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Selection of Appropriate Tracers for the Source Identification of Airborne Particulate Matter by Fisher Weight and Factor Analysis

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Abstract

A large data set was generated following the chemical determination of 40 components of airborne particulate matter (PM) on 120 samples. PM10 and PM2.5 samples were simultaneously collected at different sites in the area of Lazio (Italy) and analysed for inorganic ions (IC), total organic and inorganic carbon and major elements (ED-XRF); the same samples were further subjected to two-step chemical fractionation based on differences in elemental solubility (ICP-AES). Prior to apply receptor modeling, analysis of redundancies was performed. To this aim two approaches were applied: Fisher weight and Factor Analysis. The discriminating power of chemical components as PM source tracers was evaluated by combining results from both approaches. This led to select 23 of initial 40 variables. Fisher weight selection made it possible to evidence chemical components relevant for the identification of local sources (e.g. re-suspension of road dust). However, only by Factor analysis the role of Cr, Ni, Mn and Zn as selective tracers of two different non local sources of PM was evidenced.

Introduction

Chemical characterization of airborne particulate matter (PM) is of main relevance in environmetric approaches of source identification and apportionment, e.g. receptor modeling methods based on multivariate statistics. It is recently recognized that evaluating the solubility of major and trace elements in different PM sizes improves PM source identification, with respect to considering total element content. When chemical characterization of PM includes two- (or multi-) step chemical fractionation, large dataset are produced, requiring thus a large number of PM samples to ensure statistical robustness of results. In these cases, when cost/effectiveness evaluations are done, analysis of redundancies is determinant to reduce dimensions of data matrix. In this paper, two approaches to evaluate redundancies, Fisher weight (W_F) [1, 2] and Factor analysis (FA), are applied to a large dataset generated from chemical characterization and two-step fractionation [3] of PM10 and PM2.5. Samples were collected during a large-scale field campaign at different sites in the area of Lazio region (Italy) to the aim of identifying main PM sources. In the case of W_F an absolute and independent measure of the discriminating ability of each variable is determined [2], whereas by FA mutual correlations between variables are considered for selection. Results from both approaches are compared and combined to select relevant PM components for source identification and apportionment.

Materials & Methods

The W_F is calculated as the average of the ratios between the squares of the difference between means and the sum of the variances for all combinations of two categories into which the objects have been subdivided [1, 2]. In this paper, PM10 samples were categorized by site. Varimax rotated FA with retention of principal components was performed by STATISTICA 7.1 software; principal components with eigenvalues greater than unity were retained.

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Results



Fig. 1(left): W_F for PM10 components calculated over the three collection sites. Fig. 2(right): FA loadings for source identification at urban background site. Soluble/insoluble element fractions are respectively indicated by subscripts e and r. Al, Si, K, OM and EC were determined as total content. F1: traffic combustion/resuspension; F2: source of total Mn and Zn; F3: sea spray; F4: secondary inorganic aerosol; F5: crustal material; F6: source of soluble Cr and Ni.

Three sites were chosen for this study: traffic (MZ), urban background (VA) and rural background (FC). W_F selection was carried out by considering PM10 components having $W_F > 0.1$ (fig. 1). FA was performed under different combinations of variables: a) -all 40 components, b) - removing minor components one at a time (this allowed the selection of 30 variables which explained about 86% of total variance at each site and evidenced the influence of two non-local sources, i.e. affecting all sites irrespective of type), c) -only W_F -selected components, d) -the 17 variables selected by both approaches (Al, Si, K, OM, EC, As_e, Cu_e, Fe_e, Mg_e, Sb_e, Cu_r, Cr_r, Fe_r, Sb_r, Snr).

Conclusions

The 17 variables selected by both approaches allowed the identification of local sources (crustal, secondary inorganic aerosol, sea spray, traffic) but the two non-local contributions were not evidenced. Only after including Cr_e , Ni_e , Mn_e , Zn_e , Mn_r , Zn_r (selected by FA but not by W_F) it was possible to recognize these two sources, as reported in fig. 2.

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