The role of PIXE in the AIRUSE project "Testing and Development of air quality mitigation measures in Southern Europe"

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MEAN PM10 & PM2.5 LEVELS IN EUROPE

ESCAPE

Eeftens et al. (2012) Atmospheric Environment
PM10 daily limit value
2012

90.4 percentile of PM$_{10}$ concentration in 2012, based on daily average with percentage valid measurements $\geq 75$ % in $\mu$g/m$^3$

- $\leq 20$
- 20-40
- 40-50
- 50-75
- $> 75$

- No data
- Countries/regions not included in the data exchange process

European Environment Agency
19/11/2014
THE AIRUSE PROJECT AIMS

• Characterizing similarities & differences in PM sources & contributions across S-EU (5 cities)
• Once the main sources of PM10 and PM2.5 are identified, the strategic goal of the AIRUSE project is to develop, test and propose specific measures to abate urban ambient air PM in S.-EU, to meet AQ standards & to approach WHO guidelines.

Specific objectives

• Obtaining harmonized source contributions to PM for AIRUSE cities & to identify those responsible for exceedances of the PM limit values and WHO guidelines
• Develop, test and propose cost-effective air mitigation measures for South European countries
• Support adaptation of control strategies for reducing PM exposure in South Europe

Specific PM mitigation measures

• Street washing & dust suppressants for road dust and deposited African dust
• Biomass burning
• Industrial emissions (channelled and fugitive)
• Strategies from other European countries (LEZ, eco-efficient vehicles, labelling, shipping, biomass burning...)

## B2. HARMONIZED 2013 PM10 & PM2.5 SOURCE APPORTIONMENT

### Long term measurements

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*Intercomparison between PIKE and ICP on Teflon filters
*Intercomparison between Teflon (PIKE) and quartz (ICP) filters
*Intercomparison between PIKE and XRF on Teflon and MCE filters

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### Maps

- Barcelona
- Athens
- Porto
- Florence
- Milan
Sampling

BARCELONA

1 year sampling
daily time resolution
  (1 day every 3*)
- PM10 e PM2.5
- quartz and teflon

Shorter samplings
1 hour time resolution
- ~ 2 weeks in winter and summer
  - fine and coarse

ATHENS

PORTO

FLORENCE

* All the days if saharan intrusions foreseen (Hysplit, Skiron)
Analysis

DAILY SAMPLES
- PM2.5 and PM10 concentrations (gravimetric analysis)
- Ionic composition (IC)
- EC-OC (thermo-optical methods)
- Major and minor elements (PIXE, ICP-MS, ICP-AES, AAS)
- Levoglucosan (Milan), organic compounds and carbonates on a reduced number of samples

HOURLY SAMPLES
- Elements Z>10 (streaker sampler + PIXE)

STATISTICAL ANALYSIS FOR SOURCE APPORTIONMENT
(PMF, Positive Matrix Factorization) on daily and hourly data
### B2. HARMONIZED 2013 PM10 & PM2.5 SOURCE APPORTIONMENT

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*Intercomparison between PIXE and ICP on Teflon filters
*Intercomparison between Teflon (PIXE) and quartz (ICP) filters
*Intercomparison between PIXE and XRF on Teflon and MCE filters
B2. HARMONIZATION & OBTENTION OF 2013 PM10 & PM2.5 SOURCE APPORTIONMENT

- **BCN UB**
  - Primary: 35%
  - Secondary: 65%

- **H UB**
  - Primary: 30%
  - Secondary: 70%

- **MLN UB**
  - Primary: 32%
  - Secondary: 68%

- **AIE SUB**
  - Primary: 18%
  - Secondary: 82%

- **POR TR**
  - Primary: 62%
  - Secondary: 38%

- **AIV TR**
  - Primary: 34%
  - Secondary: 66%

Legend:
- Secondary organics
- Secondary inorganics
- Primary OM + EC
- Primary: Mineral dust
- Primary: Sea salt

**PM2.5**
PMF results: Florence

**FI-UB PM10**
- Unaccounted: 0.2; 1%
- Vehicle exhaust: 2.5; 13%
- Vehicle non-exhaust: 1.5; 10%
- Secondary nitrate: 2.2; 11%
- Secondary sulphate and organics: 3.9; 20%
- Heavy oil combustion: 0.9; 5%
- Local dust: 2.3; 12%
- Saharan dust: 0.7; 4%
- Fresh sea salt: 0.8; 4%

**FI-UB PM2.5**
- Unaccounted: 0.7; 5%
- Vehicle exhaust: 2.5; 13%
- Vehicle non-exhaust: 0.4; 2%
- Secondary nitrate: 1.9; 14%
- Secondary sulphate and organics: 4.0; 29%
- Heavy oil combustion: 0.8; 6%
- Local dust: 0.3; 2%
- Saharan dust: 0.2; 1%
- Fresh sea salt: 0.1; 1%

**FI PM10 >50 μg/m³**
- Traffic: 31.1; 43%
- Biomass burning: 22.2; 30%
- Local dust: 1.8; 2%
- Heavy oil combustion: 1.9; 3%
- Secondary nitrate: 4.9; 7%
- Secondary sulphate & organics: 6.4; 9%
- Unaccounted: 0.2; 0%
- Fresh sea salt: 0.4; 0%

**FI PM2.5 (PM10 >50 μg/m³)**
- Traffic: 22.5; 32%
- Biomass burning: 22.5; 33%
- Local dust: 0.1; 0%
- Heavy oil combustion: 1.9; 3%
- Secondary nitrate: 4.2; 6%
- Secondary sulphate & organics: 4.2; 6%
- Unaccounted: 13.8; 20%
- Fresh sea salt: 0.3; 0%
- Saharan dust: 0.0; 0%
PMF results: Barcelona

BA PM10 >40 μg/m³

BA PM2.5 (PM10 >40 μg/m³)
PMF results: Athens

AT PM10 >50 μg/m³

AT PM2.5 (PM10 >50 μg/m³)
PMF results: Porto

PO PM10 >50 \( \mu g/m^3 \)

PO PM2.5 (PM10 >50 \( \mu g/m^3 \))
Quality Assurance
Quality Assurance

ICP = 0.99 * PIXE
$r^2 = 0.82$

Pb (PIXE)

Pb (ICP-AES)

Ni (PIXE)

Ni (ICP-AES)
SOIL
Si concentrations

Florence

PM10
PM2.5

Athens

PM10
PM2.5

Porto

PM10
PM2.5

Barcelona

1.35 Na + 1.66 Mg + 1.89 Al + 2.14 Si + 1.40 Ca + 1.43 Fe + 1.67 Ti + 1.21 K

- K and Fe corrected for anthropogenic contributions by EF calculations
- Na and Mg corrected for sea-salt contributions
**Soil dust**

- **Florence**
  - PM10: 2.2 (12%)
  - PM2.5: 0.5 (4%)
  - Ratio: 0.23
  - All the days with exceedances were dust events!

- **Athens**
  - PM10: 4.3 (20%)
  - PM2.5: 1.1 (9%)
  - Ratio: 0.26
  - All the days with exceedances were dust events!

- **Porto**
  - PM10: 4.0 (11%)
  - PM2.5: 2.1 (8%)
  - Ratio: 0.52
It is important both to identify the Saharan days and to assess the ground level contribution of this natural source.

The maximum allowed number of exceedances of the 50 µg/m³ daily limit value (DLV) is 35/year. However, if an exceedance can be attributed to a natural event it can be discounted by the State Members of the European Union after scientific validation.

As a consequence, in case of DLV exceedance the estimate of African dust contribution to PM10 concentration has become a primary task for both scientists and policy makers.

A EU directive suggest to calculate the net contribution of African dust to PM10 on a daily basis, by subtracting the PM10 regional background (RB) level from the PM10 concentration values measured in rural background sites only on dust-days.

The net contribution from African dust can be obtained by the subtraction of an estimated dust background (monthly moving average excluding Saharan days) from the soil dust concentration obtained by PIXE data.
Elemental ratios (Florence)
STREAKER
STREAKER CMA
K concentrations

Florence

Saharan dust

WB for domestic heating

Athens

Porto

Wildfires and Saharan dust

Barcelona
Zn-Pb (PM2.5)

Zn

Pb

ng/m³

ng/m³

ATENE  
PORTO  
FIRENZE  
"BARCELONA"


Winter 2013 (3 weeks): **FLORENCE**: 21/01 - 12/02/2013  
**PORTO**: 25/01 - 1/02 + 19/02 - 4/03

- EPA PMF 3.0, input data prepared using the Polissar approach
- solutions from 5 to 10 factors (and different rotations) explored; Q values, scaled res., F and G matrices examined to find the most reasonable solution

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Biomass burning

**FLORENCE**

- K_F
- Biomass burn. (PMF)

**PORTO**

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**Graphs:**

- Time series graphs showing variations in concentration over time for K, K_F, and Biomass burn. (PMF) in FLORENCE and PORTO.
Traffic source
Soil dust source

FLORENCE

PORTO
Marine sources

FLORENCE

PORTO
Industrial source (Porto)
Conclusions

- AIRUSE sampling campaign concluded

- Preliminary analysis of elemental PIXE data shows many interesting results; in particular, hourly time resolution data allows us to follow in detail the time evolution of PM sources

- These data should be integrated by results obtained by the other analytical techniques…

WORK IN PROGRESS!
Thank you for your attention !!!

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calzolai@fi.infn.it