



UNIVERSITÀ
DEGLI STUDI
FIRENZE

DIPARTIMENTO DI
FISICA E ASTRONOMIA



Istituto Nazionale
di Fisica Nucleare

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Le tecniche di analisi con fasci di ioni
per lo studio del contributo
dell'aerosol di origine naturale

<http://labec.fi.infn.it>

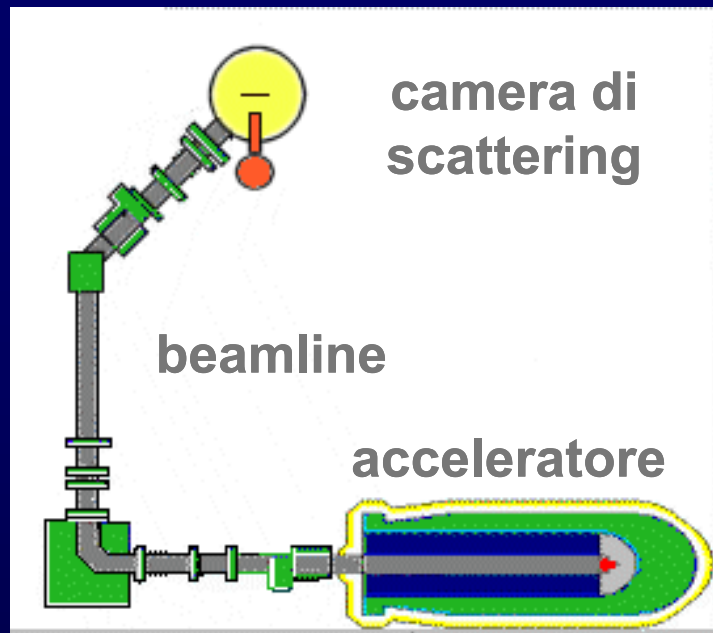
LABECO

Laboratorio di
Tecniche Nucleari
per i Beni Culturali
- Firenze

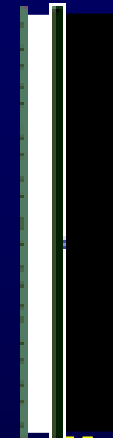
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TECNICHE DI ANALISI CON FASCI IONICI (IBA)

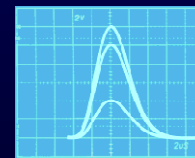
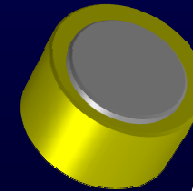


bersaglio



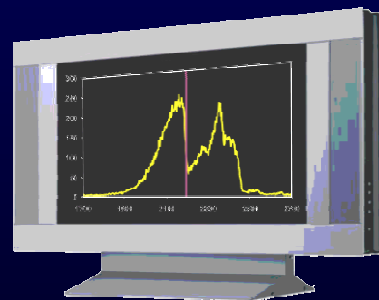
protoni

**radiazione
caratteristica**



segnale

rivelatore



**spettro di
energia**

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STUDI DI FIRENZE

External PIXE set-up at the LABEC laboratory (Florence)

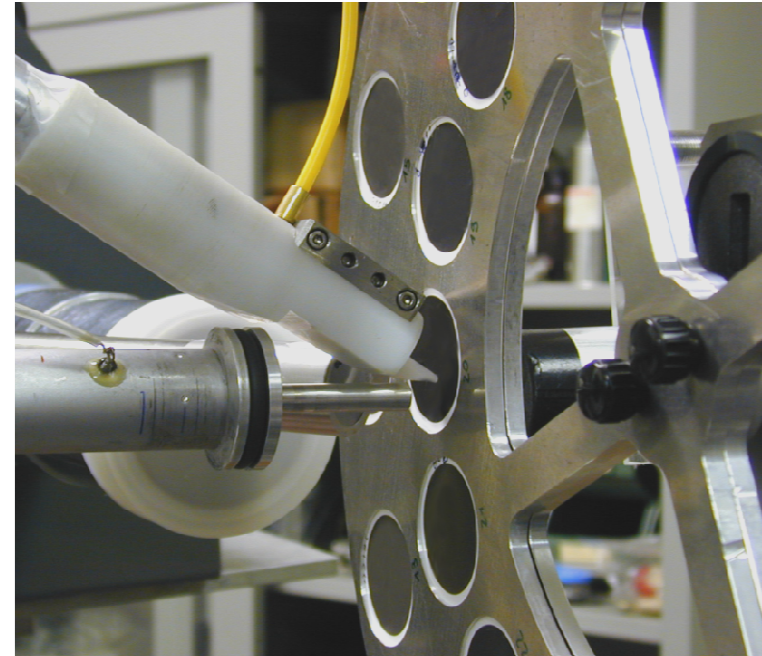
Particle Induced X-ray Emission (PIXE)

→ elemental concentrations for $Z > 10$

- good sensitivity (MDL $< 1-10 \text{ ng/m}^3$)
- no sample preparation required
- not destructive
- 2 new detectors: no problems with Teflon filters like with the traditional PIXE setups

Simultaneous detection of all the elements that compose mineral dust (Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Sr, Zr) with high sensitivity

“daily samples”



$i \sim 50-100 \text{ nA}$
Measuring time: $\sim 0.5 - 3$ minutes
Samples measured in 1 day



150- 300

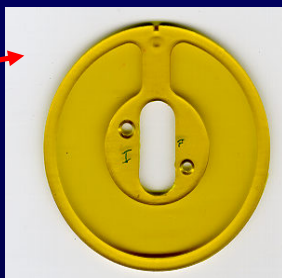
Campionatore "streaker"

"Campioni orari"



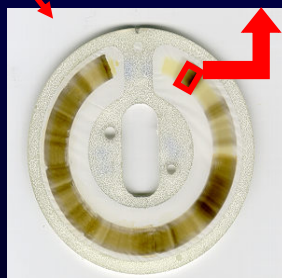
- Foglio di Kapton
- Nuclepore

PM2.5÷10



PM2.5

1 ora



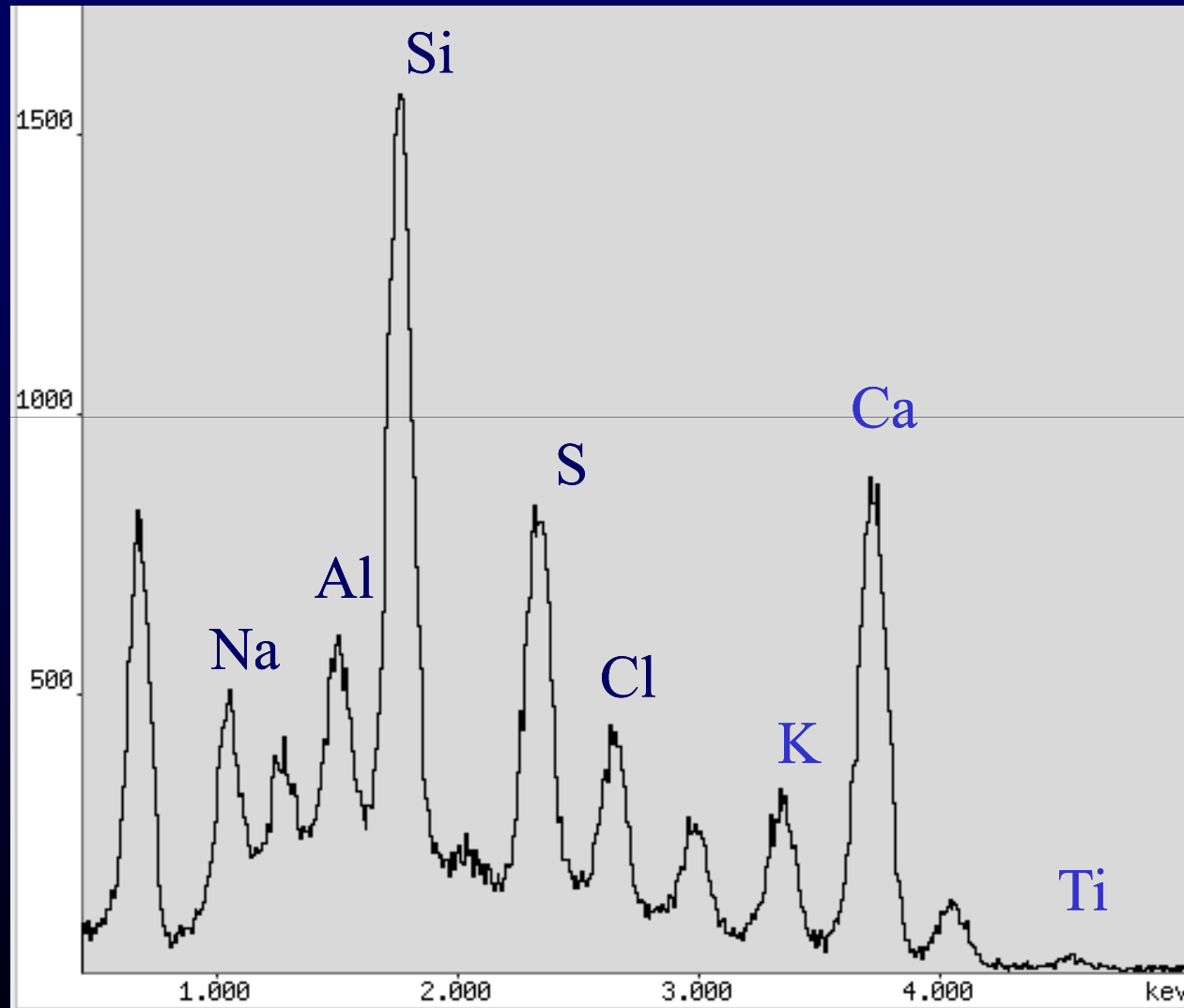
100 mm



Il fascio copre un settore di filtro uguale a 1 ora di campionamento. L'analisi della traccia punto per punto dà la concentrazione degli elementi con risoluzione oraria

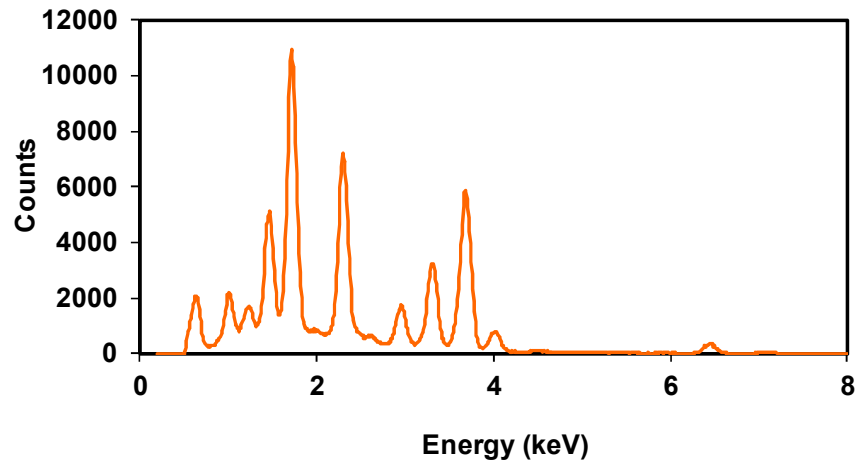
- Dimensioni del fascio: 1mm x 2 mm
- Tempo di misura: ~ 1-3 min.
- ➔ 1 settimana con risoluzione 1 h (168 punti) ~ 3 - 9 ore

PIXE spectra: 45 sec acquisition!

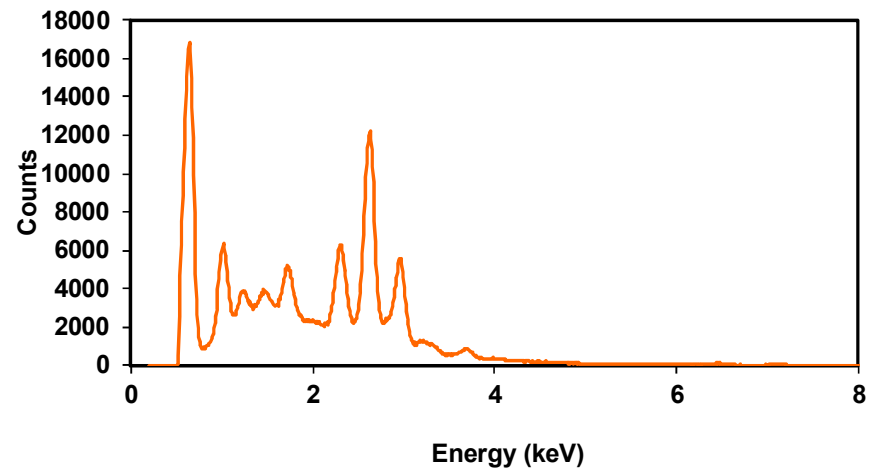


Esempi di spettri da EMEP

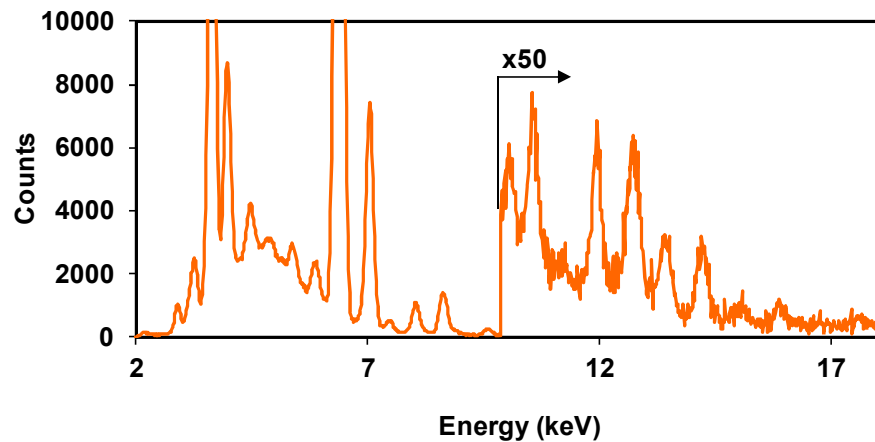
EMEP teflon MONTELIBRETTI 50nA 120s



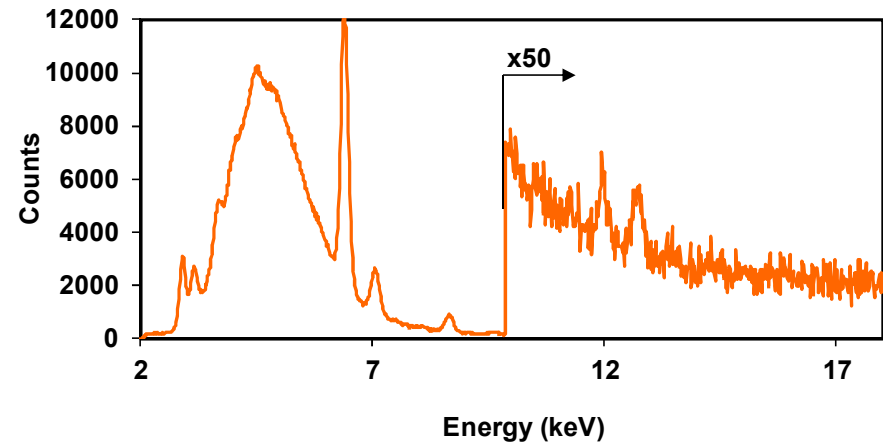
EMEP teflon AUCH MOSS 100nA 240s



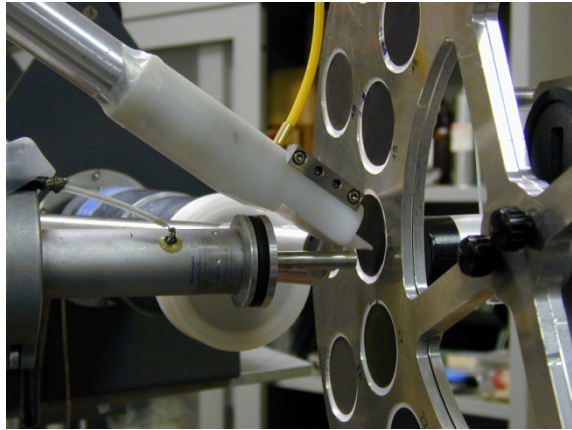
EMEP teflon MONTELIBRETTI 50nA 120s



EMEP teflon AUCH MOSS 100nA 240s



ANALISI: Filtri in Teflon



Cromatografia Ionica :

Componente solubile degli ioni inorganici

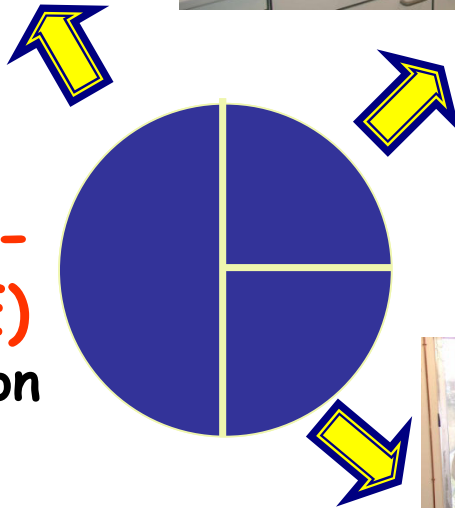
Na, NH₄, K, Mg, Ca, Cl, NO₃, SO₄, MSA, Ac, For, Gly, Ox

ICP-OES:

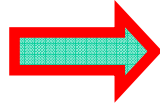
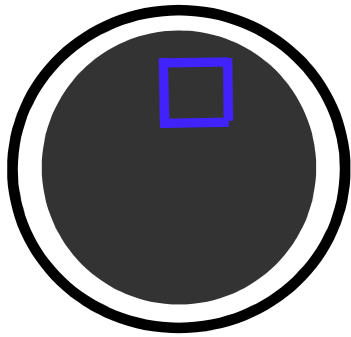
Frazione solubilizzabile in HNO₃ e H₂O₂ di alcuni metalli:

Al, Fe, Mn, Cu, Cd, V, Ni, Cr, Pb, Mo, As, Hg, Zn

Particle Induced X-ray Emission (PIXE)
(Acceleratore Tandetron del LABEC-INFN)
→ concentrazioni elementali for Z>10



ANALISI: Filtri in Quarzo



Su un quadratino:
Thermo Optical
Transmission analysis
(SUNSET) OC/EC

Sul resto del filtro:

**Analisi dei composti organici
mediante
GC-MS**



n-Alcane



IPA

Come e' possibile identificare gli eventi naturali più importanti?

Eventi naturali, quali il trasporto di aerosol marino e di polveri sahariane, possono essere identificati :

- dall' incremento della concentrazione di alcuni composti/elementi

Polveri del suolo: Al, Si, Sr, Ti, Ca, Fe, ...

Aerosol marino: Na, Cl, Mg, ...

- dai rapporti relativi fra diversi composti/elementi nella composizione del particolato
- dallo studio del trasporto delle masse d'aria (studio delle retrotraiettorie, modelli).



Campagne di campionamento



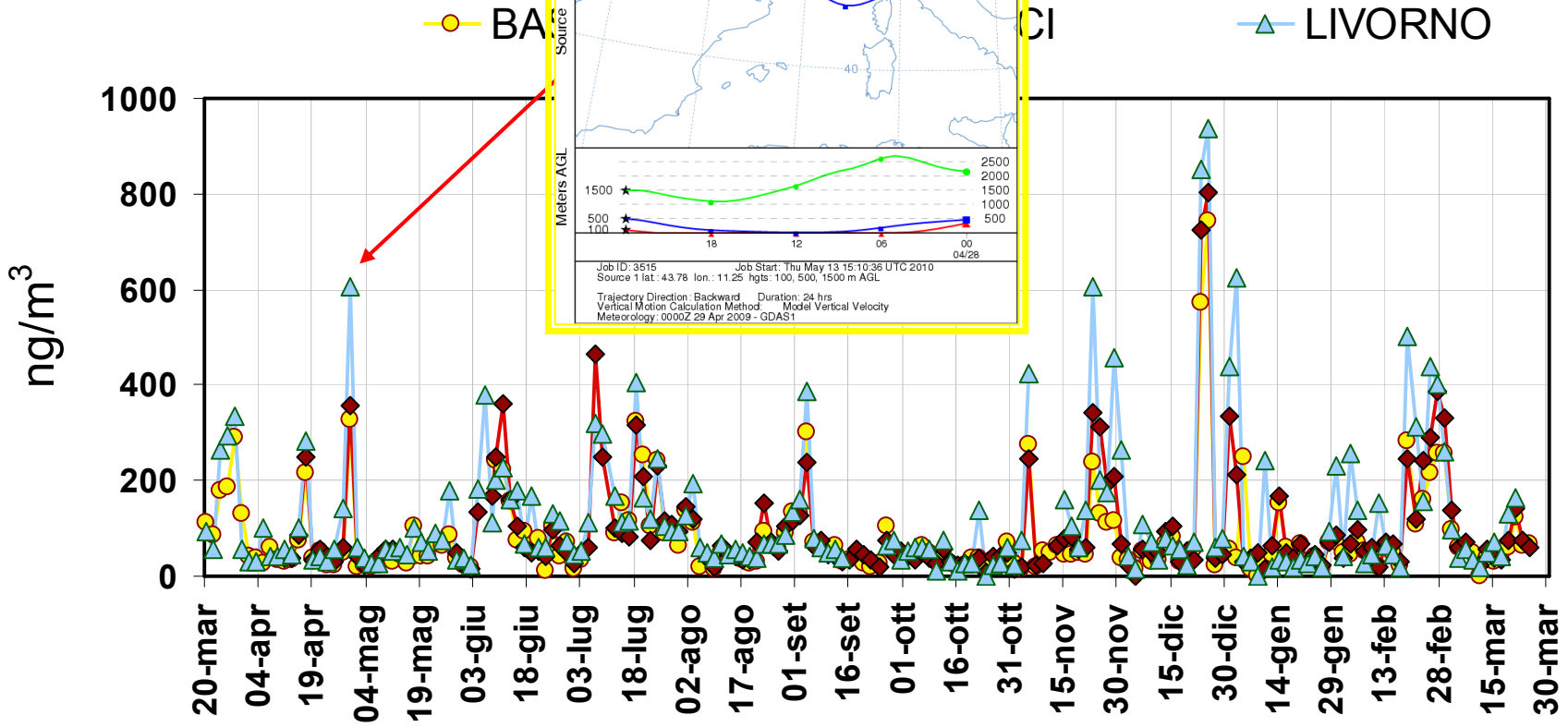
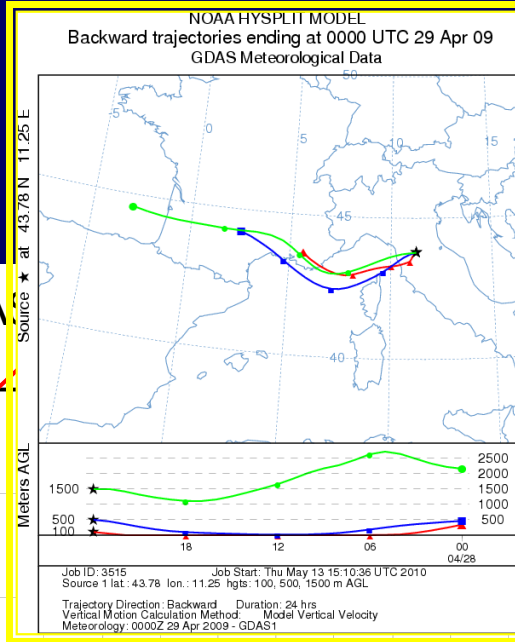
Gennaio 97- Gennaio 98
250 campioni di PM10

Sett. 02 - Giugno 03
180 campioni di PM10
1-20 Nov: PM10 e PM2.5

PATOS 1
Sett. 05 - Sett. 06
1034 campioni di PM10
Firenze: 90 camp. PM2.5

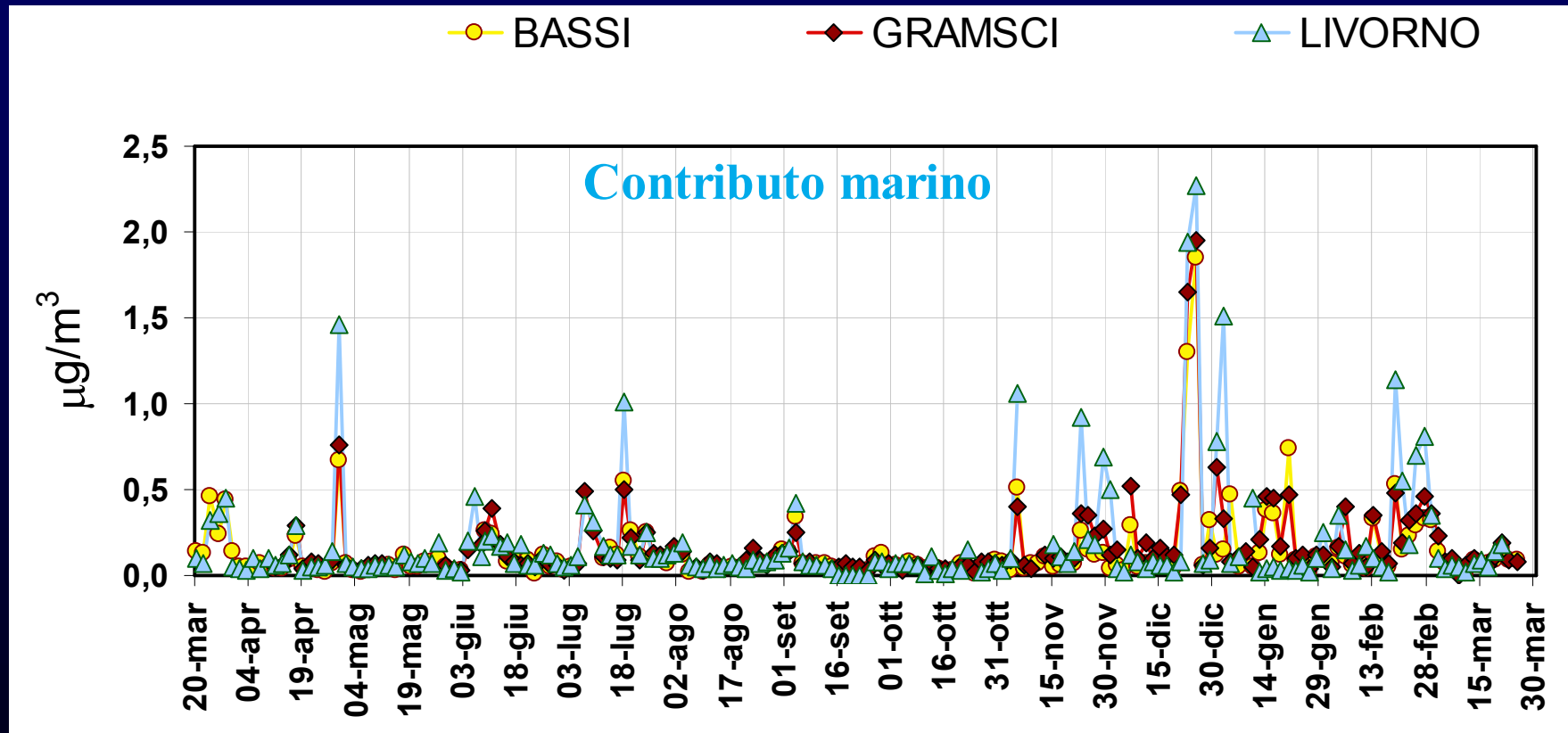
PATOS 2
Marzo 09 - Marzo 10
500 campioni di PM2.5

Campionamenti giornalieri con campionatori sequenziali LV con teste di prelievo PM10 e PM2.5



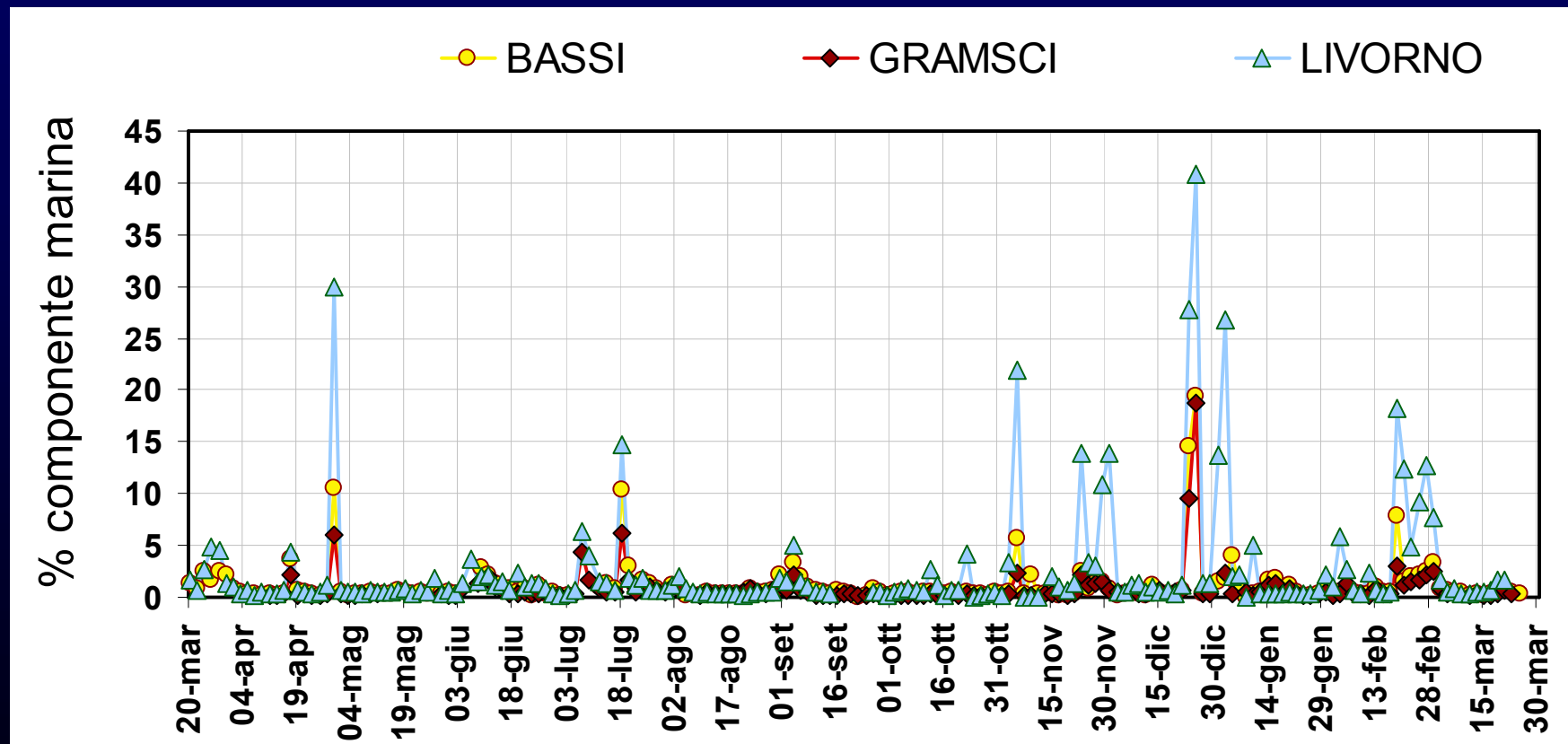


Contributo aerosol marino

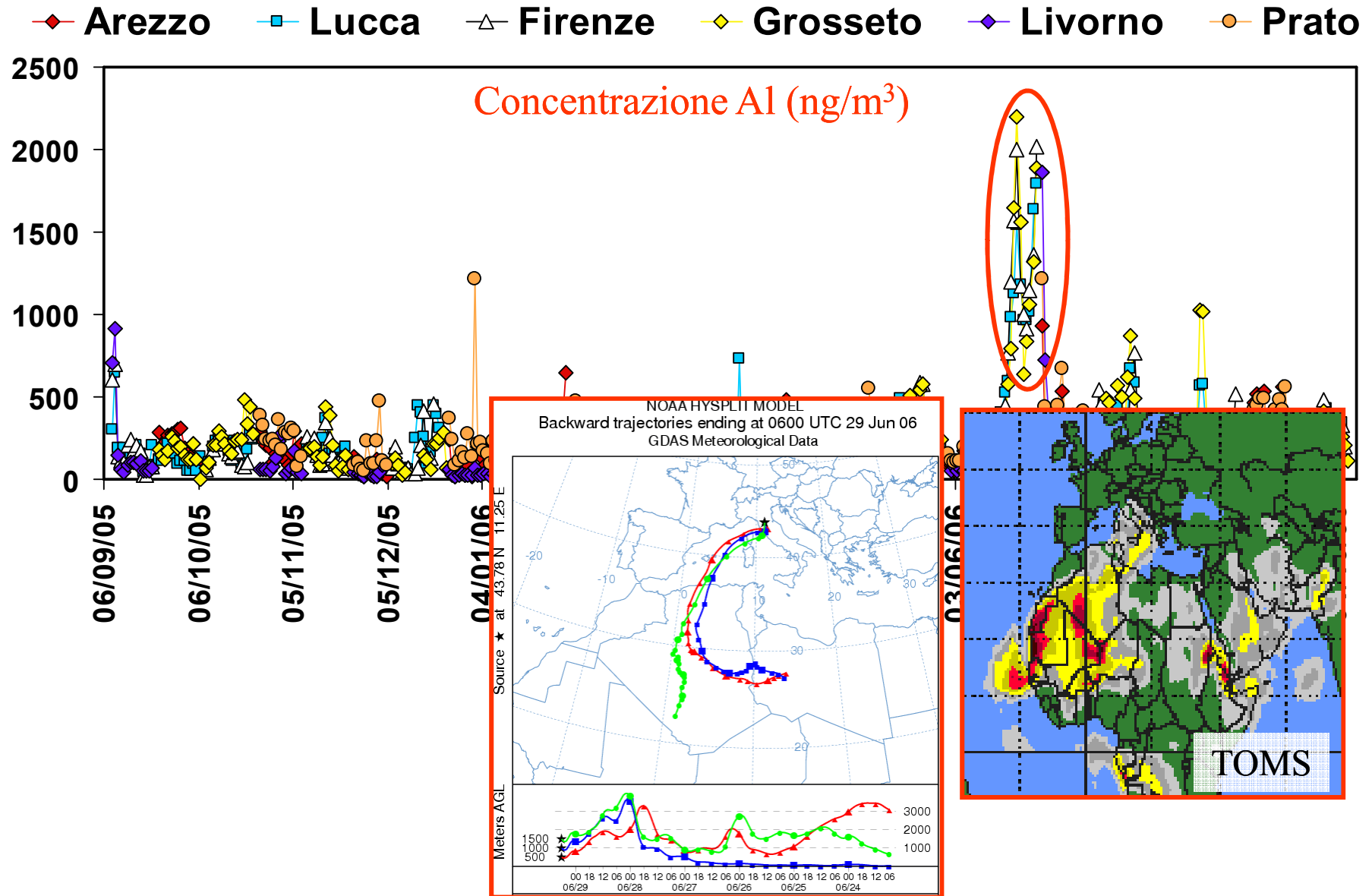




Contributo % della componente marina

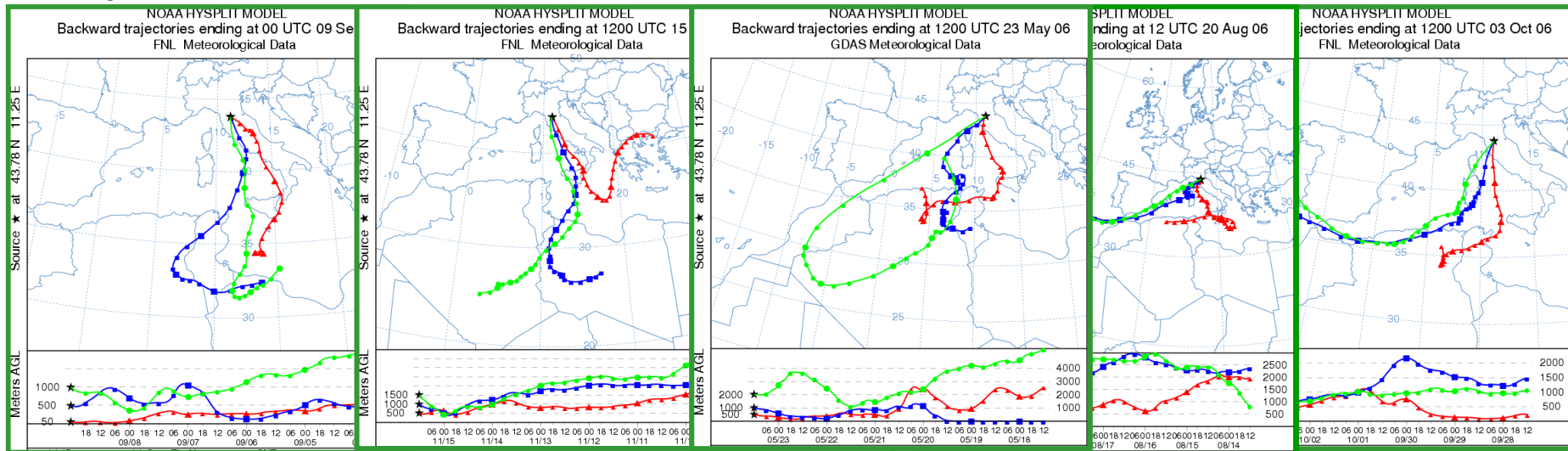
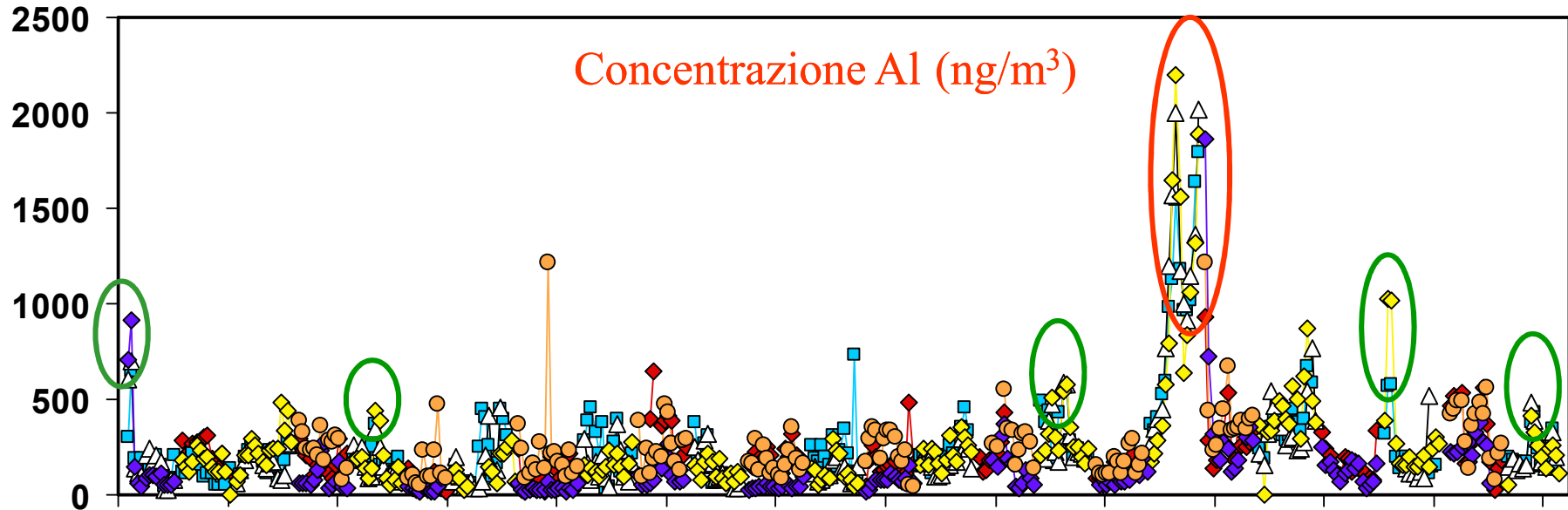


PATOS: andamenti elementali



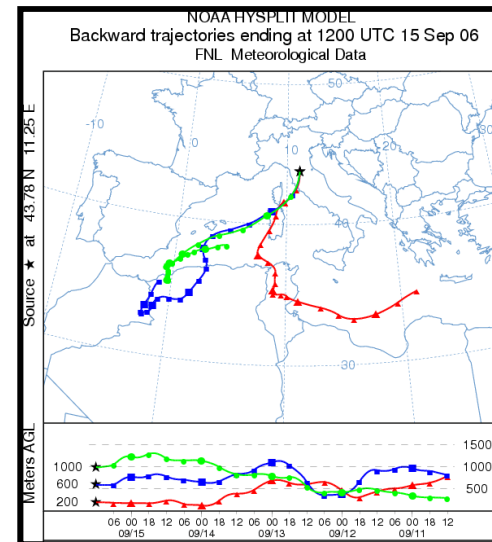
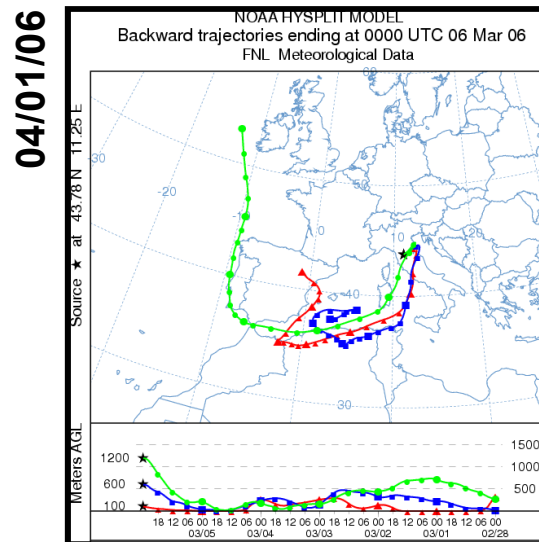
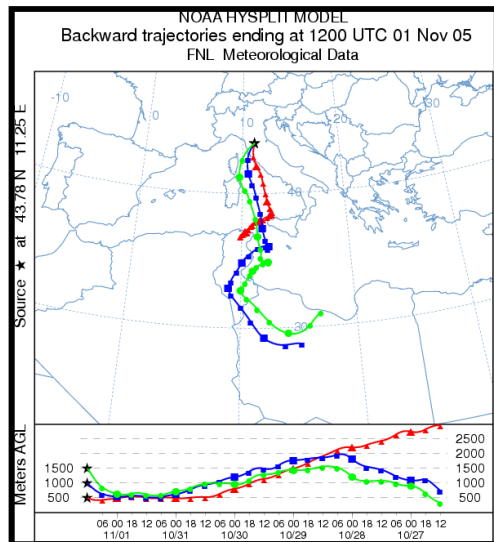
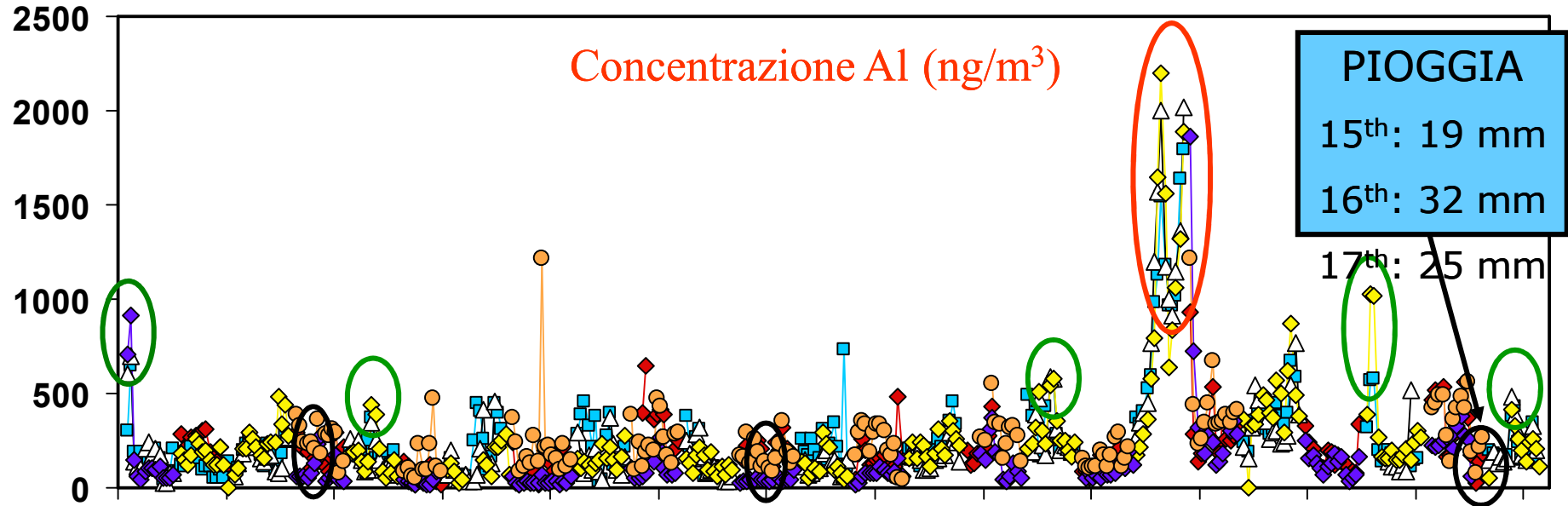
PATOS: andamenti elementali

◆ Arezzo □ Lucca △ Firenze ◇ Grosseto ◆ Livorno ○ Prato



PATOS: andamenti elementali

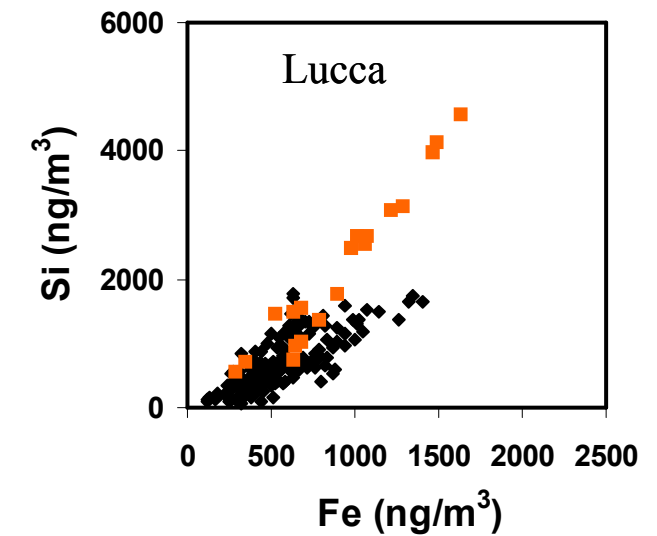
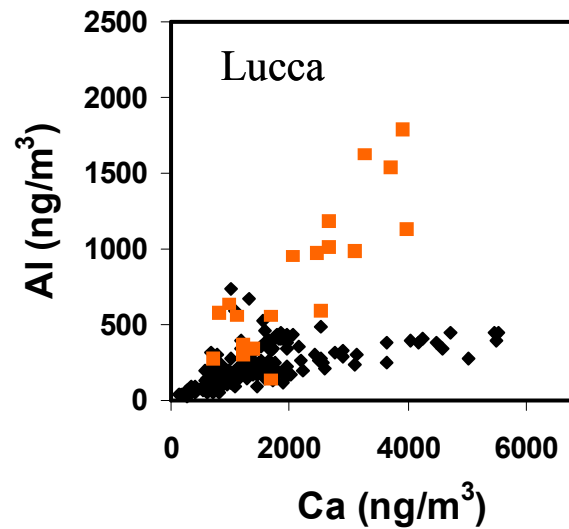
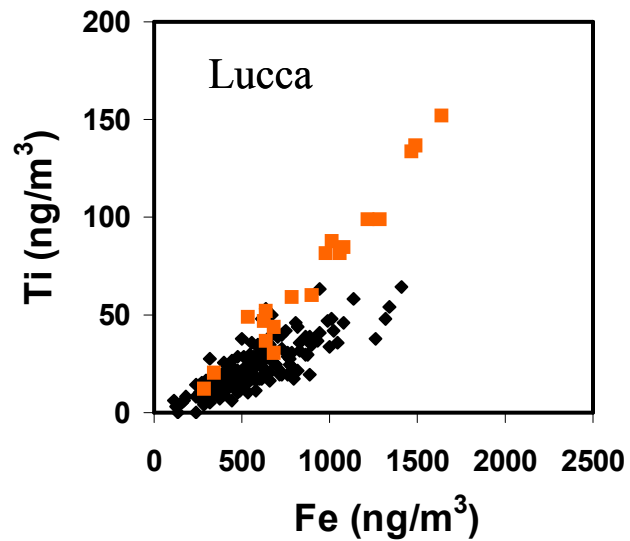
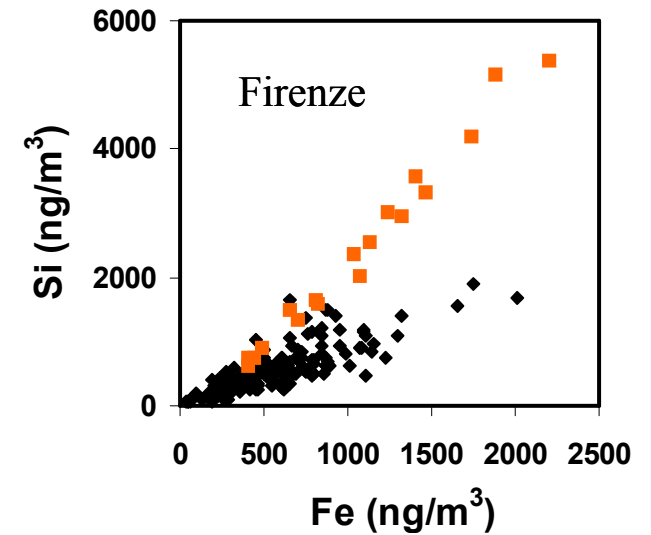
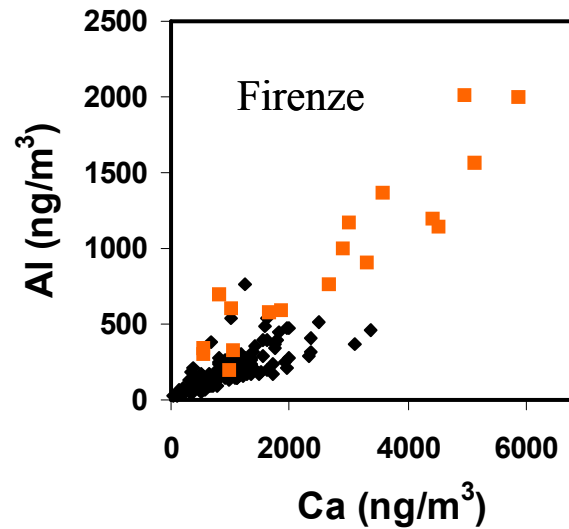
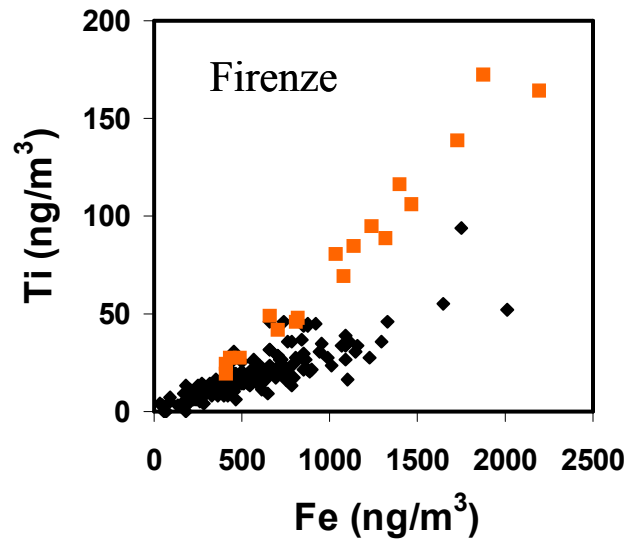
◆ Arezzo
 ■ Lucca
 △ Firenze
 ◇ Grosseto
 ◇ Livorno
 ● Prato



04/01/06

01/10/06

PATOS: rapporti elementali



Traiettorie dal Sahara

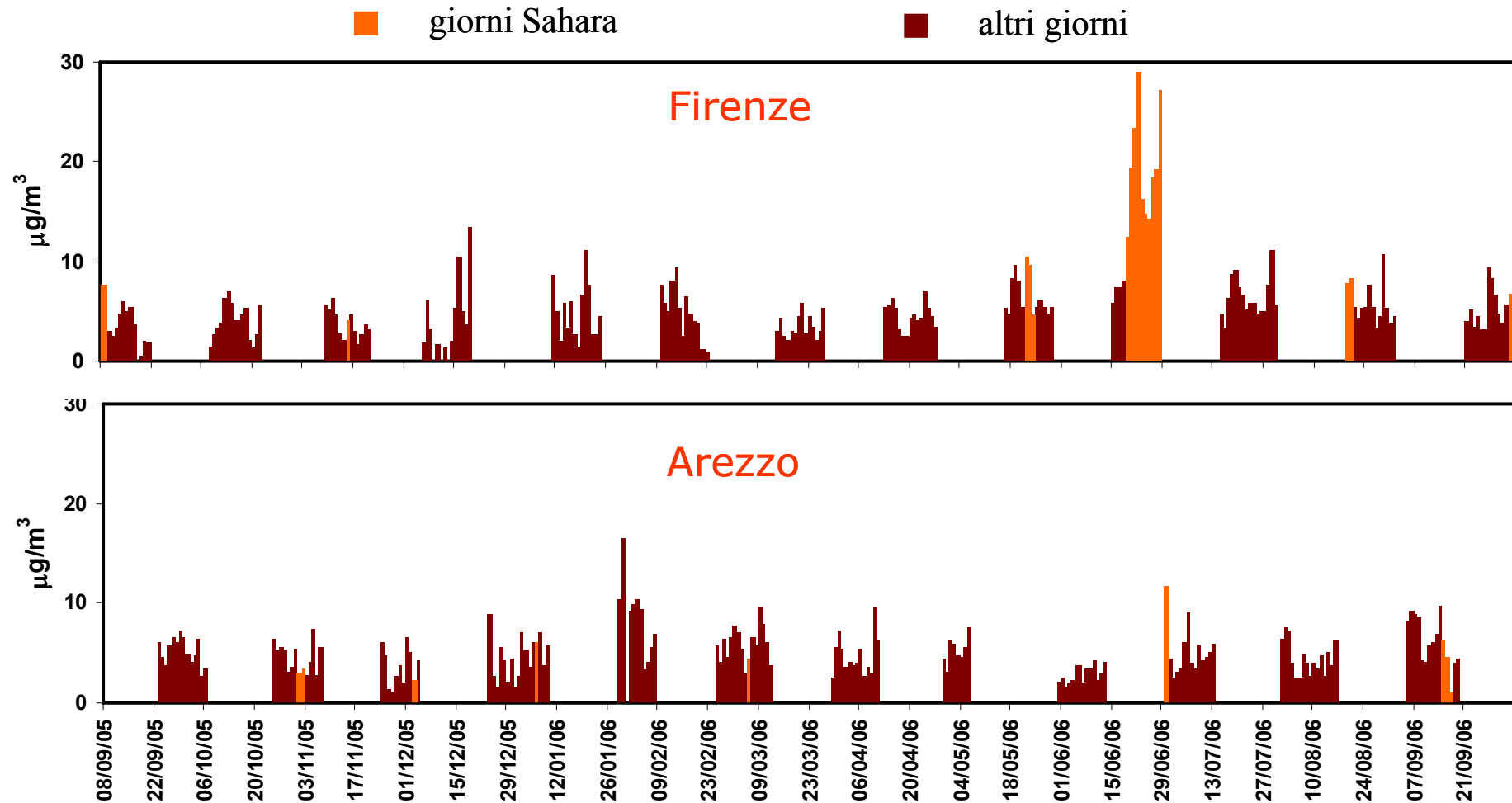
Traiettorie NON dal Sahara

PATOS: rapporti elementali

		Al/Fe	Si/Fe	Ti/Fe	Al/Ca	Si/Ca	Ti/Ca	Si/Al
Firenze	Sahara	0.88	2.3	0.072	0.39	1.0	0.031	2.6
	Altri giorni	0.36	1.0	0.036	0.22	0.6	0.022	3.0
Lucca	Sahara	0.95	2.5	0.081	0.44	1.1	0.037	2.6
	Altri giorni	0.39	1.2	0.040	0.17	0.5	0.018	3.2
Grosseto	Sahara	1.09	2.7	0.088	0.49	1.2	0.039	2.5
	Altri giorni	0.53	1.5	0.052	0.20	0.6	0.020	2.9

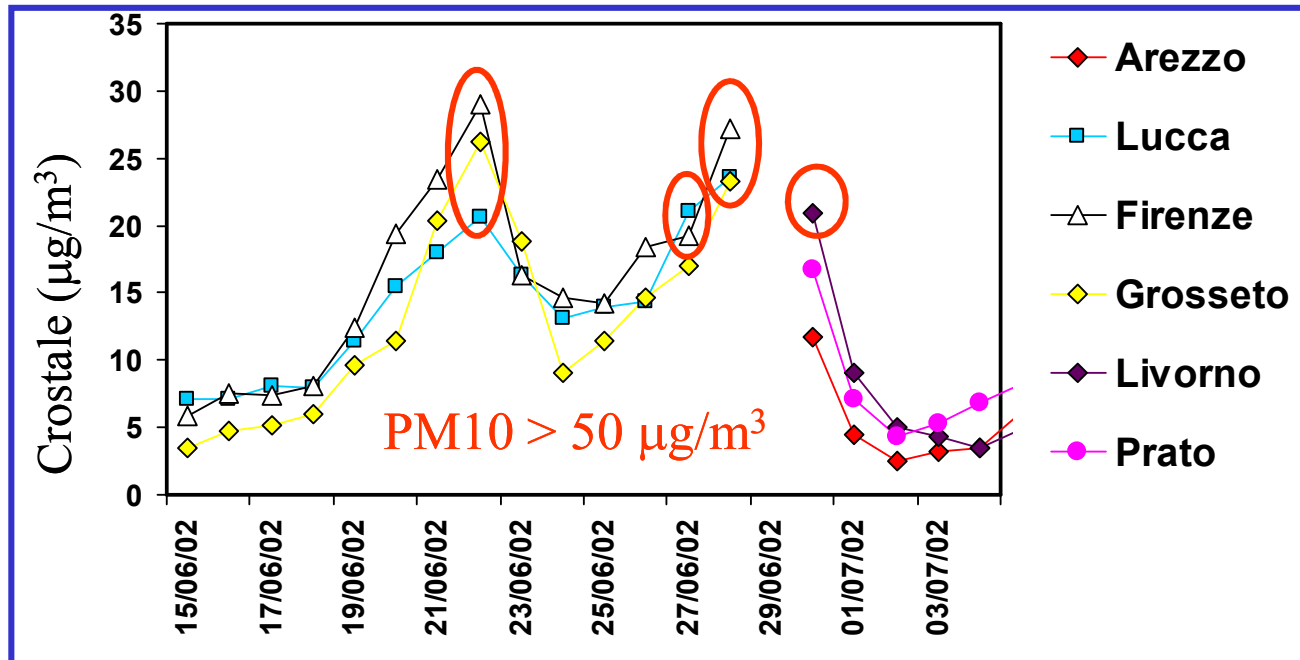
- Rapporti simili nei diversi siti di campionamento
- Cambiamenti significativi nei giorni "Sahariani" per alcuni rapporti
- Cambiamenti meno evidenti per altri rapporti elementali (Ti/Si, Ca/Fe)

PATOS: componente crostale



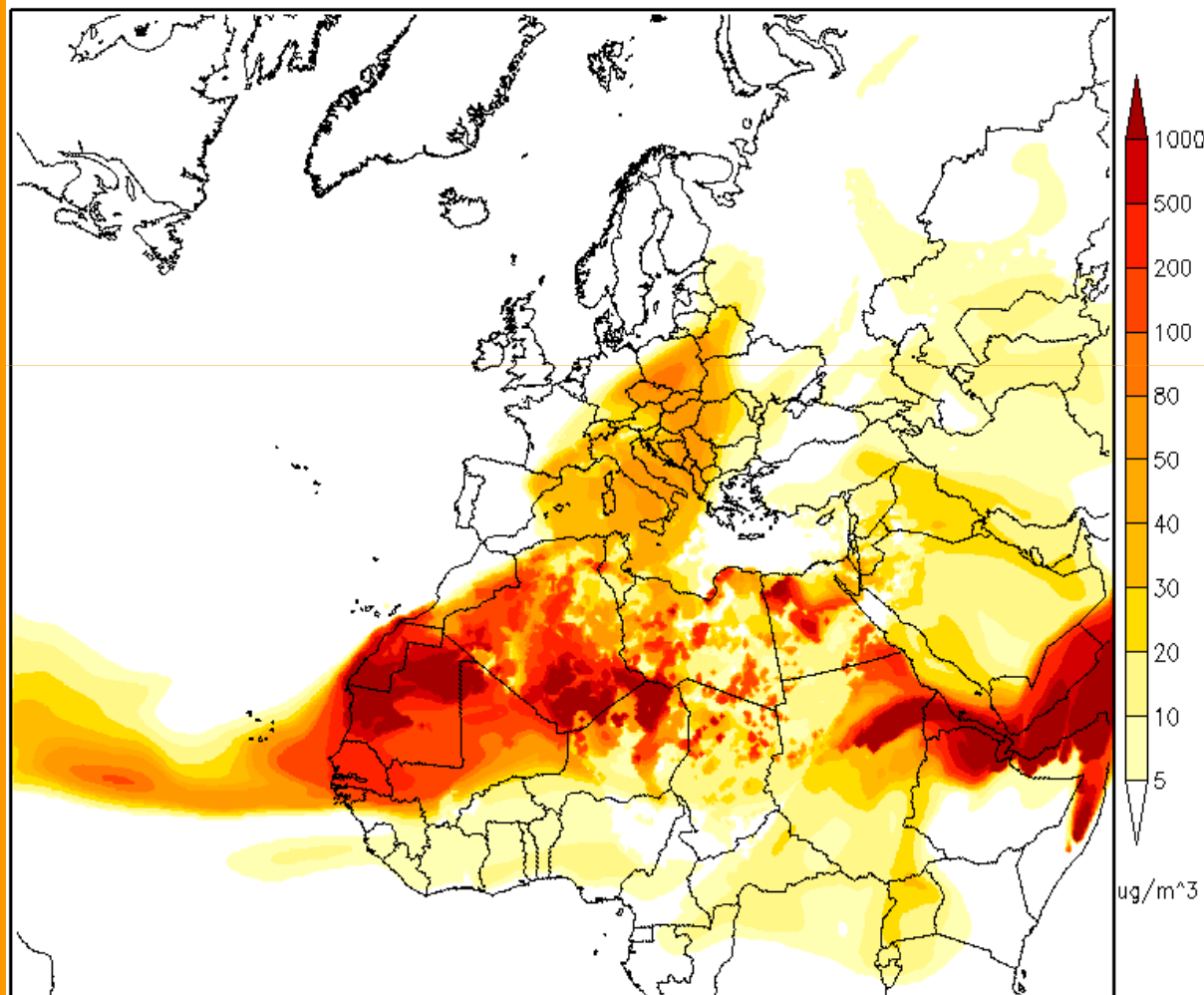
Contributo che varia da pochi $\mu\text{g}/\text{m}^3$ a $\sim 10 \mu\text{g}/\text{m}^3$
con l'eccezione dell'episodio di Giugno

PATOS: episodio di Giugno



Crostale (µg/m ³)	FIRENZE	LUCCA	GROSSETO	LIVORNO
22/06/06	29 (52%)	21 (43%)	26 (51%)	-
27/06/06	19 (38%)	21 (43%)	17 (39%)	-
28/06/06	27 (48%)	24 (46%)	23 (47%)	-
30/06/06	-	-	-	21 (42%)
Media giorni non Sahariani	5.8 (21%)	6.9 (17%)	5.9 (25%)	3.2 (19%)

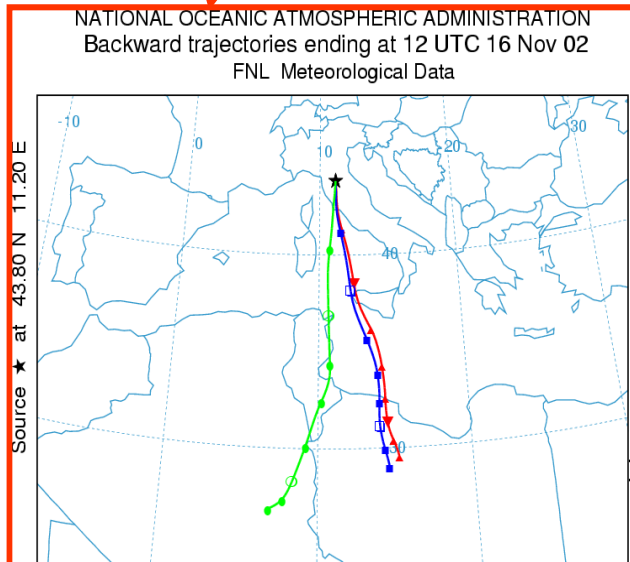
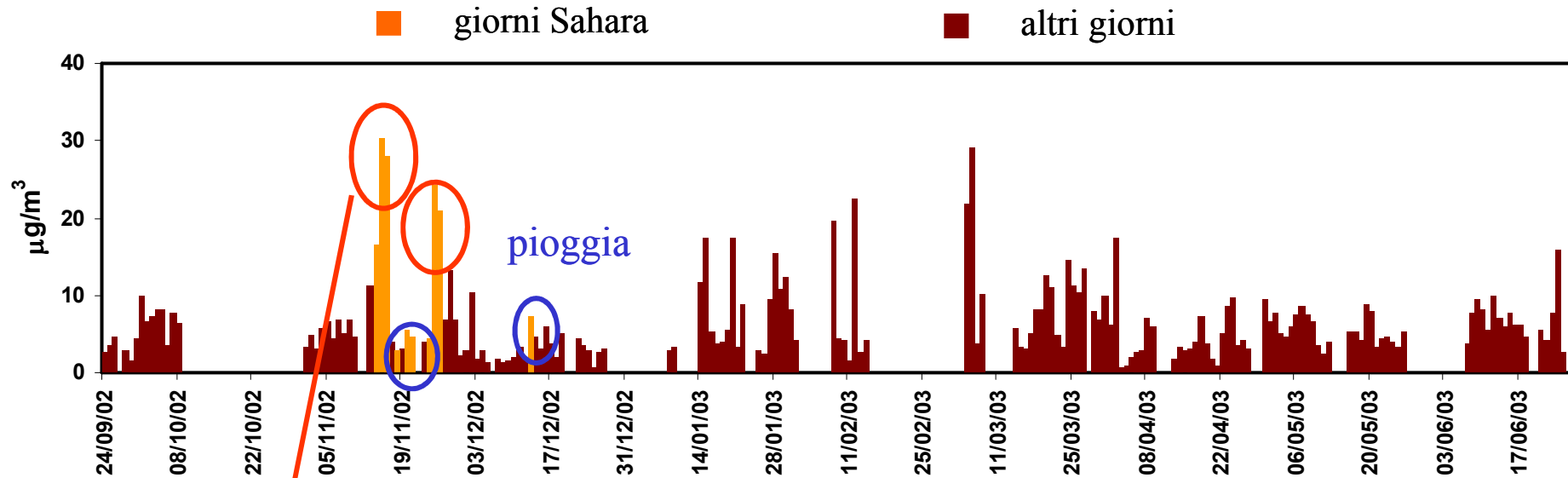
Daily average dust(>1um-<20um) conc. 28-06-2006



*Simulazione
episodio
Sahariano*

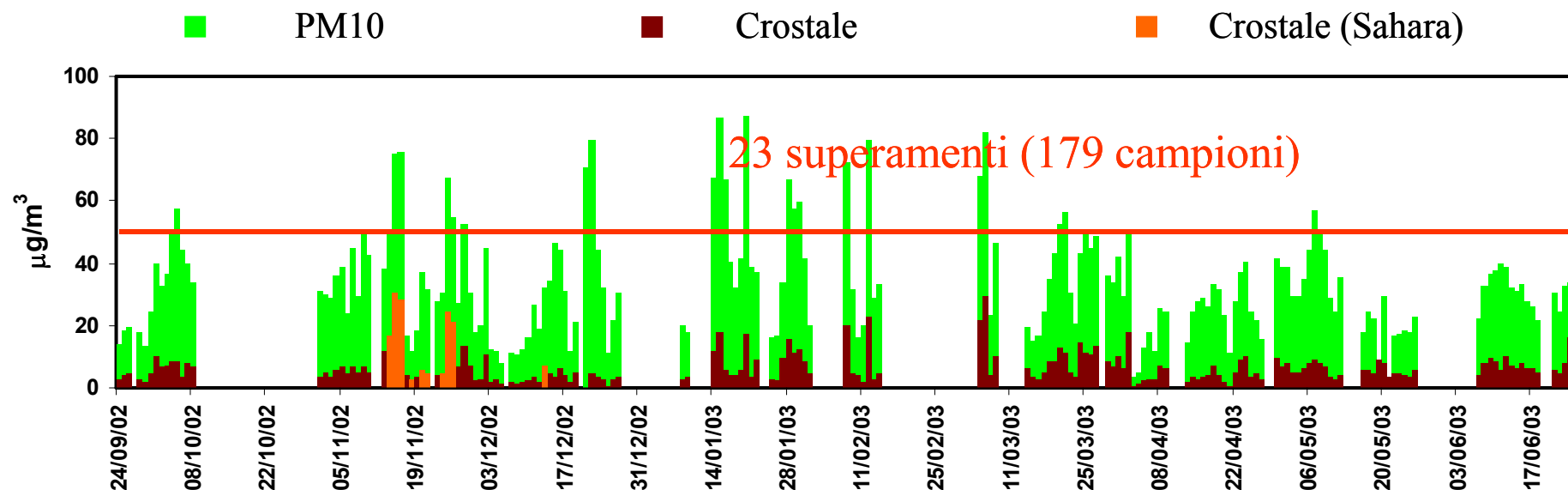
Giugno 2006

Montelupo (FI) 2002-2003



	Al/Ca	Si/Ca	Al/Fe	Si/Fe
Sahara	0.35	0.93	1.03	2.8
Altri giorni	0.24	0.72	0.57	1.7

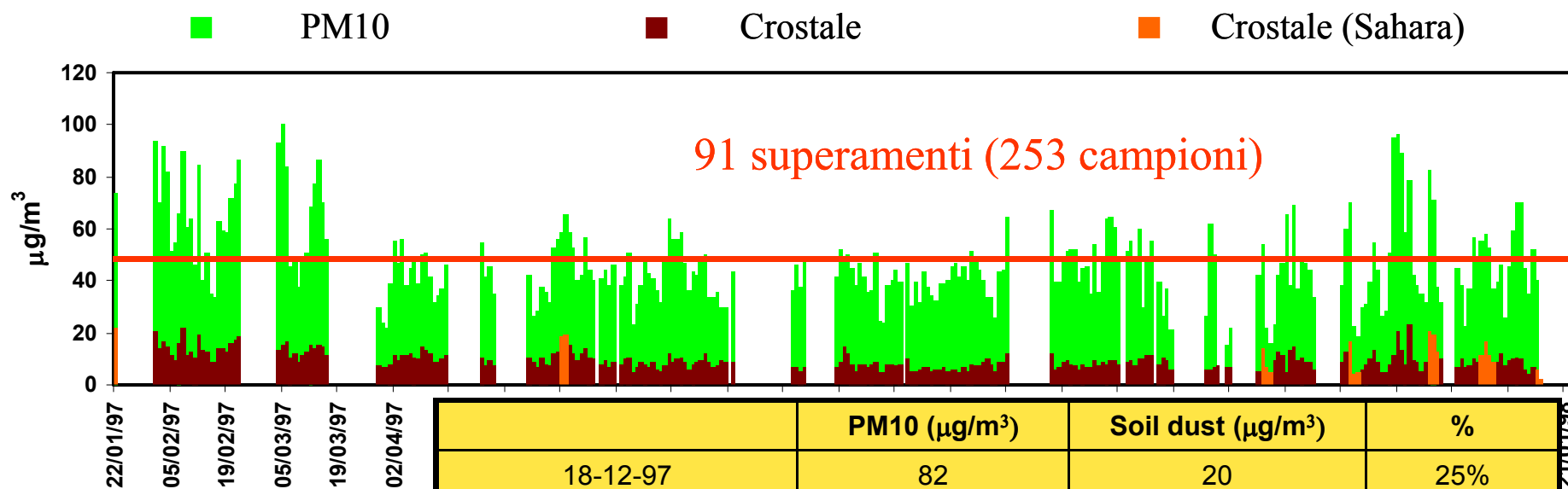
Montelupo (FI) 2002-2003



Superamenti
durante giorni
Sahariani

	PM10 ($\mu\text{g}/\text{m}^3$)	Soil dust ($\mu\text{g}/\text{m}^3$)	%
16-11-02	75	28	37%
15-11-02	75	30	40%
25-11-02	67	24	36%
26-11-02	55	21	38%
14-11-02	49	17	34%
Media giorni non Sahariani	33	6.1	19%

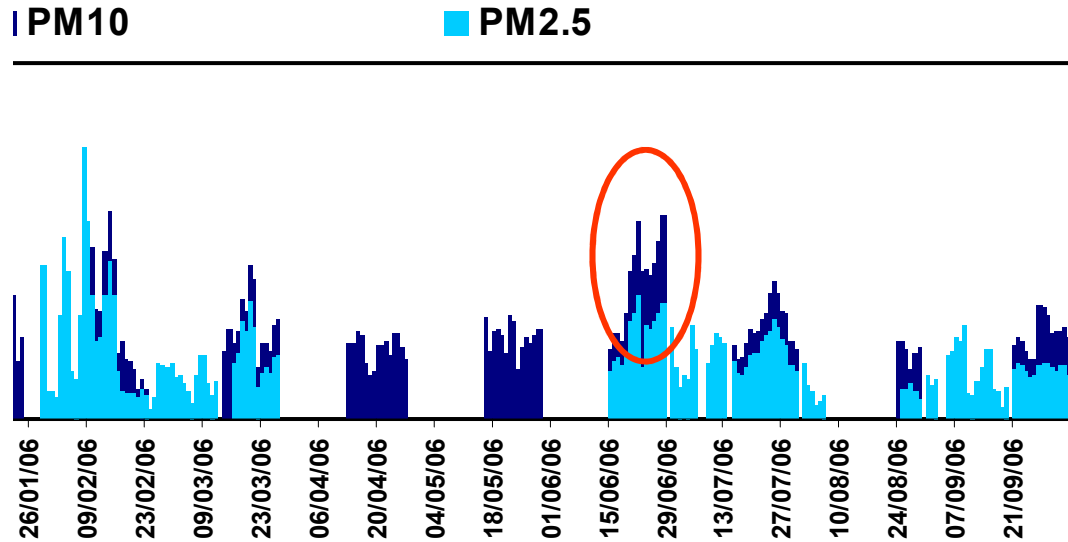
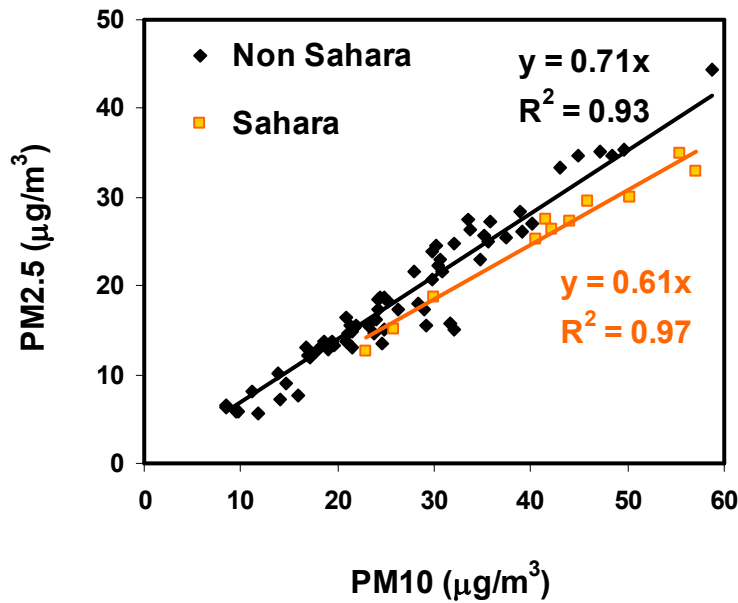
Firenze 1997-1998



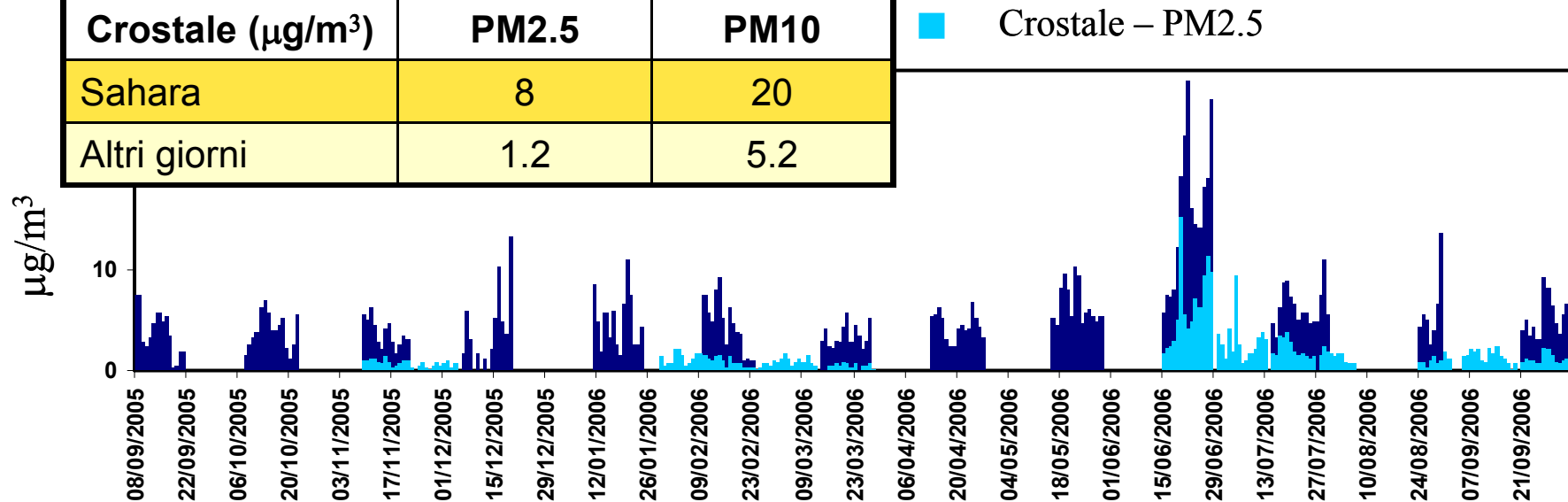
Superamenti
durante giorni
Sahariani

	PM10 ($\mu\text{g}/\text{m}^3$)	Soil dust ($\mu\text{g}/\text{m}^3$)	%
18-12-97	82	20	25%
22-01-97	74	22	29%
19-12-97	71	19	27%
28-11-97	70	16	23%
15-05-97	65	19	29%
14-05-97	58	18	31%
01-01-98	58	16	28%
31-12-97	55	11	20%
06-11-97	54	14	26%
02-01-98	53	11	21%
18-12-97	82	20	25%
Media giorni non Sahariani	47	9.3	20%

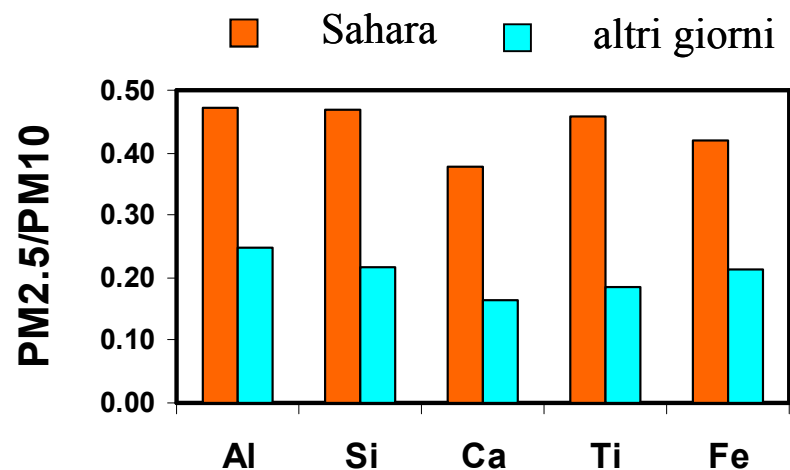
PM10-PM2.5 (PATOS)



Crostale ($\mu\text{g}/\text{m}^3$)	PM2.5	PM10
Sahara	8	20
Altri giorni	1.2	5.2



PM10-PM2.5 (PATOS) concentrazioni elementali



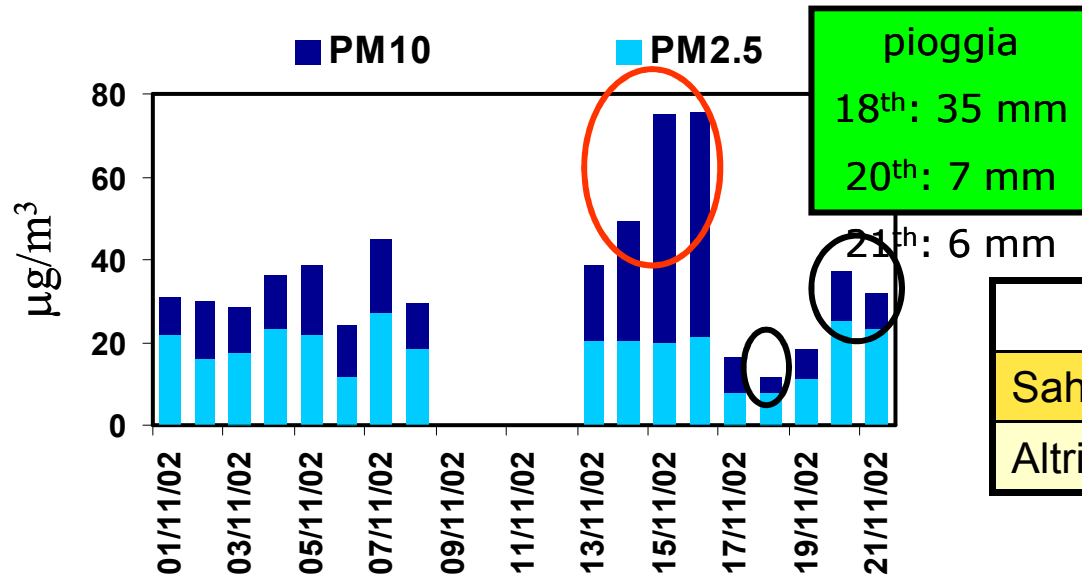
Aumento del rapporto fine/coarse durante l'episodio Sahariano

Rapporti elementali

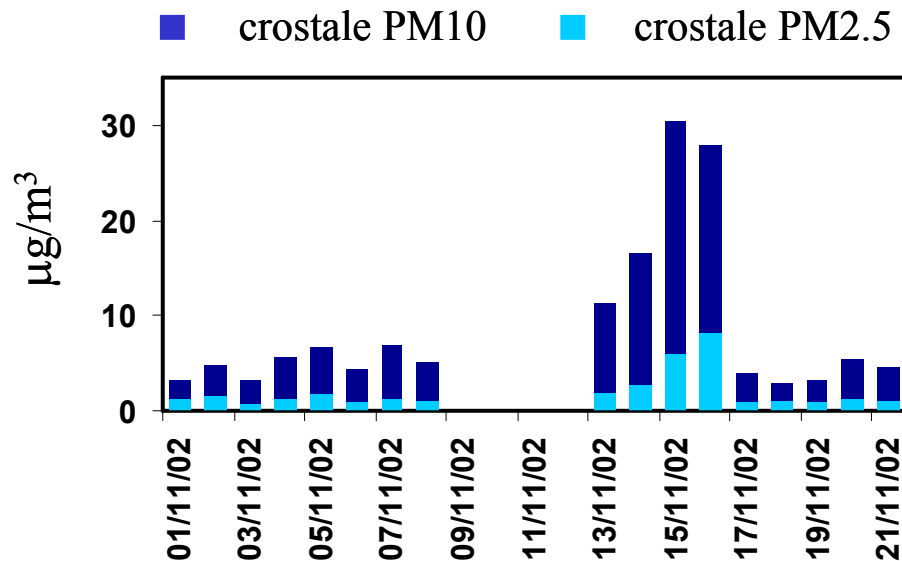
PM2.5	Si/Fe	Ti/Fe	Al/Ca	Si/Ca
Sahara	2.6	0.08	0.44	1.12
Altri giorni	1.1	0.04	0.39	0.96

PM10	Si/Fe	Ti/Fe	Al/Ca	Si/Ca
Sahara	2.4	0.08	0.33	0.86
Altri giorni	1.0	0.03	0.23	0.68

PM10-PM2.5 (Montelupo)

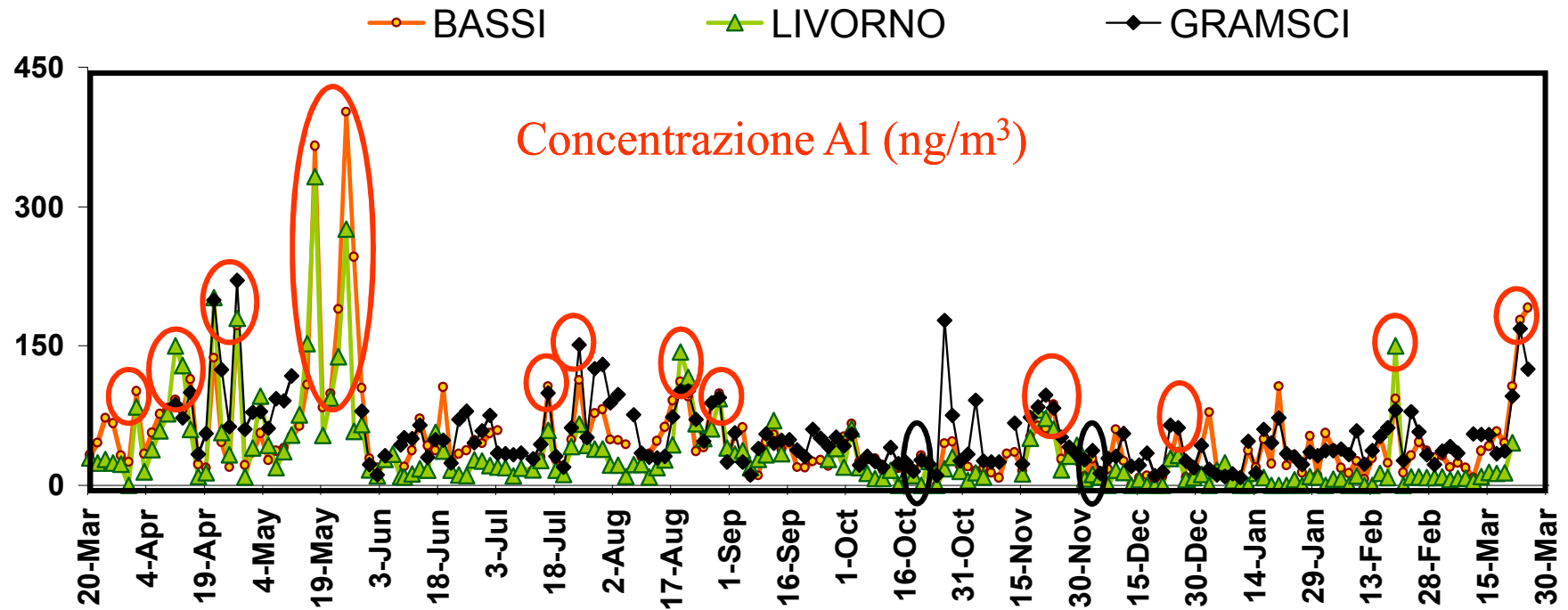


	PM2.5/PM10
Sahara (14 th -16 th)	0.32 (± 0.08)
Altri giorni (01 st -8 th)	0.59 (± 0.07)



Crostale ($\mu\text{g}/\text{m}^3$)	PM2.5	PM10
Sahara (14 th -16 th)	5.6	25
Altri giorni (01 st -8 th)	1.2	5.0

PATOS 2: PM2.5



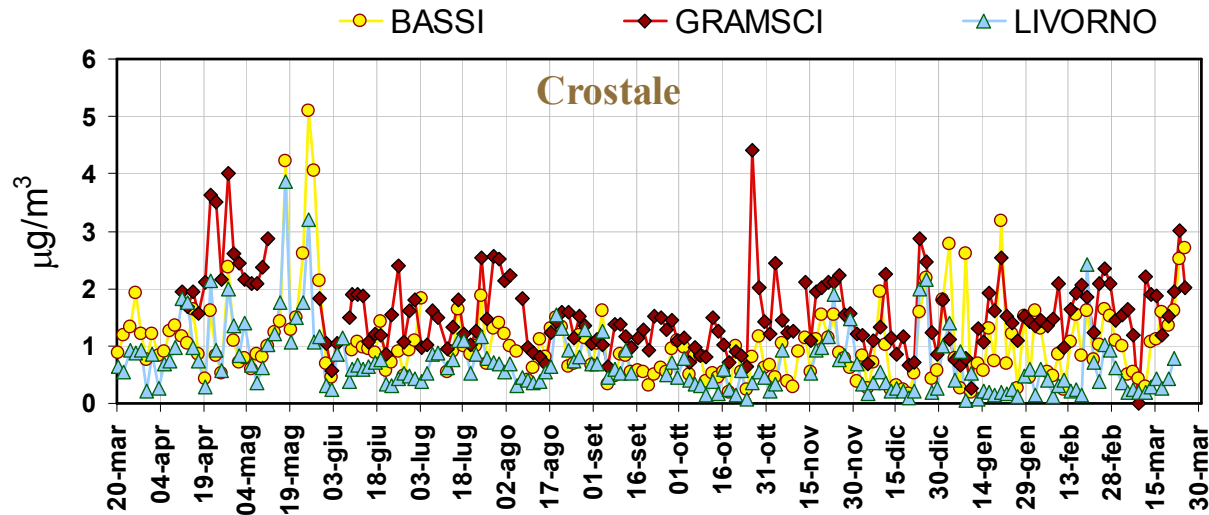
14 picchi simultanei imputabili al trasporto di polveri desertiche

PATOS 2 (PM2.5): rapporti elementali

PM2.5		Al/Fe	Si/Fe	Al/Ca	Si/Ca	Si/Al
Livorno	Sahara	1.37	3.4	1.05	2.6	2.5
	Altri giorni	0.70	2.4	0.55	1.9	3.7
FI-BA	Sahara	0.91	2.4	0.71	1.8	2.6
	Altri giorni	0.43	1.3	0.36	1.2	3.5
FI-GR	Sahara	0.42	1.1	0.60	1.5	2.7
	Altri giorni	0.16	0.5	0.27	0.9	3.5

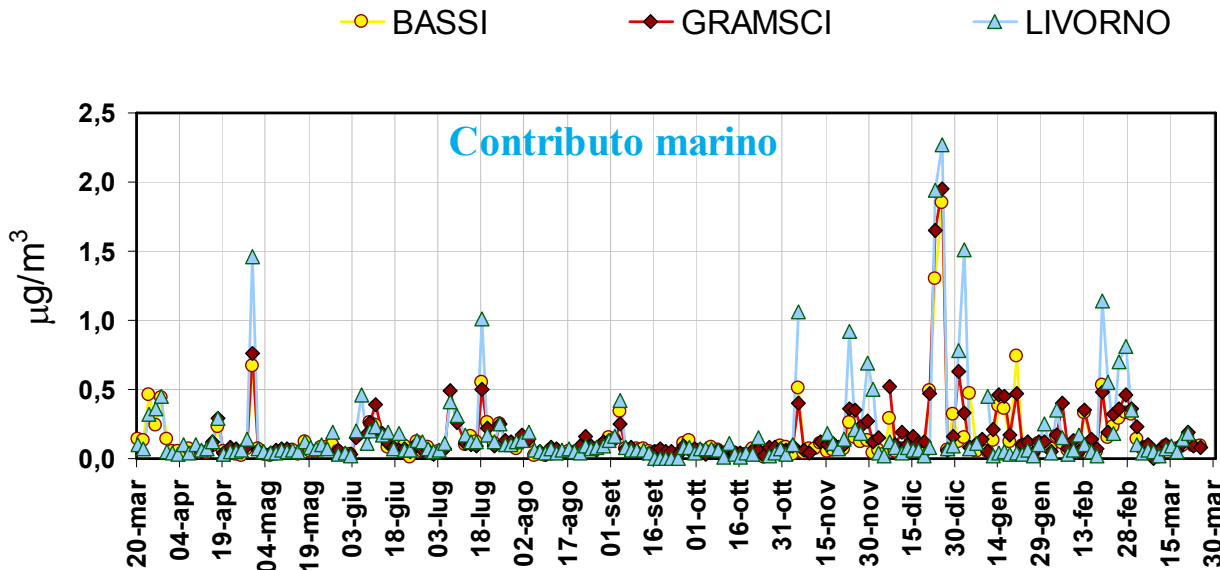
PM2.5		Al/Fe	Si/Fe	Al/Ca	Si/Ca	Si/Al
FI-BA Patos1	Sahara	1.0	2.6	0.44	1.12	2.6
	Altri giorni	0.47	1.1	0.39	0.96	2.8

Contributo naturale



GRAMSCI
 Crostale: $\sim 1.5 \mu\text{g}$
 Marino: $\sim 0.1 \mu\text{g}$
 Max naturale: $\sim 5 \mu\text{g}$

BASSI
 Crostale: $\sim 1.0 \mu\text{g}$
 Marino: $\sim 0.1 \mu\text{g}$
 Max naturale: $\sim 5 \mu\text{g}$



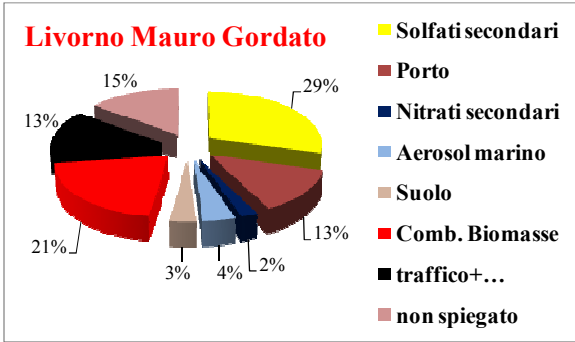
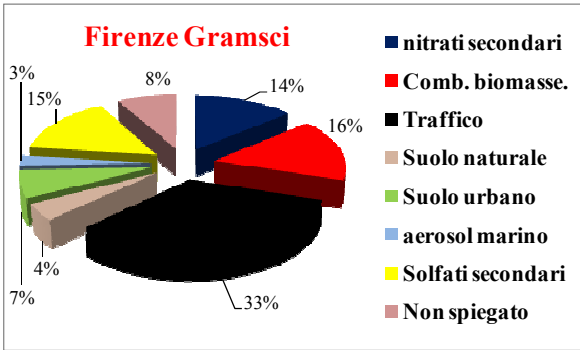
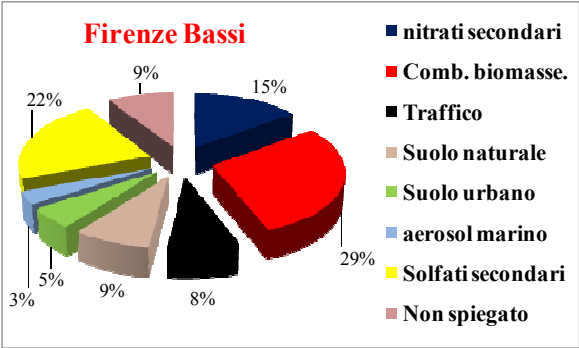
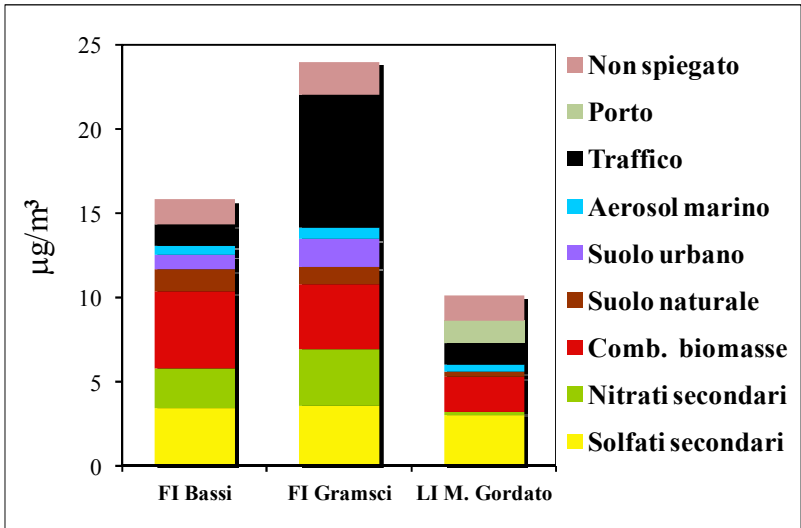
LIVORNO
 Crostale: $\sim 0.7 \mu\text{g}$
 Marino: $\sim 0.2 \mu\text{g}$
 Max naturale: $\sim 4 \mu\text{g}$



$\sim 8 \div 10 \%$

Contributo delle sorgenti al PM2.5 (media annuale)

Identificate
7 sorgenti
nei tre siti

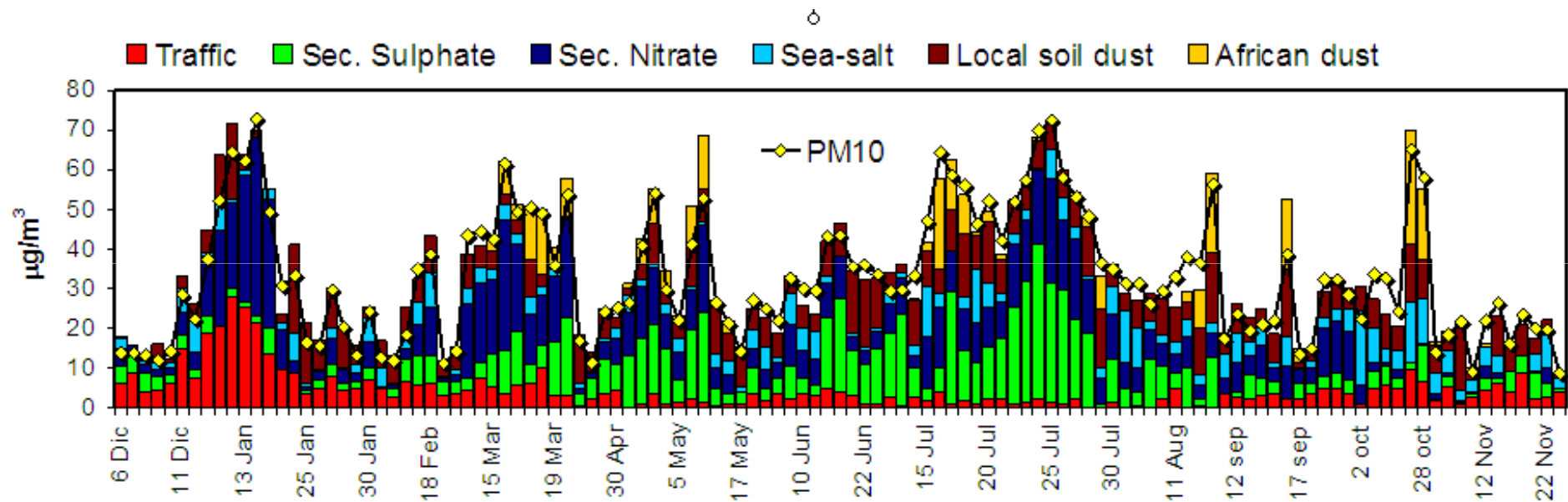


Saharan dust impact in a semi-arid zone of Spain (Elche)

- ~225,000 inhabitants
- mediterranean climate
- **Very arid zone with frequent intrusions of African dust**
- PM10 and PM2.5 daily samples, collected simultaneously for 1 year
(Dec. 2004 – dec. 2005)
- Site: urban background location, 12 m above ground level
- Samplers: low volume IND LVS.3.1 (EN 12341)



Elche (Spain): contribution to PM10

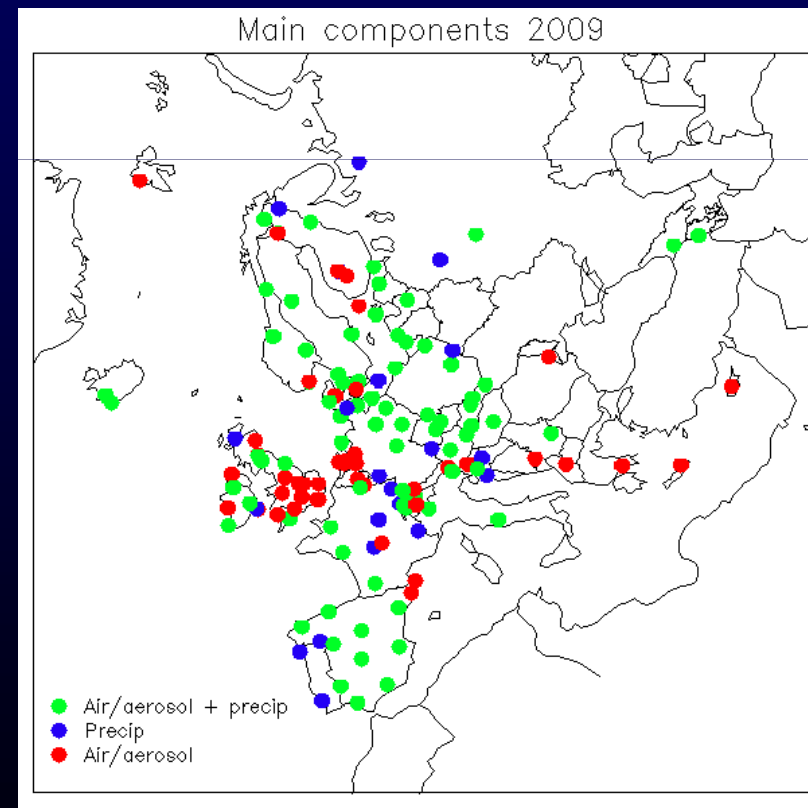


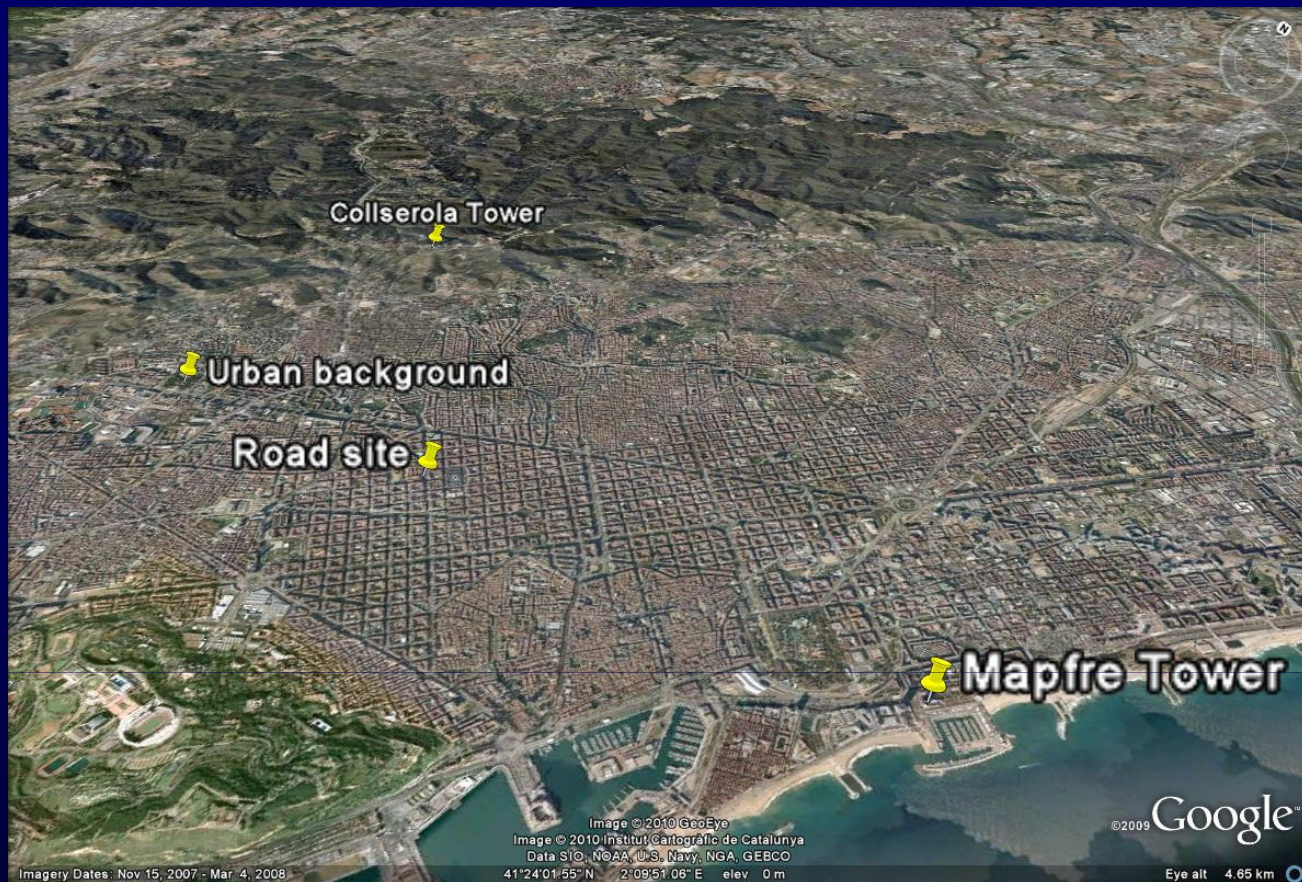
- PMF succeeded in disentangling the African dust contribution (7%) from local soil dust (21%)
 - Soil dust weight is predominant in most of the $50 \mu\text{g}/\text{m}^3$ limit exceedances.

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.

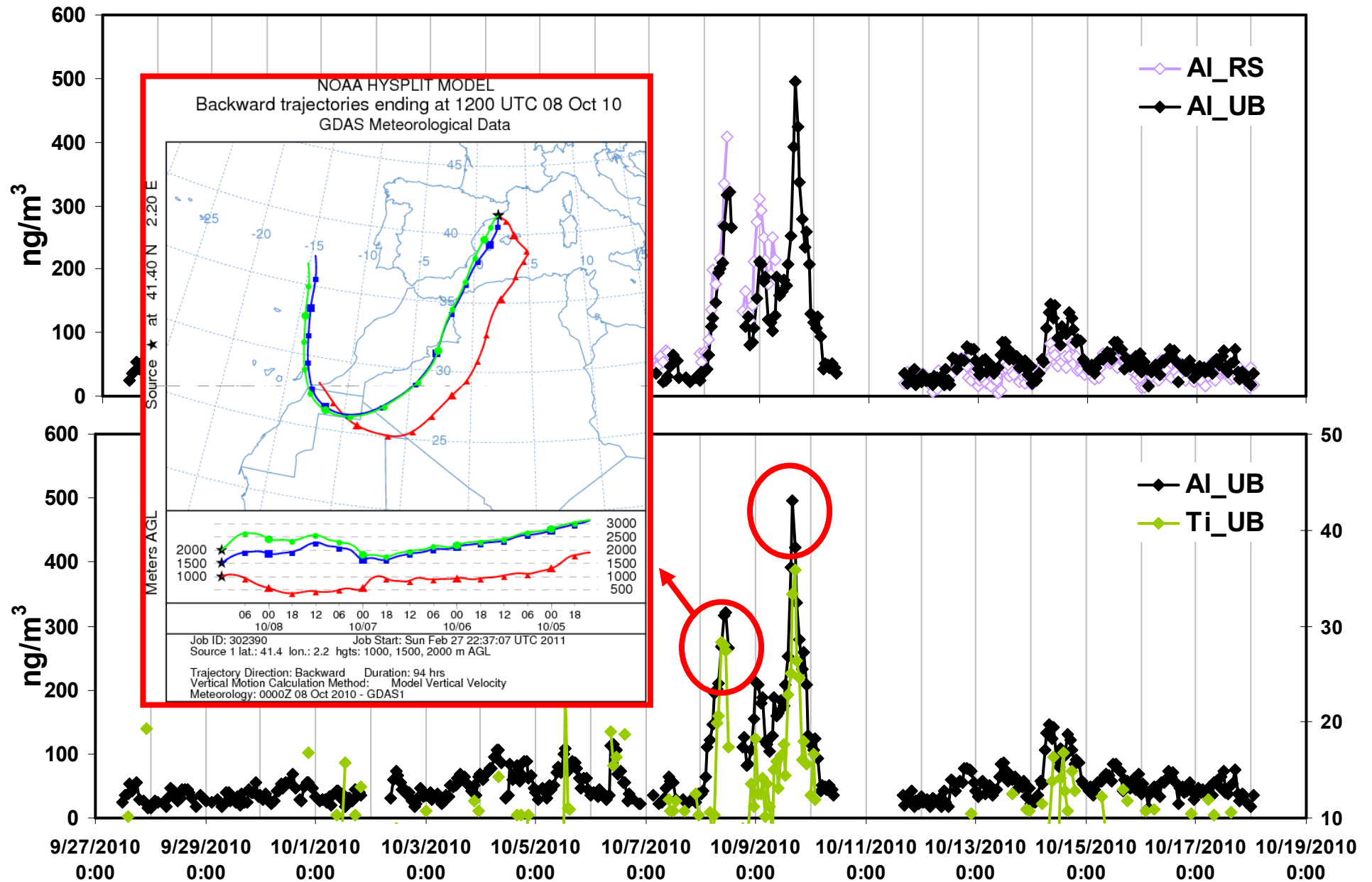
**2 campagne di un mese
(estate/inverno) in circa
15 stazioni per un totale
di circa 1000 campioni**





HR-TOF-AMS , ATOFMS (Birmingham), hourly inorganic PIXE analysis(Florence), 12 hours PM1,PM2.5 and PM10 off line filters on which we apply inorganic and organic speciation (Barcelona), CPC 3022, CPC 3025, SPMS, APS, grimm, NOx, Ozone, MAAP, Meteo.

Crustal dust



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Atmospheric
Chemistry
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Daily and hourly chemical impact of springtime transboundary aerosols on Japanese air quality

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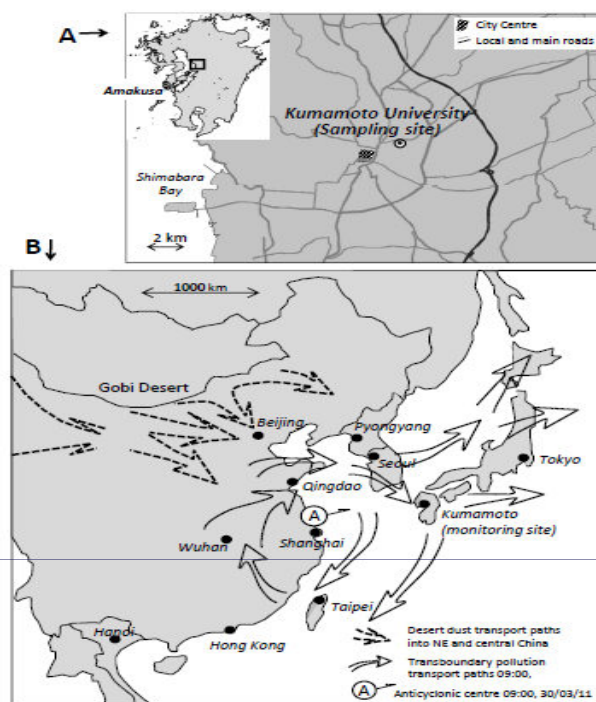


Fig. 1. Top: a simplified map of the area around the sampling site (rectangle in the inset) showing major roads including the Kyushu Expressway (darker line). Bottom: location map showing Kumamoto monitoring site and overviewing the area affected by the transboundary expulsion of anthropogenic aerosols from China into the NW Pacific region. Arrows depict typical atmospheric circulation patterns driving the pollution eastward out from the mainland, in this case by an anticyclone centred near Shanghai during the sampling period at the end of March 2011. The main source areas of springtime desert dust intrusions into the area are also shown (Wang et al., 2004).

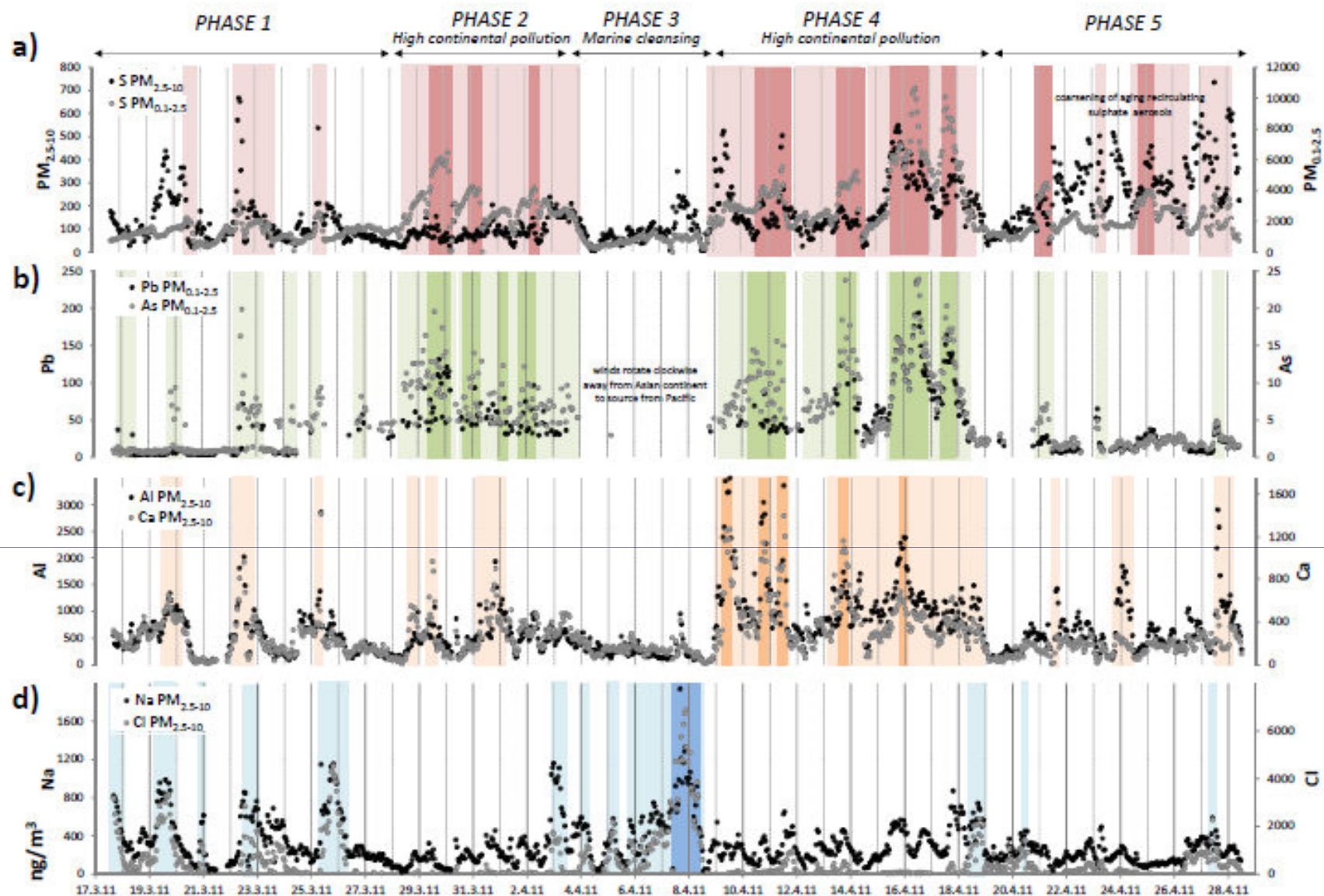


Fig. 4. Hourly selected elemental concentrations (ng m⁻³) obtained with the Streaker sampler for the five air quality phases identified during the monitoring campaign, with coloured bands highlighting main episodes of continental pollution and advection of salty marine air across Kumamoto. (a) shows both coarse (PM_{2.5-10}) and fine (PM_{0.1-2.5}) sulphatic aerosol intrusions, (b) uses Pb and As to illustrate how toxic metallic aerosols accompany the sulphatic intrusions, (c) uses Al and Ca to reveal the rise and fall of Gobi Desert PM introduced by NW winds crossing NE China, and (d) uses Na and Cl to identify marine aerosol episodes.



OBJECTIVES

The overall goal of the 'AIRUSE' project is to develop, demonstrate and adapt cost-effective and appropriate measures to ensure better air quality in urban areas. It aims to identify the most effective mitigation measures to reduce PM levels to within acceptable limits and thus to contribute to meeting current and future EU targets around air quality. Specific actions to achieve this overall goal include:

- Harmonising methods for identifying the sources of PM in the air;
- Determining the relative contribution of different emission sources of PM;
- Identifying those sources that are responsible for exceeding PM limits in specific areas;
- Evaluating the effect of current air quality mitigation measures;
- Developing targeted mitigation measures for the most important and relevant PM sources in Southern European urban areas;
- Assessing how different mitigation measures impact on PM sources and overall air quality; and
- Further adapting and optimising targeted mitigation measures.

The project thus hopes to identify the most practical and cost-effective strategies for reducing particulate matter in the air in southern European urban areas. This should support and encourage concrete actions to reduce PM exposure levels at local levels and assist national and regional authorities in implementing the "Thematic strategy on Air Pollution" and meeting the requirements of the EU Air Quality Directive (2008/50/EC).

Expected results

- The demonstration of effective PM mitigation strategies for southern Europe;
- The achievement of important reductions of PM10 and PM2.5 levels towards the limits set in the Air Quality Directive;
- Technical guides for implementing the demonstrated mitigation strategies in other regions in southern Europe and beyond; and
- Improved possibilities for implementing the Thematic Strategy on Air Pollution in southern Europe and for meeting current EU limit values for PM concentration levels and stricter PM limits in the future.

IDAEA_CSIC, Barcellona

N.C.S.R. Demokritos, Atene

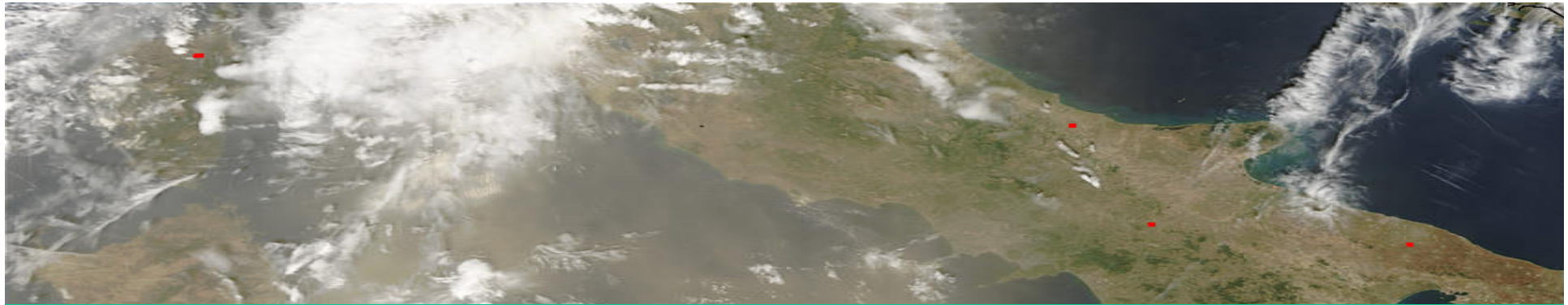
University of Aveiro

Università di Firenze

Asociación de Investigación de

las Industrias Cerámicas

University of Birmingham



Grazie per l'attenzione !!!

S. Nava, S. Becagli, G. Calzolari, M. Chiari, R. Traversi, R. Udisti



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