CHEMICALS

List of chemicals

1. Sulphur dioxide and other sulphur compounds (SO_2, SO_3, H_2SO_3)
2. Oxides of nitrogen and other nitrogen compounds (NO, NO_2, HNO_3)
3. Carbon monoxide
4. Volatile organic compounds
5. Metals and their compounds
6. Dust including fine particulate matter
7. Asbestos (suspended particulates, fibres)
8. Chlorine and its compounds (Cl_2, HCl)
9. Fluorine and its compounds
10. Arsenic and its compounds
11. Cyanides ($C\equiv N$) and Methyl isocyanate (CH_3NCO)
12. Substances and mixtures which have been proved to possess carcinogenic or mutagenic properties or properties which may affect reproduction via the air
13. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans

AIR POLLUTANTS – classifications

By the preceding definitions, any solid, liquid or gas present in the air in a concentration that causes some deleterious effect is considered an AIR POLLUTANT.

However, there are several substances that, by virtue of their massive ***rates of emission*** and ***harmful effects***, are considered the most significant pollutants.

CLASSIFICATION of pollutants can be based on:

LEGISLATION	***Criteria (Regulated) Air Pollutants***
ORIGIN	***Primary/Secondary Pollutants***
EMITTED QUANTITY	***Major Pollutants***
SOURCE	***Natural/Antropogenic Pollutants***
PHYSICAL STATE	***Gaseous/Particulate Pollutants***
SCALE	***Local/Global Pollutants***

AIR POLLUTANTS – types and nature

Classification based on emitted quantities and environmental effects

Macro*pollutants (conventional or criteria)*

- *Relevant* emissions
- *Less harmful* for human health
- Affordable and well grounded *control technologies* at state of the art

Pollutant	Spatial impact scale
SO_2	Local, regional
NO_x ($NO+NO_2$)	Local, regional
CO	Local
CO_2	Global
Particulate matter	Local
Hydrocarbons (VOC)	Local

Trace *pollutants (hazardous)*

- *Lower* emissions
- *More harmful effects (toxicity, accumulation, environmental persistence)*
- *Control technologies* recently developed and continuously updated
  - Trace metals (Cd, Pb, Hg, As, Se)
  - Persistent organic pollutants → POPs (PAH, PCDD/Fs, PCBs, organohalogen compounds)

AIR POLLUTANTS – types and nature

Classification based on physical state

- **gaseous**
  issue: quantity → concentration
- **particulates** (solid and liquid)
  issues: quantity → concentration
  dimensions → size distribution

Particles diameter d_p	Typical sources
> 10 µm	mechanical processes, natural (erosion, wind) or not
1 - 10 µm	natural sources (soil and marine aerosol) combustion, industrial processes photochemical secondary aerosols
0,1 - 1 µm	combustion, industrial processes photochemical secondary aerosols
< 0,1 µm (UFP)	combustion processes industrial (nanotechnologies) secondary aerosols

$d_p < 10$ µm → **inhalable particles**

AIR POLLUTANTS – types and nature

Classification based on the origin

- **Primary** pollutants → directly emitted from the sources
  - SO_2
  - CO
  - VOC (hydrocarbons)
  - particulate matter (TSP, PM_{10}, $PM_{2,5}$)
  - NO_x ($NO+NO_2$)

- **Secondary** pollutants → derived from transformation processes of primary pollutants in the atmosphere caused by
  - complex *photochemical mechanisms* depending on the specific site (solar radiation, sources characteristics)
    - O_3
    - NO_2
    - reactive organics (ROG)

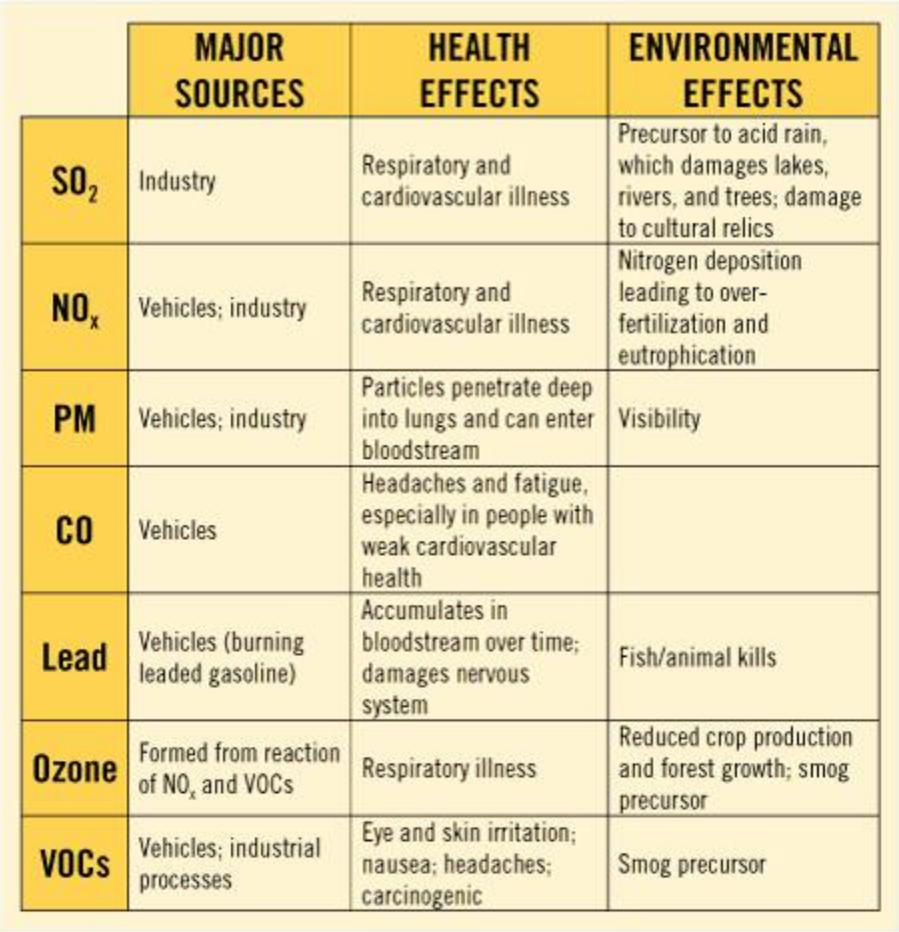
    Photochemical smog
  - combination of physico-chemical, chemical and photochemical conversion
    - fine particulates ($PM_{2.5}$, PM_1, ultrafines)

AIR POLLUTANTS – cause, source, effects

CAUSE of pollutants: explains WHY or HOW a pollutant is formed (Refers to Fundamental aspects)

SOURCE of pollutants: identify what type of process, industry or device discharge a particul pollutant (Refers to Locational Aspects → See Unit1C)

EFFECTS of pollutants:
On the Environment
On Goods
On Human health

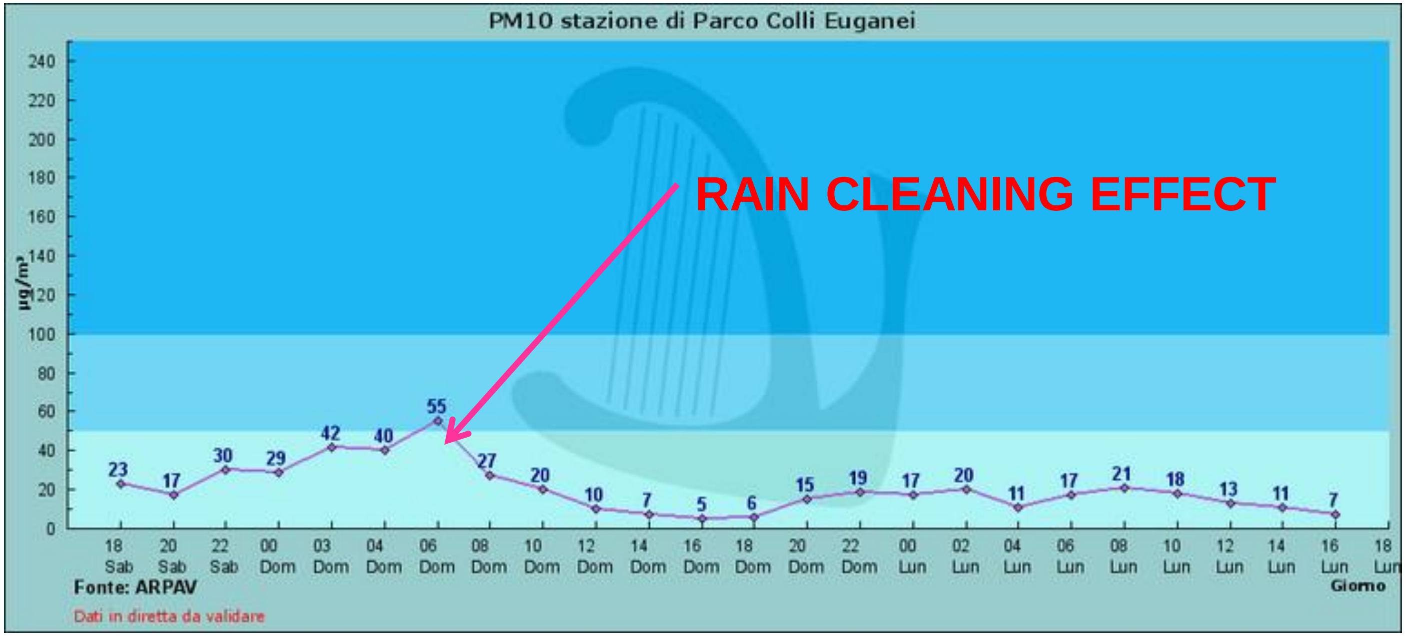


	MAJOR SOURCES	HEALTH EFFECTS	ENVIRONMENTAL EFFECTS
SO_2	Industry	Respiratory and cardiovascular illness	Precursor to acid rain, which damages lakes, rivers, and trees; damage to cultural relics
NO_x	Vehicles; industry	Respiratory and cardiovascular illness	Nitrogen deposition leading to over-fertilization and eutrophication
PM	Vehicles; industry	Particles penetrate deep into lungs and can enter bloodstream	Visibility
CO	Vehicles	Headaches and fatigue, especially in people with weak cardiovascular health	
Lead	Vehicles (burning leaded gasoline)	Accumulates in bloodstream over time; damages nervous system	Fish/animal kills
Ozone	Formed from reaction of NO_x and VOCs	Respiratory illness	Reduced crop production and forest growth; smog precursor
VOCs	Vehicles; industrial processes	Eye and skin irritation; nausea; headaches; carcinogenic	Smog precursor

In the table: a detail on Criteria Air pollutants
(sources and effects on human health)

WET CLEANING OF THE ATMOSPHERE

Stazione di Rilevamento: Parco Colli Euganei – PD
(Sat. 25th – Monday 27° - March 2017)
Valori di PM_{10} rilevati nelle ultime 48 ore



RAIN CLEANING EFFECT

Fonte: ARPAV

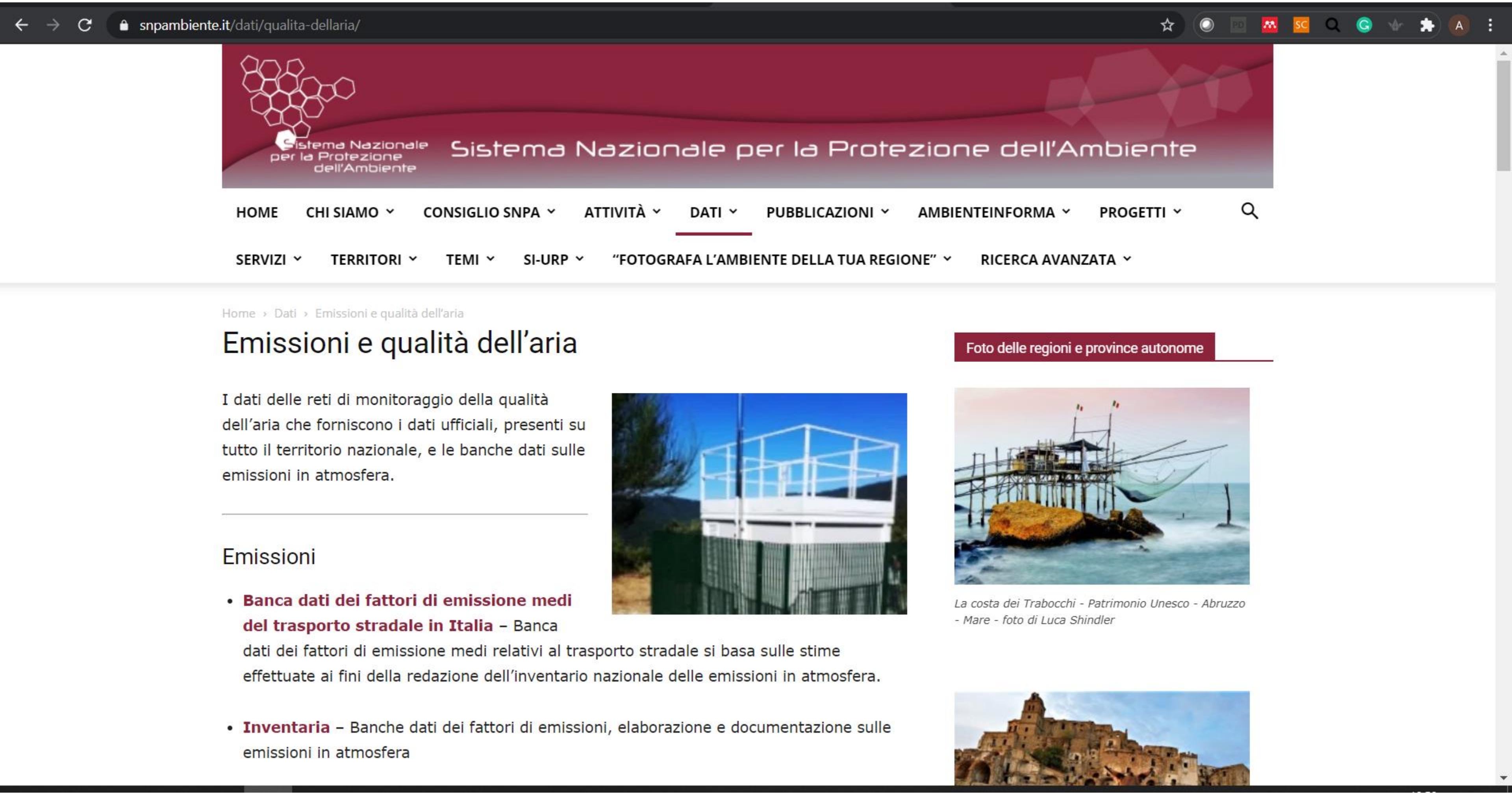
Dati in diretta da validare

Q: What about the simultaneous removal of gaseous pollutants: CO, NOx, SO_2, HCl, NH_3, …and what about CO_2 removal?

Does the solubility of some of them depend on pH of the rain?

DATA

https://www.snpambiente.it/dati/qualita-dellaria/



Emissioni e qualità dell'aria

I dati delle reti di monitoraggio della qualità dell'aria che forniscono i dati ufficiali, presenti su tutto il territorio nazionale, e le banche dati sulle emissioni in atmosfera.

Emissioni

- **Banca dati dei fattori di emissione medi del trasporto stradale in Italia** – Banca dati dei fattori di emissione medi relativi al trasporto stradale si basa sulle stime effettuate ai fini della redazione dell'inventario nazionale delle emissioni in atmosfera.
- **Inventaria** – Banche dati dei fattori di emissioni, elaborazione e documentazione sulle emissioni in atmosfera

La costa dei Trabocchi - Patrimonio Unesco - Abruzzo - Mare - foto di Luca Shindler

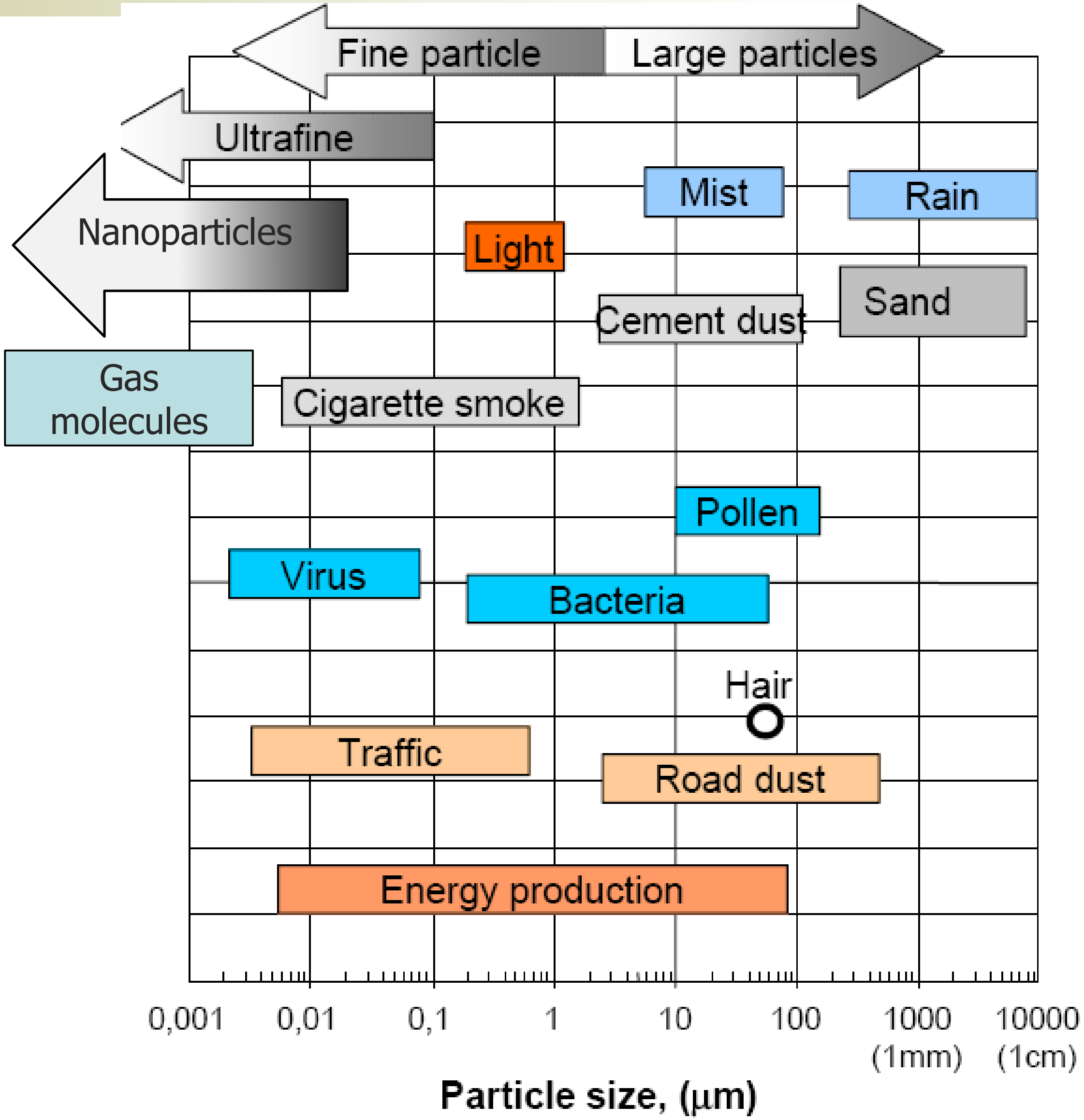
PARTICULATE POLLUTANTS

General characteristics: size

Size characteristics

origin

- ultra coarse fractions (> 10 µm): mechanical processes
- coarse (< 10 µm), fine (< 2.5 µm), ultrafine (< 0.1 µm) fractions
  - primary: combustion, evaporation, condensation
  - secondary: physical, chemical, physico-chemical processes



General characteristics: size

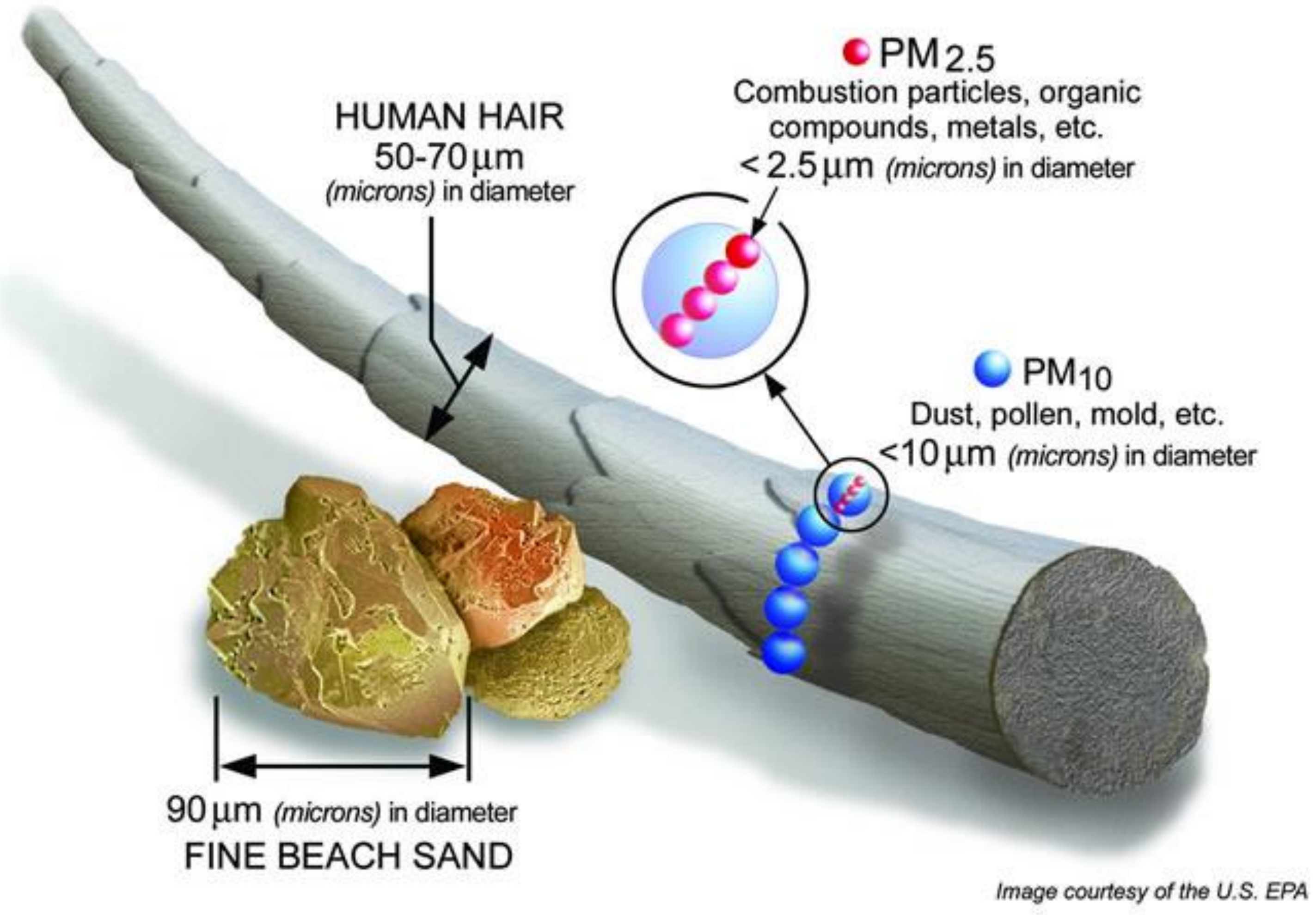
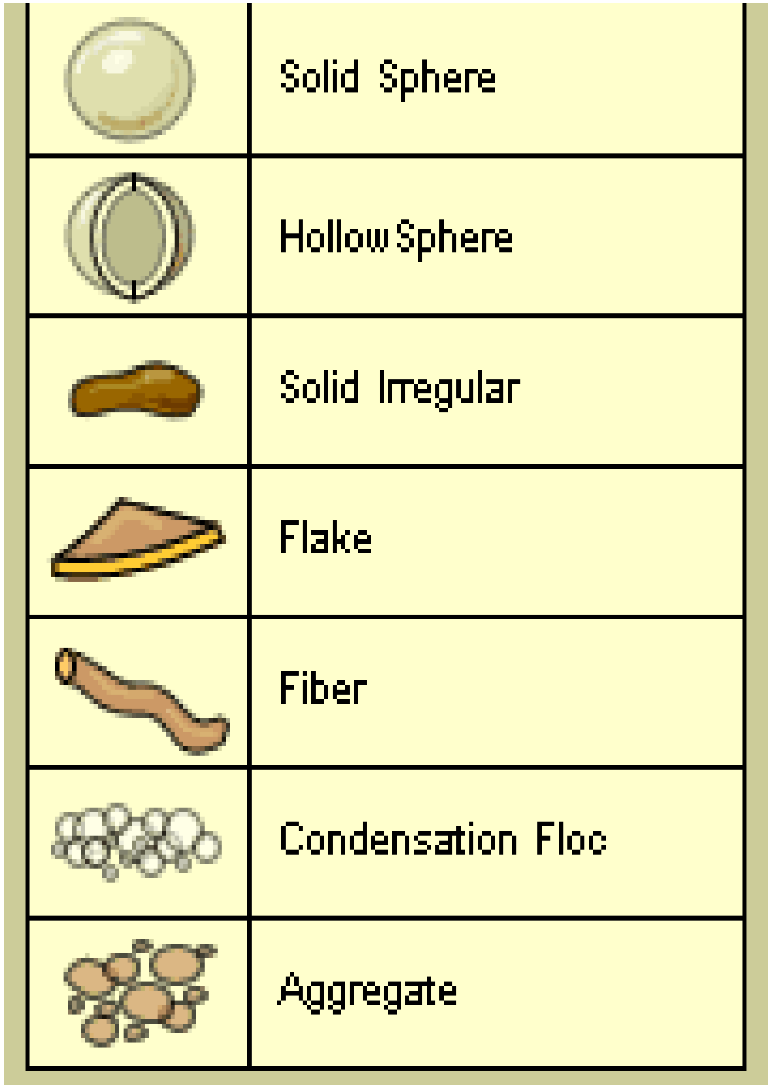


Image courtesy of the U.S. EPA

General characteristics: shape



Solid Sphere

Hollow Sphere

Solid Irregular

Flake

Fiber

Condensation Floc

Aggregate

Mineral ash residues

Cenospheres (coal combustion)

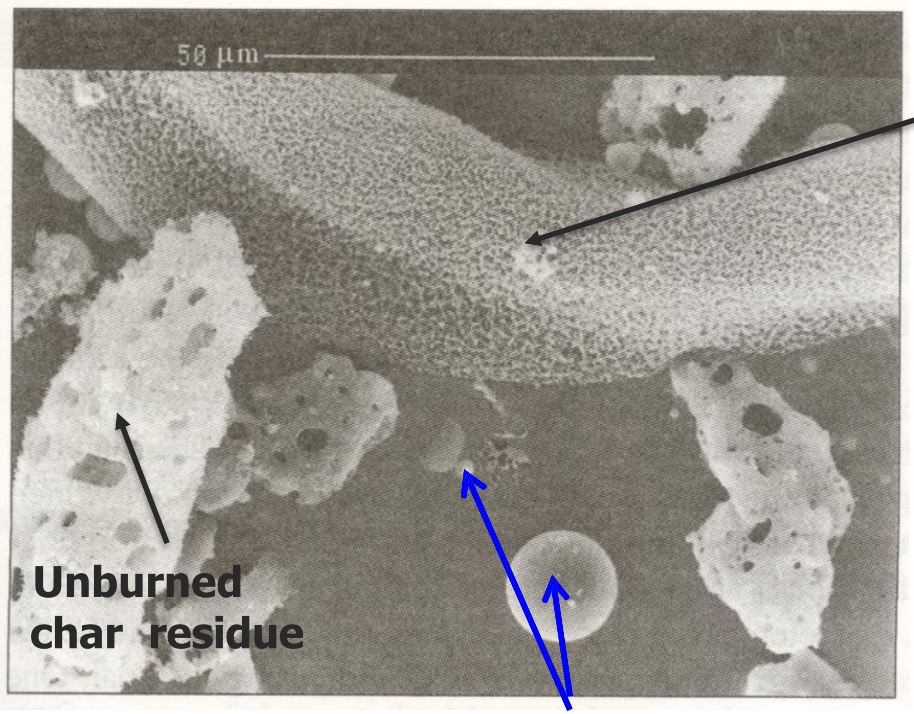
Soot (incomplete combustion)

Asbestos

Finer combustion residues,
nanoparticles

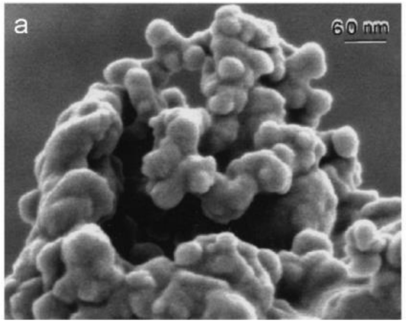
Chars, soot (incomplete combustion),
nanoparticles

General characteristics: size and shape from fuel-rich coal combustion

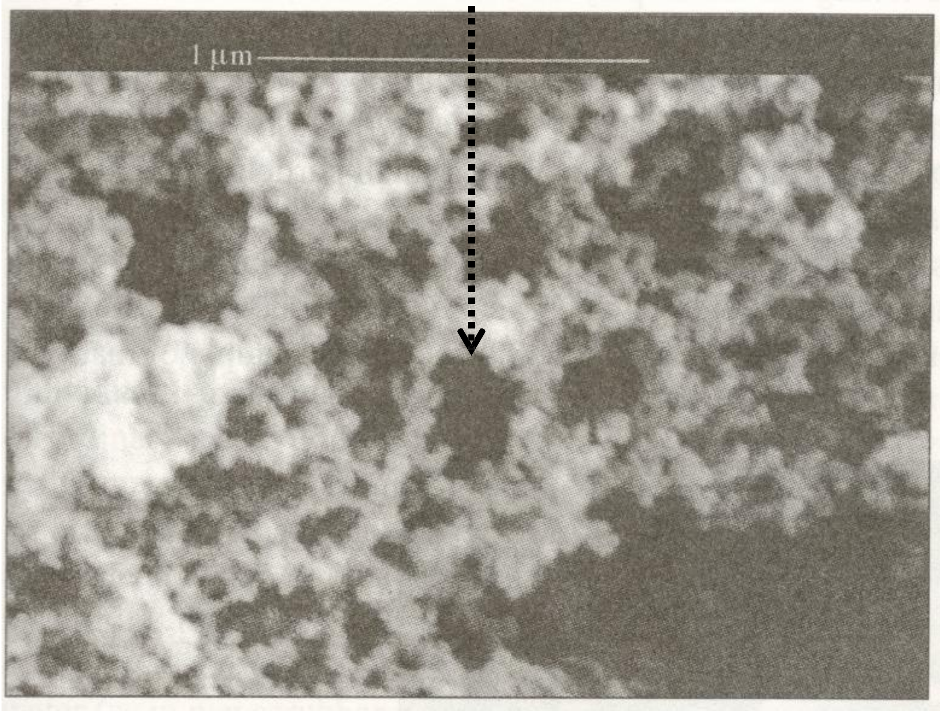


Unburned char residue

Soot

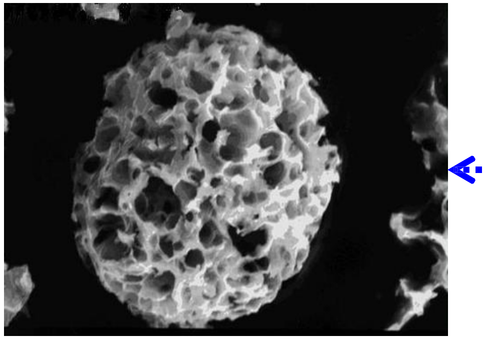


Agglomerate of spherical particles
(mostly unburned HC)

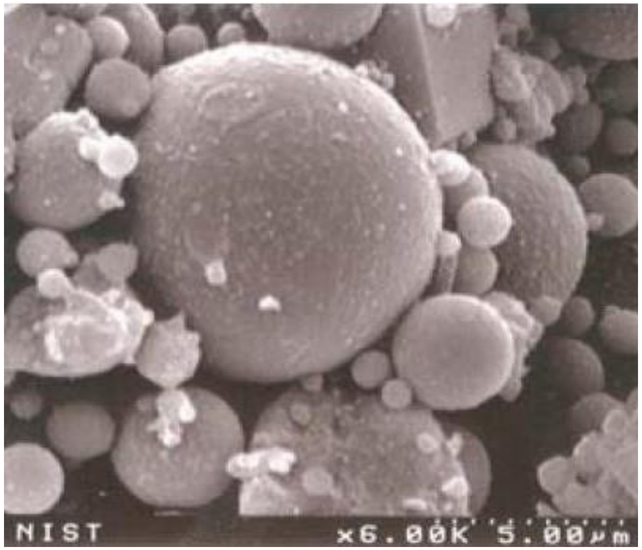


Mineral flyash

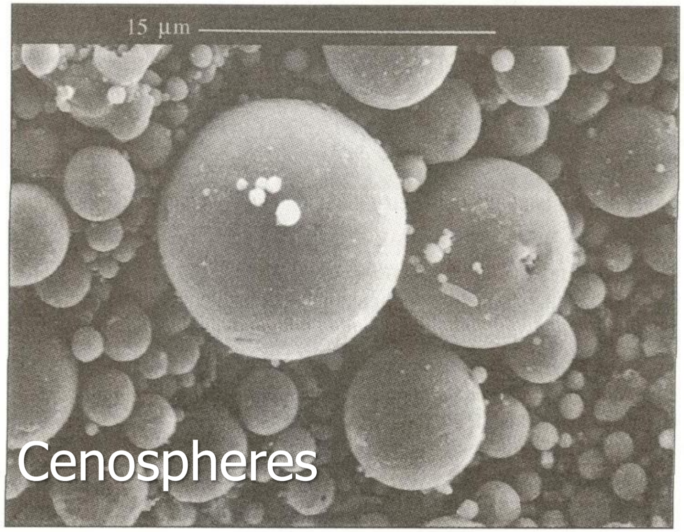
Cenosphere



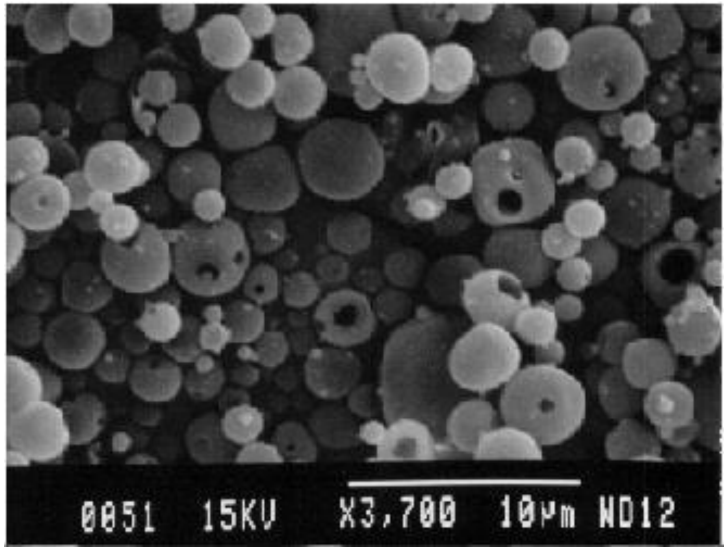
General characteristics: size and shape from optimized combustion



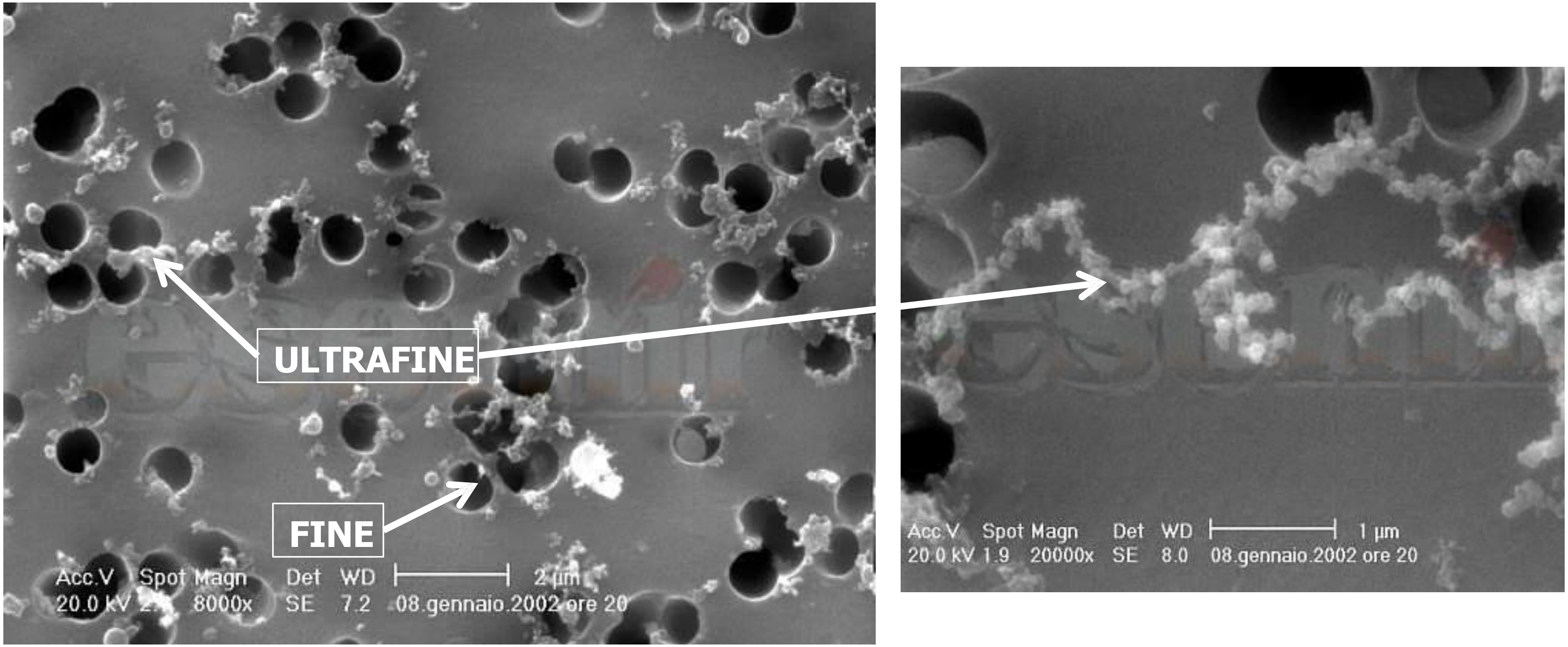
Pulverized coal



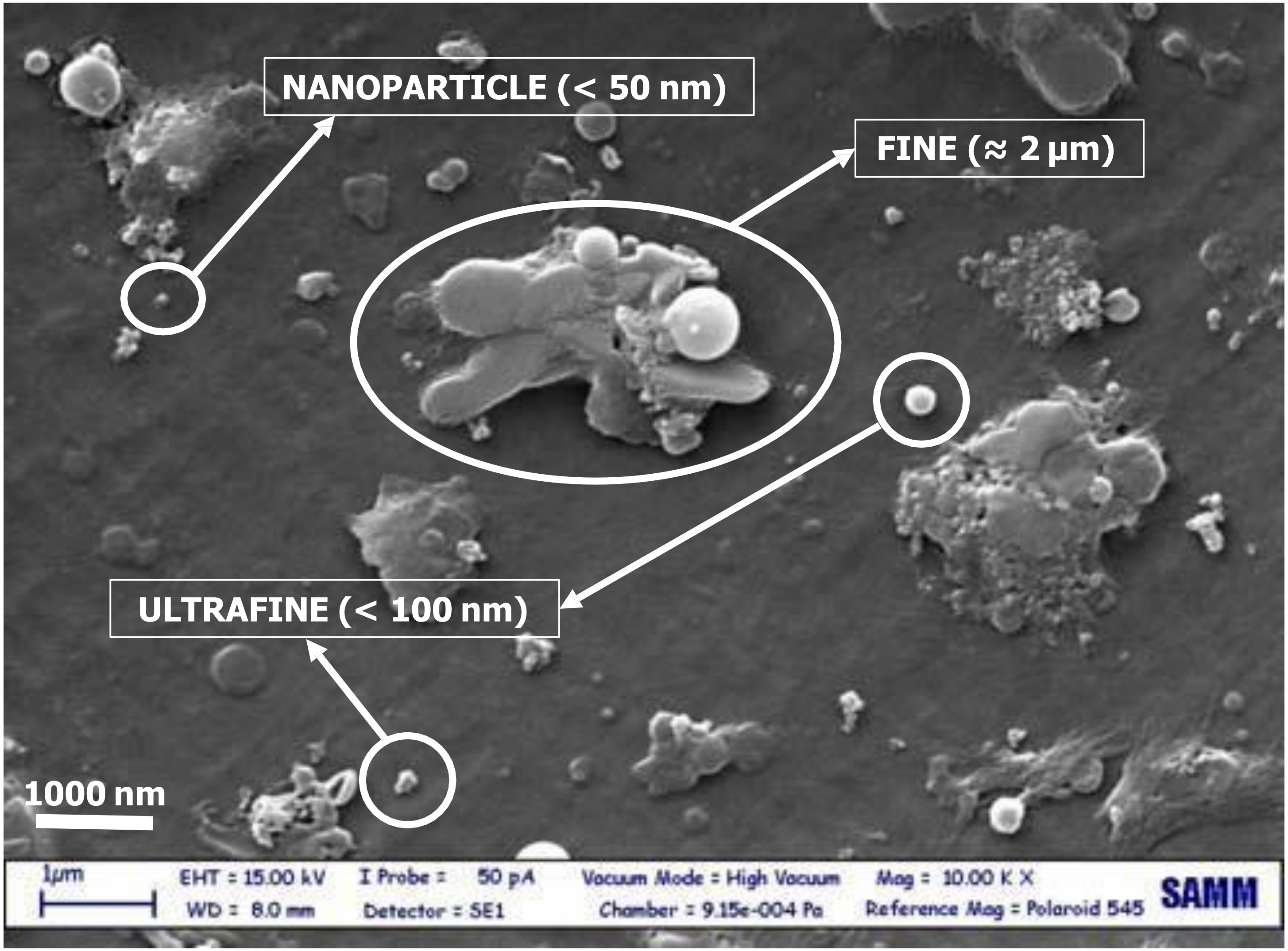
Urban waste



General characteristics: size and shape - fine/ ultrafine particles



General characteristics: size and shape – fine/ ultrafine/ nanoparticles



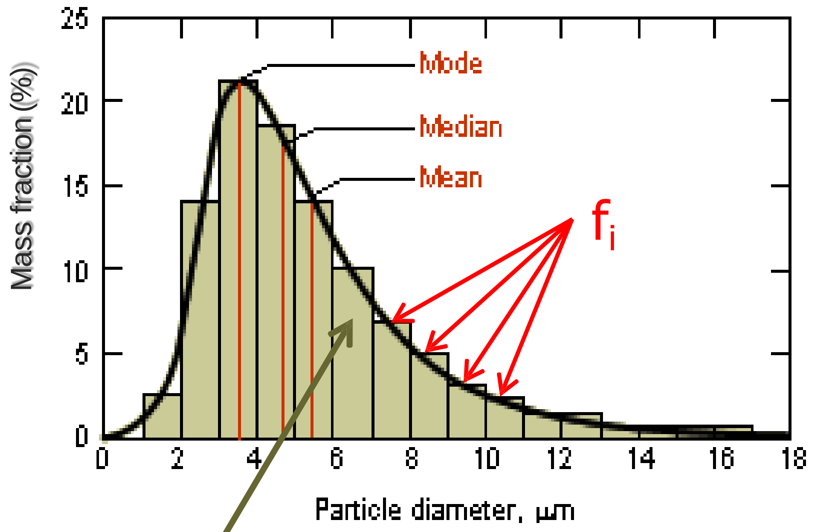
Size distribution

Particulate emissions: particles dimensions extended over variable size ranges

size distributions

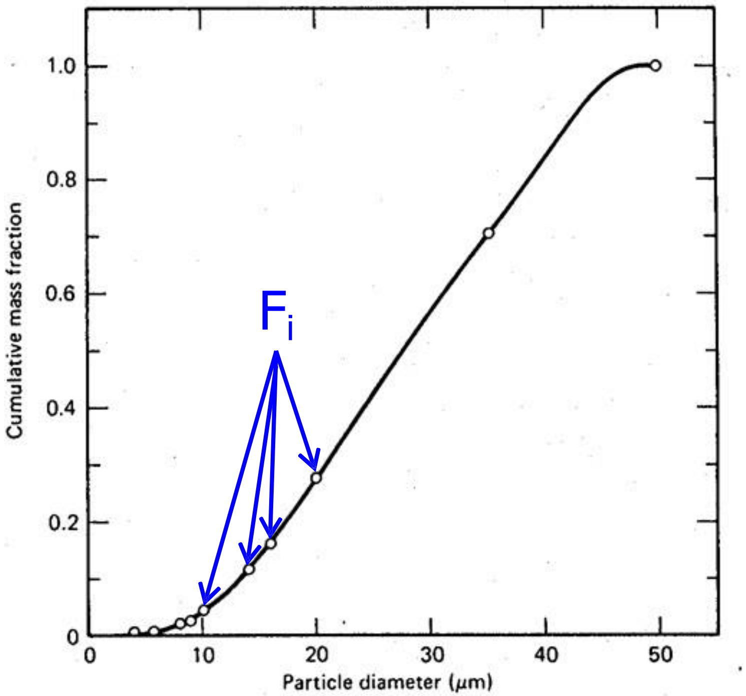
relative frequency or cumulative relative frequency distribution for size bins (size intervals)

Frequency distribution (by mass) $f_i(d_p)$



size classification measurements → histogram

Cumulative frequency distribution (by mass) $F_i(d_p)$



Size distribution

The "**mean**" is the "average" you're used to, where you add up all the numbers and then divide by the number of numbers. The "**median**" is the "middle" value in the list of numbers. To find the median, your numbers have to be listed in numerical order from smallest to largest, so you may have to rewrite your list before you can find the median. The "**mode**" is the value that occurs most often. If no number in the list is repeated, then there is no mode for the list.

dp,i (µm)			dp,i (µm)			
7.5			7.5		**Mean**	32.2
80.0			10.0		**Mode**	17.5
12.5			12.0		**Median**	22.5
17.5			12.5			
10.0			15.0			
12.0			17.5			
22.5			17.5			
27.5			17.5			
15.0			22.0			
32.5			22.5			
37.5			27.5			
42.5			32.5			
17.5			37.5			
47.5			42.5			
52.5			47.5			
17.5			52.5			
22.0			57.5			
57.5			80.0			
80.0			80.0			

Size distribution - Discrete distribution: from histogram

- n size ranges
- g_i = weight of particles within i^{th} size range
- frequency f_i distribution:

  f_i = fraction of particles with diameter included within lower (d_i) and higher (d_{i+1}) limit of i^{th} size range

$$f_i = {}^{g_i}\!/_{G} = \text{weight fraction of } i^{th} \text{ size range} = \text{frequency of } i^{th} \text{ size range}$$

$$\text{Since: } \sum_1^n g_i = G = \text{total weight of particles sample} \Rightarrow \sum_1^n f_i = \sum_1^n \left({}^{g_i}\!/_{G}\right) = \frac{\sum_1^n g_i}{G} = 1$$

- cumulative frequency Fi distribution:

Fi = fraction of particles with diameter ≤ higher limit of j_{th} size range

$$F_i = \frac{\sum_1^j g_i}{\sum_1^n g_i} = \frac{\sum_1^j g_i}{G} = \sum_1^j f_i$$

$$\Rightarrow F_n = \sum_1^n f_i = 1 \text{ where } n = \text{total number of size bins}$$

Size distribution - Continuous distribution

- $F(d_p)$ = continuous cumulative mass fraction distribution function → cumulative mass probability density function
- $f(d_p)$ = continuous mass fraction distribution function → mass probability density function

By definition: $f(d_p) = \frac{dF(d_p)}{d(d_p)}$

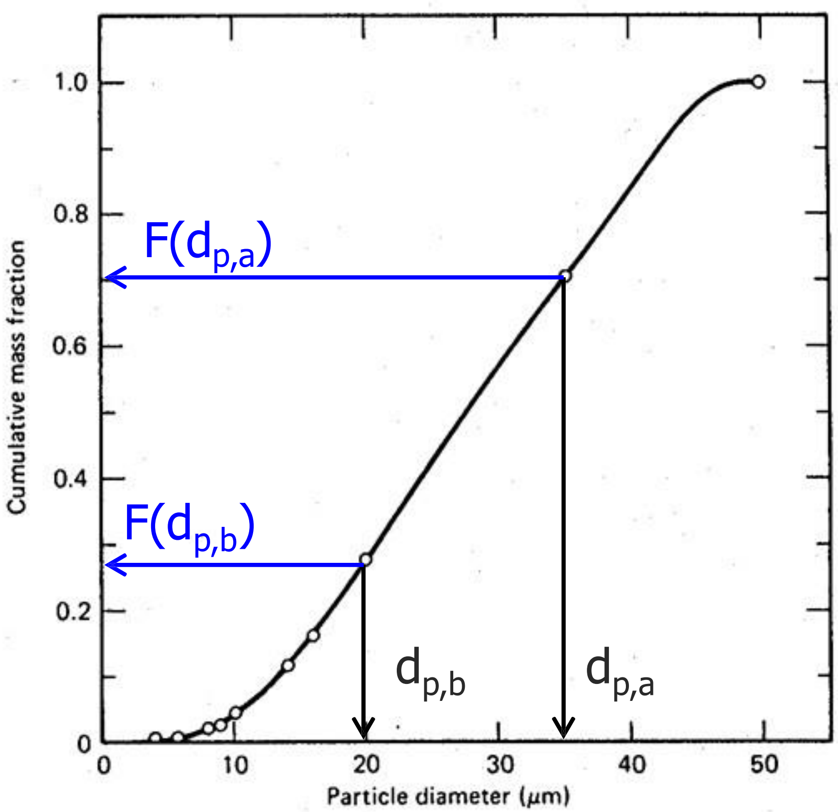
Therefore: $F(d_p) = \int_0^{d_p} f(d_p)\, d(d_p) \approx \sum_1^j f_i$

$$\int_0^\infty f(d_p)\, d(d_p) = 1 \Leftrightarrow \sum_1^n f_i = 1$$

where n = total number of size bins

In terms of a <u>discrete distribution</u>:

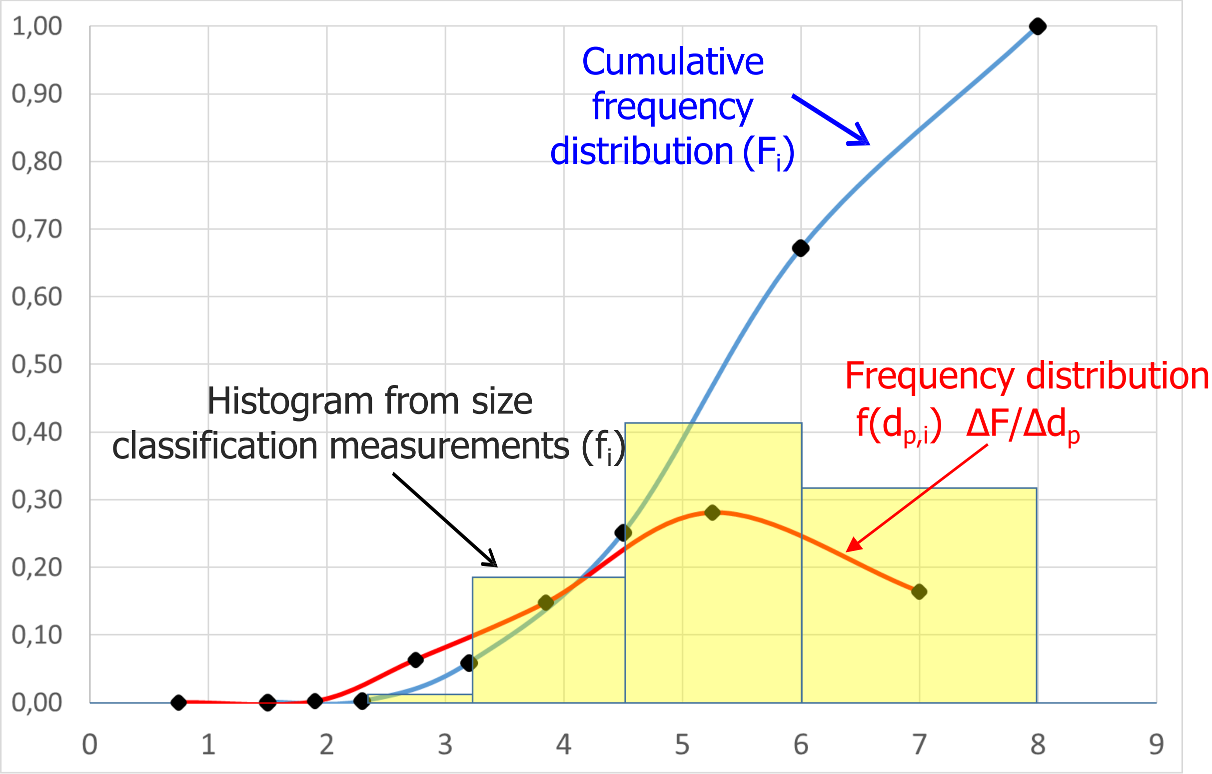
$$f(d_p) \approx \frac{\Delta F}{\Delta d_p} = \frac{F(d_{p,a}) - F(d_{p,b})}{d_{p,a} - d_{p,b}}$$



utilized for evaluating $f(d_p)$ from size classification measurements

Size distribution: example

Size bin	Diameter range of size bin (μm)	Central diameter of size bin (μm)	Weight fraction of size bin (f_i)	Cumulative weight fraction of size bin (F_j)	$\Delta F=F_b - F_a$	$\Delta d_p=d_{p,b} - d_{p,a}$	$\Delta F/\Delta d_p$
1	0 - 1.5	(0+1.5)/2=0.75	$5\cdot10^{-4}$	$5\cdot10^{-4}$	$5\cdot10^{-4}$	1.5	$3,5\cdot10^{-4}$
2	1.5 - 2.3	(1.5+2.3)/2=1.90	0.0015	$0.0015+5\cdot10^{-4}=0.0016$	0.0015	0.8	0.0019
3	2.3 - 3.2	(2.3+3.2)/2=2.75	0.057	0.057+0.0016 = 0.059	0.057	0.9	0.063
4	3.2 - 4.5	(3.2+4.5/2=3.85	0.192	0.192+0.059 = 0.251	0.192	1.3	0.148
5	4.5 - 6.0	(4.5+6)/2=5.25	0.421	0.421+0.251 = 0.672	0.421	1.5	0.281
6	6.0 - 8.0	(6+8)/2=7.00	0.328	0.672+0.328 = 1	0.328	2	0.164
			1.000				



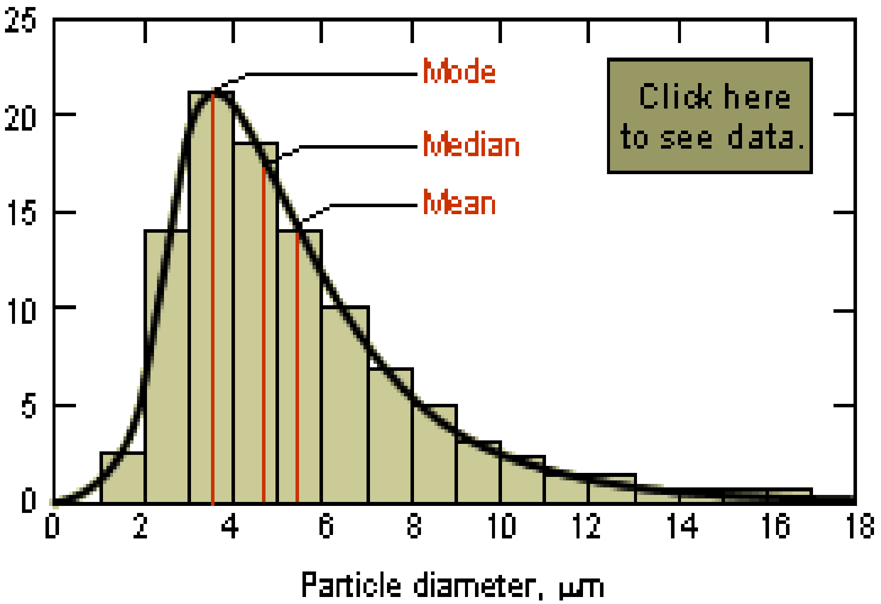
Cumulative frequency distribution (F_i)

Histogram from size classification measurements (f_i)

Frequency distribution $f(d_{p,i})$ $\Delta F/\Delta d_p$

Size distribution: Statistical distribution

- synthetic characterization of size distributions → location, dispersion
- location
  - arithmetic mean M_a: mean diameter of the mass size distribution
  - median diameter M_d: diameter of particle corresponding to a cumulative mass fraction F of 50% (particle size splitting the distribution into two equal mass fractions) → 50th percentile of cumulative mass size distribution
  - mode diameter d_{max}: diameter of particles corresponding to the maximum mass fraction f (more frequent size of particles in the distribution) → $df(d_p)/d(d_p) = 0$



Size distribution: Statistical distribution

Location parameters

- arithmetic mean Ma
  - Continuous distribution : $M_a = \int_0 f(d_p)\, d(d_p)$
  - Discrete distribution : $M_a = \sum f_i \cdot d_{p,i}$
- median diameter M_d: derived graphically from cumulative mass fraction distributions $F(d_p)$
- mode diameter d_{max}: derived graphically from mass fraction distributions $f(d_p)$

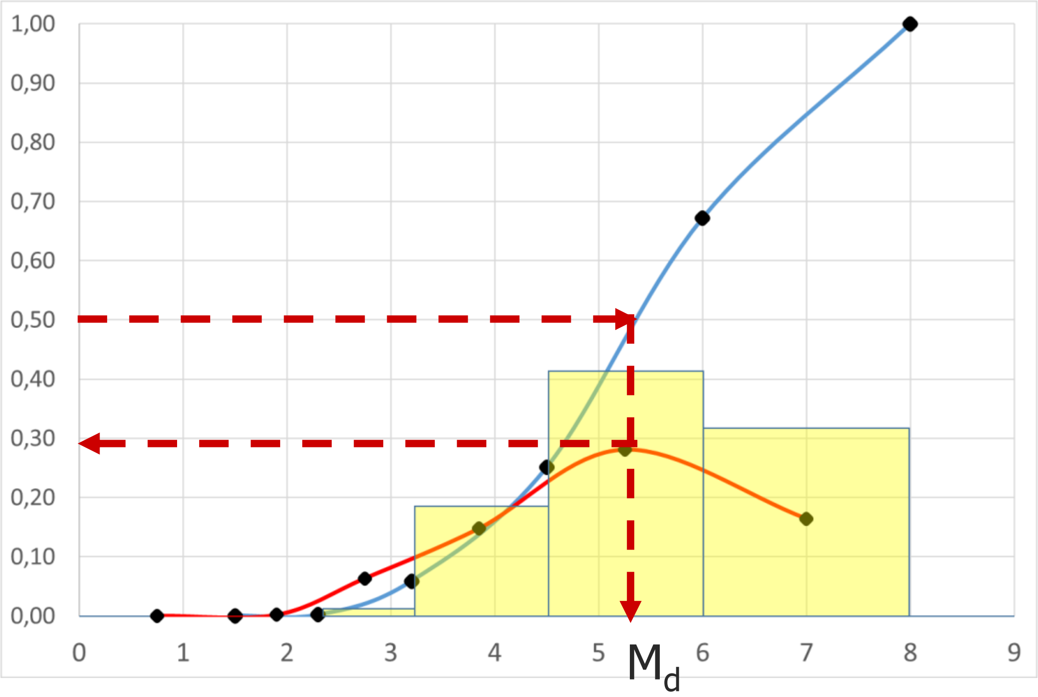
Dispersion parameters

- standard deviation S_a
  - Continuous distribution: $S_a = \left[\int_0^\infty (d_p - M_a)^2 f(d_p) d(d_p)\right]^{1/2}$
  - Discrete distribution: $S_a = \left[\sum_1^n (d_{p,i} - M_a)^2 f_i\right]^{1/2}$
- dispersion coefficient D: $D = S_a / M_a$
- range R: $R = d_{p,max} - d_{p,min}$

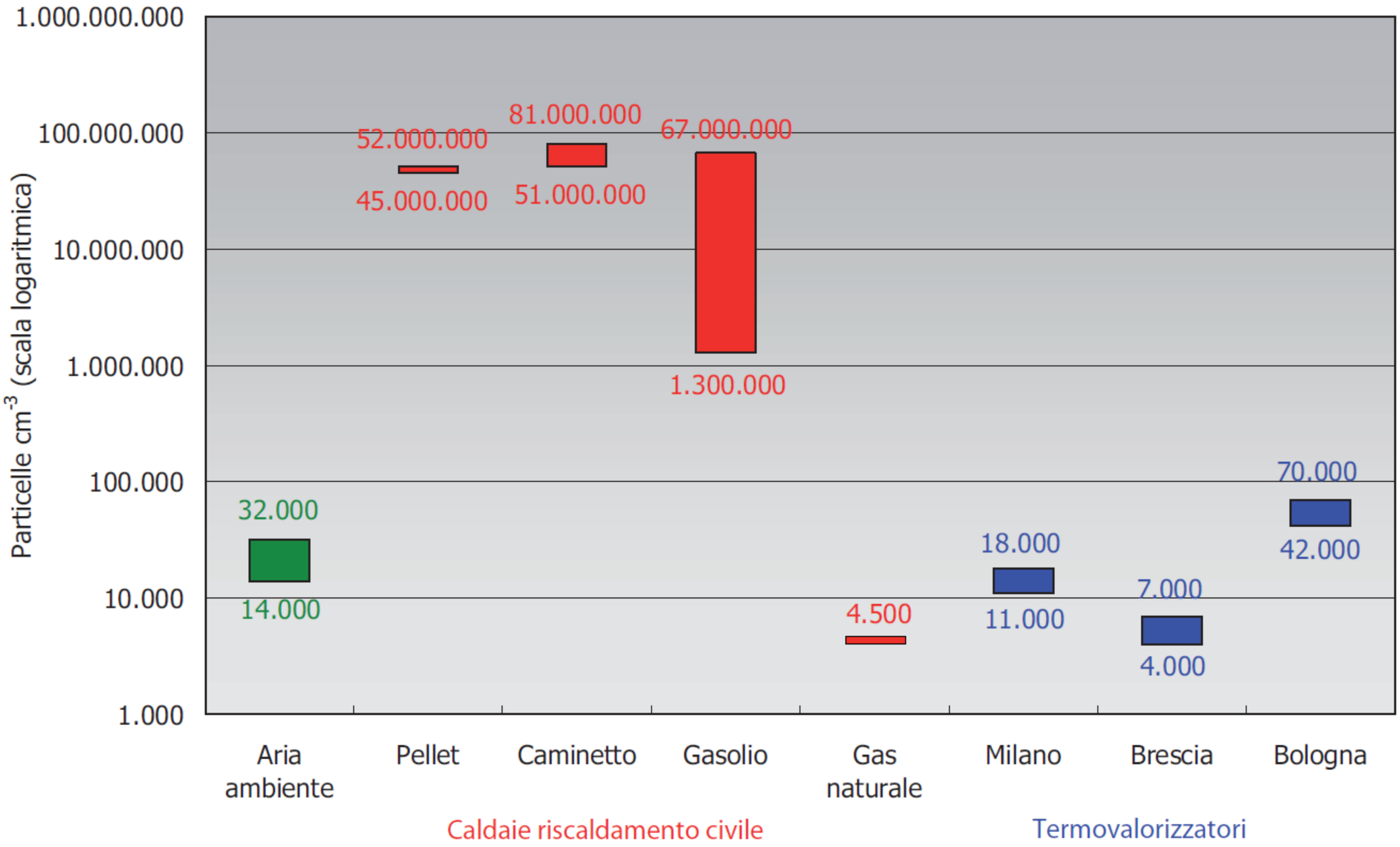
Size distribution: Statistical distribution

Size bin	Diameter range of size bin (µm)	Weight fraction of size bin (f_i)	Cumulative weight fraction of size bin (F_j)	$\Delta F/\Delta d_p$
1	0 - 1.5	$5\cdot10^{-4}$	$5\cdot10^{-4}$	$3{,}5\cdot10^{-4}$
2	1.5 - 2.3	0.0015	0.0016	0.019
3	2.3 - 3.2	0.057	0.059	0.063
4	3.2 - 4.5	0.192	0.251	0.148
5	4.5 - 6.0	0.421	0.672	0.281
6	6.0 - 8.0	0.318	1	0.164

M_a = 5.4 µm
S_a = 2.5 µm
M_d = 5.3 µm
d_{max} = 5.3 µm
f_{max} = 0.28

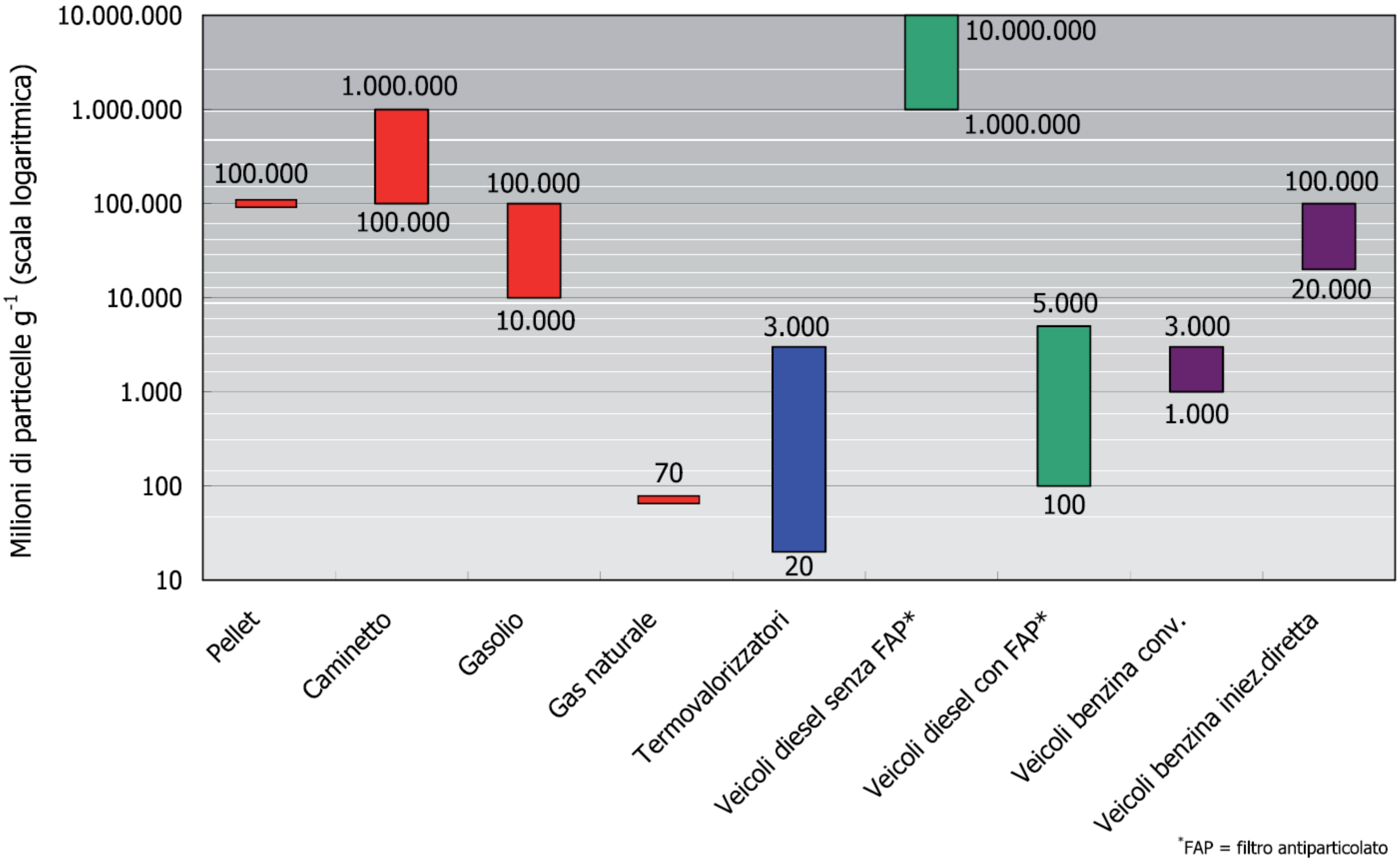


Ultrafine (< 0.1 µm) particulates



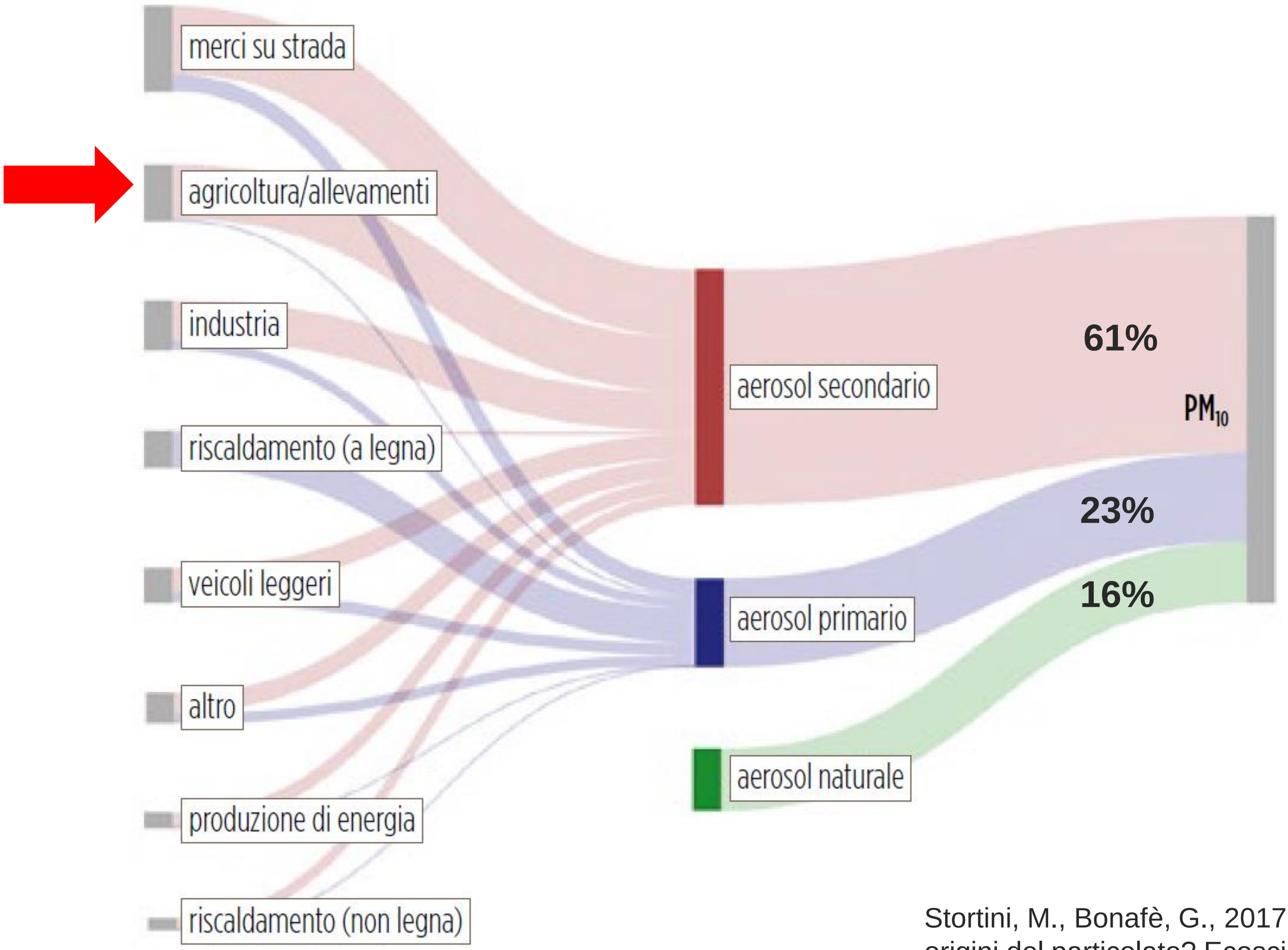
Reference: Stefano, P., Michele, P., Consonni, P.S., Coghe, P.A., Apostoli, P. Pietro, Sperimentale, M., Bergamaschi, P.E., Medica, C., 2010. Emissioni di Polveri Fini e Ultrafini da impianti di combustione. Sintesi finale.

Ultrafine (< 0.1 µm) particulates



Reference: Stefano, P., Michele, P., Consonni, P.S., Coghe, P.A., Apostoli, P. Pietro, Sperimentale, M., Bergamaschi, P.E., Medica, C., 2010. Emissioni di Polveri Fini e Ultrafini da impianti di combustione. Sintesi finale.

Source of PM10 in Emilia Romagna Region



Stortini, M., Bonafè, G., 2017. Quali sono le origini del particolato? Ecoscienza 12–13.

NO and NO_2

NO and NO_2

ALL COMBUSTION PROCESSES PRODUCE NO (a precursor of NO_2)

The way NO is produced: $N_2 + O_2 = 2\ NO$

Note:

1. Kp at ambient temperature is very, very low. (in addition, the constant velocity is also very low) → no production of NO at ambient temperature!
2. The process is endothermic (high temperatures shift the eq. towards right, thus increasing Kp and the production of NO) → maximum temperature control is important to prevent NO production!
3. NO is the main component of flue gases (about 90%, the remain. is NO_2)
4. Conversion (or oxidation) of NO to NO_2 is favored after the emission to the air, because $NO + 1/2\ O_2 = NO_2$ is an exothermic process.

NO and NO_2

Nitric oxide (NO) is formed by either of both of two mechanisms – Thermal NOx or fuel NOx:

- **Thermal NOx** is the NOx formed by reactions between nitrogen and oxygen in the air used for combustion. The rate of formation of thermal NOx is extremly temperature sensitive and becomes rapid only at «flame» temperatures (3000-3600 °F)
- **Fuel NOx** results from the combustion of fuels that contain organic nitrogen in the fuel (primarily coal or heavy oil). Not all organic nitrogen is converted to NOx. The oxidation of fuel nitrogen to NO is highly dependent on the air/fuel ratio.

Successful control of NOx depends on an understanding of the fundamental principles (thermodynamic and kinetics) of NOx formation.

Thermal NOx - equilibrium

The three principal reactions (the extended Zeldovich mechanism, 1946) producing thermal NOx are:

1) $N_2 + O \leftrightarrow NO + N$
2) $N + O_2 \leftrightarrow NO + O$
3) $N + OH \leftrightarrow NO + H$

If we consider only the thermodynamics of NO_X formation, we can begin

$N_2(g) + O_2\ (g) = 2\ NO\ (g)$ ***Kp1*** Endothermic reaction

$NO\ (g) + ½\ O_2\ (g) = NO_2\ (g)$ **Kp2** Exothermic reaction

$$Kp1 = \frac{(P_{NO})^2}{P_{N_2} * P_{O_2}} = \frac{(y_{NO})^2}{y_{N_2} * y_{O_2}}$$

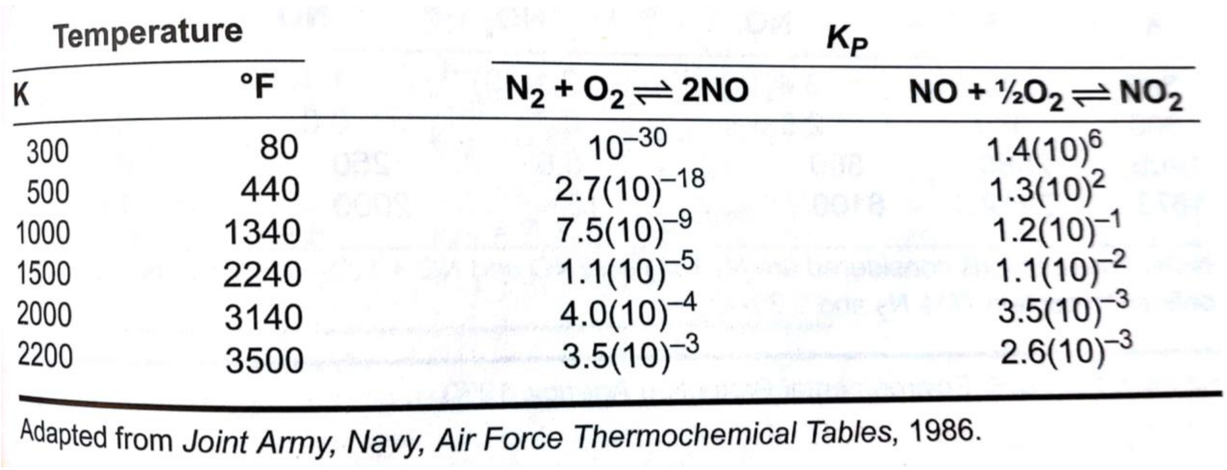
$$Kp2 = \frac{P_{NO_2}}{(P_{NO}) * (P_{O_2})^{1/2}} =$$

$$= (P_T)^{1/2} * \frac{y_{NO_2}}{(y_{NO}) * (y_{O_2})^{1/2}}$$

Where:

- Kp= equilibrium constant
- Pi=partial preassure of component i (atm)
- yi= mole fraction of component i
- Pt= total preassure (atm)

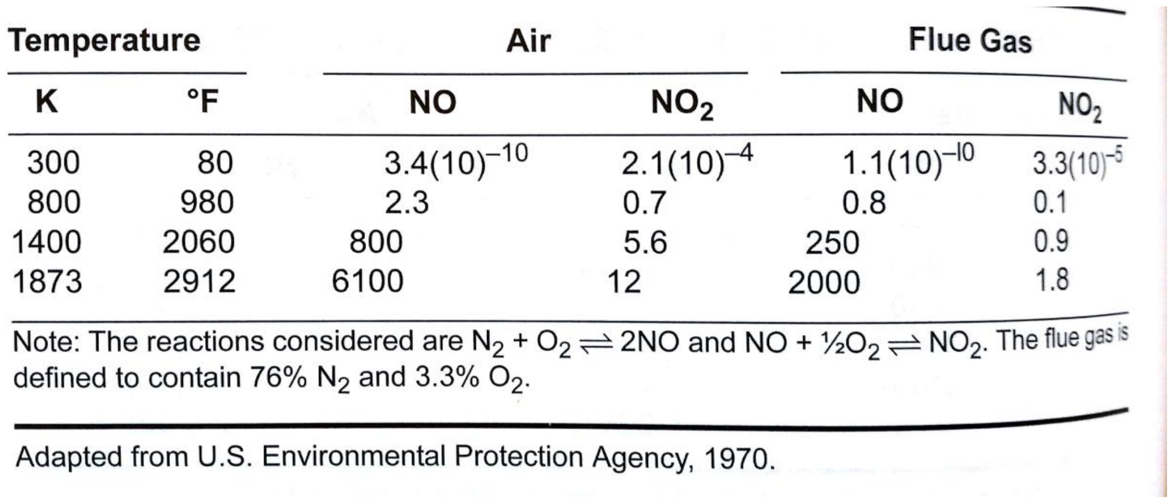
Thermal NOx - equilibrium



Temperature		K_P	
K	°F	$N_2 + O_2 \rightleftharpoons 2NO$	$NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$
300	80	10^{-30}	$1.4(10)^{6}$
500	440	$2.7(10)^{-18}$	$1.3(10)^{2}$
1000	1340	$7.5(10)^{-9}$	$1.2(10)^{-1}$
1500	2240	$1.1(10)^{-5}$	$1.1(10)^{-2}$
2000	3140	$4.0(10)^{-4}$	$3.5(10)^{-3}$
2200	3500	$3.5(10)^{-3}$	$2.6(10)^{-3}$

Adapted from *Joint Army, Navy, Air Force Thermochemical Tables*, 1986.

Equilibrium Constants for the formation of NO and NO_2



Temperature		Air		Flue Gas	
K	°F	NO	NO_2	NO	NO_2
300	80	$3.4(10)^{-10}$	$2.1(10)^{-4}$	$1.1(10)^{-10}$	$3.3(10)^{-5}$
800	980	2.3	0.7	0.8	0.1
1400	2060	800	5.6	250	0.9
1873	2912	6100	12	2000	1.8

Note: The reactions considered are $N_2 + O_2 \rightleftharpoons 2NO$ and $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$. The flue gas is defined to contain 76% N_2 and 3.3% O_2.

Adapted from U.S. Environmental Protection Agency, 1970.

Calculated Equilibrium concentrations (in ppm) of NO and NO_2 in Air and Flue Gas

- Incineration of MSW: T> 850°C; NOX ↑
- Incineration of MSW with clorinated compunds: T> 1100°C; NOX ↑↑

In flue gas: NO 90-95% v/v
NO_2: 5-10%

NOx control for stationary sources

Combustion modifications in order to:

- Reduce peak temperatures of the flame zone
- Reduce gas residence time in the flame zone
- Reduce oxygen concentrations in the flame zone

Flue gas treatment techniques

- Selective Catalytic reduction (SCR)
- Selective Noncatalytic reduction (SNR): high temperature
- Wet absorption with SOx: low solubility of NO

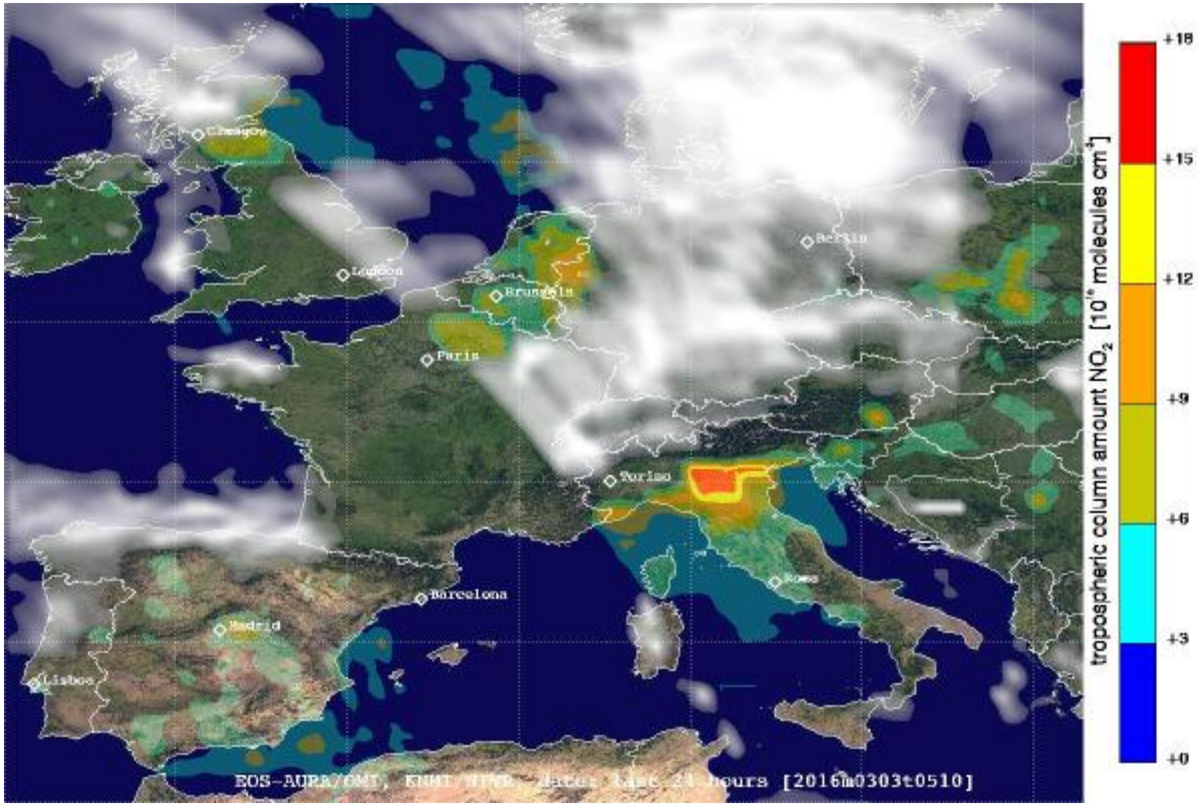
NO and NO_2

WINTER

TROPOSPHERIC NO_2

Daily OMI tropospheric NO_2 (air pollution and air quality) satellite measurements.

NO_2 Air pollution over Western Europe – 03.03.2016

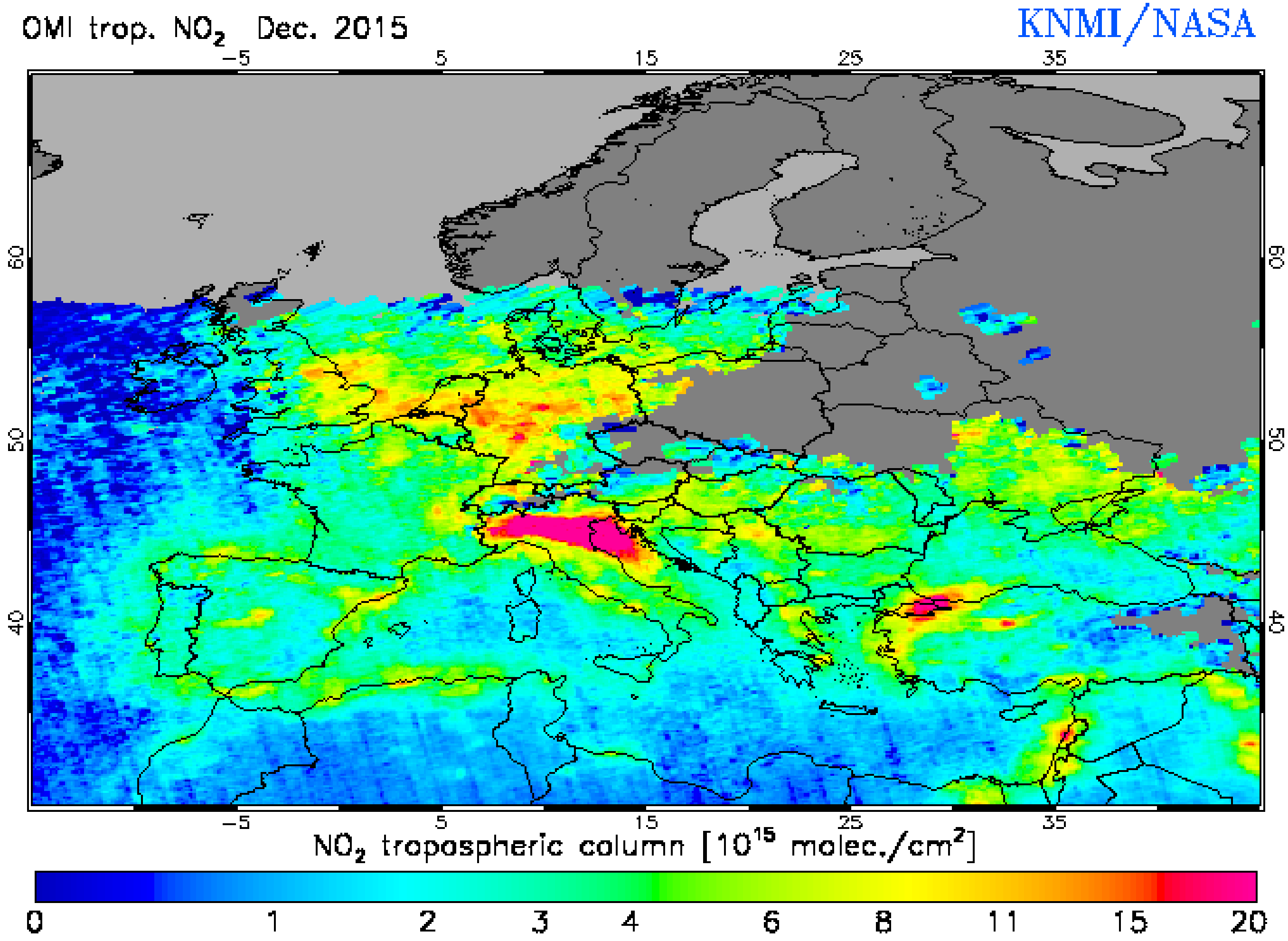


NO and NO_2

WINTER

TROPOSPHERIC NO_2

NO_2 Air pollution over Western Europe – December 2015

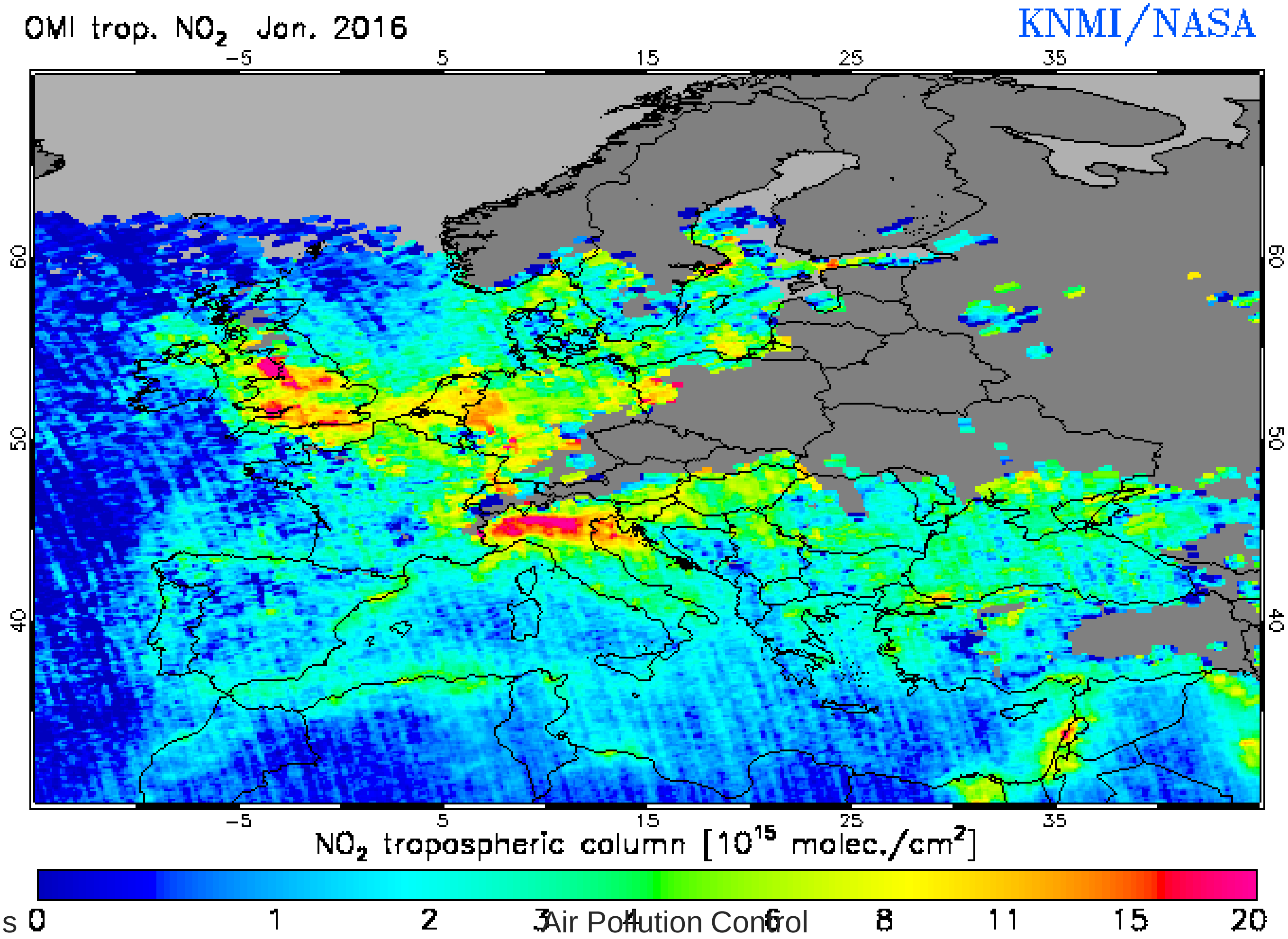


NO and NO_2

WINTER

TROPOSPHERIC NO_2

NO_2 Air pollution over Western Europe –January 2016

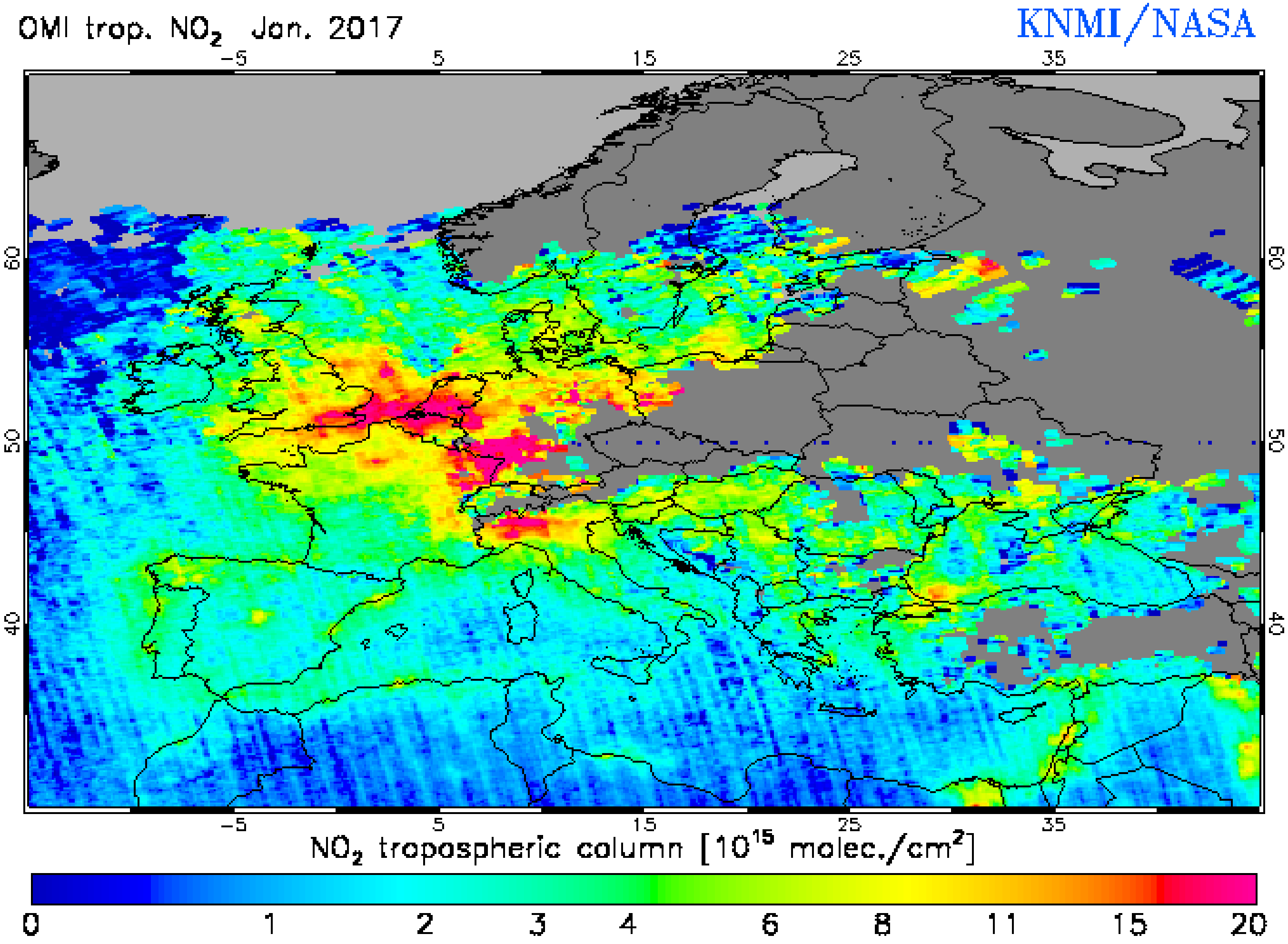


NO and NO_2

WINTER

TROPOSPHERIC NO_2

NO_2 Air pollution over Western Europe – JANUARY 2017 (monthly mean)

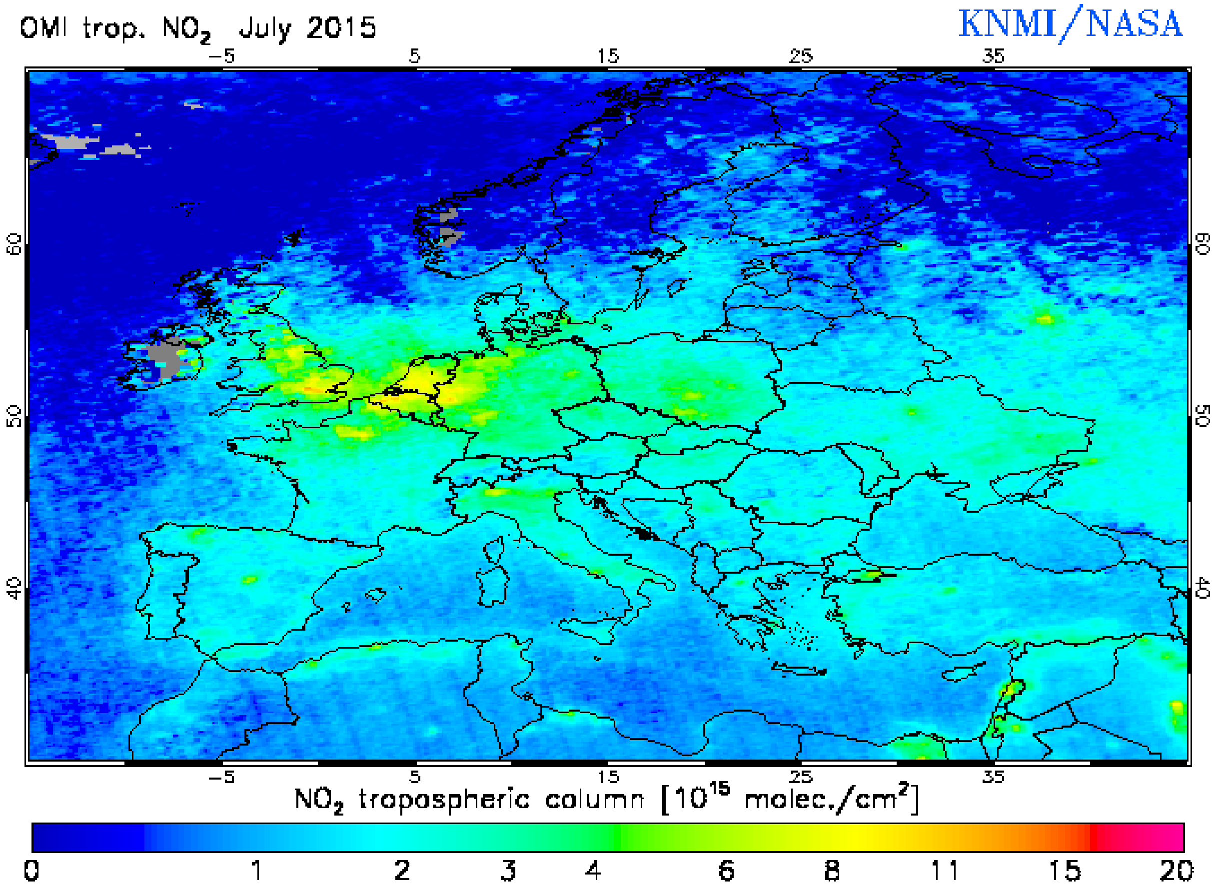


NO and NO_2

SUMMER

TROPOSPHERIC NO_2

NO_2 Air pollution over Western Europe –July 2015

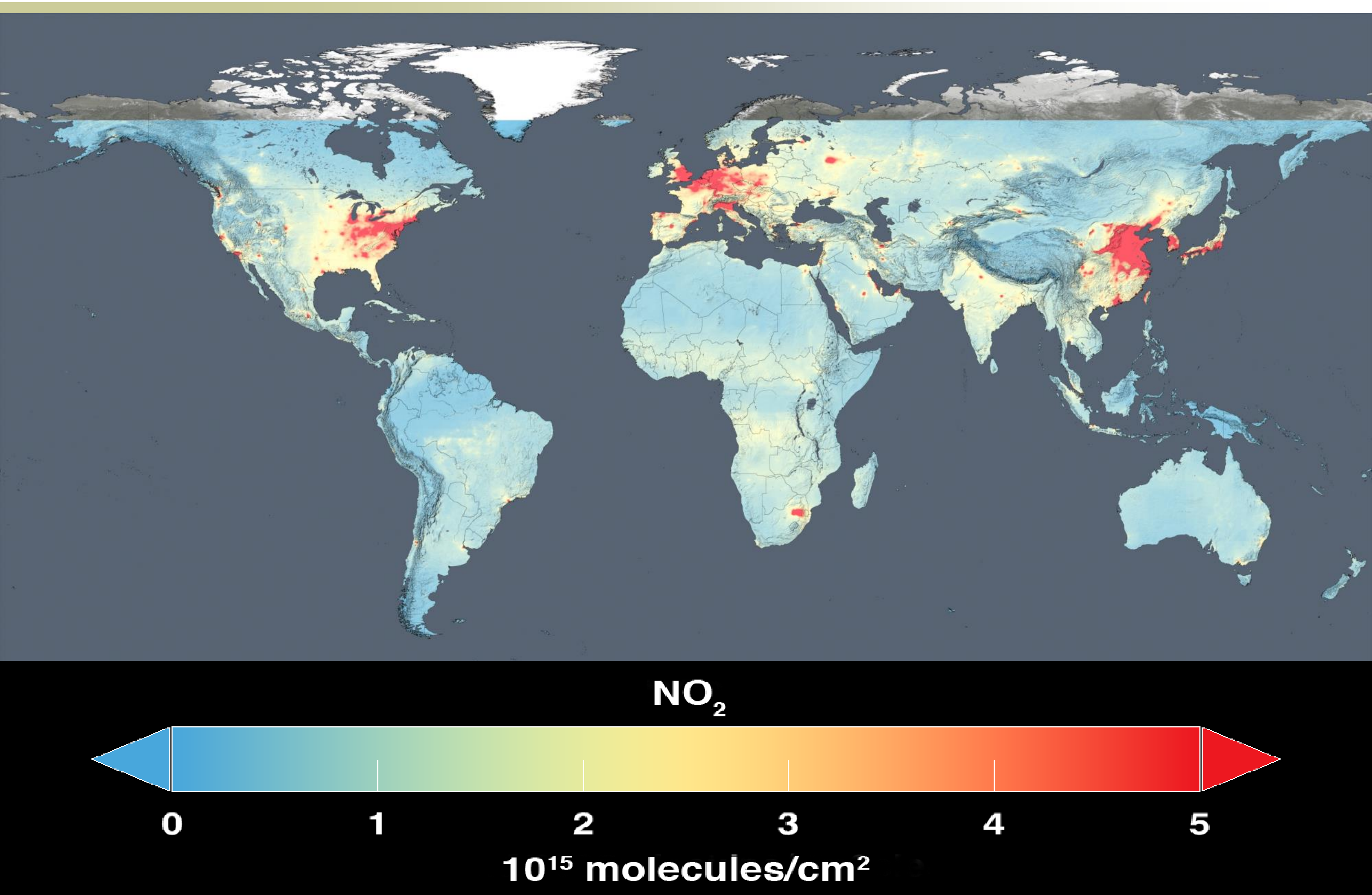


IN THE SUMMER THE NO_2 LEVEL IN PIANURA PADANA IS ABOUT ONE THIRD OF THAT IN THE WINTER

WHY?

NO and NO_2

This global map shows the concentration of nitrogen dioxide in the atmosphere as detected by the Ozone Monitoring Instrument aboard the Aura satellite, averaged over 2005. (https://svs.gsfc.nasa.gov/12094)



SO_2

Sulfur dioxide

SO_2 is the main sulfur oxide emitted into the atmosphere, where it is slowly oxidized to SO_3. Both SO_2 and SO_3 (SOx) can form **acids** when they hydrolyze with water. Make up 5 to 20% of total suspended particles.

CAUSES:

SOx are caused by burning sulfur or processing material containing sulfur.

SOURCES:

- Fossil fuel combustion for electric power generation (the main source by far)
- Industrial processes (petroleum refining, nonferrous metal smelting).

EFFECTS:

Environment. They react in the atmosphere to form acids, sulfates and sulfites: Contributes to acid rain.

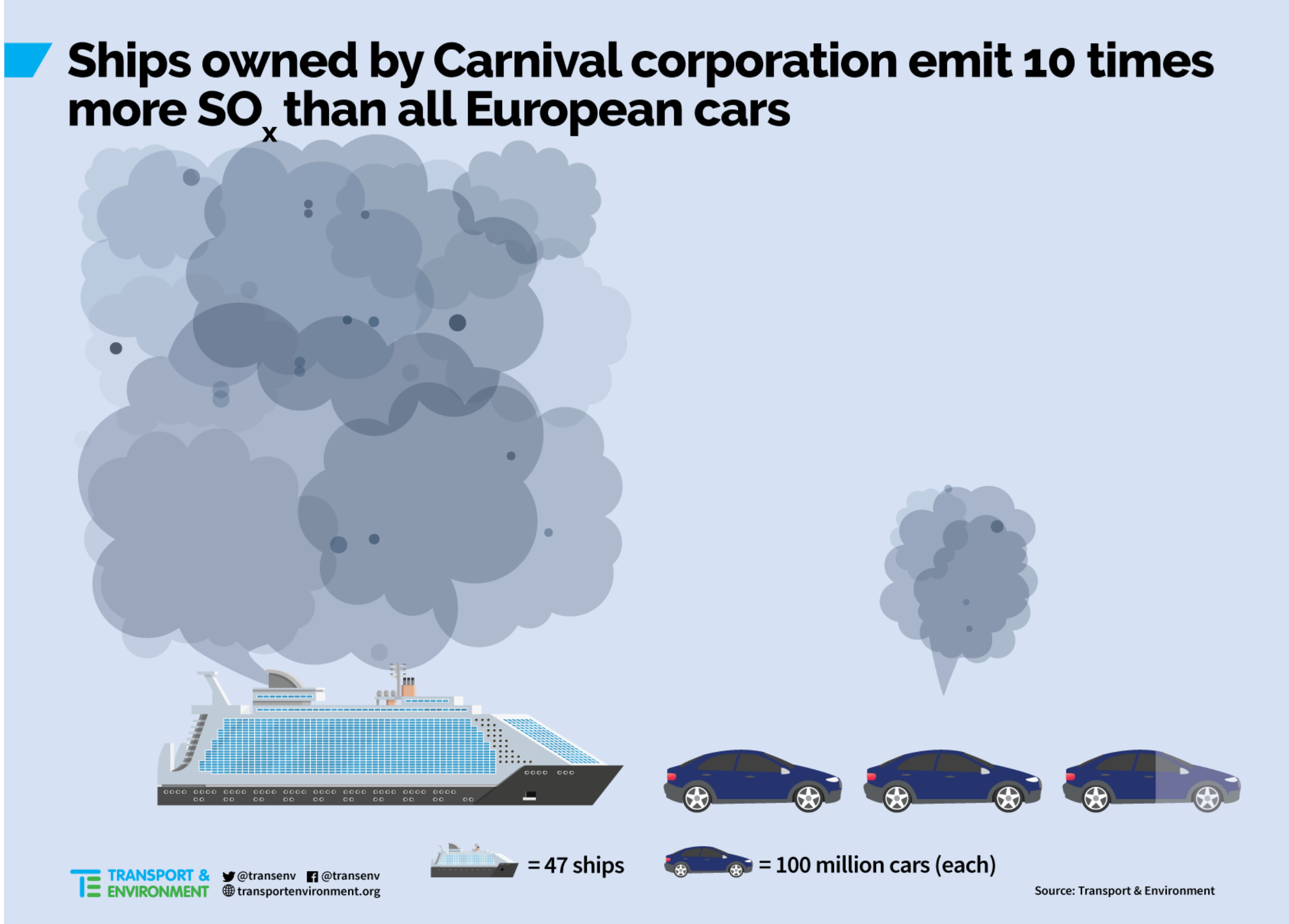
Goods. Major damage to materials (corrosion).

Health. **Humans and animals**: SO_2 is soluble and it is readily absorbed in the upper respiratory tract (bronchoconstriction; eye, nose, throat irritation).

SO_2 effects are intensified by the presence of other pollutants, especially particulates. Particulate SO_2 (or inert particulate with adsorbed SO_2) can penetrate deep into the lungs and induce severe effects.

Plants: Chlorosis (loss of chlorophyll); Plasmolysis (tissue collapse of leaf cells); reduced growth in presence of acid deposition.

Transport & Environment, 2019. One Corporation to Pollute Them All.



Source: Transport & Environment

High emissions are due to insufficient stringency of the marine fuel quality and engine emissions standards.

CO

Carbon monoxide

Odorless, colorless gas.

CAUSES:
Caused by incomplete combustion of any carbonaceous fuel.

SOURCES:
Most of it comes from motor vehicles (power plants/large furnaces are usually designed and operated carefully enough to ensure (nearly) complete combustion). Thus the major source is the transportation sector. A significant fraction is also produced by residential heating and some industrial processes.

EFFECTS:
Goods. None.
Health. Inert for materials (but also for plants), but very toxic for **humans**.
Since it reacts with hemoglobin, it reduces the transport of O_2 through the bloodstream (Hemoglobin has 210 times affinity for CO as for oxygen).
Effects on humans range from slight headaches to nausea to death.
Poses immediate health risk in high concentrations (> 750 ppm).
Affects mental functions and visual acuity, even at low levels.

Pb

Lead

Long known as one of the worst toxics in common use.

CAUSES:

Present as additive in gasoline as TEL - tetraethyl lead, (used as octane rating booster), now banned in most industrialized countries.

Present in batteries factories and many products.

SOURCES:

Emitted from battery factories and non-ferrous smelters (metal processing), gasoline additives (especially in the recent past).

EFFECTS:

Health. Affects various organs and can cause sterility and neurological impairment, e.g. retardation and behavioral disorders.

Infants and children especially susceptible.

<u>Control of mobile sources has been exceptionally successful</u>, but there is plenty left in solid form.

H_2S

Background

H_2S, is a common source of odour complaints. Typical H_2S diffuse sources: WWTP - waste water treatment plants (sewer gas), landfill plants (landfill gas), biotreatment plants (biogas), tanning industries, ..

Production of H_2S should be expected from many S-containing materials – particularly organics - under anaerobic conditions (biologic anaerobic degradation → S(-II) minimum Oxn. Number; a parallel behaviour we have with organic C-materials → CH_4!, where C(-IV), and N-cont. → NH_3, …

Cysteine and methionine are **sulfur-containing amino acids;** some vegetables contain sulfur, too.

H_2S has a very low, 0.3 ppmv, odour threshold; it is source of 'rotten egg' odours; similar behaviour have the R-SH (mercaptanes; thioalcohols) and R_2S (Disulfides).

Very low odours have also many organic compounds.

Many Air Pollution problems concern the emission of low concentrations of compounds with very low odour threshold.

Often diffuse sources, that is nonpoint sources (NPS), are concerned.

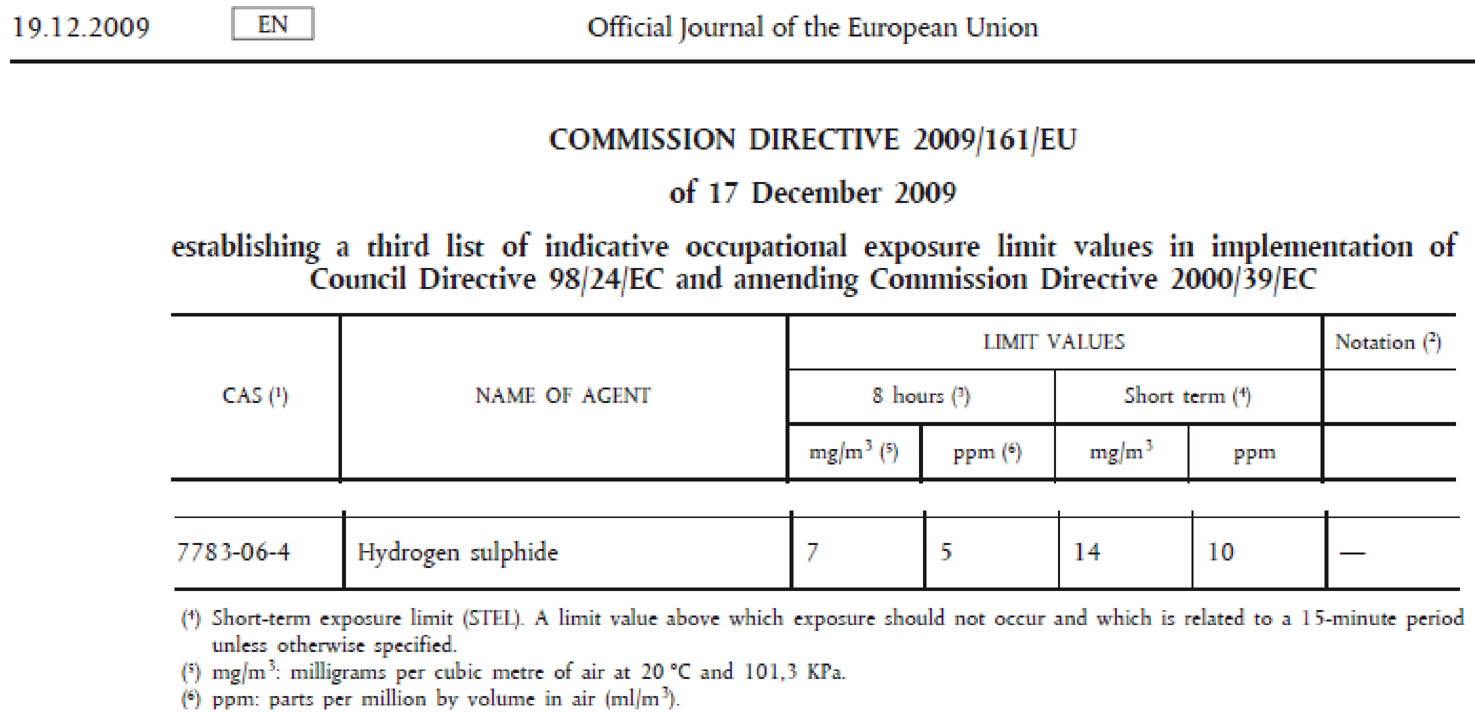
Background

Hydrogen sulfide is HARMFUL → exposure limits (EU, but more from US: ACGIH, OSHA and NIOSH) have been set for workers. TLV – Threshold Limit Values.

EU: 8-hours time-weighted average (**TWA**): 14 mg/m^3 ; short-term exposure limit (**STEL**): 7 mg/m^3.

SAFETY FIRST! Engineers **MUST** know it! **You may be responsible of the lives of the workers**!

Many lethal accidents in industrial and maintainance (O&M) activities! H_2S is a by-product from anaerobic bacterial action on sulfur compounds present in the WW/mud/etc. in closed containers (i.e. SO_4^{2-}). H_2S is a gas slightly solubile in water at pH < 7.



19.12.2009 EN Official Journal of the European Union L 338/87

COMMISSION DIRECTIVE 2009/161/EU

of 17 December 2009

establishing a third list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Commission Directive 2000/39/EC

CAS (1)	NAME OF AGENT	LIMIT VALUES				Notation (2)
		8 hours (3)		Short term (4)		
		mg/m^3 (5)	ppm (6)	mg/m^3	ppm	
7783-06-4	Hydrogen sulphide	7	5	14	10	—

(4) Short-term exposure limit (STEL). A limit value above which exposure should not occur and which is related to a 15-minute period unless otherwise specified.

(5) mg/m^3: milligrams per cubic metre of air at 20 °C and 101,3 KPa.

(6) ppm: parts per million by volume in air (ml/m^3).

Background

H_2S is a <u>weak acid</u> *(weaker than CO_2 $pKa_{1\ CO2} = 6.4$).*

H_2S acid dissociation constants are, at 25 ºC: $pKa_1 = 7.0$

$Ka_{1\ CO2} / Ka_{1\ H2S} = 4$

$$CO_{2(g)} + HS^-_{(aq)} = H_2S_{(g)} + HCO_3^-{}_{(aq)}$$ *(EQ. SHIFTED TO RIGHT)*

$$K_{eq} = Ka1_{(CO2)} / Ka1_{(H2S)} = 10^{-6.4} / 10^{7.0} = 10^{0.6} = 4$$

Corrosion of sour gas under transportation

During the production and transportation of the natural gas, H_2S and CO_2 can cause corrosion in the pipelines. **Generally, the limit for H_2S content is set to 16 ppm for natural gas networks**, but in some areas is 1/4th, that is 4 ppm.

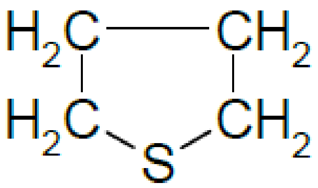
'Pipeline quality' specifications of dry natural gas vary for different EU Countries.

For transportation of liquefied natural gas, the concentrations of CO_2 must be less than 50 parts per million volume (ppmv) to prevent blockage of flow lines and other operational problems that result when CO_2 freezes (*freezing point* of *CO_2* is -78.5 °C. ….*dry ice*) during the chilling of the gas to approximately –160 °C.

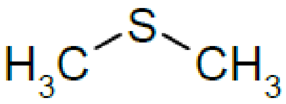
Porto Viro (Rovigo): an example of LNG regassification platform.

Natural gas odorization

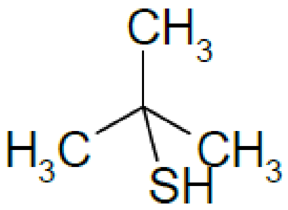
Natural gas odorization. *Bad smelling compounds are added for safety reasons to the NG in the pipelines…(mercaptane, organic sulphides, …)*



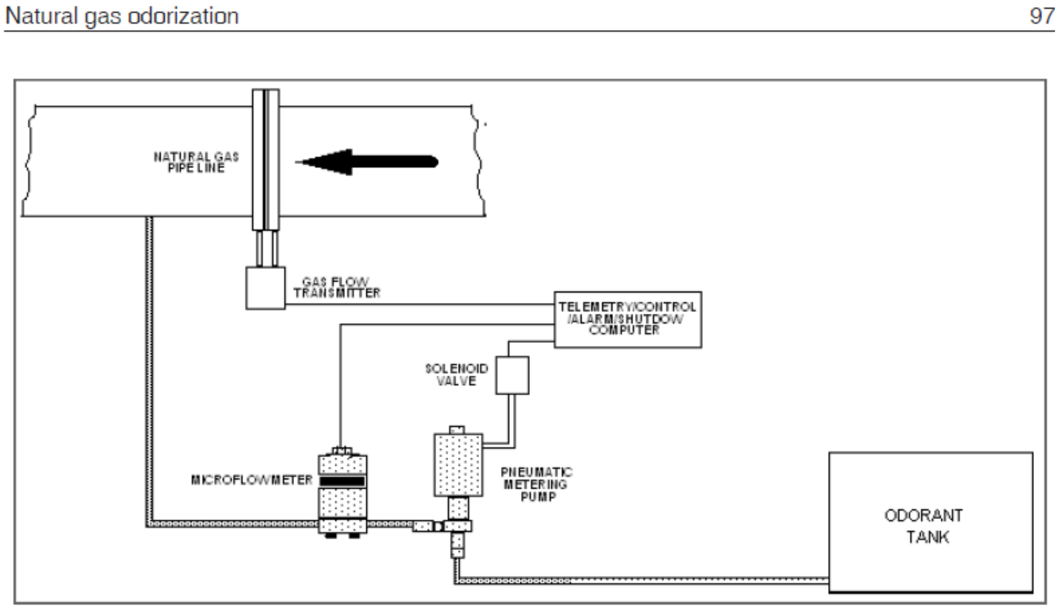
Tetrahydrothiophene



Dimethyl Sulfide



Tert-Butyl Mercaptan



Natural gas odorization 97

TECHNIQUES FOR H_2S REMOVAL FROM DIFFERENT GAS FLOWS

1. Sulphur Recovery from *high gas flows* (*Claus process, e.g. sour natural gas treatment*) *– oil/gas applications only (e.g. Oil refineries)*
2. *LO-CAT → production of S (It is a WS control technique)*
3. “Dry” absorption (*$Fe(OH)_3$ / Fe_2O_3*) *– e.g. Biogas treatment*
4. Wet scrubbing (*NaOH, or NaOH + NaClO*) *– common applications for low gas flows*


Tips To Improve
Your
Knowledge
Knowledge

Brush up

For a brush up on, please visit:

http://ec.europa.eu/environment/air/cleaner_air/index.html#introduction

Cleaner air for all

Every year, more than 400 000 people in the EU die prematurely due to the consequences of air pollution: this is more than 10 times the toll of road traffic accidents. Another 6.5 million people fall sick as air pollution causes diseases such as strokes, asthma and bronchitis. Air pollution also harms our natural environment, impacting both vegetation and wildlife: almost two-thirds of Europe's ecosystems are threatened by the effects of air pollution.

It is time to act to prevent further damage. Find out below how the European Commission proposes to address air pollution in Europe.

Brush up

For a brush up on, please visit:

http://www.minambiente.it/pagina/gli-inquinanti

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