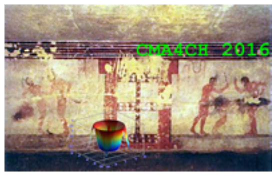
CMA4CH 2016, Mediterraneum Meeting
Straightforward approach in Cultural Heritage and Environment studies - Multivariate Analysis and Chemometry
6th ed., Rome, Italy, Europe, 18-20 December 2016



Chemical Characterization Of Atmospheric Particulate Matter In Friuli Venezia Giulia Region (NE Italy) through Exploratory Data Analysis

A. Mistaro*, A. Felluga, F. Moimas***, A. Abatangelo*, T. Asquini*, R. Bruno*, L. Celic*, M. Guidarelli*, A. Pastrello*, A. Semec Bertocchi***

Agenzia Regionale per la Protezione dell'Ambiente (ARPA FVG) del Friuli Venezia Giulia (ITALY)
*Laboratorio Acque Marino-Costiere e Qualità dell'Aria, via La Marmora 13 – Trieste; **Pressioni sull'Ambiente, via La Marmora 13 – Trieste; *** Qualità dell'Aria, via Cairoli 14 – Palmanova

Abstract

The chemical composition of atmospheric particulate (PM10) in the Friuli Venezia Giulia (FVG) region (NE Italy) has been characterized for the first time with the help of Exploratory Data Analysis (EDA) techniques (uni-, bi- and multivariated - i.e. PCA), molecular and elemental diagnostic ratios and their seasonal trends. Despite the available analytical data were limited to the parameters routinely analysed on PM10 by ARPA FVG (11 elements and 16 PAHs congeners), the applied data analysis techniques allowed us to extract useful latent information from the data set, leading to a greater knowledge of the environmental characteristics of the local area monitored, pointing out similarities and differences among them, and recognizing chemical signatures of the different point or areal sources, both industrial (foundries and coke oven) and urban (traffic and domestic heating).

Introduction

2569 samples were collected throughout the year 2014 by ARPA FVG (Regional Environmental Protection Agency) in 9 automatic stations located in the major cities (Trieste, Udine, Pordenone and Monfalcone) and near the most important industrial plants (including a coke oven and two steel plants – foundries – characterized by different processes) of Friuli Venezia Giulia (FVG) regions (NE Italy).

All samples have been chemically analysed by ARPA FVG dedicated laboratory located in Trieste (Laboratorio Acque Marino Costiere e Qualità dell'Aria - AMCQA Lab) and subsequently characterized according to their molecular (Policyclic Aromatic Hydrocarbons, PAHs) and elemental contents using multiple techniques (uni-, bi- and multivariated (i.e. PCA) analysis; molecular and elemental diagnostic ratios and their seasonal trends).

Materials & Methods

Sampling and chemical analyses have been performed by method required by EU and Italian regulations [1]. Daily PM10 samples (24 h exposition) were collected by ARPA FVG SOS "Qualità dell'Aria" and analysed by ARPA FVG SOS "Laboratorio Acque Marino Costiere e Qualità dell'Aria" according to official methods required [2]. Analyses of PAHs were performed by Soxhlet extraction and HPLC-FLD analysis (Agilent) extending the method for the determination of Benzo[a]pyrene (BaP) to other 15 PAHs congeners. Analysis of elements were performed by ICP-MS (Agilent) after mineralization of the samples, using the official method required for the four toxic metals (As, Cd, Ni, Pb) optimized for the mineralization of further metals (V, Cr, Mn, Fe, Cu, Zn, Sb). ARPA FVG AMCQA Lab is accredited by Italian National Accreditation Body (ACCREDIA) for determination of BaP and the four compulsory metals.

Statistical analyses have been performed by MS Excel 2010 (for uni- and bi-variate analysis), IBM SPSS Statistics 23 (bivariate analysis) and Past 3.0 (univariate and Principal Component Analysis).

Results

Despite the analytical data available were limited to the parameters routinely analyzed on PM10 by ARPA FVG (4 compulsory elements plus other 7 additional; BaP plus other 15 PAHs congeners), the applied data analysis techniques allowed us to extract useful latent information from the data set.

Interesting results have been obtained both in capturing and analysing the regional variability and in identifying chemical signatures of the different point or areal sources, both industrial and urban, leading to greater knowledge of environmental characteristics of each local area.

With regard to PAHs, the use of different indexes (the concentration of the only regulated congener BaP, total PAHs concentration, BaP equivalent toxicity) gave slightly different results; the degree of information conveyed by the last two parameters, by the use of molecular diagnostic ratios (MDRs) and multivariate analysis (PCA) proved to be – obviously - much larger, permitting to identify the most critical stations according to PAH concentration, toxicological concern, and successfully differentiating, in some cases, between an urban *versus* industrial (coke oven) molecular pattern, or between traffic and domestic heating as the major source of urban pollutants. Some interesting considerations have been additionally pointed out regarding the degree of correlation of the 16 congeners analysed, which proved to be essentially independent from the sampling site, but very different according to the molecular weight/volatility of selected PAHs congeners.

With regard to elements, univariate analyses were sufficient to highlight that the main concentrations of some element are - expectedly - found near steel plants. Correlation analyses (Spearman's ϱ) have been afforded singularly for each sampling site, leading in this case (contrary to PAHs correlations study) to discover very different correlation patterns, which in most cases have been successfully interpreted accordingly to the specific features of each station. Correlation studies, PCA and some elemental diagnostic ratios (EDRs) helped not only in affording the (not always trivial) distinction between urban and industrial features of each station, but in the case of foundries allowed to recognize different chemical signatures due to slightly different industrial processes and quality of raw starting materials (Fig. 1). Some other features have been highlighted by EDA, whose environmental reasons seems more difficult to account for.

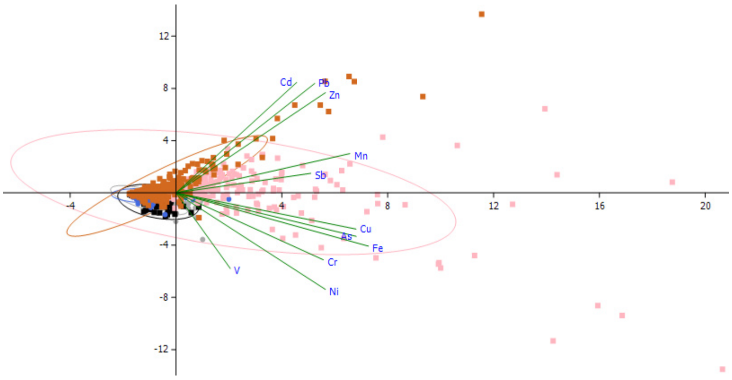


Fig. 1; Biplot from PCA for metal concentrations in PM10 collected in urban and industrial areas. PC#1 explains 51% of variance; PC#2, 18%. The two different foundries are plotted in brown and salmon filled squares, urban stations (mainly covered) are in the remaining colors.

Conclusions

The data analysis techniques employed proved to be useful to recognize similarities and differences among the different areas, helping to define the mainly-urban or mainly-industrial feature of some questionable sampling stations, checking for eventual industrial inputs in some urban stations.

Due to the high correlation among PAHs "heavier" congeners, BaP proved to be a quite good proxy for the toxicological concern of PAH mix at all stations, but the information conveyed by this parameter (the only one regulated in PM10) is necessarily incomplete. Even concerning metals, a survey limited to the four toxic regulated elements would prevent from recognizing the contributions of pollution sources and, ultimately, the understanding of the environmental pressures and impacts.

Finally, a great importance has been given to the ability of the used data analysis techniques to convey the larger possible information in simple graphic forms, in order to allow not scientifically trained people (citizens, decision makers, …) to understand some characteristics of the complex and variegated environmental system whose air they breathe.

References

1) EU 2008/50/CE (Italian D. Lgs. 155/2010)
2) UNI EN 12341:1999, Determinazione del particolato in sospensione PM10. Metodo di riferimento e procedimento per prove in campo atte a dimostrare l'equivalenza dei metodi di misurazione rispetto al metodi di riferimento. UNI EN 15549:2008, Metodo normalizzato per la misurazione della concentrazione di benzo[a]pirene in aria ambiente. UNI EN 14902:2005, Qualità dell'aria ambiente - Metodo normalizzato per la misurazione di Pb, Cd, As, Ni nella frazione PM10 del particolato in sospensione.