Lo studio del particolato atmosferico al laboratorio LABEC mediante tecniche IBA

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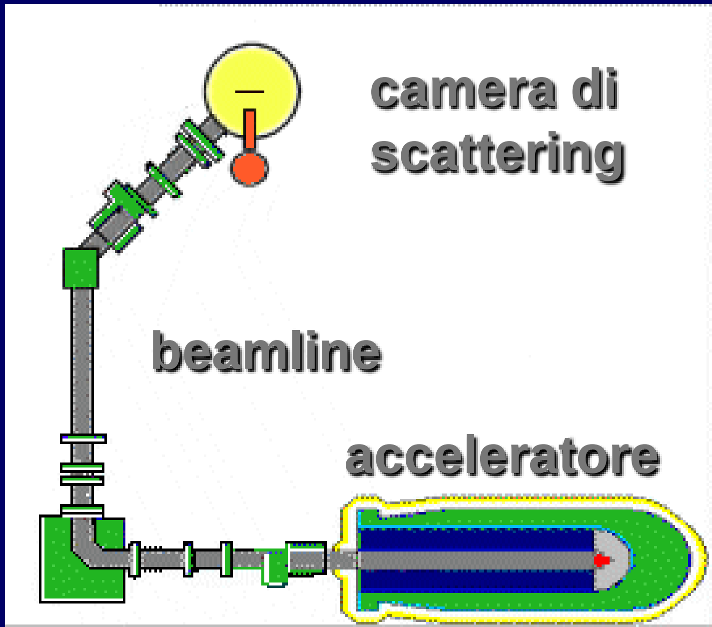
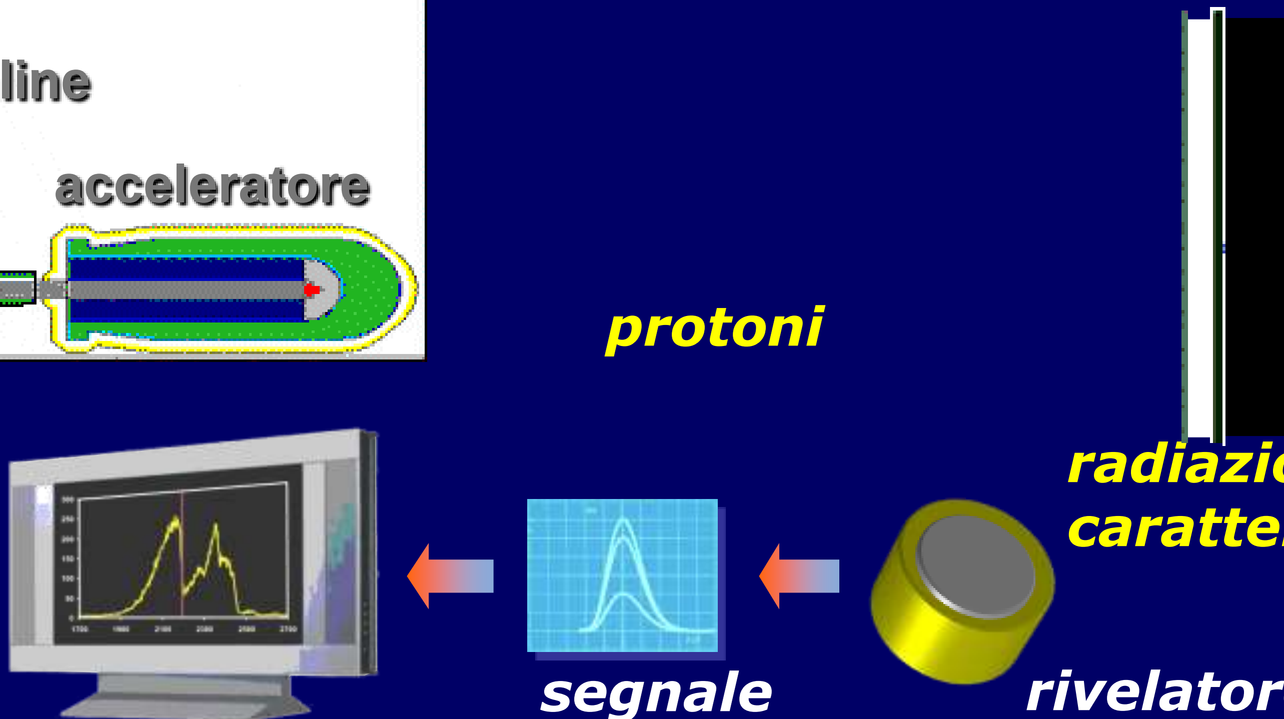
TECNICHE DI ANALISI CON FASCI IONICI (IBA)





PIXE for aerosols analysis

\+
- <u>1-10 min</u> bombardment to detect up to 20 elements (Na to Pb)
- Good detection limits down to µg/g (ng/m^3)
- Possibility to analyze sample with little mass
- Non-destructive analysis <u>without</u> any sample preparation
- It can be complemented with other IBA techniques

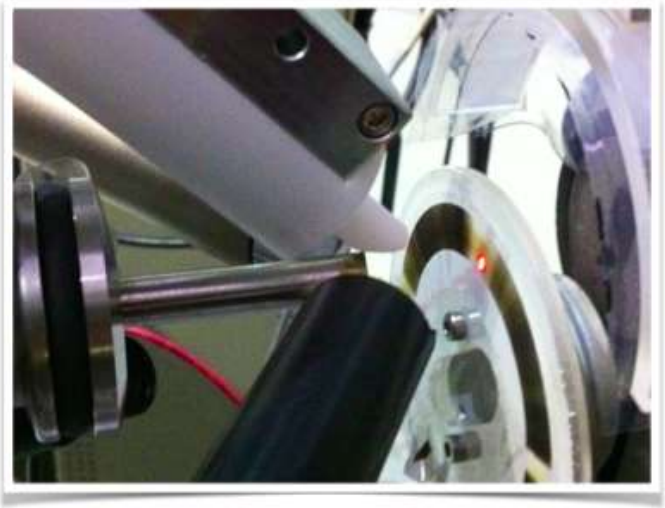
\-
- PIXE provides only part of the desired information
- Other competitive techniques: ICP-MS
XRF
SR-XRF

When PIXE on aerosols?

Other competitive techniques...

PIXE must be used when its application can give unique information or can give final results in a far simpler way with respect to other competing techniques.

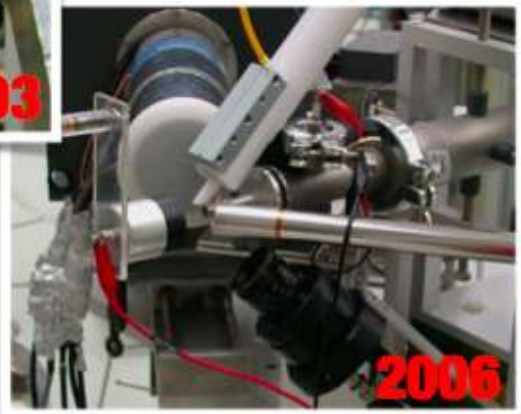
- Very short measuring time
  (~ 60 s vs. several m or h)
- Analysis of very low mass samples
  high time resolution samples (e.g. 1h) →
- Detection of all soil elements
  study of Saharan dust episodes or natural aerosol
- No sample pre-treatment
  fundamental for very low mass samples (e.g remote sites aerosol) ⟶ minimized possible contaminations



A prerequisite is the use of a proper experimental set-up which fully exploits PIXE potentialities.

Evolution of PIXE set-up for aerosols

2 Si(Li):
$10\ mm^2$, 3 mm
$80\ mm^2$, 5 mm



SDD: $7\ mm^2$, 0.3 mm
Si(Li): $80\ mm^2$, 3 mm

Funded by INFN grants (NUTELLA, NUMEN, MASAI) and EU LIFE+ AIRUSE project

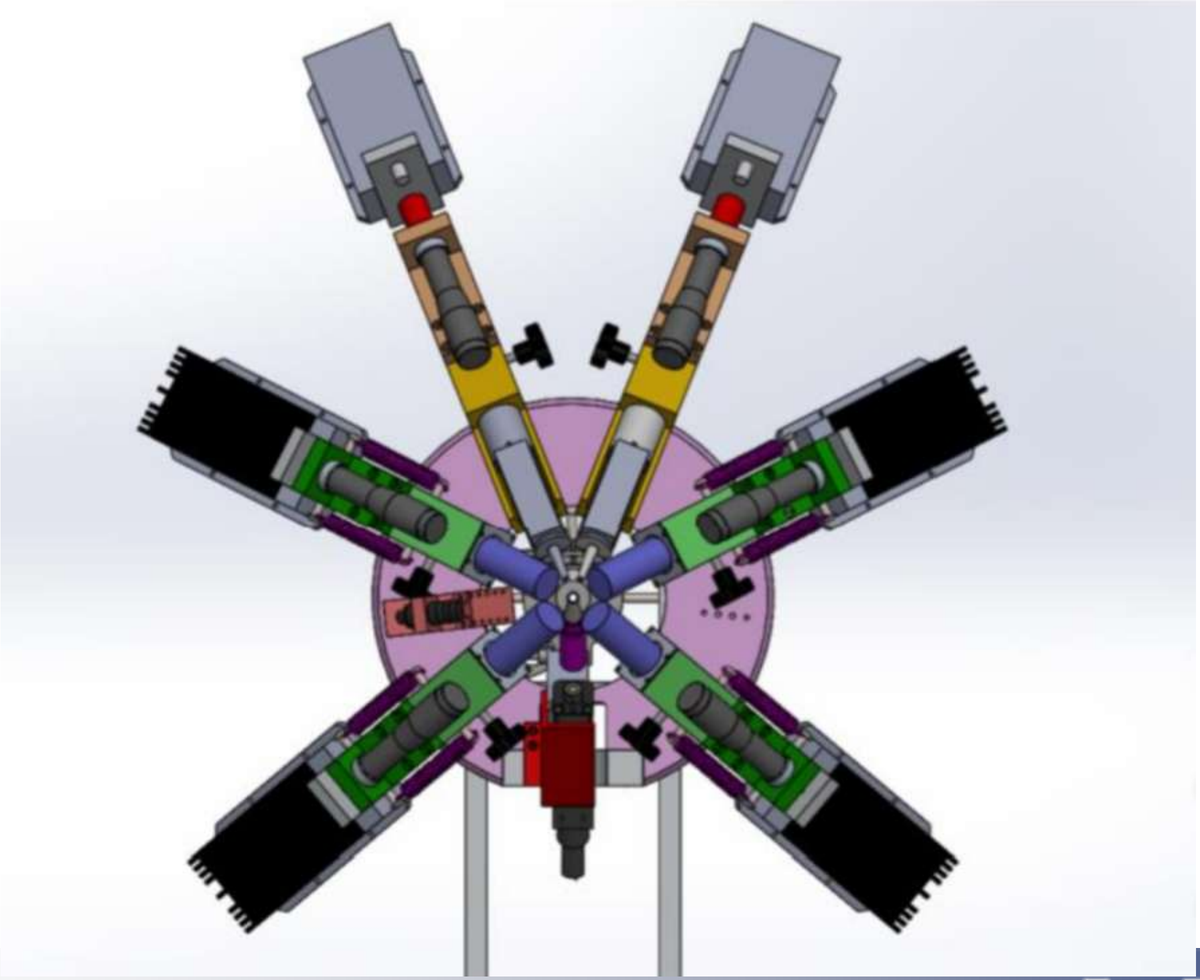
2 SDDs: $7\ mm^2$, 0.3 mm
$80\ mm^2$, 0.5 mm

3 SDDs:
$30\ mm^2$, 0.5 mm
2x $80\ mm^2$, 0.5 mm

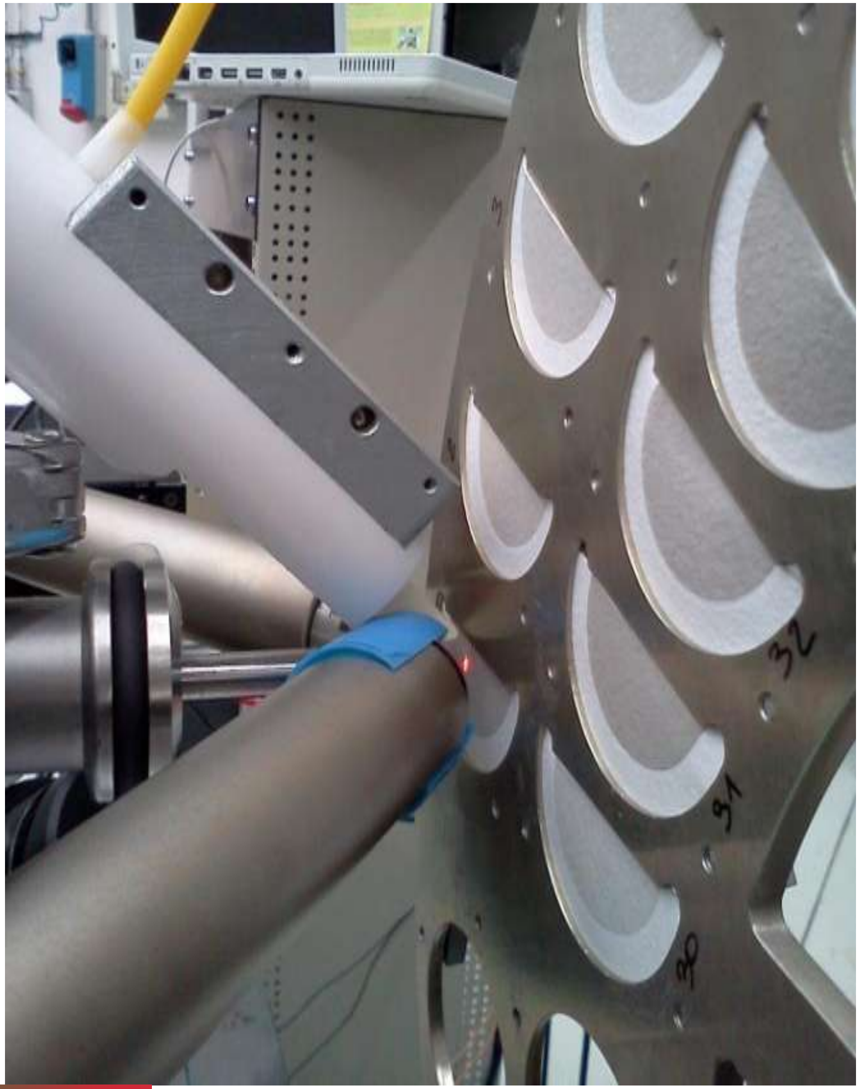
Calzolai et al., NIM B B 249 (2006) 928

Lucarelli et al., NIM B 318 (2014) 55

Prossimo set-up di misura al Labec



"Daily samples"



Ep ~ 3 MeV

i ~ 5-100 nA

Measuring time:
30-60 seconds/sample

1 year ~ 1 day

Samples with hourly resolution

- Many particulate emissions change within few hours (industrial emissions, traffic rush hours, construction works, …).

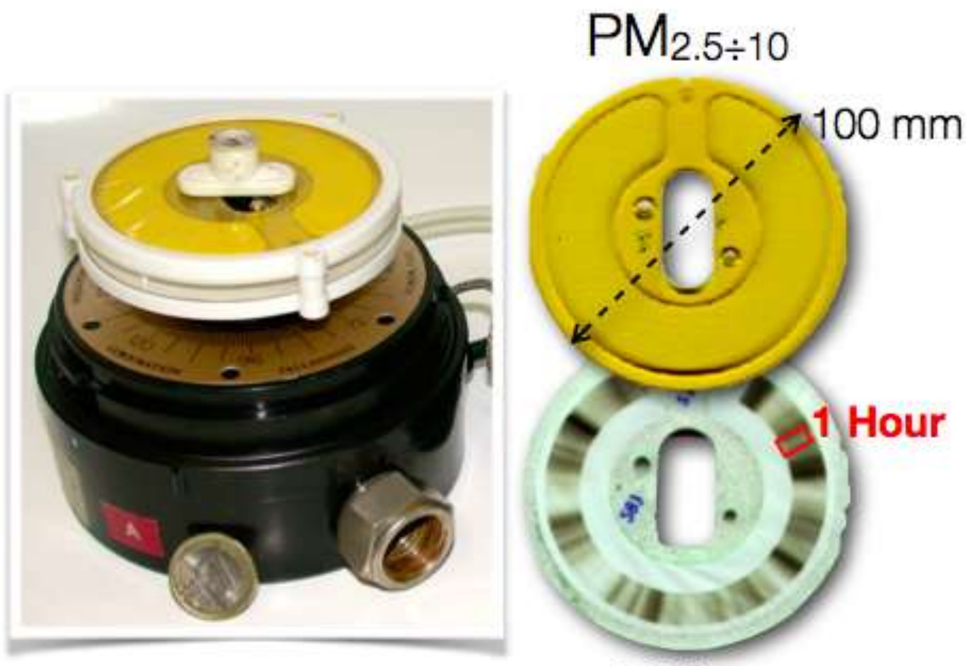
- Moreover, as many meteorological parameters, like wind intensity and direction, change within a 1-h time scale and the boundary layer evolution shows strong diurnal patterns, atmospheric transport and dilution processes change within few hours
- As a consequence, the aerosol concentration and composition may significantly change within few hours and daily samples are not capable of tracking these rapid changes

⇩

The measurement of the PM composition with high time resolution is important to: assess health and environmental effects, understand transport processes and determine source contributions.

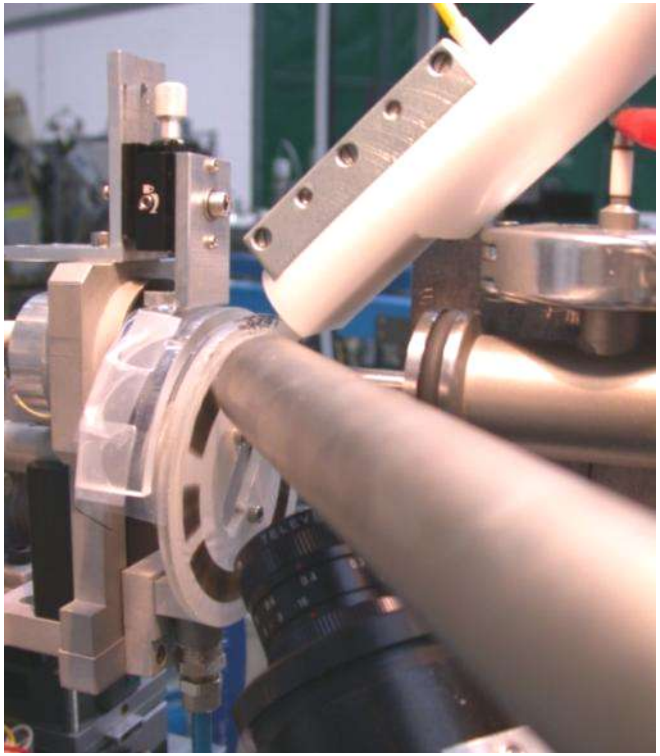
Samples with hourly resolution

Continuos “streaker” sampler
(*PIXE International*)



Kapton foils
Nuclepore filters

beam size (1 x 2 mm^2)
corresponding to 1h point



1 week of sampling =
168 (x2) hourly samples!

“Hourly samples”

E_p =2.7 MeV

i ~ 50-300 nA

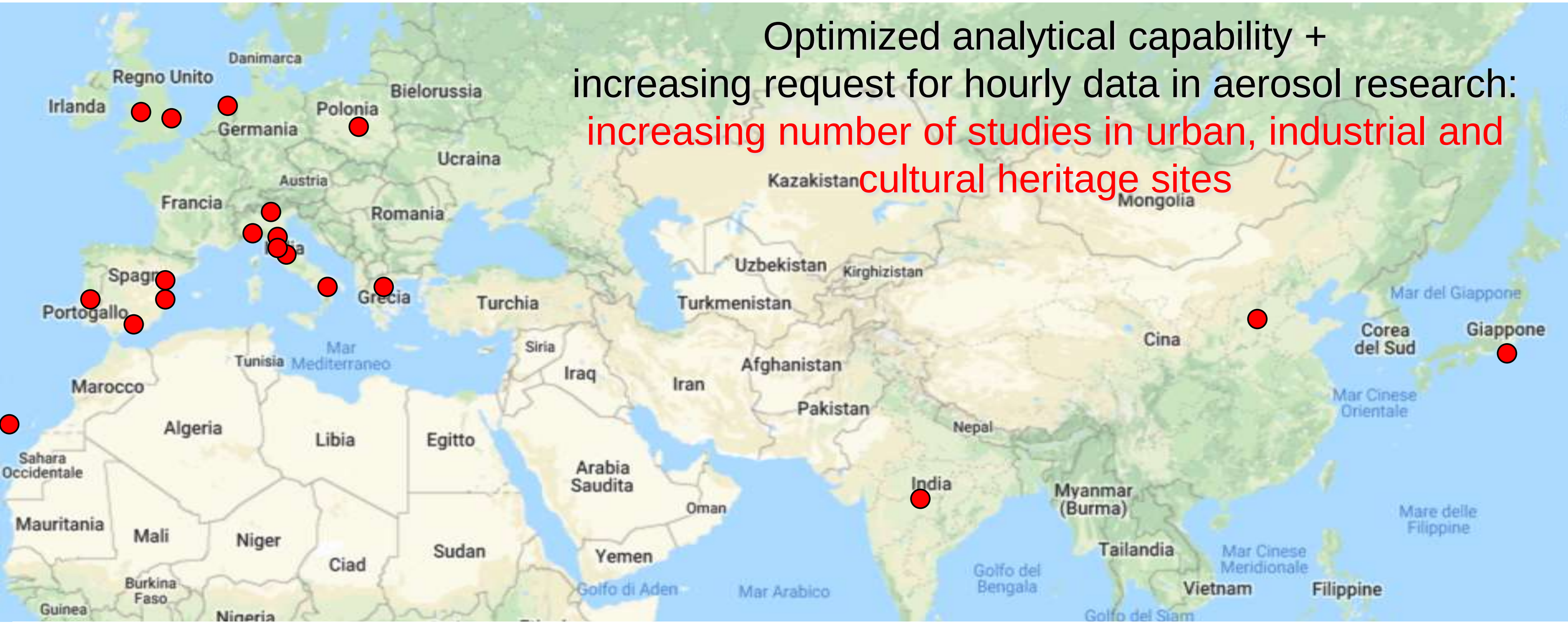
Measuring time:
60-90 seconds/sample

1 week =168 h

1 filter <5 hour

Streaker + PIXE campaigns

Optimized analytical capability +
increasing request for hourly data in aerosol research:
increasing number of studies in urban, industrial and cultural heritage sites



Many campaigns have been carried out, usually within projects involving longer daily samplings and/or in parallel with other high time resolution instruments (AMS, field EC-OC, etc.)

The streaker+PIXE contribution has been important to identify sources like traffic, biomass burning, industrial emissions, pyrotechnic events, and also the transport of desert dust.

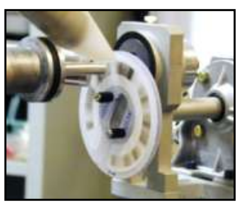
***STRAS*: Size and Time Resolved Aerosol Sampler**

Gruppi INFN Firenze, Milano, Genova, Dadolab

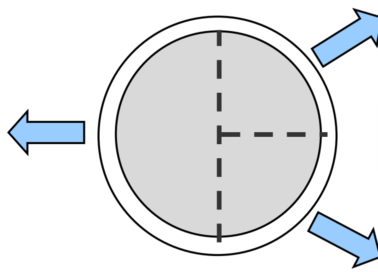
SAMPLE ANALYSIS

PM10 concentration: gravimetry

PIXE
(Particle Induced X-ray Emission)
Elements with Z>10



IC
(Ion Chromatography)
Main soluble ions
Na^+, NH_4^-, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, MSA, Ac, For, Gly, Ox

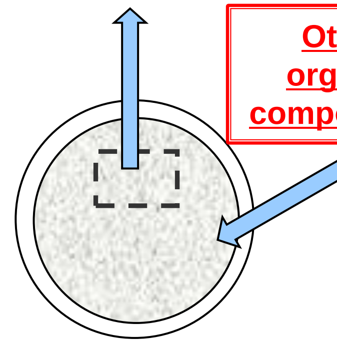


Teflon Filter

ICP-AES
Metals soluble in HNO_3 pH=1.5
Al, Si, P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, La, Ce

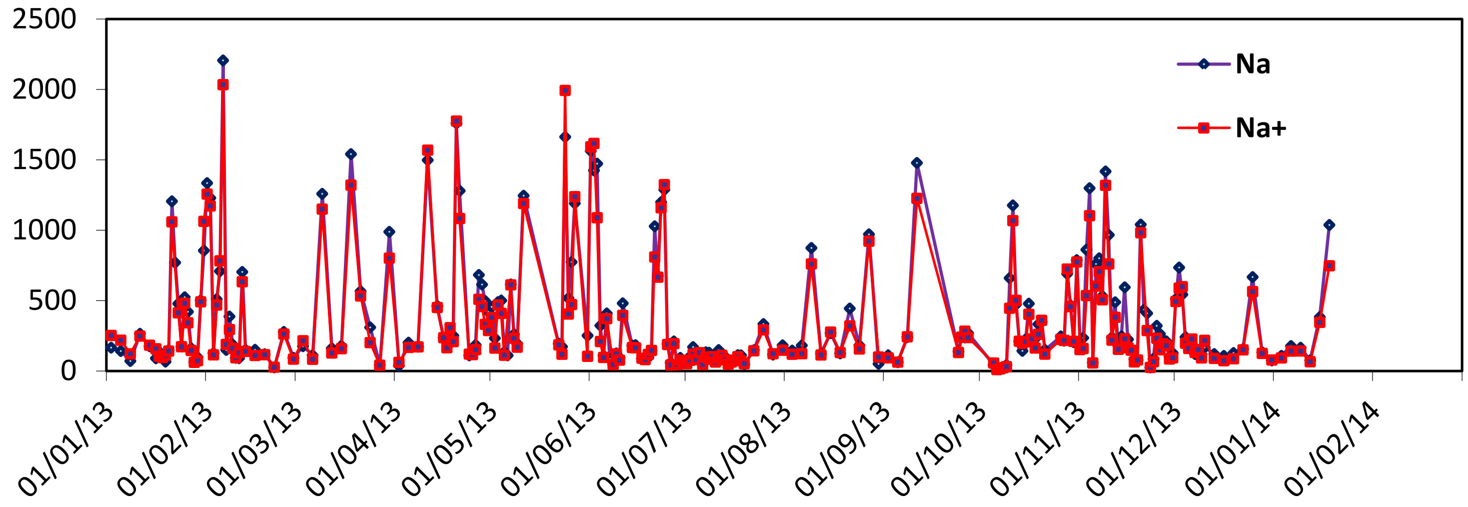
Thermo Optical-Analyzer
(Sunset)
Carbon (OC, EC, TC)

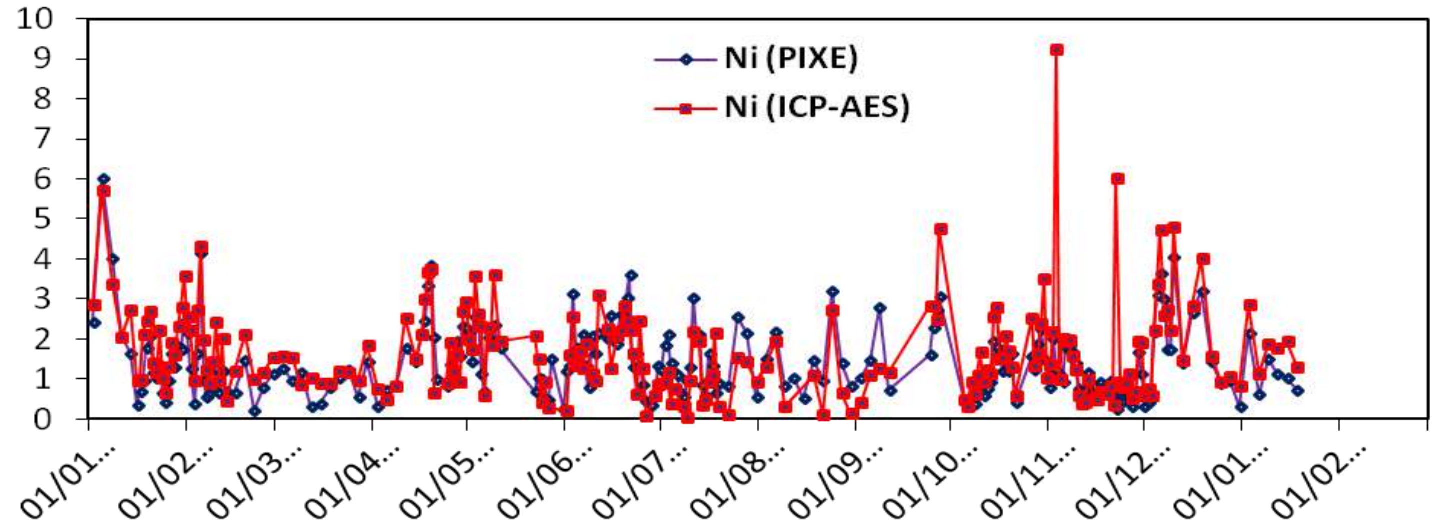
Other organic components

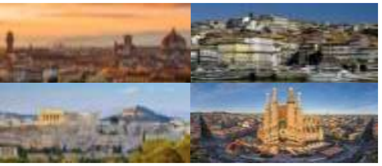


Quartz Fiber Filter

Quality Assurance







http://airuse.eu/en/

THE AIRUSE PROJECT AIMS

- Characterizing similarities & differences in PM sources & contributions across S-EU (5 cities)
- Once the main sources of PM10 and PM2.5 are identified, the strategic goal of the AIRUSE project is to develop, test and propose specific measures to abate urban ambient air PM in S.-EU, to meet AQ standards & to approach WHO guidelines.

Specific objectives

- Obtaining harmonized source contributions to PM for AIRUSE cities & to identify those responsible for exceedances of the PM limit values and WHO guidelines
- Develop, test and propose cost-effective air mitigation measures for South European countries
- Support adaptation of control strategies for reducing PM exposure in South Europe

Specific PM mitigation measures

- Street washing & dust suppressants for road dust and deposited African dust
- Biomass burning
- Industrial emissions (channelled and fugitive)
- Strategies from other European countries (LEZ, eco-efficient vehicles, labelling, shipping, biomass burning…)

AIRUSE

AIRUSE SAMPLINGS

Long term measurements			BCN-UB	FI-UB	MLN-UB	POR-TR	ATH-SUB
Daily	PM10	Mass	122	226	379	123	197
		Elements	122	226	241§	123*	197‡
		Ions	122	226	337	123	197
		ECOC	122	226	348	123	197
		CC	122	226	89	123	197
		Levoglucosan			324		243
	PM2.5	Mass	126	243	378	126	243
		Elements	126	243	361§	126	243
		Ions	126	243	374	126	243
		ECOC	126	243	370	126	243
		Levoglucosan	126	243	356	126	888
Hourly	PM2.5-10	Elements	716	504		504	888
	PM2.5	Elements	714	504		504	197

*intercomparison between PIXE and ICP on Teflon filters
‡intercomparison between Teflon (PIXE) and quartz (ICP) filters
§ intercomparison between PIXE and XRF on Teflon and MCE filters

- PIXE
- ICP
- SUNSET
- XRF
- Infrared
- IC
- GC

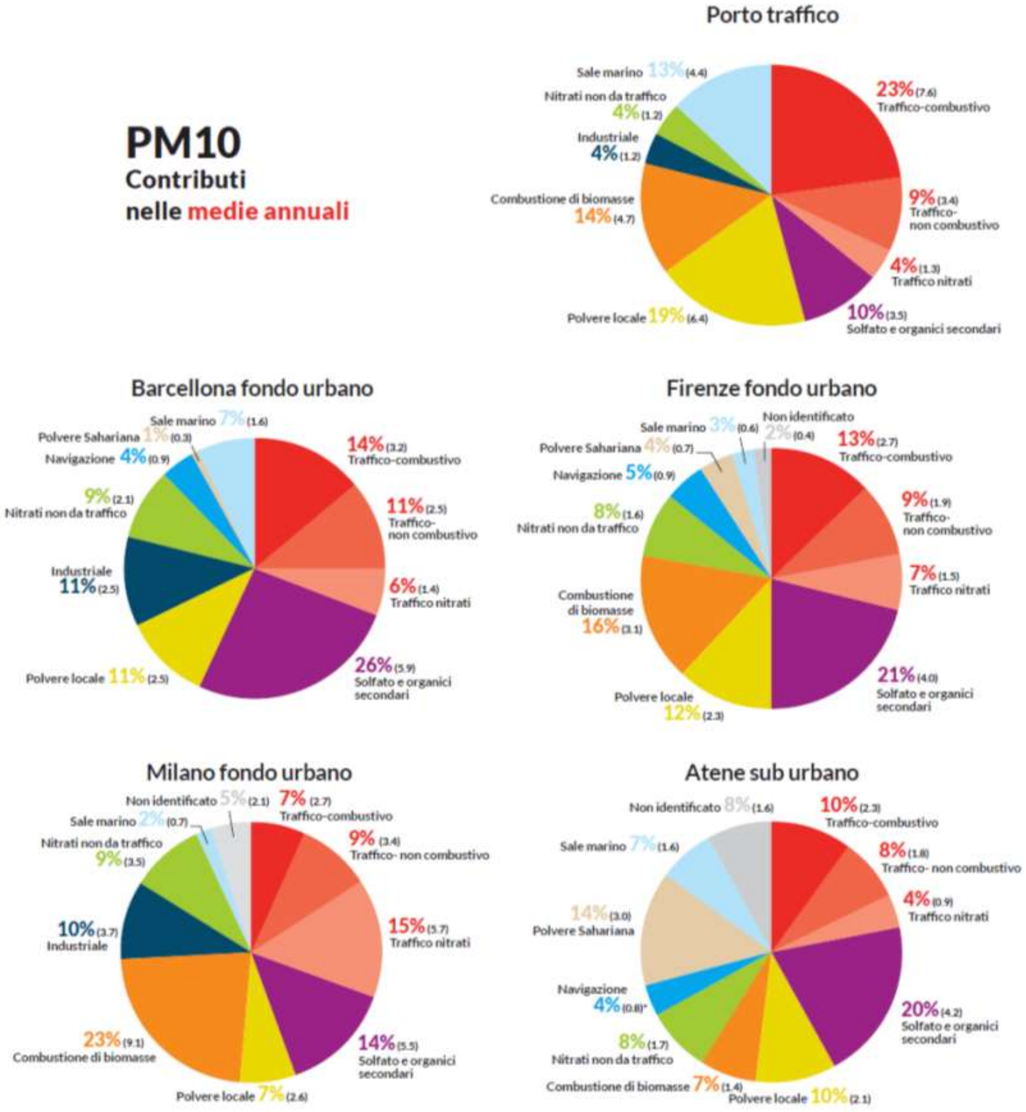
1 year daily sampling of PM10 and PM2.5
- Jan.2013 - Jan.2014 (every 3rd day*)
-quartz and teflon

Shorter samplings 1 hour time resolution
- ~ 2 weeks in winter and summer
- fine and coarse

7400 analysed samples!

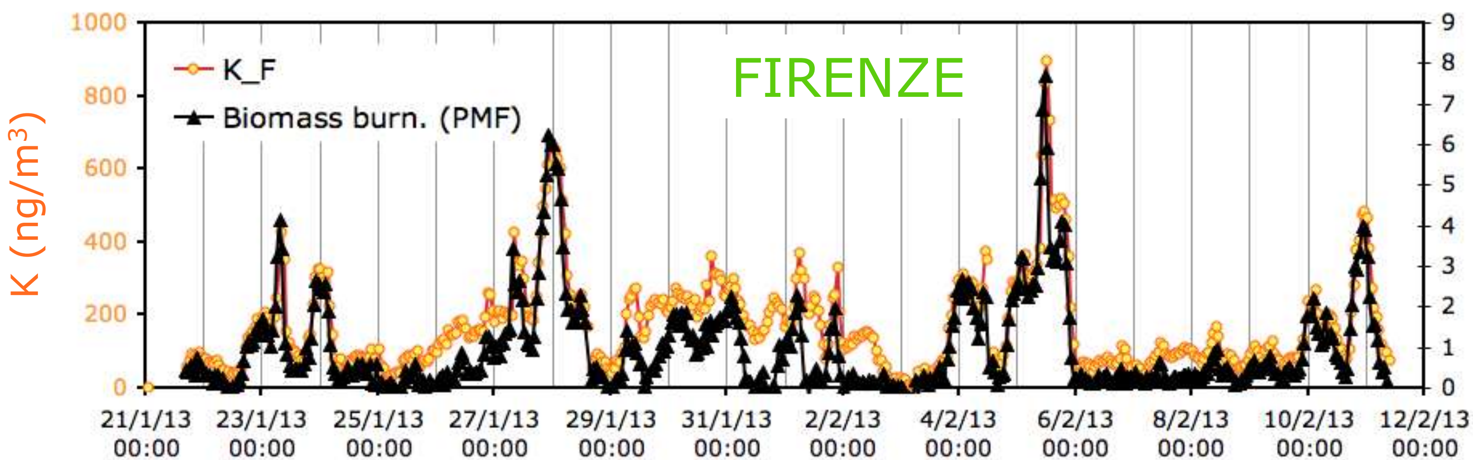
* All the days if saharan intrusions foreseen (Hysplit, Skiron)

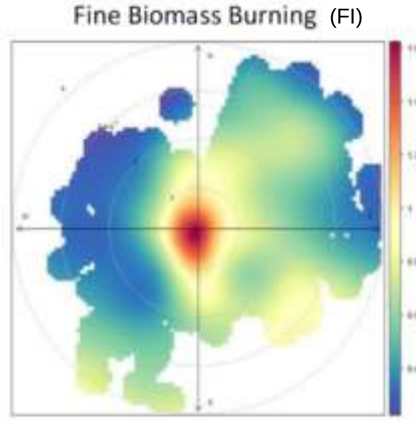
Contributo delle sorgenti al PM10

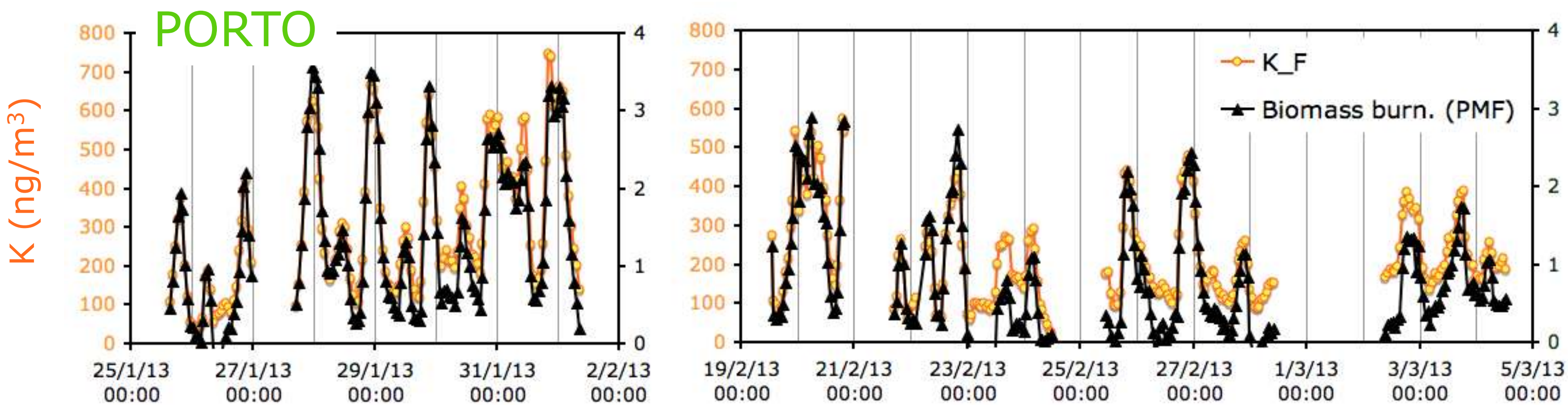


BIOMASS BURNING: HOURLY RESOLUTION

Periodic time pattern with
peaks during the evening-night hours in the
fine fraction, suggesting the use of biomass burning for domestic heating







Highly polluted urban environments: Delhi

Delhi was recently ranked the most polluted city in the world for air pollution by the WHO

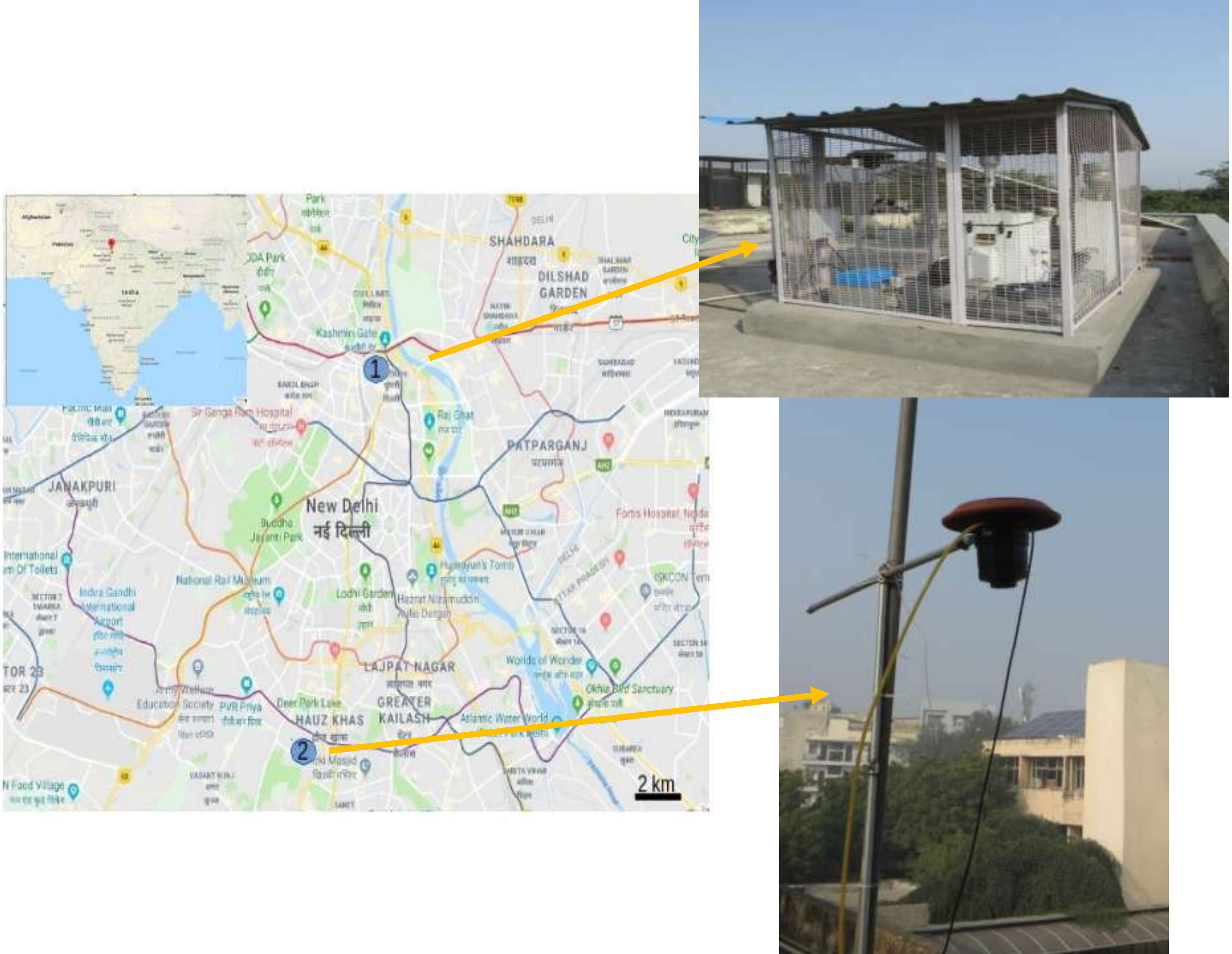
ASAP Collaboration (Birmingham University)

The aerosol was collected in two sites:

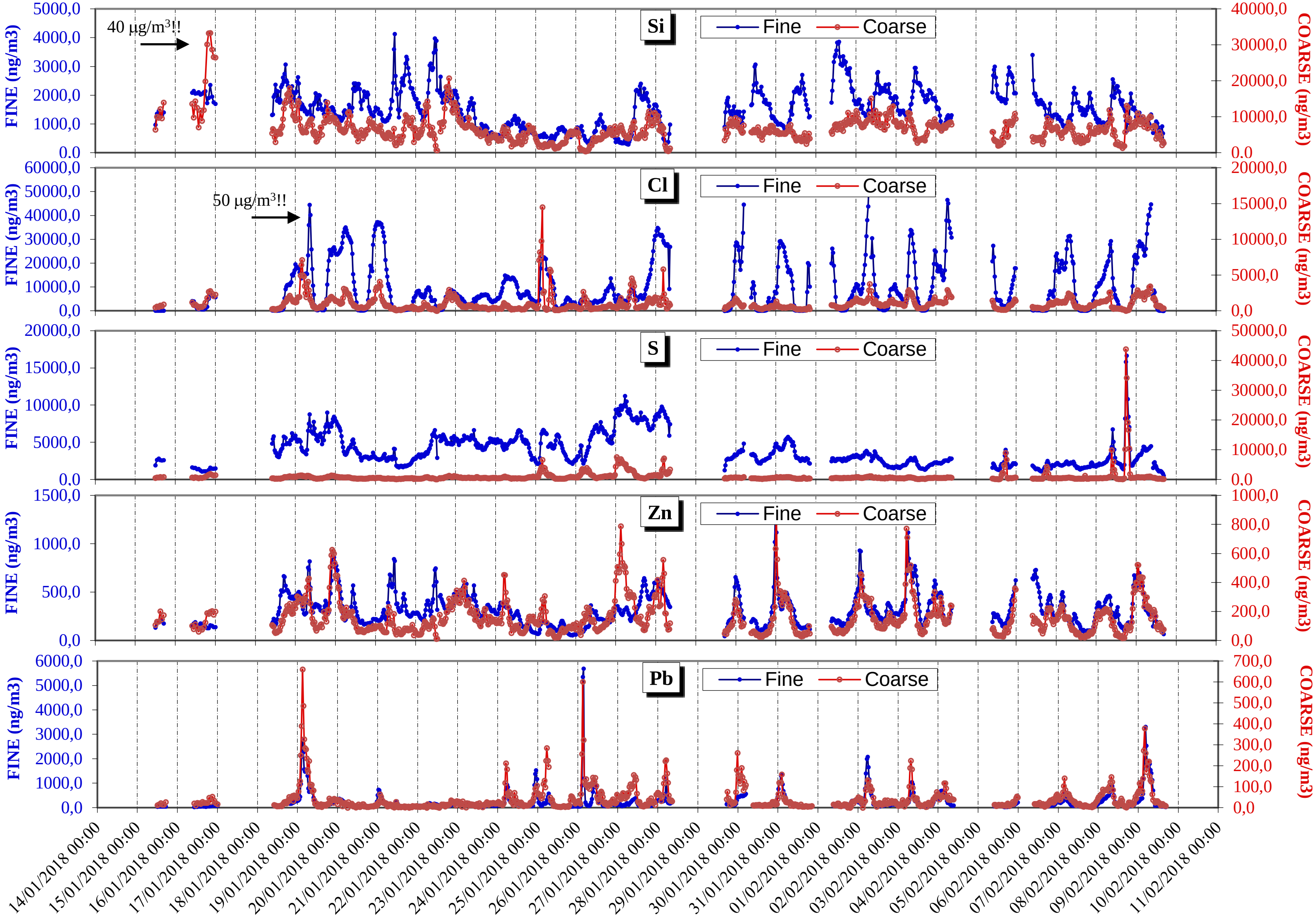
- The urban baseline site in Delhi at the Indian Institute of Technology IIT campus (a “supersite” heavily instrumented)
- The urban centre site at IGDTW which will directly sample emissions from Old Delhi.

Two month-long intensive field campaigns :

- ✓ 10 January - 10 February
- ✓ 20 May - 20 June


SHAHDARA
DILSHAD GARDEN
Kashmiri Gate
1
Sir Ganga Ram Hospital
Raj Ghat
PATPARGANJ
JANAKPURI
New Delhi
नई दिल्ली
Buddha Jayanti Park
Fortis Hospital Noida
Humayun's Tomb
National Rail Museum
Indira Gandhi International Airport
Lodhi Garden
Hazrat Nizamuddin Aulia Dargah
ISKCON
LAJPAT NAGAR
Worlds of Wonder
Okhla Bird Sanctuary
Army Welfare Education Society
PVR Priya
Deer Park Lake
GREATER KAILASH
HAUZ KHAS
Atlantic Water World
2
2 km

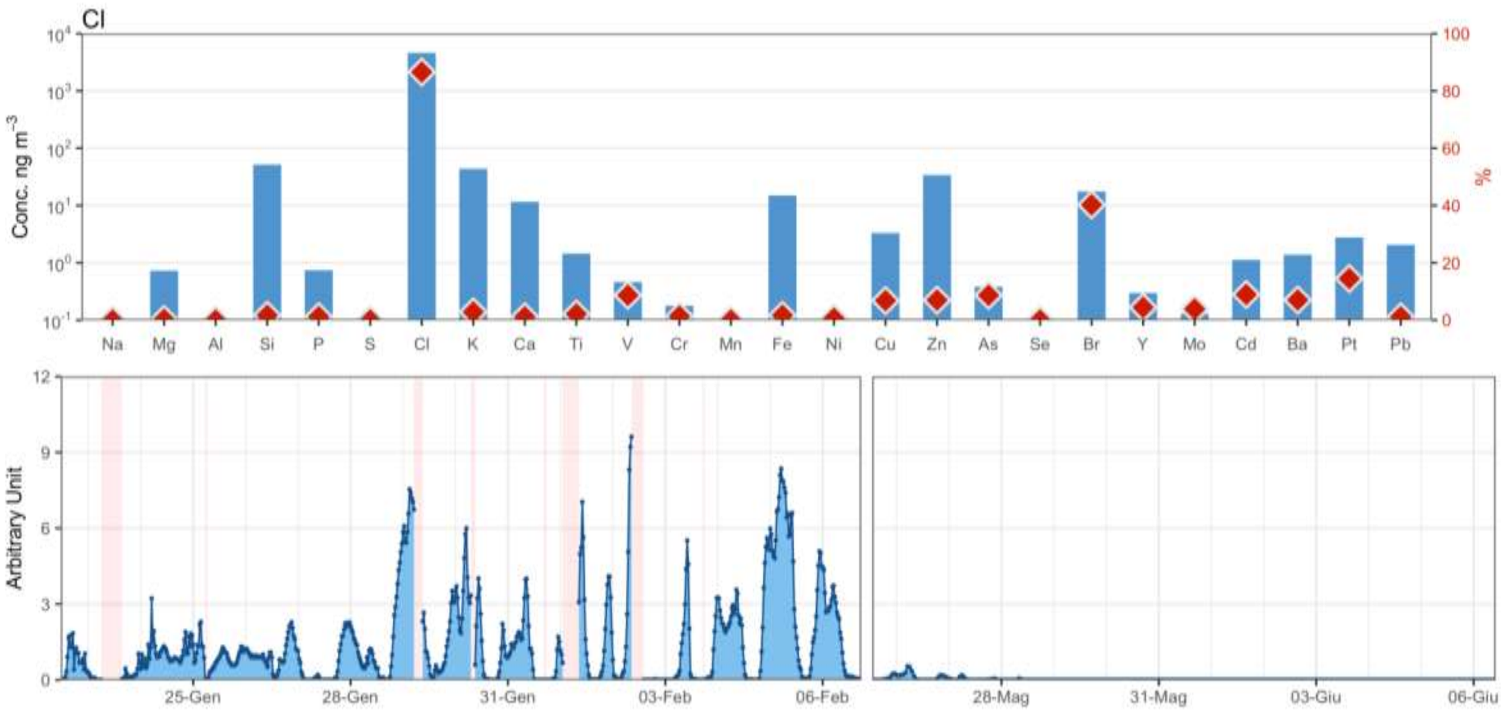
Highly polluted urban environments: Delhi

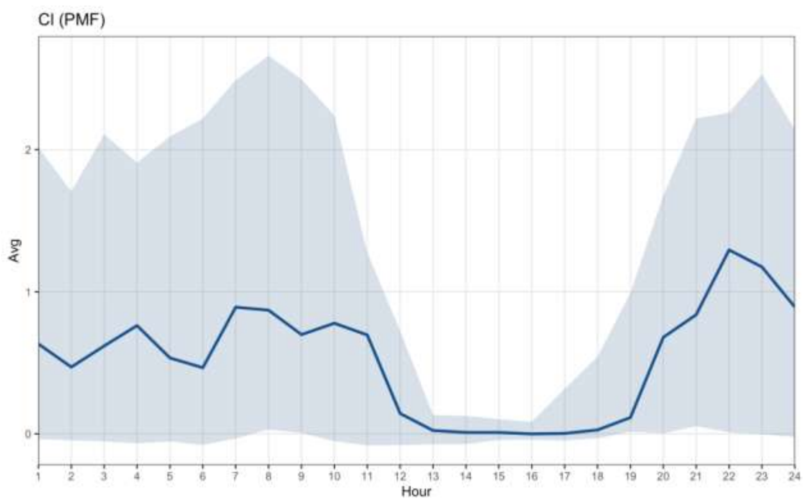


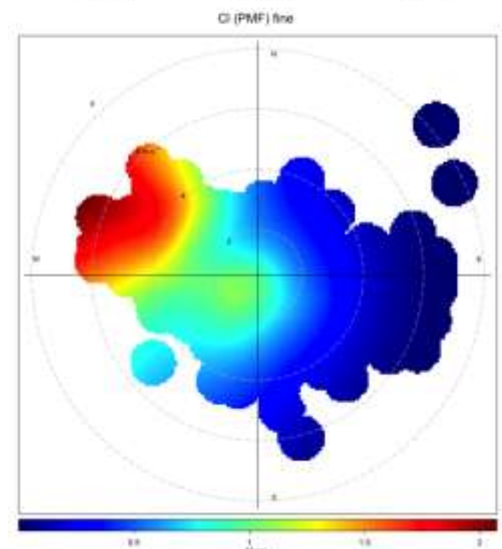
Delhi: identified sources

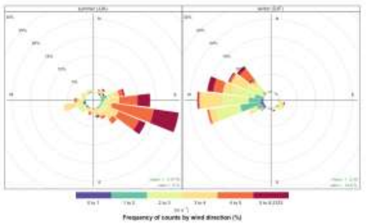
Source	*WoC (F)*	*WoC (C)*	*IIT (F)*	*IIT (C)*
Mineral dust	X	**X**	X	**X**
Urban dust	X	**X**	X	**X**
Biomass burning	**X**		**X**	
Cl (metal processing plants)	**X**	X	**X**	X
Zn (galvanizing/metallurgy ind.)	**X**	X	**X**	X
Pb (smelters,pigments,glass ind.)	**X**		**X**	
Cr-Ni (electroplating plants)	**X**	X	**X**	X
Cu (traffic-non exhaust)	X	**X**	X	**X**
S (Secondary sulphates F, sulphuric acid C)	**X**	**X**	**X**	**X**

Cl (metal processing plants)

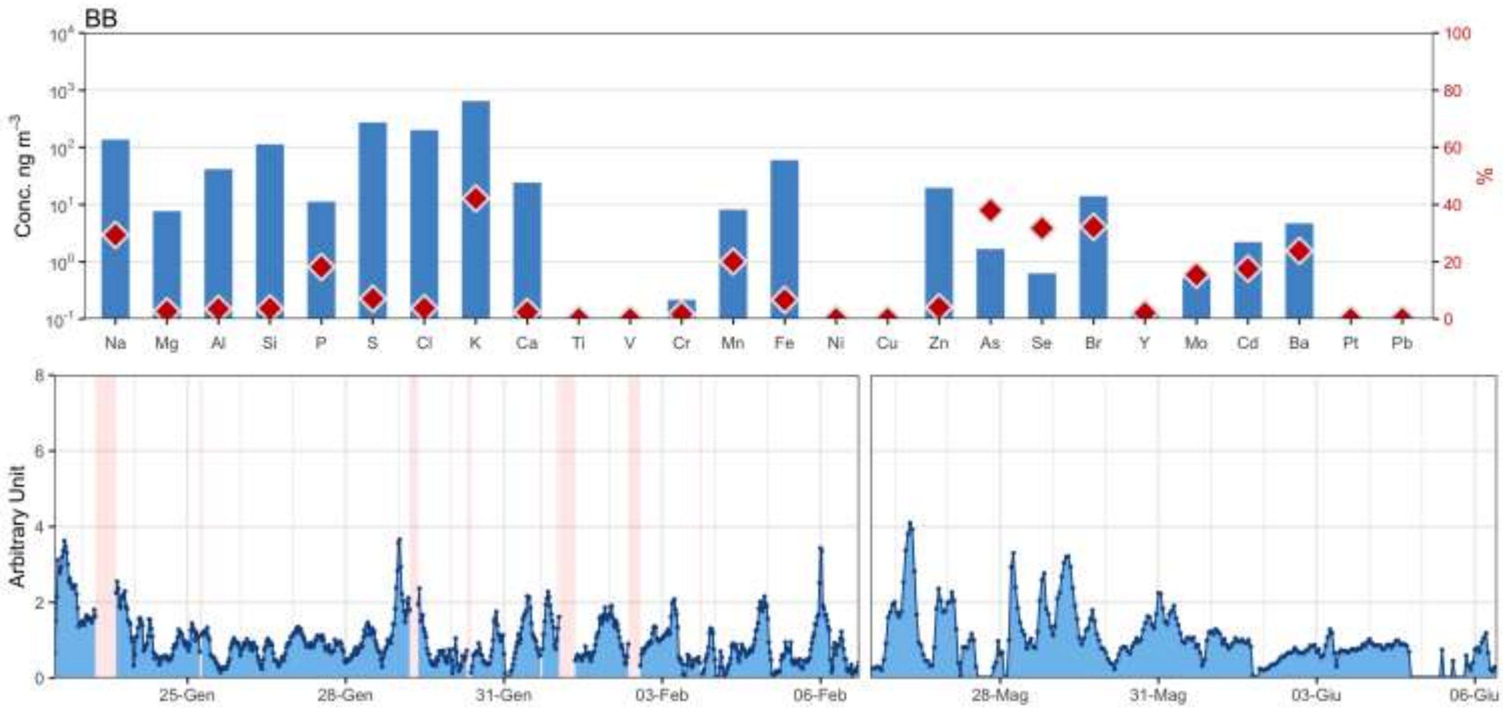


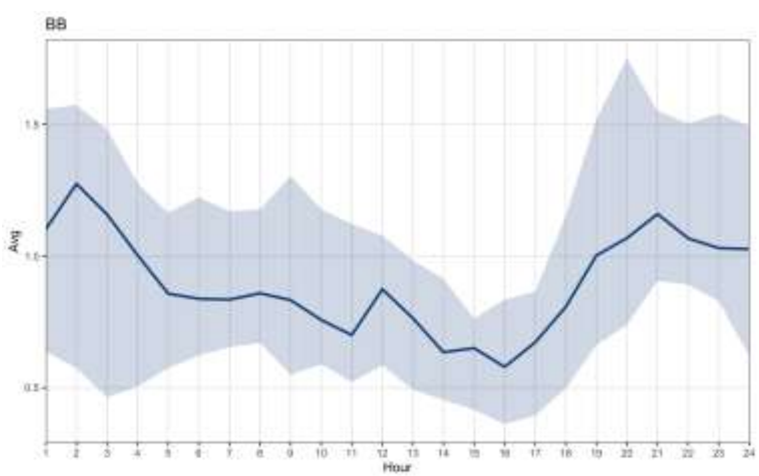


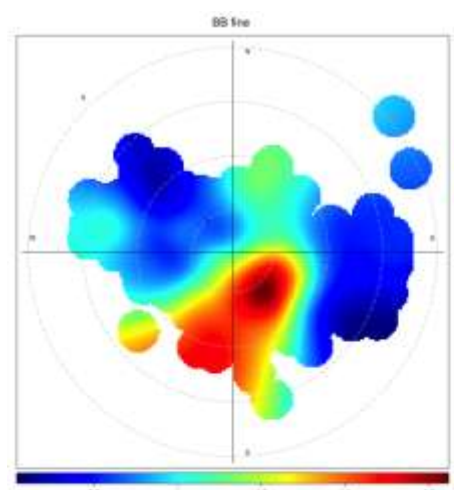




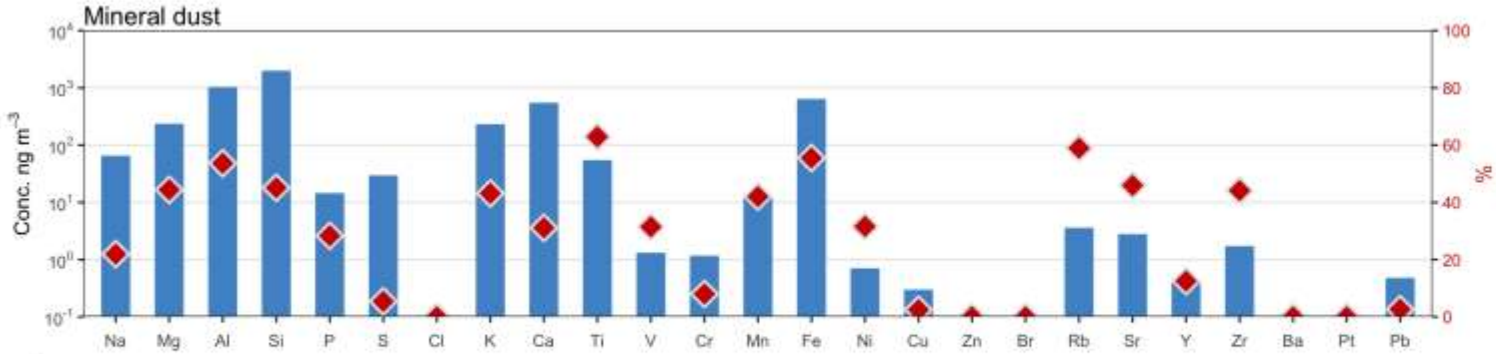
Biomass Burning

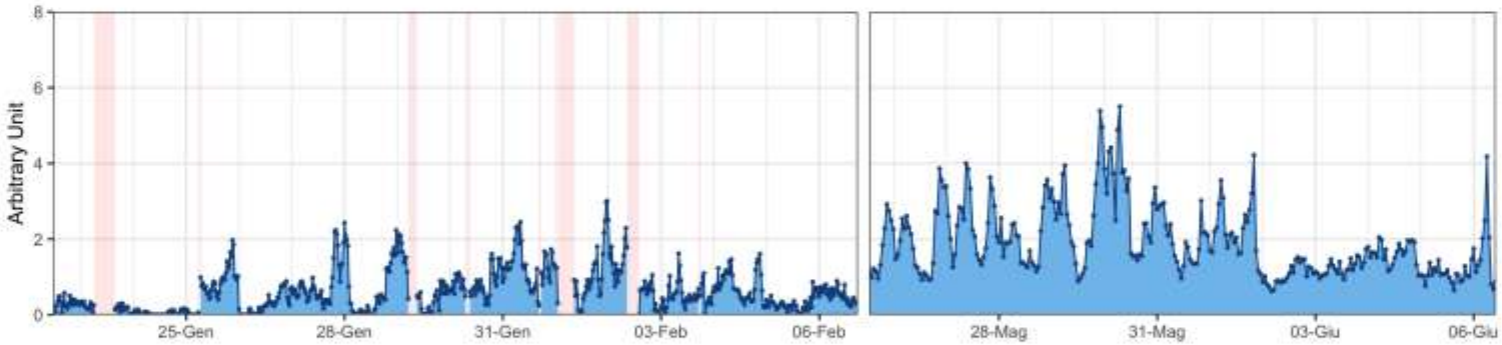


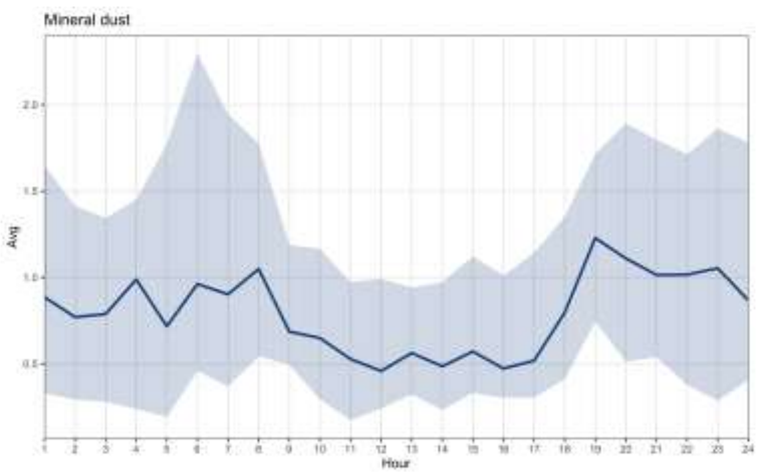


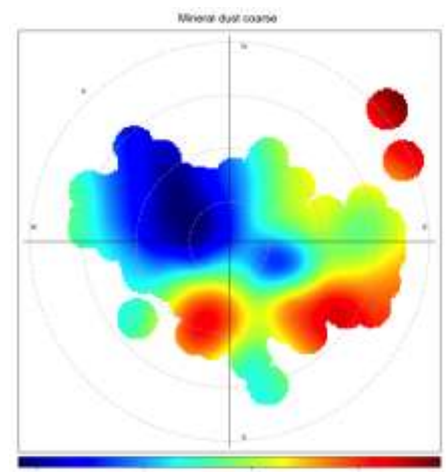


Mineral Dust

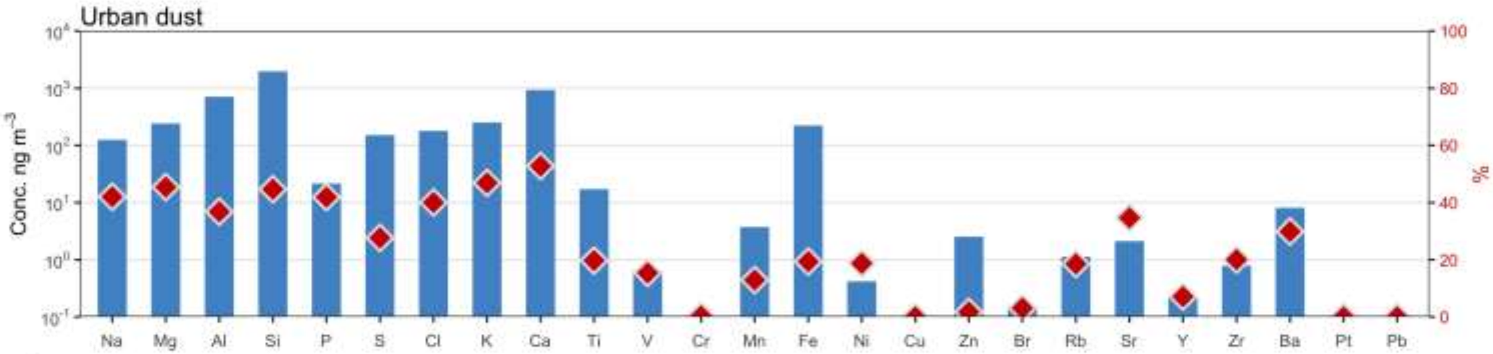


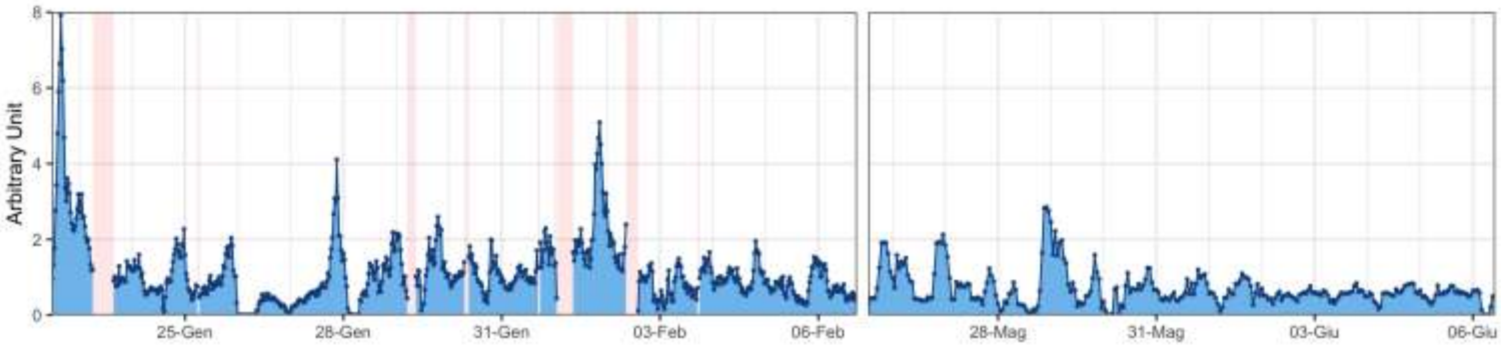


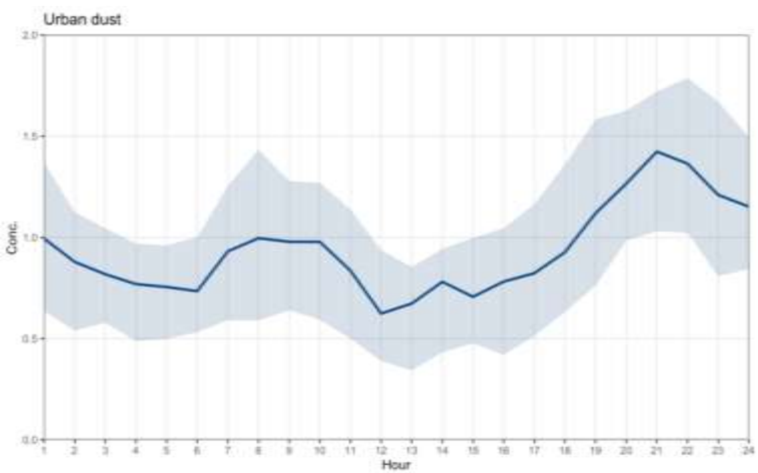


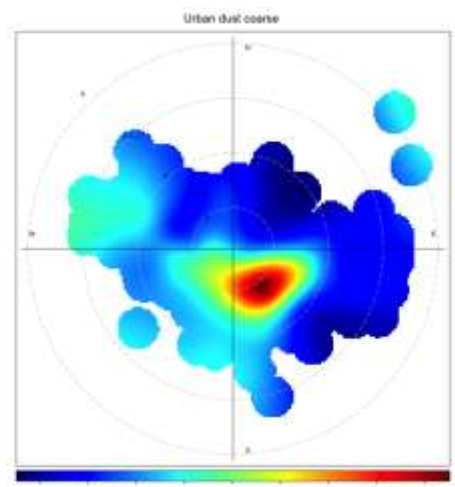


Urban dust

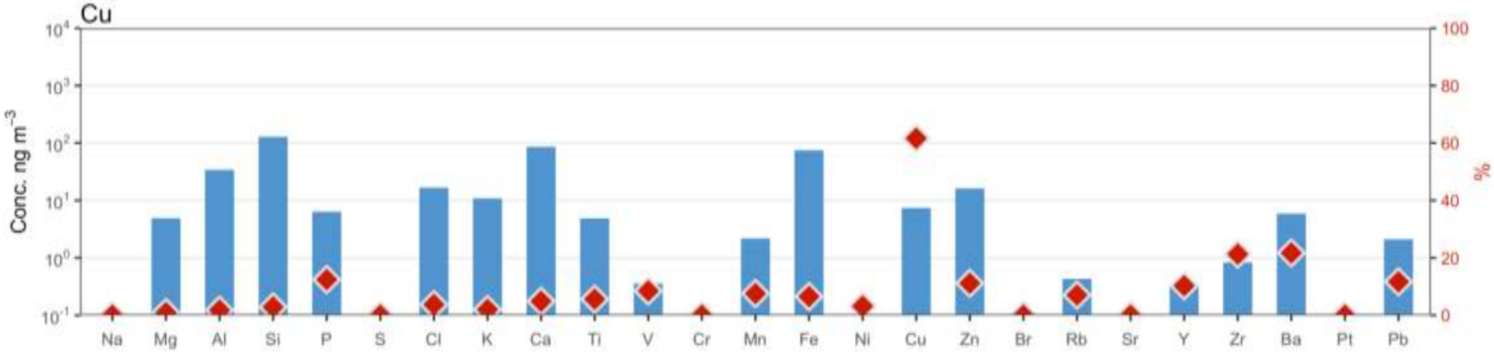

Urban dust
Conc. ng m^{-3}
%
Na
Mg
Al
Si
P
S
Cl
K
Ca
Ti
V
Cr
Mn
Fe
Ni
Cu
Zn
Br
Rb
Sr
Y
Zr
Ba
Pt
Pb

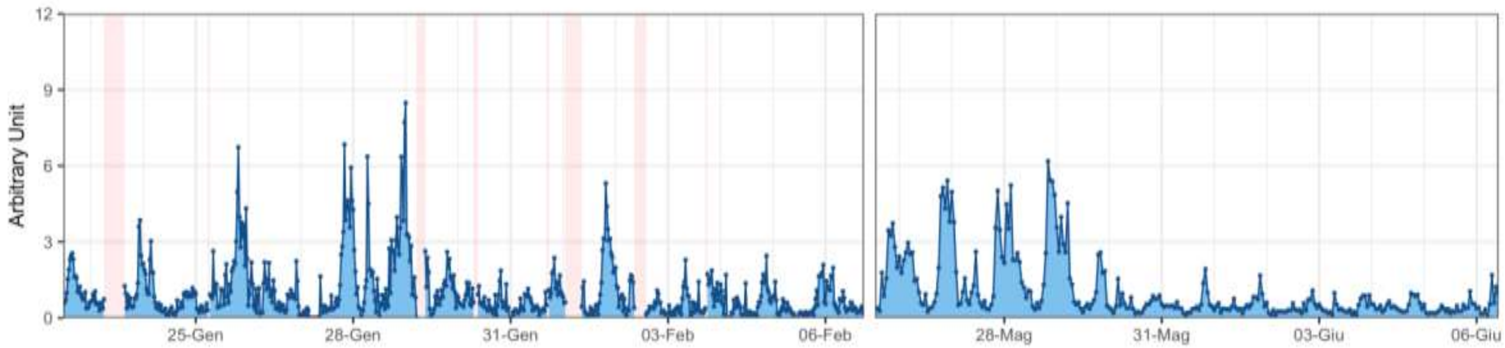

Arbitrary Unit
25-Gen
28-Gen
31-Gen
03-Feb
06-Feb
28-Mag
31-Mag
03-Giu
06-Giu

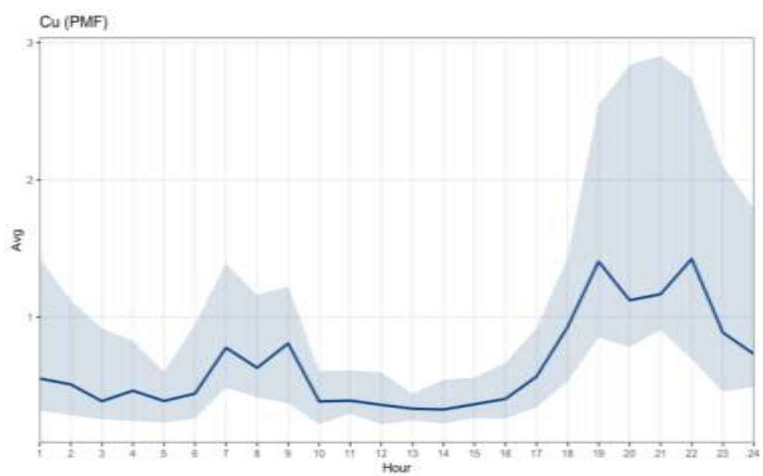

Urban dust
Conc.
Hour

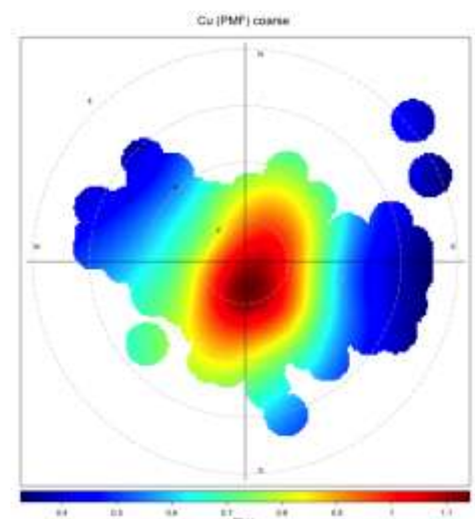

Urban dust coarse

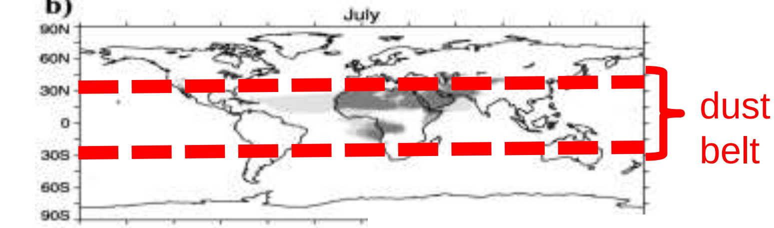
Traffic- non Exhaust (Coarse)







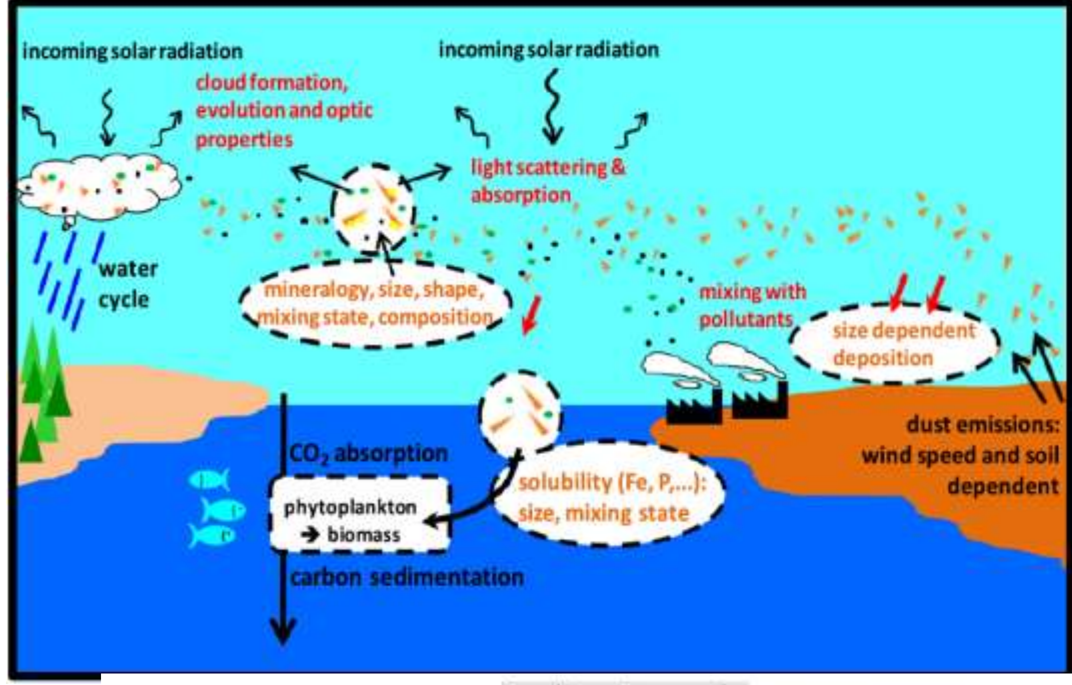




Prospero, 2002

Influence of dust on the Earth system:

-size distribution
-mixing state with pollutants
-mineralogy
-solubility

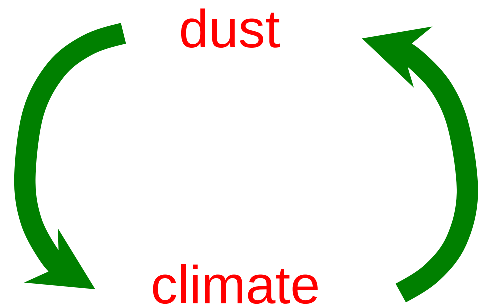


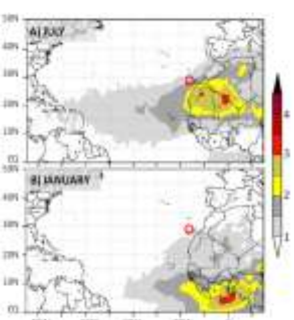
Review Article Aeolian Research Aeolian Research 6 (2012) 55–74

A review of methods for long term in situ characterization of aerosol dust

Sergio Rodríguez[a,*], Andrés Alastuey[b], Xavier Querol[b]

-direct with radiation
-cloud formation (radiation, rain)
-fertilization of ocean
➔ marine biomass ➔ CO_2 absorption



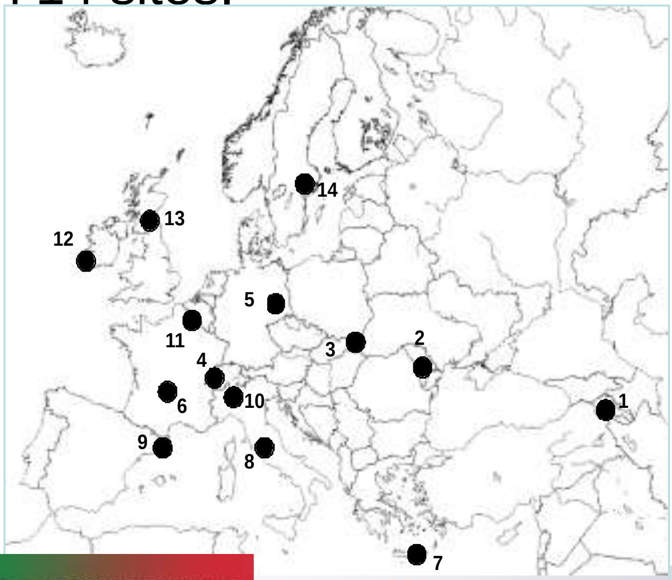


- In southern Europe it gives an important contribution to PM (~100 Mt/y) and it can episodically increase significantly the PM10 and PM2.5 levels. Sometimes it causes the exceedance of the 50 μg/m³ daily limit


EMEP

EMEP (European Monitoring and Evaluation Programme) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution for international co-operation to solve transboundary air pollution problems.

EMEP periodically arrange intensive monitoring periods; in 2012-2013 one of the major focus was to measure chemical speciation in PM_{10} with special emphasis on mineral dust, with daily samplings for two one-month periods in 14 sites.



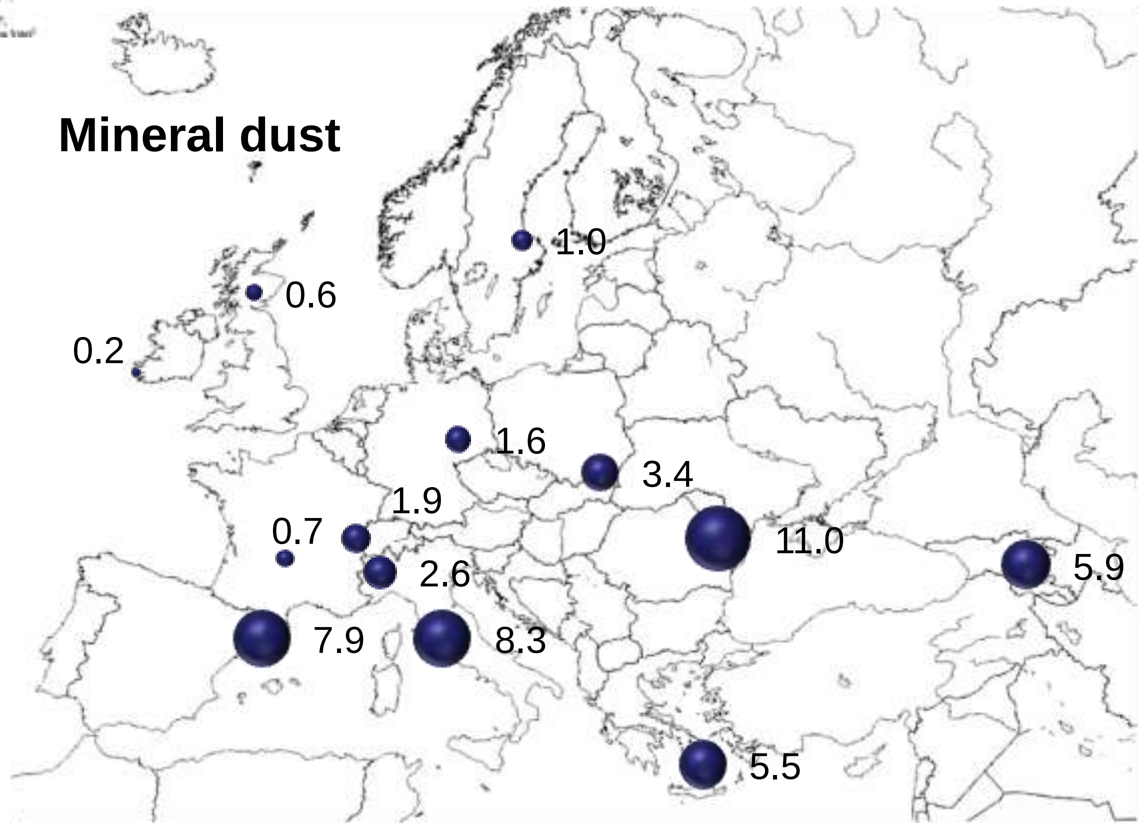
The Chemical coordinating Centre decided to assign to LABEC the measurement of all the filters collected in the two intensive campaigns for the determination of all the soil-related elements to assess the contribution of natural episodes (like Saharan dust transport).

~ 1000 Teflon filters to be analyzed

Mineral dust (μg/m³)

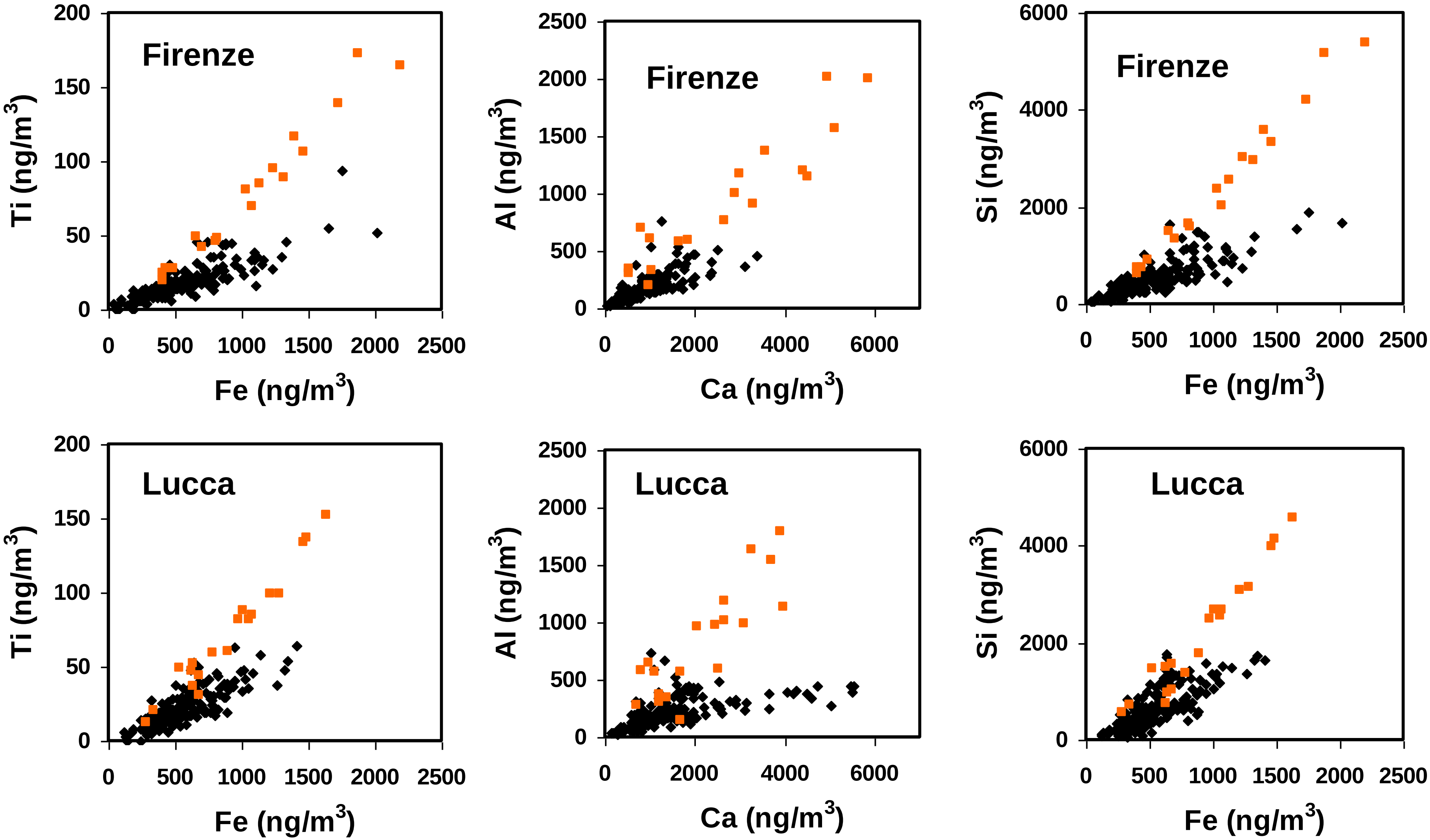
Atmospheric Chemistry and Physics EGU

Geochemistry of PM_{10} over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013



Mineral load: obtained by the addition of the SiO_2, Al_2O_3, Fe_2O_3 concentrations, and the dust contribution of Na_2O, K_2O, CaO and MgO after the subtraction of their marine contribution from the bulk concentrations

PATOS: elemental ratios



Backtrajectories from Sahara

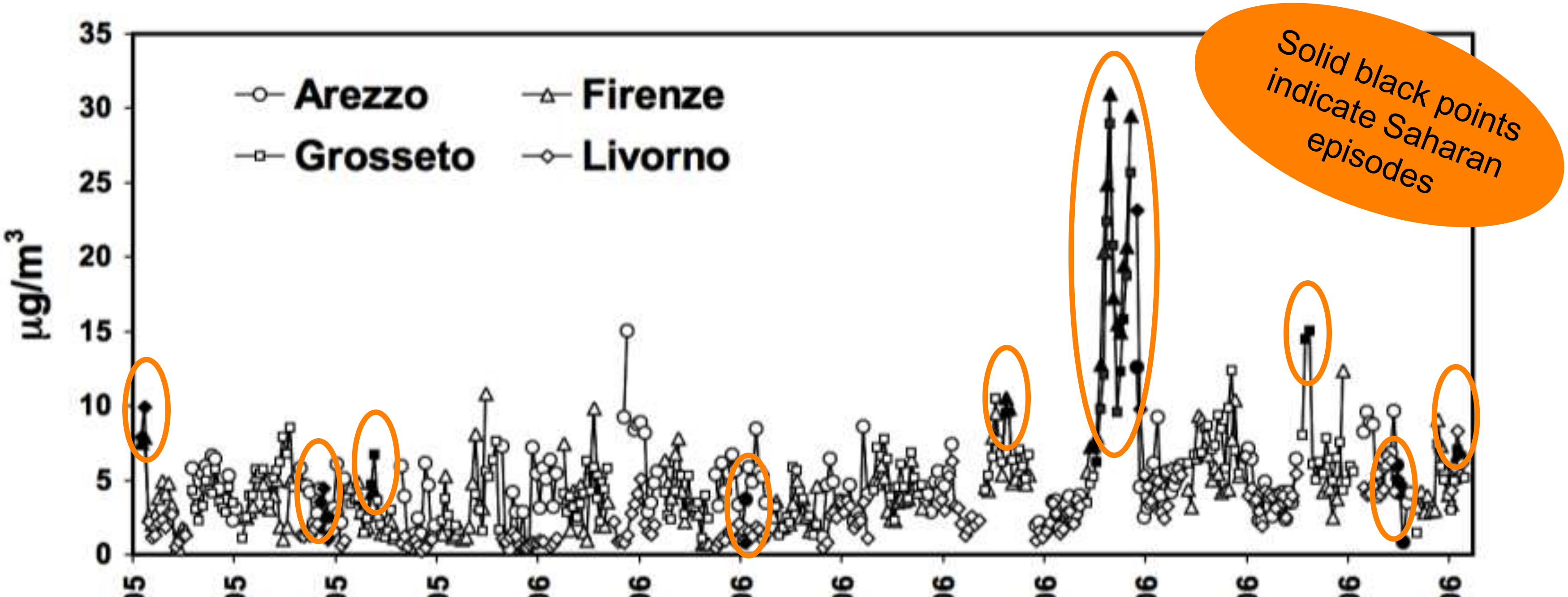
Backtrajectories NOT from Sahara

Soil dust concentration (PATOS1)

1.35 Na + 1.66 Mg + 1.89 Al + 2.14 Si + 1.40 Ca + 1.43 Fe + 1.67 Ti + 1.21 K

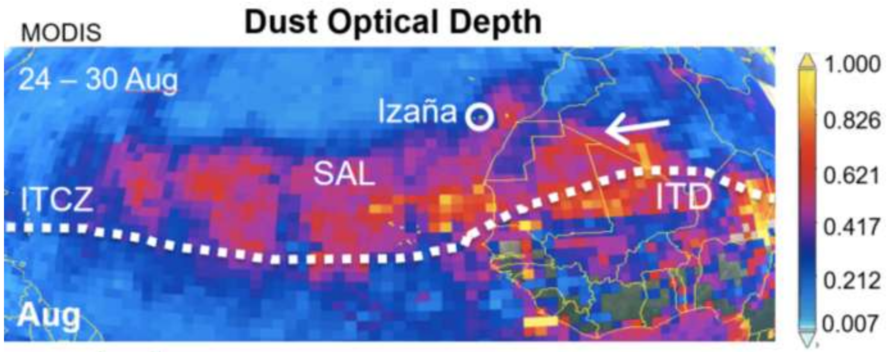
- K and Fe corrected for anthropogenic contributions by EF calculations
- Na and Mg corrected for sea-salt contributionsC

African dust obtained by subtraction of an estimated dust background (monthly moving average excluding Saharan days)



- Soil dust during non-Saharan days was about ~ 5 µg/m³ (15-20% of PM10)
- Desert dust contributions ranged from few µg/m³ up to 25 µg/m³
- Desert dust contribution > 1 µg/m³ in 6 episodes (16 days)
- Desert dust "annual average" was ~ 0.5 µg/m³

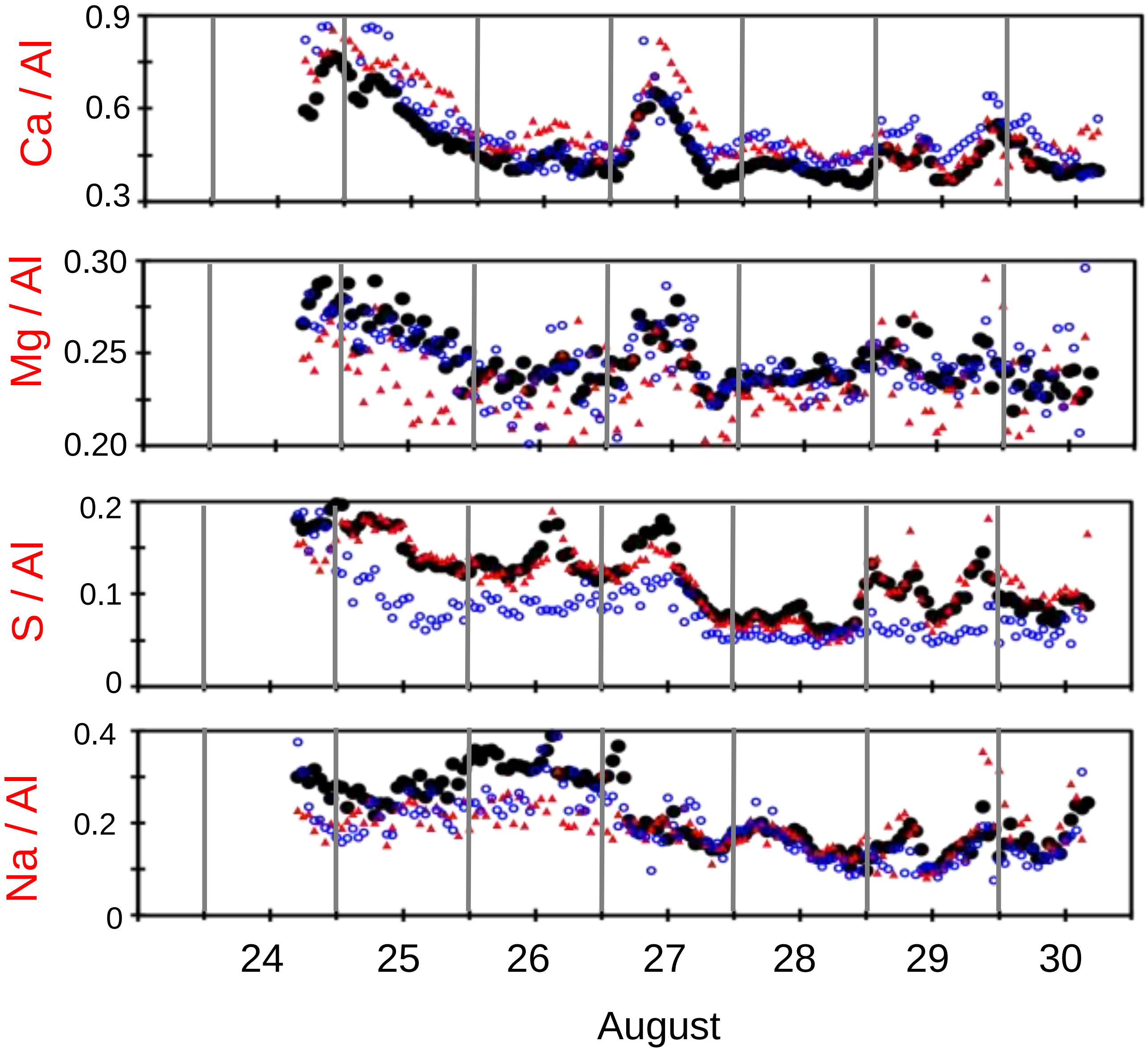
At Izaña Observatory (Tenerife), we performed the first high-resolution measurements of elemental composition of dust exported to the North Atlantic addresses three questions:



- how quick does dust composition change in the SAL?
- what is the connection to dust sources?
- and what is the role of meteorology?

Izaña Observatory (IZO) , 2367 m a.s.l.

Saharan Air Layer

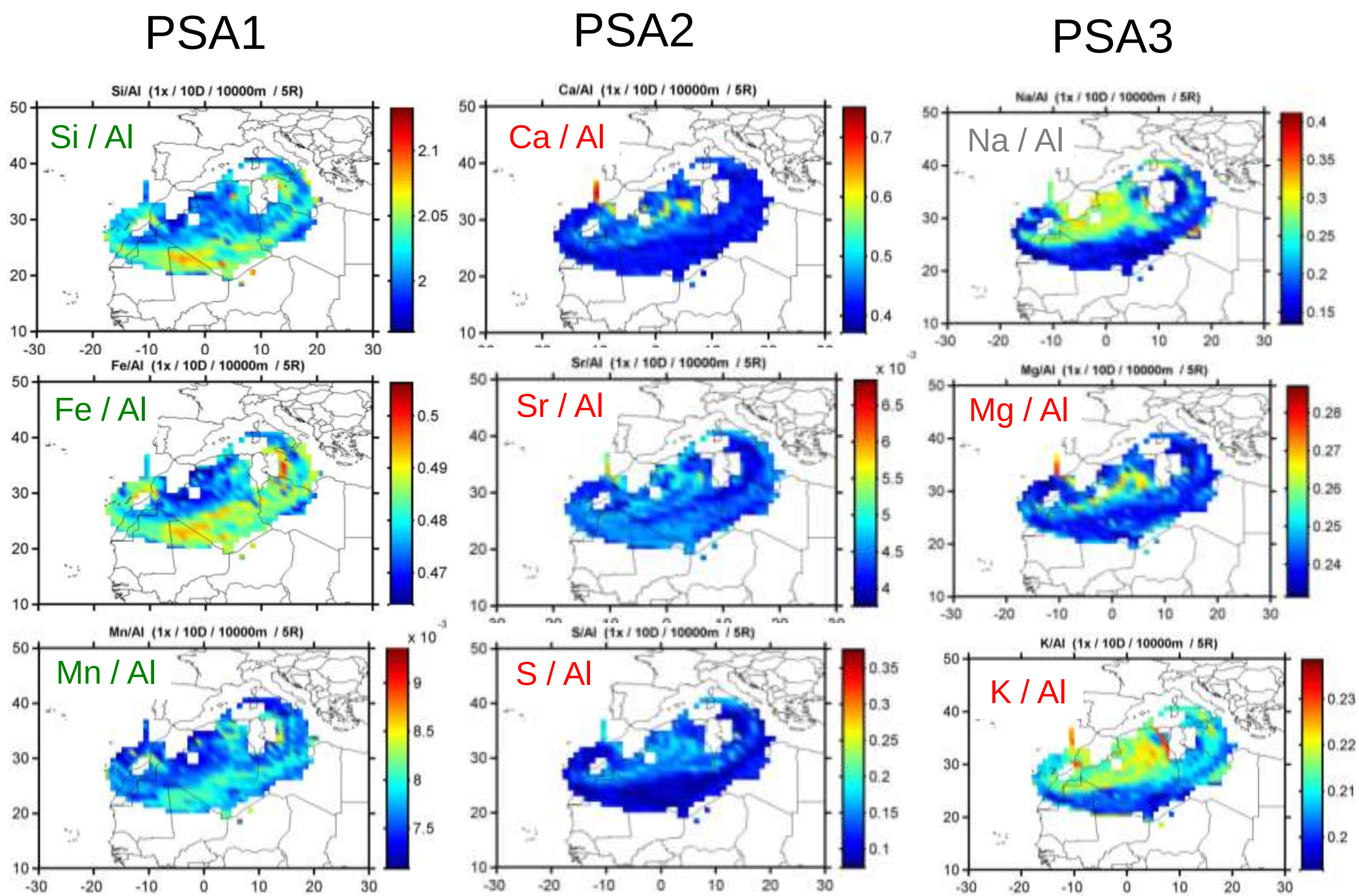


6h, change in factor 2

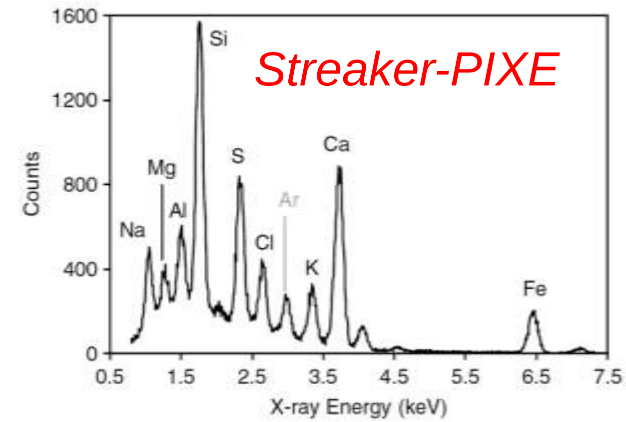
Along 1-week of continuous dust presence at Izaña (50 – 200 µg/m^3), 7 concatenated impacts, which were traced by the variability in the ratios of the different elements to Al.

This variability was induced by the alternated impacts of **three of the large North African dust sources**

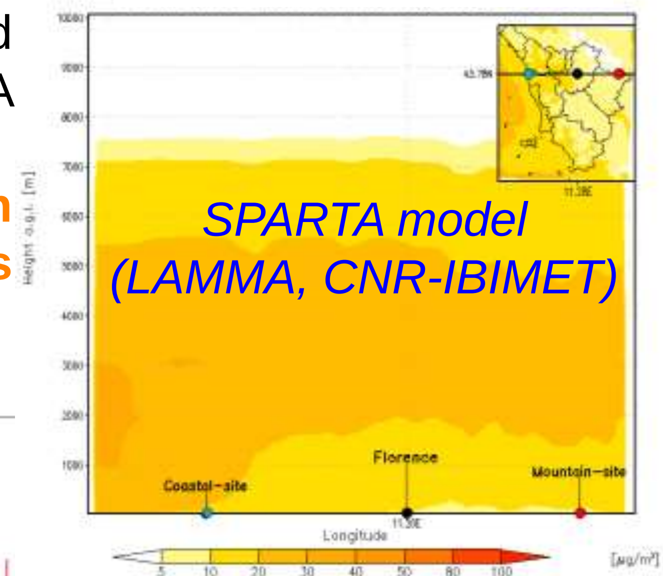
The potential source areas of dust were identified by **analysing** the "Median Ratios At Receptor" (MRAR) plots, **the median ratio of each X/Al** measured at the receptor site (Izaña) **when the air mass was previously passed above each 1◦ × 1◦ degree pixel over North Africa**. Back-trajectories were calculated with HYSPLIT software

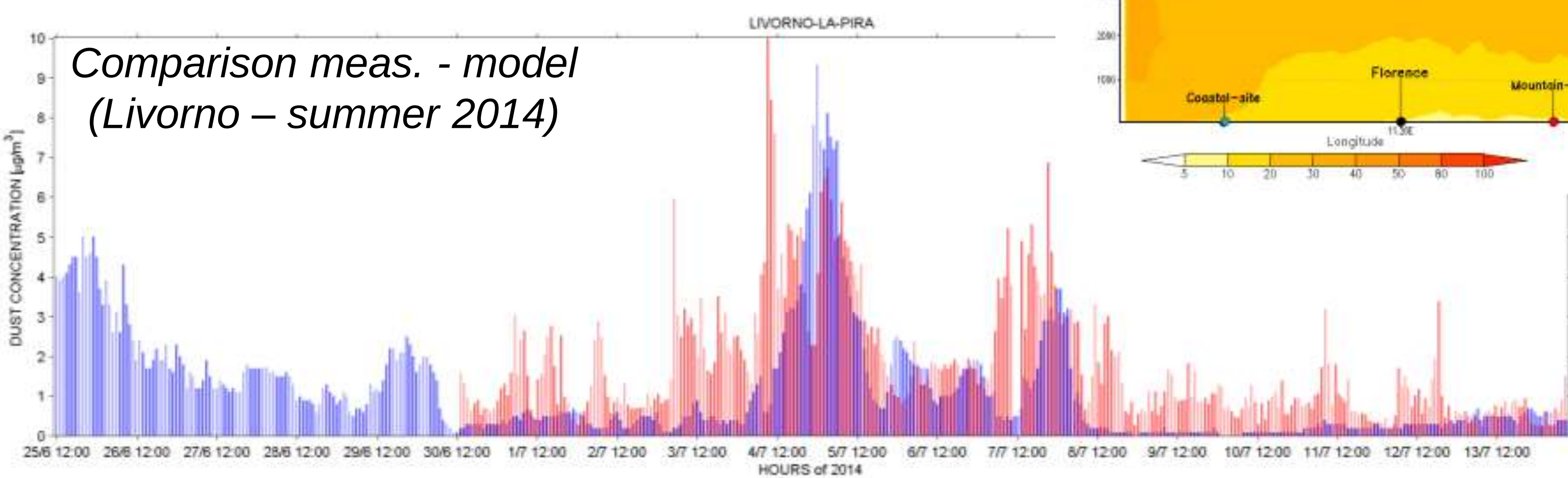


Saharan dust intrusions: validation of models

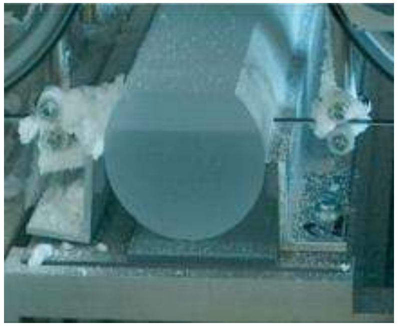


- Saharan dust outbreaks are observed over Mediterranean region several times a year and contribute to the exceedance of PM10 legal limit value.
- The characterization of the main Saharan dust outbreaks affecting the Tuscany Region was performed using the SPARTA model chain developed by LaMMA Consortium.
- **Hourly resolution allows a better comparison between measured data and the model predictions respect to daily data**





Paleoclimatic research: dust from Antarctic ice cores



- Polar ice cores are extensive archives of records of past atmospheric compositions, as they contain traces of the gases and the aerosols being in the atmosphere at the deposition time.

- Ice cores drilled in the East Antarctic plateau in the frame of the European Project for Ice Coring in Antarctica (EPICA) aimed at reconstructing global paleo-climate and paleo-environmental conditions.
- Samples from the main cold events of the last 220 kyr and Holocene

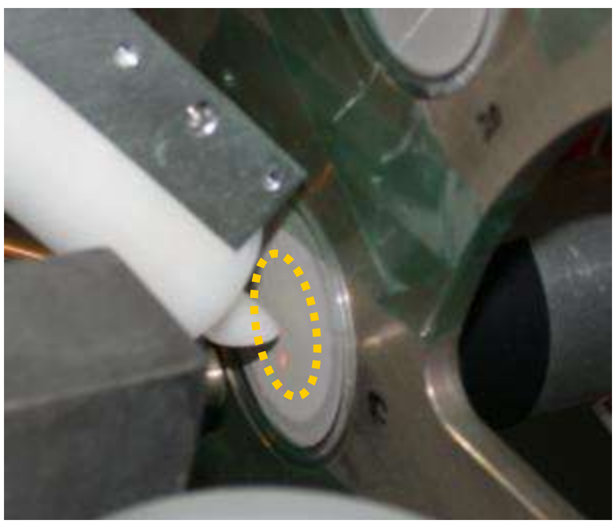
  ✓ Very low elemental concentrations: ng÷mg/kg of ice

  ✓ Ice cores are melted and the liquid is filtered through Nuclepore membranes on a 1 cm^2 area

* EPICA community members, Nature 429 (2004), 623
EPICA community members, Nature 444 (2006), 195

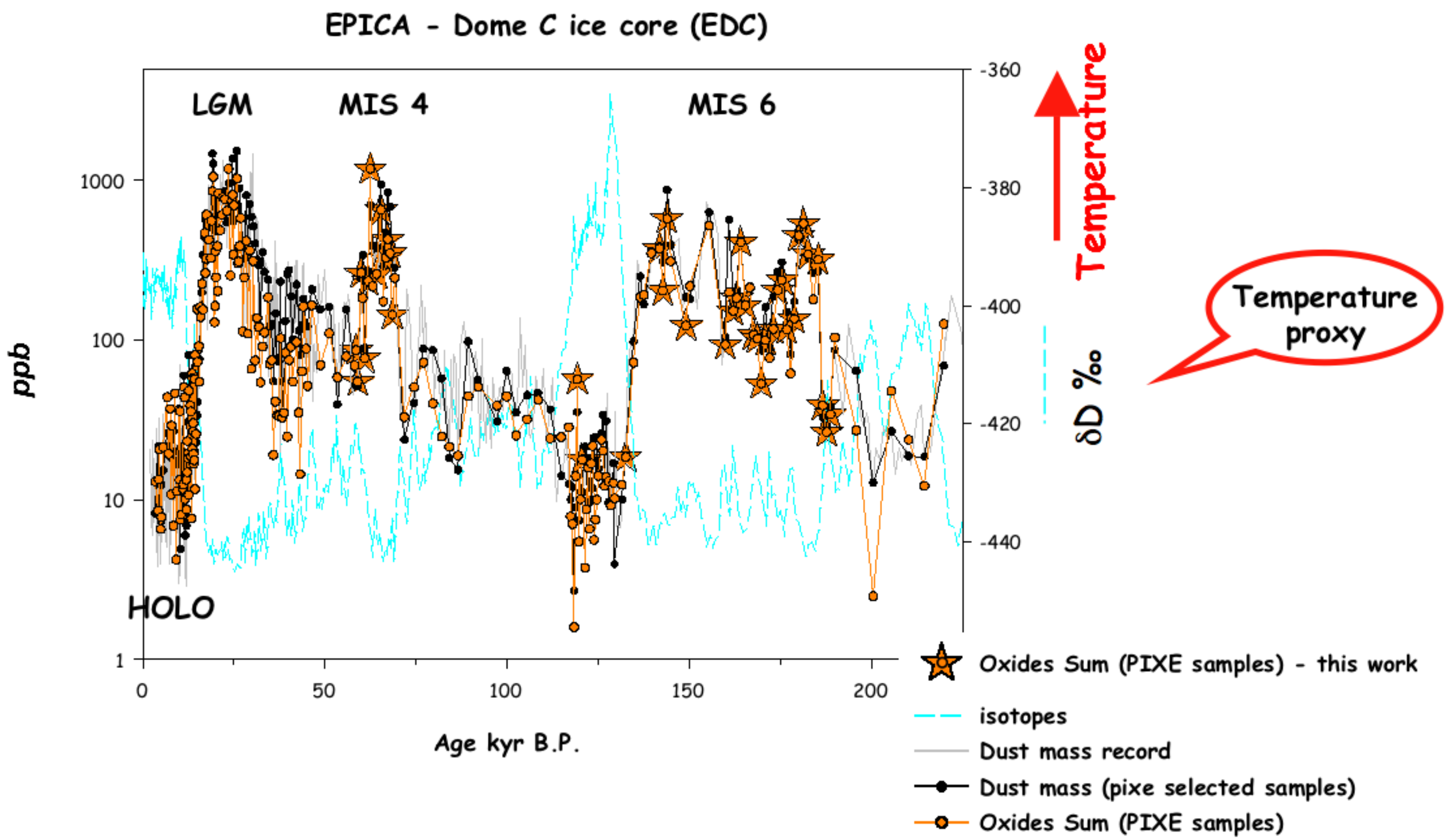
PIXE measurements

- PIXE: a reliable tool for major and minor elements investigation of ice-core dust.
- After ice melting and filtering, no pre-treatment is required: contaminations are minimized!



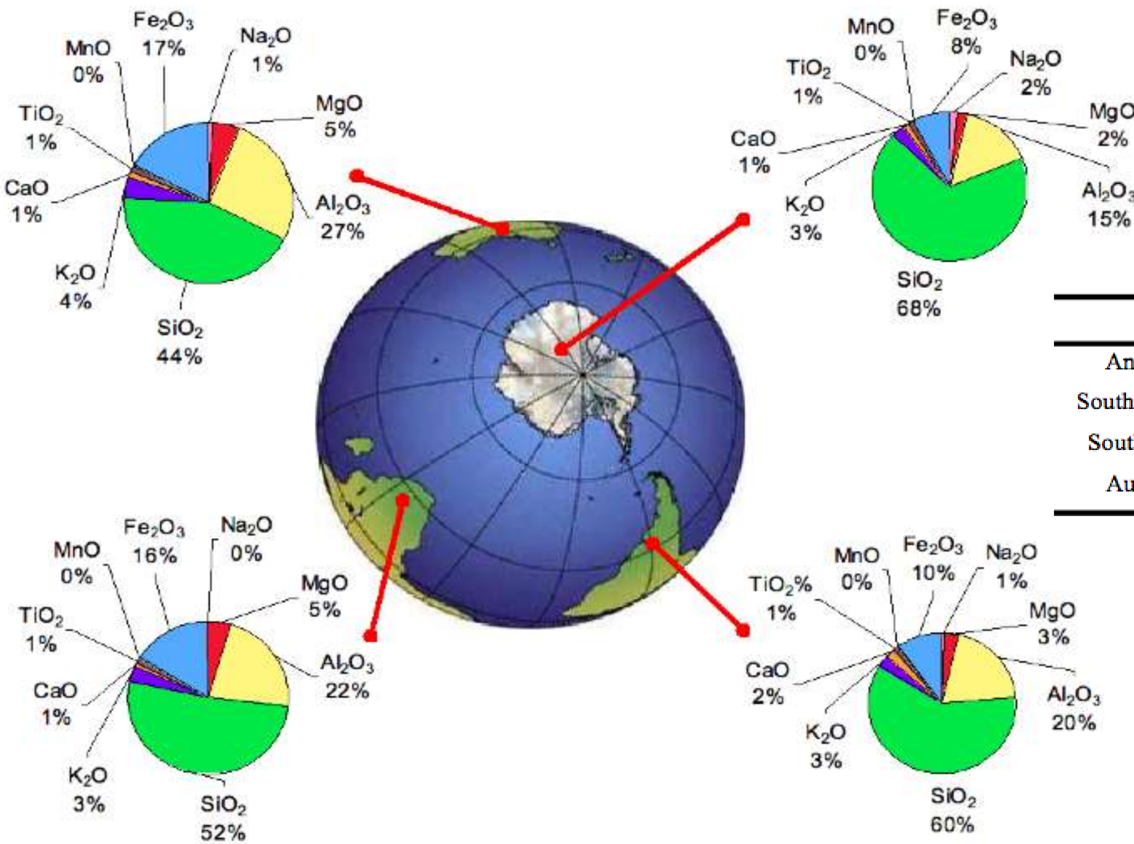
- Irradiation time per sample: ~1000 s.
- Beam current: from 5 nA to 30 nA.
- Beam collimated to 2x1 mm^2.
- Target moved in front of the beam to scan all the deposit area

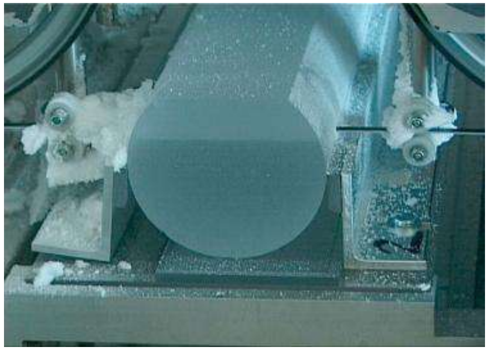
Dust concentrations



- The oxides sums calculated from the PIXE measured elemental compositions agree very well with the dust mass measured with other techniques.
- There is evidence that, during the cold periods (LGM, MIS4 and MIS6), dust concentrations are much higher than during hot periods.

Paleoclimatic research: dust from Antarctic ice cores

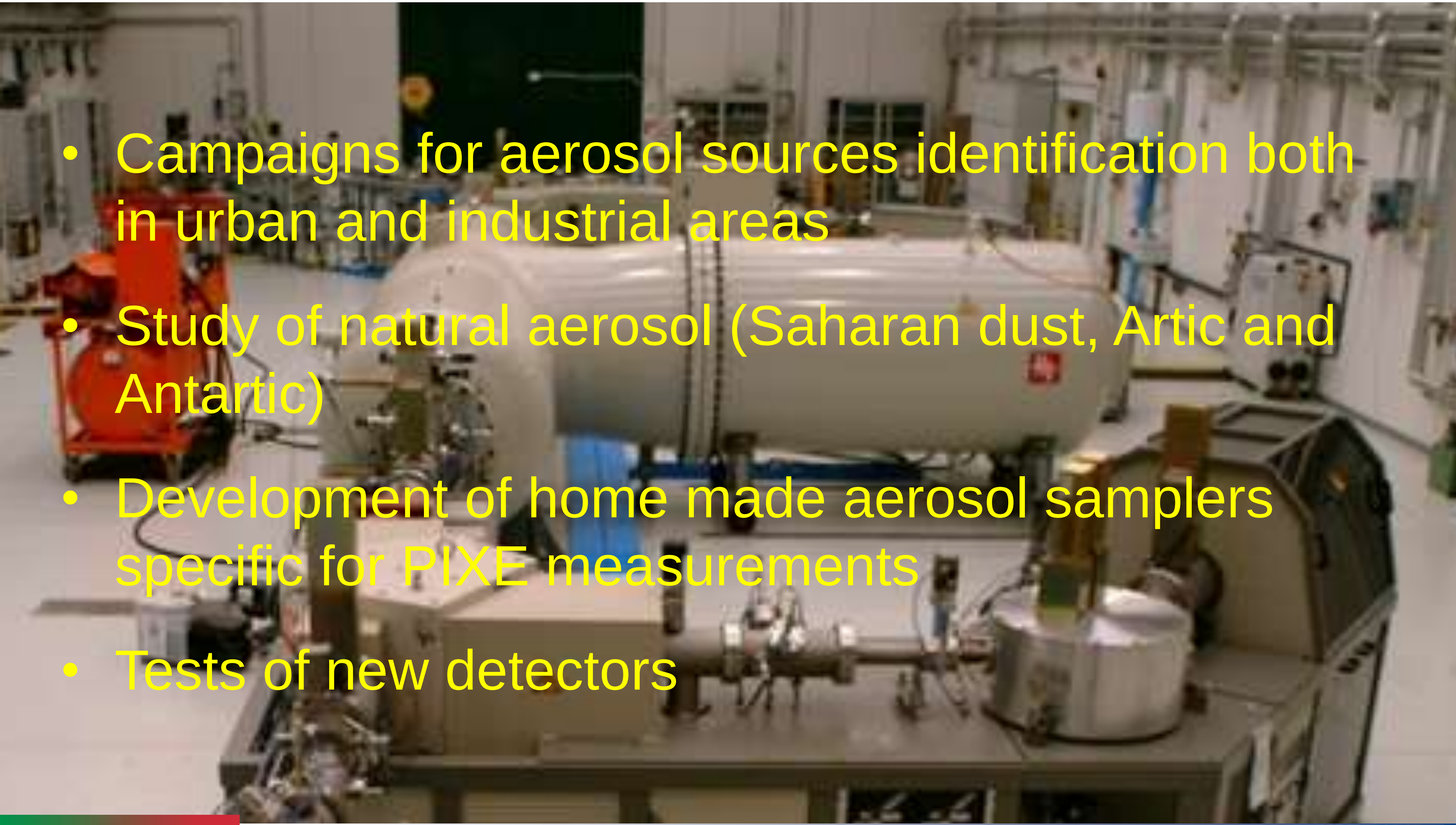




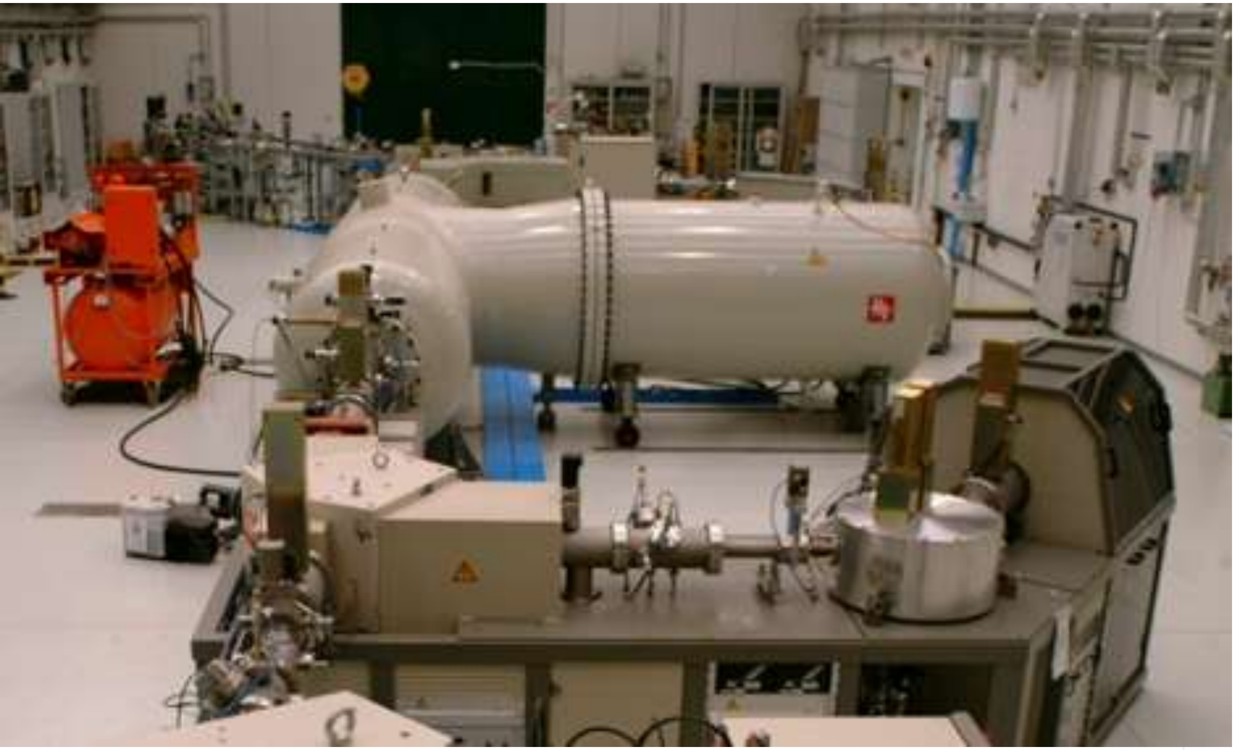
	Al_2O_3/SiO_2	Fe_2O_3/SiO_2	Al_2O_3/Fe_2O_3
Antartica	0.22 (± 0.04)	0.12 (± 0.02)	2.0 (± 0.4)
South America	0.33 (± 0.04)	0.17 (± 0.02)	2.0 (± 0.3)
South Africa	0.43 (± 0.09)	0.31 (± 0.07)	1.4 (± 0.4)
Australia	0.61 (± 0.12)	0.39 (± 0.12)	1.5 (± 0.5)

Glacial periods– South America
Holocene - Australia

Future studies at LABEC



- Campaigns for aerosol sources identification both in urban and industrial areas
- Study of natural aerosol (Saharan dust, Artic and Antartic)
- Development of home made aerosol samplers specific for PIXE measurements
- Tests of new detectors



<u>*The "Aerosol" group at LABEC:*</u>

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+
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Thank you for your attention!

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