

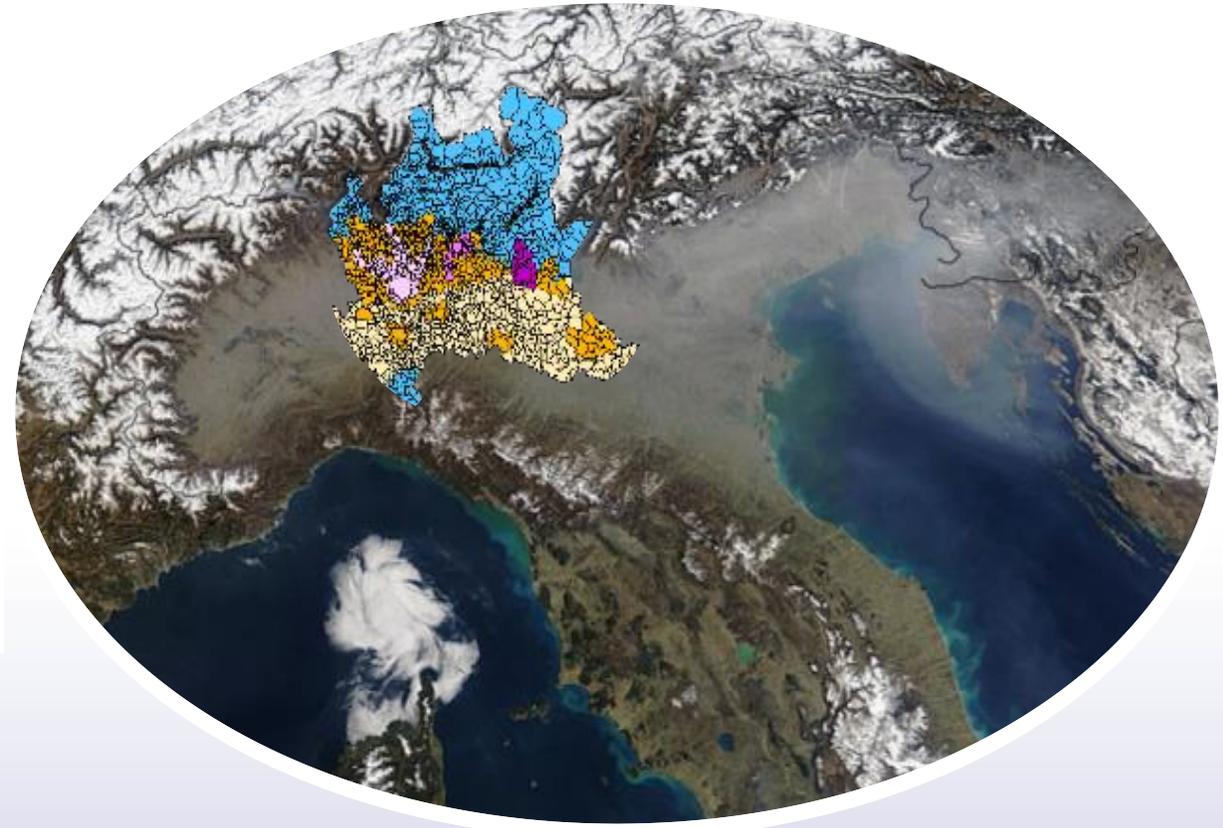
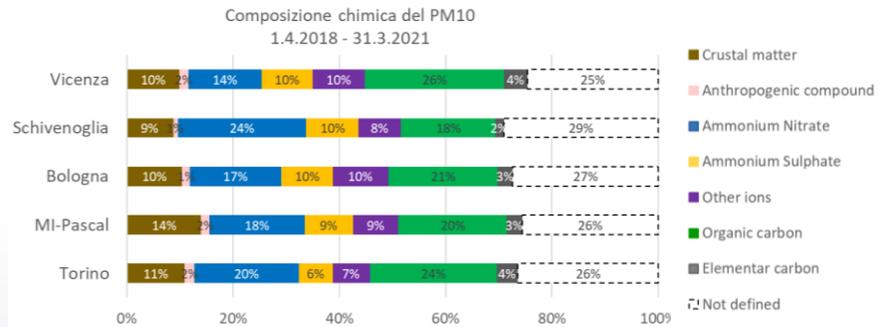
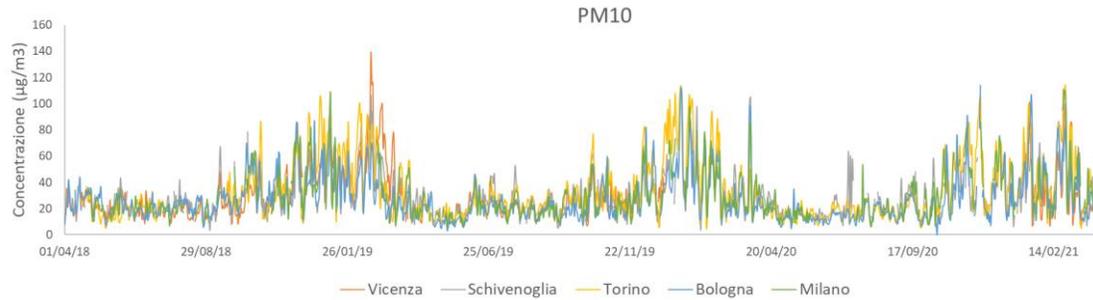


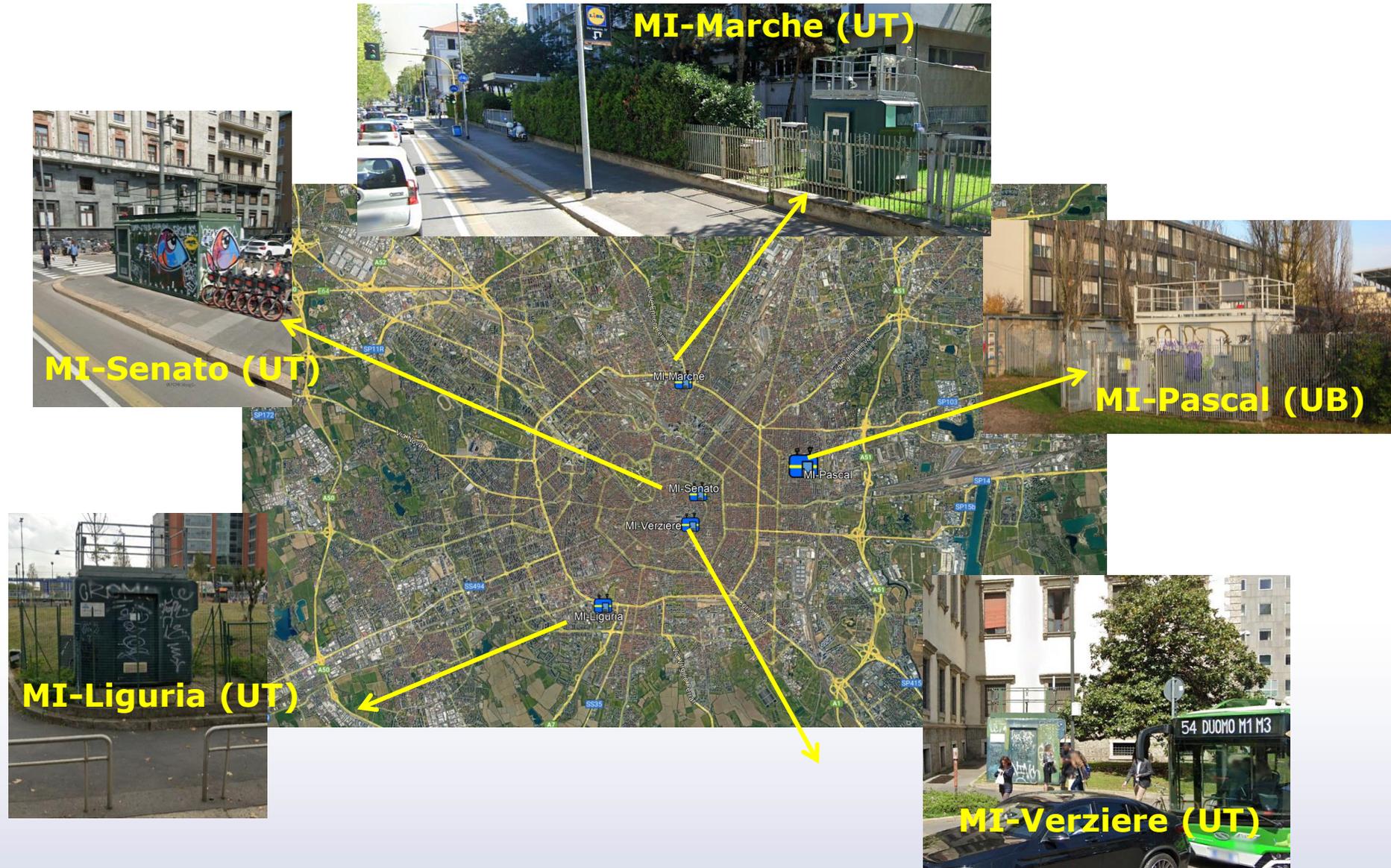
Collaborazione tra ARPA e progetti europei: RI-URBANS e il caso ARPA Lombardia

Cristina Colombi, Guido Lanzani
DG Generale – UO Aria e SPDM - ARPA Lombardia

Base di partenza

Per la sua orografia, la Pianura Padana è una delle aree europee con la più alta concentrazione di inquinanti. Per molti di questi, tuttavia, da diversi decenni si nota una costante diminuzione dei valori.







Room A:

PM10&2.5 FAI-DC

PM10&2.5&1 Fidas Palas

NO, NO₂, NO_x API

SO₂ TEI

O₃ TEI

VOC C6-C12 GC

NH₃ API

NH₃, CH₄ Ap2E

NH₃ Picarro G2508

CO₂ Picarro G2508

N₂O Picarro G2508

CH₄ Picarro G2508

VOC C2-C6 AMA

VOC C6-C12 AMA

Room B:

BC MAAP

Nephelometer

BC AE33

TC TCA08

ACSM-ToF-x

SMPS 3938W50 CEN

2 CPC 3750

APS 3321

outside:

4/6 LVS PM10&PM2.5

2 HVS PM10&PM2.5

XACT

Dal 2013 ARPA Lombardia effettua quotidianamente la caratterizzazione chimica dei campioni PM10 e PM2.5 provenienti dai supersiti.

Dal 2023 sono state aggiunte le analisi orarie delle componenti del PM (OC, EC ed Elementi).

1-year measurements: Agreement fra diversi gruppi di ricerca dal 2023



- Misure RI-Urbans: CNR Bologna (Angela Marinoni)
- Post-analisi misure ottiche e SA multi-size: UniMI (Roberta Vecchi)
- Misure h di elementi con XACT: PSI Zurich (Andre Prevot)
- Misure di OP su PM10 e PM2.5: PSI Zurich (Kaspar Daellenbach)
- Misure componenti organici: Frankfurt University (Alex Vogel)
- Misure NPF con NAIS e SMPS: University of Helsinki (Federico Bianchi, Myriam Agrò)

Diverse pubblicazioni RI-Urbans:

- ❖ *A European aerosol phenomenology – 9: Light absorption properties of carbonaceous aerosol particles across surface Europe*, J. Rovira et al., 2025
- ❖ *Recommendations for reporting equivalent black carbon (eBC) mass concentrations based on long-term pan-European in-situ observations*, Savadkoohi et al., 2024
- ❖ *Aerosol source apportionment uncertainty linked to the choice of input chemical components*, Amato et al., 2024
- ❖ *Variability of ambient air ammonia in urban Europe (Finland, France, Italy, Spain, and the UK)*, Liu et al., 2024
- ❖ *The variability of mass concentrations and source apportionment analysis of equivalent black carbon across urban Europe*, Savadkoohi et al., 2023
- ❖

<https://riurbans.eu/results/#publications>

Altre pubblicazioni in corso gruppo '1-year':

- ❖ *Phaenomenology of the atmospheric aerosol scattering and absorption properties in Milan*, Rimoldi, 2024, Tesi di Laurea UniMI
- ❖ *Low pollution and ventilation enhancing new particle formation in Milan, Italy*, Agrò et al., in fieri
- ❖ *Intercomparison of online and offline XRF spectrometers for determining the PM10 elemental composition of ambient aerosol*, Cadeo et al., in press
- ❖

Laboratorio in-house:

2 ED-XRF Panalitycal

**Mg, Al, Si, S, Cl, K, Ca,
Ti, V, Cr, Mn, Fe, Ni,
Cu, Zn, Br, Rb, Pb, Ba,
As**

1 complete chromatographic
line IC Metrohm (anions,
cations and sugars)

About 10.000 samples/year

1 TOT/TOR Sunset for EC, OC

1 TOT/TOR Sunset for EC, OC
with autosampler

Laboratorio in-house:

2 ED-XRF Panalitical

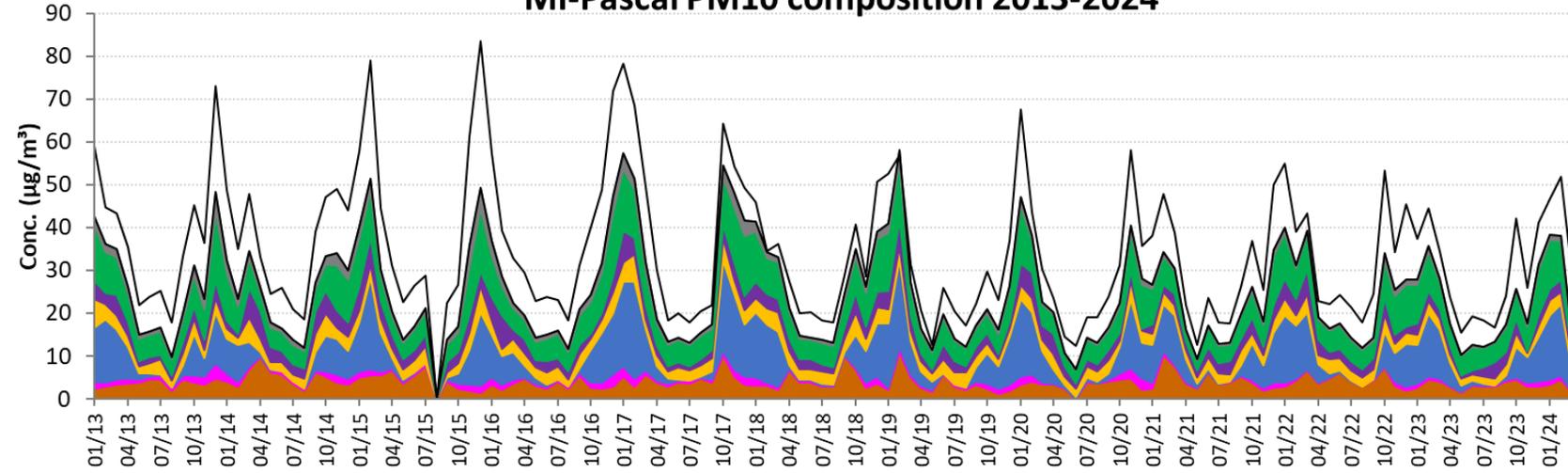
**Mg, Al, Si, S, Cl, K, Ca,
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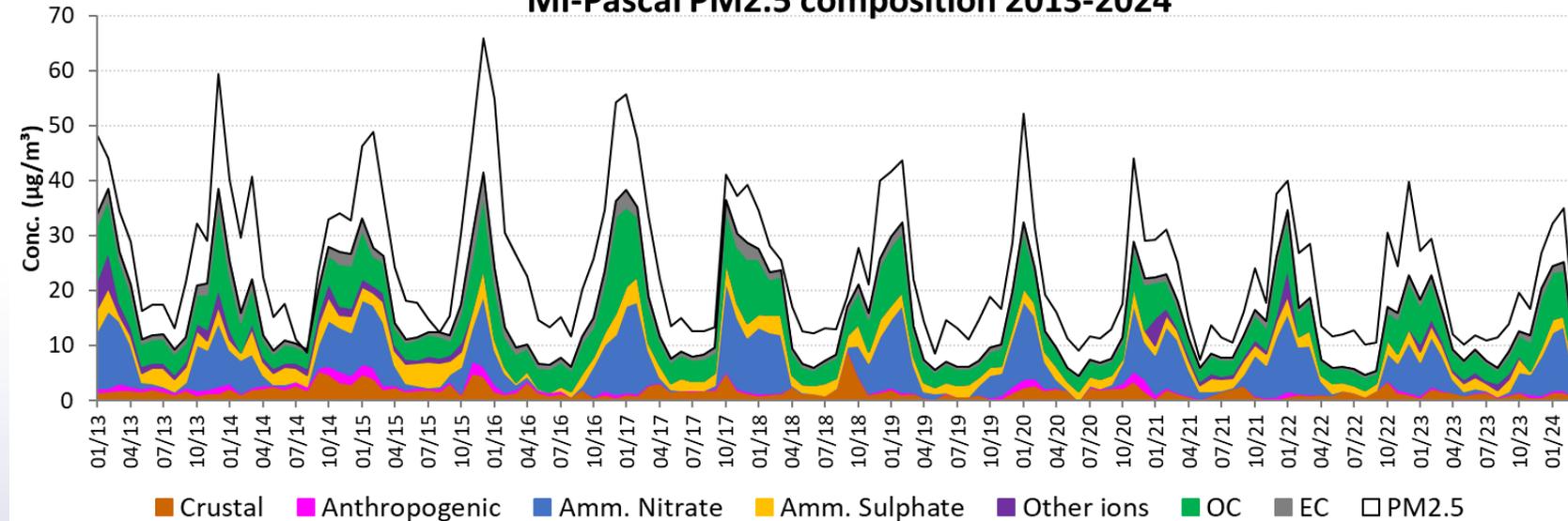
1 TOT/TOR Sunset for EC, OC

1 TOT/TOR Sunset for EC, OC
with autosampler

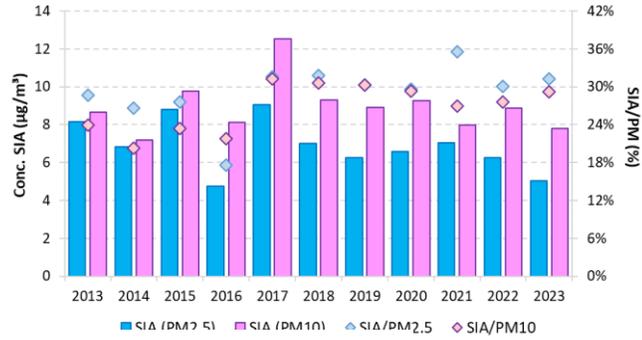
MI-Pascal PM10 composition 2013-2024



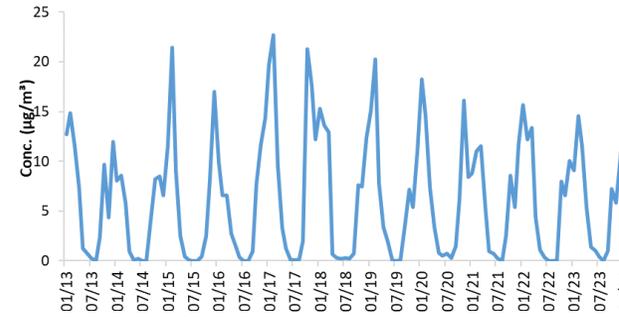
MI-Pascal PM2.5 composition 2013-2024



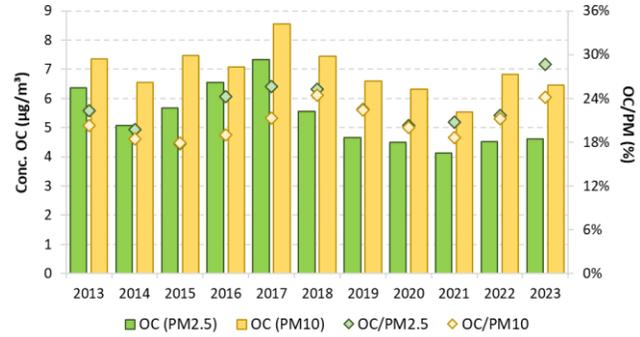
MI-Pascal SIA 2013-2023



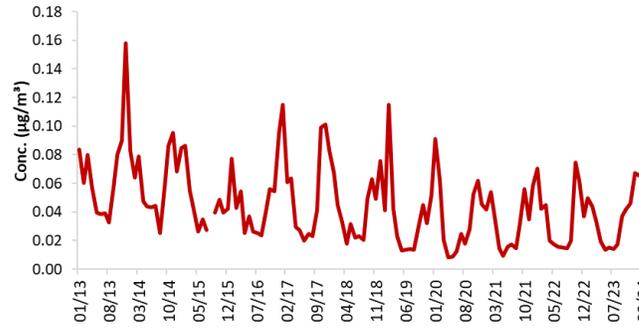
MI-Pascal Amm. Nitrate 2013-2024



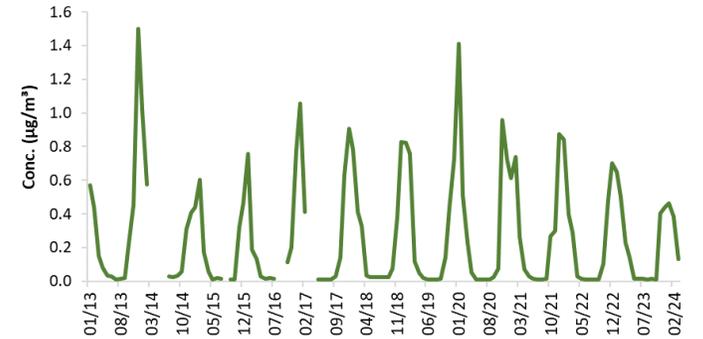
MI-Pascal OC 2013-2023



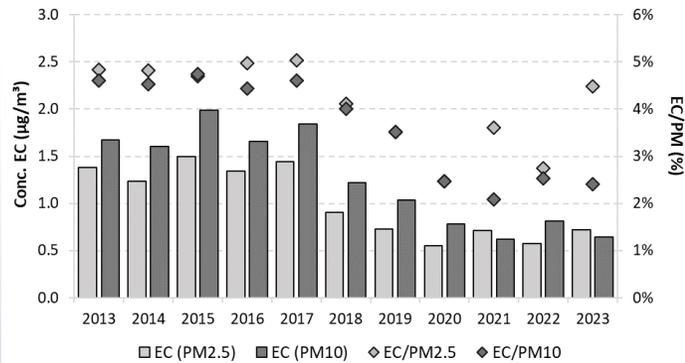
MI-Pascal Copper 2013-2024



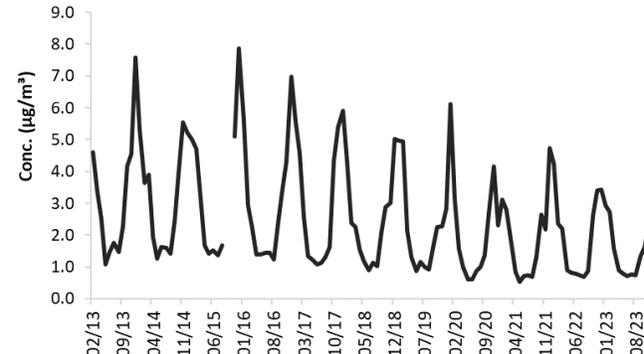
MI-Pascal Levoglucosane 2013-2024



MI-Pascal EC 2013-2023

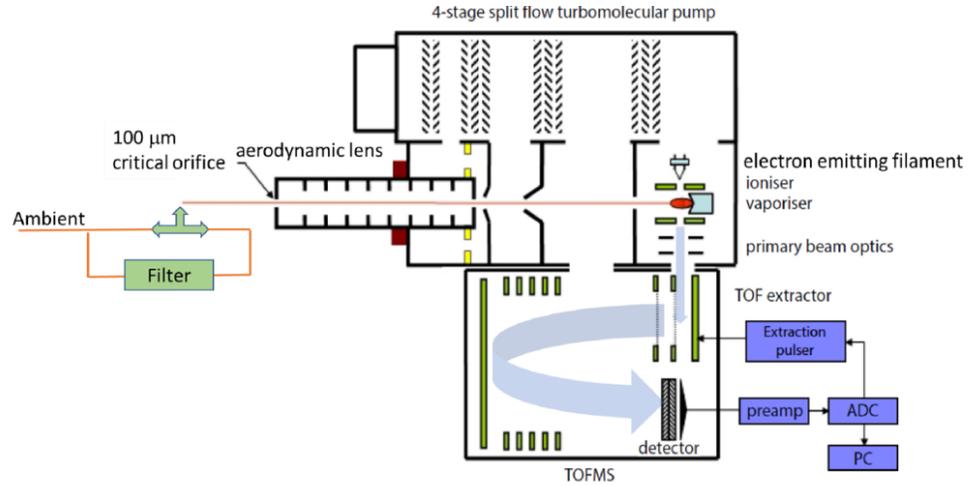


MI-Pascal BC-MAAP 2013-2024



Effetto del FAP

Time-of-Flight Aerosol Chemical Speciation Monitor with eXtra resolution (ToF-ACSM X)



Risoluzione temporale = 0.5 Hz

Monitoraggio continuo e in tempo reale della composizione chimica dell'aerosol con risoluzione di massa migliorata per una migliore quantificazione delle specie H:C, O:C e NH₄⁺.

Total Carbon (TCA08) accoppiato a BC-AE33

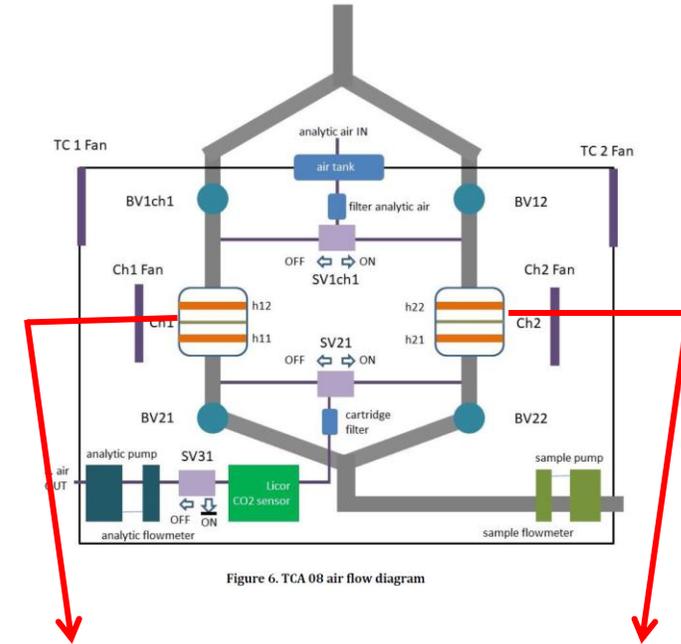
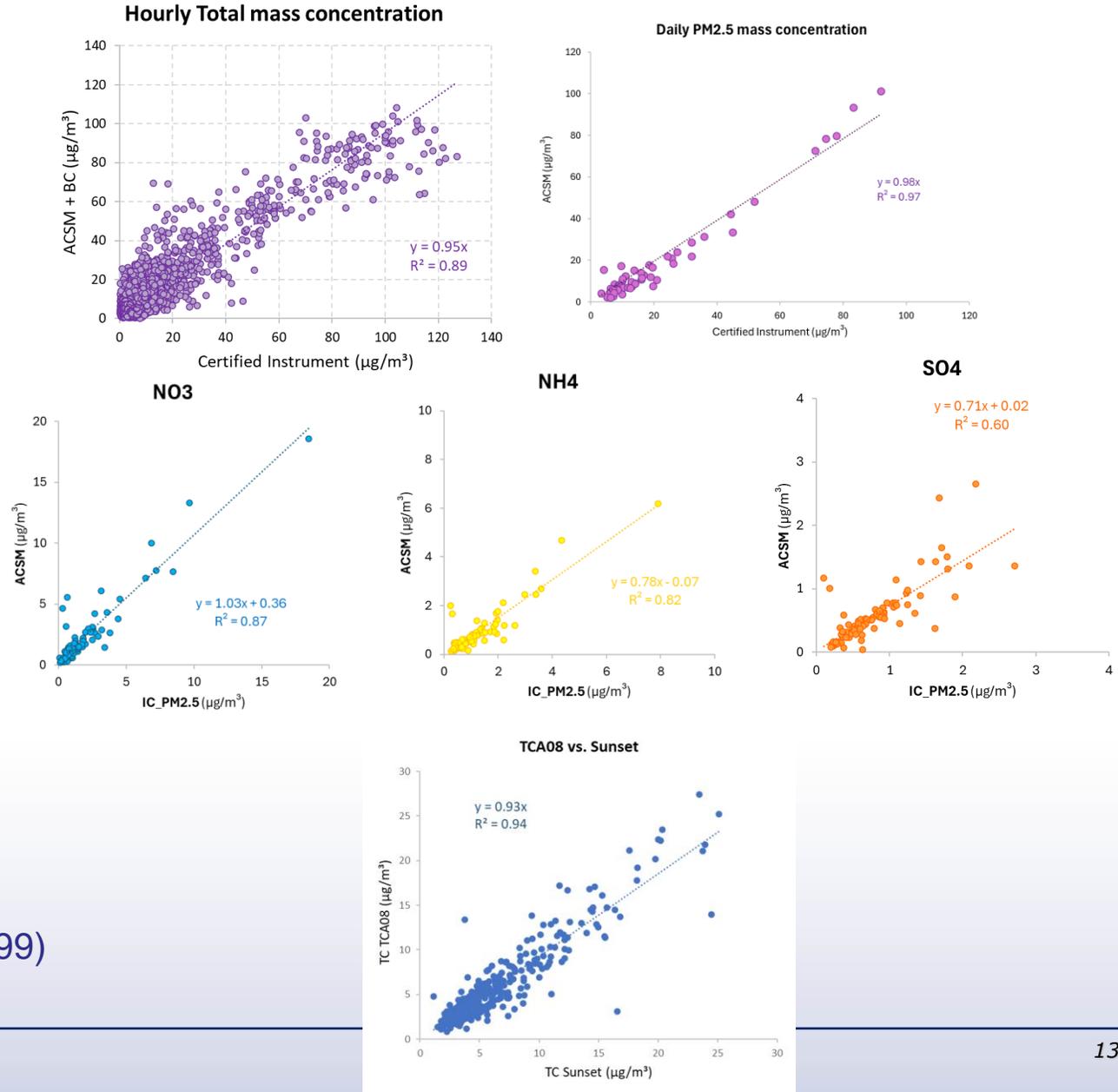
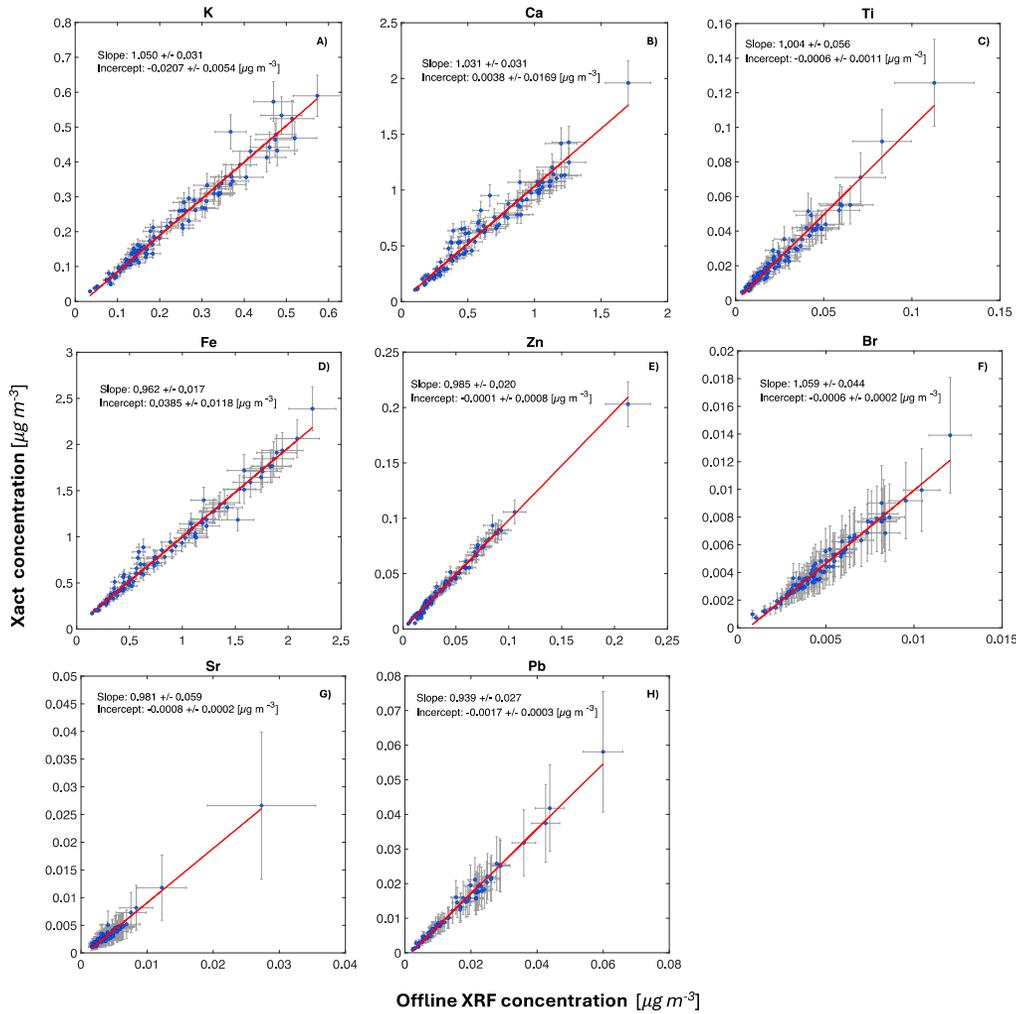


Figure 6. TCA 08 air flow diagram

While it is sampling, the other is analysing

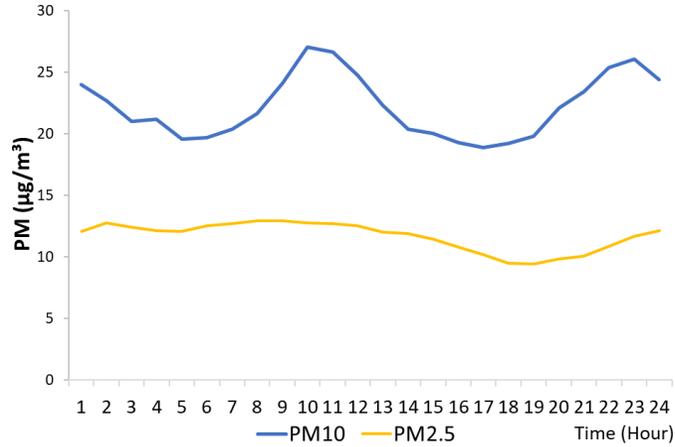
Complete combustion of all C compounds into CO₂

$$OC = TC - b \cdot BC$$

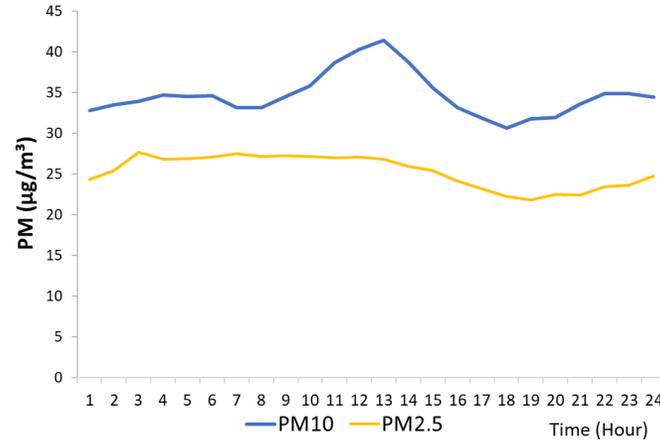


Xact® 625i altamente correlato con XRF-offline ($R^2 = 0.67 \div 0.99$)
sebbene con pendenze comprese tra 0.79 e 1.70

MI-Pascal - Summer



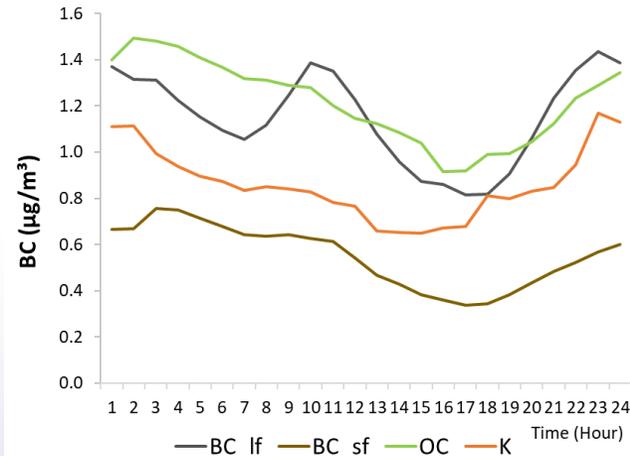
MI-Pascal - Winter



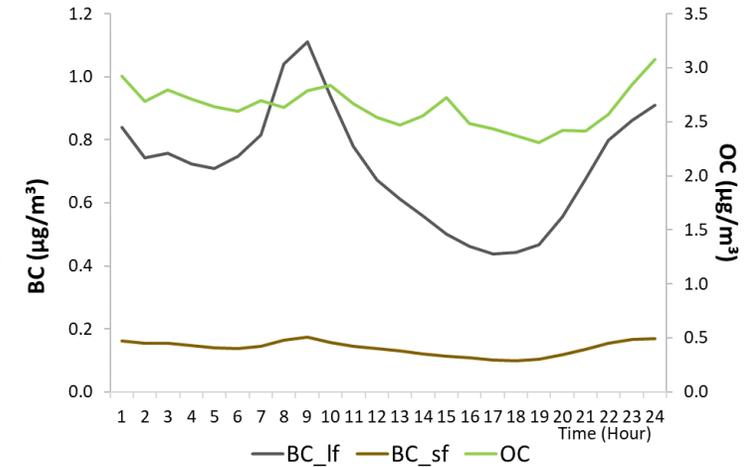
Il ciclo giornaliero del PM ne conferma la complessità per la sua origine primaria e secondaria e l'importanza dell'effetto dell'Height Mix Level (H_{mix}) sugli inquinanti.

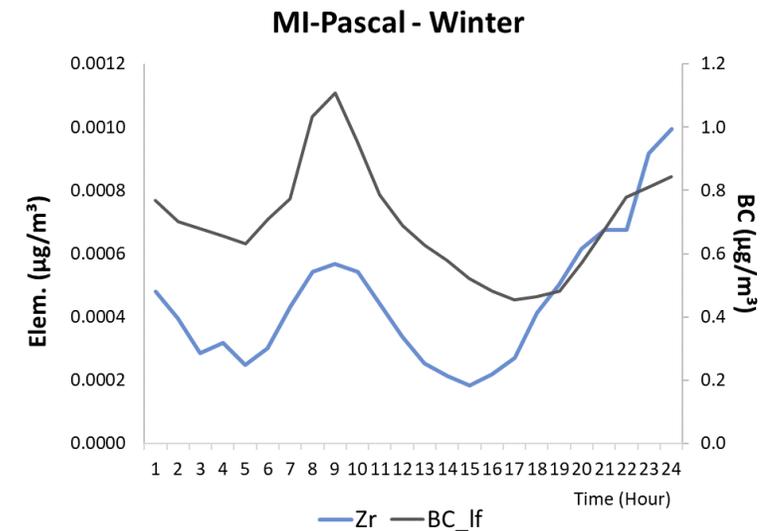
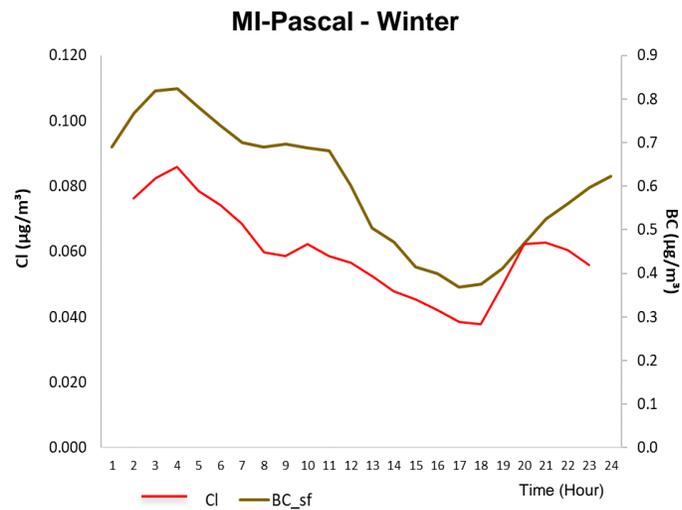
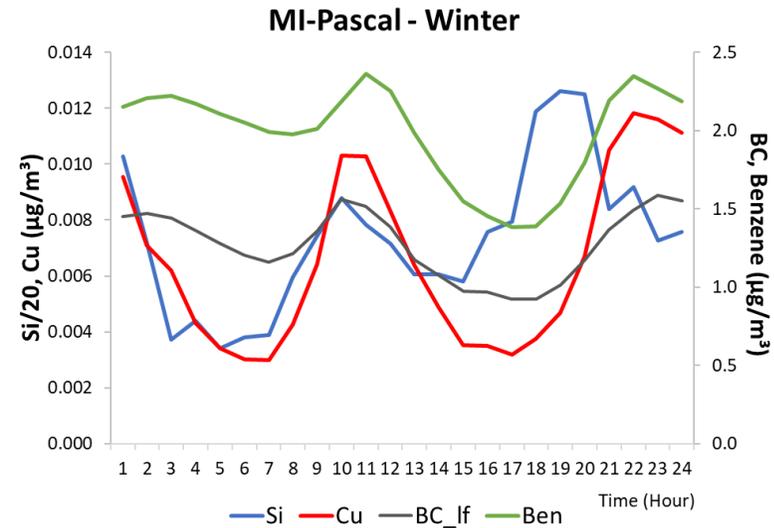
Il ciclo dell'OC sembra più correlato alle fonti di combustione, come la combustione di biomassa, avendo un'impronta simile ai suoi marker (K e BC_SF)

MI-Pascal - Winter

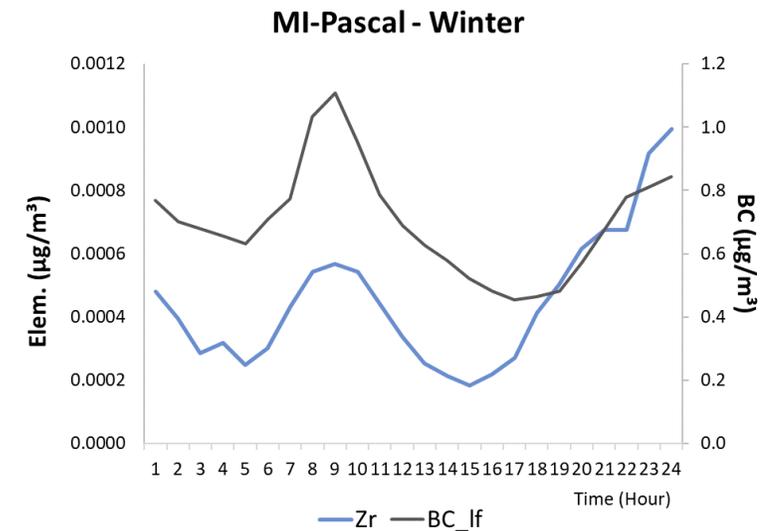
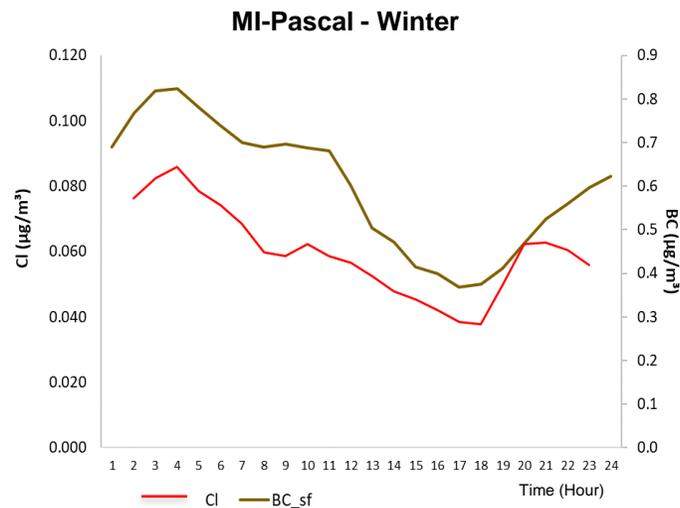
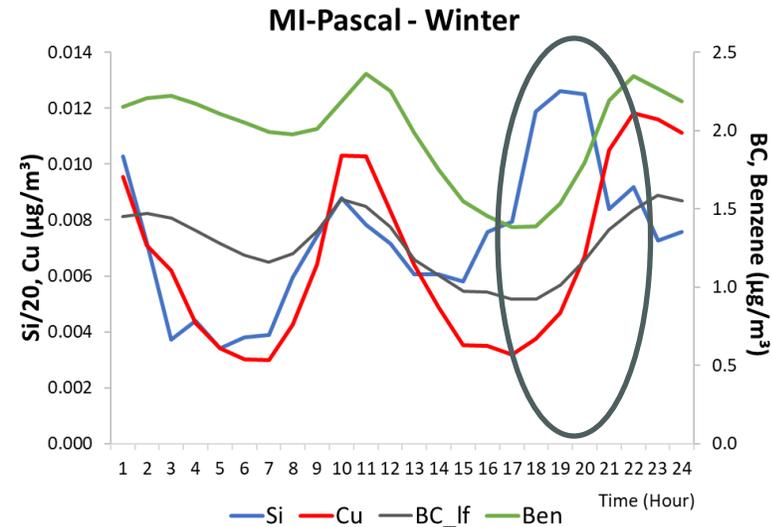


MI-Pascal - Summer



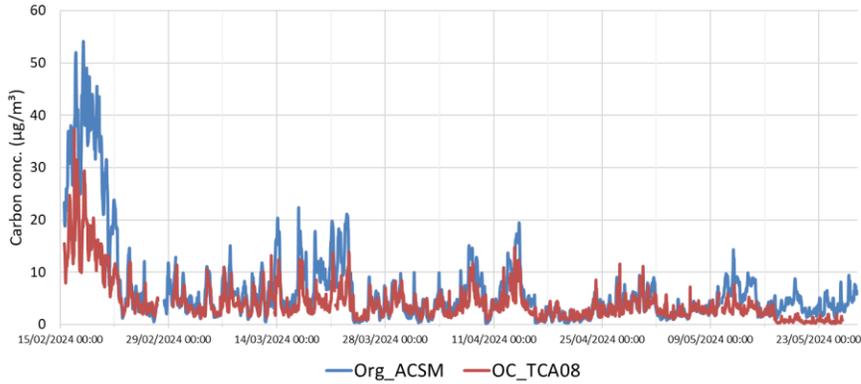


- Il ciclo del Cl suggerisce la possibilità di esplorare il fattore PMF “sale” cercando di separare il suo contributo alla combustione della biomassa
- Inoltre, l’osservazione del ciclo giornaliero suggerisce l’opportunità di migliorare l’analisi XRF offline attraverso l’aggiunta di nuovi standard, come Zr, che sembra ben correlato con BC_liquid fuel e quindi aggiungere altri marcatori per il profilo di traffico

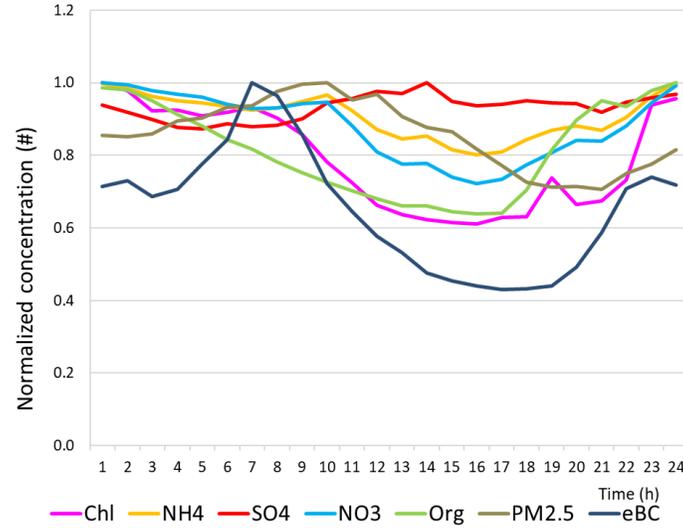


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- Analogamente al Cl, anche per il Si può esserci la possibilità di sfruttare la modulazione oraria per poter separare il risollevarimento da passaggio veicolare rispetto al contributo naturale

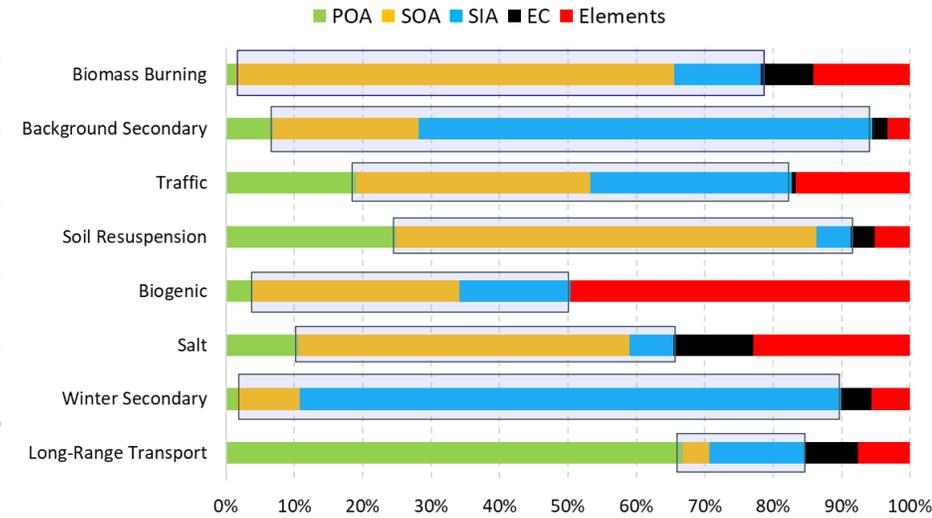
Hourly OM-OC in Milan



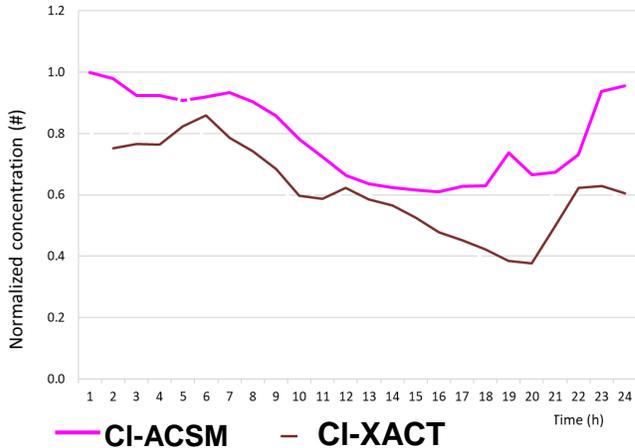
Diel variation in Milan 2024



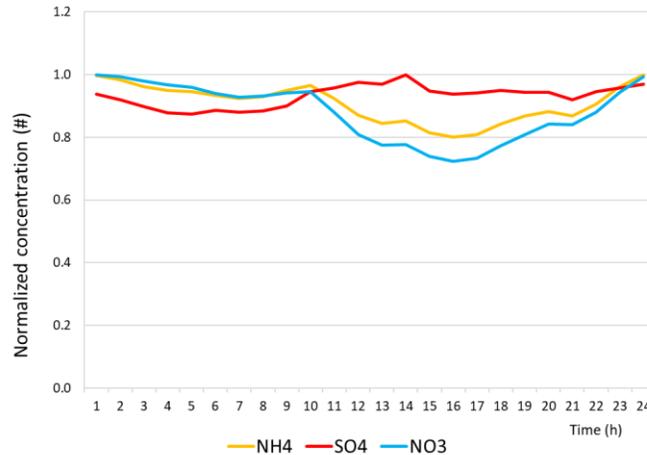
PMF Source Composition in Milan



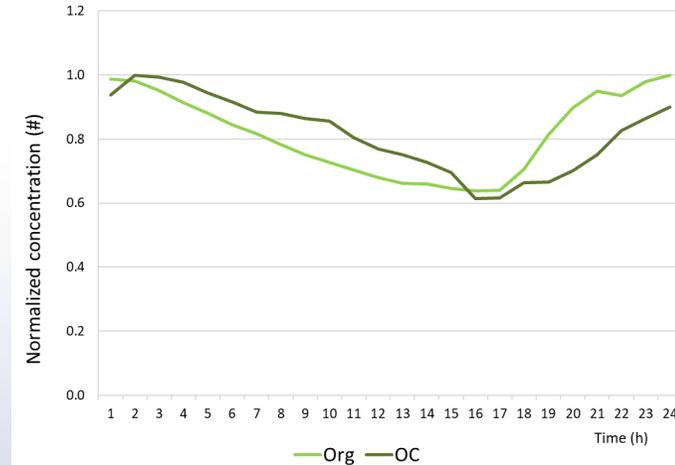
Diel variation in Milan 2024



Diel variation in Milan 2024



Diel variation in Milan 2024



ABSORPTION

radiative energy is converted into other forms of energy (thermal)

ABSORPTION COEFFICIENT

$$\sigma_{abs} = \frac{\sum_{i=1}^n C_{abs_i}}{V} [Mm^{-1}]$$

V = volume

n = number of particles in V

C_{abs_i} = absorption cross-section for the i-th particle

SCATTERING

light is deflected and redistributed in different directions

SCATTERING COEFFICIENT

$$\sigma_{sca} = \frac{\sum_{i=1}^n C_{sca_i}}{V} [Mm^{-1}]$$

V = volume

n = number of particles in V

C_{sca_i} = scattering cross-section for the i-th particle

ABSORPTION

radiative energy is converted into other forms of energy (thermal)

ABSORPTION COEFFICIENT

$$\sigma_{abs} = \frac{\sum_{i=1}^n C_{abs_i}}{V} [Mm^{-1}]$$

V = volume

n = number of particles in V

C_{abs_i} = absorption cross-section for the i-th particle

BC: $m(550nm) = 1.96 - 0.66i$ FF, WB

BrC: $m(550nm) = 1.67 - 0.27i$ WB

MinDust: $m(550nm) = 1.56 - 0.006i$ soil

$AAE_{FF} \approx AAE_{BC} \approx 1$

$AAE_{WB} \approx 2$

INFORMATION about COMPOSITION and SOURCES

SCATTERING

light is deflected and redistributed in different directions

SCATTERING COEFFICIENT

$$\sigma_{sca} = \frac{\sum_{i=1}^n C_{sca_i}}{V} [Mm^{-1}]$$

V = volume

n = number of particles in V

C_{sca_i} = scattering cross-section for the i-th particle

$\sigma_{sca}(\lambda) \sim \lambda^{-SAE}$ SAE = Scattering Ångstrom Exponent

SAE < 1 coarse fraction (> 1 µm)

1 < SAE < 2 accumulation mode

SAE > 2 ultrafine particles (< 100 nm)

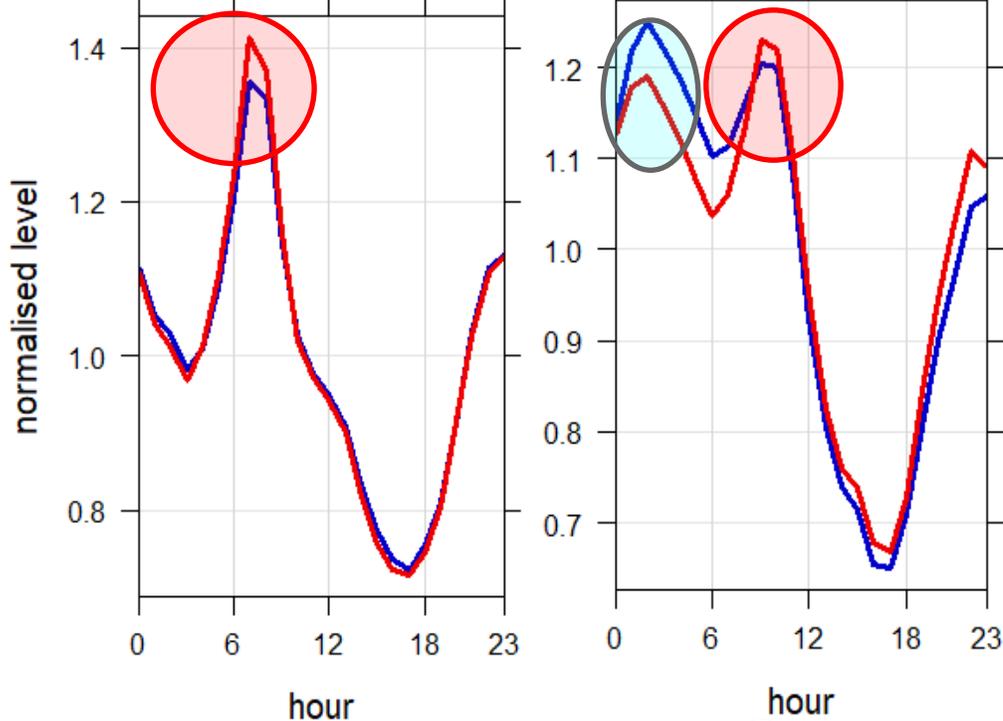
INFORMATION about DIMENSIONS

ABSORPTION

> assorb. rosso ↔ < AAE ↔ FF
 > assorb. blu ↔ > AAE ↔ WB

summer 2023

winter 2024



○ **TRAFFIC PEAK**

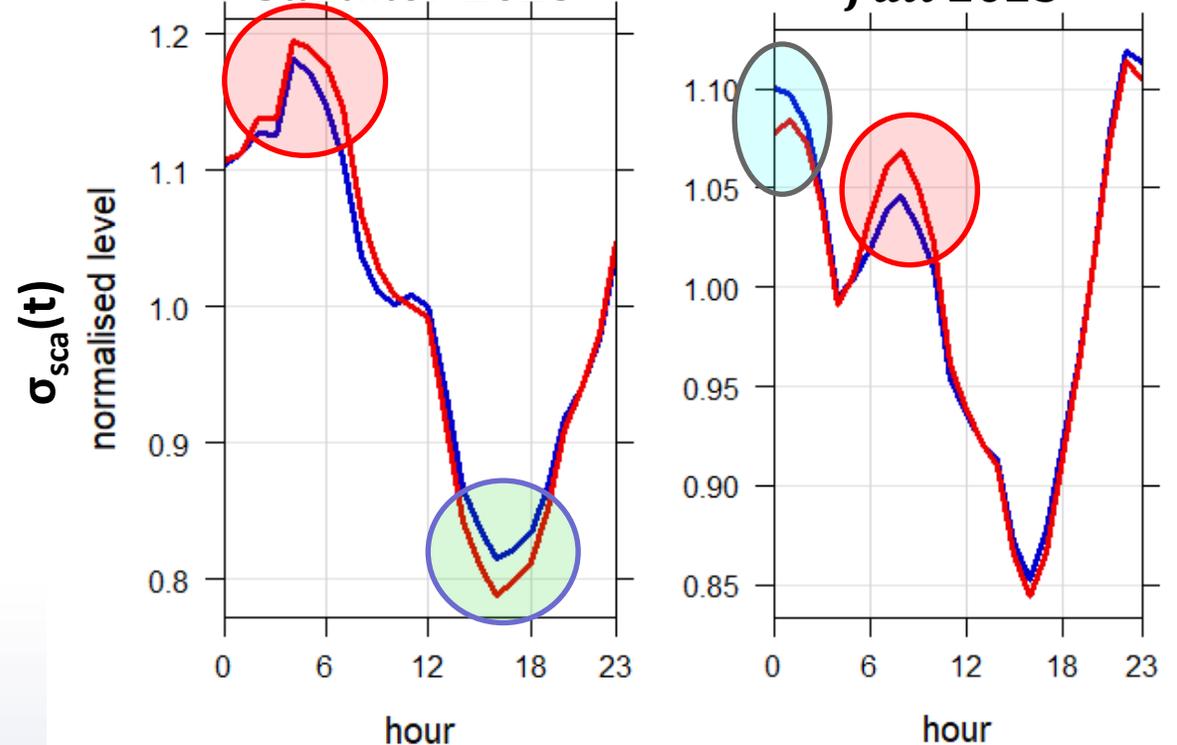
○ **DOMESTIC HEATING (only in fall/winter)**

SCATTERING

> scattering rosso ↔ < SAE ↔ COARSE
 > scattering blu ↔ > SAE ↔ Accumulaz.

summer 2023

fall 2023



○ **PHOTOCHEMISTRY (only in summer)**

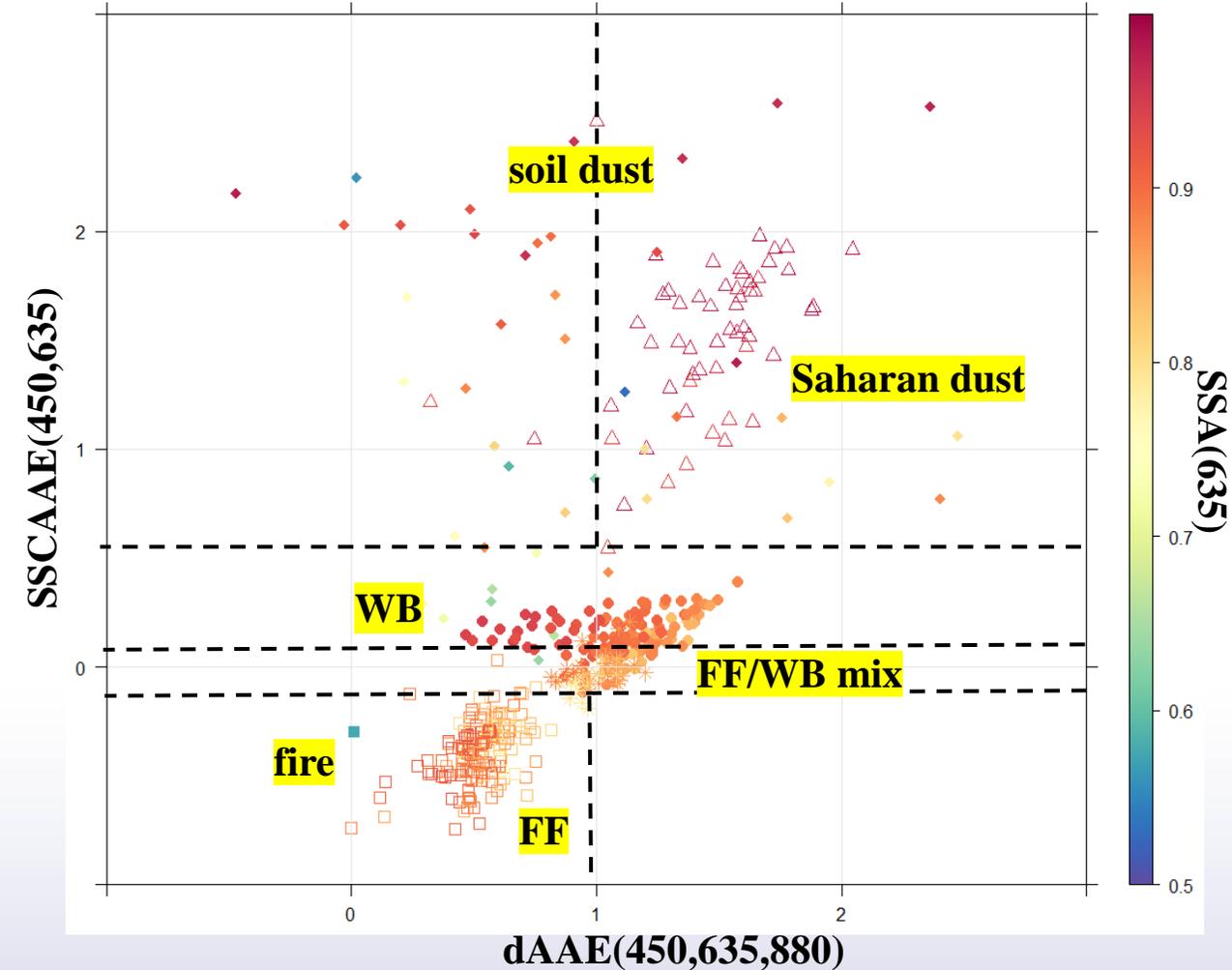
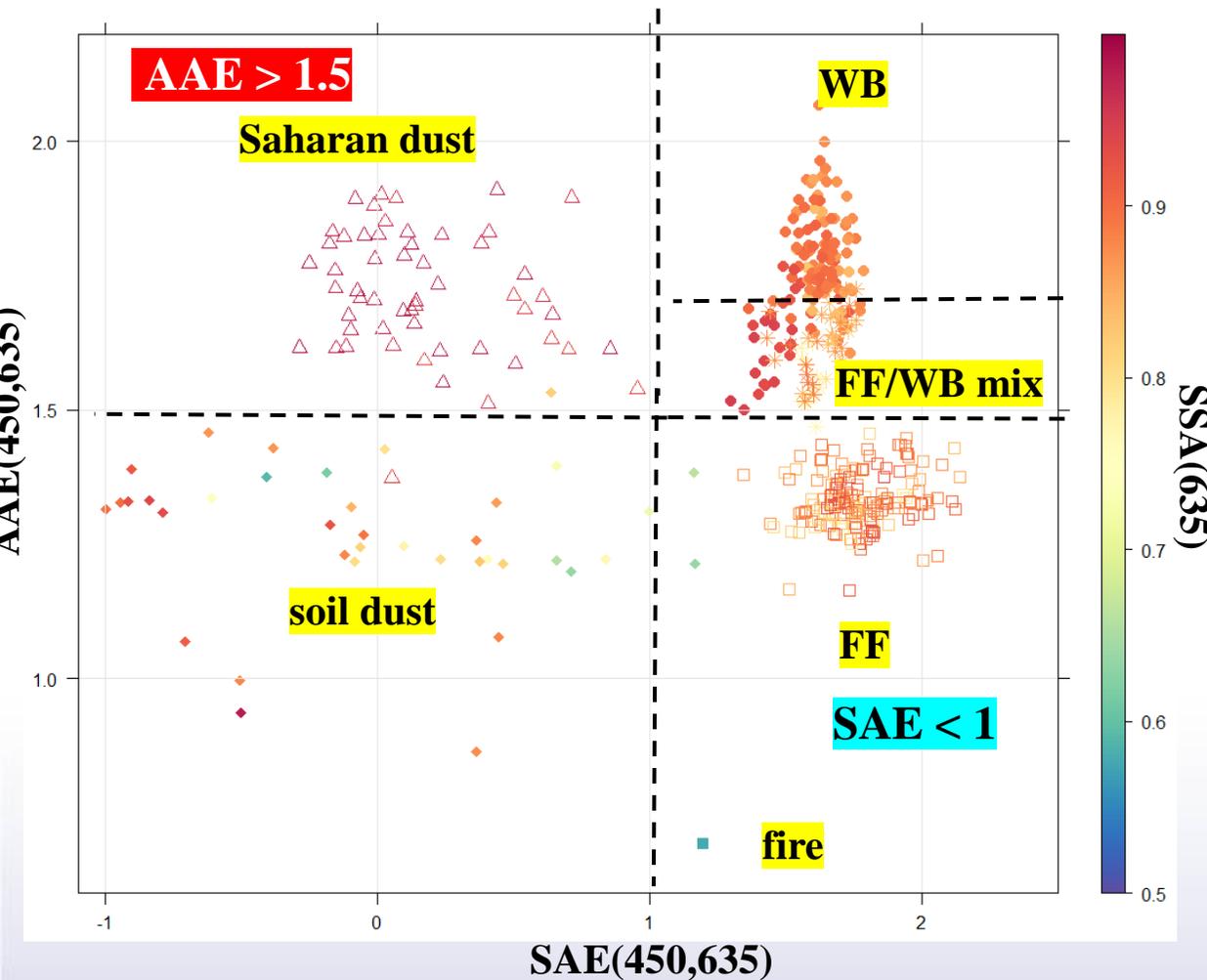
■ $\lambda = 950 \text{ nm}$

■ $\lambda = 370 \text{ nm}$

■ $\lambda = 635 \text{ nm}$

■ $\lambda = 450 \text{ nm}$

Episodi confermati dai cfrt con: X-ACT, back-trajectories, MWA model



(Russel et al., 2010 - Cazorla et al., 2013 – Valentini, 2020)

Modello MWAA (Massabò et.al., 2015)

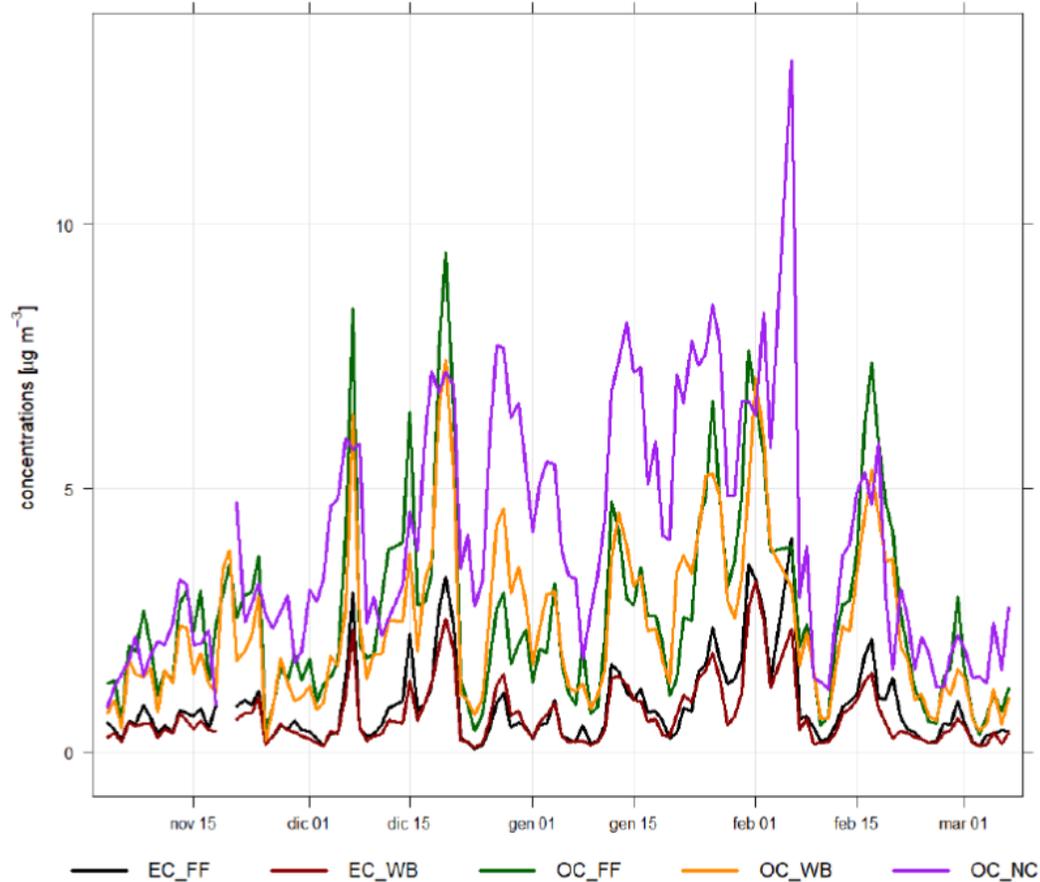


Figure 4.9 Mass apportionment by the MWAA model. The colors refer to: EC_{FF} (black), EC_{WB} (dark red), OC_{FF} (dark green), OC_{WB} (orange) and OC_{NC} (purple).

This means, in terms of relative contributions (Figure 4.10):

$$EC_{FF} = (8 \pm 7) \%$$

$$EC_{WB} = (7 \pm 6) \%$$

$$OC_{FF} = (25 \pm 17) \%$$

$$OC_{NC} = (38 \pm 21) \%$$

$$OC_{WB} = (22 \pm 15) \%$$

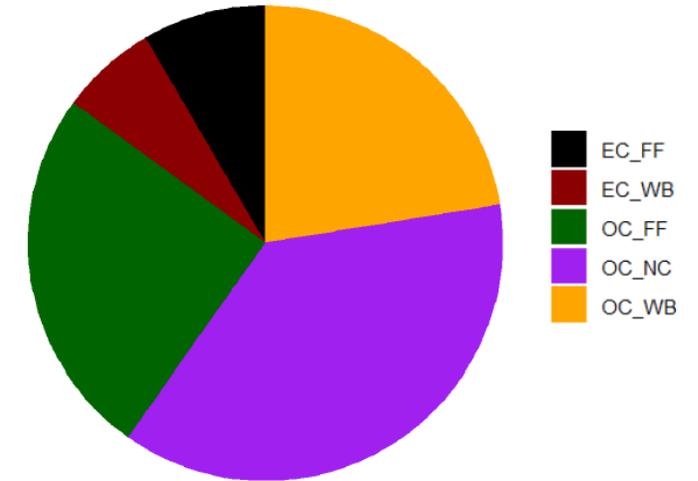
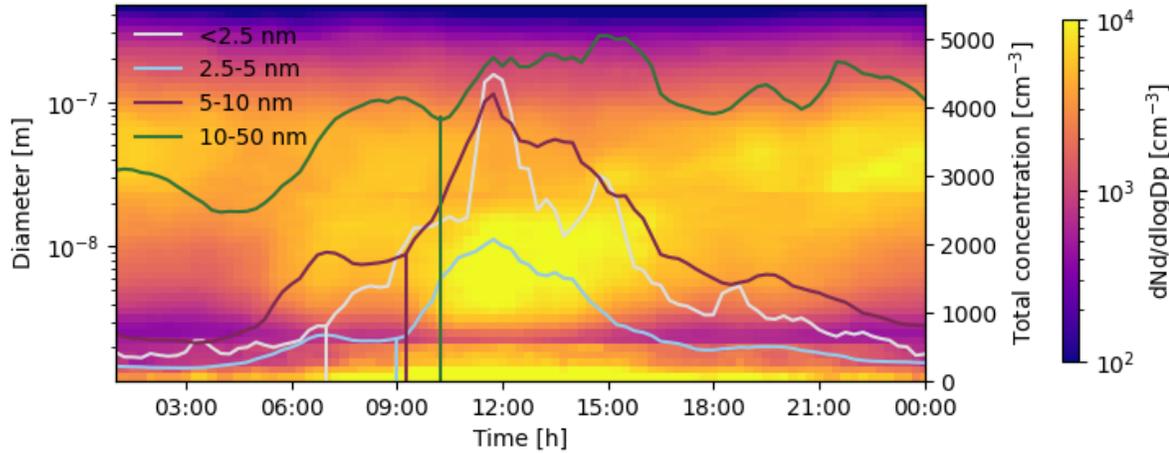
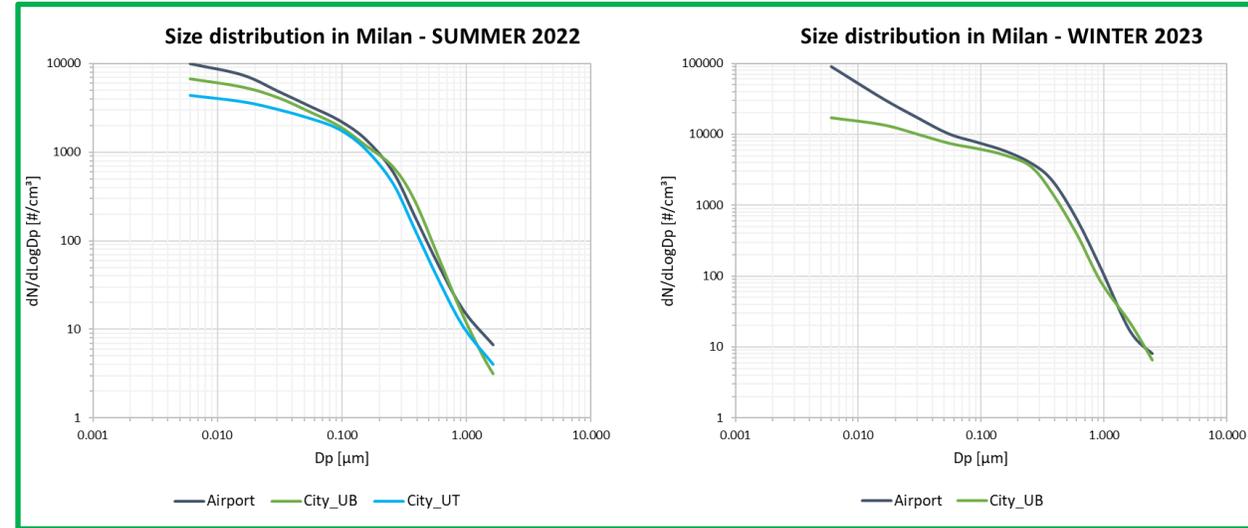
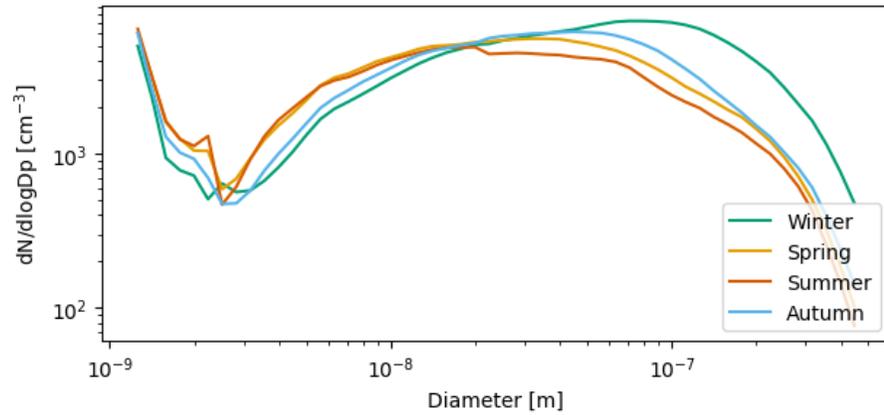
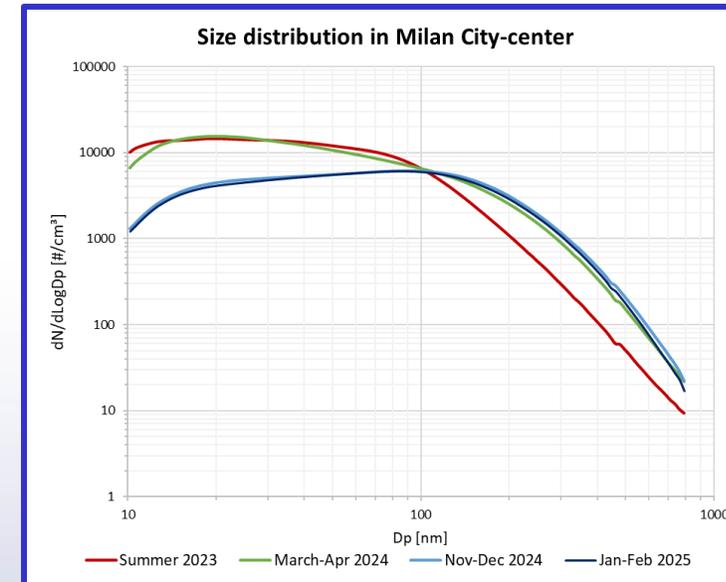


Figure 4.10 Mass apportionment by the MWAA model and relative contribution to total carbon (TC)

period	FF	WB	FF_AE33	WB_AE33
1/6/2023 – 31/10/2023	85 ± 5 %	15 ± 5 %	82 ± 4 %	18 ± 4 %
3/11/2023 – 7/3/2024	69 ± 10 %	31 ± 10 %	66 ± 6 %	34 ± 6 %



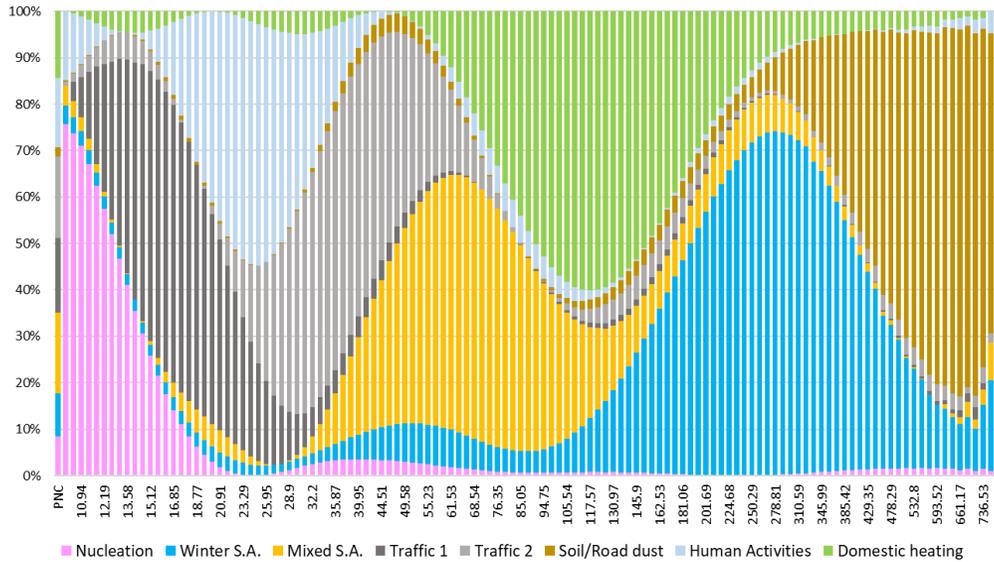
ELPI+



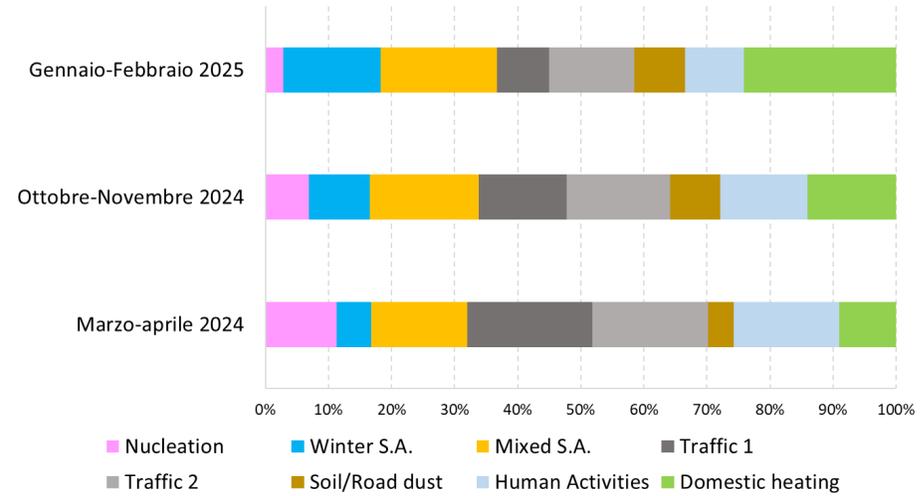
SMPS

Median particle number size distribution surface plot for the 80-100 percentile rank class and total concentrations for <2.5, 2.5-5, 5-10, 10-50 nm particles. The vertical lines represent the time when the concentrations increase due to NPF.

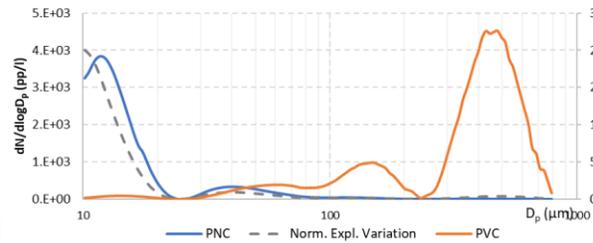
Factors fingerprint



Risultati SA UFP Milano



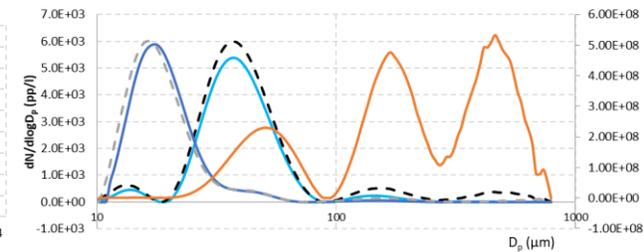
Milano Factor 1: Nucleation



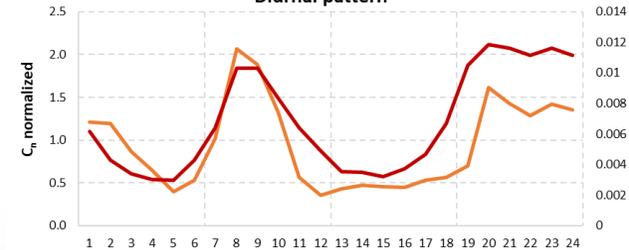
Milano Factor 1: Nucleation
Diurnal pattern



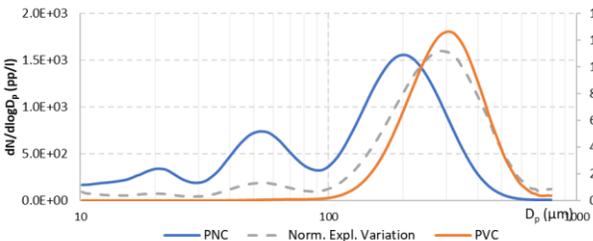
Milano Factor 4: Traffico 1 + 2



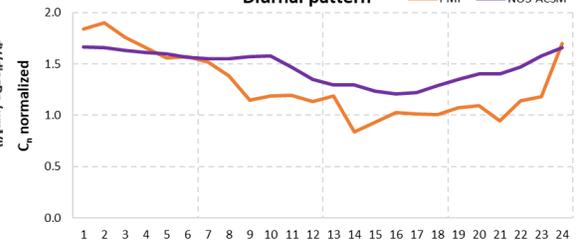
Milano Factor 5: Traffico 2
Diurnal pattern



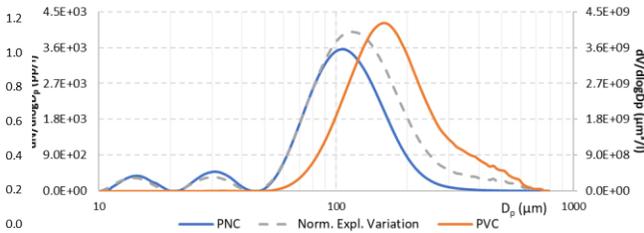
Milano Factor 2: Winter S.A.



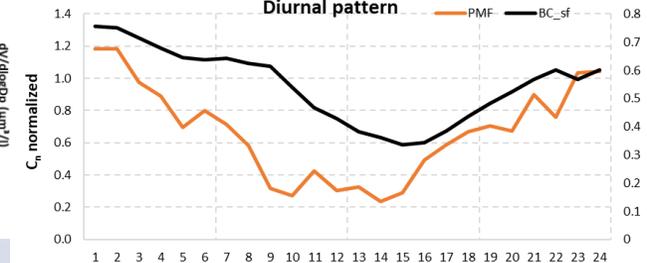
Milano Factor 2: Winter S.A.
Diurnal pattern



Milano Factor 8: Domestic Heating



Milano Factor 8: Domestic Heating
Diurnal pattern



Positive Matrix Factorization

EPA-PMF5

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}$$

Hopke, 2003

Input data:

- daily PM concentrations and chemical composition
- uncertainties by Polissar, 1998

Input data:

- Hourly UFP concentrations
- uncertainties by Ogulei et al., 2007

Positive Matrix Factorization

EPA-PMF5

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}$$

Hopke, 2003

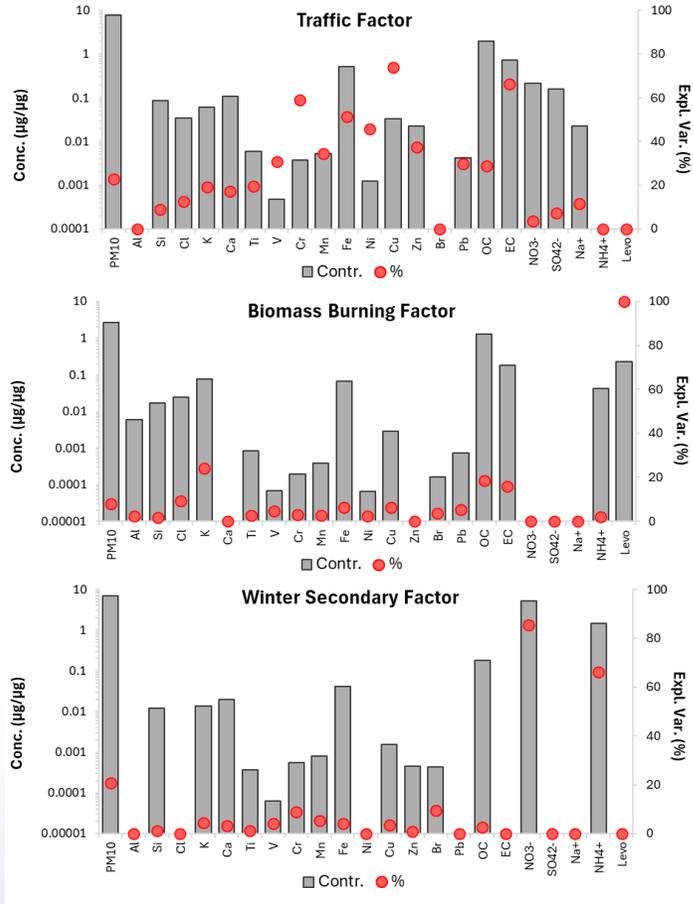
Input data: - daily PM concentrations and chemical composition

- uncertainties by Polissar, 1998

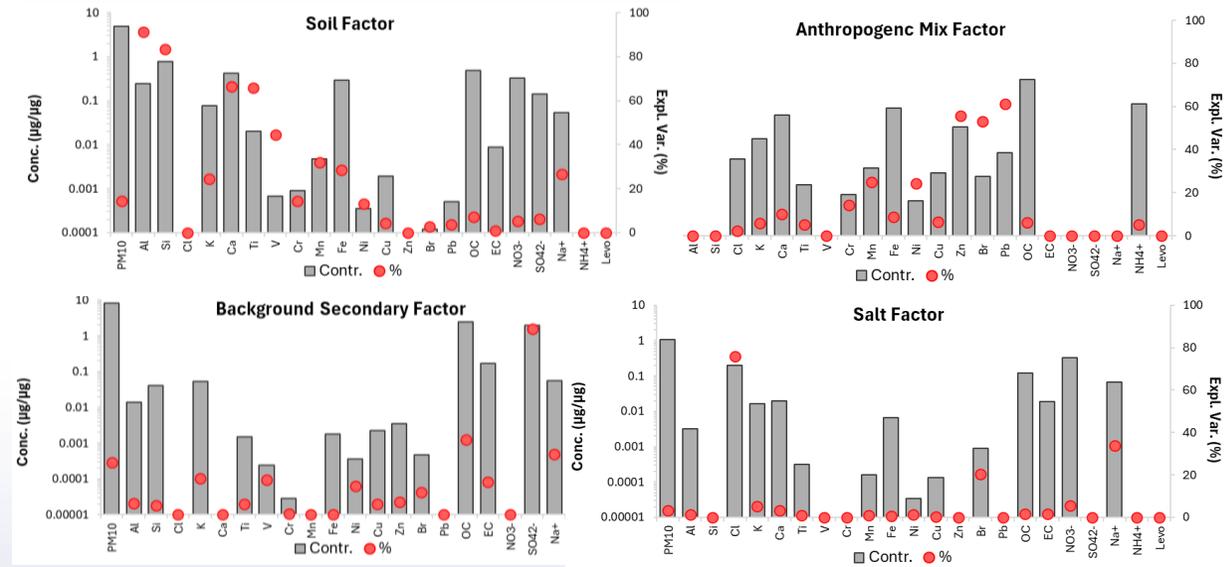
Complete dataset from 1st Jan 2013 to 31st Mar 2024 (1)

A sort of rolling approach: 2 years window size (total of 10 input dataset) (2)

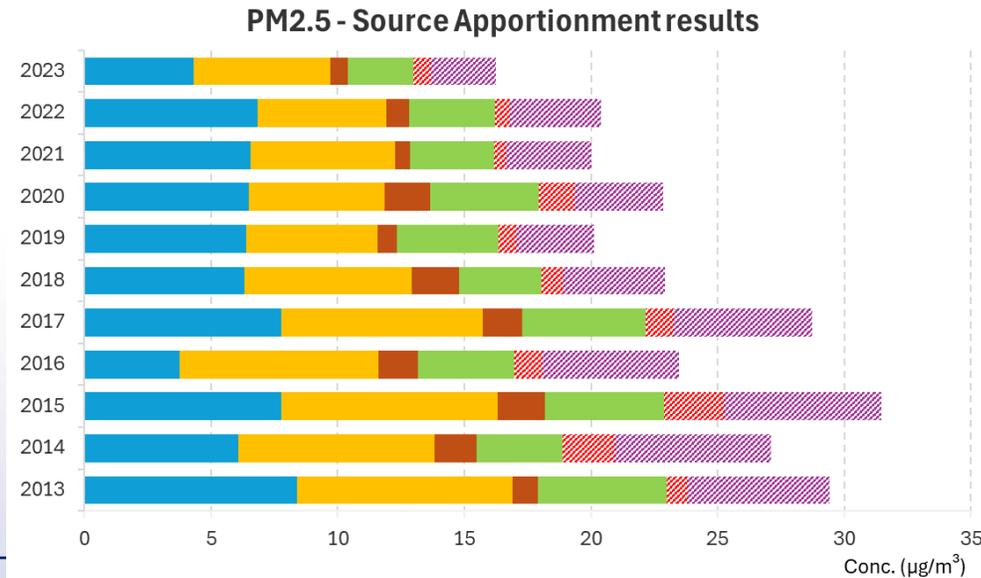
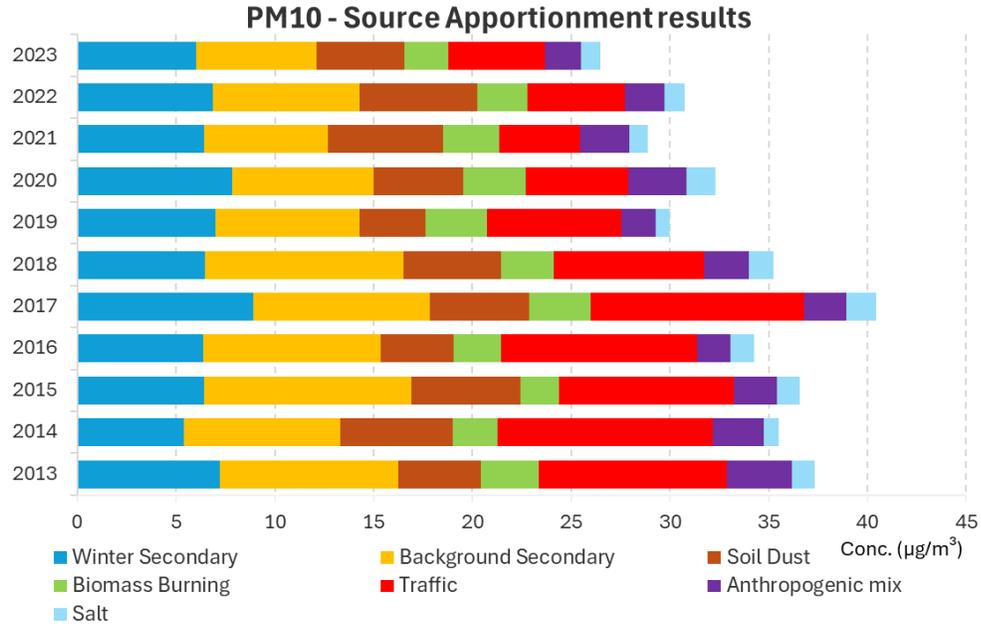
F-Matrix: Factors



- PM2.5 6 fattori
- PM10 7 fattori
- Risultati consistenti: profili dei fattori totalmente confrontabili.



1 PM10&PM2.5 SA results from 2013 to now

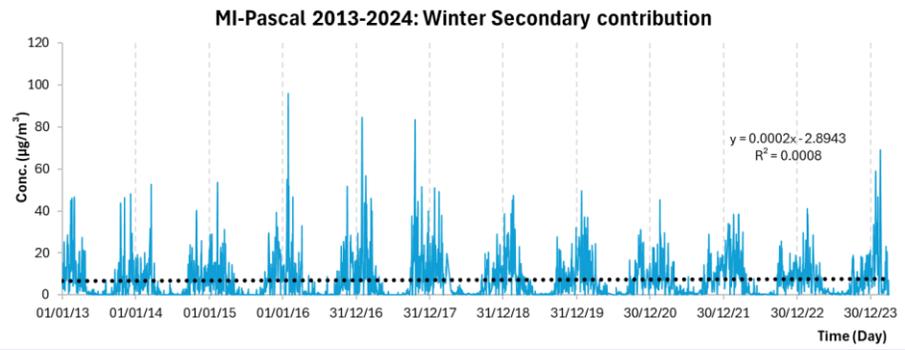
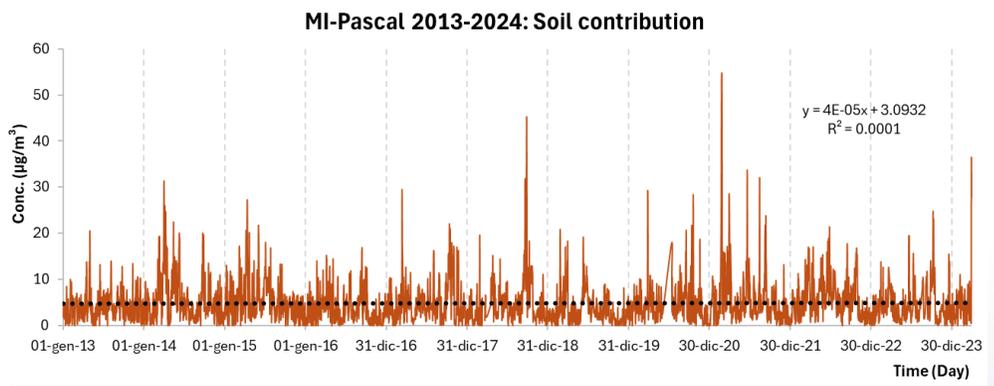
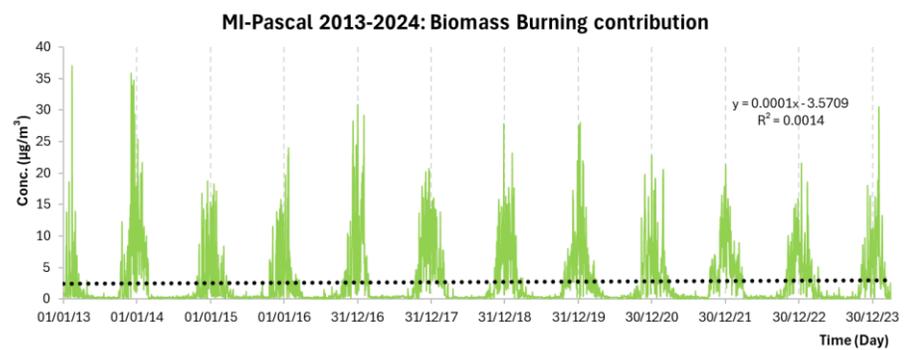
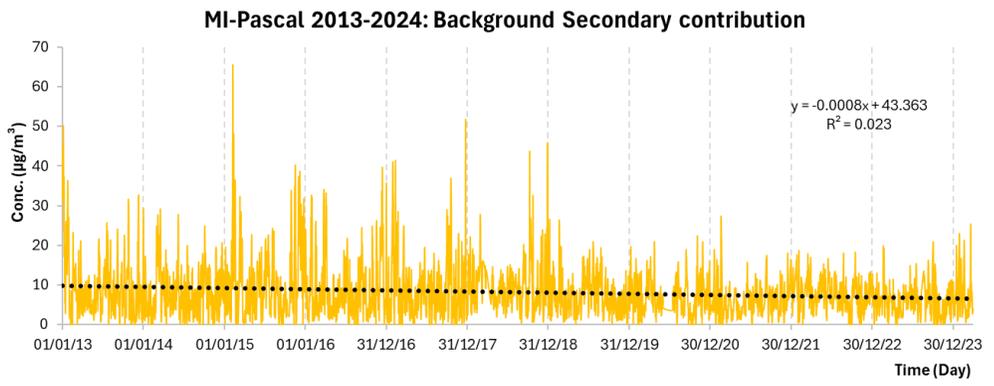
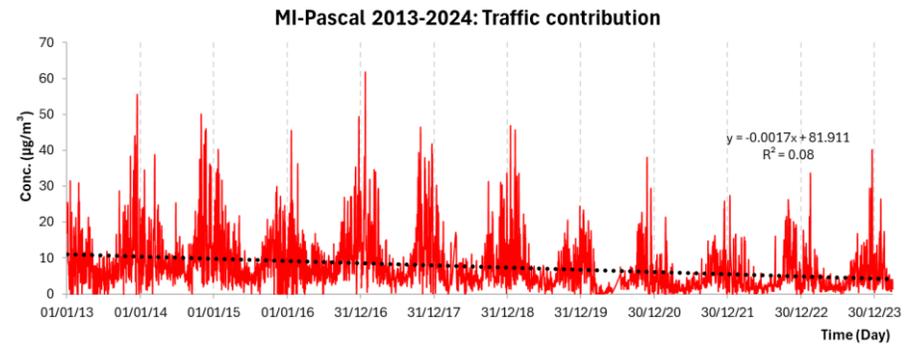


G-Matrix: Contributions

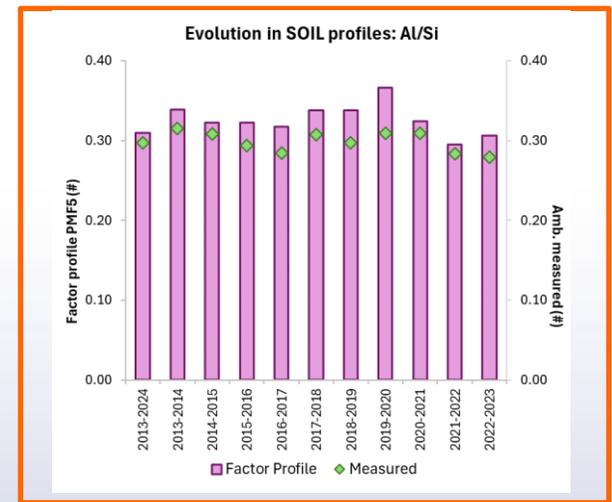
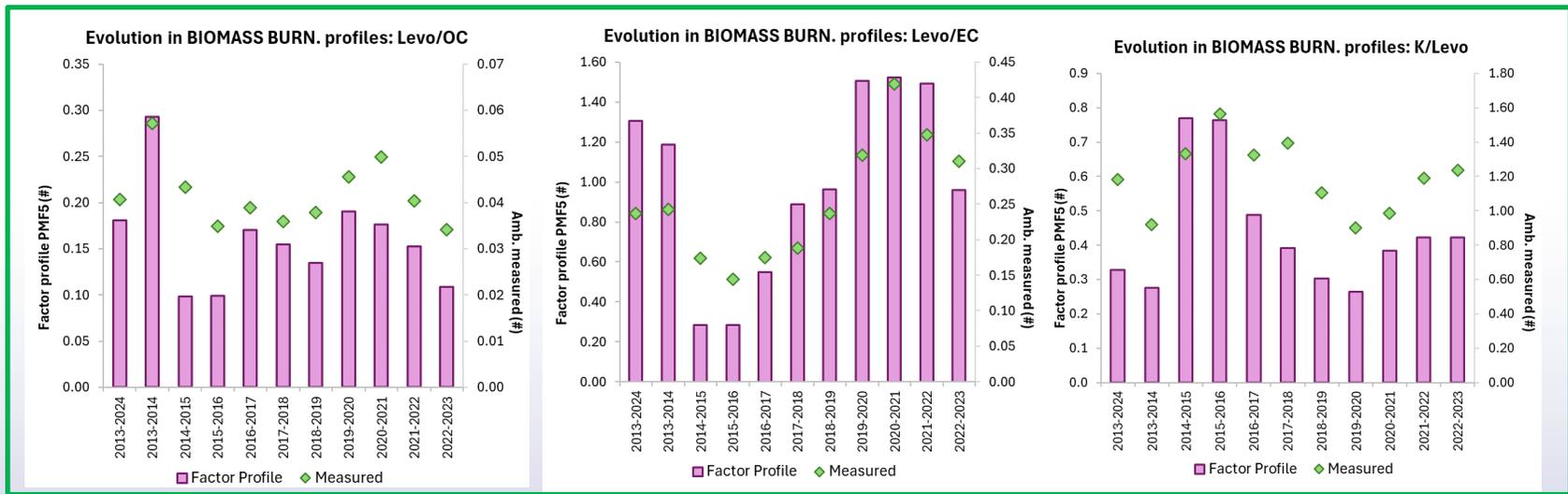
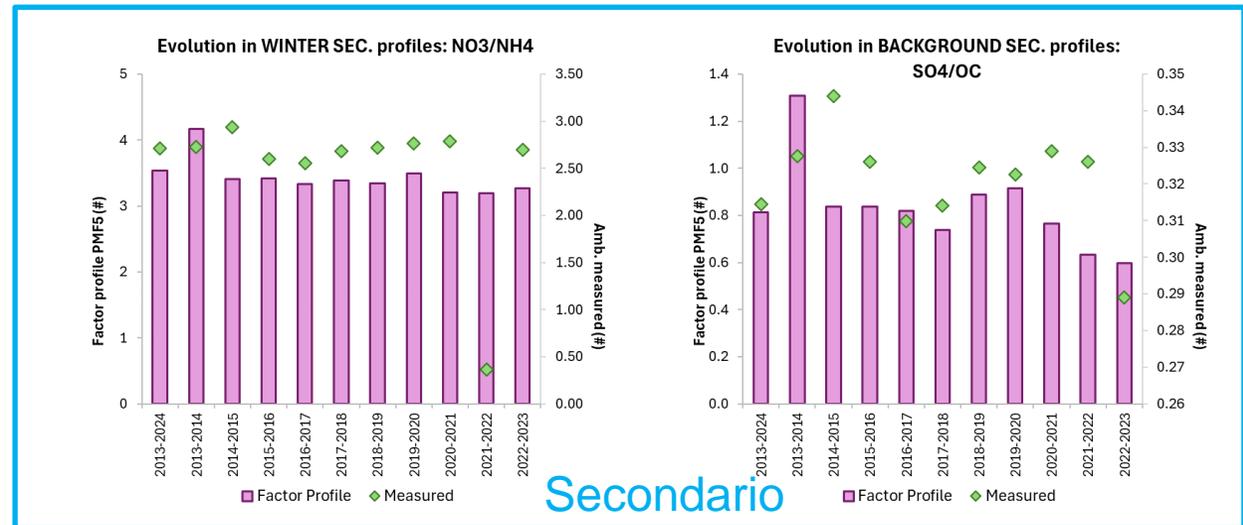
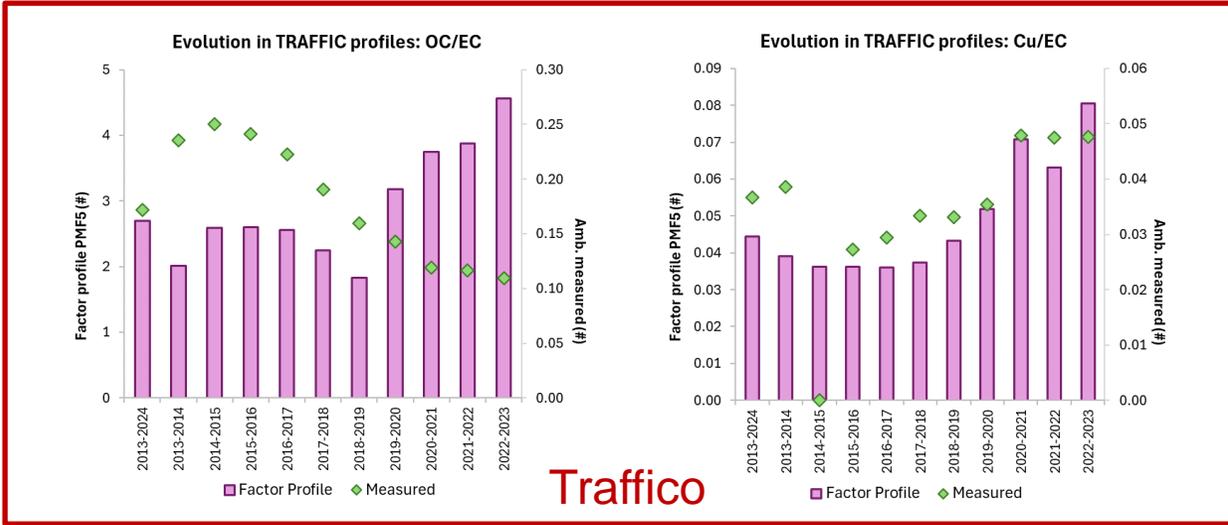
Mix Antropogenico: metalli derivanti da attività di vario tipo (produzione industriale), che non possono essere ulteriormente separati.

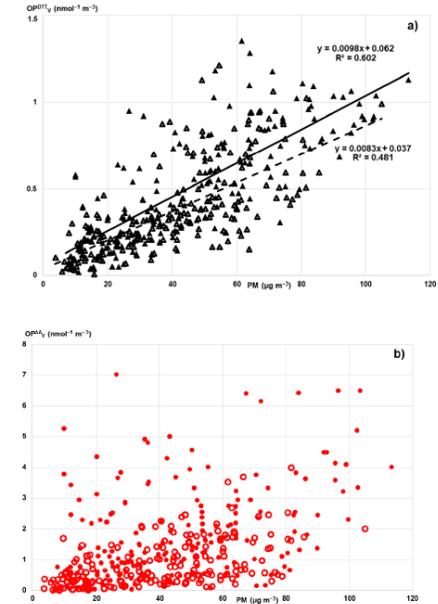
Sul dataset PM2.5, questo fattore raccoglie la maggior parte del traffico non-Exhaust; questo è il motivo per cui i 2 profili (Traffico e Mix Antropico nel PM2.5) non sono ben separati.

Trend storico dei fattori nel PM10



Risultati del Rolling approach





Pietrogrande et al., diversi paper tra i quali:

- ❖ The impact of COVID-19 Lockdown Strategies on Oxidative Properties of Ambient PM₁₀ in the Metropolitan Area of Milan, Italy,
- ❖ Seasonal and spatial variations of PM₁₀ and PM_{2,5} Oxidative Potential in five Urban and Rural Sites across Lombardia Region, Italy

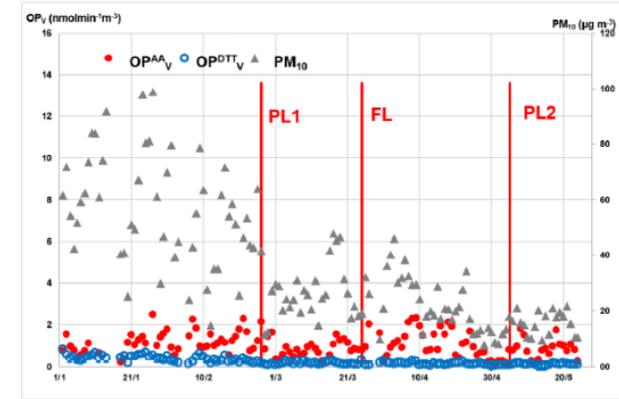
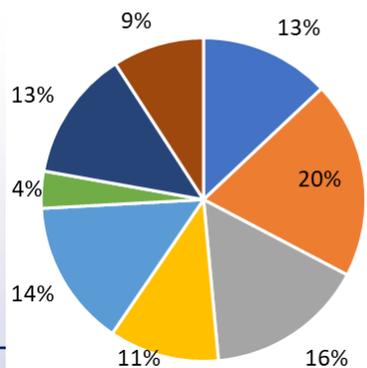


Figure 1. Temporal evolution along the whole investigated time of the extrinsic volume-based OP^{AA}_V (red points, left Y scale) and OP^{DTT}_V (blue circles, right Y scale) responses and the PM₁₀ concentrations (grey triangles, right Y scale). The vertical lines indicate the first day of each lockdown period, namely 26 February for PL1, 25 March for FL, and 5 May for PL2.

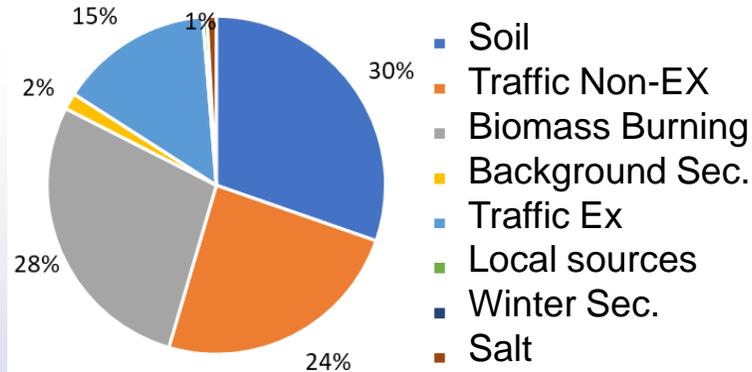
I tentativo di SA dell'OP seguendo approccio Cesari et al., 2019:

Milan UB

PM10 Source App.

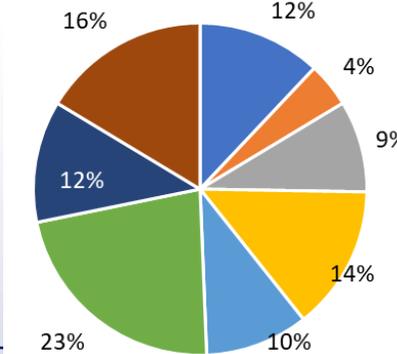


OP Source App.

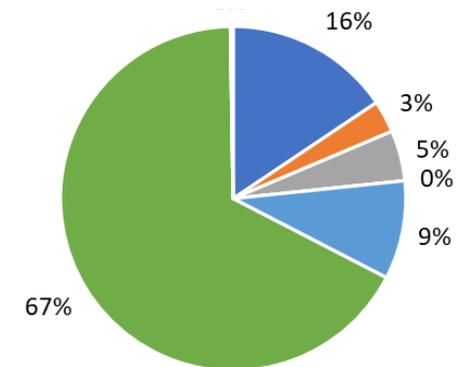


Bertonico RB

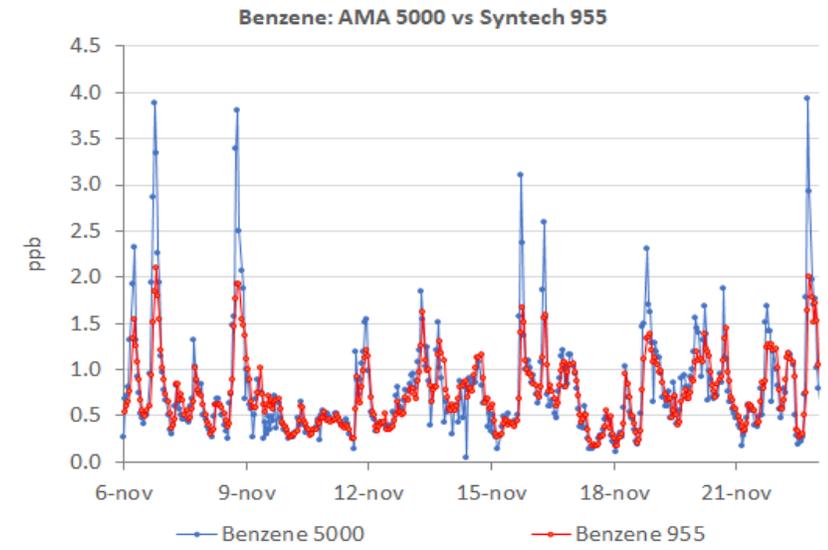
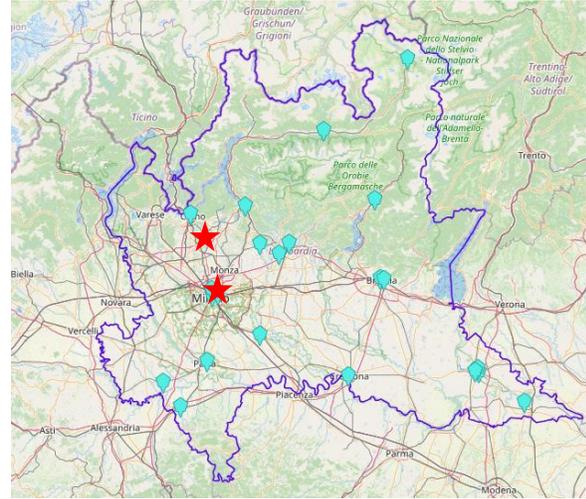
PM10 Source App.



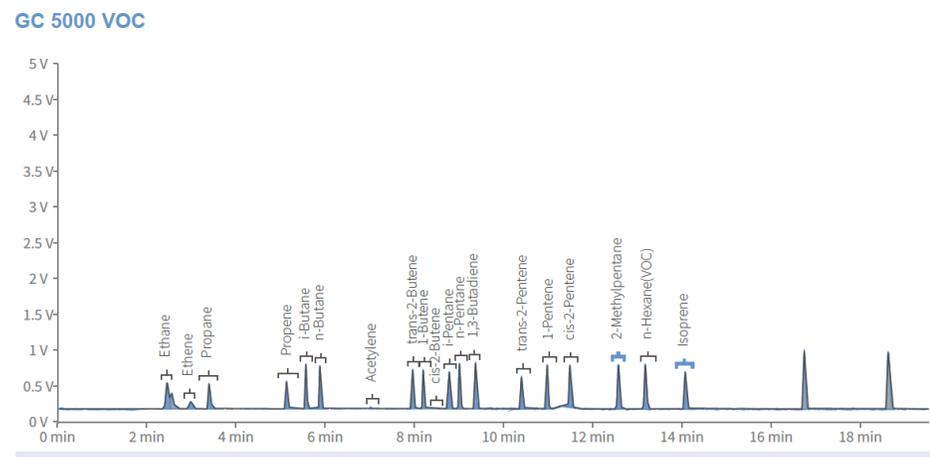
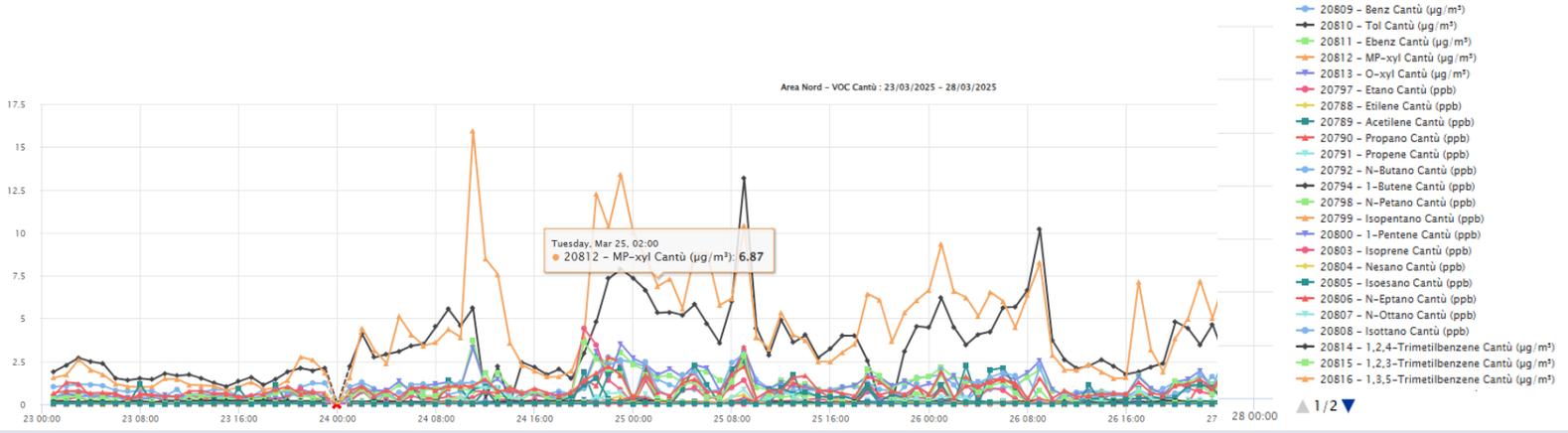
OP Source App.



- 23 BTX analyzers
- + 2 AMA GC 5000 BTX + GC 5000 VOC
- Milano
- Cantù (CO) sottovento alle emissioni



Calibrazione strumentale complessa e piuttosto costosa
In corso approfondimenti per applicazione Source Apportionment



Grazie per l'attenzione!

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