Fire Toxicity of
Construction And Building Materials

Presented by:-

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Fire toxicity assessment

- The growing need to address the flammability of synthetic polymeric materials, as substitutes for natural-based materials, has led to an increase in the use of fire and flame retardant (FR) systems.

- Most of the recent research in development of fire safe materials is focussed on preventing ignition and fire growth, shifting the focus of the fire safety towards reducing peak heat release rates.

- It is important to understand the range of concentrations of chemical species likely to be present in any fire and can have a negative effect on the environment as well as posing a serious hazard to human health.

- Quantitative data on environmentally hazardous components of fire effluent cannot routinely be obtained from accidental fires, data is obtained from real-scale fire tests and simulations involving physical fire models.

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Issues – Regulatory Guidance

UK (England) Building Regulations 2015– Part B – Fire Safety.

B1. Mean

The bu … are …
approp … to a place of
safety … **ectively**
used a

PD 7974 Th … Fire Safety
Design of Bu … es **does**
provide so … **t people.**

FACTORS AFFECTING FIRE COMBUSTION AND TOXICITY

Harmful Effects

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FACTORS AFFECTING FIRE COMBUSTION AND TOXICITY

- Harmful Effects
- Fire Scenarios and Combustion Conditions

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FACTORS AFFECTING FIRE COMBUSTION AND TOXICITY

- Harmful Effects
  - Asphyxiants
  - Irritants
  - Smoke
  - Particulates
    PAH
    Dioxins
- Fire Scenarios and Combustion Conditions

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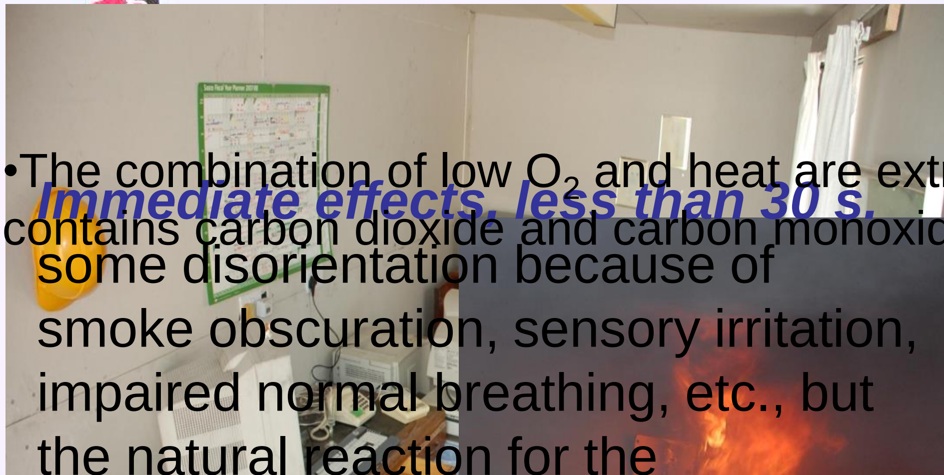
FACTORS AFFECTING FIRE COMBUSTION AND TOXICITY

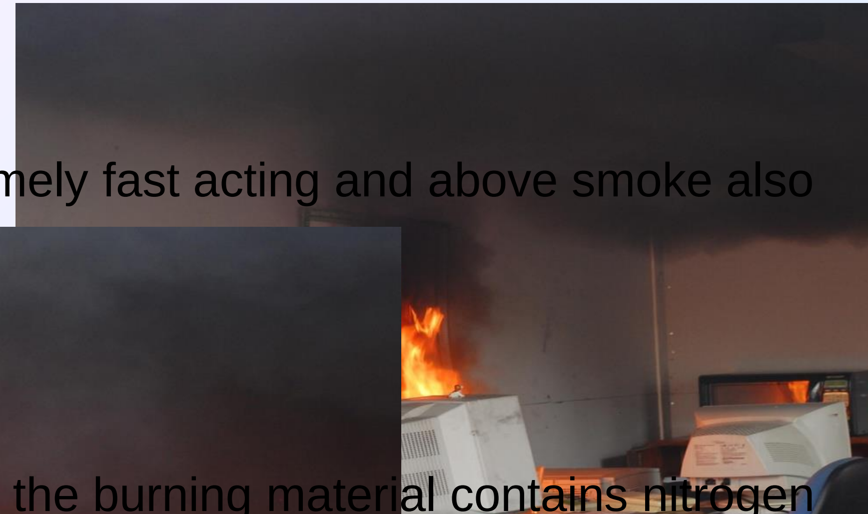
Harmful Effects

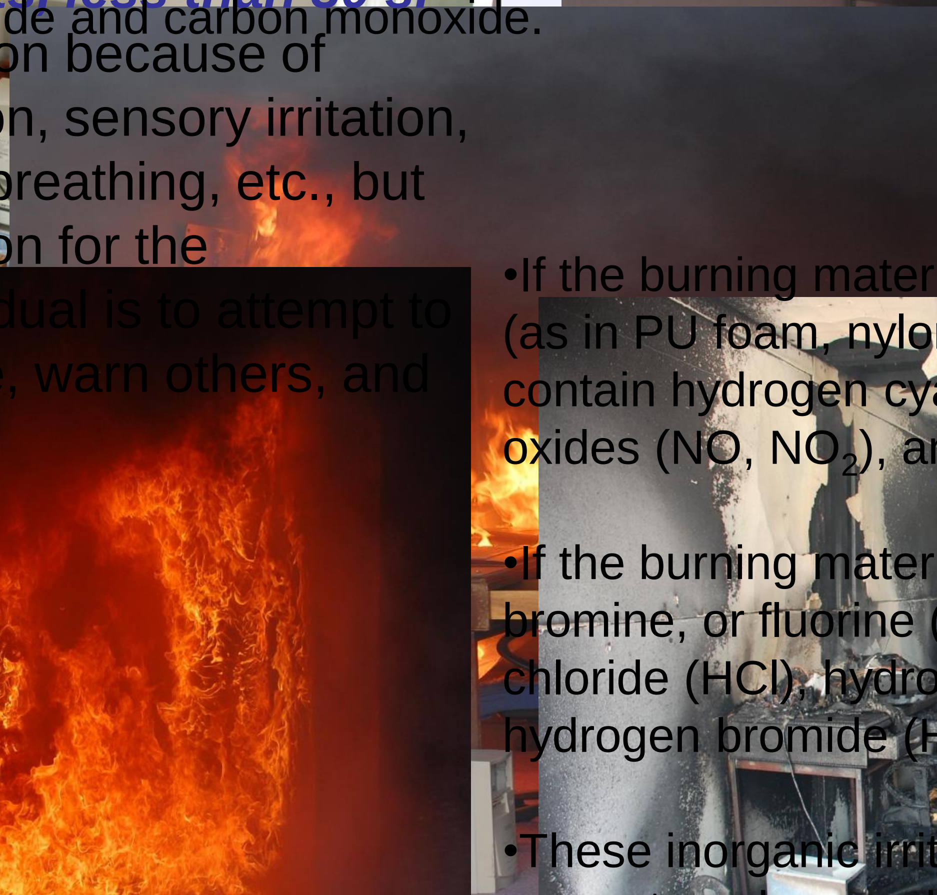
- Asphyxiants
- Irritants
- Smoke
- Particulates
  PAH
  Dioxins

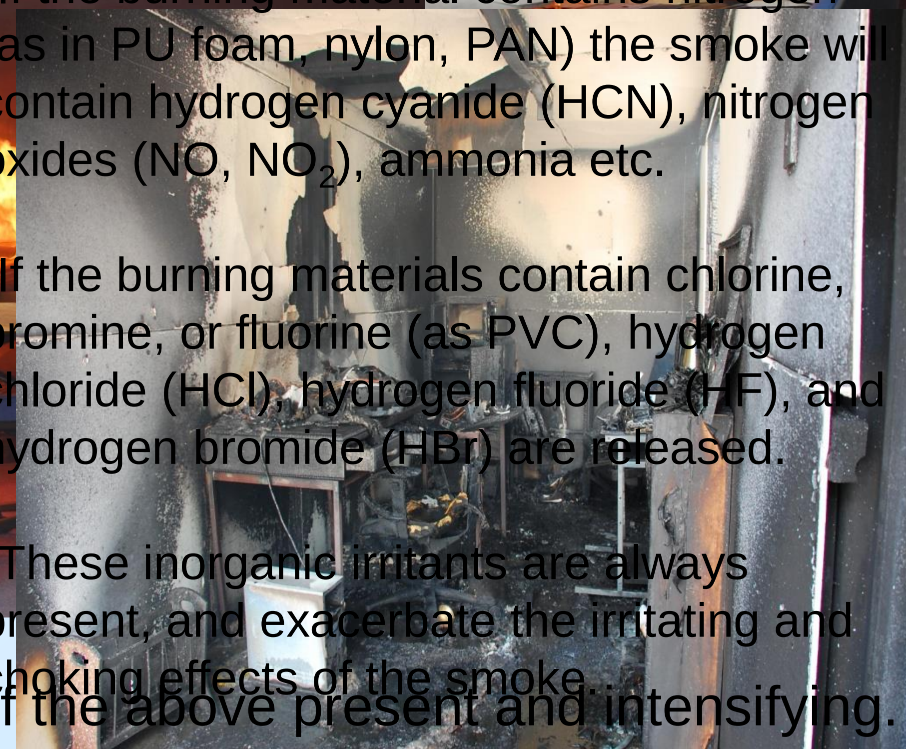
Fire Scenarios and Combustion Conditions

- Oxidative Pyrolysis
- Well-Ventilated
- Under-Ventilated









•The combination of low O_2 and heat are extremely fast acting and above smoke also contains carbon dioxide and carbon monoxide.

Immediate effects, less than 30 s. some disorientation because of smoke obscuration, sensory irritation, impaired normal breathing, etc., but the natural reaction for the unimpaired individual is to attempt to extinguish the fire, warn others, and try to escape.

•If the burning material contains nitrogen (as in PU foam, nylon, PAN) the smoke will contain hydrogen cyanide (HCN), nitrogen oxides (NO, NO_2), ammonia etc.

•If the burning materials contain chlorine, bromine, or fluorine (as PVC), hydrogen chloride (HCl), hydrogen fluoride (HF), and hydrogen bromide (HBr) are released.

•These inorganic irritants are always present, and exacerbate the irritating and choking effects of the smoke.

Immediate effects, within 2 min - All of the above present and intensifying. spreading smoke, accumulating and forming a hot layer at the ceiling level but rapidly descending toward the floor.

Harmful Effects

- **Smoke obscuration**
  - impaired vision due to the smoke and particulates presence
- **Irritant gases**
  - HCl, HBr, HF, NOx, Acrolein, Formaldehyde
  - Depending upon the concentration cause painful stimulation of the eyes, nose, mouth, throat and lungs with some hypoxia due to breathing difficulties which impedes escape and can be fatal
  - Depending upon dose inhaled cause lung inflammation and oedema which may be fatal usually some hours after exposure
- **Asphyxiation gases**
  - CO, HCN, CO_2, Low Oxygen
  - Cause confusion and loss of consciousness followed by death from asphyxia when a sufficient dose has been inhaled
  - For asphyxiants effects depend upon an exposure dose. There is little effect until a threshold dose is inhaled after which confusion occurs rapidly followed by collapse

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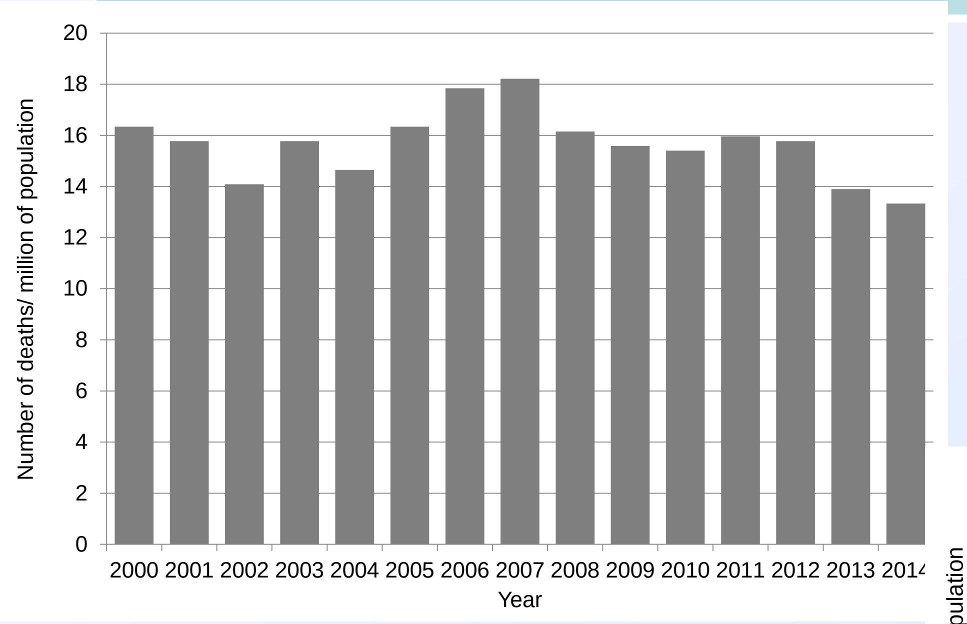
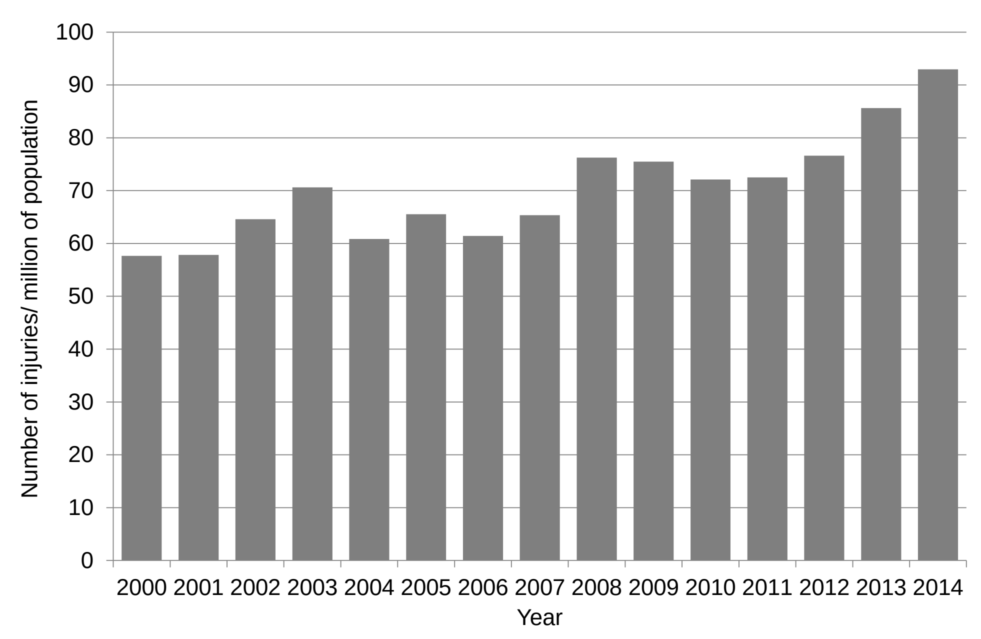
Analysis of Polish Fire Statistics

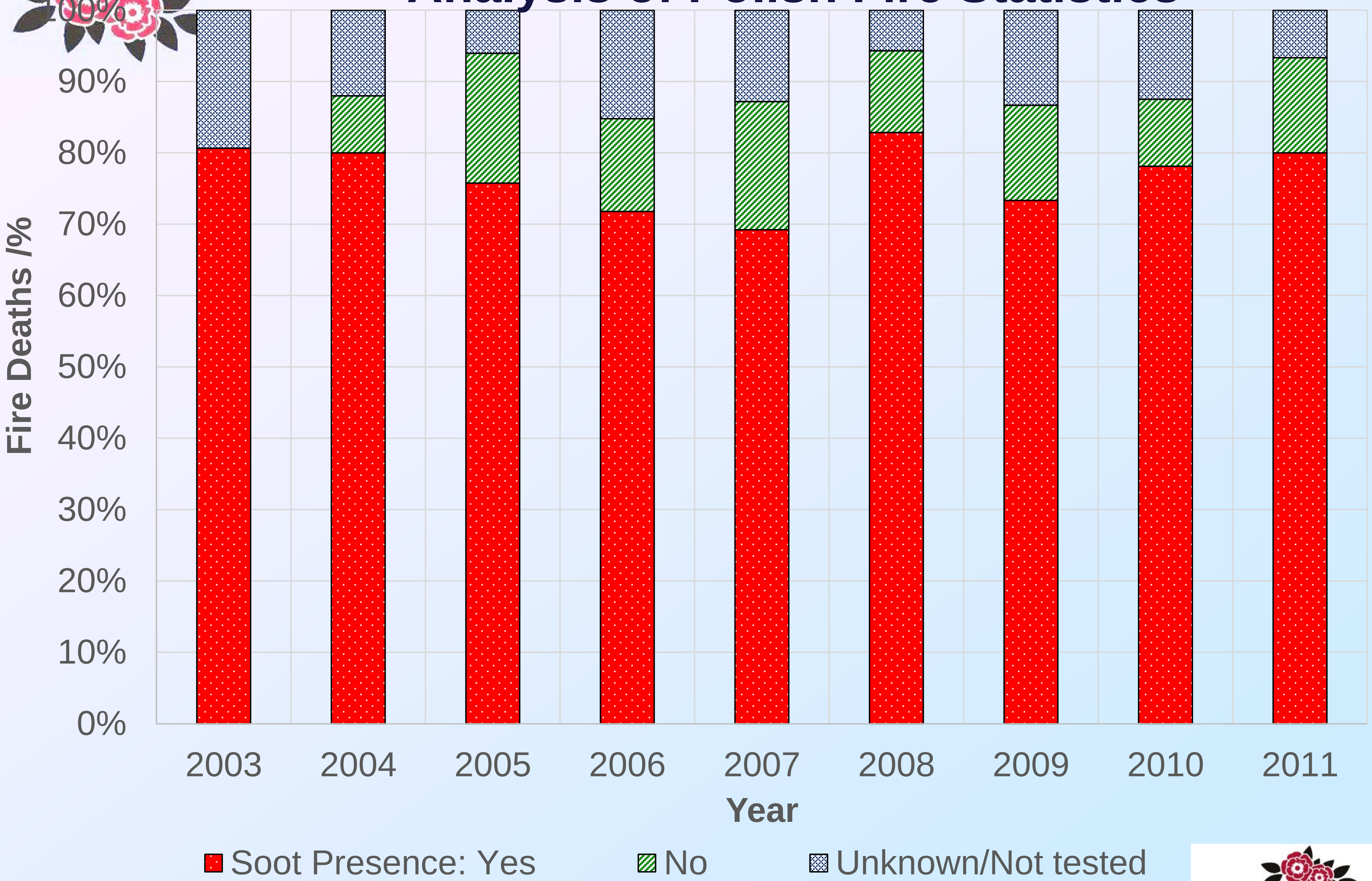
Deaths/million	Injuries/million





Stec et al. Forensic Science International, Volume 277, August 2017, Pages 77-87

Analysis of Polish Fire Statistics



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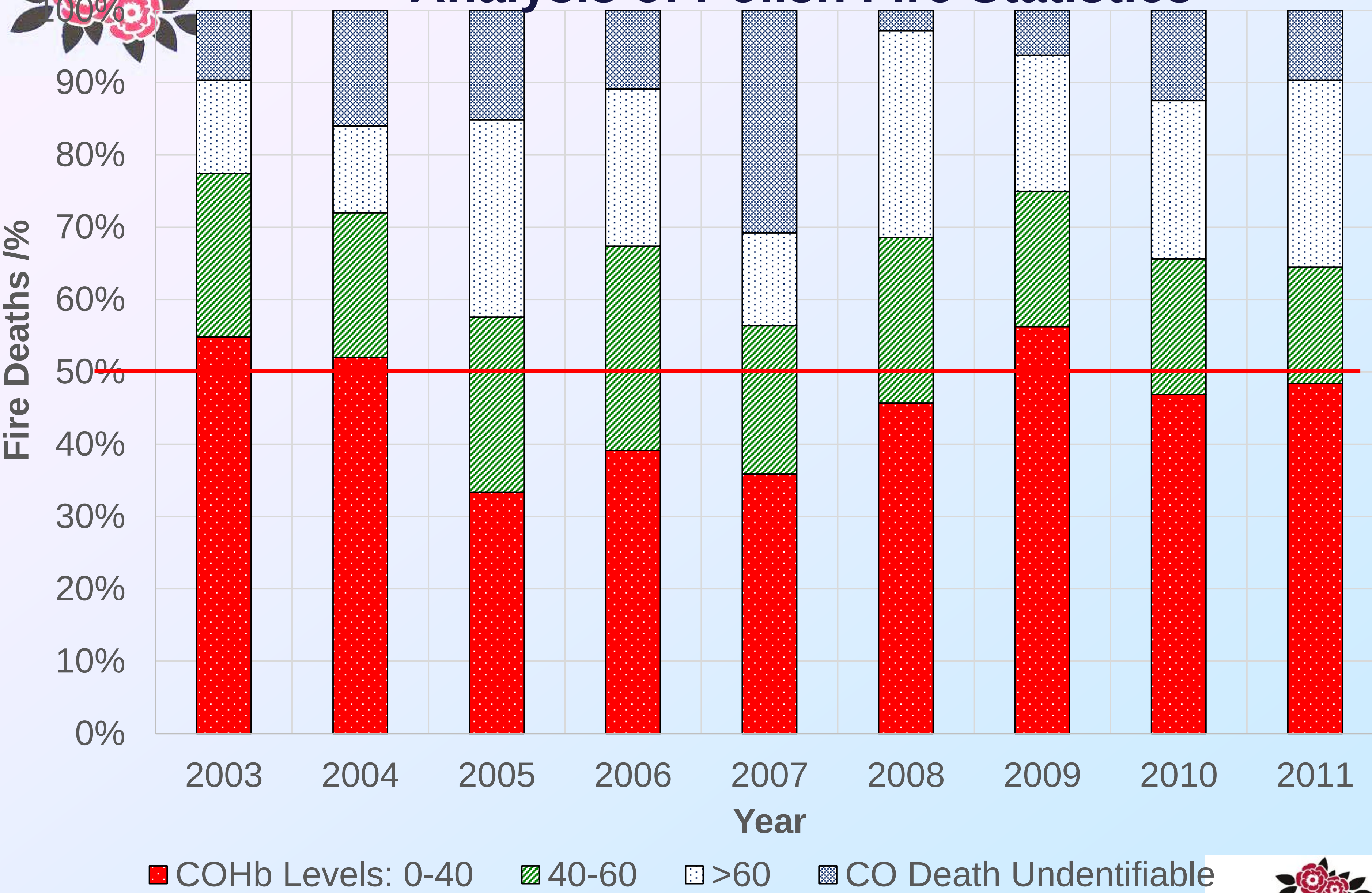
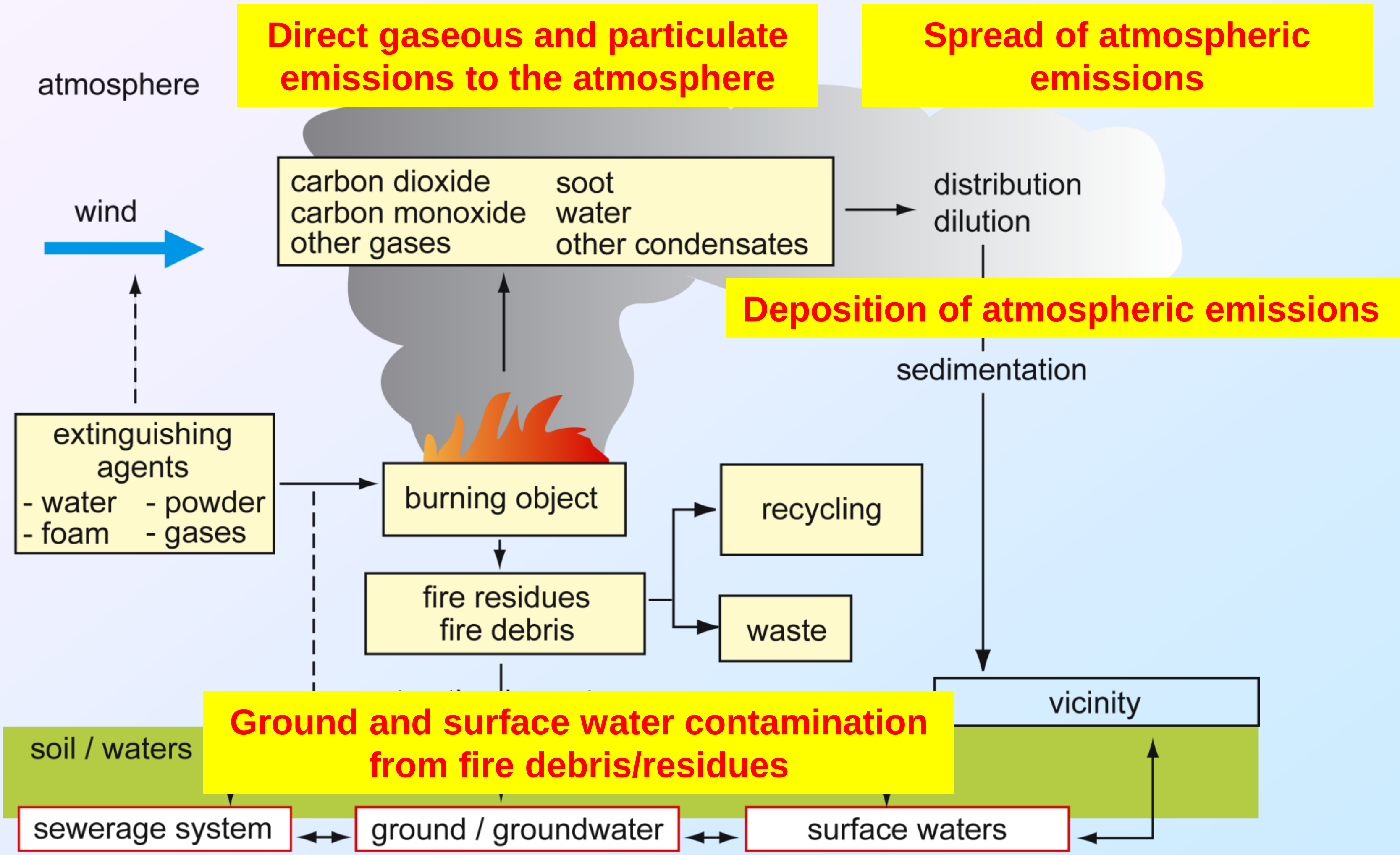


Stec et al. Forensic Science International, Volume 277, August 2017, Pages 77-87

Emission pathways from fires



ISO TC92 SC3 - PWI 26367-2: Guidelines for assessing the adverse environmental impact of fire effluents

Identification of potential environmental impact

Ecotoxicants with acute effects

Ecotoxicants with long-term effects

Metals

Particulates

Polycyclic aromatic hydrocarbons (PAHs)

Perfluorooctanesulfonates (PFOS)

Polychlorinated and polybrominated dioxins and furans (PCDD/PCDF, PBDD/PBDF)

What’s in Smoke and what are the Impacts

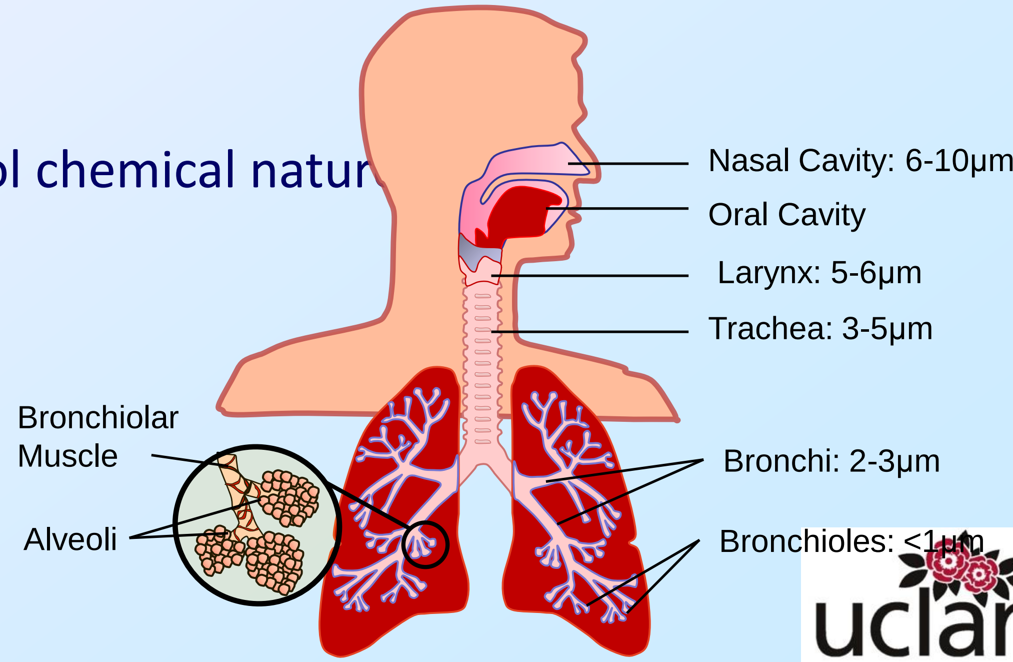
Smoke particles: small, less than one micron in diameter; behave like a gas

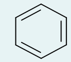
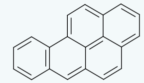
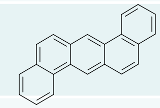
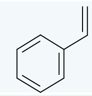
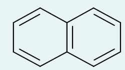
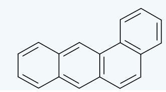
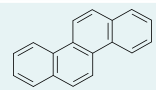
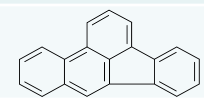
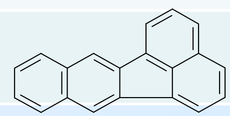
Penetrate indoors and deep into the lung

Have high surface area: adsorb other combustion products, catalytic surface

Solid and liquid aerosols are characterized by:

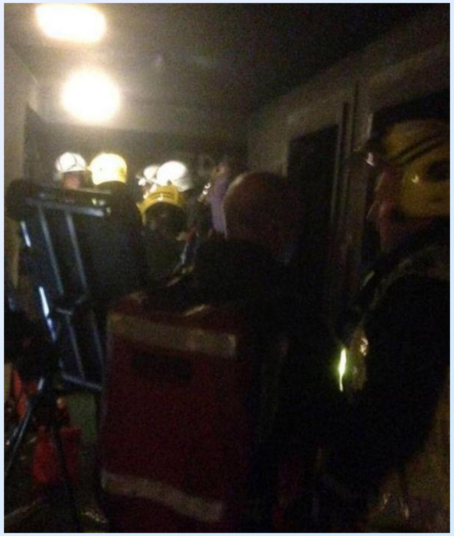
- Concentration,
- Particles size distribution,
- Chemical nature
- Morphology (depending on aerosol chemical natur



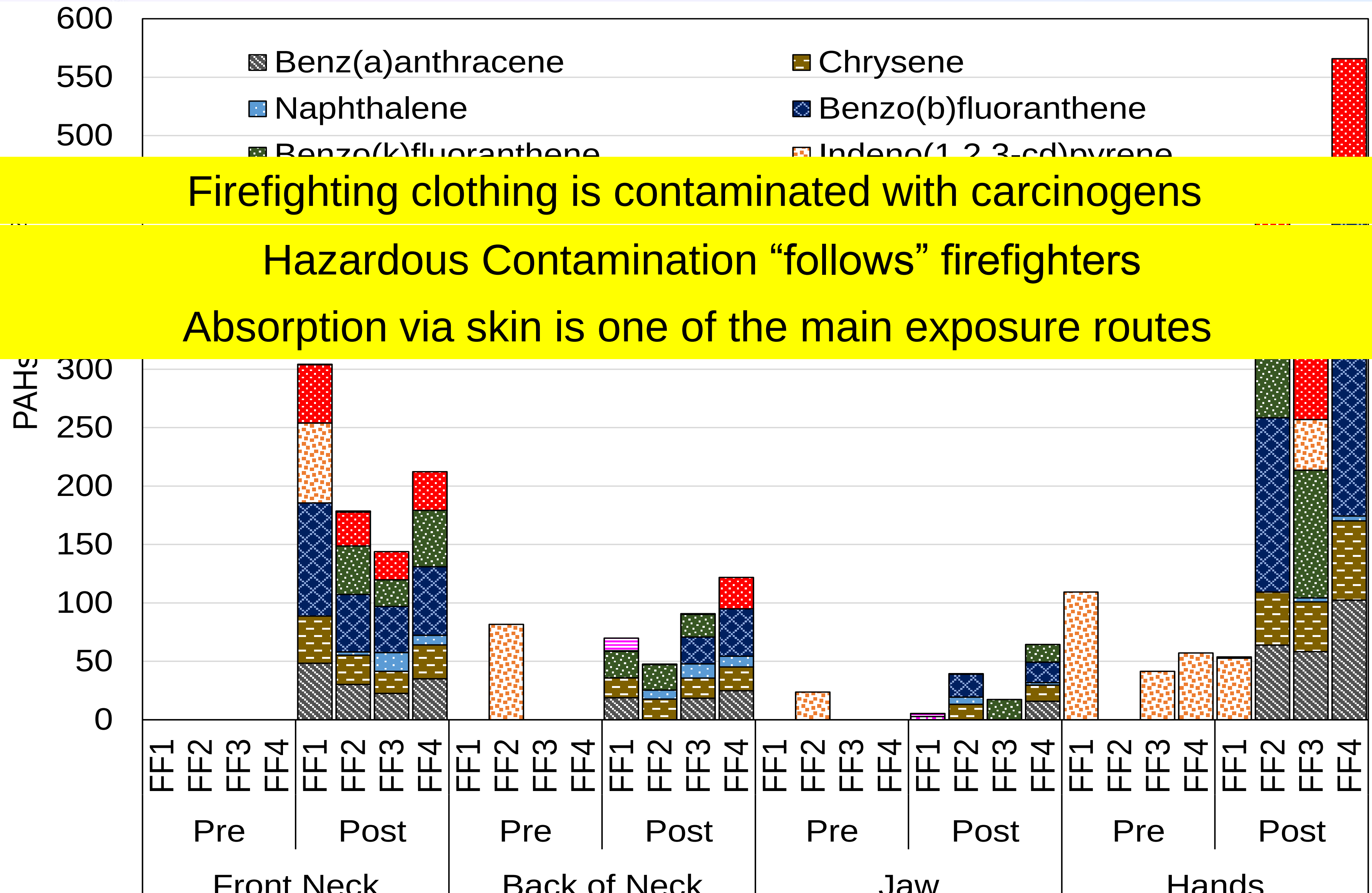
Cyclic and Polycyclic Aromatic Hydrocarbons	Structure	IARC
Benzene		1 (2012)
Benzo[a]pyrene		1 (2012)
Dibenzo[ah]anthracene		2A (2010)
Styrene		2B (2002)
Naphthalene		2B (2002)
Benzo[a]anthracene		2B (2010)
Chrysene		2B (2010)
Benzo[b]fluoranthene		2B (2010)
Benzo[k]fluoranthene		2B (2010)

Group	General description	Bases of evaluation
1	Carcinogenic to humans	Sufficient evidence of carcinogenicity in humans.
2A	Probably carcinogenic to humans	Limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals.
2B	Possibly carcinogenic to humans	Limited evidence of carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals.

What strategies are in place to minimise risk of getting cancers?



Firefighters and routes of exposure: Inhalation or Absorption or both?



Firefighting clothing is contaminated with carcinogens

Hazardous Contamination “follows” firefighters

Absorption via skin is one of the main exposure routes

AA. Stec , et. al Scientific Reports, volume 8, Article number: 2476(2018)

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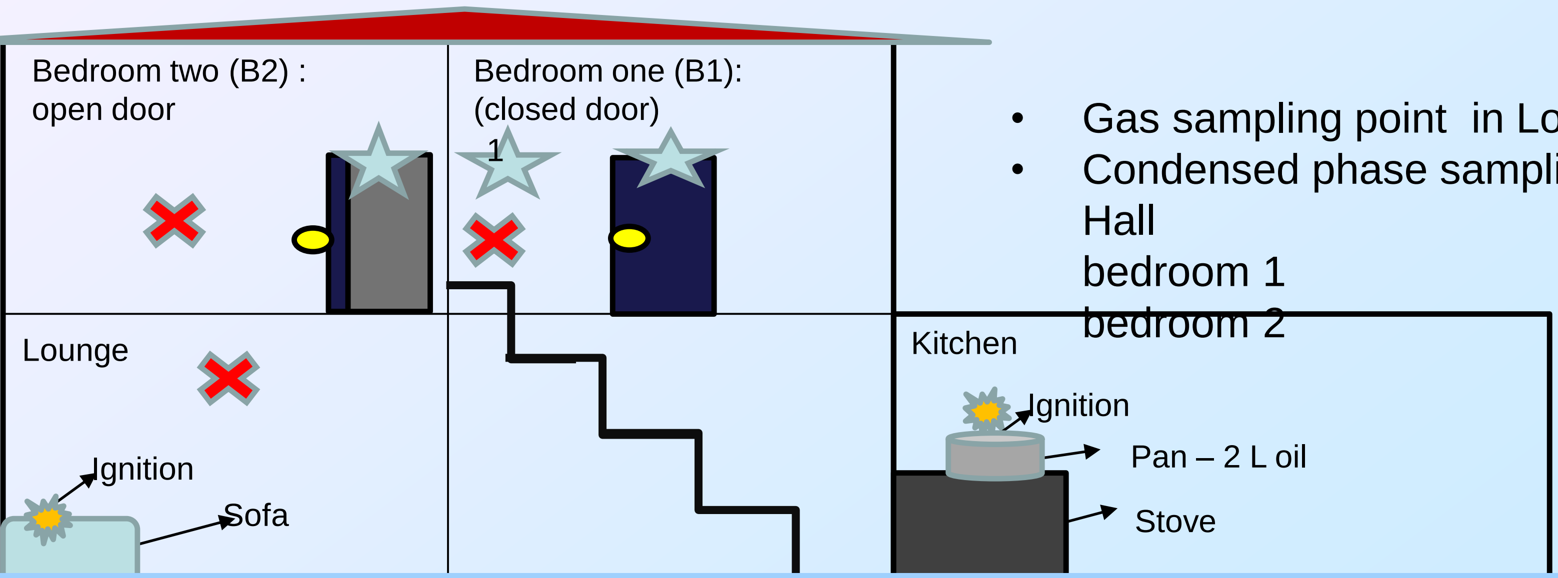
PAHs Release

- New sofas, meeting the UK furniture flammability regulations, were used either solely or with additional furnishings (carpet, curtains, television set).
- The ventilation conditions were varied(well- to under-ventilated) by varying door and/or window openings (in bedrooms/lounge).
- Two sheets of newspaper were ignited on the sofa.
- Gaseous effluents and particulate deposits were measured



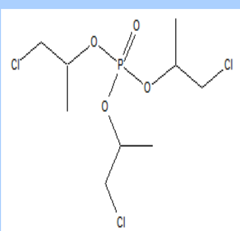
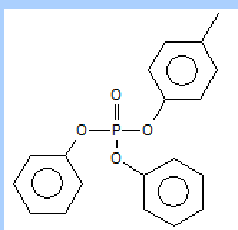
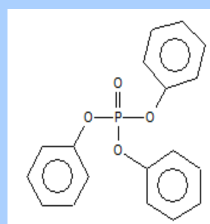
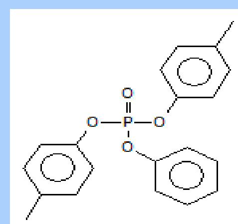
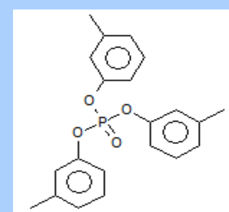
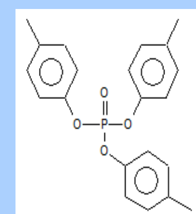
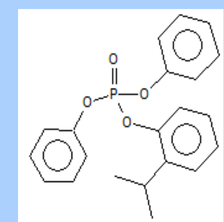
- Gas sampling point in Lounge
- Condensed phase sampling :
  Hall
  bedroom 1
  bedroom 2

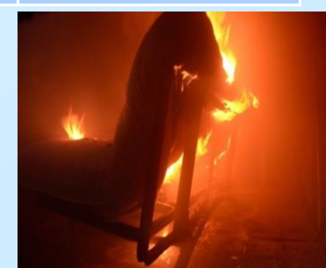
F. Hewitt , A. Christou, K. Dickens, R. Walker, AA. Stec , Chemosphere, 173:580–593, 2017

OPFRs and PAHs Release During House Fires

The most toxic PAH: benzo[a]pyrene was identified in the gas phase samples.

Phosphorus-based compounds were detected in both gas and condensed phases from burning sofas or the fully-furnished lounge.

Tris (1-chloro-2-propyl) phosphate	4-Methylphenyl diphenyl phosphate	Triphenyl phosphate	Bis(4-methylphenyl) phenyl phosphate	Tri-m-cresyl phosphate	Tri-p-cresyl phosphate	Isopropylphenyl diphenyl phosphate
						



F. Hewitt , A. Christou, K. Dickens, R. Walker, AA. Stec,, Chemosphere, 173:580–593, 2017

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- Harmful Effects
  - Asphyxiants
  - Irritants
  - Smoke
  - Particulates PAH Dioxins
- Fire Scenarios and Combustion Conditions
  - Oxidative Pyrolysis
  - Well-Ventilated
  - Under-Ventilated
- Experimental Methods

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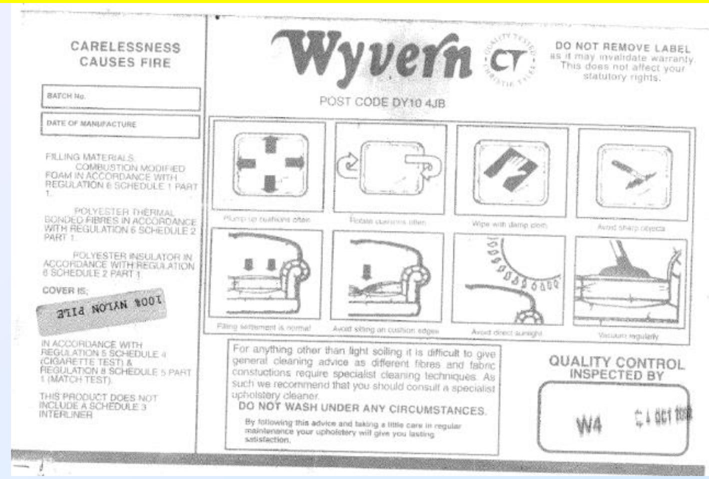
  - Bench and Large scale methods

Residential House Fire Test on Tenability



The sofa was constructed from polyurethane (PU) foam and was timber framed. The label showed that it conformed to UK fire-safety regulations

Crewe RJ, Stec AA, Walker RG, Shaw JE, Hull TR, Rhodes J, Garcia-Sorribes T., *Experimental results of a residential house fire test on tenability: temperature, smoke, and gas analyses,* J Forensic Sci., 2014 Jan;59(1):139-54

Equivalence Ratio-Classification of the fire stages

$$\phi = \frac{\text{Actual fuel / Air ratio}}{\text{Stoichiometric fuel / Air ratio}}$$

Combustion condition	Temperature (°C)	Equivalence ratio	Oxygen from fire %	CO_2/CO ratio
Smouldering	350	not applicable	>21	1-5
Well-ventilated flaming	650 or 700	$\phi < 0.75$	5 to 21	2-20
Under ventilated flaming: small vitiated fires post-flashover fires	 650 825	 $\phi > 1.5$ $\phi > 1.5$	 0 to 12 0 to 12	 2-20 2-20



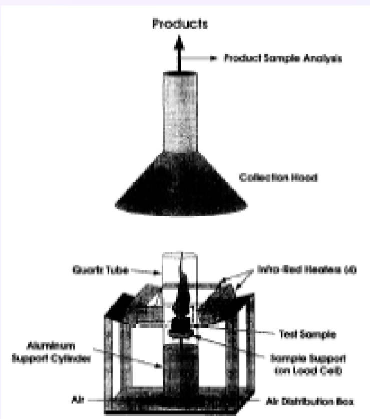

How is Fire Toxicity Measured?

3 general approaches:

Well-ventilated (e.g. Cone calorimeter)

Closed box tests (e.g. NBS Smoke Box, ASTM E1678, NES 713)

Tube furnaces (e.g. NFX 70-100, DIN 53436, IEC 60695-7-50, Fire Propagation Apparatus)



Heat flux (kWm^2)	Pilot flame	ISO fire stage depends on test material and thickness
25		adiation (?)
25		
50		(3b) Post flashover (?)

3 Conditions: each with air flow 2 litres min^{-1}

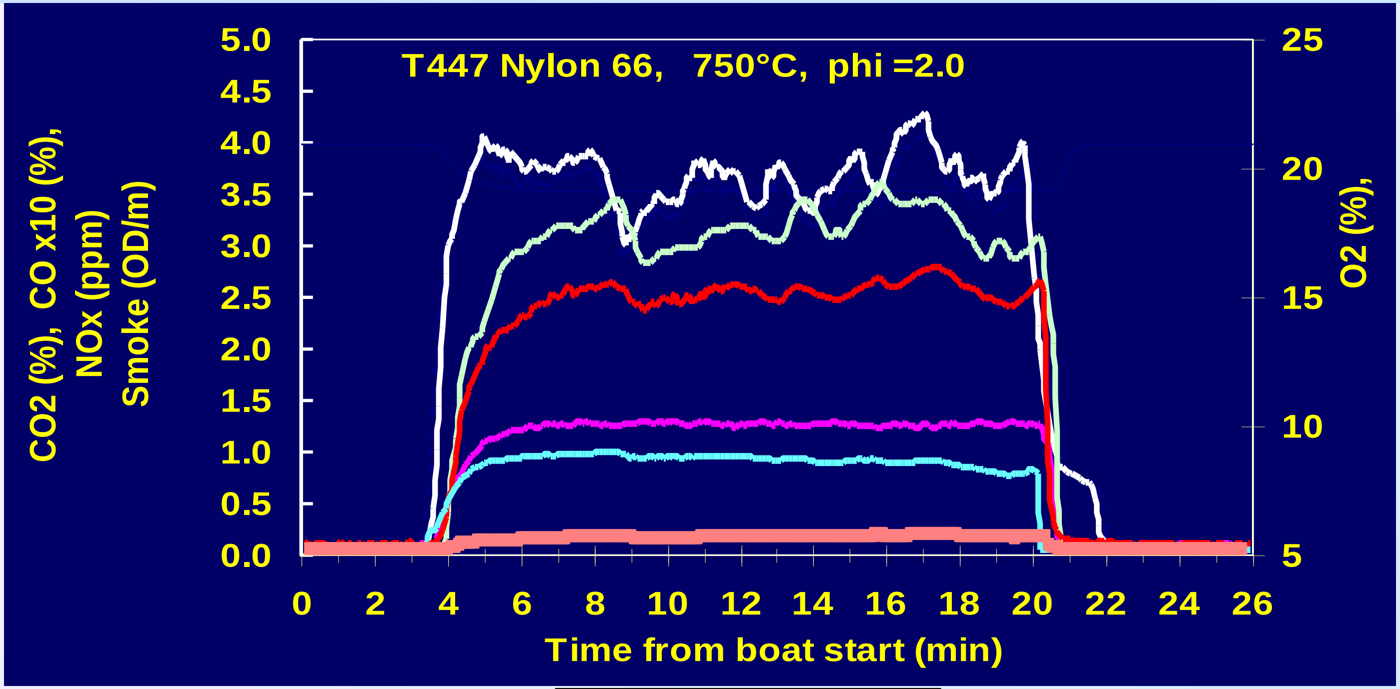
400°C Oxidative Pyrolysis (?)

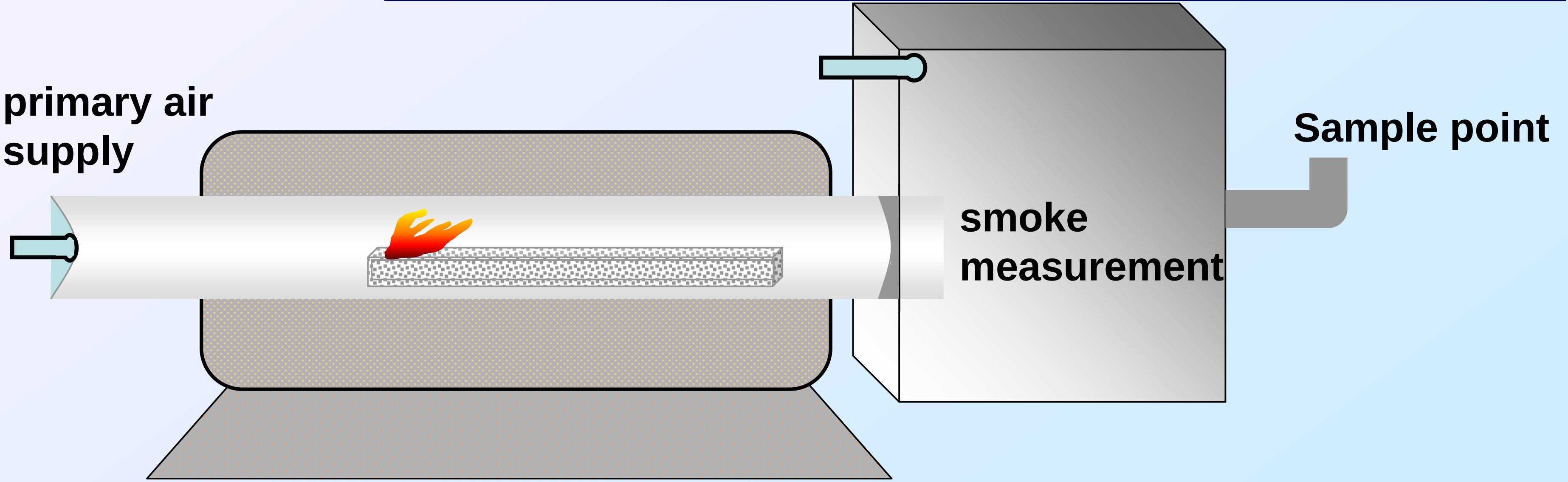
600°C Well-ventilated (?)

800°C Under-ventilated (?)

T R Hull and K T Paul, *Bench-Scale Assessment of Combustion Toxicity – A Critical Analysis of Current Protocols* Fire Safety Journal, 42, 340-365 (2007).

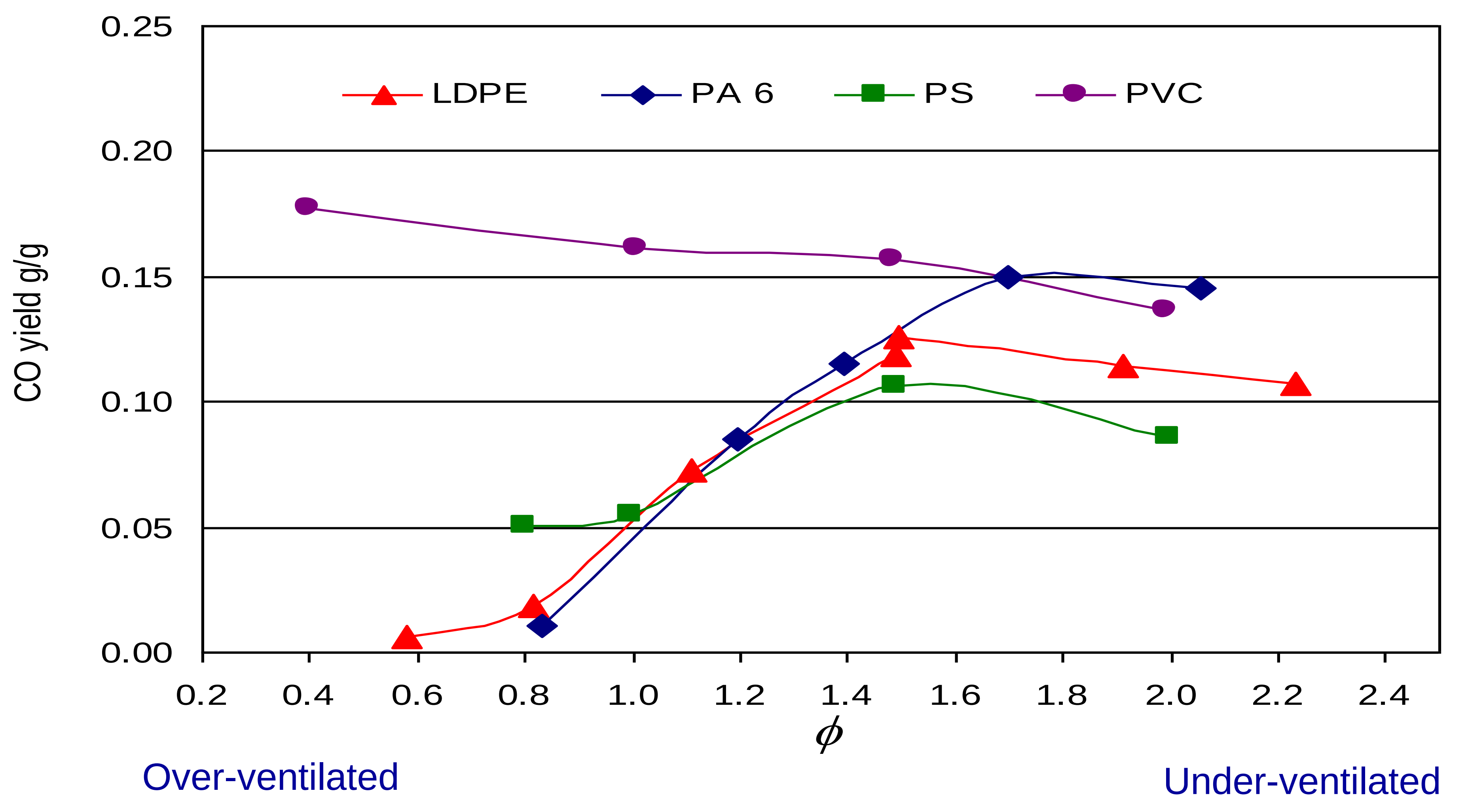
ISO 19700 The steady state tube furnace method



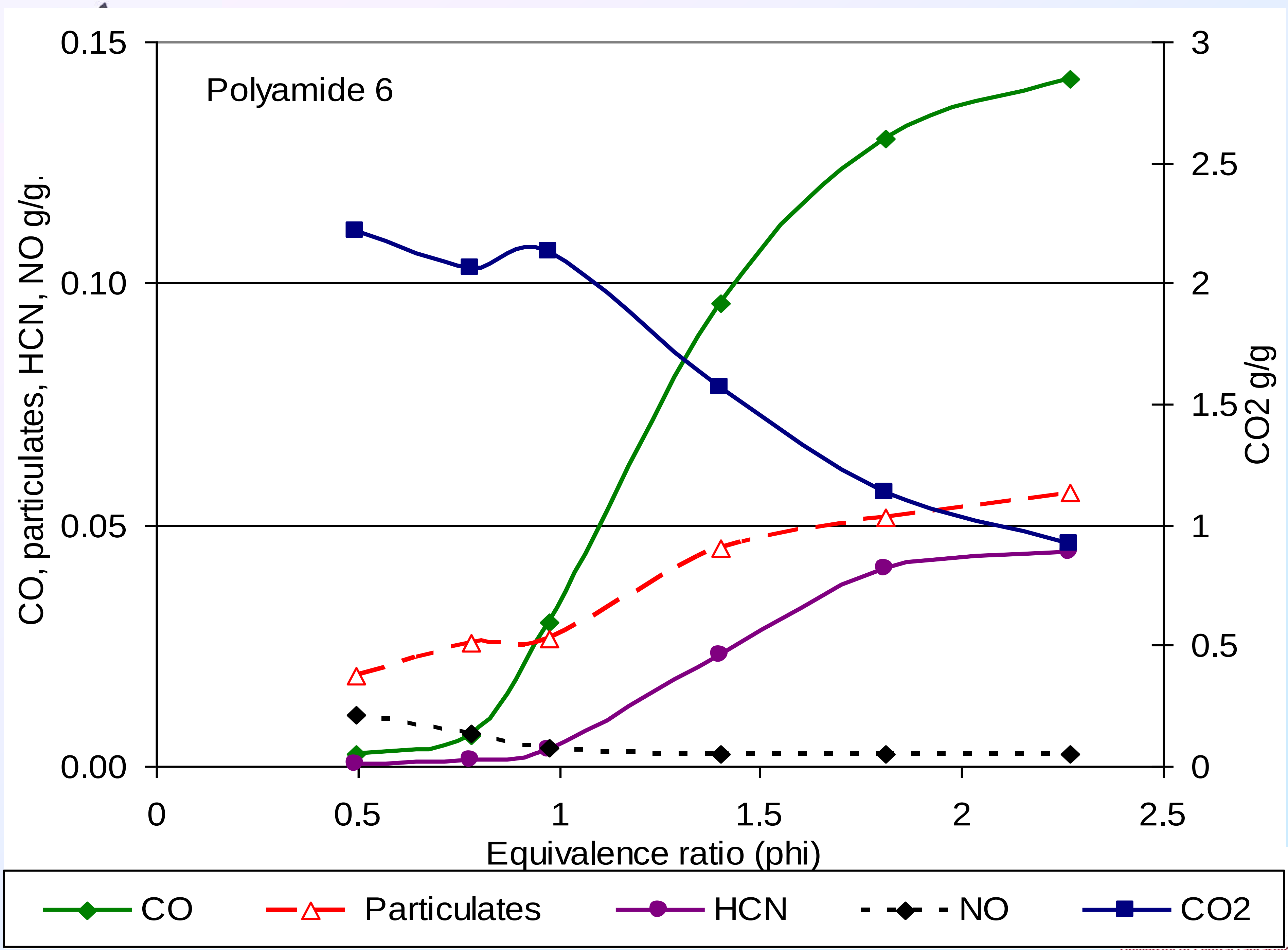


A.A. Stec, T.R. Hull, K. Lebek, *Characterisation of the Steady State Tube Furnace*, Polymer Degradation and Stability, Vol. 93, pp. 2058–2065, 2008.

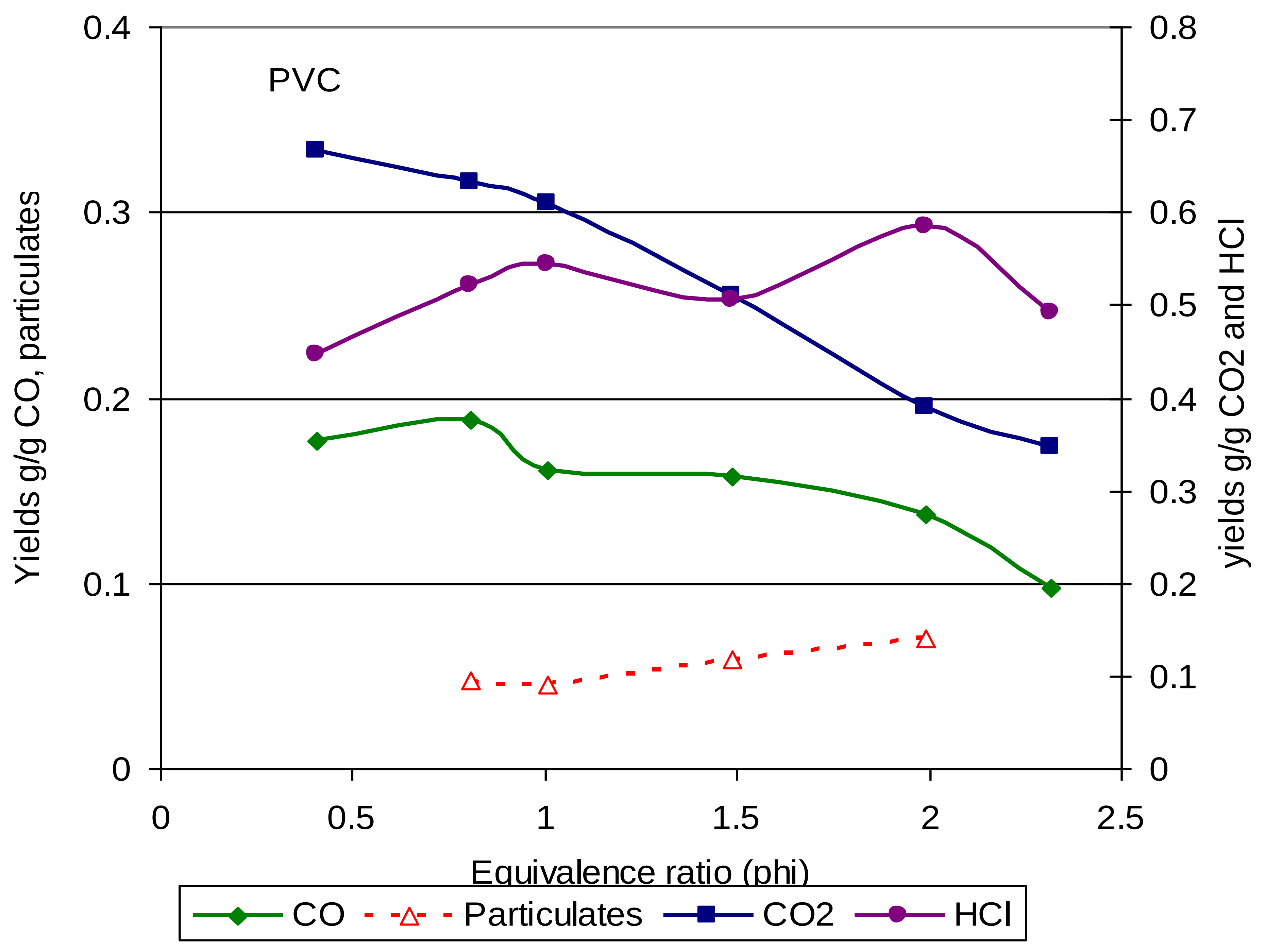
CO Yield from Steady State Tube Furnace



A.A. Stec, T.R. Hull, K. Lebek, J.A. Purser, D.A. Purser The effect of ventilation condition on the toxic product yields from burning polymers, Fire and Materials, Vol. 32, Issue 1, pp.49-60, January/February 2008.

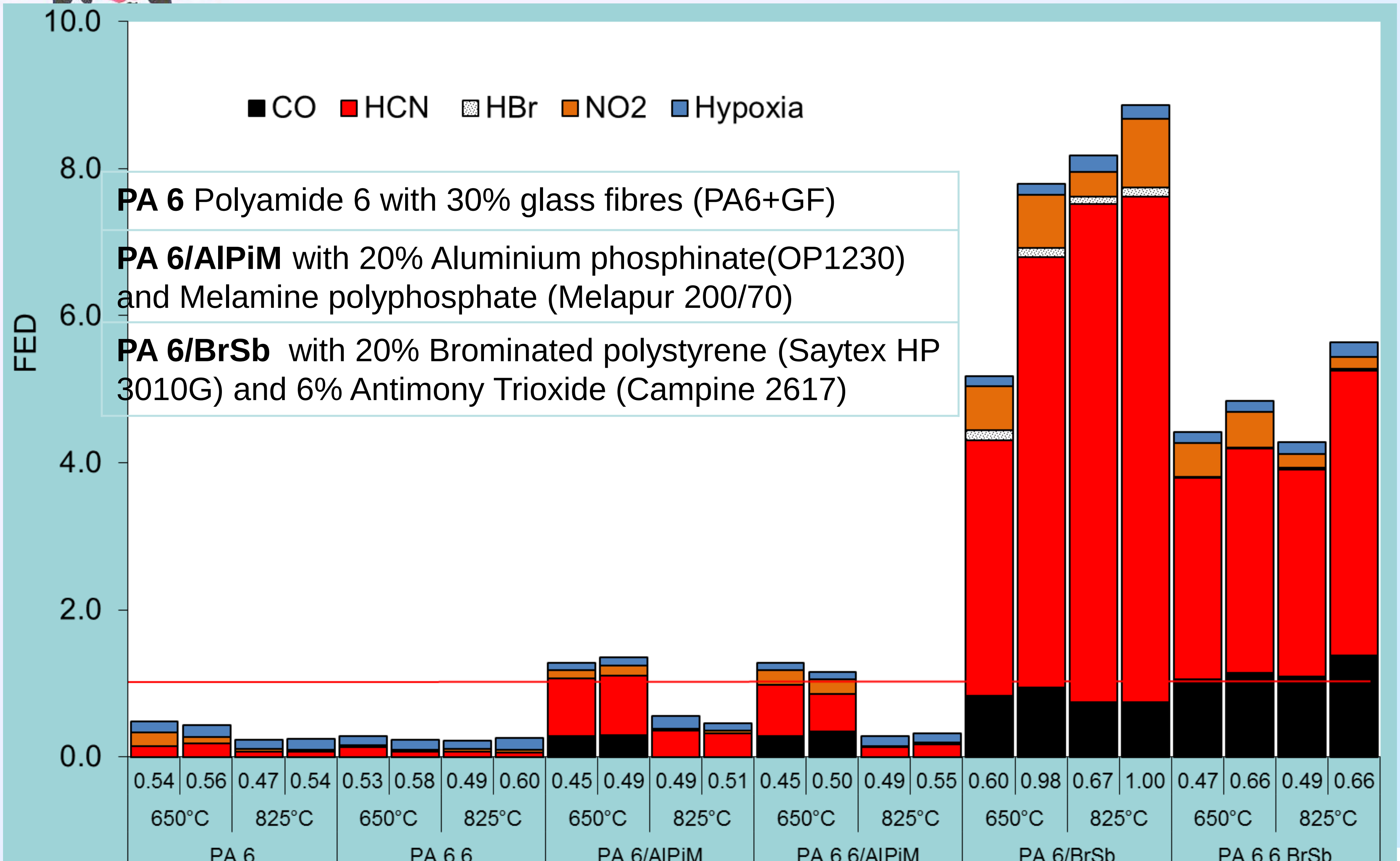


Polyamide 6
CO, particulates, HCN, NO g/g.
CO2 g/g
Equivalence ratio (phi)
0.15
0.10
0.05
0.00
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
CO
Particulates
HCN
NO
CO2



PVC
Yields g/g CO, particulates
yields g/g CO2 and HCl
Equivalence ratio (phi)
0.4
0.3
0.2
0.1
0
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
CO
Particulates
CO2
HCl

Fire Toxicity FR polyamides (20 g/m^3)



S Molyneux, A A Stec and T R Hull,, *Polymer Degradation and Stability, In Press, September 2013*
http://dx.doi.org/10.1016/j.polymdegradstab.2013.09.013

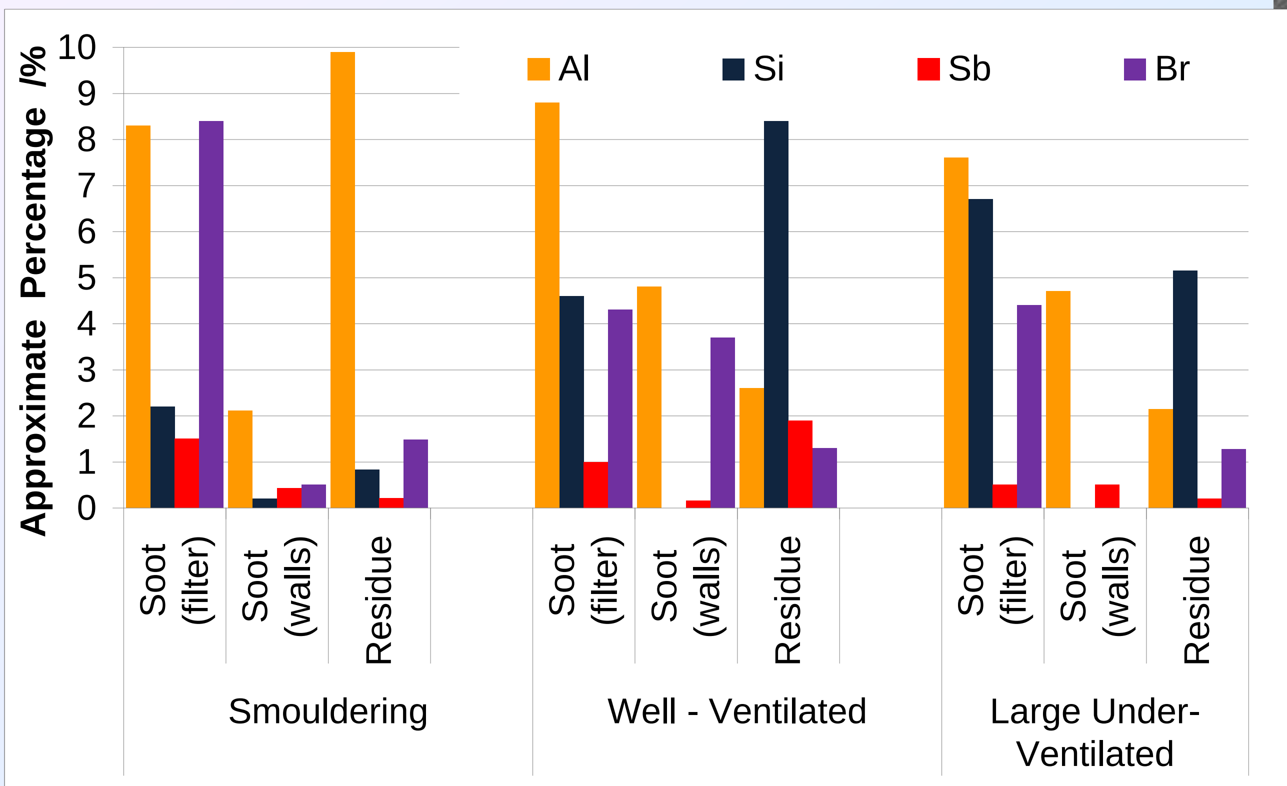
SEM-EDAX showing non-carbon in airborne particles Si, Al etc.

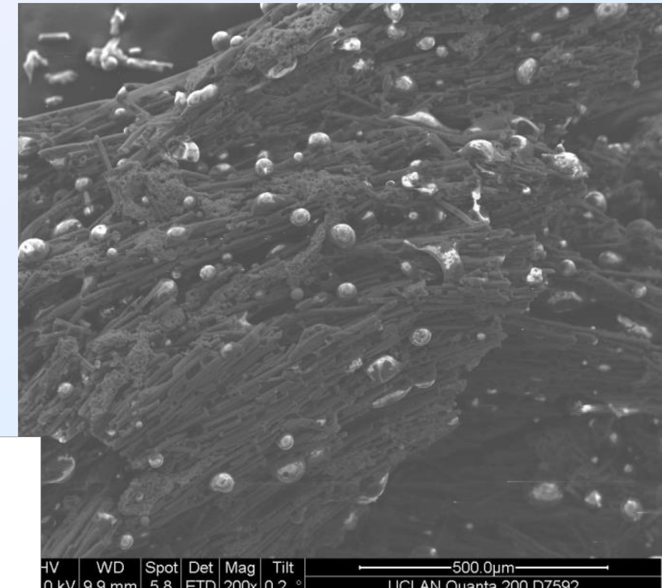
44% Polyamide 66

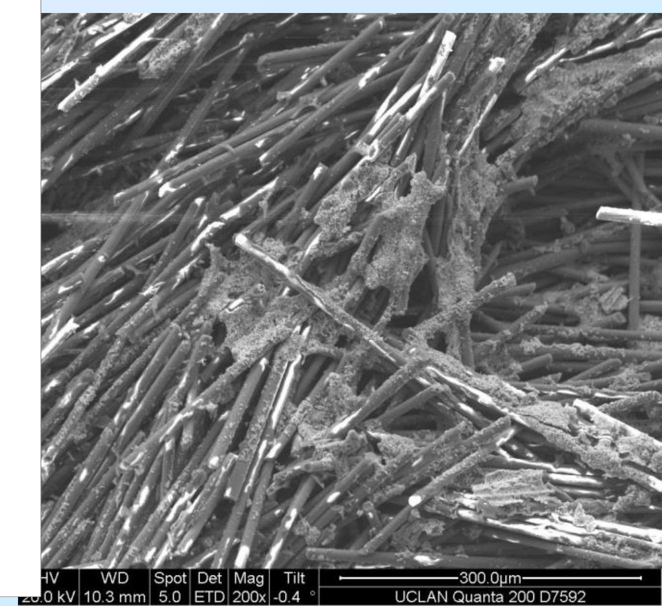
30% Glass fibres

20% Brompolystyrene

6% Antimony Trioxide







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  - Bench and Large scale methods
- **Toxicity Assessment**
  - Animal and Chemical Assessment
  - FED, FEC

Estimation of fire toxicity- ISO 13344

FED - the fraction of a lethal dose (for 50% of the population)
When FED = 1 then 50% of the population will die.

$$FED = \frac{m[CO]}{[CO_2]-b} + \frac{21-[O_2]}{21-LC_{50,O_2}} + \frac{[HCN]}{LC_{50,HCN}} + \frac{[HCl]}{LC_{50,HCl}} + \frac{[HBr]}{LC_{50,HBr}} + \frac{[SO_2]}{LC_{50,SO_2}} ....$$

$$FED = \frac{m[CO]}{[CO_2]-b} + \frac{21-[O_2]}{(21-5,4)\,\%} + \frac{[HCN]}{150} + \frac{[HCl]}{3\,700} + \frac{[HBr]}{3\,000}$$

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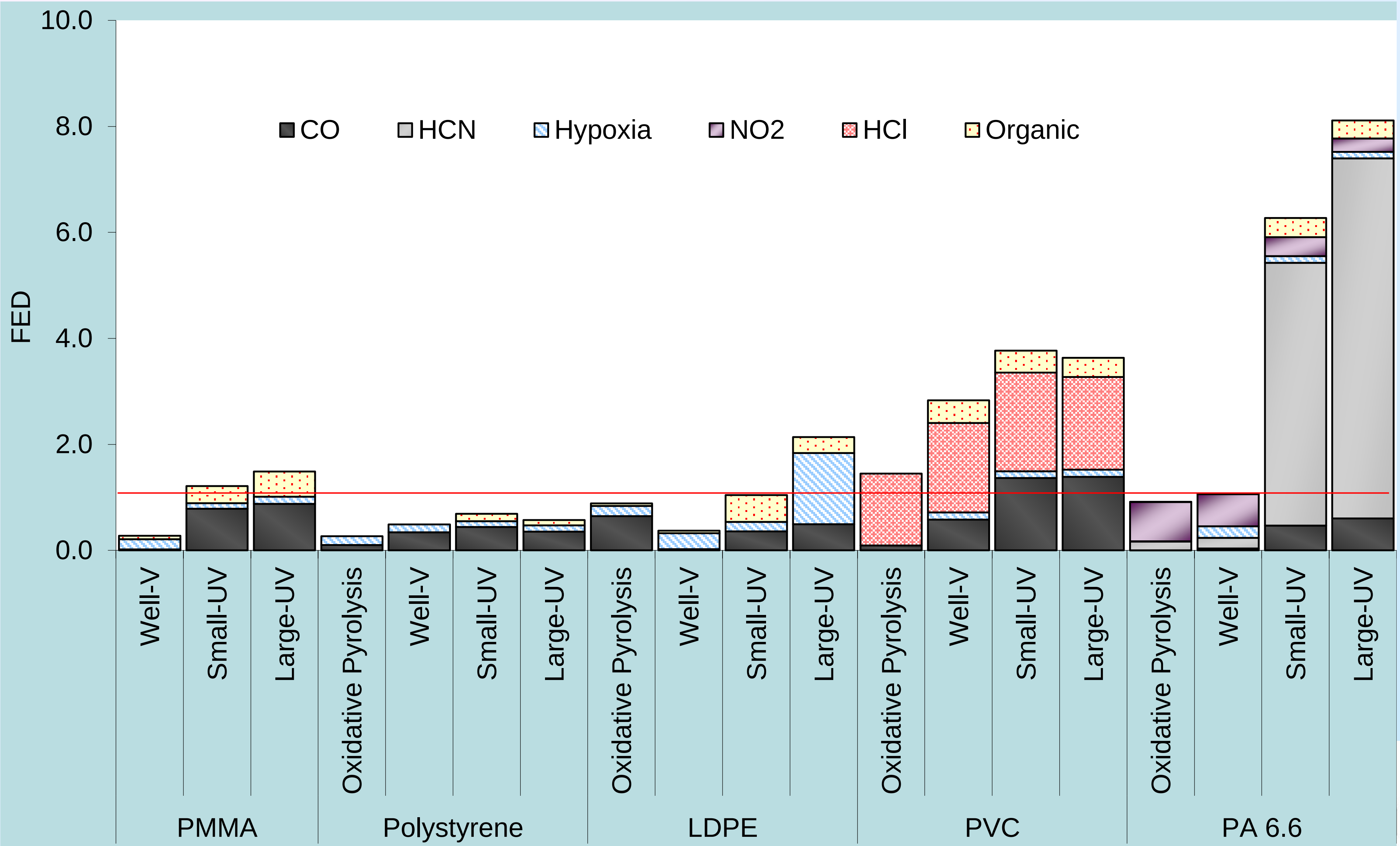
Fire toxicity of Common Polymers at 20 g/m³ loading



The fire toxicity of six insulation materials (20 g/m³)

Glass Wool (GW)

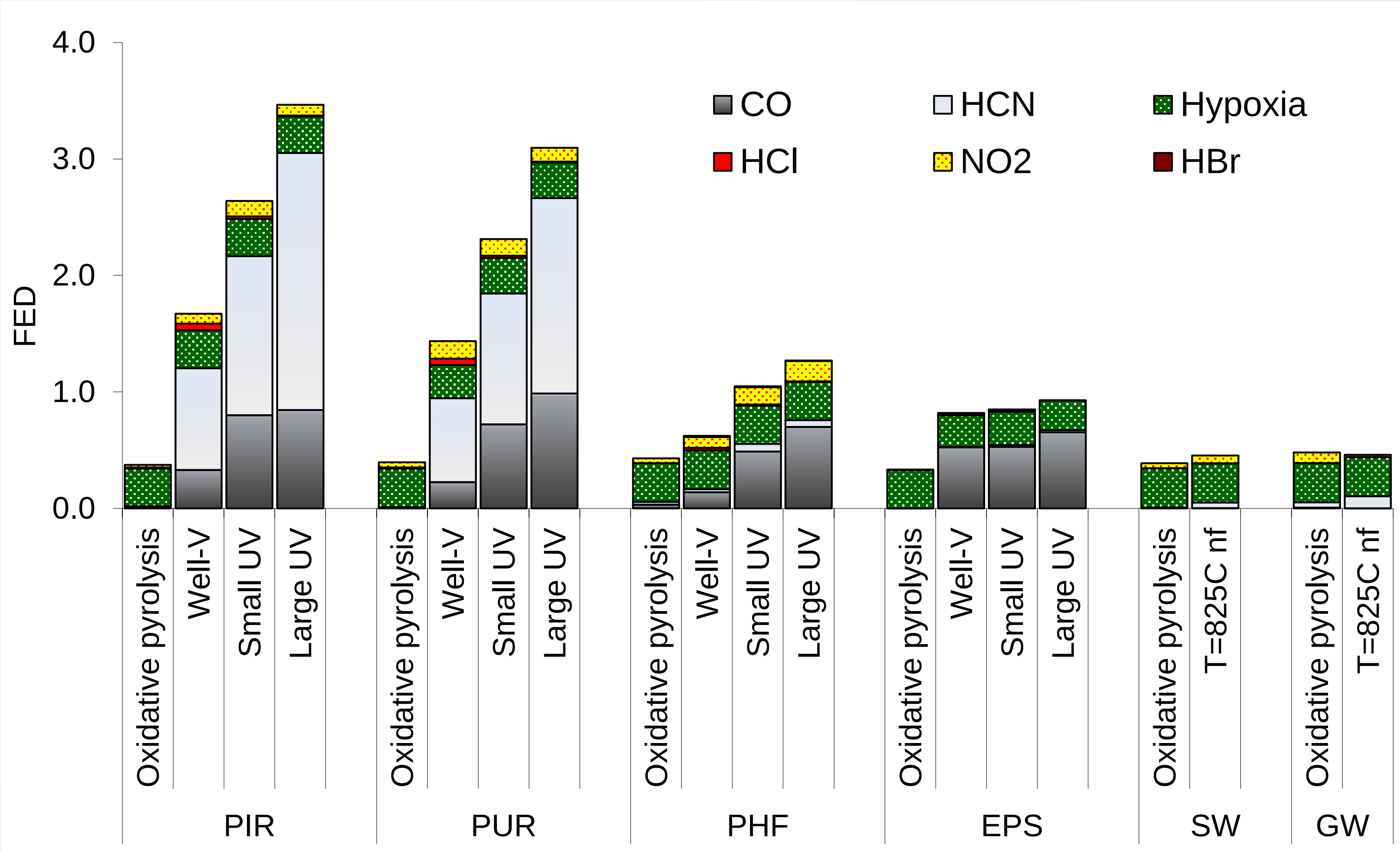
Stone Wool (SW)

Phenolic Foam (PhF)

Expanded Polystyrene Foam (EPS),

Polyurethane Foam (PUR)

Polyisocyanurate Foam (PIR)



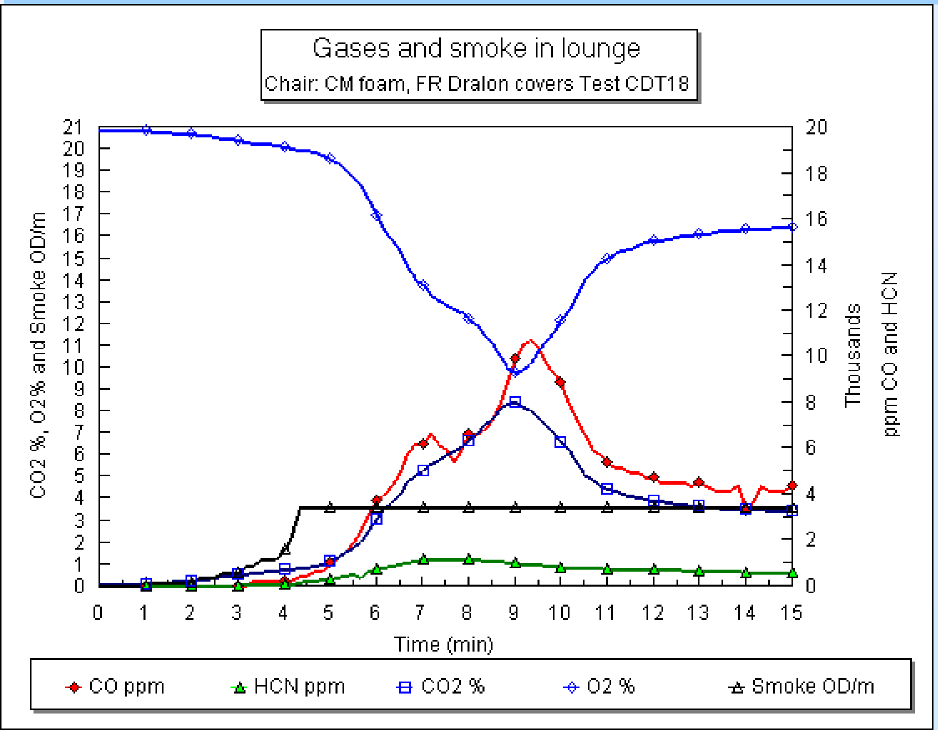
A.A. Stec and T.R. Hull, *Assessment of The Fire Toxicity of Building Insulation Materials,* Energy and Buildings, 43, pp. 498-506, 2011

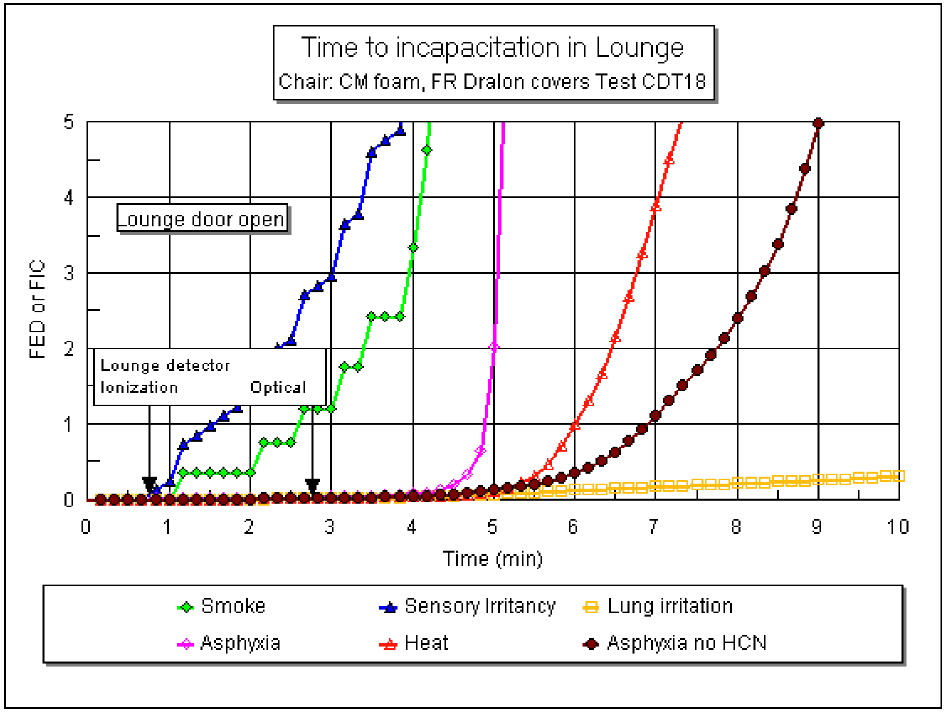
Estimation of fire toxicity

ISO 13571

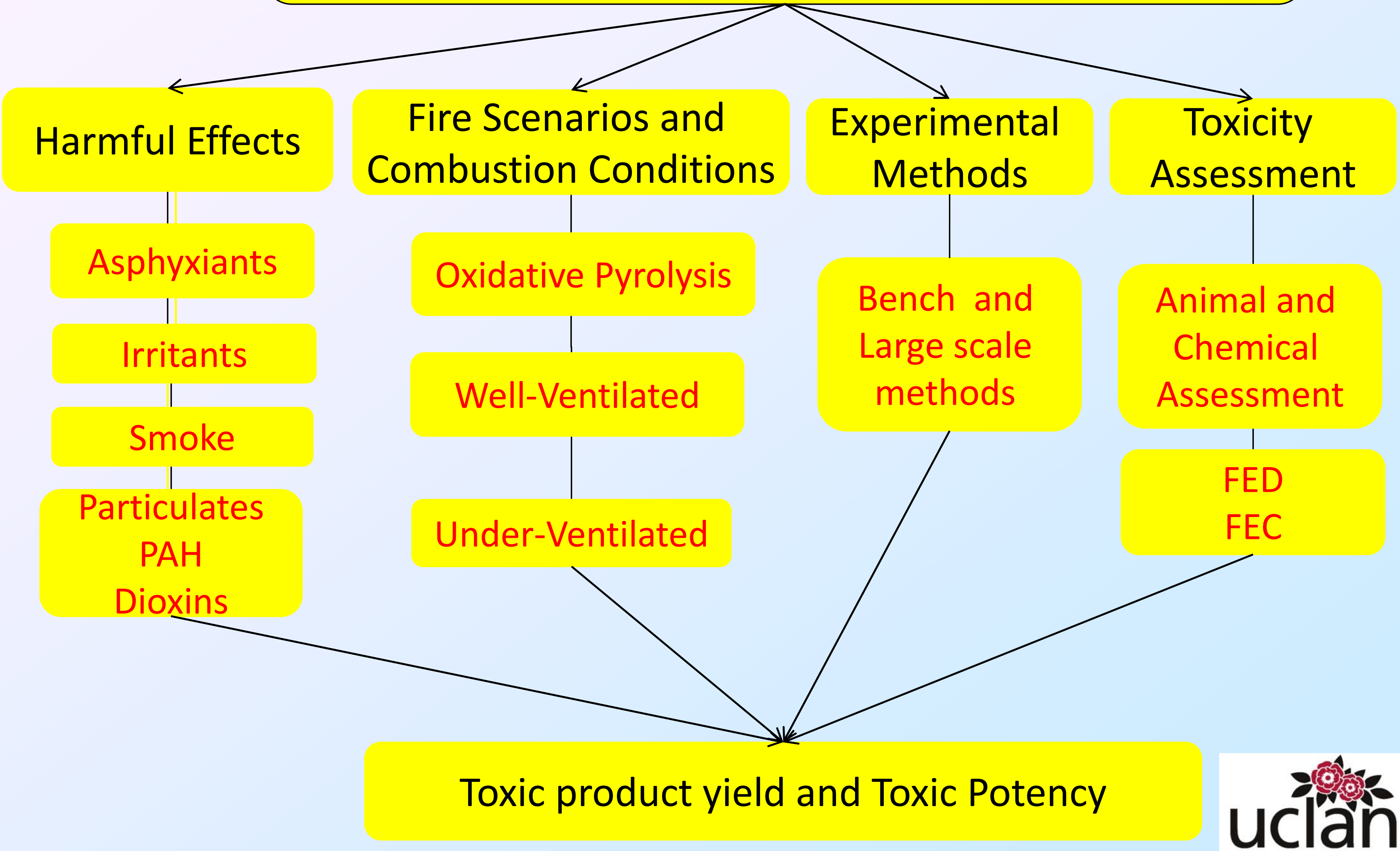
$$FED = \sum_{t_1}^{t_2} \frac{[CO]}{35000} \Delta t + \sum_{t_1}^{t_2} \frac{\exp([HCN]/43)}{220} \Delta t$$

$$FEC = \frac{[HCl]}{IC_{50,\,HCl}} + \frac{[HBr]}{IC_{50,\,HBr}} + \frac{[HF]}{IC_{50,\,HF}} + \frac{[SO_2]}{IC_{50,\,SO_2}} + \frac{[NO_2]}{IC_{50,\,NO_2}} + \frac{[acrolein]}{IC_{50,\,acrolein}} + \frac{[fomaldehyde]}{IC_{50,\,fomaldehyde}} + \sum \frac{[irritant]}{IC_{50,\,irritant}}$$





FACTORS AFFECTING
FIRE COMBUSTION AND TOXICITY



CONCLUSIONS

- Fire toxicity is dependent on both material and fire conditions.
- Yields depend on conditions, and underventilated fires are the most toxic.
- Fire toxicity data is best related to ventilation conditions in terms of equivalence ratio ϕ.
- CO is a good indicator of incomplete combustion however, it is not always the major toxicant. CO and HCN are much more prevalent in developed flaming.
- Irritants (HCl, organics and smoke particles) can prevent escape, but CO will be recorded as the cause death. HCl is independent of fire condition and NOx is favoured by well-ventilated conditions.
- Fire retardants which act in the gas phase often increase fire effluent toxicity. Brominated flame retardants increase the yield of both CO and HCN.
- Bench-scale methods rarely distinguish particular fire conditions. SSTF and FPA show acceptable agreement with large scale data over the range of fire conditions.
- Toxicity is often seen as too complex for fire safety assessments: a methodology to incorporate it at the design stage has already been under development.

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Thank you for your attention

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