# Aerosol source apportionment in two contrasting Italian sites: a comparison between physical and chemical PMF in Aosta and Lecce

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## Introduction:

- Air pollution negatively affects human health, climate and the environment. Consequently, the identification of air pollutants and emission sources is crucial for air quality assessment and abatement strategies.[1,2]
- Source apportionment (SA) is a widely used modelling approach designed to identify the primary sources of pollutants and quantify their respective contributions to overall emission concentrations.
- Traditionally used on chemical speciation data, it has been also performed on physical aerosol properties such as size distributions or light absorption data, which offer advantages like cost-effectiveness and higher temporal resolution.

## Aim of Study:

- Testing the applicability of physical source apportionment on two contrasting sites: advantages and limits.
- Comparing results of physical-PMF to chemical-PMF results.

**Table 1: Physical-PMF: Measured quantities and instruments**

| Meaured quantity | Instrument | AOSTA | LECCE | RI-URBANS reccomendations[2] |
|---|---|---|---|---|
| Particle size distribution (PSD) ultrafine | SMPS Tropos | ✗ | ✓ (2016-2017) | ✓ |
| PSD fine-coarse and $PM_{10}$ | OPC (Palas Fidas 200 (AO), OPC FAI (LE)) | ✓ (2020-2024) | ✓ (2016-2017) | ✗ |
| Eq. black carbon (eBC) (one wavelength) | MAAP Thermo Scientific 5012 | ✗ | ✓ (2016-now) | ✓ |
| eBC(λ) (multiwavelength) | 7l Aethalometer Magee Scientific AE33 | ✓ (2020-2024) | ✗ | ✓* |
| NOx concentration | NO-$NO_2$ Analyser Thermo 42i-TL | ✓ (2004-now)** | ✓ (2016-now) | ✓ |

*RI-URBANS recommends conducting SA of equivalent black carbon (eBC), but does not currently advocate for combining it with PSD.**NOx in the Aosta site were used as post-PMF ancillary data.

**Dataset used:**

Physical-PMF: **Table 1**

Chemical-PMF: **Table 2**

**Table 2:Chemical-PMF: Measured quantities and instruments**

| Meaured quantity | Instrument | AOSTA | LECCE (published) [4] |
|---|---|---|---|
| Water-soluble anion-cation daily conc. | Ion chromatograph (Dionex) | ✓ (2019-2022) | ✓ (2017) |
| EC/OC on PM10 samples | Thermo-optical analyser (Sunset) | ✓ (2019-2021) | ✓ (2017) |
| Levoglucosan on PM10 samples | GC (Thermo Scientific Trace 1300 | ✓ (2019-2021) | ✗ |
| Metals on PM10 samples | ICP-MS (Varian 820-MS (AO), Thermo XII (LE)) | ✓ (2019-2022) | ✓ (2017) |

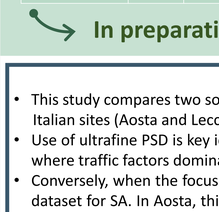
## Methods: Positive Matrix Factorization

- PMF is a receptor model used to identify and quantify source contributions to measured samples, based on their chemical or physical 'fingerprint'.
- Using EPA PMF 5.0, the datasets were analysed as matrix ***X*** (samples × species) with associated uncertainties ***u***. The model resolves ***p*** source profiles ***f*** and their contributions ***g*** (Eq.1) by minimizing an objective function ***Q*** (Eq.2), incorporating uncertainties per Ogulei et al (Eq.3).

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (Eq.1) \qquad Q = \sum_{i=1}^{n}\sum_{i=1}^{m}\left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}}\right]^2 \quad (Eq.2) \qquad u_{ij} = \sigma_{ij} + (C_3 \times N_{ij}) \quad (Eq.3)$$

- Identification of emission sources was supported by seasonal and diurnal trends, polar plots(Fig 3a,b), comparison between phys- and chem-PMF, remote sensing data and case studies.

# AOSTA



## Site Description:

- Capital city of Aosta Valley region (North-western edge of Italy)
- Population of around 33K inhabitants
- Surrounded by mountains exceeding 3500 m
- Urban background measurement station
- Transport events from Po valley (pollution hotspot)[5]

## Results - Aosta

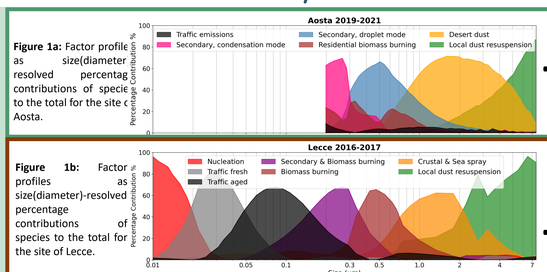



**Figure 1a:** Factor profiles as size(diameter)-resolved percentage contributions of species to the total for the site of Aosta.

**Figure 2b:** Additional PMF data in terms of percentage contributions of species sum for the site of Aosta. BC2-BC7 are the light absorpion from AE33. AAE was calculated a-posteriori. PM10 is PM10 concentration and Delta-C = eBC(370 nm) – eBC(880 nm).




**Figure 1b:** Factor profiles as size(diameter)-resolved percentage contributions of species to the total for the site of Lecce.

**Figure 2a:** Additional PMF data in terms of percentage contributions of species sum for the site of Lecce, namely eBC (equivalent black carbon), NO and NOx gas and Ntot (total number of particles) (see also Table 1)

## Phys-PMF

- **Traffic emissions:** Major eBC source (>50%) with near-zero Delta-C, suggesting aged traffic and non-exhaust sources. AAE ≈ 1 indicates fossil fuel origin. Clear daily/weekly cycles with a weekend dip.
- **Residential biomass burning:** Minor eBC source but dominates Delta-C (~100%). AAE ≈ 1.8 and broad particle size. Peaks at night, especially in winter; weak weekend effect.
- **Secondary, condensation mode:** Sulphate-rich, from gas-phase processes. Peaks linked to transport from Po valley and local particle formation.
- **Secondary, droplet mode:** Nitrate-rich, winter-dominant. Similar daily pattern to condensation mode, linked to mixed-phase processes.
- **Desert dust:** Seasonal peak in July, low in December. Flat daily trend due to random arrival time; size ~2 µm. Confirmed via remote sensing.
- **Local dust resuspension:** pronounced weekend effect suggesting correlation with anthropic activities. Size ~5–6 µm. Winter rise likely due to road salting.

## PHYS vs CHEM

| Phys-PMF | Traffic | BB | Secondaries (cond. + drop.) | Coarse (dust + local |
|---|---|---|---|---|
| **Chem-PMF** | Traffic | BB | Sulphate + Nitrate | Road salt + crustal |
| **$R^2$** | **0.45** | 0.91 | 0.70 | 0.67 |

→ **In preparation: Diemoz et al. 2025 [6]**

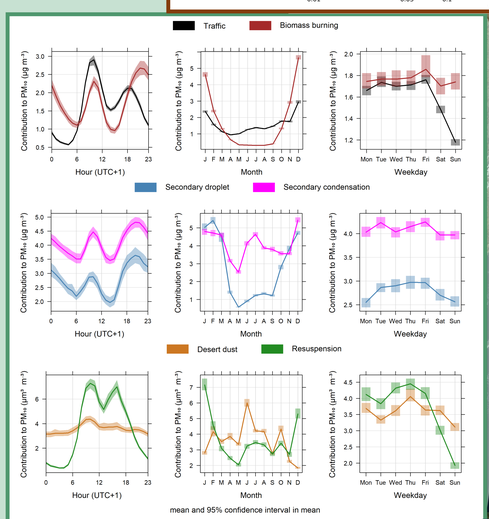



**Figure 3a:** Diurnal, monthly and weekly time variation of Phys-PMF factors for Aosta.

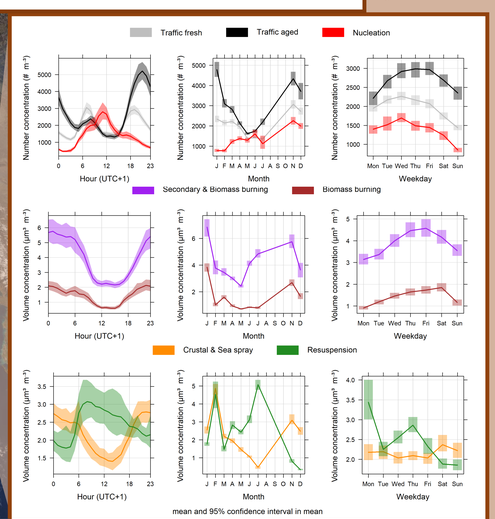



**Figure 3b:** Diurnal, monthly and weekly time variation of Phys-PMF factors for Lecce.

# LECCE

## Site Description:

- City in the Apulia region (South-western edge of Italy)
- Population of around 95K inhabitants
- Coastal flat area, 10 Km from Adriatic and 20 Km from Ionic sea
- Urban background measurement station
- Downwind some of the largest industrial settlements of southern Italy

## Results - Lecce

## Phys-PMF

- **Nucleation:** NSD peaks at 0.01 µm. Noon photochemical peak, especially in summer. Increase in Nov–Dec likely traffic-induced. No eBC; high NO. NW transport.
- **Traffic fresh:** NSD peak at 0.03 µm. Diurnal pattern tied to emissions/mixing layer. Winter increase, strong weekend effect. High NOx, some eBC. Local source.
- **Traffic aged:** NSD peak at 0.08 µm. Diurnal delay vs. fresh traffic. Higher in winter, clear weekend effect. Strong eBC/$NO_2$. Local source.
- **Secondary & biomass burning:** VSD peak at 0.25 µm. Secondary particles mixed with biomass burning (some eBC).
- **Biomass burning:** VSD peak at 0.35 µm. Linked to heating/agriculture. Winter peak. Moderate BC.
- **Crustal & Sea spray:** VSD max at 2 mm. Dust particles mixed to sea spray. Max in Feb (dust event) and higher in winter because of sea spray. Transport from SE.
- **Local dust resuspension:** VSD max at 3 mm. Higher in summer due to dry soils. Transport form SE.

## PHYS vs CHEM

| Phys-PMF | Traffic aged | Sec. & BB | BB |
|---|---|---|---|
| **Chem-PMF** | Traffic, EC, OC | $PM_{2.5}$ | BB, $PM_{2.5}$ , OC, K, $NO_3^-$ |
| **$R^2$** | 0.58, 0.64, 0.48 | 0.54 | 0.47, 0.65, 0.61, 0.43, 0.41 |

→ **In preparation: Mapelli et al. 2025 [7]**

## Summary & Conclusions

- This study compares two source apportionment (SA) models based on aerosol physical properties at two contrasting Italian sites (Aosta and Lecce) alongside chemical SA.
- Use of ultrafine PSD is key identify and quantify the factors that contributes more to number distribution, as shown in Lecce, where traffic factors dominated PNC.
- Conversely, when the focus is reconstructing particulate matter (PM), the use of PSD from fine to coarse modes is a valuable dataset for SA. In Aosta, this approach revealed that secondary and coarse factors were the most impactful sources in terms of PM10.
- Multiwavelength light absorption was crucial for distinguishing BB from traffic emissions in Aosta, whereas in Lecce PMF, these sources are likely more mixed.
- Comparing phys- and chemi-PMF confirmed complementarity and underscored the value of physical-PMF's temporal resolution.
- At the marine site of Lecce, the coarse factors are expected to be dominated by salt particles although desert dust (episodic) may impact the same size range.
- WORK in PROGRESS: future work will be done to refine the physical-based PMF.

***References and Acknowledgements:***

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*7) Mapelli et al., Aerosol source apportionment at the site of Lecce (Italy): a comparison between physics- and chemistry-based PMF, 2025*

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