

CHARACTERIZATION AND IDENTIFICATION OF THE SOURCES OF CHROMIUM, ZINC, LEAD, CADMIUM, NICKEL, MANGANESE AND IRON IN PM₁₀ PARTICULATES AT THE TWO SITES OF KOLKATA, INDIA

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Abstract. Monitoring of ambient PM₁₀ (particulate matter which passes through a size selective impactor inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter) has been done at residential (Kasba) and industrial (Cossipore) sites of an urban region of Kolkata during November 2003 to November 2004. These sites were selected depending on the dominant anthropogenic activities. Metal constituents of atmospheric PM₁₀ deposited on glass fibre filter paper were estimated using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). 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 PM₁₀ concentrations. The 24 h average concentrations of Cr, Zn, Pb, Cd, Ni, Mn and Fe from ninety PM₁₀ particulate samples of Kolkata were found to be 6.9, 506.1, 79.1, 3.3, 7.4, 2.4 and 103.6 ng/m³, respectively. The 24 h average PM₁₀ concentration exceeded national ambient air quality standard (NAAQS) as specified by central pollution control board, India at both residential (Kasba) and industrial (Cossipore) areas with mean concentration of 140.1 and 196.6 $\mu\text{g}/\text{m}^3$, respectively. A simultaneous meteorology study was performed to assess the influence of air masses by wind speed, wind direction, rainfall, relative humidity and temperature. The measured toxic trace metals generally showed inverse relationship with wind speed, relative humidity and temperature. Factor analysis, a receptor modeling technique has been used for identification of the possible sources contributing to the PM₁₀. Varimax rotated factor analysis identified four possible sources of measured trace metals comprising solid waste dumping, vehicular traffic with the influence of road dust, road dust and soil dust at residential site (Kasba), while vehicular traffic with the influence of soil dust, road dust, galvanizing and electroplating industry, and tanning industry at industrial site (Cossipore).

Keywords: aerosol, factor analysis, meteorology, toxic trace metals, urban region

1. Introduction

Rapid urbanization and industrialization led to increase in air pollution level of cities worldwide. The population of megalopolis cities, motor vehicles, motor fuel consumption increases and finally air pollution level increased (Ghose *et al.*, 2004).

Exposure to air pollution, especially particulate pollution, PM₁₀ (particulate matter which passes through a size selective impactor inlet with a 50% efficiency cut-off at 10 μ m aerodynamic diameter) is now an almost inescapable part of an urban life throughout the world. Dust from paved and unpaved roads, construction and demolition, and bare ground sites are important contributors to PM₁₀ (Chow and Watson, 2002).

Urban air pollution problems are aggravated by meteorological and topographical factors that often accumulate pollutants in the city and prevent proper dispersion and dilution. Several epidemiological studies have demonstrated a direct association between atmospheric PM₁₀ and respiratory diseases, pulmonary damage, and mortality among population (Brits *et al.*, 2004; Celis *et al.*, 2004; Dockery and Pope, 1994; Thomaidis *et al.*, 2003; Yang *et al.*, 2004; Zhao and Hopke, 2004). Ambient particulate matters also have adverse impact on environment including change in cloud formation, scattering solar radiation and visibility impairment. Toxicological studies show that the health effects of particles are dependent on their chemical composition (Mugica *et al.*, 2002). Heavy metals have a great ecological significance due to their toxicity and cumulative behavior (Mesa *et al.*, 1999).

Shortness of breath, coughing, wheezing, septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory disorders have been observed from chronic exposure of chromium (Cr) (Mugica *et al.*, 2002). Lead (Pb) can affect adversely to nervous system, the hemo group syntheses and the vascular system, especially to children (Mugica *et al.*, 2002). Cadmium (Cd) is a possible carcinogen and its chronic exposition to high concentrations can result in respiratory illness. Continuous and prolonged exposure to Nickel (Ni) may produce dermatitis and disorders to respiratory system. Manganese (Mn) is a neurotoxic element whose prolonged exposure leads to neurological disease called manganism. Zinc and iron deteriorates human metabolism. Iron is a potentially toxic element that acts as a catalyst in the development of the highly poisonous free oxygen radicals in living organisms (Hemminki *et al.*, 1995).

The trace elements are released into the atmosphere both by natural and anthropogenic sources (Bem *et al.*, 2003; Wang *et al.*, 2001). Therefore, source apportionment study is an important step for identification of the sources of toxic elements in urban atmosphere. The knowledge of the physical and chemical characteristics of particles allows identification of the emission sources.

The present study characterizes the levels of Cr, Zn, Pb, Cd, Ni, Mn and Fe in PM₁₀, collected from residential and industrial sites of an urban region of Kolkata during November 2003 to November 2004. Statistical analysis has been performed to evaluate the seasonal behavior of toxic trace metals, and correlations of their concentrations with different meteorological parameters. Factor analysis, a receptor modeling technique has been performed to identify the possible sources that contribute to PM₁₀ 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 2001 census report. It is the second largest metropolis in south Asia and is one of the worst polluted cities in the world (Ghose *et al.*, 2004). Rapid and unplanned urbanization, and uncontrolled vehicular density on insufficient badly cared road space and higher use of leaded petrol fuel increased the air pollution in Kolkata (Ghose *et al.*, 2004).

The city is bounded to the west and north-west by the Hugly river spread along 80 km, which divides it from Howrah on the western bank. The city has a tropical savannah climate with a marked monsoon season. Average relative humidity (RH) is 66% and 69% in winter and summer, respectively. Mean monthly temperature ranges from 20–31 °C, and the maximum temperatures often exceed 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 7 km/h blowing throughout the year. The monitoring locations of study area are shown in Figure 1.

The residential and industrial sites have been selected based on the predominant activities of the local areas. Residential location (Kasba) is typically residential area and air quality is mainly influenced by domestic activities, vehicular movement, solid waste dumping and open burning of leaves and garbage. Industrial location (Cossipore) has mainly thermal power plant, ordnance factory, heavy vehicular traffic, galvanizing and electroplating industry, and dyeing industry.

2.2. SAMPLE COLLECTION

At each monitoring site, concentrations of PM₁₀ were measured by respirable dust sampler (Envirotech). Ambient air laden with suspended particulates enters the system through the inlet pipe. As the air enters the cyclone, coarse and non-respirable dust is separated from the air by centrifugal forces acting on the solid particles. These coarse particulates fall through the cyclone and get collected in the sampling bottle fitted at its bottom. The air stream deposited on the filter paper carries PM₁₀. The instrument was operated at a flow rate of 0.8–1.4 m³/min. The 24 h monitoring was done once in a week at each site. Particulate samples were collected at a height of 3.0 m at residential site and 3.1 m at industrial site. Meteorological parameters like wind speed, wind direction, rainfall, relative humidity and temperature were collected from Indian meteorological department, Kolkata.

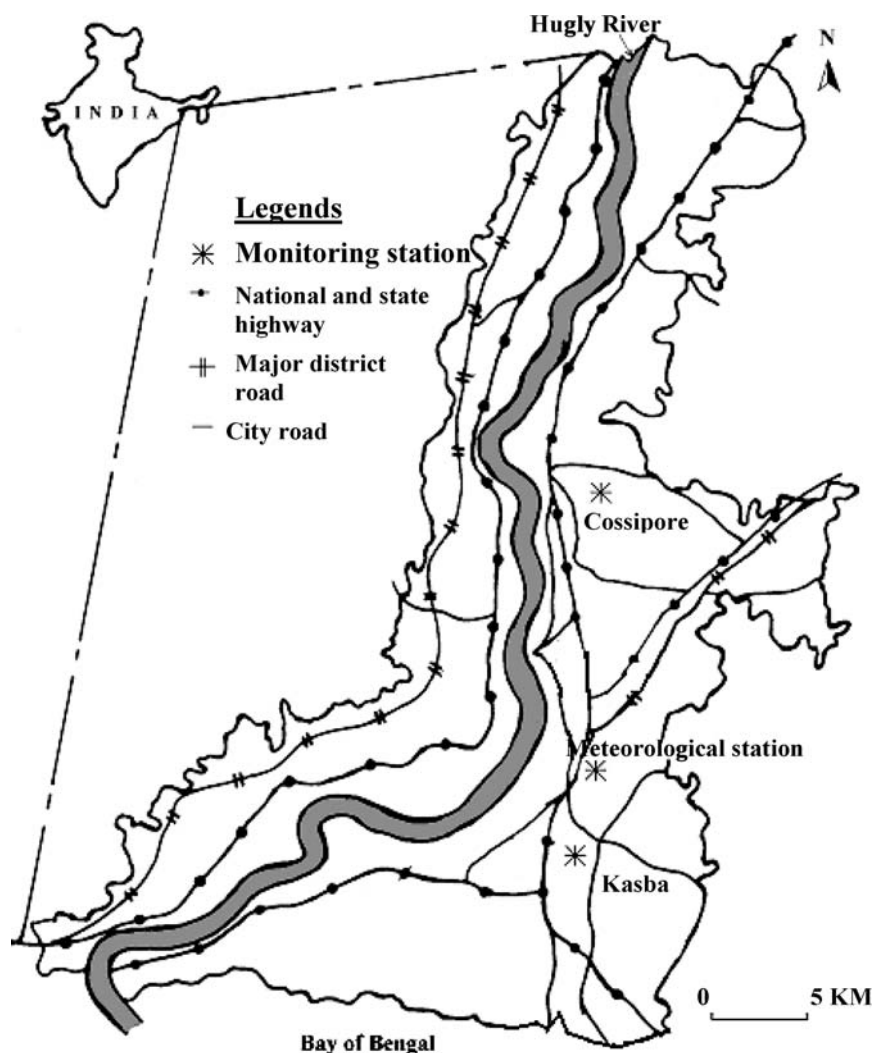


Figure 1. Monitoring locations of study area.

2.3. SAMPLE ANALYSIS

In the present study, Whatman glass fibre filter papers were used for collecting ambient PM_{10} samples and further analyzing for trace metals. The PM_{10} concentrations were measured gravimetrically by weighing the particulate mass collected and knowing the total volume of air sampled. Filter papers were kept in desiccator for 24 h before and after the sample collection. Field and laboratory blank filter samples were routinely analyzed for PM_{10} to evaluate analytical bias and precision.

It is assumed that PM₁₀ deposited on the glass fibre filter papers were uniformly distributed over the entire area. A known portion of the exposed filter paper sample is taken and digested in concentrated nitric acid (APHA, 1977). Cooled filtrate is made to a known volume using distilled water and is analyzed for metal constituents using Inductively Coupled Plasma Atomic Emission Spectrometer, Jobin Yvon JY-24. Standard solution is selected to match the sample matrix as closely as possible. During sample analysis, standard solution is repeatedly aspirated to ensure that the calibration is within the limits of control chart. Blank concentrations were always deducted from sample results.

2.4. FACTOR ANALYSIS

Multivariate analysis technique, factor analysis called principal component analysis (PCA) 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). 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). Factor analysis is a statistical technique that can be applied to a set of variables in order to reduce their dimensionality.

In factor analysis, set of variables is first normalized as X_{it} as shown in Equation (1) so that their variances are unity.

$$X_{it} = (C_{it} - C_i)/d_i \quad (1)$$

where C_{it} is the concentration of the variable i in the sample t , C_i and d_i are the arithmetic mean and standard deviation of the variable i for all samples included in the analyses. These common factors are typically characterized as pollutant source types in air pollution studies. The factor analysis model applied in the field of air pollution is given in Equation (2).

$$X_{it} = \sum_{j=1}^N L_{ij}S_{jt} + E_{it} \quad (2)$$

where L_{ij} is the factor loading of the variable i in the source j with N number of sources, S_{jt} is the factor score of the source j for sample t and E_{it} is the residual of variable i in the sample t not accounted by the j sources or factors.

The two vectors L and E are unknown in factor analysis (FA) and are obtained by assuming various covariance relationships between the vectors S and E and finally solving the covariance matrix as an eigenvalue-eigenvector decomposition problem. In this study, FA was carried out on seven toxic trace metals and PM₁₀. The factors that have been determined is rotated to transform the initial matrix to

easily interpret. The sum of the eigen values is not affected by rotation but rotation will alter the eigenvalues of particular factors and will change the factor loadings. The varimax rotation of the matrix was selected which attempts to minimize the number of heavy metals that have high loadings on a factor. This enhanced the interpretability of the factors. Unusual events or errors 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, since they do not represent the normally observed situation (Kumar *et al.*, 2001).

Factor analysis determines factor F in such a way so as to explain as much of the total variation in the data as possible with as few of these factors as possible (Kleinbaum and Kupper, 1978). In factor analysis, F_i is the i th factor as calculated by Equation (3).

$$F_i = \sum_{j=1}^p w_{ij} X_j = w_{i1} X_1 + w_{i2} X_2 + \dots + w_{ip} X_p \quad (3)$$

where the w 's are the factor weights (to be estimated from the data) chosen so as to maximize the quantity and the X 's are the original variables in standardized form.

The second factor F_2 is such that weighted linear combination of the variables which is uncorrelated with F_1 and which accounts for the maximum amount of the remaining total variation not already accounted for by F_1 . The higher the factor weight for a given variable, the more that variable contributes to the overall factor score and the higher the factor loading. Higher factor loadings of particular element can help in identifying the possible sources (Henry *et al.*, 1984). The factors obtained are rotated to achieve the meaningful underlying vectors with more interpretability.

In the present study seven toxic trace metals (Cr, Zn, Pb, Cd, Ni, Mn, and Fe) and PM_{10} have been included for PCA with 45 number of samples. Henry *et al.* (1984) suggested that the minimum number of samples (n) for factor analysis should be such that $n > 30 + (V + 3)/2$, where V represents the number of variables. Several researchers have applied PCA study for identification of sources with limited number of elements. Boruvka *et al.* (2005) in Czech Republic performed PCA with only nine variables of toxic elements and identified possible emission sources. In another study by Banerjee (2003) in Delhi, India, an attempt has been made to define the possible origin of six toxic trace metals from street dust using Principal Component Analysis.

3. Results and Discussion

The one year study indicates that the 24 h average mass concentration of PM_{10} at industrial area is 1.4 times than that of residential area. The higher particulate pollution at industrial area may be attributed due to resuspension of road dust, soil dust, automobile traffic and nearby industrial emissions. The daily average PM_{10}

concentration exceeded national ambient air quality standard (NAAQS), as specified by central pollution control board (CPCB), India at both the residential and industrial areas with mean concentration of 140.1 and 196.6 $\mu\text{g}/\text{m}^3$, respectively. The NAAQS for 24 h average PM_{10} concentrations at residential area is 100 $\mu\text{g}/\text{m}^3$, while 150 $\mu\text{g}/\text{m}^3$ at industrial area, as specified by CPCB, India. PM_{10} was clearly higher during the winter season as compared to the other seasons. Winter concentrations of PM_{10} were higher than other seasons, irrespective of the monitoring sites. It indicates a longer residence time of particulates in the atmosphere during winter due to low winds and low mixing height.

Lead concentration decreases from November 2003 to November 2004 probably due to the use of unleaded vehicular fuels. Lead analysis has a special importance because it has a specified NAAQS of 1.0 and 1.5 $\mu\text{g}/\text{m}^3$ at residential and industrial areas, respectively. As a result of the particulate sample analysis, Cd is the metal with lowest concentration varying in the range of 0.95 to 12.0 ng/m^3 at residential site (Kasba) and 1.0 to 19.0 ng/m^3 at industrial site (Cossipore). Zinc is the metal with maximum concentration varying in the range of 112 to 944 ng/m^3 at Kasba and 135 to 1679 ng/m^3 at Cossipore. High Zn values at the monitoring sites may be due to emissions from soil dust, galvanizing and electroplating industries, and garages. Table I shows the average, maximum and minimum values for metals in PM_{10} at both the monitoring sites.

3.1. SEASONAL VARIATIONS

The seasonal variations of the 24 h average concentrations of the measured trace metals are shown in Table II for the study area. The average mass and standard devi-

TABLE I
Statistical analysis of the toxic trace metals of PM_{10} measured during the study period

Site	Parameter	Average \pm SD (ng/m^3)	Max, Min (ng/m^3)
Kasba	Cr	7 \pm 6	30, 1
	Zn	483 \pm 214	944, 112
	Pb	40 \pm 49	235, 7
	Cd	2 \pm 2	12, 1
	Ni	7 \pm 4	20, 2
	Mn	2 \pm 2	9, 1
	Fe	85 \pm 74	315, 21
	Cossipore	Cr	6 \pm 4
Zn		529 \pm 330	1679, 135
Pb		118 \pm 144	462, 3
Cd		5 \pm 3	19, 1
Ni		8 \pm 4	25, 1
Mn		3 \pm 2	6, 1
Fe		122 \pm 85	375, 17

TABLE II

Seasonal average concentrations for toxic trace metals in PM₁₀ at the monitoring sites from November 2003 to November 2004

Parameter	Residential site (Kasba)				Industrial site (Cossipore)			
	Winter	Spring	Summer	Monsoon	Winter	Spring	Summer	Monsoon
Cr (ng/m ³)	8.4	13.7	3.2	4.3	4.4	8.3	7.2	5.7
Zn (ng/m ³)	452.2	309.8	542.2	587.9	407.3	613.8	646.6	451.3
Pb (ng/m ³)	66.9	49.7	18.5	17.3	244.4	134.0	41.5	40.1
Cd (ng/m ³)	4.8	3.5	1.8	1.2	6.5	4.1	2.5	5.2
Ni (ng/m ³)	7.3	9.5	4.5	5.2	6.4	10.4	7.7	8.0
Mn (ng/m ³)	3.8	1.2	1.9	1.7	3.7	2.1	2.1	2.1
Fe (ng/m ³)	116.7	102.6	52.0	62.1	144.9	144.2	89.2	106.5
PM ₁₀ (μg/m ³)	159.4	166.7	135.1	95.5	232.3	291.9	154.3	107.7

ation of the summation of all the studied metals during November 2003 to November 2004 is $0.63 \pm 0.18 \mu\text{g}/\text{m}^3$ and $0.79 \pm 0.19 \mu\text{g}/\text{m}^3$ at Kasba and Cossipore, respectively. In order to study the seasonal variations for PM₁₀ and its chemical constituents, data were sorted into four seasons: winter (October–December), spring (January–March), summer (April–June) and monsoon (July–September). Lead, Cd, Mn and Fe showed higher concentration during winter at both the sites, while Cr has higher concentration during spring season. Chromium is an important solid waste pollutant parameter (Borai *et al.*, 2002). This can be verified with comparatively higher average value of Cr concentration at residential site (Kasba) than industrial site (Cossipore) with ratio 1.16 because Kasba has a municipal solid waste dumping site. Concentration of Cd at Cossipore is approximately 2.5 times than that of Kasba.

At Cossipore, Pb, Cd, Mn, Fe, Ni and Zn concentrations were 2.95, 2.50, 1.50, 1.44, 1.14 and 1.10 times than Kasba. The concentration obtained shows large variations in their data set. The highest average concentration was found in January, may be due to temperature inversion and lowest in June, probably due to washout of the particles. During the rainy season, particulate matter concentration diminished at both the monitoring sites. Nevertheless, the metal diminishes during the rainy season is not very transparent, this suggests that metals are not precipitated and washed by the rain in a big proportion because most of them are in the finer fraction of respirable size and stay in the atmosphere inspite of the pluvial precipitation.

3.2. CORRELATION AMONG TOXIC TRACE METALS AND METEOROLOGICAL PARAMETERS

Total ninety PM₁₀ samples were analyzed for toxic trace metals (Cd, Cr, Ni, Mn, Pb, Zn and Fe). Average PM₁₀ concentration ranged between 68.16 to 280.56 $\mu\text{g}/\text{m}^3$ at Kasba, while 62.40 to 401.21 $\mu\text{g}/\text{m}^3$ at Cossipore.

TABLE III
Correlation coefficients of measured metallic constituents of PM₁₀ and meteorological parameters

Site		Cr	Zn	Pb	Cd	Ni	Mn	Fe	WS ^c	Rain ^d	RH ^e	Temp ^f
Kasba	Cr	1.00										
	Zn	0.02	1.00									
	Pb	0.07	0.23	1.00								
	Cd	0.26	0.05	0.61 ^b	1.00							
	Ni	0.51 ^b	0.36 ^b	0.45 ^b	0.40 ^b	1.00						
	Mn	0.27	0.28	0.66 ^b	0.51 ^b	0.35 ^a	1.00					
	Fe	0.15	0.34 ^b	0.61 ^b	0.48 ^b	0.45 ^b	0.51 ^b	1.00				
	WS	0.26	0.10	-0.40 ^b	-0.25	0.06	-0.08	-0.18	1.00			
	Rain	0.42	-0.12	0.11	0.34	0.37	0.50	0.49	0.07	1.00		
	RH	-0.03	0.12	0.13	0.29 ^a	0.11	0.28	0.09	-0.01	0.23	1.00	
	Temp	0.14	-0.06	-0.62 ^b	-0.36 ^b	-0.19	-0.30	-0.45 ^b	0.62 ^b	-0.27	0.01	1.00
Cossipore	Cr	1.00										
	Zn	-0.34 ^a	1.00									
	Pb	0.73 ^b	-0.53 ^b	1.00								
	Cd	0.53 ^b	-0.38 ^b	0.62 ^b	1.00							
	Ni	0.81 ^b	0.13	0.58 ^b	0.42 ^b	1.00						
	Mn	0.49 ^b	-0.14	0.53 ^b	0.34 ^b	0.52 ^b	1.00					
	Fe	0.64 ^b	-0.13	0.56 ^b	0.25	0.71 ^b	0.63 ^b	1.00				
	WS	-0.46 ^b	0.24	-0.47 ^b	-0.11	-0.36 ^a	-0.33 ^a	-0.40 ^b	1.00			
	Rain	0.41	0.53	-0.17	0.58 ^b	0.23	0.51	0.31	0.05	1.00		
	RH	-0.14	0.24	-0.21	-0.46 ^b	-0.05	0.05	0.09	-0.02	0.19	1.00	
	Temp	-0.75 ^b	0.51 ^b	-0.68 ^b	-0.40 ^b	-0.41 ^b	-0.41 ^b	-0.55 ^b	0.64 ^b	-0.32	0.02	1.00

^aCorrelation is significant at the 0.05 level (2-tailed). ^bCorrelation is significant at the 0.01 level (2-tailed). ^cWind speed. ^dRainfall. ^eRelative humidity. ^fTemperature.

Spearman rank correlation coefficients were obtained between toxic metals measured in PM₁₀ aerosol and meteorological parameters at both the monitoring sites as shown in Table III. The non-parametric Spearman rank correlation is a first insight into the sources of the toxic metals in PM₁₀. Moderate to weak correlation among toxic metals could be the result of the concentrations of different correlation behavior in urban atmosphere, especially in metropolitan city, where various emission sources coexist. Several researcher obtained similar ranges of correlation coefficients in their study of identifying possible emission sources by using PCA method. Thomaidis *et al.* (2003) observed the Spearman rank correlation coefficients values in the range of 0.22–0.69 between toxic metals, and major cations and anions of possible sources in PM_{2.5} in Athens.

Chromium has moderate correlation ($r > 0.50$, $P < 0.01$) with Ni at Kasba, while good correlation ($r > 0.70$, $P < 0.01$) with Pb and Ni at Cossipore. It has inverse relationship with relative humidity at both the sites. As the Cossipore is situated in an industrial area with moderate to heavy traffic flow, a mixture of

vehicular and industrial emissions were possible sources of the particulate matter. All the measured trace metals are either weakly or negatively correlated to meteorological parameters. Lead was moderately correlated ($r > 0.50$, $P < 0.01$) to Cd, Mn and Fe at both the monitoring sites. Human population in urban areas are generally exposed to manganese released into the air by the combustion of fuels in the automobiles, steel production, dry-cell batteries, matches, power plants, coke-oven, etc. Manganese has moderate correlation ($r > 0.50$, $P < 0.01$) with Fe at both the monitored sites.

3.3. FACTOR ANALYSIS AND SOURCE IDENTIFICATION

In the present study, varimax rotated factor analysis has been performed. Total 8 variables and 45 samples (after removing outliers) at each site were considered for factor analysis. Varimax rotated factor analysis was carried out using SPSS software (SPSS, 2003) with PM_{10} and measured toxic trace metals as variables for both the sites. Four factors were selected based on the criteria of cumulative percentage variance $> 80\%$ and eigenvalue > 1.0 . Varimax rotated factor analysis showed four possible factors (based on factor loading > 0.70) representing four different contributing sources for the trace metals at residential (Kasba) and industrial (Cossipore) sites. The total percentage variance explained by these factors was more than 80% at both the sites as shown in Tables IV and V.

The ambient airborne suspended particulates contain major fraction of loose dust particles emitted from road, soil, solid waste dumping site, burning of waste and other sources. The solid waste dumping site near Kasba receive all sort of compostible organic as well as non-compostible inorganic material, i.e., dredged material, incinerator ash, electroplating waste, municipal waste and other industrial

TABLE IV
Rotated factor matrix at residential site (Kasba), $n = 45$

	Factor 1	Factor 2	Factor 3	Factor 4
PM_{10}	0.13	0.98	-0.47	0.26
Cr	0.91	0.01	-0.17	0.28
Zn	-0.05	0.04	0.92	0.04
Pb	0.10	0.82	-0.18	0.25
Cd	0.21	0.06	-0.01	0.92
Ni	0.95	0.11	0.01	0.16
Mn	0.19	0.86	0.20	-0.19
Fe	0.83	0.45	-0.01	-0.07
Eigenvalue	3.29	1.37	1.18	0.86
%Variance	31.69	23.13	14.65	14.40
Cumulative% variance	31.69	54.82	69.47	83.87

TABLE V
Rotated factor matrix at industrial site (Cossipore), $n = 45$

	Factor 1	Factor 2	Factor 3	Factor 4
PM ₁₀	-0.02	0.95	0.15	0.08
Cr	-0.02	-0.09	0.01	0.94
Zn	-0.08	0.01	0.92	-0.23
Pb	0.39	0.81	0.04	-0.33
Cd	0.78	0.01	-0.04	0.28
Ni	0.10	0.21	0.85	0.32
Mn	0.76	0.02	0.01	-0.15
Fe	0.71	0.37	0.04	-0.13
Eigenvalue	2.53	1.66	1.33	0.96
%Variance	23.33	21.78	19.92	16.00
Cumulative% variance	23.33	45.10	65.02	81.03

wastes from Kolkata city and nearby suburban areas. As the monitoring site at Kasba is impacted by the nearby dumping site, efforts were made to separate the contribution of ambient PM₁₀ from solid waste dumping site and loose soil material. Also, chromium is an important solid waste pollutant (Borai *et al.*, 2002). Hence, the factor 1 represented by Cr, Ni and Fe with 32% variance can be attributed to solid waste dumping at residential site (Kasba).

Factor 2 at residential site comprises PM₁₀, Pb and Mn with a variance of 23%. This factor represents vehicular traffic with the influence of road dust. PM₁₀ dominates in diesel soot containing carbonaceous particles and heavy metals. Manganese has been used as an additive in vehicular fuel. The presence of Mn and Pb suggests the influence of vehicular traffic. Manganese has been used as an additive to enhance automobile performance (Pellizari *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). Although direct emissions of Pb from the vehicular exhaust had ceased for more than one year at the time of study because of phasing out of lead from vehicular fuels, Pb is still persistent in road dust from earlier vehicular exhaust emissions because of its longer residence time in the environment. A study performed in Delhi, India by Banerjee (2003) during December 1999 observed 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.

Factor 3 at Kasba has higher loading of Zn with 15% variance. Particulate Zn in ambient air may have its origin from automobile sources, i.e., wear and tear of vulcanized rubber tyres, lubricating oil and corrosion of galvanized vehicular parts (Banerjee, 2003). Significant amount of road dust is present on the road and also on

the road shoulders being deposited from automotive exhaust and kept in suspension by vehicular movement. Hence, this source can be identified as the road dust.

Cadmium at residential site suggests that the origin of this metal was not primarily from localized activity but it has been carried to soil particles by the action of wind from industrial emissions. Factor 4 with higher loading of Cd consisting of 14% variance represents soil dust.

At Cossipore (industrial site), the factor loading in factor 1 comprises Cd, Mn and Fe with 23% variance in the observations of the measured data. This factor has been identified as vehicular traffic with influence of soil dust. Cadmium is being emitted mainly from industrial activities and carried to soil particles by the action of wind. Manganese is used as an additive in vehicular fuel. Iron is emitted as a result of wear and tear of brake pads and other automobile parts.

Factor 2 at industrial site with higher loading of PM₁₀ and Pb represents road dust having variance of 45%. Automobile exhausts, especially diesel fuelled vehicles result in considerable amount of PM₁₀. Particulate Pb in road dust still persists from earlier vehicular emissions because of its longer residence time in the environment.

Factor 3 consists of Zn and Ni with 20% variance in the data set. This factor represents galvanizing and electroplating industry. Zinc is used in galvanization process, while Ni is used in electroplating industries. Monitoring site at Cossipore has nearby clusters of galvanizing and electroplating industries.

Factor 4 having 16% variance is uniquely associated with Cr and is likely to be from Cr plating operation, especially tanning industry. Chromium emissions may occur from chromate reduction, handling of basic chromic sulphate powder and from buffing process. Particulate Cr may be emitted during storage handling, and mixing of the dry chromic sulphate. The buffing operation also releases particulate Cr. Factor four represents tannery. Park and Kim (2005) also observed factor with uniquely associated with Cr having factor loading of 0.975 and variance of 7.1% in PM₁₀ in Seoul, Korea. In absence of more number of variables (trace metals) it is difficult to ascertain the exact sources.

4. Conclusions

Using the experimental data of the present study for various toxic trace metallic species, the extent of metal pollution and the seasonality in their distribution characteristics are determined. Results showed that each metal exhibited their occurrences in diverse concentration ranges of magnitude such that mean values ranging from 0.95 ng/m³ for Cd to 1679.10 ng/m³ for Zn. Moreover to explain the factors regulating their mobilization properties, the data were analyzed through the application of correlation analysis. Results of the correlation analysis showed that most of the metals exhibit moderate to weak relationship with each other. These metals tend to be inversely correlated with the meteorological parameters such as wind speed, relative humidity and temperature. Seasonal distribution patterns indicate that most

of the metals tend to exhibit maximum during winter season, probably due to the temperature inversion. The variation of toxic trace metallic concentration shows diminution of the particle concentrations during rainy seasons. This behavior is not so marked for the metals, may be due to the reason that they are not washed by the rains, although the lowest values are found during July to August. A multivariate receptor model of factor analysis was applied to PM₁₀ data measured from November 2003 to November 2004 at two sampling sites in Kolkata. Four components were extracted by factor analysis at residential site (Kasba), including solid waste dumping, vehicular traffic with influence of road dust, road dust and soil dust. Four sources were identified at industrial site (Cossipore), comprising vehicular traffic with influence of soil dust, road dust, galvanizing and electroplating industry, and tanning industry. Based on the overall study, it can be concluded that the monitoring sites may have strong impact by anthropogenic sources.

References

- APHA: 1977, *Methods of Air Sampling and Analyses*, 2nd Edition, APHA Publication, Washington, DC.
- Banerjee, A. D. K.: 2003, Heavy metals and solid phase speciation in street dusts of Delhi, India', *Environmental Pollution* **123**, 95–105.
- Borai, E. H., El-Sofany, E. A. and Abdel-Halim, A. S.: 2002, 'Speciation of hexavalent chromium in atmospheric particulate samples by selective extraction and ion chromatographic determination', *Trends in Analytical Chemistry* **21**, 741–745.
- Bem, H., Gallorini, M., Rizzio, E. and Krzeminska, M.: 2003, 'Comparative studies on the concentrations of some elements in the urban air particulate matter in Lodz City of Poland and in Milan, Italy', *Environment International* **29**, 423–428.
- Boruvka, L., Vacek, O. and Jehlicka, J.: 2005, 'Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils', *Geoderma* **128**, 289–300.
- Brits, E., Schoeters, G. and Verschaeve, L.: 2004, 'Genotoxicity of PM₁₀ and extracted organics collected in an industrial, urban and rural area in Flanders, Belgium', *Environmental Research* **96**, 109–118.
- Bruno, P., Caselli, M., Gennaro, G. and 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. and Inzunza, J. C.: 2004, 'A study of the particulate matter PM₁₀ composition in the atmosphere of Chillan, Chile', *Chemosphere* **54**, 541–550.
- Chio, C. P., Cheng, M. T. and 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.
- Chow, J. C. and Watson, J. G.: 2002, 'Review of PM_{2.5} and PM₁₀ apportionment for fossil fuel combustion and other sources by the chemical mass balance model', *Energy and Fuels* **16**, 222–260.
- Dockery, D. W. and Pope, C. A.: 1994, 'Acute respiratory effects of particulate air pollution', *Annual Review Public Health* **15**, 107–132.
- Ghose, M. K., Paul, R. and Bannerjee, 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.

- Guo, H., Wang, T. and 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.
- Hemminki, E., Horvath, M. and Schuler, D.: 1995, 'Impact of iron fortification of milk formulas on infants growth and health', *Nutrition Research* **15**, 491–503.
- Henry, R. C., Lewis, C. W., Hopke, P. K. and Williamson, H. J.: 1984, 'Review of receptor model fundamentals', *Atmospheric Environment* **18**, 1507–1515.
- Kleinbaum, D. G. and Kupper, L. L.: 1978, *Applied Regression Analysis and Other Multivariable Methods*, North Scituate, Massachusetts, Duxbury press, North Scituate, Massachusetts.
- Kumar, A. V., Patil, R. S. and Nambi, K. S. V.: 2001, 'Source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India', *Atmospheric Environment* **35**, 4245–4251.
- Marcazzan, G. M., Ceriani, M., Valli, G. and Vecchi, R.: 2003, 'Source apportionment of PM10 and PM2.5 in Milan (Italy) using receptor modelling', *Science of Total Environment* **317**, 137–147.
- Mesa, L. M., Mendez, E. P., Sanchez, M. S. and Montelongo, F. G.: 1999, 'Interpretation of heavy metal data from Mussel by use of multivariate classification techniques', *Chemosphere* **38**, 1103–1111.
- Mugica, V., Maubert, M., Torres, M., Munoz, J. and Rico, E.: 2002, 'Temporal and spatial variations of metal content in TSP and PM₁₀ in Mexico City during 1996–1998', *Journal of Aerosol Science* **33**, 91–102.
- Park, S. S. and 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. and Lynam, D.: 1999, 'Particulate matter and manganese exposures in Toronto, Canada', *Atmospheric Environment* **33**, 721–734.
- SPSS: 2003, *Advanced Statistics Manual*, SPSS/PC+V 3.0. SPSS Inc., 444 North Michigan Avenue, Chicago, IL 60611.
- Thomaidis, N. S., Bakeas, E. B. and Siskos, P. A.: 2003, 'Characterization of lead, cadmium, arsenic and nickel in PM_{2.5} particles in the Athens atmosphere, Greece', *Chemosphere* **52**, 959–966.
- Thurston, G. D. and Spengler, J. D.: 1985, '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*. Oxford, UK, Blackwell.
- Wang, C. X., Zhu, W., Peng, A. and Guichreit, R.: 2001, 'Comparative studies on the concentration of rare earth elements and heavy metals in the atmospheric particulate matter in Beijing, China, and in Delft, the Netherlands', *Environment International* **26**, 309–313.
- WHO: 1981, *International Programme on Chemical Safety, Environmental Health Criteria 17*, World Health Organization, Geneva.
- Yang, C.-Y., Chang, C.-C., Chuang, H.-Y., Tsai, S.-S., Wu, T.-N. and Ho, C.-K.: 2004, 'Relationship between air pollution and daily mortality in a subtropical city: Taipei, Taiwan', *Environment International* **30**, 519–523.
- Zhao, W. and Hopke, P. K.: 2004, 'Source apportionment for ambient particles in the San Geronio wilderness', *Atmospheric Environment* **38**, 5901–5910.