



Atmospheric Mineral Dust and Trace Metals over Urban Environment in Western India during Winter

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ABSTRACT

Trace metal concentrations in PM_{2.5} and PM₁₀ are studied from Ahmedabad, an urban location in western India. During winter, concentrations of Zn, Cd and Pb are in the range of 16.5–290, 0.1–5.4, 28–1023 ng/m³ in PM_{2.5} and 38–459, 0.21–8.4, 48–1223 ng/m³ in PM₁₀, respectively. Enrichment Factor (EF) analysis with respect to Al showed significant enrichment of elements like Cd, Pb, Zn and Cu in fine mode particles, suggesting their strong anthropogenic contribution. About 43% of PM₁₀ mass is constituted by mineral dust, and the dominant fraction (~88%) of the same exists in coarse fraction with a characteristic Fe/Al ratio of 0.53. The Ca/Al ratio is ~1.1 in PM₁₀ and ~0.8 in PM_{2.5} indicating that aerosol over this region is rich in Ca minerals compared to the average upper continental crust. Positive Matrix Factorization (PMF) analysis using trace metal and major components reveals five sources for PM_{2.5} and six for PM₁₀. The PMF results suggest anthropogenic sources contribute ~80% and 40–50% of the PM_{2.5} and PM₁₀ mass, respectively. Incineration/industrial emission, biomass burning, vehicular emissions and re-suspended/long range transported dust are the other prominent sources identified in this work. These source contributions exhibit large temporal variations during winter, as the sampling location is influenced by air masses from different source regions.

Keywords: Trace elements; Mineral dust; PM₁₀; PM_{2.5}; Positive Matrix Factorization.

INTRODUCTION

Atmospheric aerosols have significant influence on human health, ecosystem biogeochemical cycles and climate. As a result of increasing population and growing urbanization, regional air pollution problems like reduced visibility and acid deposition are apparent in the South Asian region which is of interest both in regulatory as well as scientific perspectives. This region is considered as one of the significant source regions of anthropogenic emissions in the world. In addition, this region has substantial natural aerosol sources like mineral dust from deserts and arid regions and sea-salts from marine environment. Several studies have revealed that aerosols, especially fine mode particles, can lead to serious human health effects like cardiovascular and respiratory disorders (Dockery and Pope, 1994). Also, absorbing or scattering nature of aerosols, depending on their composition, makes it a potential agent to modulate the energy balance of Earth atmosphere system. Thus, it is necessary to understand the different sources of aerosols, formation processes and concentration levels of toxic

pollutants in order to assess their environmental impact and implement effective control strategies.

Ambient aerosols consists of mineral dust, metals, sea salts as well as organic (EC and OC) and inorganic pollutants. Relative abundance of these components is highly variable both temporally and spatially. During winter, inhalation of trace-metal bearing particles is of particular health concern due to the toxicity of heavy metals and their potential to cause oxidative stress through generation of free radicals (Davidson *et al.*, 2005; Duzgoren-Aydin, 2008). Recent studies in urban atmosphere showed that concentrations of PM_{2.5} and PM₁₀ (atmospheric particles with aerodynamic diameter less than 2.5 and 10 μm, respectively) exhibit direct relation with traffic-related pollutants (both diesel and gasoline vehicles) and their health effect through respiratory and cardiac diseases (Lee *et al.*, 2006). Under favourable meteorological conditions, these metal-bearing particles can be transported along with other constituents to distant locations from source regions, including remote marine environment. It is well documented that atmospheric depositions of trace metals (viz., Cd, Pb, Cu and Zn) to open oceans could exceed those of riverine fluxes (Kokack *et al.*, 2005) and thus assessment of their probable sources and concentrations in polluted source regions are essential. Several studies have documented aerosol concentrations and major chemical constituents in this important source region in south-east Asia, however, comprehensive studies

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including trace element distribution in different size fractions are limited from Indian region (Kulshrestha *et al.*, 2009). Recent studies from India addressing the problem of pollution by heavy metals were based on short-term studies of total suspended particulates (TSP) (Tripathi *et al.*, 2004; Srivastava *et al.*, 2009; Sridhar *et al.*, 2010) and on trace metal composition of PM₁₀ (Karar and Gupta, 2006; Nair *et al.*, 2006; Kulshrestha *et al.*, 2009).

In this paper we report selected trace metal concentrations along with major crustal elements in PM₁₀ and PM_{2.5} samples collected during winter from Ahmedabad, an urban location in a semi-arid region in western India, in order to delineate their relative abundances in fine and coarse particles and evaluate the different source contributions in relation to the prevailing meteorological conditions. The approach relies on analysis of aerosol mass and trace metal composition to highlight the contribution of long-range transport of polluted air masses with possible changes in trace metal emission sources and local influences. To this purpose, the temporal variation of the distribution between the coarse and fine fractions was studied; in addition, enrichment factors were calculated based upon abundances of these elements of the Earth's crust in relation to Al. In order to better understand the causes of particulate levels and associated trace metals, the comprehensive aerosol data collected from Ahmedabad were investigated by applying positive matrix factorization (PMF).

MATERIALS AND METHOD

Site Description

Ahmedabad (23°02'N, 72°32'E) is one of the largest urban areas in western India with a population of more than 6 million. The location of sampling site is surrounded by large number of residential areas and shopping complexes as depicted in the Fig. 1 and has both small scale and large

scale industrial establishments in the eastern region within an arial distance of ~100 km. There are two thermal power plants in north and northeast directions of the sampling site within ~40 km distance. The Thar Desert is on northwest side and the Arabian Sea is on southwest side of Ahmedabad within ~200 km radius. Potential local pollutants are limited to emission from traffic, coal-based power plants and industrial areas. Generally during winter, surface wind direction over Ahmedabad is north easterly or northwesterly and the sampled air masses predominantly are of continental origin. During the sampling period, the prevailing winds were moderate northeasterly and wind speed ranged from 2 to 5.5 m/s. Ambient temperature was between 16 to 28°C and relative humidity varied from 30 to 60%.

Sampling and Analytical Procedures

Simultaneous sampling of PM_{2.5} and PM₁₀ was done at Ahmedabad using mass-flow controlled high volume samplers (Tisch, USA) from 8 December 2006 to 6 January 2007 on quartz filters (8" × 10" size, Tissuquartz, Pall Life Sciences), details of which are described elsewhere (Rengarajan *et al.*, 2011a, b). Meteorological parameters (temperature, pressure, relative humidity, wind velocity and direction) were obtained from India Meteorological Department.

Three circular sub-samples of the quartz filters (1 cm diameter) were placed in a Teflon pressure vessel with a mixture of 1.5 mL 8N teflon-distilled HNO₃ and 0.5 mL 16N teflon-distilled HF. The samples were heated with a microwave oven to 180°C in 9 min. followed by 10 min. hold at that temperature and 60 min. of ventilation/cooling. After cooling, digests were diluted to 22 mL with MilliQ water. The solution was stored in acid-cleaned polypropylene bottles (25 mL) until analysis. Cd and Pb were analyzed with Graphite Furnace AAS (Perkin Elmer AA 100) and Fe, Al, Ca, Mg, Ba, Sr, Cr, Cu, Mo, Zn, Ni, Co and Mn

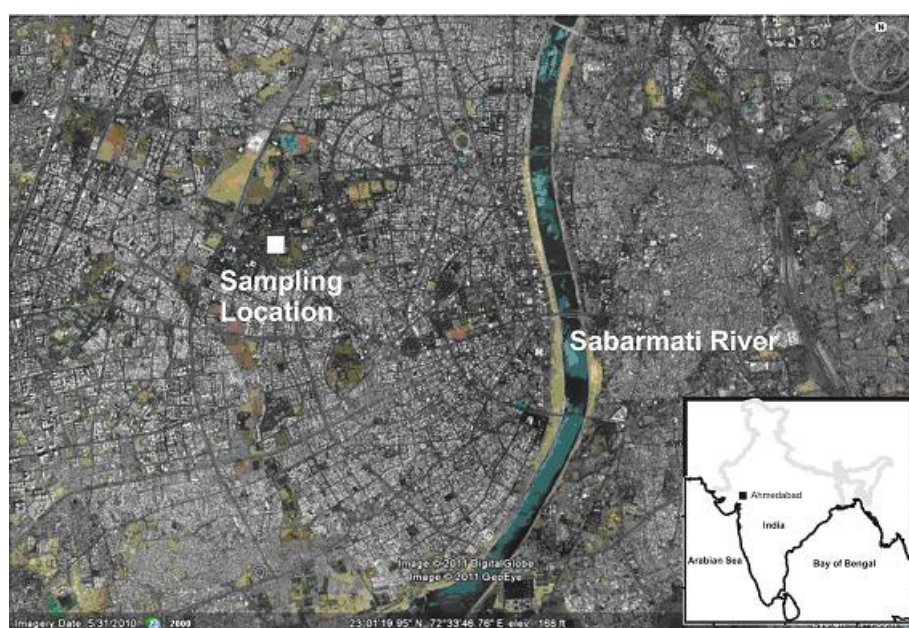


Fig. 1. Map showing the location of sampling site at Ahmedabad.

were measured using ICPMS (Thermo-X series). Elemental standards (Merck®) were diluted with 1N HNO₃ and used for calibration. The measurements were done with a precision of better than ±5%. The analytical procedures (mineralization + analysis) were regularly checked using Certified Reference Materials (W-1 and G-2 rock standards). The water-soluble ionic constituents (Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻) and carbonaceous species (Water soluble organic carbon (WSOC), elemental carbon (EC) and organic carbon (OC)) were measured in these samples using Ion Chromatograph (Dionex®), TOC analyzer (Shimadzu®) and EC/OC analyzer (Sunset®) as described in the earlier publications (Rengarajan *et al.*, 2011a, b).

RESULTS AND DISCUSSION

Particulate Matter Mass Concentrations

Time-series plot of particulate matter concentrations for both PM_{2.5} and PM₁₀ is presented in Fig. 2. Daily variations of mass concentration in relation to different chemical constituents like water-soluble and carbonaceous species during December 2006 are discussed in detail elsewhere (Rengarajan *et al.*, 2011a, b). The average values of PM₁₀ and PM_{2.5} are 171 and 56 µg/m³ respectively. Tiwari *et al.*, 2009 reported annual average of PM₁₀ and PM_{2.5} concentrations in Delhi, are 219 and 97 µg/m³ respectively. The average mass exceeded ~2 times (annual average: 60 µg/m³) and 1.3 times (annual average: 40 µg/m³) for PM₁₀ and PM_{2.5} respectively, of National Ambient Air Quality Standard (NAAQS) as specified by Central Pollution Control Board, India. These values are ~7 times higher for PM₁₀ and ~5 times higher for PM_{2.5} in comparison with World Health Organization (WHO) air quality guidelines (20 µg/m³ and 10 µg/m³, annual average for PM₁₀ and PM_{2.5} respectively; WHO, 2005).

Trace Metals Concentration

Table 1 provides statistical summary of trace metal

concentrations observed in PM_{2.5} and PM₁₀ during observation along with reported data for urban and industrial regions. The average abundances of measured metal contents in PM_{2.5} and PM₁₀ are in the following decreasing order: Al > Ca > Mg, Fe > Pb > Zn > Mn > Ba > Cu > Cr > Sr > Ni > Cd > Co and Ca > Al > Fe > Mg > Pb > Zn > Mn > Ba > Sr > Cu > Cr > Ni > Cd, Co respectively. Among these metals, average concentrations of Cd, Pb, and Zn are 2.8, 228 and 159 ng/m³ respectively in PM₁₀ samples and their daily variations are depicted in Fig. 3. Trace metal distribution among fine and coarse mode is assessed based on ratios of their concentrations in PM_{2.5} versus PM₁₀ which indicate the dominance of fine mode contribution for Cd, Pb and Zn. Sources of these trace metals can be primarily anthropogenic, associated with combustion emissions, causing their enrichment in fine particles. Concentrations of these metal species exhibit large variability during the sampling period (Fig. 3) indicating significant day to day variations in source strength of these pollutants. Studies on atmospheric input of trace metals to the northeast Atlantic Ocean revealed Zn and Pb are mobilized to the atmosphere generally through anthropogenic activities (Spokes *et al.*, 2001). Lee *et al.* (2007) reported annual average concentrations of Cd, Pb and Zn in an urban location in China as 1.6, 57 and 298 ng/m³ respectively on analysis of TSP samples. Kumar *et al.* (2001) reported 150, 370, 160 and 1060 ng/m³ for Cr, Cu, Ni and Pb respectively in PM₁₀ samples from two traffic junctions in Mumbai. At Kanpur, Sharma and Maloo (2005) reported concentrations in the range of 70–1030, 200–1630, 40–270, 2–43 and 32–400 ng/m³ for Pb, Zn, Ni, Cd and Cr in PM₁₀ samples. For Ba, Ni and Mn, ~25% contribution is from fine mode particles (Table 1), demonstrating dominance of coarse particle sources for these metals. Sr is found only ~8% present in fine particles. Coarse particles are generally produced by natural mechanical processes like wind-blown dust and sea-salts whereas it is reported by Rengarajan *et al.* (2011) that sea-salt content is less than 1% at this

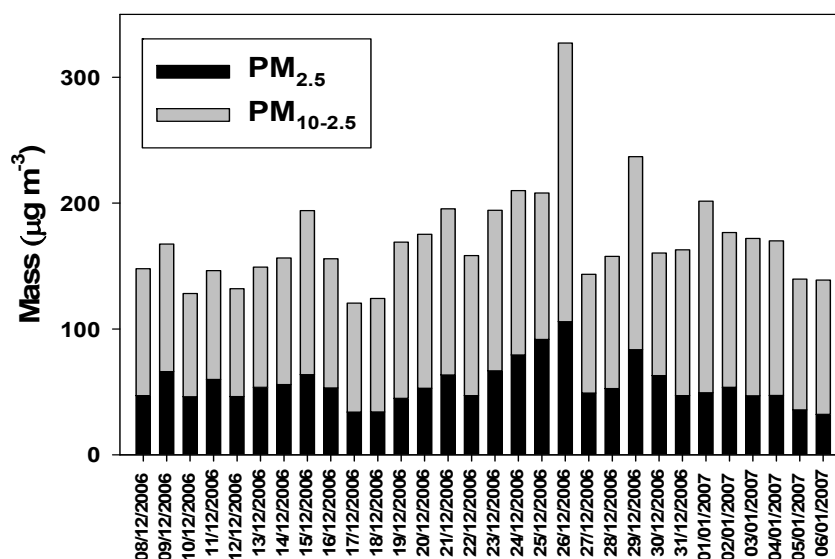
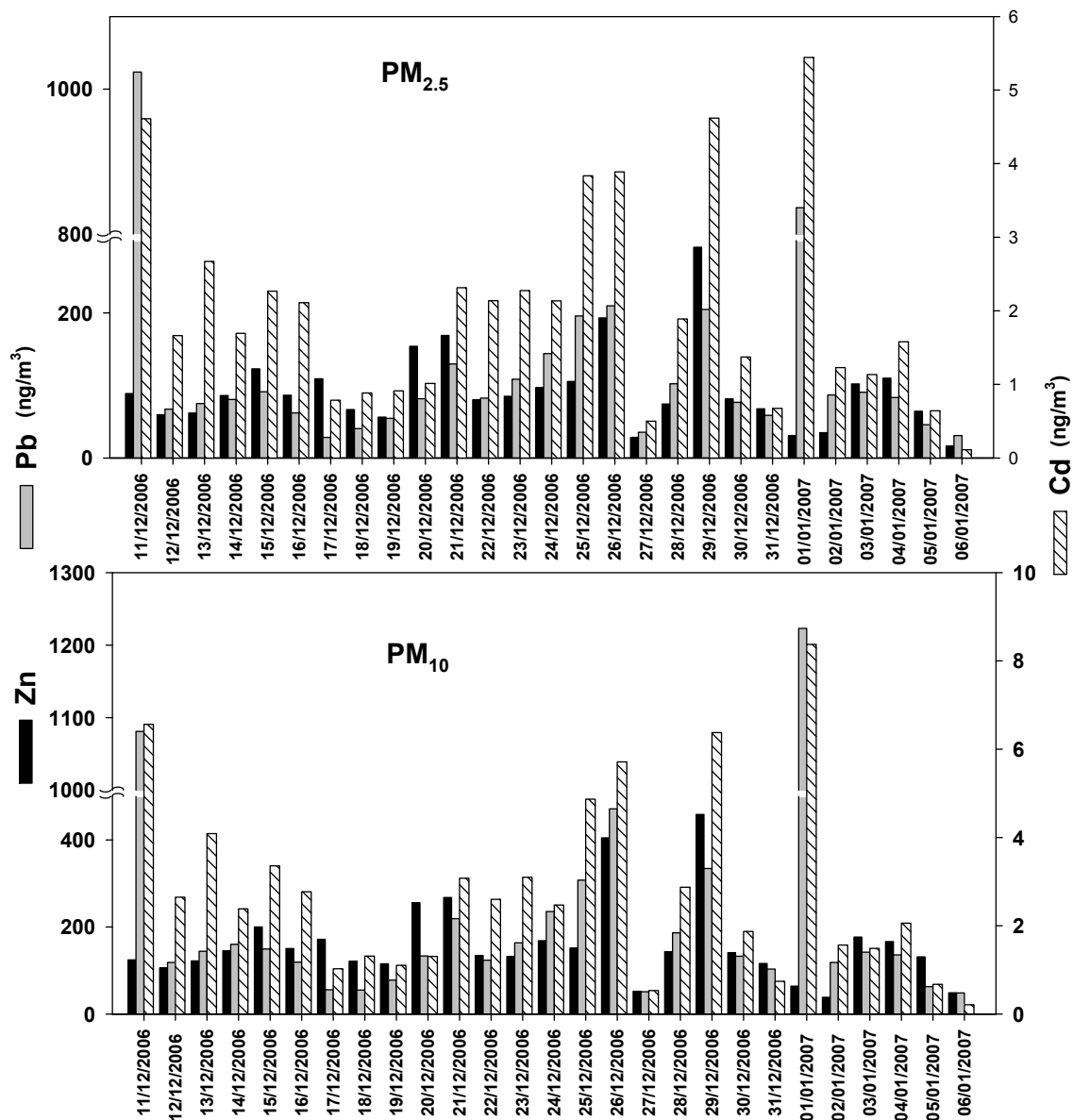


Fig. 2. Time series plot of mass concentrations of PM_{10-2.5} and PM_{2.5} at Ahmedabad during December 2006.

Table 1. Mean and range of trace element concentrations observed at Ahmedabad December 2006 to January 2007 and comparison with reported data from urban locations. Concentrations are expressed in ng/m^3 .

	PM _{2.5}			PM ₁₀			PM _{2.5} / PM ₁₀	Oxford, UK (TSP) ^a	Ispra, Italy (PM ₁₀) ^b	Hong Kong (TSP) ^c	Tirupati (PM ₁₀) ^d
	Mean	Geo Mean	Range	Mean	Geo Mean	Range					
Al	668	689	424–1159	5916	5802	3594–8774	0.12	229	-	-	-
Ba	16.4	14	3.8–38.3	67	63.8	41.4–116	0.22	-	19.9	-	-
Sr	3.4	3.1	1.2–8.4	39	37.9	24.6–66.4	0.08	25.4	-	-	-
Zn	93	79.2	16.5–290	159	137	38–459	0.58	30	149	298	-
Cu	12.4	10.5	2.3–32.8	28	25.2	11.3–63.1	0.42	39.5	10.5	70.8	25
Ni	2.9	2.5	< 1–7.2	9.7	9	4.4–21.0	0.28	67.3	10.2	-	32
Mn	36	26	5.5–226	119	120	69–550	0.22	3.5	14	-	38
Cd	2	1.6	0.1–5.4	2.8	2.1	0.21–8.4	0.76	1.06	0.51	1.6	3.4
Pb	153	94	28–1023	228	153	48–1223	0.61	186	98	56.5	20
Cr	11	5	< 1–38.4	11	9	< 1–88	0.56	1.2	6.5	15.3	8.6
Fe	283	302	70–539	398	3908	2634–6046	0.08	122	551	-	269

^aWitt *et al.*, 2010; ^bRizzio *et al.*, 1999; ^cLee *et al.*, 2007; ^dChandra Mouly *et al.*, 2006.

**Fig. 3.** Time series plot of trace elements Cd, Pb, and Zn in PM_{2.5} and PM₁₀ at the sampling site.

location during the sampling period. Hence these elements are likely to be associated with mineral dust. Spokes *et al.* (2001b) reported occurrence of Mn in both fine and coarse mode particulates and attributed soil erosion source for coarse mode and high temperature combustion for fuel or smelting for fine mode Mn. Al concentration can be taken as a representative index for mineral dust component assuming its anthropogenic sources are insignificant. A linear regression analysis of Sr, Ba, Ni and Mn with Al exhibits significant correlation for Sr, Ba, and Ni ($p < 0.05$) in PM_{10} although for Mn, the relation is statistically insignificant and it may have additional sources. EC represents anthropogenic combustion emissions which show a significant linear trend with Mn and its atmospheric abundances may be controlled by combustion sources. The average concentrations of Ba, Sr, Ni and Mn in PM_{10} are 67, 39, 10 and 119 ng/m^3 , respectively where as those in $PM_{2.5}$ are 16, 3.4, 3.0 and 36 ng/m^3 respectively. The linear regression analysis of Pb, Cd, Mn, Ni and Zn with EC in $PM_{2.5}$ suggests these elements can have significant anthropogenic combustion sources.

Average Cu concentration in $PM_{2.5}$ is 12 ng/m^3 and exhibits a linear trend with Fe but not with Al, suggesting both Fe and Cu may have significant non-crustal sources. Co and Cr concentrations in $PM_{2.5}$ are below detection limits ($< 1 ng/m^3$) in most of the days of sample collection and measurable levels were found in PM_{10} samples for a few days. The atmospheric abundances of these metals are significantly higher compared to the reported values from other urban/industrial locations (Table 1). For instance, Cr and Co concentrations reported from Oxford in UK are 1.2 and 0.22 ng/m^3 respectively for TSP samples (Witt *et al.*, 2010) whereas the corresponding concentrations in PM_{10} at Ahmedabad are 15 and 3 ng/m^3 respectively. Sternbeck *et al.* (2002) demonstrated that road traffic emissions are major contributor to total suspended particulate mass at Gothenberg, Sweden, and Cu is significantly correlated with Pb, Ba and Cr. The correlations coefficients for Pb and Ba with Cu in Ahmedabad are 0.76 and 0.764 ($p < 0.001$) respectively, indicating a noticeable impact of road

traffic sources of aerosol on these metals. But Cu does not show a significant trend with Cr indicating there could be a different source. In India, use of Pb in gasoline has been discontinued from the year 2000 onwards. Tripathi *et al.* (2004) reported Pb concentration of 101 ng/m^3 at a relatively clean residential location at Mumbai (a coastal metropolitan city) in western India. According to National Ambient Air Quality Standards (NAAQS, Government of India), the permissible limit of Pb and Ni concentrations (annual) for residential areas are 500 ng/m^3 , and 20 ng/m^3 respectively (CPCB, 2009). The average concentrations of Pb and Ni in this study are well below these upper limits.

Mineral Dust

Based on Al concentrations, mineral dust content in the aerosol samples is calculated (considering 8% Al of average upper continental crust value; McLennan, S., 2001) as: mineral dust ($\mu g/m^3$) = Al ($\mu g/m^3$) \times 100/8. This constitute ~16% of $PM_{2.5}$ and ~43% of PM_{10} mass suggesting dominant fraction of mineral dust exists as coarse particles. Average Al concentrations were 0.7 and 6 $\mu g/m^3$ in $PM_{2.5}$ and PM_{10} , respectively (Table 1). Mineral dust concentration estimated from Al abundances are depicted in Fig. 4. The dust concentration varied from 44 to 109 $\mu g/m^3$ in PM_{10} where as its range in $PM_{2.5}$ is 1.2–14.4 $\mu g/m^3$. Fe concentration in $PM_{2.5}$ samples ranged from 70 to 540 ng/m^3 and the corresponding range for PM_{10} is between 2630 and 6050 ng/m^3 . Fe and Al are significantly correlated (Fig. 5(a)) in PM_{10} with a slope of 0.53 comparable to Fe/Al crustal ratio of 0.44, indicating the dominant source of Fe as mineral dust. The Fe/Al ratio in north Indian plains ranged from 0.55 to 0.63 (Sarin *et al.*, 1979). Kumar and Sarin (2009) reported Fe/Al ratio of 0.59 for coarse mode particles ($PM_{2.5-10}$) in a remote high altitude location in Western India. Hence it can be inferred that the characteristic Fe/Al ratio for mineral aerosol of Northern/Western Indian origin is between 0.5 and 0.6. On the contrary, there was no significant relation between Fe and Al in $PM_{2.5}$ (Fig. 5(b)). The large scatter can be attributed to major sources of Fe

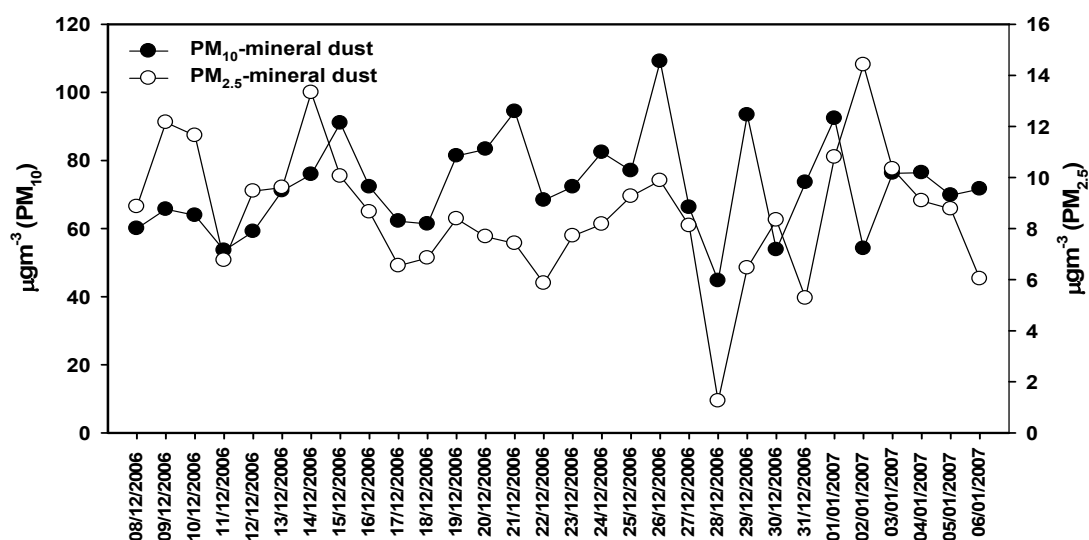


Fig. 4. Time series plot of mineral dust concentration at the sampling site.

other than mineral dust that can be of anthropogenic. In this case, the average Fe/Al ratio will be higher than typical crustal value (0.44), although the average Fe/Al ratio in PM_{2.5} samples of Ahmedabad (0.43 ± 0.15) is not different. Ca and Mg exhibit a significant linear trend with Al in PM₁₀ samples whereas large scatter is observed for PM_{2.5} samples. The average Ca/Al ratio in PM₁₀ is 1.15 and that of PM_{2.5} is 0.82; whereas the corresponding ratio in upper continental crust is 0.38 (McLennan, 2001). This suggests that mineral dust present in the ambient atmosphere is considerably rich in Ca compared to average crustal abundance. Kumar and Sarin (2009) reported Ca/Al ratio of 0.73 in fine mode aerosol, and 1.74 in coarse mode from a high altitude, remote location in western India during winter. The Thar and the Oman Deserts are potential sources of mineral aerosol containing minerals enriched with carbonates which can be transported towards this semi-arid region at different seasons. During winter, direction of surface wind is favorable to transport mineral dust from the Thar Desert towards the sampling location. Hegde *et al.* (2007) reported transport of atmospherically processed dust from Oman region under favorable meteorological conditions towards the western coastal region of India. Such long-range transport of mineral aerosols rich in carbonates has implication on the capability of dust to neutralize acidic species present in atmosphere thereby reducing acidity of

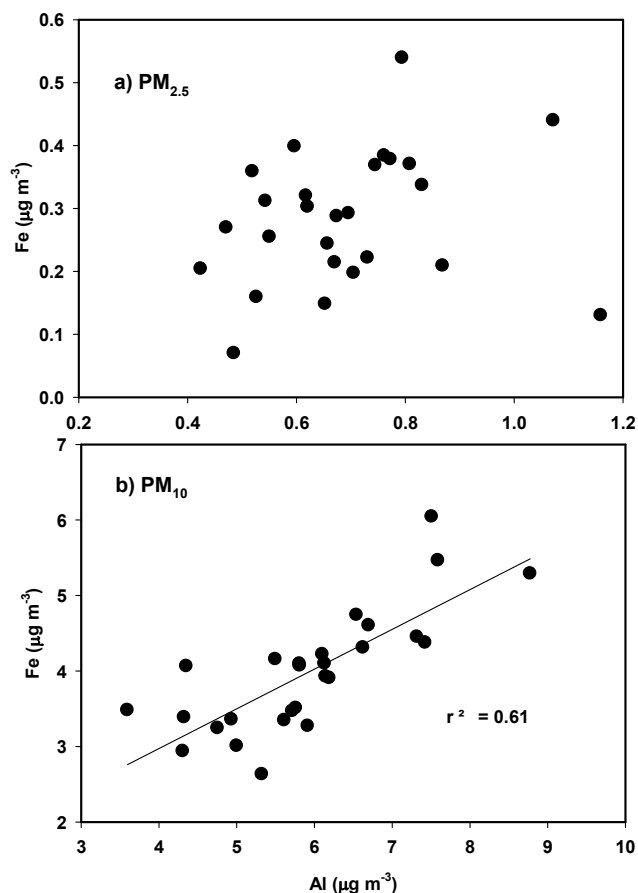


Fig. 5. Scatter plot of Fe vs. Al concentration in PM_{2.5} and PM₁₀.

wet deposition. Rastogi and Sarin (2005) reported that rain water at Ahmedabad is generally alkaline, based on chemical composition studies of wet deposition.

Enrichment Factors

In order to delineate the origin (anthropogenic or crustal) of trace metal abundances in atmospheric aerosols, average enrichment factors (EF) have been estimated in PM₁₀ and PM_{2.5} at the monitoring site. EF is the ratio of concentration ratios of element in the aerosol samples normalized to crustal concentrations. Al is commonly used as crustal source indicator and EF_x is calculated by using the equation:

$$EF_x = (C_{xs}/C_{Als})/(C_{xc}/C_{Alc}) \quad (1)$$

where C_{xs} and C_{Als} are concentrations of the element x and Al in samples and C_{xc} and C_{Alc} are that in the average crust (Taylor and McLennan, 1995). This calculation assumes that contribution of anthropogenic Al is insignificant at this sampling region. If the EF approaches 1, crustal sources are predominant and generally a value > 5 indicates large fraction can be attributed to non-crustal or anthropogenic sources (Wu *et al.*, 2007). Fig. 6 represents the enrichment factors for each element over Ahmedabad for PM_{2.5} and PM₁₀. Cd, Pb and Zn exhibit EF almost one order of magnitude higher in PM_{2.5} compared to that in PM₁₀ indicating dominant anthropogenic origin of these elements in fine mode, consistent with the information derived from distribution of these elements in fine and coarse mode particles. Lee and Hieu (2007) reported EF for these elements 9940, 276 and 174 in PM_{2.5} during spring time at a residential region in Korea and the corresponding EF for PM₁₀ are 3366, 263 and 199. Vasconcellos *et al.* (2007) reported enrichment factors for Pb, Zn and Cd of 174, 34 and 26042 in PM₁₀ samples from Sao Paulo, Brazil. EF for Mn and Cr in PM_{2.5} are 5 and 17 and that for PM₁₀ are 1.7 and 2.5 respectively at Ahmedabad indicating negligible contribution to coarse mode particulates from anthropogenic sources and moderate anthropogenic source for Cr in fine mode. Kothai *et al.* (2011) reported insignificant enrichment for Mn in coarse mode and EF of ~ 100 for fine mode at a residential area in Mumbai. The corresponding values for

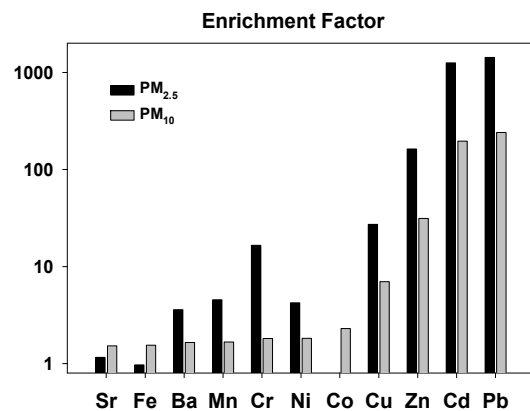


Fig. 6. Enrichment factors using the metal concentrations during winter at Ahmedabad.

Cr at Ahmedabad are < 10 and slightly > 10 , respectively. For Mn, Ba, Fe, Ni, Co and Sr, EF is not significant both in PM_{10} and $PM_{2.5}$ (< 5), hence anthropogenic sources for these metals are negligible. Thus, based on EF and elemental characteristics, source identification of particulate matter and different constituents cannot be achieved quantitatively with a reasonable accuracy.

Source Identification Using PMF Analysis

PMF is a bilinear multivariate receptor model that can identify sources of particulate matter and provide source contributions which is widely used in source apportionment studies of atmospheric aerosol in the absence of prior information on source profiles (Paatero, 1997; Polissar *et al.*, 2001; Lee *et al.*, 2003; Jeong *et al.*, 2008; Karanasiou *et al.*, 2009). EPA PMF 3.0.2.2 version was used in this study, detail of which is given by Kim *et al.* (2003) and Norris *et al.* (2008). PMF analysis yielded five factors for $PM_{2.5}$ and six factors for PM_{10} and the relative contributions of measured parameters for each factor are depicted in Figs. 8(a) and (b) respectively. The modeled and measured mass concentrations are in good agreement ($r = 0.974$, slope = 0.97 for $PM_{2.5}$ and $r = 0.988$, slope = 0.96, for PM_{10} ; Figs. 7(a) and (b)). Temporal variation of each factor is depicted in Figs. 9(a) and (b). HCO_3^- , Cl^- and NO_3^- data were removed from $PM_{2.5}$ analysis since there were many

samples whose concentrations were below detection limits. Two data points from Pb and one from Mn were replaced with the species median and assigned error of 4 times of measurement uncertainty (Chan *et al.*, 2011) because they were unrealistically high compared to other values (beyond $5 \times$ standard deviation from average concentration). Number of factors from 3 to 7 was examined on the basis of linearity of fit as indicated by the residual distributions as well as interpretability of the resulting profiles.

The factor 1 for $PM_{2.5}$ is characterized by 53% loading from Zn, 47% from Ni and 42% from Na^+ . This factor is not associated with mineral dust indicators like Al and Ca as their loading are 5.2 and $< 1\%$ respectively, and hence can be considered as industrial or/and incineration emissions. On an average, this factor contributes 11% to total measured $PM_{2.5}$ mass. The factor 2 represents mineral dust as Al, Mg-total, Ca-total, soluble Mg and soluble Ca loadings are 39, 24, 35, 44 and 58% respectively, which are indicators for mineral aerosol or soil dust. On an average, this factor contributes 10% to the $PM_{2.5}$ mass where as estimate based on simple assumption of Al as indicator for mineral dust yielded 16% as discussed in the previous section. This discrepancy may be due to additional sources of Al other than natural origin. Factor 3 is characteristically loaded with Cd and Pb (71 and 46%) and a moderate contribution from Fe, Mn, Cu and Zn (34, 39, 33 and 30%, respectively). Association of Pb and Cd as well as carbonaceous aerosols and SO_4^{2-} with this factor may be due to the coal-based power stations (Lindberg and Harriss, 1980) and industrial/vehicular emissions. This factor contributes an average mass of 31% of $PM_{2.5}$. Factor 4 is having loading from Ba and Sr (53 and 68%) and also associated with Ni (45%) and crustal elements. This may be associated with re-suspended dust along with contributions from emissions from automobiles and break-linings. EFs of these elements suggest that they are not having significant contribution from anthropogenic sources. The temporal trend suggests that during initial days of sampling the mass loading from this factor is significantly higher than after 21 December. The back-trajectory analysis has shown that from 6–21 December, air mass arrived at sampling site originated and transported from northern region and afterwards, it was from eastern region passing through central part of India (Rengarajan *et al.*, 2011b). This difference is reflected in the temporal variation of contribution of factor 4. This factor is likely to be associated with long-range transported dust. All carbonaceous species show maximum loading in factor 5 along with K^+ indicating that this represents biomass burning sources. This source contributes $\sim 33\%$ of total mass to $PM_{2.5}$. The temporal variation of this factor exhibits an opposite trend compared to that of factor 4 (Fig. 9(a)). Particulate mass from biomass burning factor increased considerably when air mass from eastern regions of Ahmedabad reached the sampling site during the latter period of observation.

Factor 1 for PM_{10} is characterized by Na (47%) and Cl (76%), with insignificant contribution from other constituents. From the Na concentration it was estimated that sea-salt contribution is very small ($< 1\%$) as discussed in previous

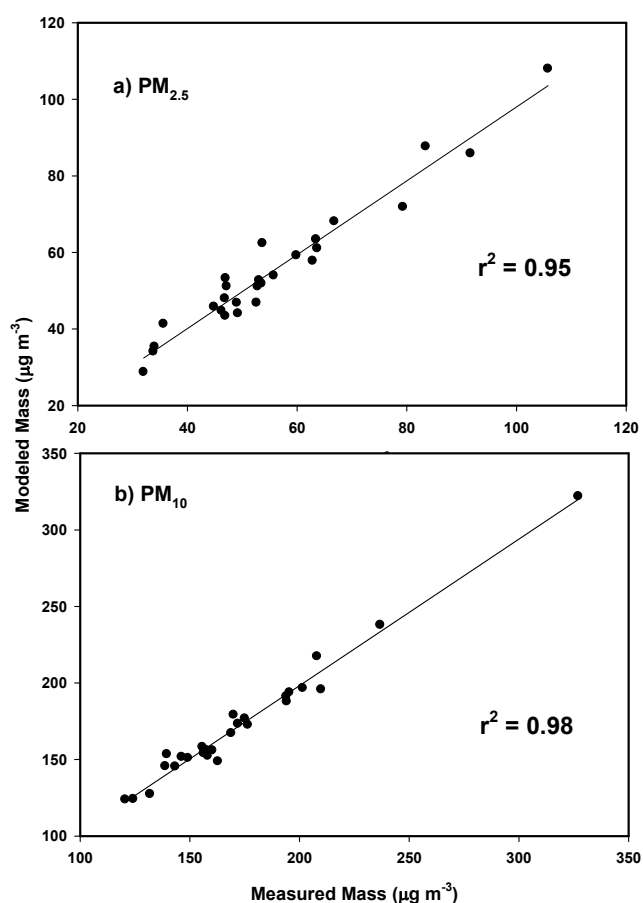


Fig. 7. Correlation between measured and modeled mass concentrations (a) $PM_{2.5}$ and (b) PM_{10} .

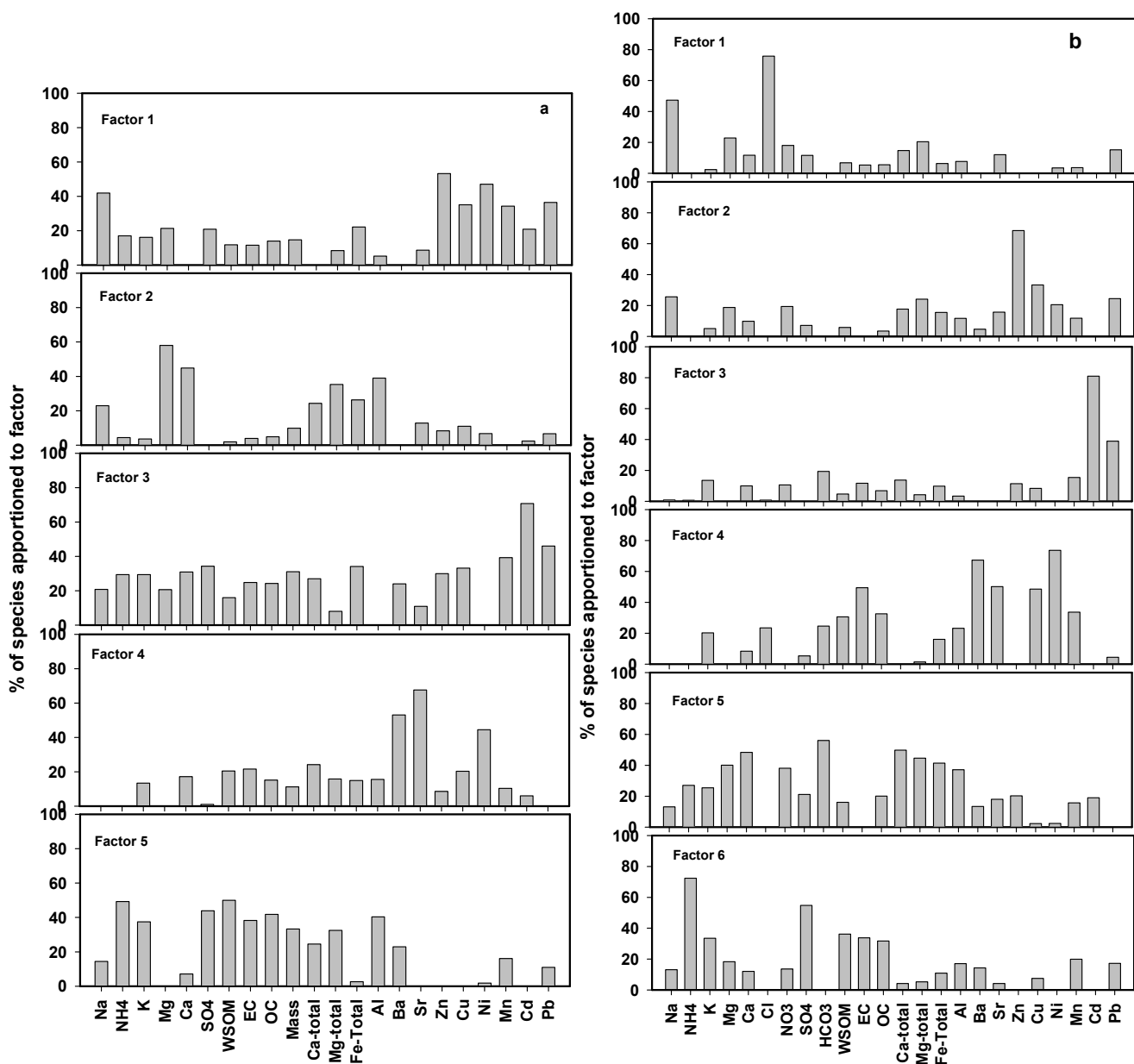


Fig. 8. Source profiles resolved from (a) $PM_{2.5}$ and (b) PM_{10} .

section and hence it is very unlikely this factor be marine aerosols. Long-range transport of re-suspended soil/salts from vast fields of salt farming in the western regions (~200 km from sampling location) may be a probable source identified by this factor. Second factor is similar to that found for $PM_{2.5}$ with characteristic contributions from Zn and Cu related to incineration/industrial emissions. Factor 3 is related exclusively to Pb and Cd, but the size distribution of these metals shows dominant existence in fine mode. Factor 4 is associated with anthropogenic industrial/vehicular emissions as characterized by metals like Cu (~49%) and Ni (~74%) along with moderate loading of carbonaceous species. Factor 5 can be designated as mineral dust with dominant loading of all soil derived species. This factor contributes ~34% to the total mass of PM_{10} whereas the estimate based on Al concentration is ~43%. The factor

6 represents biomass burning sources as evidenced by high loading from K^+ (~33%).

CONCLUSIONS

Trace element concentrations and major chemical constituents were studied in PM_{10} and $PM_{2.5}$ samples from an urban location (Ahmedabad) in western India during December 2006. Significant contribution of mass from mineral dust is observed in PM_{10} which is expected to be dominant component of coarse particles. Enrichment factors calculated for trace metals with respect to crustal Al reveal that Pb and Cd are highly enriched in fine mode particles. Anthropogenic sources contribute to trace metals like Cu, Zn, Pb and Cd. Fine mode Fe is not found in close association with crustal indicator Al, suggesting that

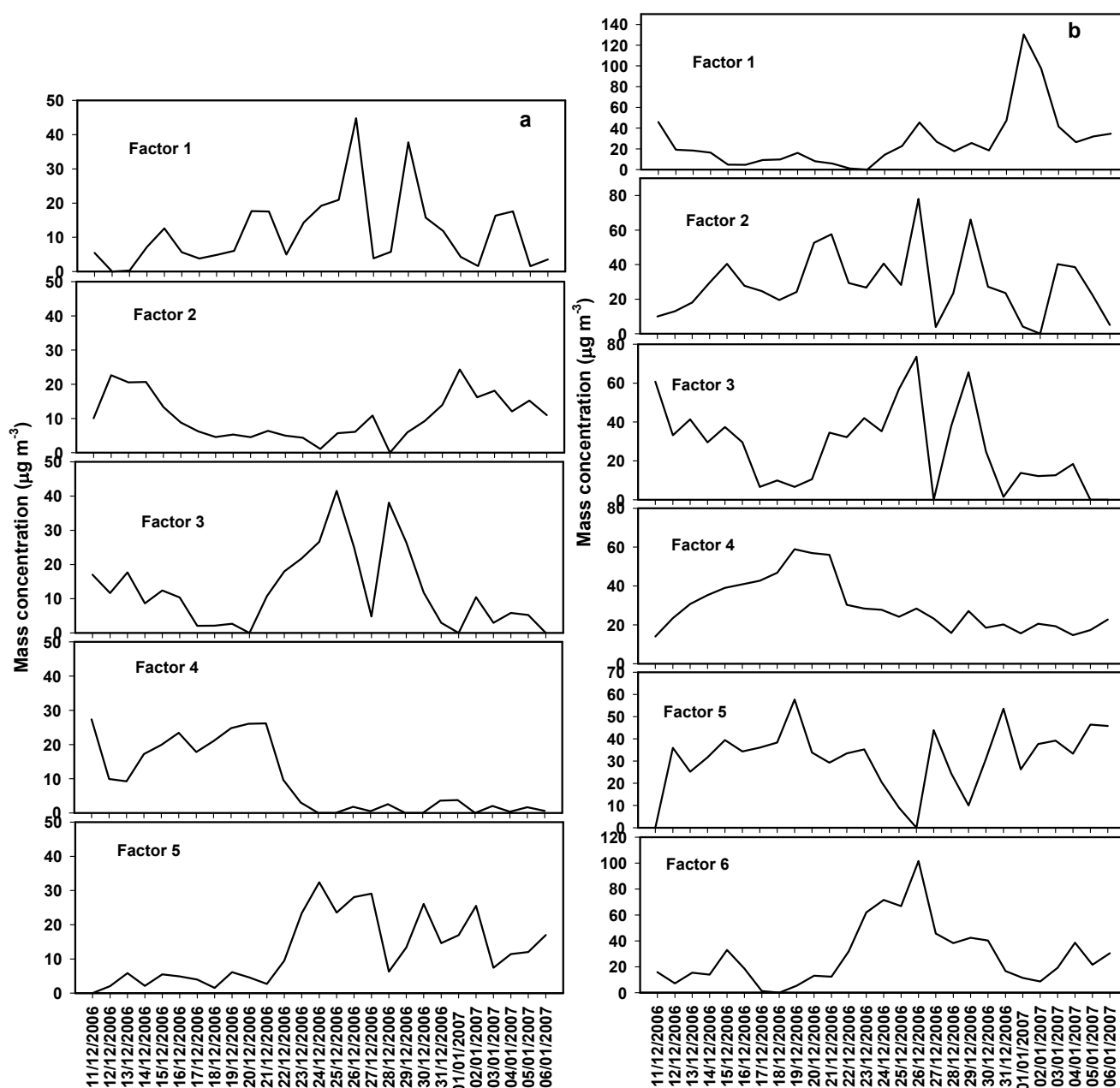


Fig. 9. Time series plot of source contributions for (a) $PM_{2.5}$ and (b) PM_{10} mass concentrations.

anthropogenic sources are contributing to its concentration. Source apportionment studies using EPA PMF 3.0.2.2 with major and trace constituents including particle mass concentrations as independent variables, suggested five factors for $PM_{2.5}$ and six factors for PM_{10} . More than 80% of $PM_{2.5}$ mass is found to be from anthropogenic sources and that of PM_{10} is between 40–50%. Such observation and analysis of changes in atmospheric aerosol chemical components could help in assessing the environmental impact of anthropogenic activities.

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