# New trends in urban air quality monitoring: ultrafine particles and black carbon

**Querol X.**[a], Alastuey A.[a] Viana M.[a], Moreno T.[a], Reche C.[a], Minguillón M.C.[a], Dall'Osto M.[a], Ripoll A.[a], Pandolfi M.[a], Amato F.[a], Pérez N.[a], Pey J.[a], Cusack M.[a], Karanasiou A.[a], Vázquez R.[a], de la Rosa J.[b], Sánchez de la Campa A.[b], Fernández-Camacho R.[b], Rodriguez S.[c], Pío C.[d], Alados-Arboledas L.[e], Titos G.[e], Atíñano B.[f], Salvador P.[f]

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A review of the European urban air quality levels evidence that particulate matter and $NO_2$ are the two critical parameters. Member states identified emissions from road traffic and domestic and residential (including biomass burning) sources as the major causes of exceedances of air quality standards on these parameters. The presentation shows how different air quality metrics evidence the impact of such sources, especially road traffic, on air quality. Special attention is paid in source contributions of black carbon and ultrafine particles and on the variability of levels of these parameters in remote, rural and urban environments. Other contribution sources of ultrafine and nano-particles to exposure are also shown.

The analysis performed evidenced the following conclusions:

1. PM10 (mixture of source contributions) and EBC (equivalent black carbon as obtained from aethalometre or MAAP measurements calibrated with EC thermo-optical simultaneous measurements, a source tracer for traffic and biomass burning) offer a good combination for AQ monitoring, specially because exceedances are registered in traffic and biomass burning hotspots.
2. Given that emission levels of EBC from road traffic have decreased as a consequence of the effectiveness of diesel filter traps, EBC also decreased in urban ambient air. Also organic compounds have shown to have relevant health impacts. Thus in future EBC may be substituted by total carbon measurements. However currently, online total C measurements are not so advanced as BC measurements.
3. 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, EBC measurements yield similar information, with real time data, low operational cost and easily to standardize method.
4. Source apportionment analysis on size-number concentration and speciation measurements yield quantitative information on N contributions from sources and atmospheric processes (Figure1).
5. Not all current PMx and $NO_2$ limit values protect exposure for high UFP episodes.

6. The ratio $NO_2$/OC+EC has changed (Figure 2) a lot in the last decade, and probably $NO_2$/UFP. This has to be taken into account when using $NO_2$ as a proxy of AQ impact of traffic PM and N. In any case UFP measures are necessary currently. May we still use EBC measurements as a proxy for UFP?
7. 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, specially if toxicity is high

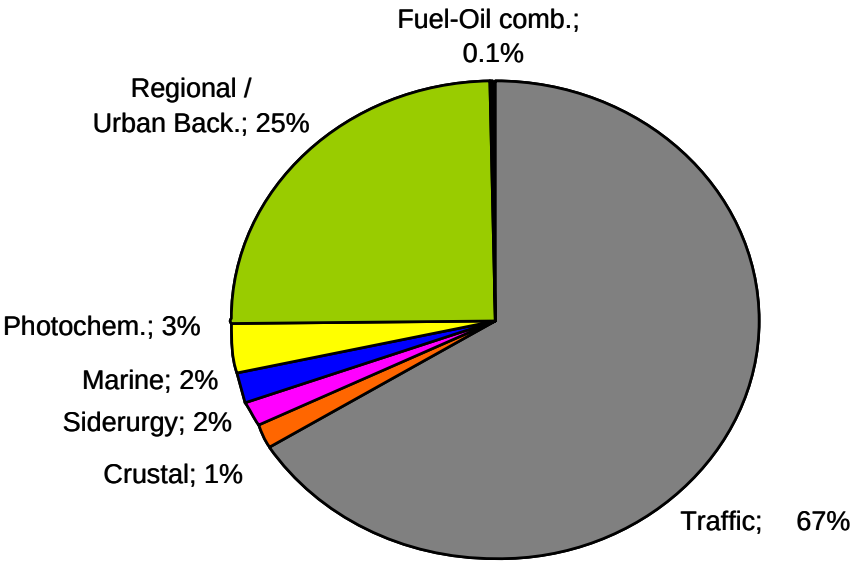


**Fig.1.** Results from source apportionment análisis carried out with receptor modelling showing the 2004 annual average source contributions of UFP (10-800 nm) to the ambient air levels at a urban background site in Barcelona

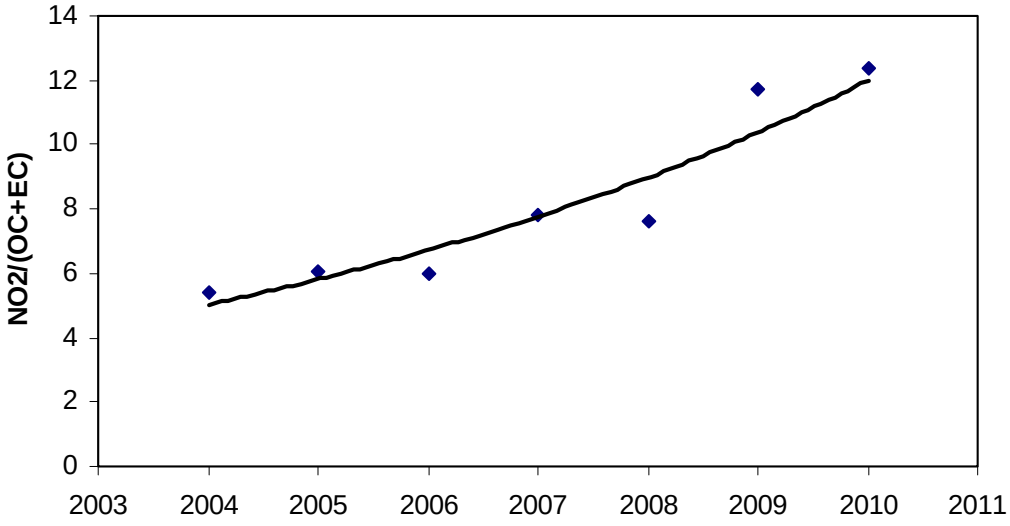


**Fig.2.** Mean annual NO2/OC+EC ratios measured in Barcelona from 2004 to 2010. NO2 measured at Ciutadella urban background and OC+EC measured at CSIC urban background site.

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16th ETH Conference on Combustion Generated Nanoparticles, Zurich 27th June 2012

# Outline

- Road traffic, air quality and aerosol measurements
    1. PMx
    2. Carbonaceous aerosols
    3. BC (EBC)
    4. EBC & N
    5. UFP
    6. PM speciation and receptor modelling
    7. Receptor modelling and UFP
- Future trends
- Conclusions

Air Pollution Monitoring Technologies for Urban Areas

SEVENTH FRAMEWORK PROGRAMME

AirMonTech

CGL2010-19464/CLI

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Contract S-G D Air Quality and Industrial Environment

SAPUSS

MARIE CURIE ACTIONS

# Road traffic, air quality and aerosol measurements

**PM components**

**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**

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

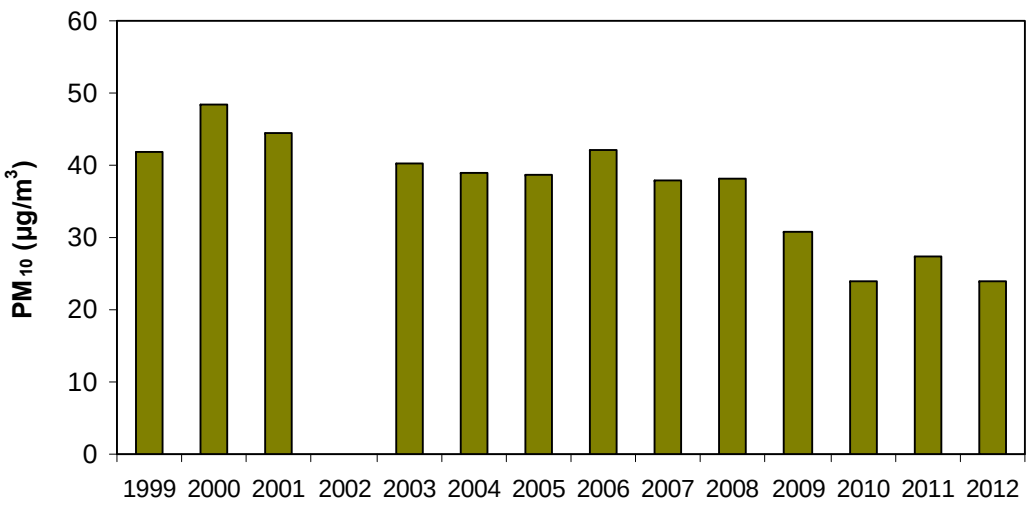
**Trace elements**

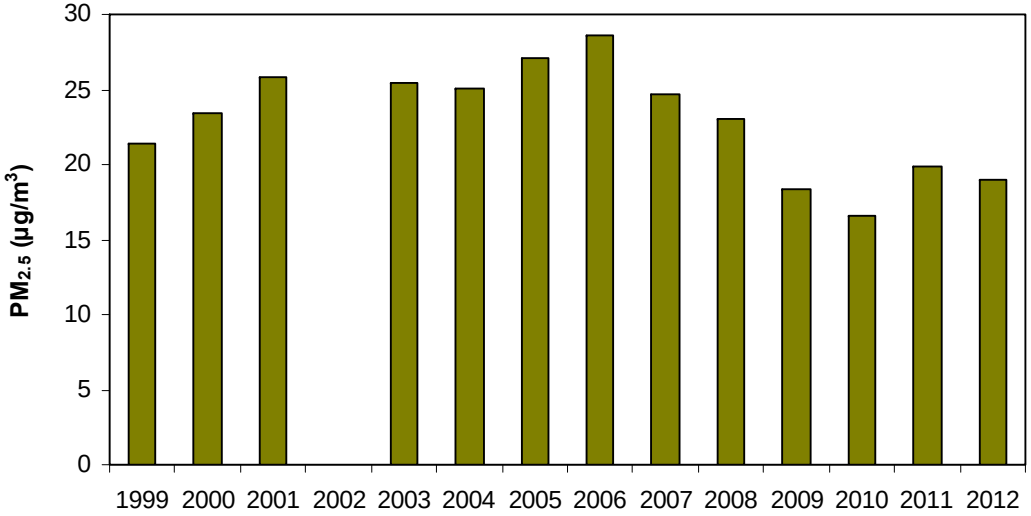
As, Ba, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Ga, Gd, Ge, Hf, La, Li, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Yb, Zn, Zr

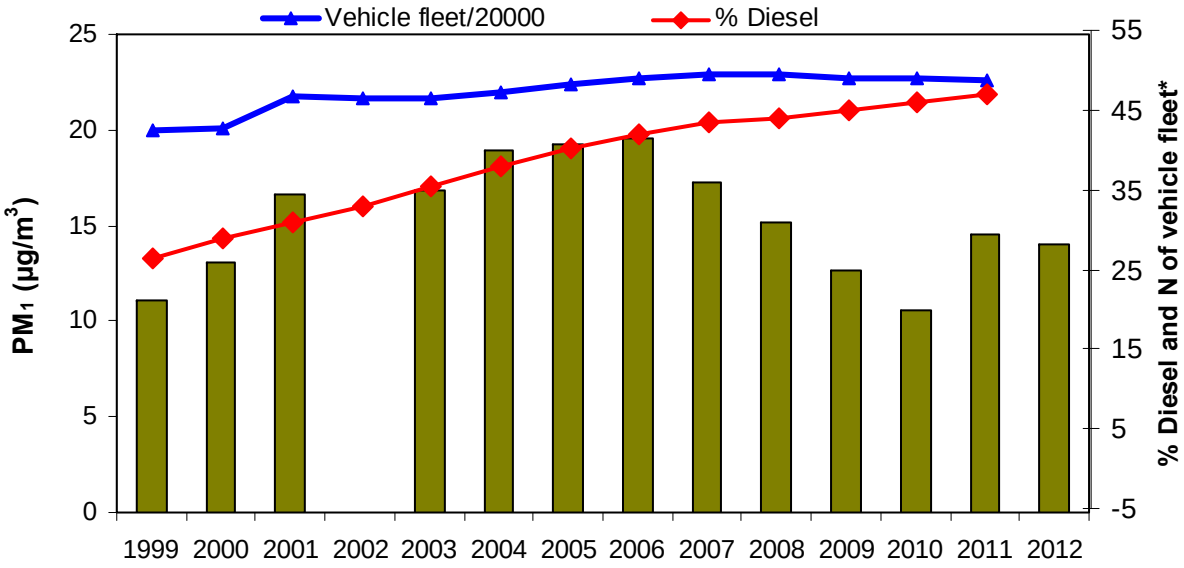

**Large proportion of PMx exceedances**

# Road traffic, air quality and aerosol measurements

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

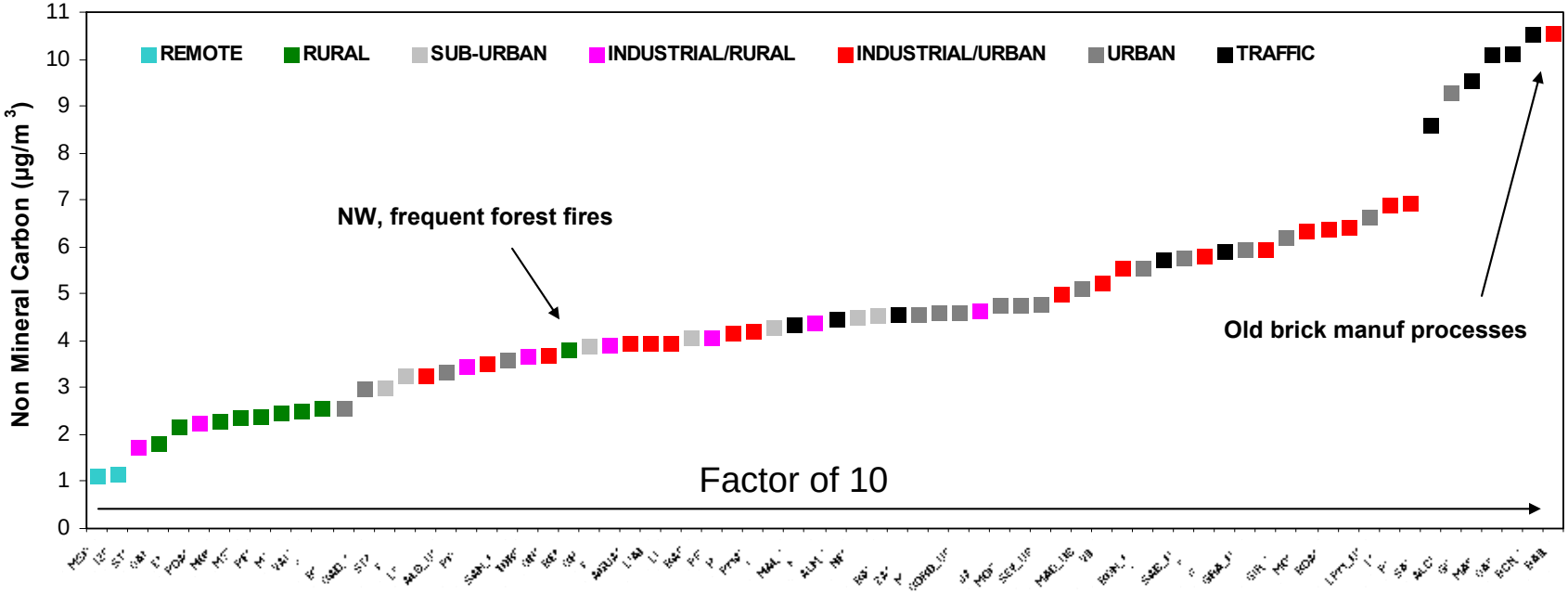


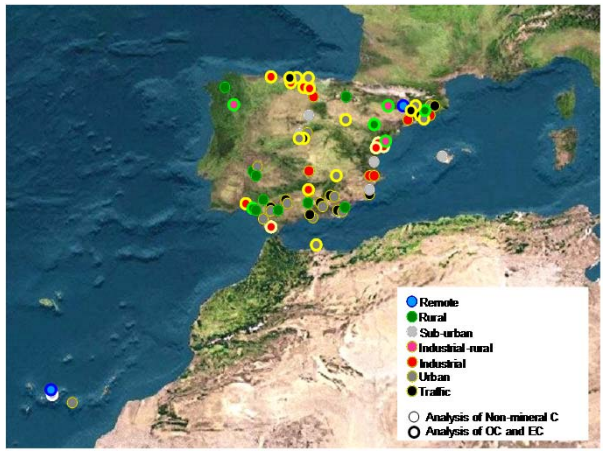



# Road traffic, air quality and aerosol measurements

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

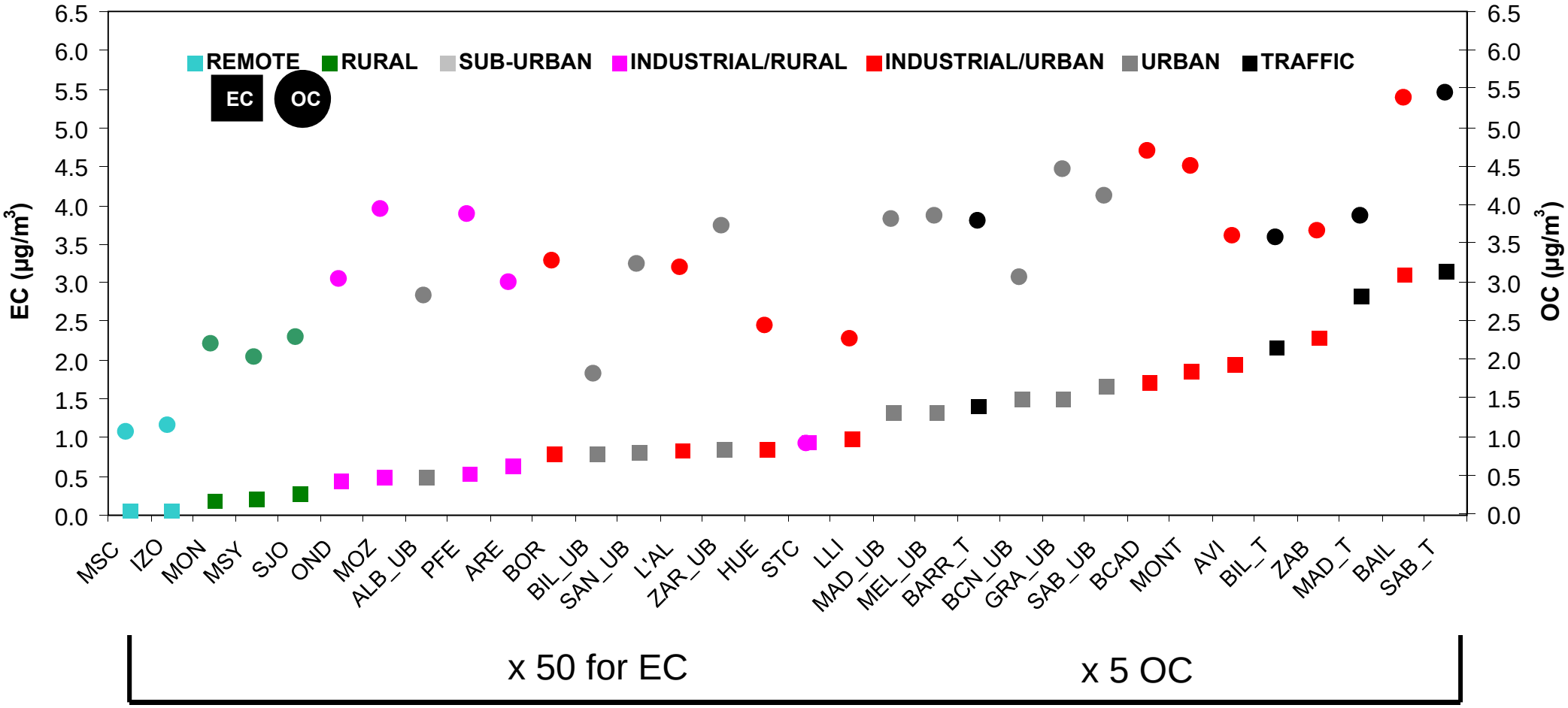


# Road traffic, air quality and aerosol measurements

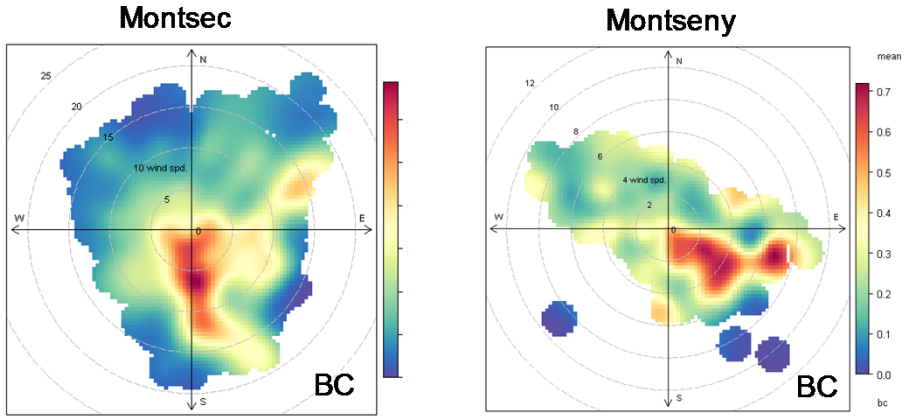
## 3. BC: Levels of EC and OC in Spain (Thermo-optical analysis)

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

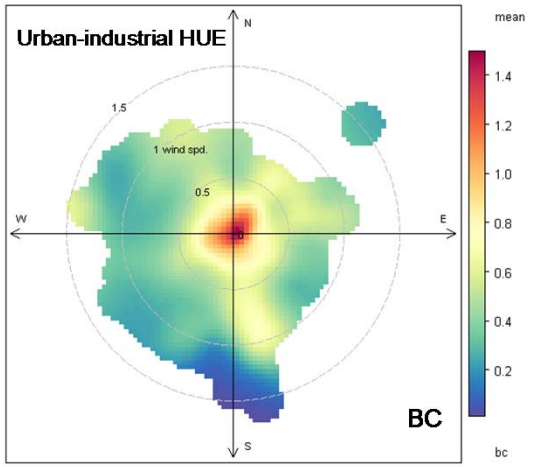


# Road traffic, air quality and aerosol measurements

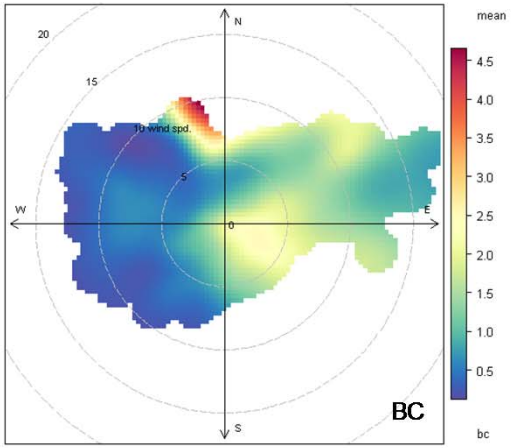
## 3. EBC: Origin, local vs external





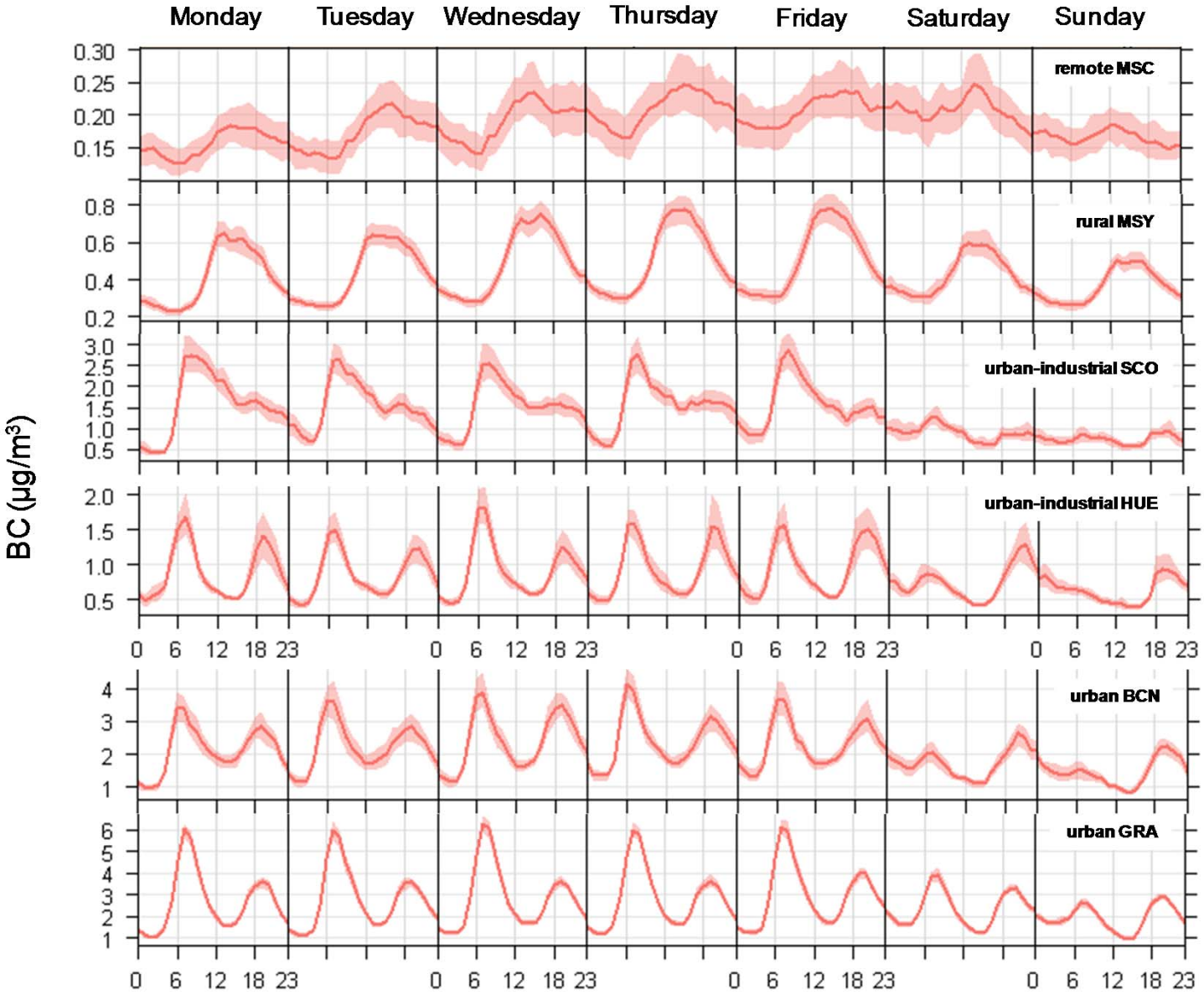




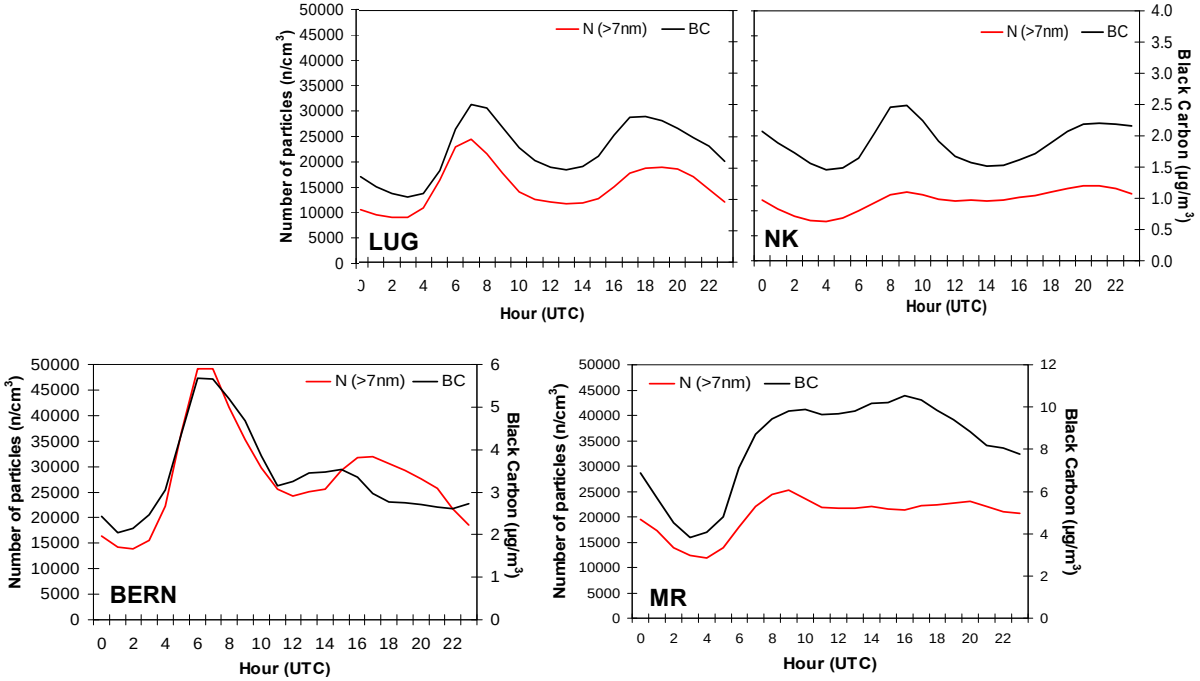
# Road traffic, air quality and aerosol measurements

## 3. EBC: Origin (daily patterns)



# Road traffic, air quality and aerosol measurements

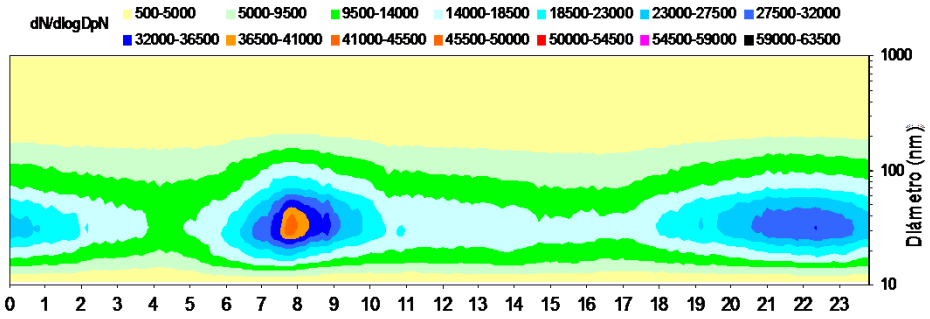
## 4. EBC & N: Origin of N (UFP) and EBC



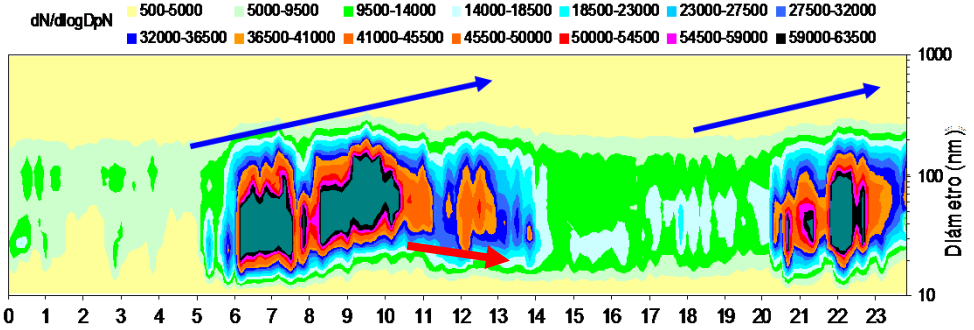

*Reche et al., 2011. Atmospheric Chemistry and Physics*

# Road traffic, air quality and aerosol measurements

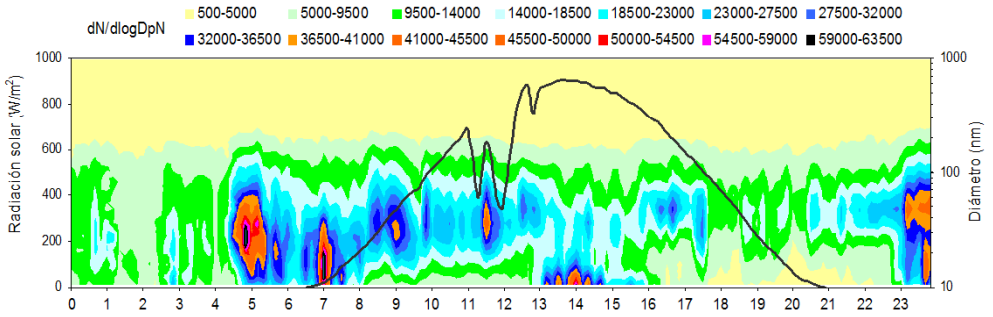
## 5. UFP: Major urban scenarios of Barcelona: Urban aerosols



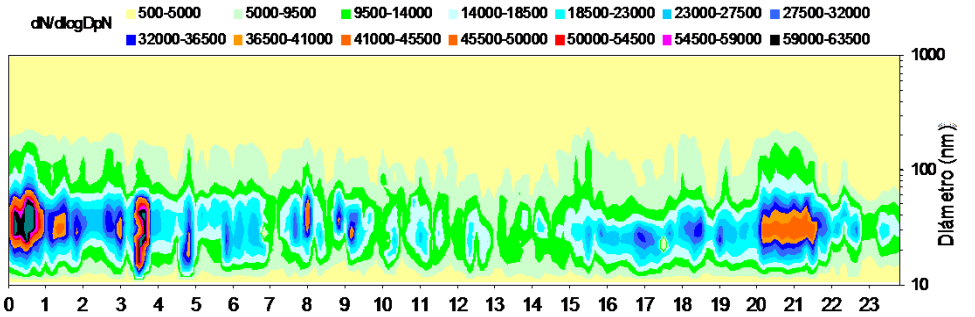

Annual mean




High pollution (condensation)




Photochemical nucleation




High dispersion

*Pey J. et al., 2008. Atmospheric Environment*

# Road traffic, air quality and aerosol measurements

## 5. UFP

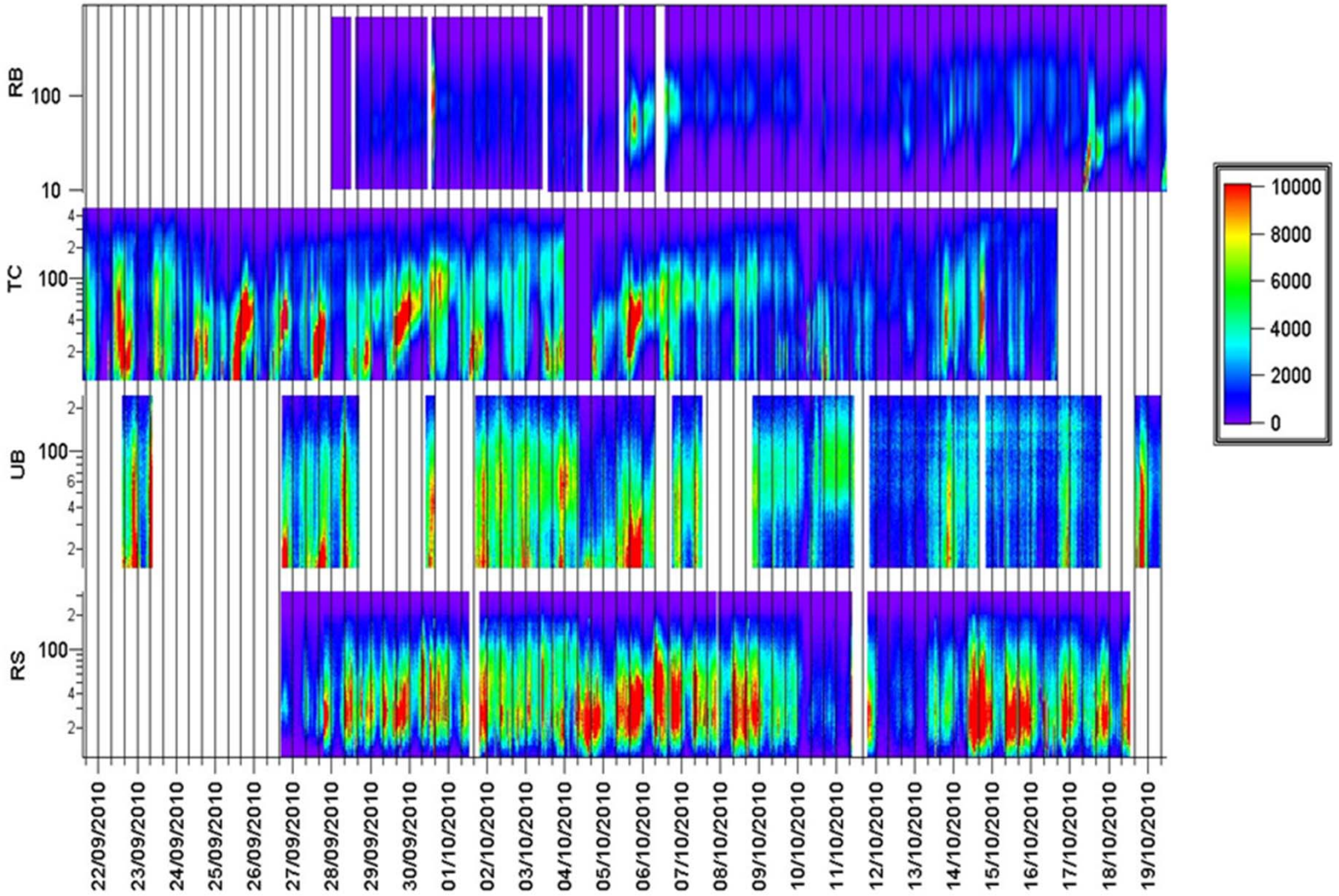
*Barcelona 2010*

RURAL

SUBURBAN

URBAN B.

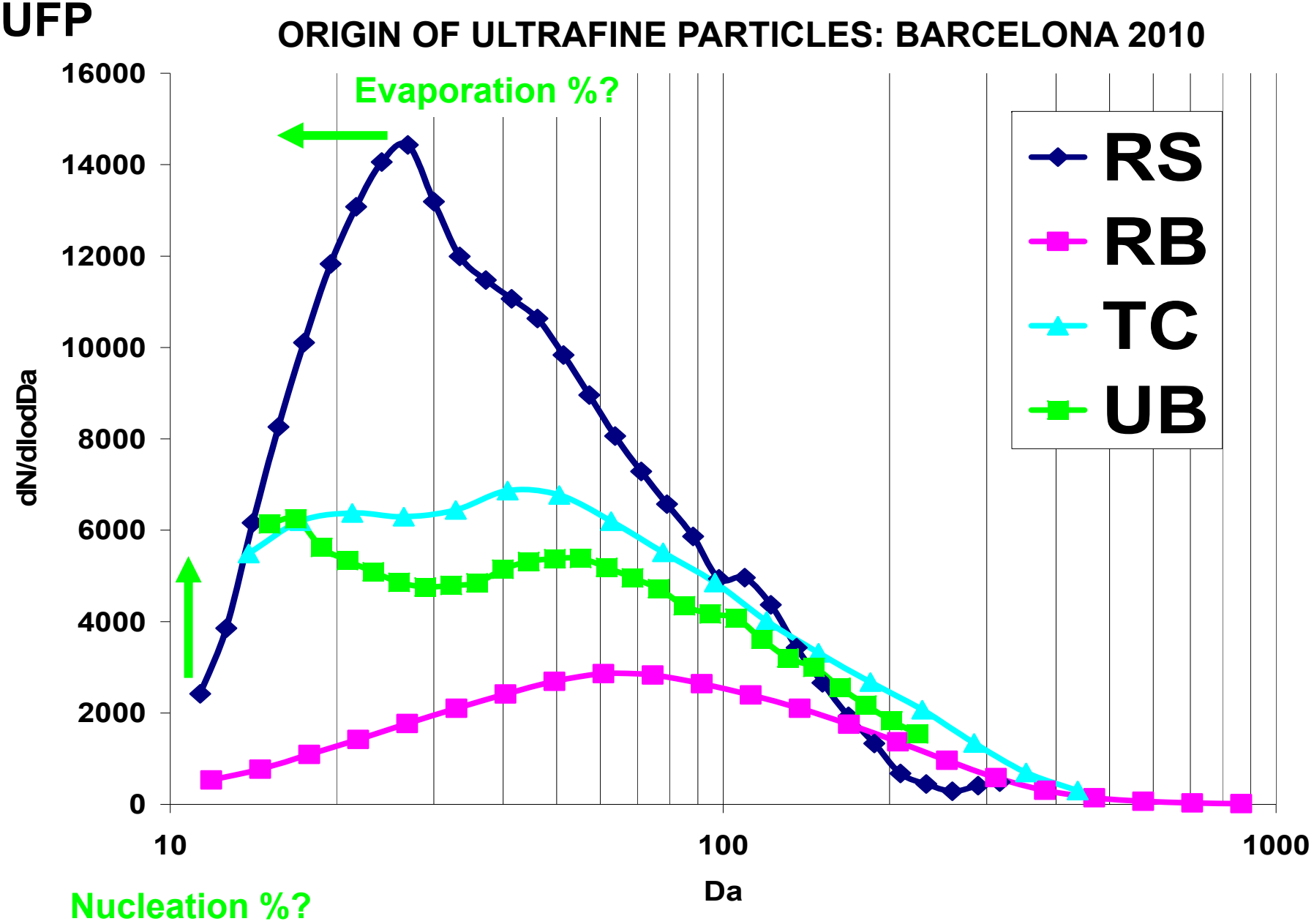
TRAFFIC




*Dall'Osto et al., 2012a Atmospheric Chemistry and Physics Discussions*

# Road traffic, air quality and aerosol measurements

## 5. UFP

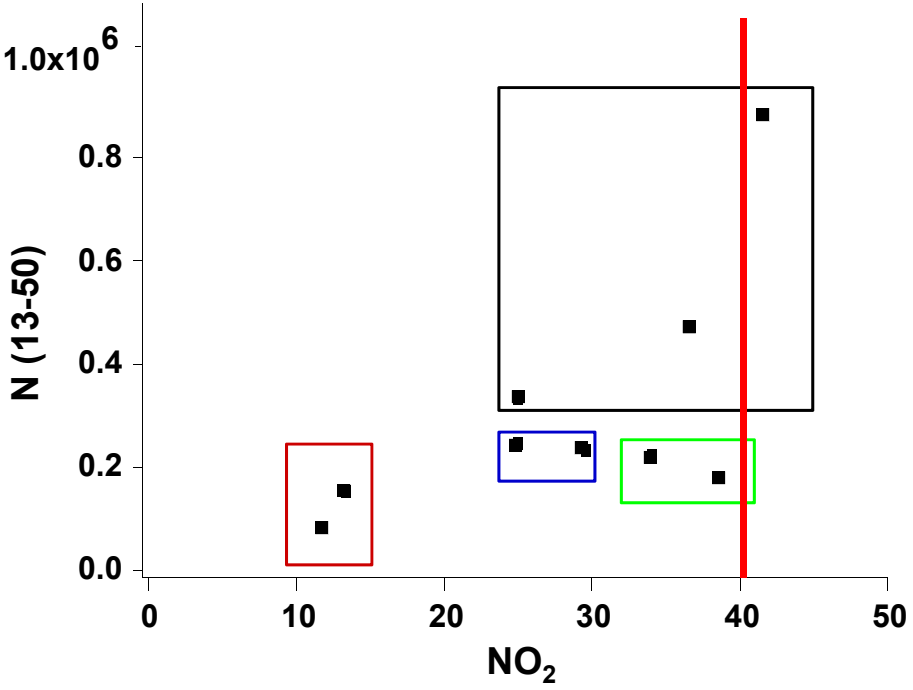



*Dall'Osto et al., 2012a Atmospheric Chemistry and Physics Discussions*

# Road traffic, air quality and aerosol measurements

*Dall'Osto et al., 2012b Atmospheric Chemistry and Physics Discussions*

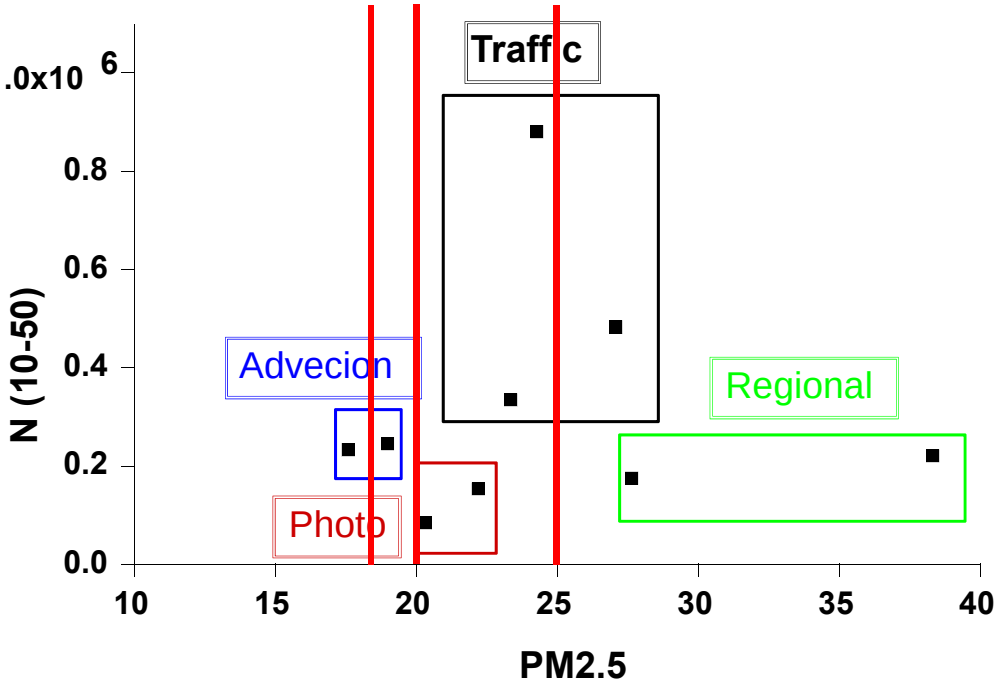
**Barcelona 2004, Cluster analysis using k-means >6000 hourly size distributions $N_{10\text{-}800}$**



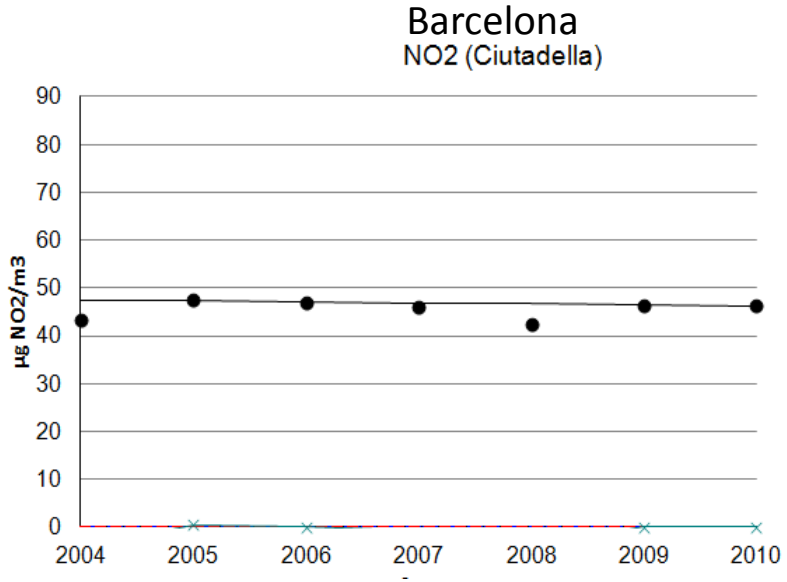

In our study characterisation of photochemical nucleation limited by N>13nm DLI!!!

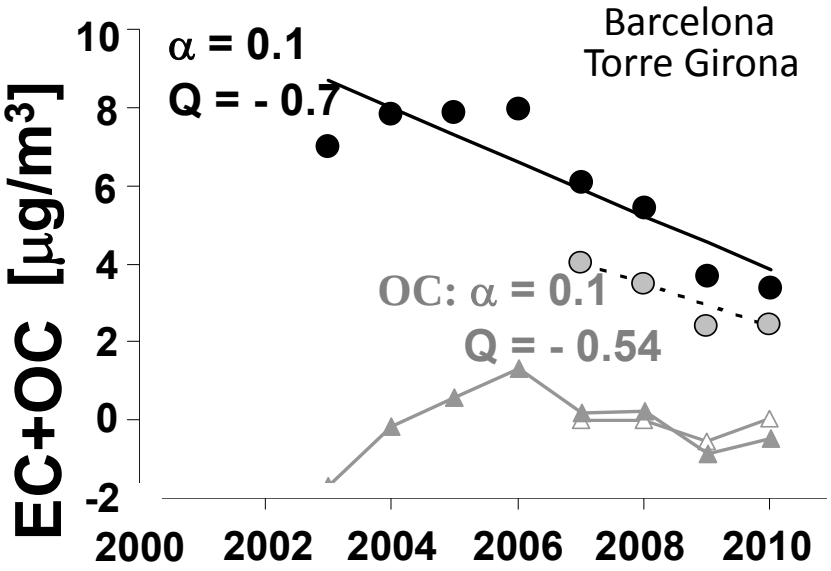
Not only N is relevant but also toxicity of the type of UFP from the 7 clusters!!!

**AQ limit and target values in Europe**

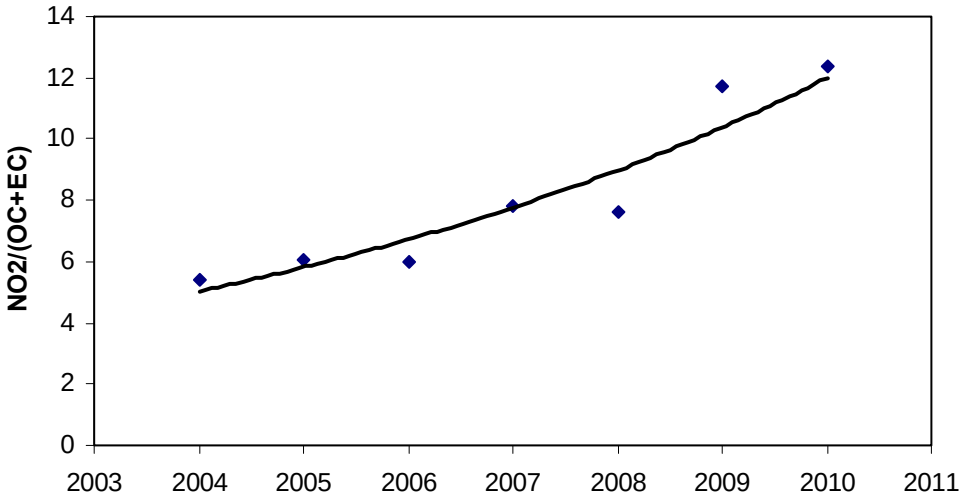


# Road traffic, air quality and aerosol measurements

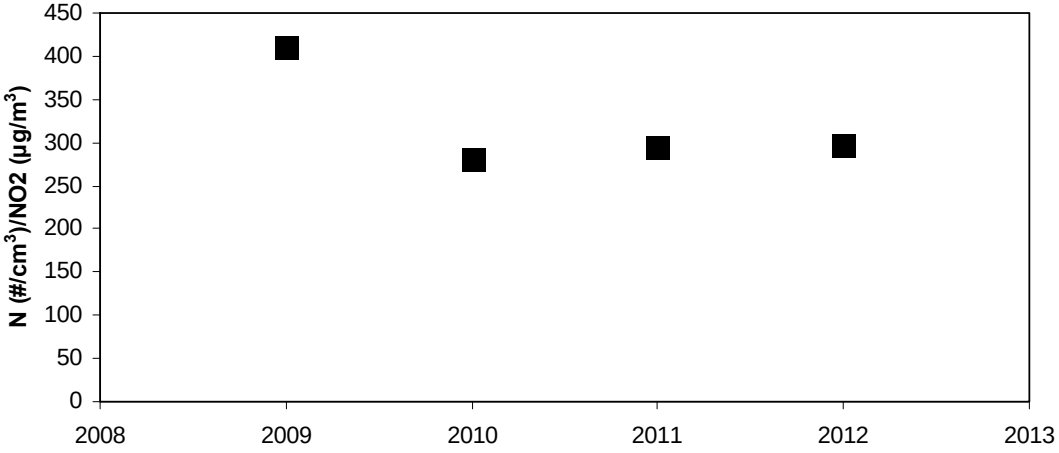



## Changing NO2/OC+EC!!!!




## NO2/UFP??????



# Road traffic, air quality and aerosol measurements

## 6. 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**

| | |
|---|---|
| $Al_2O_3$ | 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**

**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

**Accounted**
**75-85 % mass PM**

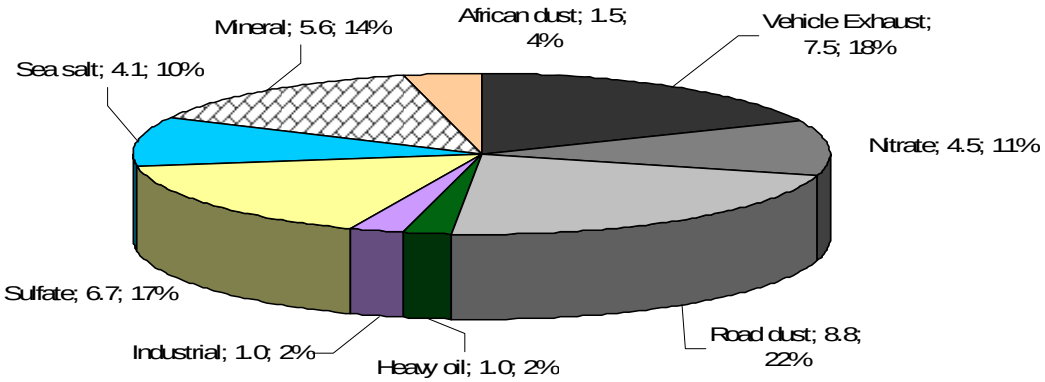
# Road traffic, air quality and aerosol measurements

**Non road resuspension 14%**

**Road traffic 45%**

**Biomass b. 3%**

**PM10**



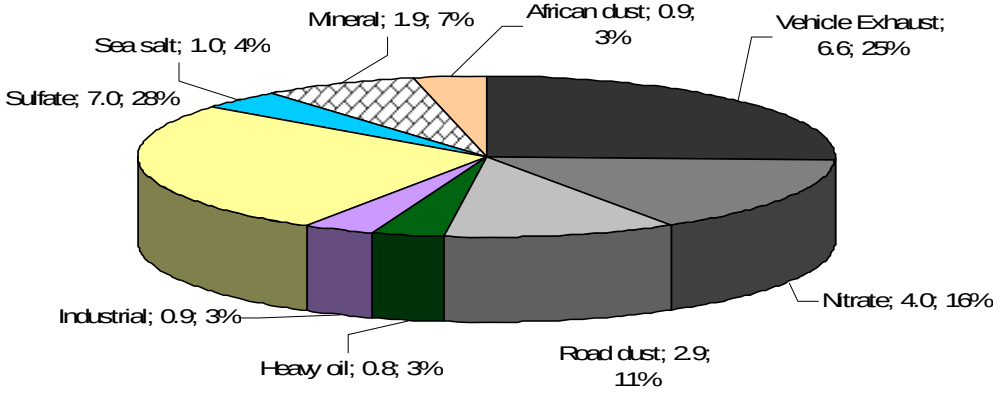

**Shipping 2%**

**Non road resuspension 4%**

**Road traffic 49%**

**Biomass b. 3%**

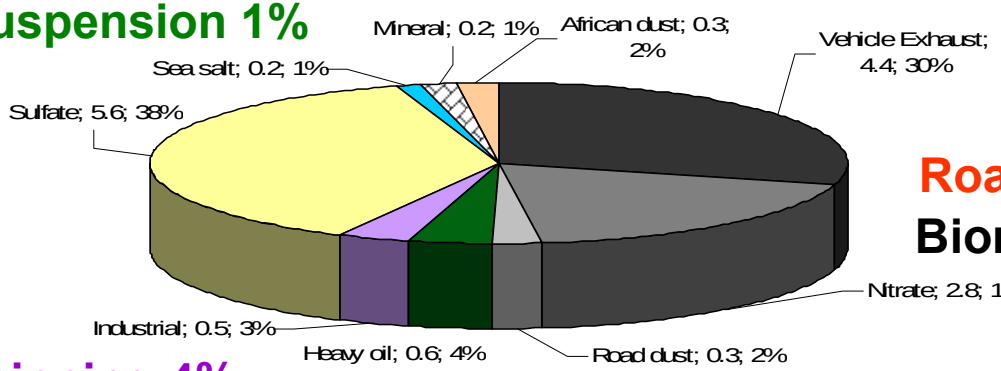
**PM2.5**




**Shipping 3%**

**PM1**

**Non road resuspension 1%**




**Road traffic 46%**

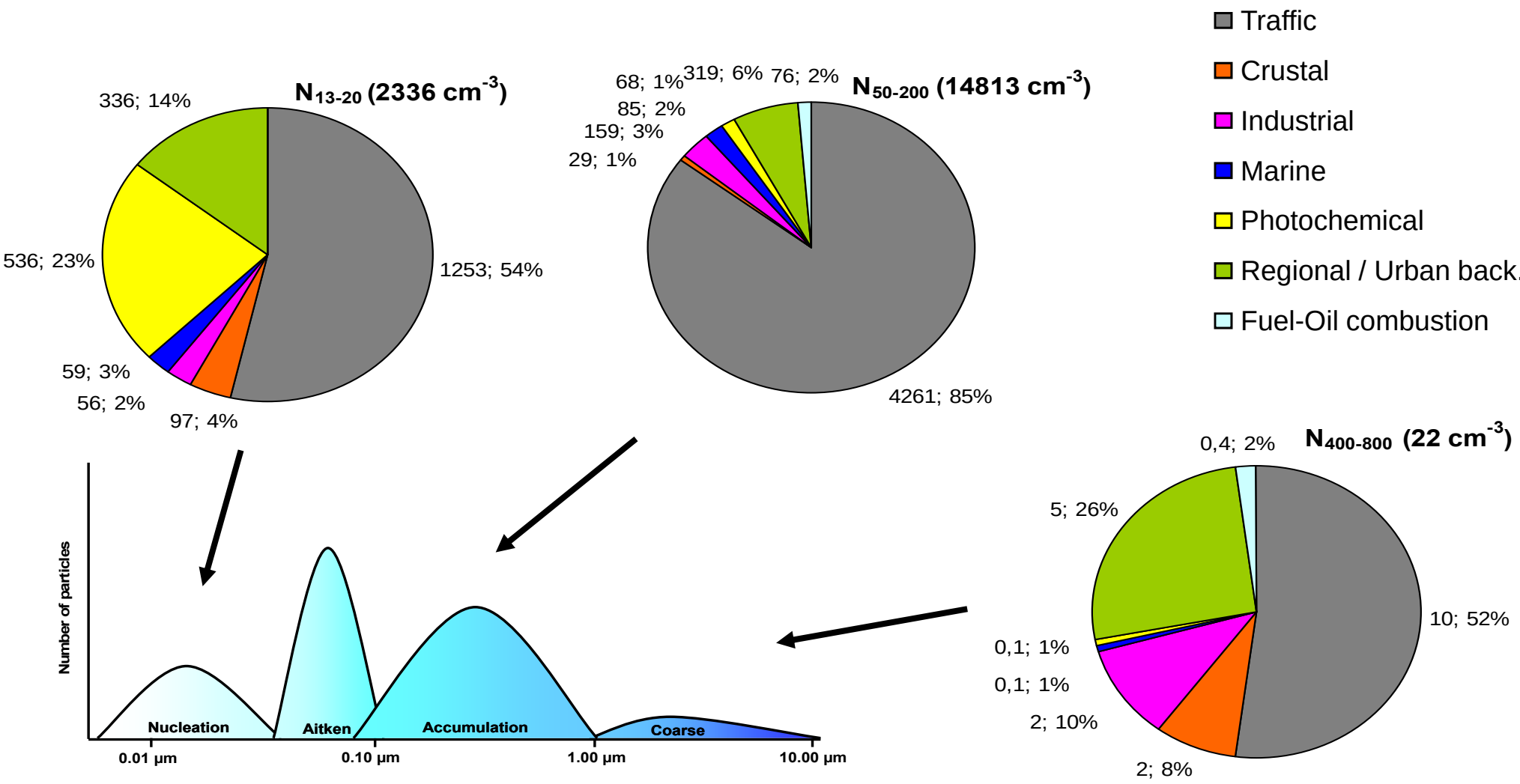
**Biomass b. 5%**

**Shipping 4%**

***Amato, et al., 2009. Atmospheric Environment, and Reche et al., 2012. Atmospheric Environment***

# Road traffic, air quality and aerosol measurements

## 7. Receptor modelling for UFP Barcelona, 2004



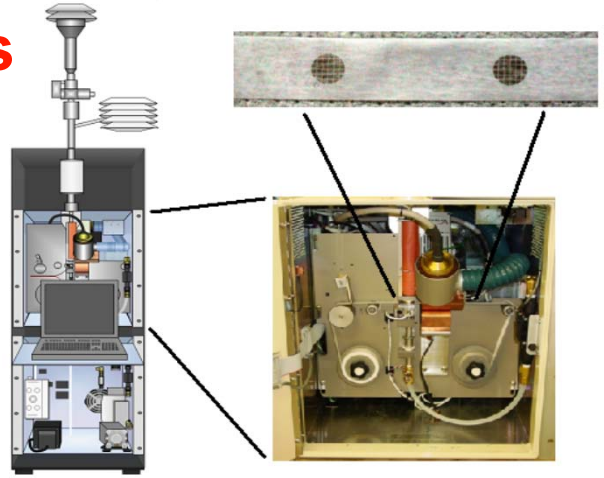

*Pey J., et al. 2009. Atmospheric Environment*

# Future trends

**Mini-AMS:** OM, sulphate, nitrate, chloride, ammonium

**BC:** insitu callibreted with EC EUSAAR-2

**On-line XRF analyser:** Metals



**High time resolution** 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
EPIDEMIOLOGY STUDIES NEEDED!!

# Conclusions

- **PM10 (mixture of source contributions) and EBC (as a source tracer for traffic and biomass burning) offer a good combination for AQ monitoring, specially because exceedances are registered in traffic and biomass burning 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, EBC 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 N contributions from sources and atmospheric processes.**

- **Not all current PMx and $NO_2$ limit values protect exposure for high UFP episodes**

- **The ratio NO2/OC+EC has changed a lot in the last decade, and probably NO2/UFP. This has to be taken into account when using NO2 a s a proxy of AQ impact of traffic PM and N**

- **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, specially if toxicity is high**

**Acknowledgements: ETH (Dr. Künzli and Dr. Mayer), 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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# Critical (URBAN) Air Quality problems in EU

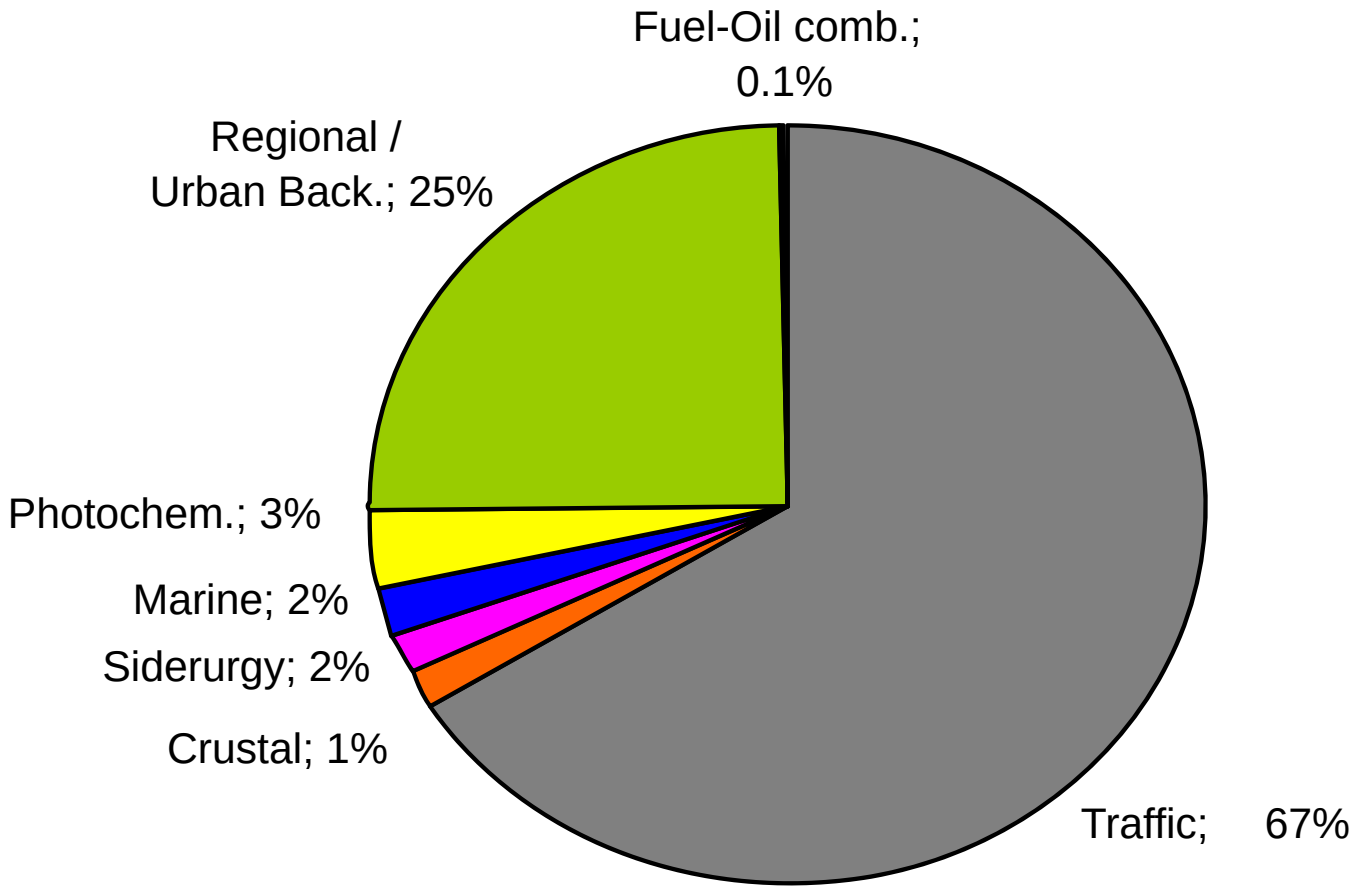
| | | 293 °K , 101,3 kPa |
|---|---|---|
| **Directive 2008/50/CE** | | **except PM and metals, Evriron. Cond.** |
| Hourly | 350 µg/m³ $SO_2$ | 24 times per year |
| Daily | 125 µg/m³ $SO_2$ | 3 times per year |
| Annual prot. ecos. | 20 µg/m³ $SO_2$ | not exceeding annual and mean 1 Oct-31 Mar |
| Hourly | 200 µg/m³ $NO_2$ | 18 times per year from 2010 |
| Annual | 40 µg/m³ $NO_2$ | not exceeding from 2010 |
| Annual prot. vegetation | 30 µg/m³ $NO_x$ | (reported as $NO_2$) not exceeding, from 2010 |
| Annual | 30 (5) µg/m³ Benzene | not exceeding from 2010 |
| Mean 8-h max. in a day | 10 mg/m³ CO | not exceeding |
| Annual | 500 ng/m³ Pb | not exceeding |
| Annual | 40 µg/m³ $PM_{10}$ | not exceeding |
| Daily | 50 µg/m³ $PM_{10}$ | n<35 per year |
| Annual | (25 y 20 (18) µg/m³ $PM_{2.5}$) | not exceeding |
| 2010-2020 | (reducing 20% $PM_{2.5}$ triennial for mean of urban background) | |
| **2004/107/CE** | | |
| Annual | 6 ng/m³ As | not exceeding |
| Annual | 20 ng/m³ Ni | not exceeding |
| Annual | 5 ng/m³ Cd | not exceeding |
| Annual | 1 ng/m³ Benzo[α]pirene | not exceeding |

**CRITICAL PARAMETRES**

# Road traffic, air quality and aerosol measurements

## 7. Receptor modelling for UFP Barcelona, 2004

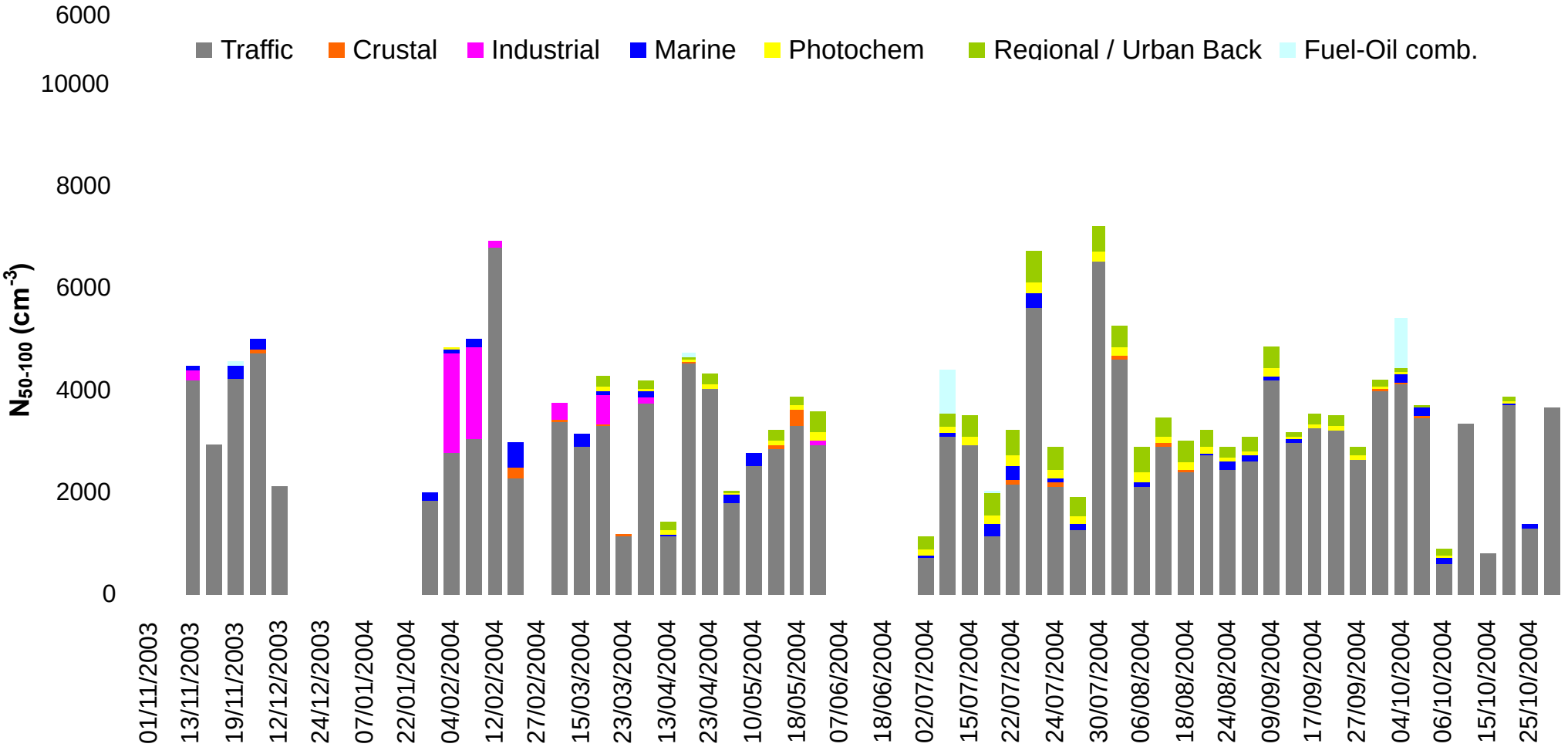
**Source contribution to the mean annual $N_{10-800}$**



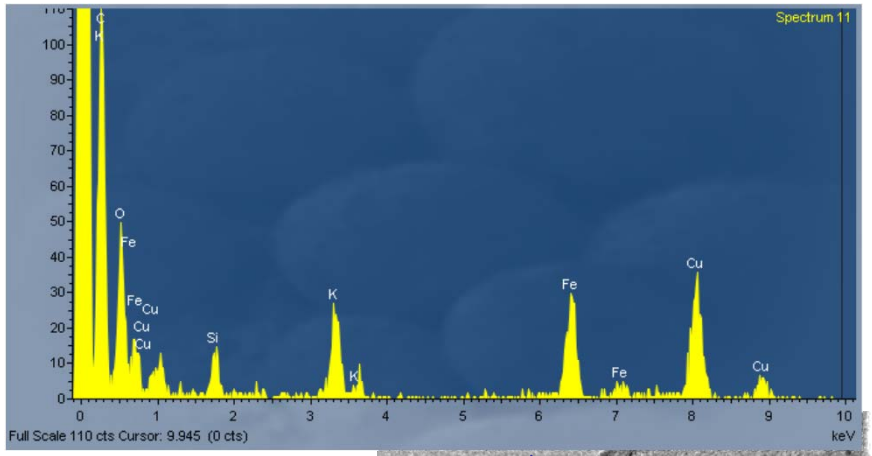

***Pey J., et al. 2009. Atmospheric Environment***

# Road traffic, air quality and aerosol measurements

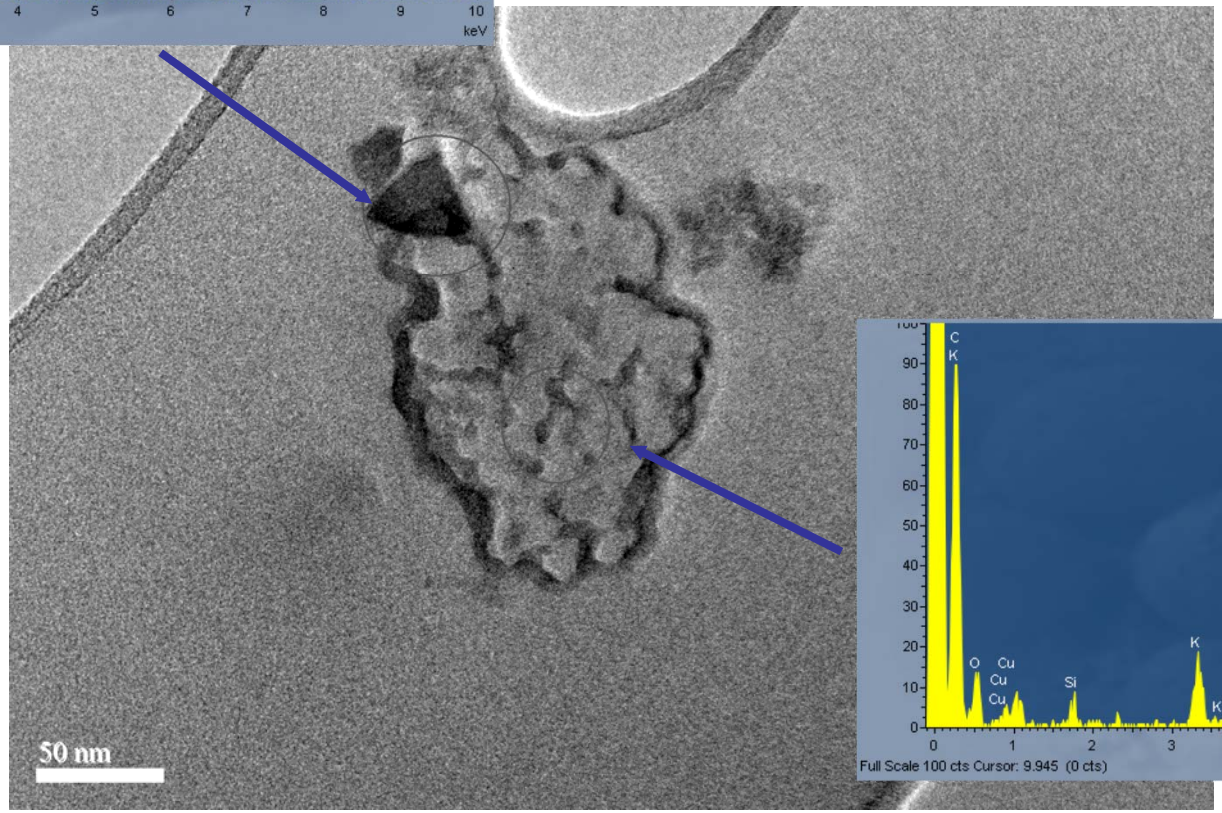
## 7. Receptor modelling for UFP Barcelona, 2004

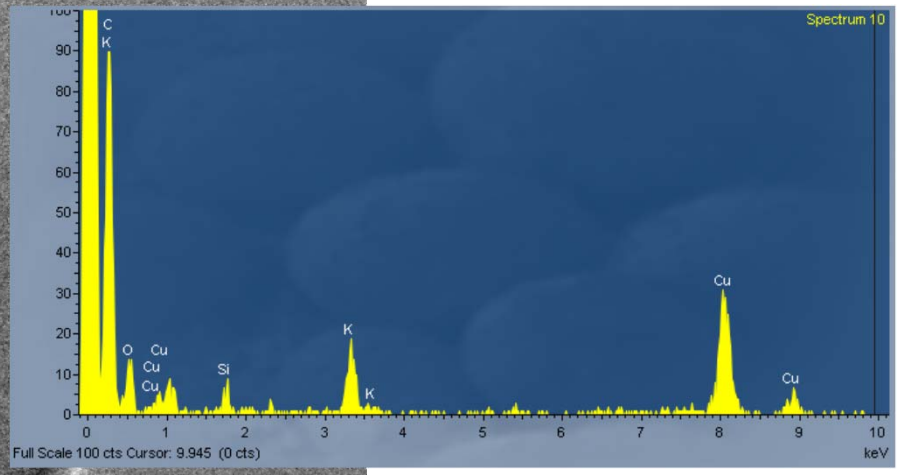


# Road traffic, air quality and aerosol measurements



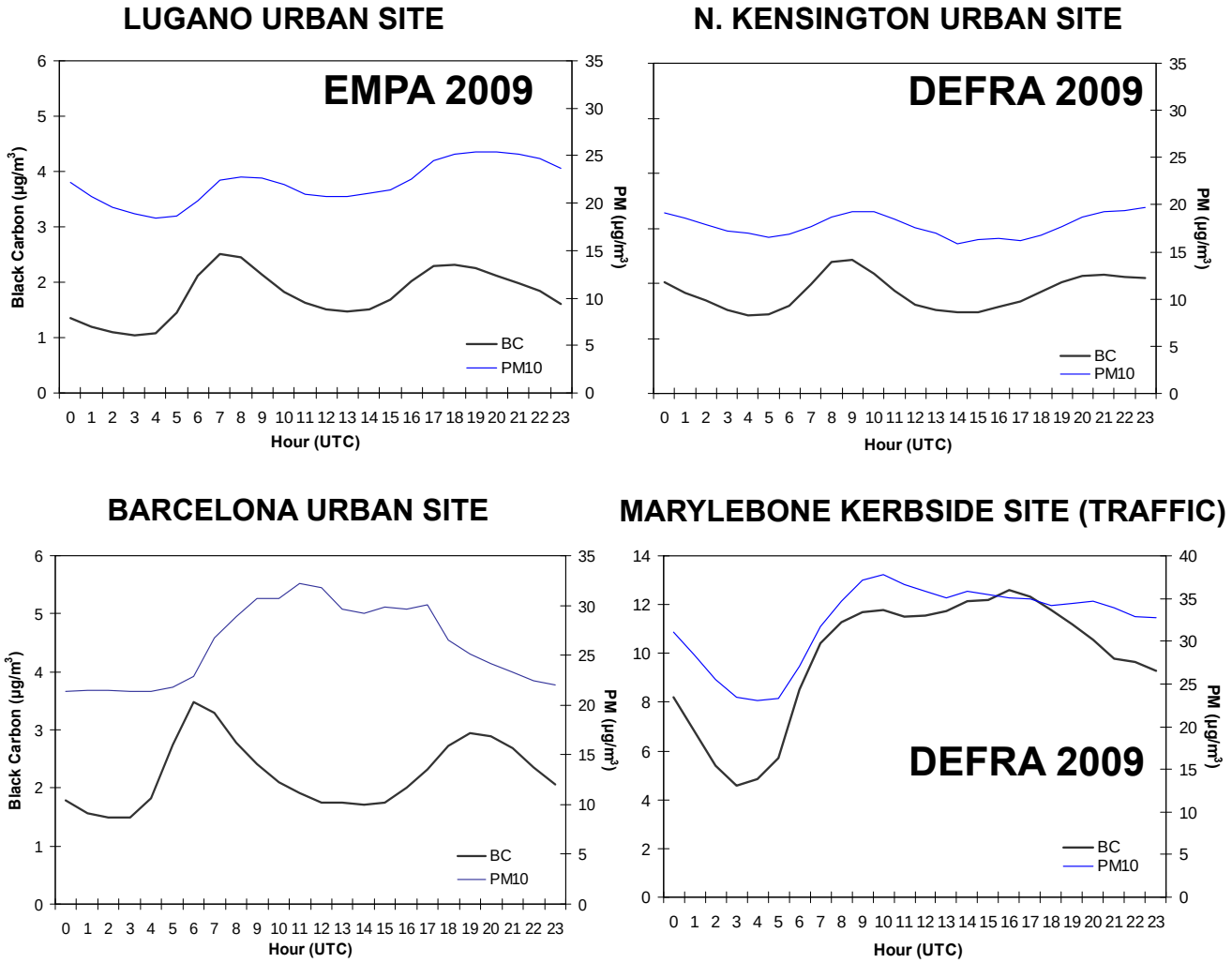

TEM-EDX analysis
Sample from Diagonal Avenue, Barcelona



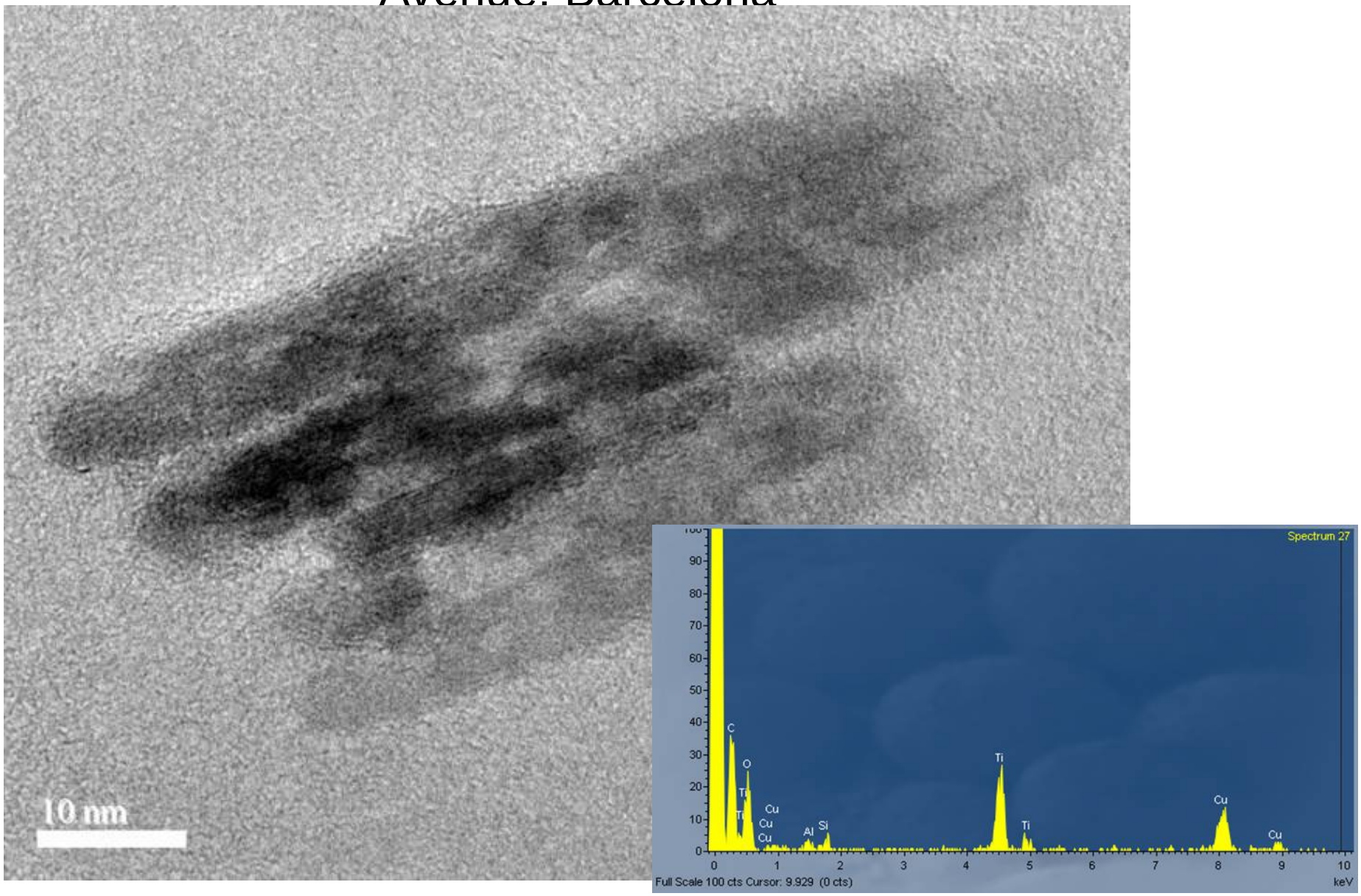
# Road traffic, air quality and aerosol measurements

## 5. PMx, BC: PM10 does not always co-vary with traffic



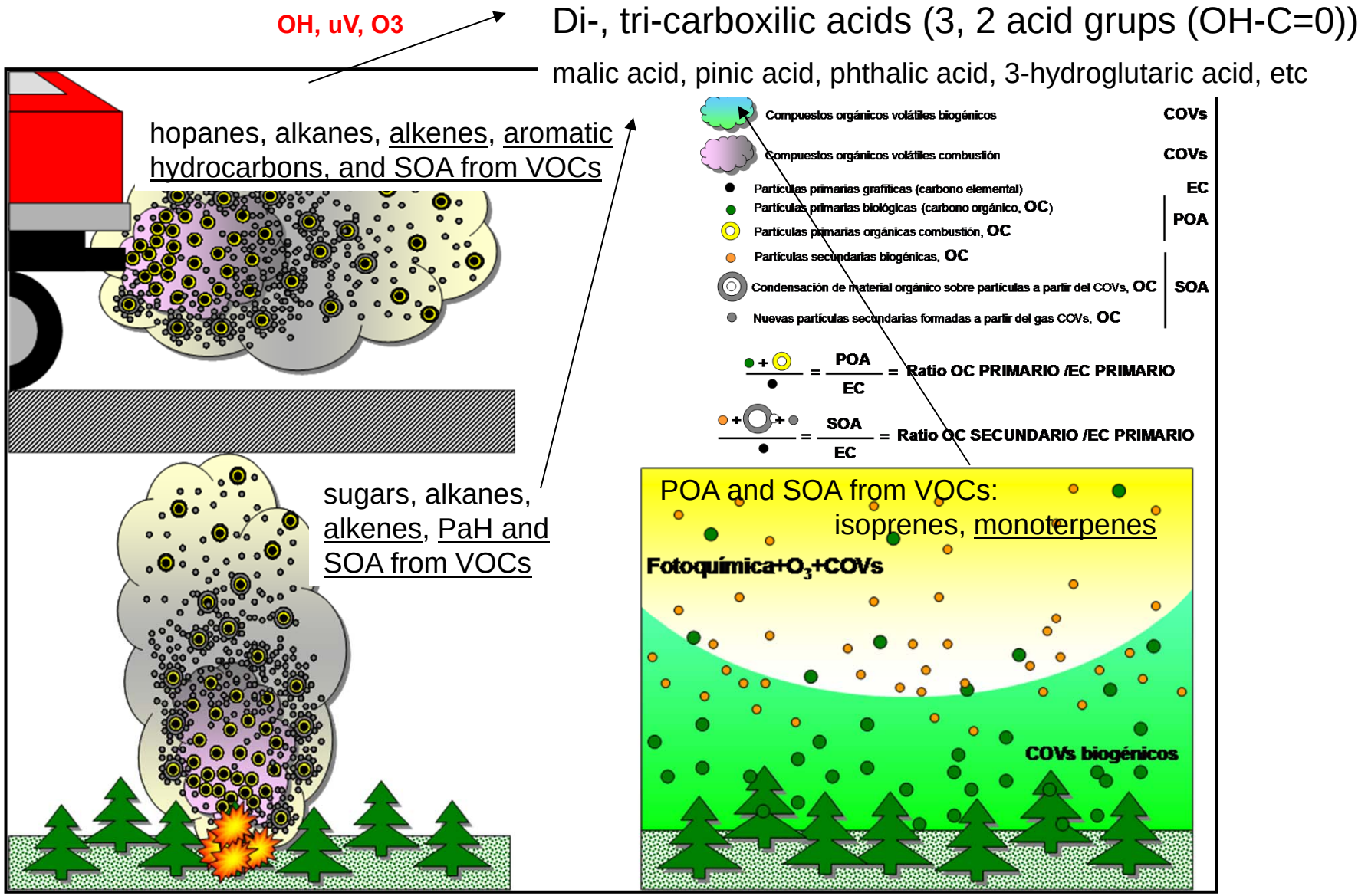

*Reche et al., 2011. Atmospheric Chemistry and Physics*

# TEM-EDX analysis, Sample from Diagonal Avenue, Barcelona



# Road traffic, air quality and aerosol measurements

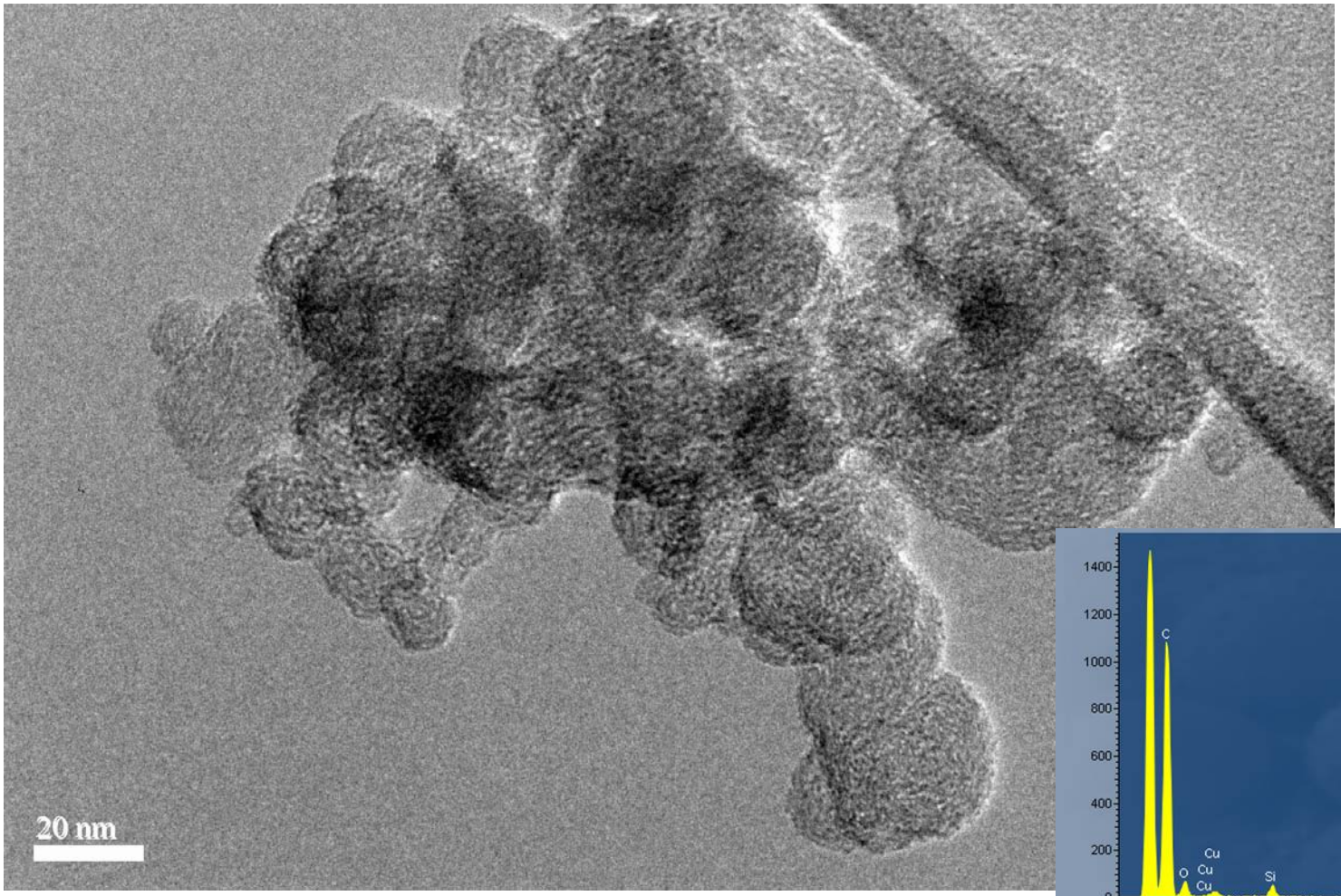
## 2. Carbonaceous aerosols: Organic and elemental carbon

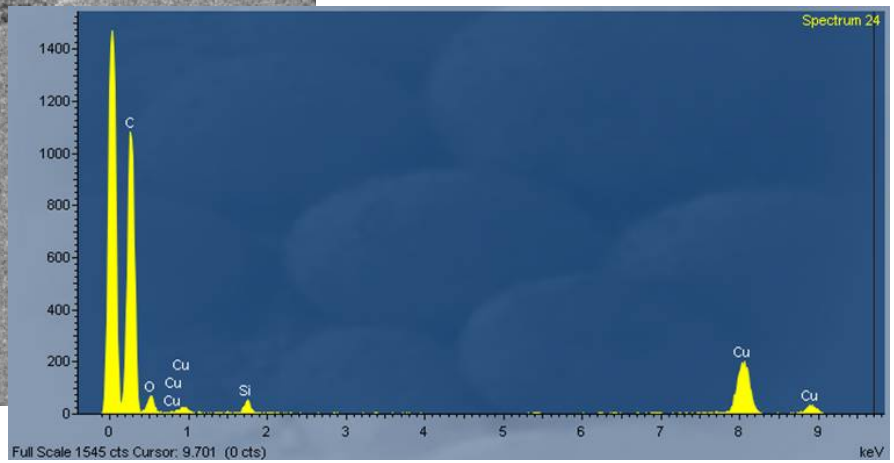


# Road traffic, air quality and aerosol measurements

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

TEM-EDX analysis,
Aerosol sample Diagonal Av., Barcelona

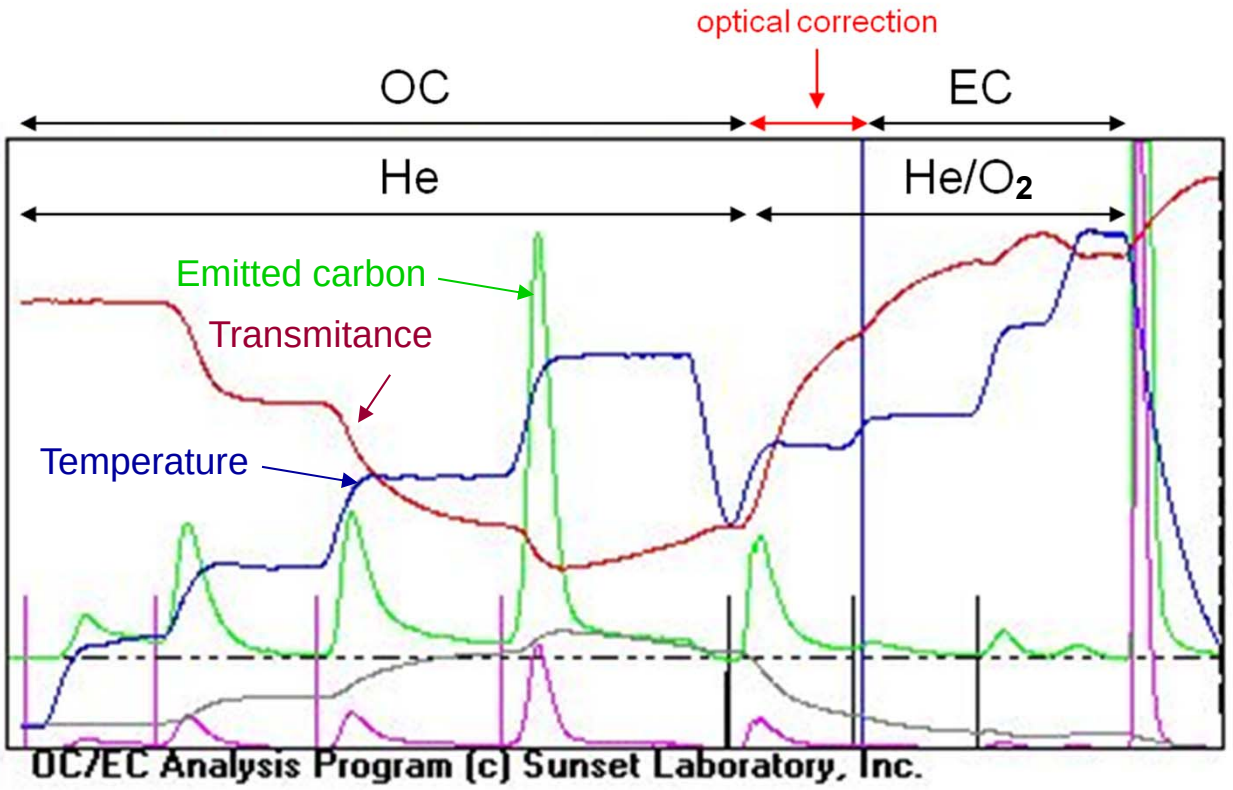


# Road traffic, air quality and aerosol measurements

## 2. Carbonaceous aerosols: Organic and elemental carbon

### Thermo-optical transmittance analysis (TOT)




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

# Road traffic, air quality and aerosol measurements

## 3. BC: On line BC optical measurements: Optical absorption of particles (collected on filters)

### 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-1) 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*
*$I_o$ 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 165º)

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

*$\omega_0$ is the single scattering albedo, dependent of the particle absorption and filter matrix scattering*
*Tr, transmitance 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. EBC: On line BC optical measurements: MASS ABSORPTION CROSS SECTION (MAC)

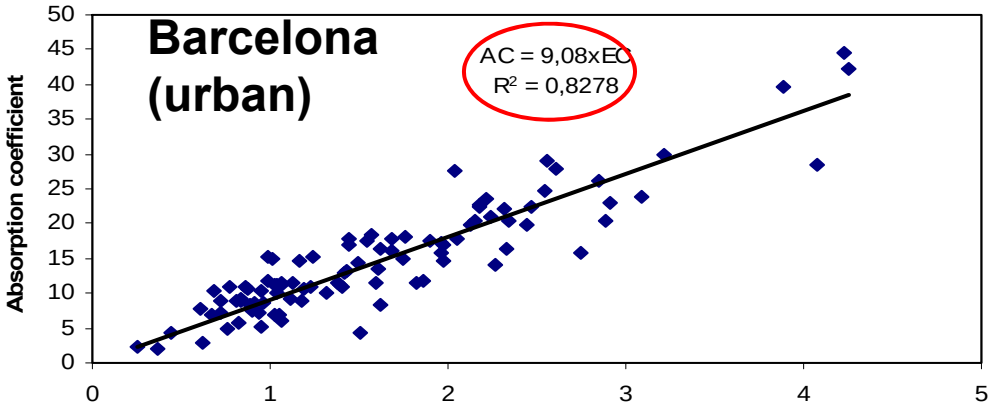
$$Abs_{BC}^{\lambda}(m^{-1}) = \sigma_{BC}^{\lambda}(m^{2}g^{-1}) \times [EBC](\mu g\, m^{-3})$$

MAC

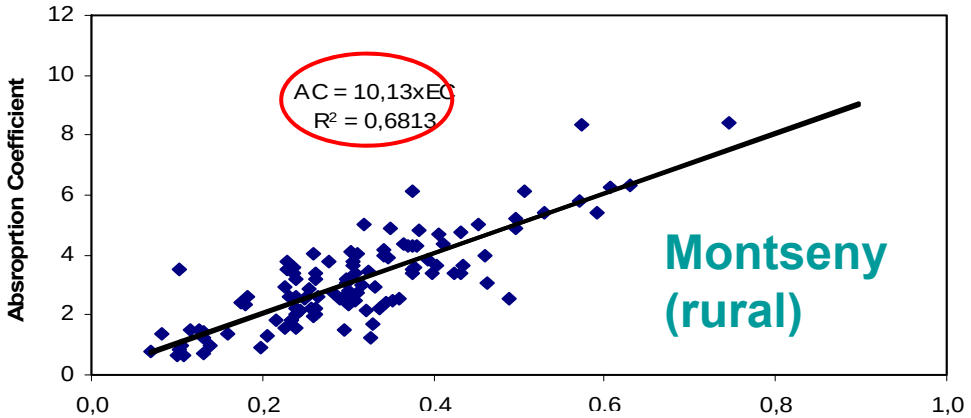
(MAAP)

(EC; SUNSET)

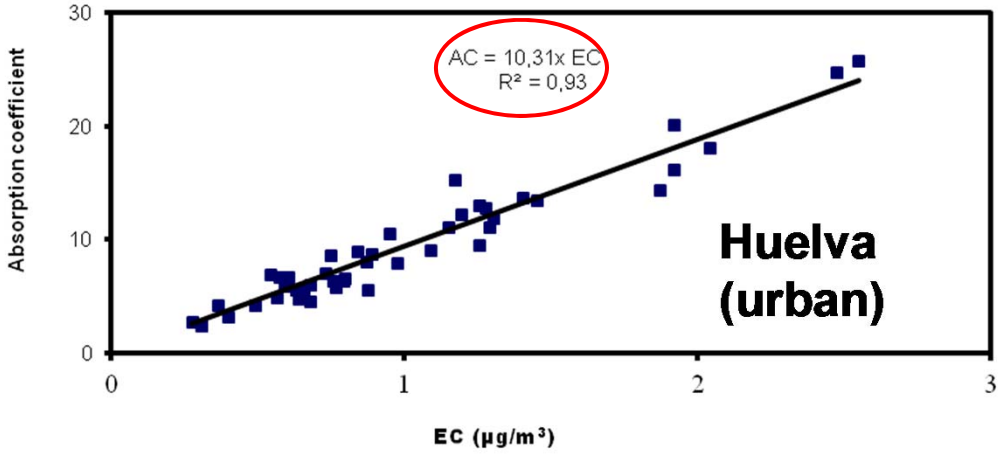
**EC=AC/9**



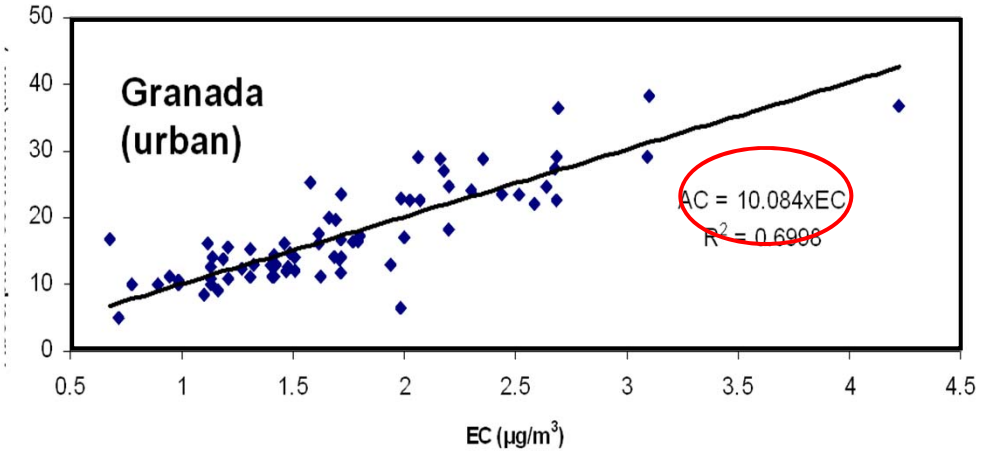

**EC=AC/10**




**EC=AC/10**



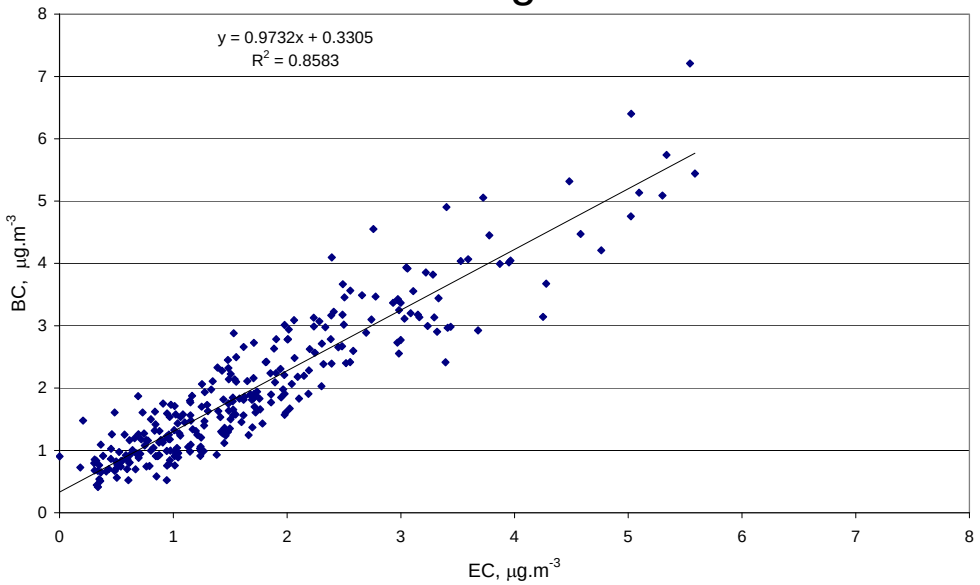

**EC=AC/10**



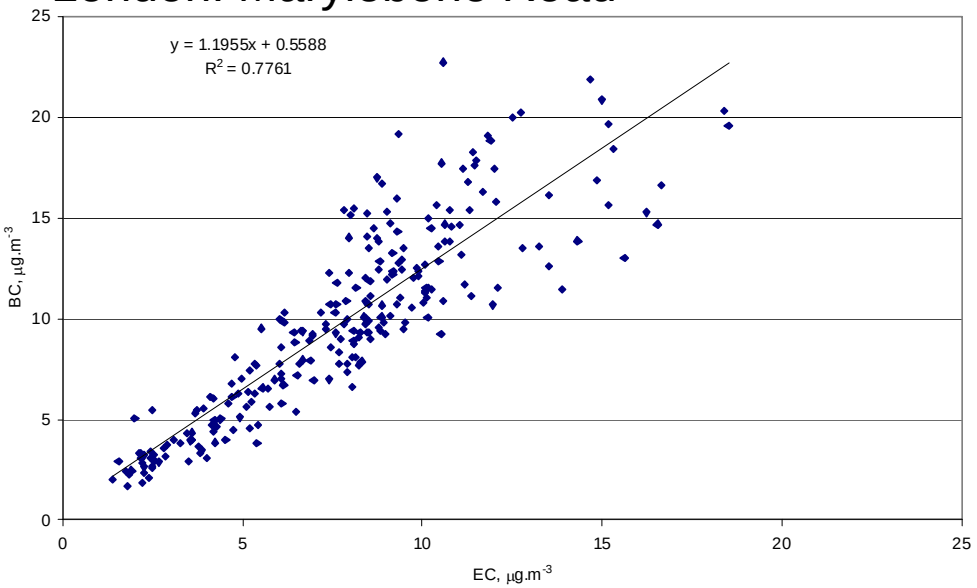
# Road traffic, air quality and aerosol measurements

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

London: North Kensington




London: Marylebone Road




***Courtesy: P. Quency & DEFRA***

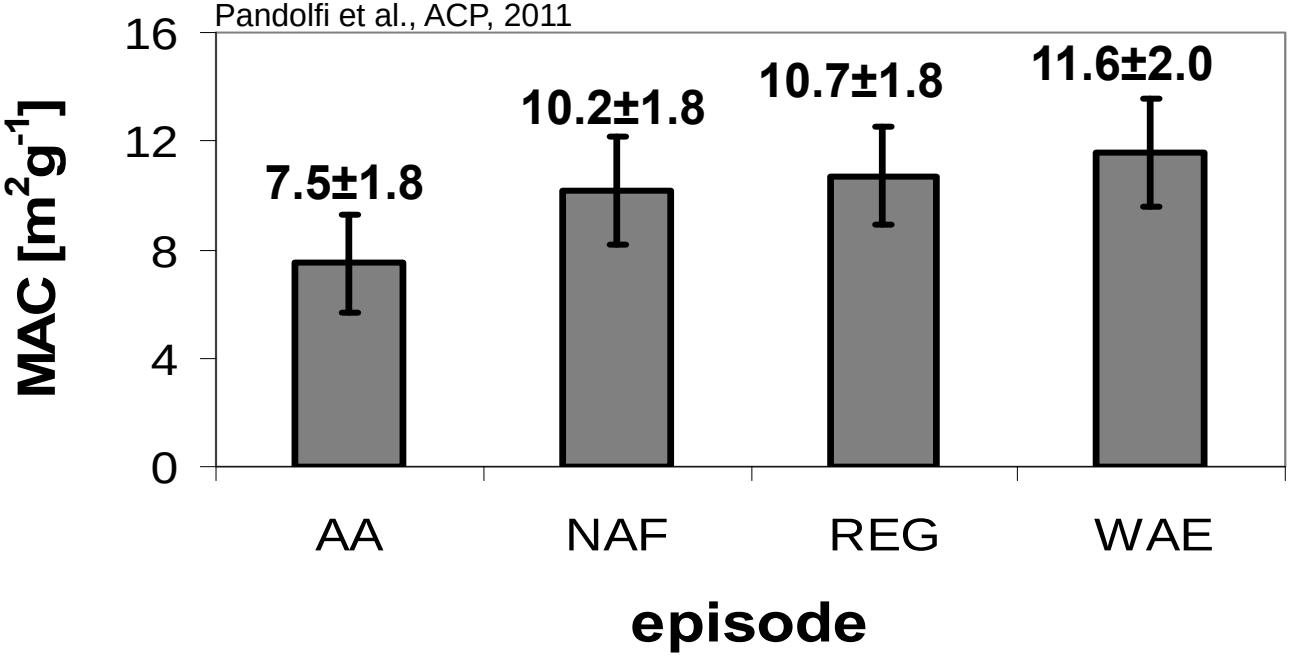
# Road traffic, air quality and aerosol measurements

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

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

**7 – 15 $m^2g^{-1}$**

MSY (04/2008 – 02/2010)





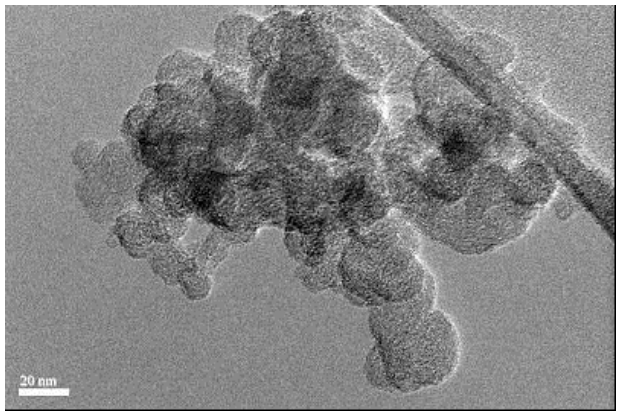
***Pandolfi et al., Atmospheric Chemistry and Physics, 2011***

# Road traffic, air quality and aerosol measurements

## 2. Carbonaceous aerosols: Organic and elemental carbon

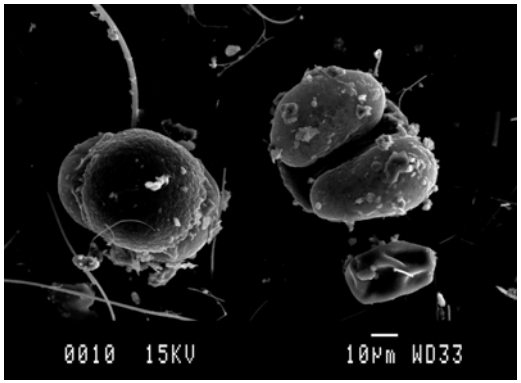
### Elemental carbon

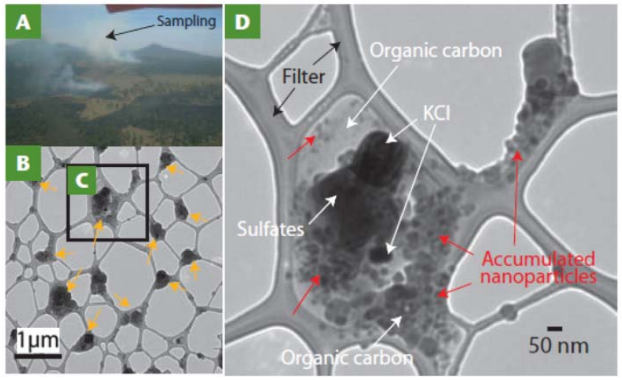
Instrumentally defined parameter for mass concentration of graphitized C (unburned and char)

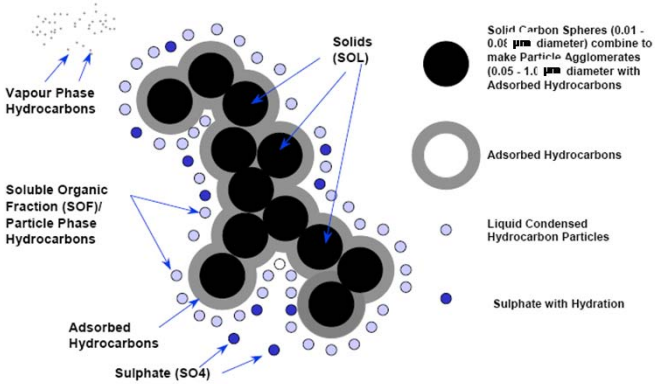



### Organic carbon

Instrumentally defined parameter for mass concentration of organic matter carbon



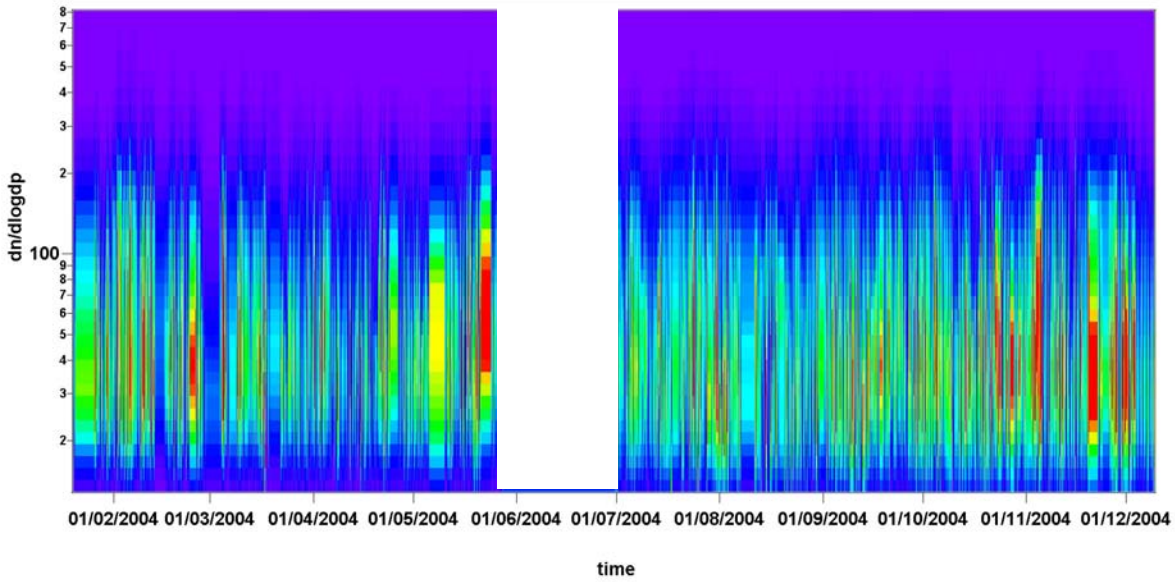



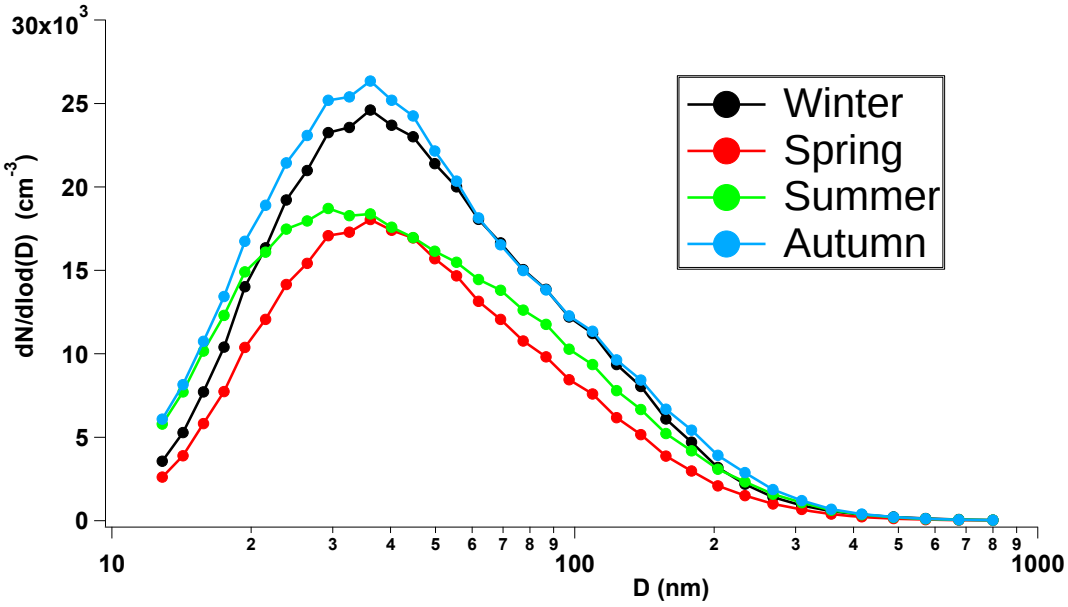




**Buseck and Adachi, 2008. Elements, 4.**

# Road traffic, air quality and aerosol measurements

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



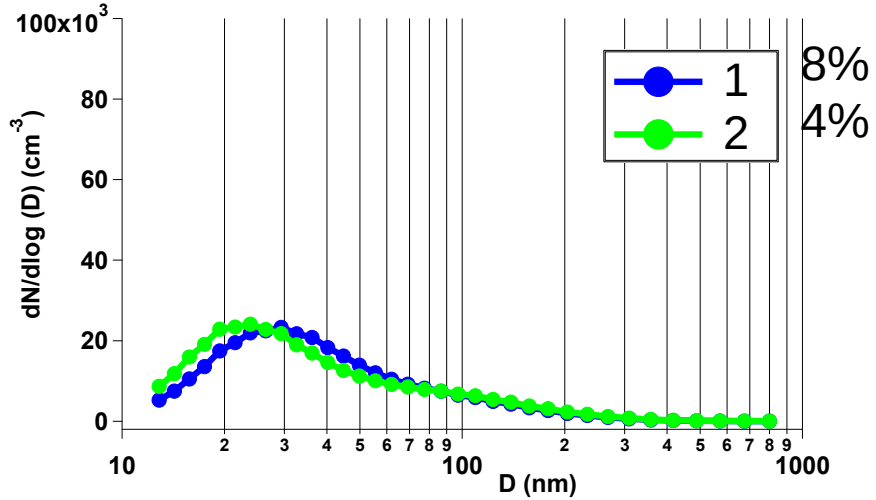

*Dall'Osto et al., 2012b*
*Atmospheric Chemistry and Physics Discussions*

# Road traffic, air quality and aerosol measurements

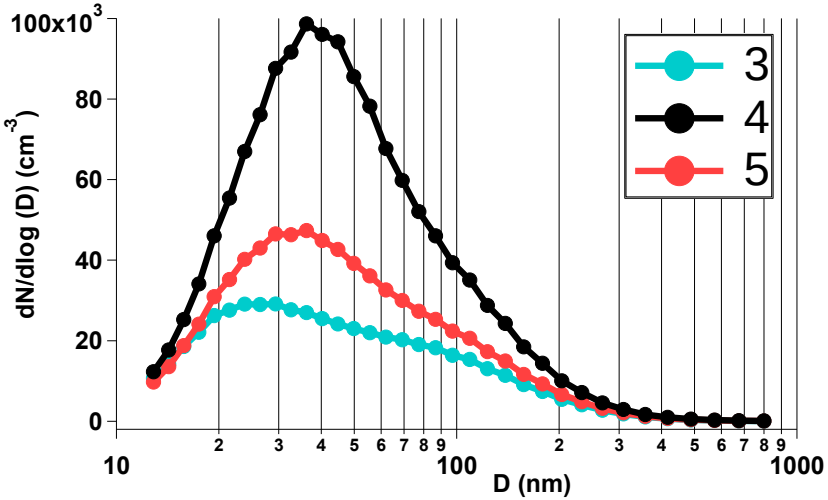
*Dall'Osto et al., 2012b Atmospheric Chemistry and Physics Discussions*

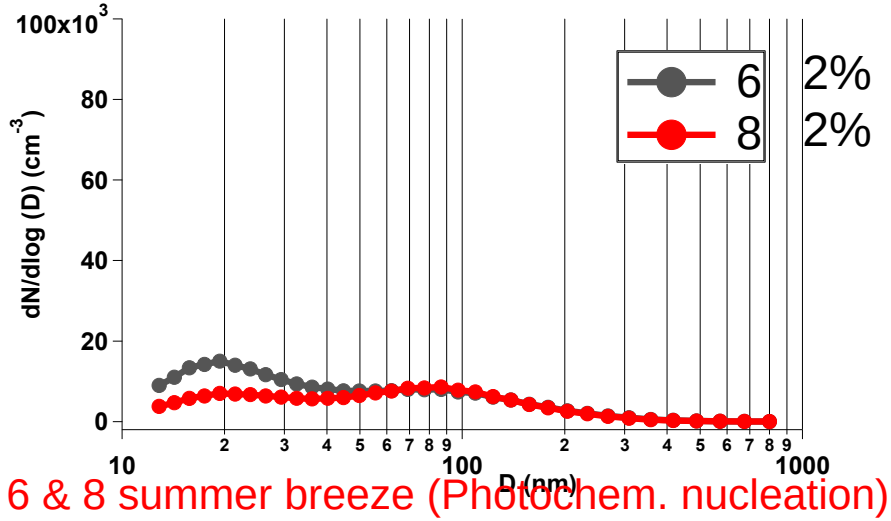
**Barcelona 2004, Cluster analysis using k-means >6000 hourly size distributions $N_{10\text{-}800}$**

1 & 2 clean atlantic advection

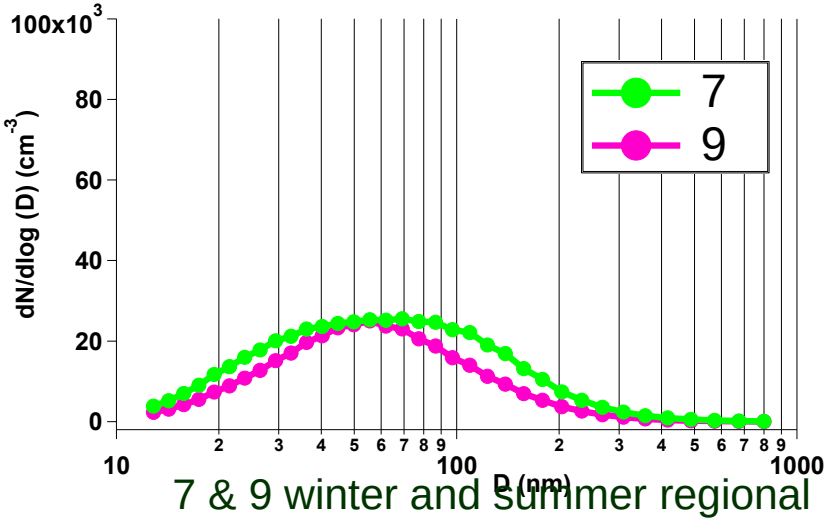



3 to 5 traffic pollution



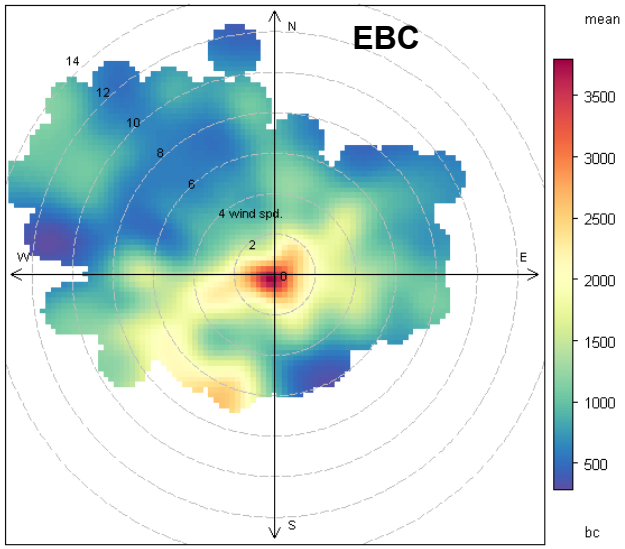

6 & 8 summer breeze (Photochem. nucleation)




7 & 9 winter and summer regional

# Road traffic, air quality and aerosol measurements

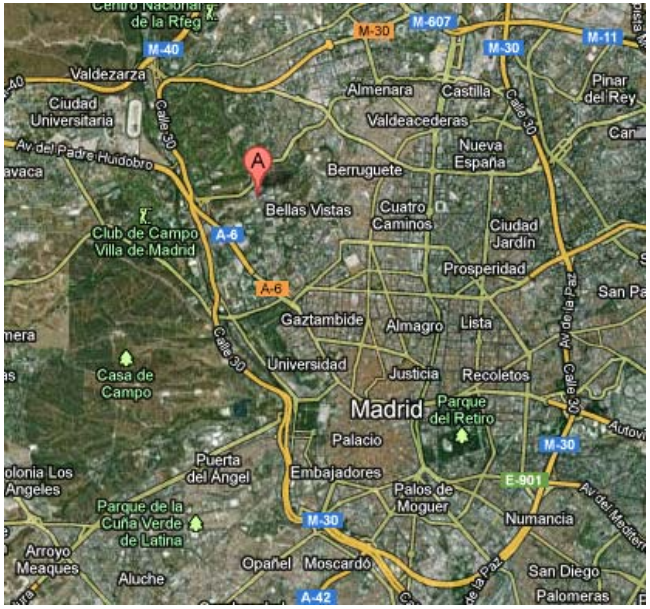

Barcelona IDAEA

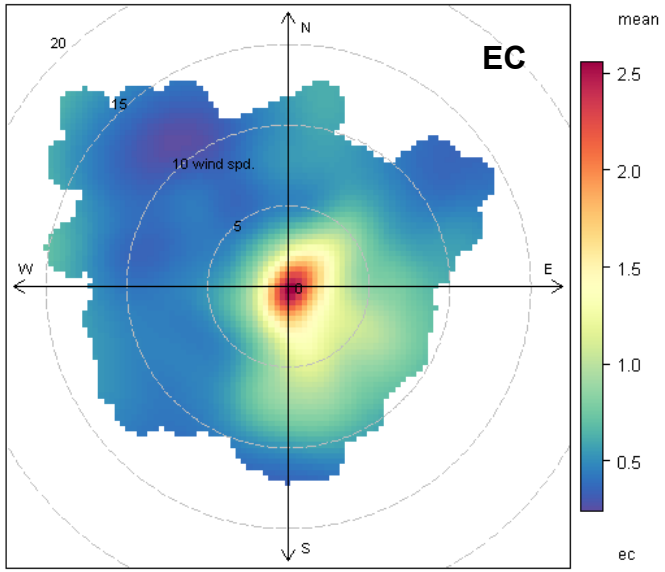



## 3. EBC:

## Local vs external

## Madrid CIEMAT

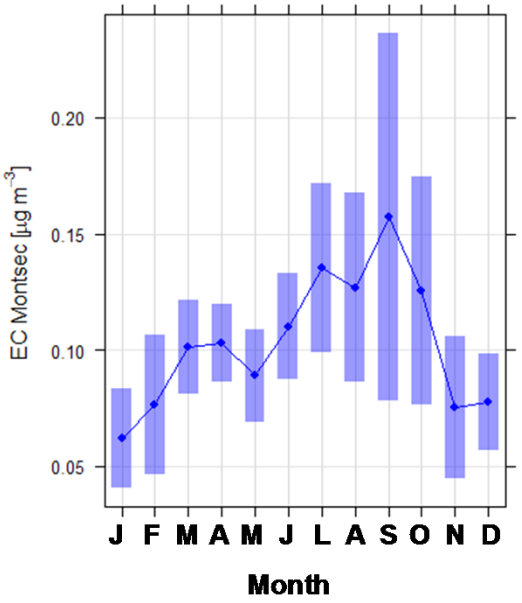


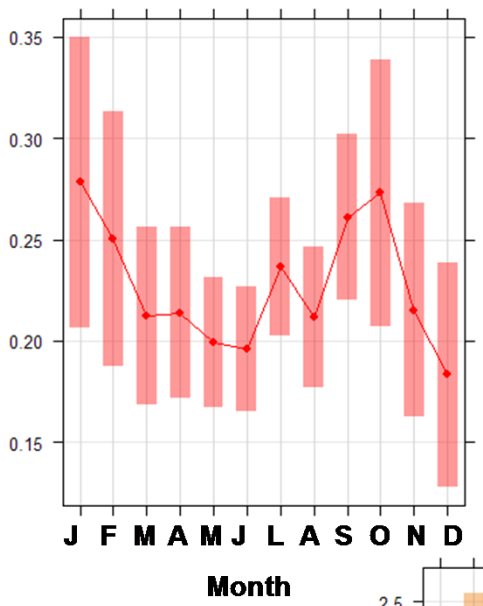
# Road traffic, air quality and aerosol measurements

## 3. EBC: Origin (seasonal patterns)

Montsec



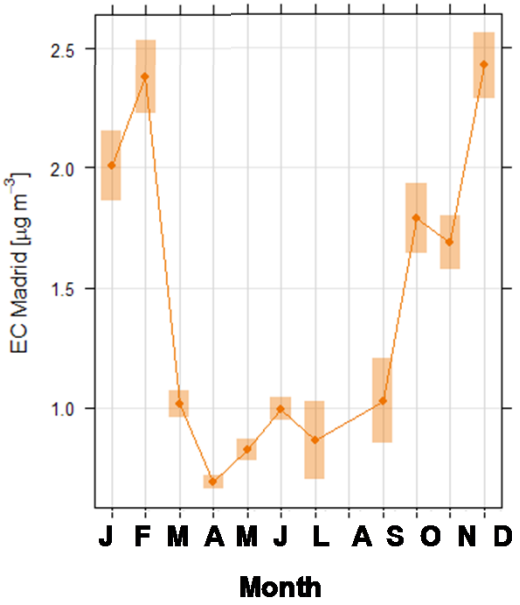

Montseny



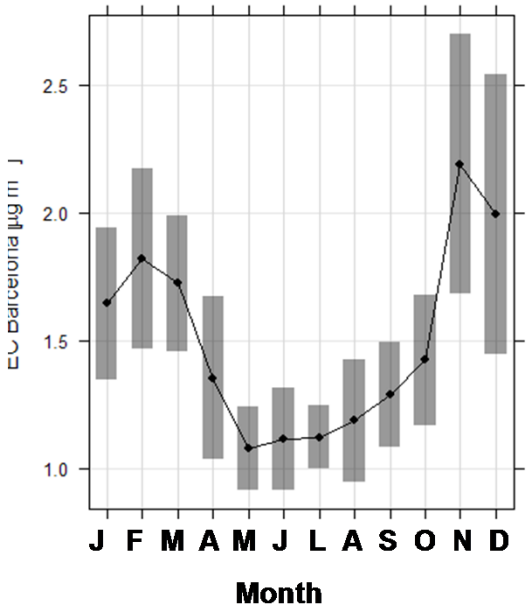

Remote & Regional background

Urban background

Madrid



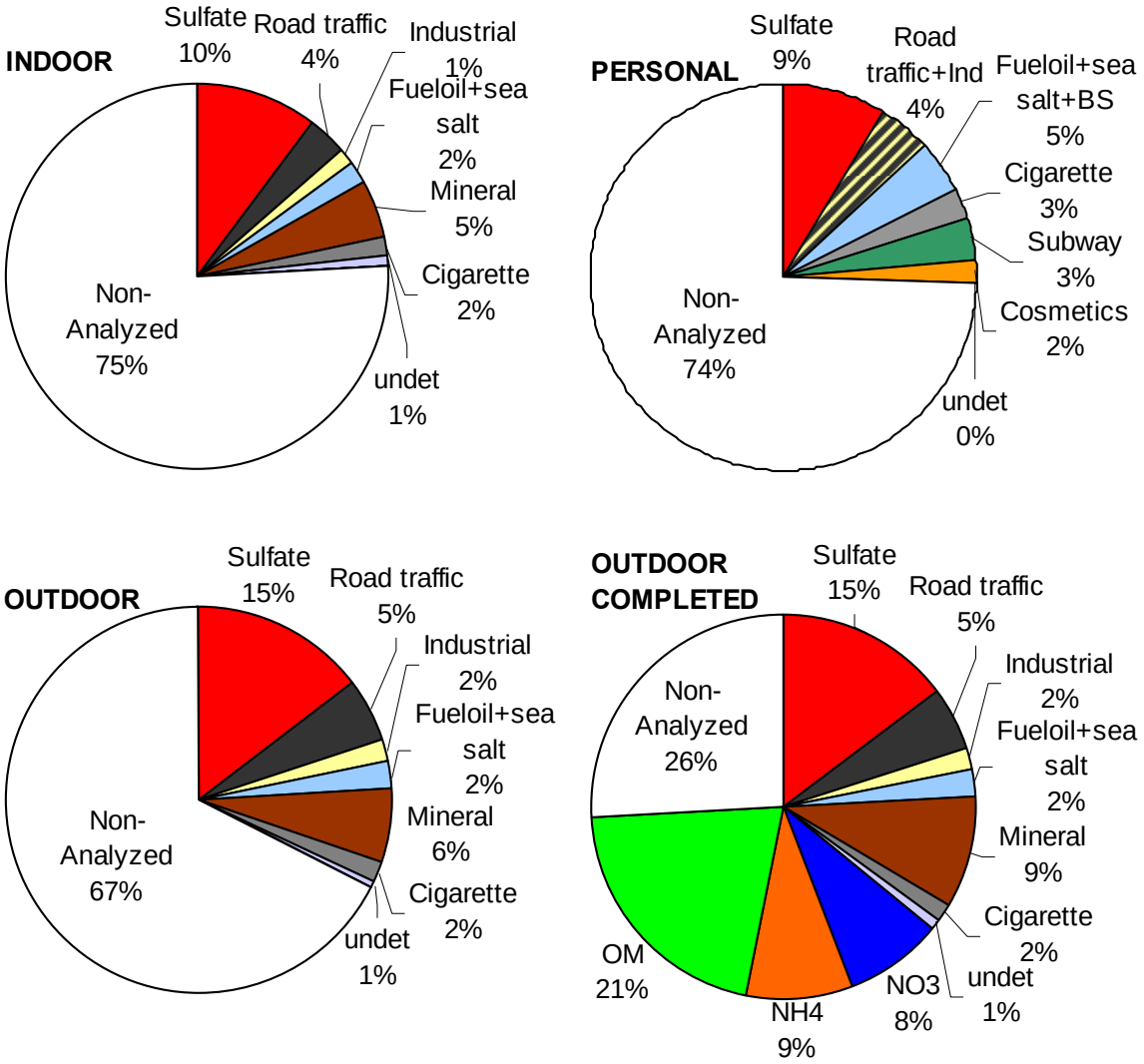

Barcelona

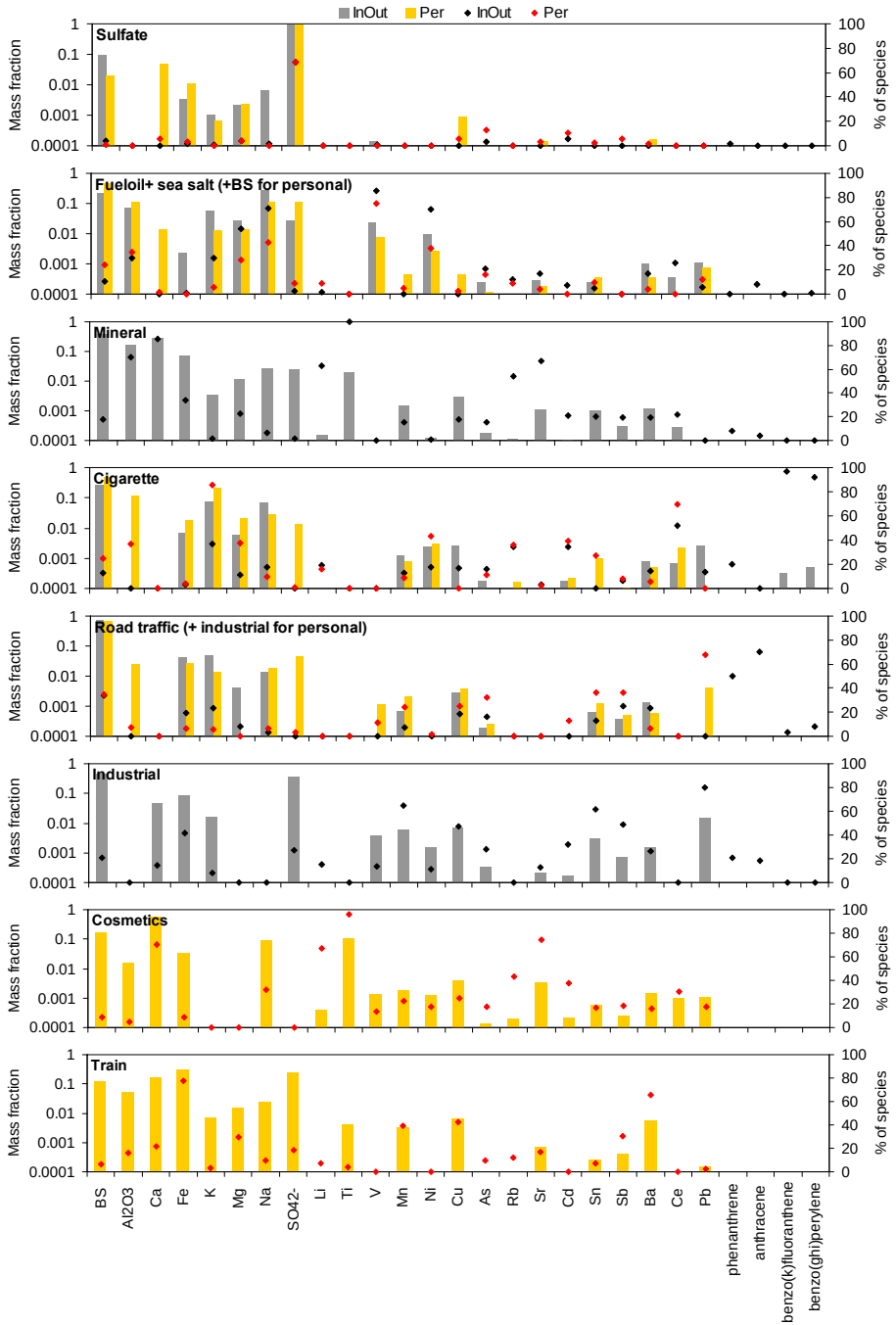


# Road traffic, air quality and aerosol measurements

## 5. UFP: Engineered nanoparticles

PM2.5 Barcelona, 54 women ARIBA project
Minguillón M.C., Schenbari A. et al., Atmospheric Environment, 2012






# ENGINEERED NANOPARTICLES

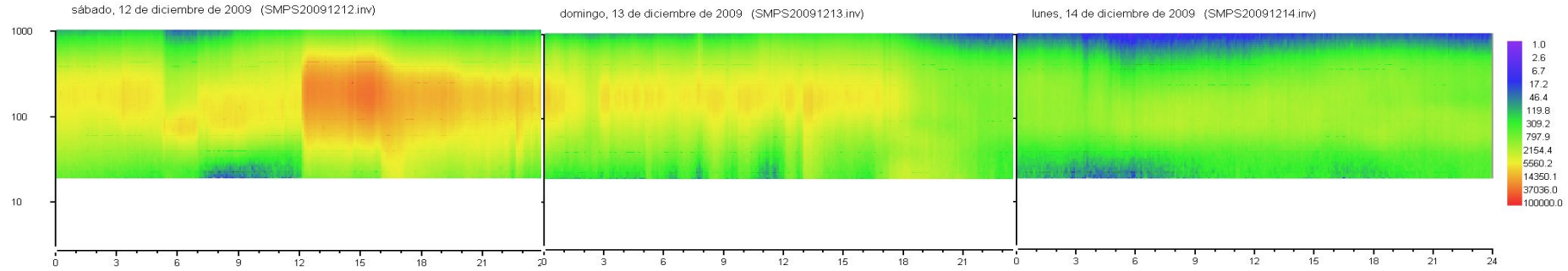
# Road traffic, air quality and aerosol measurements

## 5. UFP: Major rural scenarios: Montseny

*Cusack et al., IAE, 2010*

### Regional background aerosols

### Accumulation, max. N induced by mountain breeze




### Advection (without breeze)

### Photochemical nucleation and growth