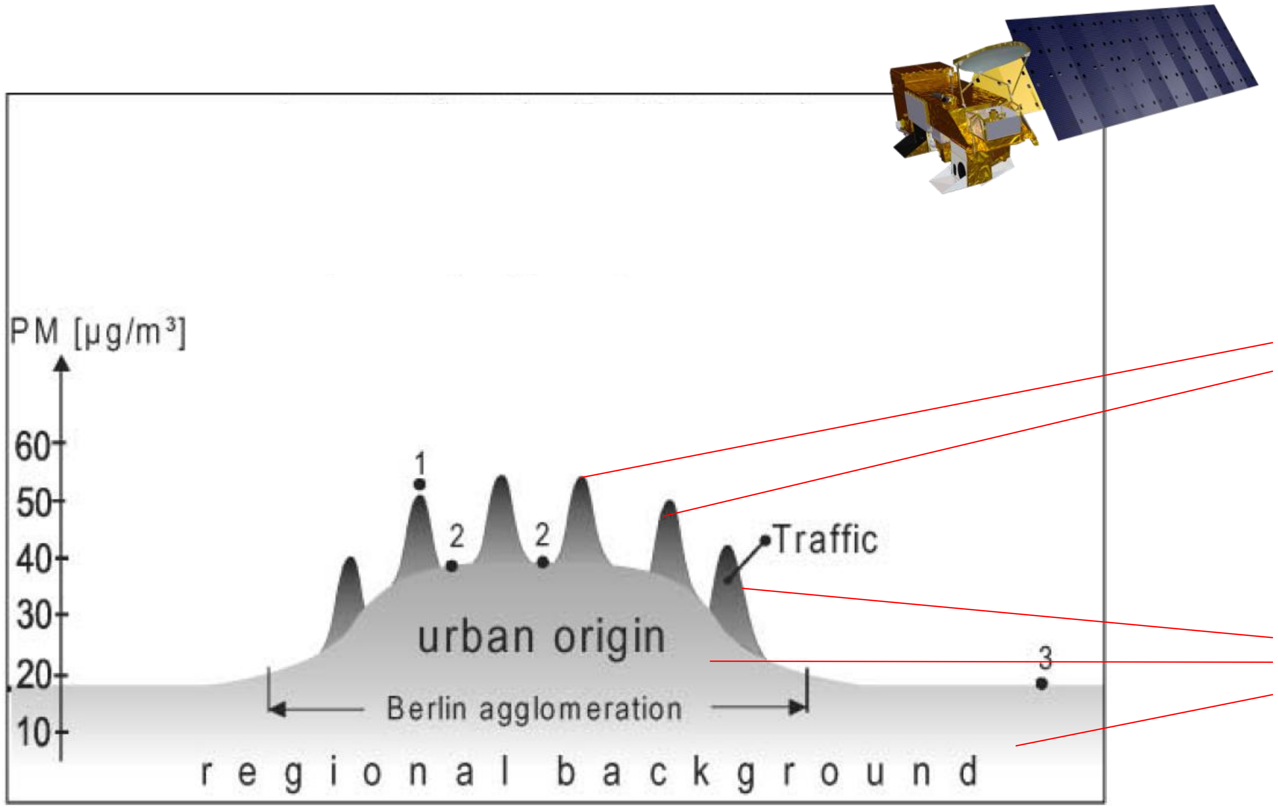
Aerosol chemical analysis

ENV-409

Complementary monitoring strategies



Aerosol concentration

Spatial extent of urban city

Satellite observation
(*intermittent, clear-sky coverage)*

Low-cost sensors
(*high spatial coverage, low data quality)*

Reference monitors
(*high data quality,*
"chemical fingerprint" of sources)

Figure from Lenschow et al., *Atmos. Environ.*, 2001

Ground-based aerosol measurements

Advanced scientific instruments

- High chemical resolution
- Deploy in short, intensive campaigns
- Expensive

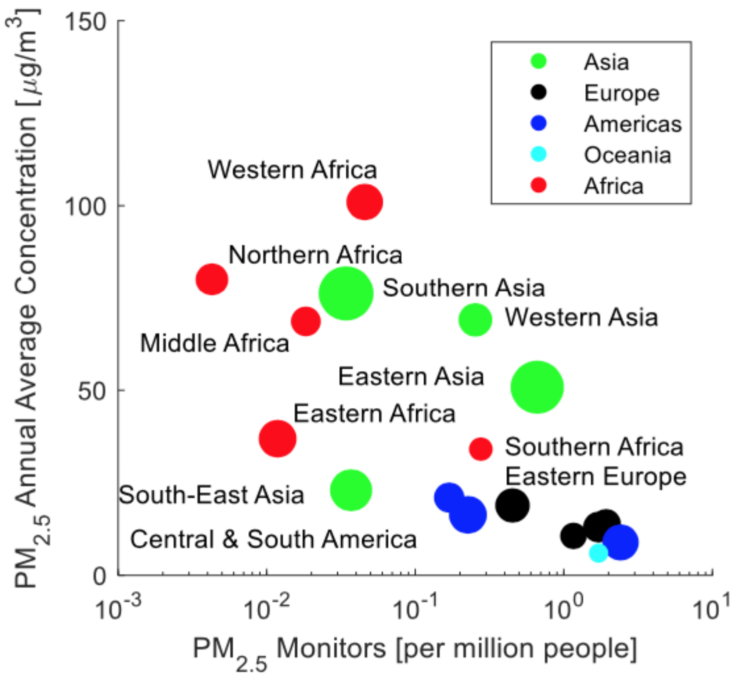
Low-cost sensors

- High spatial (and time) resolution
- Personalized information (“citizen science”)
- No chemical information, low accuracy

Regulatory monitors

- Reliable, standardized
- Accurate
- Cost-effective
- Chemical speciation

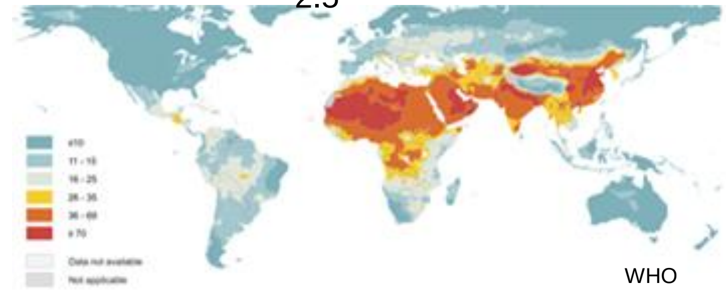
Need for cost-effective monitoring of air pollution



Lack of monitors in high population areas

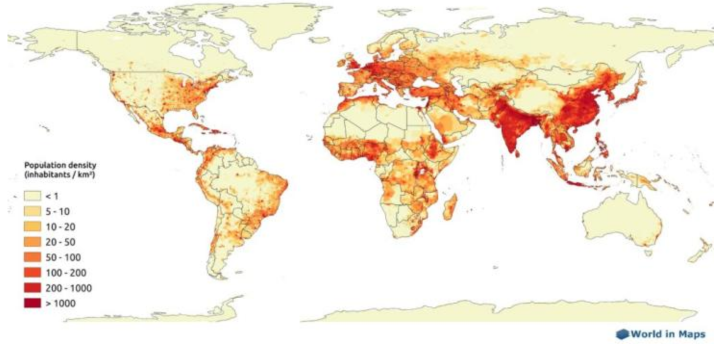
Malings et al., 2020

Estimated $PM_{2.5}$ concentrations

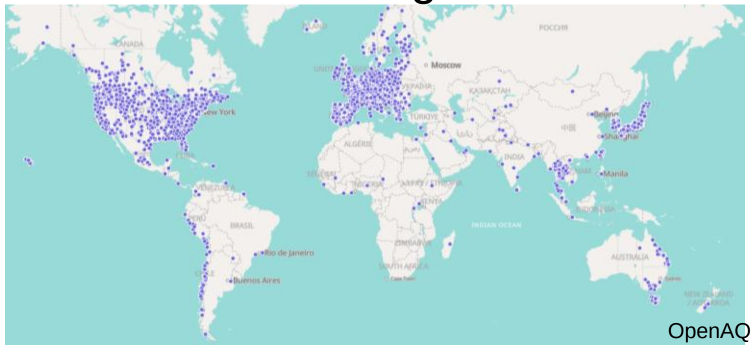


WHO

Population density



Available monitoring data

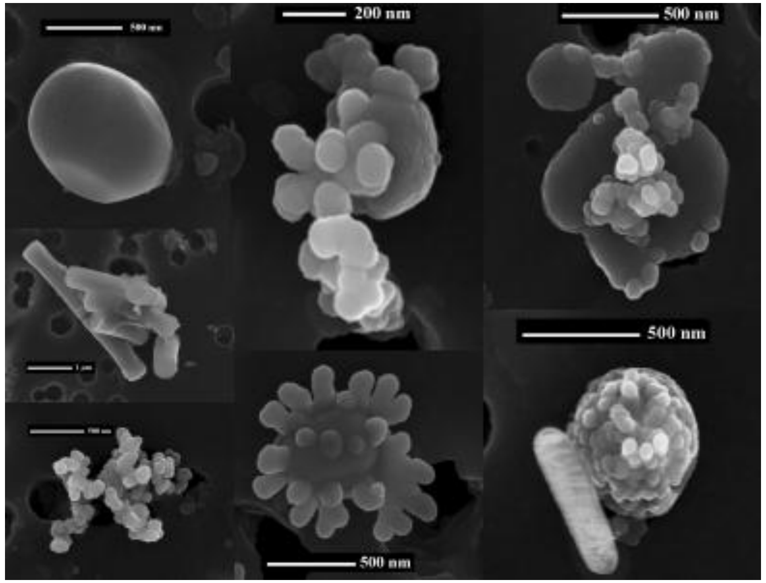


OpenAQ

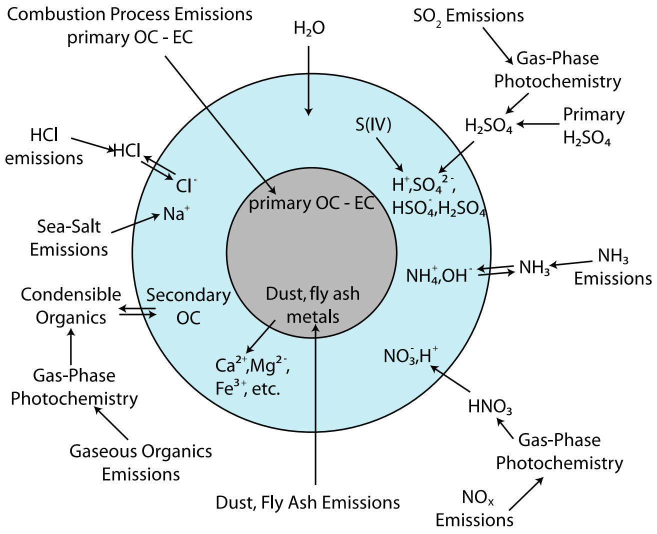
Atmospheric aerosols

Varies in
- size
- shape
- phase
- composition

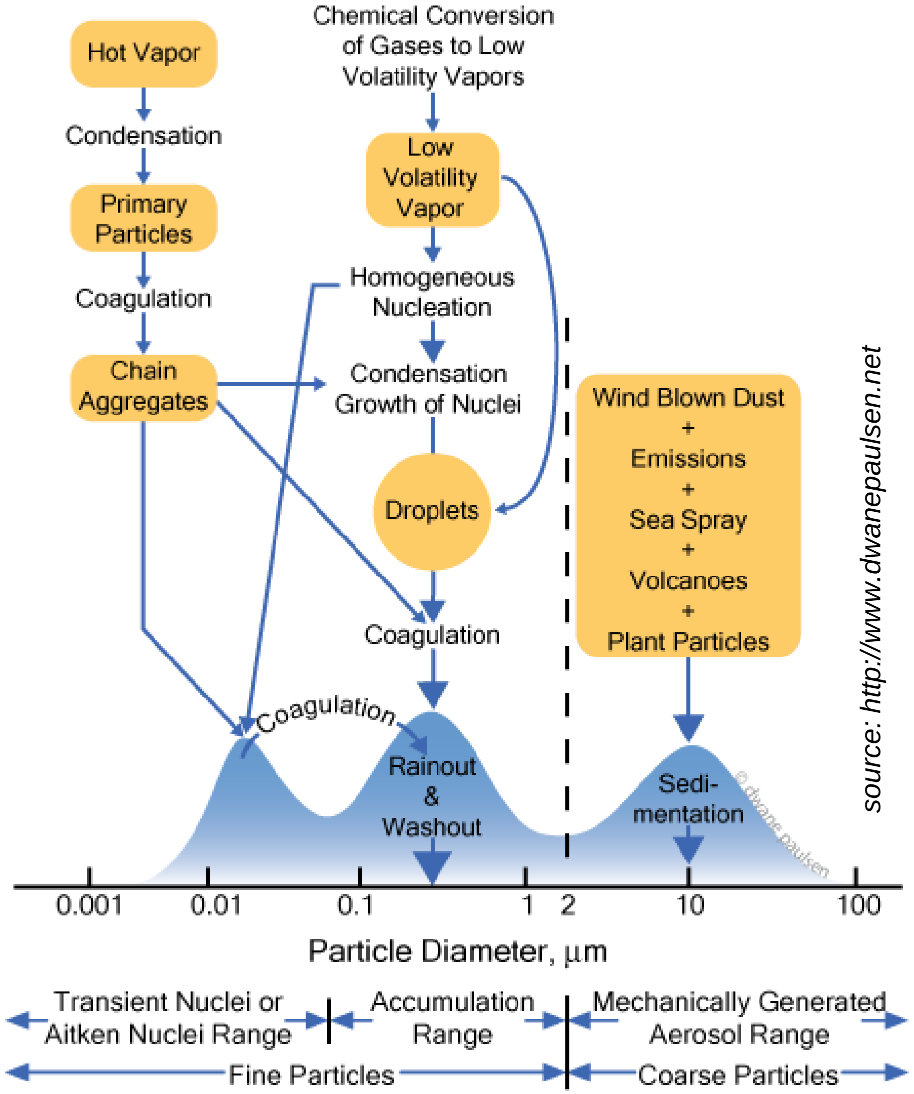
Scanning electron microscopy images



Coz et al., *Aerosol Sci. Tech.*, 2008

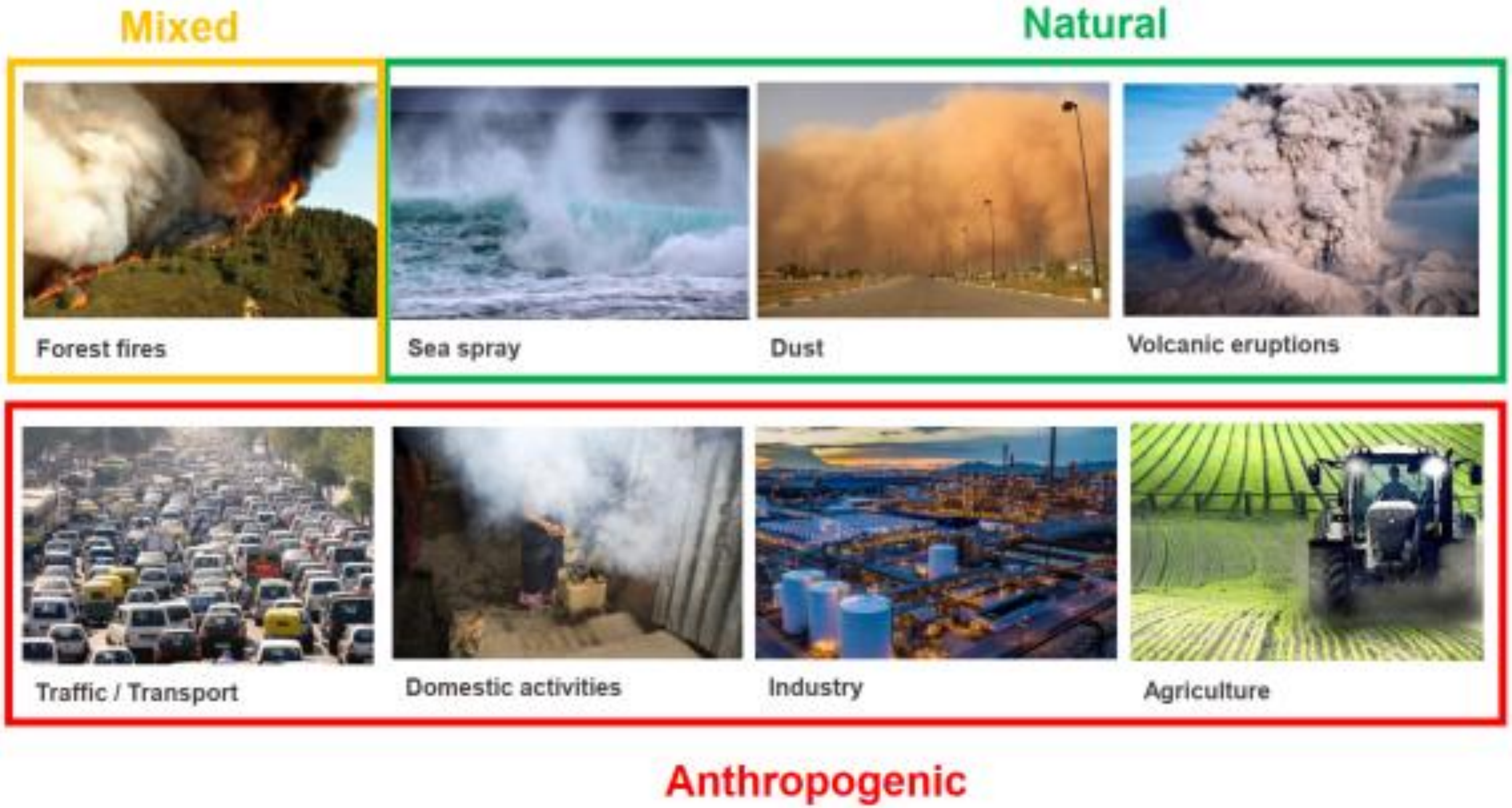


adapted from Pandis et al., *J. Phys. Chem.*, 1995



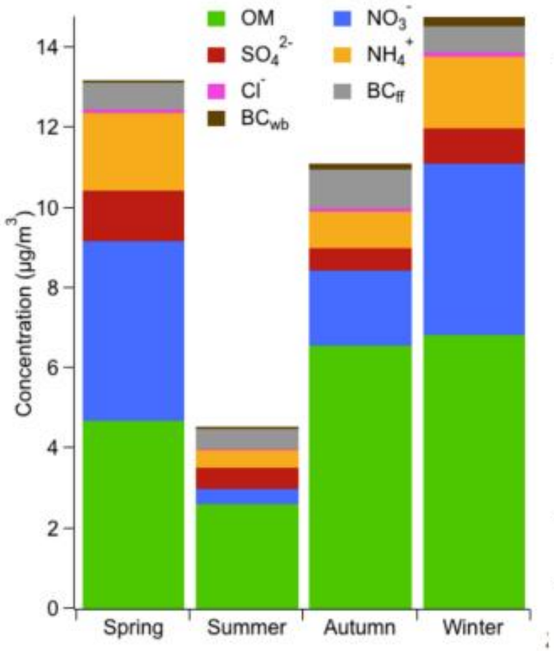
source: http://www.dwanepaulsen.net

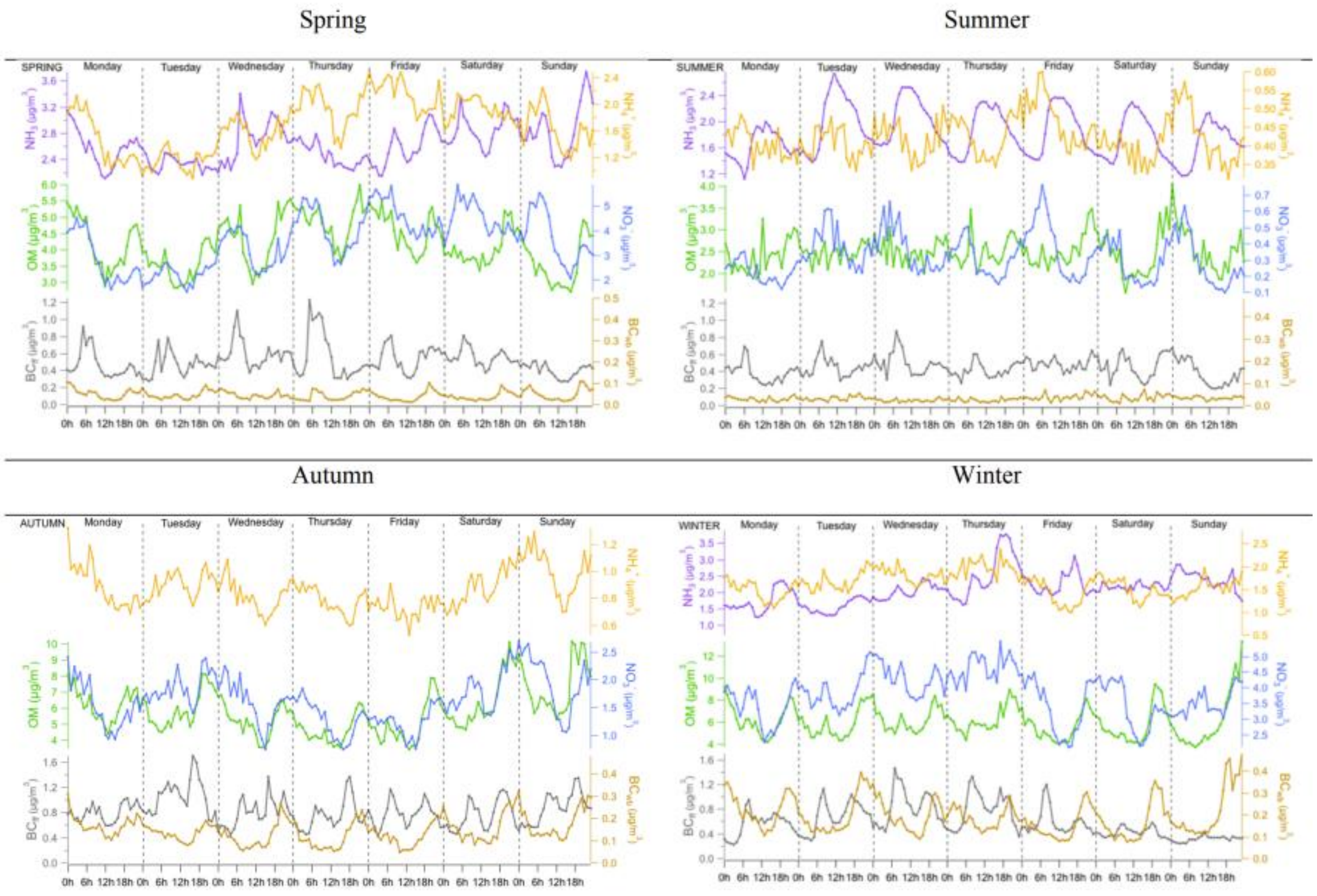
Aerosol sources



(slide from Julia Schmale)

High variation in aerosol composition





Paris, France
2011-2013

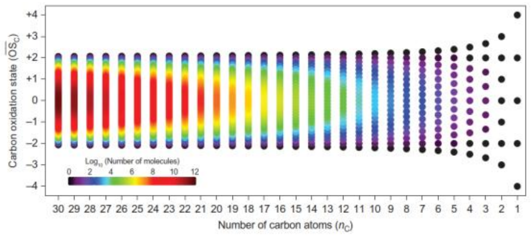


Figure 3 | Chemical complexity of organics as a function of oxidation state and carbon number. Points are coloured by the logarithm (base 10) of the number of possible compounds at a given $\overline{OS}_C$ and n_C, assuming an unbranched, acyclic carbon skeleton, and the addition of carbonyl, alcohol and acid groups only. Including a wider range of carbon skeletons or functional groups will lead to a dramatically steeper increase in chemical complexity with $\overline{OS}_C$ and n_C (ref. 31).

Kroll et al., *Nat. Chem.*, 2011

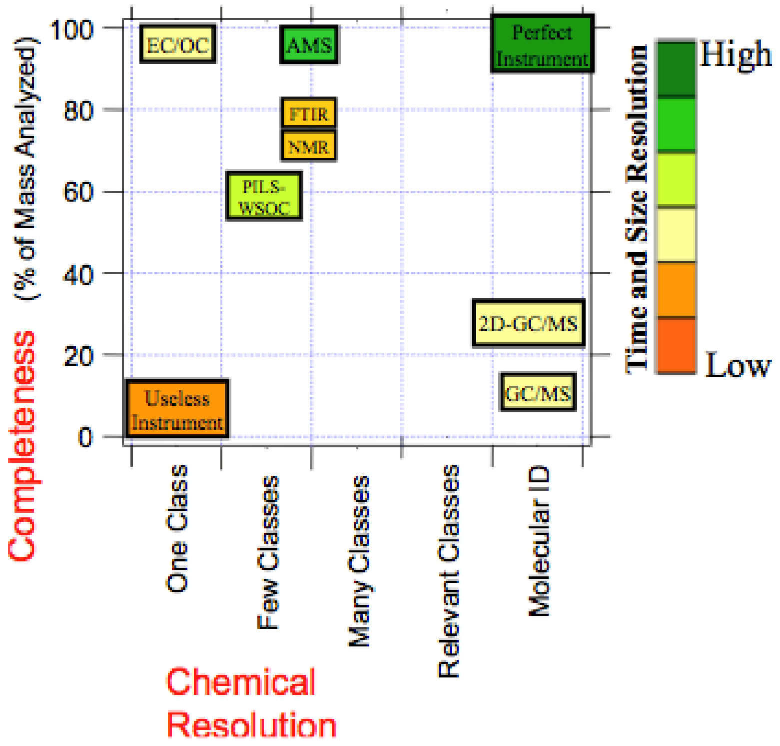
Petit et al., *Atmos. Chem. Phys.*, 2015

Chemical measurement technology tradeoffs

Diverse range of molecular classes, size, polarity in atmospheric particles

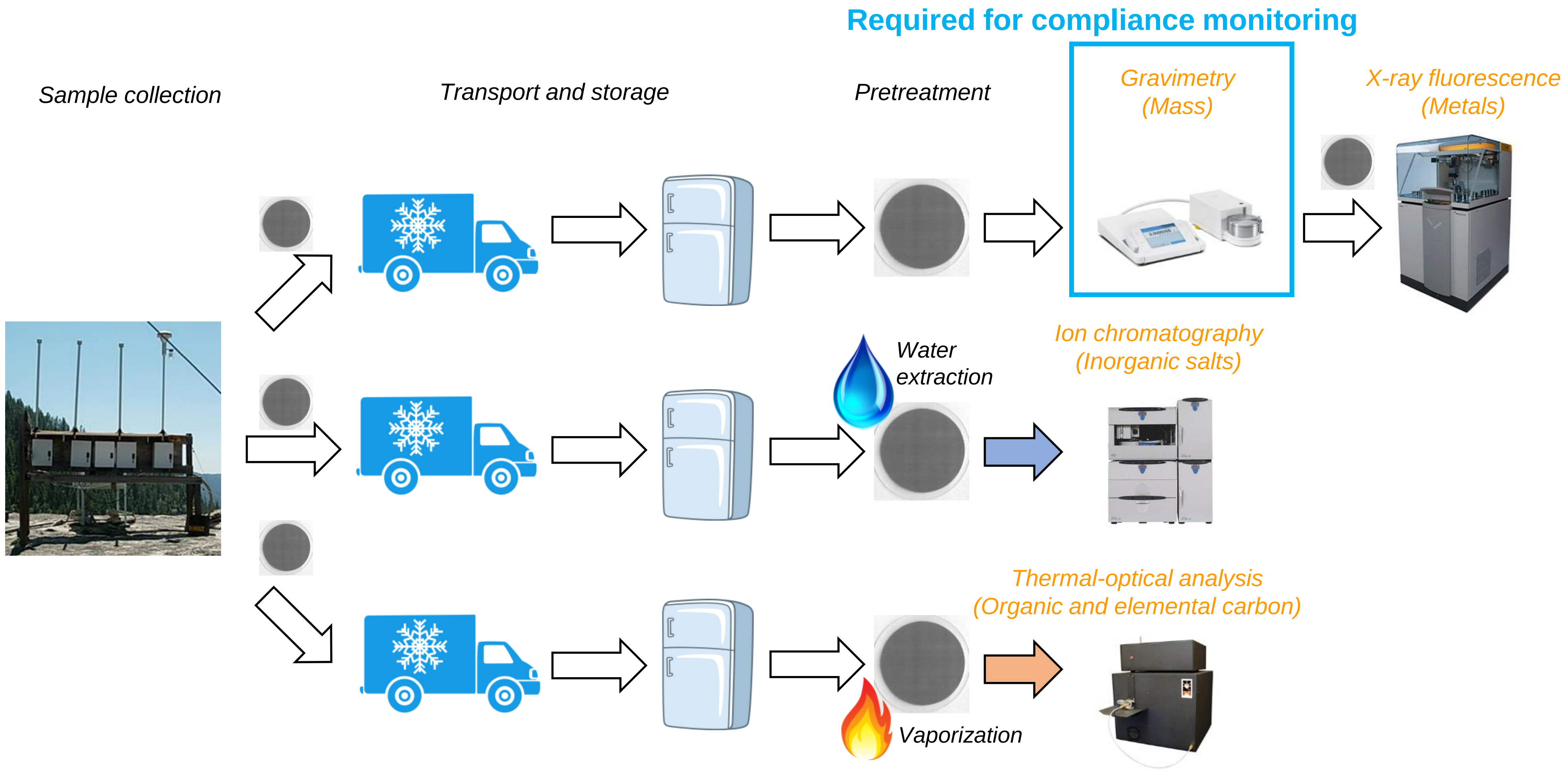
No single measurement technique for measurement of all molecules. Tradeoffs:

- offline / online
- time resolution
- chemical resolution (number of species or classes)
- completelness
- quantitative / qualitative
- Separation
  - physical / chemical
  - algorithmic
- scalability – labor and cost

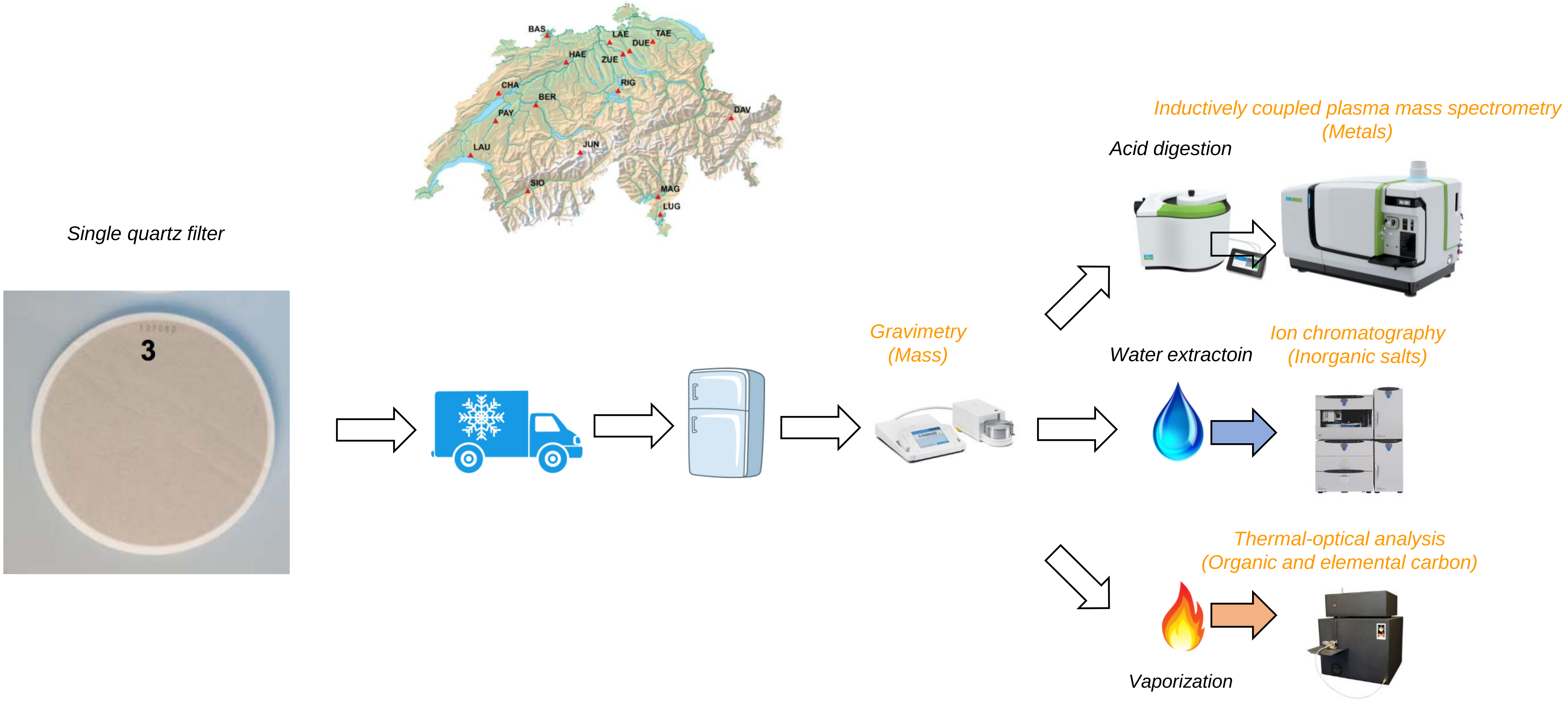


Hallquist et al., *Atmos. Chem. Phys.*, 2009

Conventional chemical speciation methods

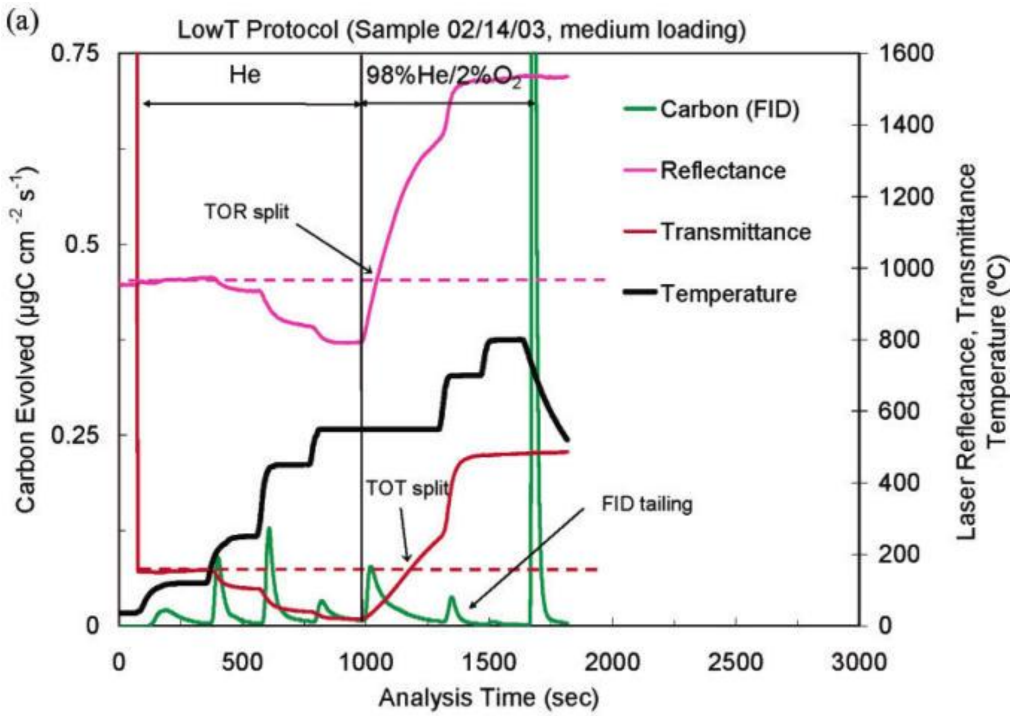


NABEL Network



Thermal optical methods

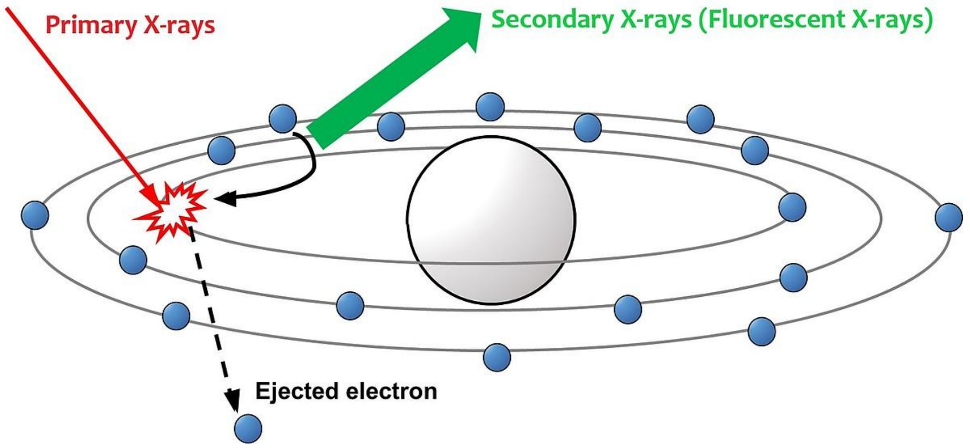
- Thermal Optical Reflectance (TOR) and Thermal Optical Transmission (TOT)
- Detector (flame ionization detector or non-dispersive IR) measures total carbon (TC)
- TC is split into organic carbon (OC) and elemental carbon (EC) via *evolved gas analysis*
- Organic matter mass can be ~1.4-2.5 times OC

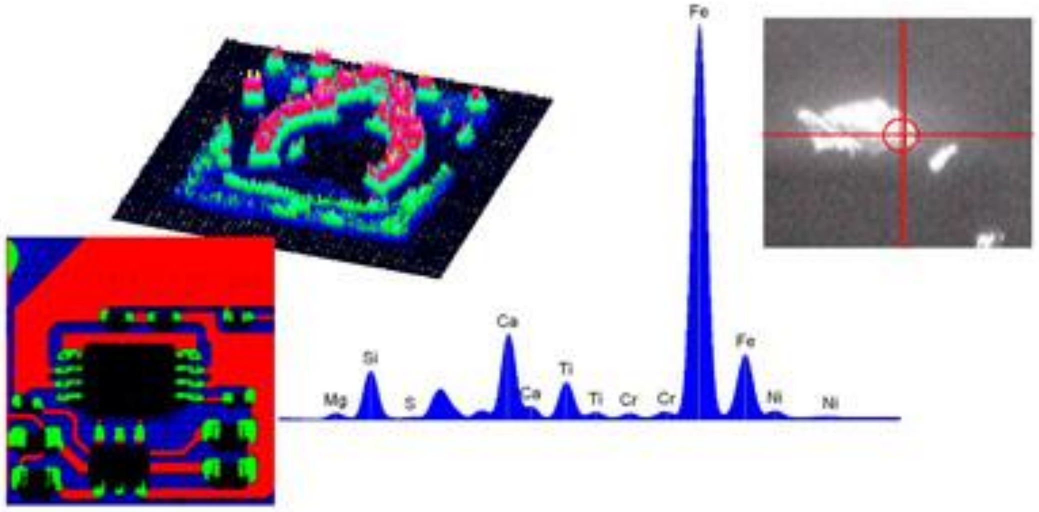


Chow et al., *Environ. Sci. Tech.*, 2004

X-Ray fluorescence

- Analysis of ~40 elements
- Most comprise a few percent of the total mass

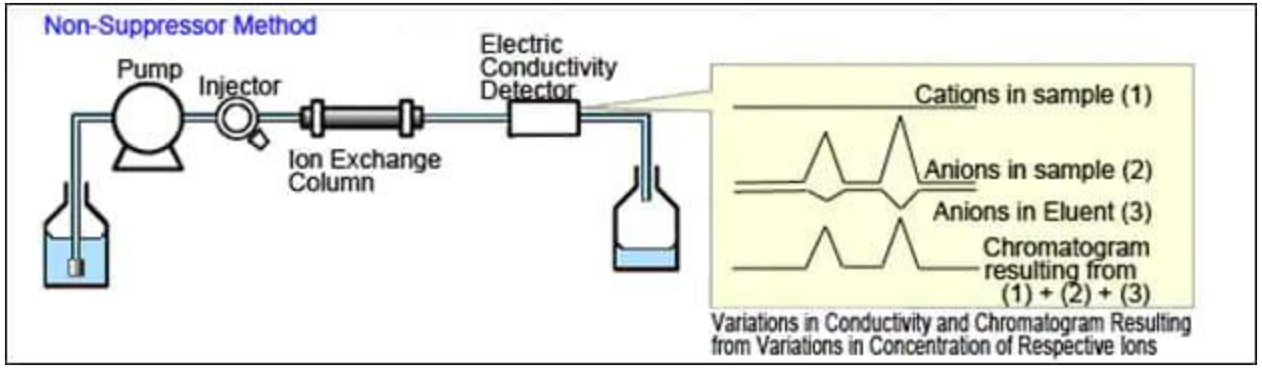


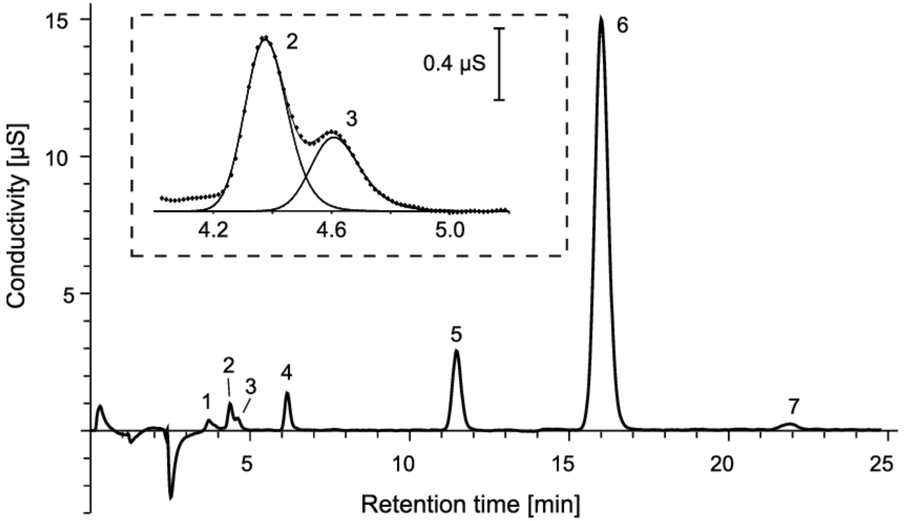


https://www.horiba.com/int/scientific/technologies/energy-dispersive-x-ray-fluorescence-ed-xrf/what-is-x-ray-fluorescence-xrf/

Ion chromatograph

- Major water-soluble ions (inorganic salts, dust)
- Cations and anions require separate columns and mobile phases – both are not always analyzed

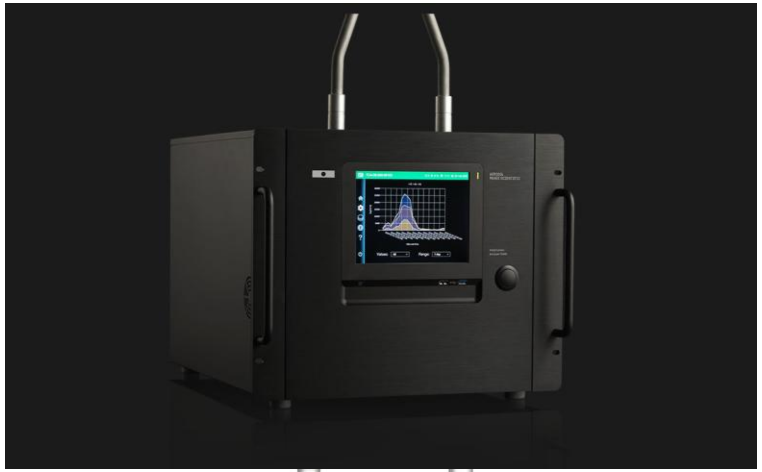




Lukács et al., *Atmos. Chem. Phys.*, 2008
https://www.ssi.shimadzu.com/industries/environment/ion-chromatography/index.html

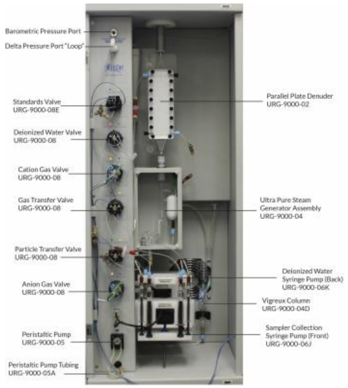
Automation

Carbon analyzer



Magee Scientific

Ion monitors
(ICs not shown)



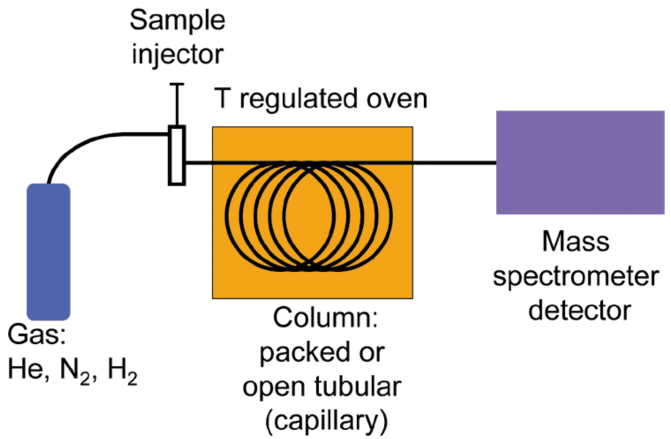
Metrohm
URG Corporation

Metals analyzer

Cooper Scientific

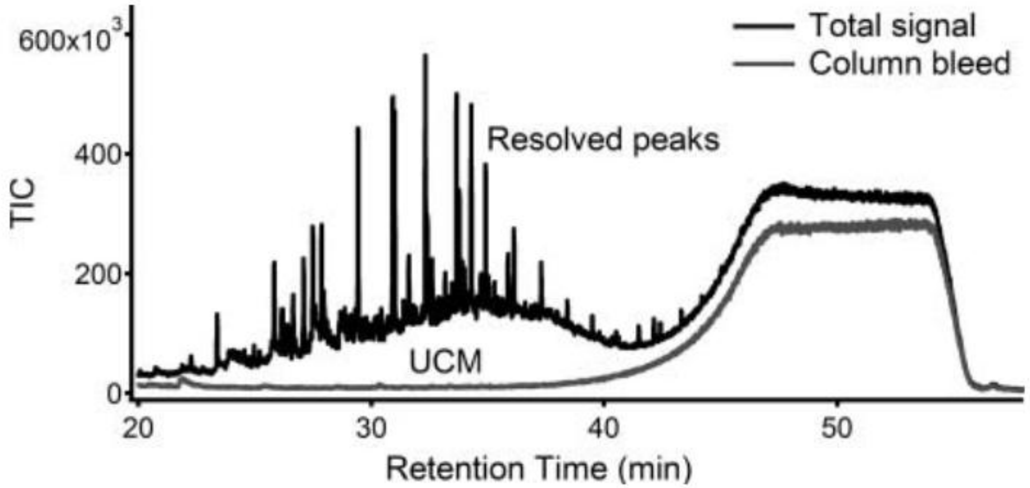
Scientific workhorses

Gas chromatography
- Preparation: extraction / derivatization / vaporization
- Molecular identification possible with mass spectrometer
- 10-20% mass recovery

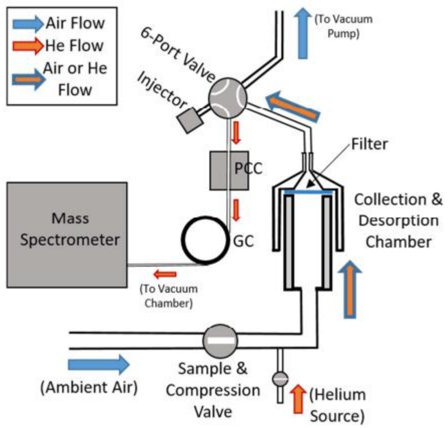


Wikipedia.com

Zhang et al., *Aerosol Sci. Tech.*, 2014



Online version



Cropper et al., *Atmos. Environ.*, 2017

Agilent Technologies

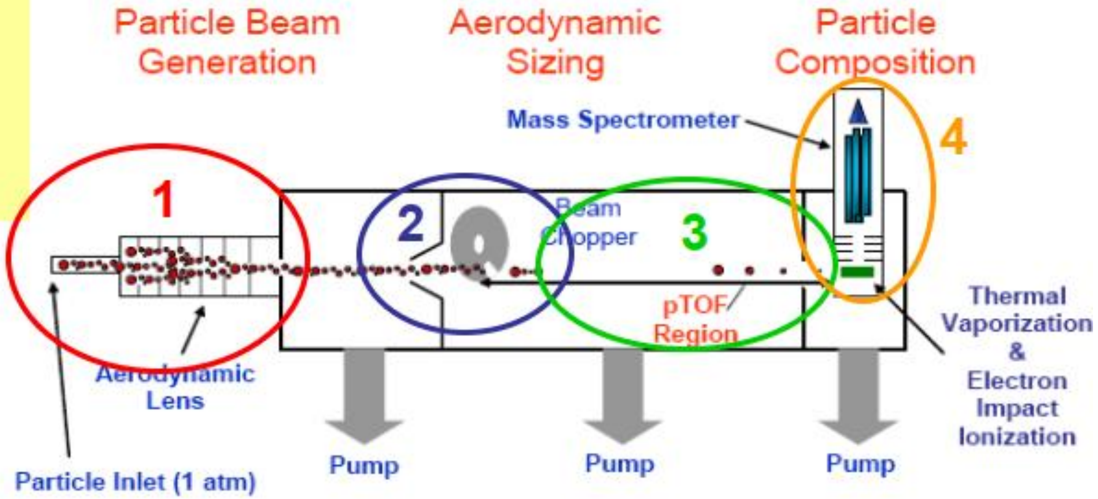
measurement of particle ingredients
Aerosol Mass Spectrometer (AMS)

on-line analysis of particulate composition

elements: C, H, O, N , Fe, Zn, Pb, Hg

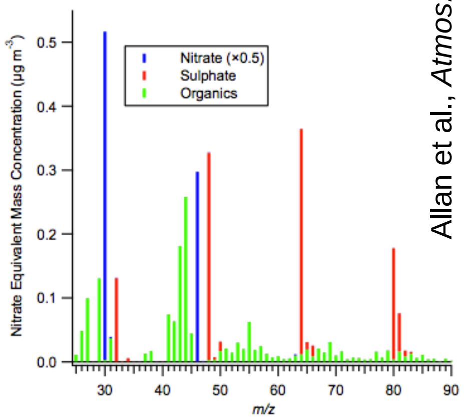
and PAHs

- High time resolution
- Inorganic + organics (typically not dust)
- Collection efficiency (50-100%)
- Molecular mass fragments



1. Aerosol particles (0.04-1µm) are sampled into a vacuum system and focused
2. A rotating beam chopper provides packages of particles
3. Size separation with the time-of-flight (TOF) technique
4. Detection of elements by quadrupole mass spectrometry *(or time of flight mass spectrometer)*

Aerodyne and TSI



Allan et al., *Atmos. Chem. Phys.*, 2004