Inorganic tracers of source pollution of PM

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Particulate matter and health in 2020, Are we on the right track?, Brussels, March 13, 2008

CSIC

COST ACTION 633
Particulate Matter:
Properties Related to Health Effects

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Outline

- PM and sources
- Tracers of pollution sources
  - Levels-time variation
  - Spatial variation
  - Physical tracers (size)
  - Mineralogy and morphology
  - Chemical tracers
- Main applications
- Conclusions

PM is made of a complex (and sometimes reactive) mixture of different components emitted by different sources, especially in the urban environment

Components of PM

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

The PM mixture and interaction

Natural Background

- Marine aerosols
- Natural minerals
- Bioaerosols + biogenic

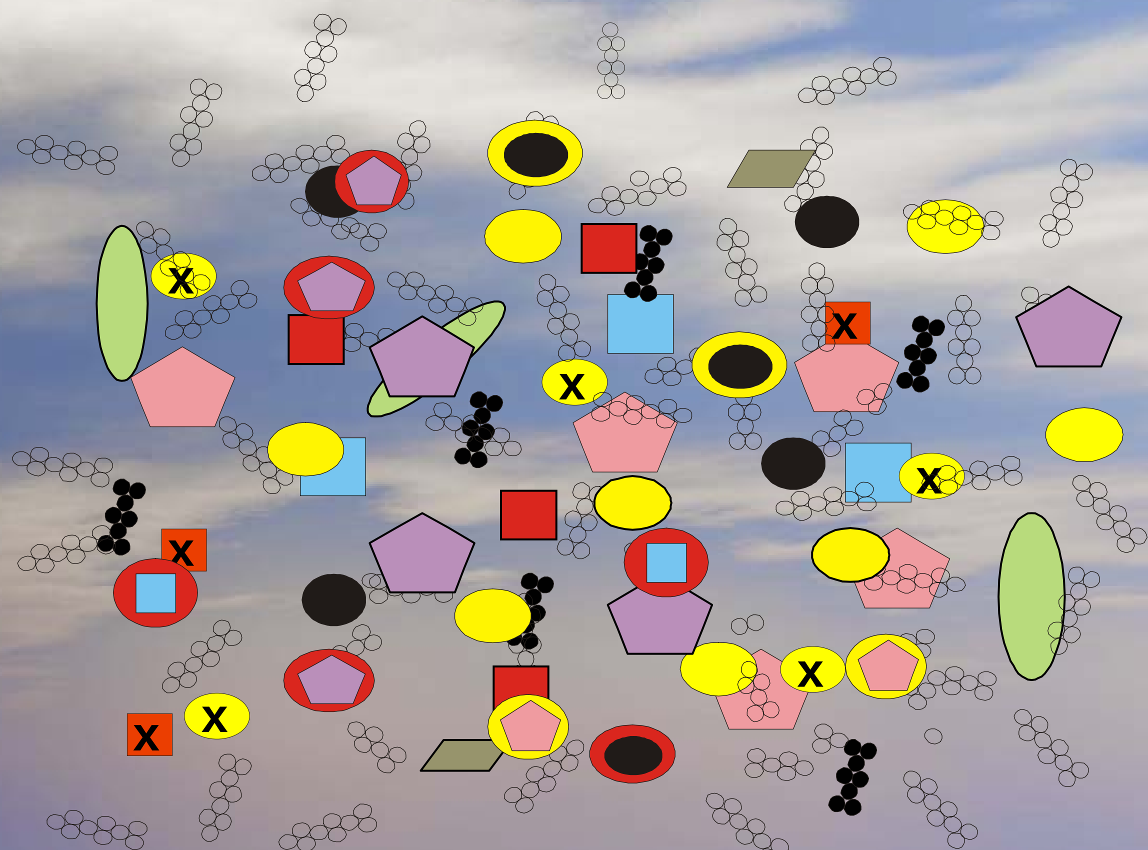
Local emissions

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

Long Range Transp.

- NH_4NO_3
- $(NH_4)_2SO_4$
- Carbonaceous

Interaction among species



PM emission sources and tracers

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

Stationary sources
Fossil fuel combustion

Power plants, heating, industry

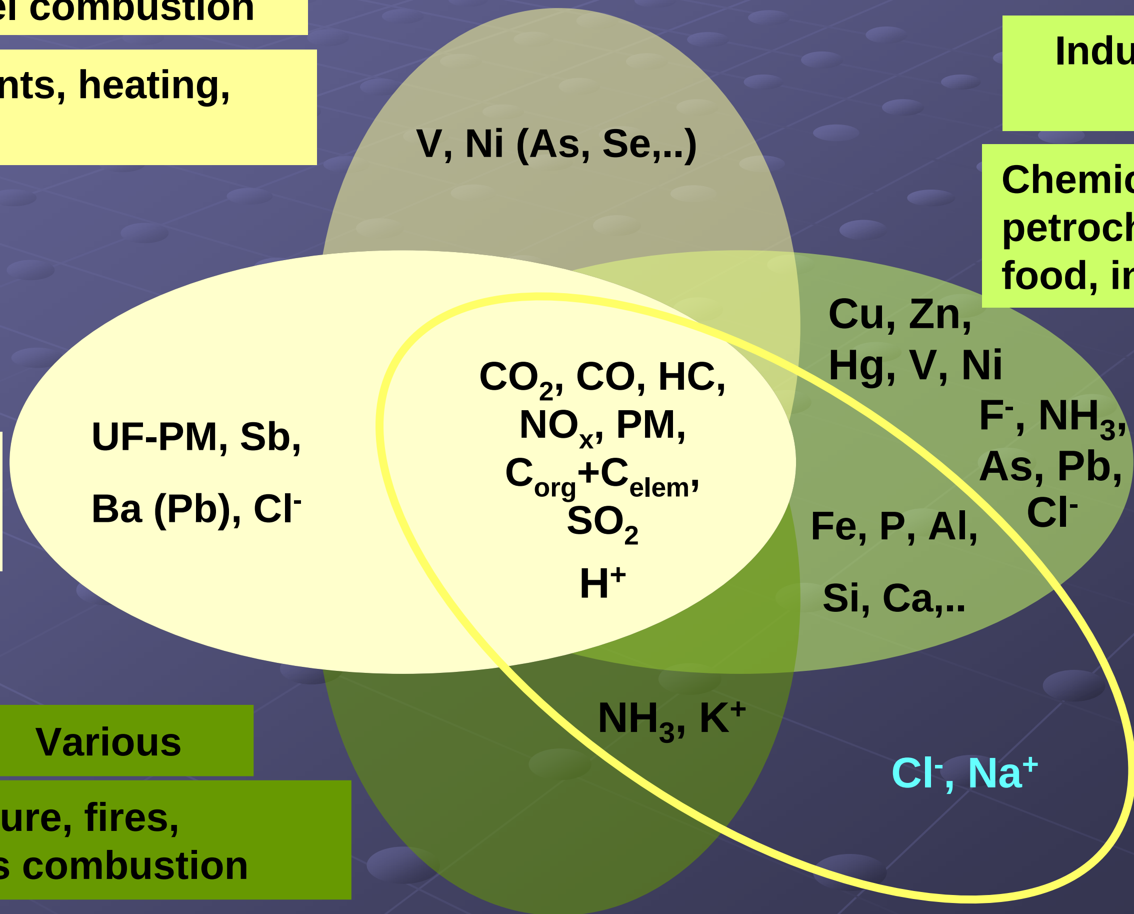
Industrial processes, incineration

Chemical, metallurgical, petrochemical, mineral food, incineration

Transport

Road, air, rail,

Fuel storage



Various

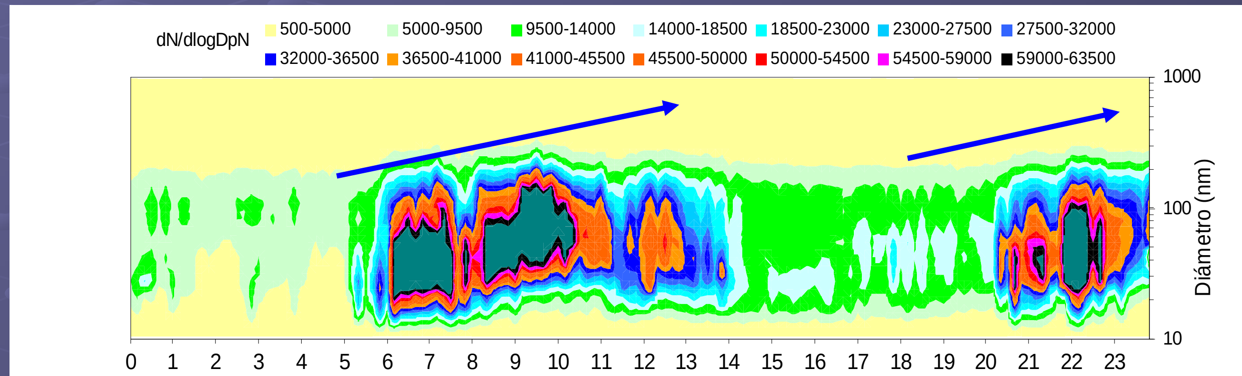
Agriculture, fires, biomass combustion

Natural emissions

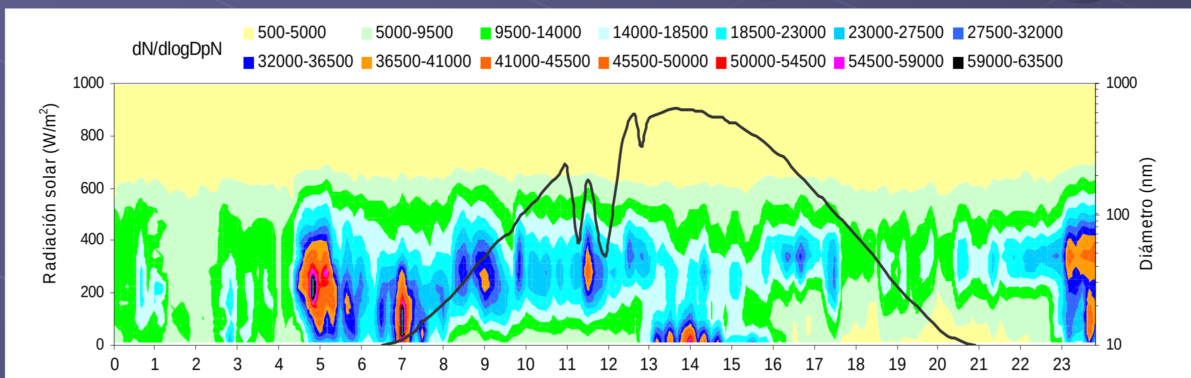
Biogenic, re-suspension, marine, lightening, volcanoes, fires

Tracers of PM sources

1. Time variation and correlation with other components: Number or mass vs. time, traffic flow, insolation NOx,….



Rush hours traffic, followed by interaction among particles and gas-particles: accumulation-condensation

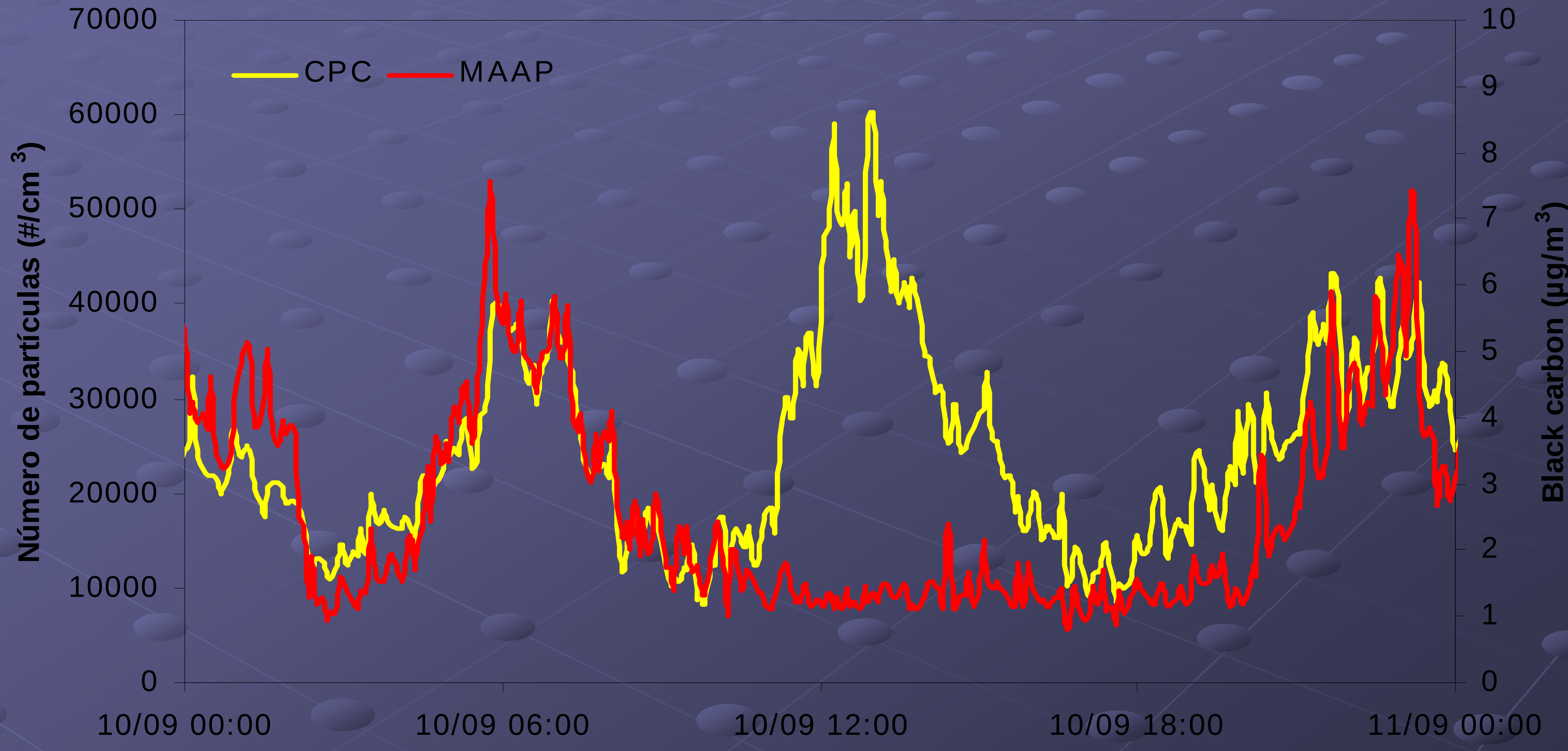


Nucleation typical from summer days at midday: photochemistry

PhD J. PEY-CSIC, 2007

Tracers of PM sources

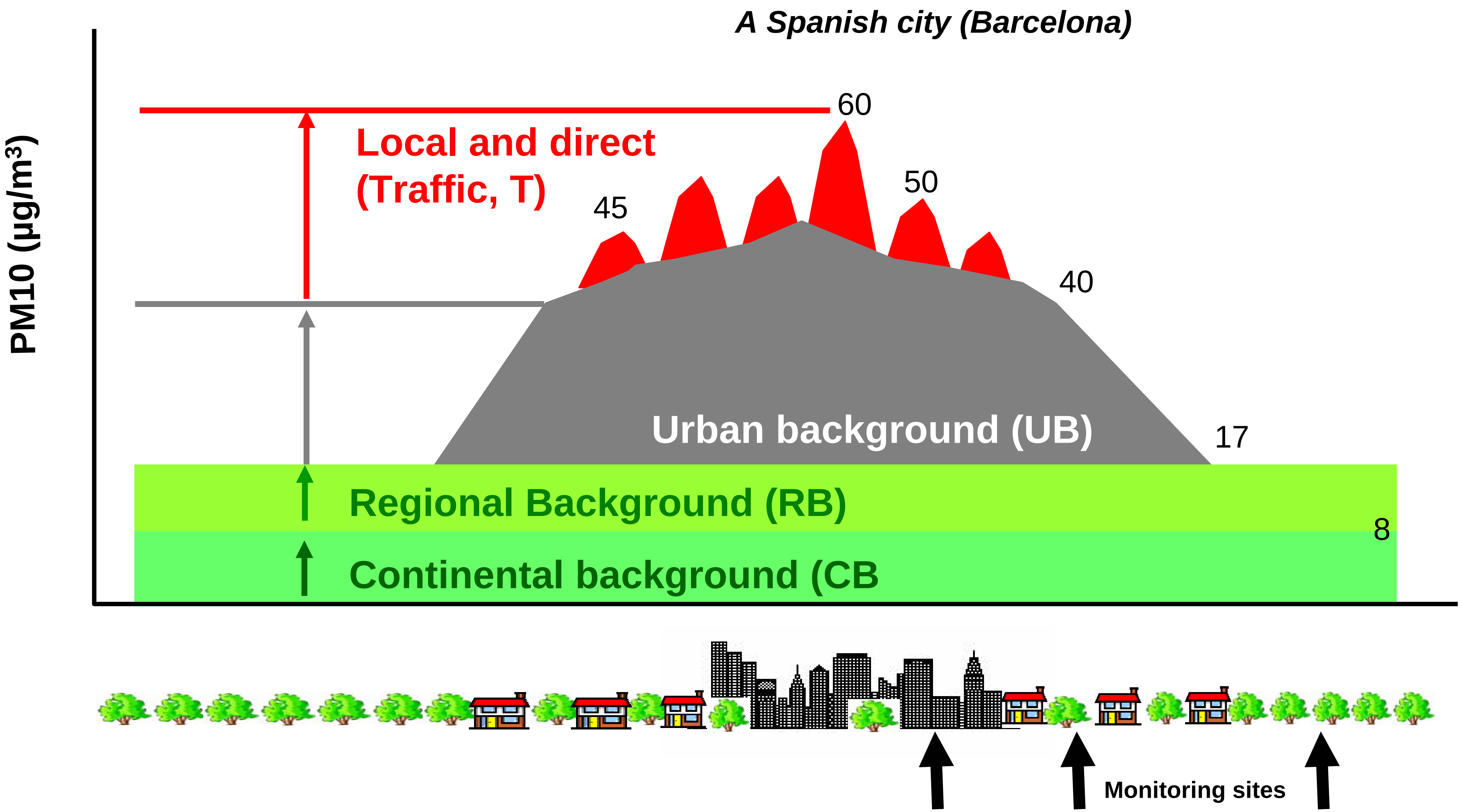
1. Time variation and correlation with other components: Black carbon (MAAP) vs. time and number concentration



Tracers of PM sources

2. Spatial variation: local-regional scale

The Lenschow et al. (2001) approach



Tracers of PM sources

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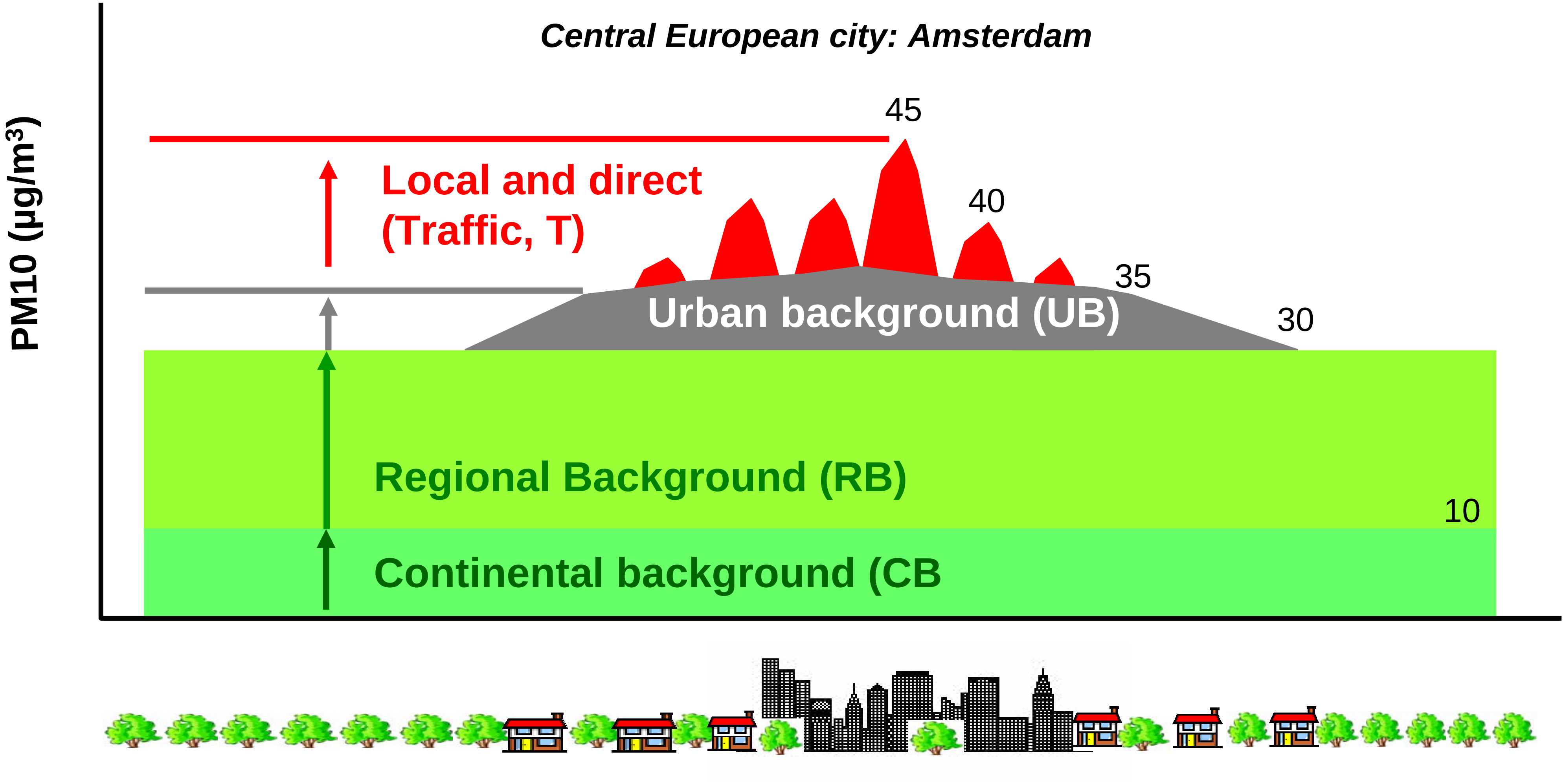
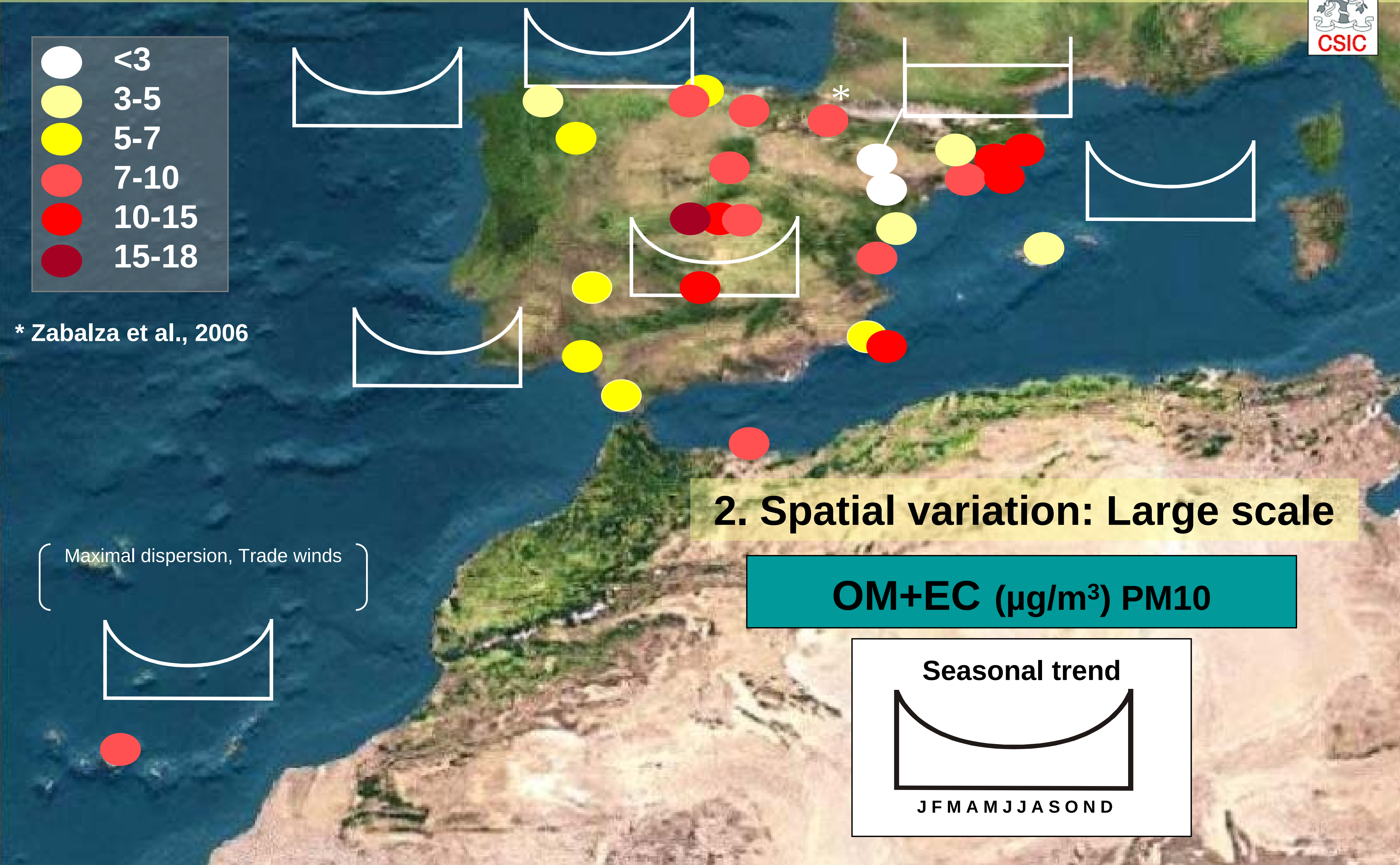
The Lenschow et al. (2001) approach



Tracers of PM sources



Tracers of PM sources

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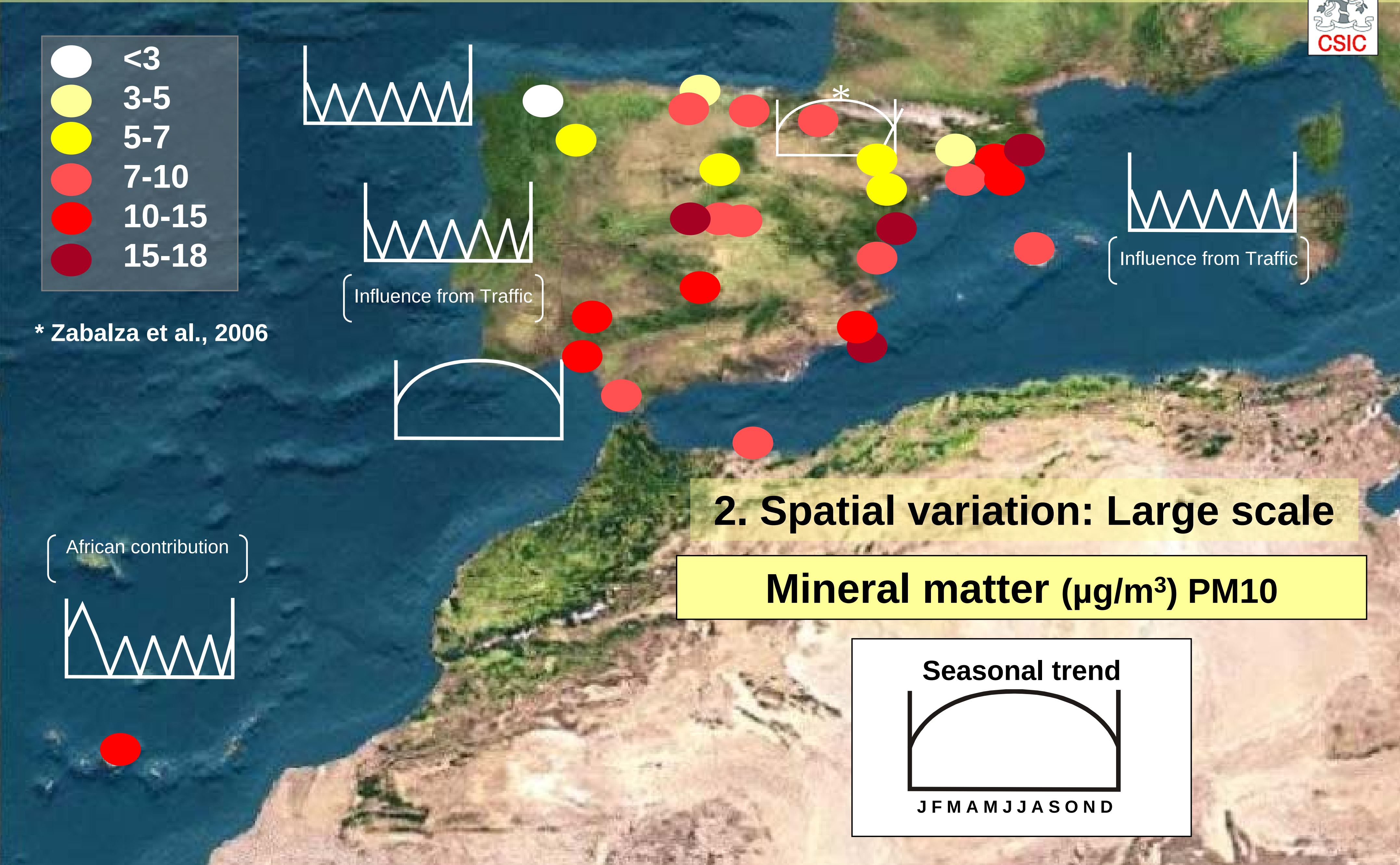
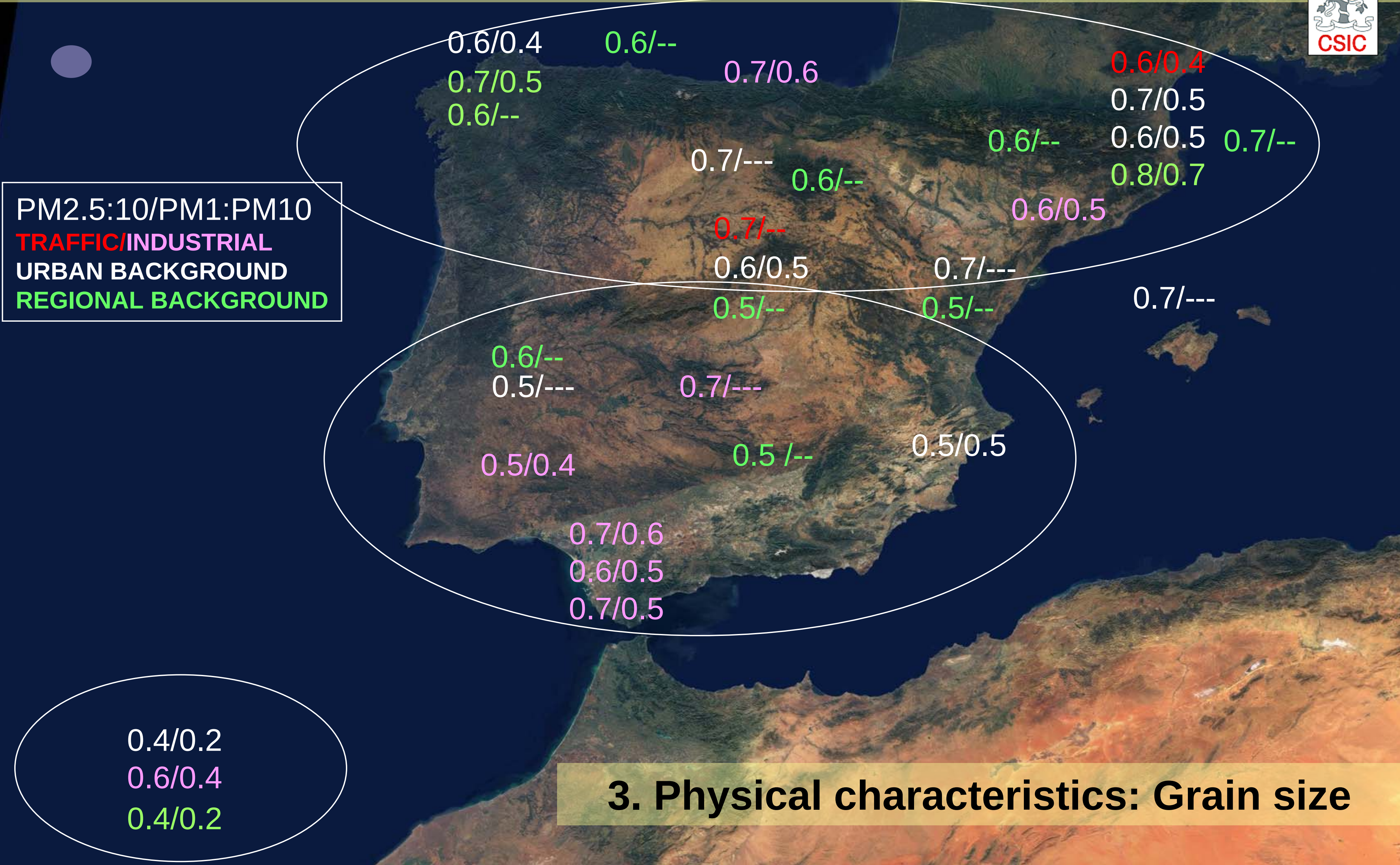


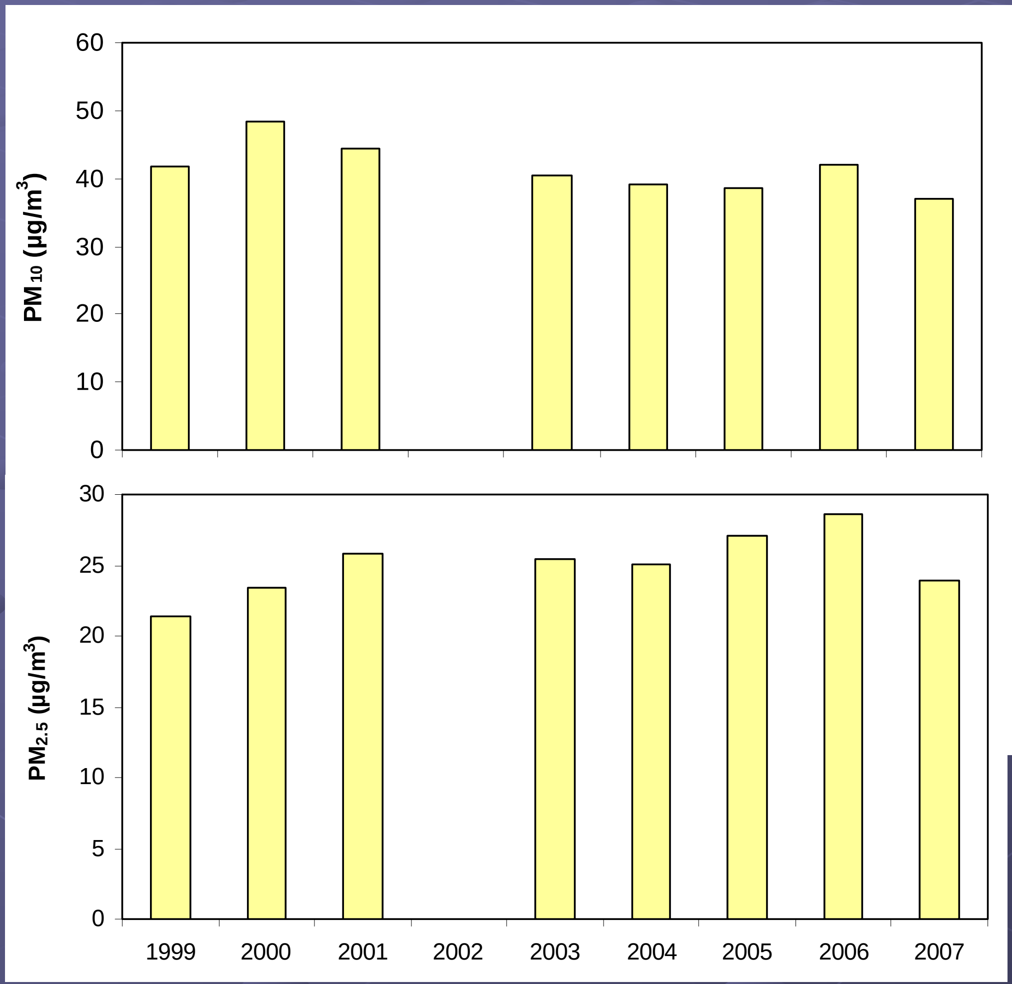
Tracers of PM sources



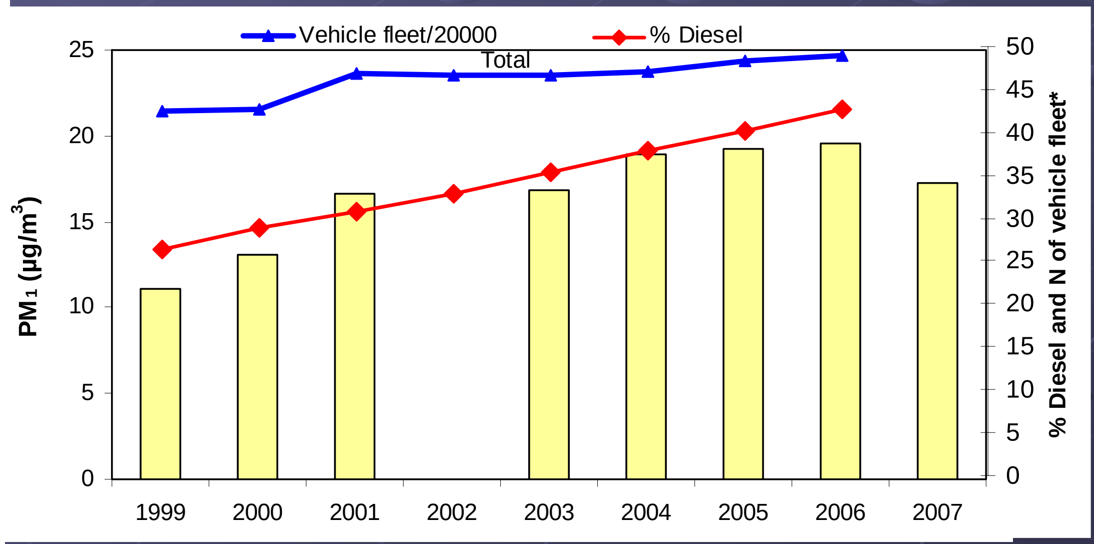
3. Physical characteristics: Grain size

Tracers of PM sources

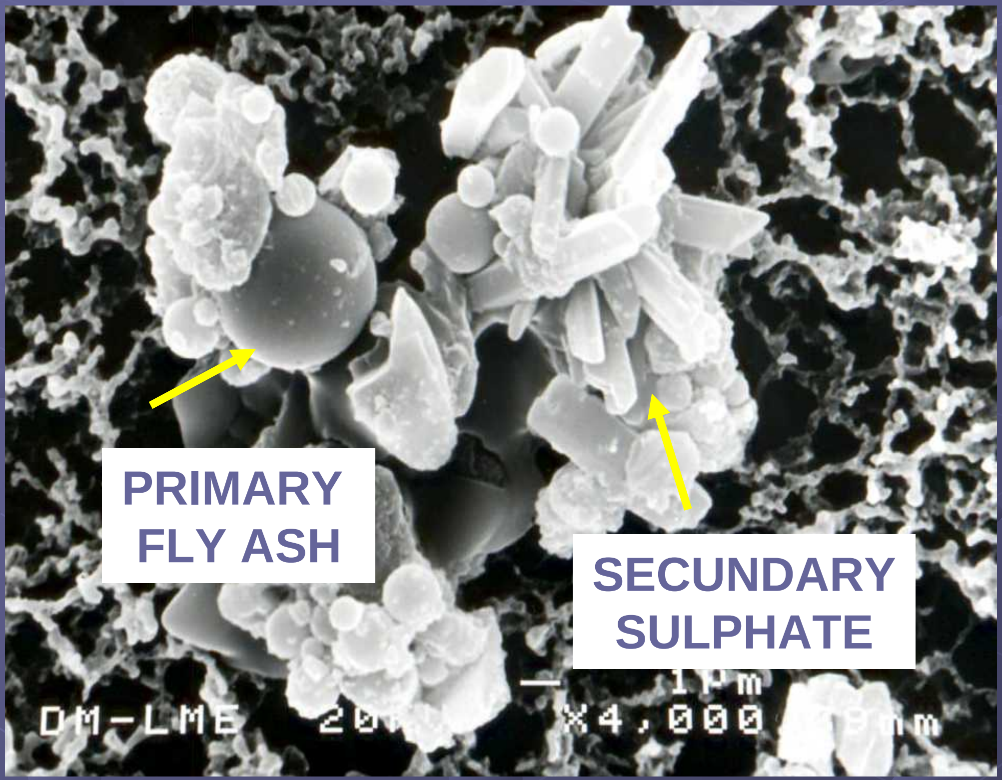
3. Physical characteristics: Grain size

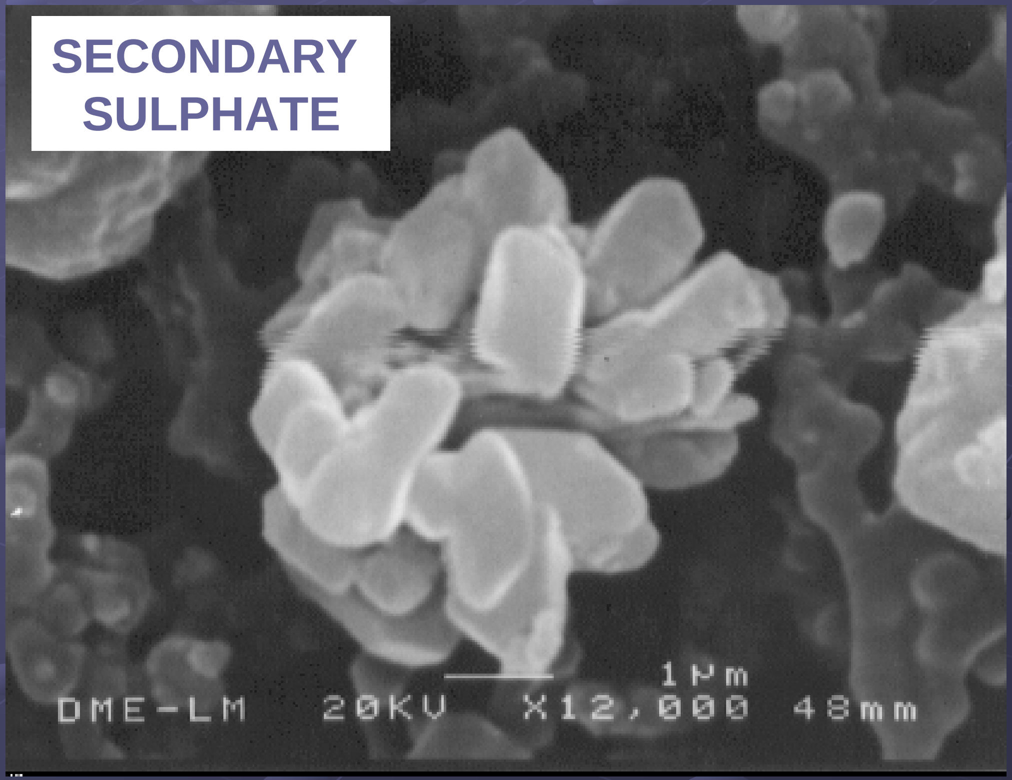


Barcelona 1999-2007



4. Other (non chemistry) tracers: SEM-EDS





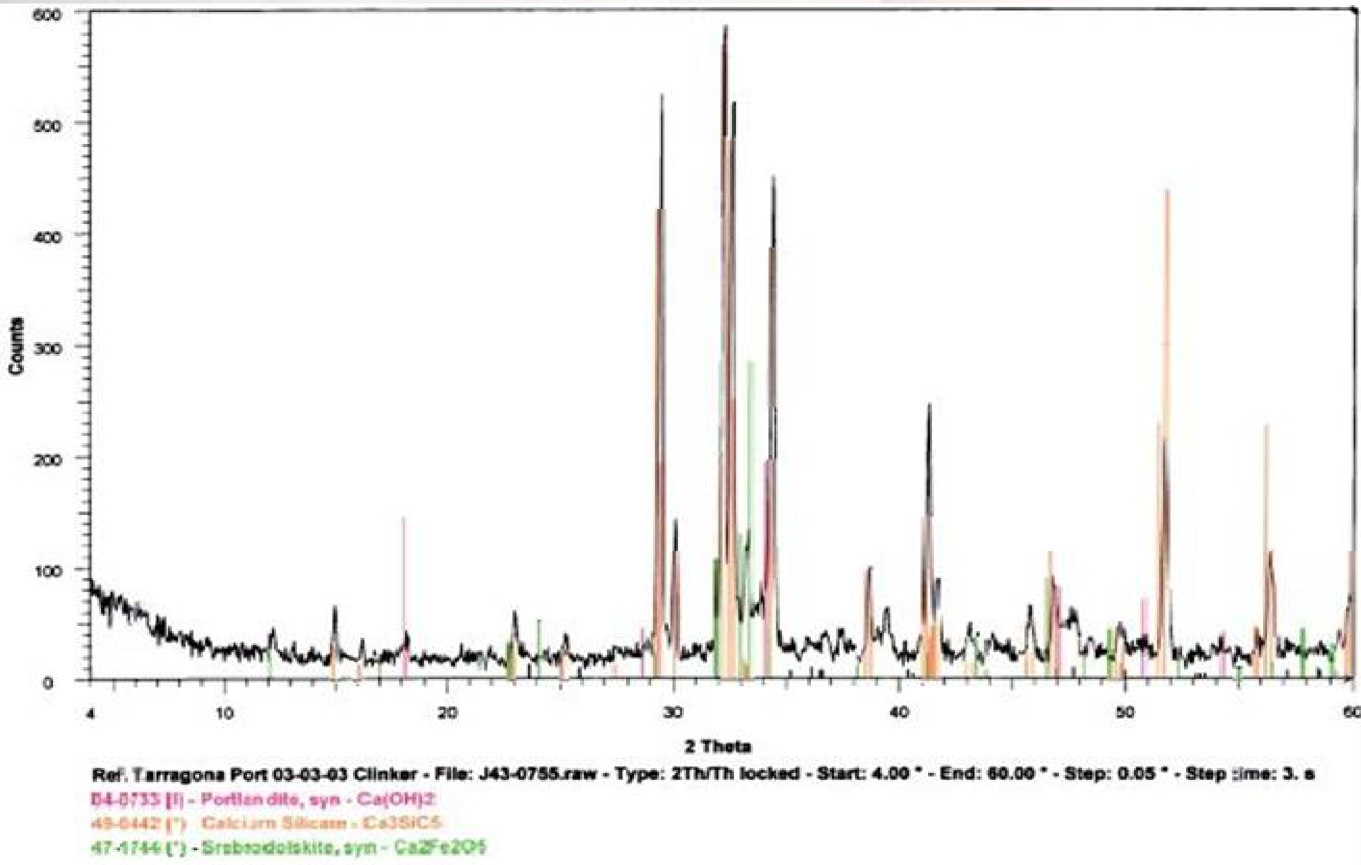
Tracers of PM sources

4. Other (non chemistry) tracers: XRD

Mineral Characterisation XRD

Ca_3SiO_5,	larnite
$Ca(OH)_2$,	portlandite
$Ca_2Fe_2O_5$,	srebrodolskite

Clinker



Tracers of PM sources

5. Chemical tracers from PM speciation

Crustal-mineral

Al_2O_3	ICP-AES
Ca	ICP-AES
K	ICP-AES
Mg	ICP-AES
Fe	ICP-AES
Ti	ICP-AES
P	ICP-AES
CO_3^{2-}	ind. Ca
SiO_2	ind. $3*Al_2O_3$

Marine aerosol

Na^+	ICP-AES
Cl^-	Ion Cromat.
SO_4^{2-}	ind. Na

Anthropogenic

Cnm A. Elemental

OC & EC Thermo-optical

Inorganic Secondary Species

NH_4^+	C.FIA
SO_4^{2-}	Ion Cromat.
NO_3^-	Ion Cromat.

40 Metals (ICP-MS)

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

Unaccounted
75-85 % mass PM

Source	Tracer	Reference
Crustal	Sc, Ce, Sm, Fe, Al	Lee et al., 1994; Koistinen et al., 2004
Soil/crustal	Si	Chan et al., 1991
Soil-related	Si, Fe	Janssen et al., 1997
Soil	Mn, Al, Sc	Huang et al., 1994
Soil dust	Al, Si, Fe	Maenhaut et al., 1989
Mineral-crustal	Al, Si, Fe, Ca, (Mg), Mn, K, Ti, REEs, Zr, Rb, Sr, Sc, Cs, U, Th, Li	Querol et al., 1996, 2001, 2004, 2007 Alastuey et al., 2005 Viana et al., 2005 Moreno et al., 2005
Sea salt, marine, sea spray	Soluble Na, Cl, (Mg)	Most studies
Traffic	TC, BC, Cu, Zn, Pb	Laschober et al., 2004
Traffic	Zn, Ba, Al, Cr, Fe, Hg, La, Mg, Mn, Na, Sb, Sc, V, OC, BC	Allen et al., 2001
Traffic	Cu, Zn, Ba	Chellam et al., 2005
Traffic	Cu, BC, Fe, Zn	Yli-Tuomi et al., 2005
Traffic	OC, EC, NO_3^-, Sn, Sb, Ba, Cu	Querol et al., 2001, Rodriguez et al., 2003, Viana et al., 2007
Brake dust	SiO_2, Fe_2O_3, Mg , Ba	Hildemann et al., 1991
Tire wear	Zn	Harrison et al., 1996
Tire dust	di-pentene(limolene), styrene	APEG, 1999
Road salt	Cl^-	APEG, 1999
Vehicle wear	Cu, Zn, Pb, Ba, Mo	Harrison et al., 2003
Mainly from wear; Cu, Ba, Sb brakes	Cu, Zn, Pb, Ba, Cd, Sb, (Fe)	Sternbeck et al., 2002

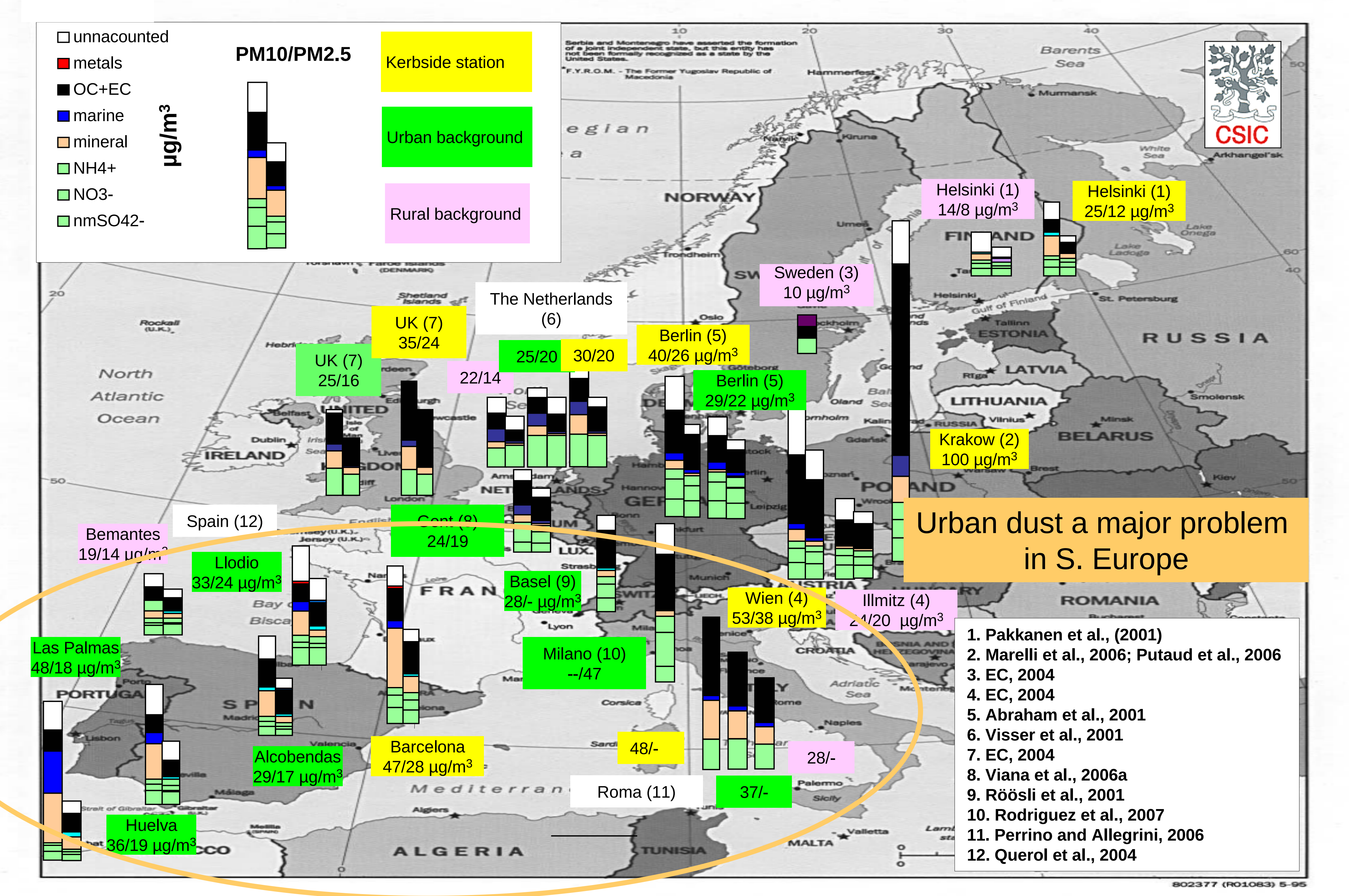
Tailpipe diesel	PM10, V, and Cd (Ca, Cr, Zn, Sr, and Pb)	Schauer J.J. et al., 2006 HEI report
Tailpipe gasoline and tire wear	V, Cr, Zn, Sr, Pb, Mo, Ag	Schauer J.J. et al., 2006 HEI
Road dust	S, Mg, Al, K, Ca; Fe and Ti, Sr, Cd, Pb	Schauer J.J. et al., 2006 HEI
Brake dust	Fe, Cr, Mn, Cu, Zn, Sb, Ba	Schauer J.J. et al., 2006 HEI

Tables modified from Y. Bruinen de Bruin, 2006. JRC EUR 22349 EN report

It may differ from one region to the other (example Mg: sea spray or dolomite)

Exhaust emissions: Before and after unleaded gasoline, currently an important signature from tire and brake wear

Tire and brake wear emissions coupled with high traffic volumes: new scenario where metals are emitted in urban agglomerations


unnacounted
metals
OC+EC
marine
mineral
NH4+
NO3-
nmSO42-
µg/m³
PM10/PM2.5
Kerbside station
Urban background
Rural background
CSIC
Helsinki (1)
14/8 µg/m³
Helsinki (1)
25/12 µg/m³
Sweden (3)
10 µg/m³
The Netherlands
(6)
UK (7)
35/24
UK (7)
25/16
22/14
25/20
30/20
Berlin (5)
40/26 µg/m³
Berlin (5)
29/22 µg/m³
Krakow (2)
100 µg/m³
Spain (12)
Bemantes
19/14 µg/m³
Gent (8)
24/19
Llodio
33/24 µg/m³
Basel (9)
28/- µg/m³
Wien (4)
53/38 µg/m³
Illmitz (4)
24/20 µg/m³
Urban dust a major problem in S. Europe
Las Palmas
48/18 µg/m³
Milano (10)
--/47
Alcobendas
29/17 µg/m³
Barcelona
47/28 µg/m³
48/-
28/-
Roma (11)
37/-
Huelva
36/19 µg/m³
1. Pakkanen et al., (2001)
2. Marelli et al., 2006; Putaud et al., 2006
3. EC, 2004
4. EC, 2004
5. Abraham et al., 2001
6. Visser et al., 2001
7. EC, 2004
8. Viana et al., 2006a
9. Röösli et al., 2001
10. Rodriguez et al., 2007
11. Perrino and Allegrini, 2006
12. Querol et al., 2004
NORWAY
FINLAND
RUSSIA
ESTONIA
LATVIA
LITHUANIA
BELARUS
POLAND
IRELAND
UNITED KINGDOM
FRANCE
SPAIN
PORTUGAL
ROMANIA
CROATIA
ALGERIA
TUNISIA
North Atlantic Ocean
Mediterranean
Barents Sea
802377 (R01083) 5-95

Tracers of PM sources

5. Chemical tracers from PM speciation

Tables modified from Y. Bruinen de Bruin, 2006. JRC EUR 22349 EN report

Coal-fired powerplant	As, Se, S, Mo, Hg (much reduced with FGD systems)	Pacyna, 1984; Huang et al., 1994; Ojanen et al., 1998; Harrison et al., 1996; Fung and Wong 1995
Oil-fired power plants and petrochem.	V, Ni, La, Sm, S	Pavyna, 1984; Ojanen et al., 1998, Huang 1994;
Waste incineration	Zn, Cu, Hg, Pb, Sb,	Pacyna, 1984, Van Borm et al., 1990; Harrison et al., 1996; Sweet et al., 1993; Parekh et al., 1987
Wood burning	K, volatile C, elemental C	Huang et al., 1994; Janssen et al., 1997; Ojanen et al., 1998; Chan et al., 1991
Steel industry	Fe, Mn, Cr, Ca	Ojanen et al., 1998; Huang et al., 1994
Steel	Fe, Cr, Mn, Ni, Zn, Se, Mo, Cd, Sn, Pb	Viana et al., 2006, Querol et al., 2004
Stainless steel	V, Cr, Ni, Mo	Querol et al., 2004
Smelting	Fe, Zn, Pb, Mn	Swietlicki et al., 1996
Zinc smelter	Zn, Cd, Pb, Sn	Sweet et al., 1993
Pyrite smelter	As, Cu	Pio et al., 1996
Copper smelter	As, Cu, Bi	Querol et al., 2004, 2007; Alastuey et al., 2007; Sánchez et al., 2007
Glaze and Ceramics (tile manufacturing)	Zn, As, Se, Zr, Cs, Tl, Pb, Bi	Querol et al., 2007; Minguillón et al., 2007

ng/m^3	Fondo rural		Fondo urbano		Acero	Acero inoxidable	Metalurgia del cobre	Petroquímica		Cerámica	
	min	max	min	max	media	media	Media	min	max	min	max
Li	0.1	0.3	0.2	0.7	0.4	0.6	0.2	0.2	1.0	0.6	1.3
Be	0.01	0.02	0.02	0.05	0.06	0.03	0.07	0.01	0.07	0.02	0.05
Sc	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.1	0.3	0.3	0.5
Ti	7	22	18	83	24	36	60	23	62	33	57
V	2	5	2	15	8	**28**	7	7	**25**	4	5
Cr	1	2	2	8	**25**	**24**	2	2	6	3	8
Mn	5	5	4	23	**87**	17	11	8	11	6	8
Co	0.1	0.1	0.2	0.5	0.5	0.6	0.4	0.2	0.8	0.4	0.7
Ni	2	3	2	7	**33**	**20**	3	3	**11**	3	5
Cu	4	8	7	**81**	33	11	**70**	23	33	4	10
Zn	16	30	14	**106**	**417**	73	51	35	54	45	**183**
Ga	0.1	0.2	0.1	0.3	0.4	0.2	0.3	0.2	0.4	0.2	0.3
Ge	0.1	0.3	0.04	0.3	0.2	0.3	0.1	0.1	0.2	0.03	0.1
As	0.3	0.4	0.3	1.5	1.8	0.9	**5**	0.5	1.9	1.7	**5**
Se	0.3	0.5	0.3	1.1	**3**	0.8	1.5	0.5	0.6	1.0	**3**
Rb	0.5	0.6	0.5	1.8	1.1	0.8	1.5	0.6	1.6	1.2	2.4
Sr	1	5	3	10	3	6	4	4	5	3	5
Y	0.1	0.1	0.1	0.4	0.1	0.3	0.3	0.1	0.3	0.2	0.3
Zr	4	4	2	10	2	5	2	2	6	10	**20**
Nb	0.04	0.1	0.05	0.4	0.1	0.2	0.2	0.1	0.3	0.2	0.3
Mo	2	3	2	5	**15**	**15**	2	2	7	1	2
Cd	0.2	0.2	0.1	0.7	1.2	0.3	0.8	0.1	0.8	0.6	1.5
Sn	1	2	1	6	**38**	1	2	2	2	1	1
Sb	0.6	0.6	1	**11**	4	1	3	1	7	1	6
Cs	0.01	0.04	0.03	0.13	0.1	0.1	0.1	0.04	**0.2**	0.1	**0.3**
Ba	5	11	4	**41**	14	15	16	12	16	12	16
La	0.1	0.2	0.2	0.6	0.3	0.6	0.5	0.3	0.9	0.3	0.6
Ce	0.2	0.4	0.4	1.3	0.4	0.7	0.9	0.5	1.2	0.7	1.9
Pr	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2
Hf	0.1	0.2	0.1	0.3	0.1	0.2	0.2	0.1	0.2	0.2	0.4
W	0.01	0.03	0.05	0.6	0.7	0.2	0.06	0.04	0.2	0.10	0.3
Tl	0.1	0.1	0.05	0.4	0.3	0.0	0.2	0.03	0.3	0.5	**2.8**
Pb	5	10	7	57	**102**	13	37	8	37	35	**103**
Bi	0.1	0.1	0.1	1.0	0.5	0.1	**1.6**	0.1	0.2	0.4	**1.5**
Th	0.1	0.2	0.1	0.3	0.1	0.1	0.4	0.1	0.4	0.1	0.2
U	0.1	0.2	0.1	0.3	0.3	0.1	0.3	0.1	0.3	0.1	0.1

Mean annual levels

Trace elements

PM10

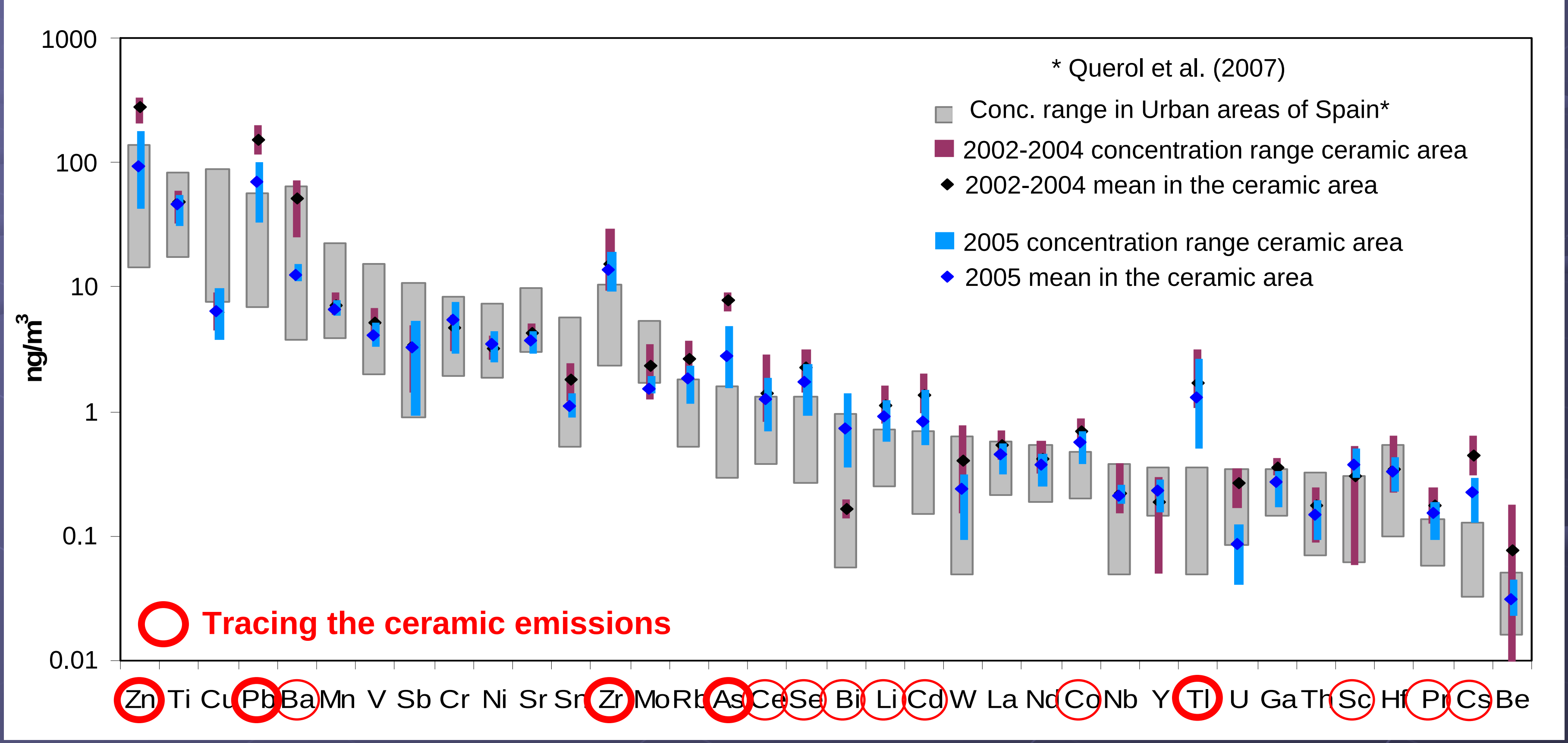
37 sites Spain

1999-2007

(ng/m^3)

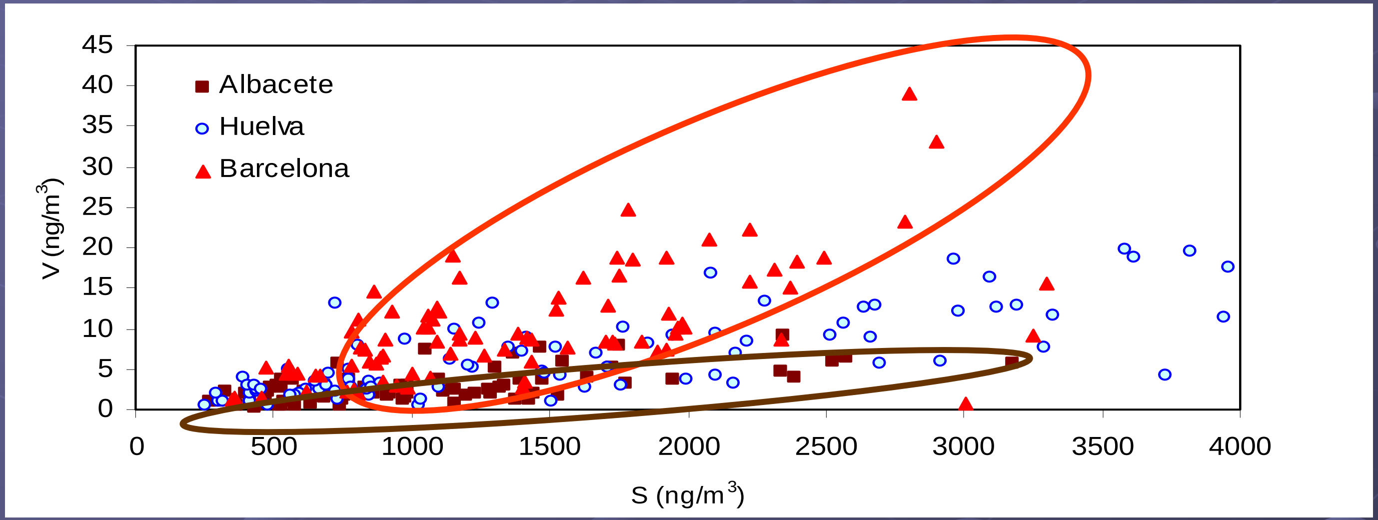
Tracers of PM sources

5. Chemical tracers from PM speciation



Tracers of PM sources

5. Chemical tracers from PM speciation
Ratios between tracers



Viana M. et al. (2007) ATMOSPHERIC ENVIRONMENT, 41, 1395-1406.

Tracers of PM sources

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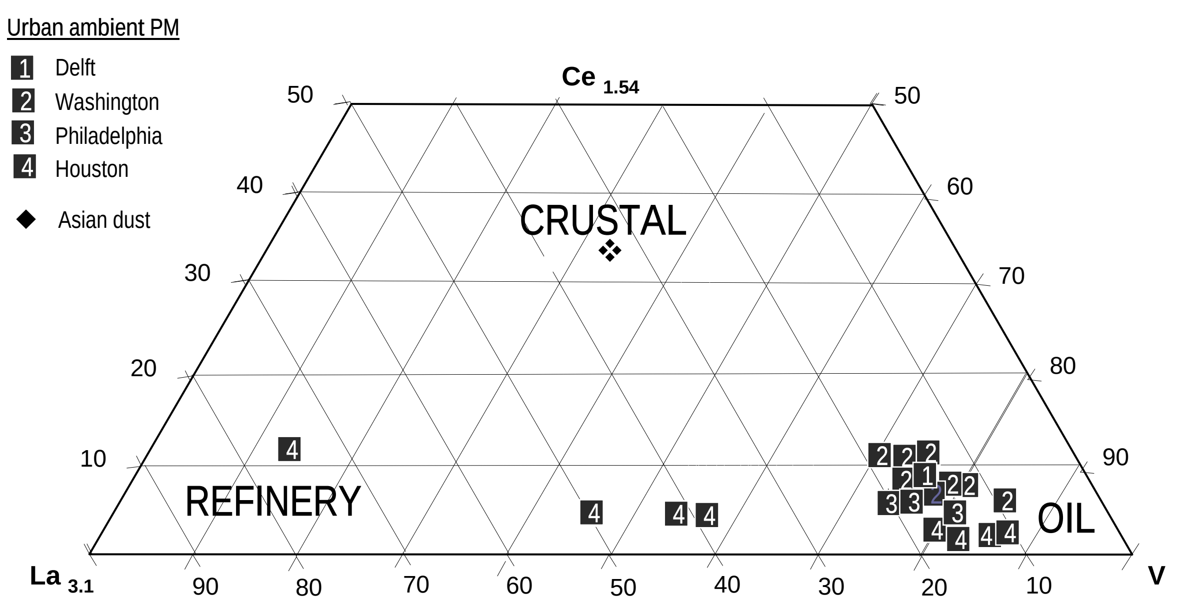

Moreno T. et. al. (2008) Environmental Science and Technology (submitted)

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Receptor models

$$\underset{p \times 1}{\mathbf{X}_t} = \underset{p \times k}{\Lambda}\ \underset{k \times 1}{\mathbf{f}_t} + \underset{p \times 1}{\mathbf{e}_t}$$

Little — **Knowledge about pollution sources** — **Complete**

Multivariate Receptor Models

Principal Component Analysis

Positive Matrix Factorization

UNMIX

Confirmatory Factor Analysis Models

Bayesian Models

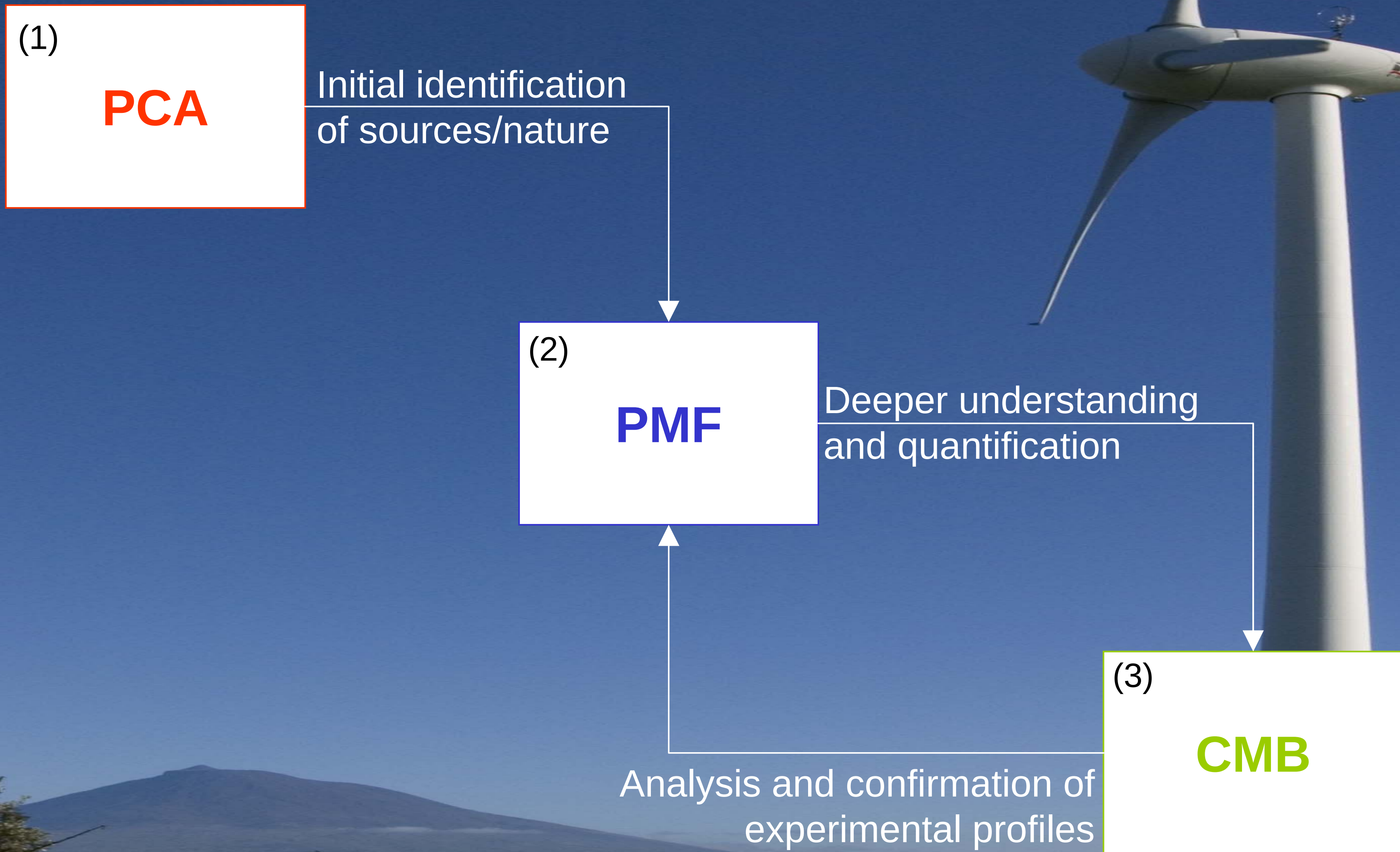
Measurement Error Models

Regression Models

Chemical Mass Balance (CMB)

Modified from Schauer et al. (2006)

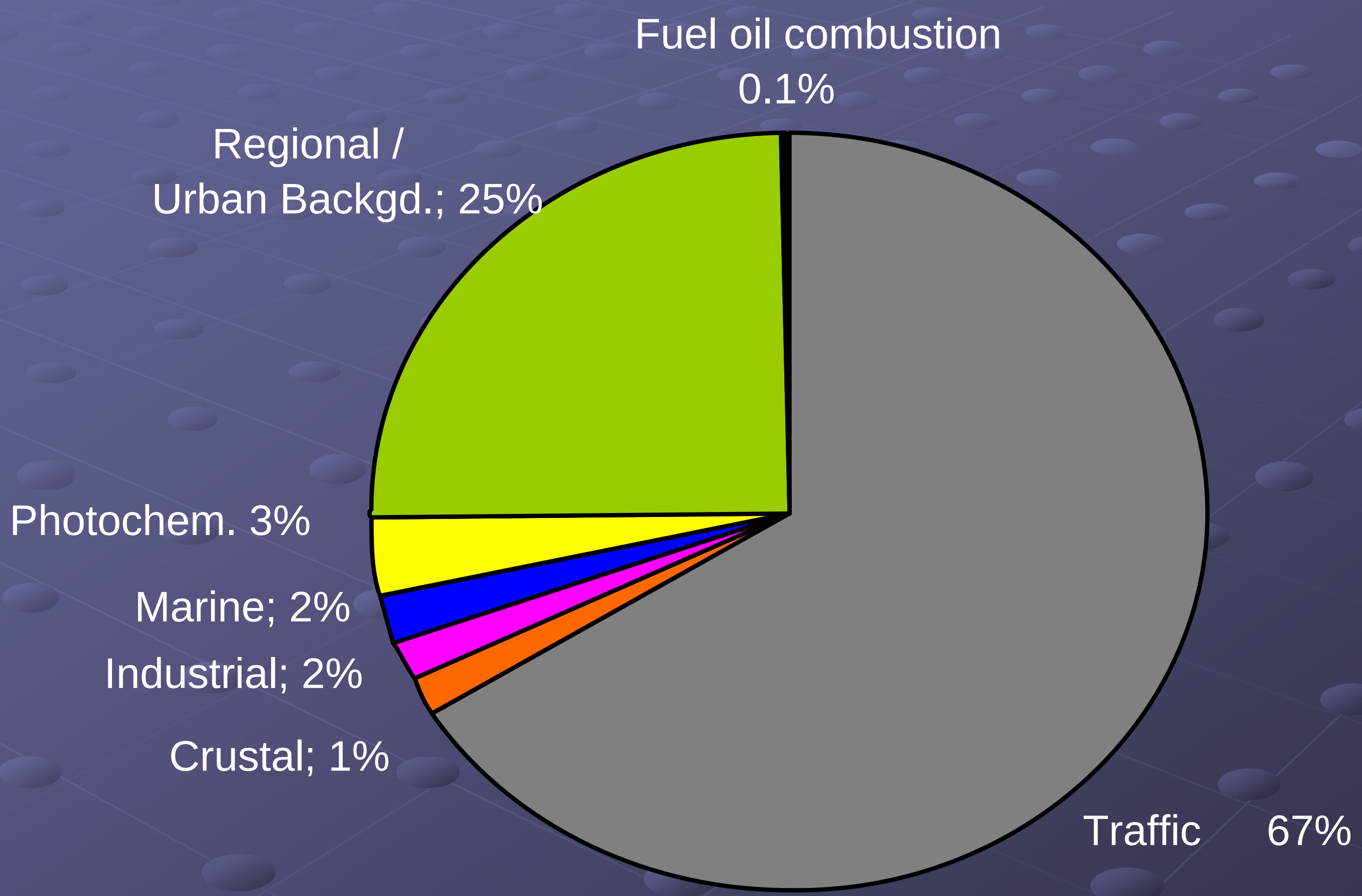
Receptor models: Suggested approach



Quantitative Applications

Receptor models: Suggested approach

Source contribution to N_{13-800}



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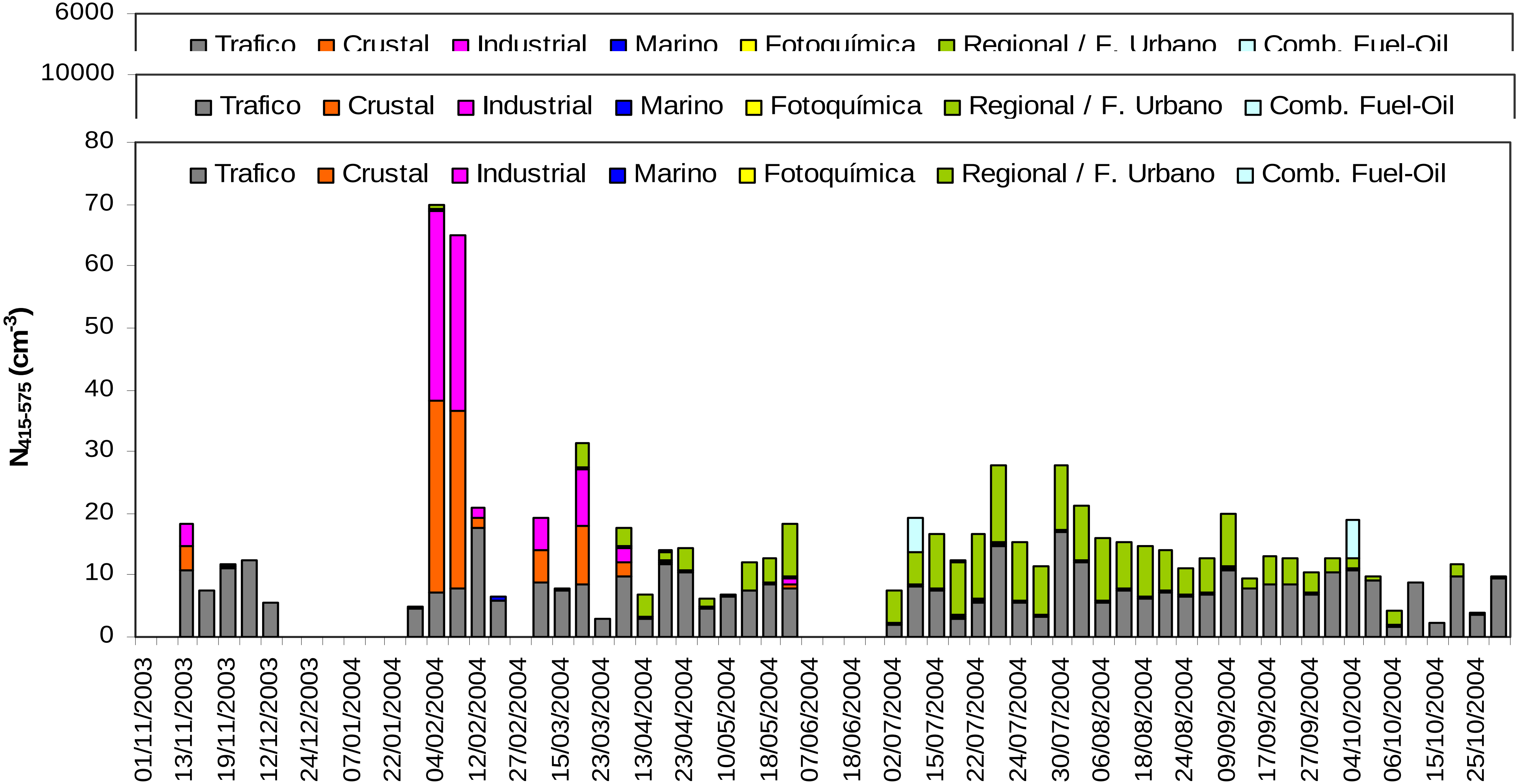
Quantitative Applications

Receptor models: Suggested approach



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Conclusions

1. PM is a complex and sometimes reactive mixture of components and in many cases scienti tools are need to identify main sources of pollution
2. We reviewed a number of qualitative and quantitative tracers of PM origin, including time and spatial PM variability, correlation with levels of other pollutants or physical parameters, grain size, SEM-EDS, XRD, and chemical tracers from speciation studies.
3. The speciation studies may allow a complete and detailed quantification of source apportionment, specially CMB, but a chemical profile library is necessary for Europe (NOWADAYS MISSING)
4. A new scenario for metals in Europe

4.1. V and Ni the tracing group SO_4^{2-}, NH_4^+, V, Ni is found in most Europe, even in rural or regional background sites: The signature from oil combustion, in the past coal combustion was traceable over all EU (now only in specific areas)

4.2. Tire and brake wear emissions coupled with high traffic volumes bring relatively high Fe, Mn, Cu, Sb, Ba and Zn levels to urban agglomerations, in the past restricted to specific hotspots with low population (smelting, steel,….)

5. Studying tracers may also help to improve monitoring of emission (the case of Tl in the ceramic area)

Main questions to be solved:

1. Secondary organic components (tracers and origin)
2. Secondary inorganic components (quantify specific origin by SRM is difficult)
3. Identification and source contribution quantification for the ‘crustal mixture’ in relatively dry areas
4. Missing a library for source PM chemical profiles

Thank you for your attention !

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Acknowledgements:

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Particulate Matter:
Properties Related to Health Effects

Ministry of the Environment of Spain, Ministry of Education and Sciences of Spain

Regional AQ monitoring networks: Generalitat Valenciana, Generalitat de Catalunya Andalucía, Baleares, Canarias, Castilla-León, Castilla la Mancha, Euskadi, Extremadura, Galicia, Madrid, Murcia