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FIRE GAS TOXICITY AND POLLUTANTS IN FIRES THE ROLE OF FLAME RETARDANTS

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ABSTRACT

Decomposition products from flame retardants like HBr, HCl, HCN and dioxins do not play a role in the acute toxicity of fire gases which is driven by carbon monoxide. Regarding the chronic toxicity of pollutants, in two well documented German fire catastrophes, the Lengerich and Dusseldorf airport fires, it was found that the cancer risk from polycyclic aromatic hydrocarbons is up to 500 times higher than that of polyhalogenated dioxins and furans. As both pollutants are strongly bound to soot and therefore of low bioavailability, no chronic toxicity effects were reported from the general population or people professionally involved in fires. The hazard from dioxins and furans in fires is highly overestimated. The chronic toxicity of polybrominated dioxins and furans from the flame retardants involved in these two fires is negligible.

INTRODUCTION

In virtually all applications for building, electrical engineering, electronics and transportation, plastics have to meet fire safety requirements. The most economic way to achieve a high level of fire safety in combustible products is the use of flame retardant systems. They ensure that ignition sources of low intensity like a match or of higher intensity like a burning waste paper basket will either prevent ignition, or if ignition has eventually occurred, that flame propagation will be substantially reduced allowing people involved in a fire to escape. Thus, flame retardants help to save lives and property.

However, particularly halogenated flame retardants have come under suspicion to be harmful to people involved in fires and to contaminate the fire site and its surroundings by the release of toxic gases and pollutants. In order to find out whether these allegations are founded, firstly, the role of acutely toxic components in fire gases and secondly, pollutants formed in fires will be discussed.

ACUTE TOXICITY OF FIRE GASES

All gases formed in a fire are deadly toxic irrespective of the products burning. The acute toxicity of fire gases is controlled by carbon monoxide (CO), a highly toxic, non irritating gas, present in significant amounts in virtually all fires and responsible for over 90% of fire deaths. Its concentration in fires depends on many factors, particularly the availability of oxygen. CO concentrations measured in real fires can reach up to 7.500 ppm. In simulated furniture fires under smouldering conditions, CO concentrations of up to 200.000 ppm were measured.

Other components of acute toxicity found in real fires play a secondary role: hydrogen cyanide was measured at levels between 5 and 75 ppm and for irritants like hydrogen chloride 1 – 280 ppm and acrolein 0.3 – 15 ppm were found [1]. The acute toxicity of some fire gas components is summarised in Table 1 [2].

1. Acute toxicity of pure gases

Substance	Lethal concentration [ppm] within 5 min	10 min	30 min
CO	12,500	7,600	4,600
HCN	570	290	110
HCl	12,000 – 16,000	10,000	2,000 – 4,000
Acrolein	500 – 1,000	150 - 690	50 – 135
CO_2	100,000	-	90,000

The deadly role of carbon monoxide in fires was demonstrated again in the Dusseldorf Airport Fire catastrophe, where all fire victims died of CO intoxication [3].

There is no contribution of polyhalogenated dibenzodioxins and –furans (PHDDs/PHDFs) to the acute toxicity of fire gases because they are formed in extremely low quantities and immediately bound to the soot produced in the fire effluents.

There is no evidence that the generation of decomposition products from flame retardants like HCl or HBr, phosphorous compounds, hydrogen cyanide or ammonia has a major influence on the acute toxicity of fire gases.

POLLUTANTS IN FIRES

The most important pollutants generated in fires are the polycyclic aromatic hydrocarbons (PAHs) and the PHDDs/PHDFs. While the PAHs may be produced by the combustion of all natural and synthetic carbon-based materials, PHDDs/PHDFs can only be formed if inorganic or organic halogenated compounds are available.

Polycyclic aromatic hydrocarbons

PAHs are generated in all fires, particularly under pyrolysis and smouldering conditions. This group of several hundred substances contains many carcinogenic compounds. The compound with the highest carcinogenic activity is benzo[a]pyrene (BaP) which has been attributed the toxicity equivalent of 1. The other most important carcinogens and their toxicity factors ranging from 0.1 to 0.001 are summarised in Table 2 [4]. In addition, the US Environmental Protection Agency EPA covers two more compounds, naphthalene and benz(a)anthracene. These 16 PAHs are referred to when PAH toxicity factors are calculated according to EPA.

PAHs are found in high amounts up to the percent range in the soot after fires. The percentage of Benzo(a)pyrene in PAHs is around 5 %. The reason for the generation of high PAH amounts is that they are precursors which form soot by condensation or agglomeration; One part of the PAHs remains unreacted and is strongly bound onto the soot particles [5].

2. Toxicity equivalence factors of PAHs

Substance	Abbreviation	Toxicity equivalence factor
Benzo(a)pyrene	BaP	1
Dibenzo(ah)anthracene	DahA	1
Benzo(j+b)fluoranthene	BjbF	0.1
Benzo(k)fluoranthene	BkF	0.1
Indeno(1.2.3-cd)pyrene	IND	0.1
Anthracene	Ant	0.001
Chrysene	Chr	0.001
Benzo(ghi)perylene	BgP	0.001
Acenaphthylene	Aceny	0.001
Acenaphthene	Ace	0.001
Fluorene	Flu	0.001
Phenanthrene	Phen	0.001
Fluoranthene	Fluor	0.001
Pyrene	Pyr	0.001

Polyhalogenated dibenzodioxins and furans

The generally used term "dioxin" in reality refers to a group of chemicals with 210 compounds composed of polychlorinated and polybrominated dibenzodioxins (PCDDs and PBDDs with 75 species each) and dibenzofurans (PCDFs and PBDFs with 135 species each). All 17 dioxins and furans with chlorine or bromine atoms substituted in 2,3,7,8 position are toxic. The most toxic substance is 2,3,7,8-tetrachlorodibenzodioxin (TCDD), the so-called Seveso poison, with the toxicity factor 1. The other 2,3,7,8-PCDD/PCDFs are less toxic by factors varying between 0.5 and 0.001. In order to determine the toxic potential of these substances Toxic Equivalents (TE) were introduced. The concentration of each congener is multiplied by the respective TE and all congeners found are summed up. The result is 2,3,7,8-TCDD Toxic Equivalents. They are internationally used to assess the toxic potential of the "dioxins" analytically found and the basis for limit values set by the authorities.

No toxicity equivalents for 2,3,7,8-PBDD/Fs have been internationally introduced so far. In Germany, however, eight 2,3,7,8-PBDD/PBDFs were regulated in the German Dangerous Goods Exception Ordinance for the "transportation of solutions and mixtures with polyhalogenated dibenzodioxins and –furans". For practical reasons, the corresponding PCDD/Fs equivalence factors were taken over.
The toxicity equivalence factors are summarised in Table 3.

3. Toxicity equivalence factors for polyhalogenated dibenzodioxins and -furans

Substance	Toxicity equivalence factor (TE)
Polychlorinated dibenzodioxins and –furans (PCDD and PCDF)	
2,3,7,8-Tetra-CDD	1
1,2,3,7,8-Penta-CDD	0.5
1,2,3,4,7,8-Hexa-CDD	0.1
1,2,3,7,8,9-Hexa-CDD	0.1
1,2,3,6,7,8-Hexa-CDD	0.1
1,2,3,4,6,7,8-Hepta-CDD	0.01
1,2,3,4,6,7,8,9-Octa-CDD	0.001
2,3,7,8-Tetra-CDF	0.1
2,3,4,7,8-Penta-CDF	0.5
1,2,3,7,8-Penta-CDF	0.05
1,2,3,4,7,8-Hexa-CDF	0.1
1,2,3,7,8,9-Hexa-CDF	0.1
1,2,3,6,7,8-Hexa-CDF	0.1
2,3,4,6,7,8-Hexa-CDF	0.1
1,2,3,4,6,7,8-Hepta-CDF	0.01
1,2,3,4,7,8,9-Hepta-CDF	0.01
1,2,3,4,6,7,8,9-Octa-CDF	0.001
Polybrominated dibenzodioxins and –furans (PBDD and PBDF)	
2,3,7,8-Tetra-BDD	1
1,2,3,7,8-Penta-BDD	0.5
1,2,3,4,7,8-Hexa-BDD	0.1
1,2,3,7,8,9-Hexa-BDD	0.1
1,2,3,6,7,8-Hexa-BDD	0.1
2,3,7,8-Tetra-BDF	0.1
2,3,4,7,8-Penta-BDF	0.5
1,2,3,7,8-Penta-BDF	0.05

Risk comparison of different pollutants

A possibility to compare different pollutants is given by the "Unit Risk" model [6,7]. For some carcinogenic substances "Unit Risk Factors" have been derived from epidemiological studies. These data show how many people, when exposed to the same quantity of the substances (inhalation of 1 µg pollutant per m³ of air) over their lifetime, would contract cancer. The Unit-Risk Factors for some carcinogenic air pollutants are summarised in Table 4.

4. Unit-Risk Factors for selected carcinogenic air pollutants

Pollutant	Unit-Risk-Factor $[1/(\mu g/m^3)]$
Arsenic	$4 \cdot 10^{-3}$
Asbestos	$2 \cdot 10^{-5}$
Benzene	$9 \cdot 10^{-6}$
Cadmium	$1.2 \cdot 10^{-2}$
Diesel soot particles	$7 \cdot 10^{-5}$
Benzo(a)pyrene (BaP)	$7 \cdot 10^{-2}$
2,3,7,8-TCDD	1.4

When comparing 2,3,7,8-TCDD (1.4) to BaP (0.07), it comes out that 2,3,7,8-TCDD is 20 times more carcinogenic than the latter. The Unit-Risk-Factor is multiplied by the actual measured concentration of the relevant substance to obtain the lifetime risk from carcinogenic pollutants in the air. The results showed that the risk from BaP is 10,000 times higher than from 2,3,7,8-TCDD. If a comparison between all carcinogenic PAHs and PCDD/Fs is made, factors of 2,000 and more remain. Therefore, compared to PAHs, the impact of dioxins on our health can be neglected in this field.

THE IMPACT OF POLLUTANTS AND THE ROLE OF BROMINATED FLAME RETARDANTS IN TWO MAJOR FIRES IN GERMANY

The role of pollutants like PAHs and particularly PHDD/Fs formed in fires has been controversially discussed in recent years, particularly in Germany after catastrophic fires like the Lengerich fire in 1992 and the Dusseldorf Airport fire in 1996. These two fires were extensively investigated and comprehensive reports published [3,8]. The reports not only contain a series of analytical results for PCDD/Fs, but for PBDD/Fs and PAHs which for the first time helped to better assess the relevance of all these pollutants to humans and the environment.

In the Lengerich fire, more than 500 tons of PVC and a major amount of plastics containing brominated flame retardants burnt. Measurements made in the fire gases showed that around 5 mg toxic equivalents (TE) per m^3 were found for PCDD/Fs. The values for PBDD/Fs were about 60 times lower and therefore, no further measurements were made for this group of substances. ThePCDD/F levels found in soot in rooms and outside in the vicinity of the fire source (0.5 – 5.6 ng 2,3,7,8-TCDD TE/m^2) were much lower than initially expected and lay under the sanitation value of 10 ng 2,3,7,8-TCDD TE/m^2. The corresponding PAH values lay in the range of 240 – 2800 ng TE/m^2 and under the sanitation value of 10,000 ng TE/m^2. Table 5 shows the measured concentrations of the 2,37,8-TCDDs and PAHs, their respective cancer risk and the PAH/TCDD cancer risk relation. The outcome is that the PAHs have an up to 500 times higher cancer risk than the TCDD/Fs.

5. Cancer risk of soot in the Lengerich fire

Samples pollutants No.	Toxic equivalents (TE) [ng/m²]	Cancer risk (Unit-Risk-Factor · TE)	Cancer risk factor PAHs/PCDD/Fs
1 PAHs	2,800	196	25
PCDD/Fs	5.6	7.84	
2 PAHs	4,600	322	575
PCDD/Fs	0.4	0.56	
3 PAHs	740	51.8	264
PCDD/Fs	0.14	0.196	
4 PAHs	230	16.1	115
PCDD/Fs	0.1	0.14	
5 PAHs	240	16.8	24
PCDD/Fs	0.5	0.7	

In the 1996 Dusseldorf airport fire, around 24 tons of combustible products were involved in the fire (Table 6). PCBs from old fluorescent tubes transformers and PVC were the primary source of PCDD/Fs. In addition, lower amounts of PBDD/Fs from brominated flame retardants were detected.

6. Combustible materials involved in the Dusseldorf airport fire

Material	Weight [kg]	Weight [%]
Polystyrene	11,400	47
Polystyrene adhesive	780	3
PVC cables	5,900	24
Conveyor belts	1,200	5
Baggage, furniture, other	5,000	21
Total	24,280	100

The concentrations of PCDD/F, PBDD/F and PAH found in various soot samples and the reference values are summarised in Table 7.

7. Dusseldorf airport fire. Concentrations of PCDD/F and PAH measured in various soot samples and German limit values

Compound	Unit	Measured value	Limit value
PHDD/PHDFs			
PCDD/Fs Toxic equivalents ITE	µg/kg	43	
PCDD/Fs + PBDD/Fs Sum of 25 congeners	µg/kg	377	100
PCDD/Fs Sum of 17 congeners	µg/kg	376	100
PBDD/Fs Sum of 8 congeners	µg/kg	1.1	5
PAHs (16 PAHs according to EPA)			
PAHs	µg/kg	5,000,000	
BaP	µg/kg	260,000	50
PAHs Toxic equivalents	µg/kg	468,000	

The concentrations of the 2,37,8-TCDDs and PAHs in toxic equivalents, the respective cancer risk and the PAH/TCDD cancer risk relation show again that the PAHs have an up to 500 times higher cancer risk than the TCDD/Fs.

The amounts of PBDD/Fs generated from brominated flame retardants in the soot samples tested are negligible. This indicates that brominated flame retardants contained in polymers involved in fires do not contribute to environmental pollution or health risks.

No chronic toxicity effects from dioxins or other soot-bound pollutants like polycyclic aromatic hydrocarbons (PAHs) were reported to date from persons accidentally involved in a fire (generally one exposure). For professional fire fighters and persons carrying out sanitation measures after a fire and involved in the disposal of fire residues, no chronic toxicity effects were reported either. This is consistent with a German study which showed that professional fire fighters have no higher dioxin blood levels than the dioxin background levels of the general population [9].

CONCLUSIONS

Decomposition products from flame retardants like HBr, HCl and HCN do not play a role in the acute toxicity of fire gases which is driven by carbon monoxide. This is also true for the formation of dioxins and furans.

PAHs are found in high amounts in all fires and contain strong carcinogens. Polyhalogenated dibenzodioxins and –furans are generated from organic or inorganic compounds in fires at usually 3 orders of magnitude lower amounts.

The impact of PAHs and PHDD/Fs in two major fires in Germany (Lengerich and Dusseldorf airport fires) showed that the cancer risk from PHDD/Fs is substantially lower than that of the PAHs.

Both pollutants are strongly bound to soot and they are of low bioavailability. This explains why no chronic toxicity effects from these pollutants were reported to date, not only from people accidentally exposed to fire gases with one exposure, but from frequently exposed professionals like fire fighters and sanitation personnel.

The findings of these two fires indicate that the chronic toxicity potential from dioxins and furans is highly overestimated and that the contribution of polybrominated dioxins and furans released from the flame retarded plastics is negligible.

REFERENCE LIST

[1] K Buff. Procedure Development for the Assessment of Health Consequences from Large Fires. Report Prepared by the Institute of Toxicology of the Technical University of Munich for a Research Project Commissioned by the German Federal Civil Protection Agency, October 1996. (in German).

[2] HR Sasse, Hj Einbrodt, FH Prager, Development of a Safety Concept for Assessment of the Toxicity of Combustion Products, J Fire Sci. (1988), P. 42-60.

[3] Independent Experts Commission for the Minister President of the State of North Rhine Westphalia for Investigating the Consequences from the Dusseldorf Airport Fire. Report - Part I. Analysis of the 11 April 1996 Fire. Recommendations and Consequences for the Dusseldorf Airport. 14 April 1997.

[4] C Nisbeth, P LaGoy, Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). Reg. Toxicol. Pharmacol. (1992), P. 290-300.

[5] M Pasternak, BT Zinn, RF Browner, The Role of PAHs in the Formation of Smoke Particulates During the Combustion of Polymeric Materials. 18th Symposium on Combustion, The Combustion Institute (1981), P. 91-99.

[6] German Federal Committee for Emission Control, Cancer Risk Due to Air Pollution, 1991 (Volumes I and II Published by the Ministry for the Environment, Planning and Agriculture of the State of North Rhine Westphalia, 1993) (In German).

[7] EJ Spindler, Soot from Fires – A Risk Assessment. Chemische Technik 49(1997)4, P. 193-196 (In German).

[8] Major Fire in a Plastics Warehouse in Lengerich, October 1992 - Documentation. Published by the Ministry for the Environment and the Ministry of the Interior of the State of North Rhine Westphalia and the town of Lengerich. June 1994. (In German).

[9] Environmental Medical Studies on Fire Fighters. Ruhr-University Bochum and Heinrich-Heine University Dusseldorf on Behalf of the Ministry of Labour, Health and Social Affairs of the State of North Rhine Westphalia. October 1992. (In German).