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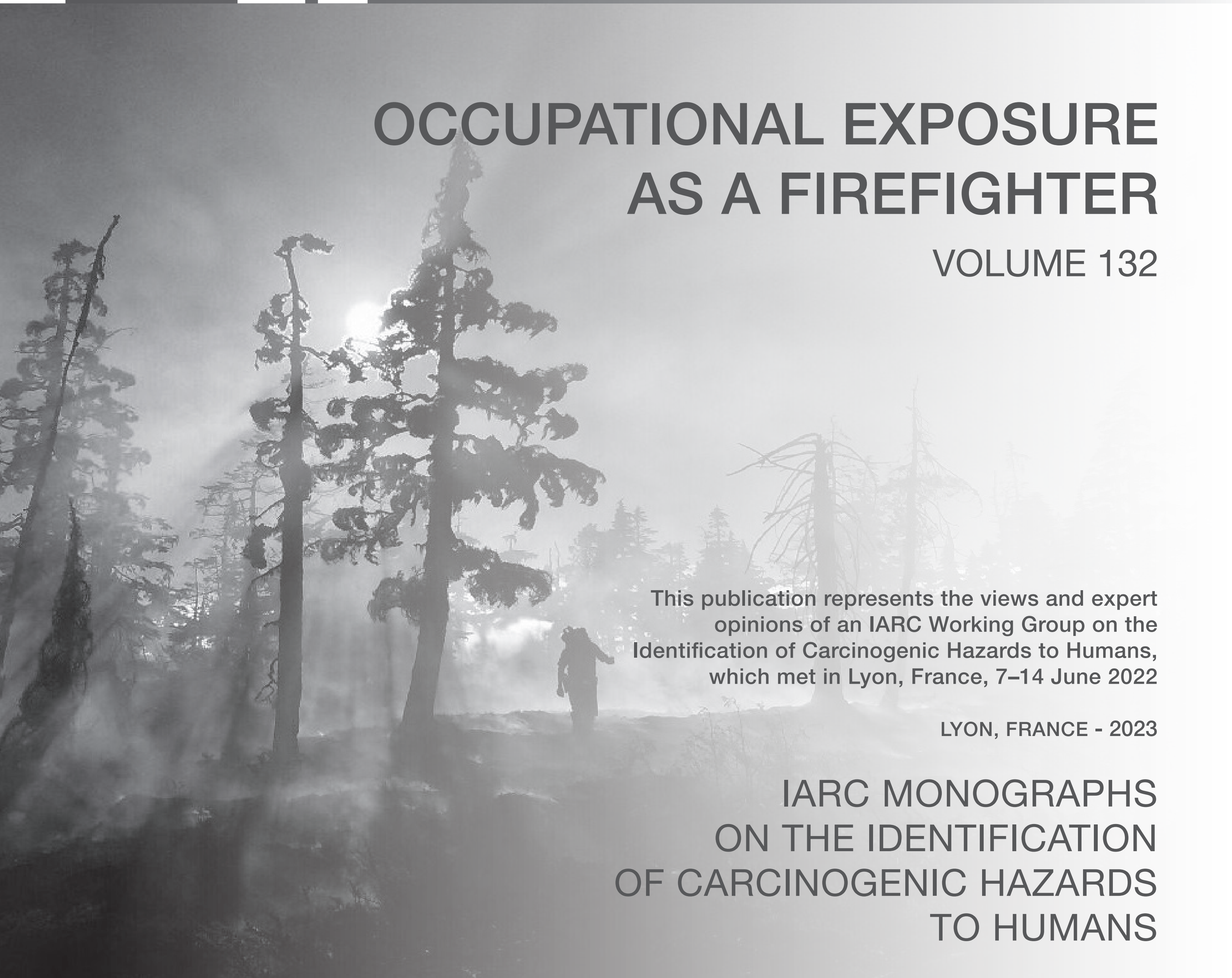

OCCUPATIONAL EXPOSURE AS A FIREFIGHTER

VOLUME 132

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1. EXPOSURE CHARACTERIZATION

1.1 Definition of the agent

The agent under evaluation is "occupational exposure as a firefighter". Firefighters' occupational exposures are complex and involve a highly heterogeneous mix of chemical, physical, biological, and psychosocial hazards resulting from fires, and from activities for training, controlling fires, and protecting life and property during emergencies (NFPA, 2021a; US BLS, 2021). The present monograph applies to any firefighter (career or volunteer) who has prepared for and participated in activities aimed at controlling fires (whether structure, vehicle, vegetation, or other types of fire), while acknowledging that firefighters are involved in numerous other occupational activities.

The occupation of firefighting can involve various roles and responsibilities, training requirements, and employer types. This variety may have an impact on the magnitude and character of occupational exposures. Firefighters respond to different types of fire and other emergency events (e.g. vehicle accidents, medical incidents, hazardous material releases, and building collapses). They also participate in non-emergency events, such as building inspections, training, and maintenance of the station or apparatus (engine) (Kales et al., 2007; Guia das Profissões, 2020; Pravaler, 2020; Fire and Rescue New South Wales, 2021a; United Kingdom National Careers Service, 2021; US BLS, 2021; Canadian Centre for Occupational Health and Safety, 2022). Specific types of firefighter may be characterized by the types of fire for which they are trained and that they are likely to encounter (e.g. structure, industrial, aircraft, marine, and wildland). Firefighters may also be defined by their employer (e.g. municipal, federal, military, tribal, or private), their employment status (e.g. full-time, part-time, volunteer, on-call, or seasonal), or their primary duties (e.g. investigator, instructor, engineer/pump operator, and hazardous materials specialist) (Hwang et al., 2019a, b; United Kingdom Home Office, 2020; US BLS, 2021; Miami Dade College, 2022). Note that fire investigators, hazardous materials specialists, or others who have not fought fires at any point in their tenure are not included in the definition of the agent (i.e. occupational exposure as a firefighter) in the present monograph. [The Working Group noted that, although terminology varies throughout the world, these general categories or types of firefighter exist in many regions. However, specialization in a particular area of firefighting may be less likely in low- and middle-income countries.]

Firefighters' tasks vary with their job assignments, rank or seniority, and location. For example, municipal firefighters in large cities may respond to more structure fires than do firefighters in rural areas, whereas firefighters near major roads or highways may respond to more vehicle fires than structure fires (Kales et al., 2007; US Fire Administration, 2018; NFPA, 2020b, 2021b). Wildland firefighting requires a different skillset to that required for municipal firefighting and has its own subspecialities (USDA Forest Service, 2021a; Forest Fire Management Victoria, 2022). Responsibilities change as firefighters advance or are promoted within the fire service. For example, a fire chief or commissioner is involved in management activities and is less likely to be directly engaged in fire suppression or rescue operations (Fleming & Zhu, 2009) (see Section 1.2 for more details about the occupation of firefighting). [The Working Group noted that there is a paucity of data with respect to promotional systems and advancement among firefighters in low- and middle-income countries.]

Firefighters can be exposed to a very wide range of airborne chemical exposures. The most common exposures are to combustion products from fires and exhaust from diesel or petrol engines. The chemical composition and airborne concentrations of combustion products depend on the materials being burned, the duration of the fire, and the ventilation conditions (Stec, 2017). Combustion products may include (but are not limited to) fine and ultrafine particulates; oxides of carbon, nitrogen, and sulfur; hydrocarbons, aromatic hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs) with or without functional groups such as amine, thiol, alcohol, or carbonyl groups; halogenated compounds including acid gases; and metals and metal oxides (Austin et al., 2001a; Baxter et al., 2010; Blomqvist et al., 2014; Fent et al., 2018; Keir et al., 2020) (see Sections 1.3.1 and 1.4 for more information on the composition of fire smoke). Firefighters may also be exposed to silica (Reinhardt & Broyles, 2019) and building materials affected by structure fires, such as asbestos and synthetic fibres (Bendix, 1979; Bolstad-Johnson et al., 2000; Lioy et al., 2002; Stec et al., 2019). Chemical flame retardants added to furnishings and other products may be released into the environment unaltered (Hewitt et al., 2017; Fent et al., 2020a). Firefighters may also be exposed to chemicals they use during firefighting, such as per- and polyfluoroalkyl substances (PFAS) contained in some aqueous film-forming foams (AFFF) (Khalil et al., 2020; Leary et al., 2020) (see Section 1.5.1 for more information on exposures other than fire smoke). Depending on the properties of compounds released, use of personal protective equipment (PPE), contamination of skin, and decontamination measures, firefighters can potentially inhale, ingest, and/or dermally absorb a variety of chemicals during or after fire responses (Fent et al., 2017, 2020b; Stec et al., 2018; Burgess et al., 2020) (see Sections 1.4.5 and 1.6 for more information on routes of exposure and control methods).

Wildfires predominantly involve the combustion of timber, brush, and other vegetation but can also produce many of the same combustion products as structure fires (e.g. aromatic hydrocarbons, aldehydes, and particulates) (Adetona et al., 2016; Cherry et al., 2021a). As wildfires encroach on urban areas (known as the wildland–urban interface, or WUI), firefighters – both wildland and municipal – have increasingly been simultaneously fighting structure and vegetation fires (Radeloff et al., 2018) (see Section 1.4.2 for more information about exposures during wildfires).

Firefighters who rarely respond to emergency fires or other chemical incidents (e.g. airport firefighters) may still have exposures from live-fire training, use of chemicals (e.g. AFFF), or from contamination of previously used protective equipment or workplace surfaces (Fent et al., 2017, 2019a; Engelsman et al., 2019; Leary et al., 2020). Most fire departments have diesel-fuelled vehicles and equipment, so firefighters can also be exposed to diesel engine exhaust (Bott et al., 2017) (see Section 1.5.1(d)). There are also non-chemical carcinogenic hazards to which many firefighters may be exposed. These include night shift work, infectious agents, and ultraviolet (UV) radiation from working outdoors (Mahale et al., 2016; Jang et al., 2020) (see Sections 1.5.2(a), 1.5.2(b), and 1.5.1(f)).

The PPE worn by firefighters around the world shares many similarities. The turnout gear of municipal firefighters typically includes self-contained breathing apparatus (SCBA), helmet, hood, gloves, and insulating clothing consisting of multiple layers of protective fabric (NFPA, 2018; CEN, 2020), although there can be notable differences in the design of each of these components according to geographical location. Wildland firefighters, in comparison, wear much lighter protective clothing and may not wear any respiratory protection (Carballo-Leyenda et al., 2018; Navarro et al., 2019a) (see Section 1.6 for more details on PPE).

Firefighters may have second jobs in occupations within or outside the fire service discipline (Beaton & Murphy, 1993; Murphy et al., 1999; Baikovitz et al., 2019; Pedersen et al., 2019, 2020). For example, it is not uncommon for a firefighter to be assigned to a municipal fire department as a full-time municipal firefighter/paramedic and also work part-time as a fire instructor or in another industry, such as construction or landscaping. Second jobs are possible because firefighters often work extended shifts, sometimes in excess of 24 hours, but with several rest days between shifts (Billings & Focht, 2016). [Career firefighters may also serve as volunteer firefighters in their community. Second jobs outside of the fire service discipline are not included as part of the agent under evaluation (i.e. occupational exposure as a firefighter). The proportion of firefighters with second jobs probably varies throughout the world.]

The present monograph will consider studies spanning firefighting activities from 1915 to the present. The occupation of firefighting has changed over this period, and advances in PPE and other control technologies may have reduced firefighters' exposures; however, the introduction of synthetic materials (e.g. foams, plastics, and glues in engineered wood products) has resulted in fire smoke that contains additional and more abundant hazardous chemicals and fires that propagate more rapidly (Kerber, 2012; Pedersen et al., 2019) (see Section 1.2 for more information on how the fire service has changed over time). Chemicals (e.g. PFAS) added to materials and equipment used by firefighters may also add to their potentially harmful exposures. The present evaluation was focused primarily on exposures (e.g. combustion products including particulates and metals, PAHs, volatile organic compounds (VOCs), semi-volatile organic compounds (sVOCs), PFAS, flame retardants, diesel exhaust, heat, UV and other radiation, and shift work) that commonly apply across the firefighting occupation and could potentially have an impact on carcinogenesis (see Table 1.1 for potential firefighter exposures classified by IARC). Highly specific exposures that would be rare for the rest of the firefighting discipline (e.g. ionizing radiation from nuclear accidents) or other known hazards that are unlikely to be directly associated with carcinogenesis (e.g. noise and psychosocial factors) are only briefly reviewed here.

1.2 Qualitative information about firefighting

1.2.1 Types of firefighter and firefighting activity

A firefighter is an individual who has been educated and trained in the prevention and suppression of fires that threaten life, property, and the environment. The fire service can be made up of different firefighter occupational subgroups and specializations, such as municipal firefighters, volunteer firefighters, fire trainers, wildland firefighters, WUI firefighters, fire cause investigators, and industrial, airport, or military firefighters. In some countries, firefighters may be

Table 1.1 Potential exposures in firefighting that have been evaluated by IARC

Exposure	Overall evaluation (IARC Group)[a]	Volume	Year	Evaluation for cancer in humans	
				Cancer sites with *sufficient* evidence in humans	Cancer sites with *limited* evidence in humans
Acetaldehyde	2B	71	1999		
Acrolein	2A	128	2021		
Acrylonitrile	2B	71	1999		
Arsenic and inorganic arsenic compounds	1	100C	2012	Lung, urinary bladder, skin	Liver, bile duct, prostate, kidney
Asbestos (all forms)	1	100C	2012	Larynx, lung, mesothelium, ovary	Pharynx, stomach, colon, rectum
Benz[*a*]anthracene	2B	92	2010		
Benzene	1	120	2018	AML, other acute non-lymphocytic leukaemia	Lung, childhood AML, chronic myeloid leukaemia, chronic lymphocytic leukaemia, NHL (all combined), multiple myeloma
Benzo[*b*]fluoranthene	2B	92	2010		
Benzo[*j*]fluoranthene	2B	92	2010		
Benzo[*k*]fluoranthene	2B	92	2010		
Benzofuran (coumarone)	2B	63	1995		
Benzo[*a*]pyrene	1	100F	2012		
Bromochloroacetic acid	2B	101	2013		
1-Bromopropane	2B	115	2018		
1-Bromo-3-chloropropane	2B	125	2020		
1,3-Butadiene	1	100F	2012	Leukaemia (all combined), lymphoma (all combined), multiple myeloma or haematolymphatic organs	
Cadmium and cadmium compounds	1	100C	2012	Lung	Prostate, kidney
Carbon black (total)	2B	93	2010		
Carbon nanotubes, multiwalled MWCNT-7	2B	111	2017		
2-Chloronitrobenzene	2B	123	2020		
4-Chloronitrobenzene	2B	123	2020		
Chromium(VI) compounds	1	100C	2012	Lung	Nasal cavity and paranasal sinus
Chrysene	2B	92	2010		
Cobalt(II) oxide	2B	131	2023		
Crotonaldehyde	2B	128	2021		
Dibenz[*a*,*h*]anthracene	2A	92	2010		

Table 1.1 (continued)

Exposure	Overall evaluation (IARC Group)[a]	Volume	Year	Evaluation for cancer in humans	
				Cancer sites with *sufficient* evidence in humans	Cancer sites with *limited* evidence in humans
Dibenzo[*a*,*i*]pyrene	2A	92	2010		
Dibromoacetic acid	2B	101	2013		
1,3-Dichloro-2-propanol	2B	101	2013		
Dichloroacetic acid	2B	106	2014		
Dichloromethane (methylene chloride)	2A	110	2017		Bile duct, NHL (all combined)
2,4-Dichloro-1-nitrobenzene	2B	123	2020		
1,4-Dichloro-2-nitrobenzene	2B	123	2020		
1,2-Dichloropropane	1	110	2017	Biliary tract (cholangiocarcinoma)	
Diethanolamine	2B	101	2013		
N,*N*-Dimethylformamide	2A	115	2018		Testis
Engine exhaust, diesel	1	105	2014	Lung	Urinary bladder
Engine exhaust, gasoline	2B	105	2014		
Ethyl acrylate	2B	122	2019		
Ethylbenzene	2B	77	2000		
Ethylene oxide	1	100F	2012		Breast, chronic lymphocytic leukaemia, NHL (all combined), multiple myeloma
Formaldehyde	1	100F	2012	Nasopharynx, AML, other acute non-lymphocytic leukaemia, chronic myeloid leukaemia	Nasal cavity and paranasal sinus
Furan	2B	63	1995		
Hepatitis B virus	1	59	1994	Liver	Bile duct, NHL (all combined)
Hepatitis C virus	1	59	1994	Liver, NHL (all combined)	Bile duct
HIV type 1	1			Anus, uterine cervix, endothelium (Kaposi sarcoma), eye, Hodgkin lymphoma, NHL (all combined)	Liver, skin (malignant non-melanoma), vulva, vagina, penis
Hydrazine	2A	115	2018		Lung
Indeno-1,2,3-[*cd*]pyrene	2B	92	2010		
Isoprene	2B	71	1999		
Lead compounds, inorganic	2A	87	2006		Stomach
Molybdenum trioxide	2B	118	2018		
3-Monochloro-1,2-propanediol	2B	101	2013		
Naphthalene	2B	82	2002		

Table 1.1 (continued)

Exposure	Overall evaluation (IARC Group)[a]	Volume	Year	Evaluation for cancer in humans	
				Cancer sites with *sufficient* evidence in humans	Cancer sites with *limited* evidence in humans
Nickel compounds	1	100C	2012	Lung, nasal cavity, paranasal sinuses	
Night shift work	2A	124	2020		Breast, prostate, colon, rectum
2-Nitroanisole (*ortho*-nitroanisole)	2A	127	2021		
Perfluorooctanoic acid (PFOA)	2B	110	2017		Testis, kidney
Polybrominated biphenyls	2A	107	2016		
Polychlorophenols	2B	71	1999		
2,3,4,7,8-Pentachlorodibenzofuran	1	100F	2012	All cancers combined	
3,4,5,3′,4′-Pentachlorobiphenyl (PCB-126)	1	100F	2012		
Pentachlorophenol	1	117	2019	NHL	
2,4,6-Trichlorophenol	2B	117			
Polychlorinated biphenyls	1	107	2016	Malignant melanoma	
Pyridine	2B	119	2019		
Radioactivity (γ activity)	1	100D	2012	All sites combined	
Radionuclides (α-particle-emitting)	1	100D	2012	All sites combined	
Radionuclides (β-particle-emitting)	1	100D	2012	All sites combined	
Silica (crystalline: quartz or cristobalite)	1	100C	2012	Lung	
Styrene	2A	121	2019		Leukaemia (all combined), lymphoma (all combined), multiple myeloma
Styrene-7,8-oxide	2A	121	2019		
Sulfuric acid[b]	1	100F	2012	Larynx	
Tetrabromobisphenol A	2A	115	2018		
2,3,7,8-Tetrachloro dibenzo-*para*-dioxin (2,3,7,8-TCDD)	1	100F	2012	All cancer sites combined	Lung, soft tissue, NHL
Tetrachloroethylene (perchloroethylene)	2A	106	2014		Urinary bladder
1,1,1-Trichloroethane	2A	130	2022		Multiple myeloma
Toluene diisocyanates	2B	71	1999		
Trichloroethylene	1	106	2014	Kidney	Liver, bile duct, NHL (all combined)
Trichloromethane (chloroform)	2B	73	1999		

Table 1.1 (continued)

Exposure	Overall evaluation (IARC Group)[a]	Volume	Year	Evaluation for cancer in humans	
				Cancer sites with *sufficient* evidence in humans	Cancer sites with *limited* evidence in humans
Trivalent antimony	2A	131	2023		Lung
Ultraviolet radiation	1	100D	2012	Cutaneous malignant melanoma, squamous cell carcinoma of the skin, basal cell carcinoma of the skin	
Vinyl chloride	1	100F	2012	Angiosarcoma of the liver, hepatocellular carcinoma	
Vinylidene chloride	2B	119	2019		

AML, acute myeloid leukaemia; HIV, human immunodeficiency virus; NHL, non-Hodgkin lymphoma.

[a] Group 1, *carcinogenic to humans*; Group 2A, *probably carcinogenic to humans;* Group 2B, *possibly carcinogenic to humans*.

[b] Strong inorganic acid mists.

trained to serve in many of these subgroups (i.e. wildland, municipal, investigation, etc.), whereas in other countries, a fire department (also known as a fire brigade) may have a workforce with firefighters working solely in one subgroup. [The Working Group noted that the tasks carried out by firefighters have changed over time, which may influence exposures. In particular, medical emergency call responses have been an increasing responsibility for firefighters in some countries.]

(a) Employment status of firefighters

The International Association of Fire and Rescue Services reported that there are more than 15 million firefighters (including 1.49 million career firefighters) in 57 countries, including most high-income countries and some low- and middle-income countries, such as China (CTIF, 2021; see Table S1.2, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). In the USA, two thirds of firefighters are volunteers or part-time paid per call (which includes paid on-call or paid per call) (Fahy et al., 2021). In England, about one third of firefighters are retained (i.e. paid on-call) (United Kingdom Home Office, 2021a). Higher proportions of all firefighters were reported to be volunteers in the Netherlands (80%), Canada (83%), and Australia (89%) (Haynes & Stein, 2018; Australian Government Productivity Commission, 2022; CBS, 2022). Career and volunteer firefighters perform the same basic jobs and tasks, but career firefighters usually work more hours and may have more advanced training than do volunteers (Hwang et al., 2019a; Fahy et al., 2021; NFPA, 2022). Volunteer firefighters are likely to attend fewer fires on average than do career firefighters (Monash University, 2014), but this is not always the case (Fig. 1.1).

[The Working Group noted that payment structures and employment status vary by country and that some fire departments may contain both volunteer and career firefighters.] Volunteer firefighters may not have the same resources as career firefighters. For example, in some geographical locations in the USA, volunteer firefighters are less likely than career firefighters to be equipped with turnout gear, helmets, and even SCBA that are compliant with the recommendations of the National Fire Protection Association (NFPA). Volunteers also tend to be firefighters in smaller departments, in more rural communities, and may lack the resources or finances to properly maintain or decontaminate their equipment or safety gear (Hwang et al., 2019a; NFPA, 2022). [The Working Group noted that it is not well understood how these organizational factors impact volunteer firefighters' exposures.]

(b) Minority and under-represented groups

Traditionally, the firefighter workforce has been a male-dominated profession. Women are under-represented in firefighting (see Table S1.2, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Among career firefighters, the proportion of women in the workforce reported ranged from 2% (Germany) and 4% (USA, Canada) up to 8% (New Zealand) (Statistics Canada, 2018; Fire and Emergency New Zealand, 2021; German Network of Female Firefighters, 2022). In an Australian cohort study covering employment from pre-1970 to 1995 and later, 4% of the full-time career firefighters and 8% of part-time career firefighters were women (Monash University, 2014). Among volunteer firefighters, 10% were women in the USA and Germany (Fahy et al., 2021; German Network of Female Firefighters, 2022). In Australia, this was 19% (Monash University, 2014). Among all firefighters in Portugal, 13% were reported to be women (Lam, 2009).

Minority groups (e.g. racial and/or ethnic groups that make up a small proportion of the regional or national population being studied) are also often under-represented in firefighting.

Fig. 1.1 Distribution of the number of incidents attended by individual firefighters (career full-time and part-time and volunteer)

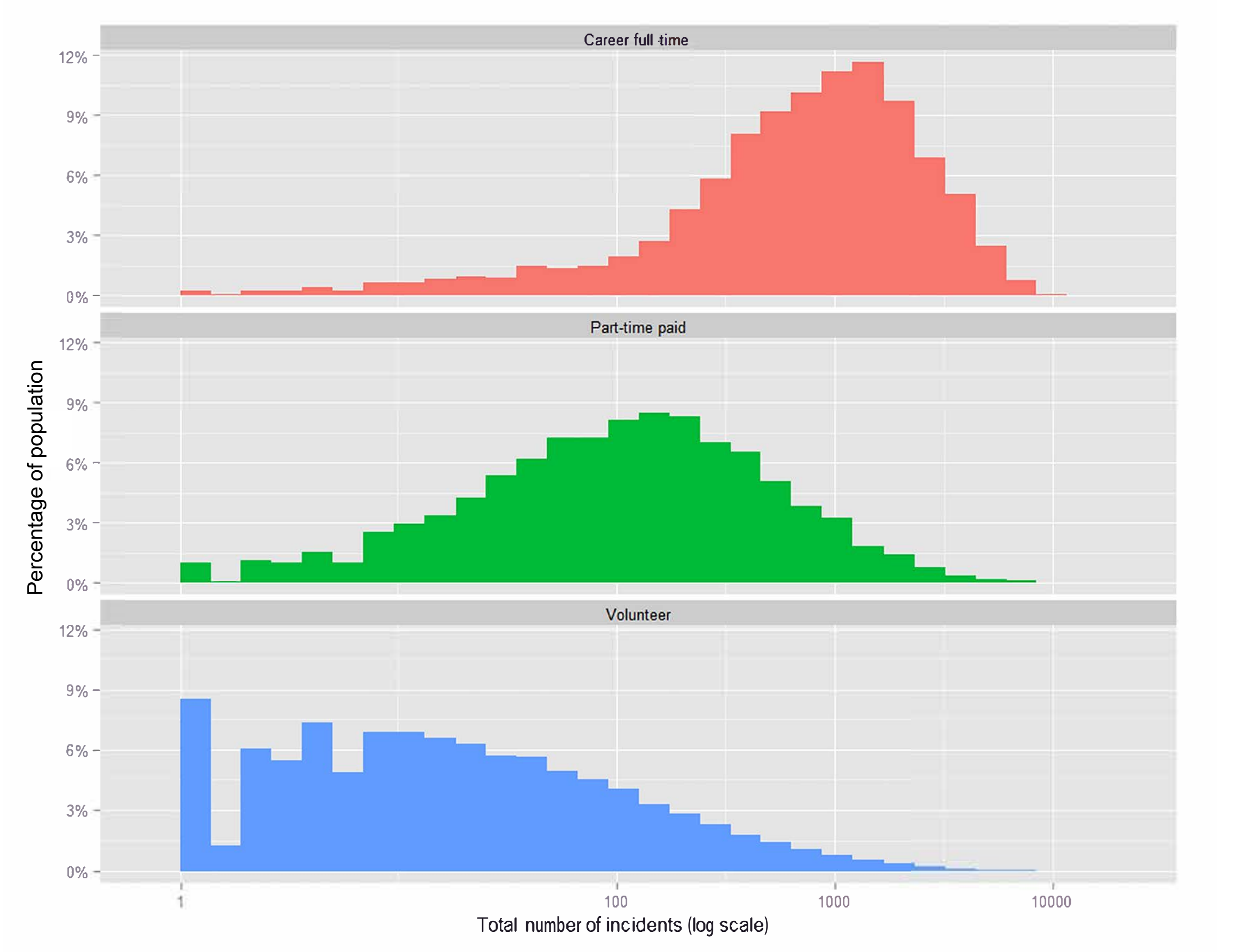


Fig. 1.1 shows that most career full-time firefighters attended more incidents than did part-time firefighters, and the volunteer firefighters attended fewer incidents than did part-time firefighters. For career full-time, volunteer, and part-time firefighters, respectively, 47%, 53%, and 78% of incidents attended were fires.
From Monash University (2014), with permission.

In the USA, the Bureau of Labor Statistics documented that in 2015 more than 1.2 million people were employed as firefighters and other first responders; the majority were White, non-Hispanic men, and aged between 25 and 54 years (Schafer et al., 2015). In England in 2020, 93% of firefighters were men and only 4% were members of an ethnic minority group (United Kingdom Home Office, 2021b). [The Working Group has identified a lack of information on firefighter exposures by race, ethnicity, and sex.]

(c) *Municipal firefighters*

Municipal (also referred to in the literature as "structural" or "urban") firefighters are an occupational subgroup of firefighters who engage in activities of fire suppression, rescue, and property conservation in buildings and enclosed structures that are involved in a fire or emergency situation. These firefighters may work for urban, suburban, or rural fire departments or agencies, and may have complex and variable work histories and exposures because of their changing occupational roles and fire responses (Fahy et al., 2021).

Potential assignments for firefighters at a structure fire incident include attack, search and rescue, outside ventilation, overhaul, backup or rapid intervention, engineer or pump operation, rehabilitation, and incident command (US Fire Administration, 2008; Fent et al., 2017) (Fig. 1.2, Fig. 1.3). Attack involves advancing a hose line and suppressing all active fire. Search and rescue may involve forcible entry into the structure and then a search for any victims. Outside ventilation typically involves creating openings at the windows and roof for horizontal and vertical ventilation of smoke and gases. Backup teams often set up a second hose line and are available for additional suppression or support as needed. Rapid intervention teams typically set up just outside the structure and are available for emergency rescue or support services as needed. Overhaul is performed after the fire has been suppressed and involves the active search for and suppression of any residual flames or smouldering items that could reignite the fire. Rehabilitation is a component of incident response in which firefighters are typically checked after an interior fire response and hydrated to prevent more serious conditions such as heat exhaustion or heat stroke. The engineer (also known as a vehicle/pump operator or chauffeur) is responsible for operating the pump and ensuring that hose lines are charged, and the incident commander directs the response activities (US Fire Administration, 2008; Horn et al., 2018; Engel, 2020).

Other job assignments are possible depending on the size and height of the structure and spread of the fire, the capabilities and resources of the responding fire companies, and incident management at the scene. A structure fire response may be very different in low- and middle-income countries where resources and technology are limited. For example, interior fire attack and search and rescue are mainly possible where firefighters have the appropriate PPE, such as coat, trousers, gloves, boots, helmet, and SCBA. [The Working Group noted that little research on job assignments and fire structures in low- and middle-income countries, including detailed information on safety gear and PPE, was available in the literature.] In addition to responding to structure fires, firefighters can respond to other emergencies, e.g. vehicle and waste container (dumpster) fires, building collapse, and medical emergencies (Kinsey & Ahrens, 2016), and have other specialities within their department, including emergency medical technician, paramedic, urban search and rescue, and hazardous materials (“hazmat”) specialist (Miami Dade College, 2022).

(d) Life at the fire station

Municipal firefighters are typically assigned to a fire hall or station that mimics a residential home and includes a kitchen, living room, shower facilities, and sleeping quarters (Kitt, 2009; Markham et al., 2016). Typically, firefighters will start their shift conducting daily equipment checks, preparing their PPE and equipment, and liaising with the outgoing shift. During their shift, firefighters may perform station duties (cleaning, maintenance, cooking), engage in physical activity, participate in training activities, and have free time, depending on the number of emergency events received during their shift. Firefighters often work extended shifts (Section 1.5.2), so some departments allow firefighters to sleep during shifts (Firefighter Connection, 2022).

(e) Wildland firefighters

Wildland firefighters are tasked with combatting and preventing wildfires in wildlands and at the WUI (Theobald et al., 2007; Mell et al., 2010).

Fig. 1.2 Municipal firefighters during exterior attack of a structure fire

Fighting structure fires involves suppressing active fires and advancing a hose line.
From © Scott Stilborn/Ottawa Fire Services.

Fig. 1.3 Firefighter performing overhaul

Overhaul involves the suppression of any remaining flames or smouldering items after the main fire has been suppressed.
From Professor Anna A. Stec, Centre for Fire and Hazards Sciences, University of Central Lancashire, UK.

They may be career or volunteer firefighters and are often seasonal workers. Deployments of thousands of wildland firefighting personnel to wildfires have been reported within a single country across a fire season (e.g. 7373 firefighters during the 2019–2020 Australian bushfires) (Parliament of Australia, 2020) or on single days (e.g. in the USA) (NIFC, 2022a). [Data on the number of wildland firefighters are not systematically documented in most countries. In the USA, estimates of the number of wildland firefighters employed by federal agencies are around the tens of thousands (Butler et al., 2017; Broyles et al., 2019).]

Factors that may have an impact on exposure, including fire behaviour, release of fire effluents, and firefighting technique, may vary across wildfires, since wildfires occur in wildlands with varying vegetation types (e.g. peat forest, conifer forest, grassland) and sometimes in the WUI, with structures and vehicles that also contain synthetic materials (HomChaudhuri et al., 2010; Caton et al., 2017; Cruz et al., 2018; Kganyago & Shikwambana, 2020). In addition to wildfire suppression, wildland firefighters carry out fire prevention by performing prescribed burns, which are controlled fires that are intentionally set to achieve resource management objectives, including fuel reduction and ecological purposes (Navarro et al., 2019a). [It is likely that the cumulative occupational smoke exposure of wildland firefighters has been increasing since the annual acreage of wildfire burns (NIFC, 2022a), number of workdays spent at wildfires per year (Navarro et al., 2019a), and/or the total area of land managed by prescribed burns (NIFC, 2022a) have probably increased, as trends in the USA indicate. Similar trends have also been observed in other countries (see Section 1.2.2).]

Job assignments during wildland fire responses differ substantially from structure fire responses (Semmens et al., 2016; Belval et al., 2017). However, municipal firefighters in areas where wildfires are common (e.g. western USA and parts of rural Australia) may be trained and involved in wildfire response activities, and 86% of the 26 000 local (municipal) fire departments in the USA in 2010 were estimated to have wildland firefighting duties (Butler et al., 2017). Wildland firefighters working at wildfires and prescribed burns are typically assigned to hand crews or engine crews (Department of Interior, 2022). Hand crews are responsible for clearing brush and other burnable vegetation along the expected pathway of the fire to construct a fire line or linear fire barrier. Hand crews often use gasoline-powered chainsaws, shovels, and other hand tools to construct the fire line; this is strenuous, time-consuming work and may involve hiking long distances (Reinhardt & Ottmar, 2004; Williamson et al., 2016). After a fireline has been secured, mop-up can proceed; this involves the extinction of any burning or smouldering vegetation, usually by covering the material with soil. Mop-up may also involve the removal of partially burned vegetation, including the felling of standing dead trees (USDA Forest Service, 2021b). Wildland firefighters may also use hand drip torches fuelled by a mixture of gasoline and diesel for backfiring (burning out unburned fuels between an active wildfire and a defensible perimeter) during wildfire suppression or for lighting vegetation during prescribed burns or backburns (Reinhardt & Ottmar, 2004; Adetona et al., 2019; McCormick & May, 2021).

Engine crews work with diesel-powered fire engines that carry water or foam and are used to suppress active fires where access is possible (USDA Forest Service, 2021c). There are other speciality disciplines in wildland firefighting, such as smoke jumpers and helitack crews, who parachute, rappel, or land near the wildfires to provide more targeted interventions (USDA Forest Service, 2021d). [Numerous other tasks beyond those discussed here may also be carried out to control the spread of wildfires or manage prescribed burns.]

Wildland firefighters usually carry their equipment with them in backpacks and wear light protective clothing, such as long-sleeved fire-resistant shirts, trousers, and gloves, mountaineering boots, and hard hats. Respiratory protection is not commonly used (see Fig. 1.4). However, the type of protective gear worn and the way in which wildfires are managed may differ between countries.

Studies have shown that wildland firefighters are exposed to high physiological workloads, extended work hours, and dangerous environmental weather extremes (Carballo-Leyenda et al., 2017; Vincent et al., 2017; Hemmatjo et al., 2018). During a wildfire, these fire crews must provide around-the-clock fire suppression to protect life and property, which may last days, weeks, or months. For example, there is a standard 14-day wildfire assignment for federally employed wildland firefighters in the USA, but this may be extended up to 30 days (with a 2-day break in the middle of the period) under certain circumstances (NWCG, 2004). These extended response times in remote locations not only increase exposure duration, but also make it difficult to clean protective clothing and skin (Cherry et al., 2019). Wildland firefighters are temporarily housed at base camps in the proximity of wildfires during fire suppression deployments (McNamara et al., 2012). They may experience additional exposures at these base camps because of the transport of wildfire smoke

Fig. 1.4 Wildland firefighter during a controlled forest fire in northern Portugal

It is common for wildland firefighters not to wear self-contained breathing apparatus, despite proximity to fire effluents.
From Marta Oliveira (4FirHealth Research Team).

plume over the camps, vehicle and power generator exhausts, and road dust (McNamara et al., 2012).

(f) Fire instructors

Fire instructors play a critical role in the development and training of firefighters (Reeder & Joos, 2019). When the firefighter recruit begins training, their first experience with live or simulated fire is led by an instructor. In many countries, a fire instructor is required to possess certification as a fire service instructor and/or subject matter expertise in subject areas of fire science demanded by fire departments and organizations. Fire service instructors teach in both classroom and laboratory settings (training grounds) from prepared lesson plans and under the direct supervision of or in collaboration with another senior fire service instructor (IFSTA, 2022). Fire instructors can be involved in multiple fire-training exercises on a given day.

Live-fire training may involve different types of fuel. Live-fire training environments in which an unconfined open flame or device propagates fire to the building or structure are designed to simulate the operational fire environment, but the specific chemical exposures to instructors may be quite different from those of real-world fires (Kirk & Logan, 2015a). For example, using plywood and chipboard as the fuel in training fires produces more pollutants than do pure pine or spruce, whereas the exposures measured during propane-burning training fires are lowest (Laitinen et al., 2010). A different study found that training exercises burning a certain type of oriented strand board (as well as pallet and straw) produced higher concentrations of certain chemicals (some of those already classified by IARC as *carcinogenic to humans*, Group 1) than did training exercises burning pallet and straw alone (Fent et al., 2019a).

Fire instructors may also experience cumulative exposure to air contaminants that far exceeds that of firefighters in operational fire environments (Kirk & Logan, 2015a; Fent et al., 2019a). Additionally, the behaviours and role of fire instructors in the training environment are different from those at an active fire scene. The non-emergency situation may not elicit the same work rate and physiological response, therefore increasing the length of exposure to chemicals (Kirk & Logan, 2015a). [The Working Group noted that evaluating the difference between air contaminant concentrations in the training environment and those in the microenvironment inside the instructor's firefighting ensemble, from which the majority of dermal uptake would occur, has received little research attention.]

(g) Fire cause investigators

A smaller subgroup of the firefighter workforce comprises fire cause investigators, who have responsibility for investigating and analysing incidents involving fires and explosions (NFPA, 2021c). They conduct root cause analysis of fire incidents and render an expert opinion as to the origin, cause, responsibility for, or prevention of fire incidents. Fire cause investigators are educated and trained in several topics, including fire science, fire chemistry, thermodynamics, thermometry, fire dynamics, explosion dynamics, computer fire modelling, and fire investigation and analysis (IAAI, 2018).

Fire cause investigators may work in either the public or private sector. Typically, those in the public sector are employed by municipalities, such as fire or police departments, or by state or federal agencies. Those working in the private sector may be employed by insurance companies, lawyers, or private firms. Many fire investigators come up through the firefighter ranks, starting out as municipal firefighters, and gaining experience in various aspects of fire behaviour before specializing in fire cause investigations. Some may begin in law enforcement and gain experience or training in arson investigations but do not necessarily have any direct firefighting experience (Belfiglio, 2022). Only fire cause investigators who have worked as or are working as firefighters are considered in the present monograph.

Although fire cause investigators usually report to the fire scene to conduct their analysis immediately after either the fire suppression and overhaul phases of a fire incident response, their attendance and investigation can be delayed hours or days post-fire suppression (Horn et al., 2022). A fire investigation can take from a few days up to a few months (Firefighter Insider, 2022). Fire cause investigators will use scientific methods to systematically review the fire scene, determine the circumstances as to the cause of the fire, and issue a determination, such as natural, deliberate, accidental incendiary, or undetermined cause (Daeid, 2005). Depending on the jurisdiction and standard operating procedures for the fire department, a fire investigator may use different approaches to conduct the investigation. Fire cause investigators generally attend more fire scenes than do most firefighters; however, they typically wear less PPE than firefighters, despite potentially harmful exposures at the investigation scene well after the fire is extinguished. [The Working Group noted that little research on exposure of fire cause investigators in high-income countries or in low- and middle-income countries (including the use of safety gear and PPE) was available in the literature.]

(h) Other subspecialities in the fire service

Firefighters can be employed in other work settings, including airports, military environments, and industrial complexes. Aviation rescue and firefighting is a type of firefighting that involves the emergency response, mitigation, evacuation, and rescue of passengers, crew, and property from aircraft involved in aviation accidents and fire incidents (Braithwaite, 2001; Smith et al., 2018). Although variations across countries can occur, airports with scheduled passenger flights are required to have firefighters and firefighting apparatus at the airport ready to respond at any time to an aircraft fire incident (Blocker, 2020). Airports may have regulatory oversight by an arm of their individual national governments or voluntarily under standards of the International Civil Aviation Organization (National Academies of Sciences, Engineering, and Medicine, 2011). Military firefighters are first responders in emergencies and may be required to perform fire suppression activities, rescue operations during a fire or other emergencies, or respond to hazardous spills in the military environment or war theatre (Moore et al., 2022). Industrial firefighters are specially trained firefighters who serve at manufacturing facilities, petrochemical plants, and refineries, among other industrial settings (Shelley et al., 2007; Ghasemi et al., 2021). They encounter unique challenges not commonly encountered by municipal firefighters, such as site-specific hazards, access areas, equipment, business priorities, and personnel, that will impact their fire suppression approach and tools at the industrial fire.

Firefighters at airports use AFFFs to extinguish class B fires, which are fires that arise from petroleum products or flammable liquids or gases, such as oil, gasoline, jet fuel, and other fuels (Rotander et al., 2015b; Milley et al., 2018; Environmental Litigation Group PC, 2020) (see Fig. 1.5). Until 2021, airports in the USA were required to use AFFF that contains fluorinated surfactants (Andrews et al., 2021; Shepardson, 2021). Additional information on PFAS use is included in Section 1.5.1(b). All United States (US) military branches were required to use fluorinated firefighting foams at bases located in the USA. Fluorinated AFFFs have also been used in other countries, such as Germany, Sweden, and the United Kingdom (UK) (Hu et al., 2016; Allcorn et al., 2018; Nordic Council of Ministers, 2019). Local municipalities also use and store AFFF. In the USA, almost 75% of AFFF is used by the military, and the remaining 25% is used by organizations such as refineries, fuel tank farms, municipal airports, and other industries (Andrews et al., 2021; Environmental Litigation Group PC, 2020). See Section 1.7 for regulations on use of firefighting foams.

1.2.2 Changes in frequency and intensity of fires

[Global trends in structure fires are difficult to ascertain because fire statistics are not available in all countries. These statistics do not include training fires or chemical incidents, which may also contribute to firefighters' exposures.] In the USA, there were 4.2 fires per 1000 population in 2020, which is about the same rate as in 2010, but more than 60% lower than the rate in 1980. Of those fires, approximately 35% were structure fires, 15% were vehicle fires, and 50% were outdoor or vegetation fires (Ahrens & Evarts, 2021). In England, firefighters responded to more than 151 000 fires in the year ending March 2021, which is a 34% decrease compared with 10 years previously. More than 40% of those fires occurred in a building, vehicle, or outdoor structure, or involved a fatality or casualty (Government of the United Kingdom, 2021). In Australia, there was a trend towards increased

Fig. 1.5 Firefighters using fire suppression foam on a class B fire at an airport

From Rich/Adobe Stock.

frequency of bushfires between 2011 and 2016 (Bushfire and Natural Hazards CRC, 2019). In Asia, Tishi & Islam (2018) reported that of all the fires in Bangladesh in the years 2010–2013, the fire incidence in Dhaka Metropolitan Area corresponded to the mean of [16.5%], and the highest frequency (36%) occurred in residential areas. The highest density of fire incidents occurred in areas of commercial and mixed use (38% and 26%, respectively). For other regions, e.g. Latin America and Africa, no information was available.

[Wildfire statistics are presented both on area burned and number of fires, and these may appear contradictory.] In southern Europe (Portugal, Spain, France, Italy, and Greece), the annual area burnt in forest fires has decreased from around 600 000 hectares in the 1980s to less than 400 000 hectares in the 2010s (San-Miguel-Ayanz et al., 2022). From the 1950s to the 2000s, the average annual area burnt in forest fires in Finland has decreased from 5760 hectares to 643 hectares (Suokas, 2015). According to one analysis, the global area burned by wildfires appears to have declined overall over past decades; however, the probability and severity of wildland fire is increasing in some regions of Europe (Doerr & Santín, 2016; Fernandez-Anez et al., 2021; San-Miguel-Ayanz et al., 2022).

Other analyses also suggest that the frequency of wildfires is increasing in some parts of the world. In the UK, peat, grass, and wildfires are becoming increasingly common, reflecting the changing weather patterns that are making the UK hotter and drier (Belcher et al., 2021). According to the European Forest Fire Information System, there is wide variation in the number of wildfires and the area burned each year (San-Miguel-Ayanz et al., 2022). Spatial and temporal trends in the incidence and severity of wildfires in Canada is tracked by the Canadian National Fire Database (Government of Canada, 2021); more than 8000 fires per year burn an average of more than 2.1 million hectares. Recent research suggests that climate change is responsible for noteworthy increases (i.e. 1.5- to 6-fold) in the frequency of extreme burning conditions and, by extension, the incidence and severity of wildfires in Canada (Coogan et al., 2020).

During the last decade, the USA has experienced exceptionally large fires, California being one of the most affected regions (Keeley & Syphard, 2021; State of California, 2021). During the 2017 wildfire season, a total of 71 499 wildfires was reported in the USA (National Interagency Coordination Center, 2017). These wildfires consumed 10 026 086 acres [4 057 413 hectares] of land (153% of the 10-year average) nationally and a total of 12 306 structures were destroyed, meaning that the 2017 wildfire season was the worst on record in terms of total structures lost. In Australia, the length and severity of the wildfire season are also increasing across much of the country, as measured by annual indices of the Forest Fire Danger Index (AFAC, 2021). Regarding Latin America, some studies suggest that there has been an increase in the frequency and length of wildfires over the last decade (González et al., 2018; Urrutia-Jalabert et al., 2018; Barni et al., 2021).

WUI fires are similarly becoming more common (Mell et al., 2010; Stein et al., 2013; Ribeiro et al., 2020). In the USA, significantly destructive WUI fires occurred in Florida in 1998, and in California in 2003, 2007, and, most recently, 2017. WUI fires have also had an impact in Europe, particularly in Portugal, France, Spain, and Greece. This has resulted in large losses of property and numerous human casualties (Ferreira-Leite et al., 2013; Darques, 2015; Tedim et al., 2015; Cardoso Castro Rego et al., 2018; Oliveira et al., 2020a).

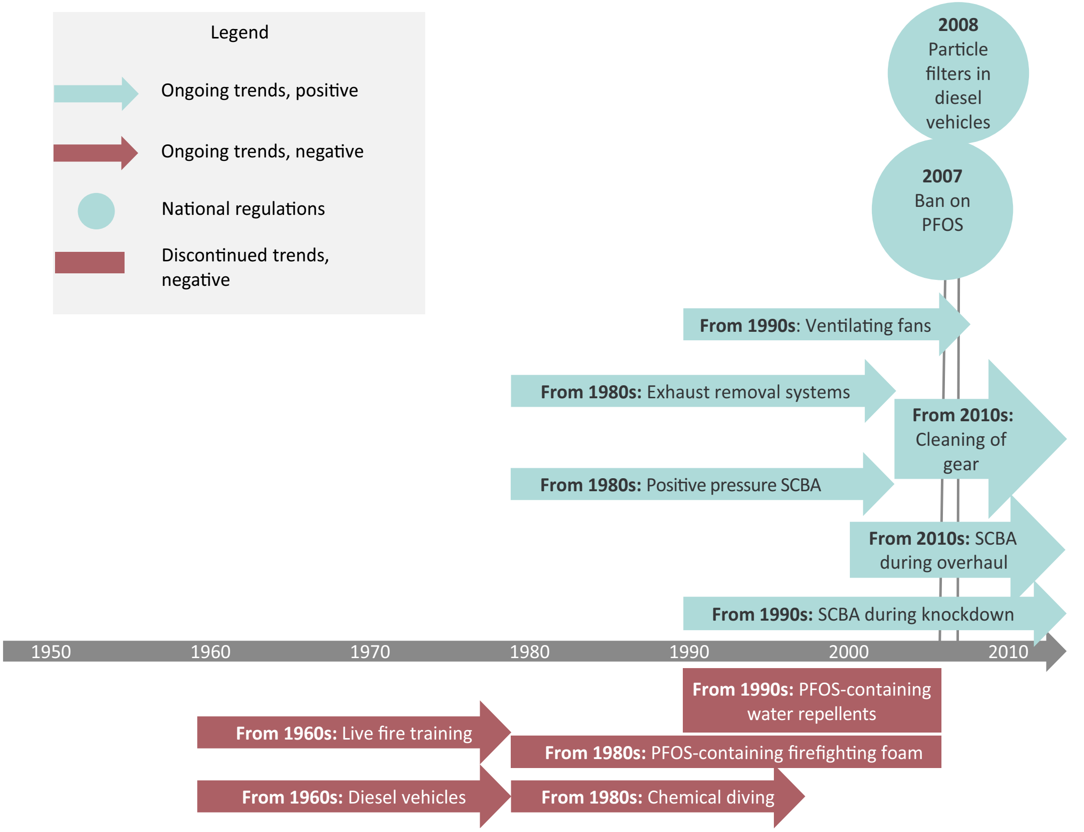
1.2.3 Temporal changes in personal protective equipment

The types of respiratory and dermal protection worn by municipal firefighters have changed over time. A major advancement in respiratory protection occurred around the 1960s when compressed-air demand-type SCBA was adapted for use by municipal firefighters, although it took another decade or longer for these respirators to gain widespread acceptance and use among fire departments (Spelce et al., 2018; Pedersen et al., 2019; London Fire Brigade, 2022). Many firefighters now wear SCBA during overhaul, but this was not common practice before the 2000s (Jakobsen et al., 2020) (see Fig. 1.6 for work-related trends observed in fire departments in Norway). [The Working Group noted that variability in this practice probably exists in fire departments throughout the world.]

Personal protective clothing has also changed from long rubber trench coats and three-quarter length rubber boots to the first iterations of modern turnout gear consisting of full-length trousers and jacket made of multiple layers of protective textiles capable of meeting heat-resistance and other performance specifications in the early 1970s (with broad adoption and standardization occurring over the next 10–20 years) (British Standards Institution, 2006, 2019b, 2020; Hasenmeier, 2008; NFPA, 2018). [Before the late 1970s, it is possible that asbestos was used in firefighter PPE; there are reports of asbestos in helmet covers (Lumley, 1971), respirators, and protective clothing.]

Fire departments began adding protective hoods to the turnout gear ensemble in the 1990s

Fig. 1.6 Changes in work conditions for firefighters from the 1950s until 2010 in Norway



PFOS, perfluorooctane sulfonate; SCBA, self-contained breathing apparatus.
Timeline of changes in policies, standards, or practices that have probably had an impact on carcinogenic exposures for firefighters in Norway. Many of these changes have also been undertaken for firefighters in other countries over similar periods. Chemical diving is part of the clean-up under water after chemical spills or accidents and firefighters/hazardous materials specialists wear special protective equipment.

(Prezant et al., 2001). In the late 2010s, PFAS were identified as constituents in the manufacture of firefighting turnout gear in the USA (Peaslee et al., 2020).

Greater awareness of contamination of turnout gear resulting from firefighting activities developed in the 2010s. New policies and procedures on turnout-gear cleaning after firefighting activities soon followed. According to a survey of fire departments in Norway, since the 1990s every department (*n* = 16) has responded that turnout gear should be washed after it has been used in a contaminated environment (Jakobsen et al., 2020). [However, variability in this practice probably exists in fire companies throughout the world. In addition, some firefighters perform on-scene gross decontamination of their gear, some launder their gear, and some do both after use in a contaminated environment. Having a second set of turnout gear and onsite extraction washers is also helpful for allowing this practice, which is not common in under-resourced fire departments.] See Section 1.6 for more information on PPE cleaning practices.

1.2.4 Other temporal changes that could affect firefighters' exposures

Building materials and the items within buildings have also changed over time (Stec & Hull, 2008; Stec et al., 2019; Jones et al., 2021; Peck et al., 2021). Once built and furnished with natural materials, like wood, clay, cotton, wool, and minerals (including asbestos), residential and commercial structures today commonly include laminated or engineered wood products (e.g. containing glues and resins), polymeric cladding, and numerous other synthetic materials, such as plastics and foams. These synthetic materials, along with open floor plans, can cause the fires to propagate, consume oxygen, and produce toxic gases at much faster rates than in the past (Stec & Hull, 2011; Kerber, 2012; McKenna et al., 2019; Stec et al., 2019). Some of these synthetic materials also contain chemical additives to provide certain desirable properties, such as plasticizers (e.g. phthalates), stain-resistant coatings (e.g. PFAS), and flame retardants (e.g. organophosphorus compounds). These substances may present their own unique exposure hazards. Foam insulation used within or outside the building envelope can also contribute to fire spread (e.g. the Grenfell Tower in London, UK) (Grenfell Tower Inquiry, 2019; McKenna et al., 2019; Jones et al., 2021; Peck et al., 2021). [Although asbestos is no longer used as an insulating material, and lead is no longer used in paint (having been banned for more than four decades in most countries), these compounds are likely to be present in many older homes and buildings and could still be released during structure fires.]

Diesel engines were largely introduced in the 1960s, hence diesel exhaust exposure has been prevalent in the fire service since that time. However, fire departments began installing diesel-exhaust capture systems in the 1980s to control these exposures in the apparatus bays (see Fig. 1.7). [The Working Group noted that the implementation of diesel-exhaust capture systems in fire stations has taken time and varies between and within geographical locations. Fire stations in low- and middle-income countries are unlikely to have these systems, and even some stations in high-income countries (especially in under-resourced departments) may not have them. The efficacy of these systems is highly dependent on proper use and maintenance (Chung et al., 2020).] More recently (in the mid-2000s), diesel-engine emission controls (e.g. diesel particulate filters) became available in the marketplace (IARC, 2013; Jakobsen et al., 2020). Battery electric vehicles (BEV) are now available, including BEV or hybrid-electric fire trucks, which may also reduce diesel exhaust exposure for fire personnel. Additional controls that have been implemented include general exhaust ventilation, diesel fuel additives, separations between the vehicle bay and living quarters, and various administrative policies, such as idling restrictions. See Section 1.5.1(d) for more information on diesel exhaust.

BEVs and hybrid-electric vehicles are growing in popularity and, like combustion engine vehicles, occasionally catch fire. Battery storage facilities can also catch fire (Gilbert, 2021). The lithium-ion batteries in these vehicles and storage facilities may produce very hot fires that require tremendous amounts of water and time to fully extinguish (Wang et al., 2012). [These types of fire may become more common as the population transitions to BEVs and back-up battery power.] See Section 1.5.1(h) for more information on lithium-ion battery fires and other emerging concerns in the fire service.

1.2.5 Health and health behaviours

Health behaviours can have an important impact on health status and cancer risk (Klein et al., 2014). Risky health behaviours, such as smoking, drinking alcohol, and sedentary behaviour, have been documented in firefighters. Studies have investigated obesity and overall

Fig. 1.7 Fire station in Chicago, USA, with diesel-exhaust capture system attached to a fire truck

The diesel exhaust extractor can be seen in yellow.
From Beatrice Prève/Adobe Stock.

health in firefighters. In a survey of 677 male firefighters from the midwestern USA, the prevalence of obesity (body mass index, BMI ≥ 30) was 32.6% and 38.5% for career and volunteer firefighters, respectively, compared with the age-standardized prevalence in US adults (33.8%) at the time of the survey (Poston et al., 2011). Munir et al. (2012) surveyed 735 male firefighters from the UK and discovered that 53% were overweight and 13% were obese; these were higher percentages than in the general population in England. In contrast, a survey of female career (n = 2398) and volunteer (n = 781) firefighters in the USA and Canada found an age-standardized prevalence of obesity in both career (17.2%) and volunteer (32.8%) firefighters that was lower than in women in the general population (41.1%) (Jahnke et al., 2022). A pilot study using actigraphy to objectively measure occupational and non-occupational physical activity among paid career firefighters found varying levels of physical activity during a typical work week, and these levels varied according to firefighter weight status categories (Kling et al., 2020). The study found that healthy-weight firefighters spent more time engaged in light and moderate physical activity than did overweight and obese firefighters, whereas overweight and obese firefighters spent more time engaged in vigorous physical activity than did their healthy-weight counterparts.

Firefighters have also been reported to experience workplace stress, have poor sleep quality, and have high levels of comorbidities. A survey of 1244 US firefighters (> 94% volunteers) revealed important statistics regarding health determinants and conditions (NVFC, 2010). For example, 54% of respondents said they experienced some or a lot of stress, 26% reported having trouble falling asleep, 28% reported having trouble staying asleep, 37% reported having high blood pressure, and 34% reported having high blood cholesterol.

Studies have also evaluated tobacco use and alcohol consumption among firefighters. A study of tobacco use among 677 male firefighters in the central USA found that career and volunteer firefighters had current cigarette smoking rates (13.6% and 17.4%, respectively) that were below national unadjusted averages between 2008 and 2010 (23.4% for adult men). However, rates for use of smokeless tobacco (18.4% and 16.8%, respectively) were above national unadjusted averages (7.0% for adult men) (Haddock et al., 2011). In the NVFC (2010) survey of mostly volunteer US firefighters, only 10% of respondents were current smokers, but 12% were current users of smokeless tobacco. Phan et al. (2022) examined trends in current smoking and smokeless tobacco use among US firefighters and law enforcement personnel and compared smoking and smokeless tobacco use prevalence in firefighters and law enforcement personnel to that in US adults in non-first-responder occupations. During the study observation period (1992–2019), the authors noted that smoking prevalence declined overall and was highest for individuals in other occupations, and that use of smokeless tobacco was higher among firefighters and law enforcement personnel (Phan et al., 2022). Among 1712 female career firefighters surveyed in 2015, the unadjusted rate for smoking was 5.1%, and the unadjusted rate for smokeless tobacco use was 1.2%; the age standardized smoking rates were lower than that of US adult women, which at the time of the study was estimated at 13.5% (Jamal et al., 2018; Jitnarin et al., 2019).

Firefighters, like individuals with other occupations, may engage in risky or binge drinking. Haddock et al. (2017) surveyed 1913 female firefighters in the USA and found that nearly 40% reported binge drinking in the past 30 days, well above rates reported nationally among women at the time (12–15%). Binge drinking for men was defined as five or more drinks on an occasion in this survey, and 56% of career firefighters and 45% of volunteer firefighters reported binge drinking one or more times in the past 30 days (Haddock et al., 2012), about twice the national average for adult men at the time (Kanny et al., 2013).

Some of the unhealthy behaviours reported among firefighters may be related to occupational stressors and/or peer pressure. Jitnarin et al. (2017) surveyed 1474 career male firefighters in the USA and found that nearly 16% of current users of smokeless tobacco initiated use after joining the fire service, which is substantially higher than expected compared with rates in the general population (i.e. 0.8% late initiation for adult males). Haddock et al. (2017) conducted a survey of 1913 US female firefighters and reported that those who screened positive for problem drinking (16.5% of those who drank alcohol) were 2.5 times as likely as the general population to have been diagnosed with depression or have post-traumatic stress disorder symptoms, and were 40% more likely to have experienced an occupational injury in the past year. Some of these adverse health behaviours (e.g. smoking, binge drinking, and caloric intake from alcohol – i.e. higher amounts of carbohydrates and lower amounts of fibre and vitamins) have been associated with night shift work in other worker populations (Bøggild & Knutsson, 1999; Lowden et al., 2010; Bae et al., 2017; Richter et al., 2021). See Section 1.5.2(a) for more details on shift work.

[The Working Group noted that the information on modifiable risk factors was limited, with nearly all available information stemming from a small number of cross-sectional surveys published since 2011. The representativeness of these studies was low given that the study populations were few (mainly USA) and sample sizes were relatively small. Moreover, longitudinal information was not available (with the exception of tobacco use in the USA, where data from a series of cross-sectional studies were available), although temporal trends probably varied given changes in firefighter behaviours and fire department policies over time.]

1.3 Detection and quantification

1.3.1 Composition of fire smoke

Combustion products are dependent on the chemical composition of the fuel that is burnt and ventilation conditions (temperature and oxygen availability) (Stec, 2017). Combustible materials vary across different types of fire, such as residential, industrial, vehicle, agricultural, and wildland fires, and any fire that is a combination of these (i.e. WUI). The fuel composition ranges from mostly lignocellulosic vegetative biomass in wildland and agricultural fires to various mixes of solid natural materials, solid synthetic materials including plastics, and liquid petrochemical fuels (Yang et al., 2007; Hess-Kosa, 2016). Common fire effluents in different types of fire are presented in Table 1.3.

Vegetation contains mostly carbon, oxygen, and hydrogen, and various types of vegetative biomass including wood have been measured and/or estimated to contain 36.2–58.4%, 31.4–49.5%, and 4.4–10.2% of these elements, respectively, by dry or dry ash-free weight (Parikh et al., 2007; Vassilev et al., 2010). Vegetative biomass also contains minor amounts of other elements, including 0.1–3.4% nitrogen and 0.01–0.60% sulfur. [Since vegetative biomass is mostly composed of carbon, hydrogen, and oxygen, the emissions from wildland fires are dominated by carbon monoxide (CO), hydrocarbons, and oxygenated carbon compounds (Yi & Bao, 2016; Liu et al., 2017; Hu et al., 2018). A major difference between wildland fires and other types of fire, including structure, vehicle, and WUI fires, is the presence and number of synthetic materials. Little is known about the chemical composition of consumer products used, for example, in buildings or cars. A non-targeted analysis by Phillips et al. (2018) measured numerous compounds in consumer products, of which 88% were not listed in a database of chemicals known to be used or present in consumer products.]

Fires traverse different stages and commonly evolve from non-flaming oxidative pyrolysis, to early well-ventilated flaming, through to fully developed under-ventilated flaming (Purser & Maynard, 2015; Stec, 2017). Oxidative pyrolysis generates low concentrations of partially oxidized organic species (e.g. carbonyl compounds and organic acids). [These may be significant in the case of fuels with a higher moisture content (for example, in peat fires).] Similarly, well-ventilated fires are generally small, and with an increase in temperature and decrease in oxygen concentration can turn into ventilation-controlled (under-ventilated) fires that exhibit much higher concentrations of the released fire effluents (Stec et al., 2007). It has been demonstrated that the yield of combustion products such as CO, hydrogen cyanide (HCN), and other smoke components increases by a factor of between 10 and 50 as the fire changes from well-ventilated to under-ventilated (Stec et al., 2007; Stec, 2017). The impact of ventilation conditions on the yields of major gases emitted by fires is presented in Table 1.4.

Combustion of most aliphatic materials (consisting only of carbon and hydrogen), such as polyethylene and polypropylene, follows the trend whereby CO concentration increases from a low value in well-ventilated conditions, to a much higher value in under-ventilated flaming.

Table 1.3 Common fire effluents produced by different types of fire

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

[a] Brandt-Rauf et al. (1988); Persson & Simonson (1998); Lioy et al. (2002); Landrigan et al. (2004); Stec & Hull (2008); Organtini et al. (2015); Fent et al. (2018, 2020a); Stec et al. (2018); Alharbi et al. (2021).
[b] Urbanski et al. (2008); Hu et al. (2018).
[c] Nammari et al. (2004); Lönnermark & Blomqvist (2006); National Air Quality Modelling & Assessment Unit (2009); Pivnenko et al. (2017); Cai et al. (2020); Hadden & Switzer (2020).
[d] Lönnermark & Blomqvist (2006); NIOSH (2010); Fent & Evans (2011); Caban-Martinez et al. (2018).

Partially oxidized organic compounds such as carbonyl compounds, organic acids, and PAHs are also present in the smoke from combustion of such materials. Higher yields of aromatic compounds are released in smoke from the combustion of polystyrene, which is an aromatic hydrocarbon polymer (Purser & Maynard, 2015).

A wider range of products are formed when materials containing oxygen or other elements are combusted (Purser & Maynard, 2015). More-oxidized combustion products, such as nitrogen oxides and ammonia, are released in higher concentrations than HCN when nitrogen-containing polymeric materials, e.g. polyurethane and polyisocyanurate foams, are combusted under well-ventilated fire conditions (Stec & Hull, 2008). Much higher concentrations of CO and HCN are observed for under-ventilated conditions of these materials (following the patterns for products that only contain hydrocarbons) (Stec & Hull, 2011). Also, gaseous mono-isocyanates were observed in studies of under-ventilated, fully developed enclosure fires of materials including polyurethane foam (Blomqvist et al., 2010, 2014; Stec & Hull, 2011; McKenna et al., 2019, Peck et al., 2021).

Materials containing chlorine (e.g. polyvinyl chloride, PVC) release CO and hydrogen chloride

Table 1.4 The main fire gases and their dependence on ventilation conditions

Yield largely independent of fire conditions	Yield decreases as ventilation decreases	Yield increases as ventilation decreases
Hydrogen fluoride (HF)	Carbon dioxide (CO_2)	Carbon monoxide (CO)
Hydrogen chloride (HCl)	Nitrogen dioxide (NO_2)	Hydrogen cyanide (HCN)
Hydrogen bromide (HBr)	Sulfur dioxide (SO_2)	Acrolein (C_3H_4O)
		Formaldehyde (CH_2O)

(HCl). The fire gas pattern is very different from that for all other polymers, since the yields of CO and HCl are independent of the fire scenario (Molyneux et al., 2014), and relatively low carbon dioxide (CO_2) yields and high yields of CO, particulates, and organics, and significant residues are observed in well-ventilated combustion conditions (Stec & Hull, 2008; Molyneux et al., 2014). Most of the chlorine contained in the material is released as HCl, but a small proportion of it is released as other chlorine-containing gas or vapour species, such as chloro-aliphatic and chloro-aromatic hydrocarbons. Formation of carcinogenic polychlorinated dibenzo-*para*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in residential fires commonly occurs when halogenated materials that are widely used in building construction (e.g. in pipes, siding, flooring, and wire insulation) are combusted (Ruokojärvi et al., 2000; Katami et al., 2002; Lavric et al., 2004; Zhang et al., 2015). In addition, the presence of specific metals increases the yields of polychlorinated dibenzo-*para*-dioxins and dibenzofurans (PCDD/Fs). This occurs with construction wood that is impregnated with legacy preservatives (e.g. chromated copper arsenate and pentachlorophenol) and newer preservatives (e.g. alkaline copper quaternary and copper azole) (Wang et al., 2002; Tame et al., 2009; Rabajczyk et al., 2020). The production of polychlorinated biphenyls (PCBs) has been banned since 1979 in the USA and since 1981 in the UK, and an international agreement in 1986 banned most uses; however, combustion of PCBs in existing electrical equipment and electric fires might result in emission of PCDD/Fs (Buser, 1985; Hutzinger et al., 1985).

Another fire-derived combustion product is sulfur dioxide (e.g. from phenolic foam) (Stec & Hull, 2011). Aliphatic and aromatic hydrocarbons (e.g. benzene and 1,3-butadiene), oxygenated organic compounds (e.g. formaldehyde, acetaldehyde, and acrolein), PAHs, and soot particles are found in almost all fires, and their concentrations are increased when combustion is ventilation-limited (Austin et al., 2001b; IARC, 2010; Purser et al., 2010; Hewitt et al., 2017; Bralewska & Rakowska, 2020).

Concentrations of released combustion products may change when the fuel contains fire retardants. Fire retardants that act in the gas phase and interfere with flame reactions (i.e. flame retardants) are frequently applied to insulation foams, electrical equipment, and upholstered furniture (Blomqvist et al., 2004a, b; Stec & Hull, 2011; McKenna et al., 2019). When burning PVC, a similar gas-phase inhibitory effect is observed. In terms of fire emissions, gas-phase halogenated flame retardants (e.g. organophosphate flame retardants, OPFRs) will release hydrogen bromide (HBr) or HCl, and considerable quantities of CO, HCN, smoke, and other products of incomplete combustion (e.g. acrolein and formaldehyde), as well as larger cyclic molecules such as PAHs and soot particulates (Molyneux et al., 2014; McKenna et al., 2019). Brominated flame retardants have been banned in the USA since 2004 and in the

European Union since 2003 (e.g. polybrominated diphenyl ethers, PBDEs), and those currently on the market (e.g. tetrabromobisphenol A, TBBPA; and other brominated phenols) are known to enhance concentrations of mixed polybrominated dibenzo-*para*-dioxins and furans (PBDD/Fs) (Weber & Kuch, 2003; Ortuño et al., 2014; Organtini et al., 2015; Zhang et al., 2016).

Additionally, emission of fine and polydisperse particles that are mostly smaller than $PM_{2.5}$ and generally in the nanometre to submicron range has been reported for wildfires, laboratory combustion testing of wood, and laboratory building and automobile compartment tests simulating overhaul conditions of firefighting (Lachocki et al., 1988; Jankovic et al., 1993; Leonard et al., 2000, 2007; Shemwell & Levendis, 2000; Fine et al., 2001; Valavanidis et al., 2008; Baxter et al., 2010; IARC, 2010; Carrico et al., 2016; Kleinman et al., 2020). Smoke, soot, and particulate emissions vary greatly according to fuel composition and fire conditions (Shemwell & Levendis, 2000; Valavanidis et al., 2008; Blomqvist et al., 2010). However, it is recognized that more and larger-sized particles tend to be generated by fires with less ventilation or oxygen (Shemwell & Levendis, 2000; Blomqvist et al., 2010; Carrico et al., 2016). This effect is enhanced in the presence of halogens, which tend to increase the distribution and concentrations of particulate matter and other volatiles (Blomqvist et al., 2010).

Various metals (e.g. cadmium, cobalt, chromium, copper, nickel, lead, antimony, thallium, and zinc) and persistent free radicals are also found in the particulate soot and ash residues resulting from wildland, structure, or vehicle fires (Smith et al., 1982; O'Keefe et al., 1985; Jankovic et al., 1993; Leonard et al., 2000, 2007; Dellinger et al., 2007; Valavanidis et al., 2008; Organtini et al., 2015). Carbon- and oxygen-centred radicals in the particles and ash residue persist for up to 6 months, with electron paramagnetic resonance signals in the samples remaining the same across the period. Persistence has also been attributed to trapping within and adsorption to the polymeric carbonaceous matrix (Valavanidis et al., 2008).

Various types and quantities of gaseous species are also often found to be attached to particulates. This includes, for example, acid gases (HCl, HBr), isocyanates, and various metals (Blomqvist et al., 2010, 2014; Stec et al., 2013).

Vehicle fires, in addition to having an increased yield of released metals, can release acid gases (HCl and HF), carbonyl fluoride (COF_2), and phosphoryl fluoride (POF_3); however, the fire composition may change depending on the type of battery in the vehicle (Lönnermark & Blomqvist, 2006; Larsson et al., 2017; Sturk et al., 2019).

[Although emissions from diesel engine exhaust are not fire smoke components, gases such as nitrogen oxides (NO_x) and particulate matter are released by a combustion process in equipment (the fire engine) that is essential to firefighting operations; these gases are hazards both in firefighting environments and at fire stations, if not captured through local exhaust ventilation (e.g. an exhaust capture system).]

1.3.2 Air sampling and analytical methods for fire effluents

The choice of sampling and analytical method used to characterize airborne contaminants at a fire incident depends on the contaminant(s) of interest, the physical nature of the airborne samples (i.e. vapour and/or aerosol), the estimated concentrations of contaminants, and any potential interactions with or interferences from other contaminants (Ronnee & O'Connor, 2020). The choice of sampling and analytical method is also strongly influenced by the activities of firefighters at the scene, e.g. whether they are engaged in attack or overhaul activity; the extinguishing agents used; the method of extinguishing agent application; and physical placement, which will have an effect on both the concentration and state of airborne contaminants, as well as the practicality of sampling device placement (Materna et al., 1992; Fent et al., 2018; Alharbi et al., 2021; Banks et al., 2021a).

[While tremendous advances in analytical chemistry have been observed over the past 30 years, little progress has been made in the detailed analysis of combustion chemicals. The major limiting factors to such progress are access to real (accidental) fires, and the complexity involved in sampling and measuring fire effluents, leading to significant difficulties in assessing firefighters' chemical exposures while attending a fire incident.]

Analysis of fire smoke at a particular incident involves prior identification of which of these (pre-defined) chemicals are considered to be the most significant or major components of the smoke (e.g. based on knowledge of fuel sources, specific fire conditions, etc.). The choice of specific gases or chemicals to monitor is based on the availability of methods that reliably collect and analyse air-contaminant samples in the fire environment (Caban-Martinez et al., 2018; Fent et al., 2018; Sjöström et al., 2019b). The most common methods are listed in Table 1.5.

Ambient or personal-monitoring air samples can be collected either actively or passively. In active sampling, a pumping device actively draws air into a container or through a medium such as a filter, solid adsorbent, denuder, solution, or reagent, and determination of the total volume of air sampled is required (NIOSH, 1994a; Bolstad-Johnson et al., 2000; Fent et al., 2019b). In passive sampling, molecular diffusion and gravity are exploited to collect analytes onto a medium or adsorbent, and no pump is required (Mayer et al., 2022).

Samples can also be classified as integrated, continuous, or grab samples. For integrated samples, the analyte is collected over time (e.g. 15 minutes, 8 hours, full shift, or task) and the average concentration is calculated over the whole measurement period. This does not allow for observations of peaks or troughs in the exposure over time. Continuous samples are collected using a direct reading instrument (i.e. real-time monitor) that provides exposure measurements at set time intervals (e.g. 10 seconds, 1 minute), indicating changes in exposure over the measurement period, such as peaks (Jankovic et al., 1991; Fabian et al., 2014; Evans & Fent, 2015). Grab samples are collected in a bag or container (e.g. evacuated canister) at a specific point in time (Treitman et al., 1980; Reinhardt et al., 2000; Booze et al., 2004; Dills & Beaudreau, 2008). They are a representative sample of the environment from which they are drawn, usually over short periods (e.g. less than 5 minutes), although samples can be collected over longer periods (i.e. hours).

Air samples can be collected over different time periods – a few seconds (e.g. peak measurements), several minutes (e.g. 15–30 minutes, task-based sampling), or longer (e.g. several hours, work-shift sampling). A series of samples or continuous measurements can also be collected and then integrated (i.e. integrated sampling) to calculate a time-weighted average (Bolstad-Johnson et al., 2000; Slaughter et al., 2004; Fabian et al., 2010; Adetona et al., 2013a; Wu et al., 2021).

The choice of analytical method will vary according to the sampling method and sample type (Ronnee & O'Connor, 2020). Selectivity of the analytical method (i.e. avoiding matrix effects and/or interference from other fire species), limit of detection (LOD) and limit of quantification (LOQ), and levels of sensitivity and accuracy between different methodologies also need to be carefully considered when selecting from the large number of analytical methodologies currently available for characterizing fire effluents (NIOSH 1992a, b; Bolstad-Johnson et al., 2000; Fabian et al., 2010; Fent et al., 2020a) These methods are summarized in Table 1.5, which highlights types of fire effluent identified and

Table 1.5 Air sampling and analytical methods available for characterizing firefighters' exposure to fire effluents

Fire effluent(s)	Sampling method(s)	Analytical method(s) (LOD and LOQ[a])	Selected reference(s)
Aldehydes	• Impregnated sieves • Gas collection tubes • Sorbent tubes • XAD-2 tube/ORBO23 sorbent tube impregnated with 2-(hydroxymethyl) piperidine • DNPH sorbent tubes, C-18 silica gel Sep-Paks • UMEX 100 passive sampling badges • XAD-2 sorbent tubes (2-hydroxymethyl piperidine) • Direct gas (multigas) detector	• GC desorption (chromotropic acid) • Infrared spectroscopy • NIOSH Method 2016 formaldehyde (LOD, 0.07 µg/sample), NIOSH Method 2539 aldehydes (LOD, 2 µg aldehyde/sample), NIOSH Method 2541 formaldehyde (LOD, 1 µg/sample) • EPA TO-11 (acrolein LOD, 0.017 ppm, formaldehyde LOD, 0.033 ppm); (acrolein LOD, 3 ppb, 2 hours, formaldehyde LOD, 6 ppb, 2 hours), • OSHA 52 formaldehyde (LOD, 482 ng/sample) and acrolein (LOD, 291 ng/sample) • EPA IP-6 A (active sampling) C (passive sampling) formaldehyde and other aldehydes (LOD, 0.03 µg/sample)	Treitman et al. (1980); Lowry et al. (1985); NIOSH (1992a, b; 1994a; 2010); Materna et al. (1992); Bolstad-Johnson et al. (2000); Reinhardt et al. (2000); Booze et al. (2004); Reinhardt & Ottmar (2004); Slaughter et al. (2004); Reisen et al. (2006); Dills & Beaudreau (2008); Reisen & Brown (2009); Fabian et al. (2010); Reisen et al. (2011); Fent & Evans (2011); Fent et al. (2019b)
Ammonia	• Direct gas detector	• Infrared spectroscopy: FTIR	Fabian et al. (2010); Caban-Martinez et al. (2018); Alharbi et al. (2021)
Asbestos	• Mixed cellulose ester filters	• NIOSH Method 7400 (LOD, 7 fibres/mm^2 filter area)	Bolstad-Johnson et al. (2000)
Carbon monoxide	• Gas sampling (Tedlar) collection bags • Gas collection tubes • Diffusion tubes • Direct gas detector	• Infrared spectroscopy: NDIR, FTIR analysers	Gold et al. (1978); Treitman et al. (1980); Lowry et al. (1985); NIOSH (1992a, b; 1994a); Reinhardt et al. (2000); Booze et al. (2004); Reinhardt & Ottmar (2004); Slaughter et al. (2004); Naeher et al. (2006); Reisen et al. (2006, 2011); Dills & Beaudreau (2008); Reisen & Brown (2009); Fabian et al. (2010); Adetona et al. (2013a); Alharbi et al. (2021); Wu et al. (2021)
Carbon dioxide	• Gas sampling (Tedlar) collection bags • Direct gas detector	• Direct analyser (LOD, 7.6 ppm, 2 hours)	Gold et al. (1978); Treitman et al. (1980); Reinhardt et al. (2000); Reinhardt & Ottmar (2004); Dills & Beaudreau (2008); Caban-Martinez et al. (2018)
Flame retardants	• Glass fibre filter with XAD-2 sorbent tubes	• UPLC-APPI, • EPA 23A PBDEs and NPBFRs (LOD depends on the substance, sampling conditions and analytical procedures)	Fent et al. (2020a)

Table 1.5 (continued)

Fire effluent(s)	Sampling method(s)	Analytical method(s) (LOD and LOQ[a])	Selected reference(s)
Hydrogen cyanide	• Gas collection tubes • Disposable syringes • Gas sampling (Tedlar) collection bag • Soda lime sorbent tubes • Multiple colorimetric detectors • Direct gas (multigas) detector	• Colorimetric method (pyridine) • Infrared spectroscopy: UV-VIS spectrophotometric method, FTIR • NIOSH Method 6010 (LOD, 1 µg/sample), NIOSH Method 7904 (LOD, 2.5 µg)	Gold et al. (1978); Treitman et al. (1980); Lowry et al. (1985); Caban-Martinez et al. (2018); Bolstad-Johnson et al. (2000); Dills & Beaudreau (2008); Fabian et al. (2010); Fent et al. (2018, 2019b); Alharbi et al. (2021)
Hydrogen sulfide	• Direct gas (multigas) detector		Fabian et al. (2010); Alharbi et al. (2021)
Inorganic acids (HCl)	• Multiple colorimetric detectors • ORBO53 tube • Direct gas (multigas) detector	• Mercuric thiocyanate method • Zall colorimetric method • NIOSH 7903 (LOD, 0.6–2 µg/sample)	Gold et al. (1978); Treitman et al. (1980); NIOSH (1994a); Bolstad-Johnson et al. (2000); Dills & Beaudreau (2008); Fent et al. (2018, 2019b); Alharbi et al. (2021)
Isocyanates	• Denuder attached to polypropylene cassette impregnated with a dibutyl-*n*-amine filter (glass fibre, impregnated); or • Impinger; or impinger + filter	• ISO 17734-(2013) • NIOSH Method 5525 (0.2 nmol NCO per species/sample (0.2 nmol NCO equals 0.017 µg HDI/sample)	NIOSH (2010); Fent & Evans (2011); Fent et al. (2019b)
Metals	• PVC and cellulose ester filters • Teflon filter • Hyder tube (mercury) • XAD-2 sorbent tube between PUF disks	• NIOSH Method 7300 ICP-AES (Cd LOD, 0.3 ng/mL; Cr LOD, 0.8 ng/mL; Pb LOD, 2.5 ng/mL) • Airborne mercury: NIOSH Method 6009 (LOD, 0.03 µg/sample) • ICP-MS (LOD, 0.027 µg/g for Sb to 51.62 µg/g for K)	Bolstad-Johnson et al. (2000); Fabian et al. (2010); Wu et al. (2021)
Nitrogen oxides	• Molecular sieve coated with triethanolamine sorbent tubes • Diffusion tubes • Direct gas (multigas) detector	• Saltzmann method • Infrared spectroscopy: FTIR analyser • NIOSH Method 6014 (1 µg NO_2/sample)	Gold et al. (1978); Treitman et al. (1980); NIOSH (1994a); Dills & Beaudreau (2008); Fabian et al. (2010); Caban-Martinez et al. (2018)

Table 1.5 (continued)

Fire effluent(s)	Sampling method(s)	Analytical method(s) (LOD and LOQ[a])	Selected reference(s)
Particulate matter	• Glass fibres, PTFE or PVC filters • Aluminium cyclone • Cyclone with PVC or Teflon filters • Filter-cassette with a nylon cyclone • Cyclone with PTFE filters • Cascade Impactor with PVC filters • Cascade Impactor with aluminium foil substrates and glass fibre filter • HEPA and/or quartz fibre filters • Electrical low-pressure impactor	• NIOSH Method 0500 (LOD, 0.03 mg/sample), • NIOSH Method 0600 (LOD, 0.03 mg/sample) • Gravimetric measurements (LOD, 10–100 µg) • Condensation particle counter • Environmental β attenuation monitor • Personal aerosol monitor • Particle size spectrometer • Particle counter • Aerosol sensor • Diffusion charger • Photoelectric aerosol sensor	Gold et al. (1978); Treitman et al. (1980); NIOSH (1992a, 1994a, 2010, 2013a); Materna et al. (1992); Reinhardt et al. (2000); Booze et al. (2004); Reinhardt & Ottmar (2004); Slaughter et al. (2004); Naeher et al. (2006); Reisen et al. (2006, 2011); Reisen & Brown (2009); Baxter et al. (2010); Fabian et al. (2010); Fent et al. (2018, 2019b); Adetona et al. (2013a); Evans & Fent (2015); Navarro et al. (2019b); Sjöström et al. (2019b); Nelson et al. (2021); Wu et al. (2021)
Polycyclic aromatic hydrocarbons (PAHs)	• Evacuated canister • Teflon or quartz filter • PUF cartridge • PTFE filter and sorbent tube (XAD-2 resin/ORBO43 sorbent tube) • Teflon filter with XAD-2 sorbent tube • Aluminium cyclone and XAD-2 sorbent tube • XAD-2 sorbent tubes with glass fibre filter • XAD-2 sorbent tube with quartz fibre filters and XAD-4 sorbent tube • XAD-7 sorbent tube	• NIOSH Method 5023 various organic-soluble compounds (LOD, 0.05 mg/sample), NIOSH Method 5506 LOD depends on the substance (e.g. naphthalene LOD, 0.20–0.80 µg/sample), NIOSH Method 5515 (LOD, 0.3–0.5 µg/sample), NIOSH Method 5528 (LOD 0.08–0.2 µg/sample, • EPA 1625 (LOD depends on the substance) • GC-MS (LOD, 1.71–7.14 ng/m^3; LOQ, 1.0–5.3 ng/m^3) • HRGC-MS • GC-TQMS	Materna et al. (1992); NIOSH (1992b, 1994a, 2013a); Bolstad-Johnson et al. (2000); Dills & Beaudreau (2008); Fabian et al. (2010); Keir et al. (2017); Navarro et al. (2017); Fent et al. (2018, 2019b); Navarro et al. (2019b); Sjöström et al. (2019b); Banks et al. (2021a)
Polychlorinated, polybrominated dibenzo-*para*-dioxins and furans (PCDD/Fs and PBDD/Fs)	• Fire debris • Glass fibre filter with XAD-2 sorbent tubes	• APGC-MS/MS: Ontario Ministry of Environment E3418 (LOD, 0.15–1.4 pg/g for tetra- through octa- halogenated dioxins and furans) • EPA 23A	Organtini et al. (2015)

Table 1.5 (continued)

Fire effluent(s)	Sampling method(s)	Analytical method(s) (LOD and LOQ[a])	Selected reference(s)
Semi-volatile and volatile organic compounds (sVOCs and VOCs)	• Tedlar bag • Evacuated canister • Cylindrical PUF • Pressurized vacuum canisters • Evacuated glass bottles • Charcoal sorbent tubes • Carbotrap 317 tubes • Catecholamine-treated charcoal tube • Thermal desorption tubes (qualitative, Carbopack Y/Carbopack B/Carboxen), charcoal tubes • Adsorbent Carbopack X 60/80 tubes • Sorbent tubes (Carbograph 1TD/ Carboxen 1000) • Direct gas (multigas) detector	• Thermal desorption GC-MS • GC-MS, GC-FID • NIOSH Method 1003 (LOD depends on the substance), NIOSH 1500 (LOD depends on the substance), NIOSH Method 1501 (LOD depends on the substance), NIOSH Method 2549 volatile organic compounds (LOD, 100 ng/tube) • EPA TO-15 (LOD depends on the substance) • GC-MS (benzene LOD, 0.1 µg; styrene LOD, 1.2 µg; VOCs and sVOCs LOD, 1–5 ppm)	Treitman et al. (1980); Lowry et al. (1985); NIOSH (1992b, 1994a, 2010, 2013a); Materna et al. (1992); Bolstad-Johnson et al. (2000); Reinhardt et al. (2000); Booze et al. (2004); Reinhardt & Ottmar (2004); Reisen et al. (2006, 2011); Dills & Beaudreau (2008); Reisen & Brown (2009); Fabian et al. (2010); Fent & Evans (2011); Caban-Martinez et al. (2018); Fent et al. (2018, 2019b); Sjöström et al. (2019b); Alharbi et al. (2021)
Silica	• Cyclone with PVC filters	• NIOSH Method 7500 (LOD, 0.005 mg SiO_2/ sample)	Materna et al. (1992); NIOSH (1992a, b)
Sulfur dioxide	• Diffusion tubes, • Filter with mixed-cellulose ester with sodium carbonate • Direct gas (multigas) detector	• NIOSH Method 6004 (LOD, 3 µg SO_2/ sample) • Infrared spectroscopy: FTIR	NIOSH (1992a, b, 1994a); Dills & Beaudreau (2008); Fabian et al. (2010); Caban-Martinez et al. (2018); Alharbi et al. (2021)

AES, atomic emission spectrometry; APGC-MS/MS, atmospheric pressure gas chromatography-tandem mass spectrometry; Cd, cadmium; Cr, chromium; DNPH, 2,4-dinitrophenylhydrazine; EPA, US Environmental Protection Agency; FID, flame ionization detector; FTIR, Fourier transform infrared spectroscopy; GC-FID, gas chromatography-flame ionization detector; GC-MS, gas chromatography-mass spectrometry; GC-TQMS, gas chromatography-triple quadrupole mass spectrometry; HEPA, high-efficiency particulate air filter; HRGC-MS, high-resolution gas chromatography-mass spectrometry; ICP-AES, inductively coupled plasma-atomic emission spectroscopy; ICP-MS, inductively coupled plasma-mass spectrometry; ISO, International Organization for Standardization; K, potassium; LOD, limit of detection; LOQ, limit of quantification; MS, mass spectrometry; MS/MS, tandem mass spectrometry; NCO, isocyanate; NDIR, non-dispersive infra-red spectroscopy; NIOSH, National Institute for Occupational Safety and Health; NO_2, nitrogen dioxide; NPBFR, non-PBDE brominated flame retardant; OSHA, Occupational Safety and Health Administration; Pb, lead; PBDE, polybrominated diphenyl ether; ppb, parts per billion; ppm, parts per million; PTFE, polytetrafluoroethylene; PUF, polyurethane foam; PVC, polyvinyl chloride; Sb, antimony; SiO_2, silicon dioxide; SO_2, sulfur dioxide; sVOC, semi-volatile organic compound; UPLC-APPI, ultra-performance liquid chromatography-atmospheric pressure photoionization; UV-VIS, ultraviolet visible spectroscopy; VOC, volatile organic compound.

[a] Only included when available.

measured, sampling methods, analytical techniques, and LOD/LOQ, when available.

In the 1980s, sampling and analytical methodologies were refined for several different gases, such as CO, HCN, and aldehydes, using colorimetric or charcoal sorbent tubes followed by infrared spectroscopy, and gas chromatography (gas chromatography-mass spectrometry, GC-MS, and/or gas chromatography-flame ionization detection, GC-FID) (Gold et al., 1978; Treitman et al., 1980; Lowry et al., 1985; Reisen et al., 2006; Navarro et al., 2017, 2019b). Methods for the collection and analysis of particulate matter have been developed continuously, with the implementation of different sampling media (e.g. different types of filter), particle collection devices (e.g. cyclones or cascade impactors) for investigating particle size distribution, and more reliable and robust analytical methodologies (NIOSH, 1992a, 1994a, 2013a, 2019; Fent & Evans, 2011; Evans & Fent, 2015; Fent et al., 2019b). Research in the 1990s was dominated by the characterization of firefighters' exposures in forest or wildland fire settings and subsequently by increasing interest in the characterization and effects of diesel exhaust emissions (at fire stations) and the effectiveness of SCBA (Jankovic et al., 1991; NIOSH, 1994a, 1998b; Than et al., 1995). A wealth of research has also been published on simulated residential fires (NIOSH, 1992a, b, 1994a; Materna et al., 1992). Sampling and analytical methodologies included the use of sampling bags, charcoal tubes for the monitoring of VOCs and PAHs (analysis by chromatography, e.g. GC-MS or GC-FID), silica gel tubes for acid gases (high-pressure ion chromatography, HPIC), soda lime tubes for HCN (spectroscopy), or polymer tubes for aldehydes (GC-FID), or high-performance liquid chromatography (HPLC) coupled with UV or diode-array detection (HPLC-UV-DAD). Analysis of particulate matter was also enhanced using cyclones or cascade impactors for investigating particle size distribution. During this time, long-term diffusion tubes (colorimetric tubes) were used together with continuous direct reading sensors or multigas analysers (for CO, CO_2, and methane, CH_4) (NIOSH, 1992a, b, 1994a; Materna et al., 1992; Naeher et al., 2006).

The implementation of more sophisticated analytical methods, principally spectroscopic and chromatographic methodologies (e.g. gas-phase Fourier transform infrared spectroscopy, FTIR; gas chromatography-nitrogen–phosphorus detection, GC-NPD; high-resolution gas chromatography-high-resolution mass spectrometry, HRGC-HRMS, atmospheric pressure gas chromatography-tandem mass spectrometry, APGC-MS/MS; and high-performance liquid chromatography with ultraviolet or fluorescence detection, HPLC-UV, HPLC-FL) allowed the quantification of standard pollutants with higher sensitivity (lower LODs/LOQs) and accuracy, thus extending analytical capacity to detect and quantify the presence of pollutants that could not previously be determined (e.g. PCBs, PBDEs, OPFRs, PCDD/Fs, etc.) (Organtini et al., 2015; Fent et al., 2020a). More recently, on-site, and real-time determination of the concentrations of airborne gaseous and particulate pollutants present in fire smoke has been achieved using portable, low-cost screening devices and sensors (e.g. multigas sensors and particle counting devices) with increasing selectivity and accuracy (Caban-Martinez et al., 2018; Alharbi et al., 2021; Nelson et al., 2021).

The use of sensor-based devices has been reported for a wide variety of air pollutants that can be detected at concentrations ranging from parts per million (ppm) to parts per billion (ppb). They include optical particle counters for measuring the size distribution of particles and electrochemical sensors used for quantitative determination of gases and vapours (CO, HCl, HCN, NO_2, SO_2, etc.) (Baxter et al., 2010; Reisen et al., 2011; Caban-Martinez et al., 2018; Alharbi et al., 2021; Nelson et al., 2021).

[The use of these sensor devices has been an important breakthrough in the monitoring of firefighters' occupational exposure to health-relevant pollutants during firefighting. Moreover, on-site and real-time portable sensors can be used in firefighters' health surveillance programmes. However, these devices have several limitations that need to be considered, including cross sensitivity and interference from environmental factors (e.g. temperature, humidity, wind, and rain).]

1.3.3 Dermal sampling and analytical methods

Skin exposure to fire effluents can occur via contaminated PPE (Stull et al., 1996; Kirk & Logan, 2015b; Fent et al., 2017). This may happen during donning, doffing, or other handling of contaminated PPE, or if contaminants are transferred from PPE or other equipment to surfaces (e.g. fire apparatus) that subsequently come into contact with the firefighter's skin. In addition, dermal exposure is possible via permeation or penetration of contaminants through or around the protective barriers of the turnout gear (see Section 1.6 for more information). In the available literature, dermal exposure samples were mostly collected using wipes or simulant patches from the face, hand, neck, forehead, wrist, or scrotum of firefighters and analysed mostly for PAHs using GC-MS standard analytical methods (NIOSH, 2013a; Baxter et al., 2014; Keir et al., 2017; Stec et al., 2018). Recently, tape stripping has been used and validated for collecting organic chemicals (PAHs) from firefighters' skin (Strandberg et al., 2018; Sjöström et al., 2019a, b). Sampling of the air under turnout gear has also been conducted as a way of measuring dermal exposure potential, as well as the attenuation provided by protective clothing, for PAHs or VOCs (Kirk & Logan, 2015b; Wingfors et al., 2018; Mayer et al., 2022). Table 1.6 provides further detail on the current body of research characterizing the measurement of contaminants on firefighters' skin.

1.3.4 Sampling and analytical methods for contaminants in fire stations

The analytical methods for the measurement of fire effluents described in Section 1.3.2 are applicable to the measurement of exposures in fire stations. No direct measurement of diesel engine exhaust as such (i.e. from fire vehicles or apparatus) was available, therefore measurement relies on the measurement of individual exhaust components (e.g. elemental carbon, CO, nitrogen oxides, sulfur dioxide, aldehydes, PAHs, and soot). Chemical species (e.g. sVOCs and VOCs, PAHs, flame retardants, and perfluorinated chemicals) detected and the corresponding sampling and analytical methods are reported in Table 1.7 (Froines et al., 1987; Than et al., 1995; NIOSH, 1994b, 1998b, 2001; Oliveira et al., 2017a; Sparer et al., 2017; Shen et al., 2018; Stec et al., 2018; Banks et al., 2020; Hall et al., 2020).

Early methods to measure the particulate fraction of diesel engine exhaust relied on gravimetric approaches; however, these methods were not specific to diesel particulate (Birch, 2002). Later methods focused on the carbonaceous fraction (i.e. elemental and organic carbon). Whereas many potential sources of organic carbon exist (e.g. tobacco smoke and cooking), there are few sources of elemental carbon, making this the better surrogate for exposure to diesel engine exhaust (Birch, 2002; NIOSH, 2016a). For more detailed information on firefighters' exposure to diesel exhaust, see Section 1.5.1(d).

1.3.5 Other sampling and analytical methods

(a) Protective clothing

Different types of firefighter PPE and its use are described in Section 1.6. Few studies (summarized in Table 1.8) have characterized the extent of contamination of firefighter PPE.

Table 1.6 Most common dermal sampling and analytical methods

Fire effluents	Fire location or activity	Sampling method	Analytical method	Reference
Polycyclic aromatic hydrocarbons (PAHs)	• Controlled building fire • Simulated/controlled residential room (structure) fires • Fire suppression activities • Smoke diving and fire extinguishing training events • Fire training events • Firefighters' work environment	• Sunflower oil wiped with cellulose ester towels • Skin simulant patches • Wipes (isopropyl alcohol, polyester) • Wipe samples saturated with corn oil • Glass fibre filter wetted with acetone • Semipermeable low-density polyethylene membranes and three tape-stripping • Tape stripping (three consecutive tapes)	• GC-MS: EPA TO-13A • GC-FID: NIOSH 5515 • HPLC (fluorescence/UV detection): NIOSH 5506 • HRGC-MS • GC-MS/MS • GC-TQMS • GPC: EPA 3640A	Laitinen et al. (2010); Kirk et al. (2011); NIOSH (2013a); Fent et al. (2014, 2017); Baxter et al. (2014); Keir et al. (2017); Stec et al. (2018); Strandberg et al. (2018); Wingfors et al. (2018); Sjöström et al. (2019a, b); Beitel et al. (2020); Keir et al. (2020); Banks et al. (2021a)
Methoxyphenols	• Burn houses (training)	• Wipes (isopropanol)	• GC-MS MDL	Fernando et al. (2016)

EPA, US Environmental Protection Agency; GC-FID, gas chromatography-flame ionization detector; GC-MS, gas chromatography-mass spectrometry; GC-MS/MS, gas chromatography-tandem mass spectrometry; GC-TQMS, gas chromatography-triple quadrupole mass spectrometry; GPC, gel permeation chromatography; HPLC, high-performance liquid chromatography; HRGC-MS, high-resolution gas chromatography-mass spectrometry; MDL, method detection limit; NIOSH, National Institute for Occupational Safety and Health; UV, ultraviolet.

Table 1.7 Sampling and analytical methods for fire effluents identified at fire stations

Fire effluents	Sampler or sampling method	Analytical method	Reference
Flame retardants	• Vacuum cleaner • PUF with glass fibre filter	• GC-MS: EPA TO-13A • GC-HRMS • HRGC-MS • GC-MS/MS • GC-HRMS-EI • HPLC-MS/MS • GC-TQMS	Brown et al. (2014); Park et al. (2015); Shen et al. (2015, 2018); Bott et al. (2017); Gill et al. (2020b); Young et al. (2021)
Nitrogen oxides	• Triethanolamine treated molecular sieve sorbent tube	• Visible absorption spectrophotometry: NIOSH 6014	NIOSH (1994b, 1998b, 2001)
Particulate matter	• Teflon glass fibre filters • Quartz fibre filters • Single stage impactor with PTFE disks	• Gravimetry • Thermal optical analysis (FID): NIOSH 5040 • Model 227B laser particle counter • $PM_{2.5}$, personal modular impactor • SidePak aerosol monitor AM510	Froines et al. (1987); NIOSH (1994b, 2001); Baxter et al. (2014); Bott et al. (2017); Oliveira et al. (2017a, b); Sparer et al. (2017)
Per-fluorinated compounds	• Vacuum cleaner	• HPLC-ESI-MS/MS • GC-MS-EI	Hall et al. (2020)
Polycyclic aromatic hydrocarbons (PAHs)	• Teflon filter followed by XAD-2 sorbent tube, • Vacuum cleaner • Glass tubes with Tenax between two PUF • PTFE disks • XAD-2 sorbent tubes • Wipe sampling with isopropyl alcohol • PUF with glass-fibre filter	• GC-MS • GC-FID: NIOSH 5515 • GC-MS-EI • LC-PAD-FLD • Ecochem PAS 2000CE	Baxter et al. (2014); Shen et al. (2015); Oliveira et al. (2017a, b); Sparer et al. (2017); Stec et al. (2018); Banks et al. (2020)
Semi-volatile and volatile organic compounds (sVOCs and VOCs)	• Thermal desorption tubes (Carbopack Y, Carbopack B, and Carboxen 1003) • Charcoal tubes	• GC-FID: NIOSH 1501 • Thermal desorption GC-MS: NIOSH 2549	NIOSH (1998b, 2001)
Sulfur dioxide	• Grab samples	• Sensidyne colorimetric detector tubes	NIOSH (2001)
Elemental/organic carbon	• Quartz fibre filters	• Thermal-optical analysis; flame ionization detector (FID): NIOSH 5040	NIOSH (2016a)
Respirable combustible dust	• Cyclone with silver membrane filter (with/without impactor)	• Gravimetry	Grenier et al. (2001)

EPA, US Environmental Protection Agency; GC-FID, gas chromatography-flame ionization detector; GC-HRMS, gas chromatography-high-resolution mass spectrometry; GC-HRMS-EI, gas chromatography-high-resolution mass spectrometry-electron ionization; GC-MS, gas chromatography-mass spectrometry; GC-MS-EI, gas chromatography-mass spectrometry-electron ionization; GC-MS/MS, gas chromatography-tandem mass spectrometry; GC-TQMS, gas chromatography-triple quadrupole mass spectrometry; HPLC-ESI-MS/MS, high-performance liquid chromatography-electrospray ionization-tandem mass spectrometry; HPLC-MS/MS, high-performance liquid chromatography-tandem mass spectrometry; HRGC-MS, high-resolution gas chromatography-mass spectrometry; LC-PAD-FLD, liquid chromatography-photodiode array-fluorescence detector; NIOSH, National Institute for Occupational Safety and Health; $PM_{2.5}$, fine particulate matter of 2.5 µm or less in diameter; PTFE, polytetrafluoroethylene; PUF, polyurethane foam.

Table 1.8 Sampling and analytical methods for contaminants in firefighters' PPE

Fire effluents analysed	Surfaces analysed	Sampling method	Analytical method	Reference
Acid gases	• SCBA mask • Respirator cartridges • Clothing	• Silica gel tube • Glass sorbent tubes packed with silica gel	• HPIC: NIOSH Method 7903	Jankovic et al. (1991); Kirk et al. (2011); Kirk & Logan (2015b)
Aldehydes	• SCBA mask • Clothing • Respirator cartridges	• Treated porous polymer tube • Formaldehyde filter • Glass sorbent tubes • DNPH sorbent tube with silica gel	• HPLC (UV): EPA TO-11 and TO-11A	Jankovic et al. (1991); De Vos et al. (2006); Anthony et al. (2007); Kirk et al. (2011); NIOSH (2013b); Kirk & Logan (2015b)
Carbon monoxide	• SCBA mask	• Direct gas monitor	• FTIR spectrometer	Jankovic et al. (1991); Austin et al. (1997)
Fibres		• Cellulose ester filter	• Phase-contrast microscopy	Jankovic et al. (1991)
Flame retardants	• Clothing	• Swab samples • Cotton wipes (hexane and cotton gauze pads) • XAD-2 sorbent tubes • Wipe sampling (isopropanol)	• GC-HRMS • GC-MS: EPA 8270D • UPLC-APPI • GC-TQMS • HPLC-MS/MS	Stull et al. (1996); Kelly et al. (2002); Park et al. (2015); Alexander & Baxter (2016); Easter et al. (2016); Mayer et al. (2019); Fent et al. (2020a); Banks et al. (2021b, c); Young et al. (2021)
Hydrogen cyanide	• SCBA mask • Clothing	• Soda lime tube • Glass sorbent tubes with soda lime	• Spectrophotometry (visible absorption): NIOSH 6010	Jankovic et al. (1991); Kirk et al. (2011); Kirk & Logan (2015b)
Metals	• Clothing	• PUF and quartz filters	• AAS: EPA 245.1 • ICP-AES: OSHA ID-125G, NIOSH Method 730, NIOSH 7303 • ICP-MS: US EPA 305B	Stull et al. (1996); Fabian et al. (2014); Keir et al. (2020)
Nitrogen oxides	• SCBA mask	• Silica gel tube	• HPIC	Jankovic et al. (1991)
Particulate matter	• Half face-piece masks • Respirator cartridges • Half-mask respirators	• Cascade impactor • Cyclones • Filter in a cassette and a carbonyl compound sorption tube • PVC filters and cellulose backup • P100 pancake-shaped filters • Battery-operated scanning mobility spectrometer • Real-time monitoring	• Gravimetric NIOSH Method 0500/0600	Jankovic et al. (1991); De Vos et al. (2006); Anthony et al. (2007); Dietrich et al. (2015)

Table 1.8 (continued)

Fire effluents analysed	Surfaces analysed	Sampling method	Analytical method	Reference
Per-fluorinated chemicals	• Turnout gear and fabric swatches		• HPLC-MS/MS	Peaslee et al. (2020)
Phthalates	• Clothing		• GC-MS: EPA 8270 • Headspace GC-MS	Alexander & Baxter (2016); Easter et al. (2016); Shinde & Ormond (2020)
Polychlorinated and polybrominated dibenzo-*para*-dioxins and furans (PCDD/Fs and PBCD/Fs)	• Clothing	• Swab samples • Glass fibre paper saturated with acetone • Cellulose wipes • Cotton twill wipes (hexane) and cotton gauze pads	• HRGC-HRMS: EPA 1613B and 8290A, Ontario Ministry of Environment Method E3418 • GC × GC-TOFMS	Kelly et al. (2002); Hsu et al. (2011); Organtini et al. (2014); Fent et al. (2020a)
Polycyclic aromatic hydrocarbons (PAHs)	• SCBA mask • Respirator cartridges • Clothing • Turnout gear fabrics	• Cloth samples • Wipe samples (heptane) • Wipe samples (isopropyl alcohol) • PTFE filter • PUF glass tubes with glass fibre filter • XAD-7 sorbent tubes • Glass sorbent tubes with PUF and glass fibre filter • XAD-2 sorbent tubes • XAD-2 sorbent tube between PUF disks • PUF and quartz filters	• GC-MS: EPA TO-13A, NIOSH Method 5528 • GC-FID • HPLC (fluorescence/UV): NIOSH Method 5506 • Headspace GC-MS • GC-TQMS	Jankovic et al. (1991); Anthony et al. (2007); Kirk et al. (2011); Fabian et al. (2014); Kirk & Logan (2015b); Easter et al. (2016); Abrard et al. (2019); Fent et al. (2017); Wingfors et al. (2018); Stec et al. (2018); Mayer et al. (2019); Shinde & Ormond (2020); Banks et al. (2021b, c); Corbally et al. (2021); Alexander & Baxter (2016); Mayer et al. (2020); Keir et al. (2020)
Semi-volatile and volatile organic compounds (sVOCs and VOCs)	• SCBA mask • Clothing • Turnout gear fabrics	• Evacuated canisters • Charcoal tubes • Tenax/Carboxen 569 tubes • Wipe samples (isopropanol, benzalkonium chloride)	• GC-MS: EPA TO1/TO2, TO-15, 8270 • Thermal desorption GC-MS: EPA TO-17 • Headspace GC-MS • GC-FID	Jankovic et al. (1991); Stull et al. (1996); Anthony et al. (2007); Kirk et al. (2011); NIOSH (2013b); Fent et al. (2015, 2017); Kirk & Logan (2015b); Shinde & Ormond (2020); Corbally et al. (2021); Mayer et al. (2020)

AAS, atomic absorption spectroscopy; DNPH, 2,4-dinitrophenylhydrazine; EPA, US Environmental Protection Agency; FTIR, Fourier transform infrared spectroscopy; GC-FID, gas chromatography-flame ionization detector; GC-HRMS, gas chromatography-high-resolution mass spectrometry; GC-MS, gas chromatography-mass spectrometry; GC-TOFMS, gas chromatography-time-of-flight mass spectrometry; GC-TQMS, gas chromatography-triple quadrupole mass spectrometer; HPIC, high-pressure ion chromatography; HPLC, high-performance liquid chromatography; HPLC-MS/MS, high-performance liquid chromatography-tandem mass spectrometry; HRGC-HRMS, high-resolution gas chromatography-high-resolution mass spectrometry; ICP-AES, inductively coupled plasma-atomic emission spectroscopy; ICP-MS inductively coupled plasma-mass spectrometry; NIOSH, National Institute for Occupational Safety and Health; OSHA, Occupational Safety and Health Administration; PPE, personal protective equipment; PTFE, polytetrafluoroethylene; PUF, polyurethane foam; PVC, polyvinyl chloride; SCBA, self-contained breathing apparatus; UPLC-APPI, ultra-performance liquid chromatography-atmospheric pressure photoionization; UV, ultraviolet.

Fig. 1.8 Wipe sampling of contaminants from a firefighter's helmet

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Sample collection in these studies, for both new and used ("soiled" or contaminated) PPE, mostly involved exposures to simulated structure fires. The locations from which samples were collected included: (i) the outer layer of turnout gear (Hsu et al., 2011; Kirk et al., 2011; Stec et al., 2018); (ii) the inner liner of turnout gear (Alexander & Baxter, 2016; Easter et al., 2016; Kesler et al., 2021); (iii) clothing or surfaces under turnout gear (Keir et al., 2020; Mayer et al., 2020); and (iv) air space around turnout gear to measure off-gassing of contaminants (Kirk & Logan, 2015b; Fent et al., 2017; Banks et al., 2021b).

A variety of contaminants were measured in these samples (e.g. PAHs, VOCs, HCN, aldehydes, acid gases, OPFRs, PCDD/Fs, PBDD/Fs, metals), and these are summarized in Table 1.8, together with the specific sampling media and analytical techniques used.

[Although PPE usage histories are usually not reported, some findings suggested that contamination of firefighter protective clothing increases with longer periods of use (Stec et al., 2018). Variations in reported results may arise not only from the sampling and analytical methods used, but also from different firefighting activities, exposure to various chemicals, and PPE age and decontamination or storage practices (Stec et al., 2018; Fent et al., 2020a; Banks et al., 2021b) (Fig. 1.8).]

Table 1.9 Other sampling and analytical methods

Fire effluents	Exposure scenario	Sampling method	Analytical method	Reference
Perfluorinated chemicals	Off-duty and on-duty firefighters	Wrist: silicone-based wristbands	LC-MS/MS	Levasseur et al. (2022)
Polychlorinated biphenyls (PCBs); phthalates, brominated flame retardants, organophosphate esters, polycyclic aromatic hydrocarbons (PAHs); semi-volatile organic compounds (sVOCs)	Off-duty and on-duty firefighters	Wrist: silicone-based wristbands	GC hybrid quadrupole-Orbitrap GC-MS/MS system	
Polycyclic aromatic hydrocarbons (PAHs)	Firefighters work environment During 24-hour shift Fire training events	Wrist: silicone-based wristbands	GC-MS	Baum et al. (2020); Caban-Martinez et al. (2020); Bakali et al. (2021)

GC-MS, gas chromatography-mass spectrometry; LC-MS/MS, liquid chromatography-tandem mass spectrometry.

(b) Wristbands

Recently, silicone wristbands (or dog tags) have been proposed and validated for collecting fire effluents while the firefighter is at work (Strandberg et al., 2018; Sjöström et al., 2019a, b; Baum et al., 2020; Caban Martinez et al., 2020; Levasseur et al., 2022). Silicone wristbands are a type of passive sampler that collect unbound VOCs and sVOCs in air, sediment, or water by diffusion into lipophilic polymers (Dixon et al., 2019). These studies are summarized in Table 1.9.

[Little information is available on the limitations of these sampling techniques, for example, information on collection efficiency or diffusion rates for various types of chemical and how the samples relate to standardized exposure monitoring methods.]

1.3.6 Biomonitoring methods

(a) Fire smoke components

Numerous studies have employed biomonitoring to assess firefighters' exposures to chemicals of concern. Biomonitoring, which has become a critical tool in occupational exposure assessment, involves measurement of the presence and levels of chemicals (or their metabolites) in human tissues (including hair and nails), bodily fluids (e.g. blood, sputum, saliva, breast milk), excreta (e.g. urine, faeces), or exhaled breath (Angerer et al., 2006, 2007; Manno et al., 2010; Scheepers et al., 2011; Arnold et al., 2013; Decker et al., 2013; Bader et al., 2021). Samples can be collected before and/or after suppression of various types of fires including, for example, intentionally set training fires, municipal structure fires, industrial fires, and wildfires. Subsequent sample analyses can examine the effect of fire suppression on the levels of selected chemicals, and/or their metabolites, in the aforementioned biological matrices (e.g. Kales et al., 1994; Dunn et al., 2009; Miranda et al., 2012; Fent et al., 2014; Waldman et al., 2016; Jackson & Logue, 2017; Keir et al., 2017, 2020; Andersen et al., 2018b; Santos et al., 2019; Grashow et al., 2020; Allonneau et al., 2021; Mayer et al., 2021).

Biomonitoring data reflect exposures from all sources (e.g. firefighting, indoor and outdoor air, drinking-water, and consumer products), and exposures via all routes of entry into the body (e.g. inhalation, oral ingestion, and dermal absorption) (Angerer et al., 2006, 2007; Laitinen et al., 2012; Arnold et al., 2013). Assessing the levels of chemicals or chemical metabolites in biomonitoring samples does not necessarily permit identification of the source(s) and/or route(s) of exposure. Moreover, the presence of a substance in a biological matrix does not necessarily mean it is causing harm, nor does the absence of a substance indicate that an individual was not exposed (Angerer et al., 2006, 2007; Arnold et al., 2013; Government of Canada, 2022).

As noted in Section 1.3.1, as well as Sections 1.4.1 through 1.4.4, firefighters are exposed to complex mixtures that can include an array of chemicals, including gases (e.g. CO and NO_2), VOCs, particulate matter, sVOCs, and fibres. Exposures to these chemicals can occur during the various phases of fire suppression (e.g. attack, knockdown, overhaul) and in the firefighters' workplace, such as the fire station (see Sections 1.1, 1.2, and 1.3.4(b)). Although firefighter PPE restricts contact with combustion-derived chemicals, exposures can occur via gear penetration, contact with exposed areas of the face, neck, and wrist, and/or contact with contaminated gear (NIOSH, 2013a; Fent et al., 2014, 2015, 2017; Andersen et al., 2018b; Wallace et al., 2019a; Beitel et al., 2020; Keir et al., 2020; Peaslee et al., 2020) (see Section 1.6).

Biomonitoring to assess firefighter exposures to gases, VOCs, and sVOCs generally involves measurement of analytes in the blood (e.g. serum), urine, or exhaled breath (e.g. Fernando et al., 2016; Wallace et al., 2017, 2019a; Andersen et al., 2018b; Wingfors et al., 2018; Cherry et al., 2019; Grashow et al., 2020). The biomonitoring strategy employed (i.e. strategy for sample collection, handling, and analysis), and the instrumentation employed to detect and quantify the chemicals or chemical metabolites, depends on the properties of the analyte, the analytical approach (e.g. targeted or non-targeted), and the parameters of absorption, distribution, metabolism, and excretion of the analyte (see Section 1.4.5). Table 1.10 provides a brief overview of analytical techniques that have been employed for biomonitoring of firefighters' exposures to selected chemicals.

Assessment of exposures to combustion-derived gases (e.g. CO, NO_2) generally involves direct analysis of exhaled breath or blood (e.g. Stewart et al., 1976; Kales et al., 1994; Dunn et al., 2009; Miranda et al., 2012; Table 1.10).

Assessment of exposures to VOCs (e.g. benzene) generally involves extraction of analytes from exhaled breath or urine using a solid adsorbent; thermally desorbed analytes are generally detected and quantified using gas chromatography or high-performance liquid chromatography coupled with tandem mass spectrometry (GC-MS/MS or HPLC-MS/MS) (e.g. Bader et al., 2014; Wallace et al., 2017, 2019a, b; Rosting & Olsen, 2020; Kim et al., 2021; Table 1.10). Biomonitoring of sVOCs generally involves examination of analytes in the serum or urine (Table 1.10); urine (e.g. spot sample, morning sample, 24-hour void) is sometimes preferred since collection is not invasive. In most cases, extraction and concentration of samples (e.g. via solid-phase or solvent extraction) is followed by detection and quantification using GC-MS/MS or HPLC-MS/MS (e.g. Moen & Øvrebø, 1997; Naeher et al., 2013; Oliveira et al., 2016; Keir et al., 2017; Gill et al., 2019, 2020a; Jayatilaka et al., 2019). It is also possible to assess exposures to some sVOCs using analyses of saliva or exhaled breath (e.g. Wallace et al., 2017, 2019a, b; Santos et al., 2019). Although targeted analyses are predominant, non-targeted approaches are becoming increasingly popular (Wallace et al., 2017, 2019b).

To determine whether firefighter biomonitoring data indicate exposure levels that differ from those of other individuals or populations, the levels of chemicals and/or their metabolites can be compared with those of control groups (e.g. fire service office workers), published population reference values, or the general population (e.g. Edelman et al., 2003; Dobraca et al., 2015; Keir et al., 2017; Grashow et al., 2020; Khalil et al., 2020; CDC, 2022; HBM4EU, 2022). Additionally, levels of chemicals or chemical metabolites

Table 1.10 Biomonitoring methods used to assess firefighter exposures to selected chemicals

Chemical component or agent	Biomarker and sample processing	Instrumentation (LOD and/or LOQ)	Comments and other relevant information	Reference
Benzene	Urinary *trans*,*trans*-muconic acid, acidification, and solvent extraction	HPLC with UV detection (LOQ, 0.02 mg/L)	Modified procedure of Angerer et al. (1997)	Bader et al. (2014)
Benzene	Urinary SPMA, acidification, and solvent extraction	HPLC with MS detection (LOD, 0.3 µg/L)	Modified procedure of Müller et al. (1997)	Bader et al. (2014)
Benzene	Unmetabolized urinary benzene	GC-MS headspace analysis (LOD, 10 ng/L)	Modified procedure of Angerer et al. (1994)	Bader et al. (2014)
Benzene and toluene	Urinary SPMA and *S*-benzylmercapturic acid, direct analysis	UPLC-MS, selected reaction monitoring (LOQ, 0.2 ng/mL)		Rosting & Olsen (2020)
Carbon monoxide	Blood carboxyhaemoglobin as carbon monoxide in exhaled breath after holding breath for set period of time	Exhaled breath monitor, electrochemical detection (LOD not reported)	Carboxyhaemoglobin level based on research conducted by Jarvis et al. (1986)	Stewart et al. (1976); Dunn et al. (2009)
Carbon monoxide	Carboxyhaemoglobin in diluted whole blood	Carbon monoxide-oximetry or manual spectrophotometry (LOD not reported)	Based on method described by Rodkey et al. (1979)	Kales et al. (1994)
Respiratory toxicants, carbon monoxide	TcDTPA, carboxyhaemoglobin and methaemoglobin in blood	Scintillation detection of ^{99m}Tc in the thigh, carboxyhaemoglobin and methaemoglobin by carbon monoxide-oximetry (LODs not reported)	^{99m}Tc-based method measures transfer of inhaled TcDTPA to blood and tissues	Minty et al. (1985)
Cyanide	Thiocyanate in blood serum	Spectrophotometric analysis of thiocyanate (LOD not reported)	Based on thiocyanate analysis method described by Bowler (1944)	Levine & Radford (1978)
Formaldehyde	Derivatized urinary thiazolidine-4-carboxylic acid, solvent extraction	GC-MS with SIM (details and LOD not reported)	Based on method of Shin et al. (2007) (MDL, 1 µg/L)	Kim et al. (2021)
Nitrogen dioxide	Exhaled breath nitric oxide (eNO) using portable hand-held NO analyser	NIOX MINO® electrochemical NO analyser, (details and LOD not reported)	Instrument designed and manufactured by Aerocine, Solna, Sweden	Miranda et al. (2012)
para-Chloroaniline	Urinary *para*-chloroaniline, alkaline hydrolysis and solvent extraction	HPLC with ECD (LOD, 2 µg/L)	Modified procedure of Lewalter et al. (1994)	Bader et al. (2014)
PAHs	PAHs in saliva, solvent extraction	Programmed temperature vaporizer GC-MS, synchronous SIM/scan mode (LOD ≤ 0.057 µg/L)	Measurement of 16 PAHs	Santos et al. (2019)
PAHs	Exhaled breath PAHs collected using dual-bed thermal desorption tubes	GC-MS following thermal desorption, SIM (LOD not reported)	Synchronous SIM/scan mode used for analyses of targeted analytes. PAH results not reported	Wallace et al. (2017, 2019a)

Table 1.10 (continued)

Chemical component or agent	Biomarker and sample processing	Instrumentation (LOD and/or LOQ)	Comments and other relevant information	Reference
PAHs	Urinary 1-OHP, enzymatic deconjugation and solvent extraction	LC-MS/MS, negative ion mode with multiple reaction monitoring (LOD, 10 ng/L)	Inter-laboratory comparison of two analytical methods	Gill et al. (2019)
PAHs	Urinary 1-OHP, enzymatic deconjugation, SPE, and derivatization	GC-HRMS with APCI (LOD, 0.64 ng/L)	Inter-laboratory comparison of two analytical methods	Gill et al. (2019)
PAHs	Urinary 1-OHP, acidification, enzymatic deconjugation, and SPE	HPLC with fluorescence detection (LOD not reported)	Based on method of Jongeneelen et al. (1987)	Moen & Øvrebø (1997)
PAHs	Urinary 1-OHP glucuronide, acidification and solvent extraction	MSI-CE-MS/MS, negative ion mode with multiple reaction monitoring (LOD, ≈7 ng/L)	Good agreement with 1-OHP determined using GC-MS	Gill et al. (2020a)
PAHs	Urinary hydroxylated PAHs, enzymatic deconjugation, solvent extraction and derivatization	GC-MS/MS with multiple reaction monitoring (LOD, 0.0007–0.04 µg/L)	Analyses of 19 hydroxylated PAH metabolites; method of Gaudreau et al. (2016)	Keir et al. (2017)
PAHs	Urinary hydroxylated PAHs, enzymatic deconjugation and solvent extraction	HPLC with fluorescence detection (LOD, 0.8 ng/L to 0.195 µg/L)	Analyses of six hydroxylated PAH metabolites	Oliveira et al. (2016)
PAHs	Urinary PAHs, enzymatic deconjugation and solvent extraction	PAH-CALUX assay, luminescence detection (LOD not reported)	Results expressed as B[*a*]P equivalents	Beitel et al. (2020)
Phenolic compounds	Urinary concentrations of seven phenolic compounds, deconjugated and concentrated by SPE	LC-MS/MS with SIM (LOD, 0.2–2.3 µg/L)	FOX (Firefighters Occupational Exposures) study	Waldman et al. (2016)
Non-targeted sVOCs	Blood serum sVOCs, concentrated via SPE	LC-MS/MS, non-targeted general suspect screen	WFBC (Women Firefighters Biomonitoring Collaborative) study. General suspect screen to identify chemicals of interest; tentatively identified chemicals subjected to confirmation	Grashow et al. (2020)
Non-targeted VOCs and sVOCs	Exhaled breath VOCs and sVOCs collected using dual-bed thermal desorption tubes	GC-MS following automated thermal desorption, SIM (LOD not reported)	Scan chromatograms used for analyses of non-target analytes	Wallace et al. (2017, 2019b)
Targeted VOCs	VOCs or VOC metabolites in urine, headspace analysis of parent compounds, SPE of selected metabolites	GC-MS or LC-MS/MS, depending on compound or metabolite (details and LOD not reported)	Based on NIOSH Method 8321 (NIOSH, 2016c) or NHANES 2011–2012 Laboratory Method (CDC, 2012)	Kim et al. (2021)

Table 1.10 (continued)

Chemical component or agent	Biomarker and sample processing	Instrumentation (LOD and/or LOQ)	Comments and other relevant information	Reference
Targeted VOCs	Exhaled breath VOCs collected using dual-bed thermal desorption tubes	GC-MS after automated thermal desorption, SIM for VOCs of interest (LOD not reported)	Synchronous SIM/scan mode used for analyses of targeted analytes, measurement of 8 targeted VOCs	Wallace et al. (2017, 2019a)
Wood smoke	Urinary levoglucosan, solvent extraction and derivatization	GC-MS/MS with multiple reaction monitoring (LOD, 10 ng/mL)		Naeher et al. (2013)
Wood smoke	22 methoxyphenols in acid-hydrolysed urine, SPE concentration	GC-MS with SIM (LODs, ≈ 0.004 µg/mL)	Based on methods of Dills et al. (2001) and Dills et al. (2006)	Neitzel et al. (2009)

APCI, atmospheric-pressure chemical ionization; B[*a*]P, benzo[*a*]pyrene; CE, capillary electrophoresis; CO, carbon monoxide; ECD, electron capture detection; GC-HRMS, gas chromatography-high-resolution mass spectrometry; GC-MS, gas chromatography-mass spectrometry; HPLC, high-performance liquid chromatography; LC-MS/MS, liquid chromatography-tandem mass spectrometry; LOD, limit of detection; LOQ, limit of quantification; MDL, method detection limit; MSI-CE-MS/MS, multi-segment injection-capillary electrophoresis-tandem mass spectrometry; NHANES, National Health and Nutrition Examination Survey; NIOSH, National Institute for Occupational Safety and Health; NO, nitric oxide; 1-OHP, 1-hydroxypyrene; PAH, polycyclic aromatic hydrocarbon; SIM, selected ion monitoring; SPE, solid-phase extraction; SPMA, *S*-phenyl mercapturic acid; TcDTPA, ^{99m}Tc diethylene triamine penta-acetate; sVOC, semi-volatile organic compound; UPLC-MS, ultra-performance liquid chromatography-mass spectrometry; UV, ultraviolet; VOC, volatile organic compound.

can be toxicologically evaluated via comparisons with reference values such as biological exposure indices (BEIs), binding biological limit values (BBLVs), or biological limit values (BLVs) (Morgan, 1997; Viegas et al., 2020) (see Section 1.7(b)).

(b) Other chemical and physical agents

Published biomonitoring methods for chemical and physical agents excluding fire smoke components are listed in Table S1.11 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). This list is illustrative and not comprehensive. Biomonitoring for exposures to diesel exhaust typically use urinary PAH metabolites, which are described in Section 1.4.5(d).

Biomonitoring for asbestos exposure is generally not conducted in firefighters, although bronchial lavage fluid analysis for macrophage asbestos fibres has been reported in a firefighter responder to the World Trade Center (WTC) disaster in New York City, USA, in 2001 (Rom et al., 2002).

PBDEs and PCBs can be measured in serum using gas chromatography-high-resolution mass spectrometry (GC-HRMS) (Park et al., 2015) and are generally expressed in units of ng/g of lipid, given their high lipid solubility. Although less commonly studied, PCBs can also be measured in urine (Haga et al., 2018). PCDD/Fs and PBDD/Fs (as well as PBDEs) have been measured by gas chromatography-isotope dilution-high-resolution mass spectrometry (GC-HRMS) (Mayer et al., 2021). PBDEs can also be measured in sweat but are more difficult to detect than in urine (Genuis et al., 2017). Non-PBDE flame retardants, such as 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) metabolized to 2,3,4,5-tetrabromobenzoic acid (TBBA), have been measured using HPLC-MS/MS in the urine of firefighters (Jayatilaka et al., 2017, 2019). These, together with chlorinated alkyl and non-chlorinated aryl OPFRs were introduced after PBDEs were phased out. In addition, dialkylphosphate metabolites of organophosphate pesticides have also been measured in firefighters' urine using the same method (Jayatilaka et al., 2017, 2019).

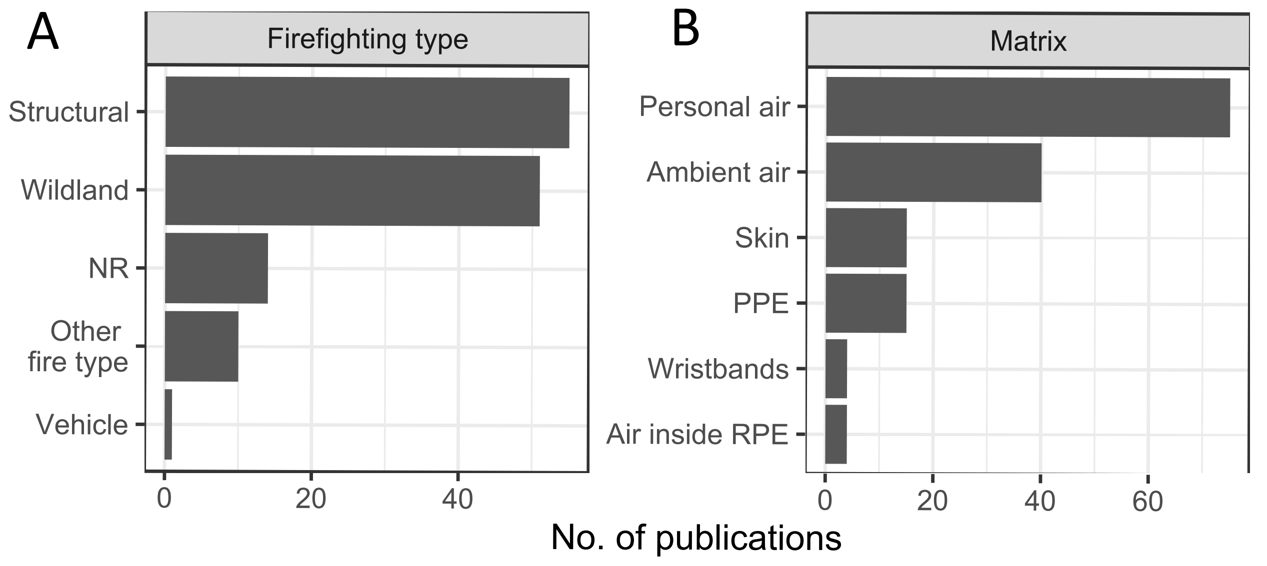
PFAS have been measured using liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Trowbridge et al., 2020). In another study using quadrupole time-of-flight tandem mass spectrometry (QTOF-MS/MS), both targeted and untargeted PFAS were measured; the LODs and LOQs for PFOS were 0.02 and 0.06 ng/mL, respectively, and for PFHxS were 0.07 and 0.35 ng/mL respectively (Rotander et al., 2015a). Targeted serum PFAS levels have been measured in 50 µL of sample using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) with an LOD of 0.05–0.04 ng/mL (Mottaleb et al., 2020).

Inductively coupled plasma-mass spectrometry (ICP-MS) has been used to measure serum total mercury, manganese, cadmium, and lead in firefighters, resulting in LODs of 0.02–0.54 ng/mL (Dobraca et al., 2015). Metals have also been measured using atomic absorption spectrophotometry (AAS) for lead, cadmium, and antimony, and the atomic absorption spectrophotometry-hydride vapour generator method (AAS-HG) for serum arsenic and mercury (Al-Malki, 2009). LODs using AAS varied according to instrument, but typical values were 1–100 ng/mL. Metals can also be measured in urine by the same methods (Wolfe et al., 2004).

1.4 Exposure to fire effluents, according to type of fire and level of exposure

Published data on exposures during firefighting activities identified by the Working Group derived primarily from studies performed in the USA (58%), Canada (9%), and Australia (9%). Limited data were also available for the

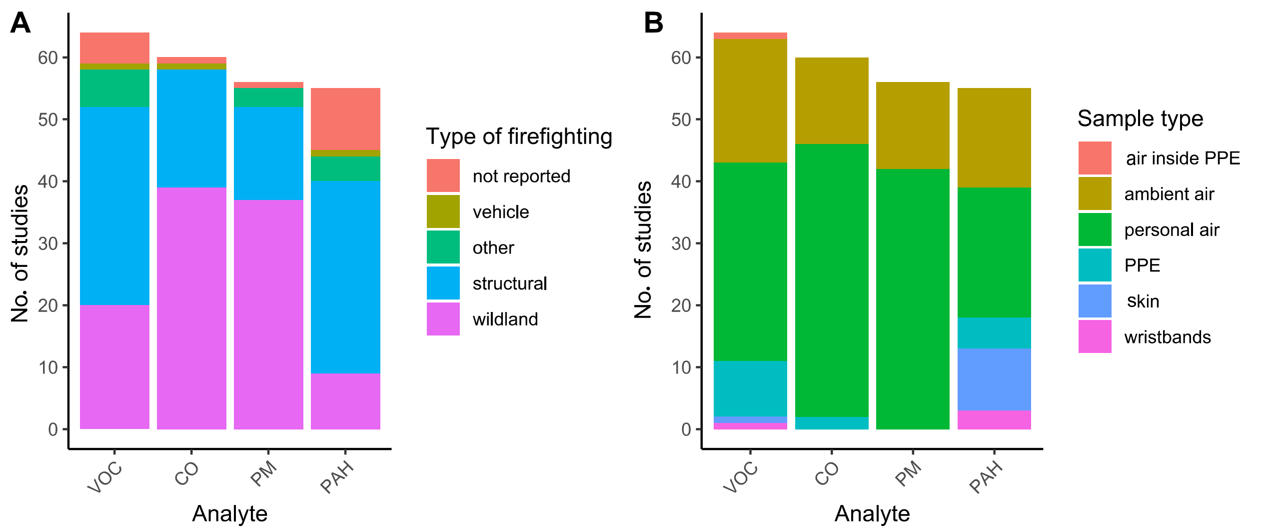
Fig. 1.9 Number of publications that report measurements of fire smoke components in firefighting context by (A) type of firefighting; and (B) sample matrix



NR, type of firefighting not specified; PPE, personal protective equipment; RPE, respiratory protective equipment. [The Working Group compiled information from all studies identified on PubMed until May 2022 that provided measurement data on firefighters' exposure.]
Created by the Working Group.

UK and some other countries in Europe (e.g. Denmark, Finland, France, the Netherlands, Poland, Portugal, Spain, and Sweden) and Asia (e.g. China, Kuwait, and Saudi Arabia), but not for Central and South America. One study was available from the Caribbean region and none from Africa (Table S1.12, Table S1.13, Table S1.14, and Table S1.15, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Most of the available information characterized the presence of different fire effluents, including particulates, VOCs, sVOCs, CO, and PAHs in the breathable air (ambient or personal) during structure and forest fires (Fig. 1.9(a)). The available information demonstrated a high degree of variability in the chemical composition of fire smoke and in the levels of exposure in different firefighting scenarios and sample types (Fig. 1.9 and Fig. 1.10). Information retrieved from the literature suggested the presence of higher concentrations of total and respirable particulate matter, VOCs and sVOCs (including benzene, toluene, ethylbenzene, and xylene, a group known as "BTEX"), and CO in structure fires than in wildfires, prescribed burns, and other types of fire (e.g. vehicles, warehouses, diesel oil, and experimental fires). Studies report considerable variability in the concentrations of PAHs in different types of fire, with the lowest levels being found during wildfires and prescribed burns (Fig. 1.11(a)). [There are several environmental factors, as well as fuel and fire conditions, firefighters' tasks on scene, and duration of exposure/shift that affect exposure during different firefighting activities.] [The data in Fig. 1.11, Fig. 1.12, Fig. 1.13, and Fig. 1.14 shown in this section are from studies that reported

Fig. 1.10 Number of publications that reported measurements of VOCs, sVOCs, CO, particulate matter, and PAHs in the firefighting context by (A) type of firefighting; and (B) type of sample



CO, carbon monoxide; PAH, polycyclic aromatic hydrocarbon; PM, particulate matter; PPE, personal protective equipment; sVOC, semi-volatile organic compound; VOC, volatile organic compound. [The Working Group compiled information from all studies identified on PubMed until May 2022 that provided measurement data on firefighters' exposure.]
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mean or median values (range values were not included). The figures do not differentiate by time period of the sample; for detailed information, consider Tables S1.12–S1.15 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).]

Approaches using biomonitoring to characterize firefighters' exposure to fire effluents are described in Section 1.4.5.

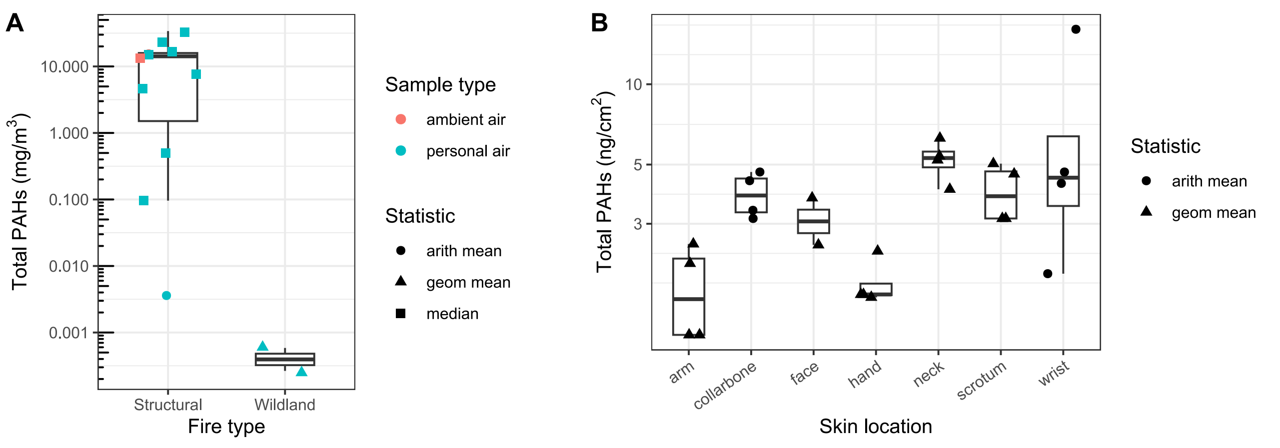
1.4.1 Structure fires

Table 1.16 presents the available studies that assessed concentrations of particulates, VOCs, sVOCs, CO, and PAHs in structure fires by sample type; detailed information is presented in Table S1.12 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

(a) Particulate matter

Measurement of environmental contamination with particulates, expressed as concentration of total particulate matter, ranged from 0.137 mg/m³ during training fires (Sjöström et al., 2019b) to 560 mg/m³ at the knockdown of training and/or urban fires involving the burning of wood, paper, kerosene, PVC plastic, stuffed furniture, tenement, and rubbish, among other materials (Jankovic et al., 1991). The maximum reported single measurement was 15 000 mg/m³ (Burgess & Crutchfield, 1995). Ambient concentrations of respirable particulate matter varied from < 0.10 mg/m³ in burned houses (with different fire origins) furnished with typical household materials during fire training exercises (NIOSH, 1998a) to 484 mg/m³ (maximum

Fig. 1.11 Concentrations of total PAHs (A) in breathable air (ambient and personal) during different types of firefighting; and (B) on different skin locations of firefighters after municipal firefighting



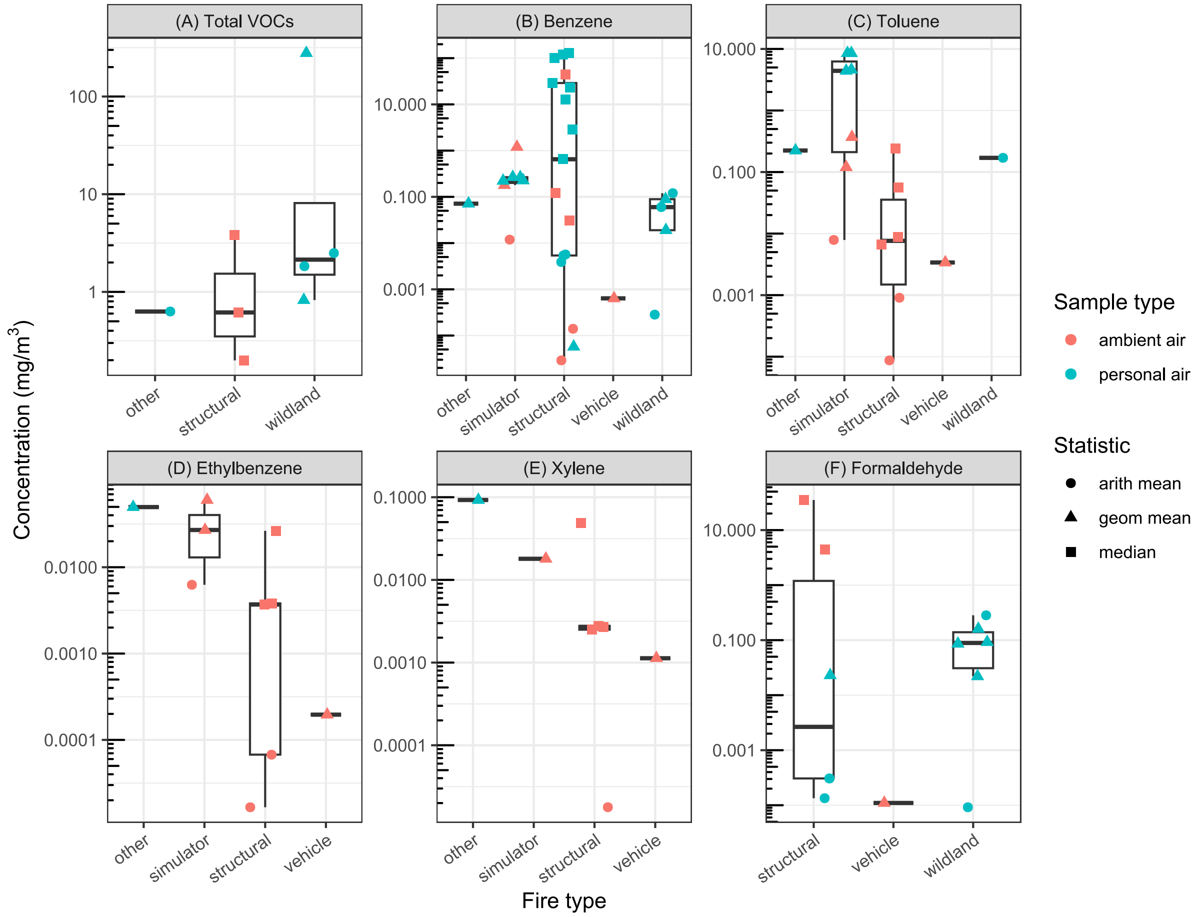
arith, arithmetic; geom, geometric; PAH, polycyclic aromatic hydrocarbon.
[The Working Group compiled information from all studies identified on PubMed until May 2022 that provided measurement data on firefighters' exposure.] Only the mean or median values are plotted in the figures. No data on other firefighting activities were available for skin exposure. Values are presented in a logarithmic scale. [Prescribed burns are usually performed under controlled conditions and so wildland fire exposure data might underestimate the real extent of exposure. See text for more information.]
Created by the Working Group.

single measurement increasing up to 715 mg/m³) during controlled residential fires inside living rooms with modern furnishings (Fent et al., 2018). Regarding total particle count, median levels ranged from 93 152 particles per cm³ during the overhaul phase of live fires (Baxter et al., 2014) to 1 580 000 (range, 102 700–2 970 000) particles per cm³ during controlled residential fires (Fent et al., 2018). Only one study (Baxter et al., 2014) evaluated environmental contamination with particulate matter with a diameter of 2.5 µm or less ($PM_{2.5}$), measuring average concentrations of 0.253–17.53 mg/m³ during firefighting at live overhaul events.

(b) Volatile organic compounds

Structure fires release several VOCs. Concentrations of total VOCs ranging between 0.10 and 107 ppm have been reported during experimental fires burning various materials frequently present in structure fires (Fig. 1.12(a); Table S1.12, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). A study performed in Saudi Arabia demonstrated that firefighters' personal air contained VOCs, including BTEX and CO, at levels that were predominantly higher during firefighting at residential fires than during firefighting at industrial fires (Alharbi et al., 2021; Table S1.12, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Ambient air concentrations of BTEX and formaldehyde ranged between 0.018 and 797 mg/m³ for benzene (maximum single value of 1027 mg/m³ at residential fires); 0.173 and 640 mg/m³ for toluene; 0.0044 and 125 mg/m³ for ethylbenzene; 0.0044 and 80.5 mg/m³ for isomers of xylene; and 0.020 and 35.2 mg/m³

Fig. 1.12 Concentrations of total VOCs, and benzene, toluene, ethylbenzene, xylene, and formaldehyde in the breathable air (ambient or personal) by type of firefighting activity reported in the literature



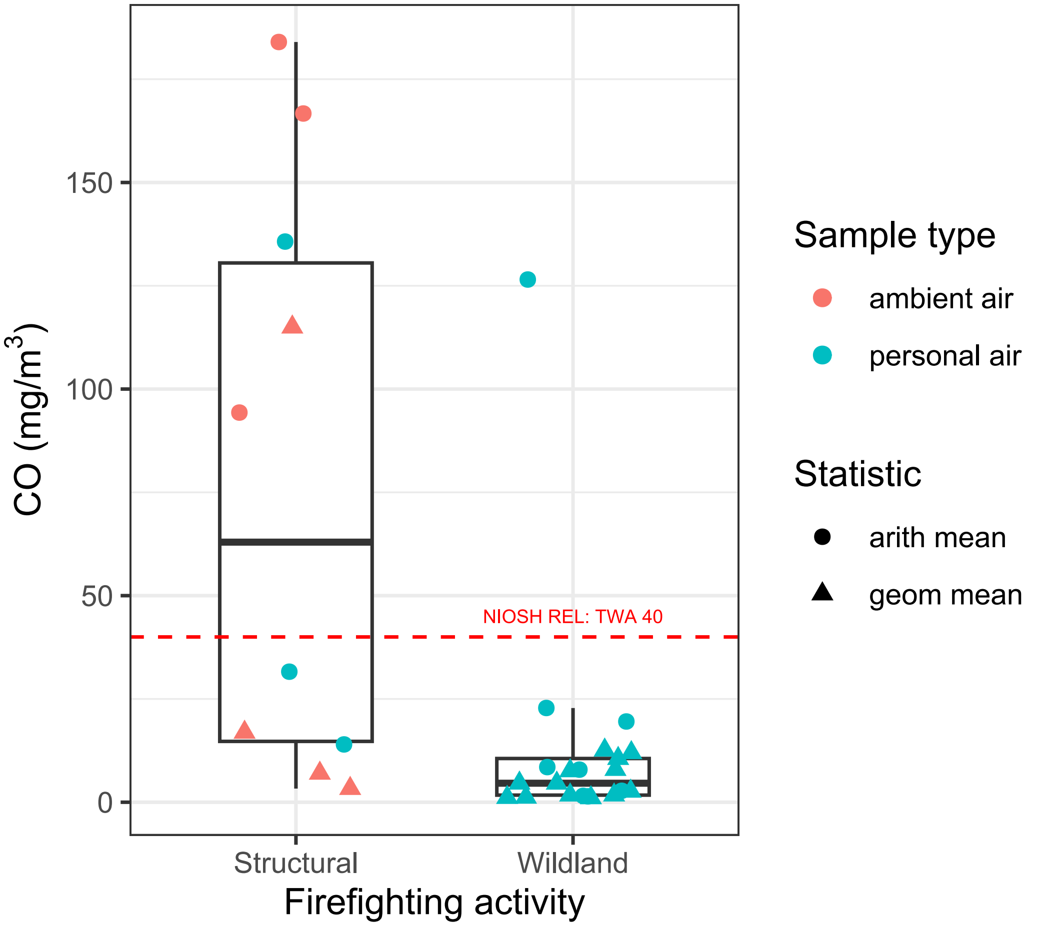
arith, arithmetic; geom, geometric; VOC, volatile organic compound.
[The Working Group compiled information from all studies identified on PubMed until May 2022 that provided measurement data on firefighters' exposure.] Only the mean or median values are plotted in the figure. Values are presented in a logarithmic scale.
Created by the Working Group.

for formaldehyde (Fig. 1.12(b–f) or Table S1.12, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Increased levels of acetaldehyde (up to 291 mg/m³), benzene (up to 101.1 mg/m³), acrolein (up to 60.6 mg/m³), and formaldehyde (up to 35.2 mg/m³) were reported during training exercises burning different fuel packaging materials, including oriented strand board, pallet, and straw, to simulate residential fires (Fent et al., 2019b).

(c) Carbon monoxide

Regarding CO, reported mean values for breathable air (ambient or personal) in structure fire environments were compiled and are presented in Fig. 1.13. Overall reported ranges reached 15 000 ppm [17 250 mg/m³] during live residential fires (Lowry et al., 1985): maximum levels reached 31 050 mg/m³ during structure fires (Burgess & Crutchfield, 1995) (Table S1.12, Annex 1, Supplementary material for Section 1,

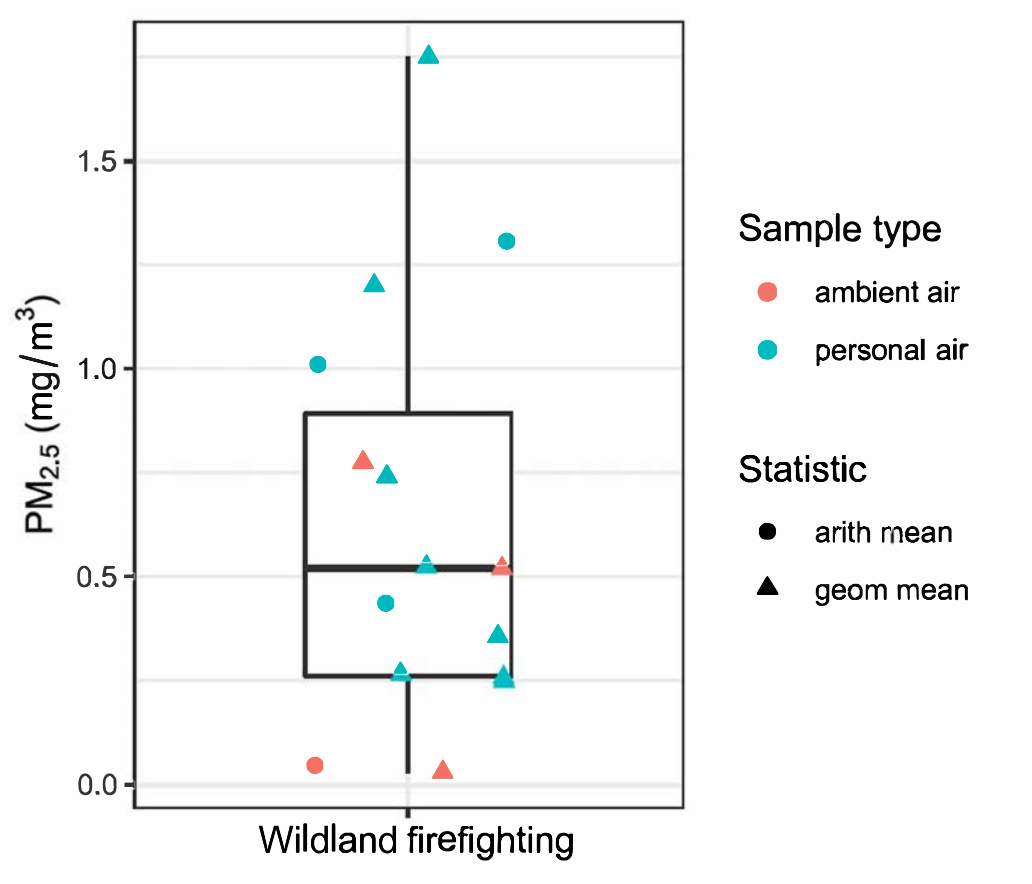
Fig. 1.13 Carbon monoxide concentrations in breathable air (ambient or personal) measured in the context of different firefighting activities



arith, arithmetic; CO, carbon monoxide; geom, geometric; NIOSH REL TWA, National Institute for Occupational Safety and Health recommended exposure limit (8-hour time-weighted average).
[The Working Group compiled information from all studies identified on PubMed until May 2022 that provided measurement data on firefighters' exposure.] Only the mean or median values are plotted in the figure. The NIOSH recommended exposure limit is indicated to allow the reader to put the values into context.
Created by the Working Group.

Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Alharbi et al. (2021) found higher concentrations of CO in the personal air of firefighters attending industrial fires than in those working on residential fires (16.43–384.2 versus 7.89–291.9 mg/m³). Several authors reported high concentrations of CO (> 1000 mg/m³) in the ambient and breathing-zone air of firefighters during firefighting at different structure fires (Table S1.12, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). In emissions from structure fires, the presence of CO was demonstrated at levels that exceeded, for instance, the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (8-hour time-weighted average, TWA) of 40 mg/m³ (Fig. 1.13).

Fig. 1.14 Concentrations of $PM_{2.5}$ in breathable air (ambient and personal) measured in the context of wildland firefighting activities



arith, arithmetic; geom, geometric; $PM_{2.5}$, particulate matter with a diameter of 2.5 µm or less.
[The Working Group compiled information from all studies identified on PubMed until May 2022 that provided measurement data on firefighters' exposure.] Only the mean/median values are plotted in the figure.
Created by the Working Group.

(d) Polycyclic aromatic hydrocarbons

The available literature highlighted structure fires as an important source of exposure to PAHs through inhalation and dermal contact (Fig. 1.11(a) and Fig. 1.11(b)). Firefighters' exposure to total PAHs through breathable air (ambient or personal) varied between 3.6 µg/m³ (geometric mean; training exercises; Sjöström et al., 2019b) and 23.8 mg/m³ (median; maximum single values reached 78.2 mg/m³) during fire combat on residential buildings (Fent et al., 2018; Fig. 1.11(a)). For benzo[*a*]pyrene (IARC Group 1, *carcinogenic to humans*; Table 1.1), personal exposure varied from 8.67 ng/m³ (geometric mean; Sjöström et al., 2019b) to 700 µg/m³ (arithmetic mean; Feunekes et al., 1997) during training firefighting exercises, the latter using heating oil. For PAHs classified by IARC in Group 2B, *possibly carcinogenic to humans* (Table 1.1), the range of exposure values was 1.811300 µg/m³ for naphthalene (maximum up to 15 916 µg/m³), 0.0026–46 µg/m³ for benz[*a*]anthracene (maximum, 236.05 µg/m³), 0.005–23.8 µg/m³ for benzo[*k*]fluoranthene (maximum, 79.2 µg/m³), 0.0108–22.3 µg/m³ for

Table 1.16 Summary of analytes monitored at structure fires, by sample type

Analyte	Sample type	References
Carbon monoxide	Ambient air	Barnard & Weber (1979); Musk et al. (1979); Lowry et al. (1985); Jankovic et al. (1991); Burgess & Crutchfield (1995); Austin et al. (2001a, b); Burgess et al. (2001); Anthony et al. (2007); Cone et al. (2008); Caban-Martinez et al. (2018)
	Personal air	Gold et al. (1978); Brandt-Rauf et al. (1988, 1989); Jankovic et al. (1991); Pośniak (2000); Burgess et al. (2002); Slaughter et al. (2004); Kirkham et al. (2011); Alharbi et al. (2021)
Polycyclic aromatic hydrocarbons (PAHs)	Ambient air	Jankovic et al. (1991); NIOSH (1998a); Austin et al. (2001a, b); Anthony et al. (2007); Kirk & Logan (2015a); Akhtar et al. (2016); Fent et al. (2018); Banks et al. (2021a)
	Personal air	Feunekes et al. (1997); Baxter et al. (2014); Fernando et al. (2016); Fent et al. (2018, 2019b); Sjöström et al. (2019b); Keir et al. (2020); Poutasse et al. (2020)
	Skin	Bolstad-Johnson et al. (2000); Laitinen et al. (2010); Baxter et al. (2014); Fernando et al. (2016); Fent et al. (2014, 2017); Wingfors et al. (2018); Strandberg et al. (2018); Andersen et al. (2018a, b); Sjöström et al. (2019b); Keir et al. (2020); Caban-Martinez et al. (2020); Banks et al. (2021a)
Particulate matter	Ambient air	Musk et al. (1979); Jankovic et al. (1991); Burgess & Crutchfield (1995); NIOSH (1998a); Burgess et al. (2001); Anthony et al. (2007); Baxter et al. (2010, 2014); Fent et al. (2018)
	Personal air	Gold et al. (1978); Brandt-Rauf et al. (1988); Burgess et al. (2002); Sjöström et al. (2019b)
Volatile organic compounds and semi-volatile organic compounds (VOCs and sVOCs)	Ambient air	Lowry et al. (1985); Jankovic et al. (1991); Burgess & Crutchfield (1995); NIOSH (1998a); Austin et al. (2001a, b); Anthony et al. (2007); Caban-Martinez et al. (2018); Fent et al. (2018, 2019b); Kirk & Logan (2019)
	Personal air	Brandt-Rauf et al. (1988); Jankovic et al. (1991); Bolstad-Johnson et al. (2000); Pośniak (2000); Burgess et al. (2001, 2002); Slaughter et al. (2004); Fernando et al. (2016); Fent et al. (2018, 2019b); Sjöström et al. (2019b); Alharbi et al. (2021)

benzo[*b*]fluoranthene (maximum, 218.59 μg/m³), 0.0158–18 μg/m³ for indeno[1,2,3-*c,d*]pyrene (maximum, 146.36 μg/m³), 0.00 457–12.9 μg/m³ for chrysene (maximum, 1062.72 μg/m³), and 0.2–7.0 μg/m³ for benzo[*j*]fluoranthene (Table S1.12, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Firefighters involved in fire combat at structure fires were also exposed to the PAH dibenz[*a,h*]anthracene (IARC Group 2A, *probably carcinogenic to humans*) (Table 1.1) at levels ranging between non-detected and 68 μg/m³ during the overhaul phase of firefighting activities on residential and commercial buildings (Bolstad-Johnson et al., 2000). Over the last few decades, information has slowly emerged related to the contamination of firefighters' skin with PAHs as a result of exposure to fire emissions (Fig. 1.11(b)). Despite being limited in number, all the studies reported increased levels of pollutants on the neck/collarbone, wrists, hands/fingers, face/forehead, back, and scrotum of firefighters after fire combat (Table S1.12, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

(e) Job assignments

[The Working Group highlighted that evidence dedicated to firefighters' exposures based on job assignments is limited.] Caban-Martinez et al. (2018) recorded a reading of 1.5 ppm for total VOCs in firefighters who were fully involved in an arson investigation into a vehicle fire and who were approximately 10 feet [3 m] from the vehicle; the reading persisted throughout the investigation. Moreover, arson investigators may re-aerosolize particulate and experience inhalation and dermal exposures to a variety of contaminants when moving debris during their investigations. Recently, Horn et al. (2022) reported concentrations of different particulate matter fractions (including submicron particles) at increased levels (based on the air quality index) during a 60-minute post-fire investigation of controlled residential fires containing furnishings currently used in the bedroom, kitchen, and living room. Those authors registered median $PM_{2.5}$ concentrations exceeding 0.100 mg/m³ (range, 0.016–0.498 mg/m³), with peak transient values reaching 23.7 mg/m³ (median, 1.090 mg/m³). Similar findings were observed for airborne aldehyde concentrations, with those for formaldehyde (median, 0.356 mg/m³; range, 0.140–0.775 mg/m³) exceeding the NIOSH limit (Horn et al., 2022).

1.4.2 Wildland fires

The available information on levels of exposure during wildland fires is presented in Table 1.17. Most of the available studies characterized prescribed burns and only some reports described participation at live wildfires or experimental/simulated wildfires (Table S1.13, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). [The Working Group noted that prescribed burns are usually performed under controlled conditions; exposure might be higher and much longer in large wildfire incidents. The wildfire exposure scenario presents challenges that make personal sampling complicated. Hence, wildland fire exposure data in the literature might underestimate the real extent of exposure.]

(a) Particulate matter

Studies reported that firefighters were exposed to increased levels of total (0.10–47.6 mg/m³) and respirable (0.02–154 mg/m³) particulate matter during wildland firefighting compared with background levels (overall range of background levels reported: total particulate matter, 0.022–0.63 mg/m³; maximum peak value, 6.9 mg/m³; and respirable particulate matter, 1.39–1.47 mg/m³; maximum peak value,

Table 1.17 Summary of analytes monitored at wildfires, by sample type

Analyte	Sample type	References
Carbon monoxide	Ambient air	Cone et al. (2005)
	Personal air	NIOSH (1991; 1992b, c, 1994a); McMahon & Bush (1992); Materna et al. (1992); Reinhardt et al. (2000); Reinhardt & Ottmar (2004); Edwards et al. (2005); Reisen et al. (2006, 2011); Swiston et al. (2008); De Vos et al. (2009b); Dunn et al. (2009); Neitzel et al. (2009); Reisen & Brown (2009); Carballo-Leyenda et al. (2010); Miranda et al. (2010, 2012); Adetona et al. (2011, 2013a, b, 2017b, 2019); Hejl et al. (2013); Dunn et al. (2013); Gaughan et al. (2014c); Ferguson et al. (2017); Reinhardt & Broyles (2019); Henn et al. (2019); MacSween et al. (2020); Wu et al. (2021)
Polycyclic aromatic hydrocarbons (PAHs)	Ambient air	Navarro et al. (2019a)
	Personal air	Materna et al. (1992); NIOSH (1992b, c, 1994a); Robinson et al. (2008); Navarro et al. (2017); Cherry et al. (2021a)
Particulate matter	Ambient air	NIOSH (1992c); Robinson et al. (2008); Cherry et al. (2019); Navarro et al. (2019a)
	Personal air	NIOSH (1991, 1992b, 1994a); McMahon & Bush (1992); Materna et al. (1992); Reinhardt & Ottmar (2000, 2004); Reinhardt et al. (2000); Slaughter et al. (2004); Edwards et al. (2005); De Vos et al. (2006, 2009b); Naeher et al. (2006); Reisen et al. (2006, 2011); Robinson et al. (2008); Neitzel et al. (2009); Reisen & Brown (2009); Miranda et al. (2010); Adetona et al. (2011, 2013a, b, 2017b, 2019); McNamara et al. (2012); Hejl et al. (2013); Naeher et al. (2013); Gaughan et al. (2014b); Ferguson et al. (2017); Reinhardt & Broyles (2019); Navarro et al. (2021); Wu et al. (2021)
Volatile organic compounds and semi-volatile organic compounds (VOCs and sVOCs)	Ambient air	Toussaint et al. (2010)
	Personal air	NIOSH (1991, 1992b, c, 1994a); Materna et al. (1992); Reinhardt et al. (2000); Reinhardt & Ottmar (2000, 2004); De Vos et al. (2006, 2009a, b); Reisen et al. (2006, 2011); Reisen & Brown (2009); Miranda et al. (2010, 2012); Navarro et al. (2021)

4.38 mg/m³) (Table S1.13, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). However, only few studies included the monitoring of background levels of exposure to particulate matter during the overall work shift of firefighters (Reinhardt et al., 2000; Reinhardt & Ottmar, 2004). Among respirable particulates, $PM_{2.5}$ is the most commonly reported fraction, with ambient values ranging between 0.029 and 435.0 mg/m³; maximum values were found in the personal air of firefighters working on prescribed burns (Fig. 1.14). Moreover, some authors demonstrated that firefighters' personal exposure to particulate matter was higher during wildland firefighting than during the regular work shift (Reinhardt et al., 2000; Reinhardt & Ottmar, 2000, 2004; Booze et al., 2004).

Some studies demonstrated undesirable, unhealthy, or even hazardous levels of exposure to airborne $PM_{2.5}$ based on the United States Environmental Protection Agency (US EPA) ambient air quality index near the fire perimeter of USA wildfire incidents where firefighters camp and rest between work shifts (McNamara et al., 2012; Navarro & Vaidyanathan, 2020).

(b) Volatile organic compounds

Measurements of firefighters' personal levels of total VOCs during wildfires varied between 0.1 and 4.0 ppm (maximum peak level of 88 ppm during an experimental forest fire; Miranda et al., 2010) and from 0.415 to 5.30 mg/m³ (maximum peak level of 7.50 mg/m³ during prescribed and experimental forest burns; Reisen & Brown, 2009) (Fig. 1.12(a); Table S1.13, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Among individual VOCs, toluene (0.038–78 mg/m³), ethylbenzene (0.027–62 mg/m³), benzene (0.01–54 mg/m³), xylene (0.018–54 mg/m³), and formaldehyde (0.010–11 mg/m³) were found at higher concentrations in ambient or breathing-zone air of firefighters (Fig. 1.12(b–f)); Table S1.13, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

(c) Carbon monoxide

Wildland firefighting activities also expose firefighters to CO at personal levels ranging from 0.92 to 345 mg/m³ during wildfires and prescribed burns (Fig. 1.13); maximum ambient air peak values reached 1483 mg/m³ during the fire episode in training forest-fire exercises (Cone et al., 2005). Concentrations of CO were mostly higher during fire attack than during overhaul (Booze et al., 2004; Reinhardt & Ottmar, 2004; Cone et al., 2005; Dunn et al., 2013).

(d) Polycyclic aromatic hydrocarbons

Levels of total PAHs in the ambient air during wildfires and prescribed burns ranged from 56 to 9103 ng/m³ (Fig. 1.11(a)), with benzo[*a*]pyrene concentrations in the breathing (personal) air of firefighters varying between 0.012 and 7 ng/m³ (maximum peak values of up to 140 ng/m³ during live wildfires; Navarro et al., 2017) (Table S1.13, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Exposures to naphthalene (range, 467–6170 ng/m³; maximum peak value, 35 900 ng/m³), benz[*a*]anthracene (range, 8–18 ng/m³; maximum peak value, 192 ng/m³), benzo[*b*]fluoranthene (range, 5–28 ng/m³; maximum peak value, 1700 ng/m³), benzo[*k*]fluoranthene (range, 4–7 ng/m³; maximum peak value, 79 ng/m³), chrysene (range, 11–31 ng/m³; maximum peak value, 250 ng/m³), indeno[1,2,3-*c,d*]pyrene (range, 3–21 ng/m³; maximum peak value, 103 ng/m³), and dibenz[*a,h*]anthracene (range, 4–10 ng/m³; maximum peak value, 50 ng/m³) were also reported in the breathing air of firefighters during firefighting at wildfires and prescribed burns (Materna et al., 1992; NIOSH, 1992b, c, 1994a; Booze et al., 2004; Robinson et al., 2008;

Table 1.18 Summary of analytes monitored at vehicle fires, by sample type

Analyte	Sample type	References
Carbon monoxide	Ambient air	Caban-Martinez et al. (2018)
Polycyclic aromatic hydrocarbons (PAHs)	Personal air	Fent & Evans (2011)
Particulate matter	Ambient air	Borgerson et al. (2011)
	Personal air	Baxter et al. (2010); Evans & Fent (2015)
Volatile organic compounds and semi-volatile organic compounds (VOCs and sVOCs)	Ambient air	Borgerson et al. (2011); Caban-Martinez et al. (2018)
	Personal air	Fent & Evans (2011)

Navarro et al., 2017, 2019b; Cherry et al., 2021a; Table S1.13, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

[The measured levels of some airborne contaminants during wildfires may appear lower than those observed during structure fires. However, the types of activity sampled, temporal and spatial variability in contamination levels outdoors, duration of the sampling period, the total exposure period, and the type of PPE used need to be taken into consideration when assessing wildland firefighters' exposure.]

1.4.3 Vehicle fires

Vehicle fires occur at very low rates in some countries (e.g. in Liechtenstein and the Russian Federation) but account for up to 13–23% of all fires or incidents in countries such as Australia, France, Japan, New Zealand, Sweden, and the USA (Monash University, 2014; CTIF, 2021). There is a paucity of information on firefighters' exposure to emissions from these fires (Fig. 1.9(a) and Fig. 1.10(a); Table 1.18). Only five studies, all performed in the USA, characterized the levels of pollutants released from these brief fire events during training activities (Table S1.14, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Other authors have also characterized vehicle fire emissions during experimental tests (Lönnermark & Blomqvist, 2006; Caliendo et al., 2013; Krüger et al., 2016; Truchot et al., 2018; Sjöström et al., 2019b). Overall, respirable particle concentrations and counts monitored in the condensed gas phase in the breathing air of firefighting forces were higher during fire combat on passenger cabins fires than on engine area fires (averages, 2.7 versus 0.36 mg/m^3 and 204 × 10^3 versus 54 × 10^3 particles per cm^3); maximum levels reached 170 mg/m^3 and 12 100 × 10^3 particles per cm^3, respectively (Evans & Fent, 2015). These values were determined during firefighting training activities performed on three salvaged vehicles; fires were suppressed with water. Evans & Fent (2015) and Baxter et al. (2010) highlighted the predominance of ultrafine particles during vehicle fire events (principally during overhaul), which may be associated with the complex mixture of materials burned in the vehicle (e.g. rubber, tyres, oil, batteries, foam, steel, electronic devices, fuel).

Ambient levels of some VOCs, including xylene, ethylbenzene, and naphthalene, were predominantly higher in engine fires than in passenger cabin fires (0.35–9.1 versus 0.45–2.7 mg/m^3, 0.15–2.2 versus 0.12–1.4 mg/m^3, and 0.930–2.4 versus 0.170–1.2 mg/m^3, respectively), whereas benzene concentrations were higher in passenger cabin fires (1.6–11 versus 0.38–60 mg/m^3) (Table S1.14, Annex 1,

Table 1.19 Summary of analytes monitored at other fire types, by sampling type

Analyte	Sample type	References
Carbon monoxide	Ambient air	Minty et al. (1985); Markowitz et al. (1989); Sebastião et al. (2021)
Polycyclic aromatic hydrocarbons (PAHs)	Ambient air	Hill et al. (1972); Ruokojärvi et al. (2000); NIOSH (1998a); Banks et al. (2021a)
	Personal air	Strandberg et al. (2018)
Particulate matter	Personal air	Dietrich et al. (2015); Andersen et al. (2017)
Volatile organic compounds and semi-volatile organic compounds (VOCs and sVOCs)	Ambient air	Hill et al. (1972); Markowitz et al. (1989); Etzel & Ashley (1994); NIOSH (1998a); Laitinen et al. (2010, 2012)

Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). [The Working Group noted that differences between VOC and sVOC concentrations may be attributed to the different materials burned in each compartment of the vehicles.]

The literature on the contribution of vehicle fire emissions to environmental levels of CO (up to 4.6 mg/m³) and PAHs (170–2400 μg/m³ for naphthalene) remains very limited (Fent & Evans, 2011; Caban-Martinez et al., 2018) (Table S1.14, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

1.4.4 Other types of fire

Table 1.19 presents the information available in the literature on other types of fire, including warehouse and training fires. Among VOCs and sVOCs, BTEX were the most characterized pollutants; concentrations ranged from 0.0091–466 mg/m³, 0.0231–2.09 mg/m³, 0.0179–1.66 mg/m³, and 0.016–2.07 mg/m³ for benzene, toluene, ethylbenzene, and xylenes, respectively (Fig. 1.12(b–e); Table S1.15, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). The highest ambient values for BTEX were reported during a large warehouse PVC fire (Markowitz et al., 1989) and a diesel-oil firefighting training exercise (Hill et al., 1972). For formaldehyde, ambient levels varied between 0.22 and 11 mg/m³ during firefighting training exercises at diving simulators and house fires (NIOSH, 1998a; Laitinen et al., 2010) (Table S1.15, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Also, the following compounds were found at concentrations higher than 2 mg/m³ during fire combat training in a diesel oil fire: acetylene/ethylene, C11 aromatics, diethylbenzene, ethylstyrene, toluene, *ortho*-xylene, and styrene (Hill et al., 1972).

Firefighters' exposure to CO ranged from 115 mg/m³ during training exercises (Minty et al., 1985) to 10 695 mg/m³ at a warehouse fire (Markowitz et al., 1989) (Table S1.15, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

Regarding ambient levels of PAHs, exposures to gaseous total PAHs reached 470 mg/m³ during simulated firefighting activities at apartment fires with pieces of chipboard and old furniture (e.g. armchair, sofas, PVC plastics, etc.) being used as fire load (Ruokojärvi et al., 2000). Ambient concentrations of benzo[*a*]pyrene isomers (0.0045–5200 μg/m³), naphthalene (1.00–54 000 μg/m³), benzofluorene isomers (0.0025–1500 μg/m³), indeno[1,2,3-*c*,*d*]pyrene

(0.0052–2000 μg/m³), and benz[*a*]anthracene plus chrysene (13–390 μg/m³) were also found in the literature; higher values were reported during simulated controlled compartment fires consisting of a diesel pan fire and a particleboard fire (Banks et al., 2021a; Table S1.15, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

Ruokojärvi et al. (2000) reported ambient levels of gaseous chlorinated pollutants, including polychlorinated phenols (14–300 μg/m³), biphenyls (2.8–56 μg/m³), chlorobenzenes (0.5–18 μg/m³), dioxins (12–83 ng/m³), and furans (21–160 ng/m³) during training exercises on simulated apartment fires. Some authors reported increased exposures at firefighting "safe zones", where individuals ease or even remove part of their PPE (e.g. SCBA), because they feel safer and need to relieve thermal and physical discomfort (Burgess et al., 2001; Andersen et al., 2017).

1.4.5 Biomarkers of exposure and considerations regarding absorption, distribution, metabolism, and excretion

Firefighters are exposed to complex mixtures at the fire suppression scene. Personal exposures to these chemicals can take place via dermal contact, inhalation, and non-dietary ingestion; biomonitoring can be used to assess the internal dose of combustion-derived chemicals, and/or their metabolites (see Section 1.3.4(a)) (WHO, 2015). Table 1.20 provides a summary of exposure biomarkers that have been employed to assess firefighters' exposures to noteworthy fire effluents, and a listing of studies that employed a variety of biomarkers.

The informativeness of biomonitoring values depends on factors such as the physical and chemical properties of the substance, the route of chemical exposure (i.e. dermal contact, inhalation, and non-dietary ingestion), as well as factors that influence absorption, distribution, metabolism, and excretion processes. These processes collectively control delivery of the chemical or its metabolite to the site of toxic action (Bessems & Geraets, 2013). In addition, such considerations influence the selection of an appropriate biomarker, the biological matrix to sample, the timing of sample collection, and the appropriate analytical method (OECD, 2022).

(a) Absorption

Absorption, which mechanistically controls bioavailability and internal dose, refers to processes that collectively move chemicals from the site of first contact (e.g. respiratory tract, dermal surface, gastrointestinal tract) to the bloodstream (Derendorf & Schmidt, 2019; Saghir, 2019).

Chemical absorption is affected by the exposure context (e.g. training versus emergency fire suppression), PPE use and post-use handling and storage, PPE design and efficiency (e.g. flash hood textile and design), site of contact (e.g. skin, respiratory tract, gastrointestinal tract), chemical form (e.g. vapour, particulate matter-adsorbed sVOCs), and firefighter duties (e.g. attack and knockdown, command and control).

Many researchers have underscored the importance of dermal absorption of substances such as PAHs and VOCs, including absorption when using turnout gear and SCBA (Feunekes et al., 1997; Laitinen et al., 2010; Baxter et al., 2014; Fent et al., 2014, 2017, 2020b; Pleil et al., 2014; Fernando et al., 2016; Oliveira et al., 2016; Andersen et al., 2017; Andersen et al., 2018a; Stec et al., 2018; Wingfors et al., 2018; Cherry et al., 2019, 2021a; Wallace et al., 2019a; Burgess et al., 2020; Keir et al., 2020; Banks et al., 2021a). Absorption of dermally deposited chemicals encountered during fire suppression, including VOC vapours and sVOCs adsorbed to airborne particulate matter, depends on PPE design and use, location and thickness of exposed skin (e.g. face, neck, wrist, forehead), physical exertion and movement, and environmental temperature

Table 1.20 Biomarkers commonly used to assess firefighters' exposures to selected fire effluents

Biomarker	Fire effluent	Selected references
Urinary biomarkers		
Urinary 2MHA	Xylenes	Fent et al. (2022)
Urinary 3HPMA	Acrolein	Fent et al. (2022)
Urinary 3MHA + 4MHA	Xylenes	Fent et al. (2022)
Urinary 4HBeMA	1,3-Butadiene	Fent et al. (2022)
Urinary BzMA	Toluene or benzyl alcohol	Fent et al. (2022)
Urinary hydroxylated PAHs	Selected PAHs	Feunekes et al. (1997); Moen & Øvrebø (1997); Caux et al. (2002); Edelman et al. (2003); Robinson et al. (2008); Laitinen et al. (2010, 2012); NIOSH (2013a); Fent et al. (2014, 2019a, 2020b); Fernando et al. (2016); Oliveira et al. (2016, 2017a, b, 2020b); Pierrard (2016); Adetona et al. (2017a, 2019); Andersen et al. (2017, 2018a, b); Keir et al. (2017); Hoppe-Jones et al. (2018); Wingfors et al. (2018); Allonneau et al. (2019); Cherry et al. (2019, 2021a); Gill et al. (2019, 2020a); Beitel et al. (2020); Burgess et al. (2020); Kim et al. (2020b); Rossbach et al. (2020); Bader et al. (2021); Banks et al. (2021a); Hoppe-Jones et al. (2021)
Urinary levoglucosan	Levoglucosan	Naeher et al. (2013)
Urinary MADA	Styrene	Fent et al. (2022)
Urinary methoxyphenols	Methoxyphenols (e.g. guaiacol, methylsyringol)	Neitzel et al. (2009); Fernando et al. (2016)
Urinary *para*-chloroaniline	*para*-Chloroaniline	Bader et al. (2014)
Urinary PHEMA	Styrene	Kim et al. (2021)
Urinary phenolic compounds	Phenolic compounds (e.g. bisphenol A, benzophenone-3)	Waldman et al. (2016); Bader et al. (2021)
Urinary PhMA	Benzene	Fent et al. (2022)
Urinary *S*-benzylmercapturic acid	Toluene	Rosting & Olsen (2020); Kim et al. (2021)
Urinary *S*-phenylmercapturic acid	Benzene	NIOSH (2013a); Fent et al. (2014); Bader et al. (2014, 2021); Rosting & Olsen (2020); Kim et al. (2021)
Urinary TZCA	Formaldehyde	Kim et al. (2021)
Urinary *trans,trans*-muconic acid	Benzene	Caux et al. (2002); Laitinen et al. (2010); Bader et al. (2014, 2021); Fent et al. (2022)
Urinary VOCs	BTEX	Bader et al. (2014); Heibati et al. (2018); Allonneau et al. (2019); Bader et al. (2021); Kim et al. (2021)
Haematological biomarkers		
Carboxyhaemoglobin in blood	Carbon monoxide	Levy et al. (1976); Loke et al. (1976); Radford & Levine (1976); NIOSH (1992c); Kales et al. (1994)
Blood cyanide	Cyanide	Jackson & Logue (2017); Edelman et al. (2003)
Blood methanol	Methanol	Aufderheide et al. (1993)
Thiocyanate in serum	Cyanide	Levine & Radford (1978)
Blood sVOCs	Selected sVOC, non-targeted approach	Grashow et al. (2020)
Blood VOCs	Selected VOCs (e.g. xylenes, dichlorobenzene)	Edelman et al. (2003)

Table 1.20 (continued)

Biomarker	Fire effluent	Selected references
Exhaled breath biomarkers		
Carbon monoxide in exhaled breath	Carbon monoxide	Stewart et al. (1976); Brotherhood et al. (1990); Cone et al. (2005); Dunn et al. (2009)
Nitric oxide (NO) in exhaled breath	Nitrogen dioxide (NO_2)	Miranda et al. (2012)
PAHs in exhaled breath	PAHs	Fent et al. (2014); Pleil et al. (2014); Wallace et al. (2017, 2019a, b)
VOCs (e.g. BTEXS) in exhaled breath	VOCs (e.g. BTEXS)	NIOSH (2013a); Fent et al. (2015, 2019a, 2020b); Pleil et al. (2014); Wallace et al. (2017, 2019a); Kim et al. (2021); Mayer et al. (2022)
VOCs and sVOCs in exhaled breath	Selected VOCs and sVOCs, non-targeted approach	Wallace et al. (2017, 2019b)
Saliva biomarkers		
PAHs in saliva	Selected PAHs	Santos et al. (2019)

2MHA, 2-methylhippuric acid; 3HPMA, *N*-acetyl-S-(3-hydroxypropyl)-L-cysteine; 3MHA + 4MHA, 3-methylhippuric acid + 4-methylhippuric acid; 4HBeMA, *N*-acetyl-*S*-(4-hydroxy-2-buten-1-yl)-L-cysteine; BTEX, benzene, toluene, ethylbenzene, and xylene; BTEXS, benzene, toluene, ethylbenzene, xylene, and styrene; BzMA, *N*-acetyl-*S*-(benzyl)-L-cysteine; MADA, mandelic acid; NO, nitric oxide; PAH, polycyclic aromatic hydrocarbon; PHEMA, *N*-acetyl-*S*-(2-phenyl-2-hydroxyethyl)-L-cysteine; PhMA, *N*-acetyl-*S*-(phenyl)-L-cysteine; sVOCs, semi-volatile organic compounds; TZCA, thiazolidine-4-carboxylic acid; VOCs, volatile organic compounds.

and humidity (Wester et al., 1990; WHO, 2006; Laitinen et al., 2010; NIOSH, 2013a; Baxter et al., 2014; Fent et al., 2014, 2017, 2020b; Andersen et al., 2018a; Stec et al., 2018; Sjöström et al., 2019b; Beitel et al., 2020; Keir et al., 2020; Rosting & Olsen, 2020).

Pulmonary absorption of inhaled chemicals, including VOCs (e.g. BTEX, methanol), sVOCs (e.g. PAHs with low molecular weight) and toxic gases (e.g. CO, NO_2) can also occur despite the use of PPE such as SCBA (Aufderheide et al., 1993; Fent et al., 2014, 2015, 2020b; Wallace et al., 2019a). Specifically, pulmonary contact and absorption can occur in situations in which SCBA is less likely to be used (e.g. during overhaul), before donning SCBA, if the SCBA is improperly used, and/or if the SCBA is prematurely doffed (Bolstad-Johnson et al., 2000; Austin et al., 2001c; Burgess et al., 2001; Fent et al., 2014, 2015; Wallace et al., 2019a; Beitel et al., 2020; Burgess et al., 2020; Rosting & Olsen, 2020). Additionally, secondary inhalation exposure can occur via contact with soiled turnout gear (Baxter et al., 2014; Fent et al., 2014, 2015; Pleil et al., 2014; Burgess et al., 2020). With respect to particulate matter and substances adsorbed to particulate matter, absorption is governed by aerodynamic diameter. Large particles (i.e. ≥ 10 μm) are generally retained by the nasopharyngeal system, i.e. they do not enter the lungs. Particulate matter in the 5–10 μm range is generally removed by alveolar macrophages (Geiser, 2010). These particles can also be inadvertently ingested after mucociliary clearance and swallowing, with subsequent absorption in the gastrointestinal tract followed by first-pass hepatic metabolism (Ramesh et al., 2004; Pambianchi et al., 2021). Importantly, small particles (i.e. $PM_{2.5}$) can penetrate the deeper regions of the pulmonary system. Particulate matter in the 1–2.5 μm range can interact with terminal bronchioles; those < 1 μm can readily gain access to alveoli (Schraufnagel, 2020). Particles < 0.1 μm have been shown to readily cross alveolar epithelia, thereby accessing the blood stream and systemic circulation (Schraufnagel, 2020). In comparison with transdermal absorption, pulmonary absorption can be rapid; thus, temporal patterns of excreted metabolites can be used to determine the relative influence of the different exposure routes (Feunekes et al., 1997; Caux et al., 2002; Laitinen et al., 2012; Pierrard, 2016; Cherry et al., 2019).

(b) Distribution

Distribution refers to the reversible movement of an absorbed chemical from the site of contact (Taveli & Bellera, 2018). Effective distribution is required to permit the use of haematological and urinary biomarkers of exposure (e.g. urinary PAH and benzene metabolites); substances that are absorbed via dermal or pulmonary contact can be rapidly distributed to the sites of metabolism or toxic action. Generally speaking, parent compounds can be detected in the blood; biomonitoring is commonly conducted using serum analyses (e.g. brominated flame retardants and PFAS, see Section 1.5.1(i)) (e.g. Shaw et al., 2013; Rotander et al., 2015a; Trowbridge et al., 2020; Mayer et al., 2021). Metabolites are commonly detected in the urine (for example, metabolites of PAHs and benzene) (see Table 1.20, e.g. Caux et al., 2002; NIOSH, 2013a; Adetona et al., 2017a; Keir et al., 2017; Rosting & Olsen, 2020; Bader et al., 2021; Cherry et al., 2021a). Levels of systemically distributed chemicals can also be monitored via collection and analysis of exhaled breath; particularly for short-term exposures (see Table 1.20, e.g. Pleil et al., 2014; Fent et al., 2015; Wallace et al., 2017; Mayer et al., 2022).

(c) Metabolism and excretion

Metabolism and excretion are controlled by a complex series of dynamic processes influenced by factors such as genotype, sex, age, diet, drug and alcohol consumption, co-exposures to therapeutic products and other chemicals, and disease (Johnson et al., 2012).

The rates of metabolism and excretion (i.e. metabolite terminal half-life) are critically important for determining the appropriate time interval between an exposure event and biomarker sample collection (Bader et al., 2021). Since terminal excretion half-lives of combustion-derived chemicals (e.g. benzene, PAHs, environmental phenols) are generally in the range of 4–16 hours, several research groups have highlighted the importance of rapid post-exposure collection of firefighter biomonitoring samples (Caux et al., 2002; Fent et al., 2015; Waldman et al., 2016; Bader et al., 2021). It can be difficult to evaluate the results of urine samples collected long after the exposure (Caux et al., 2002; Keir et al., 2017; Bader et al., 2021). For example, benzene is rapidly metabolized and cleared from the blood, permitting rapid appearance of metabolites in the urine (Rosting & Olsen, 2020); the terminal half-life of the benzene metabolite *S*-phenylmercapturic acid is only 9 hours (Bader et al., 2021). Similarly, urinary elimination half-lives for hydroxylated metabolites of phenanthrene, fluorene, and naphthalene are in the range of 3–8 hours (Oliveira et al., 2016; Keir et al., 2017). This is consistent with time-course analyses conducted by Rossbach et al. (2020), who reported post-training concentrations of urinary PAH metabolites with half-lives of 3.5–9.3 hours. Consequently, timely collection of biomonitoring samples is of paramount importance (Caux et al., 2002; Keir et al., 2017; Cherry et al., 2019, 2021a; Fent et al., 2020b; Bader et al., 2021). Urine analyses are not commonly used for biomonitoring of exposures to PAHs of higher molecular weight (e.g. benzo[*a*]pyrene), because these substances are primarily excreted via the bile and faeces (Motorykin et al., 2015) and are largely undetectable in the urine (Keir et al., 2017, 2021; Wingfors et al., 2018; Allonneau et al., 2019). Recently, new biomarkers have been used that can provide information on exposure to benzo[*a*]pyrene, such as 3-hydroxybenzo[*a*]-pyrene (3-OH-BaP), the main urinary metabolite of benzo[*a*]pyrene (Alhamdow et al., 2019). However, this requires particularly sensitive analytical procedures, because the pathway for urinary excretion of this metabolite is much less significant than that for faecal excretion; this permits use of 3-OH-BaP only in settings with high exposures, such as occupational exposure of firefighters (Oliveira et al., 2017c).

A recent published review on biomonitoring in firefighters indicated that the half-lives of noteworthy chemicals range from hours (e.g. PAH, VOC metabolites), to months or even years (e.g. PFAS, chemical flame retardants, see Section 1.5.1(i)) (Engelsman et al., 2020). There is considerable variability or uncertainty in published values for chemical half-lives, and by extension, determination of optimal timing for sample collection (Feunekes et al., 1997; Oliveira et al., 2016; Cherry et al., 2019). [The Working Group noted that there is a paucity of toxicokinetic data for many combustion-derived chemicals. Such data would facilitate interpretation of biomonitoring results in a firefighting context (Li et al., 2012; Oliveira et al., 2016, 2020b; Cherry et al., 2019; Engelsman et al., 2020). In particular, there is a need to critically examine how half-life values vary with different routes of exposure (i.e. transdermal, inhalation, and ingestion) (Li et al., 2012; Oliveira et al., 2016, 2020b).]

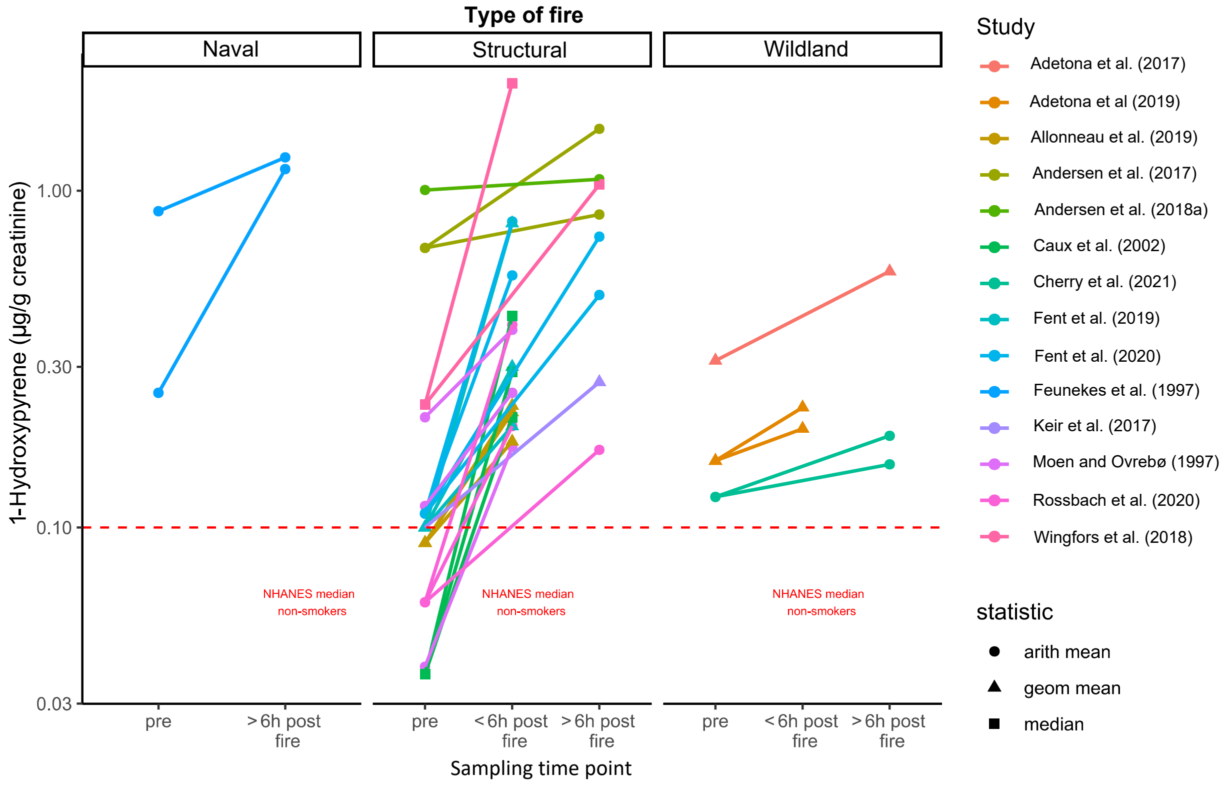
(d) Biomarkers of exposure

The studies listed in Table 1.20 collectively generated a large amount of biomarker data, particularly for urinary PAH metabolites. Although an extensive analysis of the available data was outside the scope of this section, some data patterns and deficiencies are highlighted here. Values for commonly used exposure biomarkers, e.g. 1-hydroxypyrene in urine and benzene in exhaled breath, were available from 67 studies. With respect to the predominant sources of the data, the majority of the studies were conducted in the USA (63%), followed by Canada (14%). Most of the studies (83%) involved career firefighters, and roughly half of the studies investigated structure fires. Almost 60% of the studies considered urinary biomarkers and nearly all the remaining studies examined exhaled breath (16%) or blood (18%).

Fig. 1.15 shows post-exposure changes in urinary 1-hydroxypyrene (µg/g creatinine); all the studies included in the analyses noted post-suppression increases (i.e. a fold-change of > 1.0). Seven studies noted relatively small fold-change increases (i.e. < 2) (Feunekes et al., 1997; Moen & Øvrebø, 1997; Adetona et al., 2017a, 2019; Andersen et al., 2017, 2018a; Cherry et al., 2021a); of those, three examined wildland firefighters (Adetona et al., 2017a, 2019; Cherry et al., 2021a). None of the studies that examined wildland firefighters noted fold-changes of > 2. Five studies noted fold-change increases of > 5 (Caux et al., 2002; Wingfors et al., 2018; Fent et al., 2019a, 2020b; Rossbach et al., 2020); all examined structural firefighters. The majority of studies that noted fold-change values of > 5 measured urinary hydroxypyrene levels in samples collected 3–12 hours post-exposure. This observation is well aligned with the aforementioned half-life range (i.e. 3–9.3 hours) for PAHs of low molecular weight (Oliveira et al., 2016; Keir et al., 2017; Rossbach et al., 2020). Fig. 1.16 shows the distribution of urinary 1-hydroxypyrene levels in firefighters before and after firefighting. The data indicated that, on average, levels post-exposure are 3.3-fold those pre-exposure; pre- and post-exposure levels are significantly different at $P < 0.0001$.

Fig. 1.17 shows post-exposure changes in the level of benzene in exhaled breath. Post-exposure fold-change values (i.e. post- versus pre-exposure) varied from 0.82 to 23.08 µg/m^3; 22 of the 26 values reflect a post-exposure increase (i.e. fold-change > 1.0). Twelve of the 26 values presented indicated a fold-change (i.e. post- versus pre-exposure) > 2; more than half of these (i.e. 7 out of 12) are associated with a sampling time point < 1 hour post-exposure (NIOSH, 2013a; Fent et al., 2020b; Pleil et al., 2014; Mayer et al., 2022). Indeed, all fold-change values for post-exposure sampling < 1 hour are > 1.0 (i.e. post-exposure increase in benzene in exhaled breath), with an average of 7.1 ± 2.3 µg/m^3 (n = 12). The sampling

Fig. 1.15 Urinary concentrations of 1-hydroxypyrene in firefighters before and after suppression of naval, structural, or wildland fires

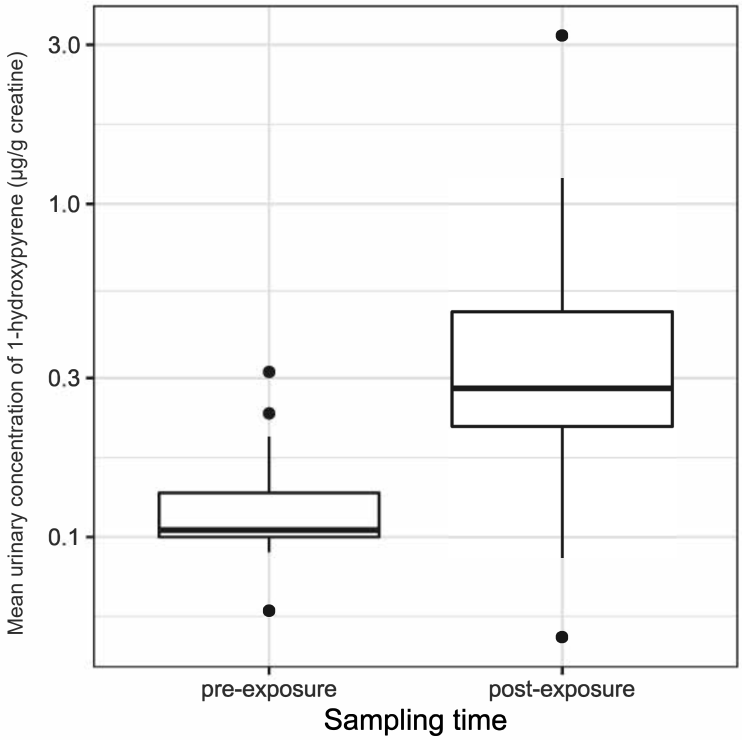


arith, arithmetic; geom, geometric; NHANES, National Health and Nutrition Examination Survey
[The Working Group compiled information from all studies identified on PubMed until May 2022 that provided biomonitoring data of firefighters' exposures.] Values are stratified by post-suppression sampling time and fire type. The median NHANES value for non-smokers is provided for comparison (CDC, 2018). Median values for European non-smokers vary from 0.046 to 0.16 µg/g (HBM4EU, 2022). Average Canadian non-smoker values are in the 0.1 µg/g range (Keir et al., 2021). All values are reported as creatinine-adjusted concentrations.
Created by the Working Group.

time-point effect was significant at $P < 0.03$. This is consistent with the rapid absorption, distribution, and exhalation of VOCs such as benzene (US EPA, 1998).

[The Working Group noted that although it is clear that biomonitoring is a valuable tool for assessment of firefighters' exposure to combustion-derived chemicals, it is also clear that numerous factors need to be carefully considered when designing an effective biomonitoring study and when interpreting biomarker measurements in a fire suppression context. Factors that need to be considered when evaluating biomarker responses include sex, hydration level, primary route of exposure, type of fire, and the participant's role in fire suppression, as well as the substance's physical and chemical properties, environmental fate, and biological half-life.]

Fig. 1.16 Distribution of urinary concentrations of 1-hydroxypyrene in firefighters before and after fire suppression



All values are reported as creatinine-adjusted concentrations; values extracted from 11 studies (i.e. Adetona et al., 2017a, 2019; Allonneau et al., 2019; Bader et al., 2021; Cherry et al., 2019, 2021a; Fent et al., 2019a, 2020b; Gill et al., 2019; Keir et al., 2017; Rossbach et al., 2020). All values are arithmetic means, except those from Bader et al. (2021), Cherry et al. (2019), Keir et al. (2017) and Allonneau et al. (2019), Adetona et al. (2017a), which are geometric means. Values are presented in a logarithmic scale. Pre-exposure values (n = 14) range from 0.060 to 0.031, with mean and median values of 0.14 and 0.11, respectively. Post-exposure values (n = 32) range from 0.050 to 3.2, with mean and median values of 0.46 and 0.28, respectively. Post-exposure values include a variety of sampling times and analytical methods. The sampling time effect (i.e. pre-exposure versus post-exposure) on urinary 1-hydroxypyrene concentrations is statistically significant at $P < 0.0001$ [figure and calculations by the Working Group].
Created by the Working Group.

1.5 Exposures other than fire effluents and polycyclic aromatic hydrocarbons

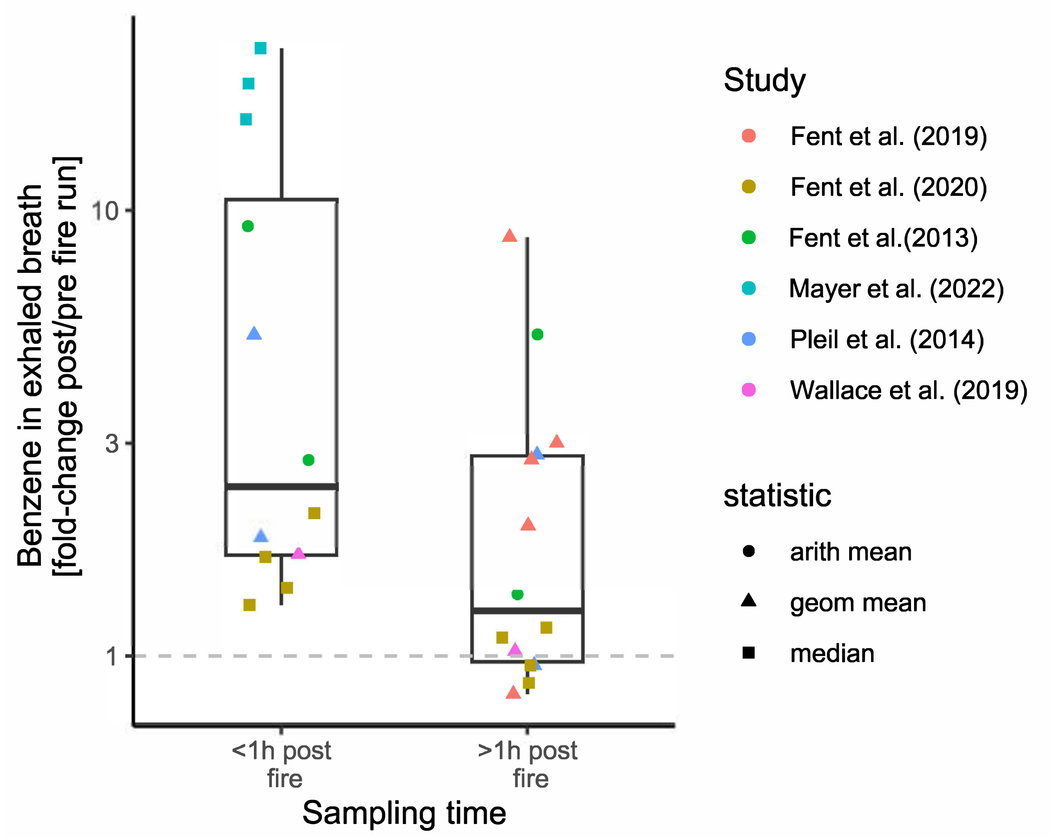
1.5.1 *Chemicals and physical factors*

(a) Asbestos and other minerals and fibres

Asbestos (IARC Group 1, *carcinogenic to humans*) is a mineral fibre used for its insulating properties in homes, businesses, and other structures that were mostly built before the 1980s. Because asbestos is ubiquitous in so many older structures, it may be encountered by firefighters during fires or other emergency incidents during which building materials are disturbed (see Table 1.21). Fire and high temperature can break down composite materials and liberate the asbestos fibres that they contain. Asbestos fibres directly exposed to high temperatures (> 400 °C) may also break down, resulting in shorter aspect ratios and less pathogenicity (Hoskins & Brown, 1994; Jeyaratnam & West, 1994).

Table S1.22 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615) provides measures of asbestos in air

Fig. 1.17 Changes in benzene concentrations in exhaled breath of firefighters before and before fire suppression



arith, arithmetic; geom, geometric.
[The Working Group compiled information from all studies identified on PubMed until May 2022 that provided biomonitoring data on firefighters' exposures.] Values are stratified by post-suppression sampling time point and presented as fold-change (i.e. post- versus pre-exposure). The average fold-change for a post-exposure sampling time of < 1 hour is 7.1 ± 2.3 (n = 12); the average for sampling time > 1 hour is 2.3 ± 0.59 (n = 14). The sampling time effect is significant at $P < 0.03$. The y-axis is presented on a log 10 scale.
Created by the Working Group.

and on surfaces associated with firefighting. During overhaul, firefighters will commonly tear down walls, ceilings, flooring, and other materials, which could disturb materials containing asbestos. In an evaluation of firefighter exposures during overhaul of structure fires in Arizona, USA, asbestos fibres were detected in 15 of 46 air samples, with an average of 0.073 fibres per cm^3, suggesting that firefighters who were not wearing respiratory protection during overhaul could inhale asbestos fibres (Bolstad Johnson et al., 2000). Asbestos may also be used in roofing materials. A factory fire in England released into the atmosphere chrysotile fibres (contained in asbestos bitumen paper covering the roof), which were later detected on firefighters' clothing and in the surrounding environment (Bridgman, 2001). Another study attempted to measure asbestiform fibres on used firefighter turnout gear from Kentucky, USA, and found evidence of actinolite and chrysotile in four of 29 surface samples, although only one sample quantified asbestos fibres (chrysotile) above the LOD for the method (1570 fibre structures per cm^2) (Hwang et al., 2019b). [Asbestos on firefighting gear could pose an inhalation hazard if the contamination were to be agitated and become airborne.]

[The Working Group noted that microscopy methods used to measure asbestiform fibres on air filters are vulnerable to interference from other substances that may also have been collected on the filter, which is likely to occur during many firefighting activities.]

Asbestos can also contaminate outdoor sites or soils. A NIOSH evaluation assessed wildland firefighters' exposures to asbestiform fibres in Libby, Montana, USA (a former site for vermiculite mines), and found task-based concentrations of 0.0013–0.13 fibres per cm^3 (NIOSH, 2019). [Contamination of soils with naturally occurring asbestos fibres is not expected to be common in most regions of the world.]

In addition to asbestos, firefighters can be exposed to other minerals, including crystalline silica (see Table 1.21). [The Working Group noted the paucity of literature on silica exposure in municipal firefighters but acknowledges the potential for silica exposure.] A study of wildland firefighters' exposures during prescribed burns and naturally occurring fires found that fire personnel were exposed to respirable quartz at concentrations that frequently exceeded the Occupational Safety and Health Administration (OSHA) permissible exposure limit of 0.05 mg/m^3, especially after adjusting for longer shifts (Reinhardt & Broyles, 2019). Firefighters can also be exposed to man-made vitreous fibres, which are fibrous inorganic materials made from rock, slag, clay, or glass (IARC, 2002). Dust samples collected from the areas surrounding the WTC disaster and from the Grenfell Tower fire contained man-made vitreous fibres (ATSDR, 2002; Lioy et al., 2002; Stec et al., 2019).

(b) Per- and polyfluoroalkyl substances

PFAS are a class of synthetic chemicals that have been used in commercial and industrial products and processes for nearly a century (US EPA, 2021a). By the 1960s, PFAS were integral in the development of a firefighting foam known as AFFF and soon after were incorporated as waterproofing agents into textiles (ITRC, 2020).

AFFFs are often used on fires involving flammable liquids or vapours (known as "class B" fires), such as jet fuel. The PFAS surfactants in AFFFs are designed to lower the surface tension, allowing the foam to quickly spread across and smother the burning liquid. AFFFs are more effective at suppressing liquid fires than is water, and they have the added benefits of reducing the water requirements and runoff potential (Magrabi et al., 2002).

In the past two decades, specific compounds used in the production of AFFFs have shifted from longer carbon chain formulae, such as perfluorooctanesulfonic acid (PFOS), to shorter and alternative formulae, such as perfluorobutane sulfonic acid (PFBS) and hexafluoropropylene oxide-dimer acid (HFPO-DA), because of emerging toxicity data and concerns over the bioaccumulation of longer-chain PFAS (Brase et al., 2021).

Although the contribution of specific pathways to a firefighter's absorbed dose is not fully understood, PFAS exposure could result from dust and products of combustion present at a fire scene; contact with firefighting foam, and PPE in which PFAS is an intentionally added component; or contaminated fire station dust (Tao et al., 2008; Shaw et al., 2013; Leary et al., 2020; Peaslee et al., 2020; Young et al., 2021). There is also the potential for firefighters to be exposed through local contamination of water with AFFF. For example, use of AFFF at fire stations, including those at airports, military bases, and training facilities, has contributed to PFAS contamination in groundwater, soil, and other surfaces (de Solla et al., 2012; Backe et al., 2013; Baduel et al., 2015; Hansen et al., 2016; Hu et al., 2016).

For many firefighters, AFFF may be the most significant source of exposure to PFAS, as supported by several biomonitoring studies in firefighters (Laitinen et al., 2014; Rotander

Table 1.21 Studies in which exposure monitoring was performed for compounds other than fire smoke[a]

Chemical agent or class	Sample type	References
Asbestos	Area air	Bolstad-Johnson et al. (2000)
	Personal air	NIOSH (2019)
	Surface (PPE)	Bridgman (2001)
	Surface (work surfaces)	Hwang et al. (2019b)
Silica	Personal air	Reinhardt & Broyles (2019)
Man-made vitreous fibres	Surface (ambient dust)	ATSDR (2002); Lioy et al. (2002); Stec et al. (2019)
Per- and polyfluoroalkyl substances	Surface (PPE)	Peaslee et al. (2020)
	Surface (work surfaces)	Young et al. (2021)
PBDEs and other brominated flame retardants	Area air	Fent et al. (2020a)
	Surface (PPE)	Easter et al. (2016); Mayer et al. (2019); Fent et al. (2020a); Banks et al. (2021c)
	Surface (work surfaces)	Shen et al. (2018); Gill et al. (2020b)
Organophosphate flame retardants (OPFRs)	Area air	Fent et al. (2020a)
	Surface (PPE)	Mayer et al. (2019); Fent et al. (2020a); Banks et al. (2021c)
	Surface (work surfaces)	Shen et al. (2018); Gill et al. (2020b)
Diesel exhaust (elemental carbon or total particulates)	Area air	NIOSH (2016b); Bott et al. (2017); Chung et al. (2020)
	Personal air	Froines et al. (1987)
Heavy metals (e.g. cadmium, arsenic, lead)	Personal air	Keir et al. (2020)
	Surface (PPE)	Easter et al. (2016); Engelsman et al. (2019)
	Surface (work surfaces)	Engelsman et al. (2019)
PCDD/Fs	Surface (PPE)	Hsu et al. (2011); Fent et al. (2020a)
PBDD/Fs	Surface (PPE)	Fent et al. (2020a)

PBDD/Fs, polybrominated dibenzo-*para*-dioxins/dibenzofurans; PBDEs, polybrominated diphenyl ethers; PCDD/Fs, polychlorinated dibenzo-*para*-dioxins/dibenzofurans; PPE, personal protective equipment.

[a] Exposure results are provided in Supplementary Table S1.22 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

et al., 2015b; Leary et al., 2020). A few studies have suggested a positive association between biological levels of PFAS and years of firefighting (Rotander et al., 2015b; Graber et al., 2021). However, because long-chain PFAS are being removed from AFFF formulations, biological levels of PFAS in firefighters who use class B foams may begin to decline (Rotander et al., 2015b). See Section 1.5.1(i) for more details on biomonitoring studies of firefighters using AFFF.

Because PFAS has been used in various commercial products, including stain-resistant carpeting and furniture, structure fires may also be associated with exposure to and contamination with PFAS. Many of the studies that have evaluated municipal firefighters' exposure to PFAS have involved biological monitoring (Tao et al., 2008; Jin et al., 2011; Shaw et al., 2013; Leary et al., 2020; Trowbridge et al., 2020; Clarity et al., 2021), and a few of these studies found associations between recent fire events or duration of exposure and specific types of PFAS in the blood (Tao et al., 2008; Shaw et al., 2013). See Section 1.5.1(i) for more information on biological levels of PFAS in firefighters.

PFAS could also be present in firefighting textiles either as part of the manufacturing process or as contamination acquired during firefighting. Evaluation of PFAS in turnout gear confirmed measurable levels of several types of PFAS in textiles. The highest levels of PFAS were found in the outer shell and moisture barriers, with evidence of migration across the protective layers in used turnout gear (Peaslee et al., 2020). Studies have also detected PFAS in dust collected from turnout-gear storage areas in fire stations, with some types of PFAS being present in higher concentrations than in dust from living areas of those fire stations (Peaslee et al., 2020; Young et al., 2021) (see Table 1.21, and Table S1.22, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

(c) *Chemical flame retardants*

Furnishings and other items containing foams, plastics, and other synthetic materials can be highly flammable. One way the furniture, textile, and electronics industries have addressed this flammability issue is by adding chemical flame retardants to their products. PBDEs were one of the first classes of chemical flame retardant to be used, starting in the 1970s (Barbauskas, 1983; McKenna et al., 2018). Use has dwindled and even been banned completely in some countries because of their persistence, ability to accumulate in the body, and toxicological effects. The Stockholm Convention on Persistent Organic Pollutants classified several congeners as persistent organic pollutants in 2009 and decabromodiphenyl ether (BDE-209) in 2017 (Secretariat of the Stockholm Convention, 2019b). Other brominated flame retardants listed for elimination in the Stockholm Convention are hexabromobiphenyl and hexabromocyclododecane (HBCDD). Several countries (e.g. China, India, Japan, and the USA) are making significant strides towards eliminating the use of these compounds. The European Union has almost completely banned the use of PBDEs, hexabromobiphenyl, and HBCDD (Sharkey et al., 2020). However, other chemical flame retardants are still being used globally, including OPFRs and other chlorinated and brominated flame retardants, in products such as foam insulation for buildings (Lee et al., 2016; Chupeau et al., 2020; Estill et al., 2020). The estimated global consumption of flame retardants in Asia, Europe, and the USA was 2.8 million tonnes in 2018 (Yasin et al., 2016).

Table 1.21 provides a summary of flame retardant measurements in area air and on surfaces associated with firefighting (see also Table S1.22, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Firefighters can potentially be exposed to all classes of flame retardant if the fires they respond involve furnishings and other items containing these compounds (such as building insulation), which will depend in part on the rules and regulations of the country where the firefighters work (Sharkey et al., 2020). Fent et al. (2020a) measured a variety of PBDEs, other brominated flame retardants, and OPFRs in the air during the live-fire portion of controlled residential fires containing modern furnishings in the USA; results included BDE-209 (median, 15.6 μg/m^3), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB; median, 7.71 μg/m^3), and triphenyl phosphate (median, 408 μg/m^3). These substances were also detected in almost every wipe sample collected from the turnout jackets and gloves worn by the responding firefighters. Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) was also detected with high frequency on turnout jackets and gloves (Fent et al., 2020a).

Other studies have measured flame-retardant contaminants on firefighting clothing from the USA and Australia (Alexander & Baxter, 2016; Easter et al., 2016; Mayer et al., 2019; Banks et al., 2021c). Studies have also measured flame retardants in dust collected in fire stations from Australia, Canada, and the USA (Brown et al., 2014; Shen et al., 2015; Banks et al., 2020; Gill et al., 2020b); some of these studies found higher levels of certain flame retardants (e.g. BDE-209 and TDCPP) than in dust collected from other occupational settings (Shen et al., 2015; Gill et al., 2020b).

Firefighters' turnout gear could also contain flame retardants added during manufacture. Alexander & Baxter (2016) measured BDE-209 from unused gloves and a knit hood available at that time in the USA (< 1 µg/g per sample). In 2019, investigators analysed new knit hoods in the USA and found that they contained no detectable flame retardants (Mayer et al., 2019). More recently, new turnout gear from South Africa was found to contain PBDEs at > 200 µg/g and HBCDD at < 0.1 µg/g (Mokoana et al., 2021). [The Working Group noted that manufacture of turnout gear with textiles containing flame retardants may have been more common in the past than today. However, the study from South Africa suggested that manufacturers may still be producing turnout gear using textiles containing flame retardants in certain regions of the world.]

Biomonitoring has also been used to assess firefighters' exposure to flame retardants. Cross-sectional biomonitoring studies of firefighters in the USA have found elevated serum concentrations of certain PBDEs (e.g. BDE-99 and BDE-209) and elevated urinary concentrations of certain OPFRs (e.g. metabolites of triphenyl phosphate and TDCPP) compared with the general population (Shaw et al., 2013; Park et al., 2015; Jayatilaka et al., 2017). In the study by Fent et al. (2020a), firefighters experienced significant increases in urinary concentrations of metabolites of triphenyl phosphate, TDCPP, and tris(2-chloroethyl) phosphate after firefighting (Mayer et al., 2021). See Section 1.5.1(i) for more information on biological levels of flame retardants measured in firefighters.

(d) Diesel engine exhaust

Firefighters can be exposed to diesel exhaust (IARC Group 1, *carcinogenic to humans*) at the fire station, when fire engines (or apparatus) are started in the bays or return to the bays after a response, and at incidents where fire engines commonly idle. Diesel exhaust is composed of particulate matter, PAHs, inorganic particles, and oxides of carbon, nitrogen, and sulfur (Pronk et al., 2009). The magnitude and composition of diesel exhaust exposures will depend on several factors, including the age and maintenance of the engines, the quality of diesel fuel (e.g. sulfur content), whether the engine includes any filtration systems, the workload or number of runs, whether the engine is running cold or warm, whether diesel-exhaust capture systems are available and being used in the bays, and if not, whether the bays include natural ventilation (e.g. drive-through bays with doors on the front and back) (Chung et al., 2020). Another important factor for living quarters of the station that are attached to the bay is whether they are under positive pressure relative to the bay [if not, there is the potential for diesel exhaust to migrate into the living areas] (NIOSH, 2016b).

Recent studies have quantified diesel exhaust in fire stations by measuring airborne elemental carbon (see Table 1.21, and Table S1.22, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Work-shift concentrations measured in fire stations have varied considerably and are generally higher in engine bays than in other areas of the fire station. One evaluation at fire stations in the USA measured elemental carbon concentrations in the engine bays at < 1–13 µg/m^3, with concentrations in the living areas ranging from 1.2 to 2.7 µg/m^3 (NIOSH, 2016b). A study in Canada measured elemental carbon in vehicle bays at concentrations ranging from < 0.5 to 2.7 µg/m^3 (Chung et al., 2020). A study in Australia measured elemental carbon at concentrations ranging from 1 to 26 µg/m³ in vehicle bays, with much lower levels in the dormitories (< 2 µg/m³). The same study quantified total PAHs (predominantly naphthalene) at concentrations ranging from ~0.05 to ~1.8 µg/m³ in the engine bays (Bott et al., 2017). No studies have specifically quantified diesel exhaust exposure at emergency incidents, but one study involving controlled residential fires measured particulate matter at > 100 000 particles/m³ before fire ignition, which the investigators attributed to the idling fire apparatus (engine) at the scene (Fent et al., 2018).

(e) Heavy metals

Firefighters can be exposed to heavy metals (some of which are classified as IARC Group 1, *carcinogenic to humans;* see Table 1.1). For example, vehicle fires would be expected to include a variety of heavy metals (present in the engine, battery, frame, and body parts), but metals could also be present in many other fires, especially fires involving older homes with lead paint or pipes or structures containing metal trusses or electronics. Airborne metal particulates or fumes produced during fires may be inhaled.

Table 1.21 provides a summary of air and surface measurements of metals associated with firefighting (see also Table S1.22, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). Keir et al. (2020) measured air concentrations of lead and found levels above the adjusted occupational exposure limit (OEL; 46.9 µg/m³) during two emergency fires in Ottawa, Canada; they also found significant increases in lead and antimony contamination on used turnout gear. Easter et al. (2016) measured metals in used firefighting hoods compared with new hoods in Philadelphia, USA, and found elevated concentrations of numerous metals, including arsenic, cadmium, chromium, and lead. Engelsman et al. (2019) measured metals on surfaces in Australian fire stations and found levels of chromium, lead, copper, zinc, nickel, and manganese that were higher than levels measured in homes or offices.

The presence of metals on firefighter gear and other surfaces does not necessarily mean that firefighters will absorb those contaminants; most metals have relatively low skin permeation coefficients (K_p, 0.001 cm/hour or less). However, there are numerous factors that can impact the permeability of metals through skin, including the valence state, the type of counter ion, and the nature of the chemical bond (organic versus inorganic) and polarity (Hostynek, 2003). [Metals and other contaminants on gear or surfaces could also become aerosolized and inhaled, or transfer to hands and be ingested, depending on hand hygiene practices after firefighting.]

Biomonitoring has also been used to assess firefighters' exposure to metals including lead, e.g. during the WTC disaster and the Notre Dame Cathedral fire, in Paris, France (see Section 1.5.1(i)).

(f) Physical factors

Physical exertion and heat stress are common among municipal and wildland firefighters (Cheung et al., 2010; Bourlai et al., 2012; Lui et al., 2014; Horn et al., 2018). Municipal firefighting ensembles, which are designed to protect firefighters from heat, will also trap metabolic heat energy produced during work and may result in increased core body temperatures (Smith et al., 2013a; Horn et al., 2018; Ghiyasi et al., 2020). Strenuous work under high-stress situations, together with increased body temperature and dehydration, may affect the sympathetic nervous system and result in cardiovascular strain (Shen & Zipes, 2014; Smith et al., 2019). How these physical stressors could impact carcinogenesis is not well understood; however, increased body and skin temperatures may result in increased dermal absorption of toxicants (Chang & Riviere, 1991; Chang et al., 1994), and dehydration can concentrate hazardous substances in the body and may place additional strain on the kidneys (Baetjer et al., 1960; Baetjer, 1969). In addition, thermoregulatory processes in the body that are part of the immune response against toxicological insults may also be affected by heat strain (Leon, 2008).

[Although the Working Group was unable to identify studies describing firefighters' UV exposure, firefighters working outdoors or working in areas with a high UV index are also likely to be exposed to UV radiation (classified in IARC Group 1) (Peters et al., 2012; Carey et al., 2014; Boniol et al., 2015).] PAHs and UV exposure may have synergistic toxic effects through photoactivation (Ekunwe et al., 2005; Toyooka & Ibuki, 2007). [Wildland firefighters will commonly spend an entire work shift (8 hours or longer) under the sun. Although their arms and legs are typically covered by protective clothing, their necks and faces may be exposed. With the growing wildfire season in various parts of the world, cumulative UV exposure is likely to worsen for wildland firefighters.]

Firefighters are also exposed to radiofrequency electromagnetic fields (IARC Group 2B, *probably carcinogenic to humans*) from the use of hand radios. [The Working Group noted that hand radios are not typically held close to the head, and the effects of radiofrequencies on the human body (e.g. increased skin temperature) drop with increasing distance (Foster & Glaser, 2007).]

In relatively rare situations, firefighters respond to radiological events, such as a dirty bomb, in which their roles could include triage, life support, and decontamination, and during which they could be exposed to ionizing radiation (Rebmann et al., 2019). One of the most well-known radiological disasters was the Chernobyl nuclear power plant disaster in present-day Ukraine in 1986. Numerous studies have documented radiation health effects among firefighters and other workers who responded to the Chernobyl disaster (Junk et al., 1999; Antoniv et al., 2017; Belyi et al., 2019). Fallout from the disaster resulted in radionuclide contamination in the exclusion zone, which presents an additional hazard for wildland firefighters (Yoschenko et al., 2006). Wildland firefighters who responded to a forest fire in the Chernobyl exclusion zone in April–May 2020 were reported to have effective internal dose maximum values of 3.5, 5.1, and 11.8 μSv, depending on the region in which they worked (Bazyka et al., 2020). Radionuclides also occur naturally in soil and vegetation. Carvalho et al. (2014) measured polonium-210 activity in wildfire smoke in Portugal; the average concentration was 70 mBq/m^3, which could theoretically result in a radiation dose for wildland firefighters of ~2.1 μSv per 10-hour workday. However, Viner et al. (2018) conducted modelling of cumulative dose for firefighters in areas of natural and anthropogenic contamination (i.e. Savannah River Site, South Carolina, USA) and found that even under worst-case conditions, the cumulative dose for firefighters exposed to potential fires would not exceed 3% of the annual guidance limit set by the US Department of Energy (0.25 mSv).

Firefighters are also commonly exposed to loud noise from alarms, sirens, personal alert safety systems, and heavy equipment and machinery (Tubbs, 1995; Hong & Samo, 2007; Kirkham et al., 2011; Neitzel et al., 2013). Wildland firefighters may use chainsaws, chippers, and even bulldozers, which can easily exceed OELs for noise (e.g. the NIOSH recommended exposure limit of 85 dB) (Broyles et al., 2017). Wildland firefighters are expected to wear hearing protection when performing tasks using this equipment; however, training on proper use and maintenance of hearing protection may vary throughout the fire service (Broyles et al., 2019).

(g) Building collapse and other catastrophic events

There were few studies reporting on the non-fire exposures received by firefighters at other major natural or man-made disasters. These publications are summarized in Table 1.23. The incidents reported in these studies include: earthquakes (where predominant exposures are assumed to be dust and particulates from collapsed buildings, or release of radioisotopes, e.g. Fukushima, Japan) (Chang et al., 2003; Fushimi, 2012; Caban-Martinez et al., 2021; Ory et al., 2021); explosions (encompassing exposures to dust, particulates, and debris in addition to products of combustion) (Slottje et al., 2005, 2006, 2007, 2008; Witteveen et al., 2007; De Soir et al., 2015); severe weather events, e.g. hurricanes (covering exposure to biologically contaminated floodwater, debris, etc.) (Tak et al., 2007); radiological events (Ory et al., 2021); chemical terrorism (e.g. the sarin nerve-agent attack in the Tokyo subway, Japan, in 1995) (Li et al., 2004); and chemical spills (encompassing exposure to specific chemical agents) (Cho et al., 2013).

Many publications (e.g. Witteveen et al., 2007; Fushimi, 2012) on non-fire exposures in firefighters have also solely focused on assessing firefighters' response to trauma by following the mental health outcomes of those attending the incident.

[The Working Group noted that there was lack of data on exposure during catastrophic events. For the site of the WTC disaster, none of the samples were collected in the immediate aftermath.]

The majority of studies on firefighters' chemical and physical exposures and their health outcomes were focused on the WTC terrorist attack (Claudio, 2001; Landrigan, 2001; Guidotti et al., 2011). Firefighters who responded to the WTC disaster had substantial and repeated exposures to dense, aerosolized dust and smoke (Nordgren et al., 2002). They were exposed to the plume created from the initial fire and building collapses, to ongoing fires that lasted at least 3 months, and to particles that were resuspended during the clean-up and transport of debris. The destruction of the WTC complex pulverized ~1.2 million tonnes of construction material (Klitzman & Freudenberg, 2003; Rom et al., 2010). This material was primarily composed of gypsum and contained calcium carbonate, silicate, and sulfate, as well as various metals. Half of the South Tower had been insulated with chrysotile asbestos (which was found in the rubble) and millions of tonnes of fibrous glass. Collapse of the twin towers (WTC 1 and WTC 2), and then of a third building (WTC 7), produced an enormous dust cloud containing coarse and fine particulate matter (Lioy et al., 2002; Rom et al., 2010).

The predominant sources of toxic gases to which firefighters were exposed included by-products of combustion or pyrolysis from burning jet fuel. The secondary reactions of these combustion products, and of those produced from the burning, vaporization, and pulverization of materials within the towers, produced an array of irritant gases, fumes, and vapours (Landrigan et al., 2004). Specific fire effluent gases measured included VOCs, HCl, PAHs, PCBs, PBDEs, PCDD/Fs), phthalate esters, etc. (Lioy et al., 2002; Litten et al., 2003; McGee et al., 2003; Offenberg et al., 2003; Landrigan et al., 2004; Dahlgren et al., 2007; Guidotti et al., 2011).

Environmental data have shown that particulate matter originating from the WTC disaster differed in composition to ambient particulate matter, being mainly composed of debris from construction buildings and therefore containing concrete, pulverized glass, calcium sulfate (gypsum) and silicates, mineral glass fibres, alkaline metals, wood, paper, cotton, and components of jet fuel (Landrigan, 2001; Lioy et al., 2002; McKinney et al., 2002; Banauch et al., 2003; Landrigan et al., 2004; Lippmann et al., 2015).

Table 1.23 Examples of firefighters' exposures during catastrophic non-fire events

Catastrophe, location, date	Exposed population	Exposures and description of event	Reference
Explosion of reactor at nuclear power plant, Chernobyl, Ukraine, 1986	Firefighters, public	Release of radioisotopes into the atmosphere	Ory et al. (2021)
Amsterdam air disaster, Netherlands, 1992	Firefighters	No specific details on chemicals released Cargo aircraft crashed into apartment buildings; firefighters and police officers assisted with rescue work	Slottje et al. (2005, 2006, 2007, 2008); Huizink et al. (2006); Witteveen et al. (2007)
Earthquake, Taiwan, China, 1999	Firefighters	No specific details on chemicals released The 12-story Tunghsing building collapsed immediately after the earthquake; more than 1500 emergency responders (including firefighters) were involved	Chang et al. (2003)
World Trade Center terrorist attack, USA, 2001	Firefighters	Structural collapse; release of chrysotile asbestos, MMVFs, particulate matter, VOCs, sVOCs, hydrochloric acid, PAHs, PCBs, PBDEs, PCDD/Fs, fire retardants, phthalate esters, and metals	Clark et al. (2001); Claudio (2001); Lioy et al. (2002); McKinney et al. (2002); Banauch et al. (2003); Edelman et al. (2003); Litten et al. (2003); McGee et al. (2003); Offenberg et al. (2003); Landrigan et al. (2004); Moline et al. (2006); Dahlgren et al. (2007); Rom et al. (2010); Guidotti et al. (2011); Lippmann et al. (2015); Weiden et al. (2015)
Ghislenghien gas explosion, Belgium, 2004	Survivors (including firefighters) Public	Debris from gas pipe and buildings projected up to 6 km away from the epicentre; air vibrations registered. Large explosion that instantly killed 24 people; only two firefighters from the first crew survived the initial blast and 132 people were wounded	De Soir et al. (2015)
Tokyo subway disaster, Japan, 1995	Firefighters	Terrorist attack with release of sarin nerve gas	Li et al. (2004)
Hurricanes Katrina and Rita, Louisiana, USA, 2005	Firefighters	Floodwater exposure associated with physical health symptoms 12 weeks after Hurricane Katrina Career firefighters involved in rescue and recovery activities while maintaining normal fire-suppression duties	Tak et al. (2007)
The Great East Japan earthquake, 2011	Firefighters	No specific details on chemicals released	Fushimi (2012)
Fukushima nuclear power plant, north-east Japan, 2011	Plant workers, public	Release radioisotopes into the atmosphere	Ory et al. (2021)

Table 1.23 (continued)

Catastrophe, location, date	Exposed population	Exposures and description of event	Reference
Hydrogen fluoride spill accident, Republic of Korea, 2012	Firefighters	Exposure to hydrogen fluoride [assumed, no measurement/quantification of exposure]	Cho et al. (2013)
Surfside building collapse, Florida, USA, 2021	Firefighters	Exposure to PAHs (from around the building pile)	Caban-Martinez et al. (2021)

MMVFs, man-made vitreous fibres; PAHs, polycyclic aromatic hydrocarbons; PBDEs, polybrominated diphenyl ethers; PCBs, polychlorinated biphenyls; PCDD/Fs, polychlorinated dibenzo-*para*-dioxins/dibenzofurans; sVOCs, semi-volatile organic compounds; VOCs, volatile organic compounds.

In data on ambient air pollution reported by nearby regional monitoring stations, airborne particulate matter mass concentrations were measured in only one or two size bands: $PM_{2.5}$ (diameter, ≤ 2.5 µm) and/or PM_{10} (diameter, ≤ 10 µm) (McGee et al., 2003; Guidotti et al., 2011). Concentrations of a mixture of airborne, respirable particulate matter were between 1 and 100 mg/m³ (Weiden et al., 2015).

Additionally, more than 95% of the mass of WTC dust particles were found to be larger than 10 µm in diameter. The high content of pulverized cement made the dust highly caustic, with a pH in the range of 9 to 11 (Lioy et al., 2002; Banauch et al., 2003; Landrigan et al., 2004). In addition to fibrous and alkaline materials, samples of larger WTC particulate matter also contained various metals (Landrigan et al., 2004; Moline et al., 2006). Samples of smaller particular matter (i.e. $PM_{2.5}$) predominantly contained calcium (or calcium carbonate/bicarbonate), chlorine, and sulfuric oxide compounds originating from construction materials such as cement, concrete aggregate, ceiling tiles, and wallboards (Clark et al., 2001; Edelman et al., 2003; Gavett, 2003).

One study of the building collapse in June 2021 in Surfside, Florida, USA, deployed silicone-based wristbands to measure ambient PAHs around the building pile. Wristbands were placed on the southern, western, and northern perimeters of the building collapse before the controlled demolition. A total of 29 wristbands were deployed for ambient sampling around the collapse, and the PAHs found at highest concentrations were phenanthrene, fluoranthene, and pyrene. Wristbands were found to be a useful passive sampling device to document levels of various PAHs in the immediate environment of the building collapse where urban search and rescue firefighters were working (Caban-Martinez et al., 2021).

(h) Other exposures

Hundreds of combustion by-products may be produced during fires, especially fires that contain various materials and chemistries. This section has covered some of the most common combustion by-products likely to be encountered by firefighters, but there are certainly others that could pose long-term health risks. The locations where firefighters work may result in other occupational exposures. For example, airport firefighters may have additional exposures from aircraft (i.e. jet engines), which are known to produce ultrafine particulate matter and other pollutants (Stacey, 2019).

One area of ongoing research is firefighters' exposure to dioxins and furans. PCDD/Fs and PBDD/Fs may be produced when burning certain types of material, including halogenated polymers and electronics. For example, Organtini et al. (2015) measured several mixed halogenated dibenzofurans (PXDFs) and PBDFs in fire debris (at levels of parts per million) from simulated household fires (which included furnishing and electronics). Electronics may also contain PCBs (some classified in IARC Group 1), which are another class of hazardous compounds to which firefighters may be exposed. See Section 1.3.1 for more information on the possible sources of these compounds during firefighting.

Only a few studies have evaluated firefighters' exposures to PCDD/Fs, PBDD/Fs, and PCBs (see Table 1.21, and Table S1.22, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615), and most involved biological monitoring. 1,2,3,4,6,7,8-Heptachlorodibenzo-*para*-dioxin (HpCDD) has been detected on firefighting equipment and clothing (Hsu et al., 2011) and measured in serum samples from firefighters in California, USA, and fire investigators in Taiwan, China, at concentrations above those for the referent general population (Hsu et al., 2011; Shaw et al., 2013). Serum concentrations of HpCDD were significantly related to firefighting activity in WTC responders (Edelman et al., 2003). These and other biomonitoring studies evaluating firefighters' exposure to PCDD/Fs, PBDD/Fs, and PCBs are discussed in Section 1.5.1(i).

Other areas of ongoing research pertain to firefighters' exposures from fires involving new technologies or materials, including lithium-ion batteries, nanomaterials, and other new compounds or chemicals. Fires involving lithium-ion batteries, for example, are intense and require tremendous amounts of water and extended time to fully extinguish (Wang et al., 2012; Larsson et al., 2014; US EPA, 2021b). [The Working Group noted that the composition of effluents from these types of fire are not fully understood. The extended response times for these fires may increase firefighters' exposures.]

(i) Biomarkers of exposure

A summary of biomarkers of exposure to agents other than fire smoke and PAHs is provided in the text below and summarized in Table 1.24. Additional details are provided in Table S1.25 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615). General considerations on absorption, distribution, metabolism, and excretion are described in Section 1.4.2(e). Most of these studies involved career firefighters in the USA, with municipal firefighters being the most frequently studied when the type of firefighter was listed; these studies reported mainly on serum measurements, followed by blood and urine.

Inhalation is the major route for asbestos exposure, and asbestos fibres are distributed predominantly into the lungs and pleura. [No studies on biomarkers of asbestos exposure in firefighters were identified by the Working Group, but specific pulmonary abnormalities can indicate exposure. In a study of 212 New York City firefighters (mean age, 57 years), 42 had pleural thickening and/or parenchymal abnormalities on chest radiograph and/or computed tomography, including 20 firefighters without reported prior exposure to asbestos (Markowitz et al., 1991).]

The major exposure route for PBDEs in the general population is ingestion, followed by dermal exposure and inhalation (Lorber, 2008). PBDEs are distributed into lipophilic tissues, and overall metabolism rates are slow; 40% of BDE-47, 16% of BDE-99, 6% of BDE-100, and 2% of BDE-153 is excreted in the urine in mice by 5 days after administration (Staskal et al., 2006). In 12 firefighters in San Francisco, USA, who had responded to a fire within the previous 24 hours, the sum of serum concentrations of PBDE was two- to threefold that reported for the general US population (Shaw et al., 2013). In 101 firefighters in southern California, USA, in 2010–2011, serum concentrations of BDE-28, BDE-47, BDE-100, and BDE-153 were significantly higher than in participants representative of the general US population in the 2003–2004 National Health and Nutrition Examination Survey (NHANES). Lower serum PBDE levels in firefighters were associated with turnout gear cleaning and storage in open rooms after fires (Park et al., 2015). In 36 US firefighters assessed before and after responding to controlled residential fires in 2015, only BDE-209 (out of 12 PBDEs quantified) pre- and post-fire serum concentrations were higher than those in the 2018 NHANES comparison population; the pre- to post-fire change was not significant (Mayer et al., 2021). In 92 male firefighters from Busan, Republic of Korea, compared with 70 male non-firefighters from the same area, the summed concentration of 27 PBDEs was higher in firefighters than in the general population, and there was a positive correlation between PBDE levels and duration of service for firefighters (Ekpe et al., 2021).

PCDD/Fs and PBDD/Fs are generated during combustion. PCDDs and PCDFs distribute predominantly to the liver and adipose tissue;

Table 1.24 Biomarkers used to assess firefighters' exposures to agents other than smoke

Analyte	Sample type	Concentration		References
		Minimum	Maximum	
Polybrominated diphenyl ethers (PBDEs)				
BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-197, BDE-207, BDE-209	Serum	0.1 ng/g lipid	253 ng/g lipid	Shaw et al. (2013); Park et al. (2015)
BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-209	Blood	NR	NR	Mayer et al. (2021)
PBDEs (sum of 27)	Serum	1.58 ng/g lipid	95.2 ng/g lipid	Ekpe et al. (2021)
*Polychlorinated dibenzo-*para*-dioxins and dibenzofurans (PCDD/Fs)*				
1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF	Serum	ND	674 pg/g lipid	Shaw et al. (2013)
2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF	Serum	2.24 pg/g lipid	NR	Mayer et al. (2021)
PCDD/Fs (sum of 17)	Serum	6.3 pg (TEQ)/g lipid	18 pg (TEQ)/g lipid	Hsu et al. (2011)
Polychlorinated biphenyls (PCBs)				
PCB-66, PCB-74, PCB-99, PCB-118, PCB-138, PCB-153, PCB-156, PCB-170, PCB-180, PCB-183, PCB-187, PCB-194, PCB-203	Serum	1.09 ng/g lipid	15.4 ng/g lipid	Park et al. (2015)
PCB-105, PCB-118, PCB-157, PCB-167	Serum	1.02 ng/g lipid	105.76 ng/g lipid	Chernyak et al. (2012)
PCBs (sum of 38)	Serum	36 ng/g lipid	317 ng/g lipid	Shaw et al. (2013)
Organophosphate and other flame retardants				
BCEtP, BDCPP, DPCP, DBuP, TBBPA	Serum	NR	NR	Clarity et al. (2021)
BCEtP, BCPP, BDCPP, DEP, DETP, DEDTP, DMP, DMTP, DMDTP, DBuP, DPhP, IPPPP, TBBA, TBPPP	Urine	< LOD	300 ng/mL	Jayatilaka et al. (2019)
Per- and polyfluoroalkyl substances				
PFHxS	Serum	0.22 ng/mL	326 ng/mL	Jin et al. (2011); Shaw et al. (2013); Laitinen et al. (2014); Dobraca et al. (2015); Rotander et al. (2015a, b); Khalil et al. (2020); Leary et al. (2020); Trowbridge et al. (2020); Clarity et al. (2021); Goodrich et al. (2021); Graber et al. (2021)
PFOS	Serum	< LOD	391 ng/mL	Jin et al. (2011); Shaw et al. (2013); Laitinen et al. (2014); Dobraca et al. (2015); Rotander et al. (2015a, b); Khalil et al. (2020); Leary et al. (2020); Trowbridge et al. (2020); Clarity et al. (2021); Goodrich et al. (2021); Graber et al. (2021)
PFDS	Serum	ND	0.1 ng/mL	Shaw et al. (2013)

Table 1.24 (continued)

Analyte	Sample type	Concentration		References
		Minimum	Maximum	
PFHpA	Serum	< LOD	1 ng/mL	Shaw et al. (2013); Dobraca et al. (2015); Rotander et al. (2015b); Trowbridge et al. (2020)
PFOA	Serum	0.25 ng/mL	7535 ng/mL	Jin et al. (2011); Shaw et al. (2013); Laitinen et al. (2014); Dobraca et al. (2015); Rotander et al. (2015b); Khalil et al. (2020); Leary et al. (2020); Trowbridge et al. (2020); Clarity et al. (2021); Graber et al. (2021); Goodrich et al. (2021)
PFNA	Serum	< 0.06 ng/mL	17.95 ng/mL	Jin et al. (2011); Shaw et al. (2013); Laitinen et al. (2014); Dobraca et al. (2015); Rotander et al. (2015b); Khalil et al. (2020); Leary et al. (2020); Trowbridge et al. (2020); Clarity et al. (2021); Goodrich et al. (2021); Graber et al. (2021)
PFDA	Serum	< LOD	20.7 ng/mL	Shaw et al. (2013); Dobraca et al. (2015); Rotander et al. (2015b); Khalil et al. (2020); Trowbridge et al. (2020); Graber et al. (2021); Clarity et al. (2021); Goodrich et al. (2021)
PFUnDA	Serum	0.1 ng/mL	10.85 ng/mL	Shaw et al. (2013); Dobraca et al. (2015); Khalil et al. (2020); Trowbridge et al. (2020); Clarity et al. (2021); Graber et al. (2021); Goodrich et al. (2021)
PFBS	Serum	< LOD	0.4 ng/mL	Dobraca et al. (2015); Rotander et al. (2015b); Trowbridge et al. (2020); Clarity et al. (2021)
PFOSA	Serum	NR	0.4 ng/mL	Dobraca et al. (2015)
Me-FOSAA	Serum	NR	3.80 ng/mL	Dobraca et al. (2015); Khalil et al. (2020); Goodrich et al. (2021); Graber et al. (2021)
Et-FOSAA	Serum	NR	1.00 ng/mL	Dobraca et al. (2015)
PFTrDA	Serum	< 0.06 ng/mL	28.5 ng/mL	Dobraca et al. (2015); Rotander et al. (2015b)
PFDoA	Serum	0.13 ng/mL	0.15 ng/mL	Dobraca et al. (2015); Graber et al. (2021)
PFBA	Serum	< LOD	0.99 ng/mL	Rotander et al. (2015b); Trowbridge et al. (2020)
PFHxA	Serum	< LOD	< LOD	Trowbridge et al. (2020)
Sb-PFOA	Serum	ND	ND	Goodrich et al. (2021)
Sm-PFOS	Serum	1.91 ng/mL	2.23 ng/mL	Goodrich et al. (2021)
Heavy metals				
Antimony	Serum	NR	NR	Salama & Bashawri (2017)
Arsenic	Serum	NR	NR	Al-Malki (2009)
Cadmium	Blood	0.18 µg/L	0.21 µg/L	Dobraca et al. (2015)
Cadmium	Serum	NR	NR	Al-Malki (2009); Salama & Bashawri (2017)

Table 1.24 (continued)

Analyte	Sample type	Concentration		References
		Minimum	Maximum	
Lead	Blood	0.87 µg/dL	64.7 µg/L	Edelman et al. (2003); Dobraca et al. (2015); Kim et al. (2020b)[a]; Allonneau et al. (2021)
Lead	Serum	NR	NR	Al-Malki (2009); Salama & Bashawri (2017)
Mercury	Blood	2.36 µg/L	3.30 µg/L	Dobraca et al. (2015)
Mercury	Serum	< LOD	16 µg/L	Al-Malki (2009); Smith et al. (2013b); Salama & Bashawri (2017)
Uranium	Urine	NR	NR	Edelman et al. (2003)

[a] [The blood lead levels reported in Kim et al. (2020b) probably have a unit error, as they are reported as mg/dL (not µg/dL), which would exceed reported fatal levels.]

BCPP, bis(1-chloro-2-propyl) phosphate; BCEtP, bis(2-chloroethyl) phosphate; BDCPP, bis(1,3-dichloro-2-propyl) phosphate; BDE, brominated diphenyl ether; DBuP, dibutyl-*n*-phosphate; DEDTP, diethyl dithiophosphate; DEP, diethyl phosphate; DETP, diethyl thiophosphate; DMDTP, dimethyl dithiophosphate; DMP, dimethyl phosphate; DMTP, dimethyl thiophosphate; DpCP, di-*para*-cresyl phosphate; DPhP, diphenyl phosphate; Et-FOSAA, 2-(*N*-ethyl-perfluorooctanesulfonamido) acetic acid; HpCDD, heptachlorodibenzo-*para*-dioxins; HpCDF, 1,2,3,4,6,8,9-heptachlorodibenzofuran; HxCDD, 1,2,3,7,8,9-hexachlorodibenzo-*para*-dioxin; HxCDF, 1,2,4,6,8,9-hexachlorodibenzofuran; IPPPP, 2-((isopropyl)phenyl)phenyl phosphate; LOD, limit of detection; Me-FOSAA, 2-(*N*-methyl-perfluorooctanesulfonamido) acetic acid; ND, not determined; NR, not reported; PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonic acid; PFDA, perfluorodecanoic acid; PFDoA, perfluorododecanoic acid; PFDS, perfluorodecane sulfonate; PFHpA, perfluoroheptanoic acid; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonic acid; PFNA, perfluorononanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFOSA, perfluorooctane sulfonamide; PFTrDA, perfluorotridecanoic acid; PFUnDA, perfluoroundecanoic acid; Sb-PFOA, branched PFOA isomers; Sm-PFOS, perfluoromethylheptane sulfonate isomers; TBBA, 2,3,4,5-tetrabromobenzoic acid; TBBPA, tetrabromobisphenol A; TBPPP, 4-((*tert*-butyl)phenyl)phenyl phosphate; TEQ, toxic equivalent quantity.

the 2,3,7,8-substituted PCDDs and PCDFs are highly retained in tissues and body, resulting in elimination half-lives of 1–7 years (Van den Berg et al., 1994). PBDD/Fs are also present as contaminants in brominated flame retardants, and their toxicokinetics are generally similar to those of PCDD/Fs (van den Berg et al., 2013). Serum PCDD/F concentrations in 16 male firefighters from Taiwan, China, were not significantly different from those in the male general population, but PCDD/F levels in four fire-scene investigators were higher than those in the general population (Hsu et al., 2011). Comparing 13 current male firefighters, 17 former firefighters, and 10 non-firefighters in eastern Siberia, Russian Federation, serum levels of HpCDD and 1,2,3,7,8,9-hexachlorodibenzofuran (HxCDF) levels were higher in current firefighters than in non-firefighters, and serum levels of octachlorodibenzofuran (OCDF) were higher in current firefighters than in former firefighters and non-firefighters (Chernyak et al., 2012). In 12 firefighters in San Francisco after a fire exposure, serum concentrations of HpCDD exceeded those found in the general population of the USA (Shaw et al., 2013). In 36 US firefighters exposed to controlled structure fires, pre-fire serum concentrations of 2,3,4,7,8-pentachlorodibenzofuran (PeCDF) (IARC Group 1, *carcinogenic to humans*) were significantly above those in the general population, as were pre- and post-fire serum concentrations of 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF (Mayer et al., 2021).

PCBs are distributed into lipophilic tissues. The rate of metabolism varies by congener; metabolism is required before clearance, and elimination is generally slow (Matthews & Dedrick, 1984). After a single dose in humans, measured elimination half-lives for PCB-138, PCB-153, and PCB-180 were 321, 338, and 124 days respectively (Bühler et al., 1988). In current firefighters from eastern Siberia, Russian Federation, previously exposed to the 1992 cable factory fire in the city of Shelekhov involving more than 1000 tonnes of PVC, polyethylene, and other plastics, serum concentrations of PCB-105 and PCB-118 were higher than in non-firefighters, and concentrations of PCB-157 and PCB-167 were higher in both current and former firefighters than in non-firefighters (Chernyak et al., 2012). In 12 firefighters in San Francisco 24 hours after a fire event in 2009, the sum of PCB serum concentrations was lower than that reported for the general population of the USA in 2003–2004 (Shaw et al., 2013). In 101 firefighters in southern California, serum PCB concentrations measured in 2010–2011 were lower than in the 2003–2004 NHANES comparison group (Park et al., 2015). [The Working Group noted that comparison of serum PCB levels in firefighters with those of the general population sampled in a different time-period can introduce a temporal bias.]

Inhalation, dermal contact, and ingestion from the diet are all important routes of exposure to OPFRs (Hou et al., 2016). OPFRs are more rapidly metabolized than PBDEs (Geyer et al., 2004; Hou et al., 2016). In the USA, urine samples collected from firefighters 20 minutes or 3 hours after performing firefighting on controlled structure fires in 2010–2011 were compared with those collected from members of the general population in Atlanta in 2015. Urinary metabolites including bis(2-chloroethyl) phosphate (BCEtP), bis(1-chloro-2-propyl) phosphate, bis(1,3-dichloro-2-propyl) phosphate, di-*n*-butyl phosphate, diphenyl phosphate (DPhP), 2,3,4,5-tetrabromobenzoic acid (TBBA), 2-((isopropyl)phenyl)phenyl phosphate, and 4-((*tert*-butyl)phenyl)phenyl phosphate, and metabolites including dimethyl phosphate, dimethyl thiophosphate, dimethyl dithiophosphate, diethyl phosphate, diethyl thiophosphate, and diethyl dithiophosphate were measured at higher concentrations in the firefighters than in the general population (Jayatilaka et al., 2019). In 36 US firefighters exposed to controlled structure fires, urinary concentrations of BCEtP and

DPhP measured before the fire were found to be significantly increased 3 hours after the fire (Mayer et al., 2021).

PFAS generally have the highest absorption through ingestion, with lower rates of absorption reported through inhalation or dermal exposure (Pizzurro et al., 2019). The elimination half-lives of PFAS vary, with a range of 44 days to 2.93 years in a study involving AFFF-contaminated drinking-water (Xu et al., 2020). In 12 firefighters in San Francisco after a fire event in 2009, perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) concentrations in serum were twice, and perfluorooctanesulfonic acid (PFOS) and perfluorohexanesulfonic acid (PFHxS) concentrations were half those in the US general population in the NHANES survey in 2003–2004 (Shaw et al., 2013).

Comparing 38 firefighters in Arizona, USA, and matched NHANES participants, firefighters had elevated PFHxS and lower PFNA and perfluoroundecanoic acid serum concentrations (Khalil et al., 2020). In eight airport firefighters training with AFFF in Finland, PFHxS and PFNA levels increased after three consecutive training sessions despite relatively low levels of these PFAS in the AFFF (Laitinen et al., 2014). In 37 firefighters in Ohio and West Virginia, USA, compared with the general population from the same area (selected as part of a PFAS-exposure related lawsuit), serum levels of PFHxS were elevated (Jin et al., 2011). In 101 firefighters in southern California examined in 2010–2011 compared with participants in the 2009 NHANES, perfluorodecanoic acid (PFDA) serum concentrations were three times as high in the firefighters, and perfluoroheptanoic acid (PFHpA) concentrations increased with use of class A firefighting foam (Dobraca et al., 2015). [The Working Group noted that levels of most legacy PFAS are decreasing in the general population of the USA, so levels in 2009 are lower than those measured in 2003–2004.] In samples collected in 2013 from 20 firefighters with AFFF exposure in Queensland, Australia, compared with samples collected in 2011–2012 from 20 non-firefighters, serum PFOS and PFHxS levels were markedly elevated in the firefighters (Rotander et al., 2015a). In 149 firefighters in Australia with AFFF exposure collected in 2013 compared with the general Australian population, serum concentrations of PFOS and PFHxS were positively associated with years of jobs with AFFF contact; study participants who had worked for ≤ 10 years had PFOS levels similar to those of the general population (Rotander et al., 2015b). In 86 female firefighters in San Francisco, USA, compared with female office workers, firefighters had higher serum concentrations of PFHxS, perfluoroundecanoic acid, and PFNA (Trowbridge et al., 2020). In 36 airport and nine suburban firefighters in Ohio, USA, enrolled in 2018–2019 compared with participants in the 2015–2016 NHANES, serum concentrations of PFHxS were elevated in the firefighters, and concentrations of PFOS were higher in airport firefighters than in suburban firefighters (Leary et al., 2020). In 116 volunteer firefighters from New Jersey, USA, in 2019 compared with participants in the 2015–2018 NHANES, serum concentrations of perfluorododecanoic acid (PFDoA), PFNA, and PFDA were elevated among the firefighters, and concentrations of both PFDoA and PFDA were positively associated with years of firefighting (Graber et al., 2021).

[The Working Group noted that for recent fire-suppression events, biomonitoring of firefighters for some organic chemicals with a long elimination half-life (e.g. PFAS or PBDEs) is extremely challenging, particularly since non-occupational exposure can be extensive (Rotander et al., 2015b; Trowbridge et al., 2020).]

The toxicokinetics of metals vary among the individual metals; ingestion and inhalation are generally the most important routes of exposure, but some metals bioaccumulate more than others (Elder et al., 2015). In 49 firefighters in Jeddah and Yanbu cities, Saudi Arabia, compared with 23 non-firefighters, there were no significant differences in concentrations of any of the metals (i.e. antimony, arsenic, cadmium, lead, and mercury) measured in serum (Al-Malki, 2009). In 66 wildland firefighters compared with 39 non-firefighters in the western USA in 2007–2009, no significant difference in whole-blood mercury concentrations was found (Smith et al., 2013b). In 101 firefighters in southern California, whole-blood mercury concentrations exceeded values for participants in NHANES 2009–2010; higher cadmium concentrations were associated with washing hands less frequently, and higher mercury concentrations with responding to brush fires in the last year (Dobraca et al., 2015). In 100 male firefighters from Dammam and Khobar cities, Saudi Arabia, compared with 50 non-firefighters, there were no differences in whole-blood metal concentrations (Salama & Bashawri, 2017). In a study of 168 firefighters who responded to the Notre Dame cathedral fire in Paris, France, only one quarter had blood lead concentrations above the 95th percentile of the general population of France, and blood lead concentrations had dropped at the 1-month and 6-month follow-up evaluations (Allonneau et al., 2021). Edelman et al. reported increased blood concentrations of lead in firefighters responding to the WTC fire and collapse compared with control firefighters (Edelman et al., 2003)

1.5.2 Organizational and psychosocial factors, and infectious agents

(a) Shift work

Shift work is a schedule of work that includes working hours other than traditional daytime hours (i.e. Monday to Friday from 08:00 to 16:00). Night shift work has been classified by IARC as Group 2A, *probably carcinogenic to humans* (see Section 1.1, Table 1.1). Other associated effects on lifestyle factors (e.g. smoking behaviour, amount of physical activity during leisure time, eating behaviour, and consumption of alcohol (Bøggild & Knutsson, 1999; Bushnell et al., 2010; Pepłońska et al., 2014) have been described in more detail in *IARC Monographs* Volume 124 (IARC, 2020).

Municipal firefighters may work 10-hour day shifts and 14-hour night shifts, 24-hour shifts or 48-hour shifts; thus, firefighters are exposed to night shift work. [There is no internationally standard shift work pattern or rotation for firefighters. Some examples from the literature are provided in this section (Table 1.26; EPSU, 2006).]

Firefighters in the Republic of Korea typically experience 3-, 6-, 9-, or 21-day cycles (Kwak et al., 2020). The 3-day cycle is 24 hours on, 48 hours off. The 6-day cycle consists of two day shifts, two night shifts, and two rest days (days off). The 9-day cycle consists of three day shifts and three night shifts; each night shift is succeeded by one rest day. In the 21-day cycle, the first week consists of five day shifts, followed by two rest days. The second week consists of 12-hour night shifts alternating with a rest day until day 14, which is a 24-hour shift. The third week starts with a rest day, followed by two 12-hour night shifts (each succeeded by one rest day). On day 20, the firefighter works a 24-hour shift. The last day is a rest day (Jeong et al., 2019).

The 1974 Salaries and Working Conditions Survey indicated that 58% of US municipal firefighters work a 24-hour shift, 41% work a 10–14-hour or 9–15-hour shift, and < 1% work a 8–12-hour or 48-hour shift (NIOSH, 1977). [The Working Group noted that schedules have changed over time. Although many schedules exist among firefighters, nowadays almost all US fire departments operate a 24-hour rotation. Typical work schedules are 24 hours on/48 hours off, 48 hours on/96 hours off, and the "Kelly shift" schedule (24 hours on/24 hours off/24 hours on/24 hours off/24 hours on/96 hours off).] In a recent cross-sectional study, 80% of female career firefighters reported schedules that involved working ≥ 24 hours per shift (Jung et al., 2021a).

Table 1.26 Examples of reported standard work shift patterns for firefighters, by country[a]

Country	Work shift pattern and other remarks	Reference
Austria	24 h on/24 h off	EPSU (2006)
Australia and some Canadian provinces	10/14 rotating shift schedule: two consecutive 10-h day shifts followed by two consecutive 14-h night shifts, then 4 days off	Bonnell et al. (2017)
Belgium	8–12-h shifts	EPSU (2006)
Czechia, Denmark	24-h shifts	EPSU (2006)
Estonia, Finland	24 h on/72 h off	EPSU (2006)
France	24-, 12- and 8-h shifts all possible	EPSU (2006)
Germany, Netherlands, Poland, Slovakia, Türkiye	24 h on, 48 h off	EPSU (2006); Demiralp & Özel (2021)
Ireland	9-h days and 15-h nights – with 2 days and 1 night followed by 2 nights and 1 day, followed by 3 days off	EPSU (2006)
Italy, Luxembourg, Slovenia	12-h day/24 h off/12-h night/48 h off	EPSU (2006)
Norway	4–7 and 7–4 shifts Monday to Friday with 24- or 48-h shifts at weekends	EPSU (2006)
Portugal	12-h shifts	EPSU (2006)
Republic of Korea	3-, 6-, 9-, or 21-day cycles	Kwak et al. (2020)
United Kingdom	2 days, 2 nights, and 3 days off	EPSU (2006)
USA and some Canadian provinces	[24-h rotation]	NIOSH (1977); Jung et al. (2021a)

EPSU, European Public Service Union.

[a] Reported standard shift patterns may not apply to wildland firefighters.

[Volunteer, retained, and on-call firefighters may not have a set shift schedule.]

In contrast to those of municipal firefighters, the work schedules of wildland firefighters vary greatly depending on the severity of the fire season. For Canadian and US wildland firefighters, for example, these schedules can go up to 14 consecutive days (up to 16 hours of service per day), with 2 or 3 days of travel at either end, before a minimum of 2 days of rest is mandated (National Multiagency Coordination Group, 2002; McGillis et al., 2017). Incidentally, assignments may be extended up to 30 days (NIFC, 2022b). In Australia, wildland firefighters are typically rostered for a 12-hour day or night shift, but this can go up to 16 hours for 3–5 consecutive days, depending on fire severity and available personnel (Vincent et al., 2016).

Shift work is inevitable in firefighting, and most firefighters work rotating or extended shifts. Firefighters may sleep during the night, unless called out to an emergency event (Pukkala et al., 2014). [However, the opportunity for and quality of sleep during the night may vary by location and employer.] For example, the self-reported sleeping duration of wildland firefighters varies between 3 and 7 hours (Vincent et al., 2018). In a study among 109 US career firefighters, 73% reported poor sleep quality, and sleep disturbance was largest for the Kelly schedule (Billings & Focht, 2016).

(b) Psychosocial factors

The firefighter work environment can be characterized as high stress, high risk, and with low control over job-related tasks and activities (Lourel et al., 2008). Adverse psychological effects of working as a firefighter may arise from working in unsafe physical conditions and witnessing traumatic incidents, and other inherent characteristics of the job (Smith et al., 2001; Brown et al., 2002; Duran et al., 2018). Firefighter working conditions include long periods of inactivity followed by periods of high activity, working night shifts, and organizational issues, including the adequacy of organizational policies, programmes, and practices, and the degree of management and co-worker support.

Research on the psychological impact of firefighting has largely focused on estimating the prevalence of post-traumatic stress disorder, depression, and other psychological illness (i.e. mood and substance-abuse disorders) (Saijo et al., 2012; Armstrong et al., 2014; Fraess-Phillips et al., 2017; Schnell et al., 2020). Prevalence varies substantially depending on the specific group of firefighters studied and the measures used to determine the prevalence of post-traumatic stress disorder. Psychological stressors are associated with an increase in alcohol, tobacco, and drug use (Kimbrel et al., 2011; Smith et al., 2011; Meyer et al., 2012; Gulliver et al., 2018; Lebeaut et al., 2020). Chronic stress can also cause corresponding changes in the body's immune function and inflammatory response; this is significant because a long-term inflammatory response and the decline of the body's immune surveillance capabilities are two out of several potential mechanisms implicated in tumorigenesis (Murphy et al., 1999; Huang et al., 2010b; Huang & Acevedo, 2011).

(c) Exposure to infectious agents

Emergency medical-response duties also put firefighters at risk of exposure to infectious agents, including hepatitis B virus (HBV), hepatitis C virus (HCV), and human immunodeficiency virus (HIV), all of which are classified in IARC Group 1, *carcinogenic to humans* (see Table 1.1) (Baker et al., 2020). In the USA, approximately 52% of protective service occupations (i.e. police officers, firefighters, transportation security screeners) are exposed at least once per month to infections in their work environment (Baker et al., 2020). Exposure to infectious agents occurs through either direct or indirect contact (Valdez et al., 2015). Through direct transmission, a pathogen (an agent that causes disease, such as a virus, bacterium, or fungus) is transmitted directly from an infected patient or victim to the firefighter. Indirect transmission occurs when an inanimate object (e.g. pen, clipboard, disposable resuscitator bag valve mask, etc.) serves as a temporary reservoir for the infectious agent.

A report from the US Centers for Disease Control and Prevention documented that first responders (including firefighters) were not more likely to be exposed to HCV than was the general population (CDC, 2000). The investigators were not able to exclude the possibility that some first responders had acquired HCV infection from job-related exposures. A literature review by Boal et al. also concluded that firefighters and emergency medical services personnel do not have an elevated seroprevalence of HCV compared with the general population (Boal et al., 2005). [The Working Group identified a paucity of scientific articles providing surveillance data on exposure to infectious agents among firefighters.]

1.6 Factors that modify or mediate effects of exposure

1.6.1 *Personal protective equipment and other control measures*

(a) Hierarchy of controls

The hierarchy of controls is a framework that supports decision-making around implementing feasible and effective control solutions in occupational settings (NIOSH, 2015). Under this hierarchy, control measures are prioritized according to their potential effectiveness. For example, elimination and substitution of occupational hazards are ranked higher than engineering controls (e.g. diesel-exhaust capture), administrative controls (e.g. decontamination of gear or skin), and PPE. PPE is considered to be the least effective type of control measure, mainly because it relies heavily on individuals to properly wear and maintain it. Nevertheless, PPE is a critically important control measure for emergency situations in which other types of controls are difficult to employ and unlikely to eliminate the hazard. Hence, firefighters rely heavily upon PPE (respiratory and dermal protection) to control their exposures to particulate matter, chemicals, and thermal hazards.

(b) Use of personal protective equipment

Variations in firefighting PPE exist across the globe and by job assignment or speciality area. For example, firefighting helmets in Europe differ from those in the USA and Japan in that European helmets are designed to integrate with a SCBA facepiece and do not have a large brim (Lee et al., 2014; Hartin, 2019). The types of PPE worn by fire-cause investigators (IAAI, 2020), industrial firefighters, hazardous material specialists, and other subspecialities of the fire service also differ. Unlike municipal firefighters, wildland firefighters typically wear light protective clothing, such as long-sleeved fire-resistant shirts, trousers, gloves, mid-calf leather boots, and hard hats, but often do not wear respiratory protection (Homeland Security, 2014; Carballo-Leyenda et al., 2018; Navarro et al., 2019a; Koopmans et al., 2022). Some wildland firefighters in certain geographical regions may wear particulate-filtering respirators (NSW Rural Fire Service, 2022); however, these types of respirator are not effective against gases and vapours, including acrolein, formaldehyde, and carbon monoxide (De Vos et al., 2009a), and do not supply oxygen.

(c) Respiratory protection

Firefighters at an incident who do not wear respiratory protection are susceptible to a variety of airborne exposures. However, municipal firefighters will often be wearing pressure-demand SCBA when battling fires, which has an assigned protection factor (APF) of 10 000 (OSHA, 2009) (see Fig. 1.18). An APF is the level of protection that a respirator should provide to employees

Fig. 1.18 Firefighters wearing self-contained breathing apparatus and other personal protective equipment

From Professor Anna A. Stec, Centre for Fire and Hazards Sciences, University of Central Lancashire, UK.

when the employer implements a comprehensive respiratory protection programme (OSHA, 2009). An APF of 10 000 means the respirator will reduce the exposure to one ten-thousandth of the concentration outside the SCBA. Atmosphere-supplying respirators (including SCBA) are the only types permitted for immediately dangerous to life or health (IDLH) environments (OSHA, 2009). On the basis of an analytical model using empirical data, Campbell et al. (1994) estimated that 95% of pressure-demand SCBA wearers would maintain a protection factor two orders of magnitude greater than 10 000. However, another study suggested that firefighters can over-breathe their SCBA during strenuous activities, highlighting the importance of fit-testing (Burgess & Crutchfield, 2015).

SCBA may not always be worn during fire emergencies. Austin et al. (2001c) tracked compressed air usage among firefighters in Montreal, Canada, and estimated that SCBA was worn 50% of the time at structure fires and only 6% of the time at all types of fire. Burgess et al. (2003) found that SCBA was used by firefighters in Arizona, USA, an average of 98%, 80%, 42%, and 15% of the time during extinguishment, entry/ventilation, overhaul, and support/standby functions, respectively. These studies are older, however, and SCBA usage has probably increased across the fire service (Burgess et al., 2020). Still, in some jurisdictions, SCBA may not be commonly worn by structural [municipal] firefighters during specific activities like vehicle fire suppression, overhaul, fire investigations, command/pump operations, or when conducting horizontal or vertical ventilation (Maglio et al., 2016; Jakobsen et al., 2020). As previously mentioned, wildland firefighters typically do not wear respiratory protection (Navarro, 2020).

Burgess et al. (2020) evaluated the impact of control interventions on exposures for different types of firefighter, including among engineers who typically set up away from the fire and often do not wear respiratory protection. When the engineers wore SCBA in the presence of smoke, they had ~40% lower PAH exposures (urinary metabolites) than they did before the intervention.

Other types of control measures in the hierarchy of controls can be implemented during emergency situations to reduce inhalation exposures for firefighters. For example, engineers, incident commanders, and support personnel may be able to approach and position themselves upwind of the fire and take advantage of natural ventilation (CFRA, 2012). Use of water as a means of controlling dust after a fire or collapse can help control the spread of airborne particles, including asbestos fibres (Kim et al., 2020a). Using fluorine-free foam as a suppression agent instead of AFFFs containing perfluoroalkyl acids can reduce firefighters' exposure to PFAS (EC/ECHA, 2020). Firefighting tactics may also impact exposure levels. For example, tactics that involve exterior suppression as a first step before transitioning to interior attack have been shown to result in less exposure for firefighters than those involving interior attack alone (Fent et al., 2020b). [The Working Group estimated that implementing these control measures together with the use of SCBA and other PPE should help to reduce the overall burden on the protective barriers of the PPE and provide greater protection to the firefighter.]

Even more control options may be available in non-emergency situations. At training academies, fire instructors can rotate positions to minimize their time within burn structures. Fuel packages can be selected to achieve training objectives while minimizing exposures. For example, simulated smoke and digital flames can be used instead of live fire for some types of training (Fent et al., 2019a, b). At fire stations, engineering controls, such as exhaust capture systems in vehicle bays, can be used to reduce firefighters' exposure to diesel exhaust (Chung et al., 2020).

Another source of inhalation exposure is the off-gassing of contaminated turnout gear (Fent et al., 2015, 2017; Kirk & Logan, 2015b; Banks et al., 2021b). This source of exposure can be minimized by quickly removing the gear, rehabilitating away from the gear, bagging or transporting the gear in a compartment other than the passenger cabin of the apparatus (engine) or personal vehicle, laundering the gear after firefighting, and storing the gear in areas outside living quarters of the fire station.

(d) Dermal protection

In addition to the inhalation route, firefighters can ingest particulate matter captured through the mucociliary escalator of the respiratory system (Lippmann et al., 1980) or directly through the oral route from hand-to-mouth transfer of contamination (depending on hygiene practices). Firefighters can also absorb hazardous chemicals via the dermal route (see Section 1.4.5 for more information on the different routes of absorption). Firefighters' skin can pick up contamination when doffing or handling contaminated gear or equipment (Kesler et al., 2021). Some contaminants may penetrate the protective barriers of the turnout gear and contact skin during the firefight. Studies have shown ingress of benzene, naphthalene, and other PAHs through openings in the turnout gear and have measured PAH contamination on skin, especially on the neck, wrist, and hands (Fent et al., 2014, 2017; Kirk & Logan, 2015b; Keir et al., 2017; Wingfors et al., 2018; Mayer et al., 2020; Banks et al., 2021a). Some chemical vapours may condense on skin as they cool under turnout gear. Compounds with low vapour pressures that contact skin are more likely to be absorbed, although the specific properties of the compounds, such as octanol/water partition coefficient, also play an important role (Frasch, 2002; Rauma et al., 2013). Dermal absorption is generally faster on areas of the body with thinner skin and a high cutaneous blood flow rate, such as the neck (VanRooij et al., 1993; McCarley & Bunge, 2001).

Turnout gear is often designed for the male anatomy, which can have an impact on its fit for female firefighters, leading to larger air spaces under the gear for females and influencing its thermal and vapour resistance (Nawaz & Troynikov, 2018; Jo et al., 2022). [The Working Group concluded that lack of properly fitting turnout gear is likely among female firefighters in general and could result in greater contaminant ingress and dermal exposure.] Tightening the interfaces around the neck, wrists, waist, and boots, and wearing particle-blocking hoods may impede the penetration of some PAH compounds (Ormond et al., 2019; Kesler et al., 2021). However, there is concern that these interventions could also increase the thermal strain for firefighters by trapping metabolic heat energy (Kesler et al., 2021). The micro-environment created under turnout gear (e.g. higher temperature and humidity levels) may facilitate the dermal absorption rate of compounds that penetrate the protective barriers of the gear (Franz, 1984; US EPA, 1992; VanRooij et al., 1993).

Most control interventions aimed at reducing dermal exposure have focused on measures that can be taken after firefighting. These interventions include gross decontamination of turnout gear and other equipment, use of skin-cleansing wipes or washing skin with soap and water at the incident, bagging and laundering of turnout gear and hoods before wearing them again, and showering as soon as possible after returning to the fire station. Fent et al. (2017) found that gross decontamination using water, dish soap, and scrubbing was able to remove a median of 85% of PAH contamination on the exterior of turnout jackets, and that use of skin-cleansing wipes removed a median of 54% of PAH contamination from the skin. Mayer et al. (2019) found a mean reduction in PAH contamination in used knit hoods of 76% after a single laundering; however, results were mixed for removal of PBDEs and OPFRs. Banks et al. (2021c) found that laundering and water-only decontamination did not significantly remove PAHs, PBDEs, or OPFRs contaminating turnout gear, with a few exceptions. Burgess et al. (2020) found that implementing several of these interventions (gross decontamination and segregation of contaminated gear with subsequent laundering, skin cleaning, and showering as soon as possible at the station) resulted in ~36% lower PAH exposures (measured as urinary metabolites) for firefighters compared with before the interventions were implemented.

While many departments have implemented PPE decontamination measures, such as gross on-scene decontamination and laundering of turnout gear that has been worn for a fire response, within the last 10 years (Horn et al., 2021), many fire departments continue to launder turnout gear infrequently (e.g. once or twice per year) as per current minimum standards or because of resource limitations (NFPA, 2020a). SCBAs are also commonly decontaminated after firefighting, but this practice is likely to vary across the fire service (Park et al., 2022). In the USA, wildland firefighters commonly wear the same protective clothing over weeks and launder these items at home (McQuerry & Easter, 2022).

1.6.2 *Other factors, including health behaviours*

Inter-individual variability in how chemicals are absorbed, metabolized, and excreted may be related to sex or genetic differences. However, these factors are complex, difficult to study, and are largely beyond the control of the individual. Personal factors that may modify or mediate the effect of exposure that individuals have control over include personal hygiene, use of sunscreen and limiting sun exposure, nutrition, exercise, sleep, limiting alcohol consumption, and not using tobacco.

(a) Personal hygiene factors

Washing or cleaning skin after firefighting will help remove contaminants before they are absorbed into the dermis or deeper layers of skin where blood perfusion occurs. However, skin-cleansing wipes, which are commonly used after firefighting, will not remove all contaminants from the skin (Fent et al., 2017). The longer chemicals stay on the skin (contact time), the more likely they are to be absorbed (Frasch et al., 2014). [The Working Group agreed that showering as soon as possible is critical to remove any residual skin contamination. Washing hands before eating will also help reduce hand-to-mouth ingestion of chemical or biological contaminants. Use of sunscreen, especially by firefighters who spend substantial time outdoors, will help reduce their exposure to harmful UV radiation. Wearing long-brim hats and long-sleeved shirts during extended times outdoors can further minimize UV exposure.]

(b) Health behaviours

Eating nutritious foods, exercising, and maintaining a healthy BMI, while important for overall health, may also help lessen the effects of exposure. Having a strong cardiovascular and respiratory system can lower an individual's breathing rate, which can extend the use of SCBA during operations and reduce the biological uptake of airborne contaminants through the lungs when respiratory protection is not worn (US EPA, 2011). Many hazardous chemicals are lipid-soluble, and increased levels of body fat can act as a reservoir to store these compounds for longer periods (Milbrath et al., 2009). Eating foods that are high in antioxidants, vitamins, and minerals can support the body's natural defences against xenobiotics and oxidative stress (Flora, 2009). Nutrition is especially important for wildland firefighters to provide the necessary calories to support their arduous work, while also providing adequate nutrients for their overall health (Brooks et al., 2021).

Not using tobacco products is also important to maintain the body's normal defence mechanisms against toxicants. Exposure to tobacco smoke has been shown to cause damage to the mucociliary escalator of the respiratory system and lessen the body's ability to clear particles inhaled into the lungs (Xavier et al., 2013).

The human body has several mechanisms in place to repair cellular and DNA damage, regardless of the cause. These mechanisms are especially active during sleep. Hence, getting adequate and consistent sleep, including uninterrupted deep sleep, is important for mitigating the effects of occupational and non-occupational exposures (Atrooz & Salim, 2020; Williams & Naidoo, 2020).

1.7 Regulations and guidelines

1.7.1 *Occupational exposure limits*

OELs for some fire effluents are presented in Table 1.27. Both the American Conference of Governmental Industrial Hygienists and the European Union (previously via the Scientific Committee on Occupational Exposure Limit

Table 1.27 Examples of occupational exposure limits for some fire effluents[a]

Fire effluents	Units	TLV-TWA		STEL	
		ACGIH	EU[c]	ACGIH	EU[c]
Acetaldehyde[b]	mg/m³		5 (LV)		45 (LV)
Arsenic	mg/m³	0.01	0.01 (IP, BV)		
Asbestos	fibres/cm³	0.1	0.1 (BV)		
Benzene[d] (on NIC)	mg/m³	0.066[e]	0.66 (BV)	0.33[e]	
1,3-Butadiene	mg/m³	4.4[e]	2.2 (BV)		
Cadmium[c]	mg/m³	0.01 TP 0.002 R	0.001 (IP, BV)		
Carbon black	mg/m³	3 IP	3 (LV)		
Carbon monoxide	mg/m³	29[e]	23 (BV)		117 (BV)
Dichloromethane (methylene chloride)	mg/m³	174[e]	353 (IOELV)		706 (IOELV)
Ethylbenzene	mg/m³	88[e]	442 (IOELV)	551[e]	884 (IOELV)
Formaldehyde	mg/m³	0.12[e]	0.37 (BV)	0.37[e]	0.74 (BV)
Tetrahydrofuran	mg/m³	150[e]	150 (IOELV)	590[e]	300 (IOELV)
Isoprene	mg/m³		8.4 (LV)		67.2 (LV)
Lead[d]	mg/m³	0.05	0.15 (BV)	0.0005	
Lead chromate	mg/m³	0.0002 (IP)	0.04 (LV)		
Naphthalene	mg/m³	50[e]	2 (LV)		8 (LV)
Particulate matter (respirable)	mg/m³	No TLV but should be < 3	0.3 (LV)		2.4 (LV)
Particulate matter (total)	mg/m³	No TLV but should be < 10			
Pentachlorophenol	mg/m³	0.5	0.05 (LV)	1	0.1 (LV)
Polychlorinated biphenyls (PCBs) (42% chlorine) (54% chlorine)	mg/m³	 1 0.5			1.5 (IOELV)
Polycyclic aromatic hydrocarbons (PAHs)[d] (benz[*a*]anthracene, benzo[*b*]fluoranthene, chrysene, anthracene, benzo[*a*]pyrene, phenanthrene, acridine, or pyrene)	mg/m³	0.2	0.0005507 (LV)		
Styrene	mg/m³	43[e]	10 (LV)	86[e]	30 (LV)
Sulfuric acid	mg/m³	0.2 TPM	0.05 TPM (IOELV)		
Tetrachloroethylene (perchloroethylene)	mg/m³	170[e]	138 (IOELV)	685[e]	275 (IOELV)
Trichloroethylene	mg/m³	54[e]	54.7 (BV)	135[e]	164.1 (BV)
Trichloromethane (chloroform)	mg/m³	49[e]	10 (IOELV)		5 (LV)

ACGIH, American Conference of Governmental Industrial Hygienists; EU, European Union; IP, inhalable particulate; LV, lowest value; ppm, parts per million; R, respirable; STEL, short-term exposure limits; TLV, threshold limit values; TP, total particulate; TPM, thoracic particulate mass; TWA, time-weighted average.

[a] Adopted from IFA (2022).

[b] Acetaldehyde – ceiling value available: ACGIH (25 ppm); EU (25 ppm, LV).

[c] When a TLV-TWA was not available, an EU binding value (BV) (Directive 2004/37/EC – carcinogens, mutagens or reprotoxic substances at work) the lowest value (LV) in place in a Member State was used or the indicative occupational exposure limit value (IOELV), when available.

[d] Substances with a biological exposure index (BEI) or EU biological limit value (BLV).

[e] Data were converted from ppm to mg/m³.

Values and now via the Committee for Risk Assessment of the European Chemicals Agency, ECHA) provide OELs. [These are both health-based limits but may not have been based on a cancer end-point.] Many countries have lists of OELs to be applied nationally (Schenk et al., 2008). The GESTIS website lists OELs from around the world (IFA, 2022).

[The Working Group noted that only some of the individual components of fire smoke (i.e. aldehydes, acid gases, sulfur dioxide, nitrogen oxides, PAHs, benzene, toluene, styrene, metals, and dioxins) have OELs, and many agents to which firefighters are commonly exposed have no OELs. There is no recommended way of adjusting for the complex and partly unknown mixtures present in fire effluents, some of which are probably composed of agents that act on the same organ and/or have the same effect, e.g. irritancy. Furthermore, OELs are typically set for a work week of 40 hours (8 hours per day for 5 days per week), so may not provide sufficient protection for workers with longer shifts. Some OELs can be arithmetically reduced for longer shifts, perhaps up to 12 hours, so that the total permitted exposure is equivalent. However, for longer shifts, depending on the agent, this may not allow sufficient recovery time between exposure periods. Firefighters often have very intense short-term exposures, during which short-term exposure limits (STELs) or ceiling limits may well be exceeded. In addition, OELs do not consider increased respiratory rates. Some more specific guidance on firefighters' exposure has been provided in Canada, the UK, and Australia (AFAC, 2019a; Government of Ontario, 2022; Government of the United Kingdom, 2022).]

1.7.2 Regulations on use of personal protective equipment

PPE including devices and garments, such as respirators, turnout gear, gloves, blankets, and SCBA are designed to protect firefighters from serious injuries or illnesses resulting from contact with fire and hazardous materials (Smith et al., 2020; McQuerry & Easter, 2022). Regulations on the use of PPE can vary worldwide. Regulation on cleaning, maintenance, and repair of PPE follows BS 8617 in the UK (British Standards Institution, 2019a). Firefighters in the UK should use municipal firefighting PPE as the common default position for fire and rescue activities initially; the PPE is modified by the incident commander based on a joint understanding of risk and information available from other responder agencies (Daniels, 2019). In Australia, PPE must comply with relevant international/Australian standards (AFAC, 2019b).

In the USA, National Fire Protection Association Standard 1971 (NFPA 1971), Standard on Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting establishes minimum levels of protection from thermal, physical, environmental, and bloodborne pathogen hazards encountered during structural [municipal] and proximity firefighting operations (American Public Health Association, 2001; NFPA, 2018). There are several other US NFPA standards that address firefighter PPE, including NFPA 1500 Standard on Fire Department Occupational Safety and Health Program (Loflin, 1989), NFPA 1851 Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting (NFPA, 2001), NFPA 1951 Standard on Protective Ensembles for Technical Rescue Incidents (NFPA, 2001), NFPA 1975 Station/Work Uniforms for Fire and Emergency Services (NFPA, 2002), NFPA 1977 Standard on Protective Clothing and Equipment for Wildland Fire Fighting (NFPA, 2015), NFPA 1991 Standard on Vapour-Protective Ensembles for Hazardous Materials Emergencies (NFPA, 2005, 2012), NFPA 1992 Standard on Liquid Splash-Protective Clothing for Hazardous Materials Emergencies, NFPA 1994 Standard on Protective Ensembles for First Responders to CBRN Terrorism Incidents, NFPA 1999 Standard on Protective Clothing for Emergency Medical Operations (EMS), and OSHA Rule 29 CFR 1910.1030 Final rule on Protecting Health Care Workers from Occupational Exposure to Bloodborne Pathogens (Denault & Gardner, 2022).

The use of PPE in Portugal is mandatory for firefighting emergency calls (Moraes et al., 2019a, b); however, different safety gear, devices, and equipment are available based on the fire scenario. There is still limited literature on and systematic investigation of the overall regulatory state of PPE (Kim et al., 2022). In the Republic of Korea, there are no comprehensive regulations governing firefighting PPE, PPE maintenance, and replacement, similar to NFPA 1851 in the USA. In Canada, the Canada Labour Code and Occupational Health and Safety Regulation (Regulation) Part 31: Firefighting, stipulate general PPE requirements, together with protective coats, trousers and hoods, station wear, and personal garments (Frost et al., 2016; Ramsden et al., 2018). [Despite the general use of PPE among firefighters worldwide, there is a need to study the impact of the makeup and design of the various types of PPE, repeated use and exposure to heat and chemicals, maintenance, and cleaning on the protective capabilities of the PPE.]

1.7.3 Regulations on firefighting foams

The use of PFAS in AFFF has been regulated in the European Union since 2006 (Banzhaf et al., 2017), and the Stockholm Convention listed PFAS (i.e. PFOA, its salts, and PFOA-related compounds; PFHxS, its salts, and PFHxS-related compounds, and long-chain perfluorocarboxylic acids, their salts and related compounds) as persistent organic pollutants that are to be phased out in 185 countries (Secretariat of the Stockholm Convention, 2019a; Pinas et al., 2020).

In the European Union, the ECHA has brought forward a restriction proposal for a European Union-wide ban on both the use and production of PFAS. In 2022, ECHA's scientific Committee for Risk Assessment and Committee for Socioeconomic Analysis are assessing the proposed restriction options (ECHA, 2022a). When adopted, the restriction could reduce PFAS emissions into the environment by more than 13 000 tonnes over 30 years (ECHA, 2022b).

1.7.4 Minimum age of firefighters

Requirements and regulations to work as a firefighter vary across countries, but many countries require an individual to be aged at least 18 years (Sluiter & Frings-Dresen, 2007; Evarts & Stein, 2020; Euroinnova, 2022). In Australia, there are no general age requirements; however, the Country Fire Authority, Victoria, has a minimum age of 16 years (16- and 17-year-olds need parental consent) for volunteer firefighters, and some brigades also run a junior programme for 11–15-year-olds (Fire Recruitment Australia, 2015; Fire and Rescue New South Wales, 2021b).

1.7.5 Regulations on maximum worker hours

The majority of US fire departments work a rotating schedule of 24-hour shifts guided by the Fair Labor Standards Act (Cohen & Plecas, 2013). In Canada, firefighters work a minimum of 48 hours per week and become eligible for overtime after working about 56 hours in a week (Ontario Association of Fire Chiefs, 2022). In Australia, working hours are a matter for trade union agreement; working hours average 38 hours per week and shifts vary over an 8-week cycle (ACT Government, 2020).

In the European Union, the Working Time Directive was introduced in 1993 to set rules on maximum weekly working time and other requirements in terms of rest breaks, daily rest periods, and shift work (Rønning, 2002; Sol & Martín, 2015; Risak, 2019). However, there are many differences regarding working time between and within countries (EPSU, 2006). Working time is negotiated nationally in Denmark, Finland, Slovakia, and the UK, while in other countries there is a combination of national and local negotiation (EPSU, 2006). Furthermore, hours are calculated on an annual basis in Belgium, Denmark, France, Slovak Republic and Spain, while they are weekly in Czechia, Finland, Ireland, Italy, Norway, Sweden and the UK. In the Netherlands, the weekly maximum number of hours is calculated over a 26-week period. The monthly calculation in Estonia is averaged over a 3-month period (EPSU, 2006).

The basic work week – the hours set out in collective agreements or statutes for which firefighters are paid at a basic rate – ranges from 36 hours in Italy and the Netherlands to 42 hours in Sweden and the UK (EPSU, 2006). However, these hours do not necessarily correspond to actual hours normally worked; for example, actual working time averaged 54 hours per week among Dutch firefighters (EPSU, 2006).

There have been a few changes to working time in recent years. In Norway, there has been a new national agreement that allows for 48-hour shifts over weekends and 24-hour shifts during the week (EPSU, 2006). In North Rhine-Westphalia, the biggest region in Germany, firefighters negotiated a reduction in the working week from 54 to 48 hours from 1 January 2007 (EPSU, 2006). The regional government agreed to bring the service into line with the Working Time Directive after pressure from the trade union.

1.8 Quality of exposure assessment in key epidemiological studies of cancer and mechanistic studies in humans

1.8.1 Epidemiological studies of cancer in humans

This section reviews the exposure assessment methods and exposure assessment quality of the epidemiological studies of firefighters. The findings are summarized in Table S1.28, and the criteria for the exposure quality rating are included in Table S1.29 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

As described in Section 1.2, Section 1.4, and Section 1.5, firefighters are exposed to a range of physical and chemical hazards that vary from day to day and have changed over time. Quantitative characterization of all these exposures is not feasible in studies of cancer in humans. The definition of exposure provided by most epidemiological studies is simply having worked as a firefighter. This definition may be refined in a variety of ways to better reflect the extent or intensity of firefighting activities. For example, those with the occupational title of firefighter but who do not actually attend to fires may be excluded. Additionally, the duration of firefighting service (e.g. < 10 years versus ≥ 10 years) may be used under the assumption that longer service will lead to more time spent in direct exposure to fires and related hazards (e.g. Aronson et al., 1994; Ahn & Jeong, 2015; Bigert et al., 2020).

Other exposure assessment metrics have been used to group firefighters by measures of the extent or intensity of exposure and reduce misclassification. For example, individual estimates of firefighting activities including number and/or types of fire (e.g. house, vehicle, etc.), probably better reflect the actual chemical and physical exposure burdens (e.g. Dahm et al., 2015) than does the simple duration of work. Other studies grouped or selected firefighters by job title or role (active or frontline) (e.g. Demers et al., 1994) and/or provided a measure of busyness, intensity, or type of firefighting role (e.g. Guidotti, 1993; Tornling et al., 1994; Daniels et al., 2015; Glass et al., 2016a).

To assess the quality of the exposure assessment and the extent of misclassification in the epidemiology studies, the following data elements were examined: (i) the study design, location, and era, or exposure period; (ii) ascertainment of firefighter status and years of engagement as a firefighter; (iii) exposure metrics for use in analyses such as a measure of intensity of firefighting work; (iv) timing of exposure relative to the outcome; (v) co-exposures to carcinogens; and (vi) potential for differential exposure misclassification (see also Table S1.28, Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

Based on these criteria, an evaluation of the exposure quality of each study is presented in Sections 2.1 to 2.6 and in the accompanying tables in Section 2 and supplementary tables in Annex 2 (Supplementary material for Section 2, Cancer in Humans, online only, available from: https://publications.iarc.fr/615).

(a) Critical review of exposure assessment methods

The 40 cohort studies reviewed all came from high-income countries, including the Republic of Korea (*n* = 2) (Ahn et al., 2012; Ahn & Jeong, 2015); Canada (*n* = 5) (Mastromatteo, 1959; Guidotti, 1993; Aronson et al., 1994; Harris et al., 2018; Sritharan et al., 2022); the USA (*n* = 16) (Musk et al., 1978; Feuer & Rosenman, 1986; Vena & Fiedler, 1987; Grimes et al., 1991; Demers et al., 1992, 1994; Burnett et al., 1994; Ma et al., 2005, 2006; Zeig-Owens et al., 2011; Daniels et al., 2014, 2015; Moir et al., 2016; Colbeth et al., 2020a; Pinkerton et al., 2020; Webber et al., 2021); Oceania (*n* = 7), (Eliopulos et al., 1984; Giles et al., 1993; Bates et al., 2001; Glass et al., 2016a, b, 2017, 2019); Nordic countries (*n* = 7) (Tornling et al., 1994; Pukkala et al., 2014; Kullberg et al., 2018; Petersen et al., 2018a, b; Bigert et al., 2020; Marjerrison et al., 2022); and other European countries (*n* = 3) (Deschamps et al., 1995; Amadeo et al., 2015; Zhao et al., 2020). The case–control studies are also mainly from high-income countries: Europe (*n* = 1) (Stang et al., 2003); North America (*n* = 9) (Sama et al., 1990; Muscat & Wynder, 1995; Ma et al., 1998; Kang et al., 2008; Tsai et al., 2015; Muegge et al., 2018; Langevin et al., 2020; Lee et al., 2020; McClure et al., 2021); and one international study that included data from China, Europe, North America, and Oceania (Bigert et al., 2016).

Most cohort studies identified career firefighters from employment records, including general municipal employment records, e.g. Vena & Fiedler (1987). Other reliable sources of employment information used in firefighter epidemiology are professional certification data (Ma et al., 2005, 2006), superannuation (pension contributions), compensation data (Mastromatteo, 1959; Sritharan et al., 2022), and retirement records (Feuer & Rosenman, 1986; Ide, 1998). Studies identifying firefighters from census data rely on self-reported employment information. They may collect data at one point in time, e.g. Zhao et al. (2020) and Harris et al. (2018), or from more than one census, which allows an estimate of employment duration (e.g. Bigert et al., 2020). Mortality studies that use death certificate data on "usual occupation," as reported to the certifying health professional often by the next of kin (for example, Burnett et al., 1994), are probably less reliable than those with employment records, for example. [The limitations of these data as a proxy for occupational exposure are well documented, e.g. Steenland & Beaumont, 1984; Schade & Swanson, 1988; Bidulescu et al., 2007.]

In some case–control studies, firefighters were largely identified from interviews or questionnaires coded to standardized occupational codes and categorized as ever/never firefighters (e.g. Stang et al., 2003; Tsai et al., 2015; Bigert et al., 2016; Langevin et al., 2020). Other sources of information on occupation for case–control studies were cancer registry records (e.g. Tsai et al., 2015), death certificates (e.g. Ma et al., 1998; Muegge et al., 2018), and linkage between cancer registry and census or employment records (e.g. McClure et al., 2021). [Occupational information from cancer and death registries is often incomplete, and there was evidence from at least one registry that the missingness was differentially distributed (McClure et al., 2021). There may also be selection bias in these studies.]

Most employment-based cohorts are from urban areas (e.g. Pinkerton et al., 2020; Webber et al., 2021), whereas other cohorts (e.g. those based on census records) are country-wide and therefore probably include both urban and rural firefighters (e.g. Pukkala et al., 2014; Bigert et al., 2020). [The exposures of rural and urban firefighters differ in type and pattern of exposure. Rural firefighters mainly fight wildland (sometimes called "landscape") fires, whereas municipal firefighters are more likely to attend structure and vehicle fires, hazardous material incidents, and false alarms. Unlike most structure fires, wildland fires can take days or even weeks to extinguish, which means that wildland firefighters may have extended firefighting periods away from home. Their equipment, such as fire trucks, clothing, and respiratory protective equipment may differ from that of municipal firefighters. Wildland firefighters probably use a different mix of fire suppression techniques, such as back burning and aerial spraying of water or flame retardants, and are less likely to use respiratory protective equipment. Section 1.2 provides further information on differences in exposure between different groups of firefighters and types of fire.]

Most cohort studies are of career firefighters, but some also included volunteers (Guidotti, 1993; Bates et al., 2001; and Petersen et al., 2018b). One study included only volunteer firefighters (Glass et al., 2017). Glass et al. (2019) included a relatively small number of career female firefighters; most of the analyses focused on volunteer female firefighters. [Assessing quality of the exposure assessment requires that firefighters be accurately identified. For career firefighters, employment records are an accurate way to identify firefighters, but similar documentation for volunteer or wildland firefighters may be unavailable in many countries. Volunteer records may not be a reliable source of duration of active firefighting, since volunteer rolls may not be updated, and volunteers may remain in the organization but not actively fight fires.]

Employment duration was often captured from employment records and used as a proxy for exposure (e.g. Petersen et al., 2018a; Glass et al., 2019; Marjerrison et al., 2022). Employment duration inferred from periodic census data is probably less reliable than that from employment records (e.g. Bigert et al., 2020). In many other studies, employment was characterized qualitatively as ever/never a firefighter, and in some cases the status was known only at a specific time point (e.g. Amadeo et al., 2015). An improvement on employment duration used by several authors (e.g. Demers et al., 1994; Ahn & Jeong, 2015; Petersen et al., 2018a) was to count only years of service in direct firefighting roles.

A few studies specified a minimum period of service as a firefighter: 1 day (Daniels et al., 2014), 1 month (Ahn & Jeong, 2015), 3 months (Glass et al., 2016b), and 1 year (Demers et al., 1992; Tornling et al., 1994; Bates et al., 2001; Kullberg et al., 2018). [This could mean that firefighters with a relatively short duration of service were included in analyses together with those with longer service, and studies were included that did not report duration of employment.]

Among the strongest exposure assessments were studies that used various sources of information to improve upon duration of service, including indicators of likelihood of high exposures from actual firefighting activities. These included Guidotti (1993), who used an exposure opportunity matrix to weigh the duration of work by proximity to the fire for various job categories. Glass et al. (2016b, 2017, 2019) grouped firefighters by the recorded number of incidents and type of fire attended (although records were incomplete and were estimated for early years). Tornling et al. (1994) grouped firefighters by the estimated number of fires they had fought. One of the exposure assessments of the highest quality was conducted for an epidemiological study of firefighters in three cities in the USA. The investigators developed a job-exposure matrix linked to participants' work history records to calculate several proxy exposure measures, including duration of exposure (cumulative time classified by exposed job title and assignment), fire-runs (cumulative events of potential fire exposure) and time at fire (cumulative hours of potential fire exposure) (Dahm et al., 2015; Daniels et al., 2015; Pinkerton et al., 2020), or specific exposures (e.g. Baris et al., 2001) assessed on diesel engine emissions.

The earliest cohort studies reviewed here included firefighters who were employed before 1930 (Musk et al., 1978; Guidotti, 1993), and the most recent studies included firefighters working in 2014 (Petersen et al., 2018a, b). A preponderance of studies examined cancer rates among firefighters working between 1980 and 2000. Analysis by era of employment may help to investigate changes in exposure over time (Glass et al., 2016a, 2017, 2019). [The wide range of eras indicated that there would have been differences in exposures between cohorts, for example, changes in the number of vehicle fires and extent of exposure to burning plastics, shift-work patterns, use of firefighting foams, and type of PPE availability and use (see Section 1.2 and Section 1.5(b) for further information.]

Information on PPE use was mentioned in only few studies. Tornling et al. (1994) included the use of SCBA in their exposure index. Wolfe et al. (2012) considered clothing in a case report of non-melanoma skin cancers. The quality and use of PPE, including respiratory protective equipment, has varied over time and so may affect the extent of exposure of individuals (Austin et al., 2001c; Austin, 2008).

Some studies examined the risk of cancer among firefighters who attended the aftermath of the WTC disaster in 2001 and were employed by the Fire Department of New York City (FDNY) (e.g. Colbeth et al., 2020a), or firefighters employed by other cities (Webber et al., 2021). Zeig-Owens et al. (2011), Colbeth et al. (2020a), and Webber et al. (2021) used earlier-developed ordinal exposure categories based on period of arrival at the scene: (1) (highest) arrived on the morning of 11 September 2001; (2) arrived afternoon of 11 September 2001; (3) arrived on 12 September 2001; (4) arrived between 13 and 24 September 2001; and (5) (lowest) arrived between 25 September 2001 and 25 July 2002. [None of these studies considered firefighting exposure that preceded the WTC response.]

The case reports and case series reviewed included limited information on exposure and are not discussed further here (Bates & Lane, 1995; Cucchi, 2003; Wolfe et al., 2012; Cormack, 2013; Schrey et al., 2013; Sugi et al., 2013; Antoniv et al., 2017; Landgren et al., 2018; Geiger et al., 2020).

(b) Other occupational exposures to carcinogens

Both career firefighters and volunteers are likely to hold or have held other jobs, either different positions within the fire service, or entirely separate occupations (Ma et al., 2006; Glass et al., 2017). For example, in a cohort of Danish paid [career] and volunteer firefighters

(Petersen et al., 2018a), more than 10% of firefighters had held jobs potentially exposing them to additional hazardous exposures in construction-related jobs, laundry or dry cleaning, the automobile industry, and rubber and plastic production. Compared with full-time firefighters, part-time or volunteer firefighters had more frequently been employed in the machine industry, fabricated metal production, the wood and furniture industry, and farming (Elbaek Pedersen et al., 2020). In a survey of career firefighters in Florida, USA, 29.7% had a second job; the most frequently reported second jobs were in education, health care, and sales (Baikovitz et al., 2019). [Most seasonal wildland firefighters also hold other jobs. These other jobs may result in exposure to other occupational carcinogens, e.g. asbestos or paint during construction work, or pesticides or solar UV in farming or forestry. Data on exposures in other jobs were not adjusted for in any cohort studies identified in the present monograph.]

1.8.2 Mechanistic studies in humans

This section reviews the exposure assessment methods used in and exposure assessment quality of the mechanistic studies of firefighters. The findings are summarized in Table S1.30 (Annex 1, Supplementary material for Section 1, Exposure Characterization, online only, available from: https://publications.iarc.fr/615).

There is no single best method for assessing exposure of firefighters for the study of key characteristics of carcinogens (Smith et al., 2016) in humans. Assessment of the quality and informativeness of the exposure assessment requires understanding the research question, the study design, and the temporal characteristics of markers of exposure and effect. To be useful, the assessment should be unbiased, temporally appropriate, sufficiently quantitatively precise to allow demonstration of a dose–response relationship, and produce a summary measure of exposure that is credibly associated with the key characteristic of interest.

The studies of firefighters selected for assessing the key characteristics of carcinogens can largely be grouped into four different study types: cross-sectional (with a single measurement), repeated measurements (without a pre-exposure measurement), pre/post comparisons, and pre/post trials (where comparisons were done on exposures in a controlled setting), each with different strengths and limitations.

Many of the key characteristics studies used cross-sectional designs in which exposure was measured at a single point in time, and reflect all previous exposures, both recent and in the distant past. These studies usually involve an exposure contrast between exposed and unexposed groups, for example, comparing firefighters and non-firefighters. A major challenge to validity in this approach is that there are likely to be many differences in health-related characteristics of the compared groups, such that the fact that one is "exposed" and the other "not exposed" may be only one of many reasons why the two groups experience different health outcomes.

The cross-sectional design may also be used to compare different groups of firefighters with varying amounts of exposure, for example, different numbers of years of employment, or time spent at fires. This is an improvement, but there are still important limitations. One of the challenges of these designs is that it is often difficult to explicitly consider exposures that have occurred at different times in the past. If the outcome measure is thought to be affected only by very recent exposures, then there may be substantial misclassification of exposure if a long-term measure of exposure such as the number of years of employment is used. In an attempt to avoid this problem, participants may be asked about their recent exposures, but these reports may be subject to recall bias, particularly if participants are aware that the hypothesis is that their recent exposures are hazardous.

Comparing groups of firefighters with varying amounts of exposure is nearly always a retrospective exercise, and it is usually not possible to estimate with any confidence the long-term or cumulative exposures to specific agents that are expected to be proportional to chronic biological effects. Even good administrative records, when they are available, will rarely provide information on PPE (what was used and how effectively). Additionally, the number of years employed as a firefighter is usually strongly correlated with age, making it difficult to disentangle exposure and age effects.

Cross-sectional designs are often used in studies of high exposures under extreme conditions after firefighters have participated in catastrophic events, such as the collapse of the WTC or certain out-of-control wildfires. These are, of necessity, post hoc, effectively prohibiting direct measurement of pre-exposure effect markers and, to a large degree (such as at the WTC), excluding contemporary measures of exposure. Moreover, the exposure experienced may have little relevance to the day-to-day exposures of the great majority of firefighters.

Studies with a repeated-measurement design examine the contrast between exposures for individuals across time. These studies have many names, but the term "repeated measurements design" will be used here for studies with two or more measurements for the same person but without a measurement before the exposure. In contrast, the term "pre/post" will be used here for studies that contrast a measurement before exposure with one or more measurements after exposure. The pre/post time interval between samples may be a work shift (8 hours, for example), but may also be many weeks or months. It is important that the exposure time window defined by the two or more time points is appropriately matched to the temporal dynamics of the outcome measure. Considerations include the half-life of circulating cells or biomarkers and any latency between exposure and response that arises from the biological mechanism of the key characteristic. The pre/post design has the strong advantage that each participant "serves as his/her own control", because it is the change in exposure over time that is studied for its association with the change in outcome, reducing risk of confounding.

An example of a good application of the pre/post design, used mainly with wildland firefighters, is the monitoring of pollutants (particles from smoke) in the breathing zone during a work shift, relating these measures to biomarkers of exposure (such as urinary 1-hydroxypyrene, reflecting PAH exposure) and to effect markers that appear rapidly (within at most 24 hours) and may have some long-term relevance to the key characteristic of interest. While in principle this design could also be used in the urban setting, it is logistically challenging, because municipal firefighters respond to fire calls only infrequently and, of course, not on a predictable schedule that would allow setting up the sampling equipment. Such a design may not take account of prior exposures over months or years of firefighting. Better studies concentrate on changes in measured biomarkers between the beginning and end of shift; although relatively straightforward to design, the importance and interpretation of changes in transient effect biomarkers may be less obvious in these studies.

The fourth type of study is the "pre/post trial"; again, a measurement before exposure is compared with one or more measurements after exposure, but in these studies the investigators assign exposures or interventions rather than simply observing whatever exposures their study participants experience. Such trials have the strong advantage of minimizing the risk of most biases since the exposure is well defined and assigned, but they are limited in their applicability, because many of the exposures of firefighters cannot ethically be delivered to human subjects. Trials have most often been conducted to evaluate effects of exposures other than breathing smoke and other combustion products, and include such factors as sleep restriction, heat exposure, physical exercise, and nutrition. Although these potentially important risk factors for cancer among firefighters can be studied in a controlled setting, findings must be interpreted cautiously, because the trial conditions may not correspond well to the actual exposures experienced by firefighters on the job.

(a) Is genotoxic

The most common approach to exposure assessment in studies of genotoxicity end-points in firefighters was to identify firefighters by employment records, sometimes supplemented with information on the duration of exposure (e.g. Ray et al., 2005). These studies are of limited use because of lack of information on the frequency or recency of firefighting activities, the timing and intensity of exposures to toxic chemicals, and the use of protective equipment.

Three studies with genotoxicity end-points involved special populations with unique exposures that are of limited relevance to the hazards of typical firefighters, and included teams who were brought to Kuwait to fight oil fires after the first Gulf War ("Operation Desert Storm") in 1990–1991 (Darcey et al., 1992), responders to a chemical plant explosion in Germany (Hengstler et al., 1995), and emergency technicians who responded to the sarin gas attack in the Tokyo subway, Japan (Li et al., 2004). Min et al. (2020) conducted a study of several mechanistic end-points among a population of firefighters on different work shifts. The hypotheses investigated were about the effects of shift work, and no other exposure information was gathered.

Higher-quality exposure assessments gathered information on the frequency or intensity of firefighting activities. Rothman et al. (1993, 1995) studied a cohort of California wildland firefighters twice, 2 months apart. Information was collected from self-reports on total hours of firefighting activity in the recent past, number of previous seasons of firefighting activity, and duration of daily exposure to diesel exhaust. Information on potential confounding exposures (including consumption of charcoal-broiled meat) was also collected by questionnaire. Self-reports of mask-wearing were also gathered. Liou et al. (1989) gathered self-reported information from firefighters on the frequency of firefighting activities in an effort to improve upon the basic firefighter/non-firefighter comparison used in the primary analyses in their papers.

(b) Induces epigenetic alterations

Four studies assessing the associations between measures of DNA methylation and firefighters' exposures used cross-sectional designs (Ouyang et al., 2012; Kuan et al., 2019; Zhou et al., 2019; Goodrich et al., 2021). There were variations in exposure assessment methods that may affect study quality. Ouyang et al. (2012) used the simplest approach, comparing firefighters to non-firefighters. Zhou et al. (2019) improved upon this simple contrast by comparing new recruits to incumbent firefighters (14 years of service, on average), and comparing incumbents by duration of service. Goodrich et al. (2021) studied only active-duty firefighting. The principle exposure contrast was created using serum concentrations of PFAS compounds, rather than any measure of firefighting experience. This approach to exposure assessment avoided problems of selection or recall bias, and even inaccuracies of official records that are found in most of the studies on firefighters. In the fourth cross-sectional study of epigenetic alterations, Kuan et al. (2019) constructed an innovative exposure metric, the exposure-ranking index, to summarize many dimensions of the exposure histories of WTC first responders. The exposure-ranking index incorporated information on the duration of exposures, as well as exposure-related tasks and use of PPE on 11 September 2001 and in the subsequent months. The information was gathered from detailed exposure questionnaires completed by firefighters and other first responders some time after the event, at enrolment into the WTC cohort. The index does not include quantitative data on specific airborne substances but should represent the inhaled burden of pollutants from the WTC event.

Among the strongest of the exposure assessments was the study of both incumbent (previously employed) and newly hired firefighters in Tucson, Arizona, USA (by Jeong et al., 2018; Zhou et al., 2019; Jung et al., 2021b; Goodrich et al., 2022). The newly-hired firefighters were followed for 2 years, and data were gathered from department records documenting for each participant the cumulative fire-hours, fire-runs (number of fires to which a participant responds), and days since the last fire call. These data were also stratified by type of fire, to attempt to distinguish different broad types of fire smoke.

(c) Induces oxidative stress

One set of studies adopted a pre/post cross-shift design, with measurement of exposure during a single work shift. Several of these came from one group (Adetona et al., 2013b, 2019; Wu et al., 2020a, b) and used data on US wildland firefighters at prescribed burns. Personal exposure to $PM_{2.5}$ was measured in the breathing zone, and exposure was also characterized by type of activity during the prescribed burn and/or by urinary markers of exposure. The exposure assessment for these was of good quality but was limited by the inclusion of only exposures during a single shift. Studies of municipal firefighters, using call-out to fire activities rather than prescribed burns, have been carried out in Denmark (Andersen et al., 2018a) and Canada (Keir et al., 2017) using a similar design but over three to five shifts. Again, particulate exposures were measured and urinary biomarkers of exposure (1-hydroxypyrene) were analysed, together with skin-wipe samples.

A second set of studies used a cross-sectional design in which exposure information was limited to being currently employed as a firefighter (Al-Malki et al., 2008; Gündüzöz, et al., 2018), or using self-reported duration of employment (Abreu et al., 2017). Such studies included wildland firefighters (Abreu et al., 2017) and firefighters carrying out more general duties (Al-Malki et al., 2008), using comparison data from non-exposed volunteers (Oliveira et al., 2020b). Gaughan et al. (2014a) studied firefighters cross-sectionally but used individual urinary levoglucosan concentrations as a measure of smoke exposure. Another group of studies used a pre/post trial design to assess the effect on oxidative stress markers of PPE-wearing (Park et al., 2016), heat exposure (McAllister et al., 2018), training (Gurney et al., 2021), physical fitness test (Macedo et al., 2015), or woodsmoke exposure among apparent non-firefighter subjects (Ferguson et al., 2016; Peters et al., 2018).

(d) Induces chronic inflammation

Pre/post trials were used for the assessment of physical and psychological stress (Huang et al., 2010a; Webb et al., 2011), heat exposure (Wright-Beatty et al., 2014; Walker et al., 2015, 2017; Wolkow et al., 2017; Kim et al., 2018; Watkins et al., 2019a, b), and sleep restriction (Wolkow et al., 2015a, b, 2016a, b), as well as interventions on time-restricted feeding (McAllister et al., 2020, 2021). [The settings were controlled, so the impact of potential confounding was limited in these studies.]

Another common design for studies evaluating chronic inflammation used measurements of an outcome pre- and post-exposure, but these were observational studies, not trials, and the investigators could not control or manipulate the exposures occurring between the two time points. This design was used in eight studies (Burgess et al., 2001, 2002; Swiston et al., 2008; Hejl et al., 2013; Main et al., 2013, 2020; Andersen et al., 2018a; Wu et al., 2020a).

There were several studies carried out during and after specific incidents: four studies on firefighters attending the WTC-site in New York after the collapse on 11 September 2001 (Fireman et al., 2004; Cho et al., 2014; Tsukiji et al., 2014; Loupasakis et al., 2015; Aldrich et al., 2016; Hena et al., 2018; Singh et al., 2018; Cleven et al., 2019; Lam et al., 2020; Goldfarb et al., 2021; Weiden et al., 2021); firefighters attending the "Black Saturday" natural disaster involving bush fires that destroyed more than 450 000 hectares in south-eastern Australia in 2009 (Main et al., 2020); and a study after the Fort McMurray fire that destroyed almost 600 000 hectares in Alberta, Canada, in 2016 (Cherry et al., 2021b; Adu et al., 2022). For the WTC studies, either presence or time of arrival was used as the measure of exposure. No further information was collected, and exposures may have varied widely. In the Black Saturday event, no further information on individual exposure was collected. In the Canadian study, environmental monitoring data were considered for $PM_{2.5}$, although these were only informative at the group level and did not allow for differentiation between workers. [For all these specific incident studies, events before and after the incident that were unmeasured may also have been of influence.]

The exposure assessment in many cross-sectional studies was simply based on being a firefighter (Orris et al., 1986; Kern et al., 1993; Bergström et al., 1997; Almeida et al., 2007; Josyula et al., 2007; Yucesoy et al., 2008; Gaughan et al., 2014b; Gianniou et al., 2016, 2018). [These studies were of limited use regarding exposure assessment, because no information was included on specific firefighting activities, or the timing and intensity of exposures experienced.] Other cross-sectional studies were based on self-reported exposures to heat (Watkins et al., 2021) and fire smoke (Greven et al., 2011, 2012). Self-reported exposures are prone to bias and misclassification, particularly with regard to identifying frequency (e.g. number of fires fought). [Among the strongest assessments of exposure were those that employed quantitative (individual) exposure measurements (Burgess et al., 2002; Swiston et al., 2008; Hejl et al., 2013; Ferguson et al., 2016; Adetona et al., 2017b; Andersen et al., 2018a, b).]

(e) Is immunosuppressive

Pre/post approaches were used to assess the immunosuppressive effects of engagement in firefighting (Smith et al., 2004, 2005) and exposure to specific firefighting-associated hazards, including heat (Walker et al., 2015, 2017), physical stress (Santos et al., 2020), and physical stress in combination with psychological stress (Huang et al., 2010a, b). The impact of potential confounding firefighting and non-firefighting exposures on the results of these studies is limited, because conditions were well-controlled in trials. The exposure–response relationships were assessed only on the basis of the presence or absence of the hazard(s). Watt et al. (2016) had high quality data on heat exposure obtained by collecting the rectal temperatures of the study participants, but these data were not used in quantitative exposure–response analyses of the study outcomes.

Potential confounding by smoking or other non-workplace exposures was not assessed in other cross-sectional studies (Bodienkova & Ivanskaia, 2003; Kudaeva & Budarina, 2005, 2007; Borges et al., 2021; Ricaud et al., 2021) or in the repeated measurement design (Montague et al., 2021). Finally, the methods used to collect exposure information and/or the metric used for quantifying exposure were not specified in three cross-sectional studies (Bodienkova & Ivanskaia, 2003; Kudaeva & Budarina, 2005, 2007).

(f) Modulates receptor-mediated effects

Exposure was limited to firefighting activity in an observational pre/post comparison study conducted by Christison et al. (2021). Qualitative categorization was used to assess the impact of job rotation (Kazemi et al., 2018; Lim et al., 2020), a semiquantitative questionnaire-based index score was used to assess repeated exposures to psychological stress, and biological monitoring was used to assess the effects of exposure to components of smoke in other observational studies (Beitel et al., 2020; Chernyak & Grassman, 2020). The potential impact of confounders was reduced in these studies by the employment of the pre/post comparison or repeated measurement study design across work-shift periods or by controlling for confounders in the analyses. However, residual confounding from non-firefighting exposures (e.g. diet) in the intervening period (17–18 years) between the exposure of interest and the measurement of effects was likely in the study that assessed the impact of exposures to PCDD/Fs and PCBs at a cable factory fire (Chernyak & Grassman, 2020). Moreover, information about the relationship between serum concentrations of the contaminants and exposures of the firefighters to smoke during the event of interest was apparently not obtained. The impact of physical stress alone (Diaz-Castro et al., 2020a) and physical stress in combination with psychological stress (Webb et al., 2011) was investigated in a randomized control trial of nutritional supplements and a pre/post trial, respectively, with exposures to equal quantities of the hazard(s) of interest under controlled conditions. Although the exposure–response relationships were assessed only on the basis of changes across specified exposures to the hazard(s) in these cases, confounding was minimized, as the participants served as their own controls.

(g) Causes immortalization, and alters cell proliferation, cell death, or nutrient supply

Quantitative assessment of exposure to constituents of smoke, including PFAS and PBDEs by biomonitoring was conducted in a cross-sectional study with appropriate control for potential confounders (Clarity et al., 2021). The biomarkers were considered appropriate for assessing the relationship between firefighting-related exposures and telomere length in the study because of the relatively long half-lives of the compounds of interest and the minimum career length of 5 years for the firefighters in the study (Clarity et al., 2021). Occupation and organophosphate flame-retardant concentration in spot urine samples were used to assess exposure in another cross-sectional study but without control for potential non-workplace exposures to products containing these chemicals (Trowbridge et al., 2022). No firefighting exposures were considered in another cross-sectional study that was available (Ranadive et al., 2021). A combination of equal exposures to physical and psychological stress under controlled conditions was investigated in a randomized control trial of a nutritional supplement (Diaz-Castro et al., 2020b). Confounding in this study was minimized since the participants served as their own controls.

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