Source Apportionment Techniques For PM

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RI-URBANS (101036245)

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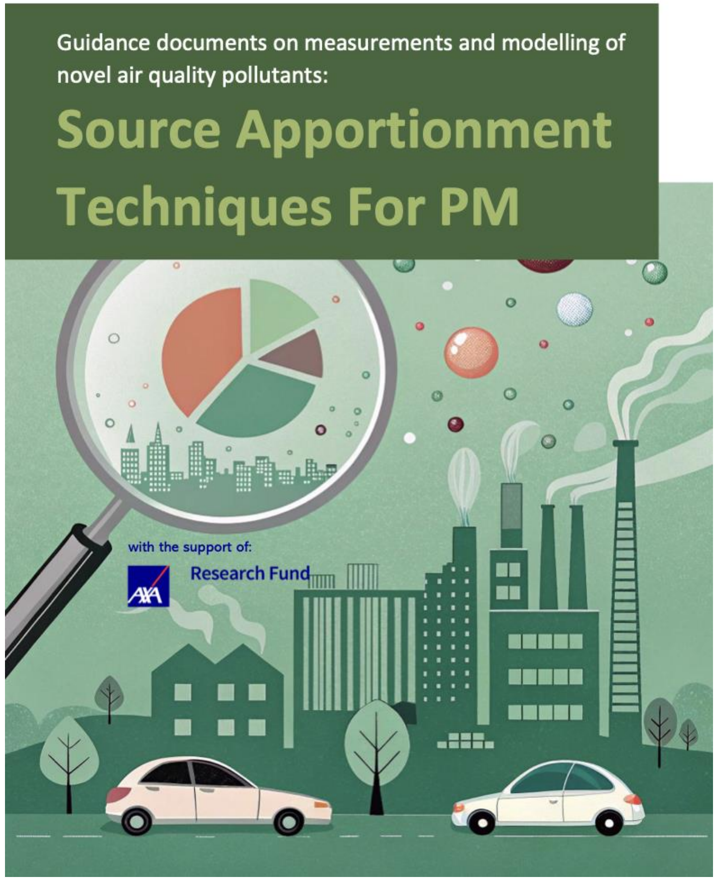
Outline

Offline SA on:

- Daily PM chemistry
- High time resolution elements
- High time resolution organic aerosol
- Combined datasets



Guidance documents on measurements and modelling of novel air quality pollutants:

Source Apportionment Techniques For PM

with the support of:

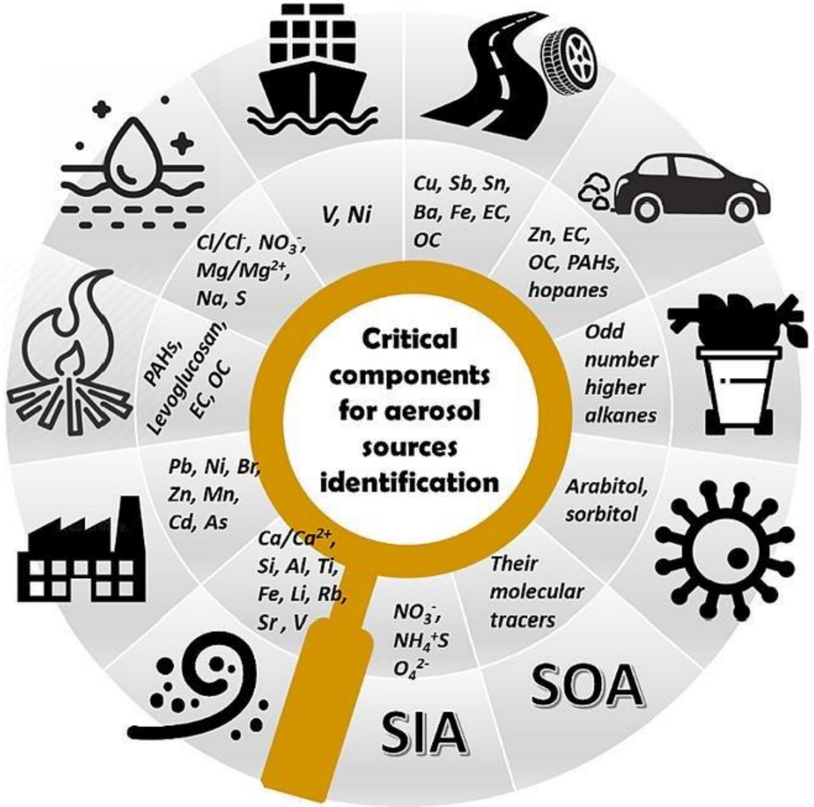
Research Fund

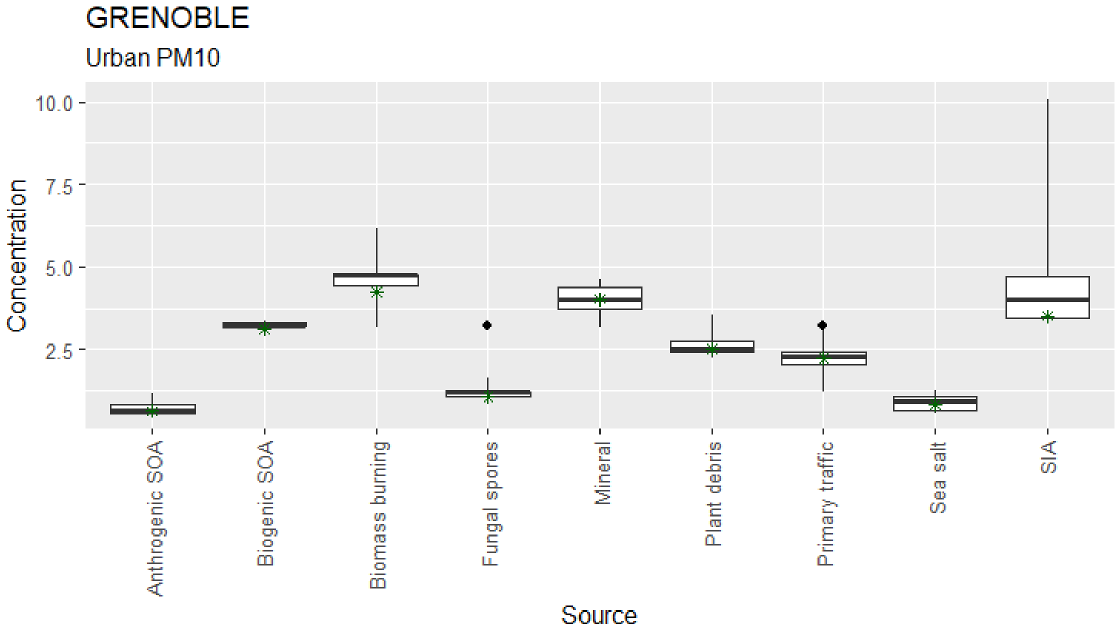
https://riurbans.eu/wp-content/uploads/2025/02/ST10.pdf

Daily PM chemistry: choice of input species

	PMx	Years	Stations	Strong components	Weak components
Barcelona (Spain)	PM10, PM1	2010, 2019, 2021	• Urban background • Traffic	PM, Al, Ca, Fe, K, Mg, Na, S, Li, Mn, Ti, V, Cr Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Cd, Sn, Sb, La, Pb, Ba, OC, EC, NO_3^-, Cl, NH_4^+, succinic acid, glutaric acid, phthalic acid, cis-pinonic acid, malic acid, 3-hydroxyglutaric acid, methylbutanetricarboxylic acid (MBTCA), 2-methylglyceric acid, galactosan, mannosan, levoglucosan, benzanthracene, chrysene, benz(b+j+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, benzo[ghi]perylene,	azealic acid, 2-methylthreitol, 2-methylerythritol, 17a(H)21β(H)-29-norhopane, 17a(H)21β(H)-hopane
Milan (Italy)	PM10	2017-2019	• Urban background	Al, Si, Cl, K, Ca, Ti, Fe, Cu, Zn, Pb, OC, EC, NO_3^-, SO_4^{2-}, NH_4^+, Levoglucosan	Mn, Ni, Br, PM10
Grenoble (France)	PM10	2013	• Urban background	OC, EC, HULIS, Na^+, NH_4^+, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, Levoglucosan, Arabitol, Sorbitol, Benzo[a]pyrene, Benzo[g,h,i]perylene, In.[1,2,3-cd]pyrene, Coronene, Acenaphthenequinone , 6H-Dibenzo [b,d] Pyran-6-one 1,8-Naphthalic anhydride, 1-Nitropyrene, Ba, Cu, Pb, Sb, Ti, Zn, Cr, V, Al, Ca, Fe, C27, C29, C31, C33, HP6, HP7, Coniferylaldehyde, Vanillic acid, Alpha-methyl glyceric acid, DHOPA, 3-Hydroxyglutaric Acid, Phthalic Acid, 2-Methyl erythritol	PM10, HP5, HP8

Daily PM chemistry: reccomendations





Amato et al., 2024 Env Int

Daily PM chemistry: reccomendations

- **At least EC-OC, major ions (using ionic chromatography), elements (by ICP), and analysis of BB tracers (either by LC-PAD or by GC-MS) should be mandatory.**
- If IC measurements include MSA and oxalate, it may lead to further determination of the main marine SOA fraction (traced with MSA) and to roughly apportion aged SOA factors originating from various origins (traced with oxalate),
- HPLC-PAD measurements for sugars alcohols (in particular arabitol and mannitol) may lead to the further determination of primary biogenic that can be a substantial PM fraction at some sampling sites, especially from Spring to late Autumn.
- A refined PMF analysis, including the determination of further sources, requires additional measurements, such as secondary biogenic emission, including tracers like 3-MBTCA, 2-MT's, etc measured with techniques like GC-MS, LC-MS, and or IC-MS.
- Inclusion of a range of PAHs measurements (or some derivatives) may lead to some improvement in some combustion sources separations but results should be studied with caution in terms of chemical profile, since these species are coming from many various origins.
- Inclusion of species like higher alkanes may also lead to some improvements in organic sources determination, especially plant debris, but results should also be considered with caution.

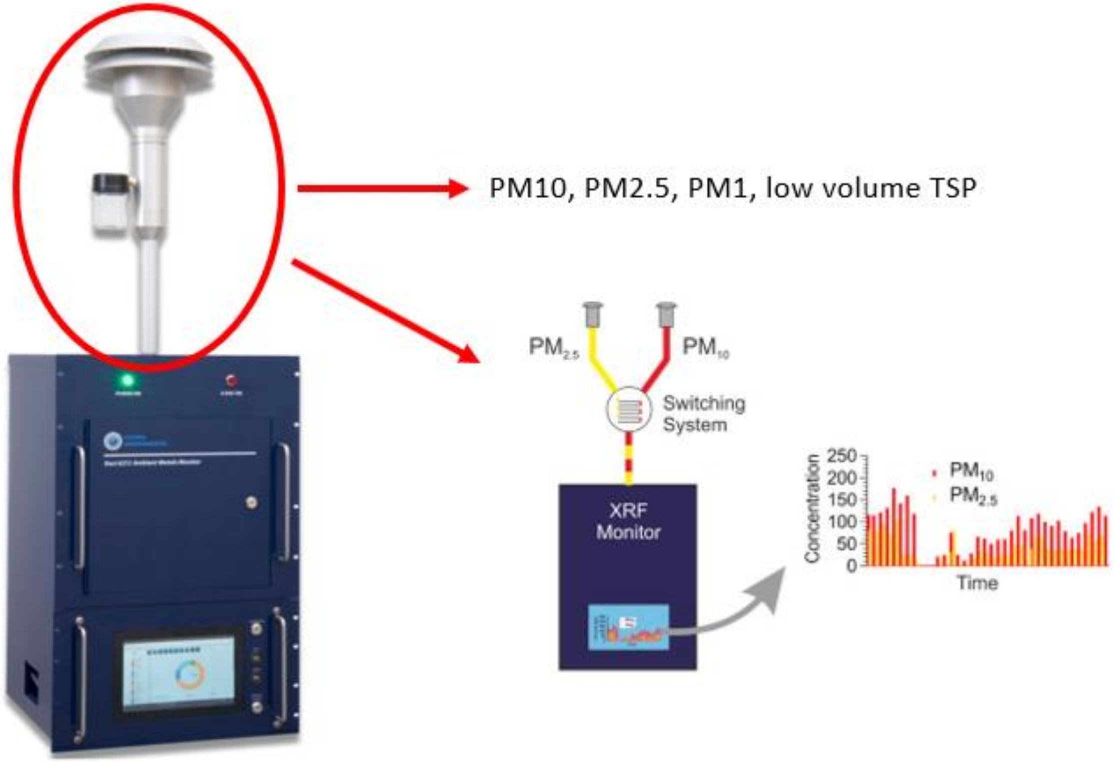
High time resolution elements

Source apportionment based on high time resolution trace elements measurements

Online XRF instruments provide data with high time resolution.

Advantages in SA use:

- ❖ Study of diurnal variations
- ❖ Possible use in RT SA approaches
- ❖ Size segregated data with one instrument


PM10, PM2.5, PM1, low volume TSP

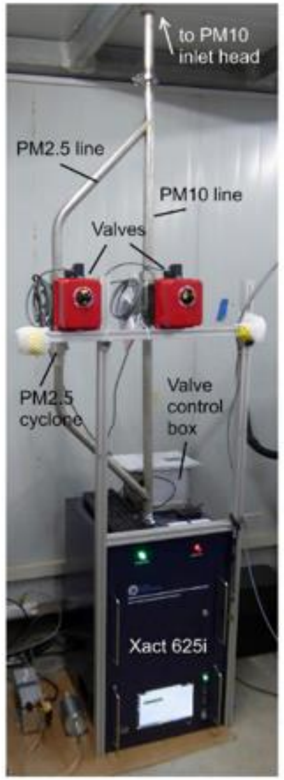


Fig. 1. Technical realization of the inlet switching system of the Xact 625i.

High time resolution elements

Overview of SA studies using HT resolution elemental data

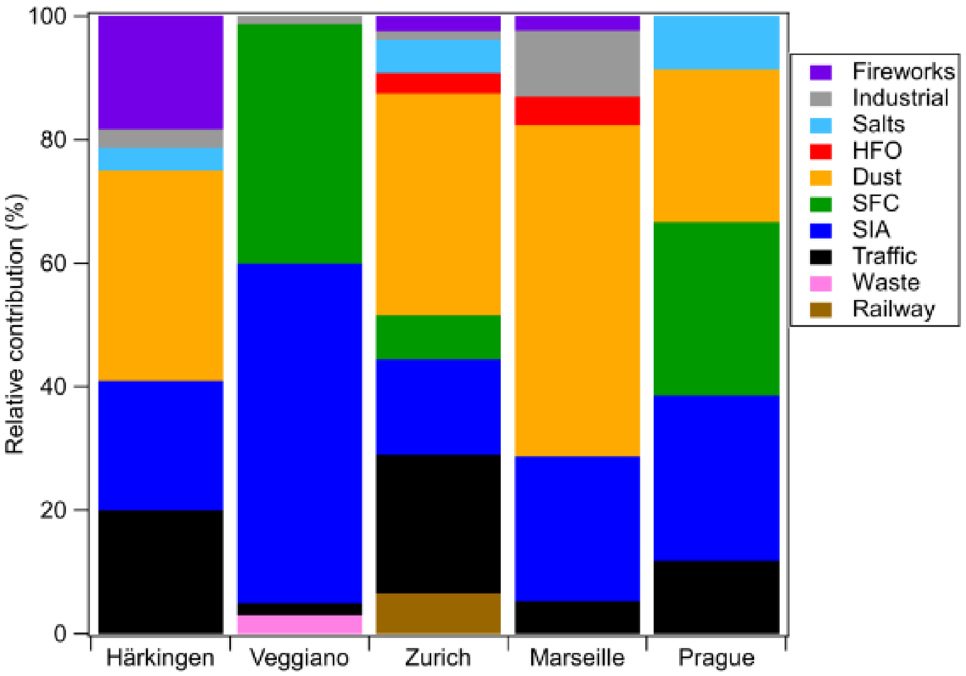
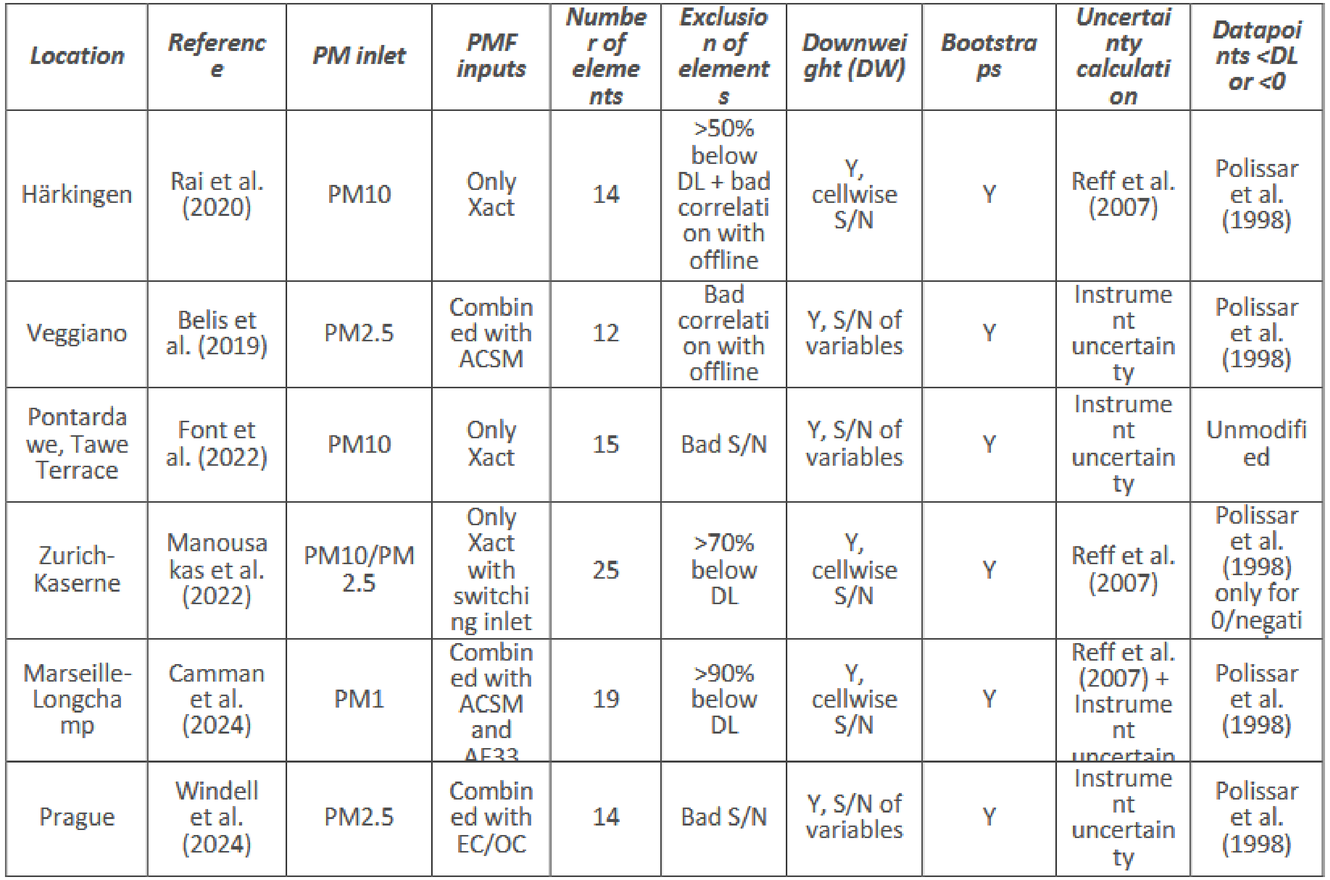


Table 7. Summary of PMF settings and data preparation from the six Xact SA studies in Europe.



Location	*Reference*	*PM inlet*	*PMF inputs*	*Number of elements*	*Exclusion of elements*	*Downweight (DW)*	*Bootstraps*	*Uncertainty calculation*	*Datapoints <DL or <0*
Härkingen	Rai et al. (2020)	PM10	Only Xact	14	>50% below DL + bad correlation with offline	Y, cellwise S/N	Y	Reff et al. (2007)	Polissar et al. (1998)
Veggiano	Belis et al. (2019)	PM2.5	Combined with ACSM	12	Bad correlation with offline	Y, S/N of variables	Y	Instrument uncertainty	Polissar et al. (1998)
Pontardawe, Tawe Terrace	Font et al. (2022)	PM10	Only Xact	15	Bad S/N	Y, S/N of variables	Y	Instrument uncertainty	Unmodified
Zurich-Kaserne	Manousakas et al. (2022)	PM10/PM2.5	Only Xact with switching inlet	25	>70% below DL	Y, cellwise S/N	Y	Reff et al. (2007)	Polissar et al. (1998) only for 0/negati
Marseille-Longchamp	Camman et al. (2024)	PM1	Combined with ACSM and AE33	19	>90% below DL	Y, cellwise S/N	Y	Reff et al. (2007) + Instrument uncertain	Polissar et al. (1998)
Prague	Windell et al. (2024)	PM2.5	Combined with EC/OC	14	Bad S/N	Y, S/N of variables	Y	Instrument uncertainty	Polissar et al. (1998)

High time resolution elements: reccomendations

- The mentioned studies performed PMF analyses on datasets including 12 to 25 elements. Some measured elements are usually excluded based on some criteria. Here, Font et al. (2022) and Windell et al. (2024) **discarded the elements having bad signal-to-noise (S/N) ratio**. Belis et al. (2019) removed elements showing **bad correlations with offline analyses on filters**. Rai et al. (2020), Manousakas et al. (2022) and Camman et al. (2024) set thresholds for the amount of data below the detection limit (DL), with elements having >50% (and bad correlation with offline analyses), >70% and >90% of data below DL excluded from their analysis, respectively.
- It is **of use to downweight (DW) observations (i.e. increase the uncertainty)** which could badly affect the model. Belis et al. (2019), Font et al. (2022) and Windell et al. (2024) applied DW based on the averaged S/N of each variable, while Rai et al. (2020), Manousakas et al. (2022) and Camman et al. (2024) performed a DW cellwise as some variables which have low S/N on average can display high S/N during specific periods (Visser et al., 2015).
- In several studies, observations <DL are treated separately. Polissar et al. (1998) suggested to replace concentrations <DL with DL/2 and the associated uncertainties by 5/6 DL. This methodology was applied by all studies except the one of Font et al. (2022), where **data inputs were reported without any modification**, as recommended by (Brown et al., 2015). Manousakas et al. (2022) also applied this recommendation for data <DL (but not below or equal to 0), since **replacing these values when the original measured values are available has no proven advantages** when the elements with low S/N are downweighted in the modeling process.
- There are several methods for setting the matrix of uncertainties for Xact data. Belis et al. (2019), Font et al. (2022) and Windell et al. (2024) used directly the instrumental uncertainties provided by the Xact software, which account for uncertainties of the sampling volume and uncertainties of the mass spectra deconvolution. Rai et al. (2020) and Manousakas et al. (2022) used the methodology described by Reff et al. (2007) including the concentrations values, fixed analytical uncertainties of 10% and DL values. Camman et al. (2024) also applied this method but introduced the instrumental uncertainties as analytical uncertainties.
- In overall, all studies used a **bootstrap resampling strategy** to explore the rotational ambiguity and the stability of the PMF solutions.

High time resolution organic aerosol

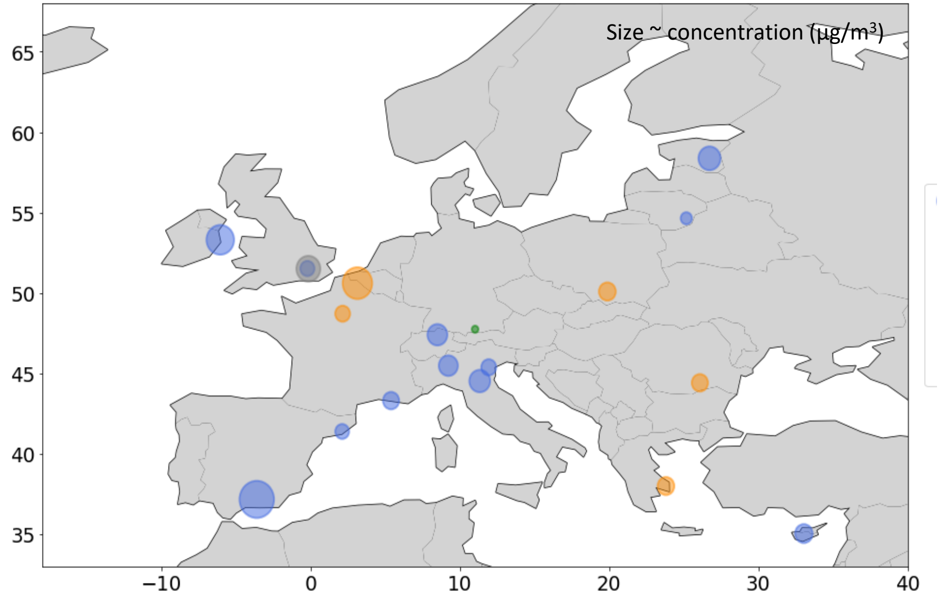
18 sites
- Type of site: Urban (13), Suburban (4), Regional background (1), Traffic (1)
- Instrument: Q-ACSM (14), ToF-ACSM (2), AMS (3)
- PMF method: Rolling +Seasonal (11), only Seasonal (8)

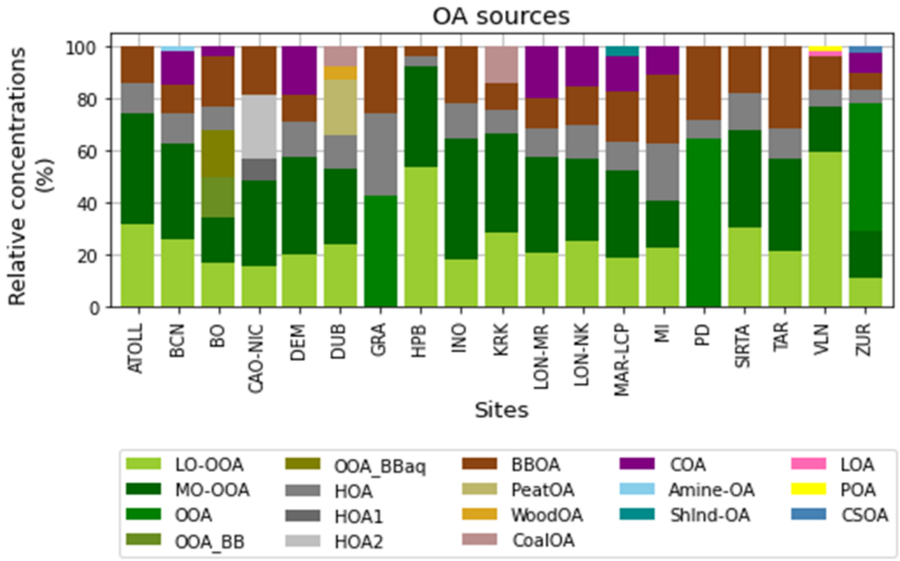
Primary

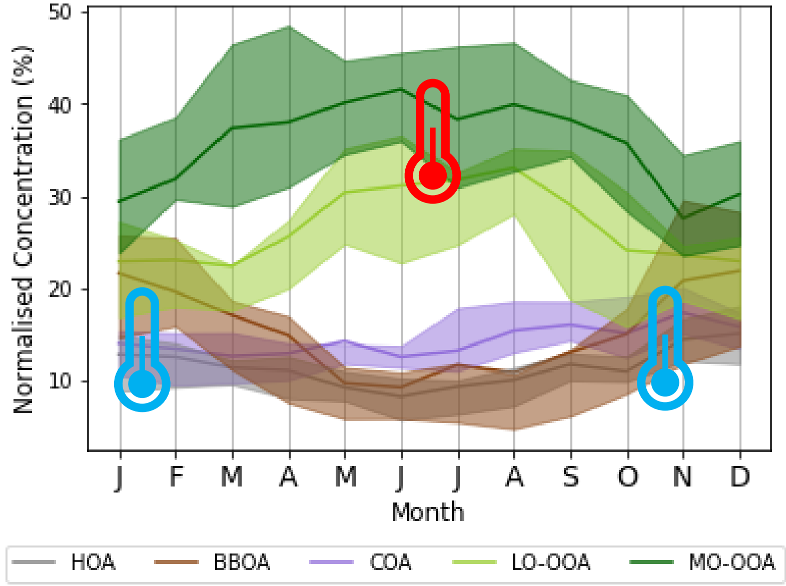
HOA BBOA COA Coal + other local

Secondary (41-92%)

LO-OOA MO-OOA +OOA + OOA-BB







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High time resolution organic aerosol: reccomendations

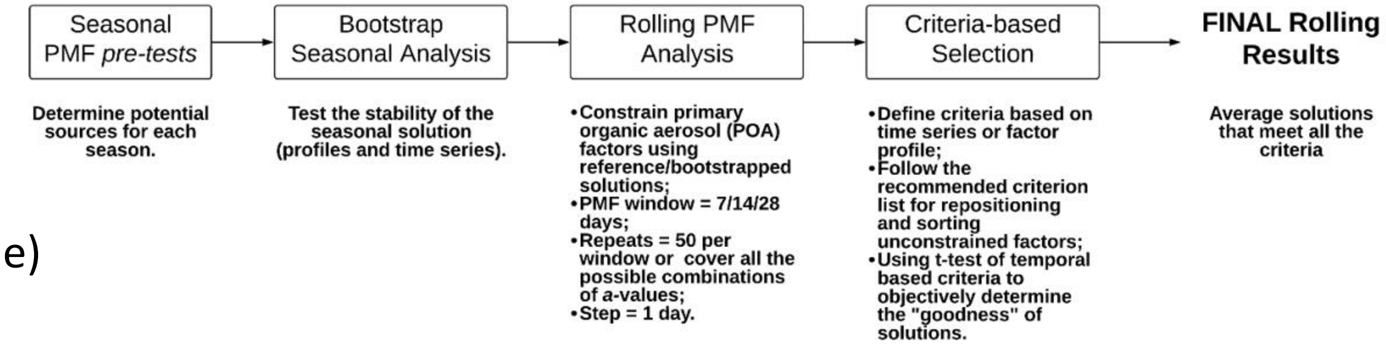
PMF protocol from Chen et al. 2022

- Rolling PMF for profile evolution.
- Seasonal PMF as basecase.
- Model guidance with *a priori* information (a-value)
    - Time series
    - Profiles
- Bootstrap

Result comparison with co-located measurements.

Possibility of RT-PMF (Chen et al. 2022b).

Other receptor models can be tested (CMB, BAMF, …).



Seasonal PMF *pre-tests* → Bootstrap Seasonal Analysis → Rolling PMF Analysis → Criteria-based Selection → **FINAL Rolling Results**

Seasonal PMF *pre-tests*: Determine potential sources for each season.

Bootstrap Seasonal Analysis: Test the stability of the seasonal solution (profiles and time series).

Rolling PMF Analysis:
- Constrain primary organic aerosol (POA) factors using reference/bootstrapped solutions;
- PMF window = 7/14/28 days;
- Repeats = 50 per window or cover all the possible combinations of *a*-values;
- Step = 1 day.

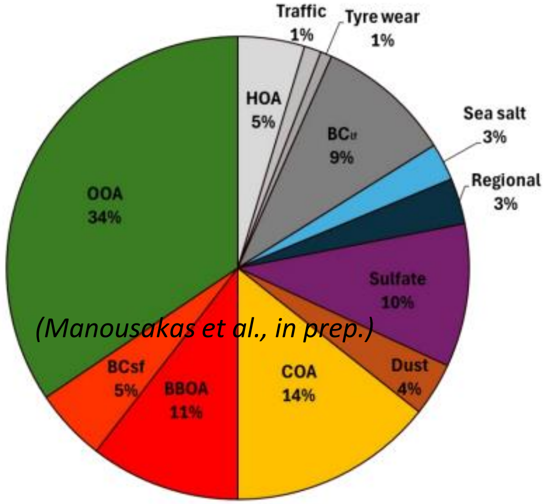
Criteria-based Selection:
- Define criteria based on time series or factor profile;
- Follow the recommended criterion list for repositioning and sorting unconstrained factors;
- Using t-test of temporal based criteria to objectively determine the "goodness" of solutions.

FINAL Rolling Results: Average solutions that meet all the criteria

Combined dataset: reccomendations

Recent interest in combining aerosol species from different types of instruments.

- OA + Secondary Inorganic Aerosol (Zografou et al. 2022)
- ACSM + Aethalometer (Forello et al. 2019)
- ACSM + XACT (Belis et al. 2019)
- ACSM + XACT + Aethalometer (Manousakas et al., in prep.)
- ACSM + filters (Srivastava et al. 2019)
- ACSM + VOCs (Kuo et al. 2014)

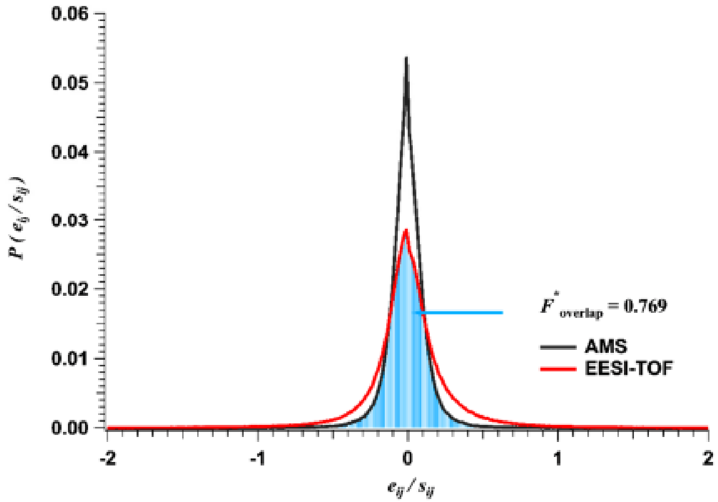


(Manousakas et al., in prep.)

Possibility to add instruments of different resolutions without averaging through the **multi-time resolution PMF** (Zhou et al. 2004)

- Implemented in SoFi (Source Finder, Canonaco et al. 2021).
- ACSM + AE33 + Filters (Via et al. 2023)
- Recommended practice instead of averaging to avoid temporal resolution loss.

Uncertainty reweigthing between instruments (Tong et al. 2022, AMS+ EESI) is <u>strongly recommended</u>.



Thank you for your attention

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Source Apportionment Webinar
29 Spetember 2025 | 10:00 -12:00 CEST

Webinar on Source Apportionment – 29 September 2025

This session will focus on tools and strategies for **Source Apportionment**, helping identify and quantify pollution sources in urban environments. Details and speakers will be announced soon.

Date: **September 29th, 10:00-12:00 CEST**

Format: **Online** (Zoom-Link)

Agenda: **will be available soon at** RI-URBANS website