Ethyl benzene	< LOR	< LOR	< LOR	< LOR	< LOR
Xylenes	< LOR	< LOR	< LOR	< LOR	< LOR
Trimethyl benzenes	< LOR	< LOR	< LOR	< LOR	< LOR
Methyl cyclohexane	< LOR	< LOR	< LOR	< LOR	< LOR
Pentane	< LOR	<b>0.033</b>	< 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	< LOR	< LOR	< LOR	< LOR	< 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 had not changed significantly. Only pentane was detected inside the protective clothing and on a single occasion at very low concentration. The other hydrocarbons not measured outside the protective clothing were also not measured inside the protective clothing.

### **Summary**

The overall results show clearly the firefighters were not exposed to any significant concentration of VOC - oxygenated hydrocarbons or VOC - hydrocarbons outside or inside their protective clothing. The measured concentrations are much less than

their respective NES values where they have been established, and similar to values typically found in the urban environment.

For the acid gases, only a single measurement of one acid gas (sulfuric acid) exceeded the established Australian National Exposure Standard (NES) for sulfuric acid ( $1 \text{ mg/m}^3$ ). However, the measurement was less than the Short Term Exposure Limit (STEL) value ( $3 \text{ mg/m}^3$ ).

The values obtained in this study for acid gases, VOC – oxygenated hydrocarbons and VOC – hydrocarbons are significantly less than the values obtained in the simulated office and room burns. These differences are likely to reflect the different fuels, external operational environment, restricted opportunities for air to enter the protective clothing. The effect of environmental conditions, such as wind and radiant heat, is also important to consider when assessing firefighter exposures in external operational environments.

The sparse results obtained for all the VOCs (acid gases, oxygenated hydrocarbons or hydrocarbons) outside and inside the protective clothing precludes any inference being drawn about whether the protective clothing affords any protection against these chemicals. This is in contrast to the results obtained about firefighter exposures during the simulated residence and office burns, which demonstrated concentrations of VOCs were significantly lower inside the protective clothing than outside.

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## CHAPTER FIVE

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

The deposition of airborne contaminants and surface-sourced contaminants onto firefighters' protective clothing at fires 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). The focus on thermal protection and performance is obvious when the properties of flammable gas-fed fires are considered. Nonetheless there is a need to describe the performance of the protective clothing against airborne contaminants whilst extinguishing flammable gas-fed fires. However, there is little if any information available, as most studies reported have focused on traditional structure fires (Gold, 1978; Burgess et al., 2001; Brandt-Rauf et al., 1988; Bolstad-Johnson et al., 2000).

There is little information reported about the likely deposition onto and movement of contaminants through firefighting protective clothing (Aust et al., 2007; Perry, 1999). Most of the knowledge has been drawn from studies addressing the performance of clothing in other industries such as the pesticide industry (Ness, 1994). In most workplace settings the most significant component of a worker's dose does not arise from penetration of the skin, but 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). It is not clear about the relative importance of the skin as an entry route during the extinguishment of external flammable gas- (LPG-) fed fires.

Previous chapters have focussed on the characterisation of firefighter exposure to a variety of airborne hazards. The results demonstrated firefighters were exposed to low concentrations of 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. No attempt was made to identify or quantify any VOCs such as benzene deposited onto a swatch because of their inherent physico-chemical properties and concentration of the airborne VOCs previously established. Nor was the influence of wetting of the garment's outer layer on the deposition of PAHs investigated.

### Results

After the extinguishment activity, the swatches did not display visible discolouration from the deposition of combustion products commonly described as soot. 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 table demonstrates clearly in all burns the PAH deposition concentration was less than the LOR.

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

PAH Deposition	Deposition concentration (ng/cm <sup>2</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Naphthalene	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthylene	< LOR	< LOR	< LOR	< LOR	< LOR
Acenaphthene	< LOR	< LOR	< LOR	< LOR	< LOR
Fluorene	< LOR	< LOR	< LOR	< LOR	< LOR
Phenanthrene	< LOR	< LOR	< LOR	< LOR	< LOR
Anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR
Pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Benz[a]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Chrysene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[b]fluoranthene / benzo[k]fluoranthene	< LOR	< LOR	< LOR	< LOR	< LOR
Perylene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[a]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[e]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Indeno[1,2,3-cd]pyrene	< LOR	< LOR	< LOR	< LOR	< LOR
Benzo[ghi]perylene	< LOR	< LOR	< LOR	< LOR	< LOR
Dibenz[a,h]anthracene	< LOR	< LOR	< LOR	< LOR	< LOR
Coronene	< LOR	< LOR	< LOR	< LOR	< LOR

It cannot be demonstrated if there is any relationship between the PAH airborne concentration/distribution and the PAH deposition distribution. The results reflect the low airborne PAH concentration and limited PAH product distribution measured during the extinguishment of the LPG fire. Deposition onto the firefighter protective clothing was insignificant. Contaminant transport processes such as emission, resuspension, transfer and redistribution are not likely to significantly affect the makeup of the final loading since the exposure is not as great (Vermeulen et al, 2000; Semple, 2004; Schneider, 1999; 2000; Thornburg, 2008). In contrast, the results obtained in the simulated residence and office burns suggest there is a relationship between the airborne PAH concentration/distribution and PAH deposition concentration and distribution.

## Summary

The results show clearly the concentration of PAHs deposited directly onto the protective clothing the firefighter activities during the extinguishment of the LPG fed fire is less than the limit of reporting. The results are not surprising for the following reasons:

- LPG fires do not generate significant quantities of aromatic hydrocarbons, polycyclic aromatic hydrocarbons or smoke as demonstrated by the results describing the airborne concentration and distribution of PAHs;

- Fire extinguishment occurred outside, rather than within a structure where smoke may become concentrated due to lack of ventilation;
- Tactical approach applied varies from the tactical approach applied inside structures;
- Water curtain readily disperses the smoke and reduces firefighter exposure to the smoke; and
- Positions adopted by firefighter are “upwind” of the fire.

The observations have implications for firefighters who specialise in extinguishing LPG fires or liquefied natural gas (LNG) fires. The deposition of PAH onto the protective clothing in these types of fires is insignificant, meaning that the firefighting protective clothing does not become as “dirty”. Hence, the protective clothing can be donned for longer periods compared with protective clothing used in internal structural firefighting.

The greatest challenge for firefighters in these circumstances is to better understand the thermal performance of their protective clothing and hence the protection afforded during the extinguishment of flammable gas fed fires.

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## 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; Bruijnzeel et al., 1995; European Centre for Ecotoxicology and Toxicology of Chemicals, 1993; Bieniek, 1998; Dankovic, 1989; Hardgraft, 2001; McDougal, 1990; Roy, 2007; Walters and Roberts, 2008; Schneider et al., 1999, 2000; Scott and Dugard, 1989; Semple, 2004; Van Rooij et al., 1993a,b). However, there is little if any information about contaminants deposited onto firefighters' skin during operational activities.

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.

Many studies have investigated the effect of chemical protective clothing as a barrier or sink for contaminants in occupational settings (Brouwer et al., 1999; Goydon and Schwoppe, 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.

The research 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. However, these exposures were insignificant compared with the exposures firefighters incurred extinguishing the simulated room and office fires. The PAH airborne contaminants were also present inside the protective clothing immediately adjacent to the skin at very low values.

### Results

Three dermal patches acting as skin surrogates were located at the chest, arm and leg of the firefighter to collect deposited PAHs. The results obtained from dermal patches are shown in Table 6.1.

**Table 6.1** Concentrations of PAHs deposited on dermal patches

	Total PAH Concentration (ng/cm <sup>2</sup> )				
	Burn One	Burn Two	Burn Three	Burn Four	Burn Five
Arm	< LOR	< LOR	< LOR	< LOR	< LOR
Chest	< LOR	< LOR	< LOR	< LOR	< LOR
Leg	< LOR	< LOR	< LOR	< LOR	< LOR

The PAH deposition concentration was less than the Limit of Reporting (LOR) on all occasions. The results reflect the low airborne concentration of PAHs measured outside and within the protective clothing.

## Summary

The results show the PAH deposition onto the firefighter skin is less than the Limit of Reporting and is not significant. The results reflect the nature of the fuel, the external environment and approaches to extinguish the fire. The water curtain reduces the radiant heat and likelihood of direct flame impingement on the firefighters. It also has some influence further dispersing the generated smoke.

Recently, Laitinen et al. (2010) reported the deposition of PAHs onto the skin of firefighter trainers during training activities using propane as the fuel. They found PAHs were readily deposited onto the firefighters, but reported only total skin doses. The most significant difference between the two studies was the internal firefighting activities in the study by Laitinen et al., compared with the external activities in this study.

The results provide a valuable insight into approaches that can be adopted to minimise the firefighters' exposure and hence their dose. Where possible a firefighter should avoid contact with the smoke. This principle applies to not only exterior operations, but also interior operations. If a firefighter cannot avoid the smoke they should adopt measures to minimise their exposure to the smoke.

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## CHAPTER SEVEN

### OUTCOMES

This study has investigated the exposure of firefighters to volatile organic compounds (acid gases, hydrocarbons and oxygenated hydrocarbons) and polycyclic aromatic hydrocarbons (PAHs) during extinguishment of LPG-fed jet fires.

No quantifiable deposition of PAHs was detected on the personal protective clothing or skin of firefighters in these tests. Historically, investigations into firefighter protective clothing have focused on the thermal performance of firefighter protective clothing, and the two most widely accepted firefighter protective clothing standards (NFPA 2007, EN 2006) also focus on thermal protective requirements. Given the firefighter exposures in this study and the significant heat generated by LPG fires, the relative focus on thermal protection from the heat and flame (as opposed to chemical protection from combustion products) is appropriate. However, it is practically impossible to avoid the deposition of some quantity of PAH onto the protective clothing and the skin. It is therefore prudent to integrate risk control measures to minimise the opportunities for contamination of the protective clothing or the firefighter, irrespective of the fuel being burned. For example, a regular protective clothing cleaning program should be implemented and firefighters should regularly shower after extinguishment activities. It must also be noted that this study did not investigate the influence of wetting of the garments' outer layers on the deposition of PAHs and other materials.

Existing standard procedures for instructors and trainees engaging in extinguishment of LPG-fed jet fires at the School of Fire and Rescue Service Training do not involve the wearing of respiratory protection. In these tests, levels of air contaminants outside and inside the firefighters' protective clothing were found to be very low, with the majority of measurements below the limit of reporting. A single atmospheric measurement of sulfuric acid outside the protective clothing was above the Australian National Exposure Standard, but below the designated Short Term Exposure Limit. Total atmospheric PAH levels were higher than typical PAH exposures reported within urban environments, but lower than mean worker PAH exposures reported in literature.

The above results support the conclusion that the risk to personnel from inhalation of toxic combustion products during extinguishment of LPG-fed jet fires at the School of Fire and Rescue Service Training is low during controlled training scenarios. However, the radiant heat and varying flame length from the burning LPG are key hazards for firefighters to consider in selection of tactics, location, and personal protective equipment requirements. Locating the firefighter behind the water curtain certainly aids the firefighter minimise the impact of the LPG flame, but the risk remains of injury to skin and the lungs from flame and radiant heat if the water curtain is breached should the firefighter have not donned appropriate respiratory protective equipment.