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The Environmental Science Education for Sustainable Human Health

8 September 2021

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Urban trees & Particulate Matter: how to estimate tree PM removal efficiency

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DIPARTIMENTO DI SCIENZE ECOLOGICHE E BIOLOGICHE

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Trees are good friends!

Improved Quality of Life

Social Benefits

Improved Air Quality

Reduced Runoff

Improved Biodiversity

Saved Energy

Urban Microclimate Amelioration

Noise Reduction

Reduced Soil Erosion

Improved Soil Quality

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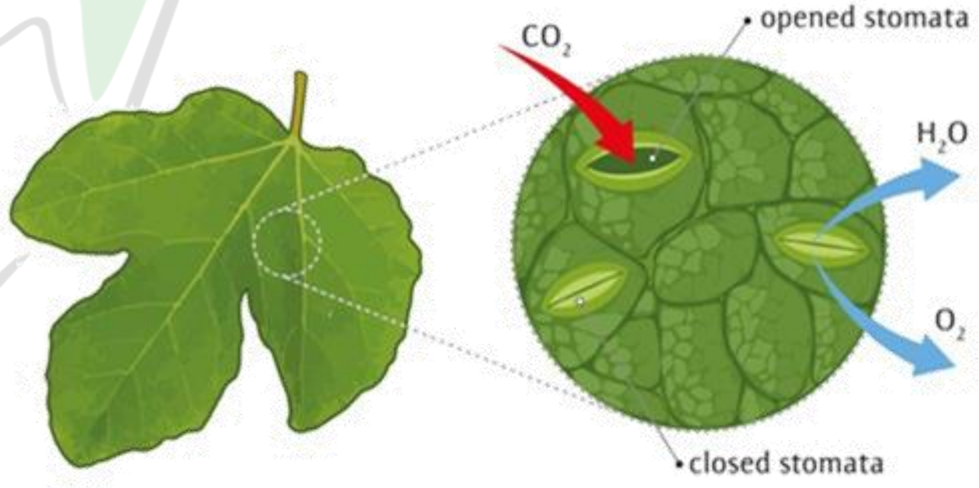
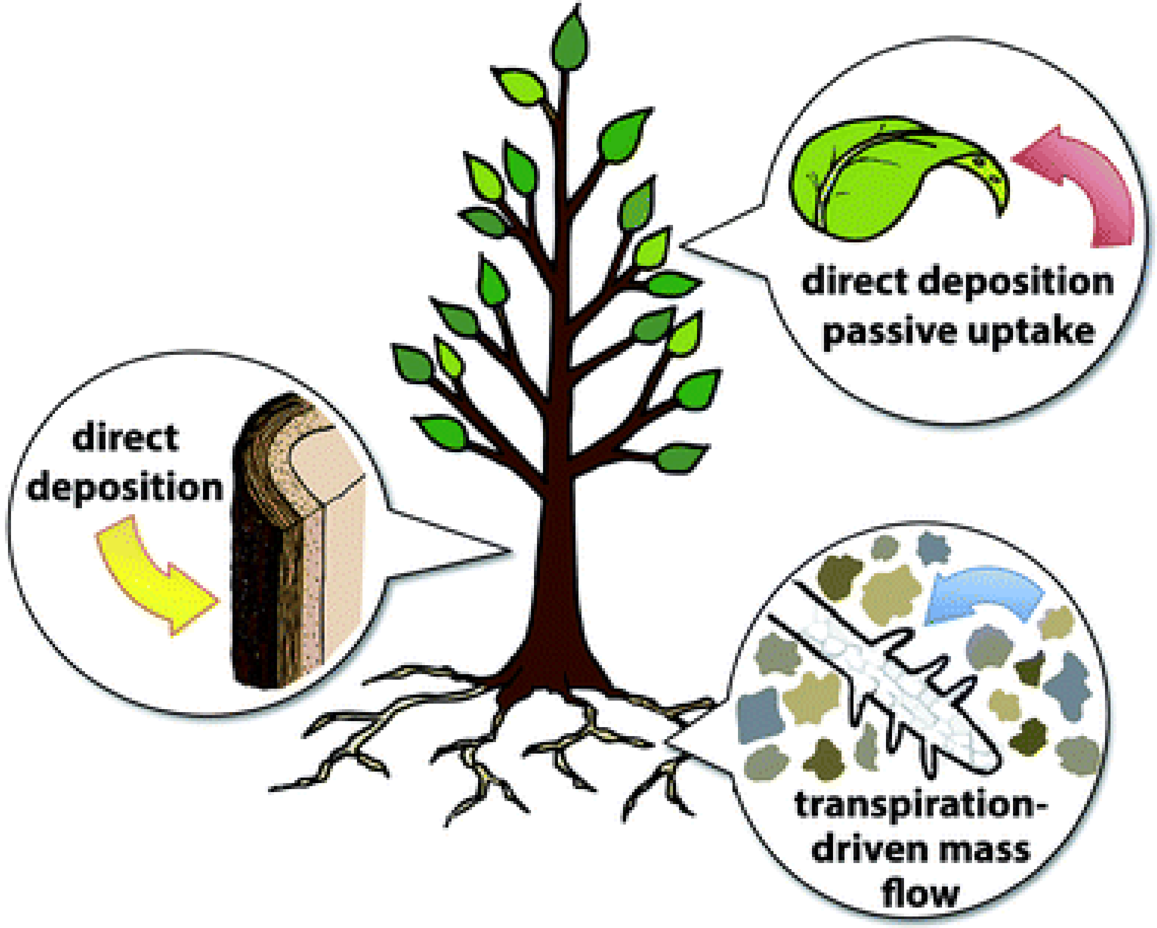
Trees capture pollutants ☺



- CO_2 from atmosphere → carbon sink
- Other gaseous pollutants (NOx, PAHs, VOCs....)
- Heavy metals form soil
- Particulate matter (PM) from atmosphere



Research highlights: natural passive samplers – plants as biomonitors
Vivian S. Lin, Environ. Sci.: Processes Impacts, 2015, **17**, 1137

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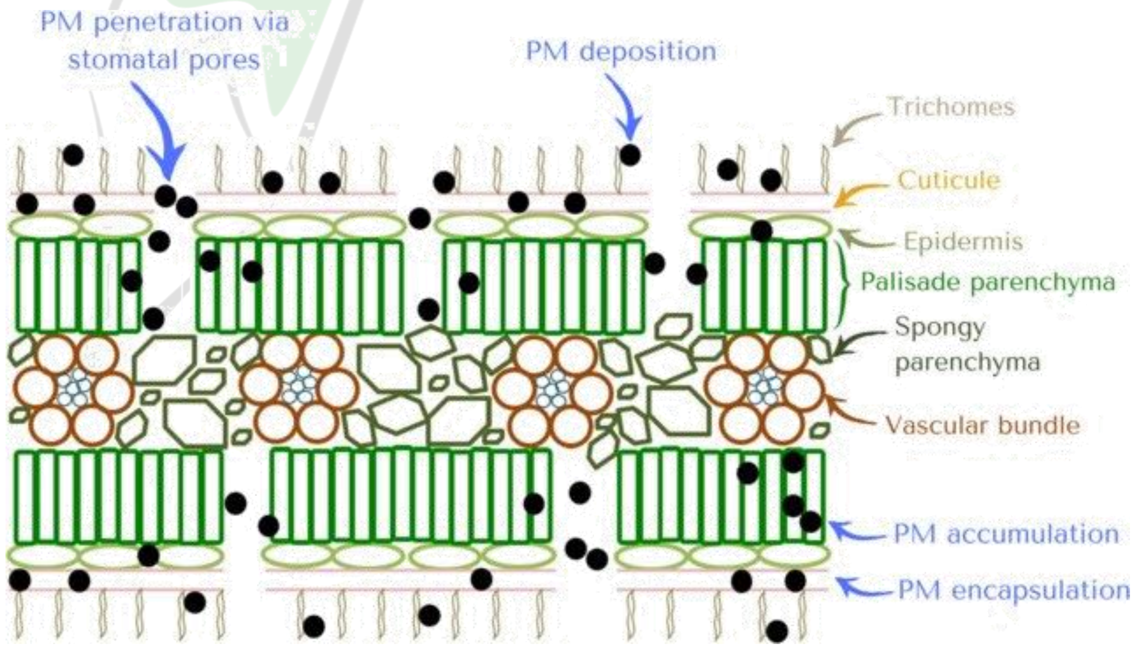
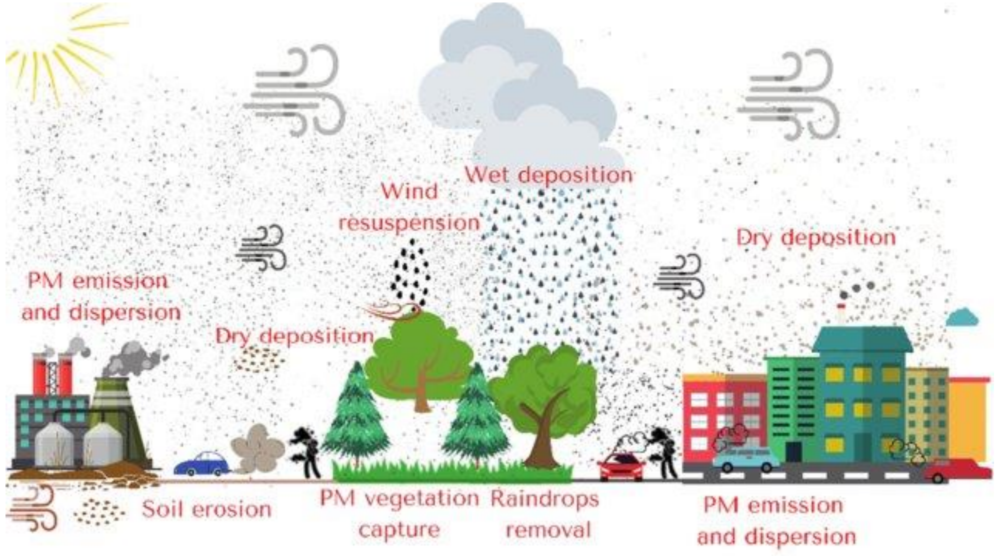
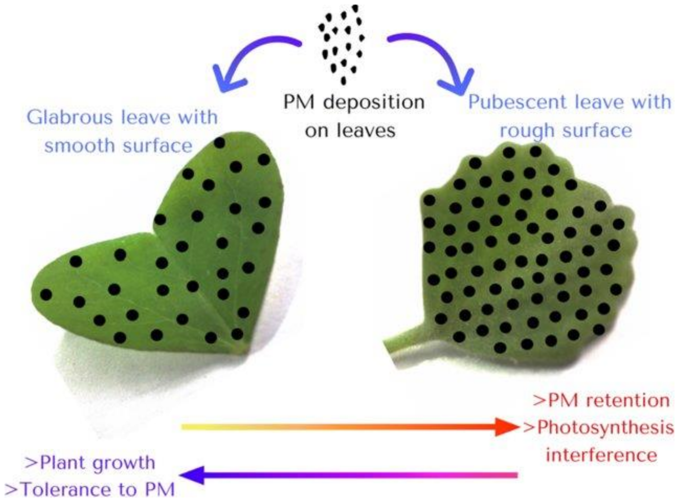
Penetration vs. deposition 😐



Particulate matter and foliar retention: current knowledge and implications for urban greening Elizabeth Chávez-García & Blanca González-Méndez, Air Qual Atmos Health (2021)





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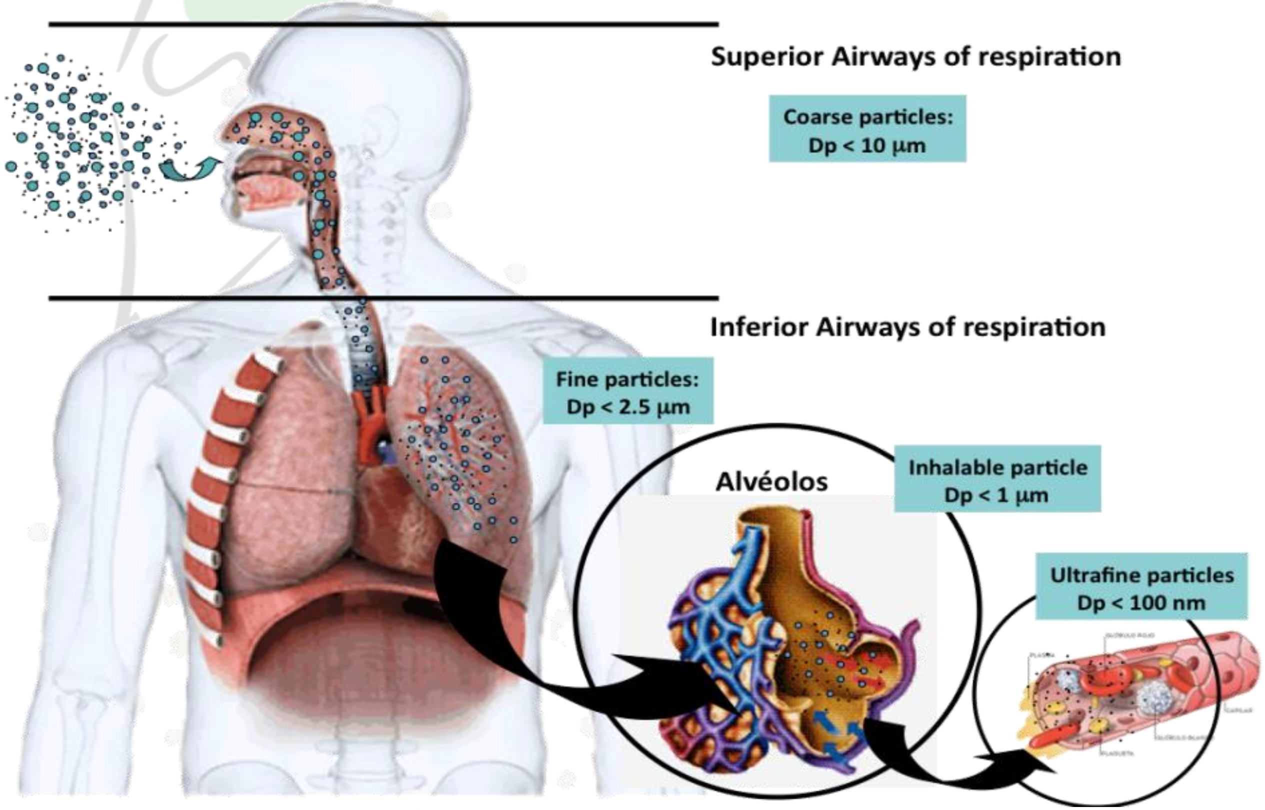
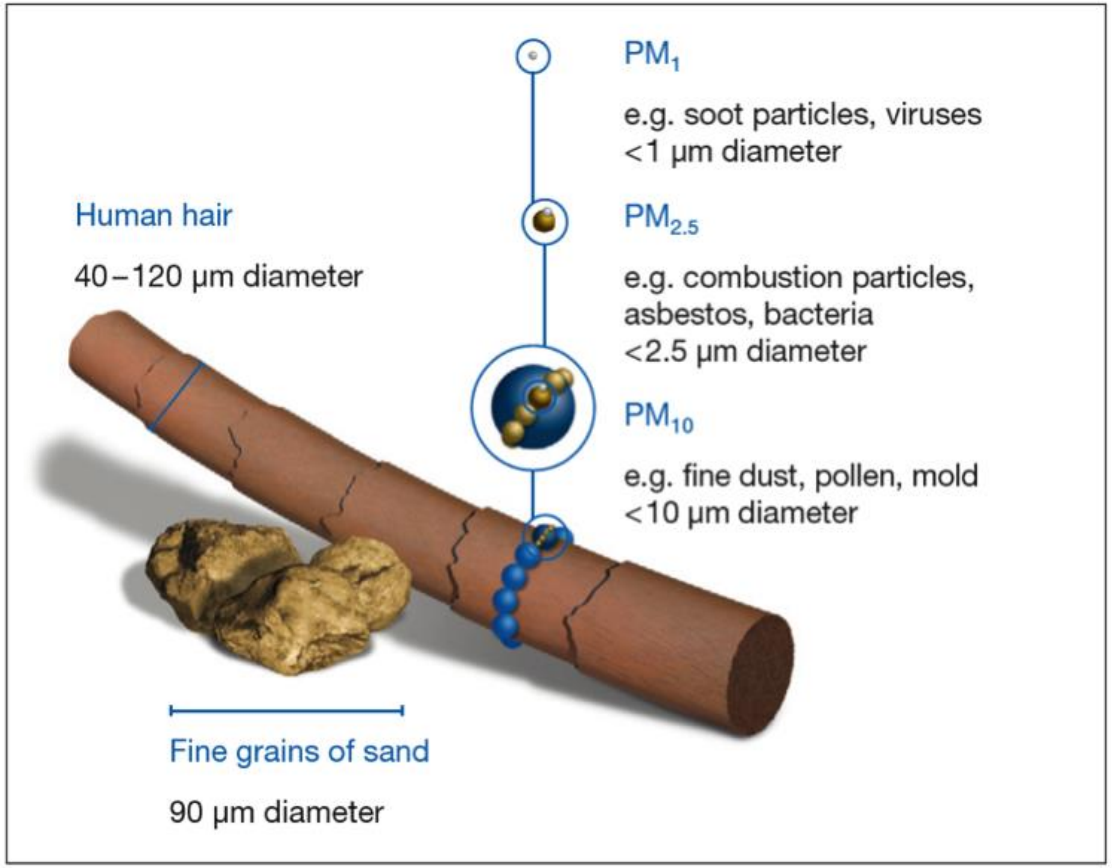
PM affects human health ☹





Main PM characteristics to know are quantity, size distribution, elemental composition

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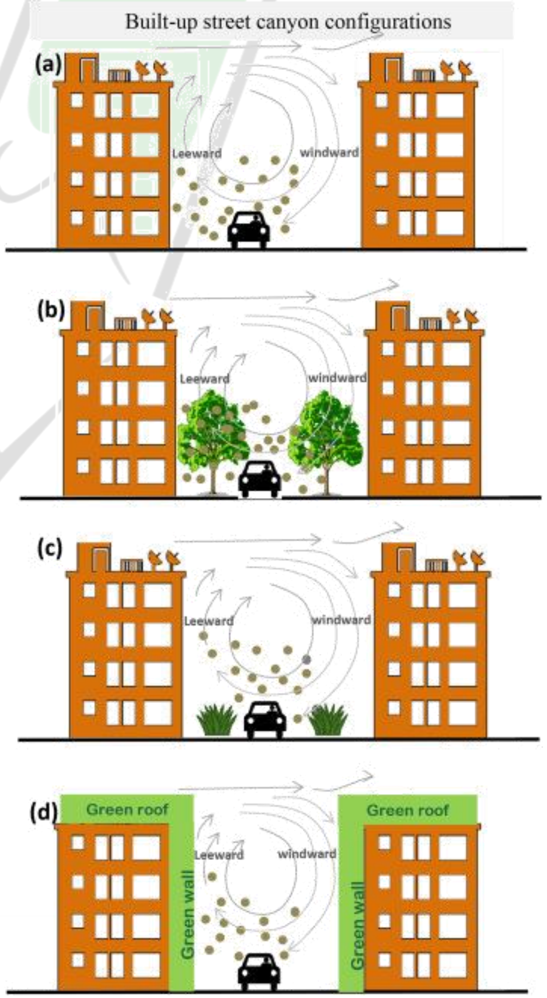
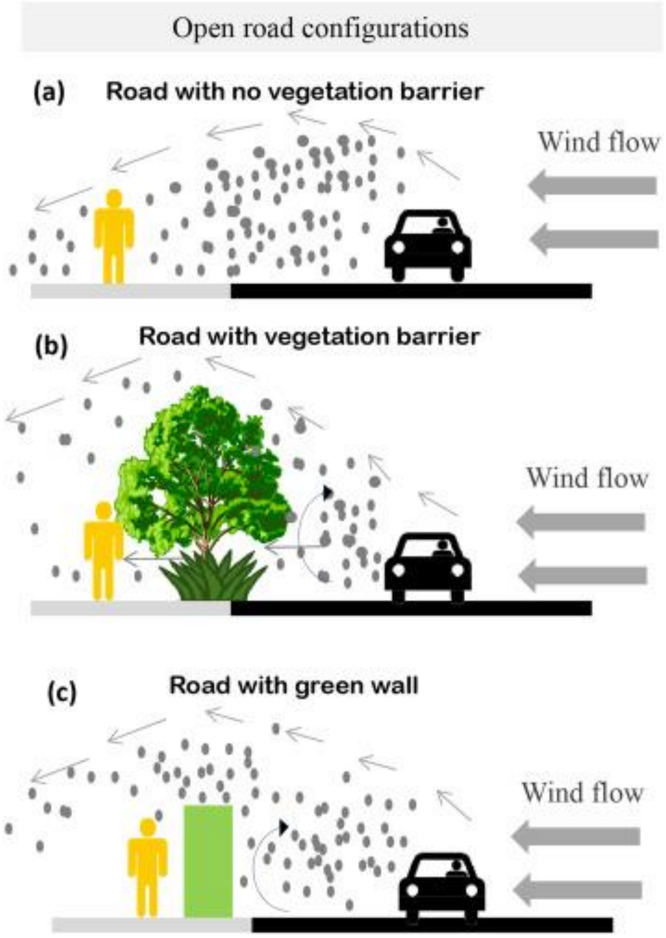
Leaves as passive filters ☺





Air quality mitigators

&

Biomonitors

Air pollution abatement performances of green infrastructure in open road and built-up street canyon environments – A review K.V.Abhijith, Prashant Kumar, John Gallagher, Aonghus McNabol, Richard Baldauf, Francesco Pilla, Brian Broderick, Silvana Di Sabatino, Beatrice Pulvirenti, Atmospheric Environment 162 (2017) 71-86.

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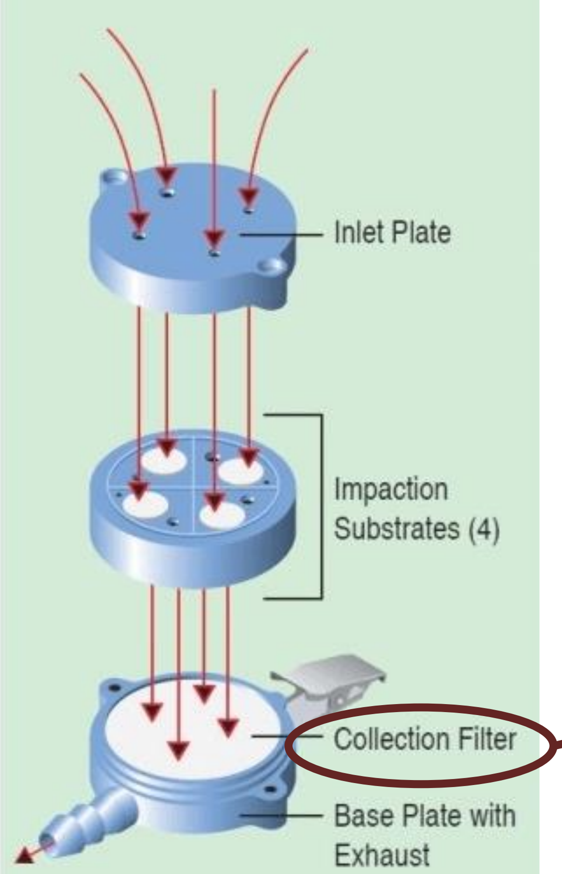
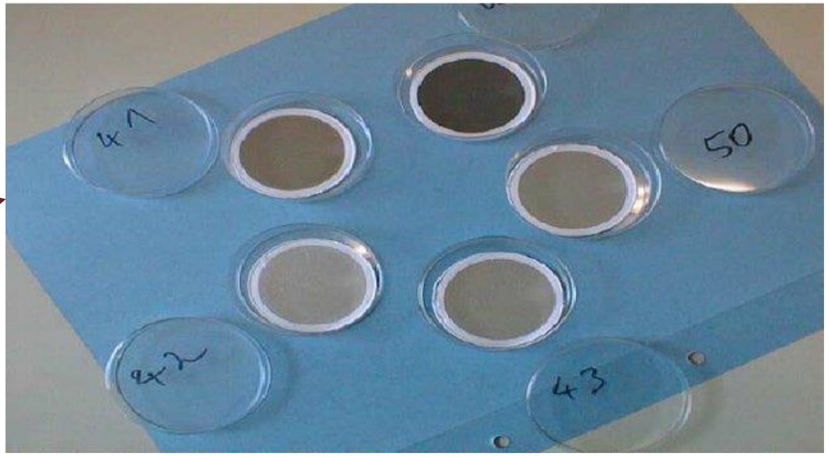
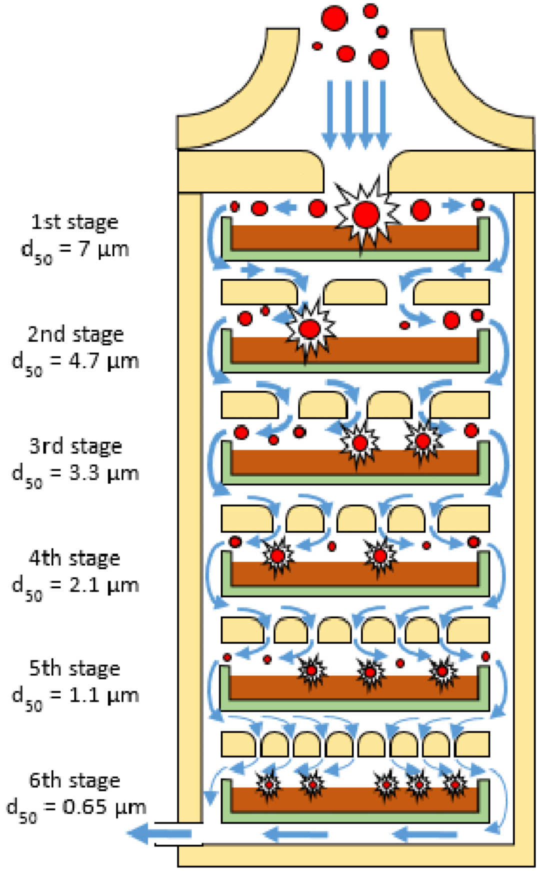
How to characteriz airborne PM ves?

Main PM characteristics to know are quantity, size distribution, elemental composition



Atomic Absorption Spectroscopy (AAS),
Gas Chromatography (GC),
… … …
↓
PM quantity
Elemental composition
and size distribution





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Could the same approach be used for leaves?

IN: Gases and penetrated PM1 from air

OUT: deposited PM from air

IN: Elements from soil

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How to characterize only leaf deposited PM?

→ washing them out!

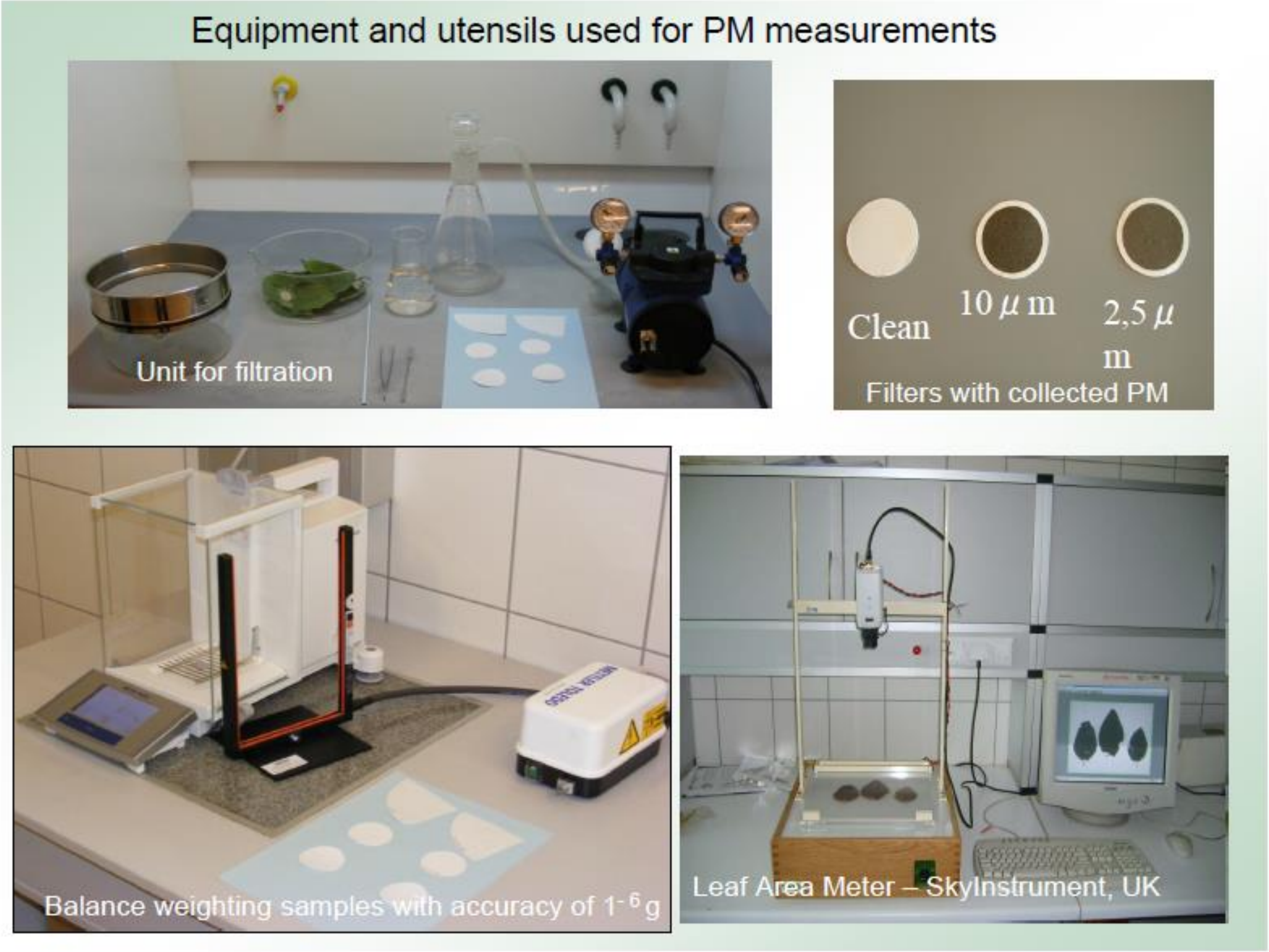
Washing & Vacuum Filtration (WF or VF)

1. Leaf Washing with water
2. Water Filtration
3. Filter Weighting
4. Leaf Area Measuring

Surface PM concentration, per size fraction:
C = weight/area [g/m²] or [mg/cm²]

Elemental composition from filter analysis

Dzierzanowski et al., International Journal of Phytoremediation 13 (2011) 1037



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Spatio-temporal variations in PM leaf deposition by VF

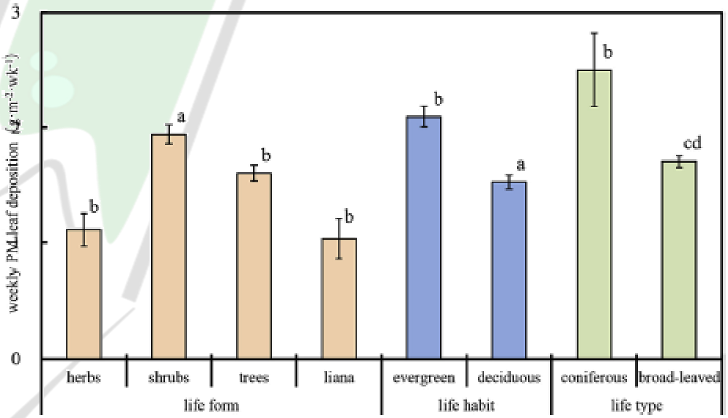


Fig. 1. Differences in PM leaf deposition among plant types.
Levels with the same letter do not significantly differ in their response to plant types, while the different letters represent the differences in PM leaf deposition among different plant types at the level of 0.05.

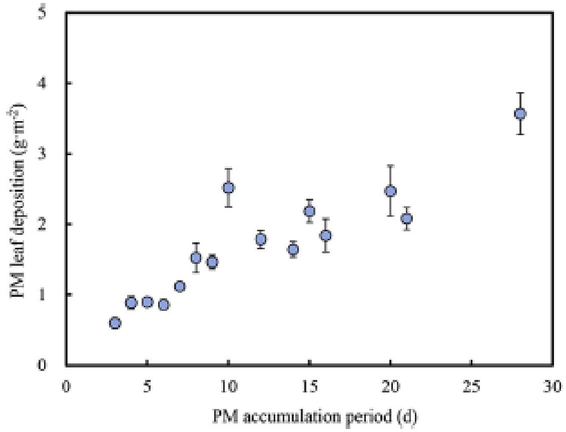


Fig. 2. Relationship between accumulation period and PM leaf deposition.

Metadata analysis by Cai et al.
Env. Poll. 231 (2017) 207-218

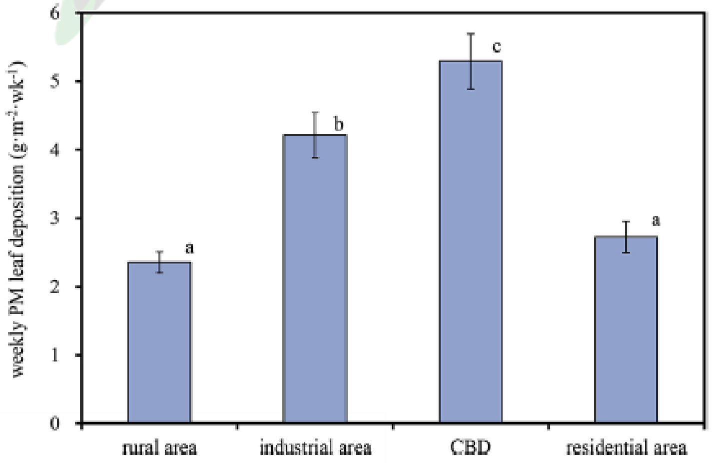


Fig. 5. Differences in weekly PM leaf deposition among land use types.

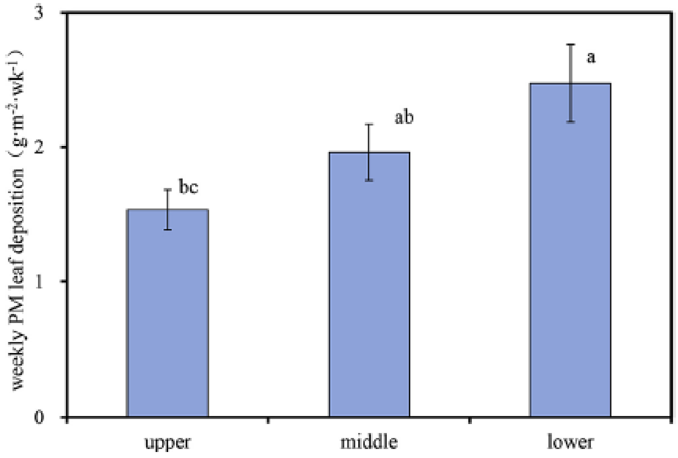
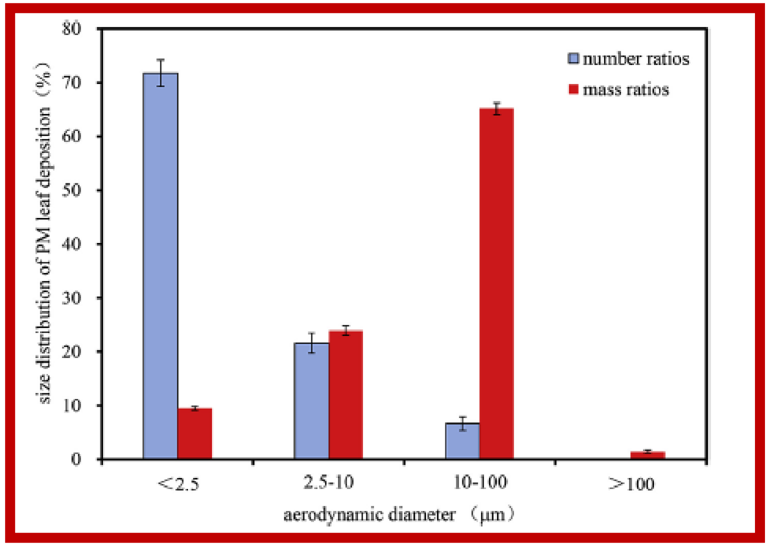


Fig 6. The influence of plant height on weekly PM leaf deposition.

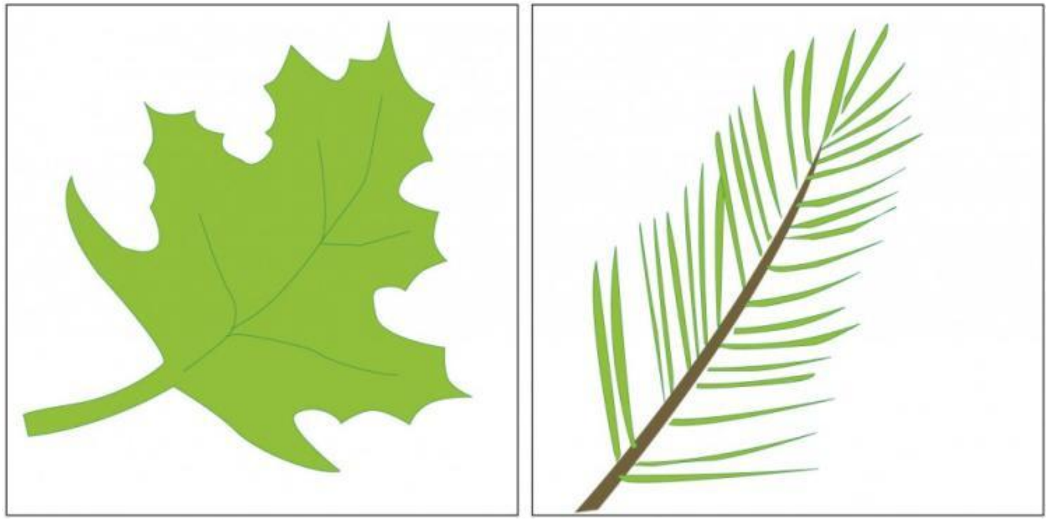


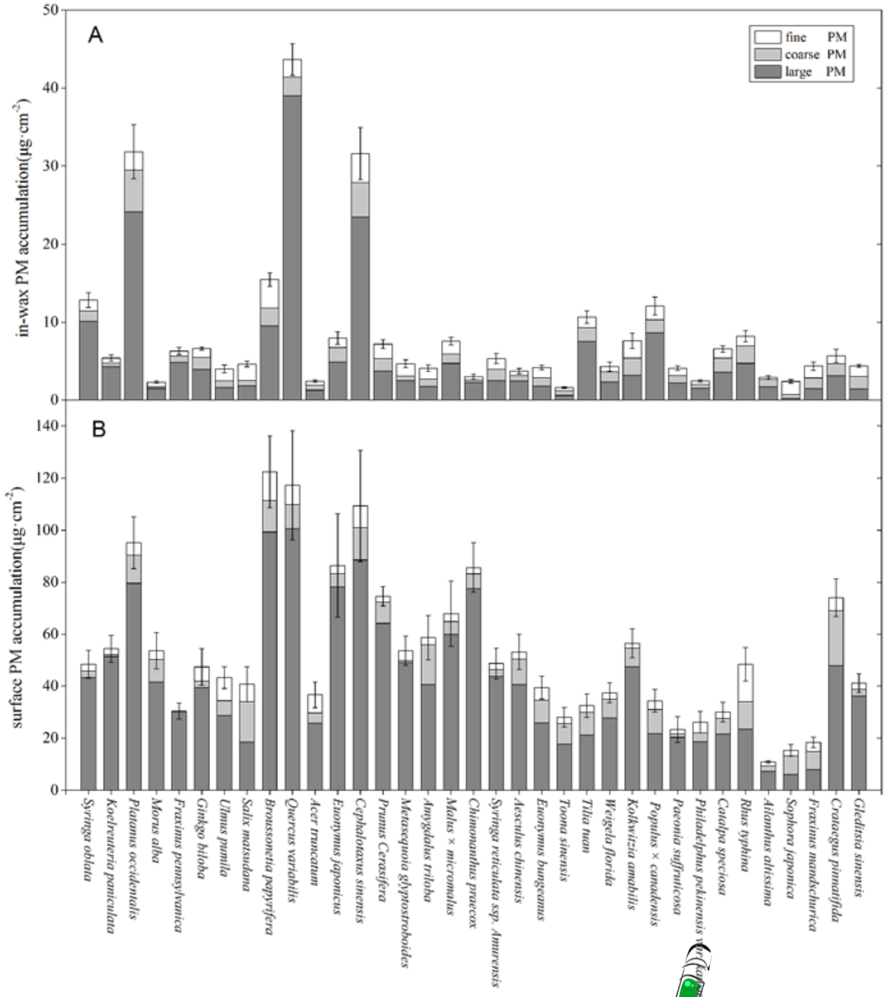
PM tree leaves capturing capability by VF

Mo et al., Plos One (2015)

Species characteristics affecting PM removal efficiency:

- Evergreen vs. deciduous
- Canopy structure
- Surface-to-volume ratio
- Leaf surface roughness and waxes





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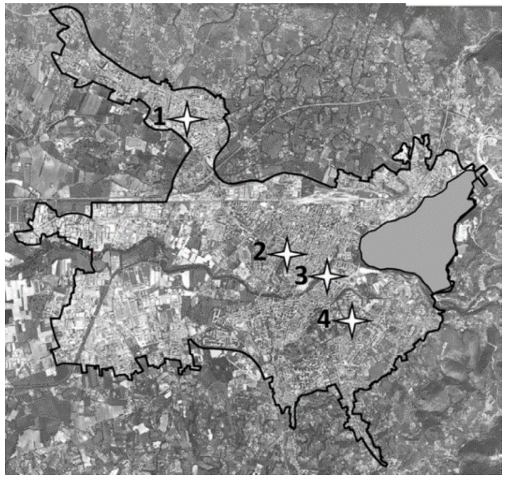
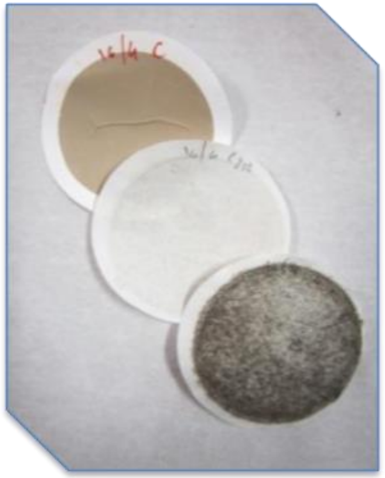
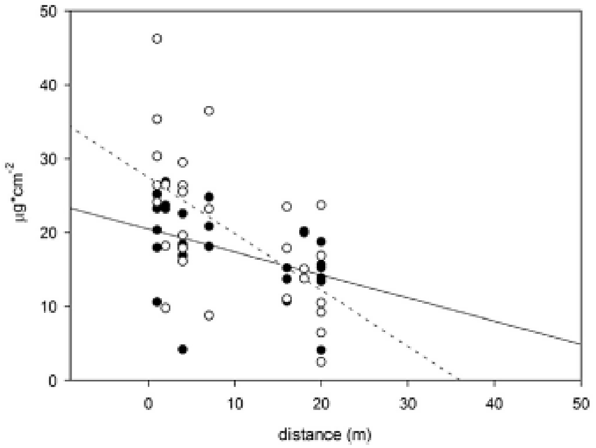
PM deposition on *Quercus ilex* leaves in an industrial city of central Italy

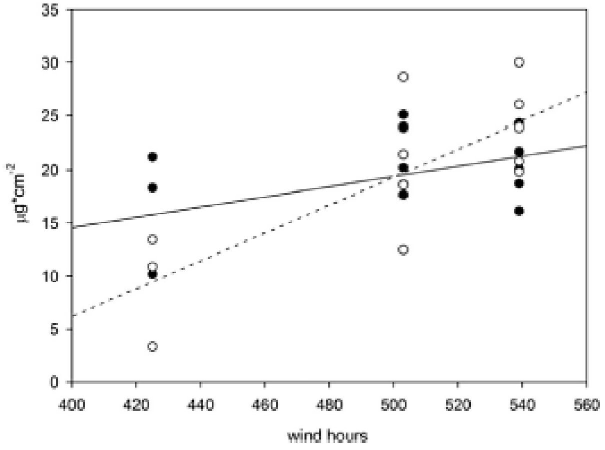
Sgrigna et al., Environmental Pollution 197 (2015) 187

- Terni: 70 day/year with PM10 concentration higher than 50 µg/m^3 in 2012
- 4 sampling sites
- 150-450 leaves per site (300-500 cm^2)
- Leaf washing in both water (surface deposited PM: sPM) and **chloroform (in-wax PM: wPM)**
- 3 filtration steps (PM>10, PM2.5-10, PM2.5-0.2)









- Street effect: OK
- Wind effect: OK
- **No correlation with air quality station data**

What is missing?

- **PM smaller than 0.2 µm**
- **Soluble PM**

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How to quantify the PM soluble part?

Electrical conductivity (EC) of solutions is a raw, but fast, method to estimate the total dissolved solid (TDS), i.e. the amount of ions present in the solution

TDS (ppm) = TDS (mg/ml) = 0.65 X EC (µS/cm)

Rusydi (2018) Correlation between conductivity and total dissolved solid in various type of water: A review. IOP Conf. Ser.: Earth Environ. Sci.118:012019

To compare TDS with the PM amount estimated by VF:

TDS (mg/cm²) = [TDS (mg/ml) x V (ml)]/[A (cm²)]

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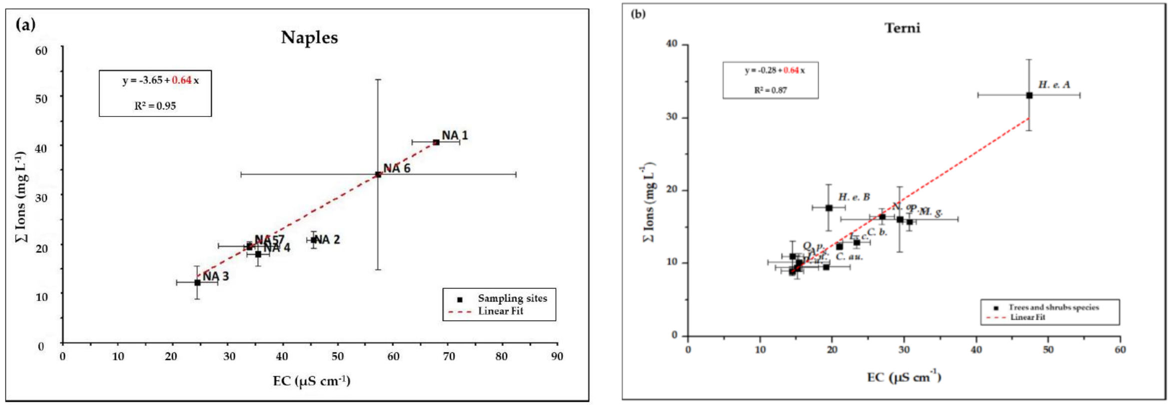
Is it reliable?

Ristorini et al., Int. J. Environ. Res. Public Health **2020**, 17, 5717

- 2 study sites: Naples (high concentration of marine salt in PM; same species, different locations) & Terni (no marine aerosol; different species in the same location)
- 3 replicates per tree
- Only water leaf washing in both cases
- EC of filtered washing solution has been measured
- Filtered leaf washing solutions were also analysed by:

- ionic chromatography (IC) for the detection of Cl, F, NO3, PO4 and SO4
- inductively coupled plasma mass spectrometry (ICP-MS) for the detection of the concentration of Al, As, B, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Si, Sn, Sr, Tl, Ti, U, V, W, Zn
- UV-Visible spectrophotometry for NH4+ detection

- Total ion mass has been obtained and compared with EC



YES! TDS (ppm) = TDS (mg/ml) = k + 0.64 X EC (µS/cm)

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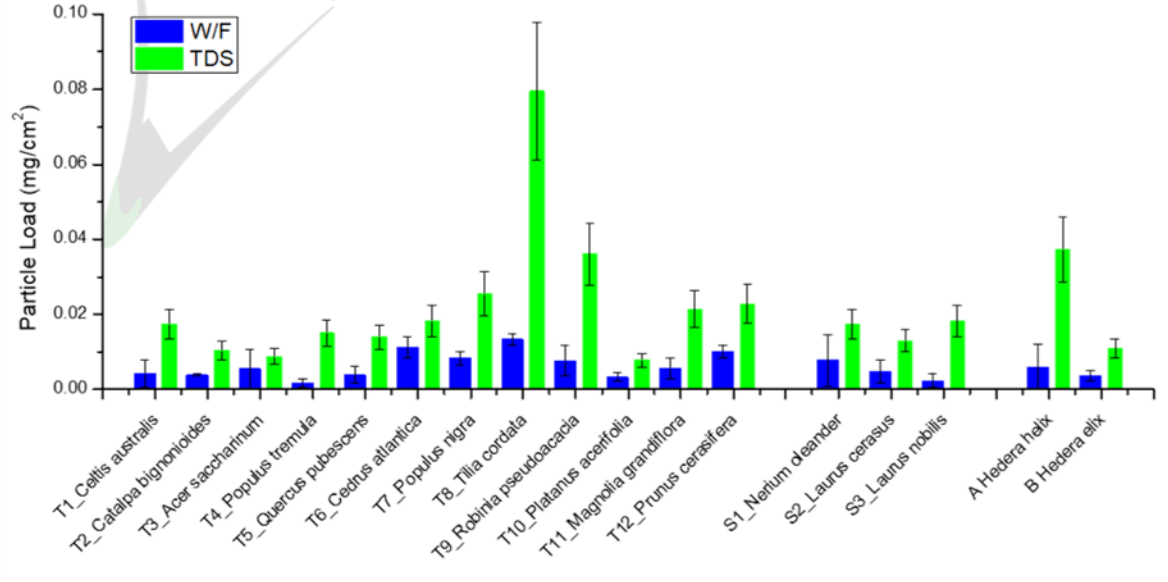
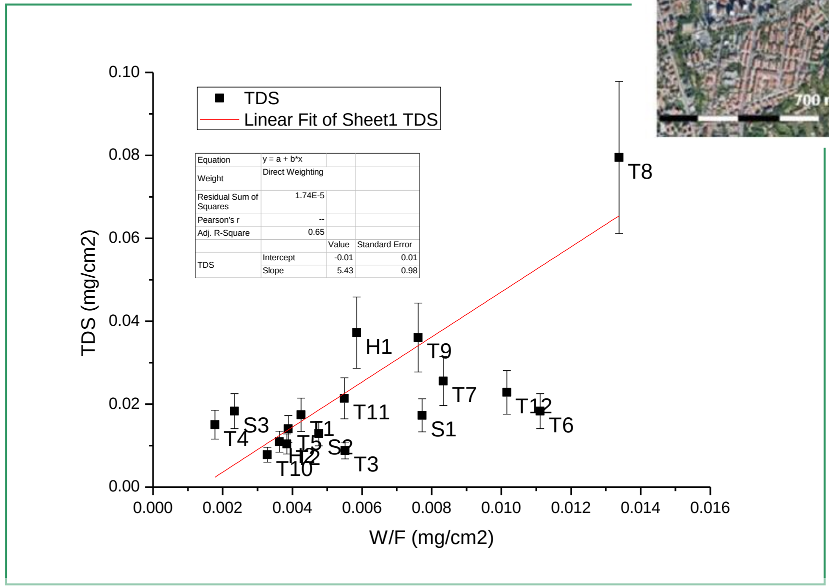
How much PM load do we lose with VF?

- Terni (no marine aerosol; different species in the same location)
- 3 replicates per tree
- Only water leaf washing in both cases
- EC of filtered washing solution has been measured
- PM load by VF has been measured and compared with TDS from EC





How can this be avoided?

- A large part of PM load is lost with VF
- Airborne PM cannot be distinguished by plant products (e.g., honeydew in Tilia cordata)

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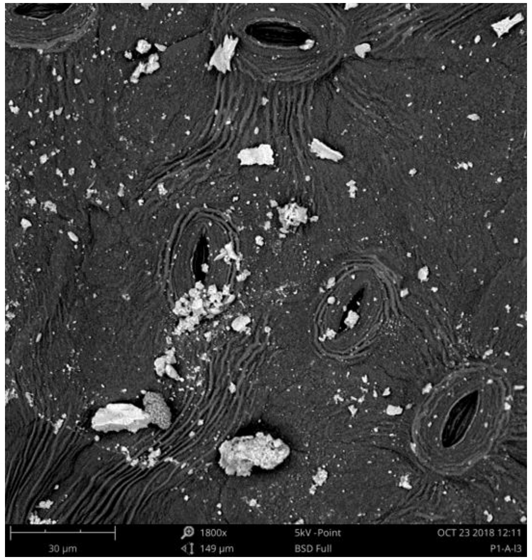
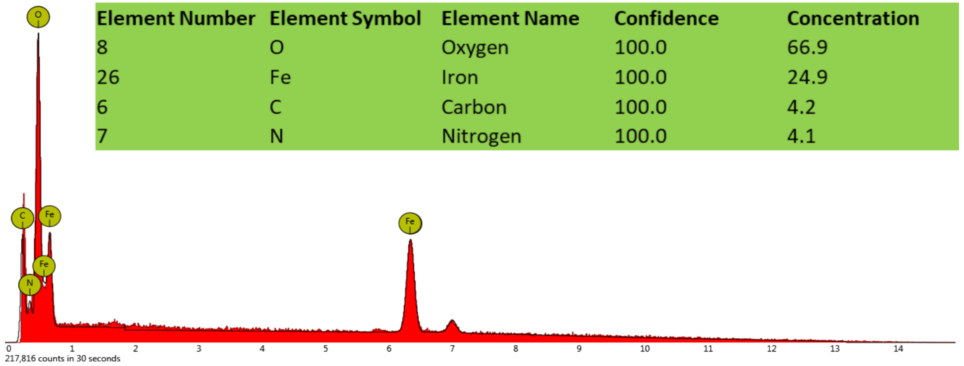
What do we need?

- To discriminate PM particles from plant secretions on the surface
- To measure how many PM particles we have on the leaf surface **without washing**
- To know their size distribution
- To characterize their elemental composition

➢ Imaging particles on the leaf surface as it is

➢ Obtaining the elemental composition of each particle





Element Number	Element Symbol	Element Name	Confidence	Concentration
8	O	Oxygen	100.0	66.9
26	Fe	Iron	100.0	24.9
6	C	Carbon	100.0	4.2
7	N	Nitrogen	100.0	4.1

Scanning Electron Microscopy (SEM)
coupled with
Energy Dispersive X-Rays Spectroscopy (EDX)

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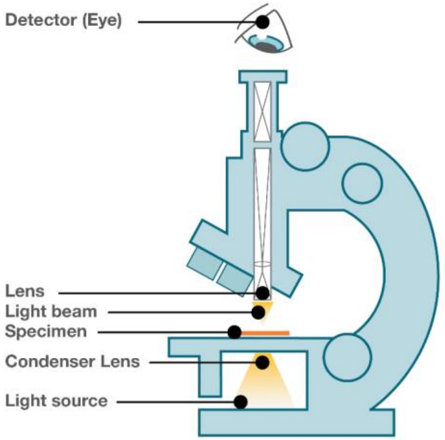
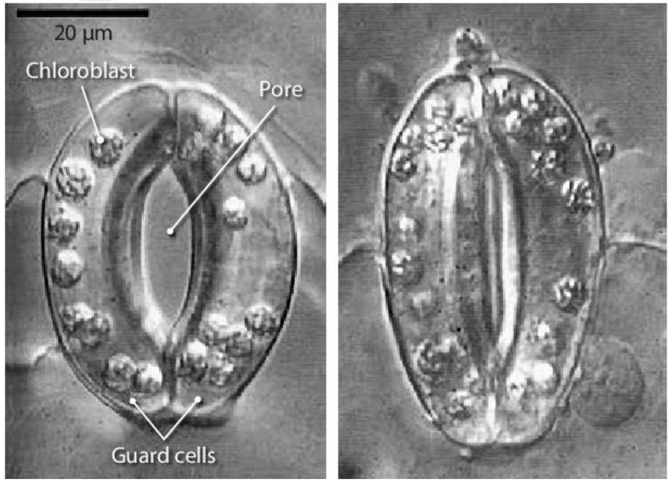
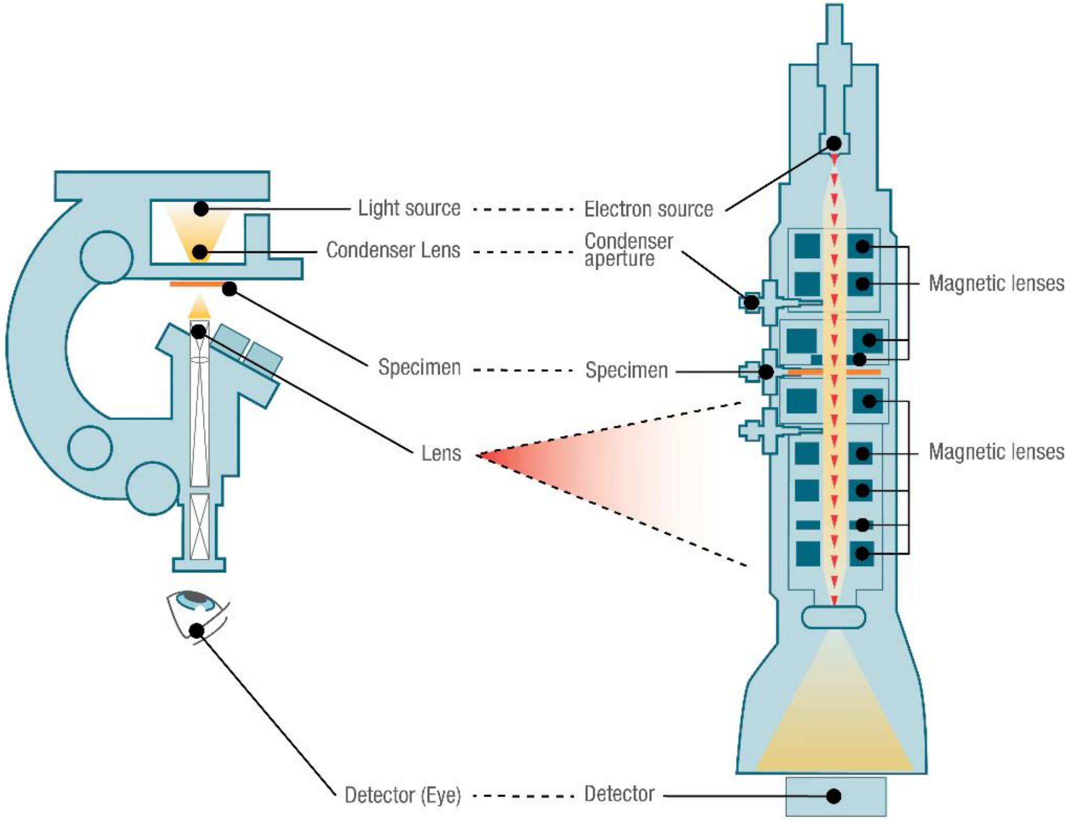
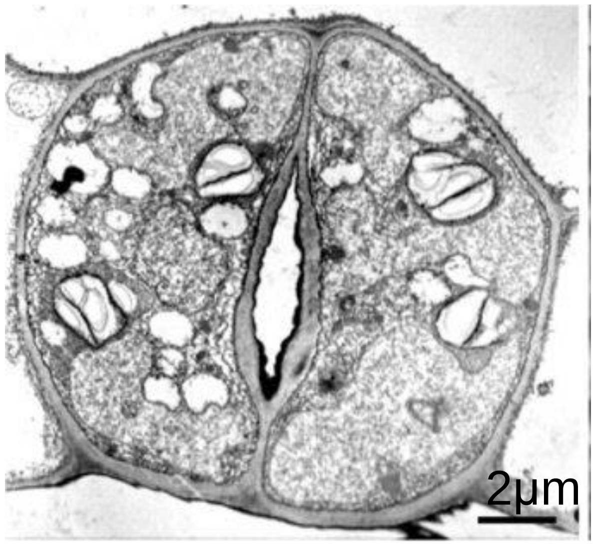
Light vs Electron Microscopy









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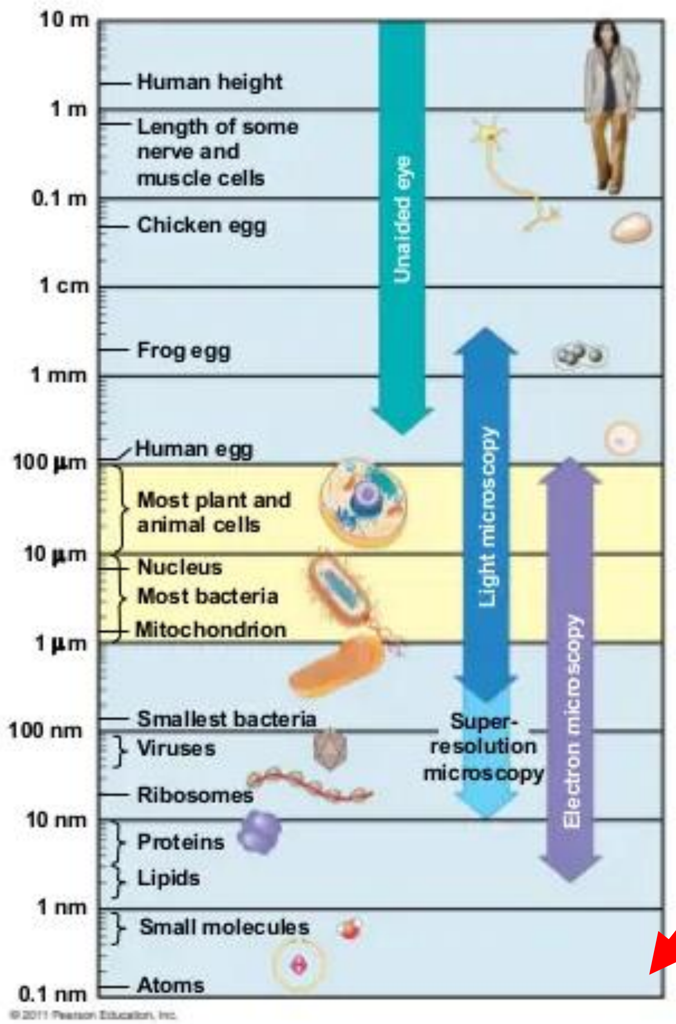
Imaging Resolution

Resolution:
minimum distance between two objects that can be discriminated



Scanning Probe Microscopies

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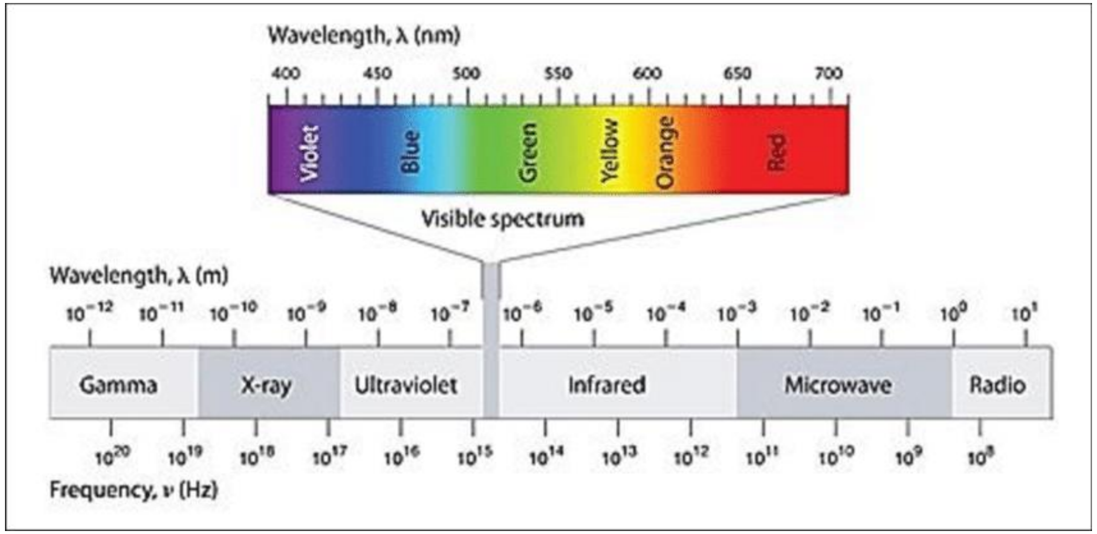
Light vs Electron Microscopy: Resolution

- Radiation-Matter Interaction
- Resolution due to "probe" wavelength

Rayleigh Formula

$$R = 0.61 \frac{\lambda}{NA}$$

	Light Microscopy (1590-1900)	Electron Microscopy (1930-1970)
Probe	Photons	Electrons
Wavelength	$\lambda = \frac{c}{\nu}$	$\lambda = \frac{h}{p} = \frac{h}{mv}$
Wavelength Range	380-780 nm	0.01-0.0005 nm
Resolution	100 nm	1 nm



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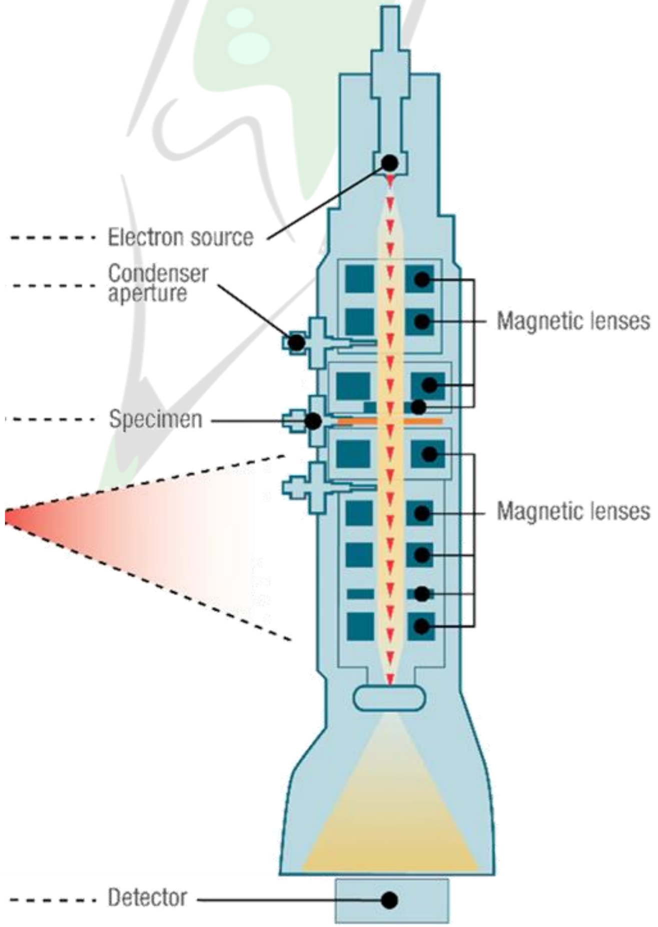
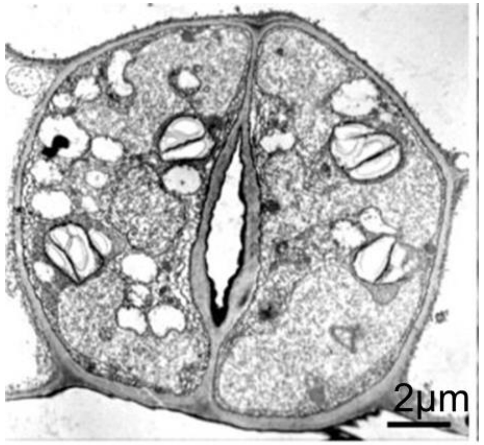
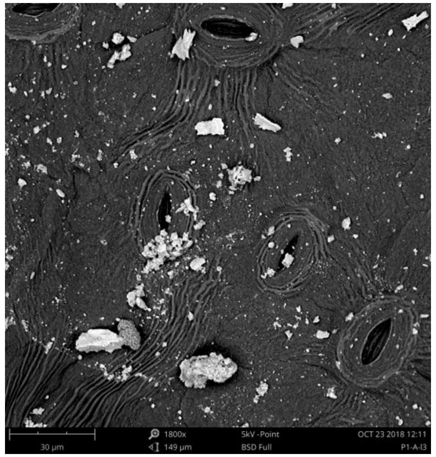
Electron Microscopy: Transmission vs Scanning

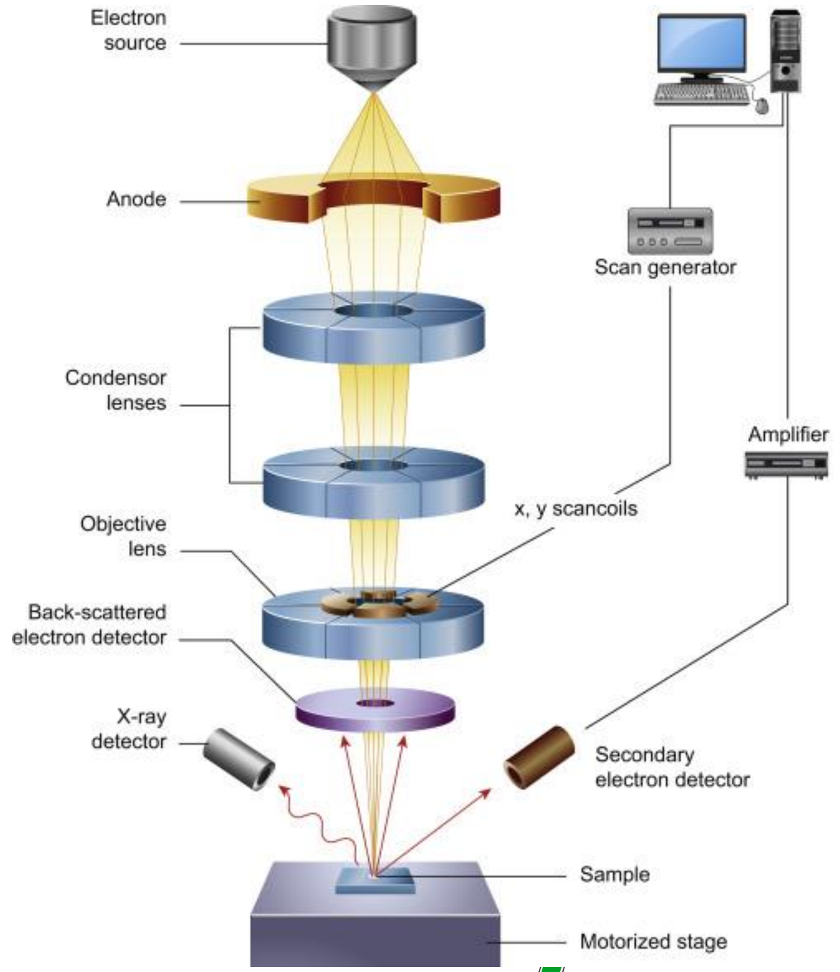




TRASMISSION



SCANNING



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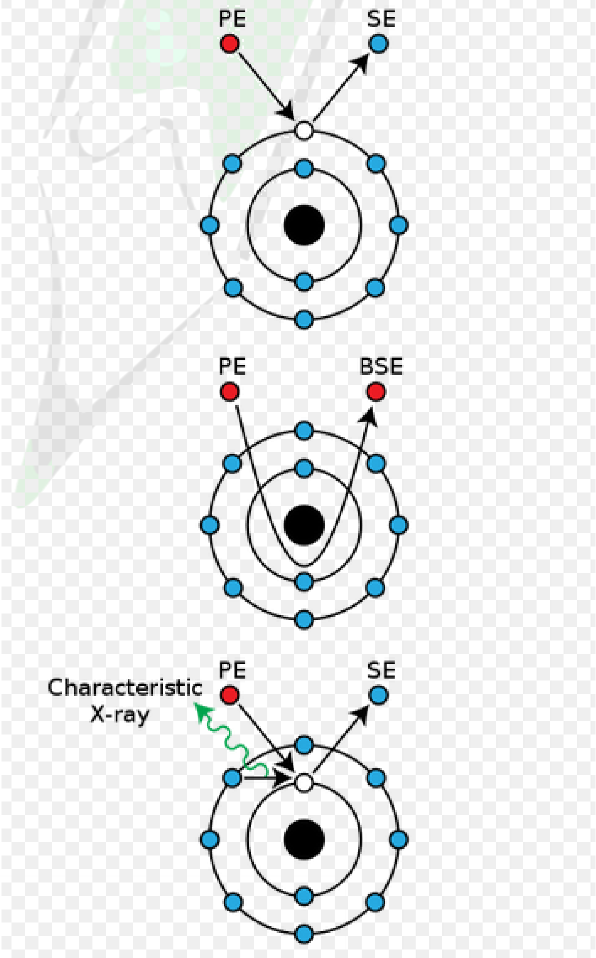
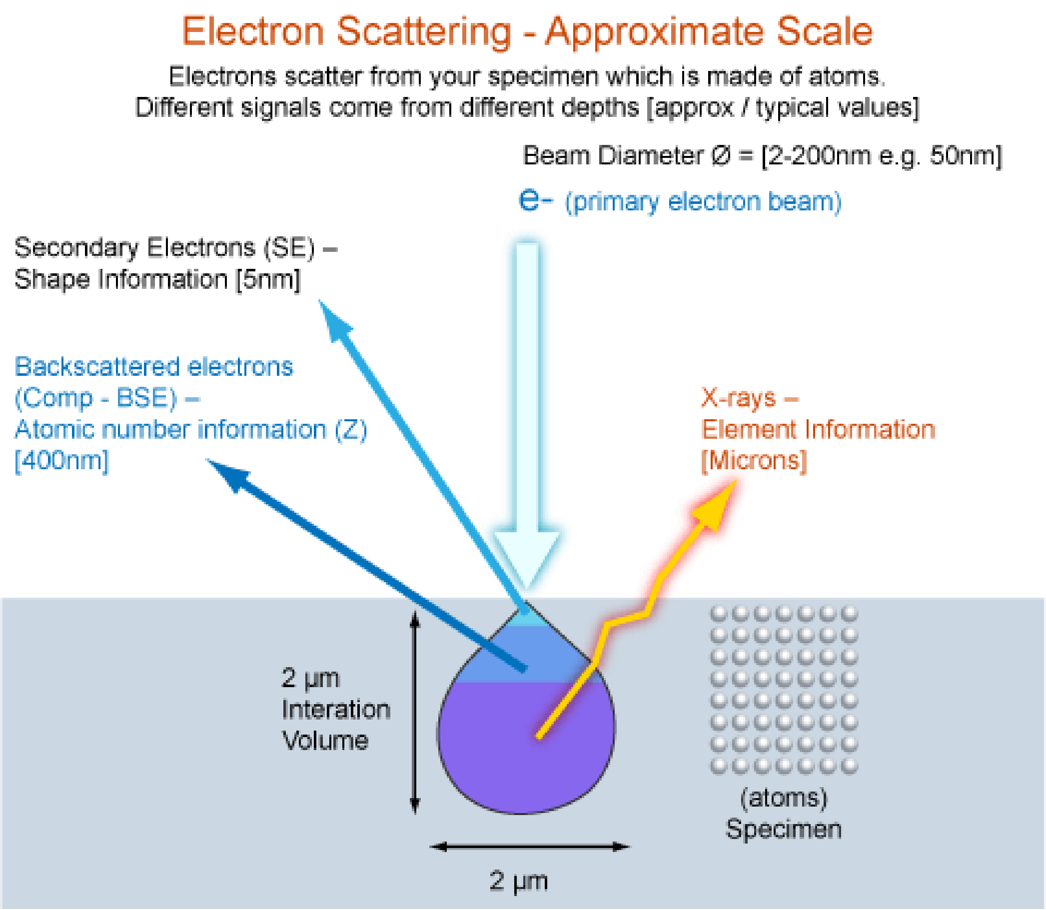
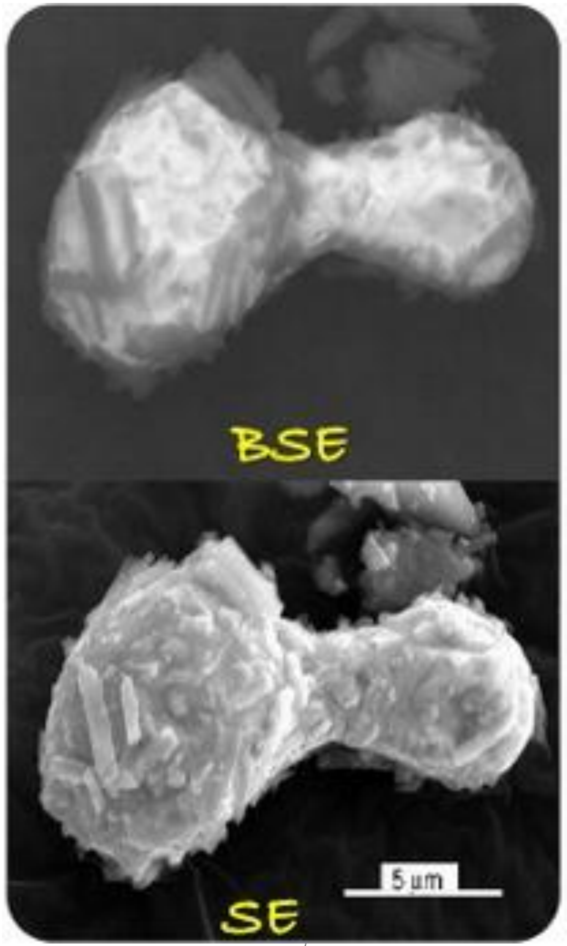
Electron-matter interaction in SEM







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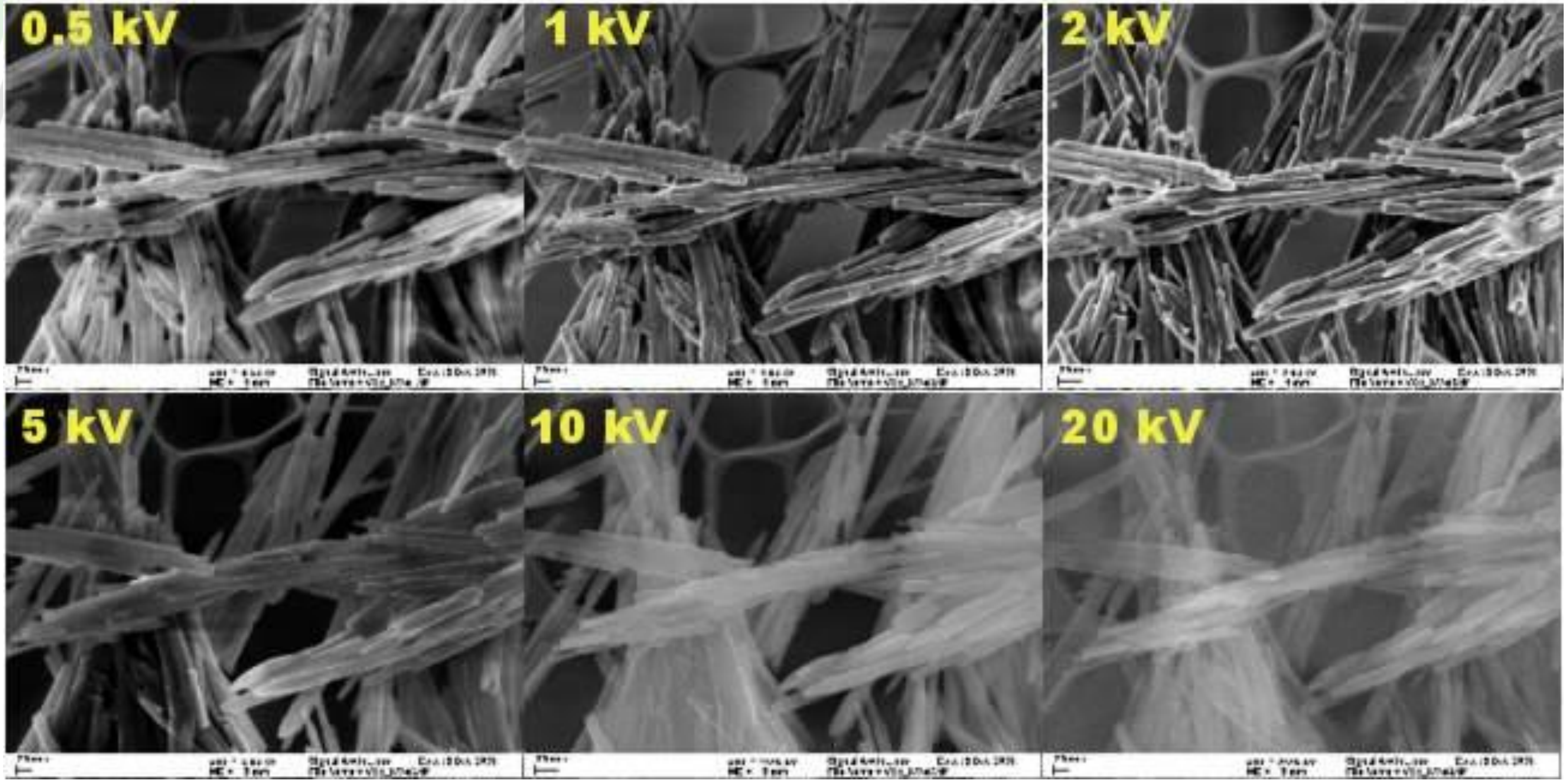
Electron energy and surface sensitivity

Decreasing the electron energy → decreasing the interaction volume



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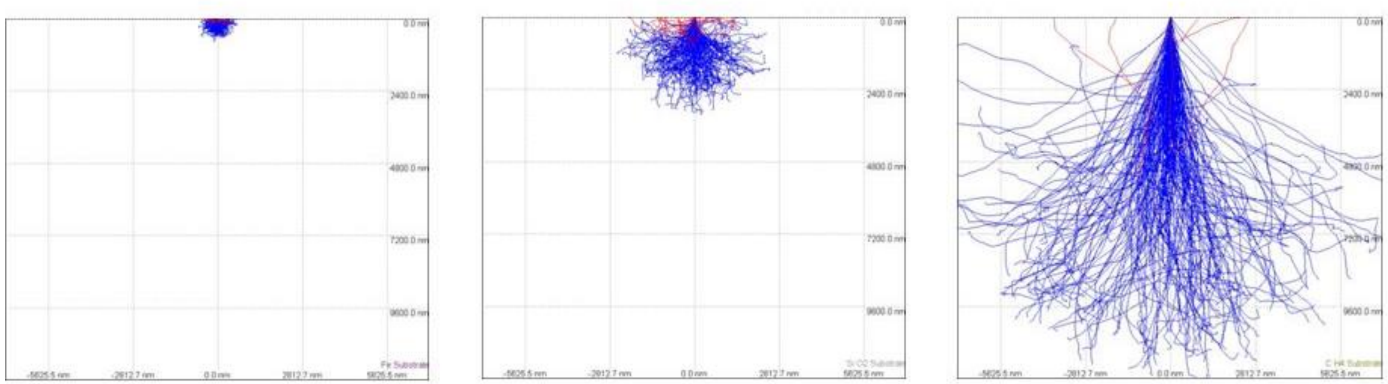
Surface atomic density and SEM sensitivity

Increasing the atomic number → decreasing the interaction volume

Electrons undergo many random *scattering events* after entering a solid specimen. The computer simulations below show the paths of 250 electrons in different materials.



Fe SiO2 Organic

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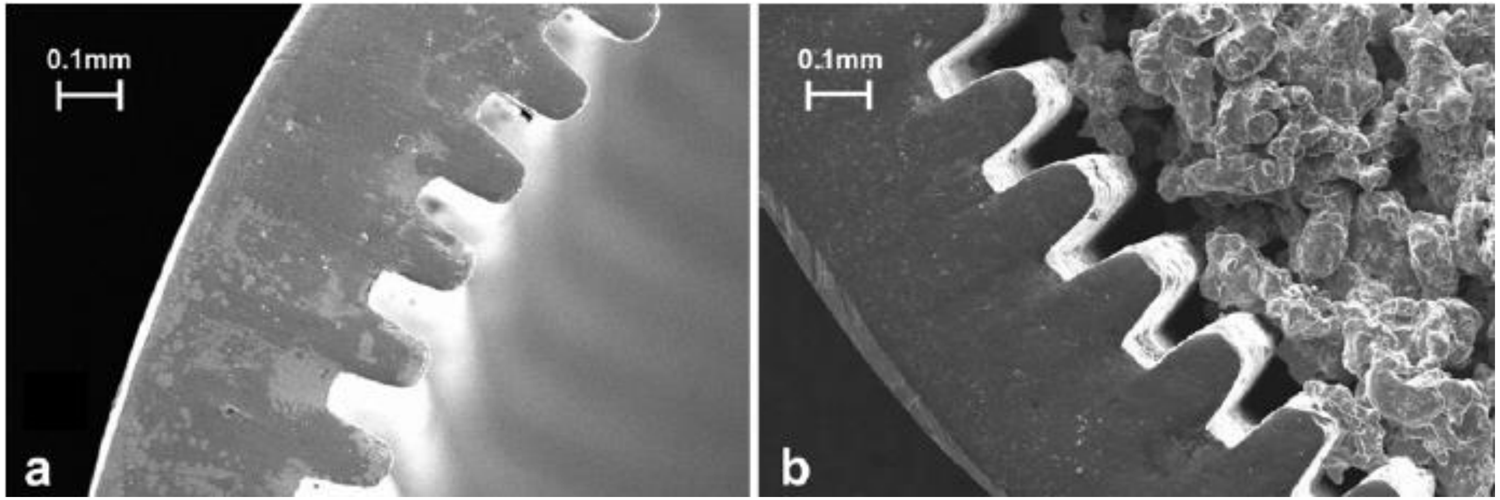
High-vacuum (Low-pressure) electron microscopy

DROWBACK: High-vacuum is required for the good functioning of both electron source and detector

Large apparatus
High cost

Injected electrons accumulate on non-conductive sample surface, disturbing the imaging process
→ **metallization and freezing are required for biological sample!**



SEM images of a sintered-grooved composite wick: (a) without copper powders sintered on, (b) with copper powders sintered on.
[Applied Thermal Engineering 50 (2013) 342-351]

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Low-vacuum (High-pressure) electron microscopy

- The high vacuum in the electron column optics is separated from the high-pressure zone by differential pumping through a pressure limiting aperture
- Surface charge effects are reduced
- No metallization is required
- Biological samples can be analyzed "as it is"
- Smaller and less expensive apparatus are required

DISADVANTAGES:

- Low-vacuum microscopes only work with Back Scattered Electrons
- Low resolution (10 nm)

STILL OK FOR OUR PURPOSE!

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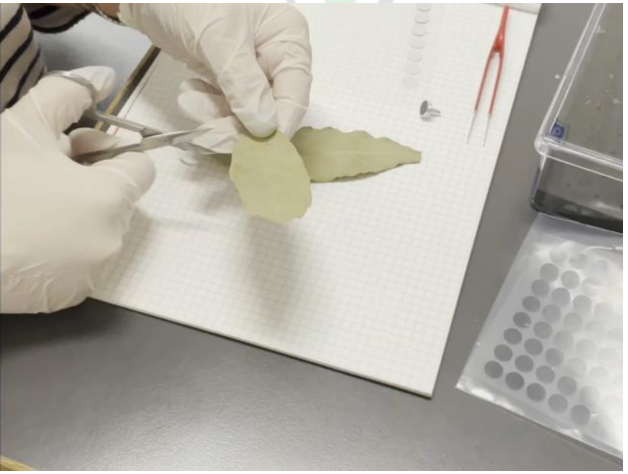
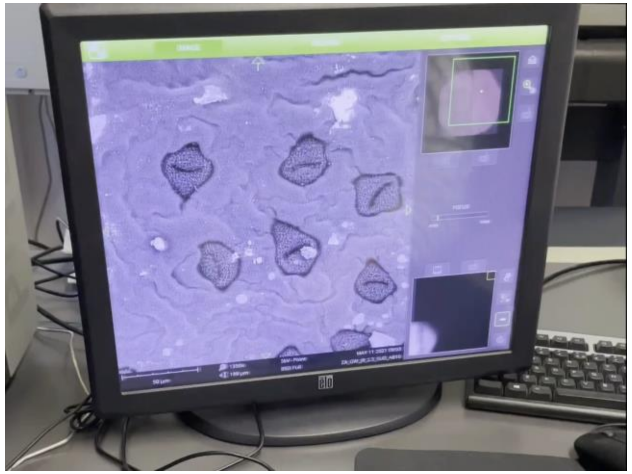
SEM characterization of “as it is” leaves





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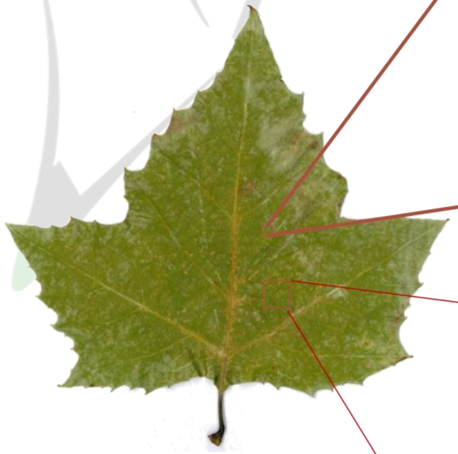
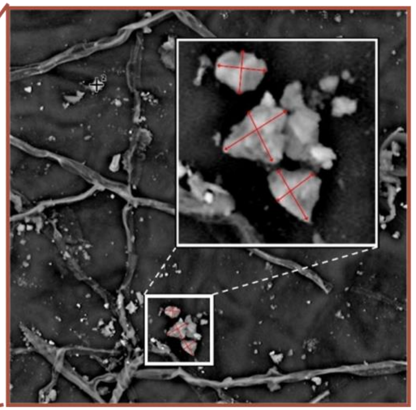
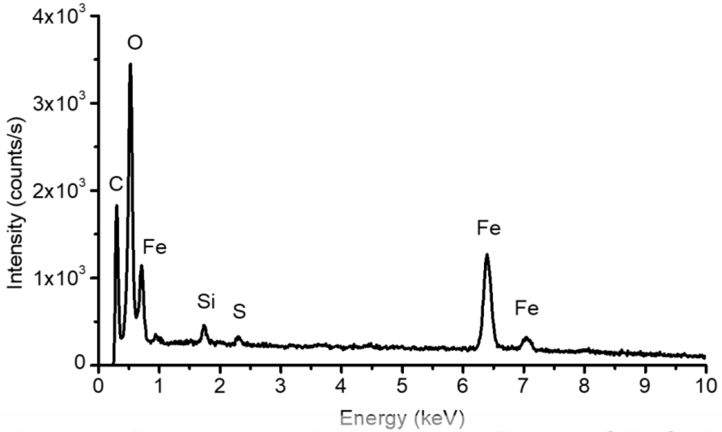
PM quantification by SEM/EDX



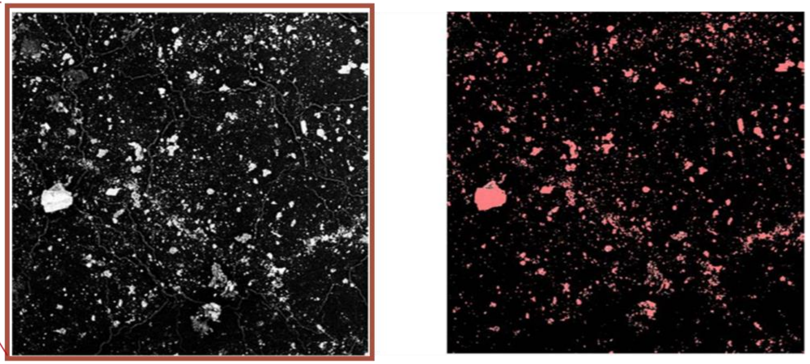




$$W_{\%_x} = \frac{\sum_{i=1}^{N} C_{x_i} \times V_i}{\sum_{i=1}^{N} V_i}$$

Baldacchini et al., ES&T 2017

Particle size (V_i) & Elemental Composition (C_{xi})→ Weighted Percentage ($W_{\%x}$)



$$M = \sum_x \frac{W_{\%x} \cdot V_{PMtot} \cdot am_x}{A_{leaf}}$$

Baldacchini et al., ESPR 2019

PM total volume (V_{PMtot}) per imaged leaf area (A_{leaf}) by grain analysis & $W_{\%i}$ → PM mass per unit leaf area (M)

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MENVIPRO

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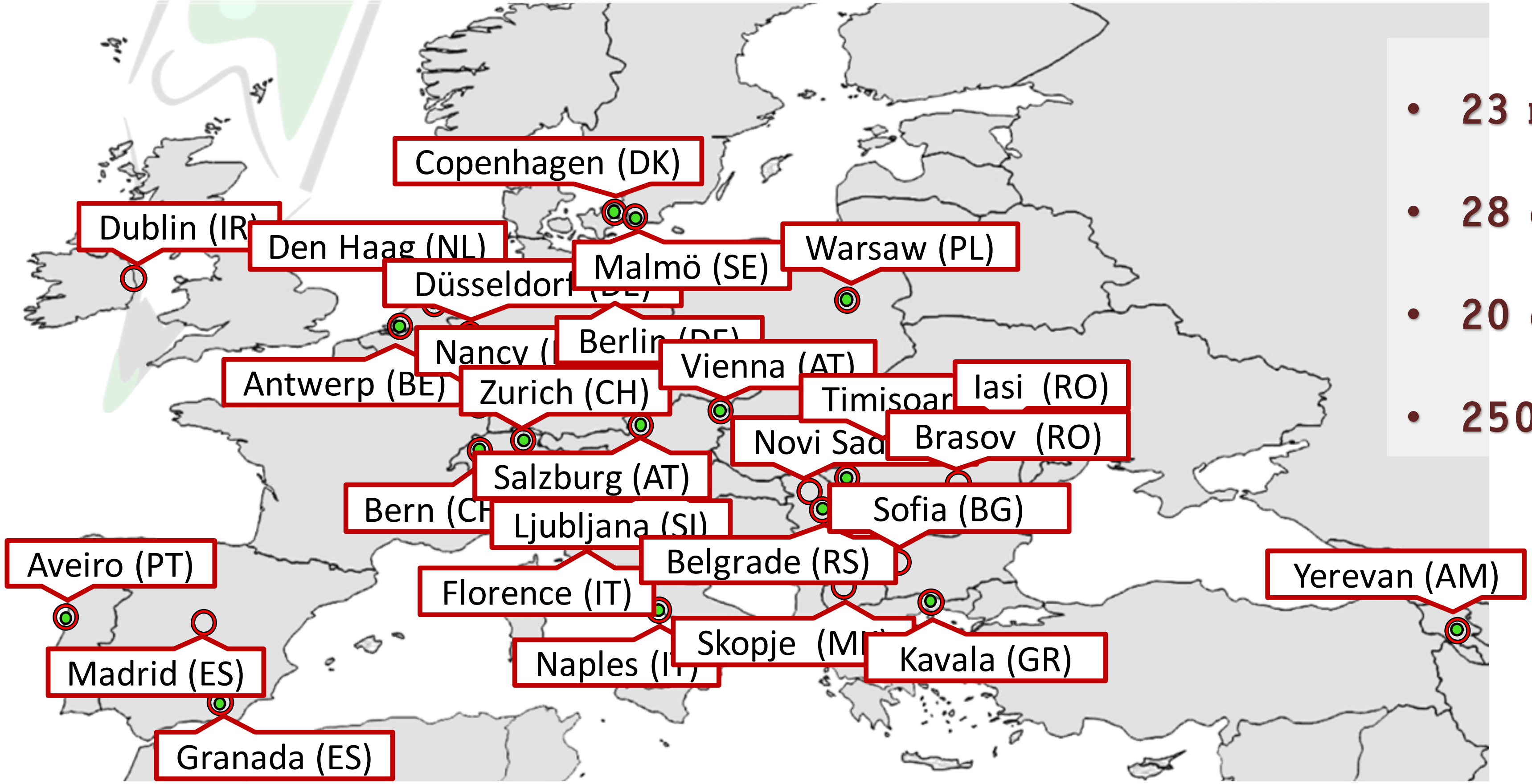
Source apportionment: A European Sampling Campaign

Same tree species in differently source-exposed sites

Baldacchini et al., ES&T 51 (2017) 1147



- 23 research groups
- 28 cities
- 20 countries
- 2500 km X 5500 km

COST FP1204 GreenInUrbs

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Source apportionment: A European Sampling Campaign

Same tree species in differently source-exposed sites

Baldacchini et al., ES&T 51 (2017) 1147

The sampling protocol

- A **street** and a **park sites** per each city
- A single **sampling species**, *Platanus acerifolia*
- **Sampling period** between August 25th and September 7th, 2014
- Sampling after a **rainless period** of at least 3 days
- **Sampling height** between 3 to 5 meters
- **5 leaves per each site**, dried and stored between clean paper sheets → Consiglio Nazionale delle Ricerche; Universiteit Antwerpen

- **Metadata** (distance from the nearest street, mean traffic density, surrounding buildings' height)
- **PM10 concentration data** provided by the nearest air quality monitoring station

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Source apportionment: A European Sampling Campaign

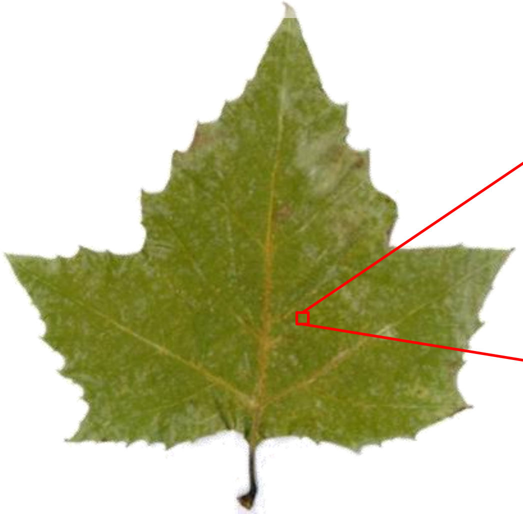
Same tree species in differently source-exposed sites

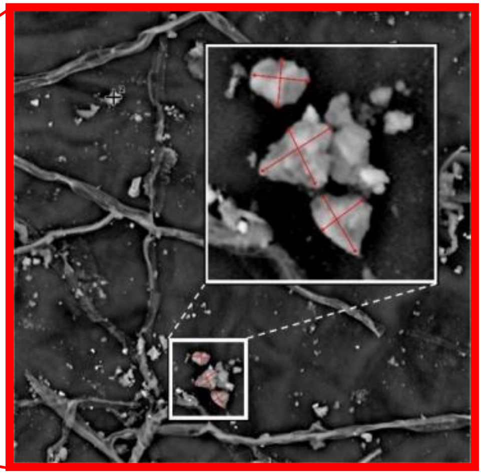
Baldacchini et al., ES&T 51 (2017) 1147

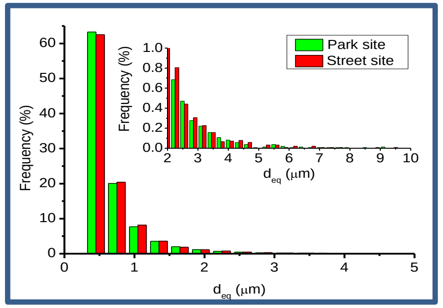
The Labs

Consiglio Nazionale delle Ricerche

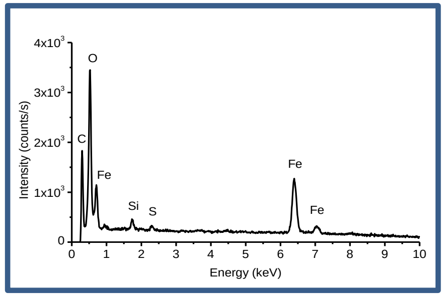
SEM/EDX





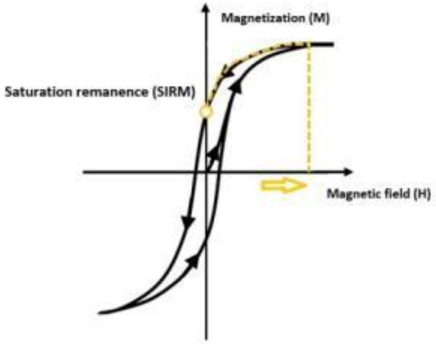


- Particle density and size distribution
- Elemental Composition



Universiteit Antwerpen

SIRM



- Leaf magnetic content
- Particle magnetic moments and chemical structure

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Source apportionment: A European Sampling Campaign

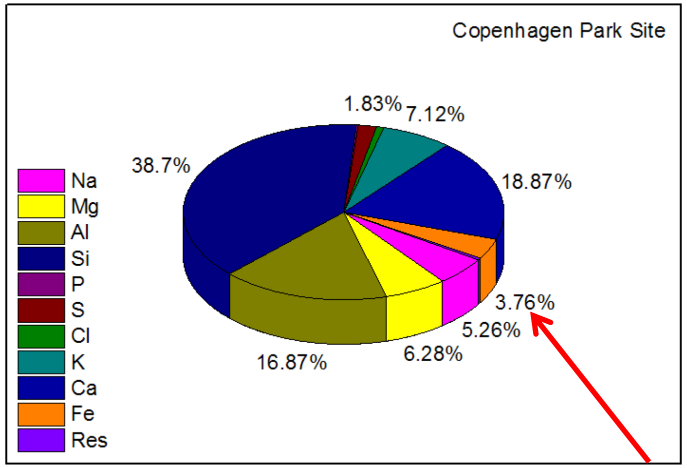
Same tree species in differently source-exposed sites

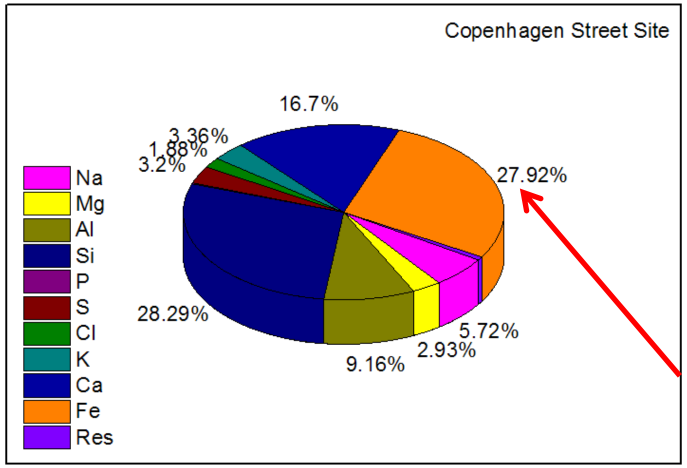
Baldacchini et al., ES&T 51 (2017) 1147

PM10 elemental composition by SEM/EDX

- **200 particles per sampling site**
- Target elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe
- Residual metals: Ti, Cr, Mn, Ni, Cu, Zn, Mo, Sn, Sb
- Semiquantitative estimation by the weigthed volume percentage $W_{\%}$

$$W_{\%_x} = \frac{\sum_{i=1}^{N} C_{x_i} \times V_i}{\sum_{i=1}^{N} V_i}$$





Most of the street sites are characterized by particles with high Fe and trace metal content

Co-funded by the Erasmus+ Programme of the European Union

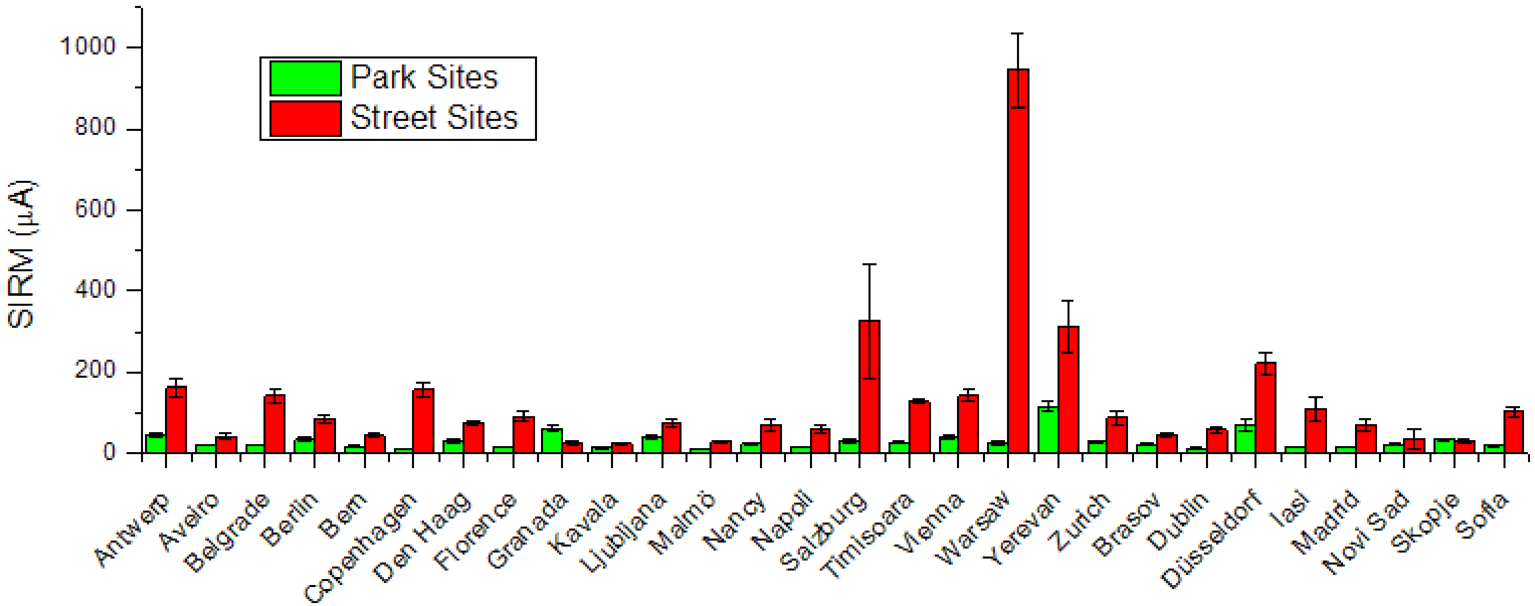
Source apportionment: A European Sampling Campaign

Same tree species in differently source-exposed sites

Baldacchini et al., ES&T 51 (2017) 1147

Leaf Fe content by SIRM

- **5 half leaves per sampling site**
- Target for ferro(i)magnetic particles (Fe-oxides, Fe-sulfides, or more rarely native Fe)
- It reflects particle composition, concentration and grain size



Most of the street sites are characterized by high SIRM values

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of the European Union

Source apportionment: A European Sampling Campaign

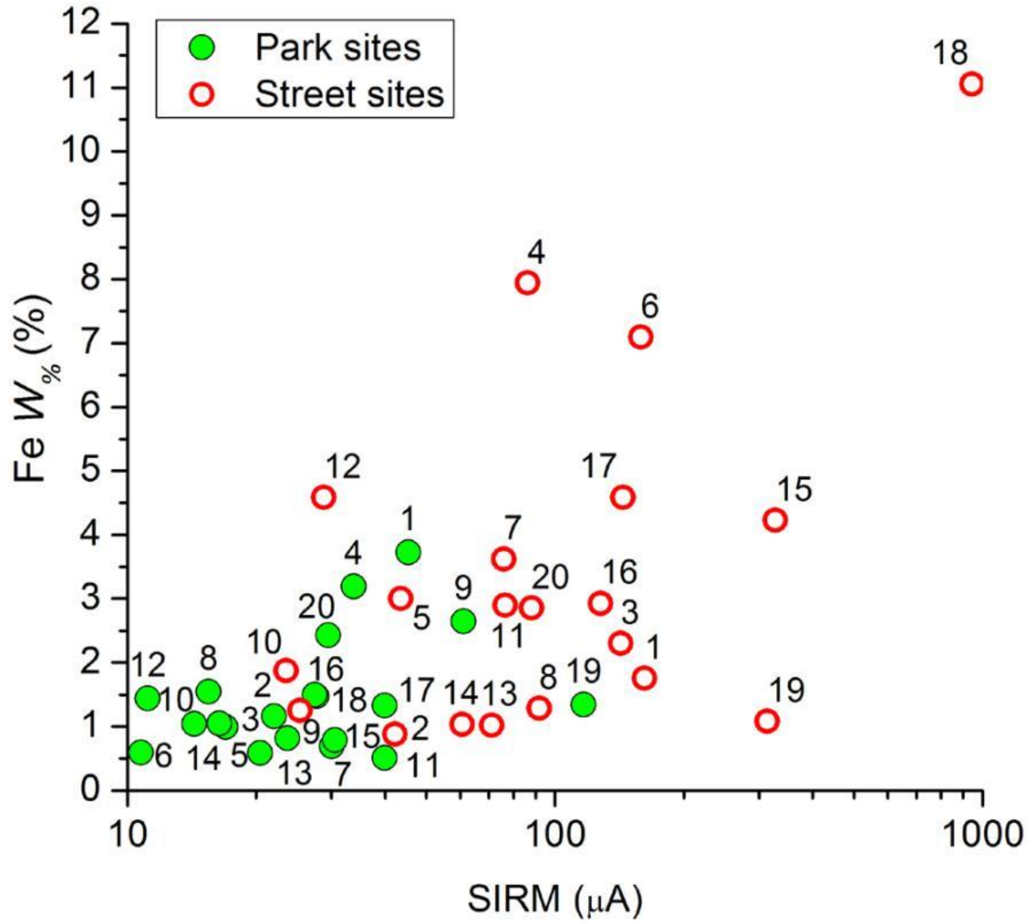
Same tree species in differently source-exposed sites

Baldacchini et al., ES&T 51 (2017) 1147

Correlation between Fe W% and SIRM value

- No correlation is obtained between Fe W% and SIRM values on the park sites' data set

- Correlation is obtained between Fe W% and SIRM values over the entire street sites' data set



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Source apportionment: A European Sampling Campaign

Same tree species in differently source-exposed sites

Baldacchini et al., ES&T 51 (2017) 1147

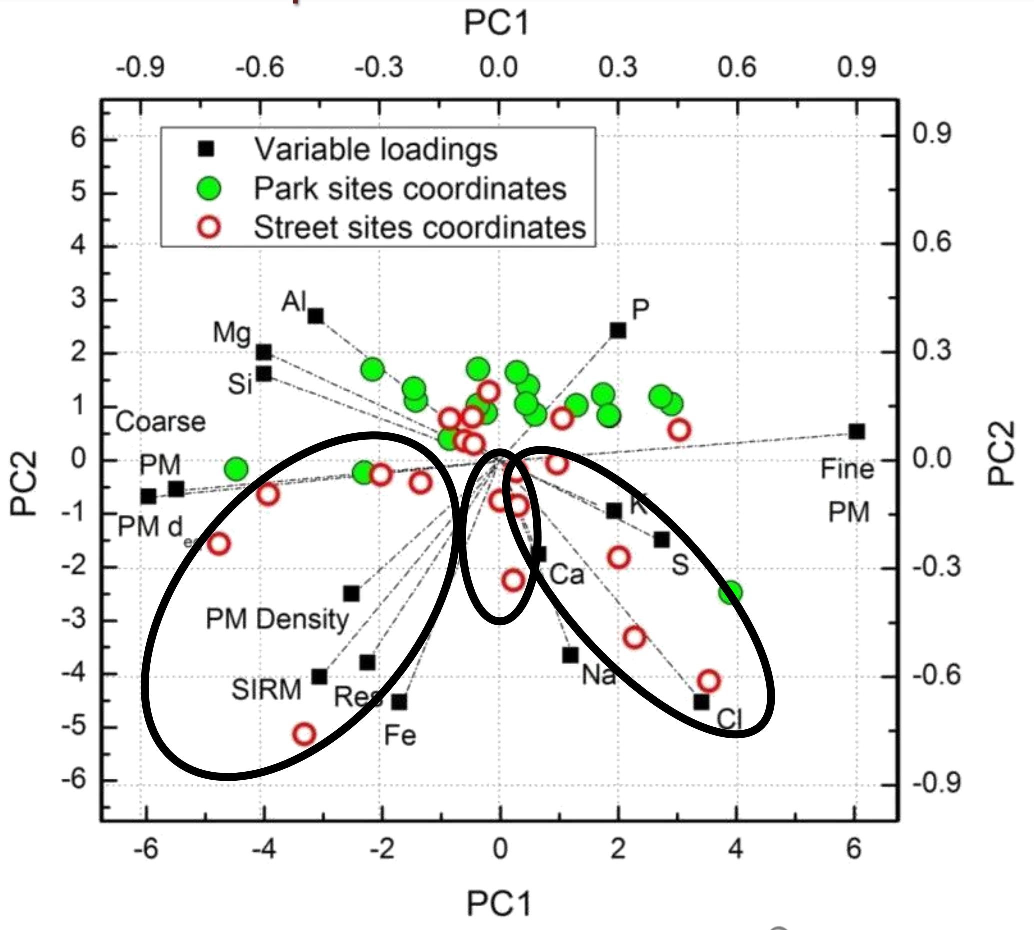
Input variables: PM10 density, percentage of fine and coarse PM, mean d_{eq}, W% of Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, and trace metals ("Res") , and SIRM value

- **PC1: particle size (fine vs. coarse particles)**
- **PC2: particle composition (natural crust components vs. pollutants)**
- **Park sites** are mainly grouped in the region of fine PM due to "crustal components" → no anthropogenic sources
- **Street sites** are divided into 3 groups

Group 1: Granada, Yerevan, Timisoara, Warsaw, Vienna. High density of coarse particles, high content of Fe and trace metals, high leaf SIRM values. → traffic related pollution

Group 2: Fine particles, low metal content, high concentrations of Na and Cl (Salzburg and Malmö), Ca (Bern and Florence sites), or Na, Cl, Ca, and S (Aveiro). → natural sources (salt, calcareous soil)

Group 3: Berlin and Copenhagen. Fine particles with high levels of Na and Fe → anthropogenic sources with high-temperature processes



In line with the results of the COST Action 633 (atmospheric PM from 33 cities over 12 countries)

Co-funded by the Erasmus+ Programme of the European Union

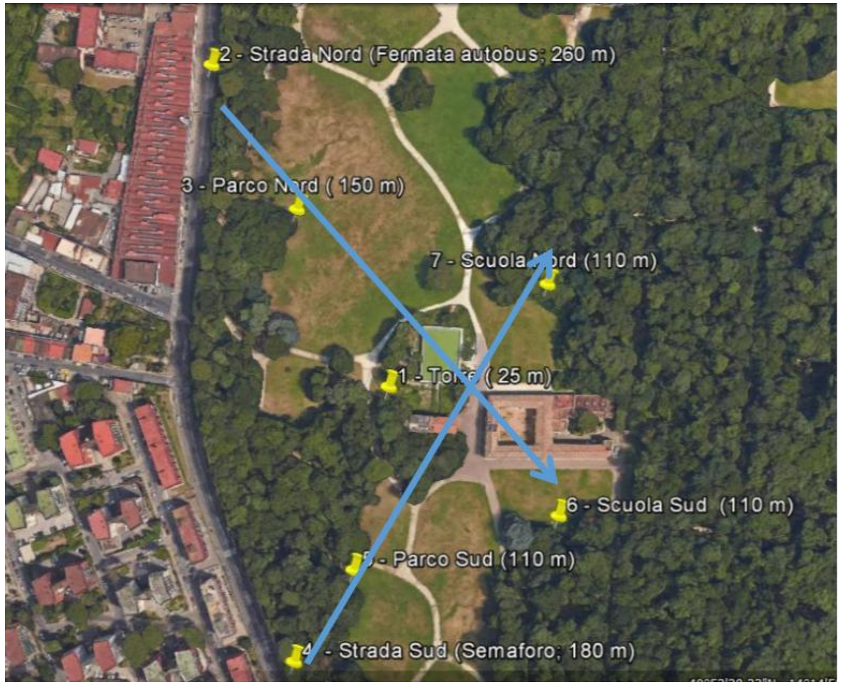
Test study: Real Bosco di Capodimonte (Naples)

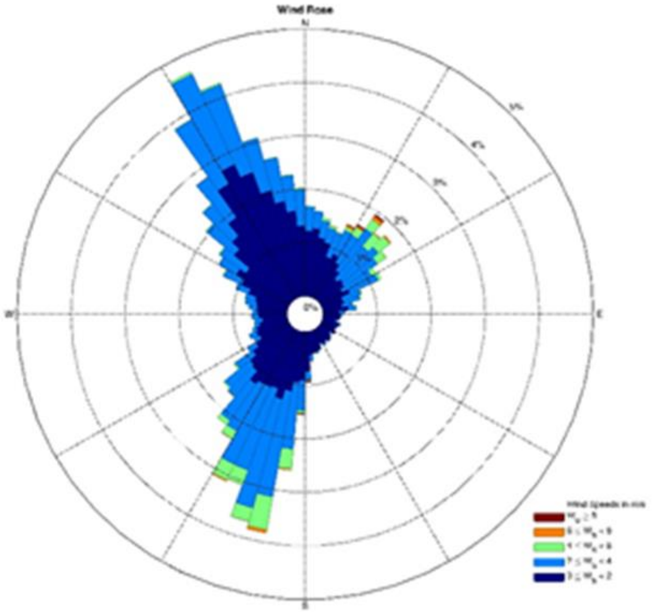
Same tree species in differently source-exposed sites

Baldacchini et al., Environ. Sci. Poll. Res. 2019

Seven *Quercus ilex* trees

- 1 Tower
-2 Street North
-3 Park North
-4 Street South
-5 Park South
-6 School South
-7 School North





Two transects along the main wind directions
First transect: 2 - 3 – 6
Second transect: 4 – 5 - 7

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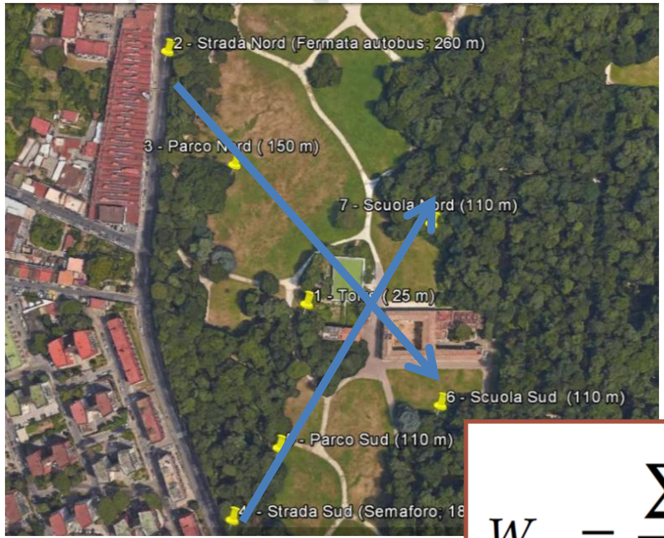
Test study: Real Bosco di Capodimonte (Naples)

Same tree species in differently source-exposed sites

Baldacchini et al., Environ. Sci. Poll. Res. 2019

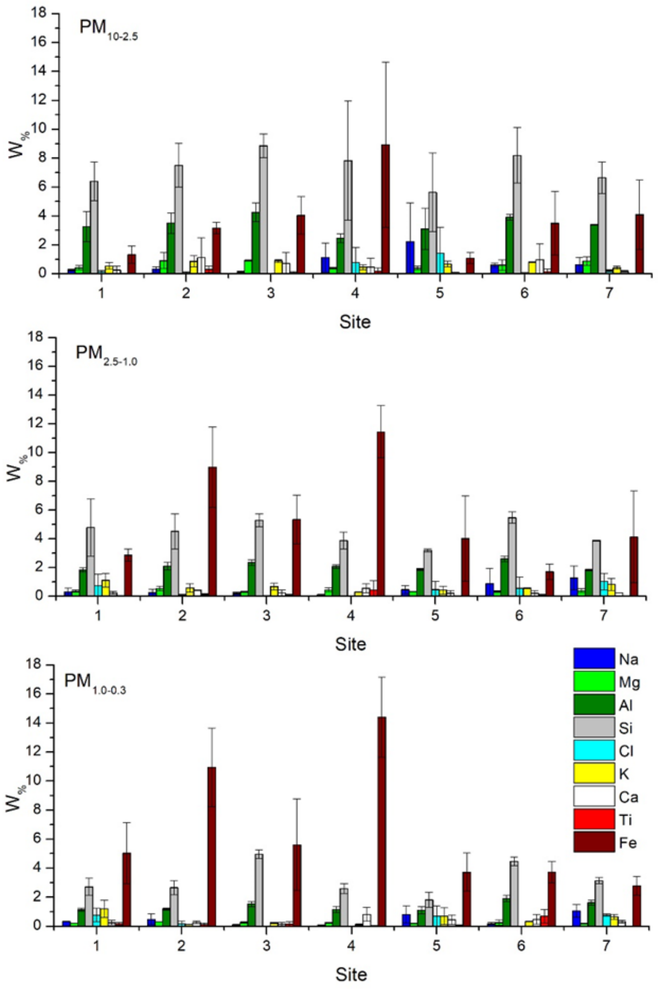
SITE DISCRIMINATION BY ELEMENTAL COMPOSITION (W%) & PCA

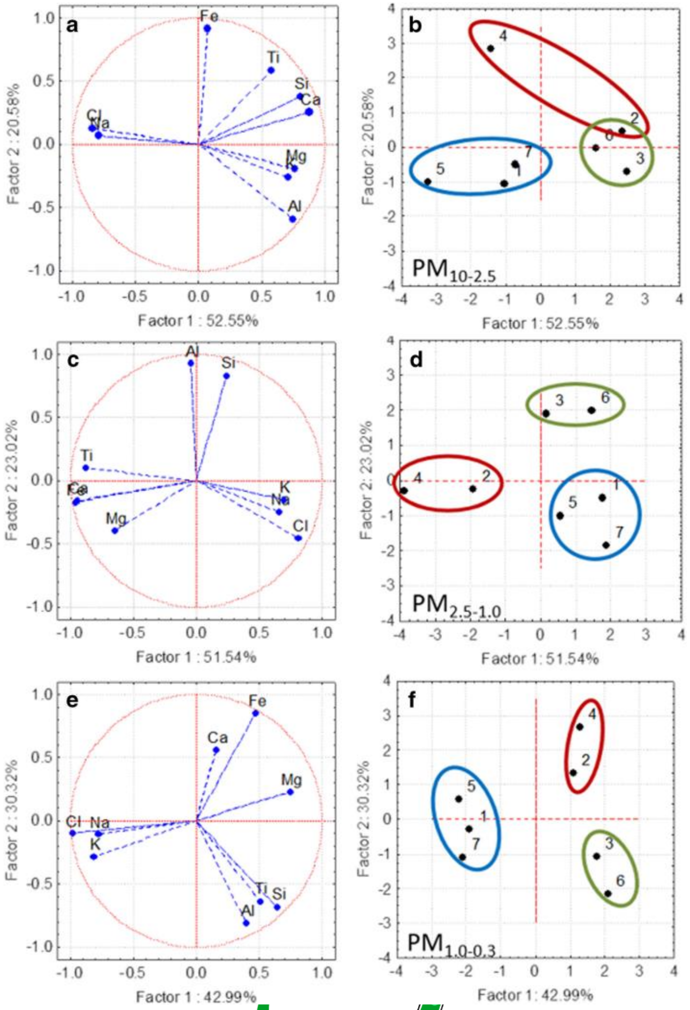


$$W_{\%_x} = \frac{\sum_{i=1}^{N} C_{x_i} \times V_i}{\sum_{i=1}^{N} V_i}$$

Baldacchini et al., ES&T 2017

Weighted Percentage ($W_{\%x}$)

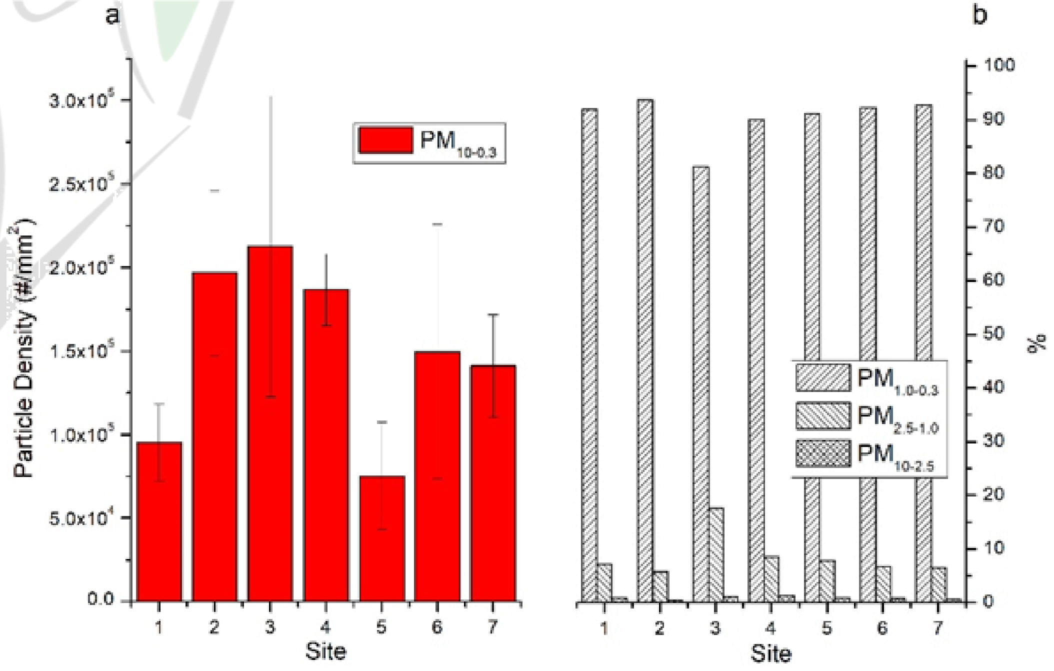


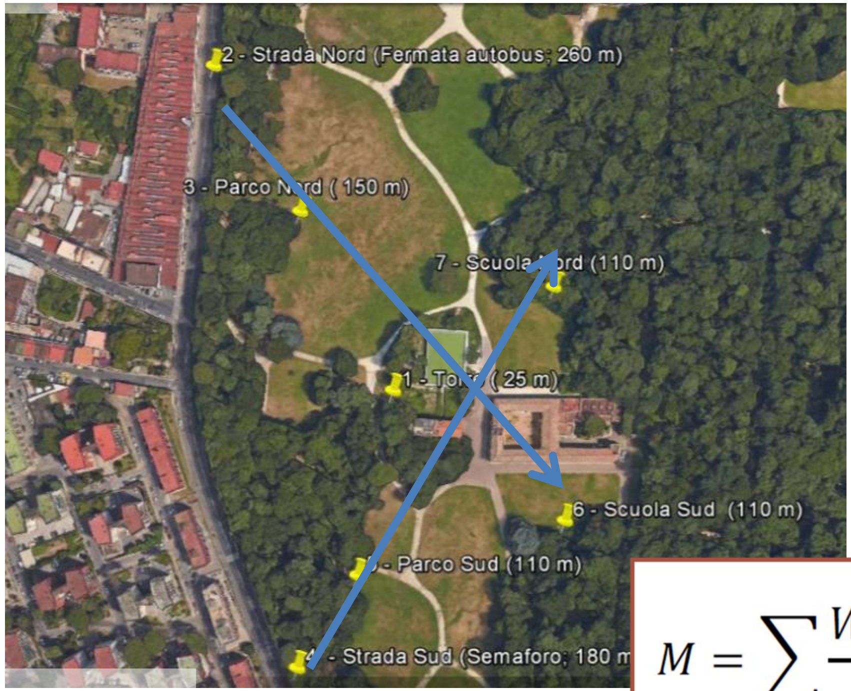


Test study: Real Bosco di Capodimonte (Naples)
Same tree species in differently source-exposed sites

Baldacchini et al., Environ. Sci. Poll. Res. 2019

PARTICLE DENSITY & PARTICLE SIZE DISTRIBUTION





$$M = \sum_{x} \frac{W_{\%x} \cdot V_{PMtot} \cdot am_x}{A_{leaf}}$$

→ **PM mass per unit leaf area (M)**

The anomalous site "3":
Old leaves: a higher number of particles and clustering of fine PM.
(this not affecting the W% elemental composition)

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Test study: Real Bosco di Capodimonte (Naples)

Same tree species in differently source-exposed sites

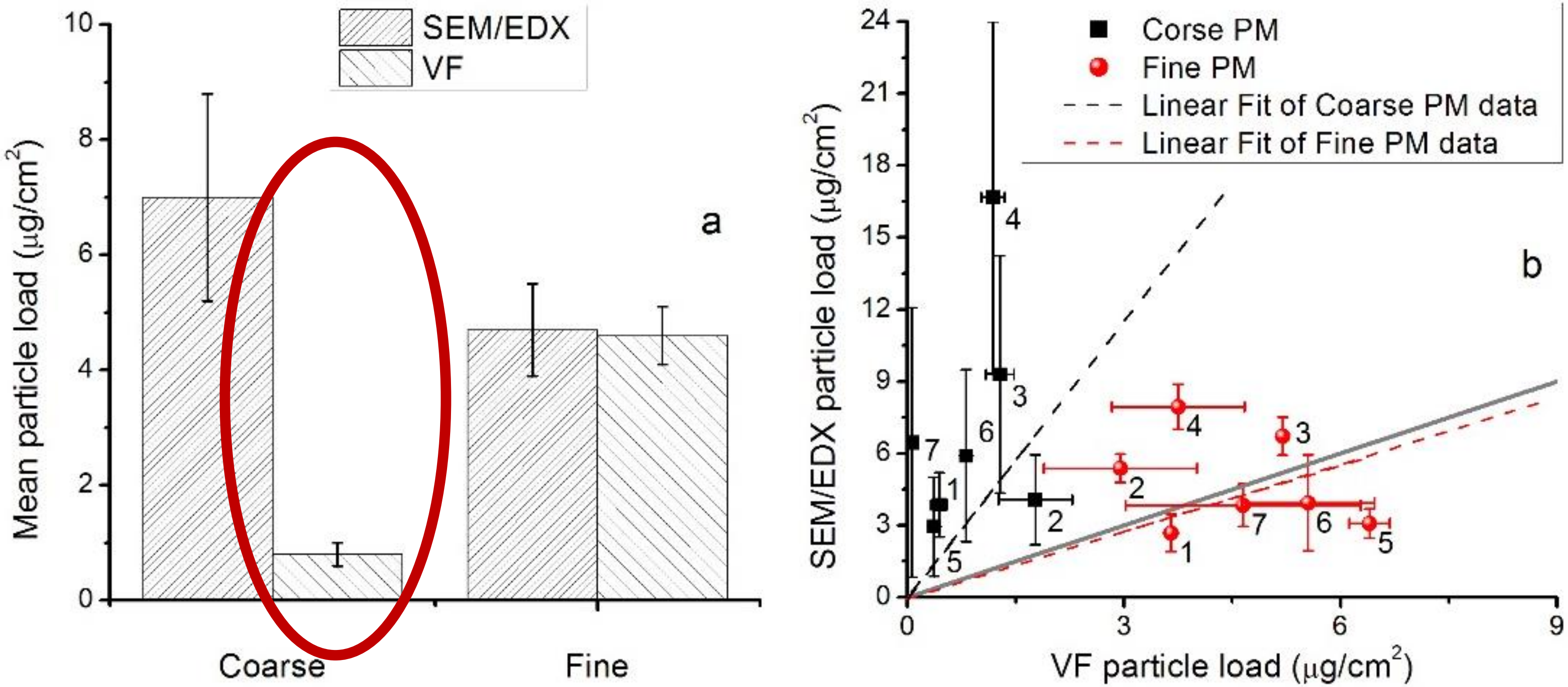
Baldacchini et al., Environ. Sci. Poll. Res. 2019

SEM/EDX vs VF PM Load

$$M = \sum_{x} \frac{W_{\%x} \cdot V_{PMtot} \cdot am_x}{A_{leaf}}$$

→ **PM mass per unit leaf area (M)**

Where are the coarse particles in VF?!



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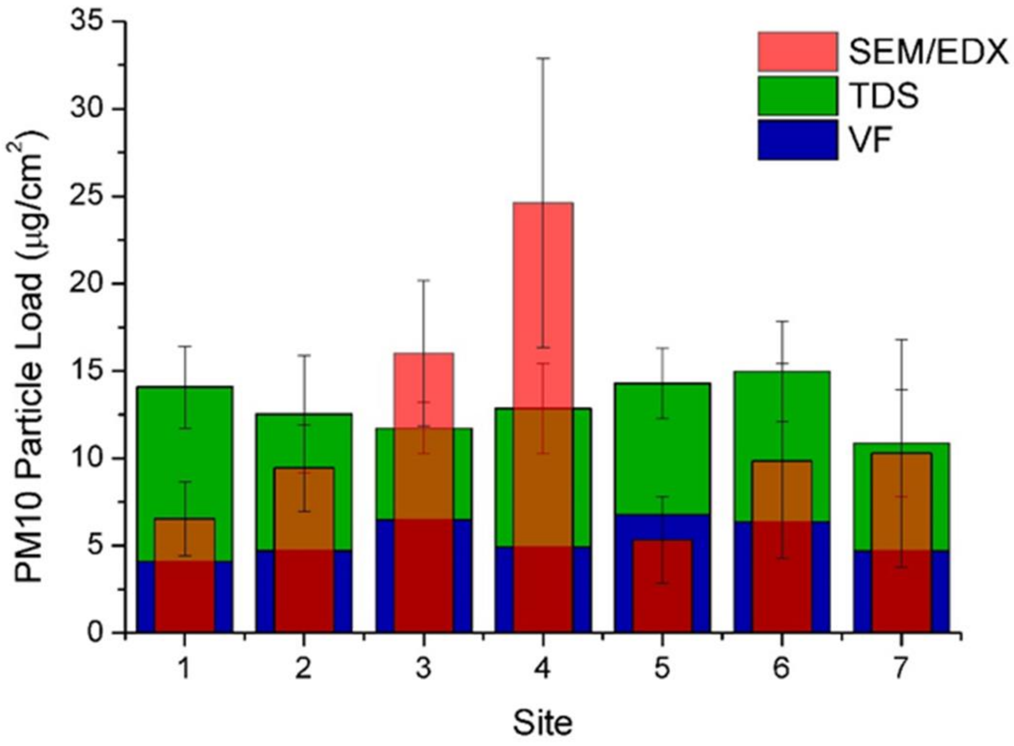
Test study: Real Bosco di Capodimonte (Naples)

Same tree species in differently source-exposed sites

Baldacchini et al., Environ. Sci. Poll. Res. 2019

SEM/EDX vs VF PM Load (+TDS)



In the water!
→ TDS

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Correlation with leaf morphology: Terni case study

Different tree species exposed to the same pollution source

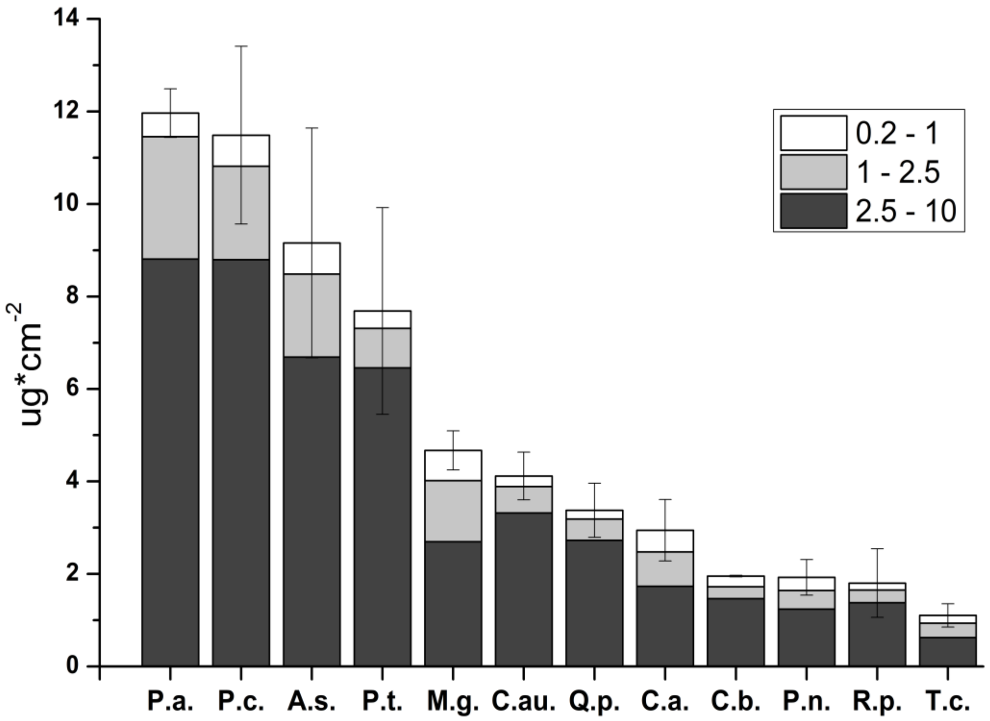
Sgrigna et al., STOTEN 78 (2020) 137310

$$M = \sum_{x} \frac{W_{\%x} \cdot V_{PMtot} \cdot am_x}{A_{leaf}}$$

→ PM mass per unit leaf area (M)

PM load by SEM/EDX per size fraction

Acer saccharinum	*A.s.*
Catalpa bignonioides	*C.b.*
Cedrus atlantica	*C.a.*
Celtis australis	*C.au.*
Magnolia grandiflora	*M.g.*
Platanus acerifolia	*P.a.*
Populus nigra	*P.n.*
Populus tremula	*P.t.*
Prunus cerasifera	*P.c.*
Quercus pubescens	*Q.p.*
Robinia pseudoacacia	*R.p.*
Tilia cordata	*T.c.*



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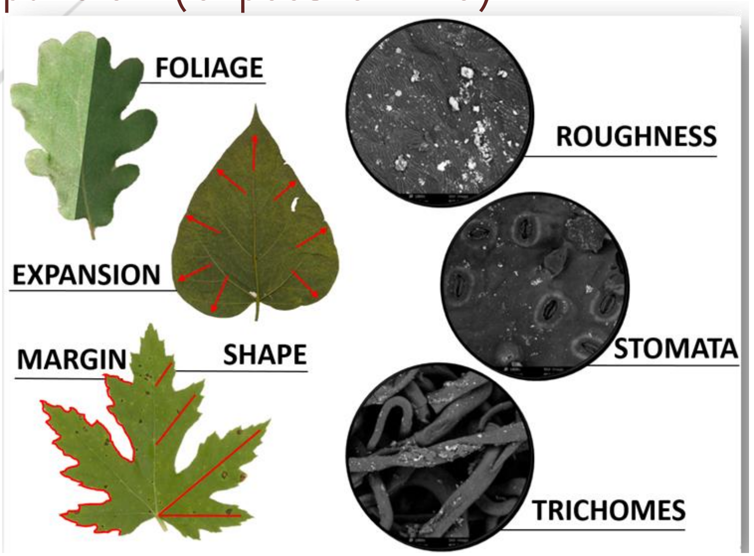
Correlation with leaf morphology: Terni case study

Different tree species exposed to the same pollution source

Sgrigna et al., STOTEN 78 (2020) 137310

MACROMORPHOLOGY
- Leaf shape and margin
- Foliage (evergreen / deciduous)
- Leaf expansion (exposure time)



	MICROMORPHOLOGY					MACROMORPHOLOGY				
	Roughness			Stomata	Trichomes	Morphology		Foliage	LGE	
Species	Type	Area	Grooves	Density	Covered area	Margin	Shape			Total Ai
A. s.	3	2	3	3	1	0	2	0	3	17
C. b.	2	2	2	1	1	0	0	0	0	8
C. a.	0	0	0	0	0	0	2	3	3	8
C. au.	3	1	1	2	0	1	0	0	2	10
M. g.	0	0	0	2	3	0	0	3	3	11
P. a.	3	3	2	2	0	0	2	0	2	14
P. n.	0	0	0	0	0	1	0	0	2	3
P. t.	3	3	3	1	3	1	0	0	1	15
P. c.	3	3	3	3	0	1	0	0	3	16
Q. p.	3	1	1	2	1	1	0	0	2	11
R. p.	1	2	2	0	1	0	1	0	2	9
T. c.	0	0	0	1	1	1	0	0	1	4

Leaf PM Accumulation index A_i

MICROMORPHOLOGY
- Roughness (Density %; Type; Dimension (um)
- Stoma (Density #*cm^{-2})
- Trichomes (Density % cover)

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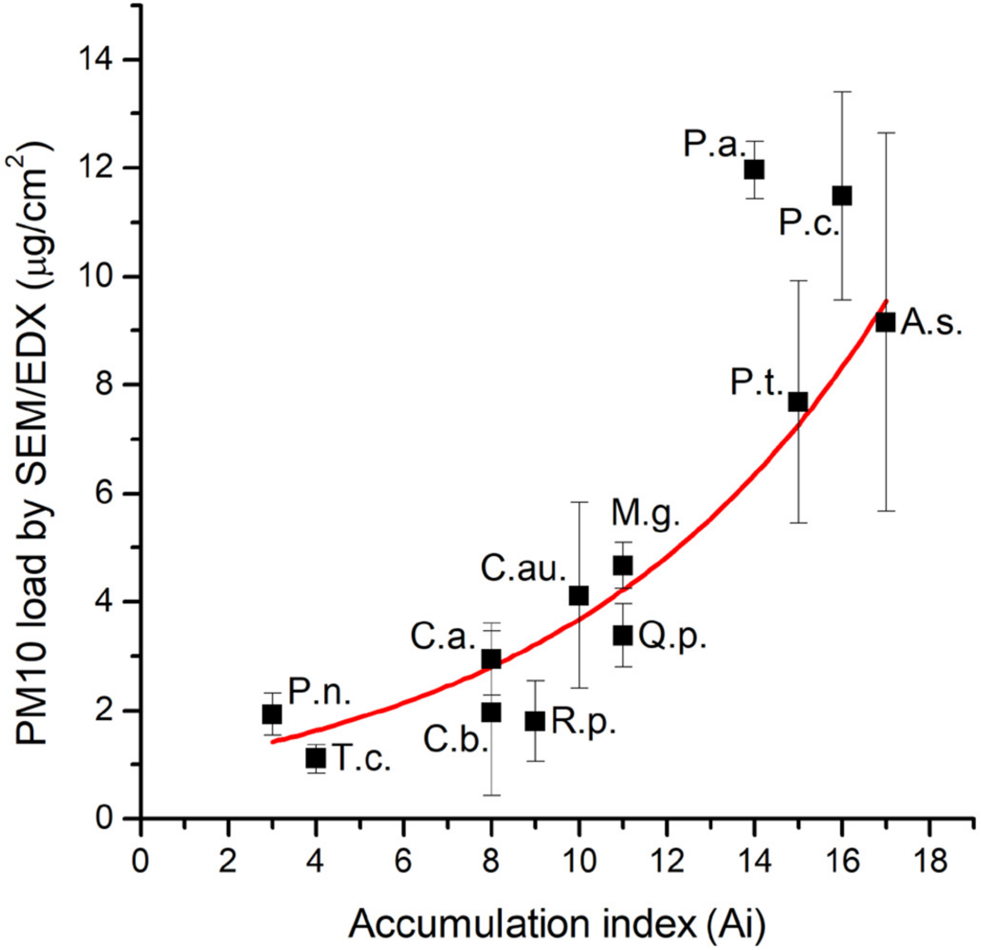
Correlation with leaf morphology: Terni case study

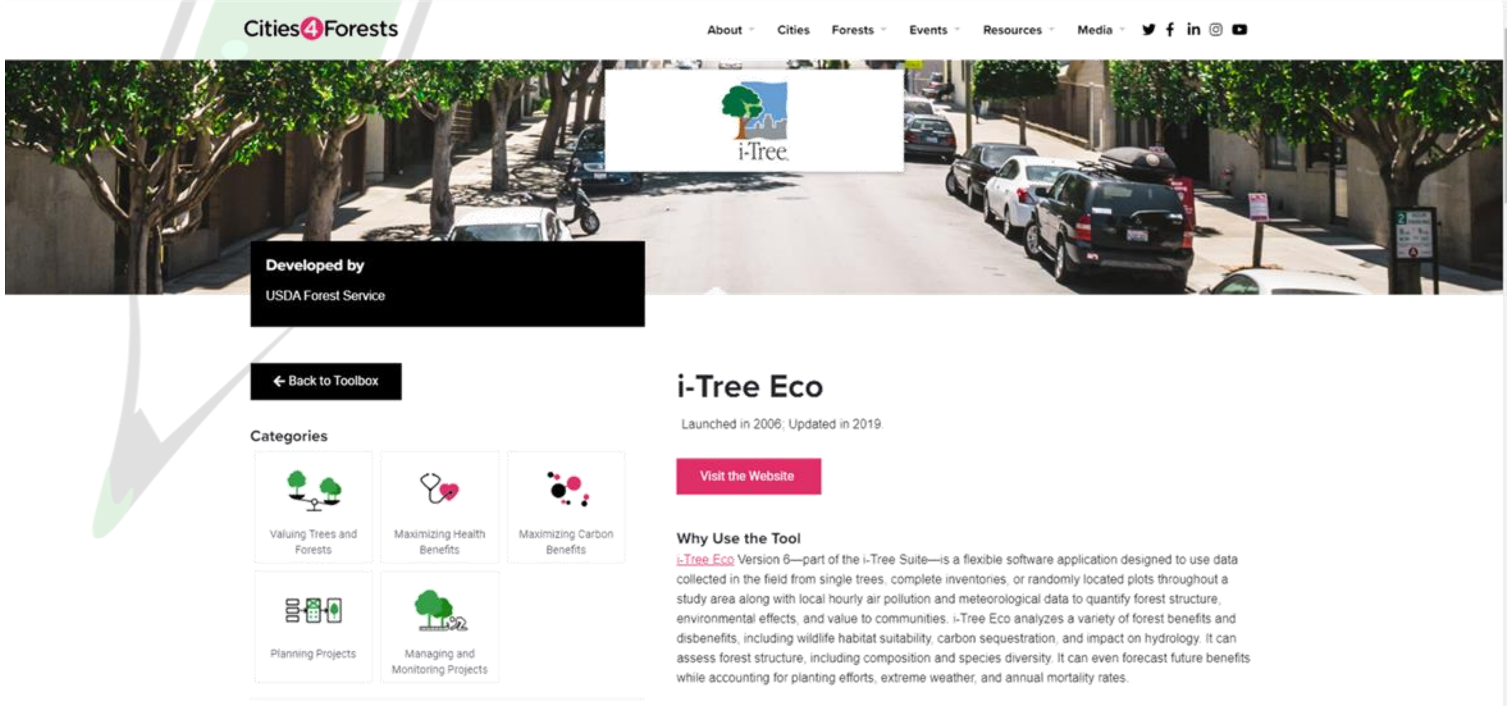
Different tree species exposed to the same pollution source

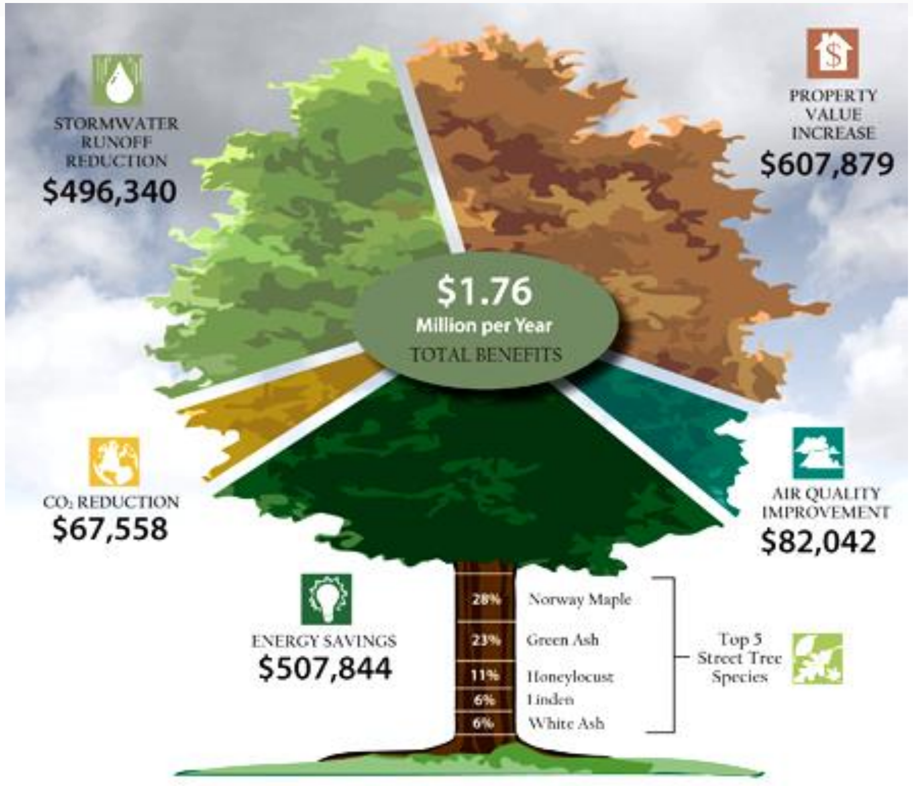
Sgrigna et al., STOTEN 78 (2020) 137310



Leaf PM retention capability strongly depends on leaf morphology, i.e. on plant species…

i-Tree model





Improving experimental knowledge helps improving models' reliability…

www.itreetools.org/resources/reports/WDNR_GreenBay_Metro.pdf

Economic benefits provided by street trees in the Green Bay Metro Area (Wisconsin, USA)

Co-funded by the Erasmus+ Programme of the European Union

i-Tree model for PM removal

INPUTS

- PM concentration in air as a function of time
- Wind speed as a function of time
- **Leaf Area Index**
- **Deposition velocity**

OUTPUTS (per m² of ground)

- PM deposition
- PM resuspension
- Net PM flux
- **PM accumulation**

Species specific results!

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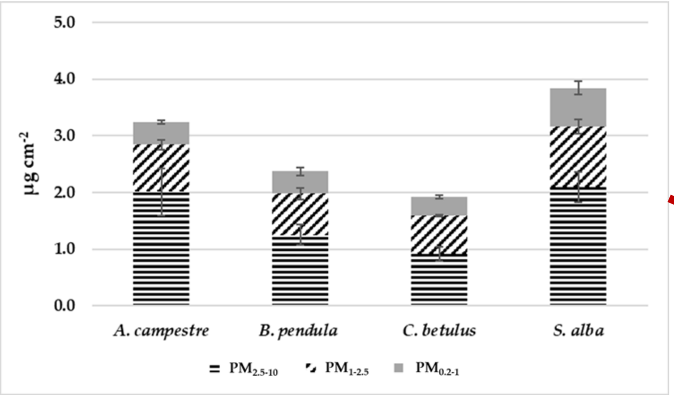
i-Tree model for PM removal
NBS Benefits' assessment – a case study in Dortmund

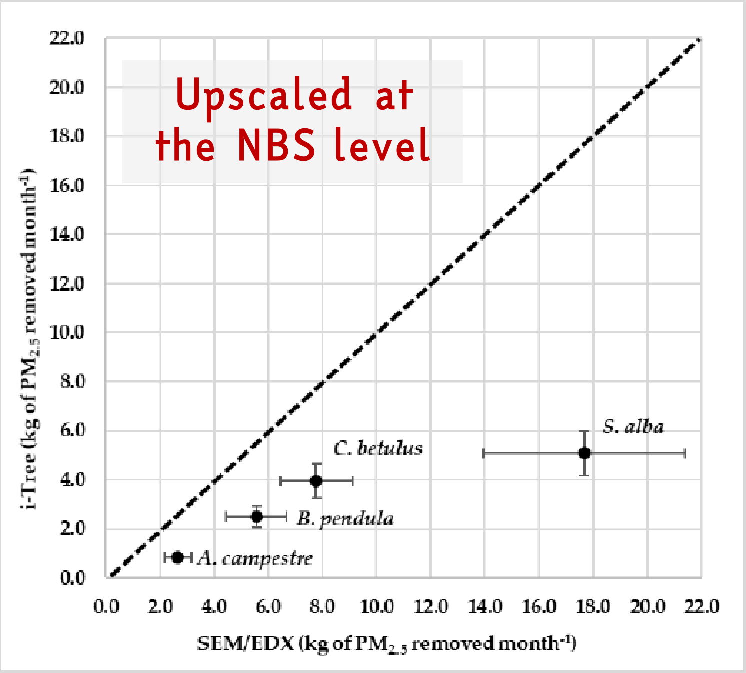
Ristorini et al., submitted UFUG

SEM/EDX (per unit leaf area)



i-Tree Eco (per tree)

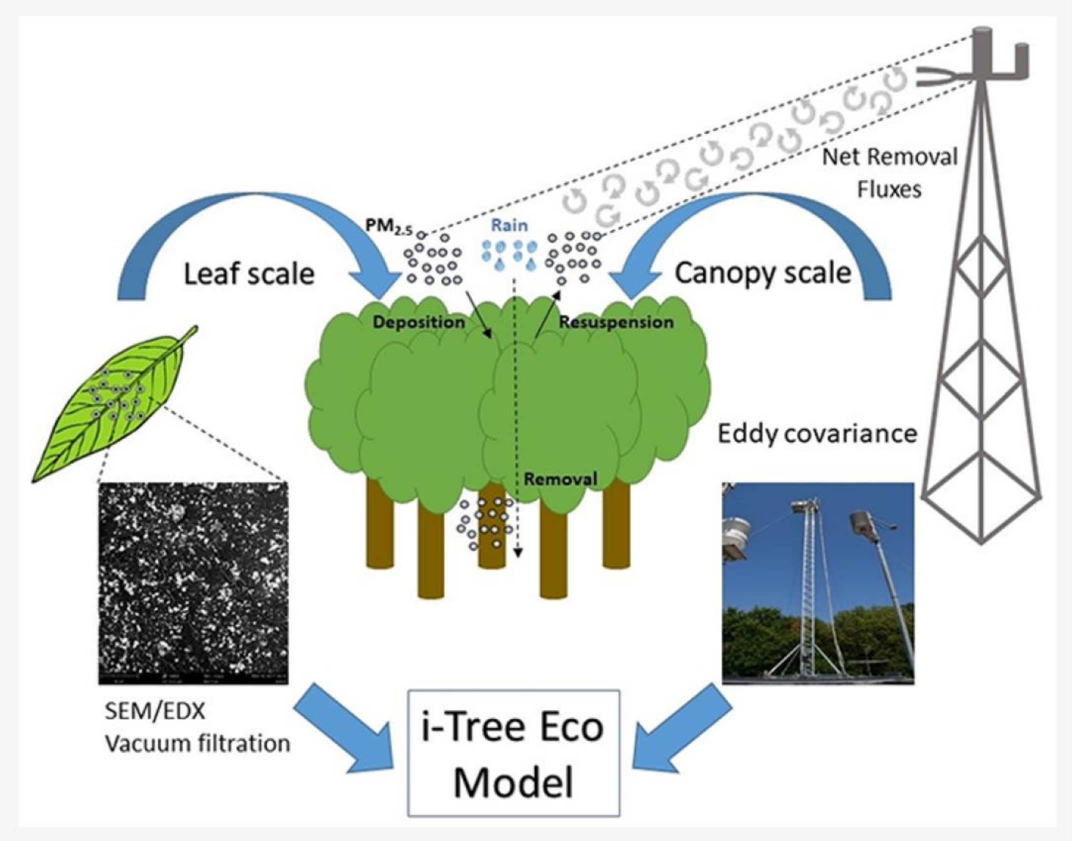
g per single tree year⁻¹	$PM_{2.5}$
S. alba L.	11.8 ± 2.1
R. pseudoacacia L.	5.5 ± 1.0
C. betulus L.	4.5 ± 0.8
A. campestre L.	2.5 ± 0.4
B. pendula Roth	1.2 ± 0.2
T. cordata MILL.	0.6 ± 0.1
S. aucuparia L.	0.10 ± 0.02



Parametrization for the selected species should be ameliorated

i-Tree model for PM removal
Leaf vs canopy scale (single species study)

Pace et al., ES&T 55 (2021) 6613



Deposition velocity
(which depends on the leaf micromorphology)
is a crucial parameter
for reproducing experimental data

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Conclusions

• Airbone **PM danger** is related to **size, elemental composition** and **quantity**

• Tree leaves can act as PM filters, ameliorating the air quality

• Tree leaves can be further used as biomonitors for source apportionment

• Many experimental approaches have been proposed up to date to characterize leave deposited PM

• The most efficient and reliable technique to quali-quantitative characterize leaf deposited PM on "as it is" leaves is SEM/EDX

• SEM/EDX can provide information on

- **particle number and concentration, per PM size**
- **elemental concentration**
- **PM mass per unit leaf area**

• At the same time, SEM/EDX provide information on the **leaf micromorphology**, which is of utmost importance for PM deposition mechanism study and model development

Co-funded by the Erasmus+ Programme of the European Union

Thank you for your kind attention!

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DIPARTIMENTO DI SCIENZE ECOLOGICHE E BIOLOGICHE

Consiglio Nazionale delle Ricerche