Fire effluent contaminants, predictive models, and gap analysis

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Buncefield Fire, 2005. Photo courtesy of Niall Ramsden

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Key words:
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Contents

Preface

The “Eco-tox” project was funded by the Swedish Fire Research Board (Brandforsk) to investigate which chemical species should be included in an eco-toxicological evaluation of fires and to catalogue the existing models and measurement methods that are appropriate to characterize the identified species. This report is intended to provide information about the eco-toxicants (chemical compounds that are harmful to people and the environment) produced in fire effluent and the predictive models and measurement techniques that can be used for determining the presence and concentrations of eco-toxicants caused by a fire incident.

The input of the Reference Group is gratefully acknowledged: Dr Anne Steen-Hansen (SP Fire Research A/S), Professor Patrick van Hees and Dr Berit Andersson (Lund University of Technology), Claes-Håkan Carlsson (Swedish Civil Contingencies Agency), Lars Brodin (Swedish Fire Protection Association, SVBF), and Dr Per-Erik Johansson (Swedish Fire Research Board, Brandforsk). The authors would also like to thank Brenda Waldekker for her extensive work on adding and updating hundreds of references to the reference database.

Summary

Fire effluent is typically comprised of many compounds and particulates that are known to be harmful to people and the environment. The extent of contamination depends on the fire conditions, the fuel, the surrounding environment, and time. There are many stakeholder groups interested in understanding the effects of fire on the environment for a variety of reasons. This report and the accompanying spreadsheet can be used as a tool by a wide range of stakeholders as guidance toward the information necessary to plan activities related to assessment of damage before (pre-planning, life cycle assessment), during (response), and after (clean-up, research, lessons learned) a fire event.

This report is essentially a literature review of the harmful effects of unwanted fire on the environment. The types of fires included are: structure fires (residential, commercial, industrial), vehicle fires (automobiles, lorries, trains), and wildland fires. Each of these types of fires may produce characteristic effluent and/or have specific traits that warrant individual consideration. Likewise, the actions of the emergency responders during a fire incident may affect the impact of the fire on the environment.

Methodologies for determining the extent (both breadth and depth) of environmental contamination are presented. These methodologies include predictive models and physical measurements. A spreadsheet accompanies this report and is designed to allow data relating to expected eco-toxicants resulting from the fire types listed above to be searched by species, formula, chemical abstract service number, or environmental phase. The spreadsheet indicates which predictive or measurement method might be appropriate to use and includes discussion, when available, of the uncertainty of the results and any limitations to its use. This information is also included in the appendices of this report for completeness, however, the strength of the spreadsheet format is that it allows sorting of the data, which greatly enhances its usefulness but is not possible to do in the static tabular format of this report. The reader is therefore strongly encouraged to use the spreadsheet to search for and cross reference the most appropriate model(s) or measurement technique(s), or the eco-toxicants that may be present for the application of interest.

A general discussion of life cycle assessment (LCA) as it applies to fire is also included in this report. Typical LCA does not consider fire as an end of life scenario, however, it is possible to use LCA thinking to compare the environmental effects of options such as the use of flame retardant chemicals, fire suppressant media or firefighting tactics.

Finally, a gap analysis is presented wherein the completeness of the data collected from literature and fire testing reports is evaluated and areas that could benefit from additional research are identified.

Sammanfattning

Utsläpp från bränder består typiskt av ämnen och partiklar som är skadliga för människa och miljö. Omfattningen av utsläppet och kontamineringsgraden från en brand beror på brandens förbränningsförhållanden, bränslet, den omgivande miljön och omfattningen av utsläppet. Det är många grupper i samhället som är intresserade av att förstå effekterna på miljön från en brand. Denna rapport och det medföljande kalkylbladet kan användas som ett verktyg för att ta fram riktlinjer för att utvärdera skadebilden: i förberedande syfte (incidentplaner, livscykelanalyser), under (respons), och efter (sanering, forskning, erfarenhetsuppföljning) en brandincident.

Rapporten är i huvudsak en litteraturstudie av de skadliga effekterna på miljön från oönskade bränder. De olika typerna av bränder som har inkluderats är: byggnadsbränder (bostäder, affärsfastigheter, industri), fordonsbränder (bilar, lastbilar, tåg), och skogsbränder. Var och en av dessa typer av bränder kan producera karakteristiska utsläpp vilket kräver individuellt beaktande. Insatsen från räddningstjänsten vid en brand är ytterligare en faktor vilken kan påverka inverkan av branden på miljön.

Metoder för att bestämma omfattningen (både vidden och djupet) av kontamineringen av miljön presenteras i rapporten. Dessa metoder innefattar både prediktiva modeller och fysiska mätningar. Ett kalkylblad medföljer rapporten vilket är utformat för att möjliggöra sökning av data om förväntade eko-toxiska ämnen relaterade till de typer av bränder som nämnts ovan. Sökningen kan göras baserat på ämnesnamn, kemisk formel, CAS-nummer, eller förekomsten i miljön, som t.ex. i mark, luft eller ytvattenvatten. Kalkylbladet indikerar vilken prediktiv- eller mätmetod som är lämplig att använda och inkluderar i vissa fall en diskussion av osäkerhet i resultaten och begränsningar i användningen. Denna information finns dessutom inkluderad i appendix i rapporten, men fördelen med kalkylbladet är att det möjliggör sortering av data vilket avsevärt ökar användbarheten. Läsaren uppmanas därför att använda kalkylbladet för att söka och korsreferera till de mest lämpliga modellerna eller mätmetoderna, eller de eko-toxiska ämnen som kan vara relevanta för den aktuella applikationen.

Rapporten innehåller också en generell diskussion om applicering av livscykel analys (LCA) på bränder. Normalt innefattar inte en LCA brand som ett end-of-life scenario, men det är möjligt att använda LCA för att t.ex. utvärdera effekterna på miljön från valet av användningen av flamskyddsmedel, släckmedel eller brandbekämpningstaktik.

Slutligen presenteras en analys där fullständigheten av informationen som insamlats från litteraturen och testrapporter utvärderas och där man också identifierar områden där kompletterande forskning skulle vara av nytta.

Abbreviations

Abbreviation	Name/Description
α, ξ	Correlation constants
ϕ	Equivalence ratio
A	Air
Aer	Aerosol
AFFF	Aqueous Film Forming Foam
AhR	Aryl hydrocarbon receptor
B(a)P	Benzo(a)Pyrene
BBR	Swedish building code
Br	Bromine
BTEX	Benzene Toluene Ethylene Xylenes
CAS	Chemical Abstract Service
CEN	European Committee for Standardization
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFC	Chlorofluorocarbon
Cl, Cl_2	Chlorine
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
COMAH	Control of Major Accident Hazards Regulations 1999
CPD	Construction Product Directive
CPh	Polychlorinated phenyls
CPR	Construction Product Regulation
C_x	Concentration of species x
decaBDE	Decabromodiphenyl Ether
EEA	European Environment Agency
EGOLF	European Group of Official Fire Laboratories
EU	European Union
EXAP	Extended Application
FEC	Fractional Effective Concentration
FED	Fractional Effective Dose
FR	Flame Retardant
F, F_x	Fluorine, F-factor for species x
GW	Groundwater
H_2S	Hydrogen Sulfide
H_2SO_3	Sulfurous acid
H_2SO_4	Sulfuric acid
HBCDD	Hexabromocyclododecane
HBr	Hydrogen Bromide
HCl	Hydrogen Chloride
HCN	Hydrogen cyanide
HF	Hydrogen Fluoride
HFC	hydrofluorocarbon
HRR	Heat Release Rate
IC	Incident Commander
ILCD	International Life Cycle Data system
ISO	International Organization for Standardization
K	Kelvin
LCA	Life Cycle Assessment
LC_{50}	Lethal concentration at which 50 % of a population dies

Li-ion	Lithium ion
MSDS	Material Safety Data Sheet
MTBE	Methyl Tert-Butyl Ether
N_2O	Nitrous Oxide
NiMH	Nickel Metal Hydride
NIST	National Institute of Standards and Technology
NO	Nitric Oxide
NO_2	Nitrogen dioxide
NOx	Nitrogen Oxides
O_3	Ozone
ODP	Ozone Depletion Potential
PAH	Polycyclic Aromatic Hydrocarbon
PBB	Polybrominated biphenyls
PBDE	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PE	Polyethylene
PFC	Perfluorinated organic compound, perfluorocarbon
PFOS	Perfluorooctanesulfonic acid
PM	Particulate Matter
POF_3	Phosphoric trifluoride
PPE	Personal Protective Equipment
PVC	Polyvinylchloride
REACH	Registration, Evaluation, Authorisation and restriction of Chemicals
S	Soil
Sed	Sediment
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
SOx	Sulfur oxides
SW	Surface water
T	Temperature
TBBP-A	Tetrabromobisphenol-A
TEF	Toxic Equivalency Factor
TEQ	Toxic Equivalent
TMTM	tetramethylthiuram monosulfide
UK	United Kingdom
US, USA	United States, United States of America
uv	Under-ventilated fire conditions
VOC	Volatile Organic Compound
WEEE	Waste Electrical and Electronic Equipment
WHO	World Health Organization
wv	Well ventilated fire conditions
Y_x	Mass fraction of species x
Δhc	Heat of combustion

1 Introduction

As people learn more about their impact on each other and the environment, new technologies are developed to replace old ones. At any given time there will exist both old and new solutions to a particular problem as the older one is phased out by the newer one. In some cases the use of a chemical or compound may be banned if it is deemed very harmful, but there may be stockpiles of it in warehouses or elsewhere for many years after the ban and which are still susceptible to fire. New and emerging technologies are also of interest because they may be an excellent solution to one type of problem and yet cause damage in other areas.

In the world of commercial research and development, new products are created based on their increased performance over existing products. Questions of weight, strength, production cost, ease of use, and other characteristics tend to be given the highest priority when decisions are made. Issues such as fire performance, while important, are not necessarily design parameters. Environmental performance is seldom an overlying design parameter, and the task of proving that the new technology or material meets environmental goals, i.e., estimating the transport mechanisms, fate, and concentrations of eco-toxicants produced by fire, is relatively ambiguous and open to interpretation.

In the case of fire, development of new environmentally friendly fire protection systems, suppression media, firefighting technologies, and fire retardant materials are active areas of research [1-5]. Evaluation of the impact of implementing these new technologies and materials is necessary if their intent is to reduce the impact of fire on the environment, e.g. fire testing or modeling should be conducted to compare the new approach with a benchmark.

The words “toxicity”, “eco-toxicity”, “environment”, and “wildland” can have different meanings depending on the context in which they are used and the audience to which they are conveyed. It is therefore important to define these terms at the outset of this report. Toxicity is the degree to which a chemical or compound can damage an organism; the term usually refers directly or indirectly to humans as the target organism. Eco-toxicity is by analogy the degree to which a chemical or compound can damage the environment. The environment consists of all organisms and their natural habitat, whether or not their natural habitat has been altered by humans. The environment may be global in scale or it could be confined to the immediate vicinity of a fire incident. Wildland is defined in accordance with the draft standard document ISO/NP 19677 as land that has never suffered human intervention, or has been allowed to return to its natural state, or land that is managed for forestry or ecological purposes [6].

In the context of this report, the term eco-toxicant will specifically refer to species (chemicals or compounds) with the potential to significantly damage the environment and which are emitted in large amounts from fires relative to other anthropogenic sources. The reason for this distinction is that numerous inorganic and organic compounds emitted from fires can have an eco-toxicological impact (e.g. methane and carbon dioxide are greenhouse gases) but their production from fires is insignificant relative to other sources [7, 8]. Thus, based on previous research conducted at SP comparing emissions from fires to emissions from other sources, eco-toxicants will be used to refer to large organic species, particulate emissions, metals, etc in this report. Many eco-toxicants belong to groups or categories of chemicals, such as polycyclic aromatic hydrocarbons (PAHs), in which the specific species are numerous and their distribution within the total PAH emission depends on the source, the burning conditions, and time. For this reason, the eco-toxicants that behave in this manner will be treated in the text collectively as groups.

Fire effluent impacts the quality of air, surface water, groundwater, sediment, and soil. Firefighting operations also impact the environment, particularly water, sediment, and soil. The work presented in this report is intended in part to assist emergency responders in making strategic and tactical decisions based on the consequences to people and the environment, therefore firefighting operations are considered separately from the fire source for structural fires, vehicle fires, and wildland fires. Timely understanding of environmental contamination is of critical importance during large fire events when emergency response strategies are planned and mass communication is necessary for public safety. Therefore the work presented in this report is also intended to support incident management decisions that affect public and environmental health, such as when to advise people not to drink their water or go outside.

Commercial developers, environmental consultants, regulators, researchers, standards developing organizations, and policymakers all have a stake in using accurate, relevant measurement techniques to support their decisions regarding new technologies and materials that affect the impact of fire on the environment. Clearly, guidance is needed concerning which models are relevant, the usefulness of the information they provide and how they can be applied. Further, researchers and standards developing organizations will benefit from a knowledge gap analysis upon which to base decisions regarding where to focus future work.

Fire is a naturally occurring process, therefore fire effluent is easily found in the environment regardless of a specific fire incident. It is important to understand that contamination of a site due to a fire is a matter of differentiating between the pre- and post- fire levels of eco-toxicants. The interaction between a fire and its surroundings or environment is illustrated in Figure 1. This figure shows how fires cause harm to the environment through:

- Direct gaseous and particulate emissions to the atmosphere
- Spread of atmospheric emissions
- Deposition of atmospheric emissions
- Soil contamination
- Ground and surface water contamination

The effect of emissions depends in part on the transfer mechanism (e.g., emission of gaseous species and the effect of weather, or the emission of contaminated firefighting water and its interaction with the drainage system) and on the specific species (i.e., small gaseous compounds, large particles and the range of species in between). It should also be noted that emissions may undergo chemical changes after emission, e.g. chemical modification of nitrogen oxides (NO_x) in the atmosphere due to ultraviolet light.

A wide variety of eco-toxicants are emitted in fire effluent. The degree to which these eco-toxicants are partitioned into different phases depends on many things, including their source, the burning conditions, the weather, and their physical characteristics. Some eco-toxicants preferentially partition into airborne particulates and agglomerate until they fall into water or soil. Other eco-toxicants remain in the gas or aerosol phase and are inhaled by people and animals. Groups of eco-toxicants, such as PAHs and VOCs, are comprised of species that partition differently according to their density, with the heavier species tending to deposit on surface water or soil while the lighter species tend to remain airborne. The characteristics of many eco-toxicants change as they are transported away from the fire. When possible, the most common environmental phase or exposure pathway is listed in the following sections.

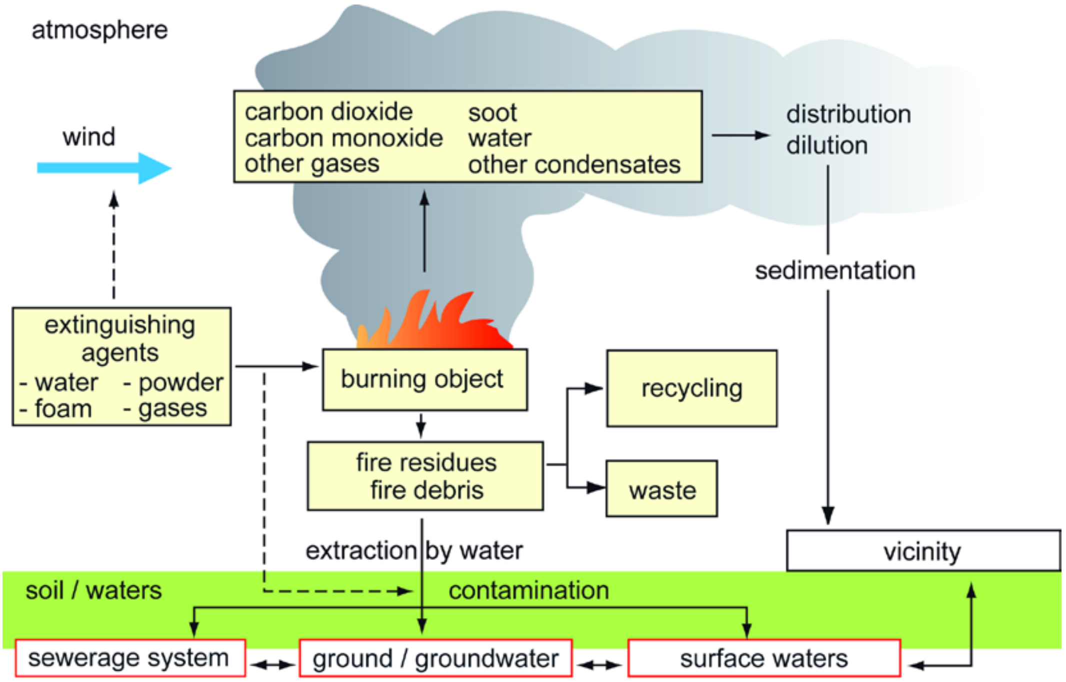

Figure 1: Emission pathways from fire. Adapted from reference [9].

Determination or characterization of fire effluent needs to be conducted in different ways depending on whether the effluent has been emitted to air, ground water or soil. Sampling of emissions to the air can only be made when the fire is on-going and sampling from the fire plume is extremely difficult. While it has been tried at times through airborne sampling from a variety of aircraft it is unclear how such point samples can be related to deposition. Ground based sampling below the plume can provide more direct input concerning potential deposition.

Emissions to the aquatic environment can be both to surface and to ground water. If extinguishing media have been used and run-off water collected, samples should be taken for analysis. Samples should also be taken of groundwater and surrounding flowing water or lakes. The location and nature of sampling should be informed by the knowledge of the pathway by which fire water run-off can spread into the environment. A detailed post incident analysis of pathways should be carried out to reveal all potential or actual routes to receptors.

Finally, emissions may occur to the terrestrial environment. Samples should be taken of soil in the downwind direction from the fire in the path of the fire plume. The exact analysis of the samples will depend on the products stored on site and their likely breakdown products as well as the firefighting agent used.

Knowledge of the potential fate and transport of eco-toxicants that could be produced by fire can be useful when comparing alternative solutions to many problems. LCA has gained popularity in recent years as a methodology that considers the environmental burden of such diverse activities as producing a product, creating or changing laws, or comparing process A to process B for a single product. Typically, fire is not considered in LCA as an end of life scenario, however, fire is an important scenario for such materials as flame retardants and fire suppressants. LCA thinking takes a viewpoint contrary to the other perspectives addressed in this report in the sense that the contamination has not happened yet. It is a “what if” exercise that will hopefully guide decision-makers toward solutions that minimize negative impact on the environment.

In the following chapters the generation, fate, transport, and other characteristics of eco-toxicants that could be produced in fire effluent from a range of fire types are discussed, as well as the effects of firefighting activities. Methods of predicting and techniques for physically measuring eco-toxicant concentrations are presented. Guidance for the implementation of the resulting data, such as LCA input or for development of new firefighting tactics, is also provided.

2 Structure fires

The environmental impact of fires in structures has been organized in this chapter according to the type of structure and the major categories of eco-toxic effluent issued by the burning structure, its contents, and firefighting operations. Residential/commercial structures are addressed in section 2.1 and warehouse/industrial fires in section 2.2.

2.1 Residential/commercial structure fires

Residential and commercial structures include single and multiple family residences, along with any other types of structures that cannot be identified as purely industrial in nature (which are dealt with separately as they potentially represent an entirely different type of fire effluent). In this section, the environmental impact of the burning structure and its contents is investigated.

2.1.1 Flame retardants

Flame retardants are present in many building materials, furniture and furnishings present in residential and commercial buildings. The term “flame retardant” (FR) refers to a broad group of chemicals with significantly varied chemical composition and potential interaction with the environment. FRs can be divided into two main groups based on chemistry:

- Organic FRs
    - halogens, predominantly bromine and chlorine
    - phosphorus-based
    - nitrogen-based
- Inorganic FRs
    - aluminum and magnesium hydroxides
    - ammonium polyphosphate
    - a variety of salts and other chemicals

The mode of action varies for different types of FRs, e.g. halogenated FRs act in the gas phase through inhibition of the combustion process; phosphorus and nitrogen based FRs often act together as intumescent FRs, creating a thermal barrier to the release of pyrolysis gases from the product or individually producing a char layer; and inorganic hydroxides act by diluting the flammable product with inflammable material and producing gaseous water to dilute the combustion gases and create third body termination species which quench the combustion process.

Each group of FR potentially contains numerous individual chemical species, in particular the organic FRs, each with individual toxicity and eco-toxicity. Further, they are used in a variety of different applications. Brominated FRs may be present in building construction materials and furnishings. Some brominated compounds are banned or their use is restricted either through regulation or voluntary industrial market removal today but they continue to exist in the field. The list of brominated FRs which may exist in products is long, over 70 species has been cited [10]. Among these compounds, those with greatest application both presently and historically include: polybrominated biphenyls (PBB, no longer on the market), tetrabromobisphenol A (TBBP-A, still in use), polybrominated diphenyl ethers (PBDEs, including decaBDE, presently being voluntarily phased out by industry), and hexabromocyclododecane (HBCDD, still in use) [11].

FRs have been used since Roman times when they prevented siege towers from catching fire. However, the first patent on a FR was the British Patent 551, patented by Obadiah Wilde in 1735 to flame retard canvas for use in theatres and public buildings. The worldwide consumption of FRs amounted to approximately 2 million tons in 2011, according to a 2012 market study by Townsend[1]. Over the past 4 years the consumption of FRs has grown substantially and is projected to continue to grow at a global annual rate of 4-5%. Use in plastics accounts for approximately 85% of all FRs used with textiles and rubber products accounting for most of the rest. North America consumed the largest volume of FRs in 2011 with a 28% share.

The global consumption in 2011 divided according to type of FR is shown in Figure 2.

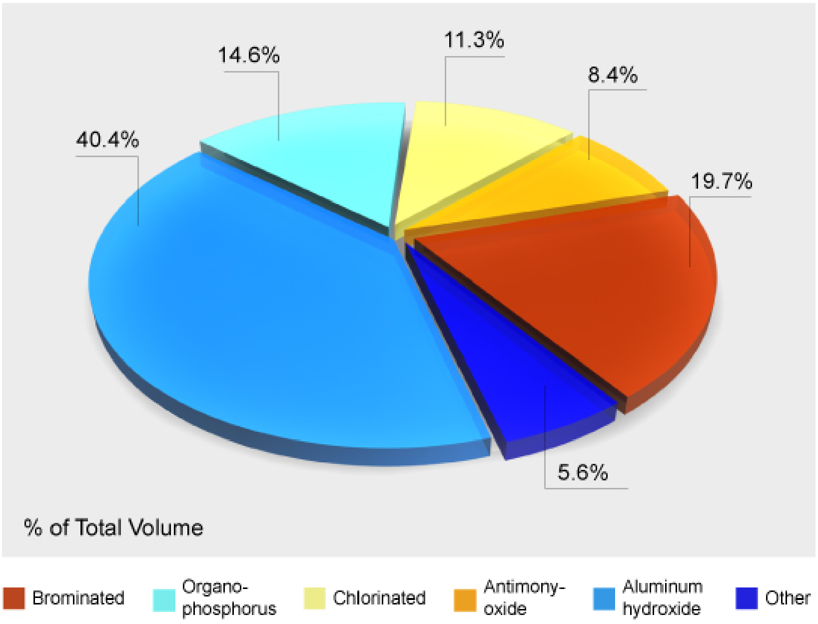

Figure 2: Flame retardant use in 2011 based on type of flame retardant. Reproduced by permission of www.flameretardants-online.com.

The presence or absence of FRs receives a significant amount of attention but typical residential and commercial premises include both flame retarded and non-flame retarded material. Further, FRs have greatest impact on the fire chemistry on incipient or small fires. Once a building fire is large the species produced will be highly dependent on the ventilation conditions and intrinsic elemental species present and only to a lesser degree determined by the presence or absence of FRs.

2.1.2 Building materials and furnishings

FR materials have received much attention due to their potentially harmful effects on humans and the environment, but there are also non-FR construction materials and furnishings that could emit compounds that exhibit harmful effects in extreme conditions and require characterization after a fire. For example, some wooden structural members are chemically treated to prevent rot. Furnishings such as cushions used in chairs and sofas may produce hydrogen cyanide (HCN) due to the presence of fuel bound nitrogen in the polyurethane foam [12]. Plastics such as polyvinylchloride (PVC) pipes used for water and sewage transfer can produce significant amounts of hydrogen chloride (HCl) when in a fire.

A good representation of the types of eco-toxicants that could potentially be released into the environment as a result of a structure fire is available in the samples collected from the World Trade Center debris. Lioy et al. made a detailed analysis of the inorganic, organic, and morphological characteristics of three samples of debris collected a few days

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[1] For more information see www.flameretardants-online.com.

after the event [13]. Among other constituents, they found PAHs, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins/furans (PCDDs/PCDFs), pesticides, phthalate esters, brominated diphenyl ethers, asbestos, heavy metals, and radionuclides. They measured the size distribution of the debris particles as well.

Household and office furniture is typically composed of a wood, plastic, or metal frame and may also include upholstered parts such as cushions and padded sections. Other furnishings may include natural and synthetic fabrics on the walls and floors. An investigation by Morikawa et al. examined the toxicity of gaseous fire effluent from house fires. They measured the gases in the story immediately above the fire (which was on the ground floor) and found that carbon monoxide (CO) and HCN were both present at significant levels. HCN was produced in greater quantities when synthetic furnishing were included in the fuel mix [14]. Similarly, Ruokojärvi et al. used simulated house fires to measure concentrations of PCBs, PCDDs/PCDFs, polychlorinated phenyls (CPh) and PAHs in fire effluent [15]. The fuel consisted of pieces of chipboard and old furniture. Concentrations of PAHs and PCDDs/PCDFs were found to be quite high in spite of the fact that there were no inherently hazardous materials used as fuel. In a risk assessment of FRs used in furniture, Chivas et al. has cited the emission of CO, carbon dioxide (CO_2), nitrogen oxides (NO_x), HCl, HCN, and sulfur dioxide (SO_2) in both FR upholstered and not upholstered furniture fires [16]. They go on to conclude that there is no toxic risk from FRs in upholstered furniture as long as the FRs are compliant with the Registration, Evaluation, Authorisation and restriction of Chemicals (REACH) regulations and the furniture complies with ignition requirements, although they also recommend more rigorous ignition testing scenarios for furniture.

A large body of work has been conducted over the past two decades at SP to identify the toxic and eco-toxic components of fire effluent [7, 8, 17-20]. In 1998 (using 1994 as a "typical year") and again in 2007 (using 1999 as a "typical year") the Swedish fire statistics were analyzed by SP to estimate the amount of pollutants emitted into the atmosphere from fire effluent during the course of a year. In the 1998 work CO_2, CO, HCN, NO_x, SO_2, HCl, and particulate matter (PM) are examined in detail while N_2O, PAHs, PCDD/Fs, and heavy metals are considered in a more general sense. This division is related to the difference between controlled combustion, which is a major source of the former list of species, and uncontrolled or accidental fires, which are a major source of the latter list of species. In both studies, the eco-toxicant sources and estimates of their concentration are collated with the fuel and fire type, e.g. house, school, apartment, wood, paper, textile, PVC, polyurethane (PUR), polyethylene (PE), rubber, petrol, oil. In the 2007 work the list of pollutants was expanded to include VOCs and focused on VOCs, PAHs, and PCDDs/PCDFs in more detail. An important conclusion of this work is that the major source of PCDD/PCDF emissions *is not* from structure fires while most PAH and VOC emissions *are* from structure fires. In addition to examining Swedish fire statistics, large-scale laboratory tests were conducted in which televisions [19] and furnished rooms [20] were burned. The fire effluent from these experiments was analyzed in detail and provides valuable information that can be used in toxicity and eco-toxicity models. For example, it was found that the application of water as a fire suppressant, underventilated conditions, and specific products in the fuel mix can lead to substantially increased production of PAHs, and that the PAH congeners were generally of low molecular weight.

In a 2011 review of thermal building insulation materials, Jelle compares the advantages and disadvantages of traditional, state of the art, and future materials [3]. While traditional PUR has a relatively low thermal conductivity, it releases HCN when burning. State of the art materials included were vacuum insulation panels, gas filled panels, aerogels, and phase change materials. Future materials included were vacuum insulation materials, gas insulation materials, nano-insulation materials, dynamic insulation materials, and either mixing of traditional structural material such as concrete with an insulation material or devising new structural materials with the desired insulation and strength characteristics. No mention was made in Jelle's study of the potential eco-toxicity of fire effluent from these state of the art or future materials (only PUR was mentioned in this respect); this is an area worthy of further investigation.

2.2 Warehouse/industrial fires

Warehouses and industrial structures are addressed separately from other types of structures due to the nature of their construction. Generally, these structures are designed specifically for their intended use with fire safety as a priority and are comprised of a minimal amount of combustible material. For this reason, the contents of the facility (warehoused goods or material being manufactured) is of primary interest rather than the actual structure. The fire effluent from warehouse and industrial structures is therefore heavily dependent on the specific use and contents of the facility. Fire effluent in smoke and fire water run-off are the two most commonly considered exposure pathways, however, another important pathway is the inappropriate disposal of fire damaged goods [21].

In the 1990s there were two large European research projects focused on characterizing the hazards of fires in chemical warehouses. Similar to this project, one of the outputs of the COMBUSTION project was a database named FIRE that contains information on fire types, substances, fire products, and smoke characteristics [22]. The other project, TOXFIRE, assessed the potential consequences from fires at chemical plants and storage facilities. Carefully selected materials (propylene, nylon, tetramethylthiuram monosulfide (TMTM), 4-chloro-3-nitrobenzoic acid, and chlorobenzene) were burned in laboratory experiments of a variety of scales and classified by ignitability, heat release, burning rate, smoke evolution, products of combustion, and the effects of packaging [23-25]. Similar work was done by Hietaniemi et al., in which a selection of compounds used in the chemical industry, liquid solvents, and polymers were burned in a cone calorimeter to determine the time to ignition, heat release rate (HRR), mass loss rate, and smoke production as a function of ventilation [26].

The number of industrial accidents per year has been roughly constant in Europe since the turn of the century and, according to the European Environment Agency (EEA), the severity of these accidents is declining [27]. The 2010 EEA report states that the ecological impact of industrial firefighting activities, which can contaminate surface and groundwater, is more severe than the smoke from the fires. The 2005 fire at the Buncefield fuel depot in the United Kingdom provides an example of this situation. A large fire, involving 23 storage tanks of various fuels and other products, emitted a smoke plume thousands of meters high. The fire burned for five days and destroyed most of the depot, during which time firefighters used 750 000 l of foam concentrate and 55 000 000 l of water for their operations. Fortunately, the weather conditions reduced the amount of smoke at ground level, however escaped fuel, foam, and water contaminated the oil and water supplies with perfluorooctanesulfonic acid (PFOS), benzene toluene ethylene xylenes (BTEX), and methyl tert-butyl ether (MTBE) [28, 29].

Real time assessment of the airborne levels of eco-toxicants is a very challenging undertaking. One possible method, using a mobile trace atmospheric gas analyzer, was used by Karellas et al. to measure airborne concentrations of HCl and Cl_2 during a fire at a pool chemical manufacturing facility in Canada [30]. On a much larger scale, real time monitoring of fire gases from the Kuwaiti oil fires in 1991 was conducted using atmospheric monitoring stations in place since 1982. Data collected from these stations shows that, in spite of many tons of gases being emitted daily from the fires, the levels of SO_2, NO_2, O_3, and H_2S remained below the Meteorological and Environmental Protection

Agency's permissible limits during the time of analysis (March – November 1991), although the levels were higher than they were before the fires started [31].

Using an approach better suited for assessing the environmental impact of a fire after the event, which is most often the only available recourse, Rasmussen et al. used a combination of laboratory tests and site evaluations [32] to estimate the concentrations of combustion products in the surroundings of a chemical plant in Denmark. The steps they followed were:

- Inspection and description of the site
- Categorization of waste types and collection of samples at the plant
- Assessment of fire causes
- Combustion experiments
- Assessment of source term concentrations from real fires
- Assessment of the plume rise and dispersion calculations
- Assessment of uncertainties

The transport mechanisms of semi-volatile groups of organic compounds, for example PAHs, have been found to depend on many factors. Meharg et al. examined the fallout of PAHs on soil and grass after a fire in a propylene warehouse and found that the lower molecular weight, least hydrophobic compounds tended to partition to the vapor phase and remain aloft longer than the heavier, more hydrophobic compounds, which tended to partition into particle phase and deposit closer to the source of the fire [33]. They also found that the soil was typically more contaminated than grass, depending on the PAH hydrophobicity. Meharg and French have found that using heavy metals as markers in soil and water to indicate the extent of localized contamination instead of organic pollutants may be a much cheaper and faster method [34]. They successfully tested this theory at four large-scale fires at plastics and pesticides warehouses. Conversely, the retention time of dye in earthworms was shown to be a useful marker for heavy metal pollution in the soil surrounding an industrial plastics fire in the United Kingdom (UK) [35].

Fires in pesticide plants and storage facilities can be particularly harmful due to the breakdown of common pesticide formulations into sulfur, nitrogen, phosphorus, and chlorine compounds that can react in the presence of fire to form very toxic effluent. In addition to posing serious human and environmental health risks, as evidenced by several notorious fires involving pesticide facilities, for example the leak of methyl isocyanate at the Union Carbide plant in Bhopal, India, the Sandoz warehouse fire in Basel, Switzerland, and the Bayer CropScience plant in West Virginia, pesticides are used in the timber industry and can also contribute to the toxicity of forest fire smoke [36]. In a recent case study, a fire in a pesticide facility provided some insight into the fate and transport of PCDDs/PCDFs when exposed to surfactants. The PCDDs/PCDFs were present as a result of the fire and the surfactants were associated with the pesticide run-off, not from foam fire suppressant. Grant et al. found that the transport of PCDDs/PCDFs was facilitated by interaction with the surfactants, traveling 2.4 m in less than 4 months [37].

Landfill fires pose a challenge from an environmental perspective, especially subsurface landfill fires that may not be easily detected. The presence of methane gas generated by waste material and the potential for methane extraction systems to draw oxygen into the waste fuel can exacerbate the situation. Landfills are designed to contain and facilitate sampling of the leachate. Smoke and leachate from landfill fires may contain PCDDs/PCDFs, PAHs, VOCs, PCBs, CO, and a host of heavy metals, depending on the composition of the fuel [38-40]. Øygard et al. found that elevated levels of chemical oxygen demand (COD) and heavy metals in leachate returned to normal within about 10 days after a subsurface landfill fire was extinguished and the excavated material returned [41]. The source of deep seated landfill fires may be difficult to find and may require extensive excavation in order to isolate and extinguish the fire. More discussion of landfill fires pertaining to firefighting tactics and exposure of firefighters is provided in Chapter 5.

The fate of specific types of waste, such as discarded tires and waste electrical and electronic equipment (WEEE), can present serious problems to the environment if they are involved in accidental fires. Regulations that control the end of life of these waste types have succeeded in minimizing their presence in landfills but have also inadvertently promoted the existence of large storage facilities for these materials until they can be properly processed. There have been numerous large tire fires in North America and Europe. Tires emit VOCs, PAHs, and PCDD/PCDFs, which are part of the fire plume but then can also deposit on soil, water, and plant life downwind of the fire plume. Burning tires also produce oil, which can contain the same pollutants and mix with water from fire suppression operations and run off into the soil and water. Steer et al. measured these pollutants during and after a major tire fire in Canada [42] and Lönnermark and Blomqvist conducted controlled tests in a laboratory setting to measure tire fire emissions [43]. Likewise, WEEE produces similar fire emissions and may also emit brominated compounds due to the use of flame retardants in the plastic components. Lönnermark found concentrations of PAHs, PCDD/PCDF, brominated compounds, and heavy metals in the effluent from WEEE fires [44].

2.3 Building regulations

Building fire regulations relate both to Fire Resistance and Reaction-to-Fire. Building fire regulations make an impact on material choices in structures and therefore also the emissions from structure fires. Fire Resistance relates to the integrity of a fire compartment under the influence of a given fire. Fire Resistance testing assesses integrity, insulation and stability of the construction under well-defined conditions. Regulations on fire resistance are put on construction products and building elements with a fire separating function. The Reaction-to-Fire of a product deals with characteristics such as ignition, flame spread, HRR, smoke and gas production, the occurrence of burning droplets and parts.

The European Commission published the building products directive (89/106/EEG) in 1989 to promote free trade of building products within the European Union (EU, and those countries outside the EU having an agreement with the EU to abide by the Construction Products Directive (CPD), e.g. Norway). The directive has recently be restructured and upgraded to a regulation – the Construction Products Regulation (CPR) which was adopted in 2011 and repeals the CPD with successive implementation between 2011-2013. The CPR contains seven essential requirements that apply to the building itself:

- Mechanical resistance and stability
- **Safety in the case of fire**
- Hygiene, health and the environment
- Safety in use
- Protection against noise
- Energy economy and heat retention
- Sustainability

In order to determine whether a building product complies with the CPR, European classification standards are devised and referred to in product standards. Classification documents are developed within CEN, the European Committee for Standardisation, which call on standards also developed within CEN (or in some cases through the

International Organization for Standardization (ISO) according to the Vienna Agreement).

The implication of the CPR is that building products must have a fire classification based on the same standards throughout Europe. The important issue is then how the classification standard is applied in each member country, i.e., the system itself is performance neutral. The European Classification Standards identify product performance but make no comment on what the performance should be for any given application. The level of safety a product must have in a building application in any member state is then the prerogative of building regulations in the specific member state.
A member state that regulates for a certain safety level will be able to identify the fire properties of a building product corresponding to that level according to the European classification standards. Products complying with the essential requirements of the directive are labeled CE. An overview of the system is given in Figure 3.

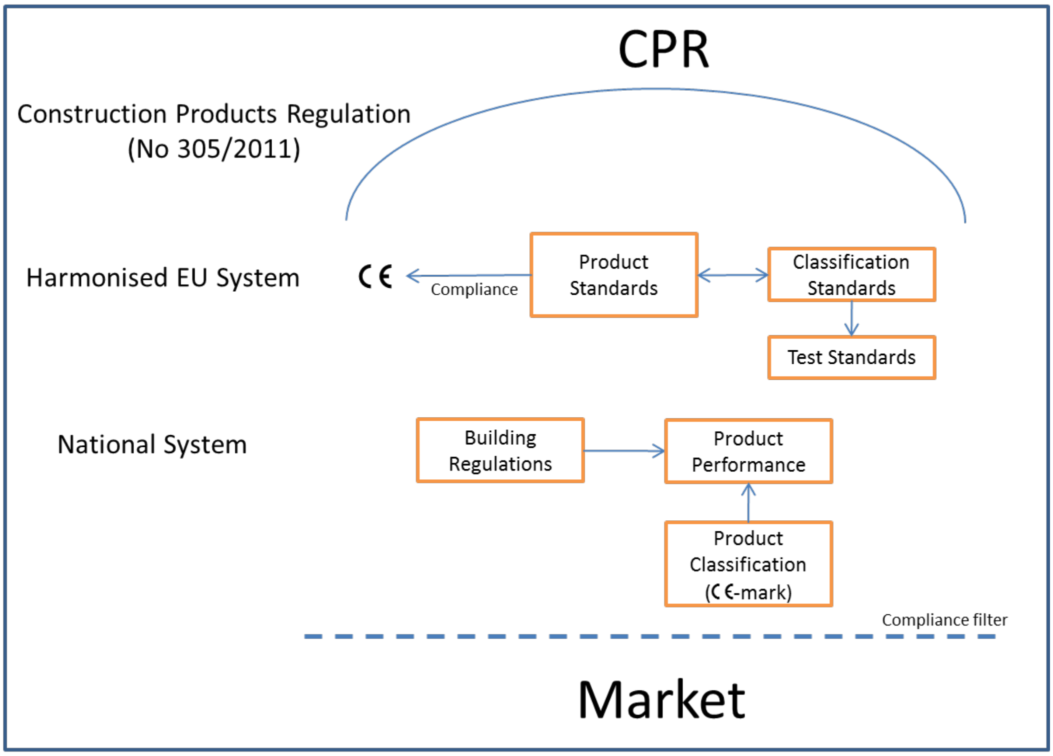

Figure 3: Schematic showing relationship between the CPR, European and national systems for building products.

Once a product standard has been developed there is a continuous need for quality assurance associated with that standard. This can include interpretation of test procedures, extended application (EXAP) of test data, technical co-operation between test laboratories, agreements of praxis between certification bodies etc. The Fire Sector Group, consisting of notified bodies[2] for testing and certification throughout Europe, is responsible for discussing these issues and defining solutions if problems arise. Technical work such as the development of good technical practice in testing relies heavily on EGOLF, the European Group of Official Fire Laboratories, and various European industrial or trade organizations.

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[2] A notified body is a body, for example a test laboratory or a certification organization, which a member state has *notified* to the European Commission as suitable for performing testing/ certification under the European system.

The European Commission published the Euroclasses in 2000 as a basis for classification of building products. The standard for Reaction-to-Fire classification of buildings products is EN 13501-1. Specific adaptations of the Euroclass system for different products have been developed and are given in the relevant product standards. The specifics can deal with the methodology for testing and determination of the Euroclass for any given product, not the definition of the Euroclass itself.

Seven main classes have been included in EN 13501-1: A1, A2, B, C, D, E and F. Additional classes apply to smoke development and the occurrence of burning droplets. In many cases the test methods used are developed within ISO and later adopted within CEN through the Vienna Agreement. These standards are well known and some of them have been in use in various countries throughout the world for many years. ISO/TC92/SC1 has, in liaison with the CEN, actively been involved in the development of European standards. These standards are called EN ISO to indicate that they are both global and specifically European.

The test requirements for the classes included in EN 13501-1 have been designed based on the large-scale reaction-to-fire performance of products from a number of product groups. In particular, correlation has been made between EN 13823 (SBI), the main test method in EN 13501-1, and ISO 9705/EN 14390 which is a room scale test for surface lining products.

Class B in EN 13501-1 represents materials that do not give flashover in the reference room test, whereas Class C - Class E do give flashover after a certain time in the reference room test. Classes A1 and A2 are the highest classes and are not explicitly correlated to the reference room but represent instead different degrees of limited combustibility of a product. Class F signifies that no Reaction-to-Fire performance has been determined.

Compliance with the CPD requires that products, where a product standard exists, are tested and CE-marked to allow access to the European market. This does not, however, define what level of performance any given product must have to be approved for use in any specific country.

The Swedish National Board of Housing, Building and Planning – BOVERKET – is a central government authority responsible for issuing building regulations and national subsidies for housing and energy efficiency measures. Boverket is responsible for detailed mandatory provisions and guidelines on essential technical requirements for construction, in particular relating to the building as a system applied to sustainable construction, reconstruction and building management. Boverket gives legal advice in the development of regulations on essential technical requirements on construction. The agency is responsible for detailed regulations on user safety as well as national essential requirements on buildings such as suitability, accessibility and usability for disabled persons.

The Euroclass system is fully implemented in Sweden and the Swedish building code (BBR) [45] sets requirements using the Euroclasses. According to BBR, classification shall be made based on the Building classification:

- BR0 – Buildings with a very high need for protection
- BR1 – Buildings with a high need for protection
- BR1 – Buildings with a moderate need for protection
- BR3 – Buildings with a low need for protection

Further, spaces in buildings shall, on the basis of the intended occupancy, be divided into the following occupancy classes:

- Occupancy class 1 – Industrial, offices, etc
- Occupancy class 2 – Places of assembly, etc
- Occupancy class 3 – Dwellings
- Occupancy class 4 – Hotels, hostels, B&B and other temporary residences
- Occupancy class 5 – Healthcare environments
- Occupancy class 6 – Premises with increased risk

The materials that may be used depend on the building classification and occupancy class.

3 Vehicle fires

In general, fires in vehicles are suppressed using hand-held extinguishers, water, and foam, depending on the nature, size, and location of the fire. If emergency services are called to respond, potentially large amounts of water and foam may be applied to the fire. Most roads are designed to divert water into a drainage collection system that might simply consist of a ditch or small channel alongside the road, perhaps leading to a holding pond. Alternatively, the drainage collection system might connect road run-off water to a treatment facility. The fact that vehicle fires can occur any place that is accessible to vehicles, including railways, can add complexity to the containment of fire suppressants.

Lönnermark and Blomqvist found that the gaseous fire effluent from an automobile fire is likely to consist of HCl, SO_2, VOCs, PAHs, and PCDDs/PCDFs [46]. Analysis of run-off water from three full-scale automobile fire tests indicated that it contained elevated levels of organic compounds and metals. Comparison with data from other research shows that lead, copper, zinc, and antimony appear to be significant in water run-off from automobile fires as well [46].

Hazardous materials typically found in automobiles that may escape into the environment in the case of a fire, but not necessarily as fire effluent, are battery acid, engine oil and fuel, refrigerant, air-bag compressed gas, hydraulic fluid from brakes, suspension, and transmission systems, paint, adhesives and sealants, and magnetic material [47].

Larger commercial vehicles, such as lorries, buses, coaches, and rail vehicles would be expected to produce similar fire effluent in larger quantities than automobiles if they are burning freely in open air, but may also produce other eco-toxicants if they are transporting cargo or are burning in an enclosed space, such as a tunnel. In 1995, Wichmann et al. burned two automobiles, a subway car, and a train car in a tunnel and examined the deposition and distribution behavior of PCDD/F and PAH residue in the tunnel [48]. He found that the homologue distribution patterns vary greatly and cannot be generalized, however, the isomer distribution patterns are in good agreement with those of incineration models. The tunnel suffered considerable contamination and the wreckage also required treatment before disposal. There is little information in the literature about the environmental impact of transport vehicle fires, however, there is some information available on the internet regarding the difficulties of responding to transport vehicle fires in which hazardous materials are present. A search of the US Office of Hazardous Materials Safety's Incident Reports Database shows that 4147 incidents have been reported since 1972 that involve highway and railway transport of materials, fire, and environmental damage[3]. A similar search of the Swedish IDA database[4] shows 5569 roadway incidents involving fire for which the emergency services responded from 1998 (for cars and "other" road vehicles) or 2005 (for buses, trucks, caravans, and rail vehicles) until 2012. It is not known if any of these incidents included transport of hazardous materials. Even if the material is not considered hazardous, the amount of suppression agent needed to extinguish a fire, especially a cargo fire, could be considerable. The pressure to extinguish this type of fire as quickly as possible is high so that roadways and railways can be re-opened, therefore time spent on proper containment of suppression media may be minimized.

Electric and hybrid electric power are emerging alternative technologies to the internal combustion engine commonly used as a power source for vehicles. Electric powered vehicles typically use batteries to deliver energy to the drive train, although future

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[3] For more information see https://hazmatonline.phmsa.dot.gov/IncidentReportsSearch/search.aspx
[4] For more information see http://ida.msb.se/ida2#page=a0087

technology may include other electro-mechanical systems such as flywheels and hydraulic accumulators [49]. The most common batteries are currently nickel metal hydride (NiMH) and lithium-ion (Li-ion), although lead acid batteries are also available. Measurements of fire effluent from Li-ion batteries, including battery packs used in vehicles, show that high levels of hydrogen fluoride (HF) and phosphoric trifluoride (POF_3) are present [50]. In a recent effort to develop best practice guidelines for emergence response to incidents involving electric vehicle batteries, Long et al. states that there is no current agreement on best practices for responding to electric vehicles fires; some sources recommend allowing the fire to burn out if the battery is involved and exposure is minimal, others suggest that large amounts of water should be applied to reduce the risk of re-ignition. Fire water run-off collected from Long's fire tests involving electric vehicles contained elevated levels of organic and inorganic carbon compounds, chloride, fluoride, and a range of metals [51]. The official guidebook for handling dangerous goods and hazardous materials incidents in the US, Canada, and Mexico (ERG2012) includes recommendations for using dry chemical, CO_2, water, or foam fire extinguishing agents for vehicle fires involving electric or hybrid electric vehicles, but also warns that extinguishment tactics depend on the types and designs of the batteries. This guidebook provides detailed instructions for responding to virtually all listed dangerous and hazardous materials that are transported within North and South America [52]. In Sweden there is online guidance available for dangerous goods (farligt gods) in a format similar to the material safety data sheets (MSDS) that are used worldwide for handling, using, and transporting chemicals and compounds[5].

There are other emerging alternative technologies on the horizon, some of which have already been implemented. Renewable bio-based fuels such as ethanol and biodiesel are becoming commonplace and the infrastructure for hydrogen fuel cell vehicles is in the early stages of implementation[6]. The environmental consequences of fires involving most of these new fuel technologies have not been fully established, although it is known that polar solvents such as ethanol can react with firefighting foams in an unproductive way [53]. Trends in best practices, recommended tactics and strategies, and standard operating procedures for responding to vehicle fires are changing as new fire risks emerge, although generally at a slower pace.

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[5] For more information see https://www.msb.se/sv/Forebyggande/Transport-av-farligt-gods/.

[6] For more information see http://www.afdc.energy.gov/fuels/.

4 Wildland fires

As defined in the introduction of this report, the term wildland is land that has never suffered human intervention, or has been allowed to return to its natural state, or land that is managed for forestry or ecological purposes. Wildland fires can be either natural wildfires and man-initiated fires, including prescribed burning and agricultural fires. Therefore the commonly used term “forest fire” is a subset of wildland fire. The smoke from wildland fires can have a widespread impact on people and the environment due to transport of the smoke gases and aerosols into the atmosphere via wind and buoyancy. Depending on the scale of the fire and the specific wind conditions, the adverse effects of wildfire smoke can be felt locally, regionally, and globally and include lung disease (which in severe cases can be fatal), visibility impairment, soil and water pollution, and global warming [54-61]. As naturally occurring phenomena, the effects of wildland fires could be considered part of the ambient environment, however, wildland fire effluent can be a threat to the health of people and other organisms, valuable natural resources, structures, and infrastructure. When wildland fires become threatening and require suppression activities the fire effluent, the fire retardants, and the firefighting tactics can be harmful to the environment. In this section, fire effluent from wildland fires is described. The additional environmental burden of wildland firefighting is examined in Section 5.

The constituents of wildland fire smoke (partitioned between gas/vapor, aerosol, and particulate phases) are very likely to include PAHs and PCDDs/PCDFs, in which partitioning and total emission depend more on the burning conditions than the fuel types. PAH partitioning has been shown to favor the gas phase and species having lower molecular weights that may adsorb onto the surface of airborne aerosols when the wildland fires are intense and well ventilated. Conversely, less vigorous fires produce more high molecular weight PAH in the particle phase that tend to deposit on soil and surface waters. Denis et al. has found that measuring high molecular weight PAH in lake sediments can provide historical information about the intensity of nearby wildland fire events [62]. No single PAH species has been found to correlate with overall PAH production in wildland fires [63]. PCDD/PCDF compositions are dependent on the specific type of biomass fuel and are formed from both vaporization of PCDDs/PCDFs bound to the fuel and (mostly) from the combustion process [64].

The constituents of wildland fire smoke have been characterized by numerous researchers [65-68]; Dokas et al. provides a good review of this work from a risk assessment point of view [69]. They identify permanent gases, VOCs, PAHs and PCDDs/PCDFs, halogenated compounds, semi-volatile organic compounds, particulates, and trace elements (including toxic and heavy metals [70]) that have been associated with wildland fire smoke. These eco-toxicants, along with PCBs, were also found in smoke from fires in storage facilities for wood chips and biomass pellets [71, 72]. Wildland fire smoke can become much more complex and take on potentially more hazardous constituents if the fire spreads into areas influenced by anthropogenic activities, as was observed by Statheropoulos and Karma in a case study in which the wildland fire they were monitoring burned a plastics warehouse [73]. Insecticides and herbicides used in timber production forests may contribute eco-toxic species to wildland fire smoke, although more research is needed to determine the extent of transport and fate of these compounds [36].

For some toxic compounds, there may not be a measureable difference between naturally occurring levels in unburned areas, levels due to a wildland fire with no fire suppressants used, and levels that may be associated with the use of fire suppressants. Crouch et al.. has shown that this was the case in four wildland fires for ammonia, phosphorus, and total cyanide in surface waters [74].

Wildland fires also have an effect on the forest floor and soil. VOCs and PM concentrations in effluent from peat fires in Australia were examined in the context of risk to human health in neighboring communities [75]. The measurements indicated that, although some carcinogenic compounds were found, concentrations of VOCs and PM were within national exposure standards.

Black et al. found that the soil beneath wildland fires can form and release PCDDs/PCDFs to air and land (as ash) if the burning conditions are severe [76-79]. The soil itself can be affected by fire in both positive and negative ways, depending on the severity of the fire. If the fire is not too severe and plants are able to re-establish quickly the soil properties can be restored or even improved by removal of undesired vegetation and short term increases of pH and nutrients. Very severe fires can cause significant loss of soil structure and organic matter as well as increased leaching and erosion, among other changes [80]. Heavy metals in ash deposited on the soil can become mobile over time and contaminate soil and water as the soil pH drops. Pereira and Ubeda found that the burning conditions and topography affect the species and concentrations in ash after a wildland fire [66].

5 Firefighting operations

The environmental impact of firefighting operations, including the use of fire suppressants and tactical operations as they relate to release of eco-toxicants into the environment, is addressed in this chapter, along with wildland firefighting operations. The eco-toxic impact of the burning structural materials and contents are considered separately in Sections 2.1 and 2.2. The impact of burning wildland fires (not including firefighting operations) is addressed in Chapter 4.

5.1 Suppressants

Aqueous film forming foams (AFFF) are used in a variety of firefighting operations, particularly for flammable liquid pool fires. They are also used as a wildland fire suppressant. If foams are not contained at a fire incident they may contaminate the soil, sediment, and surface and ground waters. Foams in general can also be disruptive to water and wastewater treatment plants and supporting infrastructure, however, the specific constituents of firefighting foams, such as perfluorinated organic compounds (PFC) used in AFFF, tend to be toxic, persistent, and bioaccumulate in the environment [81].

In addition to AFFF, there are many other types of foams used in firefighting for special fire conditions. For example, alcohol resistant protein-based foams are preferred to suppress fires involving polar solvents. The chemical composition of firefighting foam is proprietary information held by the manufacturers and is rarely made publicly available, although some of the more interesting compounds have been characterized and reported in the literature by researchers. Many countries have implemented phase-out strategies for PFCs, and some manufacturers have voluntarily followed suit, although stockpiles of these chemicals will continue to be used for some time into the future. Areas that have been contaminated by firefighting foams from fire training facilities in Norway show high concentrations of PFCs in biota, groundwater, sediments, and soil [82]. Novel formulations have been developed to replace the most harmful categories of foam constituents, such as PFOS, which have EU toxicity classifications of R51 (acutely toxic to aquatic organisms) and R53 (may cause long term adverse effects on the aquatic environment) [83, 84]. The replacement foams may still have eco-toxic characteristics, albeit to a lesser degree than the original foam, and they may break down into unknown products that could have their own set of environmental toxicity concerns [82, 85-87].

Chlorofluorocarbons (CFCs, or halons) are among the most notorious class of eco-toxic fire suppressants due to their ozone depletion potential (ODP). The Montreal Protocol, which went into effect in 1989, has effectively phased out the use of halons having the highest ODPs [88]. The Kyoto Protocol, which went into effect in 2005, is a follow-on treaty that set legally binding requirements for participating countries to reduce greenhouse gas emissions. Among the groups of affected compounds are CFCs and an additional two groups of fire suppressants: hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) [89]. Similar to the PFOS case, however, replacement compounds with marginally better ODPs have been developed that may be subject to future restrictions and stockpiles of the compounds having the highest ODPs may still exist.

Water is by far the most common fire suppressant used by the fire service for structure fires. Fire water run-off is a major transporter of eco-toxicants emitted by fires. If not contained properly on the fire ground, fire water run-off may cause damage to the environment via soil contamination and erosion or by overwhelming the capacity of natural streams or water treatment facilities.

Depending on the use of the structure, it may be equipped with deluge sprinklers, water mist systems, gaseous total flooding agents, or other fixed fire suppression systems designed specifically for the structure. In this case, the fire protection design should include containment of deployed suppressants.

While wildland fires are a natural process, they do impact the soil by removing organic matter, nutrients, the microbe and invertebrate communities that dwell in it, and by degrading soil structure and porosity [80]. When chemical fire suppressants are introduced to this depleted soil environment, nutrient regeneration may be affected, depending on the chemical content of the specific suppressant, resulting in a delay in the recovery of vegetation. If vegetation recovery is delayed, erosion of the soil is exacerbated [90]. Chemical fire retardants used for wildland fires generally consist of foams or solutions, which can have an impact on temporary wetland areas and the microbial communities in soil, although the duration and severity of the impact depends on the specific characteristics of the site [91-96].

5.2 Tactics

In order to formulate the best possible strategy in the least amount of time, especially for high risk fire events, the Incident Commander (IC) will usually have a pre-plan ready that provides guidance for responding to anticipated scenarios. For warehousing and industrial situations, the content of the pre-plan is specified in the Seveso Directive [97], which states "…in the case of establishments where dangerous substances are present in significant quantities, it is necessary to establish internal and external emergency plans and to establish procedures to ensure that those plans are tested and revised as necessary and implemented in the event of a major accident or the likelihood thereof." Annex 1, part 2, of the Seveso Directive lists the dangerous substances (as of 24/7 2012 there are 48 substances) that would cause an establishment to fall within its scope.

5.2.1 Structure fires

Firefighting tactics are used to implement the strategy developed by the IC. Some examples of tactics are: evacuating occupants; changing the ventilation of a structure by applying a fan or rupturing a roof, wall, or windows; searching for the fire source; attacking the fire by applying a suppression agent; and overhauling the fire ground after the fire has been extinguished. There may be many options to choose from for each tactic and some options will have more or less environmental impact than others.

When responding to a structure fire one of the first activities performed by emergency services is to "size up" the situation. There are many steps in this activity and they are highly dependent on the structure itself, whether or not people are inside the structure, proximity to other structures or fuels, and the availability of firefighting resources. The IC forms a strategy for dealing with the fire based on these and other factors, including environmental considerations. For example, if the structure is located directly upwind of high density housing and is likely to produce large amounts of smoke, the IC may choose to extinguish the fire as quickly as possible. In a different situation, the IC may choose to let the fire burn itself out, and in fact ventilate the structure to ensure that combustion is as complete as possible, rather than risk contaminating the surrounding environment with fire suppressants and products of incomplete combustion.

How and when structures are ventilated can affect the species, concentrations, buoyancy, and morphology of fire emissions. Allowing the fire to burn in excess oxygen tends to promote higher temperatures and more complete combustion with lower production of eco-toxicants, however, the structure may be lost or suffer extensive damage. The relatively lighter and hotter smoke will rise higher into the atmosphere and possibly be dispersed across a larger area than smoke from underventilated structure fires. Underventilated conditions tend to produce more smoke with larger soot agglomerations and lower temperatures due to oxygen-limited combustion. The smoke and ash constituents may include highly toxic compounds. A potential benefit of underventilation is that it might be possible to confine the fire to part of the structure.

When attacking the fire, containment of fire suppression agents is a critical step to reduce the environmental impact of a structure fire. Whether the suppressant is gas, foam, water, gel, a combination of these, or something else, the effect of the agent on the environment that receives it must be considered when the decision to use it is made. In most cases fire effluent will be mixed together with the suppressant.

Special training will likely be needed to protect some structures, such as landfills [38] or other waste handling facilities, when developing a pre-plan for a fire/emergency response zone. Fires can burn undetected for extended periods of time after ignition deep within stockpiles of material and may not be noticed until the material collapses upon itself or an explosion occurs. If smoke is detected, or some other indication of fire is noticed, finding the source of the fire may require removal of a significant quantity of material. The environmental impact of disturbing the material must be taken into consideration in the pre-plan, especially if it is probable that the waste contains eco-toxicants.

In spite of contingency planning, training, and other efforts to prepare for fires, events can still occur that exceed the worst anticipated case. The previously mentioned fire incident at the Buncefield fuel depot in 2005 is a good example [98]. In this incident a vapor cloud formed and exploded in an area surrounded by large fuel storage tanks, resulting in additional explosions and fires involving, and ultimately destroying, most of the site. Prior to this incident the explosion of a fuel vapor cloud was not considered to be a credible risk, nor were multiple tank fires.

Faced with an unanticipated major fire incident at Buncefield, it was necessary to form a response strategy without immediate access to meteorological, toxicological, environmental, and other necessary expertise. The environmental and human health impact of the very large smoke plume that formed over the site was uncertain; fortunately it remained aloft and did not significantly contaminate the surrounding communities. The decision was made to suppress the fire rather than let it burn out. Responders used 750 000 l of foam concentrate and 55 000 000 l of water for their operations, which exceeded the containment capacity of the site. Most of the onsite firefighting resources were damaged or rendered useless due to proximity to the explosions and fires. The response to this incident was successful in that there were no deaths and the fires were eventually extinguished, it also provided opportunities to learn and improve planning for future major fire incidents. It is instructive to review the recommendations from the incident investigations board relating to the environment resulting from the response to this event [28, 29]:

- "Communities and Local Government should complete and, where necessary, initiate an assessment of the need for national-level arrangements to provide, fund and maintain, emergency response equipment (such as high volume pumps, firefighting foam and specialist pollution containment equipment). The review could also consider criteria for allocation and use of this equipment across the UK.
- The Civil Contingencies Secretariat should review guidance to responders on assessing the extent of the impact of an incident at a COMAH[7] site to ensure

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[7] Control of Major Accident Hazards Regulations 1999

appropriate scales of response and resources are provided, at local, regional or national levels.

- [The proper government agencies] should provide local contact details to local authorities and Local Resilience Forums to facilitate emergency plan development. This will ensure local authorities have clear consultation routes for the public health and environment aspects of their off-site emergency plans.
- The Civil Contingencies Secretariat should conclude their review of arrangements for obtaining and using air quality data in an emergency.
- The Environment Agency should complete its review of methodologies for assessing the potential harm to the environment arising out of credible major incidents at COMAH sites, and from the emergency response scenarios attaching to them."

5.2.2 Wildland fires

The eco-toxic impact of firefighting tactics for wildland fires can be difficult to assess and depends to some degree on the perspective taken. One can say that any anthropogenic interference in a natural wildland fire will have a negative environmental impact for the simple reason that humans are present. Following this line of reasoning, atmospheric and noise pollution from firefighting aircraft and soil erosion and sedimentation in surface waters from ground-based humans and vehicles exacerbate fire-related stresses on the natural environment when it is most vulnerable. On the other hand, one can say that without some degree of human intervention a wildland fire could burn a larger area or burn with higher intensity, thus causing more damage than if it were left alone. In Table 1, Backer et al. provides the following list of impacts associated with firefighting activities [99].

Table 1. Impacts associated with wildland firefighting activities [99].

Environmental Phase	Impact	Potential Sources
Earth	Soil compaction	Fire camps, fire lines, heli-bases, IC posts, road construction
	Erosion	Fire lines, road construction
	Non-native species	Fire camps, fire lines, heli-bases, IC posts, rehabilitation activities (seed mixes, straw-bale check dams)
	Litter and waste	Fire camps, fire lines, extinguished fuses, line explosives, and aerial ignition devices, rehabilitation activities
	Reduction of habitat	Contour-felled logs (rehabilitation activities)
	Soil contamination	Fuel spillage
Air	Air pollution	Fossil fuel, emissions-aircraft, vehicles, machinery
	Noise pollution	Aerial support
	Visual pollution	Increase of air traffic
Water	Sedimentation	Contour-felled logs and channelization, fire camps, fire lines, road construction
	Disturbance	Amphibious aircraft, removal of water for suppression activities (heli-buckets, pumping)
	Fish mortality	Fire retardants
	Eutrophication	Fertizer use (rehabilitation activities), fire retardant
	Pollution	Fire camps, fire retardant, fuel spillage, rehabilitation activities (introduction of synthetic materials)

It is generally recognized that there is no single approach to fighting wildland fires, as with any uncontrolled fire the most effective and/or least damaging approach will depend on the specific conditions at hand. Progressive wildland fire plans incorporate methodology to ensure a balanced strategy with due consideration to minimizing the impact of firefighting tactics. Some examples of tactics that can reduce the impact of firefighting activities on the environment are listed below [99].

- Use natural barriers when possible.
- Use minimum fire line width and depth to accomplish the task.
- Avoid heavy equipment in riparian areas and meadows.
- Minimize felling of live trees and solid snags.
- Use natural openings for staging areas and camps.
- Employ "leave no trace" camping.
- Avoid the spread of non-native plants.
- Do not drop retardant or other suppressants near surface water.
- Use folding water tanks.

Following the requirements of the FLAME Act of 2009, the US Department of Agriculture published a National Cohesive Wildland Fire Management Strategy that uses a risk assessment approach to ensure that fire management decisions are based on the best available science, knowledge, and experience on a regional basis. This national strategy includes elements concerned with protection of the wildland environment, balanced with other concerns such as protection of lives and property [100]. There is also an ISO guidance document currently being developed for assessing the adverse impacts of wildland fires on the environment [6].

5.3 Firefighter exposure

While it is essentially the responsibility of firefighters and other people that may be present on the fire ground to understand the environment in which they work and to wear appropriate personal protective equipment (PPE) at all times, their exposure to fire effluent is indicative of the eco-toxicants present in the fire environment. Therefore, this section is included to briefly examine the fire environment in the immediate vicinity of firefighters.

Before firefighters leave a structural fire incident they inspect the structure to ensure that there is no hidden fire in the walls, attic, ceiling, etc… and thus no possibility of re-ignition (this is called "overhauling"). While performing this task, firefighters may be exposed to elevated levels of a variety of contaminants, including CO, PAHs, NO_2, and SO_2 if they are not wearing PPE. Similarly, fire investigators may be on the fire ground without PPE immediately after a fire and thus risk exposure to toxic chemicals [101-103].

In addition to the more common products of combustion from structure fires listed above, firefighters and others working in or near the fire debris may be exposed to VOCs, PAHs, isocyanates, and halogenated compounds, depending on the contents of the structure, if not wearing suitable PPE. A detailed treatment of firefighter exposure to fire emissions, including 9 scenarios, is given in [104]. Rescue and cleanup personnel working in the vicinity of the World Trade Center were exposed to elevated levels of benzene, PCDDs/PCDFs, and PCBs during the months after the building collapsed [13, 105]. Ruokojärvi, et al.. have found similar compounds in simulated house fires [15].

Chemical vapors and gases from vehicle fires were measured in the breathing zones of firefighters, in which aromatic hydrocarbons, aldehydes, isocyanates, and CO were found [106].

6 Predictive models

Numerous studies of fire emissions have been conducted and a large body of data is available in the open literature, some of which has been presented in the preceding chapters. This chapter will deal with both predictive models relating to emissions from fires, and models to determine the toxicological and eco-toxicological impact of these emissions. Toxicological impact is included for completeness in this report as it is significant for fire fighter environments and models concerning toxicology are often confused with eco-toxicology, by presenting both it is our hope that this confusion will be avoided.

6.1 Emissions from fires

A number of emissions models have been developed based on specific tests. Emissions from fires can consist of numerous different species as had been seen throughout this report, and can go to a variety of recipients (air, water and soil) as discussed in Chapter 1. Depending of the specific species and the recipient, the effects to health and the environment can vary. This is discussed in more detail in ISO 26367-1 Guidelines for assessing the adverse environmental impact of fire effluents - Part I: General [107].

The calculation of emissions from fires is a very complicated process and exact *ab initio* calculations are not possible for complex fuels and products. In a national project conducted in 2003-2006 emission models for fire species were developed based on a combination of theoretical calculations and empirical data from different real fires and fire tests [108].

Different species in the fire are produced in different ways. In general the emissions can be divided into five different groups, depending on their determining factors:

- Species that depend specifically on the elementary composition of the fuel
- Species that depend specifically on the combustion conditions, i.e. ventilation
- Species that depend on a combination of the two first factors
- Species that are not formed in the fire but where the fire leads to their release, e.g. chemicals in a burning warehouse etc
- Species that come from the extinguishing media.

As a first course investigation of the potential emissions from a fire it can be useful to determine the nominal maximum emission based on the available amount of a specific element to produce a specific emission. This can be expressed as:

$$Y_{i,max} = \frac{y_{x,j}}{y_{x,i}}$$

where $y_{x,j}$ is the mass fraction of the element x in fuel j and $y_{x,i}$ is the mass fraction of element x in the emitted species i.

Within the project a number of different models were developed to estimate the emission of different species based on empirical data. These models are presented for the specific species below.

6.1.1 Carbon dioxide (CO_2)

Calculation of the production of CO and CO_2 are both related to the amount of elemental carbon available in the fuel but while the production of CO_2 is only slightly dependent on the ventilation conditions, the production of CO is highly dependent on the ventilation conditions. In the core of the fire, large amounts of CO are typically produced which are rapidly oxidized to CO_2 in the outer regions of the flame where oxygen is more prevalent. Other carbon containing species are also produced in a fire but these are typically in low concentrations compared to CO_2. Under normal conditions with relatively good access to oxygen (i.e. where the global oxygen concentration exceeds that necessary for stoichiometric combustion), it can be assumed that all carbon present in the fuel will end up as CO_2. If a fire has severely restricted access to oxygen this assumption will naturally be incorrect and a correction will be needed. Tewarson [109] developed the following correlation to correct for the impact of ventilation conditions:

$$\frac{Y_{CO_2,uv}}{Y_{CO_2,wv}} = 1 - \frac{1}{e^{(\emptyset/2,15)^{-1,2}}}$$

where $Y_{CO_2,uv}$ is the mass fraction of CO_2 and uv indicates under-ventilated conditions while $Y_{CO_2,wv}$ corresponds to the same mass fraction in well ventilated conditions (*wv*), and ϕ is the equivalence ratio[8].

6.1.2 Carbon monoxide (CO)

The production of CO is largely determined by the combustion conditions, i.e. availability of oxygen, although even the temperature in the fire has an effect in room fires [110]. The main effect of increasing temperature is that production of CO is moved to lower ventilation conditions. Tewarson [109] has developed a model which does not include this temperature effect but where the type of fuel has been included, which is suitable for application to fire situations:

$$\frac{Y_{CO,uv}}{Y_{CO,wv}} = 1 + \frac{\alpha}{e^{2,5\emptyset^{-\xi}}}$$

where $Y_{CO,uv}$ is the mass fraction of *CO* and uv indicates under-ventilated conditions while $Y_{CO,wv}$ corresponds to the same mass fraction in well ventilated conditions (*wv*), ϕ is the equivalence ratio, and α and ξ are correlation constants which have been developed for different fuels as summarized in Table 2.

Table 2: Mass fraction CO for well ventilated conditions and corresponding correlation factors according to Tewarson [109].

Material/Fuel	$Y_{CO,wv}$	A	ξ
Polystyrene	0,06	2	2,5
Polypropylene	0,024	10	2,8
Polyethylene	0,024	10	2,8
Nylon	0,038	26	2,0
PMMA	0,01	43	3,2
Wood	0,005	44	3,5
PVC	0,063	7	8,0

Both the Tewarson model and the model by Gottuk and Lattimer show that the increase in production of CO as a function of the stoichiometry declines for ϕ above 1,5-2.

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[8] Note that the equivalence ratio is the ratio between oxygen needed for stoichiometric combustion and that available. ϕ =1 corresponds to stoichiometric combustion, ϕ <1 to oxygen rich combustion, and ϕ >1 to oxygen poor combustion conditions.

6.1.3 Particles

Particles have two main sources in fires: a) unburned or incombustible material from the fire, or (b) soot produced from the fire. The amount of particles and their size is therefore effected both by the type of fuel and the combustion processes. Given present models it is not possible to calculate the particles produced theoretically, rather this must be based on empirical modeling. Both the temperature of combustion and the ventilation conditions can have a major impact on the amount of particles produced. Restricted access to oxygen rapidly leads to the production of large amounts of soot. Similarly when combustion temperatures sink below a certain level large amounts of soot can be produced, e.g. in smoldering fire. It is difficult to separate the effect of temperature and ventilation as restricted ventilation also leads to a reduction in combustion temperature.

Tewarson has also proposed an empirical model for the relationship between particulate matter and the degree of ventilation based on small scale tests [109]:

$$Y_{C,uv} = Y_{C,wv} \cdot \left(1 + \frac{\alpha}{e^{2{,}5\emptyset^{-\xi}}}\right)$$

where $Y_{C,uv}$ refers to the mass fraction of particles (even though particles contain not only carbon) in under-ventilated conditions, $Y_{C,wv}$ the mass fraction of particles for well ventilated conditions, and α and ξ empirical correlation constants developed for specific fuels as presented previously for carbon monoxide.

A refinement of this model has also been developed [108] where the impact of temperature is included:

$$Y_C = Y_{C,wv} \cdot f_1(T) \cdot f_2(\emptyset)$$

where the function of temperature ($f_1(T)$) is represented by separate linear function for temperatures below 400 K, between 400 K and 1000 K and above 1000K as below:

$$f_1(T) = \begin{cases} 1 & T \leq 400K \\ -0{,}0015T + 1{,}6 & 400K < T < 1000K \\ 0{,}1 & T \geq 1000K \end{cases}$$

The ventilation dependent function is based on Tewarsons relation using the correlation factors for polypropylene (α=10; ξ=2,8).

6.1.4 Polycyclic aromatic hydrocarbons (PAH)

The production of PAH is dependent on both ventilation conditions and combustion temperature. Production of PAH increases with restricted access to oxygen, i.e. for higher equivalence ratios. Lönnermark et al. [108] recommend a model where production of PAH is estimated based on the equivalence ratio:

$$Y_{PAH} = Y_T(T) \cdot \left(Y_0 + Y_{max} \cdot \frac{1}{(1 + e^{a/\emptyset - b\emptyset})}\right)$$

where

$$Y_T(T) = \begin{cases} 0 & T > 673K \\ 0{,}0039(T - 673) & 673K < T < 937K \\ 1 & T > 937K \end{cases}$$

Where Y_0 corresponds to the mass fraction of PAH under well ventilated conditions. Y_{max} needs to be determined for specific fuels although it can be based on previous data presented by Lönnermark et al.

6.1.5 Volatile Organic Compounds (VOC)

VOC refers to a collection of organic species with a broad range of toxicity and eco-toxicity depending on the size and structure of the chemical. VOC are species which are volatile at room temperature and can travel long distances in the atmosphere. In the literature benzene is often used as an indicator for this group and therefore a model for estimation of the production of benzene is presented here. The model is based on the work by Tewarson [ref]:

$$Y_{Benzene} = Y_{Benzene,wv} \cdot \left(1 + \frac{\alpha}{e^{5\emptyset-\xi}}\right)$$

where $Y_{Benzene}$ is the mass fraction benzene, $Y_{Benzene,\ wv}$ is the corresponding mass faction for well ventilated conditions, ϕ is the equivalence ration, α and ξ are correlation parameters dependent on the fuel, e.g. for TMTM $Y_{Benzene,\ wv}=1$, $\alpha=300$ and $\xi=2,5$.

6.1.6 Nitrogen oxides (NO_x)

NO_x are comprised of a mixture of nitric oxide (NO) and NO_2. NO_x are produced by two main mechanisms: from fuel nitrogen or thermally from nitrogen molecules in air. In fires the dominant mechanism is production from fuel nitrogen due to the relatively low temperatures in fires compared to commercial combustion.

According to Lönnermark et al. the mass fraction of NO_x, Y_{NO_x} can be expressed:

$$Y_{NO_x} = \left(Y_{fuelNO_x} + Y_{thermalNO_x}\right) \cdot C_{vent}$$

where Y_{fuelNO_x} is the mass fraction of NO_x produced from fuel nitrogen, $Y_{thermalNO_x}$ is the mass fraction of NO_x produced from nitrogen in air, and C_{vent} is a ventilation factor:

$$C_{vent} = 1 - \frac{d}{e^{(\emptyset/f)^{-g}}}$$

where d, f and g are correlation factors.

The mass fraction of fuel NO_x is calculated based on an assumption of the efficiency of conversion of fuel nitrogen to NO_x while the thermal nitrogen is modeled using the following equation:

$$Y_{thermalNO_x} = \frac{(aT + bT^2 + cT^3) \cdot \Delta h_c}{1\,000\,000}$$

where a, b, and c are correlation coefficients, and Δh_c is the heat of combustion for the fuel.

6.1.7 Nitrous oxide (N_2O)

N_2O, is produced at low temperatures and is therefore highly dependent on the presence of fuel bound oxygen as it cannot be produced from nitrogen molecules in air under fire conditions. Lönnermark et al. [108] presented an empirical model for the production of N_2O based on correlation to data from combustion motors and other sources:

$$Y_{N_2O} = \begin{cases} 5 \cdot Y_{fuelN} \cdot \Delta h_c / 1\,000\,000 & T < 1173K \\ \left(\dfrac{-5 \cdot Y_{fuelN}}{100} \cdot T + \dfrac{5 \cdot Y_{fuelN}}{100} \cdot 1273 \right) \cdot \dfrac{\Delta h_c}{1\,000\,000} & 1173 < T < 1273K \\ 0 & T > 1273K \end{cases}$$

Where Y_{N_2O} is the mass fraction of nitrous oxide, Y_{fuelN} is the mass fraction of fuel bound nitrogen, Δh_c is the heat of combustion for the fuel, and T is the temperature in Kelvin.

6.1.8 Sulfur oxides (SO_x) and sulfuric acid (H_2SO_4)

Sulfur oxides are produced from sulfur bound in the fuel. These species are highly soluble in water and easily produce, e.g. sulfuric acid in run-off water or rain.

Lönnermark et al. [108] presented a model for the production of mass fractions of SO_2, SO_3, sulfurous acid, H_2SO_3 and sulfuric acid, H_2SO_4:

$$Y_{SO_2} = Y_{fuelS} \cdot \frac{M_{SO_2}}{M_S} (1 - Y_{debrisS}) \cdot \left(1 - Y_{SO_3/SO_x}\right) \cdot \left(1 - Y_{runoffSO_2}\right)$$

$$Y_{SO_3} = Y_{fuelS} \cdot \frac{M_{SO_3}}{M_S} (1 - Y_{debrisS}) \cdot Y_{SO_3/SO_x} \cdot \left(1 - Y_{runoffSO_3}\right)$$

$$Y_{H_2SO_3} = Y_{fuelS} \cdot \frac{M_{SO_2}}{M_S} (1 - Y_{debrisS}) \cdot \left(1 - Y_{SO_3/SO_x}\right) \cdot Y_{runoffSO_2}$$

$$Y_{H_2SO_4} = Y_{fuelS} \cdot \frac{M_{SO_3}}{M_S} (1 - Y_{debrisS}) \cdot Y_{SO_3/SO_x} \cdot Y_{runoffSO_3}$$

where Y_{SO_2} is the mass fraction of SO_2, Y_{SO_3} is the mass fraction of SO_3, $Y_{H_2SO_3}$ is the mass fraction of H_2SO_3, $Y_{H_2SO_4}$ is the mass fraction of H_2SO_4, Y_{fuelS} is the mass fraction of fuel bound sulfur, $Y_{debrisS}$ is the mass fraction of debris bound sulfur, $Y_{runoffSO_2}$ is the mass fraction of SO_2 in the runoff water, $Y_{runoffSO_3}$ is the mass fraction of SO_3 in runoff water, Y_{SO_3/SO_x} is the mass fraction of SO_x that is SO_3, and M_x is the molecular weight of species x (S, SO_2 or SO_3).

6.1.9 Acid gases (HCl, HBr and HF)

Acid gases are normally formed when the fuel in a fire contains halogens and can are called HX where X indicates the presence of a halogen, typically either chlorine (Cl), bromine (Br) or fluorine (F). Production of acid gases is not complete from fuel bound halogens as part of the halogen forms elemental halogen gas X_2, e.g. Cl_2 A conversion factor is typically used to estimate the amount of halogen which is transformed into its corresponding acid gas, C_{HX}. Lönnermark et al. [108] suggested the following model to determine the mass fraction of acid gas produced as a function of the mass fraction of fuel bound halogen:

$$Y_{HX} = Y_{fuelX} \cdot \frac{M_{HX}}{M_X} \cdot C_{HX} \cdot \left(1 - Y_{runoffHX}\right)$$

where Y_{HX} is the mass fraction of HX produced, Y_{fuelX} is the mass fraction of fuel bound halogen X, M_{HX} is the molecular weight of HX, M_X is the molecular weight of halogen X, C_{HX} is the conversion factor for fuel bound halogen into HX, $Y_{runoffHX}$ is the amount of HX found in the runoff water.

6.2 Models to determine the toxicological hazard

There are a small number of models which have been developed to determine the toxicological hazard of an exposure to different types of chemicals, e.g.: Fractional Effective Dose (FED) and Fractional Effective Concentration (FEC) for fire emissions; the Toxic Equivalency Factor Approach for dioxins, and the Potency Equivalency Factor approach for polycyclic aromatic hydrocarbons. The FED and FEC models are strictly for human exposure typically in close proximity to the fire. These factors are significant for fire fighter environments and are sometimes confused when determining eco-toxic hazard which is why they have been included in this report for the sake of completeness.

6.2.1 Fractional Effective Dose

The concept of the fractional effective dose model is based on the assumption that the fractional lethal doses of most gases are additive. This is based on research conducted in the early 1970's by Tsuchiya et al. (see for example [111]). The fact that the toxic potency of smoke may be approximated by the additive contribution of a selection of gases has been called the N-Gas Model and was developed by the National Institute of Standards and Technology (NIST) [112].

The predicted lethal toxic potency of test specimens or fire emissions can be calculated from the fire atmosphere at each discrete increment of time [113]. The time when the sum of each asphyxiate exceeds a specific threshold value represents the time to compromised tenability. The FED can be expressed mathematically as:

$$FED = \sum_{i=1}^{n} \sum_{t_1}^{t_2} \frac{C_i}{(C \cdot t)_i} \Delta t$$

where C_i is the concentration of species i (µL/L), and $(C \cdot t)_i$ is the concentration-time product (µL/L.min) of the dose required to produce a toxicological effect for species i, Δt is the chosen time increment (minutes) If $(C \cdot t)_i$ is represented as the LC_{50} for species i then when the FED=1 the mixture of gases should be lethal to 50% of the exposed population. It is also possible to take into account the increased rate of asphyxiate update due to hyperventilation by multiplying the FED by a frequency factor, v_{CO_2} which can be expressed as:

$$v_{CO_2} = \exp\left[\frac{\varphi_{CO_2}}{(C \cdot t)_{CO_2}}\right]$$

where φ_{CO_2} is the average volume percentage of CO_2 during the time increment, and $(C \cdot t)_{CO_2}$ is 5.

Typically LC_{50} values are based on rodent lethality data and may not be directly applicable to human exposure.

6.2.2 Fractional Effective Concentration

An irritant gas model has also been developed to assess the effect of sensory/upper respiratory irritants as these species have a concentration related impact on fire victims rather than a dose related impact [114]. To a certain degree the model will also assess the effect of pulmonary irritants as most species will ultimately penetrate into the lungs.

This model calculates a Fractional Effective Concentration (FEC) rather than an FED. In the same manner as for FED, FEC assumes direct additivity of the effects of the irritant gases included. FECs are determined for each irritant at each discrete increment of time where the time until a specific threshold value is exceeded represents the time available for egress from a fire relative to defined safety criteria. NOTE this implies that FEC calculations determine the time available until incapacitation while FED as presented in the previous section relates to 30 minute lethality of 50% of the exposed population.

The FEC can be calculated using the factors, F_x, expressed as a concentration (µL/L) at which irritant x will seriously compromise the occupants' ability to escape from the fire. The factors recommended in ISO 13571 are given in Table 3.

Table 3: F-factors determined through consensus in ISO TC92/SC3 [115].

Species	**F-factor (µL/L)**
HCl	1000
HBr	1000
HF	500
SO_2	150
NO_2	250
Acrolein	30
Formaldehyde	250

The FEC can be calculated using the following equation:

$$FEC = \frac{\varphi_{HCl}}{F_{HCl}} + \frac{\varphi_{HBr}}{F_{HBr}} + \frac{\varphi_{HF}}{F_{HF}} + \frac{\varphi_{SO_2}}{F_{SO_2}} + \frac{\varphi_{NO_2}}{F_{NO_2}} + \frac{\varphi_{acrolein}}{F_{acrolein}} + \frac{\varphi_{formaldehyde}}{F_{formaldehyde}} + \frac{\varphi_{irritant}}{F_{irritant}}$$

where φ_x is the average concentration (µL/L) of irritant gas x, F_x is the concentration (µL/L) of irritant gas x which is expected to seriously compromise the occupants ability to escape.

6.2.3 Toxic Equivalents

Toxic equivalents (TEQ) is a method to express a group of species, e.g. TCDD/TCDFs, which have different toxicity in terms of how much cumulative toxicity they represent if they were emitted as their most toxic congener based on the establishment of a Toxic Equivalency Factor (TEF). This methodology has been used for a variety of compounds. Most relevant in fire effluents are the toxic equivalents for TCDD/TCDFs, PAHs, and PCBs. For inclusion in the TEF concept it is necessary for a compound to [116]:

- Show a structural relationship to the TCDD/TCDF family of compounds
- Bind to Aryl Hydrocarbon Receptor (AhR)
- Elicit AhR-mediated biochemical and toxic responses
- Be persistent and bioaccumulative

6.2.3.1 Dioxins and furans (PCDD/PCDFs)

PCDD/PCDFs can be represented as TCDD-equivalents which represent a weighted sum of both PCDDs and PCDFs. In this sum it is assumed that 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) is the most toxic of this group of chemicals and each other member of the group is assigned a factor which describes the toxicity of the species relative to that of 2,3,7,8-TCDD. The TCDD-equivalent is then calculated using:

$$TCDD - equiv. = \sum_i [a_i(dioxin)_i + b_i(furan)_i]$$

where a_i and b_i are Toxic Equivalency Factors (TEF) for the various dibenzodioxins and furans, respectively.

The coefficients are typically determined by the World Health Oorganisation (WHO). Table 4 shows a list of the TEFs established by WHO in 1998 and again in 2005 so that it is possible to follow development of the TEF over time.

Table 4: List of common PCDD and PCDF compounds and their TEFs.

PCDD	**TEF (WHO) 1998 [117]**	**TEF (WHO) 2005 [116]**
2,3,7,8 TCDD	1	1
1,2,3,7,8 PeCDD	1	1
1,2,3,4,7,8 HxCDD	0,1	0.1
1,2,3,6,7,8 HxCDD	0,1	0,1
1,2,3,7,8,9 HxCDD	0,1	0,1
1,2,3,4,6,7,8 HpCDD	0,01	0,01
Total OCDD	0,0001	0,0003
2,3,7,8 TCDF	0,1	0,1
1,2,3,7,8 PnCDF	0,05	0,03
2,3,4,7,8 PnCDF	0,5	0,3
1,2,3,4,7,8 HxCDF	0,1	0,1
1,2,3,6,7,8 HxCDF	0,1	0,1
2,3,4,6,7,8 HxCDF	0,1	0,1
1,2,3,7,8,9 HxCDF	0,1	0,1
1,2,3,4,6,7,8 HpCDF	0,01	0,01
1,2,3,4,7,8,9 HpCDF	0,01	0,01
Total OCDF	0,0001	0,0003

6.2.3.2 Polycyclic aromatic hydrocarbons

PAH can be represented as B(a)P-equivalents which represent a weighted sum of a selection of PAH expressed in terms of their most toxic representative, benzo-a-pyrene (B(a)P). In this sum it is assumed that B(a)P is the most toxic of this group of chemicals and each other member of the group is assigned a factor which describes the toxicity of the species relative to that of B(a)P. The BaP-equivalent is then calculated using:

$$B(a)P - equiv. = \sum_i a_i (PAH)_i$$

where a_i represents Toxic Equivalency Factors (TEF) for the various PAHs, see Table 5.

Table 5: List of the TEFs established by Nisbet and Lagoy [118].

PAH	**TEF (*a_i*)**
Benzo[a]pyrene	1
Benzo[a]anthracene	0,1
Benzo[b]fuoranthene	0,1
Benzo[k]fluoranthene	0,1
Indeno[123-c,d]pyrene	0,1
Anthracene	0,01
Benzo[g,h,i]pyrelene	0,01
Chrysene	0,01
Acenaphthene	0,001
Acenahthylene	0,001
Fluoranthene	0,001
Fluorene	0,001
2-methylnathalene	0,001
Naphthalene	0,001
Phenanthrene	0,001
Pyrene	0,001

6.2.3.3 Polychlorinated biphenyls

PCB can be represented as TCDD-equivalents which represent a weighted sum of a selection of polychlorinated biphenyls expressed in terms of their equivalent in 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD). The BaP-equivalent is then calculated using:

$$TCDD - equiv. = \sum_i [a_i(dioxin)_i + b_i(furan)_i + c_i(PCB)_i]$$

where c_i represents Toxic Equivalency Factors (TEF) for the various PCBs, see Table 6. The TEFs a_i and b_i are used for dioxins and furans as defined previously.

Table 6: List of the TEFs established by WHO [116].

PCB	TEF (WHO, 1998)	TEF (WHO, 2005)
3,3´,4,4´-tetraCB	0.0001	0.0001
3,4,4´,5-tetraCB	0.0001	0.0003
3,3´,4,4´,5-pentaCB	0.1	0.1
3,3´,4,4´,5,5´-hexaCB	0.01	0.03
2,3,3´,4,4´-pentaCB	0.0001	0.00003
2,3,4,4´,5-pentaCB	0.0005	0.00003
2,3´,4,4´,5-pentaCB	0.0001	0.00003
2´,3,4,4´,5-pentaCB	0.0001	0.00003
2,3,3´,4,4´,5-hexaCB	0.0005	0.00003
2,3,3´,4,4´,5´-hexaCB	0.0005	0.00003
2,3´,4,4´,5,5´-hexaCB	0.00001	0.00003
2,3,3´,4,4´,5,5´-heptaCB	0.0001	0.00003

6.3 Models to predict the eco-toxicological hazard

Eco-toxicity is the degree to which a chemical or compound can damage the environment. In the context of this report, eco-toxicant will specifically refer to species (chemicals or compounds) with the potential to significantly damage the environment and which are emitted in large amounts from fires relative to other anthropogenic sources. The reason for this distinction is that numerous inorganic and organic compounds emitted from fires can have an eco-toxicological impact (e.g. methane and carbon dioxide are greenhouse gases) but their production from fires is insignificant relative to other sources. Thus, eco-toxicants is used to refer to large organic species, particulate emissions, metals, etc, in this report.

The perspective taken in the previous sections of this report has been to assume a fire has occurred or is presently burning. For the following section the discussion will take the viewpoint that fire could occur in the future and so decision support is needed prior to the event in order to minimize its environmental impact.

6.3.1 Life Cycle Assessment (LCA)

The information contained in this report and the accompanying spreadsheet can be used as input to build models that provide guidance for decisions that could have a potentially significant impact on the environment. LCA provides a framework for considering the cumulative environmental impact of an activity from its “birth” until its “death”, or from cradle to grave.

Recently, the International Reference Life Cycle Data System (ILCD) handbook was published to provide guidance on LCA best practices [119]. This guidance adheres to the formalized procedures found in ISO 14040 and 14044 standards on LCA, which are increasingly being included in European Union funded research projects. The primary direct applications of LCA are product development and improvement, strategic planning, public policy making, and marketing, although other applications exist.

In a typical LCA, the model follows an iterative process by which the goal and scope of the work are defined, an inventory of all the supporting data is conducted and analyzed, and the impact of the work is assessed. As the work progresses, interpretations are made and remade of all the steps until the results are acceptable. A peer review is then performed as a quality assurance measure.

Crude material extraction, production, transport and distribution, and product use, as well as product recycling, material recycling and waste handling are included in the typical cradle to grave LCA model. Occasionally it is useful to limit the scope of the LCA to cradle to gate, meaning that the LCA ends when the activity or product is ready to be used; or gate to grave, meaning that the LCA starts when use of the activity or product begins. The circular notion of a product's life is illustrated in Figure 4, including the end-of-life possibility of fire, which is not usually included in LCA.

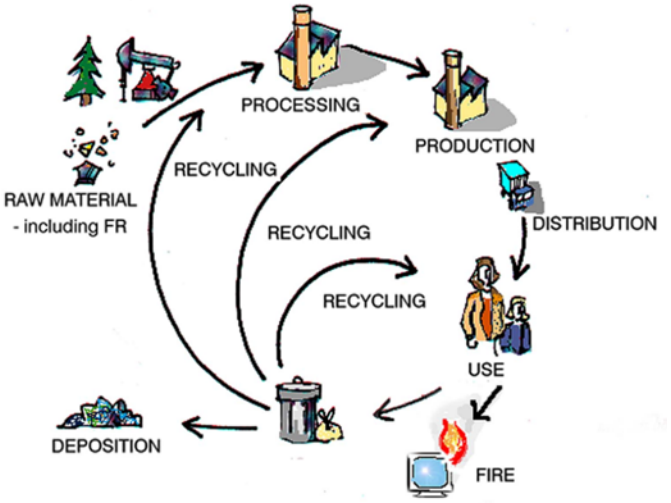

Figure 4. The life cycle of a product, including fire as an end-of-life scenario.

Accidental fire is not an end of life scenario recognized by ISO 14040 and 14044. This omission has the effect of causing FRs, fire suppressants, and emergency response to fire to appear as environmental burdens regardless of the reduction in intensity and/or number of fires. It is, however, possible to use LCA to compare the eco-toxicity of FRs, etc. Also, in Provision 6.6.I.d of the ILCD handbook "Shall – Scope of LCA"… "Other kinds of impact outside the scope of LCA that are found relevant for the analysed or compared systems may be identified and their relevance be justified". Fire-LCA is a model that describes the life cycle processes involved in accidental fire [120]. Fire-LCA uses fire statistics to quantify materials and has modules to handle the production of replacement materials needed due to the shortened life of the burned item. A diagram of the Fire-LCA model is shown in Figure 5.

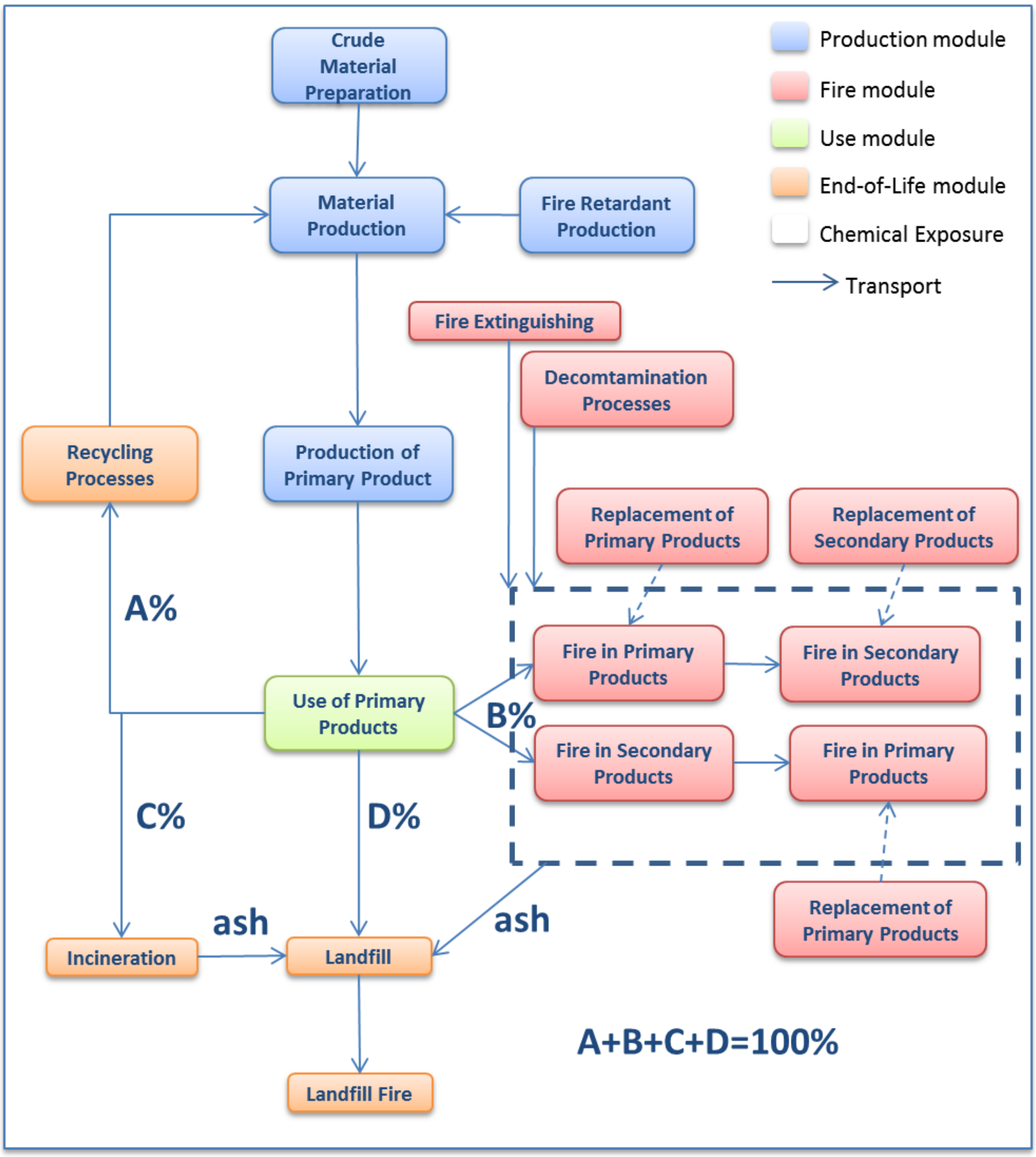

Figure 5. Diagram of the Fire-LCA model showing the life cycle processes involved in fire.

The main parts included in the Fire-LCA model are:

- Production of materials and fuels to be used in production.
- Production of the fire protection system.
- Production of the product to be analyzed (defined as the primary product).
- Use of the primary product.
- Waste handling of the primary product including:
  - Landfill
  - Incineration
  - Recycling
- Fire modules describing:
  - Fires starting in the primary product and spreading to surrounding products (defined as secondary products). These fires are called primary fires.
  - Fires starting in the secondary product and spreading to the primary product. These fires are called secondary fires.
  - Wastes from fire activities including demolition, decontamination, landfill, incineration, and recycling

  - Replacement of primary products lost in both primary and secondary fires. Replacement of secondary products that have been lost in primary fires spreading to secondary products
  - Fire extinguishing activities
  - Landfill fires in the landfilled materials

This represents a comprehensive list of the processes involved in fires. In practice it is generally not feasible to include all of the above activities. The intermediate output from a Fire-LCA model is a body of data concerning emissions to air, water and soil, energy and materials use, etc. There is, however, no well-defined or standardized way to interpret this data and make an assessment of the importance of one emission over another, or of the use of resources compared to their benefit. This makes it difficult to make a comparison between the different alternatives.

7 Gap Analysis

During the course of this investigation there were several areas in which it was difficult to find eco-toxicant information as it relates to fire effluent. These areas are briefly discussed in the following sections with the hope that the readers of this report will find them interesting topics for future work.

7.1 Decision-support tool development

This work could be considered the first step toward development of a decision support tool that consists of a current database of relevant information needed to assess the environmental impact of a fire incident. Ideally, this tool could be used after, during, or before the incident and could fulfill the needs of a variety of stakeholders. The tool would need to be accessible and easy to use and the information that it provides would need to be maintained to remain current. The tool could perhaps be web-based and could make use of other existing tools such as topographic mapping and meteorological tools.

7.2 New building materials

While there was some information available about the research and development efforts to create new building materials, there was very little discussion about how these new materials will behave when burned or the nature of their fire emissions.

7.3 Impact of vehicle fires

Most countries keep safety records, having varying levels of detail, of fire related losses. While it is possible to find statistics on the number of accidents involving fire, it was apparent that little research has been done and/or made public about the environmental impact of fires from transport vehicles. Questions about how best to respond to these types of fires and how best to prevent or prepare for them have not been answered with the same depth as similar questions about fires in structures and wildlands.

Also, fire effluent from electric and electric-hybrid vehicles has not been studied in depth yet, although the results of at least one such study is available to the public.

7.4 Pesticides in wildland fires

The presence of herbicides and insecticides in production forests may or may not cause significantly more eco-toxic fire effluent in wildland fires. More research in this area is need to understand the trade-offs involved in applying such chemicals to timber.

8 Measurement techniques

There are literally hundreds of measurement, sampling, and testing techniques for quantifying the concentration of compounds in the environment, along with many guidance documents for development of sampling/testing protocols. In this project the physical measurement, sampling, and testing techniques (collectively referenced under the general heading of "measurement techniques" in the following text) were collected from standards organizations, government regulations, and from the literature. Some of these techniques are well accepted and documented by the scientific, emergency response, governmental, testing, etc… communities and some of these techniques are somewhat obscure. Some measurement techniques address eco-toxicity in a general sense, such as ISO 17155:2002 Determination of abundance and activity of soil microflora using respiration curves. Other techniques are more specific, such as ISO 18287:2006 Determination of polycyclic aromatic hydrocarbons (PAH) - Gas chromatographic method with mass spectrometric detection (GC-MS). Every effort has been made to cite the most recent version of standardized documents. The measurement techniques cited in this report are the best available information at the time of writing. The goal of this project is to provide information in a manner that allows the user to determine the most appropriate technique(s) and document(s) to use in a given situation.

According to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (42 U.S.C. §9601)[9] a Phase I environmental site assessment is required in the USA for all commercial real estate transactions and is recommended in certain other situations. The assessment procedure for commercial or other built sites is defined in ASTM E1527-13 Standard Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process [121]. There is also an analogous standard, ASTM E2247 - 08 Standard Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process for Forestland or Rural Property [122]. If the Phase I assessment indicates the need for further investigation a much more detailed and intrusive Phase II assessment is conducted according to ASTM E1903-11 Standard Practice for Environmental Site Assessments: Phase II Environmental Site Assessment Process [123].

The CERCLA regulations (more commonly known as the Superfund regulations) and ASTM guidelines have promoted preparation of high quality, standardized environmental site assessments. Measurements performed according to the procedures outlined in ASTM E1527-13, ASTM E2247-08, and ASTM E1903-11 can be compared with other conforming measurements and with acceptance criteria for contamination levels, thus providing the scientific basis for a multi-disciplinary industry of preparers. Use of these three ASTM standards has subsequently broadened to the United Kingdom, Canada, Japan, and some parts of Europe, although perhaps not to the extent of use in the USA.

8.1 Eco-tox spreadsheet

Rather than list hundreds of measurement techniques in this document, it is more useful to describe in the following sections the methodology used to compile the information found in the tables in Appendix A, and in the accompanying "Eco-tox spreadsheet". The eco-toxicants, their phase, predictive models, measurement techniques, uncertainty of predictions or measurements, and the scope/limitations of use for the models and measurements are provided both in Appendix A (for the sake of completeness of this report), and in the "Eco-tox spreadsheet" (the spreadsheet format allows sorting of the data in many ways so that users can quickly determine which eco-toxicants are likely to be present in a given situation and how to quantify their concentration).

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[9] For more information see http://www.epa.gov/superfund/policy/cercla.htm.

8.1.1 Eco-toxicant information

In Table A1 and in the first worksheet of the Eco-Tox spreadsheet file, named “Eco-toxicant”, lists all the eco-toxicants discussed in this report. In some cases the eco-toxicants are individual species and in some cases they are groups of species. The chemical formula or common acronym and Chemical Abstract Service (CAS) reference number are given, if they exist or are publically available. This table/worksheet is keyed to more detailed information about the measurement techniques, predictive models, and literature references found in subsequent worksheets.

8.1.2 Environmental phase

The route by which the eco-toxicants are transported into the environment and/or the environmental phase in which the eco-toxicant meets its fate is given. This may involve multiple phases, for example, some PAHs may be gaseous when they are formed in the fire plume, then they adsorb onto a particle that drops out of the atmosphere and is deposited on the surface of a stream or on the soil. In this case the PAH concentration could be measured or predicted in air (A), aerosol (Aer), surface water (SW), or soil (S). Measurement techniques exist that can measure PAH concentrations in only one, two, or all of these phases, for example, ISO 19701 provides methods for sampling gaseous fire effluent in air but does not include airborne particles or aerosols [124].

8.1.3 Measurement technique

The measurement technique(s) that correspond to the eco-toxicant is provided. These measurement techniques are keyed to more detailed information found in Table A2 for air and aerosols, Table A3 for groundwater, Table A4 for sediment, Table A5 for soil, and Table A6 for surface water and in the “Measurements” worksheet of the Eco-Tox spreadsheet file. This information includes the full number and title (or literature reference) of the technique, uncertainty estimations, and comments on the scope/limitations of the technique. The keys are tied to the environmental phase targeted by the measurement technique.

8.1.4 Eco-toxicant models

The models for predicting the presence and/or concentration of selected eco-toxicants are provided in Table A7 in Appendix A and in the worksheet named “Models” in the Eco-Tox spreadsheet file. The detailed information includes the full number and title (or literature reference) of the technique, uncertainty estimations, and comments on the scope/limitations of the technique, if available. The keys are tied to the environmental phase targeted by the measurement technique.

8.1.5 References

The references to the eco-toxicants that are identified in this report are included in Table A1 of Appendix A so that they can readily be identified with a specific eco-toxicant. They are also provided in the worksheet named “References” in the Eco-Tox spreadsheet file. Note that if the references in this report are updated and renumbered they will no longer correspond to the reference numbers in the Eco-Tox spreadsheet file.

Appendix A: List of eco-toxicants

Table A1. The following table is a compilation of the eco-toxicants discussed in the preceding text, including keys to the environmental phase in which they can be expected and the models and measurement techniques that are applicable. See the following tables for additional information.

Compound	Formula (add the real formulas if possible)	CAS	Phase: (A=Air, Aer=Aerosol, GW=Ground water, S=Soil, Sed=Sediment, SW=Surface water)	Measurement technique (see following Tables 2 - 6)	Predictive model (see following Tables 7 - 11)	Comments, literature references
1-nonene	C9H18	124-11-8	A	A1, A5		[69]
1-undecene	C11H22	821-95-4	A	A1, A5		[69]
2-butanone	C4H8O	78-93-3	A	A1, A5		[69]
Aceonitrile	CH3CN	75-05-8	A	A1, A5		[125]
Acetaldehyde	C2H4O	75-07-0	A	A1, A2, A5		[69, 124]
Acetic acid	C2H4O2	64-19-7	A	A1, A5		[65, 69]
Acetone	C3H6O	67-64-1	A	A1, A5		[69]
Acetylene	C2H2	74-86-2	A	A1, A5		[65, 69]
Acrolein	C3H4O	107-02-8	A	A1, A2, A3, A5	MOD10	[69, 114, 124, 126]
Aerosols	(group)	No group CAS RN	Aer	A4, A5		[127] can include many adsorbed/absorbed compounds
Ammonia	NH3	7664-41-7	A	A1, A2, A5		[23-25, 65, 69, 124]
a-pinene	C10H16	80-56-8	A	A1, A5		[125]
Asbestos	Mg3Si2O5(OH)4	1332-21-4	A	A1, A5		[13]
Benzaldehyde	C7H6O	100-52-7	A	A1, A5		[69]

Benzene	C6H6	71-43-2	A, GW, S	A1, A5	MOD5	[28, 29, 69, 109]
Benzofuran	C8H6O	271-89-6	A	A1, A5		[69]
Benzoic acid	C7H6O2	65-85-0	A	A1, A5		[69]
b-pinene	C10H16	127-91-3	A	A1, A5		[125]
Carbon dioxide	CO2	124-38-9	A	A1, A2, A3, A5	MOD1	[7, 16, 23-25, 65, 69, 109, 124, 126]
Carbon monoxide	CO	630-08-0	A	A1, A2, A3, A5	MOD2	[7, 14, 16, 23-25, 65, 69, 109, 124, 126]
Chloro-methane	CH3Cl	74-87-3	A	A1, A5		[69]
Crotonaldehyde	C4H6O	123-73-9	A	A1, A5		[69]
Decane	C10H22	124-18-5	A	A1, A5		[69]
Ethane	C2H6	74-84-0	A	A1, A5		[69]
Ethene	C2H4	74-85-1	A	A1, A5		[65]
Ethyl-benzene	C8H10	100-41-4	A, GW, S	A1, A5		[28, 29, 69]
Formaldehyde	CH2O	50-00-0	A	A1, A2, A5	MOD5, MOD10	[65, 69, 109, 114, 124]
Formic acid	CH2O2	64-18-6	A	A1, A5		[65, 125]
Furfural	C5H4O2	98-01-1	A	A1, A5		[69]
Guaiacol	C7H8O2	90-05-1	A	A1, A5		[69]
Heavy metals, trace elements	(group)	No group CAS RN	A, S, Sed, SW, GW	A1, A2, A5, GW1, S1, S2, S3, Sed1, Sed2, SW5, SW8, SW9, SW11-SW18, SW22		[13, 17, 69, 124]
Heptane	C7H16	142-82-5	A	A1, A5		[69]
hexabromocyclododecane	C12H18Br6	25637-99-4	A	A1, A5		[11]
Hydrogen bromide	HBr	10035-10-6	A	A1, A2, A3, A5	MOD9, MOD10	[16, 108, 114, 124, 126]
Hydrogen cyanide	HCN	74-90-8	A, SW	A1, A2, A3, A5, SW19-		[7, 14, 16, 23-25, 65,

				SW21, SW23		124, 126]
Hydrogen chloride	HCl	7647-01-0	A	A1, A2, A3, A5	MOD9, MOD10	[7, 16, 23-25, 108, 114, 124, 126]
Hydrogen fluoride	HF	7664-39-3	A	A1, A2, A3, A5	MOD9, MOD10	[108, 114, 124, 126]
Isocyanates	RNCO (group)	No group CAS RN	A	A5		[18, 104, 106]
m-Cresol	C7H8O	108-39-4	A	A1, A5		[69]
Methane	CH4	74-82-8	A	A1, A5		[65, 69]
Methanol	CH4O	67-56-1	A	A1, A5		[65]
Methyl esters	(group)	No group CAS RN	A	A1, A5		[69]
Nitric oxide	NO	10102-43-9	A	A1, A2, A3, A5	MOD6	[7, 16, 24, 25, 65, 69, 108, 124, 126]
Nitrogen dioxide	NO2	10102-44-0	A	A1, A2, A3, A5	MOD6, MOD10	[7, 16, 18, 24, 25, 69, 108, 114, 124, 126]
Nitrous oxide	N2O	10024-97-2	A	A1, A2, A3, A5	MOD7	[7, 108, 128, 129]
Ozone	O3	10028-15-6	A	A1, A5		[65, 69] found downwind of fire plume
Polychlorinated Biphenols	PCBs (group)	1336-36-3	A	A1, A5	MOD13	[13, 15, 105, 130]
Polychlorinated dibenzodioxins/furans	PCDDs/PCDFs (group)	262-12-4	A	A1, A5	MOD11	[7, 8, 13, 15, 18, 37, 69, 105, 116, 117, 130]
p-Cresol	C7H8O	106-44-5	A	A1, A5		[69]
Phenol	C6H6O	108-95-2	A	A1, A5	MOD5	[18, 69, 109]
Phosphates	(group)	No group CAS RN	A	A1, A2, A5		[124]
Phosphorus (red)	P	7723-14-0	A	A1, A2, A5		[124]
polybrominated biphenyls	PBB (group)	67774-32-7	A	A1, A5		[11]

polybrominated diphenyl ethers	PBD (group)	No group CAS RN	A	A1, A5		[11]
Propene	C3H6	115-07-1	A	A1, A5		[69]
Styrene	C8H8	100-42-5	A	A1, A5	MOD5	[18, 109]
Sulphur oxides	SOx (group)	No group CAS RN	A	A1, A2, A3, A5	MOD8, MOD10	[16-18, 23-25, 69, 108, 114, 124, 126]
tetrabromobisphenol A	C15H12Br4O	79-94-7	A	A1, A5		[11]
Toluene	C7H8	108-88-3	A, GW, S	A1, A5	MOD5	[28, 29, 69, 109]
Xylene	C8H10	1330-20-7	A, GW, S	A1, A5	MOD5	[28, 29, 69, 109]
Pesticides	(group)	No group CAS RN	A, GW, SW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[13, 69]
Polycyclic Aromatic Hydrocarbons	PAH (group)	130498-29-2	A, Aer, SW, S	A4, A5, S7, SW2, SW9, SW18	MOD4, MOD12	[8, 13, 15, 17, 18, 33, 63, 69, 108, 118, 127, 131]
Particulates	PM1, PM2.5, PM10 (group)	No group CAS RN	A, Aer, SW, S	A4, A5, S1, S2, S3, S5, S6, SW1, SW8, SW9, SW10	MOD3	[17, 18, 69, 109, 127]
Volatile Organic Compounds	VOC (group)	No group CAS RN	A, Aer, GW, SW, S	A1, A4, A5, S1, S2, S3, S5, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18	MOD5	[8, 18, 28, 29, 109, 125, 127]
Methyl tert-butyl ether	MTBE	1634-04-4	GW	A5, GW1		[28, 29]
Mercury	Hg	7439-97-6	A, SW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW5, SW8, SW9, SW18		[70]
Aluminum	Al3+	7429-90-5	S	A5, S1, S2, S3, S5, S6		[66]
Iron	Fe2+	7439-89-6	S	A5, S1, S2, S3, S5, S6		[66]

Manganese	Mn2+	7439-96-5	S	A5, S1, S2, S3, S5, S6		[66]
Mineral oil (hydrocarbons)	C10-C40	No group CAS RN	S	A5, S4, S5, S6		[36, 132]
Zinc	Zn2+	7440-66-6	S	A5, S1, S2, S3, S5, S6		[66]
6:2 Fluoroteomer sulphonate	6:2 FTS	27619-97-2	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
N-Ethyl-heptadecafluorooctane sulphonamide	N-Et-FOSA	4151-50-2	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
N-Methyl-heptadecafluorooctane sulphonamide	N-Me-FOSA	31506-32-8	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
N-Methyl-heptadecafluorooctane sulphonamidoethanol	N-Me-FOSE	24448-09-7	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
N-Methyl-heptadecafluorooctane sulphonamidoethanol	N-Et-FOSE	1691-99-2	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorobutane sulphonate	PFBS	375-73-5	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluoroctanoic acid	PFOA	335-67-1	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]

Perfluorodecane sulphonate	PFDcS	67906-42-7	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorodecanoic acid	PFDcA	335-76-2	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorododecanoic acid	PFDoA	307-55-1	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluoroheptanoic acid	PFHpA	375-85-9	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorohexane sulphonate	PFHxS	355-46-4	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorohexanoic acid	PFHxA	307-24-4	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorononanoic acid	PFNA	375-95-1	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorooctane sulfonates	PFOS	1763-23-1	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[28, 29, 83, 84]

Perfluorooctane sulphonamide	PFOSA	754-91-6	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorotetradecanoic acid	PFTeA	376-06-7	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluorotridecanoic acid	PFTriA	72629-94-8	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Perfluoroundecanoic acid	PFUnA	2058-94-8	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[82]
Polyfluoroalkyl betaine also known as 6:2 fluorotelomer sulphonamide alkylbetaine	PFAB or 6:2 FTAB	34455-29-3	SW, GW, Sed, S	A5, S1, S2, S3, S5, S6, Sed1, Sed2, SW1, SW3, SW4, SW6, SW7, SW8, SW9, SW18, GW1		[85, 87]

Table A2. The following table is a compilation of the air and aerosol measurement techniques applicable to the eco-toxicants discussed in the preceding text.

Air (A) and Aerosols (Aer)			
Ref. No.	**Method**	**Uncertainty**	**Scope/comments**
A1	ASTM E800-07 Standard Guide for Measurement of Gases Present or Generated During Fires		Tool for the selection of a suitable technique from among alternatives to quantify gaseous fire effluent. It will not provide enough information for the setup and use of a procedure (this information is available in the references).
A2	ISO 19701:2013 Methods for sampling and analysis of fire effluents	Covers 18 compounds, includes measurement sensitivity and selectivity for each.	ISO 19701:2013 presents a range of sampling and chemical analytical methods suitable for the analysis of individual chemical species in fire atmospheres. The procedures relate to the analysis of samples extracted from an apparatus or effluent flow from a fire test rig or physical fire test model and are not concerned with the specific nature of the fire test. This International Standard doesn't cover aerosols and FTIR technique. The gases of environmental interest, such as PAH, dioxins, furans, endocrinal disturbers, will be developed in a future document by ISO TC92/SC3.
A3	ISO 19702:2006 Toxicity testing of fire effluents - Guidance for analysis of gases and vapours in fire effluents using FTIR gas analysis	Includes repeatability/reproducibility data for 11 compounds measured in SAFIR project.	This method is only useful to analyze molecules having a dipole moment. Can measure fire gases directly if setup is carefully arranged, otherwise gas samples are collected for later analysis. Spectral information is provided for the gases studied specifically in the SAFIR project as an aid to users to determine spectral regions of interest. Finally, applications of the analytical method are discussed.
A4	ISO 29904:2013 Fire chemistry -- Generation and measurement of aerosols	Sources of uncertainty are discussed broadly.	This standard defines apparatus and procedures for the sampling and measurement of aerosols, and provides procedures for the interpretation and reporting of the data. ISO 29904:2013 identifies the scope, applicability, and limitations of each method. The interpretation of the data from these measurements is strongly dependent on the end use of the data.
A5	ASTM D5792 - 10 Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives	Establishing the quality of data is the objective of this standard.	This practice covers the process of development of data quality objectives (DQOs) for the acquisition of environmental data. Optimization of sampling and analysis design is a part of the DQO process. This practice describes the DQO process in detail. It covers collection of data in all environmental phases.

Table A3. The following table is a compilation of the groundwater measurement techniques applicable to the eco-toxicants discussed in the preceding text.

Ground water (GW)			
Ref. No.	**Method**	**Uncertainty**	**Scope/comments**
GW1	ISO 5667-11:2009 Guidance on sampling of groundwaters		Guidance on necessary considerations when planning groundwater sampling for assessing quality. Includes saturated and unsaturated zones. Not applicable for potability measurements.
A5	ASTM D5792 - 10 Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives	Establishing the quality of data is the objective of this standard.	This practice covers the process of development of data quality objectives (DQOs) for the acquisition of environmental data. Optimization of sampling and analysis design is a part of the DQO process. This practice describes the DQO process in detail. It covers collection of data in all environmental phases.

Table A4. The following table is a compilation of the sediment measurement techniques applicable to the eco-toxicants discussed in the preceding text.

Sediment (Sed)			
Ref. No.	**Method**	**Uncertainty**	**Scope/comments**
Sed1	ISO 5667-12:1995 Guidance on sampling of bottom sediments		Provides guidance on the sampling of sediments from rivers, streams, lakes and similar standing waters and estuaries. Sampling of industrial and sewage plant sludges and ocean sediments are excluded.
Sed2	ISO 5667-15:2009 Guidance on the preservation and handling of sludge and sediment samples		Provides guidance on procedures for the preservation, handling and storage of samples of sewage and waterworks sludge, suspended matter, saltwater sediments and freshwater sediments, until chemical, physical radiochemical and/or biological examination can take place. Only applies to wet samples.
A5	ASTM D5792 - 10 Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives	Establishing the quality of data is the objective of this standard.	This practice covers the process of development of data quality objectives (DQOs) for the acquisition of environmental data. Optimization of sampling and analysis design is a part of the DQO process. This practice describes the DQO process in detail. It covers collection of data in all environmental phases.

Table A5. The following table is a compilation of the soil measurement techniques applicable to the eco-toxicants discussed in the preceding text.

Soil (S)			
Ref. No.	**Method**	**Uncertainty**	**Scope/comments**
S1	ISO 17155:2002 Determination of abundance and activity of soil microflora using respiration curves		Test method to determine activity of aerobic, hetertrophic microbial biomass in soils. Used for monitoring of soil quality and evaluation of eco-toxic potential of soils.
S2	ISO 10381-1:2002 Guidance on the design of sampling programmes		Describes general principles for designing sampling programmes for characterizing and controlling soil quality and identifying sources and effects of contamination. Emphasizes sampling locations, instrumentation, sample size, combination of samples, collection methods, and containment, storing, and transport of samples.
S3	ISO 10381-2:2002 Guidance on sampling techniques		Guidance on techniques for taking and storing soil samples. Includes information on equipment and references to groundwater and soil gas sampling. Not applicable to hard strata.
S4	ISO 16703:2004 Determination of content of hydrocarbon in the range C10 to C40 by gas chromatography		Test method for quantitative measurement of mineral oil content (C10 - C40) in field-moist soil samples. There is an annex with listed compounds.
S5	ISO 10381-5:2005 Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination		Gives guidance on the procedure for investigating urban and industrial sites where soil contamination is suspected. Useful when there is a need to establish the environmental quality of a site. Includes guidance on the collection of information for risk assessments and remediation action plans.

S6	ISO 15952:2006 Effects of pollutants on juvenile land snails (Helicidae) - Determination of the effects on growth by soil contamination		Specifies a method for determining the effects of soil contamination on the growth of young snails. Does not apply to volatile substances.
S7	ISO 18287:2006 Determination of polycyclic aromatic hydrocarbons (PAH) - Gas chromatographic method with mass spectrometric detection (GC-MS)		Specifies the quantitative determination of 16 PAHs according to the priority list of the U.S. EPA (1982)
A5	ASTM D5792 - 10 Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives	Establishing the quality of data is the objective of this standard.	This practice covers the process of development of data quality objectives (DQOs) for the acquisition of environmental data. Optimization of sampling and analysis design is a part of the DQO process. This practice describes the DQO process in detail. It covers collection of data in all environmental phases.

Table A6. The following table is a compilation of the surface water measurement techniques applicable to the eco-toxicants discussed in the preceding text.

Surface water (SW)			
Ref. No.	**Method**	**Uncertainty**	**Scope/comments**
SW1	ISO 5667-10:1992 Guidance on sampling of waste waters		Contains details on the sampling of domestic and industrial waste water, including the design of sampling programmes and techniques for collection of samples. Covers all kinds of waste water, but not accidental spillage.
SW2	ASTM D5412 - 93(2011) Standard Test Method for Quantification of Complex Polycyclic Aromatic Hydrocarbon Mixtures or Petroleum Oils in Water		This test method covers a means for quantifying or characterizing total polycyclic aromatic hydrocarbons (PAHs) by fluorescence spectroscopy (Fl) for waterborne samples. The characterization step is for the purpose of finding an appropriate calibration standard with similiar emission and synchronous fluorescence spectra.
SW3	ISO 10707:1994 Evaluation in an aqueous medium of the "ultimate" aerobic biodegradability of organic compounds		Method by analysis of biochemical oxygen demand (closed bottle test)
SW4	ISO 6341:1996 Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea)		Acute toxicity test
SW5	USEPA Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels		This method is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act.

SW6	ISO 10708:1997 Evaluation in an aqueous medium of the ultimate aerobic biodegradability of organic compounds		Determination of biochemical oxygen demand in a two-phase closed bottle test
SW7	ISO 15705:2002 Determination of the chemical oxygen demand index (ST-COD)		Small-scale sealed-tube method
SW8	ISO 5667-6:2005 Guidance on sampling of rivers and streams		Provides guidance on the design of sampling programmes, sampling techniques and the handling of water samples from rivers and streams for physical and chemical assessment. Not applicable to estuaries, coastal waters, sediment, suspended solids or biota and has limited applicability to microbiological sampling.
SW9	ISO 5667-1:2006 Guidance on the design of sampling programmes and sampling techniques		Provides guidance on the design of sampling programmes and sampling techniques for all aspects of sampling of water (including waste waters, sludges, effluents and bottom deposits).
SW10	ASTM D4189 - 07 Standard Test Method for Silt Density Index (SDI) of Water		This test method covers the determination of the silt density index (SDI) of water. This test method can be used to indicate the quantity of particulate matter in water and is applicable to relatively low (1.0 NTU) turbidity waters such as well water, filtered water, or clarified effluent samples. Since the size, shape, and nature of particulate matter in water may vary, this test method is not an absolute measurement of the quantity of particulate matter.
SW11	ASTM D2972 - 08 Standard Test Methods for Arsenic in Water		These test methods cover the photometric and atomic absorption determination of arsenic in most waters and wastewaters.
SW12	ASTM D3559 - 08 Standard Test Methods for Lead in Water		These test methods cover the determination of dissolved and total recoverable lead in water and waste water by atomic-absorption spectrophotometry and differential pulse anodic stripping voltammetry.

SW13	ASTM D3645 - 08 Standard Test Methods for Beryllium in Water		These test methods cover the determination of dissolved and total recoverable beryllium in most waters and wastewaters.
SW14	ASTM D3859 - 08 Standard Test Methods for Selenium in Water		These test methods determine the dominant species of selenium reportedly found in most natural and wastewaters, including selenities, selenates, and organo-selenium compounds.
SW15	ASTM D3919 - 08 Standard Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry		Elemental constituents in potable water, receiving water, and wastewater need to be identified for support of effective pollution control programs. Currently, one of the most sensitive and practical means for measuring low concentrations of trace elements is by graphite furnace atomic absorption spectrophotometry.
SW16	ASTM D3558 - 08 Standard Test Methods for Cobalt in Water		These test methods cover the determination of dissolved and total recoverable cobalt in water and wastewater by atomic absorption spectrophotometry.
SW17	ASTM D4190 - 08 Standard Test Method for Elements in Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy		This test method covers the determination of dissolved and total recoverable elements in water, which includes drinking water, lake water, river water, sea water, snow, and Type II reagent water by direct current plasma atomic emission spectroscopy (DCP).
SW18	ASTM D6850 - 03(2008) Standard Guide for QC of Screening Methods in Water		The determination whether to proceed with further action is useful in reducing the number of negative results for which the screening method serves as a surrogate.
SW19	ASTM D7284 - 08e1 Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection		The method detects the cyanides that are free (HCN and CN-) and strong-metal-cyanide complexes that dissociate and release free cyanide when refluxed under strongly acidic conditions.

SW20	ASTM D6888 - 09 Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection		This test method is applicable for natural water, saline waters, and wastewater effluent.
SW21	ASTM D7365 - 09a Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide		This practice is applicable for the collection and preservation of water samples for the analysis of cyanide.
SW22	ASTM D5673 - 10 Standard Test Method for Elements in Water by Inductively Coupled Plasma-Mass Spectrometry		This test method covers the determination of dissolved elements in ground water, surface water, and drinking water. It may also be used for the determination of total-recoverable elements in these waters as well as wastewater.
SW23	ASTM D6696 - 10 Standard Guide for Understanding Cyanide Species		This guide provides standard terminology for use in identifying and describing the different chemical forms of cyanide.
A5	ASTM D5792 - 10 Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives	Establishing the quality of data is the objective of this standard.	This practice covers the process of development of data quality objectives (DQOs) for the acquisition of environmental data. Optimization of sampling and analysis design is a part of the DQO process. This practice describes the DQO process in detail. It covers collection of data in all environmental phases.

Table 7. Models for predicting the concentrations of eco-toxicants in air. Note that these models do not extend to other environmental phases even though some airborne species may ultimately deposit on soil or surface water and be transported into sediment and groundwater.

Air (A)			
Ref. No.	**Method**	**Species**	**Scope/comments**
MOD1	Tewarson [109]	CO_2	Model predicts mass fraction of CO_2 in gaseous fire effluent, based on a correlation to correct for ventilation conditions.
MOD2	Tewarson [109]	CO	Model predicts mass fraction of CO in gaseous fire effluent, based on the type of fuel and includes ventilation conditions.
MOD3	Tewarson [109], Lönnermark et al. [108]	PM	Model predicts the mass fraction of PM in fire effluent as a function of ventilation conditions, later refined to include the effect of temperature.
MOD4	Lönnermark et al. [108]	PAH	Model predicts the mass fraction of PAH in fire effluent as a function of temperature, equivalence ratio, and ventilation conditions.
MOD5	Tewarson [109]	VOC	Model predicts the mass fraction of benzene as a surrogate for VOC in fire effluent as a function of ventilation conditions and equivalence ratio.
MOD6	Lönnermark et al. [108]	NO_x	Model predicts the mass fractions of thermal NO_x and total NO_x in fire effluent based on the ventilation conditions, equivalence ratio, fuel bound N, and Δhc.
MOD7	Lönnermark et al. [108]	N_2O	Model predicts the mass fraction of N_2O in fire effluent as a function of fuel bound N, temperature, and Δhc.
MOD8	Lönnermark et al. [108]	SO_x and H_2SO_4	Model predicts mass fractions of SO_2, SO_3, H_2SO_3, and H_2SO_4 in fire effluent as a function of fuel bound sulfur and debris bound sulfur.
MOD9	Lönnermark et al. [108]	HBr, HCl, HF	Model predicts the mass fraction of acid gases in fire effluent based on the fuel bound halogen and the amount of acid found in runoff water.
MOD10	ISO 13571 [114]	Irritant gases	Model calculates the FEC to predict the time available until human incapacitation in the presence of HCl, HBr, HF, SO_2, NO_2, acrolein, and formaldehyde.
MOD11	World Health Organization [116, 130]	PCDD/PCDF	Model calculates the TEQ to predict the human toxicity of groups of species, for example dioxins and furans. The model normalizes the TEF of the species by the TEF of the most toxic congener.
MOD12	Nisbet and Lagoy [118]	PAH	Model calculates the TEQ to predict the human toxicity of groups of species, for example PAH. The model normalizes the TEF of the species by the TEF of the most toxic congener.
MOD13	World Health Organization [116, 130]	PCB	Model calculates the TEQ to predict the human toxicity of groups of species, for example PCB. The model normalizes the TEF of the species by the TEF of the most toxic congener.

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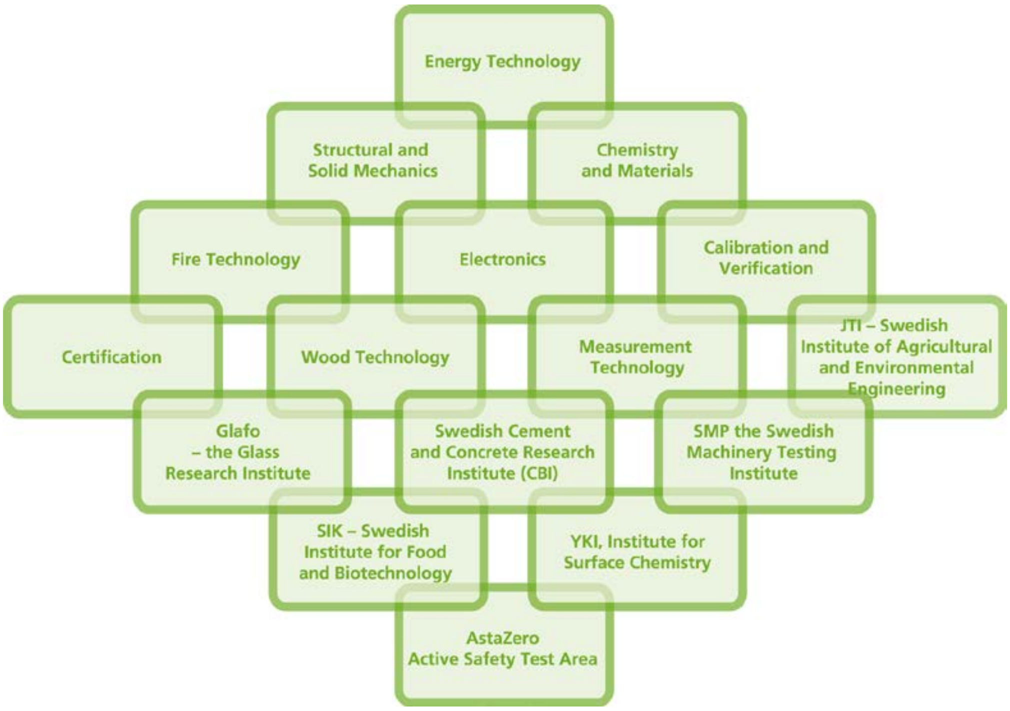

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