# Comparing methods for determination of Water-Soluble Organic Carbon

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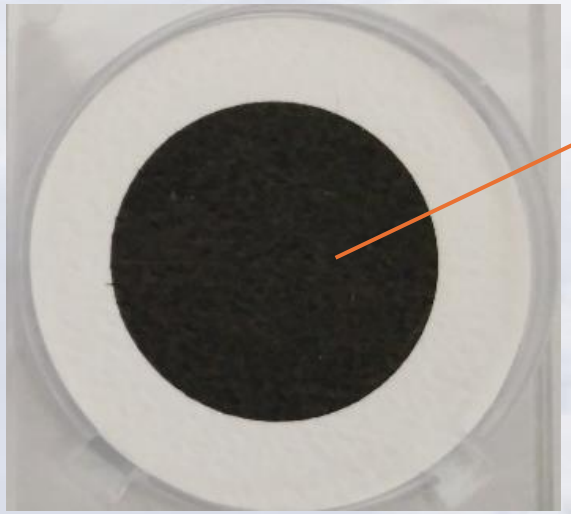
**XI convegno sul particolato atmosferico**

# Introduction

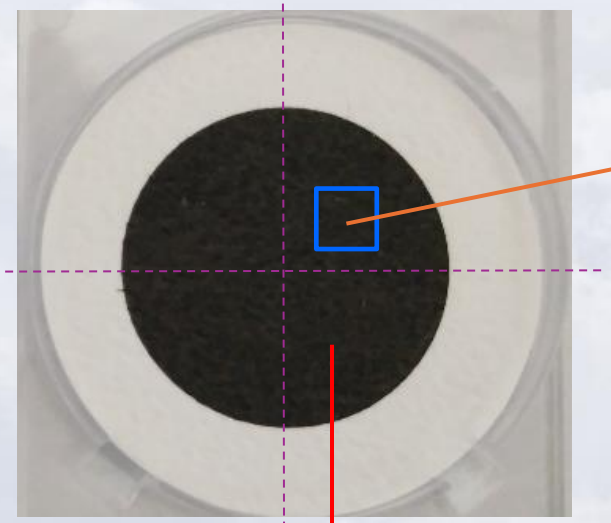
Quantifying and characterizing carbonaceous particles is crucial for understanding the origin of aerosols, their impact on air quality, human health, cultural heritage, and Earth's radiation balance.

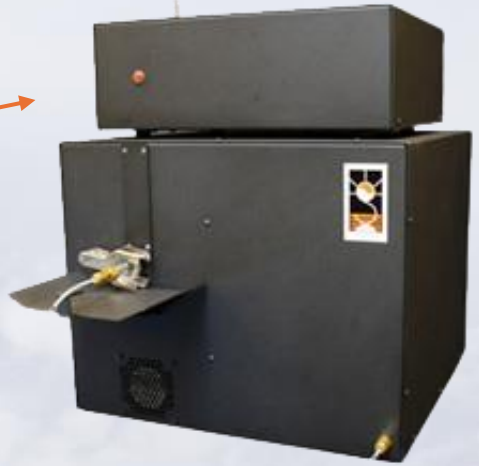


- The carbonaceous fraction is approximately 20 - 50% of atmospheric particulate matter (**PM**).
- Total carbon in **PM** is usually divided into organic carbon (**OC**), elemental carbon (**EC**) and inorganic carbon (**IC**), whose major fraction is carbonate carbon (**CC**).
- Water-soluble organic carbon (**WSOC**) is approximately 20 - 80% of **OC**, while water-soluble inorganic carbon (**WSIC**) is negligible.
- The origin of atmospheric **WSOC** can be attributed to both primary emissions from anthropogenic and natural sources and secondary formation through chemical reactions of volatile organic compounds (VOCs) in the atmosphere.
- The determination of **WSOC** is important in the characterization of atmospheric particulate matter.

This study compares two methodologies for measuring **WSOC**

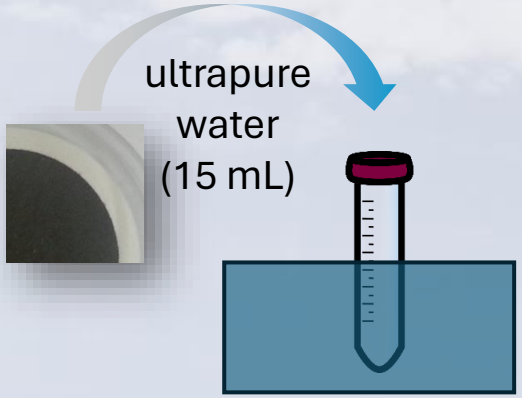
# OC and WSOC Determination





**OC/EC analyzer**
(Sunset Laboratory Inc.. OR. USA)

EUSAAR2 protocol




filtration

**TOC-L CPH instrument**
(Shimadzu Corporation. Kyoto. Japan)

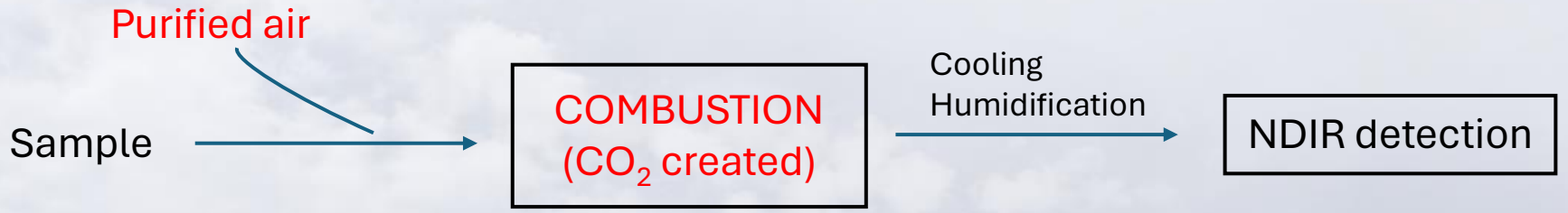
**WSOC = TOC of water extracts**

WSOC can be measured using 2 methods:

- TOC Method
- NPOC (Non-Purgeable Organic carbon) Method

# TOC Method

1) TC measurement

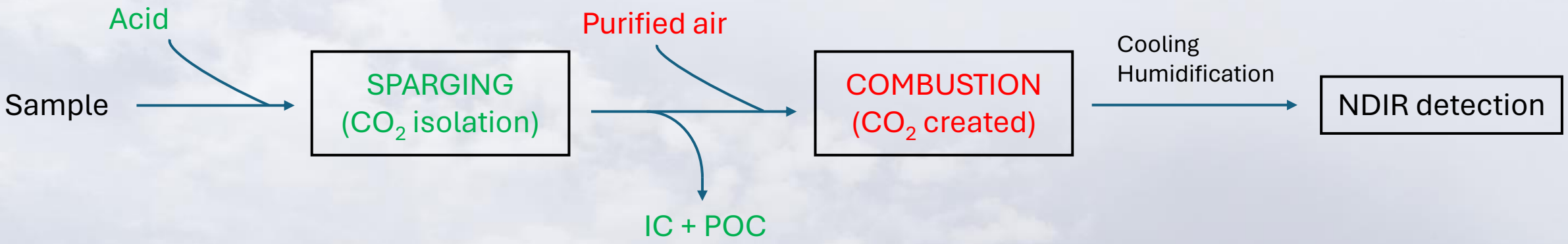



2) IC measurement


3) TOC calculation

**TOC = TC - IC**

# NPOC Method




**Sparging parameters:**

- Sparge Gas Flow
- Sparge Time
- Acid Addition

optimization

**One Variable At a Time** (OVAT)

- From an arbitrary chosen starting point one factor is varied
- At an optimum level of the first factor a second factor is varied

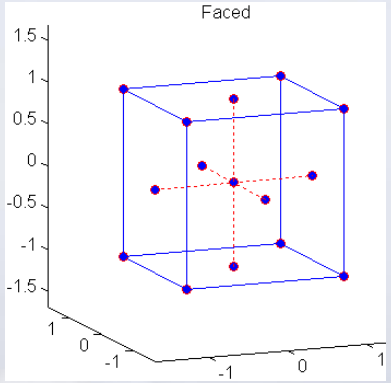
**Design of Experiments** (DoE)

- DoE is an efficient. structured way to investigate potentially significant factors and their cause-and-effect relationships on an experimental outcome

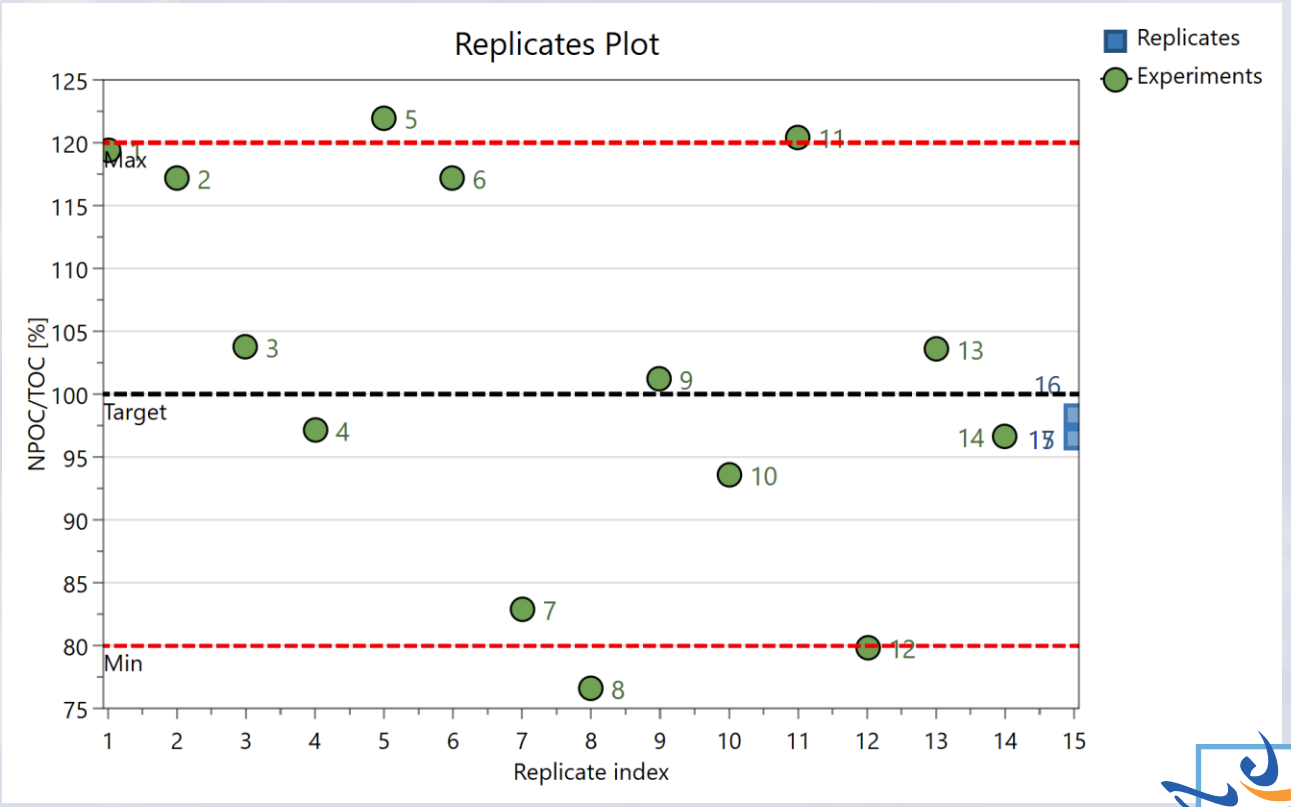
# Optimization of NPOC Method

| Design | Central Composite Face-centered (CCF) |
|---|---|

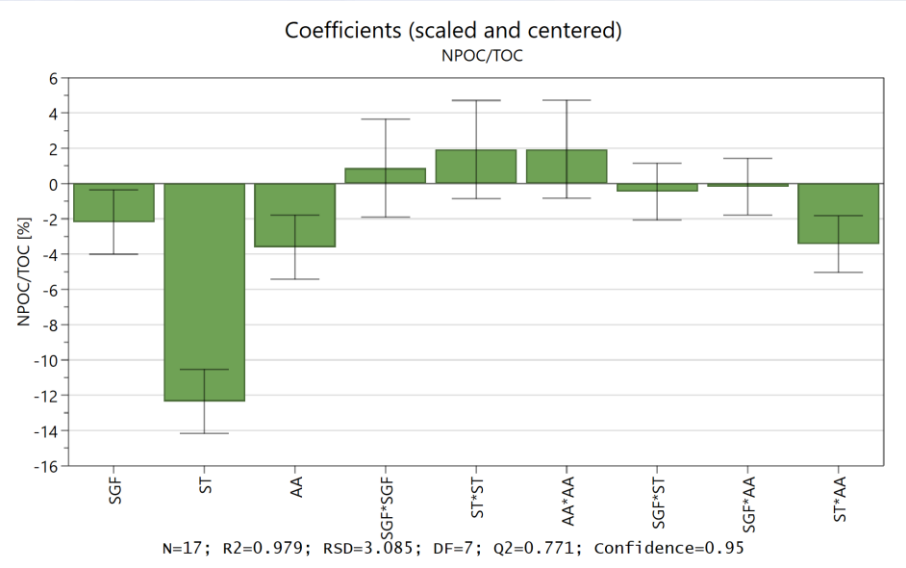
| Factors | Abbr. | Units | Low | High |
|---|---|---|---|---|
| Sparge Gas Flow | SPG | mL/min | 50 | 120 |
| Sparge Time | ST | min | 0.1 | 1.9 |
| Acid Addition | AA | % | 0.2 | 2 |

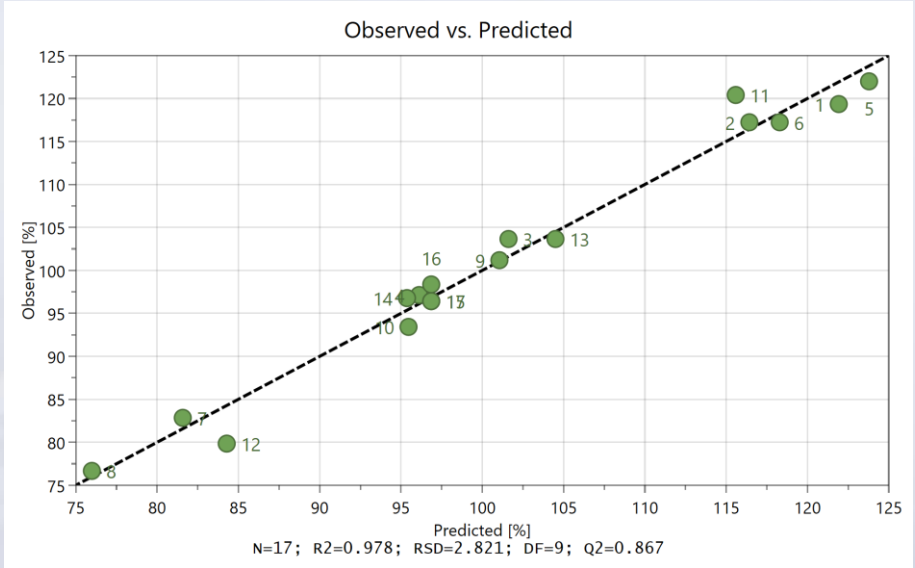



| Exp No | Run Order | SPG (mL/min) | ST (min) | AA (%) | NPOC/TOC (%) |
|---|---|---|---|---|---|
| 1 | 16 | 50 | 0.1 | 0.2 | 119 |
| 2 | 7 | 120 | 0.1 | 0.2 | 117 |
| 3 | 10 | 50 | 1.9 | 0.2 | 104 |
| 4 | 8 | 120 | 1.9 | 0.2 | 97 |
| 5 | 4 | 50 | 0.1 | 2 | 122 |
| 6 | 9 | 120 | 0.1 | 2 | 117 |
| 7 | 6 | 50 | 1.9 | 2 | 83 |
| 8 | 5 | 120 | 1.9 | 2 | 77 |
| 9 | 1 | 50 | 1 | 1.1 | 101 |
| 10 | 13 | 120 | 1 | 1.1 | 93 |
| 11 | 11 | 85 | 0.1 | 1.1 | 120 |
| 12 | 17 | 85 | 1.9 | 1.1 | 80 |
| 13 | 3 | 85 | 1 | 0.2 | 104 |
| 14 | 12 | 85 | 1 | 2 | 97 |
| 15 | 14 | 85 | 1 | 1.1 | 96 |
| 16 | 2 | 85 | 1 | 1.1 | 98 |
| 17 | 15 | 85 | 1 | 1.1 | 96 |

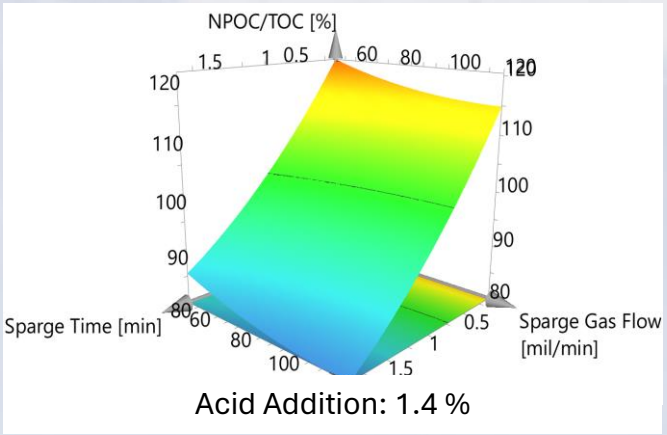


# Optimization of NPOC Method

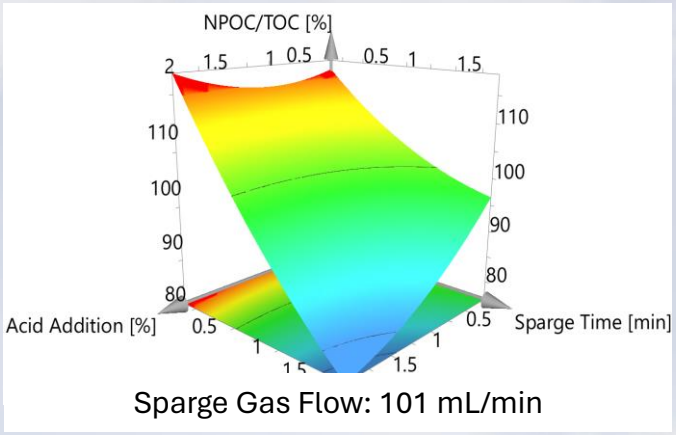


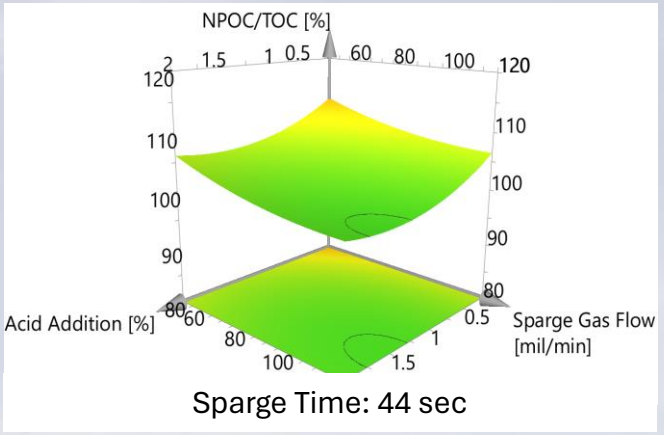

## SURFACE COUNTER PLOT



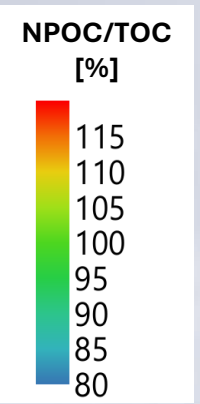

Acid Addition: 1.4 %




Sparge Gas Flow: 101 mL/min

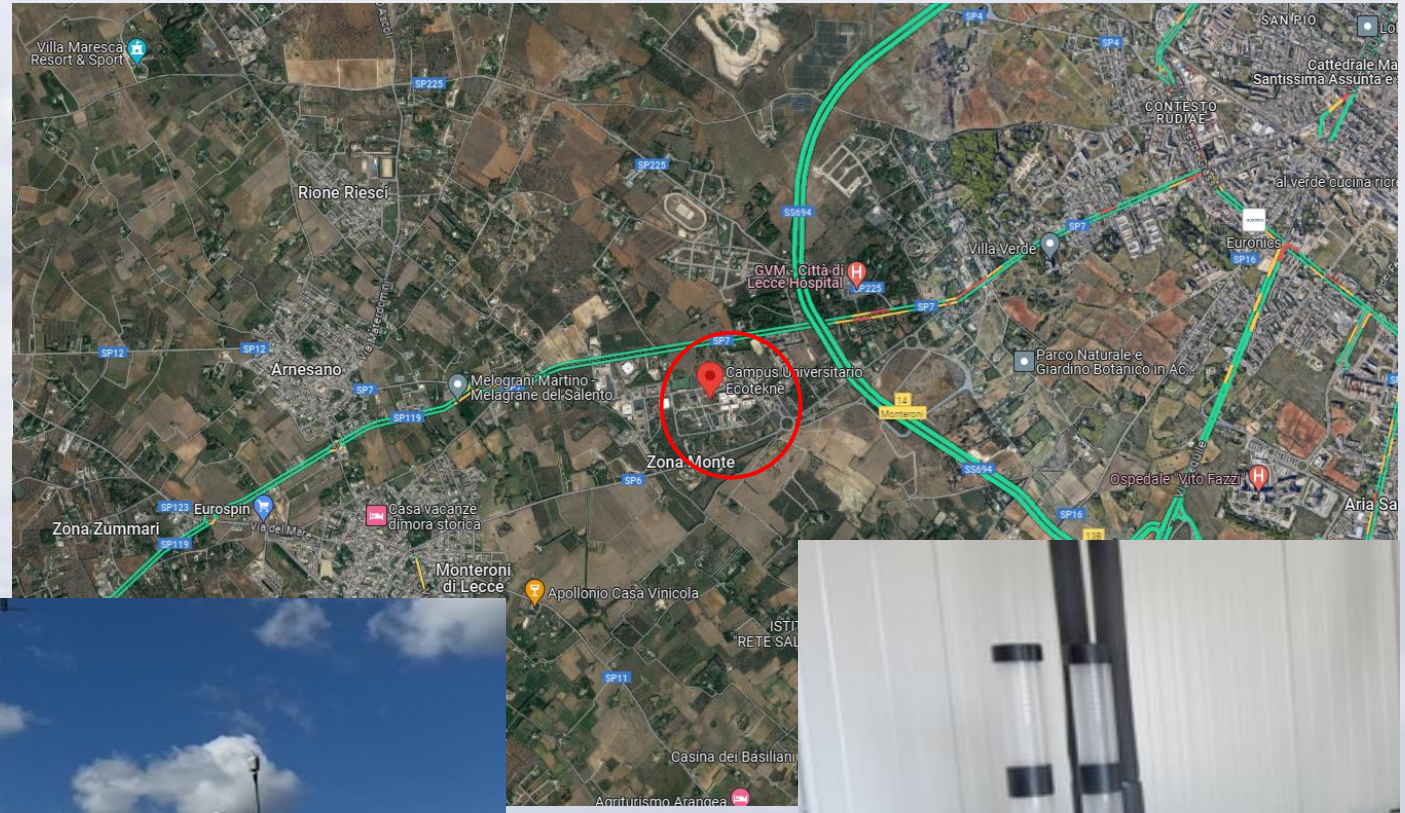



Sparge Time: 44 sec




**Sparge Time: 44 sec – Sparge Gas Flow: 101 mL/min – Acid Addition: 1.4%**

# $PM_{2.5}$ and $PM_{10}$ daily samples




## Sampler Position

- One site co-located at the ECO observatory of Lecce
- heights agl 12 m.

## Sampling campaign

Aug 2013 – Jul 2014

One sample for each month.

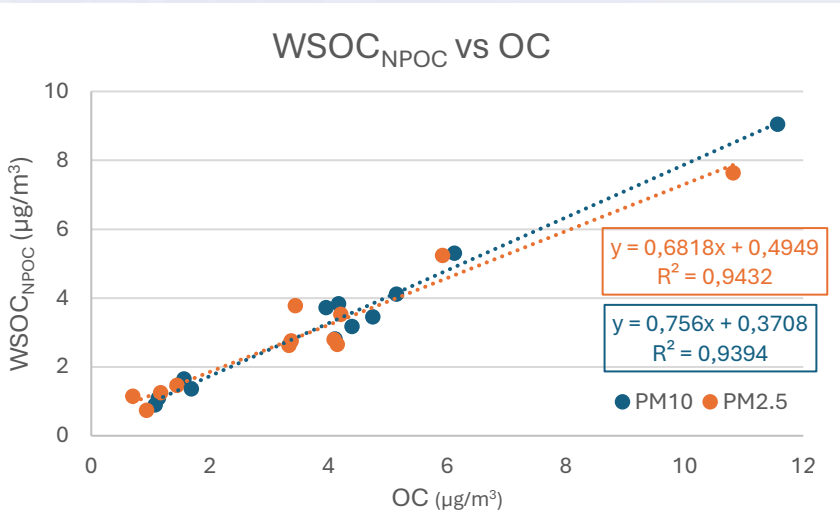
## Sampling parameters

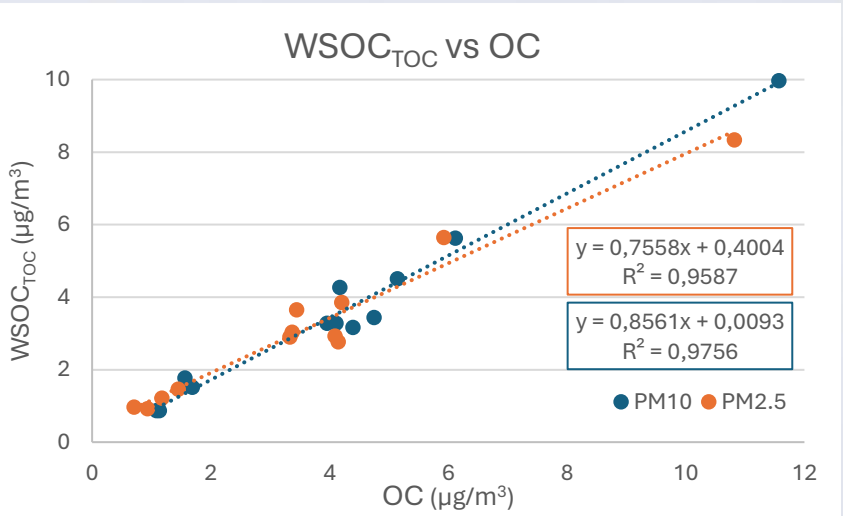
- Flow-rate: 38 L/min.
- Sampling period: 24h.
- 47 mm quartz filters (Whatman).

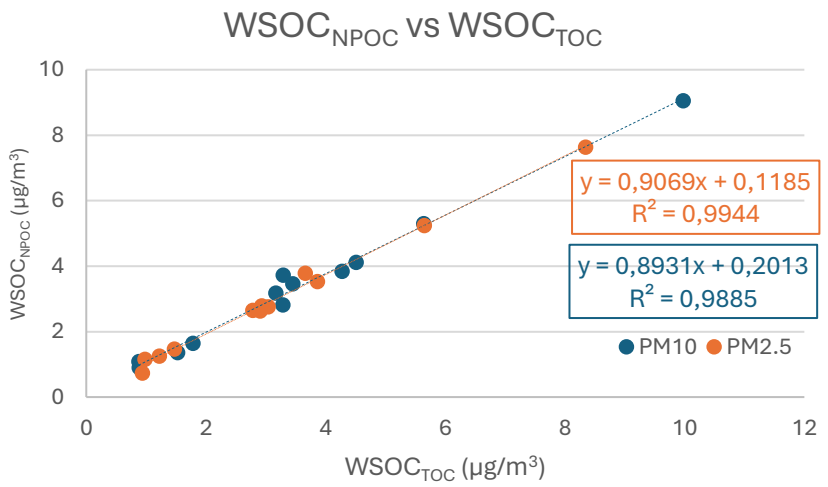
## Classification of the sites

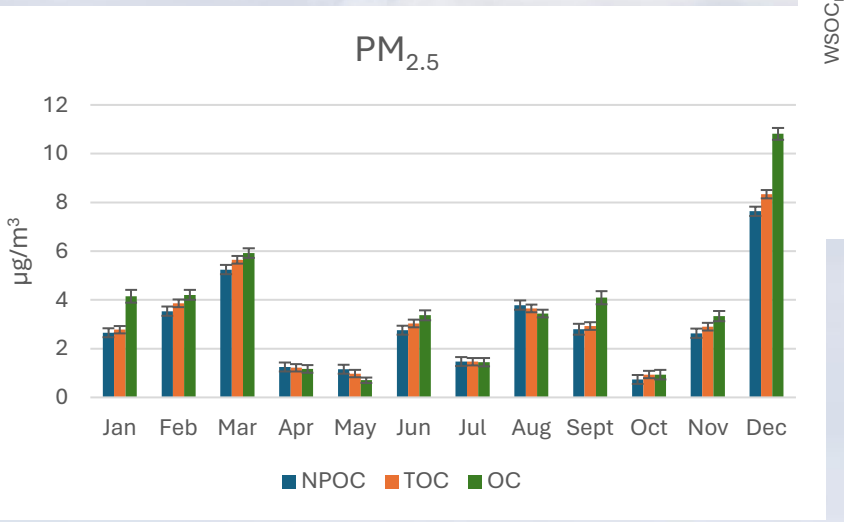
- **FU/S**: urban background.

# $PM_{2.5}$ and $PM_{10}$ daily samples



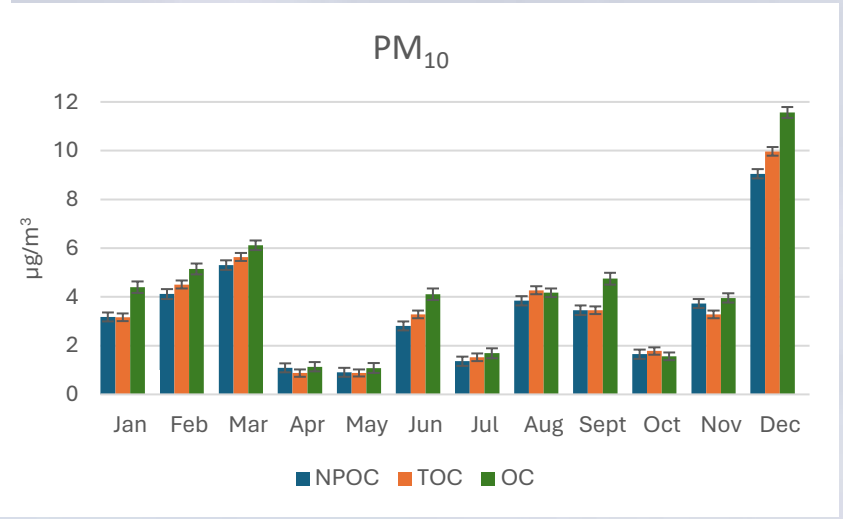



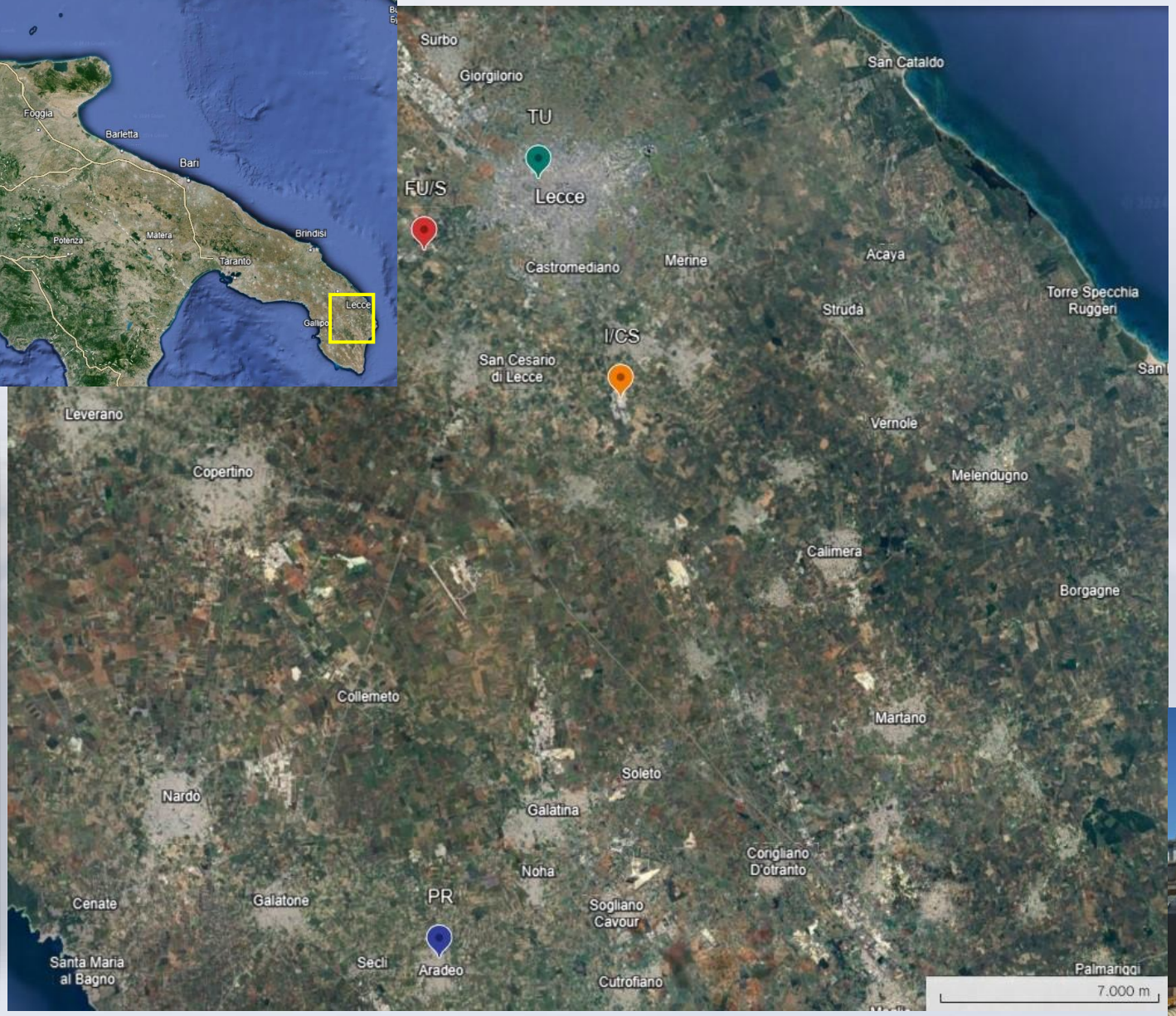

Average WSOC

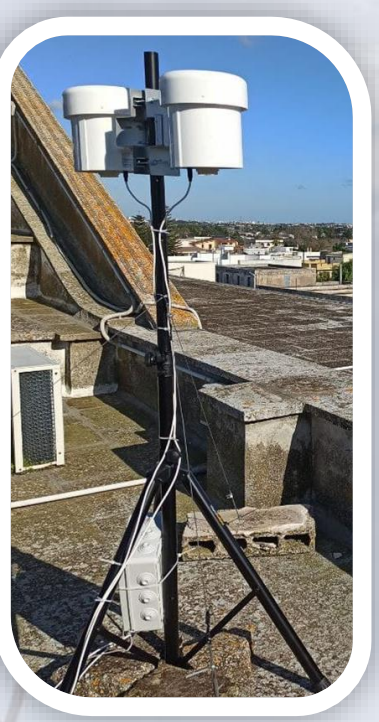
WSOC$_{TOC}$: (3.3 ± 0.5) µg/m$^3$

WSOC$_{NPOC}$: (3.2 ± 0.4) µg/m$^3$



# $PM_{2.5}$ and $PM_{10}$ monthly samples

## Samplers Position

- heights agl 9-19.5 m.
- public buildings, schools and private houses.

## Sampling campaign

- Dec 2021 – Dec 2022

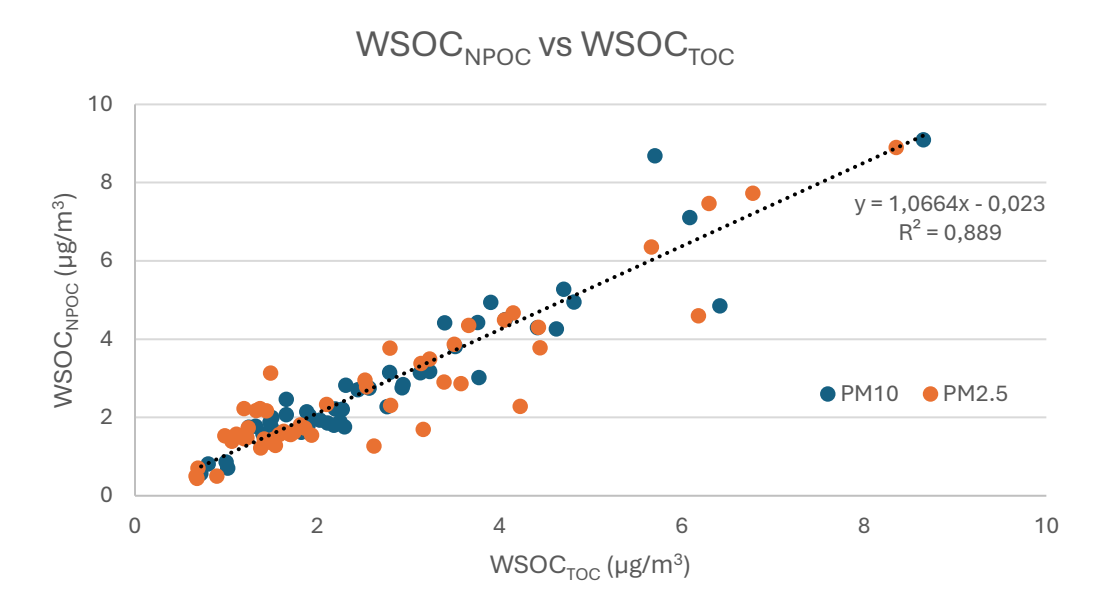
## Sampling parameters

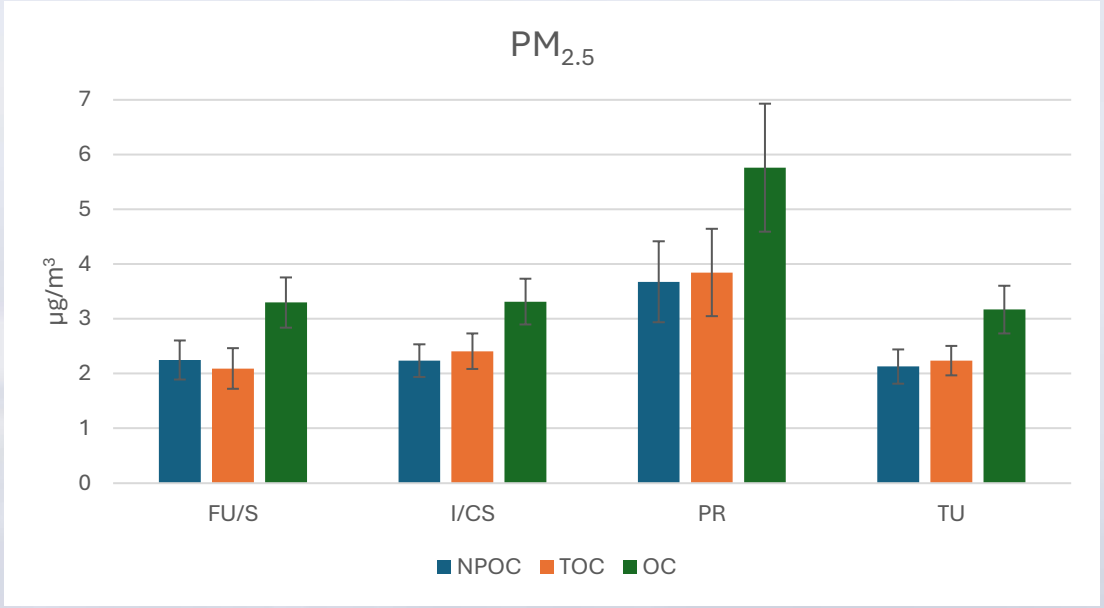
- Flow-rate 2 L/min.
- Sampling period ~30 days.
- 47 mm quartz filters (Whatman).

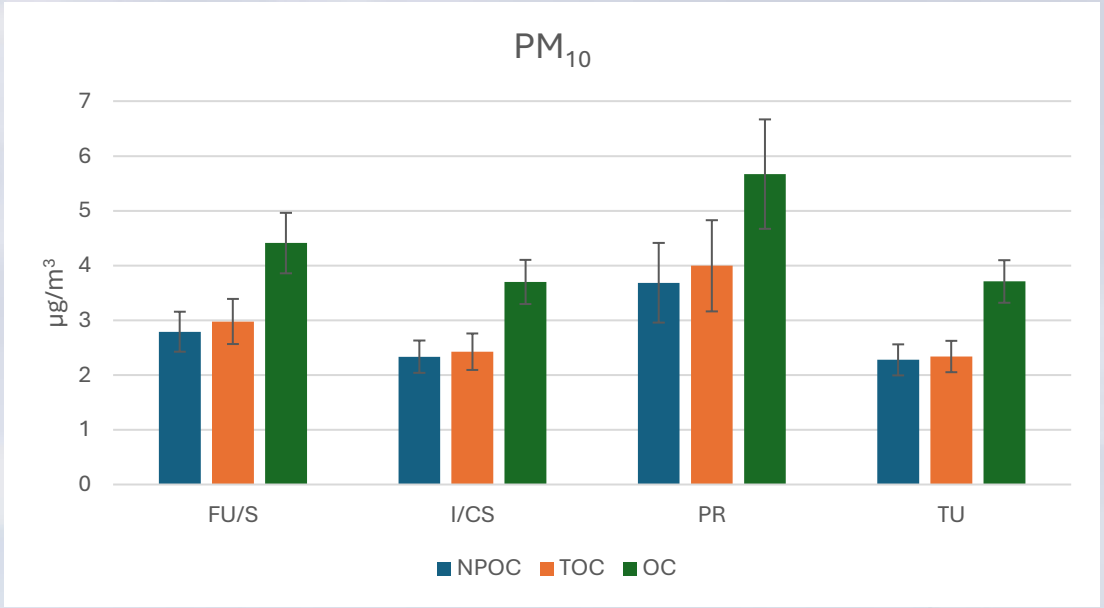
## Classification of the sites

- **FU/S**: urban background.
- **TU**: urban traffic.
- **I/CS**: commercial center.
- **PR**: site in the province

# $PM_{2.5}$ and $PM_{10}$ monthly samples



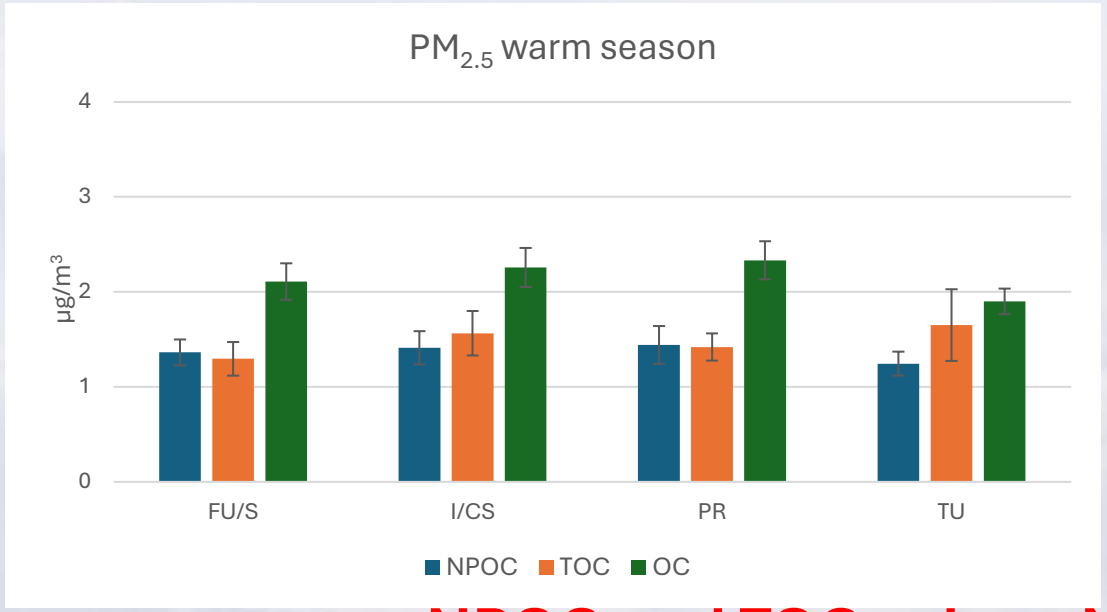



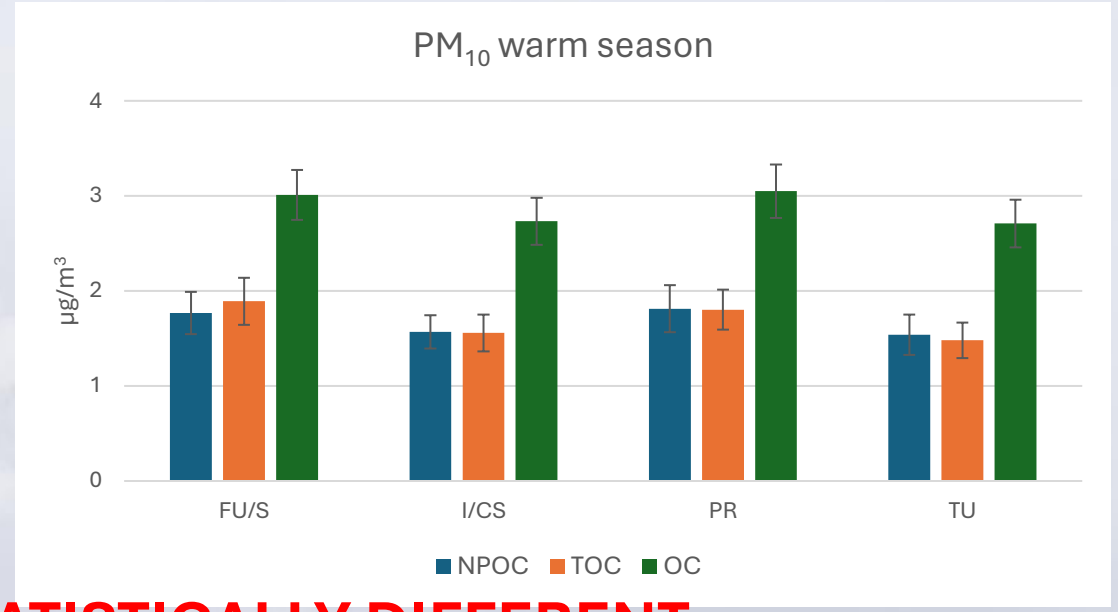




**WSOC$_{NPOC}$ and WSOC$_{TOC}$ values present:**

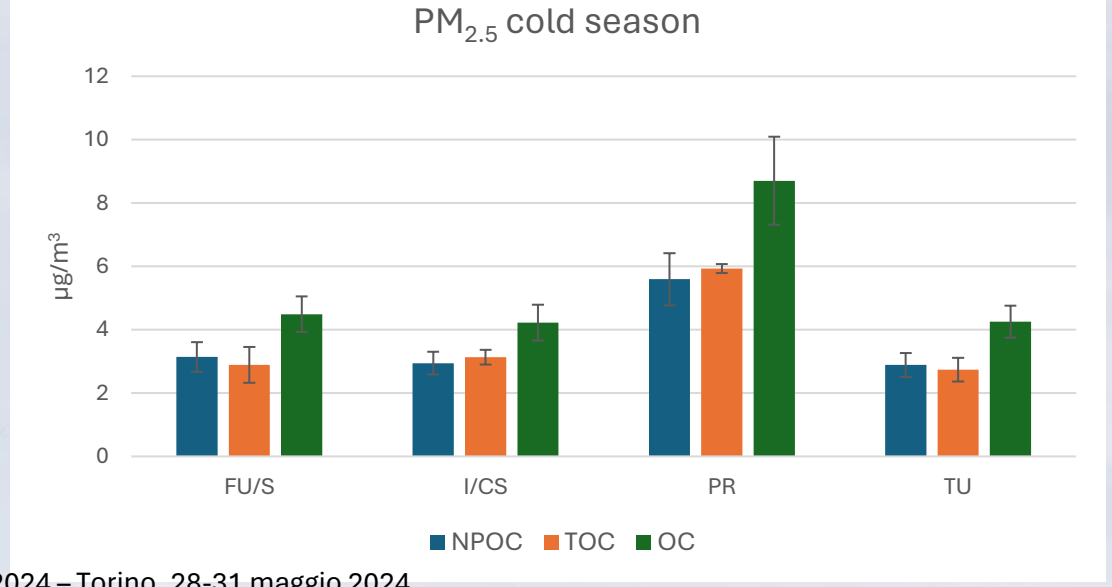
- Good correlation on $PM_{2.5}$ and $PM_{10}$ fractions
- Not statistically different

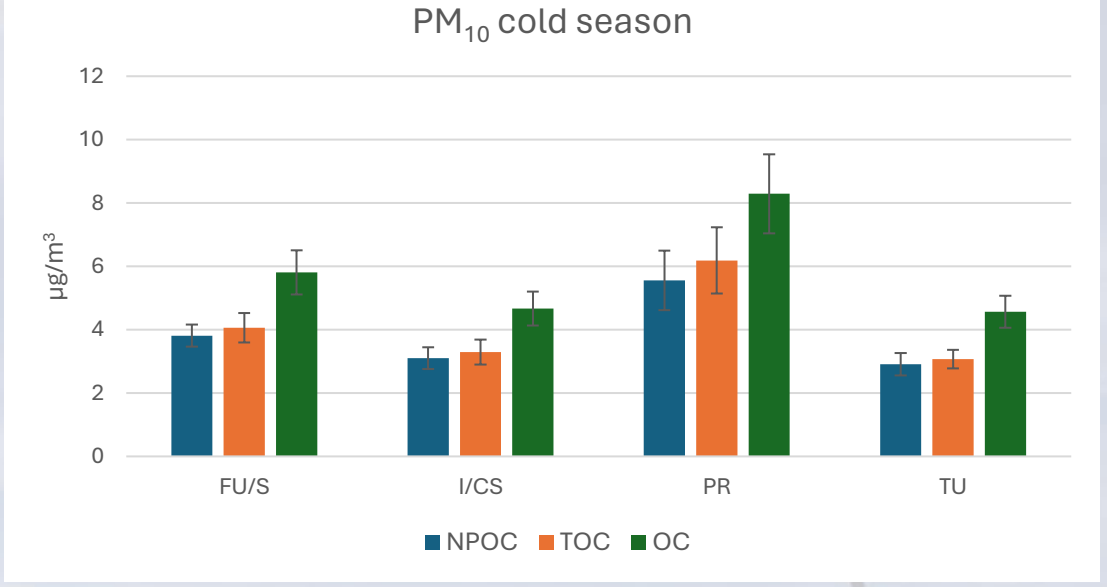
# $PM_{2.5}$ and $PM_{10}$ monthly samples



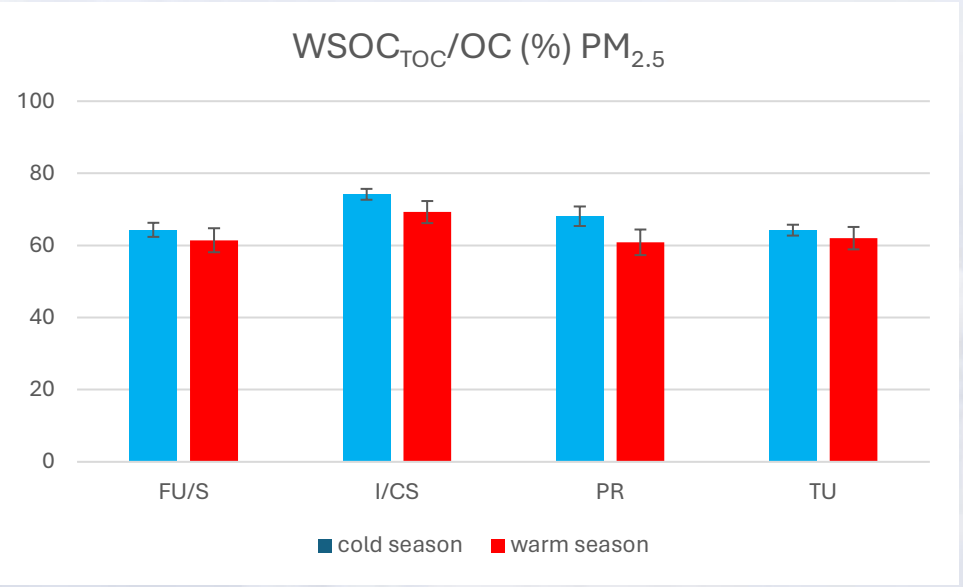




**NPOC and TOC values NOT STATISTICALLY DIFFERENT**

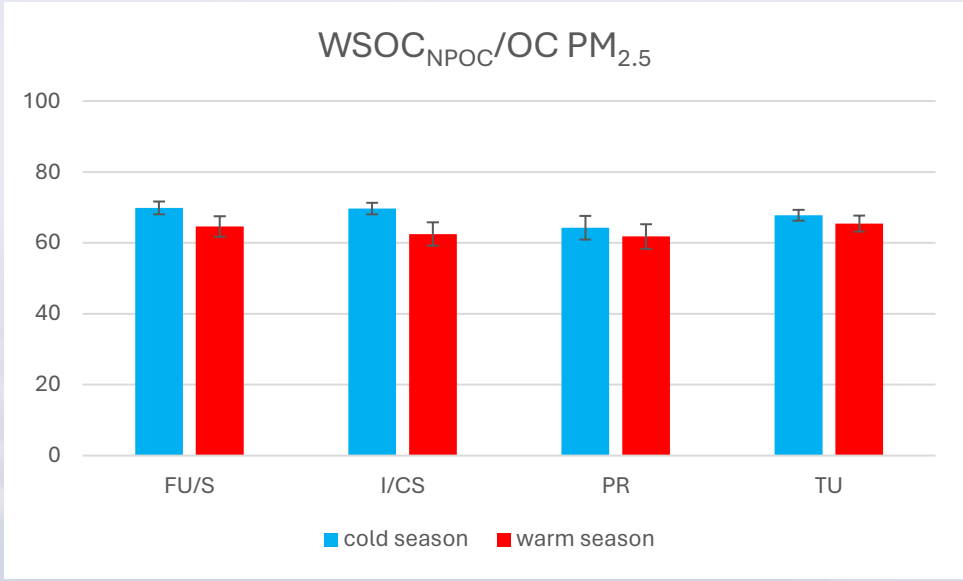


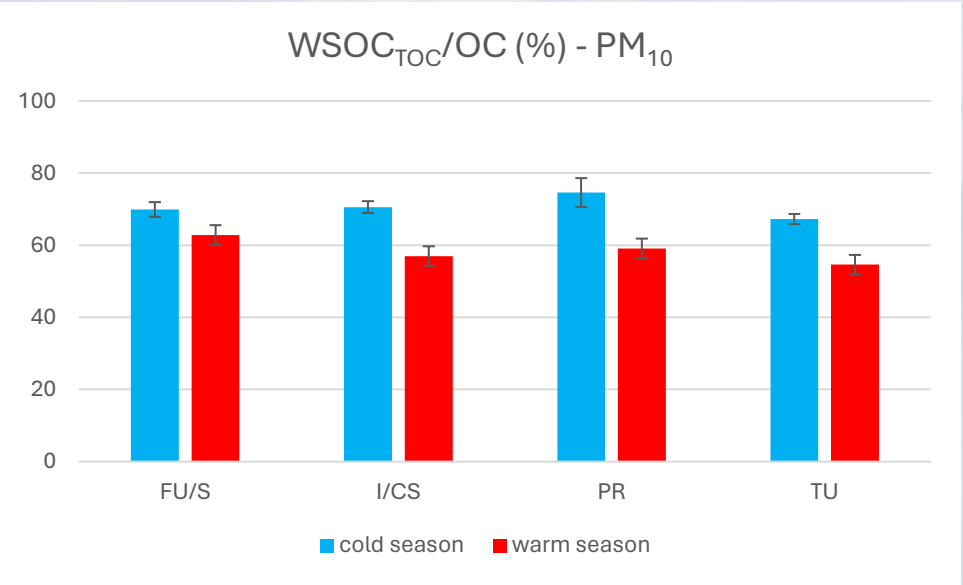



# WSOC/OC

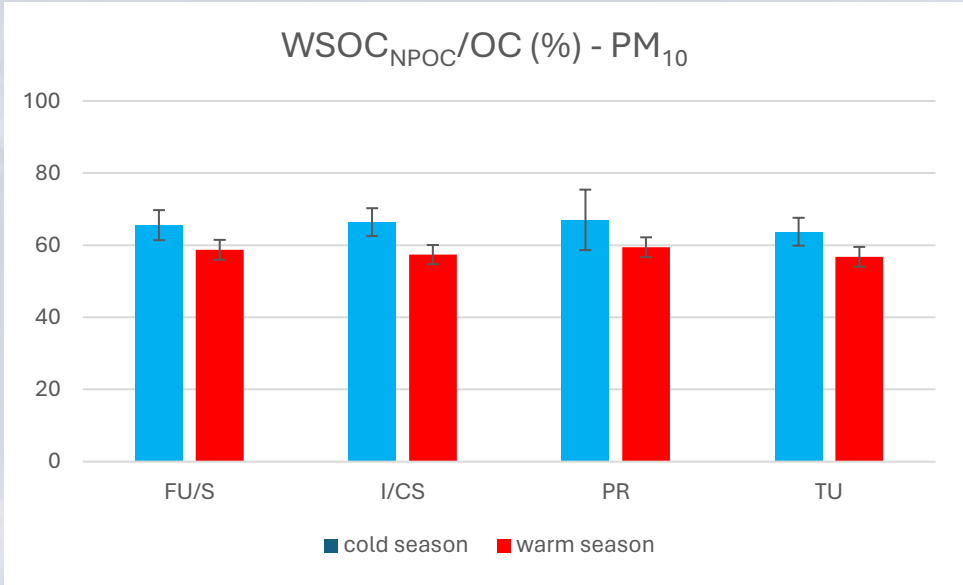



The average solubility of organic carbon is comparable in $PM_{10}$ (66%) and in $PM_{2.5}$ (65%)




Solubility of OC is greater in the cold season.



# CONCLUSIONS

- WSOC results obtained by NPOC and TOC methods do not present statistically significant differences both in terms of samples type (daily or monthly) and seasonality.
- NPOC Method requires less sample than TOC (about half).
- Average WSOC is comparable in $PM_{2.5}$ and $PM_{10}$.

# FUTURE WORK

- Estimate of intraday and inter-day repeatability on the same extract.
- Application of the two methods on future campaigns on different sites.

# Thanks for the attention!!!

With the support of the projects

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