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Workshop on Aerosol Impact in the Environment: from Air Pollution to Climate Change

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Aerosol Emissions processes

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Anthropogenic Emissions from small domestic heating plants

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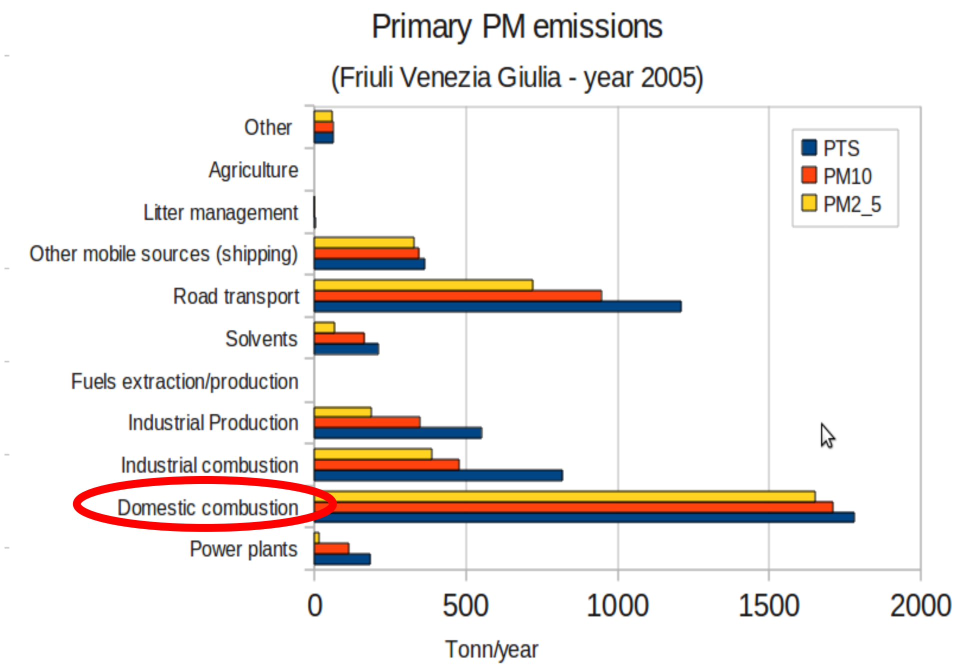
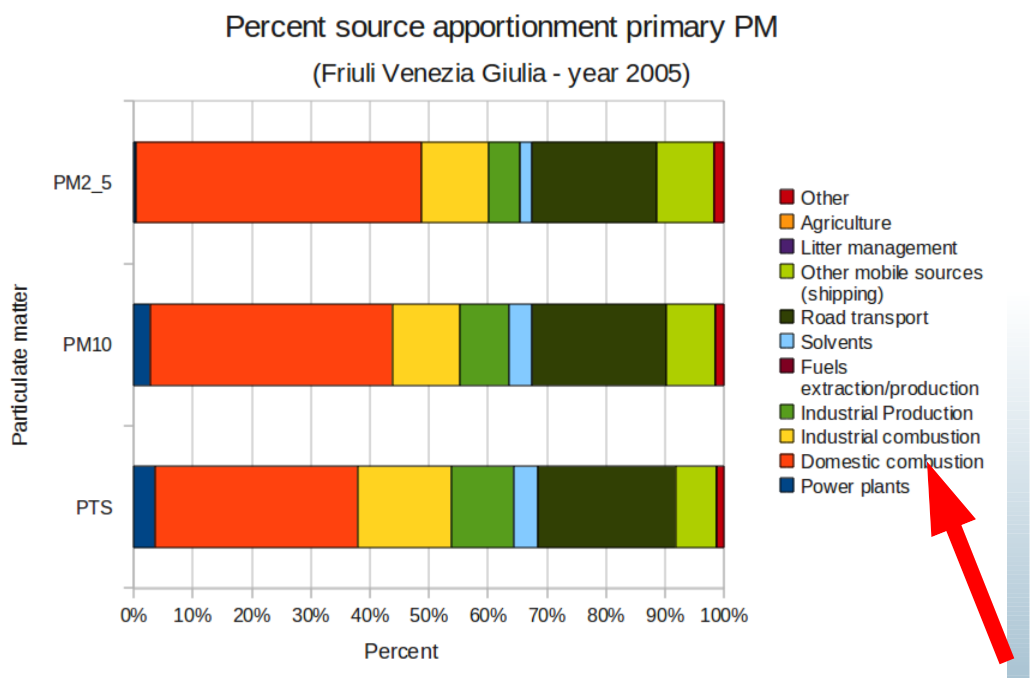
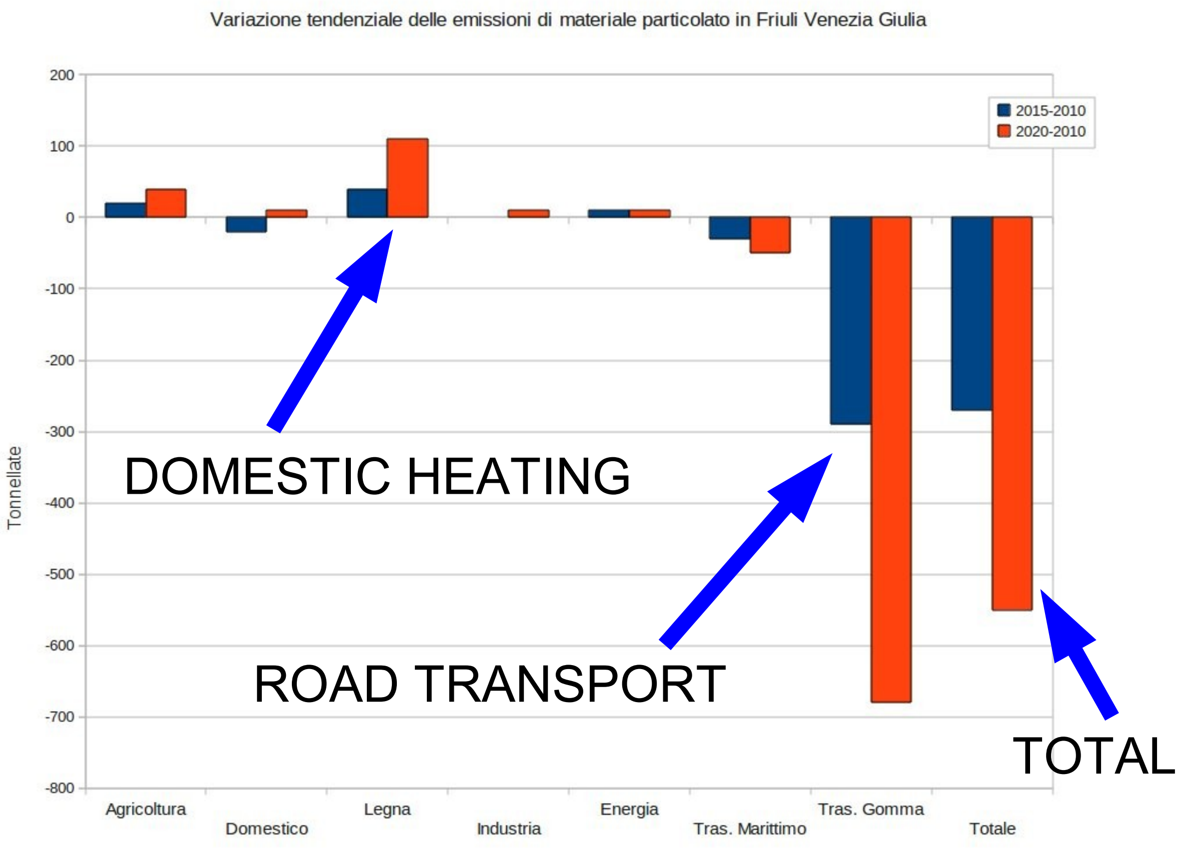
Why should we take care of "small domestic heating plants"?





Because it is one of the major anthropogenic sources of primary (and probably even secondary) atmospheric particulate matter....

Why should we take care of "small domestic heating plants"?



....and because it will become even more important in future.

GAINS-Italy energetic scenario for Friuli Venezia Giulia.

Reduction in PM10 emissions.

Blue = 2010-2015

Red = 2010-2020

Presentation Outline

- Introduction to combustion
  - anthropological aspects
  - chemical aspects
  - engineering aspects
- Types of combustions and types of emissions
- Combustion in solids
- Aerosol emission from small domestic plants
  - conceptual model
  - impacts
  - estimate
- Conclusions

Introduction to Combustion

Anthropological point of view:

Prometheus myth: stole the fire to gods and gave it to Mankind.
He was punished for that together with all Mankind through Pandora and her pot filled by all the existing evils

61^{th} A.D. Pliny the Elder (natural philosopher): air over Rome was barely breathable, this because of the emissions of its chimneys and stacks, releasing a lot of vapours and soot.

Combustion is part of worldwide experience and culture: constraints on actions

(Baumbach, 1996)

Introduction to Combustion

Chemical point of view: → combustion is an oxidation process (release energy) that occurs in relatively short amounts of time

Combustion involves atoms (Carbon, Oxygen and Hydrogen) → Number of atoms and atomic species are conserved,while molecular species vary

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 = nCO_2 + \frac{m}{2}H_2O$$

→ Aerosols do not appear in this chemical formula... complete combustion is not the answer

Introduction to Combustion

Chemical point of view:

combustion depends from the amount of available oxygen. Moreover, energy released changes fuel status

Combustion involves atoms (fuel impurities and H_2O)

SO2, SO3, H2S are often present in fuels as well as chlorides and fluorides.
We can call them Y component

$$Y + rN_2 + C_nH_m + \left(n + \frac{m}{4}\right)O_2 =$$

$$pCO_2 + \frac{q}{2}H_2O + sCO + \underline{tNOx} + \underline{soot} + \underline{ash} + \underline{vSOx} + \underline{HC}$$

Aerosols appear with a mess of other molecular species

(Warnatz et al., 2006)

Introduction to Combustion

Chemical point of view:

Rich combustion
More fuel than oxidizer

- Fuel can not be fully oxidized
- Remnants of combustion are produced (pollutants)

Lean combustion
More oxidizer than fuel

- Fuel can be fully oxidized
- Oxidizer present in exhaust air can interact with impurities present in fuel to produce new species of pollutants

How to quantify this behaviour?

With the FUEL mole fraction:

$$y_{fuel} = \frac{(moles\ of\ fuel)}{(moles\ of\ fuel) + (moles\ of\ oxidizer)}$$

Introduction to Combustion

Chemical point of view:

The **λ** (or Φ = 1/**λ**) parameter:
air number or air equivalence ratio

Complete combustion
with pure oxidizer

$$y_{stoichiometric\ ;\ pure\ oxidizer} = \frac{1\,(mole\ fuel)}{1\,(mole\ of\ fuel) + \underline{x} \cdot (mole\ of\ oxidizer)}$$

Complete combustion
with **air** (N2+O2+traces)

$$y_{stoichiometric\ ;\ air} = \frac{1\,(mole\ fuel)}{1\,(mole\ of\ fuel) + x \cdot \underline{4.76} \cdot (mole\ of\ oxidizer)}$$

Generic combustion with
air (N2+O2+traces)

$$y_{fuel\ ;\ air} = \frac{1\,(mole\ fuel)}{1\,(mole\ of\ fuel) + \underline{\lambda} \cdot x \cdot 4.76 \cdot (mole\ of\ oxidizer)}$$

λ > 1 (lean combustion) **λ = 1** (stoichiometric combustion) **λ < 1** (rich combustion)

(Warnatz et al., 2006)

Introduction to Combustion

Engineering point of view: → One of the oldest human technologies (roughly 2 Mo of years)

Combustion supplies energy → Currently 90% of the worldwide energy support comes from combustion, large majority from fossil fuels

Combustion implies interactions between chemical species and flows (fuel and oxidant), i.e. flames → Flames are the place where combustion occurs: the origin of pollutants and energy

(Warnatz et al., 2006)

Types of combustion

Engineering and chemistry → Flames

fuel and oxidizer are mixed (premixed flames)

- Turbulent
  - Spark ignited gasoline engine
  - Stationary gas turbine
- Laminar
  - Bunsen flame
  - ....

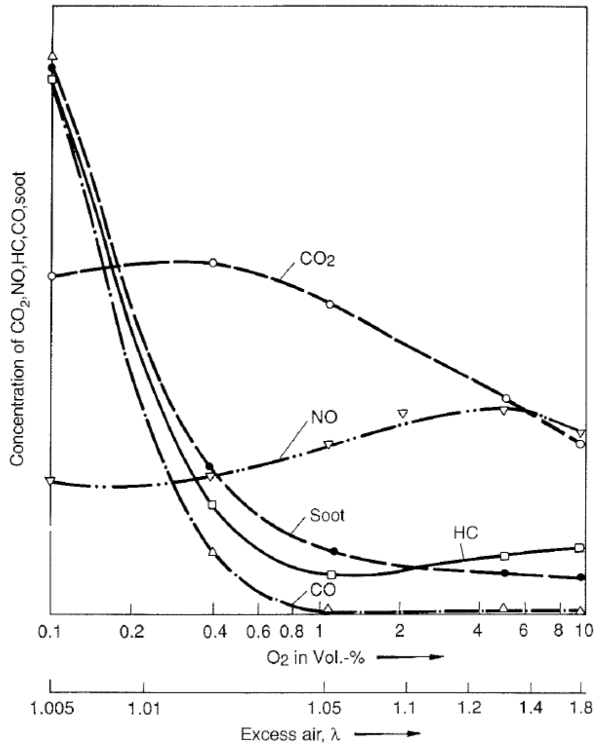
fuel and oxidizer are NOT mixed (non premixed flames)

- Turbulent
  - Aircraft turbine
  - Diesel engine
- Laminar
  - Wood fire
  - Radiant burners
  - Candles

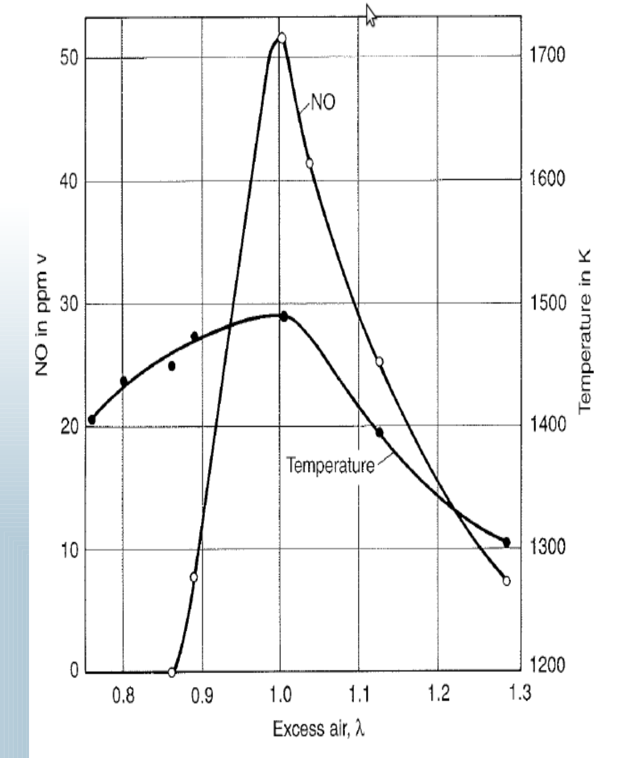
(Baumbach, 1996)

Types of emissions

Engineering and chemistry: → Emissions



Pollutants emissions from an oil furnace



NO emissions from a natural gas turbine

Combustion of solids

Combustion of solids: → Three phases

Solids are a mixture of different chemical compounds, not only hydrocarbons

1st phase: pyrolysis → Solid is heated up to the time in which it starts to release volatile organic compounds.

2nd phase: VOC oxidation → VOC are oxidized (burned) and, after total degasification of solid, a carbon rich remnant is formed, this is the **coke**

3rd phase: coke oxidation → Coke is oxidized (burned) through a surface process up to the time in which only ash remains

Combustion of solids

Combustion of solids: → 1^{st} phase: pyrolysis

This phase is even called degasification and takes place with supply of energy

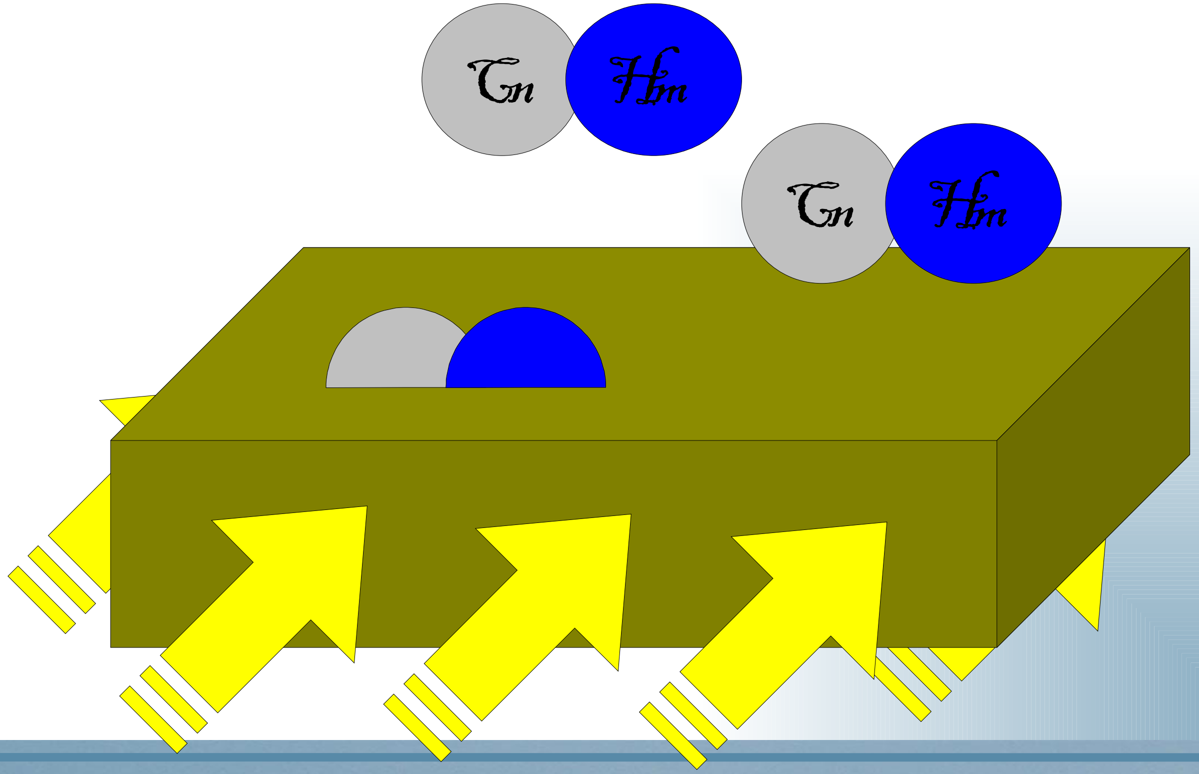
Substances with high vapour pressure are the first to be released.

Water present in the solid is emitted in this phase, subtracting energy to the system (i.e., reducing temperature)

O2 concentration is pivotal in this phase for the combustion efficiency as well as for the pollutants emissions

Combustion of solids

Combustion of solids: → 1st phase: pyrolysis



Combustion of solids

Combustion of solids: → 2nd phase: VOC oxidation

This phase usually begins while 1st phase is still active

Temperature is enough high to sustain rapid oxidation of the evaporated VOC. Energy is released in this phase and it enhances pyrolysis efficiency. Flame is formed in this case

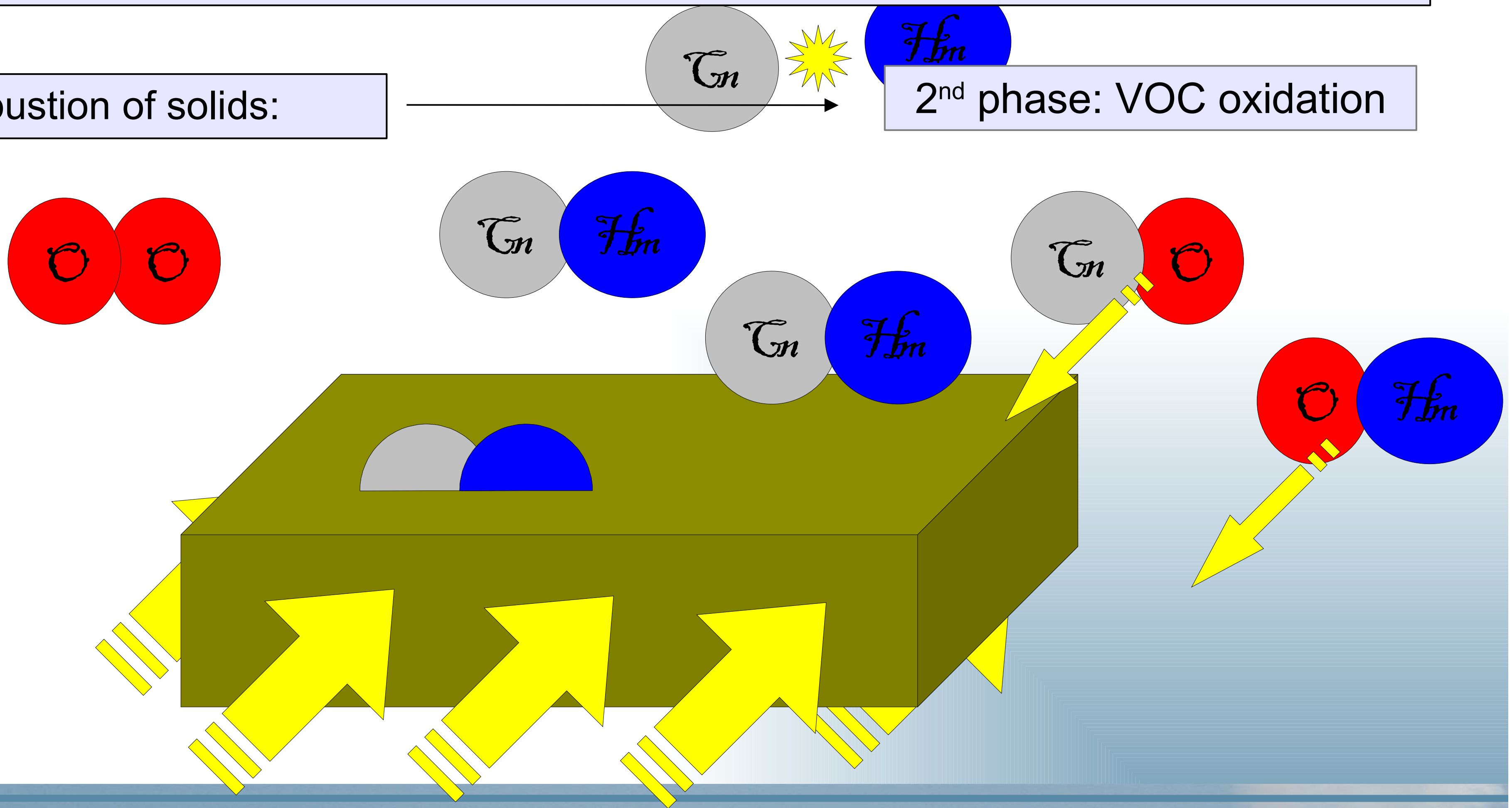
If temperature is enough high, VOC can loose their hydrogens and **soot** is formed. Soot radiates as a black body. For this reason it is at the origin of the yellow colour of flames

Fuels with an high C/H ratio are more prone to soot formation
(e.g., acetylene vs methan)

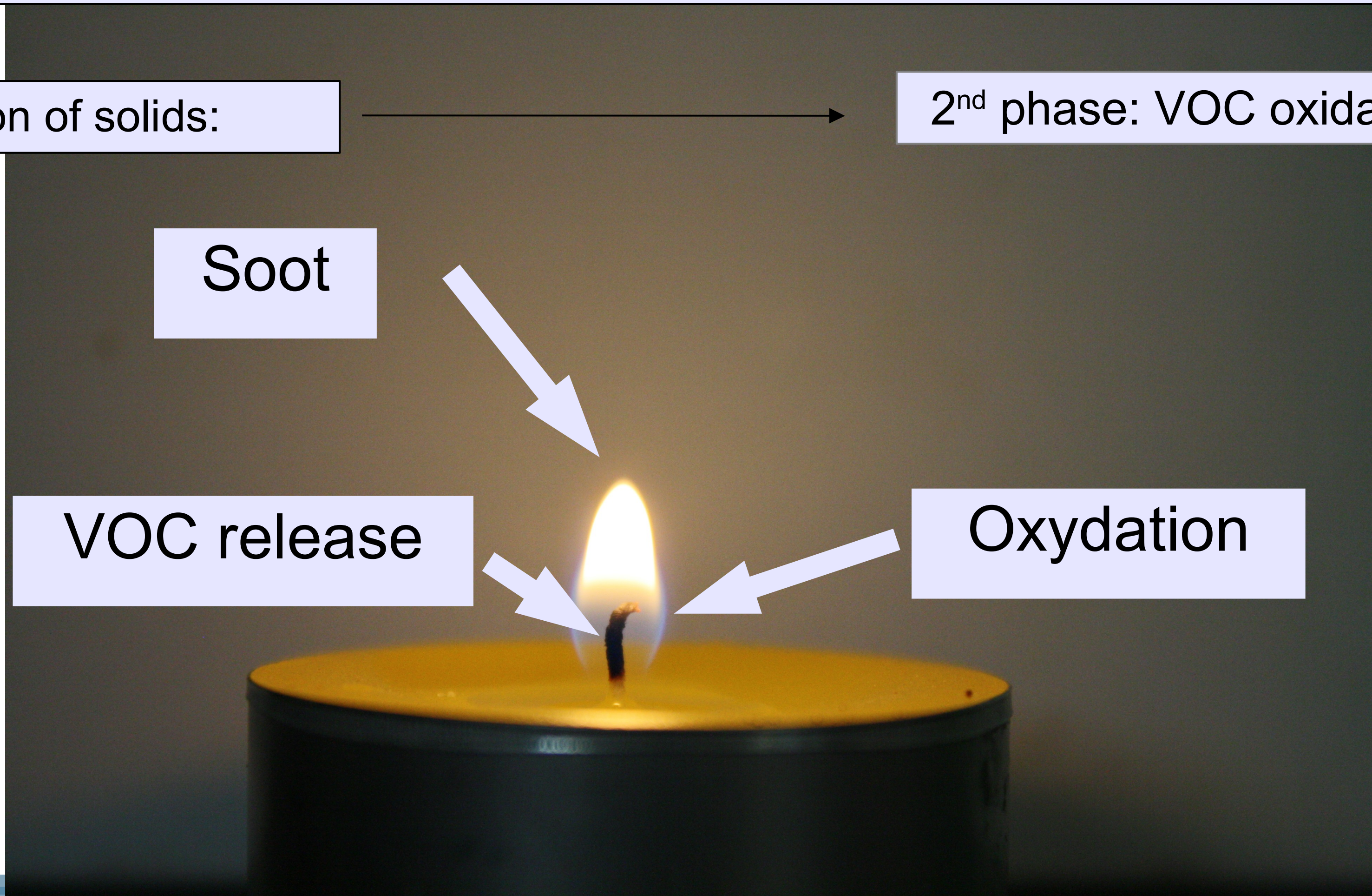
Combustion of solids

Combustion of solids:

2nd phase: VOC oxidation



Combustion of solids



Combustion of solids

Combustion of solids: → 3rd phase: coke oxidation

This phase can begins while 2nd phase is still active

Coke is composed mainly by carbon, which has a low vapour pressure

Direct emission of C can be considered as negligible

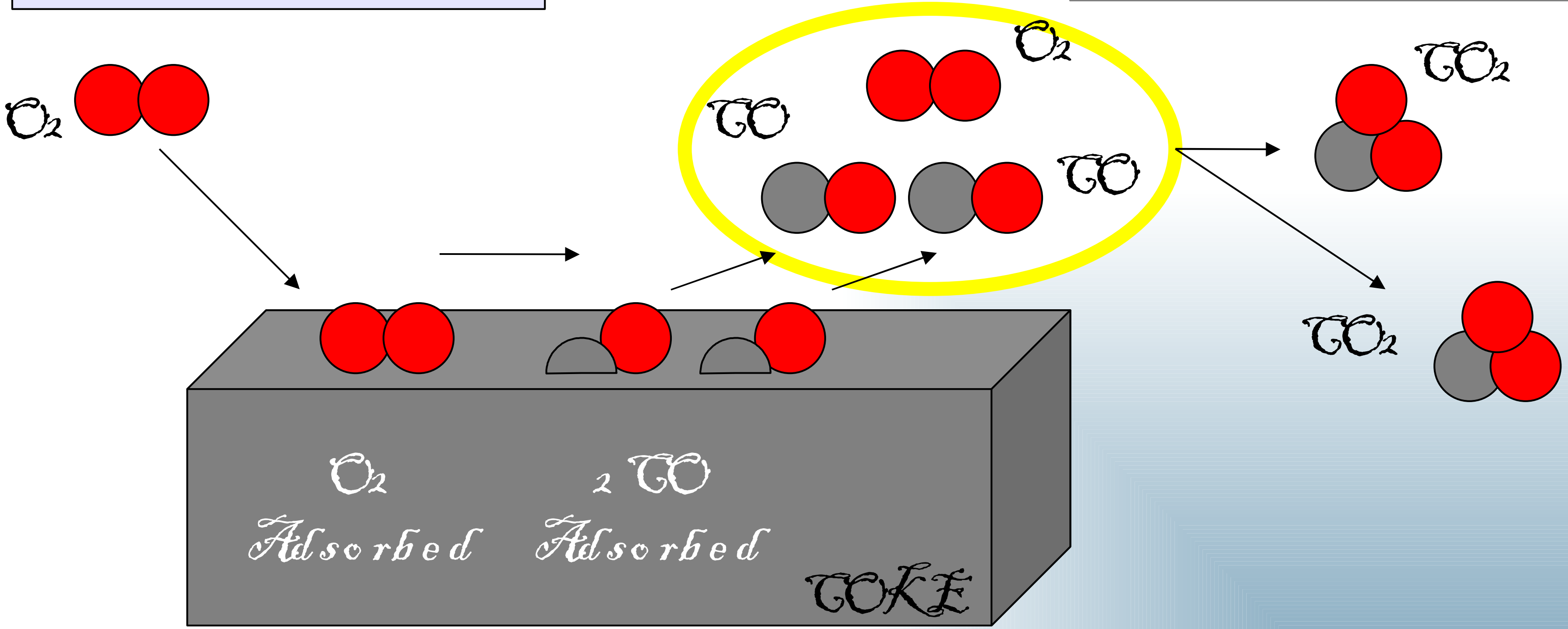
CO_2 and O_2, in this phase, can be adsorbed on the coke surface. Oxygens creates a strong bond with C on the coke surface and CO is formed

CO has an high vapour pressure and escapes from the surface. If O_2 concentration is enough, CO can be oxidized forming CO_2

Introduction to Combustion

Combustion in solids:

3rd phase: coke oxidation



(modified from Nussbaumer, 2010)

Aerosol emission – conceptual model

COC: condensable organic compounds

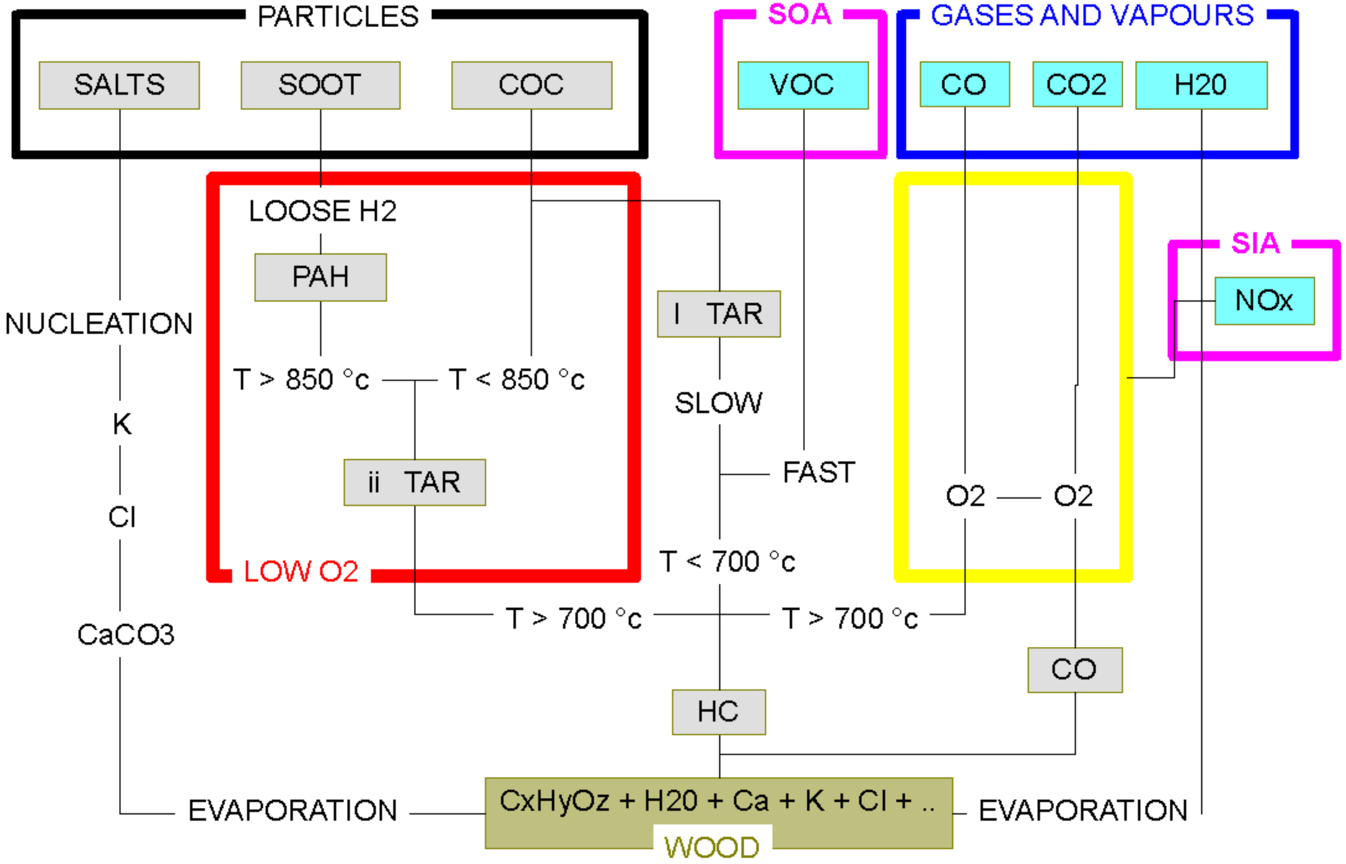
VOC: volatile organic compounds

HC: hydrocarbons (C_nH_m)

SOA: secondary organic aerosols

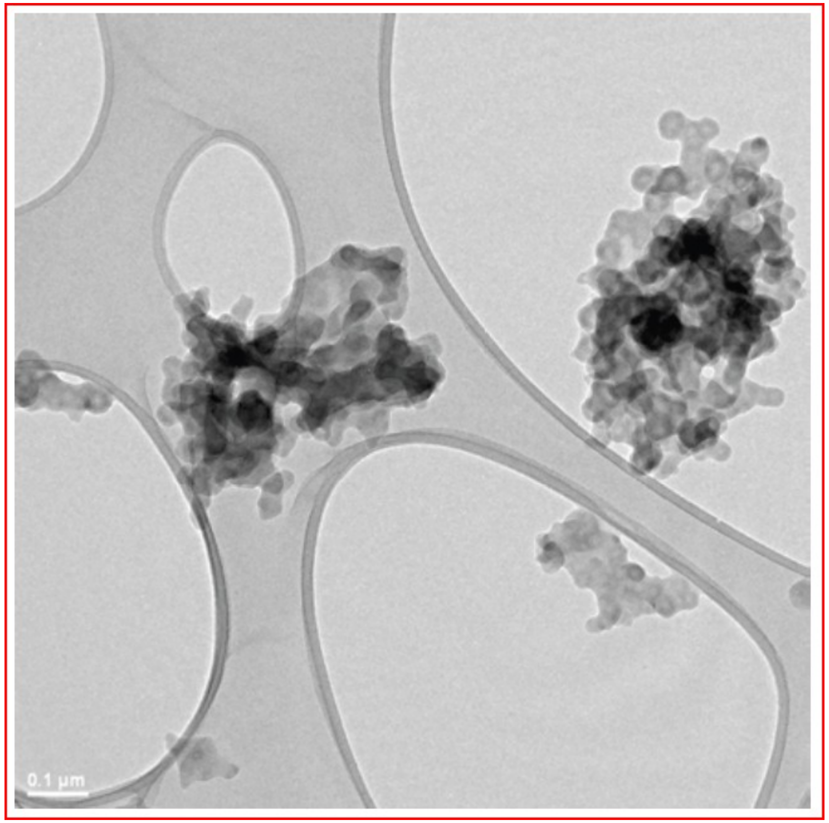
SIA: secondary inorganic aerosols

PAH: policiclic aromatic hydrocarbons

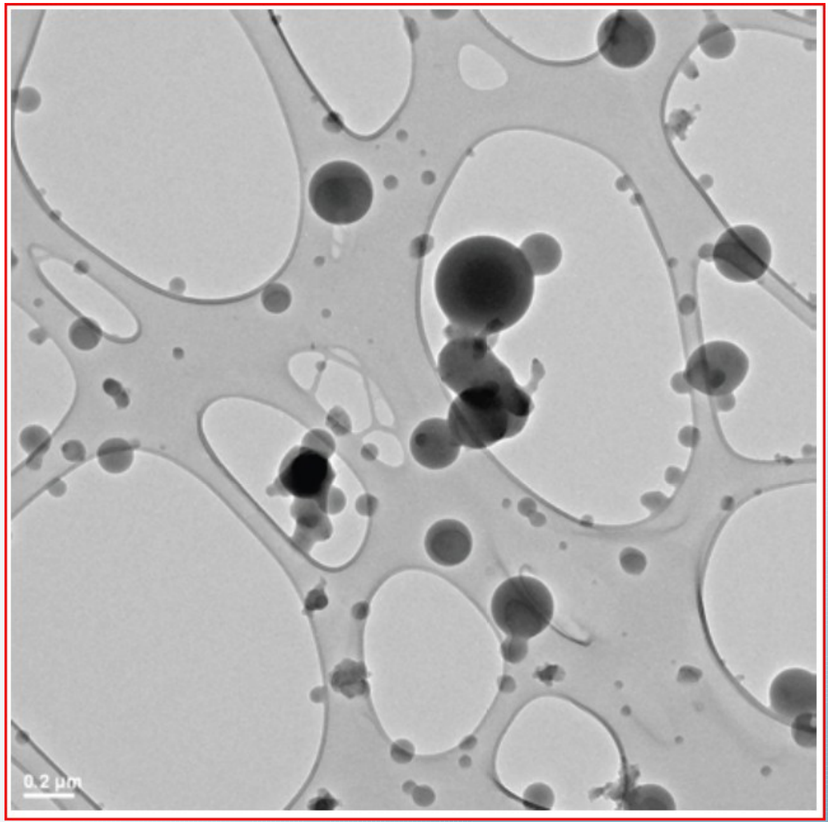


Aerosol emission – conceptual model

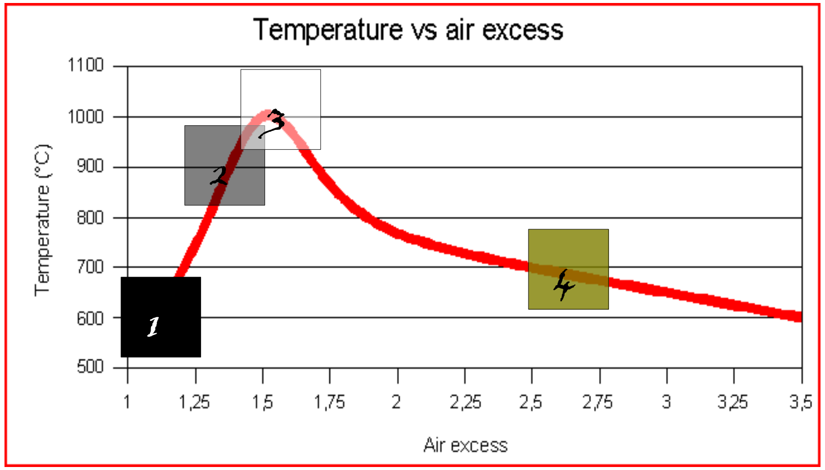
Soot

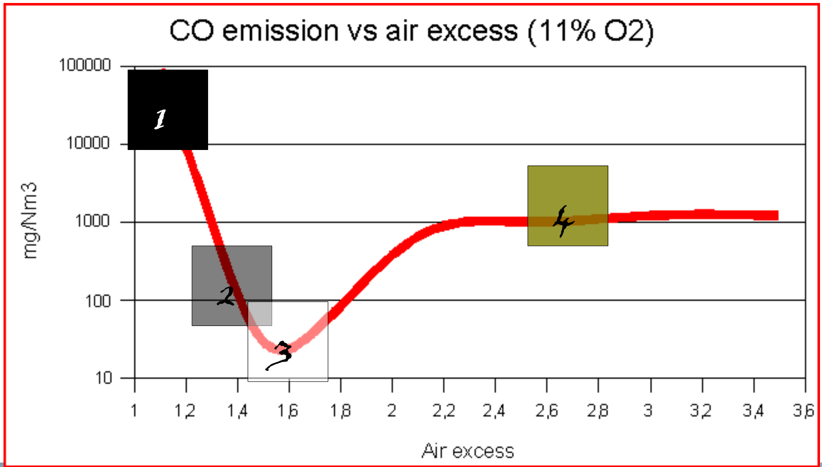


Tar (COC)



Aerosol emission – conceptual model





Pellet stove

	Flaming Combustion			Pyrolysis
	lack of O_2 in the flame	– Mix –	T and O_2 good	T low at start or high O_2, O_2 lack gas. or fl. ext.
View				
PM	**Soot**	Salts + Soot	**Salts**	**COC**
Composition	EC / BC thermo chem. / optical C/H > 6...8	↔	CC + Minerals carbonate C + inorg. M	OC = TC–EC–CC C/H < 2
Colour	black	grey	white	brown I none
Health effect		↔	–	
Climate effect	absorbs light and heats atmosphere	↔	scatters light and cools surface	weakly absorbs and scatters

1 2 3 4

Aerosol emission – impacts

Comparisons between a **wood stove** (badly operating) and a **Diesel engine** (non premixed combustion)

Emission Factors for badly operated wood stove are much larger than those for a Diesel engine (apart from naphtalene)

Even the EF of **benzo(a)pyrene** is larger for wood stoves than Diesel engines

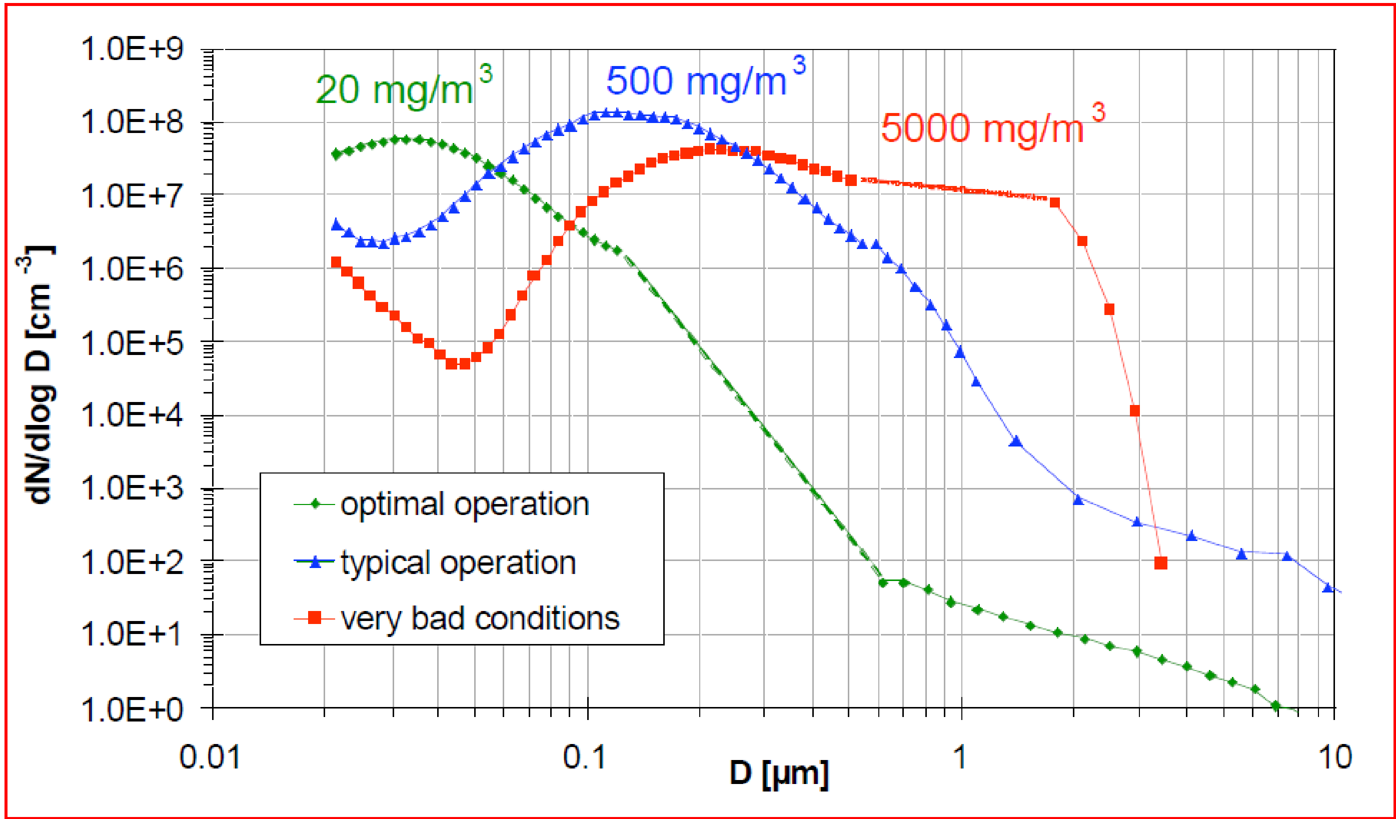
mg/kg	Wood stove	Diesel
Naphthalene	13	42
Acenaphthylene	129	7.1
Acenaphthene	17	< 3
Fluorene	173	< 3
Phenanthrene	231	3.7
Anthracene	65	< 3
Fluoranthene	154	< 3
Pyrene	170	< 3
Chrysene	54	< 3
Benzo(a)anthracen e	44	< 3
Benzo(b)fluoranthene	30	< 3
Benzo(k)fluoranthene	11	< 3
Benzo(a)pyrene	25	< 3
Indeno(1,2,3-cd)pyrene	9	< 3
Dibenzo(a,h)anthracene	< 8	< 3
Benzo(g,h,i)perylene	< 8	< 3
Total PAH	1 120	53

Aerosol emission - impacts

Aerosol size distribution for three different operating modes of a **wood stove**

Good practices reduce the bulk amount of aerosol emission

Good practices produce smaller particles



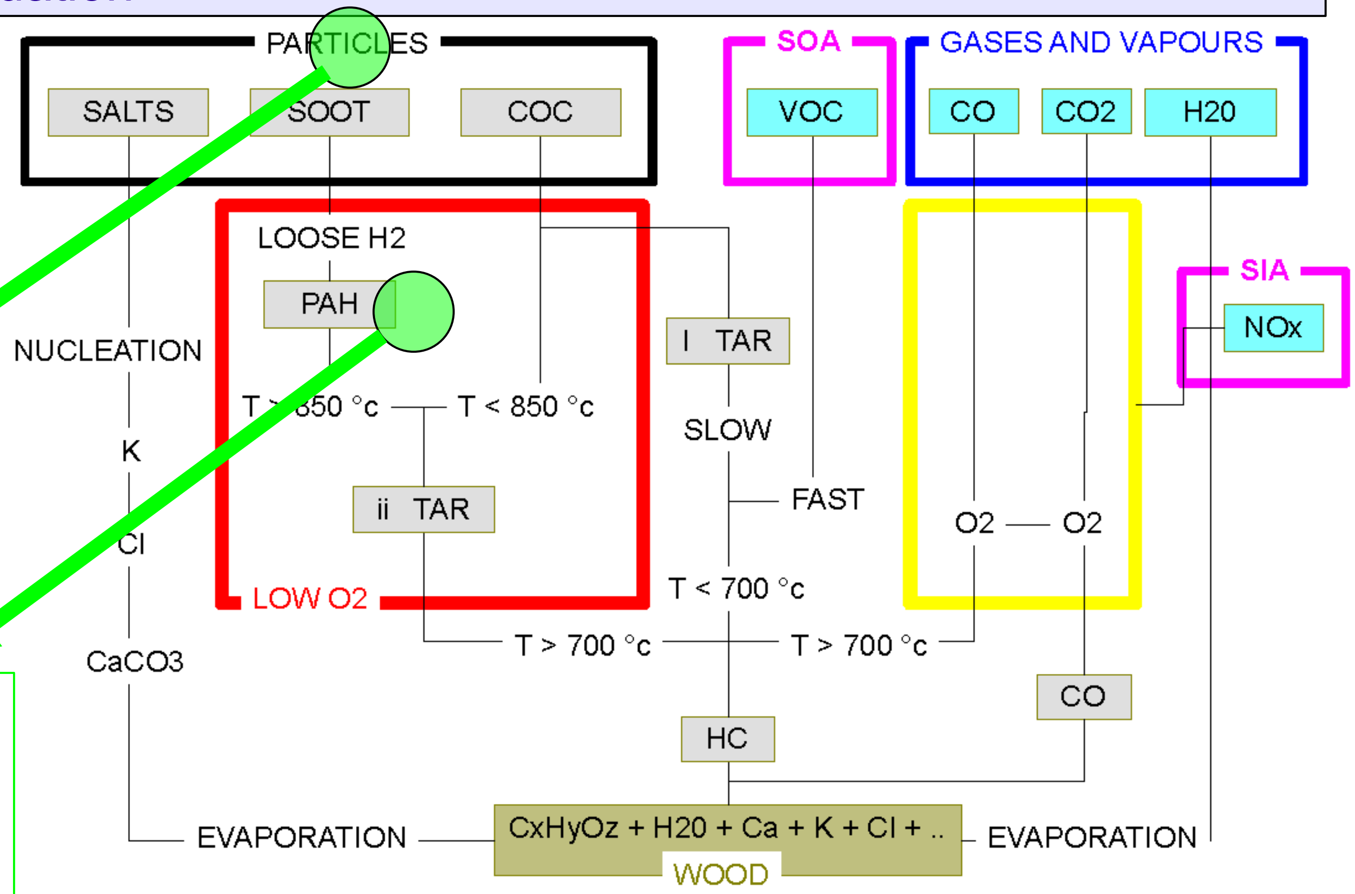
Optical counter and Scanning Mobility Particle Sizer. Mass through gravimetric method

Aerosol emission – evaluation

Emission factors depend from the point where you measure them

We loose SOA and SIA (but we have numerical models)

We loose SOA and SIA (but we have numerical models), but we loose even COC



Aerosol emission – evaluation

Currently three methods are used to measure Emission Factors (none official for EU)

WARM method: particulate matter is measured in the exhaust hot emissions. COCs do not have time to condensate.
(used, among others, by Austria and Germany)

COLD method: particulate matter is measured in the exhaust emissions after a dilution in cold air, letting COC to condensate
(used, among others, by Norway)

MIXED method: particulate matter is measured in the exhaust hot emissions, as well as VOC. It is not clear how to transform VOC in COC
(proposed by EU – discussion still open if not yet closed)

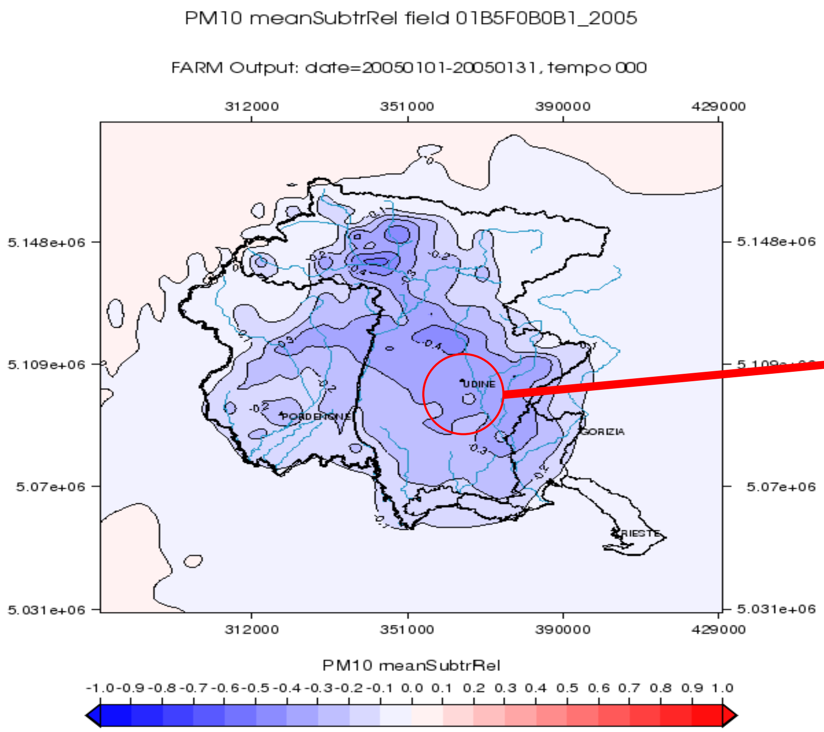
Aerosol emission – evaluation

COLD and WARM methods give dramatically different values for PM10 emissions

	WARM (g/GJ)	COLD (g/GJ)	DIFFERENCE (g/GJ)
Open Fireplaces →	500	860	360
Traditional stove →	250	810	560
Closed Fireplace →	250	450	200
High efficiency stove →	150	260	110
Pellet →	70	76	6

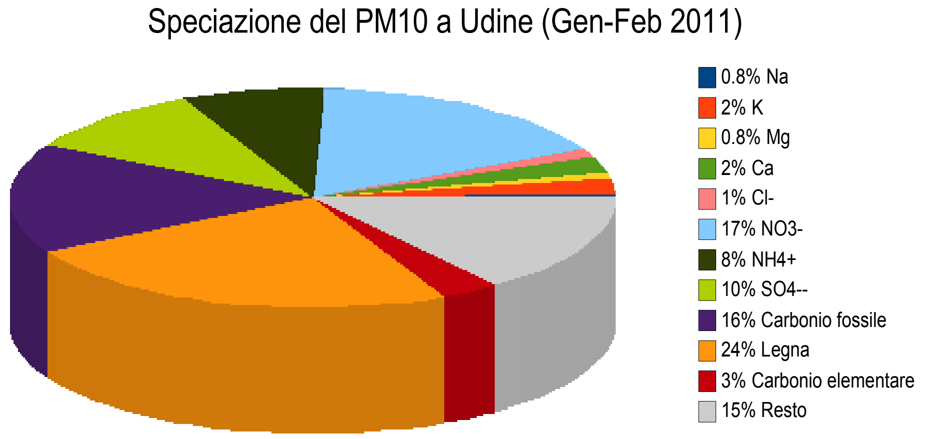
For Lombardy (Italian Region) this difference would move the total 2008 emissions from **5 500** to **11 000** t/y over a primary PM10 total amount of **15 000** t/y

Aerosol emission – evaluation



PM10
numerical simulation
(Jan 2005)

PM10 source apportionment (Jan-Feb 2011)



(fonte: progetto EU iMONITRAF!)

~ 25% of PM10 from wood combustion

~ 15% of PM10 from fossil carbon

~ 25% of PM10 from NO3- and NH4+

Conclusion

Wood represents a relevant renewable resource of energy for many EU Countries

Wood and in general biomasses are sustained by many Countries because of the climate policies

Wood usage would grow in the future for the increasing of fossil fuel cost and because of the current policies

We should start the virtuous road map for road transports and its “emission concept”

Improve knowledge, awareness and clearness in policies (proactive attitude)
By the way Prometheus means “who thinks in advance”!

THANK YOU

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