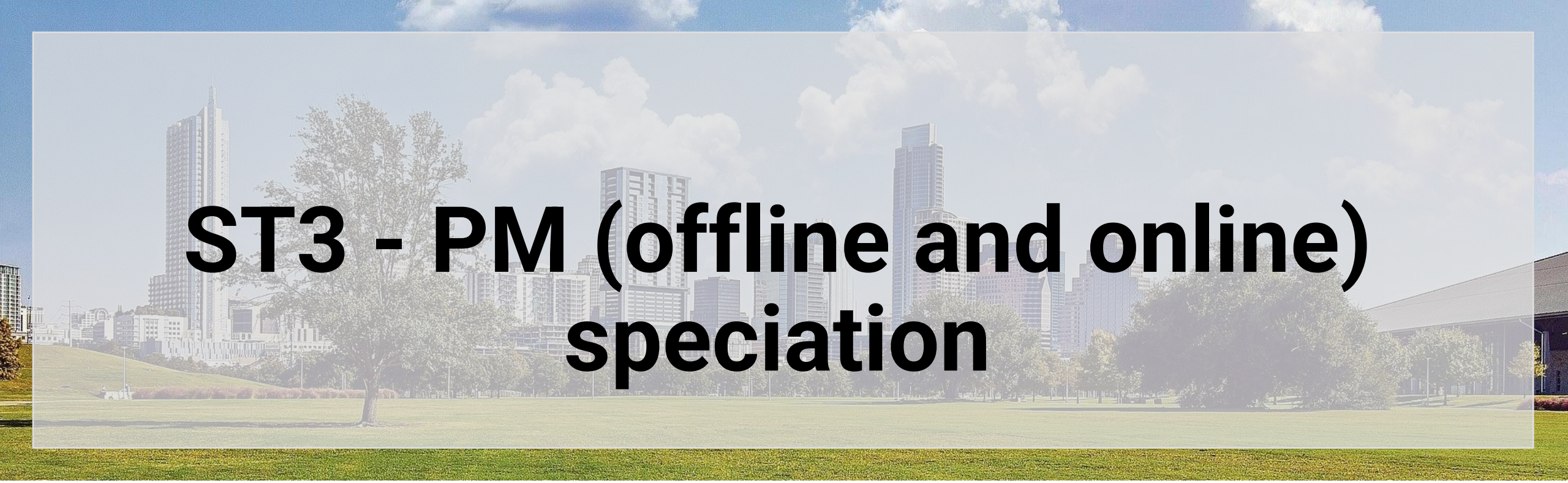

ST3 - PM (offline and online) speciation

Andres Alastuey & Benjamin Chazeau CSIC / PSI-AMU

RI-URBANS (101036245)
RI-URBANS Science meeting, 08-09 September 2025

ST for PM (offline and online) speciation

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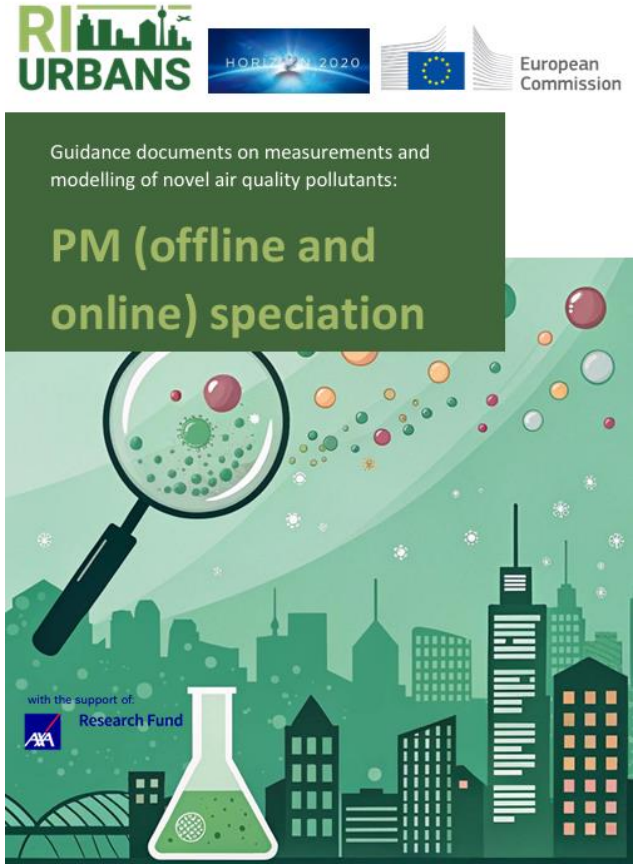

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ST for PM (offline and online) speciation

- This document **summarizes the guidance for speciation of atmospheric particulate matter (PM)** elaborated in the RI-URBANS. This guidance is based on linking the atmospheric observation and analyses expertise from ACTRIS, AQMNs and RI-URBANS.
- This guidance document includes:
  - offline PM speciation, carried out by sampling (generally 24 h) and offline analyses in laboratories,
  - online PM speciation with < 1 h resolution by using modern instrumentation

ST for PM offline speciation: recommendations on measurements (1/3)

- The new EU AQ Directive (NAQD) requires or recommends the analysis of specific PM_{10} and $PM_{2.5}$ components: As, Cd, Ni, Pb, PAHs, levoglucosan, EC/OC, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, K^+, Mg^{2+} & Na^+
- Aim: to "**assess the possible contribution from long-range transport of pollutants, support source apportionment analysis and for the understanding of specific pollutants such as particulate matter**"
- Important to use standardised measurement techniques and common criteria for the assessment of ambient air quality. Specific sampling and analytical reference protocols are available:
  - EN 14902:2005: measurement **of Pb, Cd, As and Ni in the PM_{10}** fraction of suspended particulate.
  - EN15549:2008: measurement of **benzo(a)pyrene** concentrations in ambient air **PM_{10}**
  - EN 16913:2017: measurement of **NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in $PM_{2.5}$** filters
  - EN 16909:2017: measurement of elemental carbon (**EC**) and organic carbon (**OC**) in **$PM_{2.5}$** filters.

ST for PM offline speciation: recommendations on measurements (2/3)

- Amato et al. (2024): SA studies require the analysis of tracers of specific sources: EC-OC, major ions, major trace elements (including tracers of dust and different industrial, traffic and combustion sources, such as **Al, Ca, Fe,** Ni, **V, Sb, Sn, Zn**, among others), and biomass burning tracers (e.g., PAHs, sugars, etc). For specific sources also recommended to measure **MSA, oxalate, and sugars alcohols**, among others.
- Analysis of additional PM components (not considered in the NAQD) might be required for an advanced air quality assessment: SA for cost-effective action plans, epidemiological and toxicological analyses to identify the most harmful PM components and sources…
- NAQD provided standards do not cover all the PM components of interest for an adequate source apportionment (SA) analysis.

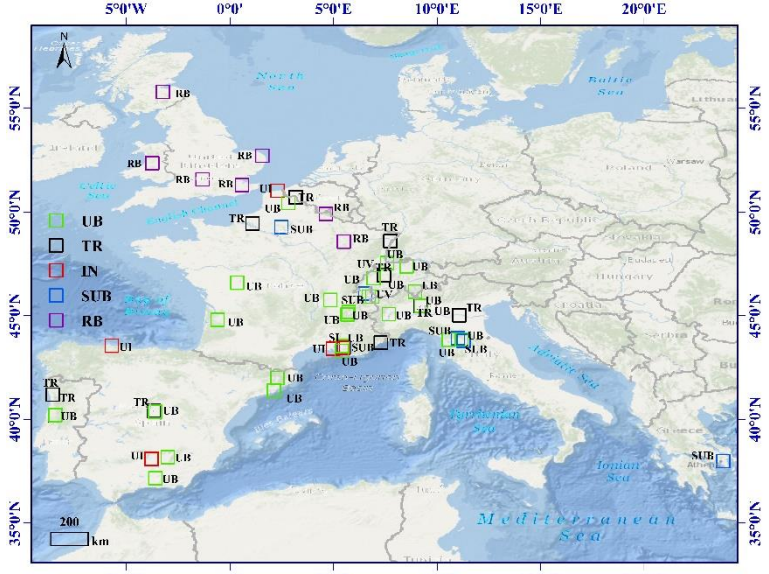
ST for PM offline speciation: recommendations on measurements (3/3)

- **Major and trace elements** in PM: not considered in the NAQD; no standards for all elements. Different methods / techniques:
  - XRF: relatively high LODs and LOQs for tracers of interest for SA (As, Cd, Sb, Se, Sn, among others)
  - PIXE: lower LODs than XRF, but requires more complex instrumentation (expensive and difficult to use)
  - ICP-MS and ICP-OES: requires acid digestion, time consuming and expensive; very good LODs for >50 elements
  - Acid digestion: EN14902 (2005) does not allow complete digestion of silicon-containing compounds and specific oxides (tracers of specific sources such as non-vehicle exhaust, road dust, desert dust, etc.). It is recommended to perform a complete acid digestion using HF:HNO_3:$HClO_4$
- **Organic compounds** in PM: standardized methodology only for PAHs (EN15549:2008 for benzo[a]pyrene). ST3 reviews existing methodologies, and proposes strategies for organic markers, including POA (polycyclic aromatic hydrocarbons, anhydro-monosaccharides, and saccharides) and SOA markers

ST for PM offline speciation: main findings (1/2)

- **Limited number of sites, and mostly from Southern Europe**: There is a lack of PM chemical composition data in central and northern Europe. This hampers the study of the spatial and temporal variability of PM levels and sources.
- **Lack of harmonization**: There is a significant lack of harmonization in measurement techniques and data reporting among the different countries and sites, which could influence the comparability and consistency of the data.
- Data availability: The **data is not openly accessible**, posing challenges for further independent analysis and validation by the wider scientific community.

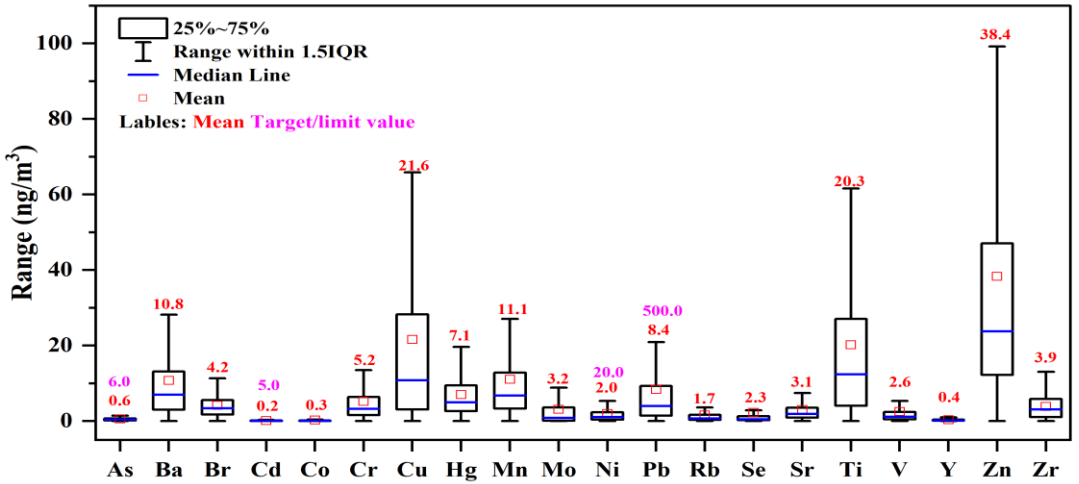
- 55 sites; 2013 to 2022, with series of data for each site covering a minimum of one year: France (24 sites), Italy (9), Spain (8), Switzerland (5), UK (5), Portugal (3), Greece (1) / 26 UB; 10 TR; 5 IND; 7 SUB; 7 RB



P1.8. Liu, X. et al., 2024a. PM10-bound trace elements in pan-European urban atmosphere. Environ. Res., 119630, https://doi.org/10.1016/j.envres.2024.119630:

ST for PM offline speciation: main findings (2/2)

- Substantial spatial heterogeneity in trace elements (TE) concentrations across Europe.
- The annual concentrations of the sum of the TEs in PM10 range 17-281 ng/m^3: diverse pollution scenarios.
- Traffic (TR) and industrial (IN) sites exhibited the highest TE concentrations, averaging 136±149 ng/m3.
- Specific relationships among TEs, highlight tthe influence of traffic, industrial activities, and natural factors.



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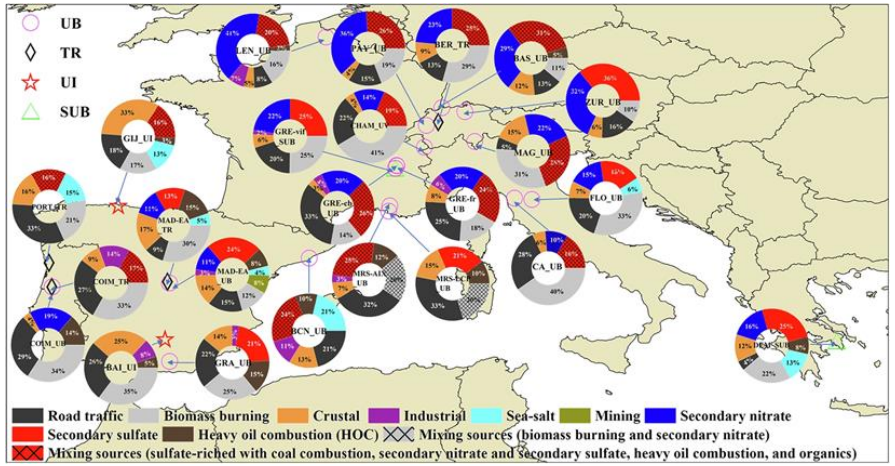


P1.47 Liu, X., et al., 2025c. Npj Climate and Atmospheric Science 2025 8:1, 8(1), 1–14. https://doi.org/10.1038/s41612-025-01097-

Online PM speciation

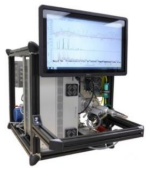
Instrumentation for online PM speciation with < 1 h resolution can be of high interest to yield information to assess short-term policy decisions, i.e., during pollution episodes.

In the ST3, the two most commonly used instruments were focused : **ACSM** and **Xact 625i**

Aerosol Chemical Speciation Monitors (Q and ToF ACSM) → Widely deployed instrument (worldwide) for NRT measurement of non-refractory **PM_1** (or **$PM_{2.5}$**) components (**OA**, **SO_4^{2-}**, **NO_3^-**, **NH_4^+** **and** **Cl^-**)

Xact 625i Ambient Metals Monitor → main commercially available instrument providing continuous, near-real-time **metals and trace elements** concentrations

Online PM speciation – QA/QC

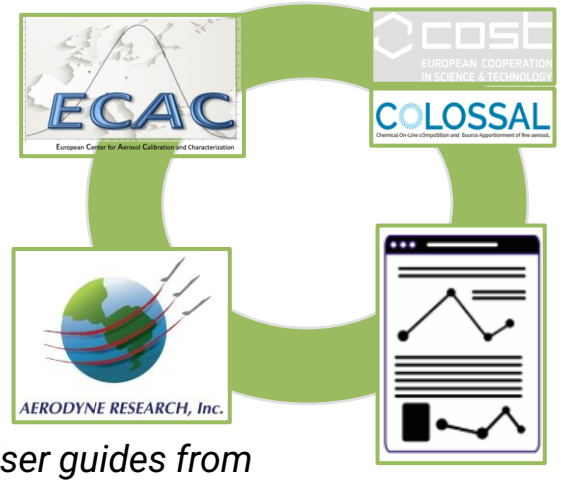


No CEN standards, but:

- ST3 on NR-PM1 speciation provided detailed guidance for method of measurements and quality control based on :

*Recommendations for operation and data processing from **ACTRIS-ECAC***

*SOP documents produced during the **COST-COLOSSAL** Action*



*User guides from **Aerodyne***

***Publications** (intercomparison, overview..)*

- Guidance in ST3 from the European WG **“ROXI” (“Real-time Online XRF Instruments”) :** supported by Sailbri Cooper and part of ACTRIS network

→ cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY →

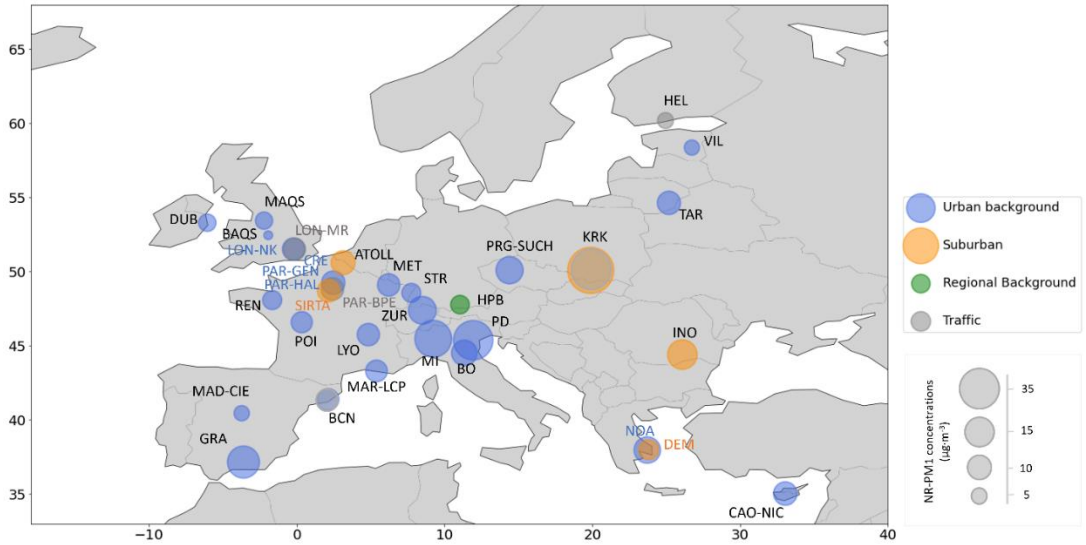
***Submission of a COST-Action project**: gathering an extended online XRF network*

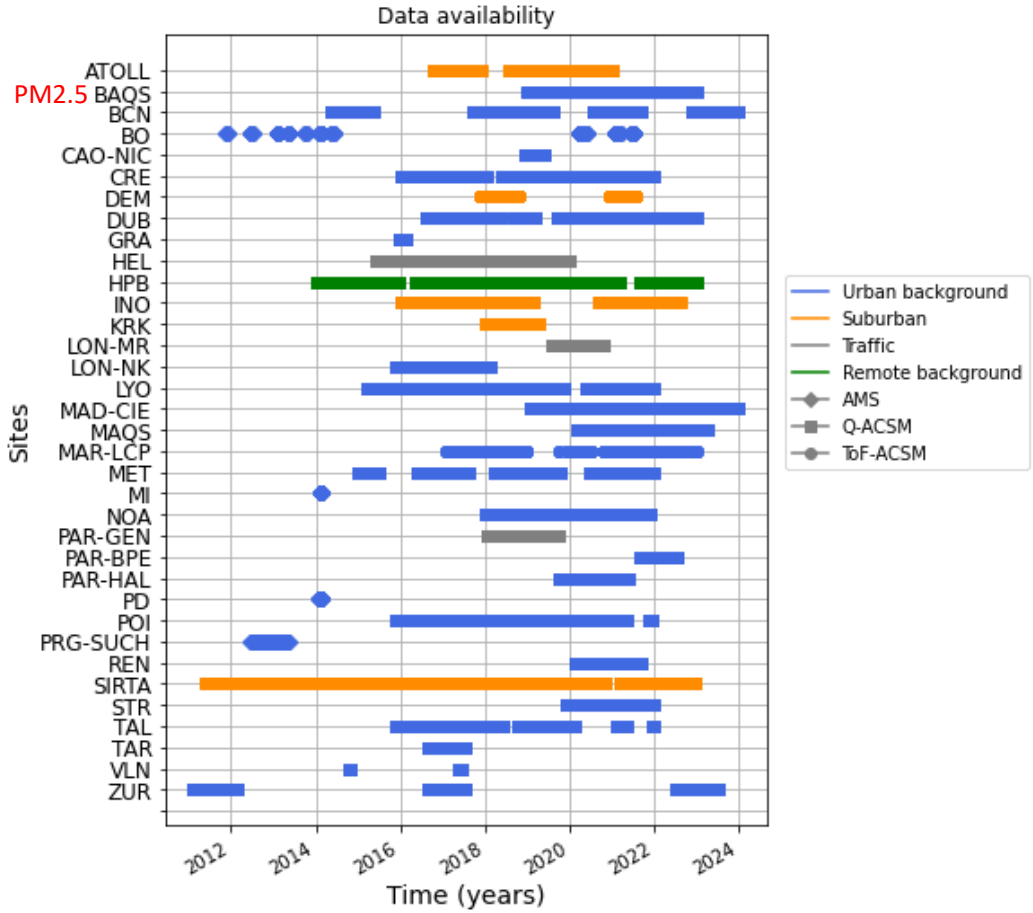
Designing future SOP and recommendations

Online PM speciation – Pan-European Overview of NR-PM1 compounds

Compiled Q-ACSM, ToF-ACSM, AMS data from 35 sites in Europe :

- 26 urban background sites, 5 suburban, 3 traffic, 1 regional background
- Mostly long-term data (>1 yr), some are short campaigns





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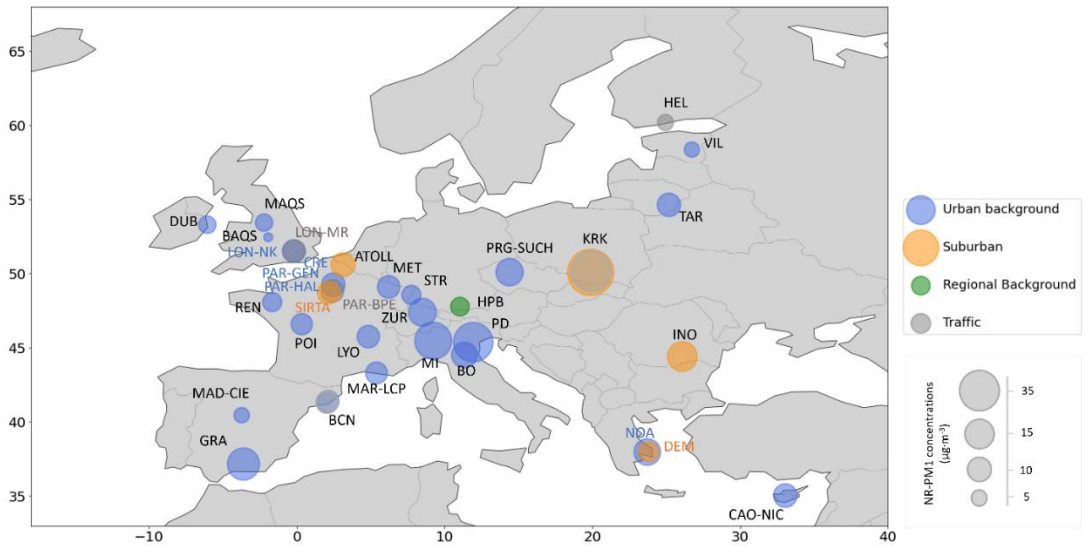
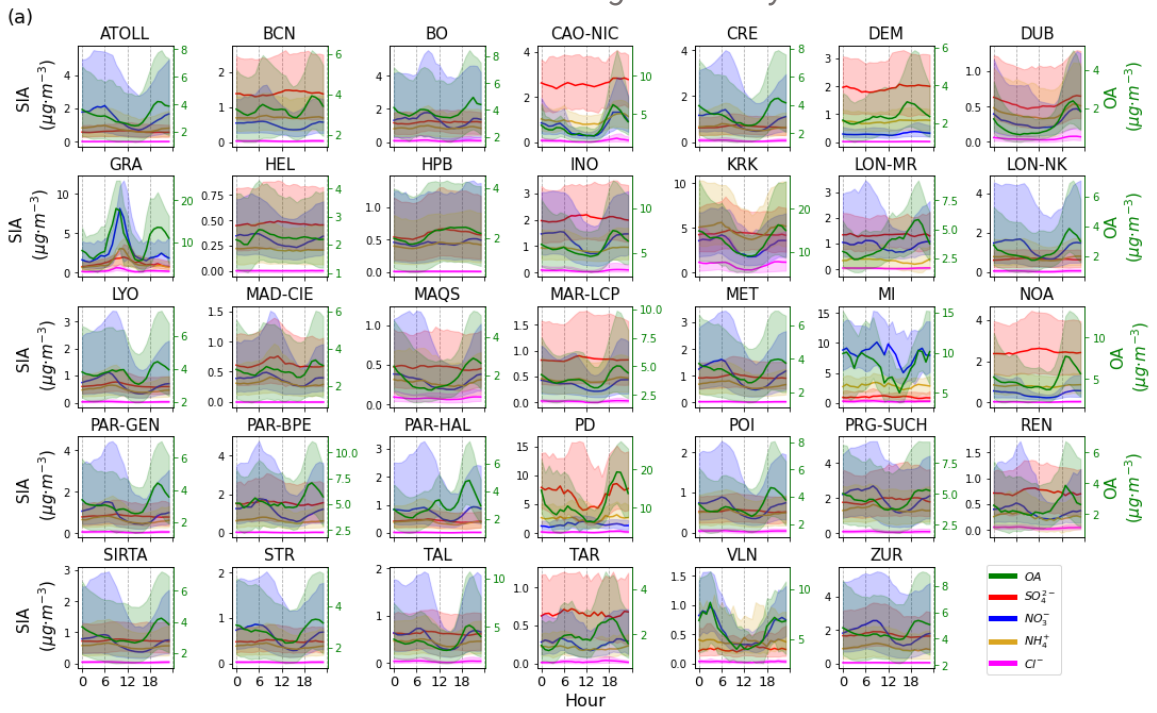
Online PM speciation – Pan-European Overview of NR-PM1 compounds

- **Very spatially heterogenous** NR-PM1 mass concentration at urban, suburban or traffic sites → more sensitive to site specific **meteorological conditions** and **emission patterns**



NR-PM1 average diurnal cycles



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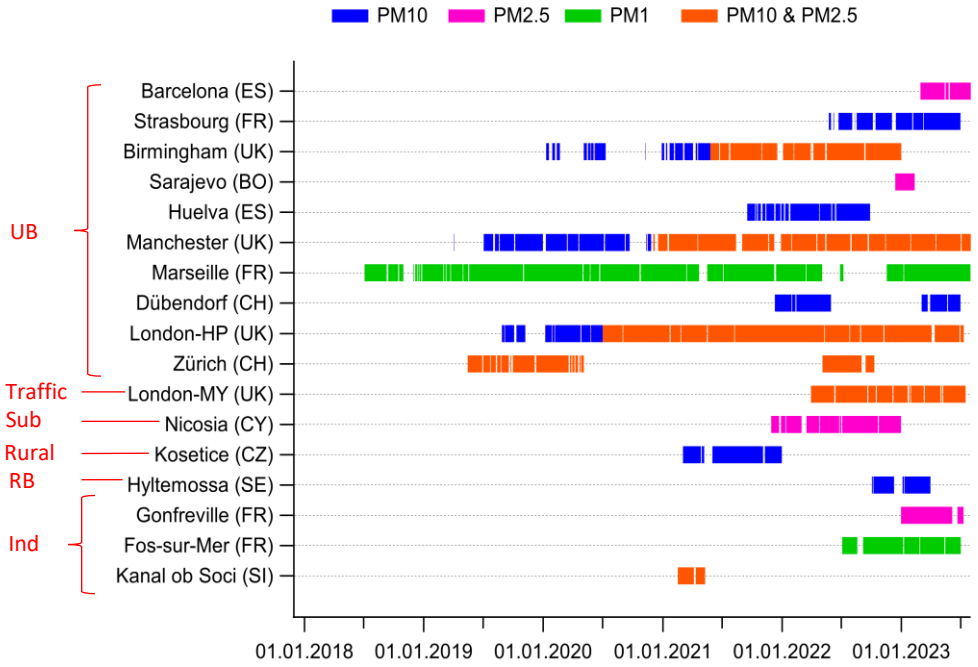
Online PM speciation – Pan-European Overview of elements

23 datasets from 17 sites in Europe :

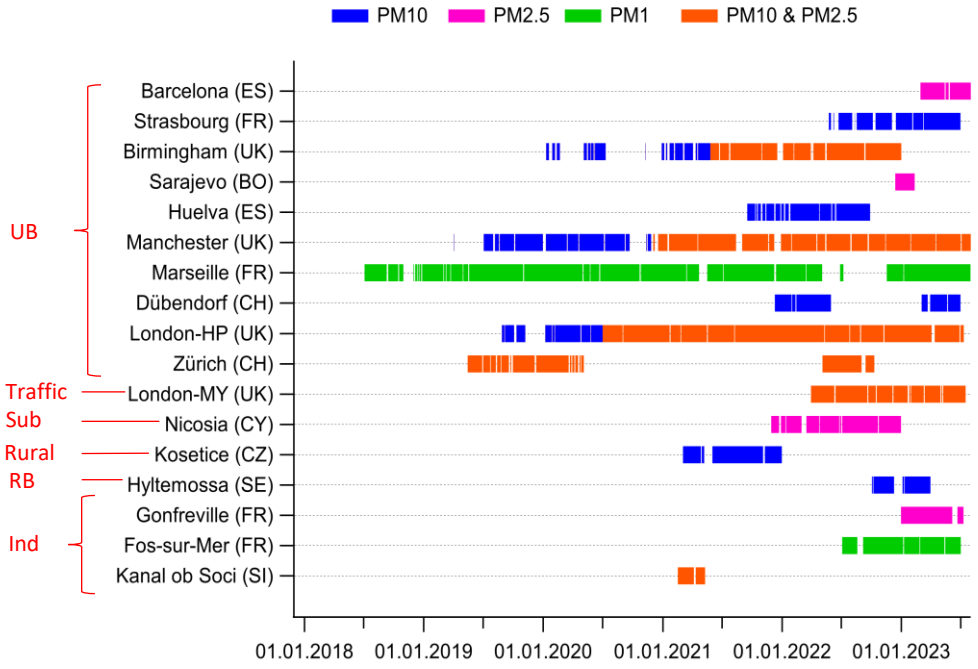
- 10 UB sites, 1 SUB, 1 TR, 3 IND, 1 RUR and 1 RB
- From some months to multi-years of data



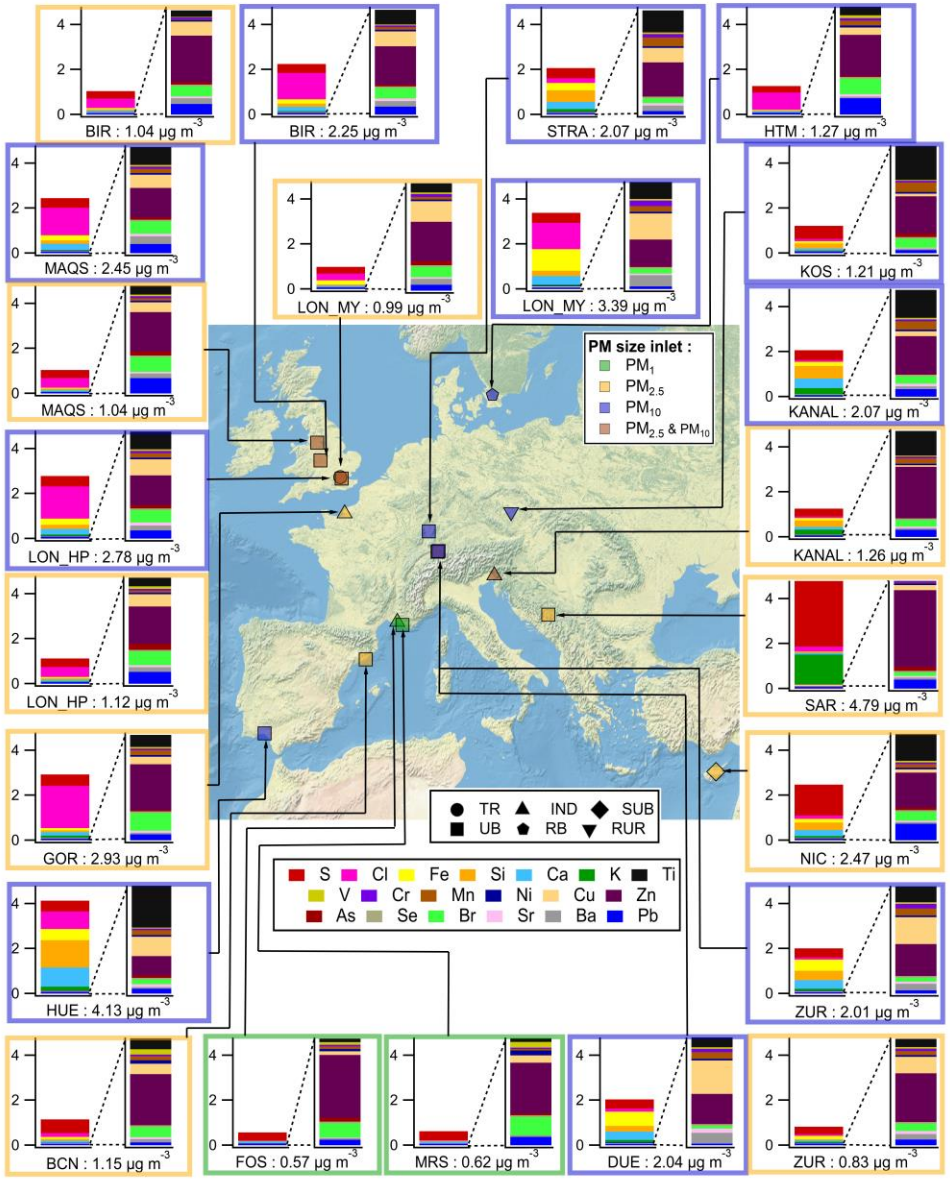
Online PM speciation – Pan-European Overview of elements

23 datasets from 17 sites in Europe :

Phenomenology of elemental composition of PM10, PM2.5 and PM10 accross Europe: size fractions, EFs, seasonal and diurnal cycles



→ *Chazeau et al., in prep (2025)*



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Online PM speciation – Recommendations

NR-PM1 compounds:

- Need to increase the number of urban sites in Europe performing online NR-PM1 measurements (only 28 for time series >1 year)
- The QA/QC procedures are not guaranteed for all sites → requirement of comparisons to collocated measurements and participation to ACTRIS intercomparisons.

PM elemental compositon:

- More users feedbacks needed for SOP development (COST-Action) and improving data management

Thank you very much for your attention!!!