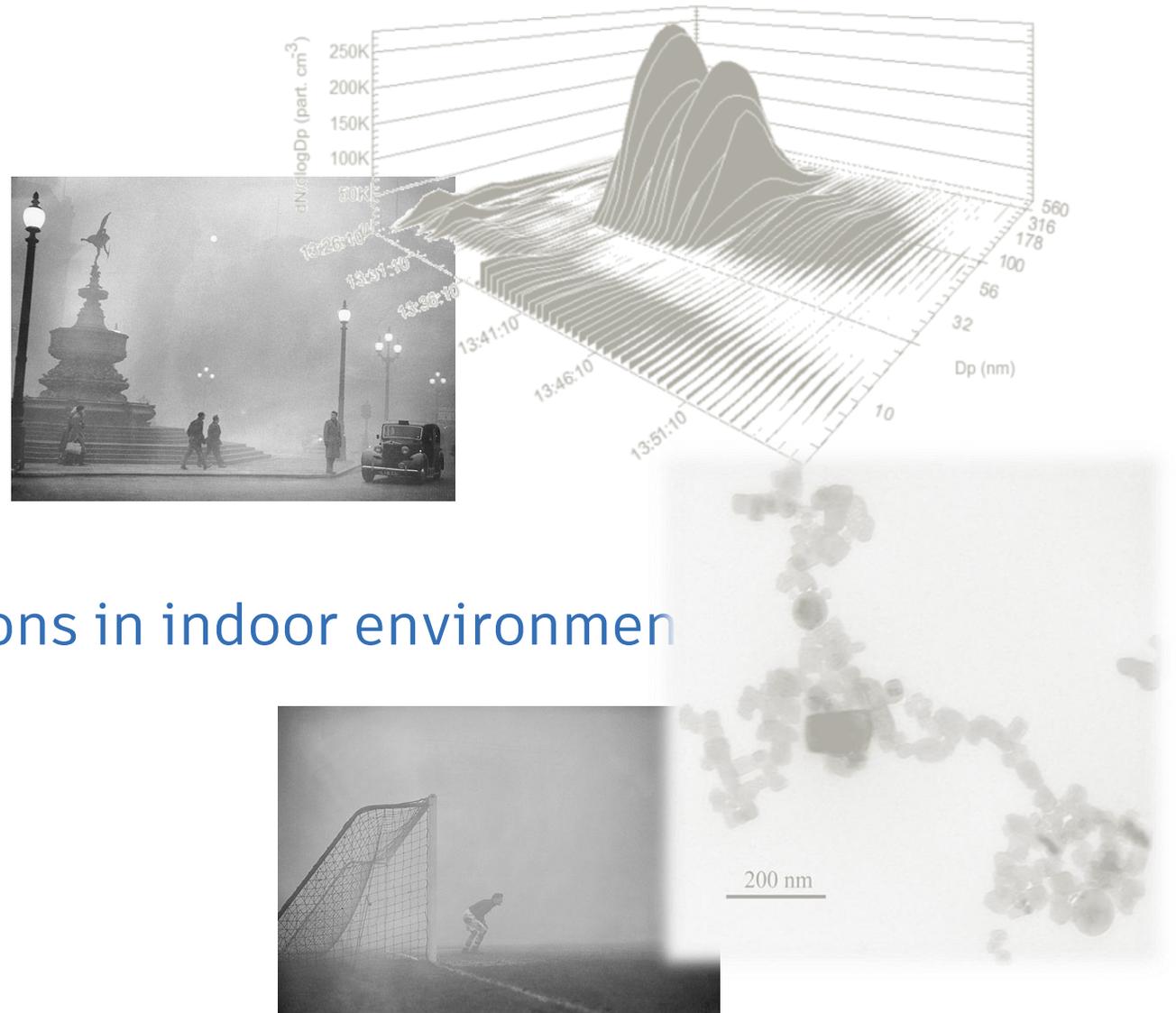


# Environmental particles

# Outlines

- Background information
- Particle thermodynamics
- Particle measurements
- Estimating exposures and emissions in indoor environments
- Research at UNICAS

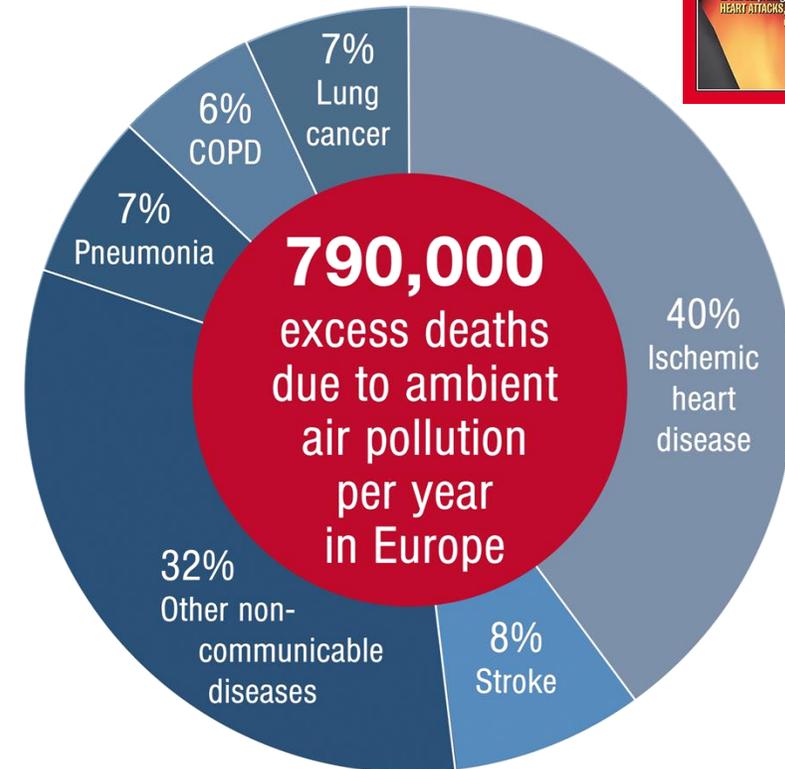


# Background information

# Why studying airborne particles

## Effects on human health

- **Health effects.** Effect on morbidity and mortality in Europe and worldwide. Classified as carcinogenic compound Group 1 (PRESS RELEASE N°221 - Lyon/Geneva, 17 October 2013)
- **Environmental effects.** Airborne particles can also impact the environment. They contribute to air pollution, reducing visibility and contributing to phenomena such as smog. Certain particles, like black carbon, absorb sunlight and can accelerate the melting of ice and snow, thereby contributing to climate change.
- **Climate Change.** Particulate matter plays a complex role in the Earth's climate. Some particles, like sulfates, reflect sunlight and can cool the Earth, while others, like black carbon, absorb sunlight and contribute to warming.



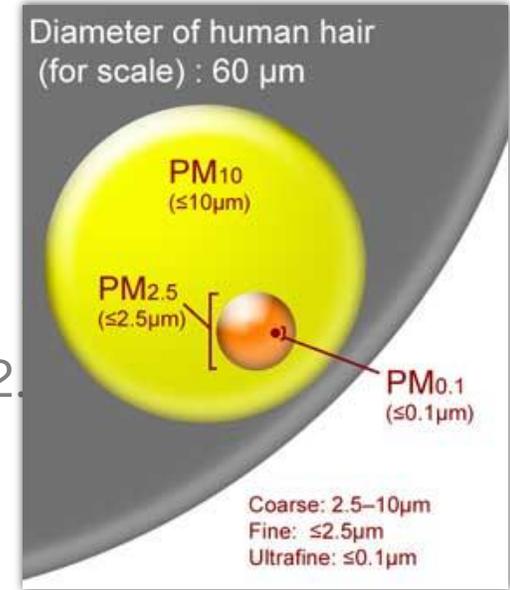
# Definition and classification

## Atmospheric Aerosol

is a metastable suspension of solid or liquid particles in a gas (e.g. air).

## Classification by size

- $PM_{10}$  mass fraction of particles with  $D_{eq} < 10 \mu m$
- Coarse Particles ( $PM_{2.5-10}$ ) mass fraction of particles with  $2.5 \mu m < D_{eq} < 10 \mu m$
- Fine Particles ( $PM_{2.5}$ ) mass fraction of particles with  $D_{eq} < 2.5 \mu m$
- Ultrafine particles (UFPs)  $D_{eq} < 0.1 \mu m$  (100 nm)
- Nanoparticles  $D_{eq} < 0.050 \mu m$  (50 nm)

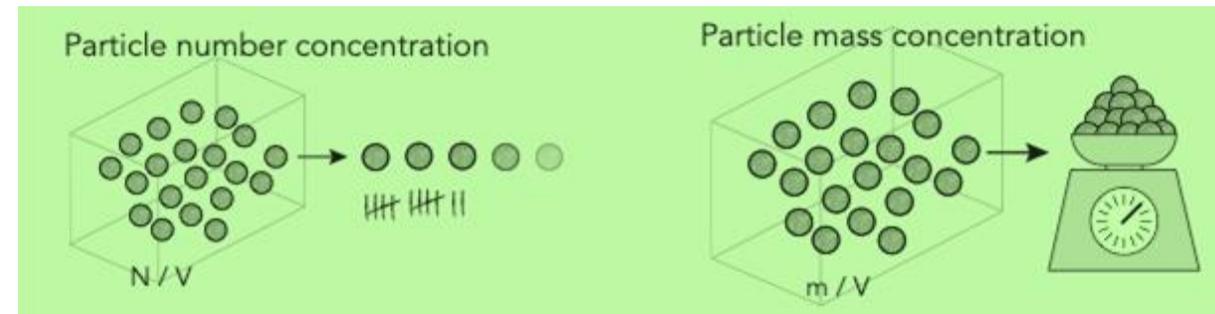


## Origins and sources

- Combustion vs. mechanical generation
- Natural vs. anthropic; primary vs. secondary

## Aerosol metrics and measurement approaches

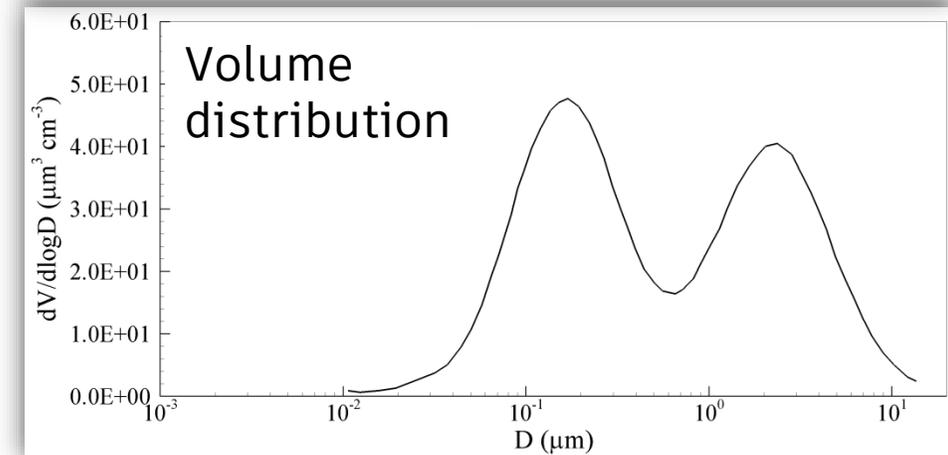
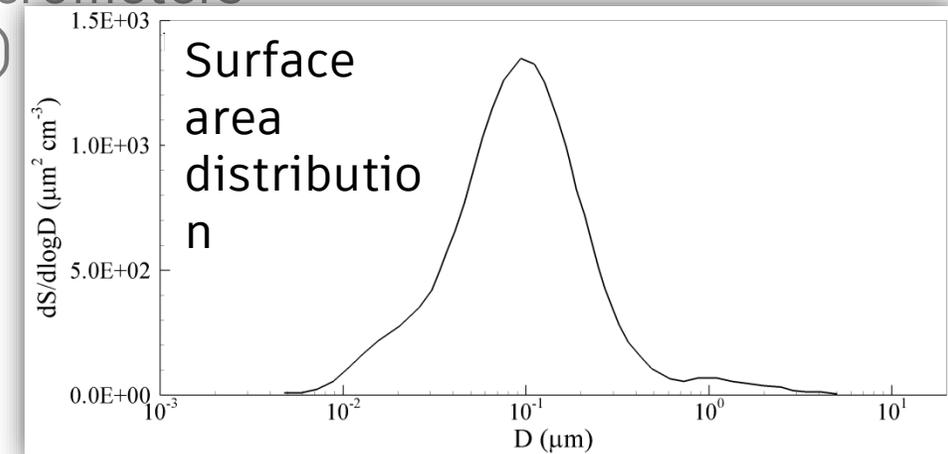
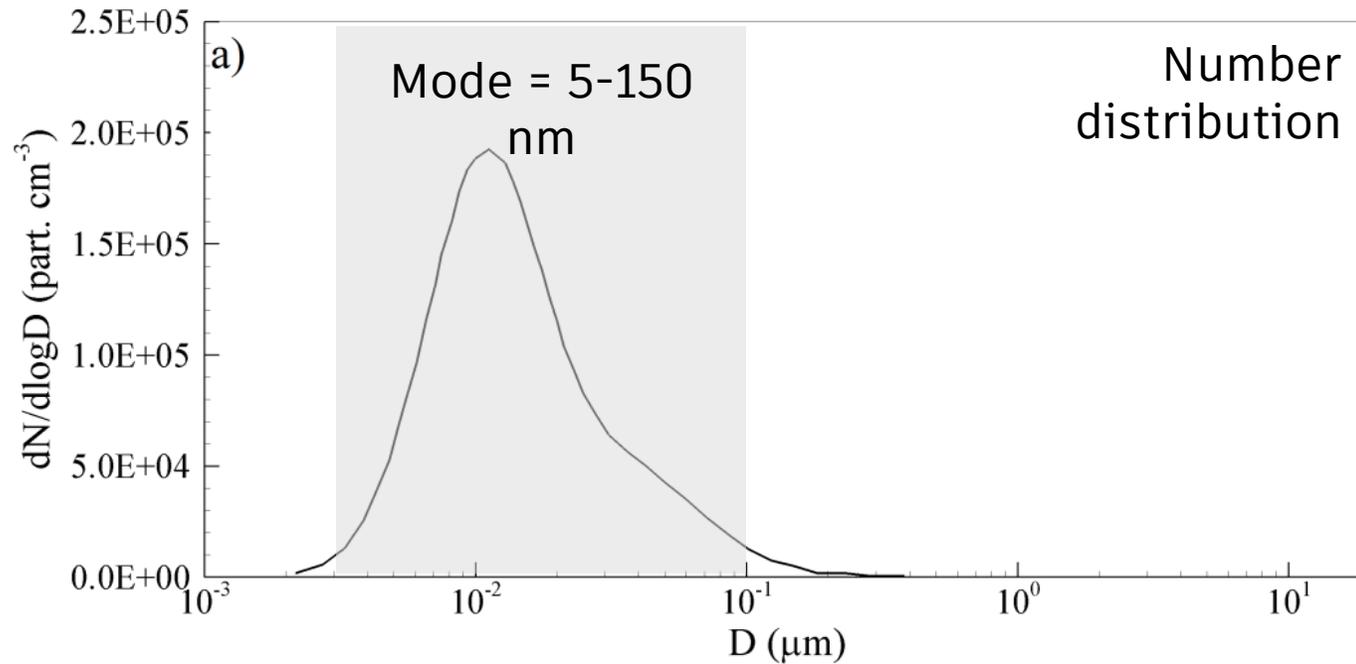
- Number, surface area vs. mass



# Definition and classification

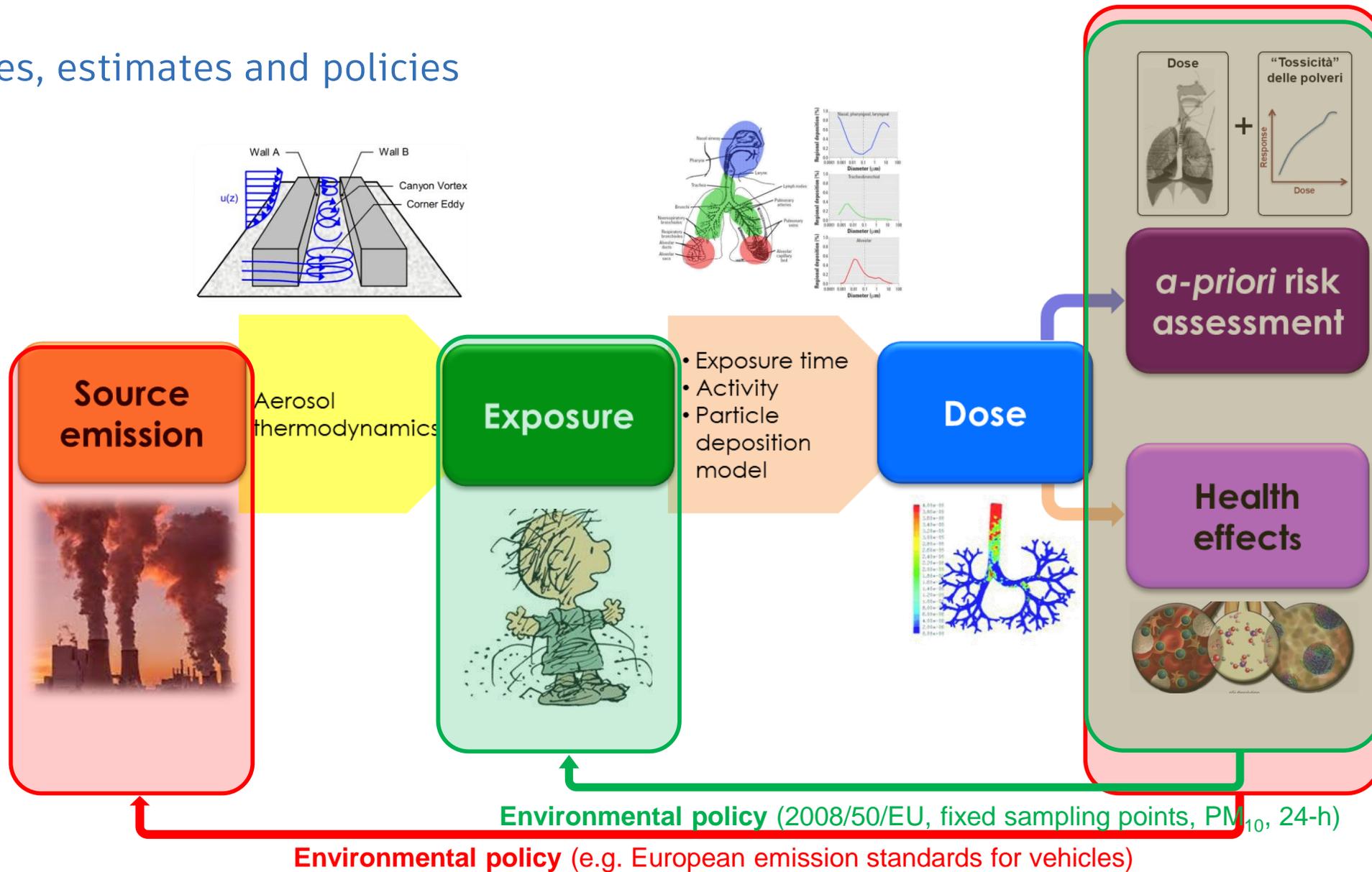
## Size distributions

- **size range** = few nanometers to tens or hundreds of micrometers
- **Modes** in different ranges (as a function of the metrics)



# From emission to risk

## Measures, estimates and policies



Brussels, 26.10.2022  
COM(2022) 542 final  
2022/0347 (COD)

Proposal for a

DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

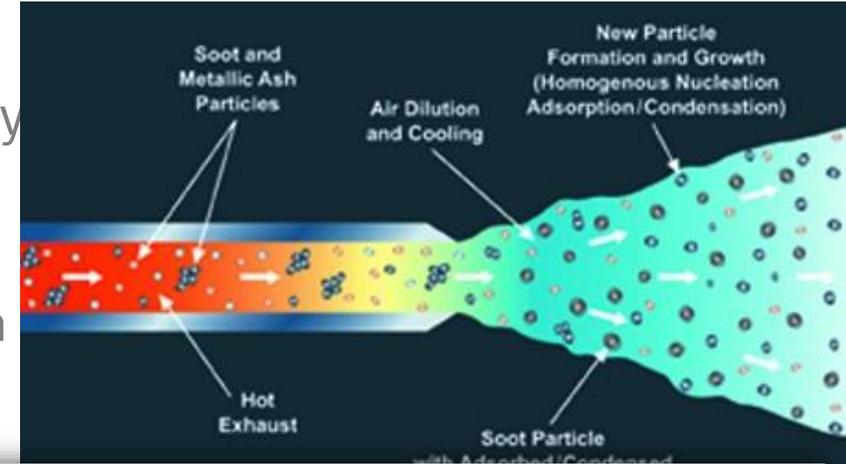
on ambient air quality and cleaner air for Europe

(recast)

- 100-1000 part. cm<sup>-3</sup>
- 1000-5000 part. cm<sup>-3</sup>
- 5000-20000 part. cm<sup>-3</sup>
- <100000 part. cm<sup>-3</sup>
- Sub-micrometric particles
- Residential heating
- vehicles;
- **short-term exposure**
- **Metrological issue**

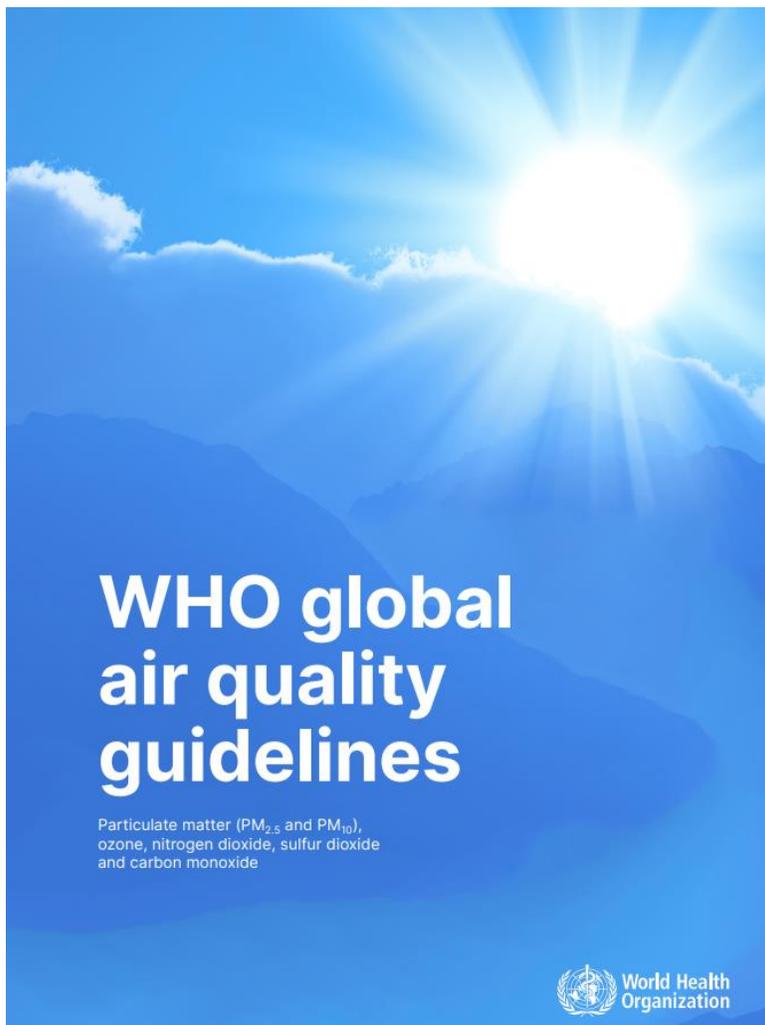
# outdoor air quality

of the outdoor air quality  
on;  
phenomena;  
on and mechanical generation



## D. Minimum number of sampling points for fixed measurements of ultrafine particles where high concentrations

Ultrafine particles shall be monitored at selected locations in addition to other air pollutants. Sampling points to monitor ultrafine particles shall coincide, where appropriate, with sampling points for particulate matter or nitrogen dioxide referred to in Point A, and be sited in accordance with Section 3 of Annex VII. For this purpose, at least 1 sampling point per 5 million inhabitants shall be established at a location where high UFP concentrations are likely to occur. Member States that have fewer than 5 million inhabitants shall establish at least 1 fixed sampling point at a location where high UFP concentrations are likely to occur.



**Table 0.1. Recommended AQG levels and interim targets**

Pollutant	Averaging time	Interim target				AQG level
		1	2	3	4	
<b>PM<sub>2.5</sub>, µg/m<sup>3</sup></b>	Annual	35	25	15	10	5
	24-hour <sup>a</sup>	75	50	37.5	25	15
<b>PM<sub>10</sub>, µg/m<sup>3</sup></b>	Annual	70	50	30	20	15
	24-hour <sup>a</sup>	150	100	75	50	45
<b>O<sub>3</sub>, µg/m<sup>3</sup></b>	Peak season <sup>b</sup>	100	70	–	–	60
	8-hour <sup>a</sup>	160	120	–	–	100
<b>NO<sub>2</sub>, µg/m<sup>3</sup></b>	Annual	40	30	20	–	10
	24-hour <sup>a</sup>	120	50	–	–	25
<b>SO<sub>2</sub>, µg/m<sup>3</sup></b>	24-hour <sup>a</sup>	125	50	–	–	40
<b>CO, mg/m<sup>3</sup></b>	24-hour <sup>a</sup>	7	–	–	–	4

<sup>a</sup> 99th percentile (i.e. 3–4 exceedance days per year).

<sup>b</sup> Average of daily maximum 8-hour mean O<sub>3</sub> concentration in the six consecutive months with the highest six-month running-average O<sub>3</sub> concentration.

## **Box 4.2. Good practice statement – UFP**

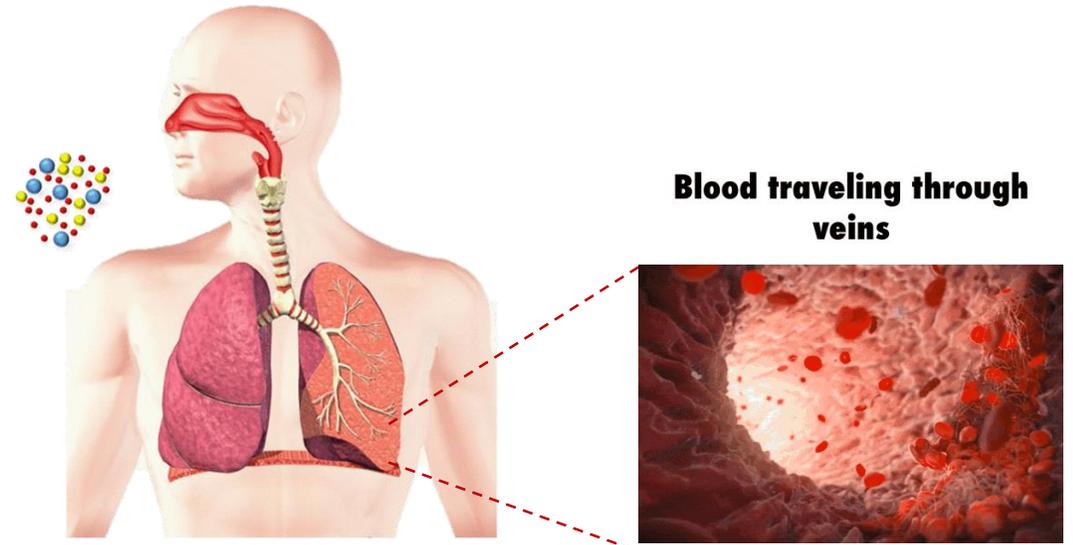
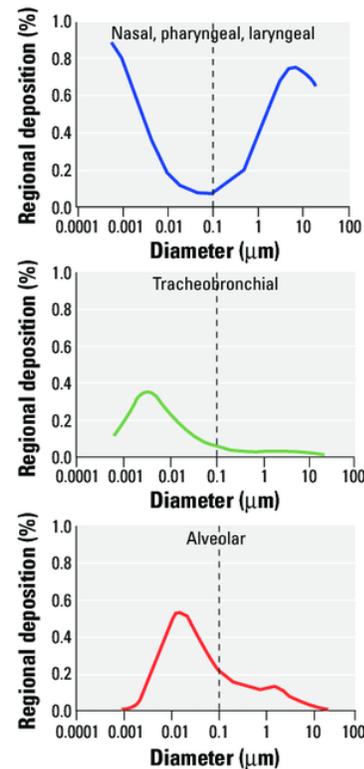
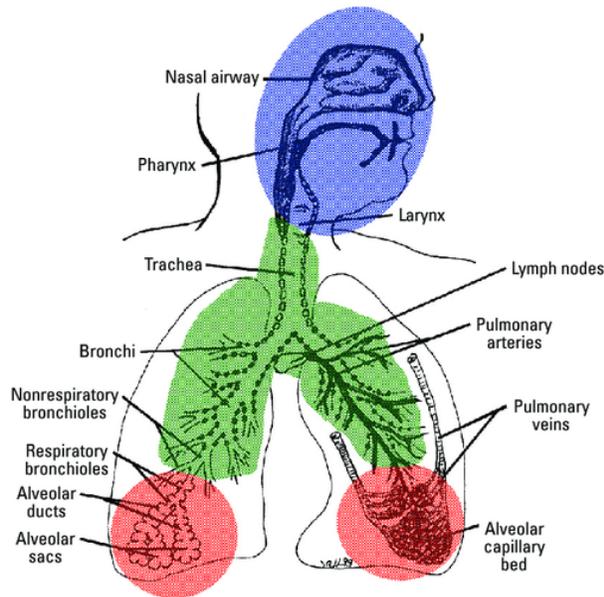
The GDG decided to formulate the following four good practice statements on UFP to guide national and regional authorities and research towards measures to reduce ambient ultrafine particle concentrations.

1. Quantify ambient UFP in terms of particle number concentration (PNC) for a size range with a lower limit of  $\leq 10$  nm and no restriction on the upper limit.
2. Expand the common air quality monitoring strategy by integration of UFP monitoring into existing air quality monitoring. Include size-segregated real-time PNC measurements at selected air monitoring stations in addition to, and simultaneously with, other airborne pollutants and characteristics of PM.
3. Distinguish between low and high PNC to guide decisions on the priorities of UFP source emission control. Low PNC can be considered  $< 1000$  particles/cm<sup>3</sup> (24-hour mean). High PNC can be considered  $> 10\ 000$  particles/cm<sup>3</sup> (24-hour mean) or  $20\ 000$  particles/cm<sup>3</sup> (1-hour).
4. Utilize emerging science and technology to advance approaches to the assessment of exposure to UFP for application in epidemiological studies and UFP management.

# Health effects

## Health effects, particle metrics

- Epidemiological studies recognized cardiovascular and respiratory issues related to the exposure to particle
- Which **size** or **property** is responsible? ( $PM_{10}$ ,  $PM_{2.5}$ , Ultrafine, surface area, assumption rate, **Deposition**) in the lungs

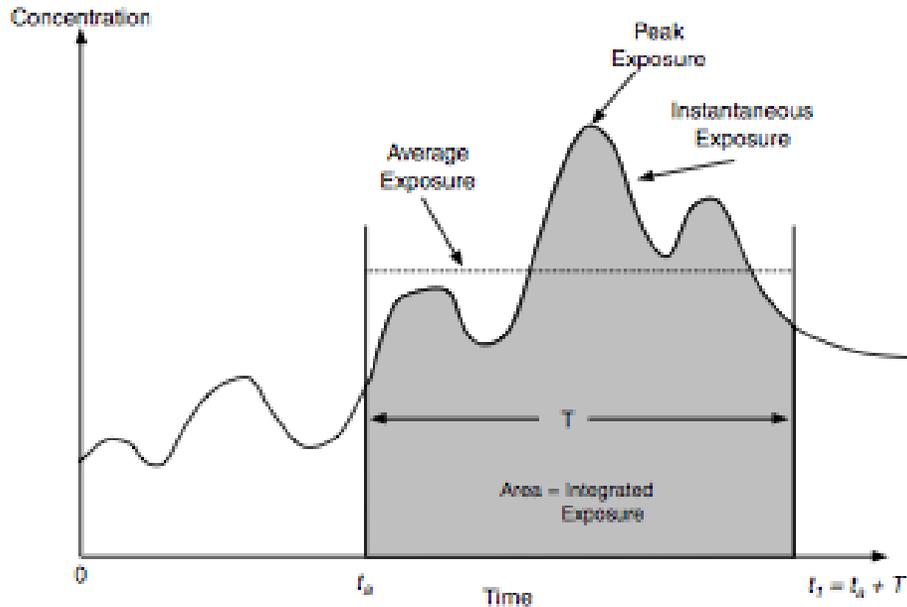


# From exposure to dose

## Take-home messages

- Huge number of small particles (sub-micrometric), very few large particles (super-micrometric);
- Exposure: **personal measurements** vs. **fixed sampling points**

Health effects are related to the dose: estimate of the **dose**?



$$DOSE_{Alv+TB} = IR \cdot S_{Alv+TB} \cdot T \quad (\text{mm}^2)$$

Inhalation rate      Lung-Deposited surface area concentration      Exposure time

# From the dose to risk

## Risk models

- e.g. Lung cancer risk model (Model by Sze-To et al. (2012))

$$\text{Risk} = \text{Toxicity} \times \text{Dose}$$

$c_f = 6.6 \times 10^{-13} \text{ mg nm}^{-2}$  (Sze-To *et al.*, 2012)  
equivalent toxicity of the particle surface area metric expressed as particle mass

$$\text{ELCR}_{extra} = \frac{1}{BW} \left( \sum_i^n \text{SF}_i \cdot \frac{m_i}{\text{PM}_{10}} \right) \cdot [c_f \cdot \delta_{Alv+TB} + \delta_{\text{PM}_{10}}] \cdot N_{day}$$

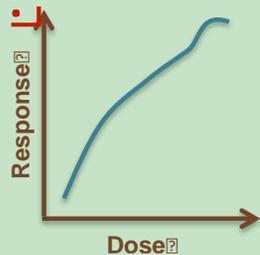
Body weight (70 kg)

Daily **extra-doses** in LDSA and  $\text{PM}_{10}$

Total exposure period (days per year)

### SF: inhalation slope factor (lifetime cancer potency)

the percent increase in the risk of getting cancer associated with exposure to a unit concentration of a chemical every day for a lifetime, here assumed equal to 70 years



Chemical	SF (kg day mg <sup>-1</sup> )
BaP	3.9
As	15.1
Cd	6.3
Ni	0.91

mass concentration of the  $i$ -th pollutant present on the  $\text{PM}_{10}$

$$\text{SF}_m = \sum_i^n \text{SF}_i \cdot \frac{m_i}{\text{PM}_{10}}$$

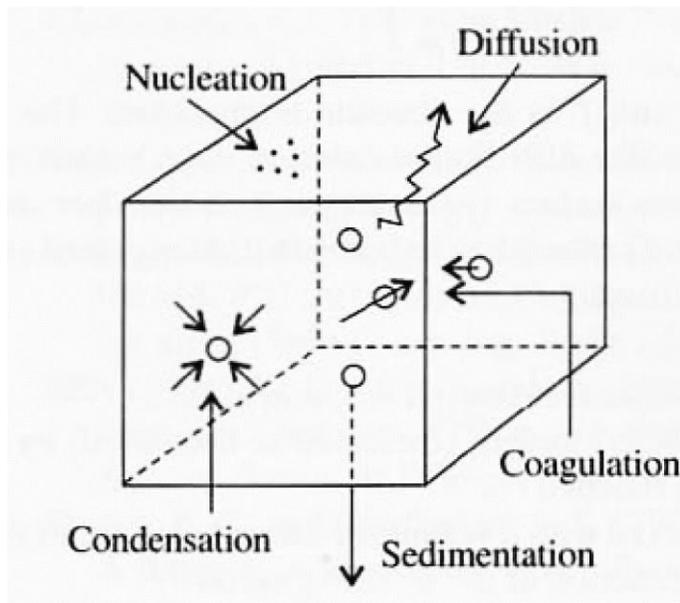
**SF of the mixture** of the  $n$  carcinogenic pollutants on  $\text{PM}_{10}$

# Particle thermodynamics

# Aerosol dynamics

## General Dynamic Equation, GDE

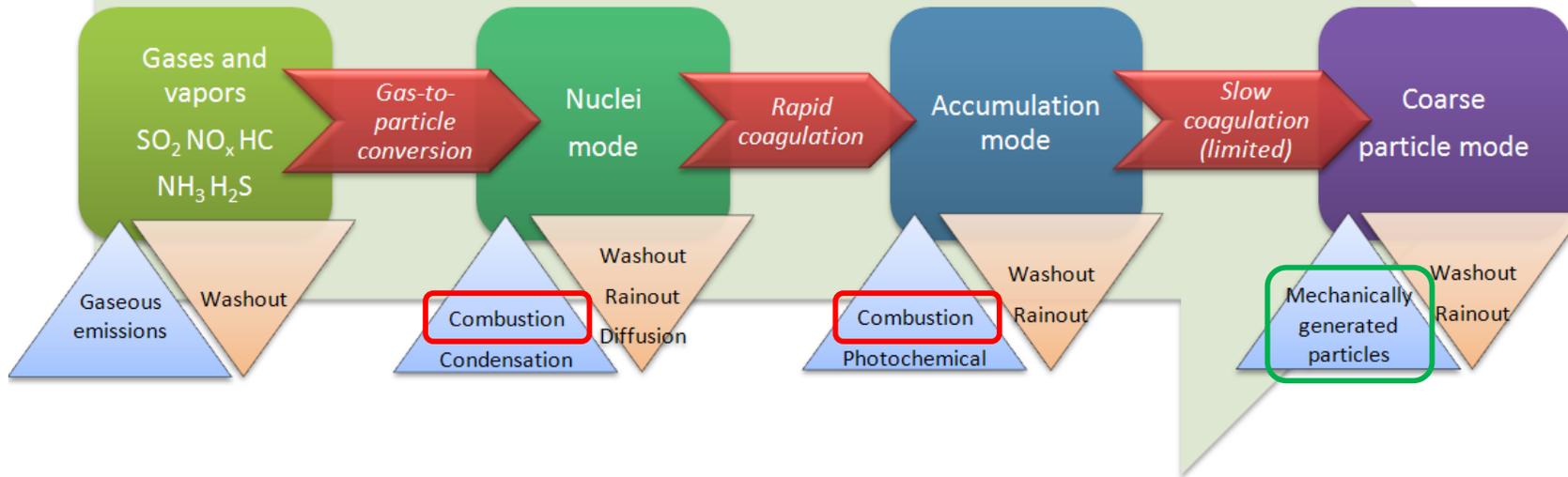
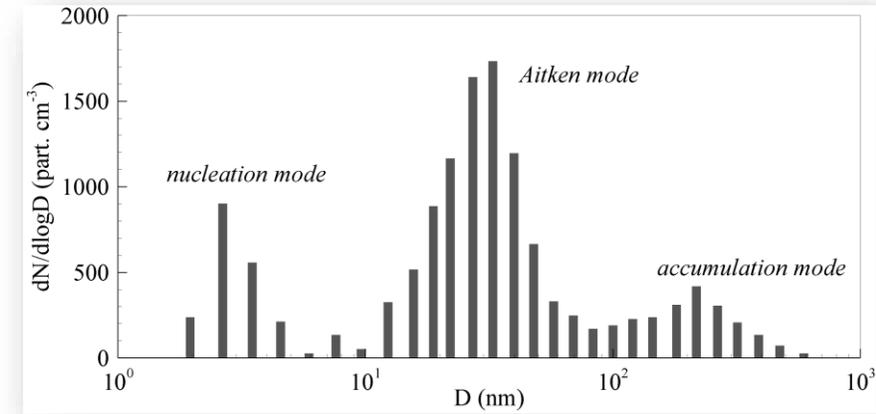
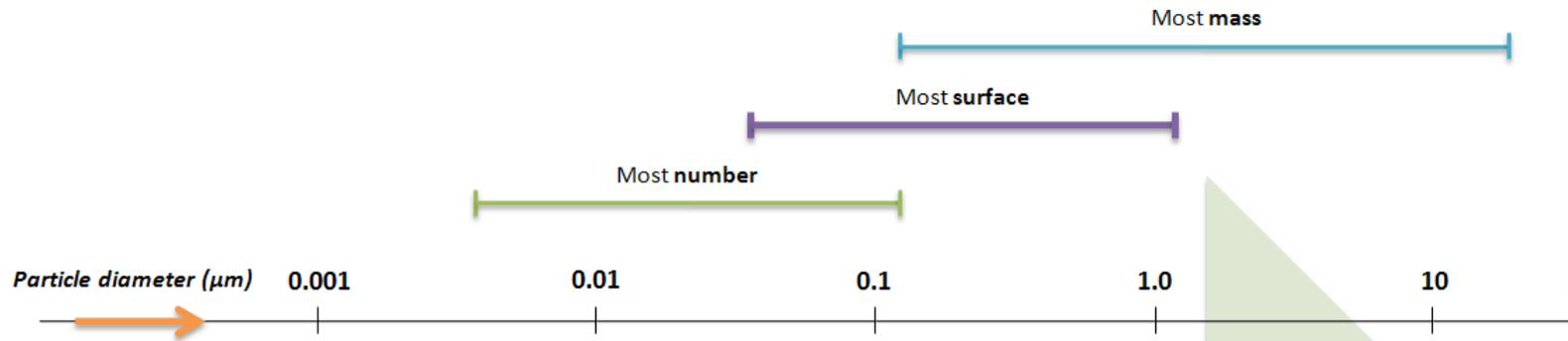
- Aerosol is characterized by dimensional, chemical and physical variations: **metastable suspension**
- Thermodynamic and physical transformations of particle **formation, growth and removal**
- The general particle dynamics equation models the influence of chemical-physical phenomena on the aerosol distribution function.



$$\frac{\partial n_d}{\partial t} = \underbrace{-\nabla \cdot n_d \bar{v}}_{\text{Particle transport}} + \underbrace{D \nabla^2 \cdot n_d}_{\text{Diffusion (Fick's laws)}} - \underbrace{\nabla(\vec{c} n_d)}_{\text{External forces}} + \underbrace{\left[ \frac{\partial n_d}{\partial t} \right]_{\text{gas-to-particle}}}_{\text{Nucleation (increases particle concentration)}} - \underbrace{\left[ \frac{\partial n_d}{\partial t} \right]_{\text{coagulazione}}}_{\text{Coagulation (reduces particle concentration)}}$$

# Aerosol dynamics

## Formation, growth and removal: particle size evolution



# Formation: nucleation

---

## gas-to-particle conversion (GPC) – ULTRAFINE PARTICLES - Nucleation

- formation of new nanoparticles from molecules in the gas phase
  - on a molecular scale, nucleation is due to the random **formation of agglomerates** of molecules that constitute stable **clusters** once a critical size has been reached
- 
- At the molecular scale, nucleation begins with the random and spontaneous aggregation of molecules.
  - These molecules might be in a vapor or a solution, and under certain conditions, they start to come together due to intermolecular forces. Initially, these clusters are unstable and can easily disband, but if they reach a certain "critical size," they become stable and can continue to grow.
  - The critical size is the point at which the cluster is energetically favorable to grow rather than shrink.

# Formation: nucleation

---

The saturation ratio plays a crucial role in nucleation. The saturation ratio is defined as the ratio of the actual concentration of molecules (in vapor or solution) to the equilibrium concentration at which the phase transition (like condensation or crystallization) would naturally occur.

- If the saturation ratio is less than 1, the environment is undersaturated, meaning that molecules are more likely to remain in their dispersed state rather than aggregate. Under these conditions, nucleation is unlikely because the energy barrier for forming a stable nucleus is too high.
- If the saturation ratio is exactly 1, the system is in equilibrium, and while nucleation can occur, it will do so at a much slower rate because the energy barrier is still significant.
- When the saturation ratio is greater than 1, the environment is supersaturated. In this state, the energy barrier for nucleation decreases, making it easier for molecular clusters to reach the critical size and become stable. The higher the saturation ratio, the more likely it is that nucleation will occur, and the faster the process will proceed.
- $S=1$  no stable condensed phase
- $S>1$  large clusters can be formed, some of them exceed a **critical size**, grow rapidly to form a stable condensed phase.

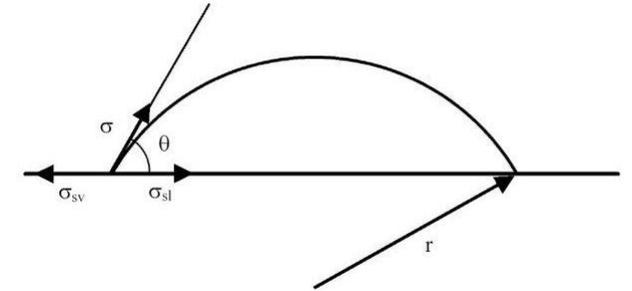
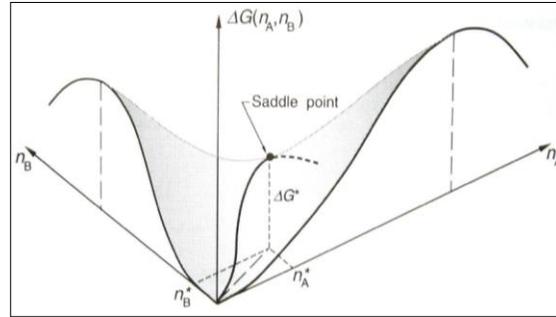
**Saturation ratio (S)**

$$S = \frac{p_A}{p_A^s} = \frac{p_A}{p_A^s(T)}$$

# Formation: nucleation

## Homogeneous nucleation

- does only occur when the vapor phase of this species is supersaturated with respect to the condensed phase of this specie



## Heterogeneous nucleation

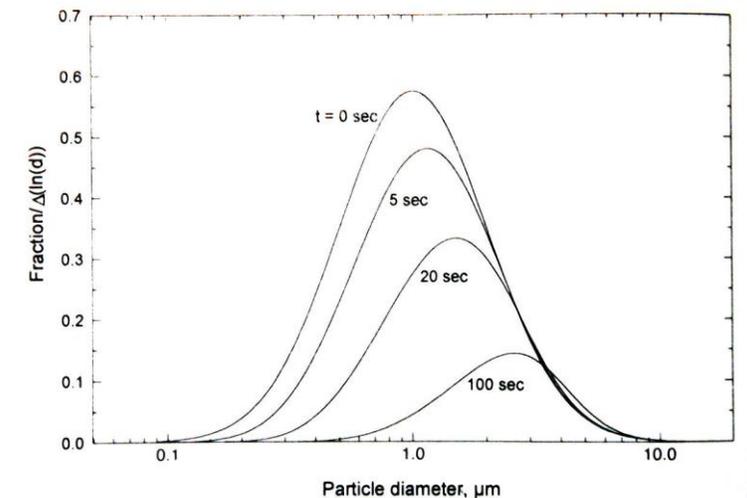
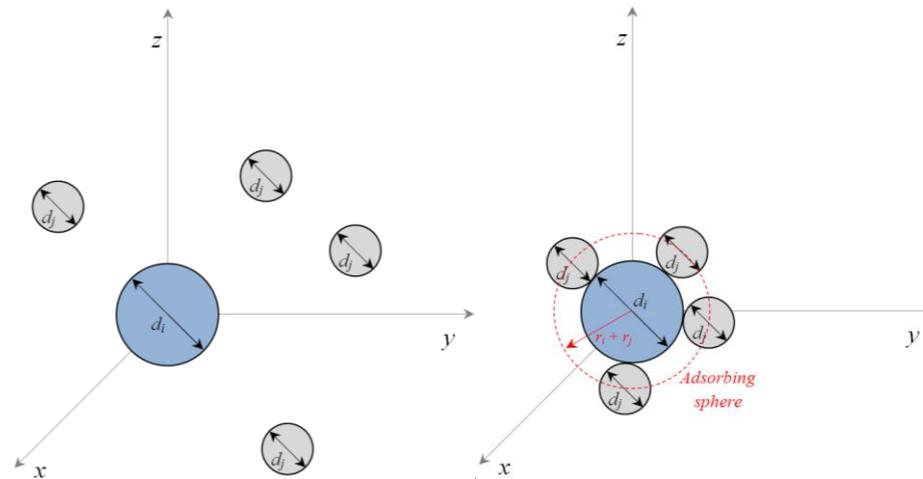
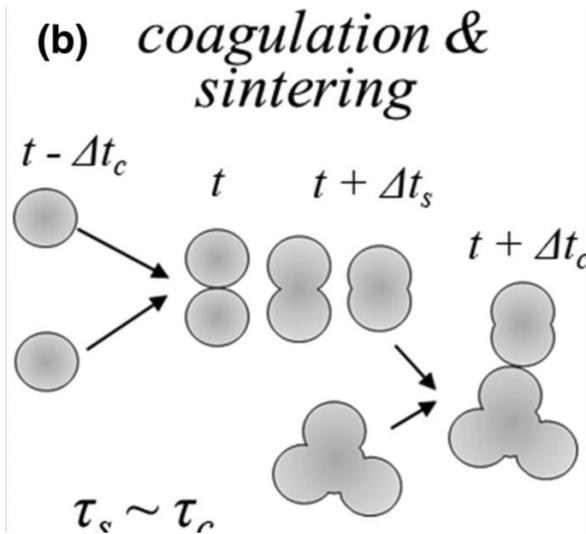
- the energy barrier for stable nucleus formation is reduced
- enables gas-to-particle conversion at even lower supersaturation
- Nucleation on an Insoluble Foreign Surface
- Ion-Induced Nucleation

Homogeneous nucleation occurs uniformly throughout the volume of a pure substance, requiring higher levels of supersaturation or supercooling to overcome a higher energy barrier, as it lacks any surfaces or impurities to facilitate the process. In contrast, heterogeneous nucleation takes place at specific sites such as surfaces, container walls, or impurities, where the presence of these interfaces lowers the energy barrier, allowing nucleation to occur more easily and at lower levels of supersaturation or supercooling. As a result, homogeneous nucleation is less common and requires more extreme conditions, while heterogeneous nucleation is more prevalent in natural and industrial contexts.

# Growth: coagulation

## Coagulation of UFPs

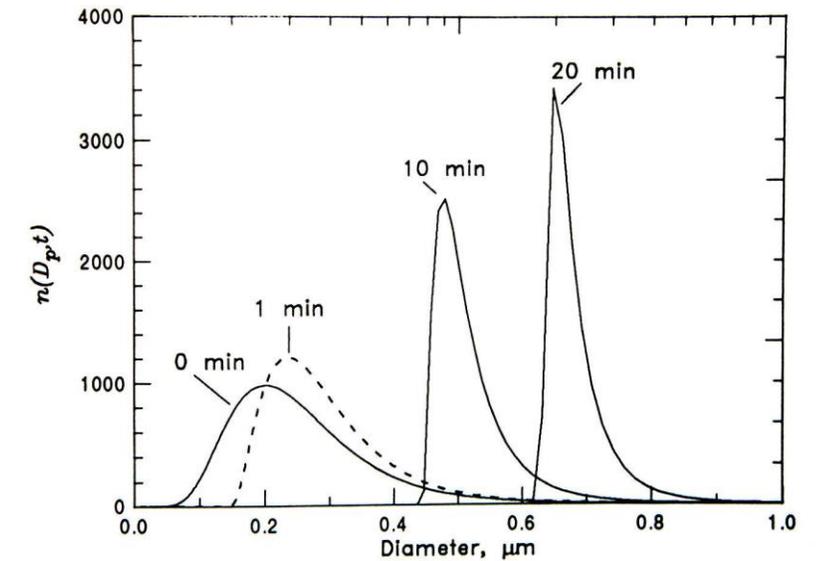
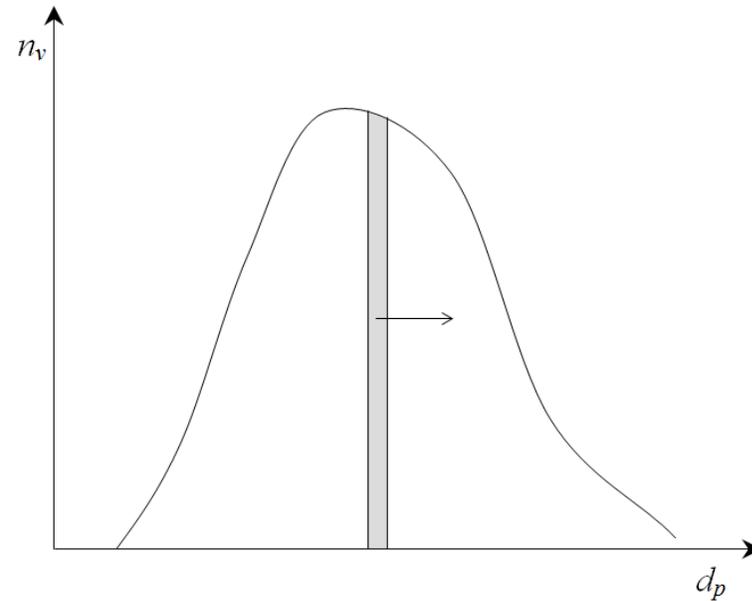
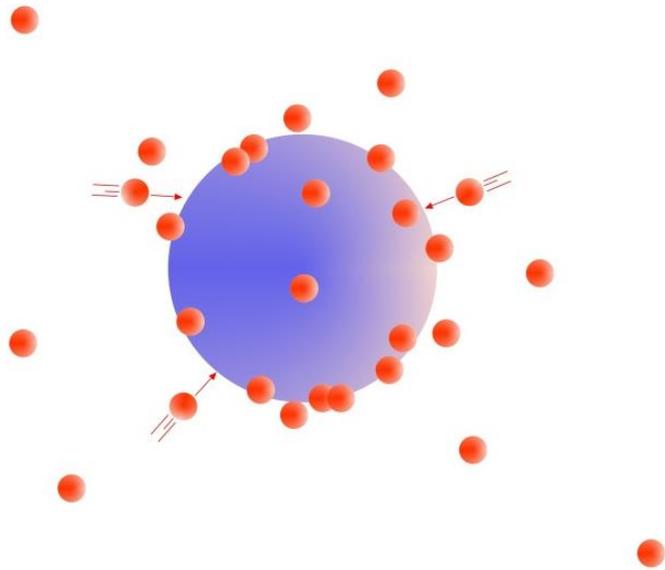
- The coagulation phenomenon is a **growth process of** particles characterized by the union of the particles themselves following their relative movement
- Consequent **decrease in the number** and surface area concentration (not mass)
- The collision, which causes coagulation phenomena, can be due to Brownian motions (thermal coagulation) or to external forces (gravitational, inertial, electrical, etc.; kinematic coagulation)



# Growth: condensation

## Condensation for sub-micron particles

- Condensation processes usually require a **supersaturated vapor** and a surface for the vapor to condense onto, e.g. existing aerosol particles
- For particles **smaller than the gas mean free path** ( $\lambda = 66 \text{ nm}$ ) the kinetic theory of gases gives us for the number of molecules colliding with particles per unit time and unit volume

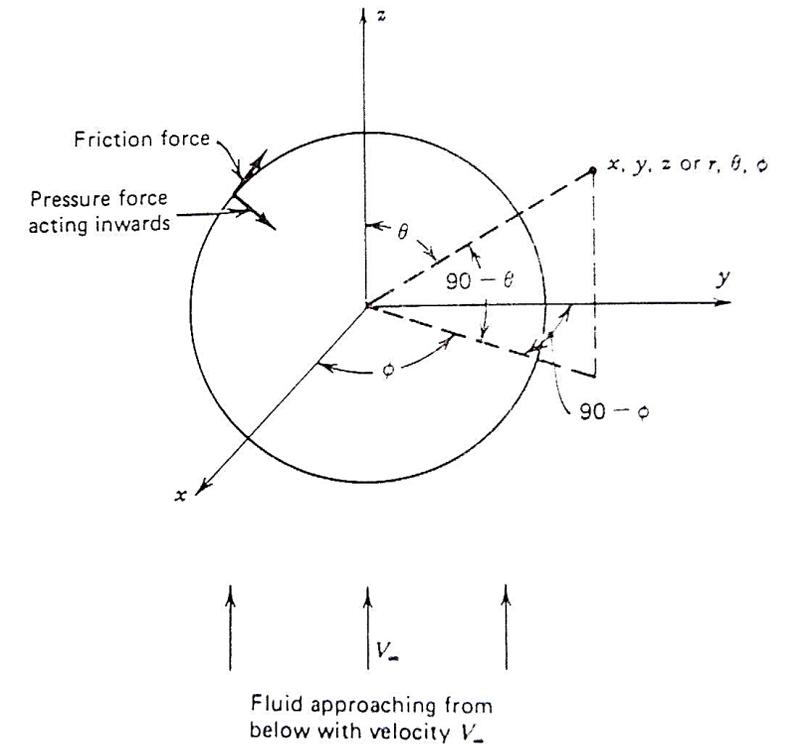
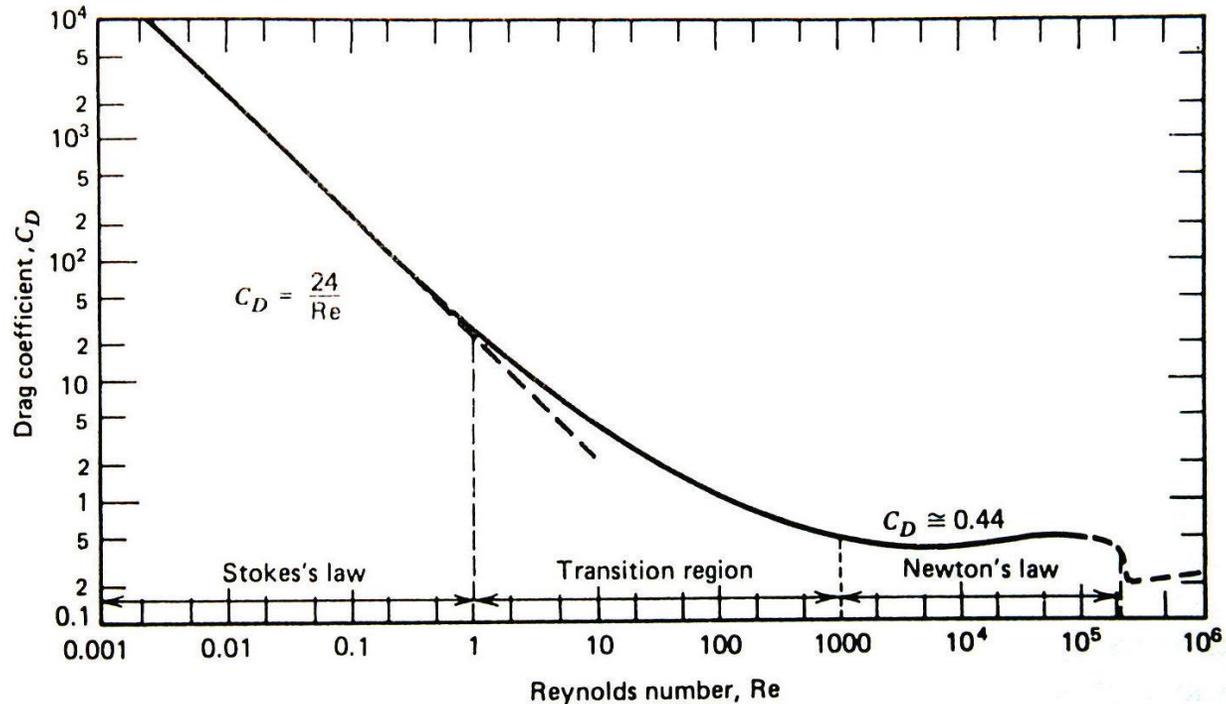


# Dynamics: particle motion

## Drag force

Stokes's law: describes the drag force on a spherical particle of diameter  $d_p$  that travels through a gas of viscosity  $\eta$  with velocity  $u_\infty$  ( $Re \ll 1$ )

$$F_d = 6\pi\eta u_\infty r_p = 3\pi\eta u_\infty d_p \quad F_d = C_D \frac{1}{8} \rho_g \pi d_p^2 u_\infty$$



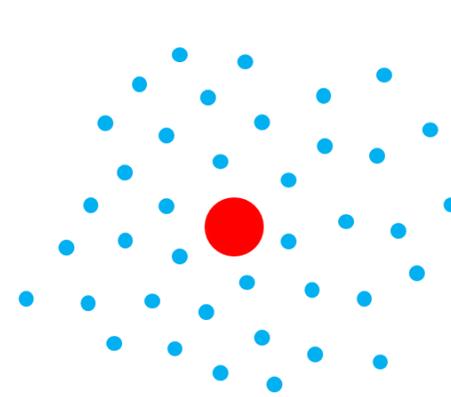
# Dynamics: particle motion

## Drag force

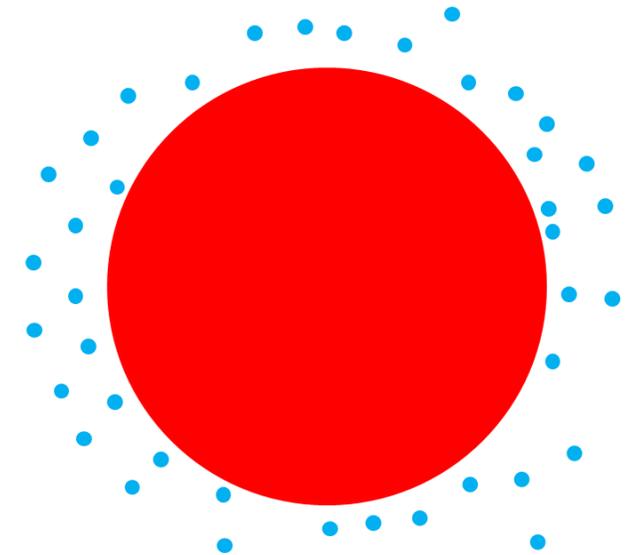
- One of the assumptions for the derivation of Stokes's law is that the relative velocity of the gas at the surface of the aerosol particle is zero (**no slip condition**). This assumption is valid for large particles where we can treat the surrounding air like a homogeneous fluid
- Particles smaller than about 1  $\mu\text{m}$  in diameter, especially nanoparticles, **settle significantly faster than predicted by Stokes's law**. This is caused by the 'slip' at the surface of the particle when the particle size approaches the dimension of the mean free path. A correction factor to account for this effect was determined by Cunningham and is called **Cunningham slip correction factor  $C_c$** .

$$F_d = \frac{3\pi\eta u_\infty d_p}{C_c}$$

$d_p$ ( $\mu\text{m}$ )	$C_c$
0.001	216
0.005	43.6
0.01	4.95
0.1	2.85
0.5	1.32
1.0	1.16
5.0	1.03
10.0	1.01



Free-molecule regime  
(slip condition)



Continuum regime  
(no slip condition)

# Dynamics: external forces

## Newton's laws and conservation of momentum

- a body tends to preserve its state of inertia
- the rate of change of the momentum of a body is equal to the net force acting on the body

Settling force Drag force	Size ( $\mu\text{m}$ )	Settling velocity (m/s)	Relaxation time (s)
	0.3	4.16E - 06	4.24E - 07
	1	3.44E - 05	3.50E - 06
	2.5	1.96E - 04	2.00E - 05
	5	7.61E - 04	7.76E - 05
• Relaxation	7.5	1.69E - 03	1.73E - 04
in external	10	3.00E - 03	3.06E - 04
• stopping	20	1.19E - 02	1.21E - 03

velocity

\*settling velocity at the equilibrium between forces

changes

$$\tau = \frac{m_p C_c}{3\pi\eta d_p}$$

when,

$$s_p = \frac{\rho_p d_p^2 C_c v_0}{18\eta}$$

starting from an initial speed due to the application of an external force, it reaches the equilibrium velocity

# Dynamics: external forces

---

The Stokes number (St) is a dimensionless number used in fluid dynamics to characterize the behavior of particles suspended in a fluid flow. It is defined as the ratio of the particle's relaxation time to a characteristic time scale of the flow. The Stokes number is given by:

$$\text{St} = \frac{\tau_p}{\tau_f}$$

Where:

- $\tau_p$  is the particle relaxation time, which represents the time it takes for a particle to adjust to changes in the fluid flow. It depends on the particle's size, density, and the viscosity of the fluid.
- $\tau_f$  is the characteristic time scale of the fluid flow, typically related to the flow's velocity and a characteristic length scale (such as the size of an obstacle or the distance over which the flow changes).

The Stokes number indicates how well particles can follow the flow of the fluid:

- **St  $\ll$  1:** Particles closely follow the fluid flow, as their relaxation time is much smaller than the flow time scale.
- **St  $\gg$  1:** Particles are less influenced by the fluid flow and tend to continue moving in their original direction rather than following the flow.

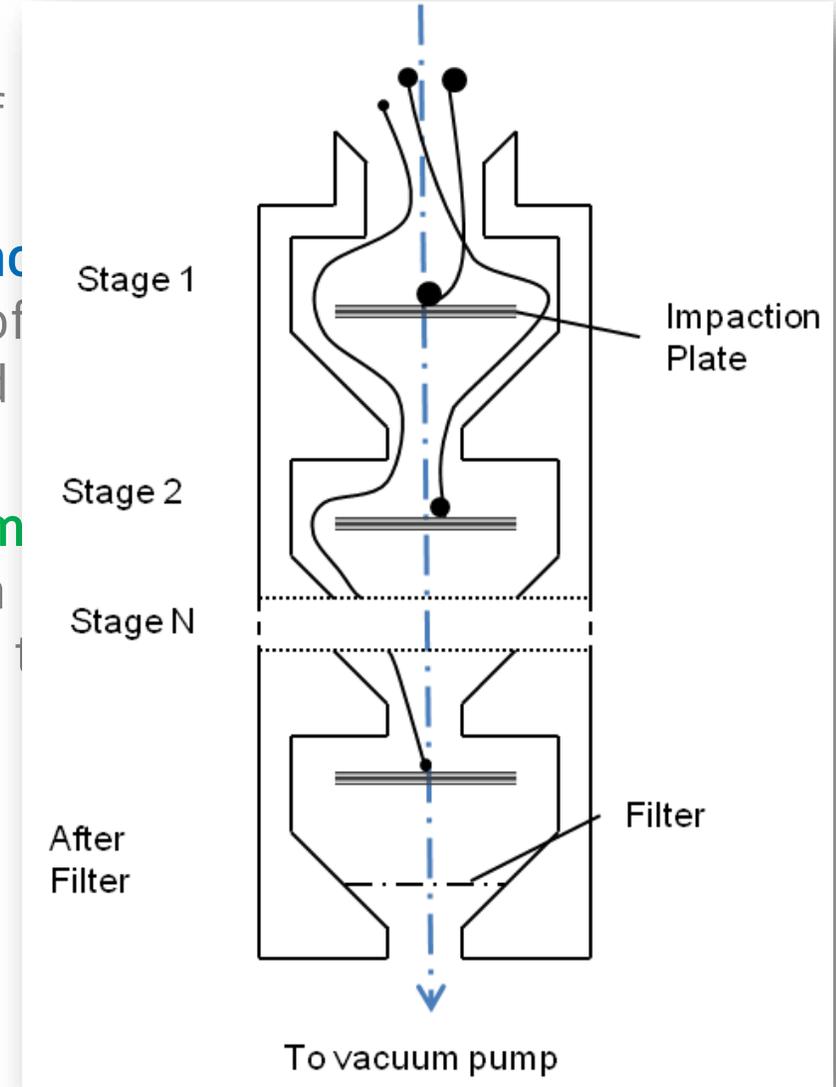
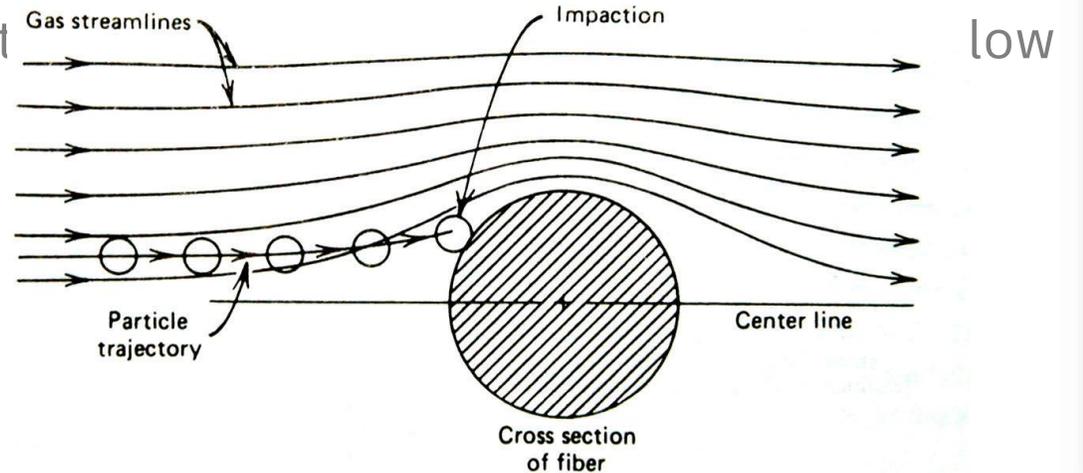
# Dynamics: external forces

## Stokes number and impaction

Stokes number gives direct information about the behavior of the obstacle.

- **Stk  $\gg 1$**  The particle **will not be able to stop within a distance m obstacle**, which also will be the dimension of the change of consequence the particle will travel in a straight line and streamlines.
- **Stk  $\ll 1$**  The particle **will be able to stop within a distance m obstacle** and consequently much smaller than the dimension gas flow. Under t deviation  $\delta_p$  only.

$$Stk = \frac{\delta_p}{L}$$



# Dynamics: external forces

## Electrical forces

Equilibrium between drag forces and electrical forces...

Terminal velocity in an electric field

$$\vec{F}_i = q\vec{E}$$

$$m_p \frac{d\vec{v}}{dt} = \frac{3\pi\eta d_p}{C_c} (\vec{u} - \vec{v}) + q\vec{E}$$

$$v_{te} = \frac{q E C_c}{3\pi\eta d_p}$$

electrical mobility  $Z_p$  gives the velocity of the particle in an external electrical field  $v_{te}$  of certain strength  $E$

$$v_{te} = Z_p E$$

$$Z_p = \frac{q C_c}{3\pi\eta d_p}$$

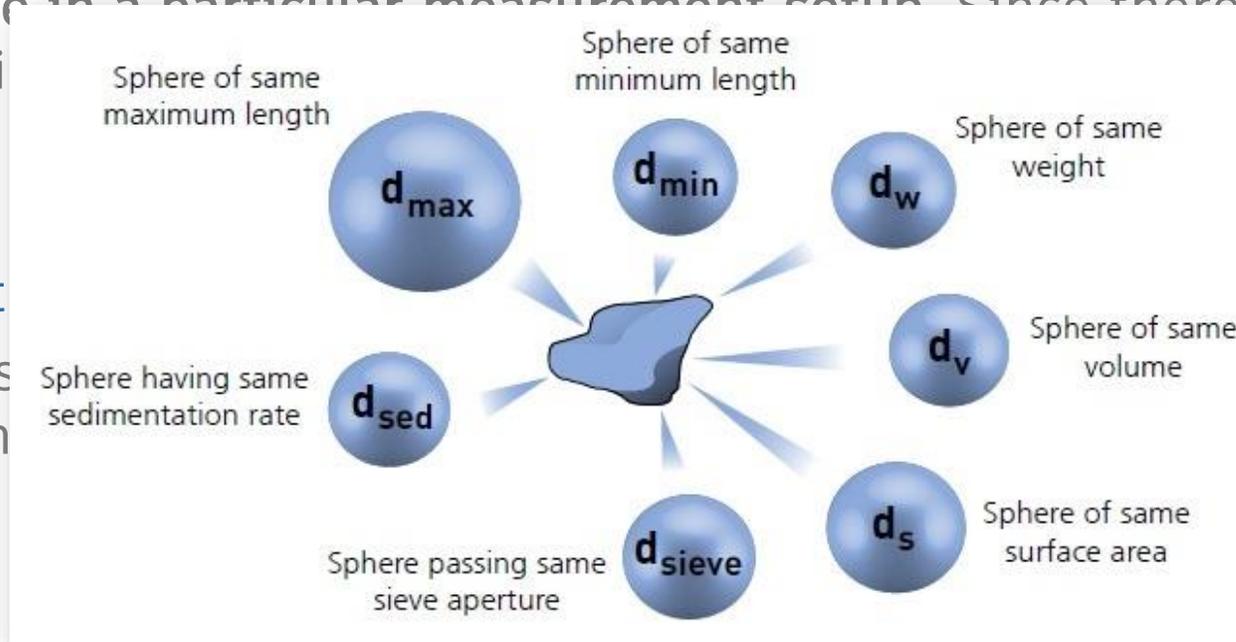
**TABLE 15.2 Electrical Mobility of Electrons, Ions, and Aerosol Particles at Standard Conditions**

Particle Diameter ( $\mu\text{m}$ )	Electrical Mobility ( $\text{m}^2/\text{V} \cdot \text{s}$ ) <sup>a</sup>	
	Singly Charged	Maximum Charge <sup>b</sup>
Electron	$6.7 \times 10^{-2}$	
Negative air ion	$1.6 \times 10^{-4}$	
Positive air ion	$1.4 \times 10^{-4}$	
0.01	$2.1 \times 10^{-6}$	$7.3 \times 10^{-4}$
0.1	$2.7 \times 10^{-8}$	$9.3 \times 10^{-4}$
1.0	$1.1 \times 10^{-9}$	$(2.5 \times 10^{-3})^c$
10	$9.7 \times 10^{-11}$	$(6.7 \times 10^{-3})^c$
100	$9.3 \times 10^{-12}$	$(1.1 \times 10^{-2})^c$

# Dynamics: equivalent diameters

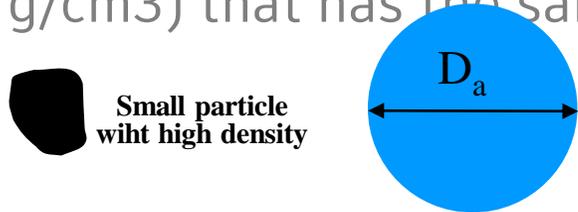
## Equivalent diameters

Equivalent diameters are defined as those of spherical particles that would behave the same as the measured particle in a particular measurement setup. Since there are a large **variety of ways** to measure particle diameters, there are a large **variety of equivalent particle diameters**.



## Aerodynamic equivalent diameter

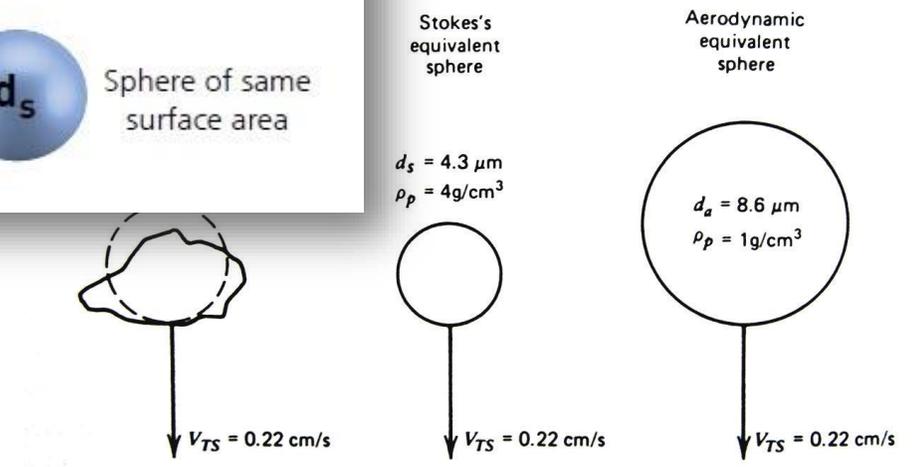
diameter of a particle is  $d_a$  (g/cm<sup>3</sup>) that has the same



## Equivalent electrical mobility diameter

diameter of a particle of unit density that has the same electrical mobility ( $Z$ ) as the particle under examination.

of unit density ( $\rho = 1$ )



# Dynamics: Diffusion

net flux or diffusion flux of particles is a result of the concentration gradient

## Brownian Motion

- Particles suspended in surrounding air are continuously **bombarded by gas molecules**.
- In every collision inertia is transferred from the gas molecule to the aerosol particle, changing the direction of motion of the particle.
- This transfer of inertia together with the statistical distribution of the gas molecules colliding with the particles results in a 'random walk' of the particles (Brownian motion).

$$m_p \frac{d\vec{v}}{dt} = -\frac{3\pi\eta d_p}{C_c} \vec{v} + m_p \vec{a}$$

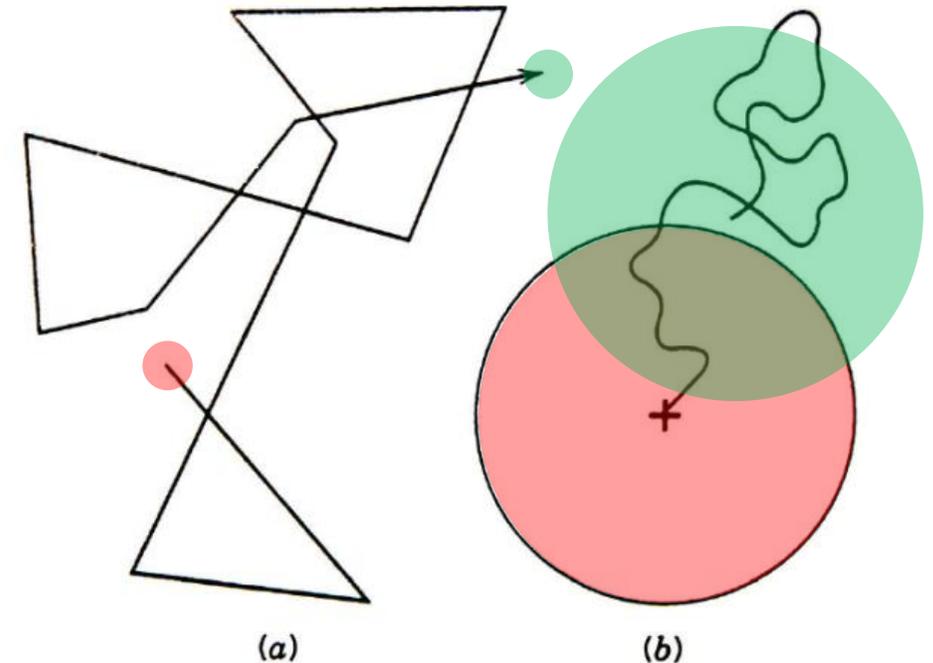


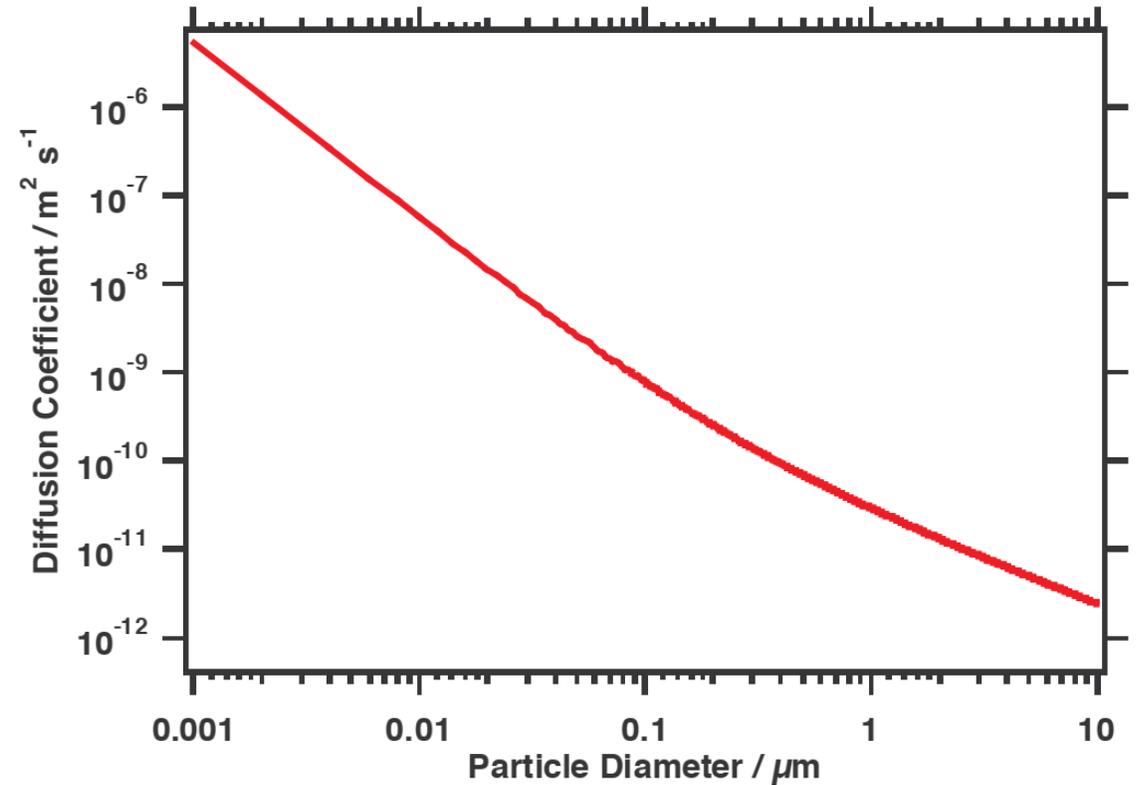
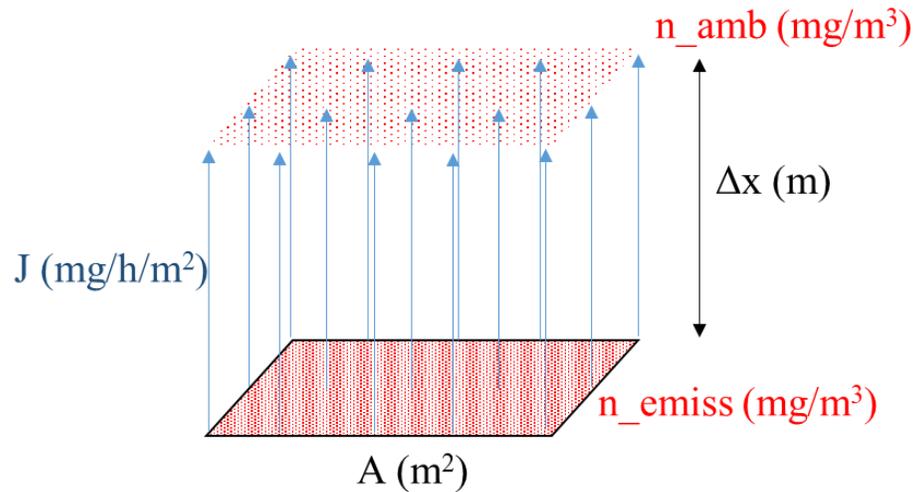
Figure 2.31: Projection of the path of (a) an air molecule and (b) of an aerosol particle of  $d_p = 0.1 \mu\text{m}$  undergoing Brownian motion. For the aerosol particle the path of motion of the center of the particle is shown. (from Hinds 1999)

# Dynamics: Diffusion

- net flux or diffusion flux of particles is a result of the concentration gradient
- Fick's laws
- **Diffusion coefficient**: the proportionality between flux and concentration gradient

$$D = \frac{kTC_c}{3\pi\eta d_p}$$

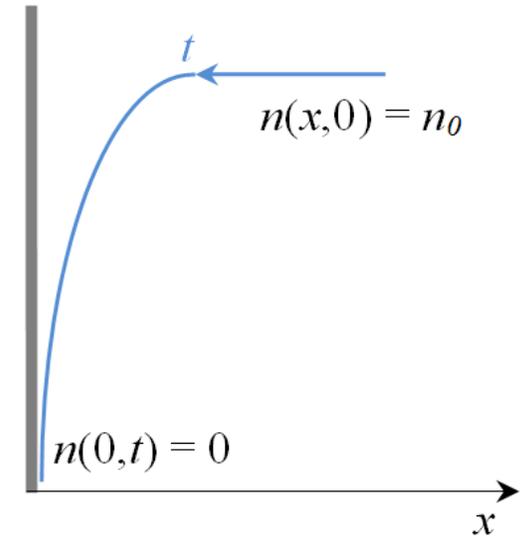
$$\frac{\partial n}{\partial t} = -\frac{\partial J_x}{\partial x} = D \frac{\partial^2 n}{\partial x^2}$$



# Dynamics: deposition

## Deposition by diffusion

- Unlike gas molecules aerosol particles (especially small ones) **stick to surfaces** when they collide with them
- **Surfaces are sinks** for the particles and that the particle concentration at the surface is zero.
- So close to a surface the particle concentration will have a gradient that causes a continuous diffusion flux of particles onto the surface



Particle diameter, $d_p$ ( $\mu\text{m}$ )	Deposition by diffusion (part. $\text{m}^{-2}$ )	Deposition by gravitational settling (part. $\text{m}^{-2}$ )	Diffusion/gravitational settling ratio
0.001	$2.6 \times 10^4$	0.68	$3.4 \times 10^4$
0.01	$2.6 \times 10^3$	6.9	380
0.1	300	88	3.4
1.0	59	3500	0.017
10	17	$3.1 \times 10^5$	$5.5 \times 10^{-5}$
100	5.5	$2.5 \times 10^7$	$2.2 \times 10^{-7}$

# Dynamics: deposition

## Deposition in ducts, transport losses

Penetration of particle in a ducts...

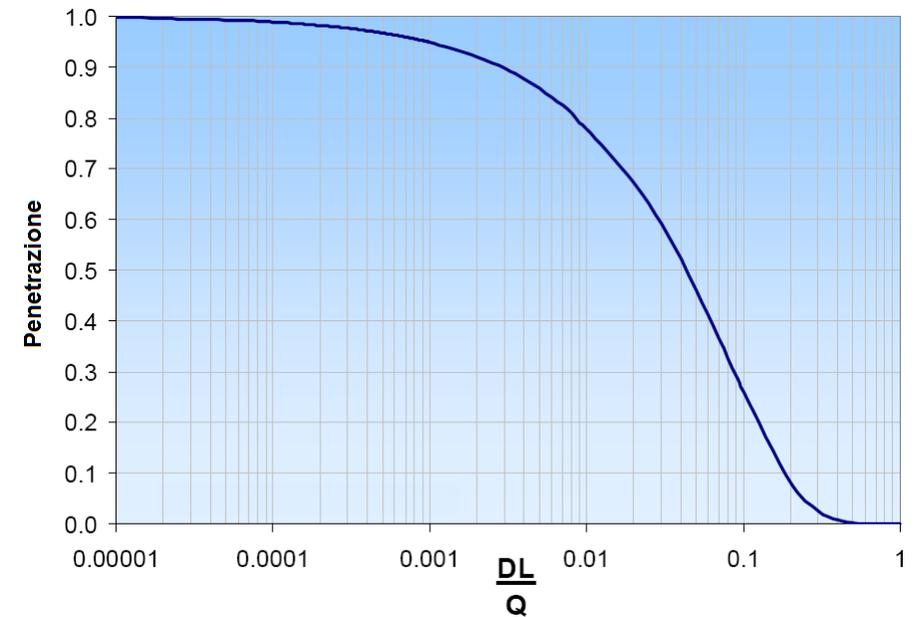
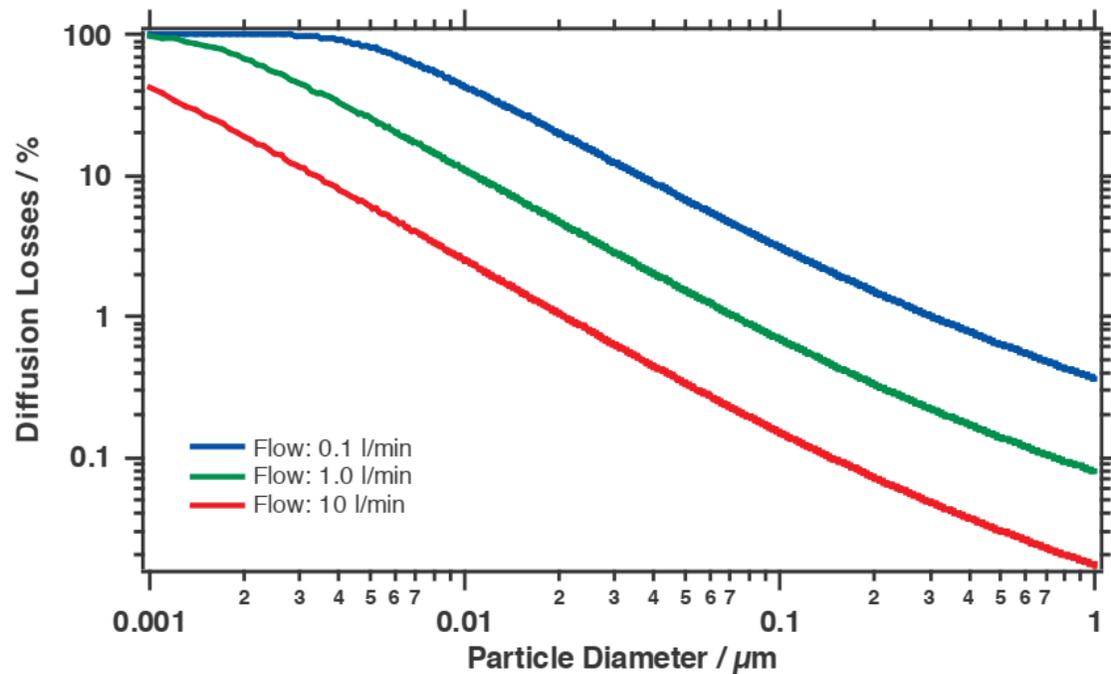
$$P = \frac{n_{out}}{n_{in}}$$

$$\mu = \frac{4DL}{\pi d_t^3 u_\infty} = \frac{DL}{Q}$$

$$P = 1 - 5.50\mu^{2/3} + 3.77\mu \quad \text{per } \mu < 0.009$$

$$P = 0.819 \exp(-11.5\mu) + 0.0975 \exp(-70.1\mu) \quad \text{per } \mu \geq 0.009$$

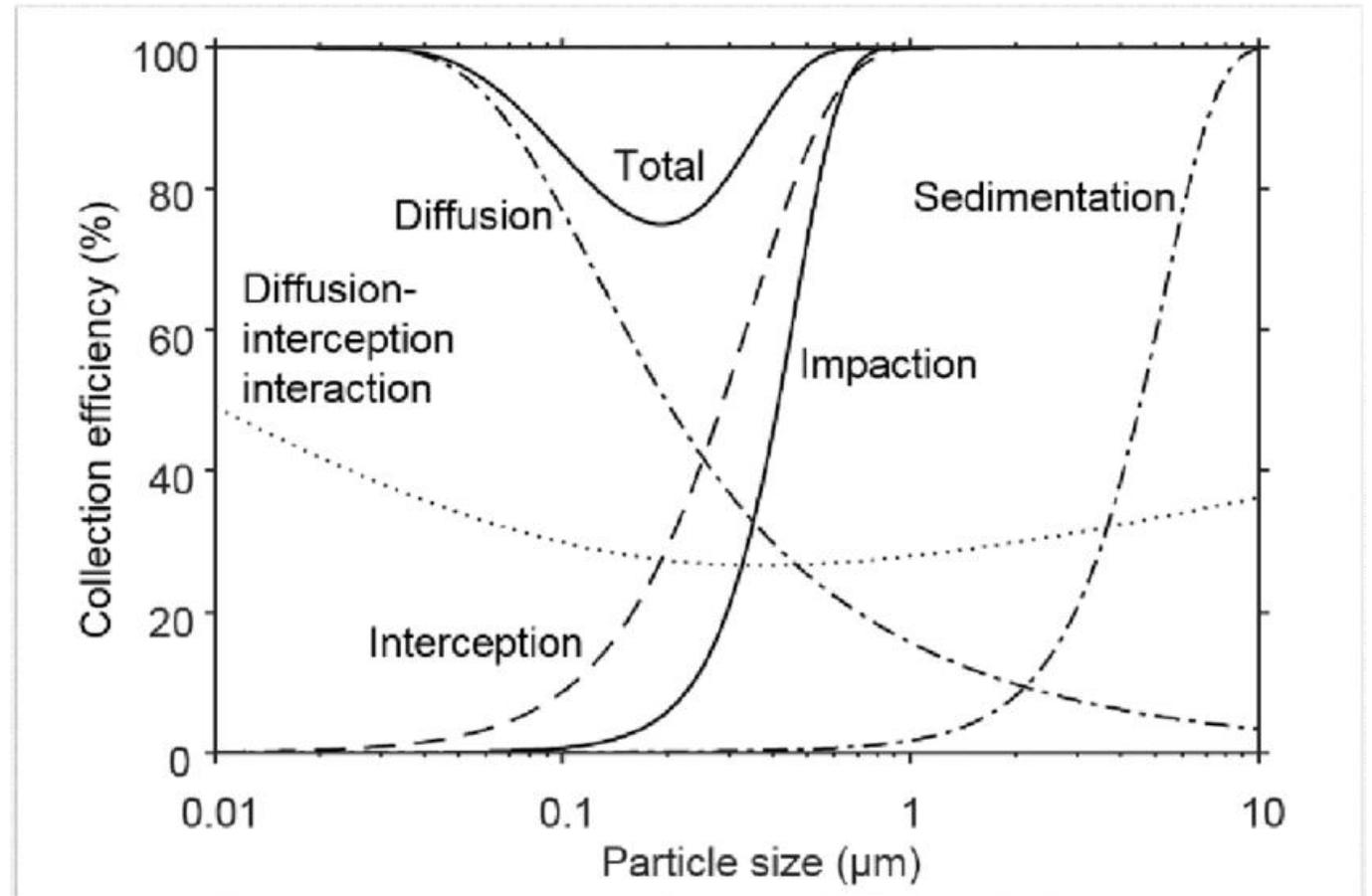
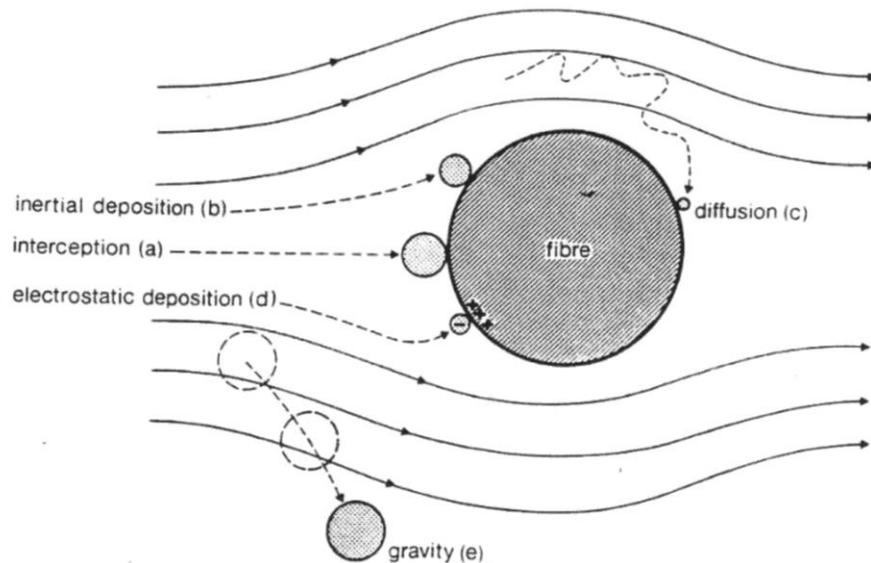
L lenght of the tube  
 $u_\infty$  average velocity  
 Q flow rate



# Dynamics: deposition

## Particle removal and deposition:

- impaction (inertia)
- diffusion
- gravitational settling
- electrostatic forces
- thermophoresis
- interception



# Particle measurements

# Laboratory at UNICAS

- **PM samplings/measurements**
  - Gravimetric samplers & heads ( $PM_{10}$ ,  $PM_{2.5}$ ,  $PM_1$ )
  - 1 Nanoparticle Aerosol Sampler TSI 3089
- **Particle number concentration/distribution measurements**
  - 2 Scanning mobility particle sizer (SMPS) TSI 3936
  - 1 Aerodynamic Particle Sizer Spectrometer (APS) TSI 3321
  - 2 CPC TSI 3775 (buthanol) + 1 CPC TSI 3750
  - 1 Fast Mobility Particle sizer (FMPS) TSI 3091
  - 1 Nanoparticle Surface Aerosol Monitor TSI 3550
  - 1 Thermodiluter for submicrometer particles
  - 1 Diluter for APS
- **Generation/calibration**
  - 1 monodisperse aerosol generation system (TSI 3940)
  - 1 Aerosol electrometer TSI 3068B
  - 1 Super-micron aerosol disperser Palas
- **Portable instruments**
  - 4 Philips Nanotracer/Testo Discmini
  - 1 CPC TSI 3007
  - 1 Nanoscan SMPS TSI 3910
  - 1 Optical Particle Sizer 3330
  - 1 DustTrak photometer 8534
  - 1 Aethalometer AE51 BC monitor



# Gravimetric measurement

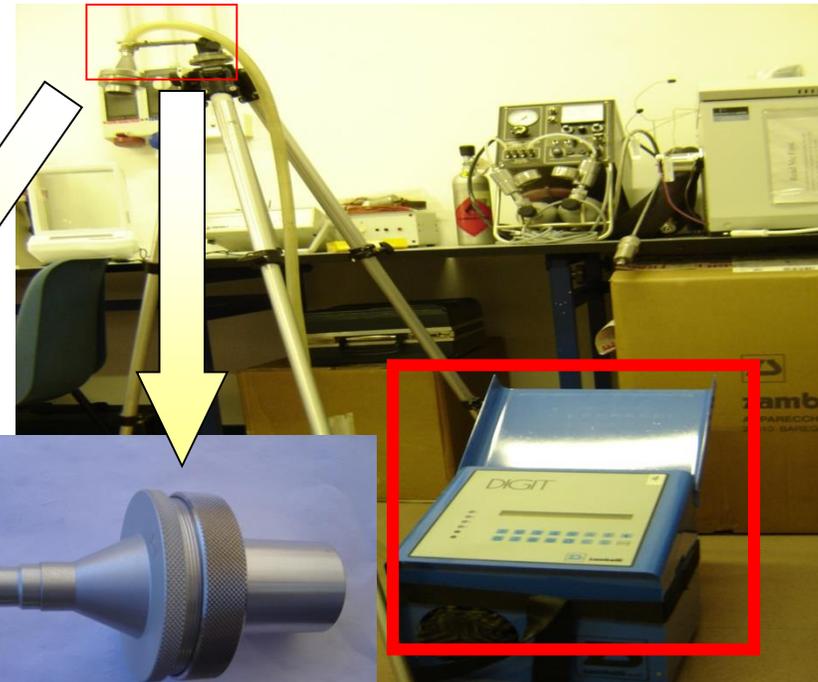
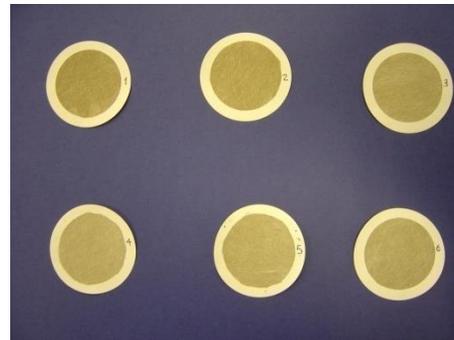
## Measurement principle

- Particulate matter is determined through air filtration resulting in the **collection** of particulate matter suspended in the air.
- The final concentration of particulate matter is obtained by determining the change in mass of the filter **divided by the volume** of normalized aspirated gas (0 °C and 101325 Pa).

## Experimental apparatus

- Analytical scale
- Constant flow volumetric sampler
- Filter holder
- Cellulose filter
- Connecting pipes

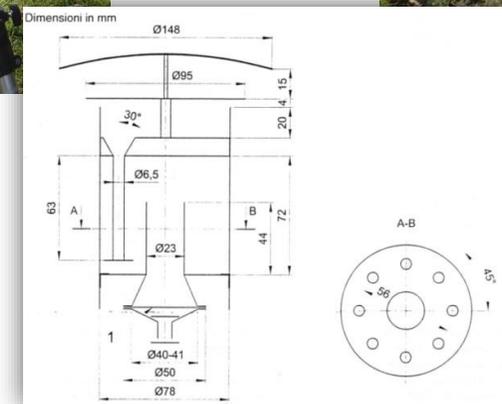
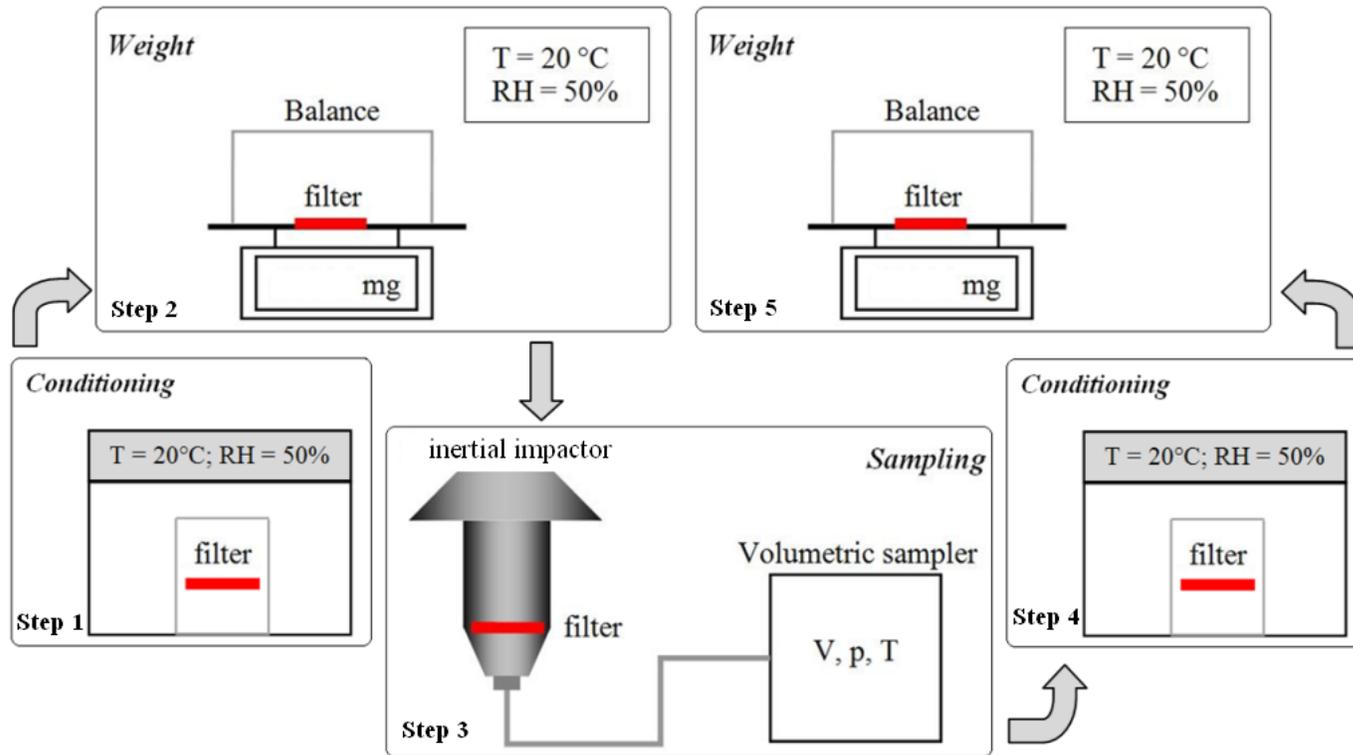
$$C = \frac{\Delta m}{V} = \frac{m_f - m_i}{V}$$



# Gravimetric measurement

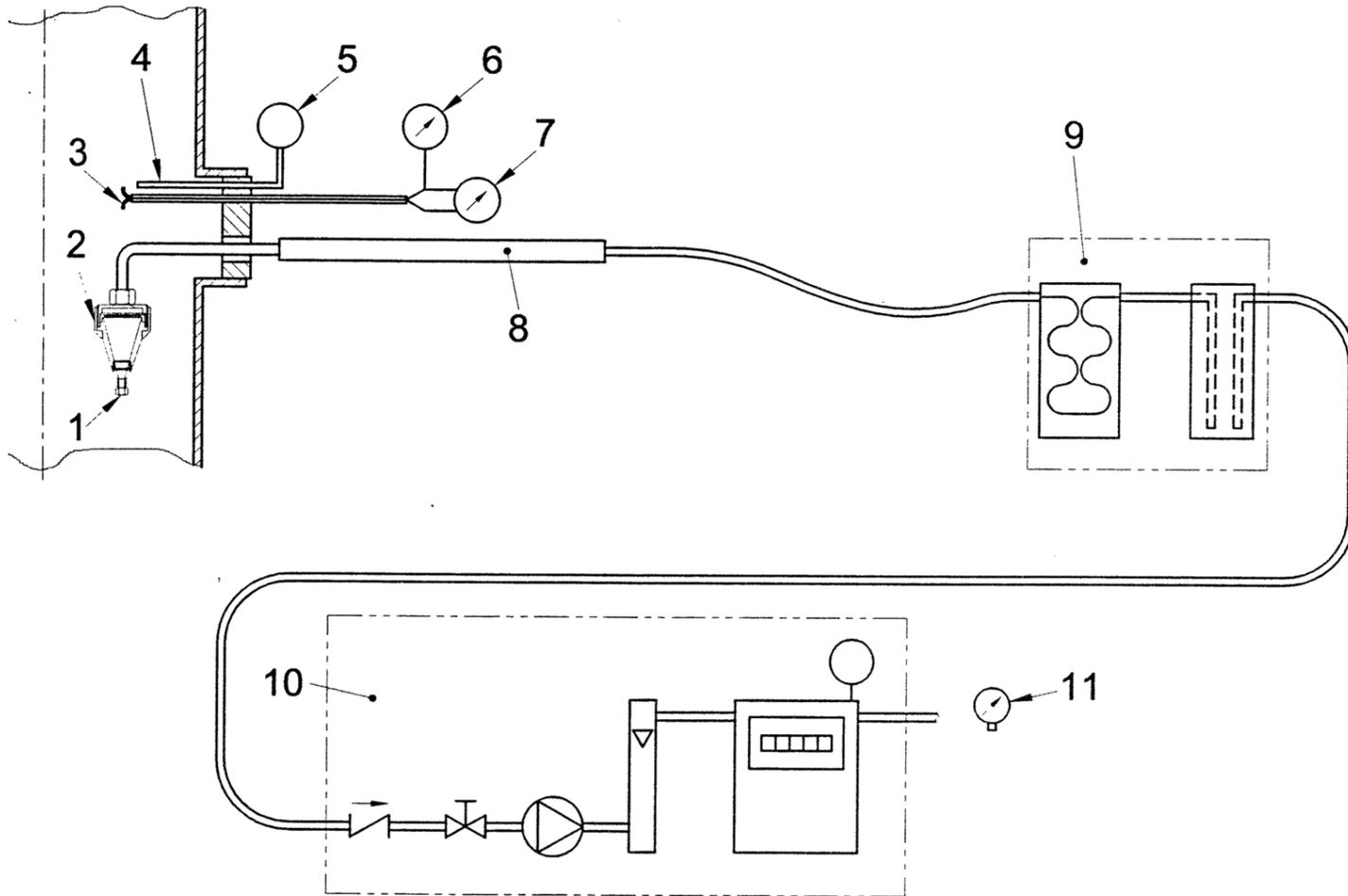
## Outdoor PM measurement

Sampling head (PM<sub>1</sub>, PM<sub>2.5</sub> or PM<sub>10</sub>) allows a “selection” by inertial impact.



# Gravimetric measurement

## Measurement at the stack of plants



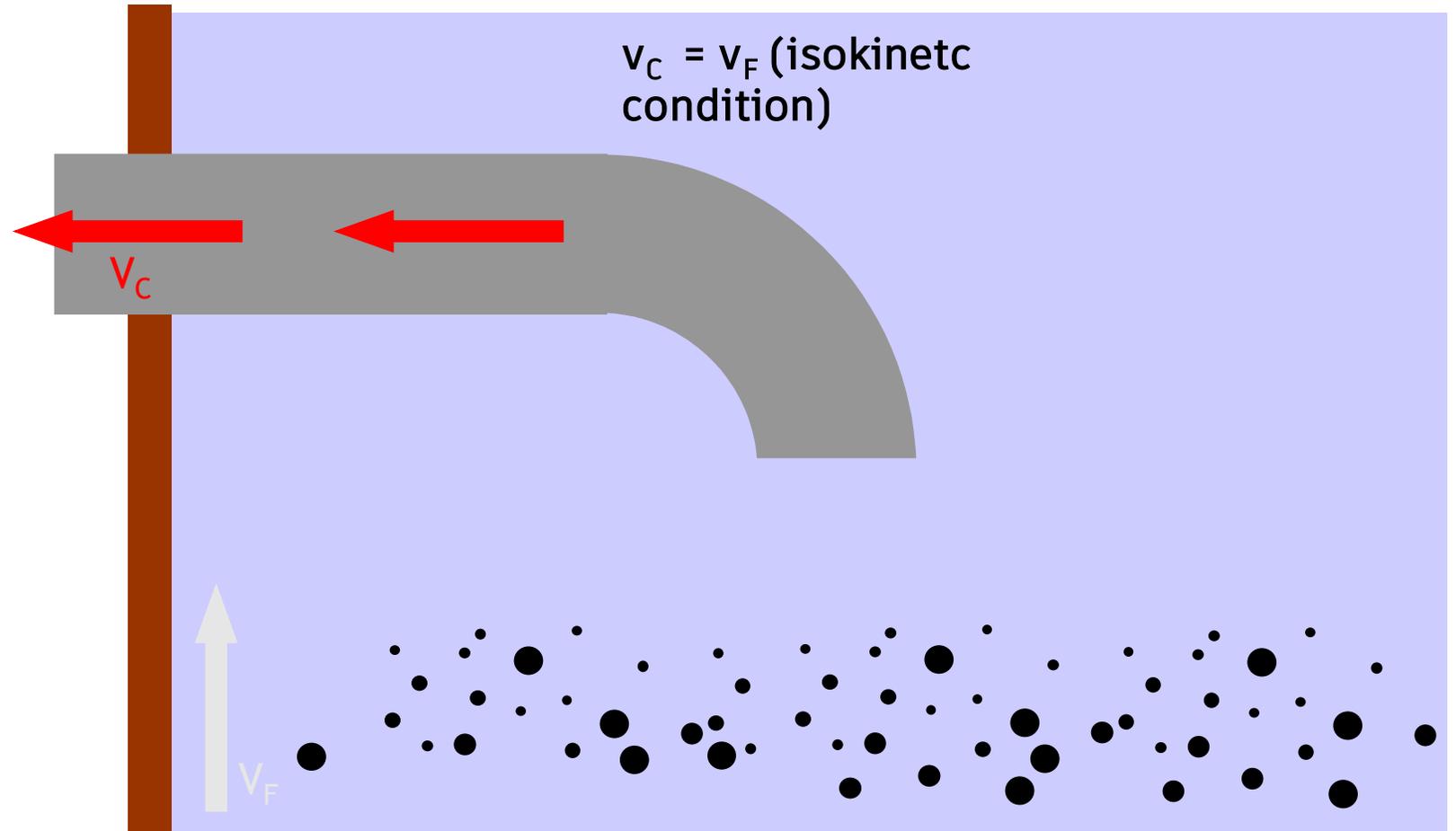
1. Inlet nozzle
2. Filter holder
3. Pitot tube
4. Temperature sensor
5. Temperature indicator
6. Static pressure measurement
7. Dynamic pressure measurement
8. Support
9. Cooling and gas collection system
10. Suction unit and gas measuring device
11. Manometer

# Gravimetric measurement

## Measurement at the stack of plants

Metrological issue: the isokinetic sampling

$v_C$  = sampling velocity  
 $v_F$  = exhaust velocity

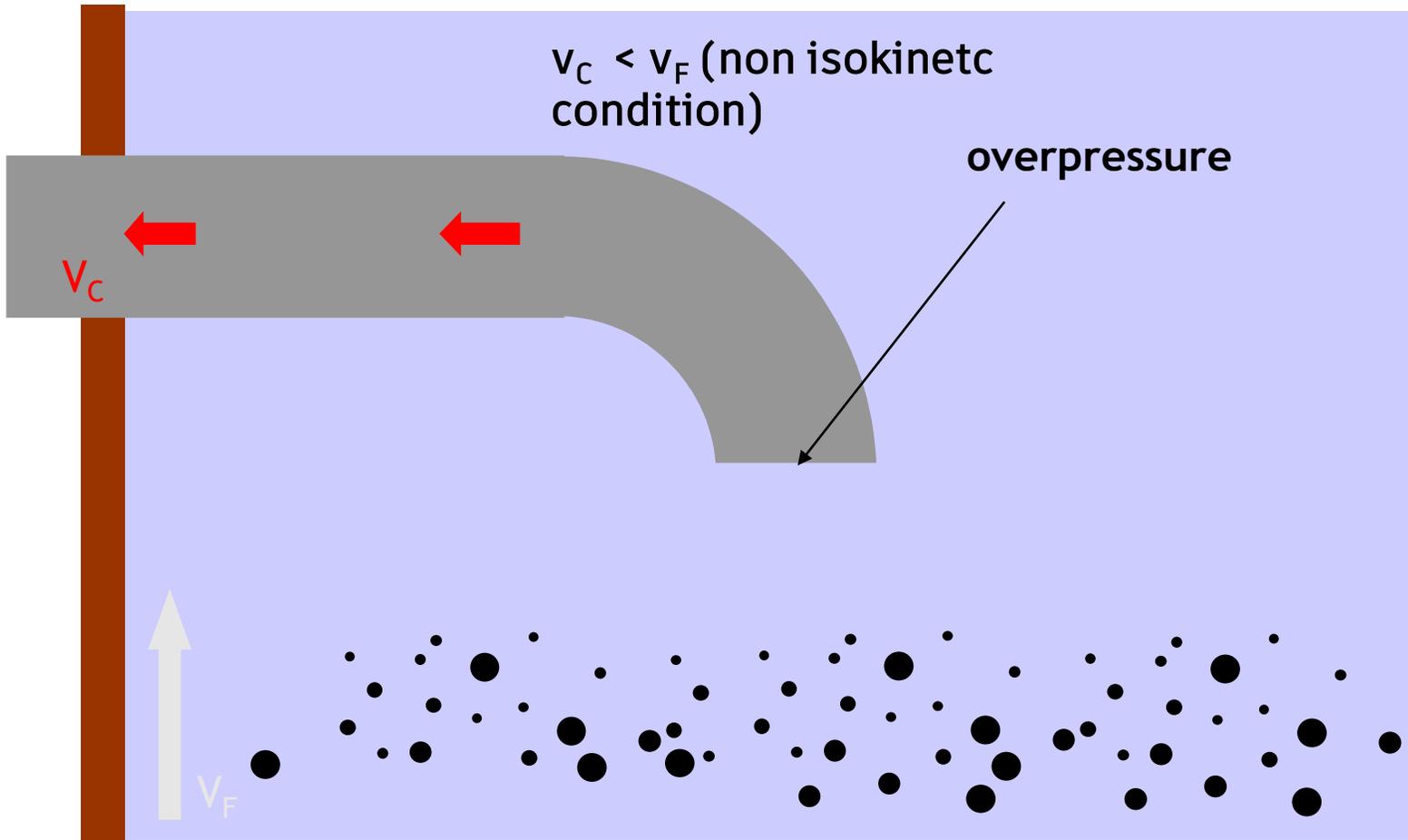


# Gravimetric measurement

## Measurement at the stack of plants

Metrological issue: the isokinetic sampling

$v_C$  = sampling velocity  
 $v_F$  = exhaust velocity

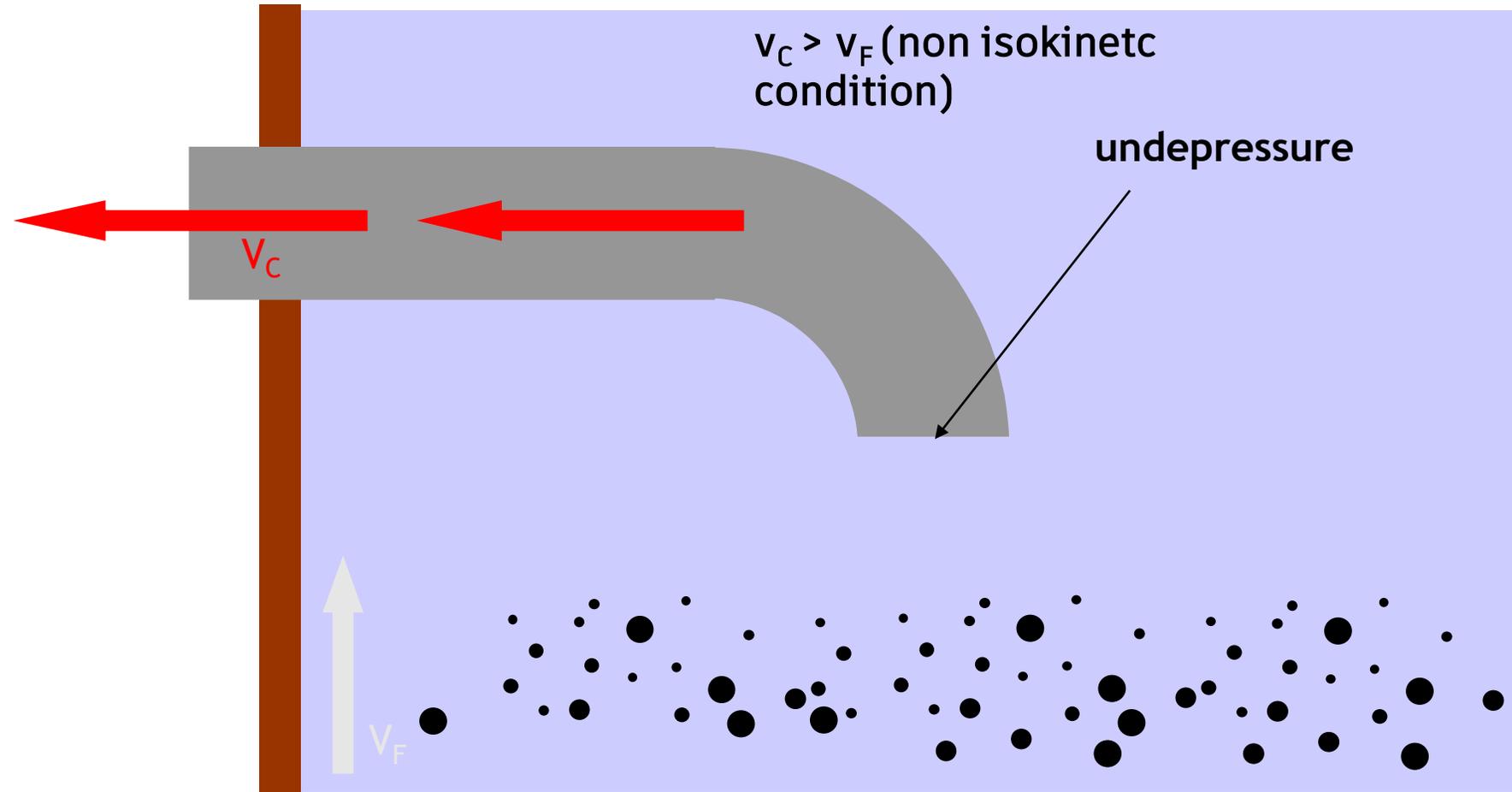


# Gravimetric measurement

## Measurement at the stack of plants

Metrological issue: the isokinetic sampling

$v_C$  = sampling velocity  
 $v_F$  = exhaust velocity



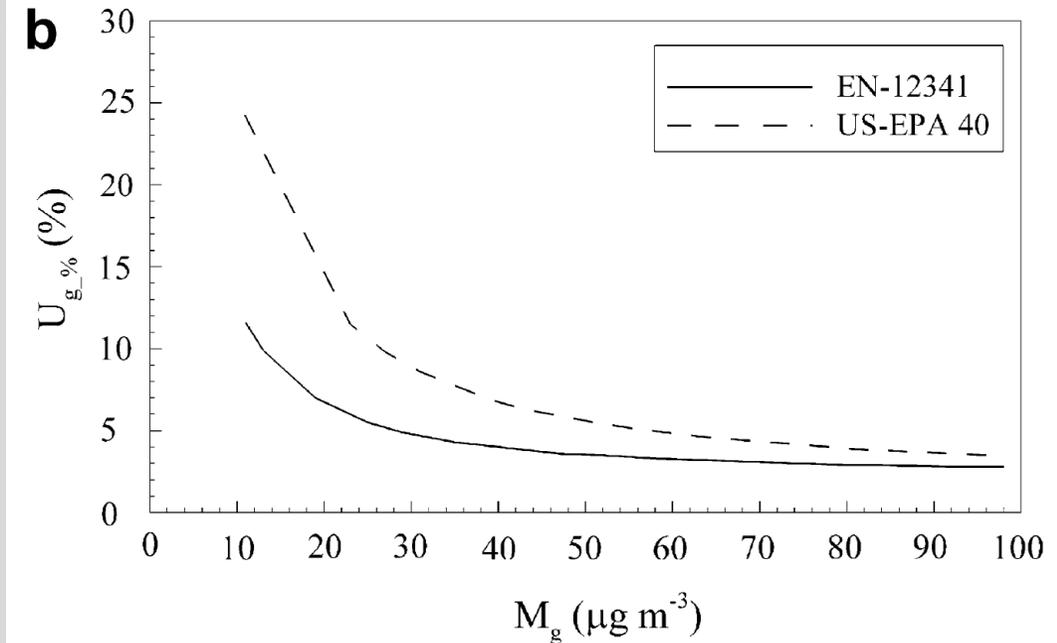
# Gravimetric measurement

## Uncertainty budget

- weighing procedure and wrong filter conditioning can generate high PM uncertainties!
- European standards guarantee lower uncertainties than US-EPA (flow rate effect!)

Uncertainty budget for PM<sub>2.5</sub> concentration in San Vittore del Lazio (Italy), May 28th, 2008.

Source of uncertainty	Value	Unit	Distribution	$k$	Standard uncertainty	Sensitivity coefficient	Absolute uncertainty contribution
Sampling	5.0	$\mu\text{g}$	Rectangular	$\sqrt{3}$	2.9	$2.0\text{E}-02$	$5.8\text{E}-02$
<i>Mass</i>							
1. Initial mass filter contribution					27.0	$2.0\text{E}-02$	$5.4\text{E}-01$
a. Conditioning	40.0	$\mu\text{g}$	Rectangular	$\sqrt{3}$	23.1		
b. Balance calibration and drift	4.09	$\mu\text{g}$	Normal	2	0.8		
c. Filter repeatability	13.9	$\mu\text{g}$	Normal	1	13.9		
2. Final mass filter contribution					23.9	$2.0\text{E}-02$	$4.8\text{E}-01$
a. Conditioning	40.0	$\mu\text{g}$	Rectangular	$\sqrt{3}$	23.1		
b. Balance calibration and drift	4.09	$\mu\text{g}$	Normal	2	0.8		
c. Filter repeatability	6.0	$\mu\text{g}$	Normal	1	6.0		
<i>Volume</i>							
a. Flow meter calibration and drift	5%		Normal	2	1.4	$3.6\text{E}-01$	$5.1\text{E}-01$
b. Pressure sensor	1%		Normal	2	509	$2.0\text{E}-04$	$1.0\text{E}-01$
c. Temperature sensor	1.0	$^{\circ}\text{C}$	Normal	2	0.5	$6.4\text{E}-02$	$3.2\text{E}-02$
Combined uncertainty		$\mu\text{g m}^{-3}$					$8.9\text{E}-01$
Statistical cover factor $K$							2
Expanded uncertainty ( $U_g$ )		$\mu\text{g m}^{-3}$					1.79
PM concentration ( $M_g$ )		$\mu\text{g m}^{-3}$					20.3
Relative expanded uncertainty ( $U_{g,\%}$ )							8.8%



# Measuring ultrafine particles

## Gravimetric method for UFPs?

- Reference method for PM (not for PN).
- representative only of the fraction of particles that have a significant **contribution in terms of mass**.

## Particle counting

- The industrial need to individually **select and count extremely small particles** has made possible the development of **optical detection techniques** and the refinement of particle size classification methodologies
- The Aitken dust counters utilized heterogeneous nucleation to grow particles in order to be detected by the human eye
- The Aitken dust counters revolutionized aerosol science by allowing measurement of concentrations of particles over a broad size range!

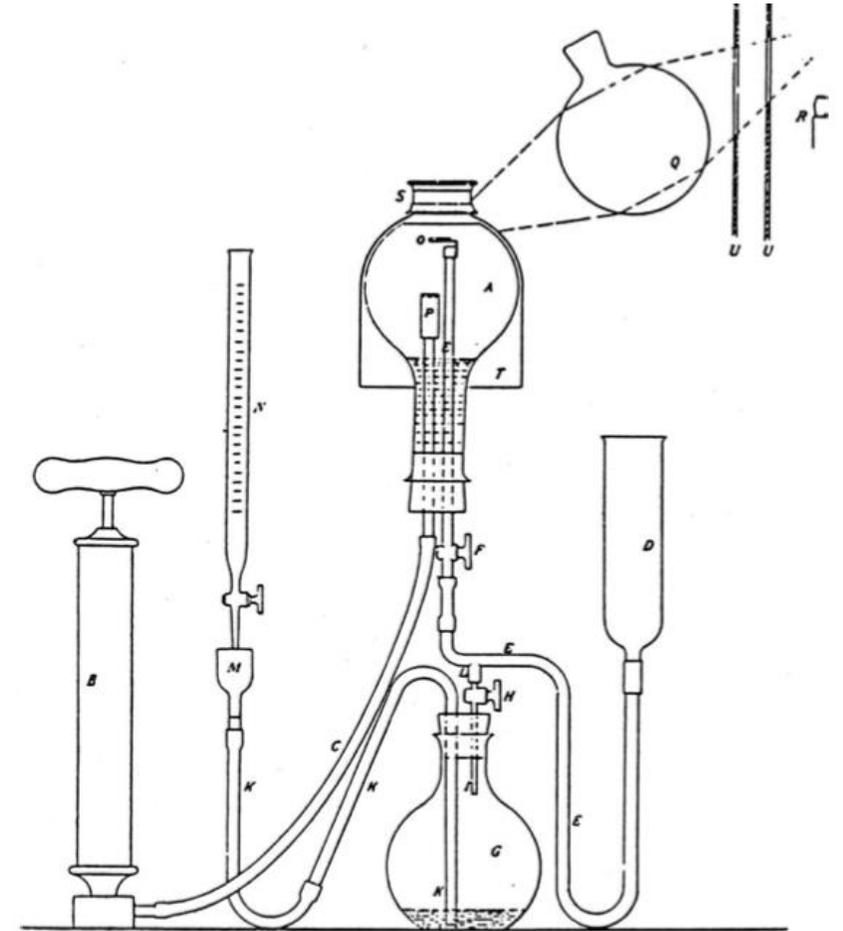


FIG. 1. Aitken's laboratory dust counter (1888): 500 cm<sup>3</sup> expansion flask (A) with a stage (O) for sedimented droplet counting with the aid of a magnifying glass (S). Sampling flask (G) and pump of 150-cm<sup>3</sup> capacity for saturated air expansion (B).

# Measuring ultrafine particles

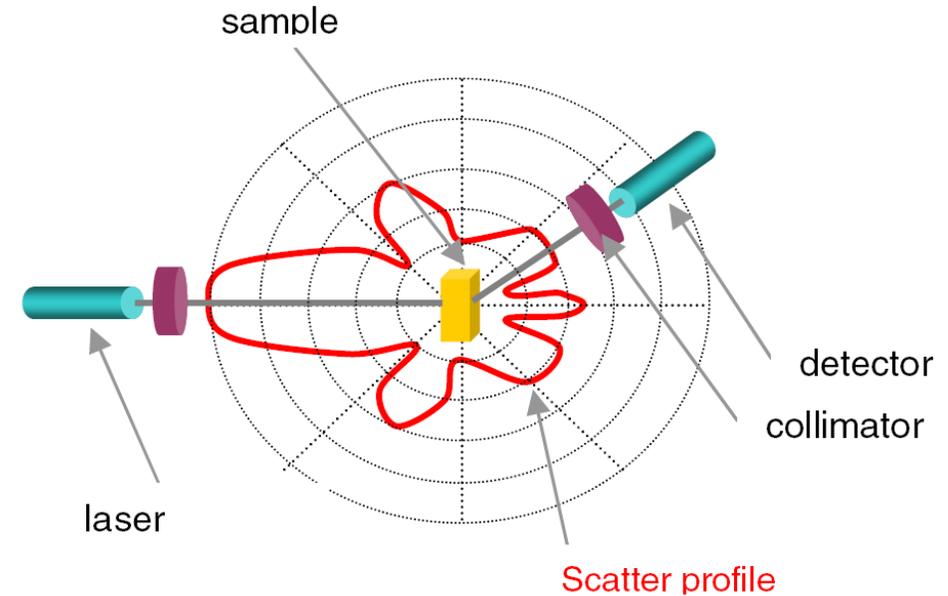
## Particle counting or...?

Direct optical sizing techniques for ultrafine particles is problematic due to:

- **weak optical diffraction** signal of light characteristic of objects of dimensions much smaller than the wavelength of the light itself,
- **non-direct proportionality** of the optical properties to a particular property of the particle over the entire dimensional range of interest.

Moreover, classification techniques exploiting inertial and gravimetric methods can only be used at pressures much lower than atmospheric ones.

Thus...ultrafine particles need to be counted and classified by electrical techniques!

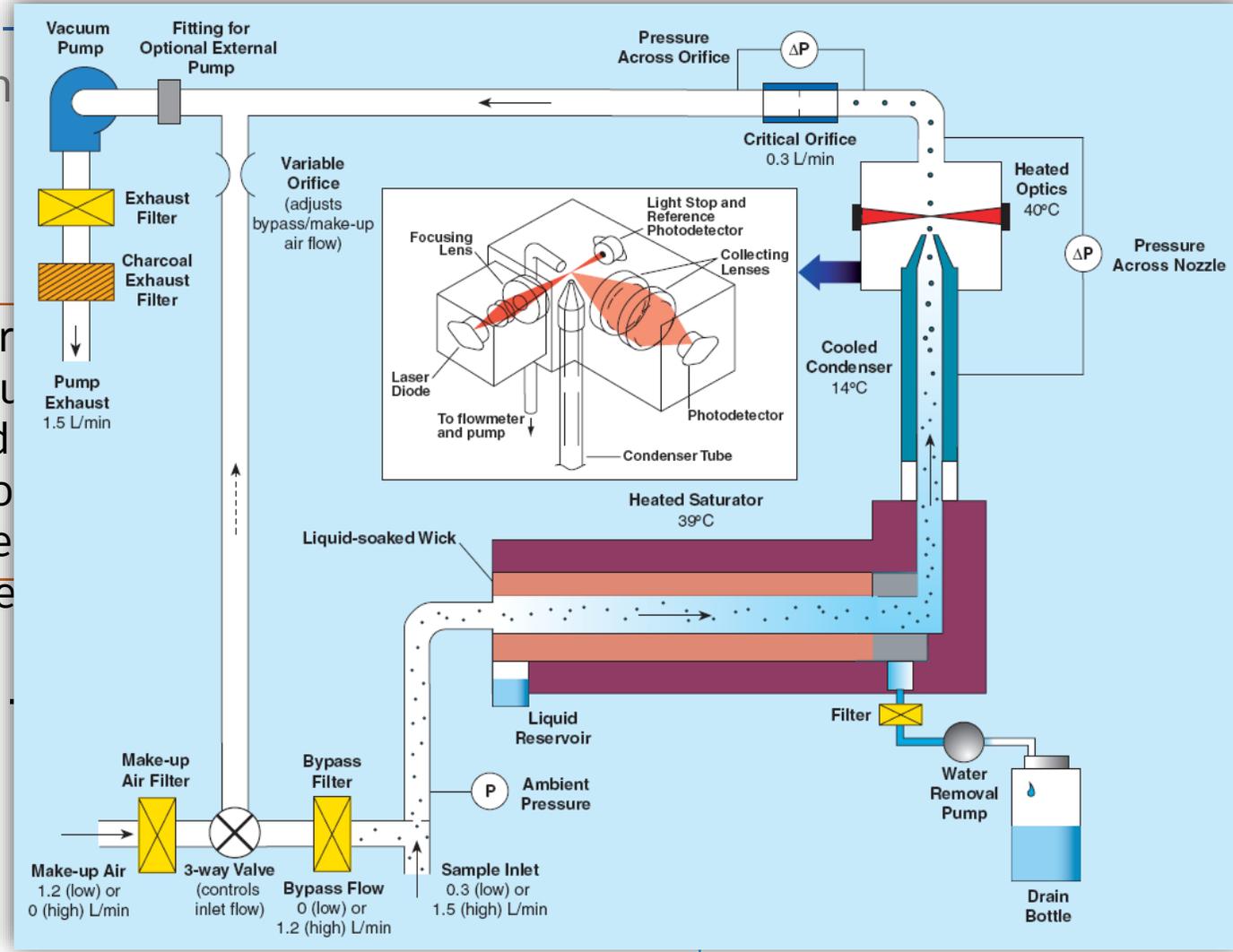


# Measuring ultrafine particles

CPC 3775 (TSI Inc.)  
Condensation technique

An aerosol sample is continuously heated butanol is diffused into the sample.

Aerosol sample



The CPC 3775 uses a laser light source and a photo-detector to collect light from particles. A microprocessor is used for instrument control and data processing.

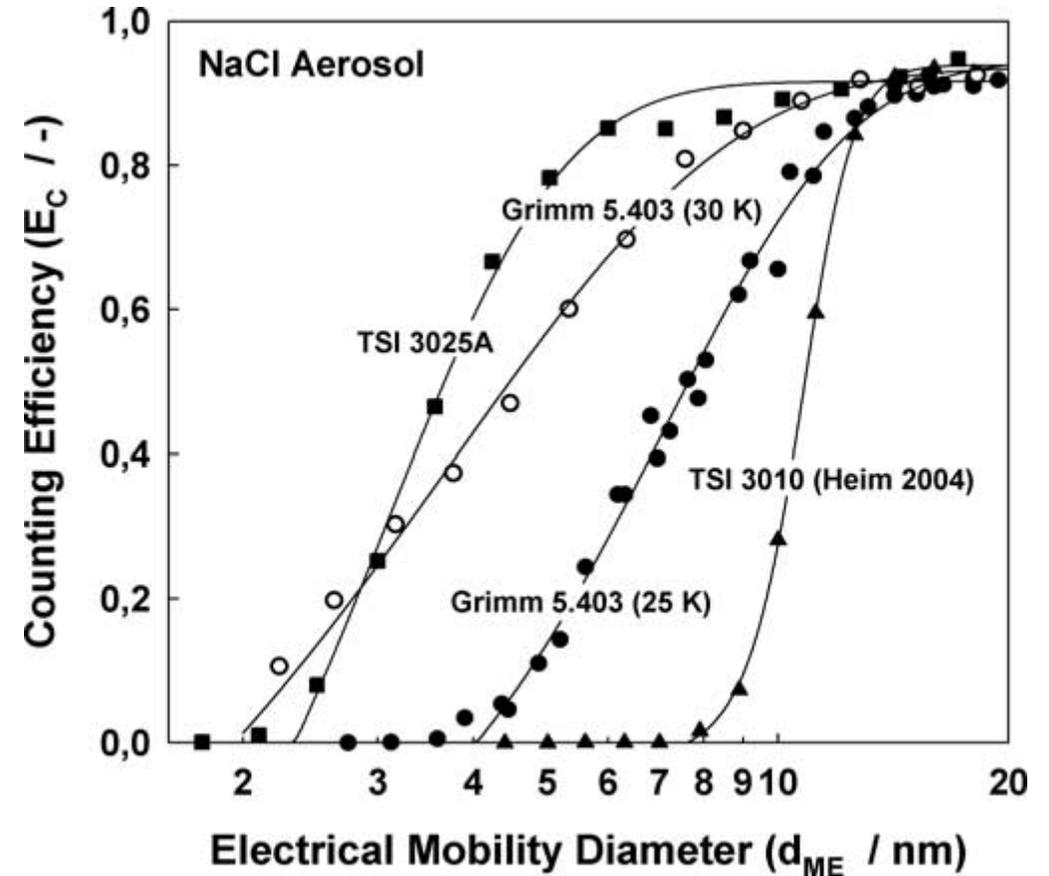
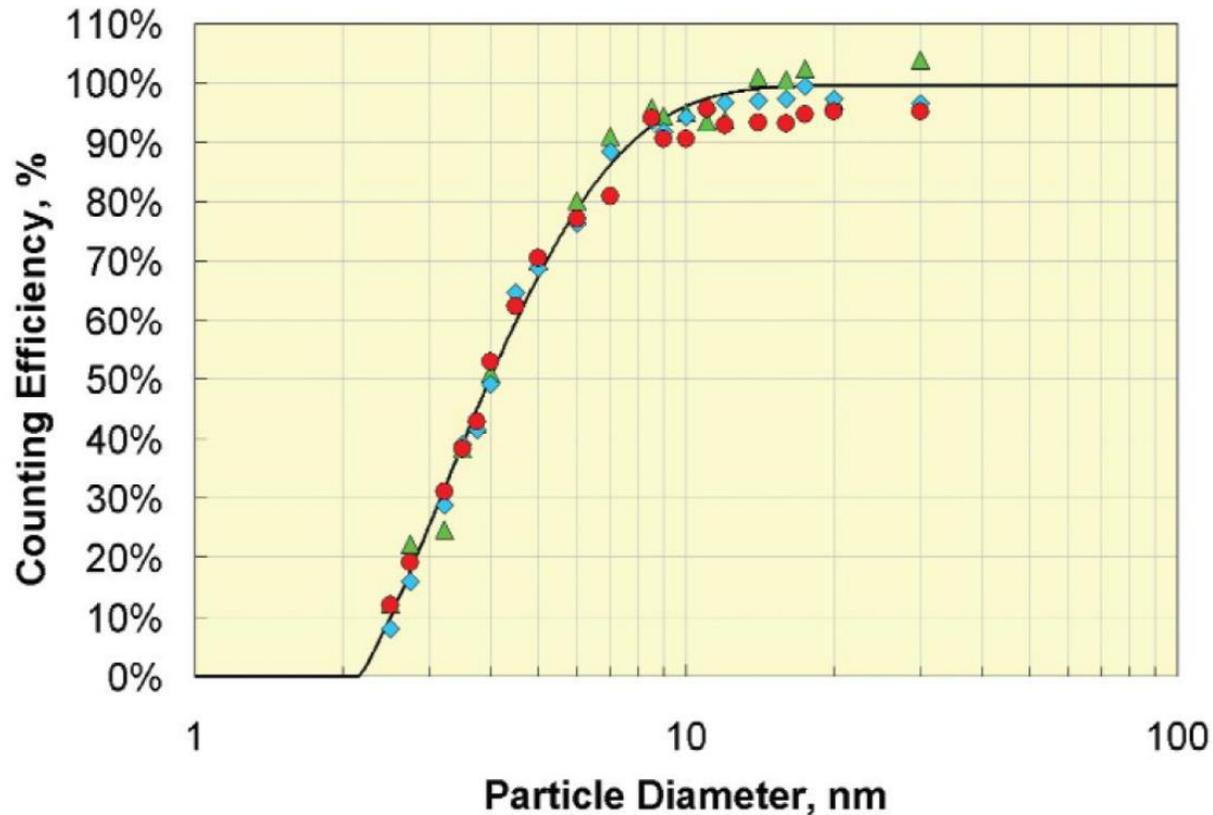
butanol is present in the saturation nuclei. Particles quickly pass through an orifice easily.

# Measuring ultrafine particles

CPC 3775 (TSI Inc.) – Condensation Particle Counter

Counting efficiency

Cut-off diameter (Kelvin effect)



# Measuring ultrafine particles

## Scanning Mobility Particle Sizer - SMPS 3936 TSI

Classification and counting

Measurement range: 0.01 – 1  $\mu\text{m}$

### How it works

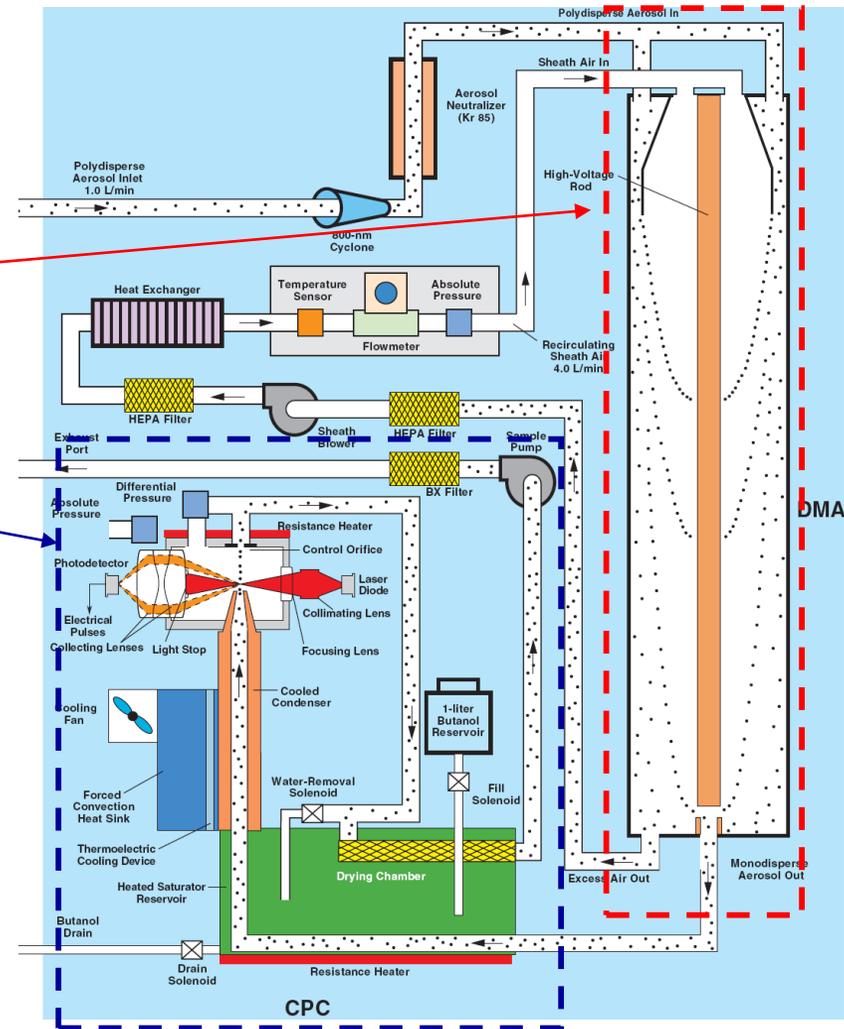
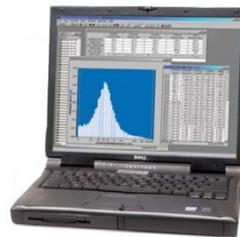
SMPS spectrometer uses electrical-mobility particle size classification (**Electrostatic Classifier**), combined with a **Condensation Particle Counter (CPC)**.



**Electrostatic Classifier**  
EC 3080 TSI



**Condensation Particle Counter**  
CPC 3775 TSI



# Measuring ultrafine particles

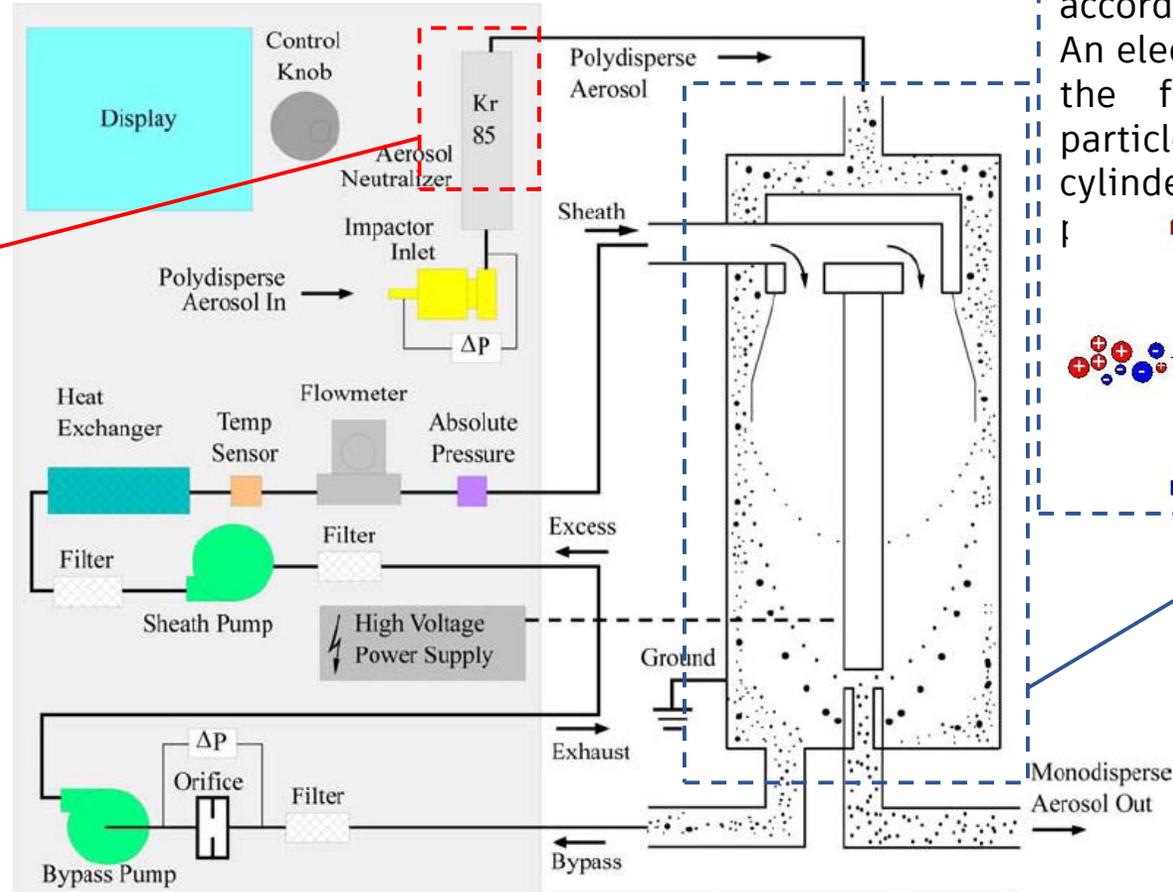
## Electrostatic classifier

Classification according to particle electrical mobility

### Aerosol Neutralizer 3077(TSI Inc.)

Polydisperse, sub micrometer aerosol passes through a radioactive bipolar charger, establishing a bipolar equilibrium charge level on the particles

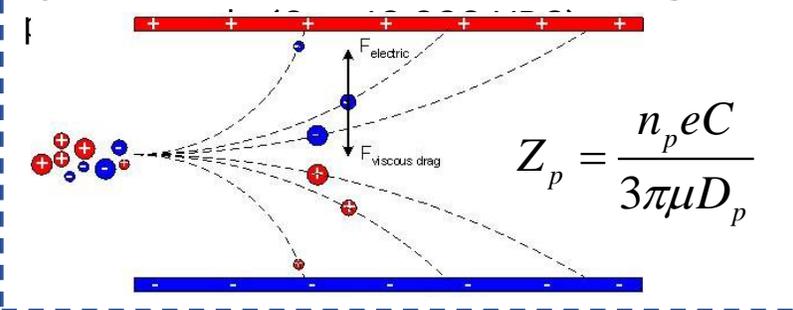
$$f(N) = \frac{e}{\sqrt{4\pi^2 \epsilon_0 D_p kT}} \exp \left[ - \frac{N - \frac{2\pi\epsilon_0 D_p kT}{e^2} \ln \left( \frac{Z_{i+}}{Z_{i-}} \right)}{2 \frac{2\pi\epsilon_0 D_p kT}{e^2}} \right]^2$$



### DMA 3081 (TSI Inc.)

The particles then enter the differential mobility analyzer (DMA) and are separated according to their electrical mobility.

An electric field inside the DMA influences the flow trajectory of the charged particles. The DMA contains an inner cylinder that is connected to a negative

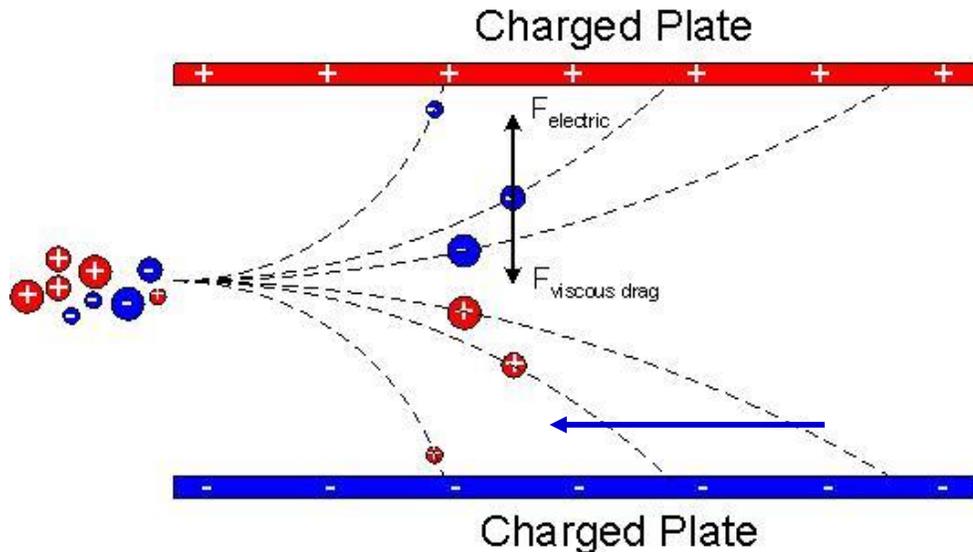


$$Z_p = \frac{n_p e C}{3\pi\mu D_p}$$

# Measuring ultrafine particles

## Electrostatic classifier

- **Smaller particles**, characterized by high electrical mobility, are attracted more quickly towards the electrode, while,
- **larger particles**, with lower electrical mobility, are influenced more by the forces of the flow field and are therefore able to complete a longer trajectory in the classification region.



$$Z_p = \frac{\text{Particle Velocity}}{\text{Electric Field Strength}} = \frac{v}{E} = \frac{n_p e C}{3\pi\mu D_p}$$

$n_p$  = number of charges/particle

$e$  = elementary unit of charge

$\mu$  = viscosity of gas

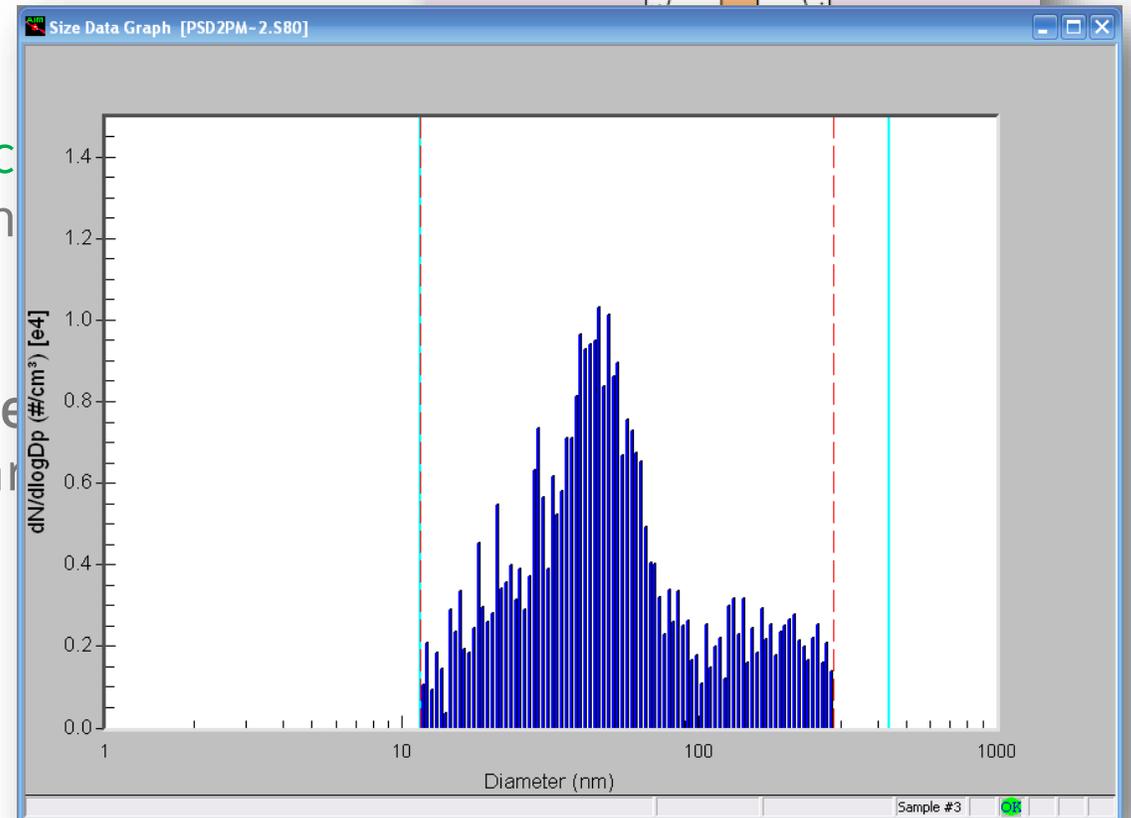
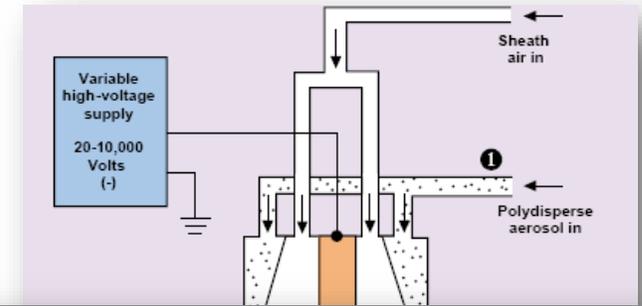
$D_p$  = particle diameter

$C$  = Cunningham slip correction

# Measuring ultrafine particles

## DMA 3081 (TSI Inc.) – Differential mobility analyzer

- The classification region is made up of two coaxial steel cylinder-electrodes: the center rod, connected to a power generator capable of providing voltages up to -10 kV
- Varying the center rod voltage **varies the electric field in the classification region** (annular region) which the particle moves.
- Only particles within a **narrow range of electric mobility** have the correct trajectory to pass through the open slit near the DMA exit.
- ...automatic scan of the entire size range!

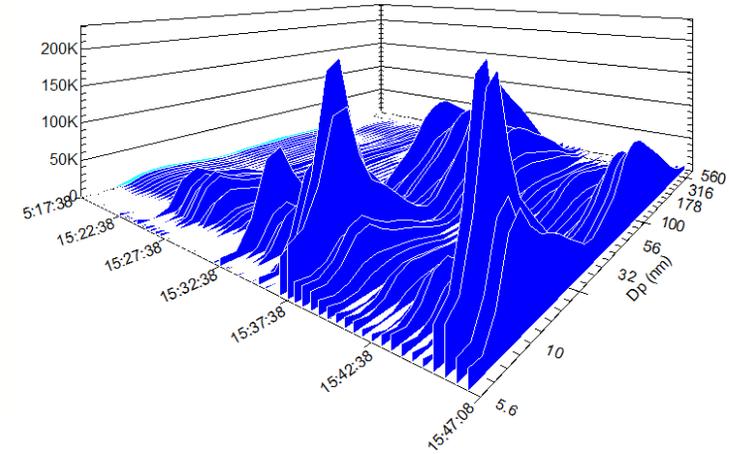
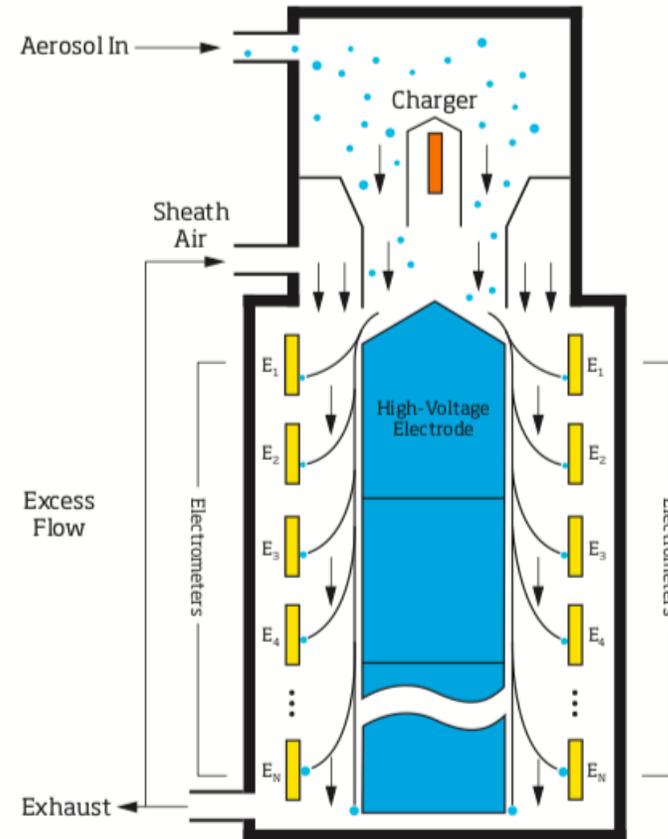


# Measuring ultrafine particles

## Fast Mobility Particle Sizer

- The FMPS™ spectrometer performs particle size classification based on differential electrical mobility classification (as with the SMPS™).
- The charged aerosol enters the analyzer column near on-axis and above the central rod.
- The particles are deflected radially outward and collected on electrically isolated **electrodes** that are located at the outer wall.
- The particle number concentration is determined **by measurement of the electrical current collected on a series of electrodes**.

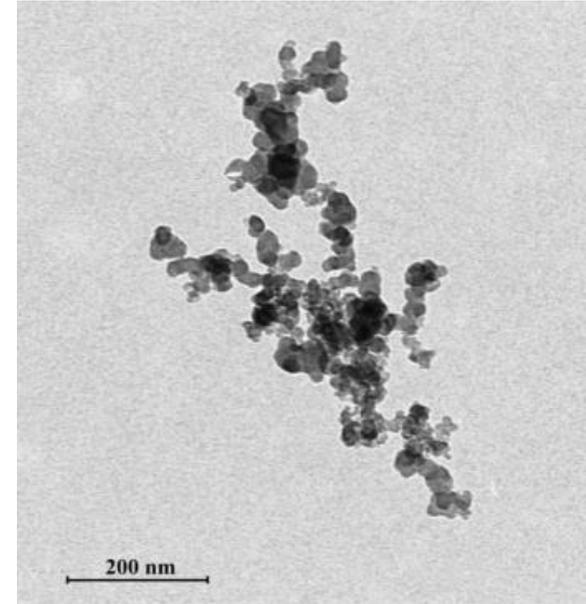
**Characterize Particle Emissions in Real-Time**



# Measuring ultrafine particles

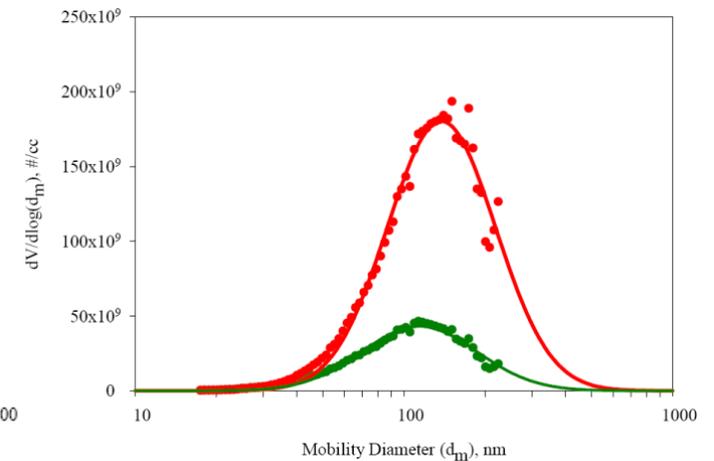
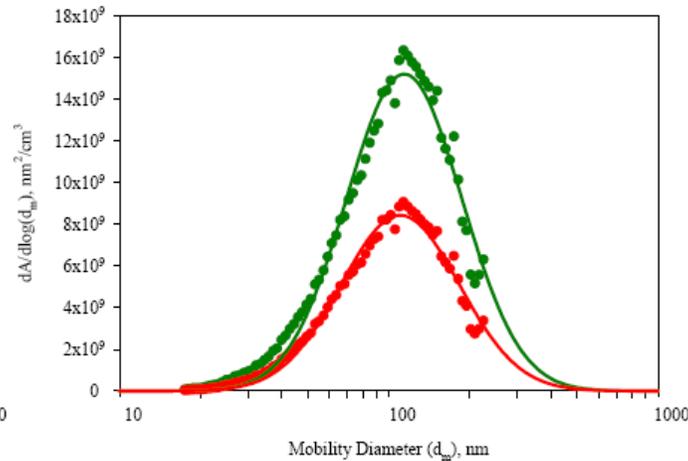
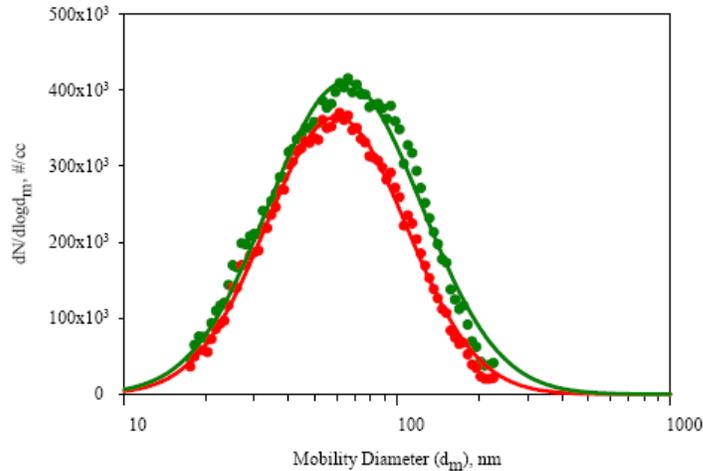
## Measurement issues

### Aggregates



### Morphological analysis

- Idealized Aggregate theory (Lall and Friedlander, 2006)
- Fractal dimension  $< 2$
- $a_c$



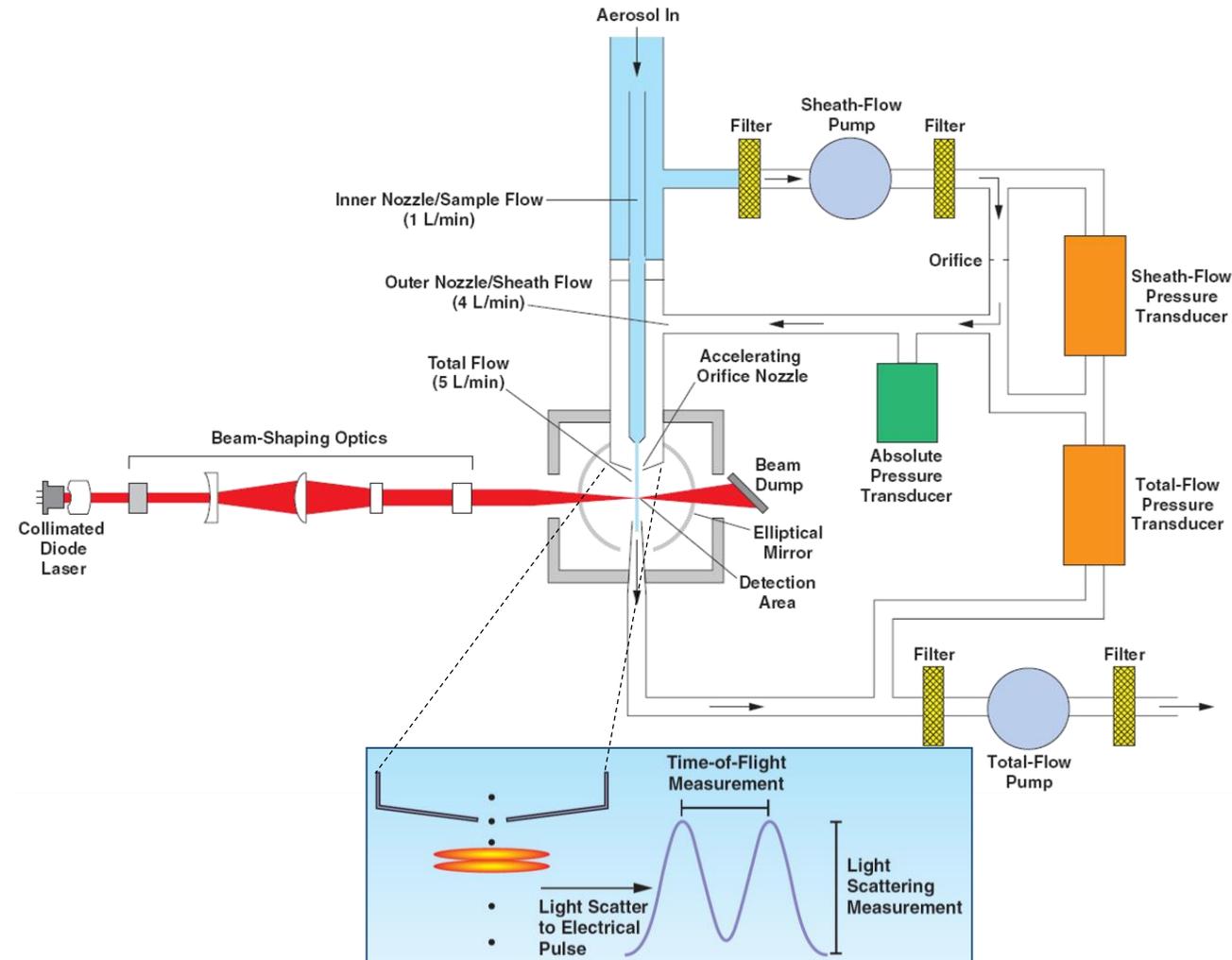
# Measuring super-micrometric particles

## Aerodynamic Particle Sizer - APS 3321 TSI

Measurement range: 0.5 – 20  $\mu\text{m}$

sizing and counting technique: *time-of-flight*

- The APS accelerates the aerosol sample flow through an accelerating orifice.
- The **aerodynamic size** of a particle determines its rate of acceleration, with larger particles accelerating more slowly due to increased inertia.
- As particles exit the nozzle, they cross through two partially overlapping **laser beams** in the detection area.
- **Peak-to-peak time-of-flight** is measured with 4 nanosecond resolution for aerodynamic sizing. The amplitude of the signal is logged for light-scattering intensity.



# Measuring super-micrometric particles

## Aerodynamic Particle Sizer - APS

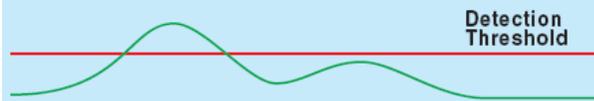
### 3321 TSI

#### Time-of-Flight Measurement Results

Every particle signal is processed in real time as one of four distinct events. The Model 3321 logs the occurrence of all events, but only Events 1 and 2 are included in size distribution results. Light-scattering intensity is recorded for Event 2 only.

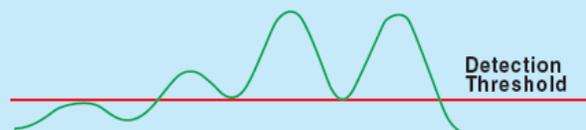
#### Event 1

This event occurs when the signal for a small particle cannot stay above the threshold and only one crest is detected. The measurement is aborted, and the time-of-flight of the particle is not recorded. However, the event is logged for concentration calculations and displayed in the  $<0.523\text{-}\mu\text{m}$  size channel in uncorrelated mode.



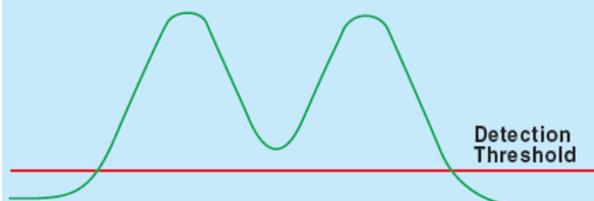
#### Event 3

This event is caused by coincidence. Although the signal stays above the threshold, three or more crests are detected. Events of this type are logged but not recorded for concentration or time-of-flight.



#### Event 2

This is a valid particle measurement. The signal stays above the threshold and two crests are detected. The time-of-flight between the two crests is recorded and the events are included in the concentration calculations.



#### Event 4

This event is outside the maximum range of the timer. The signal remains above the threshold until it moves outside the timer range, and only one crest is detected. A type 4 event is normally caused by large or recirculating particles. Again, the event is logged, but no time-of-flight is recorded.

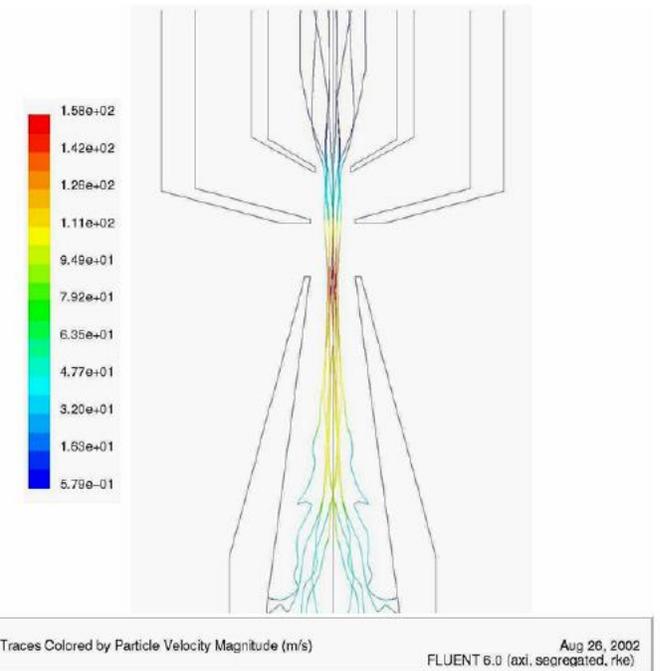
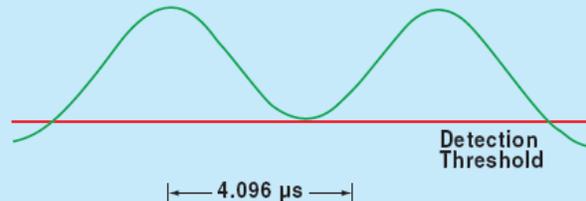
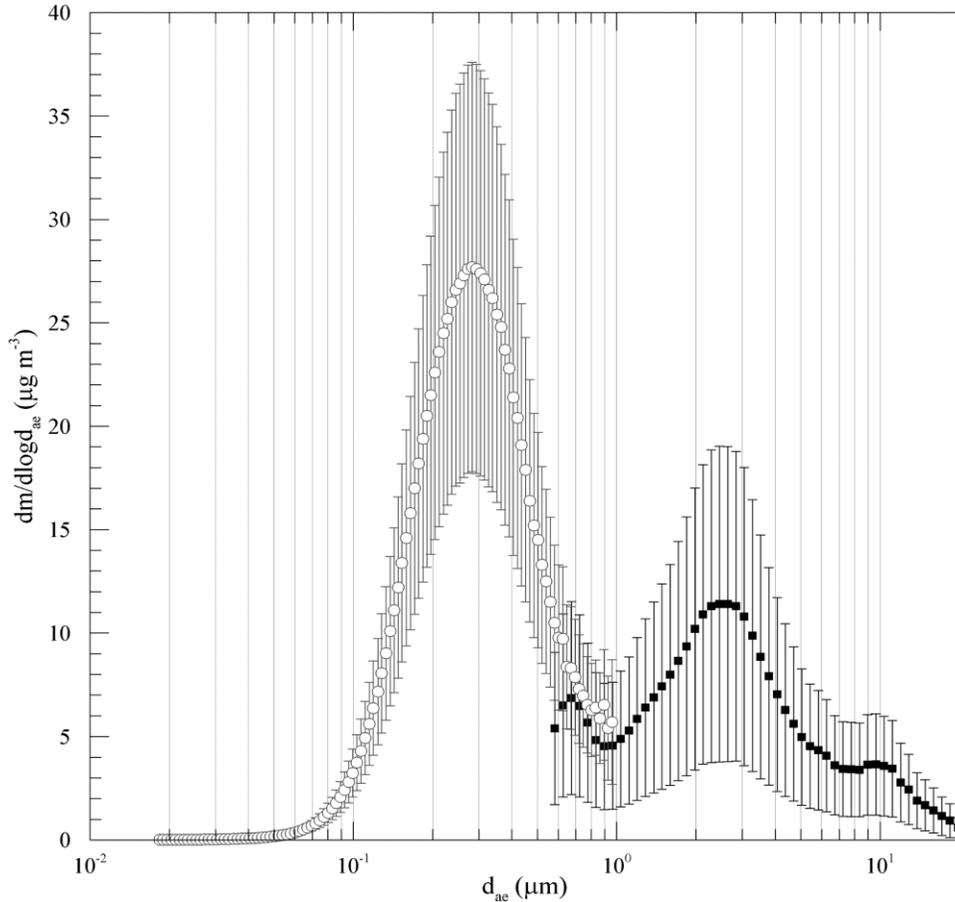


Figure 4: Flow recirculation is restricted in Model 3320 APS with a redesigned education nozzle<sup>6</sup> that is identical to the nozzle in Model 3321.

# Measuring super-micrometric particles

## SMPS-APS to measure PM



50

SMPS uncertainty contribution in the PM<sub>2.5</sub> measurement referred to the 5–10 September 2008 period

	Uncertainty value	Distribution	Uncertainty contribution $u_{m-SMPS,i}(x_i)$ ( $\mu\text{g m}^{-3}$ )
Raw count ( $c'$ )	$\pm 1/\sqrt{c'_i}$	Poisson	$1.09 \cdot 10^{-1}$
Sampling flow rate* ( $\theta$ )	$\pm 0.015 \text{ L min}^{-1}$	Normal	$3.94 \cdot 10^{-1}$
Diffusion efficiency correction ( $\eta_{diff}$ )	$\pm 10\%$		$1.26 \cdot 10^{-1}$
CPC efficiency correction ( $\eta_{CPC}$ )	$\pm 8\%$	Rectangular	$1.01 \cdot 10^{-1}$
DMA efficiency correction ( $\eta_{DMA}$ )	Included in volumetric diameter uncertainty		
Sampling time* ( $t$ )		Negligible	
Particle density* ( $\rho_p$ )	$\pm 0.5 \text{ g cm}^{-3}$	Rectangular	2.68
Volumetric diameter ( $d_{ve}$ )	$\pm 0.95\%$	Rectangular	$2.46 \cdot 10^{-2}$
Flow ratio ( $\phi$ )		Negligible	
Combined uncertainty ( $u_{M-SMPS}$ )			2.72
Statistical cover factor k			2
Expanded uncertainty ( $U_{M-SMPS}$ )			5.43
Total mass concentration ( $M_{SMPS}$ )			15.8
Relative uncertainty			34.4%

\*Fully correlated contributions.

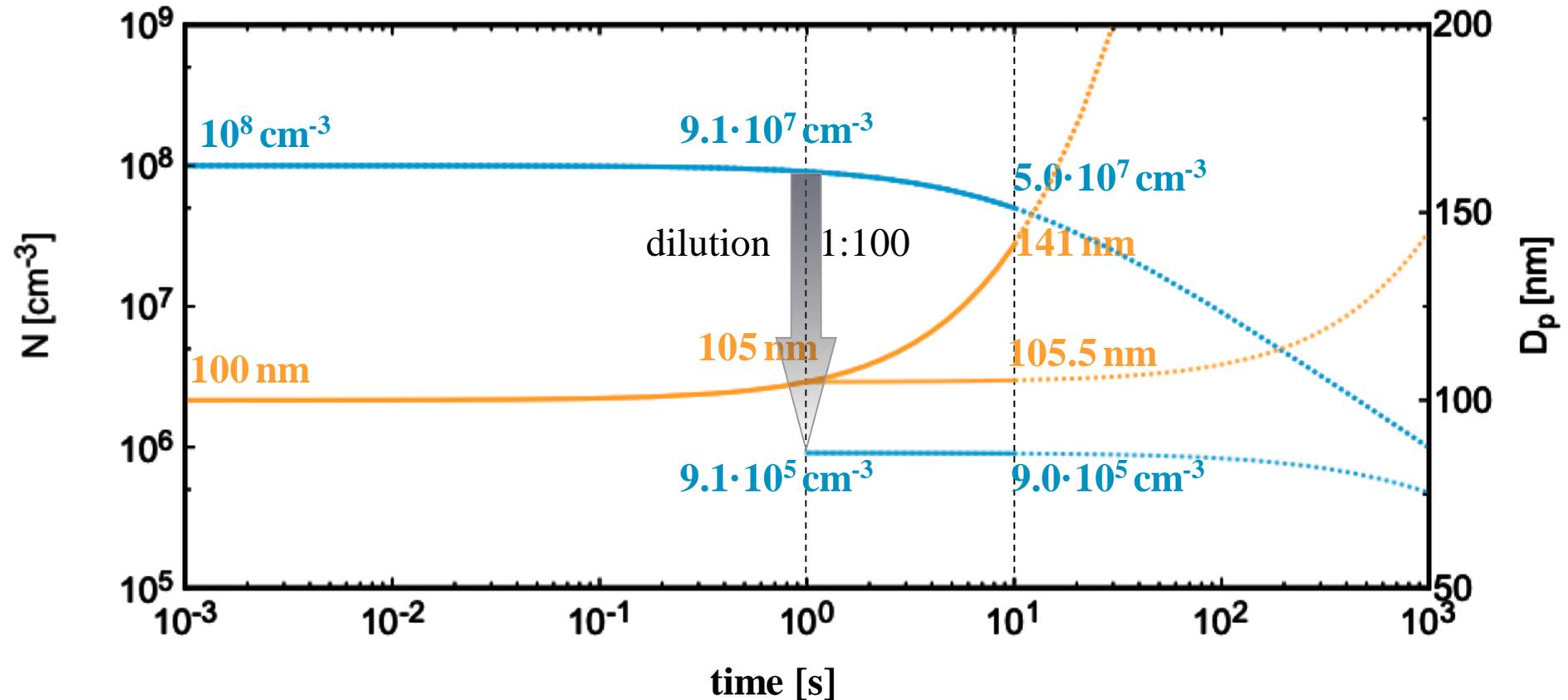
test number

# Measurement at the stack

## Sampling issues

Measurement artifacts: **coagulation, nucleation e condensation!**

Thermo-dilution of the sampled aerosol flow



# Measurement at the stack

## Thermo-dilution system

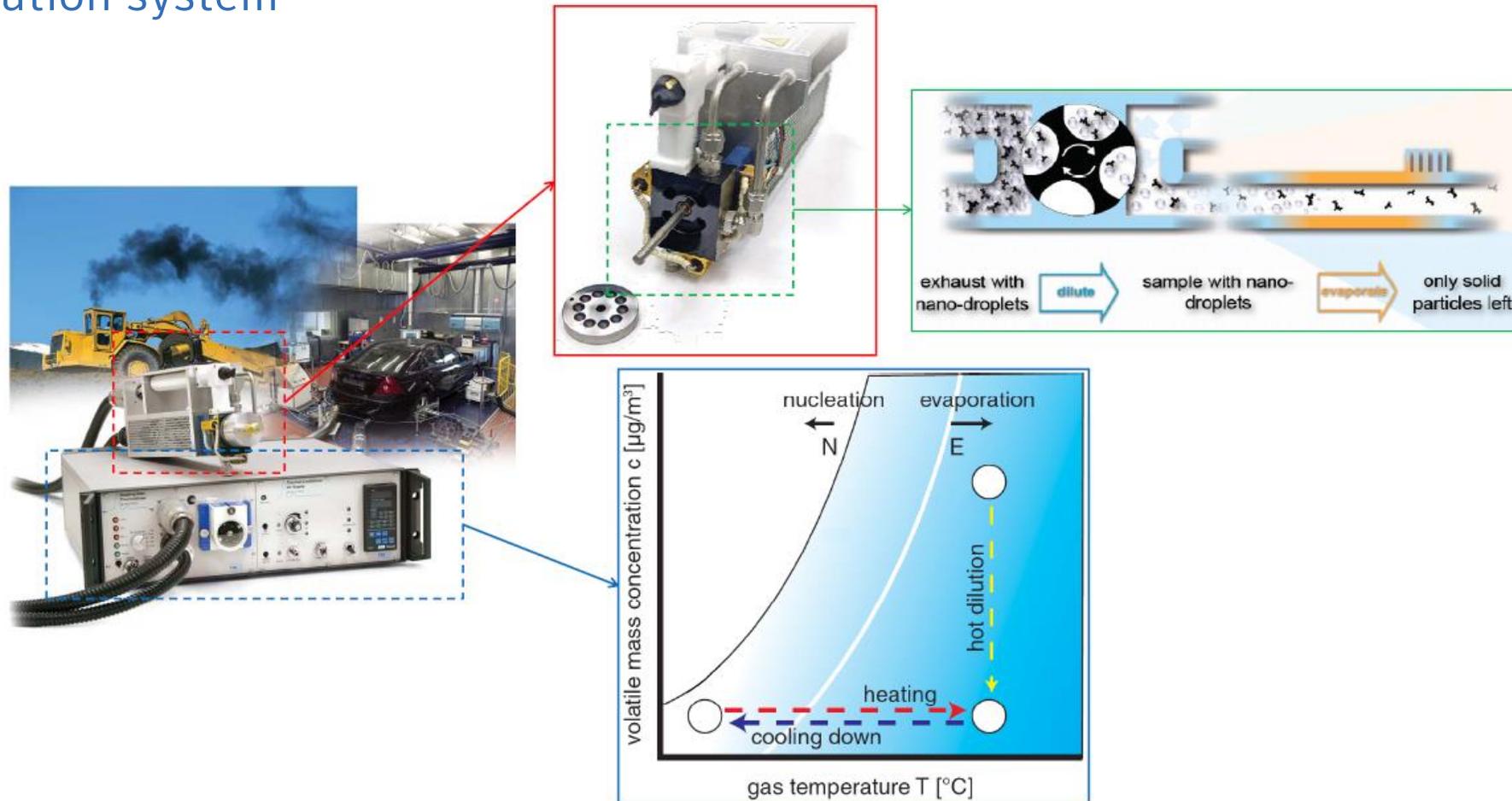
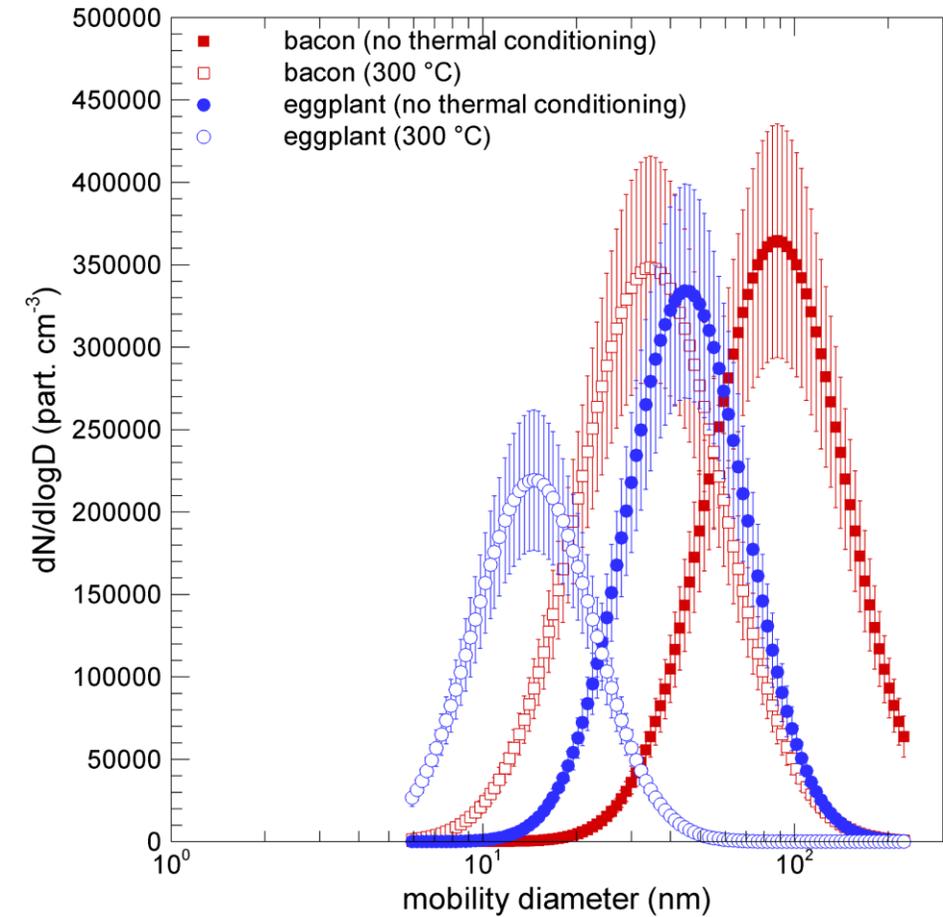
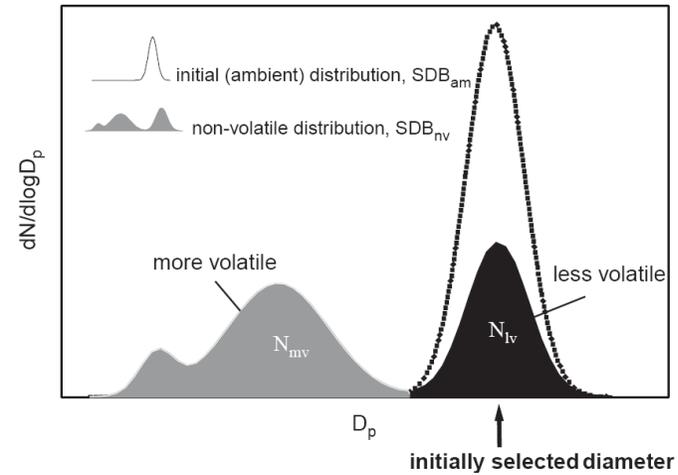
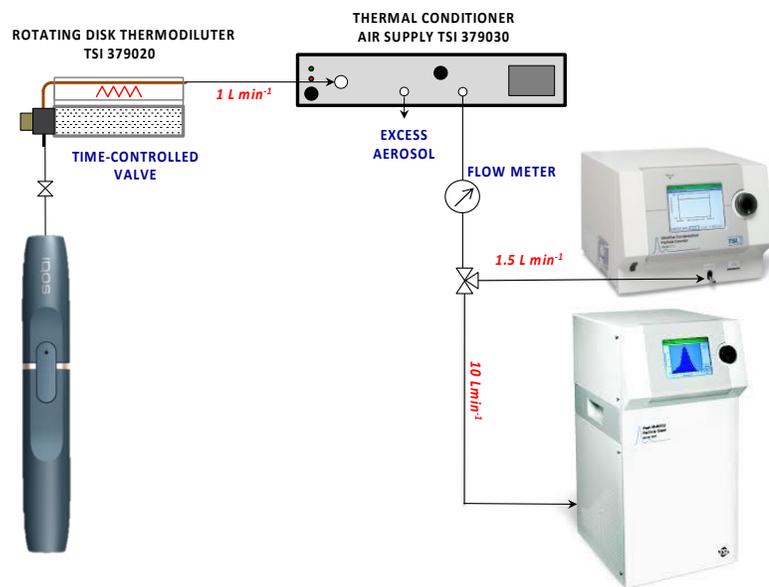


Figure 3 -Exhaust Probe Rotating Disc and Thermal Conditioner (Matter Engineering).

# Volatility analysis

## Removing volatile amount by thermodilution

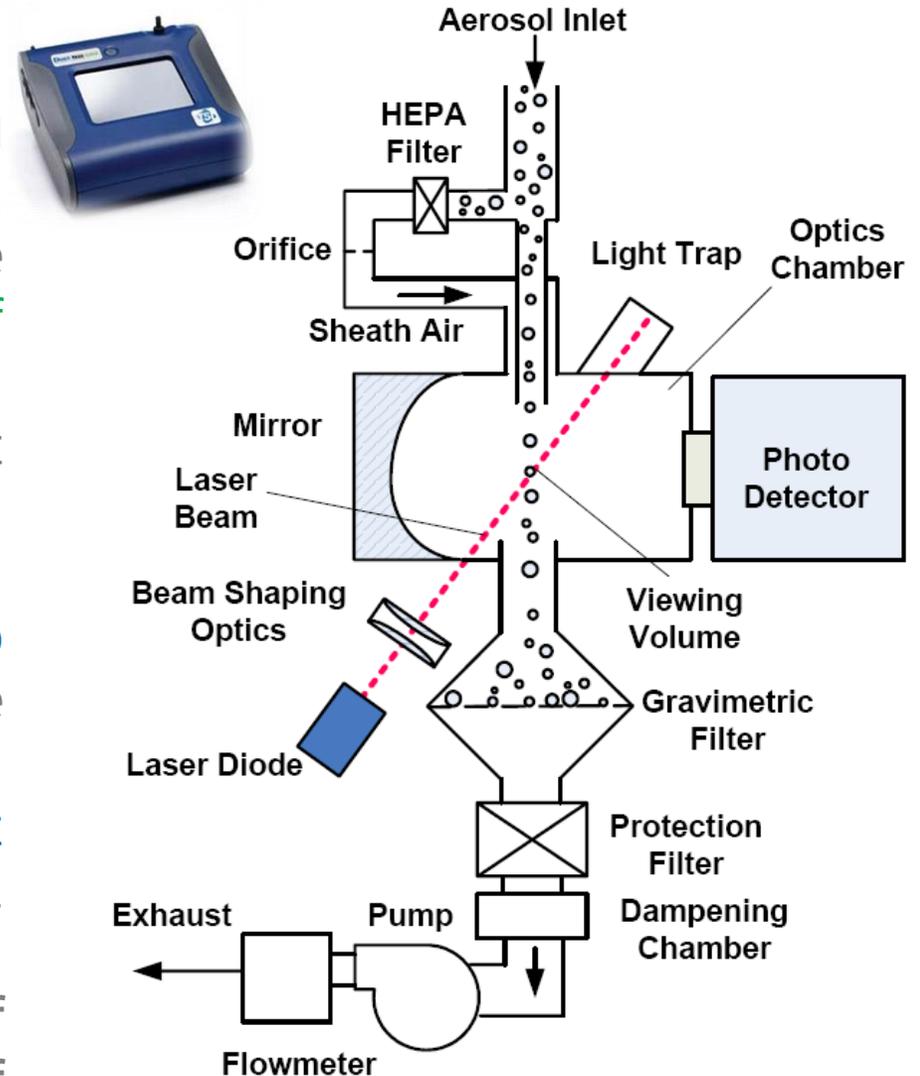


# Portable instruments: photometer for PM

## DustTrak photometer (TSI Inc.)

Measurement of PM fractions through **light scattering** technique.

- Sample flow passes through the inlet entering the sensing chamber; here, it is illuminated by a **sheet of laser light** (formed from a laser diode).
- A gold coated spherical mirror captures a significant fraction of the light scattered by the particles and focuses it on to a **photo detector**.
- The **voltage across the photo detector is proportional to the mass concentration** of the aerosol over a wide range of concentrations.
- The voltage is then multiplied by a **calibration constant** (determined from a known mass concentration, i.e. gravimetric measurement).
- The scattered light depends on the size distribution of the aerosol, refractive index, shape factor and density of the aerosol!

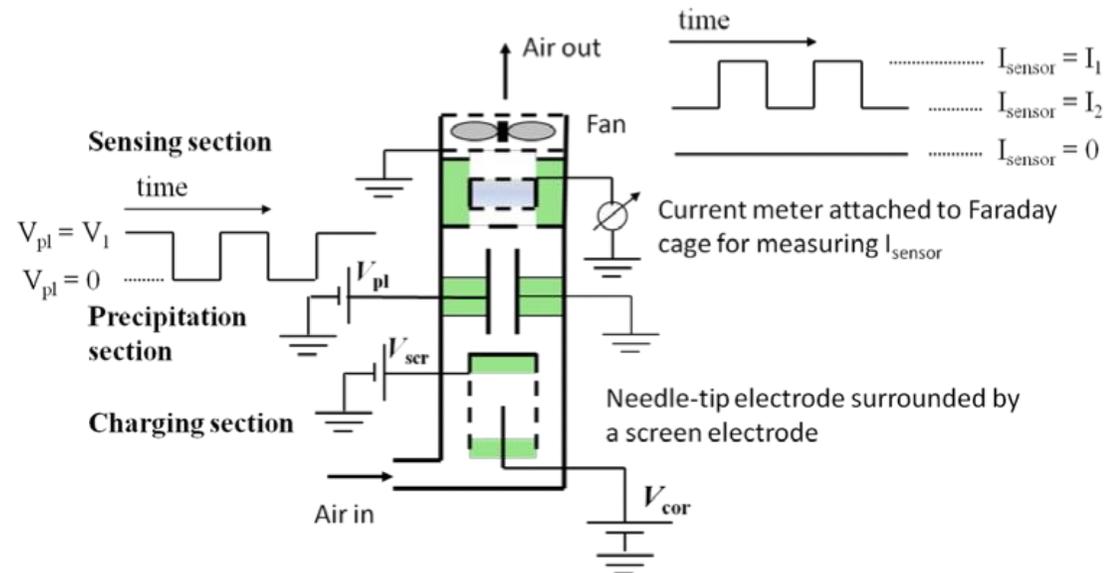


# Portable instruments: counters for PN

## Diffusion chargers

Measurement principle based on total electric charge of the particles collected.

- Particles are mixed with **unipolar ions**, which randomly collide with the particles by diffusion (hence the name) and transfer their charge to the particles.
- Excess ions are removed from the gas flow, the **charged particles are subsequently captured in a particle filter**, and a small current can be detected flowing from the filter.
- The diffusion charging process is material independent, and thus particles of different compositions cannot be distinguished.
- **The average charge  $q$  acquired by a particle in this process depends solely on its diameter.**
- Lung deposited surface area of the particles estimated (for a reference worker) – semiempirical relationships



# Estimating exposures and emissions in indoor environments

# Estimating the exposure in indoor environment

## Well-mixed simplified approach

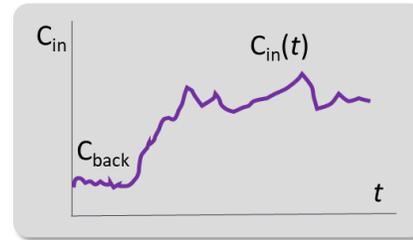
Mass balance

$$C_{out} \cdot Q_{in} \cdot P + ER = C_{in}(t) \cdot Q_{out} \cdot P + \frac{dN_{in}(t)}{dt}$$

$$C_{in}(t) = C_{back} \cdot e^{-(AER \cdot P) \cdot t} + C_{out} \cdot (1 - e^{-(AER \cdot P) \cdot t}) + \frac{ER}{V \cdot (AER \cdot P)} (1 - e^{-(AER \cdot P) \cdot t})$$

Particles entering from outdoor

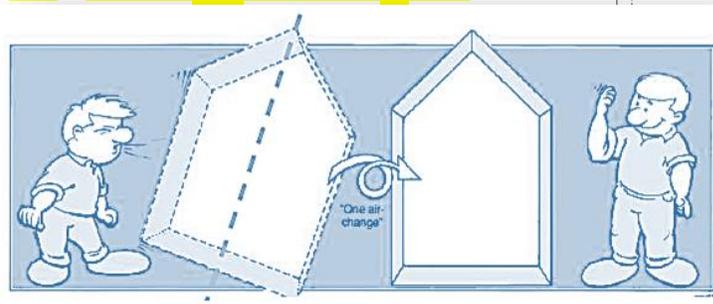
$Q_{in}$   
 $C_{out}$



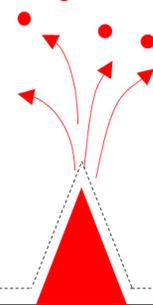
$Q_{out}$   
 $C_{in}$

Particles exiting outdoor

AER = air exchange rate  
( $h^{-1}$ ) =  $Q_{out}/V = Q_{in}/V$



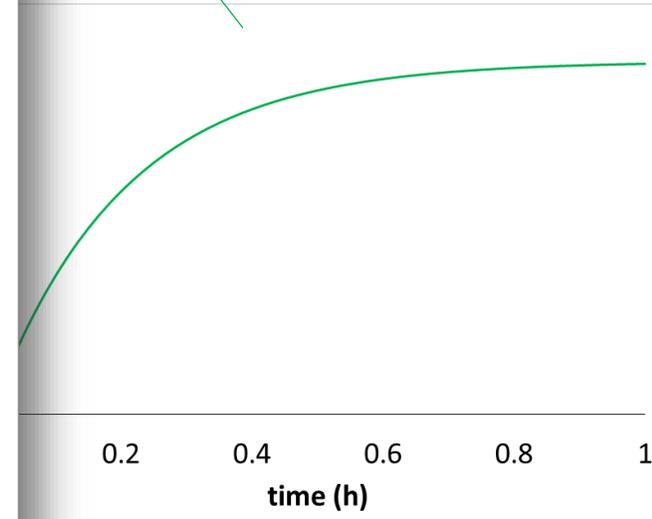
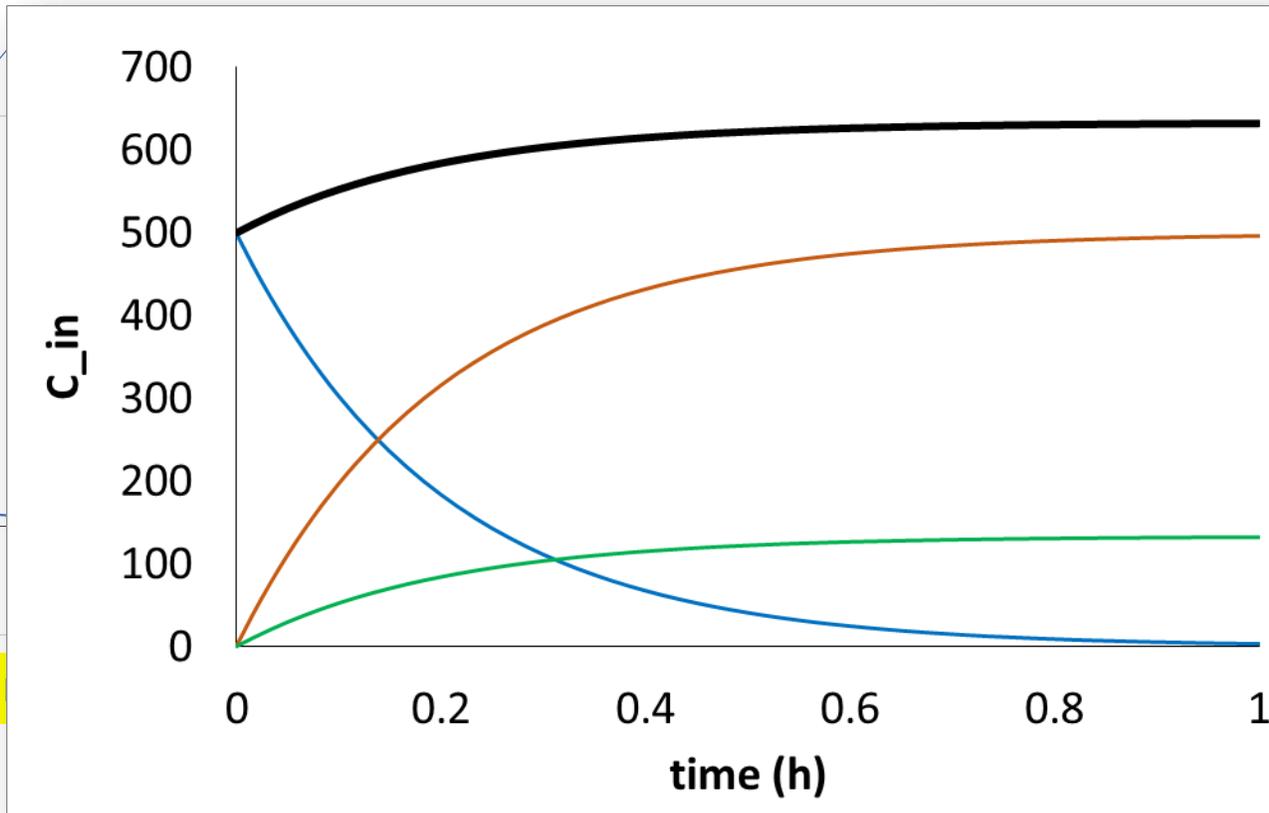
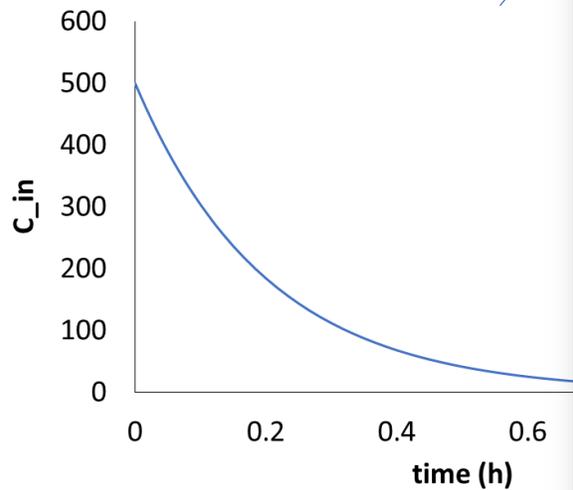
Source  
ER  
(e.g. part/s,  
• mg/s)



# Estimating the exposure in indoor environment

## Well-mixed simplified approach

$$C_{in}(t) = C_{back} \cdot e^{-(AER \cdot P) \cdot t} + C_{out} \cdot (1 - e^{-(AER \cdot P) \cdot t}) + \frac{ER}{V \cdot (AER \cdot P)} (1 - e^{-(AER \cdot P) \cdot t})$$

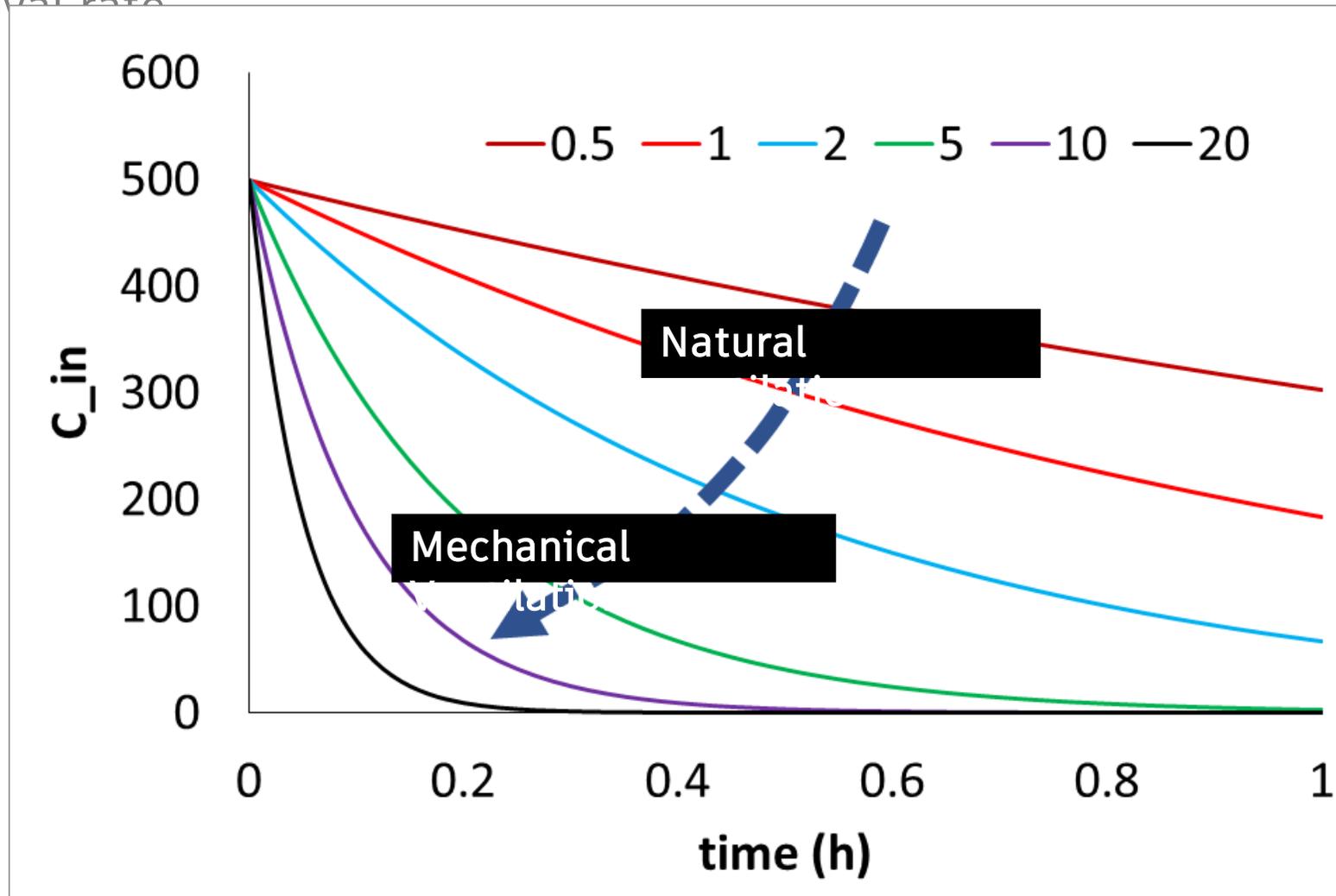


$-(AER \cdot P) \cdot t =$  "removal"

# Estimating the exposure in indoor environment

Well-mixed simplified approach

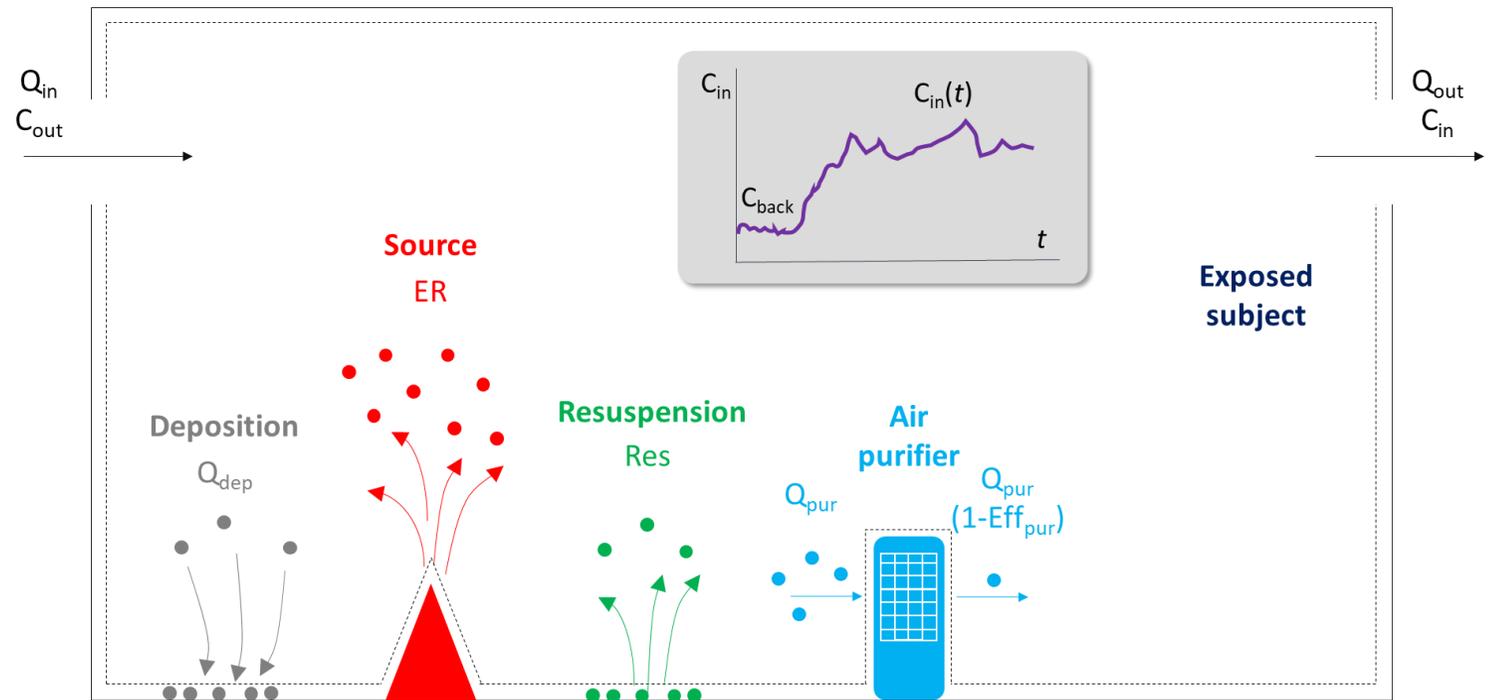
AER and removal rate



# Estimating the exposure in indoor environment

## Well-mixed simplified approach

- Deposition
- Resuspension
- Removal through air purifier
- ...



ACH = air change rate ( $h^{-1}$ ) =

$$Q_{pur}/V$$

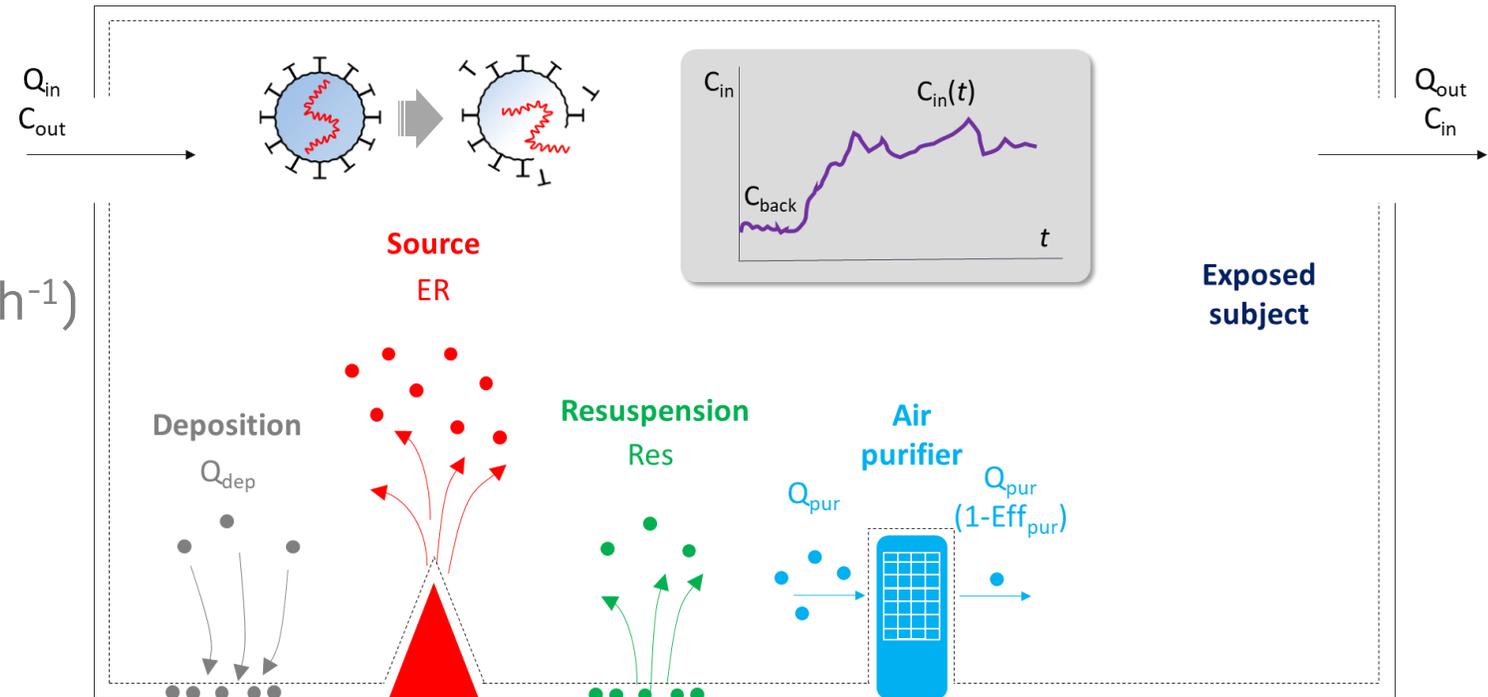
$$C_{in}(t) = C_{back} \cdot e^{-(AER \cdot P + k + ACH \cdot Eff_{pur}) \cdot t} + \frac{C_{out} \cdot AER \cdot P}{AER \cdot P + k + ACH \cdot Eff_{pur}} \left( 1 - e^{-(AER \cdot P + k + ACH \cdot Eff_{pur}) \cdot t} \right) + \frac{ER + Res}{V \cdot (AER \cdot P + k + ACH \cdot Eff_{pur})} \left( 1 - e^{-(AER \cdot P + k + ACH \cdot Eff_{pur}) \cdot t} \right)$$

$-(AER \cdot P + k + ACH \cdot Eff_{pur}) \cdot t =$  "removal rate"

# Estimating the exposure in indoor environment

## Well-mixed simplified approach

- Deposition
- Resuspension
- Removal through air purifier
- Viral inactivation - for viruses,  $\lambda$  ( $\text{h}^{-1}$ )



$$C_{in}(t) = C_{back} \cdot e^{-(AER \cdot P + k + ACH \cdot Eff_{pur} + \lambda) \cdot t} + \frac{C_{out} \cdot AER \cdot P}{AER \cdot P + k + ACH \cdot Eff_{pur} + \lambda} \left( 1 - e^{-(AER \cdot P + k + ACH \cdot Eff_{pur} + \lambda) \cdot t} \right) + \frac{ER + Res}{V \cdot (AER \cdot P + k + ACH \cdot Eff_{pur} + \lambda)} \left( 1 - e^{-(AER \cdot P + k + ACH \cdot Eff_{pur} + \lambda) \cdot t} \right)$$

$\lambda = \text{viral inactivation rate } (\text{h}^{-1})$

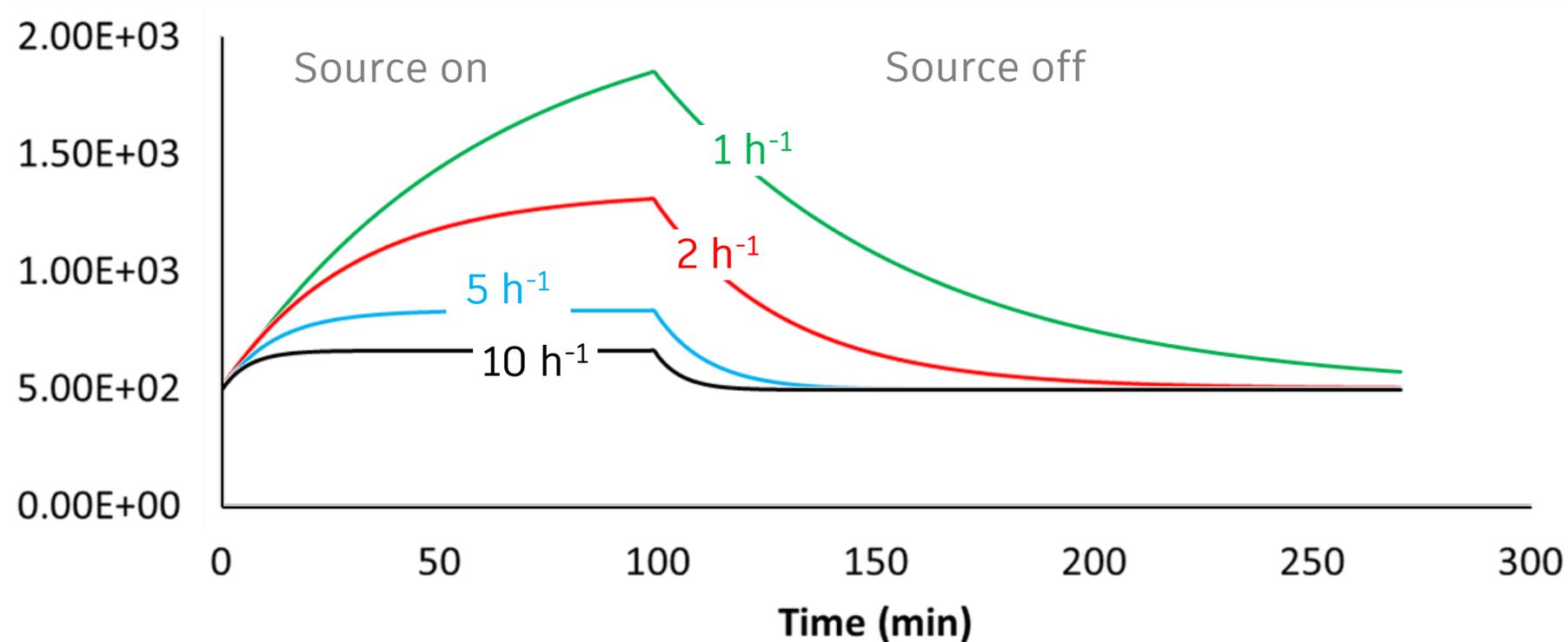
$-(AER \cdot P + k + ACH \cdot Eff_{pur} + \lambda) \cdot t = \text{"removal rate"}$

# Estimating the emission factor/emission rate

## Quantifying the emission of indoor sources

Mass balance approach

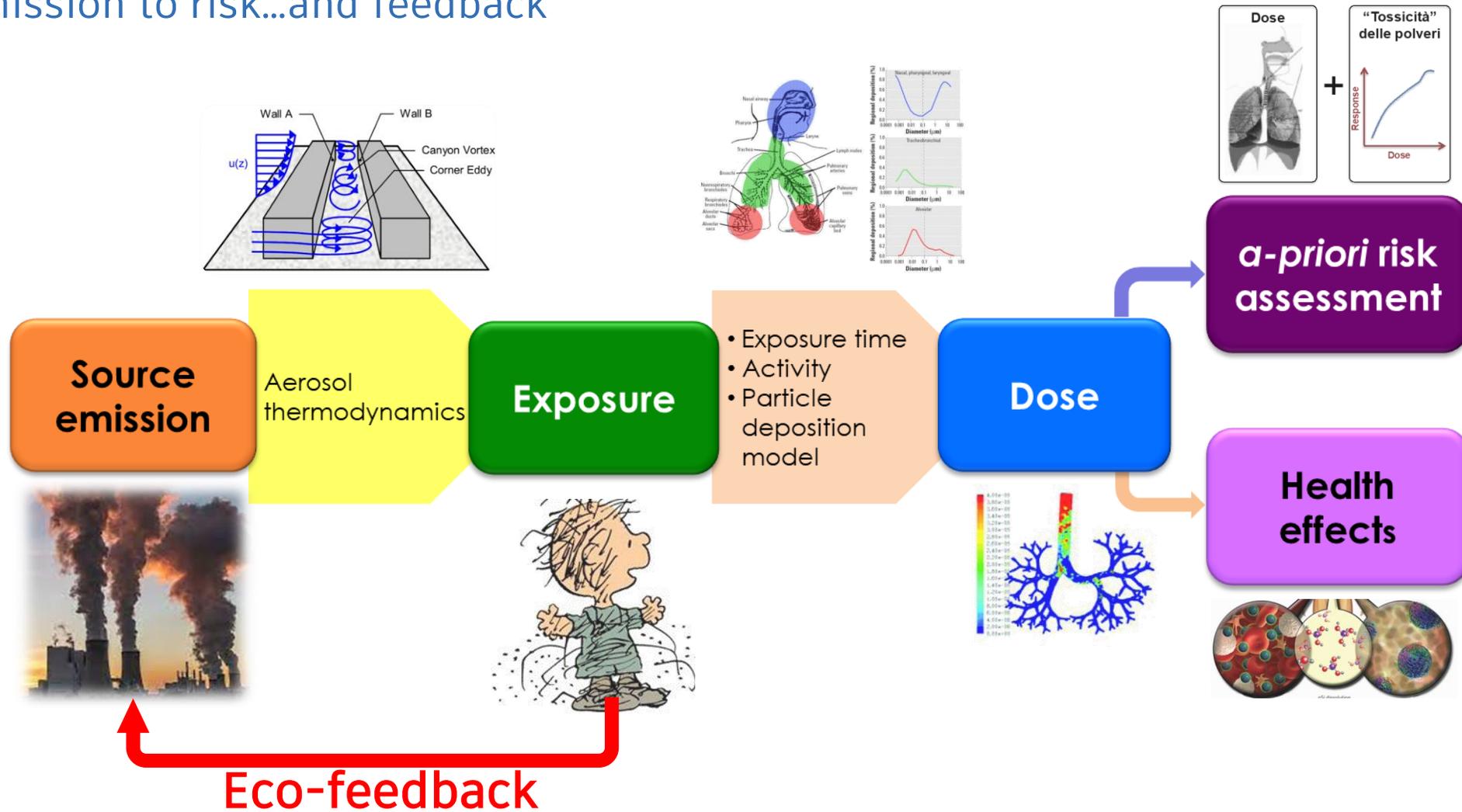
- Emission rate (emission per unit time)
- Emission factor (emission per unit mass, quantity...)



# Research at UNICAS

# Research studies

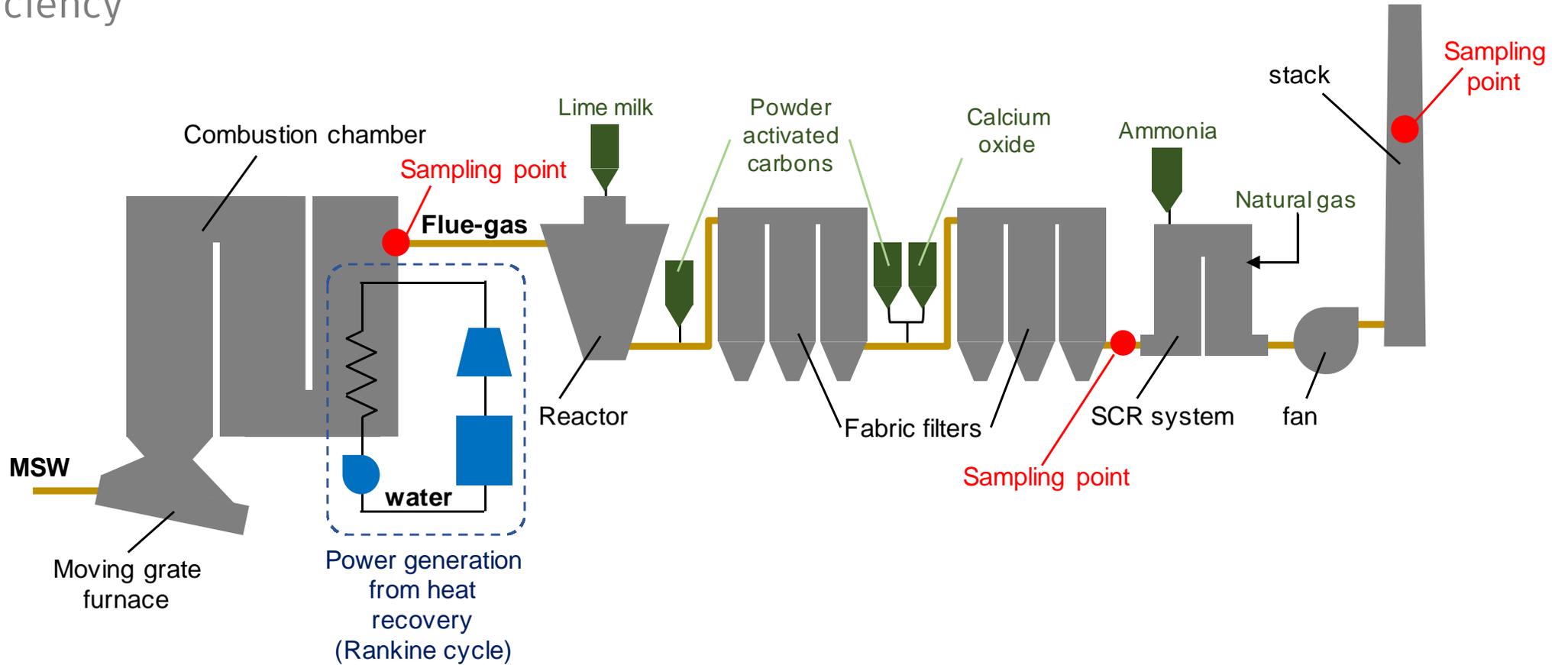
From emission to risk...and feedback



# Outdoor sources

## Incinerator plants

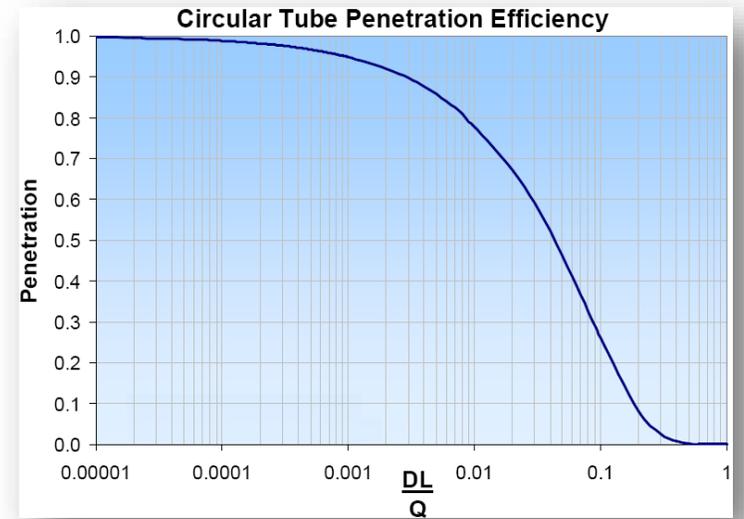
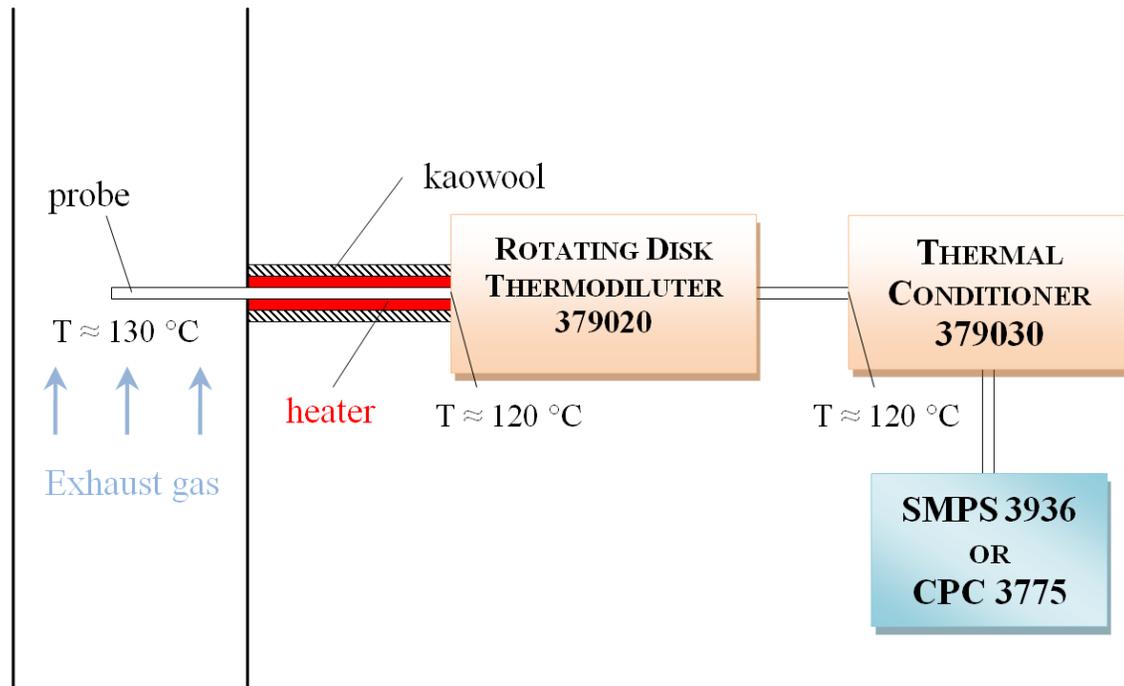
- At the stack
- Filter efficiency



# Outdoor sources

## Incinerator plants

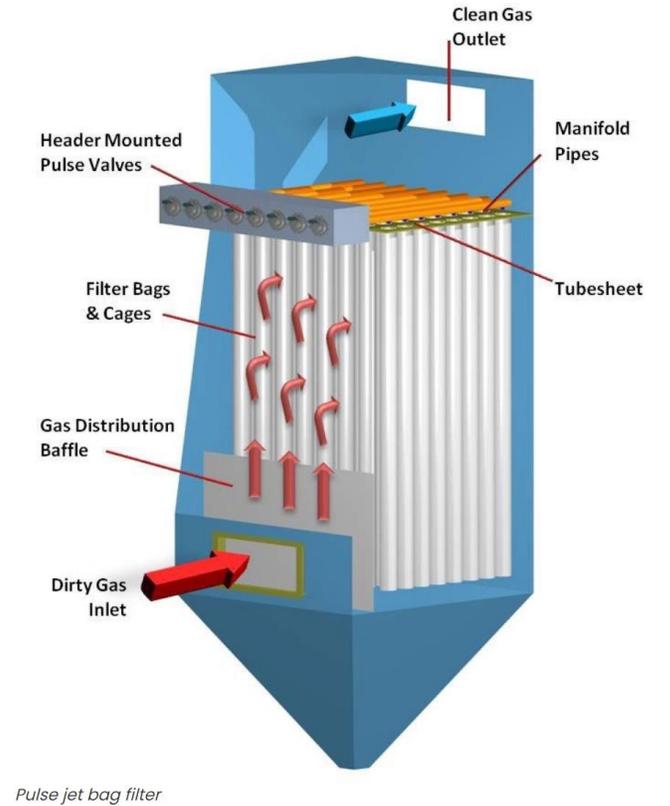
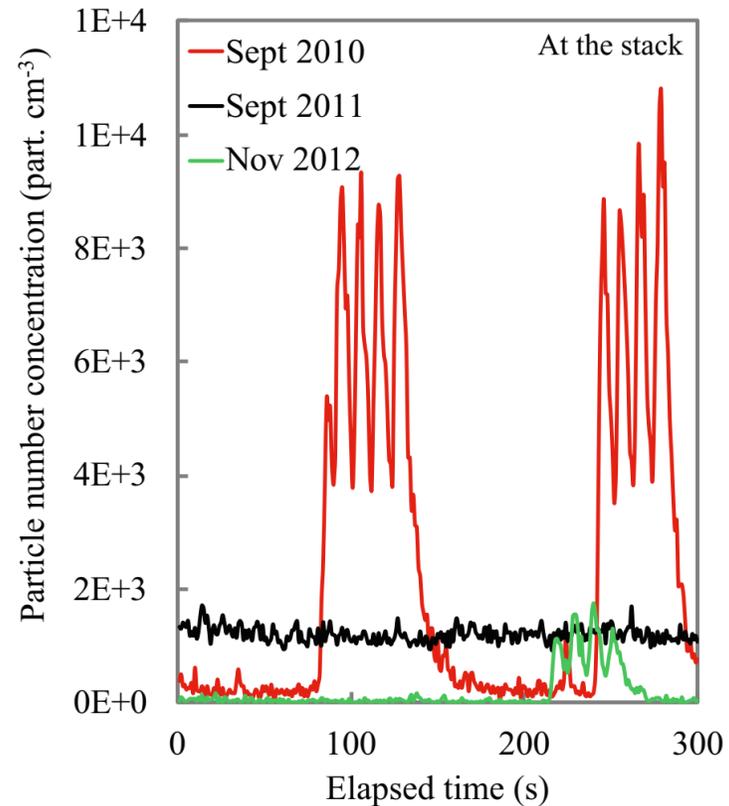
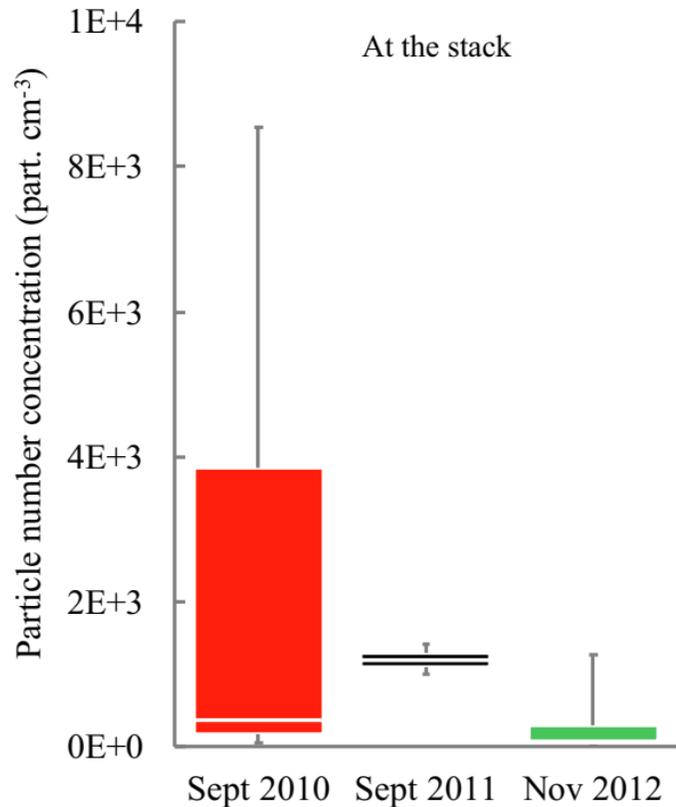
- Thermodilution
- Measurement artifacts



# Outdoor sources

## Incinerator plants

### Results



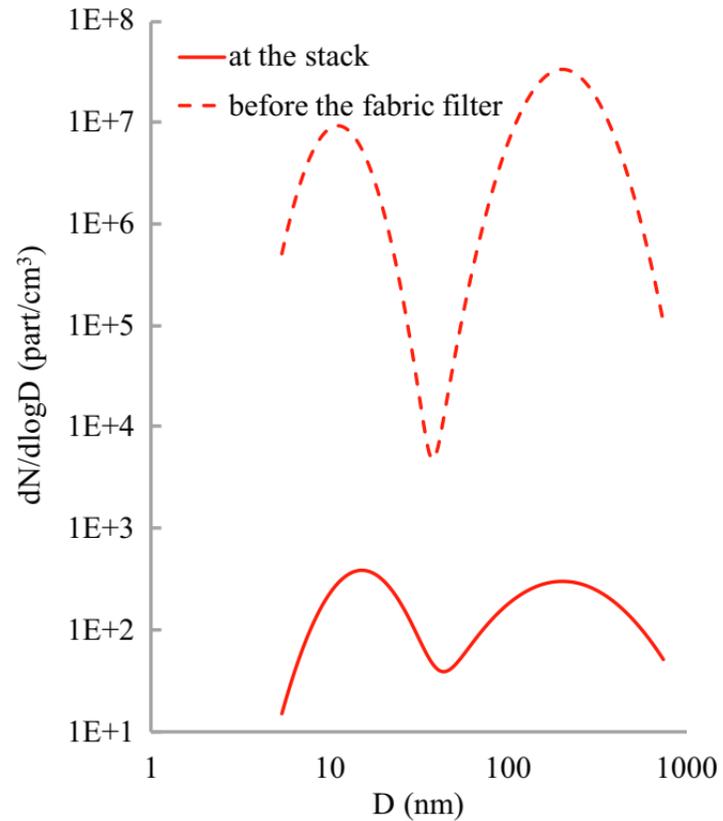
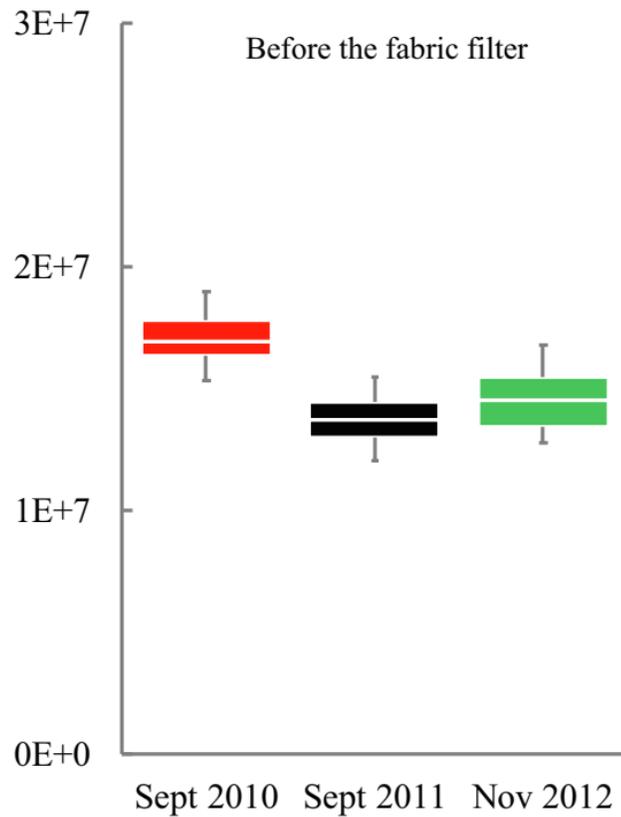
Plant equipped with Electrostatic filters:  $3.0 \times 10^5$  part. cm<sup>-3</sup>.

# Outdoor sources

## Incinerator plants

### Results

- Fabric filter efficiency for UFPs > 99.99%;



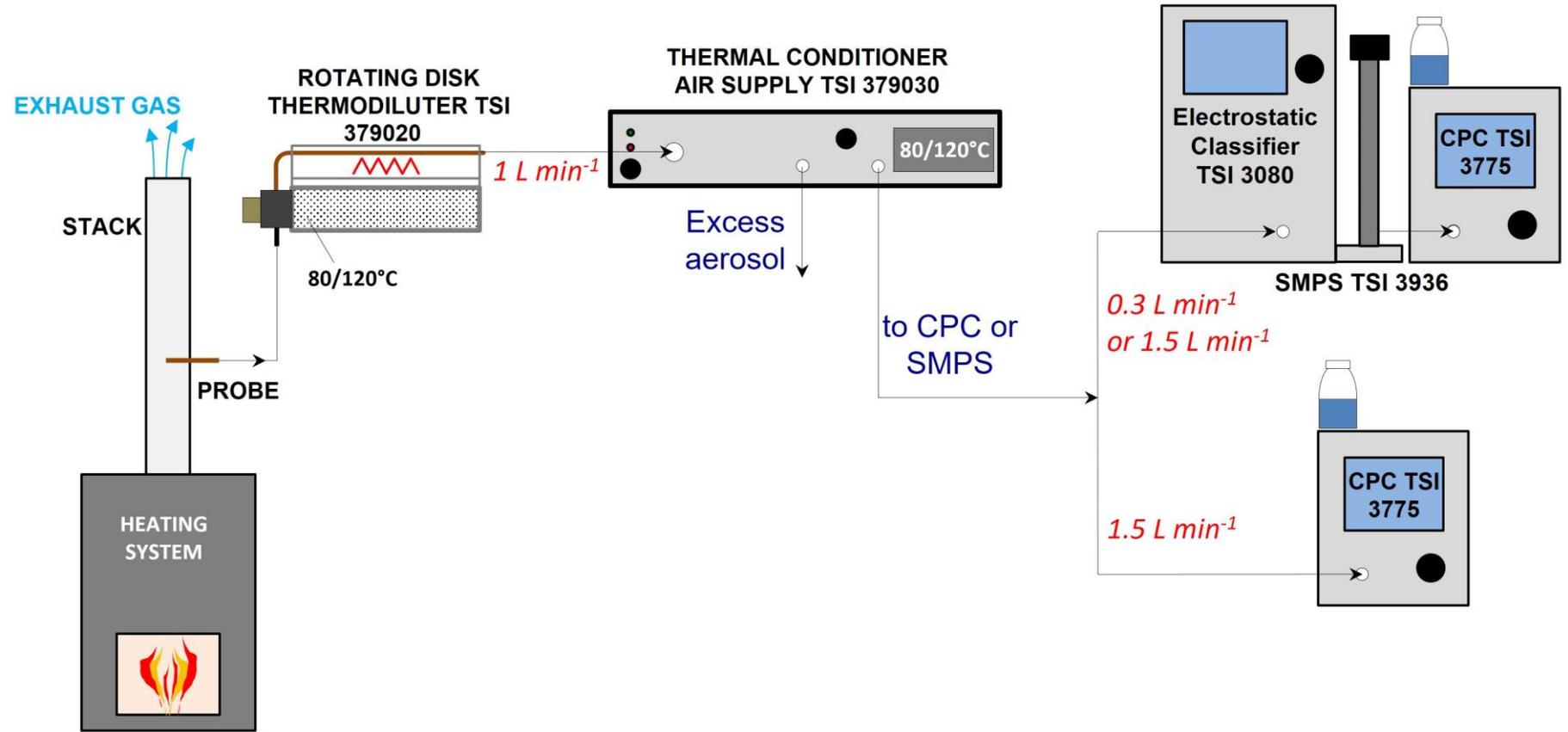
# Outdoor sources

## Thermal plants for residential heating

Boilers (LPG and methane)

Condensing Boilers (LPG and methane)

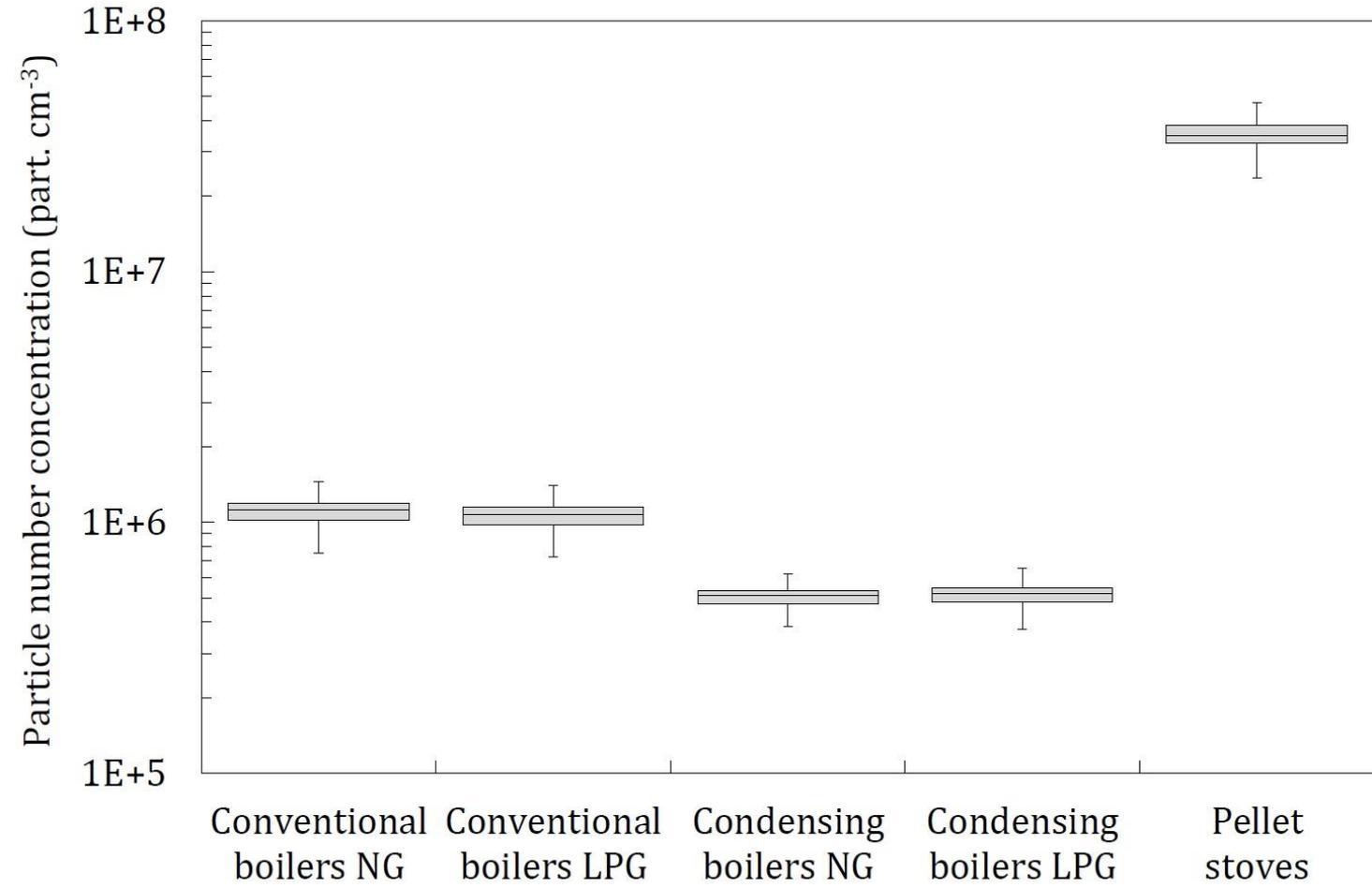
Pellet Stoves



# Outdoor sources

## Thermal plants for residential heating

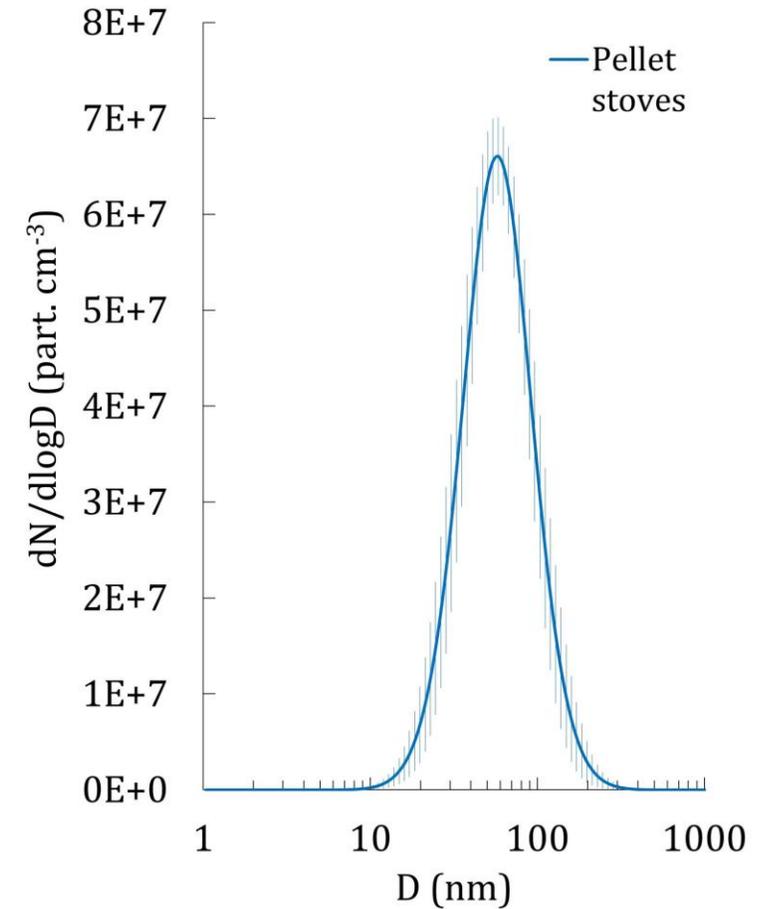
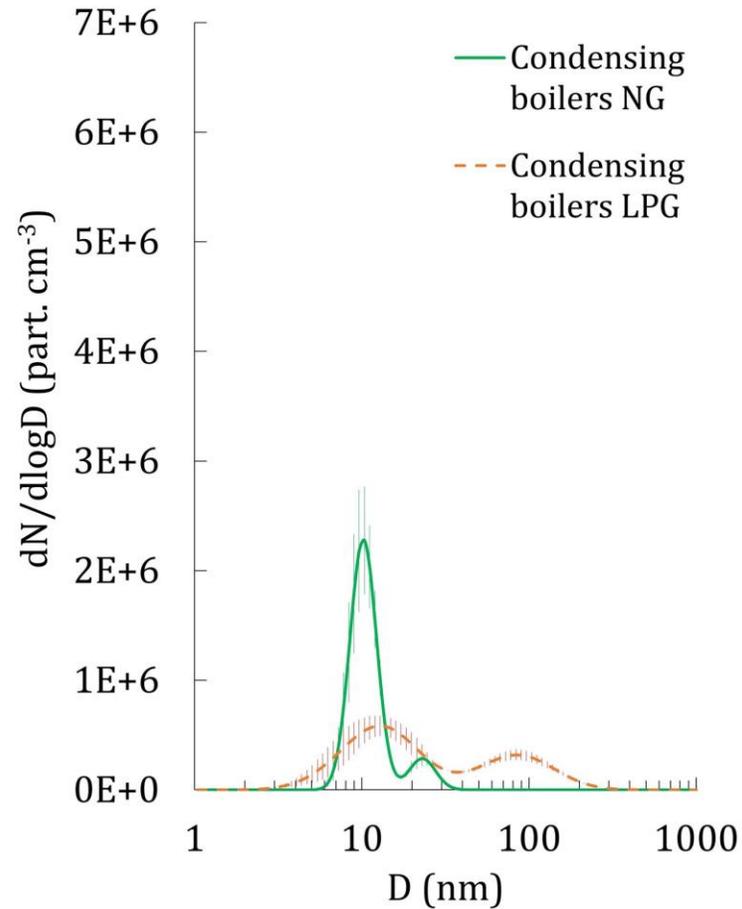
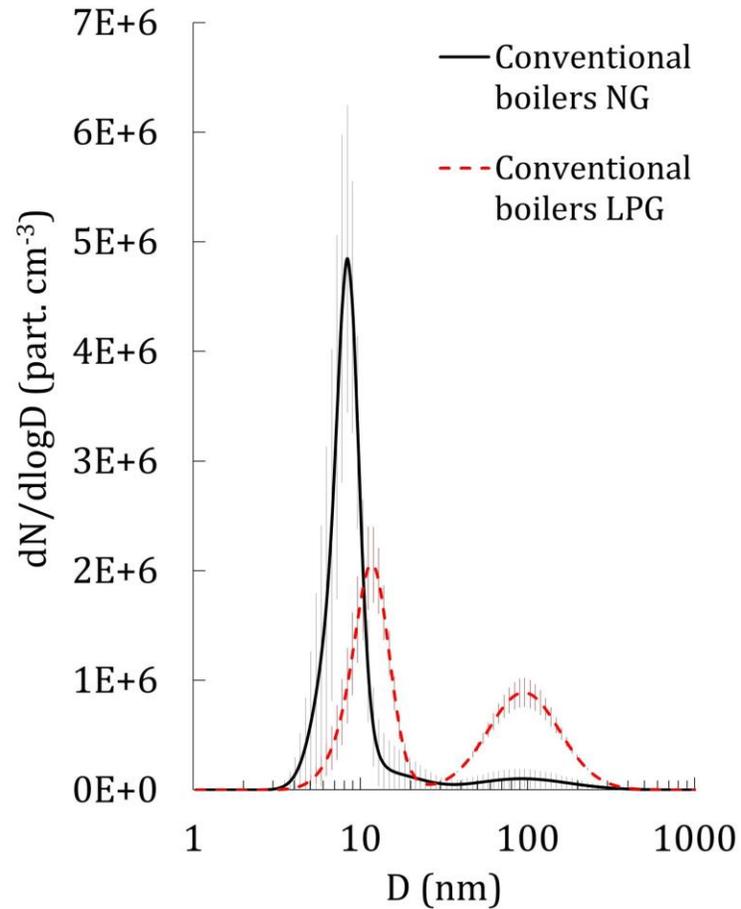
### Concentrations



# Outdoor sources

## Thermal plants for residential heating

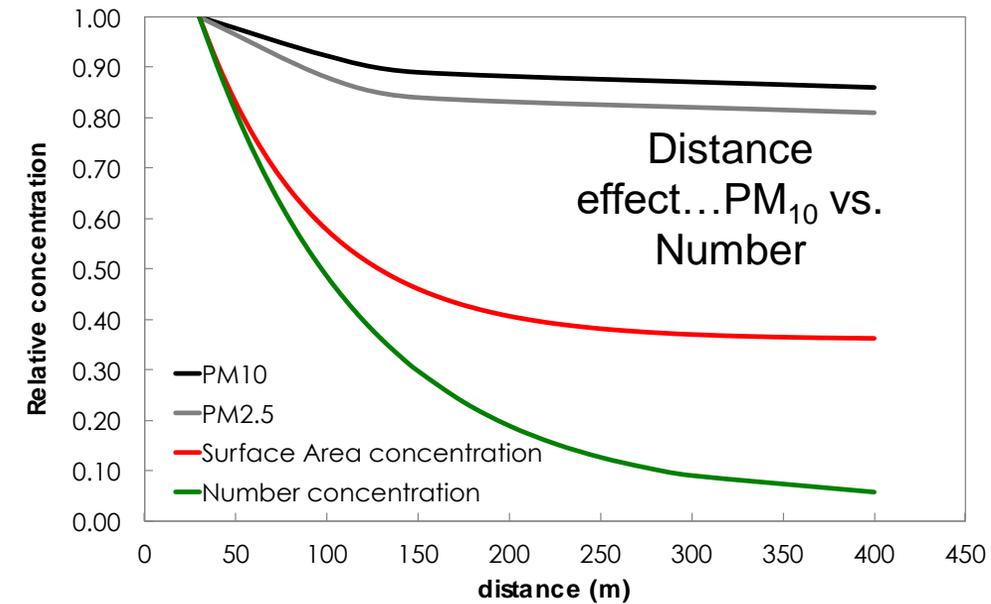
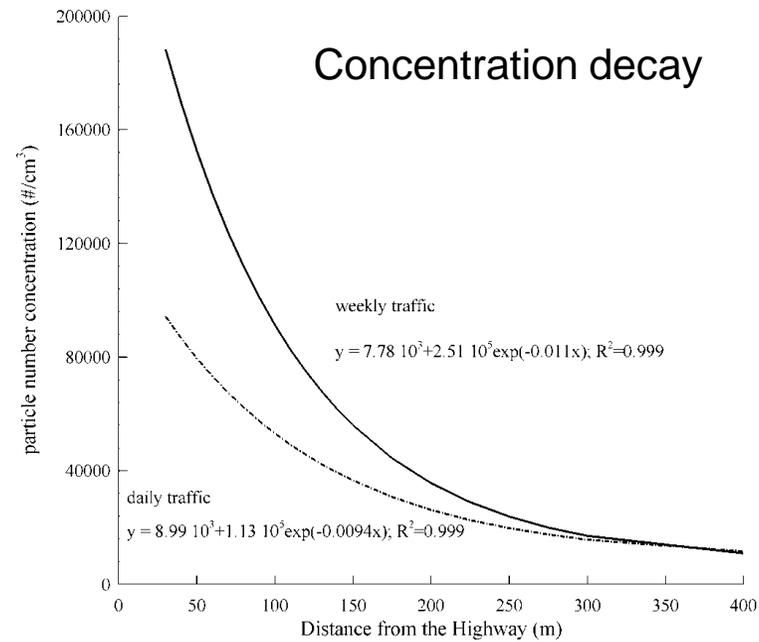
### Distributions



# Aerosol Thermodynamics: particle dispersion

## Highway

- Emission
- Dilution

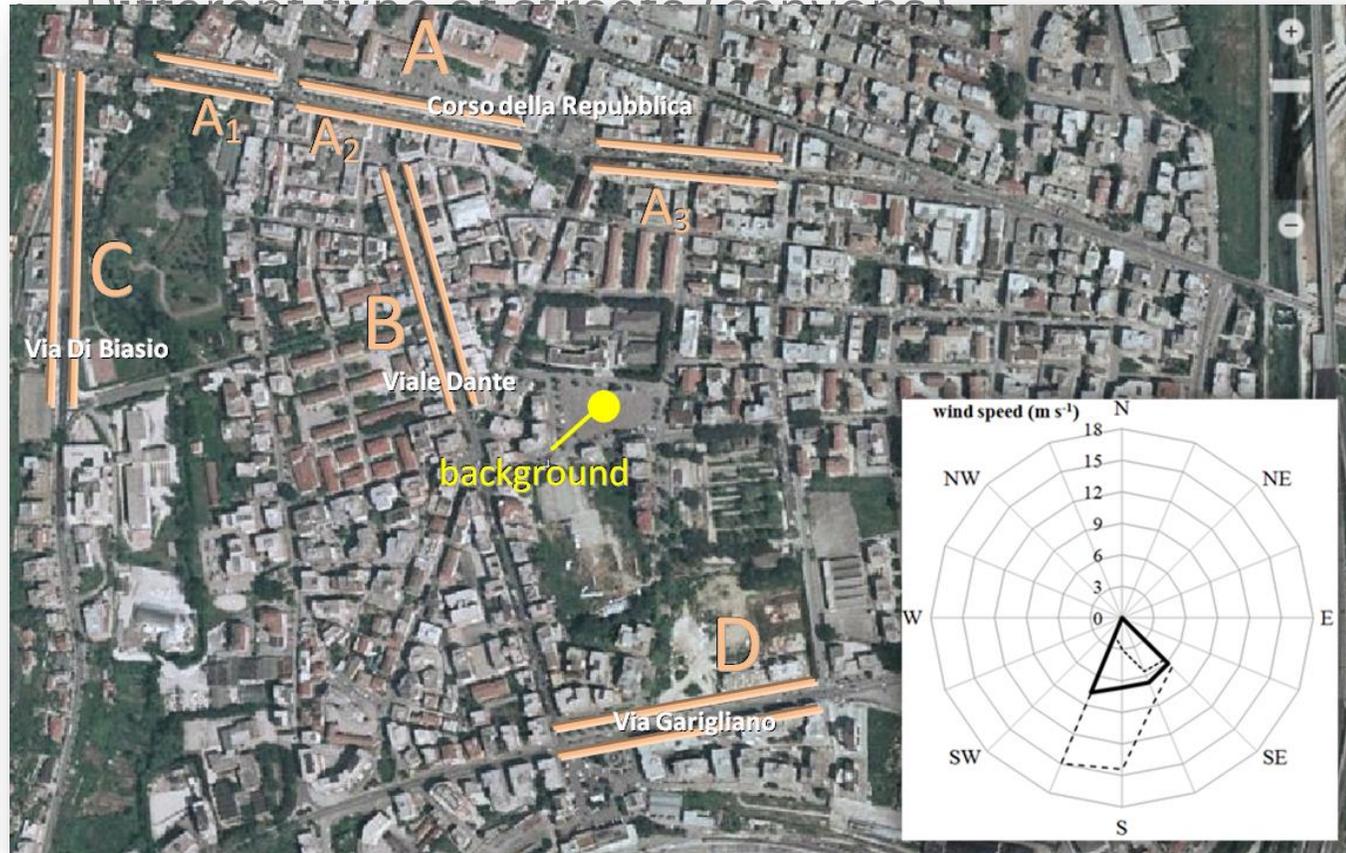


# Aerosol Thermodynamics: particle dispersion

## Urban areas

- Mobile platform to measure concentrations and distributions

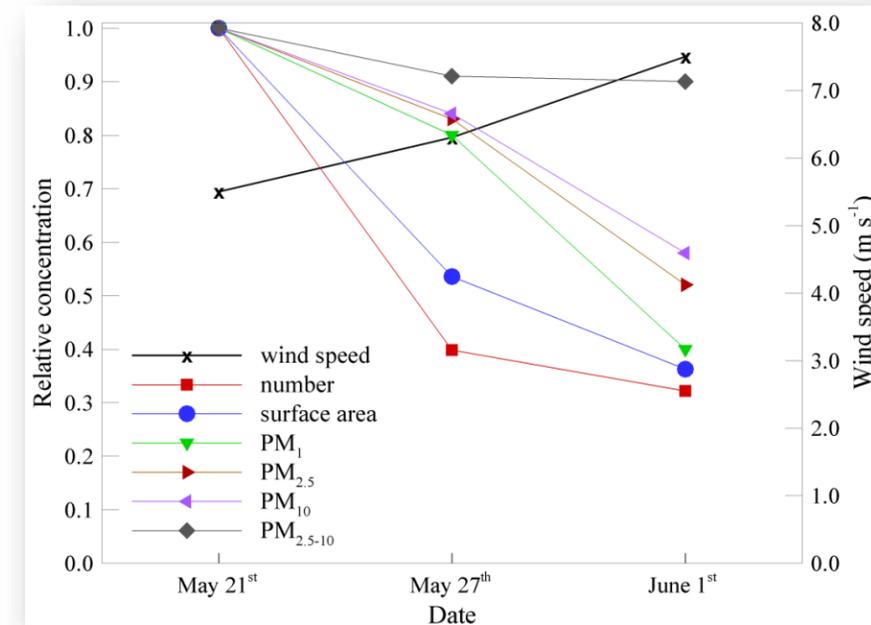
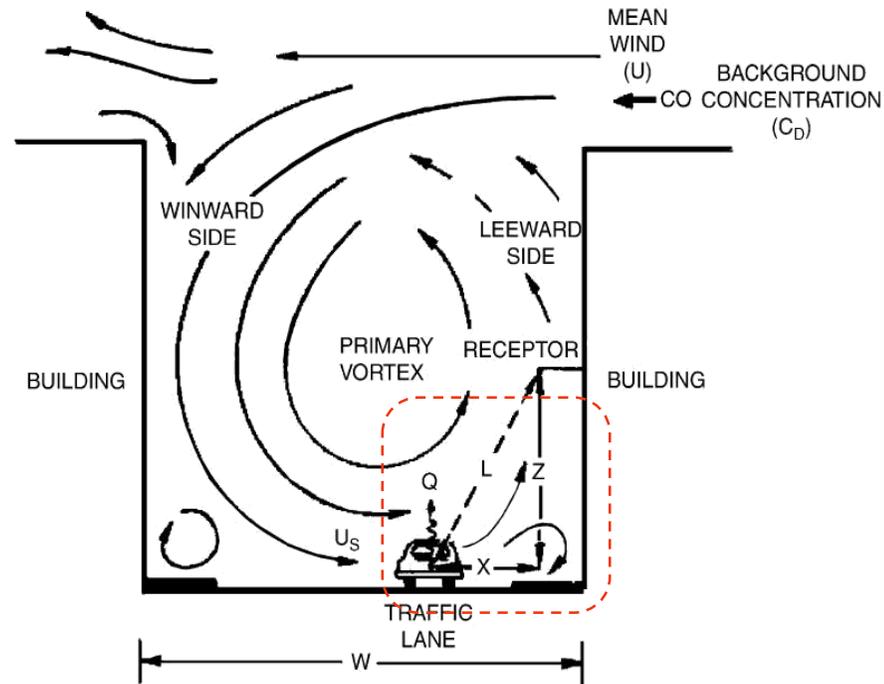
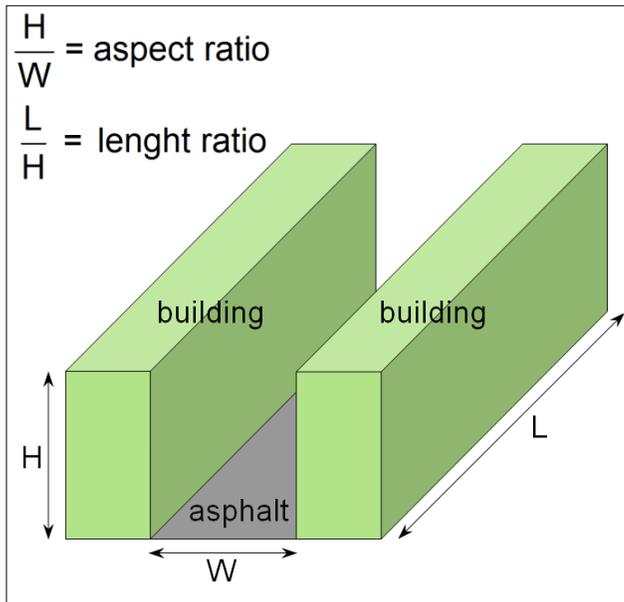
Different types of streets (geometry)



# Aerosol Thermodynamics: particle dispersion

## Urban areas

- Street canyon

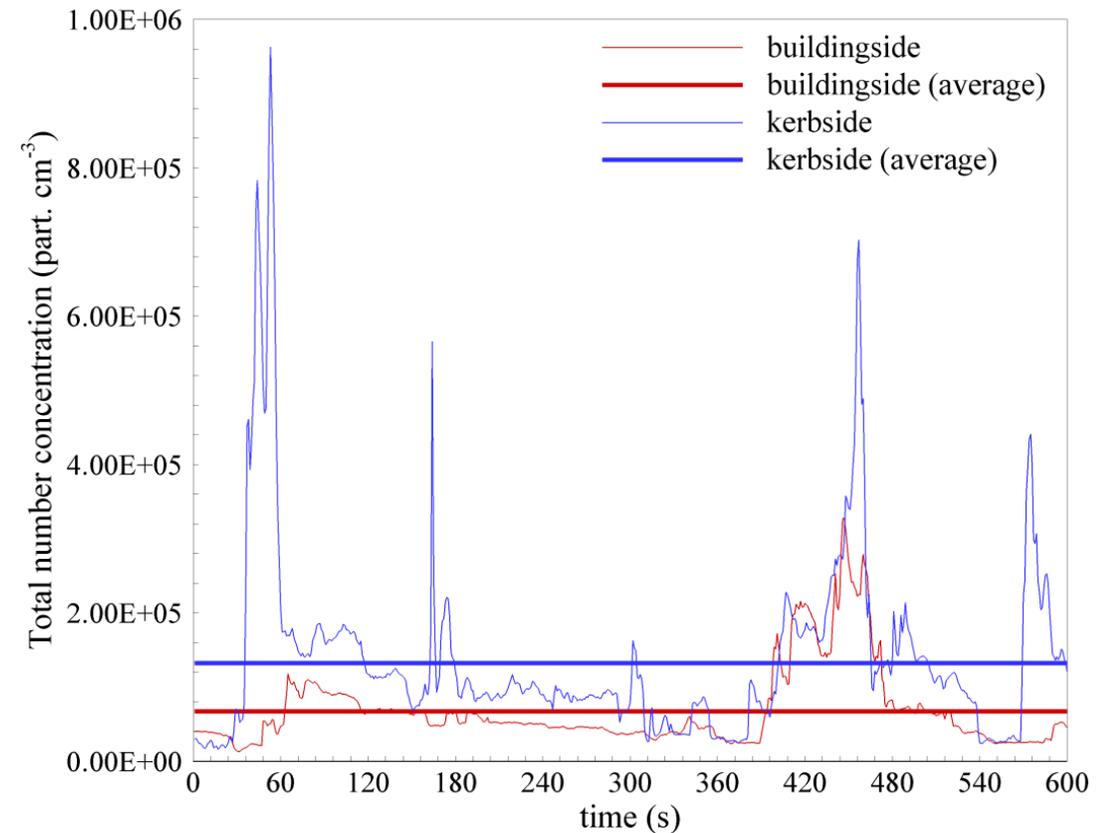
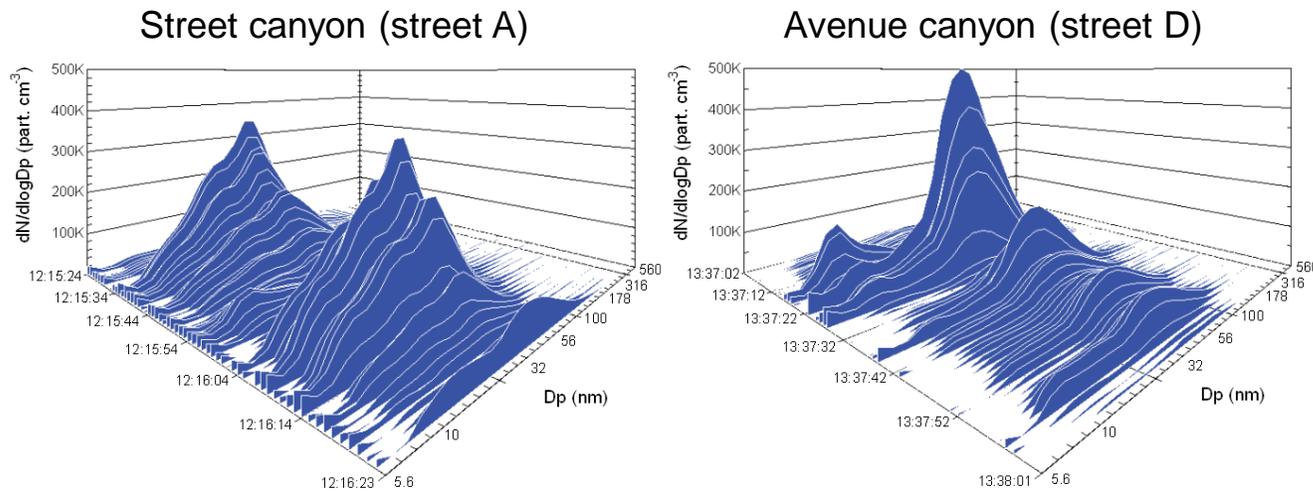


# Aerosol Thermodynamics: particle dispersion

## Urban areas

- canyon effect
- Proximity effect
- Concentration gradient of UFPs

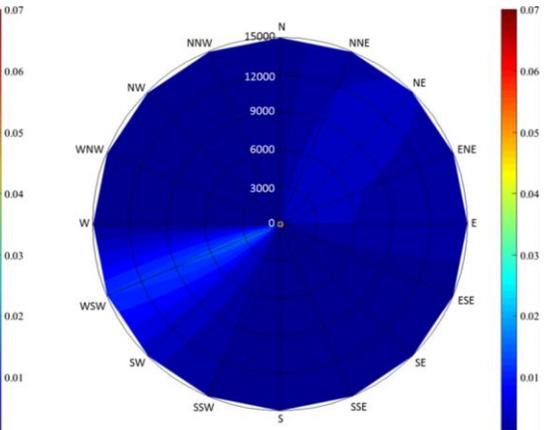
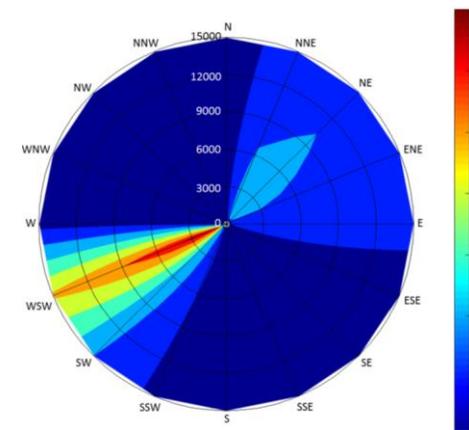
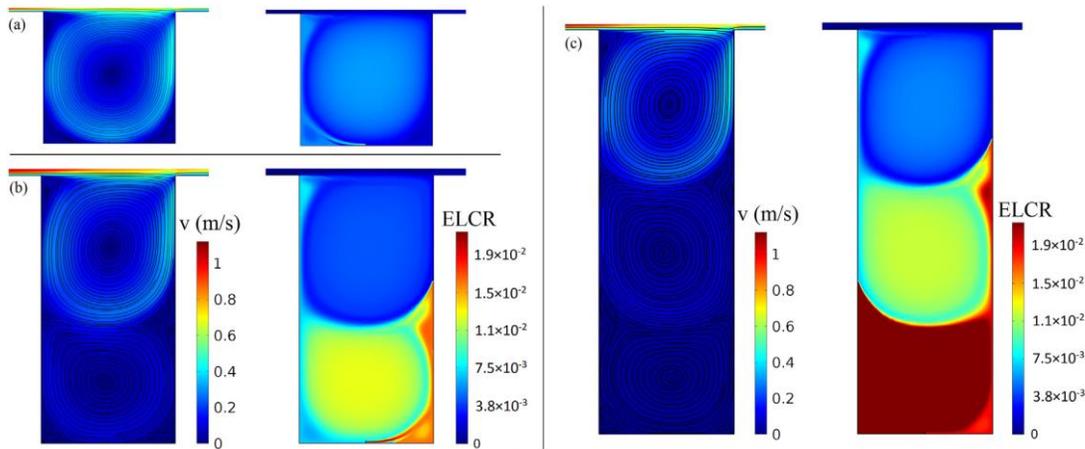
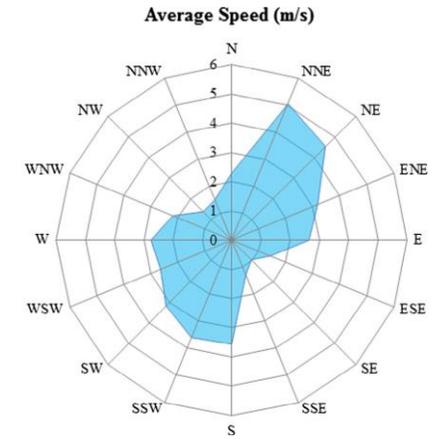
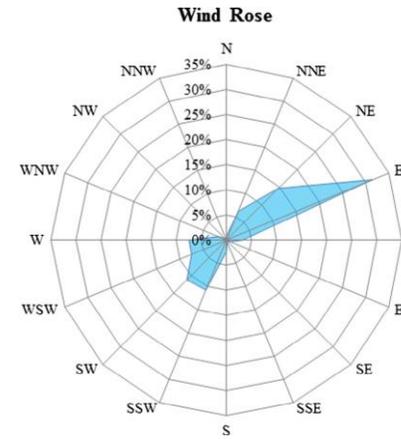
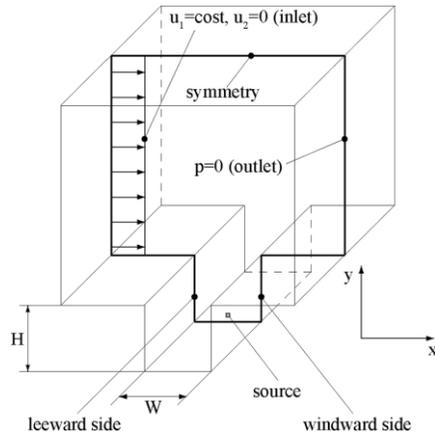
Dilution phenomena: street vs. avenue canyon.



# Aerosol Thermodynamics: particle dispersion

## CFD studies

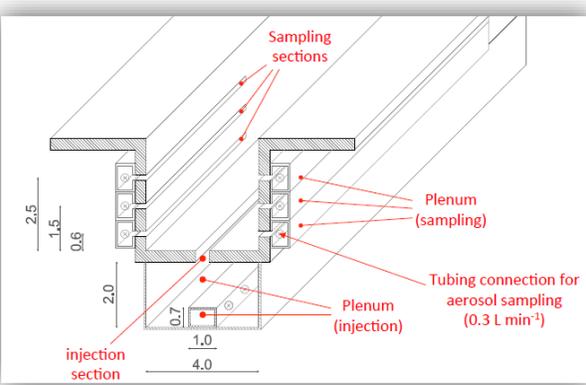
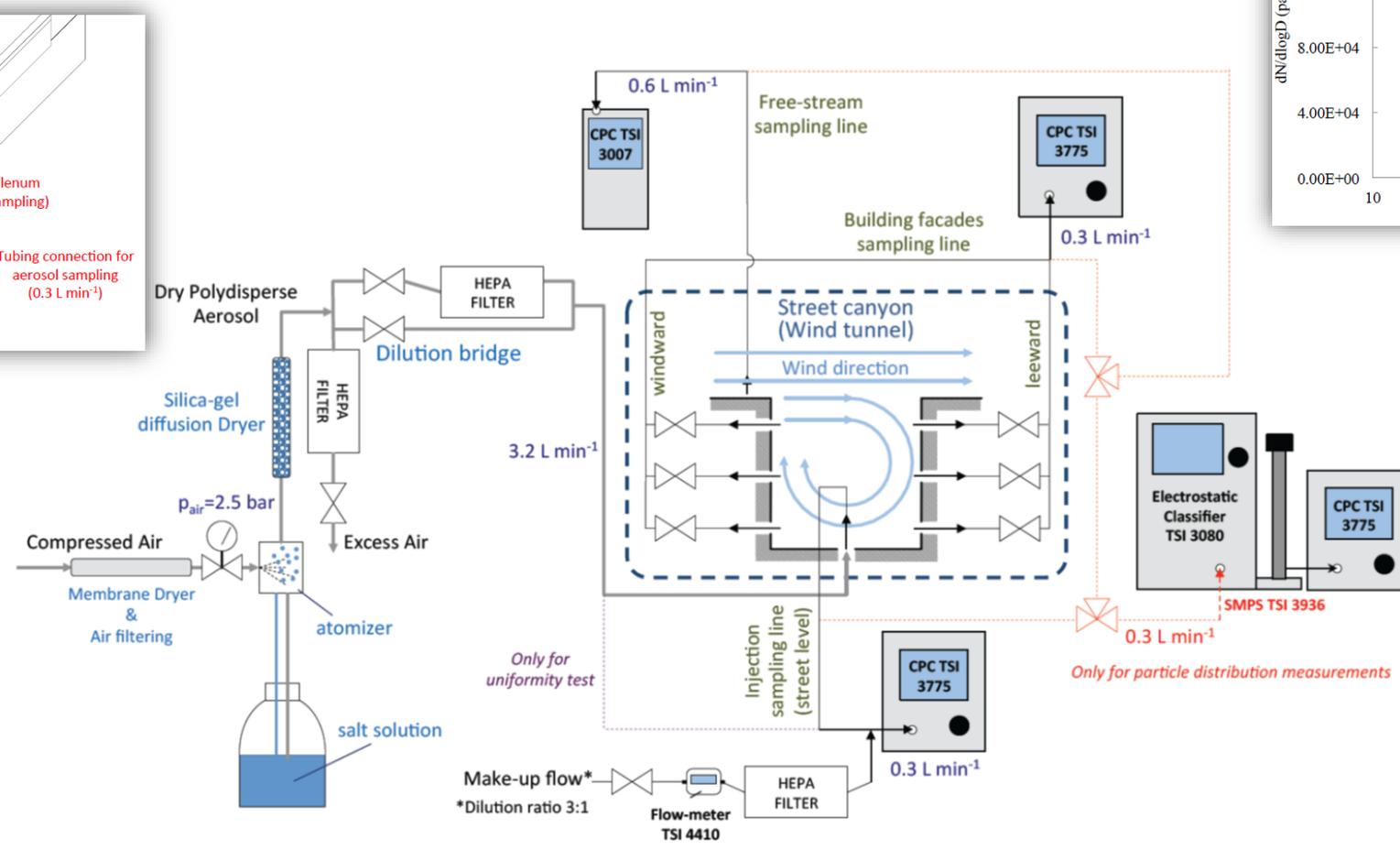
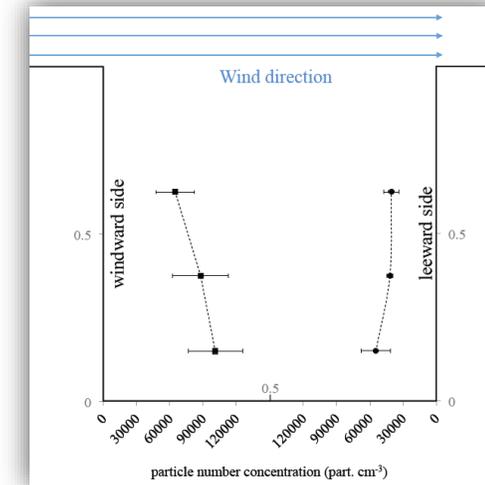
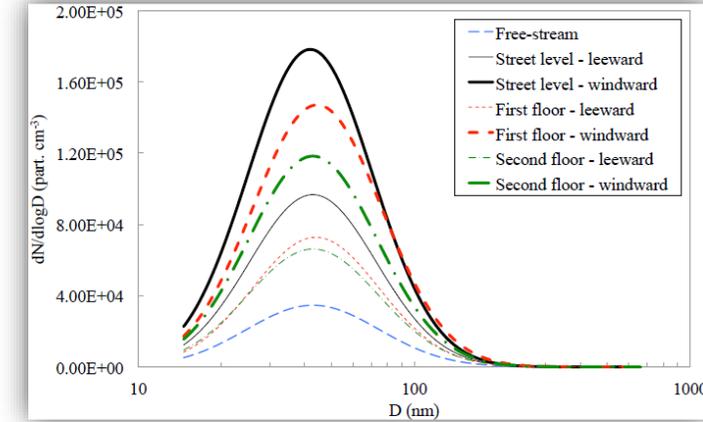
CFD analysis of particle dispersion in street-canyons...and industrial areas



# Aerosol Thermodynamics: particle dispersion

## Validation of CFD models

- Wind tunnel & particle concentration measurements



# Indoor sources

## Cooking activities

Concentrations and distribution

Different cooking activities

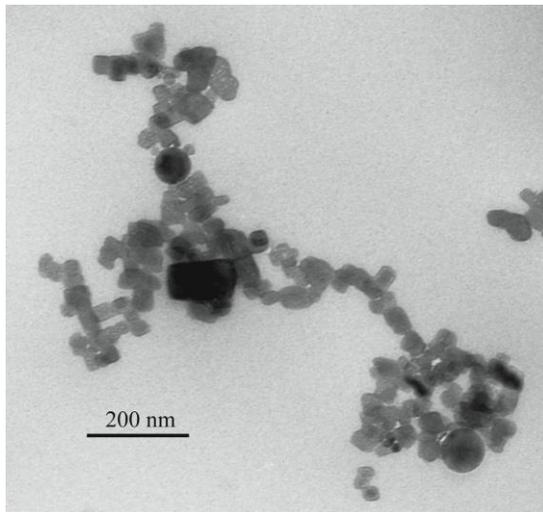
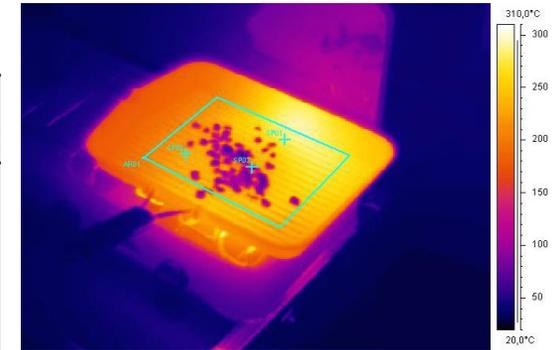
Different types of food

## Emission rate

Volatility analysis

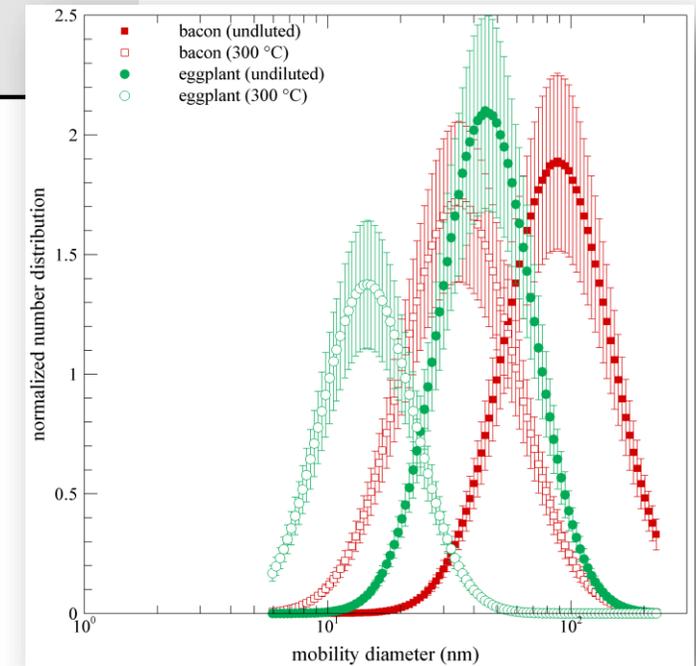
Summary of the emission factors for generated using a gas stove at maximum power for the frying of 50 g of chips: emission factor (EF), peak value (PV) and mode diameter (MD) for number ( $N$ ), surface area ( $S$ ) and mass ( $M$ ).

	Olive oil	Peanut oil	Sunflower oil (specific for frying)
NEF (part. min <sup>-1</sup> )	$1.8 \times 10^{12}$	$2.3 \times 10^{12}$	$1.1 \times 10^{12}$
SEF ( $\mu\text{m}^2 \text{min}^{-1}$ )	$2.5 \times 10^5$	$1.6 \times 10^5$	$1.2 \times 10^5$
MEF ( $\mu\text{g min}^{-1}$ )	$2.8 \times 10^3$	$1.8 \times 10^3$	$1.2 \times 10^3$
NPV (part. cm <sup>-3</sup> )	$1.2 \times 10^5$	$1.2 \times 10^5$	$1.1 \times 10^5$
SPV ( $\text{nm}^2 \text{cm}^{-3}$ )	$1.1 \times 10^{10}$	$6.8 \times 10^9$	$6.0 \times 10^9$
MPV ( $\mu\text{g m}^{-3}$ )	118	68	60
NMD (nm)	61.5	49.6	49.6
Geometric standard deviation (nm)	1.91	1.82	1.80



Summary of the size distribution of aerosols generated using a gas stove at maximum power when grilling cheese, wurstel (pork meat), bacon and eggplants (vegetable). Emission factor (EF), peak value (PV) and mode diameter (MD) for number ( $N$ ), surface area ( $S$ ) and mass ( $M$ ).

	Cheese	Wurstel	Bacon	Eggplants
NEF (part. min <sup>-1</sup> )	$3.4 \times 10^{12}$	$3.1 \times 10^{12}$	$2.8 \times 10^{12}$	$2.6 \times 10^{12}$
SEF ( $\mu\text{m}^2 \text{min}^{-1}$ )	$1.6 \times 10^5$	$1.8 \times 10^5$	$2.3 \times 10^5$	$4.8 \times 10^4$
MEF ( $\mu\text{g min}^{-1}$ )	$9.5 \times 10^3$	$1.0 \times 10^4$	$1.2 \times 10^4$	$5.2 \times 10^2$
NPV (part. cm <sup>-3</sup> )	$1.1 \times 10^5$	$1.3 \times 10^5$	$1.0 \times 10^5$	$1.2 \times 10^5$
SPV ( $\text{nm}^2 \text{cm}^{-3}$ )	$4.6 \times 10^9$	$5.8 \times 10^9$	$9.8 \times 10^9$	$2.8 \times 10^9$
MPV ( $\mu\text{g m}^{-3}$ )	283	352	389	78
NMD (nm)	41	43	49	29



# Indoor sources

## Other indoor sources

Incenses/candles

Printers

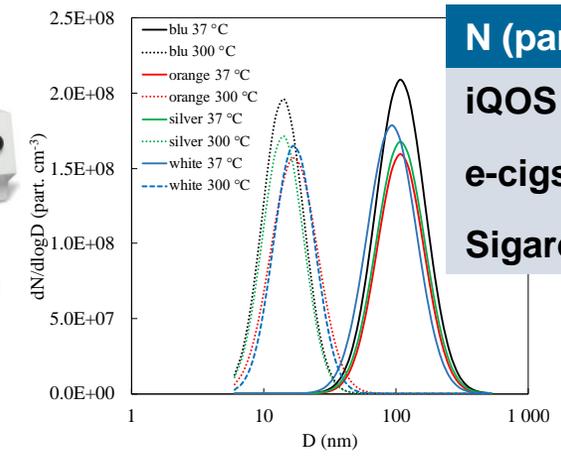
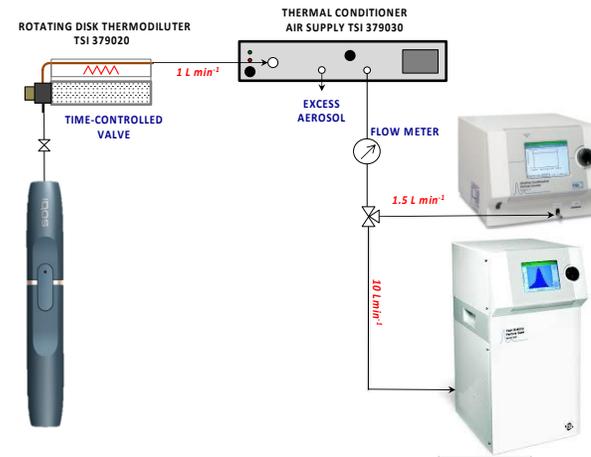
3D printers

Cigarettes & Co.

### Incense, candle

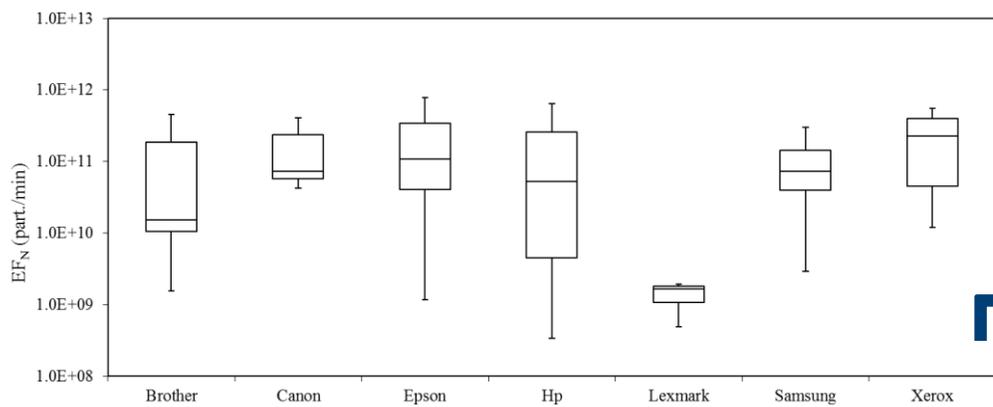
Source	$N$ (part $h^{-1}$ )
Average	
I1	$7.74 \times 10^{14}$
I2	$4.54 \times 10^{14}$
I3	$1.08 \times 10^{15}$
C1	$4.85 \times 10^{13}$
C2	$4.07 \times 10^{13}$
M1	$4.57 \times 10^{14}$
M2	$2.92 \times 10^{14}$

### cigarette, e-cigs, IQOS cigs

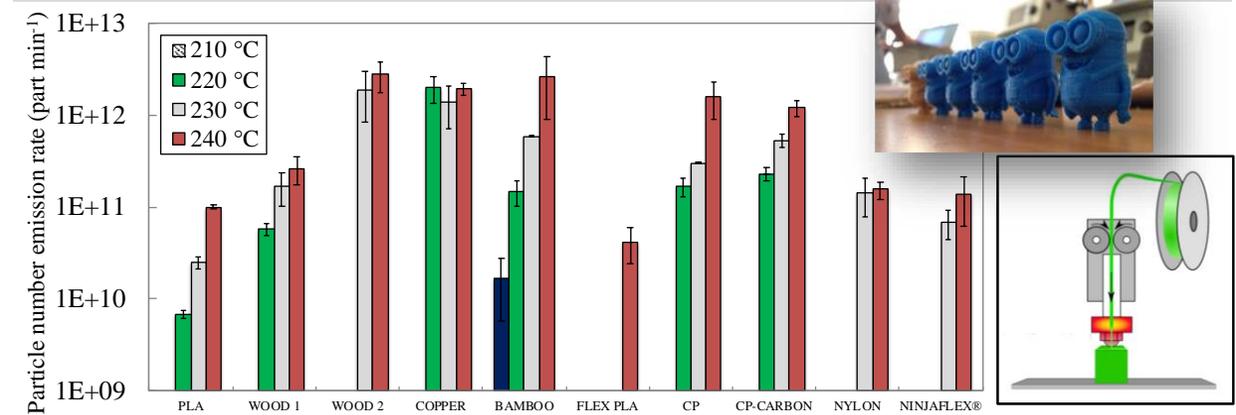


**$N$  (part.  $cm^{-3}$ )**  
**iQOS  $<1 \times 10^8$**   
**e-cigs =  $10^8 - 10^9$**   
**Sigarette  $<10^9$**

### printers



### 3D printers (material, temperature effect)



# Indoor sources

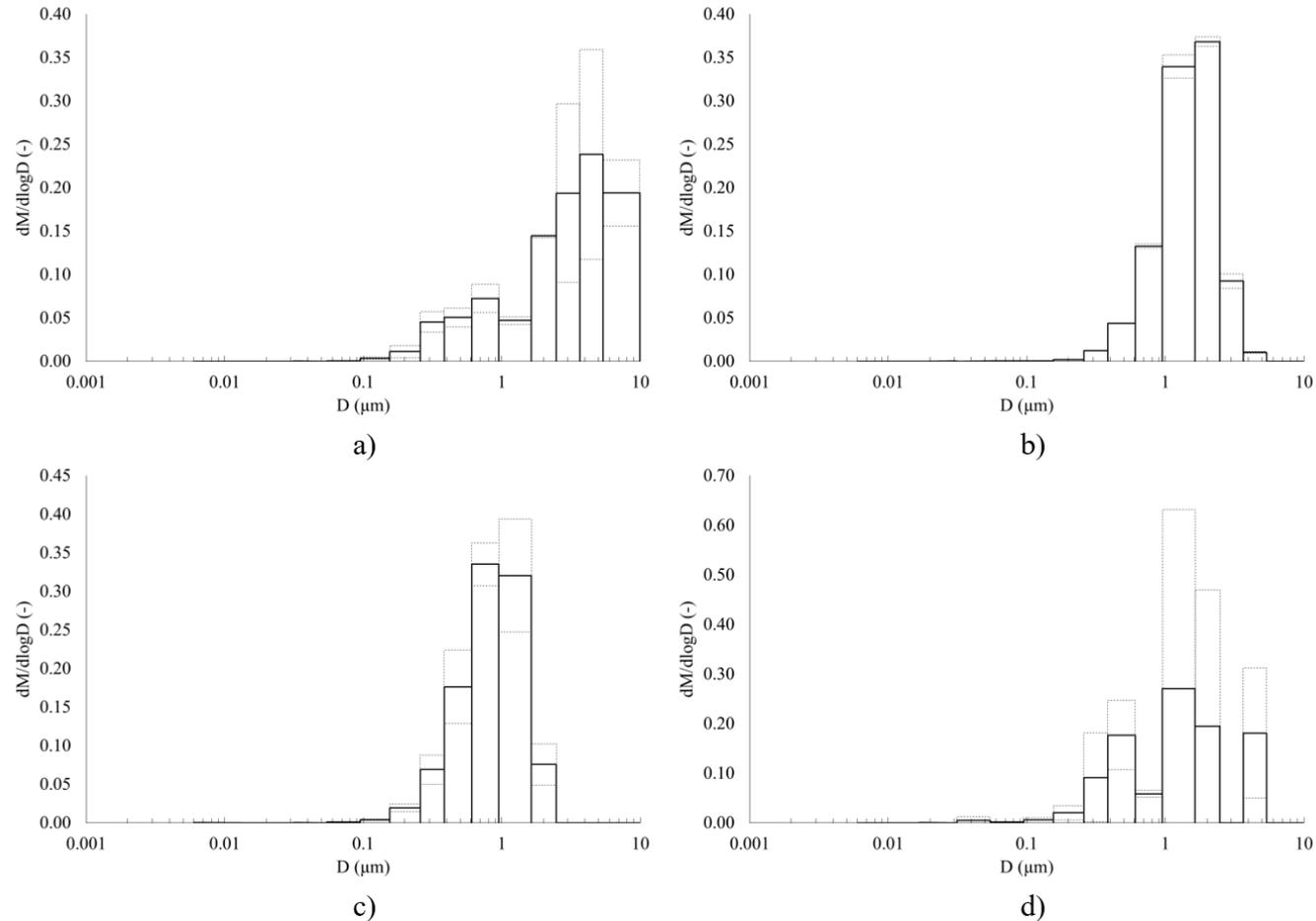
## Size-resolved chemical analysis of freshly emitted particles

Incenses

candles

Mosquito coils

Cooking activities



**Figure 1** – Particle mass distributions, normalized to the total concentration, measured during combustion of candles (a), incenses (b), mosquito coils (c), and grilling bacon (d) through the ELPI+™: solid lines represent average distributions, dashed lines represent standard deviations of the measured distributions.

# Indoor sources

## Size-resolved chemical analysis of freshly emitted particles

Incenses

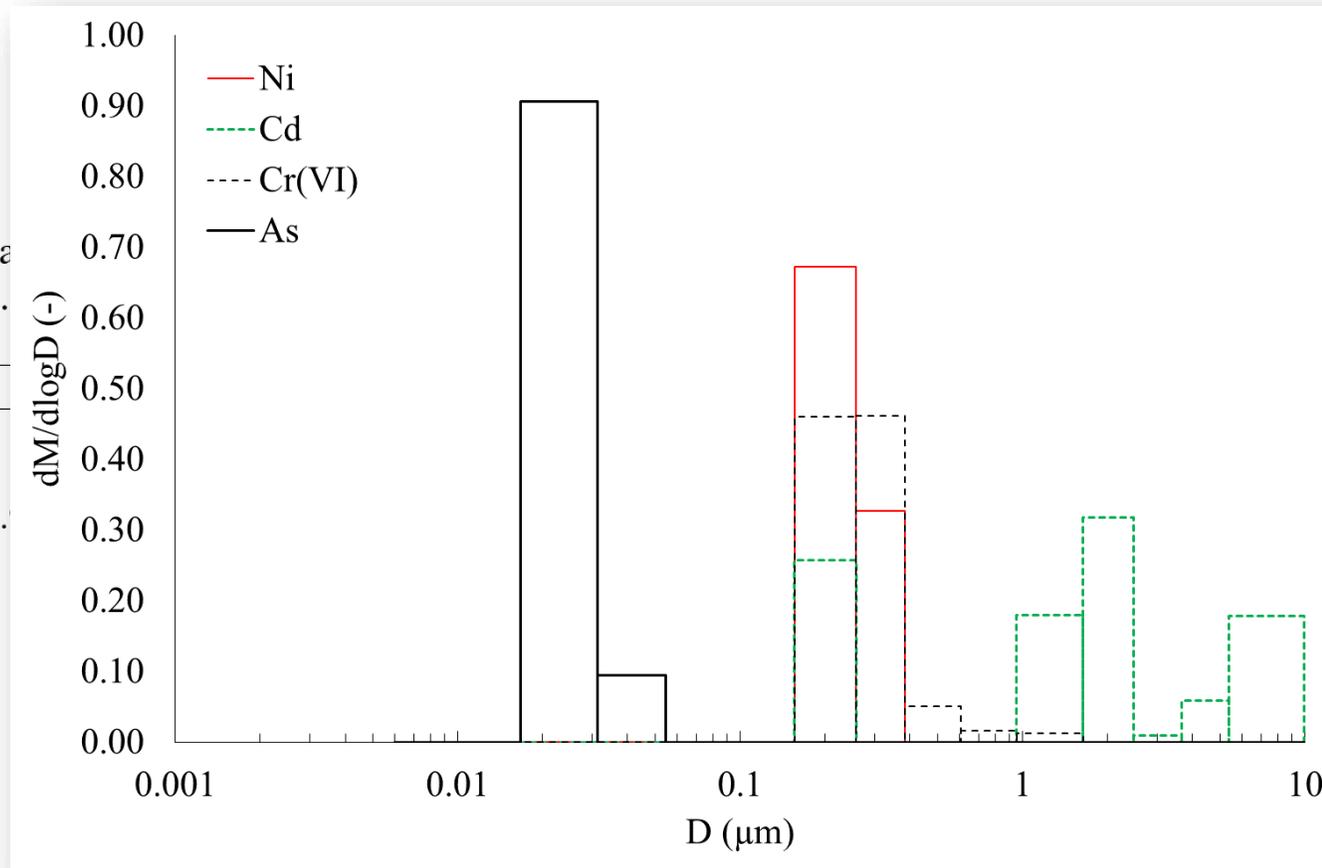
candles

Mosquito coils

Cooking activities

**Table 5** – Mass fractions of trace metals under investigation.

Source
<u>Candles</u>
<u>Incenses</u>
<u>Mosquito coils</u>



Other indoor sources  
Trace metals are

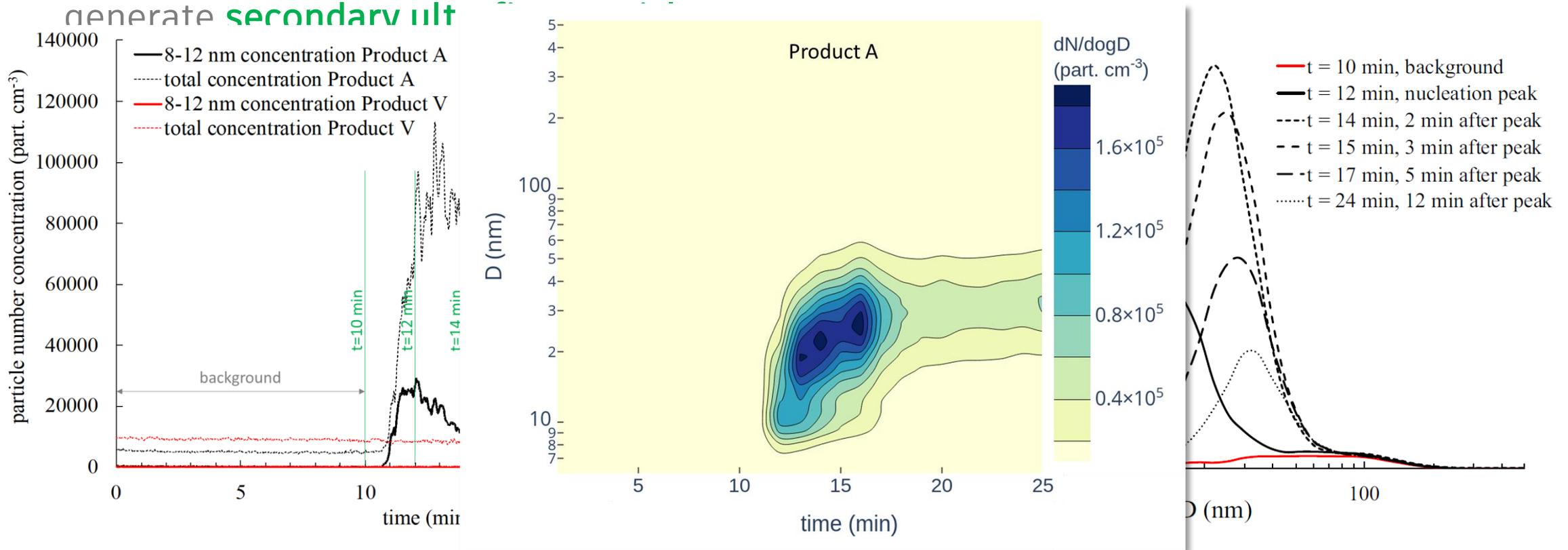
Source	Mn
Candles	$4.96 \times 10^{-7}$
Incenses	$< 10^{-5}$
Mosquito coils	$< 10^{-5}$

# Indoor sources

## Other sources (no combustion): nucleation

### Cleaning products

- Chemical reactions induced by ozone and volatile organic compounds (VOCs) produce multi-oxygenated compounds (e.g. dicarbonyls, peroxides) that, after condensations, generate **secondary ultrafine particles**



# Outdoor exposure

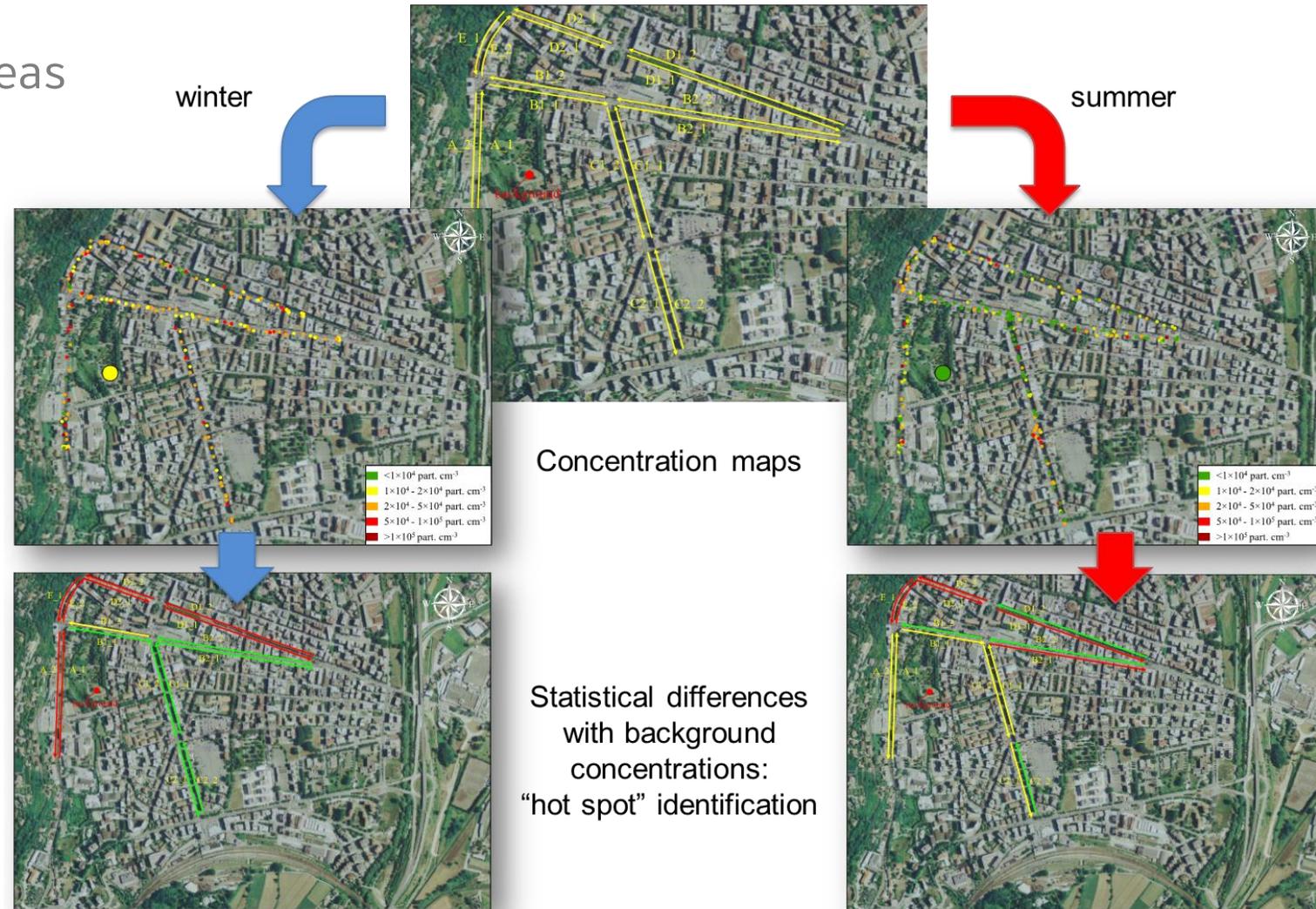
## Urban areas

### Concentration gradients in urban areas

**Table 5**

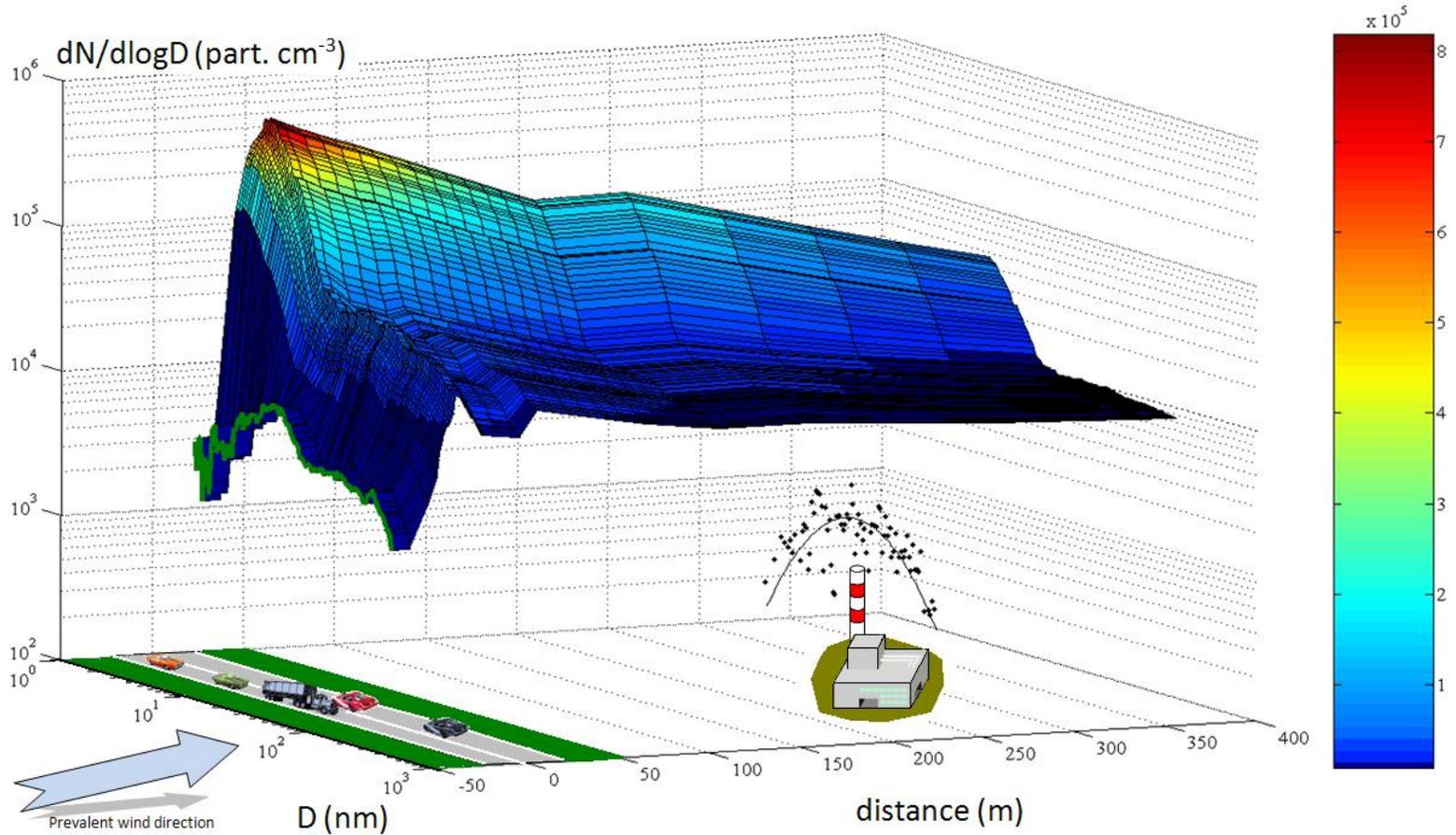
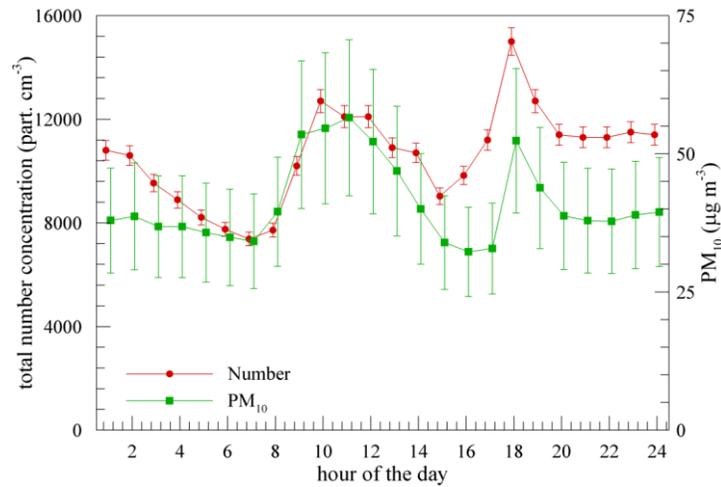
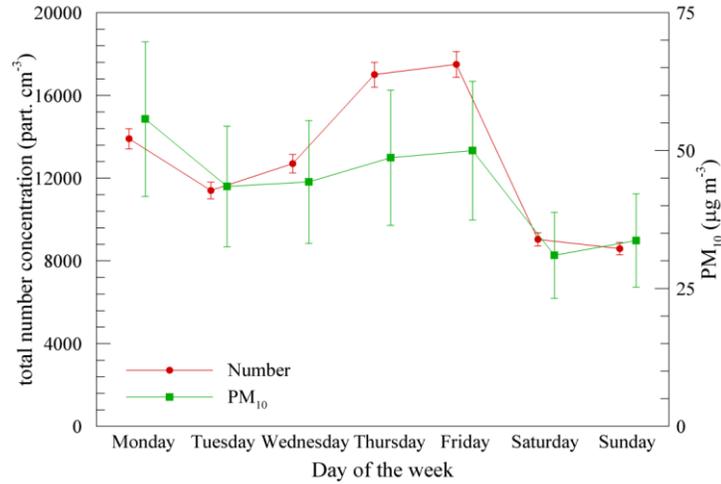
Number of road links' sides (over 16 investigated) having concentrations statistically larger than the simultaneous background levels in terms of particle number (N), alveolar-deposited surface area (S), and PM<sub>10</sub>.

Date	Run	N	S	PM <sub>10</sub>
27-Jan	1	9 of 16	11 of 16	—
	2	8 of 16	4 of 16	—
	3	3 of 16	5 of 16	—
	4	4 of 16	5 of 16	—
19-Feb	1	8 of 16	4 of 16	2 of 16
	2	2 of 16	3 of 16	2 of 16
Median Heating season		8 of 16	3 of 16	2 of 16
5-May	1	7 of 16	10 of 16	6 of 16
14-May	1	9 of 16	6 of 16	5 of 16
24-Jun	1	7 of 16	8 of 16	—
25-Jun	1	2 of 16	13 of 16	—
	2	8 of 16	12 of 16	—
29-Jun	1	9 of 16	8 of 16	—
Median Non-heating season		6 of 16	10 of 16	5 of 16



# Outdoor exposure

## Incinerators vs. streets/roads

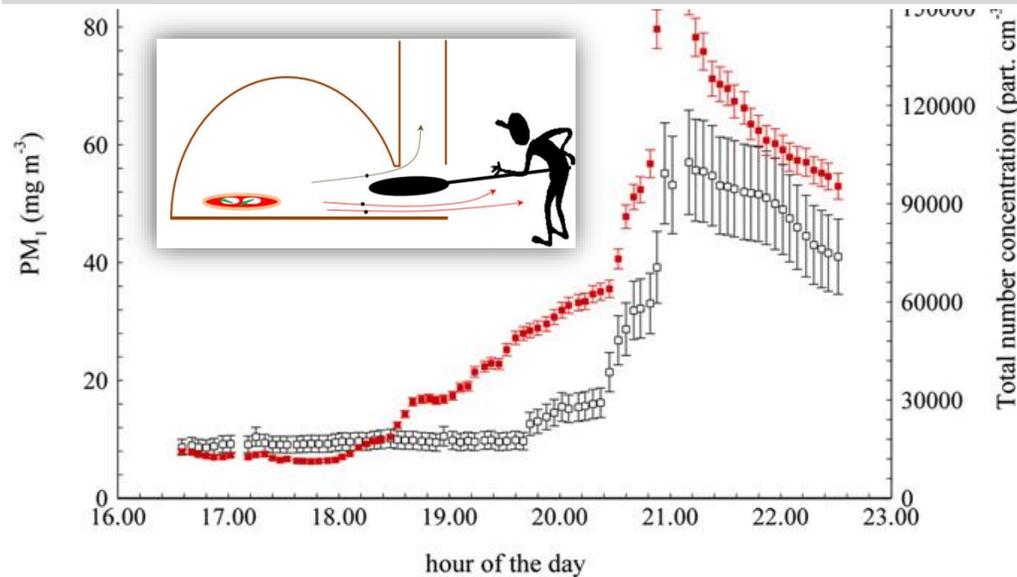


# Indoor exposure

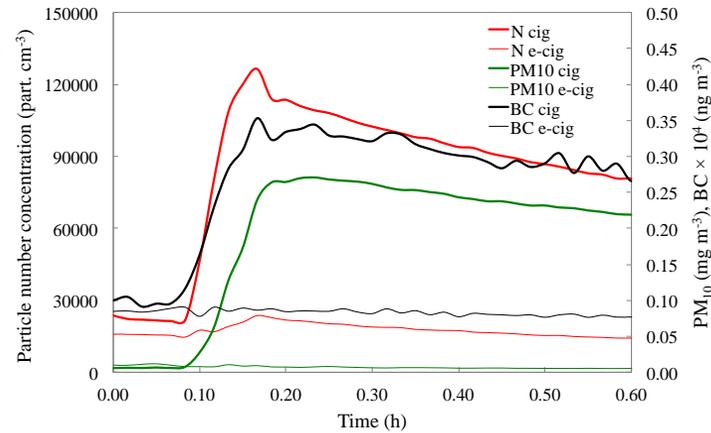
## Exposure due to indoor sources

- Homes (cooking, biomasses, cigarette)
- Workplace
- Industries (welding, etc.)
- Operating rooms
- ...

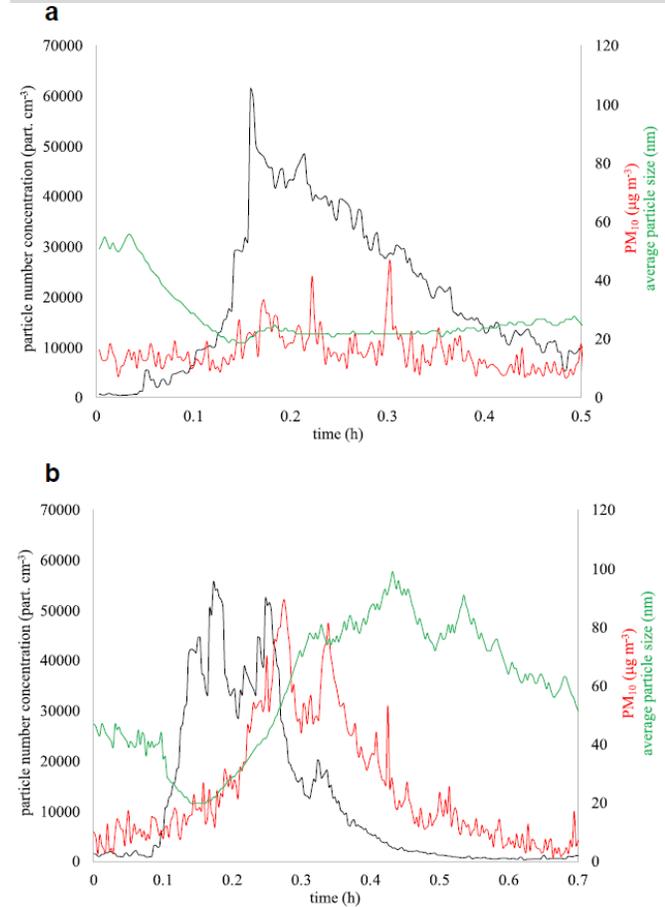
### Pizzerias/restaurants



### Second-hand smoking



### Operating rooms



### Welding sites

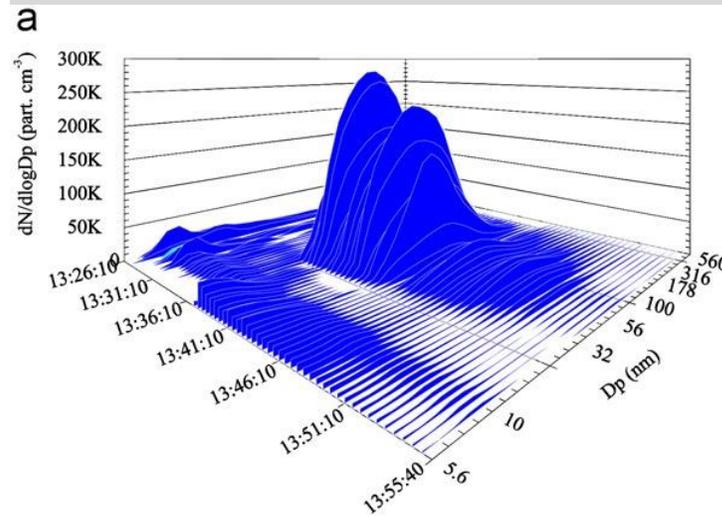


Fig. 1. Particle number concentration,  $PM_{10}$ , and average particle size as a function of time measured during a cesarean section operation (CSO 14) and an orthopedic surgery (OS 10).

# Indoor exposure

## Emission of residential heating systems

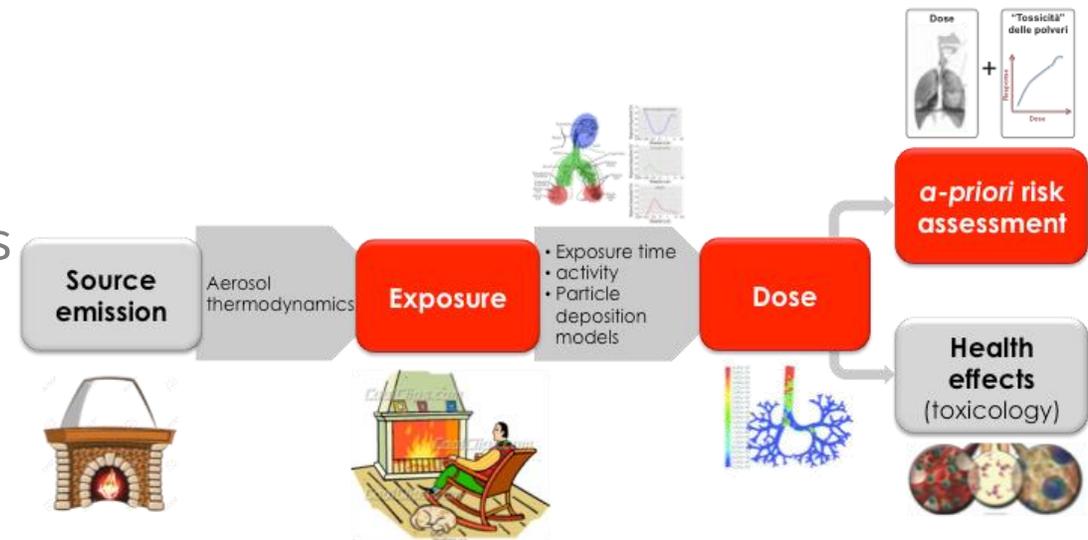
### State-of-art & Open questions

- Biomass-burning emission in outdoors
- Indoors?
- Ultrafine Particles?
- Exposure assessment?
- Dose?
- Risk?



### Aim of the research

- Indoor exposure
  - Open and closed fireplaces, pellet stoves
  - N, S, PM<sub>10</sub>
  - Carcinogenic compounds
- **Dose and risk estimate**



# Indoor exposure

## Emission of residential heating systems

### Methodology

Measurement of the exposure in 30 houses (10 per each heating system)

- Apparatus - hand-held monitors:
- diffusion charging counter (particle number & lung-deposited surface area)
- laser photometer (PM<sub>10</sub>).
- Procedure:
  - 30-60 min of background concentrations (no other sources),
  - 2-4 h of measurement during the combustion phenomena (no other sources).

### Carcinogenic compound on PM10

Quantification of di As, Cd, Ni, BaP (Group 1 IARC)

- Gravimetric sampling (PM<sub>10</sub>) emitted by wood and pellet
- GC/MS for BaP
- INAA technique for heavy metals.

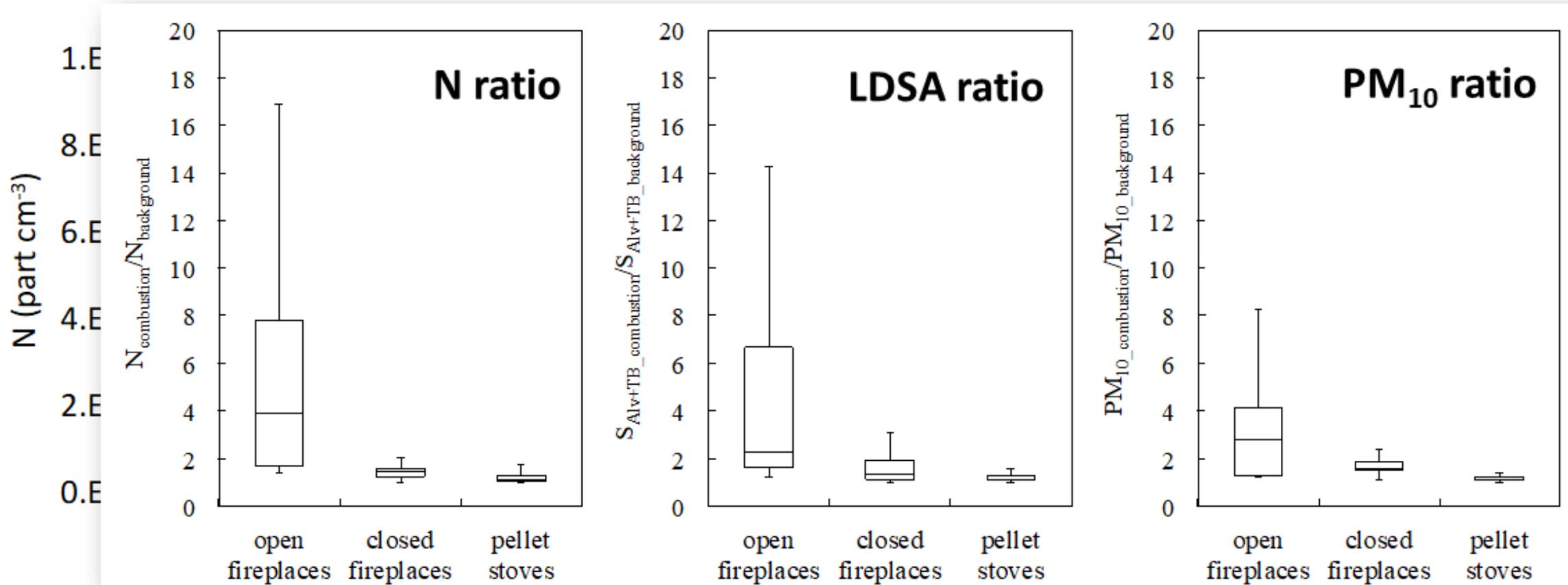


# Indoor exposure

## Emission of residential heating systems

### Results

#### Concentrations and «over-exposure»

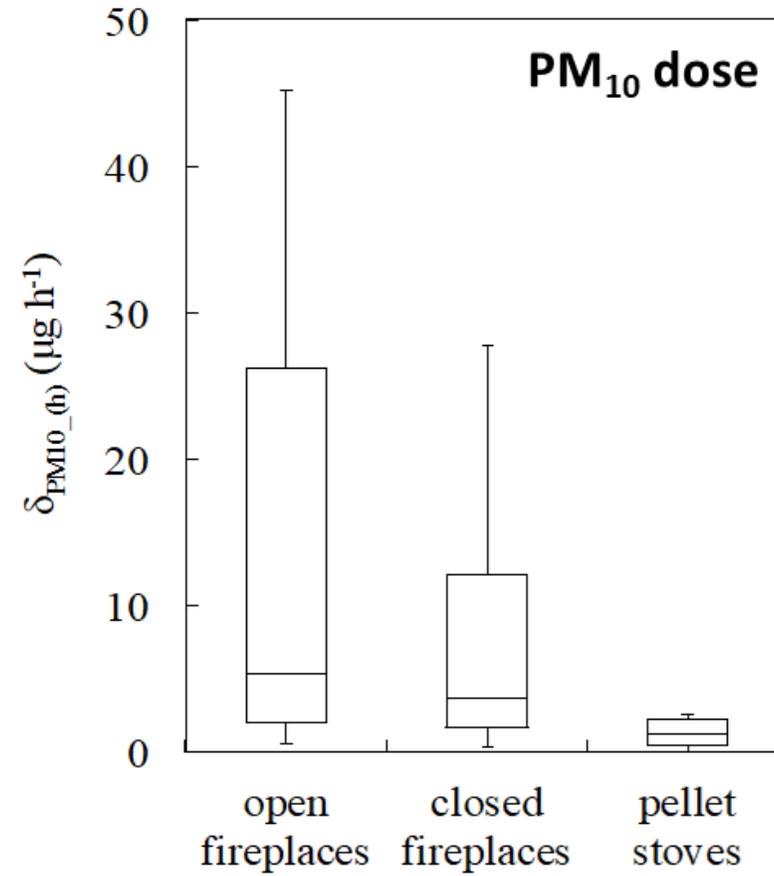
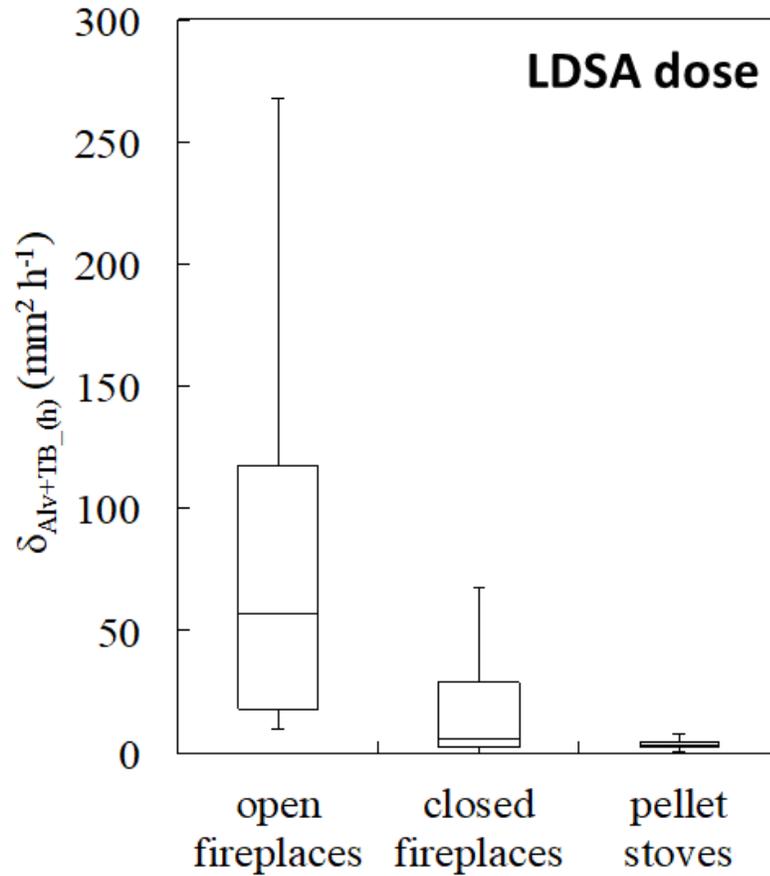


# Indoor exposure

## Emission of residential heating systems

### Results

#### Extra-doses



# Indoor exposure

## Emission of residential heating systems

### Results

#### Toxicity and risk

$$SF_m = \sum_i^n SF_i \cdot \frac{m_i}{PM_{10}}$$

	Wood	Pellet
$m_{BaP}/PM_{10}$	$6.2 \pm 0.7 \times 10^{-5}$	$4.0 \pm 0.3 \times 10^{-6}$
$m_{As}/PM_{10}$	< LOD	$9.0 \pm 1.8 \times 10^{-5}$
$m_{Cd}/PM_{10}$	$2.4 \pm 0.5 \times 10^{-4}$	$4.3 \pm 0.9 \times 10^{-4}$
$m_{Ni}/PM_{10}$	$7.2 \pm 1.4 \times 10^{-3}$	$1.2 \pm 0.2 \times 10^{-2}$
<b><math>SF_m</math></b>	<b><math>6.9 \pm 1.3 \times 10^{-3}</math></b>	<b><math>1.3 \pm 0.2 \times 10^{-2}</math></b>
<b>Contribution to the <math>SF_m</math></b>	<b>BaP=4%, As&lt;1%, Cd=2%, Ni=94%</b>	<b>BaP&lt;1%, As=11%, Cd=2%, Ni=87%</b>

	Open fireplaces	Closed fireplaces	Pellet stove
<b>Lifetime ELCR<sub>extra</sub></b>	<b><math>9.0 \times 10^{-3}</math></b>	<b><math>1.1 \times 10^{-3}</math></b>	<b><math>1.4 \times 10^{-3}</math></b>
LDSA contribution	99.97%	99.93%	99.93%
PM <sub>10</sub> contribution	0.03%	0.07%	0.07%

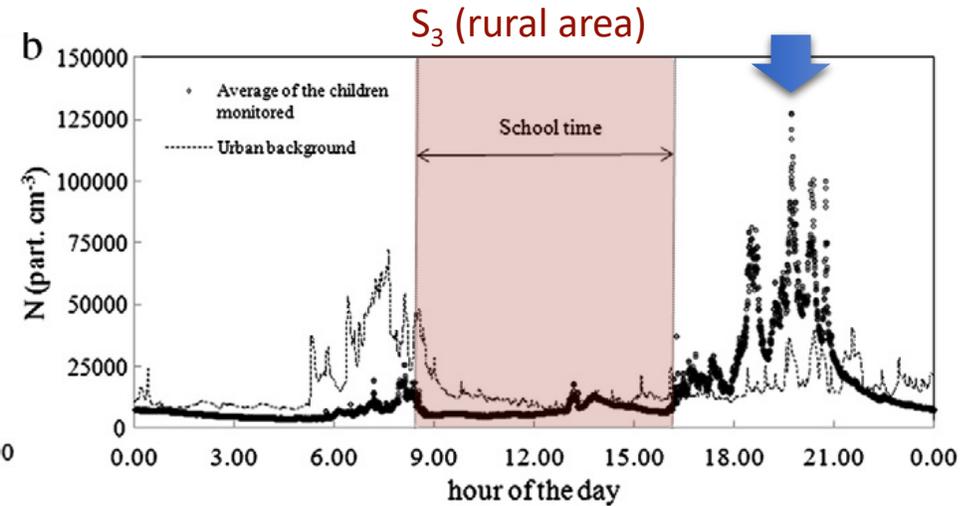
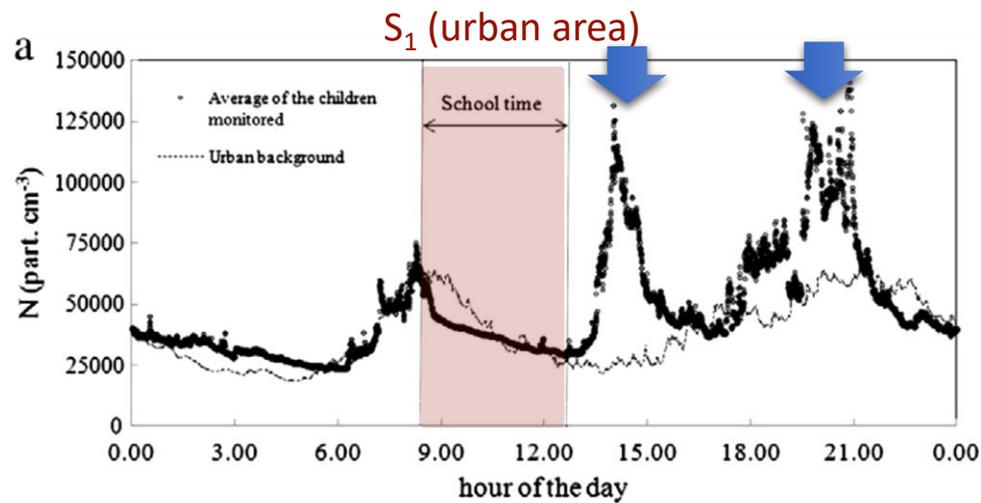
...comparison	
Exposure scenario	Risk
Italian not smoking pop.	$\approx 2 \times 10^{-2}$
Smokers	$\approx 1-5 \times 10^{-1}$
Italian students (5 yrs)	$\approx 2 \times 10^{-4}$
Downwind of incinerator	$\approx 7 \times 10^{-7}$

Maximum tolerable risk EPA-WHO =  $1 \times 10^{-5}$  (1 new case per 100000 people)

# Indoor vs. outdoor exposure

## Measurement at “personal” scale

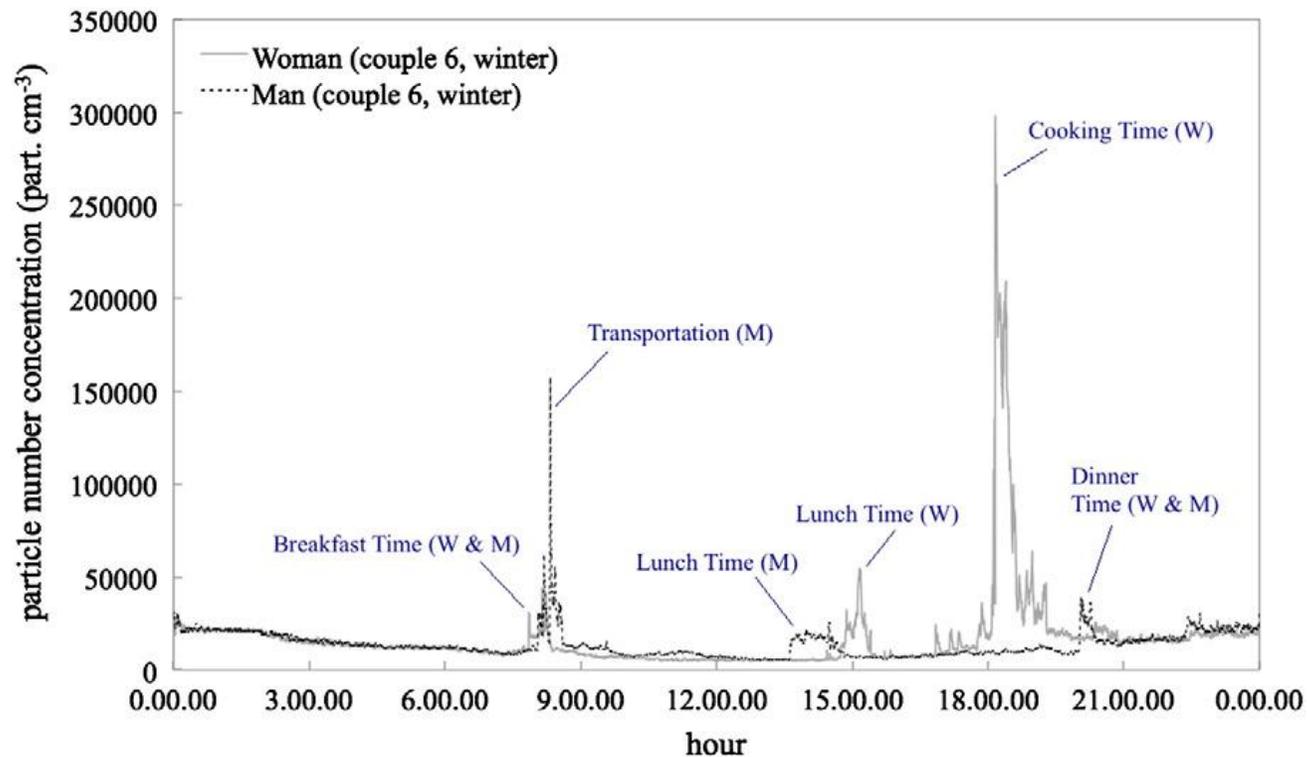
- Portable counters (Italia, Ghana, Bhutan, Australia, Brasile, Egitto, Inghilterra, Svezia, Spagna, etc.)
- Children – schools
- Adults



# Indoor vs. outdoor exposure

## Measurement at “personal” scale

- Lifestyle effect
- Average exposure of housewives 30-40% higher than workers
- Cooking contribution to the exposure



# Indoor vs. outdoor exposure

## Exposure in schools: emission vs. ventilation

- Measurements of PM<sub>10</sub>, Number concentrations, CO<sub>2</sub>
- Naturally-ventilated classrooms (pre-retrofit)



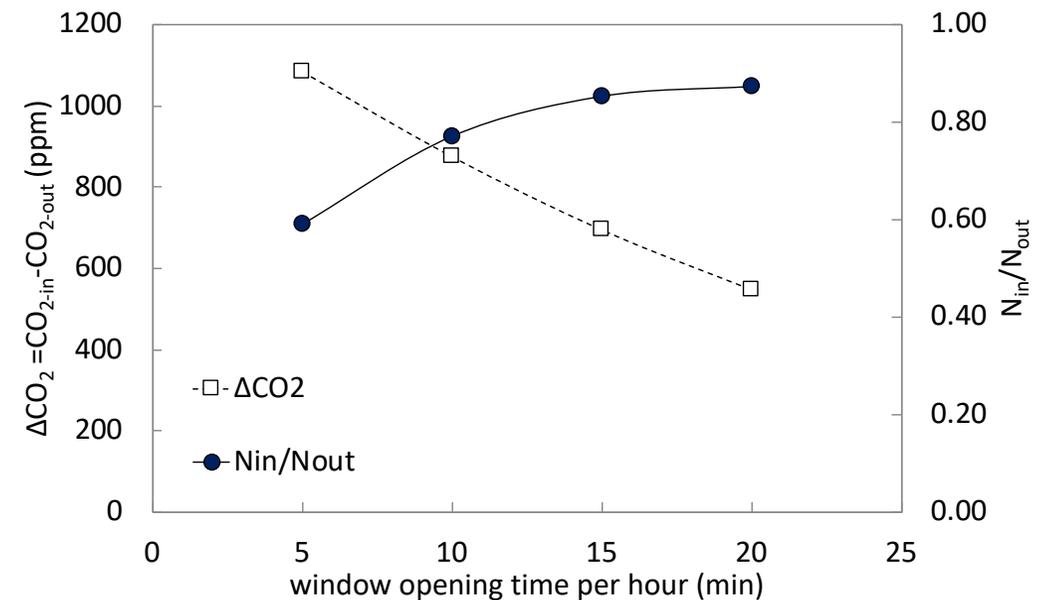
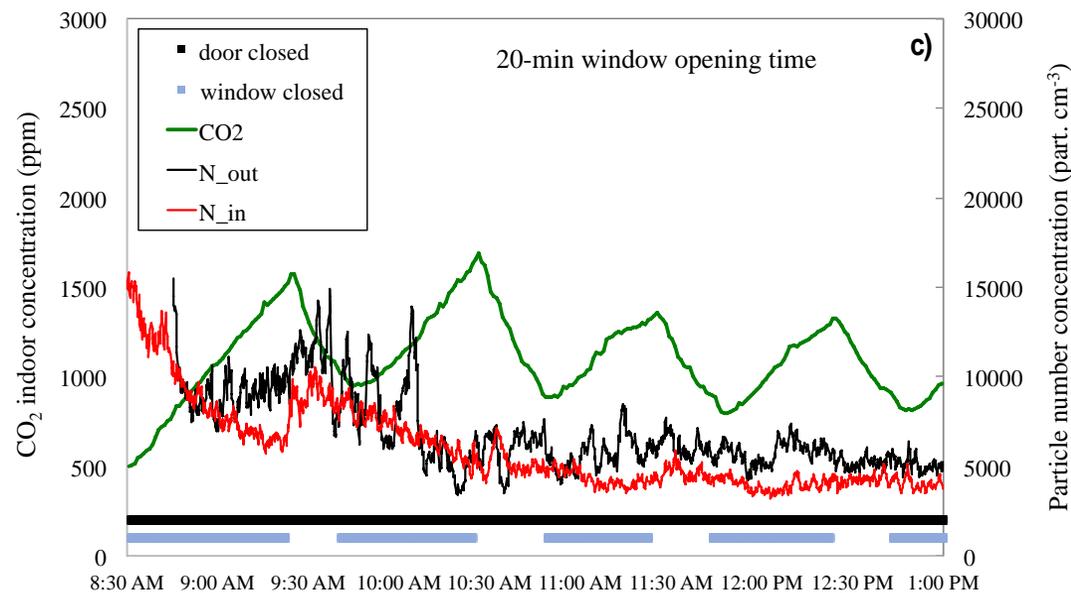
Diffusion Charger Particle Counter



DustTrak photometer 8534: PM<sub>10</sub>



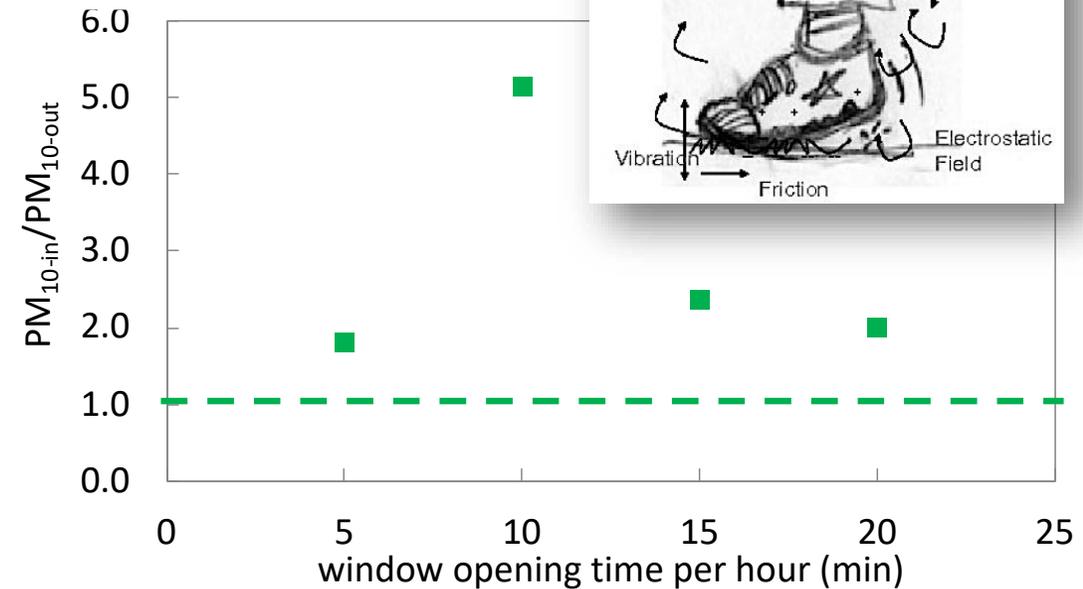
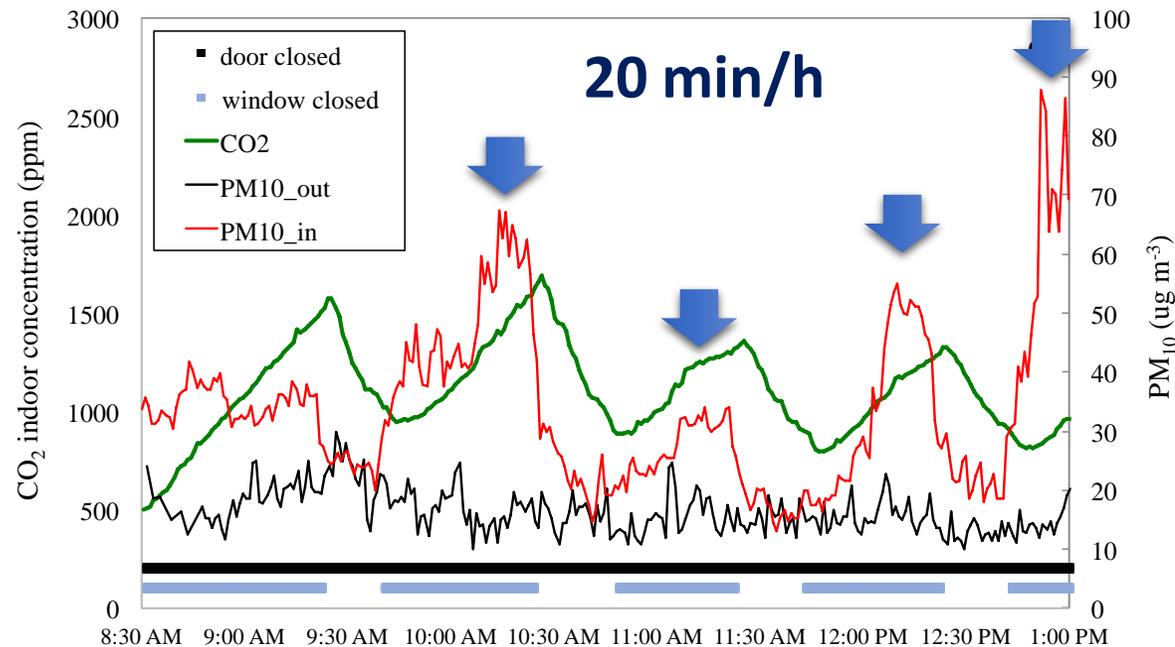
Non-dispersive infrared analyzer: CO<sub>2</sub>, T & RH



# Indoor vs. outdoor exposure

## Exposure in schools: emission vs. ventilation

- Measurements of PM<sub>10</sub>, Number concentrations, CO<sub>2</sub>
- Naturally-ventilated classrooms (post-retrofit)

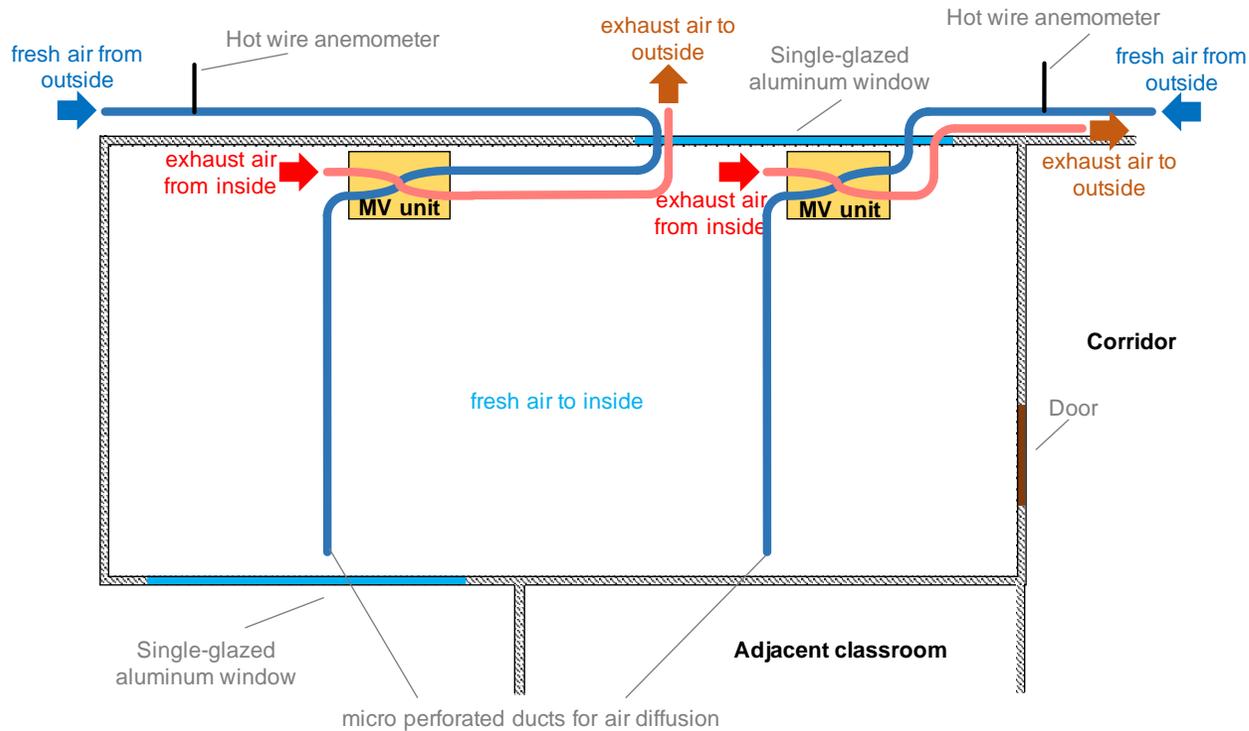


Manual airing reduces CO<sub>2</sub> (and indoor-generated gaseous pollutants) but increases sub-micrometric particles (effect on PM<sub>10</sub> negligible)

# Indoor vs. outdoor exposure

## Exposure in schools: emission vs. ventilation

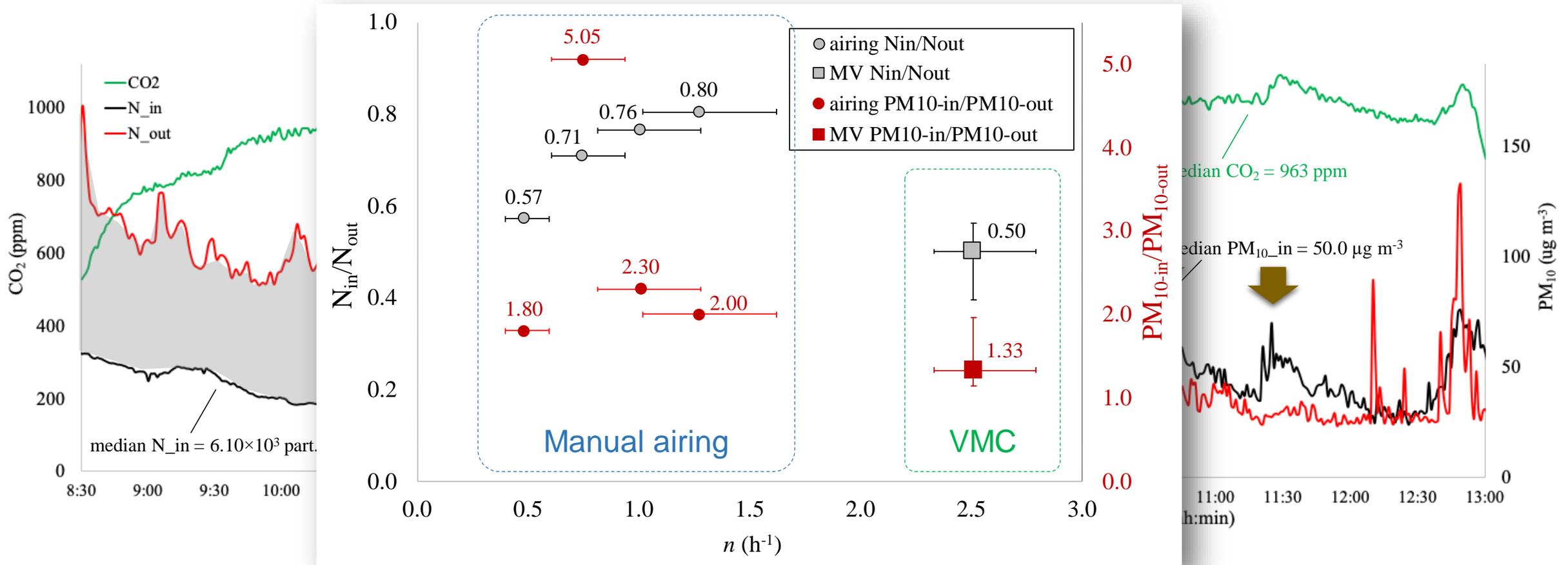
- Measurements of PM<sub>10</sub>, Number concentrations, CO<sub>2</sub>
- Mechanical ventilated classrooms (post-retrofit)



# Indoor vs. outdoor exposure

## Exposure in schools: emission vs. ventilation

- Measurements of PM<sub>10</sub>, Number concentrations, CO<sub>2</sub>
- Mechanical ventilated classrooms (post-retrofit)



# Indoor vs. outdoor exposure

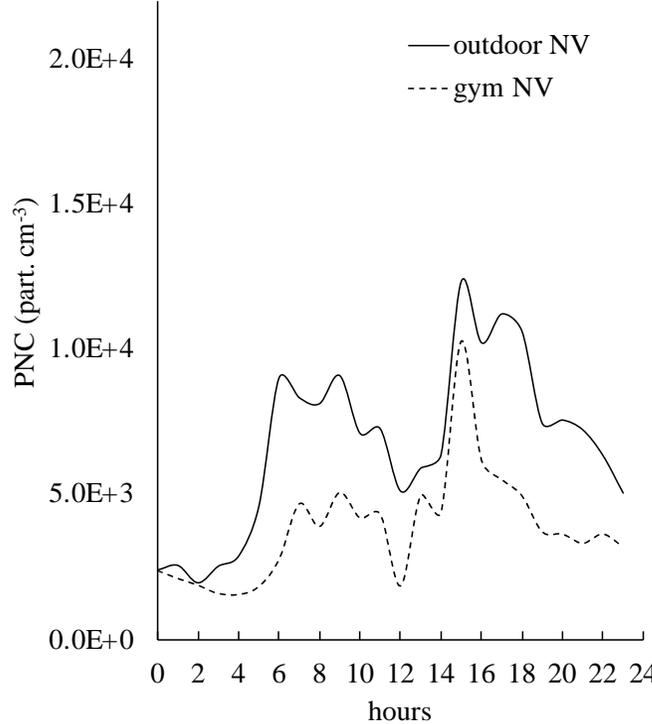
## Exposure in schools: air purifiers

School gyms in Barcelona

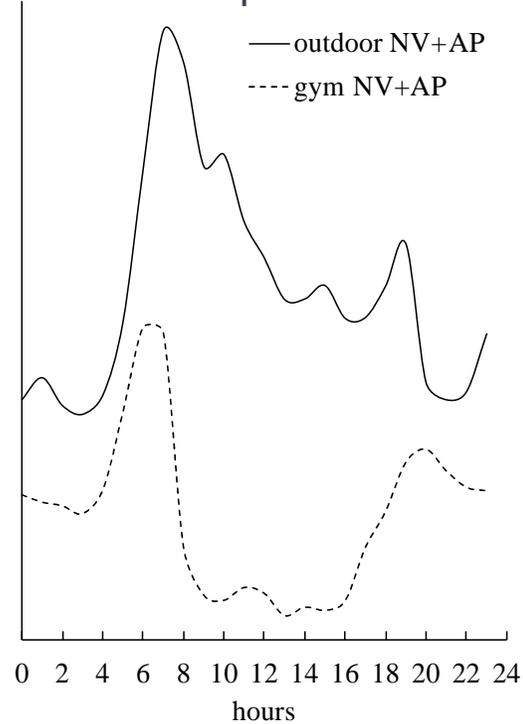


### Particle number concentrations

#### Natural ventilation

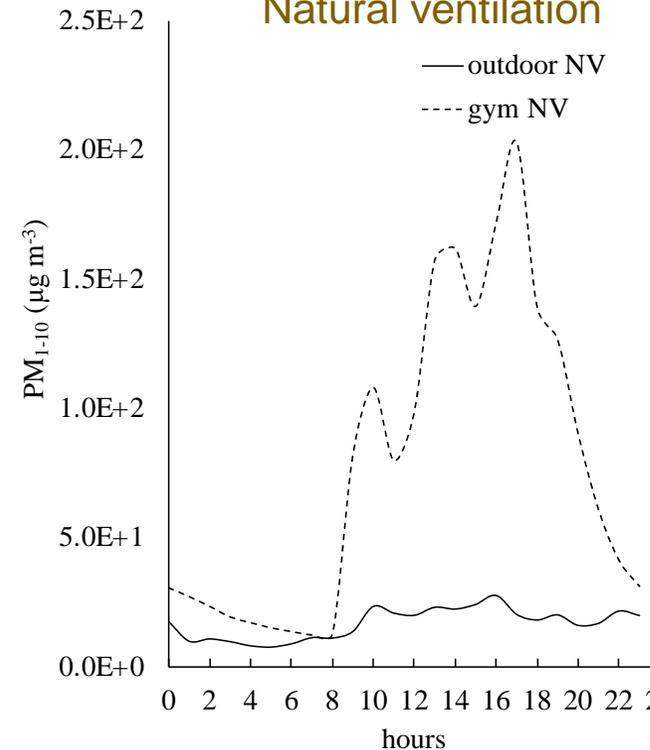


#### Air purifiers

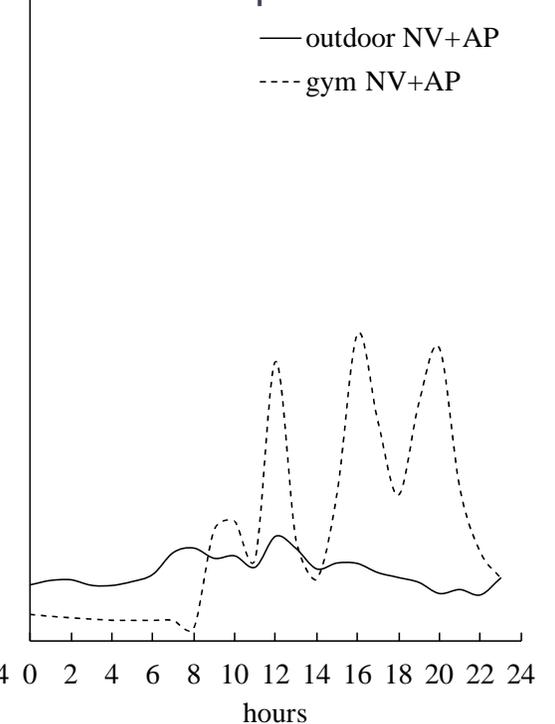


### PM<sub>10</sub>

#### Natural ventilation

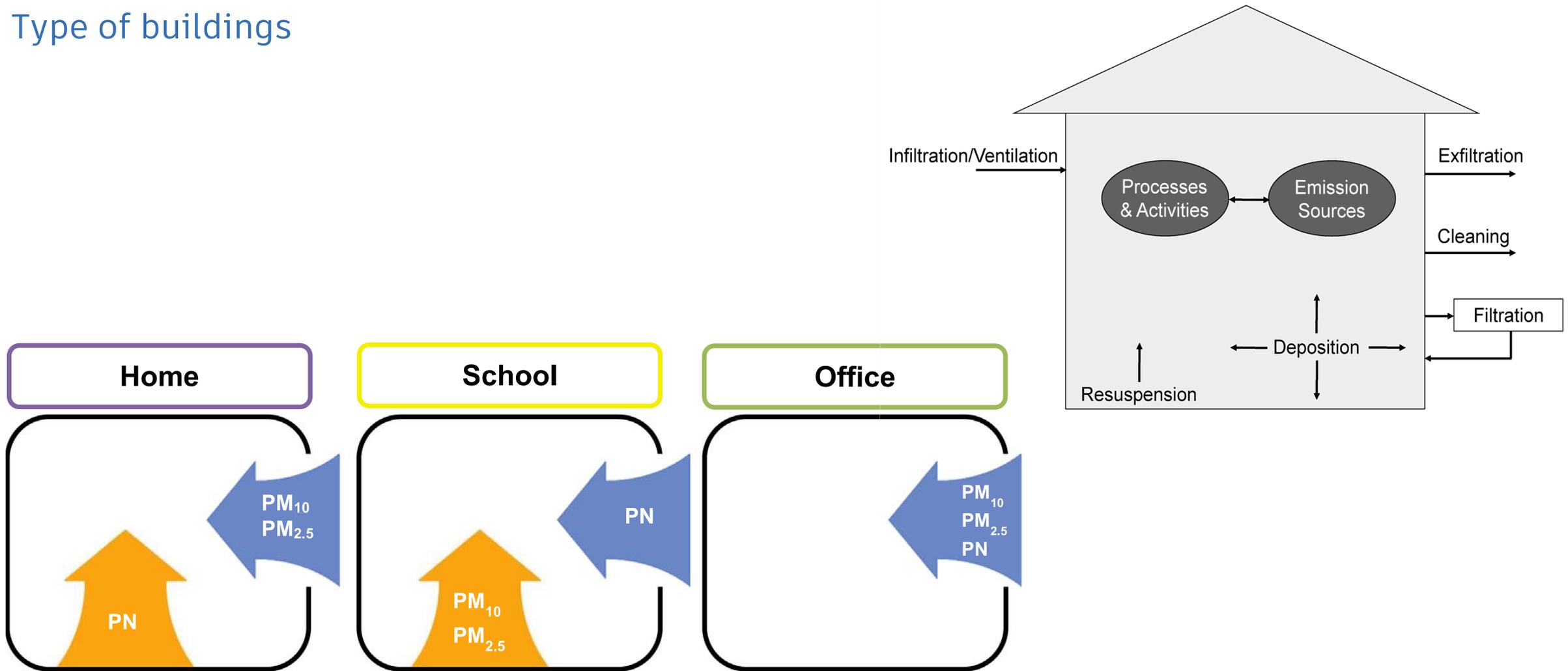


#### Air purifiers



# Indoor vs. outdoor exposure

## Type of buildings



# Dose

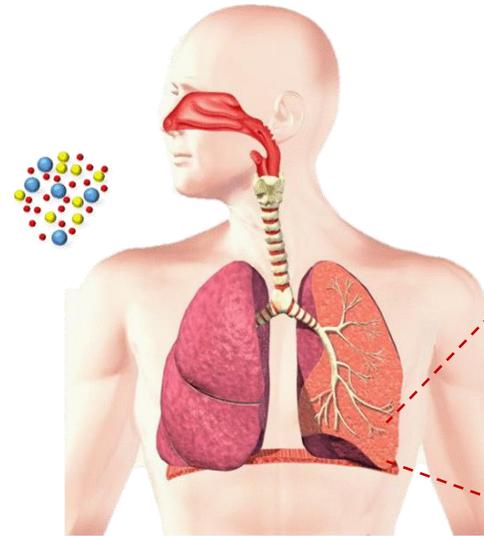
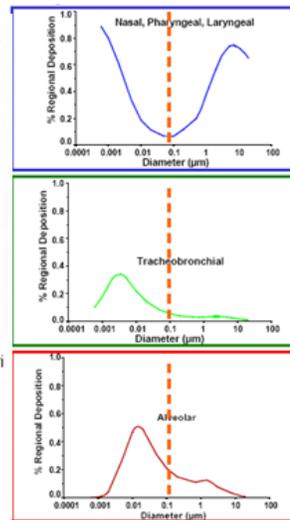
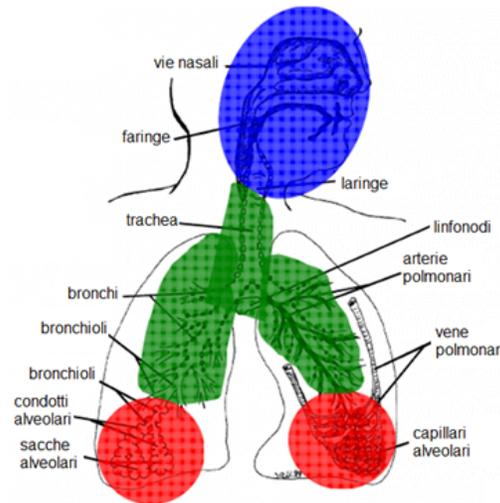
## Dose estimate from personal monitoring

$$DOSE_{Alv+TB} = IR \cdot S_{Alv+TB} \cdot T \text{ (mm}^2\text{)}$$

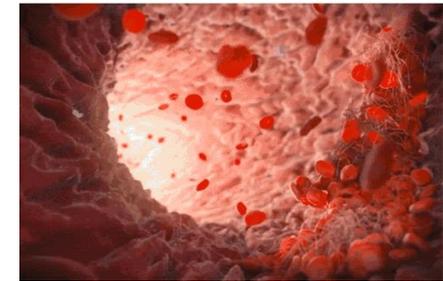
Inhalation rate

Lung-deposited surface  
area concentration

Exposure time

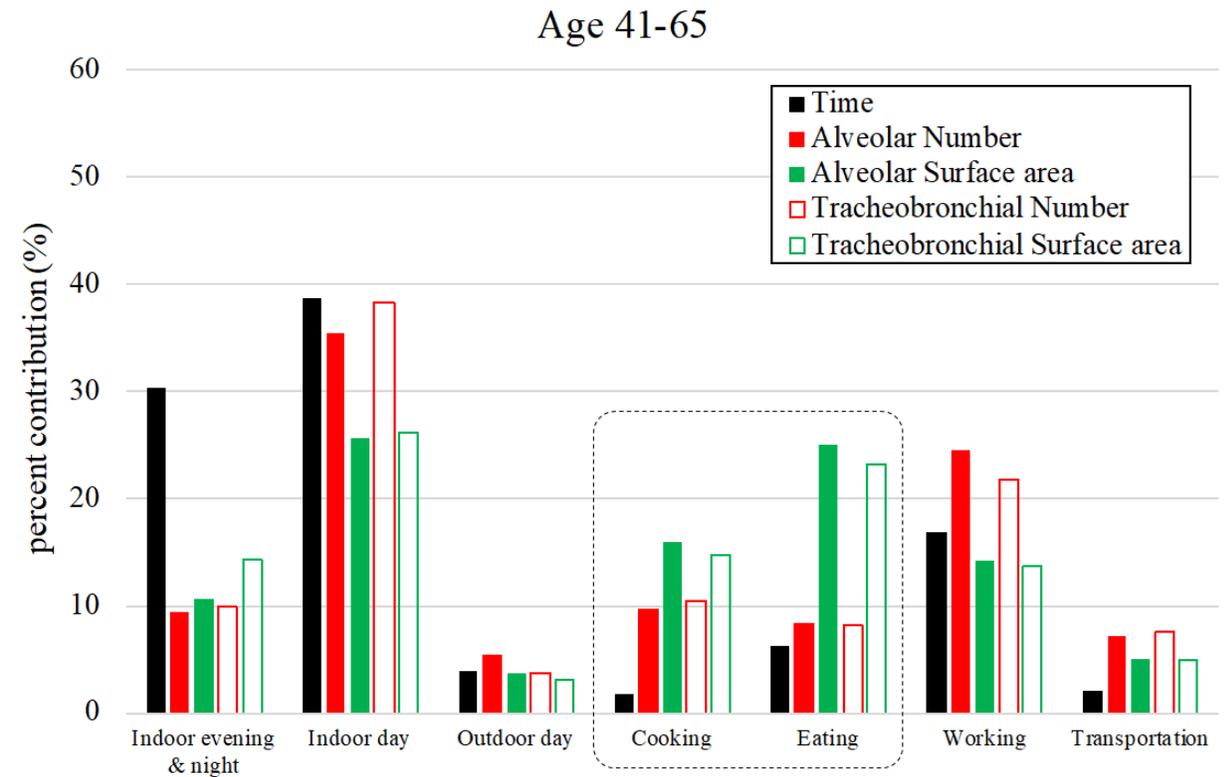
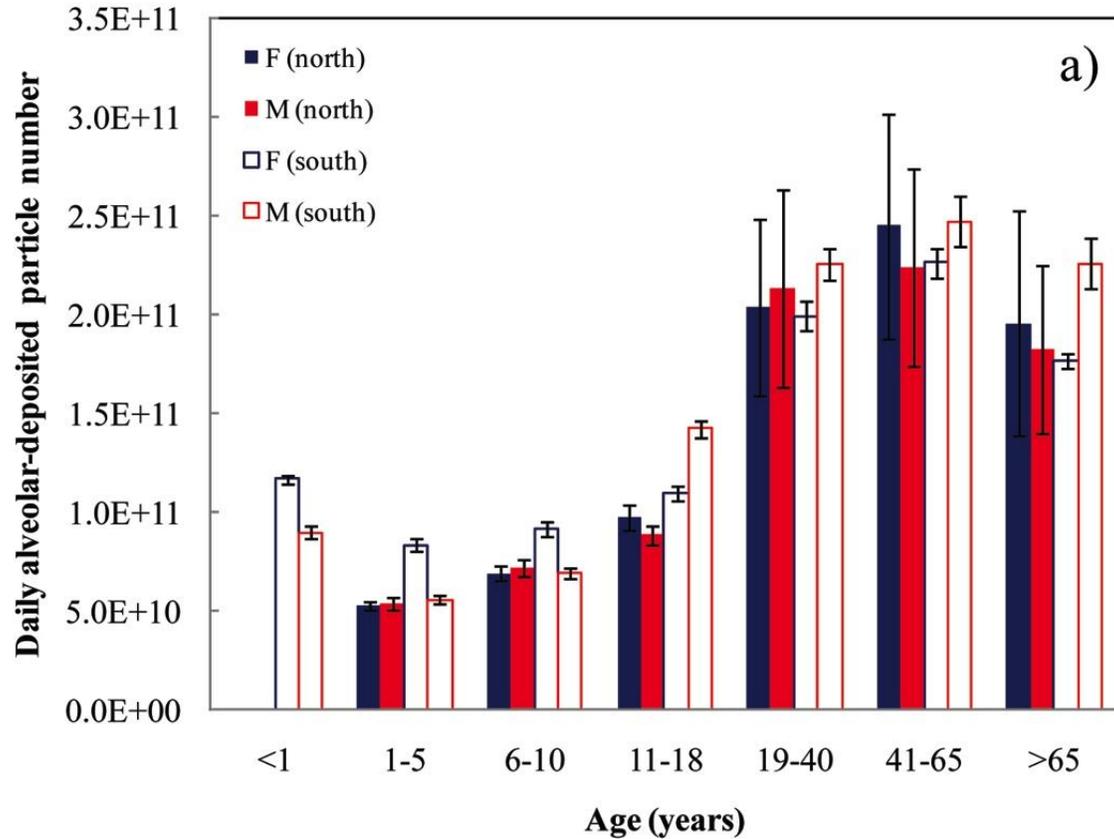


**Blood traveling through  
veins**



# Dose

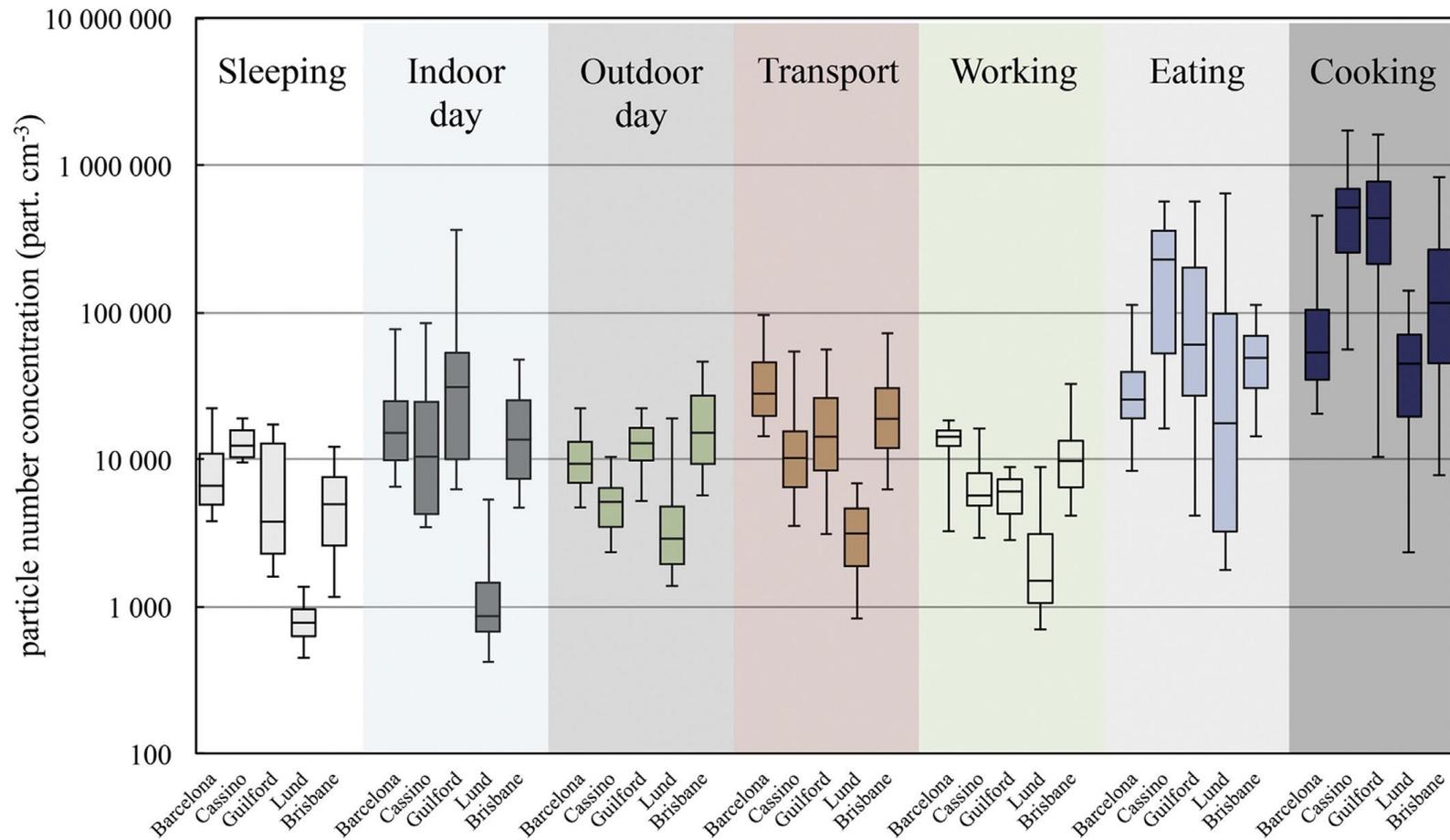
## Dose estimate from personal monitoring Age and activity effects



# Dose

## Dose estimate from personal monitoring

Different populations and lifestyles: western countries



City	Daily Dose (mm <sup>2</sup> )
Cassino (Italy)	1114-1873
London (UK)	1083-1521
Barcelona (Spain)	606-763
Brisbane (Aus)	570-782
Lund (Sweden)	52-123

# Dose

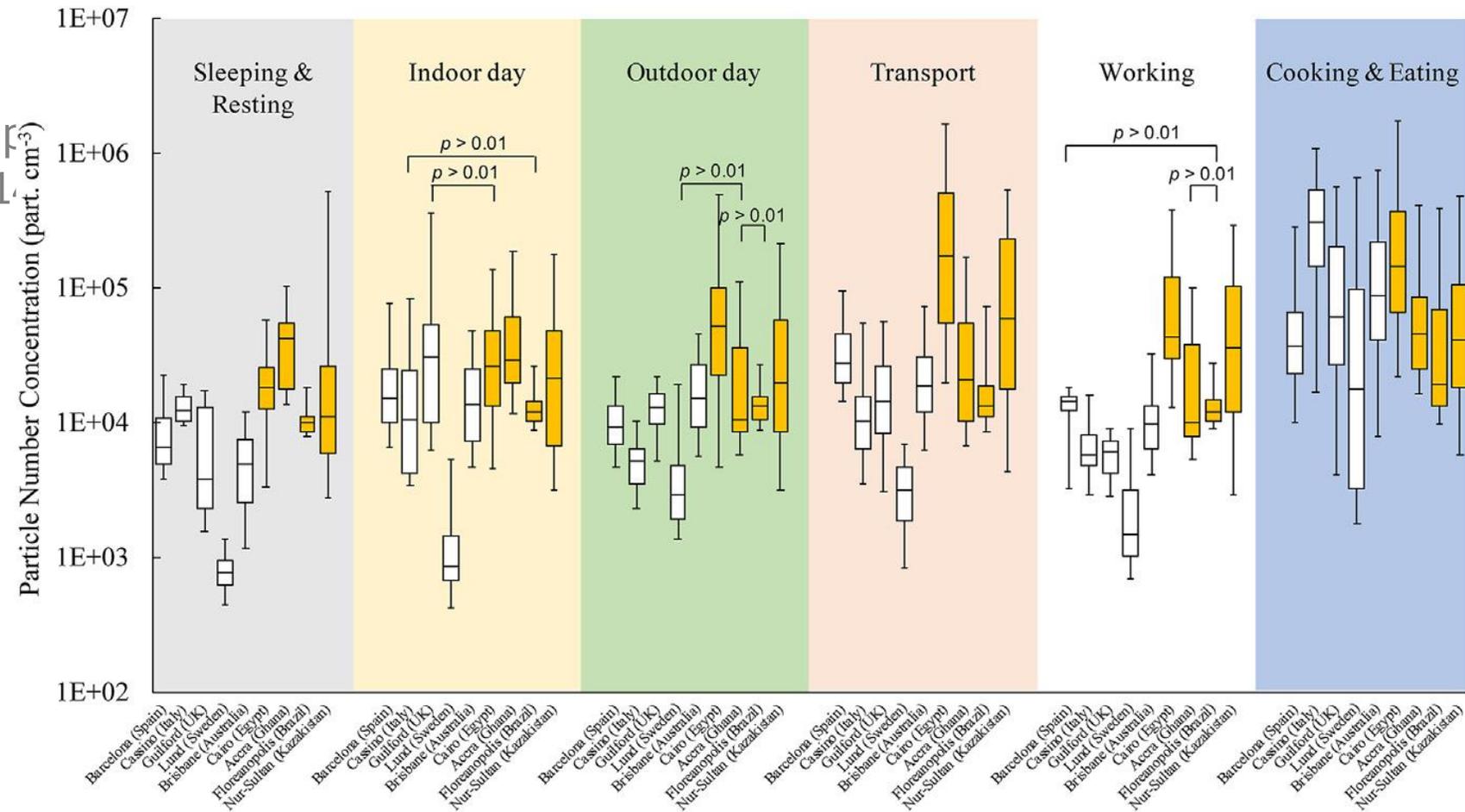
## Dose estimate from personal monitoring

Different populations and lifestyles: western countries...and other countries (e.g. low-income countries)

- Worse outdoor air quality
- Worse air quality while sleeping
- Cooking & Eating (just 8%-14% of total dose)

### Total doses:

- 1300 mm<sup>2</sup> for Egyptians
- 1100 mm<sup>2</sup> for Ghanaians
- 750 mm<sup>2</sup> for Kazakhstanis
- 450 mm<sup>2</sup> for Brazilians



# Risk

## Lung cancer risk estimate (applying models) excess lifetime cancer risk (ELCR)

Risk = Toxicity × Dose

$c_f = 6.6 \times 10^{-13} \text{ mg nm}^{-2}$  (Sze-To *et al.*, 2012)  
equivalent toxicity of the particle surface  
area metric expressed as particle mass

$$\text{ELCR}_{extra} = \frac{1}{BW} \left( \sum_i^n \text{SF}_i \cdot \frac{m_i}{\text{PM}_{10}} \right) \cdot [c_f \cdot \delta_{Alv+TB} + \delta_{\text{PM}_{10}}] \cdot N_{day}$$

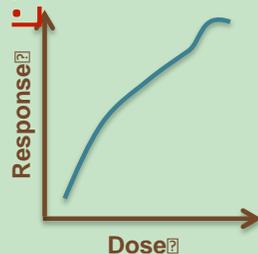
Body weight (70 kg)

Daily **extra-doses** in LDSA and  $\text{PM}_{10}$

Total exposure period  
(days per year)

### SF: inhalation slope factor (lifetime cancer potency)

the percent increase in the risk of getting cancer associated with exposure to a unit concentration of a chemical every day for a lifetime, here assumed equal to 70 years



Chemical	SF (kg day mg <sup>-1</sup> )
BaP	3.9
As	15.1
Cd	6.3
Ni	0.91

mass concentration of the  $i$ -th  
pollutant present on the  $\text{PM}_{10}$

$$\text{SF}_m = \sum_i^n \text{SF}_i \cdot \frac{m_i}{\text{PM}_{10}}$$

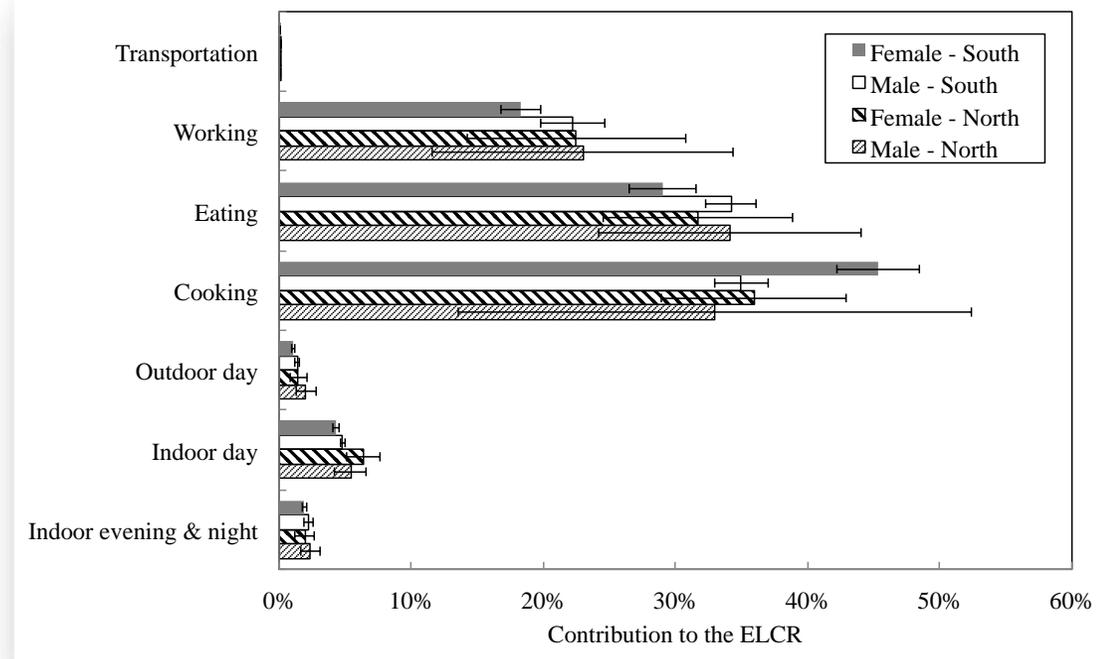
**SF of the mixture** of the  $n$   
carcinogenic pollutants on  $\text{PM}_{10}$

# Risk

Lung cancer risk estimate (applying models)  
Italian population

WHO guideline:  $ELCR < 1 \times 10^{-5}$  (one new case for 100 000 people)

Exposure	ELCR
Avarage Italian population	$1.9 \times 10^{-2}$
Avarage Italian population with <b>air quality</b>	$1.5 \times 10^{-2}$
Avarage Italian population with <b>quality</b>	$1.3 \times 10^{-4}$
Smokers	$> 1 \times 10^{-1}$
Vapers	$1 \times 10^{-4}$

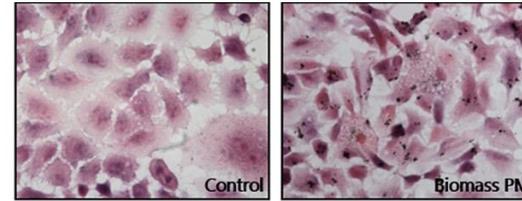
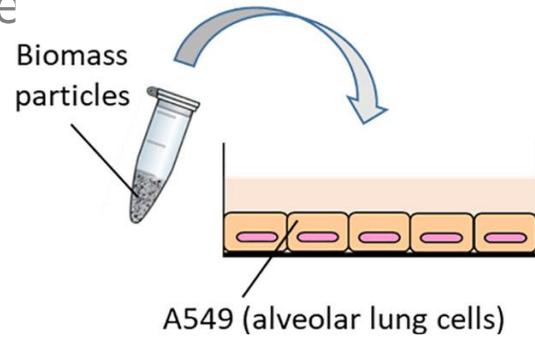


# Health effects

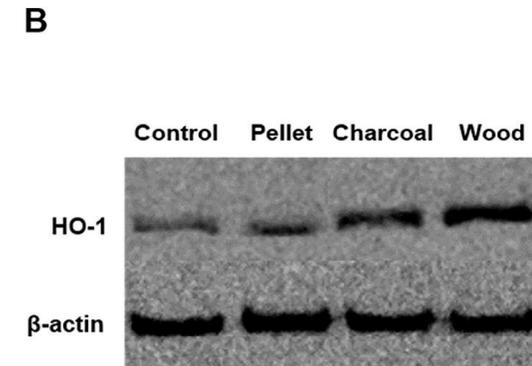
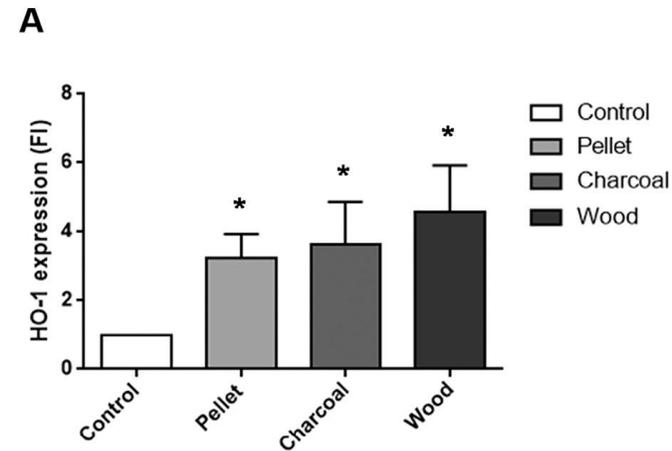
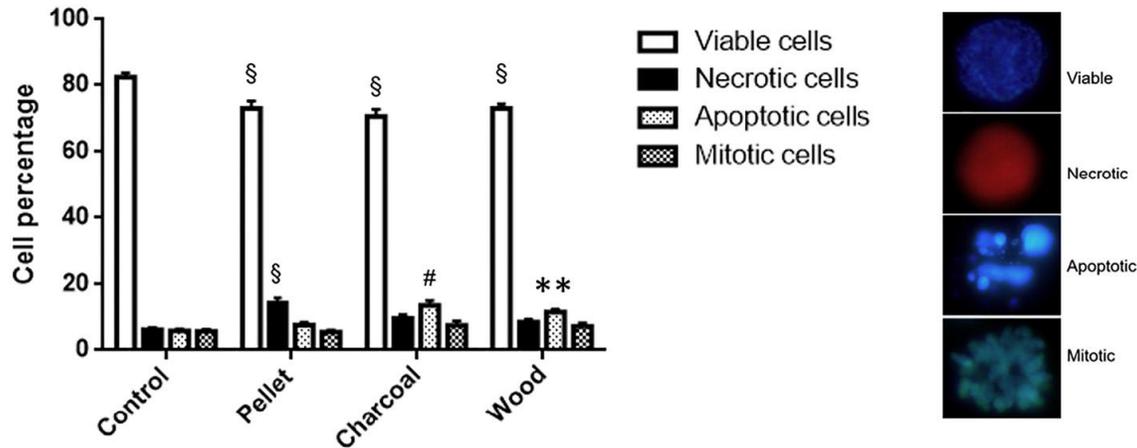
## Toxicity (In vitro) analysis of PM<sub>10</sub> emitted by combustion

Different biomass sources (pellet, wood, charcoal)

- Heavy metals is crucial in inducing acute effects related to cytotoxicity and genotoxicity
- PAHs are responsible for the induction of the xenobiotic metabolizing systems and the oxidative stress ce



- Cytotoxicity
- Genotoxicity
- Cell cycle alterations

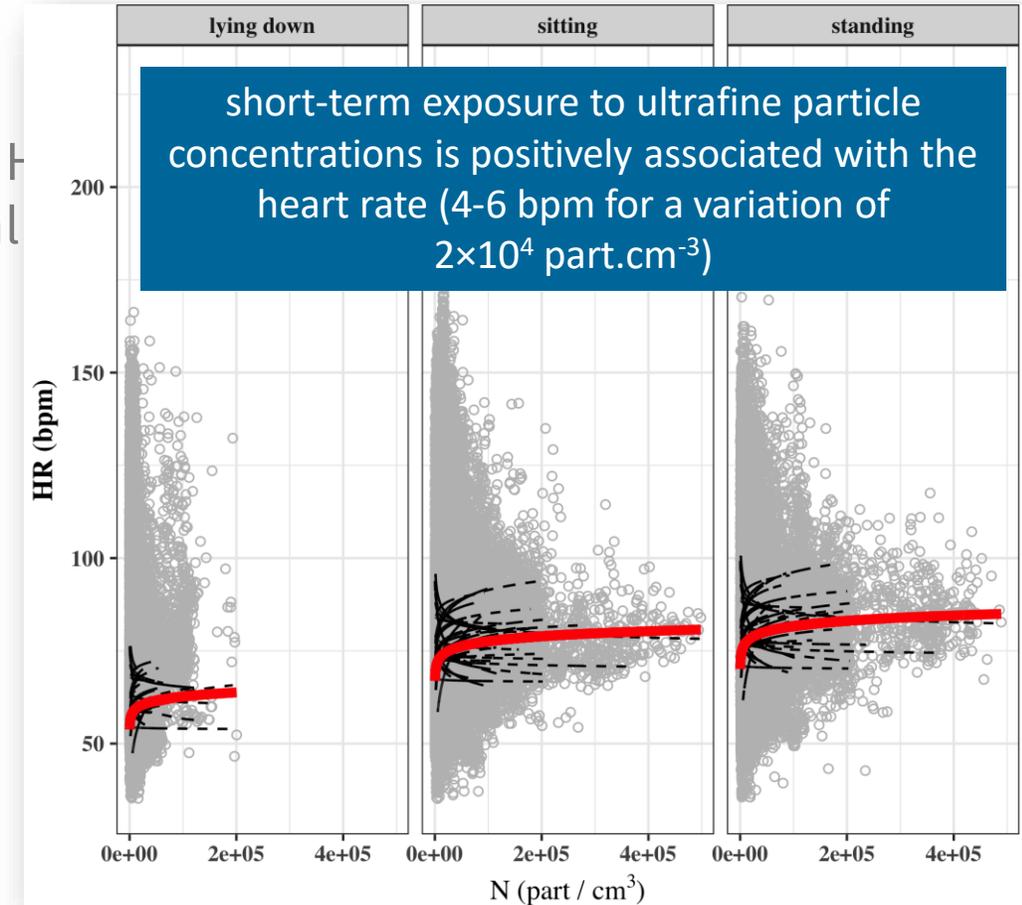
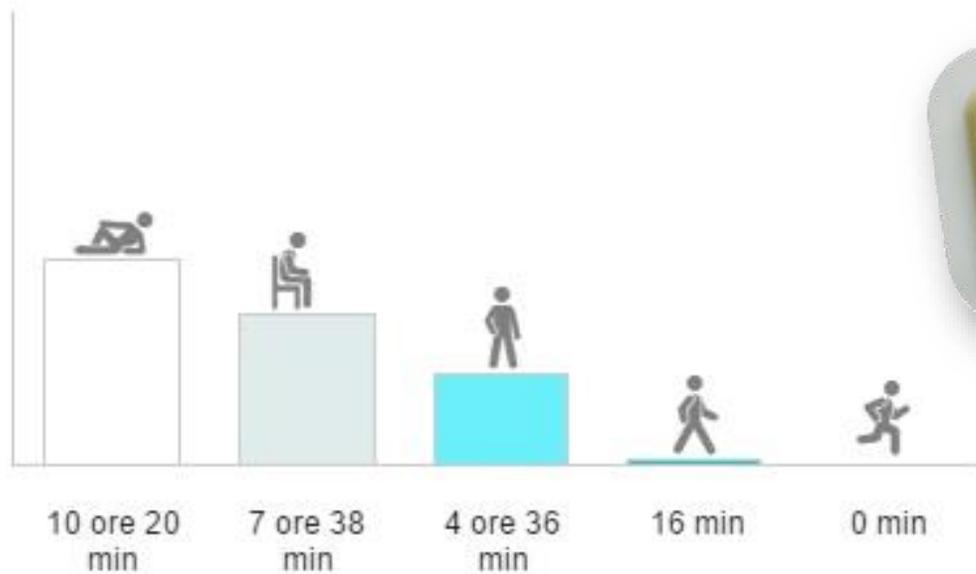


# Health effects

## Cardiovascular effects

Exposure to UFPs and heart rate

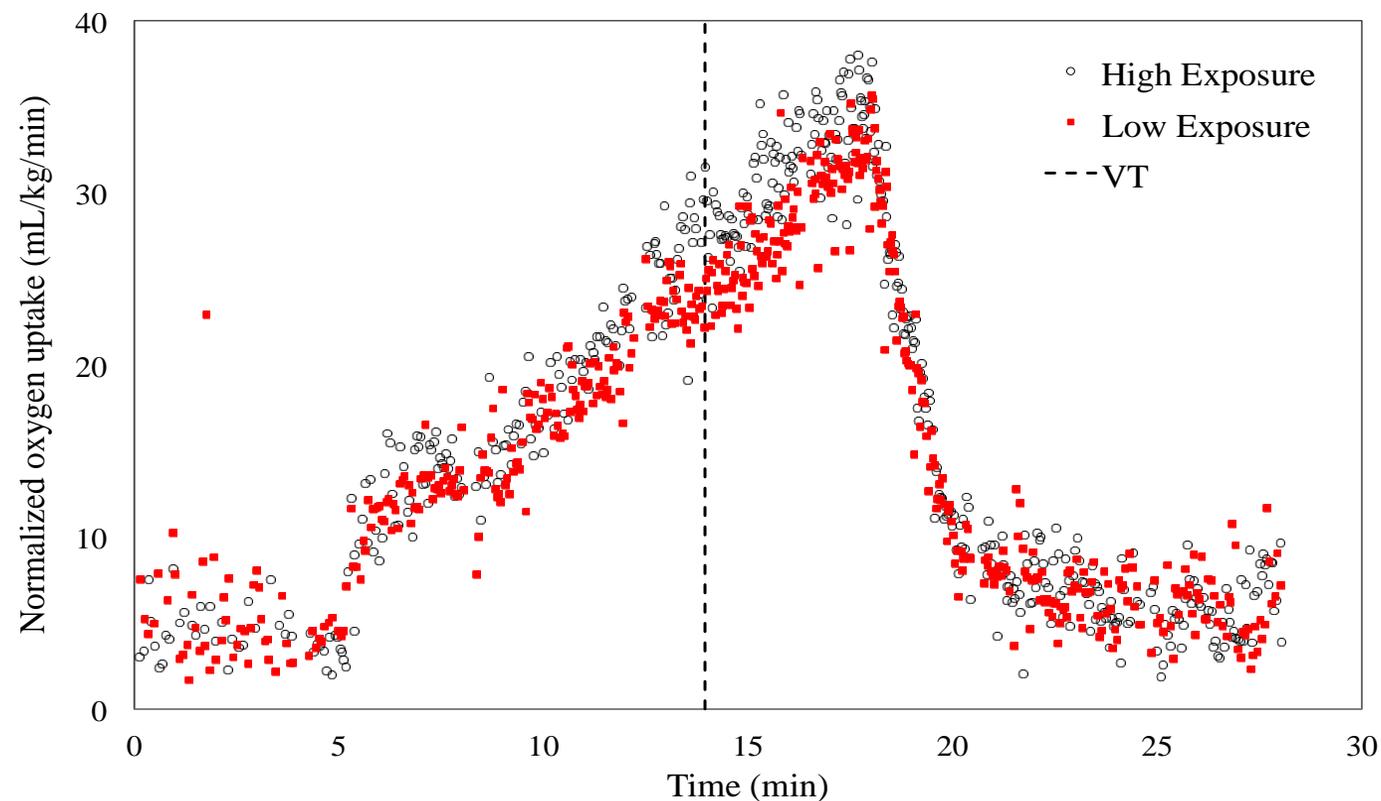
- 50 volunteers
- Measurement of exposure to UFPs
- Measurement of heart rate and activities (wearable HR)
- statistical linear mixed model to fit the experimental data



# Health effects

## Performances of athletes

Effect of the exposure to airborne particles on the physical performances achieved by athletes



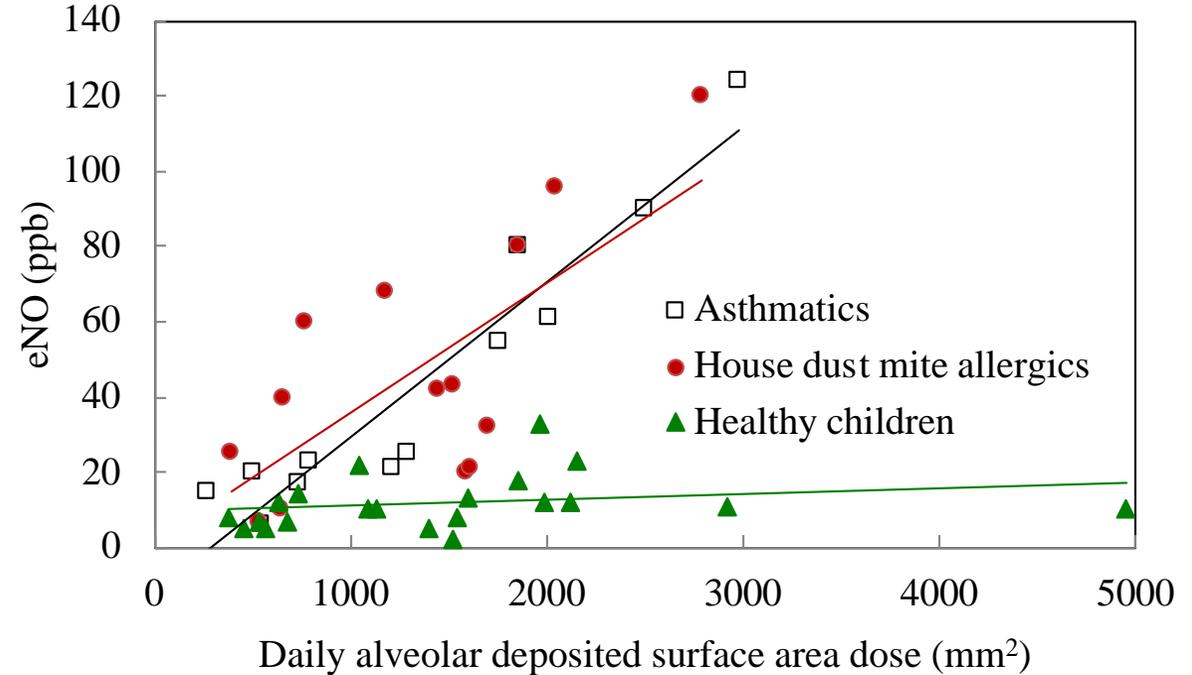
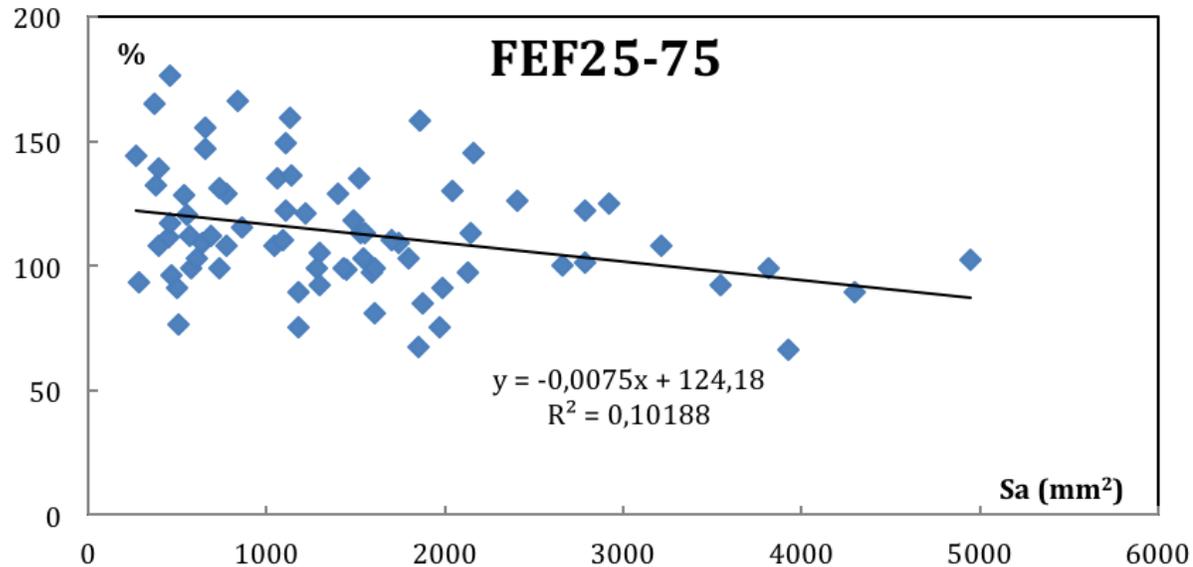
Reduction of the mechanical efficiency (oxygen uptake, peak heart rate and required metabolic power)



# Health effects

## Lung function & airways inflammation (Children)

- spirometry: an increase in daily alveolar deposited surface area dose was related to **FEV<sub>1</sub>** and **FEF<sub>25-75</sub>**, respectively (i.e. *small airway obstruction*)
- eNO test : **eNO** increase with particle doses in allergic and asthmatic children



# Feedback

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Effectiveness of eco-feedback in improving the indoor air quality in residential buildings: mitigation of the exposure to different airborne particle metrics

State-of-art

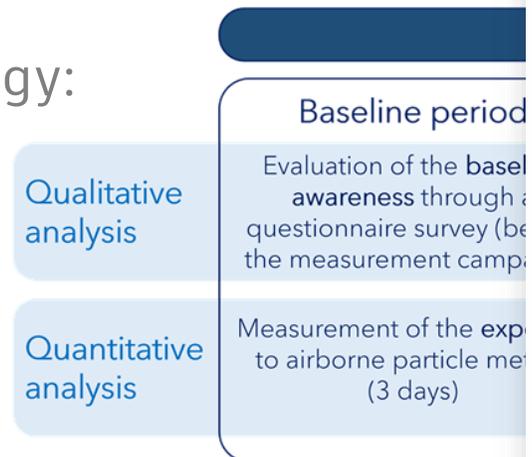
- Occupants' behavior has a significant influence on Indoor Air Quality (IAQ) and vice-versa. Acting on **behavioral change could improve the IAQ** and reduce the exposure to airborne particles in indoor environments.
- A suitable approach to provoke a behavioral change is implementing **“eco-feedback” strategies** able to bridge the gap between the lack of awareness and the understanding how their behaviors affect the environment.
- **Scientific questions on IAQ awareness to be addressed:**
  - are the occupants aware of their exposure to airborne particles in their homes?
  - is it possible to make them aware through trustworthy information?
  - and, in case, are they able to mitigate their exposure to indoor-generated airborne particles?
  - how their mitigation strategies affect the different airborne particle metrics?

# Feedback

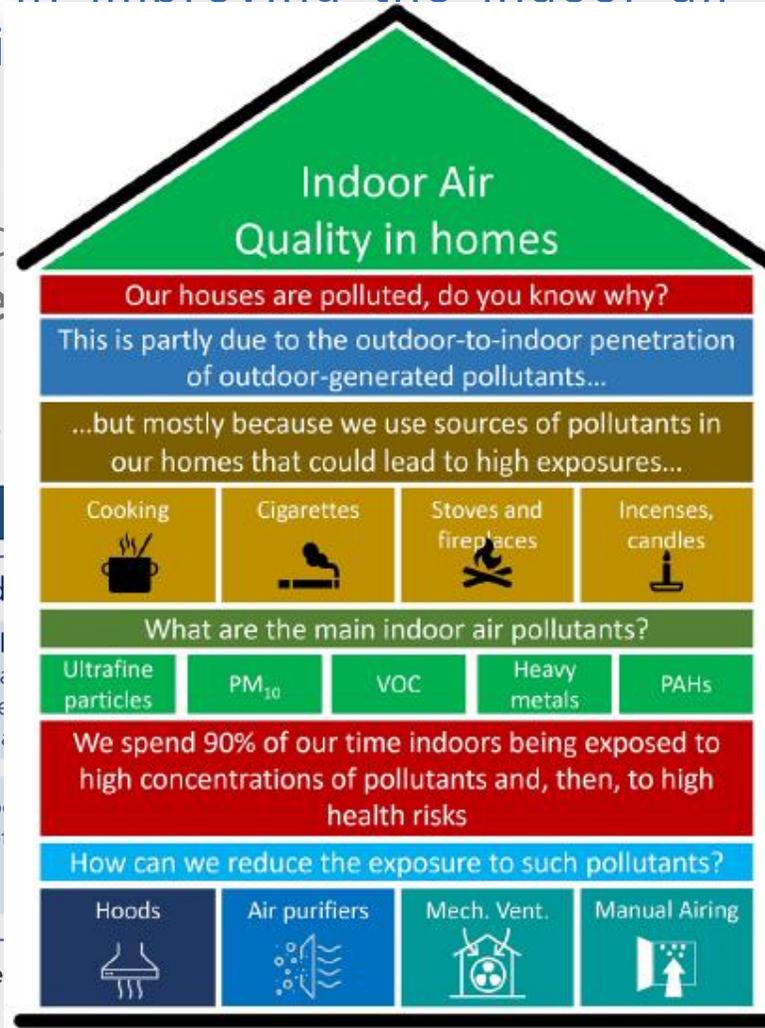
Effectiveness of eco-feedback in improving the indoor air quality in residential buildings: mitigation of the exposure to di  
 Aims:

- Investigation of the IAQ awa
- Application of an eco-feed campaign and an experime behavioral changes of the concentrations, while source

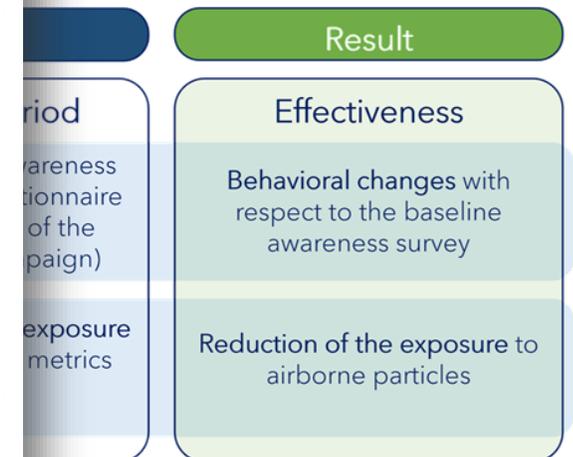
## Methodology:



Scheme of the methodology adopted to e



Questionnaire surveys;  
 with a trustworthy information  
 in the short-term the possible  
 in reducing airborne particle



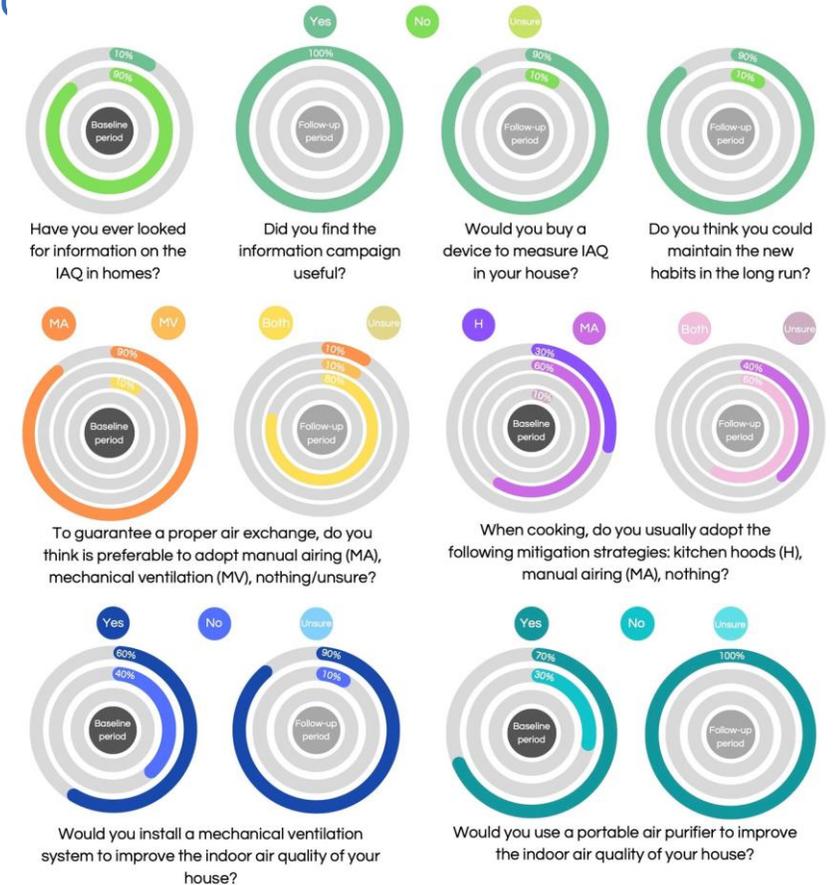
an information campaign and an experimental

# Feedback

Effectiveness of eco-feedback in improving the indoor air quality in residential buildings: mitigation of the exposure to different airborne particle metrics

Results:

- the investigated population **is not properly aware** of the IAQ in their homes and of their exposure to airborne particles; indeed, they perceive the indoor air quality mostly affected by the outdoor rather than possible indoor sources;
- the **misperception of the IAQ also affects occupants' habits and intentions**: they do not routinely use mitigation strategies while indoor sources are in operation, and, in case, their use is mainly governed by other reasons than air quality (i.e. reducing smells and relative humidity)



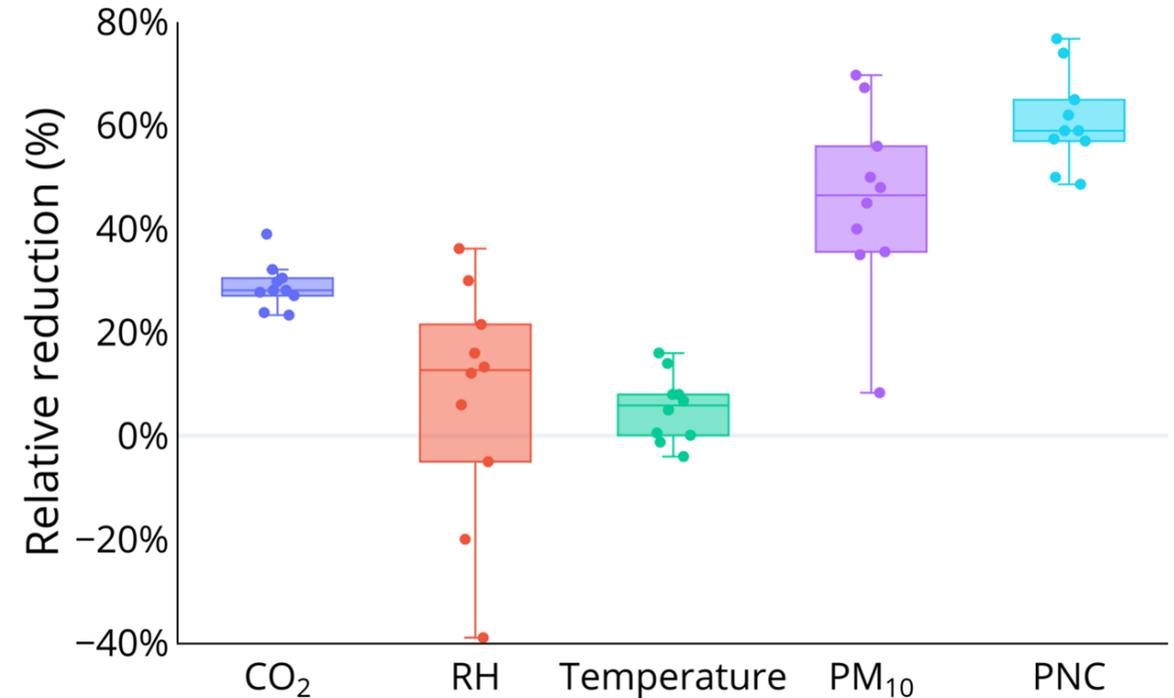
Change in perceptions, habits, and intentions of the IAQ of the ten families involved in the eco-feedback strategy

# Feedback

Effectiveness of eco-feedback in improving the indoor air quality in residential buildings: mitigation of the exposure to different airborne particle metrics

Results:

- the **eco-feedback strategy adopted resulted successful** both in terms of promoting behavioral changes of the occupants and reducing the concentration levels while airborne particle emitting sources (i.e. cooking) were in operation;
- the **exposure to airborne particle metrics while cooking** events measured during the experimental campaign carried out after the information campaign (follow-up period) **resulted lower** than the baseline exposure; relative reductions of 47% and 59% were obtained for PM<sub>10</sub> and PNC, respectively;



Relative reductions amongst median values measured during cooking activities performed within baseline and follow-up periods in the 10 homes as resulting from the quantitative analysis.

# *Thanks for your attention*

## **Giorgio Buonanno**

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University of Cassino and Southern Lazio, Cassino (FR), Italy*



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