

# Overview of environmental measurements: ATMOSPHERIC POLLUTION



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# Institute of Environmental Assessment and Water Research

<http://www.idaea.csic.es/>



**CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS  
SPANISH RESEARCH COUNCIL**

# Institute of Environmental Assessment and Water Research

IDA  
EA

## Mission:

Study the natural and anthropogenically-induced changes in the ecosystems, mainly those involving toxicity increases in organisms and humans, by means of chemical and geochemical techniques

## Leading roles in the application of:

- analytical chemistry
- geochemistry and hydrology
- molecular biology
- methods for the study of environmental problems

## Departmental structure:

2 departments:

- Environmental Chemistry
- Geosciences

# Outline

- 1. Atmospheric pollution**
- 2. The problem of NO<sub>2</sub>**
- 3. Measurement methods for NO<sub>2</sub>**
- 4. The problem of PM**
- 5. Measurement methods for PM**
- 6. Conclusions**

# Atmospheric pollution

RD, 102/2011, 28th January, 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

# Atmospheric pollution: Origin

## Wind re-suspension

Al<sub>2</sub>O<sub>3</sub>  
Mg  
Ti  
Fe  
K  
SiO<sub>2</sub>  
CO<sub>3</sub><sup>2-</sup>  
P  
Ca



## Wind emission

Na<sup>+</sup>  
Cl<sup>-</sup>  
SO<sub>4</sub><sup>2-</sup>



## Traffic, fires (OM and EC), gases



## Industry

NH<sub>4</sub><sup>+</sup>  
SO<sub>4</sub><sup>2-</sup>  
NO<sub>3</sub><sup>-</sup>  
Gases



## Industry, traffic

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

# Atmospheric pollution

## ATMOSPHERIC DIFFUSION OR DISPERSION

### Emission characteristics

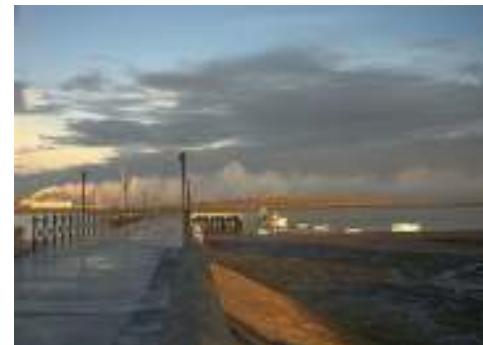
Pollutant load

T, V and height of emission



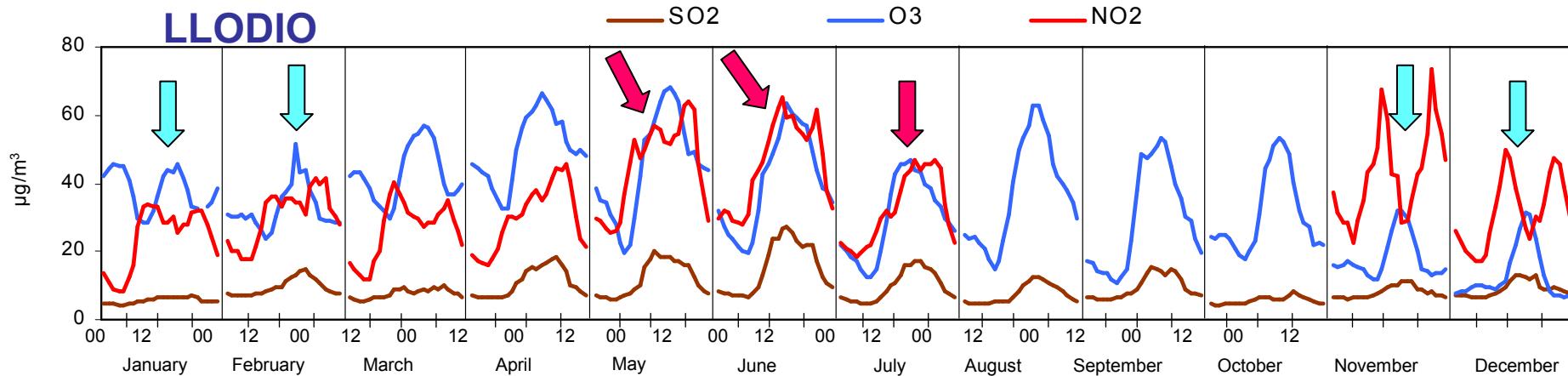
### Meteorological features

Atmospheric stratification, W-V, W-D, convection



### Topographic and local effects

Marine and slope breeze, topographic obstacles



# Atmospheric pollution

## ENVIRONMENTAL STANDARDS FOR AIR QUALITY

### Emission

#### DIRECTIVES

1996/61/EC, 2008/1/EC

2002/51/EC, 2006/120/EC

1998/69/EC, 2002/80/EC, 2007/715/EC

- ◆ IPPC Integrated Prevention and Pollution Control
- ◆ EURO standards for vehicles

### Ambient air

#### MOTHER DIRECTIVE

1996/62/CE

- ◆ Evaluation and Managing of air quality

Annex I: SO<sub>2</sub>, NO<sub>2</sub>, NOx, PM10, TSP, Pb, O<sub>3</sub>, benzene, CO, PAH, Cd, As, Ni, Hg

Directive 1999/30/EC

- ◆ SO<sub>2</sub>, NO<sub>2</sub>, NOx, PM<sub>10</sub>, Pb (PM<sub>2.5</sub>??)

Directive 2000/69/EC

- ◆ benzene, CO

Directive 2002/03/EC

- ◆ O<sub>3</sub>

Directive 2004/107/EC

- ◆ PAH, Cd, As, Ni, Hg

(PM2.5)

→ Directive Clean Air for Europe and Air Quality, 2008/50/EC & 2004/107/EC

Deadlines: 2005-2010, 2015, 2020

RD, 102/2011 (Spanish legislation)

REVISION IN 2013

# Atmospheric pollution

## ENVIRONMENTAL STANDARDS FOR AIR QUALITY

Directive 2008/50/EC, RD 102/2011

Hourly	350 µg/m <sup>3</sup> SO <sub>2</sub>	293 °K , 101,3 kPa, except PM and metals, Evriron. Cond.
Daily	125 µg/m <sup>3</sup> SO <sub>2</sub>	24 times per year
Annual prot. ecos.	20 µg/m <sup>3</sup> SO <sub>2</sub>	3 times per year not exceeding annual and mean 1 Oct-31 Mar
Hourly	200 µg/m <sup>3</sup> NO <sub>2</sub>	,8 times per year
Annual	40 µg/m <sup>3</sup> NO <sub>2</sub>	not exceeding
Annual prot. vegetation	30 µg/m <sup>3</sup> NO <sub>x</sub>	(reported as NO <sub>2</sub> ) not exceeding
Annual	30 (5) µg/m <sup>3</sup> Benzene	not exceeding
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 and 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/EC, RD 102/2011

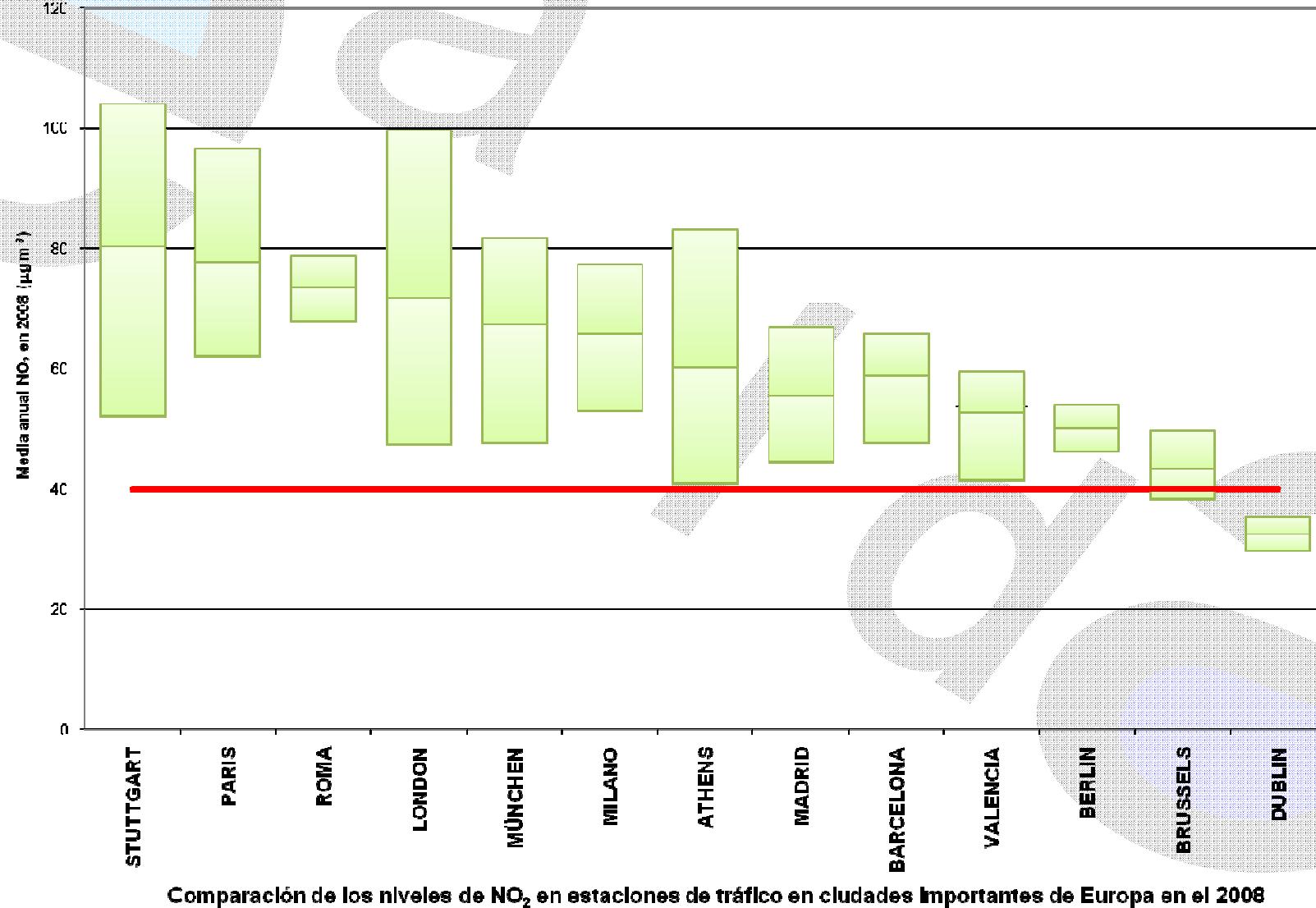
Annual	6 ng/m <sup>3</sup> As	not exceeding
Annual	20 ng/m <sup>3</sup> Ni	not exceeding
Annual	5 ng/m <sup>3</sup> Cd	not exceeding
Annual	1 ng/m <sup>3</sup> Benzo[α]pirene	not exceeding

Critical parameters (exceedances)

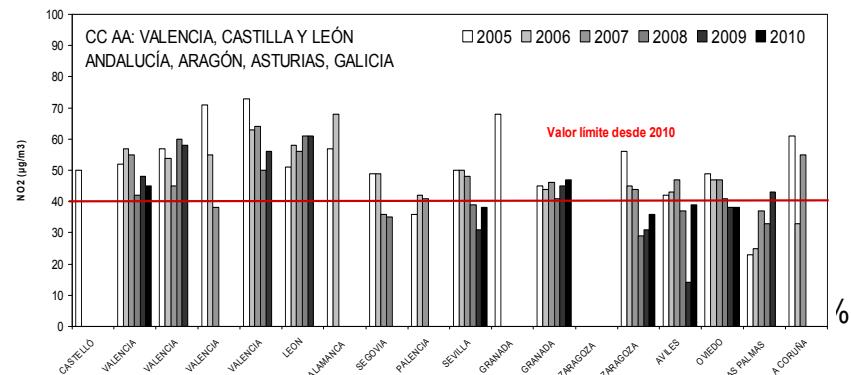
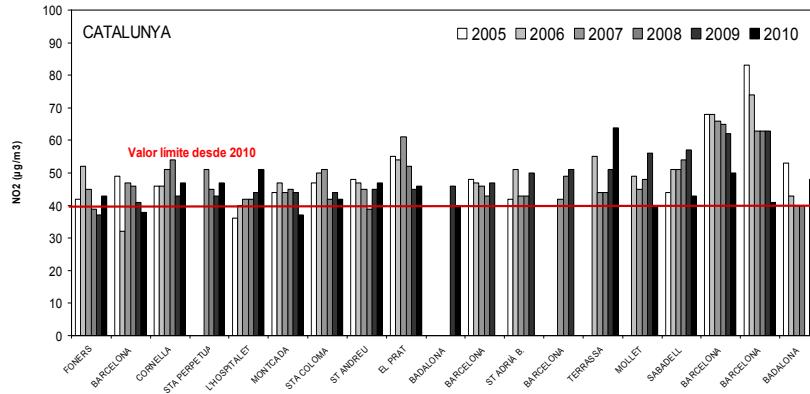
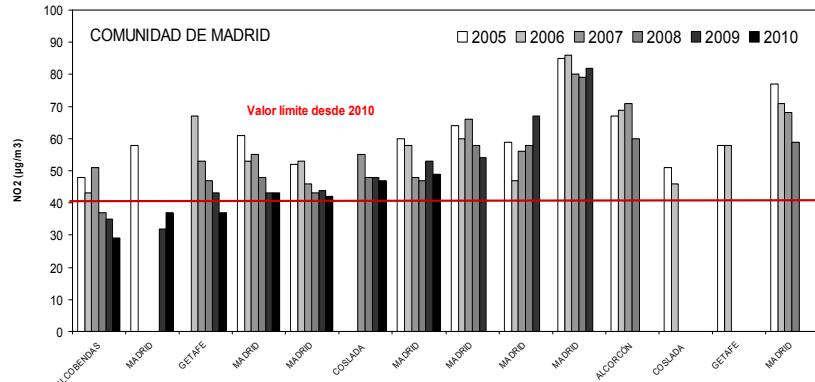
# The problem of NO<sub>2</sub>



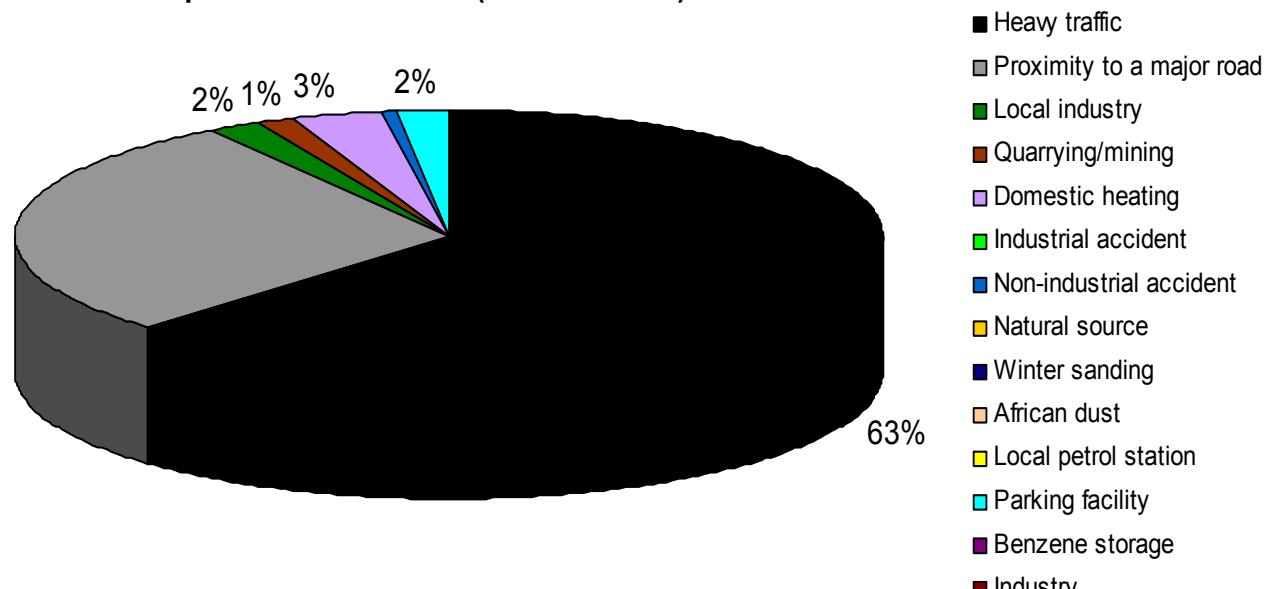
# The problem of NO<sub>2</sub>



# The problem of NO<sub>2</sub>



## Causas de superación del VLA de NO<sub>2</sub>: promedio 2001-2009 (53 estaciones)

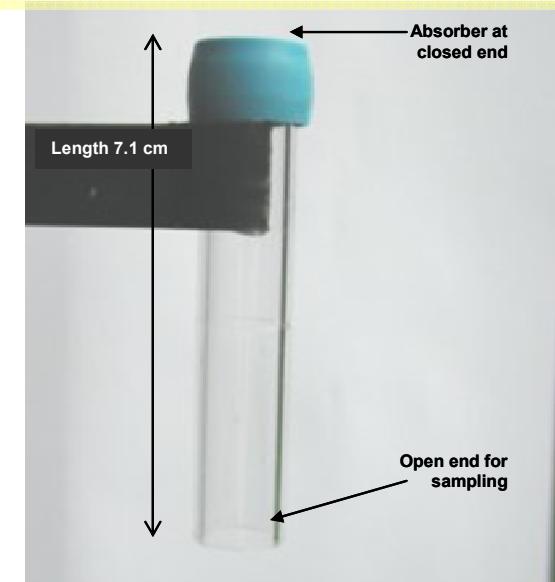


# Measurement methods for NO<sub>2</sub>

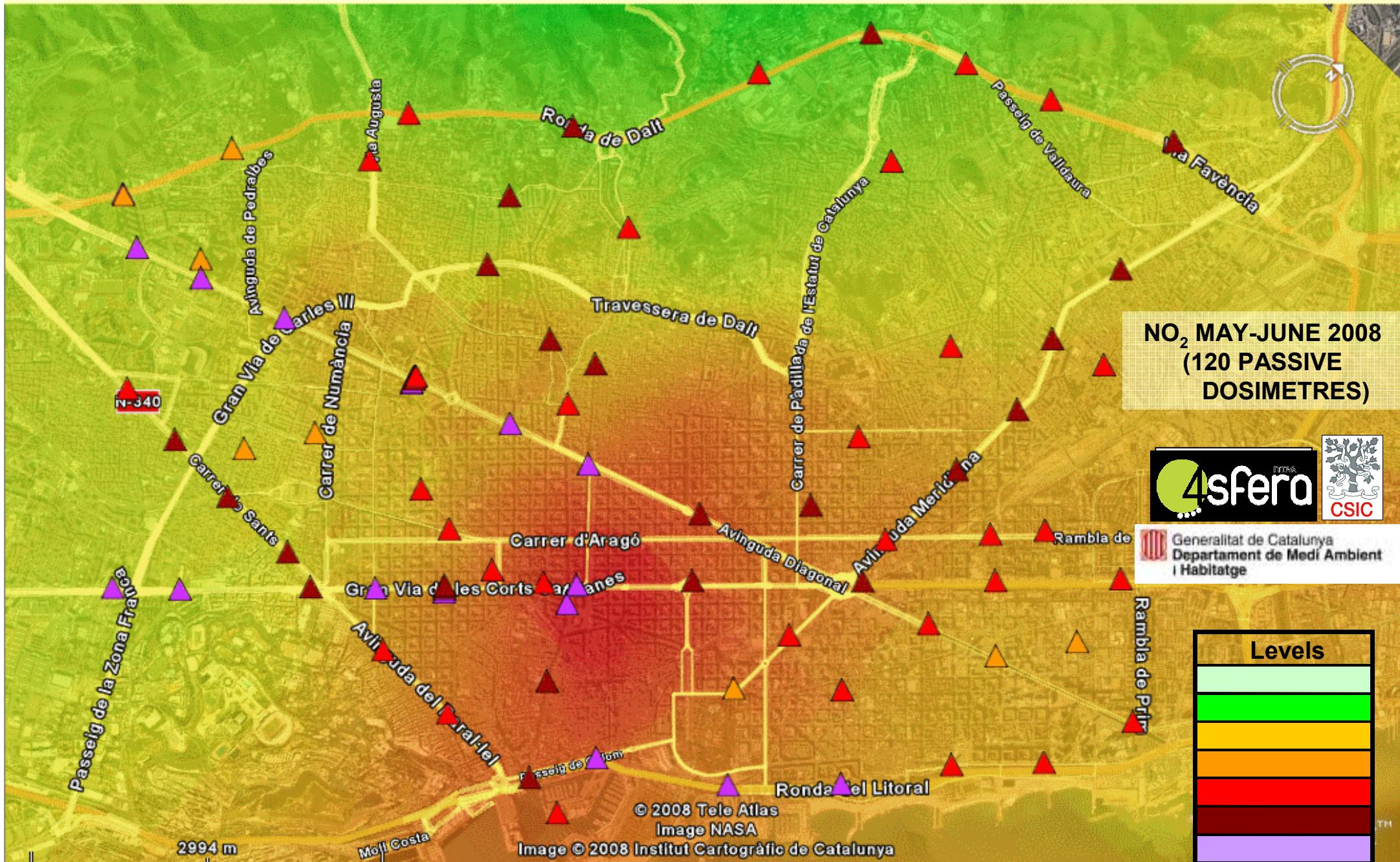
# Measurement methods for NO<sub>2</sub>



- Conventional NO<sub>2</sub> monitor
- Usually, chemiluminescence
  - Dosimeter NO<sub>2</sub>
  - Molecular diffusion
  - Analysis: colorimetry

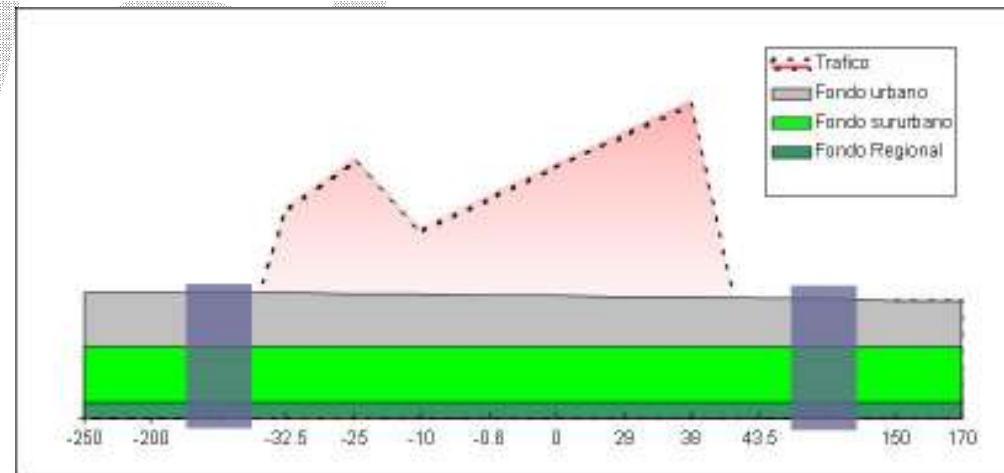


# The problem of NO<sub>2</sub>



# The problem of NO<sub>2</sub>

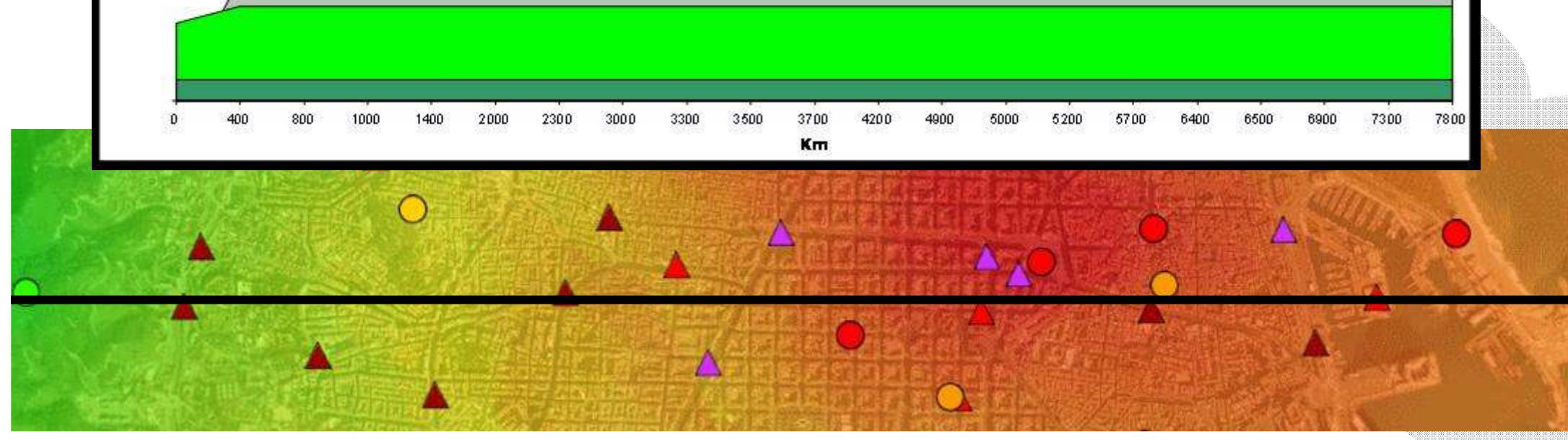
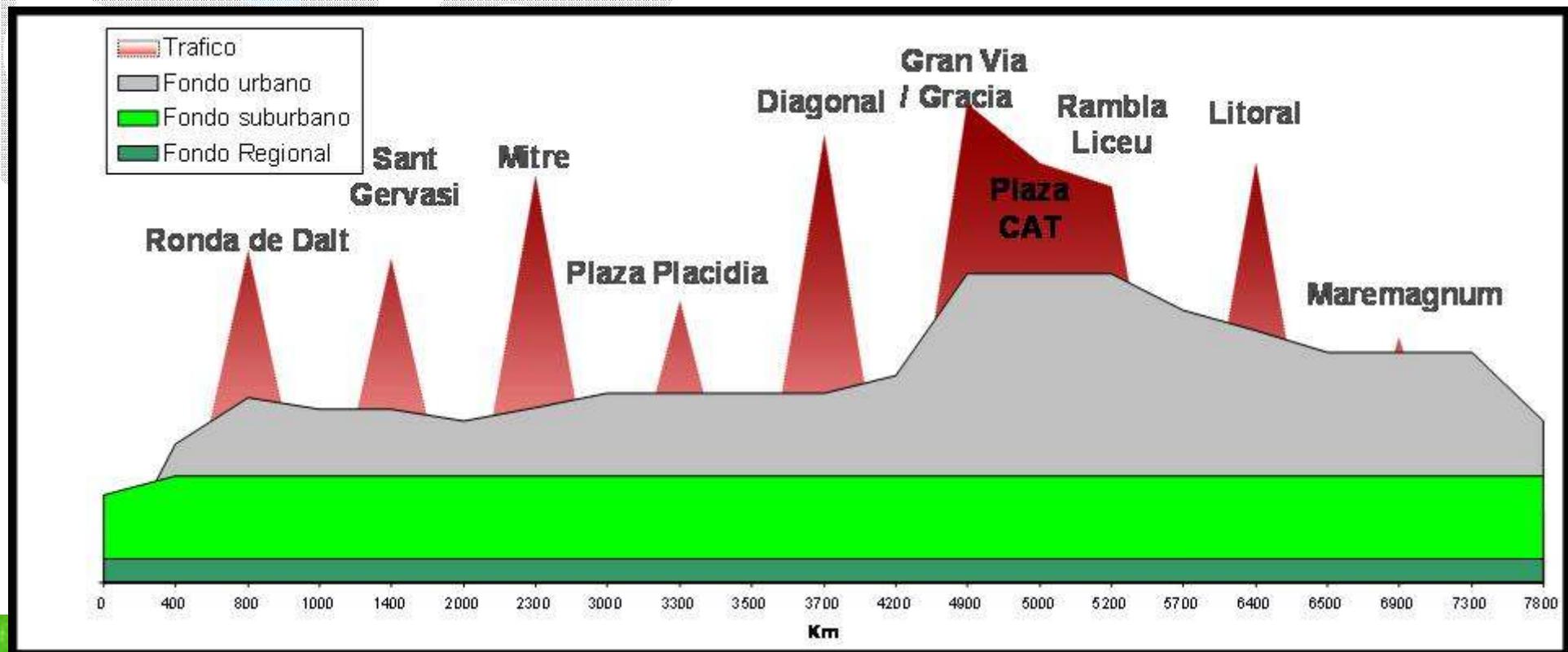
NO<sub>2</sub>, high spatial variability



# The problem of NO<sub>x</sub>

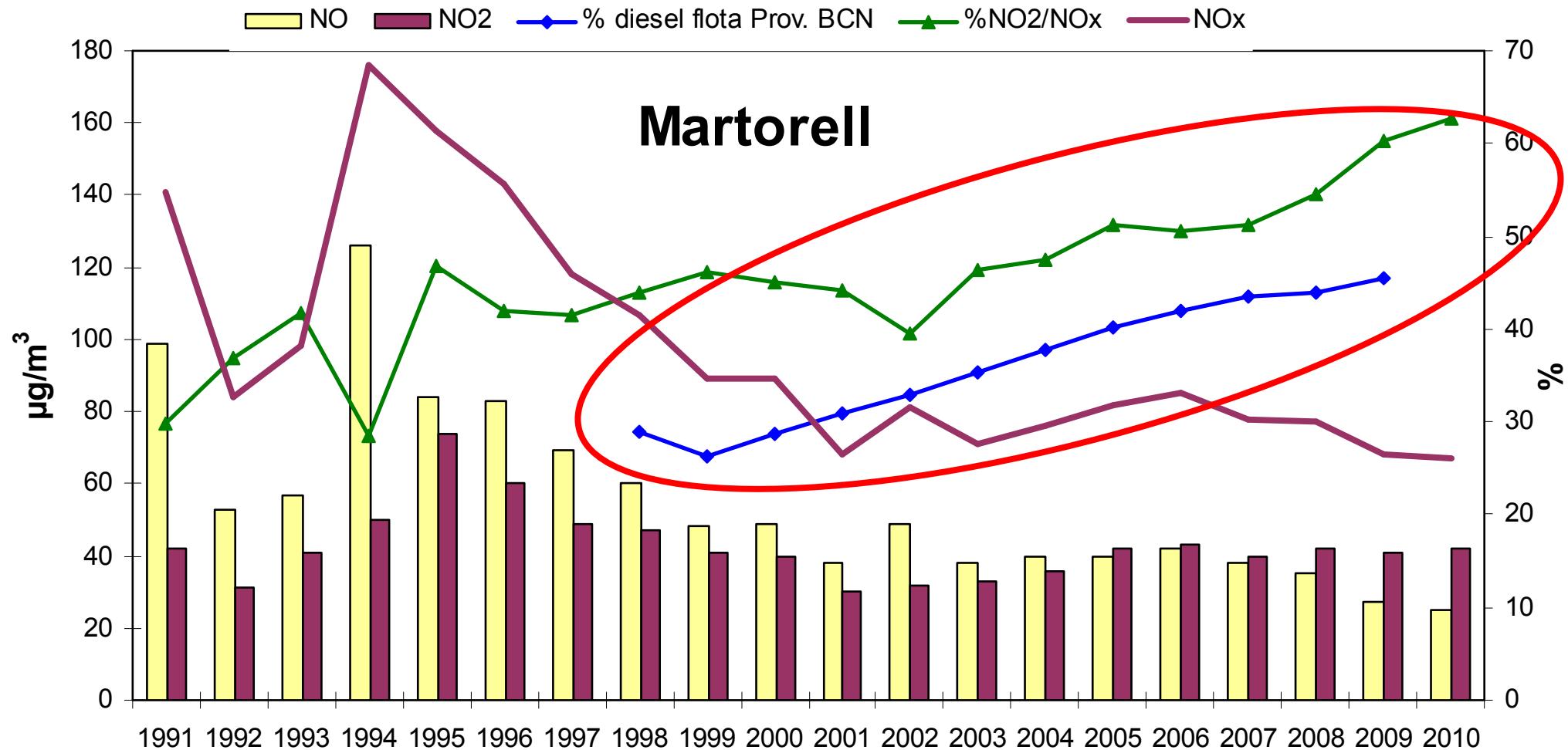
NO<sub>x</sub> MAY-JUNE 2008 (120 PASSIVE DOSIMETRES)

Fabra - Barceloneta



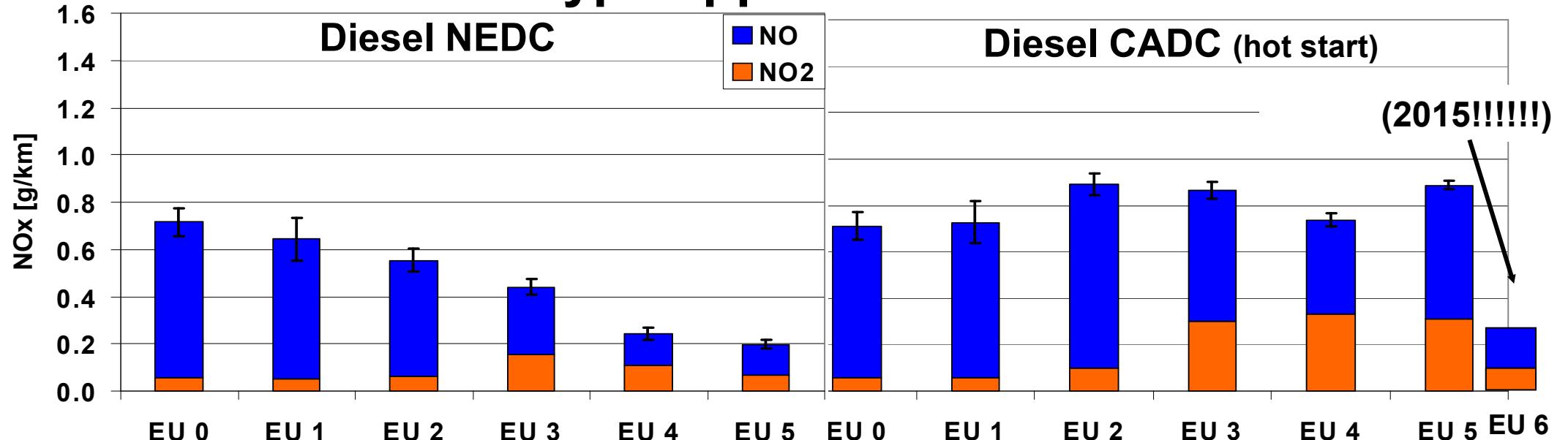
# The problem of NO<sub>2</sub>

## NO & NO<sub>2</sub> 1990-2010 TRENDS



# The problem of NO<sub>2</sub>

## Actual emissions: type approval vs.real world emissions



NEED FOR HIGH-TIME RESOLVED, PORTABLE  
LOW-COST MONITORS/SENSORS

Courtesy: Prof. Dr. S. Hausberger T.U. Graz

# The problem of PM

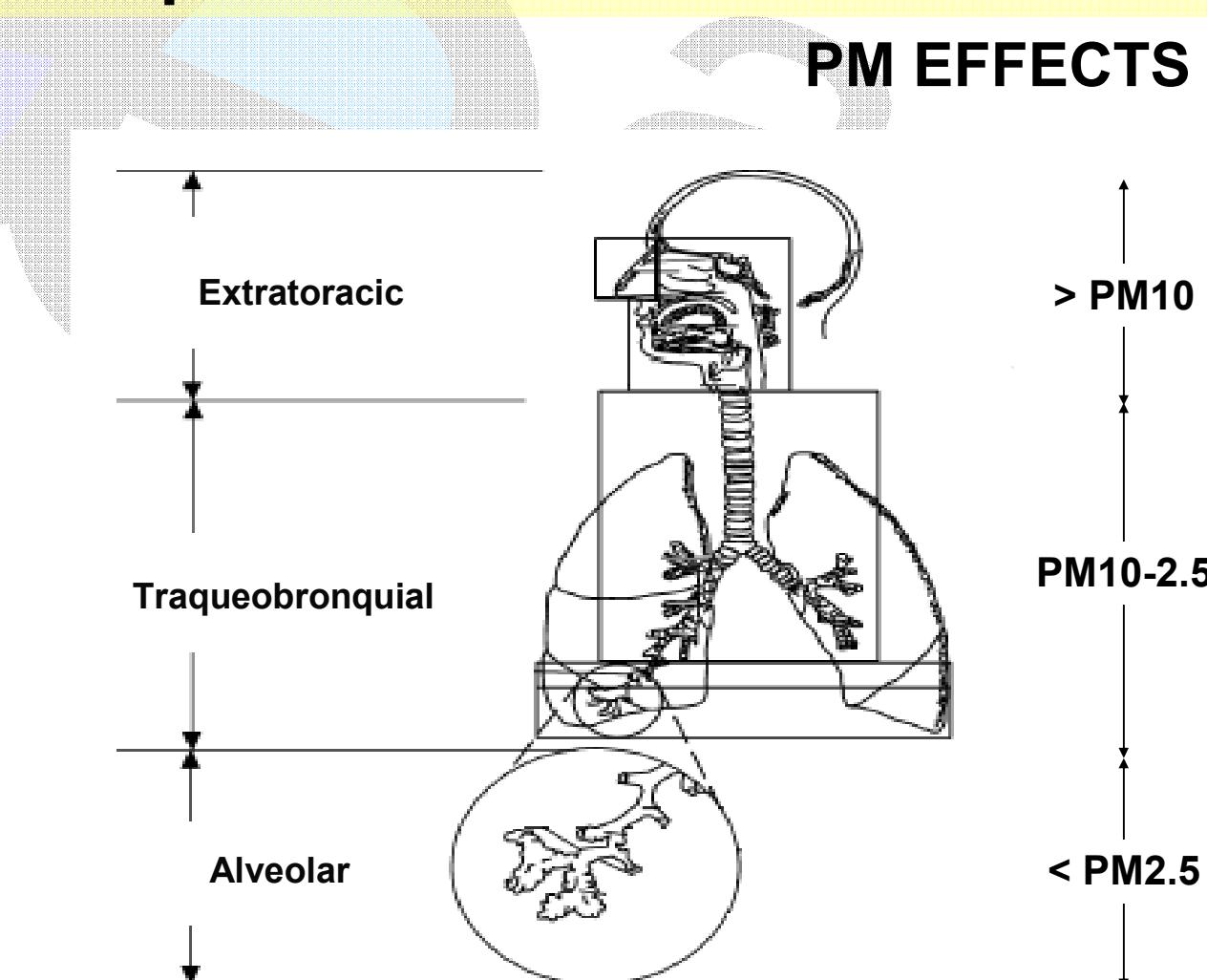
# The problem of PM

Atmospheric particulate matter (PM): heterogeneous solid and/or liquid material present in suspension into the atmosphere

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

# The problem of PM

## PM EFFECTS



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

$\text{PM}2.5\text{-}0.1$   
Additional lung physical effect

$\text{PM}0.1$   
Cardiovascular, UFP  
Reaching all important organs

# The problem of PM

## Particulate Matter and health effects in Barcelona

Perez et al., 2009 ES&T  
Selected results

Fraction	Respiratory mortality (Lag2)	Cardiovascular mortality (Lag1)	Cerebrovascular mortality (Lag1)
$\text{PM}_{10-2.5}$	1.033 (0.980-1.089)	<b>1.059</b> <b>(1.026-1.094)</b>	<b>1.098</b> <b>(1.030-1.171)</b>
$\text{PM}_{2.5-1}$	<b>1.206</b> <b>(1.028-1.416)</b>	0.984 (0.892-1.086)	0.905 (0.743-1.102)
$\text{PM}_1$	1.010 (0.963-1.059)	<b>1.028</b> <b>(1.000-1.058)</b>	<b>1.063</b> <b>(1.004-1.124)</b>

Odds ratio per 10 ug/m<sup>3</sup>

# The problem of PM

Ranking legend	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	>40											
Risk factor	Global	High income Asia Pacific	High income Western Europe	Australia	High income North America	Central Europe	Southern Latin America	Latin Europe	East Asia	Tropical Latin America	Central Asia	Andean Latin America	North Africa and Middle East	Caribbean	South Asia	Oceania	Southern sub-Saharan Africa	Eastern sub-Saharan Africa	Central sub-Saharan Africa	Westem sub-Saharan Africa
High blood pressure	1	2	3	4	5	6	7	8	2	4	3	2	1	3	6	3	6	5	6	
Smoking, including second-hand smoke	2	1	2	1	2	3	4	5	4	3	2	1	2	1	3	2	3	2	3	
Alcohol use	3	4	5	3	4	5	6	7	5	6	2	1	3	2	3	4	3	2	5	
Household air pollution from solid fuels	4	43	-	-	24	23	20	-	18	13	8	12	7	13	11	1	4	7	1	
Diet low in fruits	5	3	2	3	2	3	4	5	4	3	2	1	10	6	8	2	9	8	21	
High body-mass index	6	8	7	6	5	4	3	2	9	8	7	6	5	4	12	3	14	18	15	
High fasting plasma glucose	7	7	6	5	4	3	2	1	8	7	6	5	4	3	7	1	4	22	21	
Childhood underweight	8	2	1	2	1	2	3	4	3	2	1	2	3	2	17	1	3	34	18	
Ambient particulate matter pollution	9	9	11	26	14	12	24	14	6	20	19	11	10	24	7	19	6	32	25	
Physical inactivity and low physical activity	10	8	9	6	5	4	7	6	10	8	5	4	3	2	7	11	7	11	15	
Diet high in sodium	11	6	10	11	11	9	11	8	7	9	12	7	6	11	3	25	14	16	11	
Diet low in nuts and seeds	12	21	8	9	8	9	8	12	10	8	15	8	12	9	10	11	13	26	22	
Boron deficiency	13	20	31	21	26	22	37	29	19	14	12	13	12	4	12	6	8	11	4	
Suboptimal breastfeeding	14	-	-	-	-	11	27	-	24	23	15	24	16	9	11	12	10	10	3	
High total cholesterol	15	12	8	9	9	10	9	8	11	11	10	9	8	7	16	14	29	28	39	
Diet high in whole grains	16	10	16	16	17	13	12	11	11	12	14	16	15	14	12	15	31	31	24	
Diet low in vegetables	17	14	13	12	13	11	10	12	15	16	20	19	13	14	18	11	16	11	20	
Diet low in seafood omega-3 fatty acids	18	47	16	23	16	15	14	15	17	17	18	19	16	21	15	18	20	43	27	
Drug use	19	13	18	10	10	20	13	17	18	13	16	18	20	11	19	18	22	19	12	
Occupational risk factors for injuries	20	24	24	20	26	26	16	25	20	19	22	23	21	21	23	15	12	22	22	
Occupational low back pain	21	16	17	15	13	18	20	14	15	24	17	14	11	20	16	18	17	15	19	
Diet high in processed meat	22	20	17	14	12	15	18	15	29	17	9	22	24	15	21	24	25	21	31	
Intimate partner violence	23	18	22	23	22	25	21	22	13	23	26	22	27	19	25	23	21	25	20	
Diet low in fibre	24	16	18	18	18	20	25	16	16	25	18	20	18	22	21	21	21	26	34	
Unimproved sanitation	25	8	10	29	11	42	19	19	19	19	25	16	31	17	18	19	18	9	9	
Lead exposure	26	23	21	19	14	12	19	23	22	16	25	24	23	20	26	21	24	20	25	
Diet low in polyunsaturated fatty acids	27	19	19	17	20	23	22	18	26	24	37	21	23	29	24	25	32	23	36	
Diet high in trans fatty acids	28	25	25	24	15	23	18	15	25	21	23	23	26	15	17	20	28	34	15	
Vitamin A deficiency	29	46	49	36	31	41	42	43	41	32	33	34	34	31	33	30	21	17	13	
Occupational particulate matter, gases, and fumes	30	34	30	32	28	31	33	31	23	28	32	28	33	32	34	31	23	29	31	
Zinc deficiency	31	31	37	38	-	33	30	31	38	31	29	28	31	35	37	31	33	31	38	
Diet high in sugar-sweetened beverages	32	33	31	31	19	33	26	22	28	24	17	25	32	30	20	20	25	16	32	
Childhood sexual abuse	33	26	25	22	21	30	25	26	28	39	35	29	26	29	30	29	35	31	26	
Unimproved water source	34	42	47	41	16	42	41	42	41	41	31	35	30	39	44	31	32	34	32	
Low birth infant density	35	21	20	25	16	24	20	19	25	20	13	15	15	14	17	12	18	15	23	
Occupational noise	36	33	35	34	31	35	35	33	31	34	35	37	32	36	35	34	31	33	32	
Occupational carcinogens	37	32	38	39	34	34	32	34	31	35	38	33	30	38	30	34	42	47	42	
Diet low in calcium	38	25	28	27	26	22	29	10	31	34	30	28	25	26	32	27	26	28	35	
Ambient ozone pollution	39	36	35	41	33	36	43	-	34	40	41	41	41	41	35	42	47	39	41	
Residential radon	40	31	33	35	32	39	36	33	33	38	41	41	39	41	42	41	42	41	41	
Diet low in milk	41	22	20	20	20	29	34	32	25	30	42	36	41	42	39	42	40	39	41	
Occupational arthropagons	42	35	34	33	24	30	27	19	41	35	36	31	37	39	36	39	35	35	35	
Diet high in red meat	43	30	36	28	22	33	31	29	31	34	34	42	35	33	41	41	39	41	40	

# Risk factors ranked by attributable burden of disease for 2010

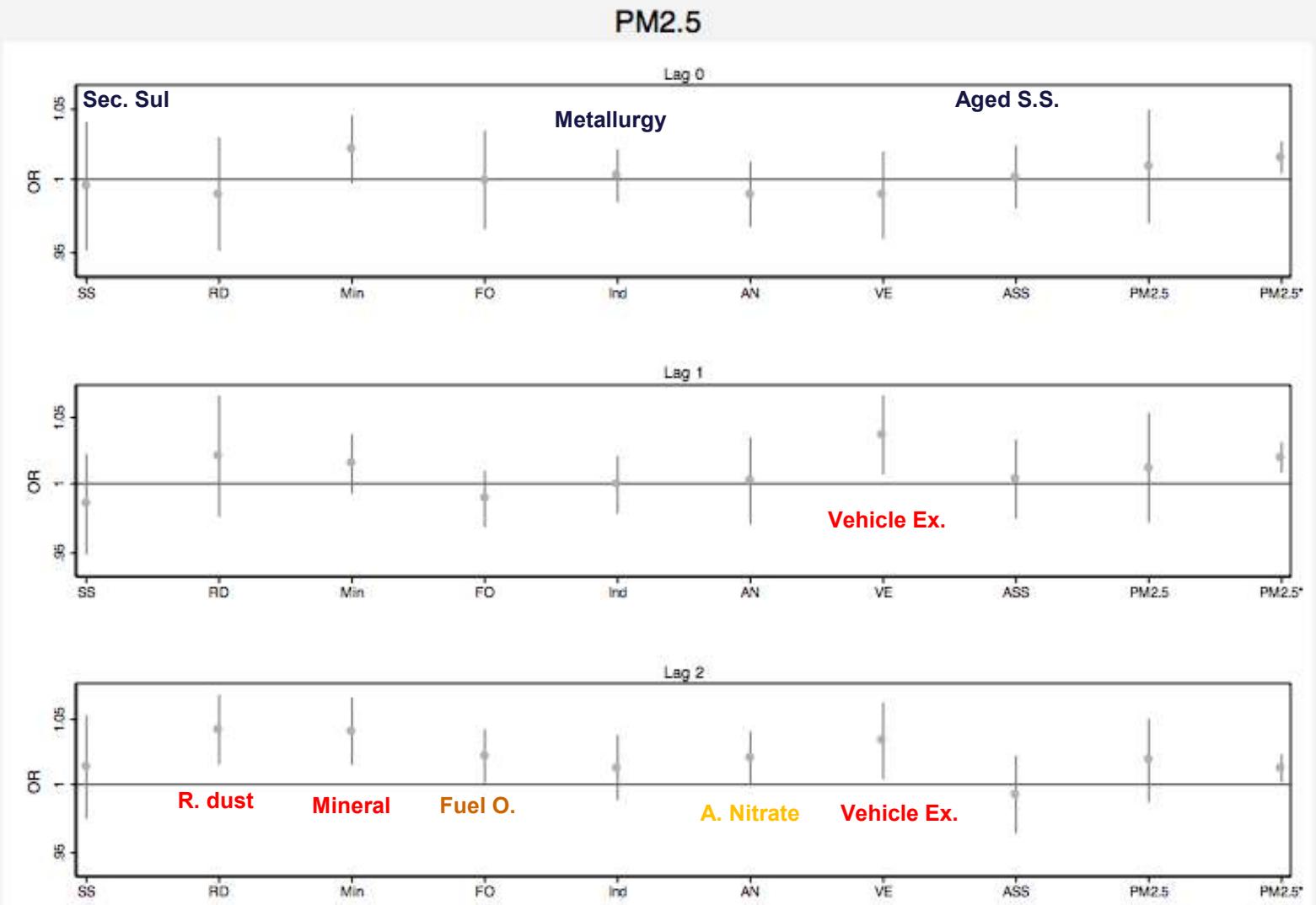
*Lim S.S., Lancet 2012; 380: 2224–60*

December 2012

# The problem of PM

## Source apportionment and mortality (Barcelona 2002-2007)

Ostro et al., 2011, EHP

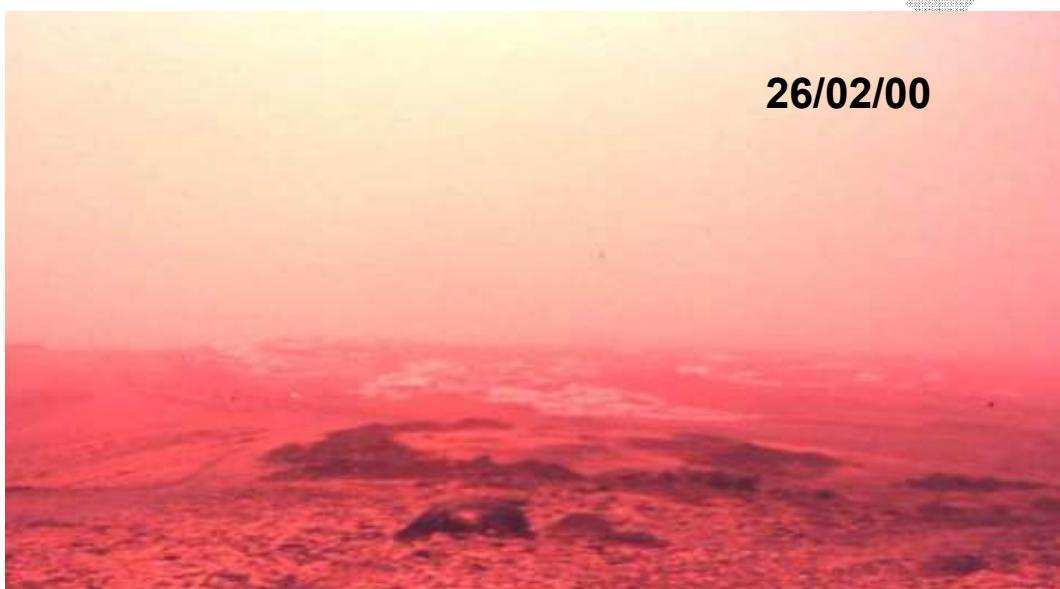


# The problem of PM

## PM EFFECTS



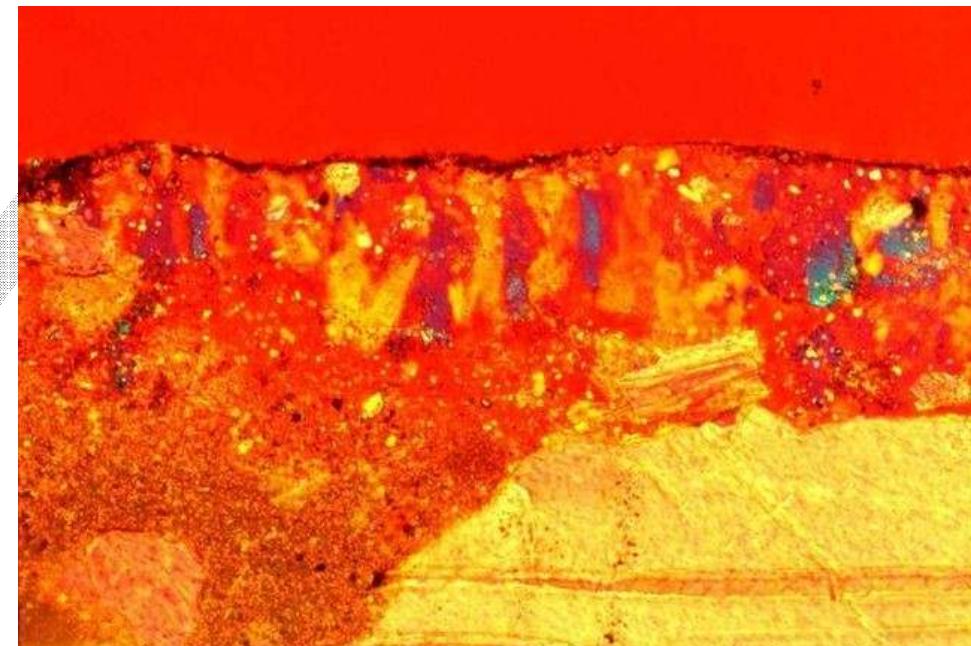
## VISIBILITY



# The problem of PM

## PM EFFECTS

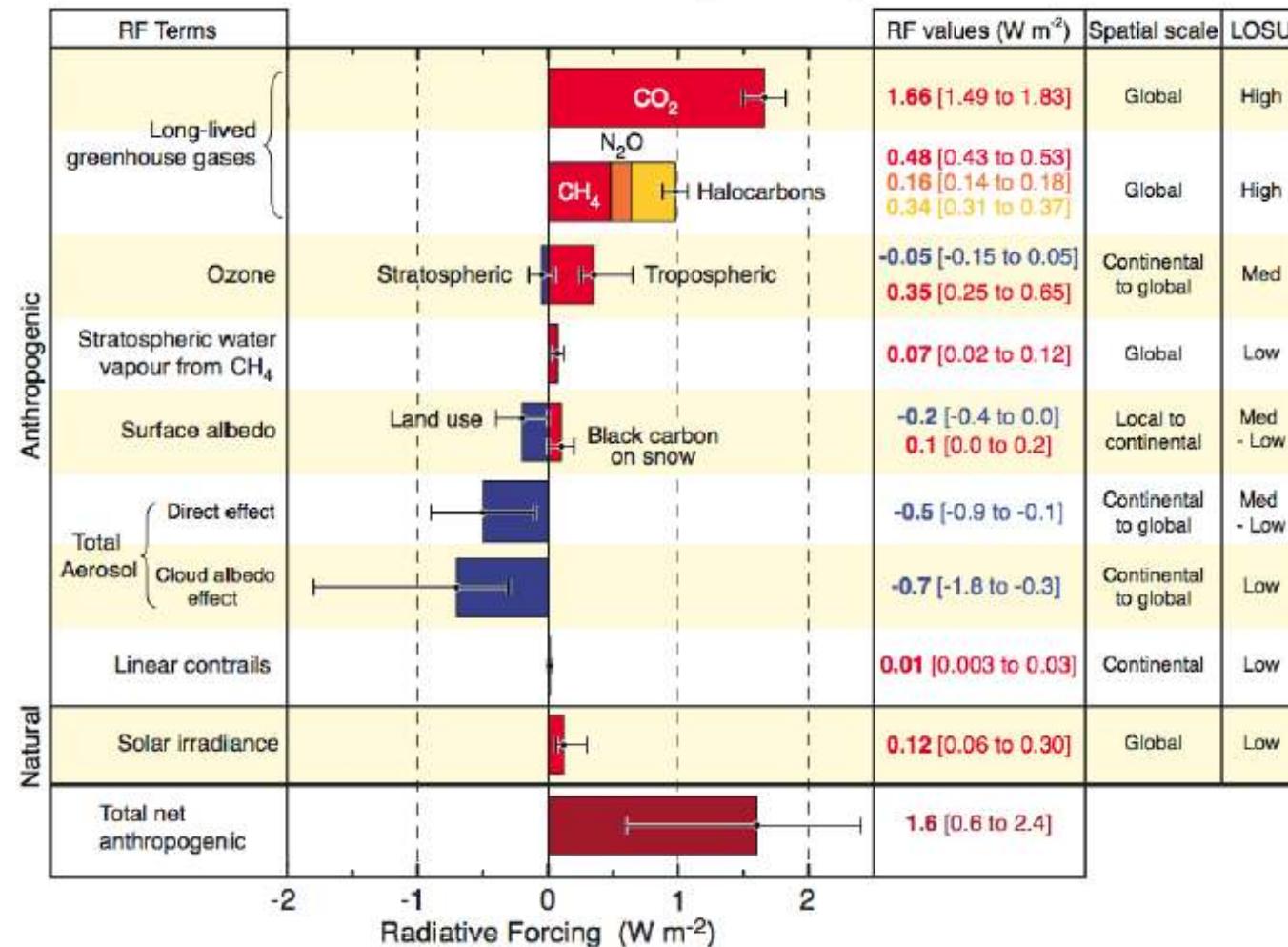
Weathering of building materials



# The problem of PM

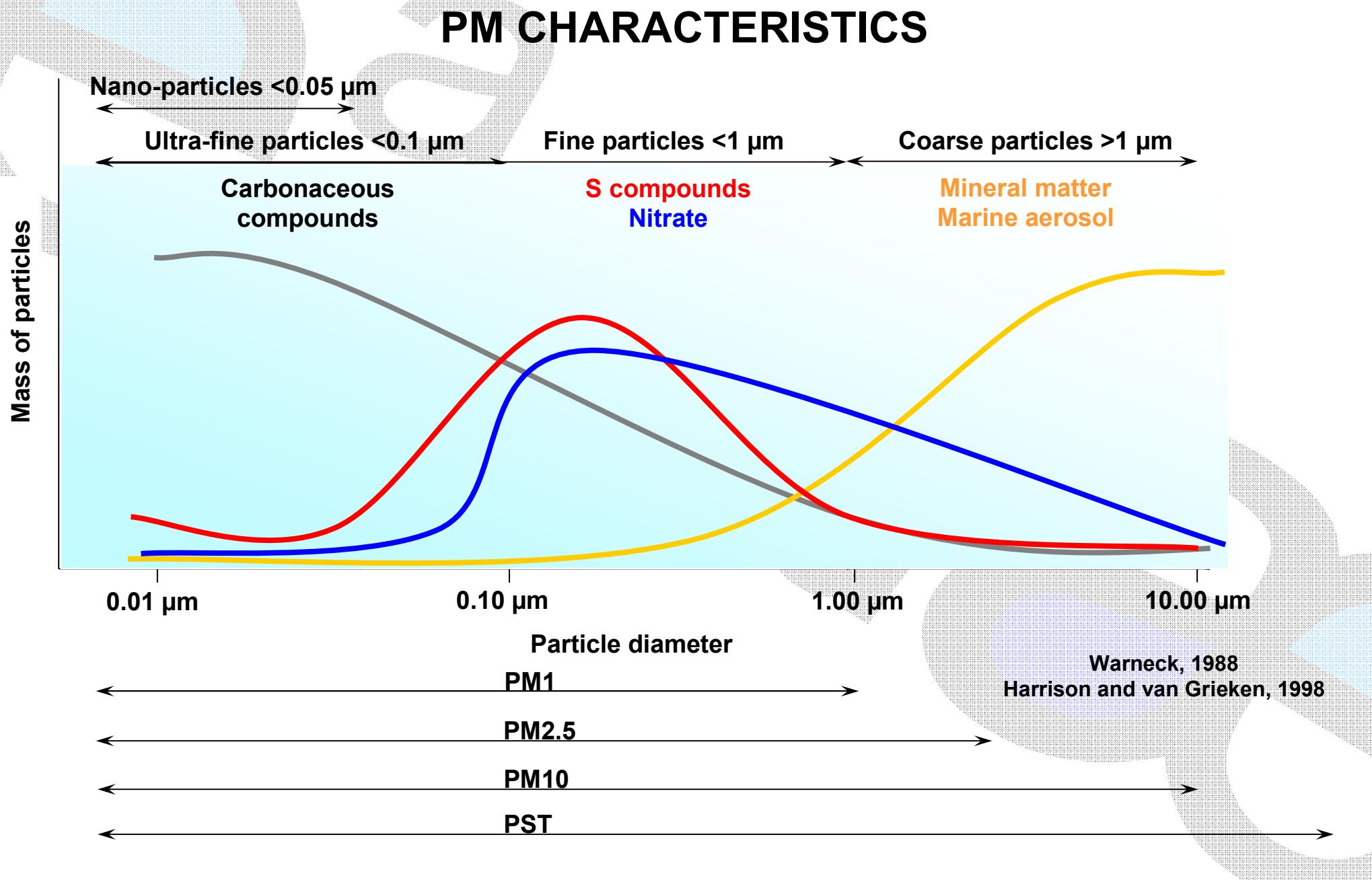
## EFFECT ON CLIMATE, IPCC (2007)

Radiative Forcing Components



©IPCC 2007: WG1-AR4

# The problem of PM



# The problem of PM

## CLASSIFICATION OF ATMOSPHERIC PARTICLES

### 1. Process of formation:

Primary particles:

Secondary particles:

directly emitted to the atmosphere as a solid  
produced into the atmosphere from gaseous  
precursors



### 2. Origin:

Natural particles

Anthropogenic particles (human activities)

# The problem of PM

## PRIMARY PM



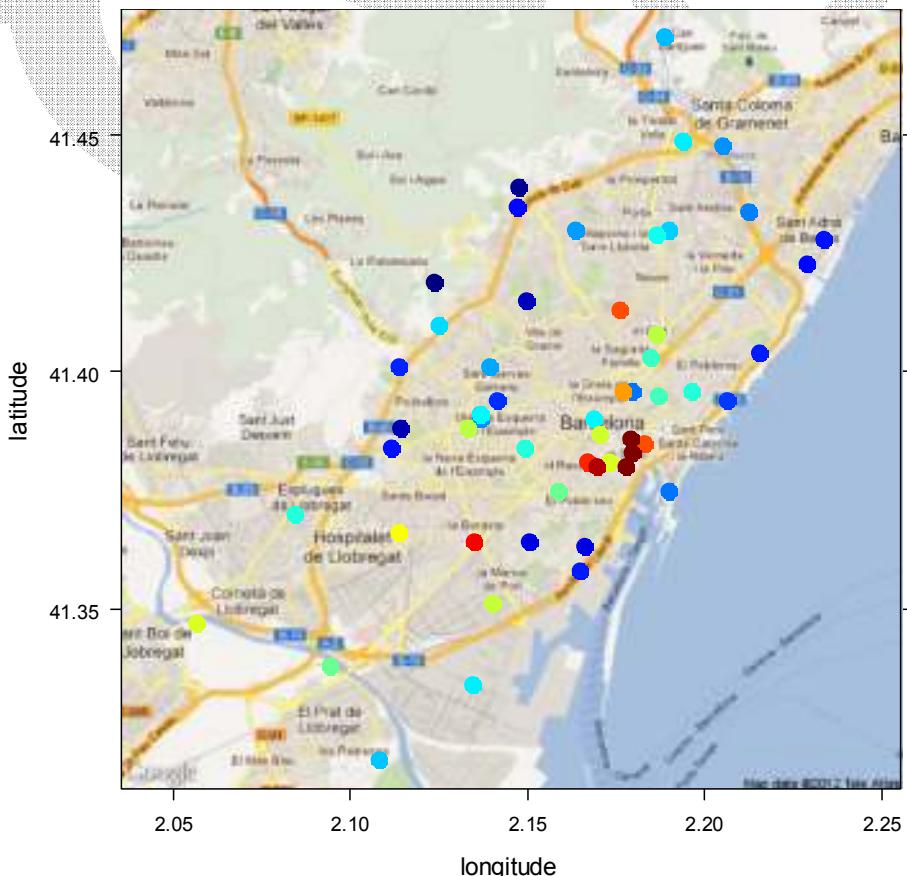
# The problem of PM

**SECONDARY PM**



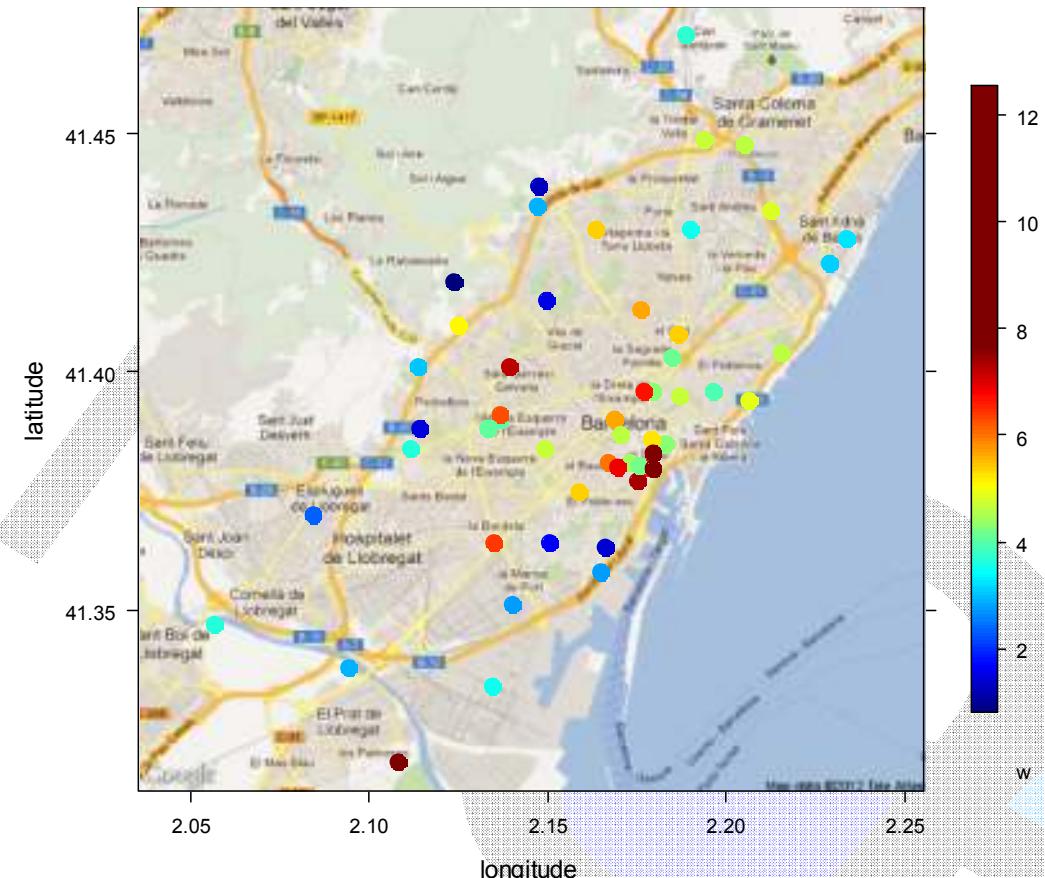
# The problem of PM

NH<sub>3</sub> ( $\mu\text{gm}^{-3}$ )  
Summer 2010



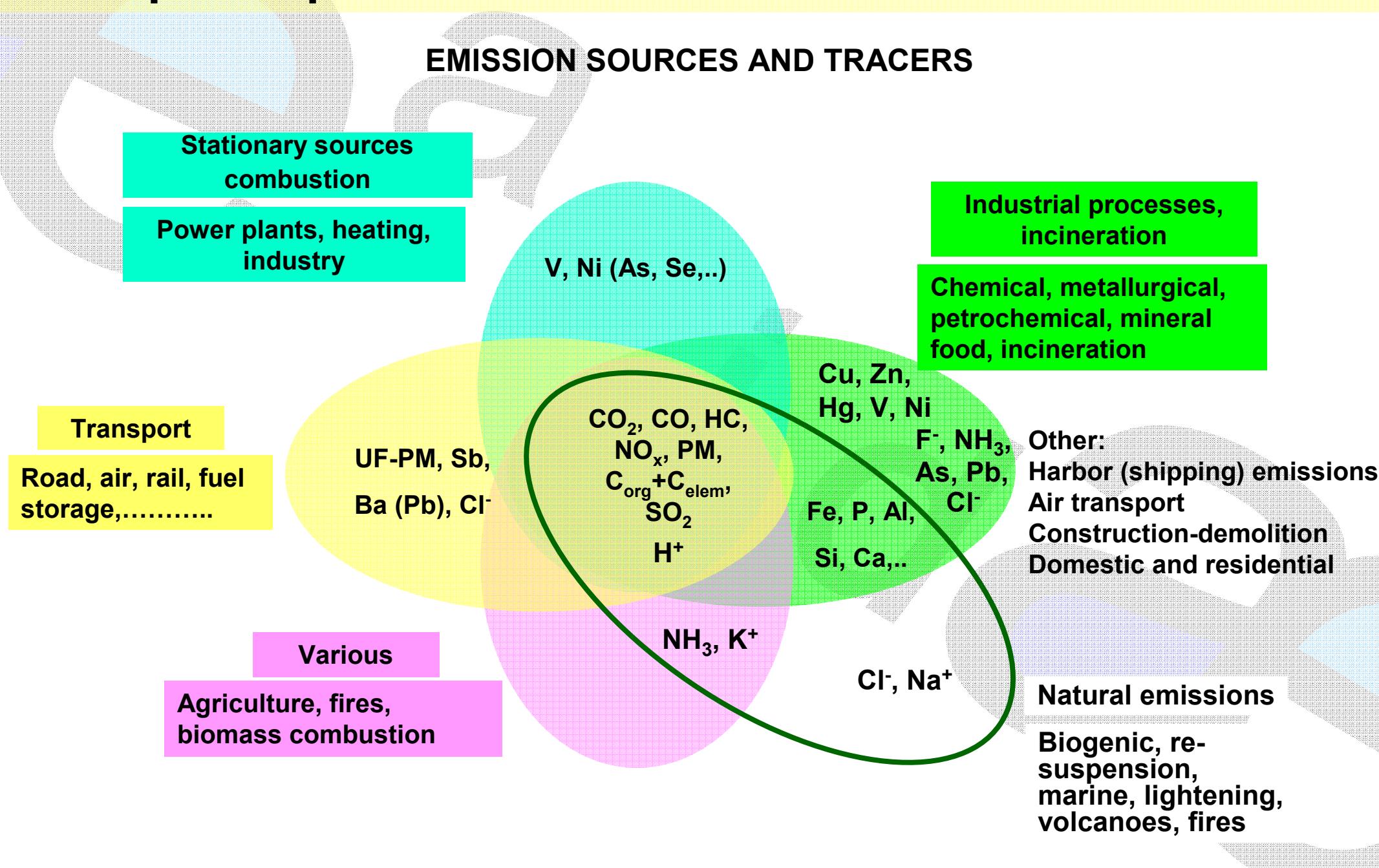
## URBAN AMMONIA

NH<sub>3</sub> ( $\mu\text{gm}^{-3}$ )  
Winter 2010

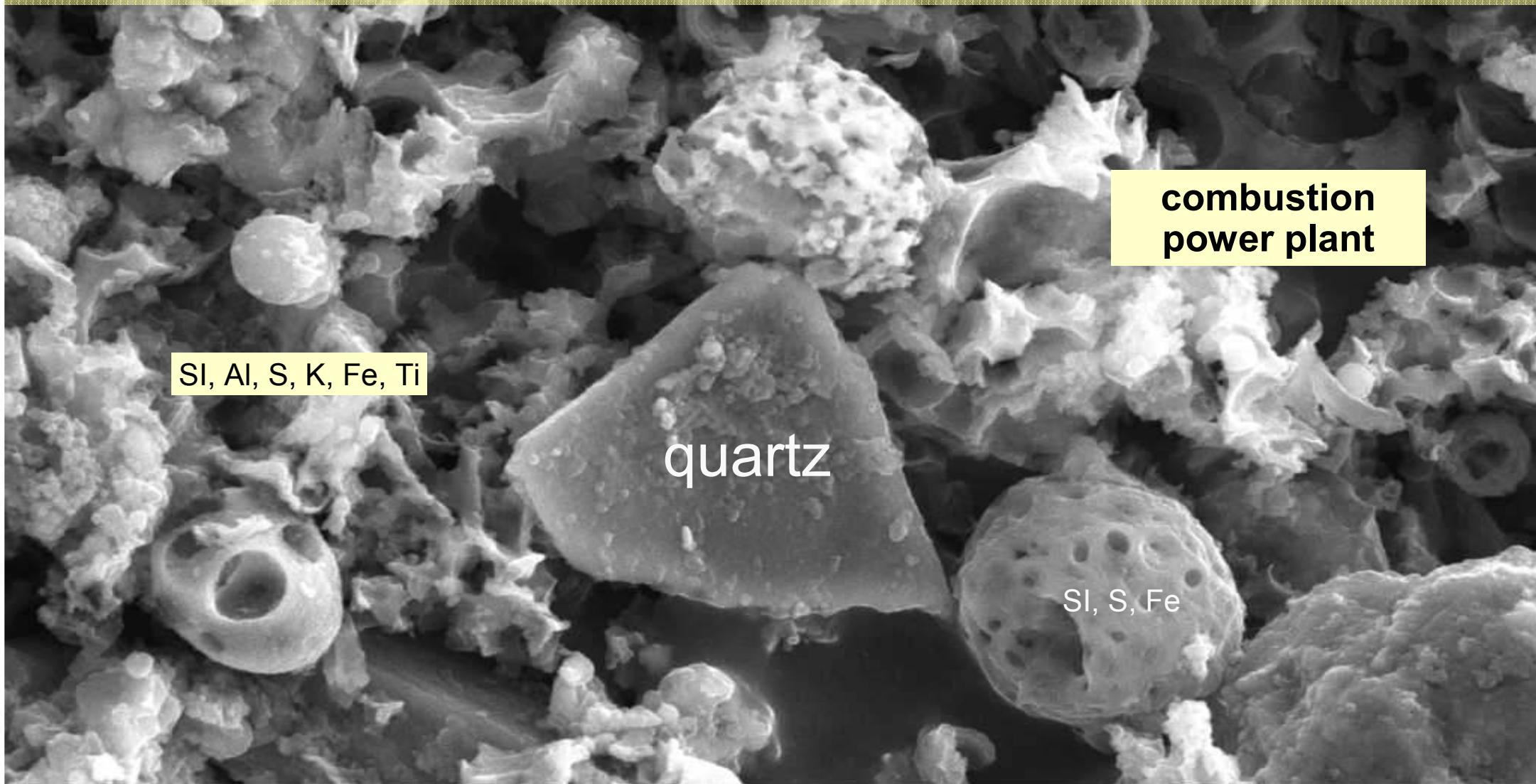


# Atmospheric pollution

## EMISSION SOURCES AND TRACERS



# The problem of PM



0011 20KU

10 $\mu$ m WD37

# The problem of PM

Bioaerosol (natural)

Vegetal debris, insects, bacteria,....

pollen

0015 20KV

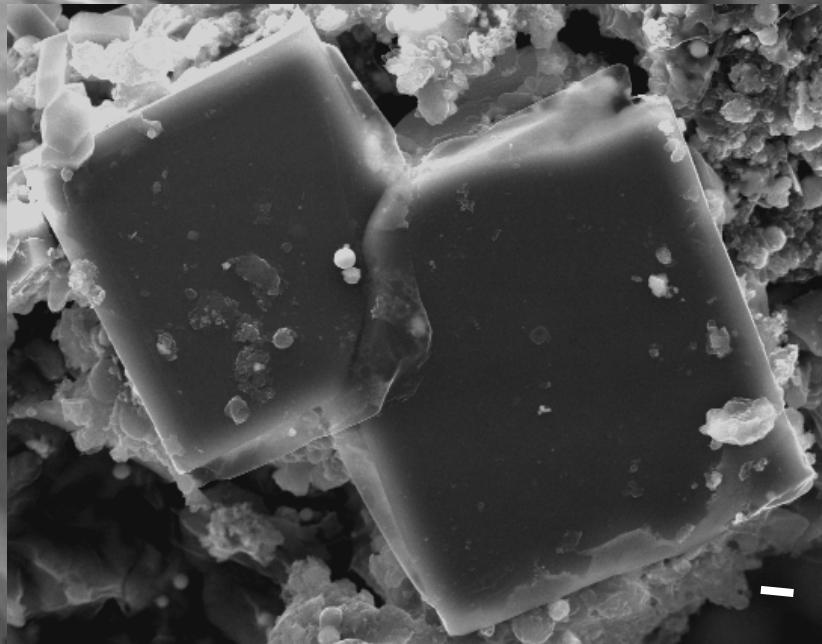
1 μm WD33

# The problem of PM

## Sea spray

Sodium, potassium, magnesium chloride, sodium, magnesium sulphate , DMS

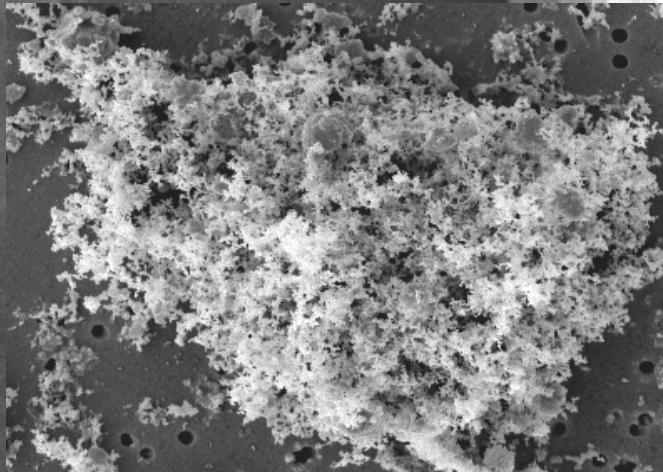
NaCl



10  $\mu$ m WD33

# The problem of PM

Diesel soot

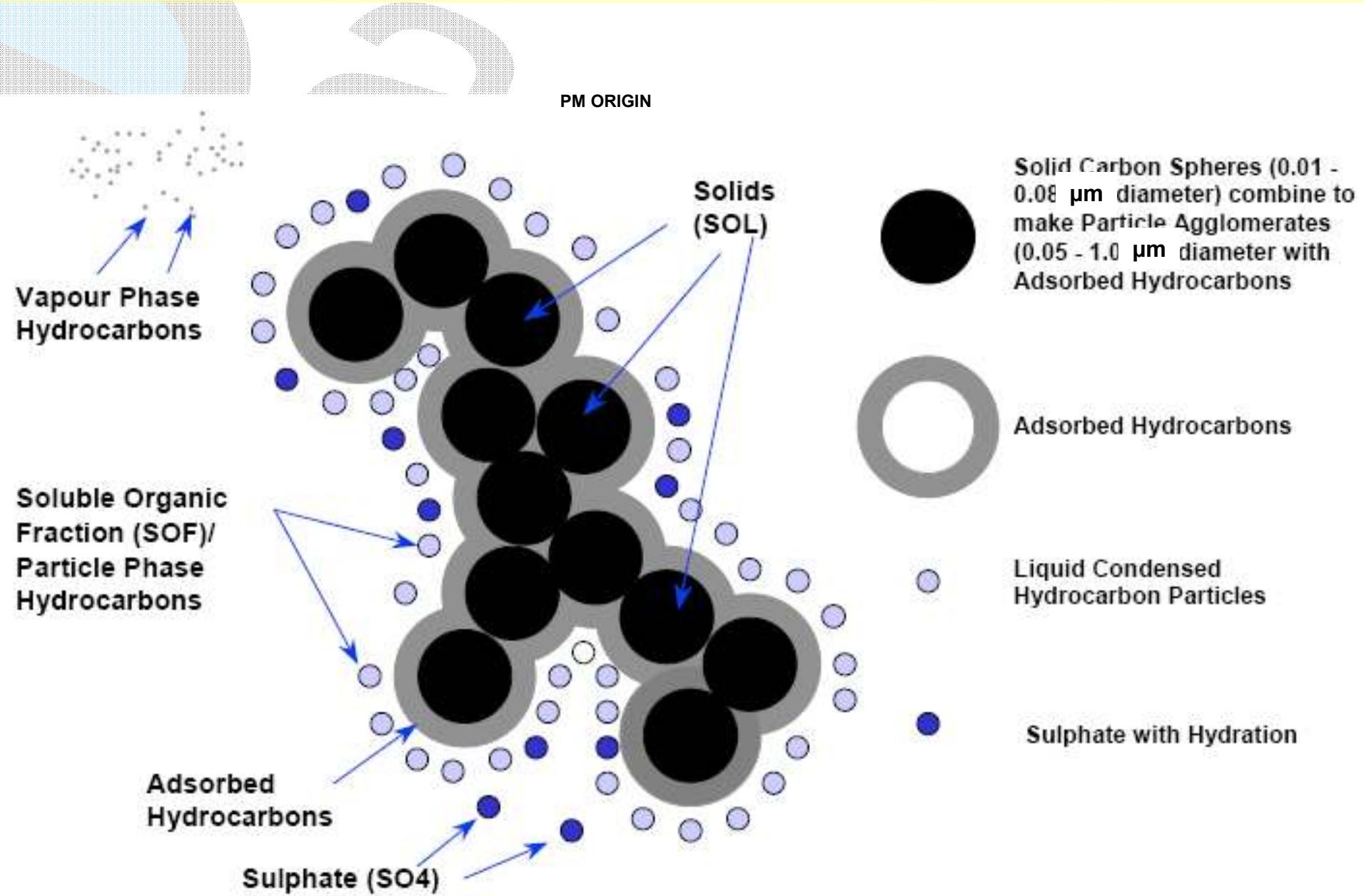


'soot'

Vehicle exhaust

Acc.V Spot Magn Det WD Exp | 1 μm  
5.00 kV 3.0 24000x SE 5.8 827 CARDIFF

# The problem of PM



# The problem of PM

Fossil fuel combustion

'char'

Fuel oil power  
plant

Si, S, Fe

NaCl

0011

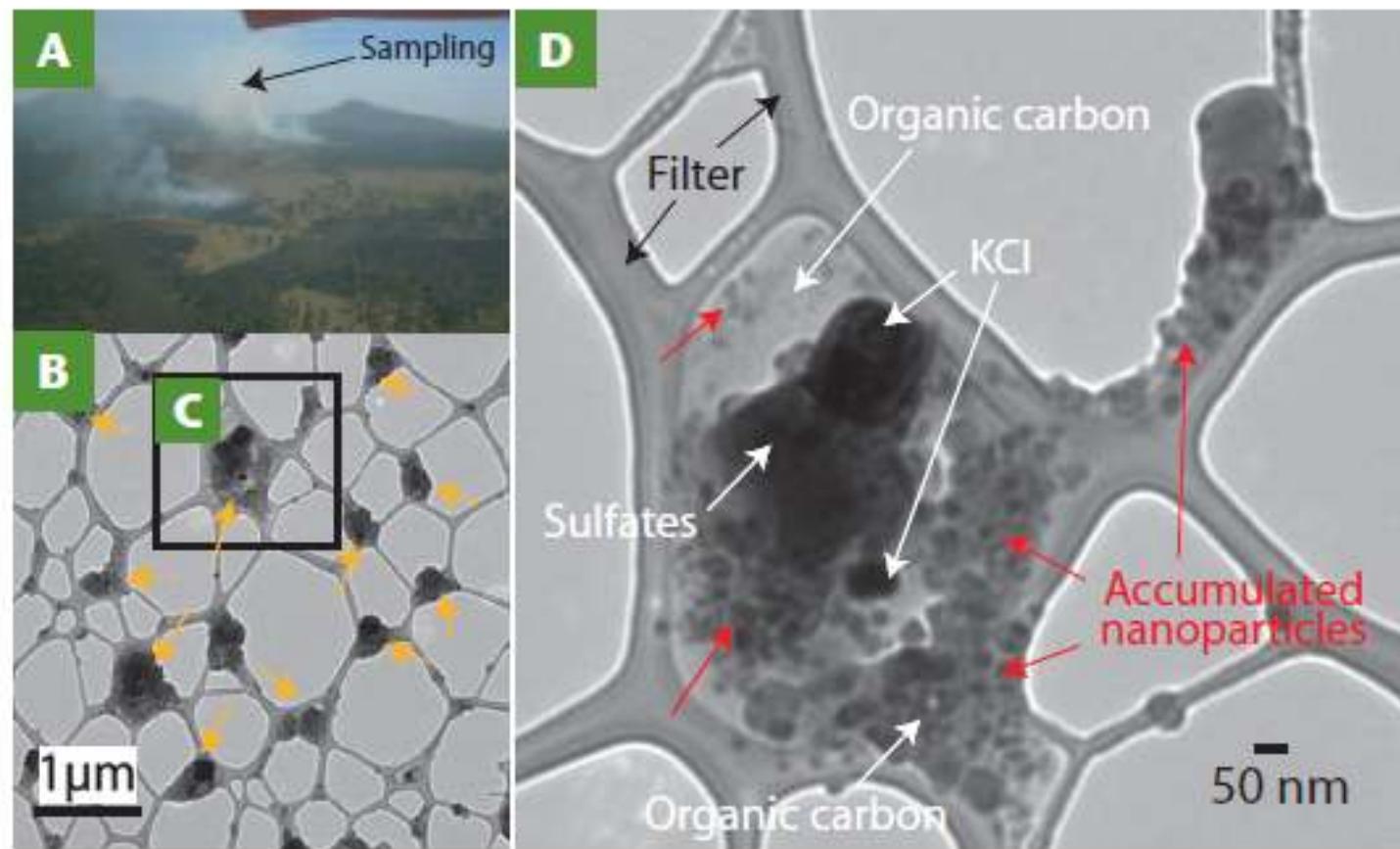
20KV

10  $\mu$ m WD33

# The problem of PM

## Biomass Combustion

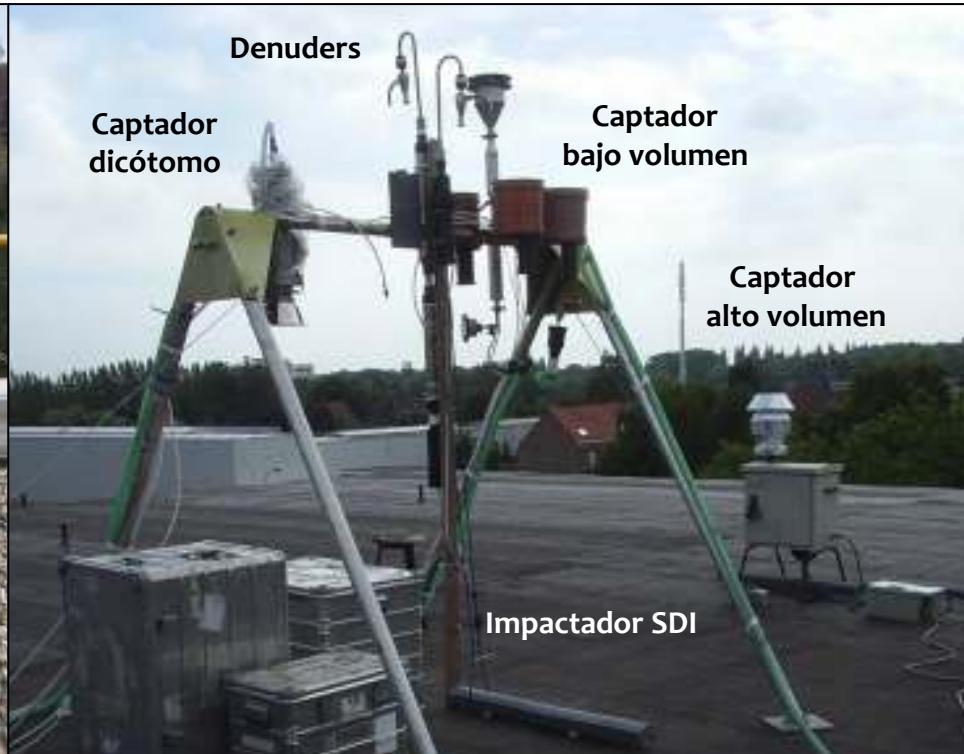
Buseck and Adachi. 2008. Elements. 4.



# Measurement methods for PM

# Characterisation of PM: Methods for measurements

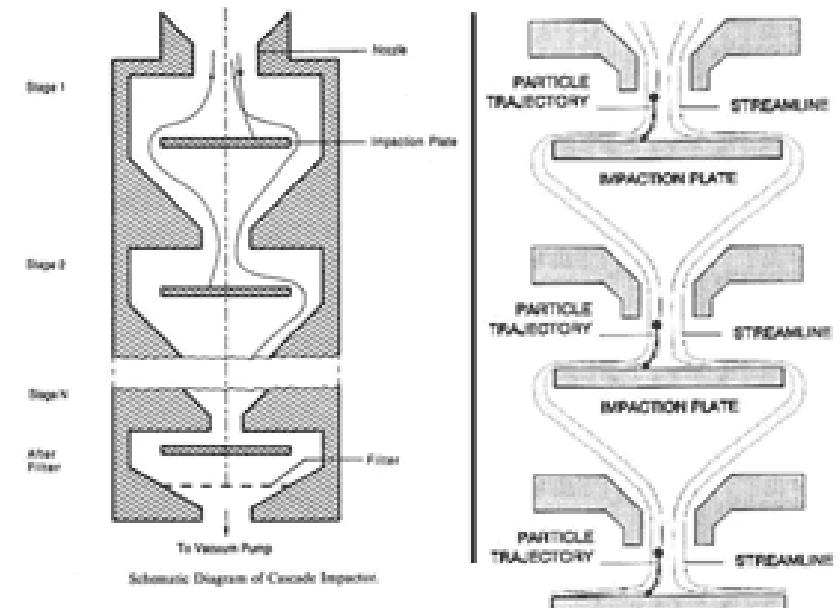
**Gravimetry:** Mass levels; EU standard; Speciation possible; Sampling artifacts



# Characterisation of PM: Methods for measurements

## Cascade impactor

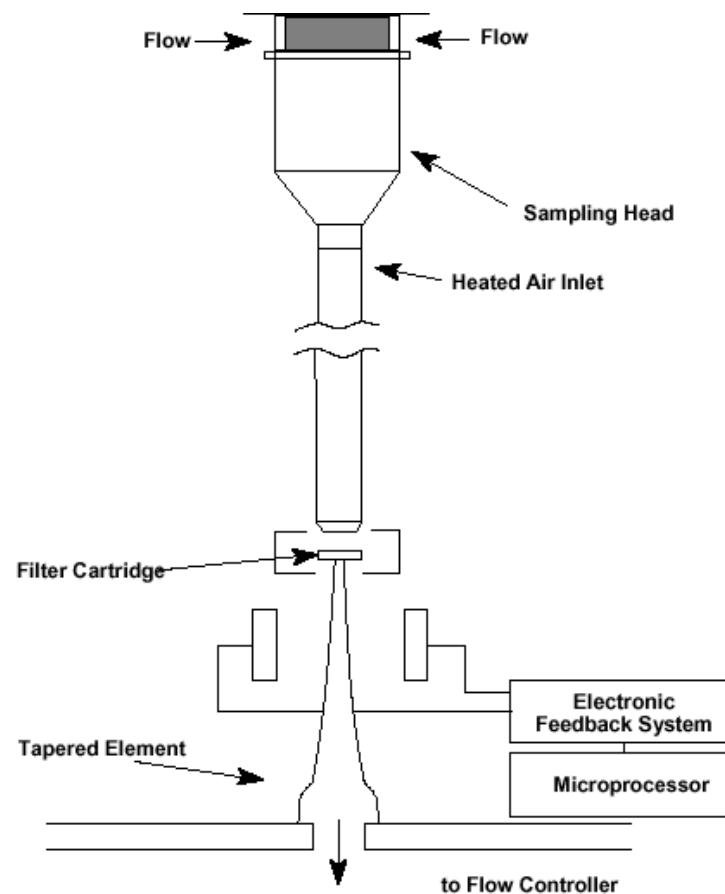
- Micro-orifice, Uniform-deposit Impactor (MOUDI)
- 30 L/min
- 0.056 – 18  $\mu\text{m}$
- Substrate requested



# Characterisation of PM: Methods for measurements

## REAL TIME: MASS

- TEOM (thermo oscillating micro-balance)

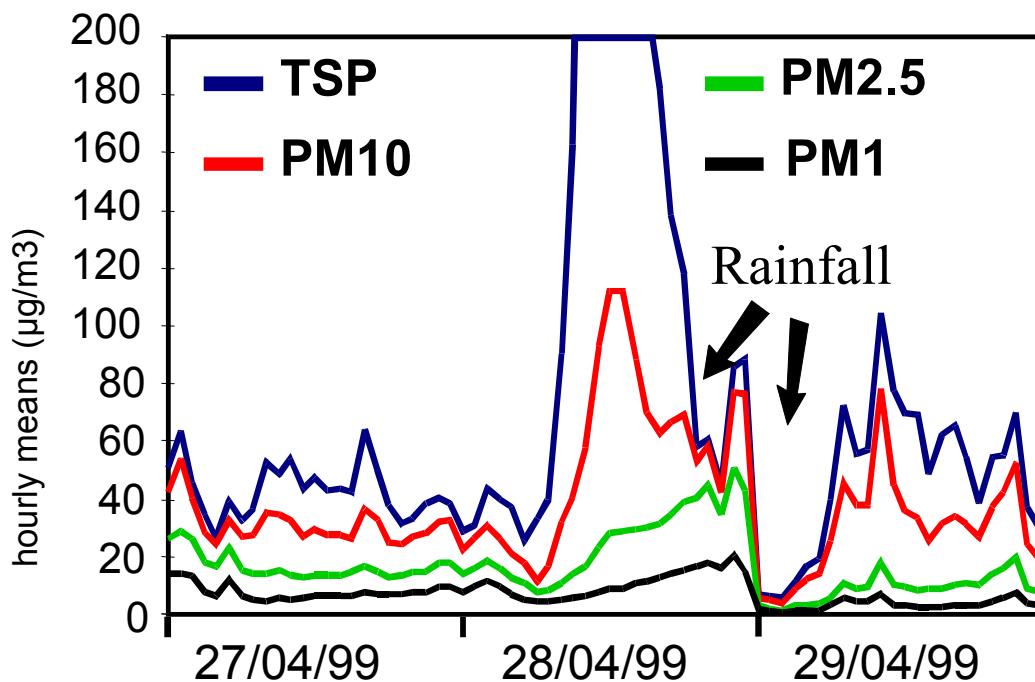


- Beta attenuation



# Characterisation of PM: Methods for measurements

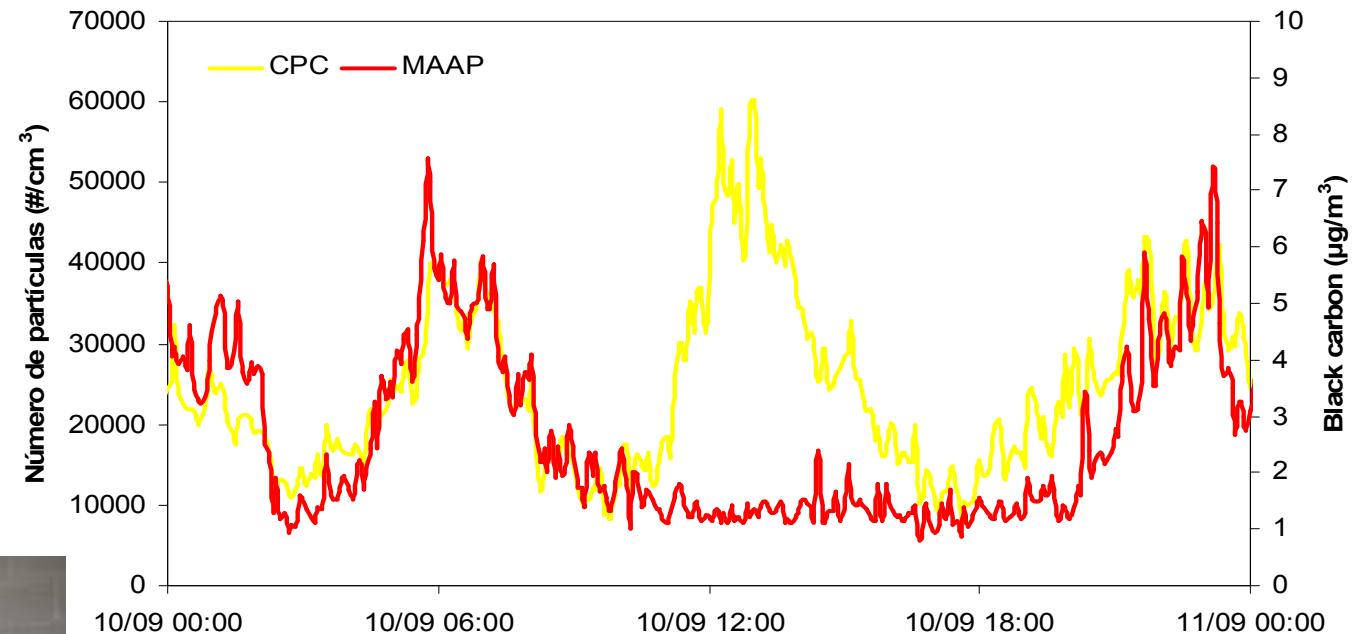
## OPTICAL COUNTERS



# Characterisation of PM: Methods for measurements

## Black carbon: MAAP: Multi Angle Absorption Photometer

Thermo Electron Corporation. Carusso/Model 5012 MAAP



Comparación medidas en tiempo real de Número de partículas y Black Carbon. Medidas experimentales realizadas en el IDAEA de Barcelona, CSIC. Noemí Pérez, tesis doctoral.

# Characterisation of PM: Methods for measurements

## Real time speciation

Soluble inorganics: **Aerosol ions & precursors**

URG 9000 IC



Taken from URG web site

MARGA



Taken from Applikon web site

PILS-IC

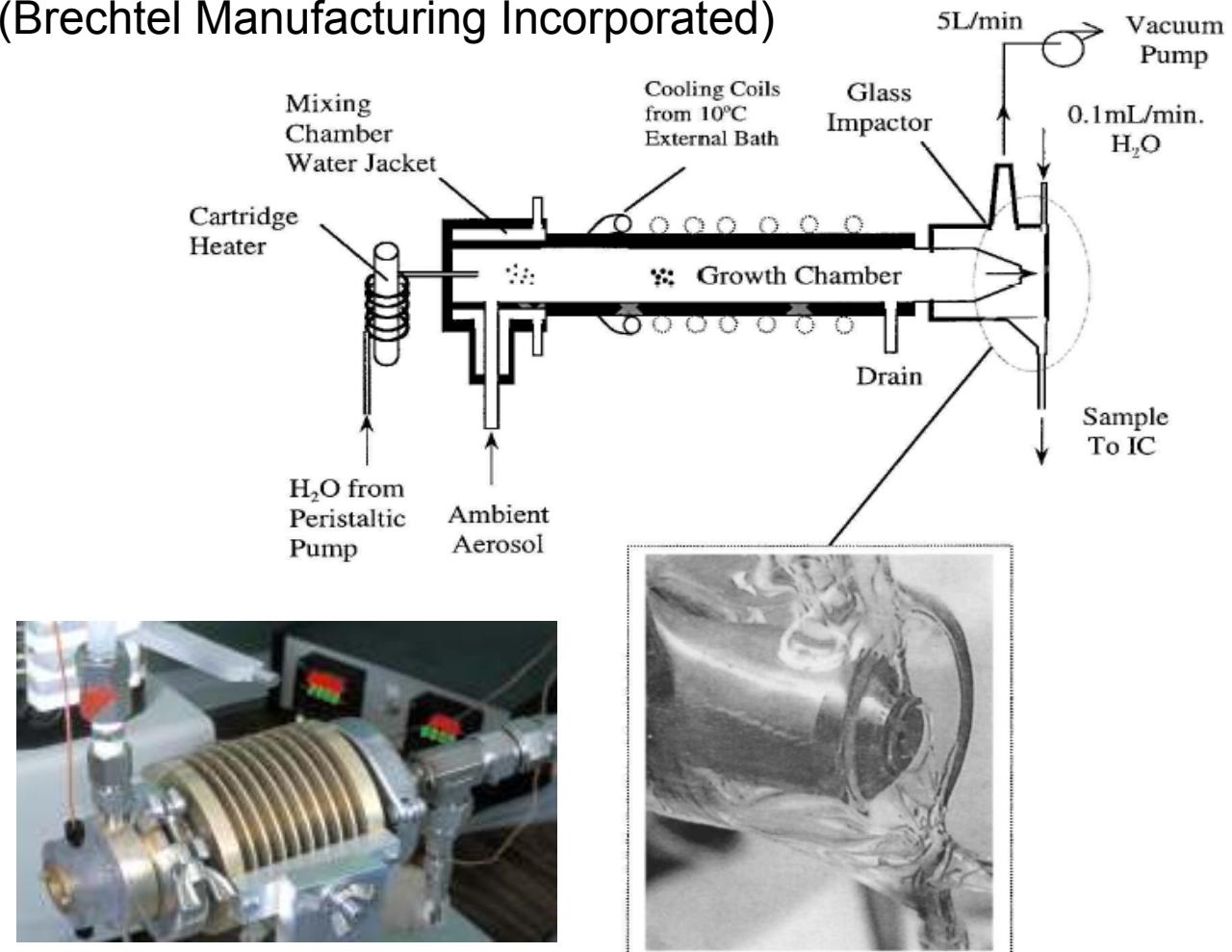


Taken from Metrohm web site

# Characterisation of PM: Methods for measurements

## Real time speciation

PILS: Particle-into-liquid sampler  
(Brechtel Manufacturing Incorporated)



Weber, R.J., D. Orsini, Y. Daun, Y.-N. Lee, P. Klotz, and F. Brechtel, A particle-into-liquid collector for rapid measurements of aerosol chemical composition, *Aerosol Sci. Tech.*, 35, 718-727, 2001

# Characterisation of PM: Methods for measurements

## Real time speciation

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



Nitrate, R&P 8400 N  
by  $\text{NO}_x$  analysis (chemiluminiscence)



Sulfate,  
Thermo 5020-SPA

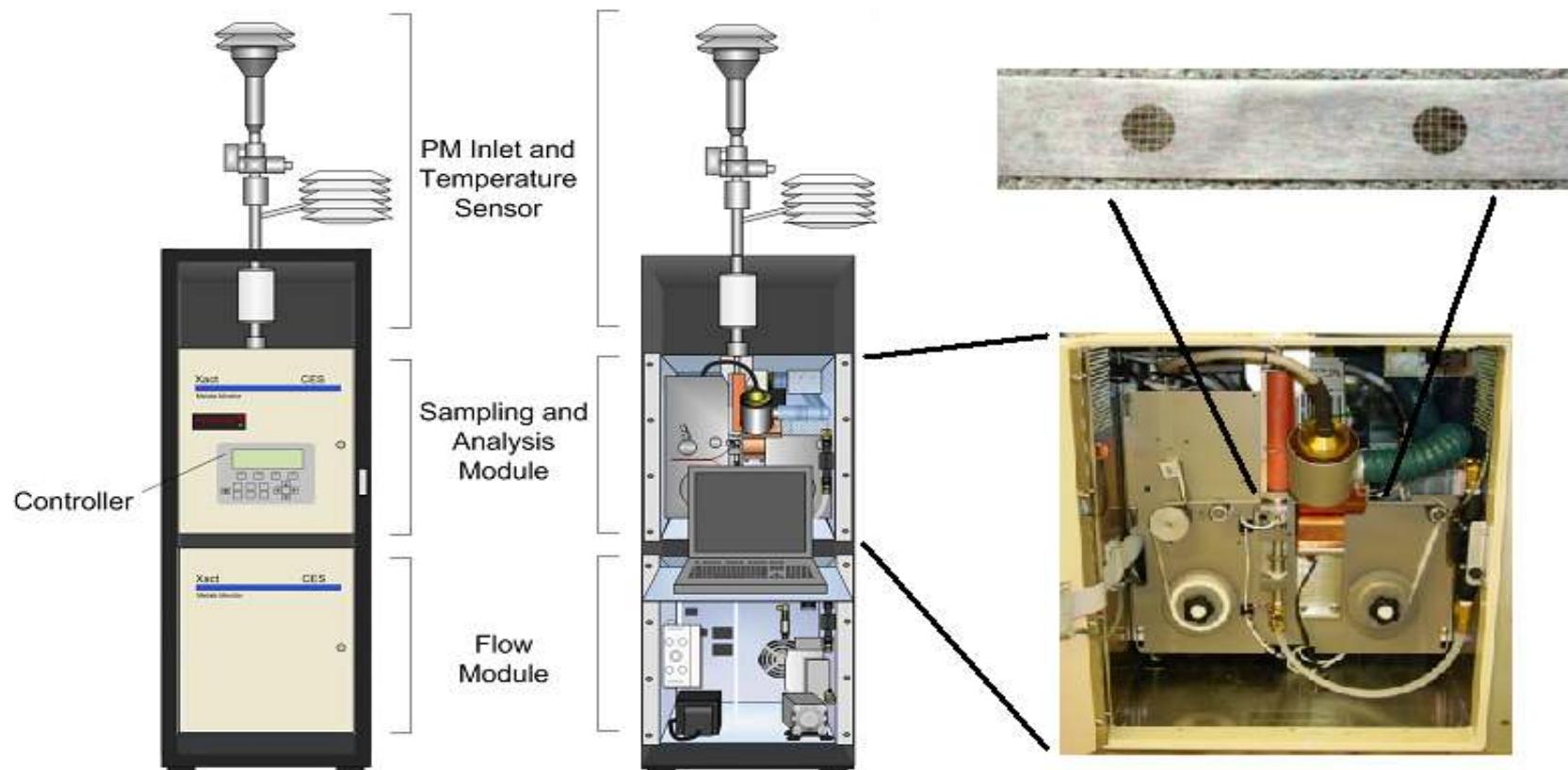


- OC and EC,
- R&P 5400 C, Sunset on-line analyzer

# Characterisation of PM: Methods for measurements

## Real time speciation

On-line XRF analyser: **Mostly metals**



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

# Characterisation of PM: Methods for measurements

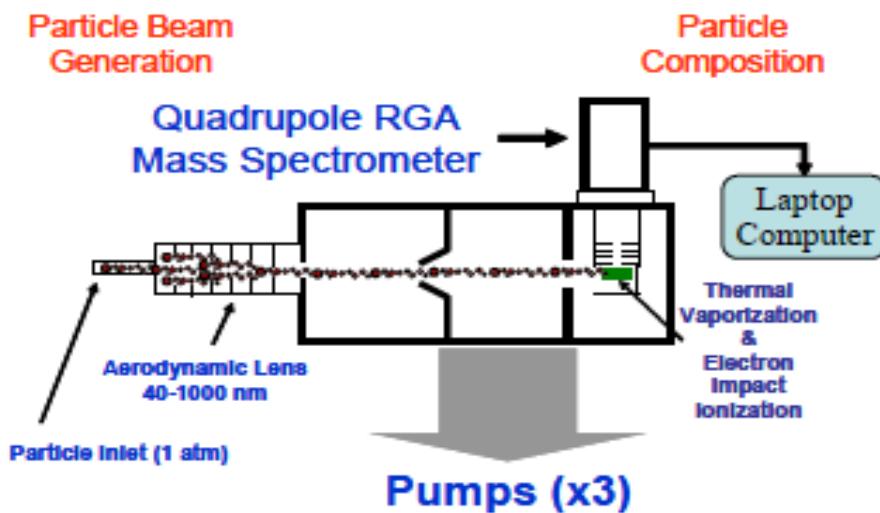
## Real time speciation

Mini-AMS: Non refractory fraction of PM1

### ACSM

Aerosol Chemical Speciation Monitor

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

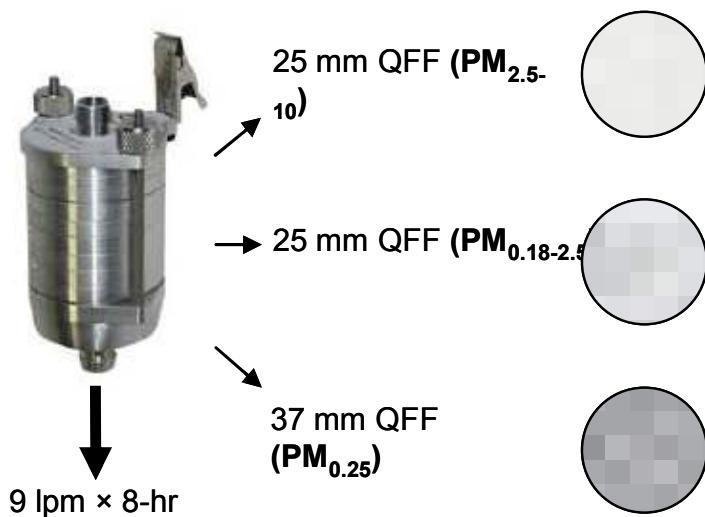


Taken from Aerodyne Research website

# Characterisation of PM: Methods for measurements

## Geochemistry of ultrafine particles

37 schools in Barcelona: exposure of schoolchildren to metals in UFPs



UFP geochemistry



Particle number



Black carbon

# **Conclusions**

# Conclusions

- Main air quality problem in urban environments: **NO<sub>2</sub>** and **PM**
- Current monitors are costly, large (size) and static
- **Future** monitoring networks will probably be based on the combination of **fixed monitoring sites** with **sensor networks**:

— — — — —

Thank you for your attention  
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representativeness (exposure)

- To this end, **sensors need to be**:
  - Low-cost
  - Portable
  - Small
  - Comparable to conventional instrumentation

**This is now YOUR job!**