Caratterizzazione chimico-fisica del particolato a Milano: il ruolo delle diverse sorgenti primarie e secondarie

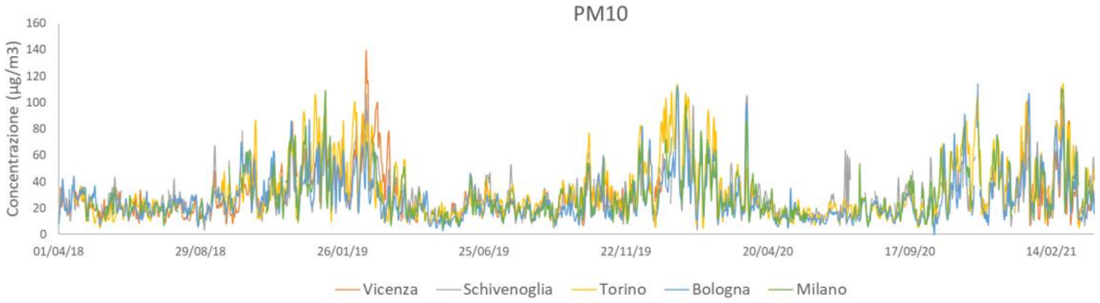
Cristina Colombi, Beatrice Biffi, Eleonora Cuccia, Luca D’Angelo, Umberto Dal Santo e Guido Lanzani

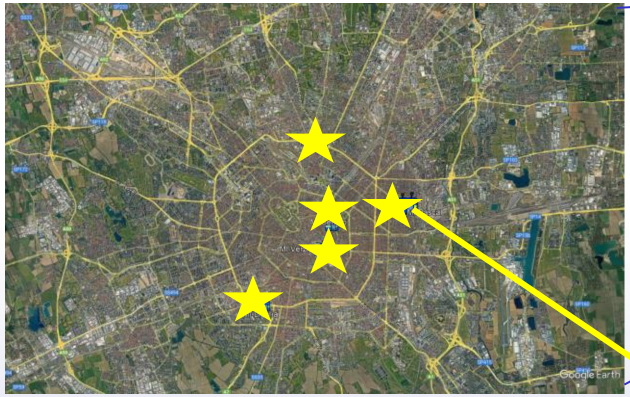
ARPA Lombardia

PM2026 – Napoli, 26-29 maggio 2026

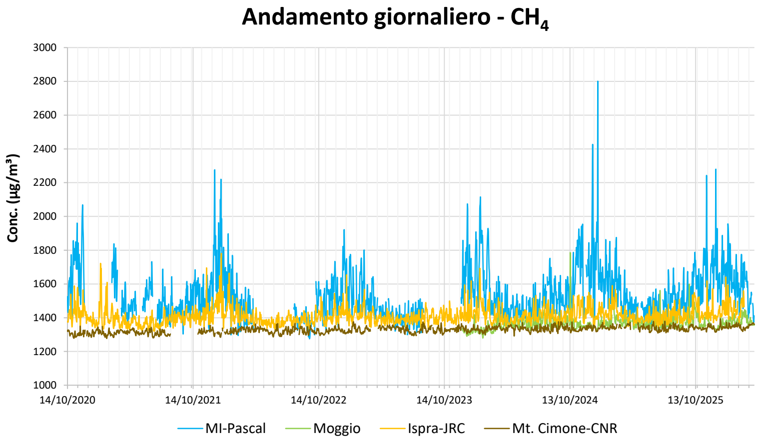
Starting Point

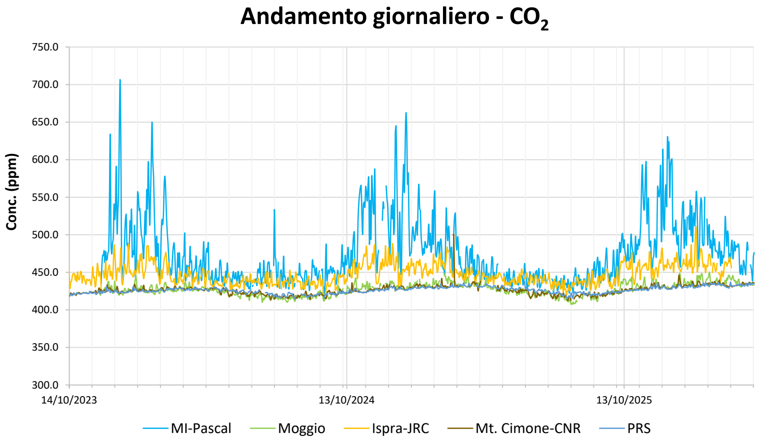
Due to its orography, the Po Valley is one of the European areas with the highest concentrations of pollutants. However, for many of these, a constant decrease in values has been noticeable for several decades.

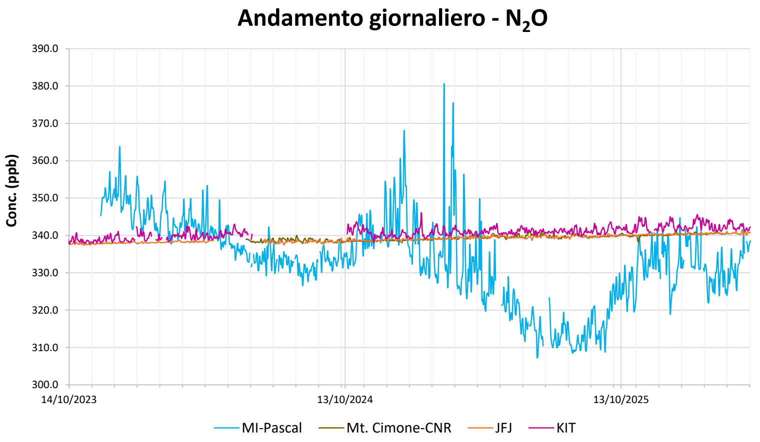


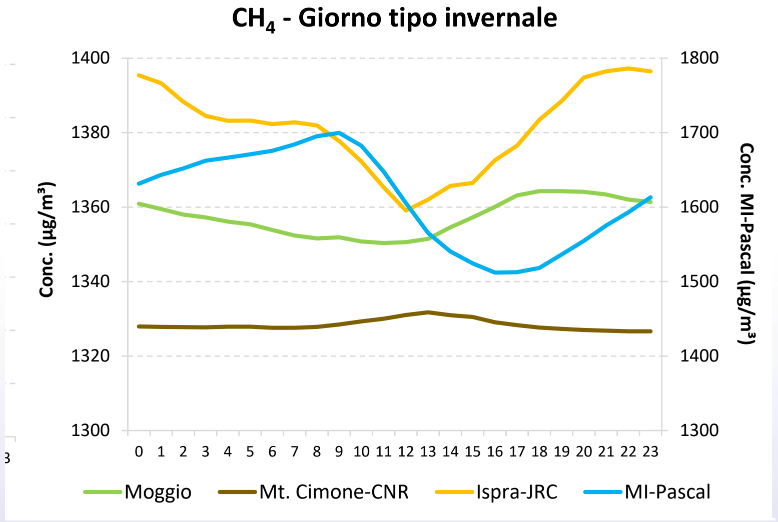


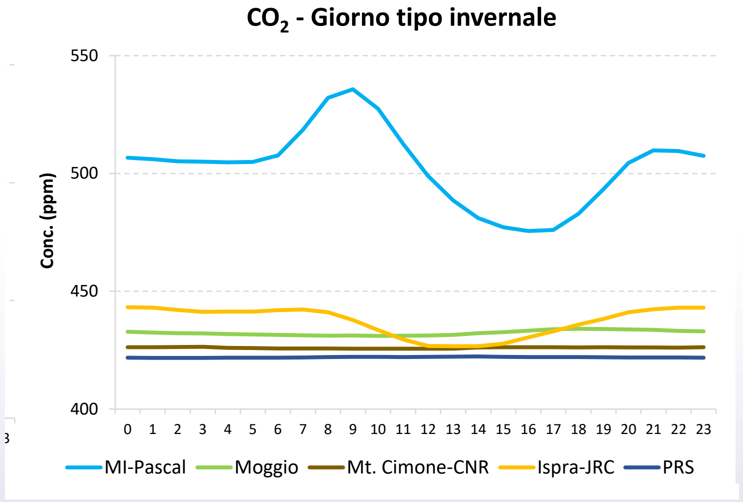
Gaseous pollutants → NO, NO2, NOx, SO2, O3, NH3, CO2, N2O, CH4

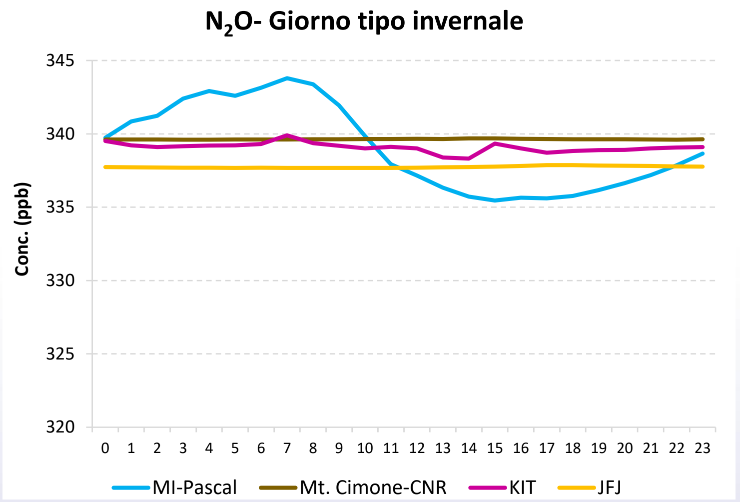












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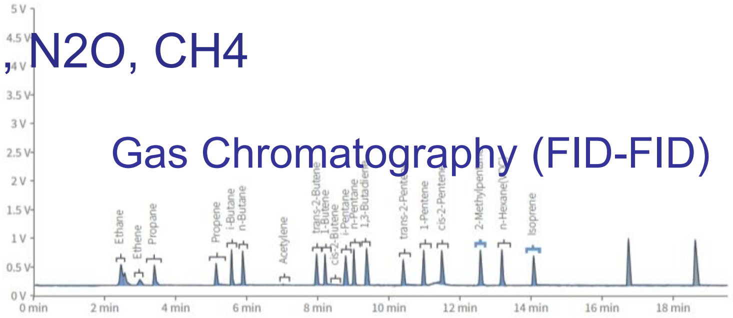
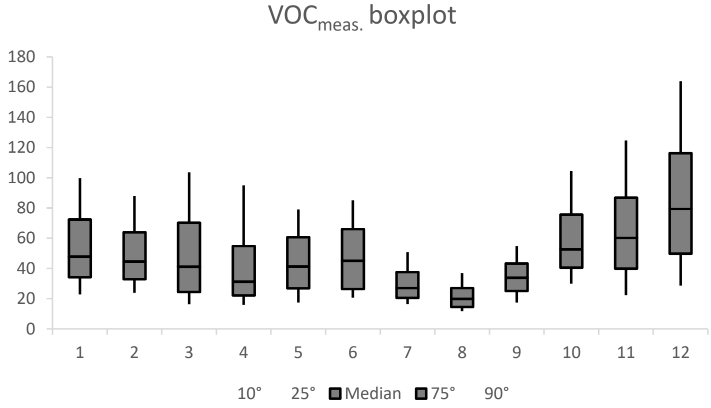
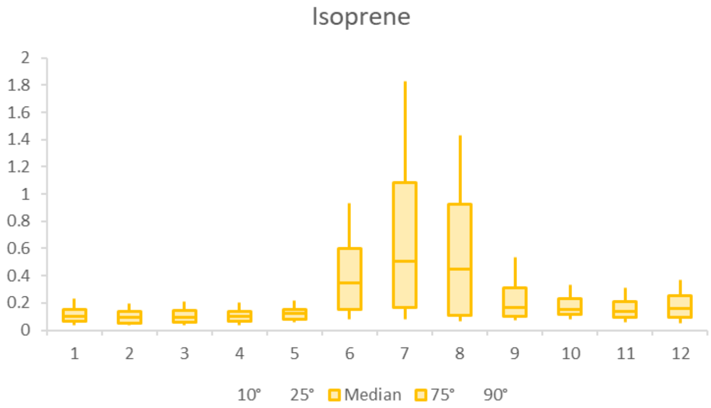
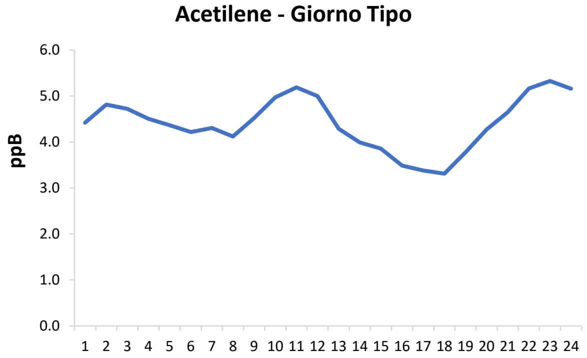
Gaseous pollutants → NO, NO2, NOx, SO2, O3, NH3, CO2, N2O, CH4

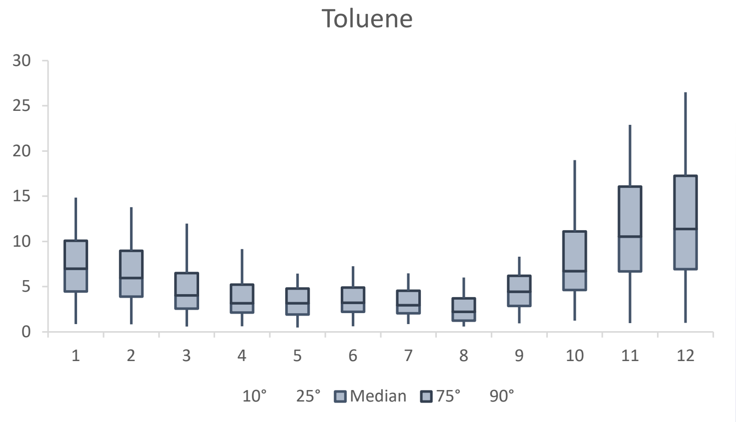
Volatile Organic Compounds → Gas Chromatography (FID-FID)

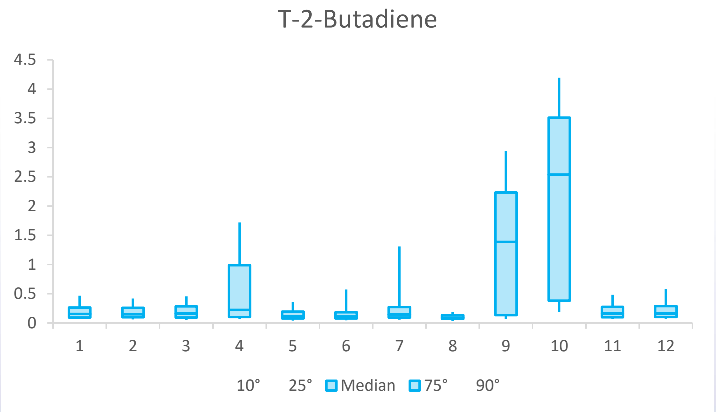


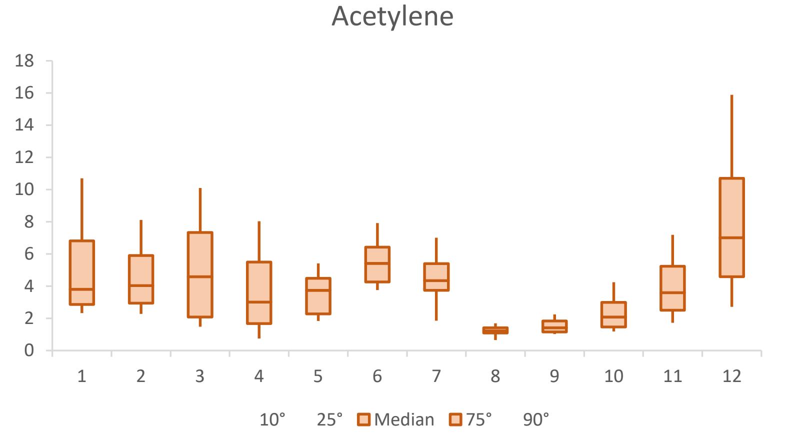












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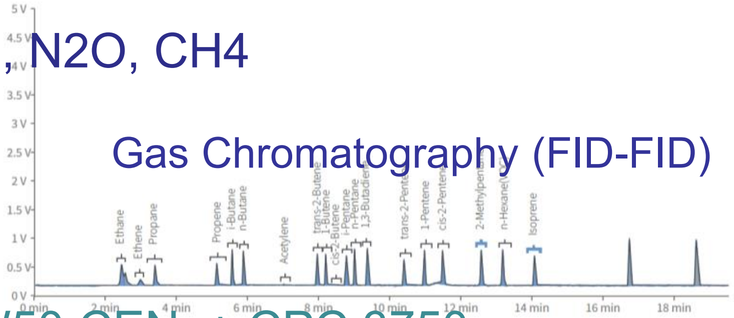
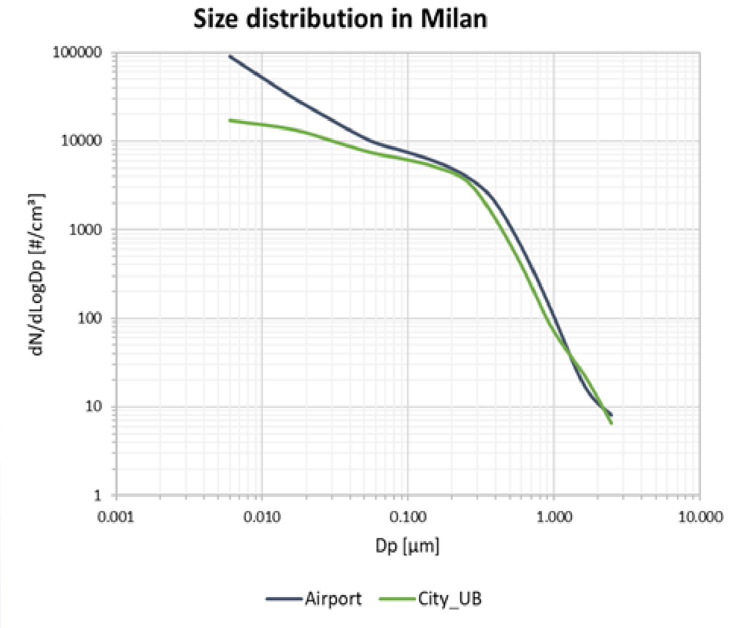


Gas Chromatography (FID-FID)

Volatile Organic Compounds →

Nanoparticles → d= 10-800 nm, SMPS 3938W50 CEN + CPC 3750

d = 6-10^4 nm, Elpi+



- *Poster, M. Agrò & WG2 IAS, Particolato ultrafine e new particle formation sul territorio italiano: un dataset della collaborazione IAS – Sessione di domani*
- *Poster, B. Biffi, Distribuzione dimensionale dell'aerosol atmosferico in un sito rurale e un sito urbano della Pianura Padana – Sessione odierna*

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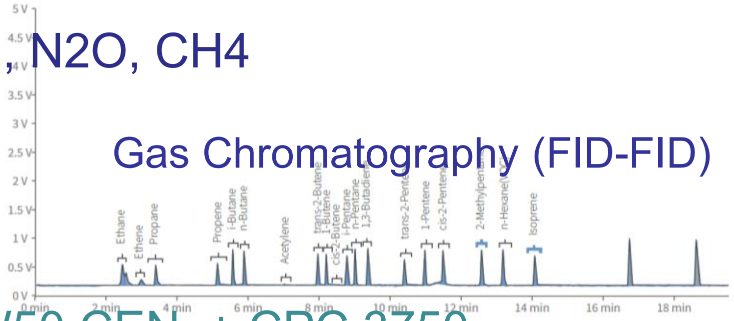

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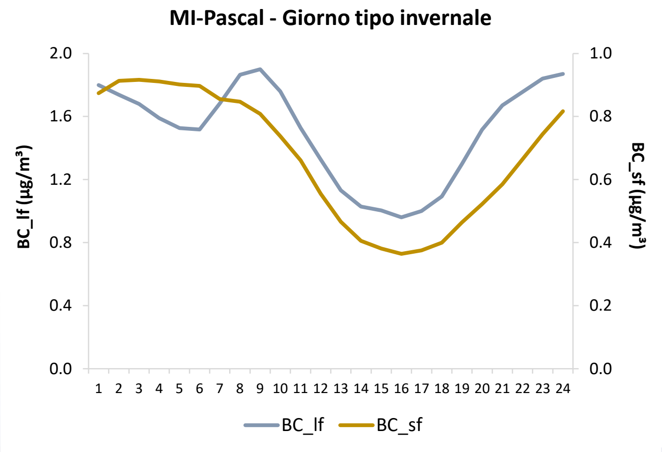
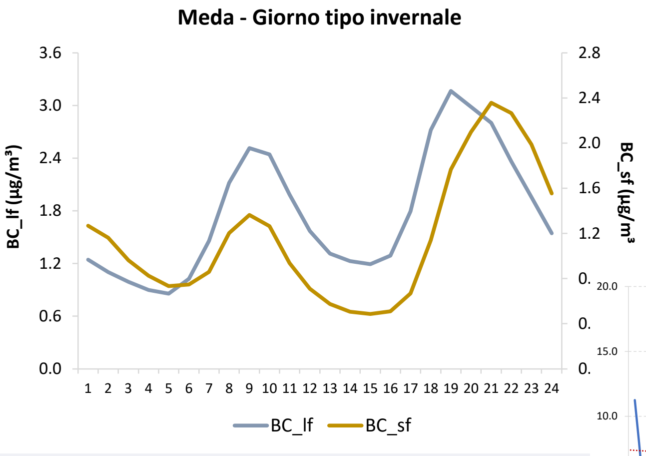
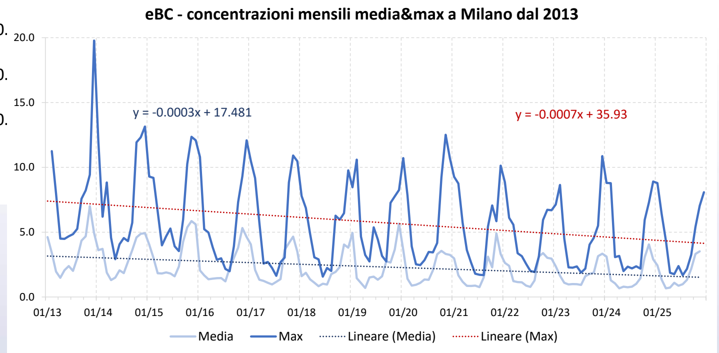
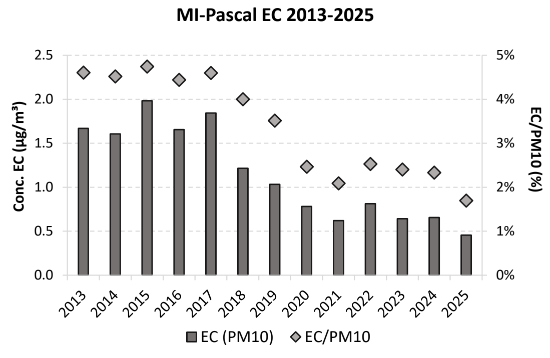




- Orale, S. Rimoldi, oggi 10:45
- Orale,V. Bernardoni, oggi 12:45
- Orale, S. Ozgen, giovedì 16:30





AQ in Milan: MI-Pascal

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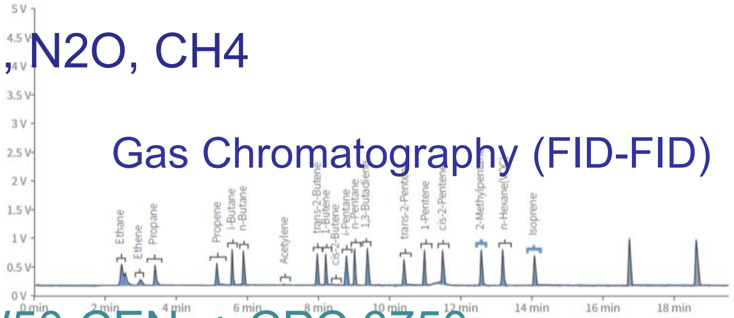

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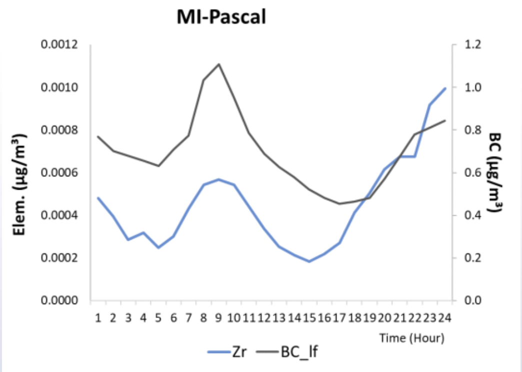
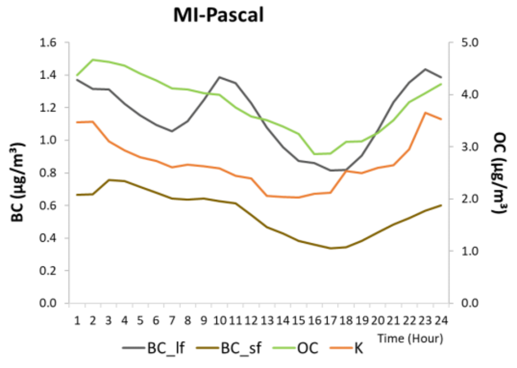
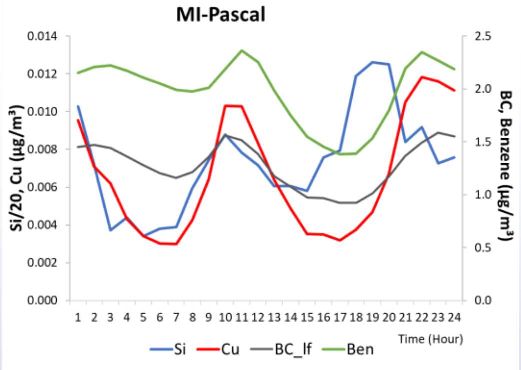
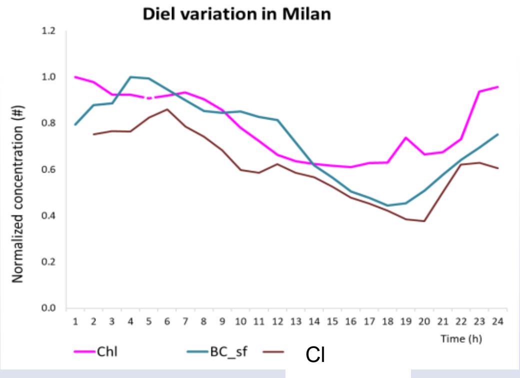
Elements (Xact) from PSI for 1 year

Elements (Xact) and MARGA ……. coming soon









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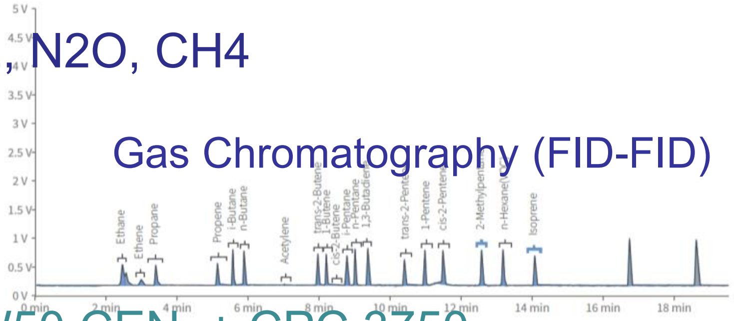

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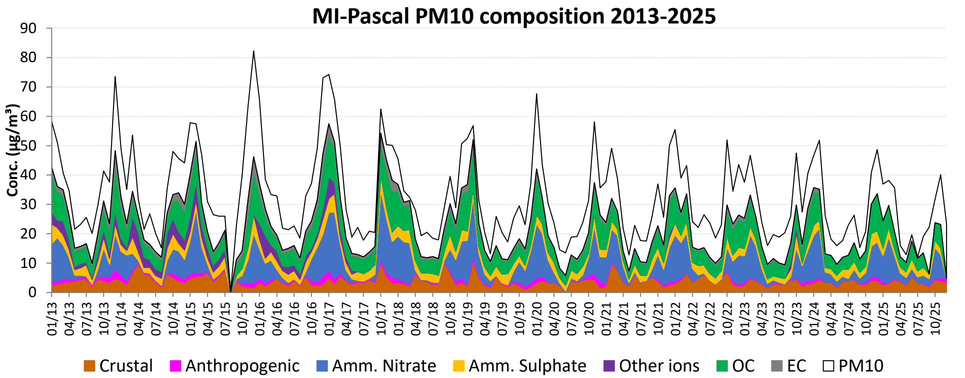
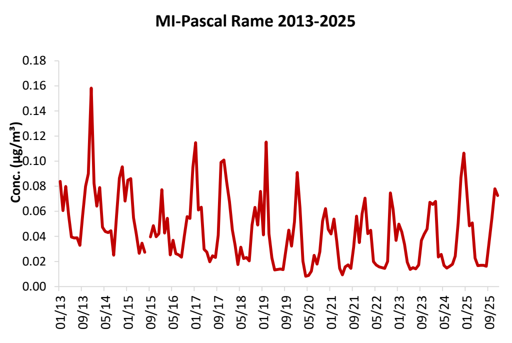
Elements (Xact) from PSI for 1 year

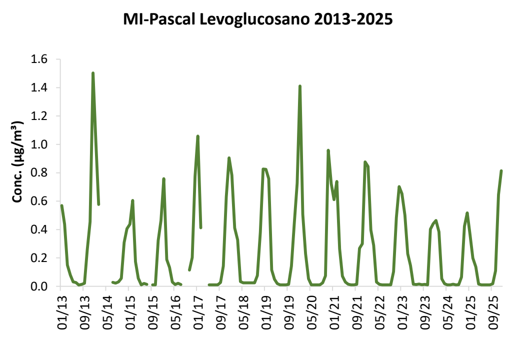
Elements (Xact) and MARGA ……. coming soon

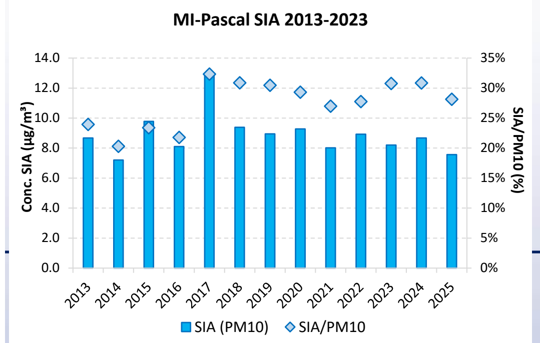
Daily PM & offline analysis → PM10&2.5 FAI-DC, 4 LVS PM10&PM2.5

Elements Z>11 (2 ED-XRF Panalitycal), ions and sugar (IC Metrohm), OC&EC (2 TOT/TOR Sunset)









Positive Matrix Factorization

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

Hopke, 2003

EPA-PMF5

Input data:
- daily PM10&2.5 concentrations and chemical comp.
- uncertainties by Polissar, 1998

DATALYSTICA - SOFI 9

Input data:
- Hourly PM conc. and chemical comp.
- uncertainties by Polissar, 1998

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

Input data:
- Hourly VOCs concentrations
- uncertainties by Polissar, 1998

PMF Other parameters

UFPs

Input data: 245 species x 10200 hours (Mar 2024 – Feb 2026) → n_{ij} >> 500.000 elements of matrix

Unc: Ogulei et al. (2007), Squizzato et al. (2019) and Hopke et al. (2024)

Unc. PNC = 3 x c_n (total variable)

$$s_{ij} = a_{ij} + C_3 * n_{ij}$$

$a_{ij} = 0.01(n_{ij} + \overline{n_{ij}})$

n_{ij} conc. sample i bin j

$\overline{n_{ij}}$ averaged conc. bin j

C_3 experimental constant ÷ [0.001; 0.15]

Atmos. Chem. Phys., 17, 12379–12403, 2017
https://doi.org/10.5194/acp-17-12379-2017

Atmospheric Chemistry and Physics

Sources of sub-micrometre particles near a major international airport

Mauro Masiol[1,2], Roy M. Harrison[1,a], Tuan V. Vu[1], and David C. S. Beddows[1]

ISSN: 0278-6826 (Print) 1521-7388 (Online) Journal homepage: http://www.tandfonline.com/loi/uast20

Modeling Source Contributions to Submicron Particle Number Concentrations Measured in Rochester, New York

David Ogulei , Philip K. Hopke , David C. Chalupa & Mark J. Utell

Environment International 135 (2020) 105345
Contents lists available at ScienceDirect
Environment International
journal homepage: www.elsevier.com/locate/envint

Source apportionment of particle number size distribution in urban background and traffic stations in four European cities

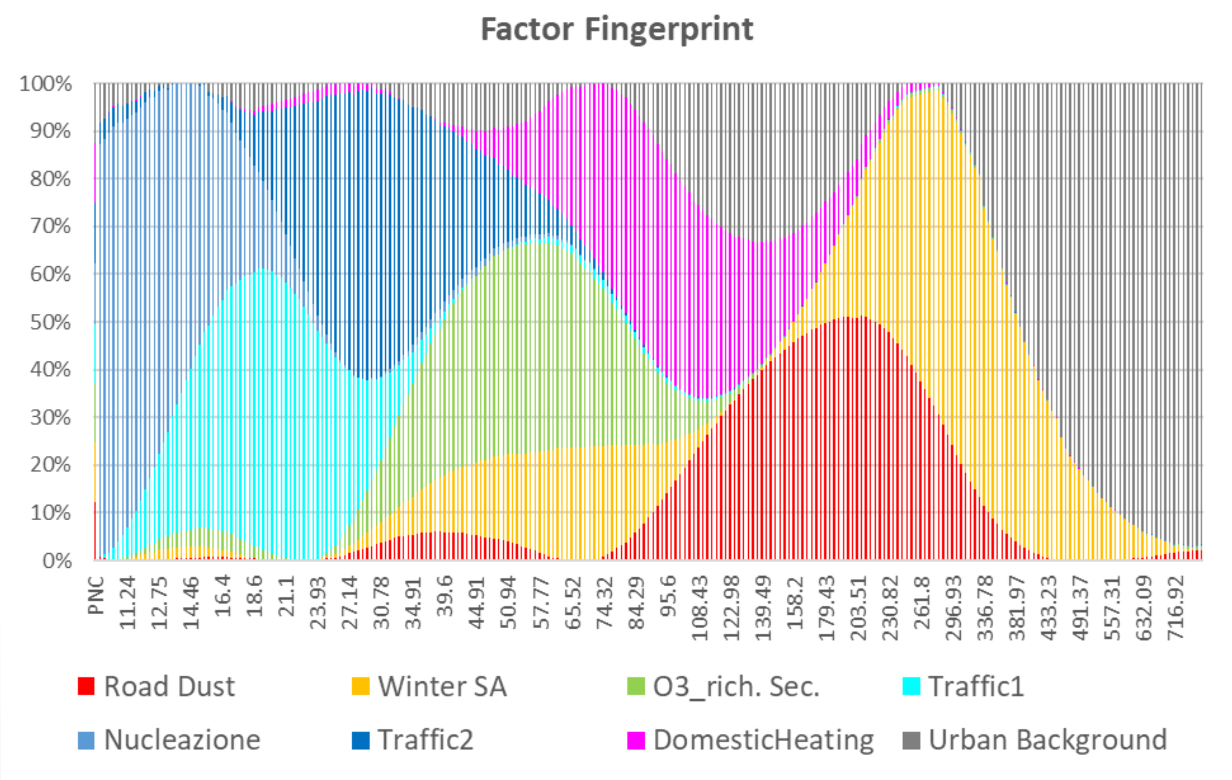
Ioar Rivas[a,*], David C.S. Beddows[b], Fulvio Amato[c], David C. Green[a], Leena Järvi[d,e], Christoph Hueglin[f], Cristina Reche[c], Hilkka Timonen[g], Gary W. Fuller[a], Jarkko V. Niemi[h], Noemí Pérez[c], Minna Aurela[g], Philip K. Hopke[i], Andrés Alastuey[c], Markku Kulmala[d], Roy M. Harrison[b,j], Xavier Querol[c], Frank J. Kelly[a]

https://www.arpalombardia.it/media/xnaj31q4/progetto-orio-relazione-20171231.pdf

+ RiUrbans_ST11

UFPs

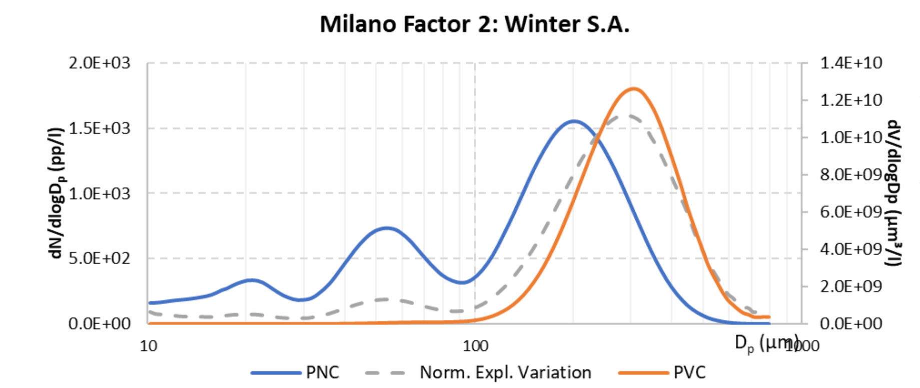
Best solution: 8 Factors

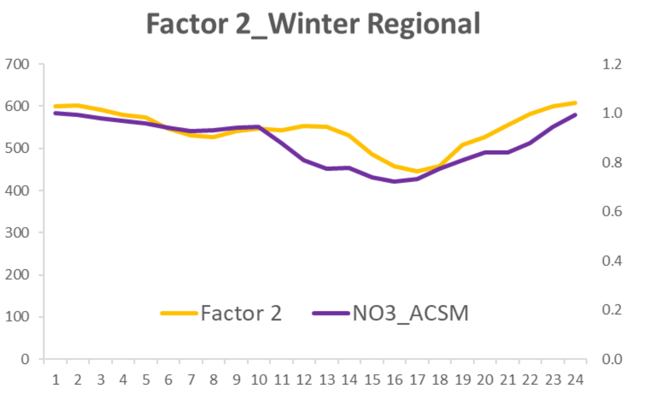


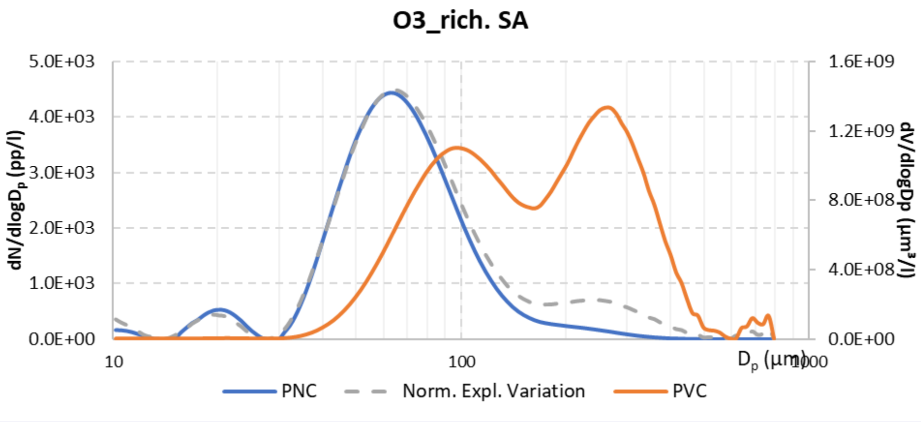
- Nucleation
- Domestic Heating
- Traffic 1
- Traffic 2
- Winter Regional Sec. Aerosol
- O3-rich. Secondary
- Road Dust
- Urban Background

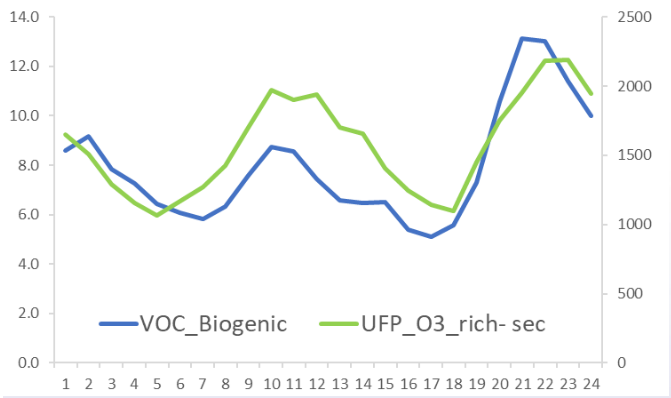
UFPs

Best solution: 8 Factors









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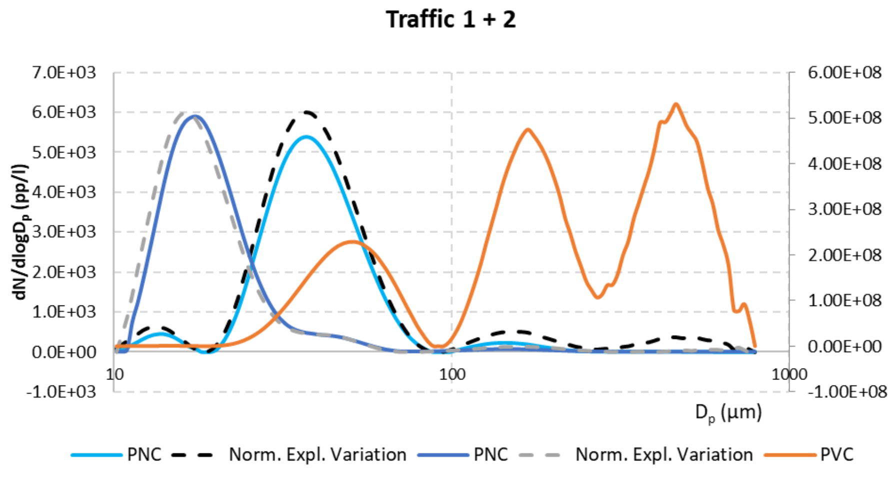

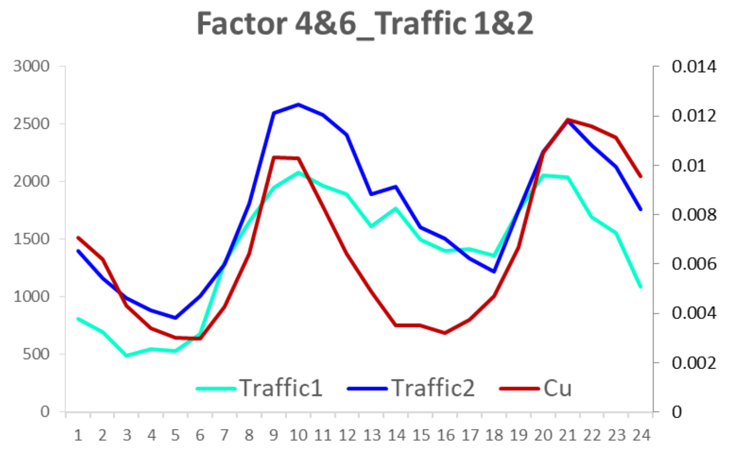

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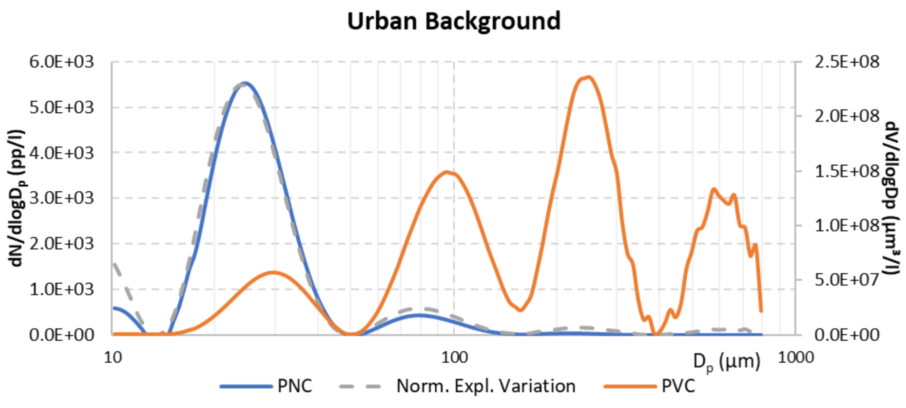

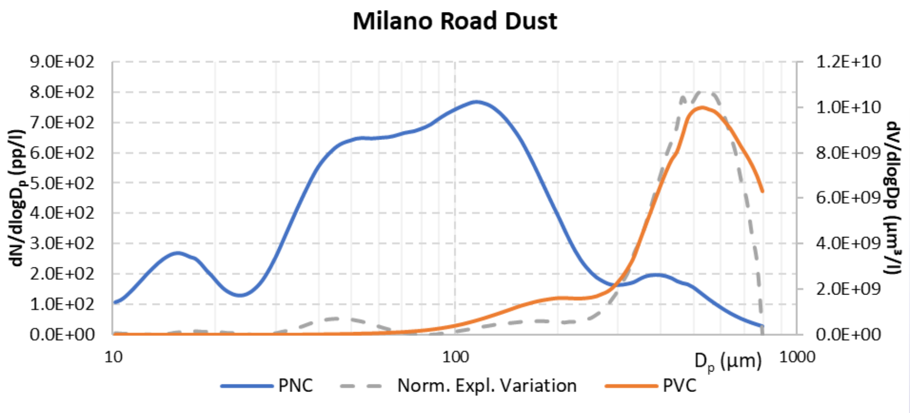

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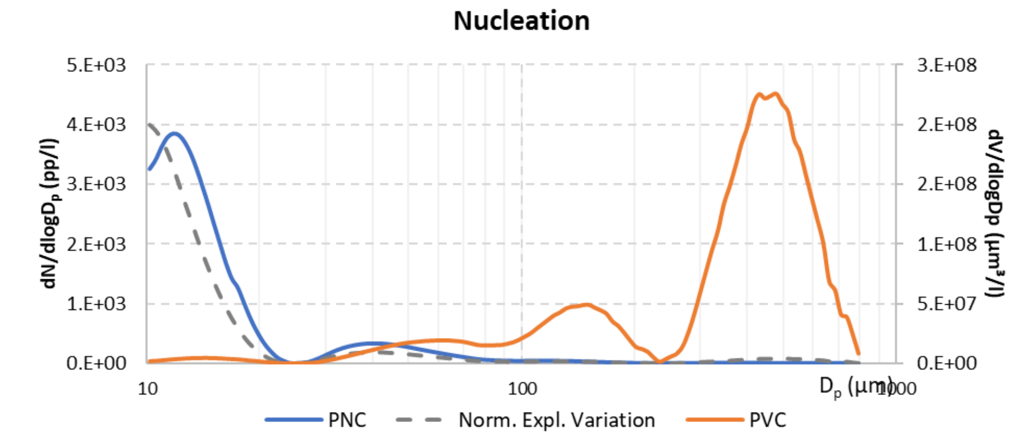

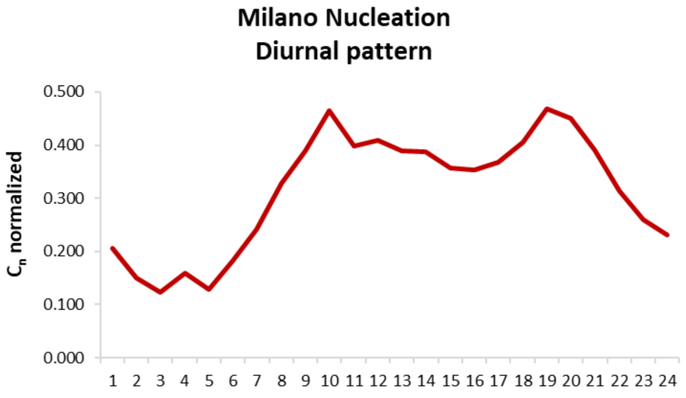

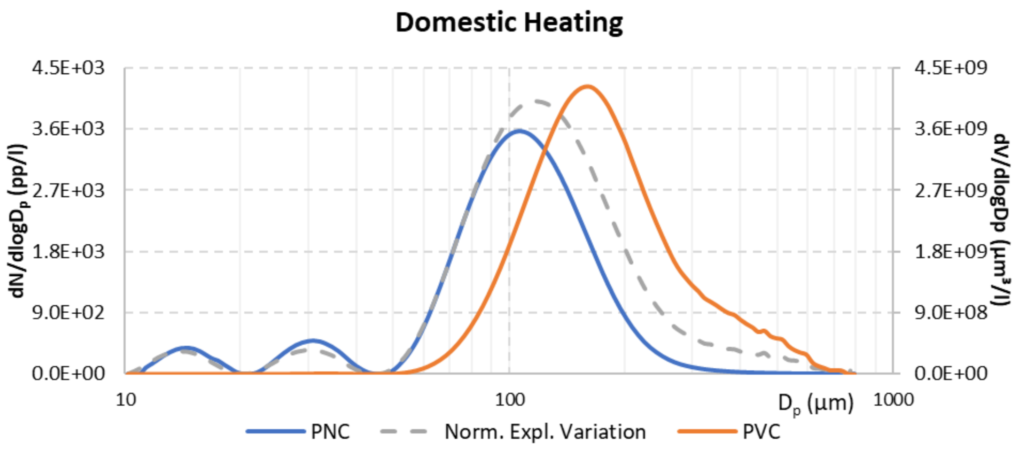

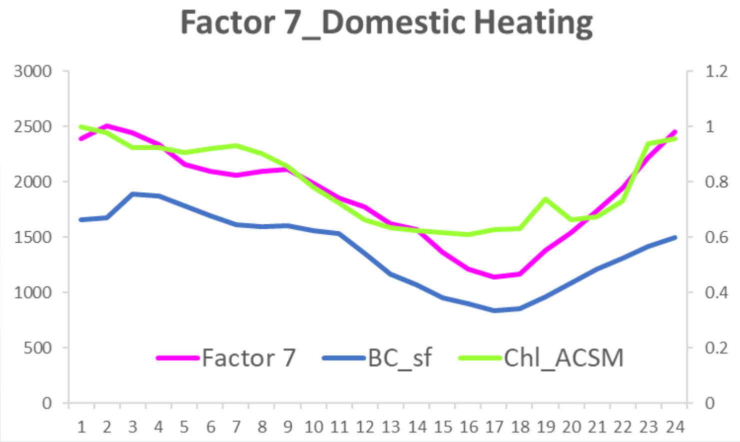

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VOCs

The possible **outliers** have to be checked by applying the lognormal law. If a value is detected as a possible outlier, this does not mean that the value is invalid (QA/QC measures should apply), but uncommon concentrations considered as outliers disrupt the performance of the PMF analysis and have to be ignored from the database used for PMF.

<u>Input data</u>: 29 species x 9239 hours (Feb. 2024 - Apr. 2025)
11 Alkanes, 8 Alkenes, 1 Alkyne, 8 Aromatics and Isoprene

<u>Unc</u>: + ACTRIS guideline (WP3 / Deliverable 3.17)
+ RiUrbans_ST11

calculated taking into account random and systematical errors during the analysis method. These were identified as errors of the integration of the peaks, of the reproducibility of the calibrations and uncertainty of the referee concentrations

$$u\chi^2_{sample} = u\chi^2_{prec} + u\chi^2_{cal} + u\chi^2_{instr} + u\chi^2_{sampling}$$

- ✓ Reproducibility
- ✓ Unc. calibration gas
- ✓ Systematic errors of the system

Atmos. Chem. Phys., 25, 5977–5999, 2025
https://doi.org/10.5194/acp-25-5977-2025

Atmospheric Chemistry and Physics

Volatile organic compound sources and impacts in an urban Mediterranean area (Marseille, France)

Marvin Dufresne[1,2], Thérèse Salameh[1], Thierry Leonardis[1], Grégory Gille[3], Alexandre Armengaud[3], and Stéphane Sauvage[1]

Journal of Hazardous Materials 459 (2023) 132138
Contents lists available at ScienceDirect
Journal of Hazardous Materials
journal homepage: www.elsevier.com/locate/jhazmat

Research Article

Source apportionment of consumed volatile organic compounds in the atmosphere

Yao Gu[a,b], Baoshuang Liu[a,b,*], He Meng[c], Shaojie Song[a,b], Qili Dai[a,b], Laiyuan Shi[c], Yinchang Feng[a,b], Philip K. Hopke[d,e]

Science of the Total Environment 906 (2024) 167159
Contents lists available at ScienceDirect
Science of the Total Environment
journal homepage: www.elsevier.com/locate/scitotenv

Identification of volatile organic compounds and their sources driving ozone and secondary organic aerosol formation in NE Spain

Marten in 't Veld[a,b,*], Roger Seco[a], Cristina Reche[a], Noemi Pérez[a], Andres Alastuey[a], Miguel Portillo-Estrada[c], Ivan A. Janssens[c], Josep Peñuelas[d,e], Marcos Fernandez-Martinez[c,d,e], Nicolas Marchand[f], Brice Temime-Roussel[f], Xavier Querol[a], Ana Maria Yáñez-Serrano[a,d,e]

Aerosol and Air Quality Research
ORIGINAL RESEARCH
https://doi.org/10.4209/aaqr.220289

Source Apportionment of VOCs and O_3 Production Sensitivity at Coastal and Inland Sites of Southeast China

Gaojie Chen[1,2,3], Taotao Liu[1,2,3], Xiaoting Ji[1,2,3], Ke Xu[1,2,4], Youwei Hong[1,2,3*], Lingling Xu[1,2], Mengren Li[1,2], Xiaolong Fan[1,2], Yuping Chen[1,2,3], Chen Yang[1,2,3], Ziyi Lin[1,2,3], Weiguo Huang[5], Jinsheng Chen[1,2*]

VOCs

Different runs: 1 on the complete dataset and 4 in each season

Best solution: 6 Factors

- Vehicle Exhaust: Alkanes C6-C9 (Isoenano 62%, N-Ottano 58%), Benzene (< 20%),
- Fuel Evaporation: 1-Pentene 70%, Acetylene 32%
- Gasoline Evaporation: Isopentane 60%
- Fugitive ONG+LPG: Ethane 58%, Etylene 66%, Acetylene 53%, Propene 50%
- Comb. Source: Trans-2-butene 72%, Cis-2-butene 64%, aromatics 52%
- Biogenic/Regional Background: Isoprene 40-100%, Ethane 28%, Propane 47%, Etylene 31%, Benzene 33%

R^2= 0.97, Slope= 0.95

PMF Other parameters

VOCs

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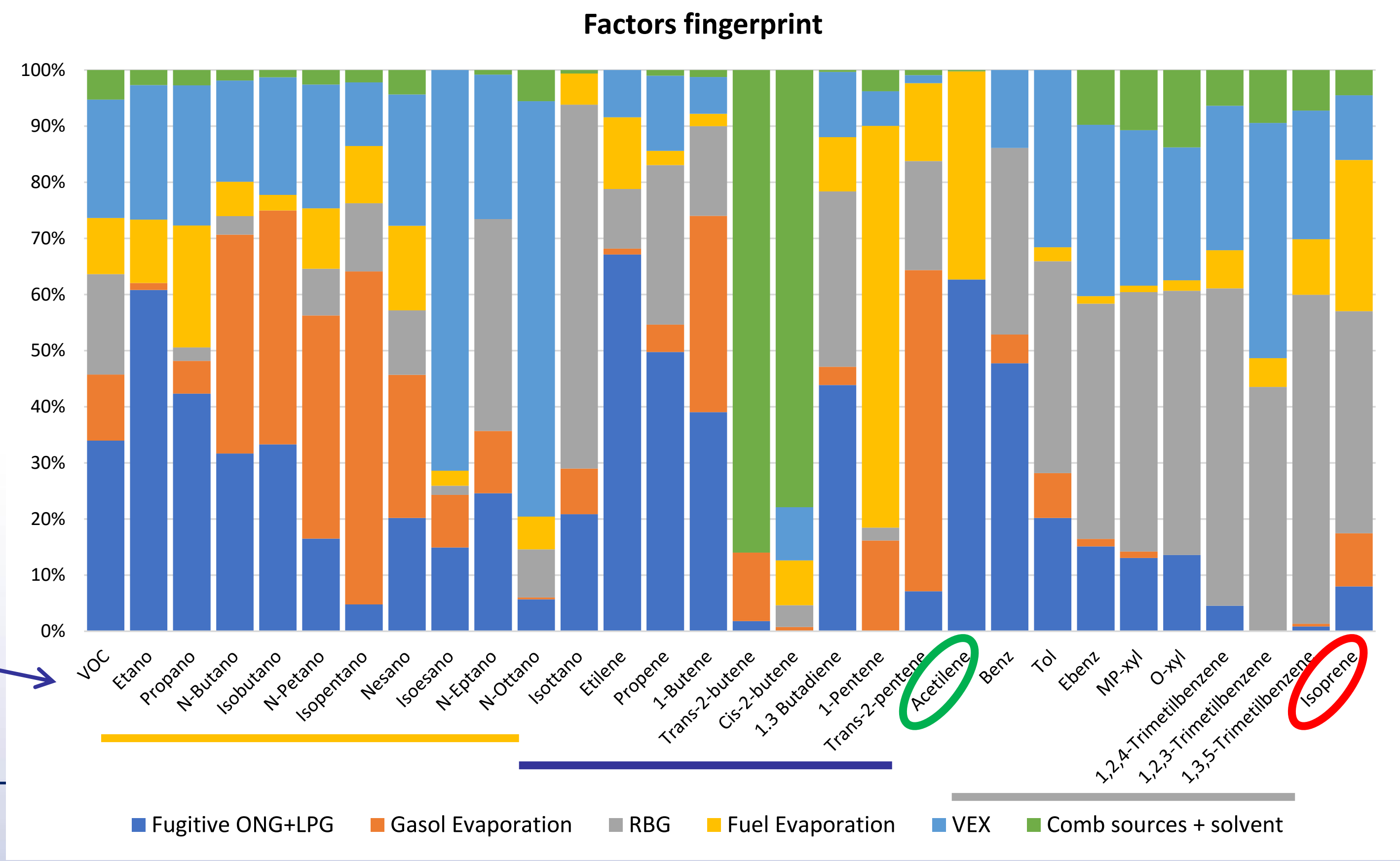
- Fugitive ONG+LPG: Ethane 58%, Etylene 66%, Acetylene 53%, Propene 50%
- Comb. Source: Trans-2-butene 72%, Cis-2-butene 64%, aromatics 52%
- Biogenic/Regional Background: Isoprene 40-100%, Ethane 28%, Propane 47%, Etylene 31%, Benzene 33%

Alcani
Alcheni
Alchini
Aromatici
Alifatici



PMF Other parameters

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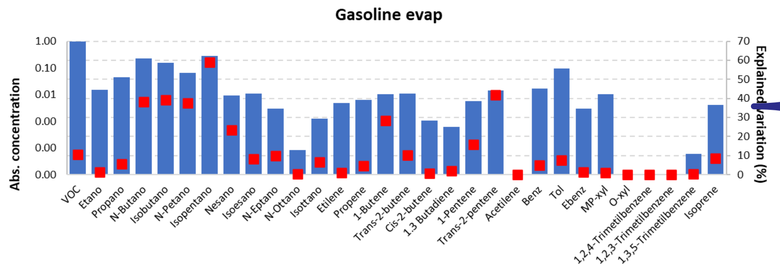
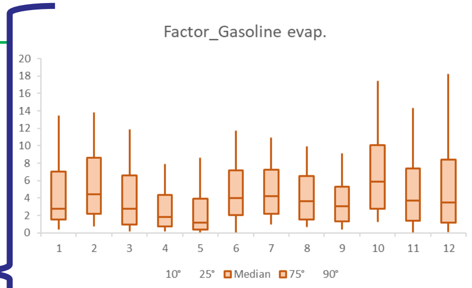
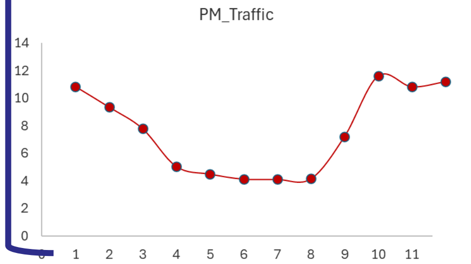
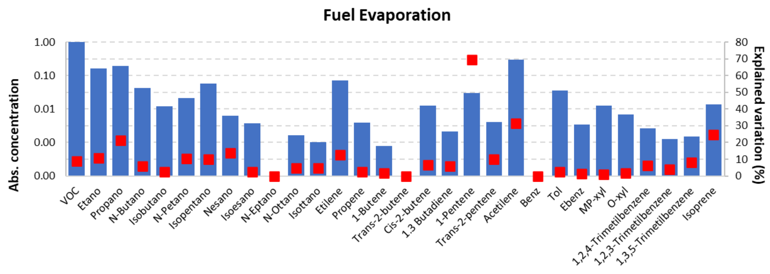
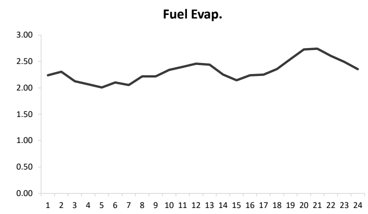
VOCs

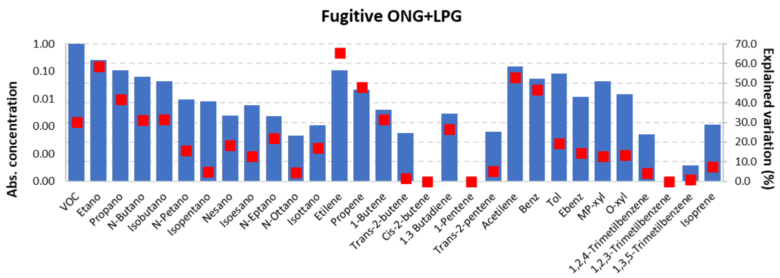


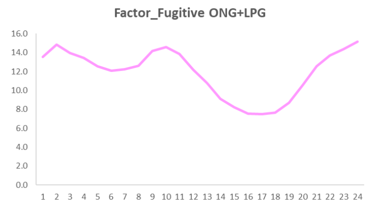


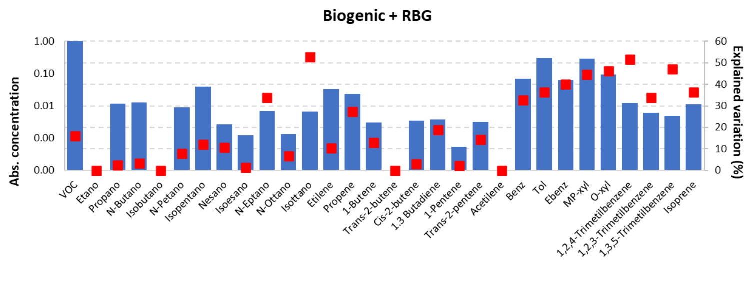


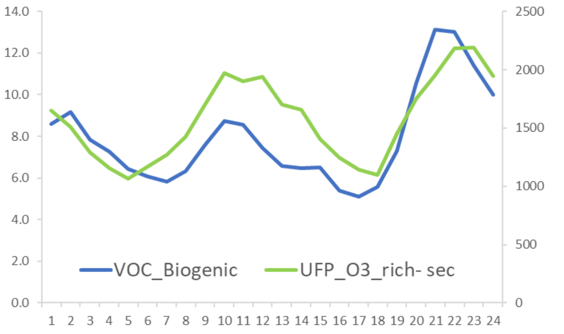


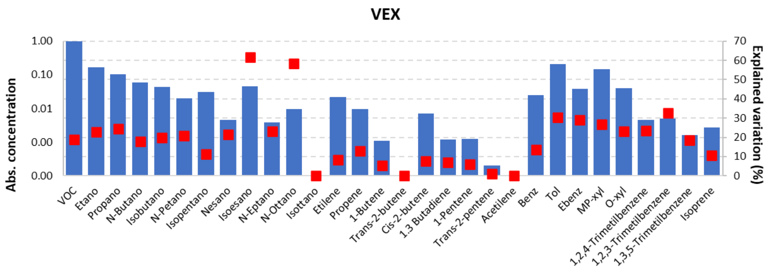


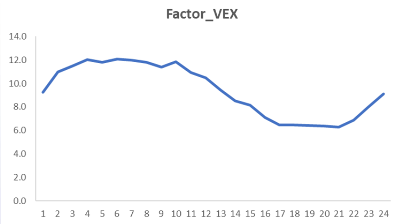


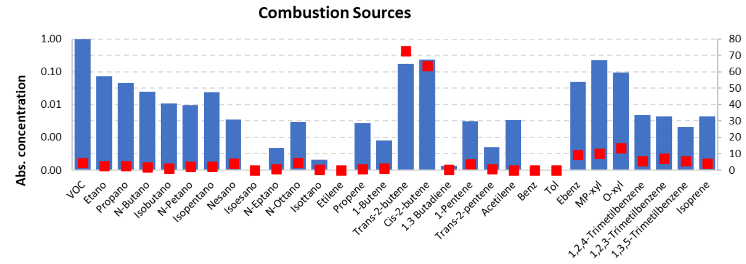


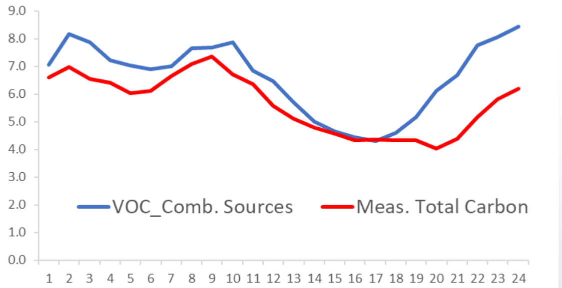












Conclusion

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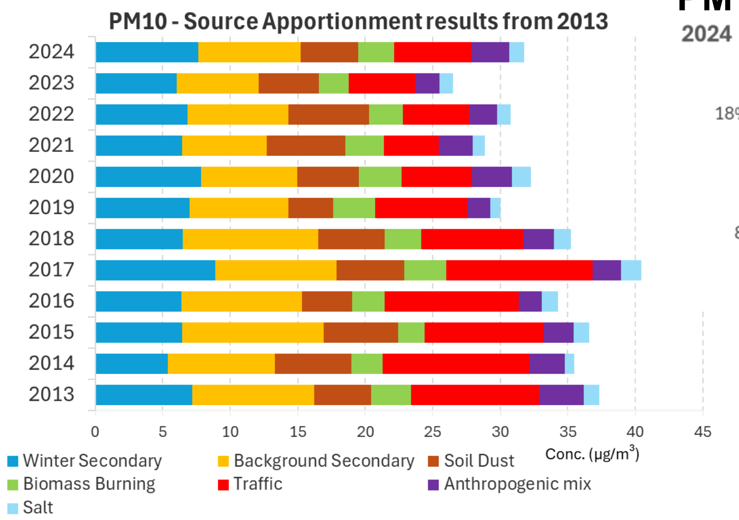
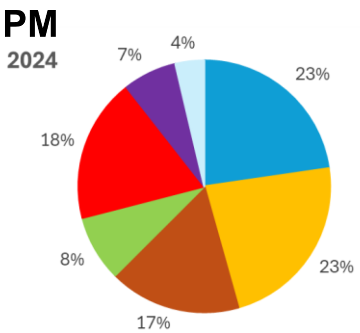
Even if the different identified sources originated different parameters (particles or gas), with different characteristics (chemical composition or particle diameters), fingerprint and behaviors are often comparable.





t Analysis

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Positive Matrix Factorization

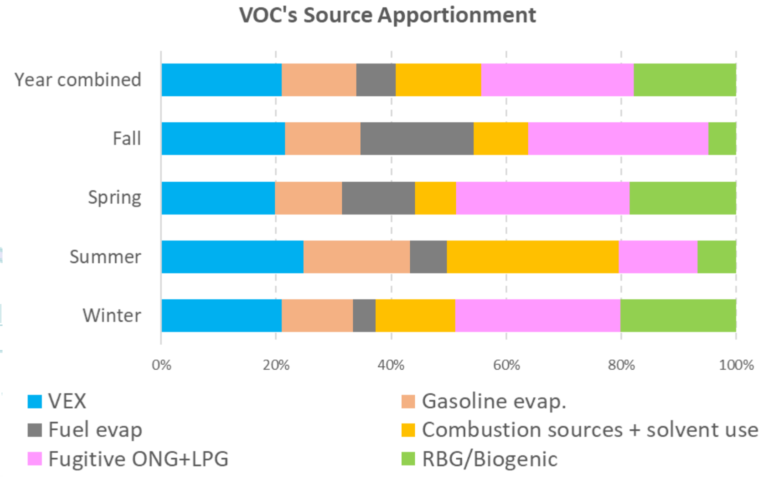
$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

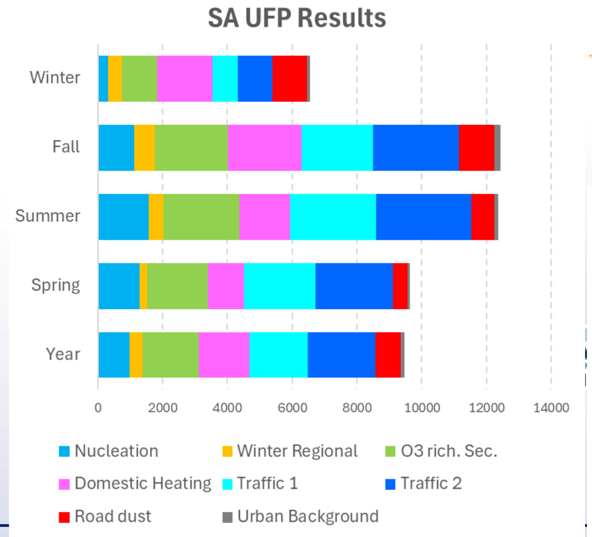
EPA-PMF5

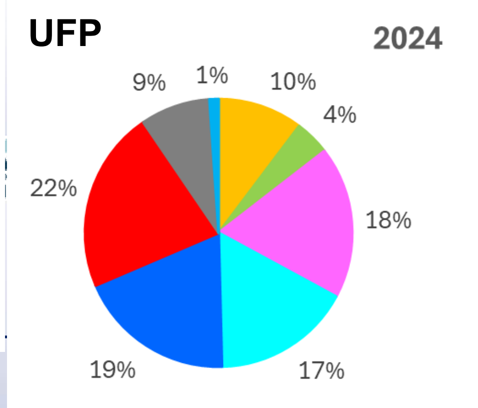
Input data:
- daily PM10&2.5 concentrations and chemical comp.
- uncertainties by Polissar, 1998

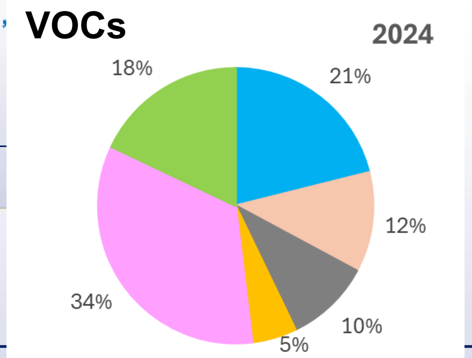
Input data:
...entrations
...lissar, 1998

Input data:
- Hourly UFP concentrations
- uncertainties by Ogulei et al.,









Thank you!

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