IN-SITU MEASUREMENT AND ANALYSIS OF ATMOSPHERIC AEROSOLS

II Lectures on Atmospheric Mineral Dust , Barcelona, 9th November 2012

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OUTLINE

PART I: ATMOSPHERE & POLLUTION

- INTRODUCTION
- EFFECTS
- MONITORING
- ANALYSIS
- SOME RESULTS

PART II: PM EPISODES IN THE WESTERN MEDITERRANEAN

- LOCAL ANTHROPOGENIC
- AFRICAN AIR MASS INTRUSIONS
- REGIONAL EPISODES
- ANTHROPOGENIC ANTICYCLONIC EPISODES

PART III: DUST OUTBREAKS

- TOOLS FOR DETECTION
- IBERIAN PROCEDURE
- HAVING IN MIND…
- OTHER APPLICATIONS

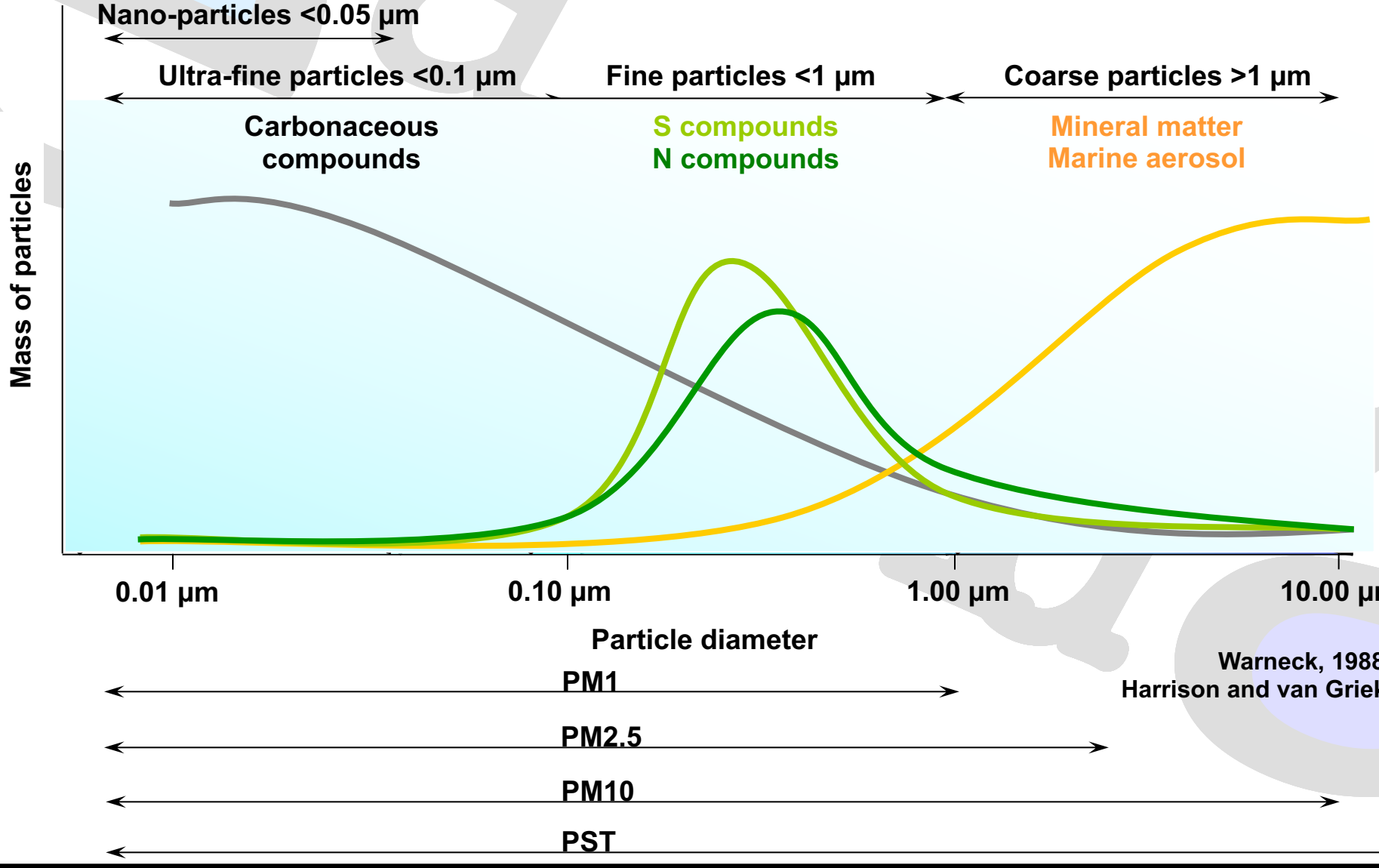
34/2007, 15th November, for Air Quality & Protection of the Atmosphere:

"Atmospheric Pollution": The occurrence in atmosphere of matter, substances or energy that may imply risk or damage for the safety or health of human beings, the environment……."

Bearing in mind:

- Not all harmful substances in atmosphere are already known
- For some components there is not a threshold for human protection
- Many activities and process (natural and anthropogenic) emit atmospheric pollutants

ATMOSPHERE & POLLUTION: introduction



Warneck, 1988
Harrison and van Grieken, 1998

CLASSIFICATION OF ATMOSPHERIC PARTICLES

1. Process of formation:

Primary particles: directly emitted to the atmosphere as a solid

Secondary particles: produced into the atmosphere from gaseous precursors

example: SO_2 (g) □ oxidation □ SO_4^{2-} (s)

2. Origin:

Natural particles

Anthropogenic particles (human activities)

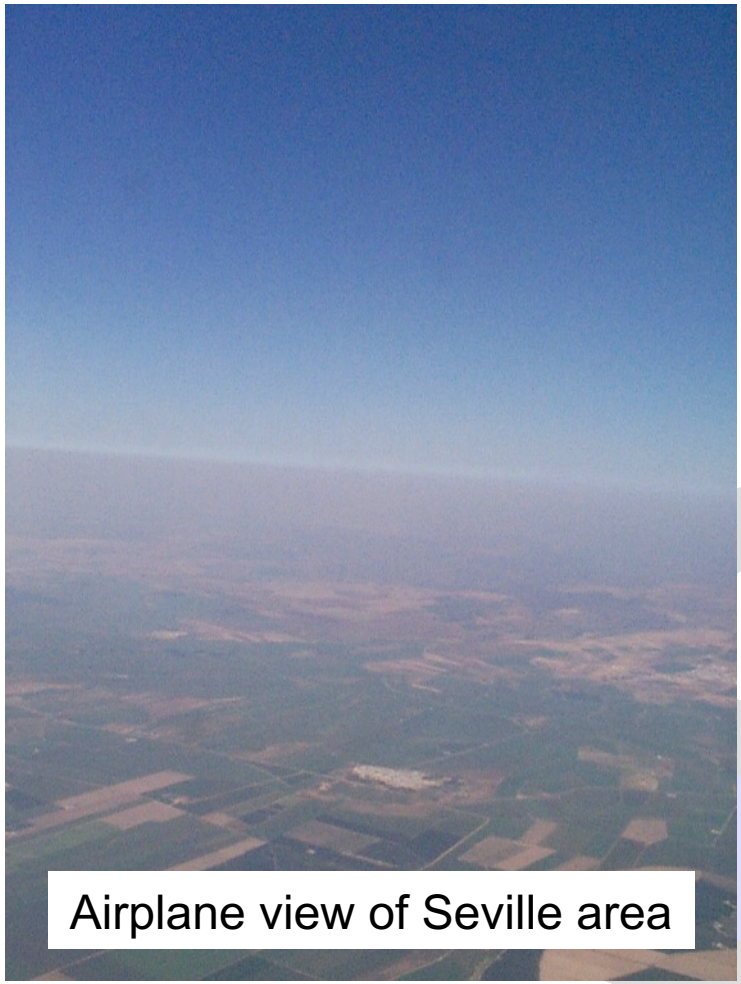
PRIMARY (ANTHROPOGENIC) PM

Handling materials in the Tarragona harbour

Industrial emissions in the Castellón ceramic area

SECONDARY (ANTHROPOGENIC) PM

Coal power plant in Andorra-Teruel



Airplane view of Seville area

FORMATION OF SECONDARY INORGANIC AEROSOLS

Process of oxidation $SO_2 \rightarrow H_2SO_4$ **and** $NO_x \rightarrow HNO_3$:

Nucleation homogeneous (gas to particle)

Nucleation heterogeneous (gas-H_2O-particle)

Reaction

2.1. Dry oxidation (main)

Generation of oxidant radicals

$O_3 + h\nu(\text{solar}) \rightarrow O^*$ $\quad O^* + H_2O \rightarrow 2OH$

Oxidation

$SO_2 + OH + m \rightarrow HOSO_2 + m$ $\quad HOSO_2 + O_2 \rightarrow HO_2 + SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

$NO + O_3 \rightarrow NO_2 + O_2$ $\quad NO_2 + OH + m \rightarrow HNO_3 + m$

Maximal velocities (summer, max hν):
6%SO_2h^{-1}, 18%NO_2h^{-1}
34%SO_2day^{-1}, 98%NO_2day^{-1}

2.2. Wet oxidation (dissolution of gases, mainly SO_2) (condensation nuclei, fog, precipitation, 'wet aerosol films')

Oxidants: H_2O_2 (pH<5), O_3 (pH>5), O_2 (catalysers, Cl, m)

Oxidation

$HCOH + h\nu$ *(solar)* $\rightarrow H + HCO^*$ $\quad HCO^* + O_2 \rightarrow HO_2 + CO^*$
(formaldehyde)

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$2SO_2 + 2H_2O \rightarrow SO_3^{2-} + HSO_3^- + 3H^+$

$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O$

Maximal velocities (summer, max hν):
270%SO_2h^{-1} (H_2O_2) 410%SO_2h^{-1} (O_3)

PM ORIGIN

PRIMARY

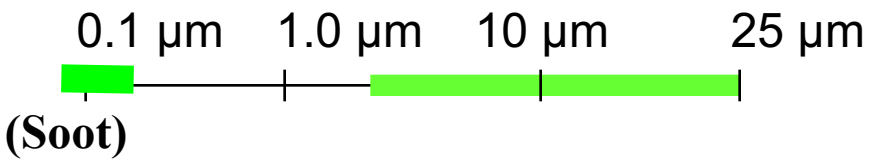
- **Natural**

  re-suspension (loc/ext)
  evap./precip.

- **Anthropogenic**

  direct emissions
  fugitive emissions

SiO_2,Al_2O_3,Fe_2O_3,TiO_2
$CaCO_3$, NaCl, C_{org}, metals



SECONDARY

- **Natural**

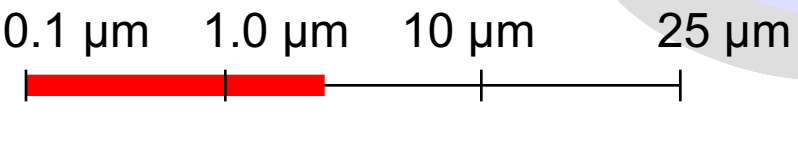
  natural sulphate

  biogenic emissions

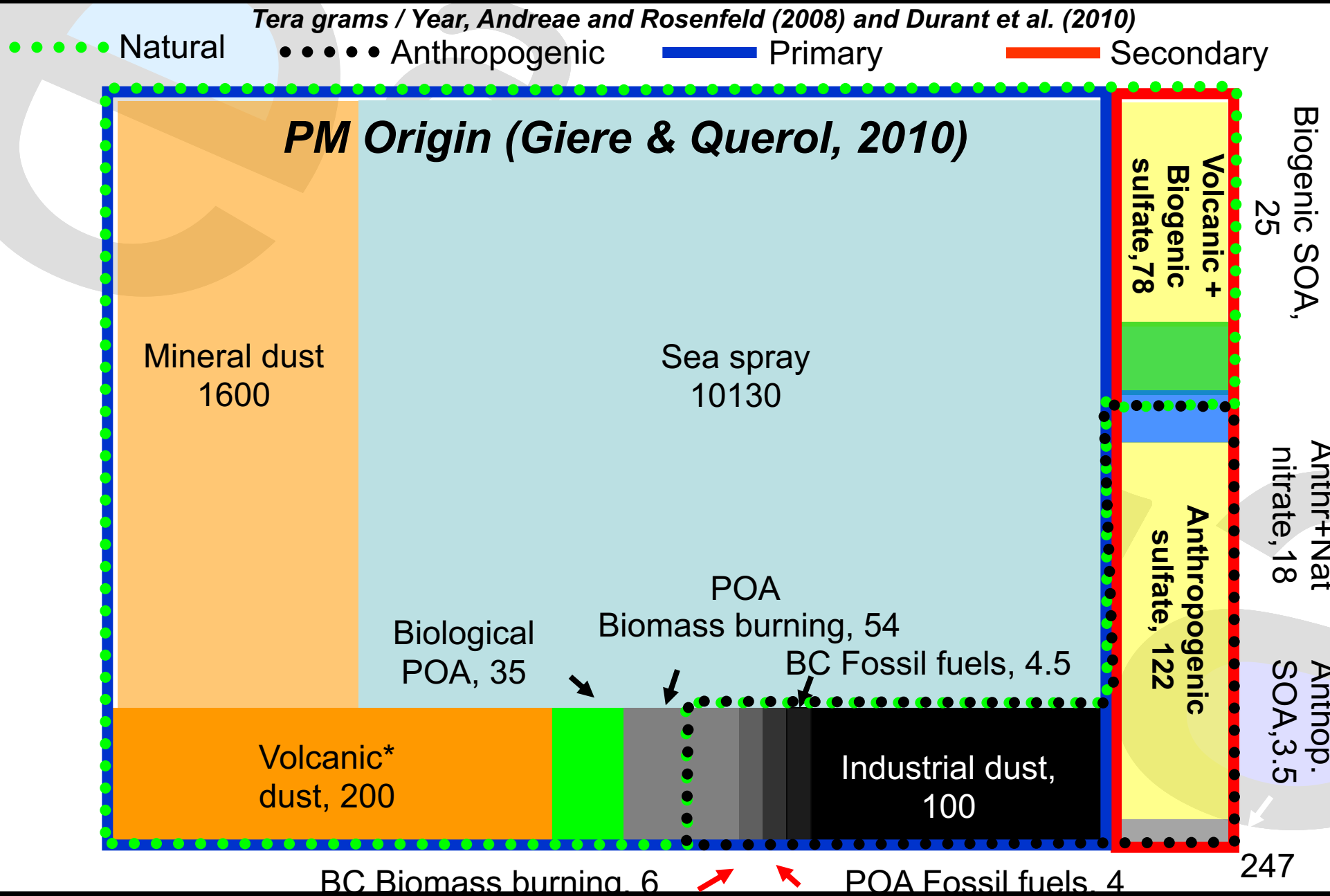
- **Anthropogenic**

  PM from gas by
  nucleation condensation
  evaporation

$SO_4^{=}$, NO_3^{-}, NH_4^{+}, H^{+}
C_{org}, metals



ATMOSPHERE & POLLUTION: introduction



PM COMPOSITION

Crustal-mineral

Al_2O_3
Mg
Ti
Fe
K
SiO_2
CO_3^{2-}
P
Ca

Carbonaceous aerosols (OM and EC)

Secondary Inorganic aerosols

NH_4^+
SO_4^{2-}
NO_3^-

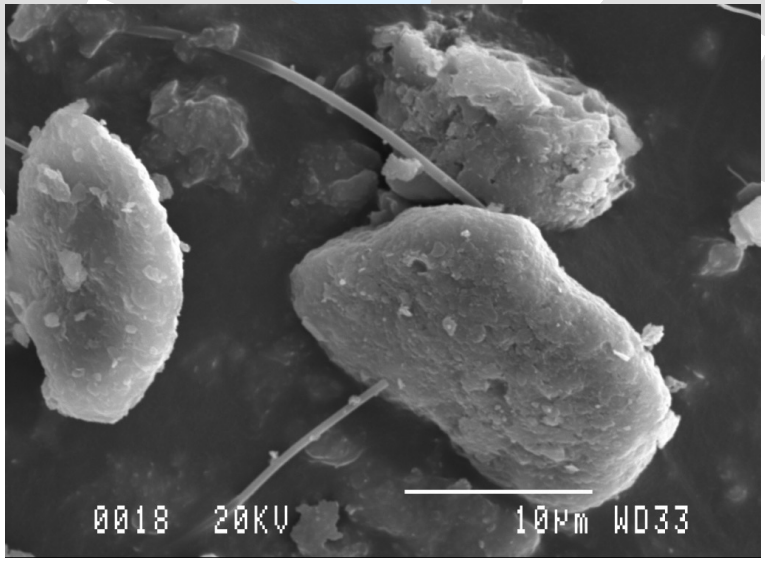
Sea spray

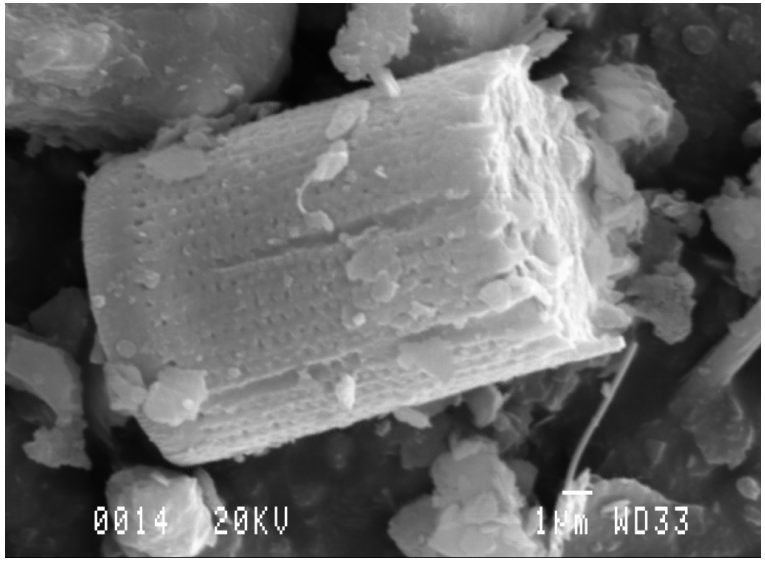
Na^+
Cl^-
SO_4^{2-}

Trace elements

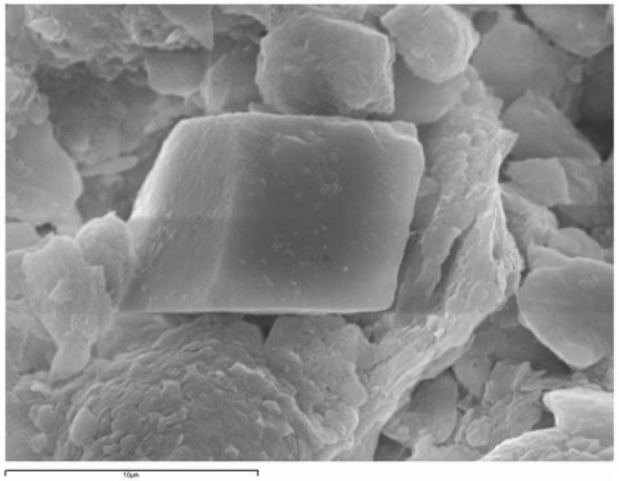
As, Ba, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Ga, Gd, Ge, Hf, La, Li, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Yb, Zn, Zr

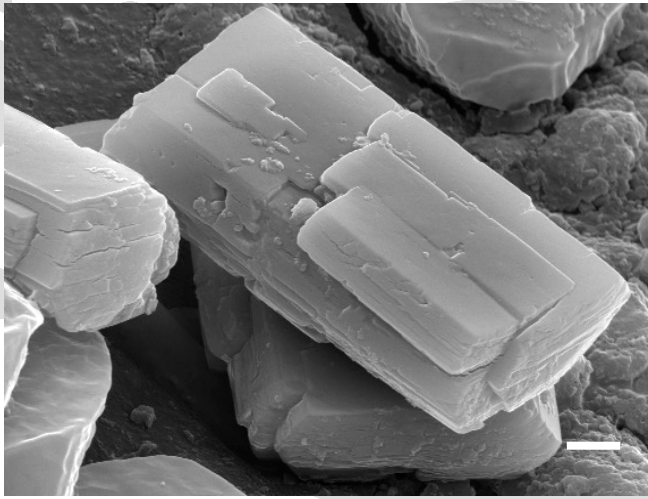
ATMOSPHERE & POLLUTION: introduction





Quartz
Clay minerals (kaolinite, Illite, Chlorite, ((Paligorskite, Smectite))
Feldespars
Other silicate minerals (talc, pirophillite,….)
Carbonate minerals (calcite, dolomite)
Phosphates, oxides, gypsum,….





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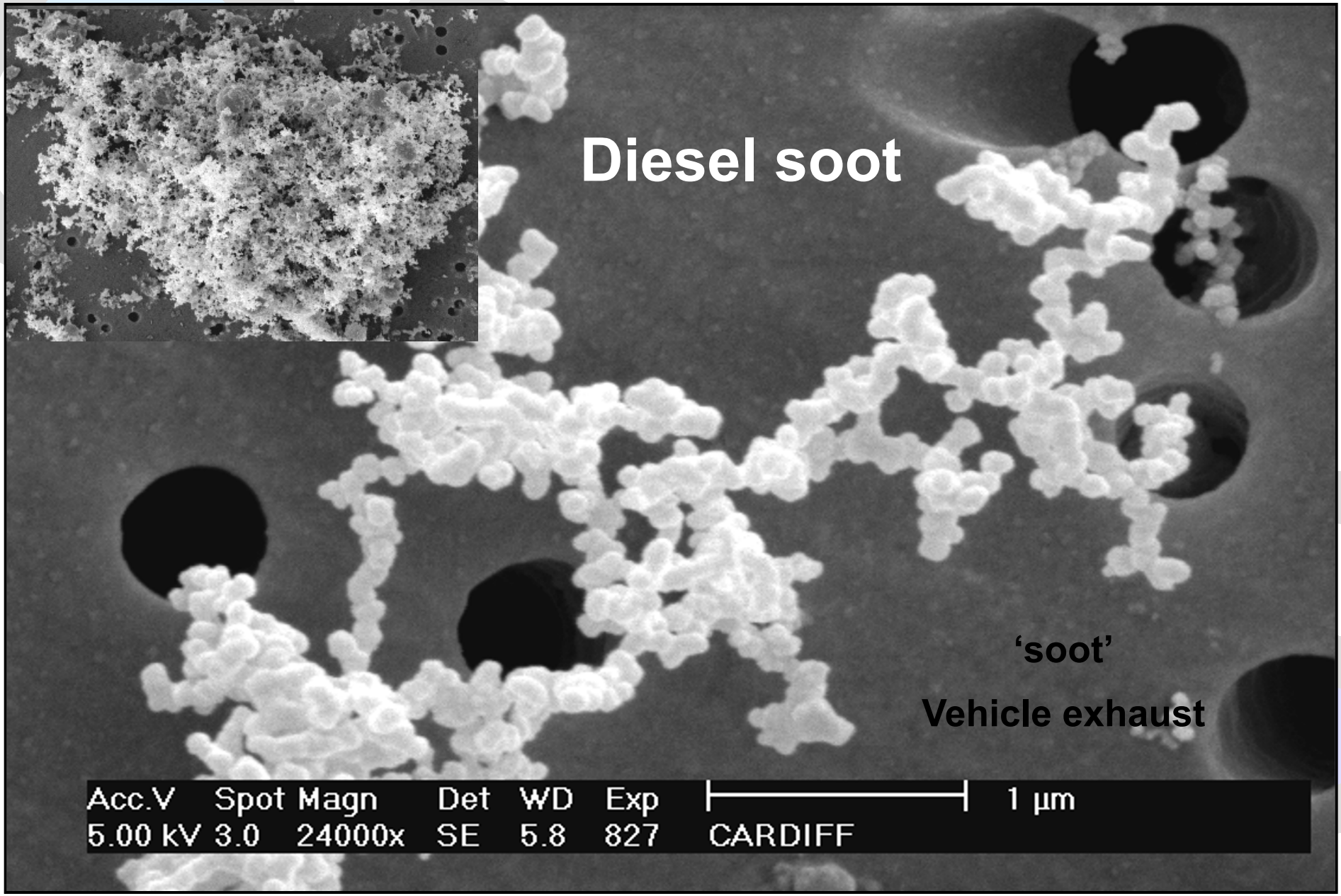
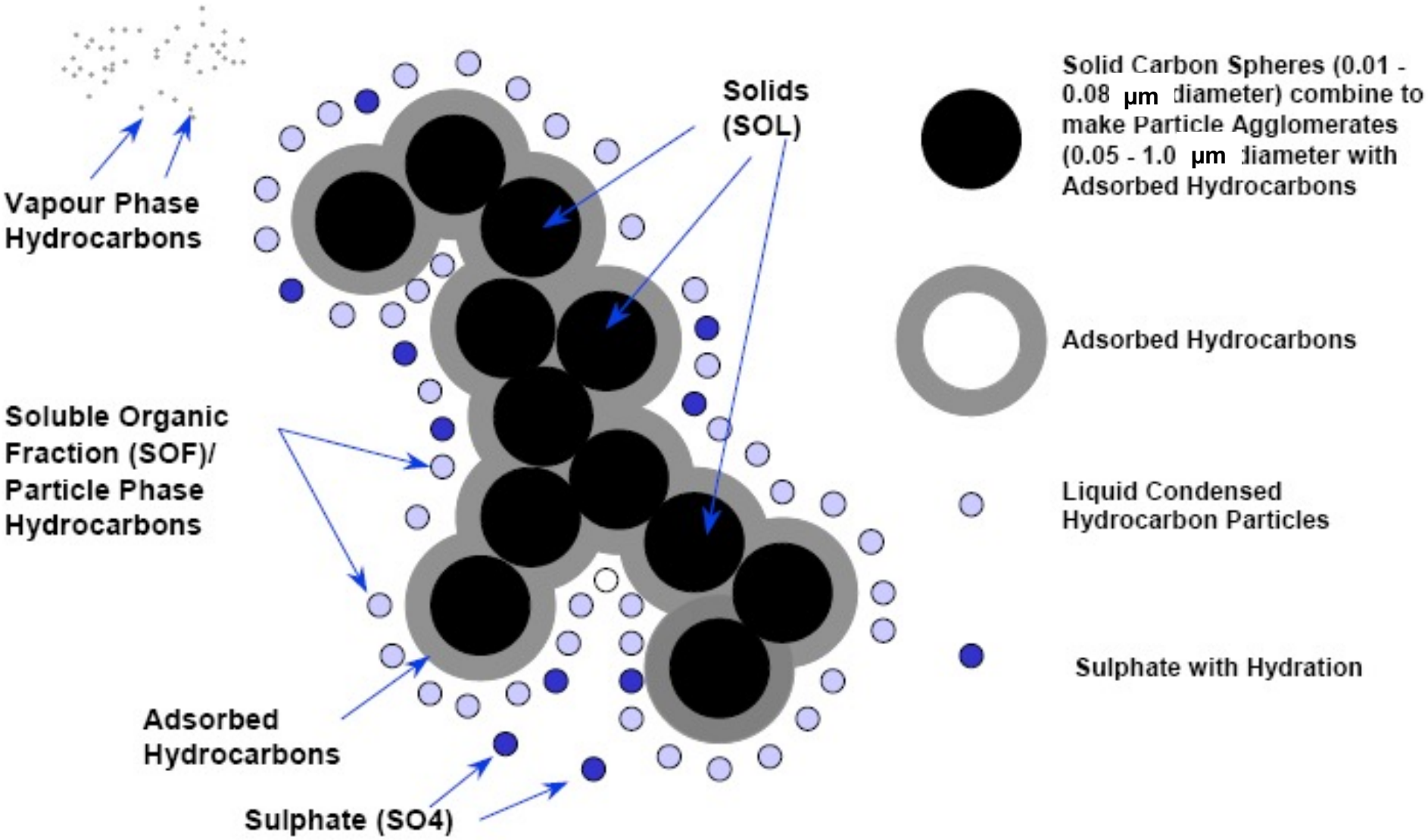
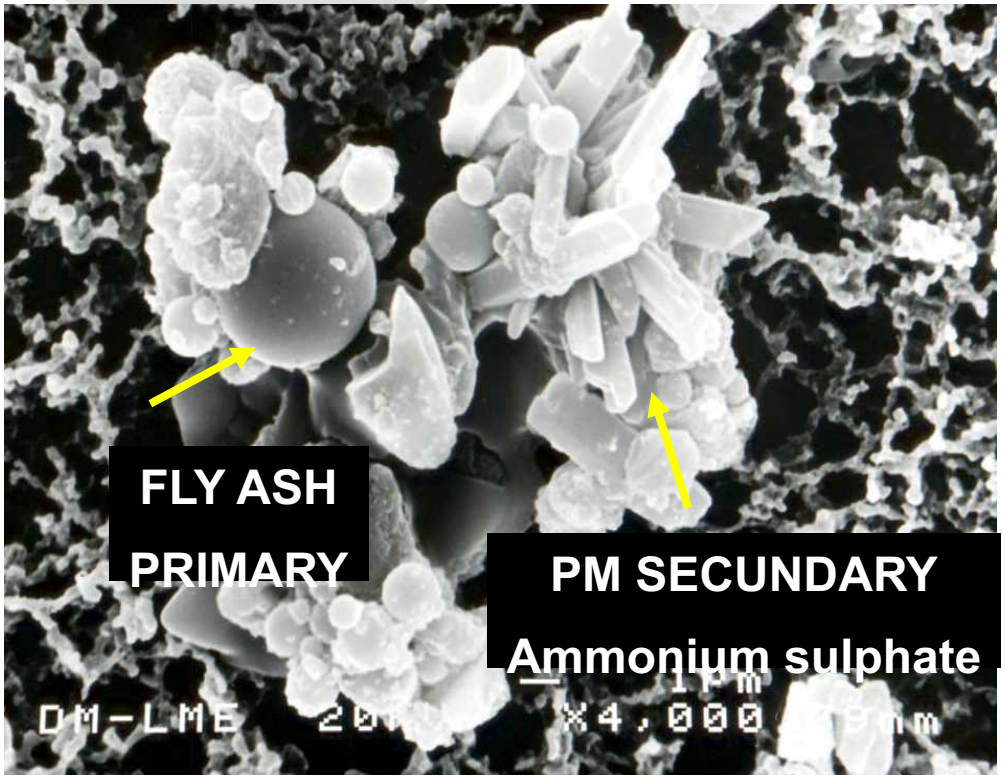


ATMOSPHERE & POLLUTION: introduction



Secondary PM from fossil fuel combustion



PM SECUNDARY

Ammonium sulphate

ATMOSPHERE & POLLUTION: introduction

Natural Background

- Marine aerosols
- Natural minerals
- Bioaerosols + biogenic

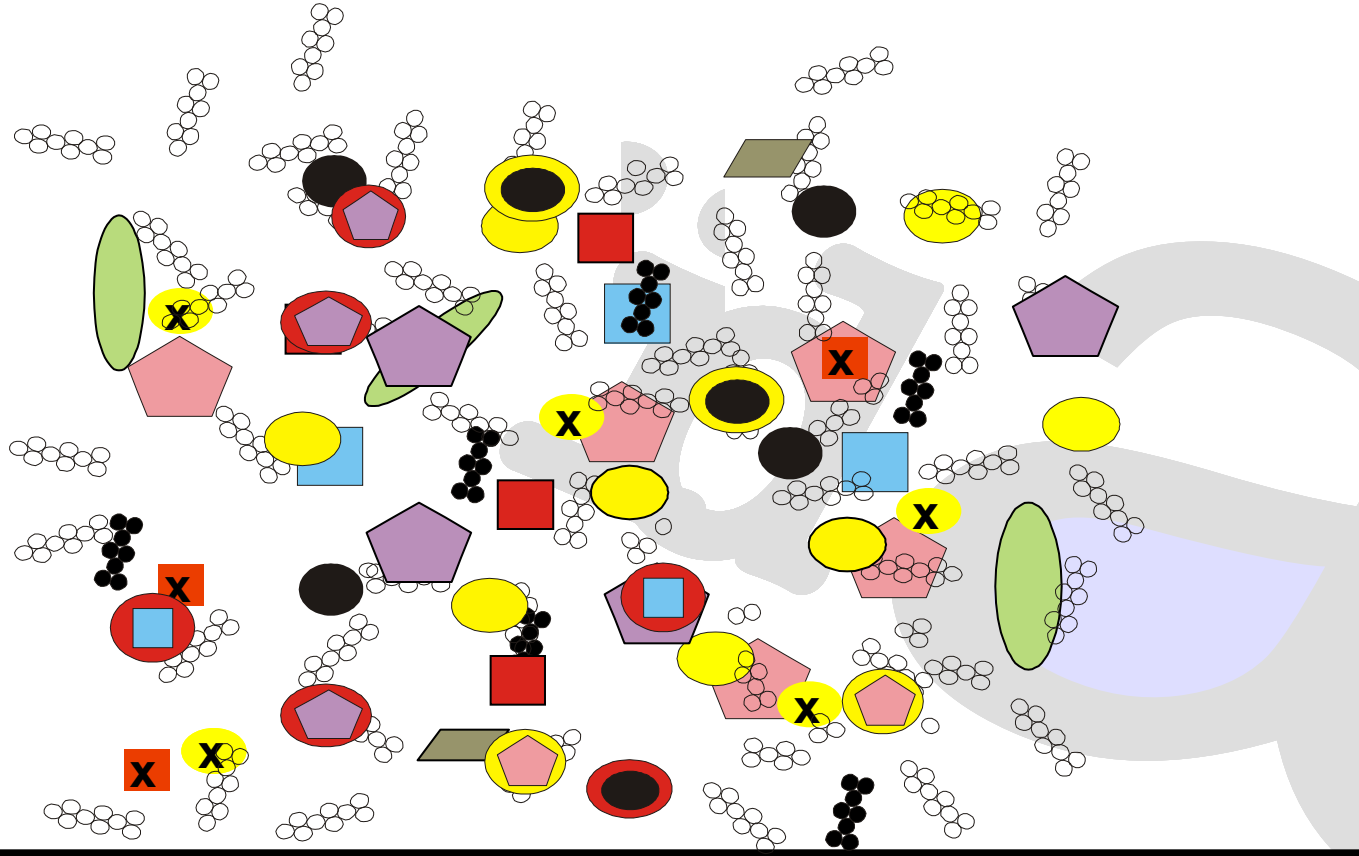
Local emissions

- NH_4NO_3
- Carbonaceous (fuel-oil ash)
- $(NH_4)_2SO_4$
- Pavement, demolition, constr.
- Carbonaceous (Soot, mainly road traffic)
- Heavy metals

Long Range Transp.

- x NH_4NO_3
- x $(NH_4)_2SO_4$
- Carbonaceous

Interaction among species



EMISSION SOURCES AND TRACERS

Stationary sources combustion

Power plants, heating, industry

Industrial processes, incineration

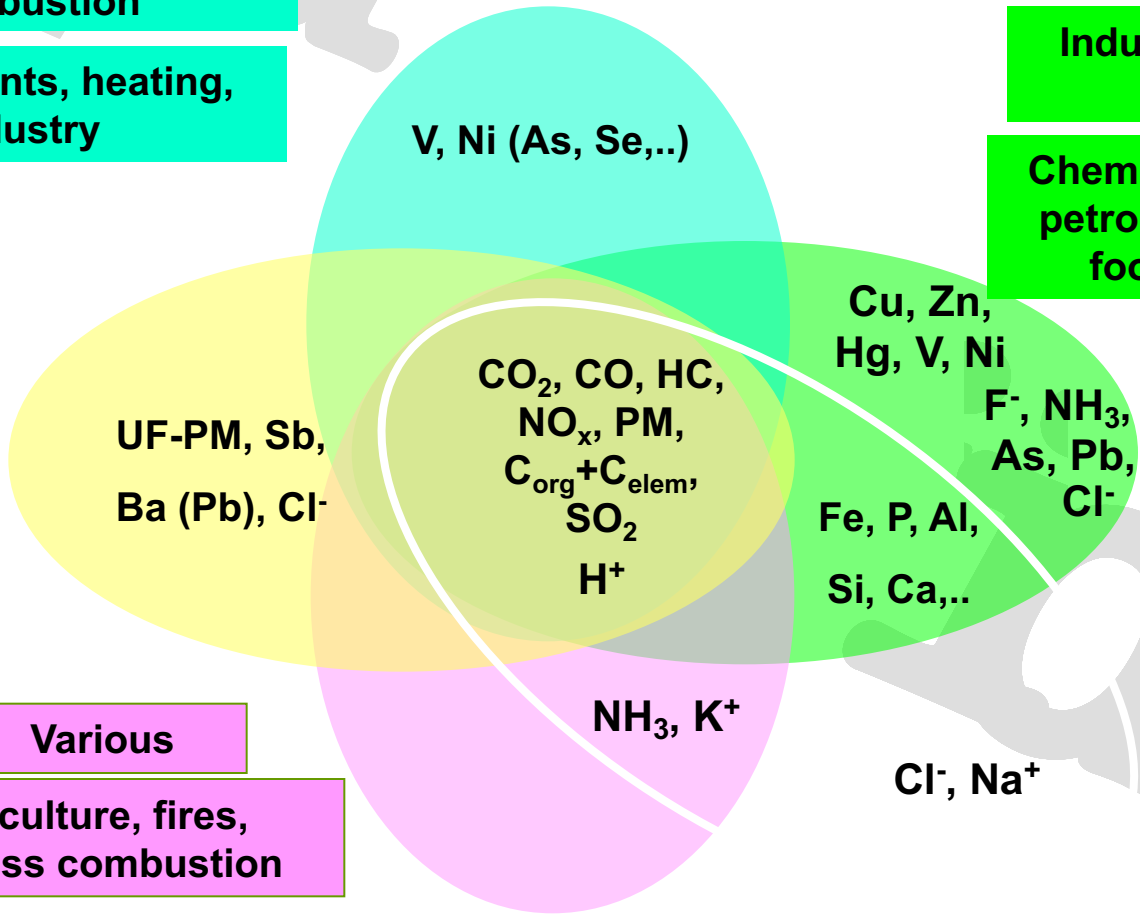
Chemical, metallurgical, petrochemical, mineral food, incineration

Transport

Road, air, rail, fuel storage,……..

Various

Agriculture, fires, biomass combustion



Other:
Harbor (shipping) emissions
Air transport
Construction-demolition
Domestic and residential

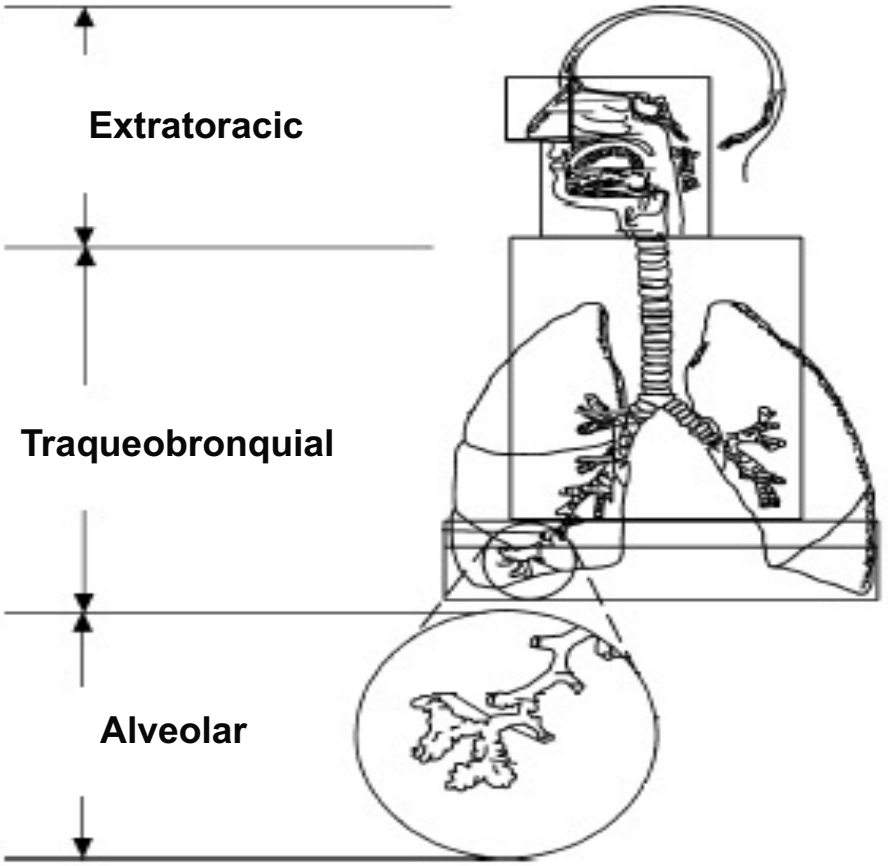
Natural emissions

Biogenic, re-suspension, marine, lightening, volcanoes, fires

Atmospheric particulate matter (PM)**: heterogeneous solid and/or liquid material (with the exception of pure water) present in suspension into the atmosphere**

- **Health impact**
- **Ecosystems**
- **Climate change**
- **Building materials**
- **Visibility**

HEALTH EFFECTS



Ultra-fine, <$PM_{0.1}$ may reach circulatory system

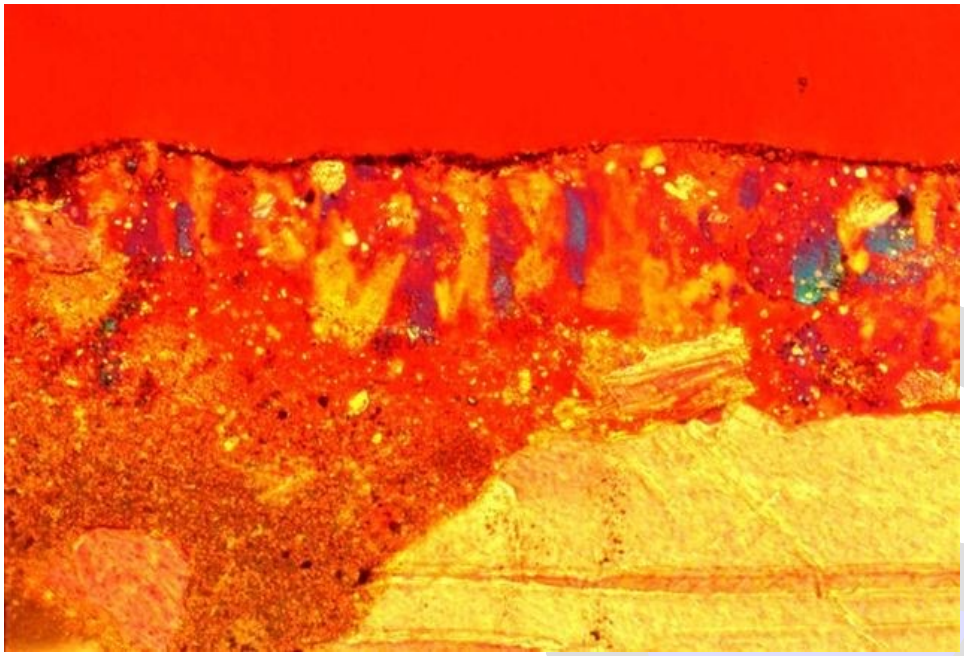
$PM_{10-2.5}$
Allergens,
inflammation, oxidative stress
Happo et al., 2008
Javala et al., 2008
Pérez et al., 2009

$PM_{2.5-0.1}$
Additional lung physical effect

$PM_{0.1}$
Cardiovascular, UFPM
Reach all important organs

EFFECTS ON VISIBILITY

WEATHERING OF BUILDING MATERIALS



NEGATIVE IMPACTS ON ECOSYSTEMS

Slamba Poremba, Poland (C. Martin, The Environmental Picture Library)

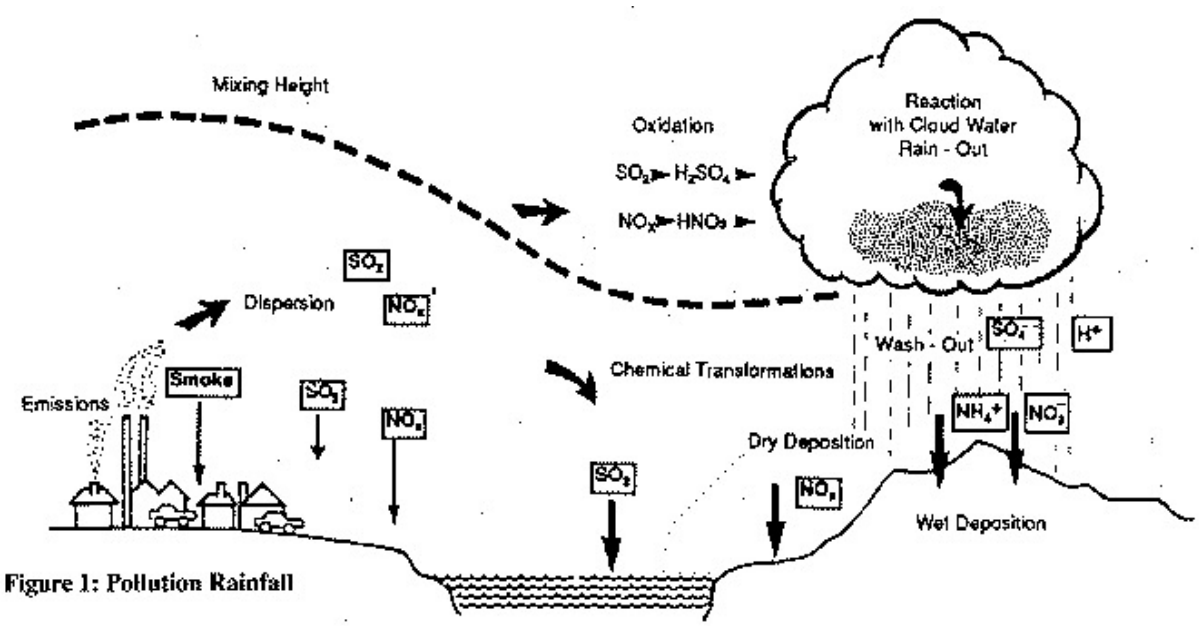
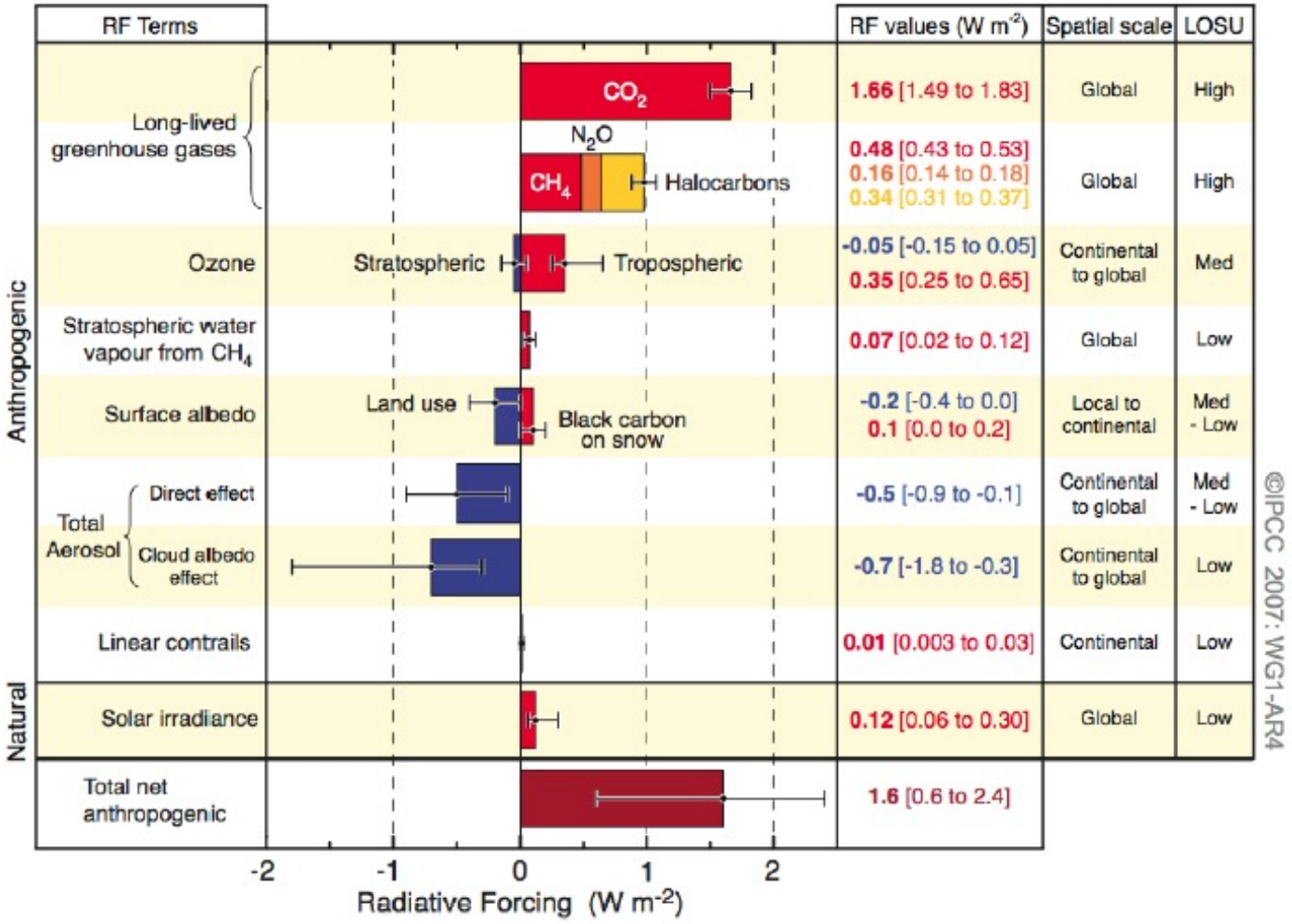


Figure 1: Pollution Rainfall

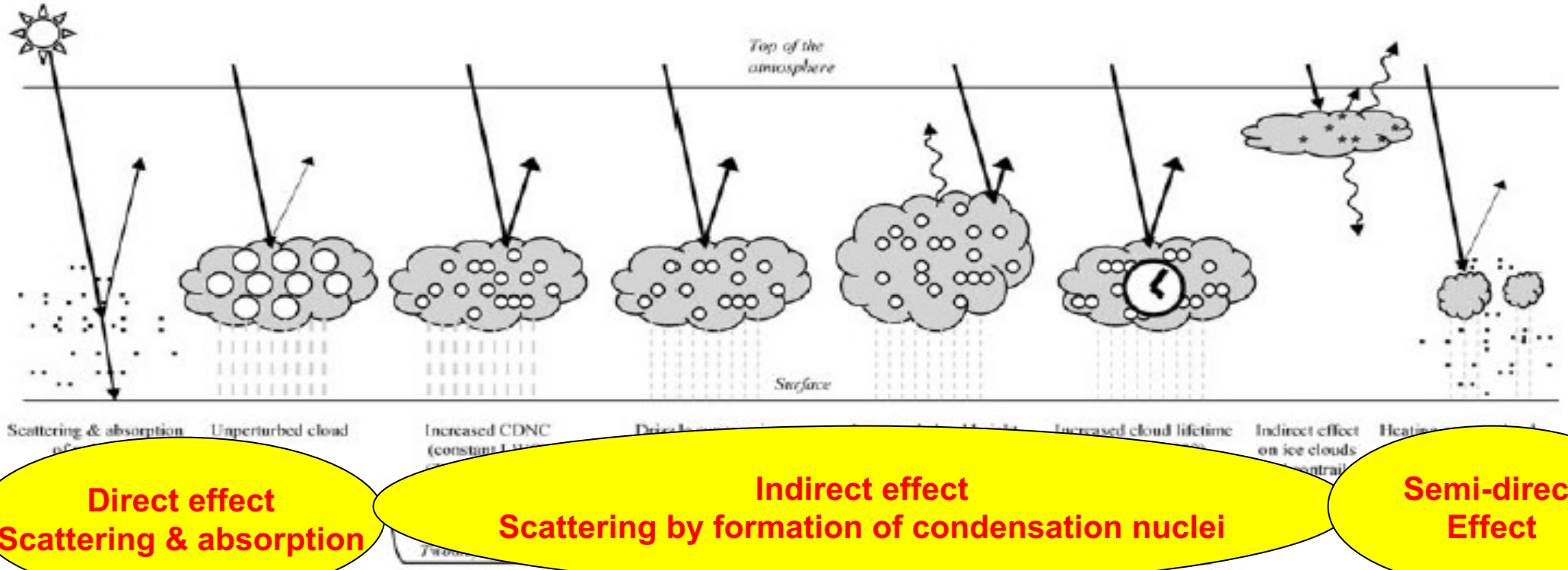
CLIMATIC EFFECTS

Radiative Forcing Components



CLIMATE EFFECT OF PM

Climate Modulation: influence in the radiative balance



Direct effect
Scattering & absorption

Indirect effect
Scattering by formation of condensation nuclei

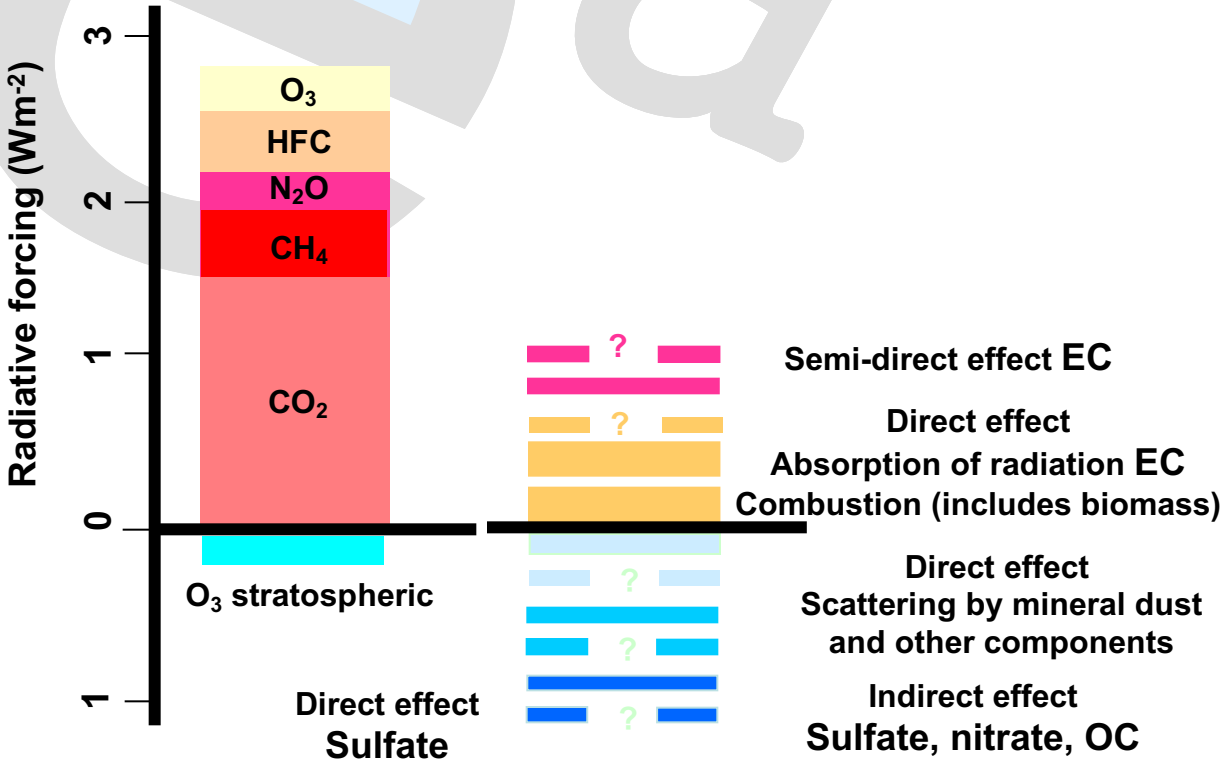
Semi-direct
Effect

Haywood and Boucher (2000)

CLIMATE EFFECT OF PM

- Warming: absorbing radiation (EC)
- Cooling: UV back scattering (sulfate, mineral, matter, OC, …)
- Warming or cooling: mineral aerosol, depending on surface (oceans or continents)
- These components are always mixed and it is very difficult evaluating the effect of the mixture

Climate effect of aerosols: Quantitative estimations



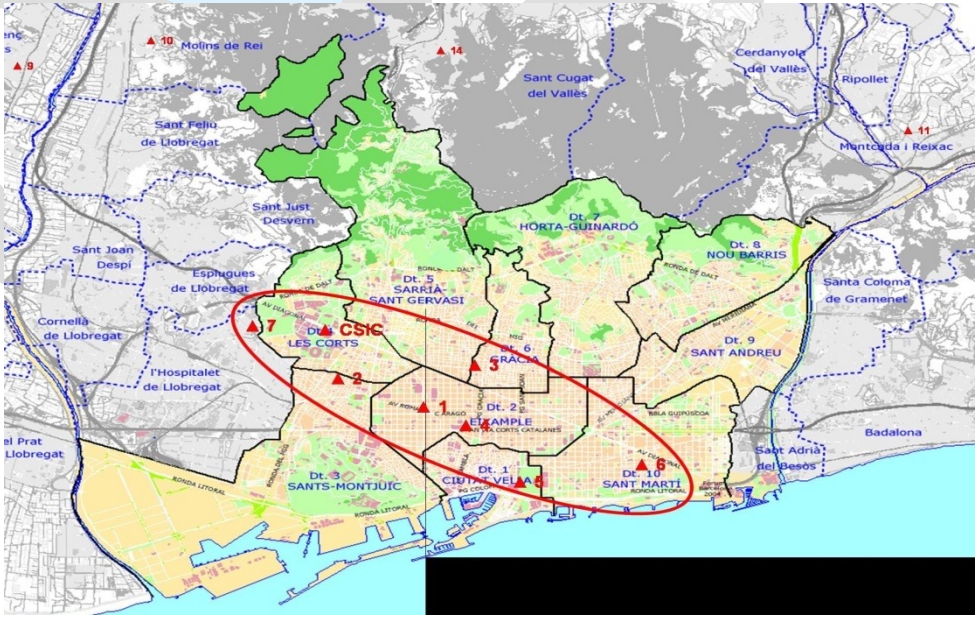
IPCC, 2007

High quantitative uncertainty
Need for research here!

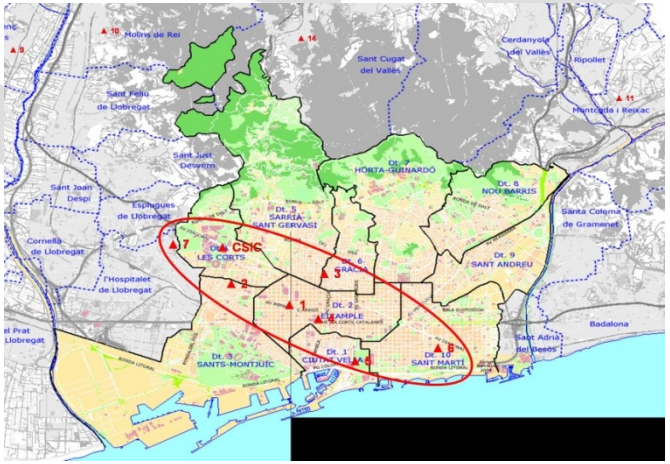
LOCATION OF MONITORING SITES

- What you would like to measure?
- Macro-implantation
- Micro-implantation

macro implantation: urban background

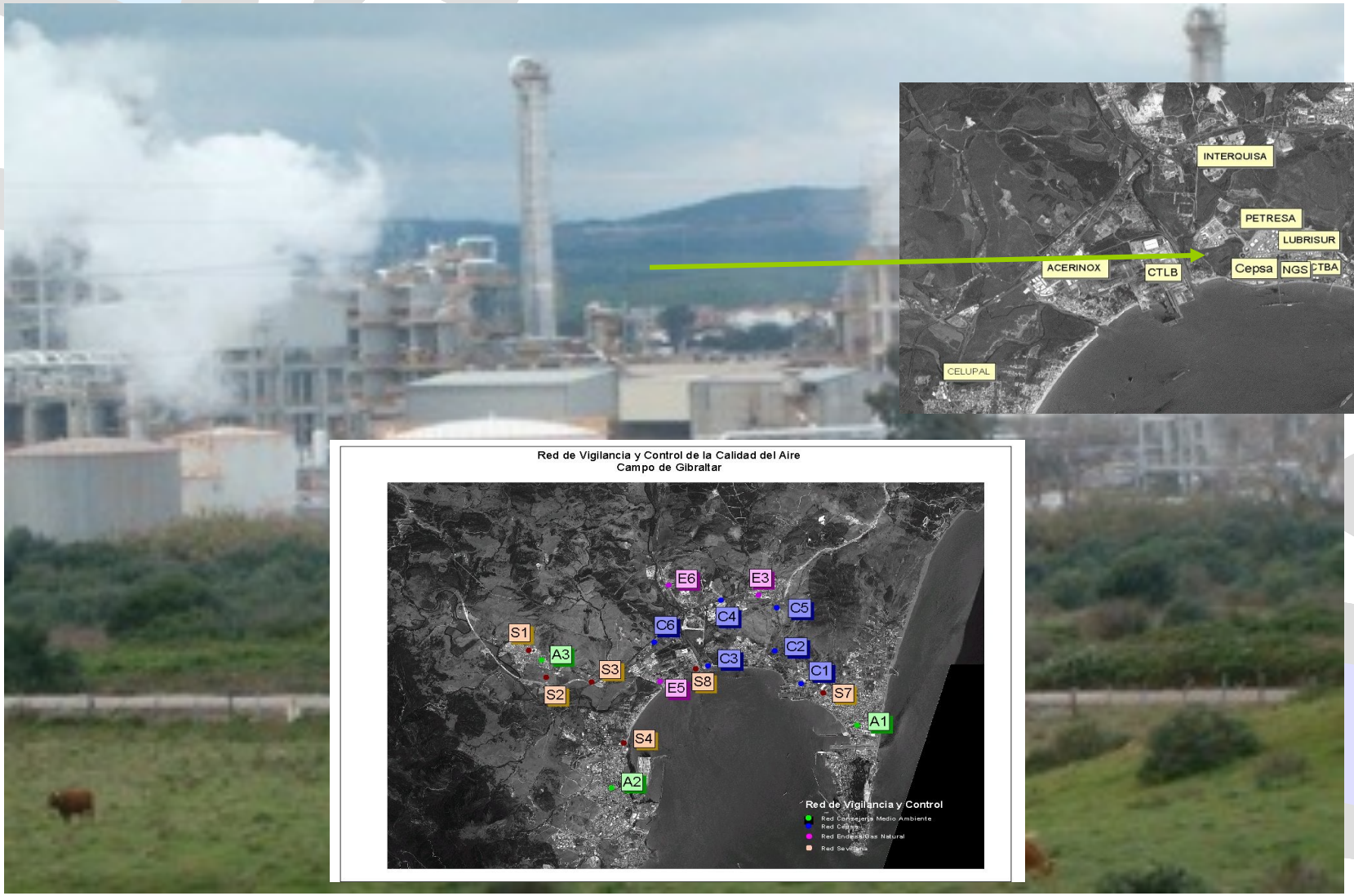


macro implantation: urban traffic



Barcelona: Universitat

macro implantation: industrial



macro implantation: regional background

Montseny-La Castanya

Operative since 2002

750 msnm

PM10/2.5/PM1 DIGITEL

GRIMM 180

Gaseous pollutants

Number concentration by size

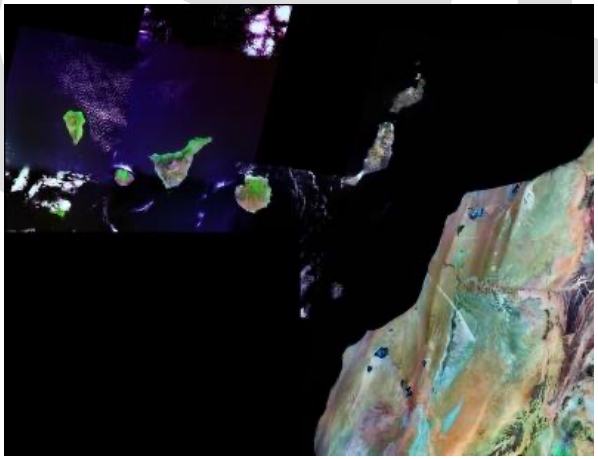
Black carbon

Scattering

PM10/PM2.5/PM1 speciation

Dry and wet deposition

macro implantation: continental background



IZO 2367 msnm

Sampling PM10/2.5 since 2002

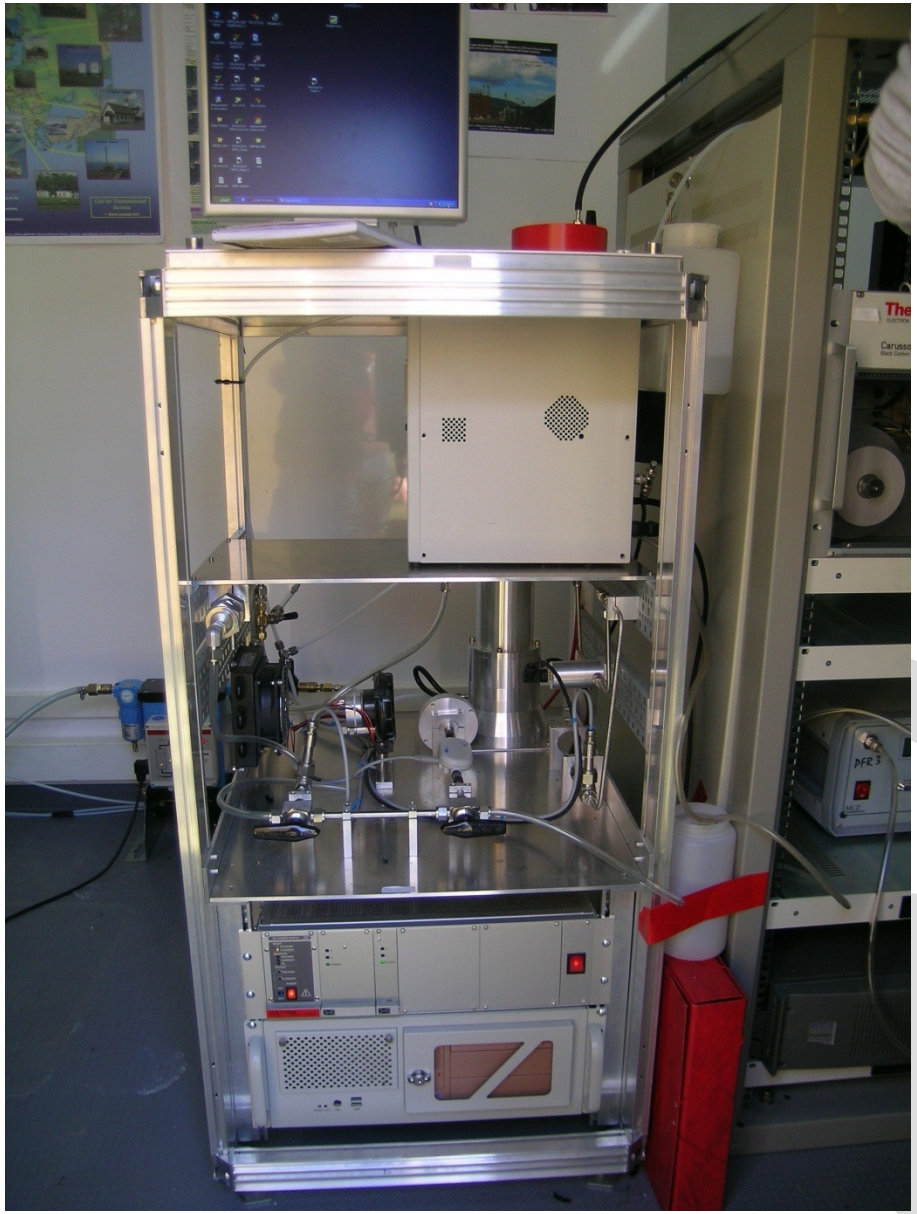
Location of monitoring sites
micro implantation

METHODS FOR MEASURING AEROSOLS

- NUMBER
- MASS
  - Gravimetric
  - Real time
- OTHER PARAMETRES
  - Semi-real time
    - PILS
    - Thermal
  - Real time: AMS

ATMOSPHERE & POLLUTION: monitoring

- Condensation particle counter (CPC)
- Number (5-1000 nm)
- Every 1 second



- SMPS (CPC+DMA)
- Number and size distribution (10-700 nm)
- Every 5 minutes

GRAVIMETRY

Captors with grain size cut off inlets

- Mass levels
- Standard in EU
- Speciation possible

- Sampling artifacts

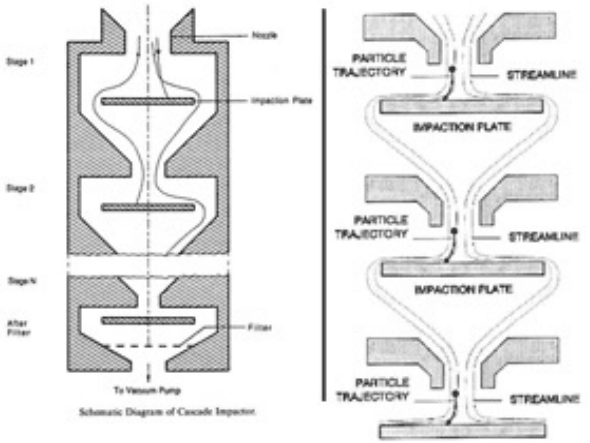
Cascade impactors

- Grain size segregation for sampling
- Variable grain size
- Substrate

- Impactor Retsch
- Impactor MOUDI
- Impactor DEKATI

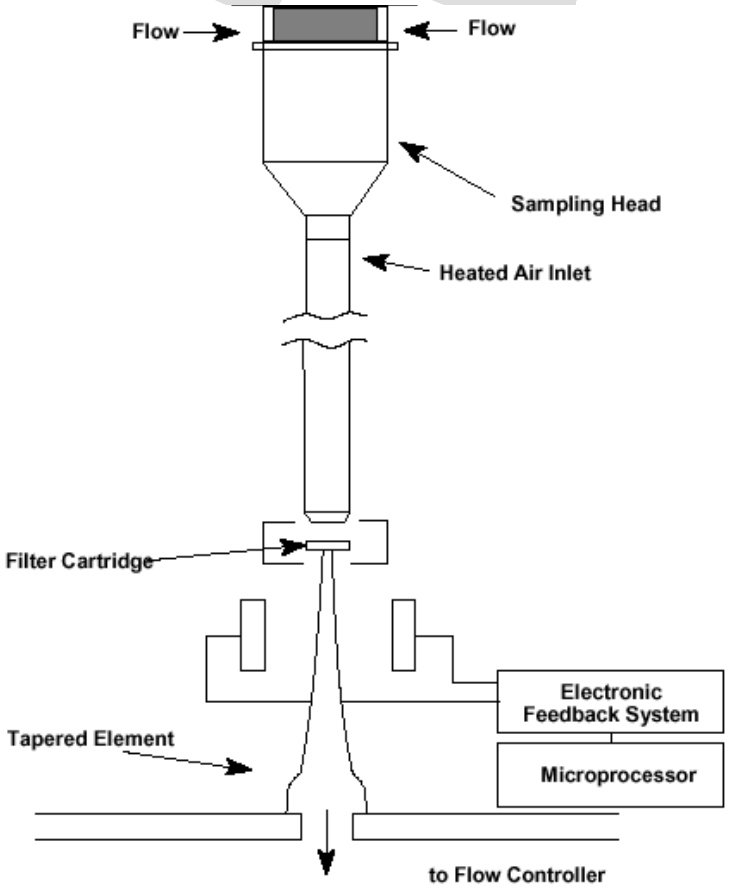
Cascade impactor

- Micro-orifice, Uniform-deposit Impactor (MOUDI)
- 30 L/min
- 0.056 – 18 μm
- Substrate requested



REAL TIME: MASS

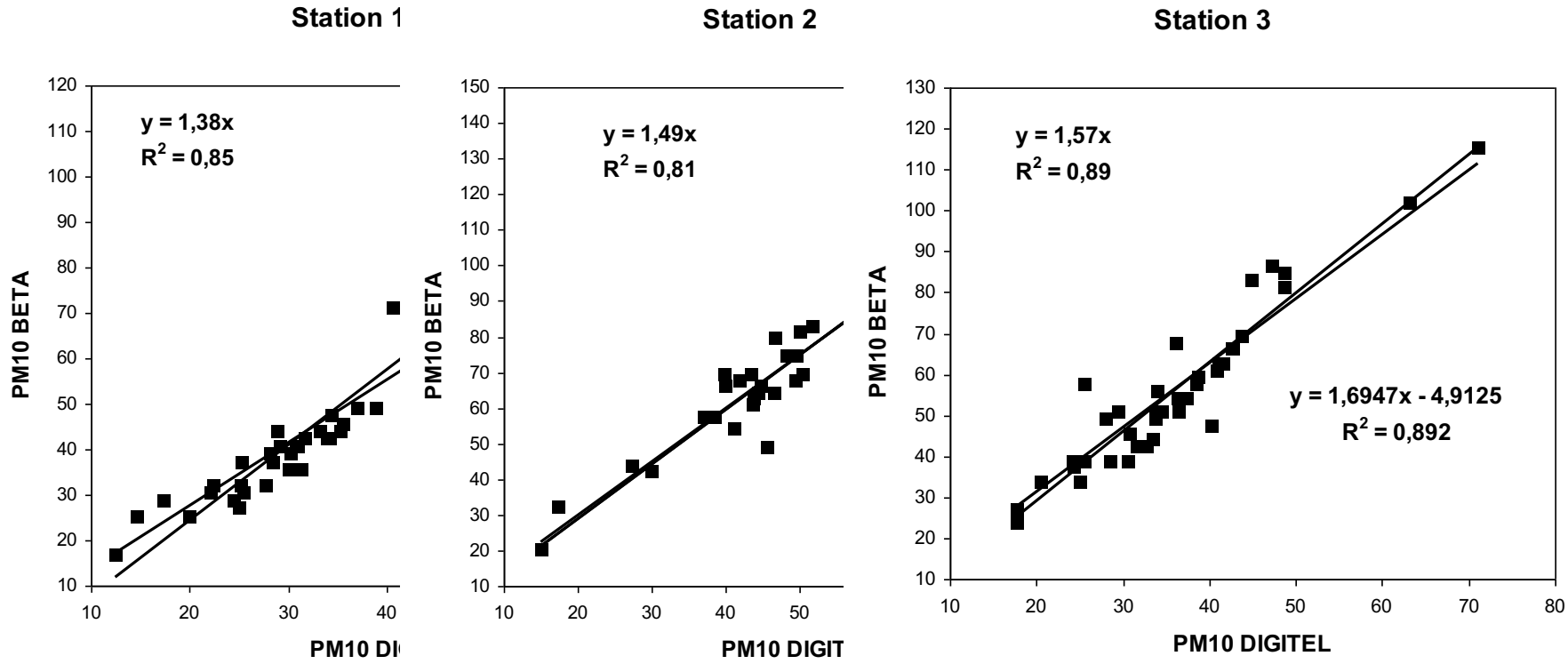
- **TEOM** (thermo oscillating micro-balance)



- **Beta attenuation**

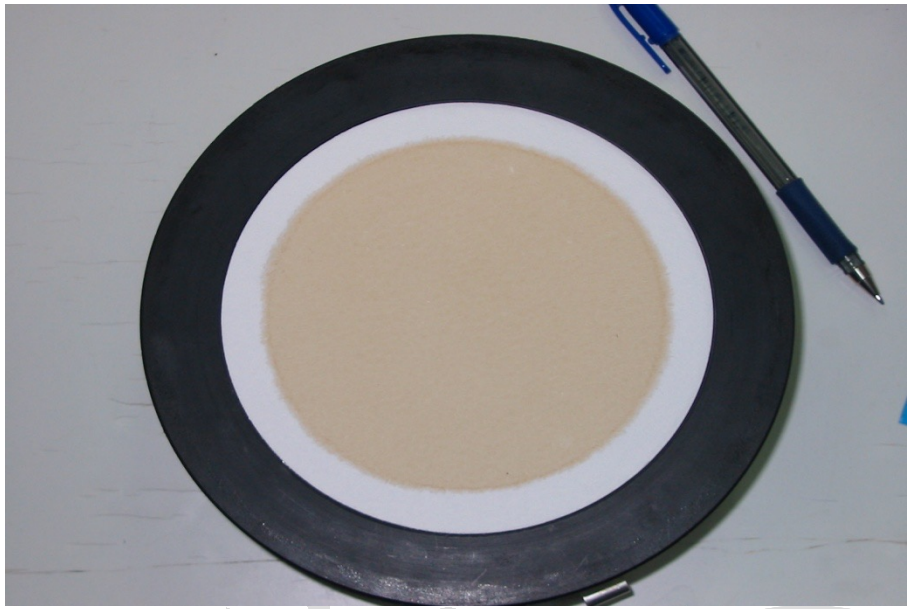
Example of 3 new instruments

- Purchased simultaneously
- Measuring in stations distant <30 km
- Maintained by the same company



Each instrument has to be corrected according individual inter-comparison exercises carried out *'in situ' !!!!!*

ATMOSPHERE & POLLUTION: monitoring



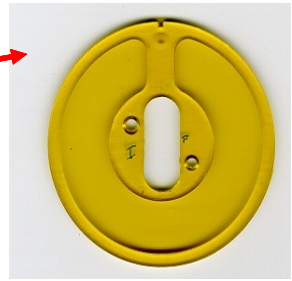
Deposition samplers

- Dry and wet
- Only wet deposition

Continuous streaker

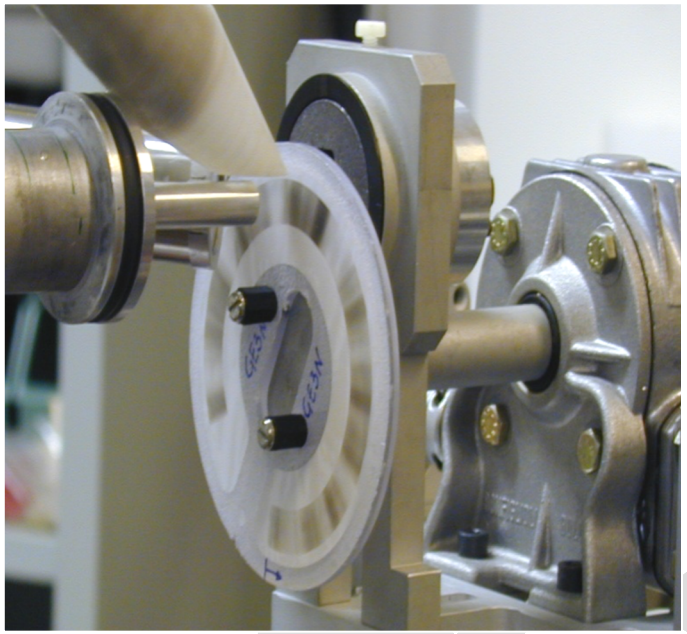
"hourly samples"

PM2.5□10



PM2.5

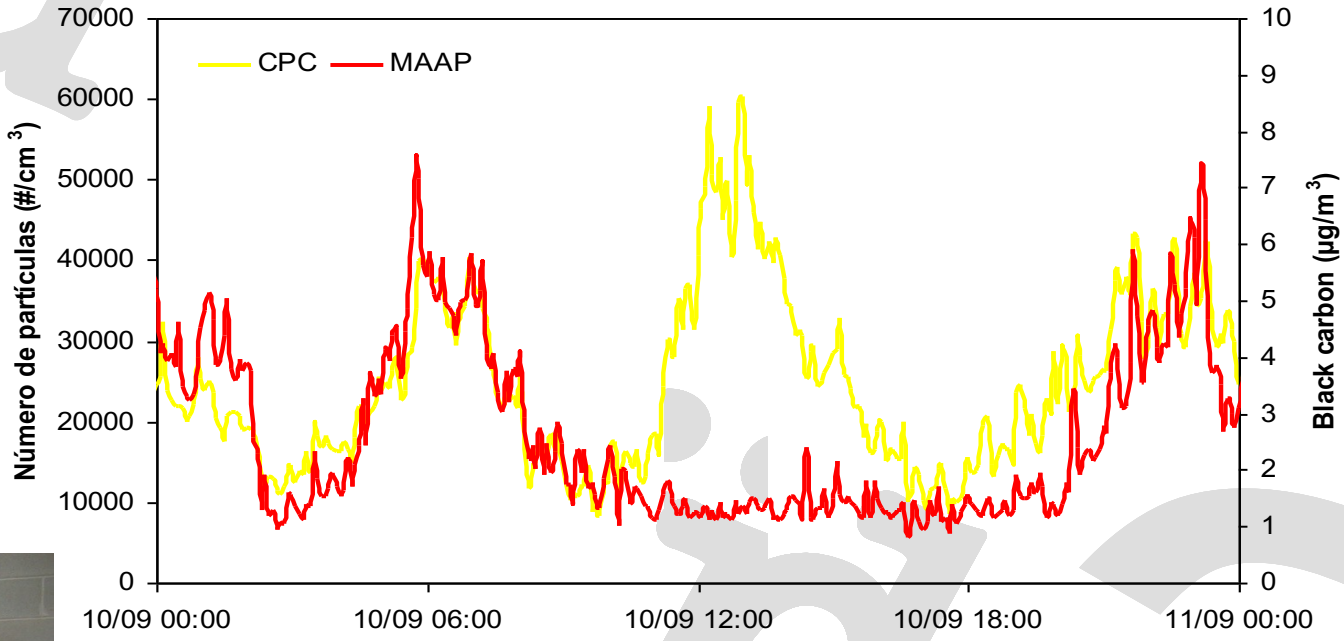
100 mm



- Kapton foils
- Nuclepore

Ø *i* ~ 20-50 nA
Ø Beam size: 1mm x 2 mm
Ø Measuring time: ~ 3 min.
1 week with 1 h
resolution (168 spots) - h

Black carbon: MAAP: Multi Angle Absorption Photometer. Thermo Electron Corporation. Carusso/Model 5012 MAAP



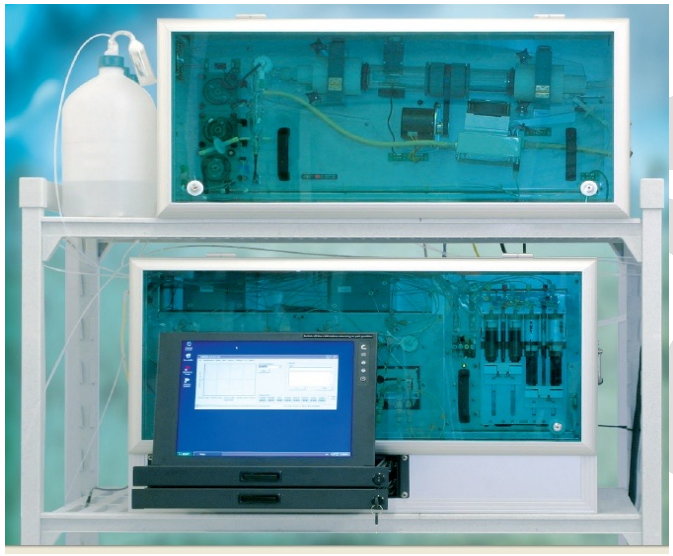
2. Real time speciation

Soluble inorganics: Aerosol ions & precursors

URG 9000 IC

Taken from URG web site

MARGA



Taken from Applikon web site

PILS-IC

Taken from Metrohm web site

2. Real time speciation

Thermal decomposition: Nitrate, sulphate, ammonium, OC, EC

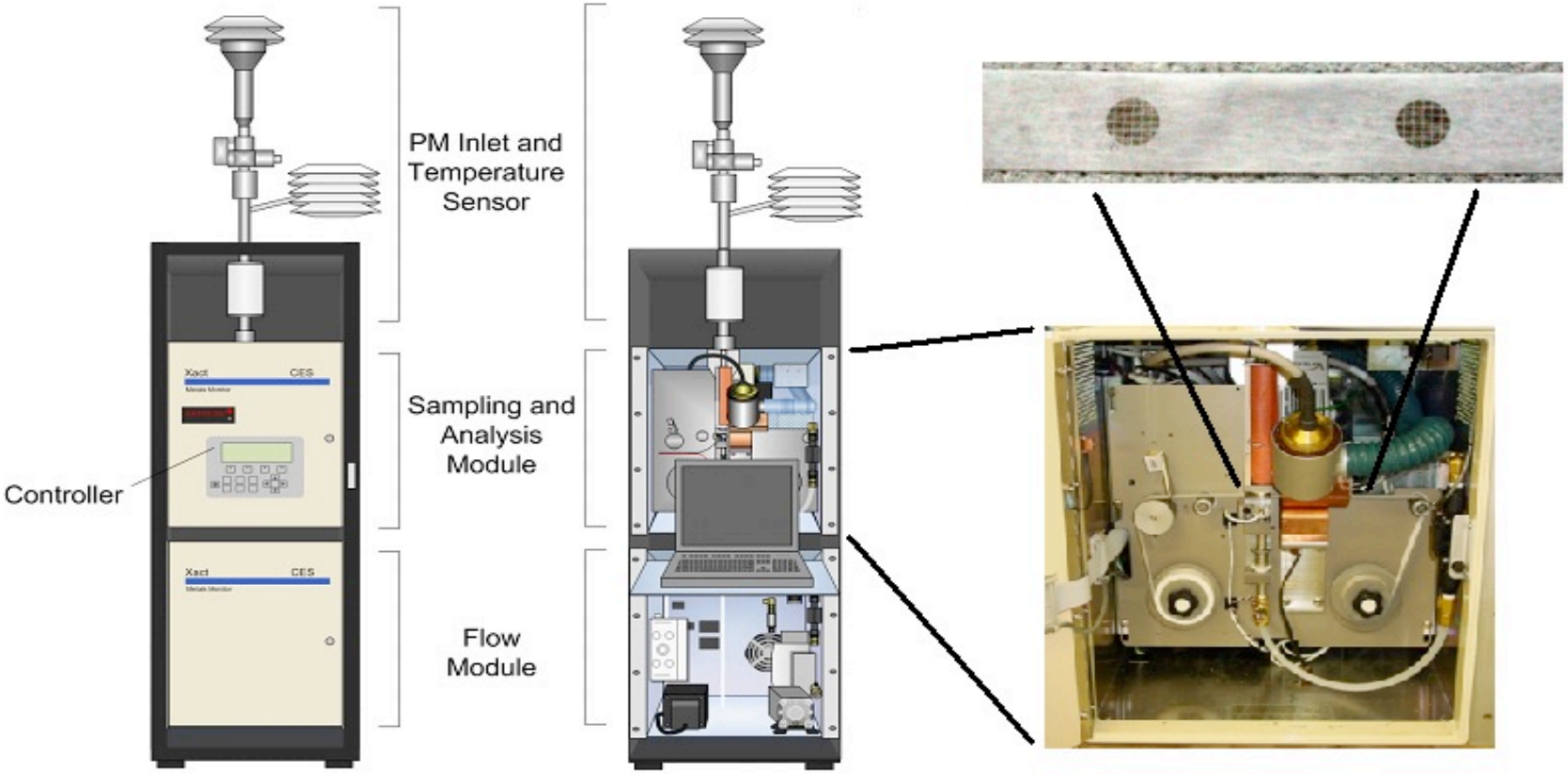
Nitrate, R&P 8400 N
by NO_x analysis (chemiluminiscence)

Sulfate,
Thermo 5020-SPA

- OC and EC,
- R&P 5400 C, Sunset on-line analyzer

2. Real time speciation

On-line XRF analyser: Mostly metals



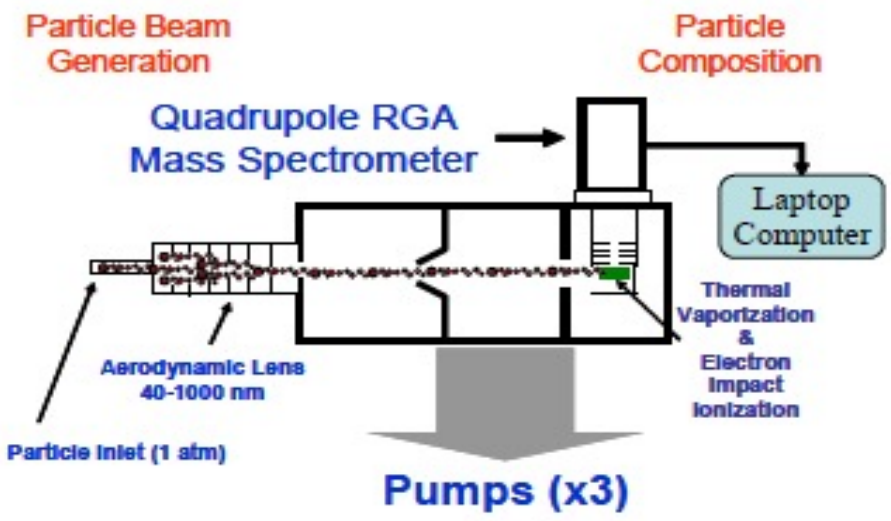
Manufacturer: Cooper Environmental Systems, Australia ;Figure taken from Yadav et al., AAAR 2010

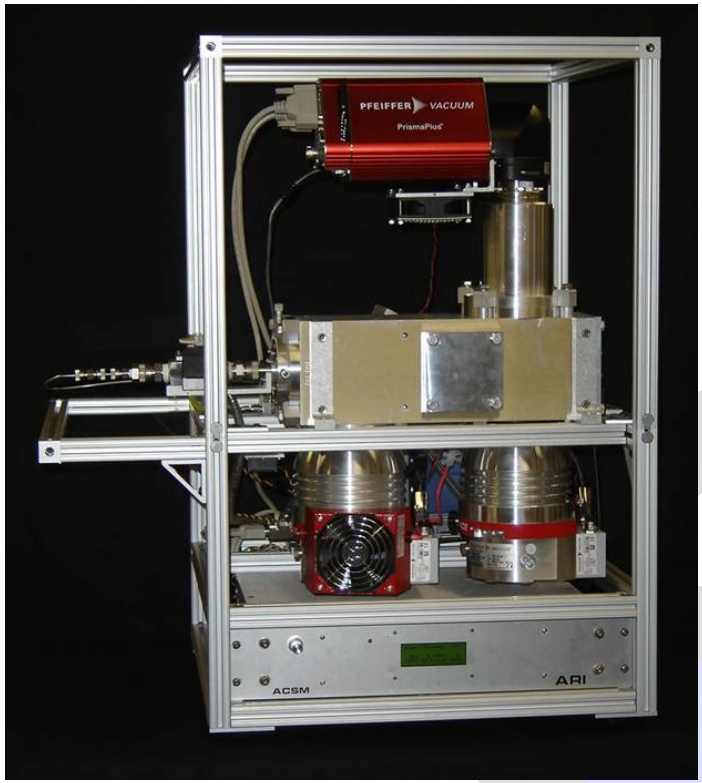
Real time speciation

Mini-AMS: Non refractory fraction of PM1

ACSM
Aerosol Chemical Speciation Monitor

Measure real-time, non-refractory aerosol particle mass and chemical composition.





Taken from Aerodyne Research website

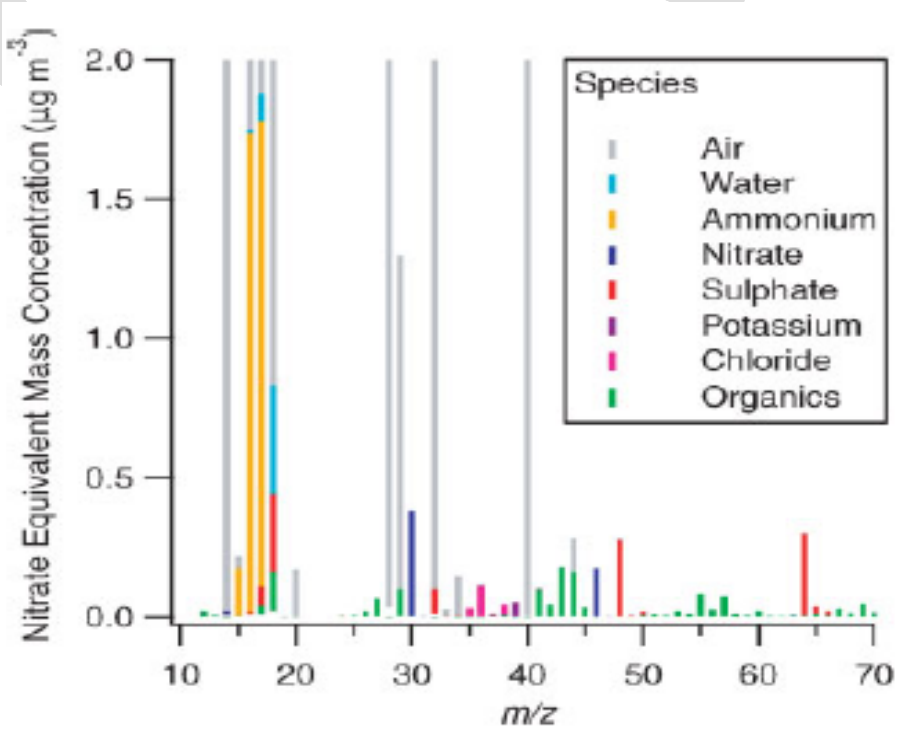
Aerodyne Aerosol Mass Spectrometer (AMS)

TABLE 1. Main ion fragments used to identify inorganic and organic aerosol species in AMS spectra. The fragments that are most useful in identifying these species are highlighted in bold text.

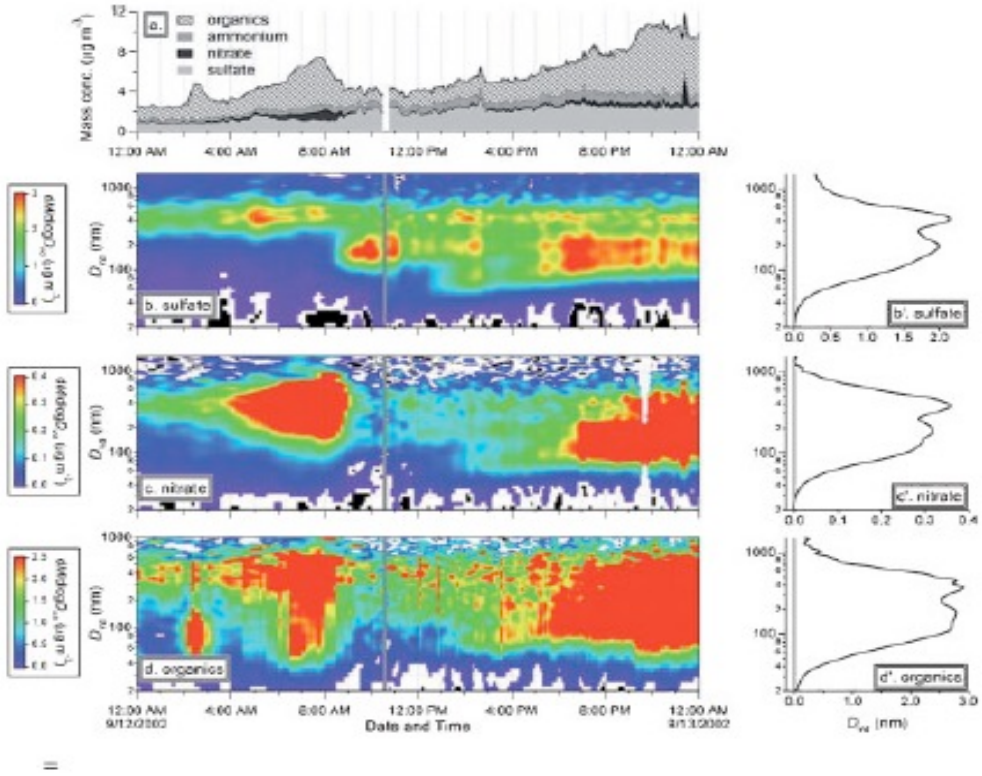
Group	Molecule/Species		Ion Fragments	Mass Fragments
Water	H_2O	$\xrightarrow{e^-}$	$\mathbf{H_2O^+}$, HO^+ , O^+	**18**, 17, 16
Ammonium	NH_3	$\xrightarrow{e^-}$	NH_3^+, $\mathbf{NH_2^+}$, NH^+	17, **16**, 15
Nitrate	NO_3	$\xrightarrow{e^-}$	HNO_3^+, $\mathbf{NO_2^+}$, $\mathbf{NO^+}$	63, **46**, **30**
Sulfate	H_2SO_4	$\xrightarrow{e^-}$	$H_2SO_4^+$, HSO_3^+, SO_3^+ $\mathbf{SO_2^+}$, $\mathbf{SO^+}$	98, 81, 80 **64**, **48**
Organic *(Oxygenated)*	$C_nH_mO_y$	$\xrightarrow{e^-}$	H_2O^+, CO^+, $\mathbf{CO_2^+}$ $\mathbf{H_3C_2O^+}$, HCO_2^+, $C_{n'}H_{m'}^+$	18, 28, **44** **43**, 45, …
Organic *(hydrocarbon)*	C_nH_m	$\xrightarrow{e^-}$	$C_{n'}H_{m'}^+$	27,29,**41**, **43**,**55**,**57**,69,71…

CANAGARATNA et al (2007). Mass Spectrometry Reviews, 2007, 26, 185– 222

Aerodyne Aerosol Mass Spectrometer (AMS)



Allan et al., 2004. J Aerosol Sci 35:909–922.



Zhang Q. et al., 2004. J Geophys Res 110: doi:10.1029/2004JD004649.

Filters: Selection according parameters…

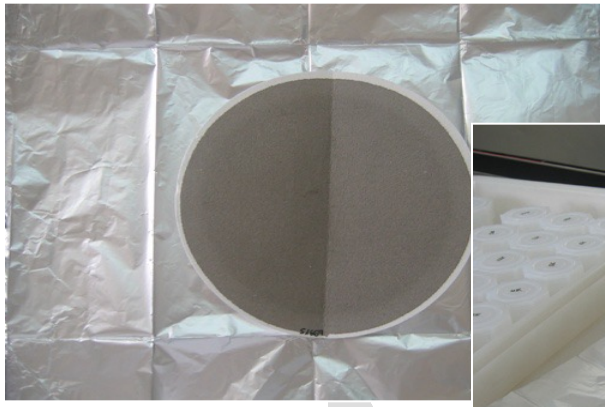
	Captor	Gravimetry	Trace elements	C analysis	NO_3^-, NH_4^+ Analysis
Glass fiber	High Vol	YES	NO	yes	YES
Quartz	High Vol	yes	Yes	Yes	YES
Cellulose nitrate	Low Vol	NO	YES	NO	NO
Teflon	Low Vol	yes	yes	NO	YES
Nylon	Low Vol	artifacts	artifacts	NO	HNO_3 (gas)

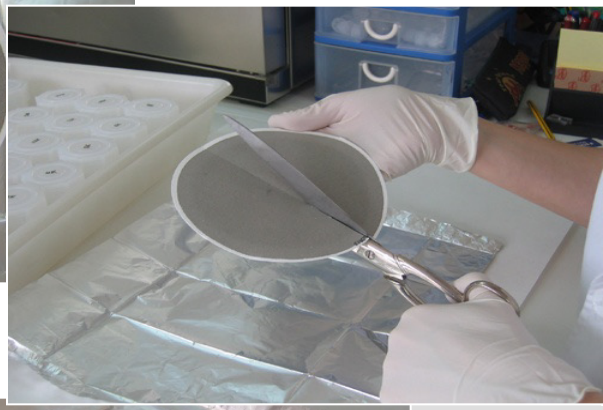
Filter treatment and analysis

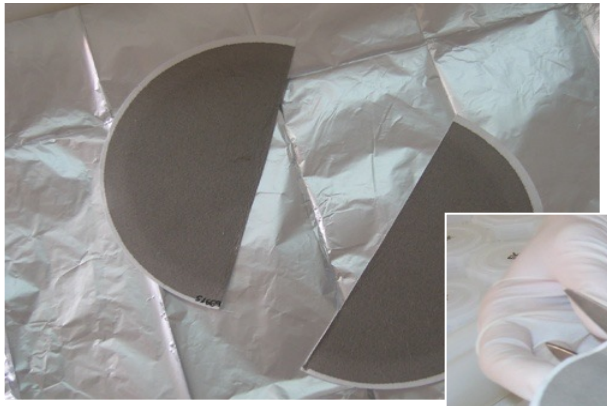
- Blank filter conditioning
- Blank filter weight
- Sampling
- Sample filter conditioning
- Acidic digestion
- Analysis of major and trace elements
- Aqueous extraction
- Analysis of soluble ions
- Analysis of C

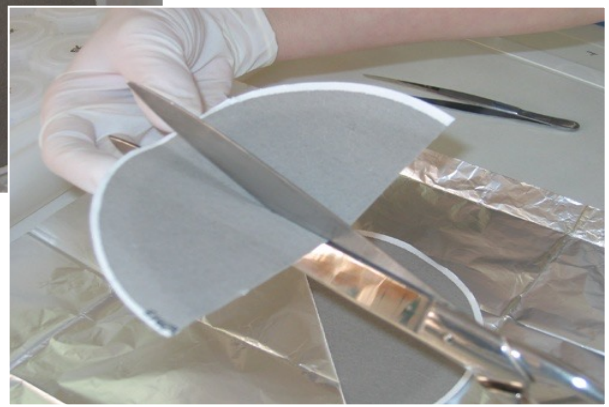
Filter treatment and analysis
Filter fractions for analysis

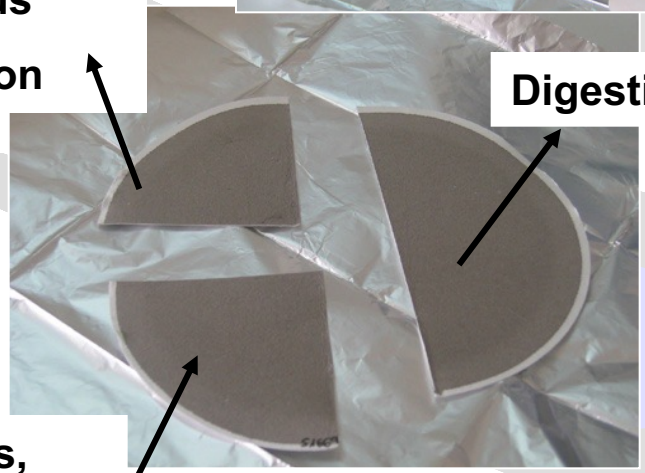
- ½ filter: acid digestion
- ¼ filter: aqueous extraction
- ¼ filter: C analysis, SEM, XRD etc











Analysis of aerosol components

Major and trace elements

In acidic digestions (5% HNO_3)

- ICP-AES: Major and some trace elements

- ICP-MS: Most trace elements

Analysis of aerosol components

Soluble ions

- Aqueous extractions
- Ion Chromatography (IC)
  NO_3^-, SO_4^{2-}, Cl^-
- FIA Colorimetry / Specific electrode NH_4^+
- ICP-AES, soluble cations

Analysis of aerosol components

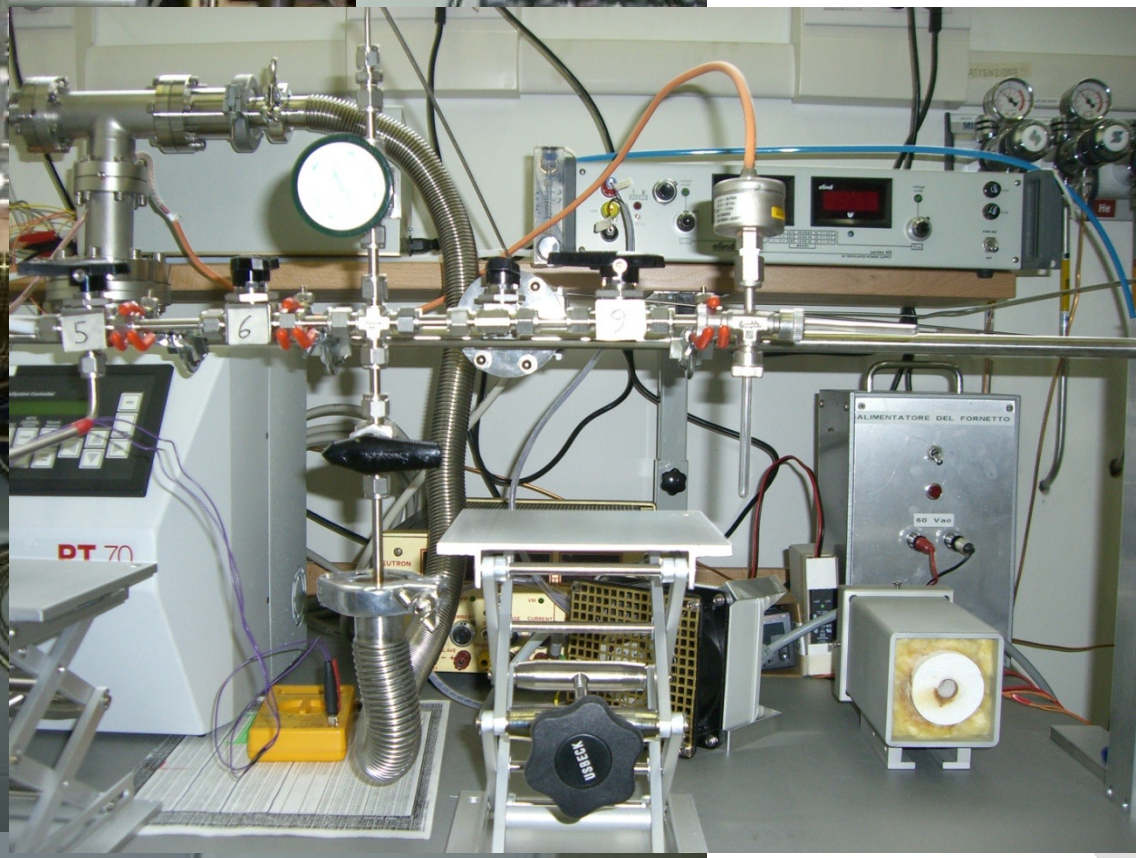
OC, EC or TC

1 inch of filter

LECO elemental analysis: C total

Thermo-optical methods for OC and EC

Isotope analysis: ^{14}C

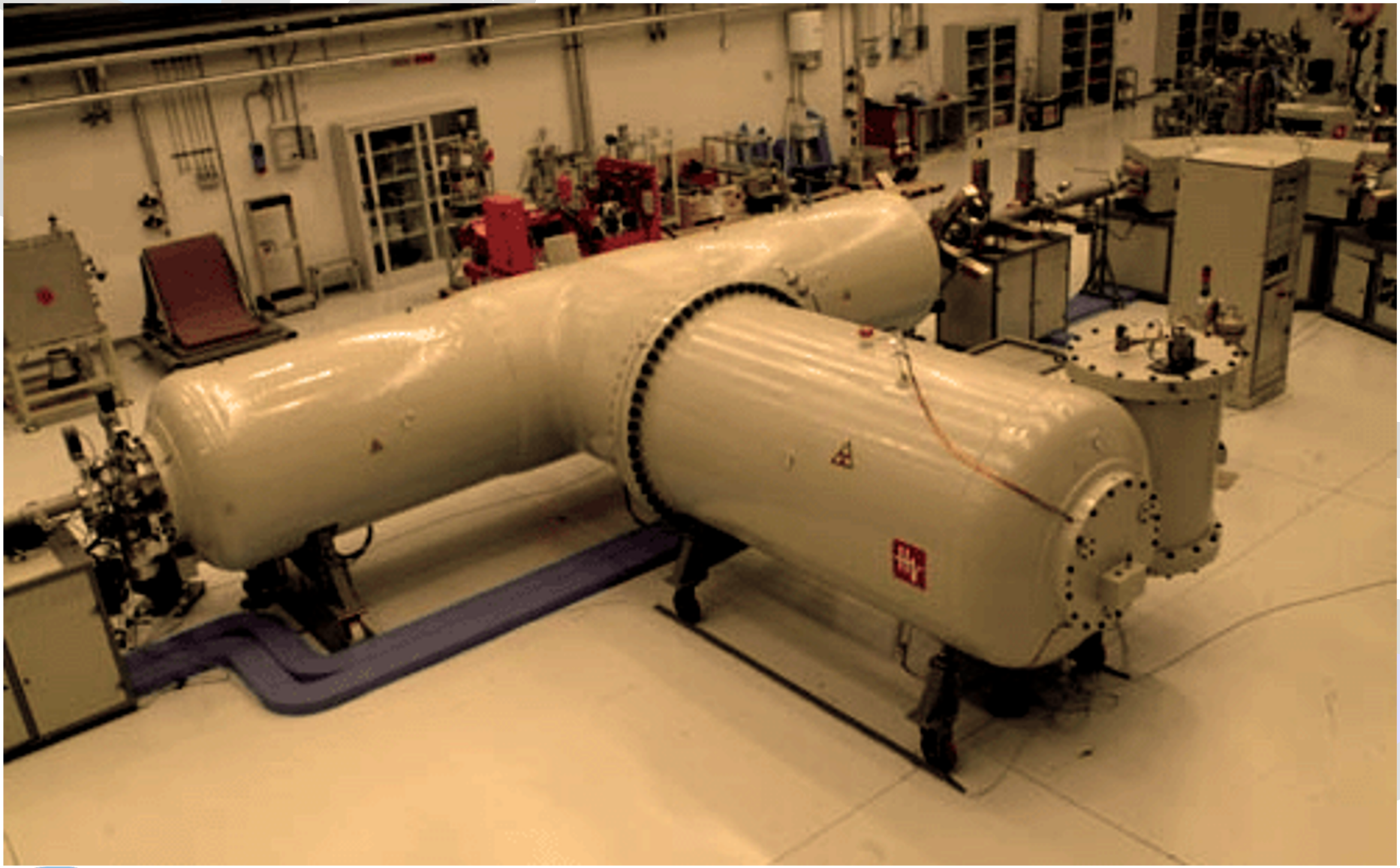


X-Ray Fluorescence

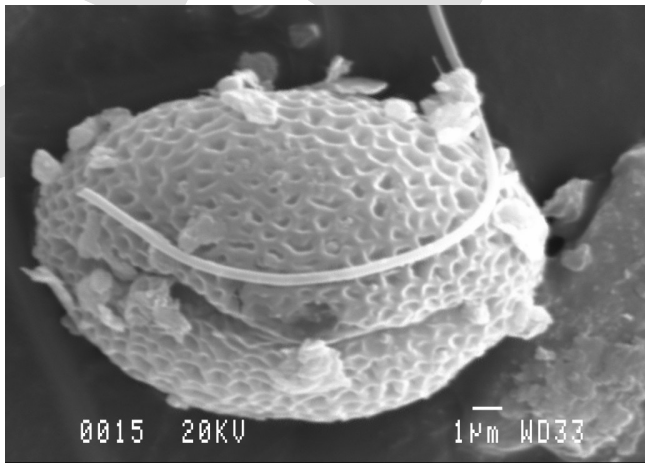
Direct analysis, non destructive (Teflon filters)

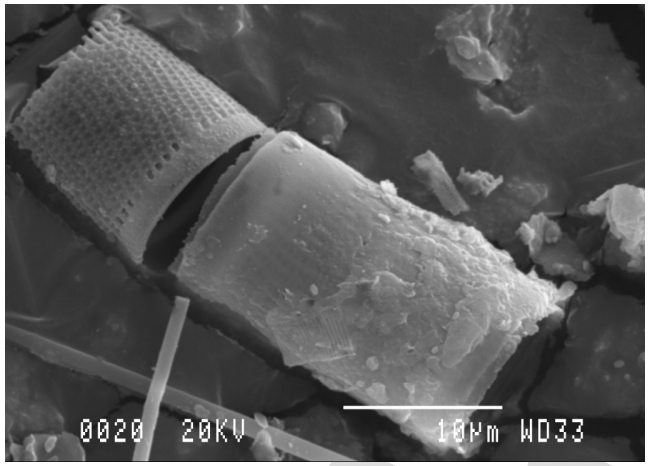
LABEC

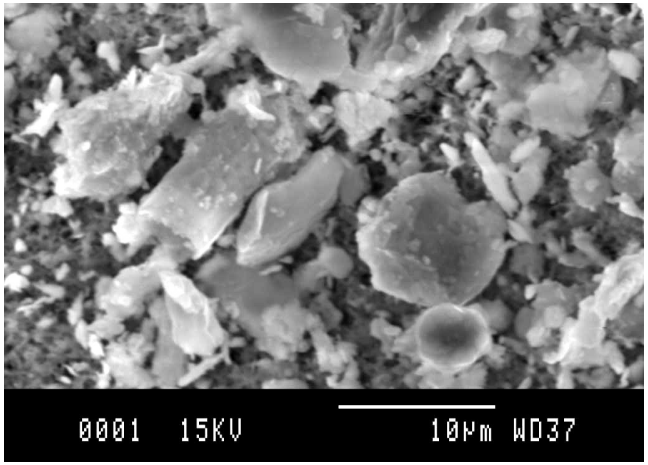
Proton Induced X-ray Emission (PIXE)

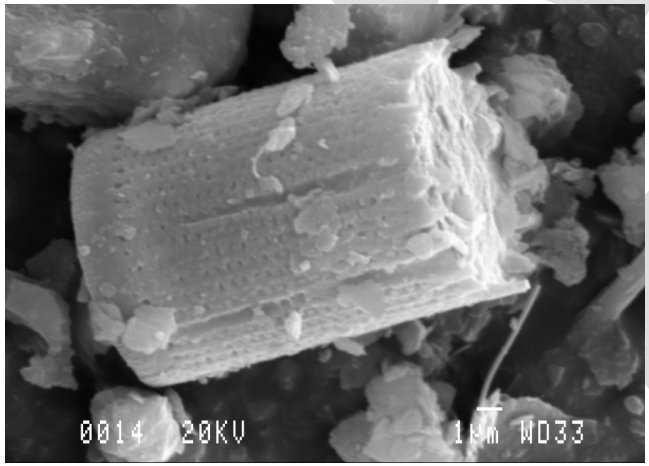


SEM-EDX analysis

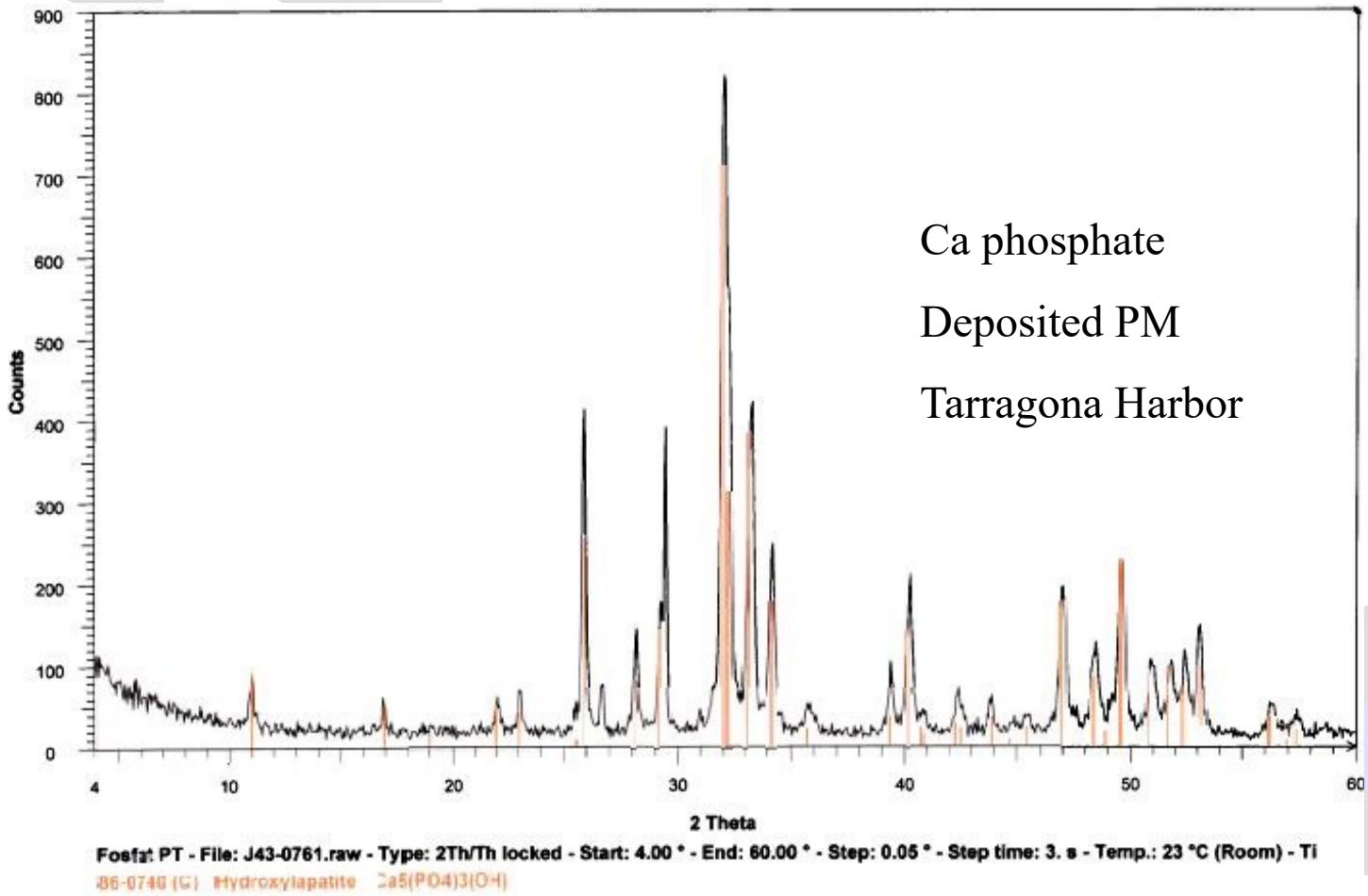




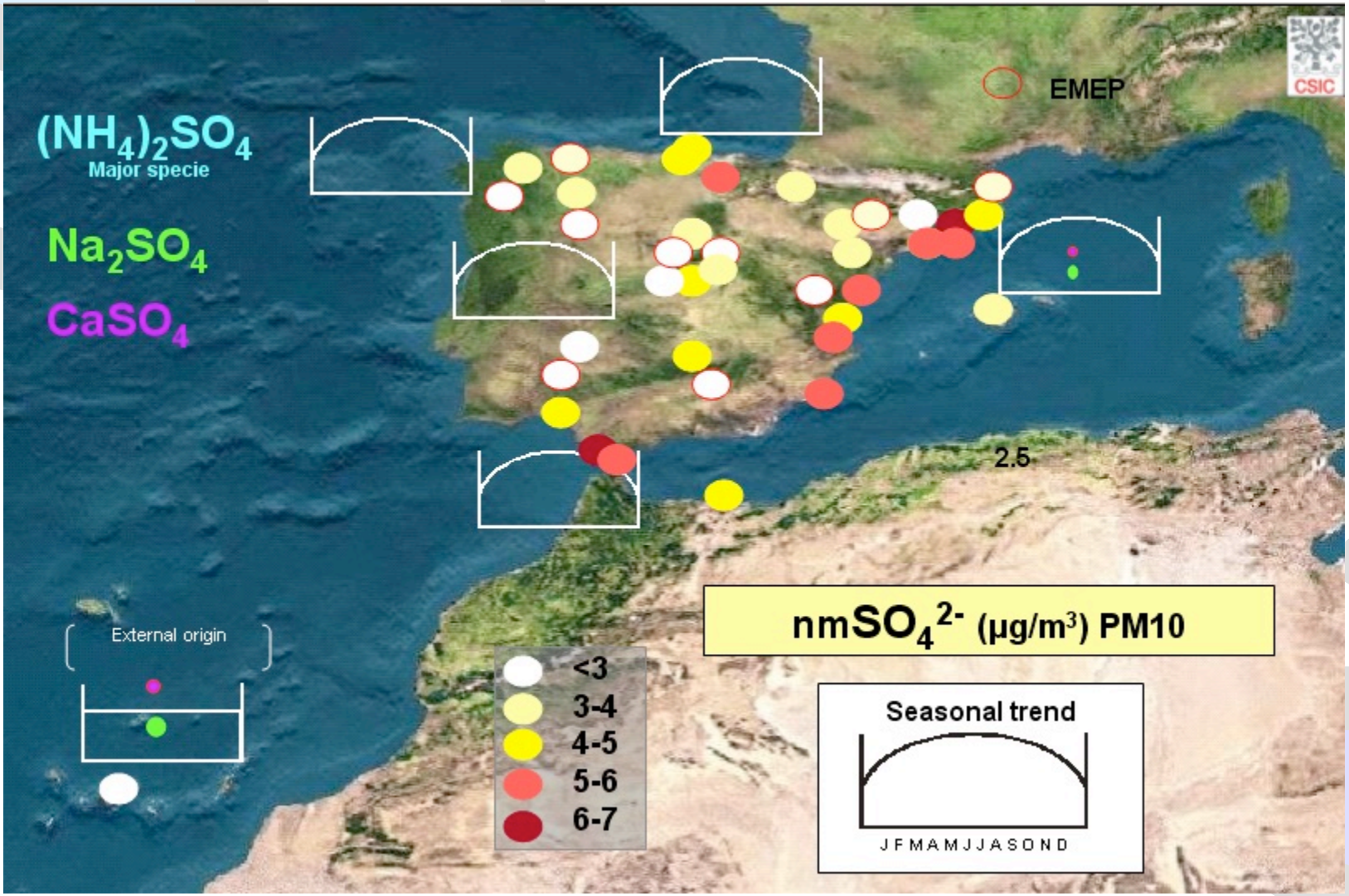




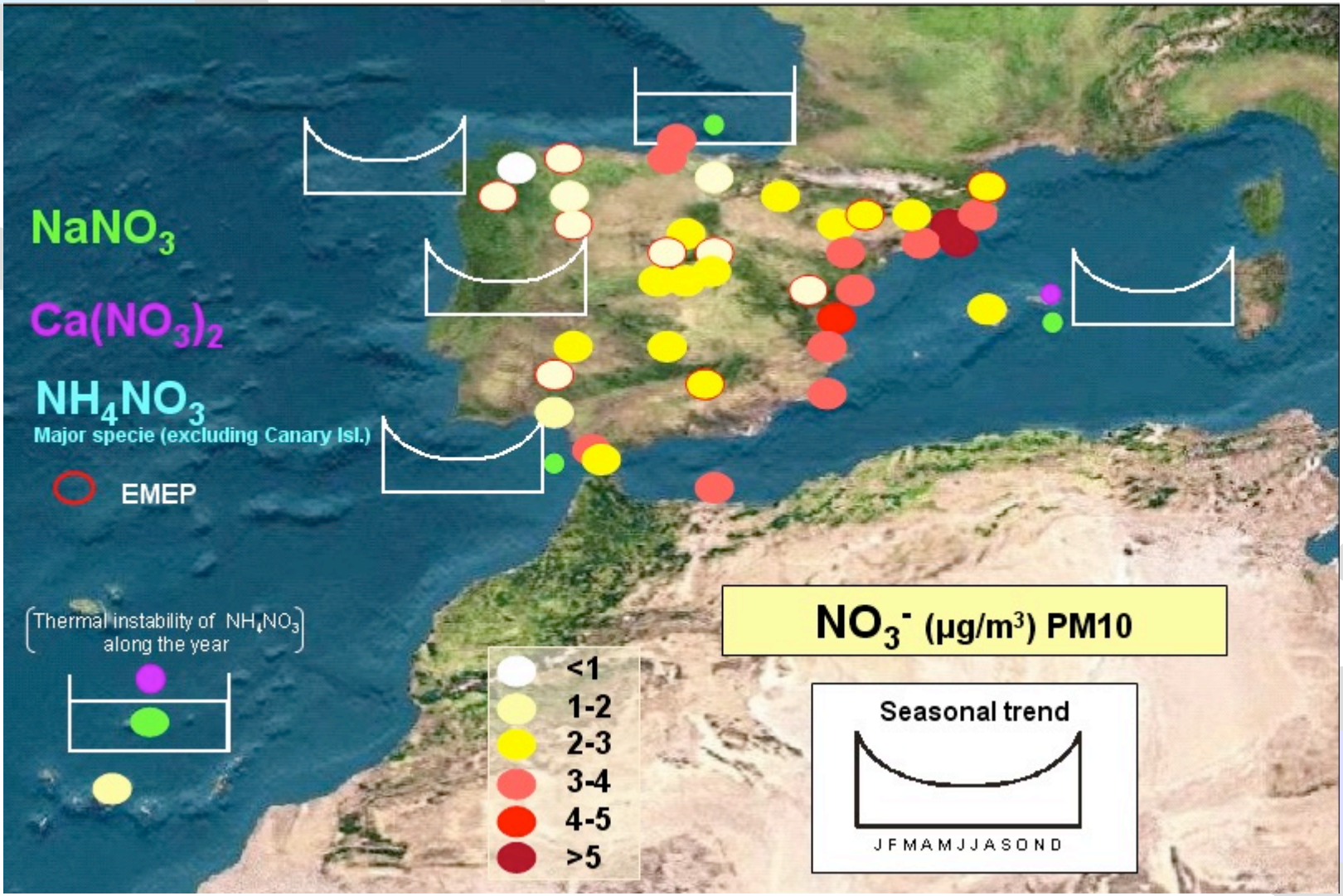
X-Ray Diffraction



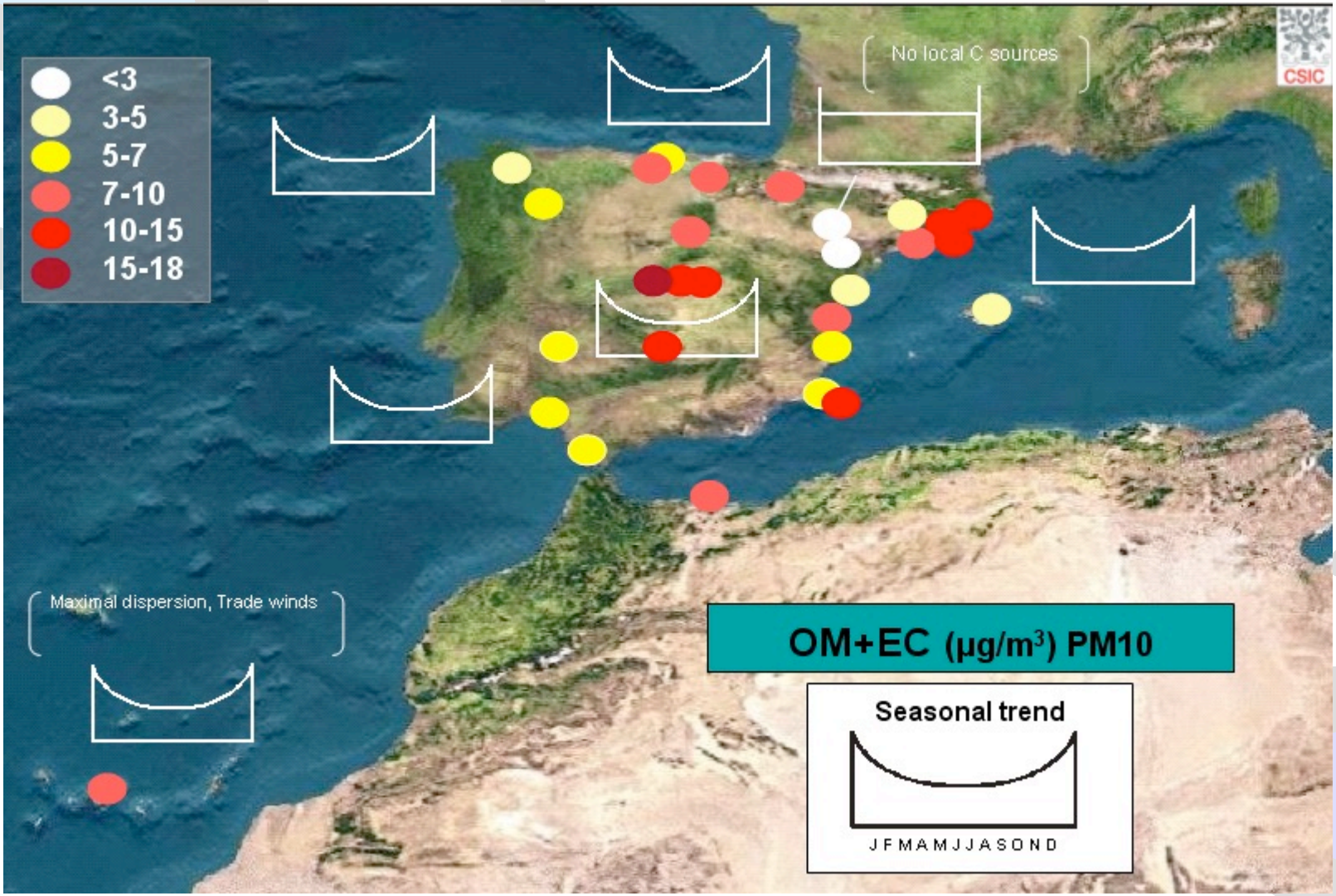
ATMOSPHERE & POLLUTION: some results



ATMOSPHERE & POLLUTION: some results



ATMOSPHERE & POLLUTION: some results



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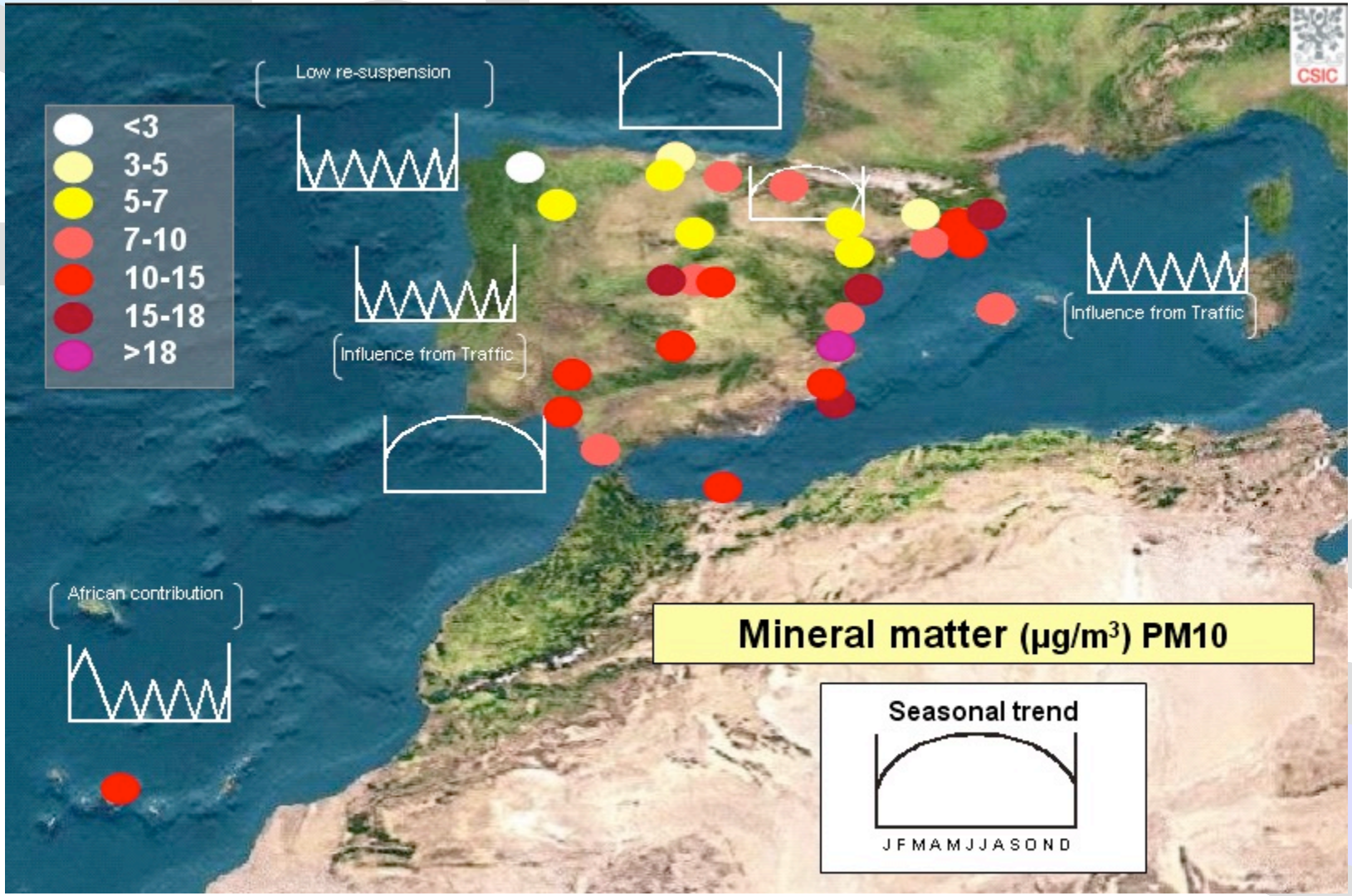
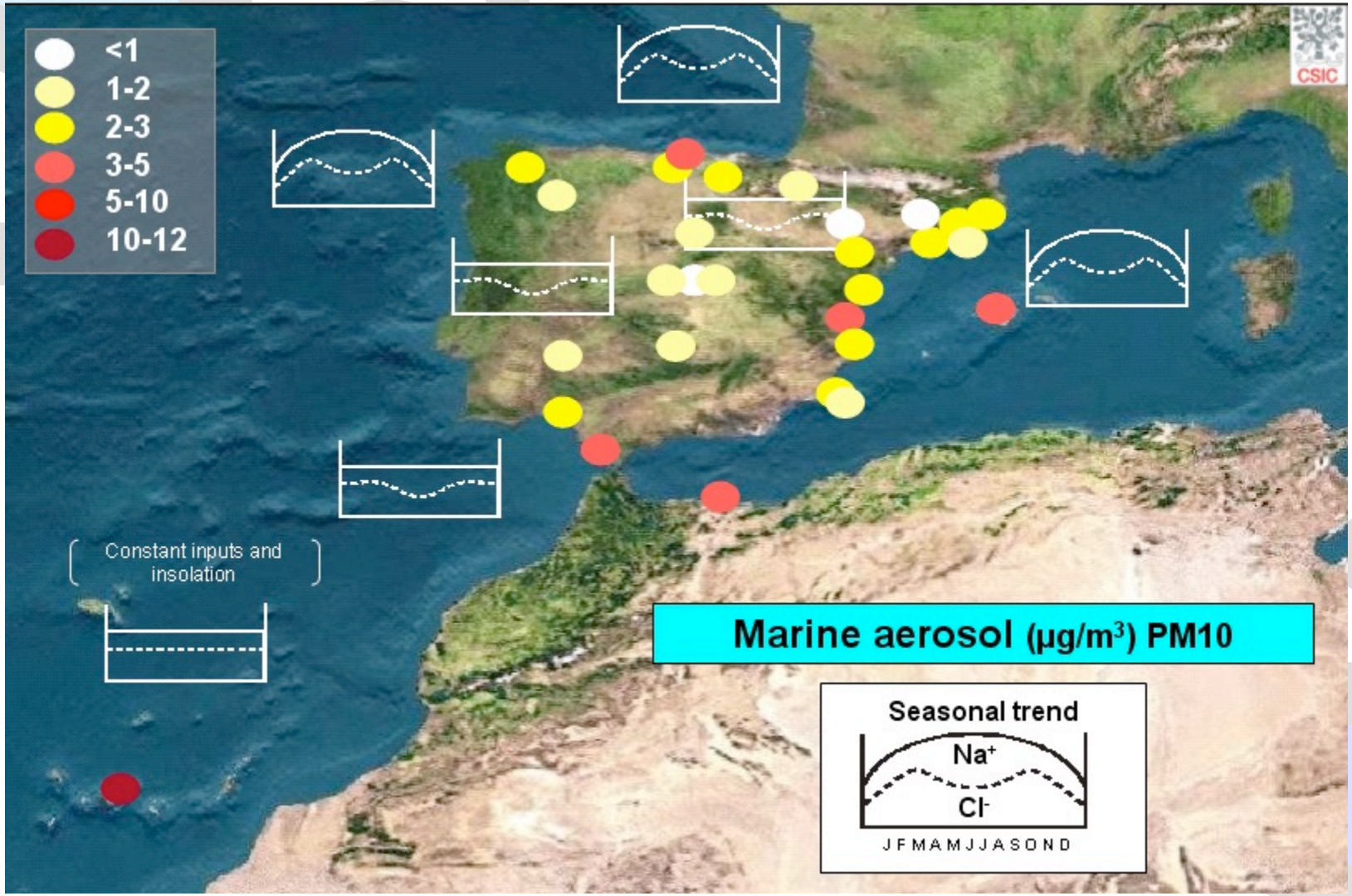


ATMOSPHERE & POLLUTION: some results



ATMOSPHERE & POLLUTION: some results

	Reg. bck		UB. bck		Steel	S. Steel	Cupper	Zinc	Petrochemical		Ceramic		Brick
	min	max	min	max	media	media	Media	media	min	max	min	max	media
Li	0.1	0.2	0.2	0.7	0.4	0.8	0.4	0.4	0.4	1.1	0.6	1.2	**2.0**
Be	0.01	0.02	0.02	0.05	0.06	0.02	0.05	0.06	0.01	0.06	0.02	0.05	**0.07**
Sc	0.1	0.1	0.1	0.3	0.1	0.1	0.4	0.1	0.1	0.3	0.3	0.5	0.3
Ti	7	19	18	**83**	25	52	71	35	22	66	33	56	**99**
V	2	5	2	12	8	**25**	6	12	8	**21**	4	6	**138**
Cr	1	1	2	8	**25**	**35**	2	3	3	5	3	7	3
Mn	5	5	4	29#	**87**	25	15	13	8	12	6	8	23
Co	0.1	0.1	0.2	0.5	0.5	0.7	0.3	0.4	0.2	**0.8**	0.4	0.7	0.6
Ni	2	3	2	7	**33**	**24**	4	7	4	**9**	3	4	**24**
Cu	2	8	7	**112**	33	15	**67**	17	20	28	4	11	**66**
Zn	12	26	14	**97**	**420**	103	41	**492**	31	56	45	**194**	21
Ga	0.1	0.2	0.1	0.3	0.4	0.3	**0.4**	0.2	0.1	0.4	0.2	0.4	**1.2**
Ge	0.1	0.3	0.04	0.3	0.2	0.2	0.3	0.04	0.14	0.22	0.05	0.2	0.1
As	0.3	0.4	0.3	**2.8***	1.8	1.2	**4.9**	1.0	0.5	2.1	1.7	**5.2**	1.6
Se	0.3	0.5	0.3	1.3	**2.8**	0.7	1.3	0.6	0.5	0.7	1.0	**2.4**	**2.2**
Rb	0.5	0.6	0.5	1.8	1.1	1.0	1.5	1.0	0.7	1.6	1.2	2.5	**5.6**
Sr	1	5	3	**10**	3	7	4	8	4.7	4.8	3	4	11
Y	0.1	0.2	0.1	0.4	0.1	0.3	0.3	0.1	0.1	0.2	0.2	0.3	0.4
Zr	3	4	2	**10**	2	5	2	2	2	7	10	**21**	4
Nb	0.05	0.1	0.05	0.4	0.1	0.23	0.2	0.14	0.1	0.3	0.2	0.3	0.36
Mo	3	4	2	5	**16**	**20**	4	2	2	8	2	5	4
Cd	0.2	0.2	0.1	0.7	**1.2**	0.3	0.6	**0.7**	0.1	0.3	0.6	**1.6**	0.3
Sn	1	1	1	6	**38**	2	2	2	1.7	2.3	1	1	NA
Sb	0.6	0.6	1	**17**	2	1.6	2	3.2	1	4	1	6	NA
Cs	0.04	0.04	0.03	0.13	0.10	0.07	0.09	0.07	0.03	**0.23**	0.14	**0.31**	**0.47**
Ba	5	8	4	**35**	14	17	18	16	8	13	12	16	16
La	0.1	0.2	0.2	0.6	0.3	0.7	0.5	0.4	0.3	**0.9**	0.3	0.6	**1.2**
Ce	0.2	0.4	0.4	1.3	0.4	0.9	0.9	0.7	0.5	1.2	0.7	**1.9**	**2.0**
Pr	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.3
Hf	0.2	0.2	0.1	0.5	0.2	0.2	0.1	0.3	0.1	0.2	0.2	0.4	NA
W	0.02	0.04	0.05	0.64	0.67	0.21	0.11	0.05	0.03	0.16	0.10	0.36	0.15
Tl	0.1	0.1	0.05	0.4	0.4	0.1	0.1	0.1	0.1	0.3	0.5	**2.7**	**2.2**
Pb	5	9	7	25	**103**	19	25	20	8	25	35	**106**	28
Bi	0.1	0.1	0.1	**1.0**	0.5	0.2	**1.0**	0.2	0.1	0.2	0.4	**1.4**	0.2
Th	0.1	0.2	0.1	0.3	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.2	0.3
U	0.1	0.2	0.1	0.3	0.3	0.1	0.2	0.1	0.1	0.3	<0.1	0.1	0.1

Mean annual levels

Trace elements

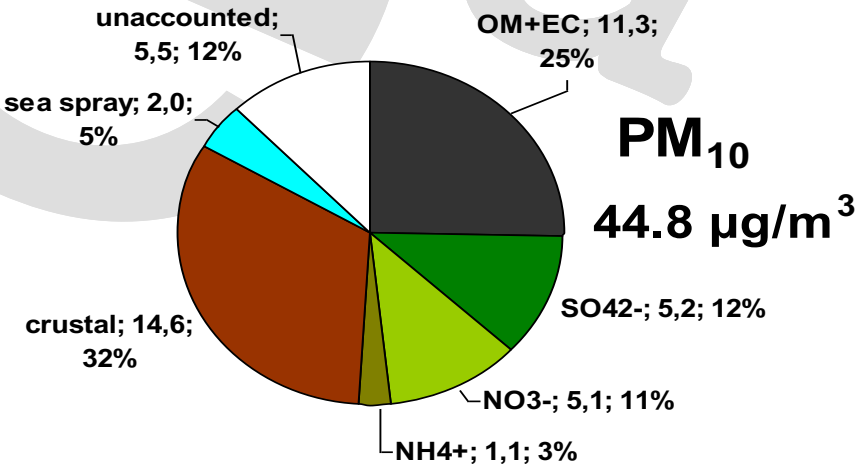
PM_{10}

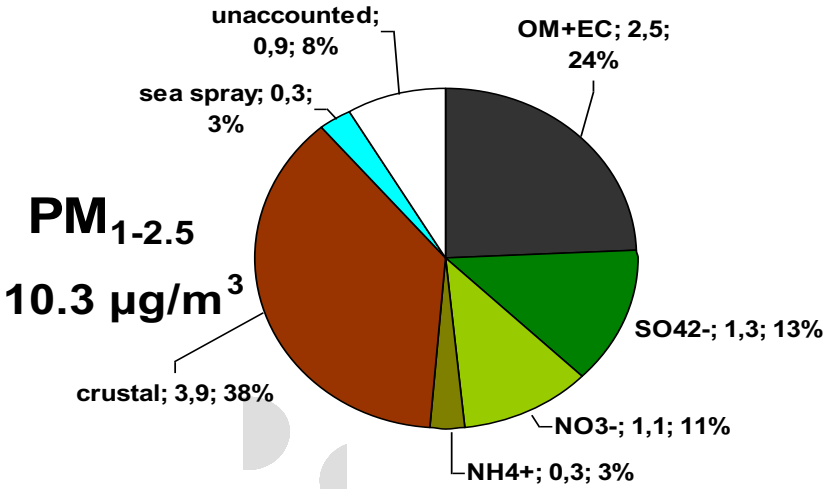
37 sites Spain

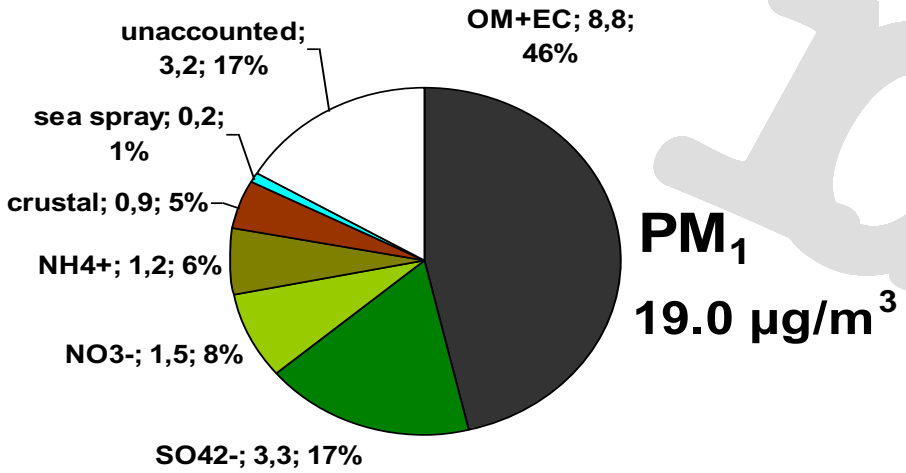
1999-2009

(ng/m^3)

Barcelona 2005-2006 (urban)

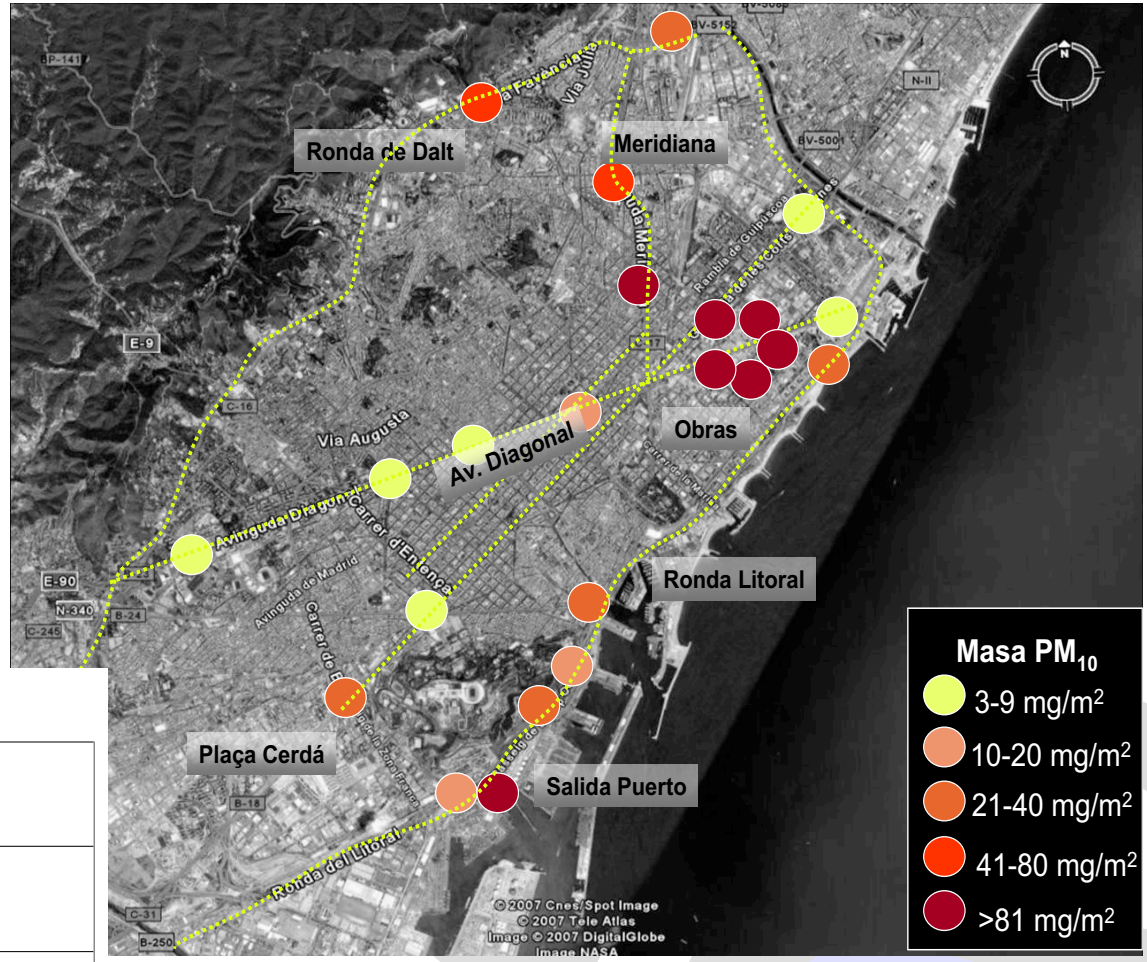


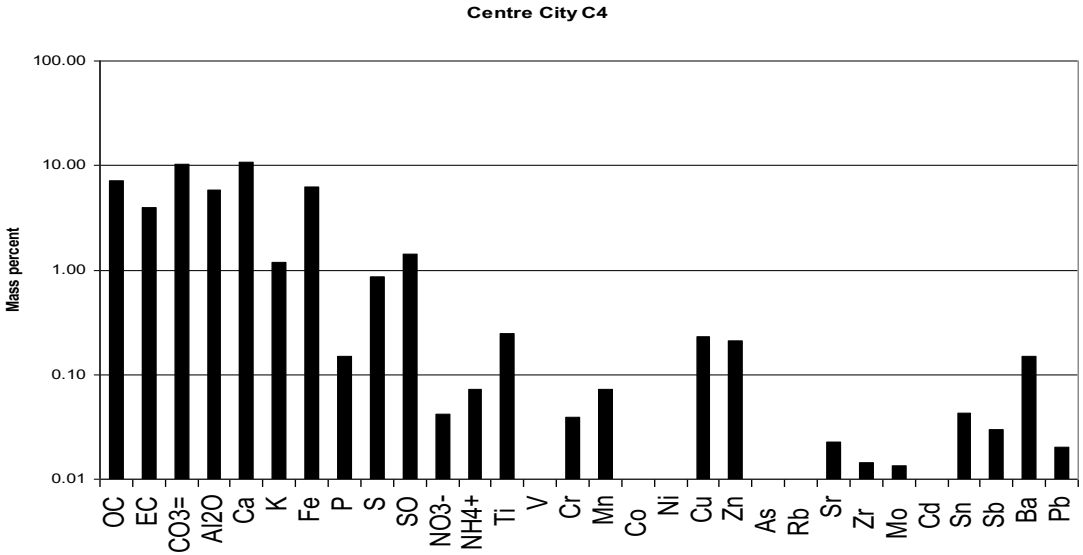




ATMOSPHERE & POLLUTION: some results

ATMOSPHERE & POLLUTION: some results

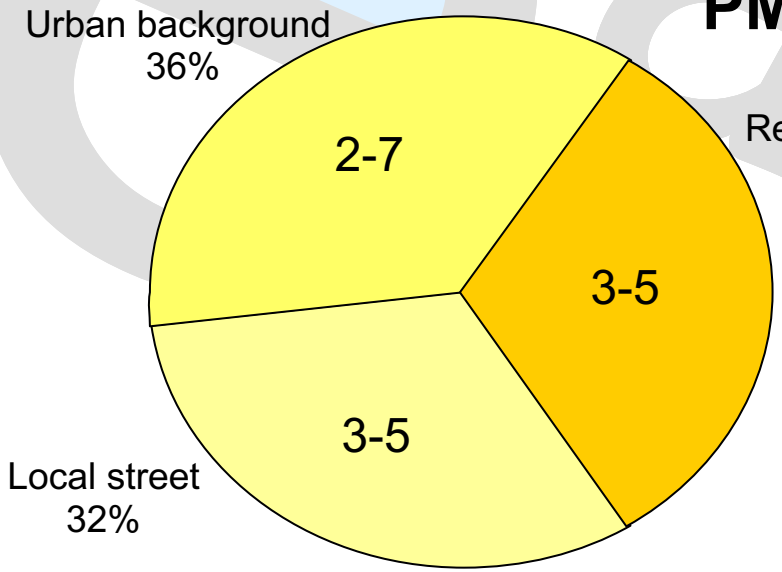


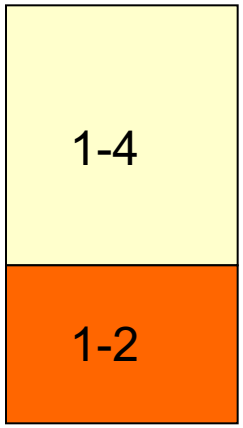


Source: PhD F. Amato

ATMOSPHERE & POLLUTION: some results

PM_{10} 12.5 µg/m³

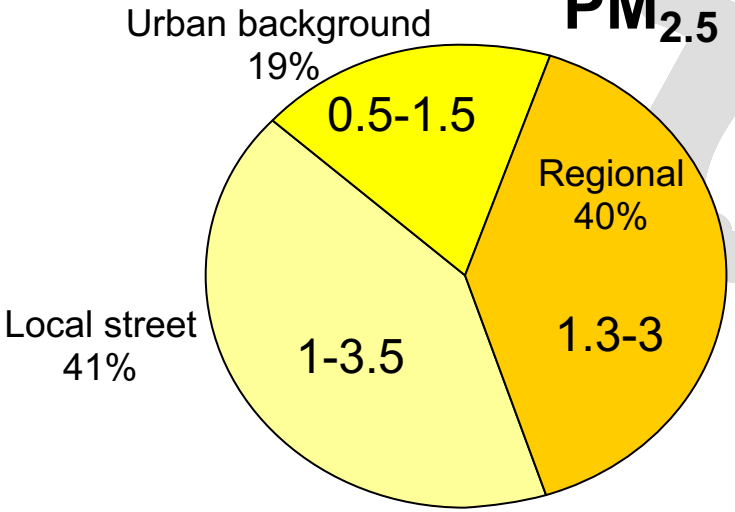


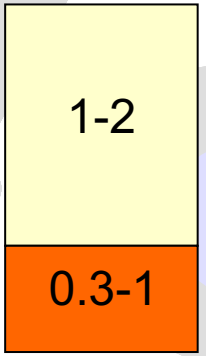


Resuspension
20%.

African dust
12%

$PM_{2.5}$ 5.4 µg/m³

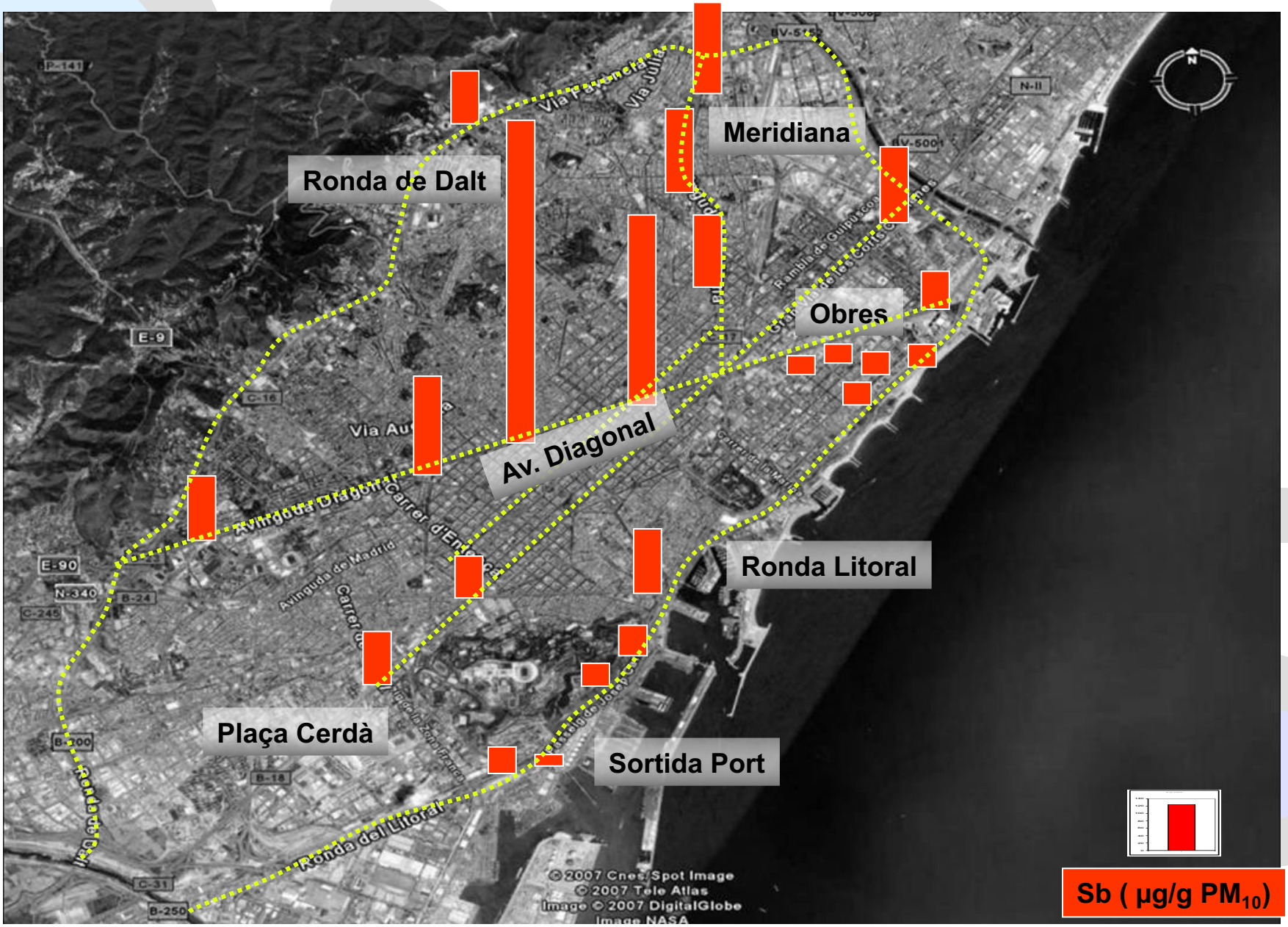




Resuspension
28%

African dust
12%

ATMOSPHERE & POLLUTION: some results



ATMOSPHERE & POLLUTION: some results

		Brake pads					Tires	
		Ferodo (A)	*Bendix*	*Road House*	*Bosch*	*Ferodo (B)*	*Bridgeston*	*Michelin*
	C tot	28	26	28	32	-	83	79
	Al	0.4	2.3	0.8	0.9	1.0	0.06	0.06
	Ca	0.4	1.8	3.6	1.7	0.3	1.31	0.46
	K	<0.1	0.4	<0.1	<0.1	<0.1	0.04	0.06
%	**Na**	<0.1	1.0	0.1	0.1	<0.1	0.03	0.03
	Mg	1.0	4.1	0.5	0.8	0.8	0.04	0.01
	Fe	50	16	33	30	26	0.02	0.03
	S	2.2	2.6	3.6	3.1	1.9	1.17	1.32
	P	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
	Li	1.8	4.4	2.4	1.1	2.2	1.4	0.1
	Sc	1	4	1	1	3	<0.1	<0.1
	Ti	605	744	567	209	335	31	17
	V	173	16	30	42	40	5	4
	Cr	210	170	1270	49	2834	1	2
	Mn	1783	1703	12636	1464	1827	3	3
	Co	26	13	14	19	10	80	94
	Ni	51	61	78	74	33	<0.1	<0.1
	Cu	82.3	24493	270	13732	117551	4.8	6.9
	Zn	66.6	4083	3462	1118	14862	19849	15073
	Ga	9.8	5.7	4.1	3.1	6.2	<0.1	<0.1
	Ge	2.8	1.4	1.2	0.8	4.1	<0.1	<0.1
	As	4.0	5.0	4.6	42	8.4	0.8	0.7
	Se	5.0	7.6	3.5	11.0	7.1	<0.1	<0.1
	Rb	30.5	38.5	14.3	1.2	4.9	1.1	3.1
	Sr	1007	857	818	1773	26	17.8	3.1
	Y	0.9	15.5	6.5	1.2	16.4	<0.1	<0.1
	Zr	4.4	1260	70.3	12.0	945	1.2	<0.1
ppm	**Nb**	<0.1	<0.1	65.8	1.7	<0.1	<0.1	0.8
	Mo	3.1	5.4	16	162	3093	0.4	0.6
	Cd	0.5	1.6	0.6	1.9	23	2.7	1.5
	Sn	2.4	31	40	147	10	2.5	2.1
	Sb	2.1	1293	14.8	7.5	6944	11.5	2.0
	Cs	1.0	1.7	0.7	<0.1	1	<0.1	<0.1
	Ba	69343	67291	39013	37213	772	10.2	15.5
	La	2.3	6.9	32.3	<0.1	5	1.8	3.5
	Ce	4.2	14.9	50.7	2.1	11.5	0.5	0.6
	Pr	<0.1	1.2	4.0	<0.1	1.2	<0.1	<0.1
	Nd	2.8	8.5	17.0	0.8	5.2	21.0	22.9
	Hf	<0.1	49.5	1.7	<0.1	36	<0.1	<0.1
	Ta	<0.1	<0.1	5.7	<0.1	<0.1	<0.1	0.9
	W	<0.1	<0.1	18.7	0.6	<0.1	<0.1	<0.1
	Tl	<0.1	<0.1	0.9	<0.1	<0.1	<0.1	<0.1
	Pb	253	173	42.0	292	6.6	20.0	25.8
	Bi	<0.1	23.6	0.0	12.2	<0.1	<0.1	0.6

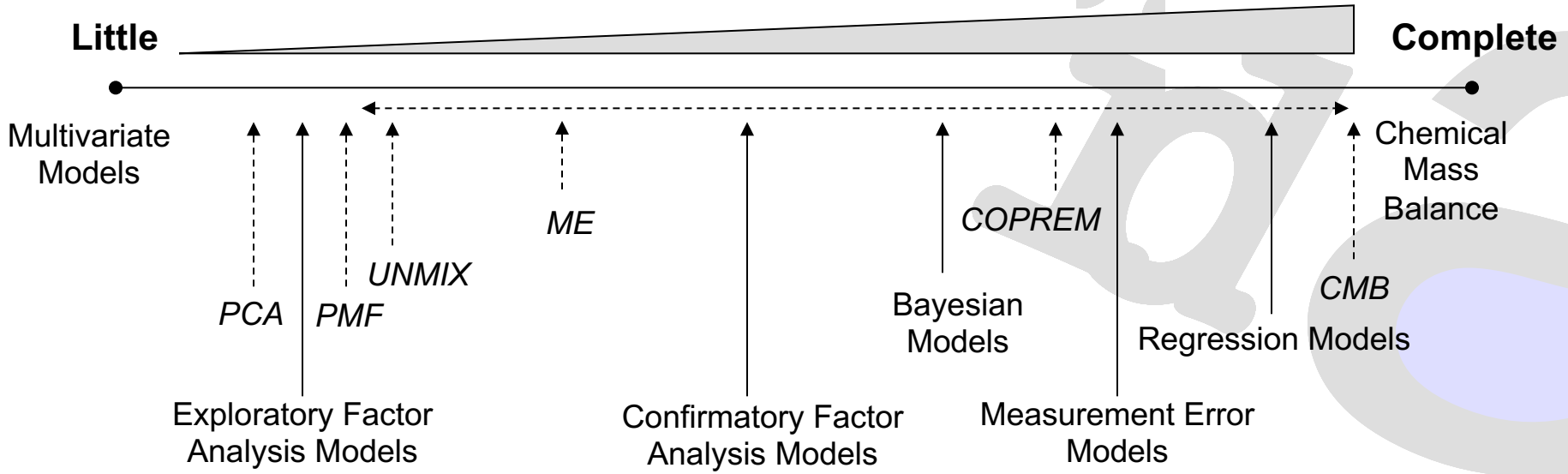
Receptor Models

Receptor models

$$X_t = \square\ f_t + e_t$$

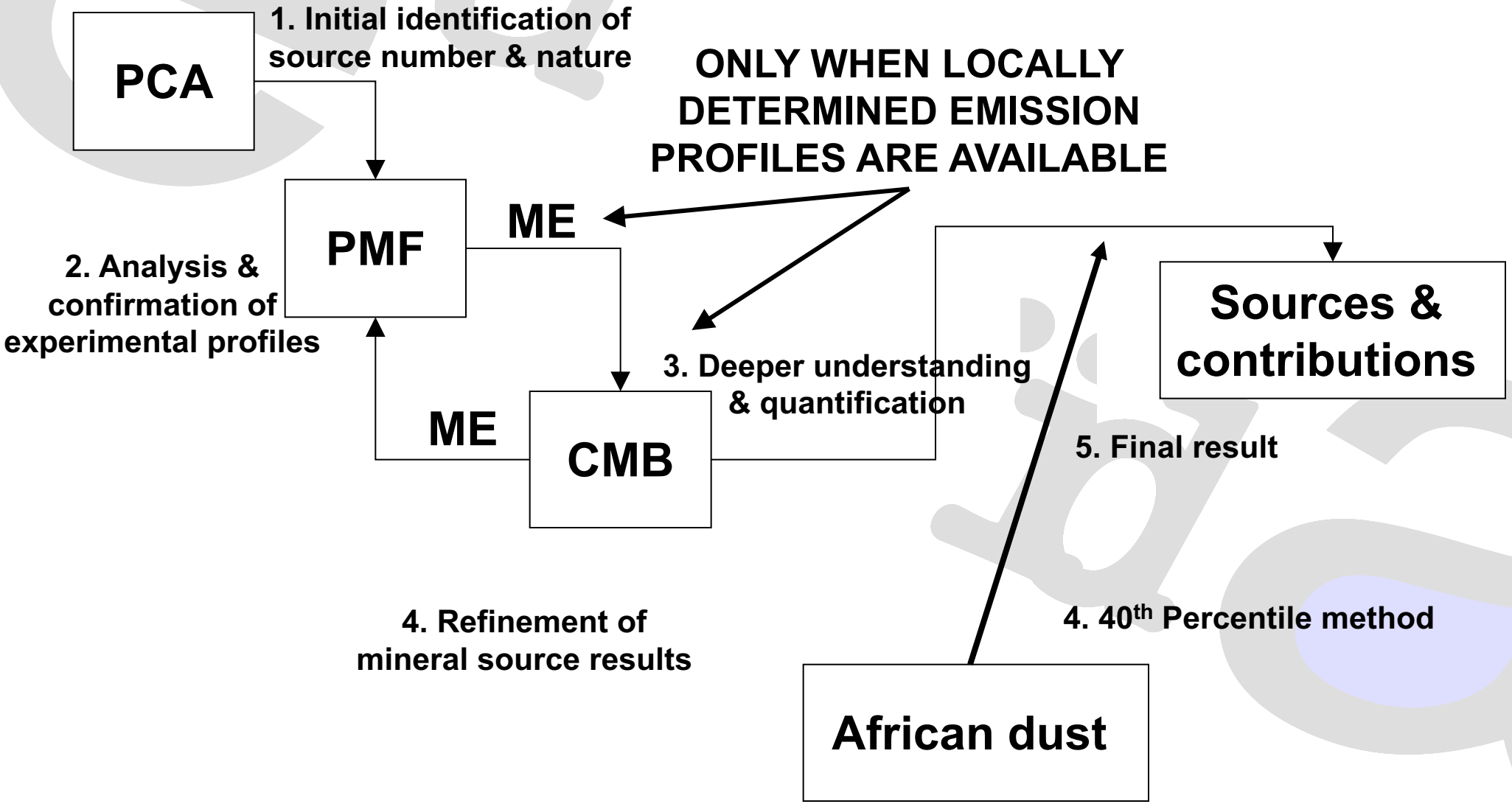
$p \times 1 \qquad p \times k \quad k \times 1 \qquad p \times 1$

Knowledge required about pollution sources prior to receptor modelling



Modified from Schauer et al. (2006)

Receptor models: Suggested approach (Spain)

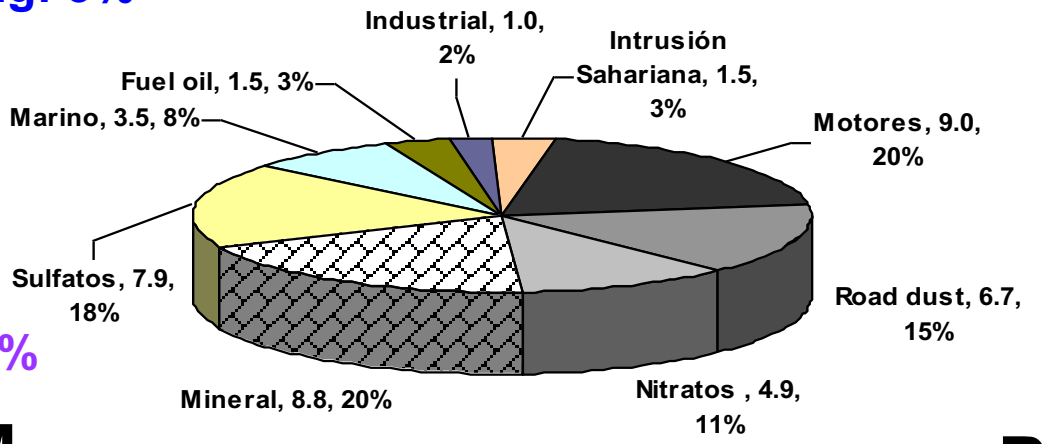


ME2: Source apportionment in Barcelona: Road dust

PM_{10}

Max. Shipping: 3%

Traffic: 43%



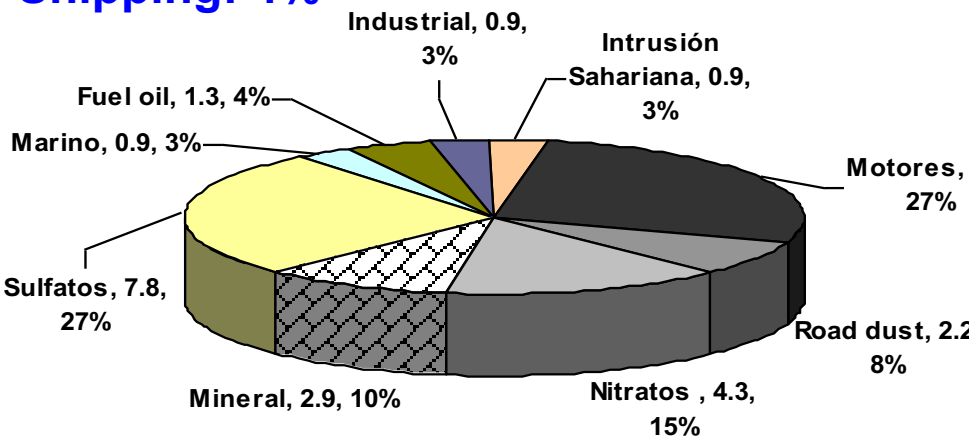
Fuente: Tesis doctoral F. Amato CSIC-IJA

Dem.-res. (reg.): 20%

$PM_{2.5}$

Max. Shipping: 4%

Traffic: 46%

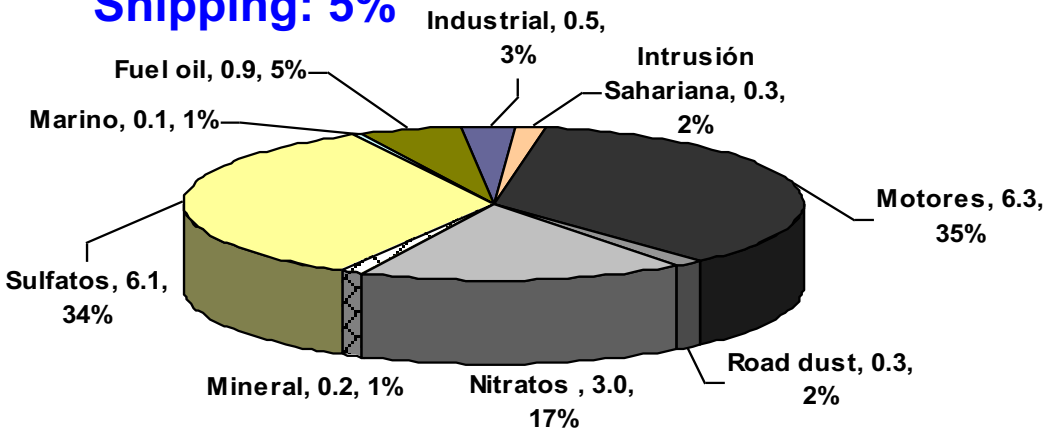


Demolition-resuspension (reg.): 10%

PM_{1}

Max. Shipping: 5%

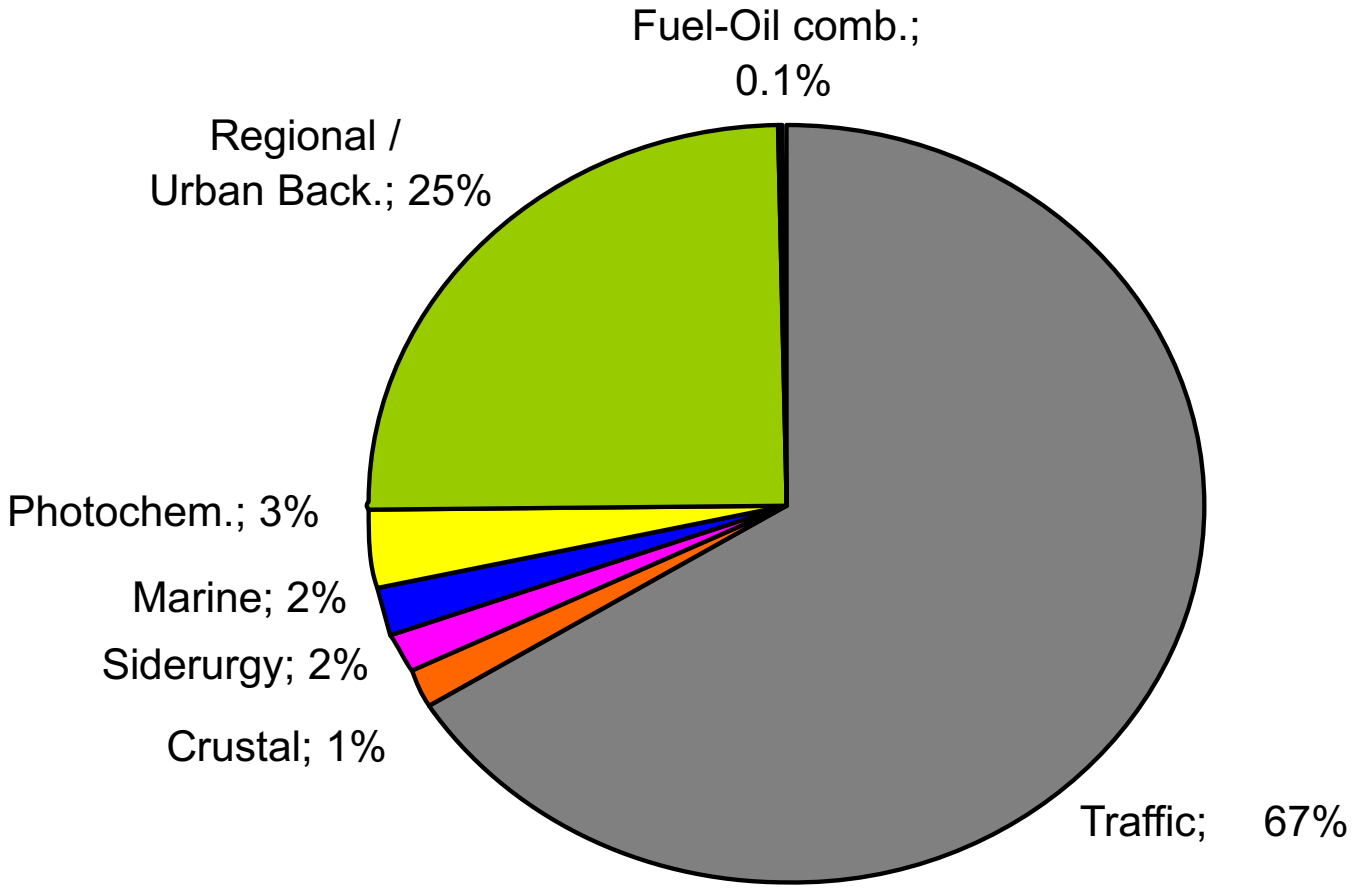
Traffic: 50%



Demolition-resuspension (reg.): 1%

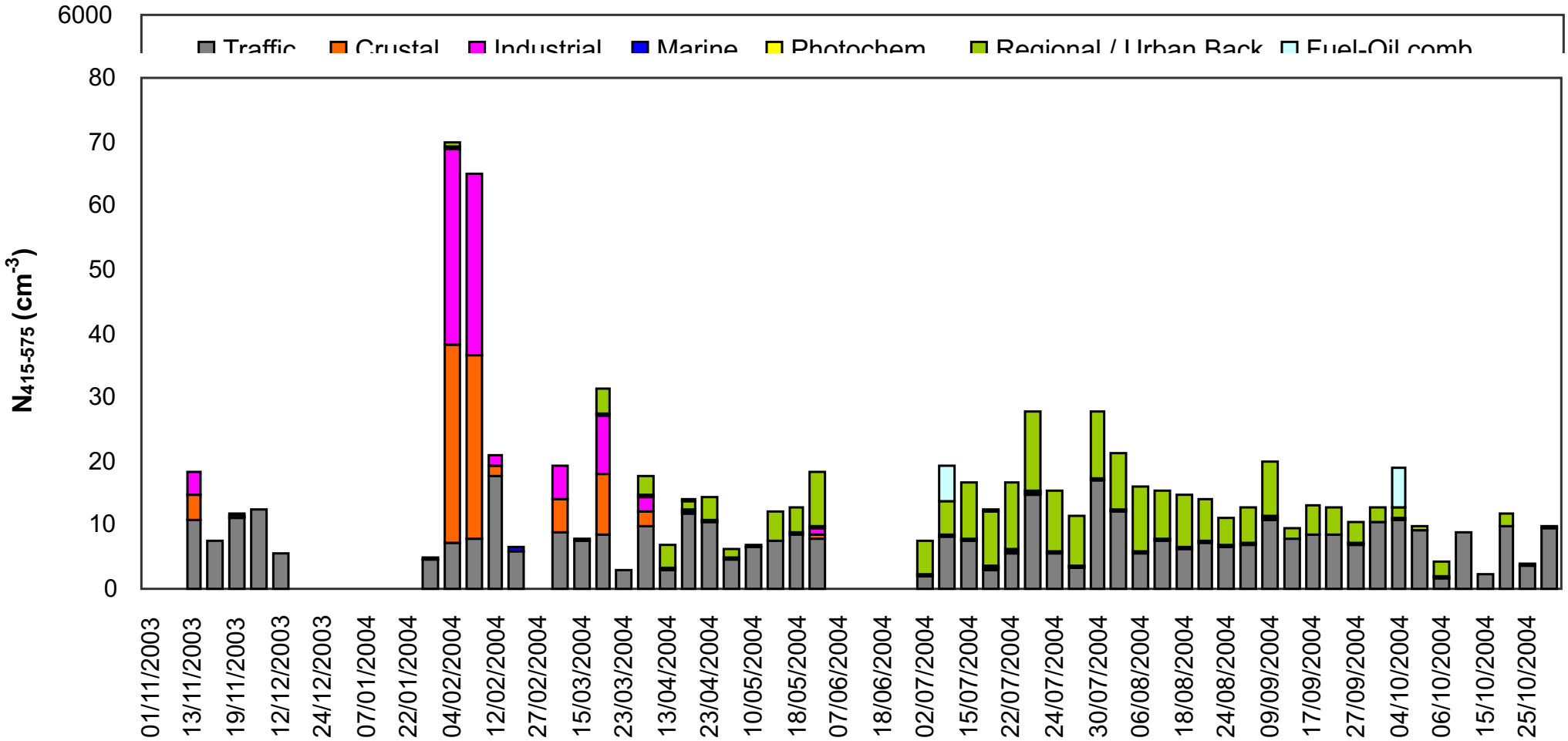
PCA-PMF Source apportionment in Barcelona: Number of sub-micronic PM

Source contribution to the mean annual $N_{13\text{-}800}$

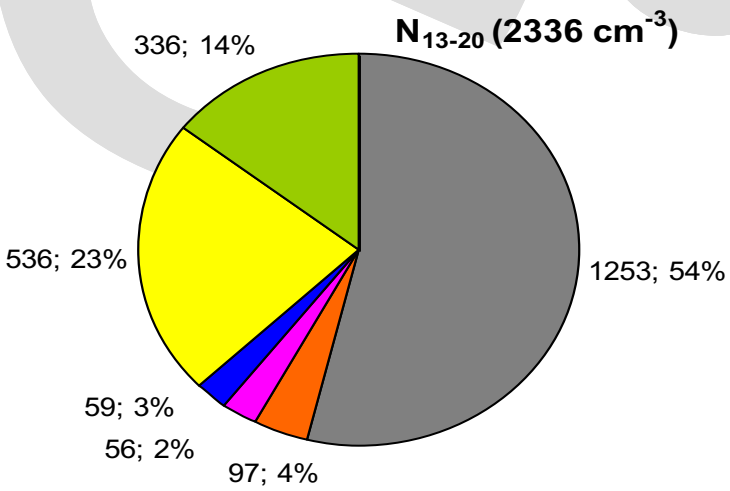


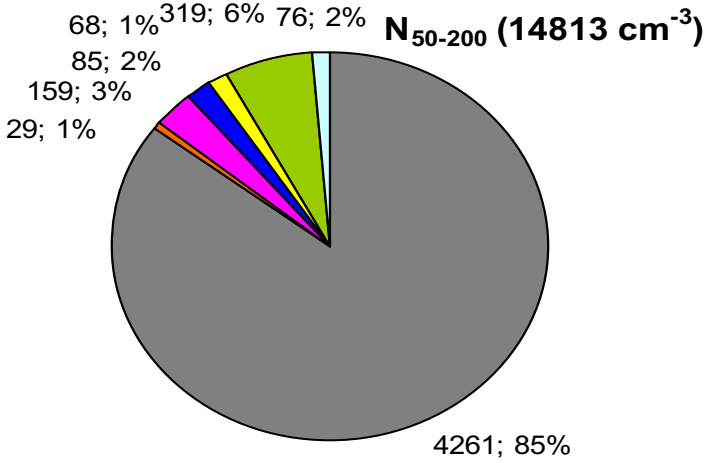
Pey et al. 2009. Atmospheric Environment

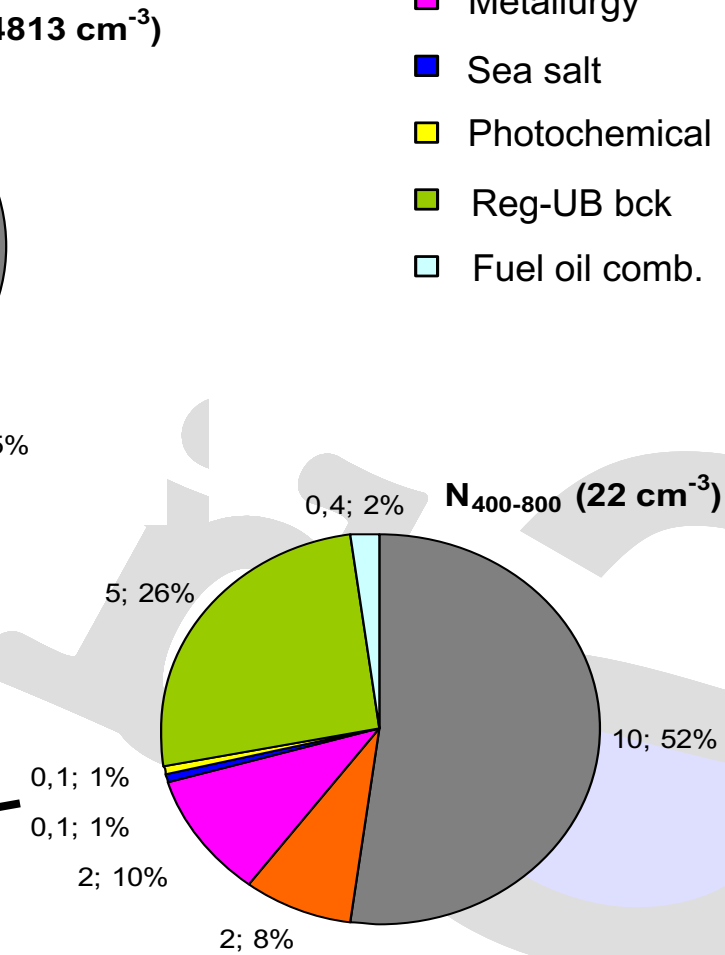
PCA-PMF Source apportionment in Barcelona: Number of sub-micronic PM

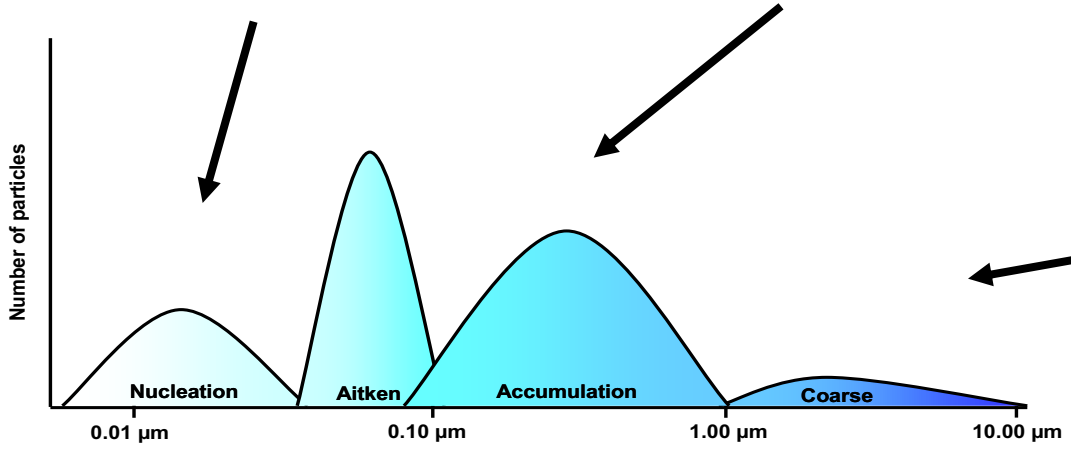


ATMOSPHERE & POLLUTION: some results





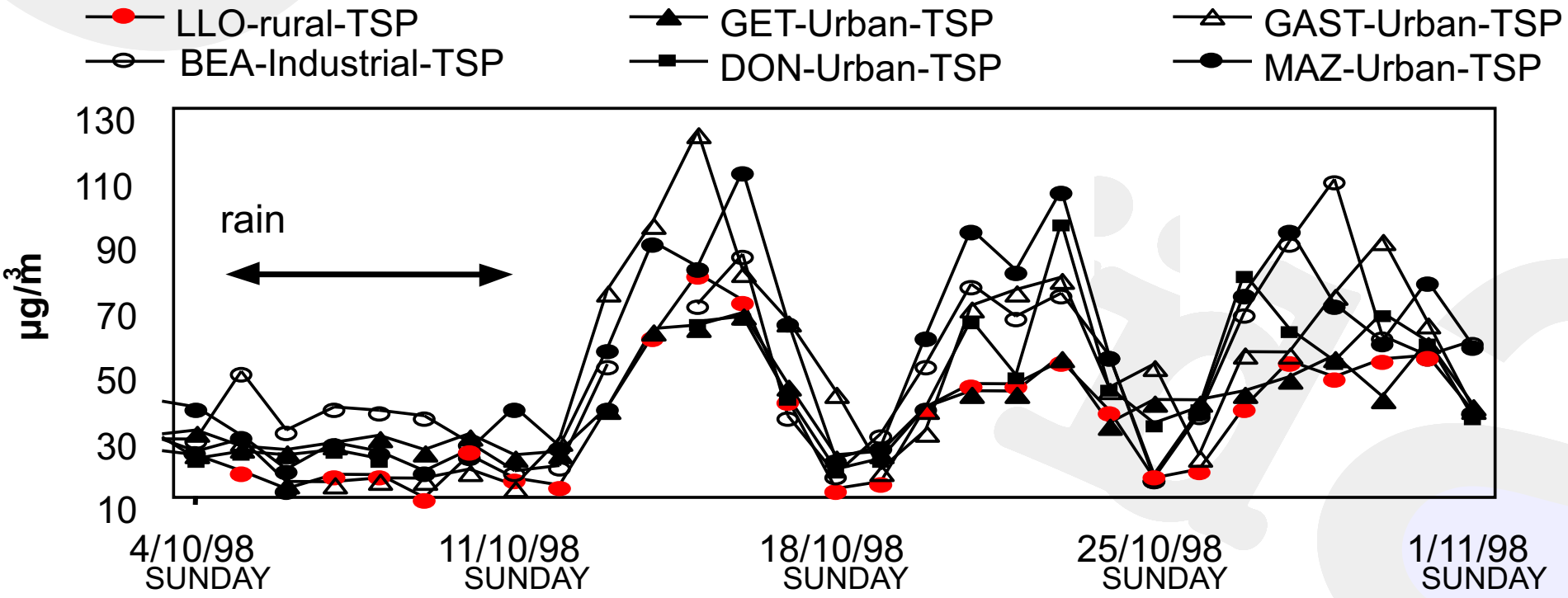




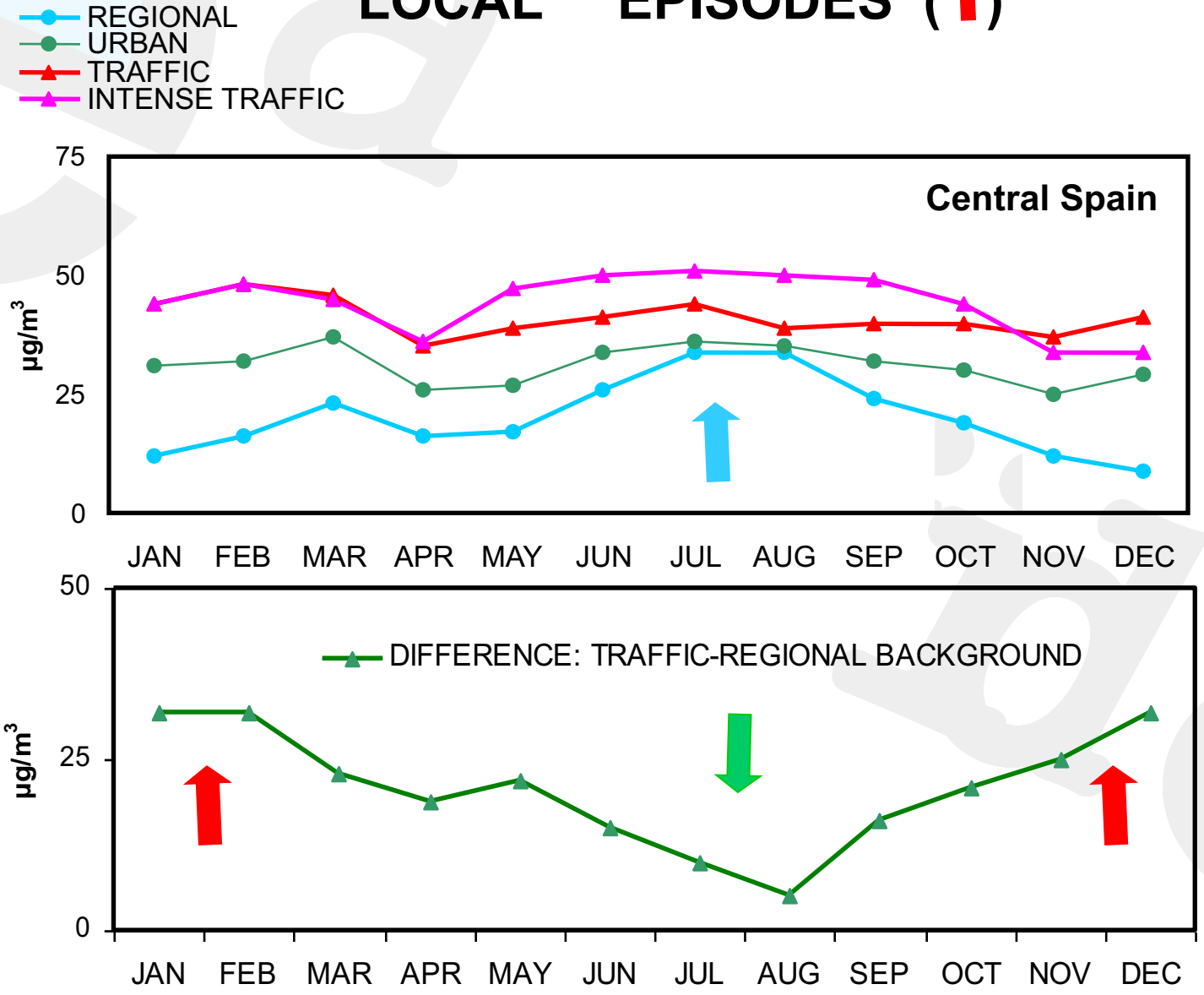
Pey et al. 2009. Atmospheric Environment

- LOCAL ANTHROPOGENIC
- AFRICAN AIR MASS INTRUSIONS
- REGIONAL EPISODES
- ANTHROPOGENIC ANTICYCLONIC EPISODES

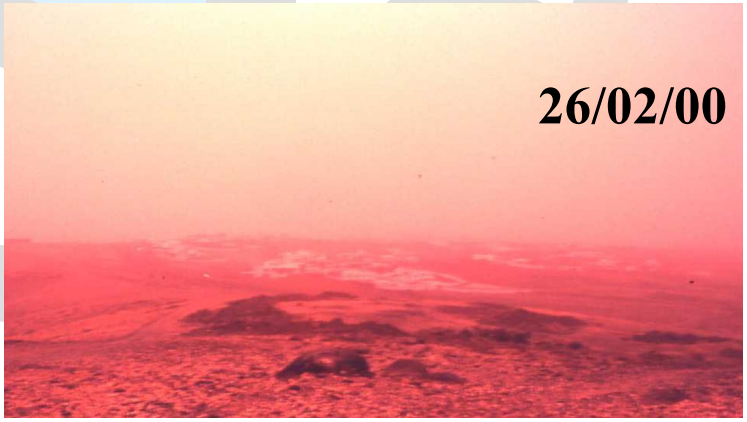
LOCAL ANTHROPOGENIC

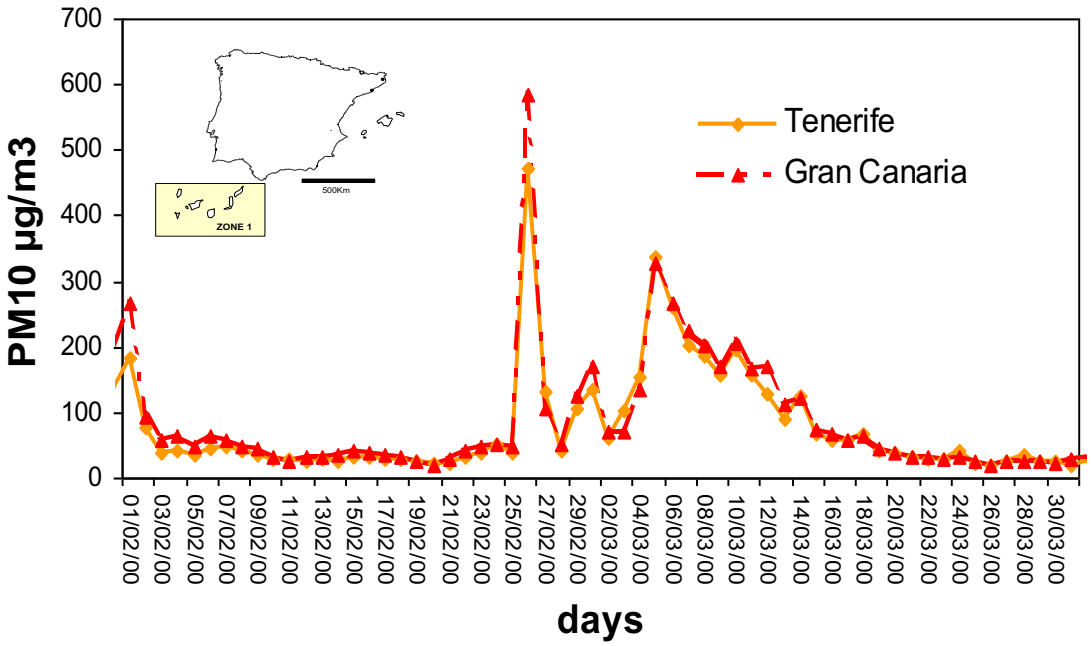


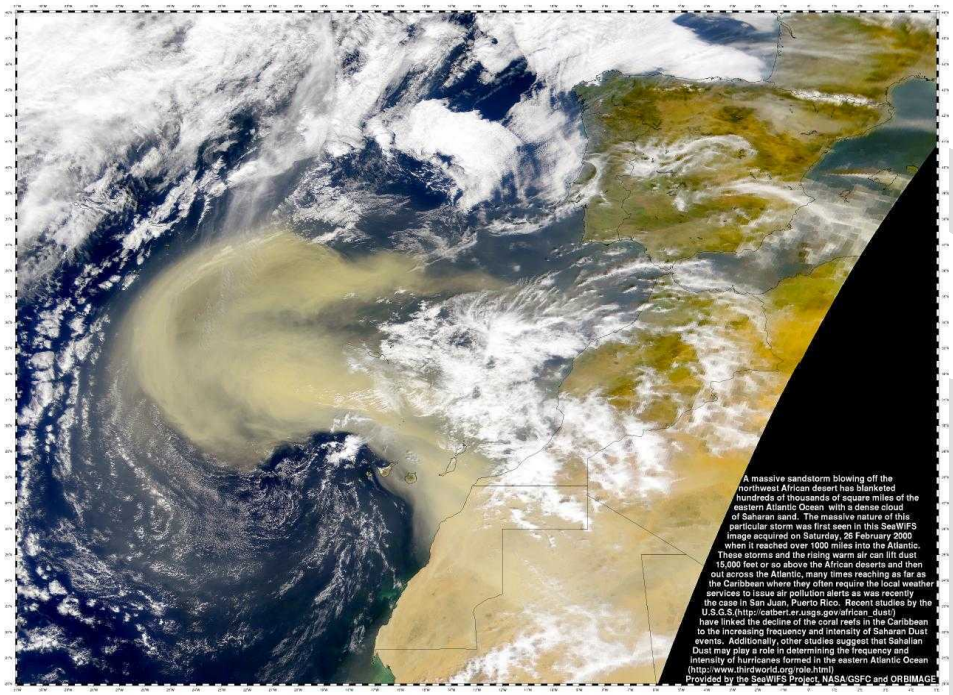
LOCAL EPISODES (↑)



PM EPISODES W. MED: African dust

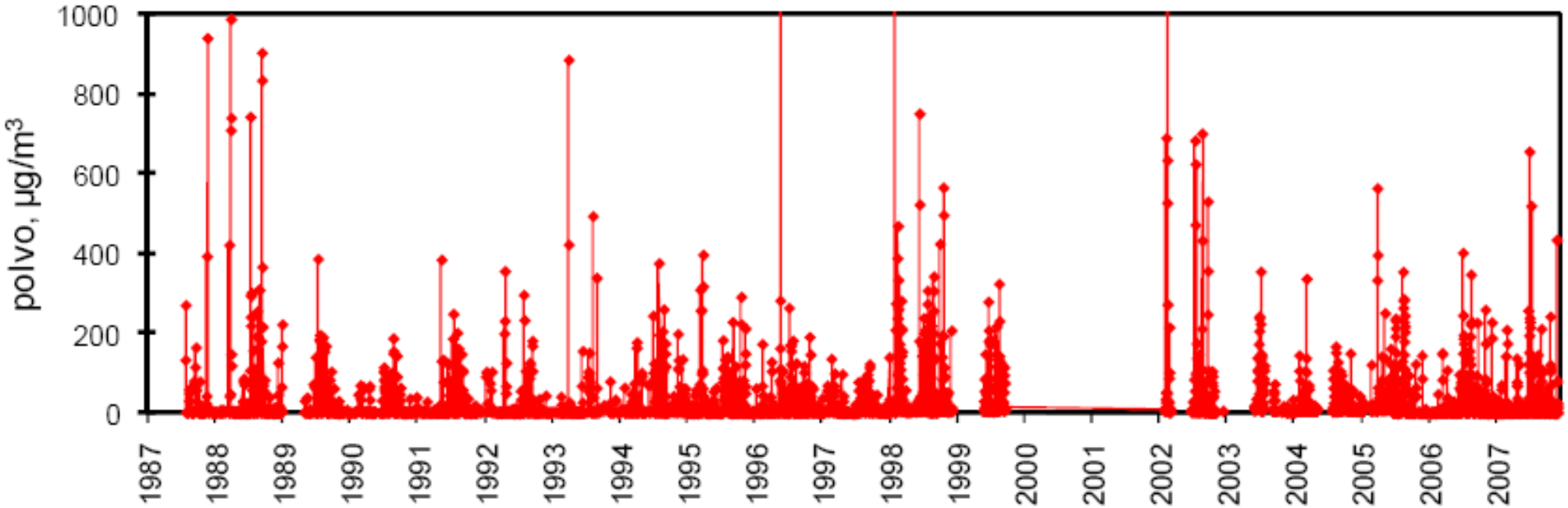




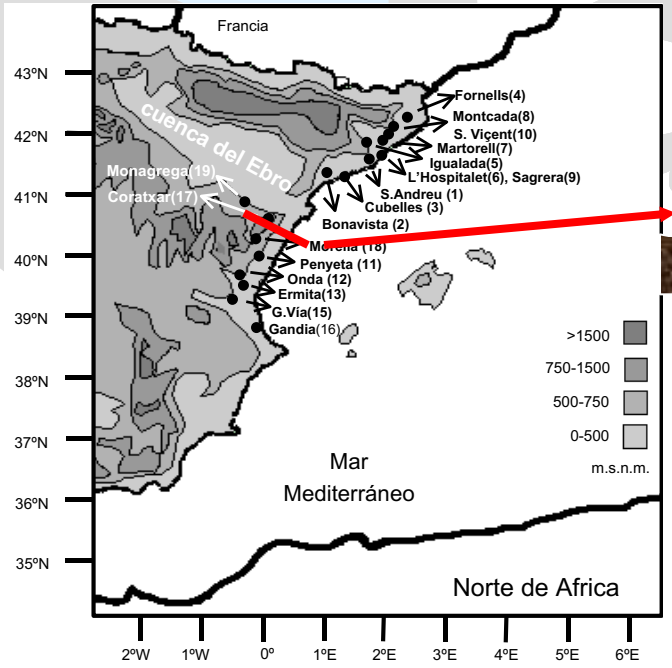


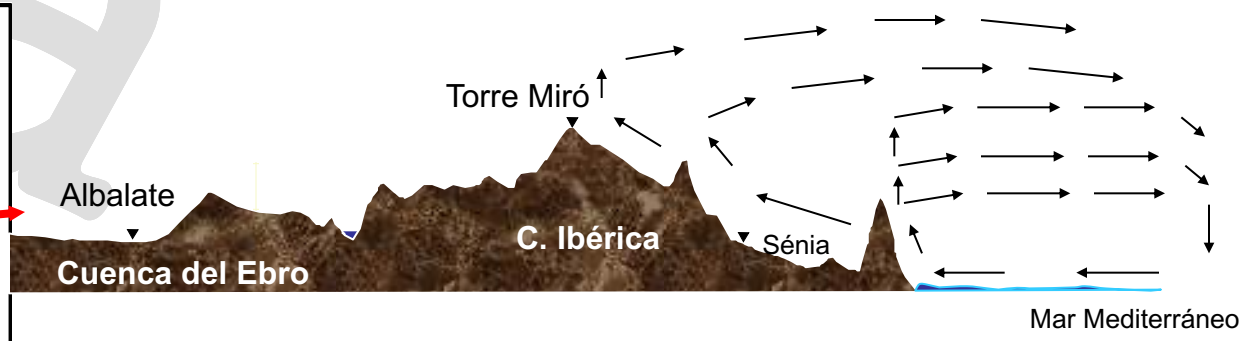
PM EPISODES W. MED: African dust

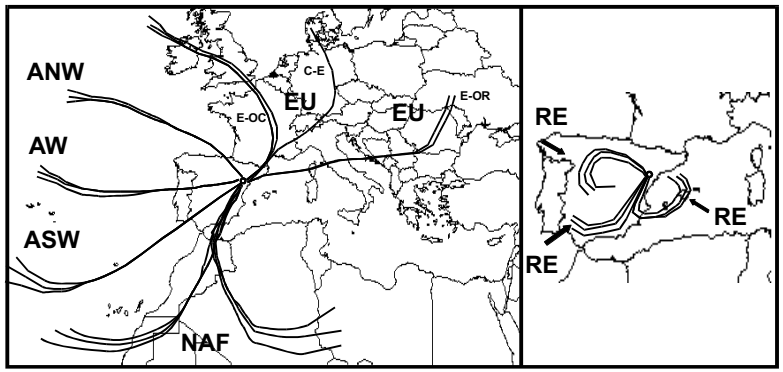
IZAÑA OBSERVATORY (Dr Sergio Rodriguez, AEMet)

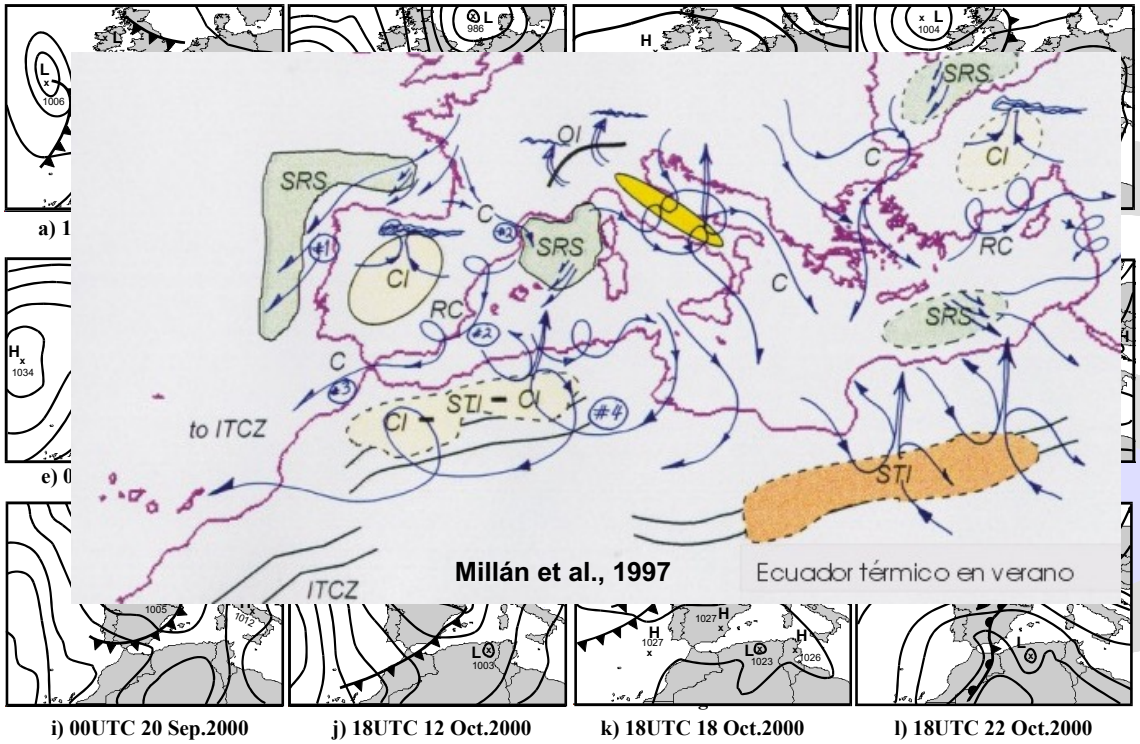


PM EPISODES W. MED: reg. recirculation

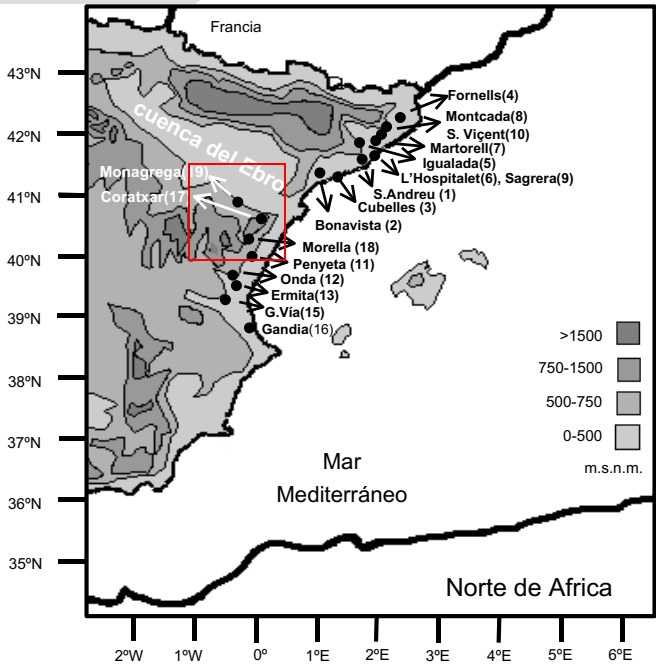


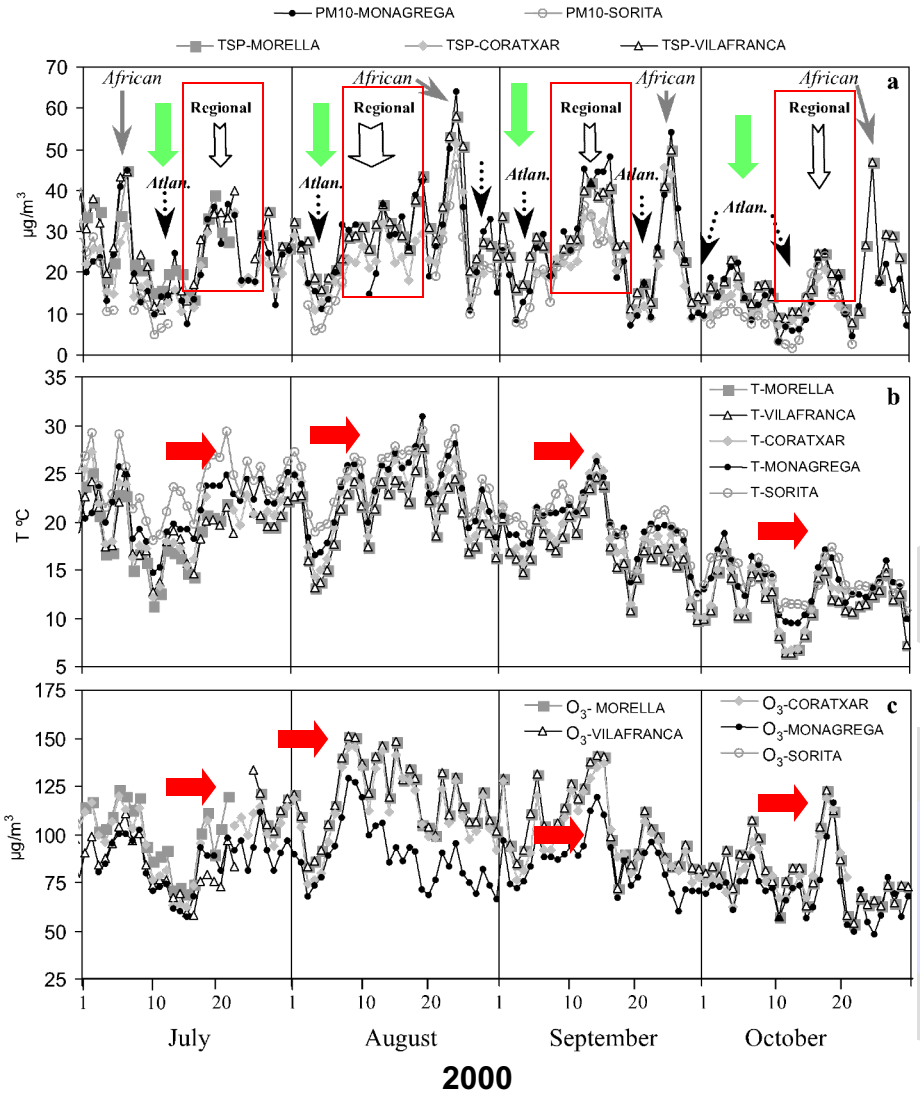




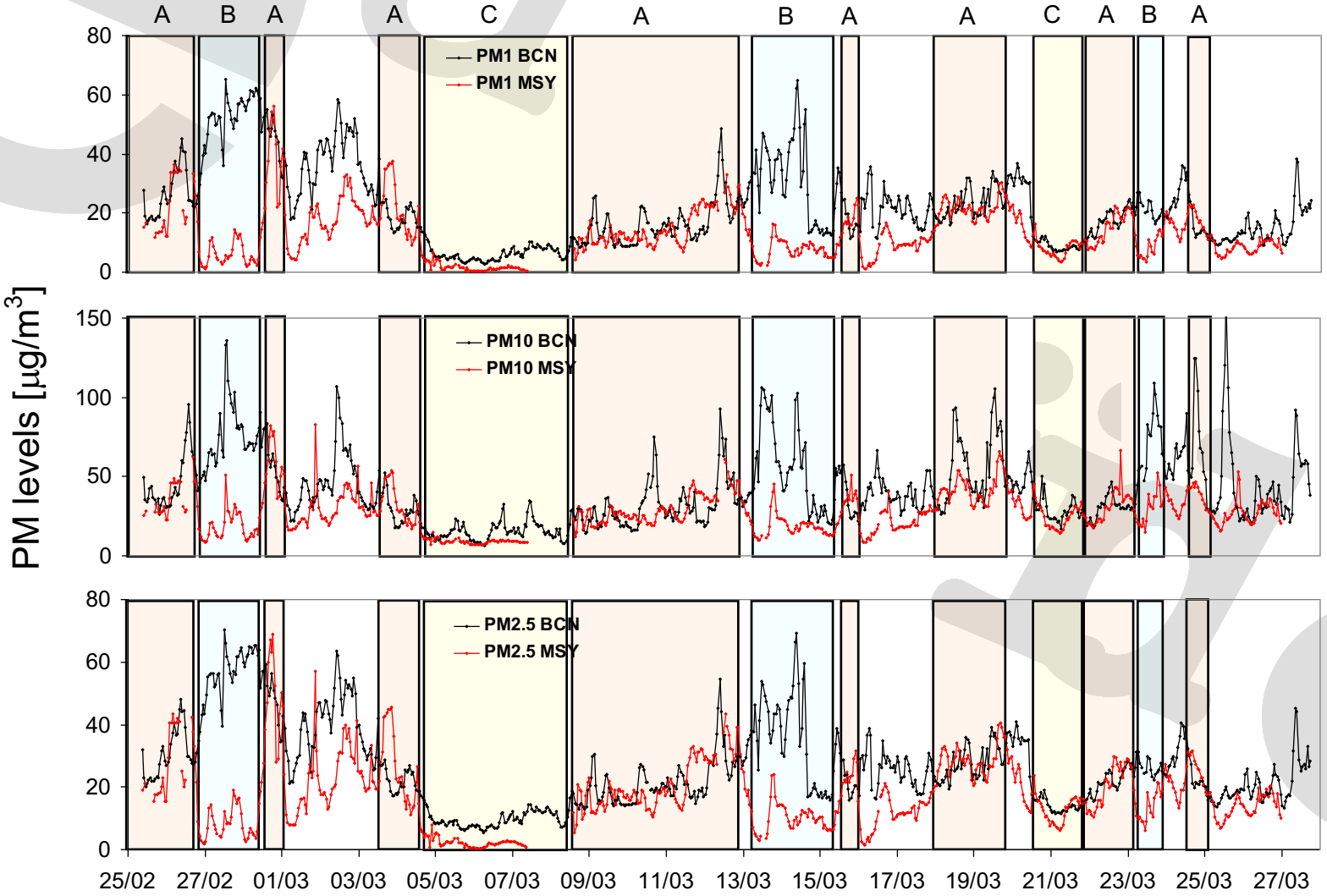


PM EPISODES W. MED: reg. recirculation



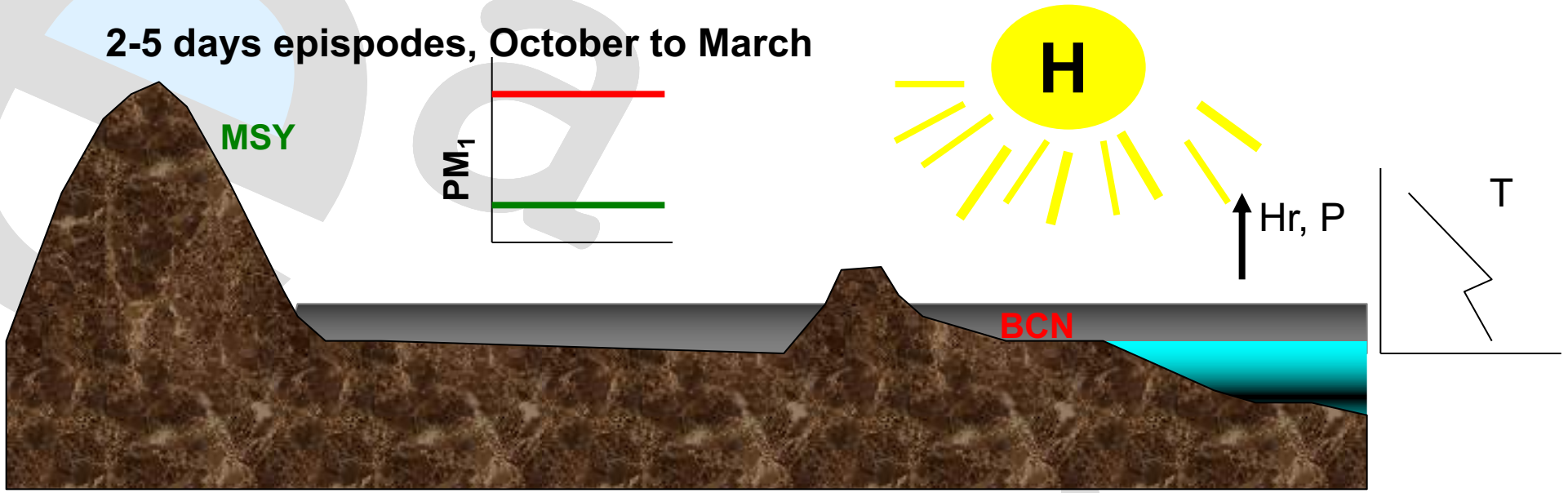


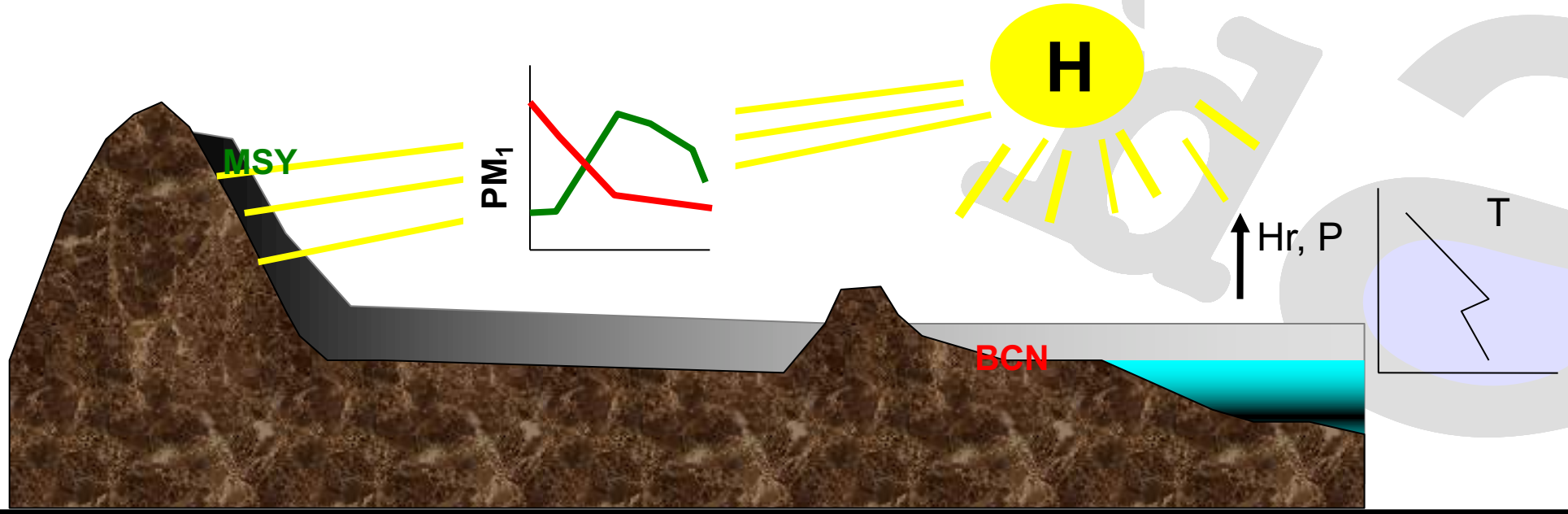
ANTICYCLONIC POLLUTION EPISODES (DAURE CAMPAIGN)



PM EPISODES W. MED: winter pollution

2-5 days epispodes, October to March

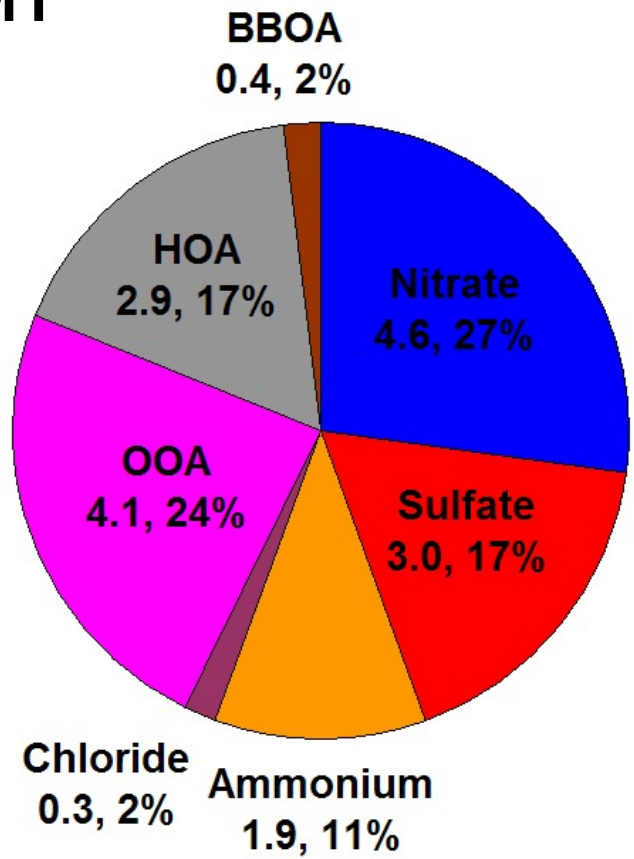




PM EPISODES W. MED: winter pollution

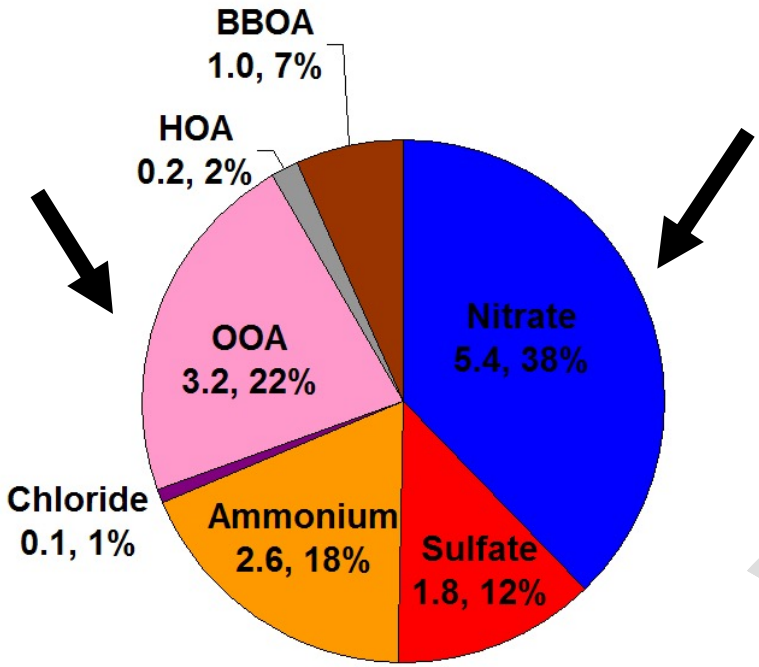
Total averages from 24/02/09 – 20/03/09

PM1



BCN ave. total =18.7 μg m^{-3}

BCN data from PSI (Mohr, DeCarlo, Heringa, Prevot et al.)

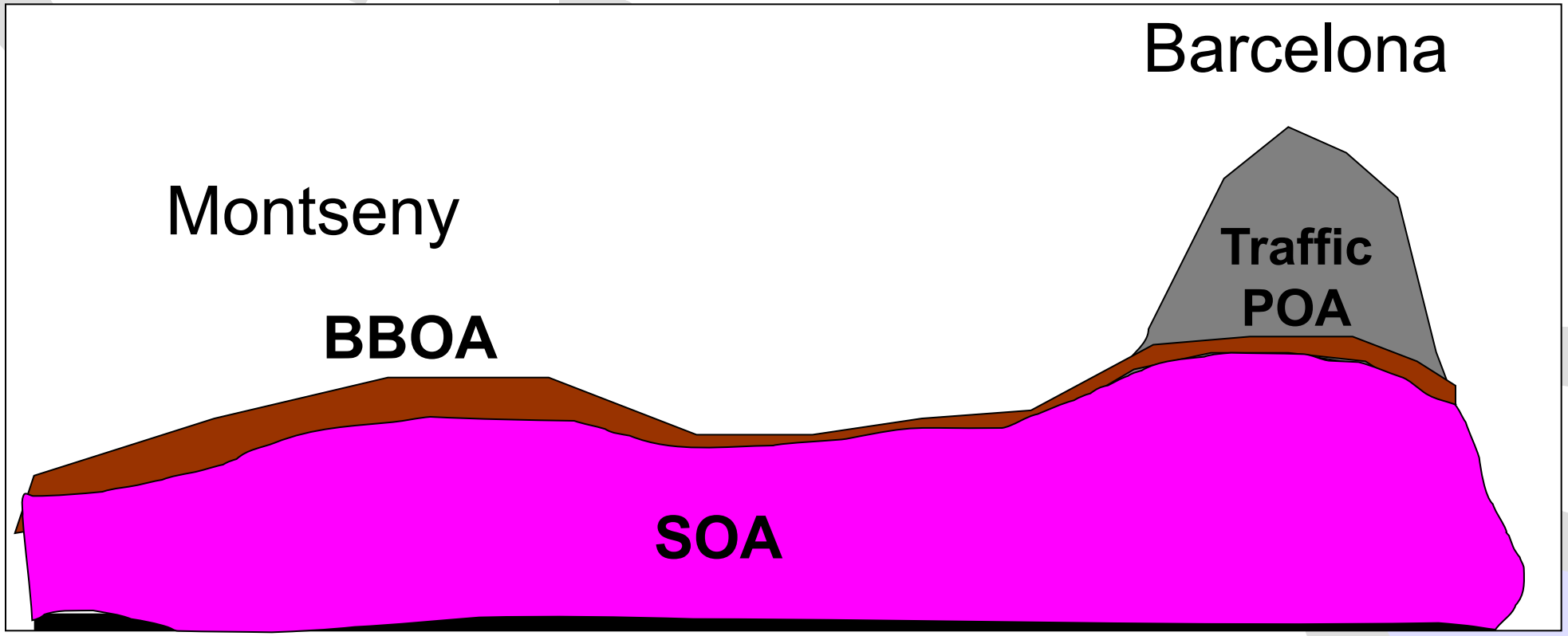


MSY ave. total =13.8 μg m^{-3}

MSY data from (Jimenez, Nemitz, et al.)

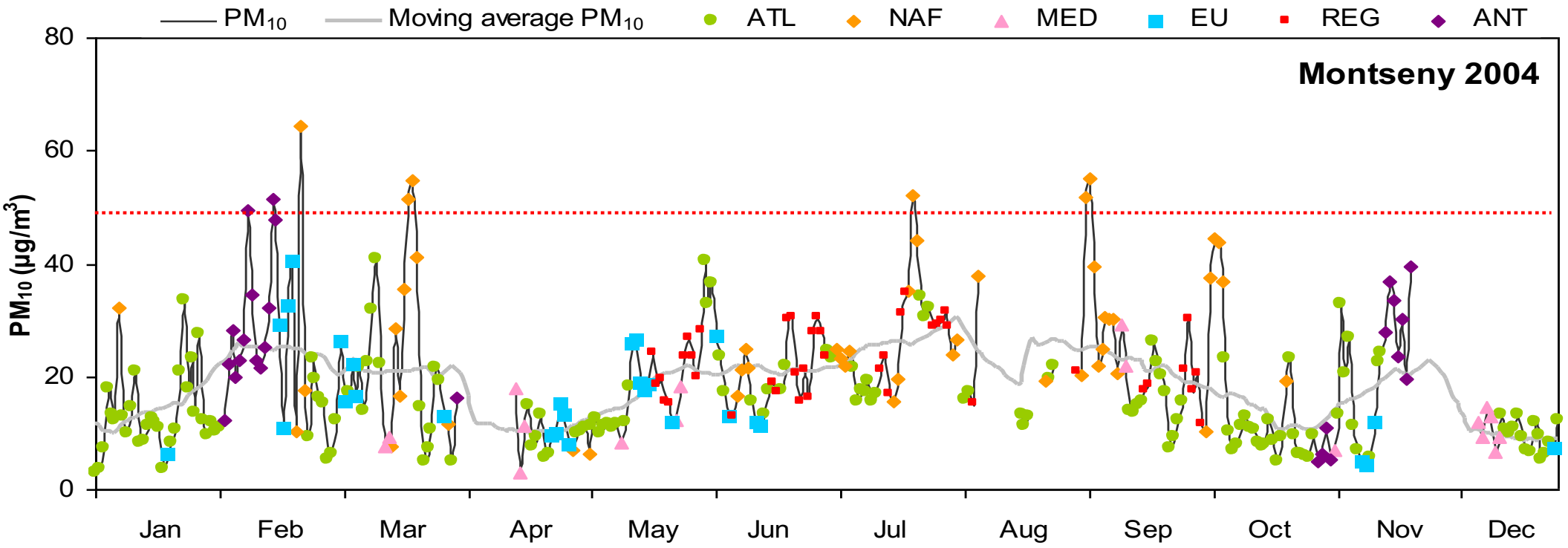
Courtesy: J.L. Jimenez, University of Colorado

PM EPISODES W. MED: winter pollution



Courtesy: J.L. Jimenez, University of Colorado

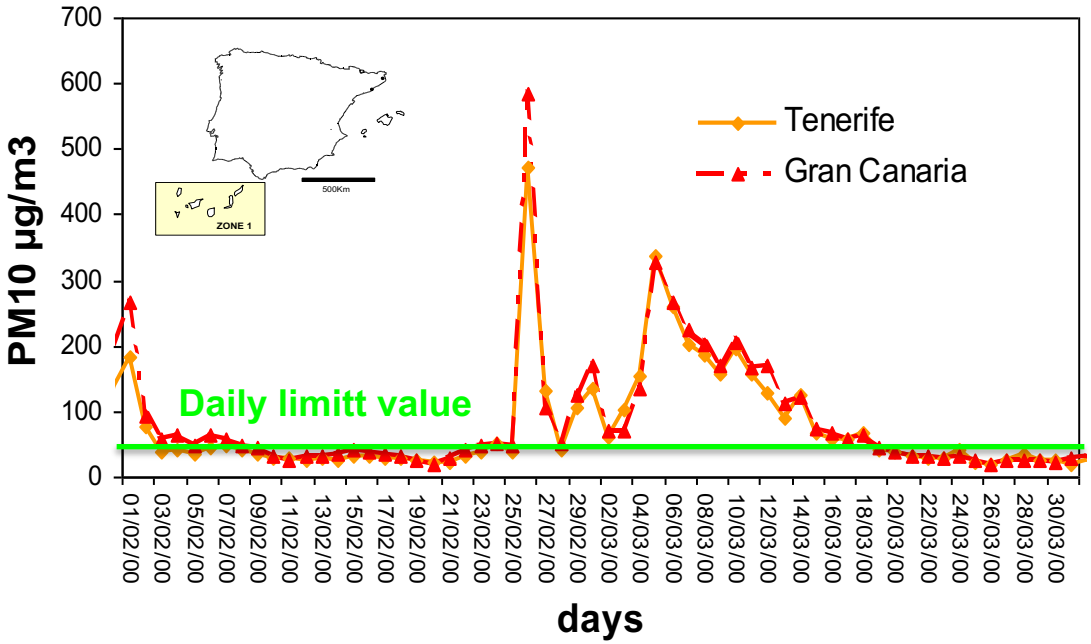
PM EPISODES W. MED: summary

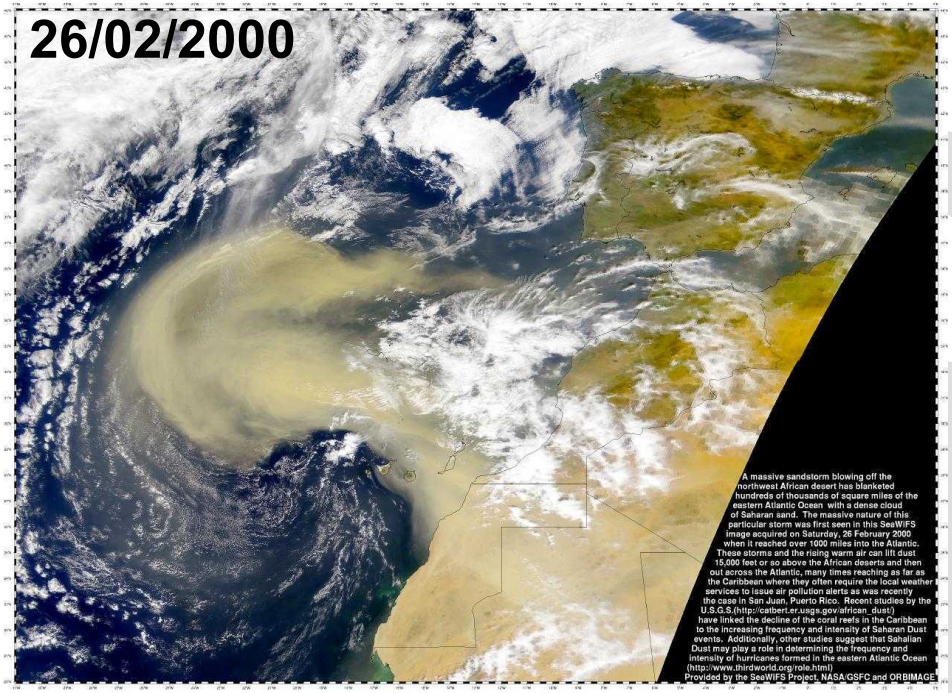


- TOOLS FOR DETECTION
- IBERIAN PROCEDURE
- HAVING IN MIND…
- OTHER APPLICATIONS

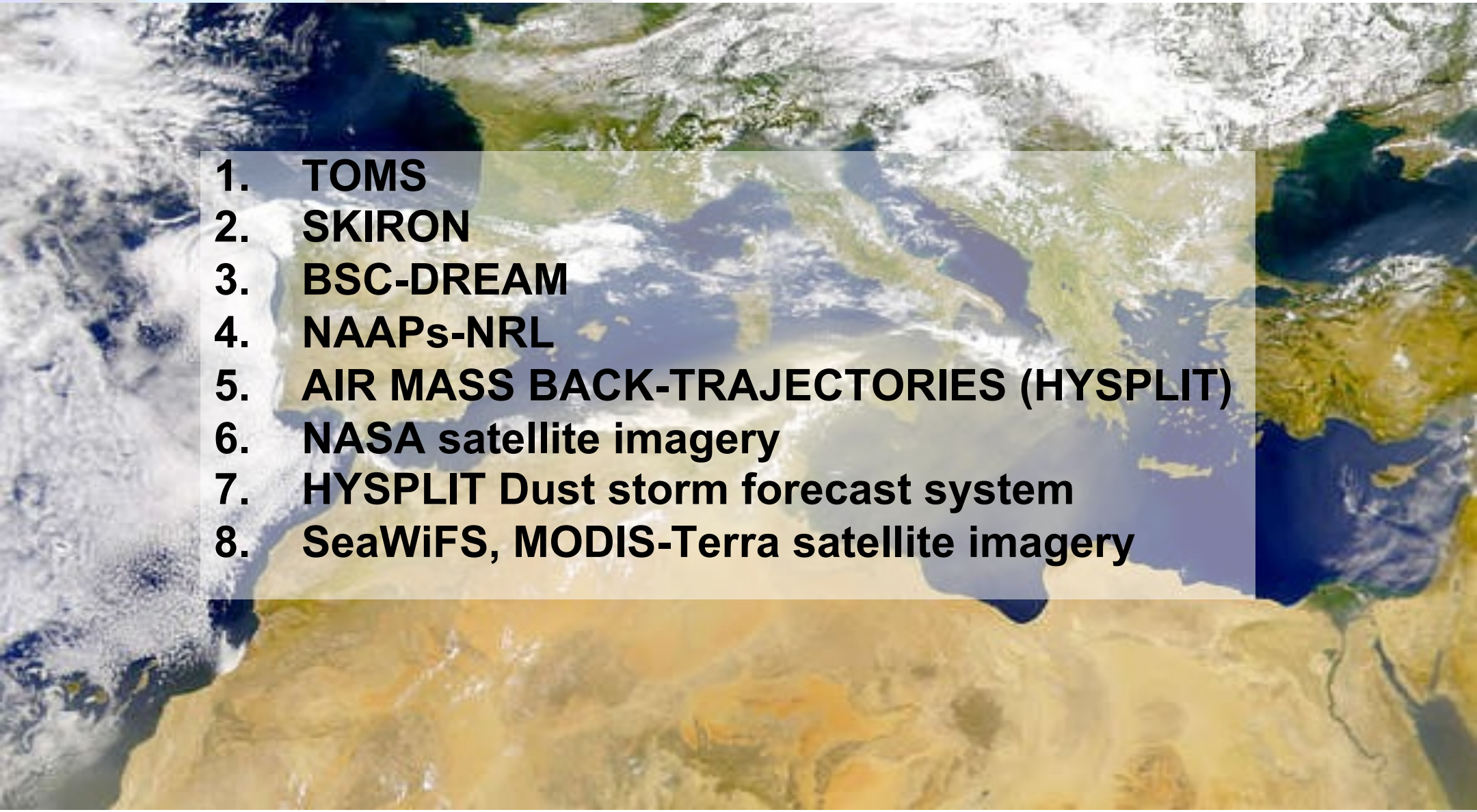
DUST OUTBREAKS

- **2008/50/CE Clean Air for Europe and Air Quality Directive, Article 2: (15) "contributions from natural sources" shall mean emissions of pollutants not caused directly or indirectly by human activities, including natural events such as volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high-wind events, sea sprays or the atmospheric resuspension or transport of natural particles from dry regions;**





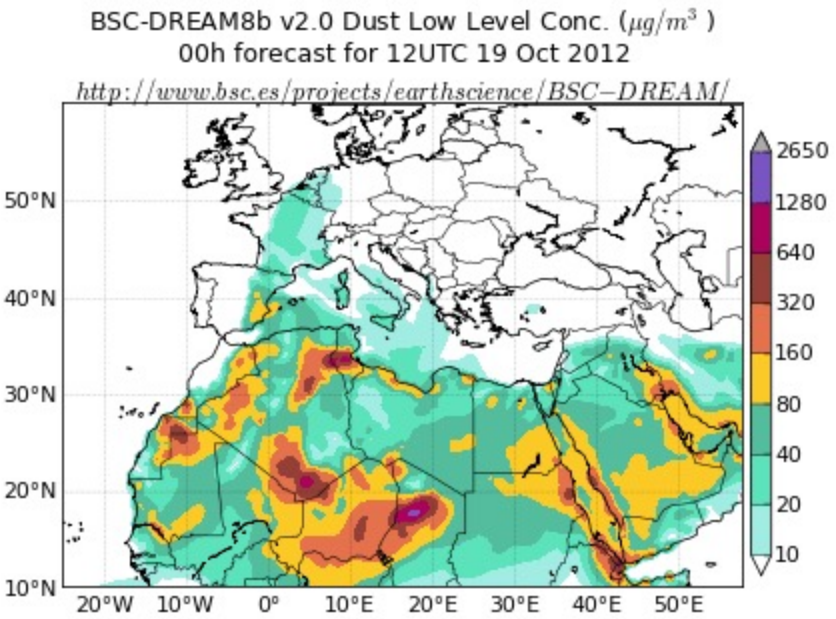
DUST OUTBREAKS: tools for detection

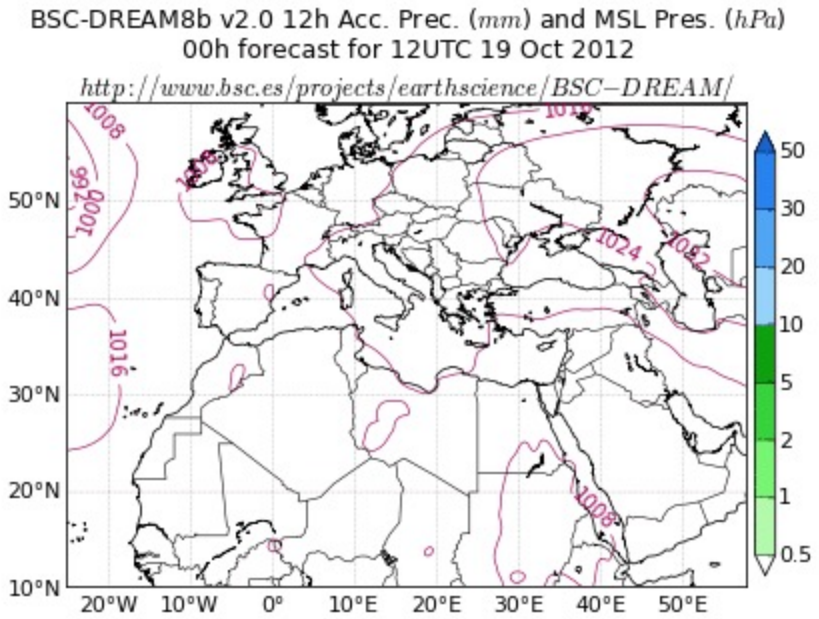


1. TOMS
2. SKIRON
3. BSC-DREAM
4. NAAPs-NRL
5. AIR MASS BACK-TRAJECTORIES (HYSPLIT)
6. NASA satellite imagery
7. HYSPLIT Dust storm forecast system
8. SeaWiFS, MODIS-Terra satellite imagery

DREAM-BSC

Surface dust concentration maps, free download from BSC

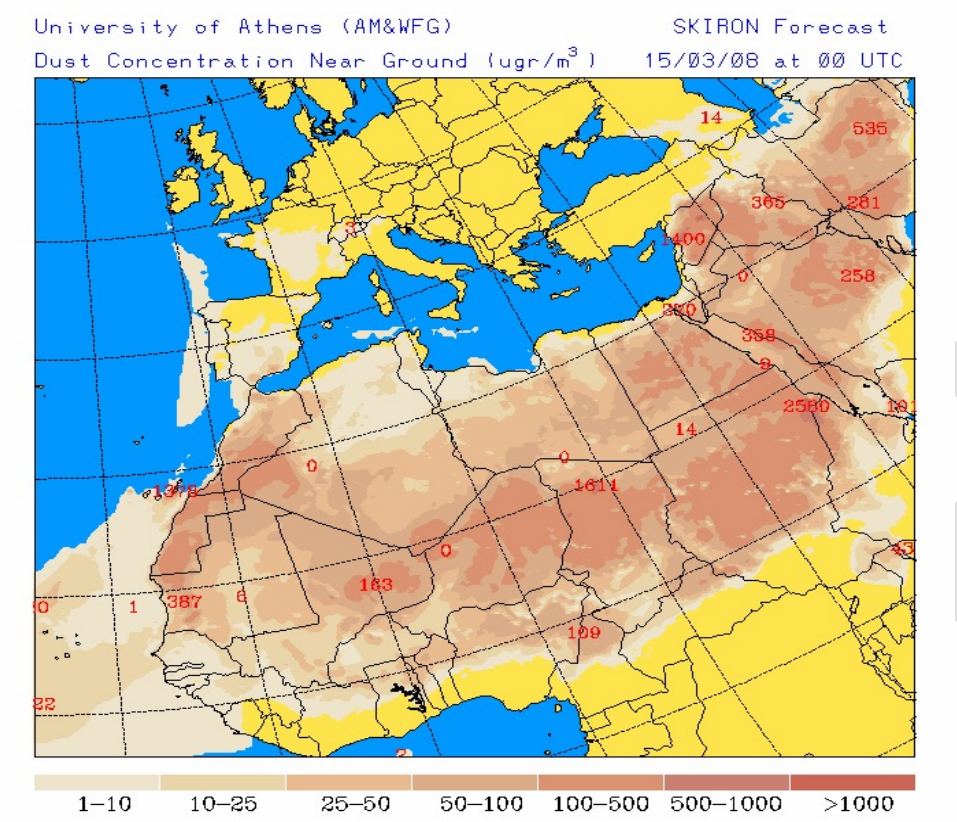




SKIRON simulations

Integrated dust load maps, free download from Athens University:

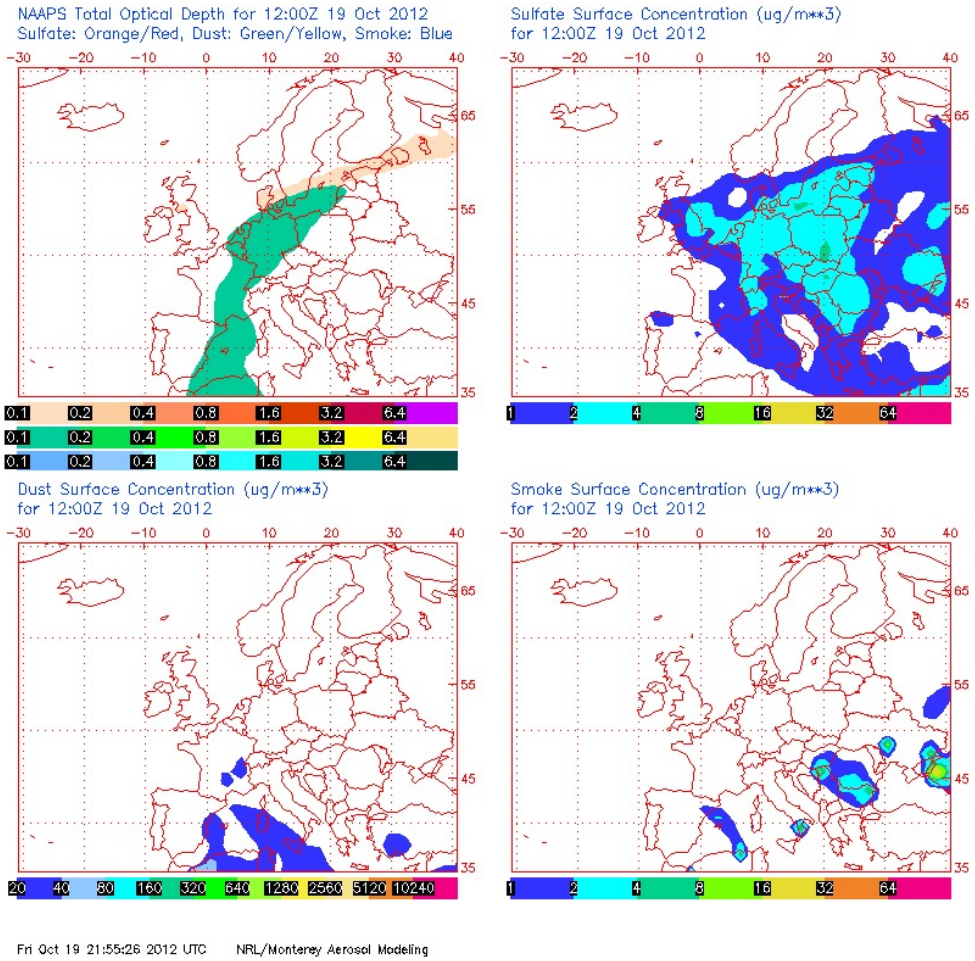
http://forecast.uoa.gr



NAAPS - NRL

Surface dust, sulfate and smoke concentration maps, free download from NRL:

http://www.nrlmry.navy.mil/aerosol/



IDENTIFICATION OF AFRICAN DUST OUTBREAKS

1. Reporting on the detection of episodes and measurement PM_{10} levels in EMEP-type sites:

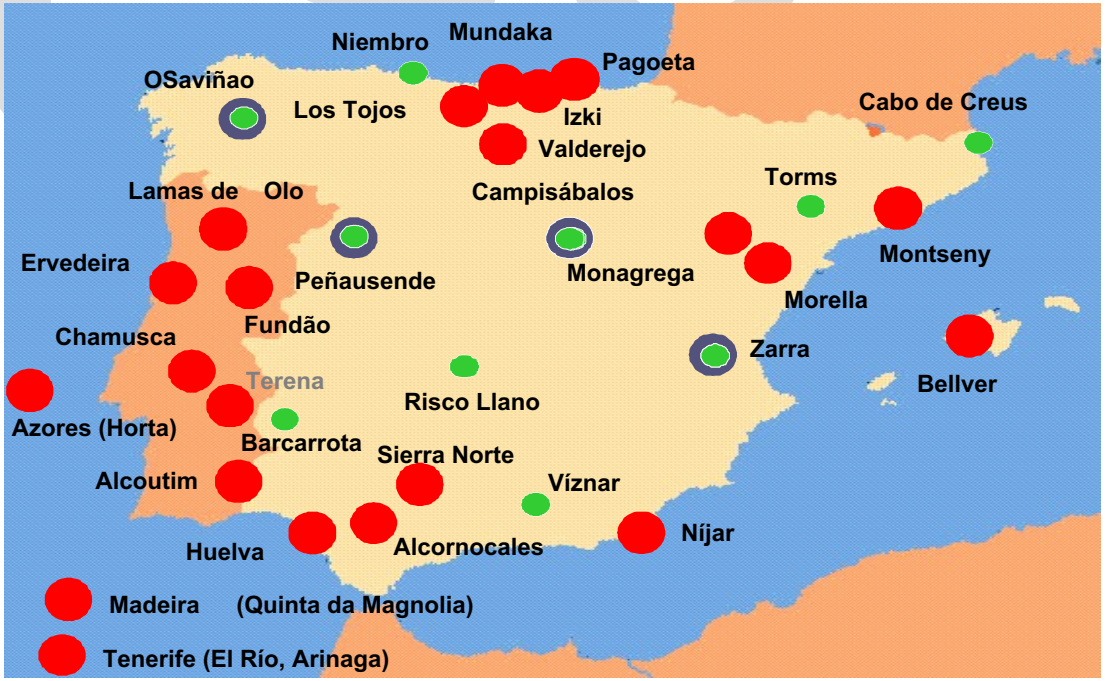
1.1. Modelling, meteo and satellite imagery tools

1.2. Daily evaluation of PM ambient concentrations recorded in a specific regional background monitoring network made of around 25 remote monitoring sites (Spain and Portugal)

1.3. Reporting on episodes detected and daily PM_{10} levels for each station of the regional background network

1.4. Three months after the end of the year a reporting on scientifically support the occurrence of each episode included in the list

ZONES AND MONITORING NETWORK

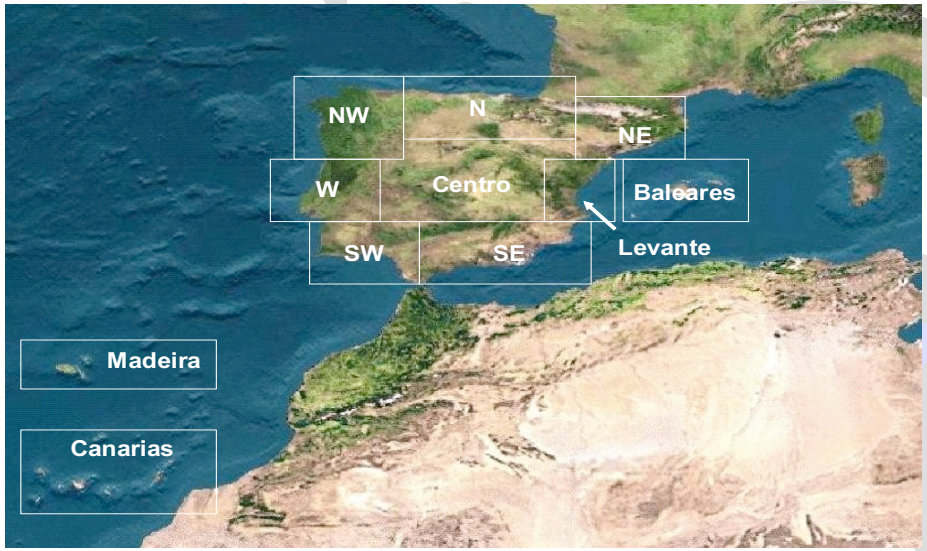


Other than EMEP

EMEP stations with real time measurements

EMEP station with gravimetric measurements

GOBIERNO DE ESPAÑA
MINISTERIO DE AGRICULTURA, ALIMENTACIÓN Y MEDIO AMBIENTE



DUST OUTBREAKS: Iberian procedure

List of episodes

ENERO 2012

ENERO 2012										
	CANARIAS (MADEIRA)	OESTE C. PORT	SUROESTE (S. PORT)	SURESTE	ESTE	CENTRO	NOROESTE (N. PORT)	NORTE	NORESTE	BALEARES
COMBUSTIÓN BIOMASA									9-11	
EUROPEO / SMOG										
AFRICANOS	3-6 9-16 18-21 30-31		25-26	25-27	26-27					

FEBRERO 2012

FEBRERO 2012										
	CANARIAS (MADEIRA)	OESTE C. PORT	SUROESTE (S. PORT)	SURESTE	ESTE	CENTRO	NOROESTE (N. PORT)	NORTE	NORESTE	BALEARES
COMBUSTIÓN BIOMASA			26-27	26-27	26-27	26-27	21-29		19 21	
EUROPEO / SMOG										
AFRICANOS	1 5-6 17 25-29		18	18						

MARZO 2012

MARZO 2012										
	CANARIAS (MADEIRA)	OESTE C. PORT	SUROESTE (S. PORT)	SURESTE	ESTE	CENTRO	NOROESTE (N. PORT)	NORTE	NORESTE	BALEARES
COMBUSTIÓN BIOMASA			28	28	28-31	1-3 28	1-3 9-16 25-31	15- 17 28	9-10 28 30-31	
EUROPEO / SMOG										
AFRICANOS	8-13 15-29		1 14-15 17 24-26 29	15 17 24-26	17 24-26	16-17 24-26	24-26	24- 26	24-26	18

QUANTIFICATION OF AFRICAN DUST TO PM LEVELS

2. Determining the natural contribution **'net dust load'** for each day of the list of African episodes

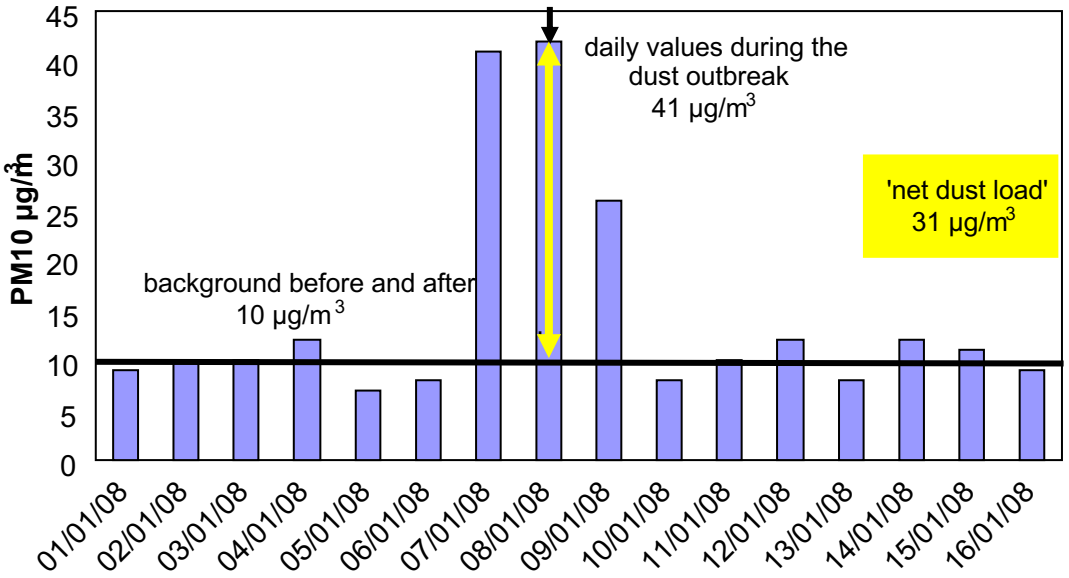
2.1. **Local-regional PM_{10} contribution (LRC, without African origin)** determined to be subtracted to the bulk PM_{10} levels during the episode

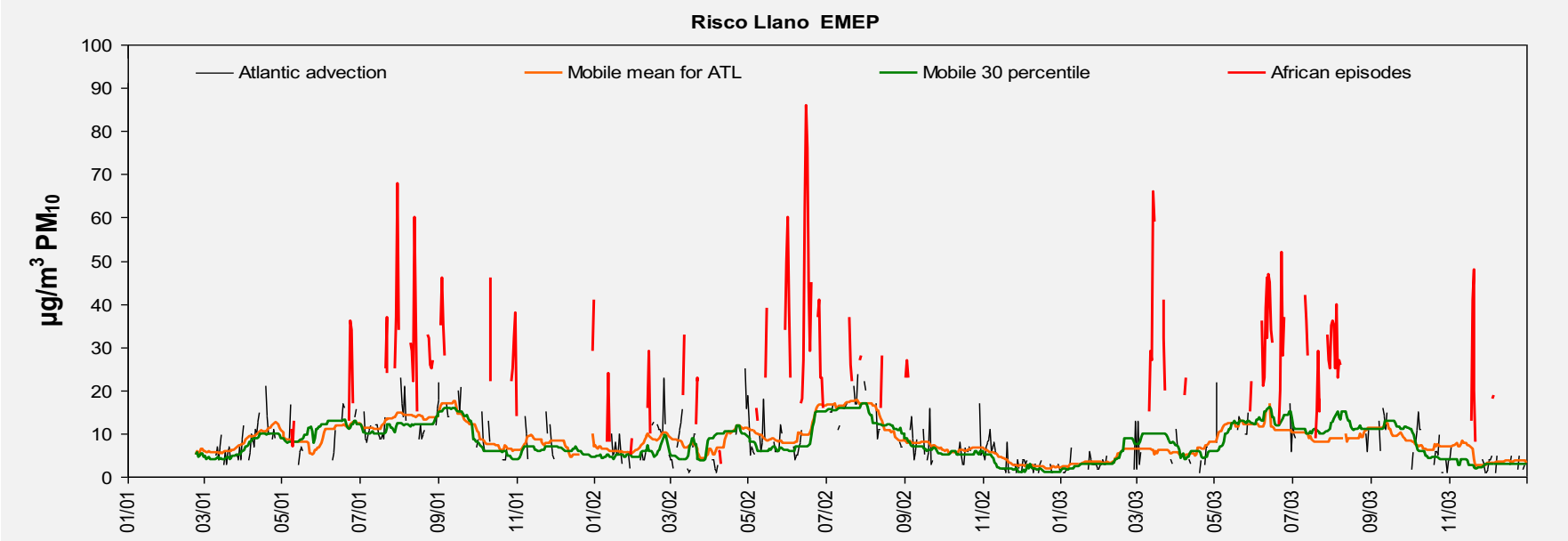
2.2. LRC daily calculated from monthly mobile **40 percentile** (centring the considered day in the middle of the month period) of the PM_{10} levels excluding the African days

2.3. Then '**net dust load**' for a given day with African dust influence in one regional background station is determined: PM_{10}-LRC

2.4. A list of 'net dust load' values for each day and regional background station is produced to be used to subtract the natural dust contribution to PM_{10} during days with exceedances of the DLV recorded at the AQ monitoring sites close to this specific regional background station. The **list** is **produced by the Ministries of the Environment from Portugal and Spain**

DUST OUTBREAKS: Iberian procedure





DUST OUTBREAKS: Iberian procedure

	S. Norte	Barcarrota	Huelva	Alcotium	Viznar	Nijar	
01/03/2005	7	6	6	6			5
02/03/2005	9	9	12	14			8
03/03/2005	9	8	16	10		8	12
04/03/2005	7	9	9	14			4
05/03/2005	12	10	8	11		8	9
06/03/2005	11	8	7	10		7	10
07/03/2005	11	9	8	15		5	9
08/03/2005	14		16	17		13	11
09/03/2005	14	18	15	18		14	12
10/03/2005	16	18		21		17	18
11/03/2005	17	22	34	41		23	21
12/03/2005	59	54	56	15		65	19
13/03/2005	31	13	22	9		23	39
14/03/2005	11	10	20	21		46	41
15/03/2005	25	27	24	56		44	36
16/03/2005	34	48	40	44		39	27
17/03/2005	32	47	31	52		36	28
18/03/2005	36	55	38	73		43	30
19/03/2005	86	181	60	128		191	35
20/03/2005	114	96	86	32		147	56
21/03/2005	96	21	21	15		81	101
22/03/2005	11	11		9		10	37
23/03/2005	12	7				11	28
24/03/2005	8	10				10	20
25/03/2005	12	10				7	22
26/03/2005	11	17				6	33
27/03/2005	13	14				10	25
28/03/2005	14	10			12	11	23
29/03/2005	13	11	18	15		8	30
30/03/2005	9	5	12	21		15	18
31/03/2005	11	11	16	23		22	16

Net dust contribution for each area

S. Norte	Barcarrota	Huelva	Alcotium	Viznar	Nijar	
6	12	25	31	15		11
48	44	45	5	56		8
21				13		27
0				36		29
14	17	11	42	34		20
23	38	25	30	29		9
21	37	15	38	26		11
24	45	23	58	33		13
75	171	45	113	180		17
103	76	71	18	136		38
85	11	5	0	69		83

Net dust contribution may also be ‘0’
If dust outbreak is weak at surface levels

Days with African dust outbreaks

MANAGMENT OF AFRICAN DUST IN A.Q. NETWORKS

3. **The AQ monitoring networks** compile a list of dates with exceedances of the DLV coinciding with the African dust outbreaks from the report by the **Ministry of the Environment**.

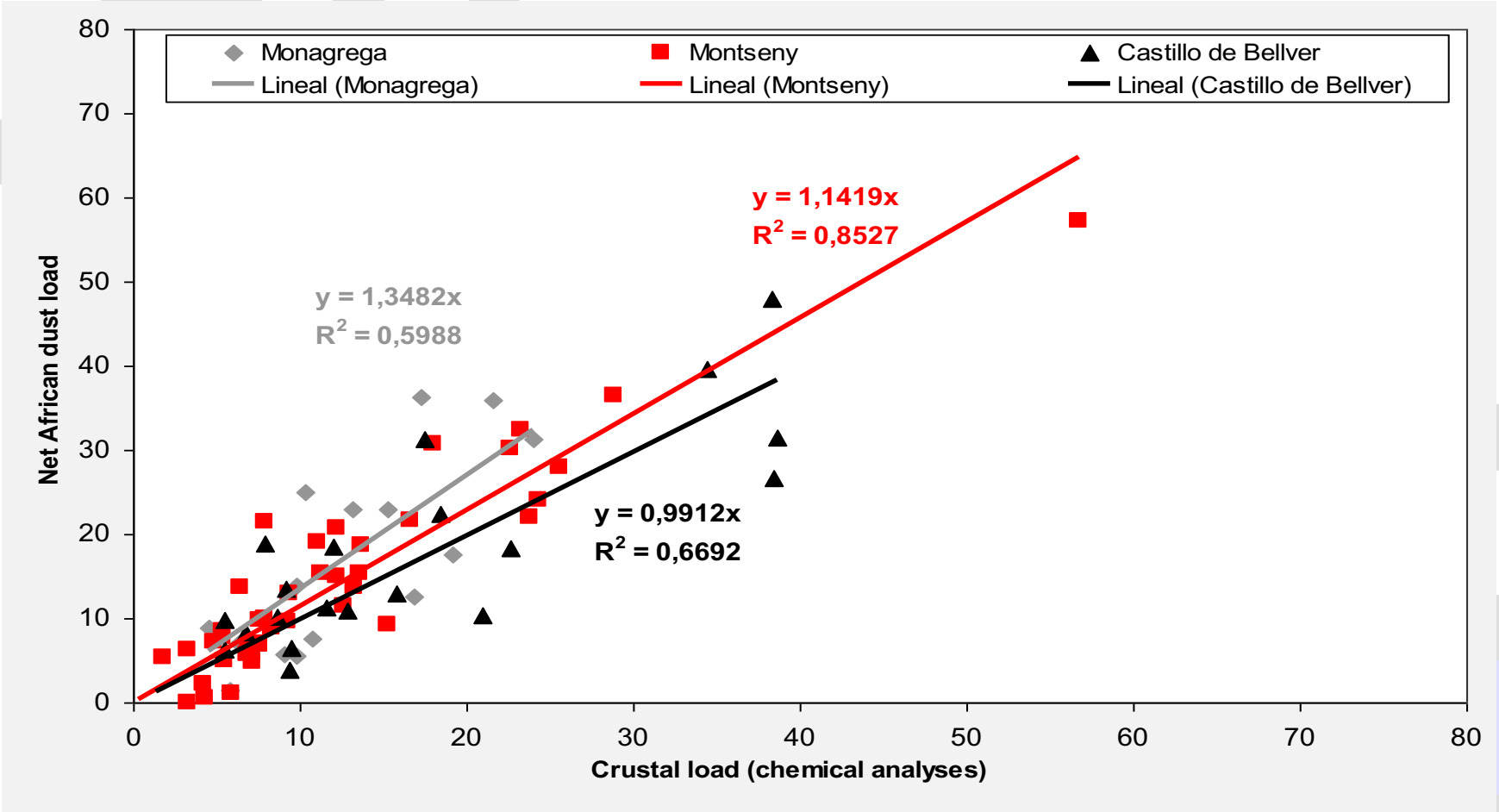
4. The 'net PM_{10} dust contribution' for the closest regional background site is subtracted from the PM_{10} levels of list produced in task 3 to discount the natural contribution

5. If after subtraction, the PM_{10} levels are < DLV (50 $\mu g/m^3$) then the exceedance will be attributed to the natural contribution, otherwise will be attributed to anthropogenic causes

6. PM_{10} levels of the days where the exceedances was attributed to natural contributions are not included in the annual average.

7. The AQ monitoring networks reports on:
7.1. Mean average PM_{10} and total number of exceedances
7.2. List of exceedances attributed to natural contributions (exceedances are not deleted!!!)
7.3. Calculated dust contribution to the annual mean (from the difference of the annual mean-annual mean with the subtractions of the calculated daily net dust loads).

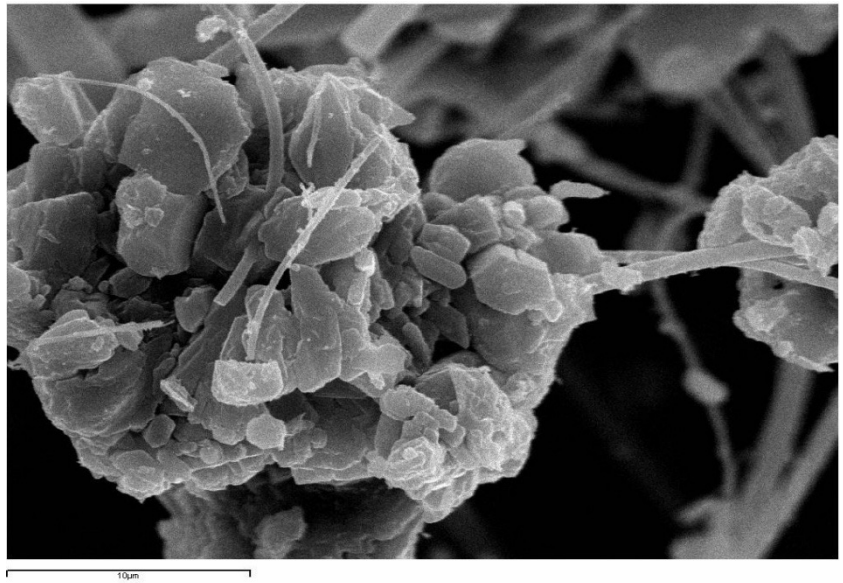
Validation of the method

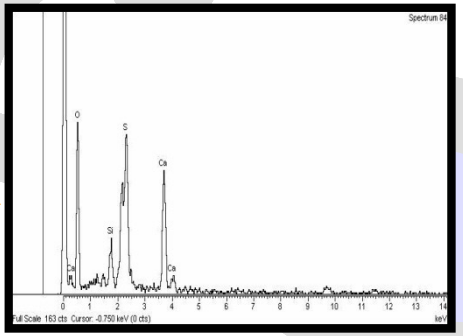


Additional considerations

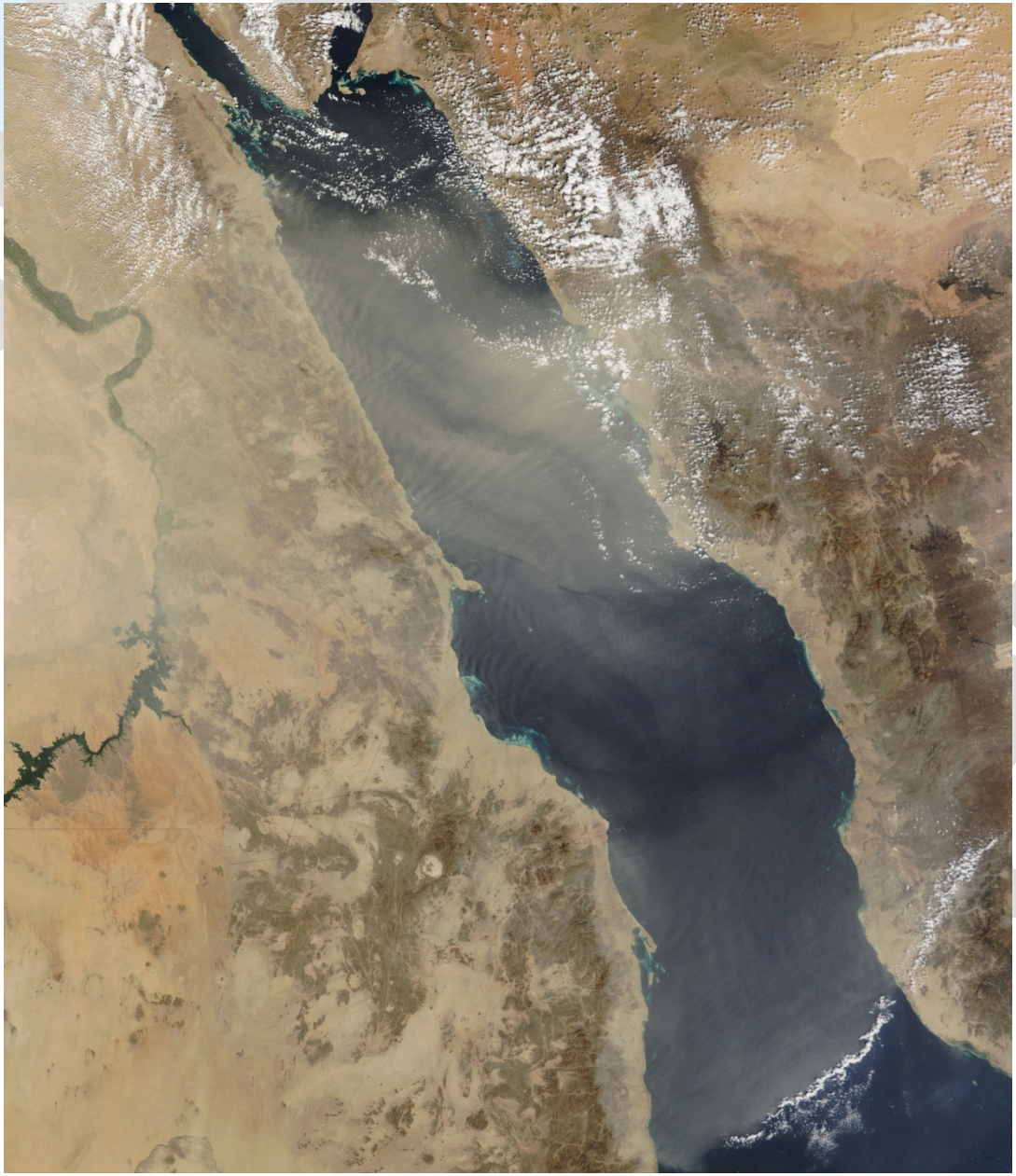
• Some African episodes finish with stagnation conditions. If up to 2 days after the episode levels are still high in EMEP-type stations, it is still considered African episode

• African dust my enhance the levels of PM not only by mass contributions but by catalysing secondary aerosol formation by interacting with gaseous precursors. This may be important in terms of mass contribution but is not taken into account in the procedure





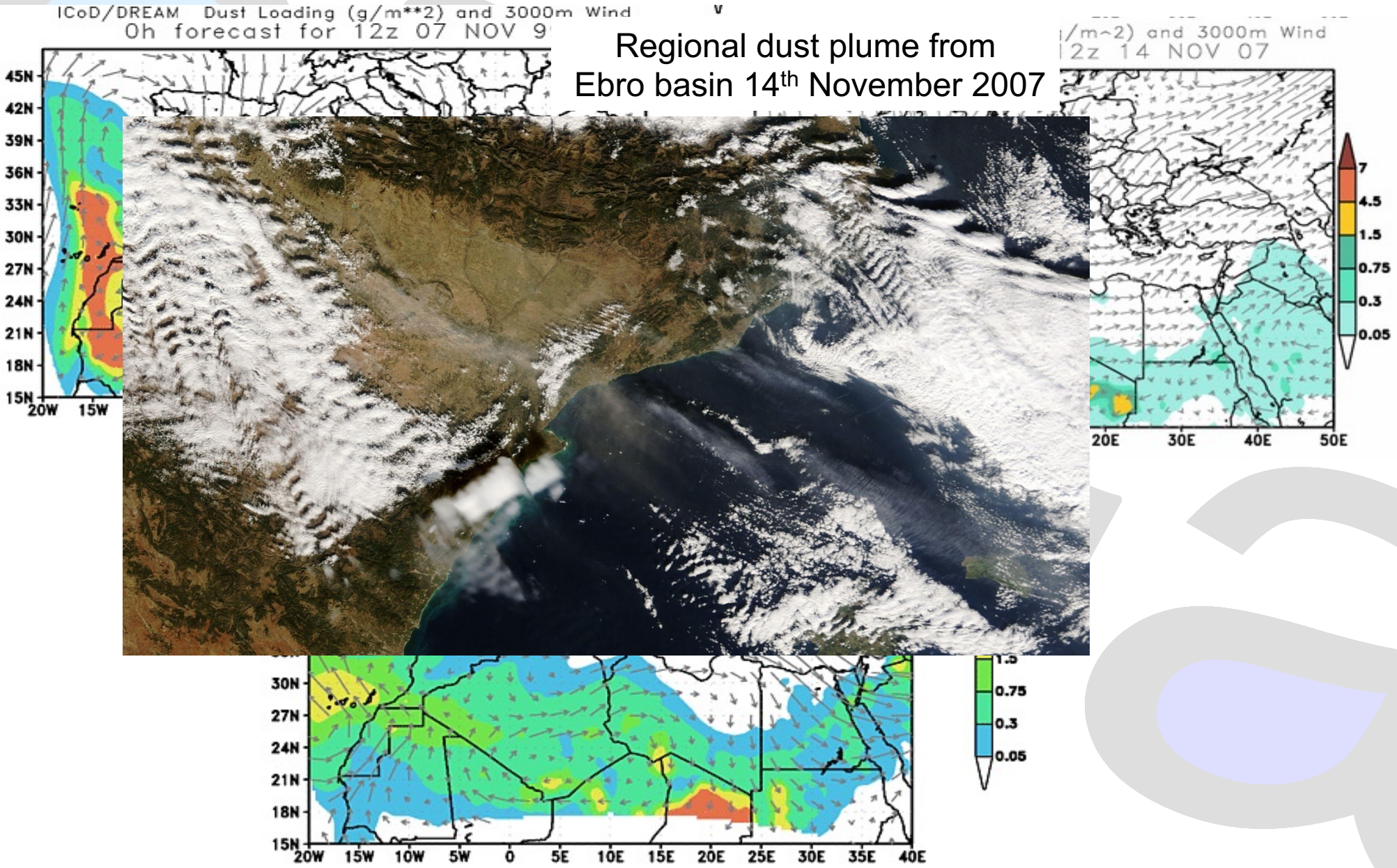
DUST OUTBREAKS: having in mind...



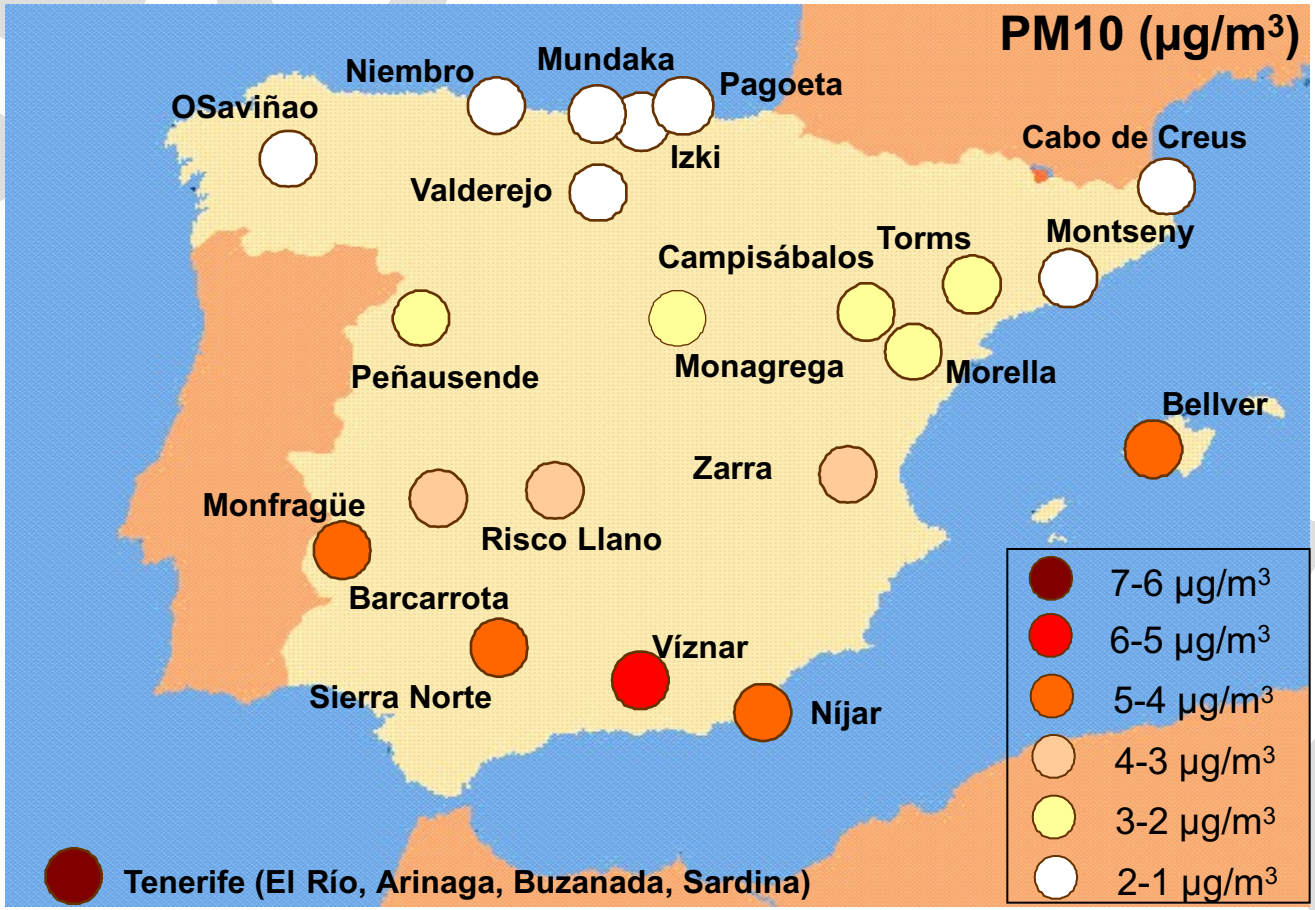
NASA- TERRA satellite
26th February 2010

DUST OUTBREAKS: having in mind...

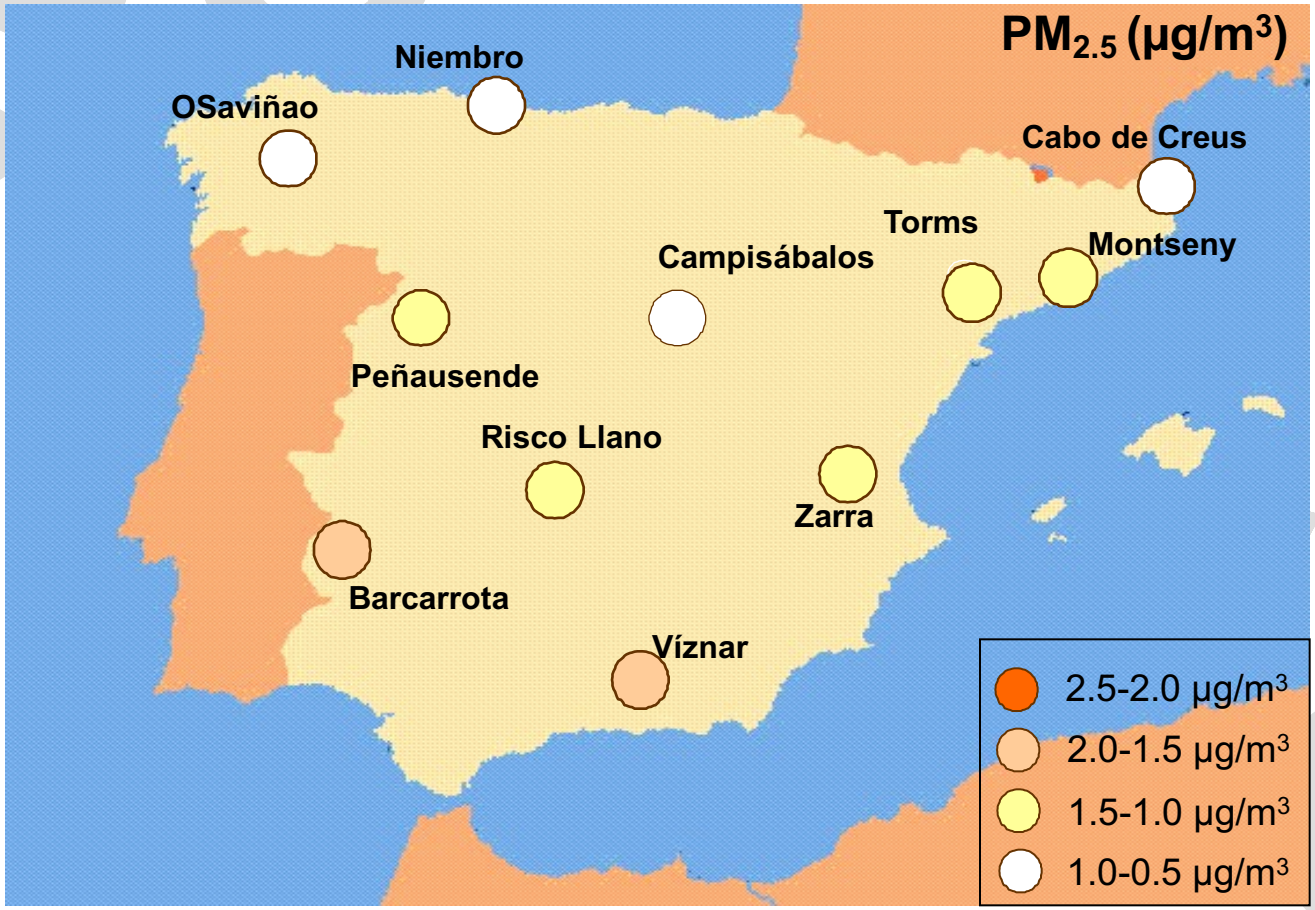
Regional dust plume from Ebro basin 14th November 2007



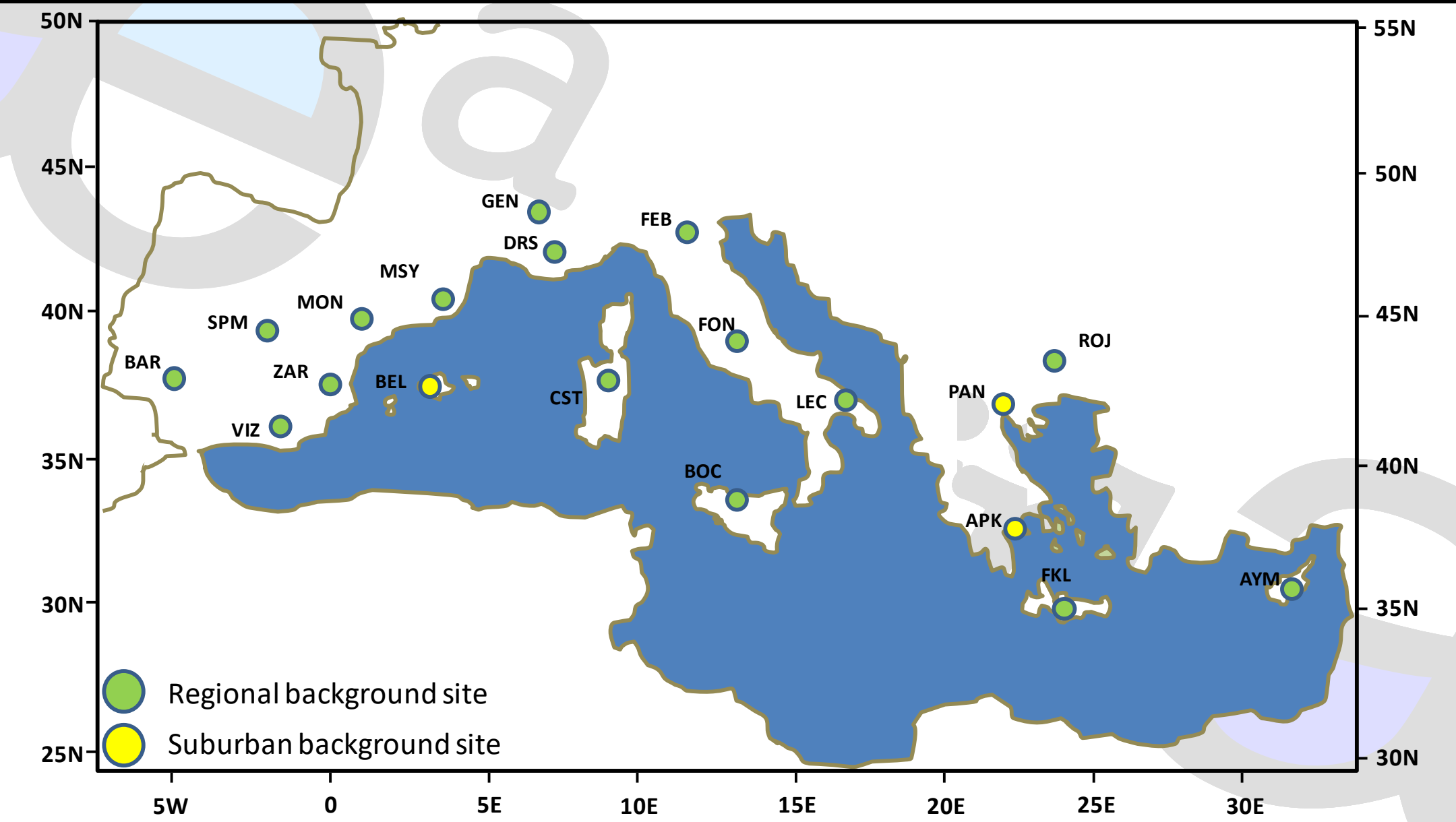
African dust contributions to the annual PM_{10} mean levels



African dust contributions to the annual $PM_{2.5}$ mean levels



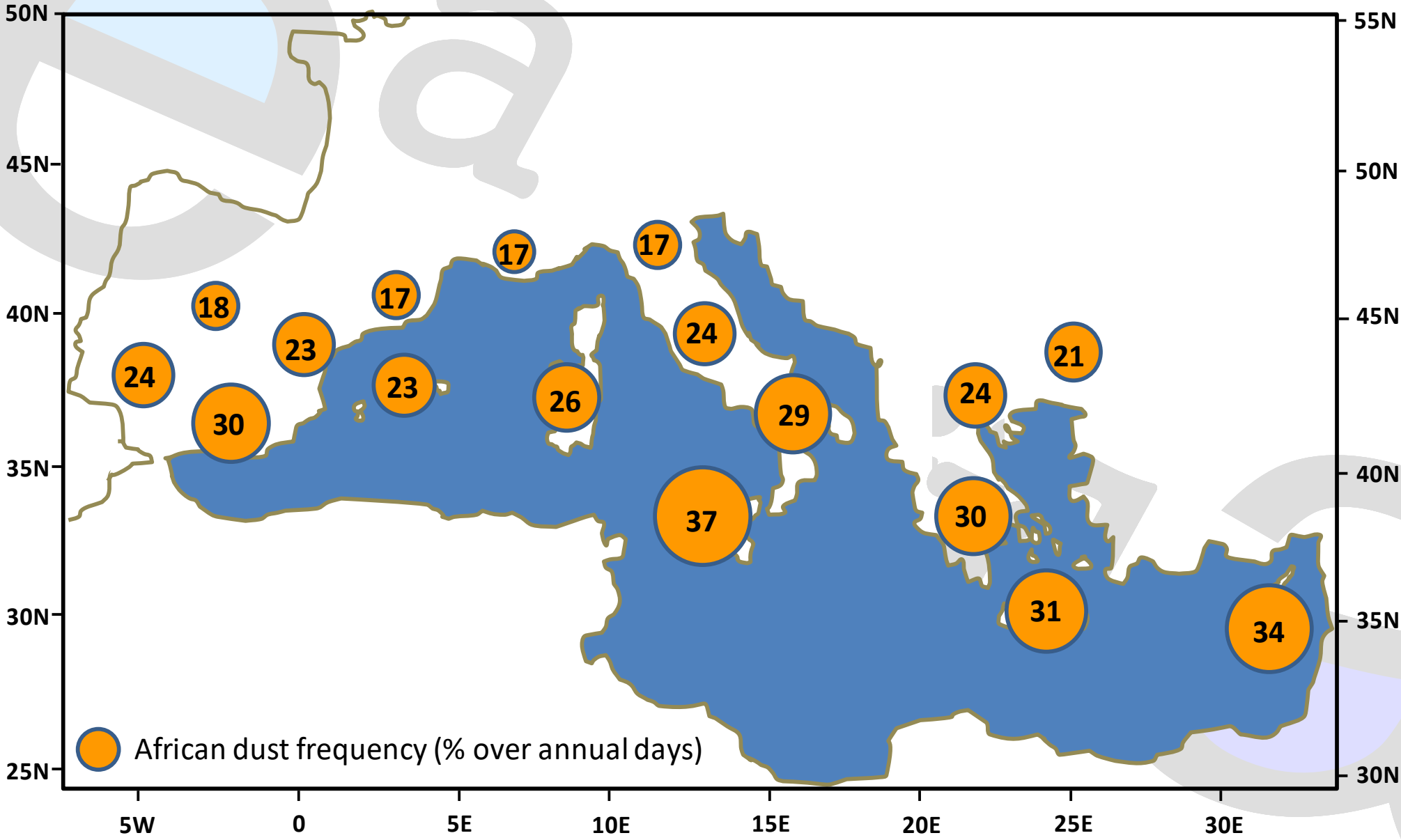
DUST OUTBREAKS: other applications



www.atmos-chem-phys-discuss.net/12/28195/2012/

Pey et al., 2012 ACPD, 12, 28195-28235

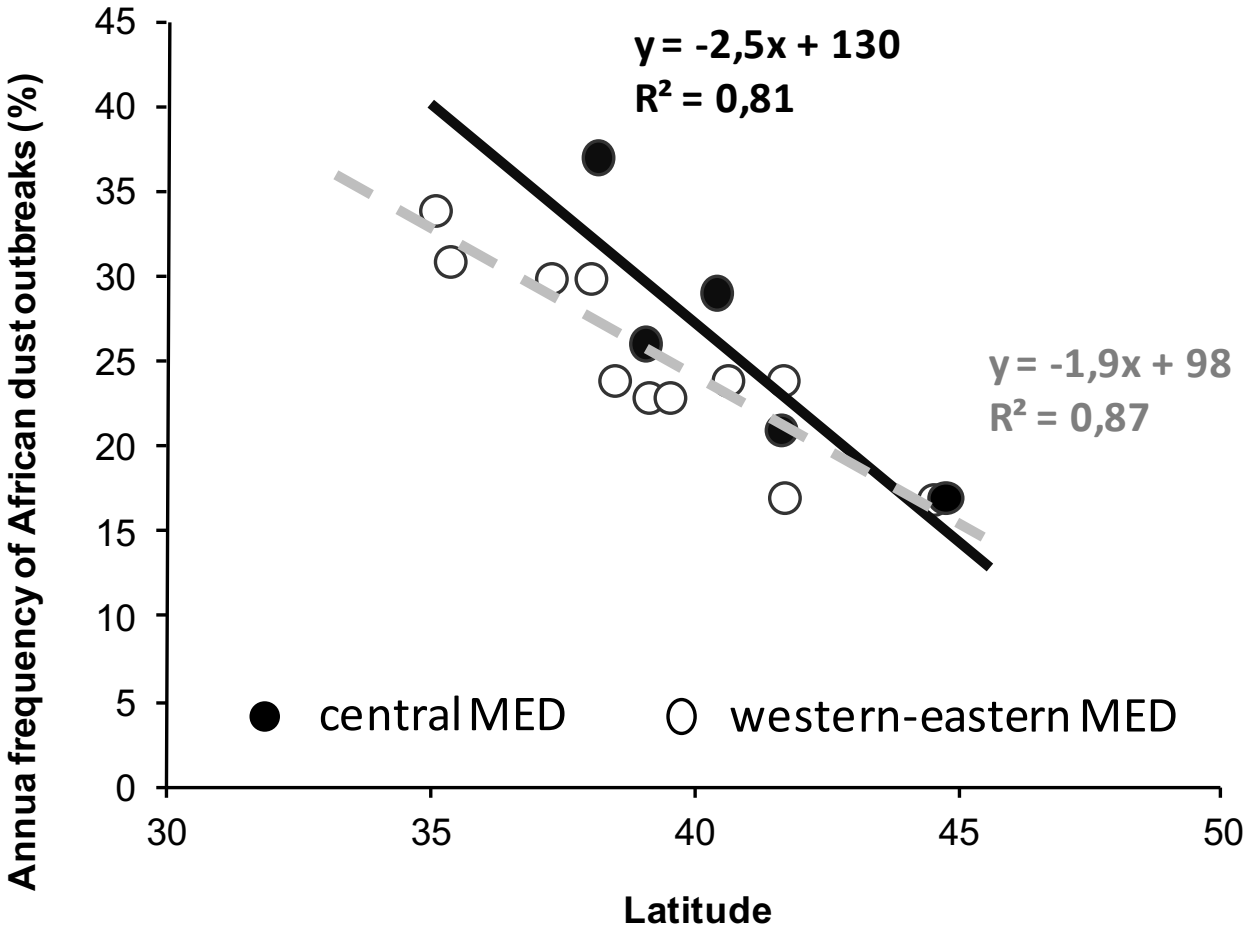
DUST OUTBREAKS: frequency



www.atmos-chem-phys-discuss.net/12/28195/2012/

Pey et al., 2012 ACPD, 12, 28195-28235

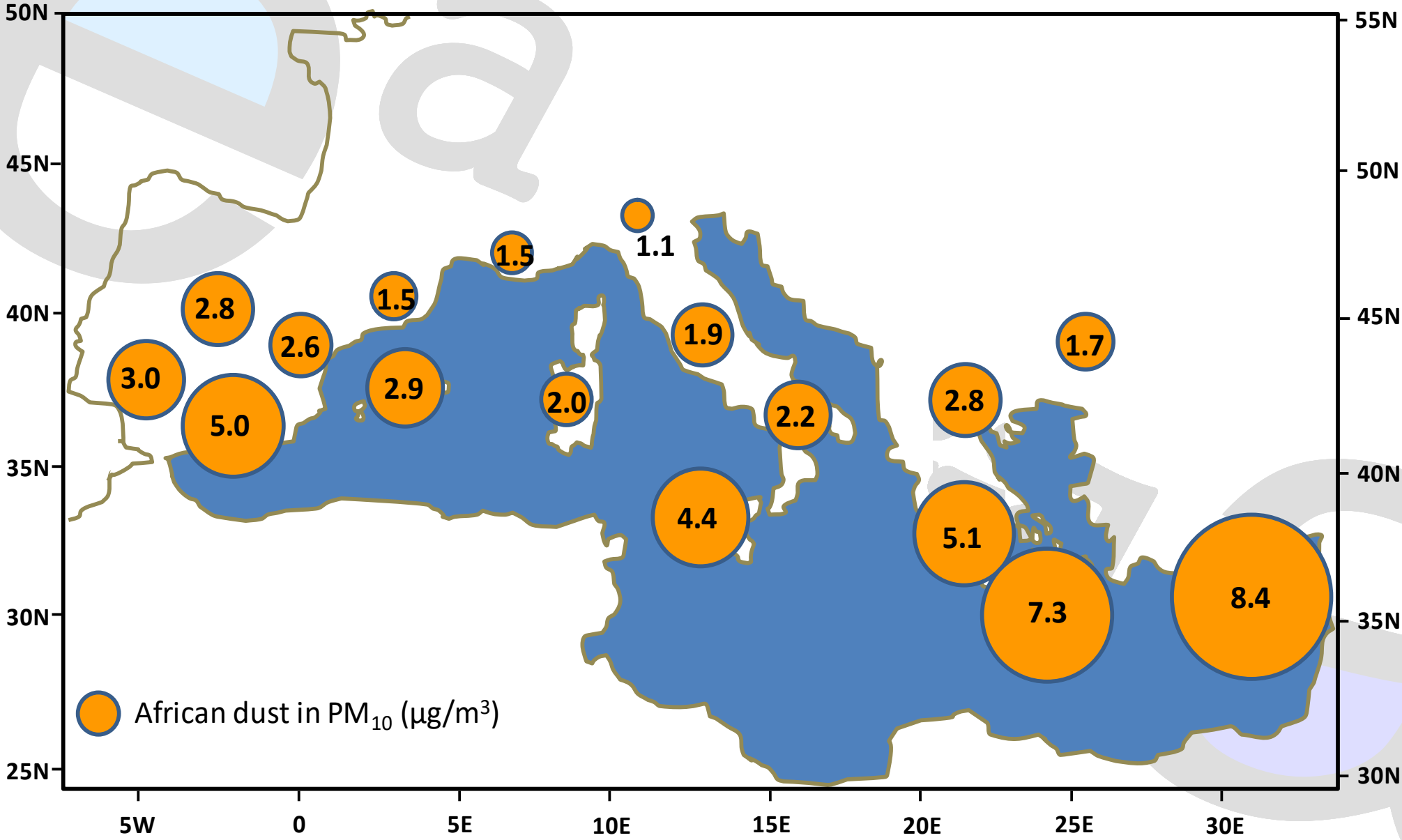
DUST OUTBREAKS: frequency-latitude



www.atmos-chem-phys-discuss.net/12/28195/2012/

Pey et al., 2012 ACPD, 12, 28195-28235

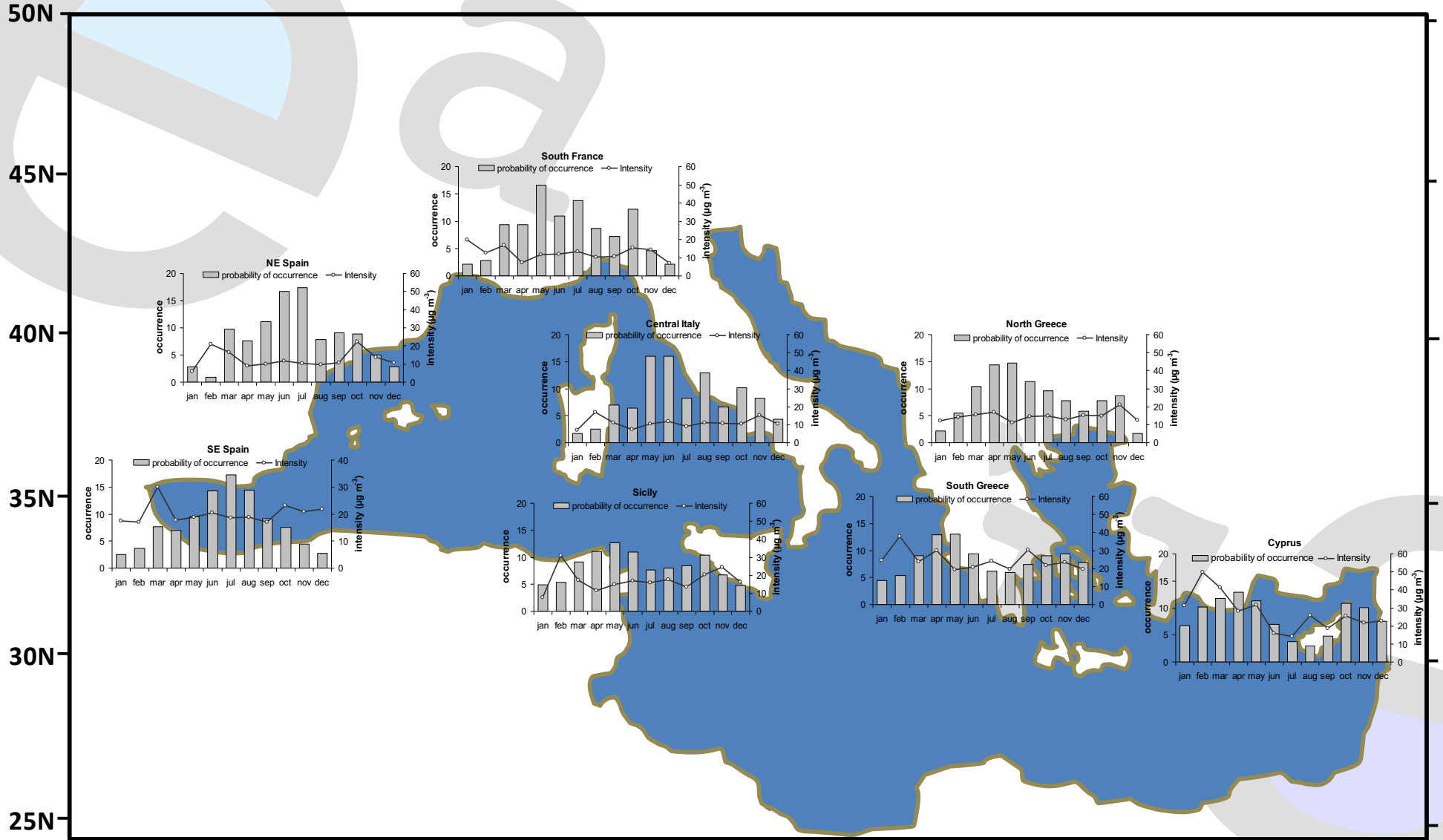
DUST OUTBREAKS: dust in PM10



www.atmos-chem-phys-discuss.net/12/28195/2012/

Pey et al., 2012 ACPD, 12, 28195-28235

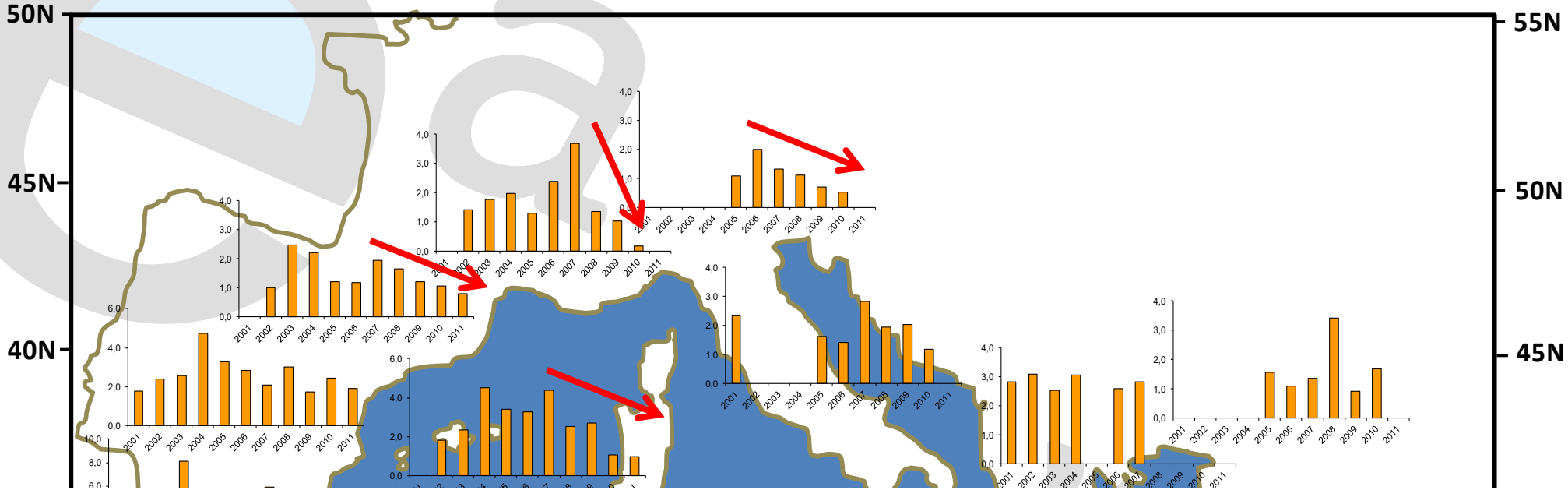
DUST OUTBREAKS: occurrence-intensity

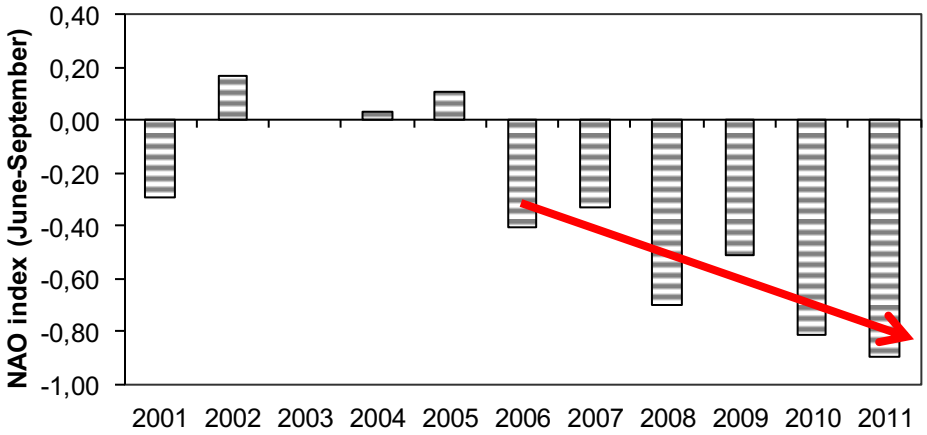


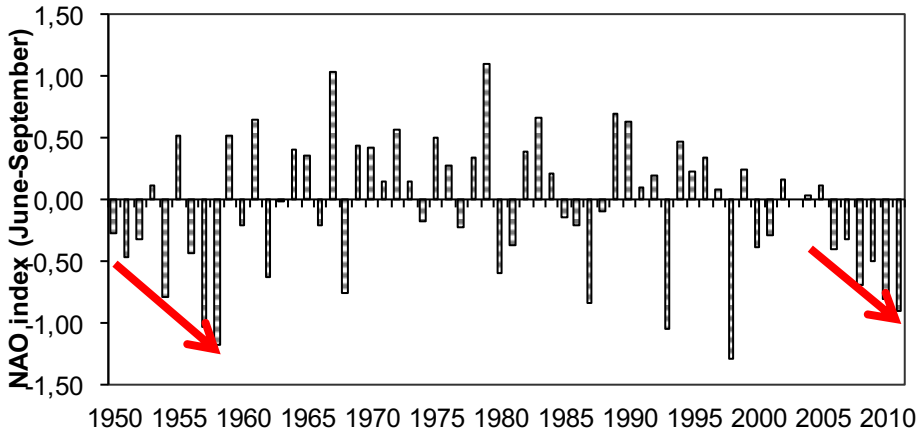
www.atmos-chem-phys-discuss.net/12/28195/2012/

Pey et al., 2012 ACPD, 12, 28195-28235

DUST OUTBREAKS: trends







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THANKS FOR YOUR ATTENTION!!