Consiglio Nazionale delle Ricerche

Compositional data analysis of element concentrations of simultaneous size-segregated PM measurements

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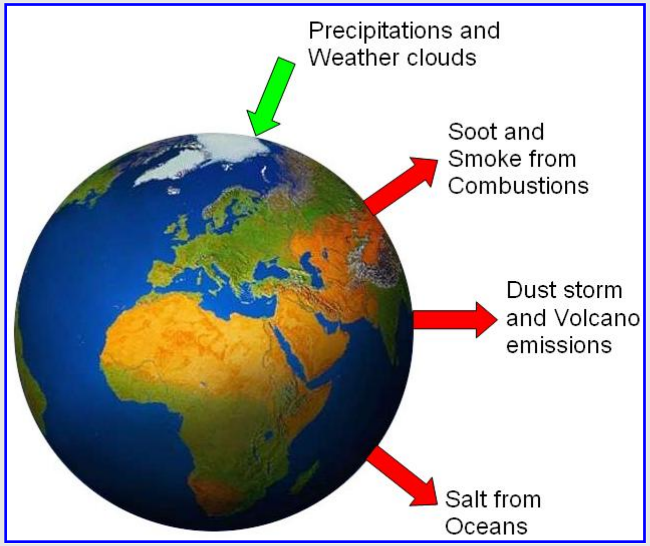
Overview

Particulate matter (or atmospheric aerosols) are solid or liquid particles or both suspended in air with diameters between about 0.002 µm and 100 µm



From https://www.google.it (modified)

Primary atmospheric aerosols are emitted directly into the atmosphere (sea-salt, mineral aerosols (or dust), volcanic dust, smoke and soot, some organics)

Secondary atmospheric aerosols form in the atmosphere by gas-to-particle conversion processes (sulfates, nitrates, some organics)

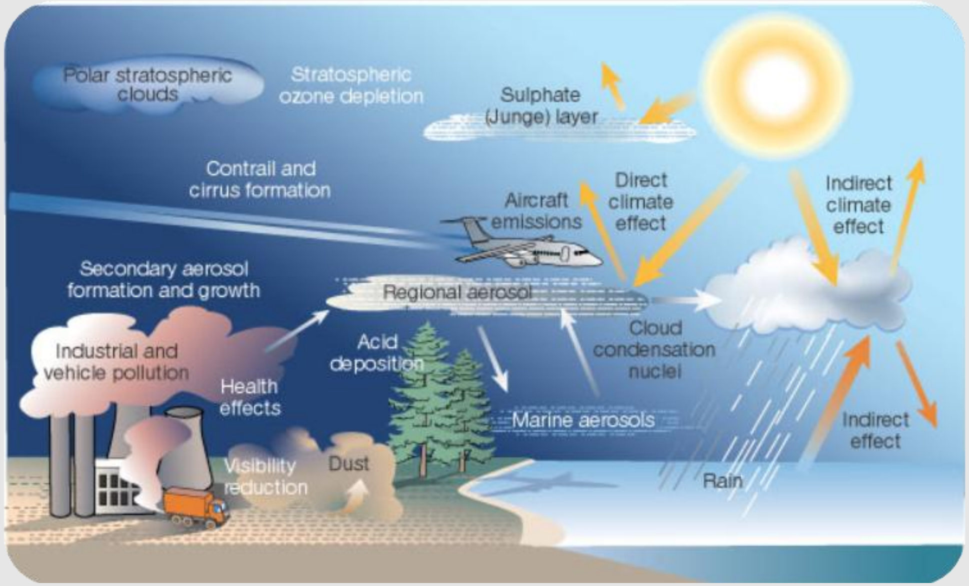
Overview

<u>Once in the atmosphere</u>, particulate matter:

✓can be transported in the atmosphere
✓can be removed from the atmosphere
(by dry deposition, wet removal, and gravitational sedimentation)
✓can change their size and composition due to microphysical transformation processes
✓can undergo chemical transformation

<u>Importance of particulate matter</u>:

✓ heterogeneous chemistry
✓ air quality and human health
✓ visibility reduction
✓ acid deposition
✓ cloud formation
✓ climate and climate change



Kolb, C.E. (2002) Nature 417, 597-598

PM elemental composition

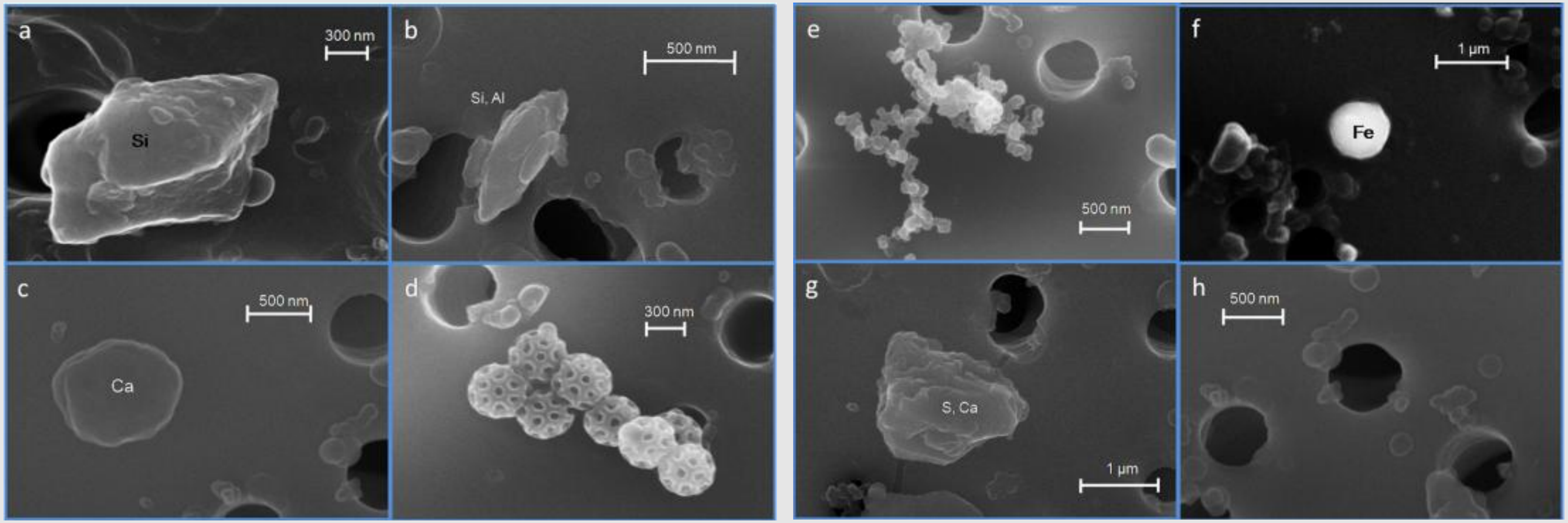
The **assessment of the chemical composition** of PM and of its size distribution in relation to its possible emission sources is a starting point to plan actions aimed at mitigating levels of PM to protect the **environment and public health**;

In the European context, selected sets of chemical elements have been attributed to specific **sources** of PM, e.g.:

- **Al, Si, Ca, Fe, Ti, Mg, Sr,** have been mainly linked to mineral matter and African dusts;
- **Na, Cl** have been mainly associated with marine sources;
- **V** and **Ni** have been mainly related to industrial and oil combustion sources.

However, the identification of a set of elements useful in the discrimination of specific **natural source** of mineral matter (e.g. such as African dusts and fugitive dusts) and characteristic **anthropogenic source** of mineral matter (e.g. resuspended road dusts and dust from construction/demolition activities), has proven to be **problematic** as these sources have the same set of elements in common.

SEM images of air-suspended particles



Margiotta et al. (2015).

SEM images of air-suspended particles: (a) quartz; (b) kaolinite; (c) calcite; (d) brocosomes; (e) soot; (f) iron oxide; (g) gypsum; (h) secondary particles.

Examples of mineral matter sources of PM

Dust storm and demolition activities. Images retrieved from: https://www.youtube.com (modified).

Fugitive dust. Ferguson and others (1999). Agricultural MU Guide, University of Missouri-Columbia, Agricultural Publication G, 1885. (modified)

Compositional data analysis 1/2

PM_{10}, $PM_{2.5}$, PM_1 aerosol particles with aerodynamic diameters smaller than 10, 2.5 and 1 μm, respectively.

$$PM_{10-2.5} = PM_{10} - PM_{2.5}$$ **Coarse size fraction**

$$PM_{2.5-1} = PM_{2.5} - PM_{1}$$ **Intermodal size fraction**

$$PM_{1}$$ **Submicron size fraction**

These fractions are converted into compositions based on weight proportions

$$x = \left(\frac{PM_{10-2.5}}{PM_{10}}, \frac{PM_{2.5-1}}{PM_{10}}, \frac{PM_{1}}{PM_{10}} \right) \%$$

Compositional data analysis 2/2

The compositional variables of this vector are non-negative and they sum to a constant c=100. Compositional data is cast into the form of a matrix where i rows represent the mineral elements and j columns represent the compositional variables.

$$x = \left(\frac{PM_{10-2.5}}{PM_{10}}, \frac{PM_{2.5-1}}{PM_{10}}, \frac{PM_{1}}{PM_{10}} \right) \%$$

The compositional data is transformed into co-ordinates using ilr (isometric log-ratio)

$$ilr_1 = \frac{1}{\sqrt{2}} ln \left(\frac{PM_{10-2.5}}{PM_{2.5-1}} \right) \qquad ilr_2 = \frac{1}{\sqrt{6}} ln \left(\frac{PM_{10-2.5} PM_{2.5-1}}{{PM_1}^2} \right)$$

Methods and Methodology

- The mineral elements concentrations of **PM_{10}, $PM_{2.5}$ and PM_1** simultaneous sampling as reported in literature have been considered and they refer to a suburban background site located in Rome with **(in-dust days**) and without **(non-dust days)** a Saharan dust episode (Matassoni et al. 2011).

- The selected mineral elements are **Al, Ti, Si, Ca, Mg, Fe, Sr,** which have been mostly and commonly interpreted as related to mineral matter (Viana et al. 2008).

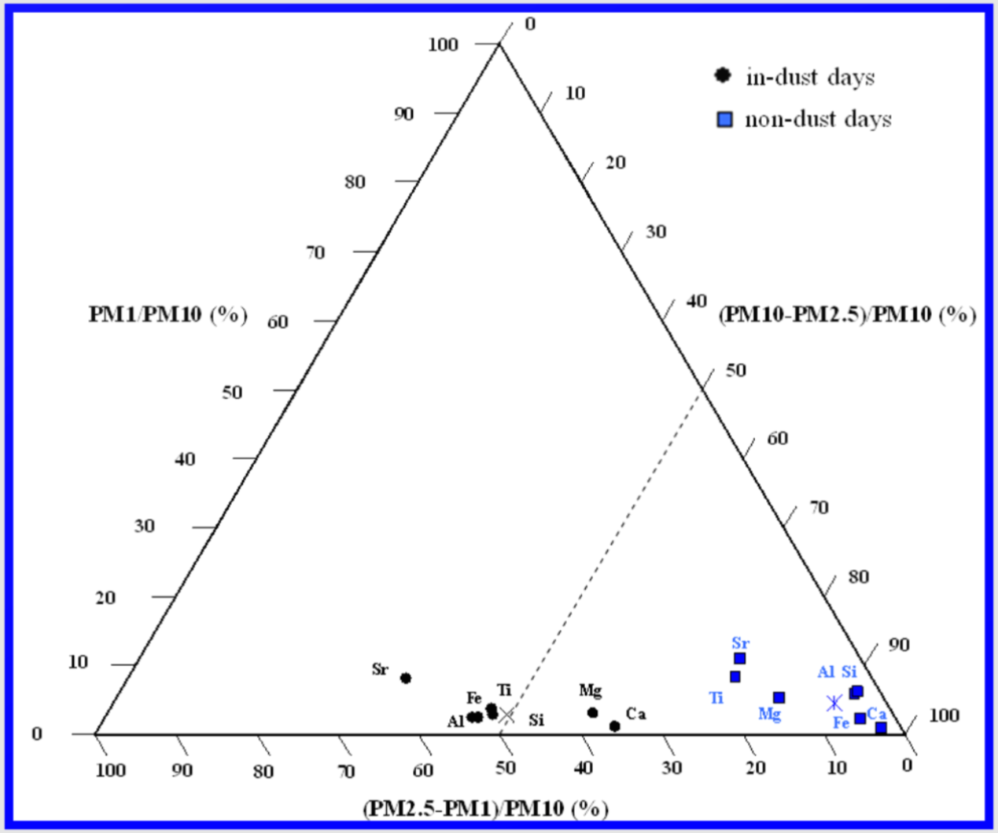
- The PM_1 solely for the Sr for in-dust and non-dust days was below the detection limits. The compositional dataset has been completed and modified using the imputation strategy described by Martín-Fernández et al., (2003) (Pawlowsky-Glahn and Buccianti, 2011).

- The compositional data sets, their centres and confidence regions can be represented using a triangular diagram.

Triangular diagram representation

The three part compositional data of **non-dust days** are displayed towards the lower right corner of the triangular diagram with high values of coarse component and low values of intermodal and submicron component. **The coarse component is more dominant.**

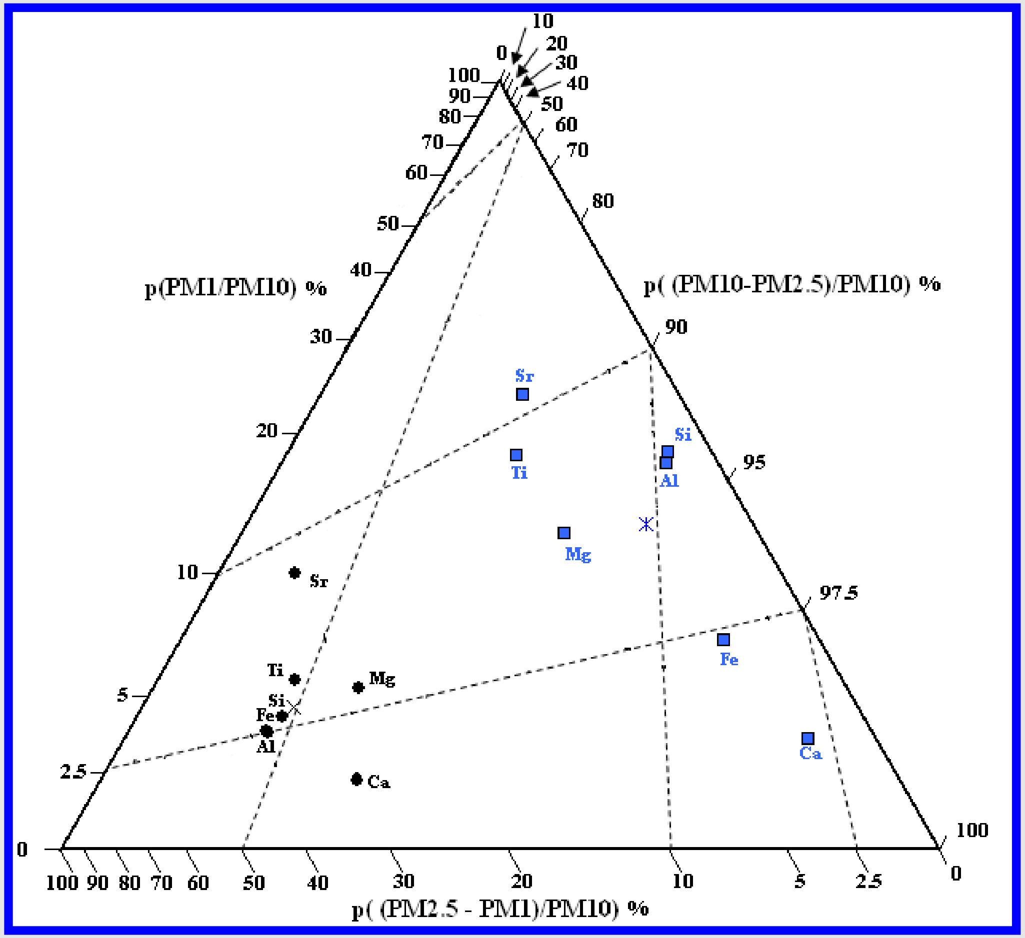
The three part compositional data of **in-dust days** are displayed along the lower border of the triangular diagram with low values of submicron component and higher values of coarse and intermodal components. **Coarse and intermodal components are dominant and comparable.**



Centering and rescaling technique

The centering and rescaling technique improve the visualization of the **two compositional** data sets.

The **two centers** are clearly distinct, however in order to validate the presence of two distinct groups, it is necessary to perform a statistical test.



Testing hypothesis and Confidence regions

The two data set related to **in-dust** and **non-dust** days are tested for equality in their centers and/or covariance structures

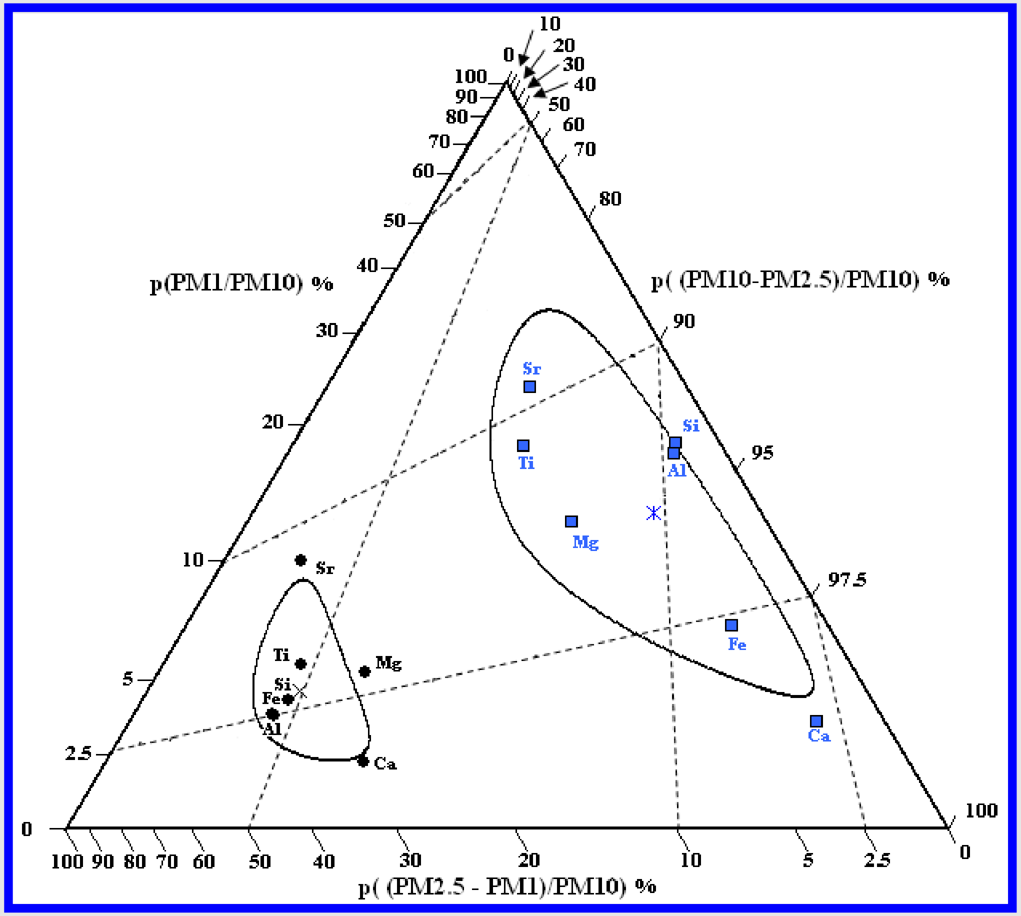
Hypothesis	Test value	χ^2 critical	df	Significance
$\mu_1=\mu_2$, $\Sigma_1=\Sigma_2$	36.870	11.07	5	0
$\mu_1\neq\mu_2$, $\Sigma_1=\Sigma_2$	9.9524	7.81	3	0.019
$\mu_1=\mu_2$, $\Sigma_1\neq\Sigma_2$	18.758	5.99	2	0.0001

$\alpha=0.05$

The equality either of covariance structures or of centres or of both has to be rejected.

The bivariate angle test and the marginal test have shown that the hypothesis of normality cannot be rejected.

The continuous lines are the confidence regions (1-α)100% α=0.05.

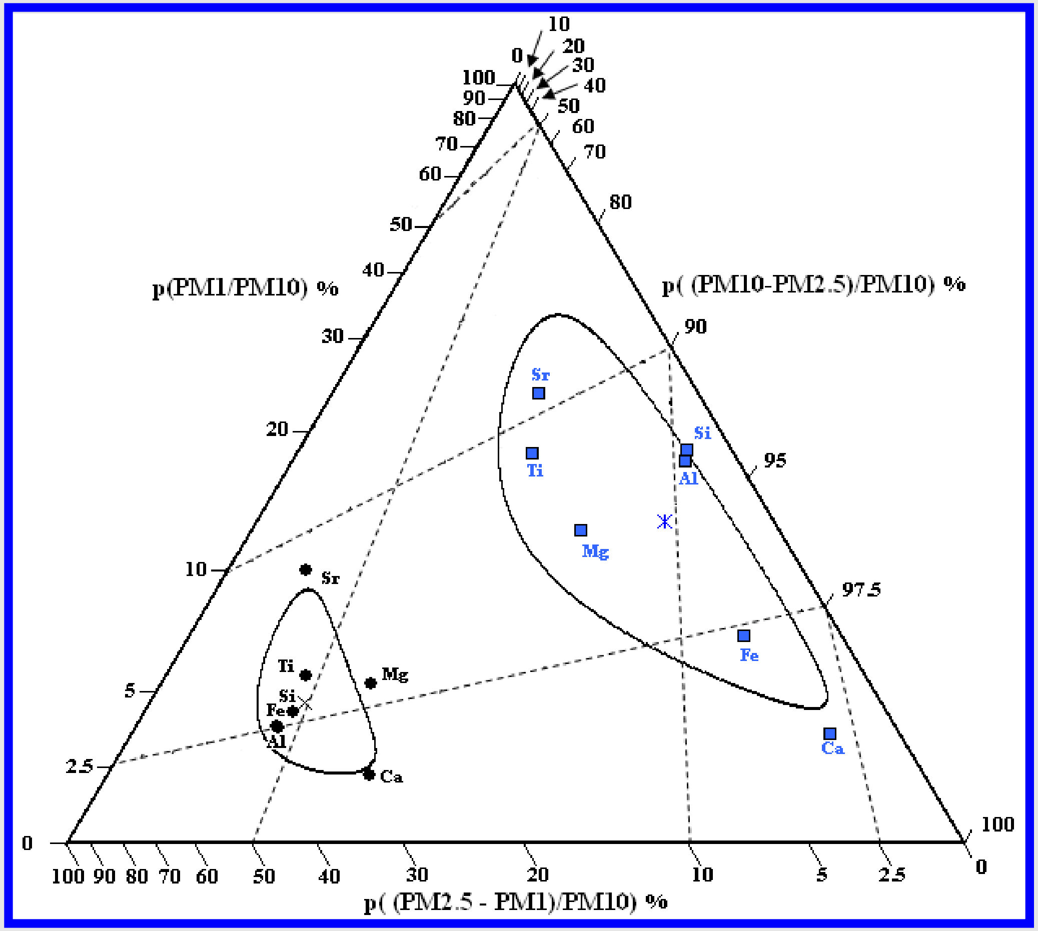


Perturbation difference

In order to evaluate the nature of the difference between the element concentrations in **in-dust** and **non-dust days** the perturbation difference was calculated between the perturbation centres related to in-dust and non-dust compositional data sets.

- The perturbation centre for **in-dust days** is (49.35,47.64, 3)$_{\text{(in-dust)}}$ whereas the perturbation centre for **non-dust days** is (89.02, 6.24, 4.73)$_{\text{(non-dust)}}$.

- The perturbation difference is (6.29,86.53,7.18)$_{\text{(in-dust)-(non-dust)}}$ suggesting that the Saharan dust event relatively increased the intermodal size fraction of the considered set of chemical tracers.



Conclusions

- The statistical methods used for the analysis of compositional data allowed the validation of the differences between the investigated data sets of the related environmental site.

- These differences can be associated with the type of mineral sources involved and possible mechanisms of addition/subtraction of materials that influences the behaviour of the environmental site.

- During in-dust days the contribution of the Saharan dust event alters the composition as well as the size distribution of PM, particularly the intermodal size fraction.

- The compositional analysis applied to PM_{10}, $PM_{2.5}$ and PM_1 tracer concentration simultaneous measurements is an effective technique which can be used to study environmental sites affected by several mineral sources.

- Moreover, the triangular diagram and centering and rescaling techniques are very important and practical tools representing compositional data of size-segregate PM mineral tracer concentration simultaneous measurements.

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Thanks for your attention

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