Fire Smoke Toxicity – What's in the Smoke

Presented by:-

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Fire toxicity assessment

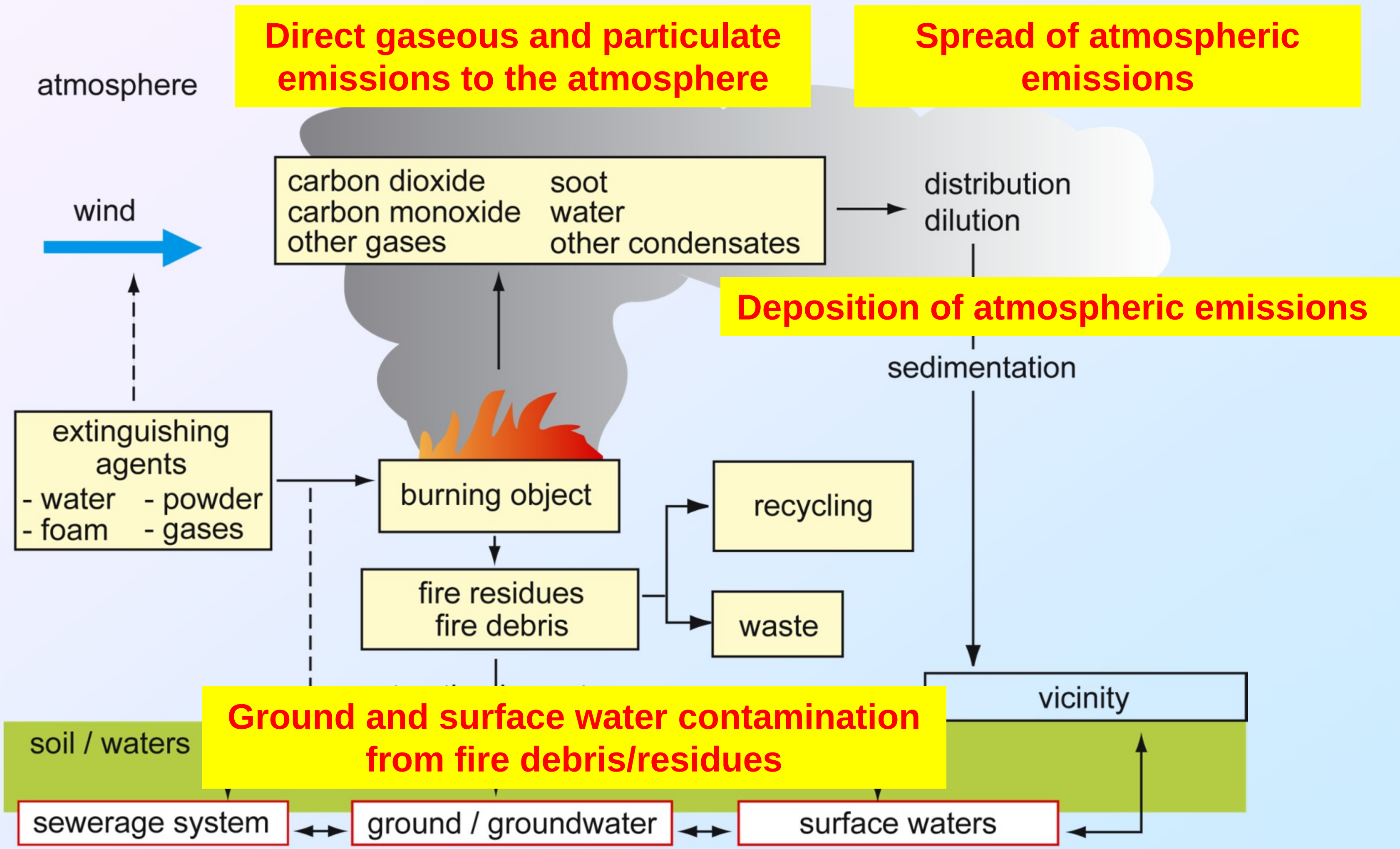
- The growing need to address the flammability of synthetic polymeric materials, as substitutes for natural-based materials, has led to an increase in the use of fire and flame retardant (FR) systems.

- 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.

Emission pathways from fires



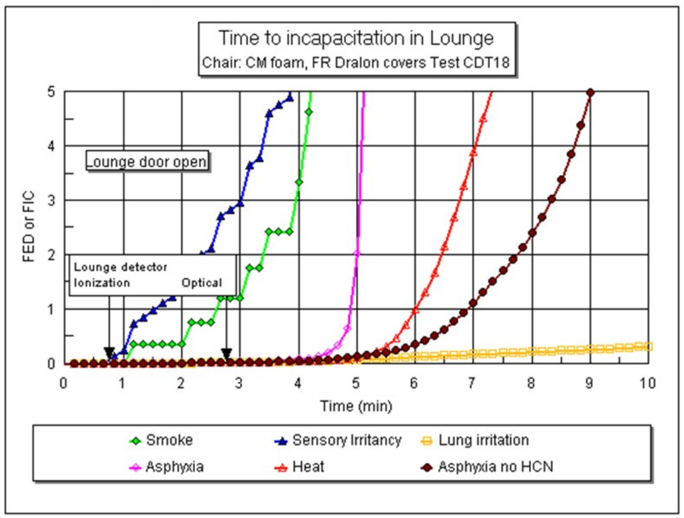
ISO TC92 SC3 - PWI 26367-2: Guidelines for assessing the adverse environmental impact of fire effluents

Toxic Hazards Assessment

The development of toxic hazards in fires depends upon the time-concentration curves of the toxic products, which in turn depends upon:

The yields of toxic gases vary considerably during different types and stages of full-scale flaming compartment fires.

The yields of each toxic product (kg/kg) from different fuels at different times during the fire.



Fire Conditions

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.

Fire Conditions

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.

Fire Conditions

•If the burning material contains nitrogen (as in PU foam, nylon, PAN) the smoke will contain hydrogen cyanide (HCN). .

•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.

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Identification of potential environmental impact

Ecotoxicants with acute effects

Ecotoxicants with long-term effects

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Sequence of fire hazards: Acute Toxicants

- 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

Asphyxiant 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

Irritant gases

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)

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What’s in Smoke and what are the Impacts

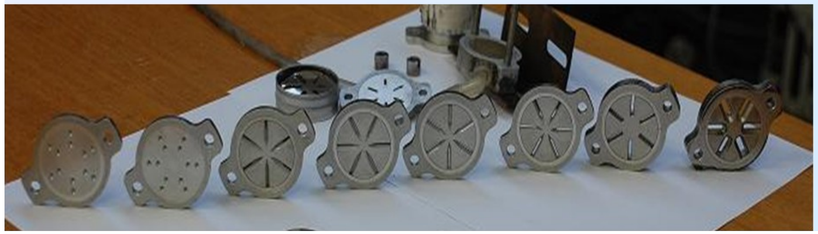
Smoke particles: small, less than one micron in diameter; behave like a gas

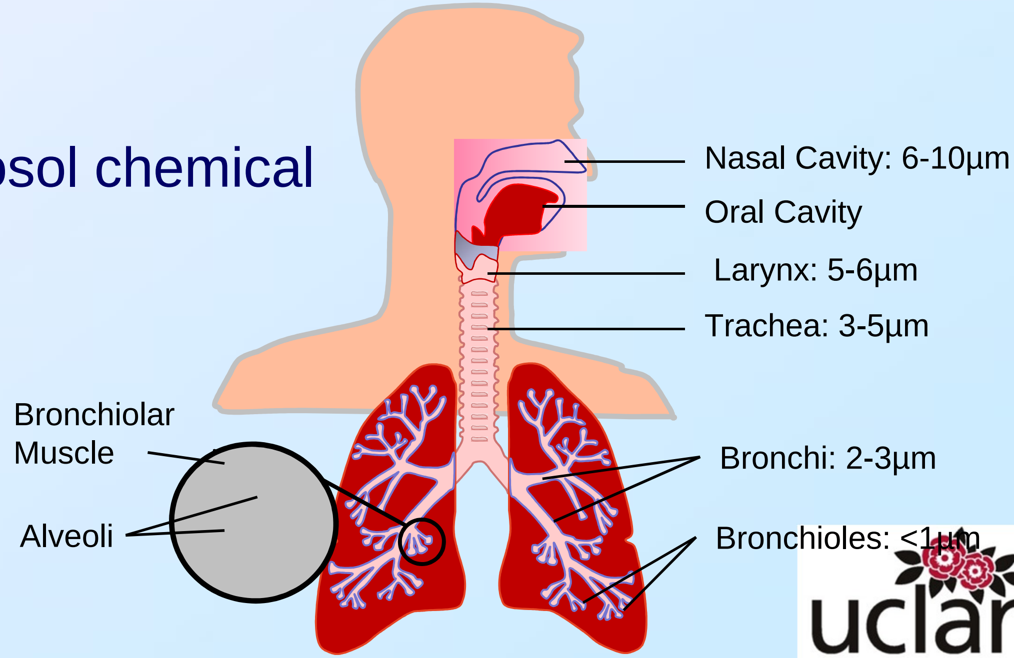
Penetrate indoors and deep into the lung

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

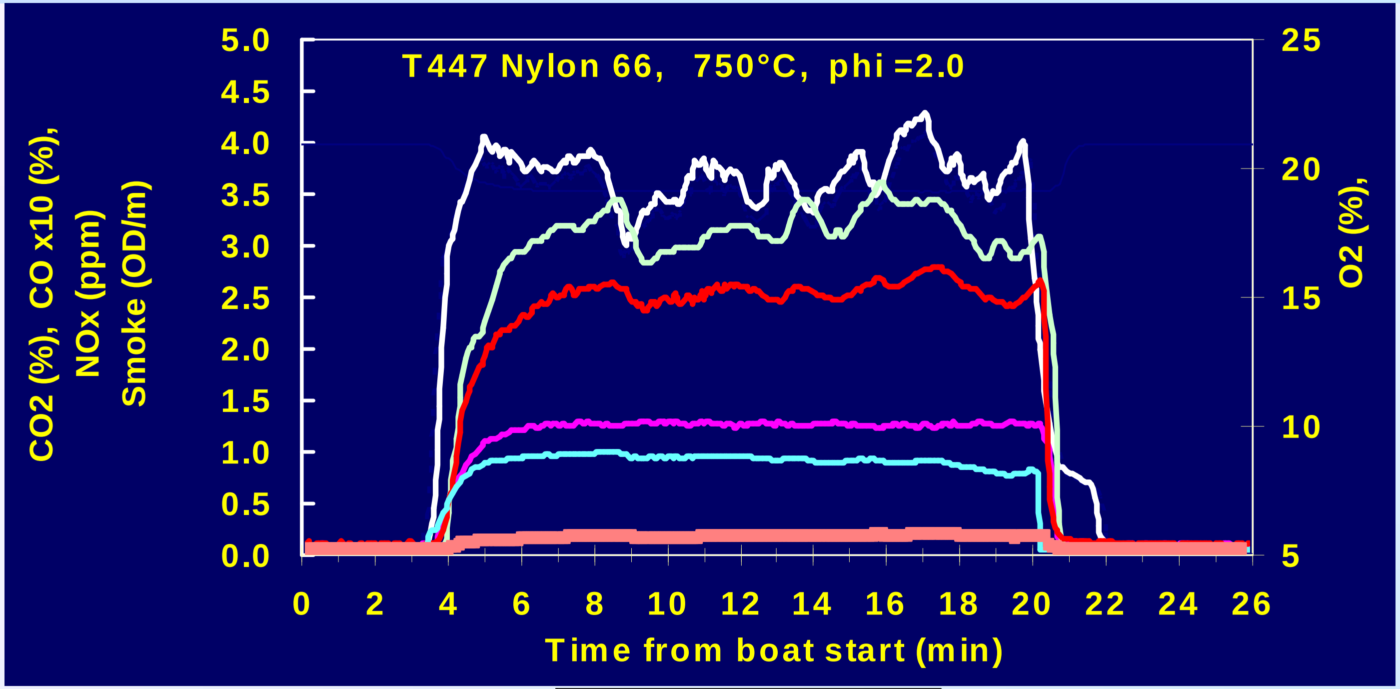
Solid and liquid aerosols are characterized by:

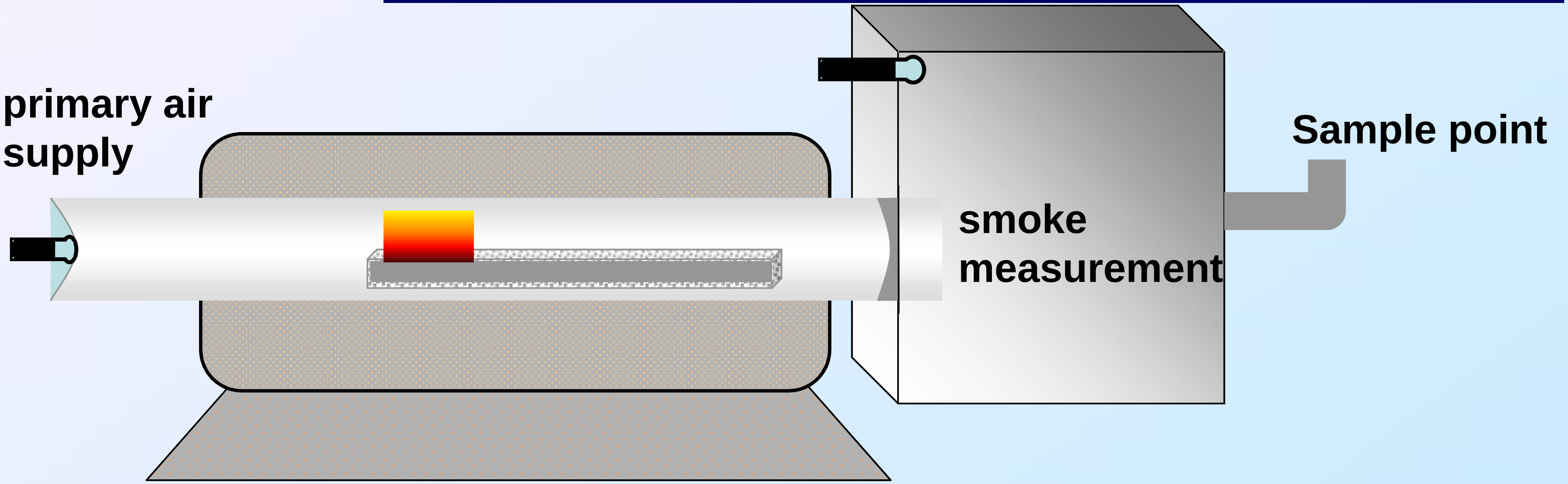
- Concentration,
- Particles size distribution,
- Chemical nature
- Morphology (depending on aerosol chemical nature).





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.

Equivalence Ratio-Classification of the fire stages

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

- $\phi = 1$ "stoichiometric" combustion
- $\phi << 1$ well-ventilated fires (fuel lean flames)
- $\phi > 1$ vitiated fires (fuel rich flames)

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

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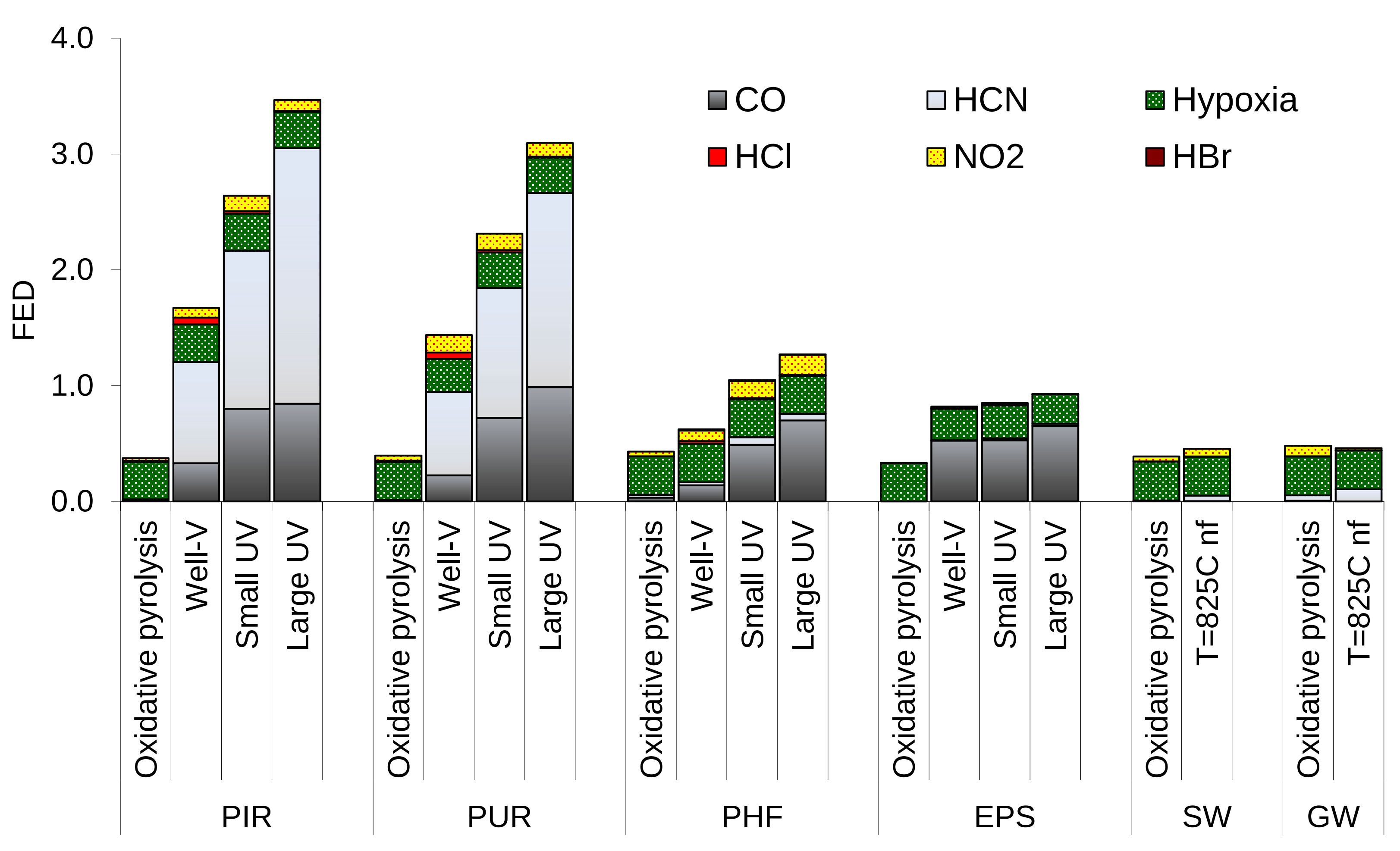
The fire toxicity of six insulation materials (20 g/m³)

Glass Wool (GW)
Stone Wool (SW)
Phenolic Foam (PhF)

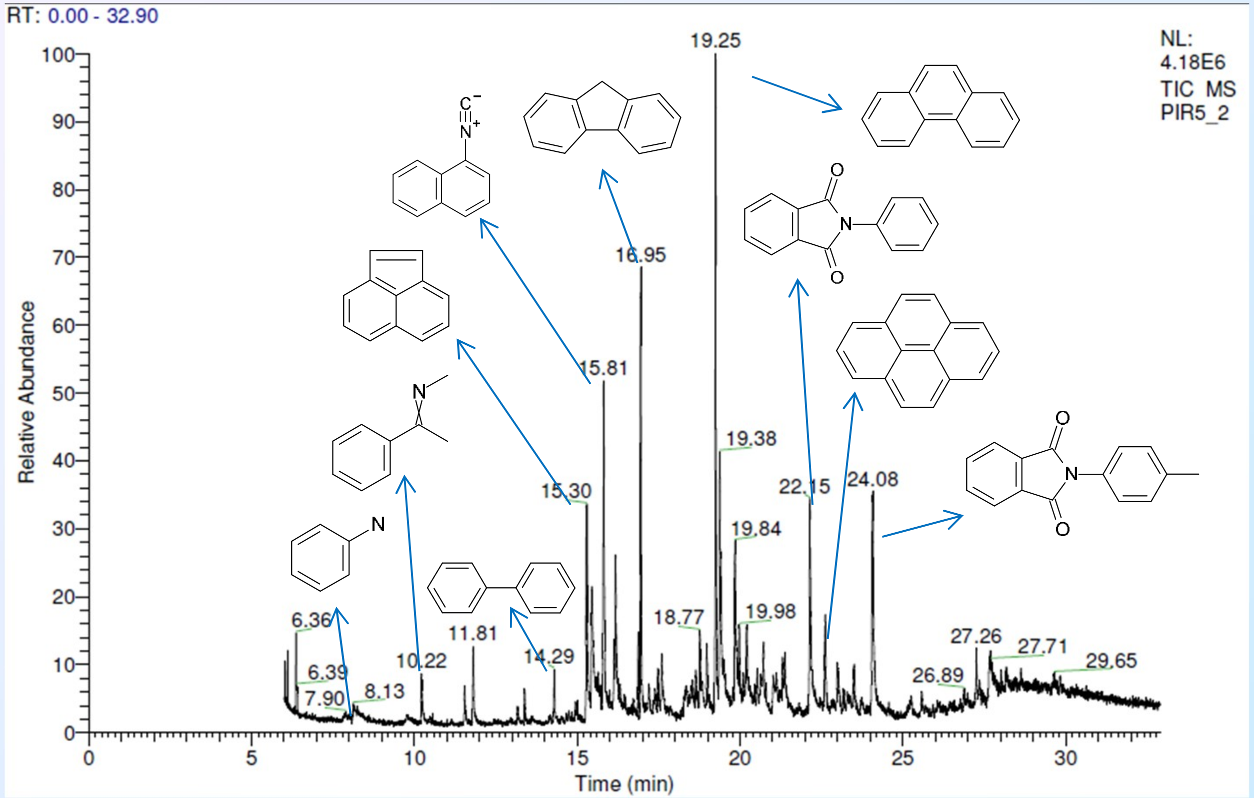
Expanded Polystyrene Foam (EPS),
Polyurethane Foam (PUR)
Polyisocyanurate Foam (PIR)



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

Semi-volatile and Volatile Sampling, Extraction and Quantification Methods Used for Smoke and Soot Analysis

PIR soot extracted using hexane/acetone (3:1) by sonication



GC/MS Solvent Extraction Results (at 600℃)

Compound	Analysed material				
	Polystyrene	EPS	PIR	PUR	Phenolic foam
Aniline			x	x	
Naphthalene	x	x			
N-(1-phenylethylidene)-methanamine			x	x	
2-Methylnaphthalene		x			
Acenaphthylene		x	x	x	x
Biphenylene	x				
1-Naphthyl isocyanide			x	x	
Biphenyl	x	x	x	x	
Fluorene	x		x	x	x
Carbazole			x		
Diphenylmethane		x			
1-Naphthalen-1-yl-ethylideneamine			x		
Phenanthrene			x	x	x
Anthracene	x	x			
1-Methylphenanthrene		x			
Fluoranthene	x			x	x
Diphenylbutadiyne			x		x
Pyrene			x	x	
1-Phenylnaphthalene		x			
2-Phenylnaphthalene	x	x			
2-Methylfluoranthene		x			
Benzo[a]fluorene	x			x	
2-Phenyl-1H-Isoindole-1,3(2H)-dione			x		
Benzo[c]phenanthrene				x	x
Chrysene	x				
p-Terphenyl	x				
2-(4-Methylphenyl)-1H-isoindole-1,3(2H)-dione			x		
Benzo[k]fluoranthene	x				
4,5-Dihydrobenzo[e]pyrene	x				
2-Phenylphenanthrene	x				

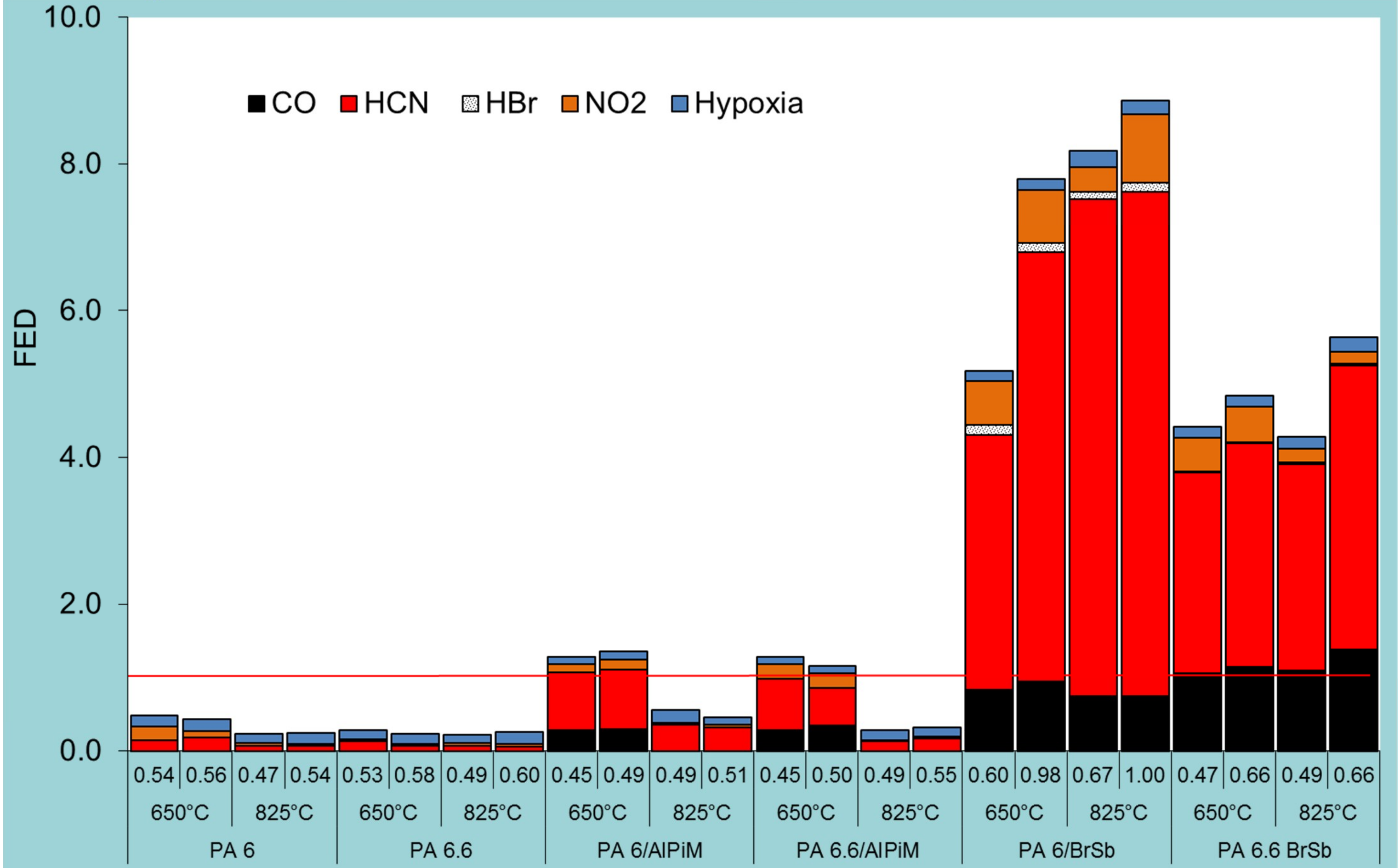
Comparison of commercial polyamide-glass fibre formulations

Industry Standard formulations to UL94 V-0 at 0.8 mm

PA 6 Polyamide 6 with 30% glass fibres (PA6 +GF)	**PA 6.6** Polyamide 6 with 30% glass fibres (PA6 +GF)
PA 6/AlPiM with 20% Aluminium phosphinate(OP1230) and Melamine polyphosphate (Melapur 200/70)	**PA 6.6/AlPiM** with 20% Aluminium phosphinate(OP1230) and Melamine polyphosphate (Melapur 200/70)
PA 6/BrSb with 20% Brominated polystyrene (Saytex HP 3010G) and 6% Antimony Trioxide (Campine 2617)	**PA 6.6/BrSb** with 20% Brominated polystyrene (Saytex HP 3010G) and 6% Antimony Trioxide (Campine 2617)

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

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



PVC Carpet

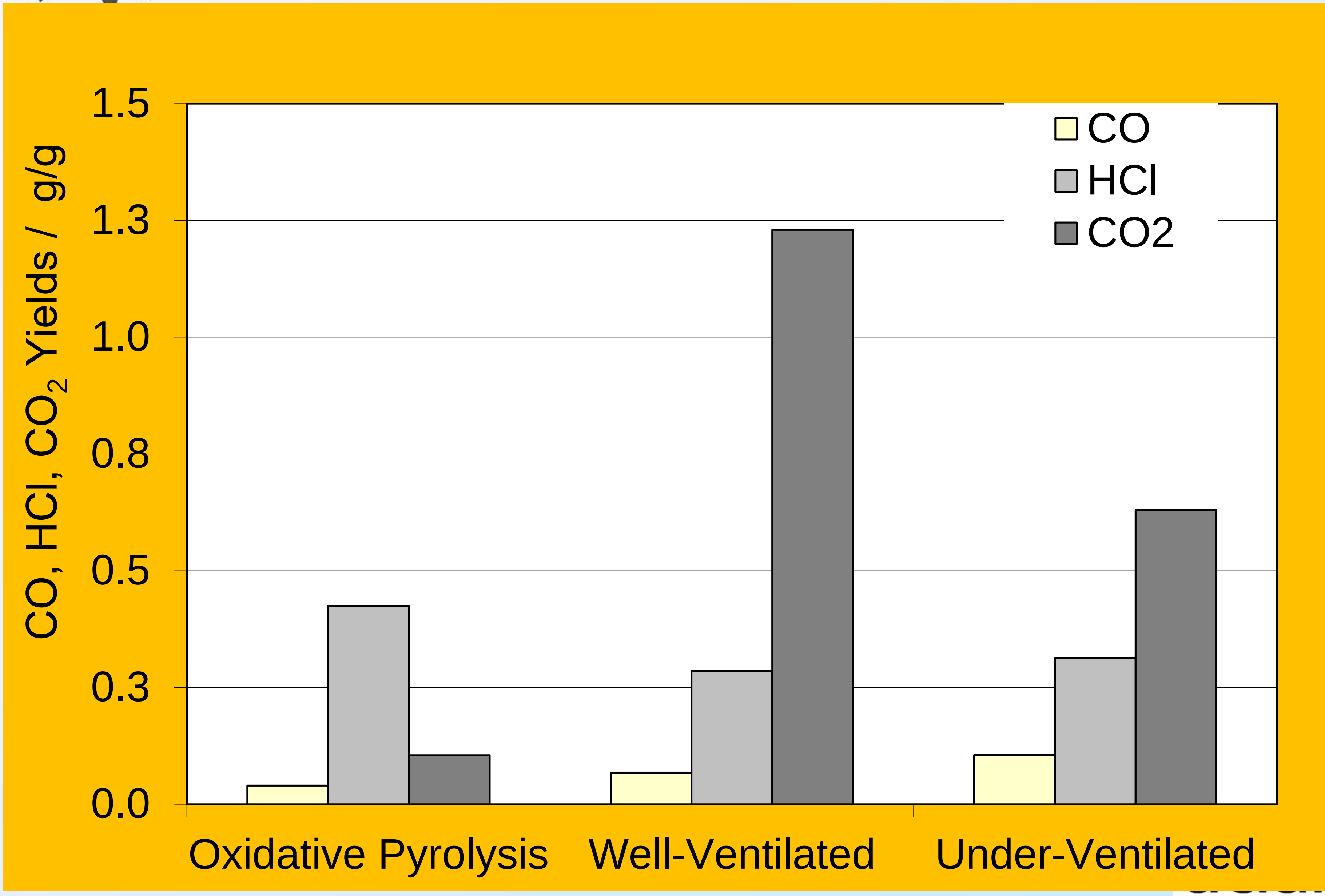
Composition of the PVC-carpet as given by the manufacturer

Component	Weight-%	Surface weight (g/m^2)
Polyvinyl chloride (PVC)	53	1490
Diisononylftalat (DINP)	18	510
Mineral fillers	24	670
Titanium dioxide	2	60
Other components	3	80

Element/characteristics	PVC-carpet
Carbon, C	38.6 weight-%
Hydrogen, H	4.96 weight-%
Nitrogen, N	Not detected
Chlorine, Cl	29.1 weight-%
Combustible part	76.2 weight-%
Density	1360 kg/m^3

A.A. Stec, J. Readman, P. Blomqvist, D. Gylenstam, D. Karlsson, D. Wojtalewicz, B.Z. Dlugogorski *Analysis of Toxic Effluents Released From PVC Carpet under Different Fire Scenarios,* Chemosphere, 90(1), pp. 65-71, 2013.

PVC Carpet- Yields



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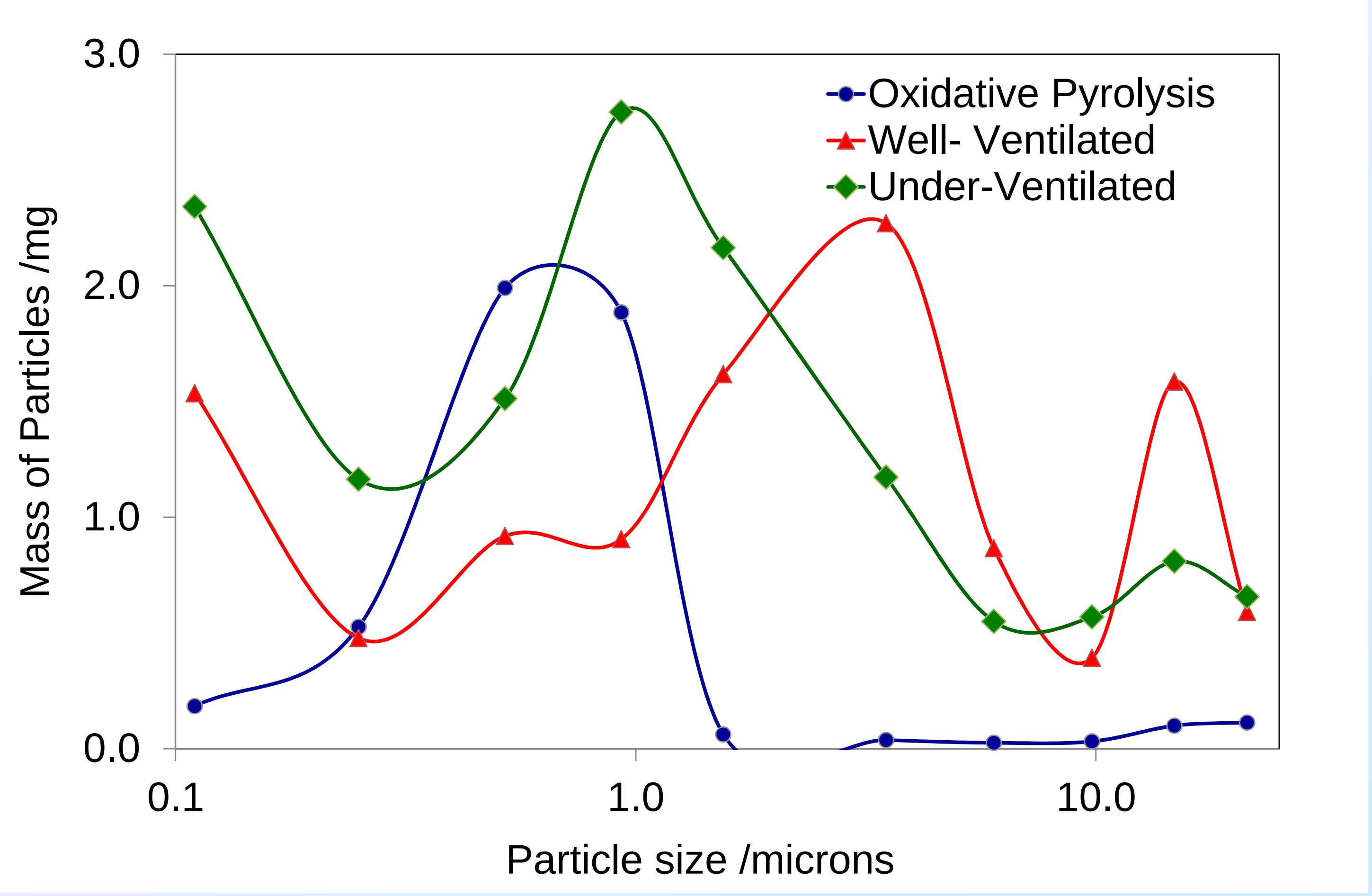
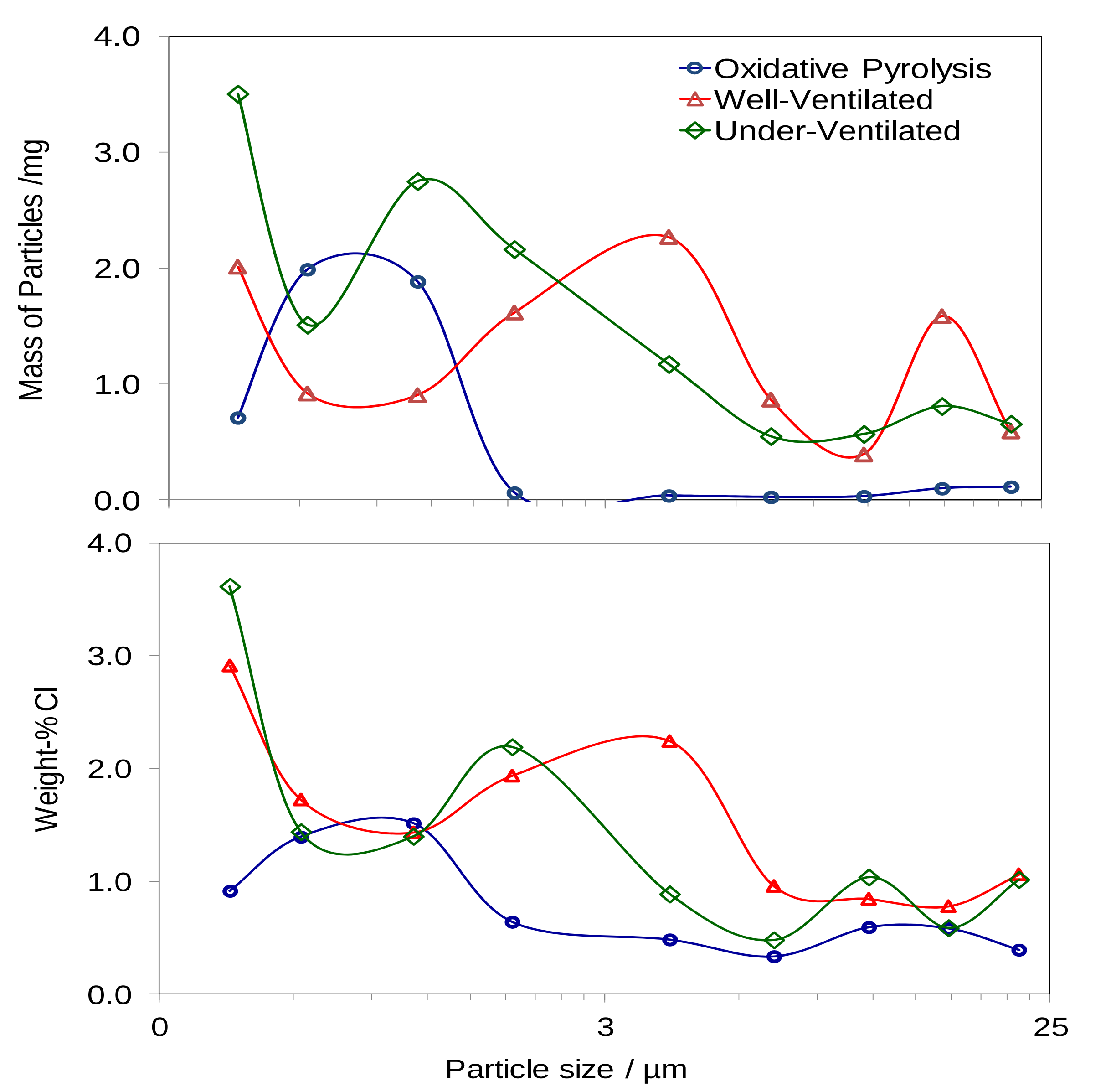
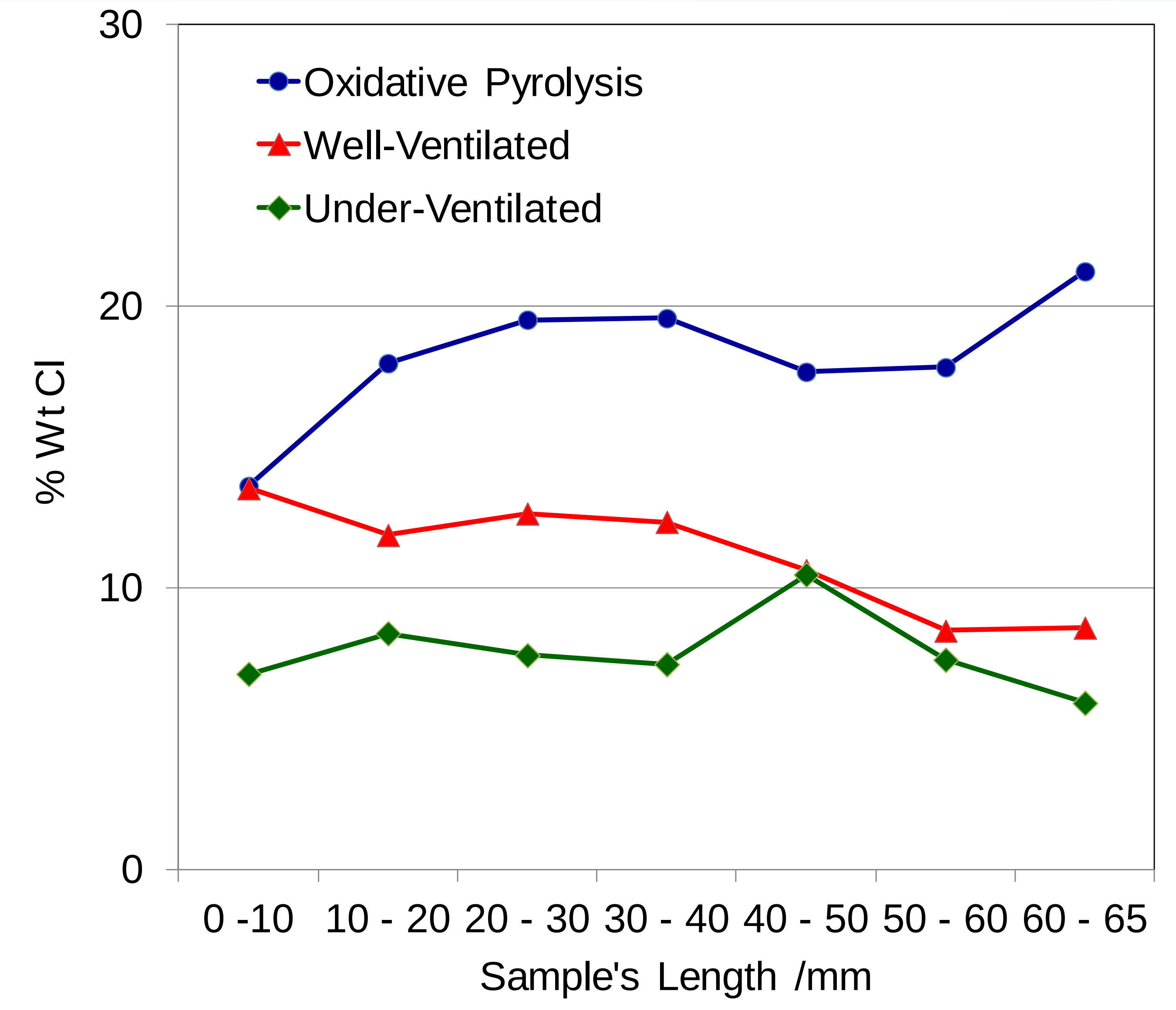
Soot Size Distribution



Chlorine content from cascade impactor plates for different fire scenarios



Chlorine content of residues as a function of sample position in furnace.

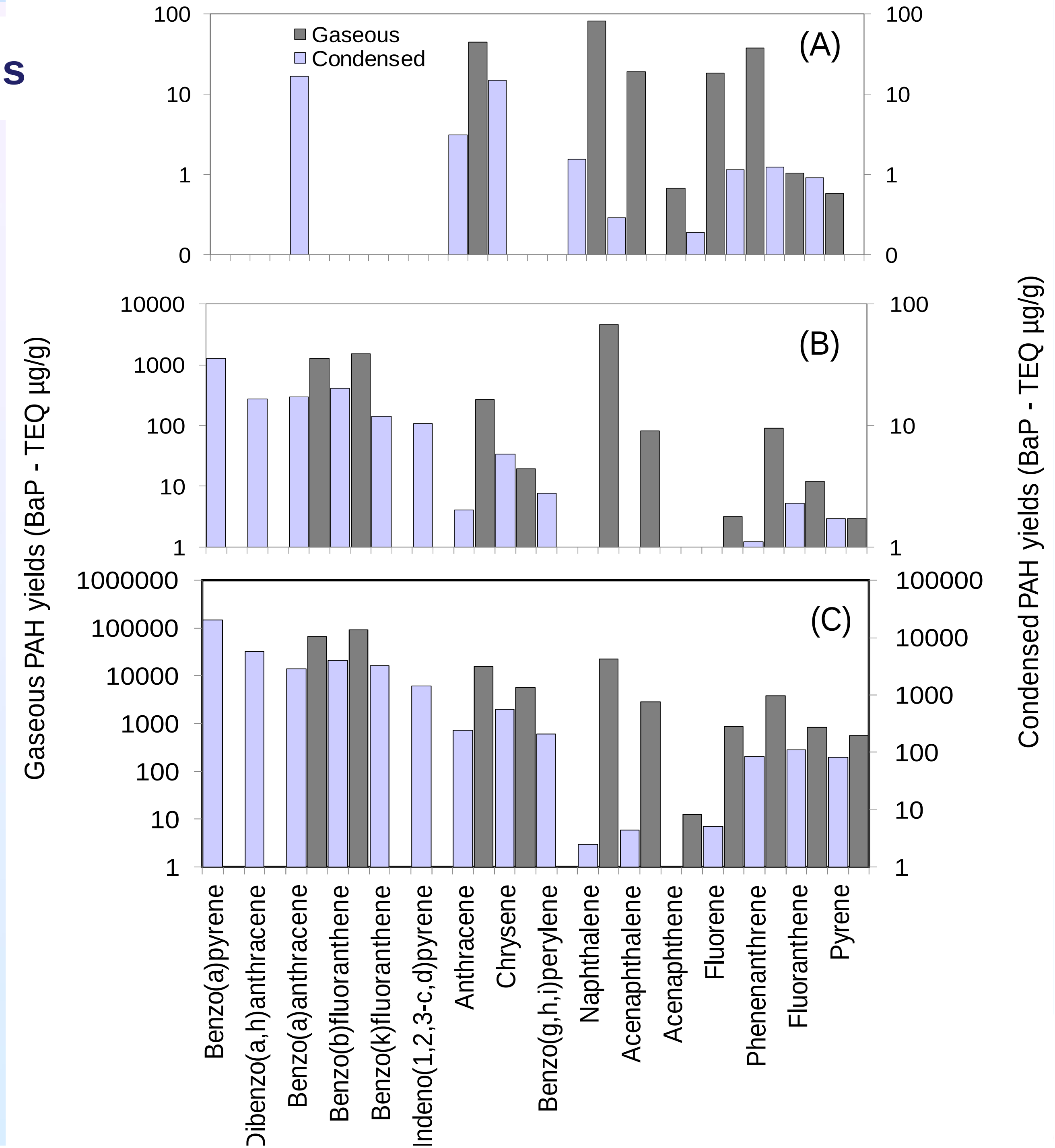


PAHs yields

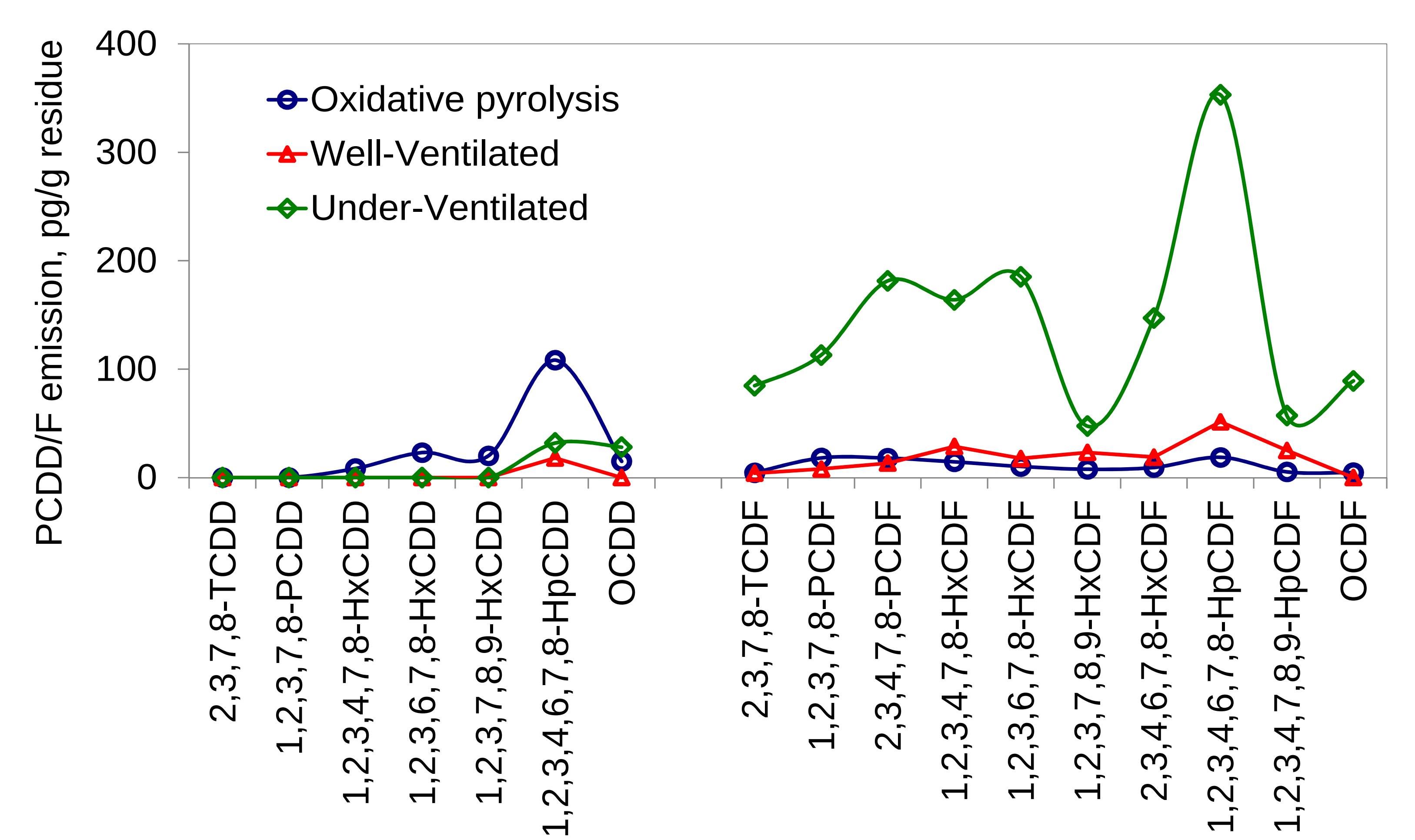
Oxidative Pyrolysis

Well Ventilated

Under-Ventilated



Concentration of PCDD/F in PVC carpet residues under different fire conditions.



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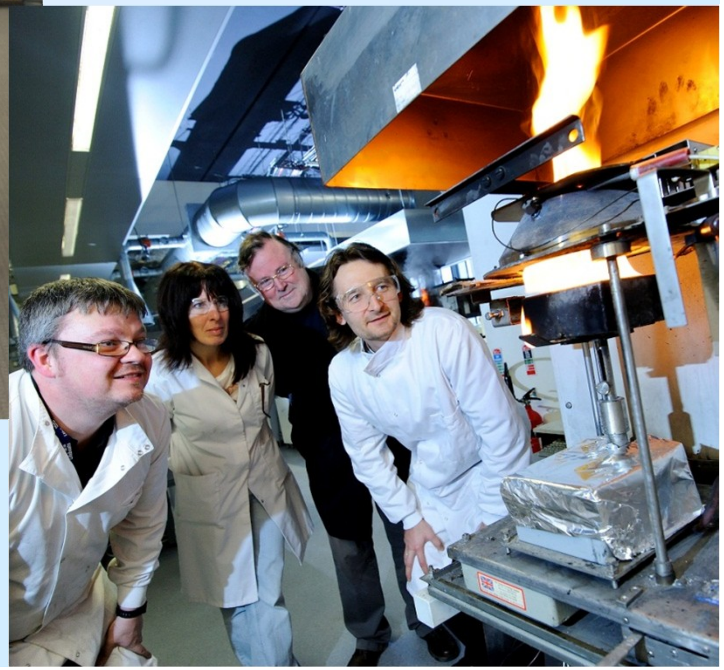
Conclusions: Acute Toxicants

- Fire retardants which act in the gas phase (“flame retardants”) often increase fire effluent toxicity.
- CO is a good indicator of incomplete combustion however, it is not always the major toxicant. The asphyxiants, CO and HCN are much more prevalent in developed flaming.
- Brominated flame retardants increase the yield of both CO and HCN, and have a more pronounced effect than aluminium phosphinate.
- Insulation materials vary widely in their toxic product yields, and potential hazard, as a function of both material and polymer
- Irritants (e.g. organics and smoke particles) are also more prevalent in developed flaming, while HCl is independent of fire condition and NOx is favoured by well-ventilated conditions.

Conclusions: Chronic Toxicants (PVC carpet)

- The chlorine content on the soot and cascade impactor plates was between 0.5 and 2.5 weight-%. There is no significant difference between the well-ventilated and the under-ventilated tests.
- A general trend towards decreasing PAHs yields with increasing molecular mass was seen for all combustion conditions studied. Both well-ventilated and under ventilated combustion of the PVC carpet produced the complete range of PAHs. In the pyrolysis tests, however, only volatile and semi-volatile PAHs were produced.
- Similar concentration of PCDD/F congeners observed for oxidative pyrolysis and well-ventilated fire scenarios. It seems that the PCDD/F toxicity of PVC residues do not depend strongly on fire condition (for T< 650 °C). For the under-ventilated fire scenario, PCDD/F concentrations are significantly higher, especially for toxic congeners of PCDF. As the temperature increased, PCDFs start to dominate over PCDD.

Acknowledgements



Thank you for your attention !

ANY QUESTIONS???

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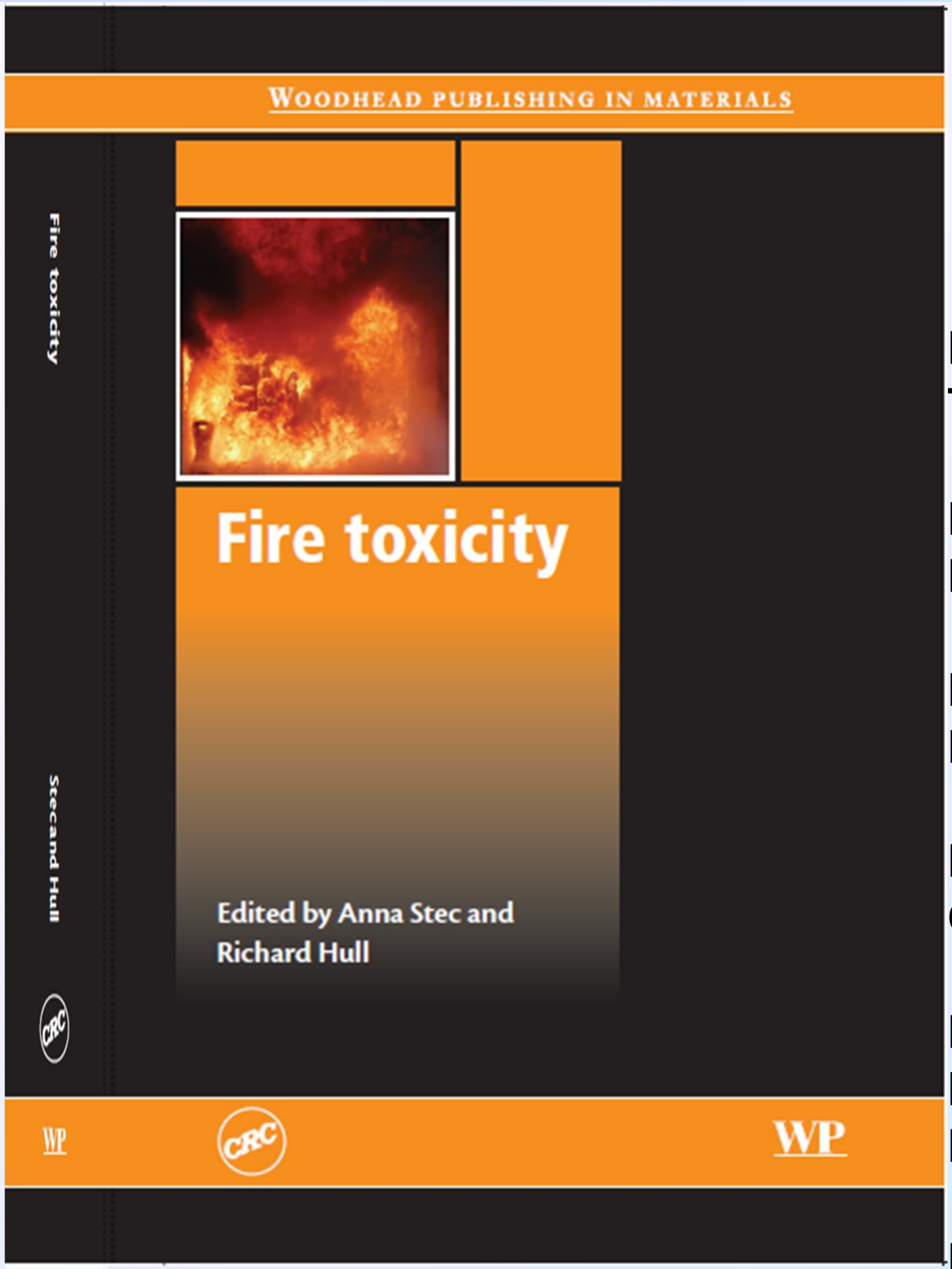

Available March 2010

PART 1 INTRODUCTION TO FIRE TOXICITY,

PART 2 HARMFUL EFFECTS OF FIRE EFFLUENTS

PART 3 BIOLOGICAL ASSESSMENT OF FIRE TOXICITY

PART 4 TOXICITY ASSESSMENT USING CHEMICAL ANALYSIS

PART 5 NATIONAL AND INTERNATIONAL FIRE SAFETY REGULATIONS

PART 6 NUMERICAL SIMULATION OF FIRES AND THEIR HAZARDS

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