

# Review of Fire Emissions from Products with and without BFRs and the Hazard of Exposure for Fire Fighters and Clean-up Crews

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## Abstract

Issues associated with the toxicity of flame retardants and the products of their breakdown in a fire situation have been discussed for some time. The diversity of flame retardants and of combustion conditions in fires make it difficult to generalise in terms of the hazard of exposure to fire emissions from flame retarded products relative to that associated with non-flame retarded products. Despite this fact there is a clear societal need for such considerations, in particular relative to firefighter exposure both during a fire and after the fact. While making such societal considerations, however, it is important to keep in mind the function of flame retardants to reduce the number and size of fires.

This project has focussed on assessing the hazard posed to a fire fighter when carrying out his duty, and whether this hazard is adversely affected by the presence of flame retardants in the products in the fire to which the fire fighter has been called.

A literature study has been conducted to identify quantitative information concerning emissions from fires. This information has been used to define a series of nine fire scenarios. The scenarios were chosen to mimic both probable (Scenarios 1-3, 5-7 and 9) and improbable (Scenarios 4 and 8) exposure situations. The hazard to fire fighters exposed to gaseous emissions was examined in detail. No risk was found to fire fighters provided full protective gear was used.

Indeed, very little difference in hazard was seen between the different scenarios (i.e., with and without flame retardants) in the case of inorganic emissions, VOCs, PAHs and isocyanates. The only case where there was a significant difference in the hazard associated with exposure to dioxins and furans from the fire scenarios with a flame retarded product was in the case of the less probable scenarios (Scenarios 4 and 8), i.e., when the flame retarded product burns as the only item burning in a room. Flame retarded items are less likely to catch fire than non-flame retarded items so the overall significance of Scenarios 4 and 8 is low. One should also keep in mind that this hazard can only be realised if the fire fighter does not wear full protective gear.

It is clear, that exposure to fire gases is hazardous independent of the presence or absence of flame retardants in the products burning in the fire. It is important to note that for all scenarios the emissions of inorganic species is close to or in excess of the NIOSH levels representing Immediate Danger to Life and Health (IDLH). In light of this alone it is clear that fire fighters should employ full protective gear on the scene of a fire independent of the presence or absence of flame retardants in the products involved in the fire. Provided full protective gear is used the hazard identified will not be realised.

Finally, even without full use of protective gear in the post-extinguishment phase, exposure to soot produced from a fire that has condensed onto surfaces, is not expected to pose a significant risk.

Key words: brominated flame retardants, degradation products, emissions, toxicity, fire fighter

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# 1 Introduction

Issues associated with the toxicity of flame retardants and the products of their breakdown in a fire situation have been discussed for some time. The diversity of flame retardants and of combustion conditions in fires make it difficult to generalise in terms of the hazard of exposure to fire emissions from flame retarded products relative to that associated with non-flame retarded products. Despite this fact there is a clear societal need for such considerations, in particular relative to firefighter exposure both during a fire and after the fact.

A significant amount of data is available in the open literature concerning emissions from fires, much of which has been produced by SP Fire Technology in the past 10 years. This data provides an excellent starting point for estimation of any potential incremental difference in emissions from fires of flame retarded and non-flame retarded products.

The emission levels in themselves, represent the hazard from exposure. In order to establish a hazard, however, it is not sufficient to discuss differences in emissions. It is also necessary to evaluate those emissions in terms of their toxicology and their potential for harm. On this basis input from a toxicologist will be required to evaluate the hazard in terms of real rather than perceived hazards.

The potential exposure of a fire fighter to fire emissions is particularly interesting as this represents an occupational exposure that will be repeated. While exposure of a fire victim cannot be expected to be kept below occupational safety limits one would strive to keep fire fighter exposure to such regulated levels. Thus, the assessment of hazard will be specifically related to the exposure scenario that a fire fighter would reasonably be expected to experience both during a fire and in post-fire clean-up, i.e. consideration will be taken of protective gear and common practice in their use.

There are numerous flame retardants on the market. The literature review in this study has restricted itself to emissions from products containing brominated flame retardants. Where possible this has been related specifically to TBBP A, HBCD and deca-BDE. Clearly a toxicological assessment can only be made provided detailed information is available concerning the composition of the emissions<sup>1</sup>.

## 1.1 Emissions from fires and their effect

Traditionally, fires have been associated with loss of life and property. In recent years the environmental effect of fires has begun to receive a considerable amount of attention. This is due in part to a heightened environmental awareness and in part to stricter environmental legislation. The legislation has both been in response to highly publicised fire incidents and their effect on the environment, and increased chemophobia in the wake of these incidents. "Silent Spring" by Rachel Carson (1962)<sup>1</sup> is widely accredited with having launched the environmentalist lobby in the west and directly resulted in the ban of DDT in the US in 1972. In modern legislation, the Precautionary Principle<sup>2,3</sup> has been defined based on such thinking, whereby chemical bans are promulgated in cases where sufficient scientific data concerning whether a chemical can be seen to be environmentally benign is lacking to make scientifically sound decisions, i.e., in lieu of definitive data, bans are promoted based on the Precautionary Principle.

Community awareness of the fact that large fires may present dramatic and persistent adverse effects on the environment has been accentuated by a number of high impact

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<sup>1</sup> In this context, "emissions" refers to fire gases, water run-off and post-fire residue.

incidents over the past half century, as indicated by a few review papers<sup>4,5,6,7,8</sup>. Perhaps the most instructive example of these was the chemical fire in an industrial warehouse near Basel Switzerland in November 1986<sup>9,10,11</sup>. This fire presented major challenges in terms of fire fighting tactics, emergency response management, crisis communication with concerned nearby countries (France and Germany), air pollution in a highly urbanised area, and water pollution. Large amounts of extinguishing water contaminated by pesticides and other toxic chemicals ran off directly into the river Rhine, killing aquatic life for several hundreds of kilometres. Moreover, the environmental problems caused by fires go far beyond pollution by run-off waters as stated as early as 1994 by Hölemann<sup>6</sup>.

The serious consequences of these disasters have confirmed that the environmental impact of fires is a real threat that urgently needs to be treated by a more systemic approach. In particular, the hazard from the emission and re-deposition in the environment of some fire effluent components having carcinogenic or mutagenic properties, and sub-lethal exposures to toxic compounds are a matter of intensive debate. Hölemann previously pointed out some of the difficulties associated with this problem and the size of appropriate mitigation measures. However, we need to better understand the relationship between these phenomena, and develop scientifically sound tools for identification of the hazard, the assessment of hazard, and the implementation of fire prevention and protection measures. Such work is just beginning within ISO/TC92/SC3 under its mandate to consider not just the local effect of fire effluent on people but also its effect on the environment<sup>12</sup>. A very limited number of papers have focussed on the environmental issues of fires until recently<sup>13</sup>.

Environmental issues associated with fires can be summarised by reporting them in terms of a history of conflict between fire safety, health and environment quality conservation officials<sup>14</sup>. This view is largely supported by numerous examples such as: the long term use of asbestos, decades of use of fire resistant PCBs (polychlorobiphenyls) in electric transformers, soil contamination at fire training academies, wildland fire management, hazardous material incident responses, water conservation measures, halon replacements that are greenhouse gases, fire retardant chemicals, alternative fuels and increased use of plastic materials in the automotive industry. Clearly, both “old problems” such as contaminated water runoff and emerging ones like determination of the degree to which fire effluents contribute to persistent organic pollutant (POP) production, show that the environmental impact of flame retardants etc needs to be clearly identified, weighed and treated in the most relevant way.

The challenge in the future is not to raise public awareness of the environmental impact of fires or the importance of fire prevention or mitigation; but to improve the interaction between the various facets of fire, environmental and toxicological science to ensure that toxicity, eco-toxicity and fire safety are dealt with together in a single holistic approach. It is only through such an approach that we can optimise any fire related situation to ensure that neither is fire safety obtained at an unacceptable cost to the environment, nor is environmental safety obtained at an unacceptable cost to fire safety.

Emissions from a fire can be comprised of a large variety of chemical species with varied characteristics and associated toxicity and eco-toxicity<sup>6,15</sup>. The majority of species emitted from a fire are formed in the fire but the elevated temperature can also cause pre-existing species in material to be released and spread in the environment. Examples of such species include flame retardants, pesticides and others. A coarse division of species according to their effect is presented in Table 1.

Table 1 Emissions from fires and their effect on health and the environment.

Effect	Types of emissions
Acute toxic	CO, HCN, Acid gases (e.g. HCl, HBr), NO <sub>x</sub> , aldehydes, isocyanates
Persistent and potentially bioaccumulative species which can give long term effects	Dioxins, PAH, PCB, particles, metals, large organic species (e.g. some flame retardants)
Acidifying	HCl, SO <sub>x</sub> , NO <sub>x</sub>
Greenhouse gases	CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O
Atmospheric Ozone	NO <sub>x</sub> , VOC

Emissions from fires can have a negative effect both close to the fire and at a great distance. Relatively few measurements have been made of emissions from real fires due to the inherent difficulties associated with such measurements. Some data exist that provide insight into the composition of fire gases based on laboratory experiments.

Exposure to fire emissions and the effect of such exposure is highly dependent on the type of emission and the susceptibility of the recipient. This project will define the types of emissions in terms of gaseous and solid to be presented to the recipient through skin contact or inhalation. More details are given of the specific emissions and the susceptibility of the recipient in Chapter 4.

## 1.2 Exposure to fire products

Exposure to fire products can occur both through inhalation and skin absorption. This study concentrates on the exposure of fire fighters to fire emissions through inhalation of gaseous emissions or particles and discusses more qualitatively skin absorption of soot, ash or debris. In all cases the fire fighter exposure is discussed depending on the presence of full personal protective gear or where less than full protective gear is used. The reason for exploring both possibilities is that while it is common practice throughout the world to require the use of full protective gear at a fire site this is not always followed by fire fighters in the field. Full protective gear is not always used because it restricts movement and increases the load for the individual afforded by any particular task. Once the acute phase of a fire incident has been managed protective gear is often removed to facilitate mobility.

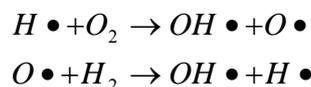
## 1.3 Background on brominated flame retardants (BFRs)

There are more than 150 different types of flame retardants of which are generally divided according to their active component, i.e.: halogenated flame retardants (including brominated and chlorinated), phosphorous based flame retardants, nitrogen based flame retardants and inorganic flame retardants. Naturally, this division is simplified and some overlap is found between the different groups based on synergies between different chemicals.

The brominated flame retardants (BFRs) have been used as flame retardants since the 1970's and are presently the largest market group due to their relatively low cost and high efficiency<sup>16</sup>. They are routinely used in a variety of plastics in a variety of applications from electronics to furniture and textiles. Worldwide, approximately 5 Mtons of bromine

are produced annually to a market value of US\$ 2 billion<sup>17</sup>. Approximately 70 different brominated flame retardant chemicals are marketed commercially, representing some 20 different groups of chemicals.

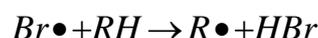
BFRs act by interfering with the radical chain mechanism taking place in the gas phase. The high energy OH and H radicals formed by the chain branching reactions:



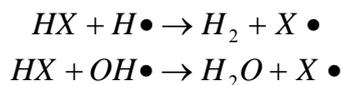
are removed by bromine radicals produced by the BFR:



The bromine radical reacts with organic products of pyrolysis to produce hydrogen bromide:



which in turn interferes with the radical chain mechanism:



Ultimately, the presence of the BFR effectively inhibits the early stages of a fire, i.e., the ignitability of the plastic matrix and reduces the hazard of ignition from a small ignition source. One should not confuse this with making the polymer non-flammable. A flame retardant polymer will ignite and burn given a sufficiently large ignition source, e.g. when it is part of a flashed-over room.

In the early 1990s, the anti-halogen stance of some environmentalist groups in Europe saw a number of legislative activities<sup>18</sup> aimed at restricting the use of certain halogenated flame retardants. Since this time all polybrominated bipheyls (PBBs) have been banned for use in the EU and the industry has voluntarily removed them from the market. Similarly, penta- and octa-BDE have been banned in the EU and the industry has voluntarily removed them from the market internationally. Presently there are risk evaluations underway for TBBP-A, HBCD and deca-BDE.

## **2 Products from brominated flame retardants in fires**

Information on combustion products from fires with materials containing brominated flame retardants (BFRs) was needed for selecting relevant exposure scenarios in this study. Detailed quantitative information was further needed to make an assessment of any significant effects on the total combustion atmosphere from materials with BFRs.

Two major experimental studies with detailed measurements of the combustion atmosphere have earlier been conducted at SP. One study including measurements of emissions from fires with flame retarded furniture<sup>19</sup>, and one earlier study with measurements on flame retarded TVs<sup>20</sup>. In both studies the products were treated with deca-BDE, and “reference tests” were made with corresponding non-flame retarded products. Both “stand-alone” and room fire tests with the product included in the fire load of the room were made. The data from these studies was in many ways suitable as input for the exposure scenarios in this study. A literature review was made to find other suitable input data if existing, and further to corroborate that the information in the furniture and TV studies was of general nature. Most information from the two experimental studies at SP concerned Deca-BDE and information was also needed for tetrabromobisphenol A (TBBP-A), hexabromocyclododecane (HBCD) and other brominated flame retardants. The lay-out and the results of the literature review are given below.

### **2.1 Lay-out of literature review**

A literature search for quantified emission data from fires with and without Flame Retardants was conducted using a search engine with access to a large number of databases including e.g. the following relevant databases: ACS (American Chemical Society), Blackwell, Cambridge journals, DOAJ (Directory of Open Access Journals), IEEE, Kluwer, Nature, Oxford journals, PubMed, ScienceDirect, Springer and Wiley.

Any literature search is a function of the search terms. All search terms and combinations are summarised in Table 2. The hits found for each combination of search terms were evaluated from the title and in many cases from reading the abstract and the relevant hits (papers) were sorted out for detailed reading. The number of hits for each combination of search terms and the relevant papers from these hits are shown in Table 2. Note that a paper is only included as a “hit with relevant info” the first time it was found.

Table 2 Summary of search parameters.

Search terms	Hits	Hits with relevant new info
brominated AND fire	120	23
brominated AND emission	50	1
brominated AND retardant AND residue	6	2
brominated AND retardant AND combustion	18	7
flame AND retardants AND smoke	59	1
flame AND retardants AND combustion	176	8
brominated AND ether AND emission	2	1
BFRs	83	9
fire AND residue	147	1
fire residues	11	2
Sum	672	55

## 2.2 Results from literature review

A total of 55 papers with some relevance regarding combustion products from BFRs were found using the search parameters given above. A number of papers were further found in the reference lists of these papers. Additionally a number of papers were found from the “shelves”, including papers/reports from SP. A total of 75 papers were read and evaluated for useful information on combustion products from brominated flame retardants. Especially quantitative information was useful. A list of these 75 papers is provided in Appendix 1.

A very limited number of the papers found gave quantitative information from fire conditions that could be relevant to designing the emissions and exposure model. These are summarised in Table 3, below. Details of direct bearing on PBDEs are summarised in section 2.2.1, those with direct bearing on TBBP-A are summarised in section 2.2.2, and those with direct bearing on HBCD are summarised in section 2.2.3.

Table 3 Summary of the articles with relevant quantitative information.

Authors	Title	Comments
<i>Papers with data from fire tests used for the exposure model:</i>		
Andersson et al. (2003)	“Fire-LCA Model: Furniture Study”, SP-Report 2003:22	Yields on a large range of products from fires tests with flame retarded (deca-BDE) sofa. Used for exposure model.
Andersson et al. (2004)	“The environmental effect of furniture”, Interflam '04.	Article summarizing the project report above.
Simonson et al.(2001)	“Fire-LCA Model: TV Case Study”, SP-Report 2001:22	Yields on a large range of products from fires tests with flame retarded (deca-BDE) TV. Used for exposure model.

<b>Authors</b>	<b>Title</b>	<b>Comments</b>
<i>Papers with data from fire tests used for the exposure model:</i>		
Blomqvist et al. (2004)	“Emissions from Fires part I: Fire retarded and non-Fire retarded TV-sets”, Fire Technology	Article summarizing the project report above.
Blomqvist et al. (2004)	“Emissions from Fires part II: Simulated room fires”, Fire Technology	Article summarizing the project report above.
<i>Papers with data from fire tests/fire conditions:</i>		
Barontini et al., 2004	“The use of TG-FTIR technique for the assessment of hydrogen bromide emission in the combustion of BFRs”, Journal of Thermal Analysis and Calorimetry	Yields on HBr release from fire retarded electronic boards using thermographic (TG) analysis apparatus.
Ebert & Bahadir (2003)	“Formation of PBDD/F from flame-retarded plastic materials under thermal stress”, Environmental International	Extensive review of production of PBDD/F from BFR treated plastics from different heating processes including fires.
Dumler et al. (1989)	“PBDF and PBDD from the combustion of bromine containing flame retarded polymers: A survey”, Chemosphere	Semi quantitative results from tube furnace tests with 17 different Br-FR plastics.
Barontini et al. (2005)	“Thermal Degradation and Decomposition Products of Electronic Boards Containing BFRs”, Ind. Eng. Chem. Res.	Qualitative data on organics and yields of inorganics from thermal degradation of printed circuit boards and resins.
Luijk, et al. (1991)	“The influence of the polymer matrix on the formation of polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs)”, Chemosphere	Yields on PBDD/F from micro pyrolysis of Br-FR HIPS.
Barontini et al. (2004)	“The Thermal Degradation Process of Tetrabromobisphenol A”, Ind. Eng. Chem. Res.	Some quantitative data on organic degradation products from TBBP-A.
Barontini et al. (2001)	“Thermal Stability and Decomposition Products of Hexabromocyclododecane”, Ind. Eng. Chem. Res.	Some quantitative data on organic degradation products from hexabromocyclododecane.

Authors	Title	Comments
<i>Papers with data on fire residues:</i>		
Zelinski et al. (1993)	“Brominated flame retardants and resulting PBDD/F in accidental fire residues from private residences”, Chemosphere	Concentrations in fire residues.
Pinkerton et al. (1989)	“A preliminary report on the investigation on the comparative toxicity of combustion products of high impact polystyrene with and without decabromo-diphenyloxy/antimony trioxide as a flame retardant using 2,3,7,8-tetrabromodibenzo-P-dioxin and 2,3,7,8-tetrabromodibenzofuran as positive controls”, Chemosphere	Concentration in char and soot.
Söderström & Marklund (1999)	“Fire of a flame retarded TV”, Organohalogen Compounds	Concentrations in fire residues.

### 2.2.1 Polybrominated diphenylethers (PBDEs)

PBDEs are a family of diphenylethers with a varying degree of the number of bromine atoms substituted to the phenyl groups. The structure formula of the fully brominated PBDE, deca-BDE, is shown in Figure 1. The products from combustion of deca-BDE could vary from a rather complete combustion resulting in a high yield of HBr, to a product spectra including BDEs with a lower degree of bromination, brominated phenols and brominated benzenes<sup>21</sup>. It is further reasonable to assume that combustion of deca-BDE could lead to the formation of brominated dibenzofurans. As can be seen from Figure 2 the structure of a brominated dibenzofuran is very similar to that of a brominated diphenyl ether.

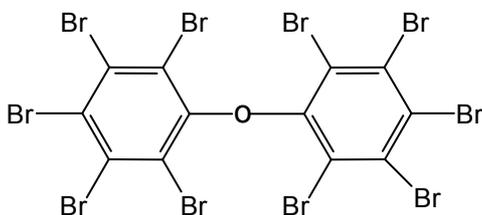


Figure 1 Structure formula of deca-BDE

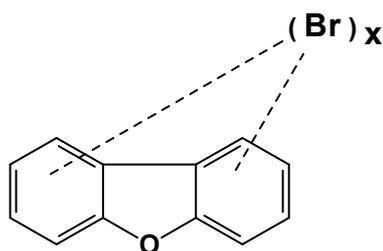


Figure 2 General structure formula for brominated dibenzofurans.  $X$  refers to the possible variations in the number of substituted BR-atoms.  $X$  could vary between 1 and 8.

Studies have shown that combustion involving PBDEs can in fact lead to the formation of PBDD/Fs. Buser<sup>22</sup> has found in micro-scale experiments with technical PBDE compounds that large fractions of the PBDE were recovered as PBDD/Fs during thermal degradation at 630°C. Luijk et al.<sup>23</sup> made similar experiments with pure PBDEs and found PBDD/F production with decreasing yields from Pn-BDE to deca-BDE. They further studied the influence of the HIPS polymer matrix in a HIPS/deca-BDE/Sb<sub>2</sub>O<sub>3</sub> system, and found that this matrix shifted the optimal PBDF formation temperature from 600°C to the HIPS depolymerization temperature (350-400°C), favoured the formation of PBDFs, and further increased the total yield of PBDFs with a factor 7 (a maximum yield of  $\sim 1.5 \times 10^6$  µg/kg PBDFs relative to polymer sample was found). Ebert and Bahadir<sup>24</sup> have reviewed published experimental data on PBDD/F production from thermal degradation (>300°C) of HIPS/deca-BDE/ Sb<sub>2</sub>O<sub>3</sub> and found yields (on polymer basis) between  $1.5 \times 10^6$  -  $150 \times 10^6$  µg/kg.

Weber and Kuch<sup>21</sup> have reviewed the formation of PBDD/Fs from thermal degradation of BFRs. This review, and also that by Ebert and Bahadir<sup>24</sup>, shows that conditions of incomplete combustion of PBDEs, i.e. conditions that occurs during a fire, can lead to the formation of considerable amounts of PBDD/Fs. The primary formation pathway under insufficient combustion conditions is most likely that from precursor compounds (i.e. degradation products of PBDEs). However, the less stable bromine-carbon bond in brominated aromatics leads to a rapid decomposition of PBDEs at high temperatures, and thus to a reduced amount of precursors during such conditions.

High concentrations of PBDD/Fs have been found in fire residues after accidental fires in private residences. Zelinski et al.<sup>25</sup> investigated three different accidental fires and found brominated substances in most samples. The fire residues from a TV gave the highest concentrations of PBDD/Fs. Söderström and Marklund<sup>37</sup> investigated a private residence after a TV and VCR fire and analysed wipe samples and ash samples. Both type of samples contained chloro-, chlorobromo- and bromo-dioxins.

Quantitative data on PBDD/Fs formation from real-scale fires involving products treated with brominated flame retardants are scarce. Fabarius et al.<sup>26</sup> conducted fire experiments with FR (penta-BDE) TV-sets by burning them in a barrel and sampling the smoke gases at the top. They did find PBDD/Fs in the smoke, but they report their results as concentrations rather than yields.

The most complete investigations of combustion products from fires involving products treated with PBDEs are the studies from SP on furniture<sup>35</sup> and TVs<sup>33</sup>. These studies report yields of combustion products found in the smoke gases, including e.g. inorganic gases, volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), chlorinated and brominated dibenzo-p-dioxins and dibenzo furans. The different fires

investigated in these studies and the compounds measured are described in detailed in section 4.1 and in Appendix 2.

In the SP study high concentrations of PBDFs were found in a stand-alone test with a TV which had a polystyrene housing treated with deca-BDE. Only traces of PBDDs were found. The total yield of PBDF homologues was  $\sim 0.8 \times 10^6$   $\mu\text{g}/\text{kg}$ , i.e. almost as much as previously have been seen from small-scale thermal degradation experiments<sup>24</sup>. The yield of individual 2,3,7,8-substituted PBDD/Fs found was  $68 \times 10^3$   $\mu\text{g}/\text{kg}$ . A yield of individual PBDFs of  $5 \times 10^3$   $\mu\text{g}/\text{kg}$  was found from a stand-alone test with a sofa<sup>35</sup> which had a covering impregnated with a PBDE which most probably was deca-BDE. No PBDDs were found. The yield was calculated from the total weight-loss of the sofa, recalculating the yield on basis of the treated covering material only, results in a yield of  $\sim 80 \times 10^3$   $\mu\text{g}/\text{kg}$ , i.e. close to the yield of individual PBDD/Fs found from the deca-BDE treated TV.

The high yields of PBDFs found in the stand-alone tests were not found in tests where the TV, respective sofa, was included as one part of the fire load in a room fire test. In a room test including a FR-sofa only 0.5% was found compared to the amount PBDF found in the stand-alone test. In the case of the deca-BDE FR-sofa only 0.006% was found in a room test compared to a stand-alone test<sup>27</sup>. The substantial decrease in PBDF yield from flash-over room fires could be explained by the weak carbon-bromine bond. The binding between the carbon backbone and the bromine atom is considerably weaker compared to the carbon-chlorine binding in a PCDF because of the greater size of the bromine atom.

## 2.2.2 Tetrabromobisphenol A (TBBP-A)

Barontini et al.<sup>28</sup> found hydrogen bromide, phenol, brominated phenols and brominated bisphenols from small-scale pyrolysis tests (180-300°C) with TBBP-A. In an investigation on electronic boards containing TBBP-A<sup>29</sup> pyrolysis experiments were carried out with temperatures between 250°C and 400°C. Also here high yields of HBr were found and the major organic products were phenol, brominated phenols and brominated bisphenols.

The production of PBDD/F from plastics containing TBBP-A was investigated by Dumler et al.<sup>30</sup> in a series of tube furnace tests. It was found that polymers with TBBP-A produced much less PBDF than polymers with polybrominated diphenyl ethers. In addition, no PBDF and PBDD with more than three bromine atoms and thus none of the toxic 2,3,7,8-bromo substituted congeners were detected. Ebert & Bahadir<sup>24</sup> show in their review paper that the yields of PBDD/F from thermal degradation of polymers with TBBP-A above 300°C gives total yields of PBDD/F in the range of  $0.1 \times 10^3$ - $80 \times 10^3$   $\mu\text{g}/\text{kg}$  (this range of values includes one set of data of  $6 \times 10^3$   $\mu\text{g}/\text{kg}$  that refers to 2,3,7,8-substituted PBDD/F only).

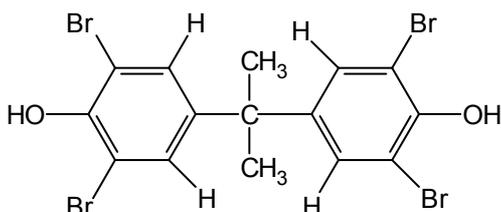


Figure 3 Structure formula for tetrabromobisphenol A (TBBP-A).

### 2.2.3 Hexabromocyclododecane (HBCD)

The thermal stability and the decomposition pathways of HBCD have been investigated by Barontini et al.<sup>31</sup> Isothermal runs at temperatures between 200 and 300 °C were performed using a thermo balance (TG). Analysis of the HBCD thermal decomposition products was carried out by TG-FTIR and GC/MS techniques. The data showed that about 75% of bromine by weight was released as HBr and that the remaining 25% is involved in the formation of high-molecular-weight bromo-organic compounds. Qualitative information on a large range of brominated and non-brominated organic compounds is given in the paper. No quantitative information is available.

PBDD/F production from plastics containing HBCD was investigated by Dumler et al.<sup>32</sup> in a series of tube furnace tests. The amounts found were comparatively small (total yield of  $5 \times 10^3$  µg /kg) or under the limit of detection, depending on experimental conditions.

## 3 Toxicity of fire products from BFRs

Brominated flame retardants (BFRs) are a structurally diverse group of chemicals. Their use and their effect on humans and the environment has been the topic of much debate over the past two decades. While the group is highly diverse and over 70 individual commercial formulations are available of BFR only a relatively small number of these are used to any great degree and very little is known about the application and effect of the vast majority of the commercially available products.

This study has chosen to focus on a small number of brominated flame retardants present in domestic products: deca-BDE, TBBP-A and HBCD. This chapter deals specifically with our present knowledge of toxicity of the PBDEs, HBCD, TBBP-A and one of their fire products, i.e. dioxins.

### 3.1 Polybrominated diphenylethers

During the last decade much attention has been given to the possible adverse health effects of brominated flame retardants. In this respect significantly more toxicological information is available from the PBDEs than, e.g., HBCD and TBBP-A. Thus, risk assessors have so far concentrated significantly on PBDEs and it is not until recently that HBCD and TBBP-A have been given more attention with respect to possible adverse effects on humans and the environment.

Several risk assessments for PBDEs have been performed and more recently been published. The WHO International Program for Chemical Safety (IPCS) published an Environmental Health Criteria (nr. 162) that was solely devoted to this group of compounds. In addition to this the EU has separately evaluated the risks of the pentabrominated, octabrominated and decabrominated diphenylethers. In these evaluations most attention has been paid to the environmental persistence and effects of these PBDEs on humans and wildlife in background situations. Although some information is available about occupational exposure to PBDEs, the information that could be used for occupational risk assessment is surprisingly scarce. Clearly, some PBDEs are more environmentally persistent and bioaccumulative than others. Furthermore, background levels can vary at least two orders of magnitudes, thereby overlapping with levels that have been reported from chronic occupational exposure. In addition, geographical differences can also be significant, most noticeably between the European and North American situation with background exposure in the latter region being often one to two orders of magnitude higher. This means that individuals in the North American background population might have PBDE body burdens, which are close or one order of magnitude less than occupationally exposed European workers. This significant geographical difference is most likely caused by the more extensive use of BFRs in North America.

Thus, hazard by exposure of fire fighters to PBDEs itself can not easily be generalized because of these large local differences in concentrations originating from consumer goods. In addition, to this possible wide range of exposure the situation in which fire fighters are exposed to BFRs, e.g. PBDEs, is very difficult to compare to exposure in other occupational settings. In the latter situation exposure is usually expected for a much longer time period e.g. many years and dermal exposure is considered a significant pathway. Due to the low volatility of these compounds inhalation has been considered quantitative less important in typical occupational exposure scenarios such as factory workers, garbage workers or disassembly worker.

At present, the only way to approach the question of fire fighter exposure and associated risk is to consider the chronic exposure situation to PBDEs in occupational settings as a worst case situation for fire fighters. For fire fighters this should be considered a worst case approach, because workers are exposed to PBDEs over an extended period of time their exposure is with less effective protection (e.g. oxygen masks and protective clothes) than fire fighters in general. Furthermore, it should be realized that in conditions with PBDEs adsorbed on smoke particles the bioavailability will be much lower than in a normal occupational setting, for dermal uptake, due to the high carbon content of smoke particles. In addition, the slow metabolic breakdown of especially the lower brominated PBDEs in a chronic occupational setting will almost invariably lead to a build up of higher body burdens. This situation is of much less importance for fire fighters, who should protect themselves with full body cover (including overalls and gloves) and breathing apparatus in relatively short exposure periods, where smoke and gases prevail. In this context it is important to keep in mind that the exposure pathway discussed is dermal absorption rather than the effect of inhalation of contaminated soot particles.

When comparing the situation of a fire fighter with that of a factory or disassembly worker, one could argue that the only moment there could be a significant exposure via inhalation is when the fire fighter is exposed to smoke without using a breathing apparatus. In this situation, the dermal exposure is very likely of minor quantitative importance relative to that of exposure via inhalation because protective clothing is usually worn continuously at a fire scene and the dermal uptake is less than the inhalation uptake.

The EU risk assessment of pentaBDE and octaBDE (2001,2002) took into account various routes of occupational exposure and different toxicological endpoints. Based on this information it was concluded that the margins of safety for pentaBDE and octaBDE were significantly below 10. This is clearly insufficient and of toxicological concern. Therefore, it was concluded that there was a need for limiting the hazards in occupational settings. However, the recent EU risk assessment (2005) for deca-BDE (which also took into account both dermal and inhalation routes for occupational exposure) calculated margins of safety (MOS) of respectively 280 and 98.

Based on these evaluations it can be concluded that if fire fighters were indeed regularly exposed via inhalation and dermal contact, similar small margins of safety for the lower PBDEs might apply. Clearly, two arguments could be brought forward that would increase the MOS significantly for fire fighters at the fire scene. First of all using breathing apparatus and protective clothes should limit the exposure with many orders of magnitude, if not reduced it to zero. Secondly, PBDE exposure through carbon containing smoke particles would be dominated by a strong reduction in bioavailability. Although the latter argument could not be supported by data from scientific literature for PBDEs, such a reduction in bioavailability of e.g. other (halogenated) polyaromatic hydrocarbons depending on the organic carbon content of the particle has been described in detail in many scientific studies.

### **3.2 Brominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs)**

One of the major toxicological problems associated with PBDEs at the fire scene is the presence and further formation of PBDDs and PBDFs. It has been commonly found that commercial mixtures of lower brominated PBDEs contain the highly toxic PBDDs and PBDFs as contaminants. As a result, previous toxicological experiments with PBDEs have erroneously been classified as having dioxin like toxicity. Recent studies with highly purified PBDEs did show that PBDEs did not possess significant Ah-receptor activity and therefore should not be classified as dioxin like compounds with a toxic equivalency

factor (TEF) relative to TCDD, the most toxic congener of dioxins. However, PBDDs and PBDFs with a 2,3,7,8-bromine substitution pattern do possess distinct dioxin like activity that is mediated through a high affinity binding with the Ah-receptor. As a result, the 2005 WHO expert consultation on toxic equivalency factors of these dioxin like compounds indicated that the 2,3,7,8 substituted PBDDs and PBDFs should have high priority to assign TEFs in the near future (Van den Berg et al., 2006).

Although, the amount of scientific information is much less extensive on the 2,3,7,8-PBDDs and PBDFs than for their chlorinated counterparts there is sufficient scientific proof available that these brominated dioxins and dibenzofurans have a similar toxicity (within one order of magnitude) compared to their 2,3,7,8-chlorinated counterparts. Based on the low dose level *in vitro* and *in vivo* toxicity of PBDDs and PBDFs, it is reasonable to suggest that their toxicity very likely overwhelms that of the PBDEs. This in spite of the fact that the latter group of compounds is present at higher concentrations. During a fire it is realistic to assume that out of the PBDEs, the formation of PBDDs and PBDFs will occur. Both 2,3,7,8 as well as non 2,3,7,8 substituted congeners can be formed in combustion processes where brominated compounds are present. The analyses done from the fire experiments described in this study show that a significant amount the 2,3,7,8-PBDDs and PBDFs can be formed. This is discussed in more detail in the next chapter.

In our semi-quantitative risk assessment we have assumed that TEF values of PBDDs and PBDFs are similar to their chlorinated congeners as established in the 2005 WHO TEF re-evaluation (Van den Berg et al., 2006). Clearly, this a worst case scenario. It might very well be that in the future more detailed *in vivo* experiments might show that these used TEF values for PBDDs and PBDFs are up to one order of magnitude lower. This could e.g. be caused by differences in toxicokinetics and metabolism between the brominated and chlorinated analogues. Thus, with respect to the described risk of chlorinated and brominated dioxins and dibenzofurans together expressed as TCDD equivalencies, a factor of approximately 10 lower should be kept in mind as a range of uncertainty (i.e. downgrade one + for hazards reported in Chapter 4)

### **3.3 Hexabromocyclododecane (HBCD) and Tetrabromobisphenol A (TBBP-A)**

No quantitative information is available from the different fire scenarios for these two BFRs. Due to the fact that HBCD might be used more in the future it is advisable to include this compound in future fire experiments if this BFR is going to be used increasingly in household articles. This BFR has been found to bioaccumulate in the foodchain and consequently there is a potential hazard for fire fighters that HBCD body-burden, similar to PBDEs, might increase over time. However, as with all the combustion products measured in the fire scenarios the use of a breathing apparatus and protective clothing, including gloves, could bring exposure probably back close to zero.

It is reasonable to assume, especially from TBBP-A, that during a fire, lower (Br<sub>1-4</sub>) brominated dioxins and dibenzofurans can be formed. This expectation is based on the fact that formation of chlorinated analogues of PCDD and PCDF invariably occurs when sufficient chlorine and aromatic hydrocarbons are available or formed. However, because of the weaker carbon-bromine bond the amount of PBDDs and PBDFs formed is expected to be lower than that of their chlorinated analogues. At present there is no indication that the combustion of TBBP-A will yield the toxic 2,3,7,8-substituted PBDDs and PBDFs. Based on the structure of TBBP-A it would actually be more realistic to expect the formation of other than 2,3,7,8 PBDDs and PBDFs, which are much less toxicological relevant. In the case of the different fire scenarios used in this study, a

differentiation between the amount of PBDDs and PBDFs is not essential, as a risk assessment was based on actual measurements of total amount of TEQs for brominated and chlorinated dioxins and dibenzofurans.

## 4 Case study on exposure scenario for fire fighters

The potential exposure of a fire fighter to fire emissions is particularly interesting as this represents an occupational exposure that will be repeated. While exposure of a fire victim cannot be expected to be kept below occupational safety limits one would strive to keep fire fighter exposure to such regulated levels. Thus, the assessment of hazard will be specifically related to the exposure scenario that a fire fighter would reasonably be expected to experience both during a fire and in post-fire clean-up, i.e. consideration will be taken of protective gear and common practice in their use.

Fire fighter exposure can occur mainly in three ways: heat exposure, gaseous exposure and exposure to soot and ash (solid exposure). In this project heat exposure with the potential for burns and harm to the fire fighter in this way will not be considered. The focus of this project is on exposure of the fire fighter to emissions from the fire, be that gaseous or solid.

Very little data could be extracted from the open literature concerning exposure to fire gases other than that generated within a series of projects which took place between 1995 and 2005<sup>33, 34, 35, 36</sup> at SP Technical Research Institute of Sweden. These projects studied the emissions from fires in products with and without flame retardants, both when burning alone and as a part of a full room fire. The data obtained from the two of these projects have been used to establish gaseous exposure data, i.e. from the TV Case Study and the Furniture Case Study. Data from a separate study by Söderström and Marklund<sup>37</sup> have been used to estimate dermal exposure to soot and ash. The proposed emission and exposure scenarios are described in more detail in sections 4.1 and 4.2.

In all cases, a fire emission model has been constructed using BRANZFIRE to determine the fire growth and volume of hot gases produced given the experimental input data and then the distribution of these hot fire gases throughout a house. Full details of the calculation are given in section 4.2.1. Gaseous exposure based on inhalation of the fire gases produced is given in section 4.2.2. Skin exposure to soot and ash is summarised in section 4.2.3.

### 4.1 Emission Scenarios

Detailed gaseous emissions data are available from a series of fire tests run at SP. While the fire gases in the experiments have been characterised to a significant degree the information available is not limitless. The specific experimental data that has been used is summarised in Table 4. The experiments conducted in these studies showed that the HRR rate in all furnished rooms was about the same. This HRR was used as input data to the BRANZFIRE calculations performed. One HRR-curve was estimated from the stand-alone TV-experiments and one from the Standalone Sofa experiments, these were then used as input to the BRANZFIRE calculations. The output from the calculations (i.e. smoke layer height and spread) was then used to calculate the dilution of the total emissions from respective experimental fire.

Particulate emissions data are available from several sources. The most relevant source relates to surface swabs made after an apartment fire in the north of Sweden. These data have been used to estimate skin exposure and are also summarised in Table 4.

Table 4 Type of emissions data used and source.

<b>Experiment</b>	<b>Data used</b>	<b>Reference</b>
Reference room furnished with non-FR sofa and nominally non-FR TV (i.e., only TBBP-A in circuit board)	HRR from experiment input to BRANZFIRE calculations Gaseous emissions data	Fire-LCA Model: Furniture Case Study
Reference room furnished with sofa treated with deca-BDE on cover and TCPP-melamine in the foam	HRR from experiment input to BRANZFIRE calculations Gaseous emissions data	Fire-LCA Model: Furniture Case Study
Free-burning sofa treated with deca-BDE in the cover and TCPP-melamine in the foam*	HRR from experiments input to BRANZFIRE calculations in a 16 m <sup>2</sup> room Gaseous emissions data	Fire-LCA Model: Furniture Case Study
Free-burning non-FR sofa	HRR from experiments input to BRANZFIRE calculations in a 16 m <sup>2</sup> room Gaseous emissions data	Fire-LCA Model: Furniture Case Study
Reference room furnished with non-FR sofa and nominally non-FR TV	HRR from experiments input to BRANZFIRE calculations Gaseous emissions data	Fire-LCA Model: TV Case Study
Reference room furnished with non-FR sofa and TV with deca-BDE in enclosure and TBBP-A in circuit boards	HRR from experiments input to BRANZFIRE calculations Gaseous emissions data	Fire-LCA Model: TV Case Study
Free-burning TV, non-FR enclosure and TBBP-A in circuit boards	HRR from experiments input to BRANZFIRE calculations, in a 16 m <sup>2</sup> room Gaseous emissions data	Fire-LCA Model: TV Case Study
Free-burning TV, with deca-BDE in enclosure and TBBP-A in circuit boards*	HRR from experiments input to BRANZFIRE calculations, in a 16 m <sup>2</sup> room Gaseous emissions data	Fire-LCA Model: TV Case Study
Apartment fire with nominally non-FR TV	Solid emissions data from post-fire surface swabs	Söderström and Marklund

\*Note that this is a worst case scenario where something large (e.g. a waste paper basket or a cushion) is burning beside the product as it will not ignite with a small open flame.

A series of nine (9) emissions scenarios have been defined based on the above data. i.e.:

1. Reference room with sofa containing non-flame retardant covering and foam, burning together with the whole room
2. Reference room with a sofa containing deca-BDE as a back-coating to the cover and TCPP-melamine foam, burning together with the whole room
3. Sofa containing non-flame retardant covering and foam, burning alone in reference room
4. *Sofa containing deca-BDE as a back-coating to the cover and TCPP-melamine foam, burning alone in the reference room*
5. Reference room with TV containing a non-flame retardant enclosure and TBBP-A in the circuit boards, burning together with the whole room
6. Reference room with TV containing deca-BDE in the enclosure and TBBP-A in the circuit boards, burning together with the whole room
7. TV containing a non-flame retardant enclosure and TBBP-A in circuit boards, burning alone in the reference room
8. *TV containing deca-BDE in the enclosure and TBBP-A in the circuit boards, burning alone in a reference room*
9. Real fire in an apartment with information concerning soot, ash and debris.

Note that Scenarios 4 and 8 (marked in italics) are less probable than the other 7 scenarios due to the lesser likelihood that a flame retarded product would ignite without a significant ignition source, i.e. a flame retarded product is not likely to be the only object burning in the room. In this context, SP data indicates that Scenario 8 is less likely than Scenario 4. The other 7 scenarios cannot be ordered in terms of probability.

In all scenarios the total amounts of emissions measured from the specific experiment has been distributed into a smoke gas layer in a normal size house (160 m<sup>2</sup>) as calculated from the BRANZFIRE software (see section 4.2.1). This resulted in a certain exposure concentrations for each emission scenario. A flow-chart of the fire emission model is showed in Figure 4.

Full emissions data and the resulting concentrations for exposure are presented in Appendix 2.

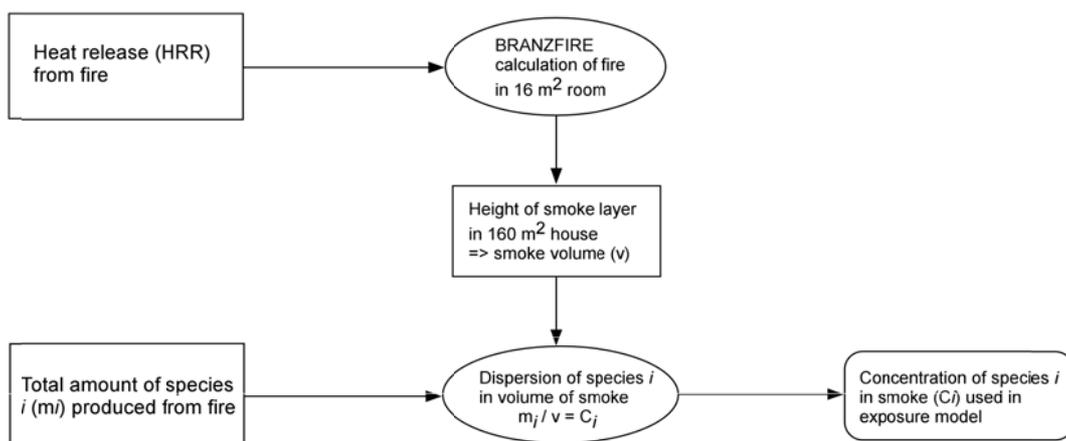


Figure 4 Flow-chart of the fire emission model.

## 4.2 Exposure data

In order to approach the possible hazard to fire fighters from the smoke developing in the different fire scenarios, it is not feasible at this stage to differentiate between different exposure situations (with or without breathing apparatus, protective clothing and gloves). The only connection that can be made with permissible occupational exposure limits and the actual situation of a fire fighters is using a worst case approach. In this worst case situation, it is assumed that the fire fighters are not using his breathing apparatus and his hands are unprotected, i.e. he is exposed to the fire emission.

In the worst case situation defined above, it is reasonable to assume that the majority of exposure of the combustion products is coming from inhalation and ingestion. To establish the hazard associated with the proposed exposure levels, the NIOSH exposure limits were used. This information was taken from the Hazardous Substances Database, that can be found directly on TOXNET ( <http://toxnet.nlm.nih.gov/>). From this database, either the OSHA or NIOSH occupational exposure standards were used. These were compared to the air levels that were actually measured in the different fire scenarios studied. Two distinct time periods could be recognized in the exposure standards: a) short term exposure of 15 min by NIOSH or, (b) 10/8 hours by NIOSH or OSHA regulations. In addition, we have included comparisons to an immediately dangerous to life (IDLH) concentrations as defined by NIOSH or OSHA.

With respect to the potential exposure of fire fighters to combustion products, including BFRs and their decomposition products, it should be noted that there is a large diversity of fire situations and time dependent differences in physical activity. As a result, the semi-quantitative hazard analysis presented in this worst case scenario also contains a significant degree of uncertainty. Clearly, the most straightforward approach to establish whether a fire fighter is indeed exposed to higher levels of BFRs or other combustion products is to determine the actual PBDE, PBDD or PBDF blood levels. This only would lead to a definite conclusion with respect to differences or similarities between fire fighters and other occupationally exposed workers, as well as providing a comparison to background body burdens in the general population.

Real life exposure is dependent on a number of important parameters including: total emissions, dilution of the emissions, breathing rate (for gaseous exposure) or time of exposure (for dermal exposure), personal protective gear, susceptibility of the subject etc. At this point many of these parameters cannot be taken into account and this coarse first hazard evaluation is the only possibility.

In order to establish the exposure levels, data from fire experiments (i.e., total emissions) have been coupled to fire modelling to estimate dilution of the emissions to a reasonable exposure to fire fighters outside of the burning room. This method relates to the assumption that the fire fighter is outside of the room of origin, fighting the fire from close proximity. Details of the fire modelling and exposure scenario development is provided below.

### 4.2.1 Fire Modelling

BRANZFIRE is a two zone model including flame spread options on walls and ceilings and is used to calculate the time dependent distribution of smoke, fire gases and heat throughout a collection of connected compartments during a fire. In BRANZFIRE, each compartment is divided into two layers, one cold layer and one hot smoke layer. The modelling equations used in BRANZFIRE take the mathematical form of an initial value problem for a system of ordinary differential equations. These equations are derived using

the conservation of mass, the conservation of energy, the ideal gas law and relations for density and internal energy. These equations predict as functions of time quantities such as pressure, layer heights and temperatures given the accumulation of mass and enthalpy in each of the two layers. The BRANZFIRE model then solves a set of equations to compute the environment in each compartment and a collection of algorithms to compute the mass and enthalpy source terms.

Two zone models have been used in the fire community for decades for calculation of smoke spread in compartments and the differences between different codes are merely differences in user interface and focus of extra features such as flame spread, number of compartments output facilities etc. Two-zone models have their limitations like in predicting temperatures in buildings with high ceilings but are accurate in normal size rooms.

In all cases the fire was assumed to occur in a 16 m<sup>2</sup> room (4 m × 4 m) with a single door opening (1,2 m × 2 m). The fire was modelled using the heat release rate from the relevant experiment from either the Furniture or TV Case Study conducted using the Fire-LCA Model (see Table 4 above). The HRR-curves used are shown in Figure 5. The fire was assumed to be situated in the centre of the room. The room was connected to a 160 m<sup>2</sup> house which was treated as a single “room”, i.e., the floor plan was not complicated by interconnecting rooms outside the room of origin. The reason for this simplistic approach was that smoke movement throughout the building was not modelled, only the extent of the smoke layer (between the ceiling and floor) and the dilution of the total emissions produced (i.e., into the total volume of the house).

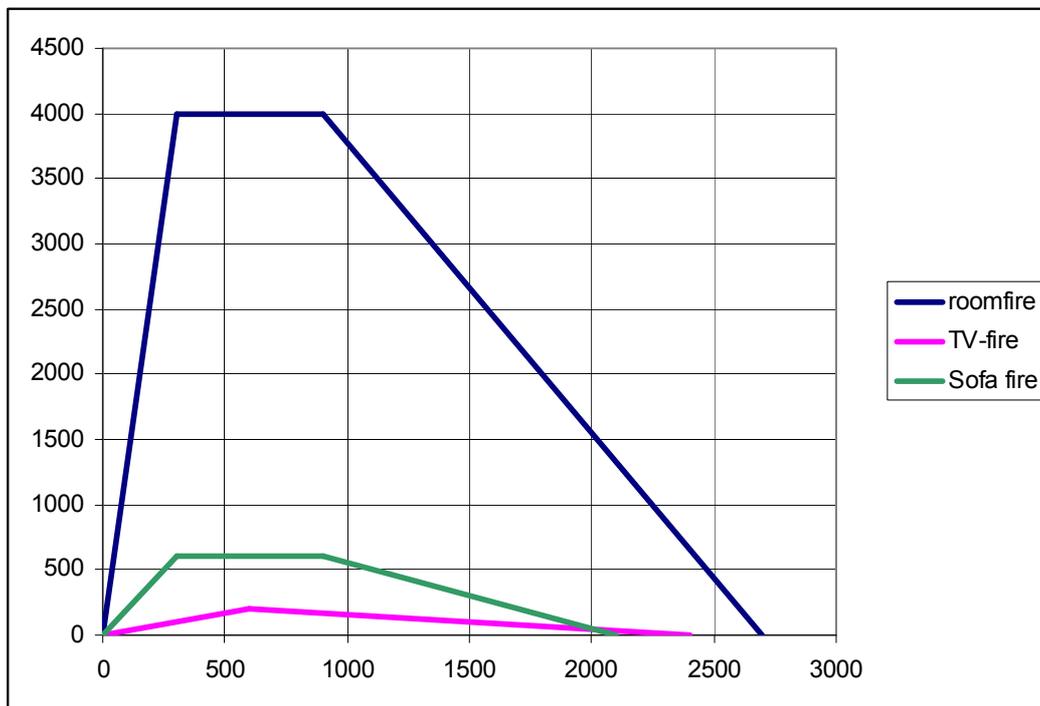


Figure 5 HRR-curves used for the calculations

In all cases the fully furnished room fires reached flash-over and the smoke layer was assumed to extend to floor level (2.4 m) by the end of the fire. This gave a total dilution volume for the fire gases of 422 m<sup>3</sup>.

In the case of the sofa burning alone in the room the smoke gas layer extended 0.68 m from the ceiling in the room of origin and 1.9 m from the ceiling throughout the dwelling,

i.e. the smoke layer is cooled outside of the room of origin and thus lowered towards the floor. This gave a total dilution volume for the fire gases in the sofa burning cases of 321 m<sup>3</sup>.

In the case of the TV burning alone in the room, the smoke gas layer extended 0.61 m from the ceiling in the room of origin and 1.35 m from the ceiling throughout the dwelling. This gave a total dilution volume in the TV burning cases of 226 m<sup>3</sup>.

## 4.2.2 Gaseous Exposure

The person exposed to the fire gases is a fire fighter at work either fighting the fire, rescuing victims or involved in post-fire clean-up or investigation. Exposure to gaseous emissions could take into account information concerning breathing rates which are available in the SFPE Handbook<sup>38</sup>. Table 5 provides a summary of the breathing rates for a 70 kg adult under different conditions.

Table 5 Summary of Breathing rates for 70 kg human under different conditions.

Object, State	Breathing rate (l/min)	Breathing rate (m <sup>3</sup> /min)
70 kg human, at rest	8.5	0.0085
70 kg human, light work	25	0.0250
70 kg human, heavy work	50	0.0500

In the exposure calculations presented in this report, however, the breathing rate could not be taken into account directly. The OSHA and NIOSH values are developed for light work. One would expect the fire fighters to be partaking in heavy work and could, therefore, consider the OSHA and NIOSH occupational health levels to be somewhat unconservative.

The full exposure data that has been used to determine hazard for the various scenarios is provided in Appendix 2.

## 4.2.3 Soot and Ash Exposure

Skin exposure to soot, ash and other fire debris is possible and in many cases far more probable than inhalation exposure. Fire fighting is dirty work and fire fighters will attest to being "covered with soot" at the end of a shift containing active duty.

Appendix 2 contains concentrations of a variety of organic species measured from soot, ash or "residue" from post-fire apartments. The concentrations have been associated with the TV or sofa exposures specifically but could really be considered as general potential exposure concentrations in the post-fire clean-up stage.

The hazard associated with the skin exposure is expected to be far less than that associated with inhalation exposure due to the small skin area exposed and the short period of the exposure and due to the fact that all species of interest are bound to soot in this type of exposure, thereby reducing their bioavailability.

#### 4.2.4 Particulate Exposure through Inhalation

We were not able to find any specific information in the open literature concerning particulate emissions from dwelling fires. Despite this fact an estimate of particulate exposure has been made as a basis for hazard and toxicity evaluation. It has been assumed that dioxin and furan concentrations on the particles are of the same order of magnitude as that found on soot in the apartment fires.

The hazard and toxicity evaluation has assumed an average particle diameter of approximately 0,4 µm and a particle yield of 0,001 – 0,1 g/g. It is clear that if breathing apparatus is used faithfully this then no particulates would be inhaled and thus not represent a problem. This data has not been used further in this report.

### 4.3 Hazards and Toxicity

As defined previously the airborne concentrations of combustion products in the different fire scenarios have been compared, postulating a worst case situation in which a fire fighter is directly exposed to such emissions when not using the breathing apparatus. It is clear that a fire fighter using correct breathing apparatus would not be exposed to these species and would not be expected to be more or less at hazard from emissions from a fire of flame retarded or non-flame retarded products.

Using the NIOSH or OSHA permissible occupational exposure standards (as far as available) for 15 minutes or 8/10 hours we compared the air concentrations and indicated hazard using a series of pluses (“+”, “++” or “+++”) showing to which extend the relevant standard level was exceeded. In this application the following definitions were used: + = 1-10 × the standard level, ++ = 10-100 × the standard level, and +++ > 100 × the standard level. If the emission exposure was below the permissible occupational exposure limit this was denoted “-“ in the Tabulated data. We have chosen not to differentiate further, if the standard was exceeded by more than a factor of 100, as levels of chemicals in these situations rapidly approach or are equal to concentrations defined as immediately dangerous to life (IDHL). The hazards associated with unprotected exposure of fire fighters to the combustion products generated in Scenarios 1-8 are given in full detail in Appendix 3. A summary of the relative hazards for Scenarios 1-8 is provided in Table 6 (for 1 day exposure) and Table 7 (for 15 minute exposure).

One should note that the concentrations which have been used to develop Tables 6 and 7 and the full data summarised in Appendix 3 are averages developed for the full fire period. One would expect these concentrations to be produced for a significantly shorter period of time than a full working day. The 8/10 hour exposure level comparison presented in Table 6 is based on an assumption that a fire fighter could (in a worst case scenario) be exposed to this level of emissions for a full working day, either due to the fact that the fire continues for an extended period of time (i.e., more than one room is involved) or the fire fighter is called to a series of domestic fires over the period of a working day.

Table 6 Summary of relative hazards for Scenarios 1-8, 1 day exposure. (empty boxes in cases when no hazard limit has been identified due to the absence of a permissible occupational exposure limit).

Scenario	1 Room Non- BFR Sofa	2 Room BFR- sofa	3 Non- BFR sofa	4 BFR- sofa	5 Room Non- BFR TV	6 Room BFR- TV	7 Non- BFR TV	8 BFR- TV
<b>Compound</b>	<b>Hazards</b>							
<b>Inorganic:</b>								
CO <sub>2</sub>	+++	+++	++	++	+++	+++	++	+
CO	+++	+++	++	+++	+++	+++	++	++
HCN	++	+++	-	++	+++	+++	-	-
HCl	++	++	+++	+++	++	+++	++	++
NH <sub>3</sub>	++	++	+	+	-	++	-	-
SO <sub>2</sub>	+++	+++	-	-	-	+++	-	-
NO	++	++	++	++	-	-	-	-
Br (from HBr)	-	+	-	+	-	++	-	+++
Sb	-	+	-	+	-	-	-	+++
<b>VOCs:</b>								
Benzene	+++	+++	++	+++	+++	+++	+++	+++
Toluene	-	-	-	-	-	+	-	+
Styrene	-	+	-	-	+	+	+	+
Phenol	+	+	-	+	-	-	+	+
Benzonitrile								
<b>PAHs:</b>								
Naphtalene	+	+	-	-	++	++	+	+
Acenaphthalene								
Acenaphthene								
Fluorene								
Phenanthrene								
Anthracene	++	++	+	+	++	+++	++	++
Fluoranthrene								
Pyrene								
Benzofluorenes								
Benzo(a)anthracene								
Chrysene	++	++	-	+	++	+++	++	+++
Benzofluoranthenes	+++	+++	+	+	+++	+++	++	
Benso(e)-pyrene								
Benso(a)-pyrene	++	++	-	+	++	+++	+	++
Perylene								
Indeno(1,2,3-c,d)pyrene	++	++	-	+	+++	+++	+	++
Benzo(g,h,i)perylene								
Dibenzo(a,h)anthracene								
Coronene								





## 5 Discussion

Very little quantitative data was available in the open literature to enable the establishment of hazard scenarios. Indeed, the only detailed quantitative data that has been published concerning fire emissions to date is from a series of projects conducted at SP from the mid-1990's to the present day. These projects allow the determination of exposure scenarios for a number of different domestic fires. The fire scenarios in themselves are all basically similar, i.e., all apply to a domestic setting and a fire in a 16 m<sup>2</sup> room and the smoke spreads to a 160 m<sup>2</sup> room. The difference between the various scenarios relates to the material burning in each case. A list of Scenarios 1-8 is given below.

Scenarios 1-4: Fire Scenarios containing sofa, with and without flame retardants

1. Reference room with sofa containing non-flame retardant covering and foam, burning together with the whole room
2. Reference room with a sofa containing deca-BDE as a back-coating to the cover and TCPP-melamine foam, burning together with the whole room
3. Sofa containing non-flame retardant covering and foam, burning alone in reference room
4. Sofa containing deca-BDE as a back-coating to the cover and TCPP-melamine foam, burning alone in the reference room

Scenarios 5-8: Fire Scenarios containing TV, with and without flame retardants

5. Reference room with TV containing a non-flame retardant enclosure and TBBP-A in the circuit boards, burning together with the whole room
6. Reference room with TV containing deca-BDE in the enclosure and TBBP-A in the circuit boards, burning together with the whole room
7. TV containing a non-flame retardant enclosure and TBBP-A in circuit boards, burning alone in the reference room
8. TV containing deca-BDE in the enclosure and TBBP-A in the circuit boards, burning alone in a reference room.

In all cases the emissions can be broken down into a small number of groups: inorganics, volatile organic compounds (VOC's), polycyclic aromatic hydrocarbons (PAH's), brominated and chlorinated dioxins and furans (PBDD/PCDD and PBDF/PCDF), brominated flame retardants (polybrominated diphenylether (PBDE) and tetra brominated bisphenol A (TBBP-A)), and isocyanates for Scenarios 1-4. The effect of the presence or absence of flame retardants on the hazard of exposure to these species, is discussed on a group basis below.

Clearly, fire gases are dangerous to fire fighters and other citizens who could be exposed, independent of the presence or absence of flame retardants. In this context it is important to note that the traditional advantage of flame retardants is in the early stages of a fire by reduction of the ignitability of the flame retarded product or delay in the time between ignition to flash-over in a room fire. This advantage is not taken into account in this study as all scenarios are considered under the assumption that they can occur, at least at some stage in the development of a fire, and the hazard associated with exposure to the fire gases is considered independent of the potential frequency of the event. Especially Scenario 4 and 8 might seem unrealistic to some readers. Statistics show however that flame retarded upholstered furniture occur as the starting item in fires. One possible explanation for this is that other material such as a blanket or a cushion might be placed in the sofa and support the fire. The fire would go on for a reasonable long time in the sofa before the entire room is flashed-over and a sofa fire is severe enough for the rescue service to be called upon. It should be emphasised, however, that the probability of

Scenarios 4 and 8 is low as flame retarded items are more difficult to ignite than non-flame retarded items. This should be kept in mind when considering the results.

The calculations are made based on the assumption that the exposed fire fighter is not wearing full breathing equipment. This is seldom the case when fighting a fire but experience show that the breathing equipment is seldom used during clean up and after extinguishment. If full protective equipment is used then the fire fighter would not be at risk. There is no specific data on emissions during the end of fires and therefore the emissions data that is available (i.e. data from the entire fire period until extinguishment) has been used for the comparison throughout.

## **5.1 8/10 hour Exposure Hazards**

Firstly, it should be noted that the NIOSH and OSHA values for 8/10 hour exposure are defined based on acceptable levels to which a worker could be exposed during a typical working day without expecting any adverse effect. A fire fighter is seldom or never on active fire fighting duty for 8 consecutive hours which implies that the 8/10 hours exposure limits are in some ways unrealistically harsh. However, short term exposure levels are only available for a restricted number of species.

The NIOSHA and OSHA values are established for normal breathing, fire fighters are probably breathing more heavily during a fire fighting and thus a comparison with the NIOSHA and OSHA values is a bit harsh. On the other hand other assumptions like the 8/10 hour exposure and not wearing full protective gear is a conservative estimate and overall the 8/10 hour comparison is deemed to be a reasonable starting point for estimating the occupational hazard fire fighters are exposed to when fighting fires or participating in post-fire clean-up.

With respect to the fire scenarios for the sofa (Scenarios 1-4) with 8/10 hour standard exposure levels, it can be noted that for most inorganic volatile compounds the hazards are approximately equal for all scenarios, and differences should be considered marginal. It is also noted that a slight increase in hazard is common from HBr in those situations where a sofa containing deca-BDE is burned.

With respect to the fire scenarios for the TV with or without deca-BDE (Scenarios 5-8) it is clear that the production of volatile inorganic gases and HBr is significantly increased in the room containing the flame retarded TV burning alone (Scenario 8) relative to the other scenarios. Indeed, the number of times these values exceed the recommended occupational standards for these volatile or gaseous compounds stands out relative to the other scenarios. One should note, however, that Scenario 8 is improbable for anything but a transition period early in a fire, as the ignition and continued burning of the flame retarded TV is not possible without a significant ignition source which would imply that other objects in the room are also burning. This would suggest that while something similar to Scenario 8 could occur early in the development of a room fire it would rapidly transition into Scenario 6.

In all the fire scenarios included in this study, the hazard of exposure to VOCs is approximately comparable and no effect can be seen, in either the sofa or TV scenarios, of the presence of deca-BDE. With respect to the hazard of exposure to PAHs, a number of observations can be made relative to the different fire scenarios. Exposure to PAH emissions from a room fire represents approximately the same hazard independent of whether the sofa contains deca-BDE or not. Thus, it must be concluded that the presences of a BFR like deca-BDE does not significantly change the production of PAHs and their

associated hazard in a typical domestic room fire situation. A similar observation can be made for the hazard estimated for a room with a TV with or without deca-BDE.

In addition, it is noted that a free burning sofa or TV containing a BFR like deca-BDE increases the hazard associated with PAH exposure, provided sustained burning does occur.

With respect to the formation of halogenated dibenzodioxins and dibenzofurans a very strong increase in hazard for the 8/10 hours exposure period can be observed when either a sofa or TV with deca-BDE is burned alone in the room, i.e., for Scenario 4 and 8. Although the formation of especially 2,3,7,8-substituted PBDDs and PBDFs coming from PBDEs is not unexpected, the very strong increase in order of magnitude is noticeable. There are several contributing explanations for this phenomenon, e.g. the molecular structure of deca-BDE which can provide the building blocks for dioxins and furans when it is broken down in a fire, and the fact that the combustion temperature in the initial stages of a fire containing deca-BDE would be expected to be lower than that of an equivalent fire without deca-BDE, thereby facilitating the formation of dibenzodioxins and dibenzofurans from these building blocks. Further, the presence of deca-BDE provides ample bromine for the aromatic bromination process. With respect to the formation of 2,3,7,8-substituted chlorinated dioxins and dibenzofurans it can be observed that in Scenarios 4 and 8 with a free burning deca-BDE sofa or TV the concentrations of the 2,3,7,8-substituted brominated dioxins and especially brominated dibenzofurans significantly exceed those of the chlorinated congeners. Ratio's for PCDD/Fs vs PBDD/Fs are  $2.8 \cdot 10^{-4}$  and  $2.7 \cdot 10^{-3}$  for Scenarios 4 and 8 respectively. However, the increase of PBDDs and PBDFs relative to formation of chlorinated analogues is not consistent for all combustion experiments in which deca-BDE is involved. In Scenarios 2 and 6 in which the whole room burns, the ratio of PCDD/Fs and PBDD/Fs has shifted more towards the chlorinated congeners with ratios of  $1.2 \cdot 10^{-1}$  and 2.6 respectively. From Scenarios 4 and 8 it might be concluded that formation of PBDDs and PBDFs is more significant with respect to TEQs when either a sofa or TV with deca-BDE is burning alone. However, if the deca-BDE sofa and TV are burning together with the whole room the total TEQ effect of PBDDs and PBDFs is found to be diminished (Scenarios 2 and 6). In practice this would mean that this increase in hazard of PBDDs and PBDFs is diminished relative to the chlorinated analogues if the whole room is burning.

In addition to the extensive formation of 2,3,7,8-substituted PBDDs and PBDFs during the fire experiments, a very strong (several orders of magnitude) and comparable increase of polyaromatic hydrocarbons (PAHs) and benzene was observed. From a toxicological point of view the carcinogenic properties of these PAHs and benzene are especially a cause for concern. Although the approach for risk assessment for these compounds varies between countries, a linear dose-effect relationship (i.e. no safe threshold level) for carcinogenicity and mutagenicity is generally accepted for these type of compounds.

When comparing the carcinogenic properties of polycyclic aromatic hydrocarbons and dioxin like compounds the presence of a threshold (safe) level is an important difference. With respect to dioxin like compounds only for 2,3,7,8-TCDD human carcinogenicity has been established (IARC 1997)<sup>39</sup>. For other 2,3,7,8-substituted dioxins and dibenzofurans such a relationship has not formally been established. However, carcinogenicity for these type of congeners could be expected because of similar mechanism of action via the Ah-receptor. In fact recent studies from the US National Toxicology Program with dioxinlike PCBs or PCDFs have confirmed this<sup>40</sup>. With respect to risk assessment and carcinogenicity of dioxin like compounds the majority the global scientific community accepts that for these compounds a threshold level exists. This justifies the use of a non linear model with a threshold for dose-response relationships with 2,3,7,8-substituted halogenated dioxins and dibenzofurans. At present only the US-EPA is still using the

linear risk assessment model for carcinogenicity of dioxin like compounds, especially 2,3,7,8-TCDD, and this approach is under heavy debate in the scientific community. In fact a recent evaluation done by the US National Academy of Sciences also criticized this approach and suggested the US-EPA to include a non linear (threshold) risk assessment for dioxin like compounds<sup>41</sup>. In summary, this means that based on the results derived from the fire experiments done in this study, the carcinogenic hazard of combustion products is significantly elevated by formation of several PAHs and benzene, which are established human or animal carcinogens. If such an increase in carcinogenic hazard is also present due to the formation of 2,3,7,8-PBDDs and PBDFs can not be established. This is caused partly by the fact that carcinogenicity for PBDDs and PBDFs has not been properly studied, but if existing it very likely has a threshold (safe) level. Consequently, for the group of PBDDs and PBDFs only an exposure of firemen higher than the threshold level might cause an increase in carcinogenic hazard. The experimental design of these studies was, however, not intended to focus quantitatively on the (carcinogenic) hazard for firemen.

Isocyanates in particular have been the subject of much debate in recent years. The effect of exposure to these dangerous combustion products has been contentious to say the least. Isocyanates are used in the manufacture of polyurethane foam in furniture and are released in relatively large quantities when the foam burns. The formation of isocyanates and amines, however, does not seem to be significantly influenced by the presence of deca-BDE, or the phosphorous based flame retardant in the foam in a flame retarded sofa.

## 5.2 15 minute Exposure Hazards

*The hazard assessment for 15 minute exposure is based on much more limited information, as no occupational exposure standard is available for many of the compounds analyzed. The only notable observation from Table 7*

Table 7 is that Scenario 4 (a free burning sofa) or Scenario 8 (a free burning TV) exhibit an increase in hazard due to the presence of deca-BDE, with respect to benzene exposure. This is in line with the hazard estimations made above for the 8/10 hour exposure period.

## 5.3 IDHL Comparison

In the discussion above it is easy to loose sight of the hazards associated with exposure to fire gases in a detailed comparison between different exposure scenarios. In this context it is important to note that for all scenarios the emissions of inorganic species is close to or in excess of the NIOSH levels representing Immediate Danger to Life and Health (IDHL). In light of this alone it is clear that fire fighters should employ full protective gear on the scene of a fire independent of the presence or absence of flame retardants in the products involved in the fire.

When discussing hazard and toxicity, it is clear that faithful use of full protective gear will provide adequate protection to fire fighters in most situations. Experience does show, however, that while fire fighters use full protective gear during an incident they are likely to relax the use of breathing apparatus in the post-extinguishment period. Exposure to fire gases in the post-extinguishment period is significantly less, however, and should represent a much reduced hazard.

## 6 Conclusions

A series of 9 scenarios have been considered in terms of the hazard of exposure to fire emissions, contingent on the presence or absence of brominated flame retardants in the products included in the fire. Scenarios 1-8 concern exposure to fire gases and the hazard to fire fighters due to inhalation of these gases. Scenario 9 concerns the hazard of dermal exposure to soot containing numerous fire products adsorbed onto the surface of the soot. In all cases, faithful use of full protective gear will provide adequate protection for fire fighters involved in active duty. Even without the use of full protective gear in Scenario 9, it is expected that exposure to soot condensed onto surfaces would not pose a significant hazard.

In the case of Scenario 9, it has been determined that there is insufficient data concerning acceptable exposure levels to allow the same kind of hazard assessment as that conducted for Scenarios 1-8. However, it is expected that the area of skin that would be exposed to the soot and the bioavailability of any products adsorbed on the soot surface imply that this scenario represents a lesser hazard than the other 8 scenarios. Thus, Scenario 9 has not been studied further. Scenarios 1-8, however, exemplify the most significant toxicological hazard a fire fighter is exposed to when fighting a common house fire and the hazard associated with such exposure contingent on the presence of a flame retardant.

Indeed, very little difference in hazard was seen between the different scenarios (i.e., with and without flame retardants) in the case of inorganic emissions, VOCs, PAHs and isocyanates. The only case where there was a significant difference in the hazard associated with exposure to dioxins and furans from the fire scenarios with a flame retarded product was in the case of the less probable scenarios (Scenarios 4 and 8), i.e., when the flame retarded product burns as the only item burning in a room. Flame retarded items are less likely to catch fire than non-flame retarded items so the overall significance of Scenarios 4 and 8 is low. One should also keep in mind that this hazard can only be realised if the fire fighter does not wear full protective gear.

One should note that Scenario 8 is improbable for anything but a transition period early in a fire, as the ignition and continued burning of the flame retarded TV is not possible without a significant ignition source which would imply that other objects in the room are also burning. This would suggest that while something similar to Scenario 8 could occur early in the development of a room fire it would rapidly transition into Scenario 6.

It is clear that exposure to fire gases is hazardous independent of the presence or absence of flame retardants in the products burning in the fire. It is important to note that for all scenarios the emissions of inorganic species is close to or in excess of the NIOSH levels representing Immediate Danger to Life and Health (IDLH). In light of this alone it is clear that fire fighters should employ full protective gear on the scene of a fire independent of the presence or absence of flame retardants in the products involved in the fire.

Clearly, fire gases are dangerous to fire fighters and other citizens who could be exposed, independent of the presence or absence of flame retardants. In this context it is important to note that the traditional advantage of flame retardants is in the early stages of a fire by reduction of the ignitability of the flame retarded product or delay in the time between ignition to flash-over in a room fire. This advantage is not taken into account in this study as all scenarios are considered under the assumption that they can occur, at least at some stage in the development of a fire, and the hazard associated with exposure to the fire gases is considered independent of the potential frequency of the event.

In conclusion, faithful use of full protective gear will provide adequate protection to fire fighters in all situations studied in this project. Even without full use of breathing apparatus in the post-extinguishment phase, exposure to soot produced from a fire that has condensed onto surfaces, is not expected to pose a significant risk. Residual gases in the fire scene cannot be evaluated at this point due to lack of information, but could be potentially more problematic.

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## Appendix 2: Emissions Data

The tables lists the emission data used for the hazard assessment in this study. The total amounts reported in the tables are taken directly from the results from the SP experiments. For some scenarios results reported as yields have been recalculated to total amounts. This applies to Scenario 1-4 and 7-8, with the following amounts of combustible materials used: Scenario 1-2: 470 kg, Scenario 3: 54 kg, Scenario 4: 55 kg, Scenario 7: 7.0 kg, Scenario 8: 6.5 kg. The average concentration is then calculated based on a dilution on the smoke gas layer volume as calculated by Branzfire.

### Average emissions from Scenarios 1-4

Compound	Scenario 1 Room, non-BFR sofa		Scenario 2 Room, BFR-sofa		Scenario 3 Non-BFR sofa		Scenario 4 BFR-sofa	
	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)
<b>Inorganic:</b>								
CO <sub>2</sub>	431222	1021	443727	1050	81702	254	76285	237
CO	15236	36	19351	46	1301	4	2112	6.57
HCN	446	1.1	640	1.5	< 22	-	50	0.15
HCl	281	0.7	293	0.7	308	1.0	402	1.25
NH <sub>3</sub>	238	0.6	497	1.2	32	0.1	39	0.12
SO <sub>2</sub>	1627	3.9	1950	4.6	-	-	-	-
NO	413	1.0	233	0.6	216	0.7	171	0.53
Br (from HBr)	0.8	0.00	2.5	0.006	1.0	0.003	3.5	0.01
Sb	<0.3	-	0.5	0.0	0.02	0.0	0.7	0.00
<b>VOCs:</b>								
Benzene	610	1.4	632	1.50	5.4	0.0168	21	0.065
Toluene	56	0.13	72	0.17	1.3	0.0040	3.4	0.010
Styrene	35	0.08	62	0.15	0.6	0.0018	2.1	0.0065
Phenol	26	0.06	34	0.08	1.3	0.0040	8.0	0.025
Benzonitrile	26	0.06	47	0.11	0.9	0.0027	5.3	0.0164

Compound	Scenario 1 Room, non-BFR sofa		Scenario 2 Room, BFR-sofa		Scenario 3 Non-BFR sofa		Scenario 4 BFR-sofa	
	Total amount (mg)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)
<b>PAHs:</b>								
Naphtalene	166000	0.39	152000	0.36	1134	0.0035	6050	0.019
Acenaphthalene	58668	0.14	49244	0.12	342	0.0011	990	0.0031
Acenaphthene	536	0.0013	304	0.001	13	0.00004	61	0.00019
Fluorene	8673	0.021	6836	0.016	52	0.00016	132	0.00041
Phenanthrene	48465	0.11	43041	0.10	259	0.00081	935	0.00291
Anthracene	5102	0.012	5317	0.013	33	0.00010	110	0.00034
Fluoranthrene	22957	0.054	17470	0.041	109	0.00034	319	0.00099
Pyrene	21682	0.051	17723	0.042	93	0.00029	253	0.00079
Benzofluorenes	2397	0.0057	1997	0.005	18	0.00005	50	0.00015
Benzo(a)anthracene	4336	0.010	3545	0.008	22.8	0.00007	72	0.00022
Chrysene	5612	0.013	4557	0.011	29.0	0.00009	94	0.00029
Benzofluoranthenes	9950	0.024	8229	0.019	41	0.00013	132	0.00041
Benso(e)-pyrene	4081	0.0097	3545	0.008	14.0	0.00004	44	0.00014
Benso(a)-pyrene	3316	0.0079	4557	0.011	15.0	0.00005	39	0.00012
Perylene	663	0.0016	734	0.002	1.7	0.00001	6	0.00002
Indeno(1,2,3-c,d)pyrene	6122	0.015	5317	0.013	18.2	0.00006	55	0.00017
Benzo(g,h,i)perylene	5357	0.013	5064	0.012	16.1	0.00005	44	0.00014
Dibenzo(a,h)anthracene	408	0.0010	405	0.001	1.8	0.00001	6	0.00002
Coronene	1607	0.0038	1798	0.004	4.9	0.00002	22	0.00007

Compound	Scenario 1 Room, non-BFR sofa		Scenario 2 Room, BFR-sofa		Scenario 3 Non-BFR sofa		Scenario 4 BFR-sofa	
	Total amount (µg)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)
<b>PCDD/PCDFs:</b>								
Chlorinated dioxins (all)	7.4	0.000000018	6.8	0.000000016	0.1	0.0000000003	51.7	0.00000016
Chlorinated furans (all)	89.7	0.00000021	1552	0.0000037	12.5	0.000000039	676	0.0000021
TCDD-eq. (I-TEQ)	1.1	0.0000000026	13.9	0.000000033	0.10	0.0000000003	8.2	0.000000026
<b>PBDD/PBDFs:</b>								
2,3,7,8 TBDD	N.D.	-	N.D.	-	N.D.	-	N.D.	-
1,2,3,7,8 PnBDD	N.D.	-	N.D.	-	N.D.	-	N.D.	-
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	408.9	0.00000097	N.D.	-	N.D.	-	N.D.	-
1,2,3,7,8,9 HxBDD	N.D.	-	N.D.	-	N.D.	-	N.D.	-
2,3,7,8 TBDF	94	0.00000022	N.D.	-	6.48	0.000000020	605	0.0000019
1,2,3,7,8 PnBDF	N.D.	-	169	0.00000040	N.D.	-	4950	0.000015
2,3,4,7,8 PnBDF	N.D.	-	169	0.00000040	N.D.	-	6545	0.000020
1,2,3,4,7,8 HxBDF	N.D.	-	517	0.0000012	N.D.	-	6050	0.000019
1,2,3,4,6,7,8 HpBDF	N.D.	-	517	0.0000012	N.D.	-	261250	0.00081
<b>PBDEs:</b>								
2,2',4,4' TBDE	< 28	-	785	0.0000019	36	0.00000011	451	0.0000014
2,2',4,4',6 PBDE	< 28	-	<28	-	12	0.000000037	324	0.0000010
2,2',4,4',5 PBDE	< 28	-	304	0.00000072	23	0.000000071	11055	0.000034
2,2',3,4,4' PBDE	< 28	-	253	0.00000060	<4.8	-	198	0.00000061
2,2',4,4',5,6' HBDE	< 28	-	329	0.00000078	35	0.00000011	401	0.0000012
2,2',4,4',5,5' HBDE	< 28	-	84	0.00000020	26	0.000000081	1458	0.0000045
2,2',3,4,4',5' HBDE	< 28	-	<28	-	9	0.000000027	440	0.0000014
Deca-BDE	400	0.00000095	76100	0.00018	259	0.00000081	3129500	0.0097

Compound	Scenario 1 Room, non-BFR sofa		Scenario 2 Room, BFR-sofa		Scenario 3 Non-BFR sofa		Scenario 4 BFR-sofa	
	Total amount (mg)	Average conc. (g/m3)	Total amount (g) (mg)	Average conc. (g/m3)	Total amount (g) (mg)	Average conc. (g/m3)	Total amount (g) (mg)	Average conc. (g/m3)
<b>Isocyanates/amines:</b>								
2,4 - TDI	87.9	0.0002	<16	-	20	0.00006	39	0.00012
2,6 - TDI	117	0.0003	<16	-	47	0.00015	42	0.00013
phenyl isocyanate	1172	0.0028	504	0.0012	47	0.00015	<	-
methyl isocyanate	1494	0.0035	1186	0.0028	258	0.00080	243	0.00076
ethyl isocyanate	<30	-	<30	-	12	0	23	0.00007
isocyanic acid	65800	0.1558	79900	0.19	5022	0.016	39050	0.12
2,4 - TAI	<30	-	<30	-	8	0	8	0.00002
2,6 - TAI	<30	-	<30	-	16	0	15	0.00005
2,4 - TDA	<30	-	<30	-	<3	-	<	-
2,6 - TDA	<30	-	<30	-	39	0	85	0.00026

### Average emissions from Scenarios 5-8

Compound	Scenario 5 Room, non-BFR TV		Scenario 6 Room, BFR-TV		Scenario 7 Non-BFR TV		Scenario 8 BFR-TV	
	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)
<b>Inorganic:</b>	<b>(g)</b>		<b>(g)</b>		<b>(g)</b>		<b>(g)</b>	
CO <sub>2</sub>	465000	1100	409000	968	22960	102	9620	42.6
CO	21600	51	23400	55.4	476	2.11	676	2.99
HCN	650	1.54	1080	2.56	-	-	-	-
HCl	230	0.54	320	0.76	49	0.22	117	0.52
NH <sub>3</sub>	N.A.	-	690	1.63	-	-	-	-
SO <sub>2</sub>	N.A.	-	3220	7.62	-	-	-	-
NO	-	-	-	-	-	-	-	-
HBr	<34	-	200	0.47	<3.5	-	279.5	1.24
Sb	N.A.	-	N.D.	-	<1.4	-	182	0.81
<b>VOCs:</b>	<b>(g)</b>		<b>(g)</b>		<b>(g)</b>		<b>(g)</b>	
Benzene	494	1.17	549	1.30	41	0.18	87	0.39
Toluene	69	0.16	87	0.21	13	0.058	81	0.36
Styrene	46	0.11	58	0.14	50	0.22	292	1.29
Phenol	-	-	-	-	5.9	0.026	12	0.053
Benzonitrile	57	0.13	72	0.17	-	-	-	-

Compound	Scenario 5 Room, non-BFR TV		Scenario 6 Room, BFR-TV		Scenario 7 Non-BFR TV		Scenario 8 BFR-TV	
	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)
<b>PAHs:</b>	<b>(g)</b>		<b>(g)</b>		<b>(g)</b>		<b>(g)</b>	
Naphtalene	262	0.62	256	0.61	10.36	0.046	31.07	0.14
Acenaphthalene	89.5	0.21	160.5	0.38	5.88	0.026	1.885	0.0084
Acenaphthene	0.9	0.0021	0.56	0.0013	0.35	0.0016	0.26	0.0012
Fluorene	11.6	0.027	14.2	0.034	2.03	0.0090	1.43	0.0063
Phenanthrene	63.2	0.152	111	0.27	10.92	0.048	18.98	0.084
Anthracene	5.3	0.016	18.5	0.0440	1.26	0.0056	0.455	0.0020
Fluoranthrene	35.3	0.084	38.9	0.0929	2.24	0.0099	5.265	0.023
Pyrene	34.7	0.082	40.1	0.095	1.19	0.0053	0.26	0.0012
Benzofluorenes	3.9	0.0092	3.21	0.0076	1.19	0.0053	1.755	0.0078
Benzo(a)anthracene	5.8	0.014	11.7	0.028	0.7	0.0031	1.625	0.0072
Chrysene	7.9	0.019	13.6	0.032	1.75	0.0078	6.305	0.028
Benzo(a)fluoranthenes	26.3	0.062	17.01	0.040	1.68	0.0074	3.64	0.016
Benzo(e)pyrene	5.8	0.014	8.02	0.019	0.42	0.0019	0.845	0.0037
Benzo(a)pyrene	3.6	0.0085	12.4	0.029	0.42	0.0019	0.585	0.0026
Perylene	0.6	0.0014	2.22	0.0053	0.07	0.00031	0.065	0.00029
Indeno(1,2,3-c,d)pyrene	14.2	0.034	14.8	0.035	0.42	0.0019	0.91	0.0040
Benzo(g,h,i)perylene	11.1	0.026	16.1	0.038	0.28	0.0012	0.455	0.0020
Dibenzo(a,h)anthracene	0.9	0.0021	1.36	0.0032	0.21	0.00093	0.91	0.0040
Coronene	6.3	0.015	6.17	0.015	0.07	0.00031	0.13	0.00058

Compound	Scenario 5 Room, non-BFR TV		Scenario 6 Room, BFR-TV		Scenario 7 Non-BFR TV		Scenario 8 BFR-TV	
	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)	Total amount (g)	Average conc. (g/m3)
<b>PCDD/PCDFs:</b>	(µg)		(µg)		(µg)		(µg)	
Chlorinated dioxins (all)	22	0.000000051	89	0.00000021	20	0.00000009	976	0.0000043
Chlorinated furans (all)	181	0.000000429	372	0.00000088	756	0.00000335	1460	0.0000065
TCDD-eq. (I-TEQ)	2.9	0.000000006	4.2	0.000000010	6.6	0.000000029	65	0.00000029
		9						
<b>PBDD/PBDFs:</b>	(µg)		(µg)		(µg)		(µg)	
2,3,7,8 TBDD	N.D.	-	N.D.	-	N.D.	-	N.D.	-
1,2,3,7,8 PnBDD	N.D.	-	N.D.	-	N.D.	-	N.D.	-
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	N.D.	-	N.D.	-	N.D.	-	189	0.0000008
1,2,3,7,8,9 HxBDD	N.D.	-	N.D.	-	N.D.	-	N.D.	-
2,3,7,8 TBDF	N.D.	-	24.07	0.000000057	6.3	0.000000028	42380	0.00019
1,2,3,7,8 PnBDF	N.D.	-	N.D.	-	2.66	0.000000012	27755	0.00012
2,3,4,7,8 PnBDF	N.D.	-	N.D.	-	3.43	0.000000015	32110	0.00014
1,2,3,4,7,8 HxBDF	N.D.	-	N.D.	-	6.65	0.000000029	62790	0.00028
1,2,3,4,6,7,8 HpBDF	11.05	0.000000026	N.D.	-	21	0.000000093	277485	0.00123
<b>Deca-BDE</b>	N.D.		N.D.		(mg)		(mg)	
					<0.02	-	53	0.00023
<b>TBBP-A</b>					(mg)		(mg)	
					191	0.00085	653	0.00289

## Skin Exposure – Scenario 9

*Samples of soot and ash from an apartment fire (Söderström and Marklund).*

Object	Species	Sample	
TV	PCDD/F	Soot (ng/m <sup>3</sup> )	Ash (ng/g)
	2378-TCDF	4.7	0.01
	∑TCDF	301	0.5
	2377-TCDD	0.1	nd
	∑TCDD	13	nd
	278-triCDF	1.3	0.01
	∑moBr triCl DF	913	1.4
	2Br 378 Cl DD	nd	nd
	∑moBr triCl DD	4.9	nd
	∑di Br di Cl DF	2456	8.4
	23 di Br 78 di Cl DD	1.7	nd
	∑di Br di Cl DD	91	0.1
	2378 TBDF	2.2	nd
	∑TBDF	1157	24
	2378 TBDD	nd	nd
	∑TBDD	33	nd
	<b>Brominated flame retardants</b>		
	TBBP-A	nd	nd
	TeBDE	190	nd
	PeBDE	nd	nd
	HxBB	nd	nd

Samples of debris from an apartment fire (Zelinski, Lorenz and Bahadir).

<b>TV</b>	<b>PB-compounds</b>	<b>Debris mg/kg</b>
	∑BrPh	8.57
	∑BRBz	7.9
	TBBP-A	3.65
	∑PBB	0.97
	∑TeBDPE-HpBDPE	118
	∑OcBDPE-DcBDPE	20.4
	PBDD/F	µg/kg (debris)
	∑MoBDF-TrBDF	18 914
	∑TeBDF-OcBDF	14 910
	∑MoBDD-TrBDD	nd
	∑TeBDD-OcBDD	50.5
	∑TeBDD/F-OcBDD/F	14 960
	TEQ	155.3
<b>Sofa</b>	<b>PB-compounds</b>	<b>mg/kg (debris)</b>
	∑BrPh	2
	∑BRBz	<0.5
	TBBP-A	nd
	∑PBB	0.16
	∑TeBDPE-HpBDPE	1.76
	∑OcBDPE-DcBDPE	nd
	PBDD/F	µg/kg (debris)
	∑MoBDF-TrBDF	126
	∑TeBDF-OcBDF	52
	∑MoBDD-TrBDD	0.2
	∑TeBDD-OcBDD	0.2
	∑TeBDD/F-OcBDD/F	52
	TEQ	0.56



Compound	Average conc. (g/m <sup>3</sup> )	NIOSH (g/m <sup>3</sup> ) Permissible Exp.	Excess Permissible Exp. Times	Hazards for Firemen 8-10 hours	NIOSH (g/m <sup>3</sup> ) Permissible Exp.	Excess Permissible Exp. Times	Hazards for Firemen 15 min	NIOSH (g/m <sup>3</sup> ) Dangerous To Life	ToxNet Information Recommended Exposure
<b>PAHs:</b>		Day	Day		Short term	Short term			
Naphtalene	0.39	0.0500	8	+	0.075	5	+	1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.14	N.I.							not established
Acenaphthene	0.0013	N.I.							not established
Fluorene	0.021	N.I.							not established
Phenanthrene	0.11	N.I.							not established
Anthracene	0.012	0.0002	60	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.054	N.I.							not established
Pyrene	0.051	N.I.							not established
Benzofluorenes	0.0057	N.I.							not established
Benzo(a)anthracene	0.010	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.013	0.0002	66	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzofluoranthenes	0.024	0.0001	236	+++					10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benso(e)-pyrene	0.0097	N.I.							not established
Benso(a)-pyrene	0.0079	0.0002	39	++	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.0016	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.0145	0.0002	72	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.013	N.I.							not established
Dibenzo(a,h)anthracene	0.0010	N.I.							not established
Coronene	0.0038	N.I.							not established

Compound	Average conc. (g/m <sup>3</sup> )	NIOSH (g/m <sup>3</sup> ) Permissible Exp.	Excess Permissible Exp. Times Day	Hazards for Firemen 8-10 hours	NIOSH (g/m <sup>3</sup> ) Permissible Exp. Short term	Excess Permissible Exp. Times Short term	Hazards for Firemen 15 min	NIOSH (g/m <sup>3</sup> ) Dangerous To Life	ToxNet Information Recommended Exposure
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	0.000000018	N.I.							
Chlorinated furans (all)	0.000000212	N.I.							
TCDD-eq.	2.6E-09	0.0000000002	13	++					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.	N.I.							
1,2,3,7,8 PnBDD	N.D.	N.I.							
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	0.000000968	N.I.							
1,2,3,7,8,9 HxBDD	N.D.	N.I.							
2,3,7,8 TBDF	0.000000223	N.I.							
1,2,3,7,8 PnBDF	N.D.	N.I.							
2,3,4,7,8 PnBDF	N.D.	N.I.							
1,2,3,4,7,8 HxBDF	N.D.	N.I.							
1,2,3,4,6,7,8 HpBDF	N.D.	N.I.							
TCDD-eq.(Br-)	1.2E-07	0.0000000002	595	+++					
Total TCDD-eq.(Cl+Br-)	1.2E-07	0.0000000002	608	+++	N.I.			0.0000000020	8h 2 ng/m <sup>3</sup>





Compound	Average con.	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	ToxNet Information
	(g/m <sup>3</sup> )	<u>Permissible Exp.</u>	<u>Times</u>	<u>8-10 hours</u>	<u>Permissible Exp.</u>	<u>Times</u>	<u>15 min</u>	<u>Dangerous ToLife</u>	<u>Recommended Exposure</u>
		<b>Day</b>	<b>Day</b>		<b>Short term</b>	<b>Short term</b>			
<b>PAHs:</b>									
Naphtalene	0.36	0.0500	7	+	0.075	5	+	1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.12	N.I.							not established
Acenaphthene	0.0007	N.I.							not established
Fluorene	0.016	N.I.							not established
Phenanthrene	0.10	N.I.							not established
Anthracene	0.013	0.0002	63	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.041	N.I.							not established
Pyrene	0.042	N.I.							not established
Benzofluorenes	0.0047	N.I.							not established
Benzo(a)anthracene	0.0084	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.011	0.0002	54	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(a)anthracene	0.020	0.0001	195	+++	N.I.				10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benzo(e)-pyrene	0.0084	N.I.							not established
Benzo(a)-pyrene	0.011	0.0002	54	++	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.0017	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.013	0.0002	63	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.012	N.I.							not established
Dibenzo(a,h)anthracene	0.0010	N.I.							not established
Coronene	0.0043	N.I.							not established

Compound	Average con.	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	ToxNet Information
	(g/m <sup>3</sup> )	<u>Permissible Exp.</u>	<u>Times</u>	<u>8-10 hours</u>	<u>Permissible Exp.</u>	<u>Times</u>	<u>15 min</u>	<u>Dangerous To Life</u>	<u>Recommended Exposure</u>
		Day	Day		Short term	Short term			
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	0.000000016	N.I.							
Chlorinated furans (all)	0.0000037	N.I.							
TCDD-eq.	3.3E-08	0.0000000002	165	+++					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.	N.I.							
1,2,3,7,8 PnBDD	N.D.	N.I.							
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	N.D.	N.I.							
1,2,3,7,8,9 HxBDD	N.D.	N.I.							
2,3,7,8 TBDF	N.D.	N.I.							
1,2,3,7,8 PnBDF	0.00000040	N.I.							
2,3,4,7,8 PnBDF	0.00000040	N.I.							
1,2,3,4,7,8 HxBDF	0.0000012	N.I.							
1,2,3,4,6,7,8 HpBDF	0.0000012	N.I.							
TCDD-eq.(Br-)	2.7E-07		1334	+++					
Total TCDD-eq.(Cl+Br-)	3.0E-07	0.0000000002	1499	+++	N.I.			0.0000000020	8h 2 ng/m3

Compound	Average con.	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	ToxNet Information
	(g/m <sup>3</sup> )	Permissible Exp.	Times	8-10 hours	Permissible Exp.	Times	15 min	Dangerous-ToLife	Recommended Exposure
		Day	Day		Short term	Short term			
<b>PBDEs:</b>									
2,2',4,4' TBDE	0.0000019	N.I.							
2,2',4,4',6 PBDE	N.D.	N.I.							
2,2',4,4',5 PBDE	0.00000072	N.I.							
2,2',3,4,4' PBDE	0.00000060	N.I.							
2,2',4,4',5,6' HBDE	0.00000078	N.I.							
2,2',4,4',5,5' HBDE	0.00000020	N.I.							
2,2',3,4,4',5' HBDE	N.D.	N.I.							
Deca-BDE	0.00018	N.I.							
<b>Isocyanates/amines:</b>									
2,4 - TDI	N.D.	0.000035			0.00014				8 hr 0.035 mg/m3 or 15 min 0.14 mg/m3
2,6 - TDI	N.D.	0.000035			0.00014				8 hr 0.035 mg/m3 or 15 min 0.14 mg/m3
phenyl isocyanate	0.0012	N.I.							liquid no vapor/gas
methyl isocyanate	0.0028	0.000050	56	++	N.I.			7.5 mg/m3	10h 0.05 mg/m3
ethyl isocyanate	N.D.	N.I.							na
isocyanic acid	0.19	N.I.							reacts quickly with other compounds
2,4 - TAI	N.D.	N.I.							no vapor
2,6 - TAI	N.D.	N.I.							no vapor
2,4 - TDA	N.D.	N.I.							no vapor
2,6 - TDA	N.D.	N.I.							no vapor

**Scenario 3: Sofa containing non-flame retardant covering and foam, burning alone in reference room**



Compound	Average conc.	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	ToxNet Information
	(g/m <sup>3</sup> )	Permissible Exp.	Times	8-10 hours	Permissible Exp.	Times	15 min	Dangerous ToLife	Recommended Exposure
		Day	Day		Short term	Short term			
<b>PAHs:</b>									
Naphtalene	0.0035	0.0500	<b>0.07</b>	-	0.075	<b>0.05</b>	-	1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.0011	N.I.							not established
Acenaphthene	0.00004	N.I.							not established
Fluorene	0.00016	N.I.							not established
Phenanthrene	0.00081	N.I.							not established
Anthracene	0.00010	0.0002	<b>1</b>	+	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.00034	N.I.							not established
Pyrene	0.00029	N.I.							not established
Benzofluorenes	0.00005	N.I.							not established
Benzo(a)anthracene	0.00007	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.00009	0.0002	<b>0.45</b>	-	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzofluoranthenes	0.00013	0.0001	<b>1</b>	+	N.I.				10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benso(e)-pyrene	0.00004	N.I.							not established
Benso(a)-pyrene	0.00005	0.0002	<b>0.23</b>	-	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.00001	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.00006	0.0002	<b>0.28</b>	-	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.00005	N.I.							not established
Dibenzo(a,h)anthracene	0.00001	N.I.							not established
Coronene	0.00002	N.I.							not established

Compound	Average conc.	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	ToxNet Information
	(g/m <sup>3</sup> )	Permissible Exp.	Times	8-10 hours	Permissible Exp.	Times	15 min	Dangerous-ToLife	Recommended Exposure
		Day	Day		Short term	Short term			
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	0.0000000003	N.I.							
Chlorinated furans (all)	0.000000039	N.I.							
TCDD-eq.	3.1E-10	0.0000000002	2	+					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.	N.I.							
1,2,3,7,8 PnBDD	N.D.	N.I.							
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	N.D.	N.I.							
1,2,3,7,8,9 HxBDD	N.D.	N.I.							
2,3,7,8 TBDF	0.000000020	N.I.							
1,2,3,7,8 PnBDF	N.D.	N.I.							
2,3,4,7,8 PnBDF	N.D.	N.I.							
1,2,3,4,7,8 HxBDF	N.D.	N.I.							
1,2,3,4,6,7,8 HpBDF	N.D.	N.I.							
TCDD-eq.(Br-)	2.0E-09		10	++					
Total TCDD-eq.(Cl-+Br-)	2.3E-09	0.0000000002	12	++	N.I.			0.0000000020	8h 2 ng/m3





Compound	Average conc.	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	ToxNet Information
	(g/m <sup>3</sup> )	Permissible Exp.	Times	8-10 hours	Permissible Exp.	Times	15 min	Dangerous ToLife	Recommended Exposure
		Day	Day		Short term	Short term			
<b>PAHs:</b>									
Naphtalene	0.019	0.0500	<b>0.38</b>	-	0.075	<b>0.25</b>		1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.0031	N.I.							not established
Acenaphthene	0.00019	N.I.							not established
Fluorene	0.00041	N.I.							not established
Phenanthrene	0.00291	N.I.							not established
Anthracene	0.00034	0.0002	<b>2</b>	+	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.00099	N.I.							not established
Pyrene	0.00079	N.I.							not established
Benzofluorenes	0.00015	N.I.							not established
Benzo(a)anthracene	0.00022	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.00029	0.0002	<b>1</b>	+	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(a)fluoranthene	0.00041	0.0001	<b>4</b>	+	N.I.				10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benzo(e)-pyrene	0.00014	N.I.							not established
Benzo(a)-pyrene	0.00012	0.0002	<b>1</b>	+	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.00002	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.00017	0.0002	<b>1</b>	+	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.00014	N.I.							not established
Dibenzo(a,h)anthracene	0.00002	N.I.							not established
Coronene	0.00007	N.I.							not established

Compound	Average conc.	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	ToxNet Information
	(g/m <sup>3</sup> )	<u>Permissible Exp.</u>	<u>Times</u>	<u>8-10 hours</u>	<u>Permissible Exp.</u>	<u>Times</u>	<u>15 min</u>	<u>DangerousToLife</u>	<u>Recommended Exposure</u>
		<b>Day</b>	<b>Day</b>		<b>Short term</b>	<b>Short term</b>			
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	1.6E-07	N.I.							
Chlorinated furans (all)	2.1E-06	N.I.							
TCDD-eq.	2.6E-08	0.0000000002	<b>130</b>	<b>+++</b>					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.	N.I.							
1,2,3,7,8 PnBDD	N.D.	N.I.							
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	N.D.	N.I.							
1,2,3,7,8,9 HxBDD	N.D.	N.I.							
2,3,7,8 TBDF	1.9E-06	N.I.							
1,2,3,7,8 PnBDF	1.5E-05	N.I.							
2,3,4,7,8 PnBDF	2.0E-05	N.I.							
1,2,3,4,7,8 HxBDF	1.9E-05	N.I.							
1,2,3,4,6,7,8 HpBDF	0.00081	N.I.							
TCDD-eq.(Br-)	9.0E-05		<b>449802</b>	<b>+++</b>					
Total TCDD-eq.(Cl+Br-)	9.0E-05	0.0000000002	<b>449930</b>	<b>+++</b>	N.I.			0.0000000020	8h 2 ng/m3





Compound	Average conc.	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	ToxNet Information
	(g/m <sup>3</sup> )	Permissible Exp.	Times	8-10 hours	Permissible Exp.	Times	15 min	Dangerous ToLife	Recommended Exposure
		Day	Day		Short term	Short term			
<b>PAHs:</b>									
Naphtalene	0.62	0.0500	12	++	0.075	8	+	1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.21	N.I.							not established
Acenaphthene	0.002	N.I.							not established
Fluorene	0.027	N.I.							not established
Phenanthrene	0.150	N.I.							not established
Anthracene	0.013	0.0002	63	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.084	N.I.							not established
Pyrene	0.082	N.I.							not established
Benzofluorenes	0.009	N.I.							not established
Benzo(a)anthracene	0.014	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.019	0.0002	94	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(a)fluoranthene	0.062	0.0001	623	+++	N.I.				10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benzo(e)-pyrene	0.014	N.I.							not established
Benzo(a)-pyrene	0.009	0.0002	43	++	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.001	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.034	0.0002	168	+++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.026	N.I.							not established
Dibenzo(a,h)anthracene	0.002	N.I.							not established
Coronene	0.015	N.I.							not established

	Average conc.	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	ToxNet Information
Compound	(g/m <sup>3</sup> )	Permissible Exp.	Times	8-10 hours	Permissible Exp.	Times	15 min	Dangerous ToLife	Recommended Exposure
		Day	Day		Short term	Short term			
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	0.00000005	N.I.							
Chlorinated furans (all)	0.00000043	N.I.							
TCDD-eq.	6.9E-09	0.0000000002	35	++					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.	N.I.							
1,2,3,7,8 PnBDD	N.D.	N.I.							
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	N.D.	N.I.							
1,2,3,7,8,9 HxBDD	N.D.	N.I.							
2,3,7,8 TBDF	N.D.	N.I.							
1,2,3,7,8 PnBDF	N.D.	N.I.							
2,3,4,7,8 PnBDF	N.D.	N.I.							
1,2,3,4,7,8 HxBDF	N.D.	N.I.							
1,2,3,4,6,7,8 HpBDF	0.000000026	N.I.							
TCDD-eq. (Br-)	2.6E-10	0.0000000002	1	+					
Total TCDD-eq.(Cl+Br-)	7.1E-09	0.0000000002	36	++	N.I.			0.000000002	8h 2 ng/m3
								0	
Deca-BDE		N.I.							



Compound	Average conc.	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m <sup>3</sup> )	ToxNet Information
	(g/m <sup>3</sup> )	Permissible Exp.	Times	8-10 hours	Permissible Exp.	Times	15 min	Dangerous ToLife	Recommended Exposure
		Day	Day		Short term	Short term			
<b>PAHs:</b>									
Naphtalene	0.61	0.0500	12	++	0.075	8	+	1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.38	N.I.							not established
Acenaphthene	0.00	N.I.							not established
Fluorene	0.03	N.I.							not established
Phenanthrene	0.26	N.I.							not established
Anthracene	0.04	0.0002	219	+++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.09	N.I.							not established
Pyrene	0.09	N.I.							not established
Benzofluorenes	0.01	N.I.							not established
Benzo(a)anthracene	0.03	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.03	0.0002	161	+++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(a)anthracene	0.04	0.0001	403	+++	N.I.				10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benzo(e)-pyrene	0.02	N.I.							not established
Benzo(a)-pyrene	0.03	0.0002	147	+++	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.01	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.04	0.0002	175	+++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.04	N.I.							not established
Dibenzo(a,h)anthracene	0.003	N.I.							not established
Coronene	0.01	N.I.							not established

Compound	Average conc. (g/m <sup>3</sup> )	NIOSH (g/m <sup>3</sup> ) Permissible Exp.	Excess Permissible Exp. Times Day	Hazards for Firemen 8-10 hours	NIOSH (g/m <sup>3</sup> ) Permissible Exp. Short term	Excess Permissible Exp. Times Short term	Hazards for Firemen 15 min	NIOSH (g/m <sup>3</sup> ) Dangerous ToLife	ToxNet Information Recommended Exposure
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	0.00000021								
Chlorinated furans (all)	0.00000088								
TCDD-eq.	1.0E-08	0.0000000002	50	++					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.								
1,2,3,7,8 PnBDD	N.D.								
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	N.D.								
1,2,3,7,8,9 HxBDD	N.D.								
2,3,7,8 TBDF	5.69839E-08								
1,2,3,7,8 PnBDF	N.D.								
2,3,4,7,8 PnBDF	N.D.								
1,2,3,4,7,8 HxBDF	N.D.								
1,2,3,4,6,7,8 HpBDF	N.D.								
TCDD-eq. (Br-)	5.7E-09	0.0000000002	28	++					
Total TCDD-eq.(Cl+Br-)	1.6E-08	0.0000000002	78	++	N.I.			0.0000000020	8h 2 ng/m3
Deca-BDE		N.I.							



Compound	Average conc. (g/m <sup>3</sup> )	NIOSH (g/m <sup>3</sup> ) Permissible Exp.	Excess Permissible Exp. Times Day	Hazards for Firemen 8-10 hours	NIOSH (g/m <sup>3</sup> ) Permissible Exp. Short term	Excess Permissible Exp. Times Short term	Hazards for Firemen 15 min	NIOSH (g/m <sup>3</sup> ) Dangerous ToLife	ToxNet Information Recommended Exposure
<b>PAHs:</b>									
Naphtalene	0.046	0.0500	1	+	0.075	1	+	1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.026	N.I.							not established
Acenaphthene	0.0016	N.I.							not established
Fluorene	0.0090	N.I.							not established
Phenanthrene	0.048	N.I.							not established
Anthracene	0.0056	0.0002	28	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.0099	N.I.							not established
Pyrene	0.0053	N.I.							not established
Benzofluorenes	0.0053	N.I.							not established
Benzo(a)anthracene	0.0031	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.0078	0.0002	39	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(a)fluoranthene	0.0074	0.0001	74	++	N.I.				10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benzo(e)-pyrene	0.0019	N.I.							not established
Benzo(a)-pyrene	0.0019	0.0002	9	+	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.0003	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.0019	0.0002	9	+	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.0012	N.I.							not established
Dibenzo(a,h)anthracene	0.0009	N.I.							not established
Coronene	0.0003	N.I.							not established

Compound	Average conc. (g/m <sup>3</sup> )	NIOSH (g/m <sup>3</sup> ) Permissible Exp. Day	Excess Permissible Exp. Times Day	Hazards for Firemen 8-10 hours	NIOSH (g/m <sup>3</sup> ) Permissible Exp. Short term	Excess Permissible Exp. Times Short term	Hazards for Firemen 15 min	NIOSH (g/m <sup>3</sup> ) Dangerous ToLife	ToxNet Information Recommended Exposure
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	0.000000091								
Chlorinated furans (all)	0.00000033								
TCDD-eq.	2.9E-08	0.000000002	145	+++					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.								
1,2,3,7,8 PnBDD	N.D.								
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	N.D.								
1,2,3,7,8,9 HxBDD	N.D.								
2,3,7,8 TBDF	0.000000028								
1,2,3,7,8 PnBDF	0.000000012								
2,3,4,7,8 PnBDF	0.000000015								
1,2,3,4,7,8 HxBDF	0.000000029								
1,2,3,4,6,7,8 HpBDF	0.000000093								
TCDD-eq. (Br-)	1.2E-08	0.000000002	58	++					
Total TCDD-eq.(Cl+Br-)	4.1E-08	0.000000002	203	+++	N.I.			0.00000000 20	8h 2 ng/m3
<b>DECA-BDE</b>	N.D.	N.I.							
<b>TBBP-A</b>	0.00085	N.I.							

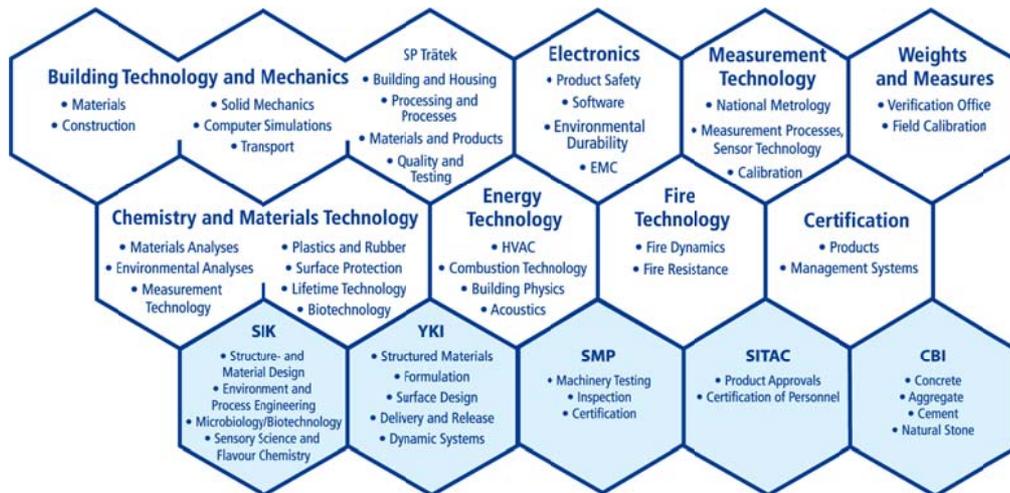


Compound	Average conc. (g/m <sup>3</sup> )	NIOSH (g/m <sup>3</sup> )  Permissible Exp.	Excess Permissible Exp.  Times	Hazards for Firemen  8-10 hours	NIOSH (g/m <sup>3</sup> )  Permissible Exp.	Excess Permissible Exp.  Times	Hazards for Firemen  15 min	NIOSH (g/m <sup>3</sup> )  Dangerous ToLife	ToxNet Information  Recommended Exposure
<b>PAHs:</b>		Day	Day		Short term	Short term			
Naphtalene	0.14	0.0500	3	+	0.075	2	+	1250.0	10h 50 mg/m <sup>3</sup> or 15 min 75 mg/m <sup>3</sup>
Acenaphthalene	0.0083	N.I.							not established
Acenaphthene	0.0012	N.I.							not established
Fluorene	0.0063	N.I.							not established
Phenanthrene	0.0841	N.I.							not established
Anthracene	0.0020	0.0002	10	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Fluoranthrene	0.0233	N.I.							not established
Pyrene	0.0012	N.I.							not established
Benzofluorenes	0.0078	N.I.							not established
Benzo(a)anthracene	0.0072	N.I.						As low as possible	suspected human carcinogen
Chrysene	0.0279	0.0002	140	+++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(a)anthracene	0.0161	0.0001	161		N.I.				10 hr 0.1 mg/m <sup>3</sup> or 8 hr 0.2 mg/m <sup>3</sup>
Benzo(e)-pyrene	0.0037	N.I.							not established
Benzo(a)-pyrene	0.0026	0.0002	13	++	N.I.			As low as possible	8 hr 0.2 mg/m <sup>3</sup>
Perylene	0.0003	N.I.							not established
Indeno(1,2,3-c,d)pyrene	0.0040	0.0002	20	++	N.I.				8 hr 0.2 mg/m <sup>3</sup>
Benzo(g,h,i)perylene	0.0020	N.I.							not established
Dibenzo(a,h)anthracene	0.0040	N.I.							not established
Coronene	0.0006	N.I.							not established

Compound	Average conc.	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	Excess Permissible Exp.	Hazards for Firemen	NIOSH (g/m3)	ToxNet Information
	(g/m <sup>3</sup> )	<u>Permissible Exp.</u>	<u>Times</u>	<u>8-10 hours</u>	<u>Permissible Exp.</u>	<u>Times</u>	<u>15 min</u>	<u>Dangerous ToLife</u>	<u>Recommended Exposure</u>
		Day	Day		Short term	Short term			
<b>PCDD/PCDFs:</b>									
Chlorinated dioxins (all)	0.0000043								
Chlorinated furans (all)	0.0000065								
TCDD-eq.	2.9E-07	0.0000000002	1450	+++					
<b>PBDD/PBDFs:</b>									
2,3,7,8 TBDD	N.D.								
1,2,3,7,8 PnBDD	N.D.								
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	0.0000008								
1,2,3,7,8,9 HxBDD	N.D.								
2,3,7,8 TBDF	0.00019								
1,2,3,7,8 PnBDF	0.00012								
2,3,4,7,8 PnBDF	0.00014								
1,2,3,4,7,8 HxBDF	0.00028								
1,2,3,4,6,7,8 HpBDF	0.0012								
TCDD-eq. (Br-)	1.1E-04	0.0000000002	526157	+++					
Total TCDD-eq.(Cl+Br-)	1.1E-04	0.0000000002	527607	+++	N.I.			0.0000000020	8h 2 ng/m3
<b>DECA-BDE</b>	0.00023	N.I.							
<b>TBBP-A</b>	0.0029	N.I.							

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