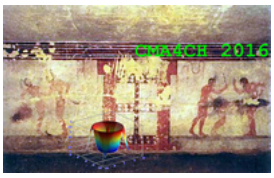
CMA4CH 2016, Mediterraneum Meeting
Straightforward approach in Cultural Heritage and Environment studies - Multivariate Analysis and Chemometry
6th ed., Rome, Italy, Europe, 18-20 December 2016



Carbonaceous Species in PM10 and PM2.5 in the Atmosphere of Three Italian Port Cities. Statistical Treatment of Data

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Abstract

It is known that carbonaceous species constitute a major, sometimes dominant, fraction of atmospheric particulate matter. Carbonaceous aerosol is commonly divided into an organic carbon (OC) and an elemental carbon (EC) fraction.

In this study the single peak components of OC/EC thermograms have been analyzed. OC/EC composition data have been acquired for PM10 and PM2.5 samples collected during 2014 and 2015 by seasonal sampling campaigns performed at three port sites in Italy. Principal Component Analysis was applied to dataset in order to evaluate differences and similitudes among the sites.

Introduction

It is known that carbonaceous species constitute a major, sometimes dominant, fraction of atmospheric particulate matter. Carbonaceous aerosol is commonly divided into an organic carbon (OC) and an elemental carbon (EC) fraction. Both of these have important roles and effects on climate and health because of their physical and chemical characteristics.

Despite the very large proportion of carbonaceous aerosols in PMx and the consequent relevance of this component for air quality, their origins are not fully understood and probably their contribution to PMx load vary largely across the different regions in Europe. The major sources of these species are biomass, bio-fuel burning emission (BBE), and fossil-fuel combustion (FFC). The origin of OC, especially of SOA (secondary organic aerosol), is a hot topic in atmospheric sciences and a recent WHO report (REVIHAAP report, WHO, 2013) indicates that further studies are needed to characterize the health effects of SOA. Another recent WHO report (WHO, 2012) also evidences clear health consequences from the increased concentrations of EC, although this is probably not due to EC per se but to the OC compounds that EC particles carry on. The importance of these different sources, however, still cannot be estimated accurately and all different source apportion methodologies have caution, because of the still limited knowledge of its molecular composition, atmospheric processes and characteristic emission profiles. A commonly used method for the indirect evaluation of carbonaceous in atmospheric particles, which had the advantage of simplicity and low cost, was based on the values of OC/EC ratios. In this study the single peak components of OC/EC thermograms have been analyzed.

Materials & Methods

OC/EC composition data have been acquired for PM10 and PM2.5 samples collected during 2014 by seasonal sampling campaigns performed at two port sites in South-Italy. In addition a second city (three sites) in Central-Italy has been evaluated in a parallel campaign on PM10 samples.

Elemental carbon (EC) and organic carbon (OC) in a 1.5 cm^2 filter punch were measured on Sunset Laboratory Thermal– Optical Carbon Aerosol analyser using NIOSH protocol (NIOSH, 1998). The OC/EC analysis proceeds in two phases. In the first phase, the carbon is volatilized in pure helium atmosphere by means of four temperature steps. During the second phase, the carbon

remaining on the filter is heated in a mixture of oxygen and helium by using six temperature steps. Carbon evolving from the filter is oxidized to carbon dioxide, and then reduced to methane for detection with a flame ionization detector (FID). Uncertainties in EC and OC measurements are of the order of 5%. For sampling of quartz filters a denuder was not used. This can lead to an overestimation of OC concentration by adsorption of gas-phase carbon component to the filter (positive artifact) and underestimation by volatilization of already collected OC from the filter (negative artifact).

Single peak components of OC/EC thermograms were analyzed and quantified: 4 OC peaks (OC1, OC2, OC3, OC4), 1 pyrolitic peak (Pyrrol) and 6 EC peaks (EC1, EC2, EC3, EC4, EC5, EC6).

Results

The compositional data matrix of the carbonaceous parameters (OC1, OC2, OC3, OC4, Pyrol, EC1, EC2, EC3, EC4, EC5 and EC6) has been treated by Principal Component Analysis, to identify groups of PMx samples that can be clustered on the basis of compositional characteristics, indicating the correlation among variables and among these and PMx samples.

The score and loadings plot in the sub-space of the first three Principal Components (PCs) is shown in Figure 1 a and b, respectively. The first three PCs explain 83% of the total variance. The PMx samples are clustered into three clusters corresponding to each PM of investigated city (cluster A, B and C in figure 1). While there is a partial overlapping of cluster A and B (city A and B), cluster C (city C) is well defined and separated. Loadings analysis explain that discrimination among clusters, leading to separation of A and B clusters from C, is mainly due to the contribution of less volatile and oxidable carbonaceous component and that OC1 and OC2 mainly characterize cluster C.

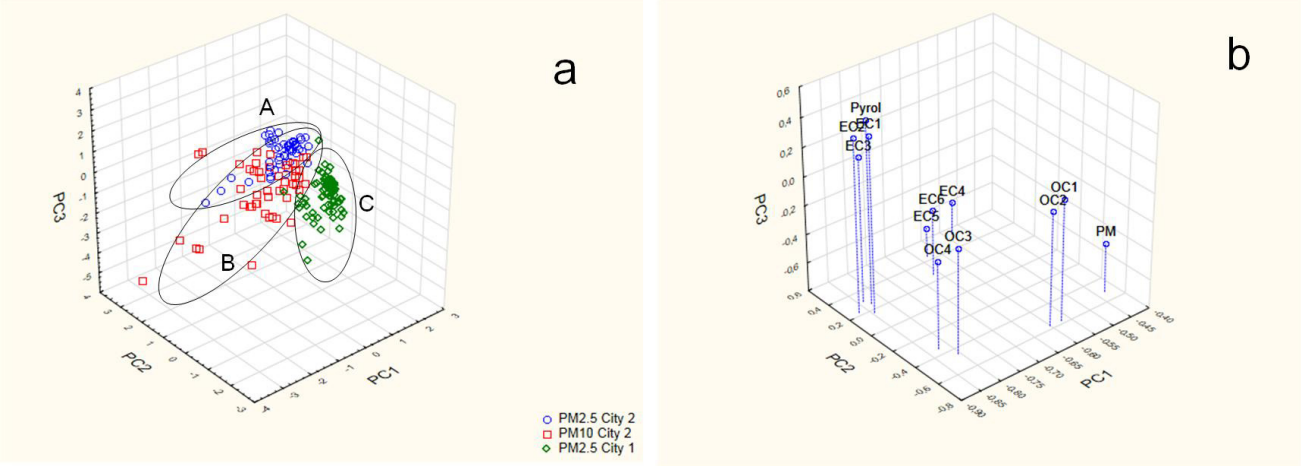

Fig.1; PMx score plot and loading plot of PC1, PC2 and PC3 space

Conclusions

The explorative investigation showed that the three cities present different amount of carbonaceous compounds which are emitted by emission sources characterized by different distribution of the single carbonaceous components. City C presents higher amounts of the more volatile and oxidable fraction, while city A and B of the ECx fractions.

References

1) WHO 2013: Review of evidence on health aspects of air pollution – REVIHAAP. First Results. WHO's Regional office for Europe, Copenhaguen, 28 pp., http://www.euro.who.int/data/assets/pdffile/0020/182432/e96762-final.pdf, 2013
2) NIOSH: Method 5040 Cassinelli ME, O'Connor PF (Eds.), NIOSH: Manual of Analytical Methods (NMAM)