ABSTRACT

In the present study, statistical methods based on multivariate analyses such as the Descriptive Discriminant Analysis (DDA) and Principal Component Analysis (PCA) were applied to determine relationships between particle sizes and the composition of the associated semi-volatile compounds, in addition to evaluating these observations in relation to the emission sources, study areas, sampling campaigns and season. Results from the DDA showed that the PAHs distributions give the best discrimination capacity within the data set, whereas the PAH distribution in intermediate particle fractions incorporates noise in the statistical analysis. The PCA was useful in identifying the main emission sources in each study area. It showed that in the city of La Plata the most important pollution sources are traffic emissions and the industrial activity associated with oil and petrochemical plants. In Leipzig, the main sources are those associated with traffic and also a power plant. The combined PCA and DDA methods applied to PAH distributions is a valuable tool in characterizing types of emissions burdens and also in obtaining a differentiation of sample identity according to study areas and sampling times.

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1. INTRODUCTION

Multivariate statistical analysis has gone beyond solely mathematical applications and has extended to several other professional branches to be used as a basic decision tool in business strategies (Chandra & Menezes, 2001; Chiu et al., 2002; Mirko, 2006) to classify animal and plant species (Ballesteros-Grijalva et al., 1996; Darland, 1975), to develop new technologies, and to design experiments and interpret results derived from exact, computational, and environmental sciences (King & Jakson, 1999; Pineda-Torres et al., 2002; Serita et al., 2005). When working with sets of variables describing a given object, it is necessary to have methods allowing the identification of mutually independent properties that are common to a given group (clusters). They can also be helpful in identifying anomalous elements in the algebraic multidimensional space (Guha et al., 2000; Slonim, 2010). There are a variety of methods that are useful for these purposes, such as Descriptive Discriminant Analysis (DDA), Classification Discriminant Analysis (CDA) and Principal Component Analysis (PCA), among others (Anderberg, 1973; Hotelling, 1993; Johnson & Wichern, 1992), allowing to derive conclusions at different specificity levels. DDA triggers a causality relationship in which the endogenous variables are non-metric and the independent variables are metric. CDA is useful for understanding differences among groups and offers an explanation, on the basis of metric observations, as to why the objects/subjects are associated with different levels of a given factor. PCA is a multivariate method in matrix algebra known as the matrix diagonalization procedure, important to finding the least number of variables to describe an object. Applications to the interpretation of the environmental behaviour of different relevant pollutants have been widely used (Kavouras et al., 2001; Khalili et al., 1995; King & Jakson, 1999; Statheropoulos et al., 1998; Zhang, 2006).

Particular interest could be given to the application of PCA to identifying pollutant sources of environmental mixtures, such as the Polycyclic Aromatic Hydrocarbons (PAHs). These are organic compounds forming in different combustion processes, which may be natural (volcanic activity, forest fires, etc.) or anthropogenic. The latter are most environmentally relevant due to their incorporation in the atmosphere from a diverse source of emissions, like mobile sources (diesel and gasoline engines), industrial activity associated with the petroleum derivatives, and domestic activity, such as home heating (Chiang et al., 2007; Khalili et al., 1995; Marr et al., 1999; Yang et al., 1998). PAHs are associated with particles arising in these processes, forming atmospheric aerosols, and consequently aiding in the transport of these compounds. Sorption/desorption-associated equilibriums with the gaseous phase are in close relationship with the ring size and molecular weight of the PAHs (Lee et al., 1981; Pankow, 1994; Storey & Pankow, 1992). There are 16 PAHs (Figure 1) that have been selected as representative priority pollutants by the Environmental Protection Agency of the USA (USEPA, 1998), which are in association with suspended particulate matter (PM) in different environments all around the world (Dallarosa et al., 2005; Fang et al., 2005, 2006; Mantis et al., 2005; Rehwagen et al., 2005; Sharma et al., 2007). The small-particle inhalable and respirable fractions (below 10 and 2.5 µm, PM10 and PM2.5, respectively) have an important epidemiologic interest because of the potential to accumulate in the respiratory system and to injure the deep respiratory tracks (Farmer et al., 2003; Gilli et al., 2007; Jacob, 1996; Viana et al., 2008). The PAH concentration in a given place depends upon some local and environmental conditions (such as UV radiation, temperature, and pressure), on the emission source, and on the type and size of the PM. Its relationship to exposure and incidence on human health, then, is given by the type of habitat (rural, residential, urban, and
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