



## Multivariate Statistical Analysis Applied to PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> Data Collected in Taranto (South Italy)

**T. Siciliano, A. Genga, L. Daniele, M. Siciliano**

Department of Materials Science, Salentum University, Via per Arnesano, 73100, Lecce, Italy

### Abstract

Principal Component Analysis (PCA), Cluster Analysis (CA) and Factor Analysis (FA) with VARIMAX rotation were applied to the whole data set of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> in order to determine the PM sources and their contributions. Daily aerosols samples of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> were collected in Taranto (south Italy) from March 31st to April 26<sup>th</sup>, 2008. The statistical multivariate analysis of the data discriminated sea spray, traffic, heavy oil combustion, secondary aerosol and industrial emissions sources.

### Introduction

Aerosol particles are recognised to have a strong impact on the environment and to cause damage to human health. For this reason, a great deal of research has focused on the metal composition of atmospheric suspended particulate matter. In this study, daily aerosols samples of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> were collected in 2008. The sampling site for this study, Taranto, is the third most densely-populated town in southern Italy. It is characterized by a high density of vehicular traffic, an important commercial and military port and an important industrial centre with petrochemical and cement plants, well-developed steel and iron foundries and some shipyards.

Multivariate statistical analysis was applied to the complete concentration data set ( $\mu\text{g/g}$ ) to evaluate the correlation among different chemical species and to find the groups of elements with similar behaviour for the identification of the sources of particulate matter.

### Materials & Methods

Daily aerosols samples were collected from March 31st to April 26th 2008 on 47mm Teflon Filters Membrane. PM mass concentration was determined by gravimetry. All filters were conditioned and weighed before and after sampling. Anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) analyses were performed using a Dionex DX600 Ion Chromatography system. Metals were determined by IPC-OES (Varian Liberty I) and by GF-AAS (Perkin Elmer Analyst 600). Principal Component Analysis (PCA), Cluster Analysis (CA) and Factor Analysis (FA) were applied to the whole data set (16 variables x 49 samples) using Statistica 6 software.

### Results

The hierarchic cluster analysis HCA (Figure 1) and the principal component analysis PCA applied to the concentration data-set revealed the presence of different groups of chemical species in the whole data set of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>. The first group contains species typical of sea spray ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{++}$ ). The second is composed of species that represents secondary inorganic components ( $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ); these species are then associated to V and Ni that are markers of heavy oil combustion and to anthropogenic elements such as Cr, Cu and Zn. The last group presents Pb,  $\text{K}^+$ , Mn, Fe and  $\text{NO}_3^-$  that could be due to vehicular traffic [1].

The score and the loadings plot in the sub-space of the three PCs (Figure 2) show how the three PCs discriminate the samples on the basis of aerodynamic diameter: there is a cluster that contains PM<sub>10</sub> samples characterized by Na<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Cl<sup>-</sup> and a cluster that contains PM<sub>1</sub> samples with high amount of V, Ni, Cr SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>. A good separation between PM<sub>10</sub> and PM<sub>1</sub> is clearly visible, while PM<sub>2.5</sub> is slightly overlapped between the other two clusters.

The application of factor analysis with VARIMAX rotation to the concentration data set, shows that five factors explain 71% of the total variance. The first factor has high loading for Na<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>++</sup> and Ca<sup>++</sup> and identifies the “sea spray” source [2]; the second factor shows high loading for Pb and identifies the “traffic” sources; the third factor presents a high loading for Ni and V and the dominance of these elements could be attributed to fossil fuel and heavy oil combustion [3,5]. The fourth factor has high loading for SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, stressing the existence of secondary inorganic aerosol.

The fifth factor comprehends only Zn identifying an industrial source, probably composed of different industrial types (metallurgic and galvanizing industry). Incineration is also the possible source for Zn[4].

## Conclusions

Application of statistical methods to a set of data of PM collected in Taranto elucidated the correlation existing among groups of elements and three different fractions of PM. The application of factor analysis to the concentration data sets lead to the identification of five main sources contributing to PM composition: sea spray, traffic, heavy oil combustion, secondary inorganic components and industrial emissions.

## References

- 1) K.Karar, A. K. Gupta, A. Kumar, A. K. Biswas, Characterization and identification of the sources of chromium, zinc, lead, cadmium, nickel, manganese and iron in pm10 particulates at the two sites of Kolkata, India, *Environ. Monit. Assess.*, 120(1-3), (2006), 347-360
- 2) D. Contini, A. Genga, D. Cesari, M. Siciliano, A. Donato, M. C. Bove, M. R. Guascito, Characterization and source apportionment of PM<sub>10</sub> in an urban background site in Lecce, *Atmos. Res.*, 95(1), (2010), 40-54
- 3) S. Rodriguez, X. Querol, A. Alastuey, M. Viana, M. Alarcon, E. Mantilla, C. R. Ruiz, Comparative PM<sub>10</sub>–PM<sub>2.5</sub> source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain, *Sci. Total Environ.*, 328(1-3), (2004), 95-113
- 4) S. Huang, R. Arimoto, K. A. Rahn, Sources and source variations for aerosol at Mace Head, Ireland, *Atmos. Environ.*, 35(8), (2001), 1421-1437
- 5) R. M. Harrison, D. T. J. Smith, L. Luhana, Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK, *Environ. Sci. Technol.*, 30(3), (1996), 825-832.

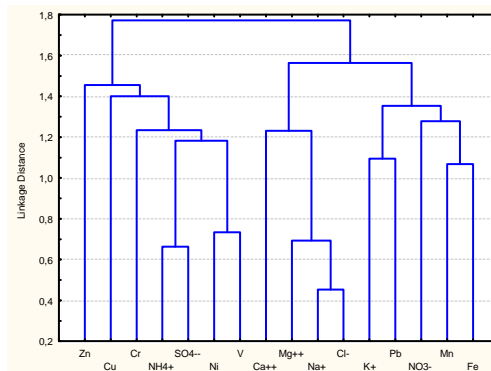


Figure 1: Dendrogram of the cluster analysis

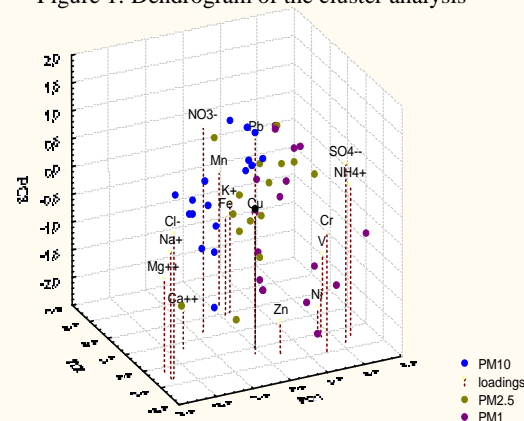


Figure 1: Graph of the three principal components and of the loadings considering the whole data set of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>.