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Review: The Use of Bench-Scale Tests to Determine Toxic Organic Compounds in Fire Effluents and to Subsequently Estimate Their Impact on the Environment

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Abstract. Generated fire effluents are toxic and responsible for the majority of fire deaths and injuries. Therefore, measures of fire safety and the assessment of toxic effects of fires on humans, which are the key factors to assess fire hazards, have been researched in the last decades. However, it is more and more recognized that there is also a need to assess the environmental impact of toxic compounds within fire effluents. Since ecotoxicology investigates the toxic effects of fire effluents on populations, interactions between ecology and toxicology are very important. These interactions may be complex and may involve research of food chains with several different trophic levels. This makes tracing of toxicants, to obtain reliable results, a real challenge. To tackle it, the bench-scale test is a cheaper and less complex method than large-scale fire simulations. Progress in the field of ecotoxicological studies is important because long-term exposure from the environment and bioaccumulation of toxic compounds in the human food chain may cause indirect health effects on humans. It is also an important tool for the general protection of the environment and biodiversity. Last, with data obtained from these studies, databases for the Life Cycle Assessment of construction materials can be improved.

Keywords: Bench-scale tests, Ecotoxicology, Fire effluents, Toxicity

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1. Introduction

A fire, involving organic substances, releases both heat and smoke. It is an uncontrolled, chaotic process in which conditions change rapidly. Depending on the fire's specific conditions, many diverse chemical compounds are produced in varying amounts. The substances, contained within fire effluents, can adversely affect human health. In principle, they are divided in four groups: asphyxiants (e.g. carbon monoxide, carbon dioxide, hydrogen cyanide), irritants (e.g. ammonia, hydrogen chloride, nitrogen oxides, phenol, sulphur dioxide), allergens (e.g. isocyanates), and carcinogens (e.g. polycyclic aromatic hydrocarbons [PAHs], dioxins, furans, certain heavy metals) [1]. The combustion of organic materials, particularly if it is incomplete, may also give rise to more complex molecules in the smoke plume, which may typically include longer carbon chains and multiple carbon-rings. The acute toxicity of these compounds is generally low and may not pose a direct health hazard during exposure [2]. In addition, fire effluents contain soot particles (particulate matter [PM]) that can penetrate deep into the lungs while carrying other, less mobile compounds. Many of these released substances are not only potentially toxic to humans but also to flora and fauna, which renders fire and fire effluent not only able to cause incapacitation, injury or death in people but also a potentially potent environmental hazard [3].

The serious consequences of disasters in recent years (e.g. California wildfires [2019], Amazon rainforest wildfires [2019] and forest fires in Australia [2020]) have highlighted the environmental impact of fires as a real threat. The emission and re-deposition of fire effluent components with carcinogenic or mutagenic properties can contribute to persistent contamination of the atmosphere, soil and water bodies, resulting in severe ecological damage [4–6]. Aerosols can be carried over long distances of tens or even hundreds of kilometres by wind before they settle on the ground or water surface. Depending on their chemical composition, their effects may include: acidification of lakes and streams, change in the nutrient balance in coastal waters and large river basins, depletion of nutrients in soil, damage to sensitive forests and farm crops or effects on diversity of ecosystems [7]. Aerosolised solid particles with less than 10 μm in diameter pose the greatest threat due to their possible deep penetration into the lungs of living organisms or potentially even the bloodstream [8–10]. These adverse health effects depend not only on the level of PM concentration in the air but also on its particular internal composition [11].

Fire effluents are not the sole potential environmental hazard. Since water is by far the most common fire suppressant used by fire services for structure fires, firefighting water runoff presents a major potential threat to the aquatic environment from fires in the short term. Along with significant water solubility of fire-generated toxic substances, fire retardants, foam suppressants and other firefighting agents were shown to be harmful to aquatic organisms [12]. The European Environmental Agency report has openly stated that the ecological impact of industrial firefighting activities, which can contaminate surface- and groundwater, is more severe than the impact of smoke from fires [13]. Until now, little research has been done on ecotoxicity of fire effluents in comparison with human toxicity studies, mainly due to complex issues related to pathways of fire-to-air transfer mechanisms and subsequent deposition in soil or water or uptake by organisms. These mechanisms are generally studied by theoretical methods or with case studies and field measurements [14–16]. Furthermore, challenges also exist in identifying and appropriately sampling toxic substances during and after a fire event. Since the extent of toxicity and environmental contamination is largely dependent on the fire conditions, the fuel, the surrounding environment, duration of burning, transmission and susceptibility of the receptor, it is also necessary to improve our understanding of the nature of fire. For example, the complexity of toxicity assessment can be demonstrated as follows: polychlorinated dibenzodioxins and furans (PCDD/Fs) are powerful carcinogenic compounds generated in fires with chlorine-containing fuel (e.g. PVC). In wildland fires, the main fuel is biomass with generally low chlorine content, resulting in fairly low PCDD/F concentrations, with PAHs being the main ecotoxic concern per mass unit of burned biomass. In residential or industrial fires, on the other hand, significantly higher quantities of chlorine-containing fuel might be available, leading to significantly higher concentrations (or even total amounts) of PCDD/Fs being produced per mass unit of fuel, even with comparatively smaller fire sizes [17–19]. Care must be taken, however, given the large volume of fuel that can be involved during wildland fires; an accumulation of these events could be a significant source of PCDD/Fs, particularly during years with extensive forest fires. Therefore, targeted experiments to establish a relationship between the controlled conditions and fire effluents production are needed to improve this understanding.

Bench-scale tests could be a useful tool for ecotoxicity tests. Bench-scale fire property measuring methods are designed for single, unique combustion conditions in a controlled laboratory environment. In this way, individual fire stages or combustion conditions can be reproduced to obtain the organic and inorganic composition of fire effluents for a specific situation or scenario of fire. Furthermore, toxicants and pollutants can be captured and manually introduced to different test environments (water, sediments, soil, dilution in air) on a lab-scale, making it possible to observe (bio)chemical changes within and their influence on targeted organisms.

In this review article, we focused on possible approaches to assess the environmental impact of toxic compounds emitted by fire effluents. Toxic substances have a strong influence on ecosystems and organisms. Whereas toxicology usually deals with the effects of toxic substances on individuals, ecotoxicology emphasizes populations. Consequently, interactions between ecology and toxicology are very important. These interactions may be complex and may involve food chains and several different organizational levels, which increases the importance of following organic and inorganic toxicants through these levels. The first level is the composition during emission of the toxicants; the second level is when the toxicant or pollutant is introduced into the environmental system, which may result in structural changes of the toxicant and biochemical changes inside organisms. On the third level, physiological alterations in organisms and population changes should be investigated. As more data on fires and impacts become available, such an approach to assessing aggregated impacts can be developed. In the last years, more research groups start to acknowledge the importance of the effect of firefighting on the environment. Martin et al. [20] already discussed the impact of fire effluents in an interesting review article. Their main focus was the different methodologies for analysing the impacts of fires (life cycle analysis, cost–benefit analysis, risk assessment, decision making tools), while the main gaps and opportunities for future research were also discussed. Also the international organization for standardization (ISO) Technical Committee TC 92, which addresses fire safety concerns, has a workgroup focusing on fire threats to the environment (ISO/TC 92/SC3/WP6). In this frame, ISO-standards were published with guidelines on the assessment of the adverse environmental impact of fire effluents [21, 22].

2. Bench-Scale Tests as a Method to Determine the Fire Effluent Toxicity

Although each fire may be regarded as unique, burning behaviour and toxic product yields depend most strongly on a few factors. Material composition, temperature and oxygen availability are normally the most important [1]. Therefore, a bench-scale method must be capable of replicating large-scale fires in the sense of reproducing individual fire stages or combustion conditions. From the obtained data, models of combustion toxicity can be prepared, and indirectly, ecotoxicity studies can be performed by introducing captured fire effluents to test environments on lab-scale. With appropriate input data, these results can be also used to make (eco)toxicity assessments for potential large-scale fires or for investigation of specific incidents. However, a constant challenge remains to establish an adequate way of conducting bench-scale tests and properly interpret the obtained data in a way that their relevance is kept to full-scale tests [23].

When conducting bench-scale tests, there are several aspects that have to be taken into account [23–25]:

- Full-scale fires simultaneously involve distinct fire stages in separate places, interlinked with chemical and thermal feedbacks.
- Combustion conditions can also change during the bench-scale test, with each condition having an unknown duration. Therefore, it is hard to correlate the results of such a test to a single, unique, controlled condition.
- The behaviour of fire may change on scale-up.
- The yield and nature of the fire effluents are a function of the fuels involved and the fire conditions. These conditions affect the burning rate and degree of oxidation of the effluent. A developed fire burns at the rate dependent on the ventilation. To obtain data to model or predict such fires, it is necessary to understand the relationship between the ventilation condition and the toxic product yields.
- One of the objectives of bench-scale testing is obtaining fundamental characteristics of materials. Unfortunately, there is not yet a methodology that can correlate the material properties with a certain fire behaviour, enabling to predict its

toxicity. This is true even for homogeneous materials, and the problems are intensified for inhomogeneous ones.
- Bench-scale toxicity tests cannot be fully and adequately specified without knowing the real-scale fire types that they are to represent (scenario). When the real-scale fire characteristics are known, an attempt should be made to match conditions in the bench-scale test.

2.1. Thermal Environment of the Test Specimen

In order to assess the validity of a particular bench-scale fire model, it is necessary to consider the parameters affecting the burning behaviour at each fire stage and the yields of toxic products that are replicated by the model. The temperature profile around a product undergoing combustion determines both the burning rate and the yields of the combustion products. The nature of this profile varies with the fire type. The challenge any bench-scale apparatus has to meet is to be capable of replicating at least one of the fire stages below [1].

The combustion process is generally divided into several stages. In wildfires pyrolysis (pre-ignition), flaming combustion and smouldering (or glowing) are the main stages [26]. Compartment fires are developed via another course of events. Once smouldering is initiated, a hot glowing char is often formed, in which the carbon oxidises exothermically. When the hot char decomposes, it heats the neighbouring material, initiating a non-flaming thermal decomposition [27]. Pyrolysis occurs when a fuel is heated and chemical material transformations occur at the fuel surface. Non-flaming fires typically produce high yields of toxic products at fairly low rate. When sufficiently high temperatures are reached, flaming fires occur. Flaming combustion involves much shorter reaction times, and for small fires converts most of the fuel to carbon dioxide and water. Fires in enclosures, such as buildings, trap the hot reacting gases below the ceiling, increasing the temperature, despite the lack of oxygen, and flaming can continue at oxygen concentrations less than 5% [28]. This is because during stable flaming, volatiles produced by the decomposing material are transported just outside the solid material into the reaction zone, with flaming combustion occurring entirely in the gas phase. Under well-ventilated conditions, mixing with cold air results in the extinguishment of the flame tip. This causes smoke particles and small amounts of partially decomposed organics to escape without being fully combusted. In ventilation-controlled flaming fires, flames are also, in part, burning in the upper, oxygen-depleted smoke layer. These processes result in inefficient, fuel-rich combustion with high yields of dense smoke and toxic chemical species. For larger fires, the flame zone is too big to allow access to sufficient oxygen so even large open-air fires are under ventilated. When flashover occurs, all fuels in the area become involved in the fire. This happens when the ventilation is sufficient to raise the upper layer temperature up to 550–600°C, and the amount of burning fuel is sufficient for the heat radiation to pyrolyse and then ignite any fuel in the neighbourhood [29, 30].

2.2. Bench-Scale Tests

There are several ISO standard methods using bench-scale tests in the assessment of fire effluent toxicity [31–33]. The most common examples are the steady-state tube furnace (ISO TS 19700), smoke density chamber (ISO 5659-2) and cone calorimeter (ISO 5660-1) tests. The steady state tube furnace was designed specifically for the assessment of smoke toxicity. The smoke density chamber was designed to assess smoke generation to regulate for visual opacity, and the cone calorimeter was designed as a tool to investigate material flammability and burning behaviour.

The steady-state tube furnace method (ISO TS 19700) [31] allows for potential atmosphere and temperature control during the experiment, using pre-decided and controlled combustion conditions. The released gases can be analysed using appropriate techniques. However, the method is limited to fairly small linear samples, typically 25 mm × 25 mm × 800 mm or less, and it is most appropriate for testing individual materials. Testing thickly layered composite materials may not be possible with this method.

The smoke density chamber test (ISO 5659-2) [32] uses test samples that are square and flatter (75 mm by 75 mm, thickness of few tens of mm). During the experiment, the sample is confined in a closed air-filled chamber. The main drawback is that after ignition, the sample burns in conditions that are not controlled but rather governed by initial conditions, the development of gases and oxygen consumption. This test also does not endeavour to represent full-scale fire performance. Therefore, interpretation of the results is key to ensure that they are not extrapolated outside of their application area.

The standard cone calorimeter method (ISO 5660-1) [33] is widely used as a flammability assessment tool. The sample burns in an open, standardised atmosphere with nominal 21% oxygen. The samples are 100 mm by 100 mm, up to 50 mm thick, and of similar mass compared to the tube furnace method, to which the toxic gas yields in well-ventilated flaming combustion are comparable. Modifications improved the working of the basic cone calorimeter method. Adding a chamber to the experimental set-up allowed the specimen to burn with a flow- and concentration-controlled amount of available oxygen. In first variations, enclosing the whole thermal part of the apparatus was considered, while later, the controlled atmosphere chamber (CAC) was used. The CAC was improved by adding a stack to allow a longer burning time of the gases before contact with cold atmospheric air. These modifications combine the positive aspects of the standard cone calorimeter method (ISO 5660-1) and the tube furnace method (ISO TS 19700). This is a promising tool that is complementary to the tube furnace as a small-scale toxicity test. Both tests have the potential to generate interesting information that could be used in modelling. However, to date, no standard apparatus design has been accepted because the major disadvantage for studying under-ventilated flaming (heat fluxes > 50 kW m^{-2}) is that the load cell becomes over-heated during the time required for the lower oxygen concentration to fill the chamber. Thus, mass losses cannot be recorded for the type of developed flaming intended. Closed chamber tests at their current state also exhibit difficulties in replicating fire effluents when the burning is in under-ventilated mode. It seems this is mainly due to the fact that part of the burning also takes place outside of the chamber; the relatively short stack may also be the reason for this increased variability.

The key difference between methods is that in the ISO TS 19700 test, the sample burns at a fixed rate as it is fed into a furnace of increasing heat flux, so the ventilation can be pre-set. In the cone calorimeter and smoke density chamber, the heat flux is fixed, and the burning rate of the sample is allowed to vary, so the ventilation condition cannot be controlled.

2.3. Toxicity and Ecotoxicity Assessment with Bench-Scale Tests

Bench-scale tests have already been proven to be a useful tool for toxicity assessments. Nonetheless, some difficulties in replicating experiments in under-ventilated conditions are indicated. For toxicity assessment, most research is based on smoke components like CO, CO_2, HCl, HCN and NO_x combined with a theoretical toxicity determination by calculating fractional effective dose (FED) and LC_{50} (lethal concentration of the fire effluent emitted to produce death in 50% of test animals) with simple mathematical equations (see Table 1) [1]. Amon et al. [76] evaluated the existing models and measurement methods and have written an excellent report summarising methods to develop toxicity and ecotoxicity data from different scale experiments. Investigations were performed to determine which chemical species should be included in the eco-toxicological evaluation of fires and catalogue the existing models and measurement methods that are appropriate to characterize the identified species. Information is provided about eco-toxicants produced in fire effluent, together with predictive models and measurement techniques that can be used for determining the presence and concentrations of eco-toxicants caused by a fire incident. The harmful effects of unwanted fire on the environment was described by using predictive models, physical measurements, gap analysis and life cycle analysis (LCA), which were found in the existing literature.

3. Analytical Techniques to Detect Toxic Compounds

Organic compounds are considered the most important products in fire effluents that can have an adverse effect on human health and the environment [1]. To assess the total hazard of an occurring fire, it is not only important to determine the initial composition of the effluent but also to investigate the possible (chemical) composition changes taking place during transport from the fire into its surroundings. If fire causes an impact to the environment, it will generally affect a large area and the ecology of that area. The impacts can be broken into pathways, over which the hazards travel from the source to the target [20]. The main pathways for environmental pollution by fires are through water, air, and soil. Since the composition of organic products, generated from fires, changes rapidly with progression of combustion, and in a manner that is dependent on the fire condition, such analyses can be challenging. First of all, it is difficult to identify all individual organic compounds and their exact concentrations produced during

Table 1
Literature review about toxicity studies performed with bench-scale tests

Furnace	Fuel	Measured parameters	Test conditions	Comparison to large scale fires	Literature References
Purser furnace (ISO TS 19700, BS 7900)	PP, nylon 6.6, PE, PS, MDF	CO, CO_2, HCN, NO_x, total hydrocarbons, particulates	Different CO/CO_2 ratios	☒	[34]
Purser furnace (IEC 60695-7-50), Static tube furnace (IEC 60754-2)	PP, PVC coated cables, PS, LDPE, acetate-ethylene copolymers, PMMA	CO, CO_2, HCl	From smouldering to post-flashover; variating ϕ	☒	[35]
Purser furnace (ISO TS 19700)	LDPE, PP, PVC, nylon 6.6, nylon 6, PS	CO, CO_2, HCl, HCN, NO_x, total hydrocarbons	T = 650°C, 750°C, 825°C, 850°C; variating ϕ	☒	[36]
Purser furnace (ISO TS 19700)	PVC, LDPE, electric cables	CO, HCl + Comparison to rat lethality data	Variating ϕ	☐	[37]
Purser furnace (ISO TS 19700)	PU foam, polyisocyanurate rigid foam, nylon 6, MDF and velour mixed fibre fabric with/without FR, acryl jersey fabric, plywood	CO, CO_2, HBr, HCN, NO_x, O_2, particulates, TUHC	T = 650°C, 700°C in air; T = 850°C + O_2 = 10, 12% Variating ϕ	☒	[38]
Smoke density chamber (ISO 5659-2), Controlled atmosphere cone calorimeter (ISO 5660), Fire propagator apparatus (ASTM E 2058), French railway test (NF X 70-100), Purser furnace (ISO TS 19700)	PP, nylon 6.6	CO, HCN	T = 650°C, 850°C Variating ϕ	☒	[39]
Cone calorimeter, NFPA 269, ASTM E 1678	PVC, PMMA, timber	CO, CO_2, HBr, HCl, HCN + EC_{50}, FED, IC_{50}, IT_{50}, LC_{50}, LT_{50}	Flashover heat 20, 50 kWm^{-2}	☐	[40]

Table 1
continued

Furnace	Fuel	Measured parameters	Test conditions	Comparison to large scale fires	Literature References
Radiant furnace + radiant smoke toxicity apparatus	Different building materials (theoretical article)	CO, CO_2, HBr, HCl, HCN, HF, NO_x + LC_{50}, Tests on animals	Post-flashover	☒	[41]
Cone calorimeter (ISO 5660), Tube Furnace (DIN 53436)	Sandwich panels of the steel-skinned type	CO, CO_2, HBr, HCl, HCN, TUHC + FED, LC_{50}	T = 500°C, 700°C Air = 100, 300 Lh^{-1} 35, 50 kWm^{-2}	☒	[42]
Cone calorimeter (ISO 5660), Tube Furnace (DIN 53436)	Rubber foam, PE foam, rock wool, phenolic foam, PU foam, polyisocyanurate foam with/without metallic face	CO, CO_2, HBr, HCl, HCN, NO_x, TUHC + FED, LC_{50}	T = 500°C, 700°C 35, 50 kWm^{-2}	☒	[43]
Purser furnace (IEC 60695-7-50), static tube furnace (NF X 70-100)	PVC or LSZH coated cables	CO, CO_2, HCl, hypoxia, organics + FED, LC_{50}	Well ventilated and under ventilated flaming	☒	[44]
Cone Calorimeter, Tube Furnace (DIN 53436)	Insecticides, Herbicides, vulcanizer, solvents, nylon, PP	CO, CO_2, HCl, HCN, NO_x, SO_2	Variating ϕ 25, 50 kW m^{-2}	☒	[45]
Purser furnace (ISO TS 19700, BS 7900), static tube furnace (NF X 70-100)	LDPE, PS, nylon 6.6, PVC	CO, HCl, HCN, organics	T = 400°C, 600°C, 800°C Air = 2 L min^{-1} Variating ϕ	☐	[46]
NFPA 269, ASTM E 1678	Sofa, particleboard bookcase, electric power cable	CO, CO_2, HCl, HCN, NO_x, formaldehyde, acrolein + FEC, FED	Pre-flashover Post-flashover	☒	[47]
Controlled atmosphere cone calorimeter	Sandwich material of balsawood and polyester skin	CH_4, C_2H_8, CO, CO_2, NO_x, formaldehyde	50 kW m^{-2} O_2 = 0, 5, 10, 15, 23%	☐	[48]

Table 1
continued

Furnace	Fuel	Measured parameters	Test conditions	Comparison to large scale fires	Literature References
Purser furnace (ISO TS 19700)	Glass wool, stone wool, expanded PS, phenolic, PU, polyisocyanurate	CO, CO_2, HBr, HCl, HCN, NO_2 + FED, LC_{50}	Oxidative pyrolysis, flaming fire Variating ϕ	☐	[49]
Purser furnace (ISO TS 19700)	Nylon 6.6 and nylon 6 glass fibre composites with/without FR	CO, CO_2, HBr, HCN, NO2 + FED, LC_{50}	T = 650°C, 825°C Well ventilated	☐	[50]
Purser furnace (ISO TS 19700, BS 7990)	LDPE, PS, nylon 6.6, PVC	CO, CO_2, HCl, HCN	T = 650°C, 750°C, 850°C Variating ϕ	☐	[51]
Purser furnace (ISO TS 19700, BS 7990)	PP and nylon 6 with/without FR	CO, TUHC	T = 650°C, 825°C Variating ϕ	☐	[52]
Purser furnace (ISO TS 19700)	PVC carpet	CO, CO_2, HCl, PAH, PCDD, PCDF	T = 350°C, air = 2 $Lmin^{-1}$ T = 650°C, air = 10 $Lmin^{-1}$ T = 825°C, air = 2.1 $Lmin^{-1}$	☐	[53]
Purser furnace (ISO TS 19700)	PP nanocomposites	CO, CO_2, hydrocarbons	T = 650°C, 825°C Variating ϕ	☐	[54]
Vaporiser + isothermal alumina tubular reactor	Captafol (sulfenimide fungicide), Folpet, Captan	$COCl_2$, $SCCl_2$, C_2HCl_3, HCl, CS_2, COS, SO_2, C_6H_6, HCN, CO, CO_2, PCDD/F, VOCs	Under and well-ventilated non-flaming fires	☐	[55–57]
Cone calorimeter	CCA-treated *Pinus radiata*	PCDD/F	Flaming combustion	☐	[58]
Vaporiser + isothermal alumina tubular reactor	Alpha-cypermethrin (insecticide)	PCDD/F, VOCs	Combustion, post combustion and cooling-down zone conditions	☐	[59]
Cone calorimeter	Fire retarded and non-fire retarded TV-sets	CO_2, CO, HBr, HCl, HCN, NO_X, Sb, VOCs, PAH, PCB, PCDD/F, PBDD/F, deca-BDE, TBBPA	35 kW m^{-2}	☒	[60]

Table 1 continued

Furnace	Fuel	Measured parameters	Test conditions	Comparison to large scale fires	Literature References
DIN furnace, Cone calorimeter	Tetramethylthiuram monosulphide, 4-Chloro-3-nitro-benzoic acid, Chlorobenzene, PP, Nylon 6.6	O_2, CO, CO_2, NO_x, HCl, HCN, SO_2, unburned hydrocarbons	Under-ventilated and well-ventilated combustion	☒	[61]
Ceramic lined furnace	Pine wood crib	Unburned hydrocarbons, NO_x, CO, CO_2, and O_2	T = 300, 400, 500°C; O2 = 14, 11.8, 8.5%	☐	[62, 63]
1.6 m^3 fire enclosure	Folded cotton towels	CO, formaldehyde, CO_2, benzene, toluene, xylene, TMB, butadiene, NO_x, SO_2, HCN, methane, acrolein, LC_{50}	Smouldering combustion	☐	[64, 65]
1.6 m^3 fire enclosure	Acrylic curtains	CO, HCN, acrolein, NOx, formaldehyde, LC_{50}	T = 350–500°C, ventilated conditions	☐	[66]
1.6 m^3 fire enclosure	Kerosine, diesel, wood cribs	23 toxic gases (e.g. N_2O, COS, HCl, HF, MeOH, trimethylbenzene, EtOH, naphthalenes, xylenes, acetaldehyde, butadiene. formic and acetic acid)	Air starved fires	☐	[67]
Tewarson calorimeter	Li-ion battery	HF, CO, NO, SO_2,HCl	35 kW m^{-2}	☐	[68]
Tube furnace	Fabrics—natural fibres: flax, cotton, wool, hemp; fabrics—synthetic fibres: polyamide, polyacrylic, polyester	CO, HCN, NO_x, SO_2, H_2S, CO_2	T = 450, 550, 750°C absence of a combustion initiating flame.	☐	[69]

Table 1
continued

Furnace	Fuel	Measured parameters	Test conditions	Comparison to large scale fires	Literature References
Tube furnace	Solid wood, flexible PUR, fire-retarded rigid PU, PVC carpet, data cable with fluorine-containing polymer, PVC based cable sheathing material, fire-retarded PE cable insulation material	CO_2, CO, HCl, HF, HCN, NO, NH_3, PAHs, isocyanates, VOCs, aldehydes	Well-ventilated and oxygen deficient combustion	☐	[70]
Cone calorimeter	24 different building materials	CO, HCl, HBr, HF, HCN, NO, NO2, NH_3, SO_2, Isocyanates, aminoisocyanates, amines	35 kW m^{-2}	☒	[71, 72]
Cone calorimeter	PVC sheated cable	CO, CO_2, HCl, acrolein, formaldehyde, LC_{50}	40 kW m^{-2}	☐	[73]
ISO/TS 19700 steady-state tube furnace, controlled atmosphere cone calorimeter, smoke chamber	Polymeric foam, organic fibre material, mineral fibre material PMMA	CO_2, CO, HCN, NO_x, SO_2, HCl, HF, HBr	Pyrolysis, flaming combustion; T = 350, 650, 700, 825°C; 25, 50 kW m^{-2}	☐	[74]
Steady-state tube furnace (ISO/TS 19700)	PVC carpet, wood board	PAHs, isocyanates	Oxidative pyrolysis, well-ventilated flaming fires, under-ventilated flaming post-flashover fires	☐	[75]

ϕ radiant flux intensity (measure for ventilation conditions), *EC50* half maximum effective concentration, *FEC* fractional effective concentration, *FED* fractional effective dose, *FR* fire retardants, *IC50* half maximal inhibitory concentration, *IT50* half inhibitory time, *LC50* lethal concentration to 50% of test group, *LDPE* low density polyethylene, *LSZH* low smoke zero halogen, *LT50* median lethal time, *MDF* medium density fibre boards, *PE* polyethylene, *PMMA* poly(methyl methacrylate), *PP* polypropylene, *PS* polystyrene, *PU* polyurethane, *PVC* polyvinyl chloride, *TUHC* total unburned hydrocarbons, *VOCs* volatile organic compounds combustion. Another problem is the large variety in the structure and, as such, the solubility of created compounds, which makes a complete extraction very difficult. Furthermore, the variety of the compounds in the fire effluent extract calls for multiple analytical methods (e.g. Fourier Transformation Infrared spectroscopy [FTIR], high pressure liquid chromatography [HPLC] and gas chromatography mass spectrometry [GC–MS], the latter two with different sampling and adsorption/desorption techniques) to be employed on the same effluent sample in order to detect as many as possible. Lastly, the lack of multi-compound standards or verified chemometric methods of analysis makes the final processing of spectra and determination of present compounds difficult and prone to errors.

There are 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 chapter, measurement techniques were collected from standards organizations, government regulations, and the literature. ISO published a document to standardize the collection and measurements in the environment of certain pollutants, which are produced during fire events [22]. Amon et al. [76] found a smart way to compile all this information into an "Eco-tox spreadsheet". The spreadsheet contains eco-toxicants, their phase, predictive models, measurement techniques, uncertainty of predictions or measurements, and the scope/limitations of use for the models and measurements.

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. To evaluate the impact of persisting organic pollutants, originating from fire effluents, on the environment, analytical procedures, which are specific for the studied class of toxic components and test environments (soil, aquatic environment, air or sediments), are required. The main problem is that most techniques are not time-resolved, which means that for each time interval a new sample needs to be collected. The concentrations found in a fire-polluted environment must be compared with a corresponding unpolluted "control" and composition of the fire effluents. In this way, it is possible to estimate the extent of toxic hazard and study transformations of organic compounds during transport into or interactions with the previously present components in a particular environment.

Sampling of emissions to the air can only be made when the fire is ongoing, and sampling from the fire plume is extremely difficult. In the air, free organic compounds, as well as organics present on PM, can be determined. Analytical techniques intended to measure ecotoxicants in the aquatic environment are described better than for other environments. Those optimised for waste or drinking water can also be applied on water in rivers and lakes or run-off water obtained from fire extinguishing, but sea water is often a more complex matrix and different analytical techniques are required. Soils and sediments are by all accounts more complex matrices to differentiate between the abundant present organic matter and the contamination. This is especially valid if the contamination is only present in lower concentrations.

Most literature for toxicity assessment is focused on the fire effluents released into the air, which can contain many corrosive, toxic, irritant or combustible chemical species together with relatively large quantities of condensable water. The standard ISO19701:2013 [77] describes how to measure CO, CO_2, HCN, HCl, HBr, HF, NOx, acrolein, formaldehyde, acetaldehyde, SO_2, CS_2, ammonia, heavy metals, phosphates, phenol, benzene, toluene, styrene, nitriles, formic acids, isocyanates and total hydrocarbons with Colorimetry, HPLC, GC–MS and inductive coupled plasma (ICP) as the main analytical tools. However, for some of these gases, FTIR spectroscopy offers an improved procedure because it provides 'in-situ' time-resolved measurements over relatively short periods. FTIR analysis of fire gases is now conducted routinely in tests in labs all over the world. Quantitative analysis of inorganic and selected smaller organic species is conducted with high precision following ISO19702:2015 [78]. The analysis of bigger organic species is, however, more challenging due to the complex fire gas mixture.

In addition to the compounds mentioned above, hundreds of different volatile organic compounds (VOCs) are also released during fires. Sampling and analysis of nonpolar VOCs is described in the U.S. Environmental Protection Agency (EPA) TO14A method [79]. Other frequently used methods for collecting VOCs are solid phase micro extraction (SPME), syringe, sorption tubes, midget impingers and Tedlar bags [80]. Several groups did a thorough study about a multitude of possible VOCs that can be released during different types of fires [81–85]. Care must be taken because VOCs can be released as free pollutants into the air or adsorbed on PM; therefore, different measurement techniques are necessary [86–88].

Carcinogenic compounds like polychlorinated biphenyls (PCBs), dioxins and PAHs are also found both as volatiles as well as adsorbed to PM in fire effluents and air. There exist several methods for capturing these compounds, mainly using XAD adsorbents and polyurethane foams (PUFs) in combination with glass-fibre or quartz filters. The standardised method for sampling of PCDD/Fs in fire effluents via the filter/condenser method is described in EN1948:1-3:1997 [89]. GC–MS is the main method for their qualification and quantification, while PAHs, if in high enough concentrations, can be analysed using HPLC. Analysis of PCDD/Fs is standardized in EPA method 23 [90], while the procedure for PCDD/Fs on PM10 or fly ash is found in RCRA method 8280 [91] and EPA Method 201a/202 [92, 93]. The EPA TO-13A [94] for sampling and analysis methods of PAHs in ambient air could be perfectly applied for determining PAHs in fire effluents and air. There have also been several reports on the determination of PAHs [95–106], PCDD/Fs [95–97, 107–111], organic pollutants [112, 113] and PCBs [95–97] in fire effluents and air following non-standardised methods or modifications of the existing standards.

Also, a whole range of unknown organic and inorganic compounds can be adsorbed on PM in addition to PCBs, dioxins and PAHs. Methods to extract and analyse PM captured on various filters have been developed by Fine et al., Garcia-Hurtado and Hays et al. [86, 114, 115].

Afterwards, these gaseous organic pollutants, which are formed in the fire plume and adsorbed onto a particle, can drop out of the atmosphere and deposit on the surface of a stream or on the soil, thereby polluting nearby surface water, soil or sediment. Another way of releasing eco-toxicants into the nearby environment is via water run-off produced from fire extinguishing agents. Several studies were performed to measure ecotoxicants inside the environment. Procedures to measure PAH concentration are described for surface water [116–118], sea water [104], soil [119] or sediments [118, 120, 121]. Methods to measure the PCDD/F concentration found in water and on the PM present in water [122–124], soils [125] and sediments [125] are also described. Procedures on how to measure VOCs are described for surface water [87, 126, 127], soils [128–130] and sediments [128]. General organic pollutants can be determined in surface water [131, 132], soils [133] and sediments [133].

4. (Eco)toxicological Assessment

In this section, the different existing approaches to estimate fire effluent toxicity on humans and their direct effects of exposure on the environment will be considered, in light of their advantages and/or disadvantages. Ultimately, it is of interest to investigate how environmental impacts of fire might aggregate: locally, regionally and globally. As more data on fires and impacts become available, such an approach to assessing aggregated impacts can be developed.

4.1. Toxicology of Fire Effluent Gasses

There is a lack of knowledge on the effect of organic products in fire effluents on the human body since it cannot be measured directly for legal and ethical reasons. Different human toxicity assessment methods were established to overcome this type of problem. In vitro studies use human cells, isolated tissues and organs outside the body to investigate the toxic and adverse reactions of substances towards them [1, 134]. These types of experiments have potential to replace animal testing [134]. Tests on animals are performed either directly, using animal exposure, or indirectly, by comparing the measured toxins' concentrations in a particular medium with information on dose-dependent effect recorded in one or several previous studies. Animal testing is not a preferred system of use since it has certain shortcomings. The data rely on the untested assumption that effects on animal subjects may be simply extrapolated to humans [135]. Sadly, there is a lack of procedures to be used to evaluate the lethal concentration limits and the lethal dose for a broad range of organic compounds.

The general approach in generating toxic potency data from chemical analysis is to assume additive behaviour of individual toxic compound and express each concentration as a fraction of the lethal concentration for 50% of the population for a 30-min exposure (LC_{50}). Summing these contributions generates a fractional effective dose (FED) [136]. The use of this additive model is almost certainly an over-simplification because the toxic effects of different gases occur in different organs [25].

The most appropriate way to determine the toxicity of fires in buildings is described in ISO 13571 [137], which predicts the incapacitation for humans exposed to fire smoke. This standard is based largely on primate exposure data.

4.2. Ecotoxicity Tests on the Nearby Environment, Contaminated by Fire Effluents or Fire Supressing Agents

Ecotoxicity is the study of how chemicals interact with organisms in the environment. Assessments of ecotoxicological effects include estimating the amount of bioaccumulation of a chemical within the food web and its persistence in the environment. These two factors affect the amount and duration of environmental exposure and help predict which organisms are most likely to be affected [138]. For this purpose, it is of extreme importance that reports of environmental contamination following major fire disasters are prepared [20, 139–141]. Such data are usually not collected due to a combination of factors: emergency services are too busy dealing with the fire to monitor the emissions, they lack necessary training to monitor emissions or to understand the impacts of firefighting on the environment. In some countries, there are other public servants that could be called to the scene of a fire to take responsibility for emissions measurements, but they are not always informed when a fire occurs.

Another way of assessing ecotoxicity is by exposure studies on organisms. Primary measurement end points for acute and chronic toxicity are organisms' survival, growth and, often, reproduction. Aquatic bioassays include water column (*Daphnia*, crustaceans, algae and fish—freshwater and marine), sediment (*Chironomus*, *Hyalella*, oyster) and amphibians (frog embryos). Terrestrial assays include standardized studies for germination and growth of plants (e.g. *Trifolium* sp.), various types of soft- and hard-bodied soil invertebrates, honeybees and birds. Soil microbial function tests are also available to determine chemical effects on respiration, decomposition and nitrogen fixation. In general, the information for toxicity to terrestrial organisms is also sparse. [129].

Avoidance response was introduced as an easy, fast and sensitive ecotoxicity test. For certain chemicals, the avoidance response could give results, which can be as sensitive as the ones obtained from reproduction tests; while for other chemicals, the results are at least as sensitive as the ones obtained by survival tests. The main advantage of avoidance tests is their relative short duration (maximum 2 days) and experimental simplicity (no specific life cycles of the animals required, easier counting, etc.). Standard avoidance test guidelines have been developed for earthworms [142] and *Collembola* (ISO 17512-2) [143], while similar tests have also been executed with enchytraeids [144–146], oribatid mites [147] and isopods [148, 149]. It was demonstrated that the avoidance behaviour is primarily determined by pollutants and not by chemical-physical soil properties. Avoidance behaviour of at least 80% of the specimens under assessment is proposed as a criterion for toxicity. Presumably such tests are limited to molecules that occur naturally, so that a detection and avoidance response has been allowed to evolve. Similar tests also exist in the aqueous environment, called the fish avoidance test [150].

For waters in natural environments, the Microtox® Toxicity Test is used to evaluate the inhibition of the luminescence in the marine bacterium *Vibrio fischeri*. In the presence of pollutant agents, the natural bioluminescence of *V. fischeri* is reduced, and the toxicity is expressed as the half maximal effective concentration (EC50) counted according to the standard procedure ISO 11348 [151]. Toxicity testing based on microorganisms is gaining popularity because it is relatively quick, reproducible, cheap and does not raise ethical issues.

Different authors have noted the influence of fire or fire extinguishing agents on the environment. Meharg et al. [5] investigated a forest ecosystem, which was contaminated as a result of a fire involving 600t of PVC. Forests effectively scrub semi-volatiles from the atmosphere, leading to elevated levels of detected contaminants in forests compared to non-forested areas. Livers of wood mice (*Apodemus sylvaticus*) caught in these areas were analysed for dioxins and furans, showing elevated residues and physiological damage in the rodents.

McDonald et al. [12] conducted acute toxicity tests of firefighting chemicals and foam-like fire suppressants on important aquatic invertebrates, such as the amphipod *H. azteca*, since disruption of ecosystem functions at lower trophic levels could, in turn, impair the health and well-being of organisms at higher trophic levels, such as fish.

Silva et al. [4] studied the deleterious effects of the ash-laden runoff from forest fires on water quality by preparing aqueous extracts of this ash (AEA). The AEA was analysed with respect to a large group of chemical compounds and the sixteen prioritized PAHs. An ecotoxicological screening of the AEA was performed with four standard aquatic species from different functional groups and trophic levels with limited results.

Hertzberg et al. [152] investigated the influence of HCl and PVC-smoke by a new method involving isolated and perfused guinea pig lungs. A rapid decline in the lung physiology parameters, conductance and compliance was observed. Additionally, PM was found at different levels in the lung tissues and chemical species from the smoke gases were found in the artificial blood solution in the lungs used in the experiments.

To ensure environmental safety of fire extinguishing chemicals used to fight forest fires, the U.S. Forest Service requested an investigation to determine the potential for UV-enhanced toxicity and environmental persistence of fire-retardant chemicals [153, 154]. Their results showed persistent toxicity of rainwater runoff, particularly from sandy or rocky surfaces, while soils high in organic matter rapidly decreased chemical persistence. Other fire-related factors, such as ash effluents, may increase the chemical toxicity of rainwater runoff.

5. The Importance of Material Toxicity Studies and Fire LCA Analysis

Materials used in buildings are generally considered for their properties from several perspectives, such as mechanical and aesthetical characteristics, durability, VOC emissions, and surface properties. From the point of view of toxicity and ecotoxicity, it is also essential to make buildings and construction products from materials that emit as little toxic compounds as possible during fires. Therefore, it is important that the toxicity of fire effluent emissions and resulting ecotoxicity of different materials is compared. No data exist about the impact of construction materials on the ecotoxicity, but in the literature, building materials were compared according to their fire effluent toxicity. The use of bench-scale tests, in particular with the ISO TS19700 steady state tube furnace, is, despite its shortcomings, currently the most suitable tool to perform toxicity assessments. As the toxic products of some materials vary as a function of ventilation conditions, it is necessary to perform assessments of fire toxicity under less-ventilated conditions, under which usually the most toxic effluents are emitted. Lack of studies done in all ventilation conditions, inconsistencies and shortcomings in the methodology, and lack of information about the conditions in a large building fire, make it difficult to extrapolate measured toxicities to real fire conditions. Care must be taken during fire toxicity studies because, in most cases, the bulk of the early stage fire hazard comes from combustion of occupant goods, not construction materials [155]. Therefore, toxicity studies should also focus on these types of materials.

The large amount of studies, which investigate the toxicity of polymers (see Table 1, [156]), can give valuable information on which construction materials, such as insulation foams, cable insulations or plastics, to use in buildings. However, making such decisions is not always straightforward since the toxicity of materials generally changes according to the fire scenario. It was found that since neither glass nor stone wool undergo flaming combustion, their fire toxicity is negligible compared to that from any of the foam products (e.g. expanded polystyrene, phenolic, polyurethane, polyisocyanurate) [49]. The fire toxicity of expanded polystyrene foam is lower than that of polyurethane, polyisocyanurate or even phenolic foam [49]. Hull et al. [46] found that Nylon 6.6 produces high concentrations of HCN in under-ventilated conditions, which makes it the most toxic plastic in such fires. PVC also shows very high levels of toxicity due to its HCl release in the fire effluent. Polyethylene shows high toxicity for smouldering and under-ventilated combustion but lower toxicity for well-ventilated combustion. The outcome of such toxicity studies can have major impacts. The results of the investigation of Hull et al. [41] about the fire toxicity of burned cables was used to persuade the regulators of the need to introduce a special classification in the Construction Products Regulation (305/2011/EU—CPR, 2011), which came into force across Europe in 2013. This has driven the switchover from toxic PVC to low smoke/zero halogen cable insulation coatings in the non-domestic sector over the last years.

Different researchers also studied the toxicity of fire effluents when natural wood and wood treated with preservatives or fire retardants were used as a building material. This is especially relevant as using wood in construction is becoming more and more popular because of its environmental friendliness (especially when compared with most other construction materials). It is well known that in the presence of halogens PCDD/F are formed during wood combustion via precursors like phenols and lignin or via de novo reactions in the presence of particulate carbon and chlorine, albeit in smaller amounts than from most other materials. It was found that combustion of the natural, uncontaminated wood leads to much lower PCDD/F emissions than of treated wood [157, 158]. An interesting review of dioxins during wood combustion was written by Lavric et al. [159] Test results about the behaviour of copper, chromium and arsenic in fire effluents of copper-chromium arsenate (CCA)-treated wood (CCA was a widely used wood preservative in the middle of the twentieth century) showed that almost all the original amounts of chromium and copper were retained in the ash, while some of the arsenic evolved into the gas phase. This phenomenon increased with increasing temperature and air supply [160]. Otherwise, the field of wood combustion is still quite unexplored. Experiments are necessary to make comparisons between different types of wood, different combustion conditions and different experimental parameters. The ultimate goal must be an accurate and reliable determination of the specific hazard posed by different wood species and wood products that are used commercially. Another area that needs further work is that of emission toxicity from burning wood treated with preservatives and/or fire retardants. There is extensive literature concerning fire retardants per se [161, 162], but very little has been reported concerning the toxicity of emissions from wood treated with fire retardants [163].

Fire retardants also tend to have unintended negative effects on the environment and human health. Less toxic alternatives appear to be available already and manufacturers of flame retardants addressed data gaps and commissioned necessary tests and studies. Studies on the influence of fire retardants on fire toxicity showed that brominated and antimony-containing flame retardants increase the yields of the two biggest killers in fires (CO and HCN) [50]. It was found that it would be a significant fire safety advantage to replace brominated flame retardants. Most phosphorus, inorganic and nitrogen containing flame retardants have a low environmental impact relative to halogenated and antimony-containing flame retardants, which means that they pose less harm to the environment and do not bio-accumulate in biota [164]. In addition, they have a low (eco) toxicity profile and will eventually mineralize in nature.

Research that investigates the combustion products of several materials is of high importance. The more detailed information from each material about the released toxic products is available, the better the picture on environmental level can be made, when combining all the data from several fire types and conditions. A great example of such research can be found in the work of Blomqvist et al. [15].

Some research groups went a step further than just comparing the toxicity and environmental impact of building materials during fires by studying emissions upon combustion and took into account the whole life cycle of these products. A standard LCA model represents the best modern method to determine the environmental impact of a series of choices concerning the life cycle of any given product, from exploitation of resources to manufacturing, through use to recycling, re-utilisation or disposal. Assuming that a certain number of fire accidents are unavoidable in any society, it is important to take fires into consideration when defining the environmental impacts from products. Therefore, a Fire-LCA model was developed by SP in Sweden [165–167]. Such a model includes modules to account for accidents, like fires, but also recognizes the extent of the damaged area, the fire-fighting efforts and the replacement of damaged materials. The model itself is generally applicable, if appropriate additions and changes are made for each new studied case. The guidelines are better developed for items usually found as equipment, appliances, fixtures, fittings or decor in a building, although this does not exclude their application to building materials. In a first case study, a TV with high fire performance enclosure material was compared to that with easily ignitable enclosure material [165, 168–170]. The second application of the Fire-LCA model focussed on a comparison between two types of electrical cables, assumed to have essentially the same fire performance [171, 172]. The third application of the Fire-LCA model has focussed on a comparison between two types of furniture, one having the minimal fire performance required on mainland Europe and the other with fire performance similar to that required in the UK [173, 174]. In all cases, the benefits of a higher fire performance are weighed against the "price" society has to pay for the production and handling of possible additives and/or other ways of production. The Fire-LCA model was later also applied by other research groups [175] or used as a basis to develop other assessment tools [176]. Another type of model is the Dynamic LCAFire and was developed by Chettouh et al. [177].

The most important aspect is that LCA-based environmental impact methods can be used to assess a wide range of environmental impact categories such as: global warming, eutrophication, resource depletion, ecotoxicity of soil and water bodies.

6. Conclusions

Ecotoxicity studies are a fascinating multidisciplinary area, investigating how fuel chemistry, conditions of complex fire processes and the effect and dynamics of produced fire effluents can have a significant influence on ecosystems. It requires understanding the stages of fire growth from ignition to ventilation-controlled burning, the behaviour of fire on different scales, the behaviour of aerosol particulates and chemical components in different environments, the response of living organisms to the components present as well as their chemical quantification and their relationship to its ecotoxicity.

Nonetheless, the current state of research in the field of fire ecotoxicity leaves a lot to be desired. Several methods are already developed to measure concentrations of organic and inorganic products that are generated during fires. However, no functional mathematical algorithms exist yet to interpolate these measured concentrations into a valid assessment of the toxicity of a fire, resulting in the fact that there is currently no way to satisfactorily assess its environmental impact. This is mainly because we do not yet really know either the short- or long-term exposure effects of many of these chemicals, which makes it hard to judge their combined effects in varying concentrations. Additionally, these compounds are spread by smoke particles generated in the fires, and the properties of these particles should also be taken into account. Finally, the fact that different compounds can interact with each other or with their environment, when conditions change, makes it even harder to create fitting models of their behaviour and toxicity.

Bench-scale methods, which create specific fire conditions on a lab-scale, can generate a lot of information on what is released during a real fire event, especially in controlled atmosphere environments. However, the largely incomplete data gathered so far is difficult to interpret to the level of an actual wildfire or residential/industrial fire. These types of tests are also useful to compare the fire toxicity effects of construction materials. In this way, engineers can focus on the use of the safest and most environmentally friendly materials in the construction of future houses. Until now, most of the data gathered experimentally is collected from burning only a single type of material. Therefore, one of the future challenges in fire toxicity will be to investigate materials' interaction of burning composites and determine its impact on the environment.

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Availability of Data and Material

Not applicable.

Compliance with Ethical Standards

Conflict of interest The researchers claim no conflicts of interest.

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