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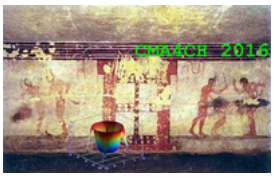

Chemometric Classification (SIMCA) of Atmospheric Particulate Matter in Friuli Venezia Giulia Region (NE Italy) According to Elemental Content

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Abstract

A large environmental dataset, consisting of elemental content in atmospheric particulate matter (PM10) collected in different typologies of sampling stations, was analysed with the SIMCA class-modelling method. All samples collected in a purely urban context proved to be successfully modelled as a single "urban" regional class, independently from sampling sites. In sites where the urban/industrial feature was questionable, for each station, it was anyway possible to assess the degree of non-urban inputs.

Introduction

The chemical composition of atmospheric particulate (PM10) collected in the Friuli Venezia Giulia (FVG) region (NE Italy) collected in 2014 was recently characterized by ARPA FVG in a previous work [1] using Exploratory Data Analysis (EDA) techniques (uni-, bi- and multivariated - i.e. Principal Component Analysis, PCA) and molecular or elemental diagnostic ratios (MDRs, EDRs). Despite the analytical data were limited to the parameters routinely analysed on PM10 by ARPA FVG (11 elements and 16 PAHs congeners), and no parameter considered was a specific marker of any pollution source, the applied data analysis techniques proved useful to characterize sampling sites and to recognize distinct patterns for sampling stations characterized by known point or areal sources, both industrial (foundries and coke oven) and urban ones (traffic and domestic heating). In particular, the use of EDRs and PCA techniques applied to elemental content in PM10 allowed us to infer the mainly-urban or mainly-industrial feature of some questionable sampling stations, checking for eventual industrial inputs in some urban stations.

Given the good results of this multivariate approach, in order to seek more quantitative results on the latter task, in the present work we analysed a larger elemental dataset (years 2014-2016) with a classification method (Soft Independent Modelling by Class Analogy, SIMCA).

Materials & Methods

3480 samples were collected throughout the years 2014-2016 by ARPA FVG (Regional Environmental Protection Agency) in 12 automatic sampling stations located in the major cities (Trieste, Udine, Pordenone and Monfalcone) and near the most important industrial plants of FVG region. Daily PM10 samples (24 h exposition) were collected by ARPA FVG (SOS "Qualità dell'Aria") and analysed for 11 elements by the ARPA FVG dedicated laboratory located in Trieste (SOS "Laboratorio Acque Marino Costiere e Qualità dell'Aria", accredited by Italian National Accreditation Body (ACCREDIA) for determination of the four compulsory metals), using methods required by EU and Italian regulations [2]. Analysis of elements were performed by ICP-MS (Agilent) after mineralization of the samples, optimizing the official method (required for the four toxic elements As, Cd, Ni, Pb) for the mineralization of further metals (V, Cr, Mn, Fe, Cu, Zn, Sb).

PCA and EDRs preliminary analyses were performed by MS Excel 2010 (for uni- and bi-variate analysis), and Past 3.0 (PCA). SIMCA was performed by MATLAB (The Mathworks, Natick, MA) using an in-house routine.

Results

We succeeded in building one single class-model for all PM10 samples of FVG region collected in an urban environment, independently from the city of the sampling stations. Despite no element considered is a specific marker of any pollution source, the model proved sensitive (95%) and quite specific (82%) with respect to samples belonging to industrial sites (Fig. 1). This suggests that, concerning its elemental content, the urban atmospheric particulate of the main cities of FVG region can be modelled in one single class (disregarding geographical and climatic differences among the cities, or site-specific features), and that this "FVG urban class" is sufficiently well defined to discriminate urban samples from other ones characterized by different (not purely urban) origins.

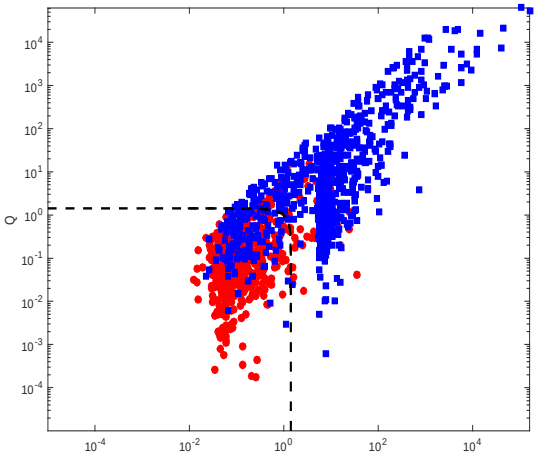

Fig. 1; Q *vs* T^2 plot from SIMCA analysis. Horizontal axis: T^2 (squared Mahalanobis distance from the center of the scores space normalized by the 95th percentiles of its distributions). Vertical axis: Q (sum of squares of residuals normalized by the 95th percentiles of their distribution). In red: urban samples; in blue: industrial samples. Sensitivity (in calibration/7-fold cross-validation): 95%/95%; Specificity: 82%/82%).

We used this model to evaluate the elemental patterns recorded in stations where the urban/industrial feature of the sampling state was questionable. The non-urban input ranged from 17 % to 62 % according to the different sampling sites.

Conclusions

The use of a chemometric classification tool (SIMCA) on a large dataset of PM10 elemental characterization resulted in, at least, two main outcomes:

i) Samples of PM10 collected in all the main cities of FVG region can be considered as belonging (concerning elemental content) to one single class, provided that the sampling station is located in a purely urban context. This outcome enforces the choice of eventually reducing – even to one only – the number of FVG urban sampling stations for elemental analysis, not only because of the low environmental levels measured in all sites for the regulated elements with respect to EU-regulations, but also in force of the *site-in*dependency of its composition; the latter feature suggests that one single regional station, chosen to be representative for all the main urban sites, could serve as a single "watch" for all FVG region, thus abating dramatically the costs of surveys.

ii) The *non-urban* contribution to PM10 sampled in *urban* stations of FVG region have been quantitatively evaluate. While *unsupervised*/exploratory multivariate techniques already proved [1] (by recognizing the different patterns in pollution sources and in sampling stations) to be pivotal to qualitatively identify the mainly-urban or mainly-industrial character of some questionable sampling stations, *supervised* pattern recognition allowed to measure, for those questionable stations, the percentage of events characterized by a non-purely-urban PM10 input. This result is of paramount importance both for policymakers and for Public Institutions dealing with environmental protection and public health.

References

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2) EU 2008/50/CE (Italian D. Lgs. 155/2010) UNI EN 12341:1999, Determinazione del particolato in sospensione PM10. UNI EN 14902:2005, Metodo normalizzato per la misurazione di Pb, Cd, As, Ni nella frazione PM10 del particolato in sospensione.