Sources identification using organic molecular markers in fine particulate matter collected at Trombay, Mumbai

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This paper received the Best Poster Award at the Workshop cum Seventeenth National Symposium on Environment on advances in Environmental Monitoring and Modeling, held at the Centre for Environmental Science & Engineering, IIT Kanpur, from 13-15 May, 2010

Abstract

Positive Matrix Factorization (PMF), a useful factor analysis method, was applied to 24-hr PM$_{2.5}$ speciation data, collected at Trombay, Mumbai. The PM$_{2.5}$ fraction was found to have mass concentration ranging between 22.7 $\mu$g/m$^3$ and 79.0 $\mu$g/m$^3$, with a mean concentration of 56.7 $\mu$g/m$^3$. In PM$_{2.5}$ samples, the total Polycyclic Aromatic Hydrocarbons (PAHs) level ranged from 12.8 ng/m$^3$ to 96.92 ng/m$^3$ and the mean concentration was 52.6 ng/m$^3$. For this study, a 5 factor model was found to provide the most physically interpretable solution, with 90.7% of the measured mass apportioned. The sources were identified as diesel combustion emissions, biomass burning and incineration, coal-fired power plant emissions, local gasoline traffic emissions and refinery emissions.

Introduction

Particulate matter has been implicated in a number of health effects, including respiratory symptoms, bronchitis, heart attack and premature deaths. The airborne Particulate Matter (PM) in an urban atmosphere, is a complex mixture of inorganic and organic substances, and their origin could be either natural or anthropogenic, or both. Among the organic compounds of anthropogenic origin, the PAHs make up an important group, because, of the way they endanger human health and also because, they can be used as source-specific marker molecules. Understanding the contribution of various emission sources is critical, to appropriately manage PAHs in the environment. Receptor models have been used, to assess contributions of PAHs from all major sources based on observations at sampling. Receptor models are the application of multivariate statistical methods to the identification and quantitative apportionment of pollutants to their sources. Positive Matrix Factorization (PMF), an advanced receptor models has been successfully used, for quantitative identification of sources of organic pollutants in aerosols. PMF rotates the matrices of factor loadings and scores with positive constraints, which makes factor axes less orthogonal and makes factor loadings and factor scores more interpretable. In this paper, organic molecular markers PAHs were used in PMF analysis, to identify possible sources of PM$_{2.5}$ measures, at an urban location in Mumbai.

Sample Collection and Analysis

PM$_{2.5}$ samples were collected, using a fine particulate sampler. Sampling was done for a 24 hour period, at a height of 8 meters from the ground level. Pre-weighted filter papers were used, to collect the samples. A strict regime of quality control and quality assurance was followed. Field blanks were collected to quantify possible contamination of the samples during collection, transport and storage. The characterization and quantification of different PAHs were carried out, using a Shimadzu HPLC
system (LC-10 AD) with UV-visible detector. Before analysis, the filter paper samples were extracted ultrasonically, with hexane as solvent.

**Results and Discussion**

The PM$_{2.5}$ fraction was found to have a mass concentration, ranging between 22.7 $\mu$g/m$^3$ and 79.0 $\mu$g/m$^3$, with a mean concentration of 56.7 $\mu$g/m$^3$. In PM$_{2.5}$ samples, the total PAHs ranged from 12.8 ng/m$^3$ to 96.92 ng/m$^3$ and the mean concentration was 52.6 ng/m$^3$. Maximum concentration of PAH was observed during winter in PM$_{2.5}$ samples, while a minimum value was observed during the monsoon. Lower concentration of PAHs was recorded during summer than in winter. This could be due to photo-oxidation of PAHs and the meteorological conditions, favoring the dispersion of these compounds during summer. Maximum concentration of fluoranthene was recorded during summer at the sampling site. Fluoranthene is the marker species of coal combustion, industrial oil burning and petrol and diesel powered vehicles. Due to longer retentivity of submicron particles in the atmosphere, Fluoranthene emitted around the industrial site shows a higher concentration during summer.

For this study, a five factors model was found to provide the most physically interpretable solution. 90.7% of the measured mass was apportioned. The sources were identified as diesel combustion emissions, biomass burning and incineration, coal-fired power plant emissions, local gasoline traffic emissions and refinery emissions. Fig.1 shows the percentage of concentrations of individual PAHs to different sources as obtained by PMF analysis.

Factor 1 explains about 30% of the sum of the measured PAHs and was dominated by Benzo(k)Fluranthene, Benzo(b)Fluranthene, Phenanthrene and Perylene. According to Hwang et al. (2003) the presence of PAHs with 3 and 4 aromatic rings, such as Benzo(k)Fluranthene, Benzo(b)Fluranthene and Phenanthrene, indicates the dominance of diesel combustion. Therefore, the presence of these compounds can be attributed to diesel exhausts. Factor 2 explains 22% of the total PAHs and was dominated by Benzo (a) Anthracene, Benzo (a) Pyrene and Dibenzo (a,h) Anthracene. Kulkarni and Venkataraman (2000) have
shown, that Benzo(a)Pyrene can be a good tracer for wood burning, while Freeman and Cattell (1990) showed that this compound could be associated with combustion of vegetation. Masclet et al. (1986) have shown that, Dibenzo(a,h)Anthracene can be a typical tracer for incineration. Therefore, it is very difficult to assign any specific source for this factor. However, it is more appropriate to attribute this factor to biomass burning and incineration. Factor 3 is responsible for 16% of the sum of determined PAHs. This factor is predominantly weighted in Anthracene and Benzo(a)Anthracene. Khalili et al. (1995) identified that Anthracene, Phenanthrene and Benzo(a)Anthracene were tracers for coal combustion. Therefore coal combustion could be characterized as the source for this factor. Factor 4 accounted for 12% of the total measured PAHs. This factor is weighted in Benzo(ghi)Perylene and Fluranthene. Miguel et al. (1998) have shown, that Benzo(ghi)Perylene is characteristic of vehicular emissions from gasoline engines. Therefore this factor could be attributed to the vehicular emissions for gasoline exhausts. Factor 5 explains 10% of the variance and has a high load for Fluorene and Pyrene. According to Masclet et al. (1986), light PAHs (3 and 2 aromatic rings) are predominant in emissions from petrol refinery and are characterized by high concentration of Fluorene and Pyrene. Thus, in this work, this factor was associated with refinery emissions.

References