

Multi-element Analysis and Characterization of Atmospheric Particulate Pollution in Dhaka

Bilkis A. Begum¹, Swapan K. Biswas¹, Philip K. Hopke^{2*}, David D. Cohen³

¹ *Chemistry Division, Atomic Energy Centre, P.O.Box164, Dhaka-1000*

² *Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY 13699-5810, USA*

³ *Institute for Environmental Research, Australian Nuclear Science and Technology Organization, Menai, NSW 2234 Australia*

Abstract

PIXE (Proton Induced X-Ray Emission) and PIGE (Proton Induced Gamma Ray Emission) have been used to measure the concentration of over 20 elements present in coarse and fine atmospheric particle samples. These samples were collected at a semi-residential site at Dhaka, Bangladesh from July 2002 to June 2003. The multi-elemental capability of PIXE and PIGE enabled the use of these elemental-concentration data to define fingerprints of various coarse and fine particle sources in the atmosphere using factor analysis along with linear regression. Biplots between a major component of a given source identified by the factor analysis with another signature element were prepared. Regression analyses could then be performed on a subset of the plot to quantify the relationship between these constituents in this fingerprint. The identified fingerprints included anthropogenic sources, such as motor vehicles, Zn source, two-stroke engine, and fugitive Pb; as well as natural sources, such as sea spray and soil dust. In this study, the chemical compositions of elements of these fingerprints were compared with the results obtained from PMF modeling that had been obtained in a previous study.

Keywords: Polycarbonate filter paper; PIXE; PIGE; Fingerprints.

* Corresponding author. Tel.:315-2683861, Fax: 315-2684410

E-mail address: hopkepk@clarkson.edu

INTRODUCTION

Air pollution has become one of the most serious environmental concerns in urban areas, especially in view of the adverse health effects that have been associated with ambient fine particles (Dockery *et al.*, 1989, Pope *et al.*, 1992, Dockery *et al.*, 1993, Dockery *et al.*, 1994, Pope, 2000, Schwartz, 2001). In the urban environment, the emissions from motor vehicles and biomass burning, lead from battery reprocessing, and paint pigment production are all transported as fine particles. Epidemiological links have been established between the concentrations of fine airborne particles ($< 2.5 \mu\text{m}$ in diameter) and the morbidity and mortality rates in large populations (Dockery *et al.*, 1993) at airborne concentrations in the range 10 to $30 \mu\text{g}/\text{m}^3$. Fine particles also affect visibility by scattering and absorbing light and influencing the public's perception of pollution. They are transported over large distances and are important in geochemical cycling of a number of elements, cloud formation and, ultimately, global climate.

The identification of various sources of airborne particulate matter (PM) and the assessment of their impact on the aerosol composition of an airshed are some of the major goals of contemporary atmospheric research. The establishment of national air-quality standards for PM in many countries around the world has also created the need to identify the particle sources so that effective control strategies could be designed and implemented. Initial efforts at the identification of particle sources focused on dispersion models of point sources, and in most cases, resulted in substantial reduction in ambient PM levels. However, additional methods were needed to identify and quantitatively apportion the particle mass to sources with better resolution. These methods are called receptor models that use the measured properties of collected ambient samples to infer the contributions of the sources to the pollutant concentrations. These methods require that samples be collected at the location of interest, the receptor site, and that the samples so collected be analyzed for the properties that are characteristic (generally chemical composition) of the pollutant sources. Therefore, the measurements of the elemental composition of atmospheric particles are needed for compliance monitoring, studies of environmental deposition, and source attribution by receptor-modeling techniques.

Accelerator-based ion beam analysis (IBA) techniques are particularly well-suited to the fast, non-destructive, multi-elemental analysis of air filters collected for ambient aerosol studies (Cohen *et al.*, 1998; 2004a, b). Typically, the particle loading on these filters may range from less than one hundred $\mu\text{g}/\text{cm}^2$ to over $1 \text{ mg}/\text{cm}^2$ thick, and therefore, can be considered to be thin targets for energetic proton beams of a few MeV. The filters themselves may only contain a total sample mass of just 100 to 500 μg , and thus, provide an extremely small sample for analysis by conventional methods. Furthermore, the yields of X-rays and gamma rays after just a few minutes irradiation by several nanoamps of 2 to 4 MeV protons were sufficient to provide elemental concentrations for the majority of elements of interest in air pollution studies. Therefore, PIXE in

aerosol studies is receiving renewed interest globally in conjunction with other nuclear methods commonly known as ion beam analysis (IBA) technique that are well-suited to particle and aerosol filter analysis (Cohen *et al.*, 1996; 1998).

In this paper, the application of PIXE and PIGE to multi-elemental characterization of both coarse and fine aerosol particles in a semi-residential (SR) area of Dhaka from July 2002 to June 2003 is discussed. Combining elements and estimates of compounds of known chemical composition to derive signatures for interesting aerosol components is also presented. Multi-elemental concentration data obtained from PIXE and PIGE analysis has also been performed to define fingerprints of various sources of atmospheric particulate matter by factor analysis (FA) method.

Factor analysis is a multivariate statistical technique used in environmental studies to identify sources from data taken at receptor sites (Hopke *et al.*, 1976; Henry, 1997; Huang *et al.*, 1999). Factor analysis generates the underlying “factors” that describe groups of variables. In environmental studies, each factor is generally treated as a source. The common version of factor analysis uses the correlation matrix to calculate a suite of factors that are rotated to generate a matrix of “factor loadings” for the variables. The main limitation of factor analysis in atmospheric science is validation; it is easy to obtain results, but it is almost impossible to check them objectively.

In this paper, the results obtained from FA were compared with the results obtained from an earlier PMF (Begum *et al.*, 2004) analysis. The emphasis of these comparisons is on the common crustal and marine factors, whose compositions are well-known and can serve as quantitative indicators for the acceptability of the present approach.

EXPERIMENTAL

Sampling site

Samples were collected in a semi-residential (SR) area of Dhaka, Bangladesh from July 2002 to June 2003 using a 'Gent' type stacked filter sampler (Hopke *et al.*, 1997) capable of collecting air particulate samples in the PM_{10-2.2} and PM_{2.2} size fractions. The sampling site located at the Atomic Energy Centre, Dhaka (AECD) campus (Fig. 1). The site was located about 50 m from a road with a moderate traffic density. The site was selected in such a way that it would provide pollution levels that are representative of the area. For each 24-hour sampling period, one fine and one coarse particle sample were obtained on 47 mm diameter nuclepore filters. At flow rates in the range of 15 to 17 Lpm, particles in the 2.2- to 10- μ m equivalent aerodynamic diameter (EAD) range were collected on the coarse filter (pore size 8 μ m), and particles with EAD < 2.2 μ m were collected on the fine filter (pore size 0.4 μ m). The effective sampling time was varied

between 6 and 20 h distributed uniformly over 24 h a day to avoid filter clogging and so that the flow rate remains within the prescribed limits of the sampler. This ensures proper size fractionation and collection efficiency (Begum *et al.*, 2005a). Samples were collected twice each week.

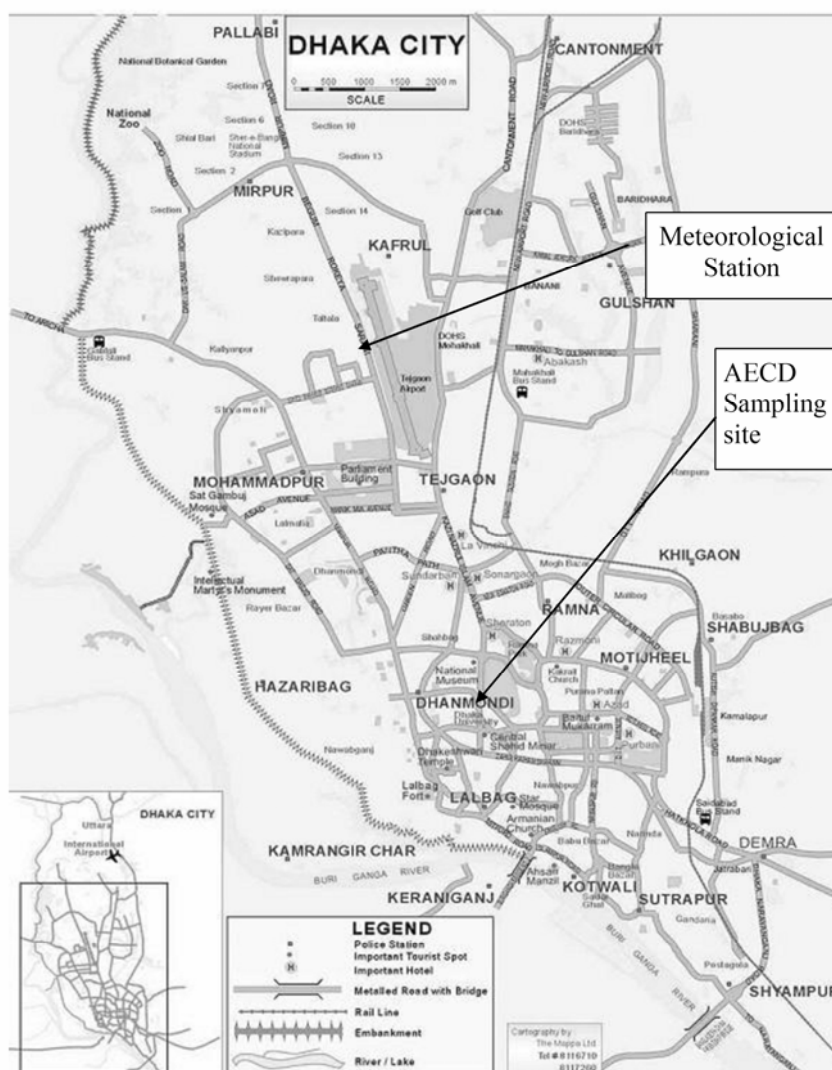


Fig. 1. Location of sites at Dhaka in Bangladesh.

PM mass and BC determination

The samples were transferred immediately to the laboratory for mass and black carbon (BC) measurements. The aerosol masses of both the coarse and fine fractions were determined by weighing the filters before and after the exposure. A Metler microbalance (Model MT5) having a readability of 1 µg was used for the gravimetric analysis and the quality assurance exercises. A standard operating procedure (SOP) was followed throughout the study (Begum *et al.*, 2006a).

Since the temperature and humidity of the ambient air of the weighing area may affect the moisture content of the filters, and thus may affect its weight, filters were equilibrated in the conditioned environment for at least 24 hours before being weighed. During this equilibration period, the relative humidity and temperature remained constant at typically ~50% relative humidity and 22 °C. A Po-210 (alpha emitter) electrostatic charge eliminator (STATICMASTER) was used to eliminate the charge accumulated on the filters before each weighing. The concentration of black carbon in the fine fraction samples was determined by reflectance measurements using an EEL (Evans Electro Selenium Limited) Smoke Stain Reflectometer. Secondary standards of known black carbon concentrations were used to calibrate the reflectometer. Details of the method has been described elsewhere (Biswas *et al.*, 2003).

Multi-elemental analysis

Accelerator-based ion beam analysis (IBA) methods have been applied throughout the present study (Cohen *et al.*, 2002; 2004a, b). Each polycarbonate filter was analyzed using the PIXE and PIGE techniques at the Australian Nuclear Science and Technology Organization (ANSTO), Australia. Data from these methods were collected simultaneously using a 2.6-MeV proton beam from a Van de Graaff accelerator. Beam diameters were typically 8 mm, and currents were kept at less than 2 nA/mm² to avoid beam damage to the filters and to reduce elemental losses. Run lengths were typically sufficient to deliver 30 µC (100 nA for 300 s) of total charge through the filter. Two analytical methods were used (Cohen *et al.*, 1998; 2002): 1) Proton-Induced X-ray Emission (PIXE), and 2) Proton-Induced Gamma Emission (PIGE). PIXE was used to analyze for 17 elements: Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Ni, Zn, Br, and Pb.

After a PIXE spectrum has been measured, there are essentially two steps in the spectral analysis. The first step is to analyze the spectrum to determine areas of characteristics of elemental peaks. The second step is to estimate the yield of X-rays so that elemental concentrations can be estimated from the peak areas and the expected yields. The first step is performed by the computer program BATTYPC. The second phase, namely the calculation of X-ray yields, is done by THIKPC for both thick and thin target (see Cohen and Clayton, 1987). For concentration determinations, a calibration curve was developed from thin-film standards excited under the same experimental conditions. Ten MicroMatter thin-film standards of Al, SiO₂, CaF₂, SrF₂, NaCl and Fe were used to span the X-ray and gamma-ray energy ranges covered by this study.

PIGE spectra were acquired up to gamma-ray energies of 8 MeV; only the peaks in the low energy portion were of interest in this study. The dominant peaks were fluorine (F 197 keV) and sodium (Na 440 keV). The PIGE detector system was calibrated against the known concentrations of aluminum, sodium chloride, calcium and strontium fluoride in the MicroMatter

thin-film samples mentioned above. The precision and accuracy of the PIXE and PIGE techniques have been discussed in detail elsewhere (Cohen *et al.*, 2002), but they are typically less than $\pm 10\%$ for PIXE and $\pm 15\%$ for PIGE for those elements whose concentrations are well above their minimum detection limits.

Meteorological conditions

In Bangladesh, the climate is characterized by high temperatures, high humidity most of the year, and by distinctly marked seasonal variations in precipitation. The year can be divided into four seasons according to meteorological conditions; pre-monsoon (March-May), monsoon (June-September), post-monsoon (October-November) and winter (December-February) (Azad *et al.*, 1998; Salam *et al.*, 2003a). Winter season is characterized by dry soil conditions, low relative humidity, scanty rainfall, and prevailing winds of low speed from the northwest. Rainfall and wind speed become moderately strong, and relative humidity increases in the pre-monsoon season when the southwesterly (marine) flow becomes dominant. During monsoon season, the wind speed further increases and the air masses are strongly marine in nature. In the post-monsoon season, the rainfall and relative humidity decrease, as does the wind speed. The wind direction starts shifting to northeasterly. The meteorological data used in this study was obtained from a local meteorological station (Fig. 1), located about 5 kilometers north of the semi-residential site.

Reconstructed mass variables (RCM)

The IBA analysis of PM samples provided opportunities to detect a sufficient number of elements, making it is easier to develop fingerprints related to a variety of PM sources. It is useful to combine some of these elements and estimate the concentrations of compounds likely to represent most of the measured elements; such as estimating the amount of ammonium sulfate from the measured sulfur concentration. Other combinations of elements that represent interesting aerosol components can be estimated using pseudo-elements, such as “soil” as described by Malm *et al.* (1994).

Sulfate can exist in the atmosphere as sulfuric acid-producing acid rain, or be partially neutralized to ammonium bi-sulfate, or fully neutralized to ammonium sulfate (Lee *et al.*, 2001). It is assumed that sulfur occurs in the atmosphere as fully neutralized ammonium sulfate (Malm *et al.*, 1994).

Sulfur, potassium, and calcium occur naturally in sea spray in mass ratios of 0.084, 0.036 and 0.038, respectively (Wilson, 1975). The ratio of chemical species present in sea spray can be used

to define the non-sea salt component of various elements in the standard way: non-sea salt sulfur where:

$$\begin{aligned}
 [nssS] &= [Stot] - 0.084 \times [Na] \text{ potassium } [nssK] = [Ktot] - 0.036 \times [Na] \text{ and} \\
 Ca[nssCa] &= [Catot] - 0.038 \times [Na]. \\
 [nssS] &= [Stot] - 0.084 \times [Na]
 \end{aligned}
 \tag{1}$$

Fine potassium is an accepted indicator for smoke from biomass burning/brick kiln. It is known that brick kilns in Dhaka burn both wood and coal, so fine potassium is also related to the production of bricks. These production facilities operate mainly in winter due to the seasonally dry conditions. They are largely situated in the northwest and southeast sides of the city. These brick kilns are a major contributor to severe air pollution in winter in Dhaka (Azad *et al.*, 1998). In order to obtain a reliable smoke indicator from fine potassium, it is necessary to subtract the fine potassium associated with soil and sea salt from the total K concentrations. Hence, smoke K is obtained by $Smoke\ K = (Ktot - 0.036 \times Na - 0.6 \times Fe)$.

It is assumed that both fine and coarse soil are composed mainly of the oxides of Mg, Al, Si, Ca, Ti and Fe, with other many trace elements (Malm *et al.*, 1994). The equation for soil is:

$$Soil = 2.20 \times Al + 2.49 \times Si + 1.63 \times Ca + 1.94 \times Ti + 2.42 \times Fe.
 \tag{2}$$

This equation assumes that the two common oxides of iron Fe_2O_3 and FeO occur in equal proportions. The factor of 2.42 for iron also includes the mass of K_2O in soil, based on the (K / Fe) = 0.6 ratio for sedimentary soils.

Principal component analysis

The process of identification and apportionment of pollutants to their sources is an important step in air-quality management. Principal component analysis (PCA) (Hopke, 1985) uses measurements of pollutant concentrations at a sampling site to identify significantly correlated variables. This method extracts components that explain the majority of the variance in the data matrix, which are then qualitatively interpreted as possible sources (Hopke *et al.*, 1976; Hopke, 1985; Wolff *et al.*, 1985). PCA is often useful for providing information regarding source characteristics in terms of the elements that are associated with a given source type. These methods are based on the analysis of the correlation between measured concentrations of chemical species, assuming that highly correlated compounds are emitted from the same source.

RESULTS AND DISCUSSION

Particulate matter mass and black carbon concentrations

The 24-hour average PM_{2.2} and PM_{2.2-10} mass fraction results for the SR site are shown in Figs. 2 and 3 as monthly box and whisker plots. The box represents 25-75% of the distributions of the monthly PM_{2.2} and PM_{2.2-10} concentrations. The horizontal bar in the box indicates the median, and (+) sign denotes the mean of the distribution for that month. The points lying outside the range defined by the whiskers (extreme events) are plotted as outlier dots. The Date axis is represented as year and month with, for example, 200207 being July 2002.

At this site, fine and coarse particulate matter was sampled on 100 days between July 2, 2002 and June 30, 2003. The average 24-hour fine-mass values ranged from 10 g/m³ to 100 g/m³ with a median of 24 g/m³. For coarse particle mass, the values ranged from 10 g/m³ to 190 g/m³ with a median value of 44 g/m³ (Table 1).

The median values presented in Figs. 2 and 3 show that in the premonsoon, monsoon, and postmonsoon periods both fine and coarse mass concentrations were relatively low; but in the winter period, the mass concentrations were high. Because of the lower temperatures during winter, the mixing height becomes lower and the particulate matter was trapped nearer to ground level. During the winter, the rainfall is minimal so that dust resuspension increases the PM mass concentrations. During the winter season, the prevailing winds in Dhaka are from the north and northwest providing transported PM from India. There were other periods of the year when the mass concentrations were particularly high. These periods have been identified and discussed in previous studies (Begum *et al.*, 2004; Begum *et al.*, 2005b).

Table 1. Summary of the coarse and fine particulate matter mass concentration at SR site in Dhaka for the study period of July 2002 to June 30, 2003.

Parameter	Semi residential site, Dhaka	
	Coarse particle	Fine particle
Mean (µg/m ³)	48	31
Median (µg/m ³)	44	24
Standard deviation (µg/m ³)	30	21
Maximum (µg/m ³)	194	106
Minimum (µg/m ³)	9	9
Number of filters exposed	100	100

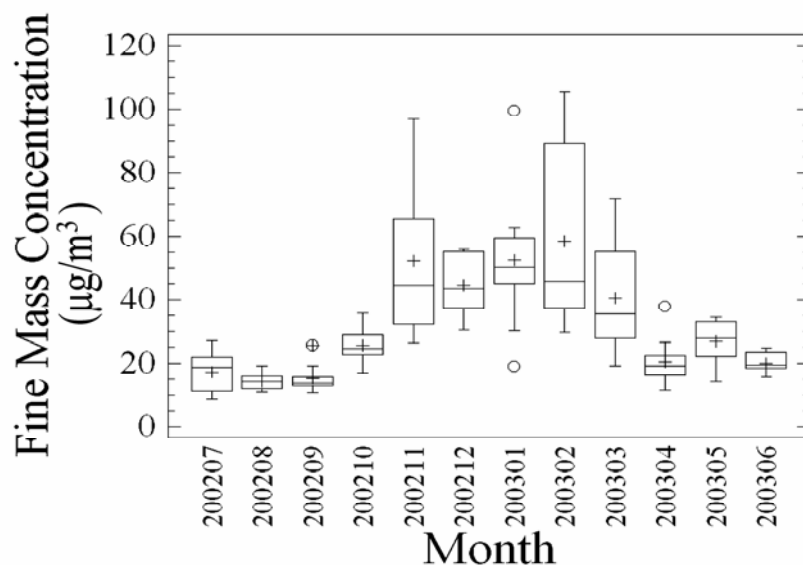


Fig. 2. Box and whisker plot for monthly fine mass (PM_{2.2}) concentration at SR site during the study period.

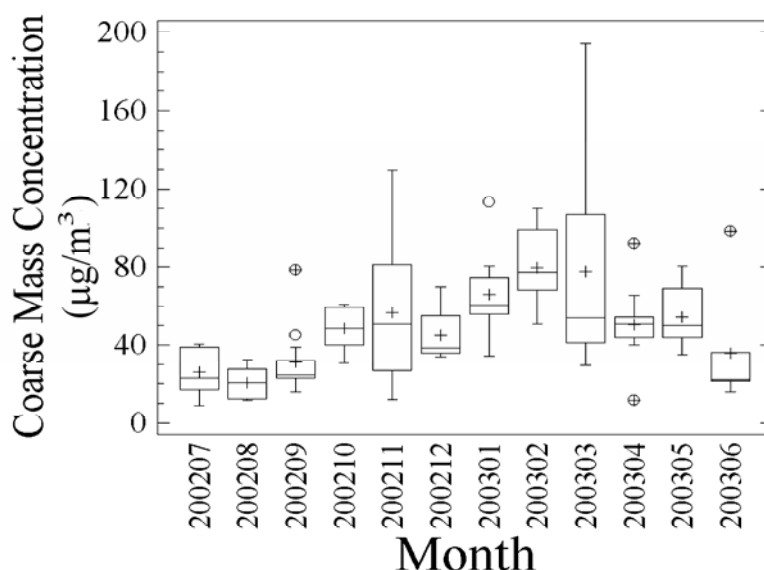


Fig. 3. Box and whisker plot for monthly coarse mass (PM_{2.2-10}) concentration at SR site during the study period.

Fig. 4 shows the monthly averaged box and whisker plot for the PM_{2.2} black carbon measurements at the SR site in Dhaka City. BC had strong seasonal variations with higher values in the winter where the concentrations were twice the summer (premonsoon) values. The reason for the high contribution during the winter period was caused by both the seasonal fluctuations in emissions and meteorological effects (precipitation rate and wind direction). During the wintertime, the wind comes mainly from the north and northwest. Air mass backward trajectories

calculated with HYSPLIT (Draxler and Rolf, 2003) using the vertical mixing model for those days which had higher contribution of concentration (both PM_{2.2} and BC mass) showed that air particulate mass concentrations were also influenced by transboundary air pollution (Begum *et al.*, 2006b). The values of the Air Quality Index (AQI) (Akhter *et al.*, 2004) in winter were very high, and the air was classified as extremely unhealthy during this period.

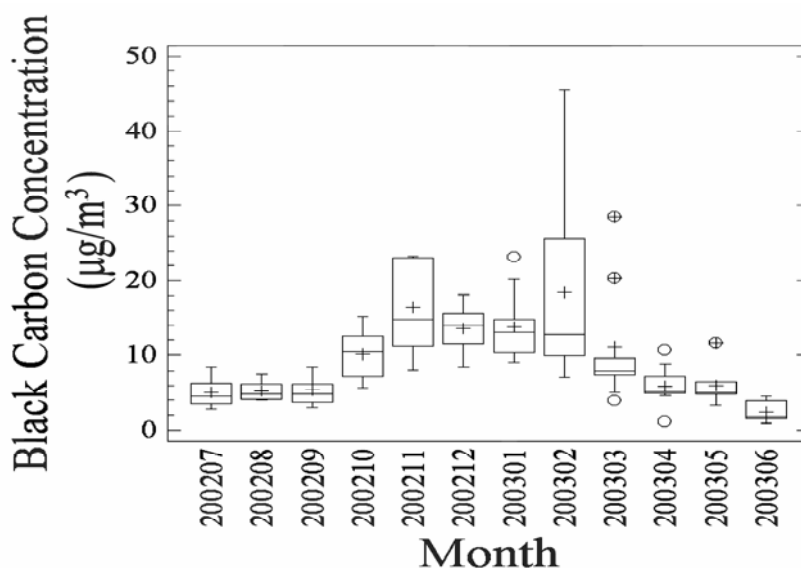


Fig. 4. Box and whisker plot for monthly black carbon (BC) concentration at SR during the study period.

Results of the reconstructed mass (RCM) variables

The variation of fine- and coarse-soil concentrations are displayed in Figs. 5 and 6, showing the monthly box and whisker plots for the coarse- and fine-soil estimates. It can be observed that during the premonsoon period, the concentrations of soil were higher than during any other period due to reduced soil-moisture effects (Begum *et al.*, 2004).

The sum of all the composite variables discussed in the previous section should provide a reasonable estimate of the total coarse and fine mass for comparison with the measured gravimetric mass of both coarse and fine particles on the filters. So, the reconstructed mass (RCM) would be the sum of the reconstructed mass variables defined above:

$$RCM = (NH_4)_2 SO_4 + Salt + Soil + Smoke + OMH + BC + Zn + Pb \tag{3}$$

where OMH represents the term for organic matter. During calculation of RCM, this OHM term has been omitted, because organic matter was not measured in this study. The RCM estimates

here will be well below 100%, but still sufficient to do reasonable source apportionment estimates, as the number of elements measured spans the full range of possible chemical species found in most particulate matter collected here.

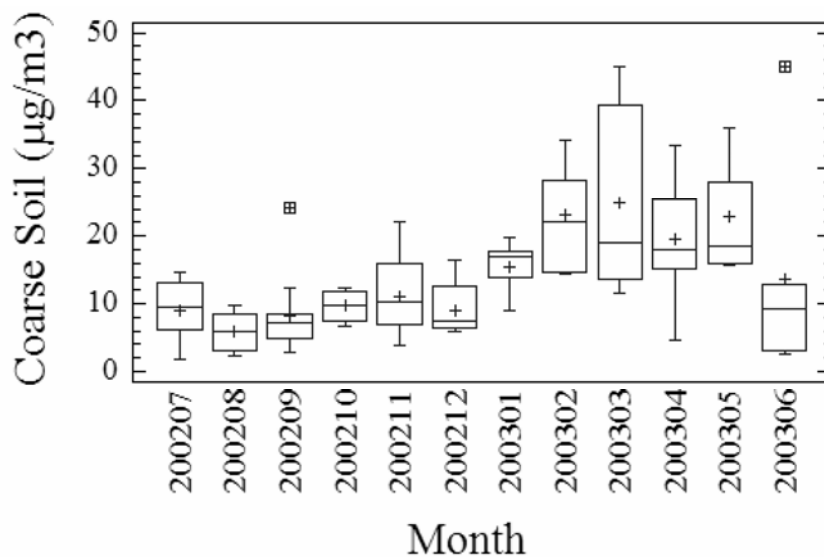


Fig. 5. Coarse soil estimates for SR during the study period.

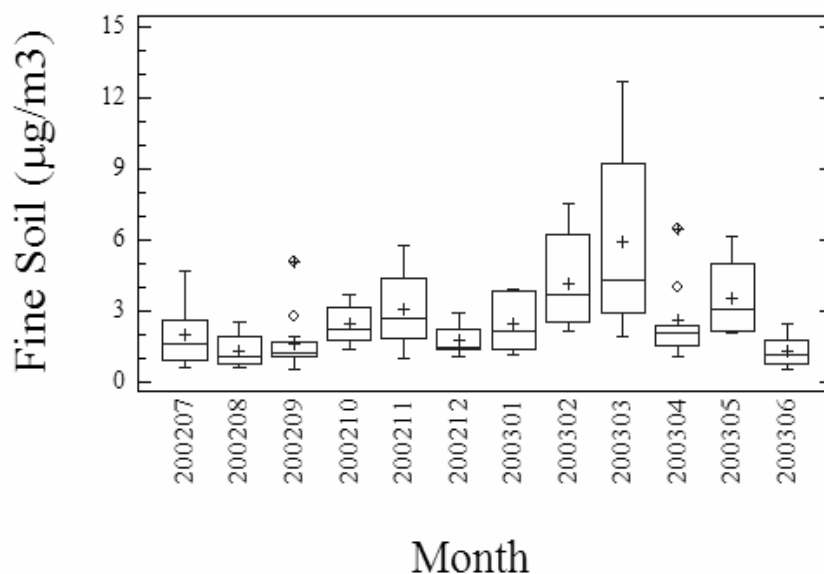


Fig. 6. Fine soil estimates for SR during the study period.

Equation (3) contains contributions from most of the major components measured in both coarse and fine mass. However, some trace elements, such as Cr, Co, Ni, Cu, and Br, are missing. These trace elements contributed on an average less than 1% to the total mass. The RCM was compared with the gravimetric weight of the filters, where the least squares fit to the data gave

$PCM = 0.43 \times Weight$ with an $R^2 = 0.73$ in the case of coarse mass (Fig. 7), and $PCM = 0.54 \times Weight$ with an $R^2 = 0.68$ in the case of fine mass (Fig. 8). The reconstructed mass is about 50% in this study because nitrate and organic matter were not included in the calculation. Table 2 gives the percentage of RCM components in the calculated RCM values for coarse- and fine-particulate matter samples.

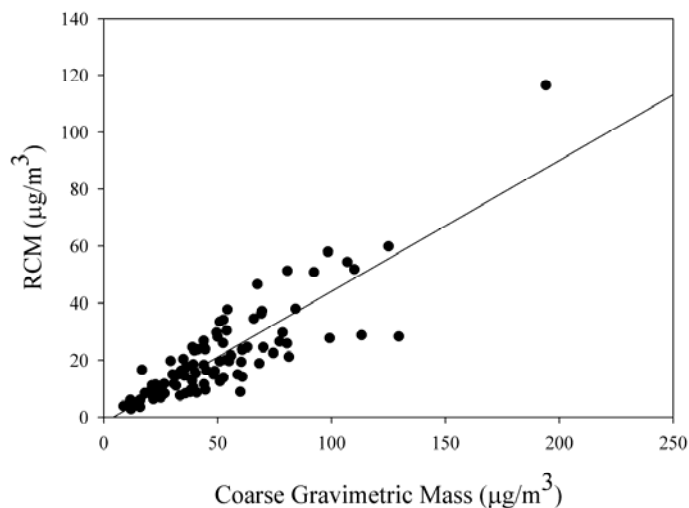


Fig. 7. The plot of RCM vs. Coarse gravimetric mass during the sampling period.

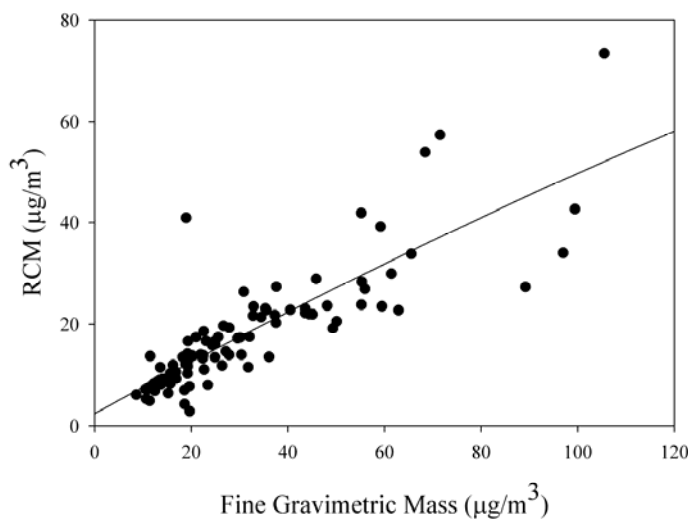


Fig. 8. The plot of RCM versus fine gravimetric mass during the sampling period.

Results from principal components analysis

This data sets include a total of 100 samples each for the coarse and fine fractions. Summary statistics for these data are presented in Table 3. In order to produce the best-possible source

resolutions, it is important to have accurate and precise measurements of the particulate mass, as well as determinations for as many as elements as possible. Of the 17 elements determined for each of the 100 samples, two elements, Cr and Sr, had values that were missing or below the detection limits in over 50% of the samples. These two elements were thus eliminated from the analysis. Since the method cannot use missing or below detection limit data, a value is required for assigning to those data values. These values were assigned a random number from a uniform random generator to provide a number between zero and the detection limit (Hopke, 1982).

In order to have a unique rotation, Hopke (1982) suggested a useful empirical criterion for choosing the number of retained eigenvectors. In a number of cases in which source identification of airborne particulate-matter composition was a problem, a stable solution was provided by choosing the number of factors containing a variance greater than one after an orthogonal rotation. The total variance in each factor was calculated as the sum of the squared loading for the given factor. A plot of these eigenvectors as a function of factor number is given in Fig. 9. There were four factors with eigenvalues greater than 1.0 for the fine particle data, and three factors with eigenvalues greater than 1.0 for the coarse particle data. However, there are additional eigenvalues of 0.85 and 0.56 for fine, and of 0.83 and 0.5 for coarse data. It can be seen that there is a smooth decrease from factor 6 up to 13 in the case of coarse data, and from 7 factors up to 14 in the case of fine data.

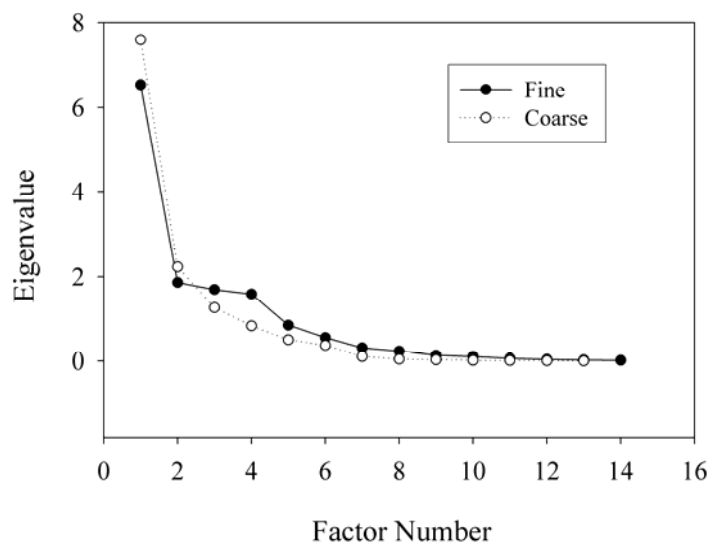


Fig. 9. Eigenvalues for the fine and coarse data sets as a function of factor number.

In order to obtain reliable estimates of the different sources contributing to the fine and coarse mass measured at the SR site, Principal Components Analysis (PCA) was used to identify major elements associated with sources. Tables 4 and 5 show the factor loadings from the PCA analysis. Factors with two or more elements having factor loadings above 0.3 have been highlighted. Five

factors were required to explain 96% of the sample variance in case of the coarse particulate matter and six factors were required to explain 93% of the sample variance in case of the fine particulate matter. Factor loadings near 1.0 demonstrate that the element has a strong association with that individual factor.

Factor 1 (Table 4) that explained 58% of the variance, includes high factor loadings for Al, Si, Ti, Ca, K, Mn and Fe in coarse particles that are identified as typical soil indicators. Factor 2 explained 17% of the variance and was labeled Sea Spray/Fresh Sea Salt as it included high loadings for Na, Cl and Br.

Table 3. The mean and standard deviations (elemental concentration in ng/m³) of coarse and fine particulate matter of a semi-residential area, Dhaka.

Parameter	Coarse particulate matter		Fine particulate matter	
	Mean	STD	Mean	STD
Mass	48461	30134	31037	20567
BC			9134	6844
F	136	163	58.9	98.3
Na	719	708	219	166
Al	1174	1167	248	390
Si	3176	2890	683	918
P	57.5	97.4	19.9	39.9
S	794	698	1111	810
Cl	556	815	83.4	96.7
K	482	411	316	206
Ca	1041	961	151	308
Ti	84.4	69.7	12.8	18.3
Mn	23.0	16.5	8.3	7.0
Fe	1035	786	200	203
Cu	9.38	6.80	4.2	3.9
Zn	350	416	259	274
Br	20.9	16.9	18.0	37.9
Pb	95.7	247	175	478

Table 4. Principal Components Analysis (PCA) with varimax rotation for all PM_{2.2-10} data from SR site.

Elt	Soil	Sea Spray	Two-stroke engine	Fugitive Pb	Motor Vehicle	Communality
Al	0.965	0.163	0.069	0.053	0.109	0.977
Br	0.038	0.675	0.502	0.019	-0.367	0.844
Ca	0.978	0.128	-0.017	0.012	0.000	0.974
Cl	0.091	0.962	0.048	-0.006	0.046	0.939
Fe	0.973	0.106	0.096	0.099	0.113	0.989
K	0.968	0.073	0.071	0.117	0.153	0.983
Mn	0.950	0.123	0.096	0.066	0.052	0.933
Na	0.262	0.939	-0.097	-0.064	0.067	0.968
Pb	0.162	-0.052	0.068	0.976	0.103	0.996
S	0.525	0.013	0.261	0.220	0.728	0.922
Si	0.979	0.113	0.060	0.057	0.127	0.993
Ti	0.962	0.067	0.072	0.117	0.192	0.985
Zn	0.126	0.023	0.936	0.067	0.150	0.920
% Var.	58.4	17.21	9.76	6.39	3.85	Total 96%
Eigen	7.59	2.24	1.27	0.83	0.50	

Factor 3 explained 10% of the variance and was labeled Zn source. It is anticipated that the contribution is mainly from motor vehicle, especially two-stroke engines, such as motor cycle/motor scooter (Begum *et al.*, 2005b). In two-stroke engine, fuel and lubricant are mixed and burnt together in the piston chambers. Zn is an additive in the lubricating oil, and thus, during combustion, Zn is emitted from two-stroke engines. In four-stroke engine, oil is not mixed with the gasoline and Zn emissions are reduced. Zn could also be emitted from galvanized materials production, tire wear and the use of zinc compounds in rubber production (Begum *et al.*, 2004).

Factor 4 explained 6% of the variance and was labeled as Fugitive or Resuspended Pb source. Although, Pb was eliminated from the gasoline in Bangladesh in July 1999 (Biswas *et al.*, 2003), there may be substantial accumulated lead in the dust near roadways. There are also some Pb battery recycling plants in the older part of Dhaka. Factor 5 explained 4% of the variance and was labeled as Motor Vehicle emissions (both diesel and gasoline engine exhaust) and shows high values of S (Begum *et al.*, 2005b).

Table 5. Principal Components Analysis (PCA) with varimax rotation for all PM_{2.2} data from SR site.

Elt	Soil	Motor Vehicle	Two-stroke Engine	Zn Source	Sea Salt	Fugitive Pb	Communality
BC	0.24	0.67	0.55	-0.15	0.00	0.22	0.89
Al	0.86	0.29	-0.01	0.29	0.18	-0.08	0.95
Ca	0.96	0.18	0.08	0.01	0.04	0.04	0.96
Cl	0.23	0.08	-0.12	0.90	0.24	0.03	0.95
Cu	0.00	0.14	0.91	0.09	0.07	-0.04	0.86
Fe	0.90	0.21	0.33	0.06	0.12	0.04	0.97
K	0.45	0.82	0.19	0.02	0.11	0.17	0.95
Mn	0.49	0.13	0.73	0.07	-0.08	-0.09	0.81
Na	0.11	0.12	0.01	0.16	0.96	0.01	0.98
Pb	-0.04	0.24	-0.06	0.03	0.01	0.96	0.99
S	0.27	0.91	0.05	0.14	0.10	0.12	0.94
Si	0.82	0.42	0.11	0.16	0.30	0.00	0.97
Ti	0.94	0.13	0.05	-0.01	-0.12	-0.04	0.92
Zn	-0.02	0.01	0.55	0.80	-0.04	0.01	0.95
% Var	46.7	13.3	12.1	11.3	6.04	3.96	Total 93%
Eigen	6.54	1.86	1.70	1.59	0.85	0.55	

Examining the fine particle results in Table 5, Factor 1 explained 47% of the variance with high factor loadings for crustal elements, including Al, Si, Ti, Ca, K, Mn and Fe. These elements are typical indicators of soil. Factor 2 explained 13% of the variance and was labeled as Motor Vehicle that shows high values of S and BC (both diesel and gasoline engine exhaust). This factor also has a high value of K that most likely comes from biomass/brick kiln along with BC. In the PCA results, it was not possible to separate this area source from the motor-vehicle emissions.

Factors 3 and 4 explained 12% and 11% of the variance, and were labeled Two-Stroke Engine and Zn source, respectively. Zn associated with Cu, Mn and BC was identified as two-stroke engine exhausts (Begum *et al.*, 2004). Zn could also be contributed from galvanizing factories, tire wear, and the use of zinc compounds in rubber production. Thus, the factor with high loadings of Zn and Cl was attributed to a Zn source that is likely to be a composite of Zn sources other than two-stroke exhaust.

Factor 5 explained 6% of the variance and was labeled Sea Spray as it included high loadings for Na and Cl. Factor 6 explained 4% of the variance and was labeled as Fugitive or Resuspended Pb.

Source related classification of the elements based on PCA analysis: Soil fingerprint

Soil has previously been identified as a significant component of Asian aerosol in many studies (Holmes *et al.*, 1996; Cheng *et al.*, 2000; Hein *et al.*, 2002; Cohen *et al.*, 2004a, b). In order to obtain a reliable estimate of the soil mass associated with the PM_{10-2.2} and PM_{2.2} mass measured, PCA was used to identify major crustal components associated with the soil fingerprints for this site. The seven elements, Al, Si, K, Ca, Ti, Mn and Fe in their oxide form, were used to define a soil fingerprint for Dhaka (Table 6).

Table 6. Slope, standard error (SE) and correlation coefficient (R²) of the biplots of soil cursor element identified by PCA analysis relative to silicon for coarse and fine particulate matter.

Element	Slope	SE	# Points	%SD	R ²	Constraints
Coarse particulate matter						
Al	0.383	0.004	100	10.5	0.99	
Ca	0.325	0.006	100	16.9	0.97	
K	0.146	0.002	100	12.3	0.99	
Ti	0.025	0.000	100	12.3	0.99	
Fe	0.300	0.004	100	13.8	0.98	
Mn	0.006	0.000	100	23.2	0.95	
O	2.605	0.008	100	2.86	1	
Fine particulate matter						
Al	0.3664	0.009	99	24.3	0.94	
Ca	0.1974	0.0066	99	33.1	0.90	
K	0.300	0.0106	46	23.7	0.95	K / Si < 0.5
Ti	0.0181	0.0009	99	49.2	0.80	
Fe	0.2735	0.0076	99	27.5	0.93	
Mn	0.010	0.0007	99	69.3	0.69	
O	2.4595	0.019	99	7.6	0.99	

Table 7. Mean elemental fractions in soil obtained from the least squares fit of each element against silicon and assuming each element occurs as its common oxide.

Element	Coarse particle		Fine particle	
	Fraction	SD	Fraction	SD
Al	0.080	0.008	0.079	0.014
Si	0.209	0.069	0.215	0.071
Ca	0.068	0.011	0.042	0.014
K	0.031	0.004	0.065	0.015
Ti	0.005	0.001	0.004	0.001
Fe	0.063	0.009	0.059	0.014
Mn	0.001	0.000	0.002	0.001
O	0.544	0.016	0.529	0.220

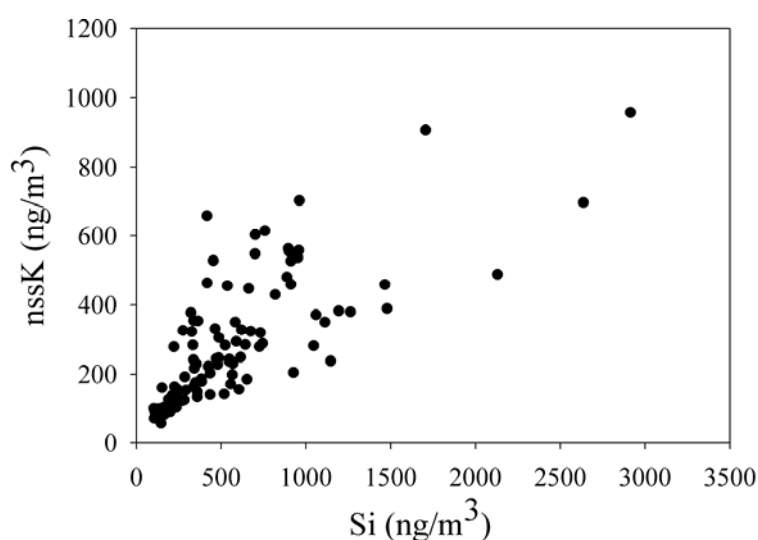


Fig. 10. Correlation plot for silicon versus non-sea salt potassium (nssK) at SR site for fine fraction.

It is important not to include elements in soil estimates that may have significant contributions from sources other than soil, because inclusion of these may tend to over estimate the soil component. It is possible to minimize this problem by two ways. First, the known components of elemental concentrations from sources other than soil are removed. For example, by removing the sea-salt component from the total potassium and calcium estimates through a knowledge of the [K/Na] and [Ca/Na] ratios in seawater. Second, by plotting the concentrations of each element against that of silicon for each sample, the most-abundant crustal species measured in this study, it is possible to obtain the minimum least squares fitted slope that excludes the contributions of

this element not associated with silicon. A good example of this problem was potassium. Potassium has three possible primary sources: smoke from biomass burning, sea salt, and windblown soil. The biplot of nssK against Si (Fig. 10) exhibits two different correlations that confirm K has sources other than soil. By using an appropriate constraint ($K/Si < 0.5$) to obtain the subset of data for the correlation analysis, the soil component was differentiated from other sources. The slopes of the least squares fit for silicon to each of the mentioned elements, together with standard errors of the fit, were used to compute the fingerprints for soil indicator (Table 7).

Motor vehicle fingerprint

The motor vehicle source fingerprint in fine PM included high loadings for BC: S, together with resuspended road dust elements, and Si and Al. Historically, lead has been the most reliable tracer of traffic. However, since July 1999, lead has been totally banned from gasoline in Bangladesh (Biswas *et al.*, 2003). Black carbon is reported to be a significant component of the PM_{2.2} mass fraction in Asian sites (Cohen *et al.*, 2004a, b). It is emitted by motor vehicles, the combustion of fossil fuels, animal waste burning, crops and vegetation fires (Salam *et al.*, 2003b; Begum *et al.*, 2004; Begum *et al.*, 2005b). Again, sulfur can serve as a tracer for traffic exhaust in Bangladesh, as there are no coal-fired power plants in the country. The sulfur content of diesel fuel is 0.7%, and for gasoline it is 0.2%. The high sulfate concentrations can also be the result of some transboundary transport. For the coarse fraction of PM, the factor associated with high factor loading of S was identified as the motor vehicle fingerprint.

An approach similar to that explained earlier was utilized for the fine motor vehicle fingerprints to exclude contributions from sources other than traffic exhaust to the concentrations of S, Al and Si. The slope of the least squares fit for black carbon to each of the mentioned elements, together with standard error of the fit, were used to develop the motor vehicle fingerprint (Table 8).

Table 8. Mean elemental fractions in motor vehicle obtained from least squares fit of each element against black carbon for fine samples.

Element	Fine particle	
	Fraction	SD
S	0.074	0.027
BC	0.868	0.521
Al	0.009	0.003
Si	0.035	0.013

Sea salt / fresh sea salt fingerprint

Sea spray/fresh sea salt included high loadings for Na, Cl and Br in the coarse fractions. Fine fraction sea spray included Na and Cl. It was observed that this source dominated during the monsoon season when the wind is normally from the south and southeast. From the PCA analyses, it was seen that Na was associated with Cl for the fine-fraction particles, and with Cl and Br for coarse-fraction particles. Cl may have sources other than sea salt, and therefore, similar constraints have been applied during the least square fits to obtain a source profile representing local sea salt contributions. The slopes of the least square fits for sodium to each of those elements, together with standard error of fit, were used to produce a fingerprint for sea salt/fresh sea salt in the case of both fine and coarse samples separately (Table 9).

Table 9. Mean elemental fractions in sea spray obtained from least squares fit of each element against sodium for fine and coarse samples respectively.

Element	Coarse particle		Fine particle	
	Fraction	SD	Fraction	SD
Cl	0.471	0.183	0.057	0.030
Na	0.518	0.311	0.249	0.150
Br	0.011	0.008		

Two-stroke engine fingerprint

Two-stroke engine emissions include high loadings for BC, Zn, Mn and Cu for fine fractions and Zn and Br for coarse fractions. Zn is characteristic of lubricating oil combustion in two-stroke engines. Although three-wheeled taxis with two-stroke engines have been completely banned since January 2003, personal two-stroke motorcycles and scooters are still in use, leading to continued Zn emissions. Zn can also be emitted from galvanized materials production, tire wear, and the use of zinc compounds in the rubber production. Since Cu, BC, Mn, and Br have sources other than two-stroke engines, the concentrations of these elements were regressed against corresponding Zn concentration with appropriate constraints. The slope of least squares fit for Zn to each of those mentioned elements, together with standard error of fit, were used to define the fingerprints for the two-stroke engine sources separately for both the fine and coarse samples (Table 10).

Table 10. Mean elemental fractions in two stroke engine obtained from least squares fit of each element against Zinc for fine and coarse samples respectively.

Element	Coarse particle		Fine particle	
	Fraction	SD	Fraction	SD
Cu			0.001	0.0005
Zn	0.507	0.405	0.056	0.033
BC			0.867	0.661
S	0.477	0.237		
Br	0.016	0.018		
Mn			0.001	0.001

Zinc-source fingerprint

The PCA analysis for fine fractions showed another factor with high Zn and Cl factor loading. The association of Zn with Cl indicates the presence of a source other than two-stroke engine emissions, which was defined as an unknown Zn source. The slope of the least squares fit for zinc to Cl, together with standard error of fit, were used as a fingerprint for this source (Table 11).

Table 11. Mean elemental fractions for the Zn source.

Element	Mean elemental fraction with SD	
	Fraction	SD
Cl	0.080	0.036
Zn	0.790	0.395

Fugitive/resuspended Pb fingerprint

PCA analysis showed a high factor loading of Pb. Although leaded gasoline was banned in Bangladesh from 1999, Pb may come from fugitive sources, for examples paint and pigment, Pb acid battery (Begum *et al.*, 2005b), or the resuspended soil dust (Harris *et al.*, 2005). Since Pb does not have any strong association with other elements, it is not possible to create a multi-elemental fingerprint for this source.

Comparison of PCA source fingerprints with PMF

In an earlier study, source apportionment was performed using positive matrix factorization (PMF) (Begum *et al.*, 2004). The PMF method develops its own source fingerprints through a least squares fit to the data. These fingerprints are used to obtain the source contributions at the receptor site. The source fingerprints obtained from the present study using PCA method have been compared with those obtained from PMF analysis in Table 12. It has been observed that the relative abundance of different elements obtained by different fingerprinting methods have comparable values (Huang *et al.*, 1999). Therefore, it is concluded that source fingerprints obtained using the PCA-regression method described above may be utilized for source apportionment study using chemical mass balance (CMB) or other similar methods.

ACKNOWLEDGEMENT

This work is financially supported partly by the RCA/IAEA, and the Ministry of Science and Information & Communication Technology (MOSICT), Government of the People's Republic of Bangladesh under a special grant. The authors acknowledge this assistance. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.arl.noaa.gov/ready.html>) used in this publication.

Table 12. Comparison of source fingerprints obtained from PCA and PMF method.

Element	Source Fingerprint							
	Soil_FA	Soil_PMF	Sea Spray_FA	Sea Spray_PMF	Soil_FA	Soil_PMF	Sea Spray_FA	Sea Spray_PMF
Coarse particulate matter				Fine particulate matter				
Na			0.518±0.311	0.203±0.009			0.451±0.27	0.152±0.04
Mg								
Al	0.08±0.008	0.042±0.004			0.065±0.011	0.057±0.004		
Si	0.20±0.069	0.10±0.008			0.1620±0.054	0.131±0.007		
S								
Cl			0.471±0.183	0.464±0.009			0.153±0.01	0.58±0.017
K	0.031±0.004	0.014±0.002			0.07±0.031	0.044±0.004		
Ca	0.068±0.011	0.058±0.003			0.047±0.015	0.052±0.001		
Ti	0.005±0.001	0.004±0.003			0.003±0.001	0.005±0.0006		
Cr								
Mn	0.001±0.000 1	0.0007±0.0001			0.001±0.0001	0.0004±0.0002		
Fe	0.063±0.009	0.034±0.003			0.039±0.01	0.028±0.002		
Ni								
Cu								
Zn								
Br			0.011±0.008	0.003±0.0007				
Pb								

REFERENCES

- Akhter, S., Islam, M.A., Hossain, A.M.S., Quadir, S.M.A., Khan, A.H., Begum, B.A., Khaliqzaman, M., and Swapan, K.B. (2004). Air Quality Monitoring Program in Bangladesh: Trends Analysis of Criteria Pollutants and Source Apportionment of Particulate Matter in Dhaka, Bangladesh. Clean Air Initiative (Asia), www.baq2004.org.
- Azad, A.K., Kitada, T. (1998). Characteristics of the Air Pollution in the City of Dhaka, Bangladesh in Winter. *Atmos. Environ.* 32: 1991-2005.
- Begum, B.A., Akhter, S., Sarker, L., and Biswas, S.K. (2006a). Gravimetric Analysis of Air Filters and Quality Assurance in Weighing. *Nucl. Sci. & Appl.* Submitted.
- Begum, B.A., and Biswas, S.K. (2005a). Comparison of PM Collection Efficiency of Gent and Airmetrics MiniVol Portable Air Sampler. *Nucl. Sci. & Appl.* 114: 79-83.
- Begum, B.A., Biswas, S.K., Kim, E., Hopke, P.K., and Khaliqzaman, M. (2005b). Investigation of Sources of Atmospheric Aerosol at a hot spot area in Dhaka, Bangladesh. *J. Air and Waste Manage. Assoc.* 55: 227-240.
- Begum, B.A., Kim, E., Biswas, S.K., and Hopke, P.K. (2004). Investigation of Sources of Atmospheric Aerosol at Urban and Semi-urban Areas in Bangladesh. *Atmos. Environ.* 38: 3025-3038.
- Begum, B.A., Swapan K, B., and Philip, K.H. (2006b). Temporal Variations and Spatial Distribution of Ambient PM_{2.2} and PM₁₀ Concentrations in Dhaka, Bangladesh. *Sci. Total Environ.* 358: 36-45.
- Biswas, S.K., Tarafdar, S.A., Islam, A., Khaliqzaman, M., Tervahattu, H., and Kupiainen, K. (2003). Impact of Unleaded Gasoline Introduction on the Concentration of Lead in the Air of Dhaka, Bangladesh. *J. Air & Waste Manage. Assoc.* 53: 1355-1362.
- Cheng, Z.L., Lam, K.S., Chan, L.Y., Wang, T., and Cheng, K.K. (2000). Chemical Characteristics of Aerosols at Coastal Station in Hong Kong.1. Seasonal Variation of Major ions, Hologens and Mineral Dusts between 1995 and 1996. *Atmos. Environ.* 34: 2771-2783.
- Cohen, D.D. (1998). Characterisation of atmospheric fine particles using IBA techniques, *Nucl. Instr. & Meth (B)* 137: 14-22.
- Cohen, D.D., and Clayton, E. (1987). A Database for thick target PIXE, *Nucl. Instr. & Meth (B)* B22: 59-63.
- Cohen, D.D., Bailey, G.M., and Kondepudi, R. (1996). Elemental Analysis by PIXE and other IBA Techniques and their Application to Source Fingerprinting of Atmospheric Fine Particle Pollution. *Nucl. Instr. & Meth (B)*. 109/110: 218-226.
- Cohen, D.D., Stelcer, E., and Garton, D. (2002). Ion Beam Methods to Determine Trace Heavy Metals Concentrations and Sources in Urban Airshed. *Nucl. Instr. & Meth. (B)*. 190: 466-470.

- Cohen, D.D., Garton, D., Stelcer, E., and Hawas, O. (2004a). Accelerator Based Studies of Atmospheric Pollution Processes. *Radiation Physics and Chemistry* 71, 759-767.
- Cohen, D.D., Stelcer, E., Hawas, O., and Garton, D. (2004b). IBA Methods for Characterization of Fine Particulate Atmospheric Pollution: A Local, Regional and Global Research Problem. *Nucl. Instr. & Methods B*219-220, 145-152.
- Dockery, D.J., and Pope, C.A. (1994). Acute Respiratory Effects of Particulate Air Pollution. *Ann Rev Public Health* 15: 107-132.
- Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., and Speizer, F.E. (1993). An Association between Air Pollution and Mortality in six US Cities. *N. Engl. J. Med.* 329: 1753-1759.
- Dockery, D.W., Speizer, F.E., Stram, D.O., Ware, J.H., Spengler, J.D., Ferris, B.G. (1989). Effects of Inhalable Particles on Respiratory Health of Children. *Am. Rev. Diseases* 139: 134-139.
- Draxler, R.R. and Rolph, G.D. (2003). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>). NOAA Air Resources Laboratory, Silver Spring, MD.
- Harris, A.R., and Davidson, C.I. (2005). The Role of Resuspended Soil in Lead Flows in the California South Coast Air Basin. *Environ. Sci. & Technol.* 39: 7410-7415.
- Henry, R.C. (1997). History and Fundamentals of Multivariate Air Quality Receptor Models. *Chemometrics and Intelligent Laboratory Systems*; 37: 37-42.
- Hien, P.D., Bac, V., Tham, H.C., and Vinh, L.D. (2002). Influence of meteorological conditions on PM_{2.5} and PM_{2.5-10} concentrations during the monsoon season in Hanoi, Vietnam. *Atmos. Environ.* 36: 3473-3484.
- Holmes, J., and Zoller, W. (1996). The Elemental Signature of Transported Asia Dust at Mauna Loa Observatory. *Tellus.* 48B: 83-92.
- Hopke, P.K., Receptor Modeling in Environmental Chemistry (Wiley: New York, 1985).
- Hopke, P.K. (1982). Comments on "Trace element concentrations in summer aerosols at rural sites in New York State and their possible sources" by P. Parekh and L. Husain and 'Seasonal variations in the composition of ambient sulfur-containing aerosols' by R. Tanner and B. Leaderer. *Atmos Environ.* 16: 1279-1280.
- Hopke, P.K., E.S. Gladney, Gordon, G.E., Zoller, W.H., and Jones, A.G. (1976). The Use of Multivariate Analysis to Identify Sources of Selected Elements in the Boston Urban Aerosol. *Atmos. Environ.* 10: 1015-1025.
- Hopke, P.K., Xie, Y., Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P., and Cohen, D. (1997). Characterization of Gent Stacked Filter Unit PM₁₀ Sampler. *Aerosol Sci. & Technol.* 27: 726-735.

- Huang, S., Rahn, K.A., Arimoto, R. (1999). Testing and optimizing two factor-analysis techniques on aerosol at Narragansett, Rhode Island. *Atmos. Environ.* 33: 2169-2185.
- Lee, J.H., Kim, Y.P., Moon, K.C., Kim, H.K., and Lee, C.B. (2001). Fine Particle Measurements at Two Background Sites in Korea between 1996 and 1997. *Atmos. Environ.* 35: 635-643.
- Malm, W.C., Sisler, J.F., Huffman, D., Eldred, R.A., and Cahill, T.A. (1994). Spatial and Seasonal Trends in Particle Concentration and Optical Extinction in the United States. *J. Geophys. Res.* 99: 1347-1370.
- Pope, C.A. (2000). Epidemiology of Fine Particulate Air Pollution and Human Health: Biologic Mechanisms and Who's at Risk. *Environmental Health Perspective*; 108: 713-723.
- Pope, C.A., Schwartz, J., and Ranson, M.R. (1992). Daily mortality of PM10 Pollution in Utah Valley. *Arch. of Environ. Health* 47: 211-217.
- Salam, A., Bauer, H., Kassin, K., Ullah, S.M., Puxbaum, H. (2003a) Aerosol Chemical Characteristics of a Mega-city in Southeast Asia (Dhaka, Bangladesh). *Atmos. Environ.* 37: 2517-2528.
- Salam, A., Bauer, H., Kassin, K., Ullah, S.M., and Puxbaum, H. (2003b). Aerosol Chemical Characteristics of an Island Site in the Bay of Bengal (Bhola-Bangladesh). *J. Environ. Monit.* 5: 483-490.
- Schwartz, J. (2001). Is there harvesting in the association of airborne particles with daily deaths and hospital admissions? *Epidemiology* 12: 55-61.
- Wilson, T.R.S., Salinity and major elements of sea water. (1975) In *Chemical Oceanography*, 2nd edition, J.P. and G. Skirrow, eds. Chapter 6, Academic Press, London, pp. 365-413.
- Wolff, G. T., Korsog, P. E., Kelly, N. A., and Fermam, M. A. (1985). Relationships Between Fine Particulate Species, Gaseous Pollutants and Meteorological Parameters in Detroit 19. *Atmos. Environ.* 19: 1341-1349.

Received for review, January 10, 2006

Accepted, September 9, 2006