

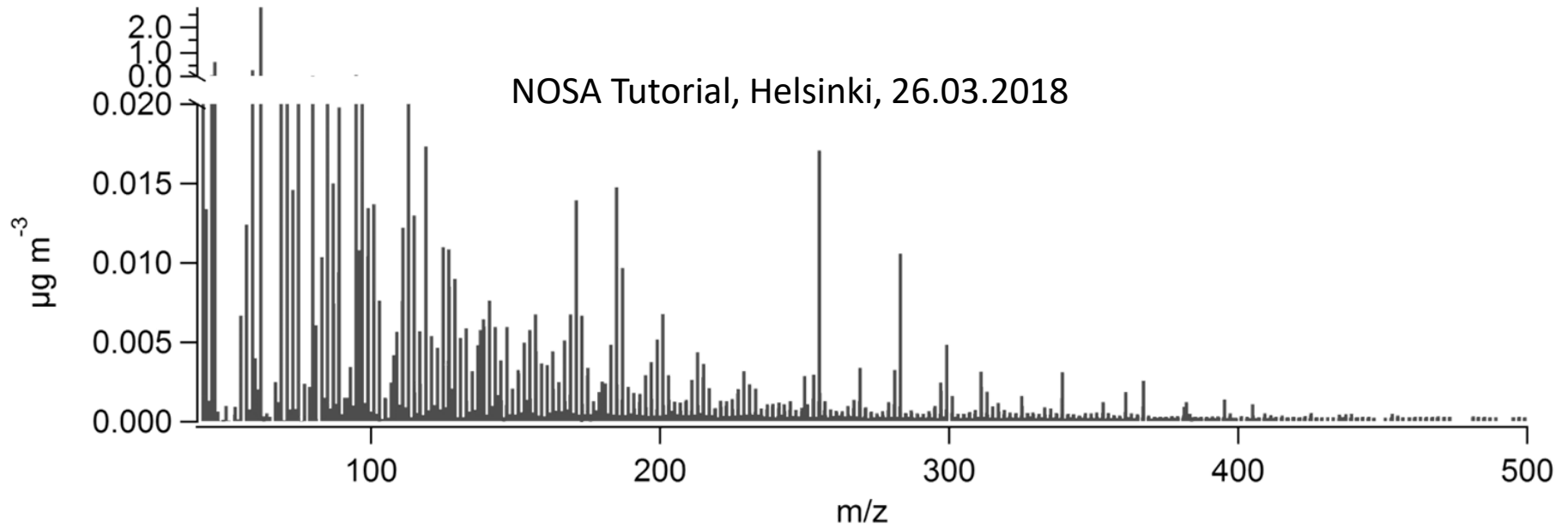
# Mass spectrometric measurements of organic aerosol particles: Applications in air quality and climate research

**Claudia Mohr**

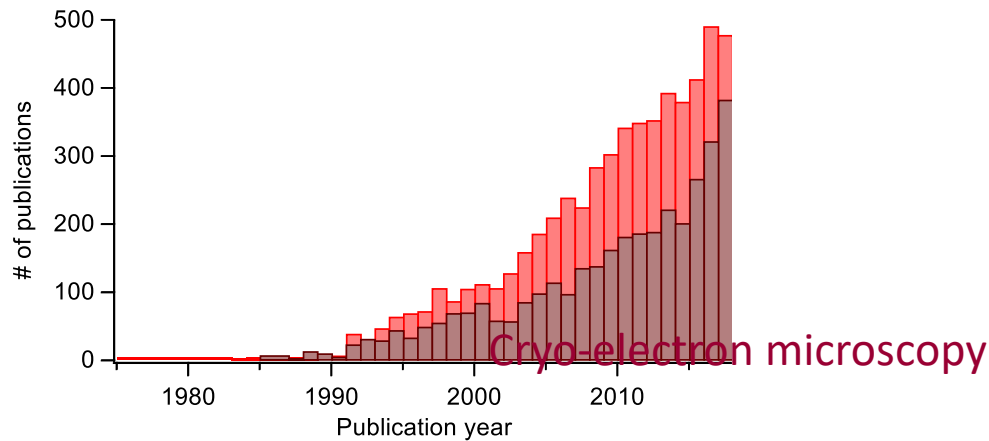
*claudia.mohr@aces.su.se*

Department of Environmental Science and Analytical Chemistry (ACES)

Stockholm University



# Number of publications with “Mass spectrometry” and “Aerosols” as topic (Web of Science), 1975 - today

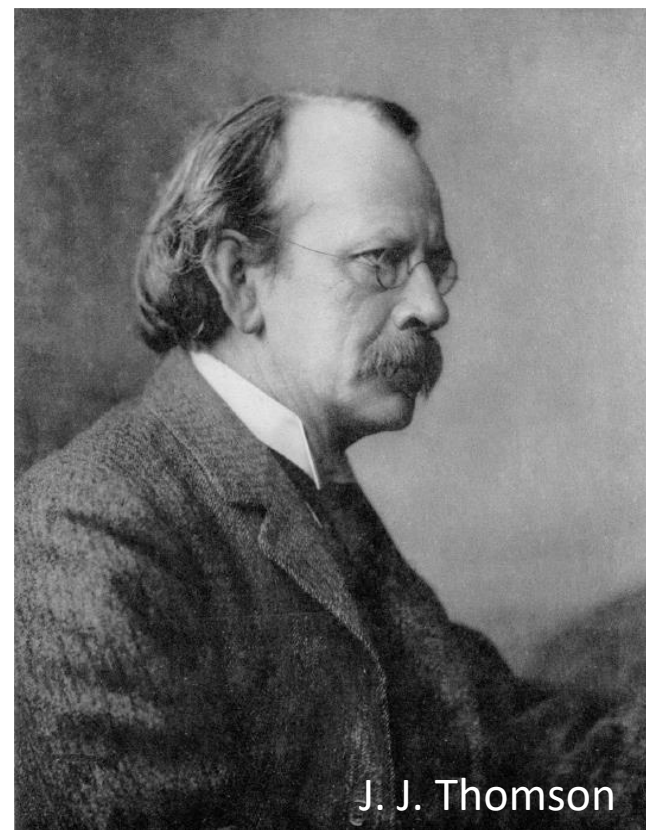


# What I'll be talking about

- Mass spectrometry is a very powerful tool in (organic) aerosol chemical analysis
  - History, main principles of mass spectrometry
  - Inlet, vaporization, ionization determine what we can analyze
- Has led to vast advances in our understanding of organic aerosol chemistry and formation
  - Chemistry and why it matters for air quality and climate
- Mass spectrometric applications in aerosol chemistry
  - Biased towards my own research; just examples and by no means complete!

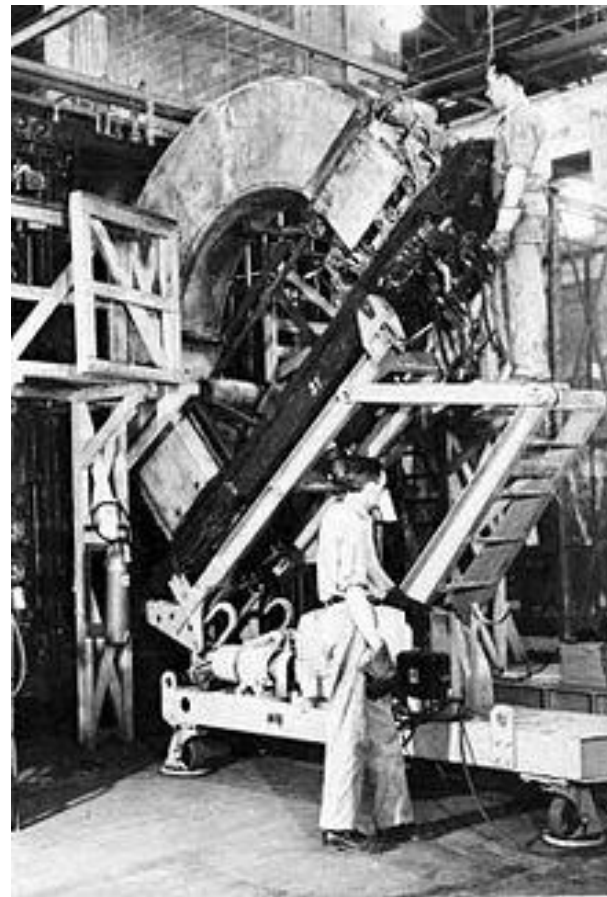
# The beginning of mass spectrometry

- Born in the field of physics
- 1899: J. J. Thomson builds an instrument that can measure  $e/m$  and  $e \rightarrow$  mass of the electron, Nobel Prize in Physics 1906.
- Later builds the “first mass spectrometer” to measure the masses of charged atoms.



# Mass spectrometry and the beginning of the nuclear age

- MS was pushed into prominence in the 1940s: World War II and the Manhattan Project
- Alfred Nier: Managed to separate  $^{238}\text{U}$  and  $^{235}\text{U}$  → uranium enrichment, nuclear age, and atomic bomb



MS used in the Manhattan Project for U enrichment

# Chemists join the game...

- “Unexplainable, voodoo, black magic kind of tool”



- 1950s: Transition from industrial chemistry to academia; research on the relationship of mass spectrum to the molecular structure
- Late 1980s: Application in aerosol research

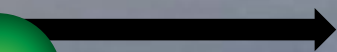
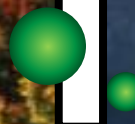
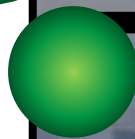
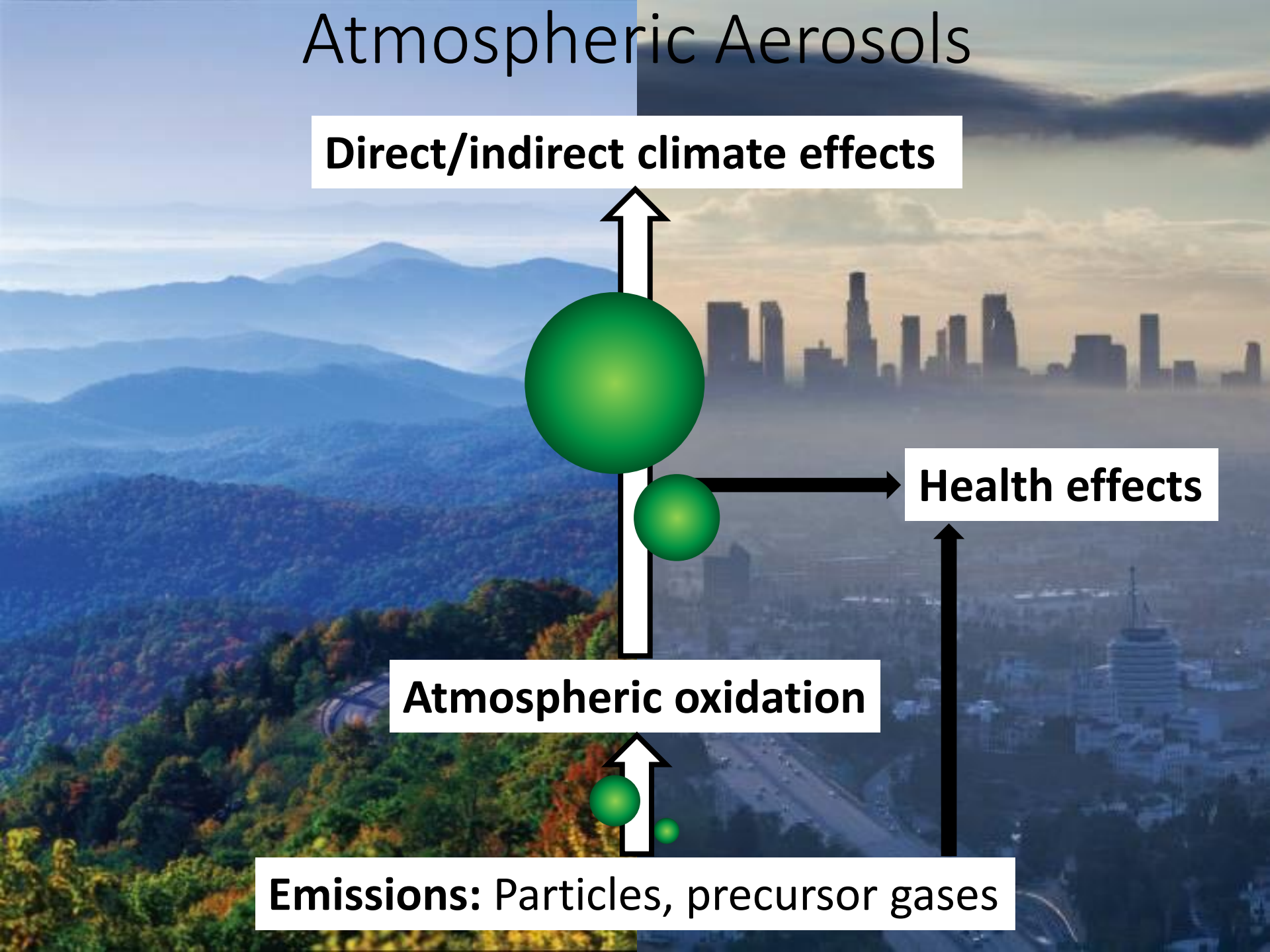
# Atmospheric Aerosols

**Direct/indirect climate effects**

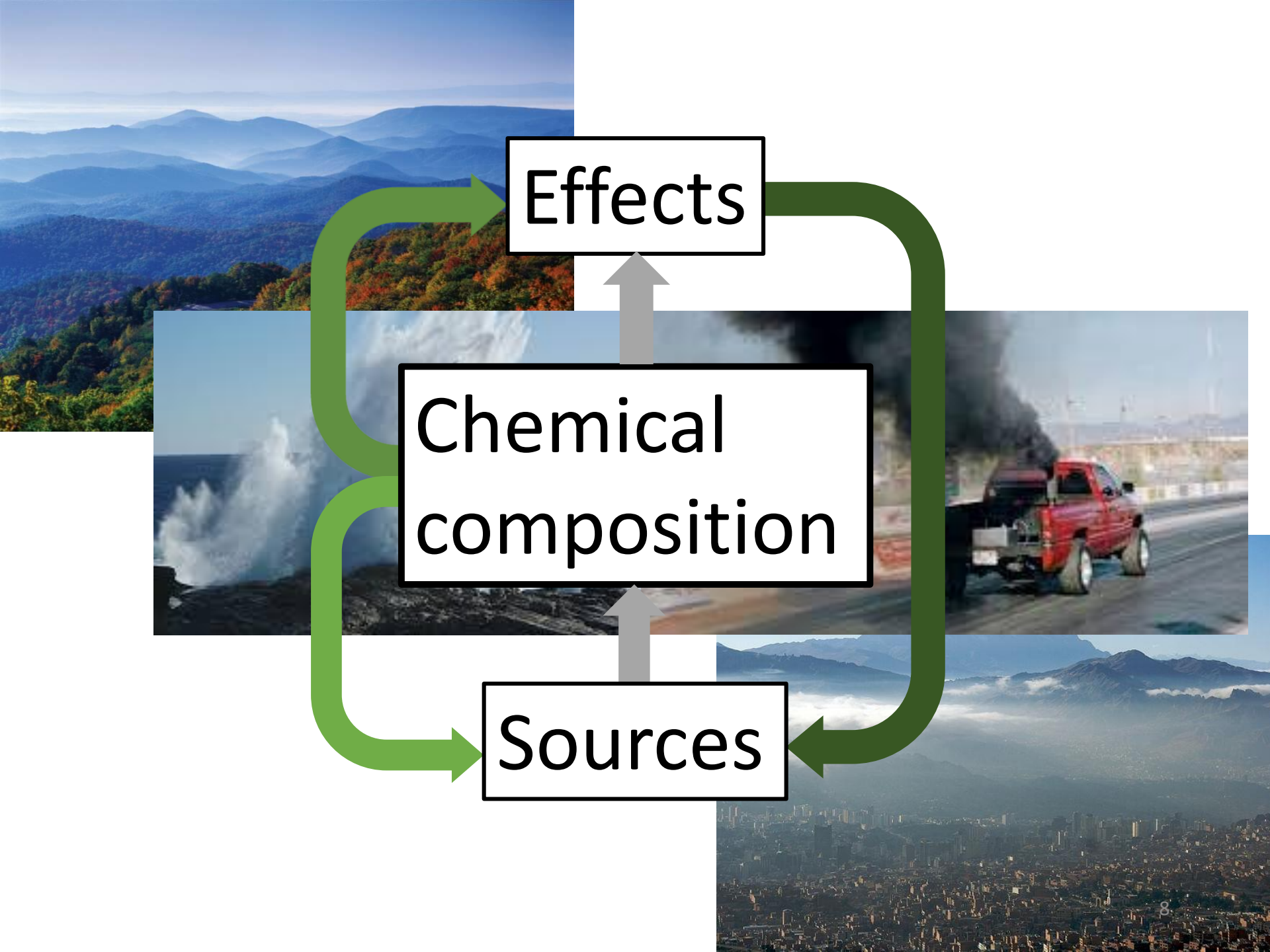
**Health effects**

**Atmospheric oxidation**

**Emissions: Particles, precursor gases**



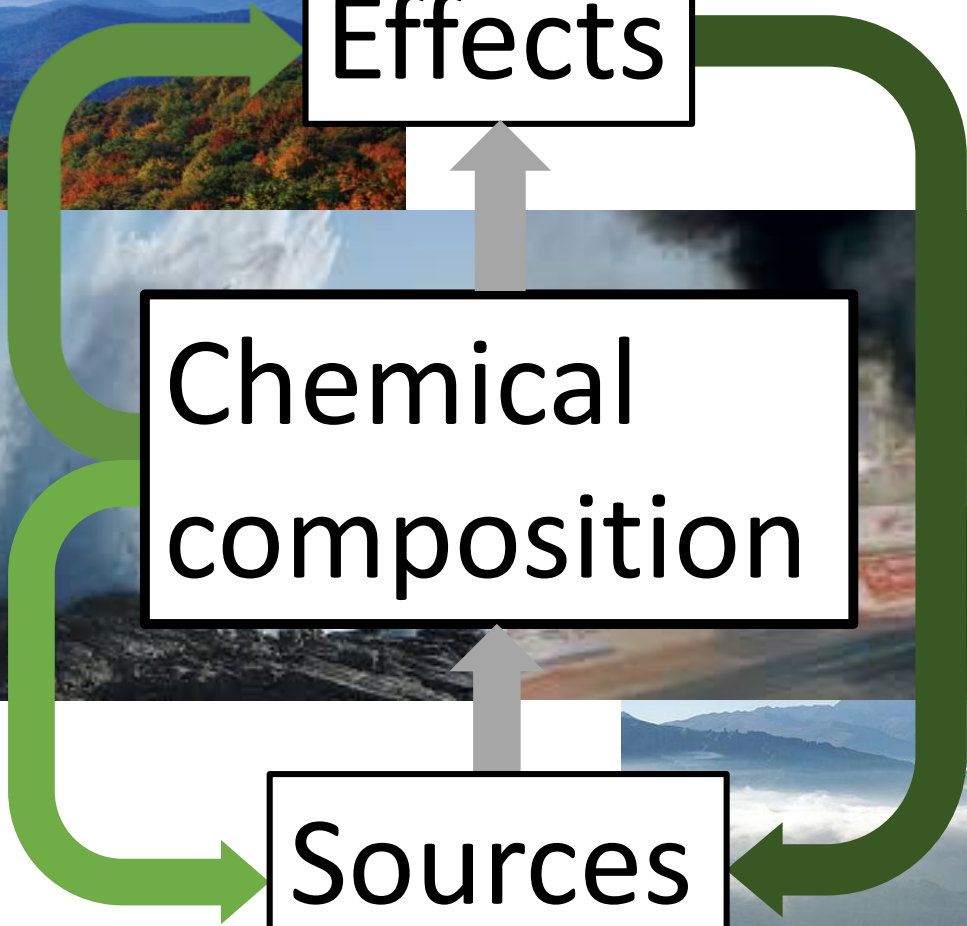




Effects

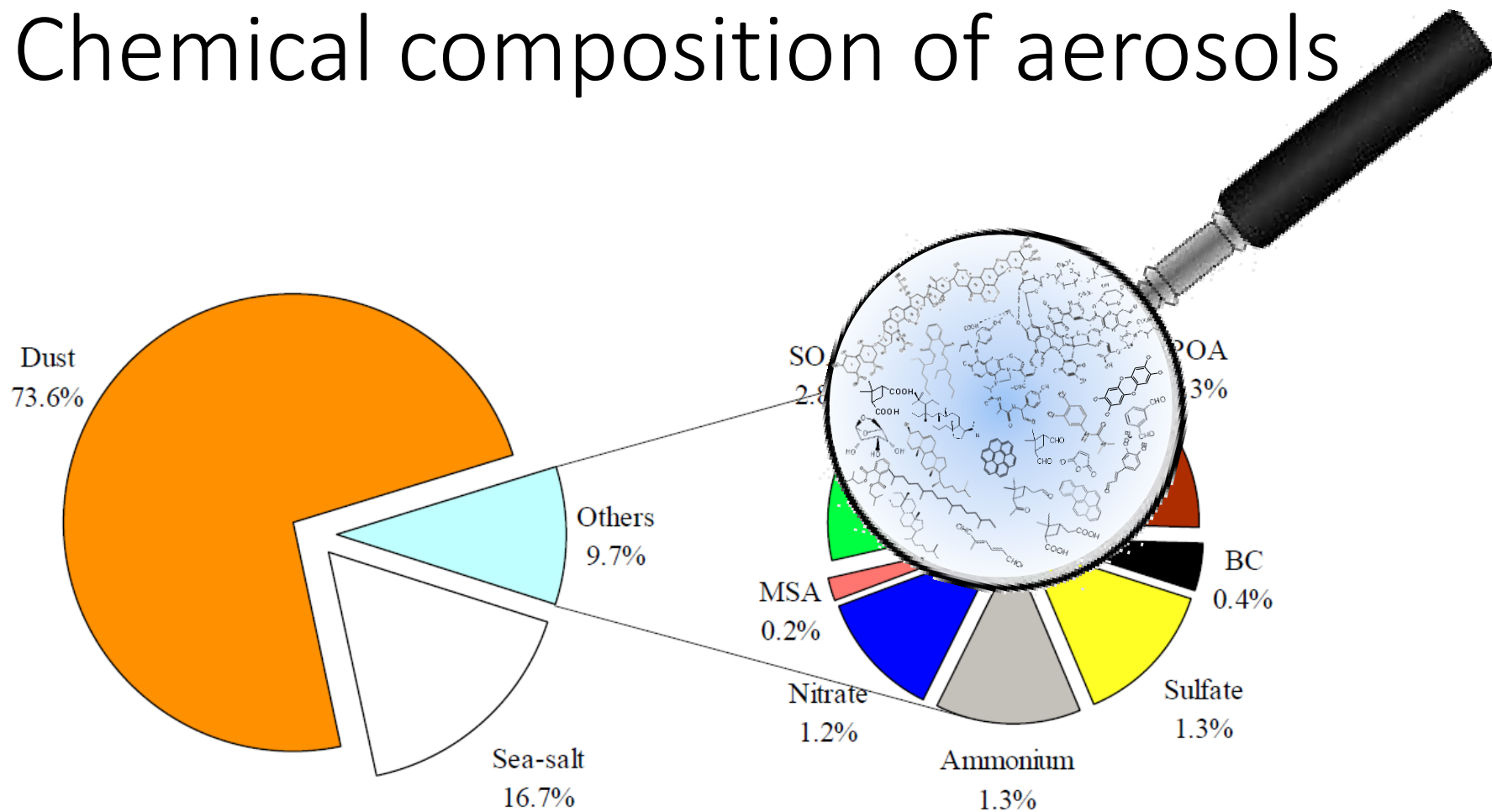
Chemical composition

Sources

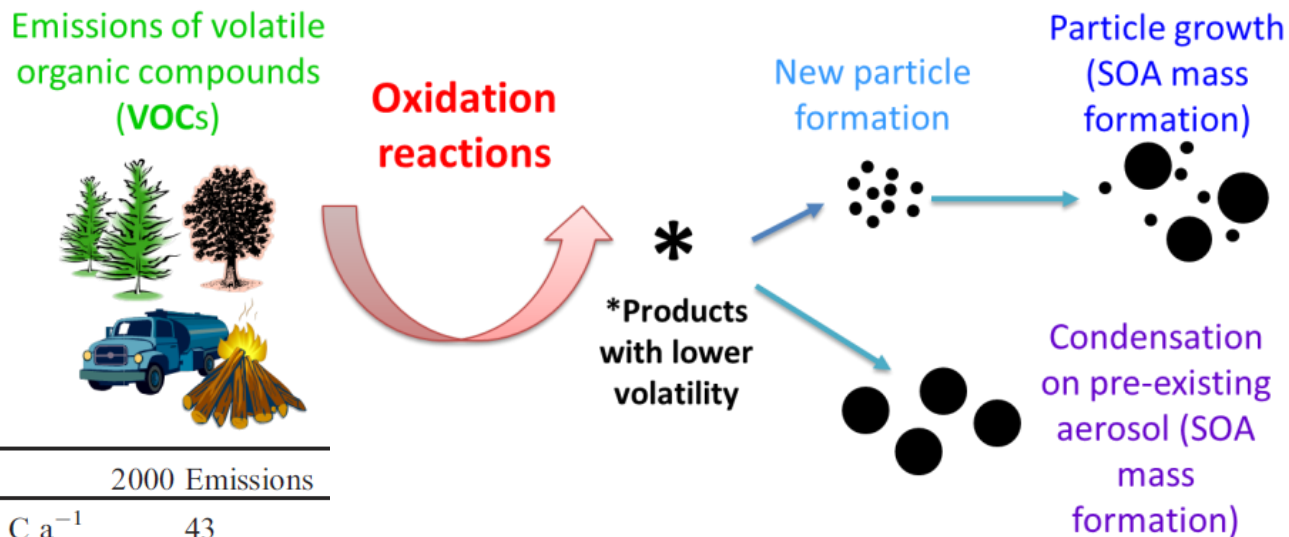




# Chemical composition of aerosols



# Secondary organic aerosols



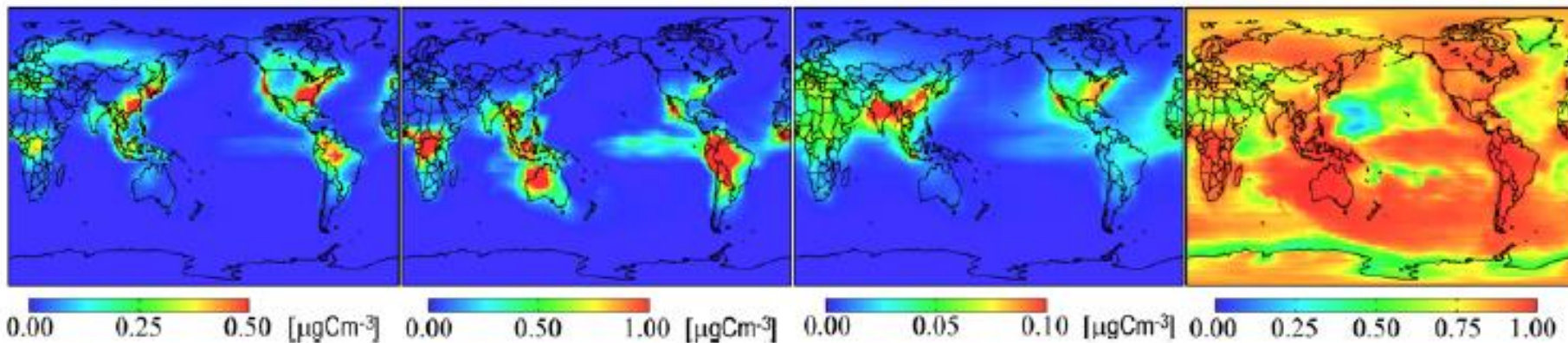
Species	2000 Emissions
Monoterpenes, Tg C a <sup>-1</sup>	43
Isoprene, Tg C a <sup>-1</sup>	496
Aromatics, <sup>b</sup> Tg C a <sup>-1</sup>	16.0

SOA (monoterpenes)

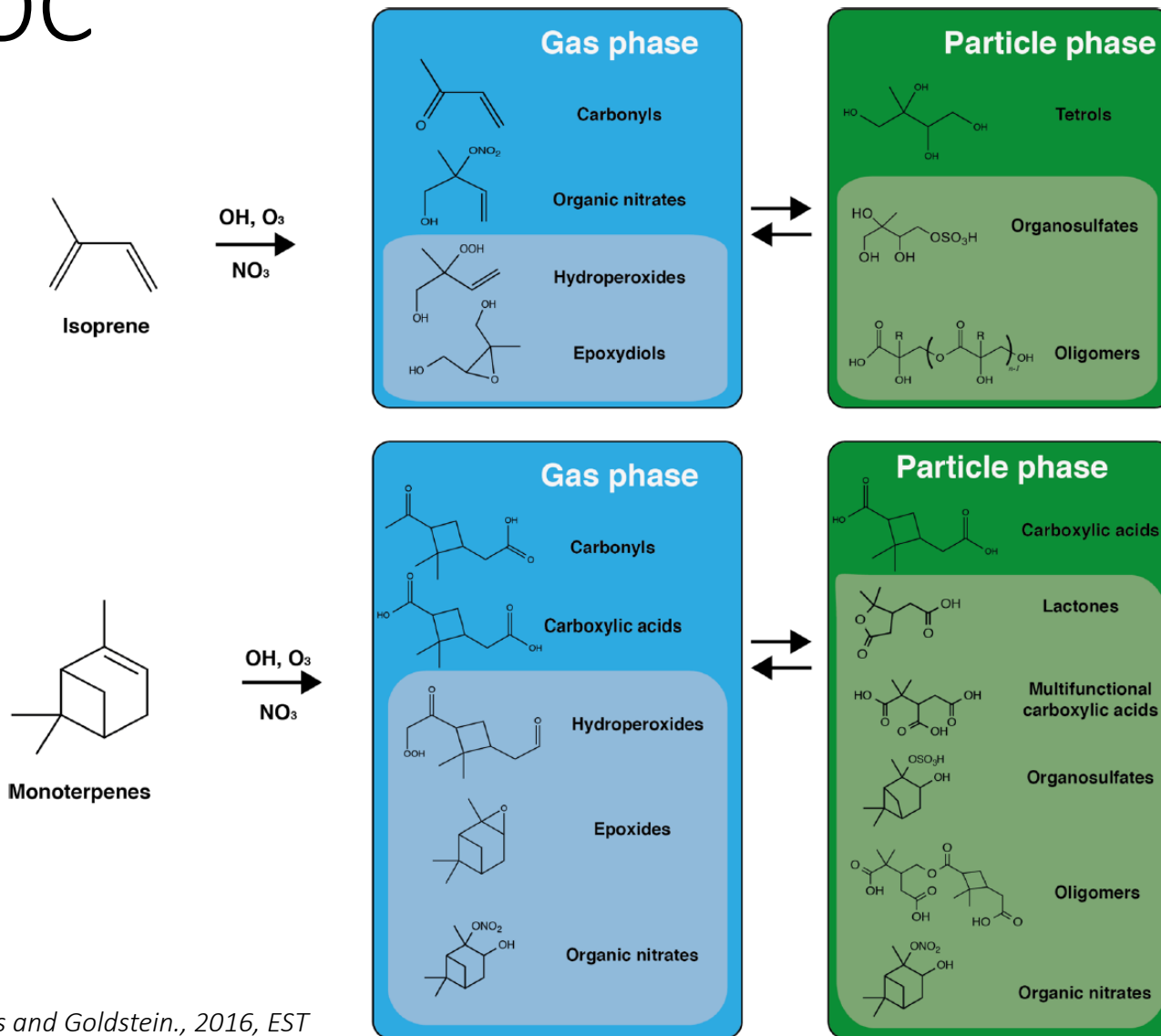
SOA (isoprene)

SOA (aromatics)

Fraction biogenic

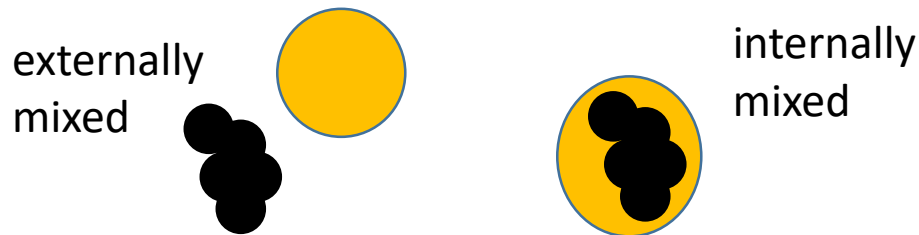


# Oxidation products of biogenic VOC



# Measuring aerosol composition: An analytical challenge

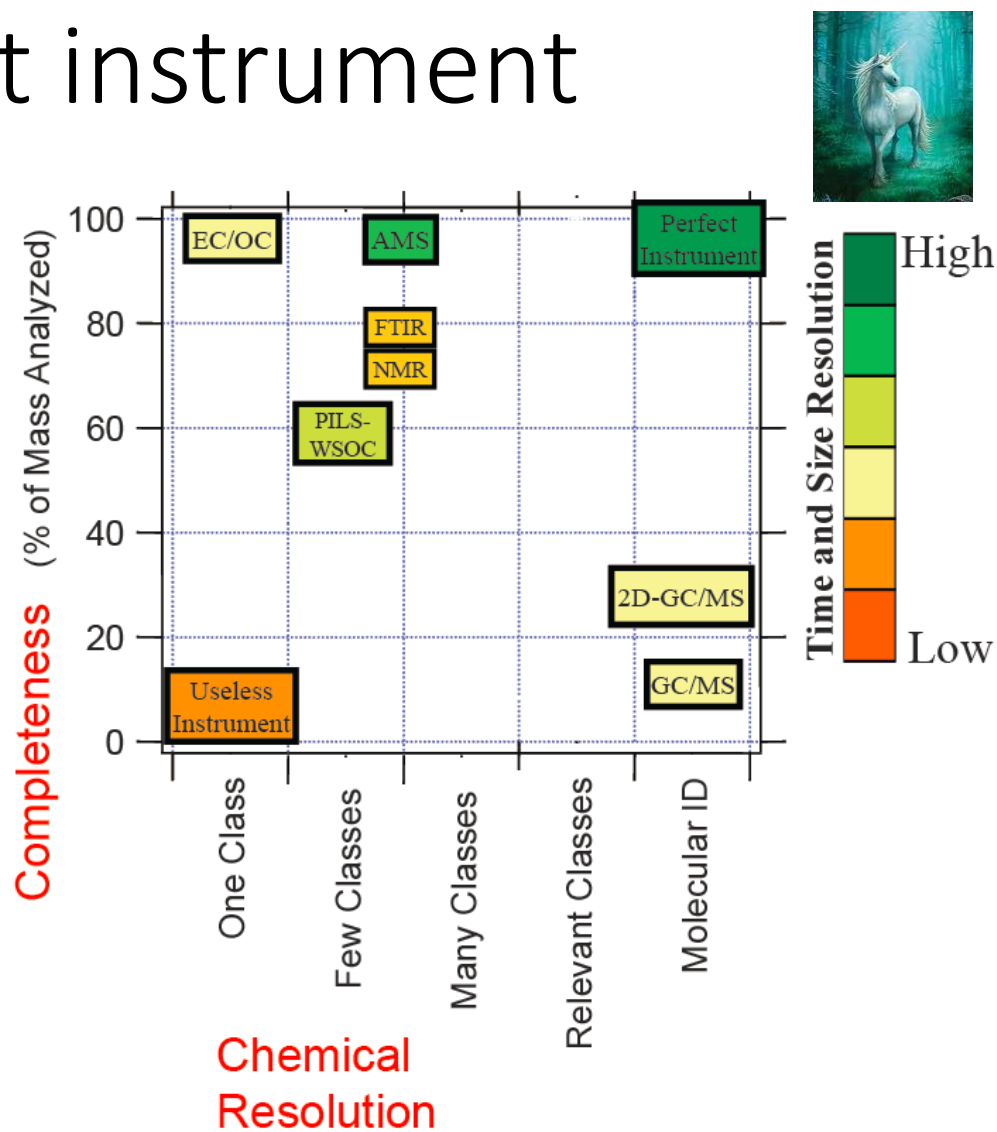
- $\sim 10^{12}$  to  $10^{15}$  molecules per aerosol particle
- $\sim 10^{-20}$  to  $10^{-6}$  g/particle of mass
- Organic carbon
  - > 10,000 organic compounds!
  - Variety of properties: consider oil vs. an alcohol
- Mixing state



# To address the challenge

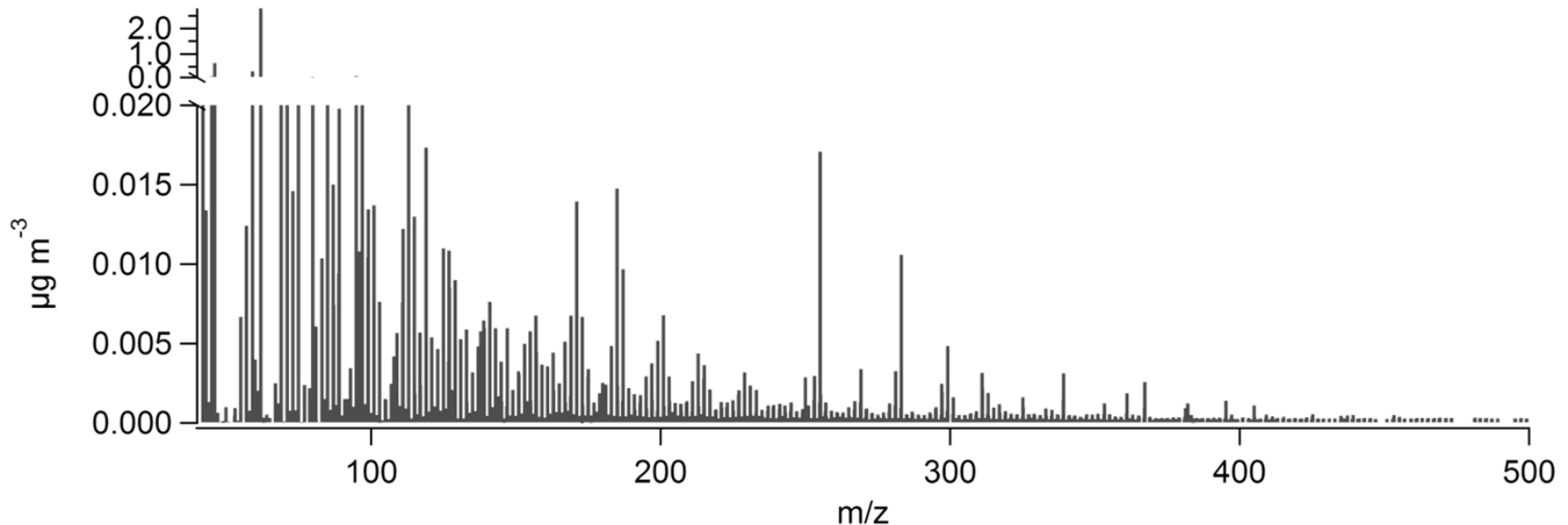
- High time resolution
- High sensitivity
- Quantitative
- Completeness/selectiveness

# Organic aerosol composition – the perfect instrument



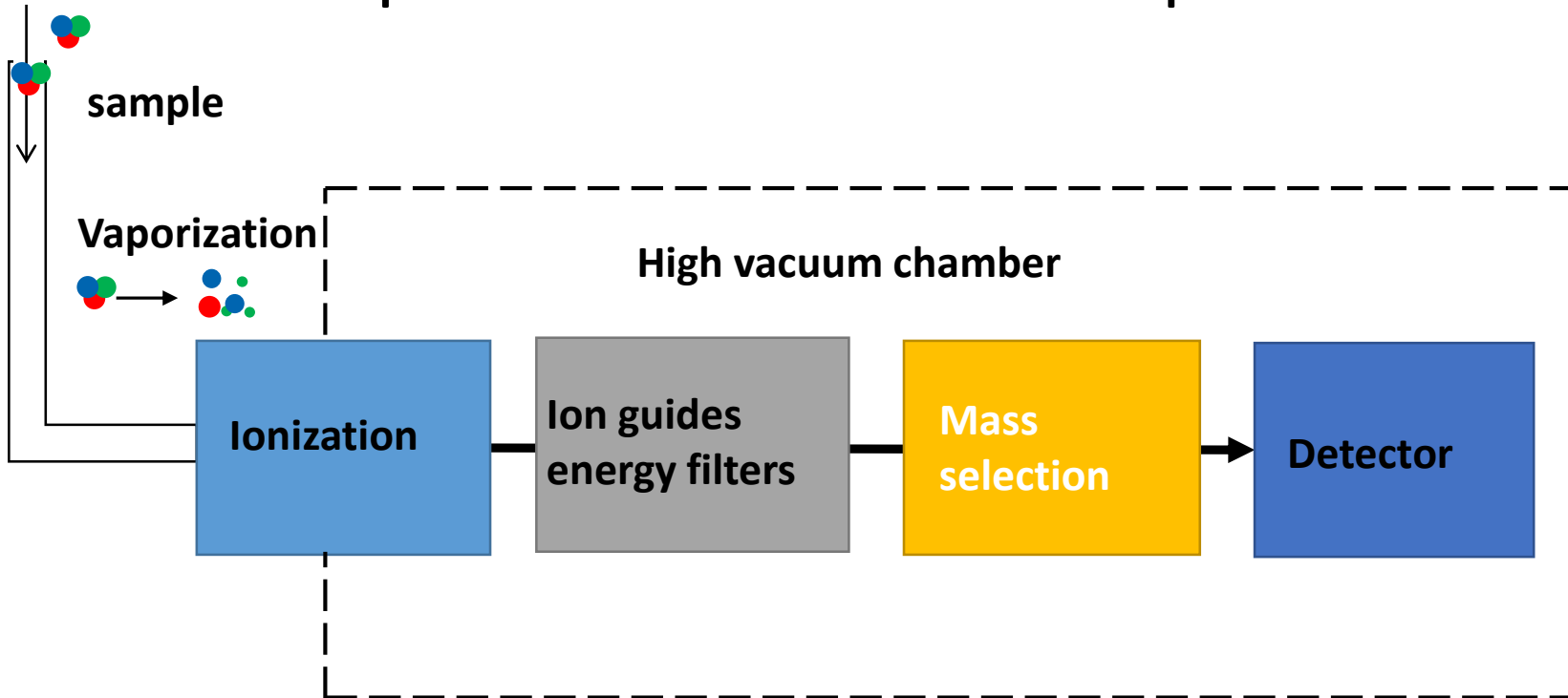
# Mass spectrometry

- Identifies compounds based on
  - elemental mass
  - molecular mass
  - mass of molecular fragments
- Involves ionization of the measured species: Separation of ions based on their motions in magnetic and/or electrical fields
- The measured entity is mass-to-charge,  $m/z$
- Particles: Vaporization





# Mass spectrometer components



Vaporization and ionization: Selective, artifacts (fragmentation)

# The importance of vacuum

- To control ion motions well, they need to be collision-free
- Collision frequency proportional to pressure
- Typical pressure (mass selector)  $<1 \times 10^{-5}$  mbar
- Disadvantage: Adds power, weight and maintenance

Vacuum range	Pressure in hPa (mbar)	Molecules / cm <sup>3</sup>	Molecules / m <sup>3</sup>	Mean free path
Ambient pressure	1013	$2.7 \times 10^{19}$	$2.7 \times 10^{25}$	68 nm <sup>[2]</sup>
Low vacuum	300 – 1	$10^{19} - 10^{16}$	$10^{25} - 10^{22}$	0.1 – 100 μm
Medium vacuum	$1 - 10^{-3}$	$10^{16} - 10^{13}$	$10^{22} - 10^{19}$	0.1 – 100 mm
High vacuum	$10^{-3} - 10^{-7}$	$10^{13} - 10^9$	$10^{19} - 10^{15}$	10 cm – 1 km
Ultra high vacuum	$10^{-7} - 10^{-12}$	$10^9 - 10^4$	$10^{15} - 10^{10}$	1 km – $10^5$ km
Extremely high vacuum	$<10^{-12}$	$<10^4$	$<10^{10}$	$>10^5$ km

# Ionization

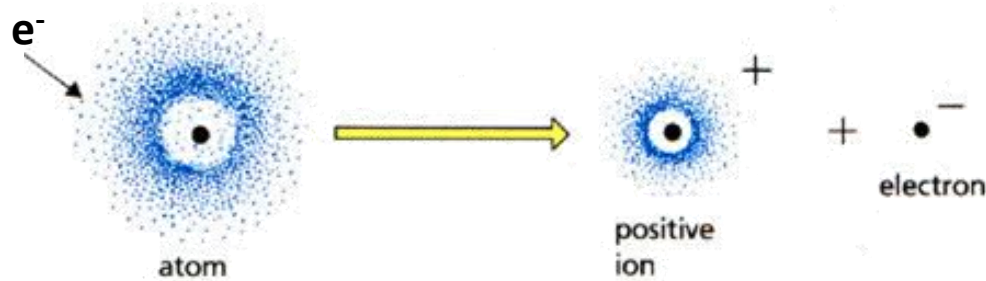
Impart a charge to a molecule or atom (+ or -)

- Widely used techniques:
  - Electron Ionization (EI)
  - Chemical ionization (CI)
  - Laser desorption
  - Inductively Coupled Plasma Ionization (ICP)
  - Electrospray
  - Glow discharge
  - ...

**Ionization techniques are selective and prone to artifacts (fragmentation of parent molecules)**

**Decide the compounds that can be analyzed**

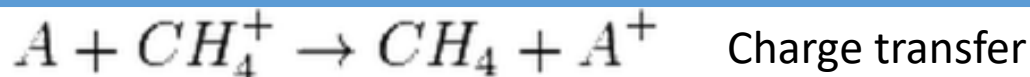
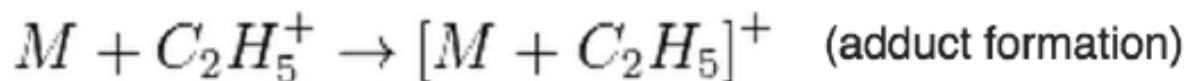
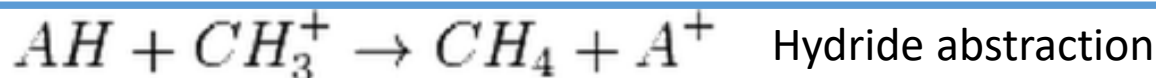
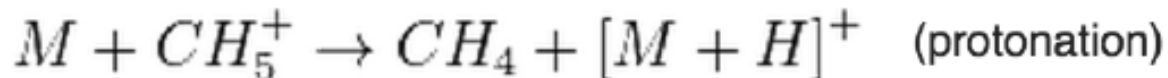
# Electron ionization



- De Broglie interaction:  $\lambda = \frac{h}{mv}$
- 70 eV  $\rightarrow$  0.14 nm, same scale as the molecular bonds for carbon
- Fragmentation

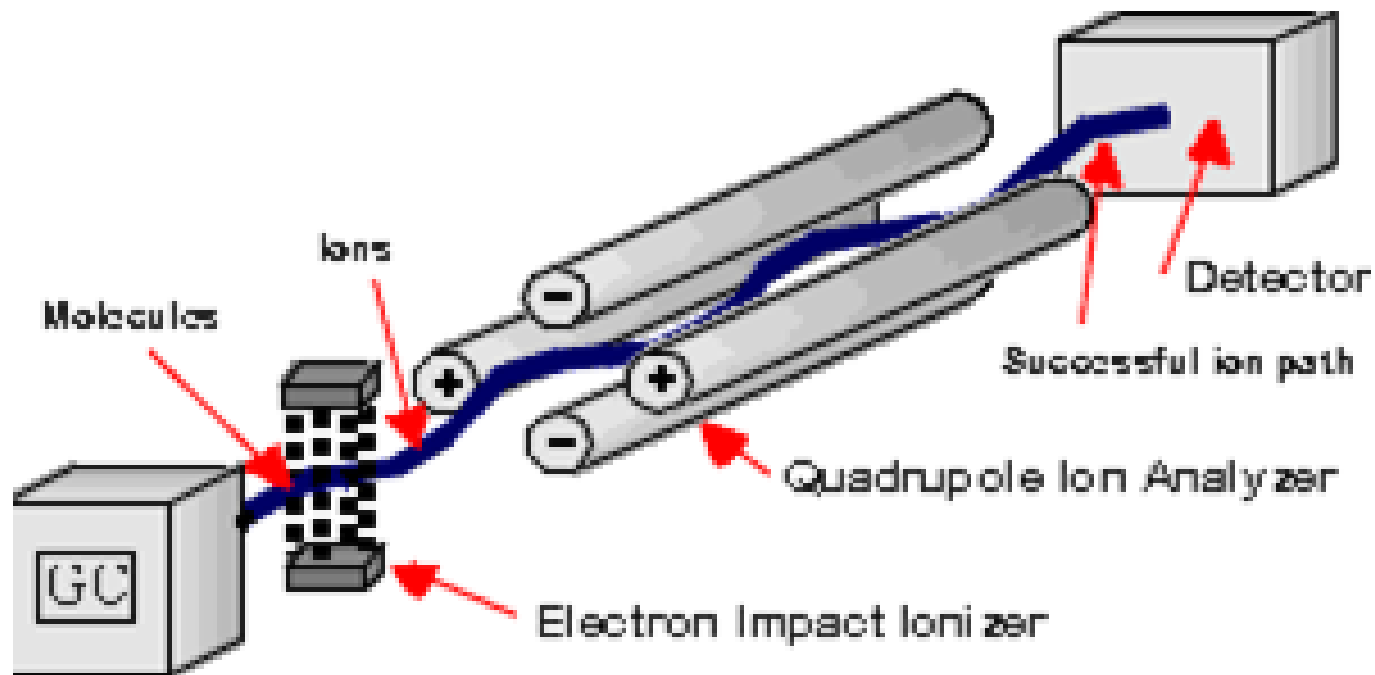
# Chemical Ionization

- Soft ionization – less fragmentation, molecules are easily recognized
- Collisions of the molecule to be analyzed with primary ions
- Chemical reactions produce positive and negative ions of the molecules to be analyzed



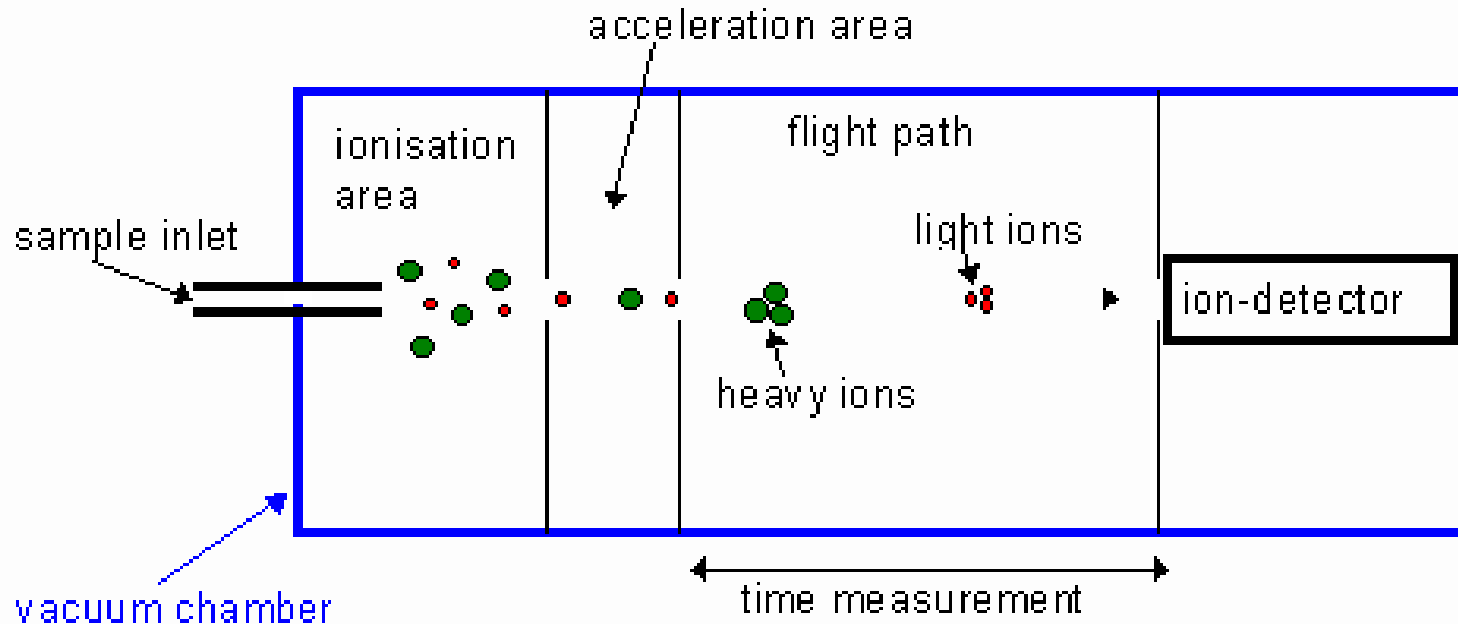
# Mass analyzer: Quadrupole

- Mass filter



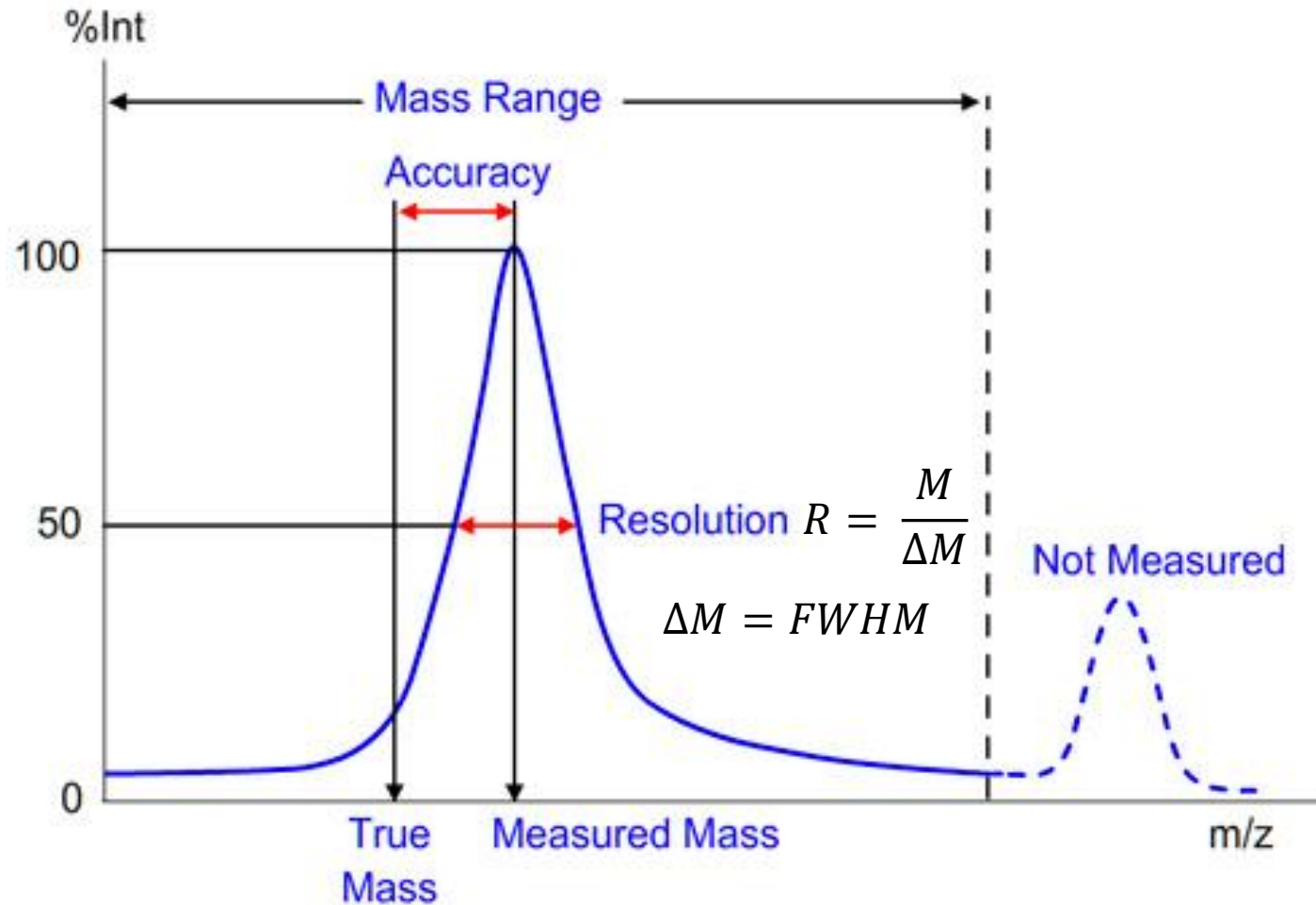
# Mass analyzer: Time of flight

- Mass separation

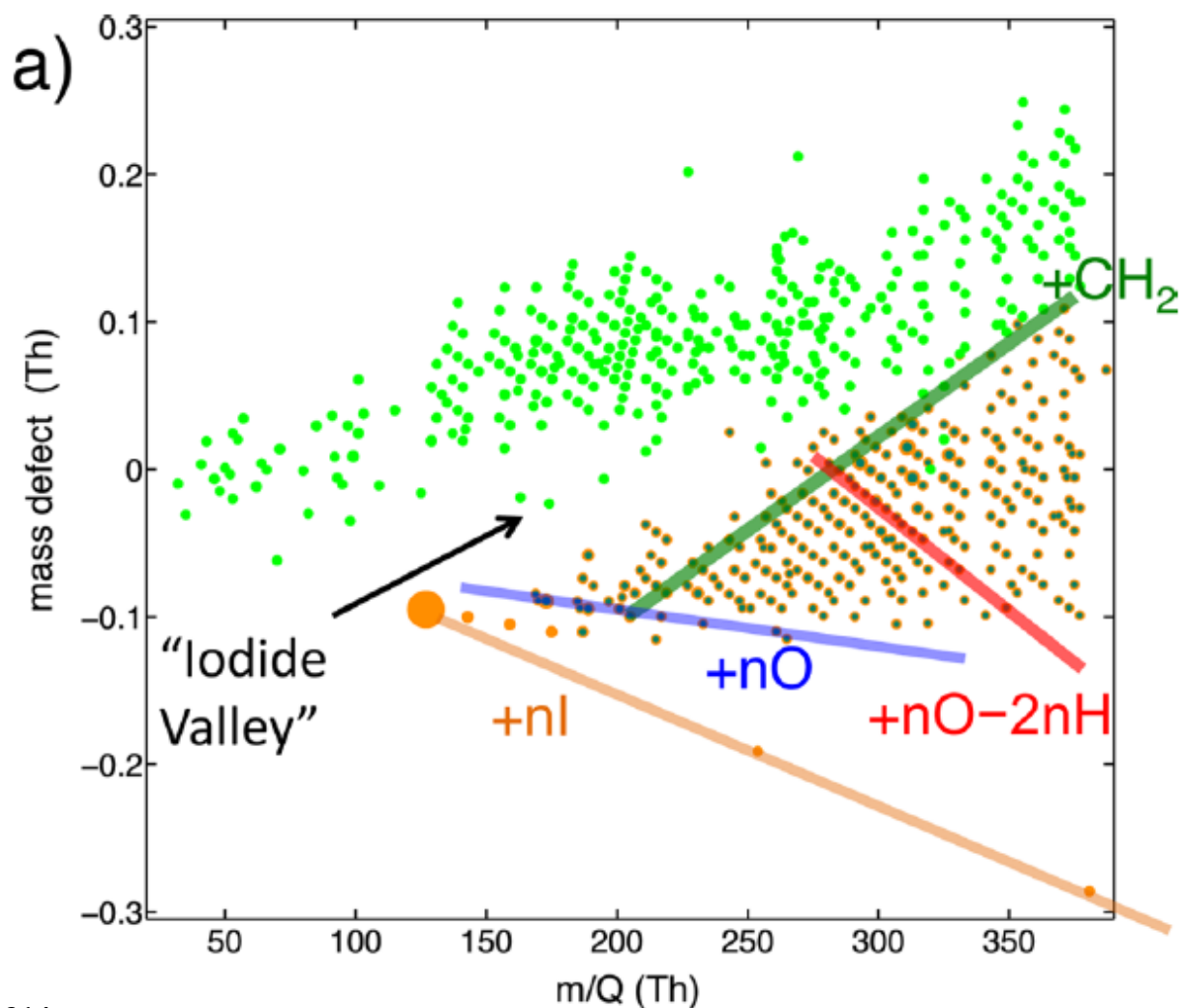




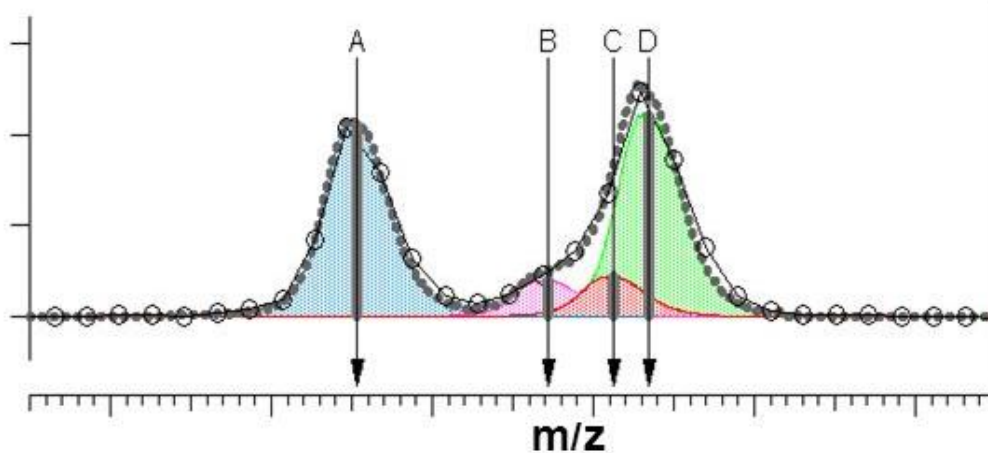
# Spectra and analysis



# Mass defect: Difference between “exact” and nominal mass



# Resolution and peak fitting



**Peaks at A,B,C,D have same 'shape' only different heights. At a peak height of 1, area under shape =  $\alpha$**

Area due to A = PeakHeightA \*  $\alpha$

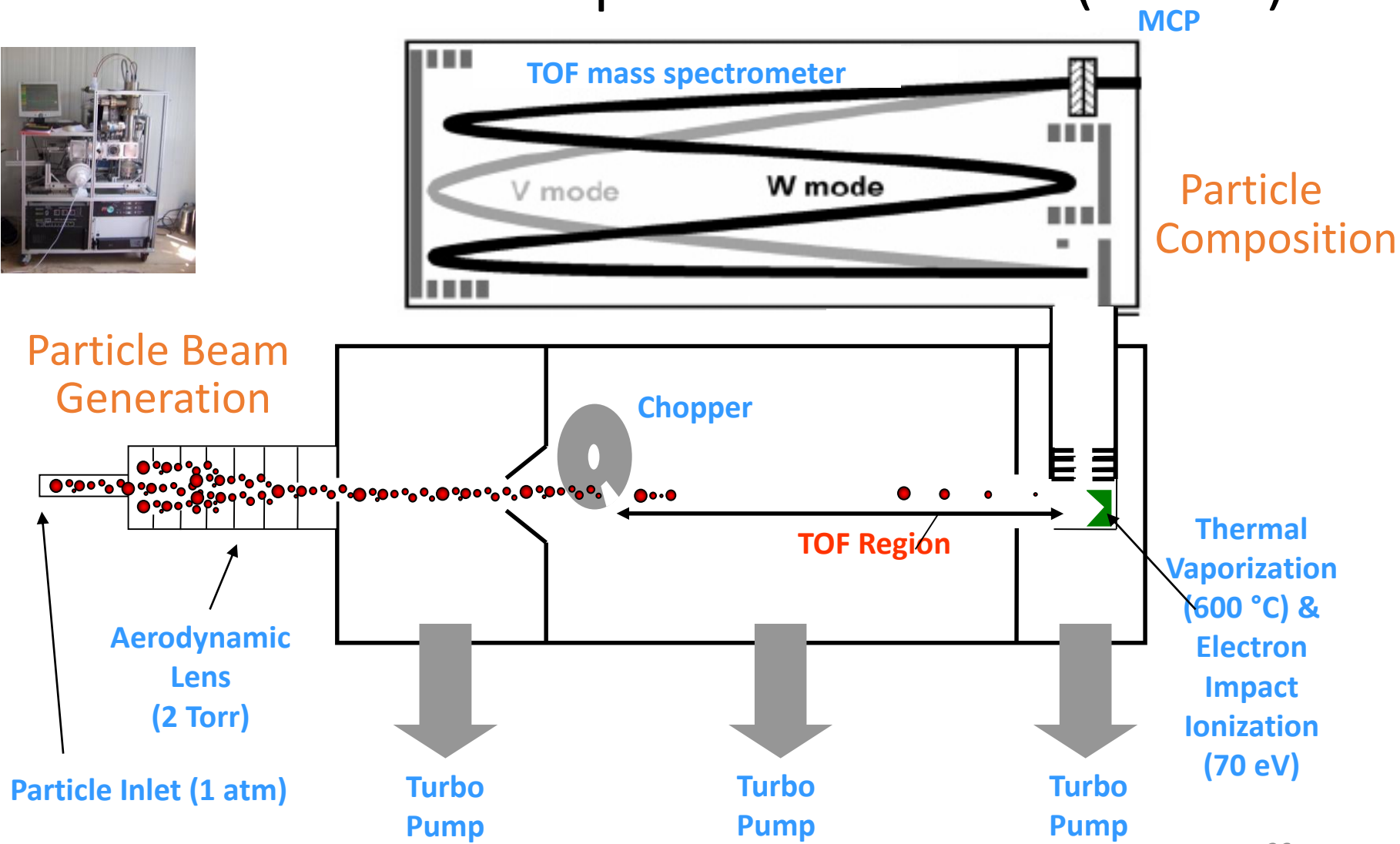
Area due to B = PeakHeightB \*  $\alpha$

Area due to C = PeakHeightC \*  $\alpha$

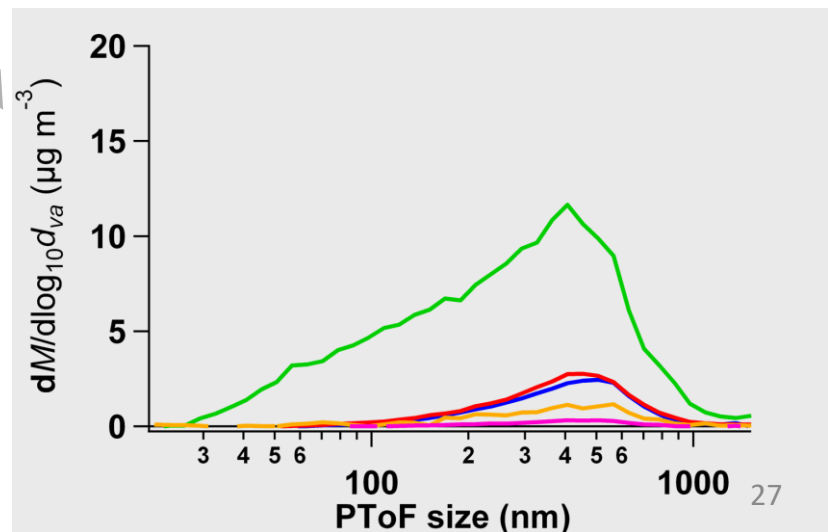
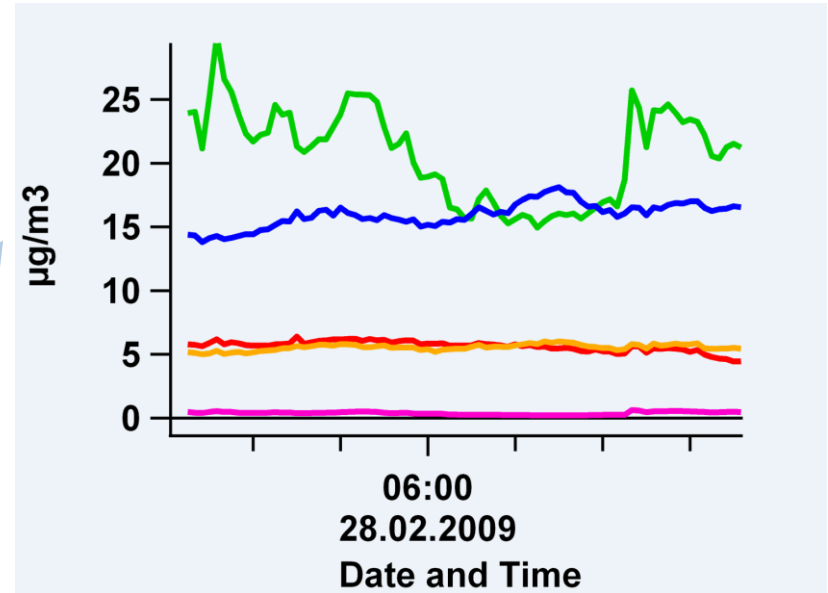
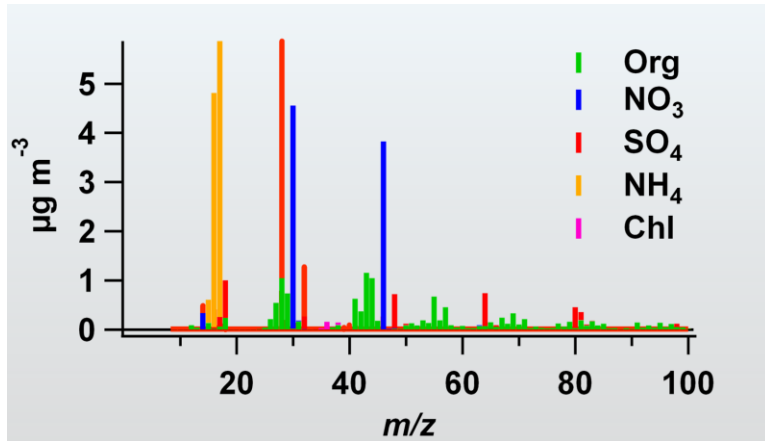
Area due to D = PeakHeightD \*  $\alpha$

As a check,  $\Sigma$  areas A,B,C,D  $\approx I_m$

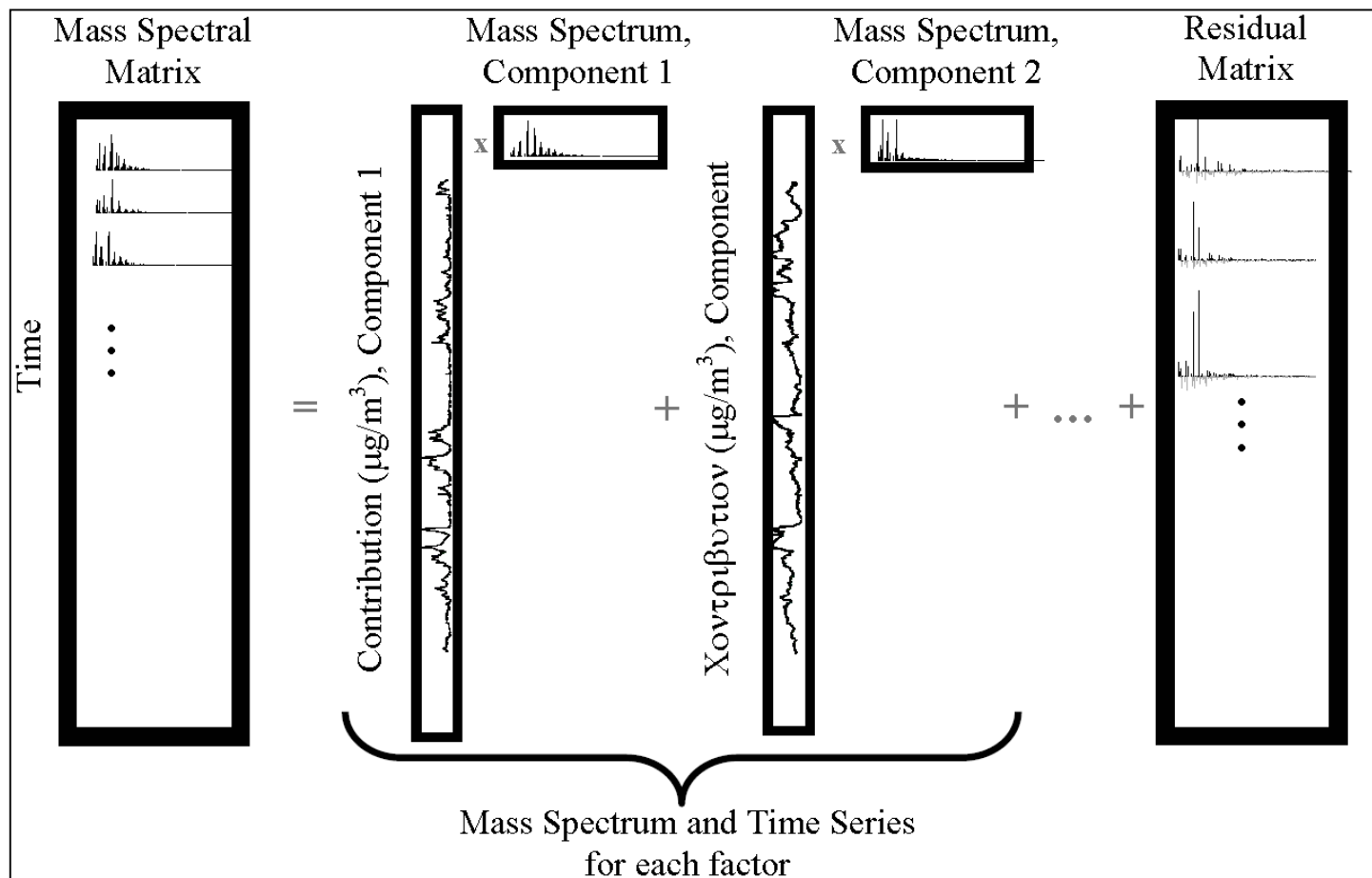
# Aerosol Mass Spectrometer (AMS)



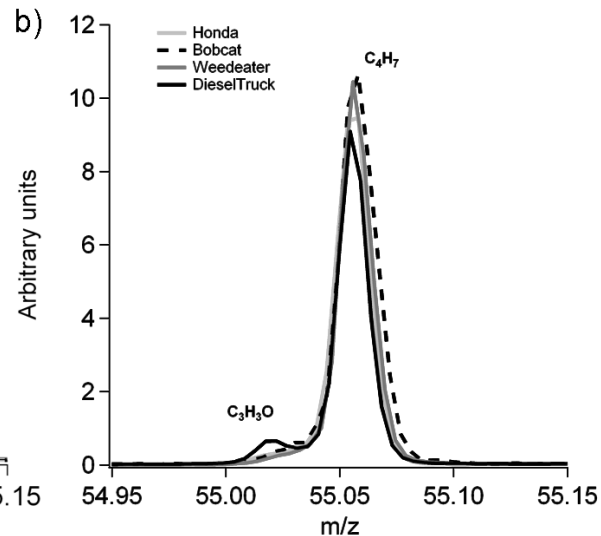
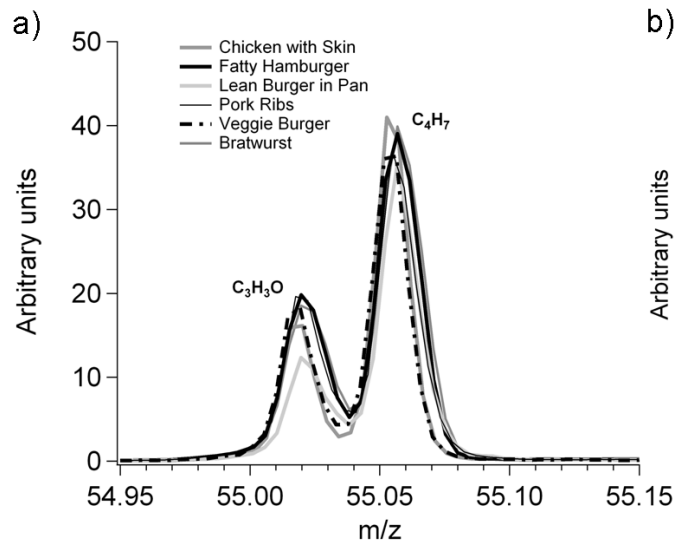
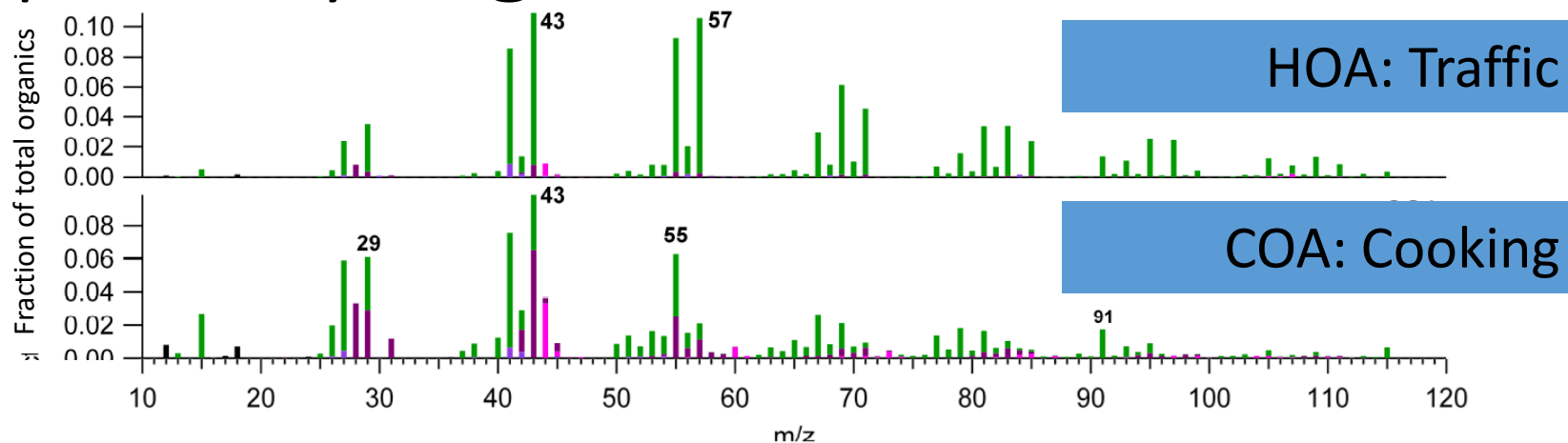
# AMS Data output



# Positive Matrix Factorization (PMF)



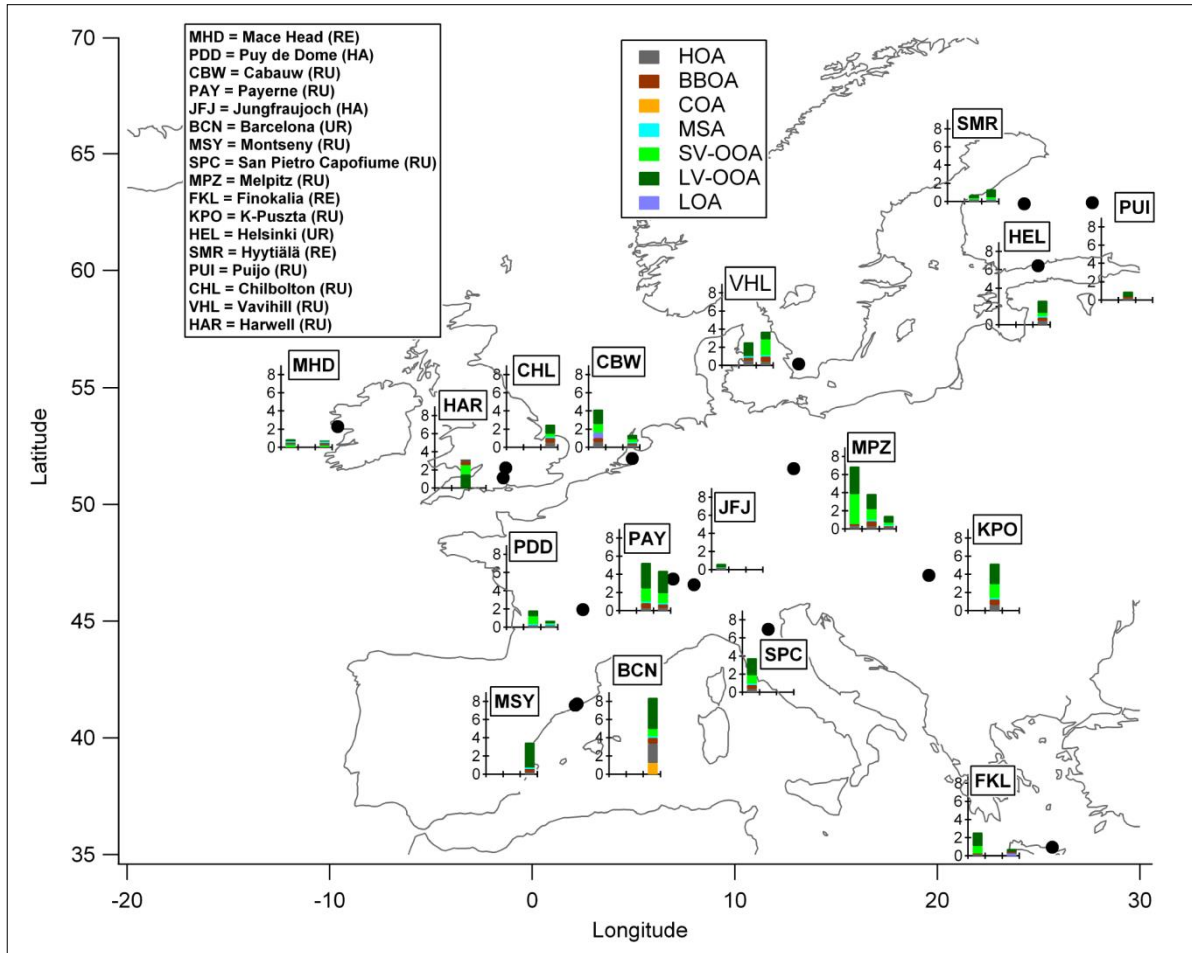
# Cooking: An important source of primary organic aerosols



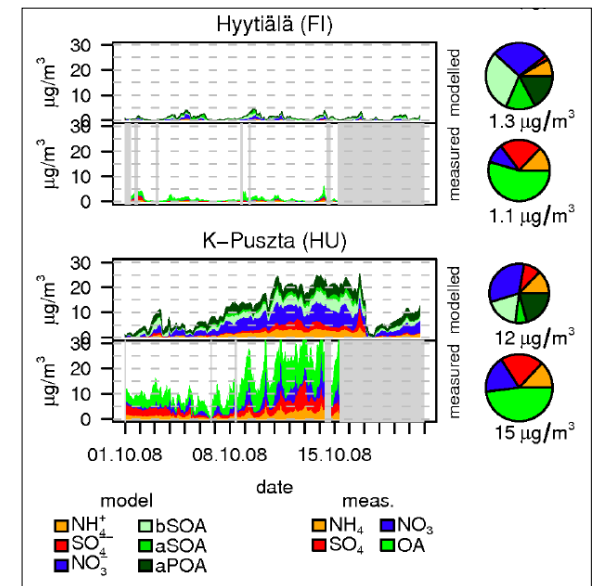


# Europe: Advances in source apportionment of primary organic aerosols

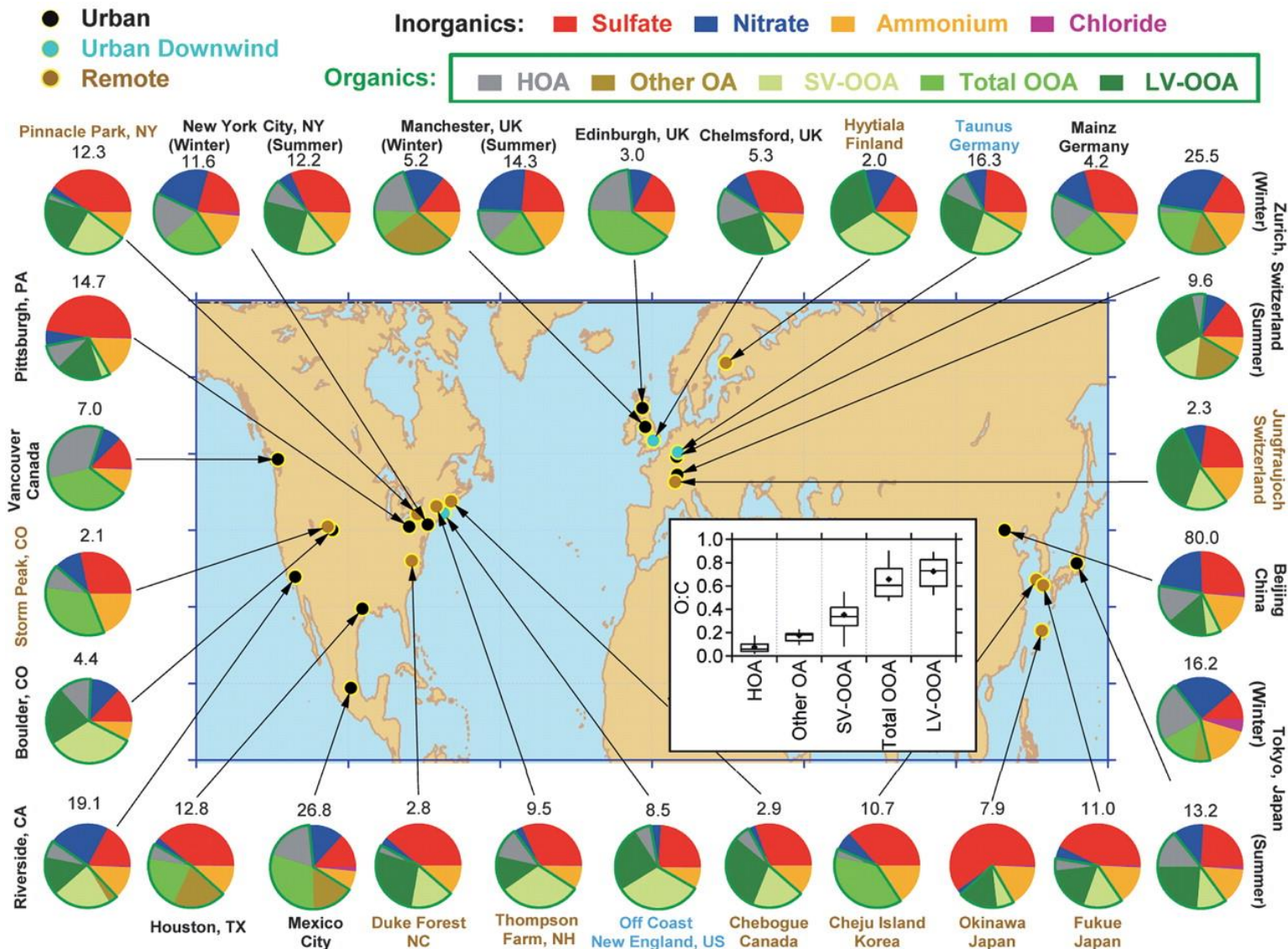
## AMS measurements + PMF



## Model evaluation

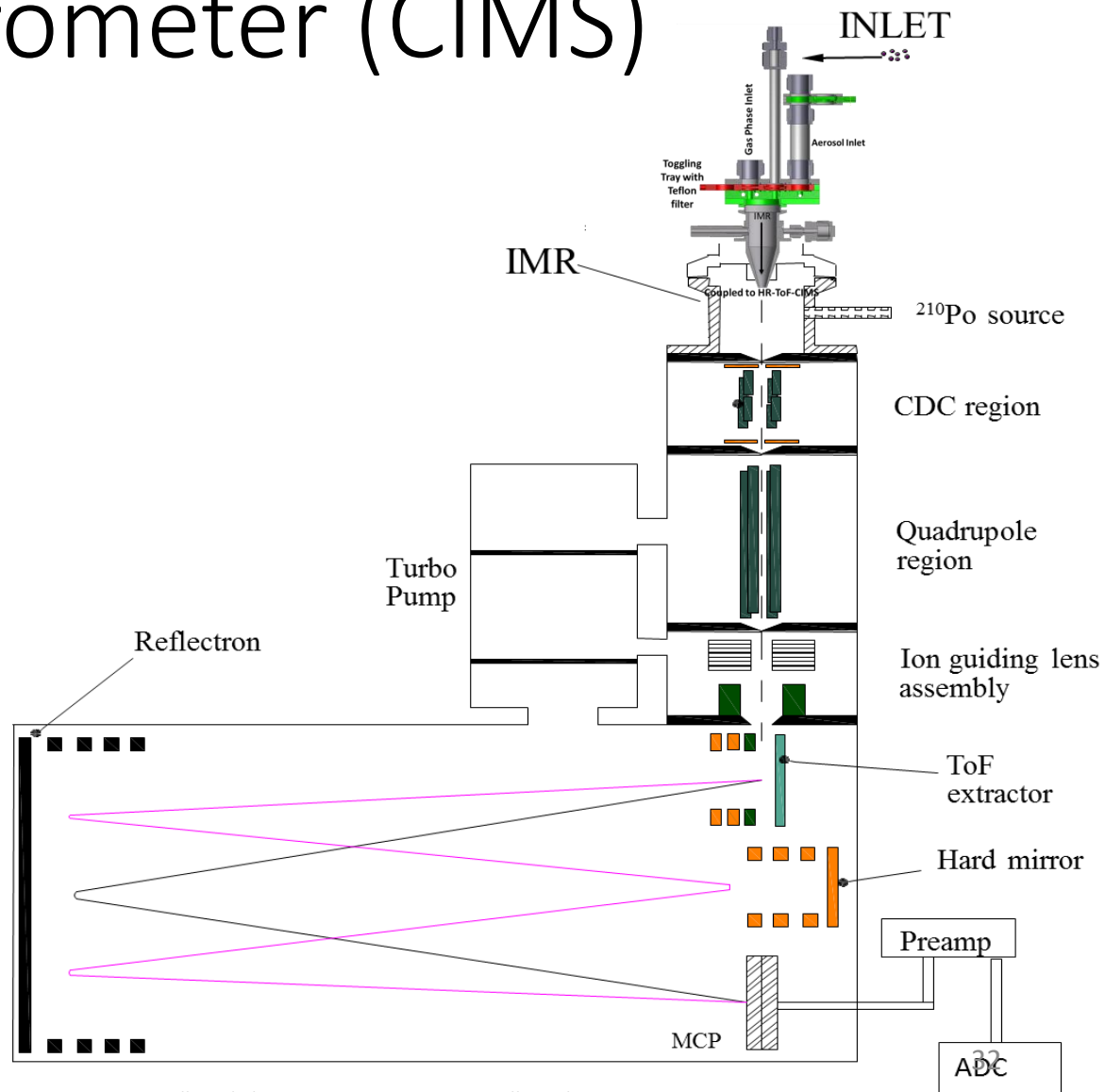
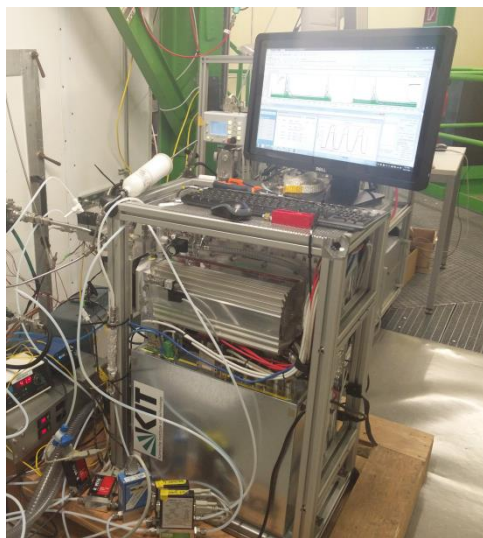


# PM<sub>1</sub> chemical composition worldwide

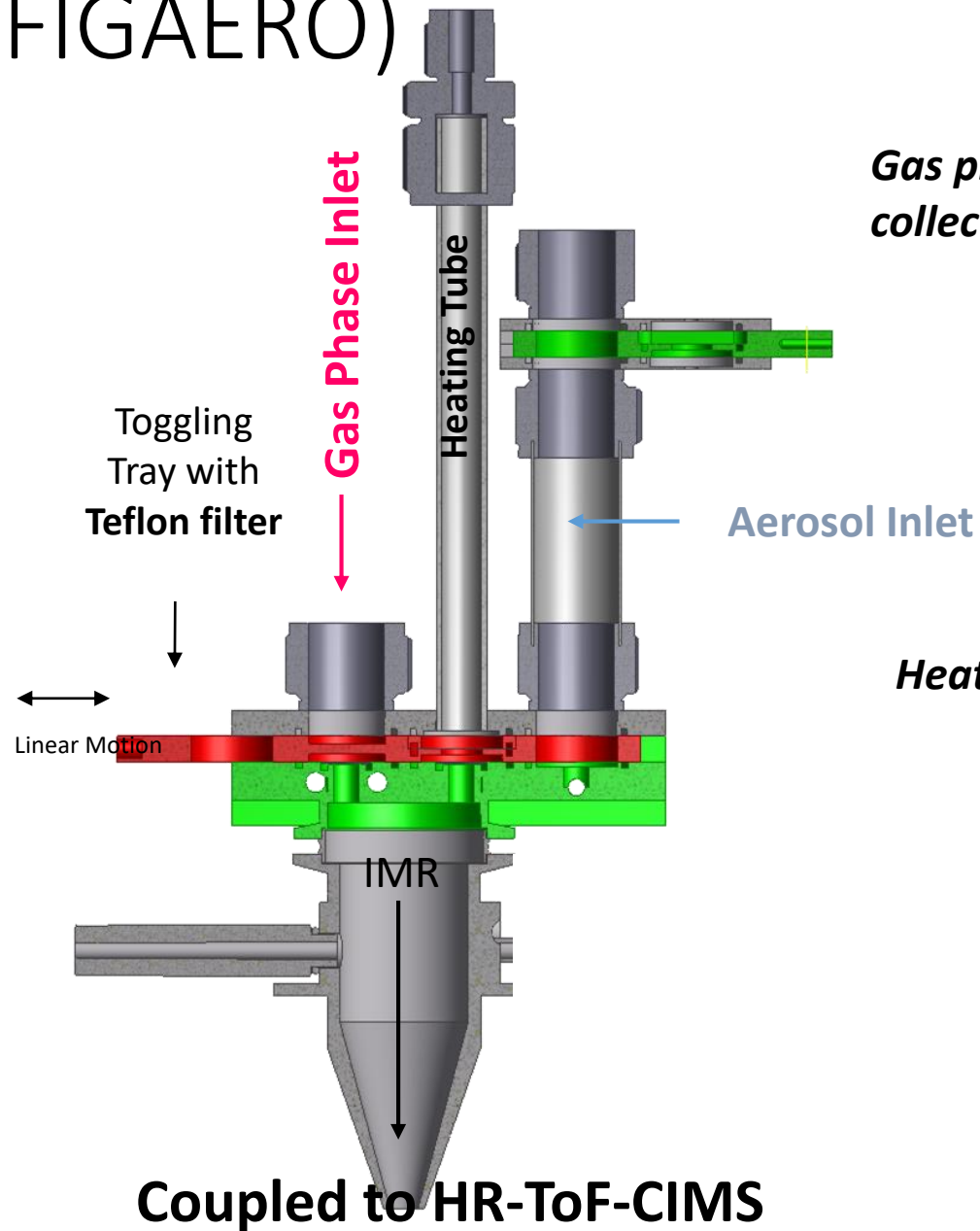


# Chemical ionization mass spectrometer (CIMS)

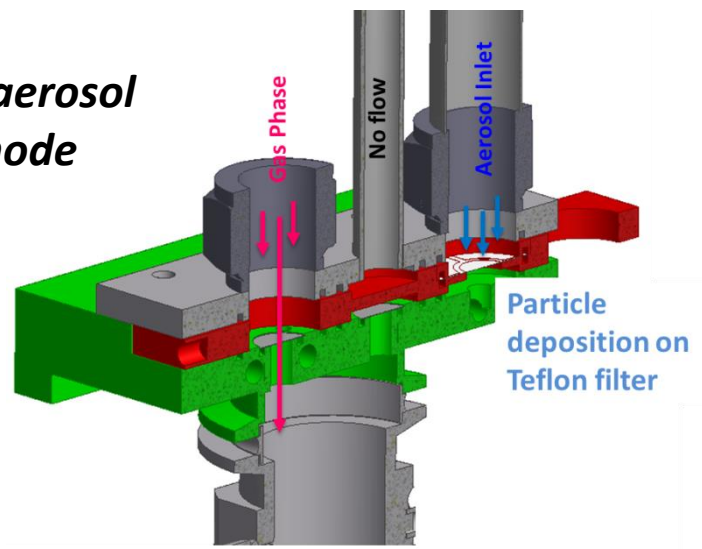
- Reagent ions:
  - Iodide
  - Acetate



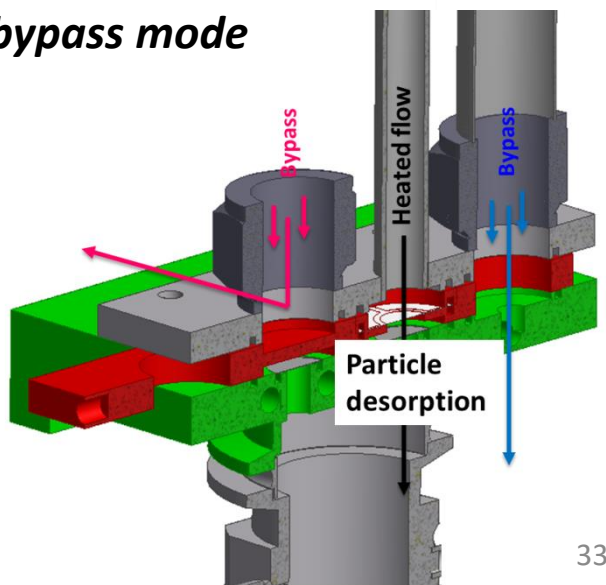
# Filter Inlet for Gases and AEROsols (FIGAERO)



*Gas phase/aerosol collection mode*

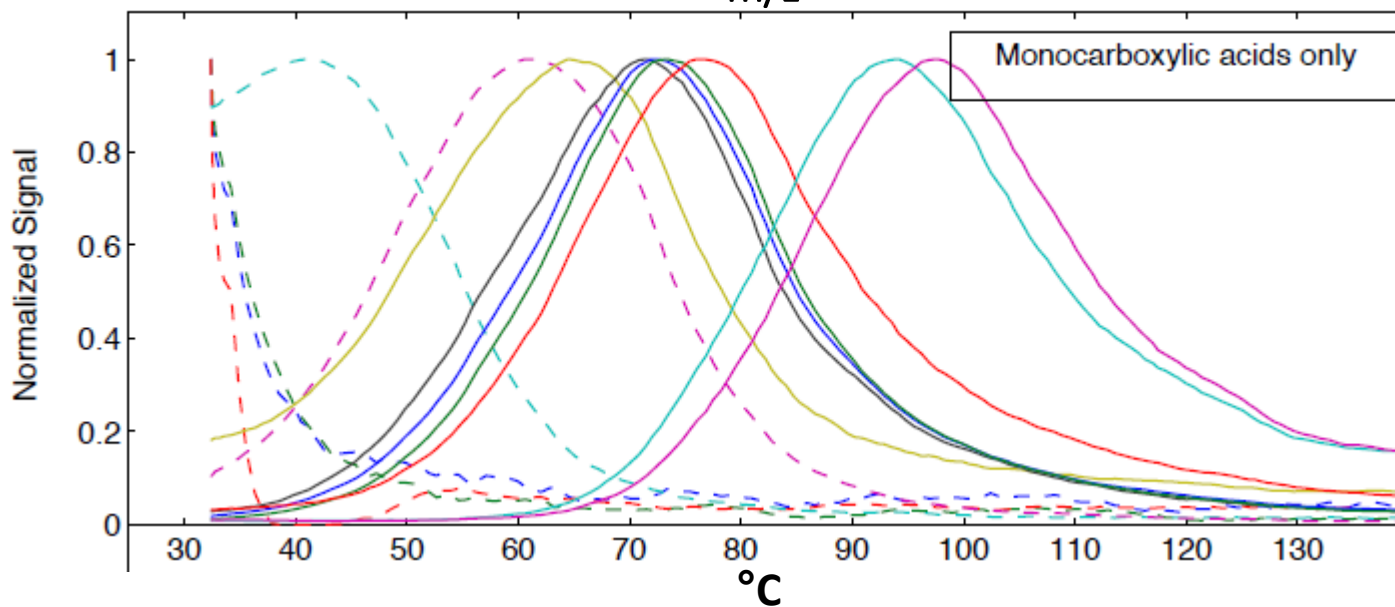
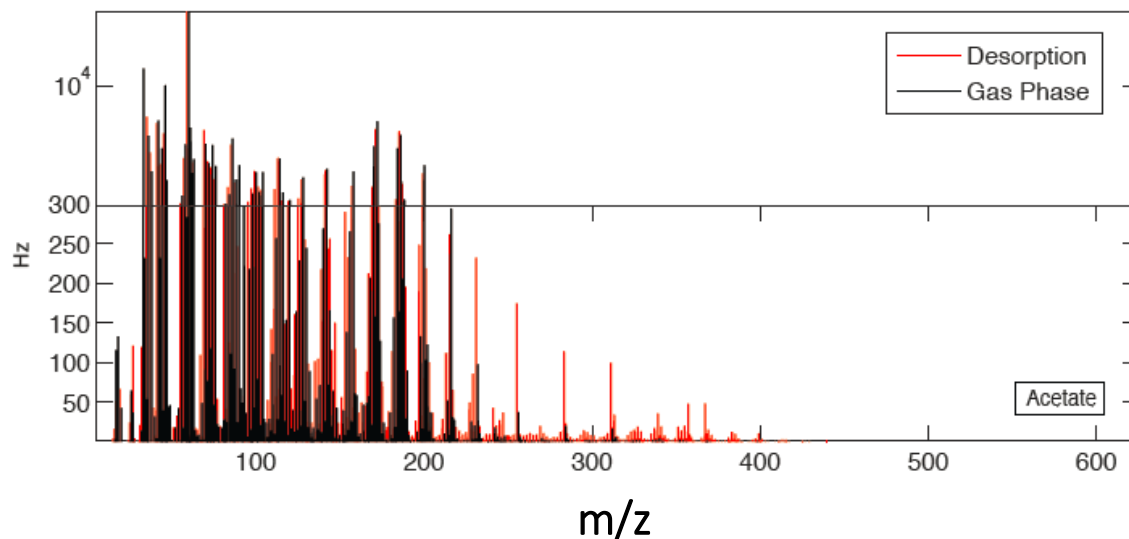


*Heating/bypass mode*





# FIGAERO-CIMS: Data output

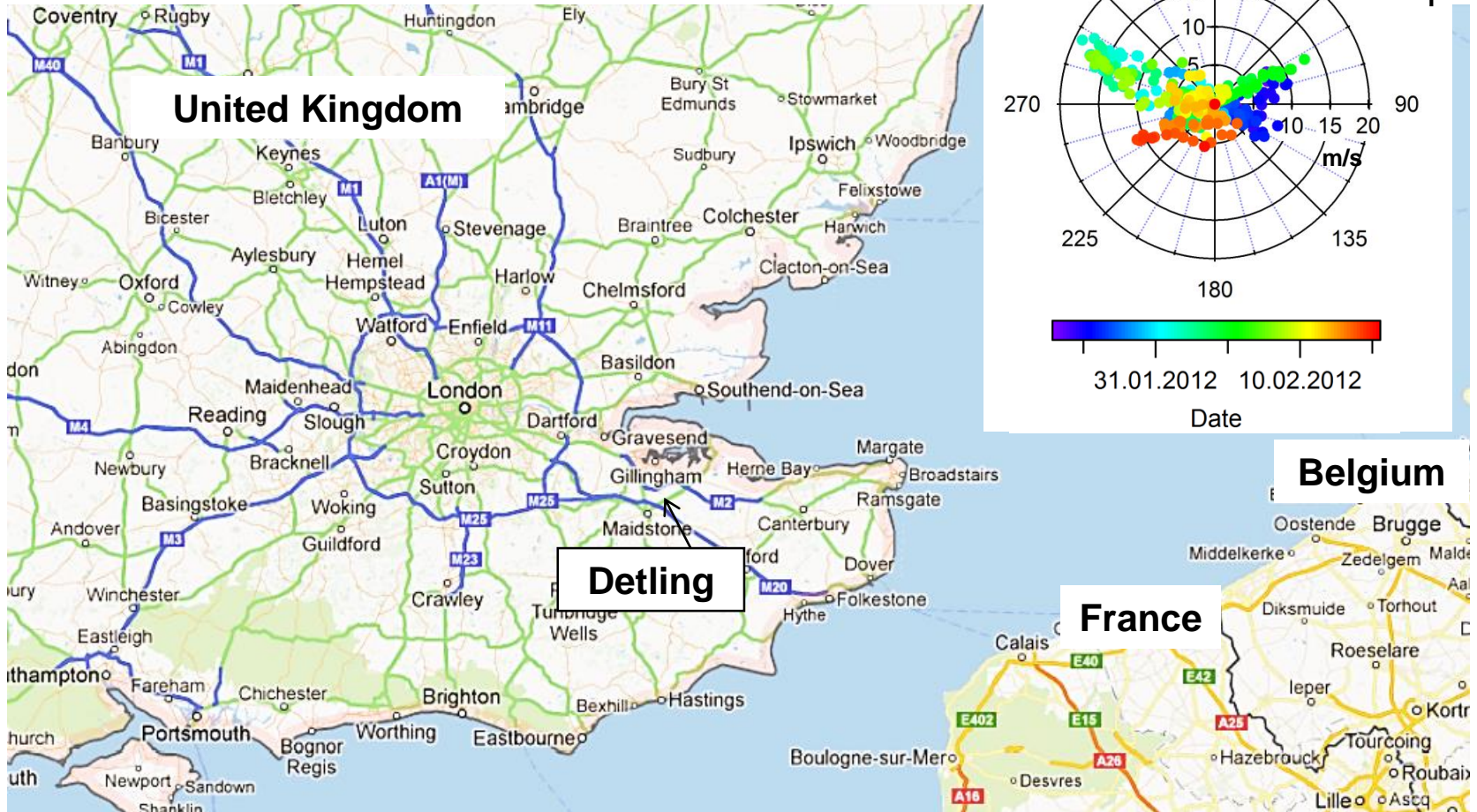


# Detling, UK

## ClearfLo Campaign 2012: Particulate matter in urban and rural areas

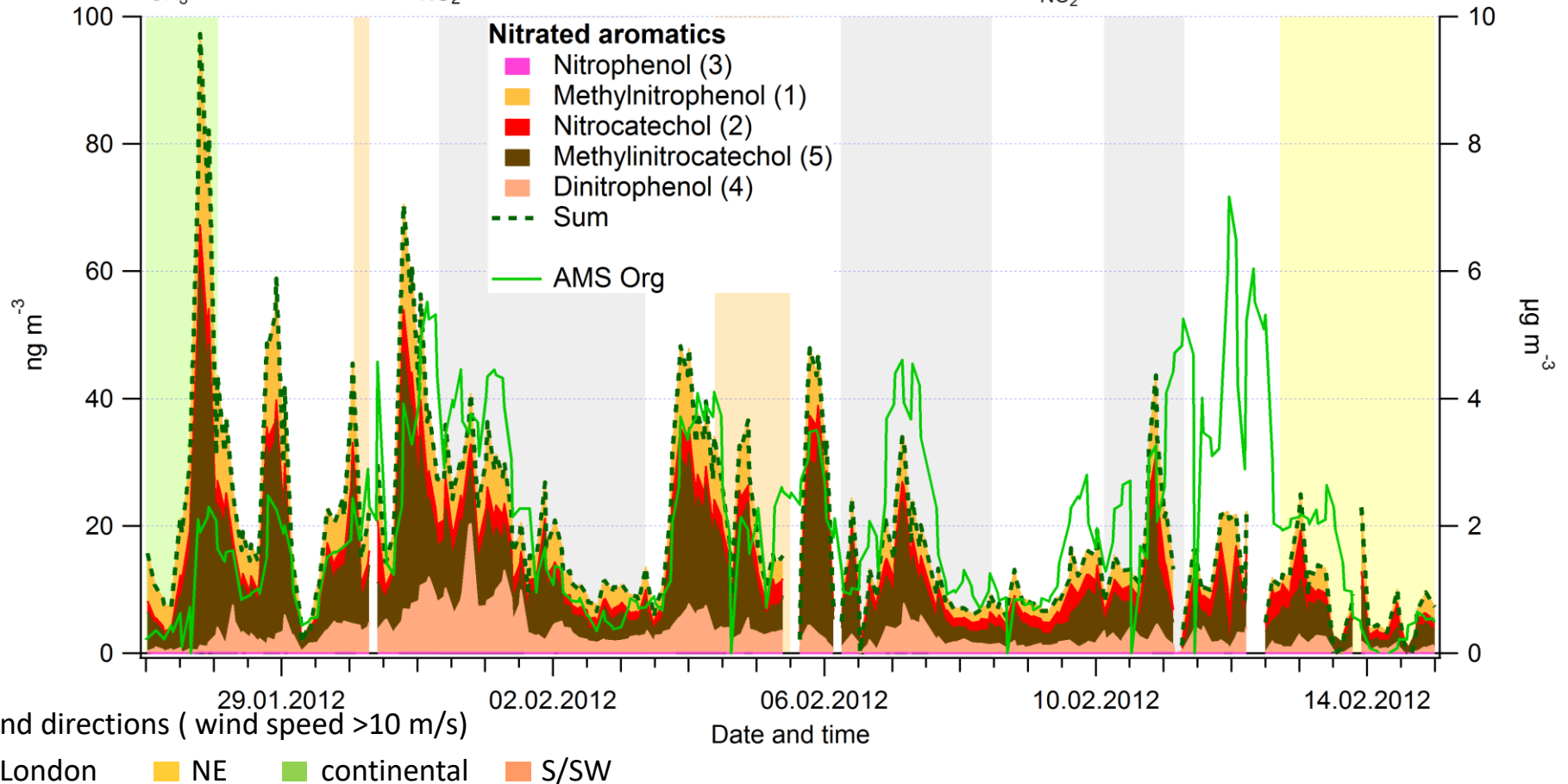
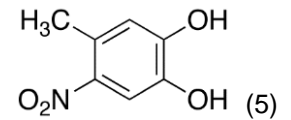
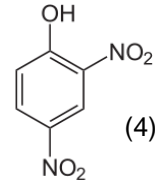
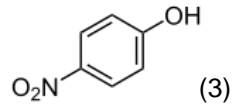
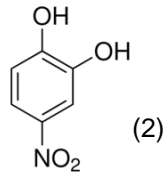
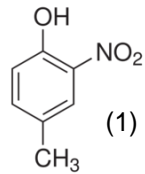


# Detling, UK: ClearfLo Campaign



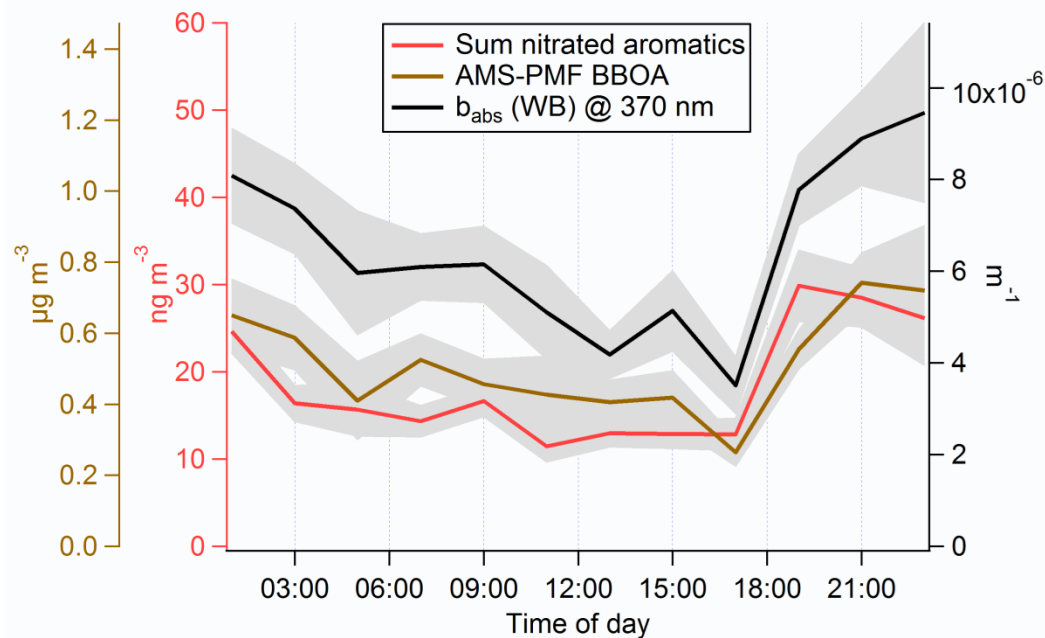
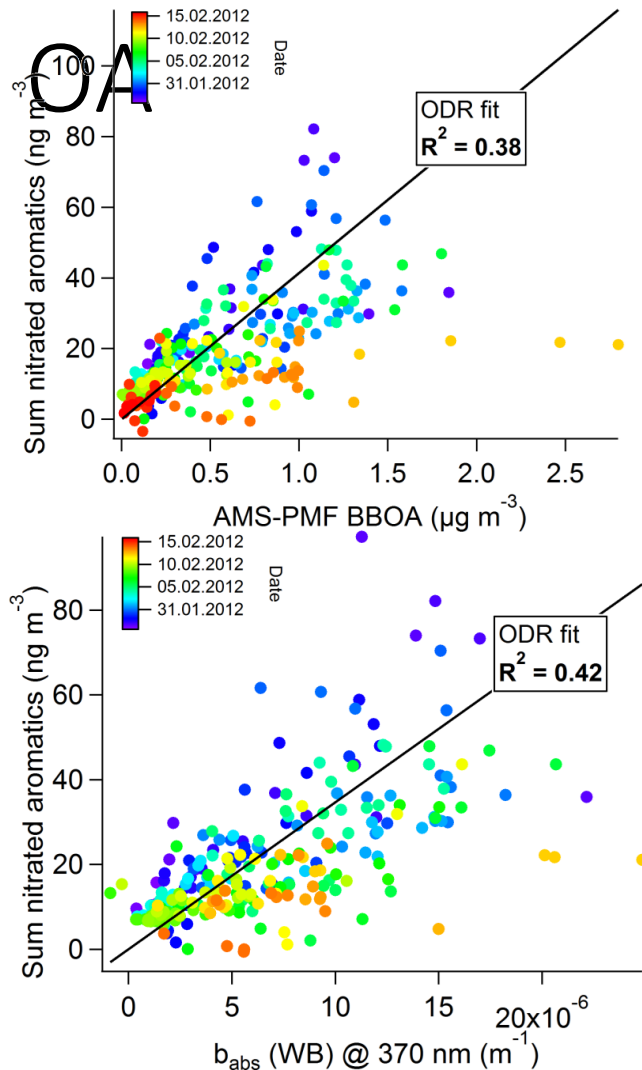


# Time series nitrated aromatics

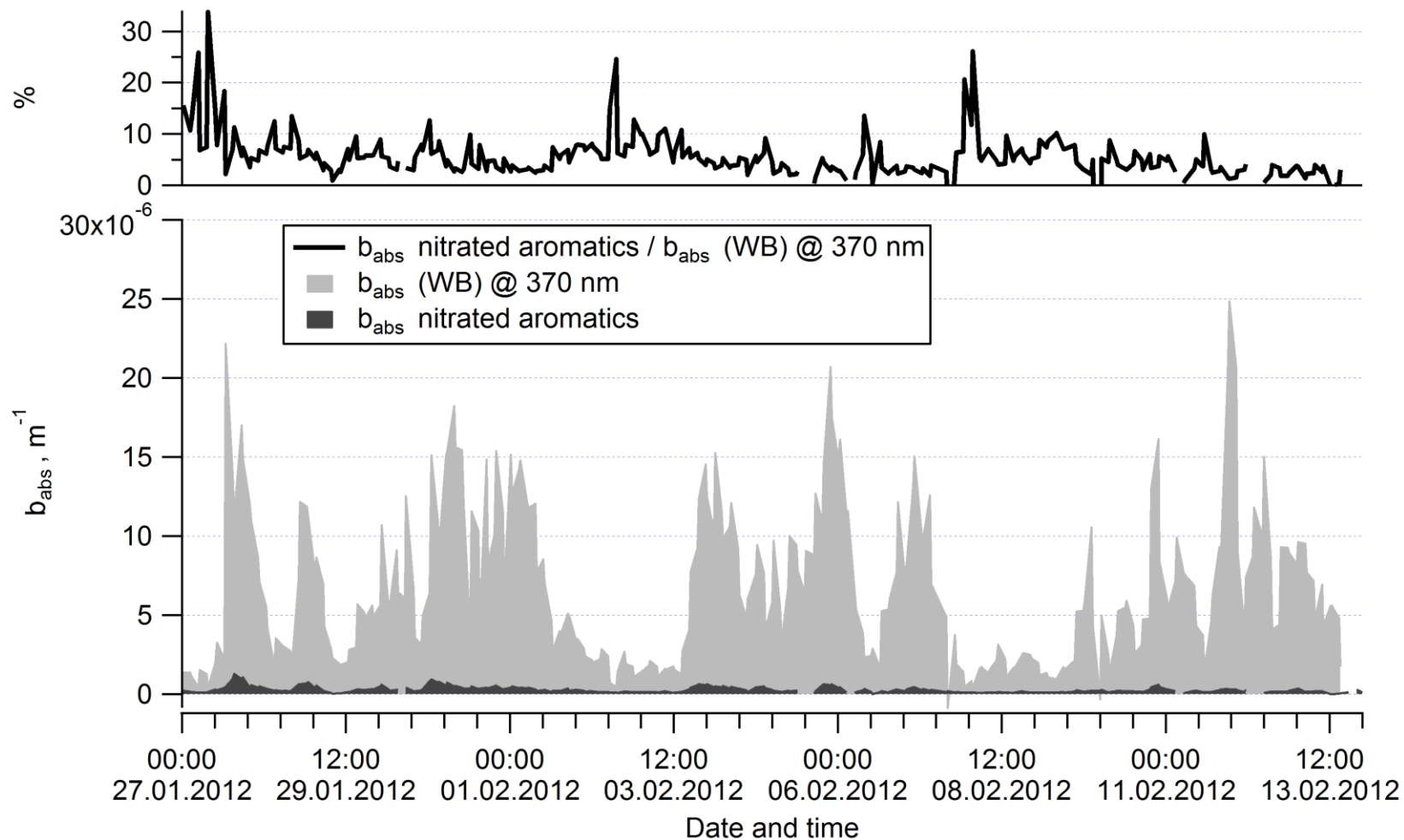




# Nitrated aromatics - light absorbers related to secondary biomass burning



# Estimated contribution of nitrated aromatics to $b_{\text{abs}}$ (WB) @ 370 nm





# Hyytiälä, Finland

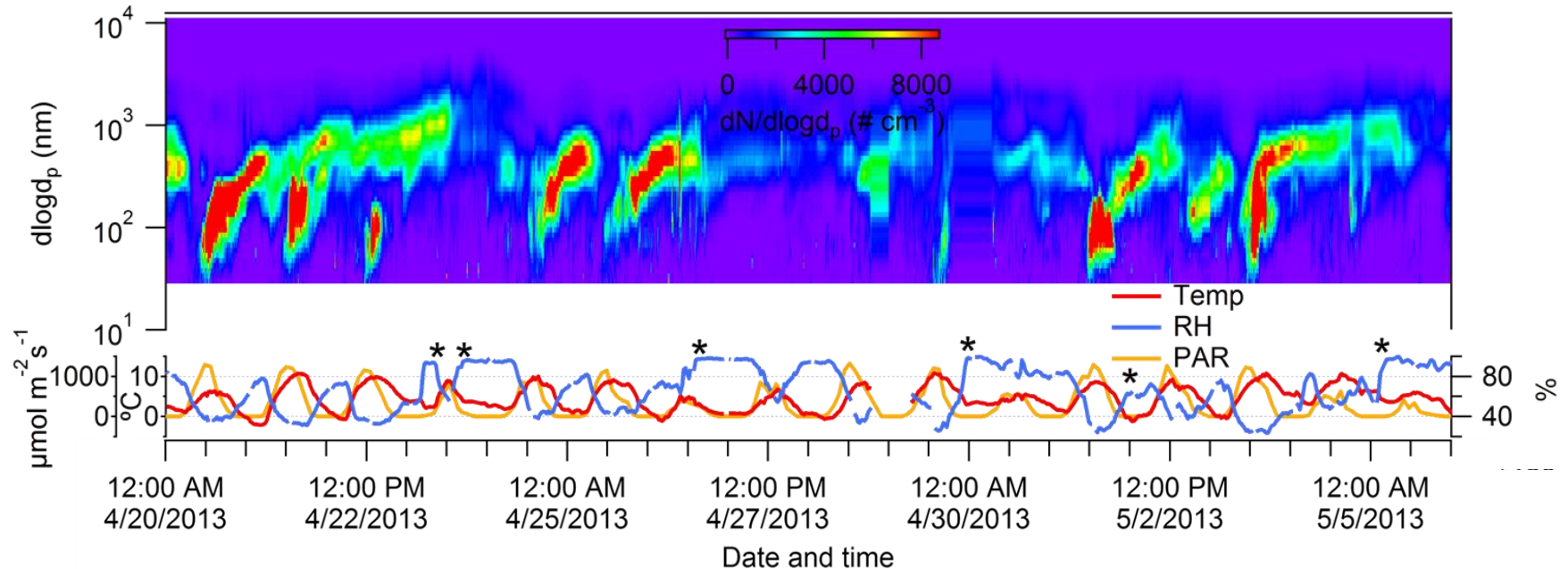




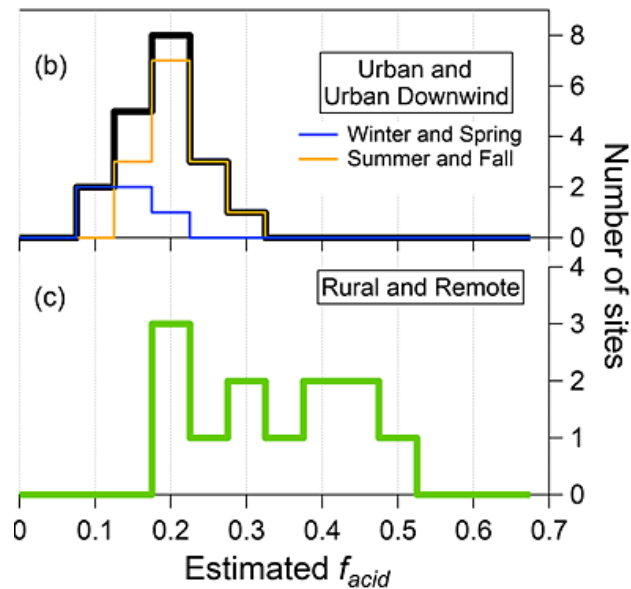
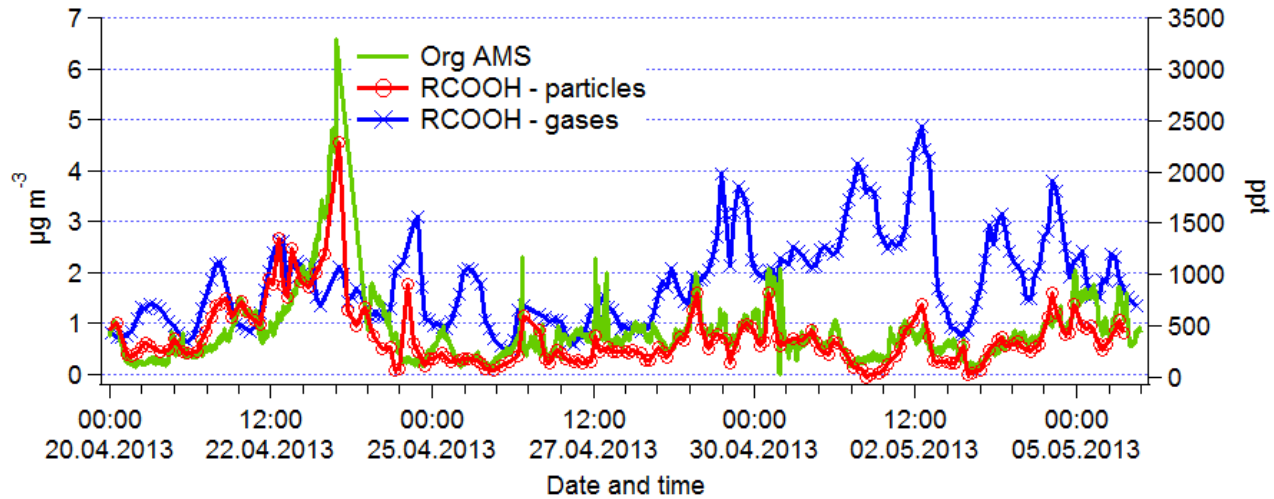
# New particle formation in the boreal forest

Spring 2013 and 2014

- Regular new particle formation events
- Analysis of chemical composition of gas and particle phase
- Acetate/iodide

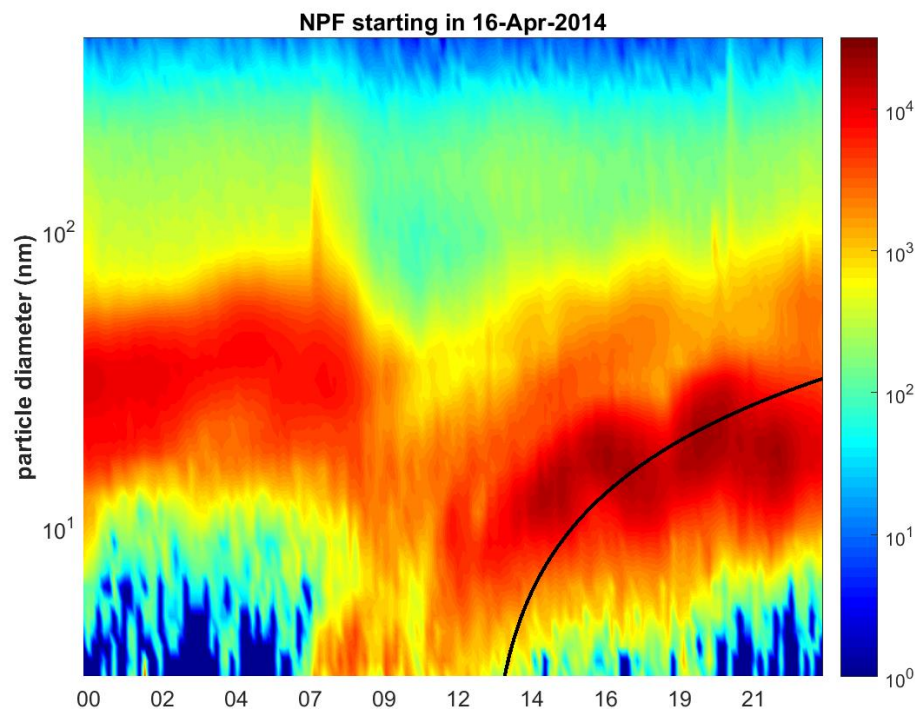


# Carboxylic acids



# Measured gas phase compounds explain particle growth rate

Model for Acid-Base chemistry in NANoparticle Growth (MABNAG)



Modelled particle growth rate based on data input from CIMS  
→ Talk tomorrow by Taina Yli-Juuti, 11:30

# Main points

- Mass spectrometry is a very powerful tool in (organic) aerosol chemical analysis (sensitivity, time resolution)
- Inlet, vaporization, ionization determine what we can analyze
- Has led to vast advances in our understanding of organic aerosol chemistry and formation
- Challenges
  - Quantitativeness
  - Data Analysis

