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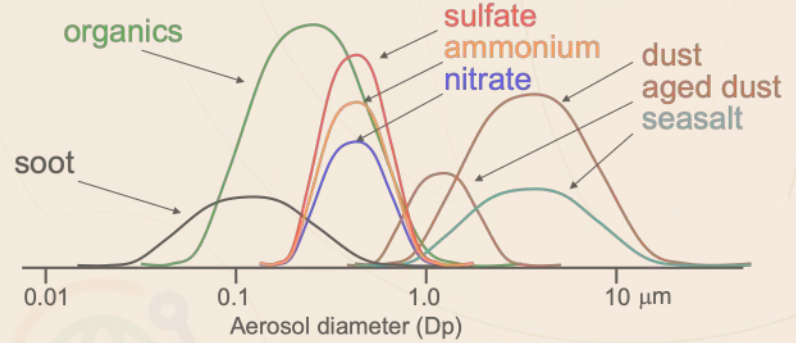
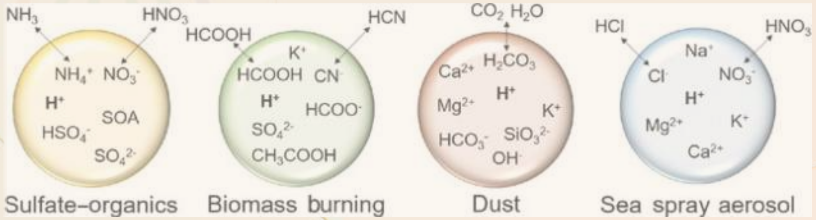
Consiglio Nazionale delle Ricerche

Istituto di Scienze dell'Atmosfera e del Clima

CNR ISAC

Training event “Atmospheric standardized observations: Methods and maintenance in observatories – In-Situ.”





Aerosol chemical composition

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Horizon Europe

CleanCloud

IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructures System
(D.D. n. 130/2022 - CUP B53C22002150006) Funded by EU - Next Generation EU PNRR-Mission 4 “Education and Research” - Component 2: “From research to business” - Investment 3.1: “Fund for the realisation of an integrated system of research and innovation infrastructures”

Finanziato dall'Unione europea NextGenerationEU

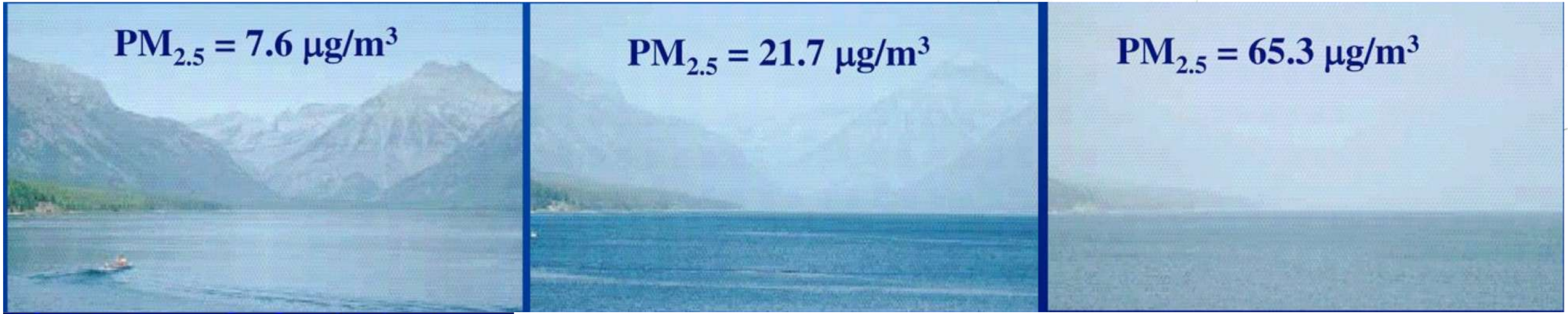
Ministero dell’Università e della Ricerca

Italiadomani

Atmospheric Aerosol

Atmospheric aerosol is the suspension of liquid or solid particles floating in the air

Microscopic and light, but VISIBLE!



Glacier National Park images are adapted from Malm, *An Introduction to Visibility* (1999) http://webcam.srs.fs.fed.us/intropdf.htm

Atmospheric Aerosol Sources

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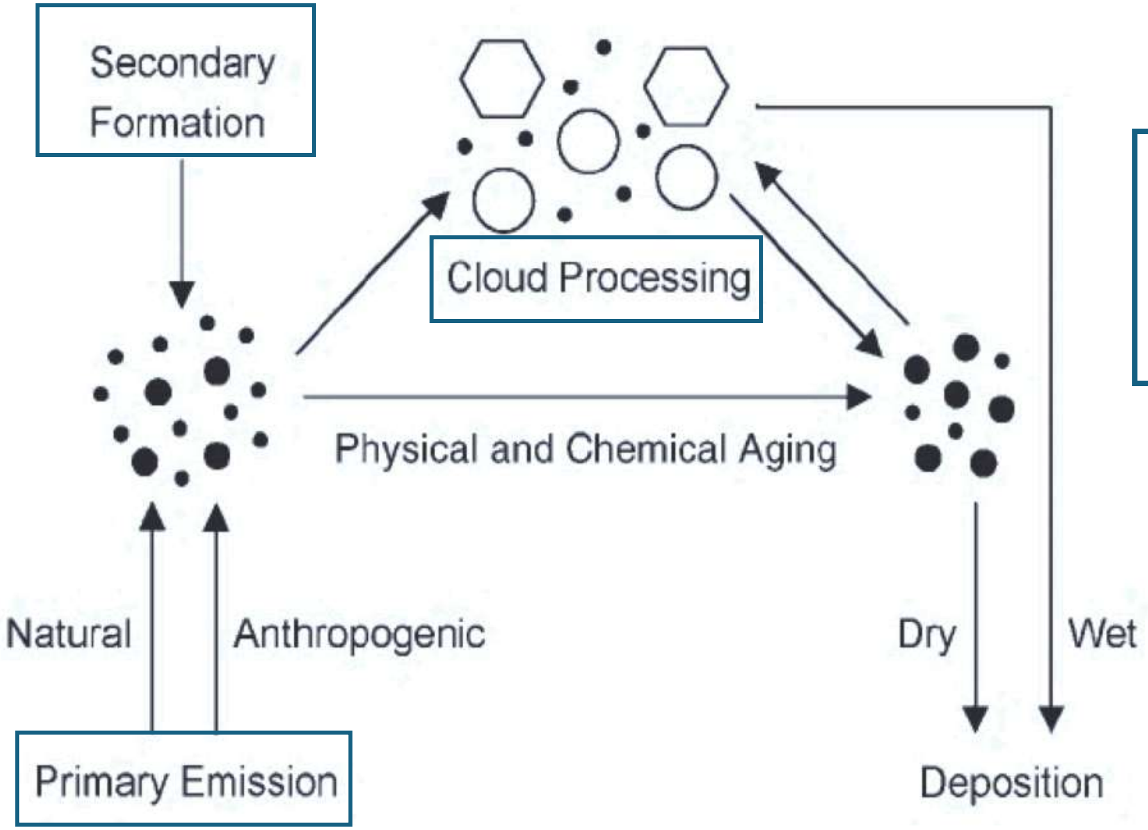
NATURAL	ANTHROPOGENIC

Different emission and formation mechanisms

PRIMARY AEROSOL = directly emitted in the form of particles

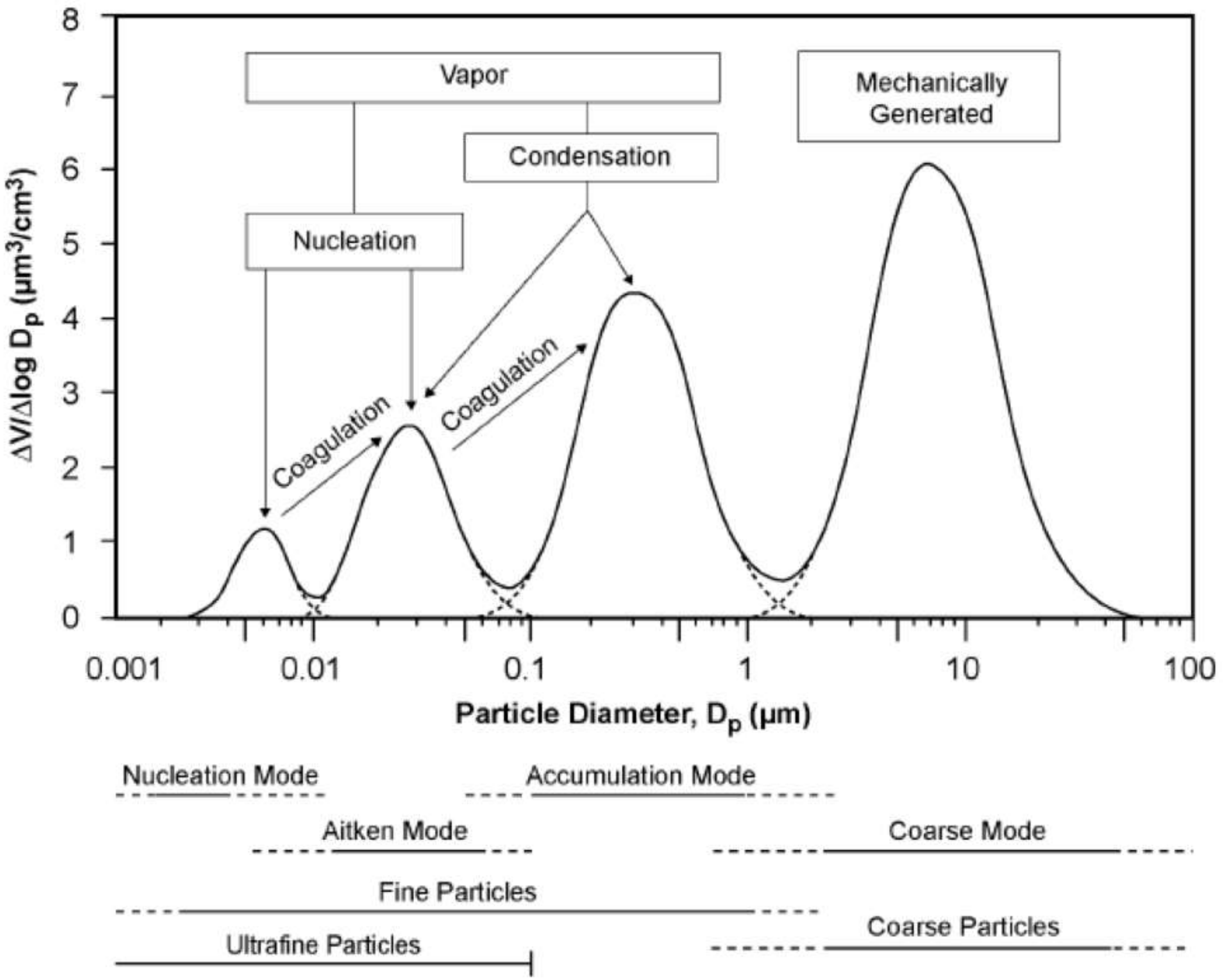
SECONDARY AEROSOL = formed/transformed in the atmosphere from gaseous precursors



The atmosphere is a dynamic system, in which aerosol undergoes countless transformations

The «family» of atmospheric aerosols is extremely **various** and **heterogeneous**

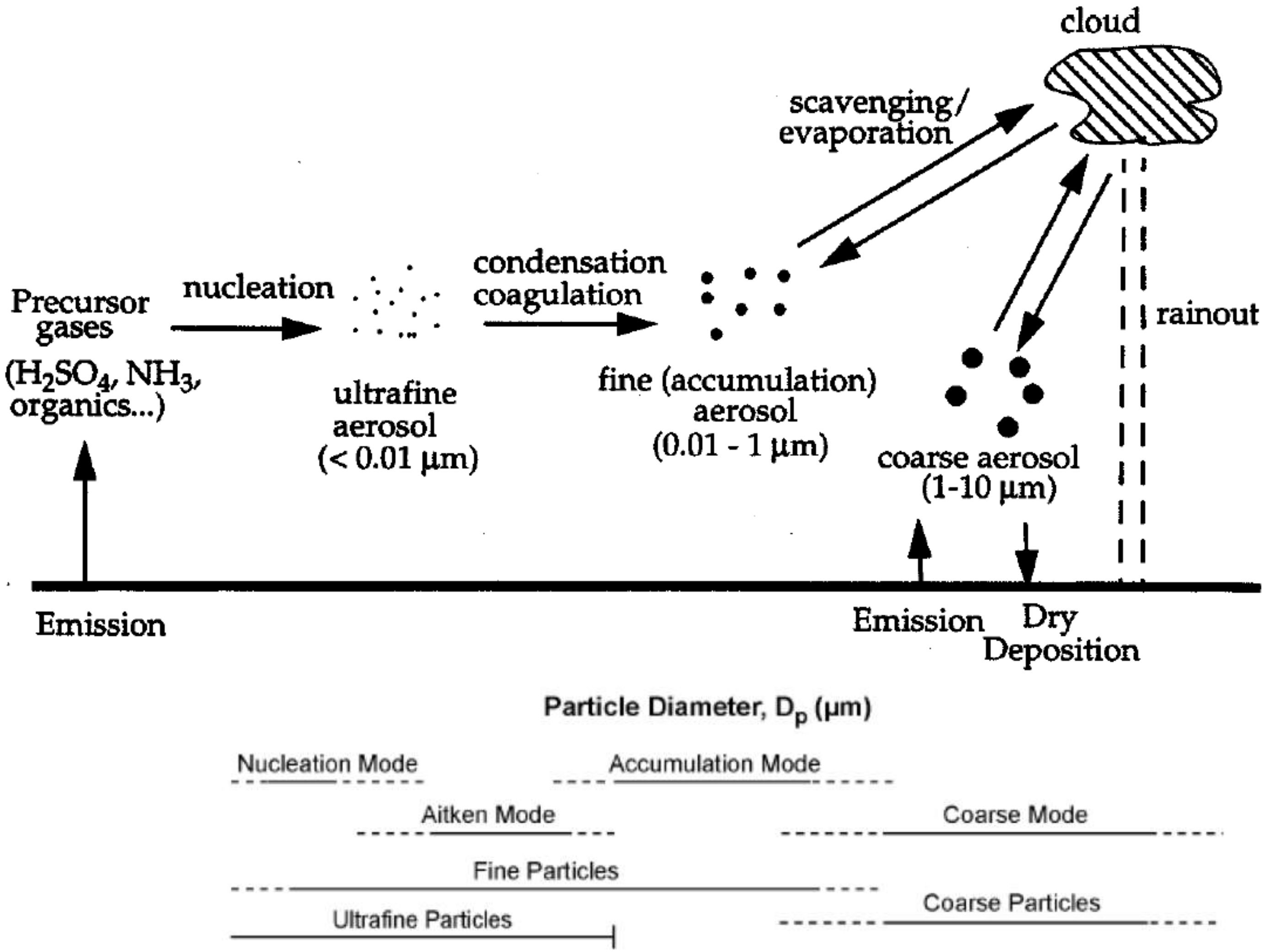
Varied size distribution



The particle sizes span several orders of magnitude!

Nucleation mode	< 10 nm
Aitken mode	10 nm – 100 nm
Accumulation mode	100 nm – 1 μm
Coarse mode	1 μm – 100 μm

Varied size distribution



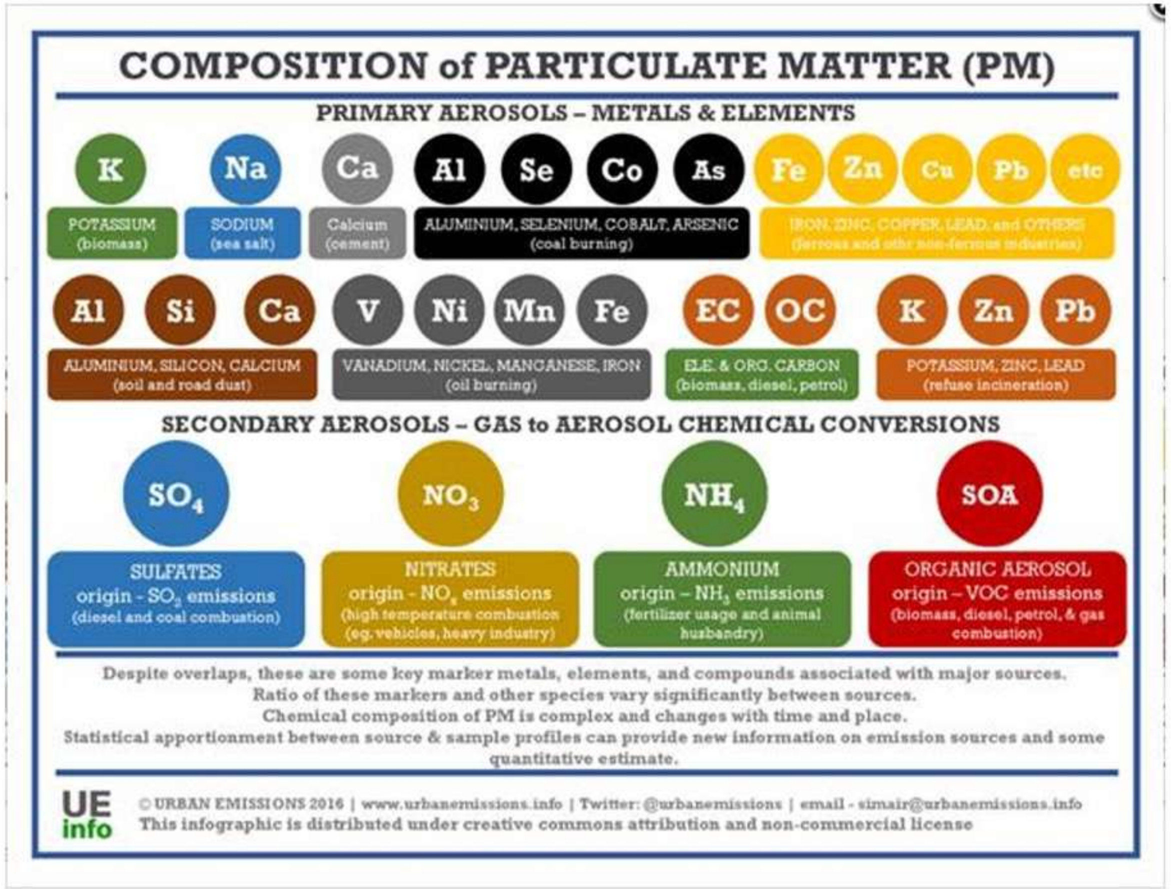
The particle sizes span several orders of magnitude!

Nucleation mode	< 10 nm
Aitken mode	10 nm – 100 nm
Accumulation mode	100 nm – 1 µm
Coarse mode	1 µm – 100 µm

…are linked to sources and formation/transformation mechanisms and in turn affect transport and removal mechanisms

Complex chemical composition

The variety of sources and formation mechanisms corresponds to an enormous chemical variability and complexity.



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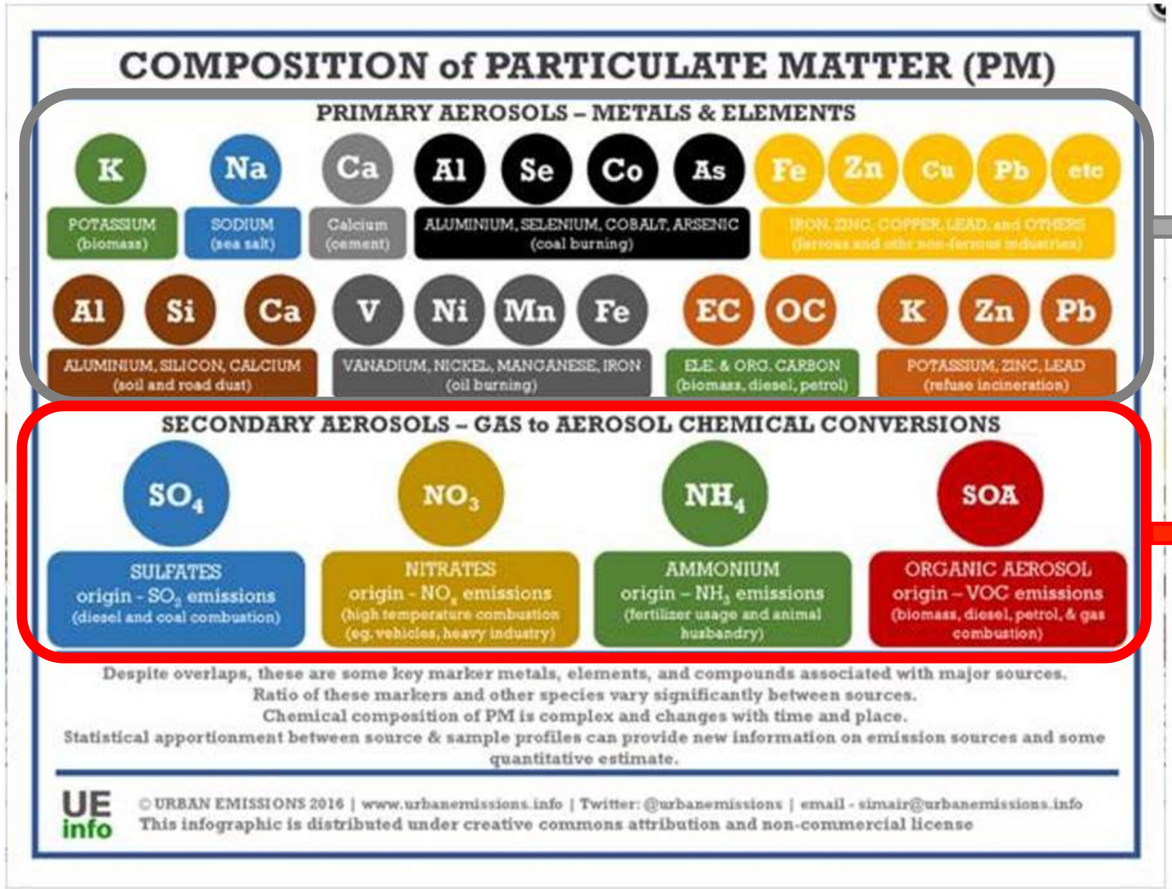
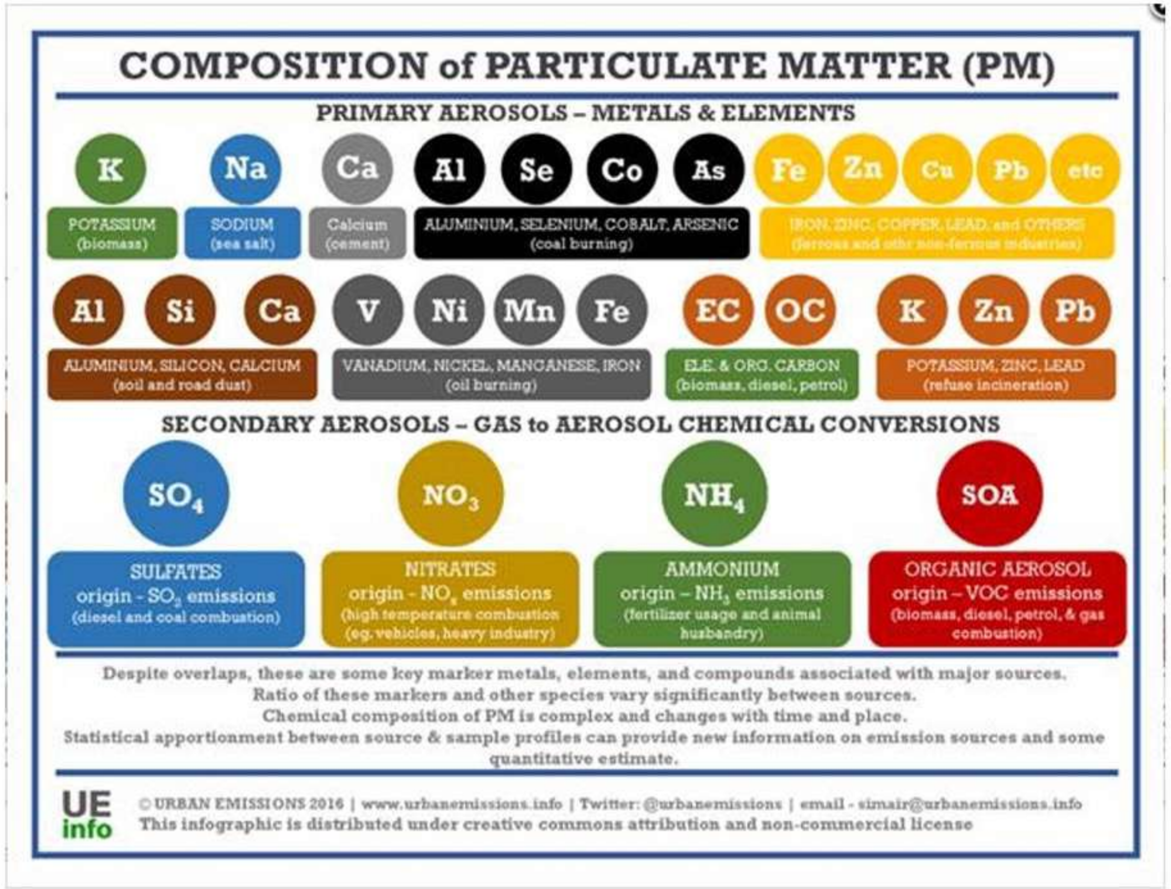


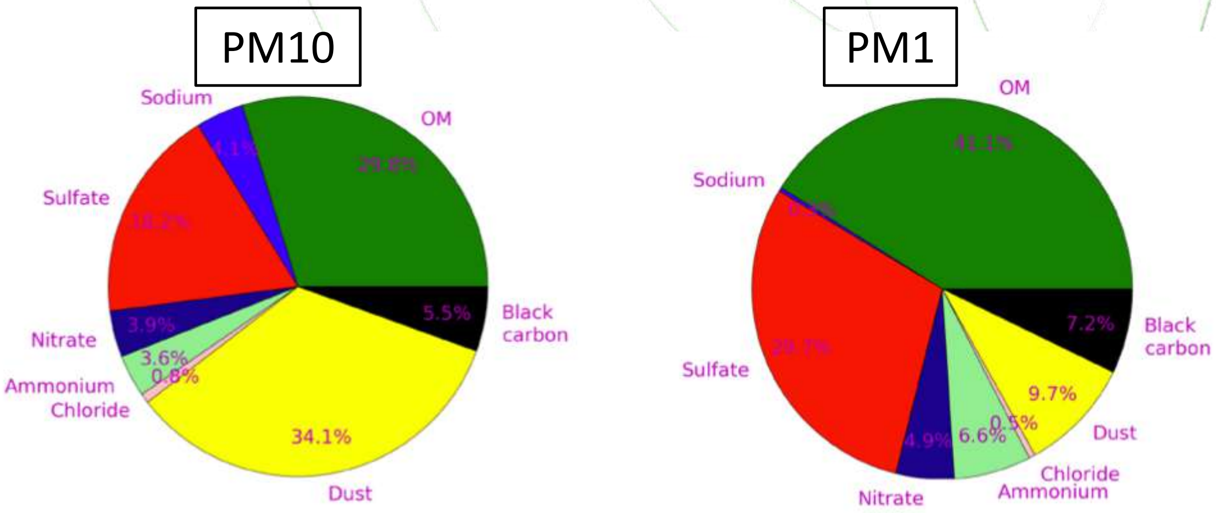
PRIMARY SPECIES = directly emitted in the form of particles

SECONDARY SPECIES = formed/transformed in the atmosphere from gaseous precursors

Complex chemical composition

The variety of sources and formation mechanisms corresponds to an enormous chemical variability and complexity.

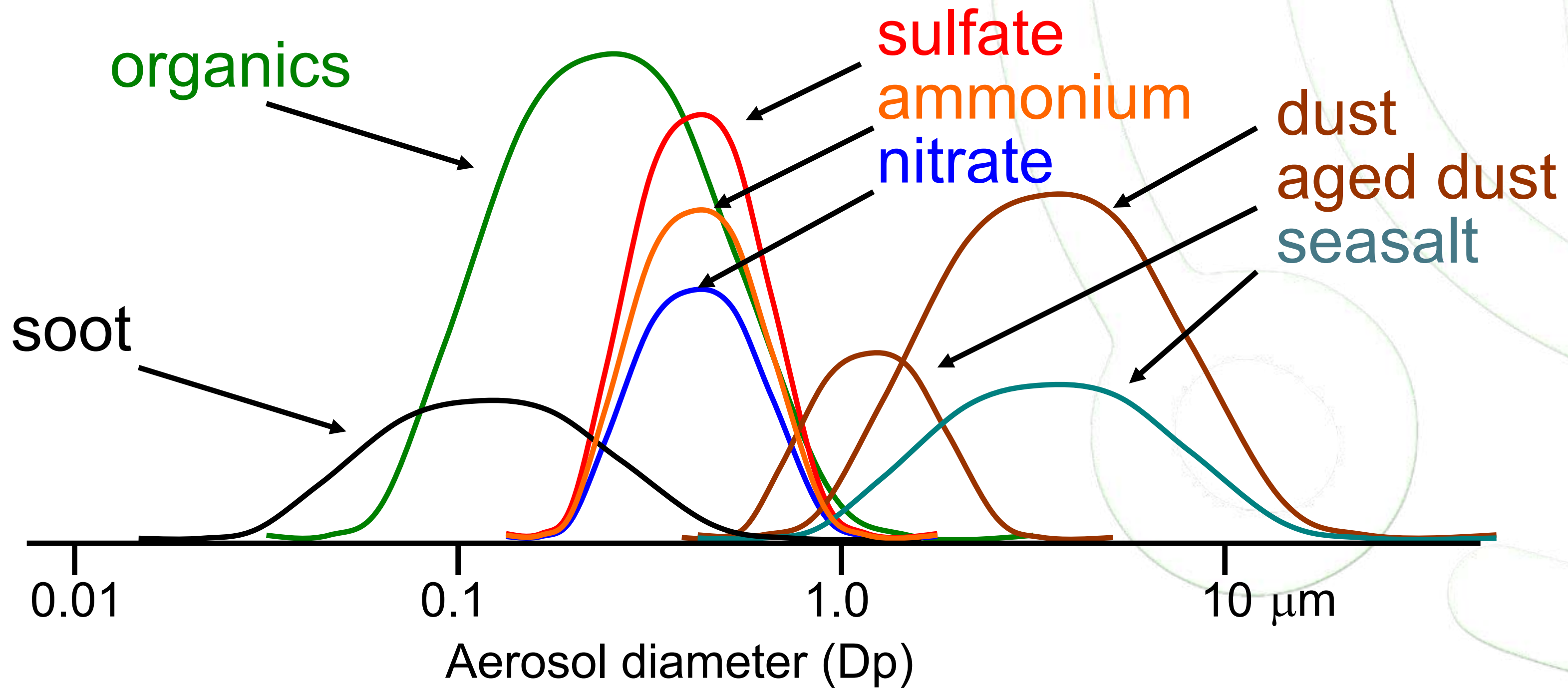




Chrit M., et al., 2018 (https://doi.org/10.5194/acp-2017-915)

Variability in the same place between different particle sizes

Mass size-distributions of the main aerosol chemical components

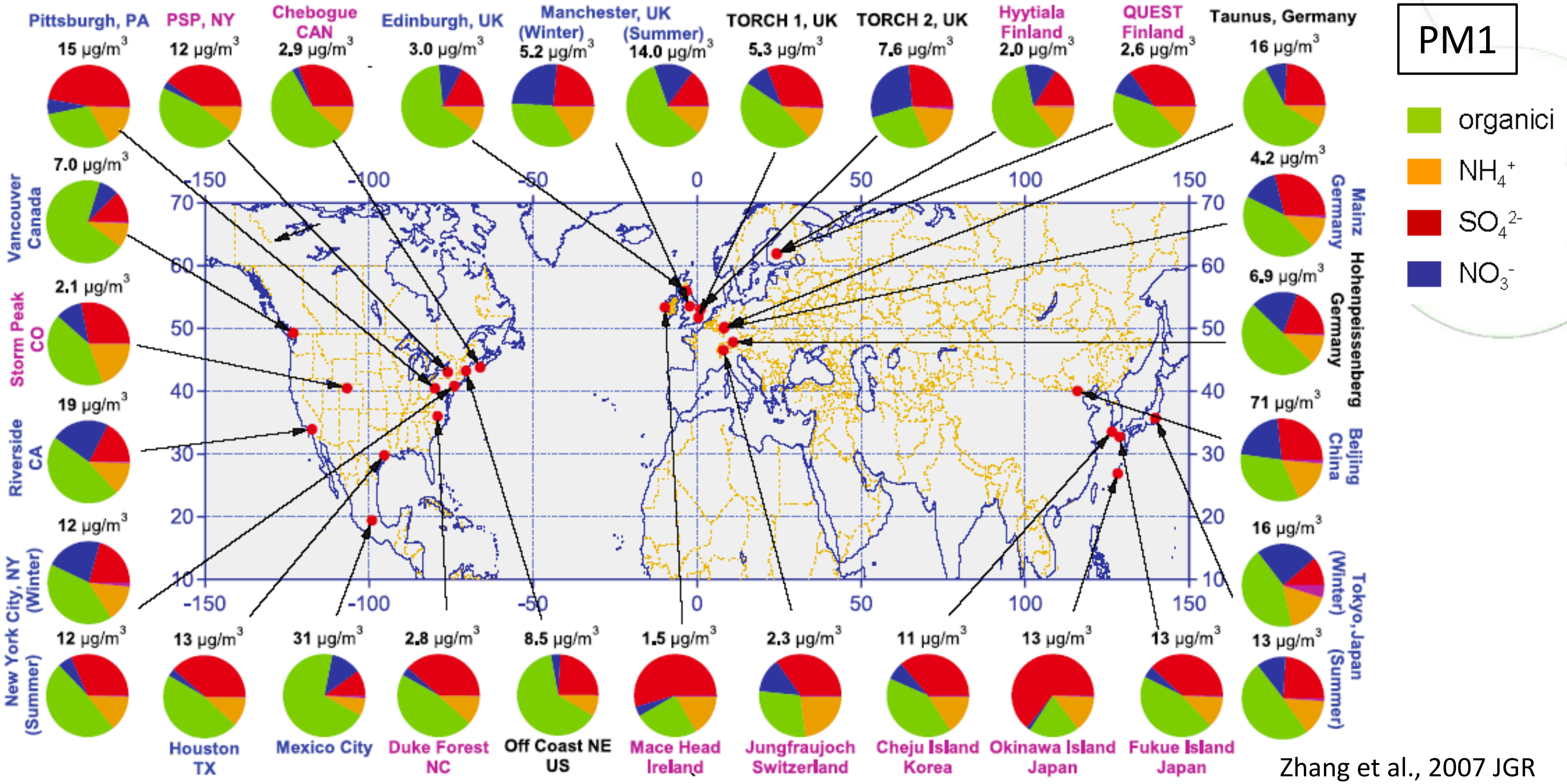


Internal mixing of A and B

external mixing of A and B

Complex chemical composition

The variety of sources and formation mechanisms corresponds to an enormous chemical variability and complexity.



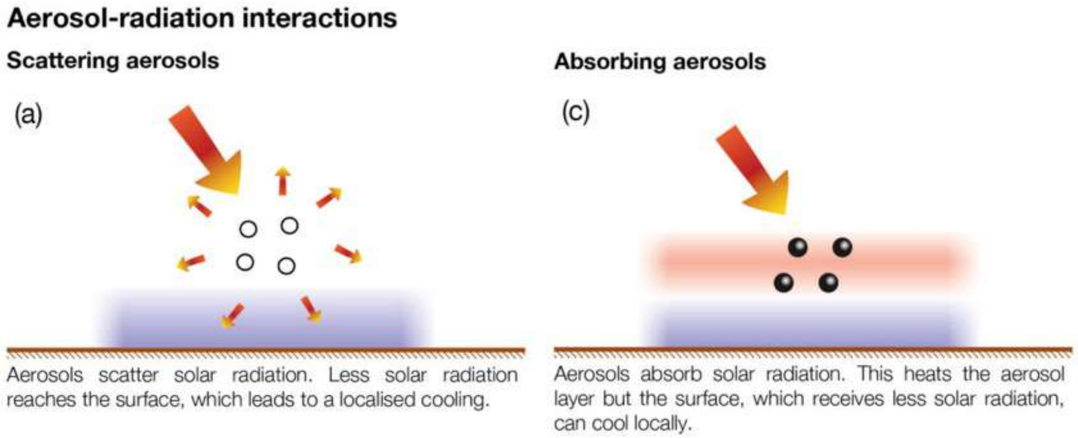
Zhang et al., 2007 JGR

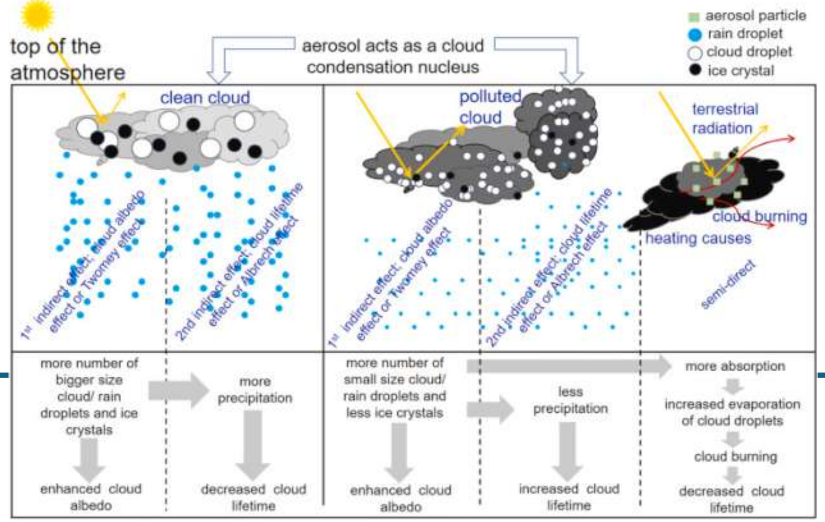
Extreme spatial and temporal variability!

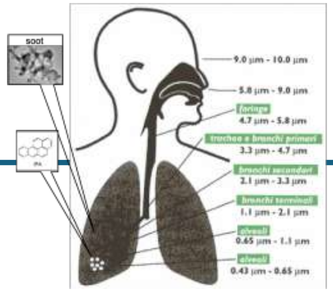
Aerosol chemical composition: why is important?

Aerosol chemical composition affects all the particles atmospheric properties/processes:

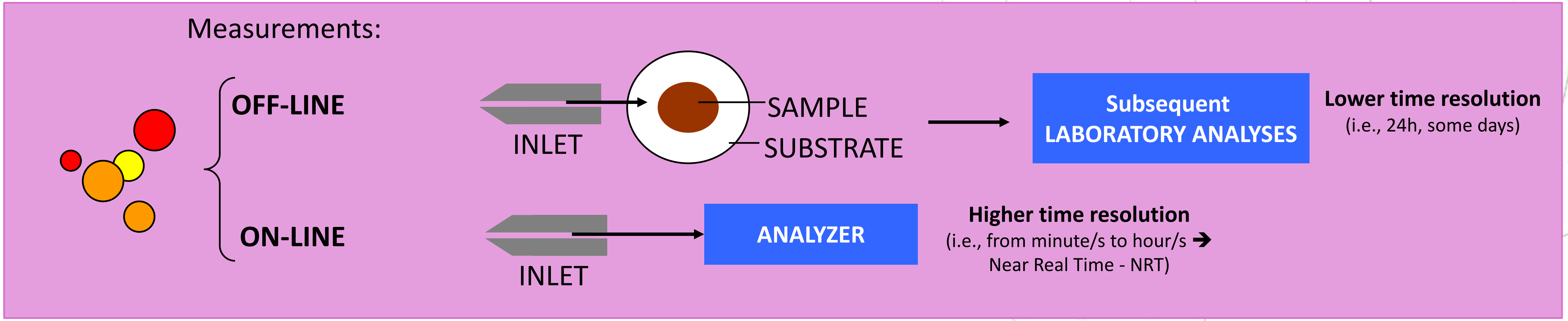
- interaction with radiation
- chemical reactivity
- scavenging processes
- interaction with water vapor
  (hygroscopic growth and cloud formation),
- health effects, etc.

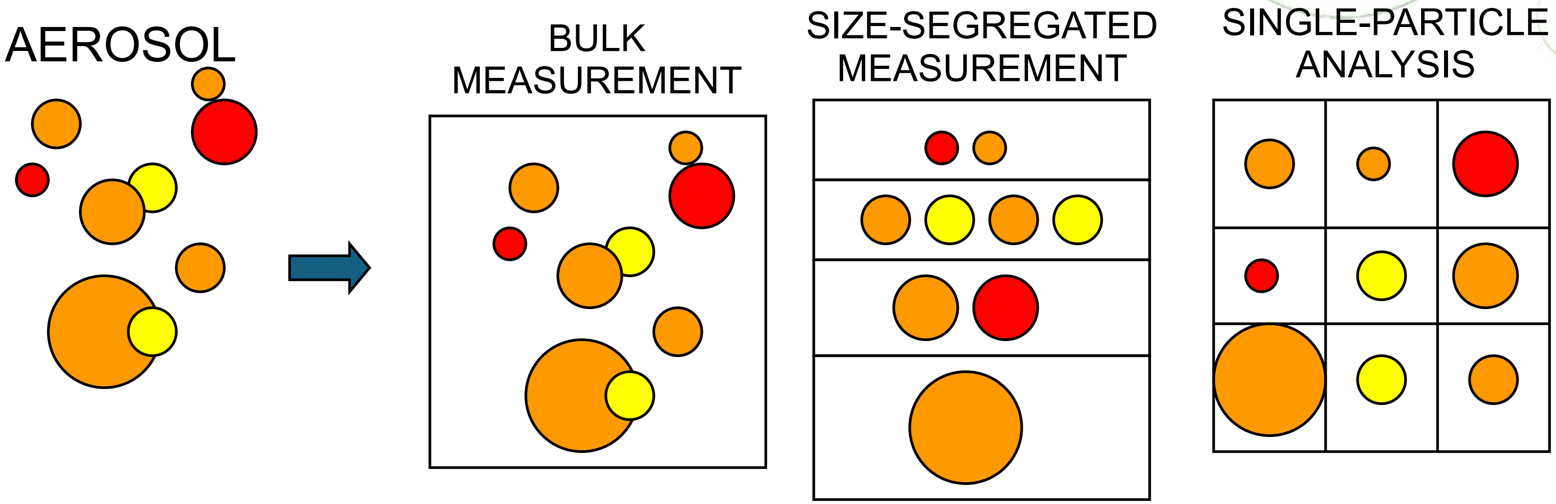






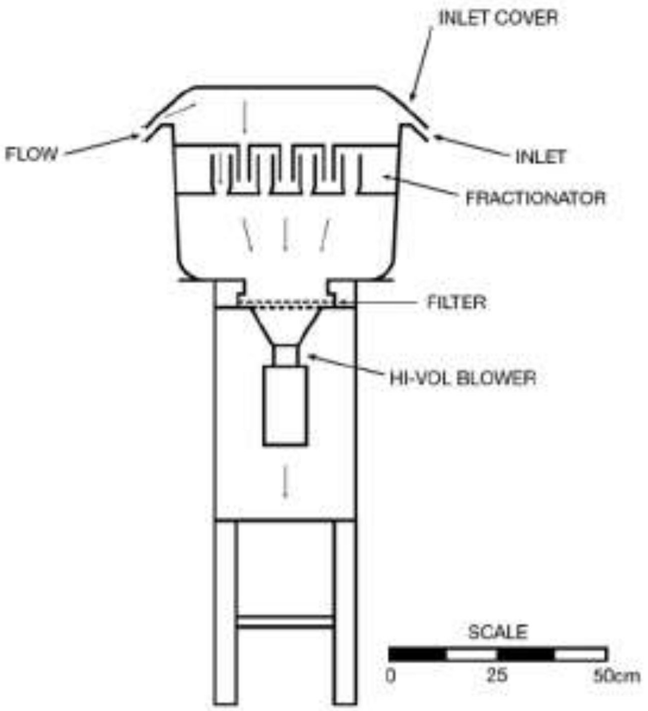
In-situ measurements of particle composition





Sampling – off-line

- Air sampling through an *inlet*;
- Heating for drying humid particles (and cloud droplets and ice particles);
- Diffusion denuders to remove gas phase components;
- Size fractionation (e.g., PM10, PM2.5, PM1);
- Particle collection on filters or other substrates.



Flow 10 100 1000 L/min

"low volume" "medium volume" "high volume"

Aerosol size fractionation

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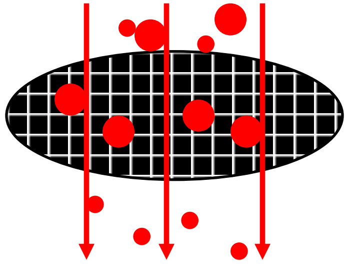
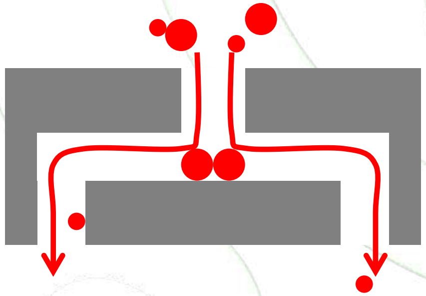
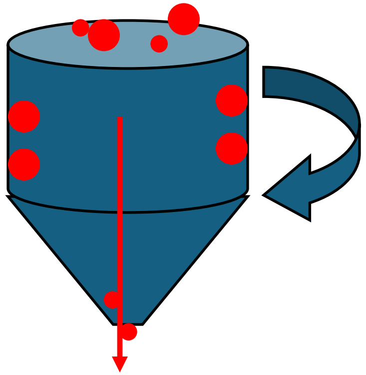
FILTRATION



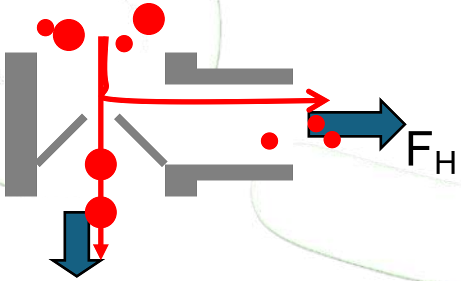
IMPACTOR



CYCLONE

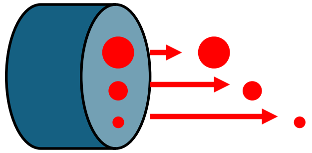


VIRTUAL IMPACTOR



$F_L << F_H$

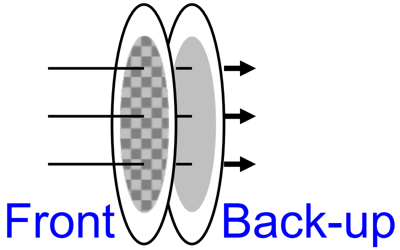
NOZZLE ACCELERATION

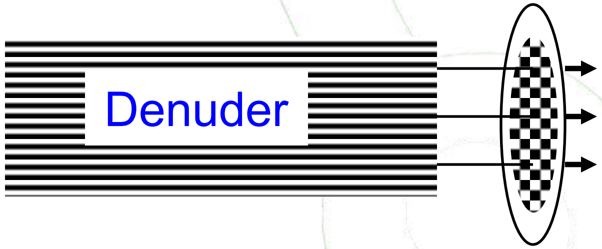


Sampling artifacts

- **Positive artifacts** (absorbtion of volatiles in fibrous filters, like quartz-fiber, Teflon, nylon) observed for VOC, SO_2 and HNO_3

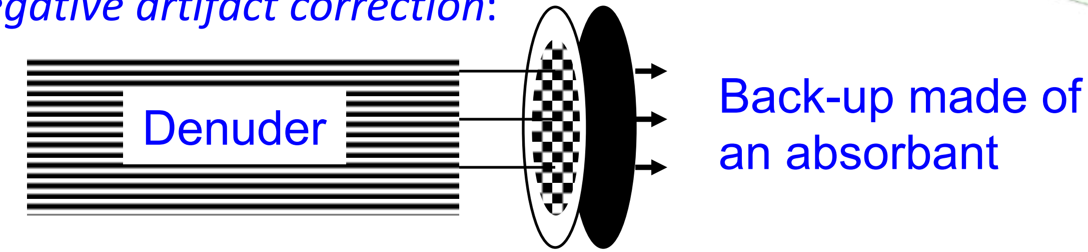
- *modifications to the sampling line for positive artifact correction*:





- **Negative artifacts** (volatilization of semivolatiles from the collected sample + particle bouncing on flat substrates) for OC, NH_4NO_3

- *modifications to the sampling line for negative artifact correction*:



- If T, RH or the aerosol concentration vary significantly during sampling, the correction for positive and negative artifacts cannot be done accurately.

Filter types more suitable for off-line chemical analyses

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***Table 3.1.1**. Comparison of filter types (modified from Bergmans et al., 2022).*

			Weighing		Chemical characterisation			
Filter type	Flow*	Hygros.	El charge	Mass	Elements	OC/EC	Organics	Ions
Glass fiber	HV, LV, VLV	(Low)	Low	High	N	(Y)	Y	Y
Quartz	HV, LV, VLV	Low	Low	High	Y*	Y	Y	Y
Teflon, PTFE	LV, VLV	Low	Low	Variable	Y	N	Y	Y
Polycarbonate	VLV	Low	(High)	Low	Y	N	N	Y
Cellulose esters	LV, VLV	High	(High)	(Low)	Y	N	N	N
PVC	LV, VLV	Low	High	Low	Y	N	N	Y
Nylon	LV, VLV	Low	(High)	Low	Artifacts	N	N	HNO_3

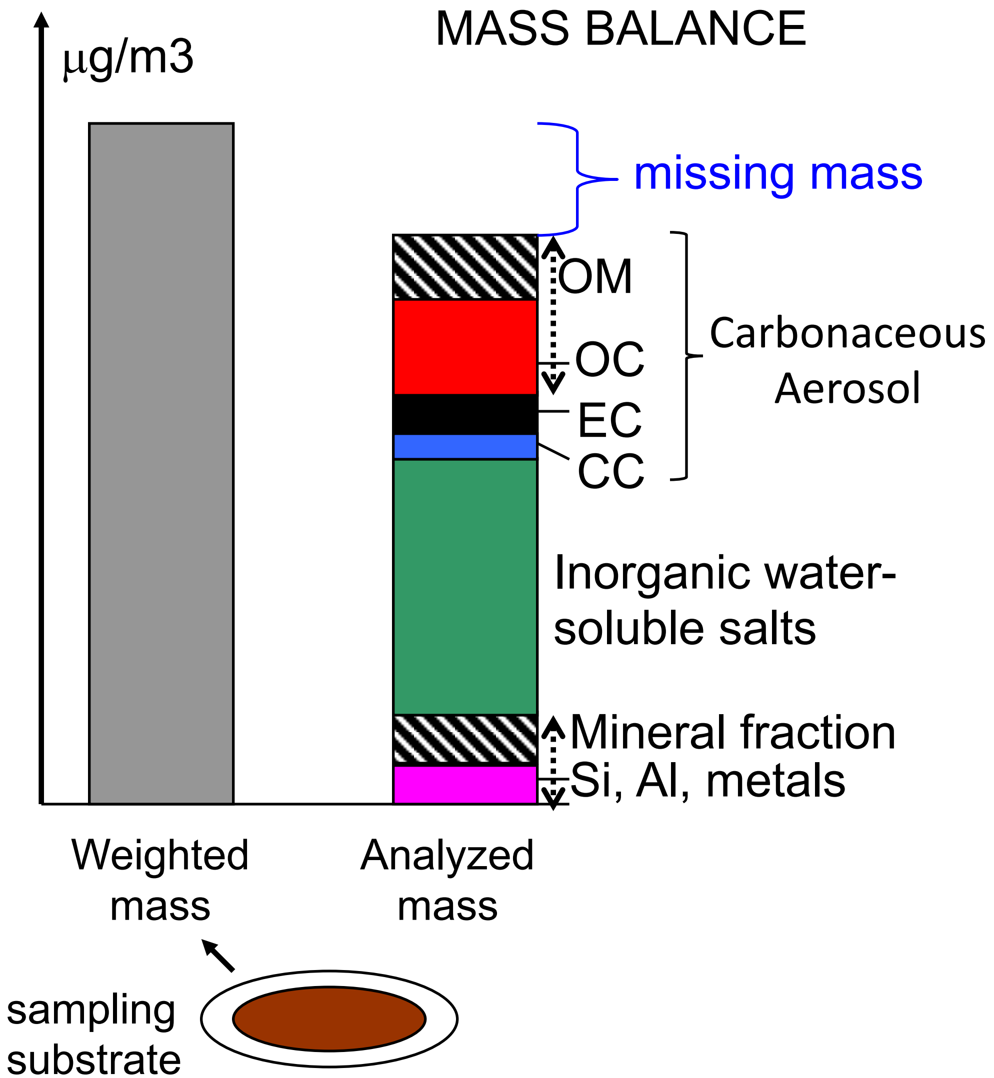
* High (HV; 30 $m^3 h^{-1}$), Low (LV; 1 – 2.3 $m^3 h^{-1}$), and Very-low (VLV; <10 L min^{-1}) volume samplers. Hygros.: hygroscopicity; El charge: electrostatic charge.

European Commission

RI-URBANS

WP7 Deliverable D55 (D7.6): PM (offline and online) speciation

Aerosol chemical analysis: main components



- Non-refractory ➔ Organic aerosol ➔ thousands of different species
- Refractory ➔ soot + carbonatic

Secondary Inorganic Aerosol - SIA:

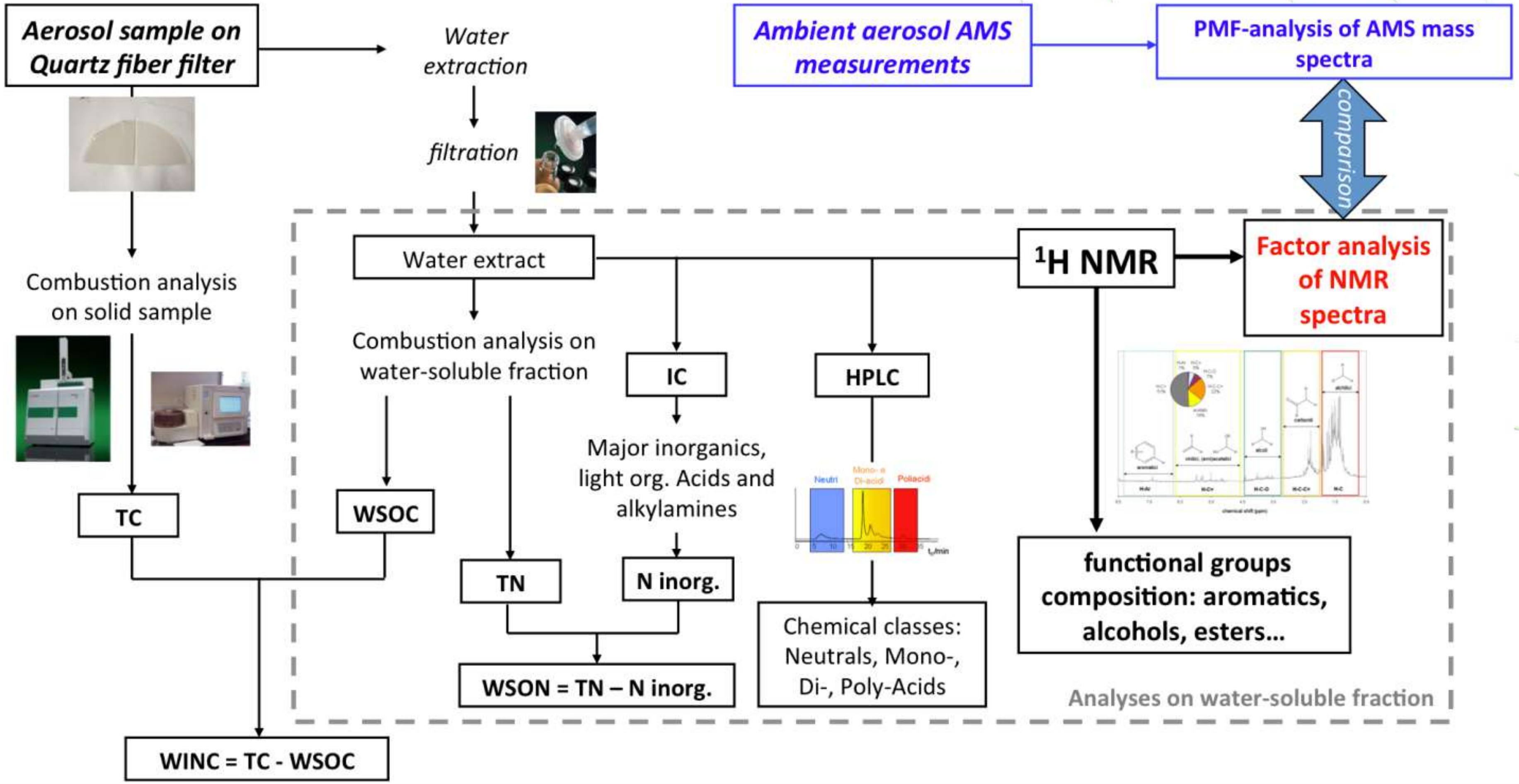
- **NITRATE** (NO_3^-)
- **SULFATE** (SO_4^{2-})
- **AMMONIUM** (NH_4^+)

Sea-salt and/or other sources:

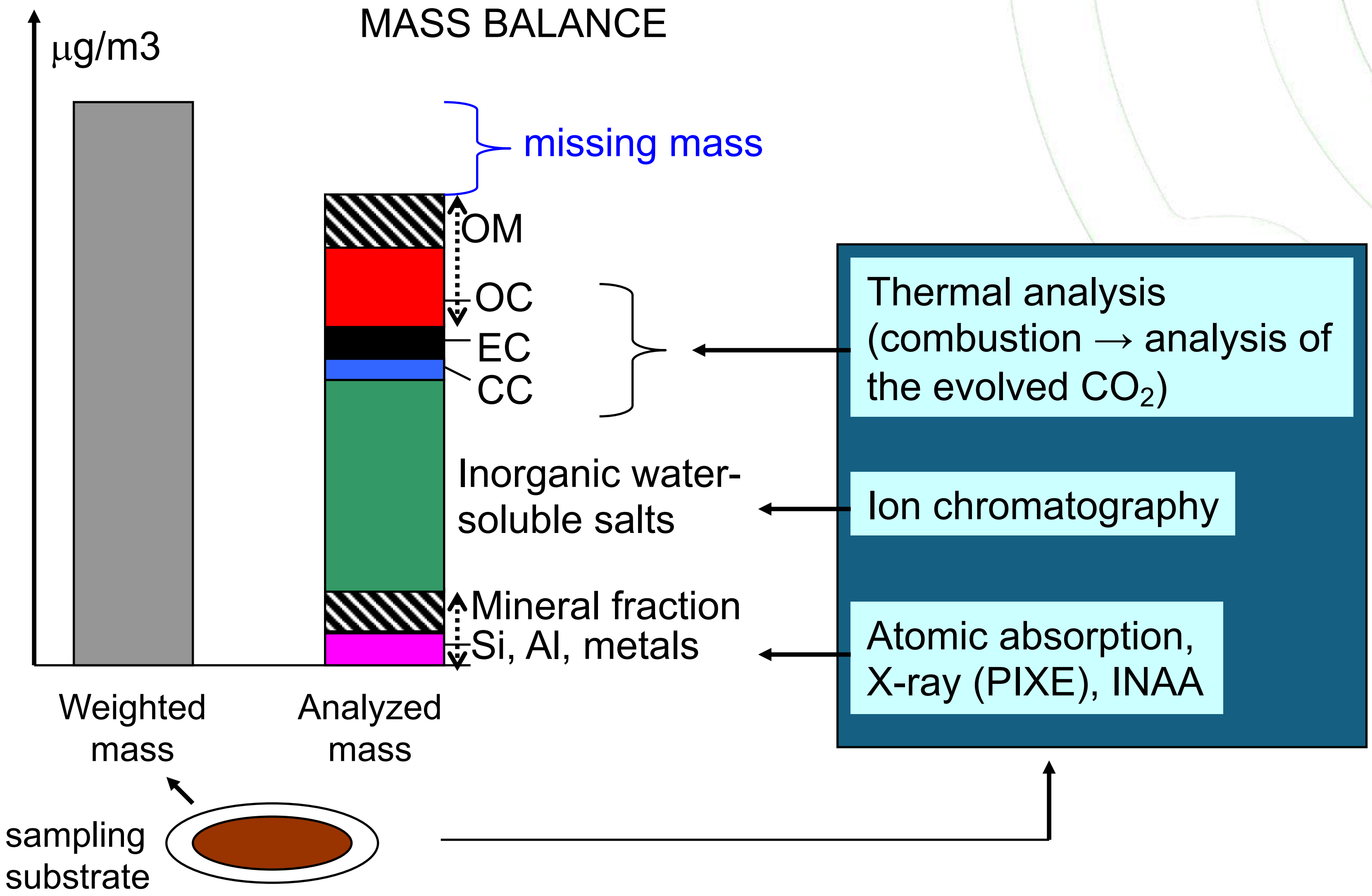
- Chloride (Cl^-)
- Sodium (Na^+)
- Potassium (K^+)
- Calcium (Ca^{2+})
- Magnesium (Mg^{2+})

Aerosol chemical analysis: many techniques in parallel

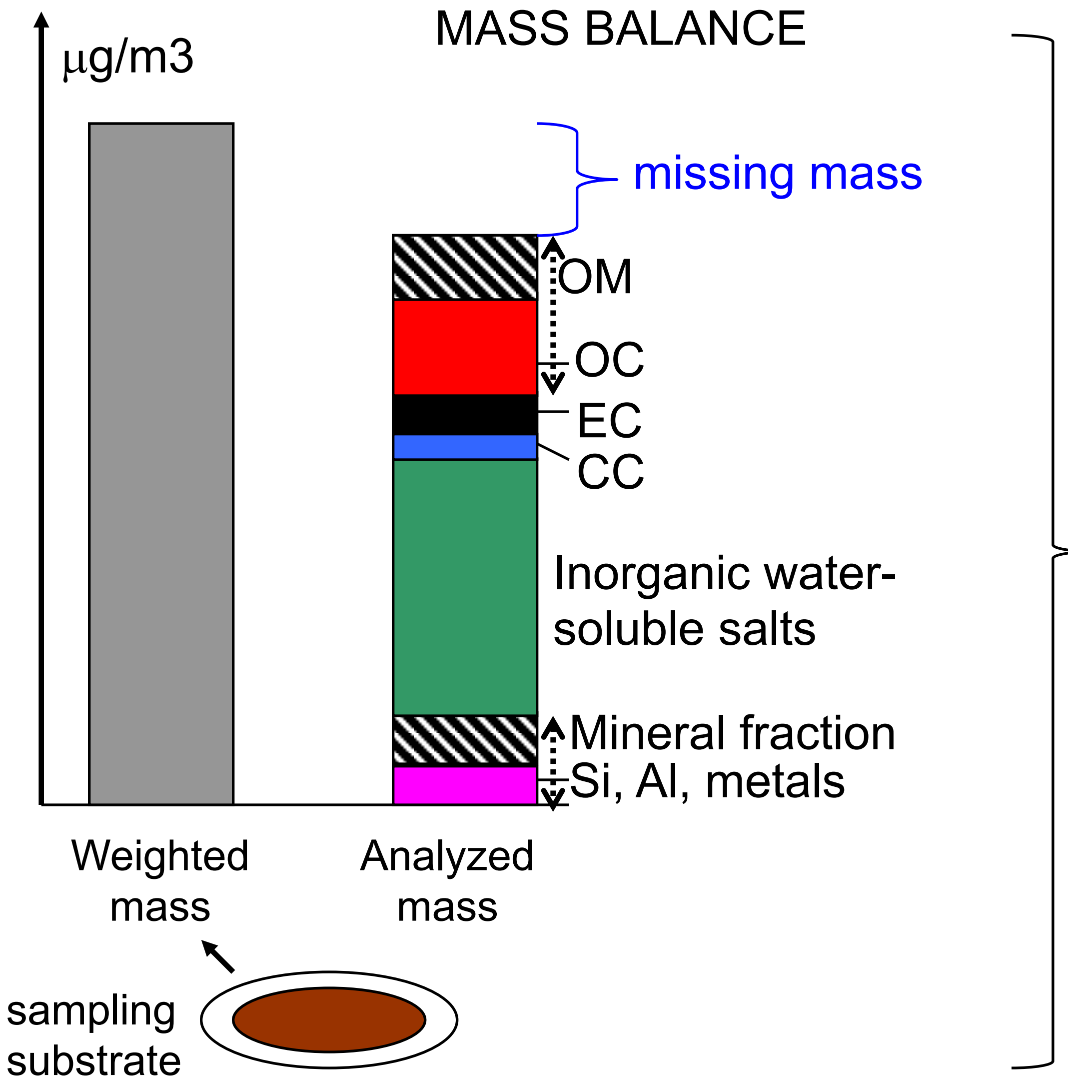
Given the chemical complexity, there is **no single analytical technique** that can characterize the entire chemistry of the particles ➔ **Different and complementary techniques are usually used in parallel**.

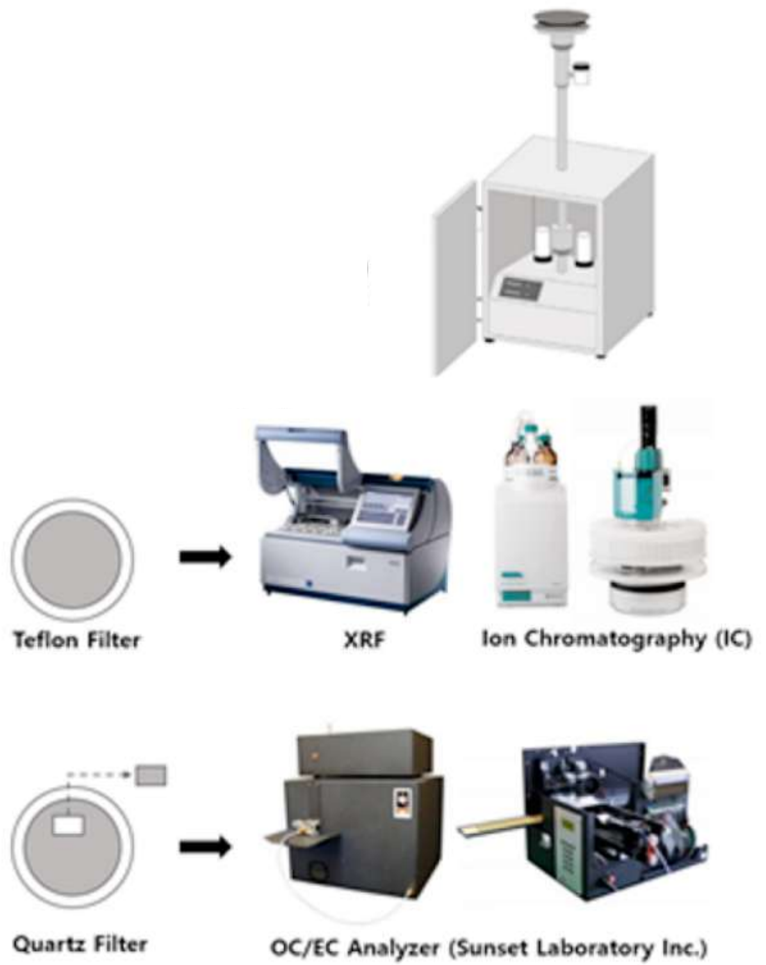


Aerosol chemical analysis: many techniques



Aerosol chemical analysis: many techniques





Lee et al., 2023 https://doi.org/10.3390/toxics11010069

Water soluble ions: ion-chromatography

Concentration of the water-soluble inorganic ions (which **account for a large fraction of PM**) is usually performed by ion-chromatography (IC) analysis of the water extract of a filter, or a fraction of the filter

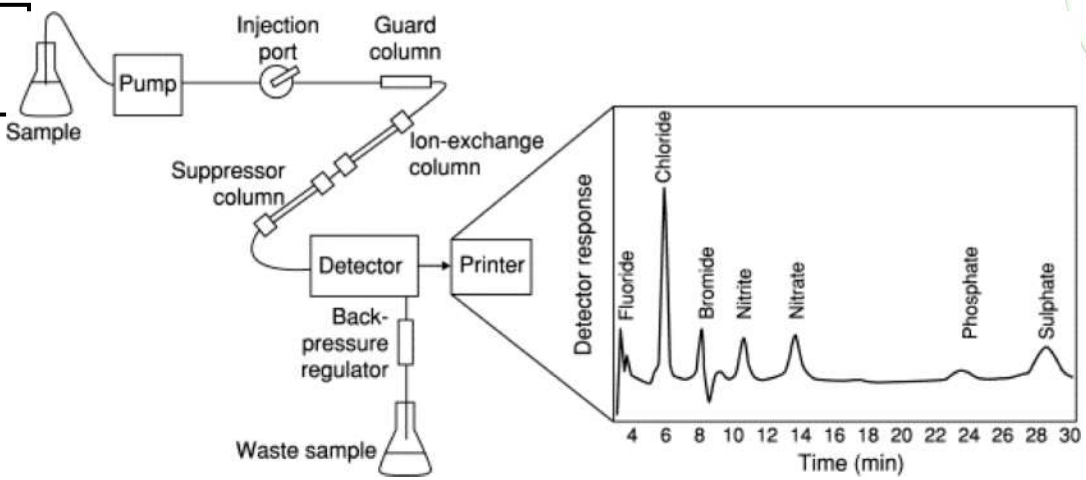
European standard EN16913:2017 ➔ water extraction of the filter followed by the analysis of the ions by IC coupled to a conductivity detector.

Measurement of **NITRATE** (NO_3^-), **SULFATE** (SO_4^{2-}), **Chloride** (Cl^-), **AMMONIUM** (NH_4^+), **Sodium** (Na^+), **Potassium** (K^+), **Magnesium** (Mg^{2+}), **Calcium** (Ca^{2+})

Extraction & filtration

PM samples on filters

Water extract



ACTRIS does not provide any guideline for the analysis of water-soluble ions in PM. The EMEP Manual (2001) provides some recommendations for sampling and analysis of ions in atmospheric particulate matter.

Major and trace elements (i.e., mineral fraction & metals)

The analysis of major and trace elements in PM is of high interest for **tracing emission sources**. Trace elements usually occur at **very low concentrations** (in the order of ng m^{-3} or lower) requiring robust analytical techniques with low detection limit.

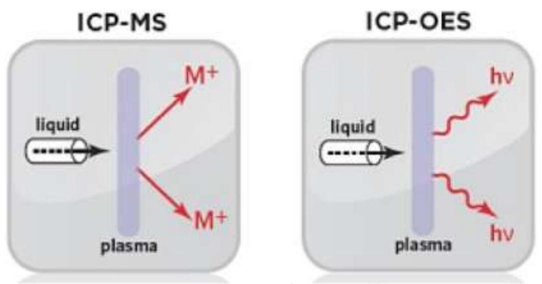
3 main types:

Atomic Spectrometric techniques

Inductively Coupled Plasma (ICP)

ICP-MS (Mass Spectrometry)

ICP-OES (Optical Emission Spec.)



PROS: **very low LODs and LOQs**

CONS: require a chemical digestion of the sample (=> **time consuming** and possible **contaminations**)

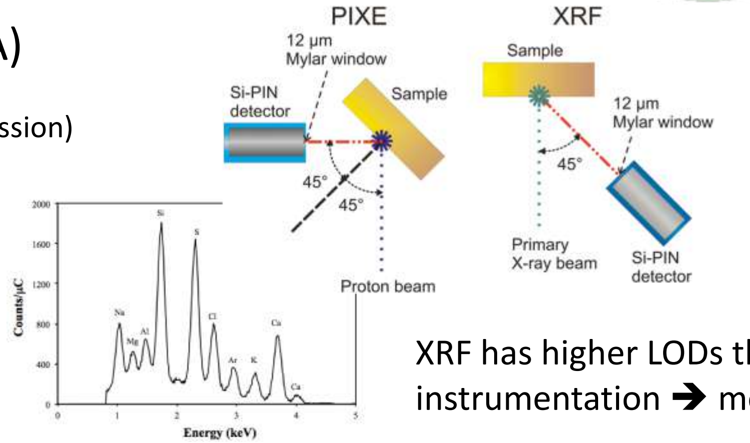
Out of these two, ICP-MS is often the technique of choice due to lower LODs/LOQs and being one of the standard methods in the EU legislation (EN 14902:2005).

X-Ray methods

Ion Beam Analysis (IBA)

PIXE (Particle Induced X-ray Emission)

XRF (X-ray fluorescence)



PROS: **non-destructive** and **fast-analysis** techniques that involve minimal sample manipulation

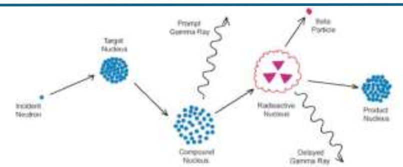
CONS: higher LODs with respect to ICP

XRF has higher LODs than PIXE, BUT it requires less complex instrumentation ➔ more affordable and easier to use.

Neutron Activation Analysis - INAA

(Duarte et el., 2021)

Samples are irradiated with neutrons to create radioactive isotopes, which then decay and emit characteristic gamma rays.



Major and trace elements (i.e., mineral fraction & metals)

ACTRIS guidelines provide some recommendations for multi-element analysis of PM filters, **mainly based on XRF and/or PIXE techniques** (https://www.actris-ecac.eu/pmc-elements.html):

•• Filters used should have low concentrations of elements of interest. They should be clean, with low contamination, and thin to reduce the background in PIXE spectra and the contribution of residual bulk contaminants.

•• The sampling should produce as much homogeneous aerosol deposit as possible.

•• After the sampling the filters should be stored in Petri slides, in order to avoid that the filter surface with the aerosol deposit on it could get in contact with materials that could results in loss of the aerosol deposit or in contamination.

•• The use of small Ziplock plastic bags or wrapped aluminium foils should be avoided.

XRF techniques can only be applied when PM samples are collected on Teflon filters, which requires the use of low-volume samplers. This technique, unlike ICP-based methods, **allows direct determination of Si**. However, the detection limits of some tracers of interest to study the contribution of sources, such as As, Cd, Sb, Se, Sn, among others, can be considered (too) high.

Major and trace elements: on-line measurements

As regards to **real-time analysis of trace elements and metals**, no guidelines have so far been produced. However, there is an increasing scientific interest in Europe in high time resolution XRF instrumentation for atmospheric aerosol measurements.

Currently there are three online XRF instruments available:

- **Xact 625i Ambient Metals Monitor** by Sailbri Cooper Inc., USA (https://cooperenvironmental.freshdesk.com)
- **EHM-X100 Atmospheric Heavy Metals On-line Analyses** by Skyray Instrument Ltd., China
- **PX-375 Particulate Monitor with X-Ray Fluorescence** by Horiba Ltd., Japan.

Xact 625i

ACTRIS established a Working Group on Online metal analysis for drafting operational recommendations (https://www.actris.eu/facilities/national-facilities/forum)

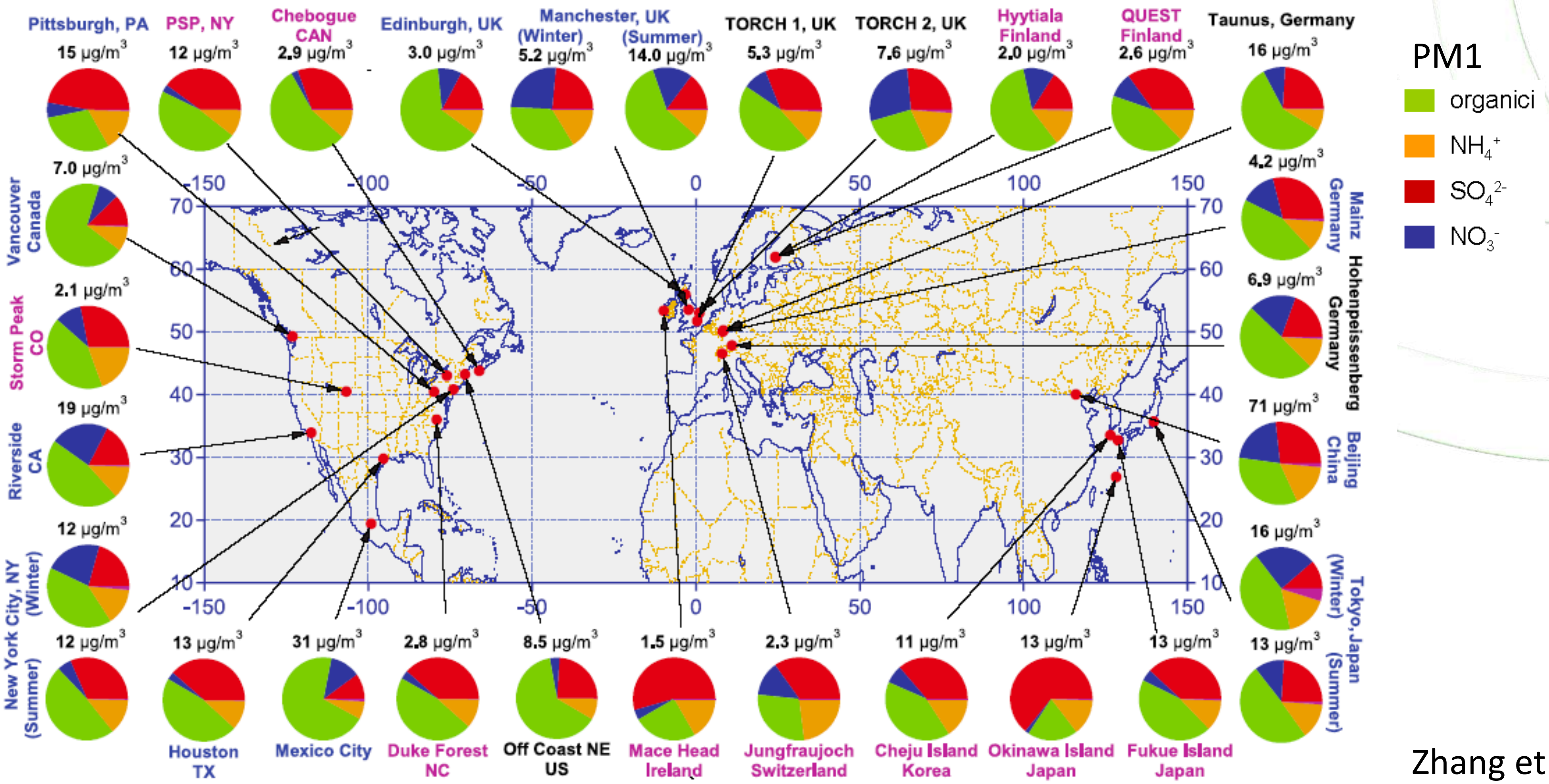
Carbonaceous aerosol: names & definitions

Total Carbon (TC), organic (OC), elemental (EC), carbonatic (CC), water-soluble OC (WSOC)

- **TC** = OC + EC (+ CC);
- **EC**: thermally refractory carbon (decomposes only at **T > 400°C** and in **oxidizing atmospheres**);
- **CC**: determinable by difference from TC or WSOC **after acidification**;
- **WSOC**: determinable in the aqueous extract with **liquid TOC techniques**.

Organic Aerosol- OA

Organic aerosol (OA) represents **20 - 50% of the fine aerosol** (PM1) mass in urban and rural environments and **up to 90% in remote sites** such as boreal forests, where organics often also dominate the coarse particulate matter (PM10) fraction.



Zhang et al., 2007 JGR

Organic Aerosol- OA

OA is a **mixture of thousands of different molecular species** including **aliphatic and aromatic hydrocarbons**, **PAHs**, **aldehydes**, **ketones**, **carboxylic acids** (and polyacids), **amines**, **alkyl nitrates**, **polyols**, **sugars**…

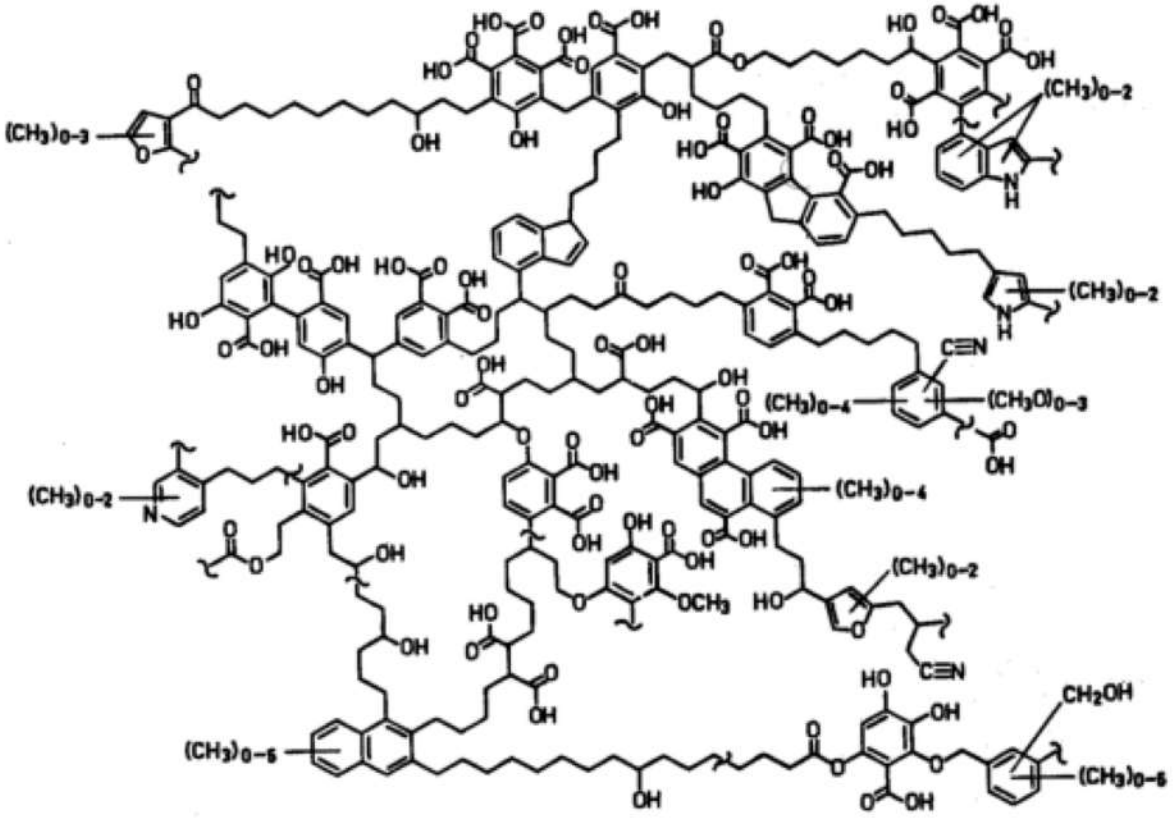
From relatively simple and linear molecules…

es. n-alcani

CH_3-$(CH_2)_{16}$-CH_3

…to very complex multifunctional molecules

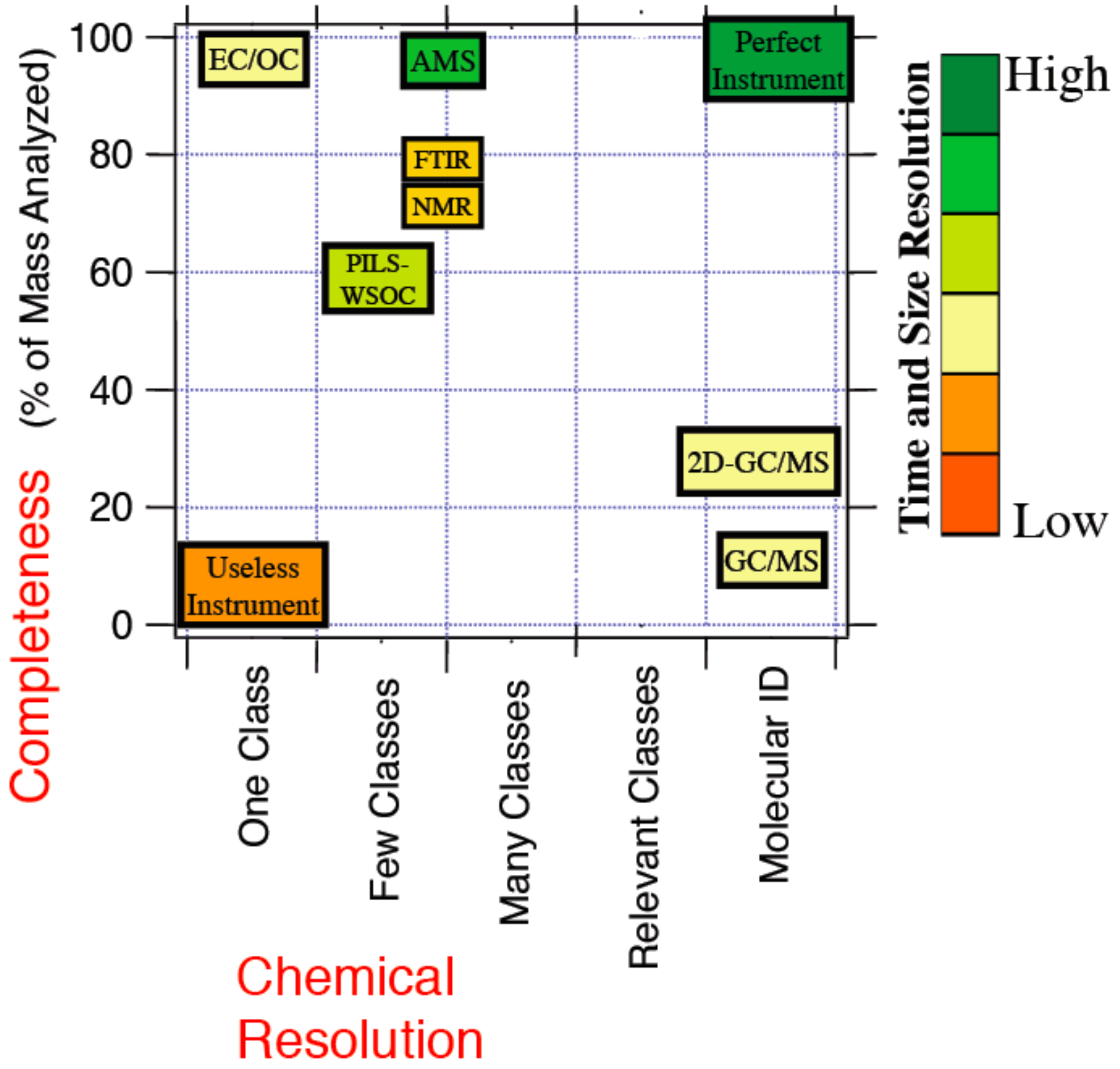
es. HULIS



…whose **SOURCES** (anthropogenic or biogenic, primary or secondary) and **CHEMICAL-PHYSICAL PROPERTIES** (e.g. polarity, volatility, size distribution) vary enormously in space and time

OA Analysis: Techniques Compared

Classification based on ability to quantify total mass, chemical and temporal resolution



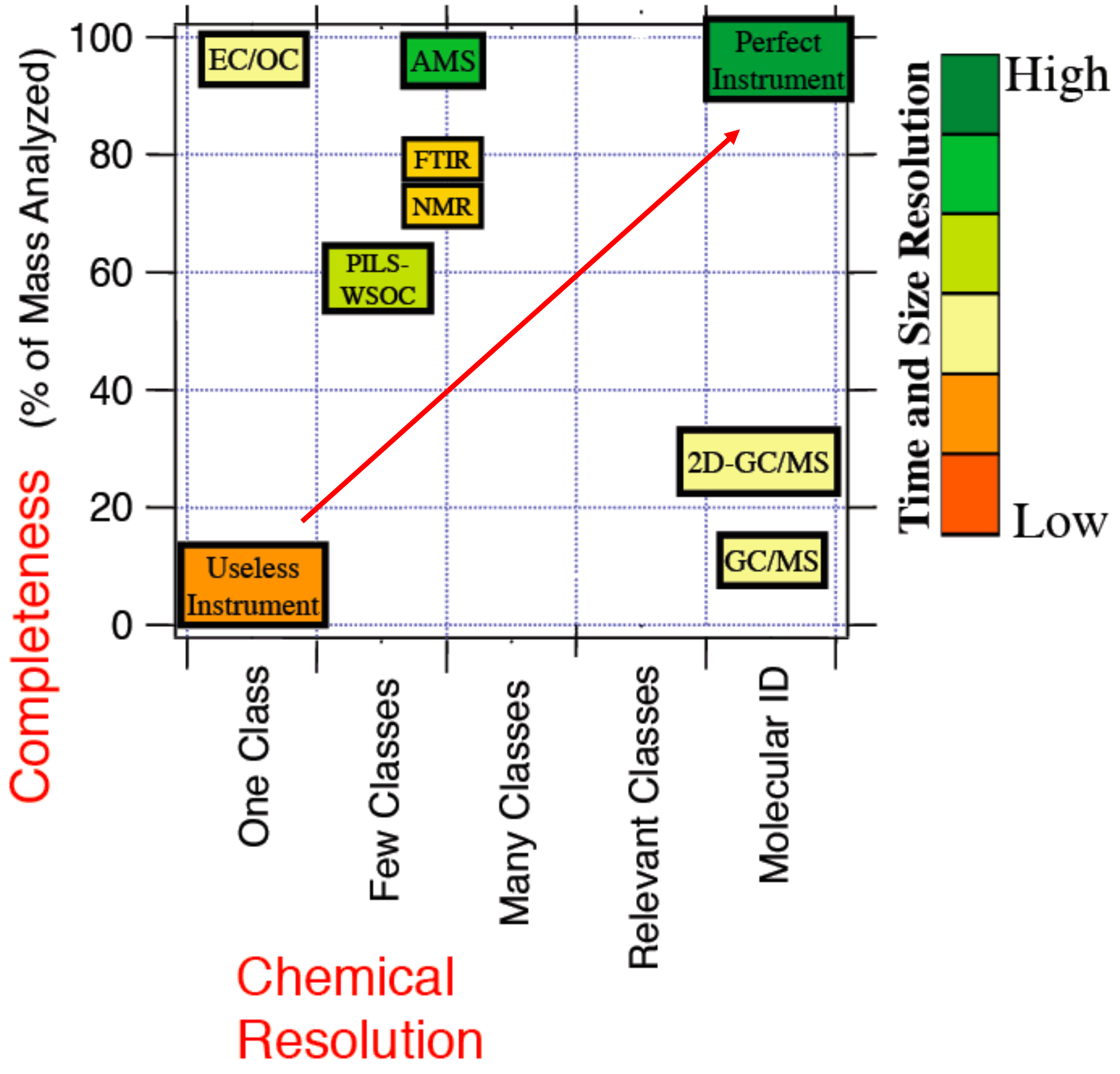
THERE IS NO PERFECT/COMPLETE TECHNIQUE…

SEVERAL COMPLEMENTARY TECHNIQUES ARE USEFUL

Hallquist et al., 2009 ACP

OA Analysis: Techniques Compared

Classification based on ability to quantify total mass, chemical and temporal resolution

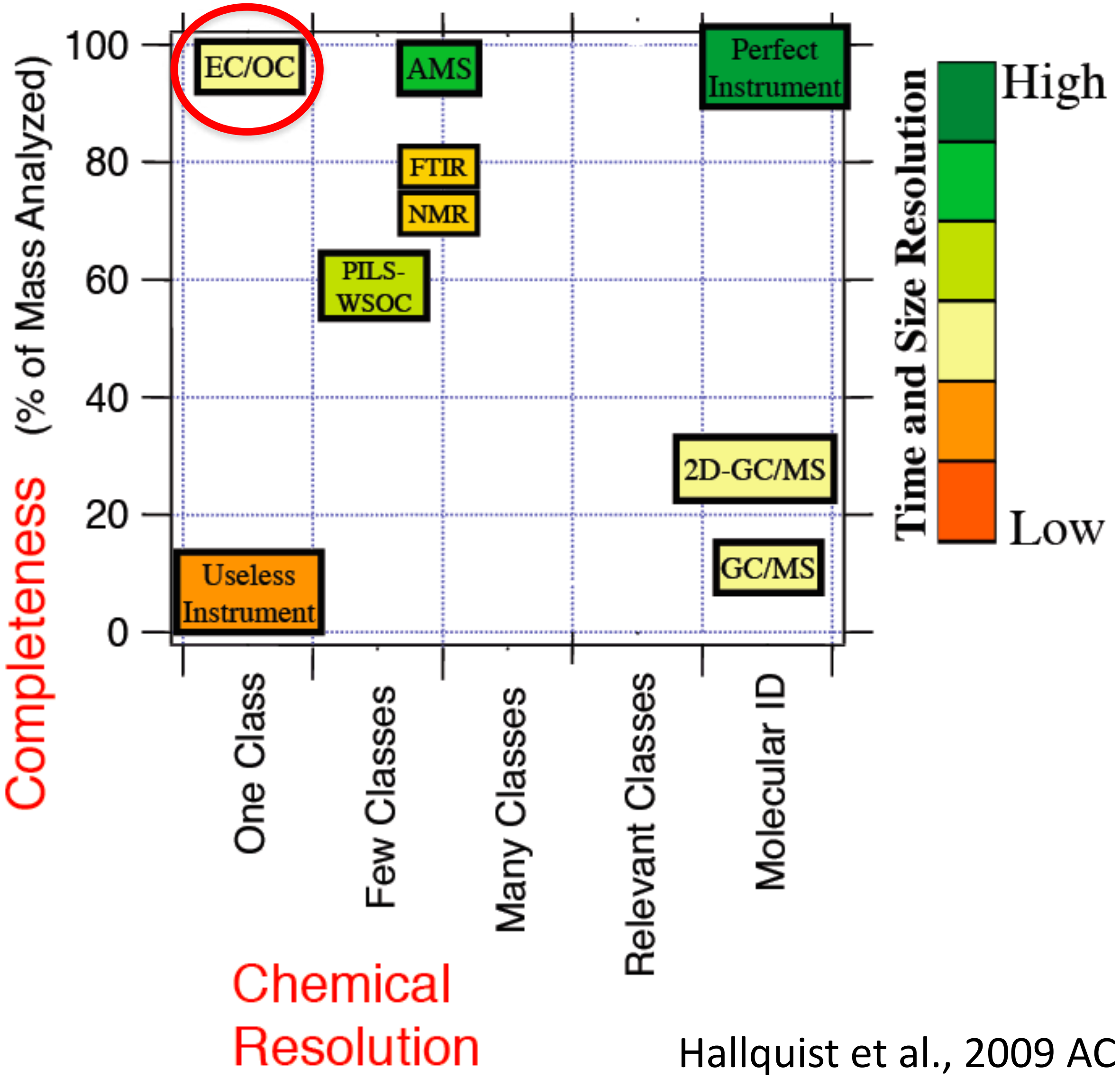


Hallquist et al., 2009 ACP

OA Analysis: Techniques Compared

Classification based on ability to quantify total mass, chemical and temporal resolution

Thermo-optical meas. (EC/OC)
identify the total organic mass, but do not allow any type of speciation into classes or individual compounds.

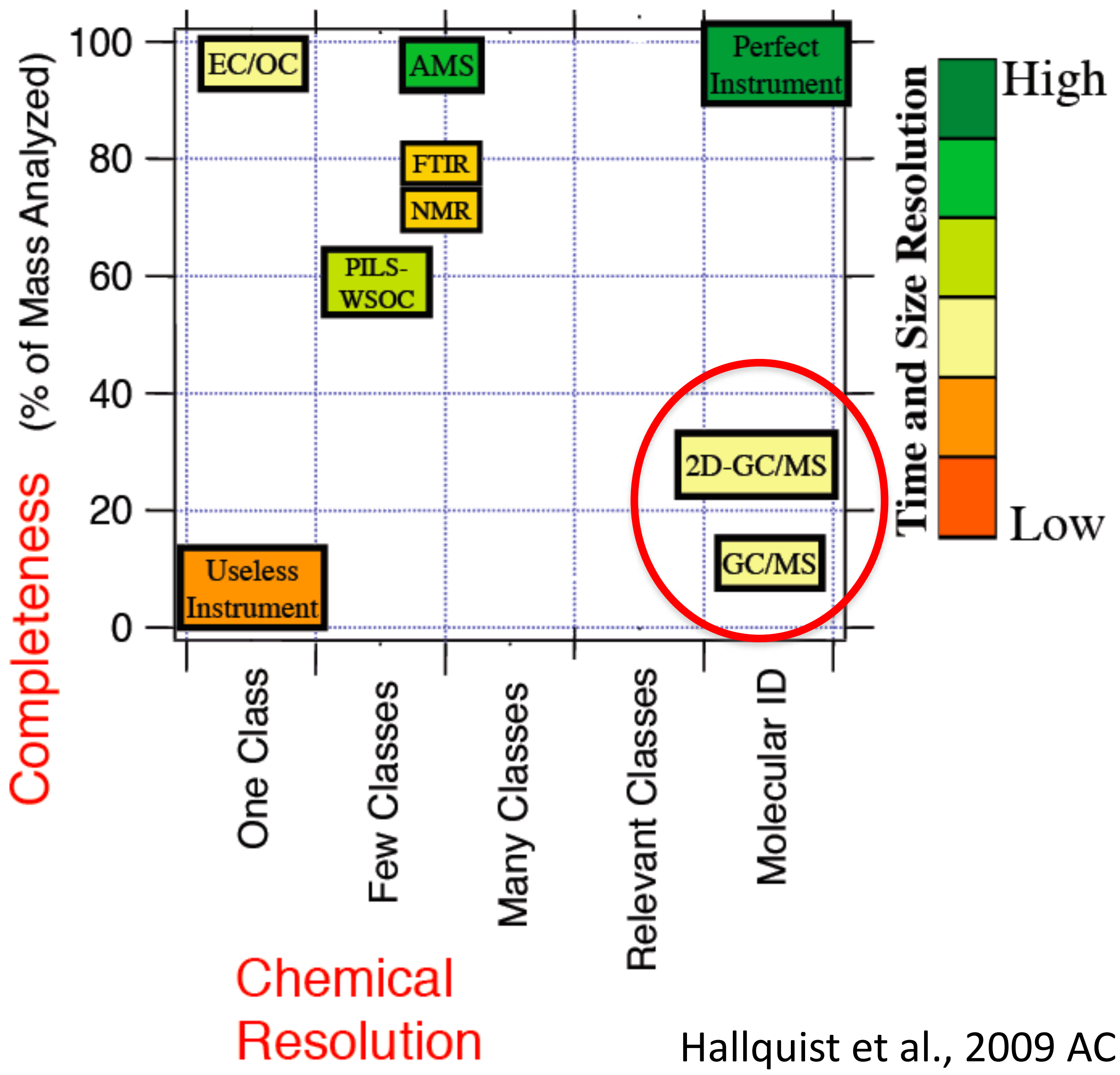


Hallquist et al., 2009 ACP

OA Analysis: Techniques Compared

Classification based on ability to quantify total mass, chemical and temporal resolution

Chromatographic methods
identify individual chemical species but resolve only a small fraction of the total organic aerosol mass (10% - 40%)

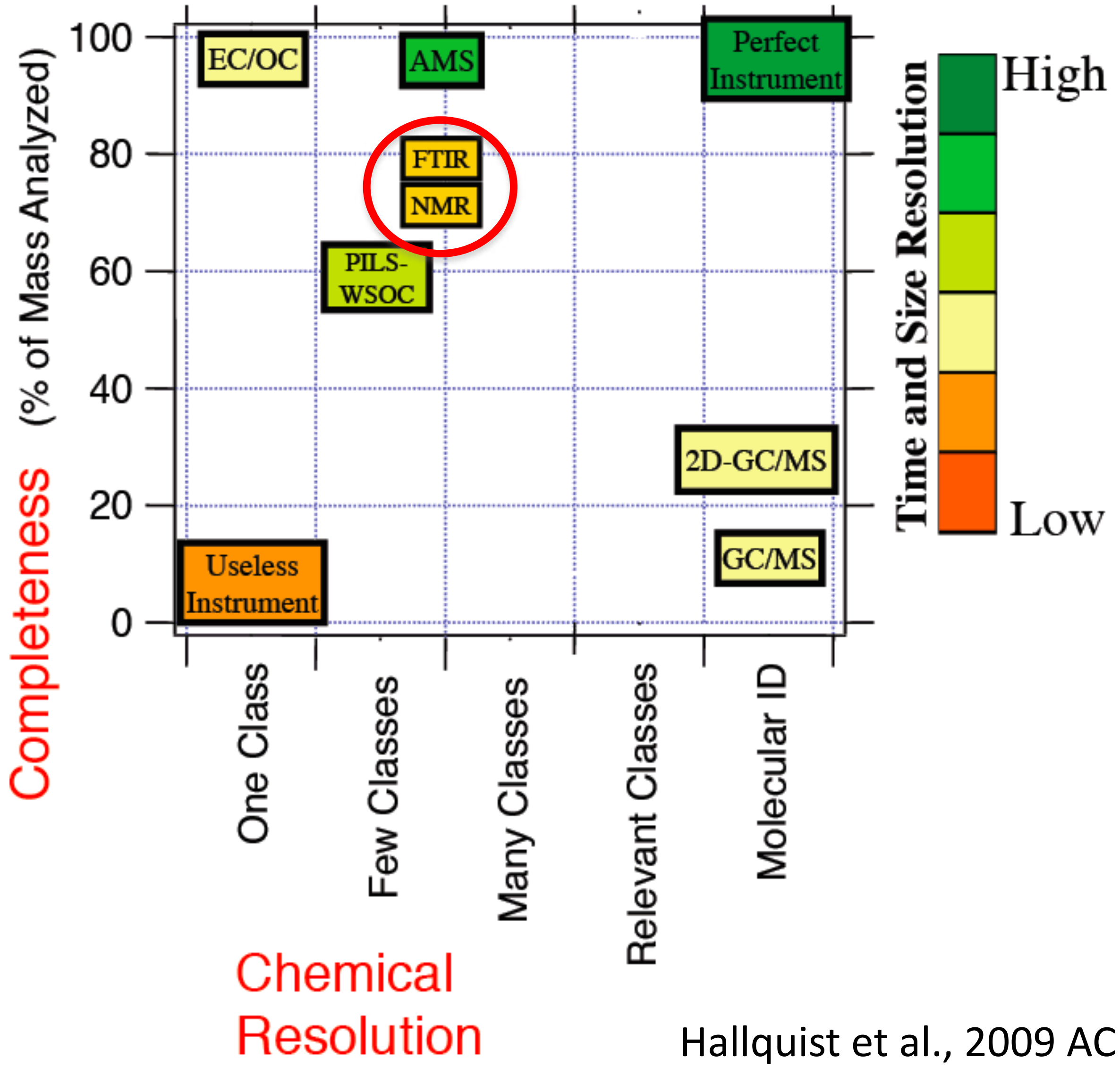


Hallquist et al., 2009 ACP

OA Analysis: Techniques Compared

Classification based on ability to quantify total mass, chemical and temporal resolution

<u>**FT-IR & NMR spectroscopy**</u>
identify organic functional groups such as carbonyls, amines, hydroxyls, aromatic rings, etc., resolving much of the mass, but give little information about individual molecules.

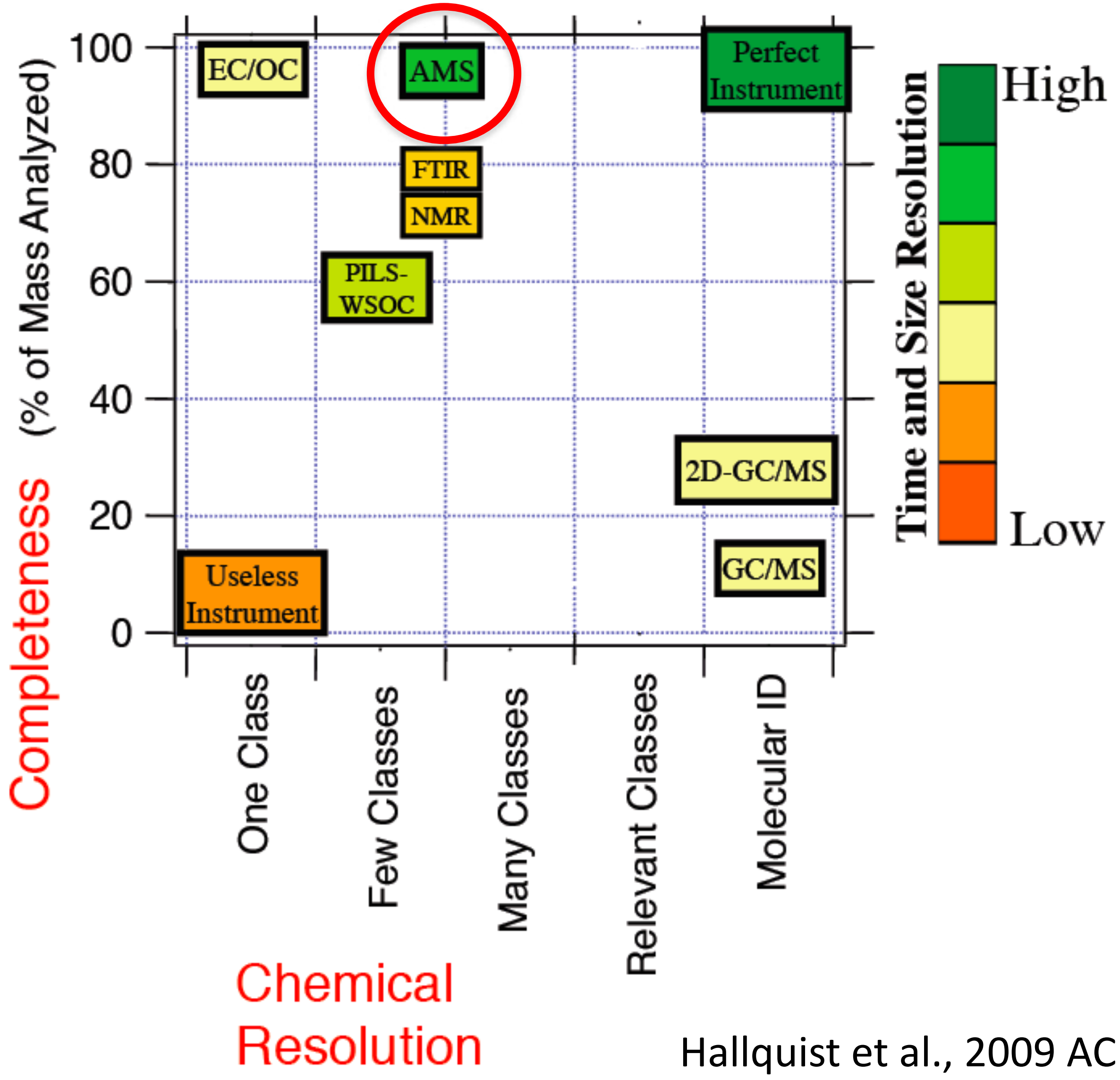


Hallquist et al., 2009 ACP

OA Analysis: Techniques Compared

Classification based on ability to quantify total mass, chemical and temporal resolution

Aerosol Mass Spectrometry (AMS)
quantifies the total organic aerosol and describes it with a few classes in particular based on their degree of oxidation (es., HOA, BBOA, OOA)

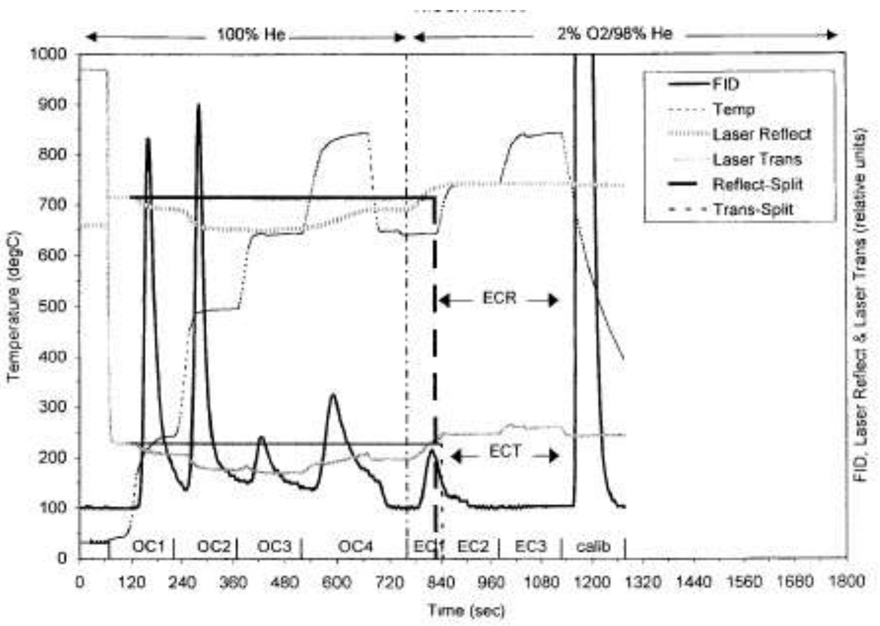


Hallquist et al., 2009 ACP

Organic and elemental carbon (OC/EC)

The concentrations of OC and EC in atmospheric PM collected on **quartz-fiber filters** are typically measured using the **thermal-optical offline analytical technique** with an optical correction of charring.

The technique consists of subjecting the aerosol collected on filter-samples to a thermal-protocol (a ramp of increasing temperatures) and following their vaporization and progressive oxidation to CO2

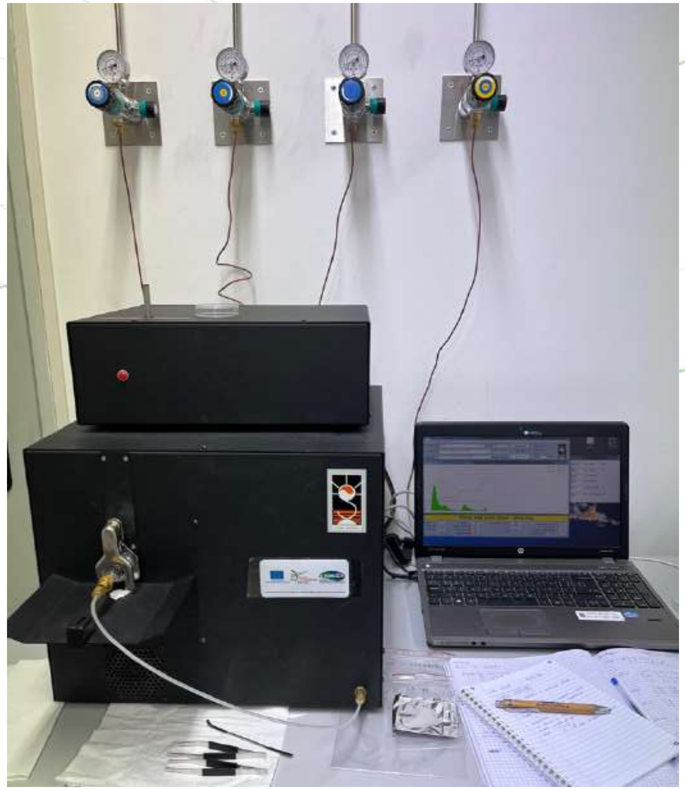


Most employed **thermal protocols** are:

- IMPROVE,
- NIOSH-like, and the
- **EUSAAR-2** (Cavalli et al., 2010).

The optical correction for charring is generally performed via filter light transmission monitoring (TOT).

SUNSET Lab OC-EC Aerosol Analyzer



NB: only glass and quartz-fiber filters are suitable for SUNSET!

Organic and elemental carbon (OC/EC)

A European standard (EN16909:2017) exists for the measurement of airborne EC and OC in PM2.5 (Karanasiou et al., 2015; Brown et al., 2017).

The recommendation by ACTRIS for OC & EC analysis is to follow the EN16909:2017.

ACTRIS guidelines highlighted specific points of EN16909 that are particularly important: on filters choice and pre-treatments, thermal protocols, etc. (please refer to: https://www.actris-ecac.eu/actris-gaw-recommendation-documents.html)

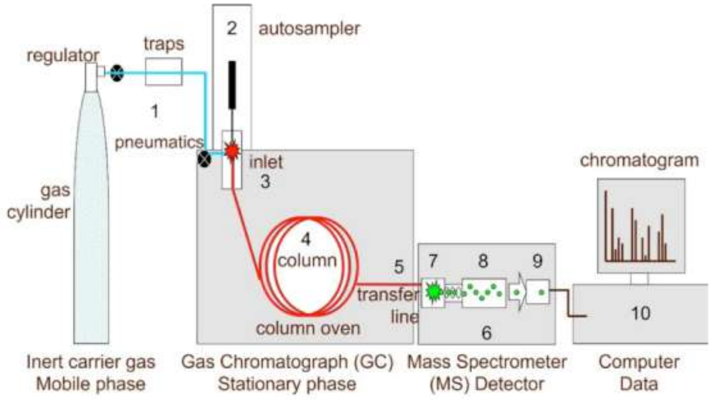
Urban and regional background supersites are also advised to follow the recommendations made to ACTRIS National Facilities (NFs)

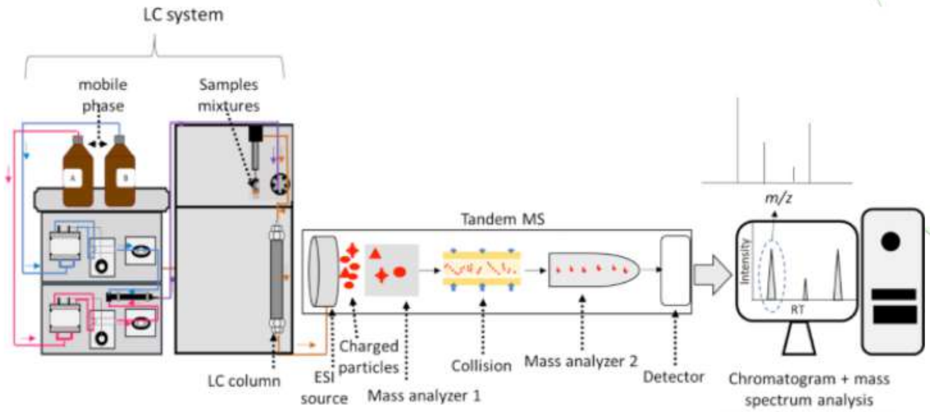
ACTRIS-ECAC also provide recommendations on **thermal-optical on-line analysis** of OC and EC using a semi-continuous field analyser in "Semi-continuous measurement of elemental carbon (EC) and organic carbon (OC)", available at www.actris-ecac.eu/pmc-oc-ec.html .

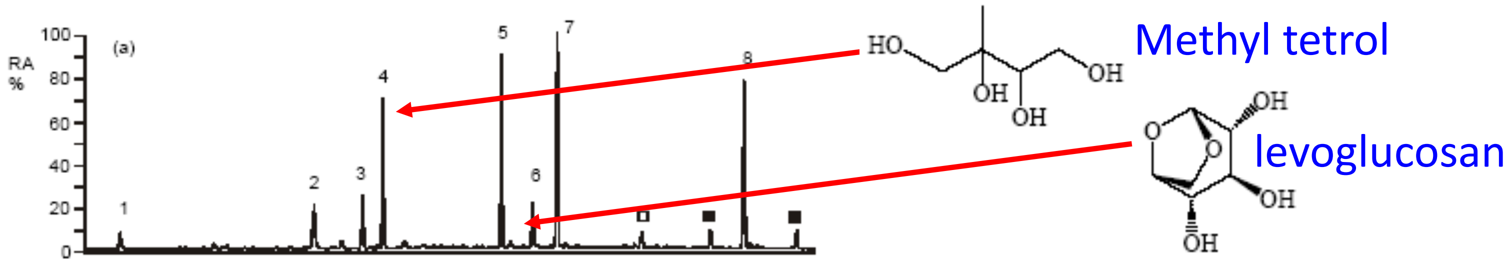
Organic markers: separation and molecular speciation

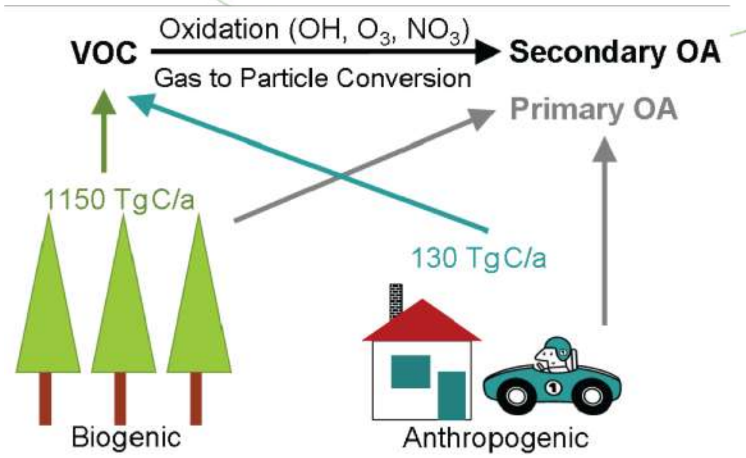
Given their association with specific emission sources, some organic compounds are used as **molecular markers** to identify the presence and contributions of the **different sources** to PM (Schauer et al., 2007).

They are usually measured in ambient air PM filter samples by solvent extraction and subsequent **Gas and/or Liquid chromatography** coupled with **mass spectrometry (GC-MS, LC-MS)**









Organic markers most commonly determined

GC-MS and **LC-MS**, allow **identification and quantification of a wide range of organic compounds**, BUT generally cover a very small fraction (often <5 %) of the total organic aerosol mass.

An overall standardised methodology is lacking, and only exists for PAHs, and in specific for **benzo[a]pyrene** (EN15549:2008, CEN/TS 16645:2014, ISO 12884:2000, USEPA TO-13A, ISO 16362:2005) and for **levoglucosan** (CEN/TS 18044:2024)

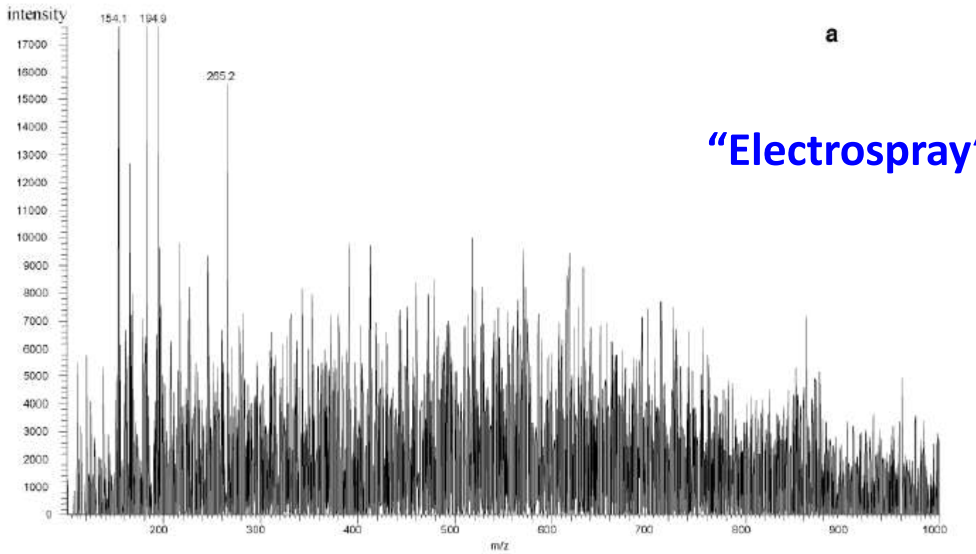
Nonetheless the mass concentration of particulate organic tracers is an **additional chemical variable within the ACTRIS aerosol in-situ framework**.

Table 3.1.2. *Molecular organic aerosol markers in atmospheric particulate matter for emission sources and SOA processing, and their analytical procedures and references.*

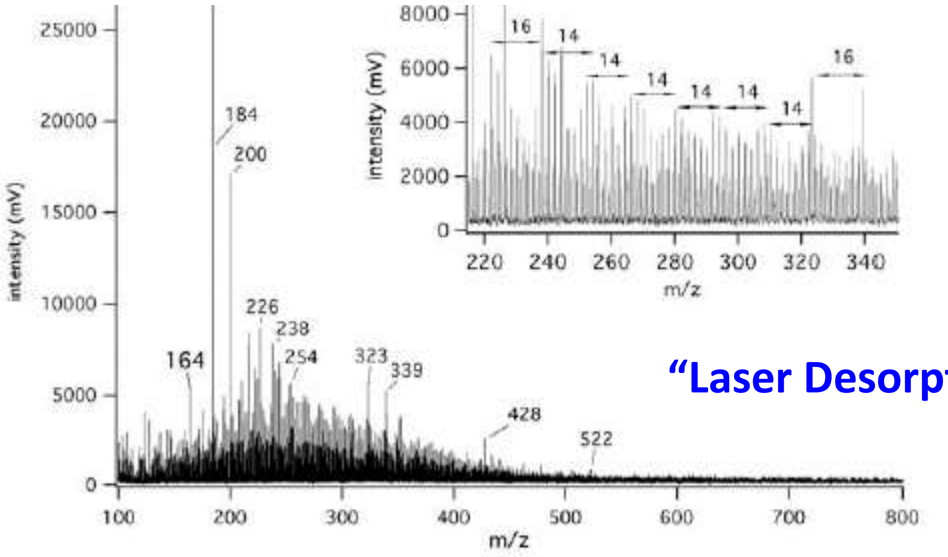
	Group	Source/Precursors	Marker compounds	Solvent	Separation /Detection	Refs.
POA	*PAH	Traffic exhaust Biomass burning Combustion	benz[a]anthracene benzo[b]fluoranthene benzo[k]fuoranthene benzo[a]pyrene benzo[ghi]perylene chrysene inden[123cd]pyrene retene	Dichloromethane Hexane Acetone Toluene	GC-MS GC-MS/MS GC-FID HPLC-FID HPLC-FLD LC-MS GCxGC-TOFMS TD-GC-GC-MS	CEN/ TS 16645:2014; EN 15549:2008; EPA TO-13A, 1999; Fontal et al., 2015; ISO 12884:2000; ISO 16362:2005; Schauer et al., 2007; van Drooge et al., 2023; Van Drooge & Grimalt, 2015)
	Hopanes	Traffic	17a(H)21β(H)-30-norhopane 17a(H)21β(H)-hopane		GC-MS GC-FID	(Alier et al., 2013; Schauer et al., 2007; Van Drooge and Grimalt, 2015)
	n-alkanes	Combustion	nC20 – nC25		GC-MS GC-FID	(Alier et al., 2013; Schauer et al., 2007; Van Drooge and Grimalt, 2015)
		Vegetation detritus Soil dust	nC27, nC29, nC31			
	Saccharides	Biomass burning	levoglucosan, mannosan, galactosan	Dichloromethane Methanol Water	GC-MS (BSTFA) GC-MS/MS (BSTFA) LC-MS HPLC-PAD IC-PAD TD-GC-GC-MS	(CEN/TS 18044:2024; Fine et al., 2004; Fontal et al., 2015; Medeiros & Simoneit, 2007; Samaké, Jaffrezo, Favez, Weber, Jacob, Albinet, et al., 2019; Van Drooge & Grimalt, 2015)
		Soil dust Vegetation detritus Fungal spores	glucose, arabitol, mannitol, sorbitol			
SOA	Acids and polyols	Biogenic and anthropogenic VOCs	succinic acid, glutaric acid, malic acid	Dichloromethane Methanol Water Acetone	GC-MS (BSTFA) GC-MS/MS (BSTFA) LC-MS HPLC-PAD IC-PAD	(Alier et al., 2013; Claeys et al., 2007, 2004; Claeys and Maenhaut, 2021; Fine et al., 2004; Heald et al., 2010; Kubátová et al., 2000; Medeiros and Simoneit, 2007; Palm et al., 2018; Paulot et al., 2011)
		Naphthalene (combustion)	phthalic acid			
		Oleic acid (food cooking)	azelaic acid			
		Isoprene (vascular plants)	2-methylglyceric acid, C5 triols, 2-methylthreitol, 2-methylerythritol			
		Alpha-pinene (pine forests)	cis-pinonic acid, 3-hydroxyglutaric acid, **MBTCA			

**PAH: polycyclic aromatic hydrocarbons; **MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.*

Organic analysis: molecules and fragments



“Electrospray” (ESI) – MS/MS

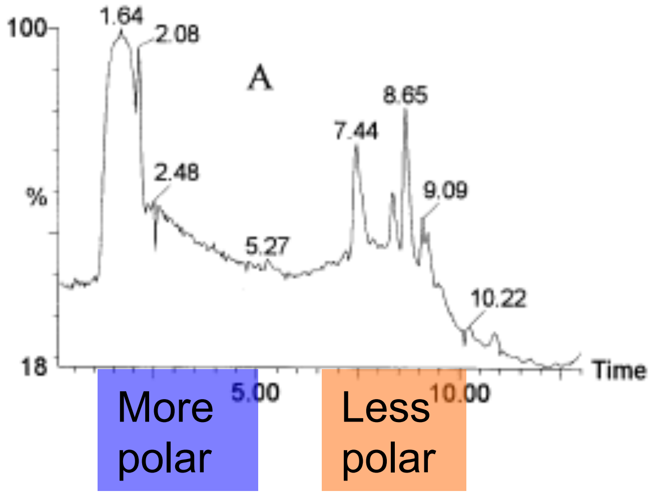


“Laser Desorption” (LDI) – TOF - MS

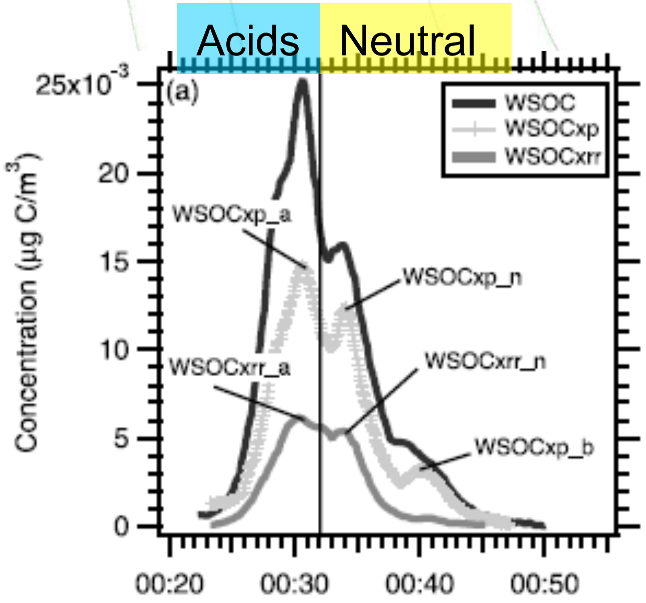
Mass spectrometry with **“soft” ionization techniques** (and without preliminary chromatographic separation), can be used to derive the “apparent” distributions of molecular weights. But the complexity of the spectra makes it difficult to obtain information on the chemical structure of the mixtures.

Organic analysis: chemical classes

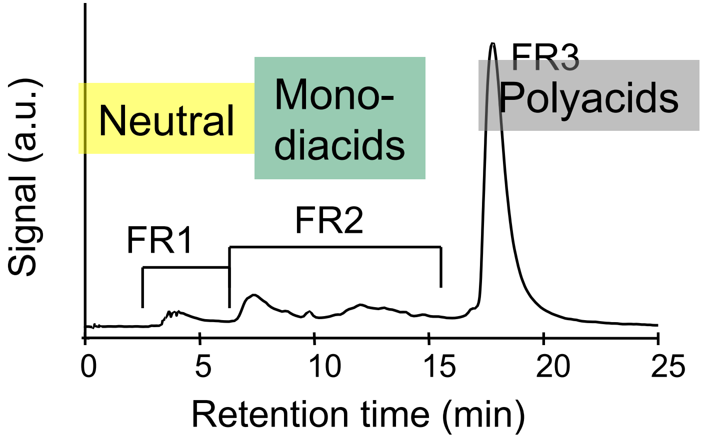
LC (RP)– ESI - MS



LC (ionic exclusion)– (UV) – TOC



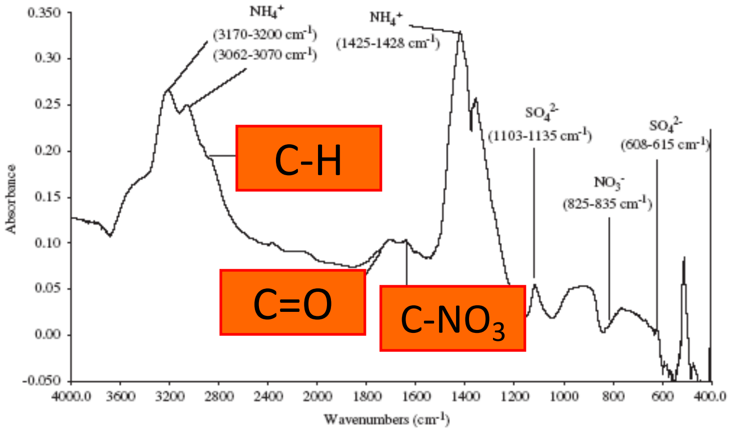
LC (ionic exchange) – UV (-TOC)



1. greatly simplifies the system;
2. OC fractions are defined operatively;
3. chemical classes which completely elude GC-MS methods are determined by LC methods

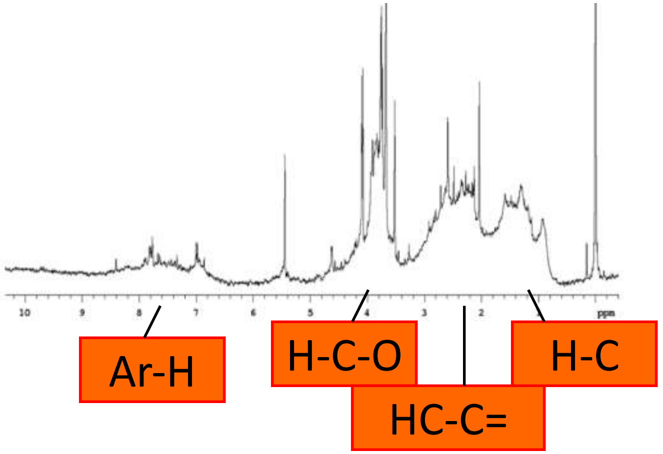
Organic analysis: functional groups

Infrared (FTIR) spectroscopy



-allows the analysis of the aerosol sample directly without extraction;
-is more sensitive than H-NMR;
-specific sampling substrates (e.g. Teflon) are needed;
-Inorganic salts interfere.

Nuclear magnetic resonance (NMR) spectroscopy



-proton (H) NMR techniques can be easily applied to the analysis of solvent (or water)- extracted OCs;
-provides better resolution than FTIR;
-does not suffer from the interference of inorganic compounds in the sample;
-Carbon (^{13}C) NMR methods are poorly sensitive and require weekly samplings with High-Vol collectors to provide sufficient loadings for the analysis.

Organic analysis: Carbon isotope analysis

Δ14C: Thermal analysis (OC/EC separation) → CO2 Isolation and reduction to C (solid) → "accellerator" (A)MS

Δ13C: Thermal analysis (OC/EC separation) → GC (CO_2 separation from N_2O) → "Isotopic ratio" (IR)MS

Isotopic analyses allow for instance to differentiate between **fossil carbon** (poor of ^{14}C, fossil fuel combustion) and recent carbon (rich of ^{14}C, biomass burning and biogenic secondary particles) sources

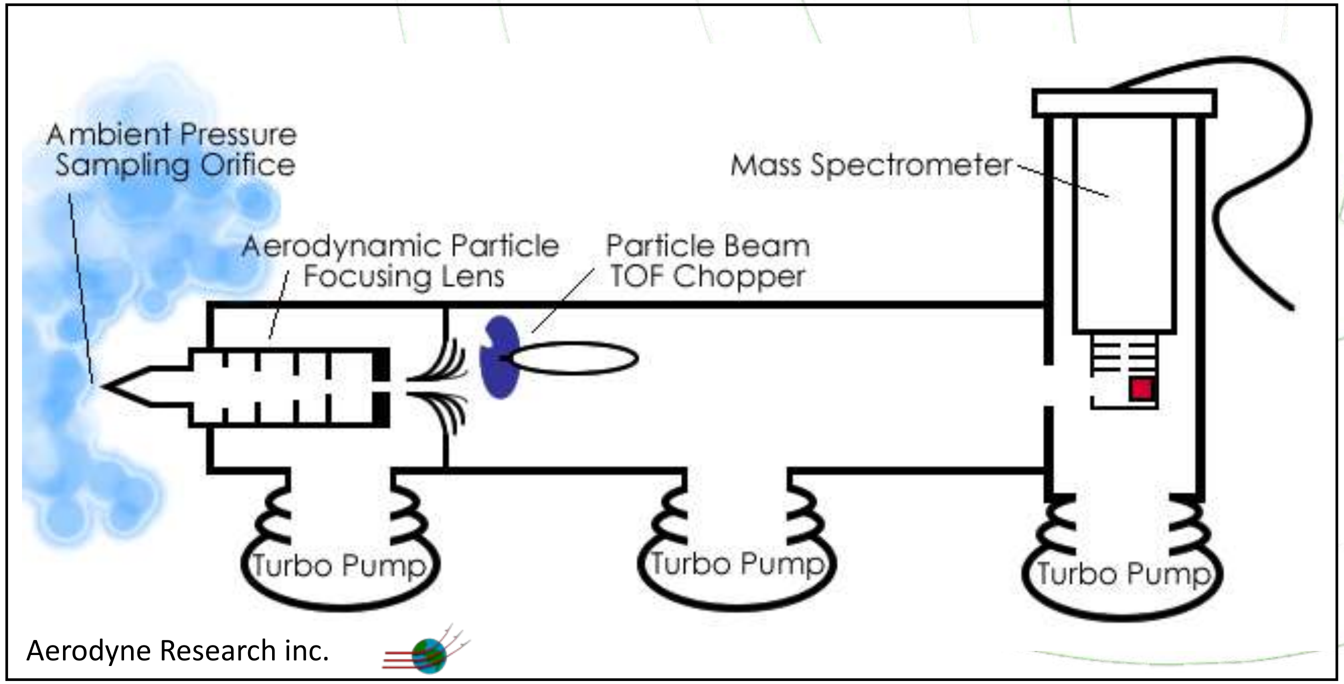
Aerosol Mass Spectrometer (r-)evolution

AMS

ON-LINE & REAL-TIME MEASUREMENTS:
real-time characterization (time resolution sec./min.) directly from the ambient air

QUANTITATIVE SPECIATION OF PM1/PM2.5:
Concentration of the main (non-refractory) components of the aerosol: Sulphate, Nitrate, Ammonium and Organics

SIZE DISTRIBUTION OF CHEMICAL COMPONENTS:
chemical composition derived from the mass spectra of all non-refractory PM

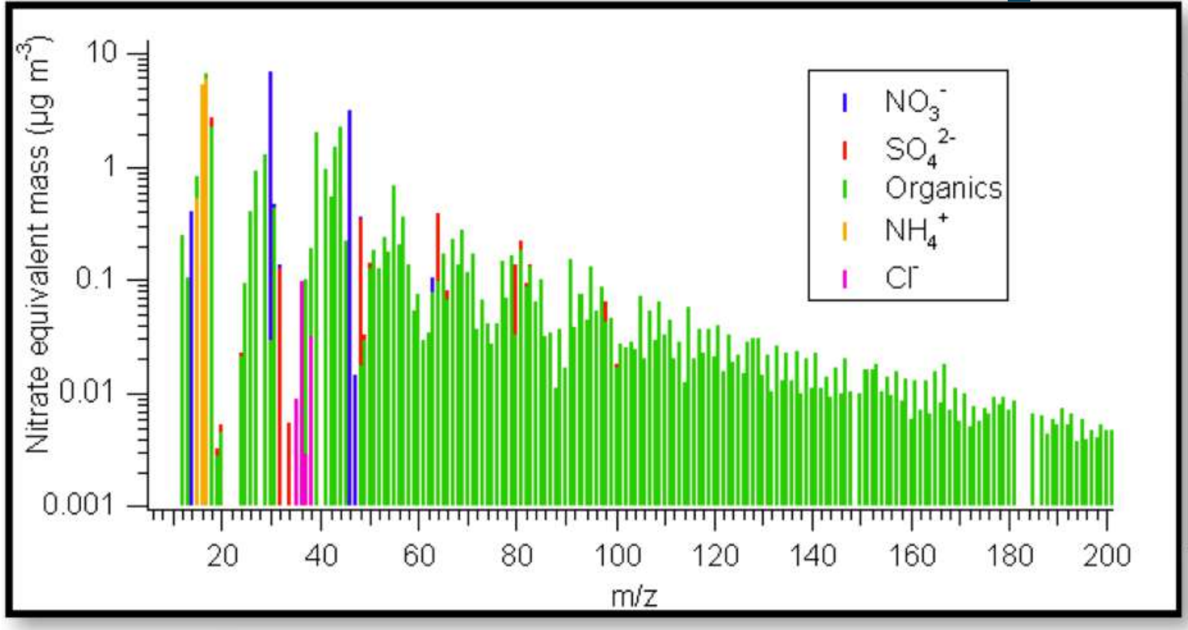


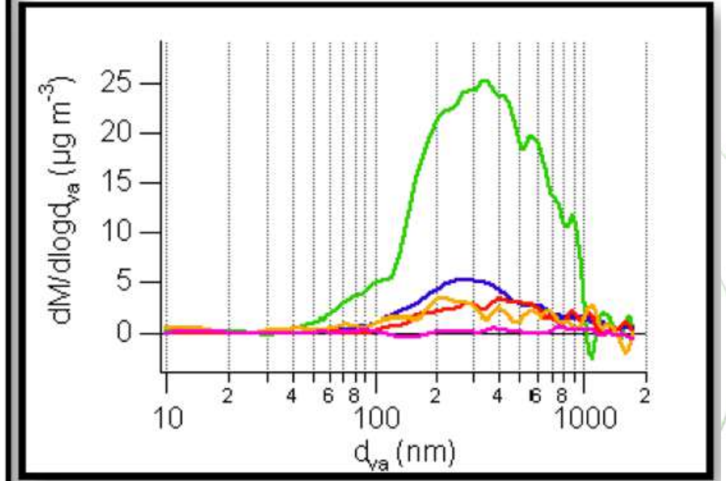
Jayne et al. (2000)

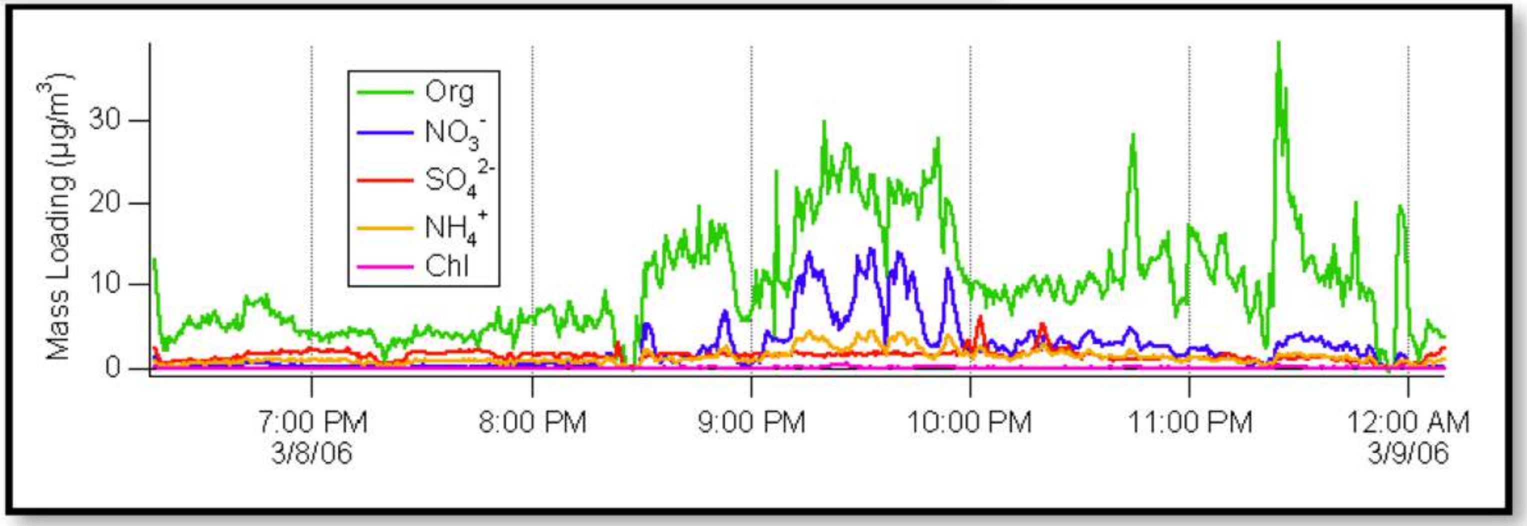
Possibility to study processes of formation and evolution of inorganic and organic species, primary and secondary

AMS: basic data

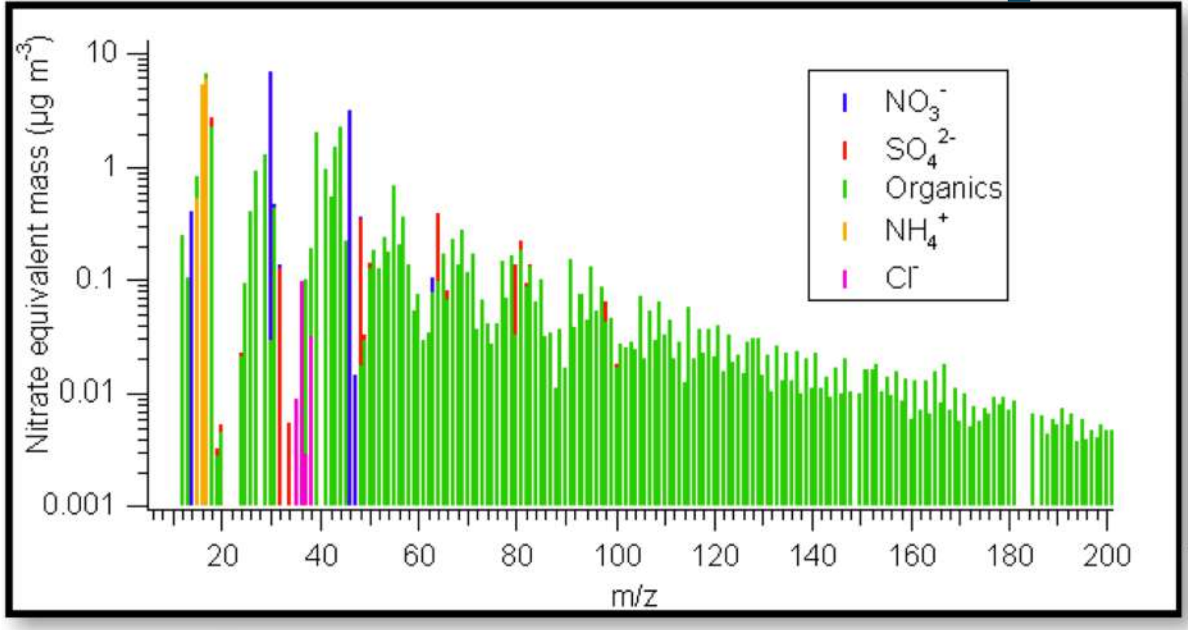
Mass spectra(MS) of the total NR-PM1 with sec/min time-resolution



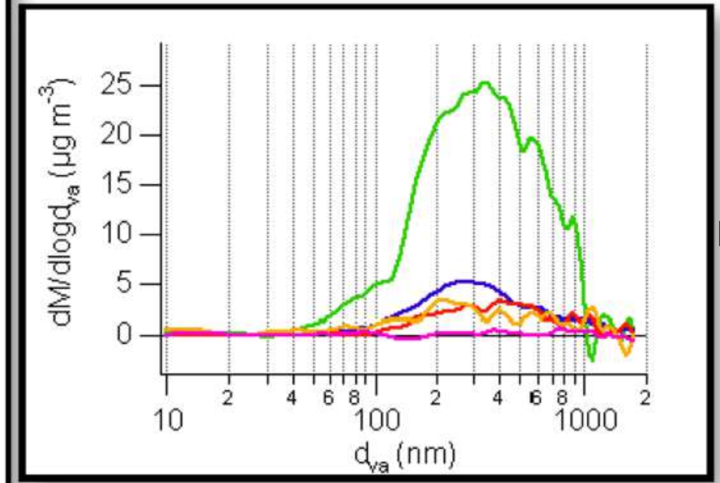




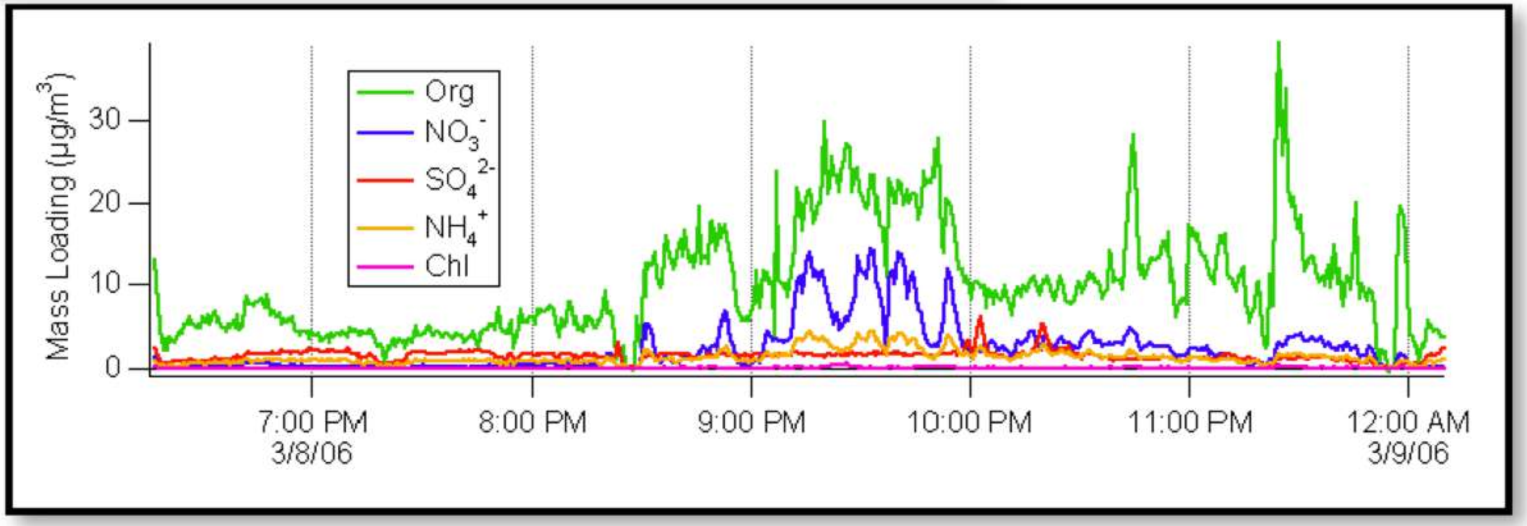
AMS: basic data



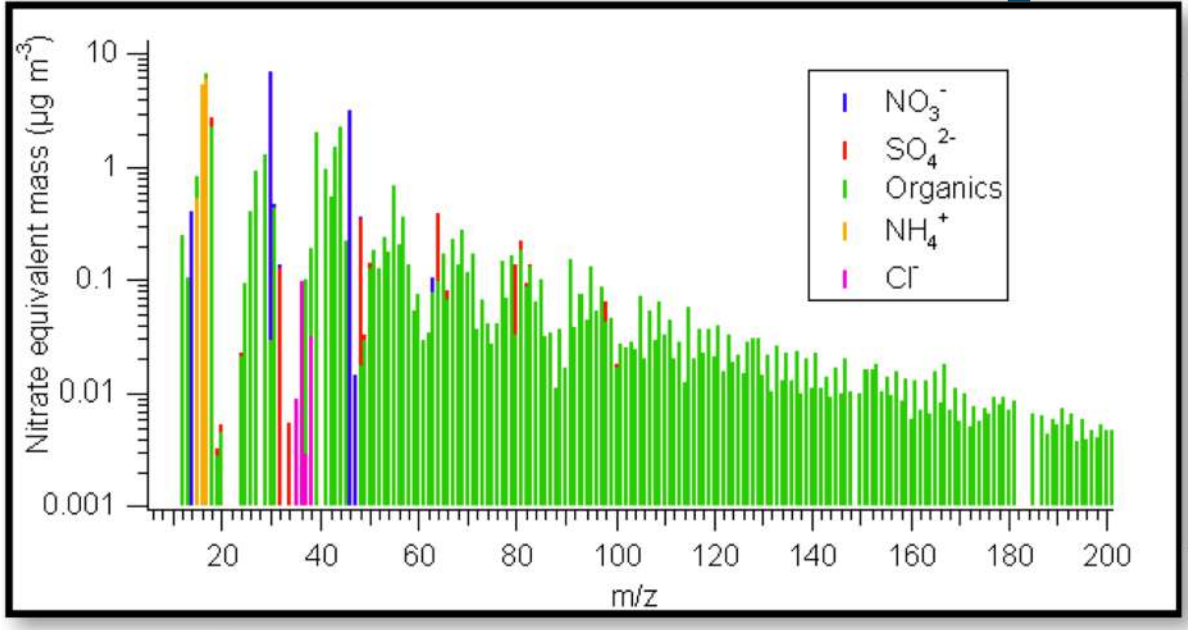
Mass spectra(MS) of the total NR-PM1 with sec/min time-resolution

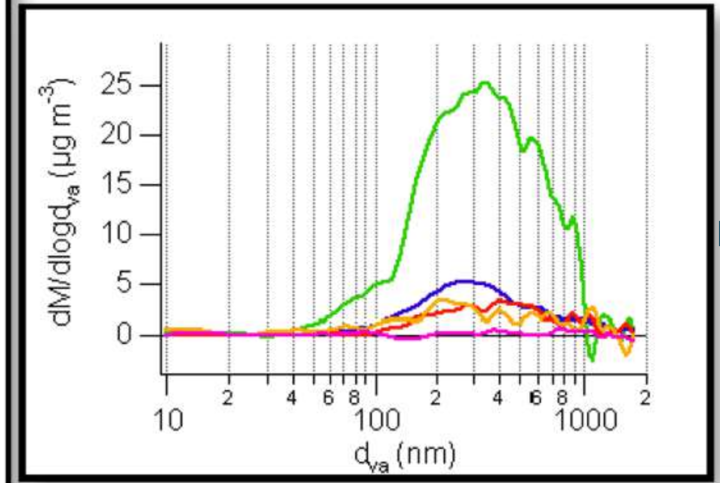


Size distribution of chemical species…



AMS: basic data

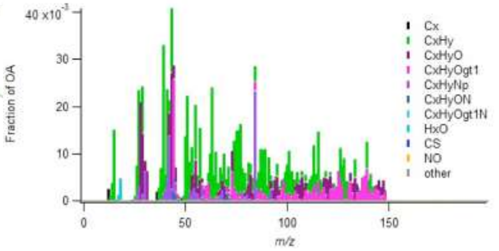


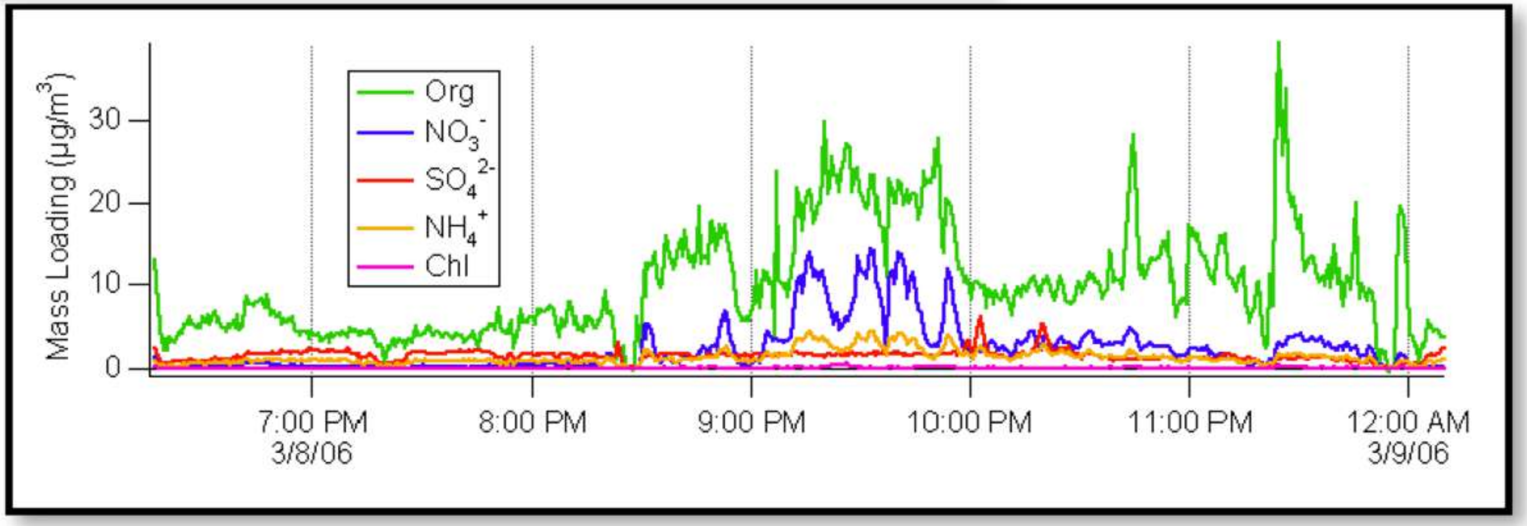


Mass spectra(MS) of the total NR-PM1 with sec/min time-resolution

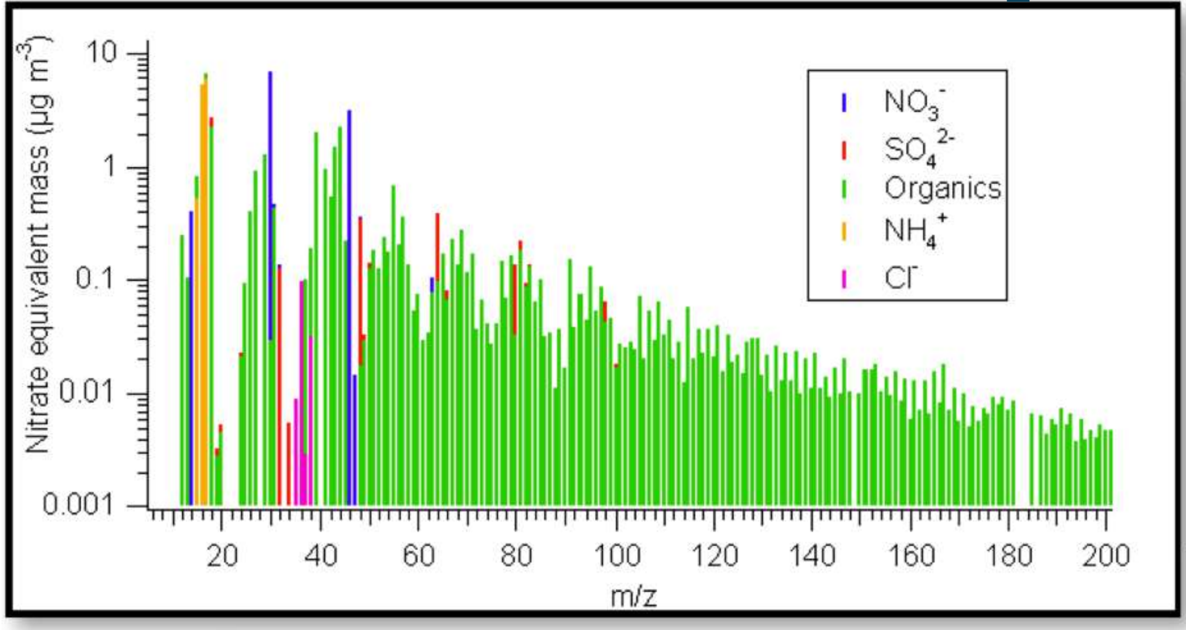
Size distribution of chemical species…

…with size-segregated mass spectra of the OA

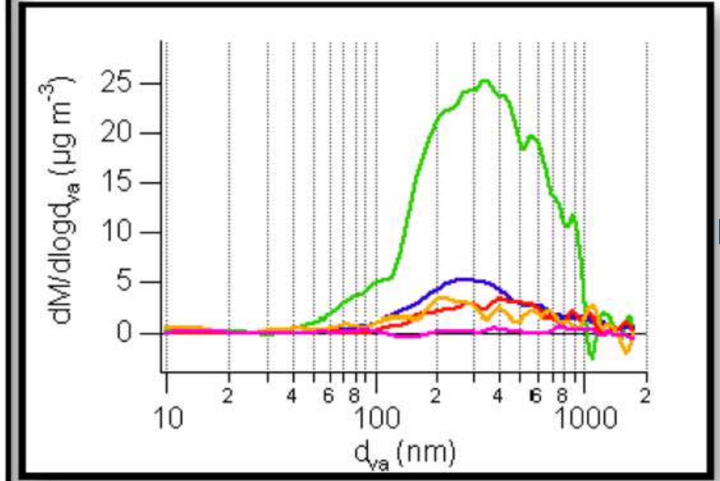




AMS: basic data

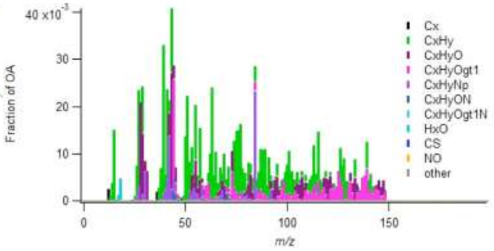


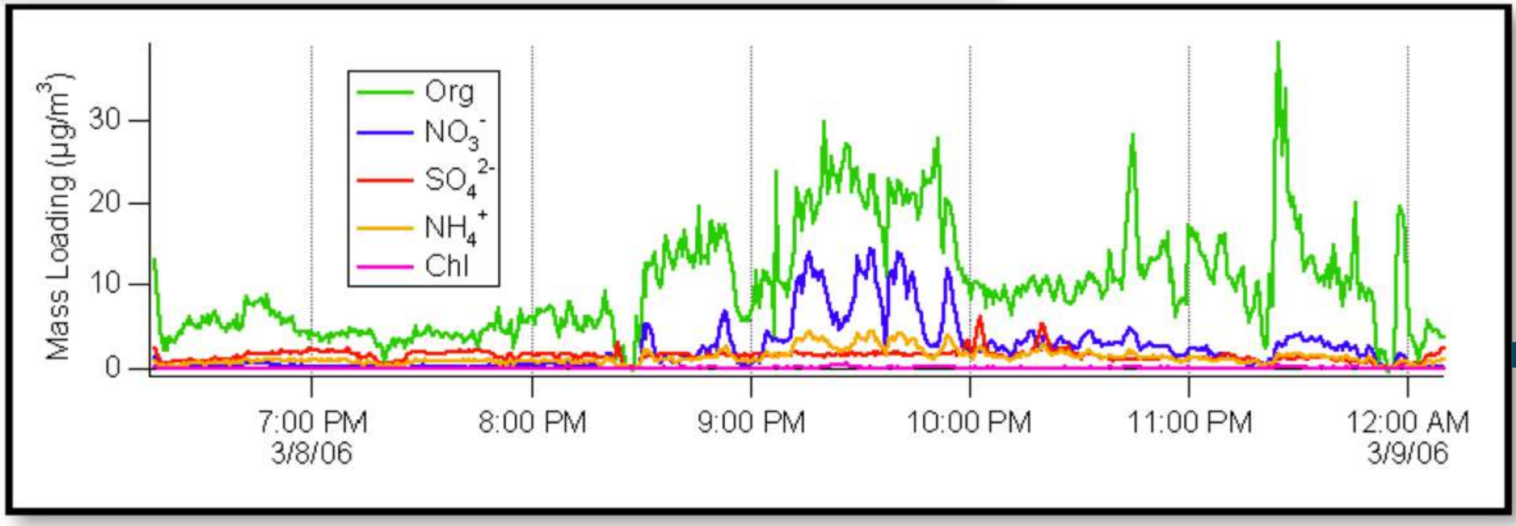
Mass spectra(MS) of the total NR-PM1 with sec/min time-resolution



Size distribution of chemical species…

…with size-segregated mass spectra of the OA

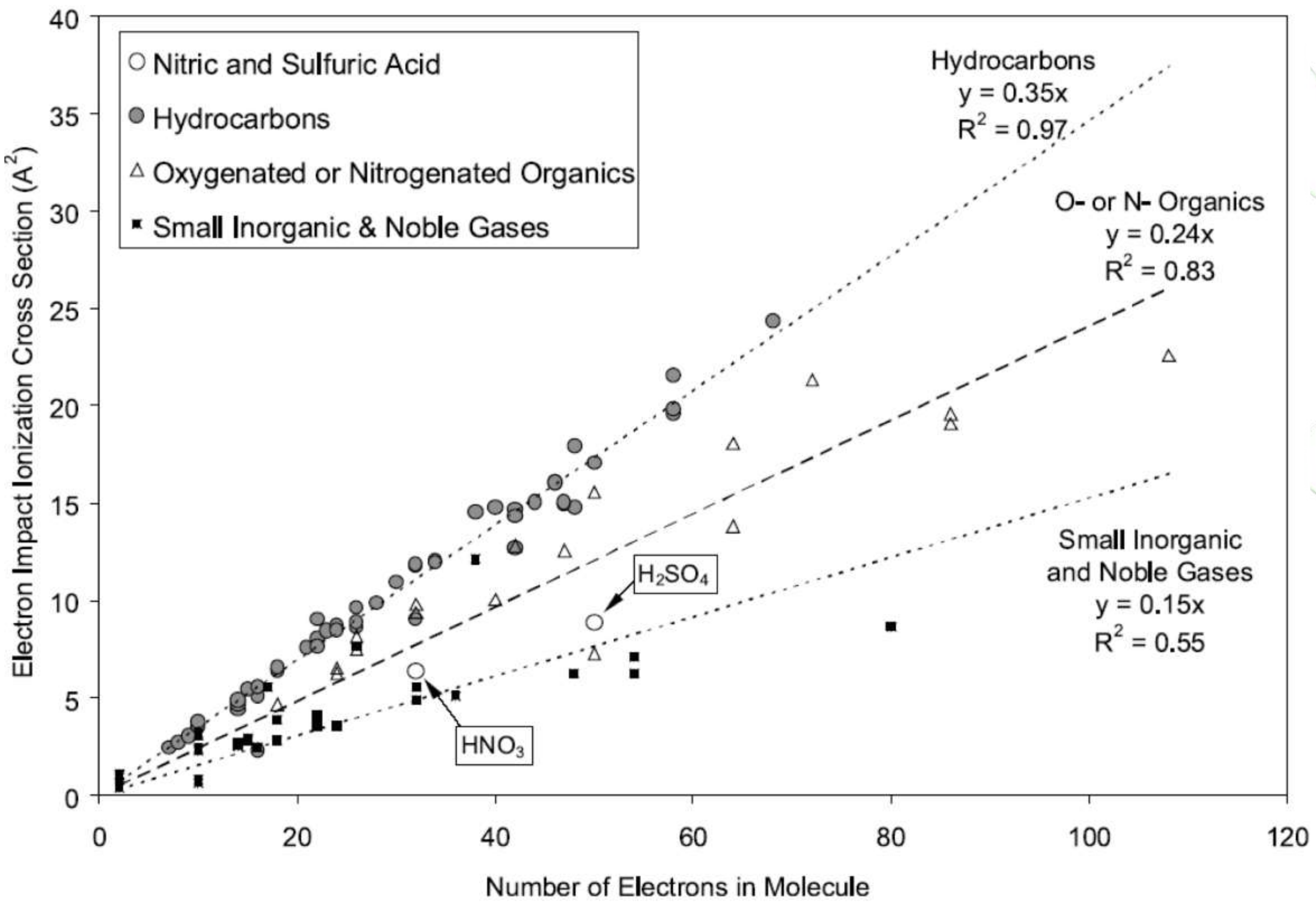




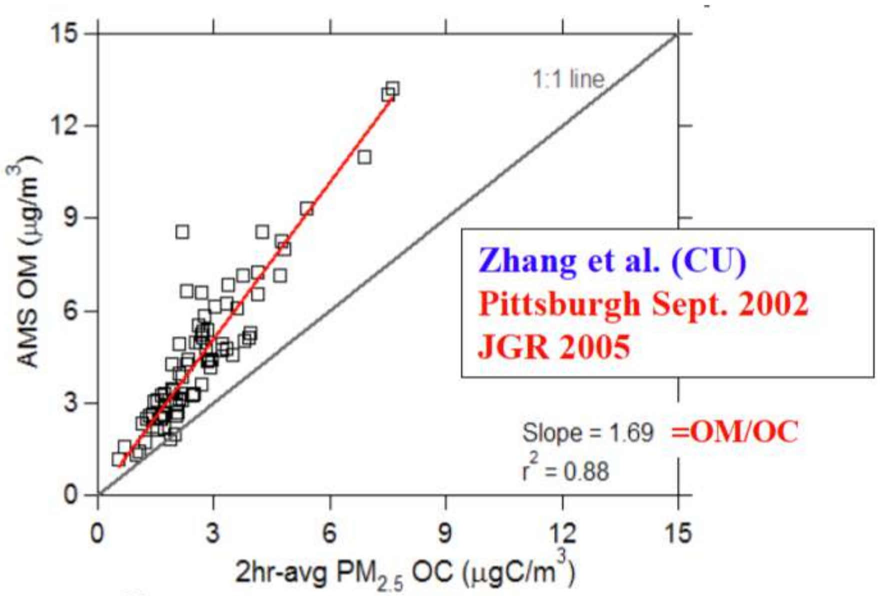
Time series of mass concentrations of the main non-refractory chemical species

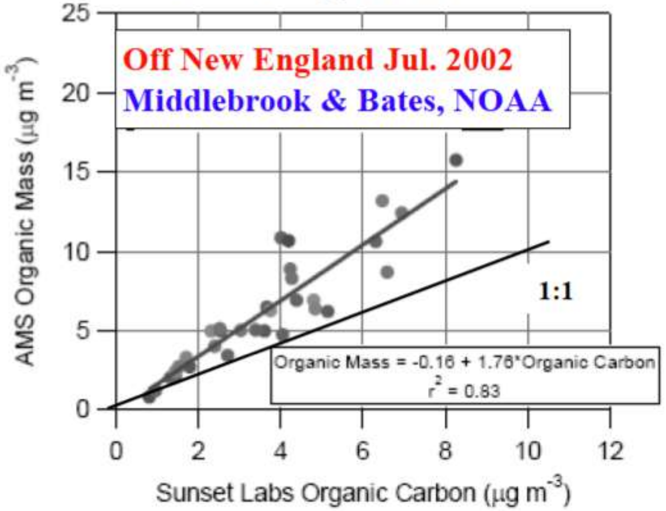
AMS: ionization efficiency ∝ electrons

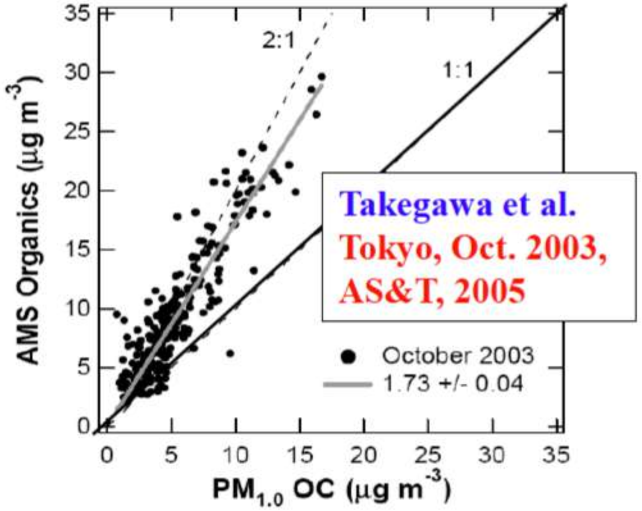
JIMENEZ ET AL.: AMBIENT SAMPLING WITH THE AERODYNE AMS

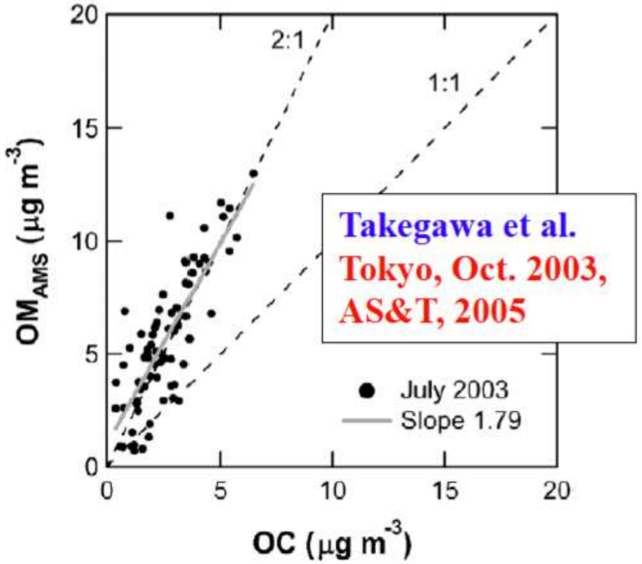


AMS Organic Mass (OM) vs Organic Carbon by OC analyzers



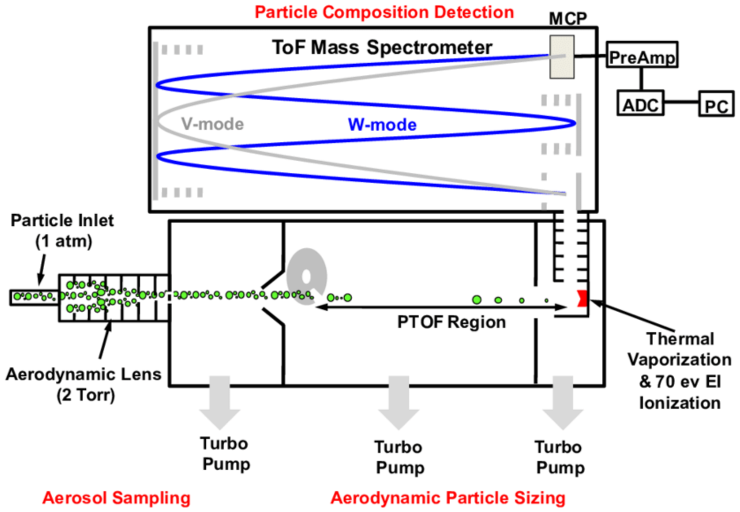






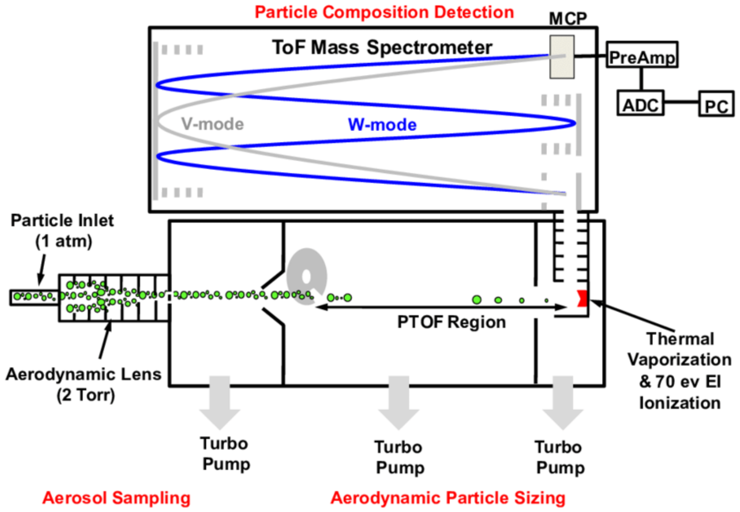
Different versions of AMS: evolution toward «simplification»

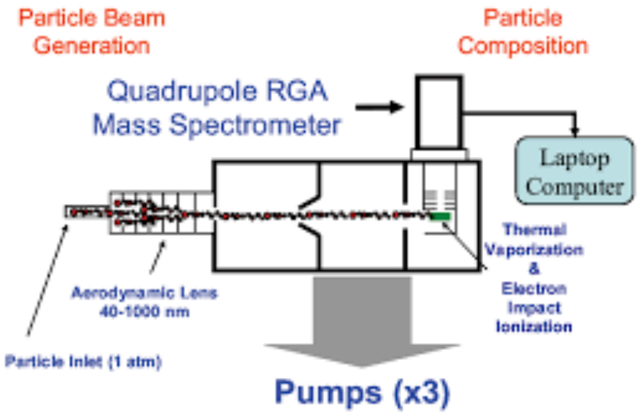
HR-TOF-AMS

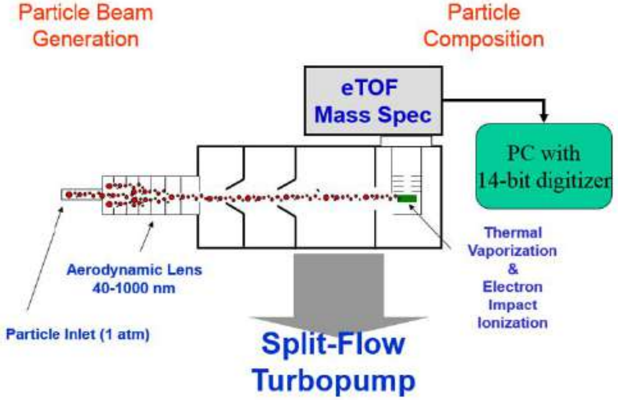


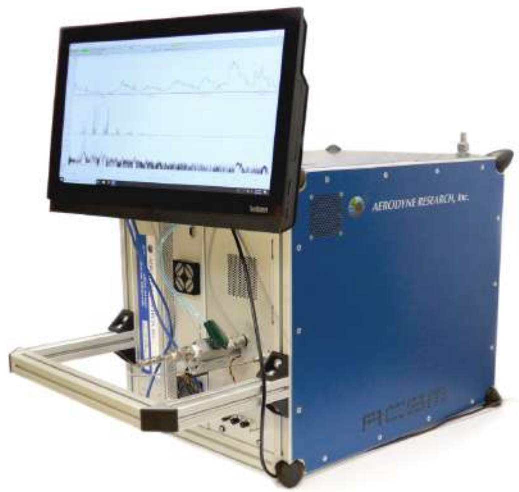
Different versions of AMS: evolution toward «simplification»

HR-TOF-AMS	Q-ACSM	TOF-ACSM









Chemical resolutions compared

Quadrupole spectrometers (first AMS and Q-ACSM) give us a resolution per unit mass (UMR): e.g. m/z 12, 13 … 200

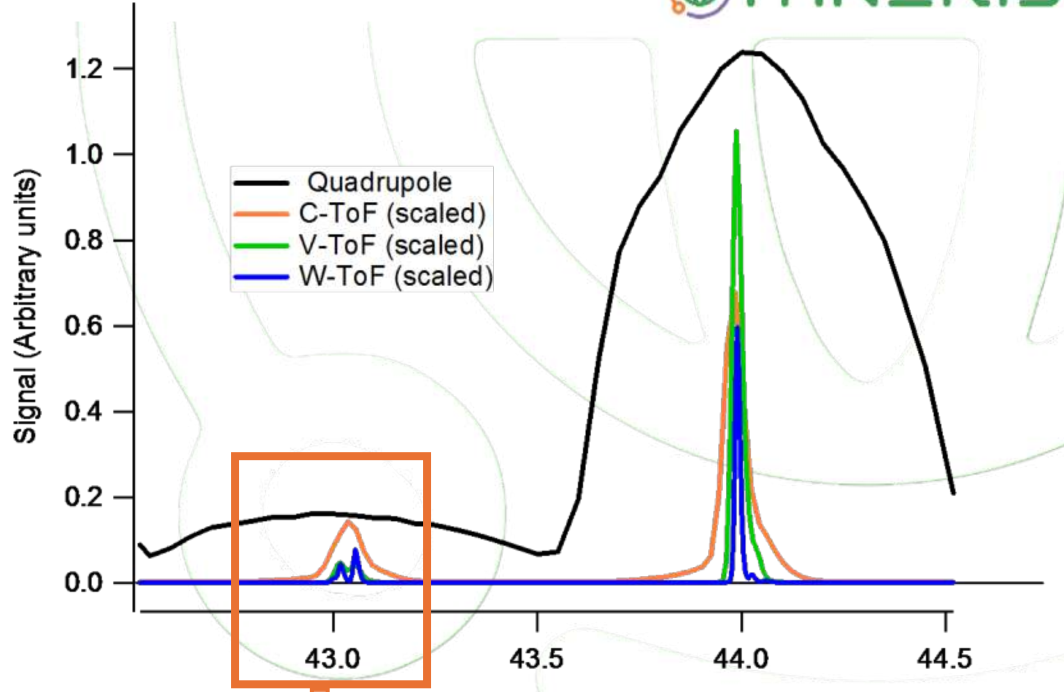
Time-Of-Flight (TOF) instead allows us to distinguish mass fractions and therefore different ions for each atomic mass unit

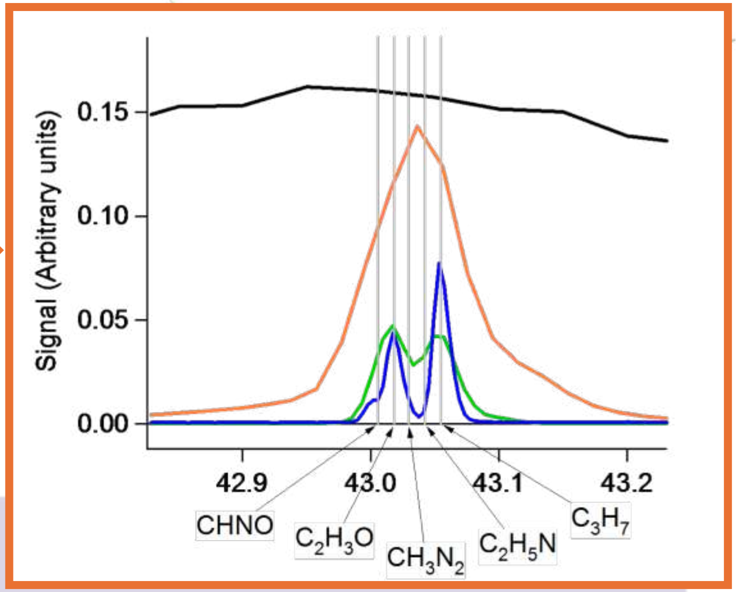
Element	Nominal Mass	Exact Mass
C	12	12.000000
H	1	1.007825
O	16	15.994915
N	14	14.003074
S	32 34	31.972070 33.967866

m/z 43	Exact Mass
CHNO	43.005814
C_2H_3O	43.018390
C_3H_7	43.054775

R. P. 3400 R. P. 1200

CHNO ↔ C_2H_3O ↔ C_3H_7



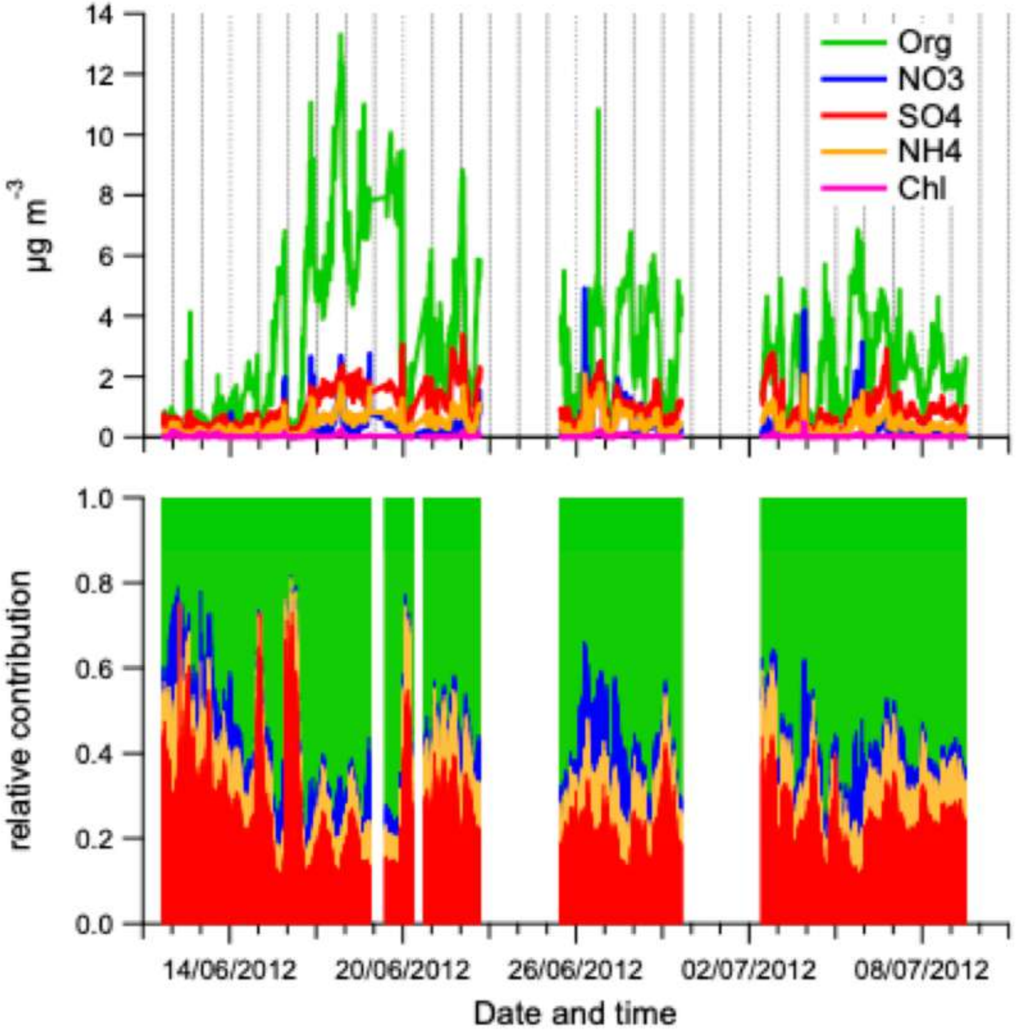


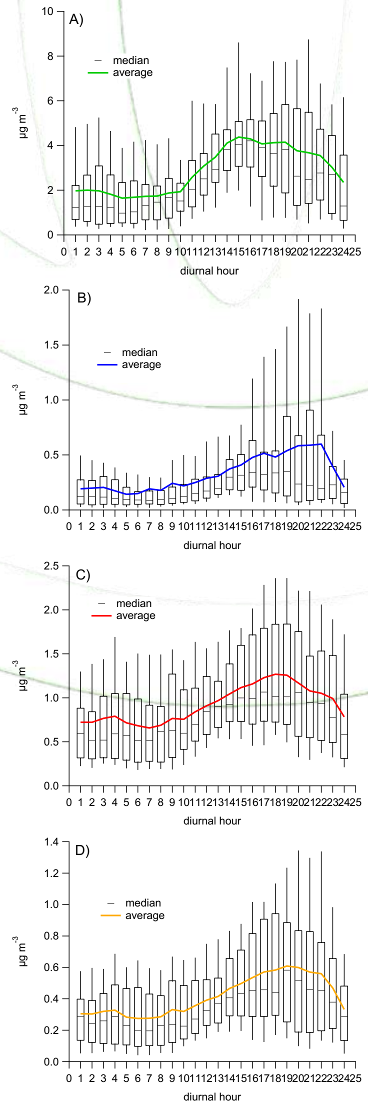
What does high resolution (temporal and chemical) allow us to do?

<u>Trend and evolution of chemical composition</u>:

Nitrate, sulfate, ammonium & organics…

… their temporal trends and diurnal cycles





Rinaldi et al., ACP 2015

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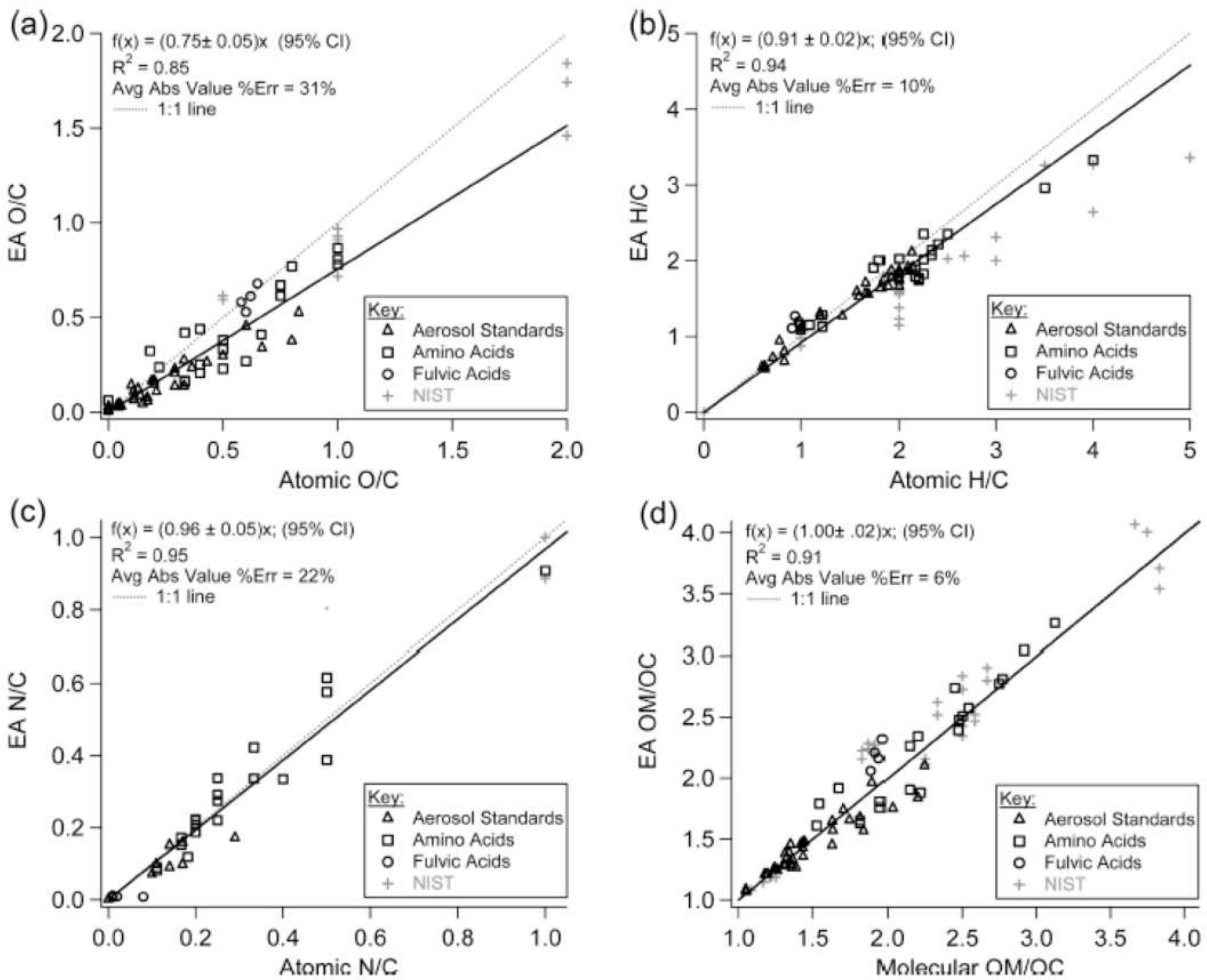
<u>OA Elemental Ratios</u>:

OM:OC, O:C, H:C, N:C & S:C



Aiken et al. Anal. Chem 2007, Aiken et al. 2008 ES&T

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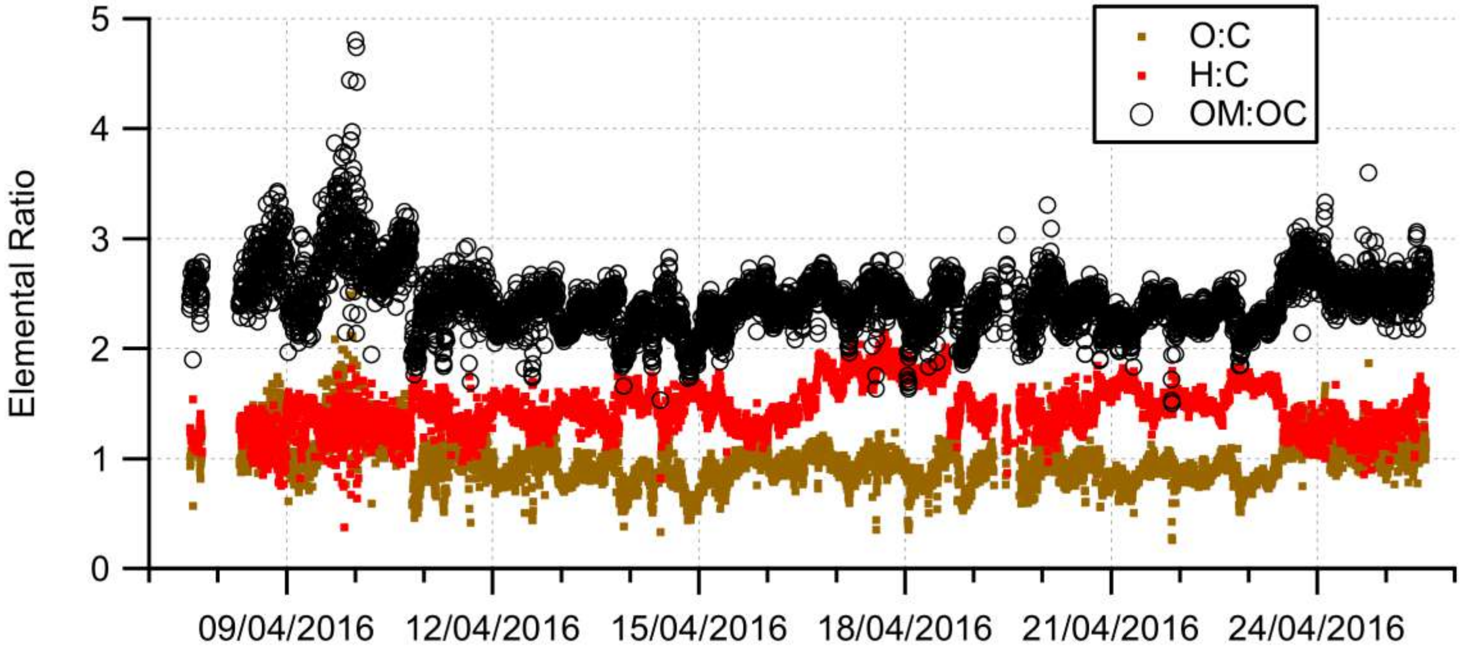
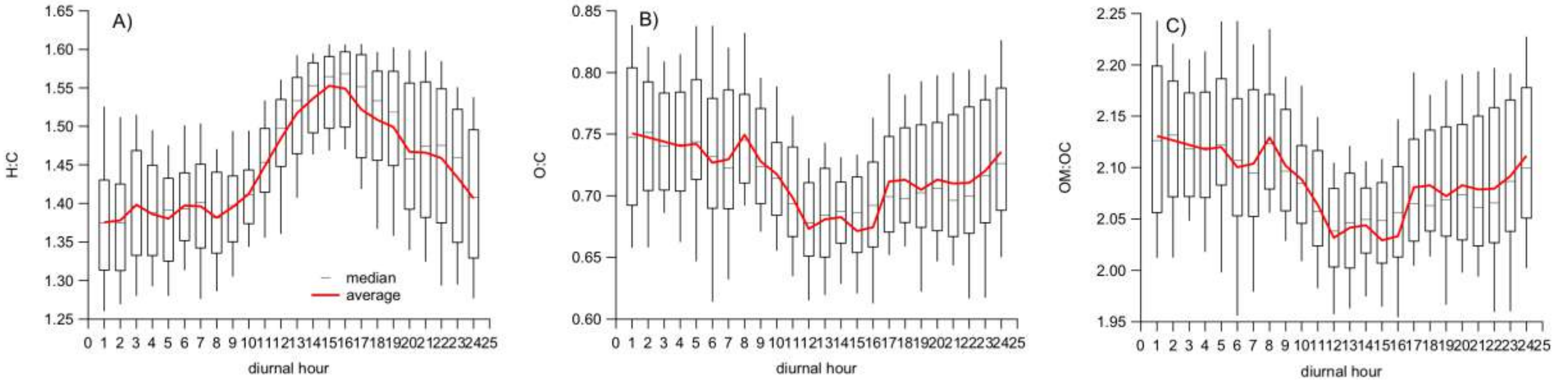


Rinaldi et al., in preparation



What does high resolution (temporal and chemical) allow us to do?

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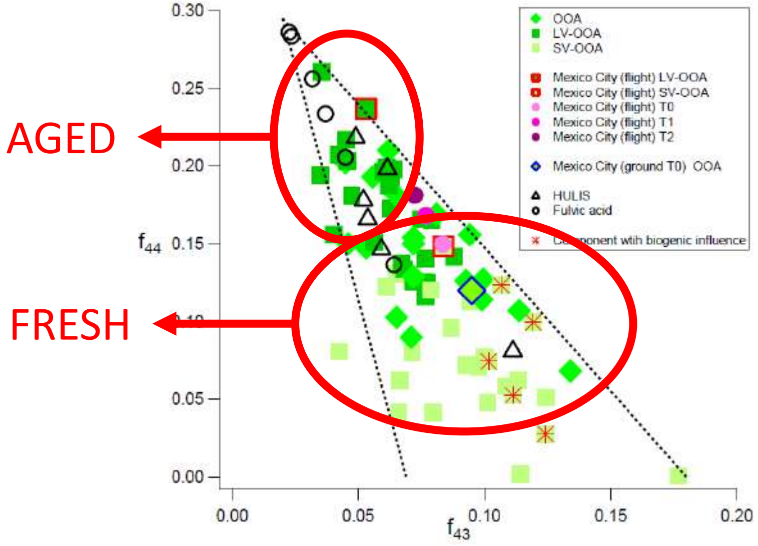
… their temporal trends and diurnal cycles

<u>OA chemical evolution</u>

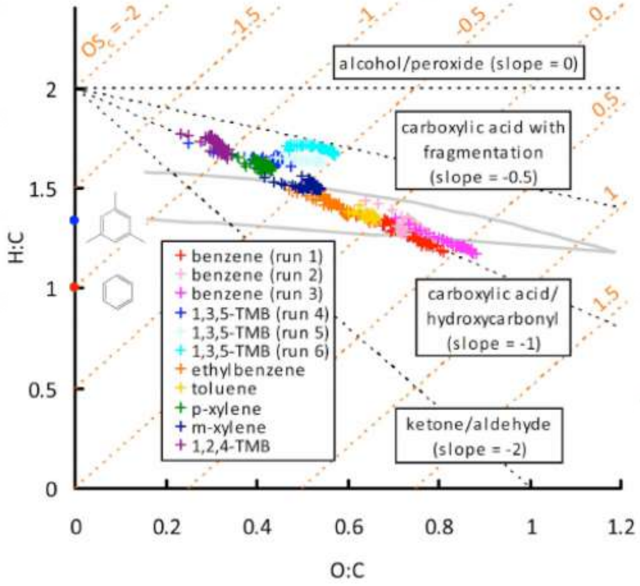
formation mechanisms and aging processes

Fractional abundance of specific fragments: Ng triangle plot



Ng et al., ACP, 2010

Van Krevelen diagram

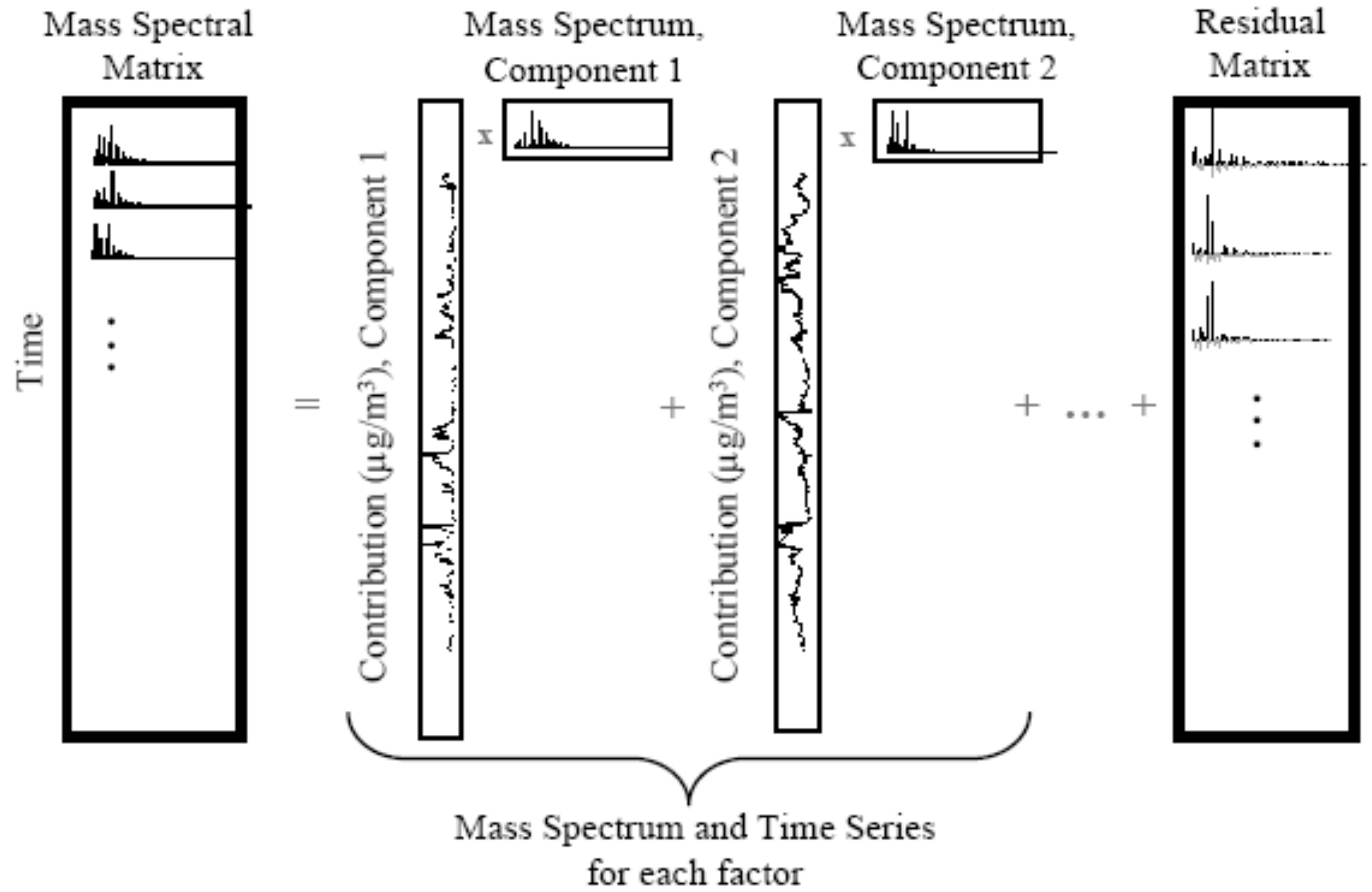


Sato et al., ACP 2012

OA Source Apportionment

Receptor models based on multivariate statistical techniques of OA mass spectra:
Positive Matrix Factorization (PMF)

Series of AMS
OA mass spectra



Factor analysis

(X = G*F + E)

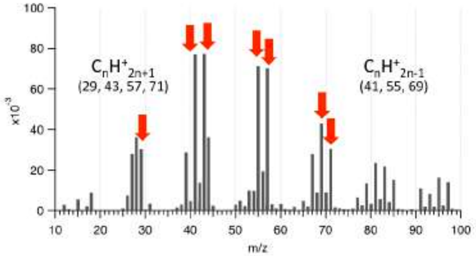
Where:
X = measurements matrix
F = factor profile vector
G = factor contribution vector
E = errors matrix

Main algorithms:

PMF2 & ME-2

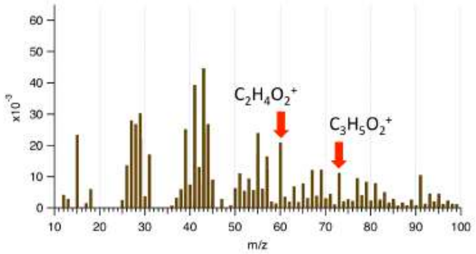
Main OA sources identified by AMS-PMF

Primary components (POA)



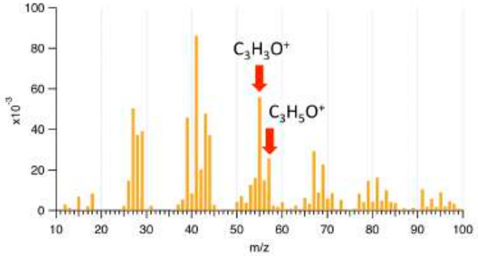
HOA
(Hydrocarbon-like)

Fossil fuels combustion = TRAFFIC



BBOA
(Biomass-burning)

Biomass burning= DOMESTIC HEATING

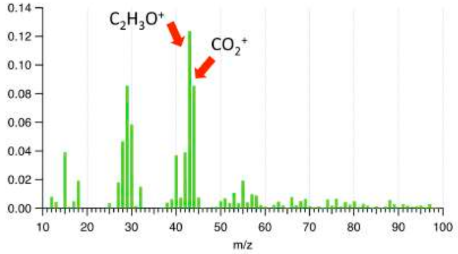


COA
(Cooking)

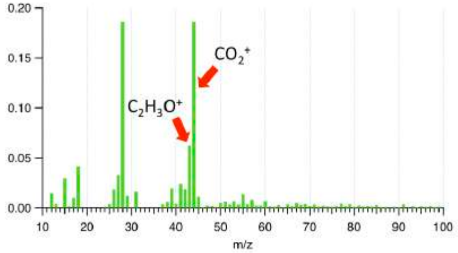
Cooking food= COOKING

Secondary components (SOA)

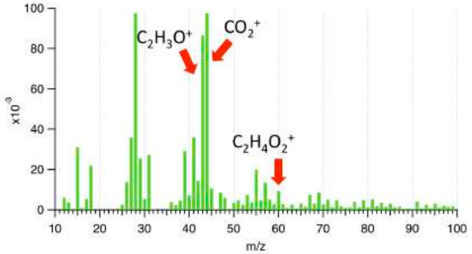
socalled Oxidized Organic Aerosol (OOA), SOA proxy



SV-OOA
(semivolatile Oxidized)



LV-OOA
(lowvolatile Oxidized)



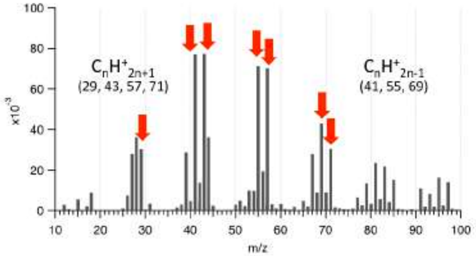
OOA-BB
(biomass-burning Oxidized)

…

Multiplicity of formation and transformation processes

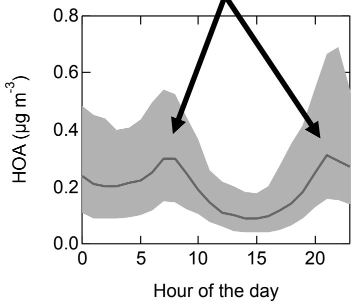
Main OA sources identified by AMS-PMF

Primary components (POA)

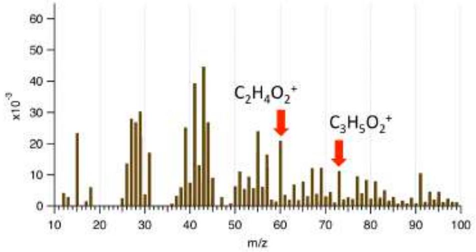


HOA
(Hydrocarbon-like)

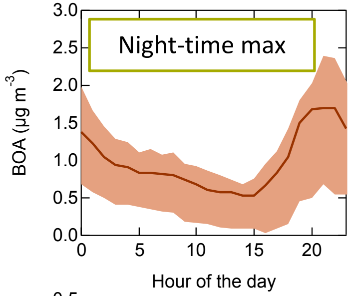
Double max =
rush hours



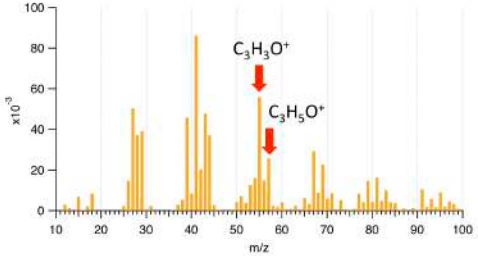
TRAFFIC



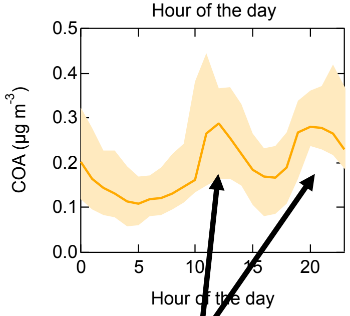
BBOA
(Biomass-burning)



HEATING



COA
(Cooking)

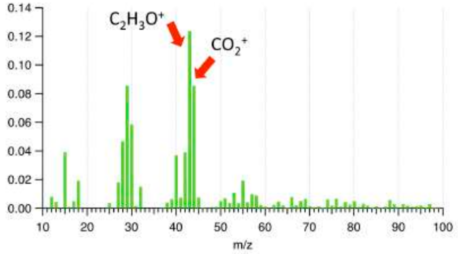


COOKING

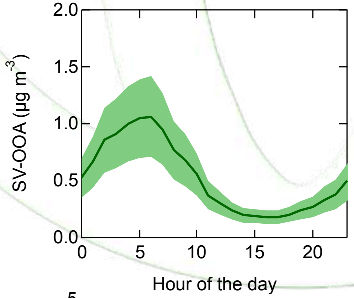
doubleo max =
meal hours

Secondary components (SOA)

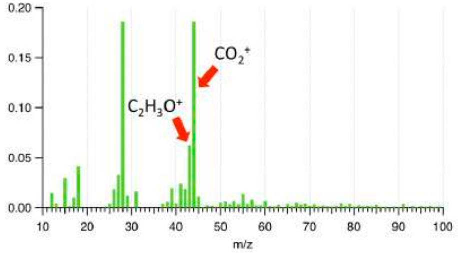
socalled Oxidized Organic Aerosol (OOA), SOA proxy



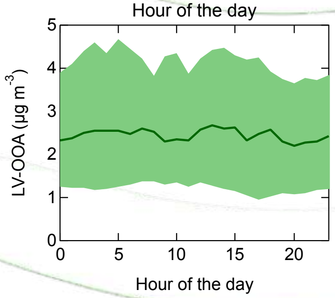
SV-OOA
(semivolatile
Oxidized)



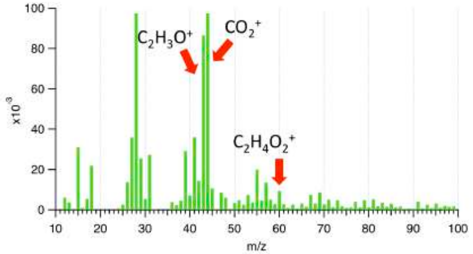
BIOGENIC
LOCAL



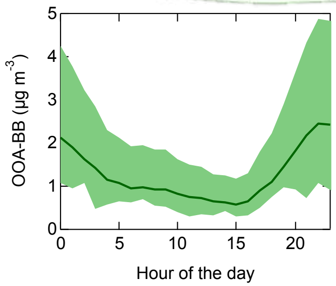
LV-OOA
(low-volatility
Oxidized)



CONTINENTAL
BACKGROUND



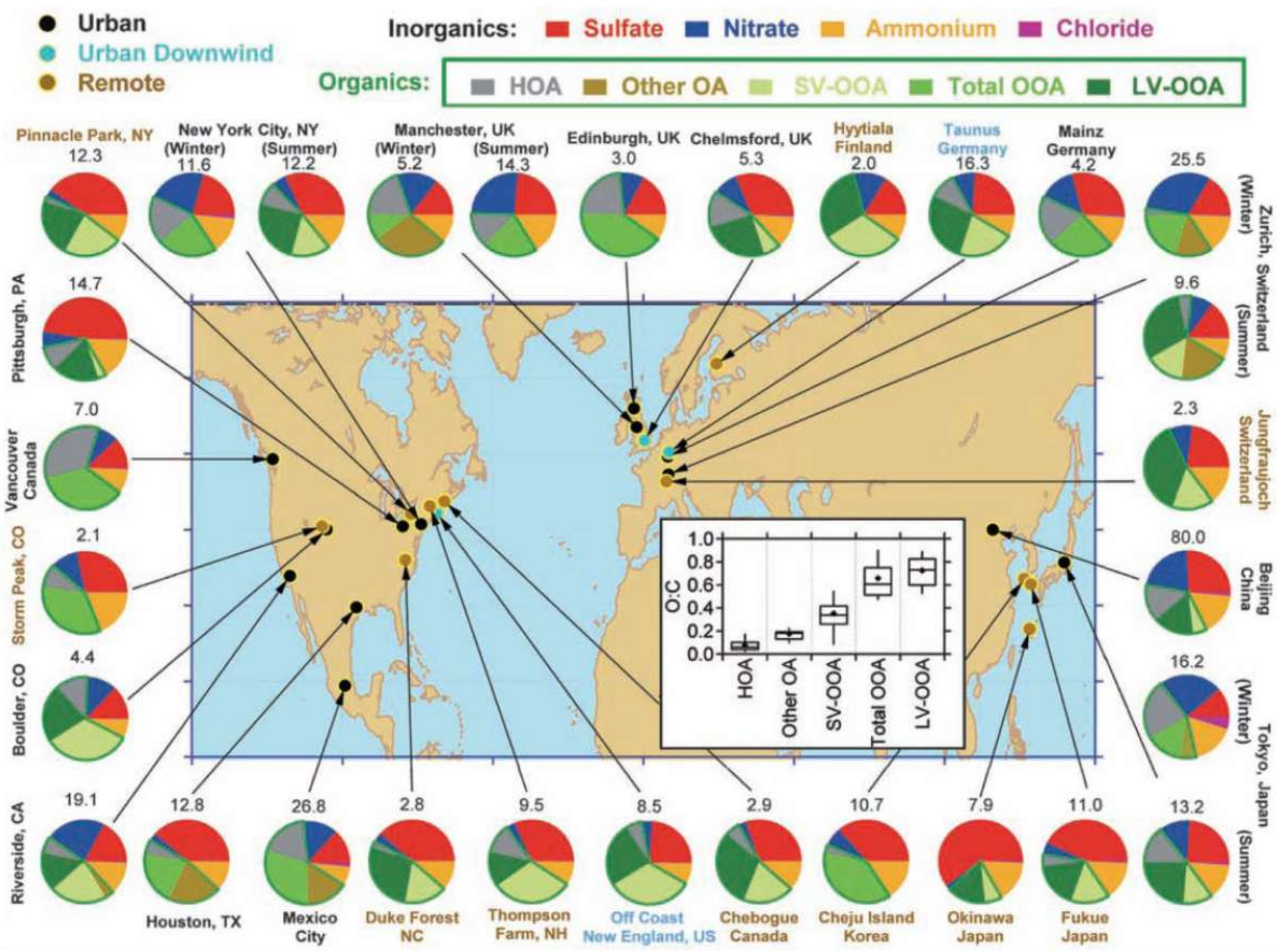
OOA-BB
(biomass-burning
Oxidized)



HEATING

...

Main OA sources identified by AMS-PMF

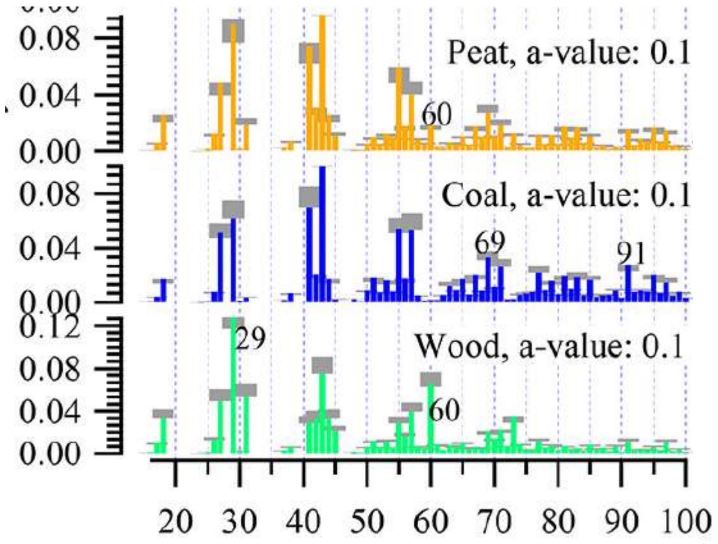


SOA often dominates over POA globally, especially (but not exclusively) outside urban environments and especially in summer

Other specific factors/sources

Primary components (POA)

Lin C. et al., ES&T, 2017

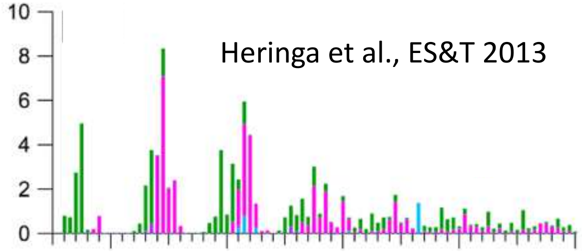


PEAT burning
(torba)

CCOA
(coal combustion)

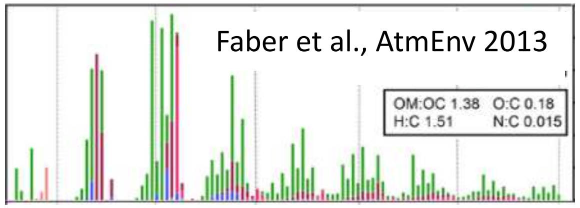
SFOA
(solid fuels)

WBOA
(wood burning)



Pellet POA

DOMESTIC HEATING



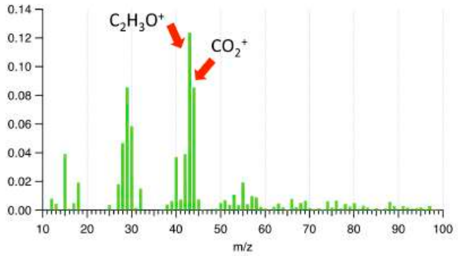
CSOA
(Cigarette-Smoke)

CIGARETTE SMOKE

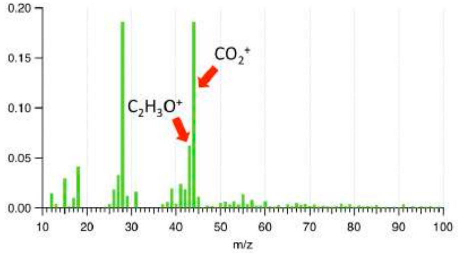
...

Secondary components (SOA)

socalled Oxidized Organic Aerosol (OOA), SOA proxy

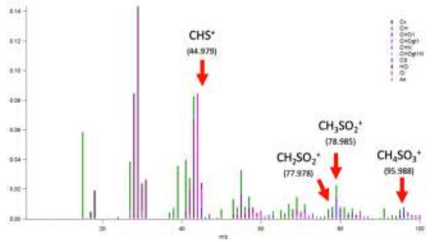


LO-OOA
(less-oxidized OOA)



MO-OOA
(more-oxidized OOA)

They may represent emission sources and/or transformation processes or degrees of aging



MOA (Marine)

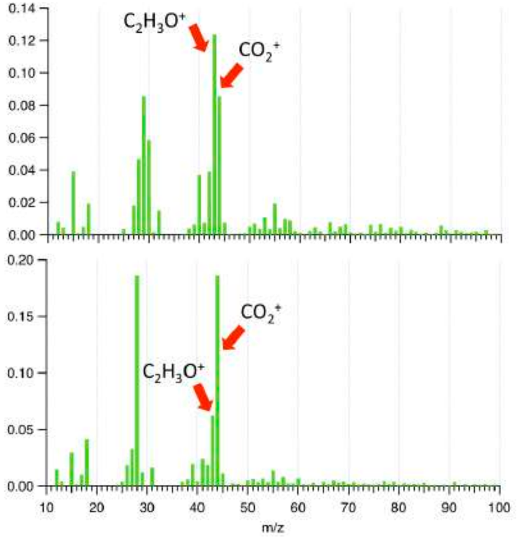
Crippa et al., JGR 2013

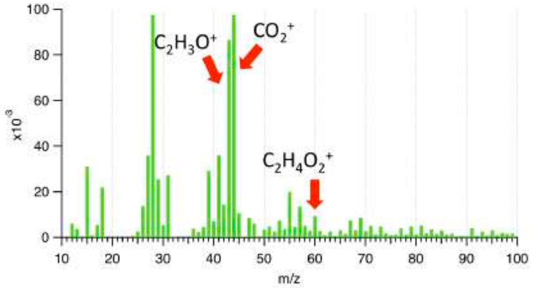
MARINE OA

...

SOA and how to distinguish them

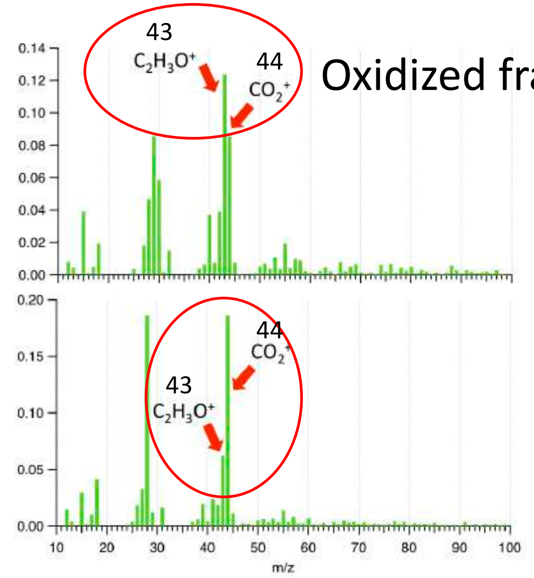
OOAs are considered to be representative of all SOAs in the complex. However, since SOAs in the environment encompass a multiplicity of formation and transformation processes mixed together, it is often difficult to distinguish different categories.





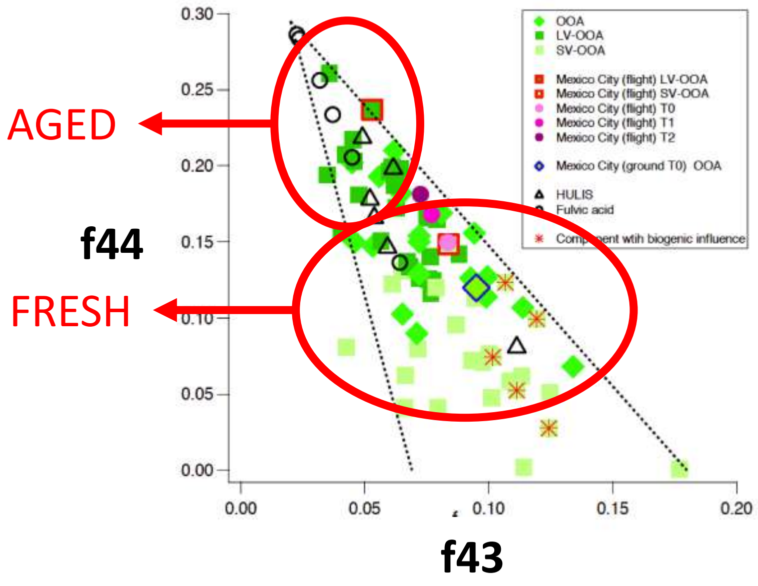
SOA and how to distinguish them

AMS provides useful information on time trends, oxidation states and some characteristic fragments…

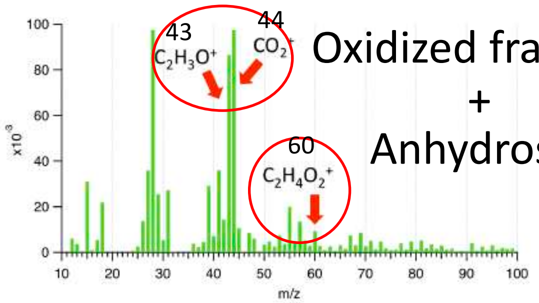


Oxidized fragments

AMS: different oxidation state/degree

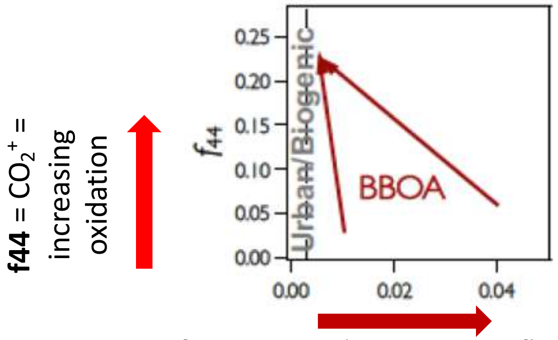


Ng et al., ACP, 2010



Oxidized fragments
+
Anhydrosugars

➔ Biomass burning influence



Cubison et al., ACP 2010

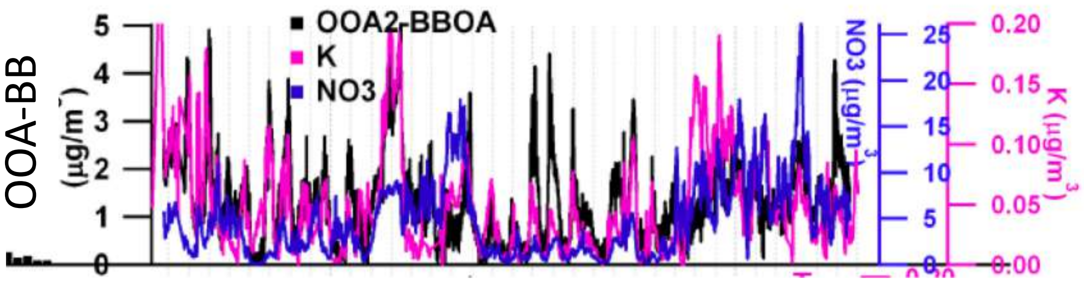
f60 = $C_2H_4O_2^+$ = growing influence of biomass combustion

SOA and how to distinguish them

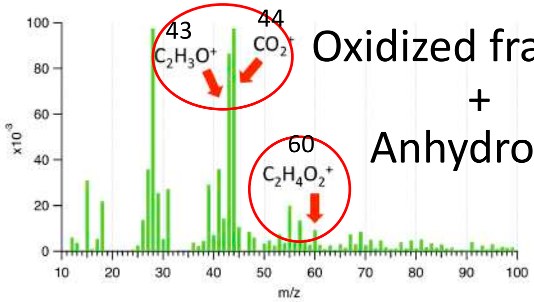
AMS provides useful information on time trends, oxidation states and some characteristic fragments…

…but by itself it is difficult to identify the origin of the OOA: **an integrated approach with other techniques is needed!**

(eg.: correlation with tracers, meteorology, backtrajectories analysis ecc.)

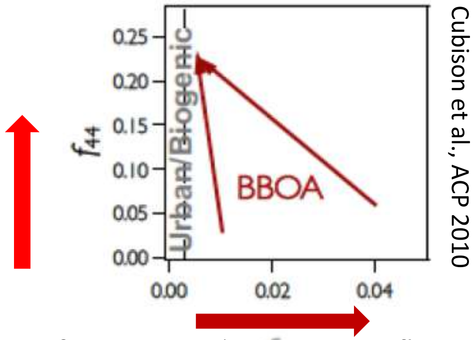


OOA-BB has fragments of anhydrosugars and correlates with K and Nitrate ➔ secondary factor with influences from biomass combustion = BB-SOA



Oxidized fragments
+
Anhydrosugars ➔ Biomass burning influence

f44 = CO_2^+ = increasing oxidation



f60 = $C_2H_4O_2^+$ = growing influence of biomass combustion

Cubison et al., ACP 2010

SOA and how to distinguish them

AMS provides useful information on time trends, oxidation states and some characteristic fragments…

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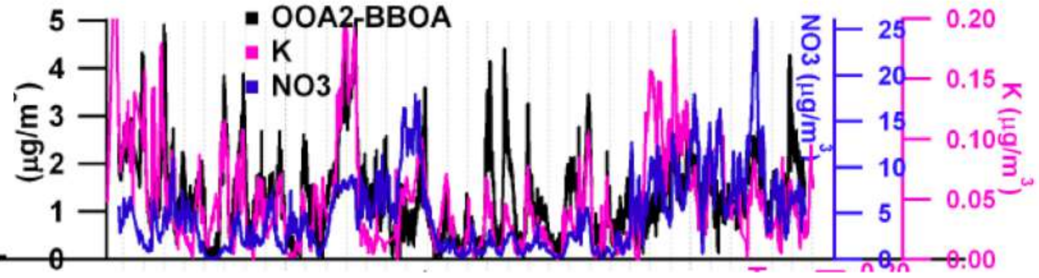
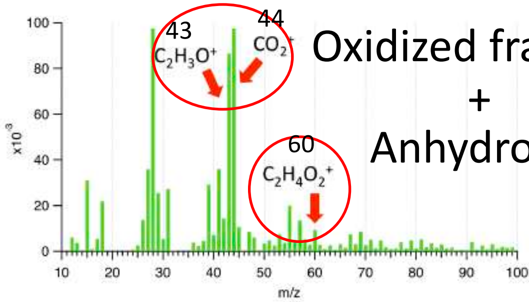
OOA-BB



<u>OOA-BB has fragments of anhydrosugars and correlates with K and Nitrate ➔ secondary factor with influences from biomass combustion = BB-SOA</u>

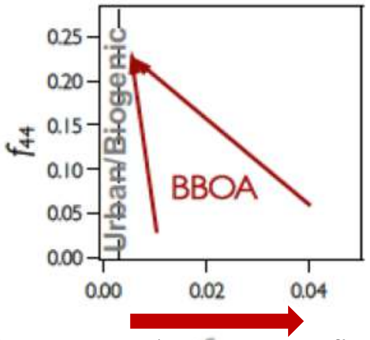


Oxidized fragments

+

Anhydrosugars ➔ Biomass burning influence

f44 = CO_2^+ = increasing oxidation



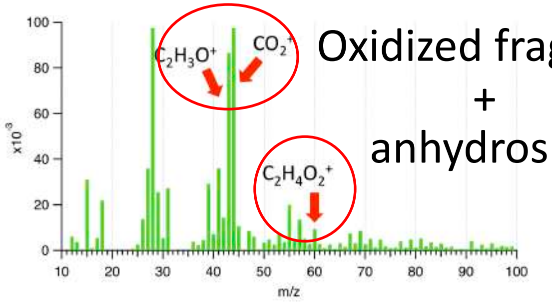
Cubison et al., ACP 2010

f60 = $C_2H_4O_2^+$ = growing influence of biomass combustion

SOA and how to distinguish them

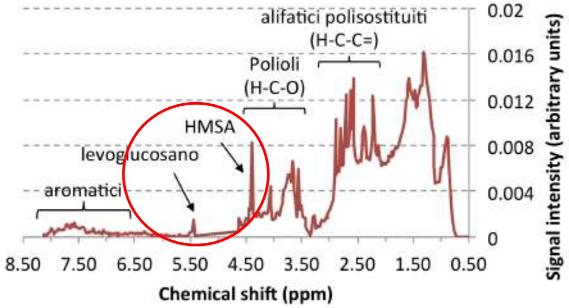
EXAMPLE: Comparison with Source Apportionment techniques on H-NMR spectra of OA

<u>OOA-BB =</u>
<u>BB-SOA</u>



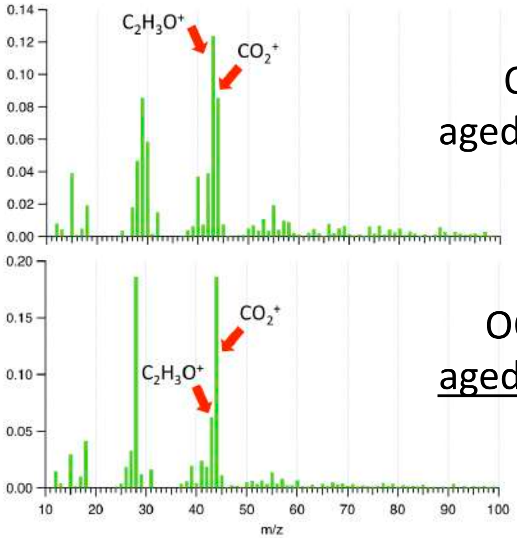
Oxidized fragments
+
anhydrosugars

Polysubstituted chains
+
aromatics
+
specific tracers



<u>Other SOA</u>: additional/complementary physical-chemical information is needed

AMS: different oxidation state



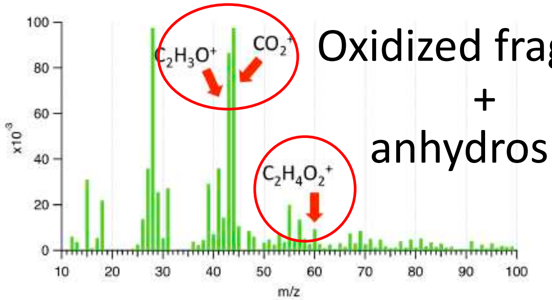
OOA<u>less</u>
aged/processed

OOA <u>more</u>
<u>aged</u>/processed

SOA and how to distinguish them

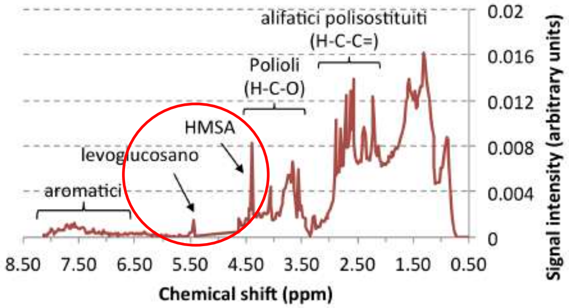
EXAMPLE: Comparison with Source Apportionment techniques on H-NMR spectra of OA

OOA-BB = BB-SOA



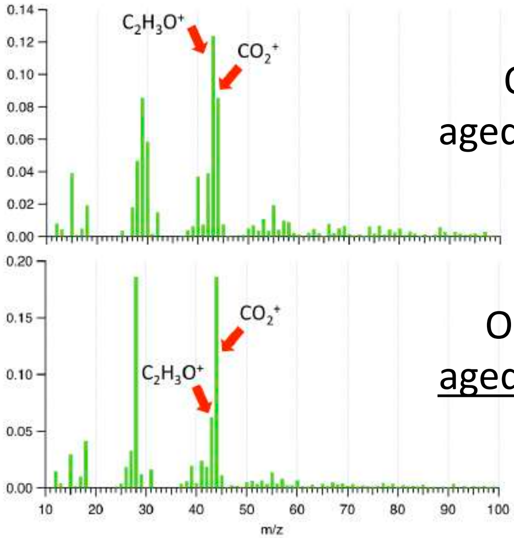
Oxidized fragments
+
anhydrosugars

Polysubstituted chains
+
aromatics
+
specific tracers



Other SOA: additional/complementary physical-chemical information is needed

AMS: different oxidation state



OOAless aged/processed

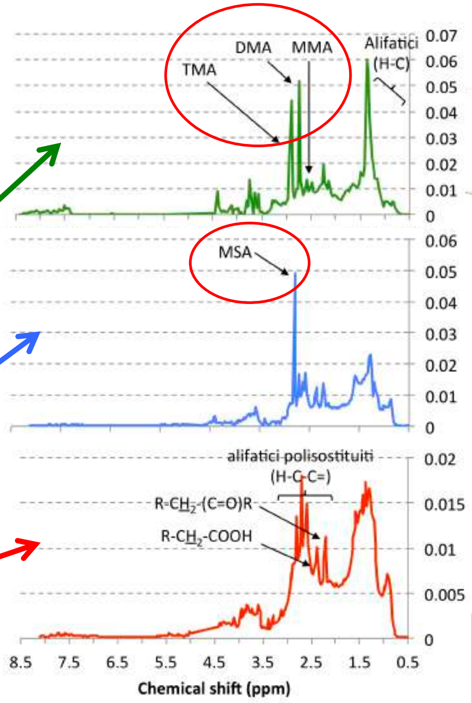
OOA more aged/processed

NMR: specific tracers and functional groups

Alkyl amines = **agricultural /livestock activities**

Methanesulfonic acid = **marine origin**

HULIS features = photochrmical ageing and transport

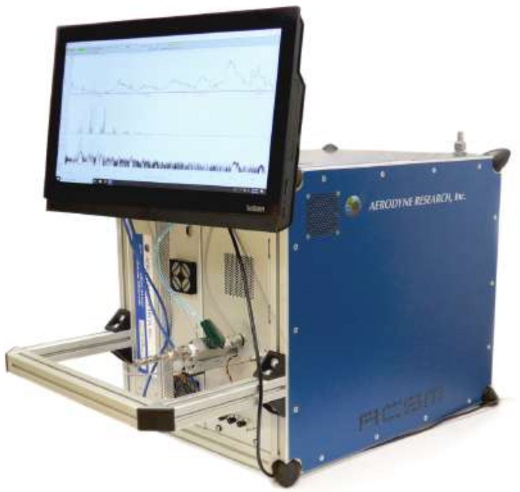


Recommandations on NR-PM1 on-line measurements by ACSM

There are currently no CEN standards for online measurements of aerosol constituents.

Regarding online measurements on NR-PM1 using ACSM, other initiatives such as the **COST-COLOSSAL Action** have produced guidelines (https://www.cost.eu/actions/CA16109/).

Standard Operating Procedures (SOP) documents both for **Q-ACSM** and **ToF-ACSM** produced during the COST-COLOSSAL Action which presents indications for the installation settings, servicing, checks, maintenance, quality assurance and quality control (QA/QC), and diagnostics are available (COST-COLOSSAL (2021), COST-COLOSSAL/ACTRIS (2022)).



These guidelines are **adopted by ACTRIS**. Also, some publications describing this instrumentation and performing intercomparisons can be found on the aforementioned webpage.

THANKS!

IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructures System
(D.D. n. 130/2022 - CUP B53C22002150006) Funded by EU - Next Generation EU PNRR-Mission 4 "Education and Research" - Component 2: "From research to business" - Investment 3.1: "Fund for the realisation of an integrated system of research and innovation infrastructures"

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Ministero dell'Università e della Ricerca
Italiadomani