Compréhension des sources et des processus de formation de la pollution particulaire en région Ile-de-France

Sources and formation processes of particulate pollution over the Ile-de-France region

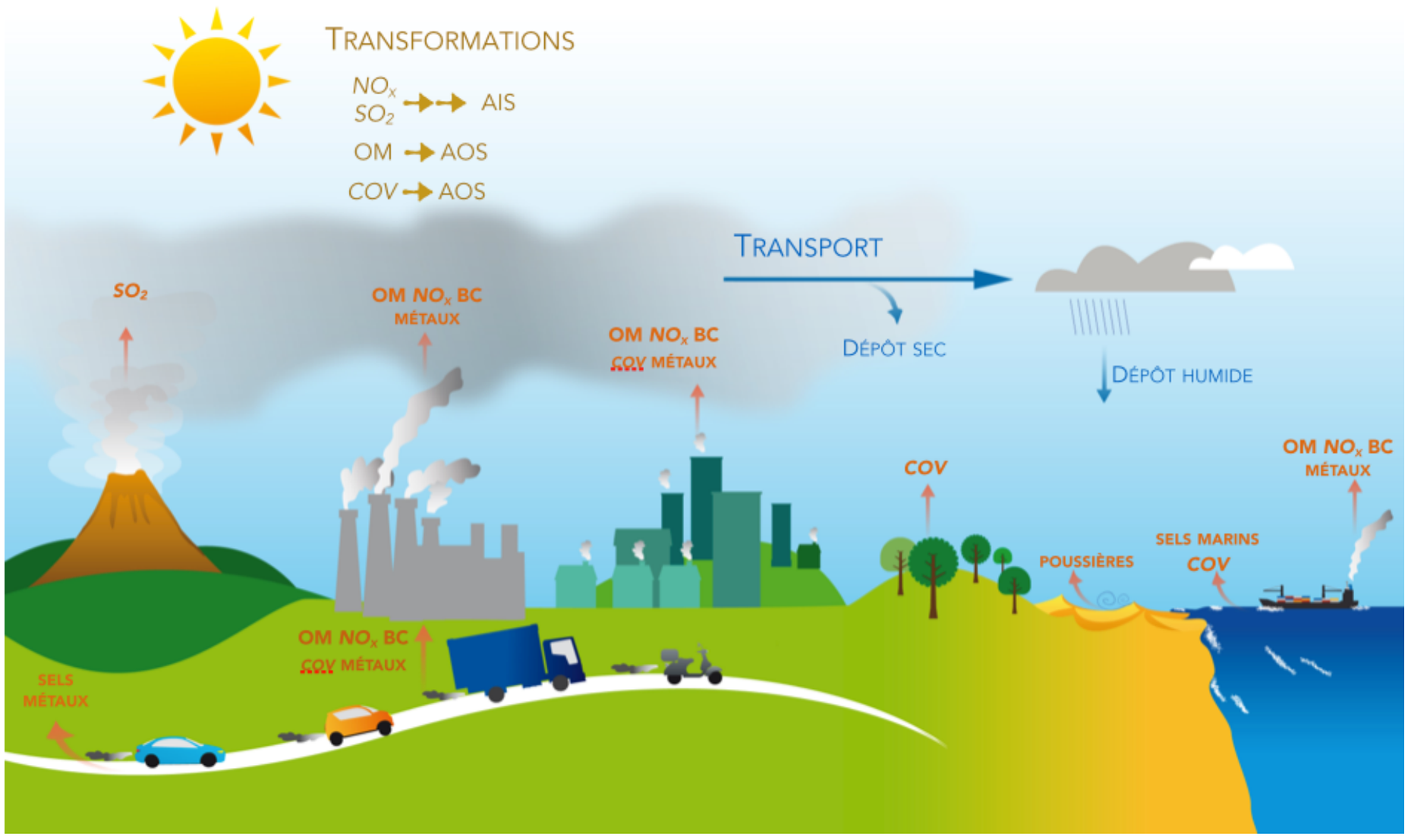
Jury

Philippe Bousquet	UVSQ / LSCE	Président
Karine Sellegri	LaMP	Rapporteur
Matthias Beekmann	LISA	Rapporteur
Paolo Laj	LGGE	Examinateur
Andre Prevot	PSI	Examinateur
Jean Sciare	LSCE	Directeur
Olivier Favez	INERIS	Co-encadrant

MOTIVATIONS, OBJECTIVES & STRATEGIES

Particulate pollution is complex by virtue of:

- the multitude of emission sources & the diversity of their chemical fingerprint
- the whole diversity of transformation processes
- meteo. parameters favoring accumulation or transport



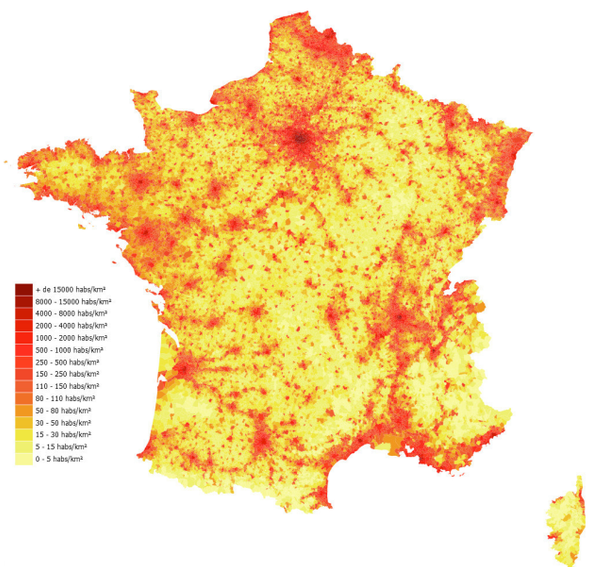
MOTIVATIONS, OBJECTIVES & STRATEGIES

HEALTH REGULATION

- Particulate pollution can be associated with cardiovascular, respiratory, cerebrovascular and neurodegenerative diseases, linked to chronic exposition (1st environmental risk in the world)

- Submicron particles have higher toxic potential, as they go deeper into bronchial tubes. Small particles are usually associated with anthropogenic emissions while bigger particles are linked to natural emissions

➡ Need of a **continuous** monitoring of the **chemical** properties of **fine** particles



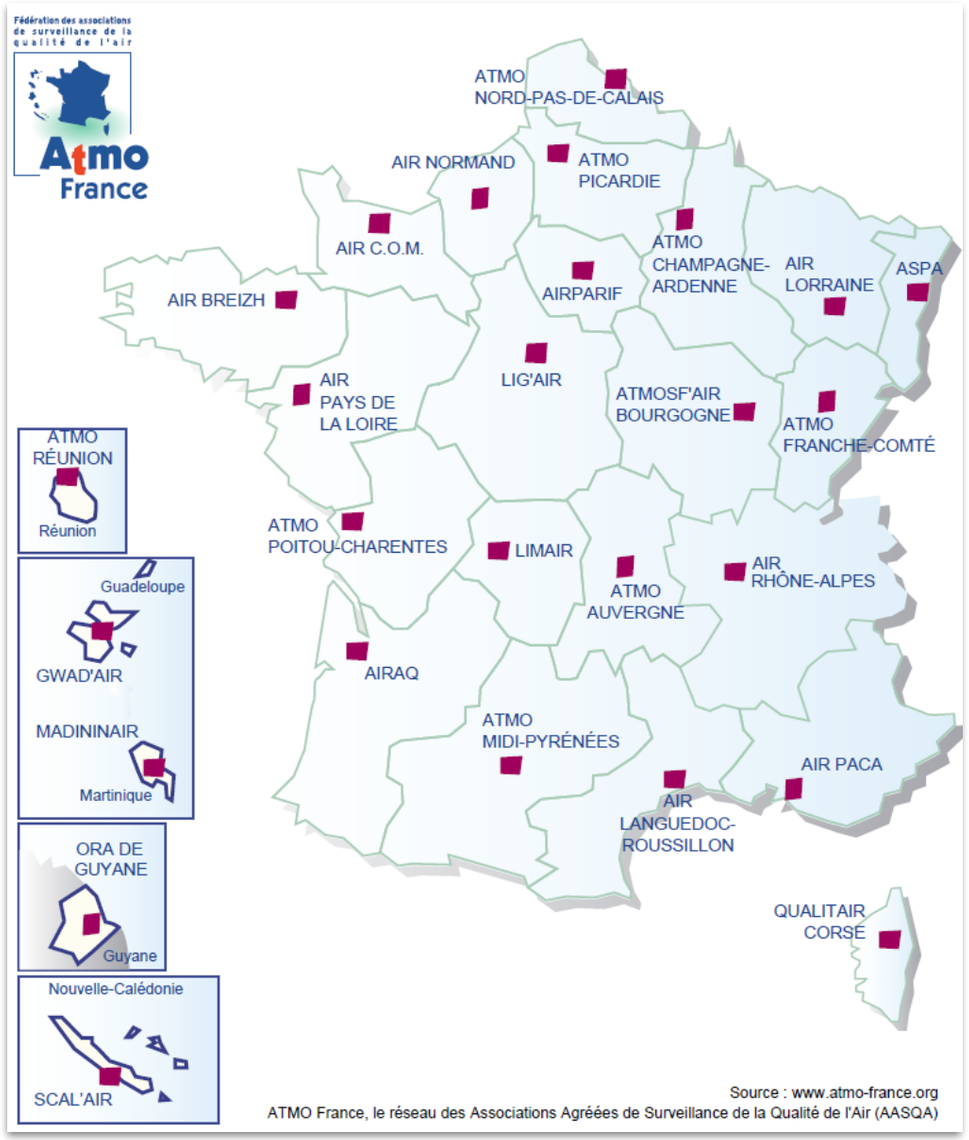
Ile-de-France is the most populated area (~12 M inhabitants) over only 2-3% of french territory

Exacerbated exposition to outdoor aerosol pollution

MOTIVATIONS, OBJECTIVES & STRATEGIES

HEALTH REGULATION

- In France, air quality is continuously monitored by regional monitoring networks (AASQA)



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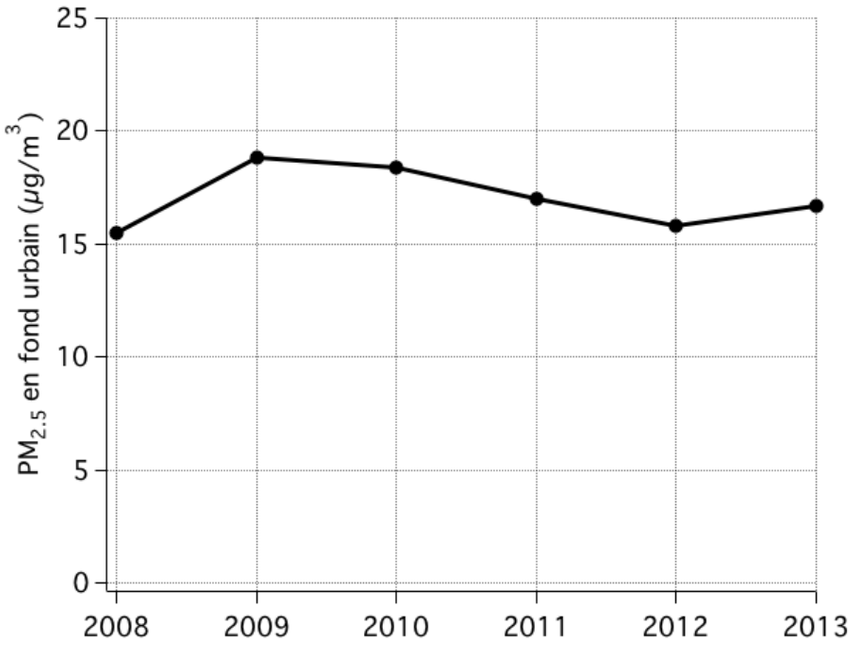
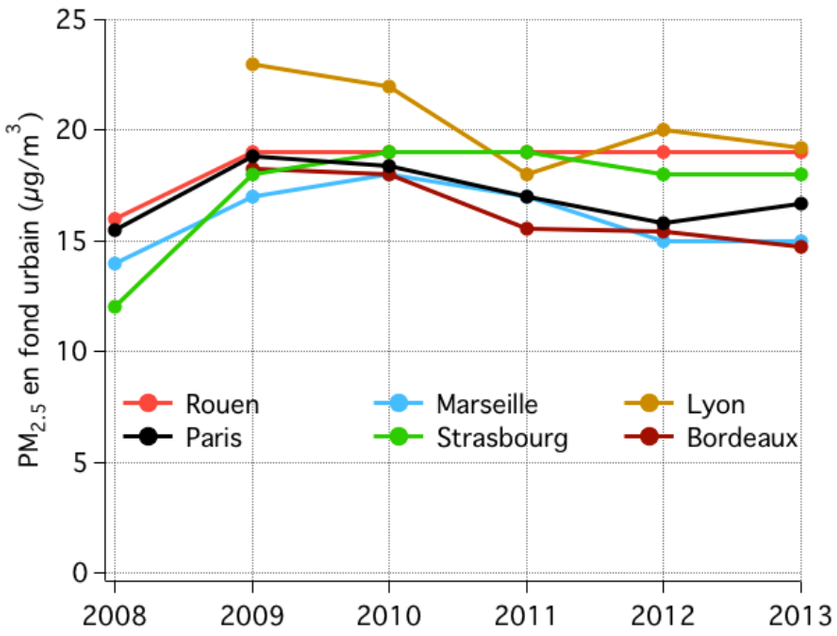


Relative stagnation of annual [$PM_{2.5}$] in IdF…



… Observed in most French cities

MOTIVATIONS, OBJECTIVES & STRATEGIES

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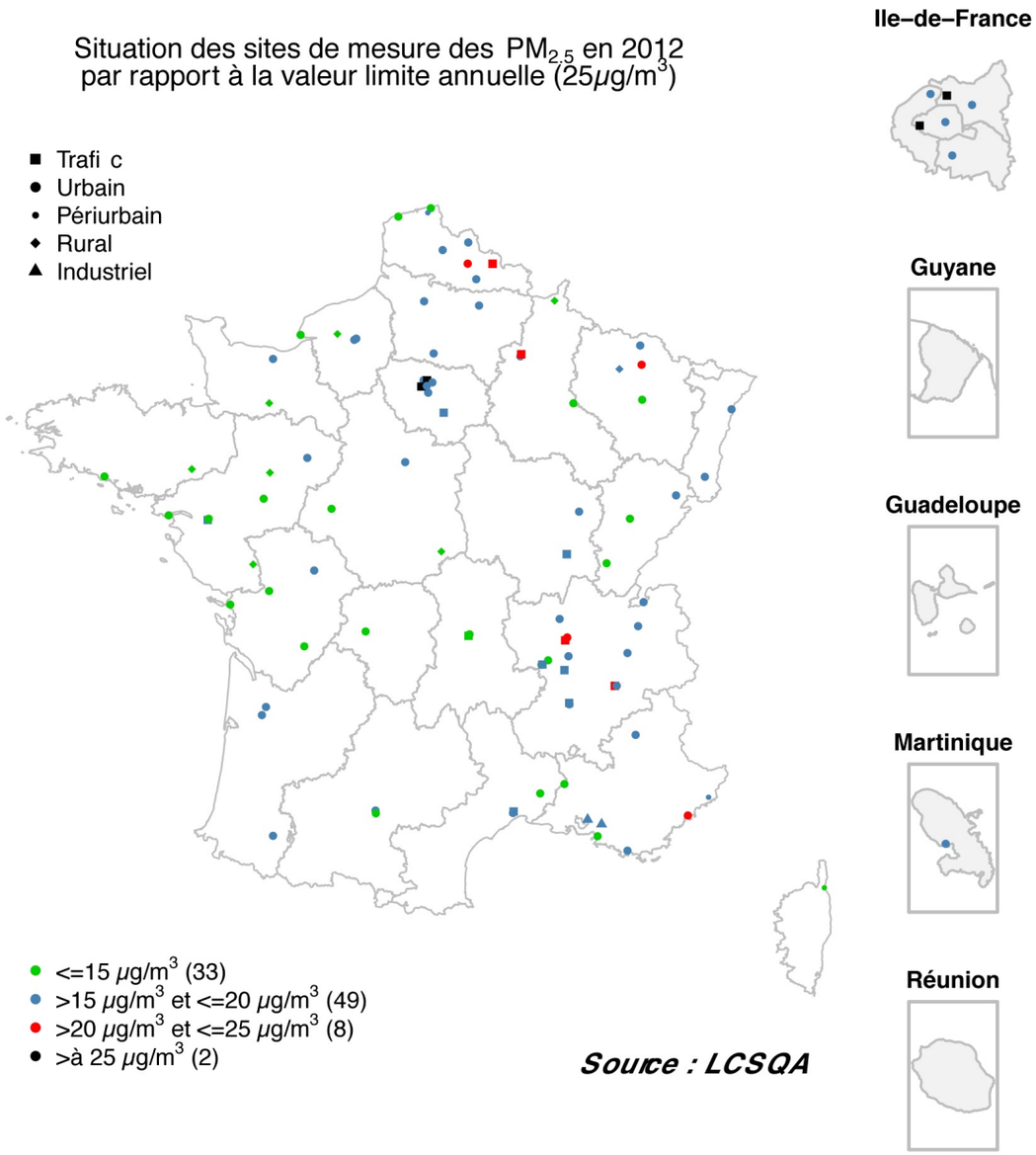


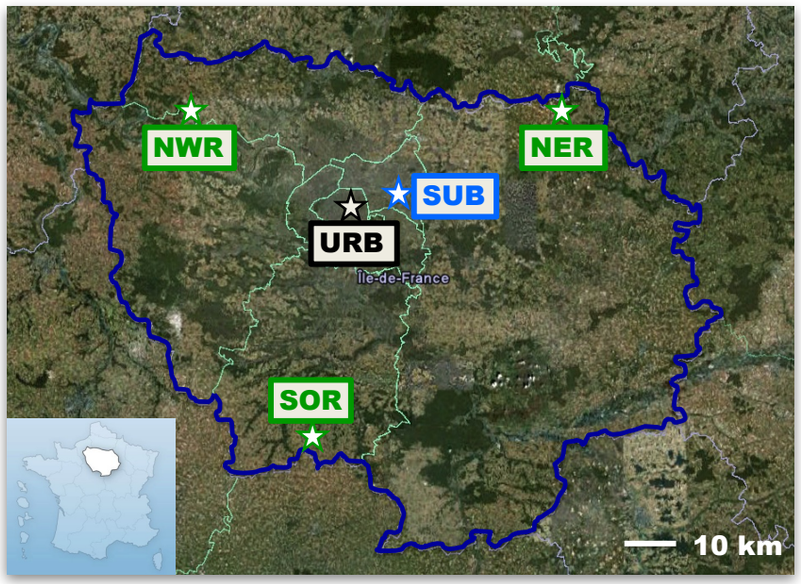
But only IdF is concerned by limit values exceeding!

MOTIVATIONS, OBJECTIVES & STRATEGIES

CONTEXT MEDIA COVERAGE STATE OF THE AIR

Programme « PARTICULES »

A year of daily filter sampling in 5 sites across IdF region between Sep. 2009 and Sep. 2010



Programme « MEGAPOLI »

MOTIVATIONS, OBJECTIVES & STRATEGIES

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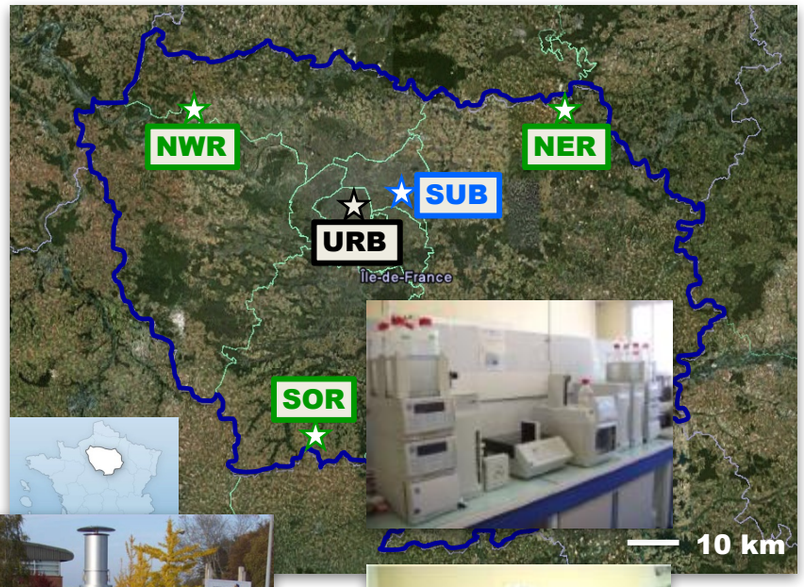

Based on off-line analyses

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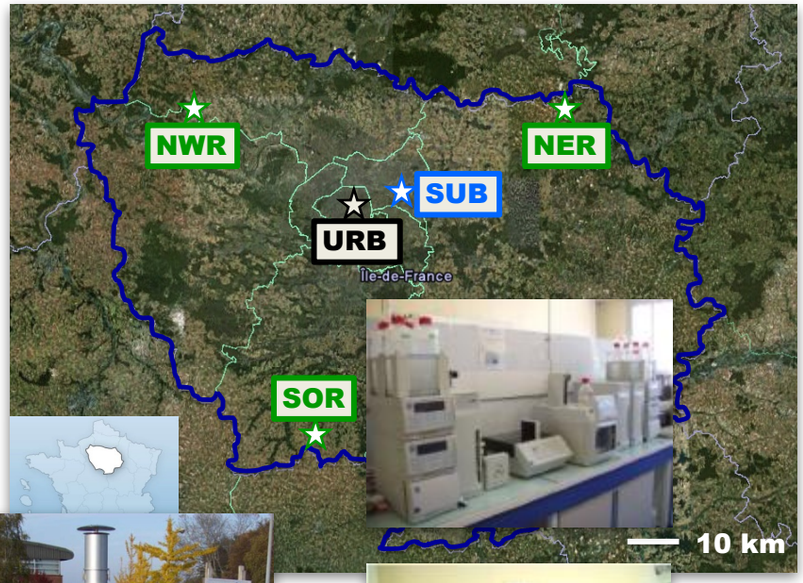

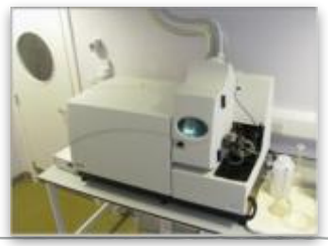

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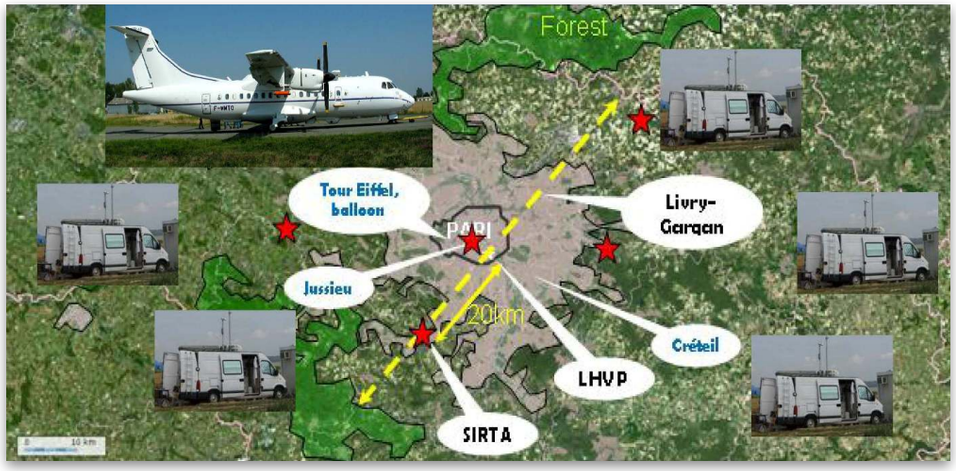
Programme « MEGAPOLI »

Two intensive field campaigns in Summer 2009 and Winter 2010 with state-of-the-art instrumentation



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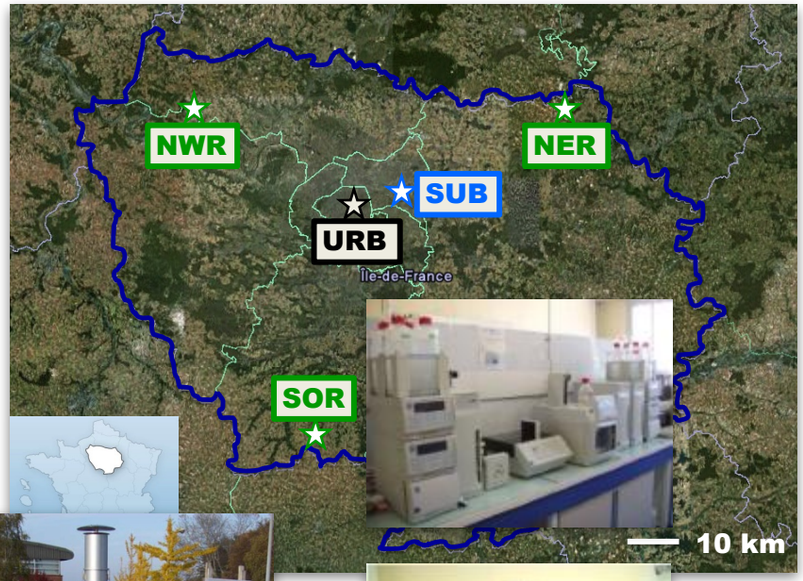

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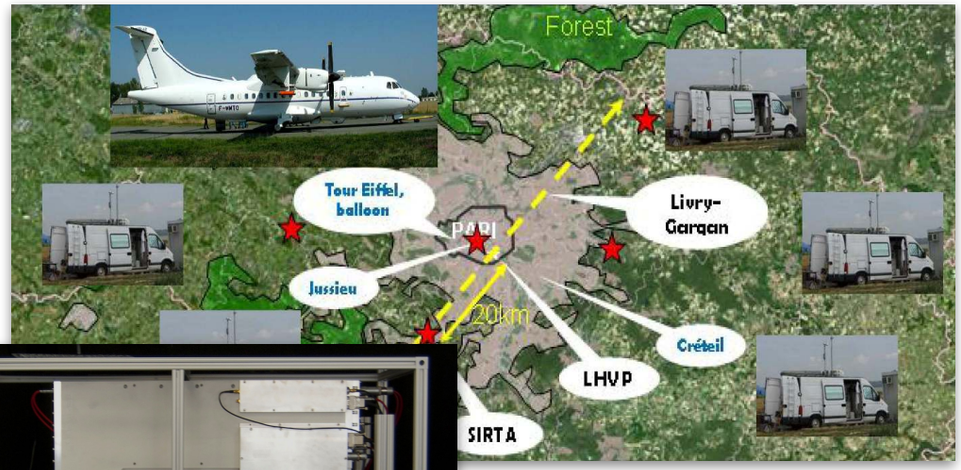

Online chemical composition and sizing *via* Aerosol Mass Spectrometer

MOTIVATIONS, OBJECTIVES & STRATEGIES

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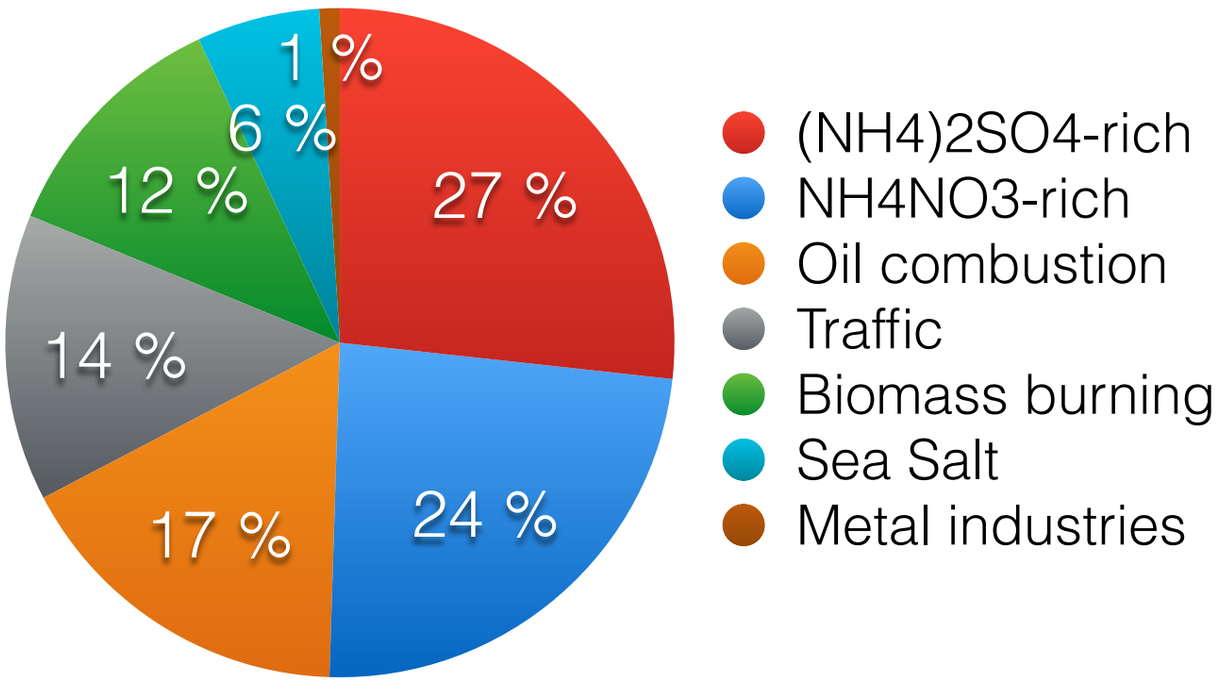
Programme « PARTICULES »

$PM_{2.5}$ source apportionment Bressi et al., 2014



- Secondary sources dominate!
- Unexpected significant contribution of oil combustion
- Unexpected relatively low contribution of traffic

SOURCE APP.

Programme « MEGAPOLI »

MOTIVATIONS, OBJECTIVES & STRATEGIES

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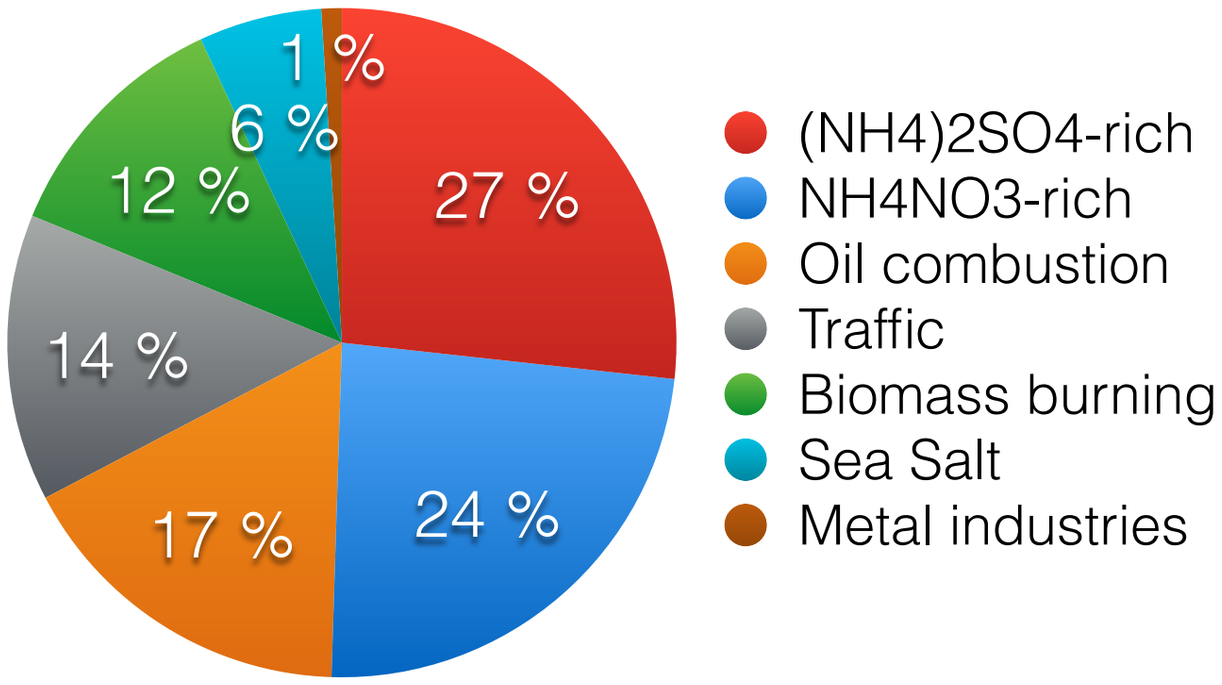

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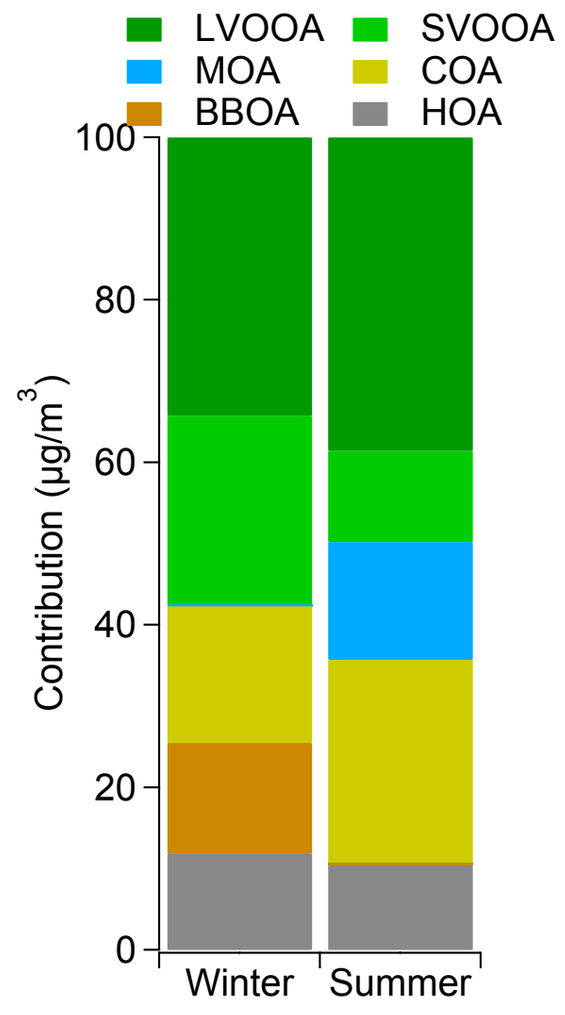
Programme « MEGAPOLI »

OA source apportionment Crippa et al., 2013a&b



- Cooking appears to be a significant source of OA
- Oxidized OA major component of OA

MOTIVATIONS, OBJECTIVES & STRATEGIES

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Programme « PARTICULES »

Programme « MEGAPOLI »

SOURCE APP.

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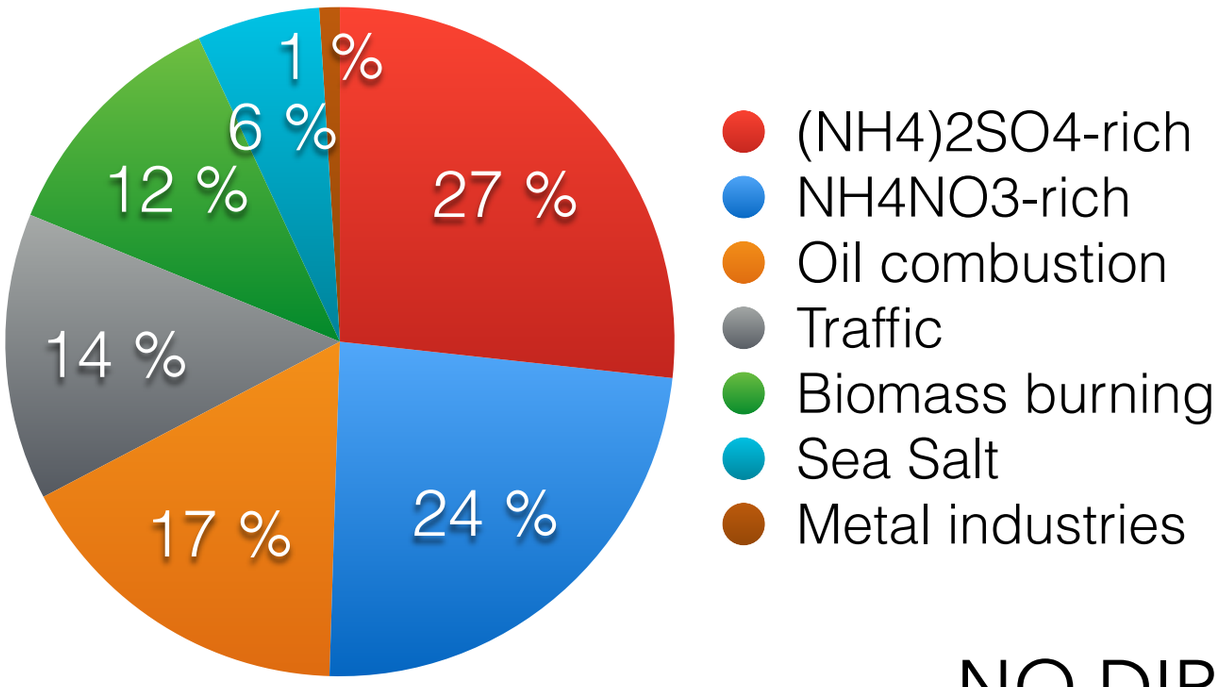
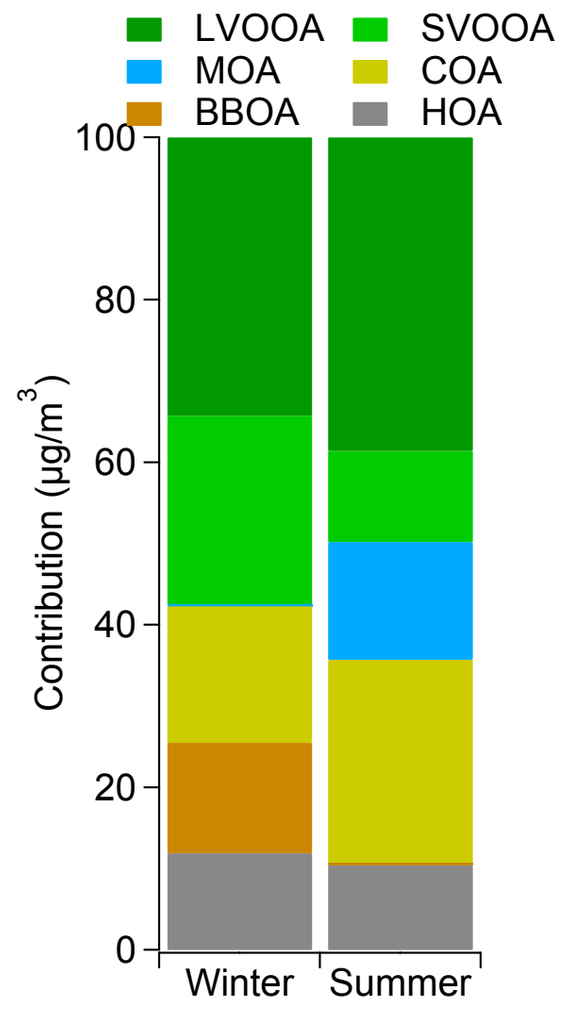


NO DIRECT LINK

OA source apportionment Crippa et al., 2013a&b



MOTIVATIONS, OBJECTIVES & STRATEGIES

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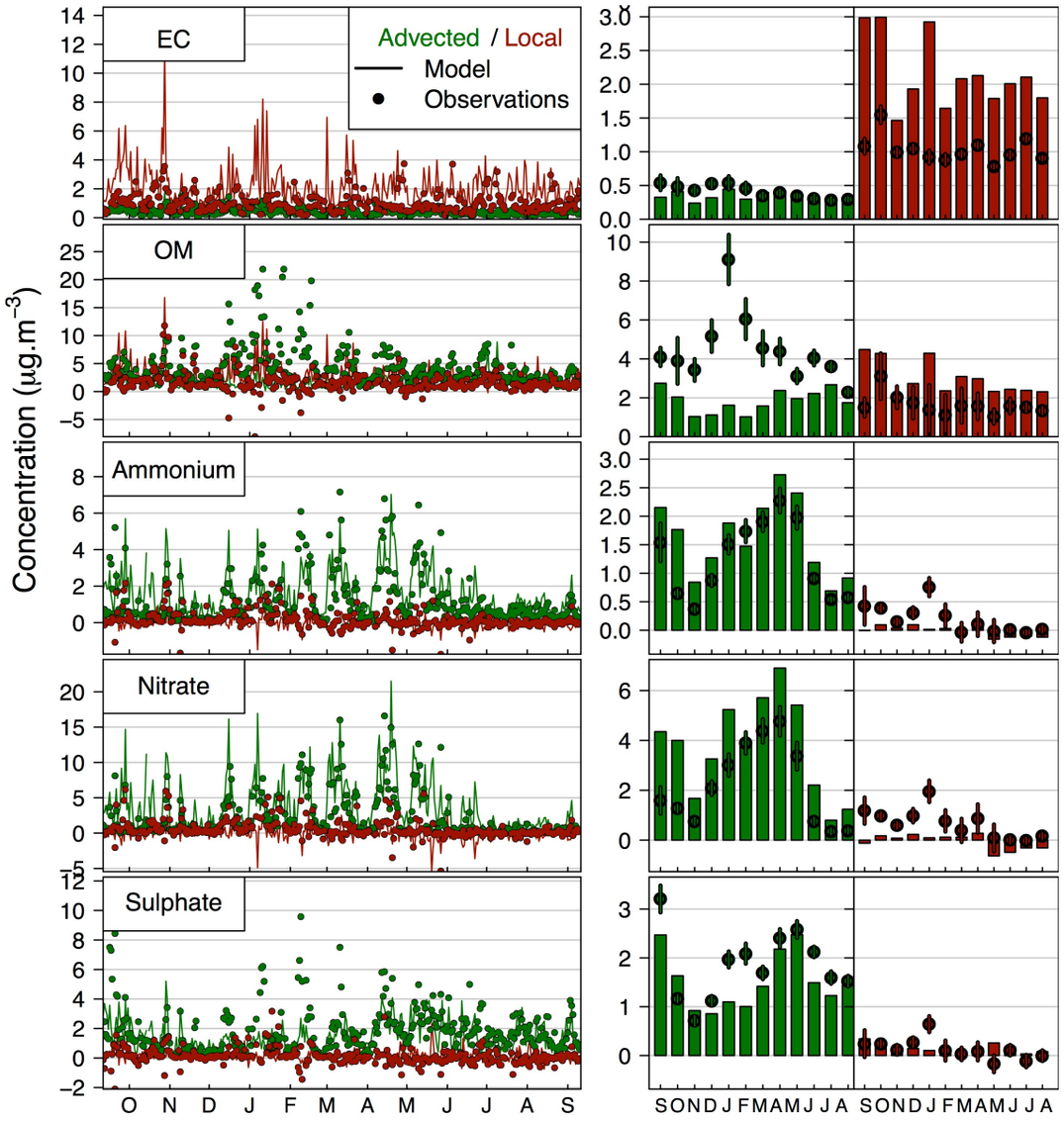
Programme « PARTICULES »

COMP. W/ MODELS

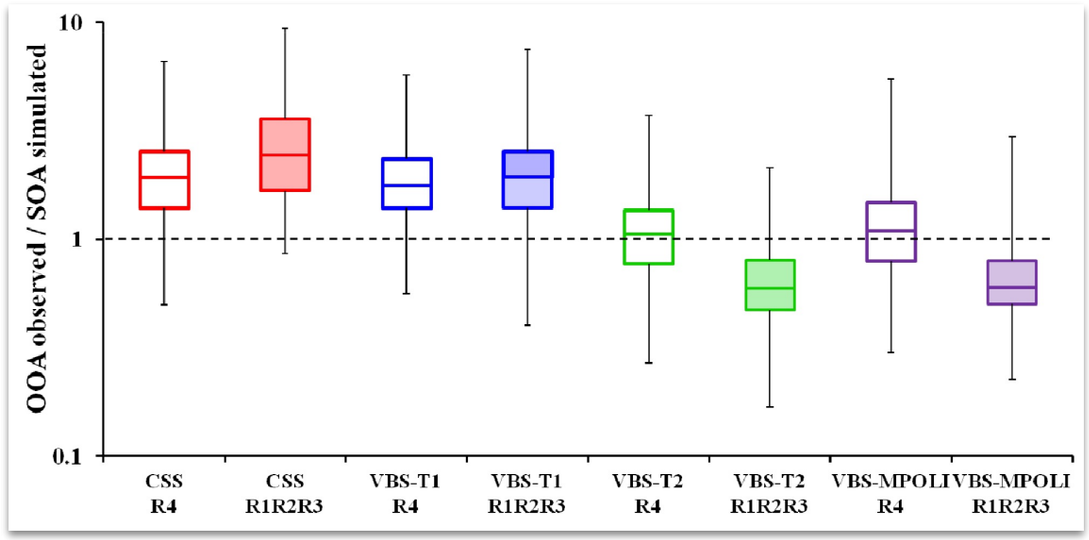
Petetin et al., 2014



Difficulties with OM and NO_3

Programme « MEGAPOLI »

Zhang et al., 2013



Difficulties of several models to reconstruct OM, and more specifically secondary OA

Motivations, Objectives & Strategies

Long term obs.
High time res.
Perennial station
Geo. origins
Source app.
Poll. episodes

MOTIVATIONS, OBJECTIVES & STRATEGIES

	PARTICULES
Long term obs.	✔
High time res.	✗
Perennial station	✗
Geo. origins	✔
Source app.	PM2.5
Poll. episodes	✔

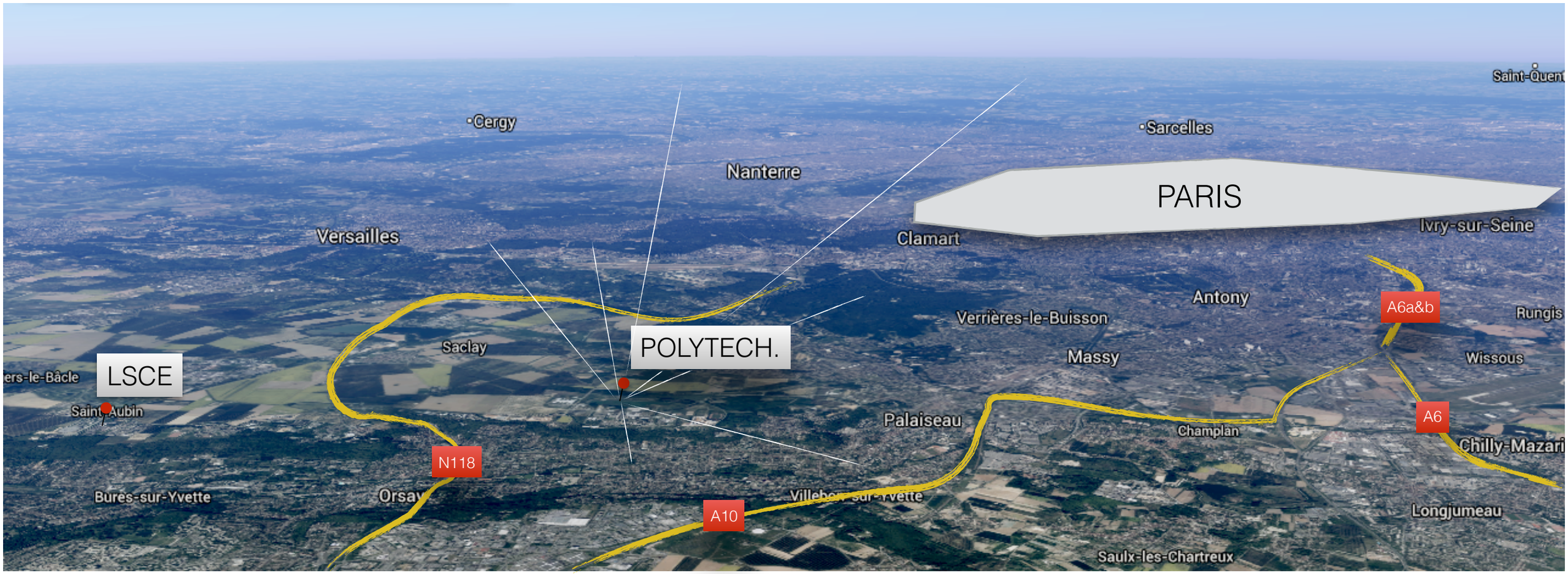
MOTIVATIONS, OBJECTIVES & STRATEGIES

	PARTICULES	MEGAPOLI
Long term obs.	✔	✗
High time res.	✗	✔
Perennial station	✗	✗
Geo. origins	✔	✔
Source app.	PM2.5	OM
Poll. episodes	✔	✔

Motivations, Objectives & Strategies

	PARTICULES	MEGAPOLI	**THIS PhD**
Long term obs.	✔	✗	✔
High time res.	✗	✔	✔
Perennial station	✗	✗	✔
Geo. origins	✔	✔	✔
Source app.	PM2.5	OM	OM
Poll. episodes	✔	✔	✔

THE SIRTA ATMOSPHERIC SUPER-SITE



The national experimental SIRTA station is composed on 5 different zones, including 4 on the campus of Ecole Polytechnique

Document and monitor radiative and dynamic processes in the atmosphere through remote sensing

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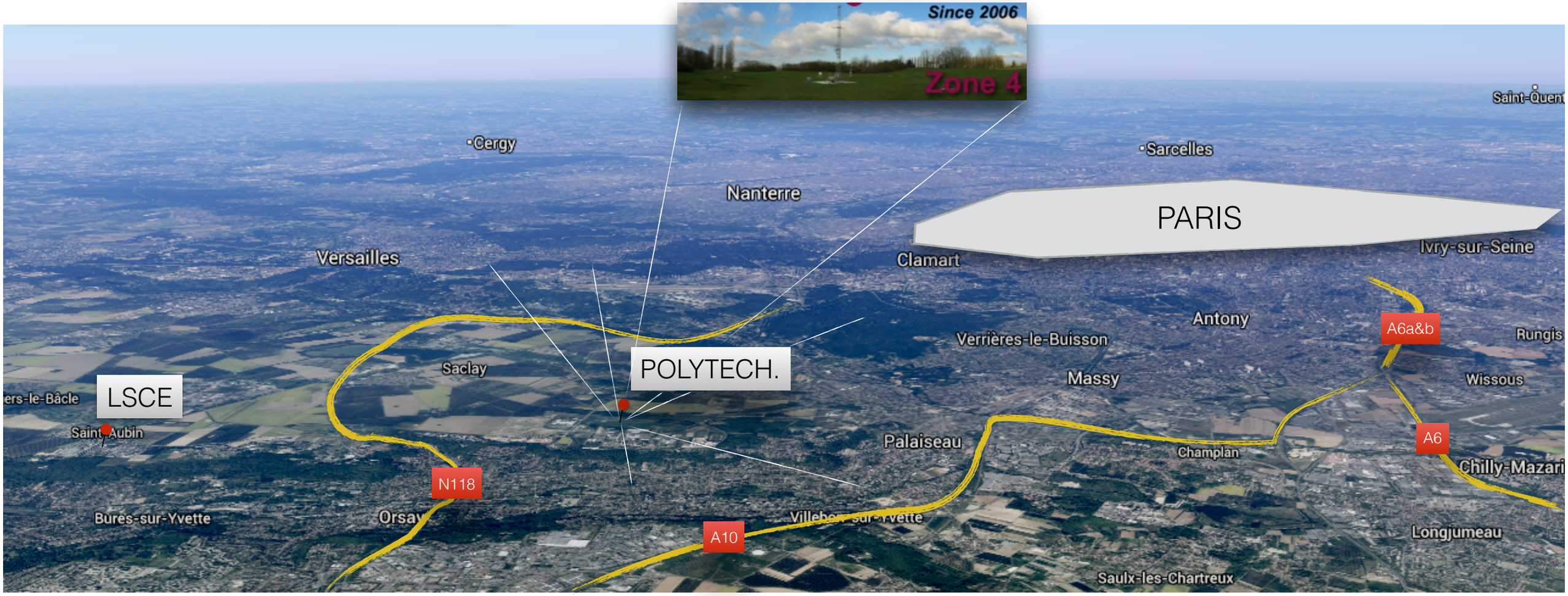

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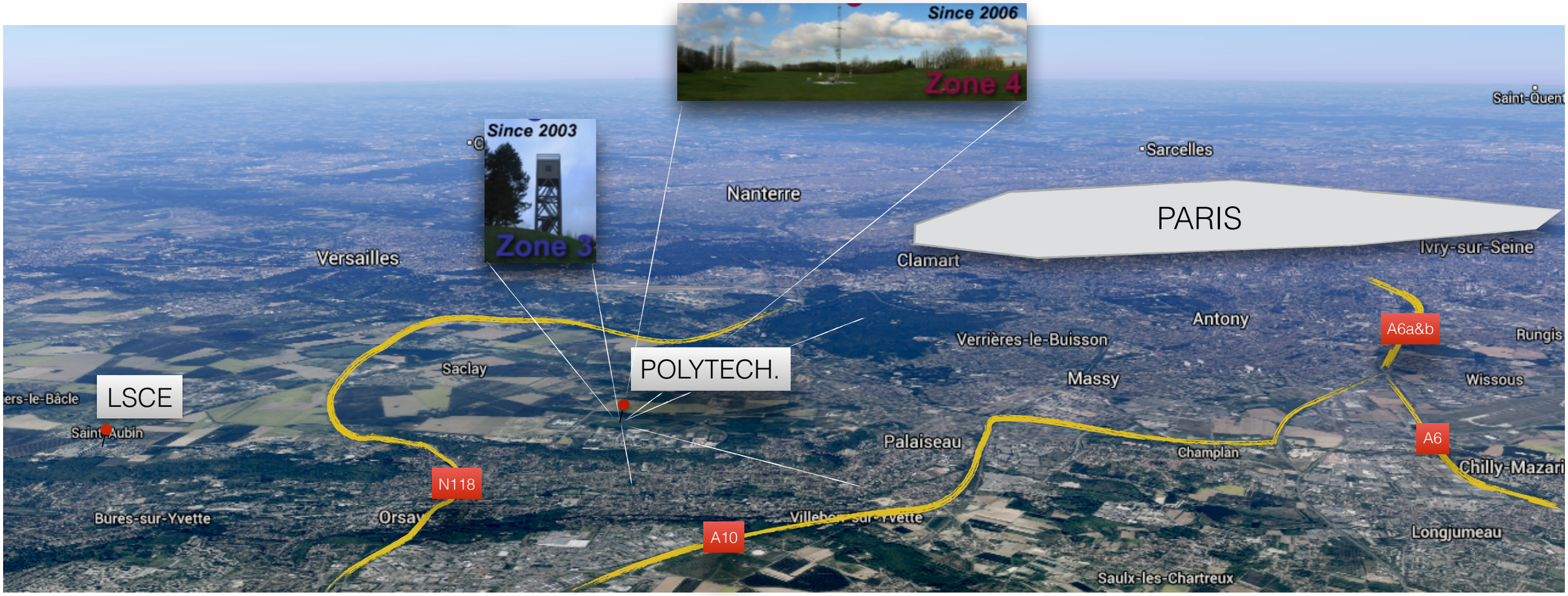

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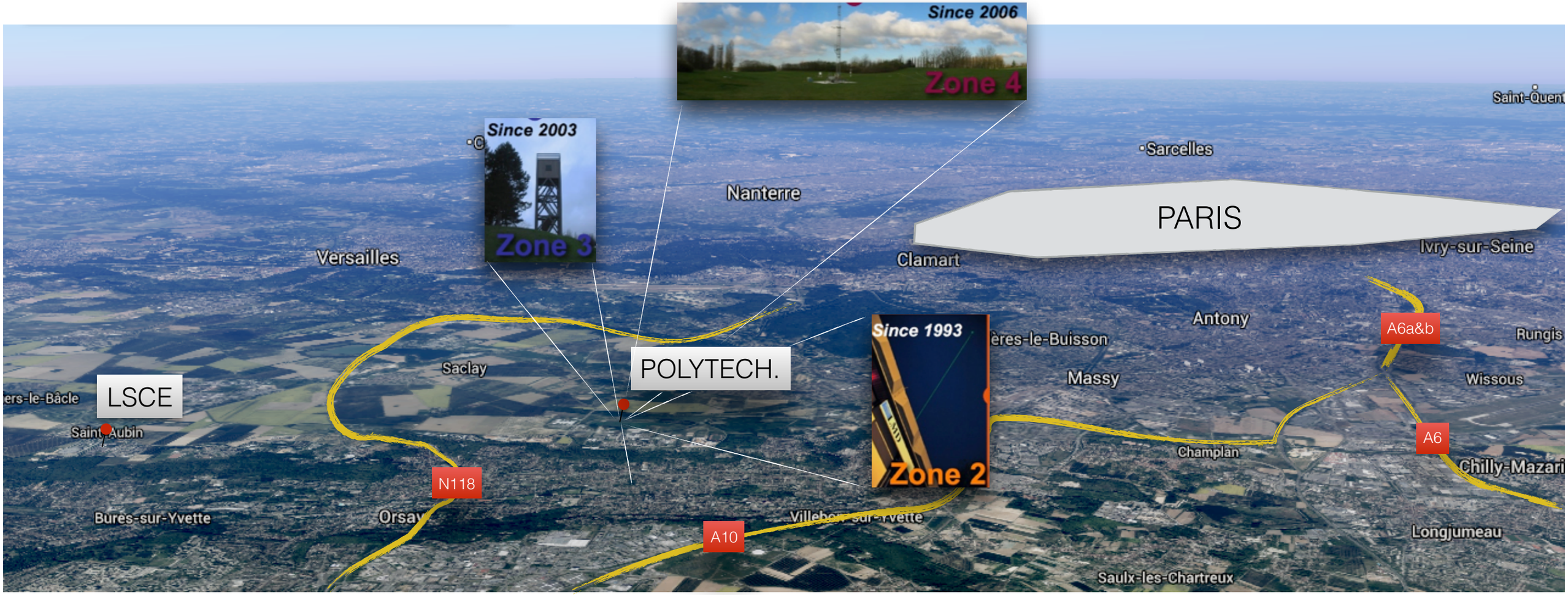

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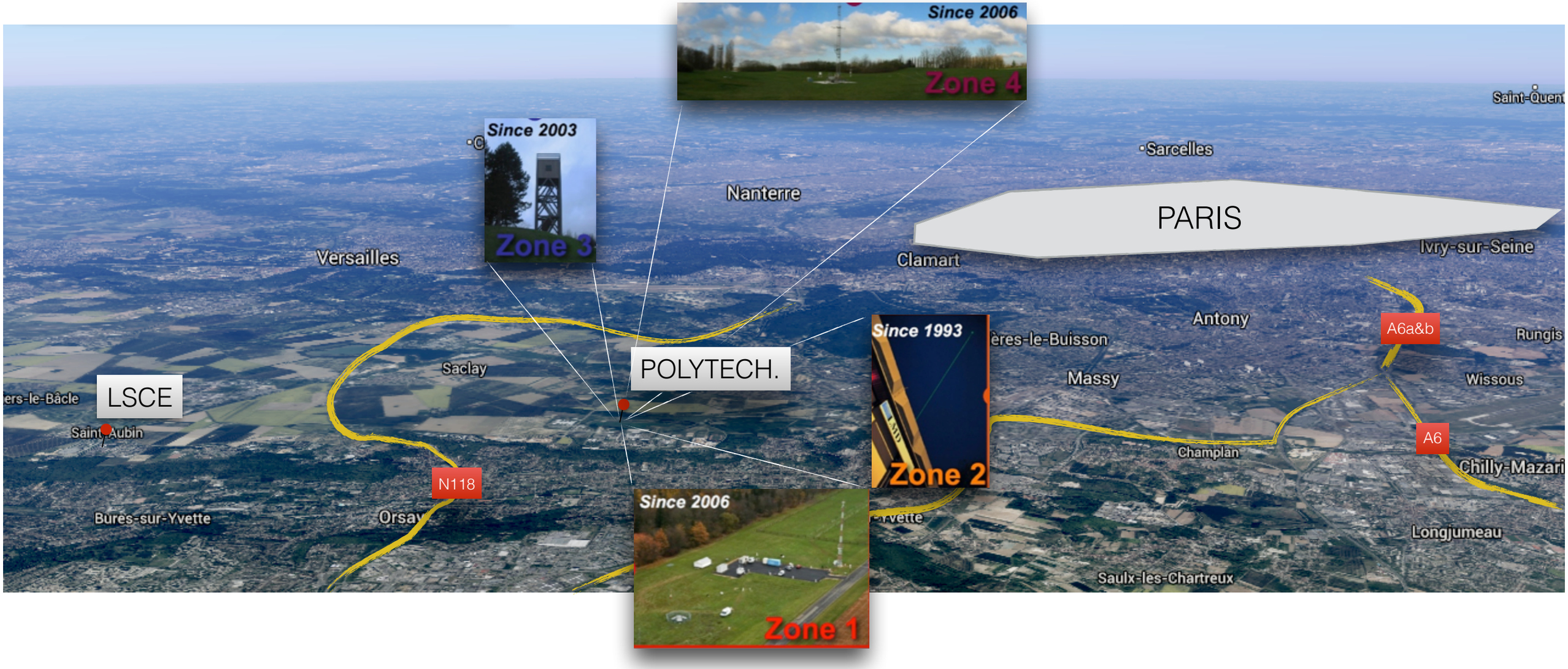

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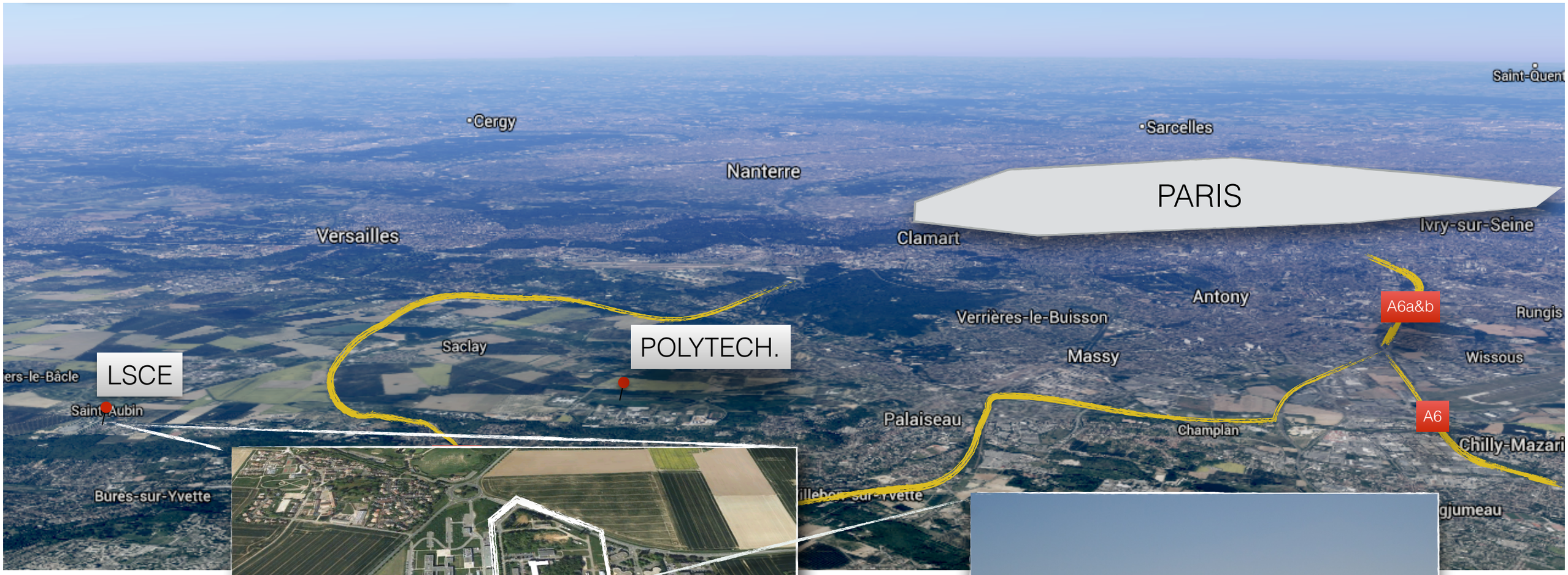
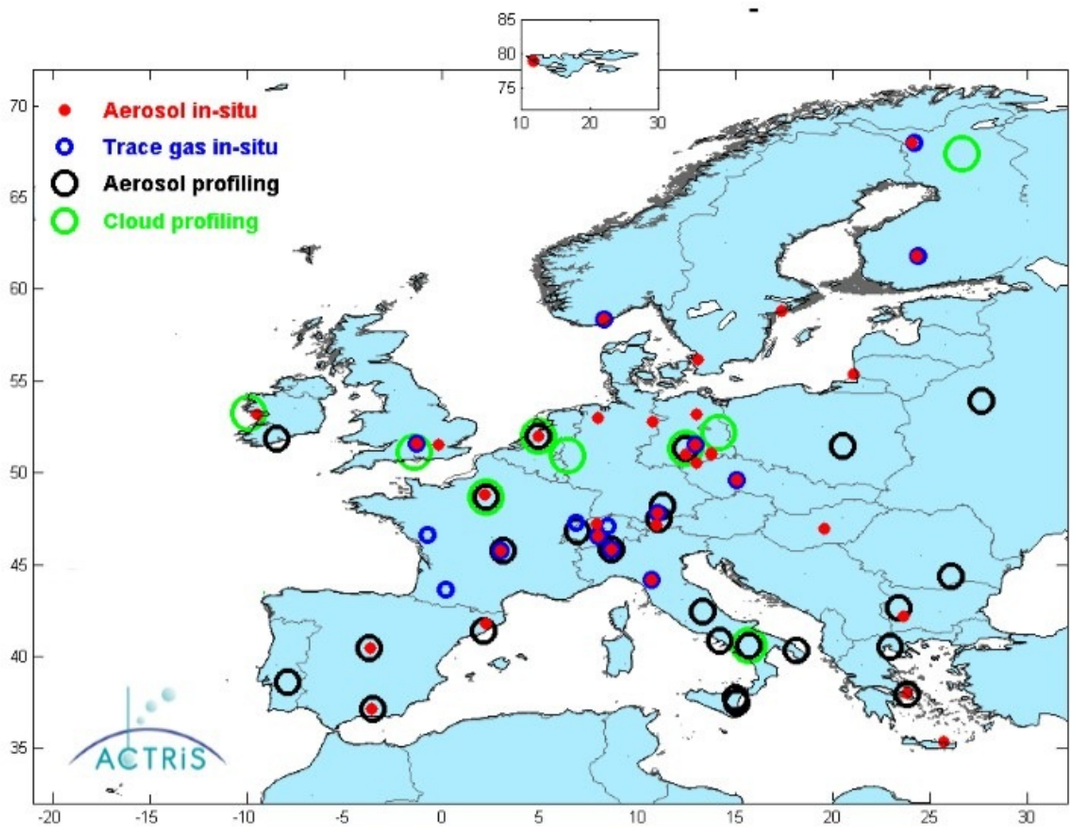
Located ~4km from Ecole Polytechnique, LSCE hosts an in-situ observation station, and has been officially part of SIRTA since 2012



THE SIRTA ATMOSPHERIC SUPER-SITE

SIRTA is part of networking activities: ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure network)

- provide high quality data throughout Europe on a single database
- promote transnational collaborations (intensive field campaigns / intercomparison exercises)
- training, meeting, sharing feedbacks
- promote the use of state-of-the-art instrumentation



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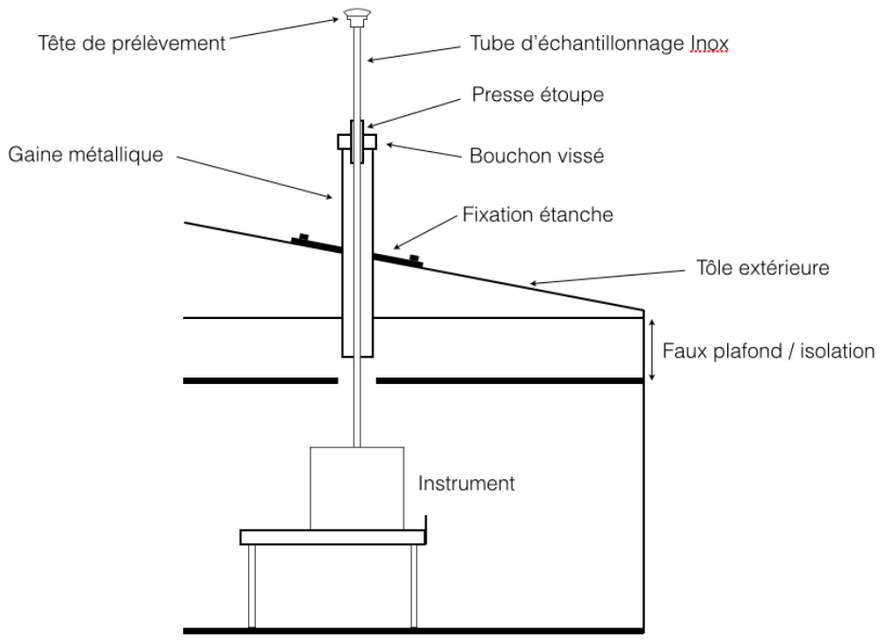
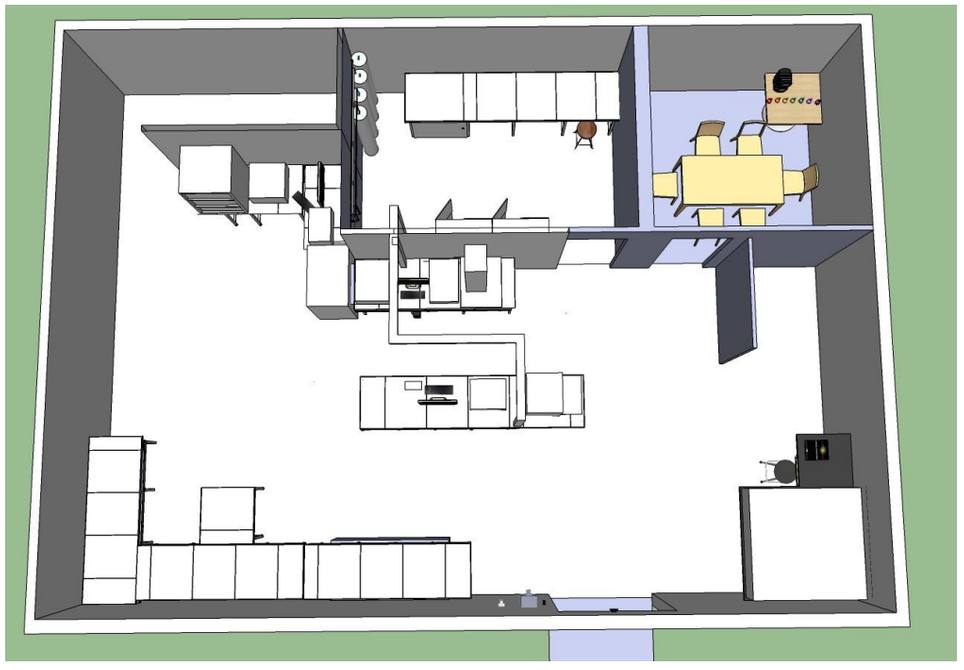
At the beginning of the PhD, the station didn't exist, as important restoration work was needed.
I took part in all different phases of the construction, from the sampling strategy and the design of the station, to the installation of the instruments.





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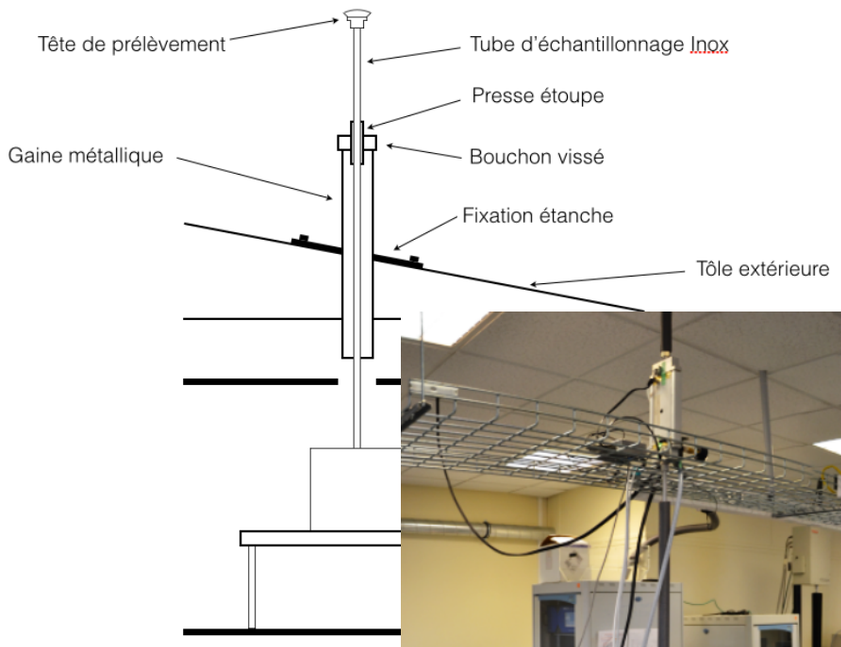

Measurements officially started in January 2013.

THE SIRTA ATMOSPHERIC SUPER-SITE

The station is equipped with state-of-art instrumentation for the chemical and physical characterization of the atmospheric pollution over the Ile-de-France region

INSTRUMENT	MODEL/BRAND	PARAMETER	RESOLUTION
ACSM	**Aerodyne**	**OM, NO**	**30 min**
Aethalo.	**Magee AE31 & AE33**	**Absorption 7λ**	**5 min**
Néphélo. 1	*Ecotech Aurora M3000*	*Diffusion 525 nm*	*5 min*
Néphélo. 2	*Ecotech Aurora M3000*	*Diffusion 450 nm*	*5 min*
TEOM-FDMS	**R&P TEOM 1400ab+ FDMS 8500c TEOM-FDMS 1405F**	**PM**	**6 min**
SMPS	**GRIMM 5.416**	**Size distribution**	**15 min**
PARTISOL	*Thermo*	*EC-OC*	*24 h*
AiRRmonia	**Mechtronics**	**NH**	**5 min**
NO	*Teledyne T200UP*	*NO/NO*	*1 min*
VOC cartridge	*Sypac V2*	*VOC*	*bi-hebdo.*

data not used in this PhD

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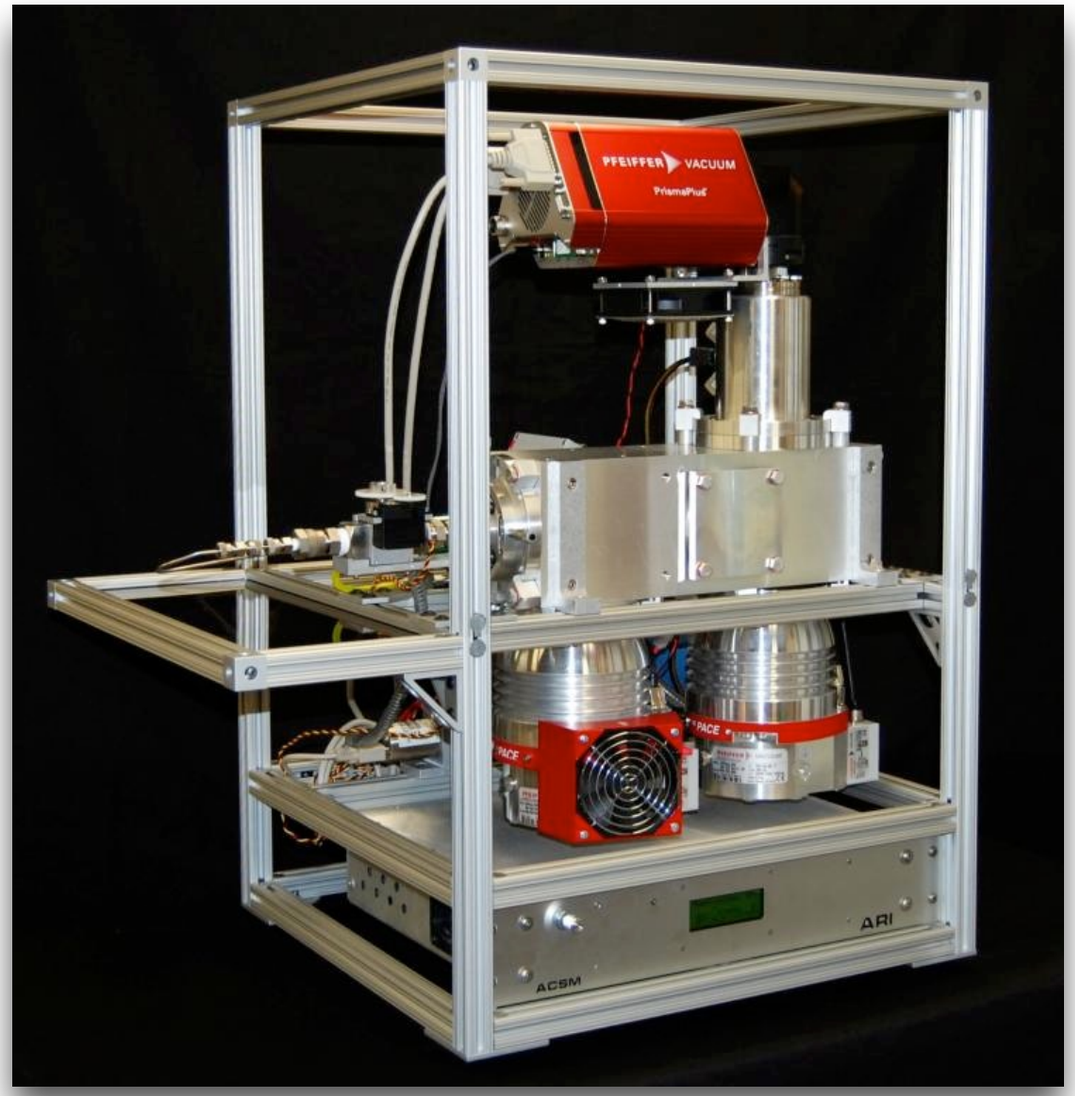
THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)



Mass Spectrometer

Designed for robust long term monitoring

Reduced maintenance

OM, NO_3^-, SO_4^{2-}, NH_4^+, Cl^- 30min

Compared to filters:

Pro:

High time resolution with less artefacts (esp. SV material)

OA source apportionment

Cons:

Data treatment is more complex

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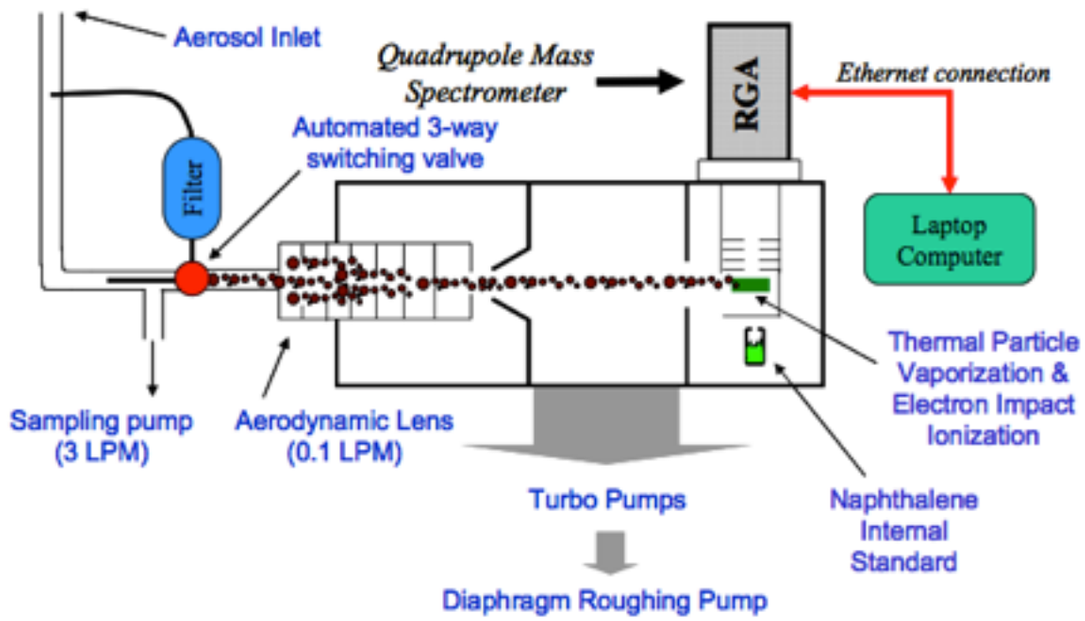
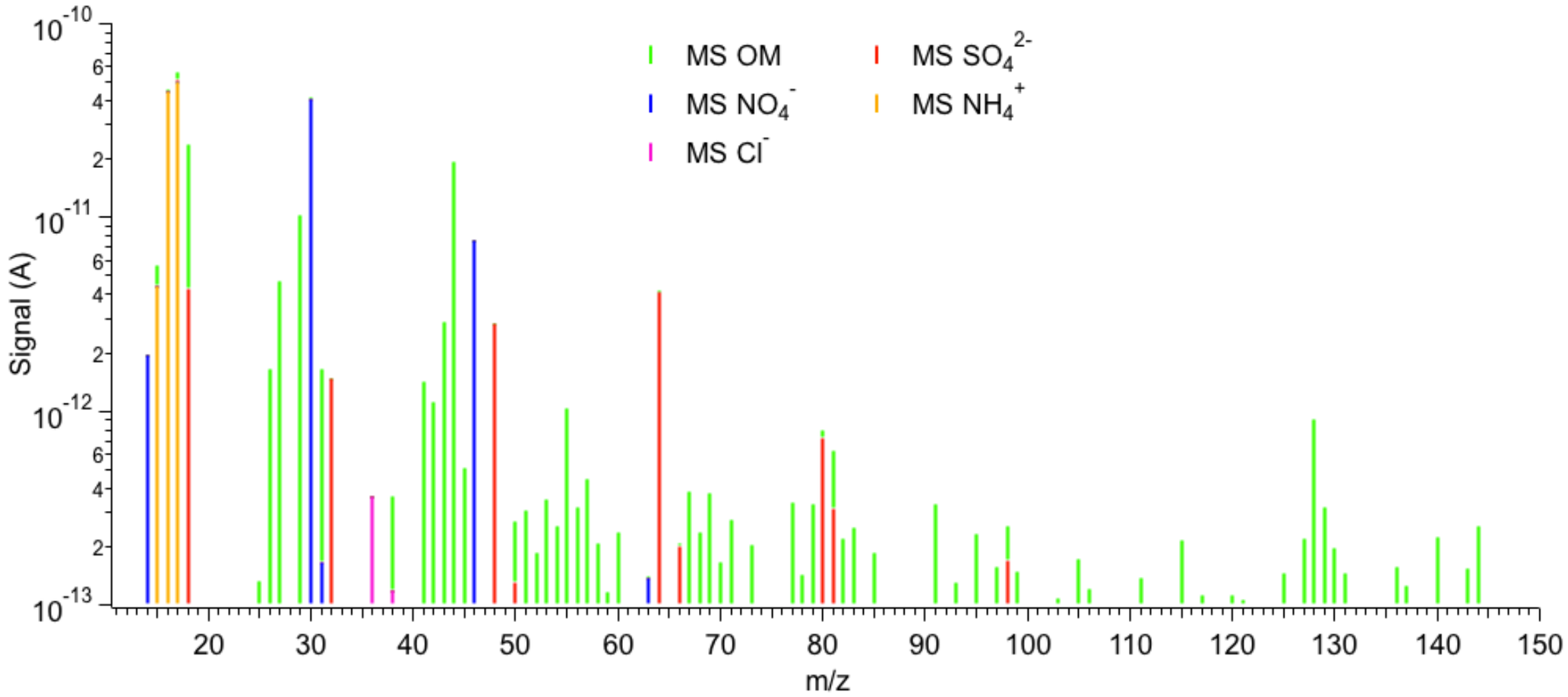


- Particle beam focused through an aerodynamic lens
- Particles are flash-vaporized on a 600°C heated conical tungsten vaporizer, and ionized with electron impact at 70 eV
- Fragments are separated through a quadrupole

- Sequential analyses, with an upstream total filter mounted in parallel allows the removal (by subtraction) of the signal due to gas-phase compounds.

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

PRINCIPLE CALIBRATION DATA TREAT. COMP. EXT. DATA



- A fragmentation panel is applied to reconstruct the concentration of organics and inorganics following reference fragmentation patterns *Allan et al., 2004*

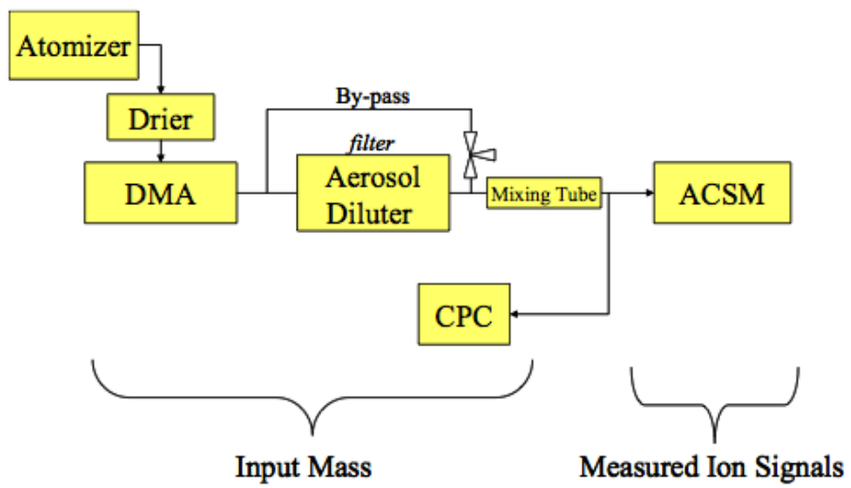
$$IC_S = \sum_i a_i^S \cdot m/z_i$$

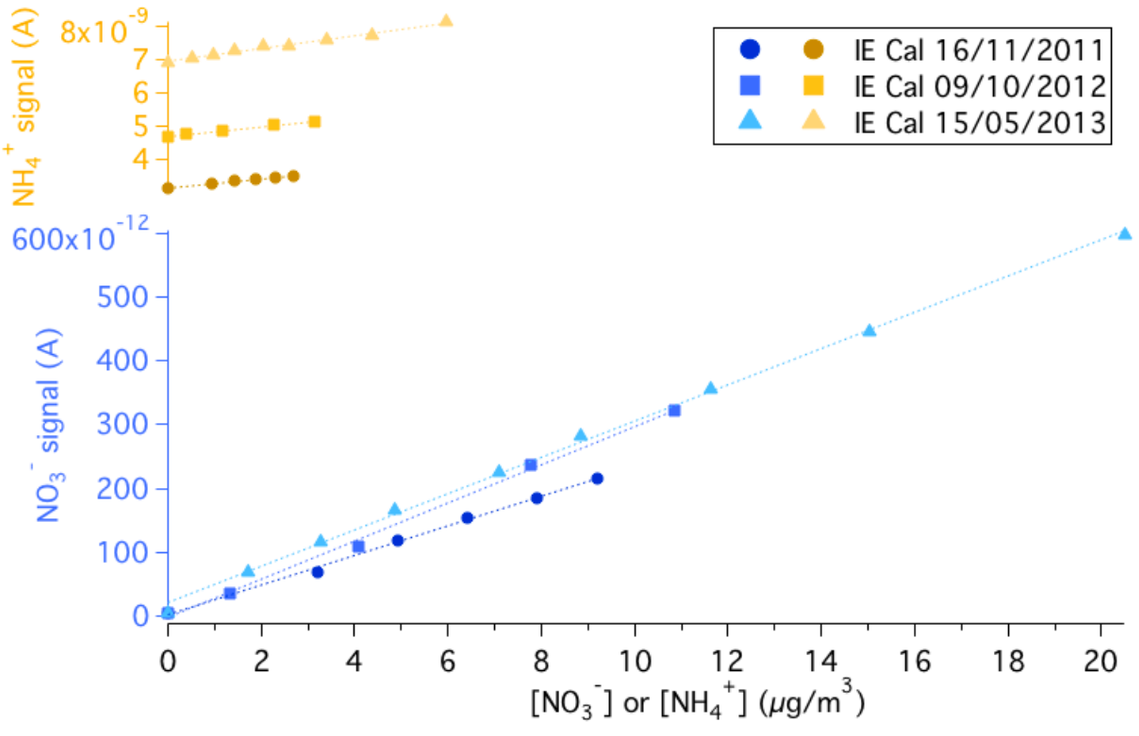
IC_S (A) —**response factor**→ [S] (µg/m^3)

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

The response factor of the instrument is determined through the direct injection of 300 nm NH_4NO_3 particles

- the CPC is used to determine the concentration of NH_4NO_3
- the by-pass total filter is used to vary the concentration





- 3 calibrations were performed in 2 years
- The consistency of the slopes allowed us to use a single averaged RF

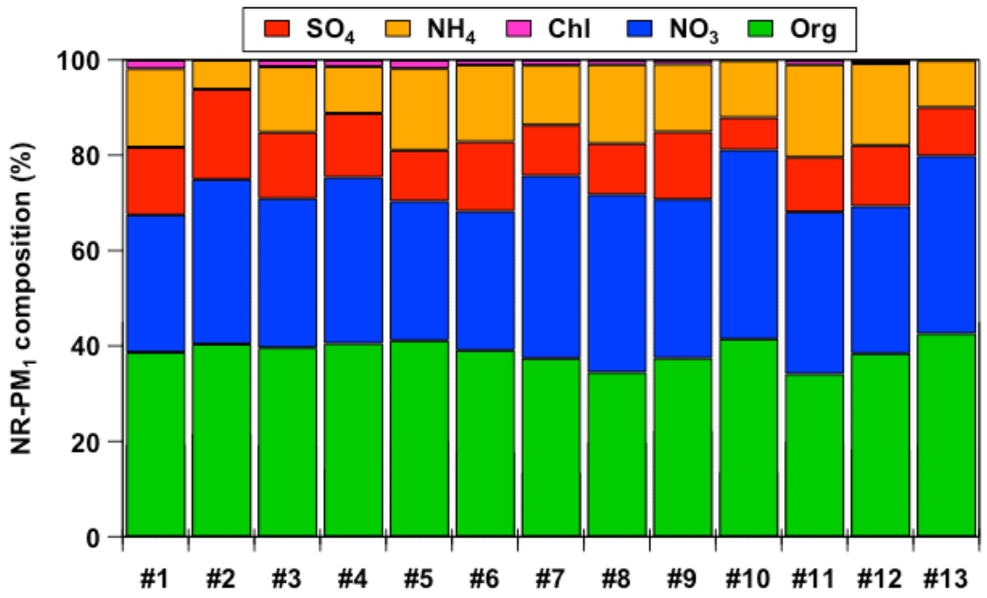
13% uncertainty

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

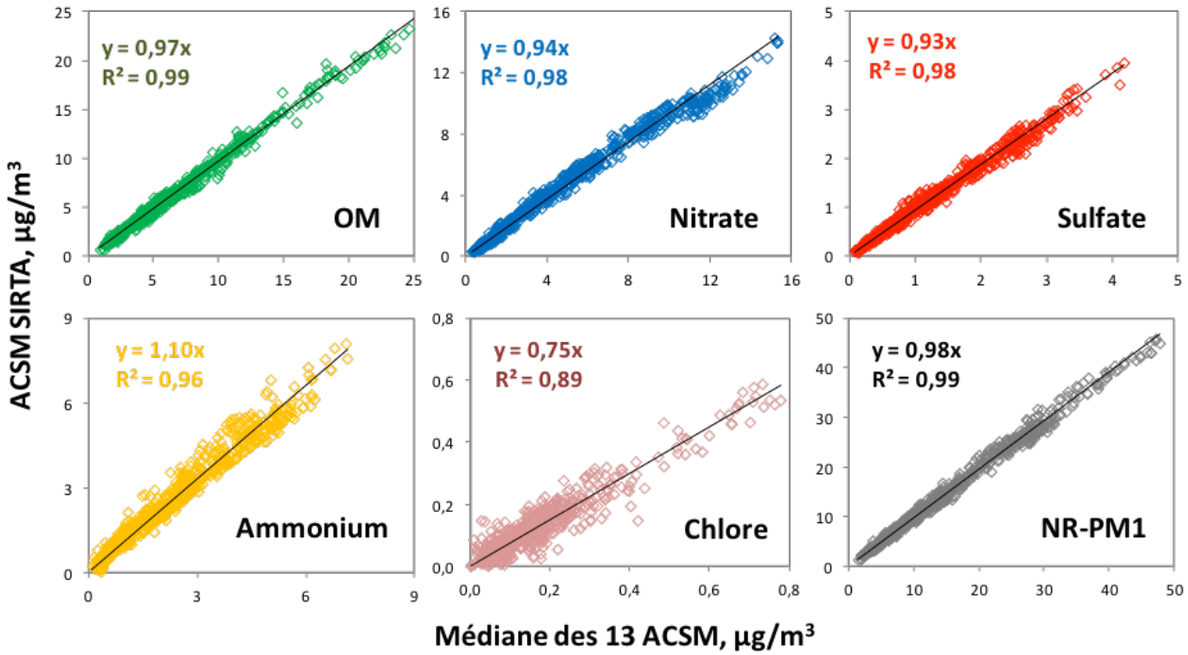
ACSM intercomparison *Crenn et al., in prep.; Frohlich et al., in prep.; Belis et al., in prep*

From 12/11 to 02/12, 13 ACSMs, 10 U.E. countries, ~20 scientists, at SIRTA

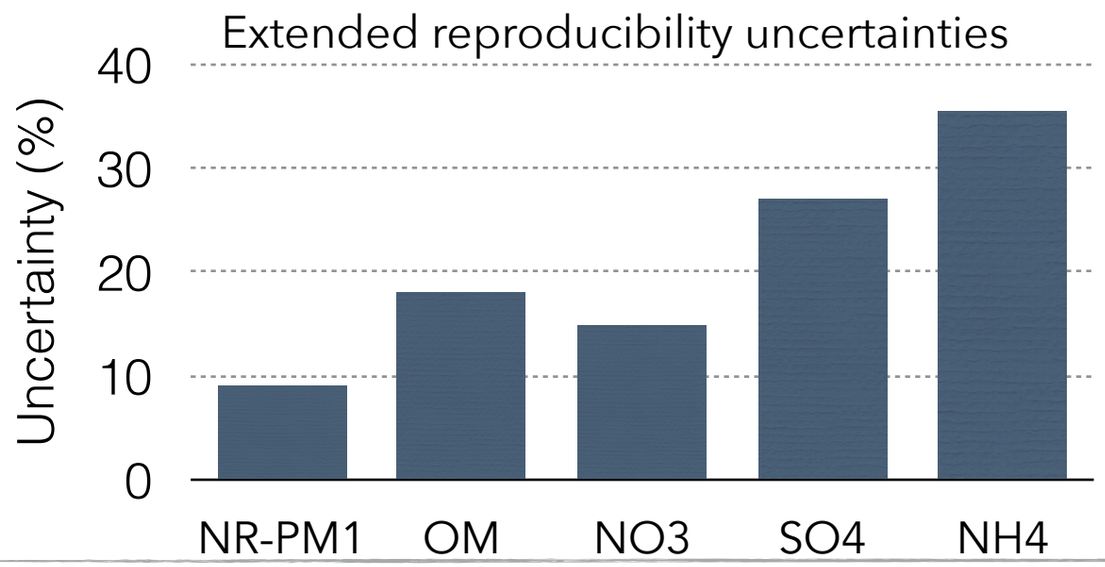
Average chemical composition



Consistency of SIRTA ACSM



Extended reproducibility uncertainties

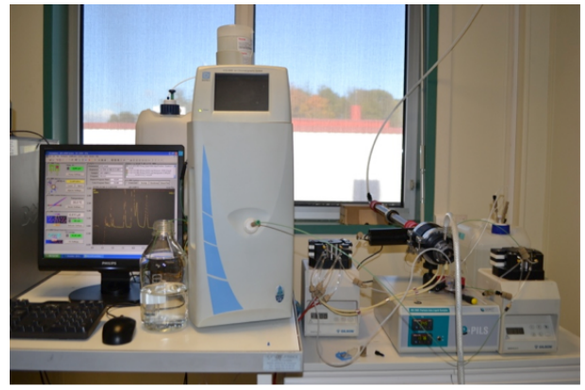


THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

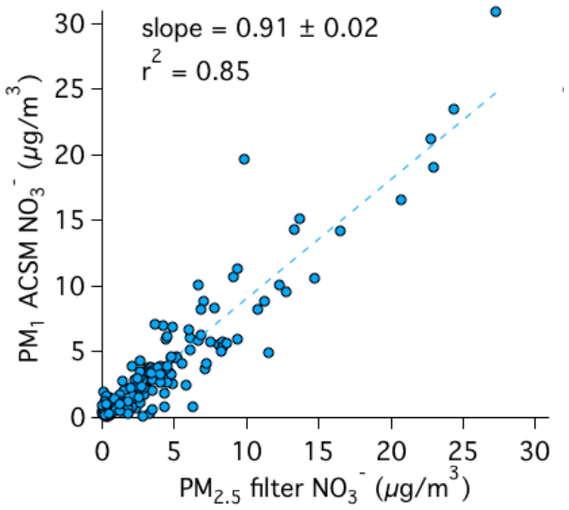
PRINCIPLE CALIBRATION DATA TREAT. COMP. EXT. DATA

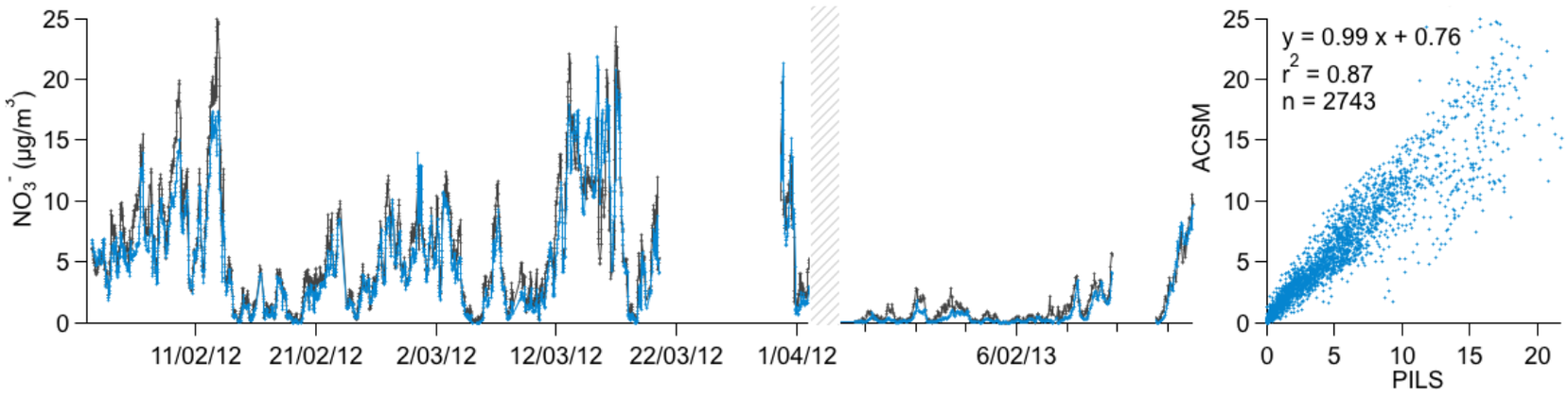
Specie by specie

FILTERS



PILS-IC



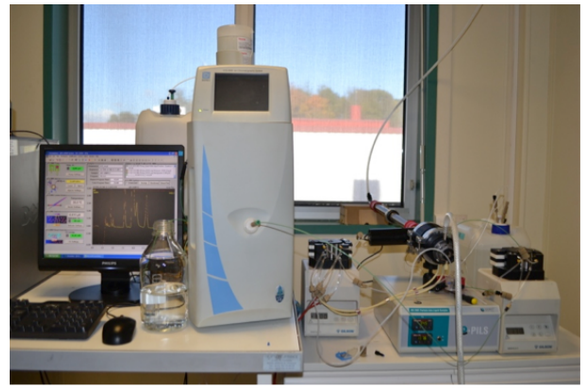


Satisfactory consistency between ACSM and PILS or filters

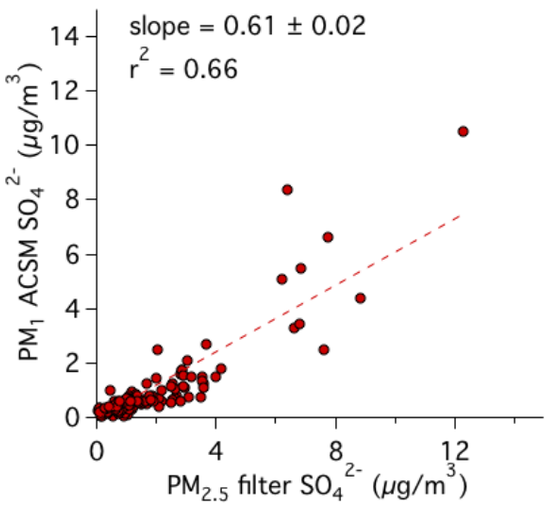
THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

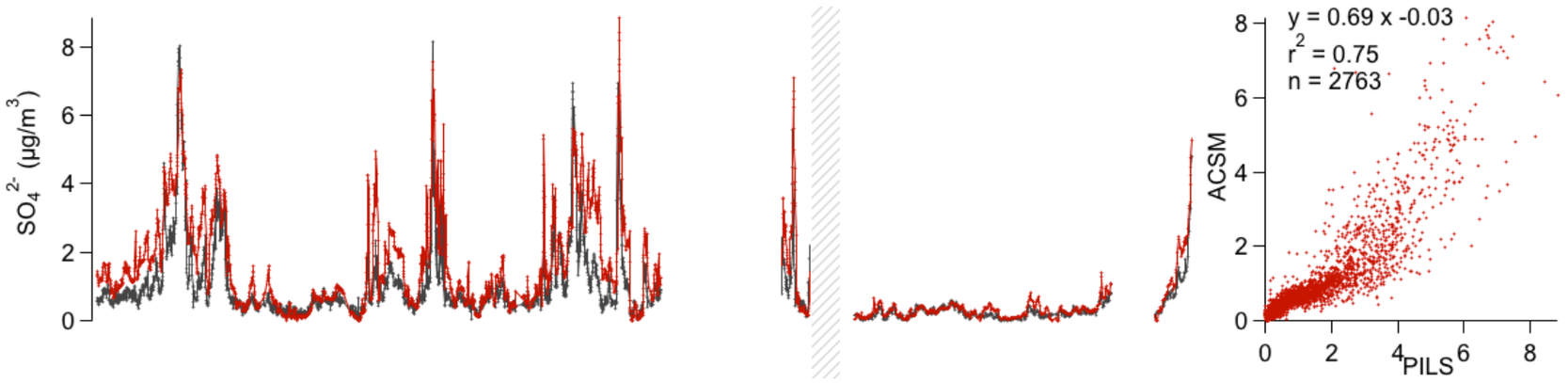
Specie by specie

FILTERS



PILS-IC





Underestimation of ACSM for SO_4. Can be due to:

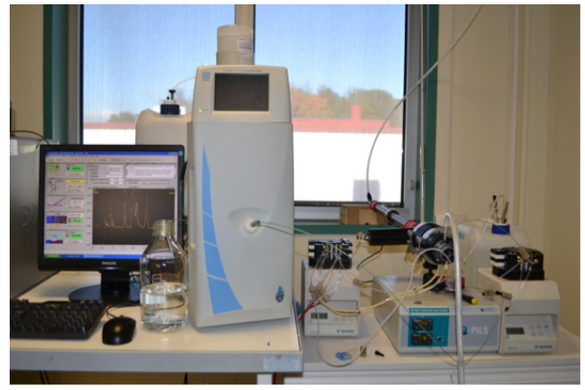
- PILS and filters takes refractory SO_4 into account
- Some SO_4 may be found between $PM_{2.5}$ and PM_1
- Bouncing effect and fragmentation issue of SO_4 particles within the ACSM (?)

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

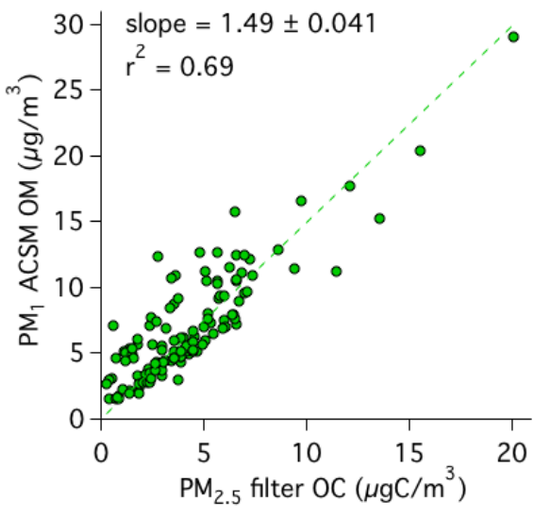
PRINCIPLE CALIBRATION DATA TREAT. COMP. EXT. DATA

Specie by specie

FILTERS



PILS-IC



Slope significantly different from Bressi et al. (2013). Can be due to:

- Sampling artefacts for filter sampling
- Some OM may be found between $PM_{2.5}$ and PM_1

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

PRINCIPLE CALIBRATION DATA TREAT. COMP. EXT. DATA

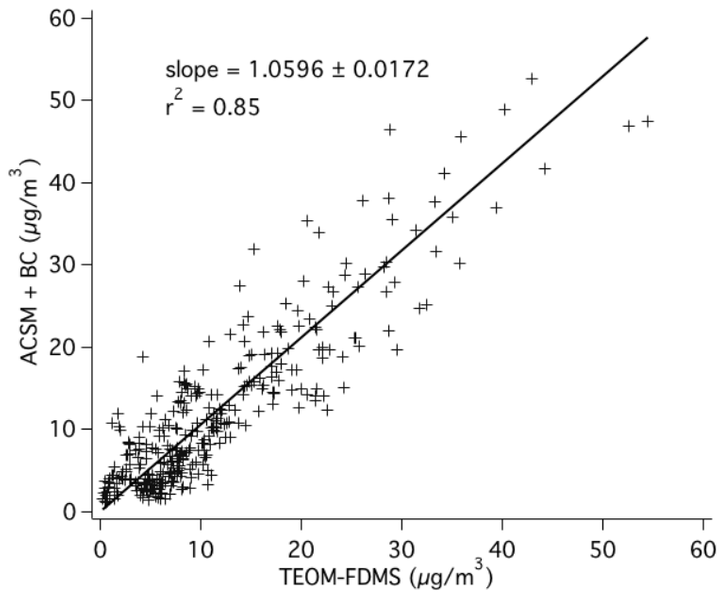
Total mass

ACSM + BC ⟷ TEOM-FDMS

Daily average

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

Total mass

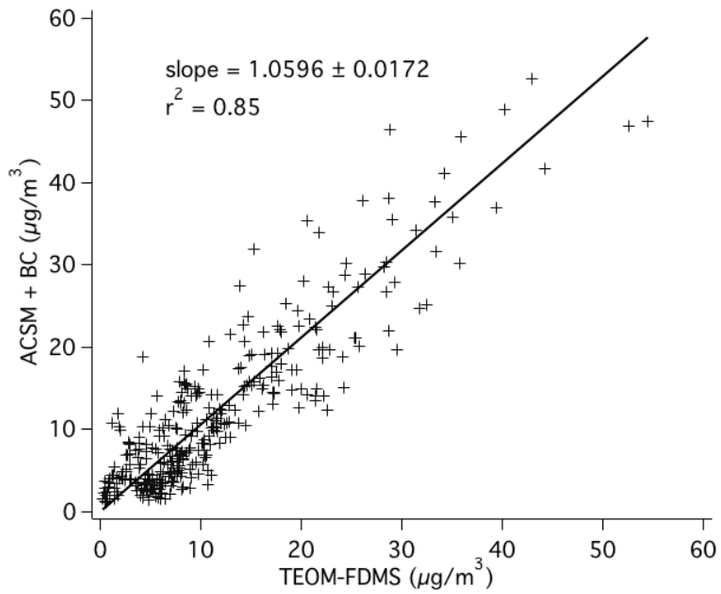


ACSM + BC ⟷ TEOM-FDMS ✔

Daily average

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

Total mass



ACSM + BC ⟷ TEOM-FDMS ✔

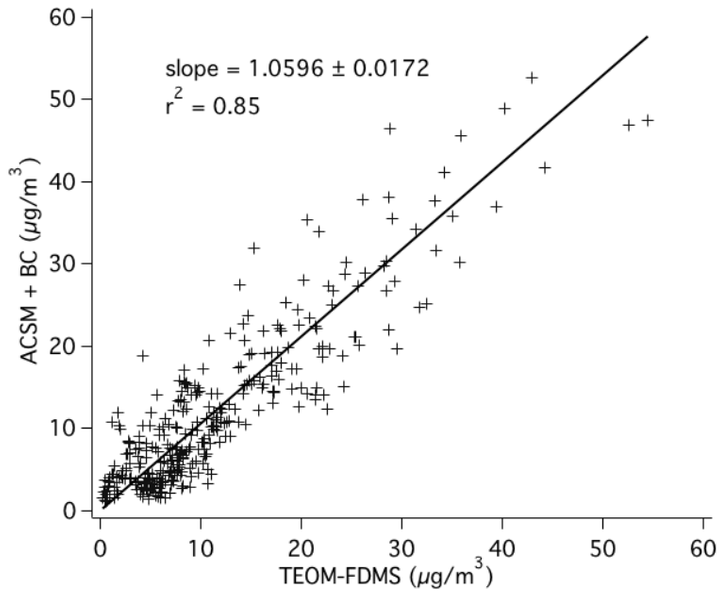
Daily average

ACSM + BC ⟷ SMPS

3-h average

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

Total mass

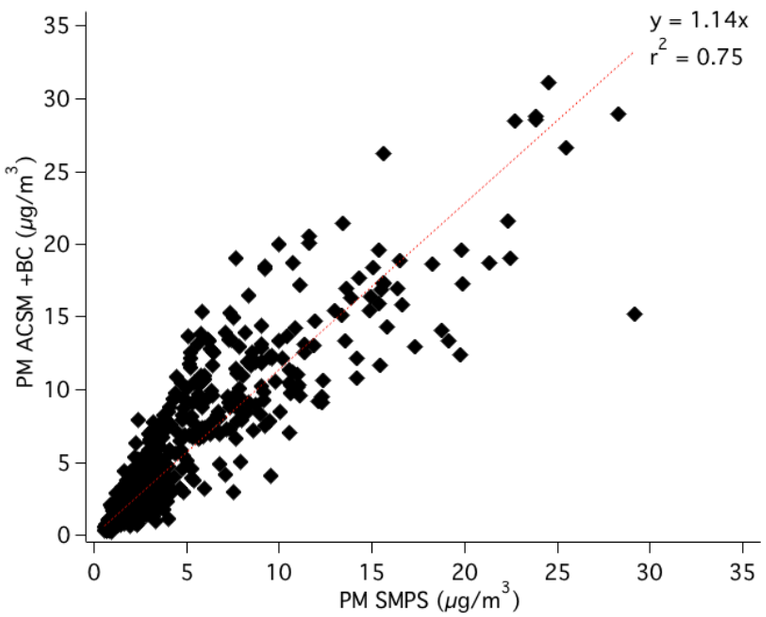


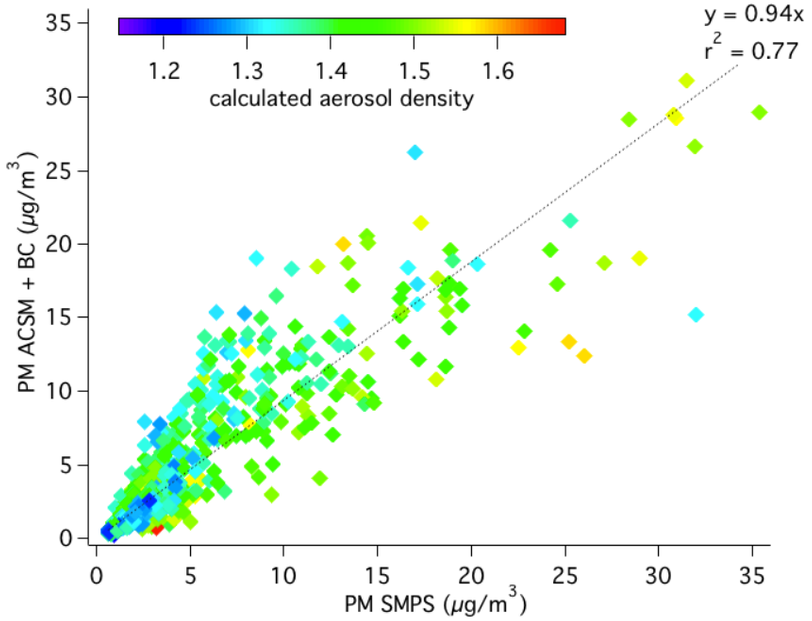
ACSM + BC ⟷ TEOM-FDMS ✔

Daily average

ACSM + BC ⟷ SMPS ✔

3-h average





Atmos. Chem. Phys. Discuss., 14, 24221–24271, 2014
www.atmos-chem-phys-discuss.net/14/24221/2014/
doi:10.5194/acpd-14-24221-2014

Atmospheric Chemistry and Physics Discussions

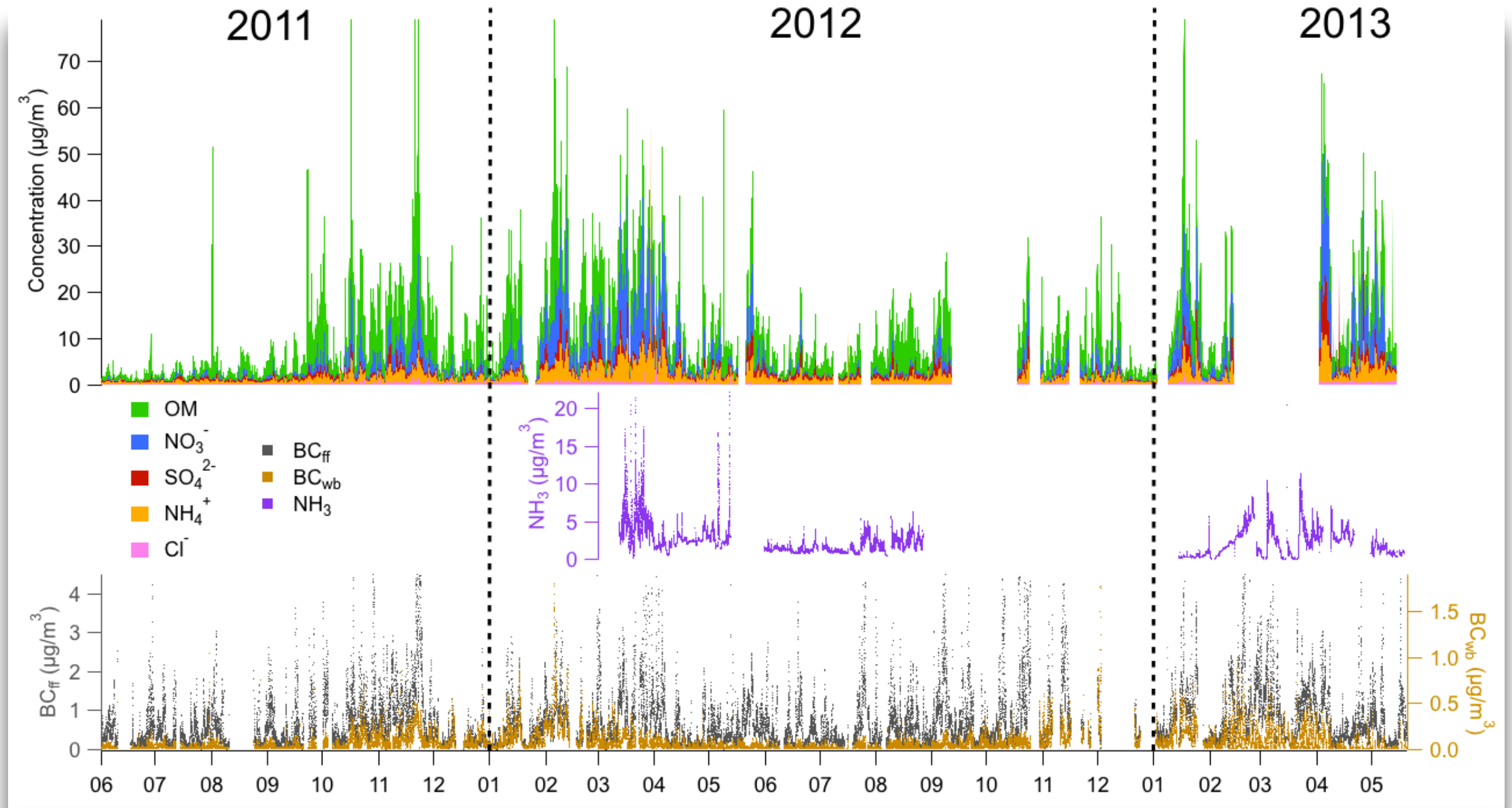
Two years of near real-time chemical composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer

J.-E. Petit[1,2], O. Favez[1], J. Sciare[2], V. Crenn[2], R. Sarda-Estève[2], N. Bonnaire[2], G. Močnik[3], J.-C. Dupont[4], M. Haeffelin[4], and E. Leoz-Garziandia[1]

[1]Institut National de l'Environnement Industriel et des Risques, Verneuil-en-Halatte, France
[2]Laboratoire des Sciences du Climat et de l'Environnement (CNRS-CEA-UVSQ), CEA Orme des Merisiers, Gif-sur-Yvette, France
[3]Aerosol d.o.o., Ljubljana, Slovenia
[4]Laboratoire de Météorologie Dynamique, Institut Pierre Simon Laplace, Ecole Polytechnique, Palaiseau, France

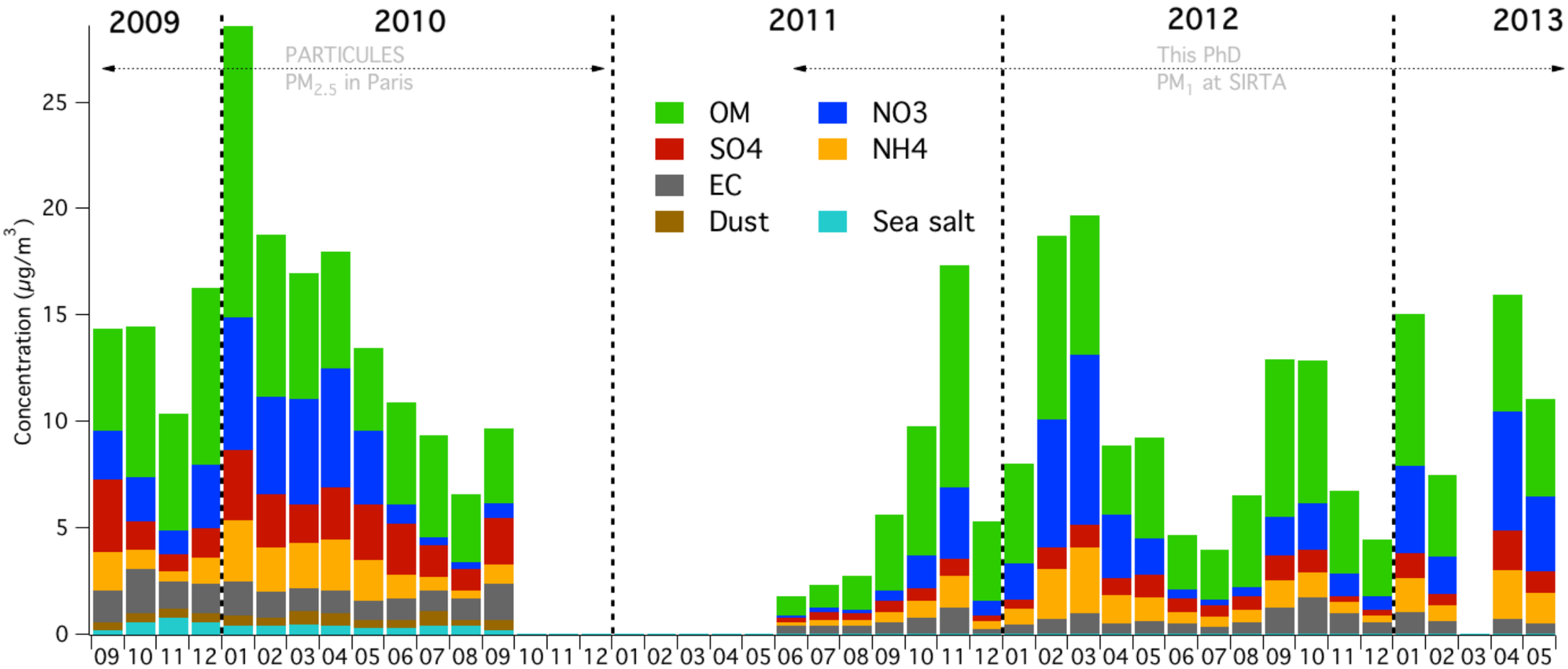
SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES



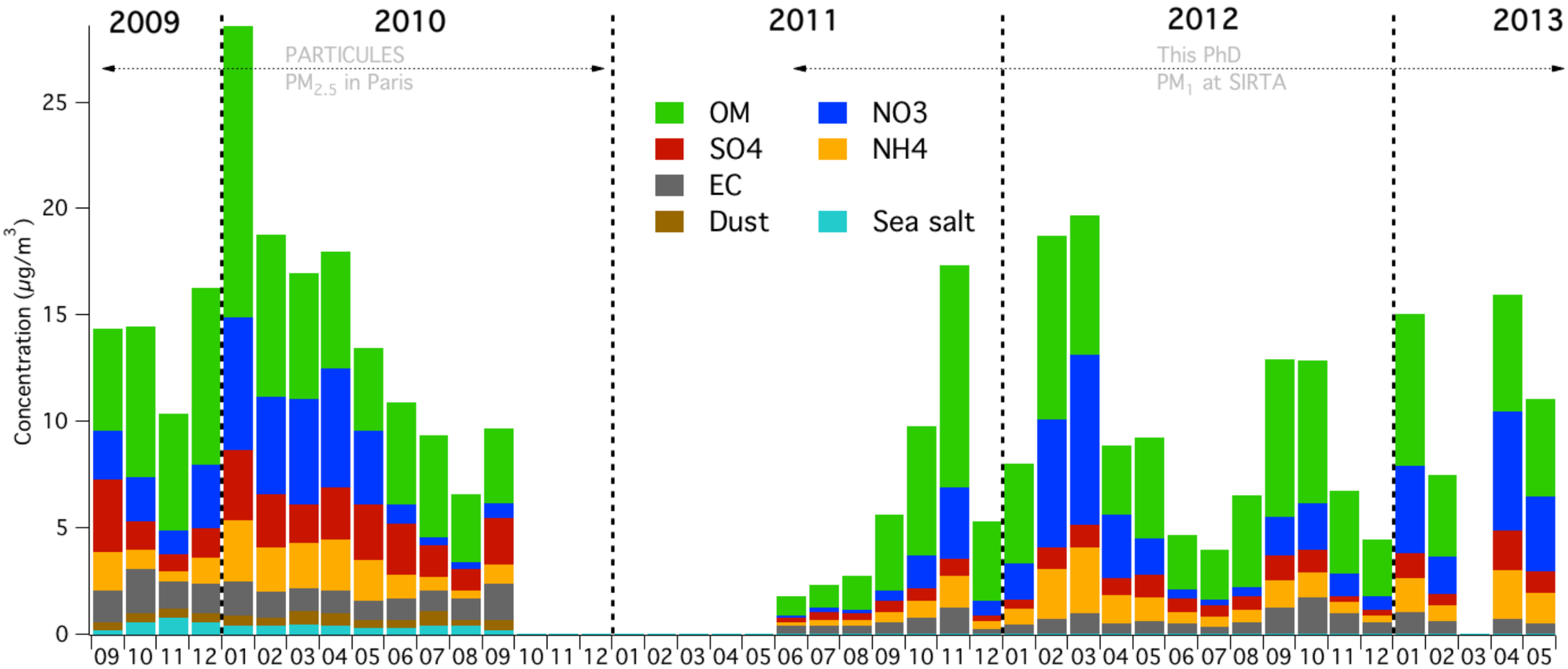
SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

SEASONALITY GEO. ORIGINS POLL. EPISODES



SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

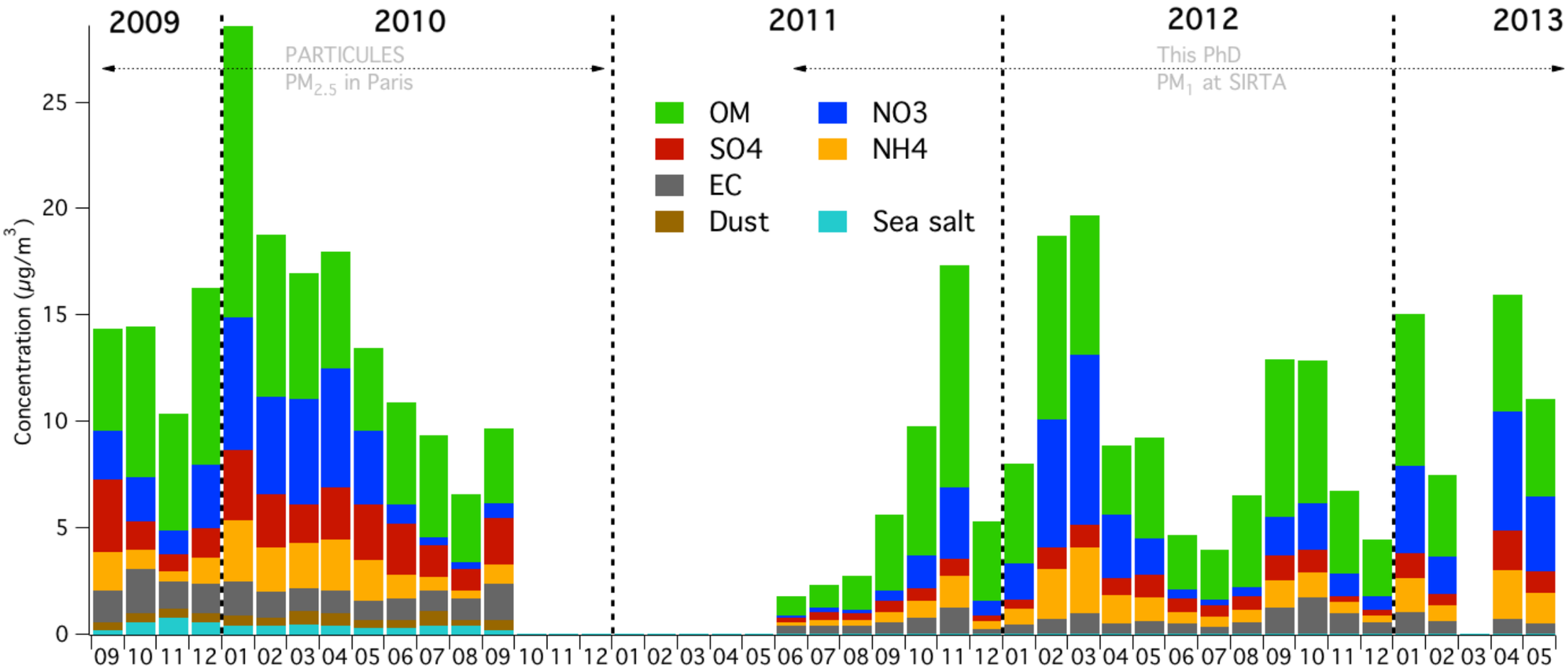
SEASONALITY GEO. ORIGINS POLL. EPISODES



Highest concentrations in late autumn/winter/early spring

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

SEASONALITY GEO. ORIGINS POLL. EPISODES



Highest concentrations in late autumn/winter/early spring

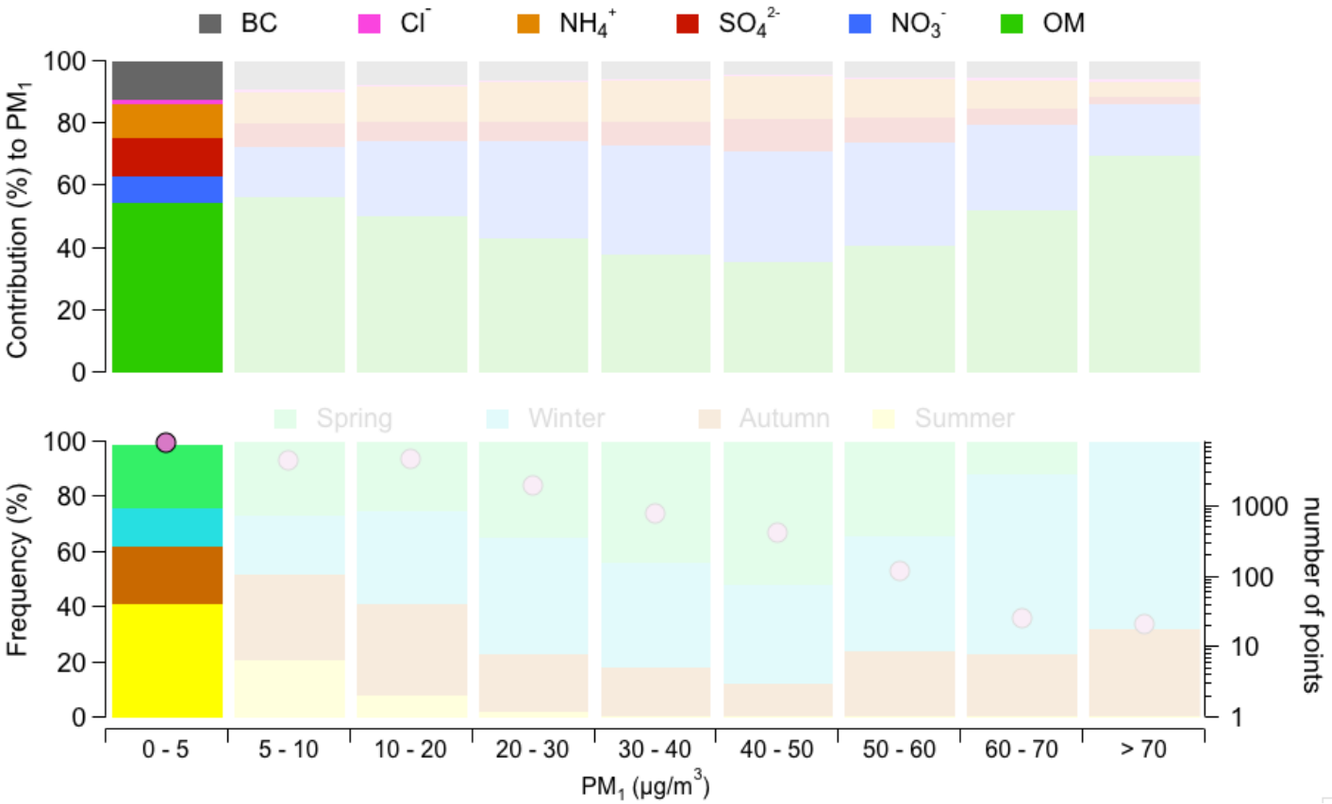
High contribution of OM in winter

High contribution of NH_4NO_3 during spring

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

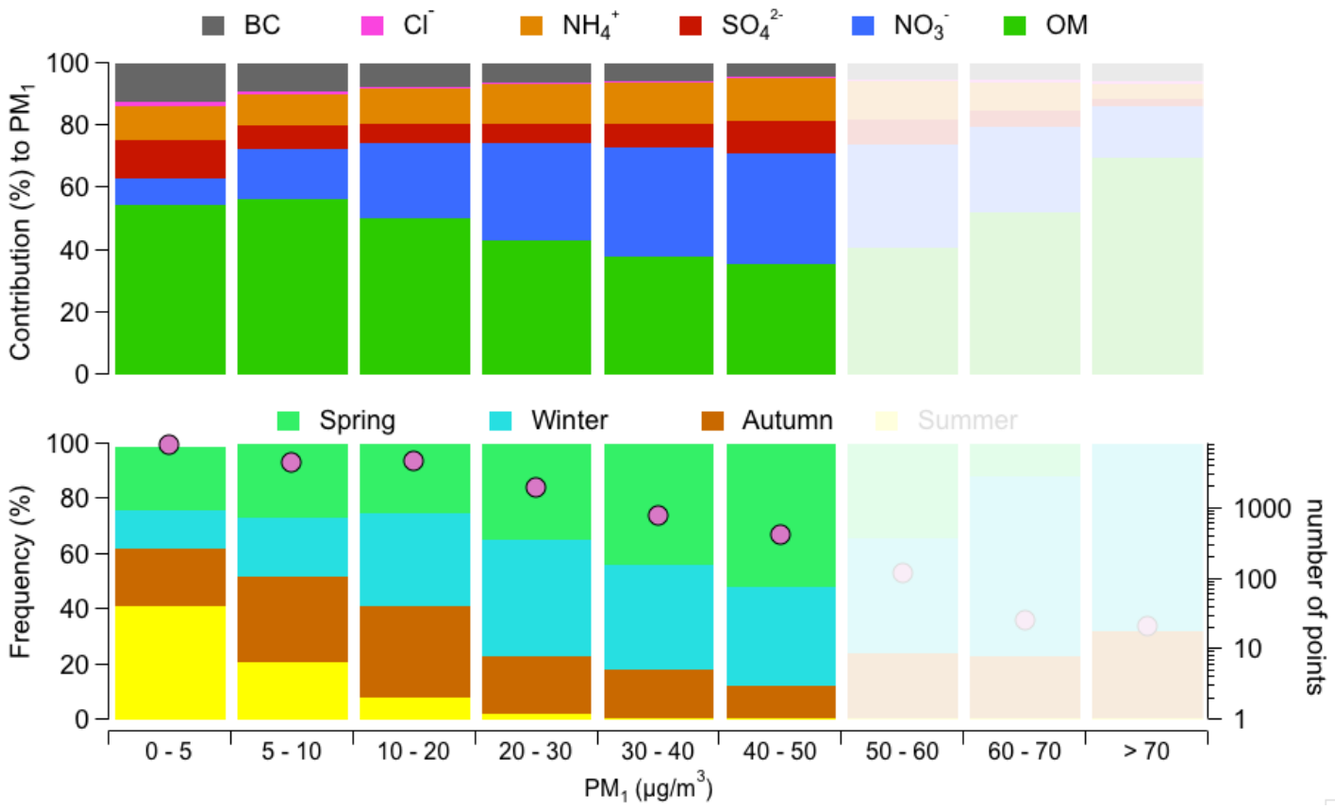
Concentration size boxes



SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

Concentration size boxes



- Increasing contribution of ammonium nitrate along with springtime data until 50 µg/m^3

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

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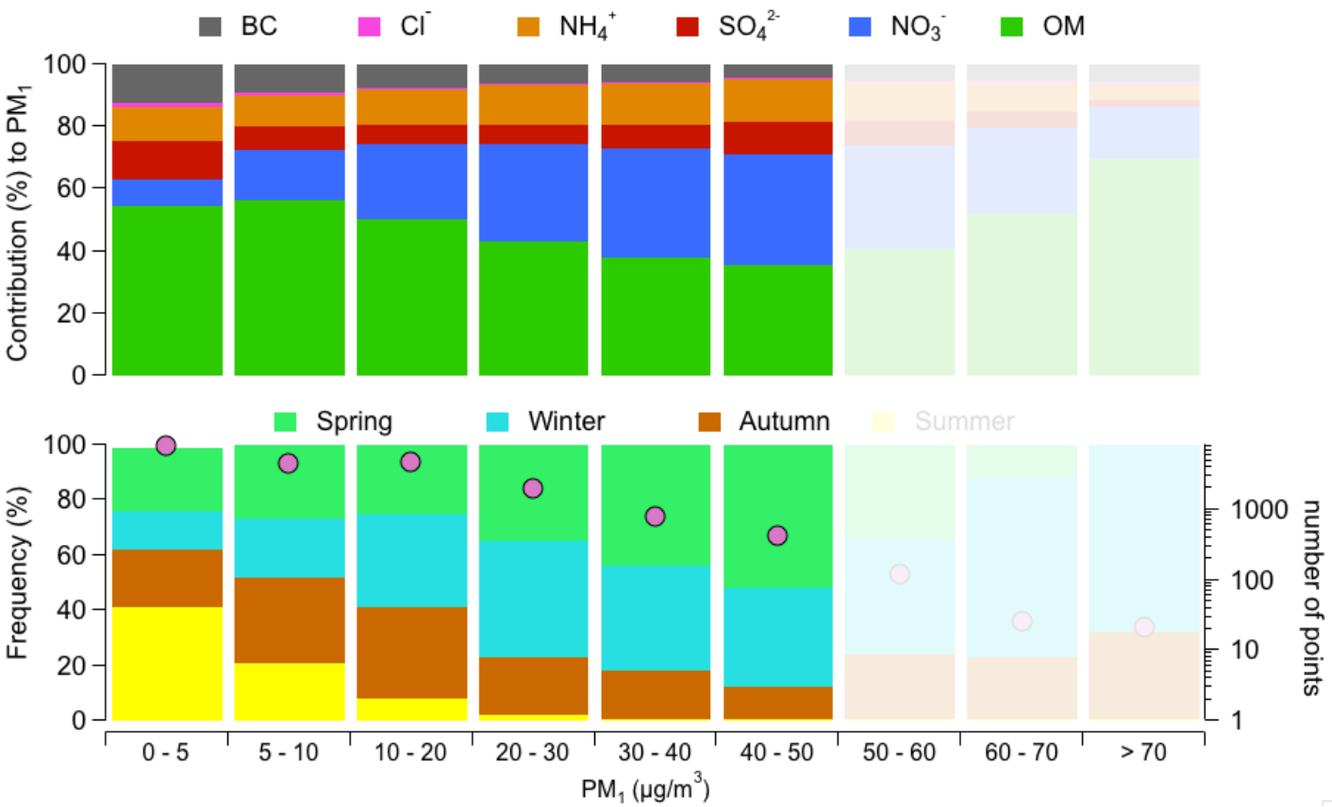

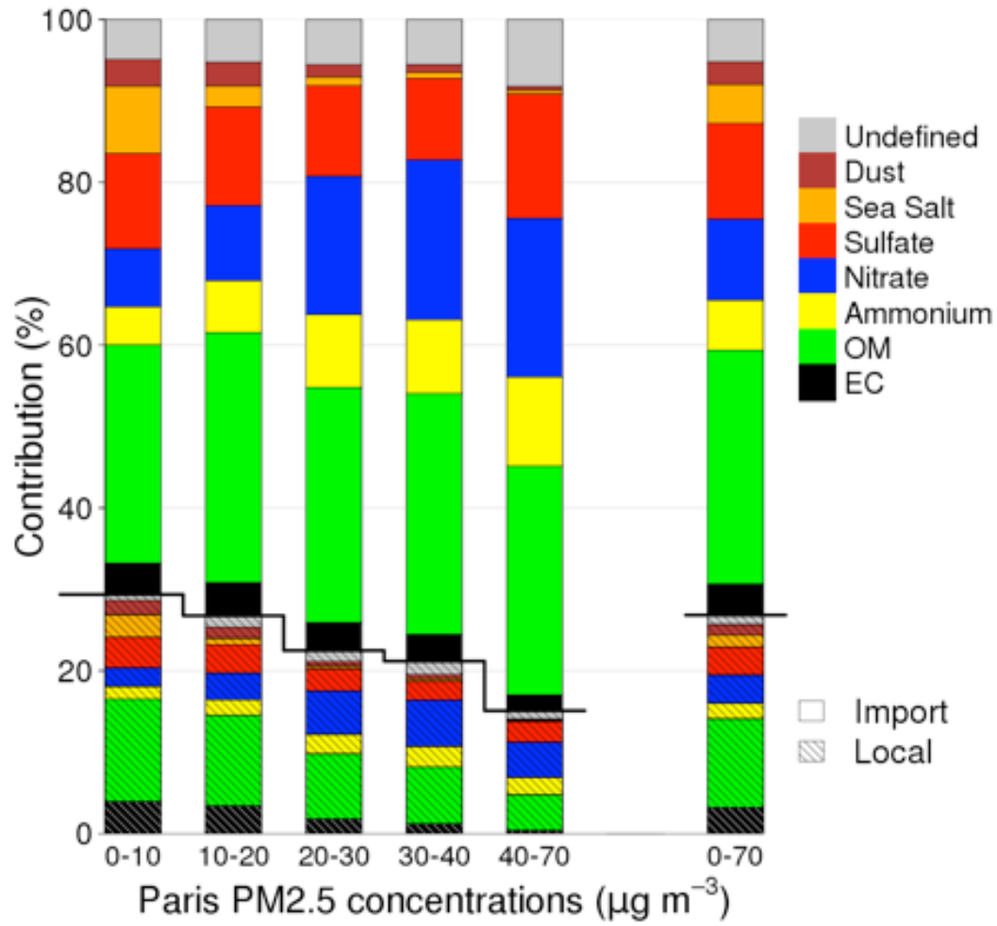

- Increasing contribution of ammonium nitrate along with springtime data until 50 µg/m^3

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

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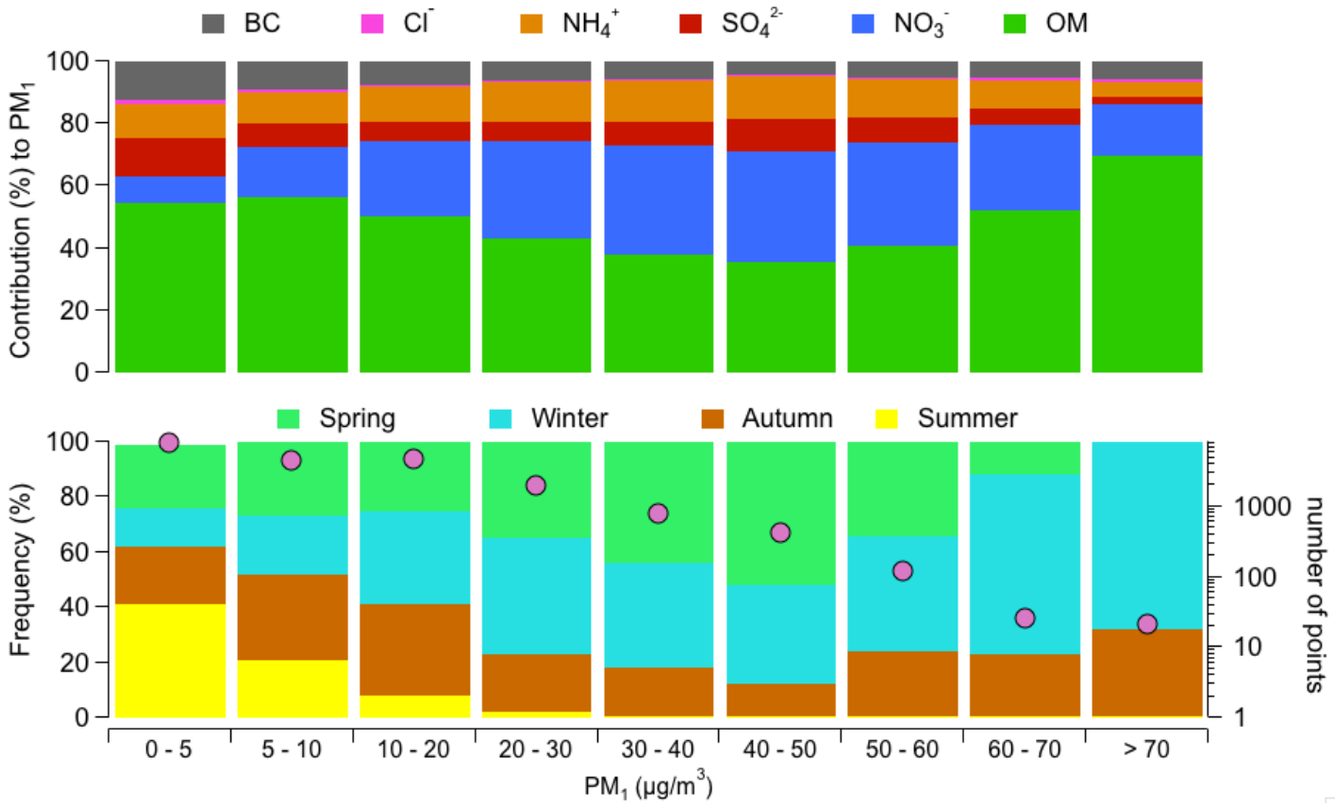

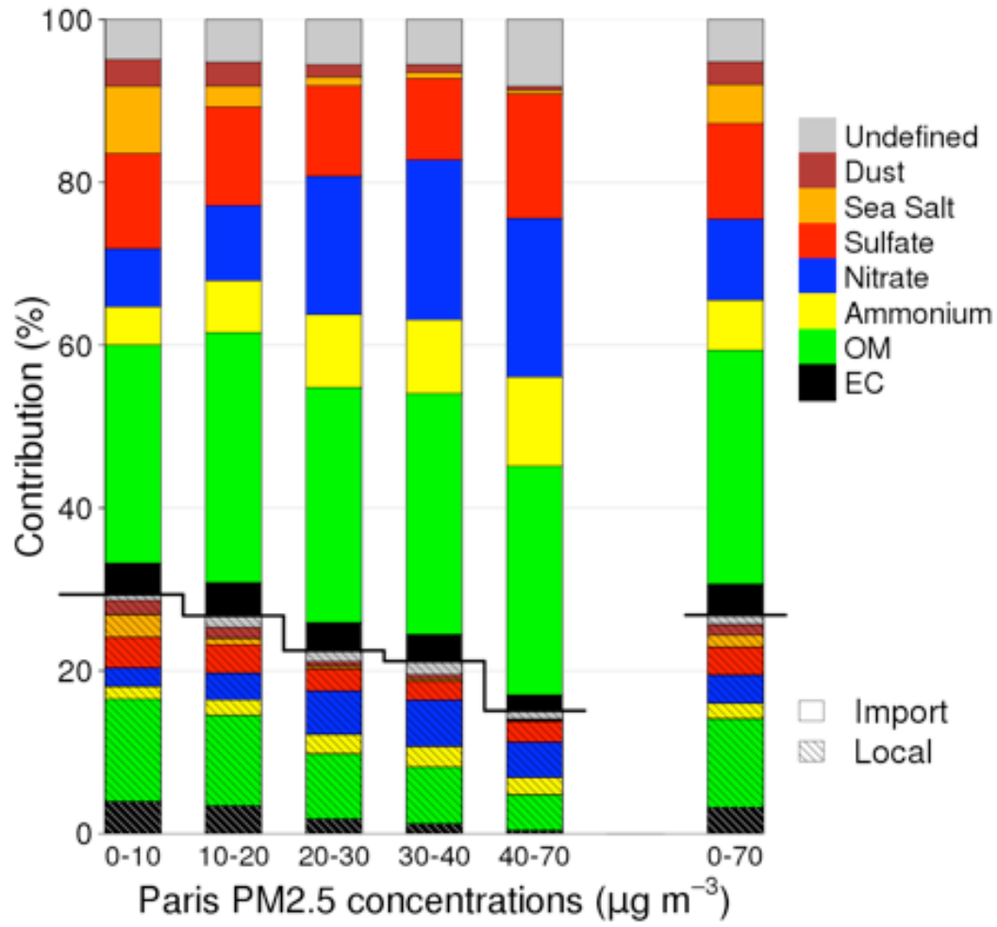

- Increasing contribution of ammonium nitrate along with springtime data until 50 µg/m^3

- Beyond, highest concentrations measured mostly in winter, with a strong contribution of OM

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

Non-parametric Wind Regression

Smoothing calculation by weighted averaged, whose coefficients are determined by kernel functions

$$E(\theta,u)=\frac{\sum_{i}^{N} K_1\left(\frac{\theta\text{-}W_i}{\sigma}\right)\cdot K_2\left(\frac{u\text{-}Y_i}{h}\right)\cdot C_i}{\sum_{i}^{N} K_1\left(\frac{\theta\text{-}W_i}{\sigma}\right)\cdot K_2\left(\frac{u\text{-}Y_i}{h}\right)}$$

- W_i: wind direction at t_i
- Y_i: wind speed at t_i
- C_i: concentration of the pollutant at t_i

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

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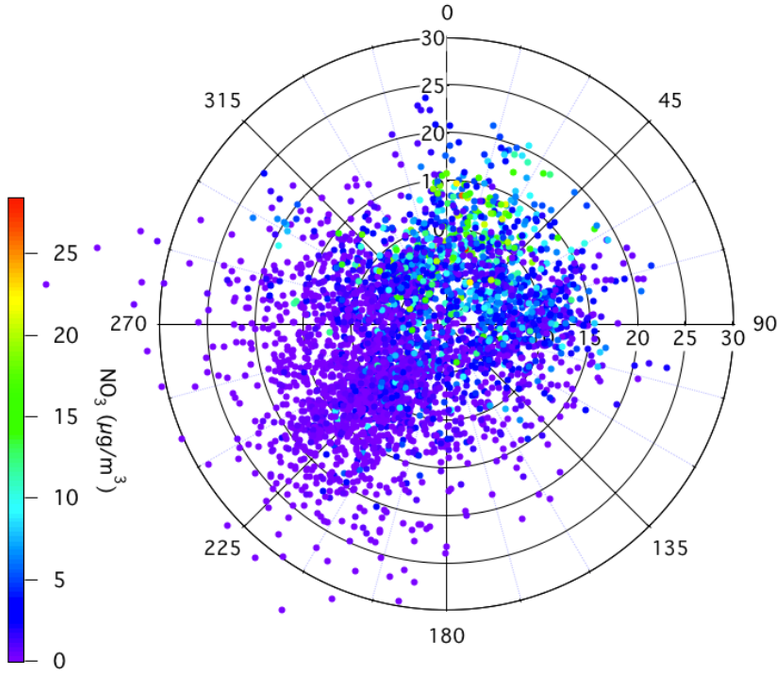

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

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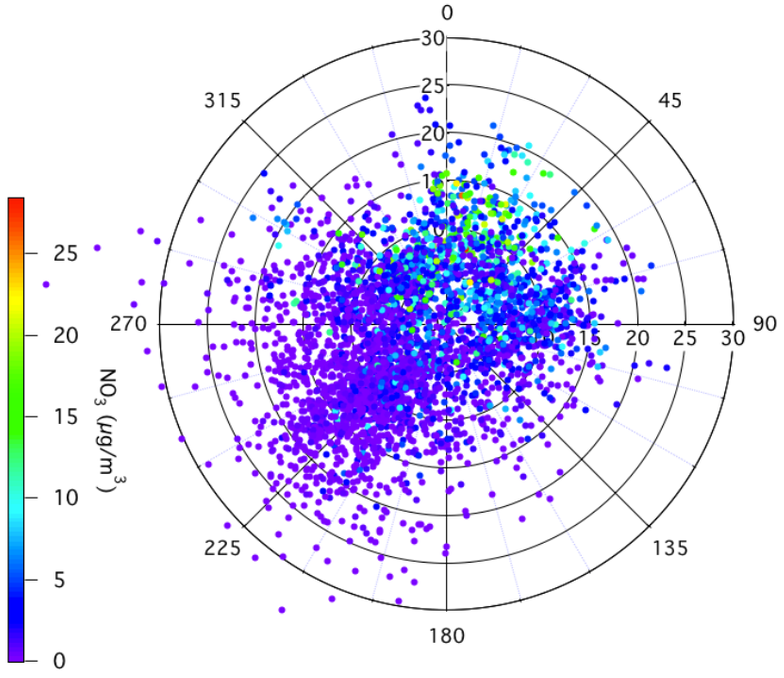
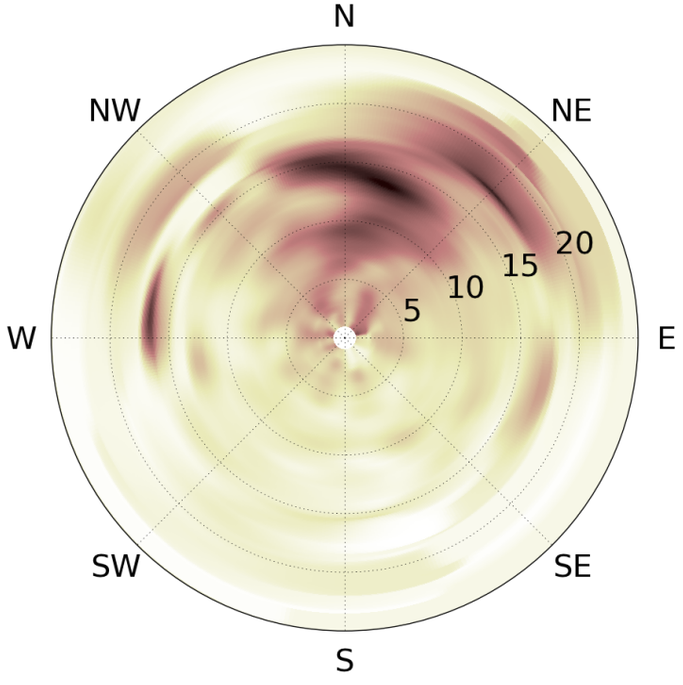


NWR



SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

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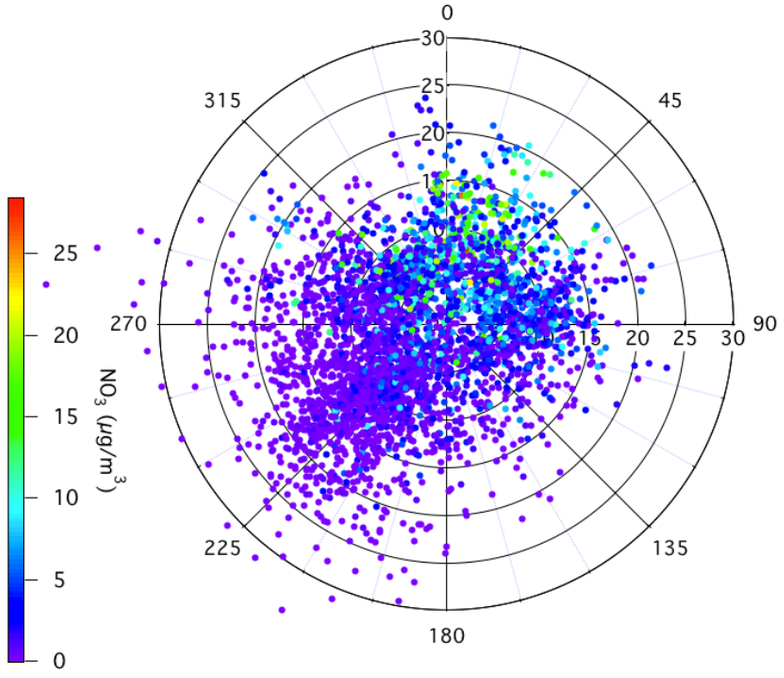

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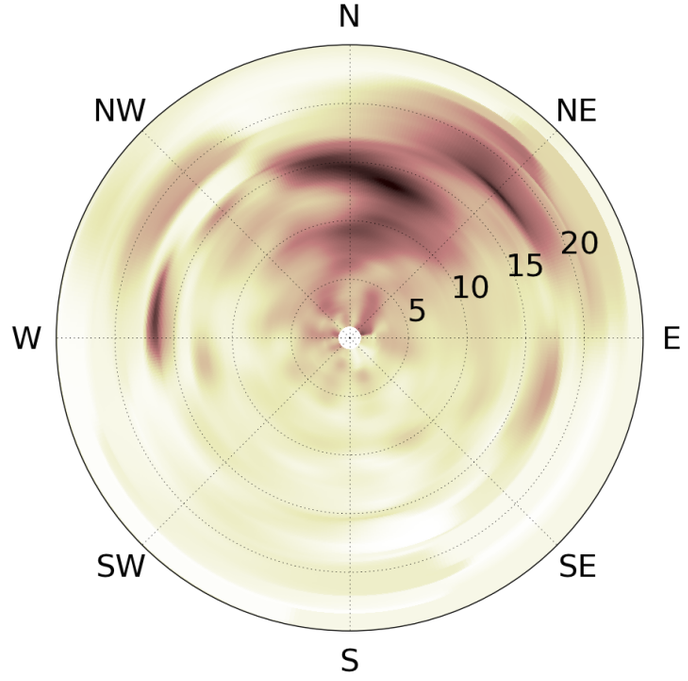


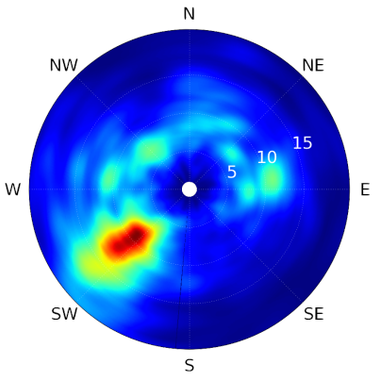
Developed by Henry et al. (2009), but I coded a custom Python script to perform the calculation.

Seasonality, Geographical Origins & Poll. Episodes

From June 2011 to May 2013:

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

rose des vents



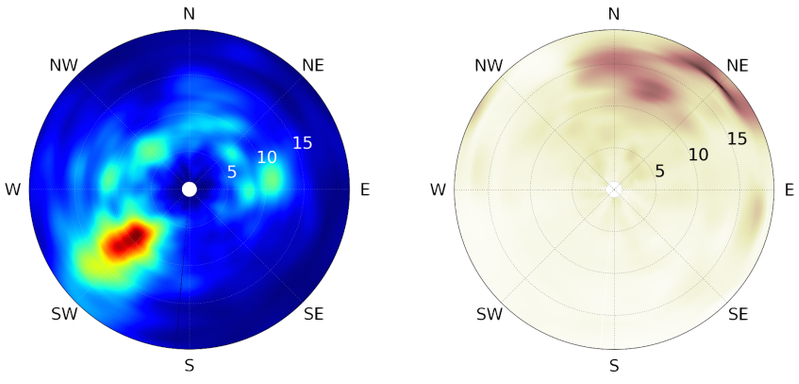
From June 2011 to May 2013:

- IdF mainly influenced by SW winds are moderate speed

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

rose des vents SO_4^{2-}



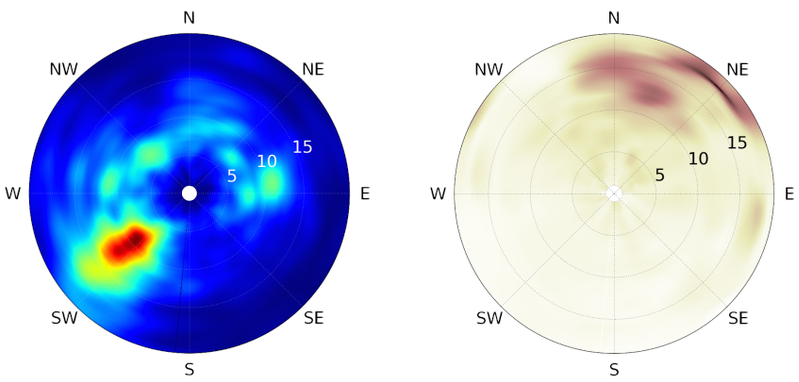
From June 2011 to May 2013:

- IdF mainly influenced by SW winds are moderate speed
- SO_4^{2-} : no major SO_2 sources in IdF; slow transformation to SO_4^{2-} ⟶ advected

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

rose des vents SO_4^{2-}



From June 2011 to May 2013:

- IdF mainly influenced by SW winds are moderate speed
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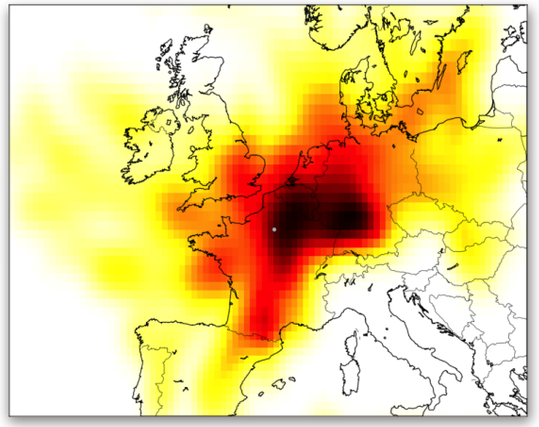
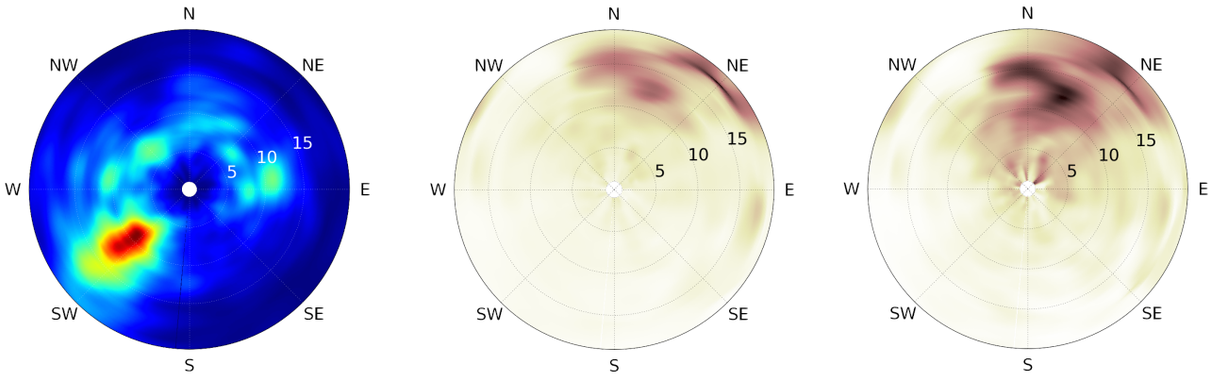
AMMONIUM SULFATE RICH SOURCE



SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

rose des vents SO_4^{2-} NO_3^-



From June 2011 to May 2013:

- IdF mainly influenced by SW winds are moderate speed
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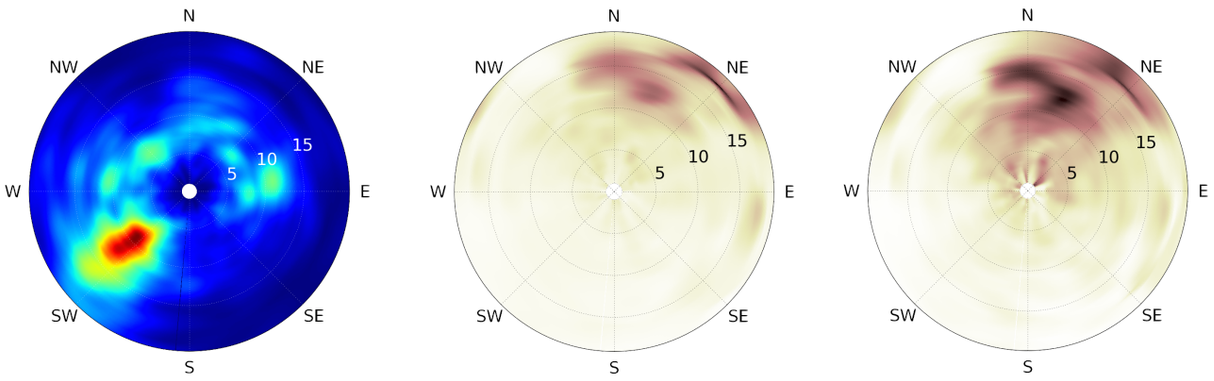
- NO_3^- : advected + Paris city plume

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

rose des vents SO_4^{2-} NO_3^-



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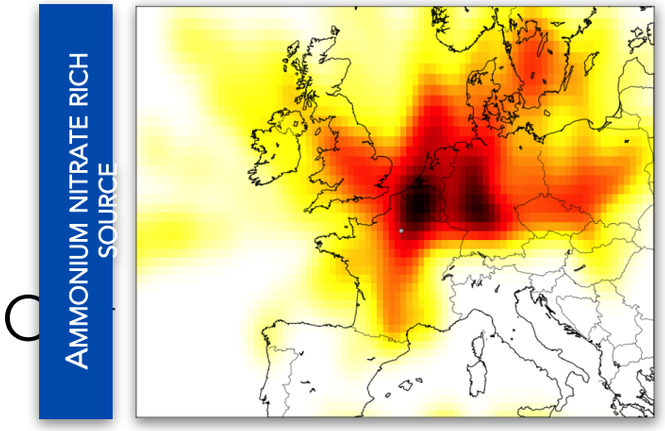
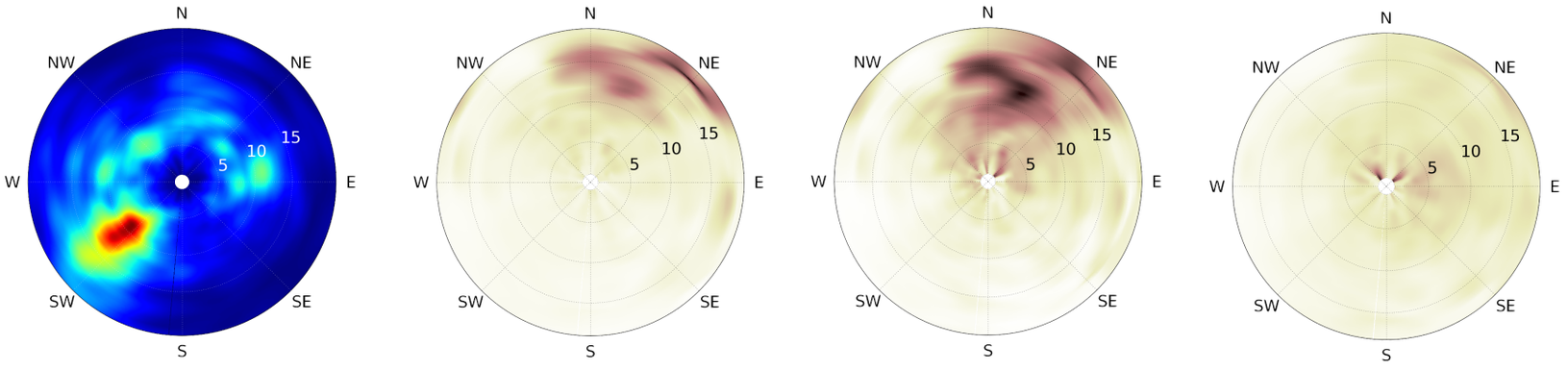


SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES | GEO. ORIGINS | POLL. EPISODES

rose des vents | SO_4^{2-} | NO_3^- | OM



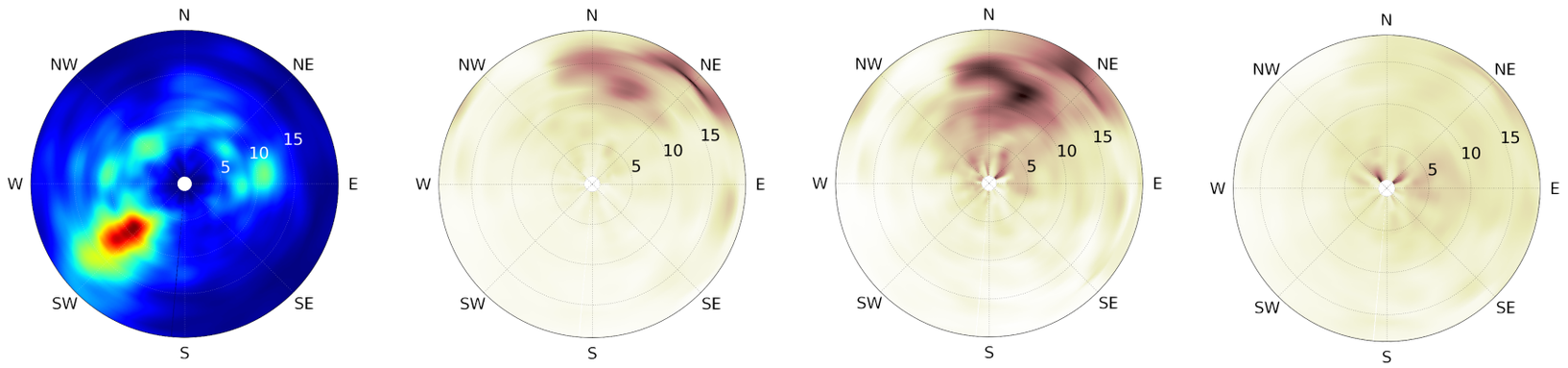
From June 2011 to May 2013:

- IdF mainly influenced by SW winds are moderate speed
- SO_4^{2-} : no major SO_2 sources in IdF; slow transformation to SO_4^{2-} ⟶ advected
- NO_3^- : advected + Paris city plume
- OM : high local concentrations, significant regional background

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

rose des vents SO_4^{2-} NO_3^- OM



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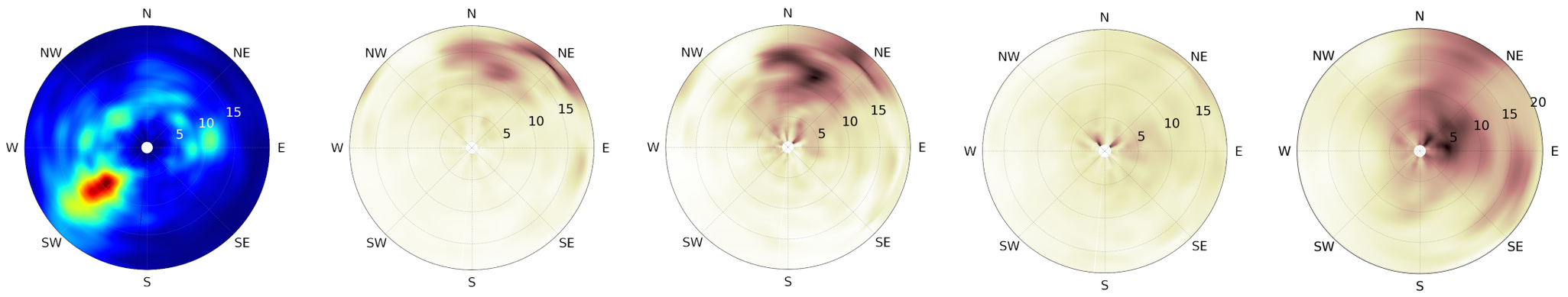
SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

rose des vents SO_4^{2-} NO_3^- OM BC



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SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES | GEO. ORIGINS | POLL. EPISODES

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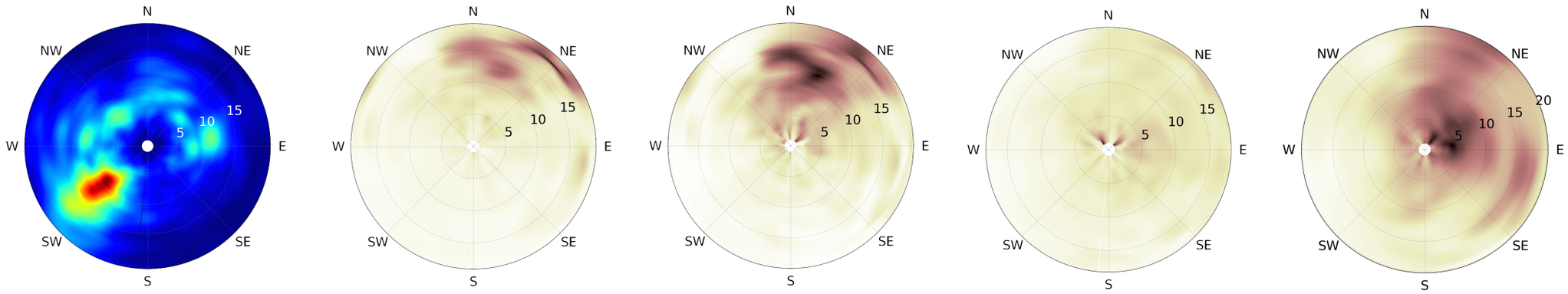

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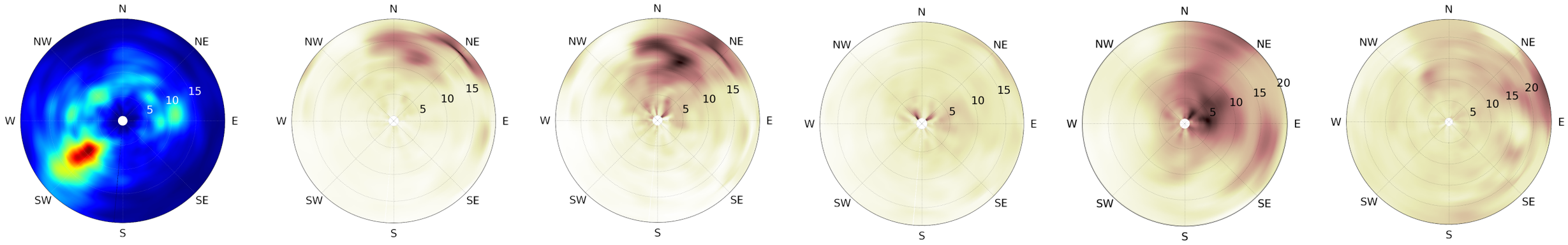
SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

rose des vents SO_4^{2-} NO_3^- OM BC NH_3



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- NO_3^- : advected + Paris city plume
- OM : high local concentrations, significant regional background
- BC: local + Paris city plume
- NH_3 : Insignificant impact of NH_3 emissions from Brittany, significant regional background

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

Clustering

Statistically compile back-trajectories into average air masses

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

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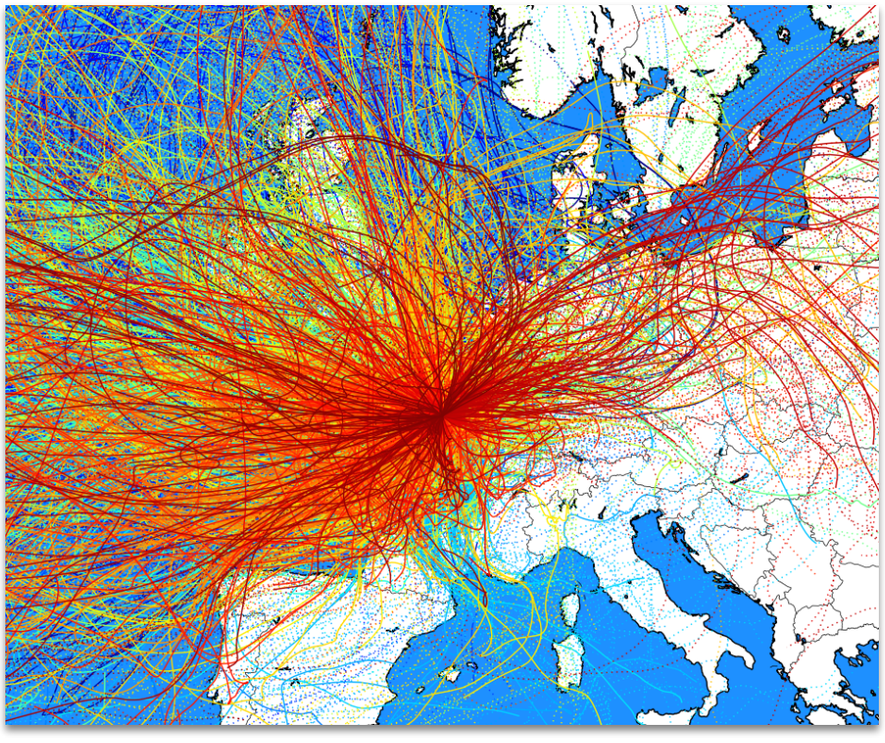
Statistically compile back-trajectories into average air masses

From 06/2011 to 05/2013, 2030 back-trajectories….



SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

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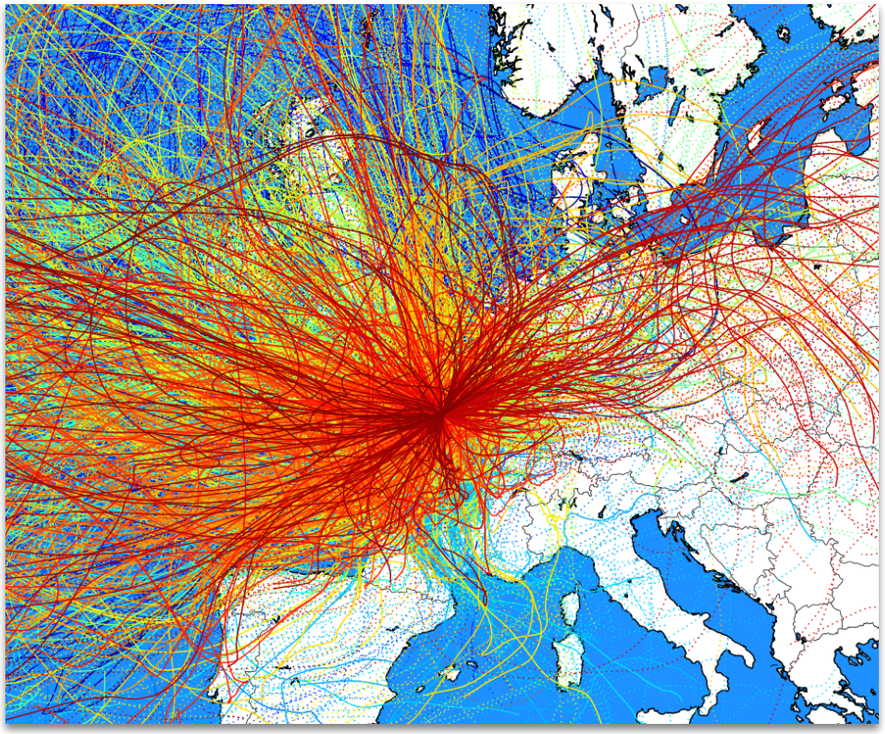
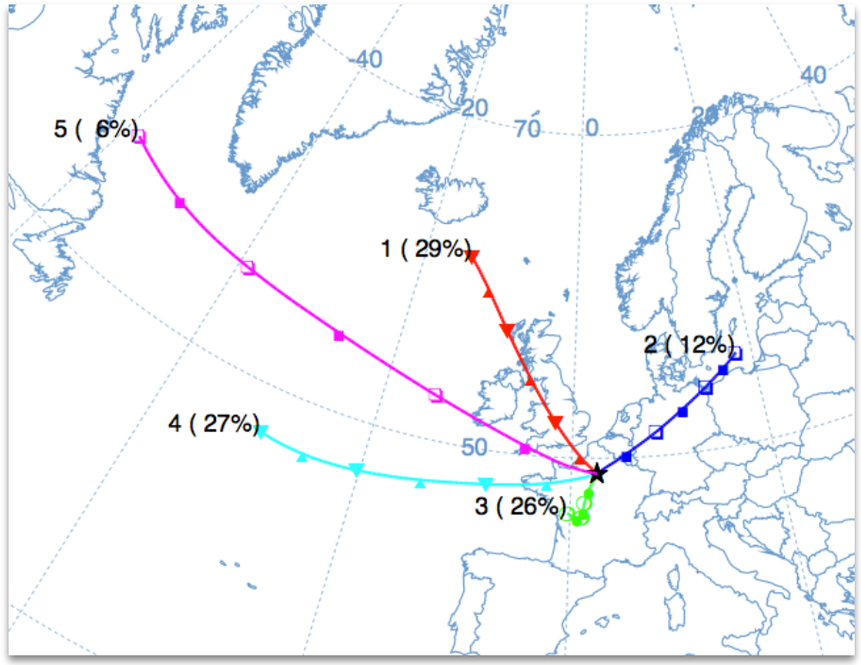


cluster



calculations performed with Hysplit 4

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

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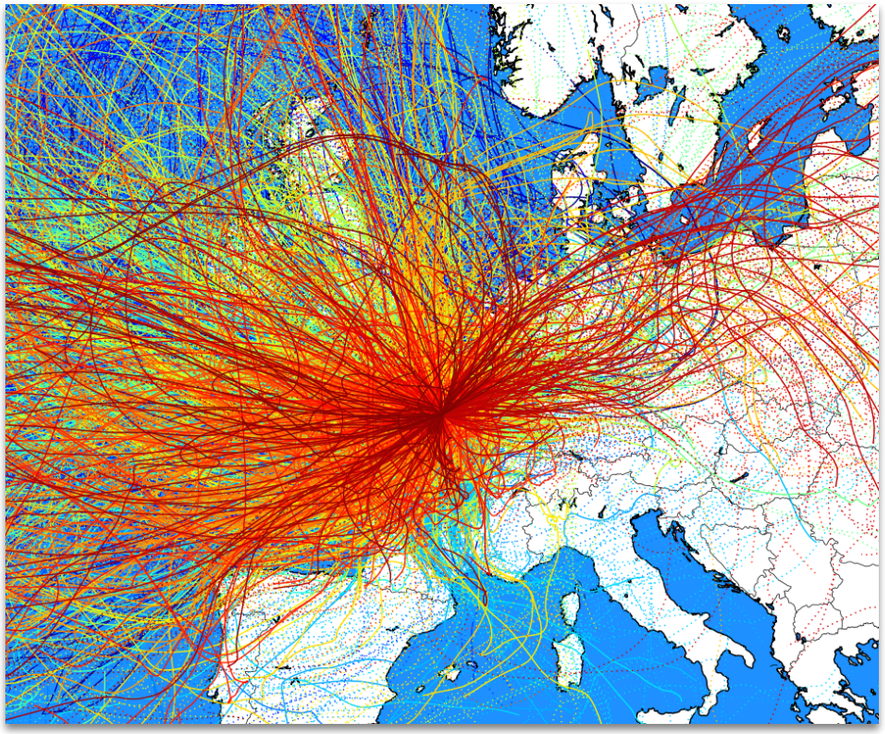

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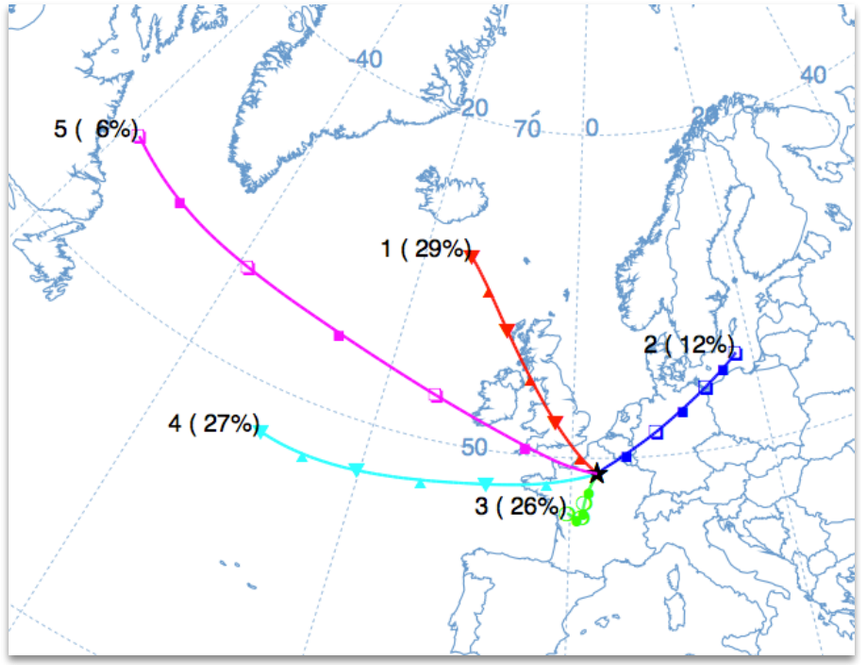


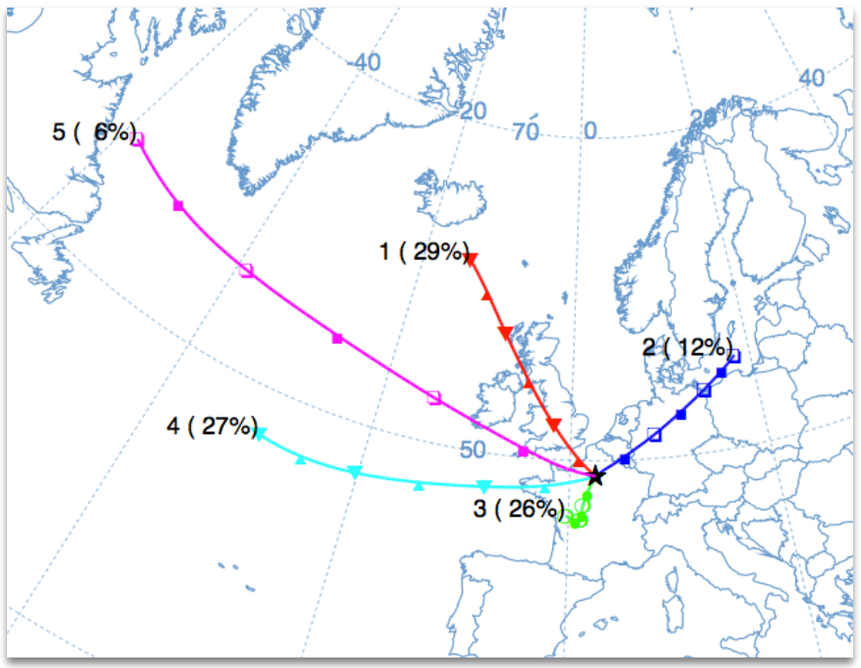
calculations performed with Hysplit 4

\+ : Uncertainties associated to each back trajectories are smoothed out

\- : Geo. origin less accurate, influence of Paris plume not trivial

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES



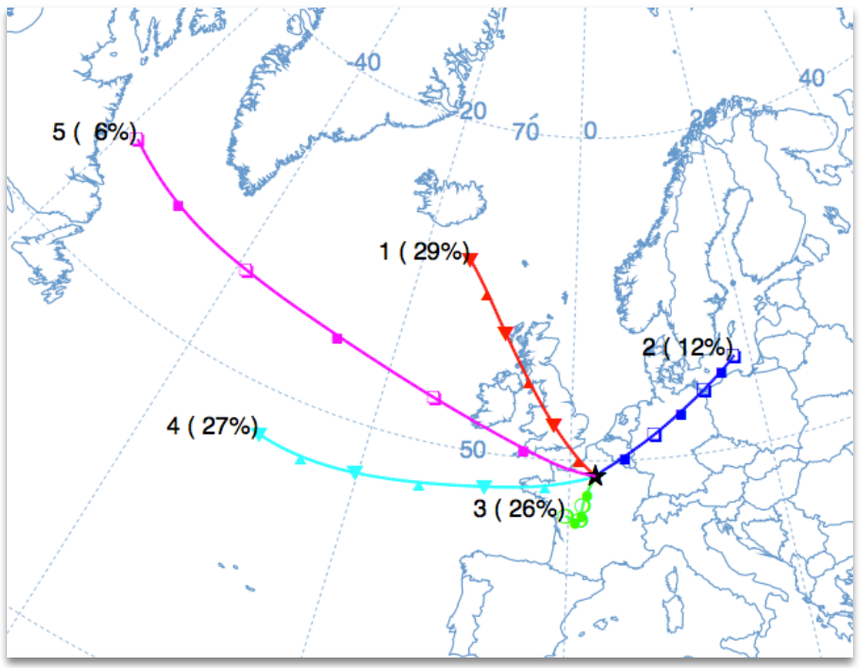
Chemical composition averaged over 6h and linked to each traj. of each cluster

→ average chemical comp. per cluster!

cluster #	OM	NO	SO	NH	Cl
1	3.3	2.1	0.6	0.9	0.06
2	8.4	6.7	1.9	2.8	0.1
3	6.7	2.8	0.81	1.3	0.06
4	2.6	0.7	0.4	0.5	0.04
5	2.33	0.6	0.2	0.3	0.05

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES



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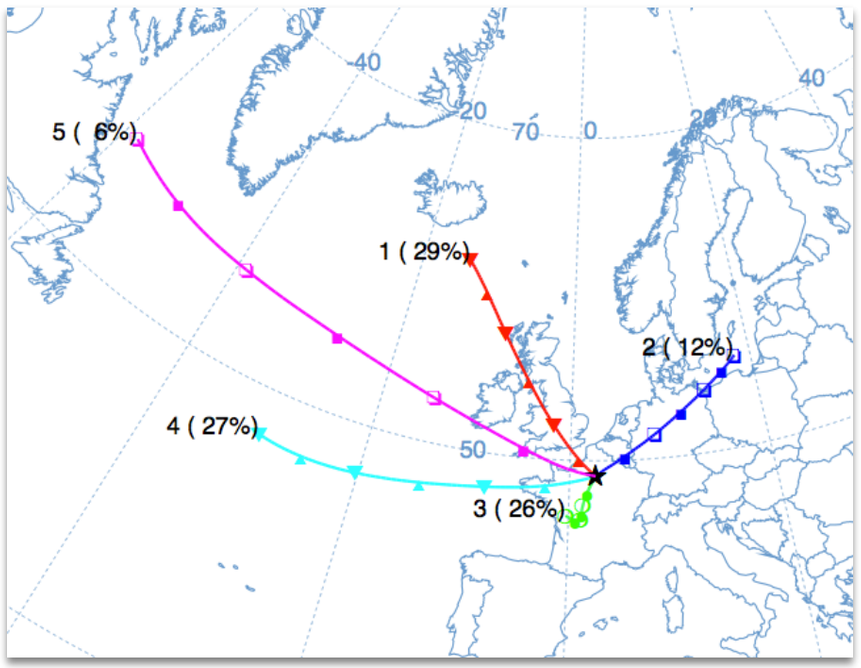
Influence of Great Britain and/or shipping and/or industries in Northern France?

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES



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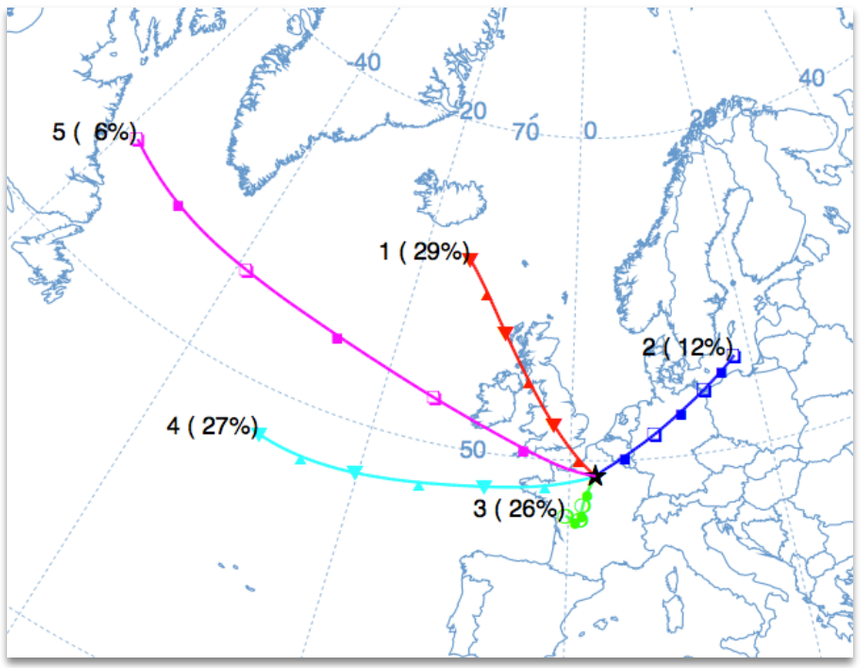
Advected pollution with highest NO_3 and SO_4, but Paris plume is uncharacterized.

These air masses are usually associated with cold temperatures in winter, favoring wood burning at local scales

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES



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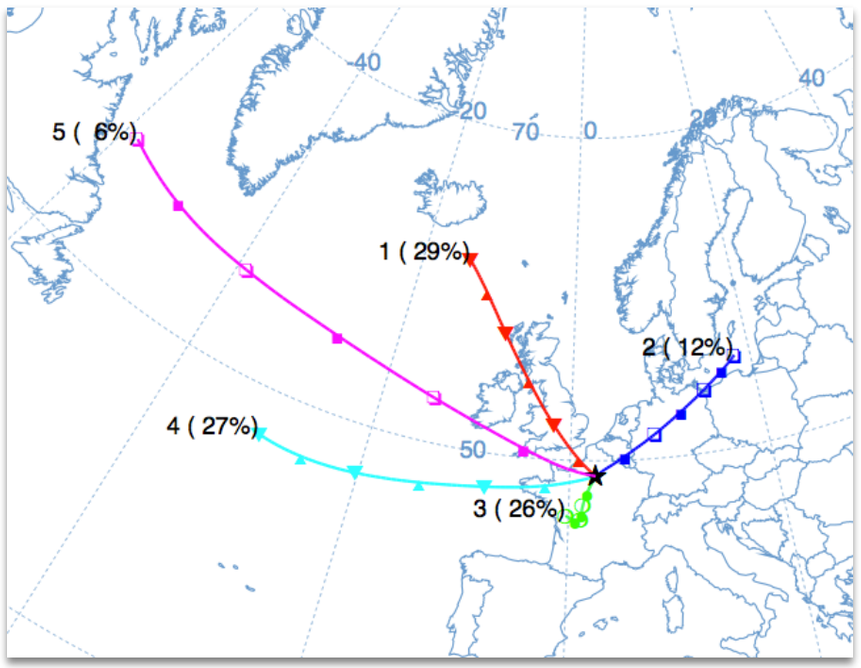
Stagnant air masses, accumulation of pollutants, concomitant with high OM and significant NO_3

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES



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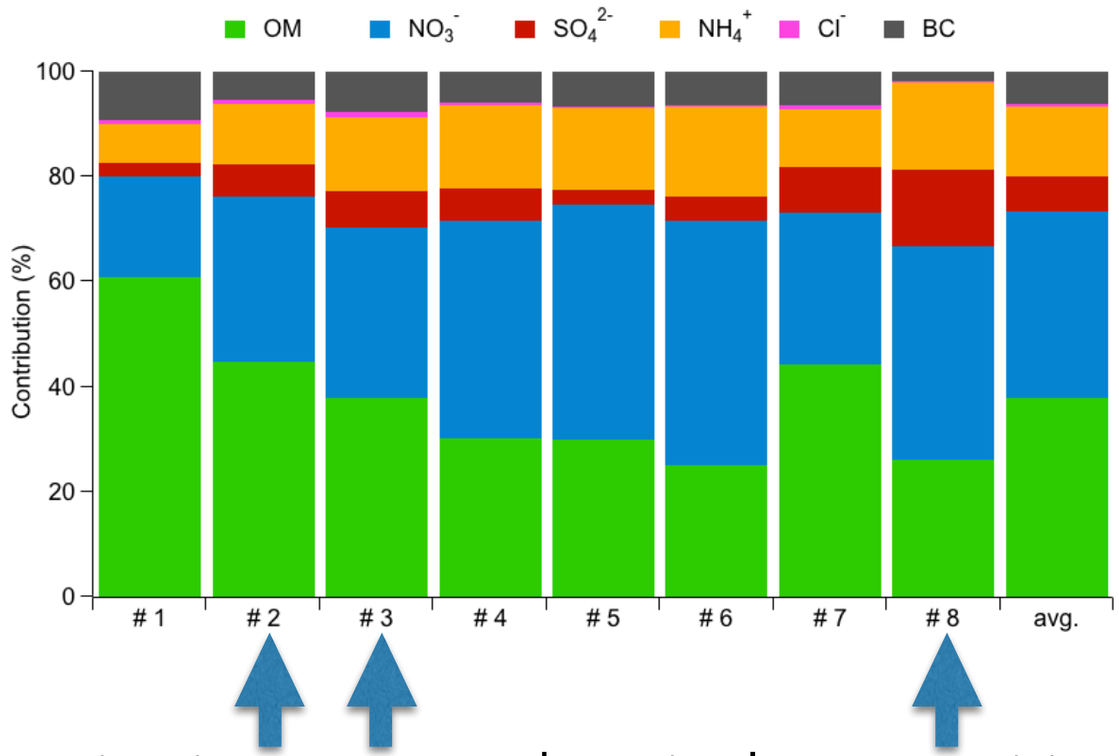
Clean air masses from the Atlantic ocean.
Low PM levels

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

Persistant pollution episode: PM_1 > 20 µg/m^3 for at least 3 consecutive days

Between June 2011 & May 2013: 8 persistant pollution episodes



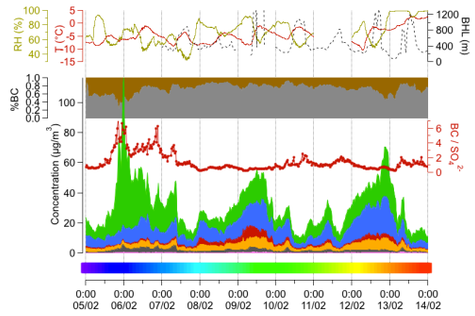
Observed discrepancies in average chemical compositions underline differences in geographical origins, and (trans)formation processes

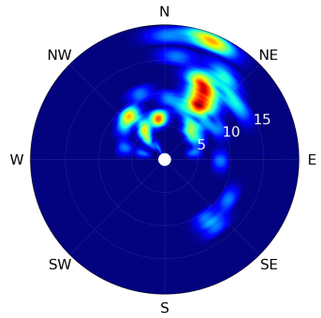
Chemical composition, BC fractions, meteo (T, RH & BLH), BC/SO_4 ratio, wind rose, and back-trajectories every 3h

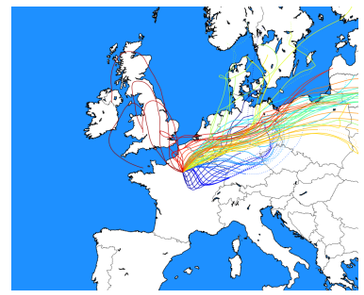
SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES

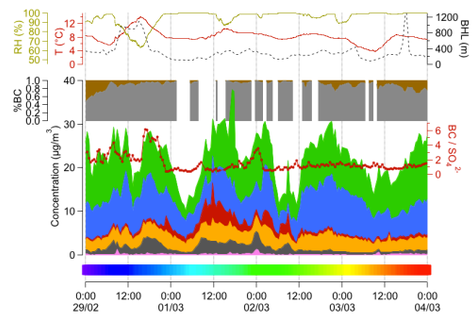
#2 05/02/2012 14/02/2012

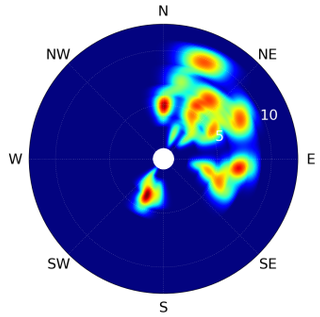


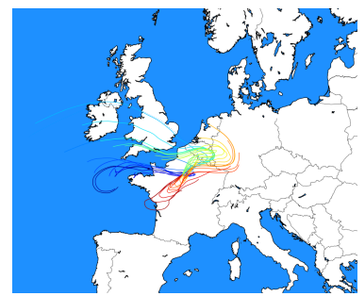




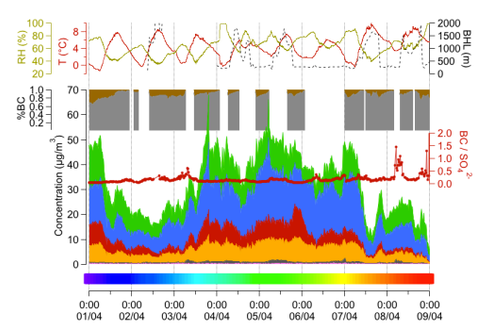
#3 29/02/2012 04/03/2012

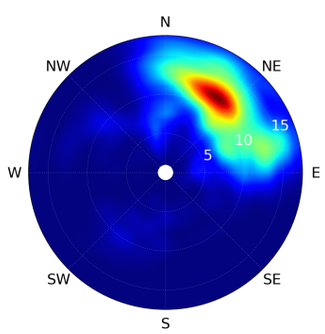


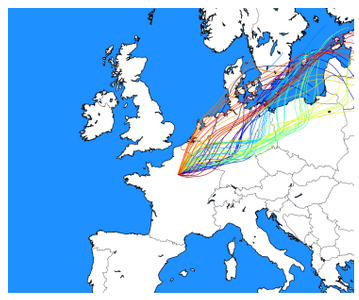




#8 01/04/2013 09/04/2013

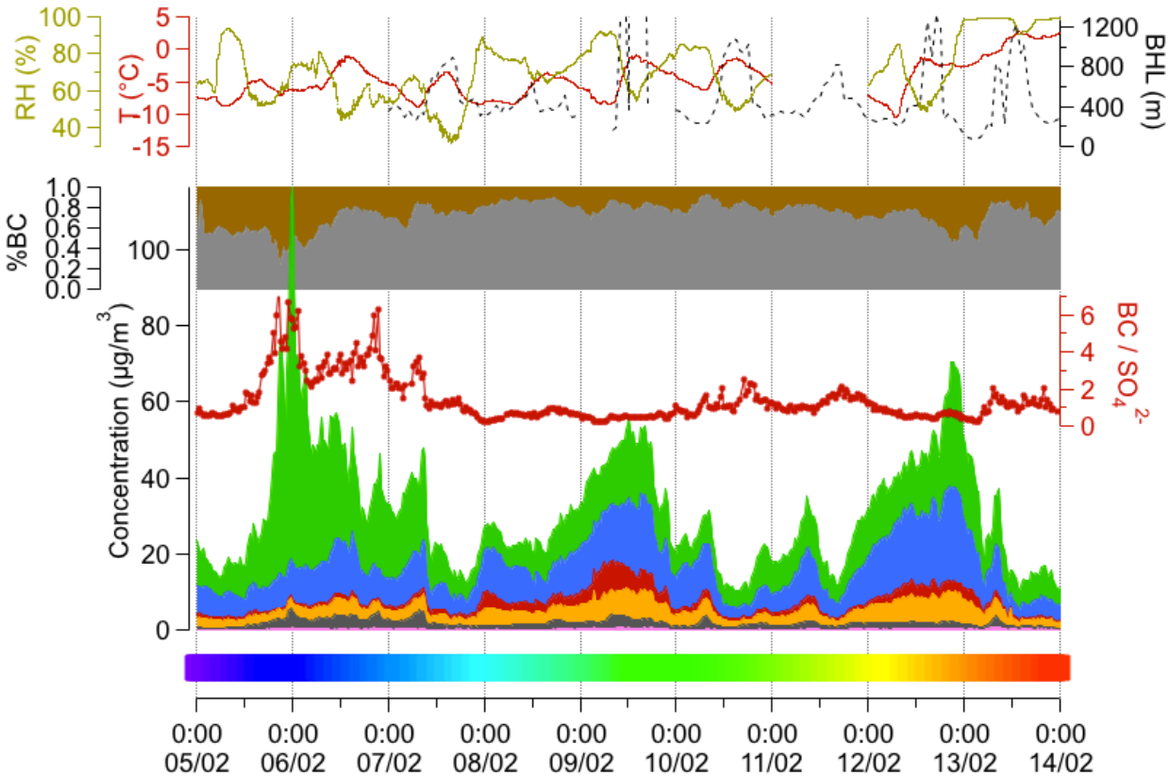


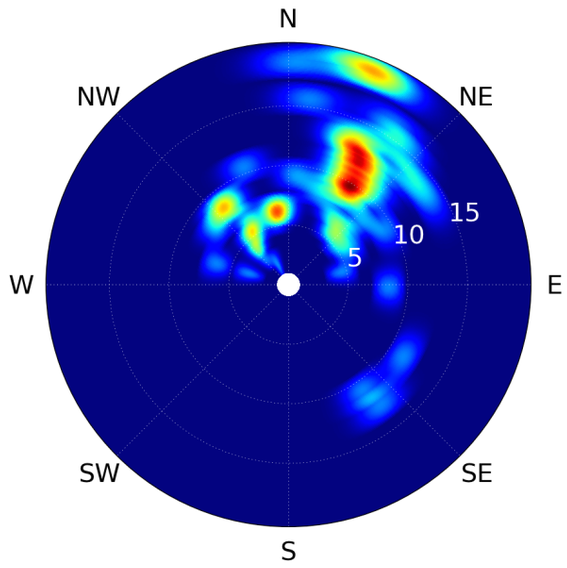


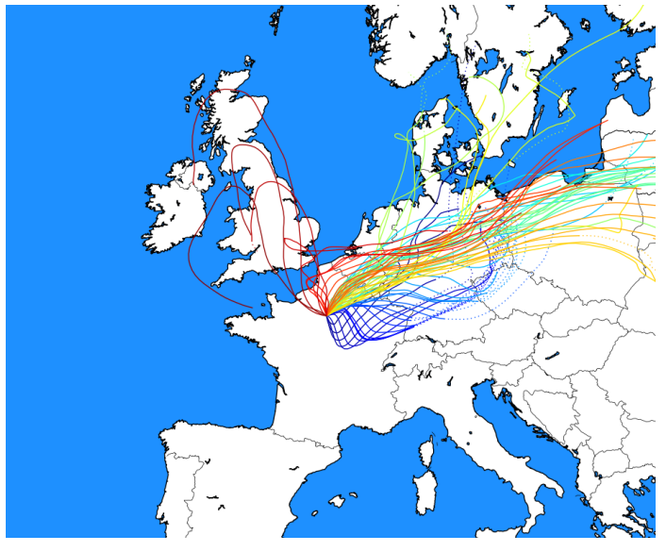


SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES







1st phase

low temperatures, high OM, BC, $\%BC_{wb}$, BC/SO_4 ratio
local wood burning emissions

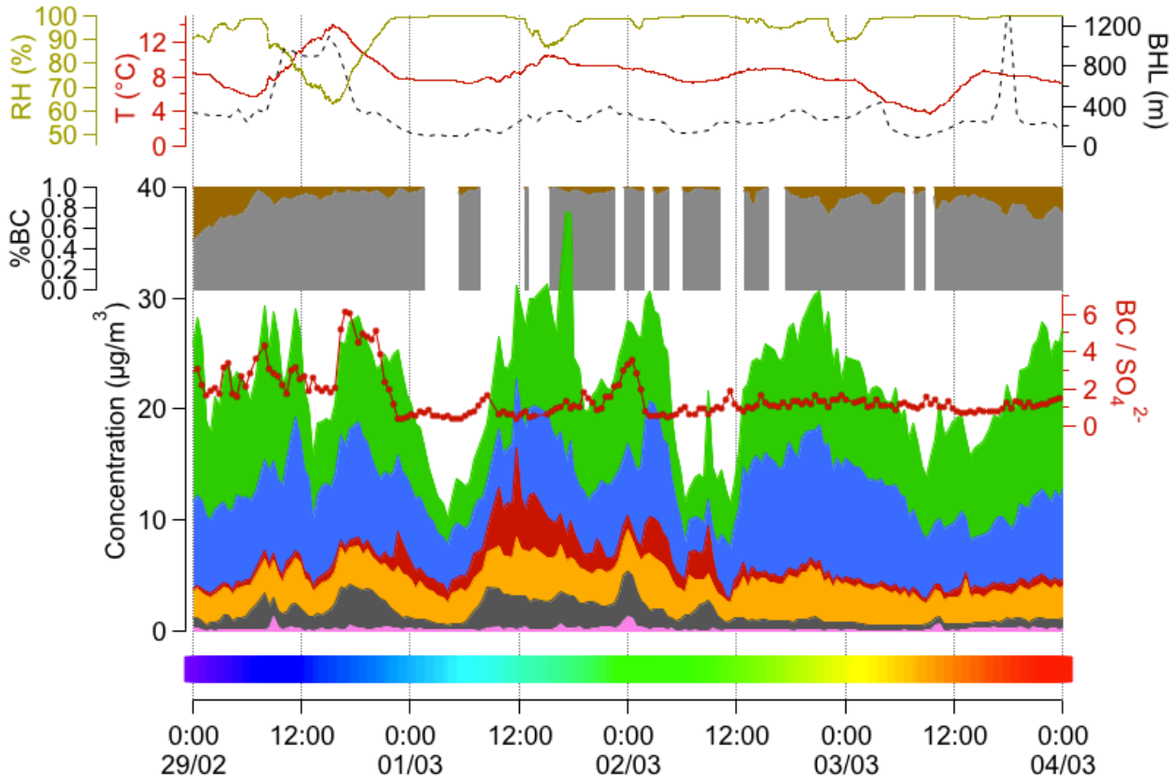
2nd phase

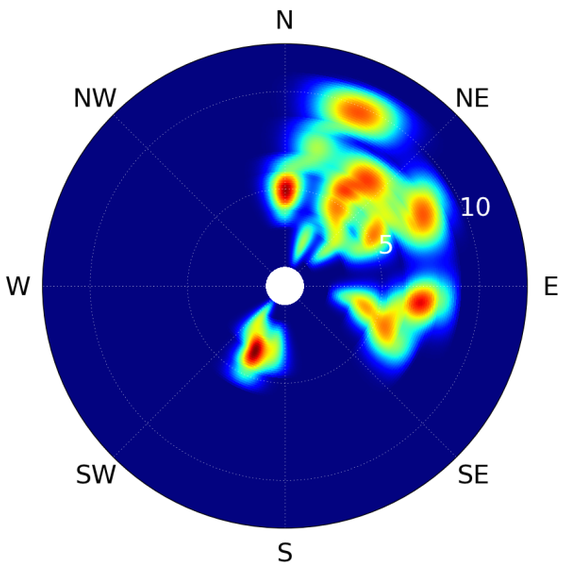
air masses coming from the NNE, high NH_4NO_3
mid- to long-range transport

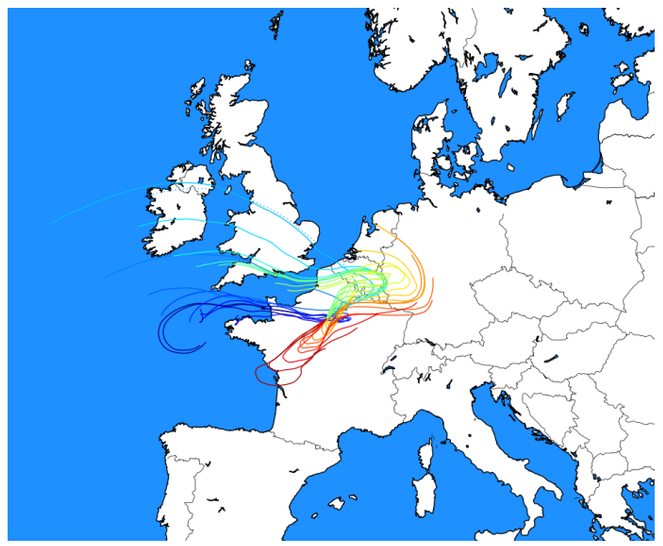
Influence of local emissions

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

GENERAL FEATURES GEO. ORIGINS POLL. EPISODES







very high RH (100% most of the time)
Concentration drops on 01/03 & 02/03 due to two stratus lowering fog events (Parifog observations) occurring during the second half of the night.
higher SO_4 after 1st fog suggests transported SO_2 (air masses near English Channel & Belgium) and local/ regional oxidation by fast fog processing
Kai et al. (2007), Rengarajan et al. (2011)

Influence of fogs regarding the chemical transformation of PM_1

SEASONALITY, GEOGRAPHICAL ORIGINS & POLL. EPISODES

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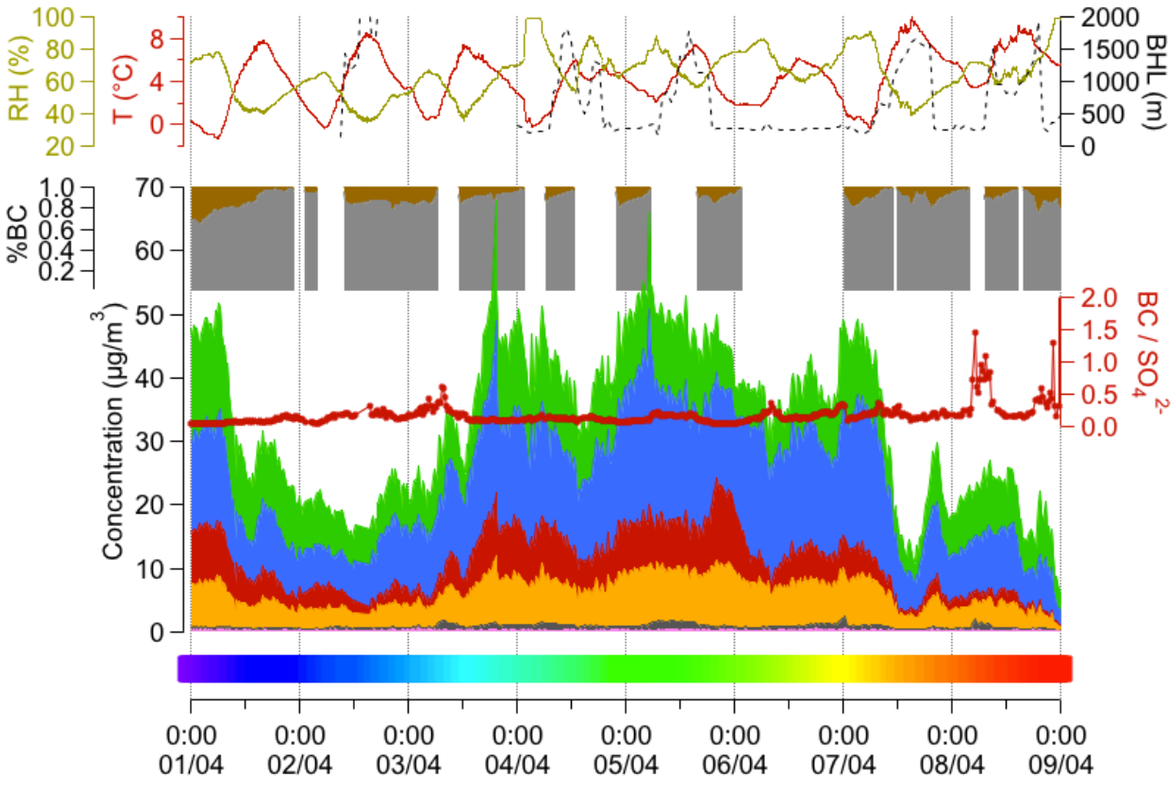

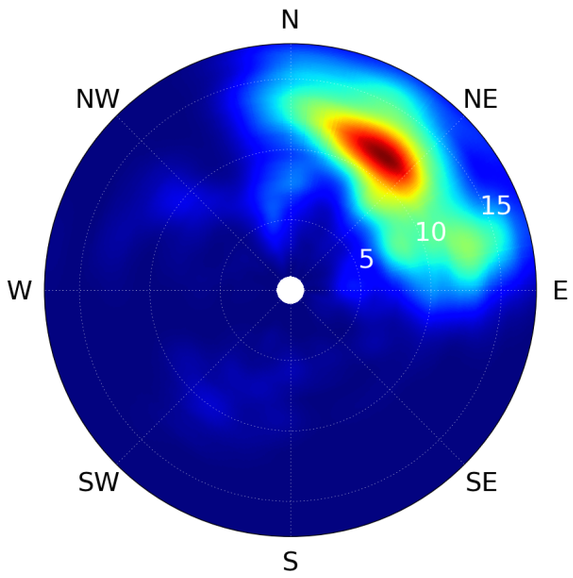

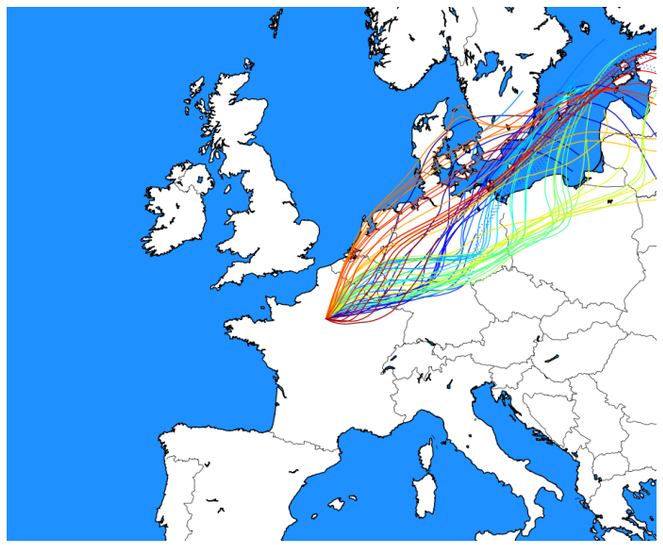

Air masses from the NE and very low BC/SO_4

Chemical composition dominated by NH_4NO_3 and $(NH_4)_2SO_4$

<u>Evidence of advected secondary pollution</u>

CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY

UNCONS. PMF

CONS. PMF

Source-receptor models

$$X = G * F + E$$

input data

temporal contribution

factor profile

residual

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CONS. PMF

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$$X = G * F + E$$

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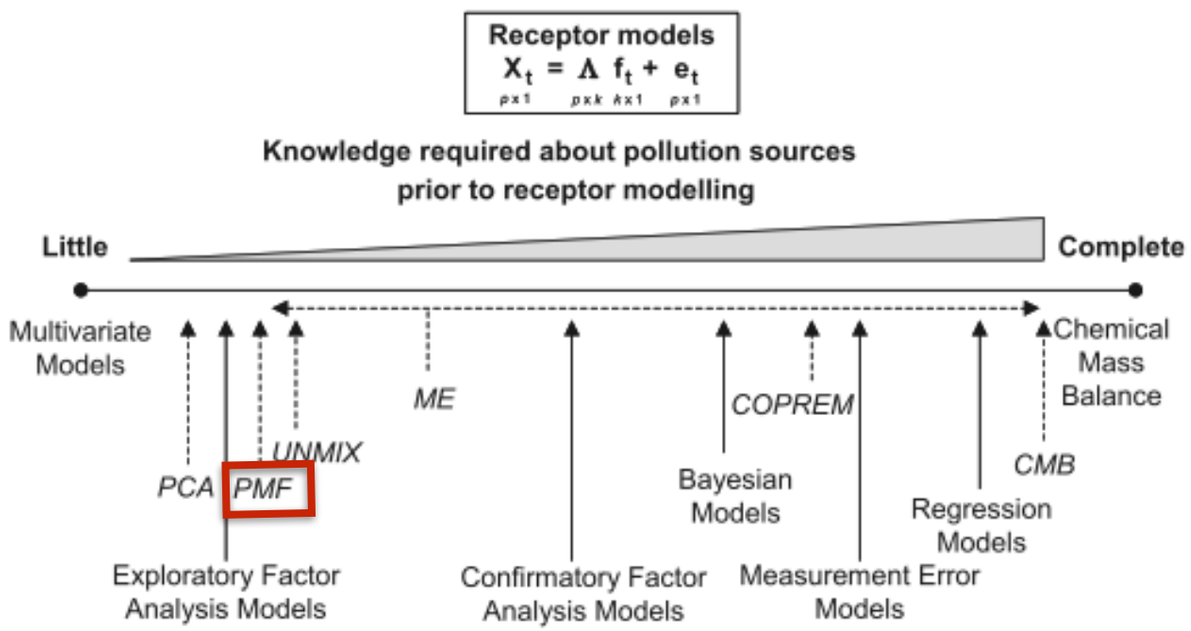

PMF:

- no *a priori* knowledge of G, F, or number of factors
- G > 0

CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY

UNCONS. PMF

CONS. PMF

Source-receptor models

$$X = G * F + E$$

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factor profile

residual

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$$X = G * F + E$$

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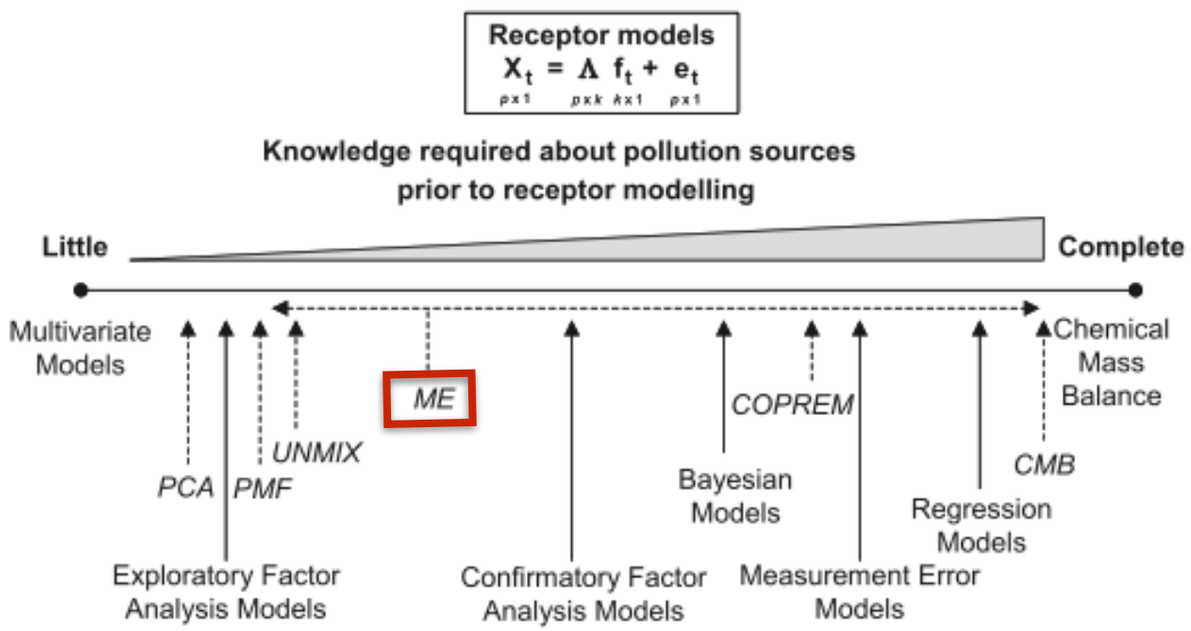

ME-2:

- possibility to constrain *a priori* information (e.g. source profile)
- $f_{j,\ solution} = f_j \pm a*f_j$ where a is the « degree of freedom » of the constrain

CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY

UNCONS. PMF

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$$X = G * F + E$$

CHARACTERIZATION OF ORGANIC AEROSOLS

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UNCONS. PMF

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OA Source apportionment

- m/z from ACSM/AMS - online data
- Grouping org. molecules following frag. pattern and sources temporality
- Igor procedure (SourceFinder)
- HOA
  BBOA
  OOA
  COA
  MOA

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- HOA
  BBOA
  OOA
  COA
  MOA

PM Source apportionment

- chem. comp. database- offline data
- Source profile
- EPA PMF v.3(5)
- Biomass Burning
  Traffic & resuspension
  Industries
  Sea Salt & marine biogenic
  Shipping
  NO_3-rich sec. aer.
  SO_4-rich sec. aer.

CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY

UNCONS. PMF

CONS. PMF

$$X = G * F + E$$

OA Source apportionment

- m/z from ACSM/AMS - online data
- Grouping org. molecules following frag. pattern and sources temporality
- Igor procedure (SourceFinder)
- HOA
  BBOA
  OOA
  COA
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  NO_3-rich sec. aer.
  SO_4-rich sec. aer.

CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY UNCONS. PMF CONS. PMF

$$X = G * F + E$$

OA Source apportionment

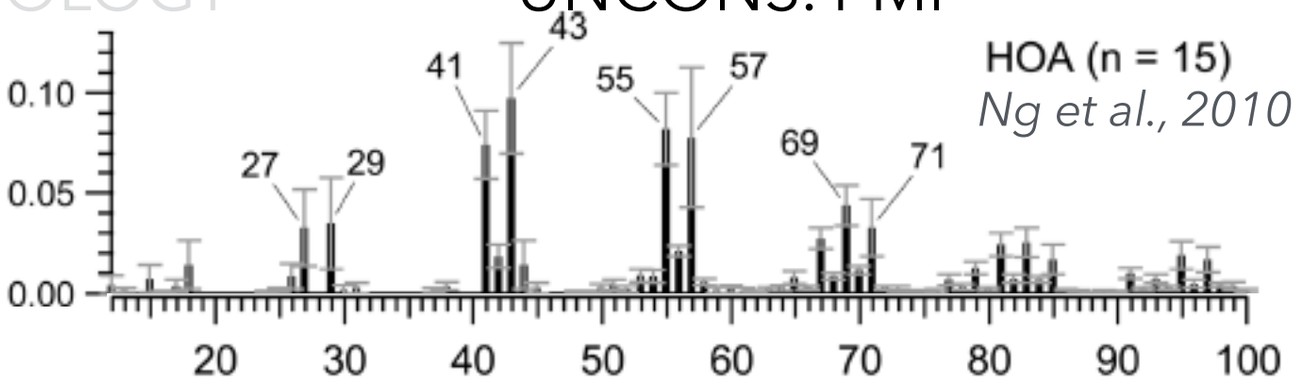
- From 01/09/2011 to 13/02/2013
- ~20 000 data points
- Mathematical indicators show that 3-4 factors can be used

CHARACTERIZATION OF ORGANIC AEROSOLS

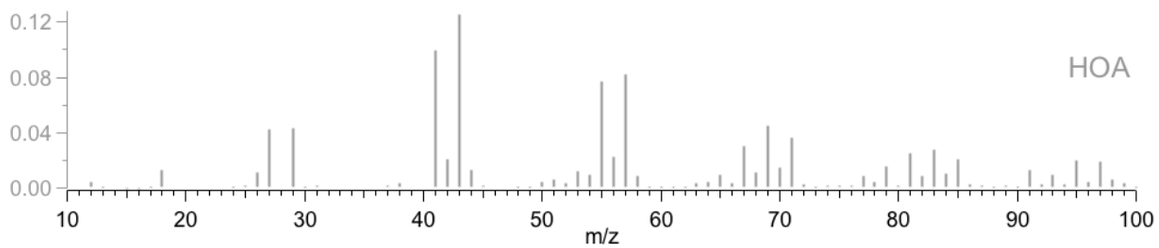
METHODOLOGY

UNCONS. PMF

CONS. PMF

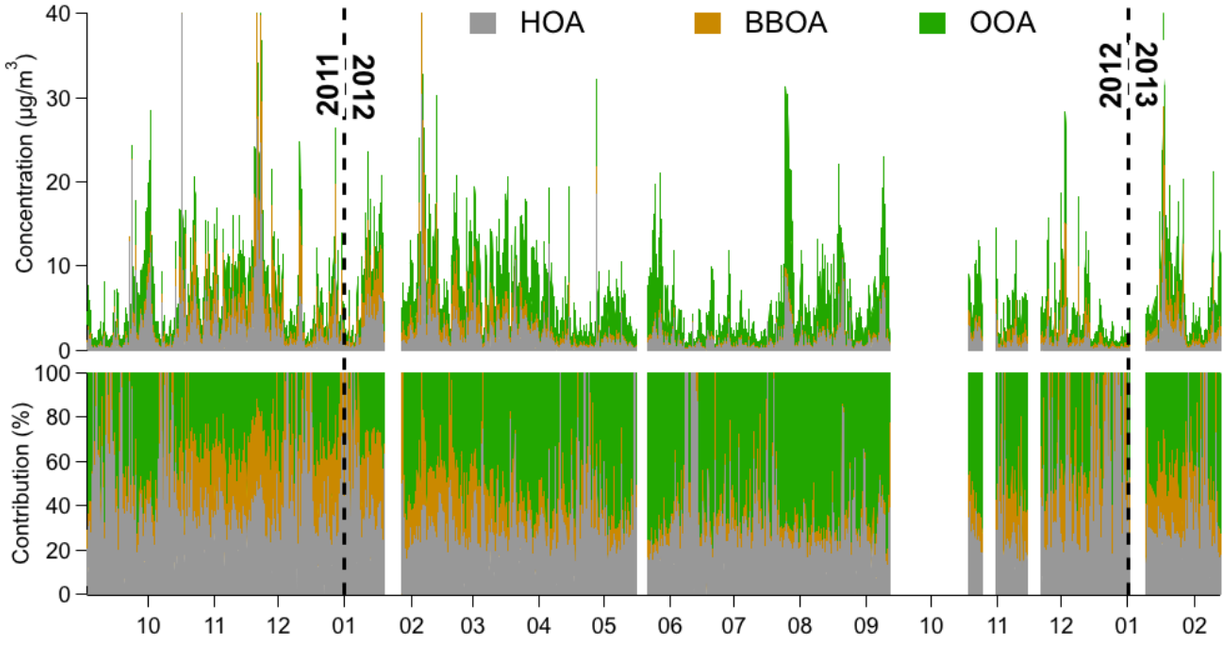


F

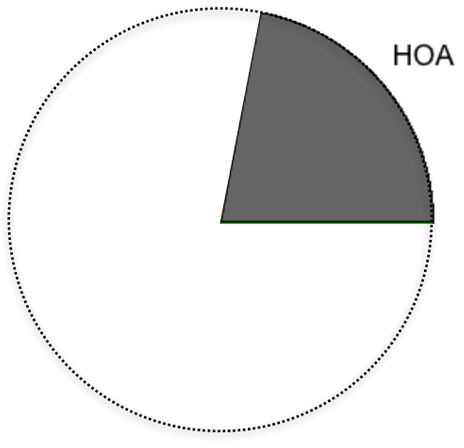


- Fragmentation characteristic of unsaturated hydrocarbons (C_nH_{2n+1})
- 22 % of OA
- Higher concentrations during autumn (more traffic)

G



- Higher contributions along with clean air masses (low PM levels)

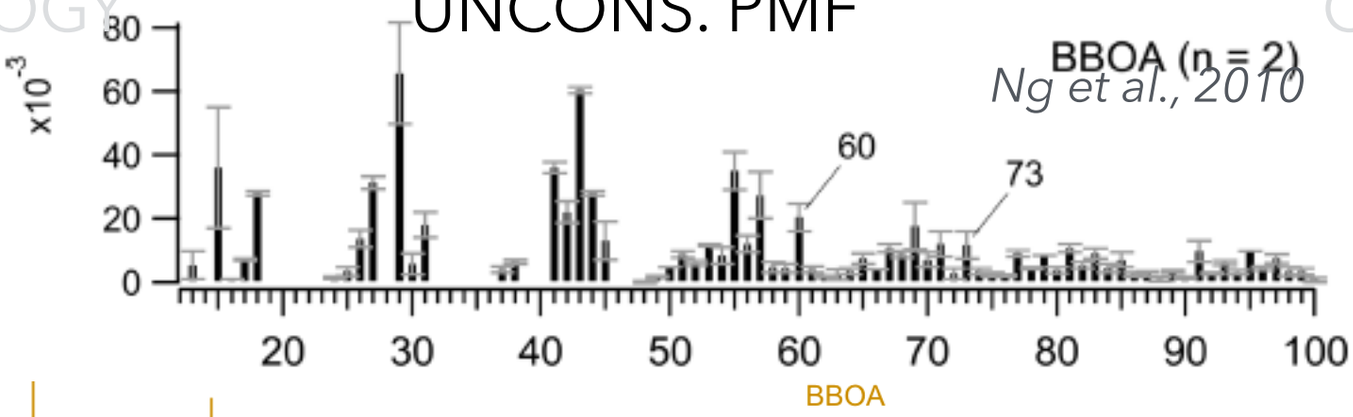


CHARACTERIZATION OF ORGANIC AEROSOLS

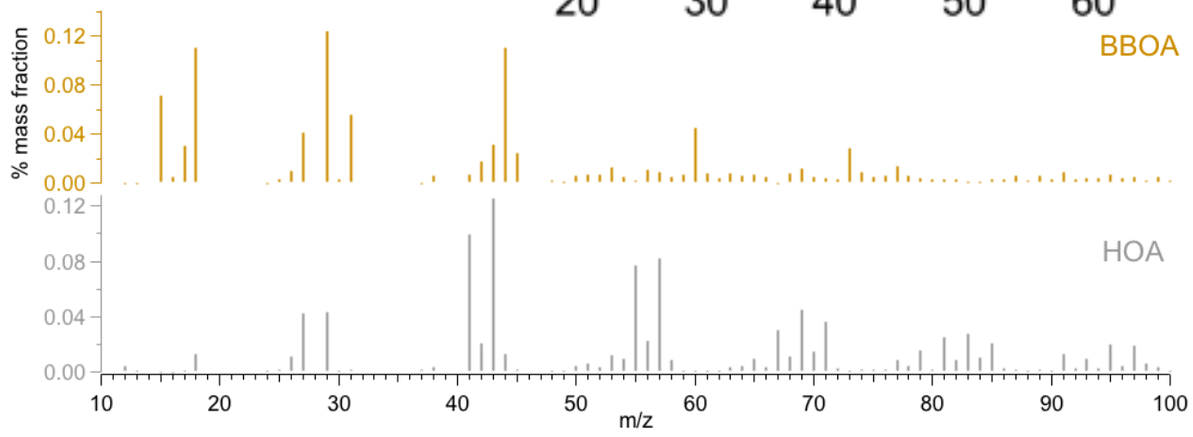
METHODOLOGY

UNCONS. PMF

CONS. PMF

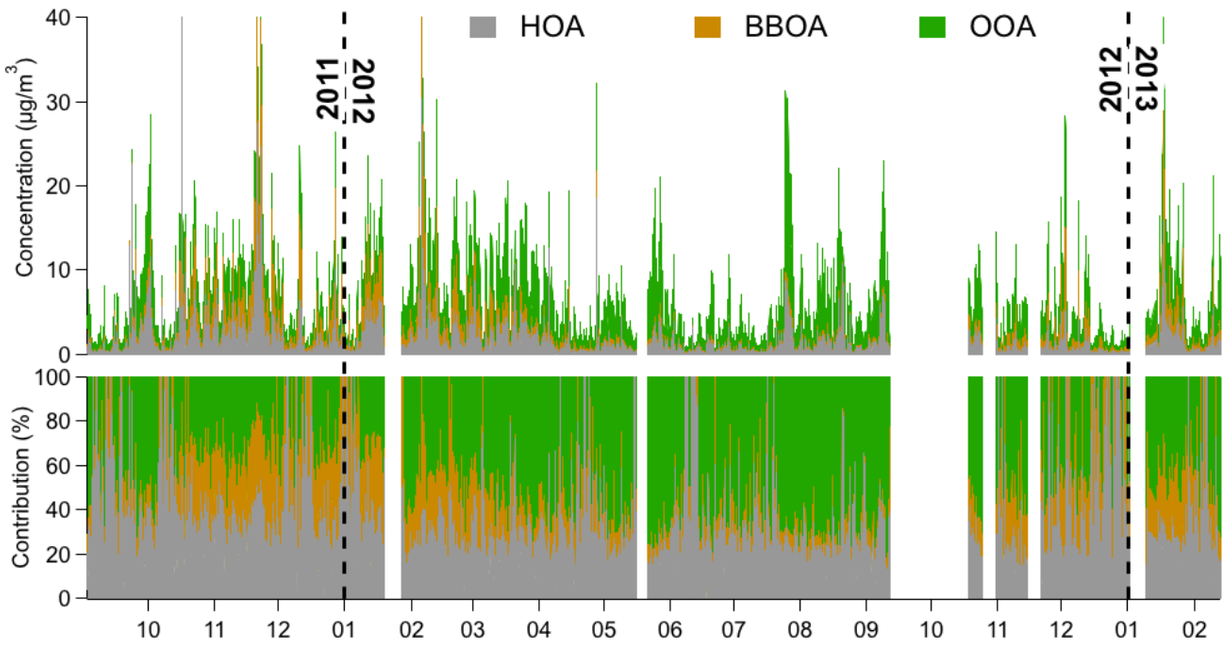


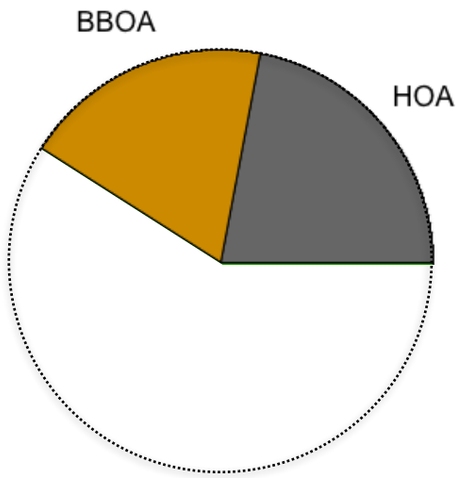
F



- Frag. characteristic of levoglucosan, tracer of biomass burning *(Simoneit et al., 1999)*
- 19 % of OA
- Strong seasonality with highest concentrations during cold seasons

G

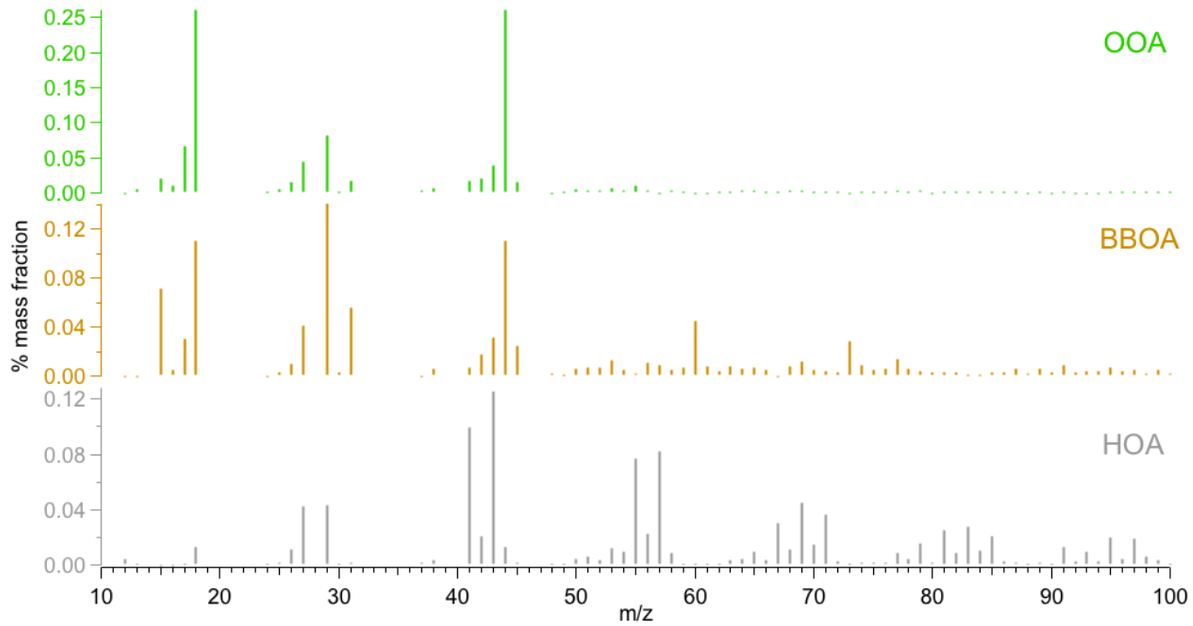




CHARACTERIZATION OF ORGANIC AEROSOLS

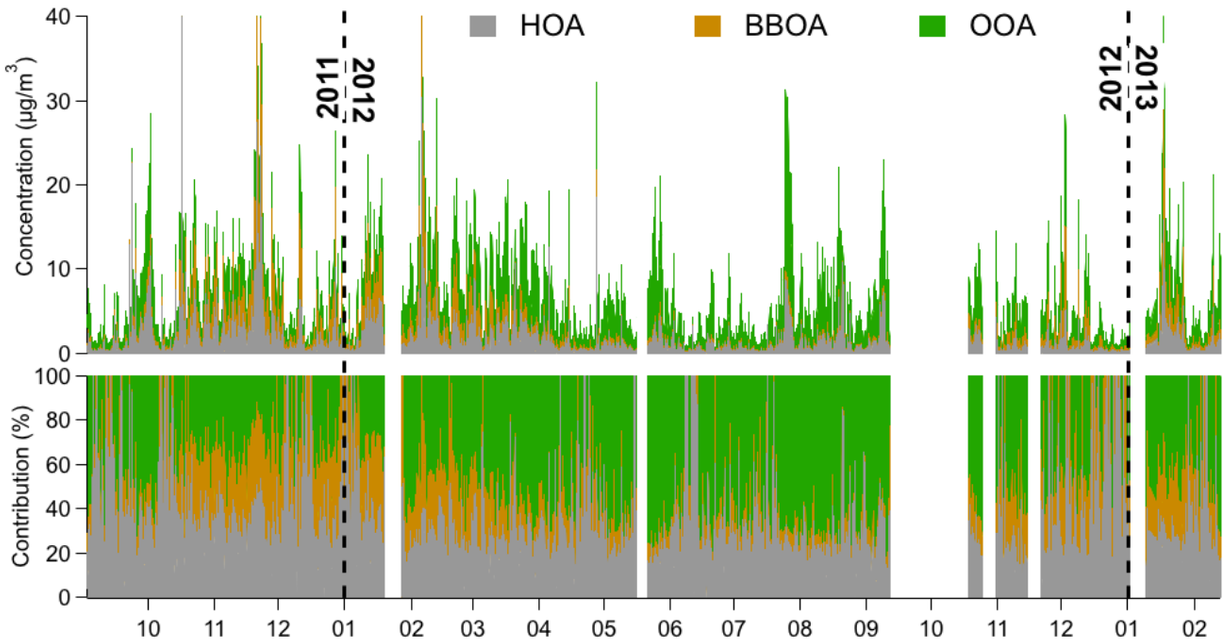
METHODOLOGY | UNCONS. PMF | CONS. PMF

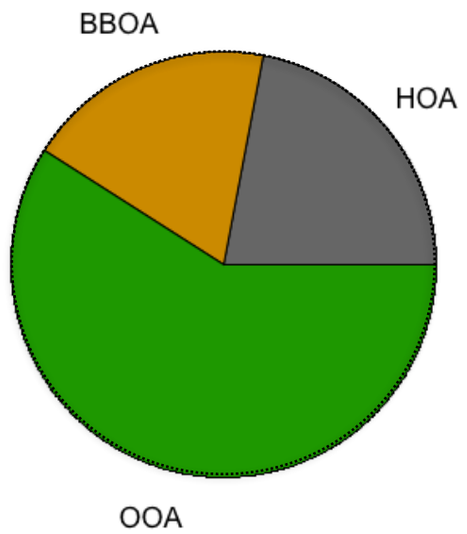
F



- Mass spectra dominated by m/z44 (CO_2^+)
- 59 % of OA

G

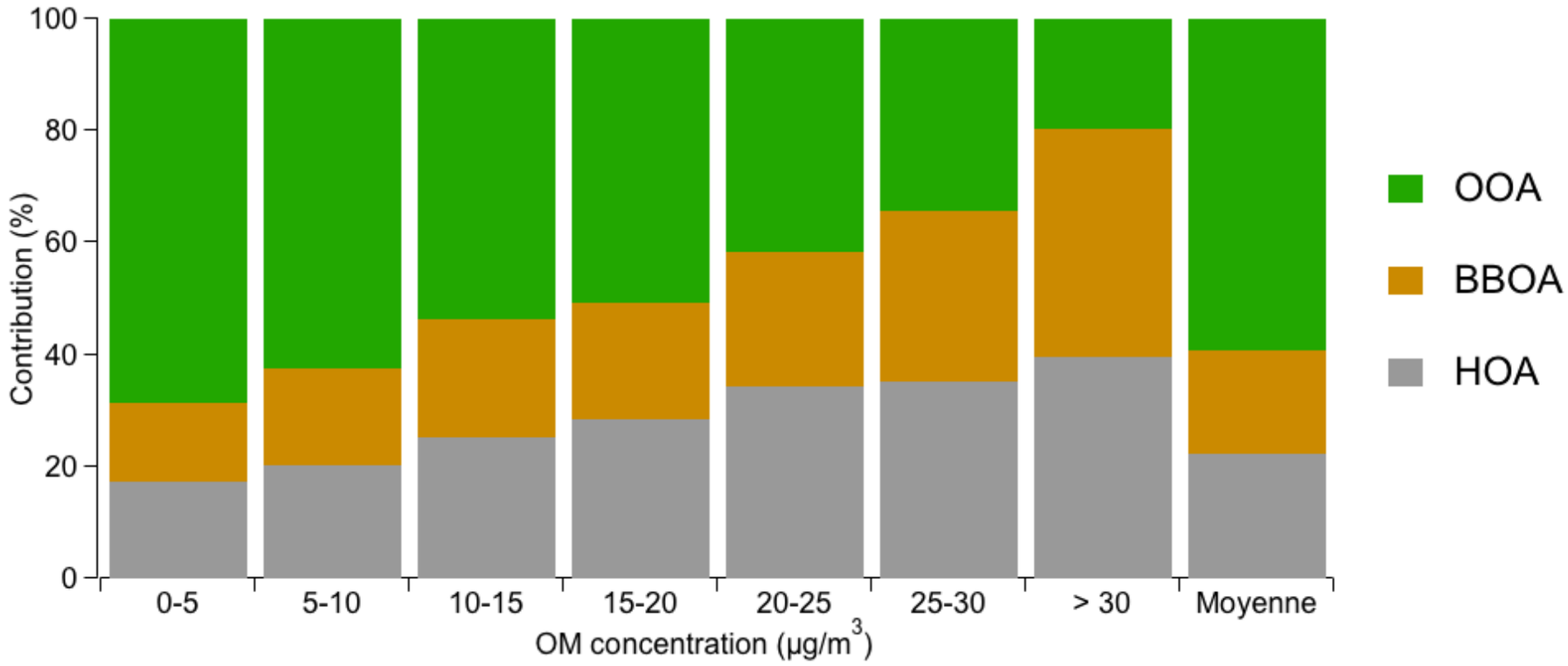




CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY UNCONS. PMF CONS. PMF

3 factors - The added value from filters

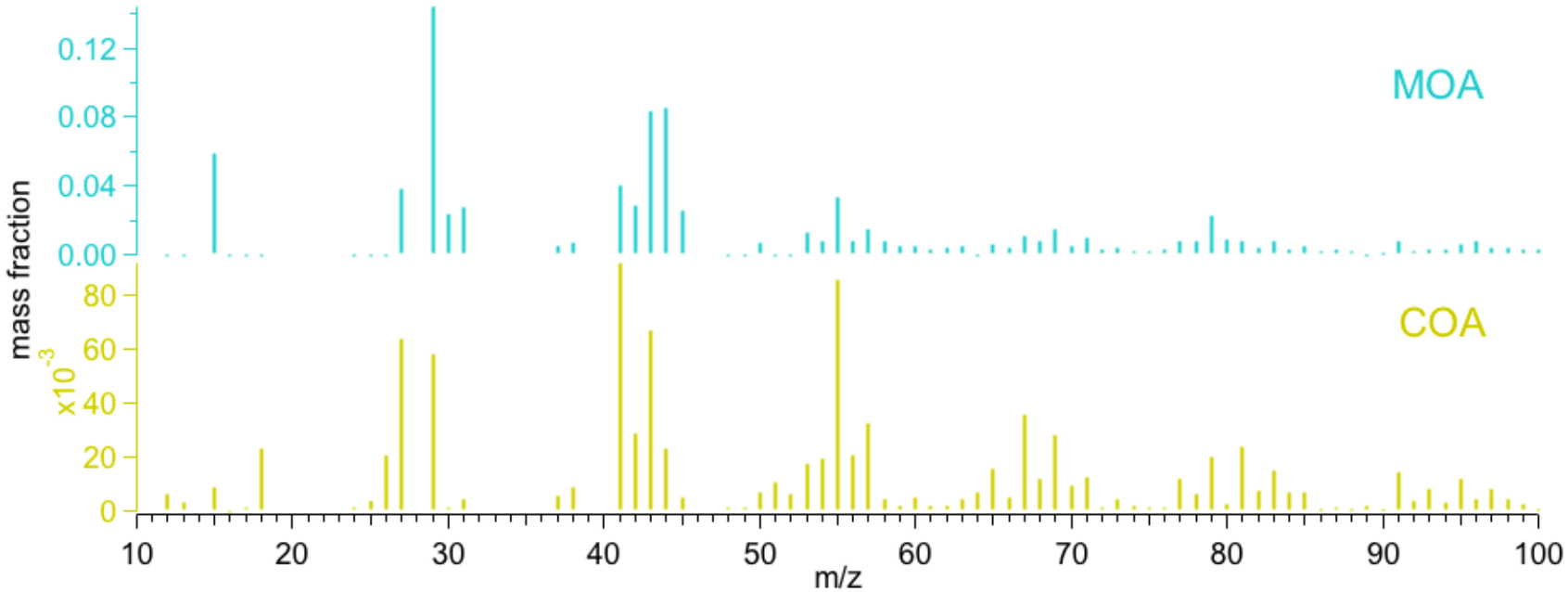


The BBOA contribution to OM gets higher with OM concentrations and correspond to sporadic spikes

CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY UNCONS. PMF CONS. PMF

COA & MOA previously identified at SIRTA with AMS instrument *(Crippa et al., 2013a&c)*



HOA, COA, MOA factors constrained with a-value=0.1

2 factors left unconstrained

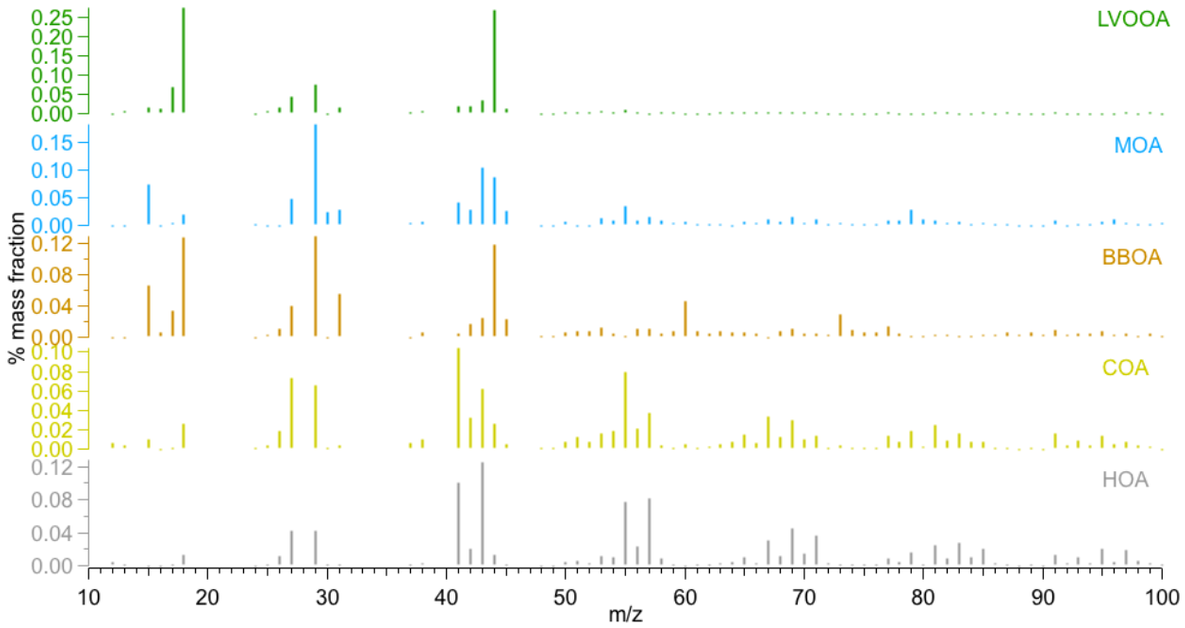
CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY

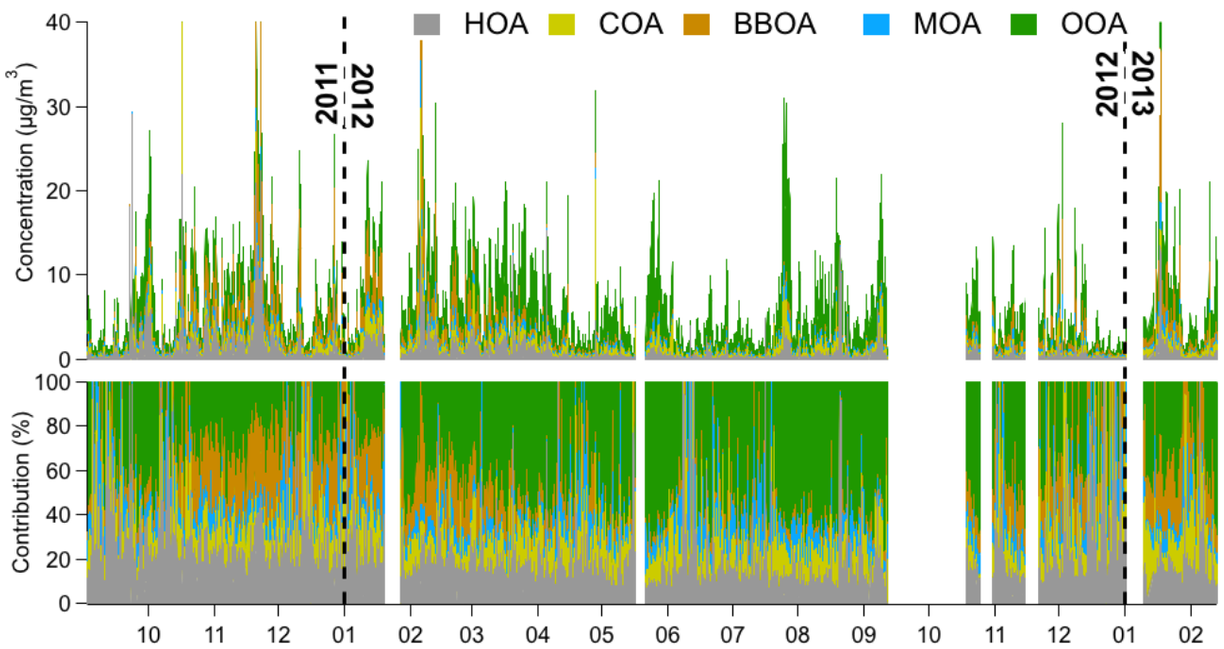
UNCONS. PMF

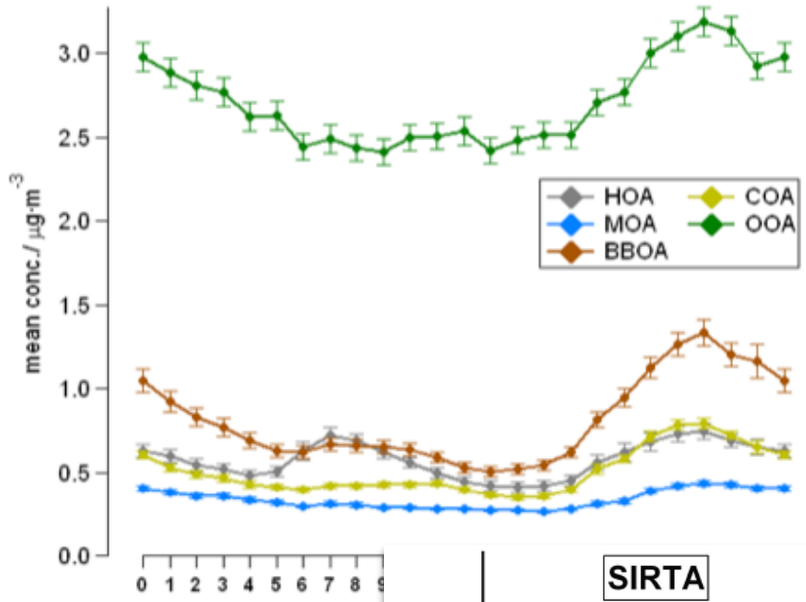
CONS. PMF

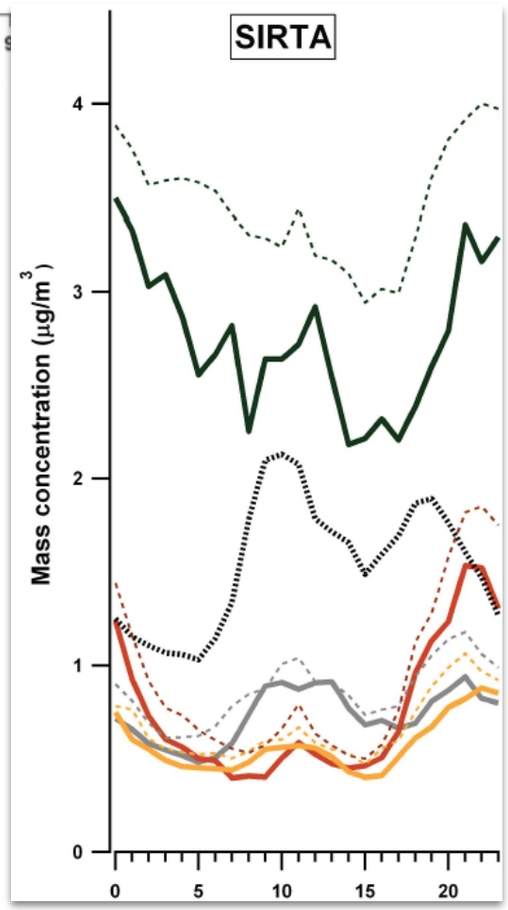
F



G







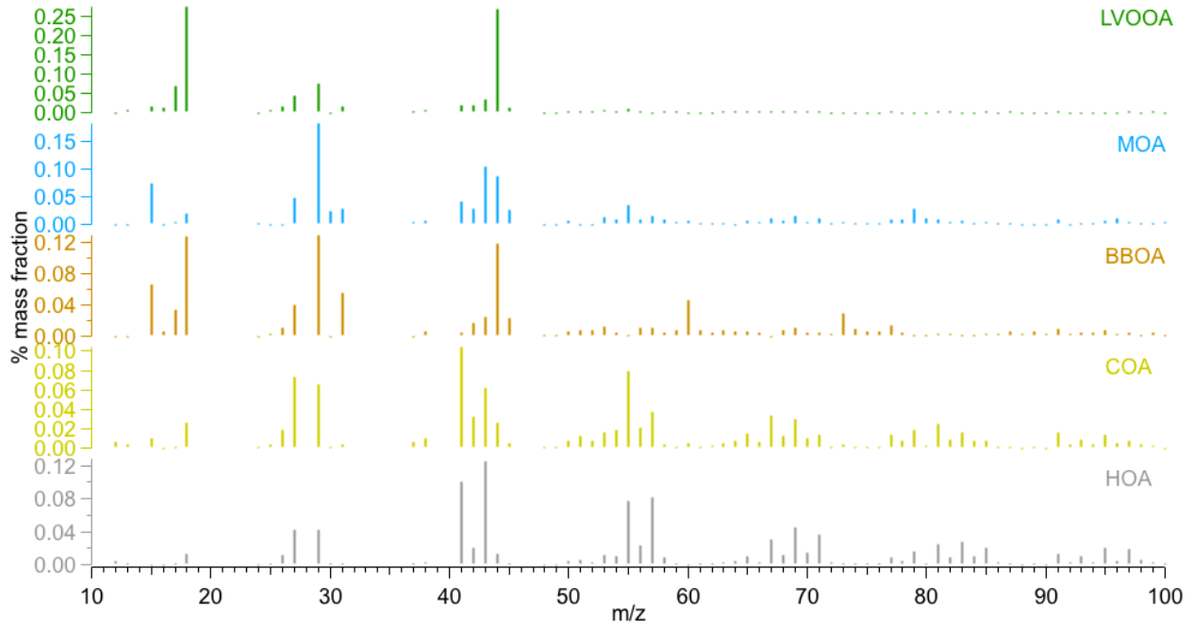
CHARACTERIZATION OF ORGANIC AEROSOLS

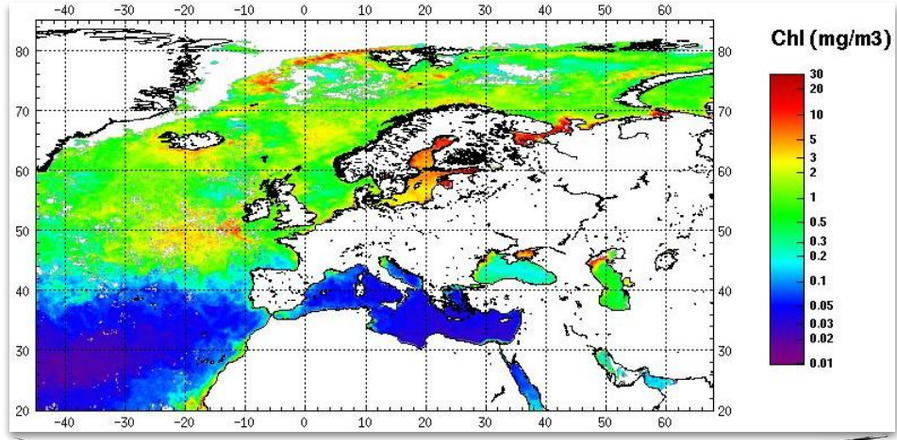
METHODOLOGY

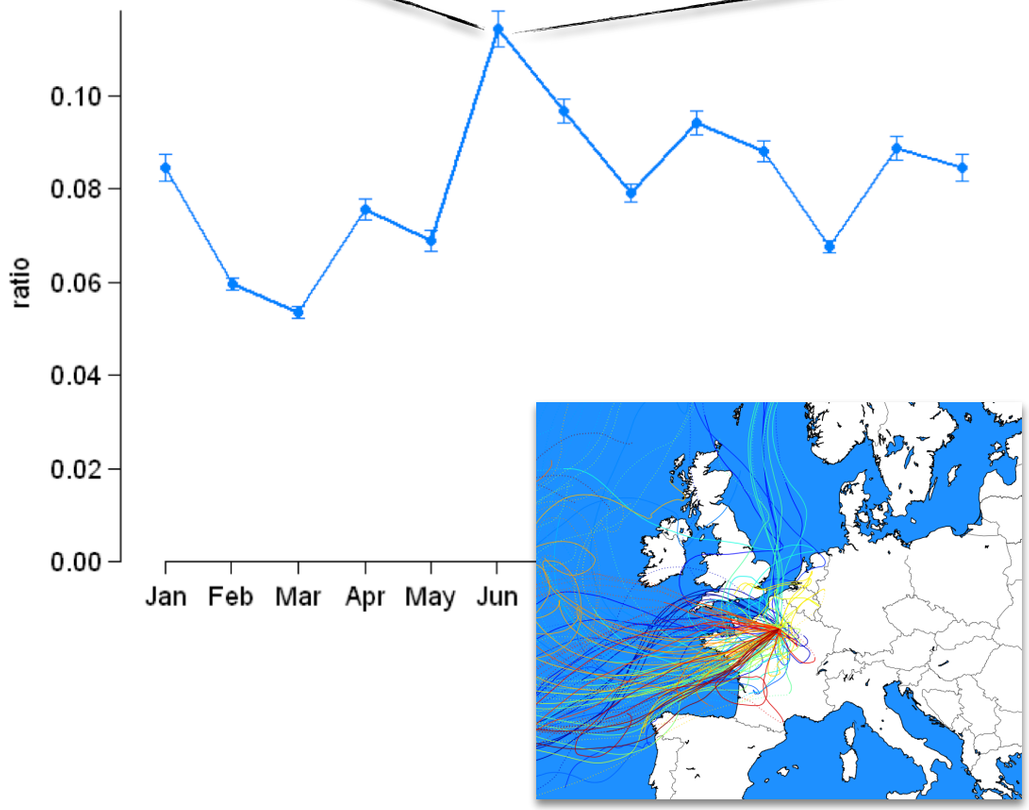
UNCONS. PMF

CONS. PMF

F







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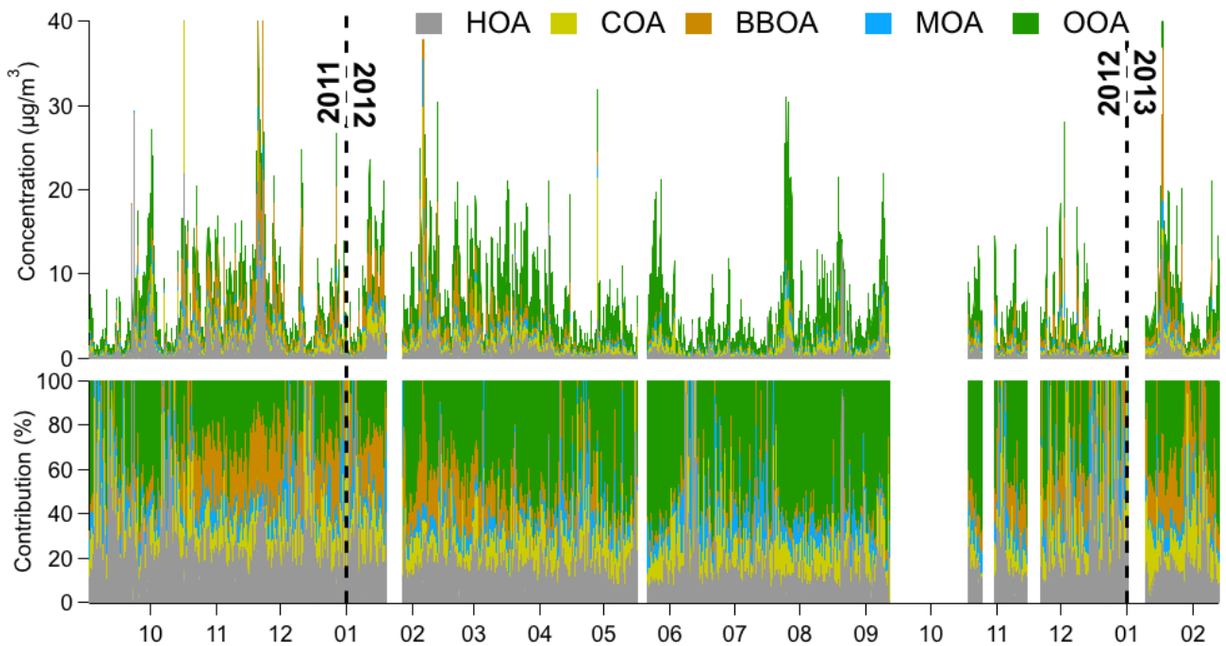
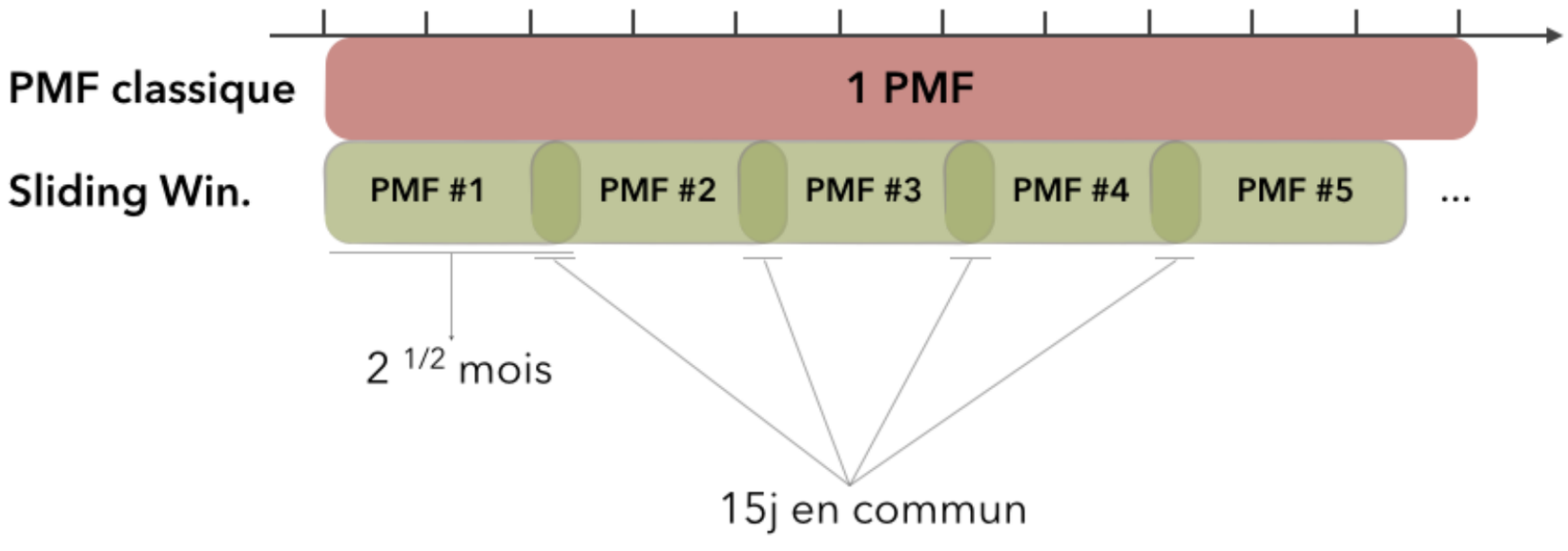


Results seem to make sense, but no external tracers are available to corroborate additional profiles (e.g. MSA for MOA, and cholesterol for COA)

There might be issues regarding the seasonality of fixed factor profiles over long term periods (could be especially true for OOA). This be explored with shorter PMF analyses

on going work with V. Crenn (LSCE) & F. Canonaco (PSI)



CHARACTERIZATION OF ORGANIC AEROSOLS

Going beyond regular PMF analysis, some novel approaches offer new perspectives towards a refine characterization of OA & non-refractory material:

- Crippa et al., 2013b: combine PTR-MS & AMS data
- Sun et al., 2012: combine OA matrix, and some m/z of NO_3 and SO_4
- McGuire et al., 2014: use of the total NR matrix

How about taking all PM_1 components (OM, NO_3, SO_4, NH_4, Cl, BC) into account to apportion PM_1 sources?

IDENTIFICATION OF PM_1 SOURCES

$$X = G * F + E$$

<u>OA Source apportionment</u>

- m/z from ACSM/AMS - online data
- Grouping org. molecules following frag. pattern and sources temporality
- Igor procedure
- HOA
  BBOA
  OOA
  COA
  MOA

<u>PM Source apportionment</u>

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Biomass Burning
Traffic & resuspension
Industries
Sea Salt & marine biogenic
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NO_3-rich sec. aer.
SO_4-rich sec. aer.

Atmos. Chem. Phys. Discuss., 14, 14159–14199, 2014
www.atmos-chem-phys-discuss.net/14/14159/2014/
doi:10.5194/acpd-14-14159-2014

Atmospheric Chemistry and Physics Discussions

Submicron aerosol source apportionment of wintertime pollution in Paris, France by Double Positive Matrix Factorization (PMF^2) using Aerosol Chemical Speciation Monitor (ACSM) and multi-wavelength Aethalometer

J.-E. Petit[1,2], O. Favez[1], J. Sciare[2], F. Canonaco[3], P. Croteau[4], G. Močnik[5], J. Jayne[4], D. Worsnop[4], and E. Leoz-Garziandia[1]

[1]Institut National de l'Environnement Industriel et des RISques, INERIS, Parc Technologique ALATA BP2, 60550 Verneuil-en-Halatte, France
[2]Laboratoire des Sciences du Climat et de l'Environnement, LSCE, UMR8212, CNRS-CEA-UVSQ, 91191 Gif-sur-Yvette, France
[3]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 PSI Villigen, Switzerland
[4]Aerodyne Research, Inc. 45 Manning Road Billerica, MA, USA
[5]Aerosol d.o.o., Kamniška 41, 1000 Ljubljana, Slovenia

14159

Accepted for ACP

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY

OA SOURCE APP. PM_1 SOURCE APP.

ACSM

→ OM matrix

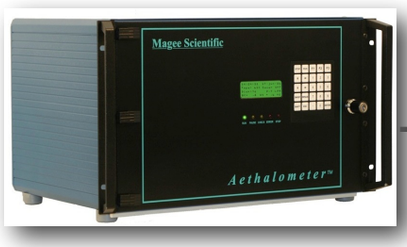
OA source app.
1st PMF/ME2 analysis

12	13	15	.....	100

→ **PM_1 source app.**
2nd PMF

- OOA
- HOA
- BBOA
- NO_3
- SO_4
- NH_4
- Cl
- (K)
- BC_{wb}
- BC_{ff}

Aethalometer AE31

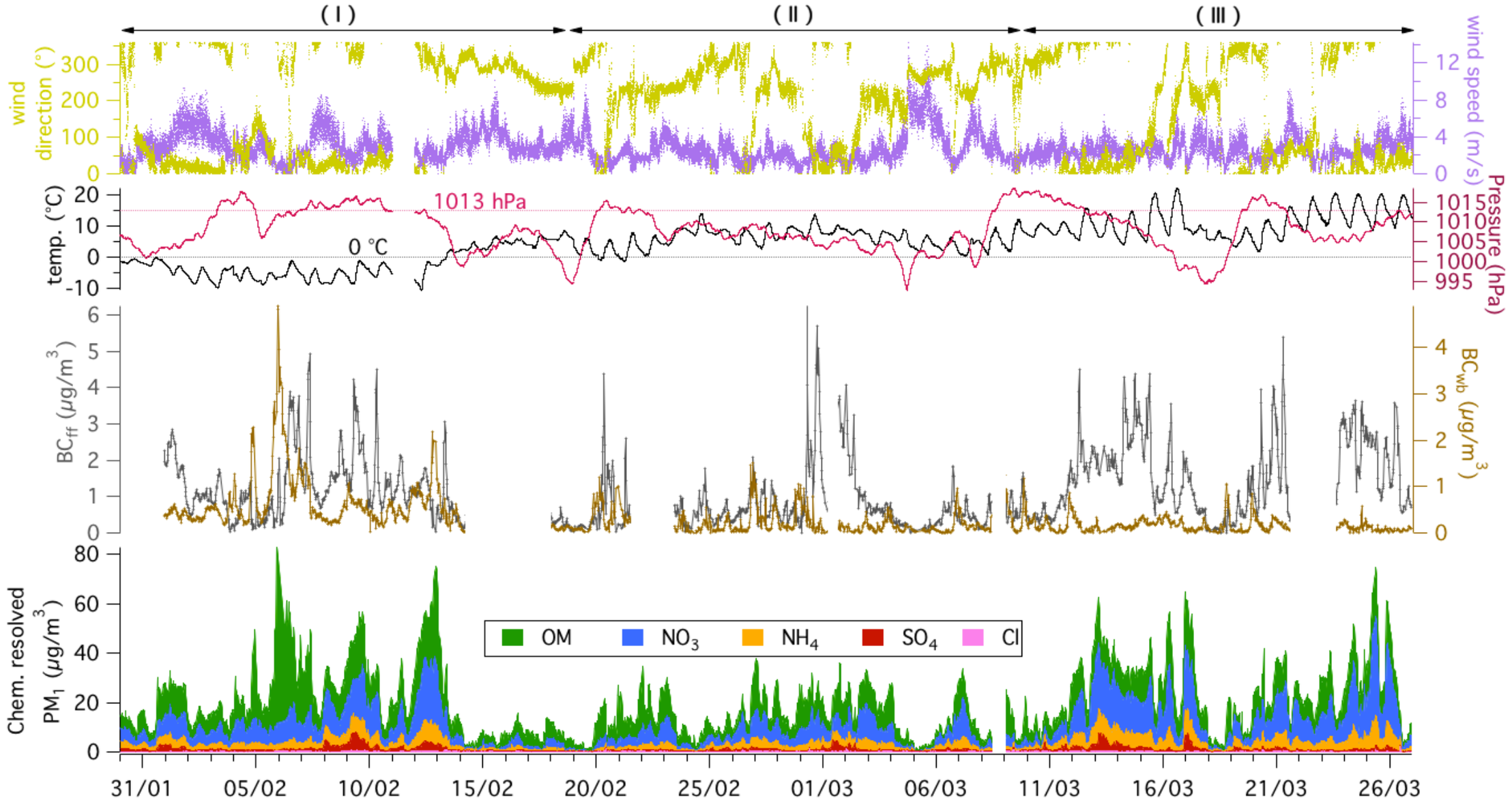


→ Multi-λ abs. coeff. → Aethalo. model Sandradewi et al., 2008 →

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Methodology applied to a 2-month dataset, from 31/01 to 27/03



IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY

OA SOURCE APP.

PM_1 SOURCE APP.

ACSM

OM matrix

OA source app.

1st PMF/ME2 analysis

12	13	15	.....	100

PM app.

2nd PMF

- OOA
- HOA
- BBOA
- NO
- SO
- NH
- Cl
- (K)
- BC
- BC

Aethalometer AE31

Multi-abs. coeff.

Aethalo. model

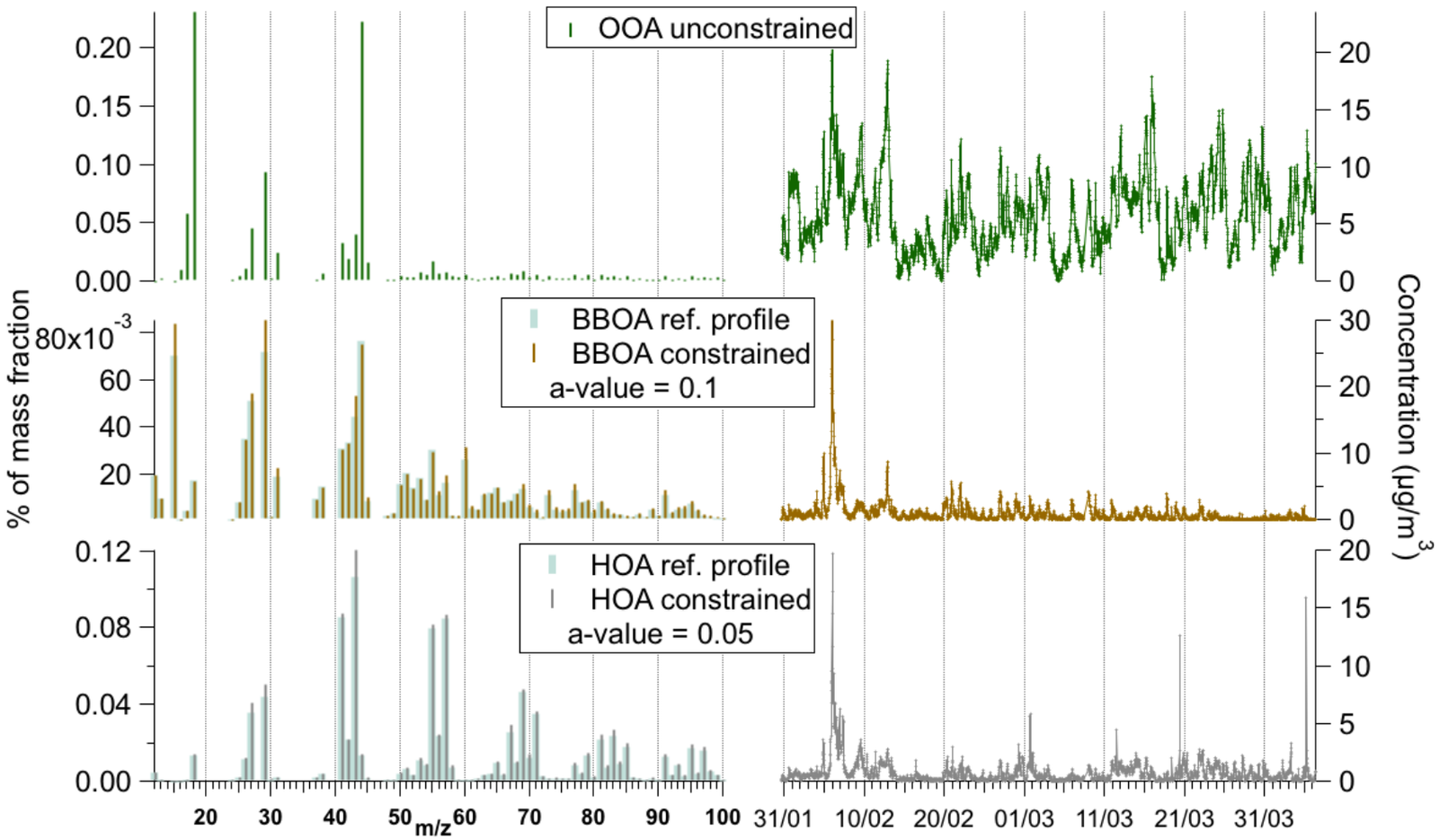
Sandradewi et al., 2008

IDENTIFICATION OF PM_1 SOURCES

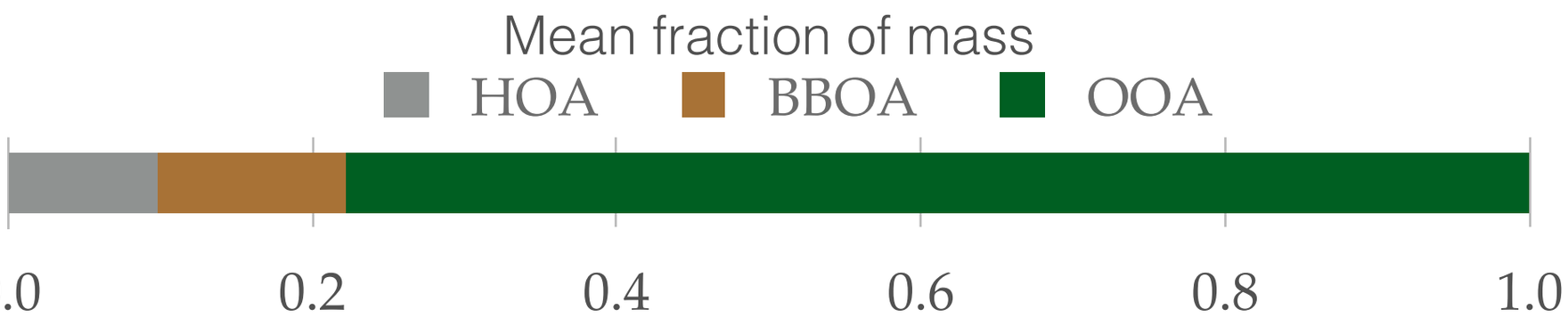
METHODOLOGY

OA SOURCE APP.

PM_1 SOURCE APP.



3 OA factors commonly observed when using AMS/ACSM



OOA represents the majority of OA, but cannot be directly linked to a pollution source !!!

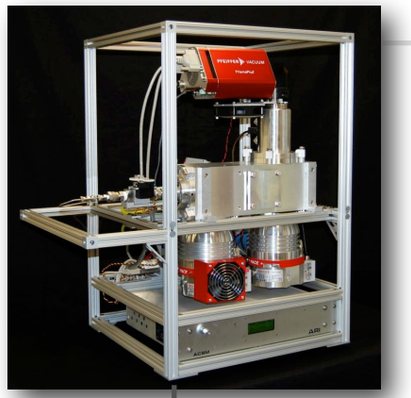
IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY

OA SOURCE APP.

PM_1 SOURCE APP.

ACSM



OM matrix

OA source app.

1st PMF/ME2 analysis

12	13	15	.....	100

PM_1 source app.

2nd PMF

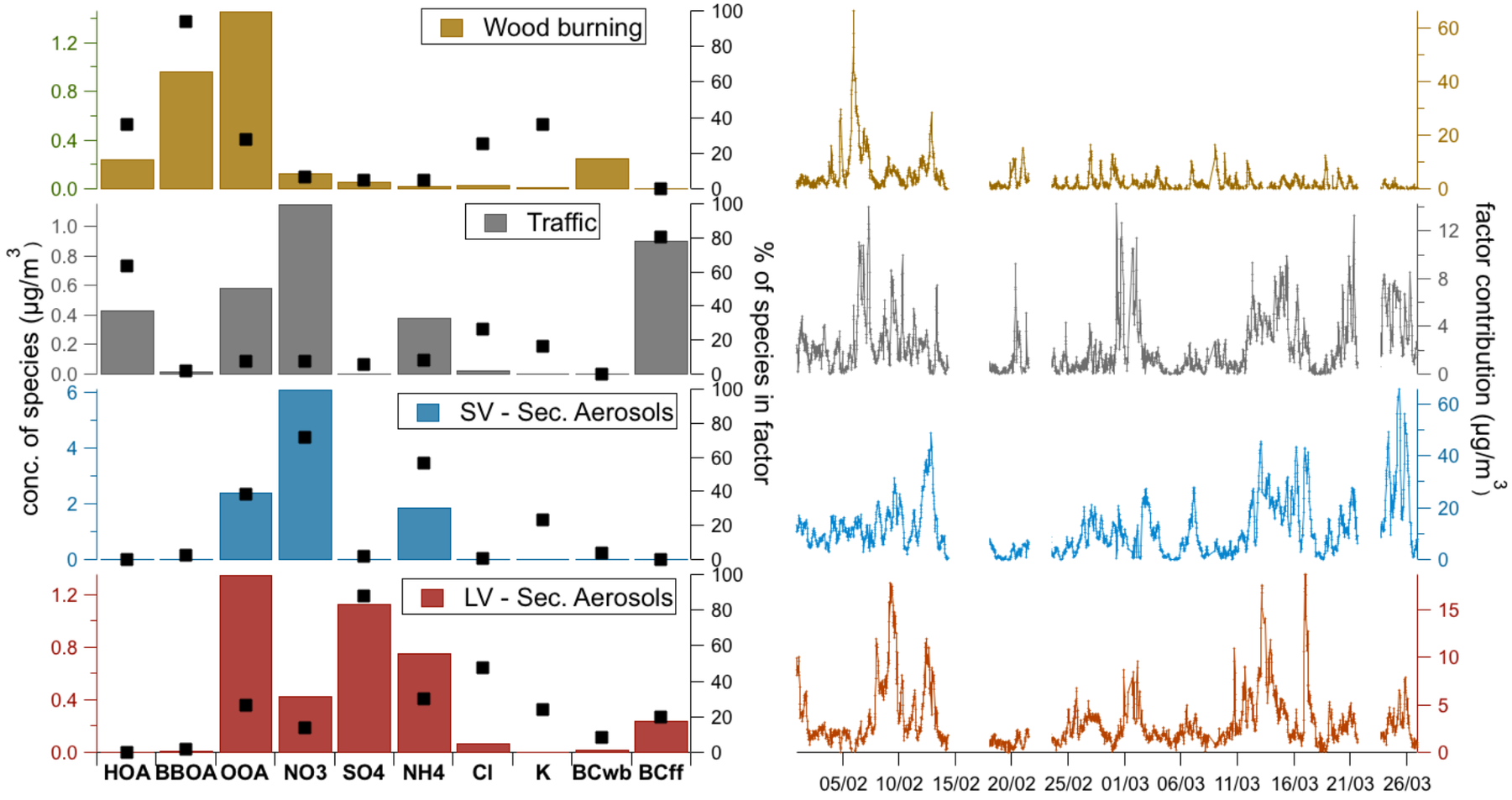
- OOA
- HOA
- BBOA
- NO_3
- SO_4
- NH_4
- Cl
- (K)
- BC_{wb}
- BC_{ff}

Aethalometer AE31

Multi-λ abs. coeff. → Aethalo. model Sandradewi et al., 2008

IDENTIFICATION OF PM_1 SOURCES

Results - profiles & time series



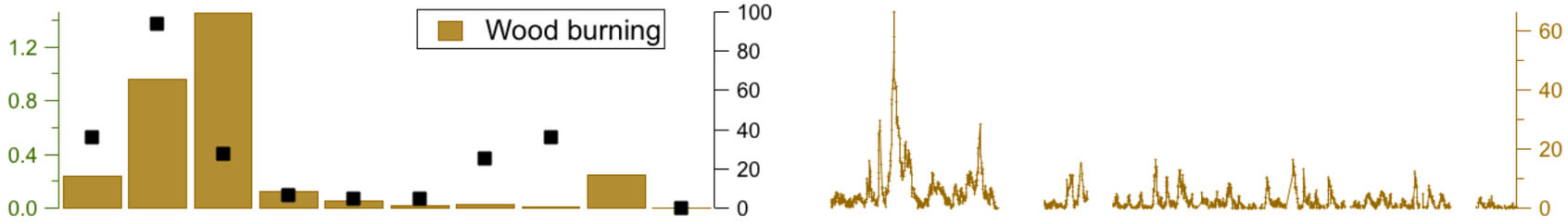
4-factor solution most realistic stability checked by bootstrap (100% for each factor)

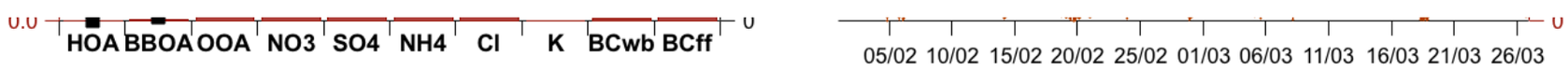
bootstrap	f1	f2	f3	f4
f1	**100**	0	0	0
f2	0	**100**	0	0
f3	0	0	**100**	0
f4	0	0	0	**100**

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Results - profiles & time series



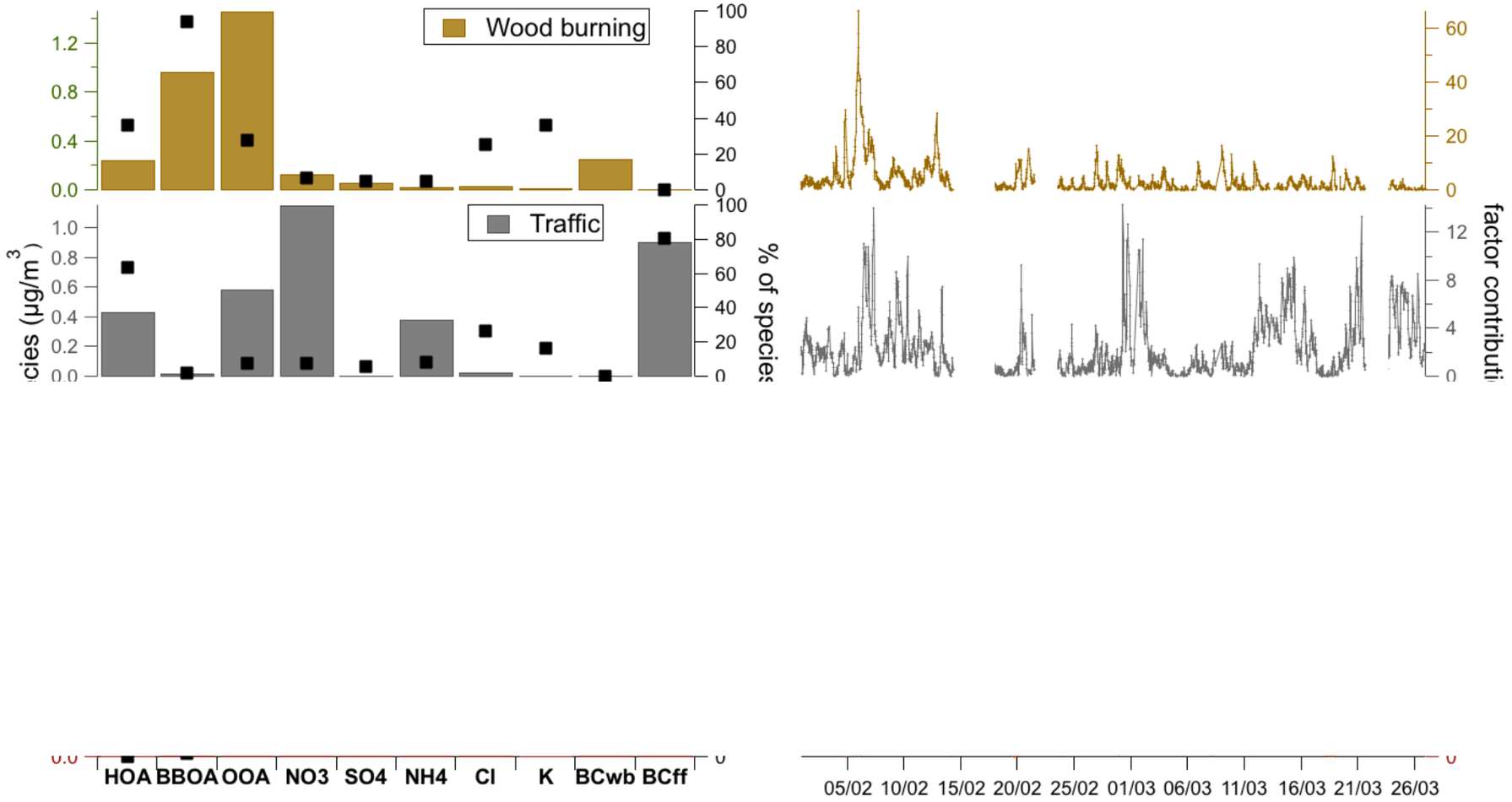


90% of BBOA & 85% of BC_{wb} explained by this factor
presence of HOA, illustrating its covariation with BBOA
OOA represents around 50% of OA_{wb} (fast condensation of VOCs? atmospheric ageing?)

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Results - profiles & time series



60% of HOA & 80% of BC_{ff} explained by this factor

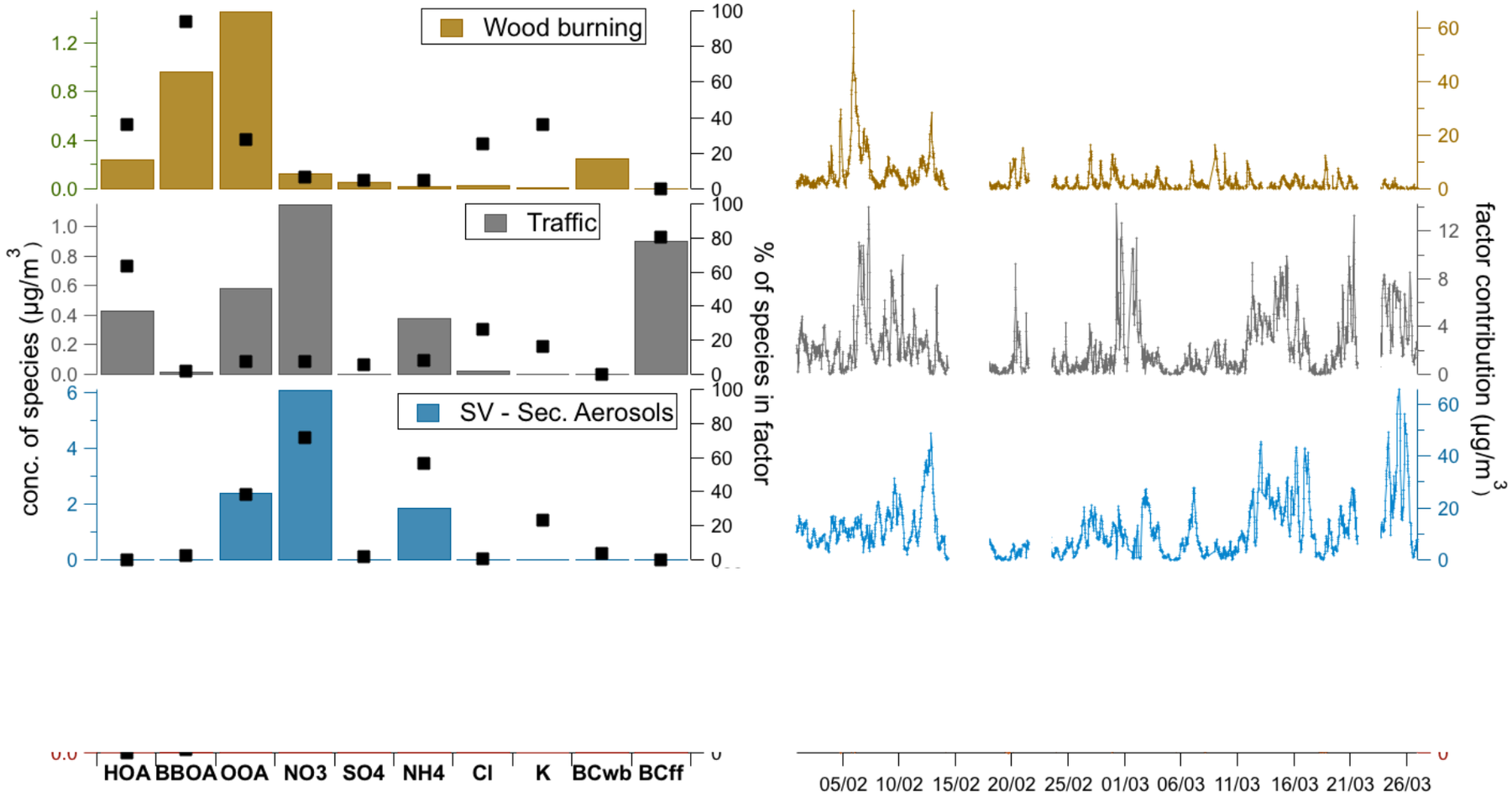
OOA represents more than 50% of OA_{ff} (fast oxidation and condensation processes?)

NH_4 & NO_3 (in stoichiometric proportion) suggest condensation with mobile emissions

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Results - profiles & time series



Profile dominated by NH_4NO_3

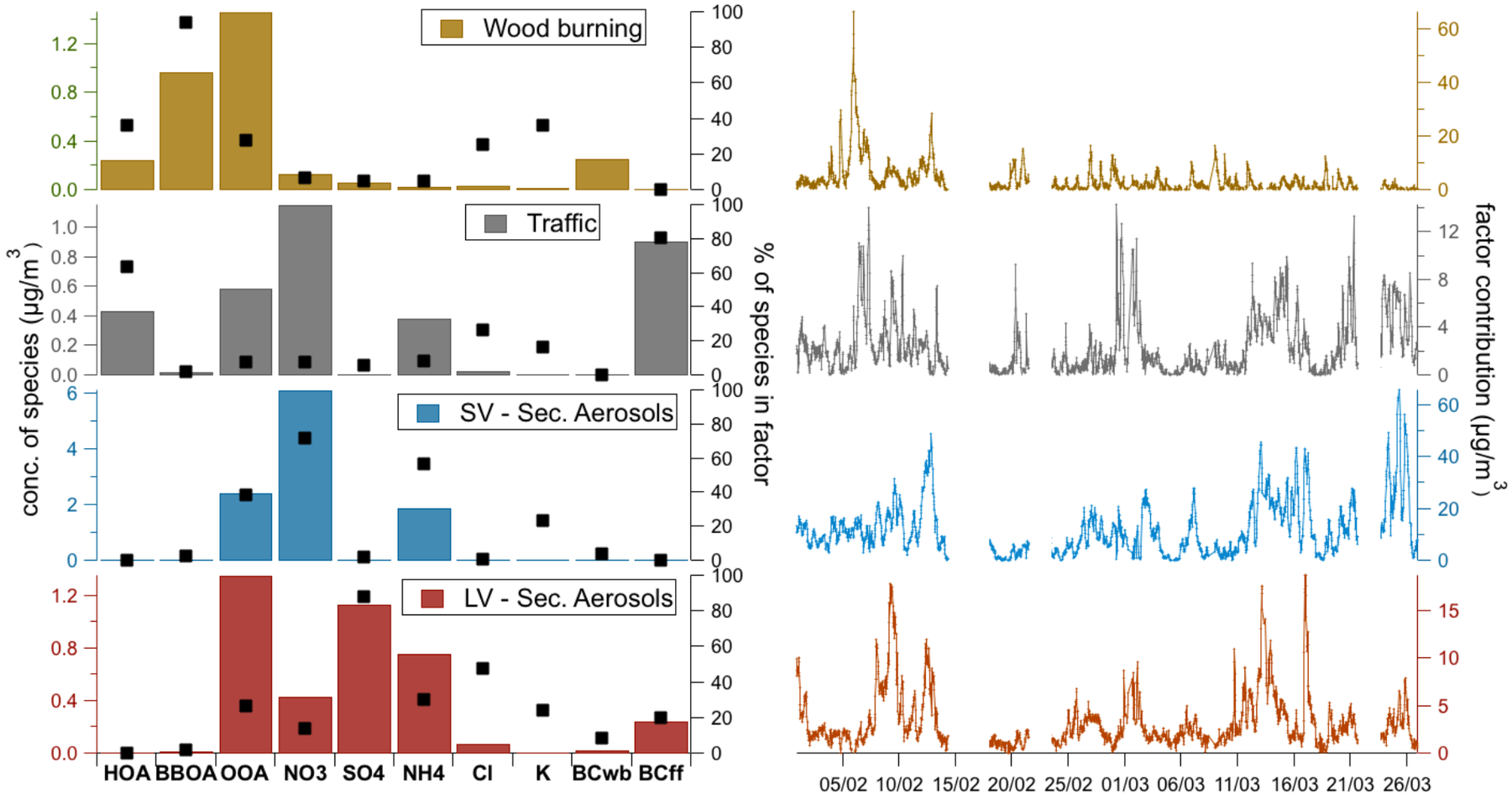
OOA in this profile should be considered as semi-volatile

not associated to a source, this factor represents semi volatile secondary aerosols

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Results - profiles & time series



Profile dominated by $(NH_4)_2SO_4$

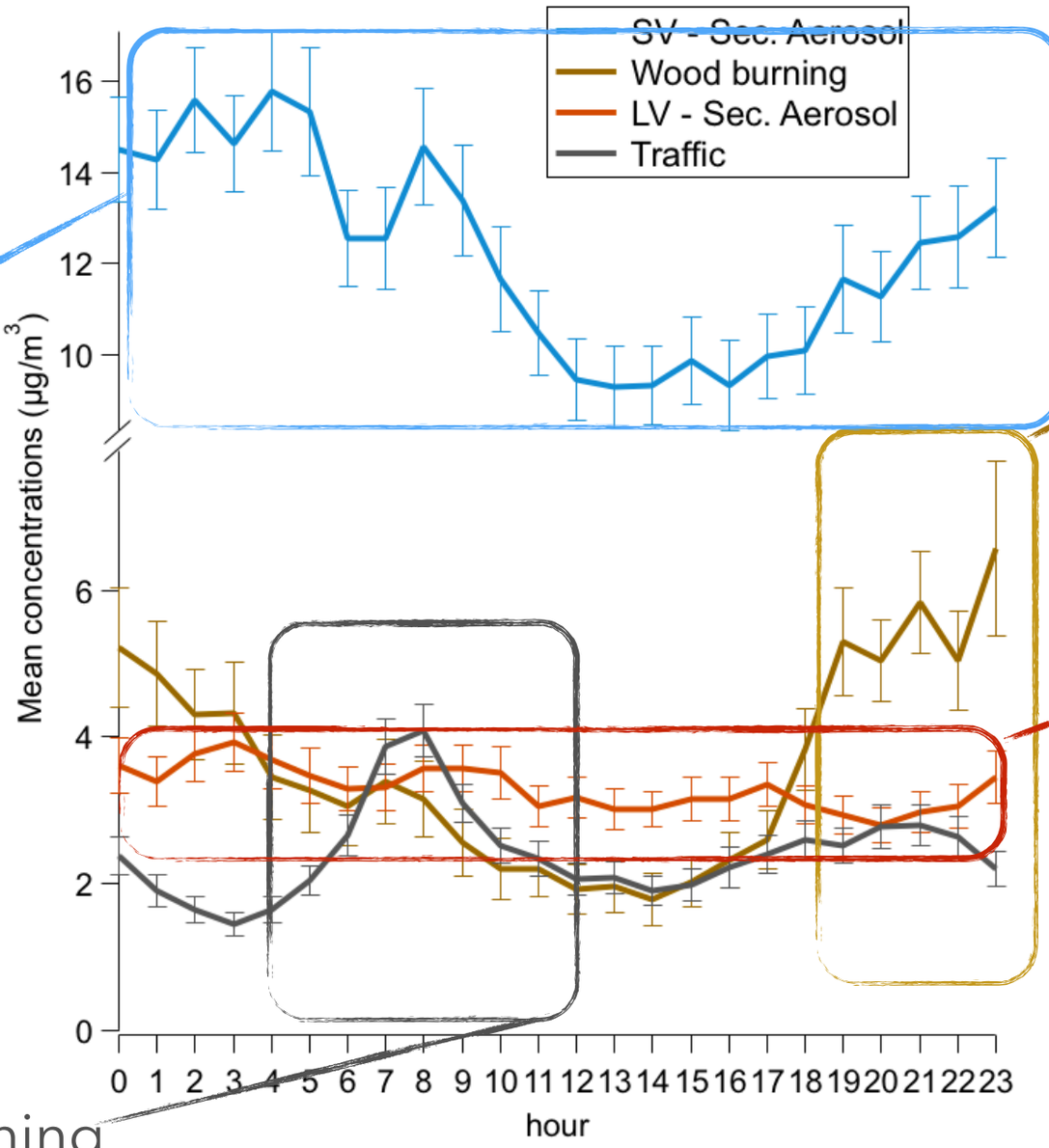
Noteworthy BC_{ff} could suggest internal mixing with SOA and sulfates

not associated to a source, this factor represents low-volatile secondary aerosols

IDENTIFICATION OF PM_1 SOURCES

Results - diurnal variations

Decrease during the day



Wb peak in the evening

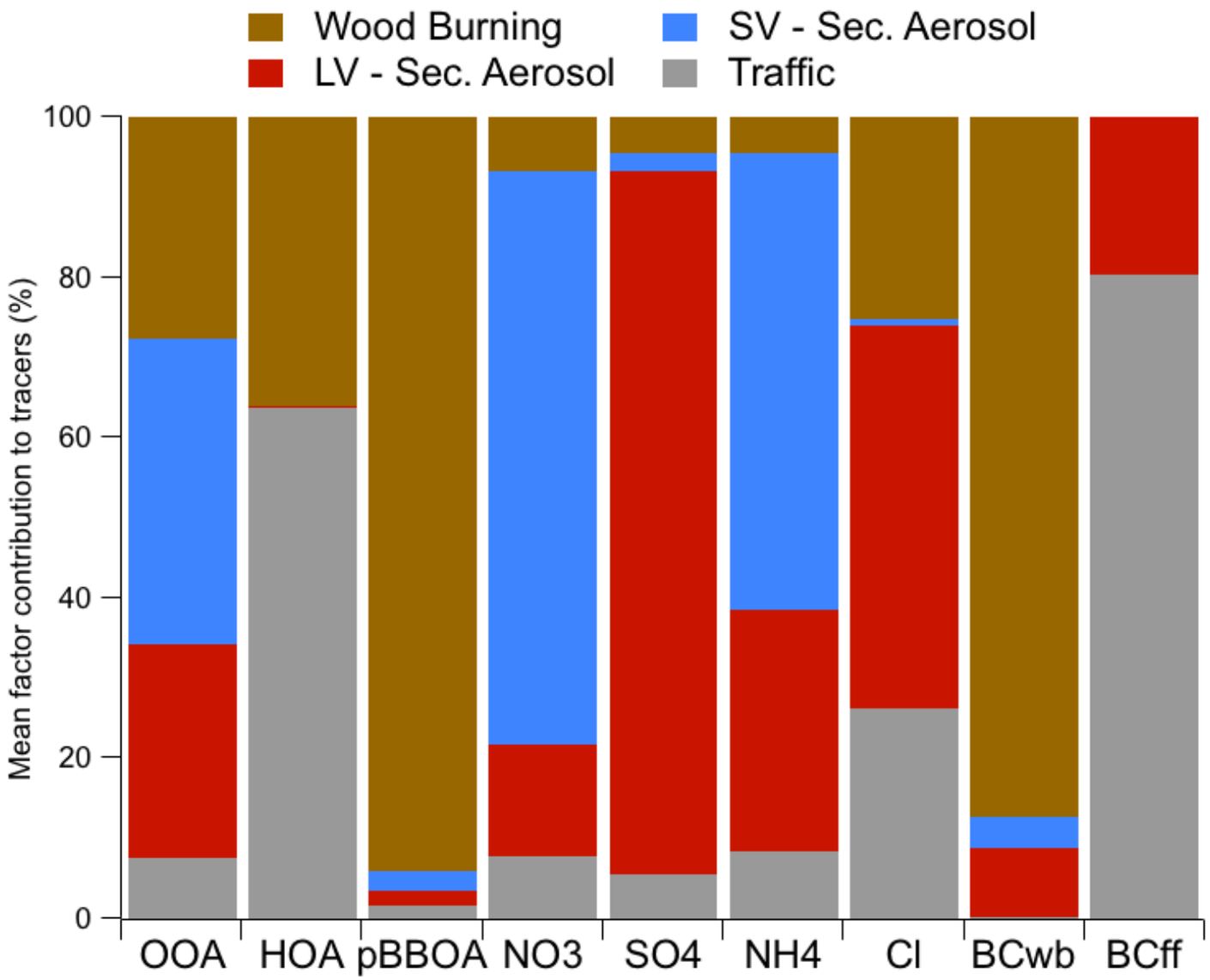
Uniform variability -> regional signal

Traffic peak in the morning

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Results - summary



- BBOA stays an excellent of wood burning emissions, but is not representative of the total mass
- HOA stays a good tracer of traffic emissions in urban areas, but is found to be significantly attributed to wood burning
- OOA is distributed in all 4 factors, but secondary material make up the major contribution. The OOA found in the wood burning and traffic factors may represent fast secondary organic formation, but should not be representative of the whole variety of wb and traffic-related SOA.

CONCLUSION & PERSPECTIVES

METROLOGICAL

METHODO. & SCIENCE

- ACSM appeared to be a credible solution for robust online monitoring of the chemical composition of sub micron aerosols over long term periods

- ACSM + Aethalometer satisfactorily close PM_1 mass

- Construction of a unique database (the longest in Europe). Strong implications for modeling studies to improve air quality forecast.

- Feasible and on-going implementation within regional operational network (Air Rhone Alpes, Air Lorraine)

CONCLUSION & PERSPECTIVES

METROLOGICAL

METHODO. & SCIENCE

- Automated Python tools to investigate geographical origins (PSCF, NWR, cluster)

- Long term characterization of OA for the 1st time in Paris (and among 1st studies in Europe) **Sliding Windows**

- First tentative of PM_1 source apportionment with online data (AMS/ACSM)

Intercomparison of PMF alternative approaches

THANK YOU!

PARTICULATE POLLUTION IN URBAN AREAS

SOURCE METEO CHEMICAL COMP.

Complex chemical composition essentially linked to the multitude of emission sources, and that each source has her inner chemical fingerprint (profile)

FIGURE JLJ

PARTICULATE POLLUTION IN URBAN AREAS

SOURCE METEO CHEMICAL COMP.

Complex chemical composition essentially linked to the multitude of emission sources, and that each source has her inner chemical fingerprint (profile)

especially true for organic matter! can be composed of >10 000 compounds!

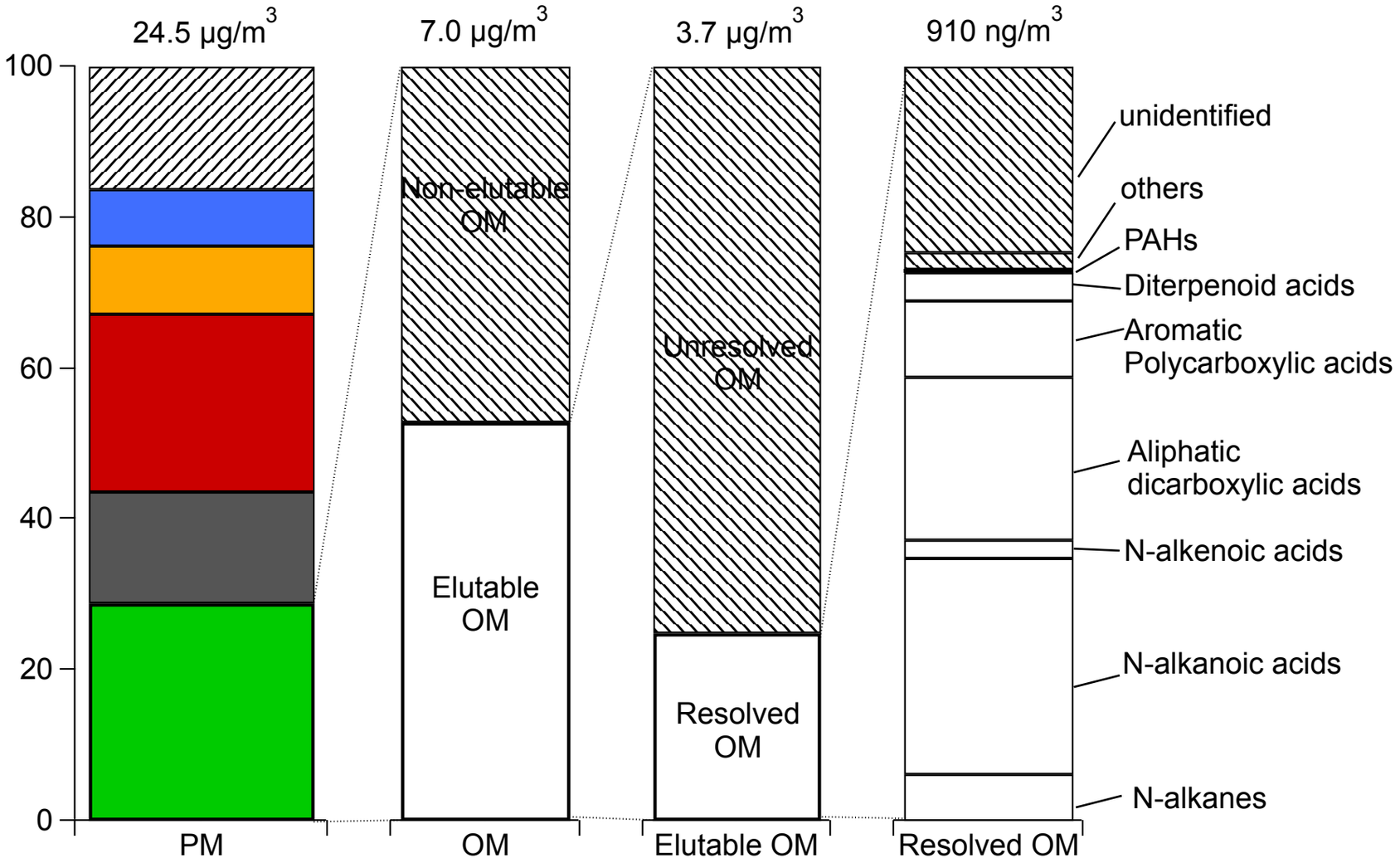
FIGURE JLJ

PARTICULATE POLLUTION IN URBAN AREAS

SOURCE METEO CHEMICAL COMP.

Complex chemical composition essentially linked to the multitude of emission sources, and that each source has her inner chemical fingerprint (profile)

especially true for organic matter! can be composed of >10 000 compounds!

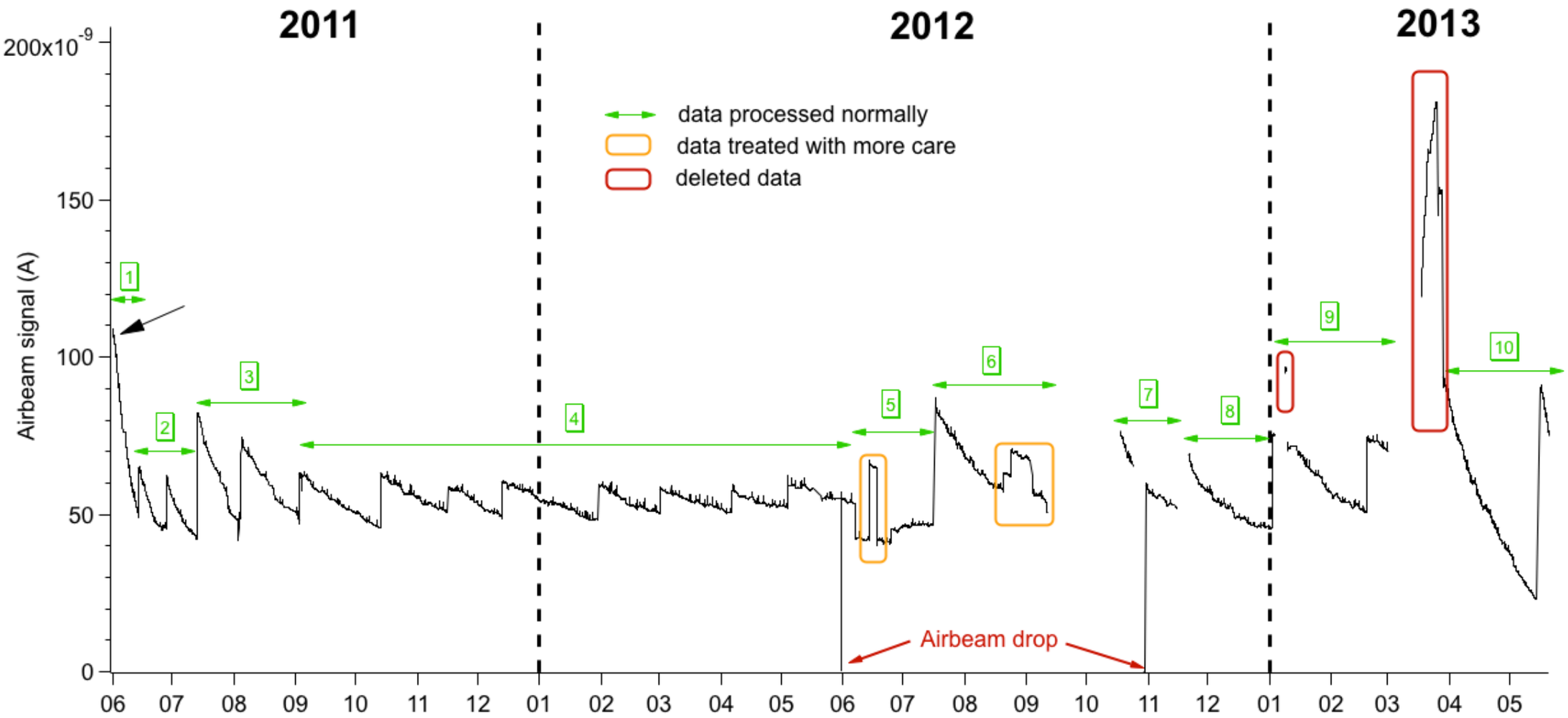


West Los Angeles, 1982

FIGURE JLJ

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

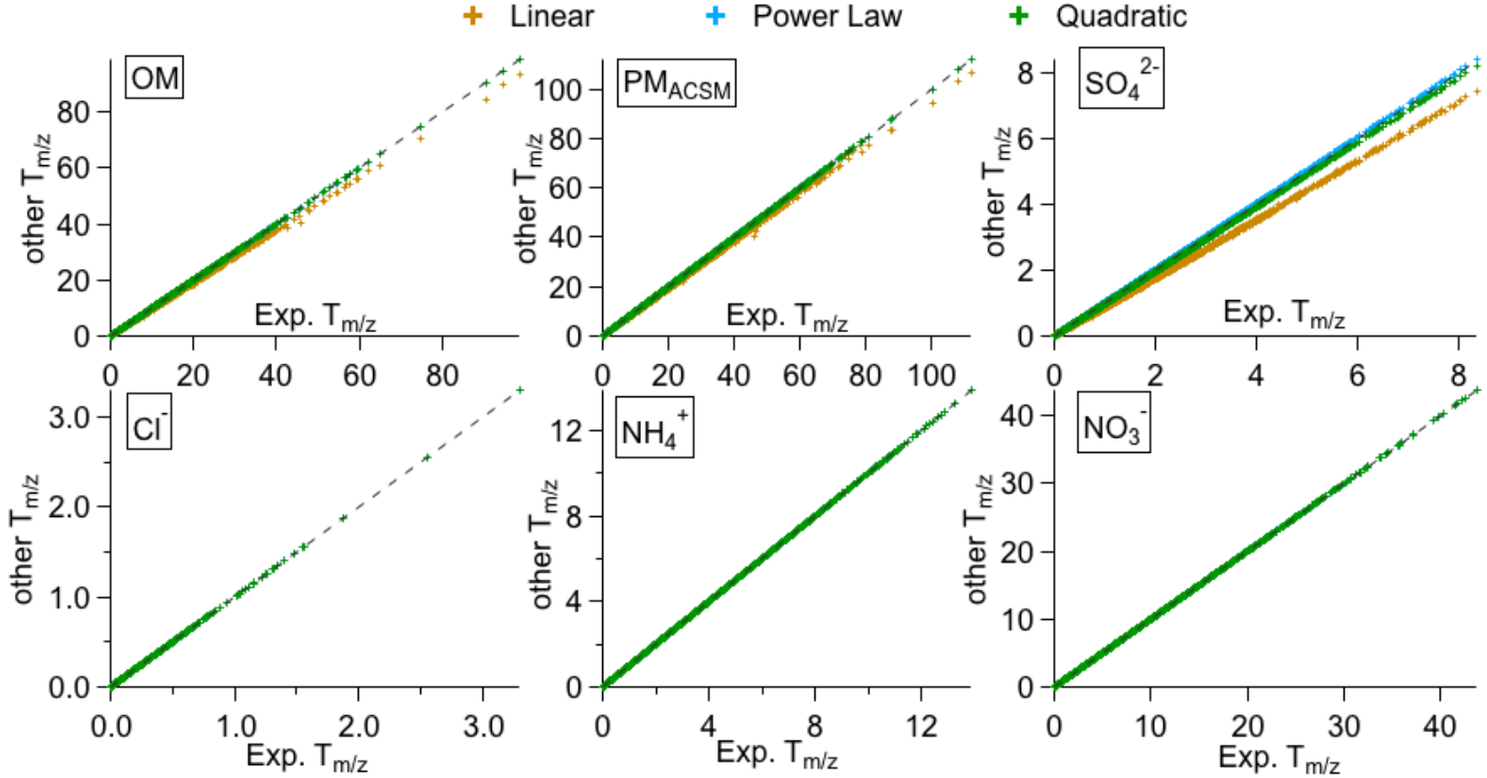
- Data treatment based on air beam (N_2^+) temporal variations *(Ng et al., 2011)*. Old versions of Igor procedures implied sequential treatments



THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

- Data treatment based on air beam (N_2^+) temporal variations. Old versions of Igor procedures implied sequential treatments

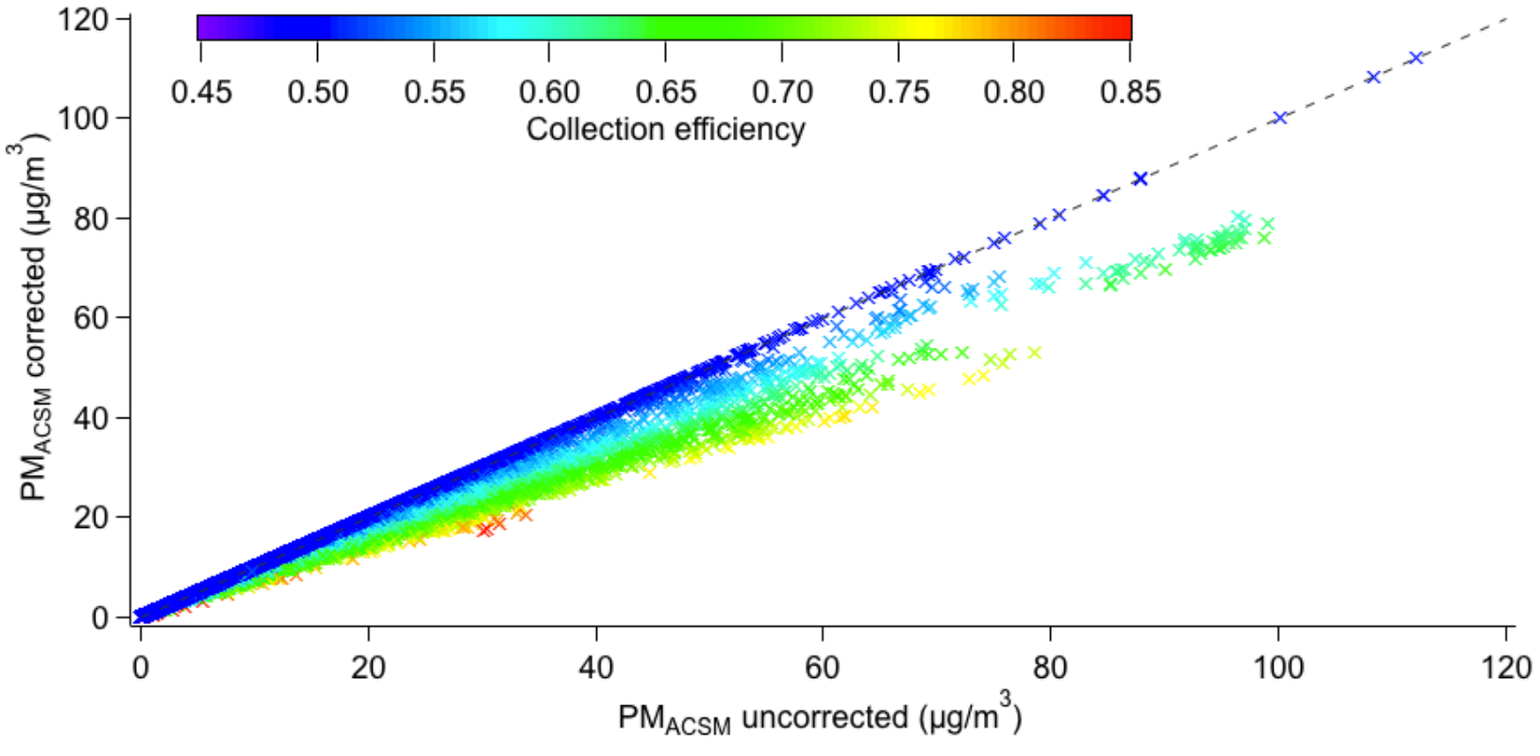
- Mass spectra need to be corrected from ion transmission through the quadrupole *(Ng et al., 2011)*



Does not affect PM_{ACSM} much, but needs to be done, especially regarding the statistical analysis of OM mass spectra

THE AEROSOL CHEMICAL SPECIATION MONITOR (ACSM)

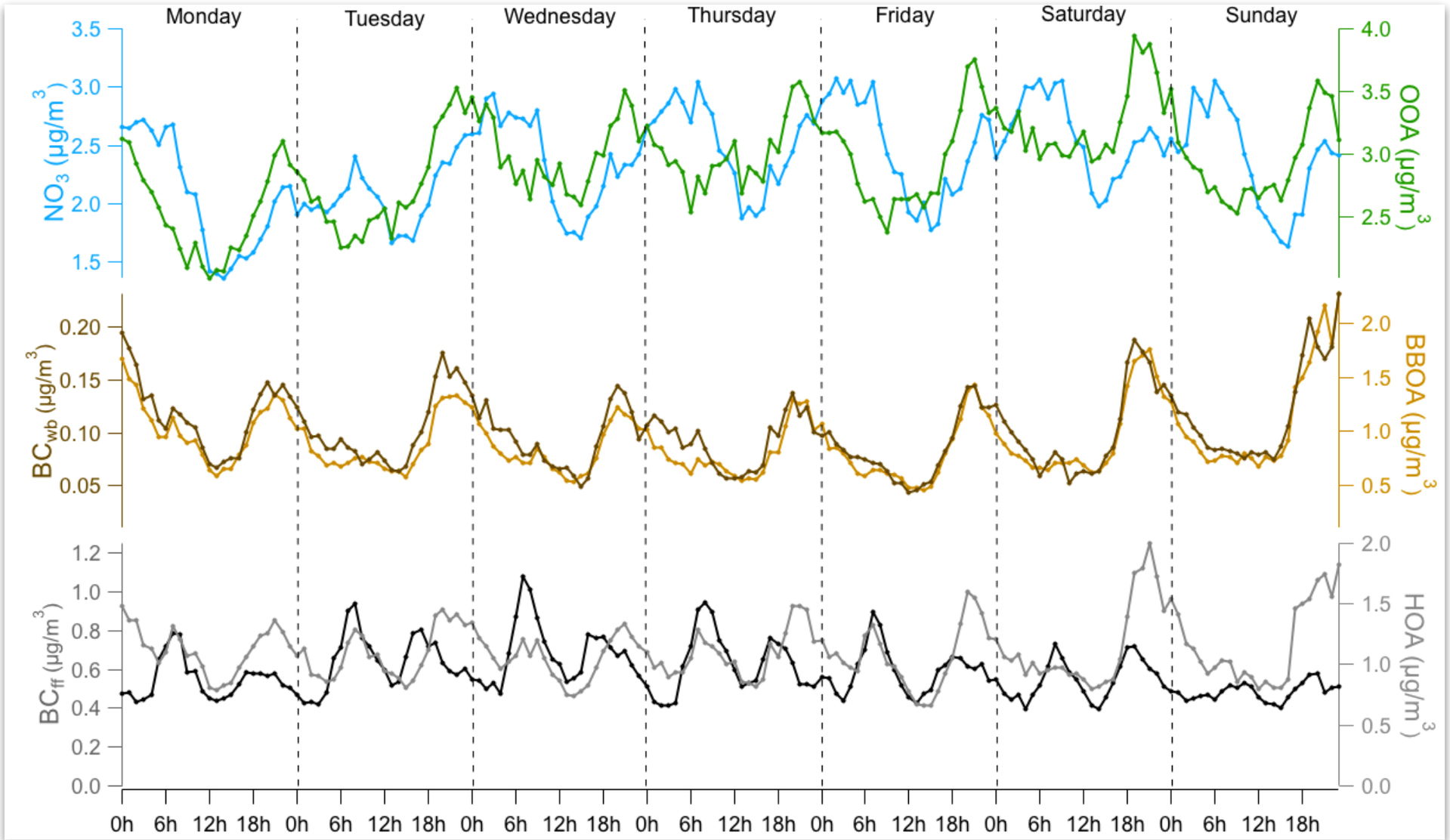
- Data treatment based on air beam (N_2^+) temporal variations. Old versions of Igor procedures implied sequential treatments
- Mass spectra need to be corrected from ion transmission through the quadrupole
- Collection efficiency need to be corrected from overestimations linked to NH_4NO_3 mass fraction *(Middlebrook et al., 2012)*



CHARACTERIZATION OF ORGANIC AEROSOLS

METHODOLOGY UNCONS. PMF CONS. PMF

3 factors - The added value from filters



IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Uncertainties

One of the most important part of a PMF analysis is to best estimate uncertainties of the dataset

Tracers

Aerodyne's uncertainties for inorganics not fully available yet (undergoing work)

«Polissar» approach (Polissar et al., 1998) promoted on the US EPA PMF soft

$$Unc. = \begin{cases} \frac{5}{6} \cdot LOD \text{ if } C \leq LOD \\ \sqrt{rel.unc.^2 \cdot C^2 + LOD^2} \text{ if } C > LOD \end{cases}$$

	NO	NH	SO	Cl	K	BC	BC
LOD (µg/m	0.12	0.51	0.28	0.1	0.02	0.1	0.1
rel. unc. (%)	15	15	15	20	50	40	40

«Weak» variable

«Strong» variable

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Uncertainties

One of the most important part of a PMF analysis is to best estimate uncertainties of the dataset

Tracers OA fractions

- No automated calculations of uncertainties for time series of PMF outputs (undergoing work)

→ «Polissar» approach

	HOA	BBOA	OOA
LOD (µg/m	0.1	0.1	0.1
rel. unc. (%)	30	30	30

«Weak» variable

«Strong» variable

- Empirical determination of LODs and rel. unc. Definitely not the best way, but best compromise to give weight to OA (otherwise, too strong weight of inorganics)

IDENTIFICATION OF PM_1 SOURCES

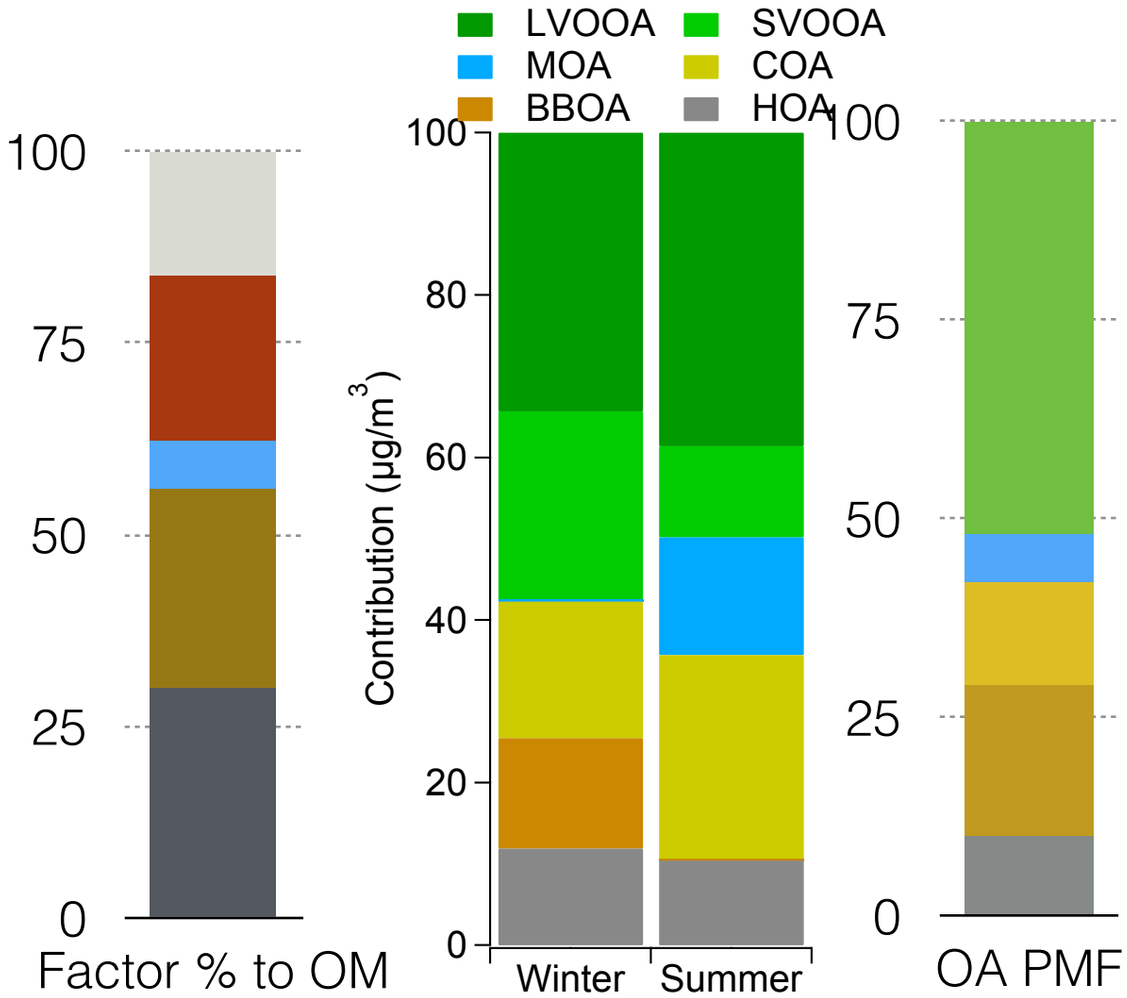
Results - sensitivity tests

- Constrained and unconstrained OA source app. give similar results. The resulting consecutive PMF analyses are not fundamentally different.
- A wide range of a-values (OA-source app.) has poor impact on OA fractions' profiles and time series.
- Residuals shows that little information stay unused from the OA source app.
- Bootstrap analysis highlight the stability of the 4-factor solution
- Several relative uncertainties used in the PM1 source app. were tested in order to refine the empirical initial guesses
- The intense wood burning peak has little impact on final results

Characterization of Organic Aerosols

METHODOLOGY UNCONS. PMF

CONS. PMF



Secondary OM from Bressi et al.: 28%

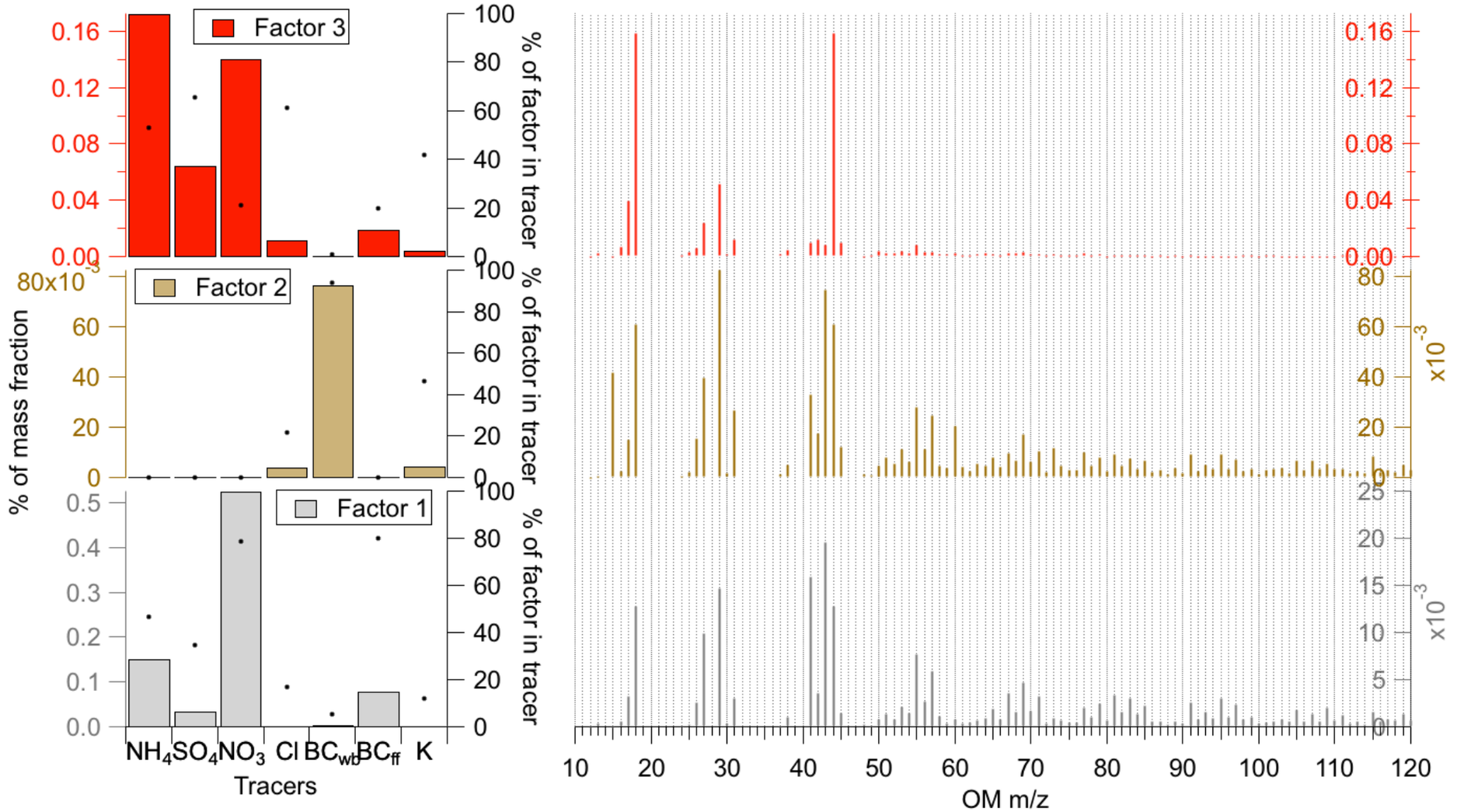
Secondary OM from OA PMF: 59%

- OM from other sources
- OM from SO4-rich source
- OM from NO3-rich source
- OM from WB source
- OM from Traffic source

- OOA
- MOA
- COA
- BBOA
- HOA

IDENTIFICATION OF PM_1 SOURCES

Other approaches - « All in one » PMF

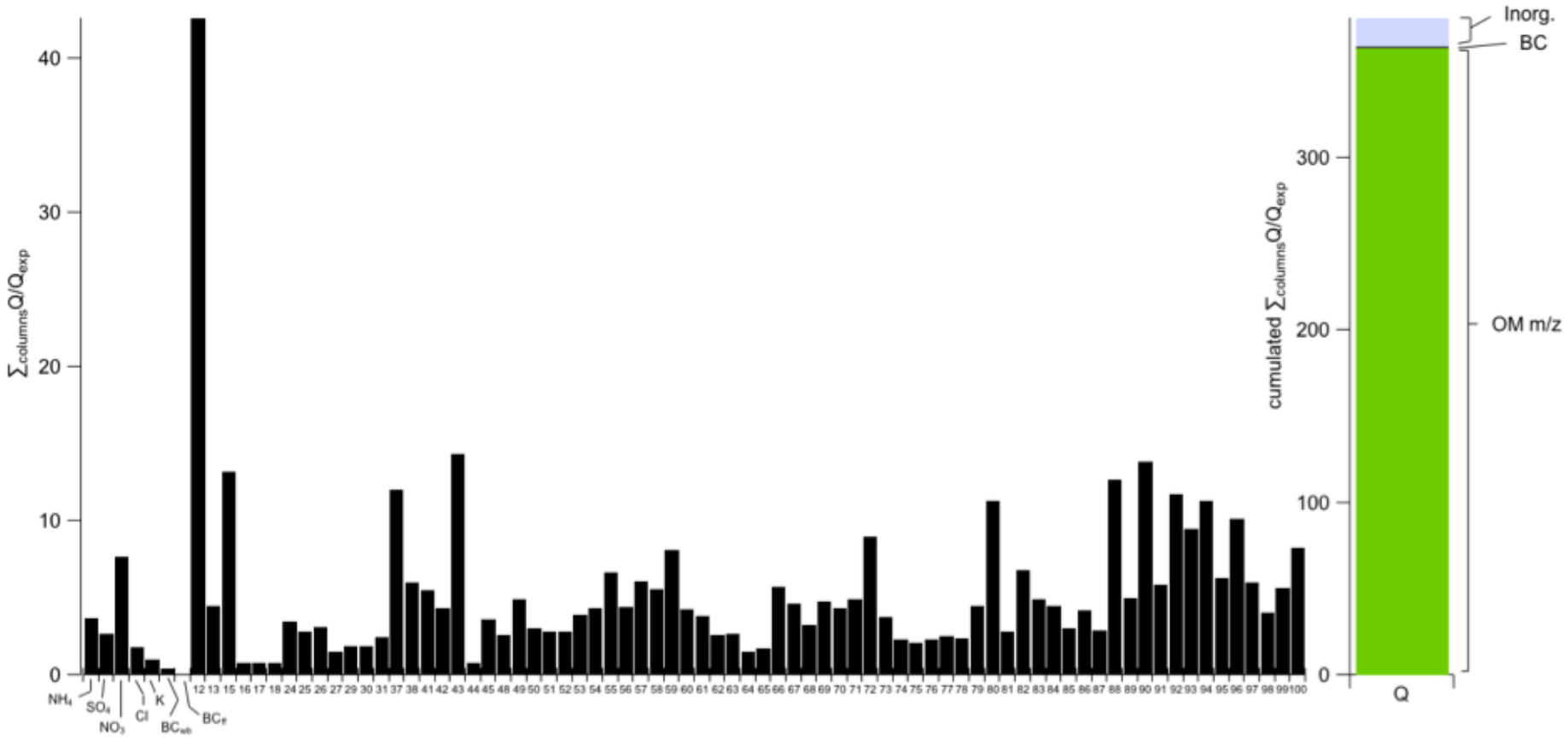


- 3-factor solution is most stable (from bootstrap analysis)
- AS-rich factor, wood burning factor, and AN-rich + traffic factor
- OA profiles make sense but AN-rich + traffic factor stay convoluted

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM1 SOURCE APP.

Other approaches - « All in one » PMF



IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Other approaches

Aethalometer AE31

ACSM

12	13	15	.....	100	NO	SO	NH	Cl	K	BC	BC

F1 F2 F3 ..... Fx

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY

OA SOURCE APP.

PM_1 SOURCE APP.

Other approaches

ACSM

OA source app.

1st PMF/ME2 analysis

12	13	15	.....	100

OOA

HOA

BBOA

multilinear regression

PM_1 source app.

OM

NO_3

SO_4

NH_4

Cl

(K)

BC_{wb}

BC_{ff}

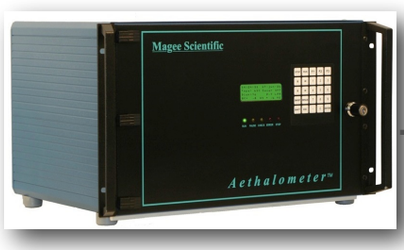
F1

F2

F3

Fx

Aethalometer AE31



Multi-λ abs. coeff.

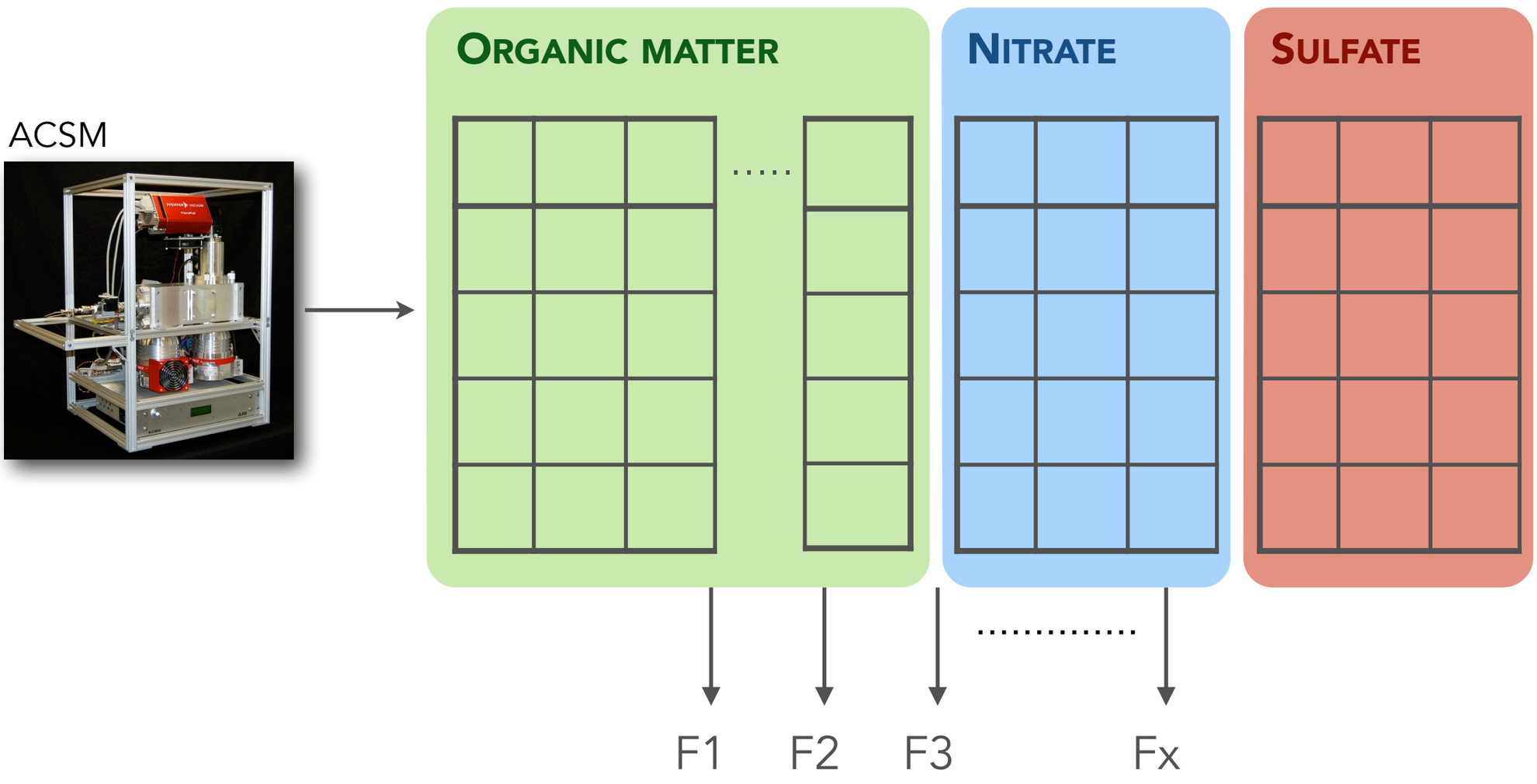
Aethalo. model

Sandradewi et al., 2008

IDENTIFICATION OF PM_1 SOURCES

METHODOLOGY OA SOURCE APP. PM_1 SOURCE APP.

Other approaches



methodology from Sun et al. 2012 - not tested yet

IDENTIFICATION OF PM_1 SOURCES

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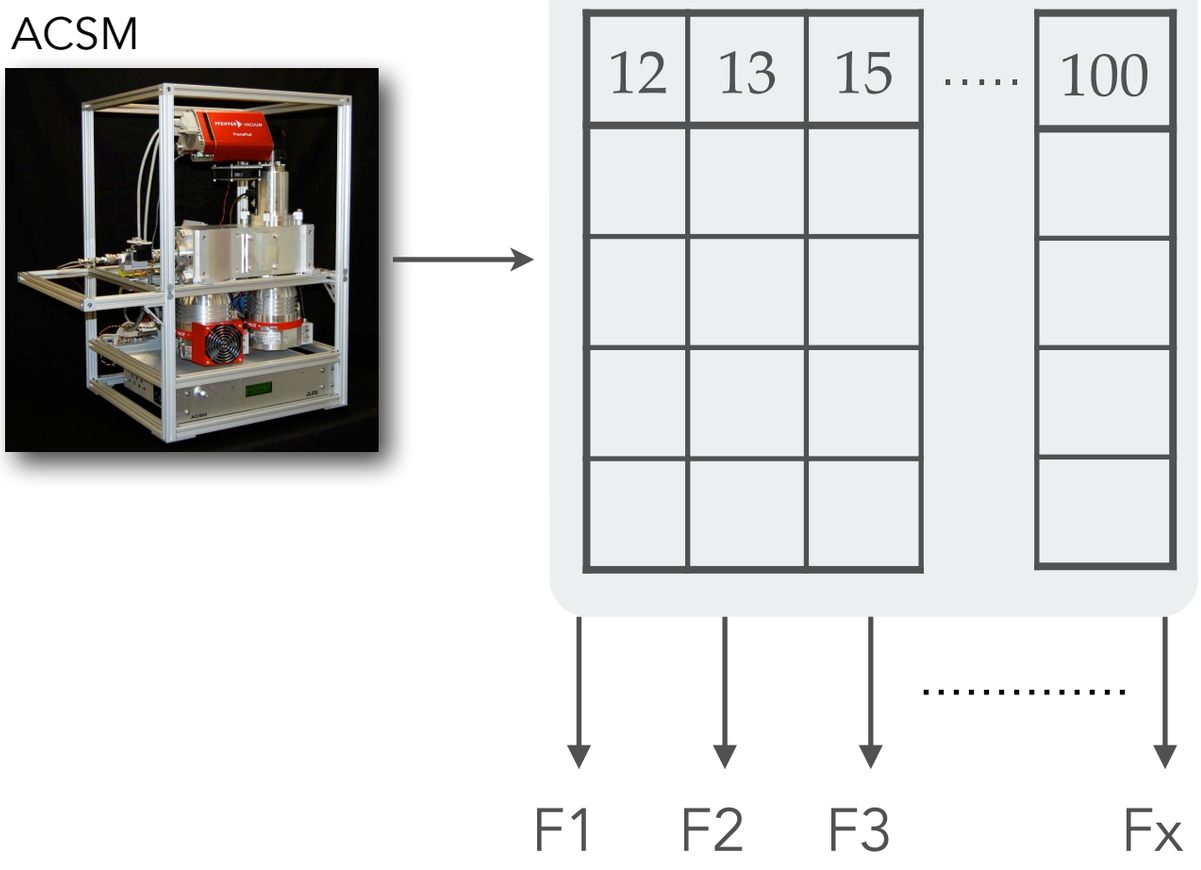
Other approaches



methodology from McGuire et al. 2014 - not tested yet