Fire Retardants and their Potential Impact on Fire Fighter Health
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Toxic Hazards to Fire Fighters, Including Effects of Fire Retardants, During Fires and Post-Fire Investigation Activities

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Issues

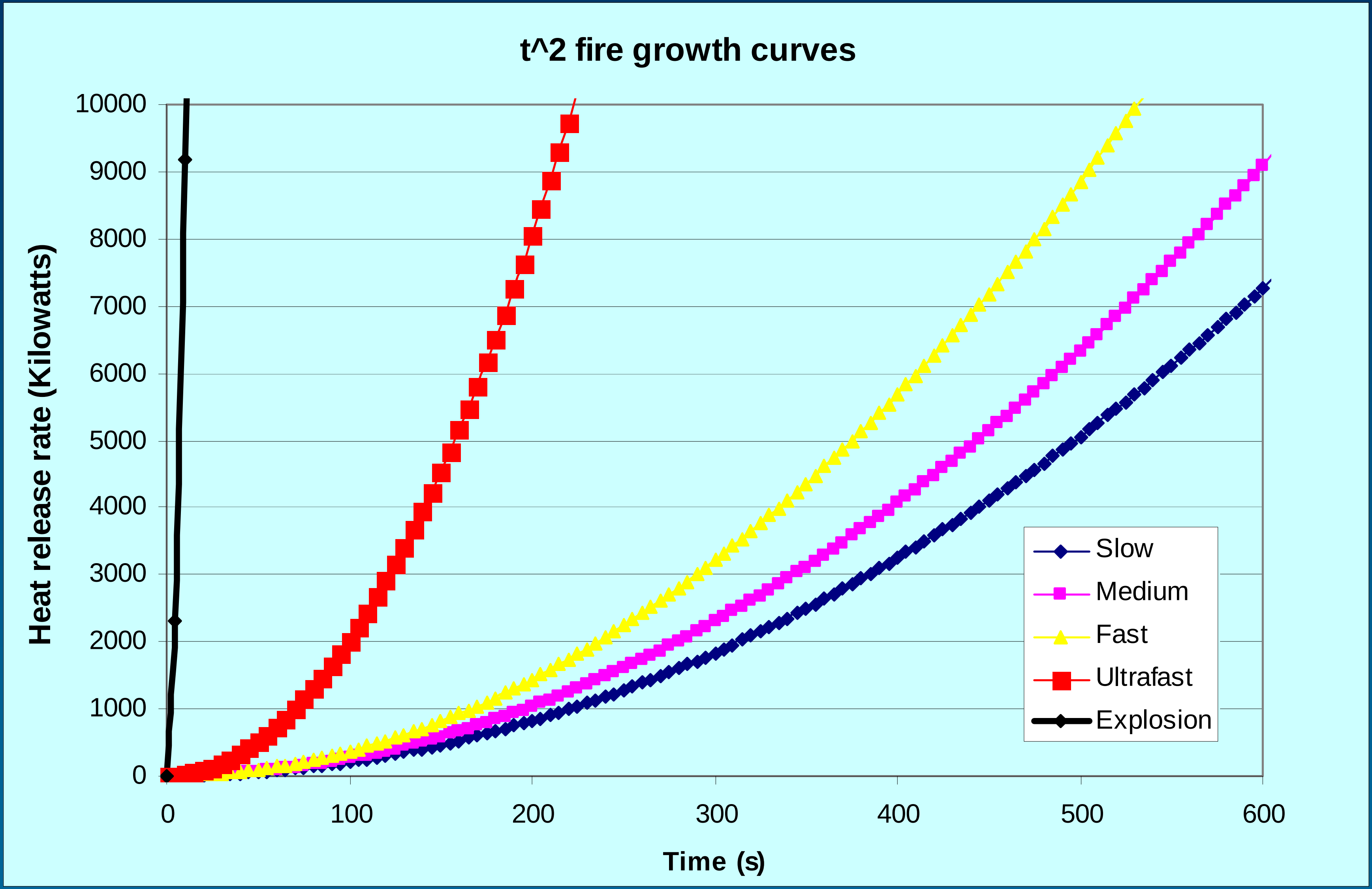
- What are potential health hazards to fire fighters from exposure to toxic fire effluents?
- What features of burning materials and fire conditions give rise to these hazards?
- What effect do fire retardants have on toxic fire hazards?

Role of fire retardant treatments

Benefits of fire retardant treatments:

1. **Reduce probability that a heat or ignition source will initiate a growing spreading fire**
    - Reduce initial ignition probability
    - If ignition does occur may result in self-extinction/failure of propagation
    - Thereby essentially eliminate the toxic and environmental hazards from fires prevented
2. **If the initial ignition resistance is overcome may reduce the rate of fire growth**
    - May result in a period of very slow growth up to a critical fire size
    - Or may provide a slower t^2 fire growth curve
    - In such cases may reduce the rate of toxic hazard development and increase the time available for escape or fire fighting

BS7974 fire growth rate curves



BS7974 fire growth rate curves

CBUF
chairs

Limitations of fire retardant treatments

- Do not provide non-combustibility, but ignition resistance to a heat source up to a design limit. If this limit is exceeded a rapidly spreading fire may occur
- During a fire (depending upon the FR system used) may increase yields of common toxic fire gases such as carbon monoxide and hydrogen cyanide, and introduce additional toxic products such as acid gases.
- Fires may release corrosive or toxic environmental contaminants (such as to a building interior or to the wider exterior environment).
- Toxic fire retardant compounds may leach out from products in general use or be released during disposal leading to environmental contamination.

Issues arising from toxic environmental contamination by combustion products

Challenge:

- ensure that the societal benefits in terms of reduced fire risk, and reduced fire hazards in some situations, are not offset by increased toxic fire hazards in other situations and by unacceptable environmental contamination, either as a result of release during the product life-cycle or during fires.
- In order to achieve this it is important that small and large-scale fire tests and methods of toxic hazard analysis are capable of providing realistic assessments of full-scale fire hazards.

Key toxic products in fires

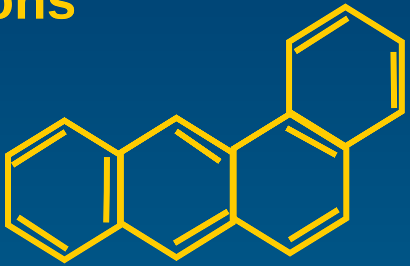
- Products threatening survival during and immediately after a fire:
  - Asphyxiant gases: CO, HCN, CO_2, low oxygen
  - Irritants: acid gases – HCl, HBr, HF, COF_2, H_3PO_4, SO_2, NOx
    organic irritants - acrolein, formaldehyde, crotonaldehyde, phenol, styrene
  - Particulates (especially ultrafine particles)
- Products causing environmental contamination, with long term health implications for repeated exposure during fire fighting or post-fire investigation
  - Benzene, isocyanates, PCBs, PAHs, doxins and furans, aldehydes
  - Inhalable fibres: asbestos, ceramic, mineral, carbon fibre
  - Particulates, metals

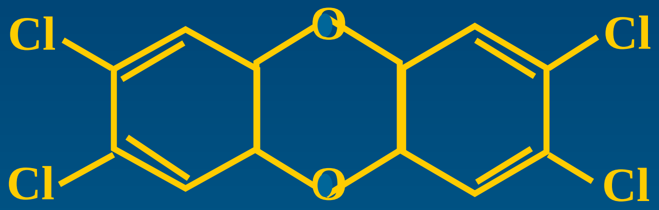
Toxic and carcinogenic compounds in fire residues and soot

Dioxins

Polyaromatic hydrocarbons

Dibenzofurans





2,3,7,8, Tetrachlorodibenzodioxin

Benz[a]anthrene

Benzene

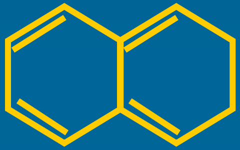
Metals Pb Cd etc

Benzo[a]pyrene

Isocyanates

acids

Polychlorinated biphenyls



Formaldehyde

Toxic smoke products

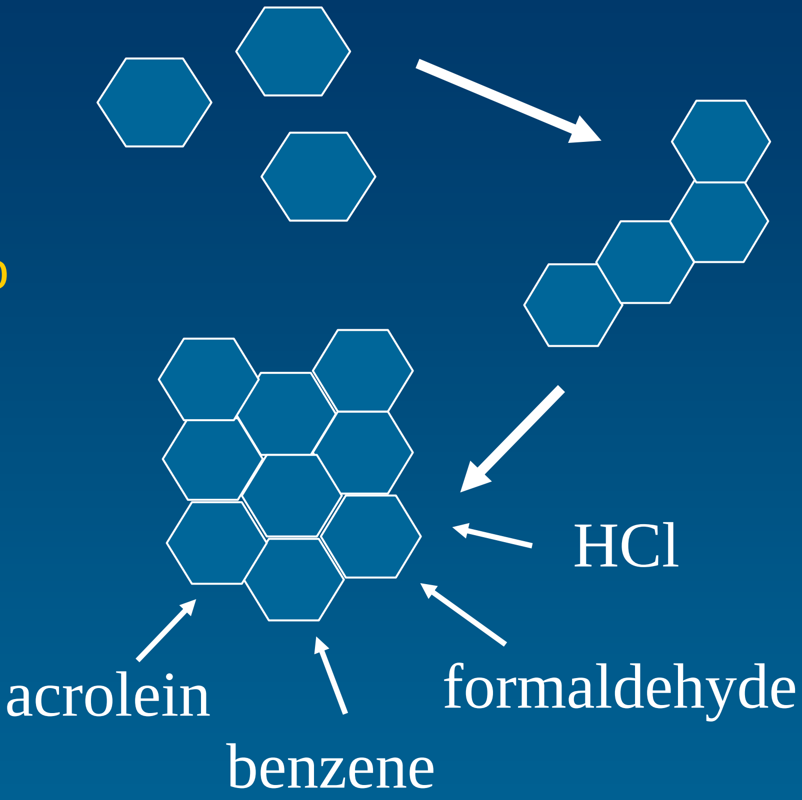
Particles:

Carbonaceous soot particles:

Organic hydrocarbon fragments undergo ring cyclization, forming aromatic ring compounds which coalesce into progressively larger molecular graphite-like plates by removal of hydrogen

Volatile toxic species including acids, organic irritants and carcinogens condense on the particles

The particles if inhaled provide a delivery system for deep lung penetration of "packets" of concentrated toxins



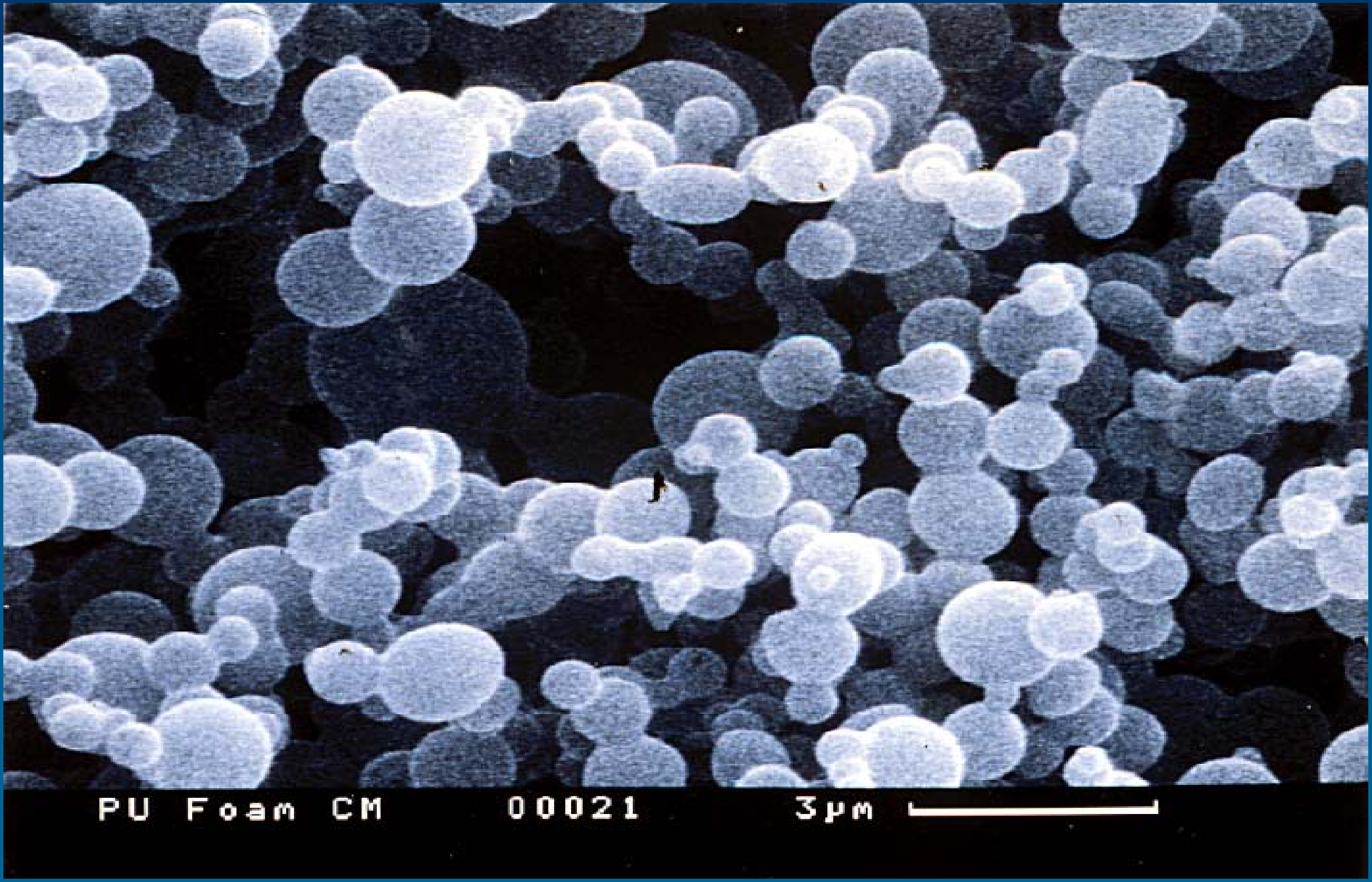
HCl

acrolein

benzene

formaldehyde

SMOKE PARTICLES



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Potential hazards to fire fighter health

Can consider three fire zones:

- Zone 1: Inside fire compartment – Exposure to effluent fire plume lethal within minutes (due to asphyxiant and irritant gases) – But Fire Fighters normally wearing BA. Potential health hazard from environmental contamination during post fire investigation and clean-up.

  Example: FF wearing helmet and visor fighting outside vehicle fire: got too close so effluent got under visor: took one breath and felt weak at knees.

  Examples: Kings Cross Underground and Mont-Blanc tunnel: FFs enter unprotected to attempt rescue in extreme emergencies and did not survive

- Zone 2: Outside immediate fire compartment or building – Exposure to effluent plume with dilution factor of 50 - 100 times that inside fire (hazard from brief exposure to more concentrated "downwashed" smoke plumes) – Fire Fighters and other emergency personnel not wearing BA. – Potential significant health hazard, especially from repeated exposures

  Example non BA FFs exposed to downwashed plume outside caravan factory fire: after a few minutes felt faint and respiratory discomfort treated at A&E but subsequent flu-like and memory problems: invalided from service

  Example non BA FFs unwell after fighting open air fire at plastics tip – turned out to be due to food from mobile canteen

- Zone 3: Surrounding area of city exposed to downwind plume) – Potential minor health hazards to large exposed population from much more diluted plume

  Example: Spike in cardio-respiratory deaths in population during episodes of poor air quality with high PM 10 and PM2.5 particulates levels

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Potential hazards to fire fighter health

- Asphyxiant gases (carbon monoxide and hydrogen cyanide) are the main Zone 1 killers, but are relatively harmless at the 50-100 dilution levels in the smoke plume outside the immediate fire zone.
- Irritant gases and associated particulates are also lethal at Zone 1 concentrations, but still present significant health hazards at Zone 2 (and to some extent at Zone 3 concentrations). Irritant gases cause inflammation of eyes and respiratory tract (potential acute and chronic bronchitis, chronic obstructive lung diseases, such as fibrosis or emphysema, RADs (reactive airway disfunction syndrome)

  Example: New York telephone exchange fire: FFs died afterwards from bronchiolitis obliterans

- Other exposures toxic at Zone 2 concentrations or during post-fire investigation:
  - Sensitisers including formaldehyde and isocyanates leading to asthma

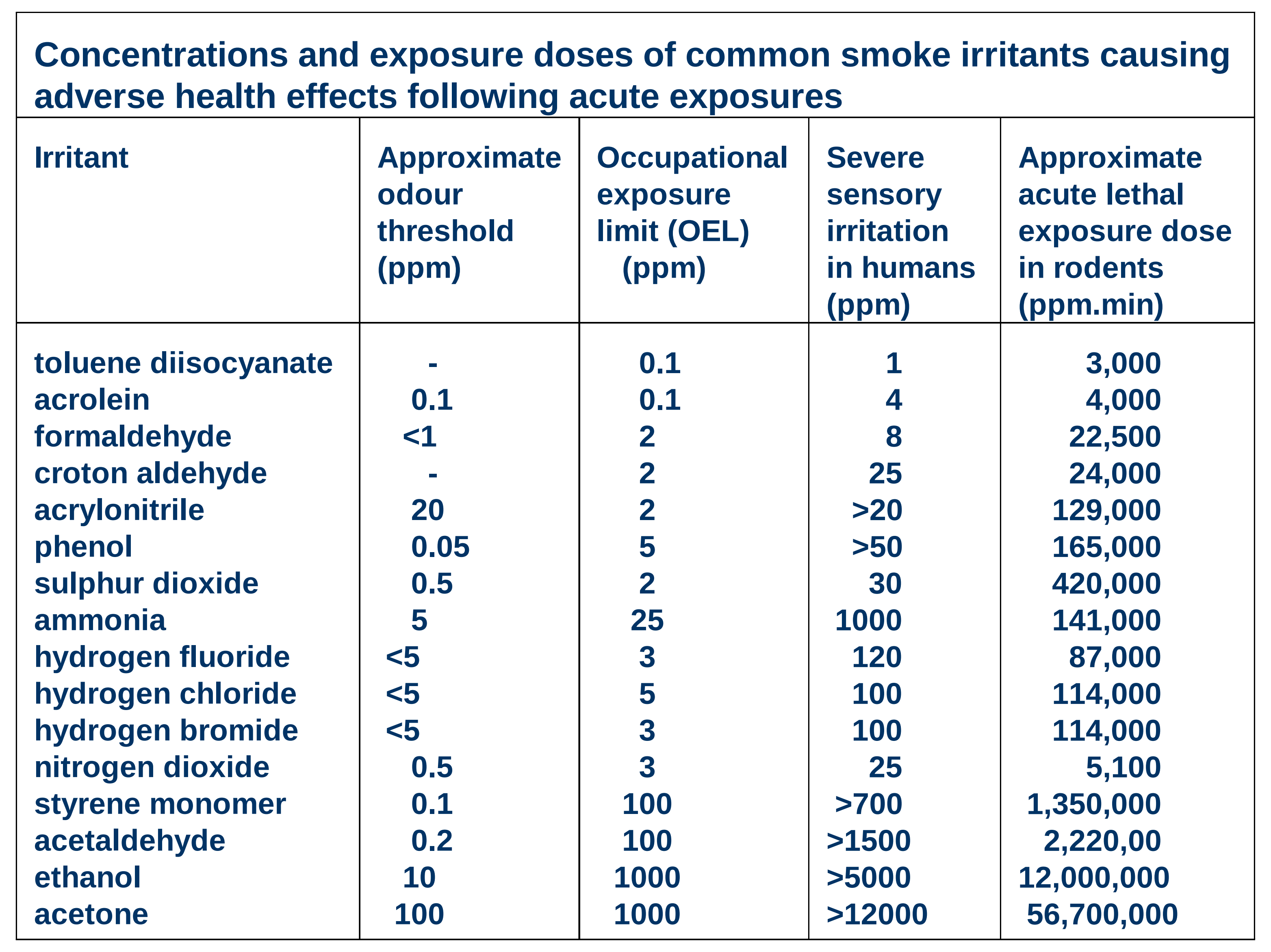
    Example: Barber in foyer of hotel fire exposed to smoke while escaping, subsequently developed asthma when went back to work in refurbished hotel

  - Organic carcinogens, PAHs dioxins, dibenzofurans, metals
  - Ceramic and asbestos fibres: lung fibrosis, pleural cancers
  - Ultrafine particulates and CO: risk of angina and heart attacks

    Hotel guest rescued by FF from smoke contaminated hotel room, next day angina and had to have bypass operation

    Basically similar to disease risk for cigarette smokers. UK FF health findings, FFs who smoke had lung and heart disease – non-smokers did not – but not followed after retirement

Ranges of toxic products and fire hazards in the vicinity of fires inside and outside buildings		
Toxic product	Low range near a small smouldering or flaming fire, or in a diluted plume outside	High range: in effluent plume from a well developed compartment fire
Carbon monoxide	100-200 ppm	4%
Carbon dioxide	0.2-0.5%	15%
Oxygen	20%	2%
Hydrogen cyanide	10-20 ppm	1500 ppm
Particulates, acid gases and organic irritants	10-20 ppm	2000 ppm
Smoke optical density	0.02-0.1	10
Temperature	Near ambient	1000°C



Concentrations and exposure doses of common smoke irritants causing adverse health effects following acute exposures

Irritant	Approximate odour threshold (ppm)	Occupational exposure limit (OEL) (ppm)	Severe sensory irritation in humans (ppm)	Approximate acute lethal exposure dose in rodents (ppm.min)
toluene diisocyanate	-	0.1	1	3,000
acrolein	0.1	0.1	4	4,000
formaldehyde	<1	2	8	22,500
croton aldehyde	-	2	25	24,000
acrylonitrile	20	2	>20	129,000
phenol	0.05	5	>50	165,000
sulphur dioxide	0.5	2	30	420,000
ammonia	5	25	1000	141,000
hydrogen fluoride	<5	3	120	87,000
hydrogen chloride	<5	5	100	114,000
hydrogen bromide	<5	3	100	114,000
nitrogen dioxide	0.5	3	25	5,100
styrene monomer	0.1	100	>700	1,350,000
acetaldehyde	0.2	100	>1500	2,220,00
ethanol	10	1000	>5000	12,000,000
acetone	100	1000	>12000	56,700,000

Zone 2 ~ 2-5 x OEL = difficult to tolerate risk to health

Zone 1 ~ 50- 100 x OEL incapacitating and acute lung damage

Toxic product yields in fires

Depend upon three major parameters:

1. **Elemental composition of material**
   - **Mass % C,H,O,N,P,Cl,Br,F,S,inert fillers (Fire Retardants)**
2. **Organic composition of material**
   - **Aliphatic or aromatic**
   - **Char forming or decomposing into gas phase**
   - **Detailed structure, isocyanates etc**
3. **Decomposition conditions in fire**
   - **Flaming/non-flaming, ventilation, temperature**

Toxic product yields from different fire retardant systems

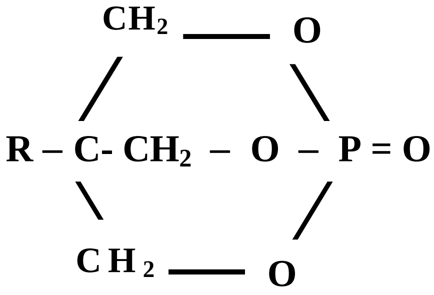
- With respect to toxic product yields the ideal fire retardant system acts in the solid phase and minimises the release of organic fuel vapours and acid gases.
- Systems that lead to reduced organic emissions relative to the parent polymer include:
  - Inert fillers
  - Alumina trihydrate systems
  - Char forming or layer forming systems locking up fuel carbon
    - Borax boric acid
    - Char forming nitrogen-phosphorus systems
  - Nano-clay systems
- Win-win situation: fewer smaller fires and less toxic products. But with nano-clays some concerns about potential release of highly toxic nanoparticles

Phosphorous-based systems

- Act partly as char formers in the solid and partly in the vapour phase depending upon the system.
- Char forming is beneficial with respect to toxic emissions but vapour phase systems tend to reduce combustion efficiency – increasing toxic product yields.
- The additives also release toxic compounds.
  - Nitrogen - HCN
  - Phosphorus – Mostly P_2O_5 - hydrolyses to H_2PO_4.
    - Phosphine PH_4 has been detected in some situations.
- One case of a neurotoxic organophosphorus product TMPP being released when any phosphorus additive is combined with a trimetholyol polyol (certain PU foams and hydraulic turbine lubricants)
- In other experiments with phosphate-retardant treated cotton, Kallonen obtained deaths in rats which cannot be explained in terms of normal toxic products.

Extreme neurotoxicity from phosphate fire retardant and foam

Toxicity of different bicyclophosphate esters



R :	CH_3	C_2H_5	C_3H_4	C_4H_9	$HOCH_2$
LD_{50} : (mg/kg i.p.)	32	1.0	0.38	1.5 0.18 ISO	>500

(Bellett and Caseda, 1975)

Trimethylol Propane Phosphate

Rat LC_{50} 0.035(mg/l) - 1 hour exposure

(From Kimmerle et al., 1976)

Phosphorous-based systems

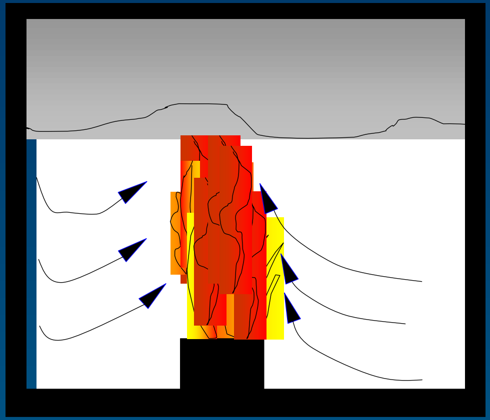
- In terms of toxic hazard it is important to consider the full-scale performance of a fire-retarded product, taking into account both the fire growth rate and the toxic product yields
- Data from full-scale tests on armchairs using different combinations of polyurethane foams (untreated and with melamine/chlorinated phosphate foam) combined with different covers (non-FR acrylic and back-coated brominated acrylic or FR-cotton).
- These show how calculated time to incapacitation for a room occupant varied with chair type.
- The results showed that when an FR-treated cover was combined with an FR-treated foam, the calculated time to incapacitation was improved by approximately two minutes
- Although melamine PU-foams contain more nitrogen than regular foams there does not appear to be an increase in HCN yield – although all PU produces high HCN concentrations (not hazardous to BA fire fighters)

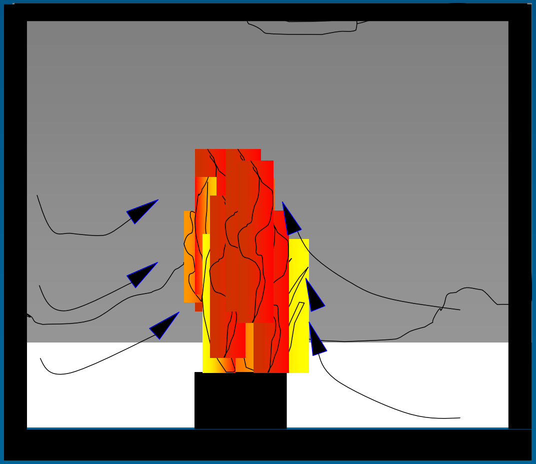
Halogen-based systems

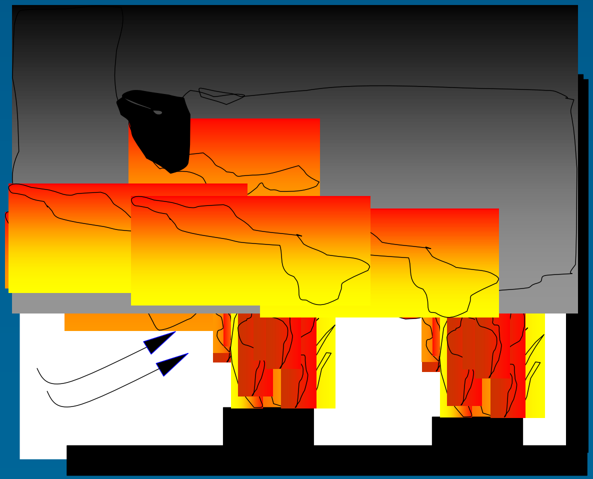
- For halogened materials and materials treated with halogen-based fire retardants (especially chlorine and bromine systems), inhibition of combustion in the vapour phase results in inefficient combustion with an increase in yields of toxic carbon and nitrogen compounds under all fire conditions.
- In addition irritant acid gases are released contributing to the toxicity
- These systems can provide an improved reaction to fire performance up to a certain fire or heat attack, but in some situations rapid fire growth can occur once this threshold is overcome

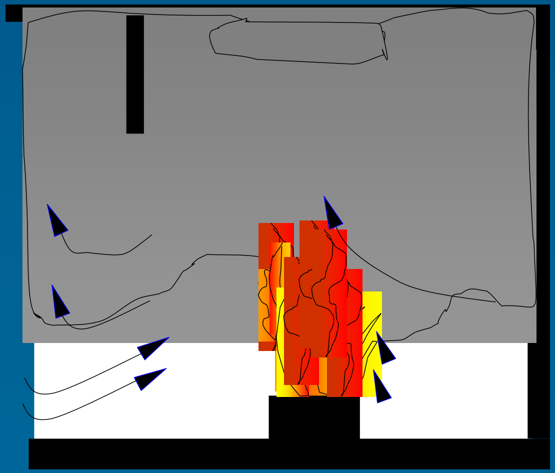
Main fires types and hazard scenarios

1. Non-flaming/smouldering fires
2. Early/well ventilated flaming fires
3. Ventilation controlled fires
    - pre-flashover vitiated flaming fires
    - post-flashover vitiated flaming fires









The Equivalence Ratio ϕ

$$\phi = \frac{Actual\ \ Fuel\,/\,Air\ Ratio}{Stoichiometric\ \ Fuel\,/\,Air\ Ratio}$$

For well-ventilated fires, ϕ < 1,

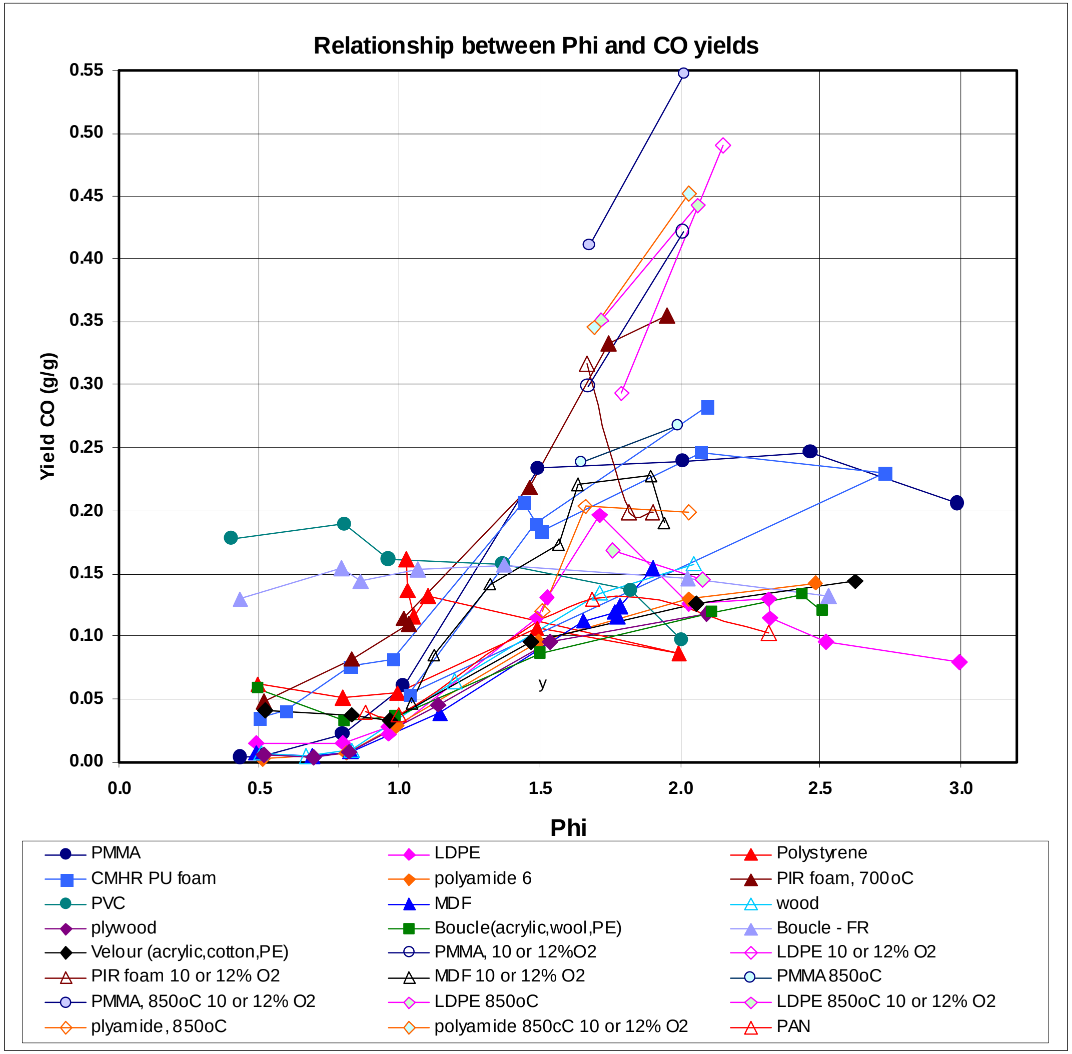
For fuel-rich (vitiated) combustion, ϕ > 1

Further factors affecting yields of CO and other products:

- Oxygen concentration
- Temperature
- Fire retardants

BS7990 – IS0/IEC TS19700 Tube Furnace

CO yields versus equivalence ratios – BRE tube furnace



- For materials leaving no residue phi was calculated from the stoichiometric oxygen demand of the whole material
- For char formers the char was considered as 100% carbon and unavailable as fuel for phi calculation
- Most materials have low CO yields (< 0.05 g/g mass loss) for phi <1 (unless heavily FR)
- Phi > 1 sigmoid with a plateau ~ phi = 1.75-2.0
- Materials fell into groups:
- High max yields up to 0.55 g/g : PMMA, Polyamide
- Low max yields up to 0.14 g/g : cellulosics
- Heavily halide FR materials (PVC, Boucle-FR) – almost constant yield across range
- Effects of oxygen: for a given phi lower CO yields in air than in 10-12% O_2/N_2 mixtures
- Effects of temperature: at 850ºC somewhat higher CO yields in some cases

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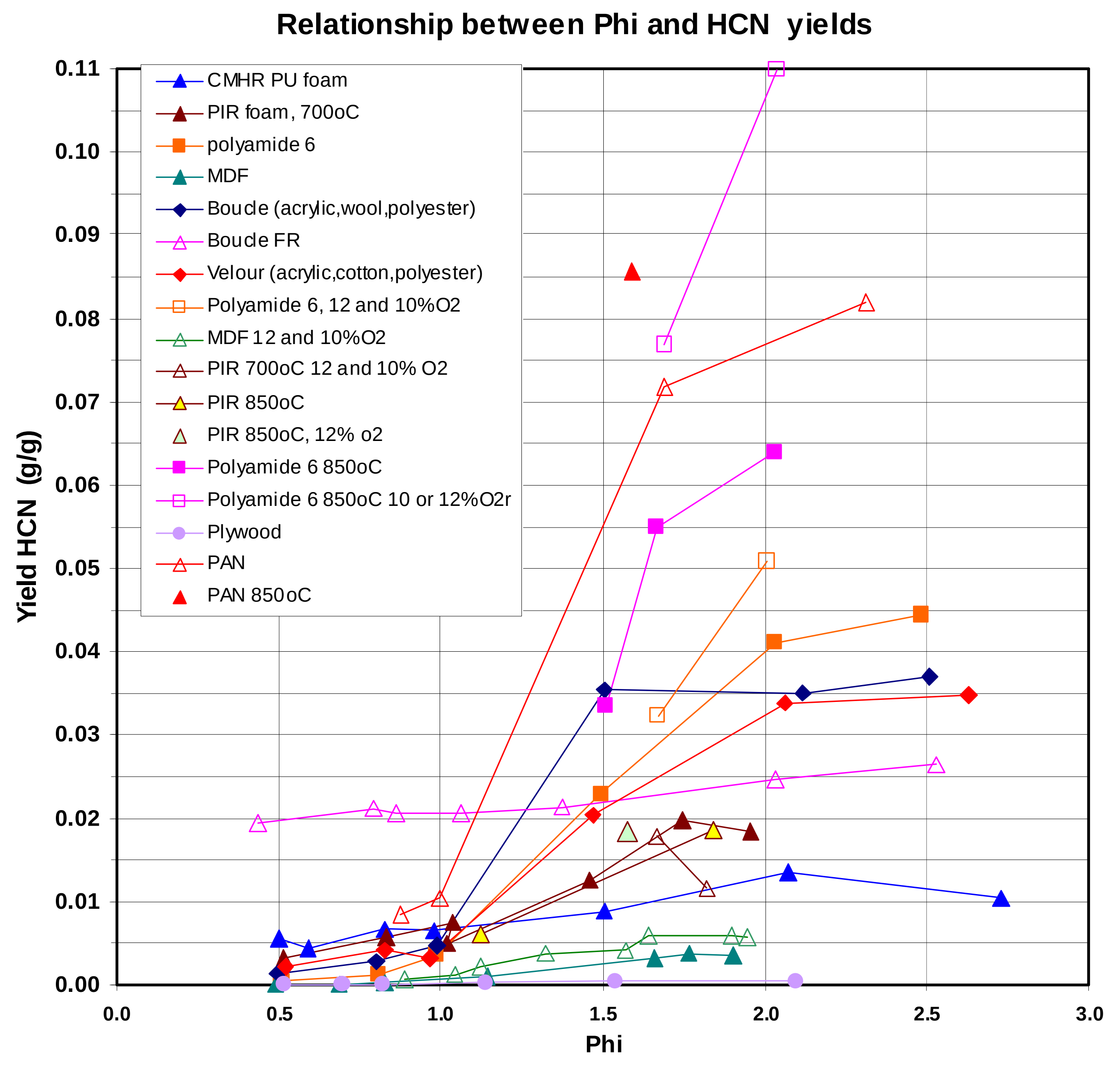
HCN yields versus equivalence ratios – BRE tube furnace



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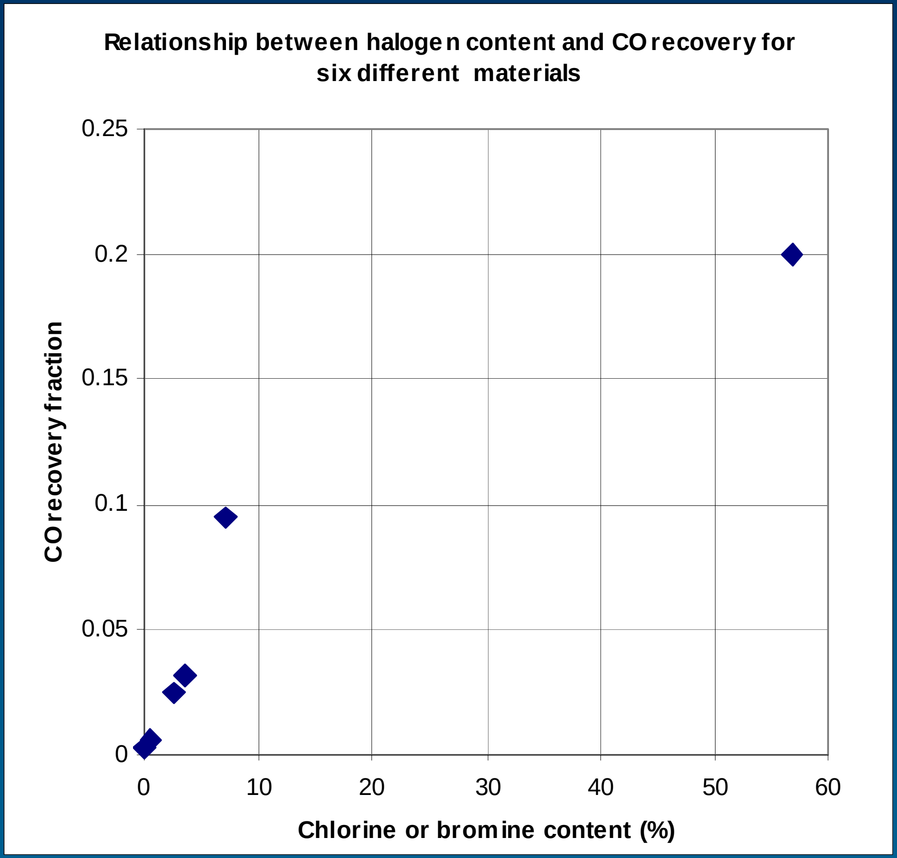
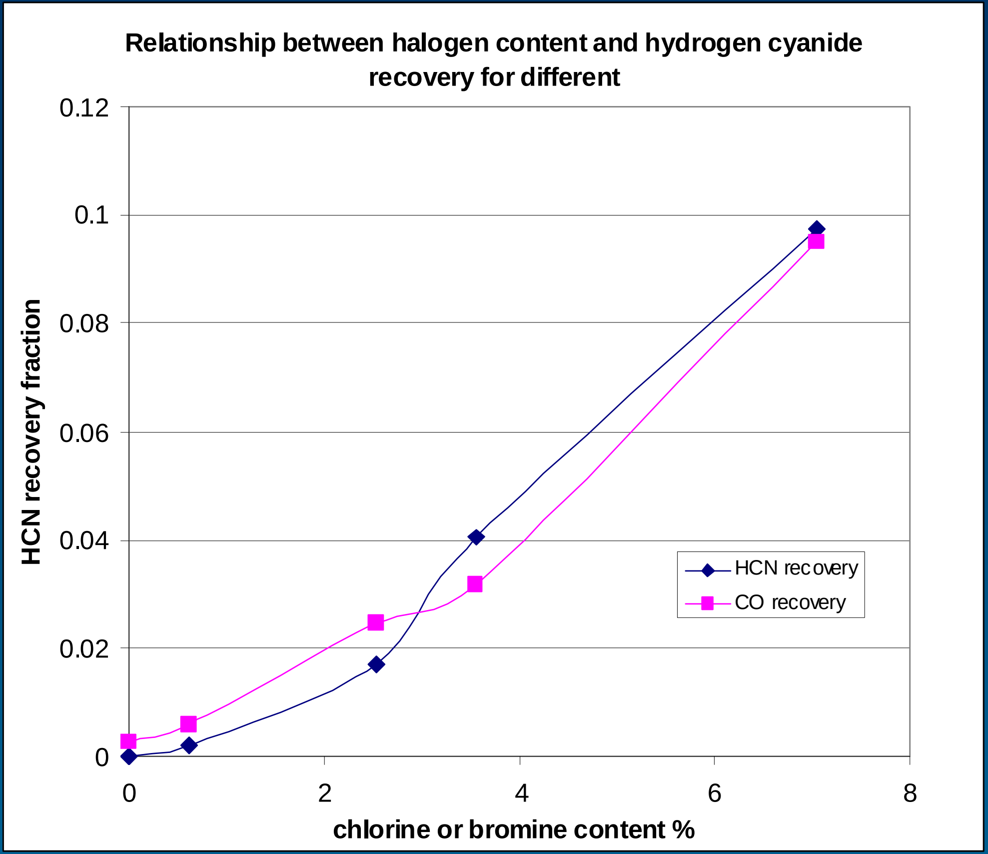
Effect of halogen content on CO yields under well-ventilated flaming conditions – BRE tube furnace





Relationship between halogen content and recoveries of hydrogen cyanide and carbon monoxide from a five different materials (PMMA, MDF, PU foam, PIR foam and Boucle FR fabric) under well-ventilated conditions (phi < 1)

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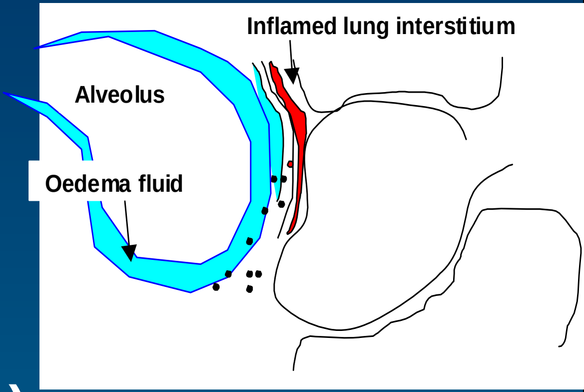
Fluoropolymers and ultrafine particles

- Fluoropolymers produce toxic acid gases COF_2, HF and perfluoroisobutylene all of which can contribute to fatal lung inflammation with a toxic potency around 10x that of most other materials
- Perfluorinated materials under certain conditions produce an ultrafine particulate which is a highly potent cause of fatal lung inflammation and (polymer fume fever).

Toxicity of thermal decomposition and combustion products of fluoropolymers



Polytetrafluroethylene (PTFE)

$$- (CF_2 - CF_2)_n -$$

Toxic potency: 0.015 - 14 g/m^3 (30- minute exposure)

Most fires: potency 10 x wood

Extreme toxicity conditions: 1000 x wood (e.g. 2 g in this room lethal to all occupants). Decomposition at 450-650ºC and recirculation through hot zone

Extreme toxicity due to ultrafine fluropolymer particles 0.01-0.15 µm

deposit in lung interstitium causing inflammation and oedema

Dioxins and furans

Table 2: Exposure limits and guidelines for dioxins and furans

Agency	Exposure limit / kg bodyweight / Day	Exposure limit / person / day (assuming 70 kg)
UK - COT	10 pg TEQ/kg/day TDI	700 pg TEQ/day TDI
WHO	1990: 10 pg TEQ/kg/day ADI	700 pg TEQ/day ADI
	now reduced to:	
	1-4 pg TEQ/kg/day TDI*	70 pg TEQ/day TDI ←
US - EPA	6.4 fg TCDD/kg/day TDI	4.5 pg TCDD/day TDI

*[13]Chemosphere 40, 1095 (May 2000)
Adapted from several sources

Dioxins and furans – sources of contamination from fires

- Asked by UK Home Office to assess health risk to fire fighters from dioxins
- As with other combustion products the yields of dioxins and furans are very dependent upon the combustion conditions in a fire. Work on the incinerator problem has shown that 300-400ºC is the optimum temperature for dioxin formation
- Doxins yields therefore depend on fire size and ventilation, as well as the nature of the fuel in terms of organohalogen compounds and total halogen content. Vitiated fires are likely to produce the highest yields and we have found high yields of halogenated benzenes and phenols (regarded as dioxin precursors) at under these conditions
- The EPA study showed very high yields of dioxins and furans from inefficiently burning fires involving the burning of household waste (4.5% PVC content) in a 55 gallon oil drum. In one experiment the total yields of PCDDs/FSDFs was 493 ng/g waste decomposed compared with 0.0035 ng/g waste decomposed in a modern incinerator a factor of more than 100,000.
- One household using this method could produce more dioxins than the entire output of a modern municipal waste incinerator.

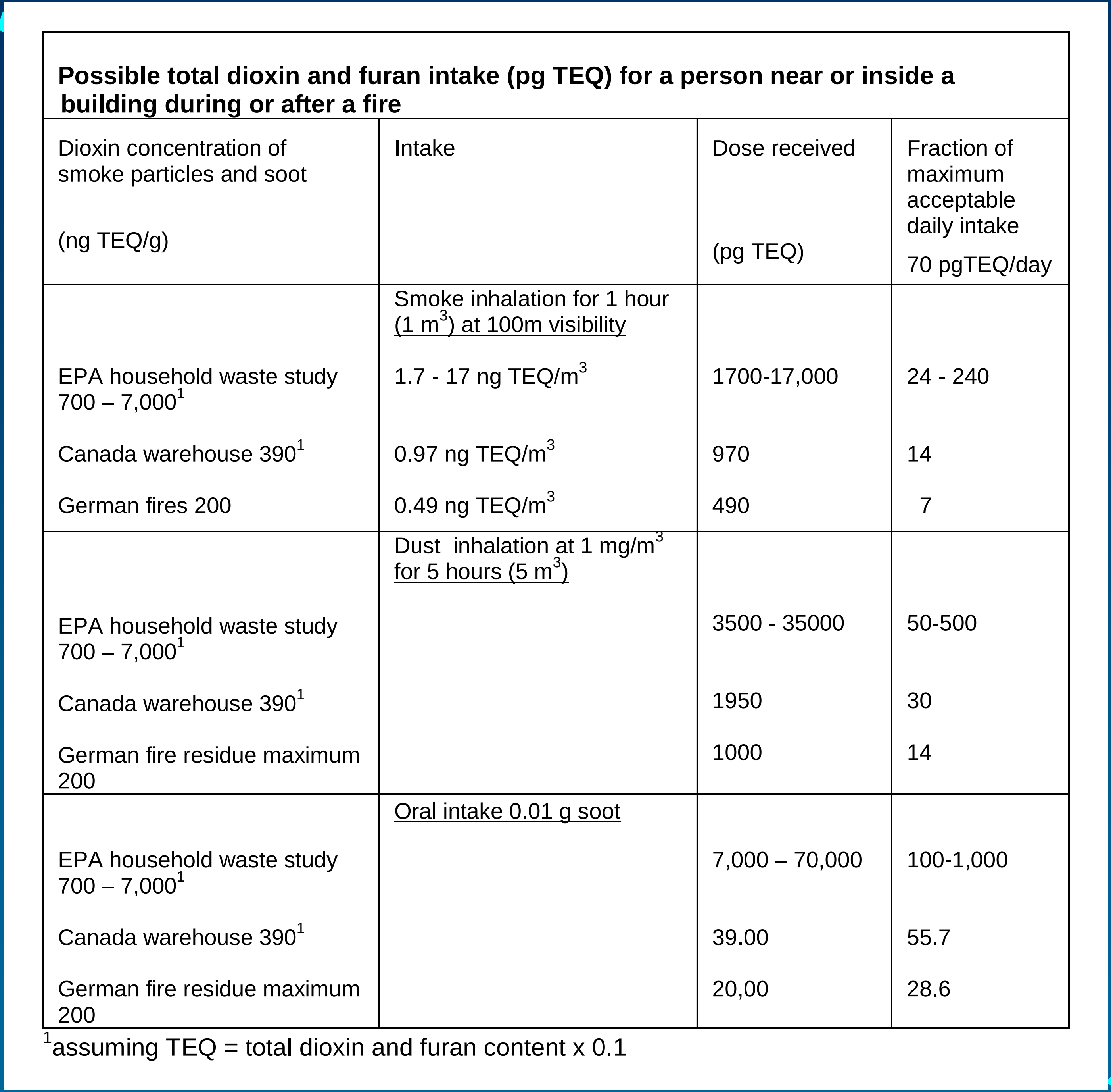
Dioxins and furans – human exposure from fires

- During and after a fire, human exposure could be via three routes:
    - Inhalation
    - Dermal absorption
    - Oral ingestion
- Concerns are concentrations in smoke effluent plumes and in soot deposits
- Soot samples from a number of fires: dioxins 5-400 ng TEQ/g soot
- Canada PVC warehouse fire up to 390 ng TEQ/g soot
- German fire survey up to 200 ng TEQ/g soot
- Dusseldorf airport (mainly from from polystyrene?) 43 ng TEQ/g soot

  EPA study 700-7000 ng TEQ/g soot

  with ~ 5-40 ng TEQ/m^3 in a dilute smoke plume (OD/m 0.01) in the vicinity of the oil barrel.

- Based on these figures it is possible to estimate hazards to a person working in the vicinity of a burning building and exposed to dilute smoke, or working inside the building after the fire and exposed to soot.



Possible total dioxin and furan intake (pg TEQ) for a person near or inside a building during or after a fire

Dioxin concentration of smoke particles and soot (ng TEQ/g)	Intake	Dose received (pg TEQ)	Fraction of maximum acceptable daily intake 70 pgTEQ/day
	Smoke inhalation for 1 hour (1 m^3) at 100m visibility		
EPA household waste study 700 – 7,000[1]	1.7 - 17 ng TEQ/m^3	1700-17,000	24 - 240
Canada warehouse 390[1]	0.97 ng TEQ/m^3	970	14
German fires 200	0.49 ng TEQ/m^3	490	7
	Dust inhalation at 1 mg/m^3 for 5 hours (5 m^3)		
EPA household waste study 700 – 7,000[1]		3500 - 35000	50-500
Canada warehouse 390[1]		1950	30
German fire residue maximum 200		1000	14
	Oral intake 0.01 g soot		
EPA household waste study 700 – 7,000[1]		7,000 – 70,000	100-1,000
Canada warehouse 390[1]		39.00	55.7
German fire residue maximum 200		20,00	28.6

[1] assuming TEQ = total dioxin and furan content x 0.1

Conclusions

- Any fire effluents present a significant potential health risk to fire fighters
- Main hazards are to non BA wearers from exposure to diluted effluents outside main fire and to environmental contamination during post-fire clean-up and investigation
- A range of toxic products and effects occur in fire effluent plumes
- The main group of fire retardants presenting a *potential* increased health risk over and above existing risks are the halogenated fire retardants
    - Unclear that significant added risk occurs
    - Potential health risks from increased exposure to lung inflammation
    - Potential health risks from increased exposure to dioxins and dibenzofurans during post-fire activities mainly via oral route
- Simple respiratory protection and hygiene precautions can significantly reduce potential health risk