How Do Fire Conditions and Synthetic Materials Affect Near Field Chemistry in Urban Wildfires?

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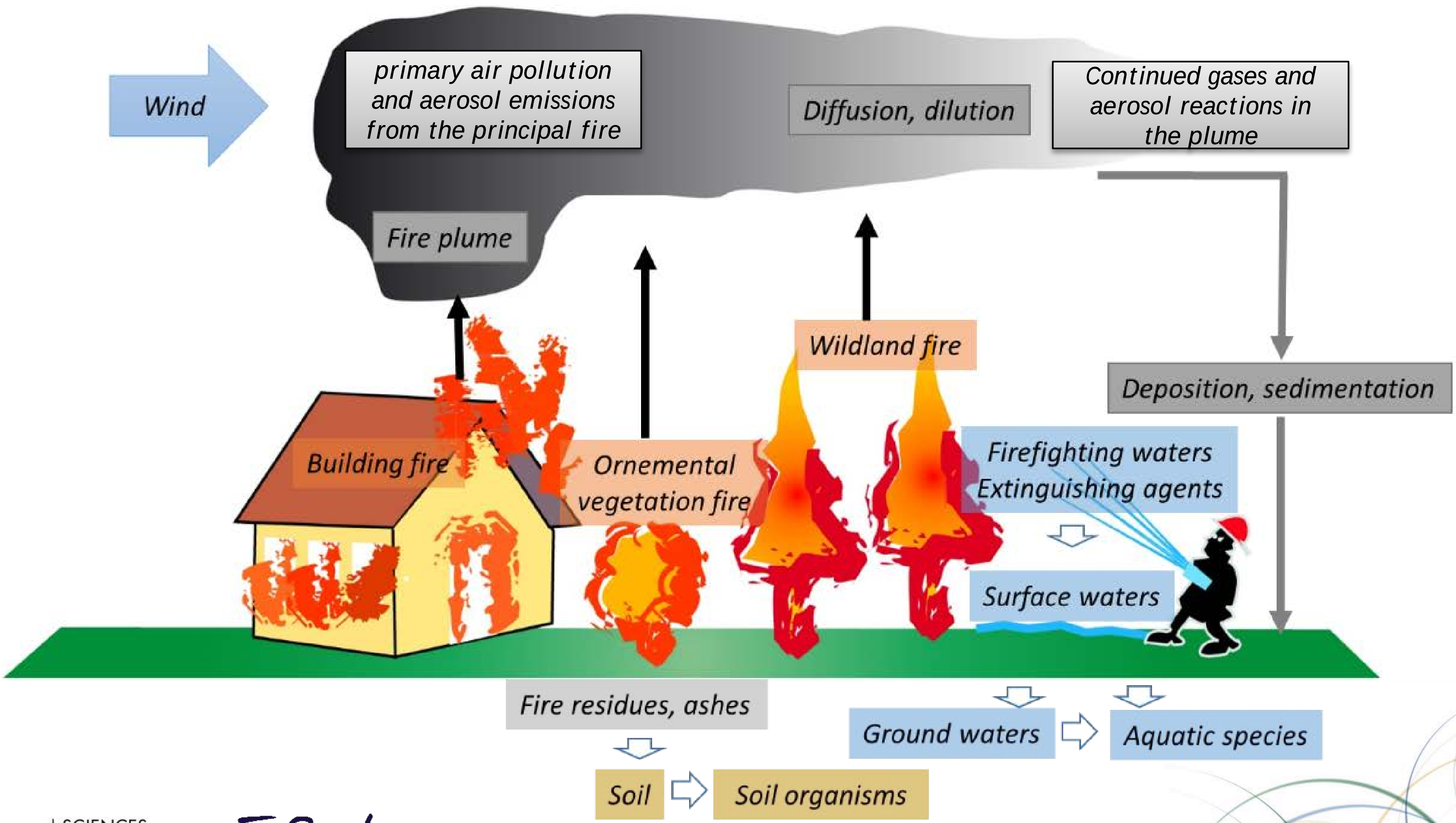
What is the ignition and fire scenario?



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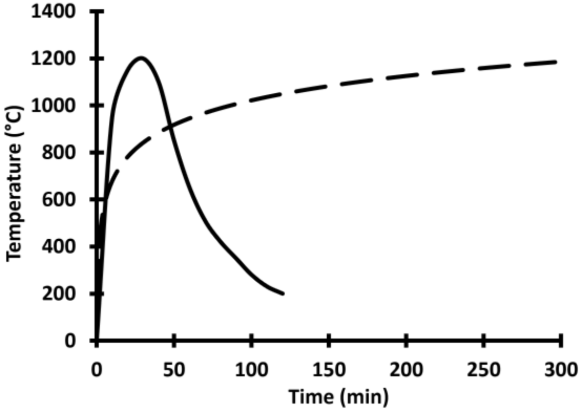
What are the main differences in thermal attack

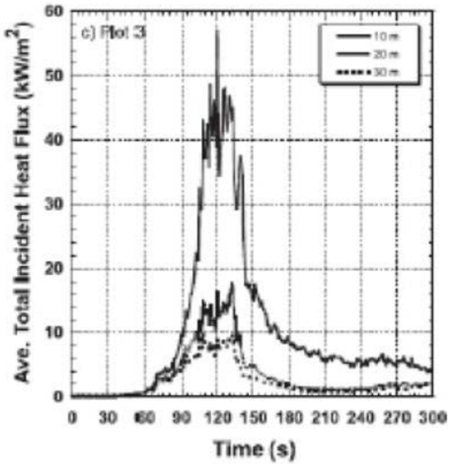
Compartment fires

- Fire growth leading to flashover
- High temperatures, high heat fluxes inside post-FO compartment leading to « incineration » of some combustion products



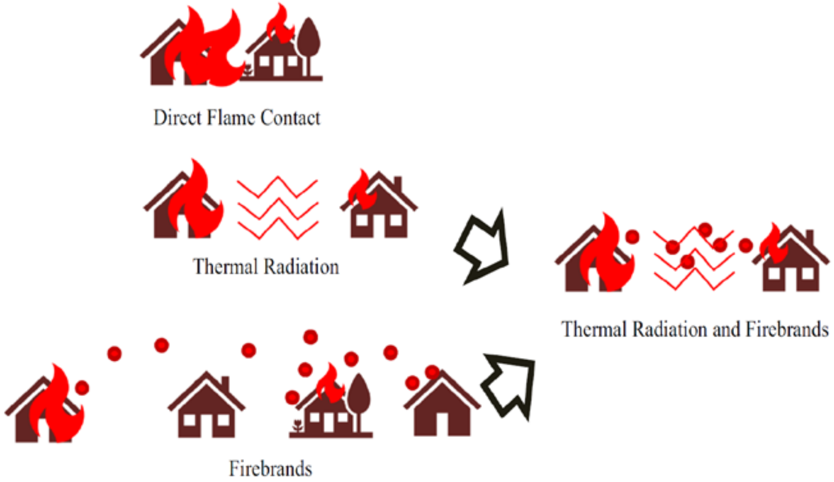
Fires at wildland-urban interface

- Short exposure times to radiation
- Potentially high intensity, pre-heating of surfaces
- Residence time in flame (direct exposure)
- Role of fire brands in heating/ignition process
- Importance of the nature of the wildland fuel:
  - Species, height
  - Ornemental species
  - Humidity



WUI ignition and fire scenarios

Example of Australian approach to define zones



S. Suzuki, et al., The Performance of Wood and Tile Roofing Assemblies Exposed to Continuous Firebrand Assault, Fire and Materials, 41: 84-96, 2017

Firebrands

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The characteristics of thermal attack at the WUI interface

Other parameters that matter:

- Nature of the interfaces and their gapiness (lacunarities)
- Land management
- Vegetation clearing at the interfaces
- Fire size (burning stratum) and propagation speed
- Firefighting and firefighters accessibility

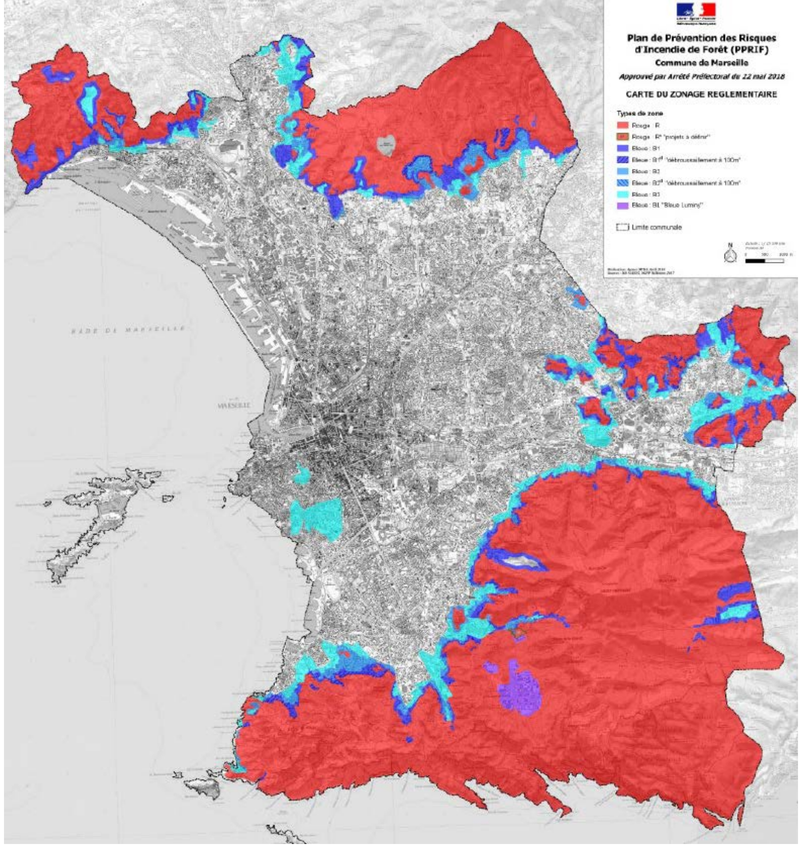
Shrubs, grass

Maquis

Canopy

Canopy

Different kinds of
interactions



Marseille city risk map

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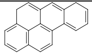
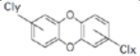
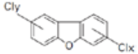
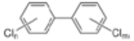
Emissions from fires at WUI

Species of interest

Carbon oxides	Carbon monoxide (CO)	
	Carbon dioxide (CO_2)	
Halogenated acids (hydrogen halides)	Hydrogen Chloride (HCl) Hydrogen Bromide (HBr) Hydrogen Fluoride (HF)	
Nitrogen-containing species	Hydrogen cyanide (HCN) Ammonia (NH_3)	
	Nitrogen Oxides (NO_x)	
	Acrylonitrile or Prop-2-enenitrile (C_3H_2N)	
Sulphur-containing species	Sulphur Dioxide (SO_2) Hydrogen Sulphide (H_2S)	
Aldehydes	Formaldehyde or methanal (CH_2O) Acetaldehyde or ethanal (C_2H_4O) Acrolein or prop-2-enal (C_3H_4O)	
VOCs	Benzene (C_6H_6) Styrene or Vinylbenzene (C_8H_8) Toluene or Methylbenzene (C_7H_8) Phenol (C_6H_5OH) Formic Acid ($CHOOH$)	
Metals	Large variety, including heavy metals	
PAHs[1]	Polycyclic Aromatic Hydrocarbons including benzo-a-pyrene	 *benzo-a-pyrene*
Dioxins, furans and PCBs[2]	Dioxins	
	Furans	
	Polychlorobiphenyl	
Aerosols	Conventionally classified as PM_{10} and $PM_{2.5}$, a mixed liquid-solid particulate matter, sometimes sub-specified in their components (black carbon, organic carbon, H_2SO_4,…)	
Firefighting chemicals	Perfluorinated compounds Diammonium phosphate Ammonium sulphate	

Acute toxicants

Chronic/long term toxicants

[1] WHO proposes conventional methods of combination of PAHs in equivalent benzo-a-pyrene to assess toxic effects (Nisbet & Lagoy, 1992).

[2] WHO proposes conventional methods of combination of dioxins, furans and PCBs in equivalent 2,3,7,8 TCDD to assess toxic effects (Kutz, et al., 1990) (World Health Organization, 1998) (Van den Berg, et al., 2006)

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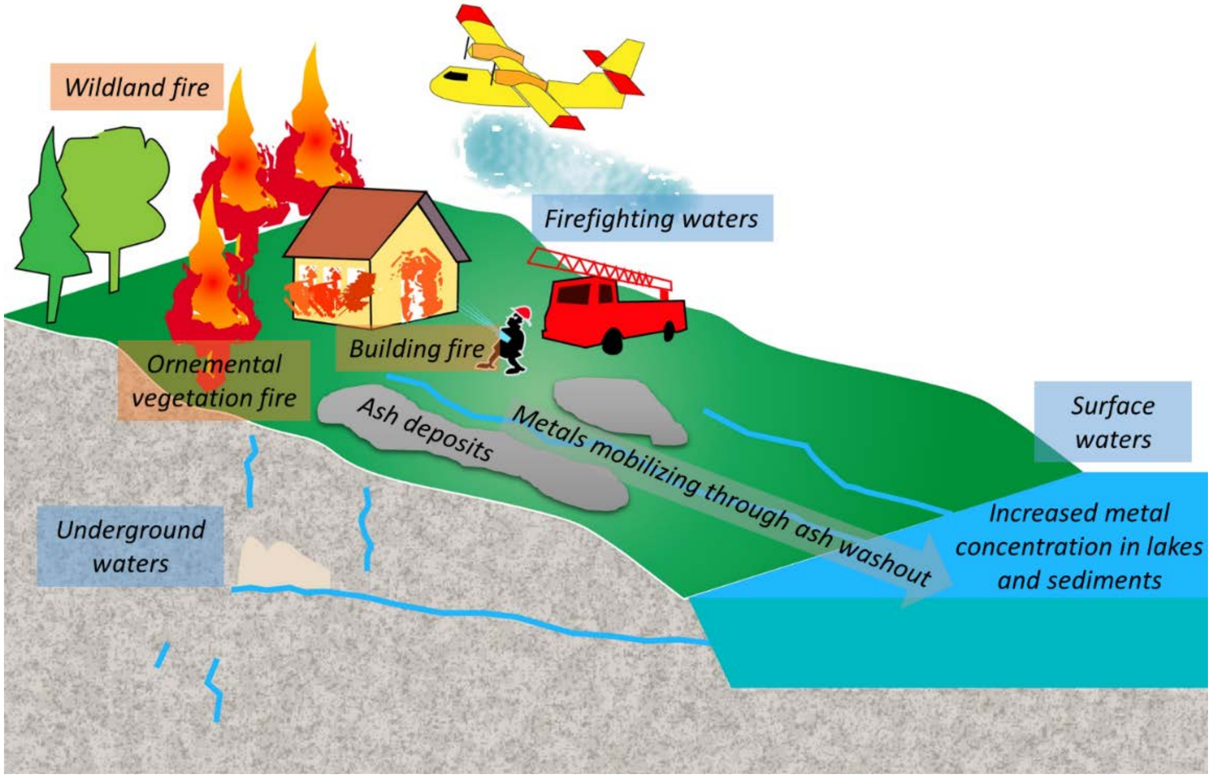
Contamination targets



Differences between wildland fires and fires at WUI, e.g. firefighting run-off waters go directly to waste water network

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How does this affects construction products pyrolysis and combustion?

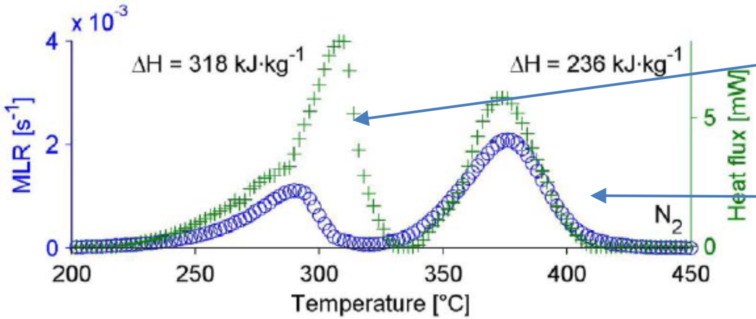
Chemical approach of gaseous fuel

- Need to study separately solid and gas phase, and consider their coupling
- Fire scientists often do not consider enough gaseous fuel as of importance
- Models often reduce gaseous FUELS to FUEL
- Accurate representation of flame requests proper knowledge of the gaseous fuel mixture
  - Turbulence calculation
  - Soot formation, radiation

Chemistry of fire pyrolysis (1)

- Description of solid phase based on mass loss rate as function of local temperature, i.e. using Arrhenius-like functions
- This is a very partial description:
  - Mass loss from the solid could correspond to various fractions simultaneously or consecutively
  - Combustibility domain of the fuels is a key parameter.
  - Combustibility domains depend on pressure and temperature

Example case: polyurethane (from Bustamante thesis)



1st released, under 300°C, is made of isocyanates. This is not combustible under 400°C

2nd released, after 350°C, is polyols-based. This is combustible

Chemistry of fire pyrolysis (2)

- Gas phase reactions are not governed by their kinetic: too fast compared to the phenomena that interrest us in fires
- The combustion in gas phase is driven by mixture, meaning **combustibility domains**
- Solid phase reactions are governed by heating rate, oxygen diffusion and their kinetics
- Residence time in flame and plume is also a key parameter

- Fuel species have several impacts on radiative balance:
  - Spectral dependance of emission / absorption down the flame
  - Influence on flame shape modifies view factors

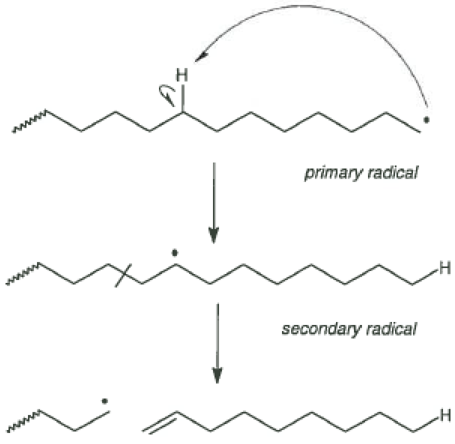
General Case for Thermoplastics

- Degradation occurs in 4 mechanisms (Bolland, 1947):
  - Random-chain scission
  - End-chain scission
  - Chain stripping
  - Cross-linking

- Scission may occur, in weak points or in end of chain, resulting to the formation of lighter chain fragments

- If these chain fragments are light enough, they could be released as a gas

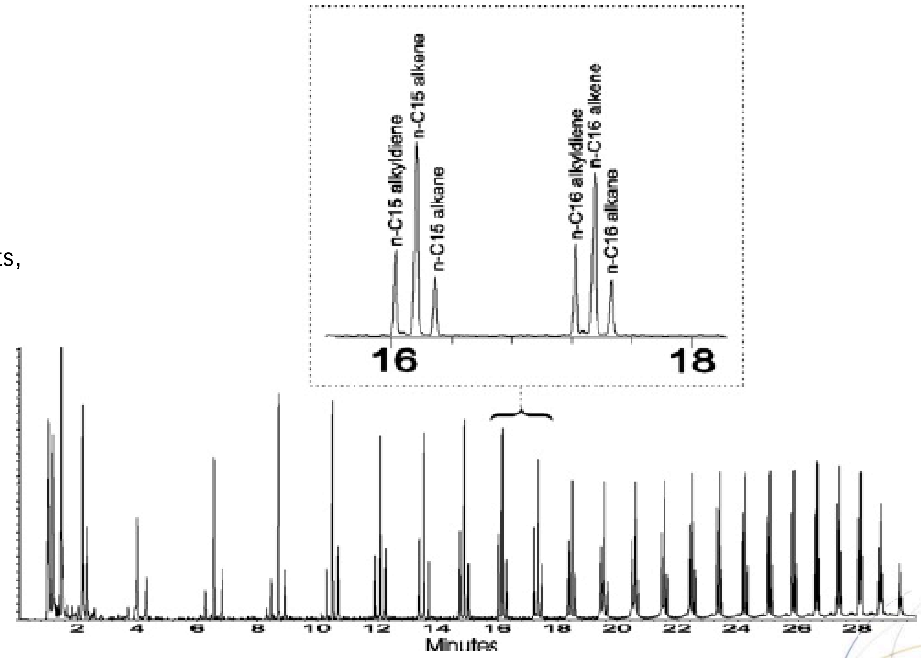
- Processes may differ in « real » materials due to crosslinking, generating unsaturated, isomeric, and aromatic fragments that then contributed much more readily to soot/aerosol formation



Typical example of scission process in a polyolefine

Polyethylene (1)

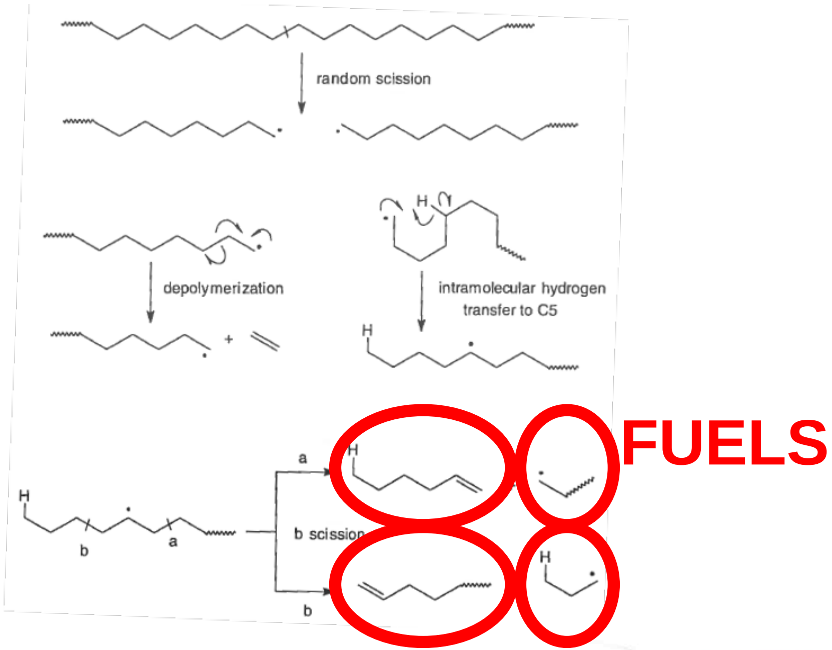
- Pyrogramm obtained by PyGC-MS
- Various hydrocarbons, all chain lengths
- Characteristic of polymer scissions:
  - from classic beta scission for normal and iso-alkyl components,
  - followed by isomerization



Polyethylene (2)

- What happens chemically ?

Thermal degradation of PE showing initial random scission, depolymerization, intramolecular hydrogen transfer and β-scission



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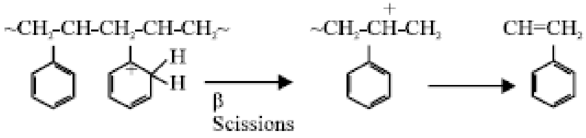
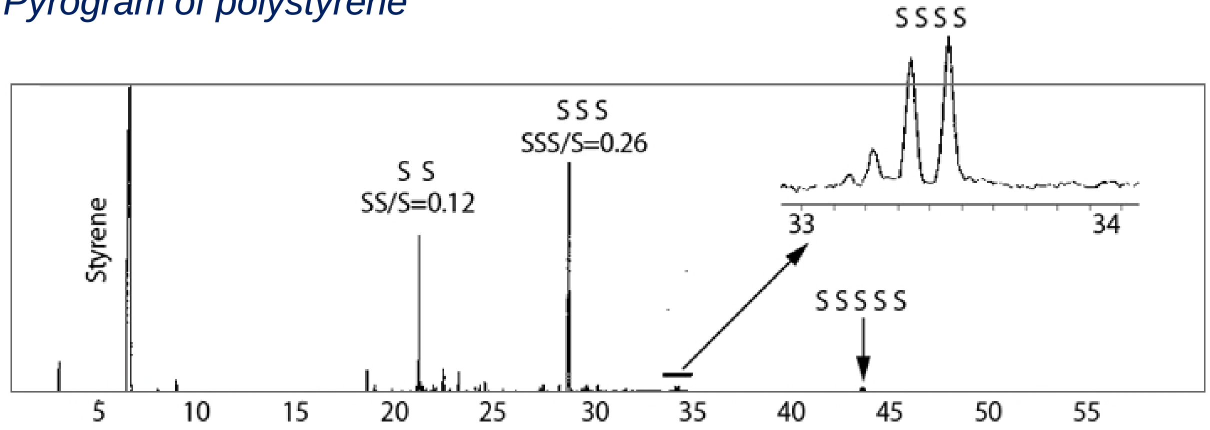
Polystyrene (PS)

- Releases mainly its monomer, styrene, and in less proportions as dimers or trimers

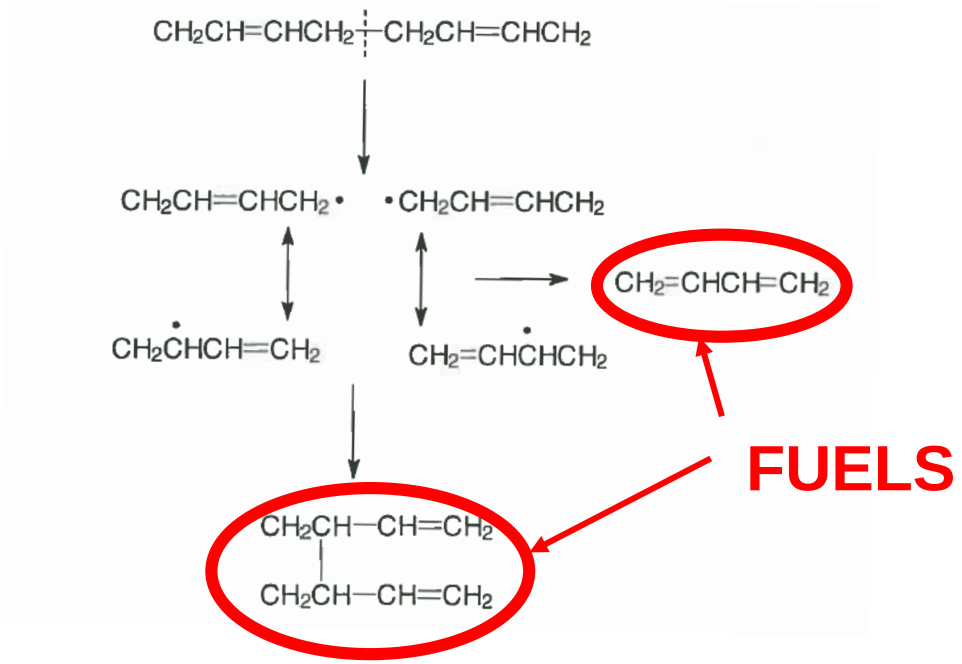


Pyrogram of polystyrene

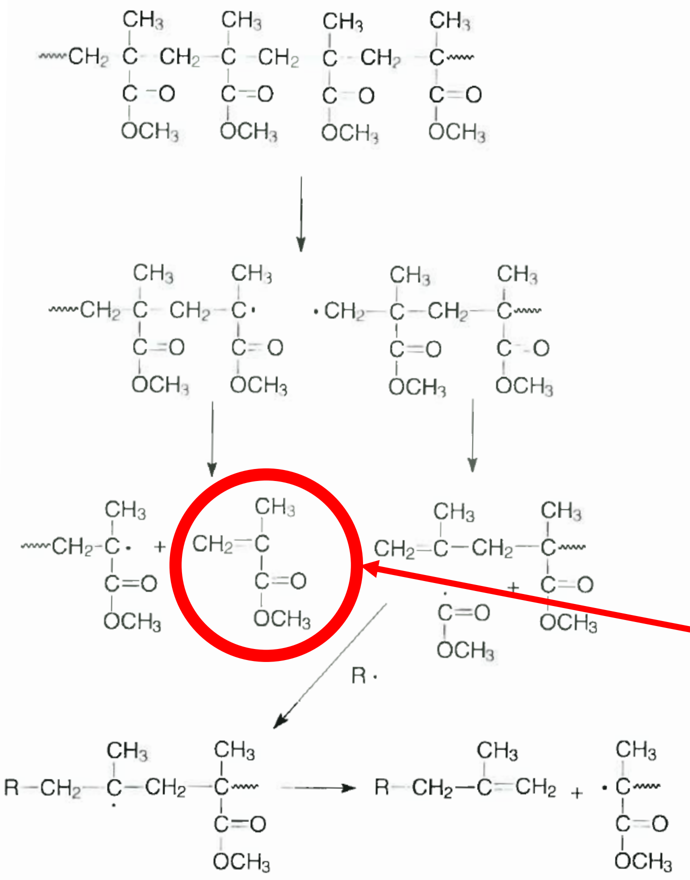


Polybutadiene

- Formation of monomere and dimere by cross-linking



PMMA



FUEL

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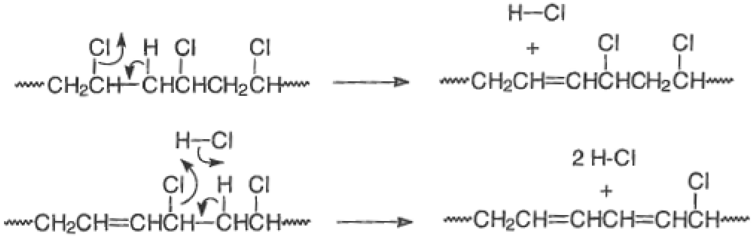
Polyvinyl Chloiride (PVC)

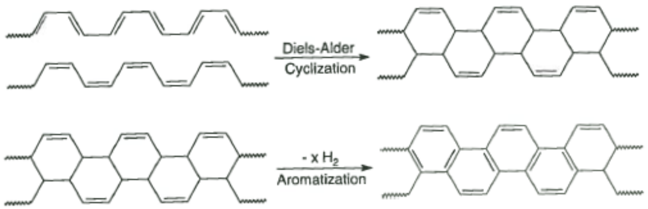
1st step: autocatalytic dehvdrochlorination. Releases HCl.

1



2nd step: cyclation and aromatization, leading to the formation of a char

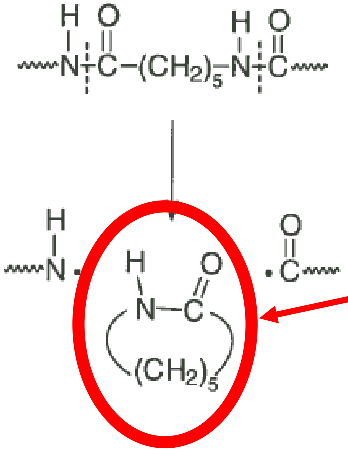
2



It means no fuel released in gas phase, except additives such plasticizers.
At 2nd step, production of dihydrogene. After, oxidation of char due to oxygen diffusion, producing CO

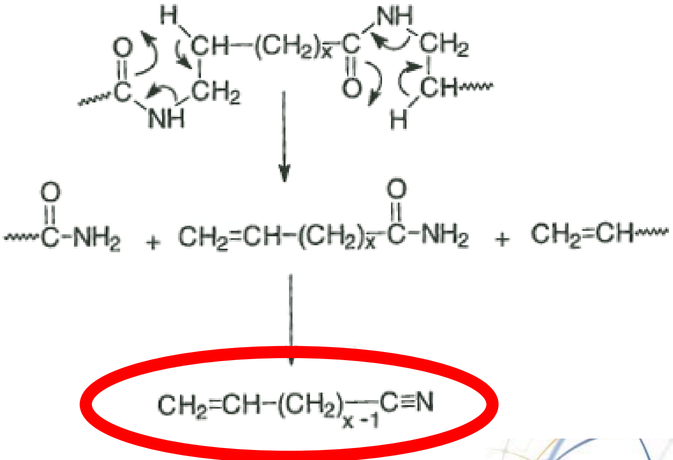
Polyamides (1)

- In the case of PA-6, fuel is Caprolactame, quite heavy molecule



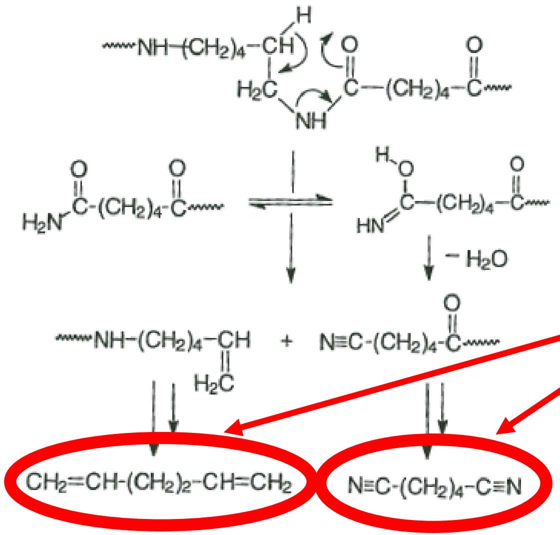
FUEL

- For larger polyamides such PA-10, the lactam is less important. Major products are nitriles and olefines (see right)



Polyamides (2)

- In the case of PA-6-6, 2 fuels are produced, close to inital monomers



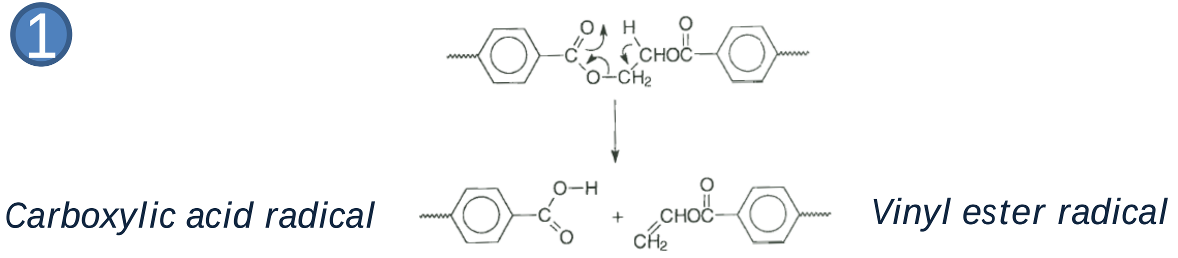
FUELS

1,5-hexadiene

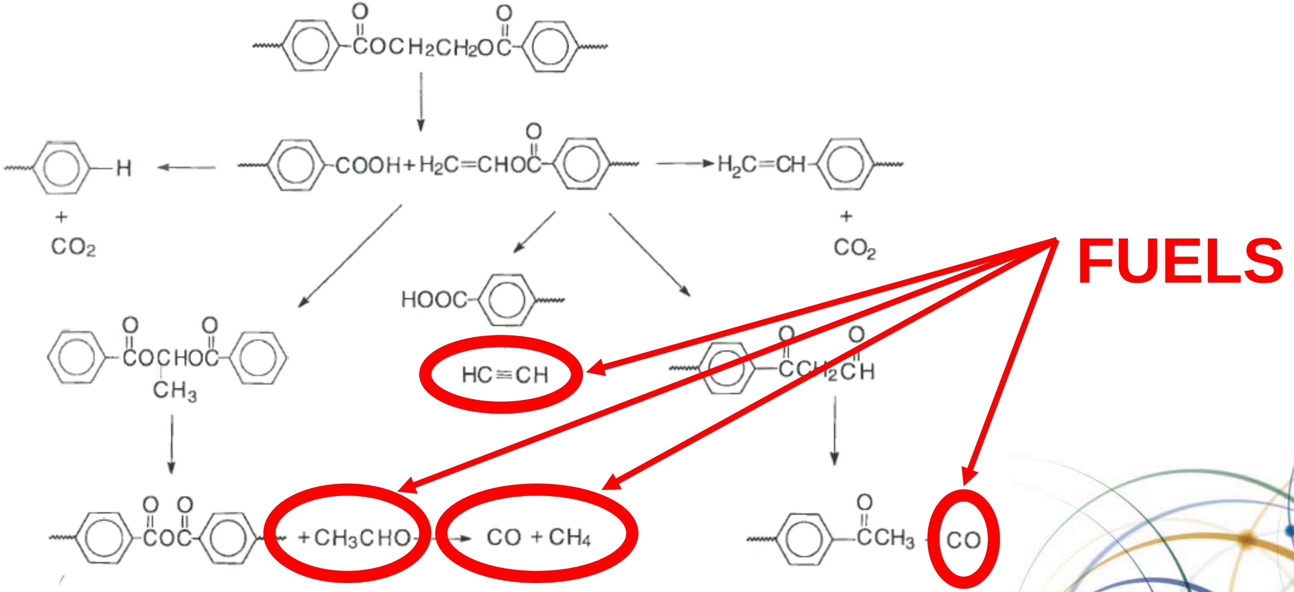
1,4-dicyanobutane

Polyesters – Polyethylene terephtalate

1



2



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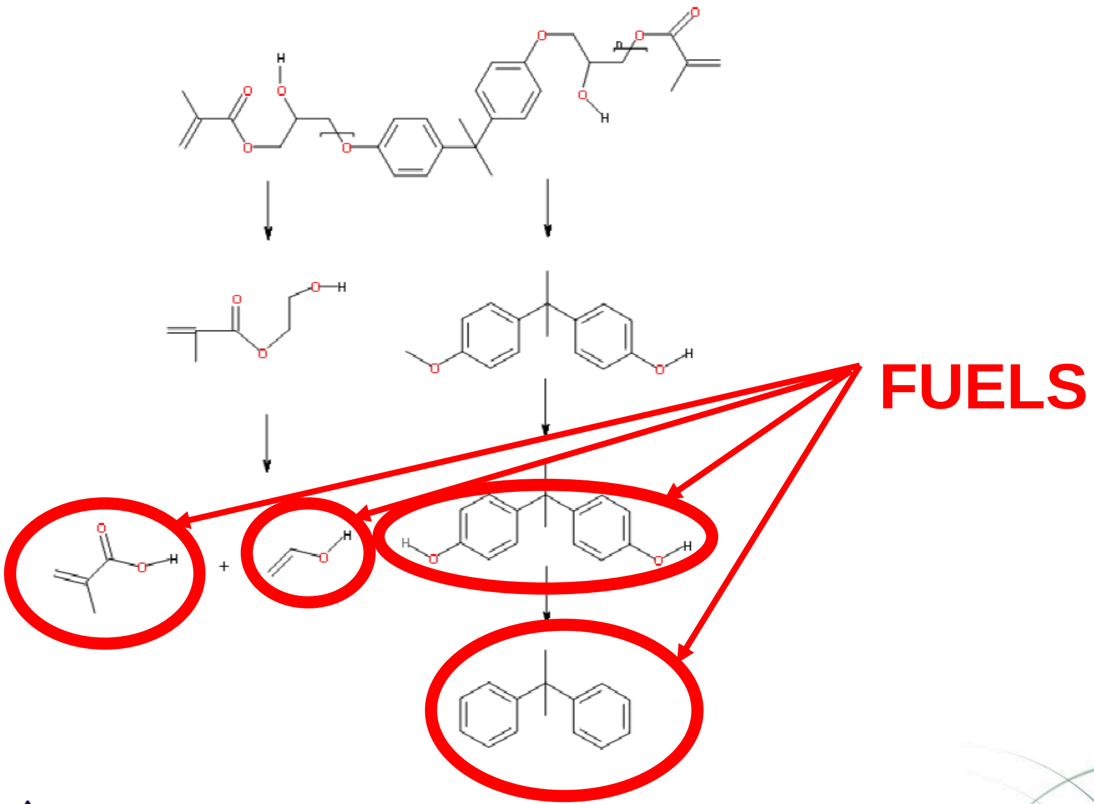
Unsaturated Polyesters and vinylesters

Vinylester



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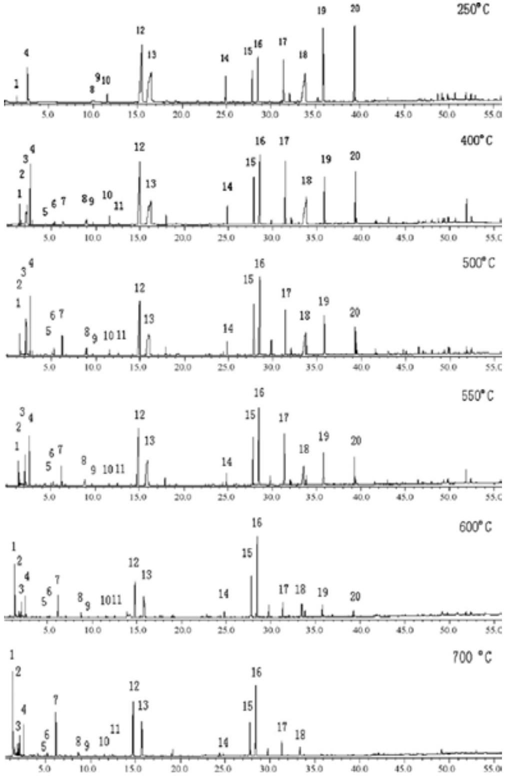
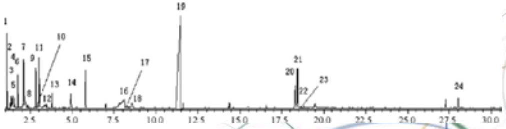
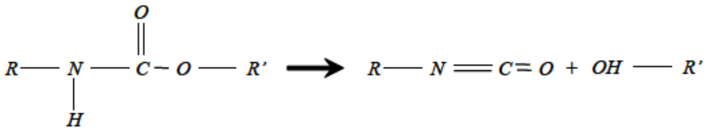
Polyurethanes



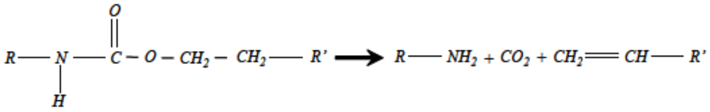


- Typical dissociation mechanisms and examples of temperature influence in pyrograms

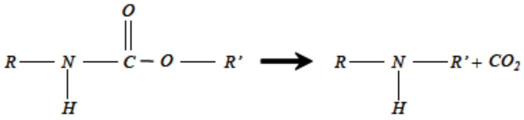
1) dissociation to isocyanate and polyol



2) dissociation to primary amine, olefin and carbon dioxide



3) elimination of carbon dioxide, leading to formation of a secondary amine



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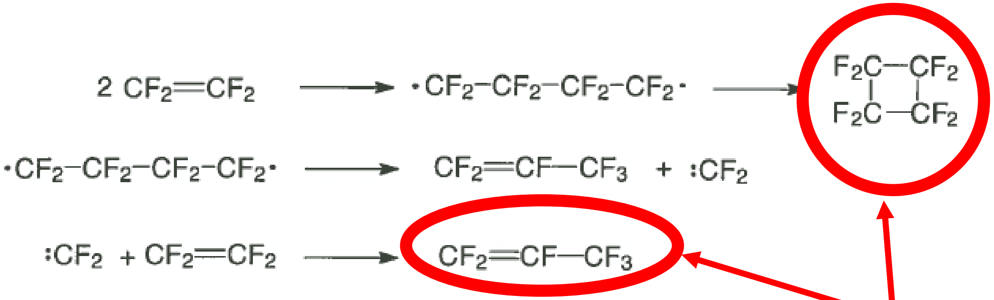
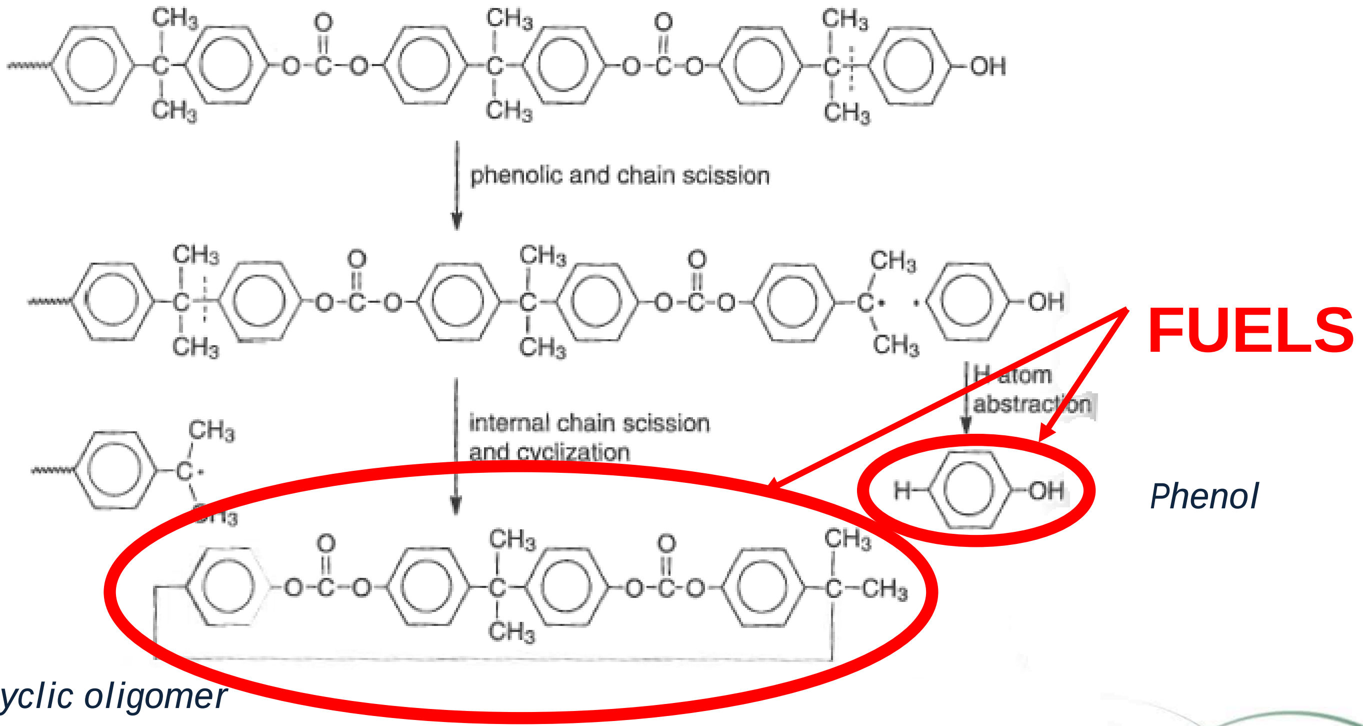
Polytetrafluoroethylene (PTFE)



Non-combustible

Polycarbonates (PC)

- Bisphenol-A based Polycarbonate



Phenol

Cyclic oligomer

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Example of PVC

- Massively used in construction for claddings, windows, shutters, rain gutters and drains
  - Rain gutters are a choice target for fire brands accumulation
  - Vertical surfaces such windows and shutters have a good view factor for radiation heating
- PVC as an intrinsic good resistance to ignition but releases much more HCl than natural fuels
- Incomplete combustion and chlorine may potentiate generation of dioxins and furanes

Anthorpic additional threats

Fire can mobilize or suspend some anthropic sources of pollution

- Flame retardants, fillers and nanofillers
- Toxic products from construction (sometimes years after installation, due to slow renewal of building stock)
  - Anti-mold or anti-rot products, e.g. Copper chrome arsenate (CCA) or antimony salts used in timber treatment
  - Asbesto used in old constructions
  - Etc,
- Pesticides and fertilizers, e.g. in gardens or farms
- Everything from past uses, e.g. chernobyl grass fires

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