Atmospheric Research 84 (2007) 30–41

ATMOSPHERIC RESEARCH

www.elsevier.com/locate/atmos

Source apportionment of PM_{10} at residential and industrial sites of an urban region of Kolkata, India

Kakoli Karar [1], A.K. Gupta *

Environmental Engineering Division, Department of Civil Engineering, Indian Institute of Technology, Kharagpur 721302, India

Received 31 January 2006; received in revised form 16 May 2006; accepted 16 May 2006

Abstract

PM_{10} and its chemical species mass concentrations were measured once in a week at residential (Kasba) and industrial (Cossipore) sites of an urban region of Kolkata for a period of 24 h during November 2003 to November 2004. At each monitoring site, 53 sets of daily average PM_{10} samples were collected during the study period. Approximately 55% of the monitoring days are weekdays, while 45% are weekends. The PM_{10} mass concentrations ranged from 68.2 to 280.6 $\mu g\ m^{-3}$ at the residential site, and 62.4 to 401.2 $\mu g\ m^{-3}$ at the industrial site. Polycyclic aromatic hydrocarbon compounds (PAH), fluoranthene (Fl), pyrene (Py), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF) and benzo(a)pyrene (BaP) have been analyzed using Gas Chromatoghaphy. Metals in PM_{10} deposited on quartz microfibre filter papers were measured using an Inductively Coupled Plasma-Atomic Emission Spectrometer. Chromium (Cr), zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni), manganese (Mn) and iron (Fe) are the seven toxic trace metals quantified from the measured PM_{10} concentrations. Total carbon (TC), inorganic carbon (IC) and organic carbon (OC) were analyzed using a Carbon analyzer. Exposed quartz microfibre filter papers were also analyzed for water-soluble anions of fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) using ion chromatography. In this study, principal component analysis (PCA)/absolute principal component scores (APCS) model was applied to the mass concentrations of PM_{10} and its chemical species. Principal component analysis with varimax rotation identified five possible sources; solid waste dumping, vehicular emission, coal combustion, cooking and soil dust at residential site. The extracted possible sources at the industrial site were vehicular emissions, coal combustion, electroplating industry, tyre wear and secondary aerosol. A quantitative estimation by principal component analysis–multiple linear regression (PCA–MLR) model indicated that solid waste dumping contributed 36%, vehicular emissions 26%, coal combustion 13%, cooking 8% and soil dust 4% at the residential site. The PCA–MLR apportioned 37% to vehicular emissions, 29% to coal combustion, 18% to electroplating industry, 8% to tyre wear and 1% to secondary aerosol at the industrial site. Due to the limitation in source marker species analyzed, 13% at Kasba and 7% at Cossipore could not be apportioned to any possible sources by this technique.

Keywords: Aerosol; Particulate matter; Principal component analysis; Multiple linear regression; Receptor model; Sources

---

1. Introduction

Urban air quality in developing countries has deteriorated gradually because of rapid urbanization, population growth, lack of sufficient public facilities and

---

* Corresponding author. Tel.: +91 3222 283428; fax: +91 3222 255303.

E-mail addresses: k_karar1@yahoo.co.in (K. Karar), akgupta@iitkgp.ac.in (A.K. Gupta).

[1] Tel.: +91 3222 281418; fax: +91 3222 255303.

0169-8095/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.atmosres.2006.05.001

industrialization. In India, air pollution has become a great topic of debate at all levels because of the enhanced anthropogenic activities (Goyal and Sidhartha, 2002). The role of anthropogenic processes as the source of atmospheric pollution has been increasing gradually with the onset of the industrial revolution (Kim et al., 2002).

Air quality in cities is getting worse as the population, traffic, industrialization and energy use increases. Even with the introduction of advanced emissions control technology, motor vehicles remain the dominant sources of urban air pollution. It is important to identify the source characteristics of air pollution for the development of air quality control strategies (Park and Kim, 2005).

Kolkata is a mega city with high population density, several business activities as well as a number of large and small-scale industries of different categories. A clinical examination and questionnaire survey of residents of the city and rural Bengal reveal that the Kolkata population is much more susceptible to respiratory disorders as compared to a similar population in rural Bengal. While 13.5% and 35% of the rural subjects surveyed suffer from upper and lower respiratory tract symptoms respectively, the corresponding figures for the Kolkata population are 41.3% and 47.8% (WBPCB, 2001).

Several epidemiological studies have indicated a strong association between elevated concentrations of PM_{10} (particulate matter which passes through a size selective impactor inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter) and increased mortality and morbidity (Arditsoglou and Samara, 2005; Lin and Lee, 2004; Namdeo and Bell, 2005). It also influences many atmospheric processes including cloud formation, visibility, solar radiation and precipitation, and plays a major role in acidification of clouds, rain and fog (Celis et al., 2004; Hong et al., 2002; Khoder, 2002; Rajkumar and Chang, 2000). Anthropogenic prime sources of PM_{10} are combustion, vehicular traffic and industrial processes. Ambient particulate matter may be the carriers of acidic or toxic species (e.g., heavy metals, acids and carcinogenic organic compounds) and may have detrimental effects on human health and ecosystems (Cheng et al., 1996). High molecular PAHs are reported to have high toxicity (Kameda et al., 2005).

The identification of air pollution sources is an important step in the development of air quality control strategies (Wang and Shooter, 2004). Abatement strategies may significantly improve the air quality after identifying the main aerosol sources. Receptor modelling has been used to determine sources of aerosols on local (Kowalczyk et al., 1982) and regional (Rahn and Lowenthal, 1984) scales. Receptor models identify the presence and quantify of source contributions to the receptor (Harrison et al., 1997; Vega et al., 2000; Srivastava et al., 2005). The mostly widely used models are the chemical mass balance (CMB), principal component analysis (PCA)/absolute principal component scores (APCS), positive matrix factorization (PMF), and graphical ratio analysis for composition estimates (GRACE)/source apportionment by factors with explicit restriction (SAFER) models (Guo et al., 2004). The great advantage of using PCA as a receptor model is that there is no need for a priori knowledge of emission inventories (Chio et al., 2004).

Over the last two decades, multivariate analysis has been widely used to identify possible sources of ambient particles. Among multivariate techniques, PCA is often used as an exploratory tool to identify the major sources of air pollutant emissions (Bruno et al., 2001; Guo et al., 2004; Marcazzan et al., 2003; Thurston and Spengler, 1985). Factor scores available as output from principal component analysis (SPSS, 2003) was unscaled and uncentred to produce absolute factor scores (AFS) using the method outlined by Thurston and Spengler (1985). This technique is known as the absolute principal component analysis (APCA). This APCA technique has been applied successively in a number of studies (Maenhaut and Cafmeyer, 1987; Kumar et al., 2001). In this technique, the AFS are regressed on the observed PM_{10} concentration to apportion the respirable particulate matter to each sample (Kumar et al., 2001).

The aim of the study was to quantitatively apportion the sources leading to high PM_{10} concentrations at residential and industrial sites of an urban region of Kolkata. At each monitoring site, concentrations of PM_{10} were monitored using a respirable dust sampler (Envirotech, APM 460). The PM_{10} concentrations were measured gravimetrically by weighing the particulate mass deposited on the quartz microfibre filters and knowing the total volume of air sampled. A varimax rotated principal component analysis identifies the probable sources affecting the composition of PM_{10}. Principal component analysis–multiple linear regression (PCA–MLR), a receptor modelling technique, has been used for quantitative apportionment of the sources contributing to PM_{10} at the monitoring sites.

2. Materials and methods

2.1. Study area

Kolkata (22°32′ N, 88°22′ E) is the second most populous city of India after Mumbai according to the

2001 census report. The city is bounded to the west and north–west by the Hugly river spread along 80 km. The core area of the city is flat with elevations ranging from 6 m above the mean sea level. Kolkata has a tropical savannah climate with a marked monsoon season. Average relative humidity is 66% and 69% in winter and summer, respectively. Mean monthly temperature ranges from 20 to 31 °C, and the maximum temperature often exceeds 42 °C. The pre-monsoon and monsoon seasons are dominated by strong southwesterly winds with greatest air ventilation potential (UNEP/WHO, 1992). Moderate northwesterly winds prevail for most of the year. Being located in a coastal area and influenced by sea-based disturbances, it has an average wind speed of 2 m/s blowing throughout the year. Fig. 1 shows the monitoring locations of the study area. Kolkata, the second largest metropolis in south Asia is one of the worst polluted cities in the world. Rapid and unplanned urbanization, uncontrolled vehicular density on insufficient badly cared-for road space, low turnover of old vehicles with too frequent breakdowns and higher use of leaded petrol fuel increases the air pollution in Kolkata (Ghose et al., 2004).

The residential and industrial monitoring stations were set up based on the importance of emission sources, sensitivity of receptors, wind directions and predominant activities of the local areas. Kasba is a typical residential area and air quality is mainly influenced by domestic activities, vehicular movement, solid waste dumping and open burning of leaves and garbage. An industrial location (Cossipore) has mainly thermal power generation plant, ordnance factory, railway yard for loading and unloading materials, heavy vehicular traffic, electroplating industry and dyeing industry and other small scale industries, such as, battery industry, tannery.

2.2. PM_{10} sampling protocol

A respirable dust sampler (Envirotech, APM 460) was deployed for monitoring ambient PM_{10} at each monitoring site. Ambient air laden with suspended particulates enters the respirable dust sampler through an inlet pipe. As the air enters the cyclone, coarse, non-respirable dust is separated from the air by centrifugal forces acting on the solid particles. It first separated coarser particles larger than 10 μm from the air stream

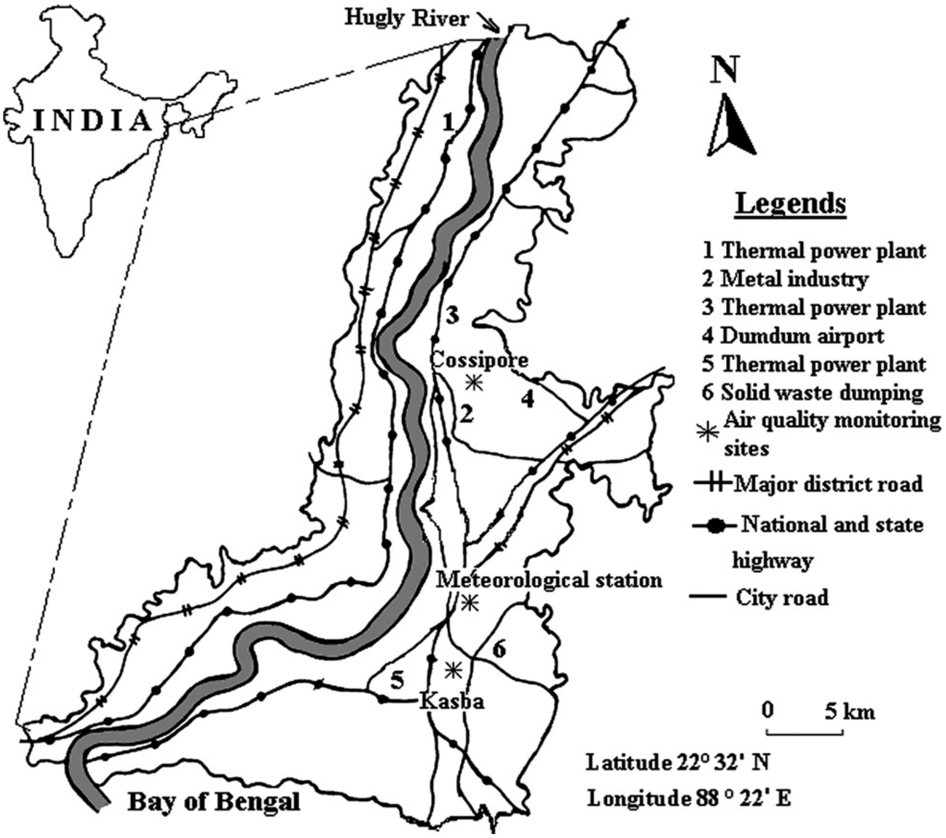

Fig. 1. Monitoring locations of the study area with major source locations.

before filtering it on the Whatman quartz microfibre filter paper (GF/A). These coarser particulates fall through the cyclone and get collected in the sampling bottle fitted at its bottom. The air stream deposited to the quartz microfibre filter paper, clamped between the top cover and filter adapter assembly, carries the fine dust forming the respirable fraction (PM_{10}) of total suspended particulate matter. The instrument was operated at a flow rate of 0.80–1.40 m^3 min^{-1}. Monitoring of the PM_{10} was carried out once in a week at each site for a period of 24 h. At each monitoring site, 53 sets of daily average PM_{10} samples were collected during the study period. The 48 sets of daily average PM_{10} samples were further analyzed for various species after removing outliers. Approximately 55% of the monitoring days are weekdays, while 45% are weekends.

2.3. Sample analysis

The PM_{10} concentrations were measured gravimetrically by weighing the particulate mass deposited on the filters and knowing the total volume of air sampled. Filter papers were stored in an envelope and kept in a dessicator containing dry silica gel for 24 h before and after the sample collection. The amount of air sampled through the weighed filter was recorded and the filters were placed in an appropriately labeled envelope and transported along with a blank filter to the analytical laboratory for analysis. Field and laboratory blank filter samples were routinely analyzed for PM_{10} to evaluate analytical bias and precision.

After gravimetric analysis, a known portion of the exposed quartz microfibre filters were digested in HNO_3 (nitric acid) and used for trace metal analysis (APHA, 1977). After digestion, a colourless solution was obtained that was evaporated to dryness. Reagent blank was also prepared by using unexposed filter paper following the same procedure. Cool filtrate was made up to a known volume using freshly prepared distilled water and was analyzed for metal constituents using Inductively Coupled Plasma–Atomic Emission Spectroscopy (Jobin Yvon, JY-24) for chromium (Cr), zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni), manganese (Mn) and iron (Fe). During sample analysis, a standard solution was repeatedly aspirated to ensure that the calibration was within the limits of the control chart. Blank concentrations were always deducted from sample results. An intensive quality control programme was implemented to maintain the accuracy and precision throughout the study.

The aliquot of PAHs samples were taken by punching out a small circular portion of the exposed filters with a stainless steel punch and immersed in 25 ml of cyclohexane (Manuel et al., 2004). The sample was released using an ultrasonic bath for 5 min and filtered through a G-4 sintered glass crucible. More cyclohexane was then added to the residue, the bath ran for a further 10 min followed by filtration. Both the filtrates were then mixed together and concentrated in a rotary vacuum evaporator using a hot water bath at 60 to 65 °C. The flask was removed from the water bath and the solvent was allowed to drain for at least 5 min while cooling. The concentrated extract was transferred into a concentrator tube. The flask was rinsed with 5 ml of cyclohexane and the washed solution was also transferred into a concentrator tube. The extract in the concentrator tube was again concentrated to 0.5 ml in a rotary vacuum evaporator using a hot water bath at 95–100 °C. The tube was cooled for at least 10 min and stored in a refrigerator until taken to Gas Chromatography for analysis (Manuel et al., 2004). The blank samples were taken by punching out equivalent small circular portions from unexposed filter papers and extracted in a similar pattern as that of the exposed filters. The concentrated extract was analyzed by Gas Chromatography equipped with a Flame Ionization Detector (Perkin Elmer, auto system XL, GC-FID) for fluoranthene (Fl), pyrene (Py), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF) and benzo(a)pyrene (BaP). The GC-FID used a Dexsil 300 column under optimized operating conditions.

Total carbon (TC), inorganic carbon (IC) and organic carbon (OC) of the PM_{10} particles were analyzed using a Carbon analyzer (SSM-5000A).

For the analysis of water-soluble anion, a known portion of the particulate loaded quartz microfibre filters were extracted by ultrasonic agitation in 25 ml double distilled water for a period of 25 min. These extracts were filtered through a filter paper (Whatman No. 42) into pre-cleaned polypropylene bottles. These were refrigerated at 4 °C and used for the analysis of major anions. All chemicals used were of analytical reagent grade and solutions were prepared in double distilled water. Ion chromatography (IC-Dionex DX-100) was employed to analyze fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}). Blank samples were also prepared from the unexposed filter papers in the same procedure as that of the exposed filter samples and analyzed for the anionic species.

2.4. Data analysis

Over the last two decades, multivariate analysis has been widely used to identify sources of ambient particles. The PCA is a statistical technique that can be applied to a set of variables in order to reduce their dimensionality. It allows the replacement of a large set of intercorrelated variables with a smaller number of independent variables. These new variables (principal components) are derived from the original variables, and are simply linear combinations of those variables (Thurston and Spengler, 1985).

Factor analysis of principal component analysis has been performed in the present study on the 24 h average PM_{10} data sets characterizing the aerosol samples collected using the SPSS statistical software (SPSS, 2003). Henry et al. (1984) suggested that the minimum number of samples (n) for factor analysis (FA) should be such that $n > 30 + (V+3)/2$, where V represents the number of variables. An important aspect in any multivariate analysis is the selection of a proper data set. Unusual errors or events in sampling and analysis results in very high or very low values (outliers) of one or more variables. These outliers have to be removed before analysis to avoid propagation of errors (Kumar et al., 2001). In this study, 20 variables and 43 samples (after removing outliers) were considered for factor analysis.

Varimax rotated factor analysis was carried out on various constituents of the ambient aerosol at the study area. The eigenvalues were used to determine the number of factors along with the variance in each factor after rotation (Park and Kim, 2005). The number of factors was selected such that the cumulative percentage variance explained by all the chosen factors is more than 80%. Only those factors that have an eigenvalue more than one were chosen to have normalized variables that carry one unit of variance (Kumar et al., 2001). Thus, if an eigenvalue is less than one, then it carries less information than one of the initial variables and is therefore not needed (Maenhaut and Cafmeyer, 1987). Since higher factor loading of particular elements in a factor can help in identifying the possible sources (Henry et al., 1984), the number of factors selected (sources identified) should represent the sources that are relevant in the receptor domain. The identification of the determined factors was achieved by examining the factor loadings of the source tracer elements in each of the factors. Here, the Kaiser criteria were adopted to decide the appropriate number of factors to be retained with eigenvalues >1 (Kaiser, 1958). Good model solutions were achieved when the fractions of pollutant variance explained by the PCA model were as close to one as possible (Guo et al., 2004).

Henry and Hidy (1979) characterized the potential sources of particulate sulfate in four U.S. cities by applying PCA analysis to a mixture of air quality and meteorological variables. Kleinman et al. (1980) identified and estimated the relative importance of sources of airborne particulates using PCA techniques. Thurston and Spengler (1985) applied PCA to Boston inhalable particle elemental composition data to estimate particle sources in Boston. Harrison et al. (1996) identified the major air pollution source categories of ambient polycyclic aromatic hydrocarbons by means of PCA in England. The PCA techniques have also been used to assess sources of gaseous atmospheric pollutants such as volatile organic compounds (VOC), carbonyls, nitrogen oxides (NO_x) and carbon monoxide (CO) (Bruno et al., 2001; Miller et al., 2002).

In this study, PCA has been applied to the PM_{10} mass concentration data collected at residential and industrial sites of an urban region of Kolkata. The species concentration matrix $X[n \times m]$ with n rows (the number of analyzed species) and m columns (the number of samples analyzed) was standardized using the Z-score. The Z-score of each element for every sample was determined by Eq. (1).

$$Z_{ik} = \frac{(C_{ik} - \overline{C}_i)}{\sigma_i} \tag{1}$$

where $i = 1,2,\ldots,n$ (n = the total number of species); $k = 1,2,\ldots,m$ (m = the total number of samples); C_{ik} is the concentration of the ith species for the kth sample; $\overline{C}_i$ is the mean concentration for the ith species over all observations; σ_i is the standard deviation concentration distribution of the ith species.

The PCA assumes that the total concentration of each species is made up of the sum of the contributions from each source for that species of PM_{10} as given by Eq. (2).

$$Z_{ik} = \sum_{j=1}^{p} W_{ij} P_{jk} \tag{2}$$

where P_{jk} is the jth source value for the kth observation with $j = 1,\ldots,p$, (p = the number of pollution sources influencing the data) and W_{ij} is the coefficient matrix of the ith species for the jth source. Henry and Hidy (1979) found the Eq. (2) may be inverted, yielding in matrix terms as given by Eq. (3).

$$[P]_{j\times k} = [B]_{j\times i}[Z]_{i\times k} \tag{3}$$

where

$$[B]_{j\times i} = {}^{[W]}j \times i/\lambda_j \tag{4}$$

and λ_j is the eigenvalue associated with P_j.

The PC scoring matrix $[B]$ is derived so that the first principal component PC(1) explains a large percent of the total variance of the original variables as possible. The coefficients for the second principal component PC (2) are, in turn, chosen so that it explains as large a percent of the remaining variance in the original variables, subject to the restriction that PC(1) and PC (2) are uncorrelated. In general, the coefficients for PC(j) explain as much of the remaining variance (that is not explained by PC(1) to PC($j-1$)), subject to the constraint that PC(j) be uncorrelated with PC(1) to PC($j-1$).

The PC equation coefficients [B] are mathematically derived from the correlation matrix as given by Eq. (5).

$$[R]_{i\times i} = [Z]_{i\times i}[Z]^{t}_{i\times i} \tag{5}$$

The objective of PCA is to find orthogonal (uncorrelated) components so that the correlation matrix [R] is diagonalized. The diagonalization finds a matrix Q as shown in Eq. (6).

$$[Q^{-1}]_{i\times i}[R]_{i\times i}[Q]_{i\times i} = [\wedge]_{i\times i} \tag{6}$$

where [$\wedge$] is a diagonal matrix of eigenvalues arranged in descending order of magnitude and Q contains the corresponding eigenvectors which diagonalize the correlation matrix. These eigenvectors are the matrix [B], which can be used in Eq. (3) to derive the PC score matrix [P] from the [Z] matrix. Empirically, it has been found that the unrotated PCs are often not readily interpretable since they each attempt to explain all remaining variance in the data set (Thurston and Spengler, 1985). For this reason, a limited number of components ($p<n$) are usually subjected to rotation using the criteria of varimax. After PCA rotation, the resulting components have been found to often be more representative of individual underlying sources of variation. The varimax rotation constitutes a maximization of the variance of the community-normalized loadings (correlations) presented in the columns of PC pattern. They preclude the emergence of a strong general component by making the variance explained by the individual components more equal, resulting in orthogonal components which are often more readily identifiable as specific source components.

Rotated PC coefficients B*, are calculated by applying the rotation transformation matrix [T] to [B],

$$B^{*}_{p\times n} = [B]_{p\times n}[T]_{n\times n} \tag{7}$$

Rotated PC scores are compared using this transformed [B] matrix,

$$[P]^{*}_{p\times m} = [B]^{*}_{p\times n}[Z]_{n\times m} \tag{8}$$

These PC scores are correlated with their respective pollution sources impacting the site. Henry and Hidy (1979) showed that the regression of a dependent variable Y_k on the daily scores of components P_{jk} is given by the Eq. (9).

$$Y_k = \overline{Y} + \sum \varsigma_j P_{jk} \tag{9}$$

where $\overline{\mathrm{Y}}$ represents the mean of Y_k. If the dependent variable Y_k is the total mass in μg m^{-3}, then ς_j are the conversion coefficients of the non-dimensional PC score deviations into mass deviations from the mean source impact.

The absolute zero PC score has subsequently been estimated for each PC by separately scoring an extra day. All the elemental concentrations are zero on that day. This is accomplished by deriving the Z-score for absolute zero concentrations as given by Eq. (10).

$$(Z_0)_i = \frac{0-\overline{C}_i}{\sigma_i} \tag{10}$$

The rotated absolute zero PC scores, P_0^*, for each of the p components as shown in Eq. (11).

$$P^{*}_{0_p} = \sum_{i=1}^{n} B^{*}_{pi}(Z_0)_i \tag{11}$$

These estimates of the PC scores for each component at absolute zero are then used to estimate Absolute PC Scores (APCS) for each component on each day as given by Eq. (12).

$$[\mathrm{APCS}]^{*}_{p\times j} = [P]^{*}_{p\times j} - [P_0]^{*}_{p\times j} \tag{12}$$

Regressing daily PM$_{10}$ mass data on these APCS gives the estimates of the coefficients which convert the APCS into pollutant source mass contributions (μg m^{-3}) for each sampling day as given by Eq. (13).

$$M_k = \varsigma_0 + \sum_{j=1}^{p} \varsigma_j \mathrm{APCS}^{*}_{jk} \tag{13}$$

where M_k is the particle mass recorded (in μg m^{-3}) during observation k, APCS$^*_{jk}$ is the rotated absolute component score for component j on observation k, ς-APCS$^*_{jk}$ is the particle mass contribution on observation k (in μg m^{-3}) made by the pollution source identified with component j, and ς_0 is the particle mass contribution (in μg m^{-3}) made by sources unaccounted for in the PCA.

3. Results and discussion

3.1. PM_{10} mass concentrations

During the study period, the 24 h average PM_{10} concentrations and standard deviations were 140 ± 43 μg m^{-3} at the residential site (Kasba), and 197 ± 88 μg m^{-3} at the industrial site (Cossipore). Daily average PM_{10} concentrations ranged from 68 to 281 μg m^{-3} at the residential site and 62 to 401 μg m^{-3} at the industrial site. The average PM_{10} concentration at the industrial site was 1.4 times higher than the residential site. High particulate concentration at Cossipore may be attributed to the heavy vehicular traffic flow, emissions from nearby industries, and resuspension of road and soil dust. The arithmetic mean and standard deviation of PM_{10} and its measured chemical species at the monitoring sites are summarized in Table 1. Daily average PM_{10} concentrations exceeded National Ambient Air Quality Standard (NAAQS) as specified by Central Pollution Control Board, India (CPCB, 1998). The PM_{10} NAAQS is 100 μg m^{-3} for the residential area and 150 μg m^{-3} for the industrial area. Approximately 85% of the monitored PM_{10} data at the residential area and 70% at the industrial area exceeded the NAAQS.

Table 1
Statistical summary of particulate mass concentrations in study area

Parameter	Unit	Residential site n=48		Industrial site n=48	
		Mean	SD	Mean	SD
PM_{10}	μg m^{-3}	140	43	197	88
Fl	ng m^{-3}	16	10	23	15
Py	ng m^{-3}	15	8	18	10
BaA	ng m^3	18	10	23	15
BbF	ng m^3	30	19	24	18
BaP	ng m^3	13	8	14	10
TC	ng m^{-3}	2062	1343	3022	1178
IC	ng m^{-3}	159	72	229	136
OC	ng m^{-3}	1902	1611	2793	1772
Cr	ng m^{-3}	7	6	6	4
Zn	ng/m^3	490	298	535	302
Pb	ng m^{-3}	40	29	119	94
Cd	ng m^{-3}	2	2	5	4
Ni	ng m^{-3}	7	4	8	4
Mn	ng m^{-3}	2	1	2	2
Fe	ng m^{-3}	87	69	123	90
F^-	ng m^{-3}	94	61	125	92
Cl^-	ng m^{-3}	712	610	1213	891
NO_3^-	ng m^{-3}	182	107	159	108
PO_4^{3-}	ng m^{-3}	198	132	18	4
SO_4^{2-}	ng m^{-3}	1186	602	1671	402

n = number of samples.

Particulate mass concentrations were higher in winter. Higher winter concentrations were due to low wind speed and low mixing height, leading to an accumulation of pollutants over the city. Minimum PM_{10} mass concentration was found in the monsoon season at the monitoring sites. The minimum monsoon concentration was due to washout of the particles by rains from the atmosphere. A similar seasonal variation of PM_{10} was observed in the port and harbour region of Mumbai, with a maximum concentration of 135.8 μg m^{-3} during winter and a minimum of 20.3 μg m^{-3} during the monsoon (Gupta et al., 2004).

Major PAH compounds at the monitoring sites were BbF with 0.03 μg m^{-3} at the residential site and 0.02 μg m^{-3} at the industrial site. Chromium (Cr), zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni), manganese (Mn) and iron (Fe) are the seven toxic trace metals quantified from the measured PM_{10} concentrations. Results identified zinc with a maximum contribution to PM_{10} among measured metals having concentrations of 0.49 μg m^{-3} at the residential site and 0.53 μg m^{-3} at the industrial site. Sulfate was found in maximum concentration among anionic species with a value of 1.2 μg m^{-3} at the residential site, and 1.7 μg m^{-3} at the industrial site.

3.2. Source apportionment

3.2.1. Source identification and apportionment at the residential site

Varimax rotated factor analysis identified five possible factors (based on factor loading of species greater than 0.7) indicating five different contributing sources for the species measured at the residential site (Kasba). The total percentage variance explained by five factors was about 95% at the residential site. The corresponding possible sources of PM_{10} in the residential area are presented in Table 2.

The first factor (F_1) at the residential site (Kasba) was heavily loaded (factor loading > 0.7) with total carbon (TC), organic carbon (OC) and nitrate with eigenvalue 6.1. Total carbon, organic carbon and nitrate in the atmosphere are assumed to be emitted by the solid waste dumping site located in Kasba. The raw materials used for composting in the dumping site represent a wide spectrum of organic wastes such as municipal solid wastes (MSW), sewage sludge, green wastes and animal manure. A probable reason for its emission can be the decomposition of organic and inorganic substances. This factor F_1 has a 31.3% variance of the data set. Nitrate aerosol originates mainly from the oxidation products of NO_x. The major source of NO_x in the study

Table 2
Varimax rotated factor matrix for residential site

Species	Possible emission sources				
	Solid waste dumping	Vehicular emissions	Coal combustion	Soil dust	Cooking
Fl	0.13	0.16	0.96	−0.16	−0.13
Py	0.59	0.10	0.75	0.10	0.25
BaA	−0.35	0.18	0.74	−0.21	0.48
BbF	−0.14	0.07	0.19	0.05	0.95
BaP	0.10	0.29	0.94	−0.10	0.05
TC	0.89	0.24	0.04	0.08	−0.30
IC	0.64	0.31	−0.04	0.61	−0.13
OC	0.89	0.23	0.04	0.05	−0.31
Cr	0.22	0.82	0.16	0.31	0.32
Zn	−0.57	−0.42	−0.23	0.14	0.63
Pb	−0.05	0.85	0.06	−0.31	−0.26
Cd	0.59	−0.10	0.06	−0.78	0.07
Ni	0.04	0.80	−0.23	0.34	0.41
Mn	0.15	0.93	0.23	−0.17	−0.12
Fe	0.05	0.88	0.37	−0.18	−0.11
F^-	−0.30	−0.39	0.56	0.36	0.40
Cl^-	0.50	−0.18	0.05	0.80	0.14
NO_3^-	0.94	−0.18	0.05	0.23	0.12
PO_4^{3-}	0.01	−0.01	0.62	−0.72	−0.19
SO_4^{2-}	0.33	−0.22	−0.17	0.90	0.05
Eigenvalue	6.1	5.1	3.5	3.1	1.2
% variance	31.3	25.4	17.6	15.3	5.9
Cumulative % variance	31.3	56.7	74.3	89.6	95.5

area is motor vehicles. Also, this source is adjacent to the city road, so the higher loading of nitrate suggests that this source is influenced by road dust.

The second factor (F_2) accounted for the variance of 25.4%. The moderate to high loading of Cr, Pb, Ni, Mn and Fe is associated with vehicular emission at Kasba. Iron was emitted as a result of wear and tear of brake pads and other automobile parts. Iron, chromium and nickel were associated with particles in tailpipe emissions that may be derived from the fuel lubricant or from engine wear. Manganese has been used as an additive to enhance automobile performance (Pellizzari et al., 1999). The manganese tricarbonyl compounds constitute the group of organomanganese compounds of toxicological significance. These manganese tricarbonyl compounds are used as additives in unleaded petrol (WHO, 1981). Lead was associated with leaded gasoline vehicular emissions. Although direct emissions of Pb from the vehicular exhaust had ceased for more than one year at the time of study because of the phasing out of lead from vehicular fuels, Pb is still persistent in road dust from earlier vehicular exhaust emissions because of its long residence time in the environment. A study performed in Delhi, India by Banerjee (2003) during December 1999 observed a significant concentration of Pb in road dust although direct emissions of Pb from vehicular exhausts had ceased for 2 years at the time of study because of the phasing out of leaded gasoline in Delhi. Pellizzari et al. (1999) found relatively higher Mn concentration near major roadways. The eigenvalue of this factor is 5.1.

At Kasba, the third factor (F_3) was heavily loaded with Fl, Py, BaA and BaP with a percentage variance of 17.6. This factor of PCA with eigenvalue 3.5 represents coal combustion. The polycyclic aromatic hydrocarbon (PAH) species were mainly emitted as a result of pyrolitic processes, especially incomplete combustion of organic materials (Brun et al., 2004). Organic compounds can be emitted directly from both higher terrestrial plants (biogenic) and manmade combustion processes. In addition, secondary organic particles can be formed by the condensation of low vapour pressure organic molecules, which were photochemically produced from biogenic volatile organic compounds (Kavouras et al., 2001).

Soil has also been identified as a source of airborne particles in PM_{10}. The F_4 (soil dust) has moderate to high loading of Cl^- and SO_4^{2-} with 15.3% variance and eigenvalue 3.1. Sulfate in the atmosphere was generally assumed to be a secondary particle aerosol component produced from gas to particle conversion of SO_2. The probable reasons for the association of these species with crustal elements can be the chemical binding in the soil dust component variation by the resuspension process. Kolkata is located in coastal areas and influenced by sea-based parameters (Cl^-).

The fifth factor (F_5) has a high BbF at the residential site with 5.9% variance and an eigenvalue of 1.2. Benzo (b)fluoranthene is a PAH compound that is mainly emitted from the burning of fossil fuel. This factor represents cooking.

3.2.2. Source identification and apportionment at the industrial site

The corresponding possible sources of PM_{10} in the industrial area are presented in Table 3. Five factors at this site were selected. The total variance explained by the five factors was about 92%.

The first factor (F_1) at the industrial area (Cossipore) was heavily loaded (factor loading$>$0.7) with Fl, BaA, BbF, BaP and IC. The first factor represents coal combustion with 30.9% variance and eigenvalue 6.2. Polycyclic aromatic hydrocarbons (PAHs) are benzene-derived molecules possessing a condensed ring skeleton (Farkas et al., 2004). A large amount of PAHs were

Table 3
Varimax rotated factor matrix for industrial site

Species	Possible emission sources				
	Coal combustion	Secondary aerosol	Vehicular emissions	Tyre wear	Electroplating industry
Fl	0.91	0.04	0.19	0.04	0.08
Py	0.36	−0.41	0.76	−0.19	−0.19
BaA	0.94	−0.15	−0.14	0.10	−0.06
BbF	0.96	−0.09	−0.13	0.12	−0.05
BaP	0.92	−0.16	0.32	−0.02	−0.02
TC	0.23	−0.09	0.23	0.94	0.06
IC	0.78	−0.31	−0.10	0.04	0.04
OC	0.19	−0.07	0.25	0.94	0.06
Cr	0.14	−0.08	−0.12	−0.02	0.91
Zn	0.51	0.35	−0.25	0.01	0.10
Pb	−0.22	−0.17	0.81	0.38	−0.27
Cd	−0.08	0.56	0.60	−0.15	0.51
Ni	0.08	0.60	−0.01	−0.56	0.45
Mn	0.06	0.08	0.96	0.14	−0.11
Fe	−0.08	0.18	0.95	0.22	0.06
F^-	−0.24	0.93	−0.06	0.07	0.24
Cl^-	−0.08	0.91	0.17	−0.23	0.05
NO_3^-	−0.08	0.93	−0.05	−0.15	−0.32
PO_4^{3-}	−0.34	−0.06	−0.30	0.49	0.68
SO_4^{2-}	0.02	0.97	−0.02	0.02	−0.12
Eigenvalue	6.2	4.1	3.9	2.5	1.7
% variance	30.9	20.6	19.4	12.7	8.7
Cumulative % variance	30.9	51.5	70.9	83.6	92.3

produced from incomplete burning processes of fossil fuels. Due to their hydrophobic nature, all PAHs are preferentially associated with carbon phases of particles, and thus adverse health effects are often evident with sediment exposure (Thorsen et al., 2004). The carcinogenic effect might be attributed to the induction produced by PAHs adsorbed in the carbon core nucleus of particulate matter. Cossipore has a thermal power generation plant using a coal fired boiler. There is a considerable amount of emissions from the stack throughout the firing cycle, particularly during coal charging and coal churning in the firing gates of the boilers.

The second factor (F_2) accounted for the variance of 20.6%. At the Cossipore site, F^-, Cl^-, NO_3^- and SO_4^{2-} were associated with secondary aerosol. F_2 has an eigenvalue of 4.1. At coastal sites where aerosol is in abundance in the atmosphere and contains NaCl and soil dust, the NO_3^{-1} concentration is higher than HNO_3. There is a possibility of NO_2 getting adsorbed on the aerosol particles and becoming oxidized to particulate NO_3^{-1} (Gupta et al., 2003). Sulfate is likely to be associated with SO_2 emissions. Most of the mass of SO_4^{2-} associated with this source result from the oxidation of SO_2.

At the industrial site (Cossipore), Py, Pb, Mn and Fe was moderate to heavily loaded with 19.4 percentage variance in the third factor. This factor, F_3 represents the vehicular emissions with an eigenvalue of 3.9. Pyrene has been emitted from incomplete burning of the fuel. The Mn and Pb suggest that it is related to local motor vehicle traffic. Mn has been used as an additive to enhance automobile performance (Pellizzari et al., 1999). The Py and Fe likely reflect a variety of vehicle-related influences such as engine and lubricating oil.

Total carbon (TC) and organic carbon (OC) dominate the factor four (F_4) with 12.7% variance and eigenvalue of 2.5 at Cossipore. Tyre wear represents the fourth factor.

The fifth factor, F_5 has high Cr with 8.7% variance. The Cr identified is likely to be from a Cr-related process. This factor represents the electroplating industry. Park and Kim (2005) obtained higher Cr loading in its sixth component of PCA analysis with only species of Cr (factor loading = 0.975) in that factor.

3.3. Principal component analysis–multiple linear regression

In the absolute principal component analysis (APCA) technique the absolute factor scores (AFS)

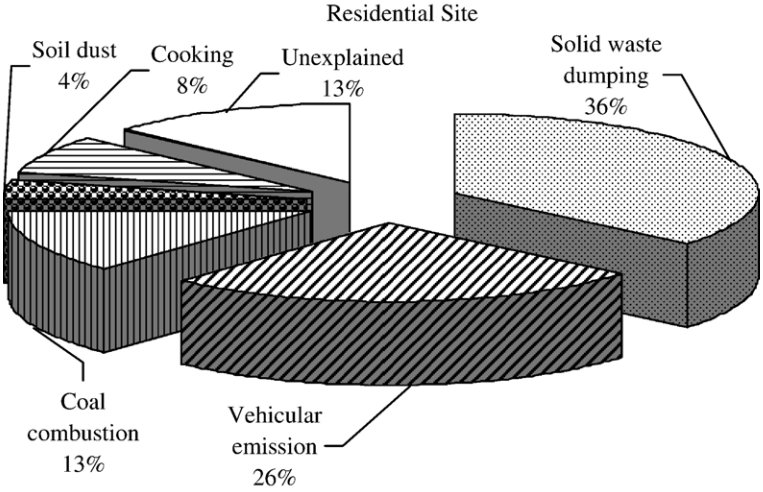

Fig. 2. Source apportionment of PM_{10} at the residential site.

are regressed on the observed PM_{10} concentration to apportion the respirable particulate matter to each sample (Kumar et al., 2001). Source apportionment to the 24 h average PM_{10} at residential and industrial sites is shown in Figs. 2 and 3, respectively. For the 24 h average PM_{10} concentration, solid waste dumping contributed 36%, vehicular emission contributed 26%, coal combustion contributed 13%, cooking contributed 8%, soil dust contributed 4%, and 13% remained as an unexplained contribution at the residential site. The 24 h average PM_{10} concentration was contributed 29% by coal combustion, 1% by secondary aerosol, 37% contributed by vehicular emission, 8% contributed by tyre wear, 18% contributed by electroplating and 7% remained as unexplained contributions at the industrial site.

The result obtained by principal component analysis–multiple linear regression (PCA–MLR) is quite comparable to existing observations. The solid waste dumping ground is located near to the residential monitoring site and PCA–MLR analysis also obtained a higher percentage contribution by solid waste dumping at Kasba. The industrial monitoring area has a nearby thermal power plant and also moderate to heavy vehicular traffic flows. The PCA–MLR obtained maximum contribution of

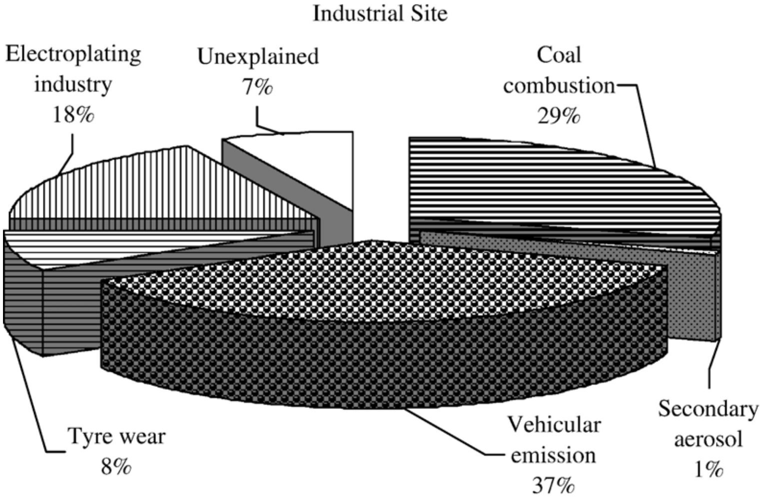

Fig. 3. Source apportionment of PM_{10} at the industrial site.

PM_{10} at Cossipore by vehicular emission and coal combustion.

4. Conclusions

Detailed chemical analysis of 24 h average PM_{10} concentrations at the two monitoring stations, namely residential and industrial sites has been performed in the present study during November 2003 to November 2004. Monitoring sites were chosen depending upon the dominant anthropogenic activities of the area. The major PAH compound of PM_{10} was BbF at residential and industrial sites. Results identified zinc with maximum contribution to PM_{10} among measured metals at the monitoring locations. Sulfate of PM_{10} was found in maximum concentration among anionic species with a value of 1.19 $\mu g\ m^{-3}$ at the residential site and 1.67 $\mu g\ m^{-3}$ at the industrial site.

The purposes of this apportionment study were to identify possible ambient emission sources and to quantify the contributions of the sources to measured particulate pollutants. Principal component analysis–multiple linear regression (PCA–MLR), a receptor model, was used to quantitatively apportion the sources leading to high PM_{10} concentrations at the two monitoring locations (Kasba and Cossipore) in Kolkata. The principal component analysis–multiple linear regression technique apportioned five possible sources for PM_{10} observed at the residential (Kasba) and industrial (Cossipore) sites. The calculated daily scores of each factor were regressed on particle mass to estimate source contribution. The PCA–MLR identified solid waste dumping (36%), vehicular emission (26%) and coal combustion (13%) are the major contributors to PM_{10} at the residential site. Vehicular emission (37%), coal combustion (29%) and the electroplating industry (18%) have been identified as the major contributors to PM_{10} at the industrial site. A quantitative estimation by the PCA–MLR model also indicated that cooking contributed to 8% and soil dust to 4% at the residential site, while 8% was produced by tyre wear and 1% by secondary aerosol at the industrial site. Due to the limitation in source marker species analyzed, 13% at the residential site and 7% at the industrial site could not be apportioned to any possible sources by this technique.

A quantitative understanding of source contributions to ambient particulate levels is needed to develop emission control strategies. The results of this study will be very useful for the environmental management of particulate concentrations that violated the standards in the study area.

References

Arditsoglou, A., Samara, C., 2005. Levels of total suspended particulate matter and major trace elements in Kosovo: a source identification and apportionment study. Chemosphere 59, 669–678.

APHA, 1977. Methods of Air Sampling and Analyses, 2nd ed. American Public Health Association, Washington, DC.

Banerjee, A.D.K., 2003. Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environmental Pollution 123, 95–105.

Brun, G.L., Vaidya, O.C., Leger, M.G., 2004. Atmospheric deposition of polycyclic aromatic hydrocarbons to Atlantic Canada: geographic and temporal distributions and trends 1980–2001. Environmental Science and Technology 38, 1941–1948.

Bruno, P., Caselli, M., Gennaro, G., Traini, A., 2001. Source apportionment of gaseous atmospheric pollutants by means of an absolute principal component scores (APCS) receptor model. Fresenius' Journal of Analytical Chemistry 371, 1119–1123.

Celis, J.E., Morales, J.R., Zaror, C.A., Inzunza, J.C., 2004. A study of the particulate matter PM_{10} composition in the atmosphere of Chillan, Chile. Chemosphere 54, 541–550.

Cheng, M.D., Gao, N., Hopke, P.K., 1996. Source apportionment study of nitrogen species measured in southern California in 1987. Journal of Environmental Engineering 122, 183–190.

Chio, C.P., Cheng, M.T., Wang, C.F., 2004. Source apportionment to PM10 in different air quality conditions for Taichung urban and coastal areas, Taiwan. Atmospheric Environment 38, 6893–6905.

CPCB, 1998. National Ambient Air Quality Standards. Central Pollution Control Board, New Delhi.

Farkas, N., Lorinczy, D., Dergez, T., Kilar, F., Belagyi, J., 2004. Effect of polycyclic aromatic hydrocarbons on erythrocyte membranes by DSC and EPR. Environmental Toxicology and Pharmacology 16, 163–168.

Ghose, M.K., Paul, R., Banerjee, S.K., 2004. Assessment of the impacts of vehicular emissions on urban air quality and its management in Indian context: the case of Kolkata (Calcutta). Environmental Science and Policy 7, 345–351.

Goyal, P., Sidhartha, 2002. Effect of winds on SO_2 and SPM concentrations in Delhi. Atmospheric Environment 36, 2925–2930.

Guo, H., Wang, T., Louie, P.K.K., 2004. Source apportionment of ambient non-methane hydrocarbons in Hong Kong: application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model. Environmental Pollution 129, 489–498.

Gupta, A., Kumar, R., Kumari, K.M., Srivastava, S.S., 2003. Measurement of NO_2, HNO_3, NH_3 and SO_2 and related particulate matter at a rural site in Rampur, India. Atmospheric Environment 37, 4837–4846.

Gupta, A.K., Patil, R.S., Gupta, S.K., 2004. A statistical analysis of particulate data sets for Jawaharlal Nehru port and surrounding harbour region in India. Environmental Monitoring and Assesment 95, 295–309.

Harrison, R.M., Smith, D.J.T., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. Environmental Science and Technology 30, 825–832.

Harrison, R.M., Smith, D.G.T., Pio, C.A., Castro, L.M., 1997. Comparative receptor modelling study of airborne particulate pollutants in Birmingham, United Kingdom, Coimbra (Portugal) and Lahore (Pakistan). Atmospheric Environment 31, 3309–3321.

Henry, R.C., Hidy, G.M., 1979. Multivariate analysis of particulate sulfate and other air quality variables by principal components—part I. Annual data from Los Angeles and New York. Atmospheric Environment 13, 1581–1596.

Henry, R.C., Lewis, C.W., Hopke, P.K., Williamson, H.J., 1984. Review of receptor model fundamentals. Atmospheric Environment 18, 1507–1515.

Hong, Y.M., Lee, B.K., Park, K.J., Kang, M.H., Jung, Y.R., Lee, D.S., Kim, M.G., 2002. Atmospheric nitrogen and sulfur containing compounds for three sites of South Korea. Atmospheric Environment 36, 3485–3494.

Kaiser, H.F., 1958. The varimax criterion for analytic rotation in factor analysis. Psychometrika 32, 443–482.

Kameda, Y., Shirai, J., Komai, T., Nakanishi, J., Masunaga, S., 2005. Atmospheric polycyclic aromatic hydrocarbons: size distribution, estimation of their risk and their depositions to the human respiratory tract. Science of Total Environment 340, 71–80.

Kavouras, I.G., Koutrakis, P., Balic, F.C., Oyola, P., 2001. Source apportionment of PM_{10} and $PM_{2.5}$ in five Chilean cities using factor analysis. Journal of the Air and Waste Management Association 51, 451–464.

Khoder, M.I., 2002. Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area. Chemosphere 49, 675–684.

Kim, K.H., Lee, J.H., Jang, M.S., 2002. Metals in airborne particulate matter from the first and second industrial complex area of Taejon city, Korea. Environmental Pollution 118, 41–51.

Kleinman, M.T., Pasternack, B.S., Elsenbud, M., Kneip, T.J., 1980. Identifying and estimating the relative importance of sources of airborne particulates. Environmental Science and Technology 14, 62–65.

Kowalczyk, G.S., Gordon, G.E., Rheingrover, S.W., 1982. Identification of atmospheric particulate sources in Washington, D.C. using chemical element balances. Environmental Science and Technology 16, 79–90.

Kumar, A.V., Patil, R.S., Nambi, K.S.V., 2001. Source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India. Atmospheric Environment 35, 4245–4251.

Lin, J.J., Lee, L.C., 2004. Characterization of the concentration and distribution of urban submicron (PM1) aerosol particles. Atmospheric Environment 38, 469–475.

Maenhaut, W., Cafmeyer, J., 1987. Particle induced X-ray emission analysis and multivariate techniques: an application to the study of the sources of respirable atmospheric particles in Gent, Belgium. Journal of Trace and Microprobe Techniques 5, 135–158.

Manuel, J.A., Phadke, K.M., Joshi, S.D., Lalwani, A., Kumar, A., 2004. Levels of benzo(a)pyrene (BAP) in ambient air of Indian metropolis. Journal of Indian Association for Environmental Management 31, 107–112.

Marcazzan, G.M., Ceriani, M., Valli, G., Vecchi, R., 2003. Source apportionment of PM_{10} and $PM_{2.5}$ in Milan (Italy) using receptor modelling. Science of the Total Environment 317, 137–147.

Miller, S.L., Anderson, M.J., Daly, E.P., Milford, J.B., 2002. Source apportionment of exposures to volatile organic compounds. I. Evaluation of receptor models using simulated exposure data. Atmospheric Environment 36, 3629–3641.

Namdeo, A., Bell, M.C., 2005. Characteristics and health implications of fine and coarse particulates at roadside, urban background and rural sites in UK. Environment International 31, 565–573.

Park, S.S., Kim, Y.J., 2005. Source contributions to fine particulate matter in an urban atmosphere. Chemosphere 59, 217–226.

Pellizzari, E.D., Clayton, C.A., Rodes, C.E., Mason, R.E., Piper, L.L., Fort, B., Pfeifer, G., Lynam, D., 1999. Particulate matter and manganese exposures in Toronto, Canada. Atmospheric Environment 33, 721–734.

Rahn, K.A., Lowenthal, D.H., 1984. Elemental tracers of distant regional pollution aerosols. Science 223, 132–139.

Rajkumar, W.S., Chang, A.S., 2000. Suspended particulate matter concentrations along the East–West Corridor, Trinidad, West Indies. Atmospheric Environment 34, 1181–1187.

SPSS, 2003. Advanced Statistics Manual. SPSS/PC+V 3.0. SPSS Inc., 444 North Michigan Avenue, Chicago IL 60611.

Srivastava, A., Sengupta, B., Dutta, S.A., 2005. Source apportionment of ambient VOCs in Delhi City. The Science of the Total Environment 343, 207–220.

Thorsen, W.A., Cope, W.G., Shea, D., 2004. Bioavailability of PAHs: effects of soot carbon and PAH source. Environmental Science and Technology 38, 2029–2037.

Thurston, G.D., Spengler, J.D., 1967. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. Atmospheric Environment 19, 9–25.

UNEP/WHO, 1992. Urban Air Pollution in Mega Cities of the world. Blakwell, Oxford, London, UK.

Vega, E., Mugica, V., Carmona, R., Valencia, E., 2000. Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model. Atmospheric Environment 34, 4121–4129.

Wang, H., Shooter, D., 2004. Source apportionment of fine and coarse atmospheric particles in Auckland, New Zealand. Science of the Total Environment 340, 189–198.

WBPCB, 2001. Green governance. Newsletter, West Bengal Pollution Control Board. Volume II, Issue III, India.

WHO, 1981. International programme on chemical safety. Environmental Health Criteria, vol. 17. World Health Organization.