Multivariate Analysis and Chemometrics applied to Environment and Cultural Heritage, Nemi (RM), 2-4 October 2006, Italy, Europe



Sources and Source Regions Effecting the Aerosol Composition of the Eastern Mediterranean

<u>G. Dogan¹</u>, G. Güllü² and G. Tuncel¹

¹Middle East Technical University, Dept. Environmental Engineering, Ankara, Turkey ²Hacettepe University, Dept. Environmental Engineering, Ankara, Turkey

Abstract

Sources and sources regions affecting aerosol components at a rural site on the Mediterranean coast of Turkey were investigated using a receptor oriented method namely, positive matrix factorization (PMF). Seven factors were identified with PMF, namely two crustal, marine, mixed anthropogenic, smelter, local pollution and fertilizer factors. Consequently, this factor is identified as local pollution factor. PMF, with seven factors explained 83% of the system variance.

Introduction

Studies performed in the region clearly demonstrated that the Eastern Mediterranean is under the strong influence of long range transport of pollutants. The sulfate levels is the highest measured in whole Europe. Concentrations of other pollutants, such as ozone, pollution derived trace elements are also high. In this study PMF is used as multivariate statistical tool to identify sources affecting chemical composition of Eastern Mediterranean aerosol. PMF uses a least square approach to solve the factor analysis problem integrating non-negatively constraints into the optimization process and utilizing the error estimates for each data values as point by point error estimates [1]. A variant of trajectory statistics namely, Potential Source Contribution Function (PSCF), which combines information provided by measured concentrations and paths of backtrajectories is used to identify locations of sources revealed by the PMF. Combination of these two powerful tools of chemometry proved very useful to identify sources that affect composition of particles in the Eastern Mediterranean and whereabouts of those sources.

Materials and Methods

The sampling station is located on the Mediterranean coast of Turkey, approximately 20 km to the east of the city of Antalya (31.0°E, 36.8°N). Particles were sampled using a Sierra Anderson Model SAUV-10H PM-10 High Volume Air Sampler. Daily aerosol samples were continuously collected between February 1992 and December 1993. During this period, approximately 600 daily aerosol samples were collected. The uncertainty estimation in PMF provides a useful tool to decrease the weight of missing and below detection limit data in the solution as well as to account for the variability in the source profiles. In this study, values below detection limit were replaced by half of the detection limit values and their overall uncertainties were set at 5/6 of the detection limit values. Missing values were replaced by the geometric mean of the measured values and their accompanying uncertainties were set at four times this geometric mean values. The concept of PSCF was used to determine geographical regions that may have a higher probability of being source areas. Statistical significance of potential source areas were tested using bootstrapping technique [2;3].

Results

The result showed that Eastern Mediterranean aerosols consists of 7 components represented by seven factors. Two of these components are crustal material with high loadings of litophilic elements. One of these crustal factors are identified as local soil and the other one, which has higher loading of Ca, is identified as Saharan dust. One of the seven factors, which include high loadings of Na, Mg, Cl and Br was a clear marine factor.

G. Dogan et al., Sources and Source Regions Effecting the Aerosol Composition of the Eastern Mediterranean

Pre issue, CMA4CH 2006, Mediterranean Meeting. Multivariate Analysis and Chemometrics applied to Environment and Cultural Heritage, Nemi (RM), 2-4 October 2006, Italy, Europe

Four of the seven factors represented anthropogenic components in the Eastern Mediterranean aerosol population. They were all loaded with pollution-derived elements. First anthropogenic factor has high loadings of NO_3^{2} , SO_4^{2} , V, Zn and Se. This factor is identified as mixed anthropogenic factor, owing coexistence of coal combustion related species, such as $SO_4^{2^2}$, Se, oil combustion related element V and Zn which is an element generally associated with industrial activities. According to the calculated PSCF values, presented in Figure 1, the major contributions to this factor are from Aegean coast, Marmara region, Balkan countries, Ukraine and regions located northern part of Ukraine. Second anthropogenic factor has high loadings of As and Sb and is attributed the local sources. The backtrajectories of the highest 20% contributing days for this factor advect to the surface as they come closer to the station site (Figure 2). The third anthropogenic factor consisted only of NH₄⁺ ion. Previous studies in the same location have clearly demonstrated that NH_4^+ in this region is strongly associated with fertilizer use [4]. Therefore this factor is recognized as fertilizer factor. The last anthropogenic factor has high loadings of Cr, Ni, Sb, Br and Pb. This factor is a second mixed anthropogenic factor as it includes well known marker of particles emitted from motor vehicles, such as Pb and Br and elements associated with particles emitted from smelters, such as Cr. Ni, and Sb. The Cr smelter in the city of Antalya, is the most likely candidate for this factor, because, the smelter is located within the city and mechanism that brings its emissions to our station is also expected to bring urban emissions. Lead and Br which are indicators of urban plume is also observed in this particular factor.



Fig. 1; Calculated PSCF values for highest 40% factor scores of sulfate factor

Fig. 2; (a)Top and (b)side view (from Africa) of backtrajectories corresponding to highest 20% of the factor scores of arsenic factor

Conclusion

In this study, positive matrix factorization was applied to the data set generated by analysis of samples collected at a station located on the Mediterranean coast of Turkey. Seven factors generated with PMF namely, local dust, Saharan dust, marine, mixed anthropogenic (sulfate), smelter, local pollution and fertilizer with a system variance of 83%. The main source region of sulfate factor is identified as Aegean coast, Marmara region, Balkan countries, Ukraine and regions located northern part of Ukraine. The smelter factor is due to the smelter activities in Antalya and the urban plume. Agricultural activities over the region signified itself with a fertilizer factor.

References

1) B.A. Begum, E. Kim, S.K. Biswas, P.K. Hopke, Investigation of sources of atmospheric aerosol at urban and semi-urban areas in Bangladesh, *Atmos. Environ.*, 38, 19 (2004) 3025-3038.

2) R. Wehrens, H. Putter, L.M.C. Buydens, The bootstrap: a tutorial, *Chemometr. Intell. Lab.*, 54 (2000) 35-52.

3) A. Lupu and W. Meanhaut, Application and comparison of two statistical trajectory techniques for the identification of source regions of atmospheric aerosol species, *Atmos. Environ.*, 36 (2002) 5607-5618.

4) G. Güllü, I. Ölmez, S. Aygün and G. Tuncel, Atmospheric trace element concentrations over the Eastern Mediterranean Sea: Factors effecting temporal variability, J. Geophys. Res., 103 (1998) 21943-21954.