



## Black Carbon Measurements for Improved Urban Air Quality Monitoring

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# Outline

- Critical Air Quality parameters in EU
- Road traffic, air quality and aerosol measurements
  - 1. PMx
  - 2. Carbonaceous aerosols
  - 3. BC
  - 4. BC & N
  - 5. PM & BC
  - 6. UFP
  - 7. PM speciation and receptor modelling
  - 8. Receptor modelling and UFP
- Future trends
- Conclusions

CGL2010-19464/CLI



Contract S-G D Air Quality and Industrial Environment

SAPUSS  
  
MARIE CURIE ACTIONS

## Directive 2008/50/CE

293 °K , 101,3 kPa

except PM and metals, Eviron. Cond.

Hourly	350 µg/m <sup>3</sup> SO <sub>2</sub>	24 times per year
Daily	125 µg/m <sup>3</sup> SO <sub>2</sub>	3 times per year
Annual prot. ecos.	20 µg/m <sup>3</sup> SO <sub>2</sub>	not exceeding annual and mean 1 Oct-31 Mar
Hourly	200 µg/m <sup>3</sup> NO <sub>2</sub>	18 times per year from 2010
Annual	40 µg/m <sup>3</sup> NO <sub>2</sub>	not exceeding from 2010
Annual prot. vegetation	30 µg/m <sup>3</sup> NO <sub>x</sub>	(reported as NO <sub>2</sub> ) not exceeding, from 2010
Annual	30 (5) µg/m <sup>3</sup> Benzene	not exceeding from 2010
Mean 8-h max. in a day	10 mg/m <sup>3</sup> CO	not exceeding
Annual	500 ng/m <sup>3</sup> Pb	not exceeding
Annual	40 µg/m <sup>3</sup> PM <sub>10</sub>	not exceeding
Daily	50 µg/m <sup>3</sup> PM <sub>10</sub>	n<35 per year
Annual	(25 y 20 (18) µg/m <sup>3</sup> PM <sub>2,5</sub> )	not exceeding
2010-2020	(reducing 20% PM <sub>2,5</sub> triennial for mean of urban background)	

## 2004/107/CE

Annual	6 ng/m <sup>3</sup> As	not exceeding
Annual	20 ng/m <sup>3</sup> Ni	not exceeding
Annual	5 ng/m <sup>3</sup> Cd	not exceeding
Annual	1 ng/m <sup>3</sup> Benzo[a]pirene	not exceeding

**CRITICAL PARAMETERS**

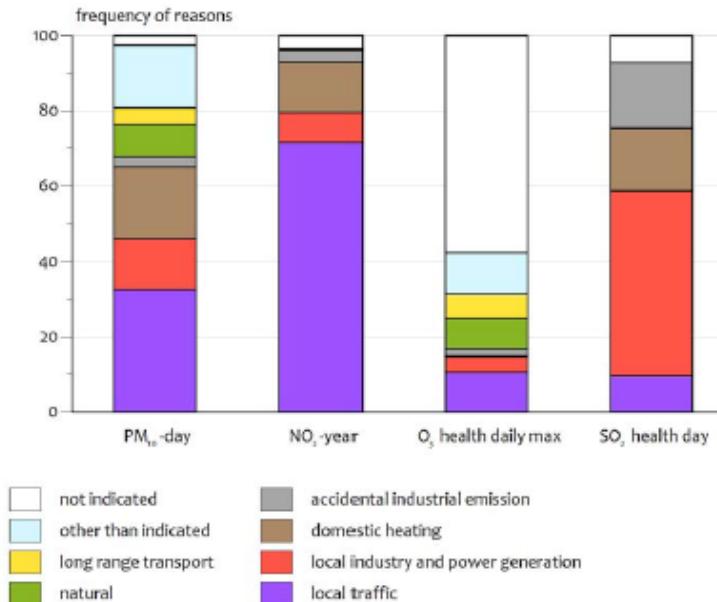
# Critical Air Quality problems in EU

## Reporting on ambient air quality assessment in the EU Member States, 2008



ETC/ACC Technical Paper 2010/11  
December 2010

Benno Jimmink, Frank de Leeuw, Erik Noordijk,  
Jana Ostatnická, Markéta Coňková



\* data extracted from form 11 and 13 of AQ questionnaire

Figure 7: Reported reasons for exceedances of limit and target values of PM<sub>10</sub>, NO<sub>2</sub>, O<sub>3</sub> and SO<sub>2</sub>, 2008

# Road traffic, air quality and aerosol measurements

## Crustal-mineral

$\text{Al}_2\text{O}_3$   
 $\text{Mg}$   
 $\text{Ti}$   
 $\text{Fe}$   
 $\text{K}$   
 $\text{SiO}_2$   
 $\text{CO}_3^{2-}$   
 $\text{P}$   
 $\text{Ca}$



## Sea spray

$\text{Na}^+$   
 $\text{Cl}^-$   
 $\text{SO}_4^{2-}$



## PM components

### Carbonaceous aerosols OM and EC



### Secondary Inorganic aerosols

$\text{NH}_4^+$   
 $\text{SO}_4^{2-}$   
 $\text{NO}_3^-$



## Trace elements

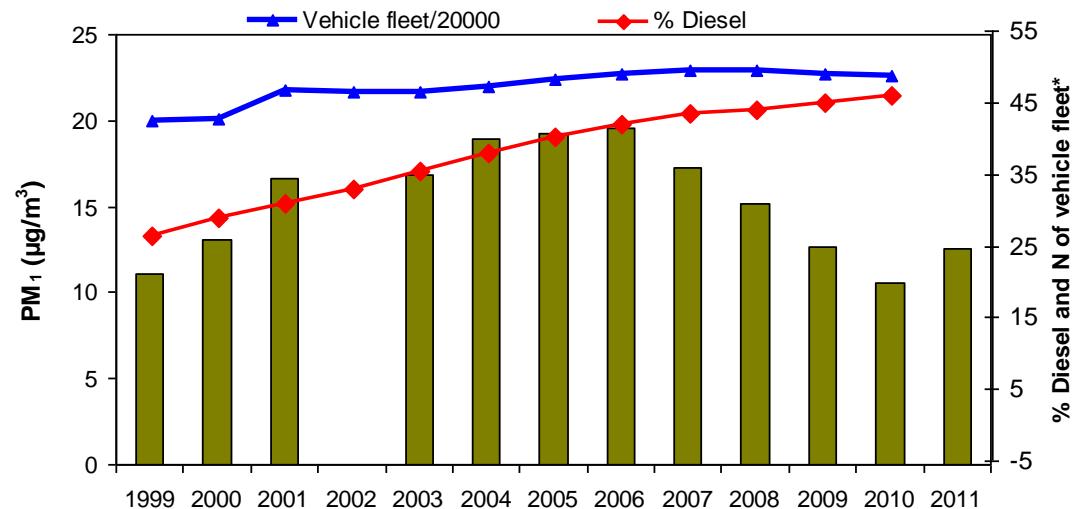
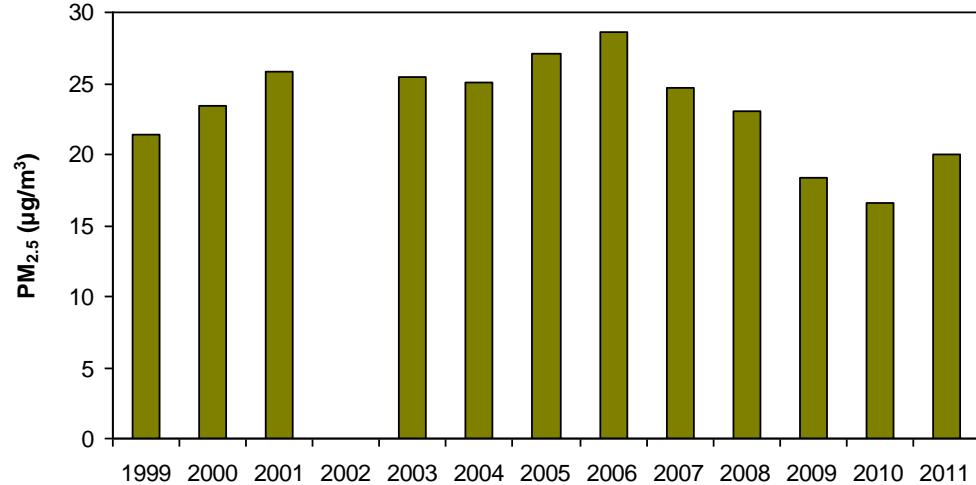
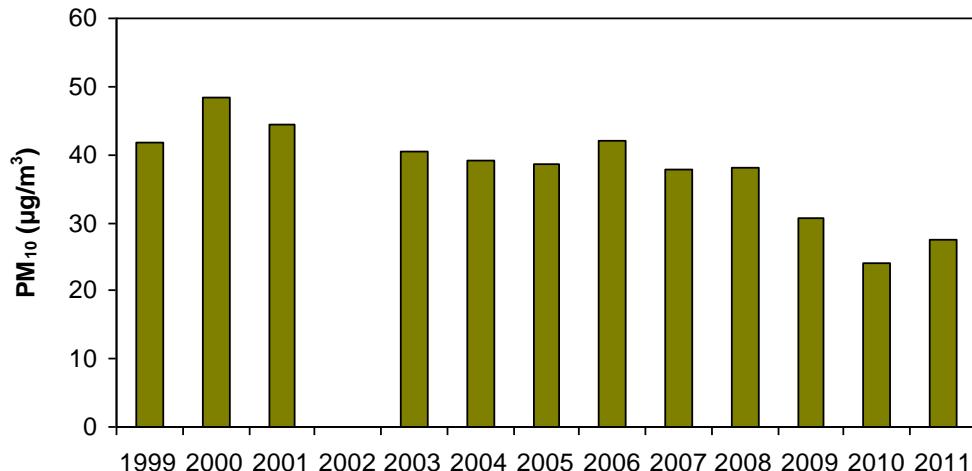
As, Ba, Bi, Cd, Ce, Co, Cr,  
Cs, Cu, Dy, Er, Ga, Gd, Ge,  
Hf, La, Li, Mn, Mo, Nd, Ni, Pb,  
Pr, Rb, Sb, Sc, Se, Sm, Sn,  
Sr, Ta, Th, Ti, Tl, U, V, W, Yb,  
Zn, Zr



Courtesy NREL

**Large proportion of PMx exceedances**

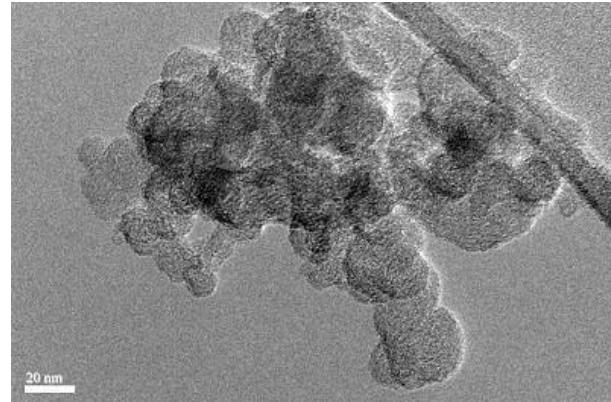
## 1. PMx: BARCELONA 1999-2011 PM10, PM2.5, PM1???



## 2. Carbonaceous aerosols: Organic and elemental carbon

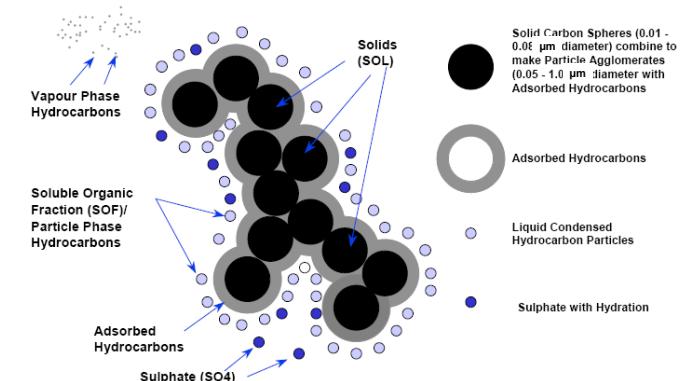
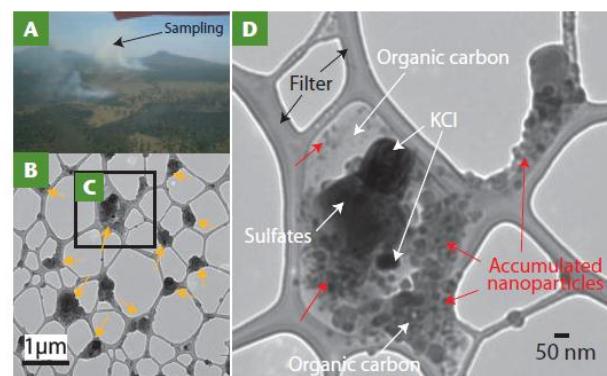
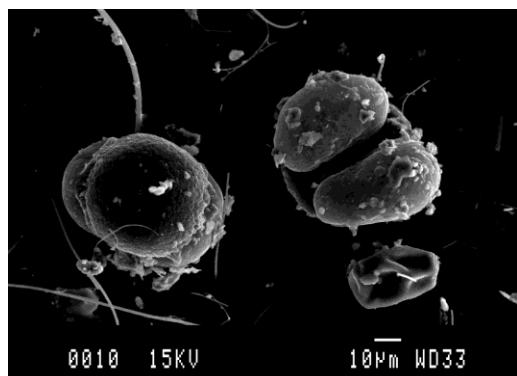
### Elemental carbon

Instrumentally defined parameter for mass concentration of graphitized C (unburned and char)

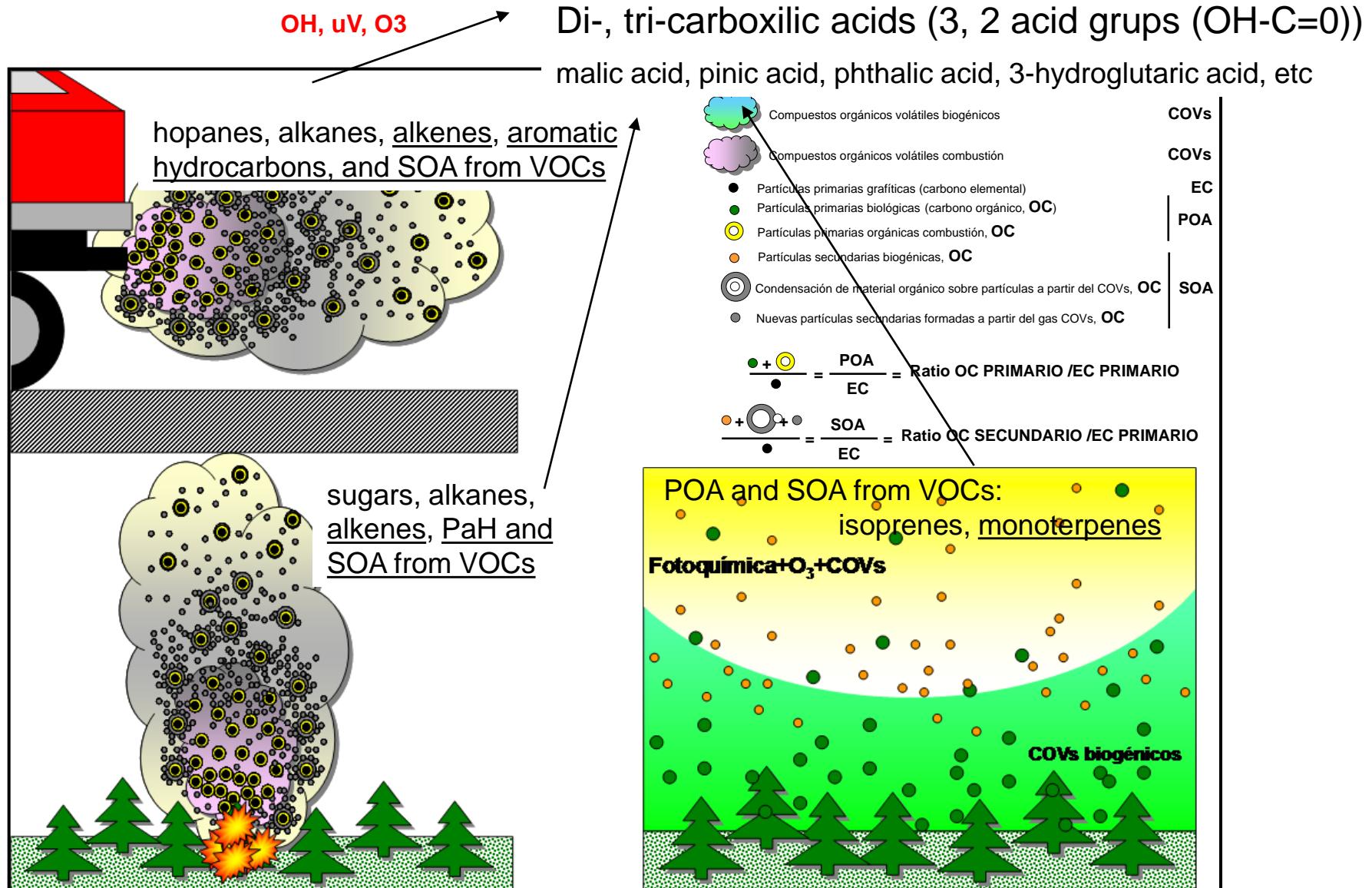


### Organic carbon

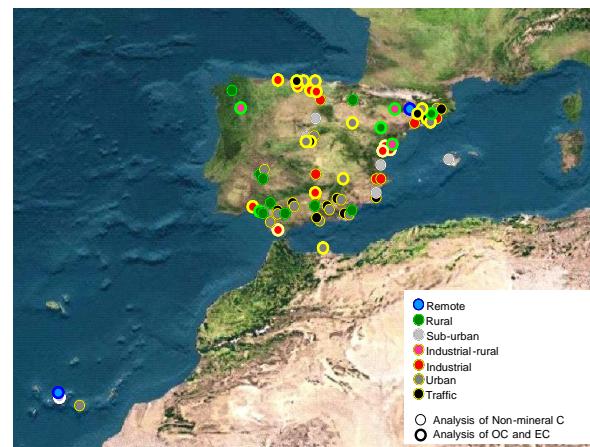
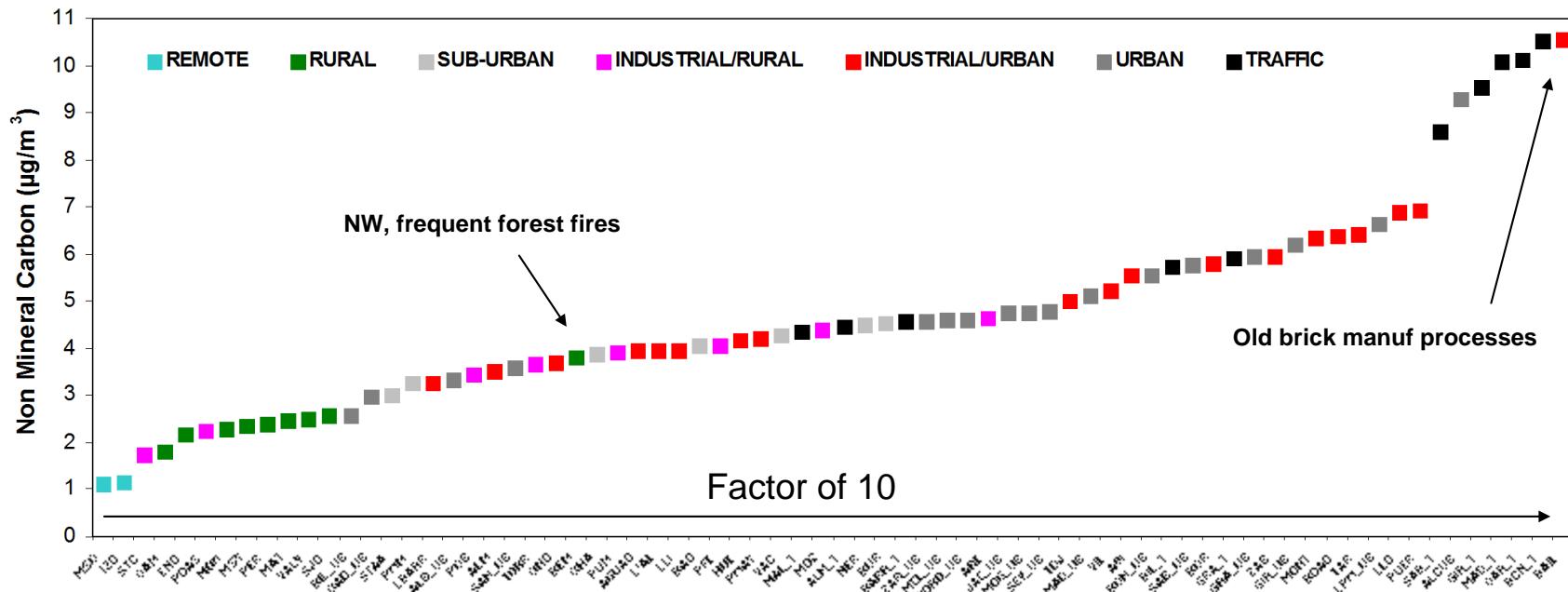
Instrumentally defined parameter for mass concentration of organic matter carbon



# Road traffic, air quality and aerosol measurements

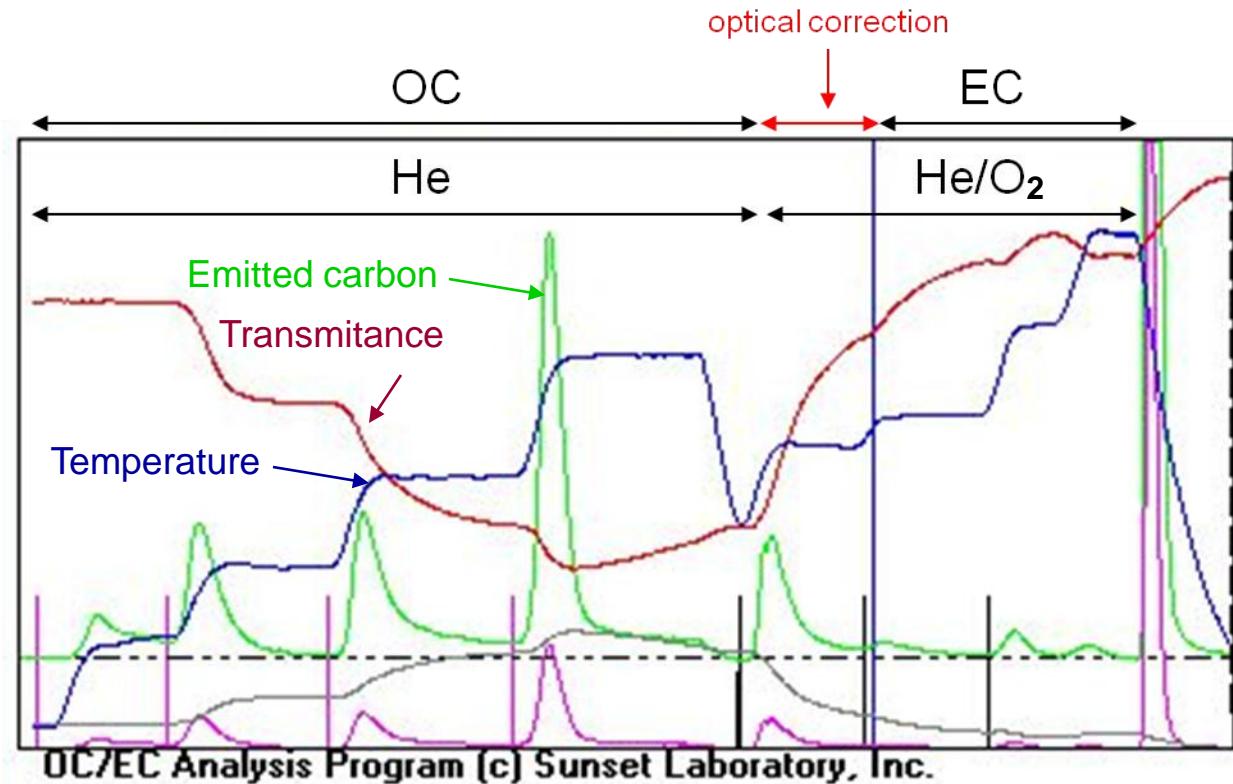


## 2. Carbonaceous aerosols: Non mineral C 1999-2011 in Spain



## 2. Carbonaceous aerosols: Organic and elemental carbon

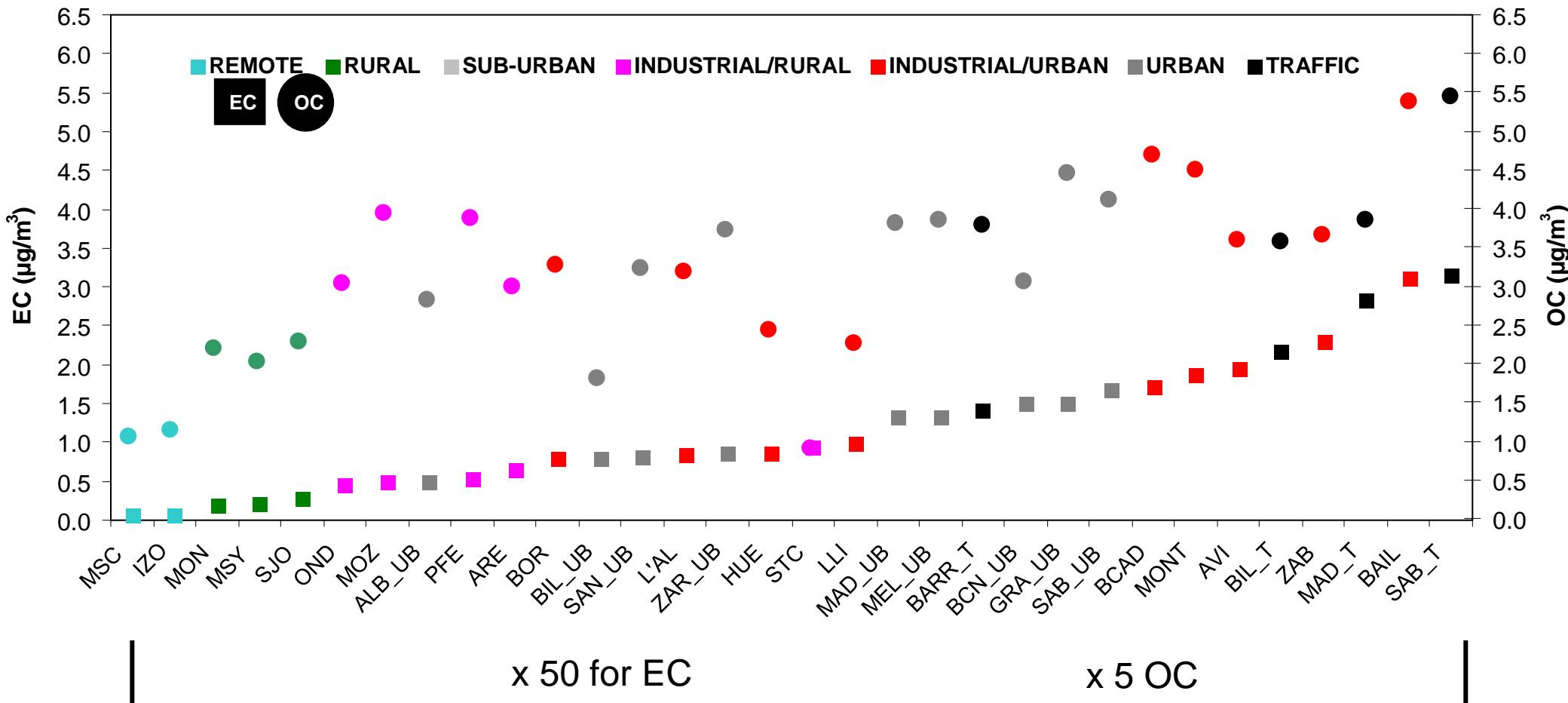
### Thermo-optical transmittance analysis (TOT)



(EUSAAR2.par temperature protocol; Cavalli *et al.*, 2010)

## 3. BC: Levels of EC and OC in Spain (Thermo-optical analysis)

BC may be proportional to contribution from traffic (+ biomass b.) and can be calibrated with EC



## 3. BC: On line BC optical measurements: Optical absorption of particles

### 3.1. TRANSMITTANCE METHOD

- Aethalometer (up to 7 wavelenghts)
- Particulate Soot Absorption Photometer (PSAP) (3 wavelenghts)
  - Measure the attenuation of a beam of light transmitted through the sample when collected on a fibrous filter.
  - Affected by the wavelength of the light.
  - The change in transmission from one measurement to the next is related to the **optical absorption coefficient (Abs, m<sup>-1</sup>)** of the aerosol:

$$\lambda\text{-dependent Abs- } (m^{-1}) = \frac{AREA}{VOLUME} \ln\left(\frac{I_0}{I}\right) f(Tr)$$

*f(Tr) filter + aerosol load correction factor*

*I<sub>0</sub> transmited intensity prior sample*

*I transmited intensity of sample*

### 3.2. MAAP METHOD

- Multi Angle Absorption Photometer (MAAP)

The **Abs** at 637nm is determined by radiative transfer considerations (multiple scattering effects and absorption enhancement by reflections). This calculation is based on directly measured values of transmission, direct and diffuse back scattering (130 and 165°)

$$MAAP\text{-Abs } (m^{-1}) = \frac{(1 - \omega_0) \ln(tr) AREA}{VOLUME}$$

*$\omega_0$  is the single scattering albedo, dependent of the particle absorption and filter matrix scattering*  
 *$Tr$ , transmittance of the aerosol layer on the filter*

$$Abs\ (637nm)\ (m^{-1}) = MAAP\text{-Abs}\ (m^{-1}) * f$$

# Road traffic, air quality and aerosol measurements

## 3. BC:

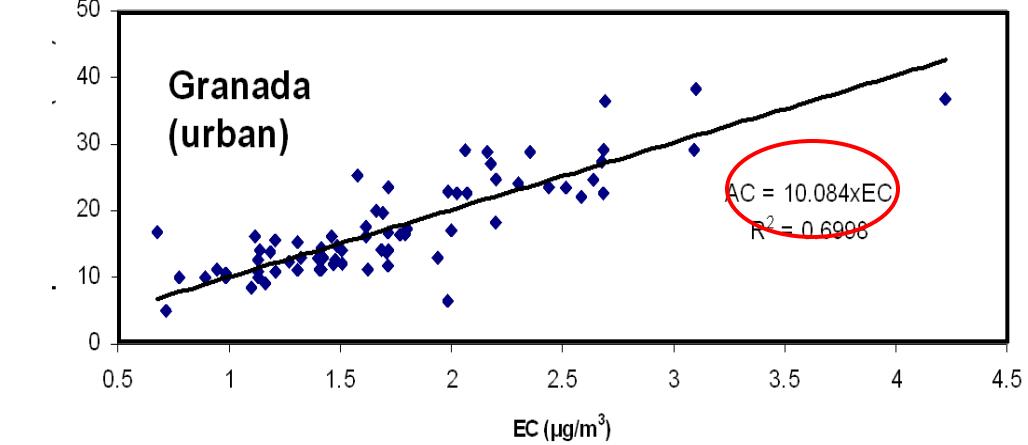
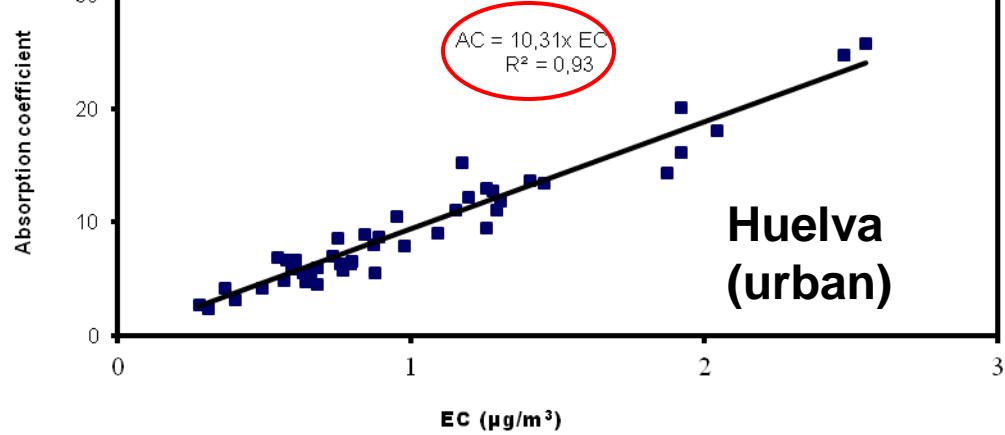
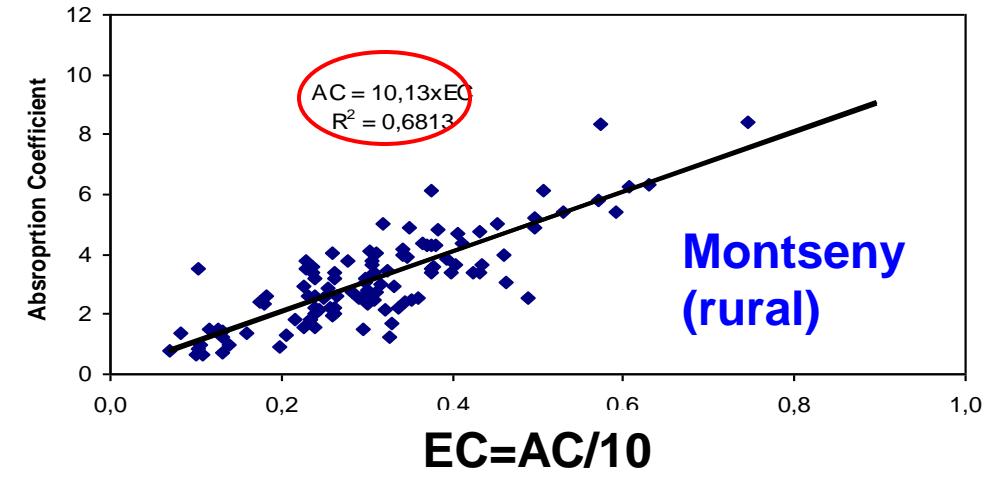
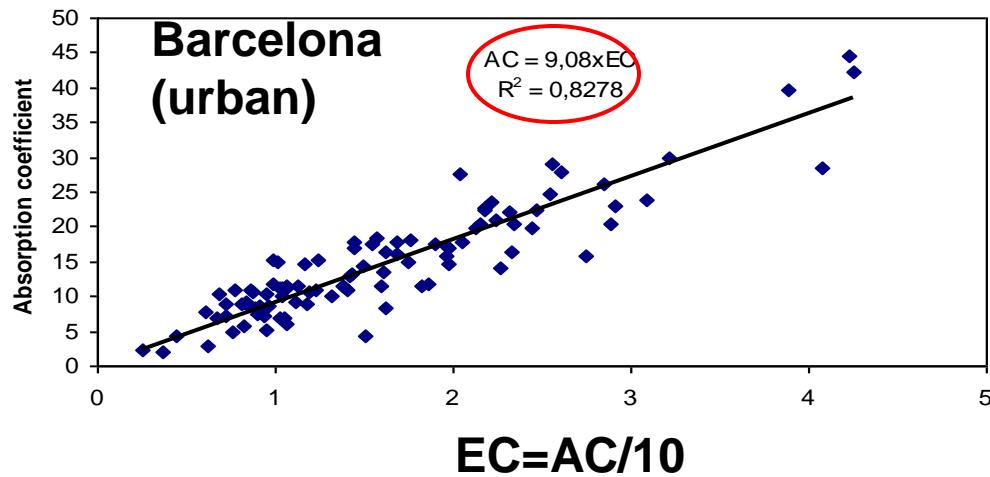
ORIGIN OF BC AND MASS ABSORPTION CROSS SECTION (MAC)

$$Abs_{BC}^{\lambda} (m^{-1}) = \sigma_{BC}^{\lambda} (m^2 g^{-1}) \times [EBC] (gm^{-3})$$

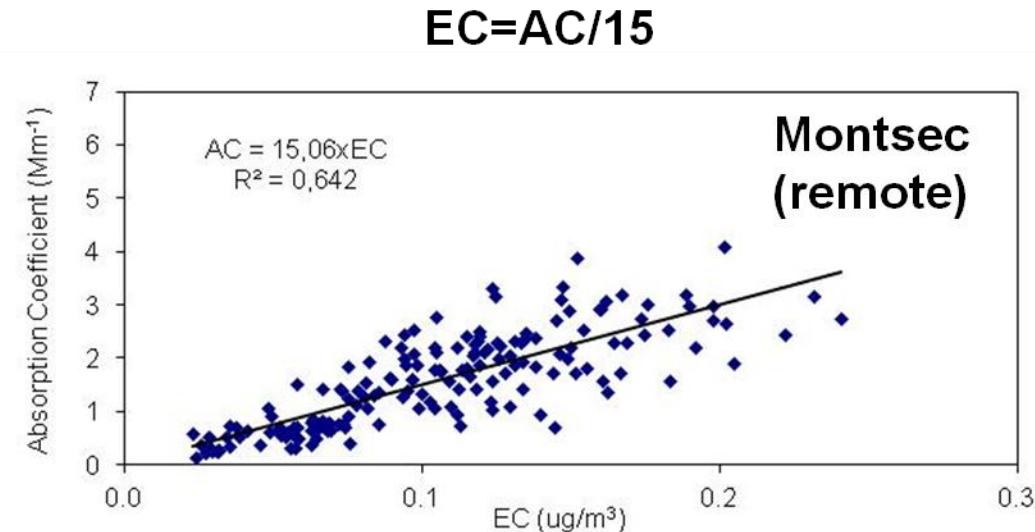
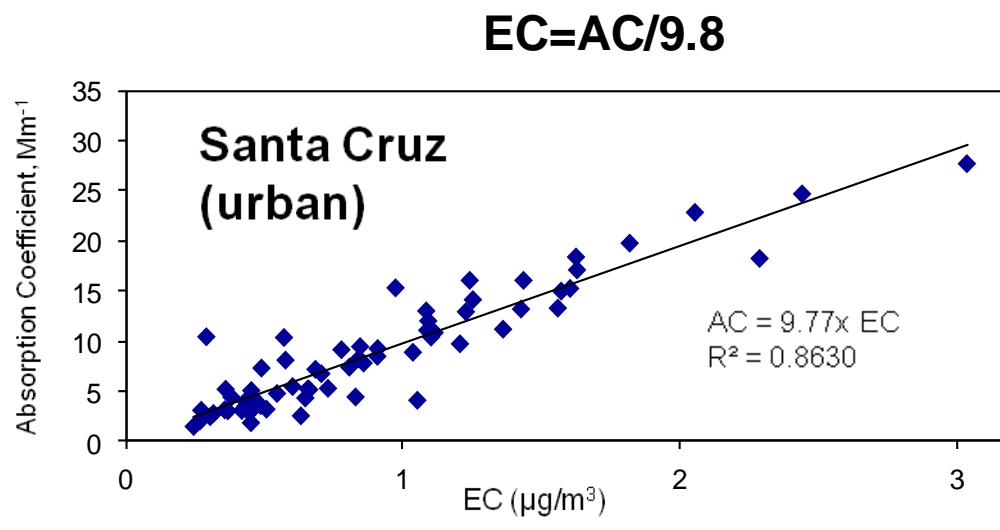
(EC; SUNSET)

(MAAP)

$$EC = AC/9$$

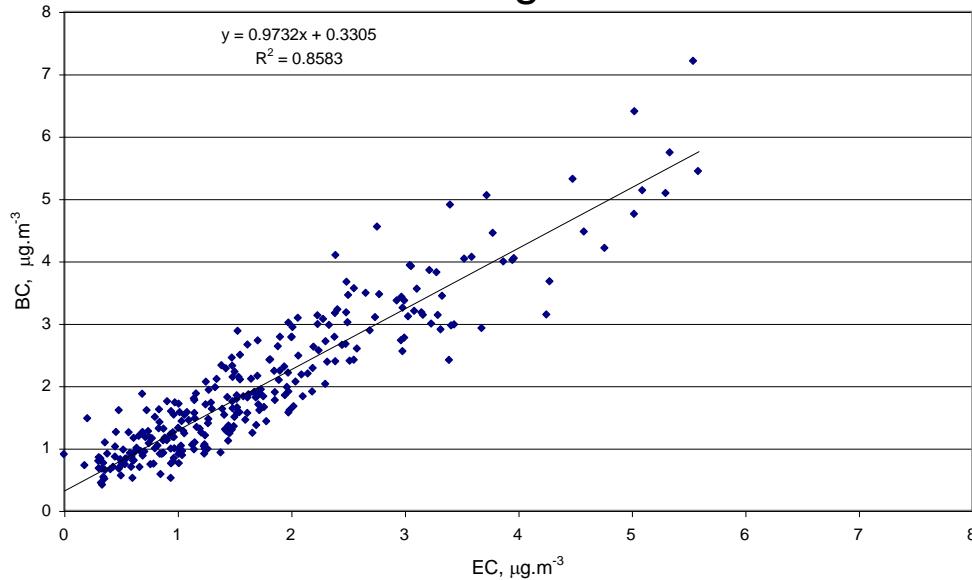


## 3. BC: ORIGIN OF BC AND MASS ABSORPTION CROSS SECTION (MAC)

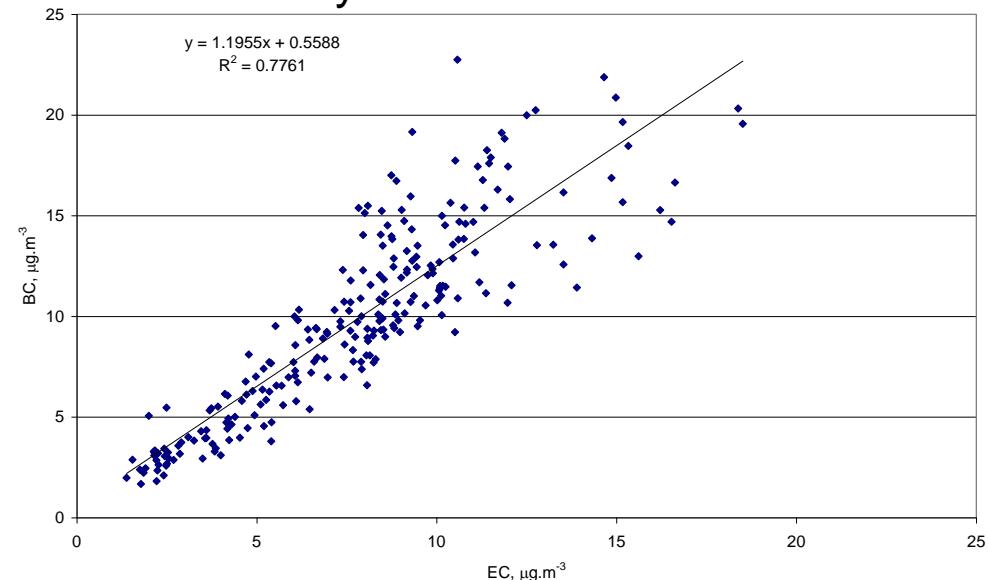


### 3. BC: Levels of BC compared with EC (EBC): Aethalometre and Sunset (NIOSH)

London: North Kensington



London: Marylebone Road



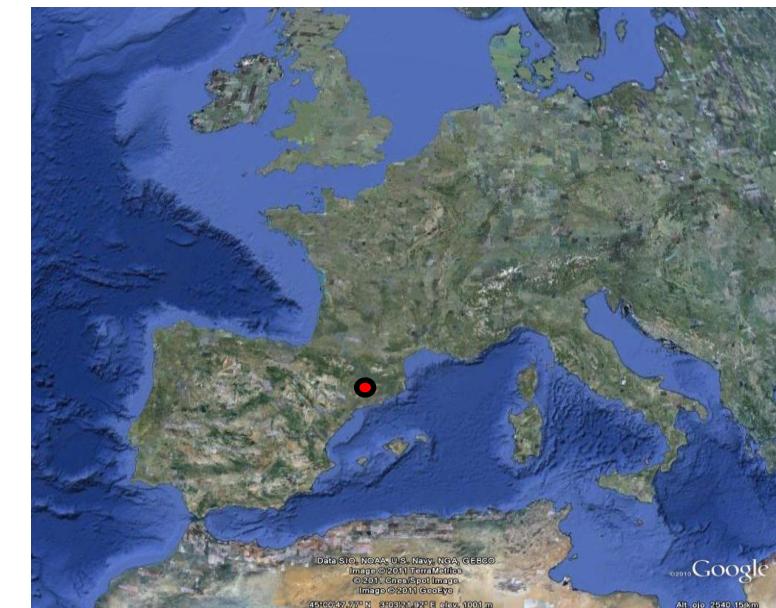
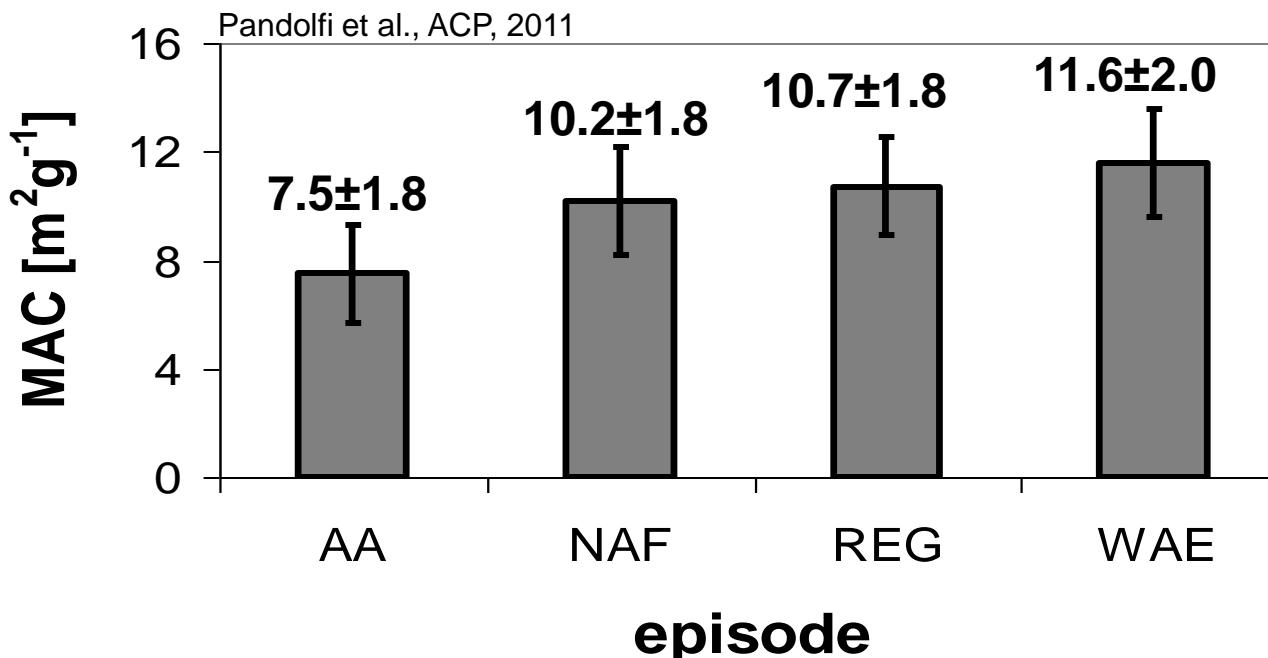
*Courtesy: P. Quency & DEFRA*

## 3. BC: ORIGIN OF BC AND MASS ABSORPTION CROSS SECTION (MAC)

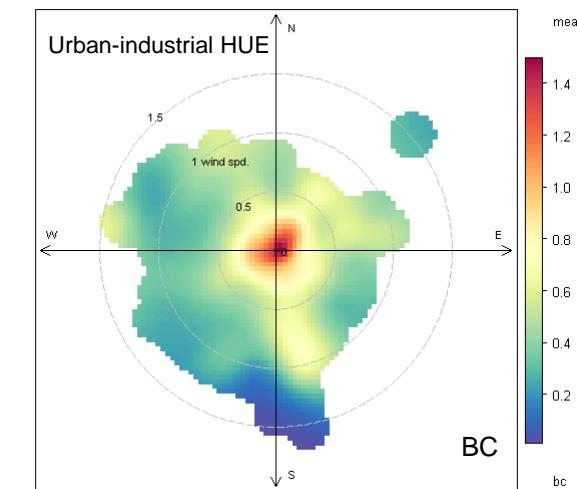
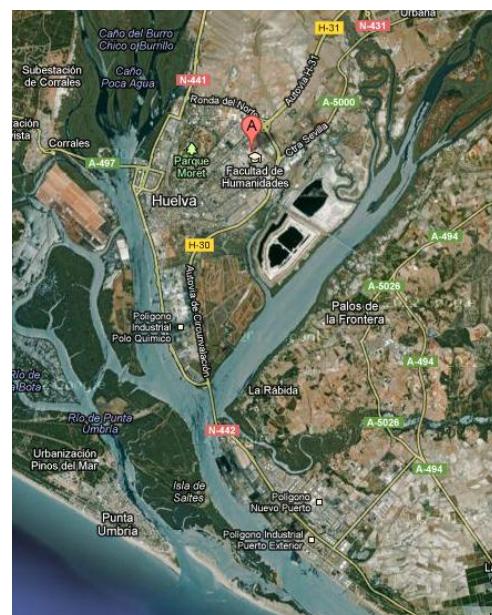
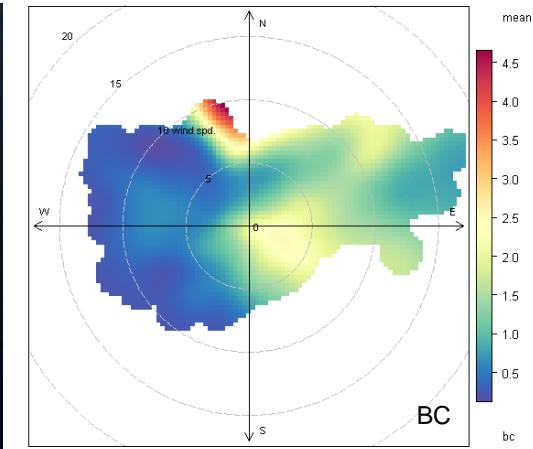
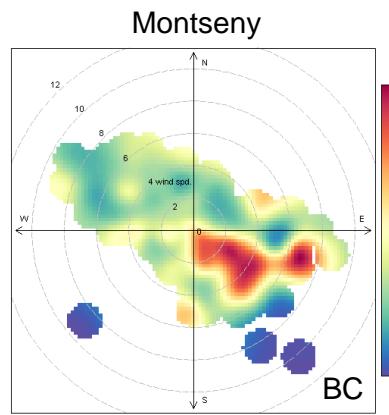
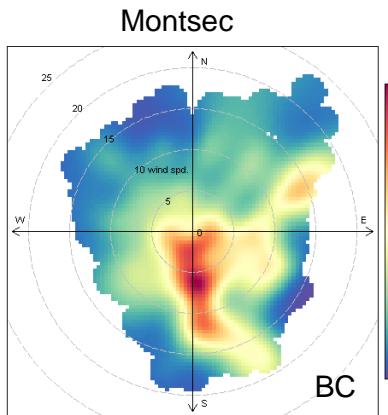
$$Abs_{BC}^{\lambda} (m^{-1}) = \sigma_{BC}^{\lambda} (m^2 g^{-1}) \times [EBC] (gm^{-3})$$

$7 - 15 \text{ m}^2\text{g}^{-1}$

MSY (04/2008 – 02/2010)



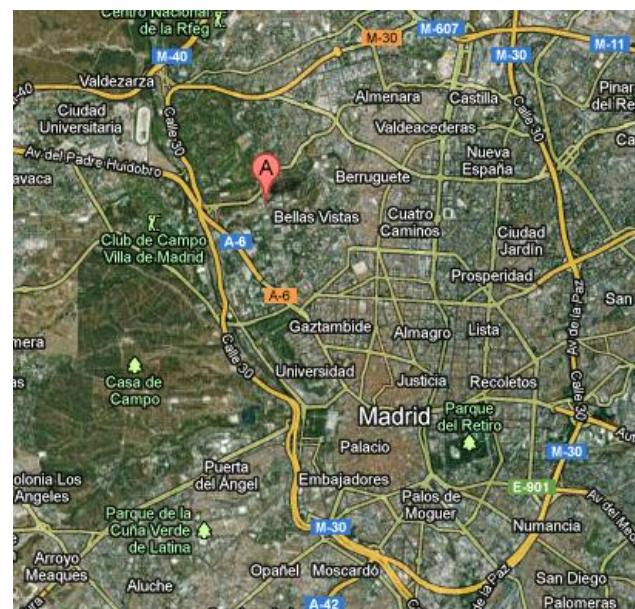
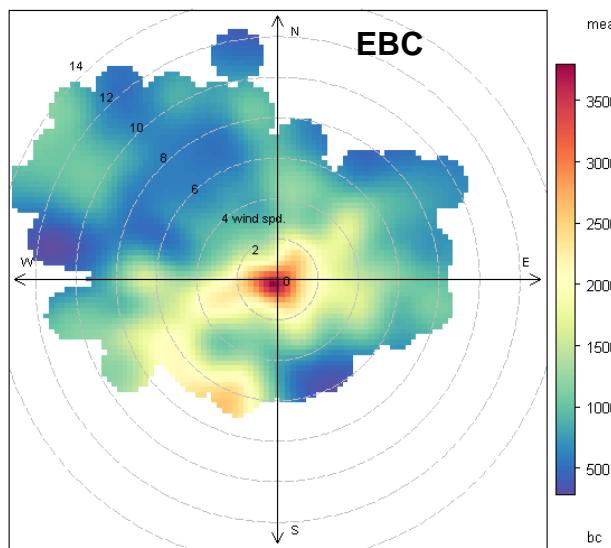
## 3. BC: Local vs external EBC



# Road traffic, air quality and aerosol measurements

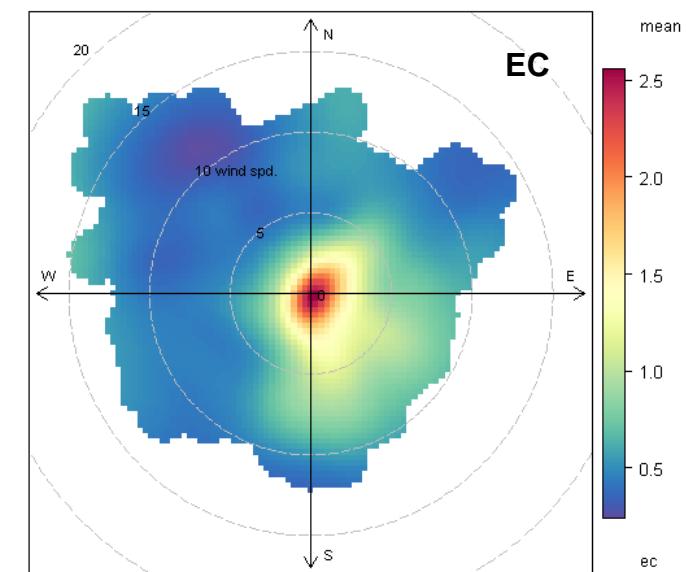


**Barcelona IDAEA**



**3. BC:**  
**Local vs external EBC**  
**& EC-OC**

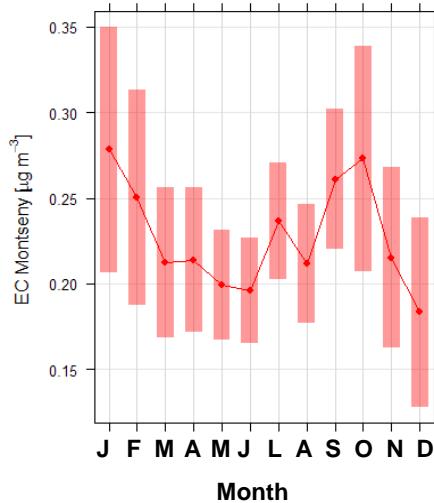
**Madrid CIEMAT**



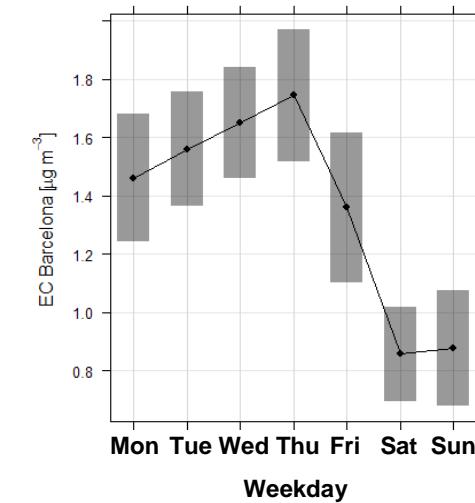
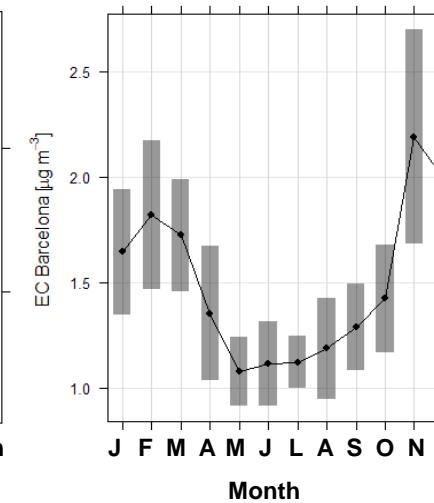
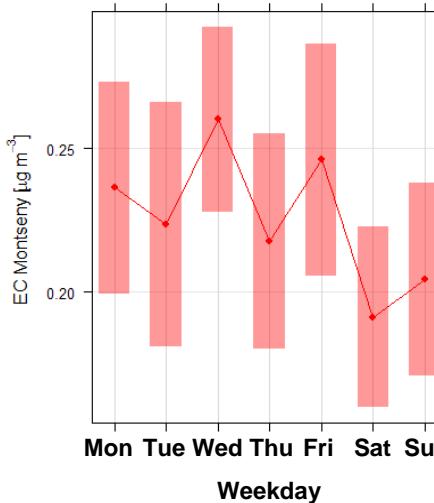
# Road traffic, air quality and aerosol measurements

## 3. BC: Seasonal and weekly patterns: EC

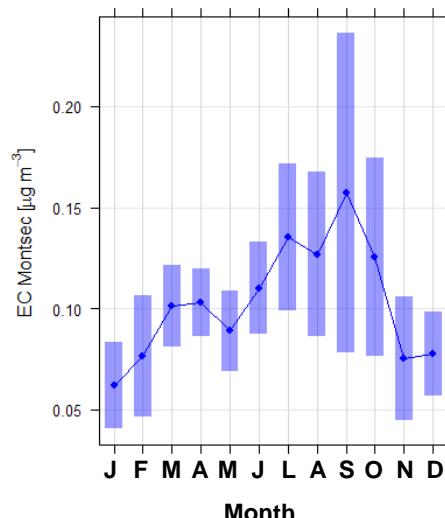
— Montseny



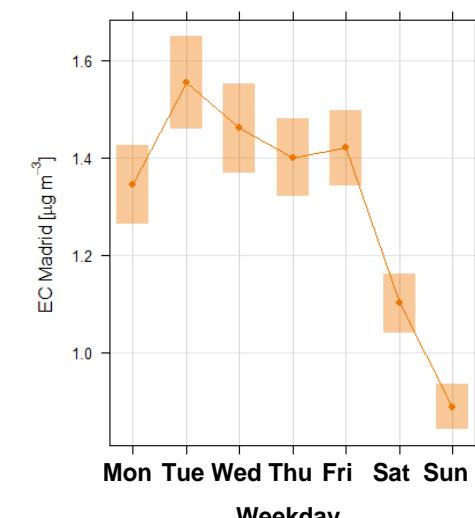
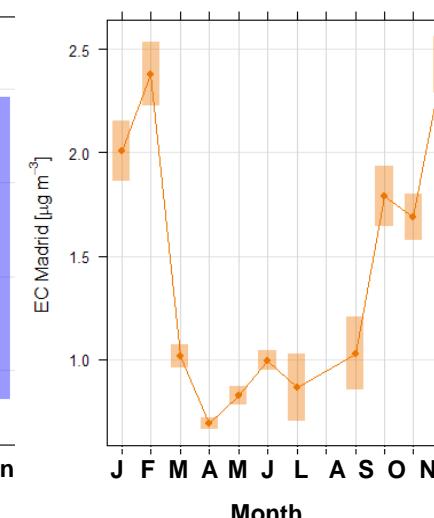
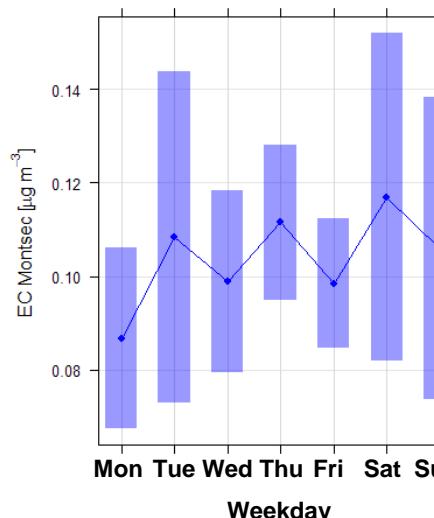
— Barcelona



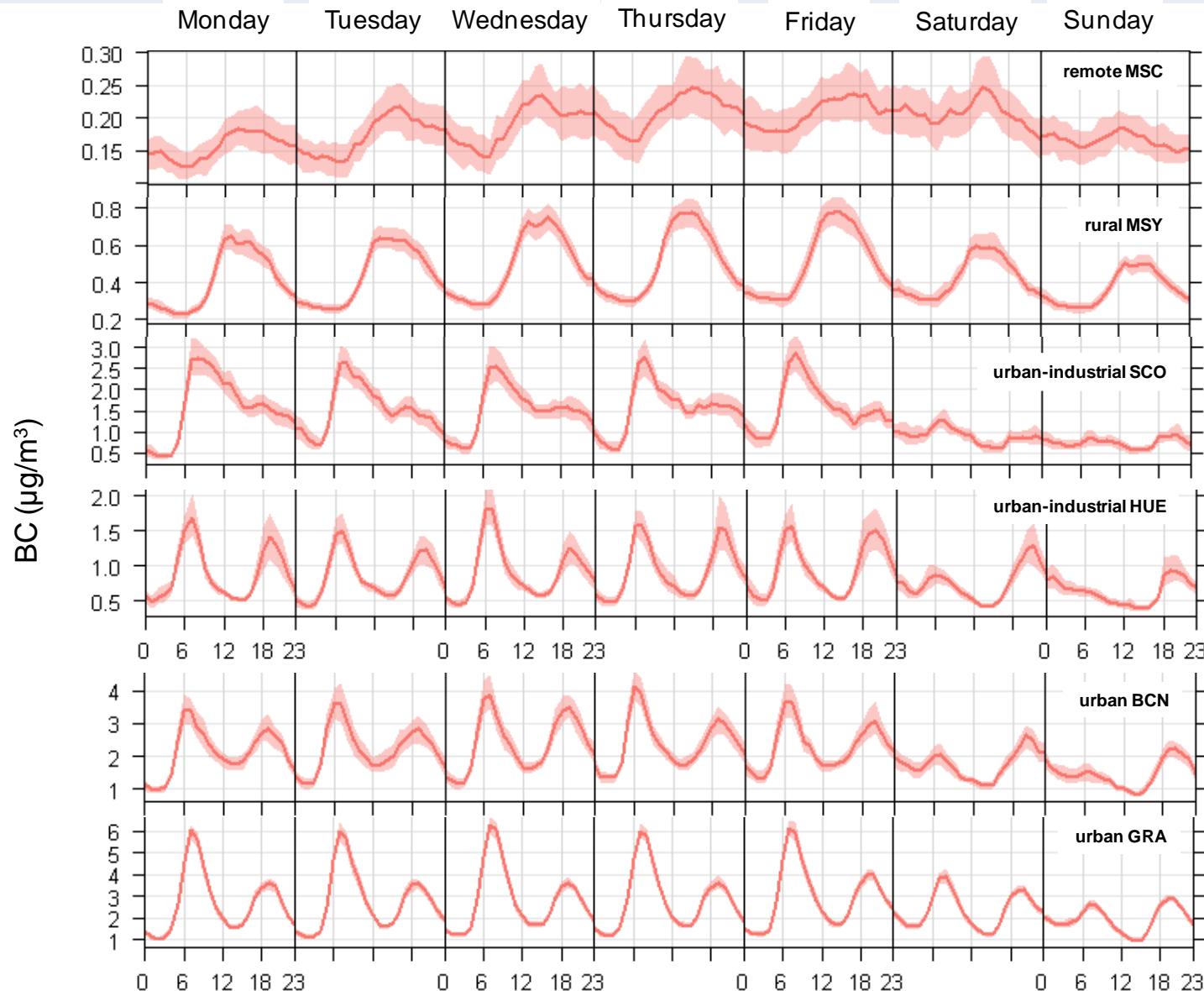
— Montsec



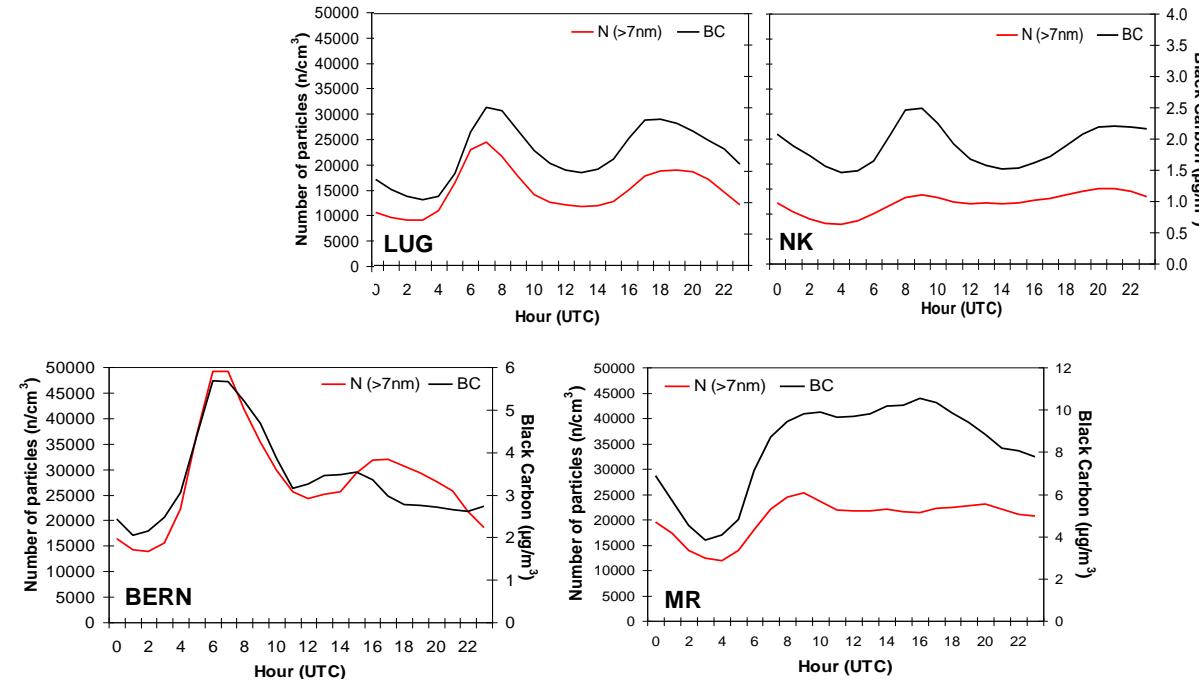
— Madrid



## 3. BC: Hourly patterns: EBC

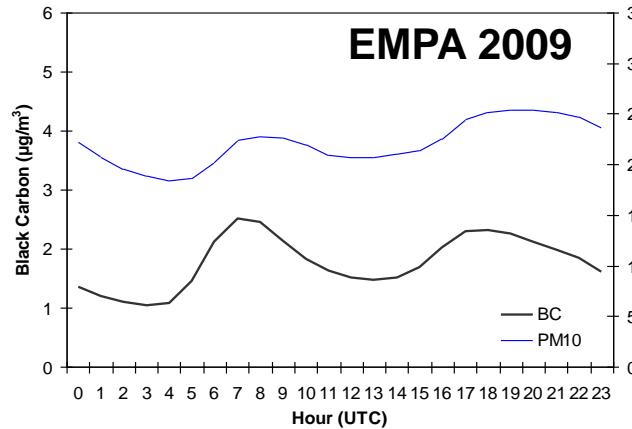


## 4. EBC & N: N vs EBC???

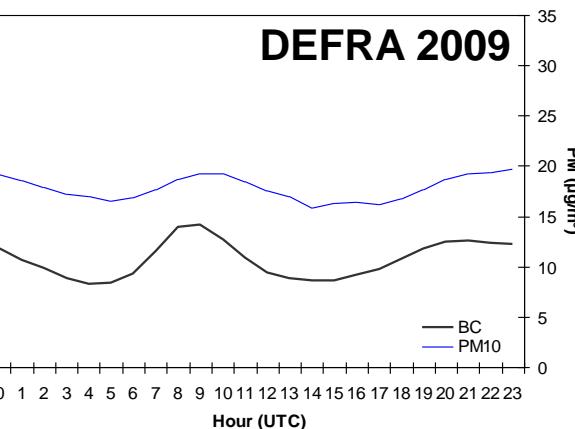


## 5. PM<sub>x</sub>, BC: PM10 does not always co-vary with traffic

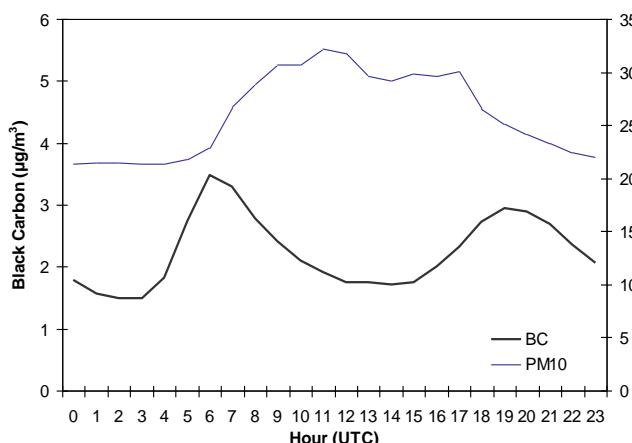
LUGANO URBAN SITE



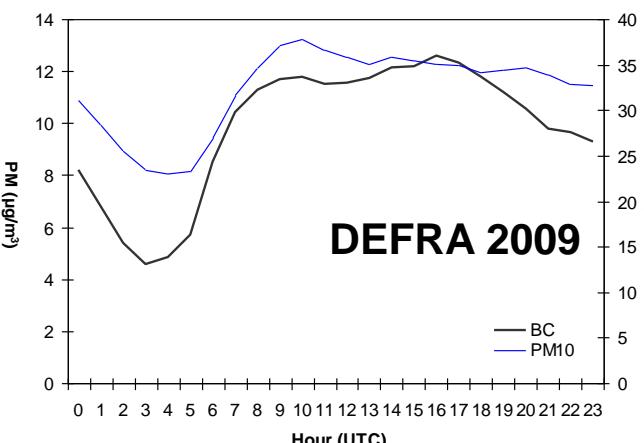
N. KENSINGTON URBAN SITE



BARCELONA URBAN SITE



MARYLEBONE KERBSIDE SITE (TRAFFIC)



# Road traffic, air quality and aerosol measurements

## Barcelona 2010

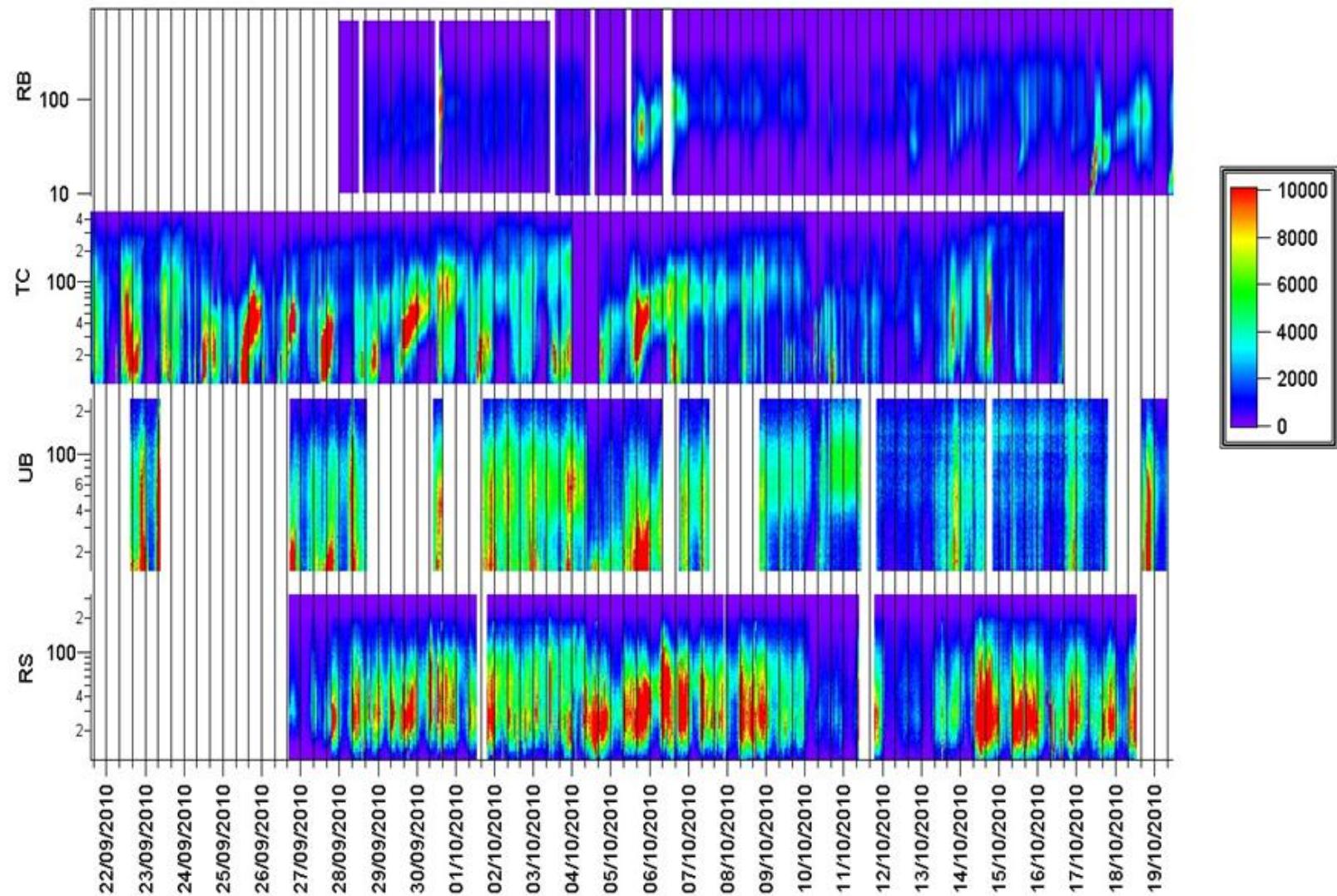
### 6. UFP:

RURAL

SUBURBAN

URBAN B.

TRAFFIC

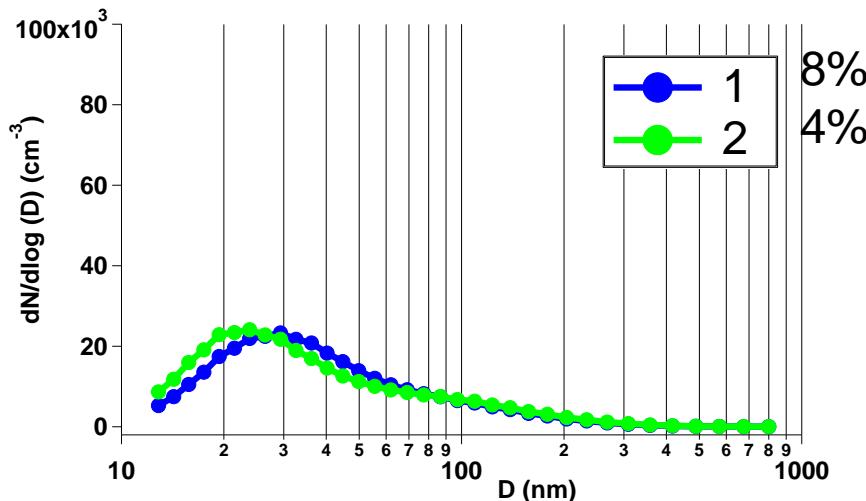


# Road traffic, air quality and aerosol measurements

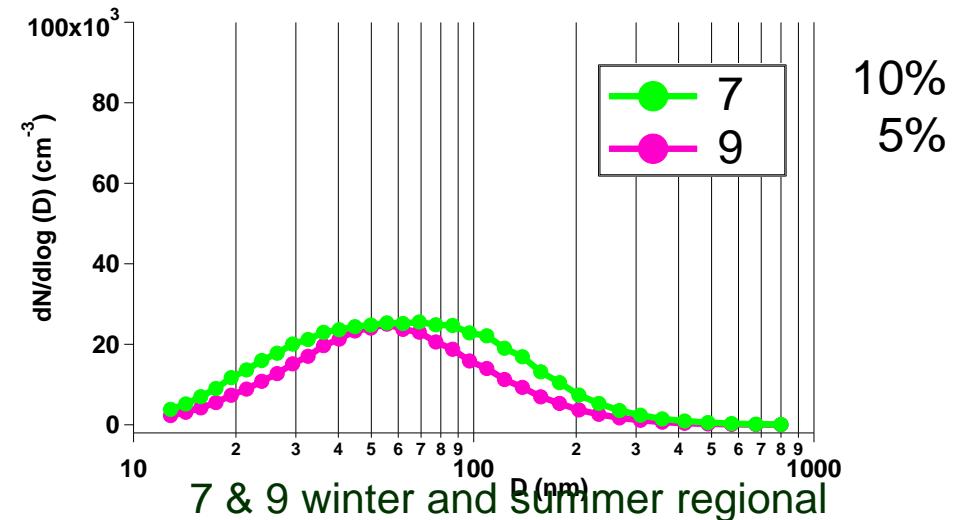
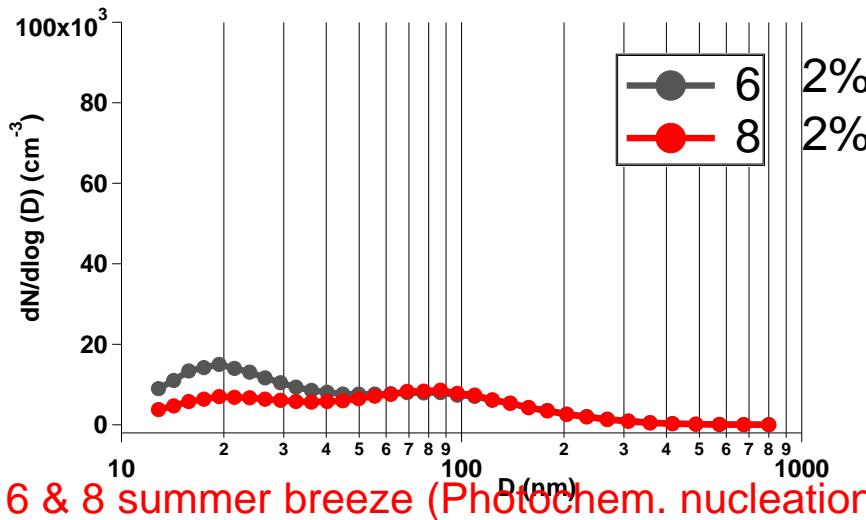
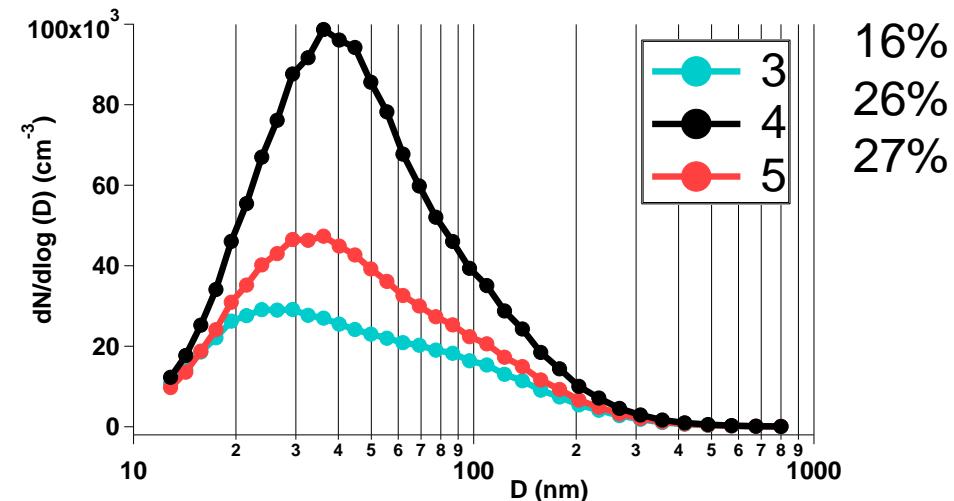
Dall'Osto et al., 2012b *Atmospheric Chemistry and Physics (submitted)*

**Barcelona 2004, Cluster analysis using k-means >6000 hourly size distributions  $N_{10-800}$**

1 & 2 clean atlantic advection



3 to 5 traffic pollution



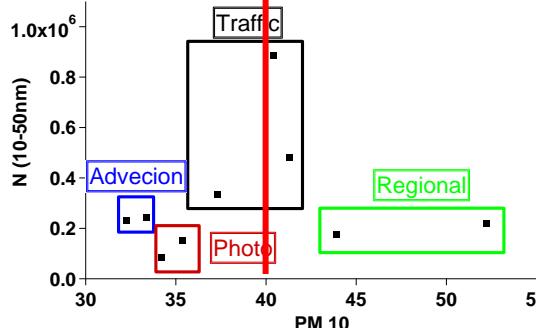
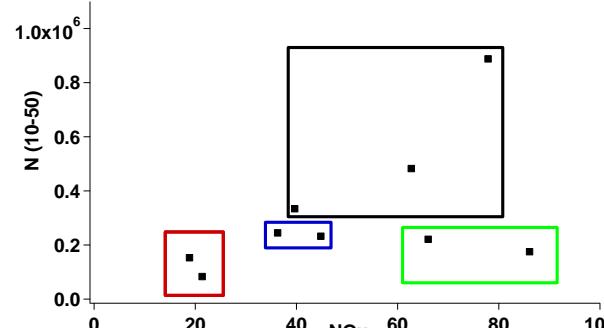
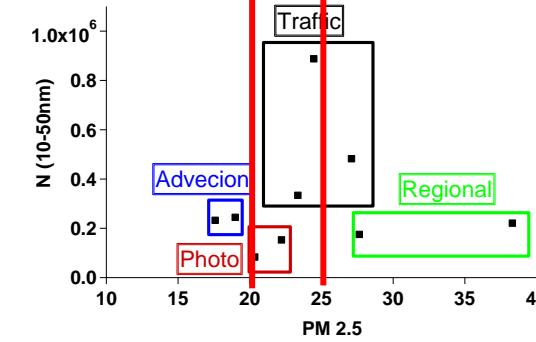
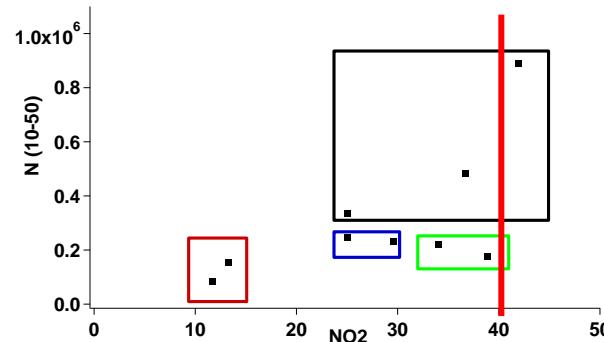
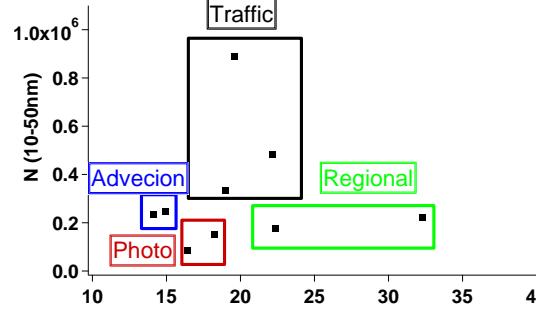
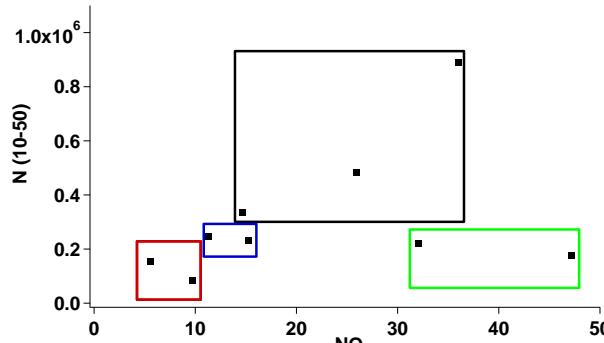
6 & 8 summer breeze (Photochem. nucleation)

7 & 9 winter and summer regional

# Road traffic, air quality and aerosol measurements

Dall'Osto et al., 2012b *Atmospheric Chemistry and Physics (submitted)*

**Barcelona 2004, Cluster analysis using k-means >6000 hourly size distributions  $N_{10-800}$**



Not only N  
is relevant but  
also toxicity of the type of  
UFP from the 7 clusters!!!

In our study characterisation  
of photochemical nucleation  
limited by  $N > 13\text{nm DLI}!!!$

## 7. PM speciation and receptor modelling

Large data set on PM speciation needed (t & \$)

(at least 100 days/year for annual representativity, all days for daily control)

Ex. Off-line inorganics, IDAEA-CSIC

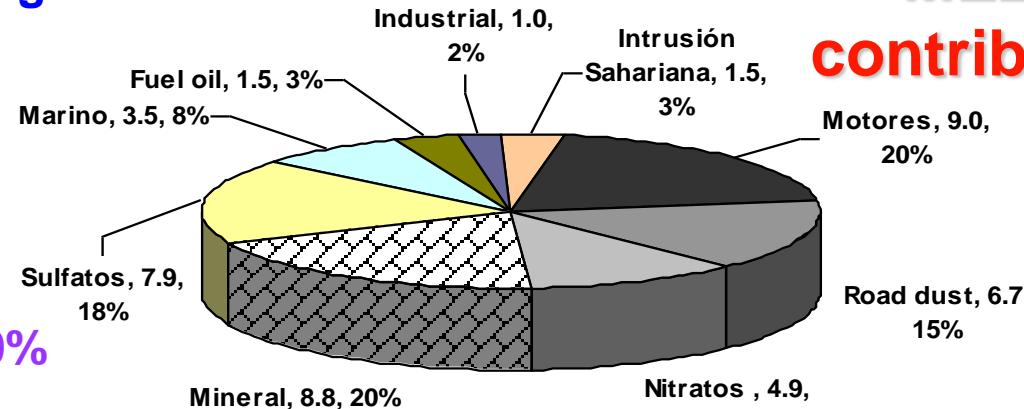
Crustal-mineral		Anthropogenic	
Al <sub>2</sub> O <sub>3</sub>	ICP-AES	OC & EC	Thermo-optical
Ca	ICP-AES	<b>Inorganic Secondary Species</b>	
K	ICP-AES	NH <sub>4</sub> <sup>+</sup>	C.FIA
Mg	ICP-AES	SO <sub>4</sub> <sup>2-</sup>	Ion Cromat.
Fe	ICP-AES	NO <sub>3</sub> <sup>-</sup>	Ion Cromat.
Ti	ICP-AES	<b>40 Metals</b> (ICP-MS)	
P	ICP-AES	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	
CO <sub>3</sub> <sup>2-</sup>	ind. Ca		
SiO <sub>2</sub>	ind. 3*Al <sub>2</sub> O <sub>3</sub>		
Marine aerosol		Accounted 75-85 % mass PM	
Na <sup>+</sup>	ICP-AES		
Cl <sup>-</sup>	Ion Cromat.		
SO <sub>4</sub> <sup>2-</sup>	ind. Na		

# Road traffic, air quality and aerosol measurements

**Max.  
Shipping: 3%**

**PM<sub>10</sub>**

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

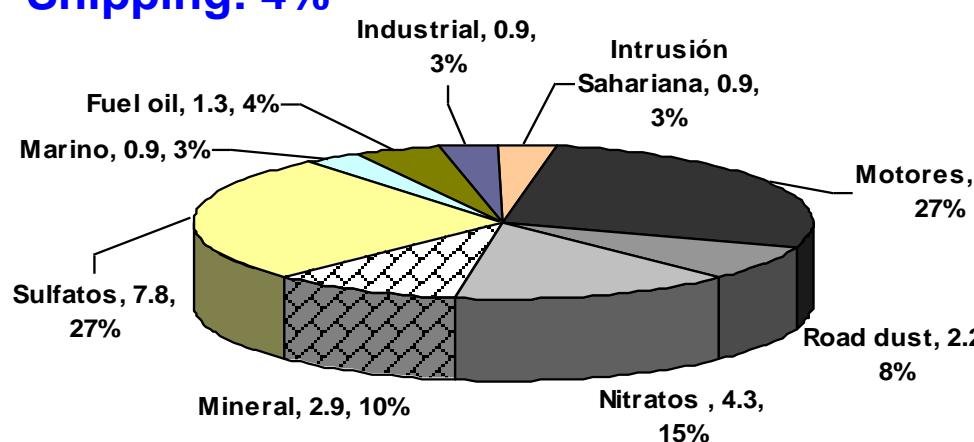


**Traffic: 43%**  
**ME2: Annual source contributions in Barcelona**

**Max.  
Shipping: 4%**

**PM<sub>2.5</sub>**

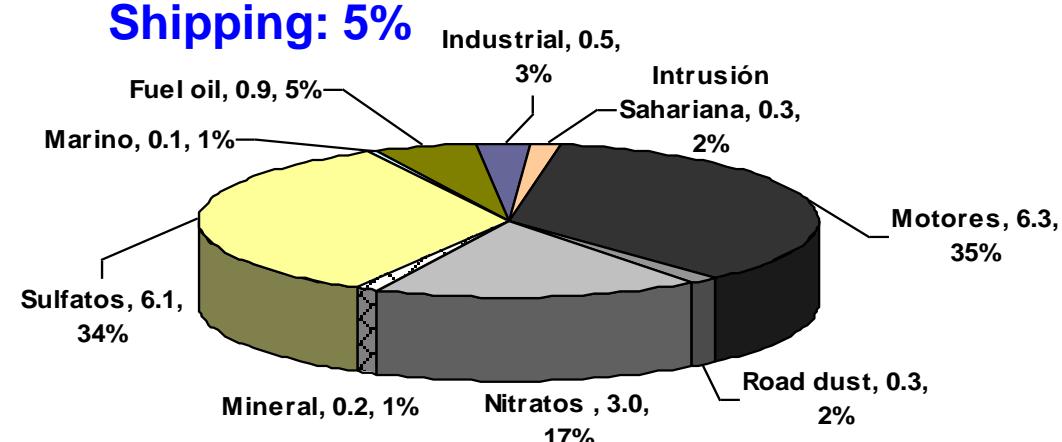
**Traffic: 46%**



**Max.  
Shipping: 5%**

**PM<sub>1</sub>**

**Traffic: 50%**

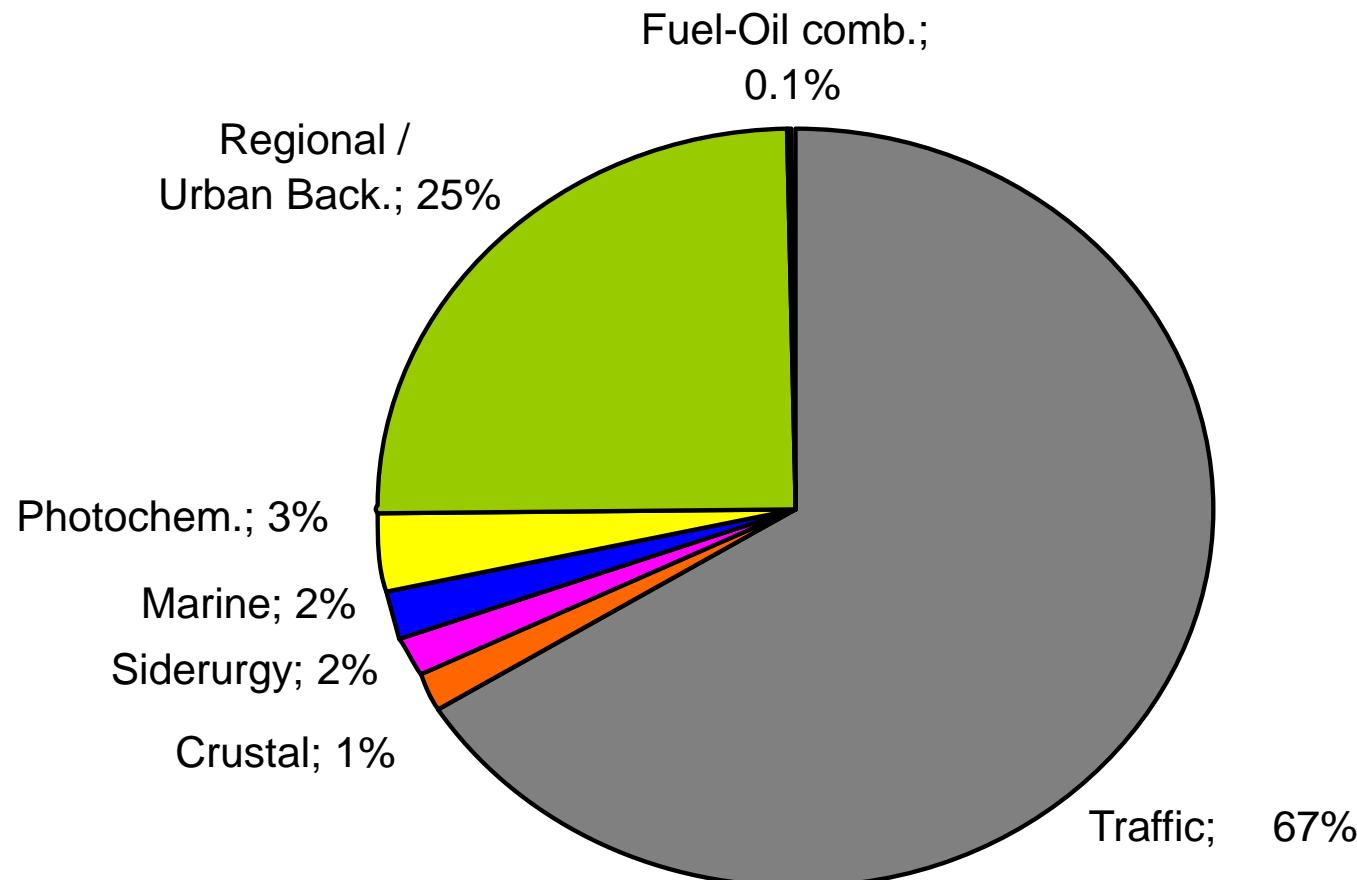


**Demolition-resuspension (reg.): 10%**

*Amato, et al., 2009. Atmospheric Environment*

## 8. Receptor modelling for UFP Barcelona, 2004

Source contribution to the mean annual  $N_{10-800}$

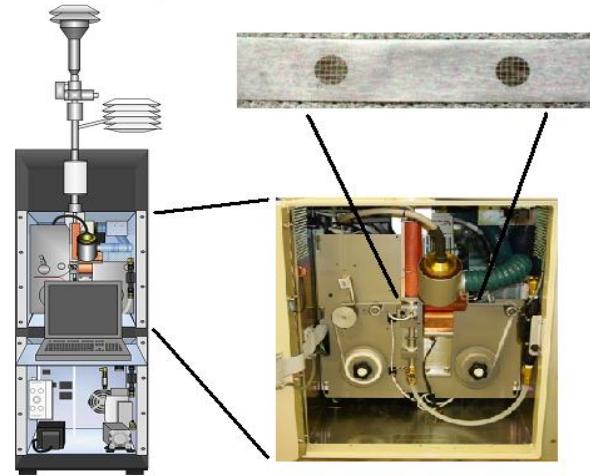


# Future trends

OM, sulphate, nitrate, chloride, ammonium

insitu calibrated with EC EUSAAR-2

Metals



source apportionment

But  $N_{50}$  not analyzed currently by AMS

Then, UFP measurements will still be necessary, specially if demonstrated that  $N_{50}$  is highly toxic or has cerebrovascular and cardiovascular effects

# Conclusions

- PM10 (mixture of source contributions) and BC (as a source tracer for traffic and biomass burning) offer a good combination for air quality monitoring, specially because exceedances are registered in traffic hotspots
- Quantitative receptor modeling applied to data sets of PM speciation may offer the possibility of setting limit values for PM contributions from road traffic (relatively homogeneous emission chemical profiles across Europe). However, BC measurements yield similar information, with real time data, low operational cost and easily to standardize method.
- Source apportionment analysis on size-number concentration and speciation measurements yield quantitative information on sources and processes contributions.
- Not all current PM<sub>x</sub> and NO<sub>2</sub> limit values protect exposure for high UFP episodes
- In future combination of Mini-AMS + BC + XRF will allow continuous monitoring of most components, but for the finest aerosols, UFP measurements will still be necessary for <50nm), specially if toxicity is high

**Acknowledgements: AIRMONTECH (VII F.P. EC)**

**Ministry of the Environment of Spain, Ministry of Sciences and Innovation of Spain**

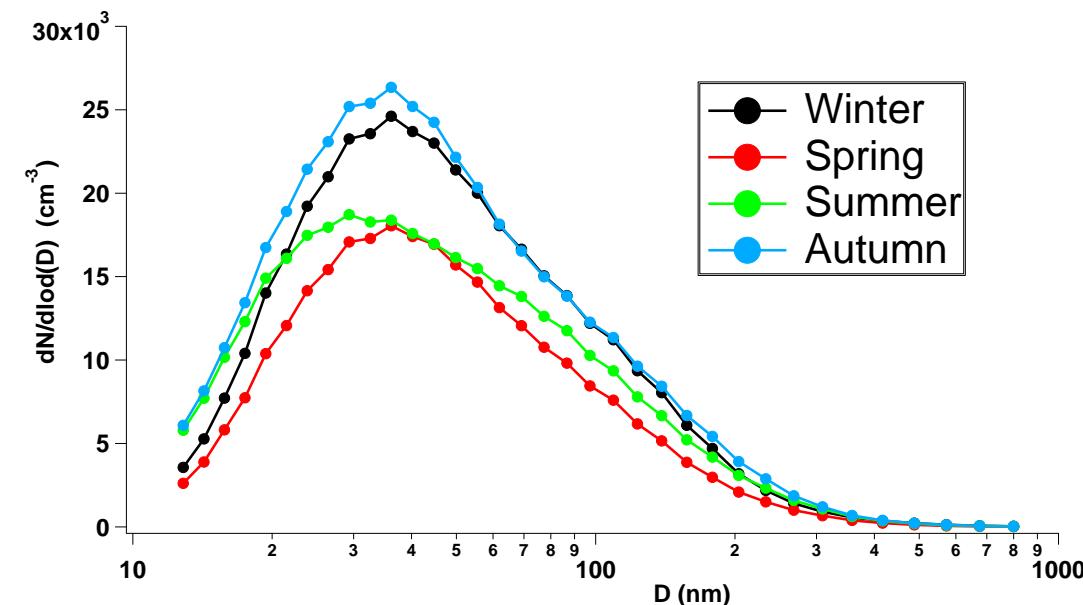
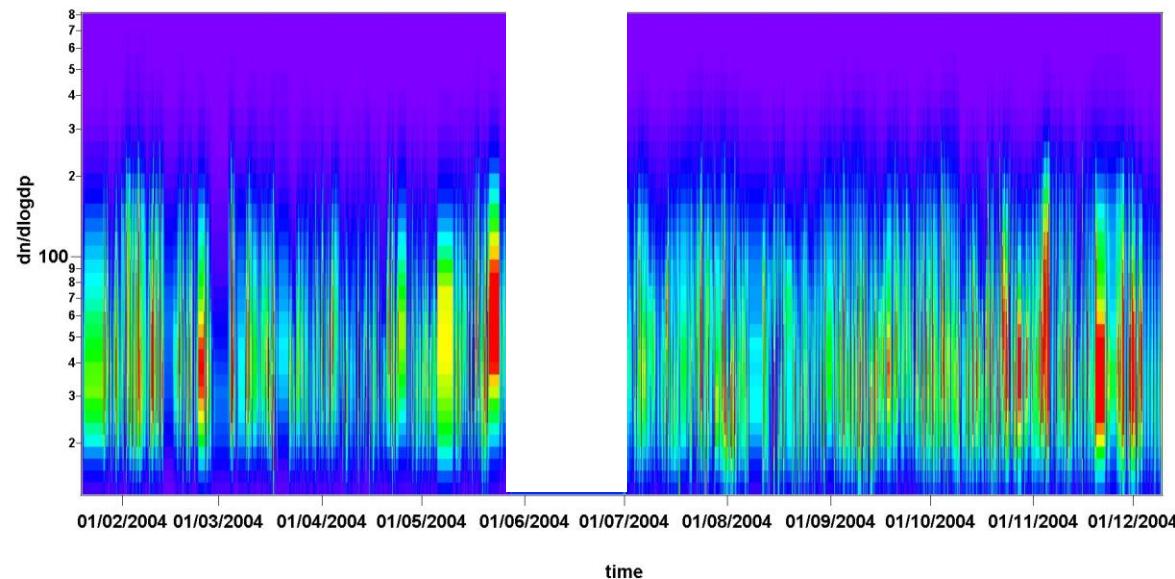
**Regional AQ monitoring networks: Generalitat de Catalunya, Andalucía, Aragón, Asturias, Baleares, Canarias, Cantabria, Castilla la Mancha, Castilla León, Euskadi, Extremadura, Galicia, Generalitat Valenciana, Madrid, Melilla, Murcia. Also to DEFRA (UK) and EMPA (CH) for providing data on BC and N, OpenAir (Carslaw & Ropkins, 2011. Environmental Modeling & Software)**

***Thank you for your attention !***

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# Road traffic, air quality and aerosol measurements

## 6. UFP: $N_{10-800}$ continuously measured 2004, Barcelona urban background



Dall'Osto et al., 2011 ACP (in preparation)

## 3. EBC: A number of pollutants co-vary along the day with traffic

A large proportion of PM exceedances occur in urban-traffic sites

BARCELONA, urban background, mean values for 2009

