



## Source Characterization of Trace Elements in Indoor Environments at Urban, Rural and Roadside Sites in a Semi Arid Region of India

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### ABSTRACT

The present study investigated the particle size distribution of trace metals (Fe, Pb, Mn, Cu, Ni, Cr, Zn, Cd, Hg, and As) in the domestic environment, and examined the relationships among the levels of these metals and identified the related sources. Five homes at each site i.e., urban, rural and roadside, were selected for sampling. PM<sub>10</sub> and PM<sub>2.5</sub> samples were collected by using an APM-550 particulate sampler. Metals were analyzed by AAS after acid digestion. The monthly average PM<sub>2.5</sub> concentration ranged from 80 to 184.67 µg/m<sup>3</sup>, while the PM<sub>10</sub> monthly concentration ranged from 167.56 to 307.95 µg/m<sup>3</sup>. PM<sub>2.5</sub> contributed 50–56% of PM<sub>10</sub>. The total contribution of the analyzed trace metals in PM<sub>2.5</sub> was 6.2% while in PM<sub>10</sub> it was 2.2%. This followed the order Fe > Zn > Pb > Cr > Ni > Cu > Mn. Pb and Ni exceeded the prescribed annual National Ambient Air Quality Standards (NAAQS) given by the Central Pollution Control Board (CPCB) by up to 5 and 36 times, respectively. For Pb and Ni it is 0.50 µg/m<sup>3</sup> and 0.02 µg/m<sup>3</sup>, respectively. The particle mass was concentrated in the coarse size fraction, and the mass of individual trace metals was concentrated in finer sizes (except Fe), which is a major issue of concern. Intercorrelations and Principal Component Analysis were used to classify the two groups of sources, one from house dust and anthropogenic activities indoors, and the other from infiltration from outdoors. Enrichment factors with respect to outdoor metal concentrations have been identified for each metal. Fe was found to be totally contributed by outdoor dust. Mn and Cr are found to be less enriched, while Pb, Ni, Zn and Cu were found to have indoor sources.

**Keywords:** PM<sub>10</sub>; PM<sub>2.5</sub>; Trace metals; Health effects; Sources; Correlation; Enrichment factor.

### INTRODUCTION

Fine particles (PM<sub>2.5</sub>), with an aerodynamic diameter smaller than 2.5 µm, is considered to be more hazardous than larger size PM due to its longer residence time in the atmosphere and can penetrate deep into the alveolus of human beings through breathing (Feng *et al.*, 2009; Massey *et al.*, 2009; Satsangi *et al.*, 2011). Contaminated, heterogeneous geosolids, when ingested, act as an important vehicle for the non-dietary intake of many toxic chemicals, including trace metals, by humans (Gupta *et al.*, 2010). Not only vehicles, which are important emitters of fine particles in the city, combustion of residential fuels for heating and cooking, construction and renovation, surface coatings and solvents (e.g., VOCs) are often of equal or greater importance

(Chow *et al.*, 2004; Masih *et al.*, 2012a, b). Indoor pollutants may originate from many sources including infiltration of outdoor pollutants, cookers and heaters, building and furnishing materials, smoking, consumer products, and incense burning (Madany *et al.*, 1994; Taneja *et al.*, 2008; Massey *et al.*, 2012a). One category of indoor pollutant, which is known to be toxic, is that of heavy metals. Heavy metals find their way into residential homes either as airborne dust or through items used or activities carried out within the house like renovation or different cooking methods. Especially vulnerable in this respect are young children, who may ingest several milligrams of indoor and outdoor dusts per day through the repetitive mouthing of non-food objects (Fergusson and Marsh, 1993). Most of the focus to date has been on soils that are contaminated by specific industrial sources or events or by more general urbanization (Madrid *et al.*, 2008) and on indoor dusts (Turner and Ip, 2007; Habil *et al.*, 2013). The makeup of the latter is often dominated by external solids, like soils and road-dusts, but also contains appreciable quantities of particulates generated internally from cooking, smoking, heating, decorating and the application of cosmetics.

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The production of radicals by soluble elements and their mediated Fenton chemical reactions between metal ions or metal complexes and hydrogen peroxide. It results in the formation of reactive oxygen species (ROS) such as hydroxyl radical and peroxy radicals which causes damage to biomolecules and plays a major role in the aging process and a multitude of diseases such as cancer, as well as neurodegenerative disorders (Barbusinski, 2009) is the primary pathway to generate oxidants, where particle size plays an important role in element bioaccessibility and therefore, finally in bioavailability and toxicity (Lingard *et al.*, 2005). Zn can induce inflammatory cells and protein in lung lavage fluid and DNA synthesis in lung cells (Feng *et al.*, 2009) and Fe, V, and Ni has been reported to be the primary determinant of acute inflammatory infection (Costa and Dreher, 1997). Pb and Cd are considered potential carcinogens (Dundar and Altundag, 2006; Massey *et al.*, 2013) and are associated with etiology of a number of diseases, especially cardiovascular, kidney, blood, nerves, and bone diseases (Jarup, 2003). Low levels of Pb and Cd also interfere with crucial nuclear functions such as DNA replication, DNA repair and gene expression through competition with nuclear uptake, homeostasis and the function of essential metal ions (Hechtenberg and Beyersmann, 1995). Although Zn and Cu are essential elements, their excessive concentration in food and feed plants are of great concern because of their toxicity to humans and animals (Kabata-Pendias and Mukherjee, 2007). Cultivation of crops for human or livestock consumption can potentially lead to the uptake and accumulation of these metals in edible plant parts with a resulting risk to human and animal health (Lim *et al.*, 2008). Carcinogenic transition metals such as Ni and Cu catalyze the generation of reactive oxygen species that may result in damage to cell membranes, mitochondria, proteins and DNA (Kasprzak, 1995). The neurotoxin effects of low-level exposure to manganese in human populations are little understood but have been noticed as of concern by some authors (Mergler, 1999; Altundag and Tuzen, 2011). The excessive Mn exposure is associated with neurologic and neuropsychiatric disorders, including the subclinical signs and symptoms of Parkinsonism, reduced speed of movements, and alterations in gait, posture and facial expressions (Davis *et al.*, 1999).

Sources of metals in aerosols are reported differently by different scientists. Motor vehicles are considered the primary source of airborne Pb (Chiaradia *et al.*, 1997; Dundar and Altundag, 2002). It is therefore expected that regions of high Pb in household dust will correspond with areas of high traffic flows. Analysis of household dust by Gulson *et al.* (1995) in Sydney suggests that lead in “contaminated” households can originate from either gasoline or paint, depending on the proximity to major traffic thoroughfares and Pb in household dust is more consistent with gasoline lead. There has been unprecedented boom in the housing sector which is expected to satisfy the demand for over 30 million new homes; hence, the increased use of lead-based paints. Studies in London concluded that road sources were the largest source of Pb household dust levels (Hunt *et al.*, 1993). Maharachpong *et al.* (2006) found elevated concentrations of

Pb in soils and house dusts in areas surrounding boat yards in southern Thailand. Here, contamination was attributed to residues of plumboplumbic oxide ( $Pb_3O_4$ ) used in the caulking mixture applied between wooden planks of the hulls of wooden boats. In the home environment, the authors suggested that boat-repairers tracked in Pb-rich dust on their clothing, skin, hair and shoes. Madany *et al.* (1994) mentioned the smoking of cigarettes, cosmetics and paint chips resulting in elevated Cd, Zn and Cr content. Fergusson and Marsh (1993) proved that worn construction, furnishing and carpet materials can lead to elevated heavy metal content. Cr is derived from yellow paints in roads and alloys in automobiles (Madany *et al.*, 1994), it is also emitted from municipal waste burning outdoors (Kulshrestha *et al.*, 2009a; Massey *et al.*, 2013) and at indoors it is emitted from burning coal and kerosene (Joshi *et al.*, 2010).

Nickel is one of many trace metals widely distributed in the environment, with both natural and anthropogenic sources. It finds its way into the ambient air as a result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources. Tobacco smoking in the form of gaseous nickel carbonyl. Stainless steel in kitchen, inexpensive jewelry utensils also contributes to lower level of nickel (Cempel *et al.*, 2006).

The objectives of the present investigations were to carry a distribution of heavy metals including Fe, Pb, Mn, Cu, Ni, Cr and Zn in the indoor air of Agra, India in two size ranges of particulate i.e.,  $PM_{2.5}$  and  $PM_{10}$  and to elucidate the relationships between the levels of metals in these sizes. The results have practical importance in identifying sources and processes that control levels of fine particulate matter in a respirable size range. The elemental constituents of respirable size range particulate matter are of public health interest, as this determines human susceptibility to pollution processes.

## EXPERIMENTAL

### Site Description

Agra, the city of Taj Mahal ( $27^{\circ}10'N$   $78^{\circ}02'E$ ), with area of 1,880.40 km<sup>2</sup> is located in the north central part of India about 204 Kms South of Delhi. It is one of the most famous tourist spots of the country. It is bounded by the Thar Desert of Rajasthan on its south east, west and north west peripheries and is therefore, a semiarid area that borders on a humid subtropical climate with a marked monsoon season. Meteorologically the year is divisible into three distinct seasons; Summer season (March–June) is associated with strong hot dry westerly winds and high temperature ranges between 30 and 46°C. Relative humidity in the summer ranges between 18 and 48%. The monsoon season (July–October) is hot and humid, temperature ranges from 24 to 36°C and the relative humidity ranges from 70 and 90%. The pre-monsoon and monsoon seasons are dominated by strong northeast and southeast winds and in the winter seasons (November–February), the temperature ranges from 10 to 25°C during day time and drops below 5°C at night. Dust storms and thunderstorms from the Asian subcontinent and the Thar Desert are frequently observed

during the period from March to June. The wind speeds vary from 2.6 to 6.9 km/h with a maximum during summer and monsoons and minimum in winters. The downward wind blew 29% in south-south-east and 6% North-East direction in summers and in winters it blew a 9.4% in west-north-west and 11.8% in north-north-west direction. The atmospheric pollution load here is high and because of the downward wind, pollutants may be transported to the different areas mainly from an oil refinery situated in Mathura (50 kms from the center of the City). It has about 1,574,542, total inhabitants and population density is about 1,093 people per sq. km (Census, 2011) with 3,86,635 vehicles registered and 32,030 diesel power generator sets. In Agra, 60% pollution is due to vehicular emission (NAAQMS, 2006; Massey *et al.*, 2012a). Three national highways crossing the city such that residences lie adjacent to it and vehicular traffic count of about  $10^5$  vehicles per day (Kulshrestha *et al.*, 2009b, Massey *et al.*, 2012b). In the city, about 700 tons of solid wastes are generated everyday that can be seen in the form of piles along roadsides and streets due to poor municipal services. The major industrial activities are ferrous and non-ferrous metal casting, rubber processing, chrome and nickel plating units, copper wire and diesel engine, tanneries, lime oxidation, pulverization, engineering works and chemicals. Apart from local sources, Mathura refinery, Firozabad glass industries and brick kiln factories are also situated within 40km from Agra.

### Sample Collection

Sampling was done at three sites to cover various areas in

the city, this includes five urban homes (UH) with commercial areas around, five roadside homes (RH) located adjacent to heavy traffic density roads and five rural homes (VH) where houses are made up of mud, grasses and are situated in areas with little traffic and lots of greenery. The roadside and urban houses were mostly located in a ten kilometers square area of the city. Whereas the rural homes are located at the periphery of the city Agra. Diesel generators are used here for irrigation purposes. Apart from agricultural activities like field plowing, irrigation and biomass burning or garbage burning, construction are other major activities near these houses as the area is now developing. Cooking is done mostly with wood, coal and other oil fuels (Fig. 1). It is not easy to draw distinct boundaries between these sites, thus sources of pollution in one area can affect other areas too. Twenty four hours sampling for  $PM_{10}$  and  $PM_{2.5}$  was done from October 2009 to March 2010, with a fine particulate dust sampler (APM 550, Envirotech), which runs at a constant flow rate of 16.6 L/min. It has a portable Wins-Anderson impactor for the sampling of  $PM_{2.5}$ . The particles were collected on 47 mm diameter, 2  $\mu$ m pore size PTFE filters. During the sampling of six months total 90 samples were collected indoors with a frequency of 30 samples at each site. A few samples (30 samples, two outside each house) were also collected outside the residences simultaneously with indoor sampling to see the impact of outdoor air on concentration of indoor pollutants. For indoor sampling, sampler was placed in living rooms where occupants spend most fraction of their time. The air inlet hood of collection sampler was kept at a height of 1–1.5 meters above the

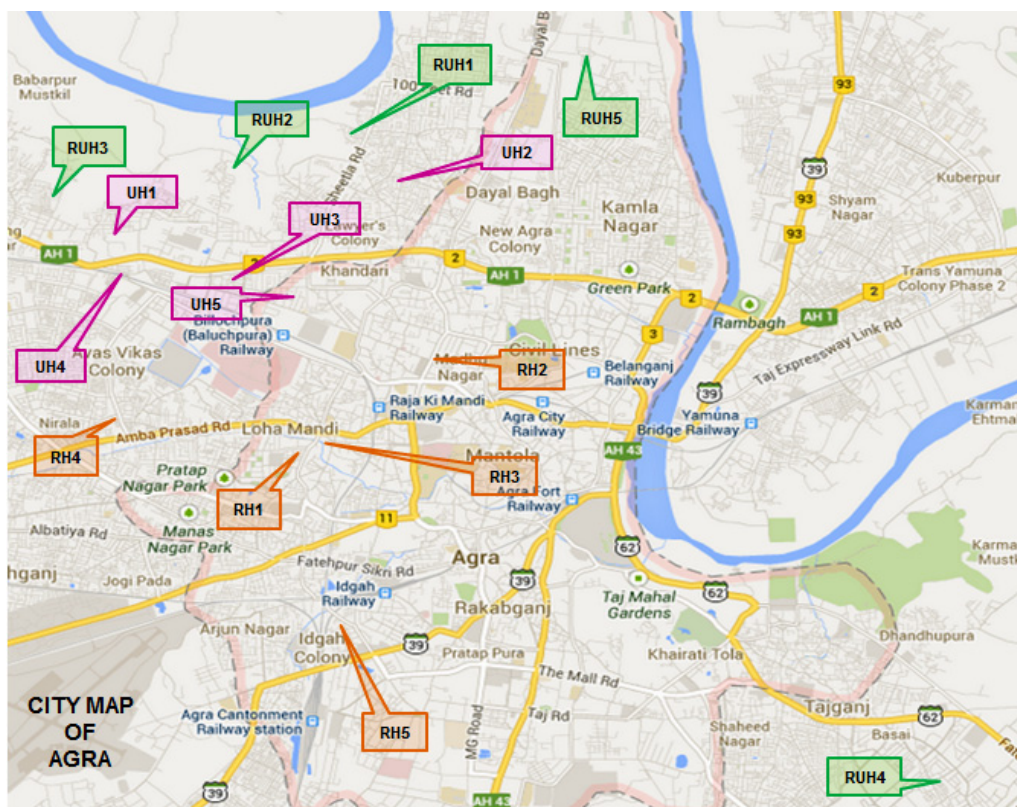


Fig. 1. Site map of Agra showing sampling sites. VH = rural site, UH = urban site, RH = roadside site.

ground level to simulate the humans breathing zone, while for outdoor sampling, it was kept at the rooftops of the houses, which are at a height of 4 m from ground level. The instrument was also kept at least 1 m away from potential sources of air pollutants. In this paper the results are discussed by averaging the data of five residences at each location.

### Analytical Procedure

Filter papers were weighed three times before and after sampling using four-digit balance (Citizen, model no. ISO 9001:2000) with sensitivity of  $\pm 0.2$  mg and in the 220–20 mg range. Before weighing the samples were equilibrated in desiccators at 20–30°C and relative humidity of 30–40% in a humidity controlled room for 24 h. Field blank filters were collected to reduce gravimetric bias due to filter handling during and after sampling. Filters were handled only with tweezers coated with Teflon tape to reduce the possibility of contamination. After weighing, samples were refrigerated till further analysis. It is assumed that particulate deposited on filter papers were uniformly distributed over the entire area. The exposed filter paper was digested in 6–8 mL analytical grade (Merck)  $\text{HNO}_3$  (APHA, 1977) and kept on hot plate at the temperature of 40–60°C for 90 minutes (USEPA, 1999). The solution was diluted up to 50 mL with distilled de-ionized water and stored in polypropylene bottles (before use these bottles were dipped overnight in 2%  $\text{HNO}_3$  and then again dipped overnight in deionized distilled water to prevent adsorption of metals on these bottles) till analysis. Analysis for ten metals was done on Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer, AAnalyst 100) regularly within two months of extraction. The minimum detection limit (MDL) of the instrument (AAS) for Lead (Pb) is 0.10, Zinc (Zn) is 0.018, Nickel (Ni) is 0.063, Iron (Fe) is 0.060, Chromium (Cr) is 0.055, Manganese (Mn) is 0.052, Copper (Cu) is 0.077, Cadmium (Cd) is 0.60, Mercury (Hg) is 0.025 and Arsenic (As) is 0.10 mg/L. Cd, Hg and As were found undetected at these sites.

### Statistical Analysis

Statistical analysis was performed using Microsoft Excel 2007 and SPSS software version 11.5. The particle concentration data were initially investigated by descriptive

statistics (mean and standard deviation). Further, skewness was applied to view whether the distribution of data is symmetric or asymmetric. Inter Particulate Ratios, Metal Concentrations, Enrichment Factor were also calculated to know whether these elements are emitted indoors or originated from outdoors. Metal Inter Correlation was used to analyze the relationship between indoor outdoor concentrations of heavy metal ions at roadside, urban and rural sites. Principal Component analysis was also performed to know the probable sources of heavy metals contamination in coarse and fine particles at different sites.

## RESULTS AND DISCUSSION

### PM Distribution

Table 1 lists the average concentration and standard deviation of particulates indoor at urban, rural and roadside sites in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  size fraction respectively. The trends of particulate mass concentration in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were road > rural > urban. This indicates that air quality in rural and roadside sites is affected by particulate matter (PM) and that urban site has relatively better air quality. On comparing average  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  concentration with WHO guidelines (10  $\mu\text{g}/\text{m}^3$  and 20  $\mu\text{g}/\text{m}^3$  annual averages respectively) for ambient air, our results exceeded 11–12 times. The  $\text{PM}_{2.5}/\text{PM}_{10}$  ratio according to WHO standards (2005) is 0.50 and that by NAAQS (2009) given by CPCB (Central Pollution Control Board, India), it is 40  $\mu\text{g}/\text{m}^3/60$   $\mu\text{g}/\text{m}^3$  i.e. 0.66. In the present study this ratio was found to vary between 0.35 to 0.62. The ratio can be different when meteorological parameters like temperature, humidity and air exchange rate change. From health point of view it may be better to have less fine particles in  $\text{PM}_{10}$ , because fine particles penetrate deep into the alveolus of human beings through breathing and are more hazardous (Pipal et al., 2011). On comparing particulate concentration during different sampling months, reported in Table 1, it can be observed that particulate levels are higher during the months of December and January and low during the month of October. It is because December and January months are marked as peak winter months in this region with low temperature and moderate relative humidity which points towards the poor

**Table 1.** Average mass concentration ( $\mu\text{g}/\text{m}^3$ ) and other descriptive of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  at three sampling sites indoors during the sampling period.

	Roadside		Rural		Urban	
	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$
October	185.49 $\pm$ 20.12	83.84 $\pm$ 14.40	167.56 $\pm$ 24.52	79.99 $\pm$ 18.32	185.42 $\pm$ 10.72	80.16 $\pm$ 8.03
November	279.29 $\pm$ 18.65	99.78 $\pm$ 16.23	220.34 $\pm$ 19.56	128.00 $\pm$ 14.27	241.10 $\pm$ 9.22	104.65 $\pm$ 6.35
December	297.54 $\pm$ 11.56	184.67 $\pm$ 17.34	274.33 $\pm$ 17.12	144.28 $\pm$ 12.19	241.99 $\pm$ 16.29	102.61 $\pm$ 14.70
January	286.32 $\pm$ 13.15	157.86 $\pm$ 16.21	280.44 $\pm$ 14.67	158.00 $\pm$ 13.38	307.95 $\pm$ 16.17	168.04 $\pm$ 17.80
February	221.88 $\pm$ 18.33	132.82 $\pm$ 13.45	267.89 $\pm$ 9.83	145.12 $\pm$ 9.36	217.74 $\pm$ 9.45	135.89 $\pm$ 6.58
March	208.60 $\pm$ 9.41	123.74 $\pm$ 6.48	213.71 $\pm$ 11.34	105.00 $\pm$ 11.14	194.27 $\pm$ 8.16	110.18 $\pm$ 8.74
Average	246.52	130.45	237.37	126.73	231.41	116.92
St.Dv	46.96	37.02	44.44	29.26	44.14	30.74
Maximum	297.54	184.67	280.44	158	307.95	168.04
Minimum	185.49	83.84	167.56	79.99	185.42	80.16
Geomean	242.68	126.034	233.62	123.54	228.11	113.74

dilution of pollutants during this season. The PM mass distribution as a function of particle size is given in Fig. 2(a) at three different sampling sites. The PM mass is concentrated in the coarse size fraction and decreases with decreasing particle size. At roadside site 52% (range 35%–62%) of  $PM_{10}$  is comprised of  $PM_{2.5}$ , at rural site 53% (range 47%–58%) of  $PM_{10}$  comprised of  $PM_{2.5}$  while on an urban site again 50% (range 42% to 62%) of  $PM_{10}$  is comprised of  $PM_{2.5}$ . On the contrary, Fig. 2(b) shows the distribution of sum of metal concentration in two size particulates. The total contribution of analyzing metals in  $PM_{2.5}$  is 6.2% of total  $PM_{2.5}$  mass concentration, while in  $PM_{10}$ , it was only 2.2% of total  $PM_{10}$  mass concentration. This shows that mass of metals is concentrated in finer sizes and decreases in increasing particle size. Contribution of metals in  $PM_{2.5}$  is found to be 1.2 to 1.3 times that in  $PM_{10}$ .

### Composition and Size Distribution of Metals

Concentrations of individual metals in  $PM_{10}$  and  $PM_{2.5}$  analyzed at three sites were compared (Fig. 3). Table 2 shows the mean concentration, range and standard deviation of each metal at individual sites. Trends of metal concentration at roadside was  $Fe > Pb > Zn > Cr > Ni > Cu > Mn$ , at rural site was  $Fe > Cr > Zn > Pb > Ni > Cu > Mn$ , at urban site was  $Fe > Zn > Pb > Cr > Ni > Cu > Mn$ . Overall the concentration trend for metals indoor is:  $Fe > Zn > Pb > Cr > Ni > Cu > Mn$ . No trend of monthly changes in metal concentration was observed for individual metals but sum of seven analyzed metals  $\Sigma$ Metals show rise in concentration after November and then fall in concentration after February at all sites in both the sizes. Compared with other metals Fe concentration was highest in both size particulates and showed maximum variation. Central Pollution Control Board, India (CPCB) prescribes annual National Ambient Air Quality Standards (NAAQS) only for Pb and Ni. These standards are  $0.50 \mu\text{g}/\text{m}^3$  and  $0.02 \mu\text{g}/\text{m}^3$  for Pb and Ni respectively. In the present study Pb concentration (average of Pb in  $PM_{10}$  and  $PM_{2.5}$ ) exceeded up to 5 times at the roadside while at the other two sites it was under the limit. Exceedance of Pb at the roadside may be due to mixing of residual Pb

in soil and its resuspension in the air due to motor vehicles at this site. Ni concentration exceeded up to 36 times at a rural site in the month of November. At roadside it was 21 times higher, at rural site it was 14 times higher and at urban site it was found to be 18 times higher in  $PM_{2.5}$  size while in  $PM_{10}$  it ranged between 2 to 9 times higher between the sites. Higher concentration of Ni is also a major issue of concern and people can easily get exposed to it by inhalation or dermal contact. It is observed that the overall concentration of metals at three sites are either higher in fine particulate sizes or have maximum contribution (more than 60%) in a finer fraction of particulate. Atmospheric concentrations of metals did not differ substantially between sites but with possible exceptions, Pb, Mn, and Cu were found higher at roadside. Cr is higher at rural site which may be due to coal and kerosene burning which carry Cr. At urban site Fe, Cu, Ni and Zn showed high concentrations.

### Atmospheric Urban Fingerprints

As the concentration levels of metals are low as compared to the total particulate concentration, they could not reveal potential main atmospheric sources. To infer the potential sources, the interelement correlations, and enrichment factors were explored.

### Correlations

Univariate Pearson correlations are determined by using SPSS 11 (Table 3) to find source related relationship among metals. Pb, Mn, Ni and Cr show good correlation with  $PM_{2.5}$  concentration (Table 3(a)) at roadside therefore most of their concentration is due to particle dust which may be composed of indoor suspended dust as well as by air seeped inside the house from outdoors. Pb, Mn, Cu, Ni and Cr together are showing good inter-correlation which indicates their common source within the house. It can be dust from the walls of the house which carry chemicals included in paints (Booher, 1988). In recent years, lead has been phased out or restricted in many consumer products due to serious health impacts, especially in children and fetuses (Kumar et al., 2008). The United States has enforced

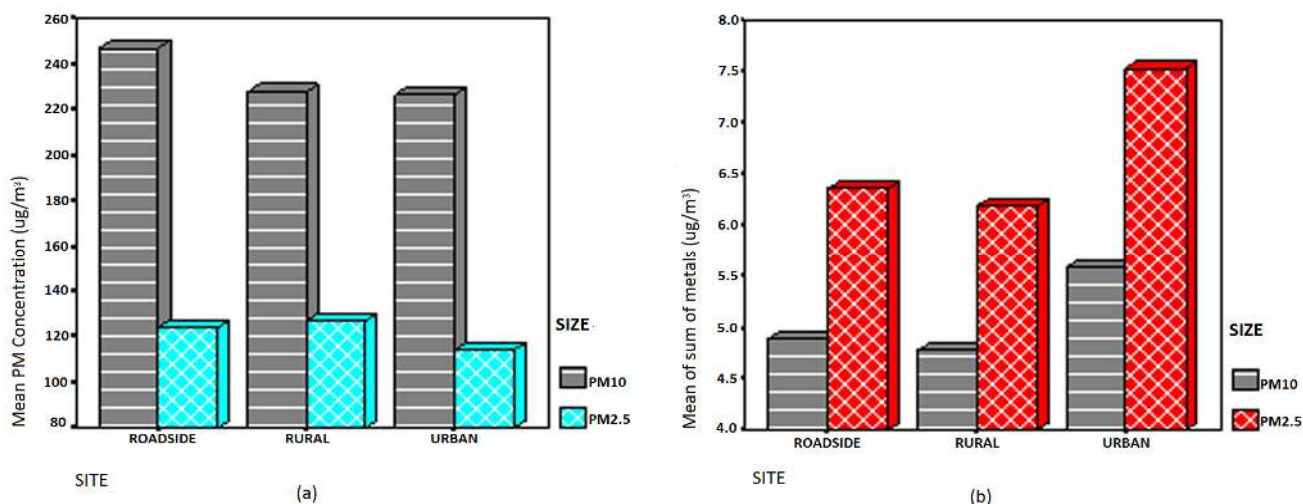


Fig. 2. Mass distribution (a) and total metal distribution (b) in  $PM_{10}$  and  $PM_{2.5}$  at urban, rural and roadside sites indoors.

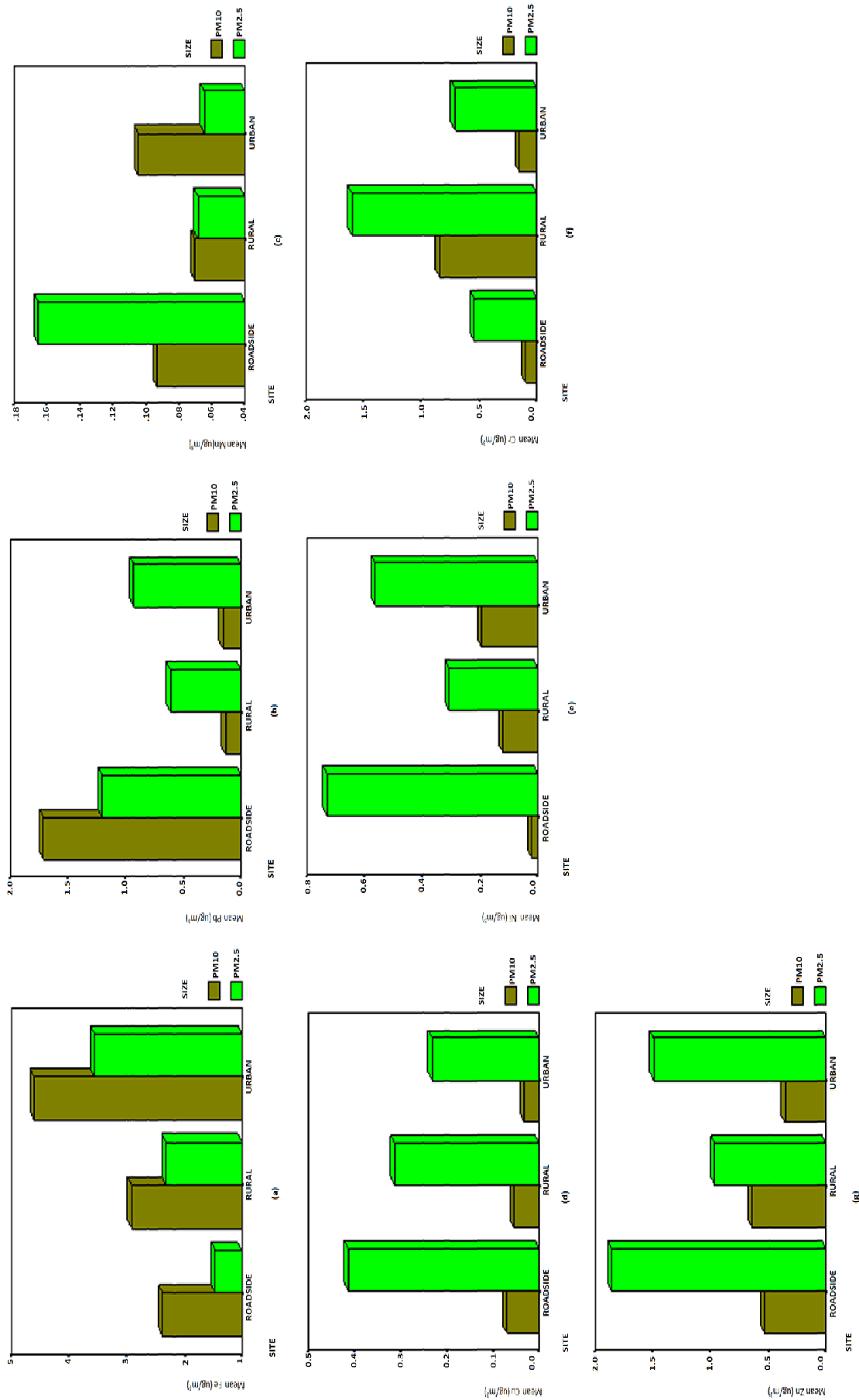


Fig. 3. Mass distribution of individual metals (Fe, Pb, Mn, Cu, Ni, Cr, Zn) in PM<sub>10</sub> and PM<sub>2.5</sub> at urban, rural and roadside sites.

**Table 2.** Average mass concentration ( $\mu\text{g}/\text{m}^3$ ) of analyzing metal parameters in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  at three sampling sites.

(a)

Months	ROADSIDE													
	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$
October	$0.12 \pm 0.06$	$0.12 \pm 0.19$	$1.45 \pm 0.66$	$0.65 \pm 0.35$	$0.01 \pm 0.02$	$0.09 \pm 0.07$	$0.08 \pm 0.03$	$0.74 \pm 0.62$	$0.05 \pm 0.04$	$0.08 \pm 0.05$	$0.10 \pm 0.01$	$0.31 \pm 0.08$	$0.07 \pm 0.13$	$0.73 \pm 0.40$
	$1.95 \pm 1.60$	$0.78 \pm 1.11$	$1.97 \pm 0.39$	$0.69 \pm 1.28$	$0.09 \pm 0.32$	$0.04 \pm 0.23$	$0.07 \pm 0.18$	$0.24 \pm 0.09$	$0.02 \pm 0.08$	$0.11 \pm 0.25$	$0.08 \pm 0.05$	$0.55 \pm 0.04$	$0.53 \pm 0.32$	$0.61 \pm 0.07$
November	$7.42 \pm 3.67$	$2.64 \pm 1.08$	$2.17 \pm 0.73$	$1.84 \pm 1.44$	$0.25 \pm 0.24$	$0.97 \pm 0.06$	$0.02 \pm 0.01$	$0.35 \pm 0.40$	$0.06 \pm 0.04$	$0.61 \pm 0.41$	$0.08 \pm 0.33$	$0.87 \pm 0.85$	$1.24 \pm 0.64$	$2.26 \pm 0.77$
	$2.73 \pm 1.44$	$2.24 \pm 0.89$	$2.03 \pm 1.20$	$1.11 \pm 1.27$	$0.12 \pm 0.26$	$0.05 \pm 0.23$	$0.10 \pm 0.17$	$0.48 \pm 0.68$	$0.03 \pm 0.01$	$0.65 \pm 0.56$	$0.11 \pm 0.06$	$1.13 \pm 0.97$	$0.74 \pm 0.53$	$1.58 \pm 0.63$
December	$1.87 \pm 0.85$	$0.84 \pm 0.59$	$1.24 \pm 1.59$	$1.07 \pm 0.25$	$0.08 \pm 0.04$	$0.05 \pm 0.28$	$0.07 \pm 0.02$	$0.39 \pm 0.03$	$0.02 \pm 0.02$	$0.56 \pm 0.36$	$0.08 \pm 0.04$	$0.67 \pm 0.07$	$0.51 \pm 0.69$	$0.72 \pm 0.01$
	$0.14 \pm 1.45$	$0.15 \pm 0.33$	$1.39 \pm 0.05$	$1.22 \pm 1.07$	$0.01 \pm 0.01$	$0.02 \pm 0.01$	$0.09 \pm 0.16$	$0.34 \pm 0.01$	$0.06 \pm 0.09$	$0.59 \pm 0.23$	$0.11 \pm 0.07$	$0.49 \pm 0.36$	$0.08 \pm 0.60$	$0.44 \pm 0.32$
Average	2.37	1.13	1.71	1.10	0.09	0.20	0.07	0.42	0.04	0.43	0.09	0.67	0.53	1.06
St.Dv	2.69	1.07	0.39	0.43	0.09	0.38	0.03	0.17	0.02	0.26	0.02	0.29	0.44	0.71
Geomean	1.04	0.64	1.67	1.03	0.05	0.07	0.06	0.40	0.04	0.32	0.09	0.62	0.33	0.89
Skewness	1.64	0.69	-0.01	0.95	1.16	2.43	-1.71	1.42	0.00	-0.92	0.21	0.61	0.65	1.25
Maximum	7.42	2.64	2.17	1.84	0.25	0.97	0.10	0.74	0.06	0.65	0.11	1.13	1.24	2.26
Minimum	0.12	0.12	1.24	0.65	0.01	0.02	0.01	0.24	0.02	0.08	0.08	0.31	0.07	0.44

(b)

Months	RURAL													
	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$
October	$1.95 \pm 1.66$	$0.39 \pm 0.86$	$0.11 \pm 0.05$	$0.88 \pm 0.79$	$0.04 \pm 0.05$	$0.03 \pm 0.03$	$0.06 \pm 0.02$	$0.04 \pm 0.28$	$0.13 \pm 0.16$	$0.33 \pm 0.56$	$0.85 \pm 0.54$	$2.59 \pm 1.42$	$0.59 \pm 0.72$	$1.69 \pm 0.63$
	$2.77 \pm 0.91$	$1.84 \pm 0.77$	$0.15 \pm 0.06$	$0.31 \pm 0.05$	$0.07 \pm 0.04$	$0.05 \pm 0.09$	$0.02 \pm 0.03$	$0.05 \pm 0.60$	$0.09 \pm 0.06$	$0.72 \pm 0.24$	$0.53 \pm 0.47$	$2.07 \pm 0.87$	$0.08 \pm 0.15$	$0.34 \pm 0.12$
November	$2.73 \pm 1.55$	$2.24 \pm 0.67$	$0.21 \pm 0.55$	$0.32 \pm 0.08$	$0.10 \pm 0.39$	$0.03 \pm 0.21$	$0.03 \pm 0.12$	$0.66 \pm 0.16$	$0.13 \pm 0.18$	$0.43 \pm 0.52$	$0.74 \pm 0.68$	$1.01 \pm 0.92$	$0.11 \pm 0.01$	$0.73 \pm 0.63$
	$3.18 \pm 2.53$	$3.19 \pm 0.81$	$0.11 \pm 0.06$	$0.51 \pm 0.16$	$0.12 \pm 0.26$	$0.08 \pm 0.07$	$0.08 \pm 0.09$	$0.14 \pm 0.29$	$0.02 \pm 0.05$	$0.01 \pm 0.02$	$0.71 \pm 0.81$	$1.85 \pm 0.71$	$1.65 \pm 1.53$	$0.59 \pm 0.03$
December	$4.45 \pm 2.61$	$4.65 \pm 1.24$	$0.18 \pm 0.07$	$0.89 \pm 0.24$	$0.01 \pm 0.06$	$0.02 \pm 0.05$	$0.08 \pm 0.06$	$0.50 \pm 0.06$	$0.33 \pm 0.17$	$0.05 \pm 0.09$	$1.61 \pm 0.98$	$1.53 \pm 0.34$	$0.10 \pm 0.05$	$0.66 \pm 0.17$
	$2.54 \pm 1.74$	$1.63 \pm 0.23$	$0.08 \pm 0.09$	$0.76 \pm 0.29$	$0.10 \pm 0.09$	$0.20 \pm 0.45$	$0.06 \pm 0.09$	$0.48 \pm 0.05$	$0.01 \pm 0.02$	$0.21 \pm 0.14$	$0.56 \pm 0.33$	$0.54 \pm 0.67$	$1.32 \pm 1.48$	$1.75 \pm 1.25$
Average	2.94	2.32	0.14	0.61	0.07	0.07	0.06	0.31	0.12	0.29	0.83	1.60	0.64	0.96
St.Dv	0.84	1.46	0.05	0.27	0.04	0.07	0.03	0.27	0.12	0.26	0.40	0.74	0.69	0.60
Geomean	2.84	1.84	0.13	0.56	0.06	0.05	0.05	0.19	0.07	0.15	0.77	1.42	0.32	0.81
Skewness	1.23	0.54	0.35	-0.14	-0.62	1.96	-0.51	0.17	1.39	0.72	1.98	-0.22	0.78	0.76
Maximum	4.45	4.65	0.21	0.89	0.12	0.20	0.08	0.66	0.33	0.72	1.61	2.59	1.65	1.75
Minimum	1.95	0.39	0.08	0.31	0.01	0.02	0.02	0.04	0.01	0.01	0.53	0.54	0.08	0.34

(c)

Months	URBAN													
	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$
October	$1.90 \pm 0.45$	$1.78 \pm 0.60$	$0.35 \pm 0.48$	$0.75 \pm 0.20$	$0.07 \pm 0.02$	$0.07 \pm 0.03$	$0.02 \pm 0.08$	$0.23 \pm 0.17$	$0.45 \pm 0.33$	$0.43 \pm 1.24$	$0.01 \pm 0.01$	$0.09 \pm 0.07$	$0.19 \pm 0.03$	$2.10 \pm 0.95$
	$1.19 \pm 0.78$	$1.05 \pm 1.42$	$0.26 \pm 0.01$	$0.91 \pm 0.56$	$0.12 \pm 0.15$	$0.04 \pm 0.03$	$0.01 \pm 0.01$	$0.39 \pm 0.50$	$0.06 \pm 0.14$	$0.09 \pm 0.07$	$0.03 \pm 0.02$	$1.16 \pm 1.52$	$0.21 \pm 0.22$	$0.90 \pm 0.82$
November	$2.72 \pm 0.21$	$2.76 \pm 0.71$	$0.03 \pm 0.07$	$0.89 \pm 0.77$	$0.09 \pm 0.07$	$0.08 \pm 0.06$	$0.05 \pm 0.07$	$0.06 \pm 0.02$	$0.06 \pm 0.21$	$0.68 \pm 0.81$	$0.08 \pm 0.14$	$1.35 \pm 1.54$	$0.65 \pm 0.22$	$0.42 \pm 0.54$
	$8.33 \pm 2.81$	$4.20 \pm 1.79$	$0.02 \pm 0.13$	$0.98 \pm 0.16$	$0.01 \pm 0.02$	$0.05 \pm 0.02$	$0.10 \pm 0.02$	$0.50 \pm 0.22$	$0.02 \pm 0.04$	$0.24 \pm 0.29$	$0.03 \pm 0.12$	$0.48 \pm 0.63$	$0.21 \pm 0.19$	$1.69 \pm 0.21$

Months	URBAN													
	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>
February	9.36 ±	5.73 ±	0.01 ±	0.73 ±	0.21 ±	0.06 ±	0.01 ±	0.23 ±	0.32 ±	0.37 ±	0.97 ±	0.72 ±	0.05 ±	2.45 ±
	3.52	2.72	0.17	0.21	0.24	0.05	0.03	0.17	0.26	0.28	0.54	0.50	0.08	0.98
March	6.79 ±	3.68 ±	0.04 ±	0.80 ±	0.16 ±	0.06 ±	0.03 ±	0.16 ±	0.11 ±	0.37 ±	0.06 ±	0.05 ±	0.96 ±	1.13 ±
	1.51	1.25	0.02	0.23	0.23	0.05	0.03	0.14	0.15	0.24	0.17	0.03	0.54	0.78
Average	5.05	3.20	0.12	0.84	0.11	0.06	0.04	0.26	0.17	0.36	0.20	0.64	0.38	1.45
St.Dv	3.54	1.70	0.15	0.10	0.07	0.01	0.03	0.16	0.17	0.20	0.38	0.54	0.35	0.77
Geomean	3.85	2.78	0.05	0.84	0.08	0.06	0.03	0.22	0.10	0.31	0.06	0.37	0.25	1.24
Skewness	0.13	0.27	1.11	0.19	0.05	0.00	1.57	0.47	1.09	0.38	2.43	0.22	1.16	0.01
Maximum	9.36	5.73	0.35	0.98	0.21	0.08	0.10	0.50	0.45	0.68	0.97	1.35	0.96	2.45
Minimum	1.19	1.05	0.01	0.73	0.01	0.04	0.01	0.06	0.02	0.09	0.01	0.05	0.05	0.42

a lead limit of 90 ppm in paint. While India does not have any mandatory norms, the voluntary limit has been set at 1,000 ppm by Bureau of Indian Standards (BIS, 2004; Dutta *et al.*, 2009). It is primarily used in paints as pigment to impart colour. It is also added to make paints more durable and corrosion resistant, and for speed drying. Lead chromate (also called chrome yellow) and lead carbonate (also called white lead) are widely used as a pigment. Lead chromate is often used to make yellow orange, red and green paints. Lead carbonate is a superior paint pigment used for its opaque quality. Others pigments like red lead and blue lead impart corrosion protection as well as colour to metal surface. Using lead substitutes increases the cost and also reduces paint performance.

The correlation between Pb, Cr, and Ni was also identified by Madany *et al.* (1994). Fe, Zn and Mn show good correlation with PM<sub>10</sub> (Table 3(b)), therefore these metals are also originated from dust outdoors at this site. Zinc normally originates from automobiles such as lubricating oils and tires outdoors while Fe, Mn is in the resuspended road dust. Mn is used in unleaded gasoline as Methylcyclopentadienyl manganese tricarbonyl (MMT) to improve the octane number and as antiknocking agent. Pb, Cu Ni and Cr showed correlation among themselves as in the case of PM<sub>2.5</sub> above which may be again due to paint and other household dust.

At rural site one set of correlation is observed among Ni, Cr and Fe in PM<sub>2.5</sub>. Possible common sources of Ni and Cr at this site can be combustion of coal and other inferior fuels such as kerosene and diesel for cooking and lightening purposes. Cempel *et al.* (2006), Joshi *et al.* (2010) and another set is observed between Zn, Pb and Mn in PM<sub>2.5</sub> which can be attributed to vehicular emission made by vehicles used for agricultural and construction activities, along with resuspension of soil dust. Zn is emitted from abrasion of tires while Mn is used as additive in unleaded gasoline (Kulshrestha *et al.*, 2009a). For PM<sub>10</sub> Fe, Cu, Ni, Cr and Pb showed one set of correlation among themselves which is due to construction activities at this site. Fe is used in construction for framing of pillars and the roofing of the building. Cement and paint are the source of lead at this site. Sharma and Pervez (2004) found concentration of Pb and other trace elements four to eight times higher in PM<sub>10</sub> near a cement plant. Cr showed a very strong correlation

with Ni (0.95) which can be attributed to the combustion of coal and other fuels at this site. Zn showed correlation with Mn and Pb showed correlation with PM<sub>10</sub> due to influence from vehicular emission.

At urban site Fe, Mn and Ni showed a correlation in case of PM<sub>2.5</sub> which is may be due to seeping of air from outdoors. Where activities like wear and tear of tires, oil burning, abrasion of mechanical parts of road vehicles, oil lubricants etc. are contributing to the emission of the above metals while for PM<sub>10</sub> Cr, Mn and Fe showed correlation which is due to solid waste incineration activities at these sites. Cr is an important solid waste pollutant (Borai *et al.*, 2002). Pb and Ni showed correlation with each other and Cu showed correlation with PM<sub>10</sub>. Possible source for it is road dust which might have entered inside the homes by penetration or be tracked into the dwelling on shoes and clothes.

#### Principal Component Analysis

Principal Component Analysis (PCA) is a well-established tool for analyzing structure in multivariate data sets (Derwent *et al.*, 1995). For the purpose of this study, varimax rotated factor analysis was performed to identify the main sources influencing the concentration of study pollutants at the sampling sites. Data are included in the matrix only if the Eigen value of the factor is greater than 1. Factors identified by factor analysis are reported in the form of Pie chart in Fig. 4.

#### Roadside Site

At roadside site we have modern types of houses, as they have been built recently, usually their environment is of high traffic during night and morning with both heavy and light motor vehicles. It is a busy place with many kinds of activities such as Petha industry (famous Indian confectionery), iron works, shoe factories, electroplating industry, railway station, oil lubricants shop, many big and small restaurants, Photostat shops, waste dumping and incineration, vehicle repairing shops, welding work, major hospitals, hotels, banks and offices along with heavy traffic and two major crossings nearby. At roadside site two sources were found, identifying 78.25% of elemental concentration in PM<sub>2.5</sub> (Fig. 4(a)). Pb, Mn, Cu, Ni, Cr and PM<sub>2.5</sub> concentration represent the factor 1 with 55.5% variance. The common source attributed is household dust. Cr is



**Table 3.** Inter correlations between analyses metals in PM<sub>2.5</sub> and PM<sub>10</sub> at three sites.

Table 3a										Table 3b														
SITE = ROADSIDE , SIZE = PM10					SITE = ROADSIDE , SIZE = PM2.5					SITE = RURAL , SIZE = PM10					SITE = RURAL , SIZE = PM2.5									
PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	
Fe	<u>0.74</u>							Fe	-0.29							Fe	-0.12							
Pb	-0.46	-0.68						Pb	<u>0.77</u>	-0.48						Pb	-0.79	-0.09						
Mn	<u>0.80</u>	<u>0.99</u>	-0.69					Mn	0.18	-0.10	<u>0.58</u>					Mn	-0.31	-0.63	0.13					
Cu	-0.45	-0.85	<u>0.80</u>	-0.79				Cu	0.33	-0.36	0.46	<u>0.63</u>				Cu	-0.64	-0.24	0.38					
Ni	-0.69	-0.98	<u>0.80</u>	-0.96	<u>0.92</u>			Ni	-0.24	-0.15	<u>0.73</u>	<u>0.94</u>				Ni	-0.24	<u>0.79</u>	-0.16	-0.28				
Cr	-0.32	-0.50	<u>0.97</u>	-0.50	<u>0.71</u>	<u>0.66</u>		Cr	<u>0.75</u>	-0.17	<u>0.65</u>	<u>0.99</u>	<u>0.97</u>			Cr	-0.24	<u>0.74</u>	-0.70	-0.84	0.21			
Zn	<u>0.82</u>	<u>0.97</u>	-0.68	<u>0.99</u>	-0.72	-0.93	-0.49	Zn	0.09	0.54	0.01	-0.31	0.11	-0.04		Zn	-0.83	-0.44	<u>0.75</u>	0.03	-0.24	-0.15		
SITE = ROADSIDE , SIZE = PM10										SITE = ROADSIDE , SIZE = PM2.5														
Table 3c										Table 3d														
PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	
Fe	0.47							Fe	-0.12							Fe	-0.12							
Pb	<u>0.62</u>	0.41						Pb	-0.79	-0.09						Pb	-0.79	-0.09						
Mn	0.23	-0.59	-0.32					Mn	0.33	-0.63	0.13					Mn	-0.31	-0.63	0.13					
Cu	0.22	<u>0.74</u>	-0.26	-0.20				Cu	0.33	-0.64	-0.24	0.24				Cu	0.33	-0.64	-0.24	0.38				
Ni	0.22	<u>0.79</u>	<u>0.67</u>	-0.88	<u>0.95</u>			Ni	-0.24	<u>0.79</u>	-0.26	<u>0.54</u>	<u>0.95</u>			Ni	-0.24	<u>0.79</u>	-0.16	-0.28				
Cr	0.29	<u>0.94</u>	<u>0.51</u>	-0.82	-0.76	-0.51		Cr	-0.24	<u>0.74</u>	0.38	0.45	-0.76	-0.51		Cr	-0.24	<u>0.74</u>	-0.70	-0.84	0.21			
Zn	-0.05	-0.23	-0.79	<u>0.69</u>	-0.76	-0.51		Zn	-0.83	-0.44	<u>0.75</u>	0.45	-0.76	-0.51		Zn	-0.83	-0.44	<u>0.75</u>	0.03	-0.24	-0.15		
SITE = RURAL , SIZE = PM10										SITE = RURAL , SIZE = PM2.5														
Table 3e										Table 3f														
PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PMCONC	Fe	Pb	Mn	Cu	Ni	Cr	Zn	
Fe	0.31							Fe	-0.29							Fe	-0.29							
Pb	-0.22	-0.46						Pb	0.07	0.14						Pb	0.07	0.14						
Mn	-0.52	0.30	-0.32					Mn	-0.22	<u>0.54</u>	0.12					Mn	-0.22	<u>0.54</u>	0.12					
Cu	<u>0.83</u>	0.43	-0.37	-0.59				Cu	0.29	-0.30	-0.20	-0.54				Cu	0.29	-0.30	-0.20	-0.16				
Ni	-0.49	-0.11	<u>0.77</u>	-0.01	0.24			Ni	-0.25	<u>0.72</u>	-0.24	-0.29	0.24			Ni	-0.25	<u>0.72</u>	-0.24	0.27	-0.48			
Cr	-0.10	<u>0.64</u>	-0.23	<u>0.71</u>	-0.36	-0.40		Cr	0.16	0.29	0.21	-0.29	-0.36	-0.40		Cr	0.16	0.29	0.21	0.26	0.10			
Zn	-0.24	0.03	-0.16	0.13	-0.36	-0.40		Zn	0.12	0.07	-0.04	0.17	-0.36	-0.40		Zn	0.12	0.07	-0.02	-0.23	-0.03	-0.21		
SITE = URBAN , SIZE = PM10										SITE = URBAN , SIZE = PM2.5														

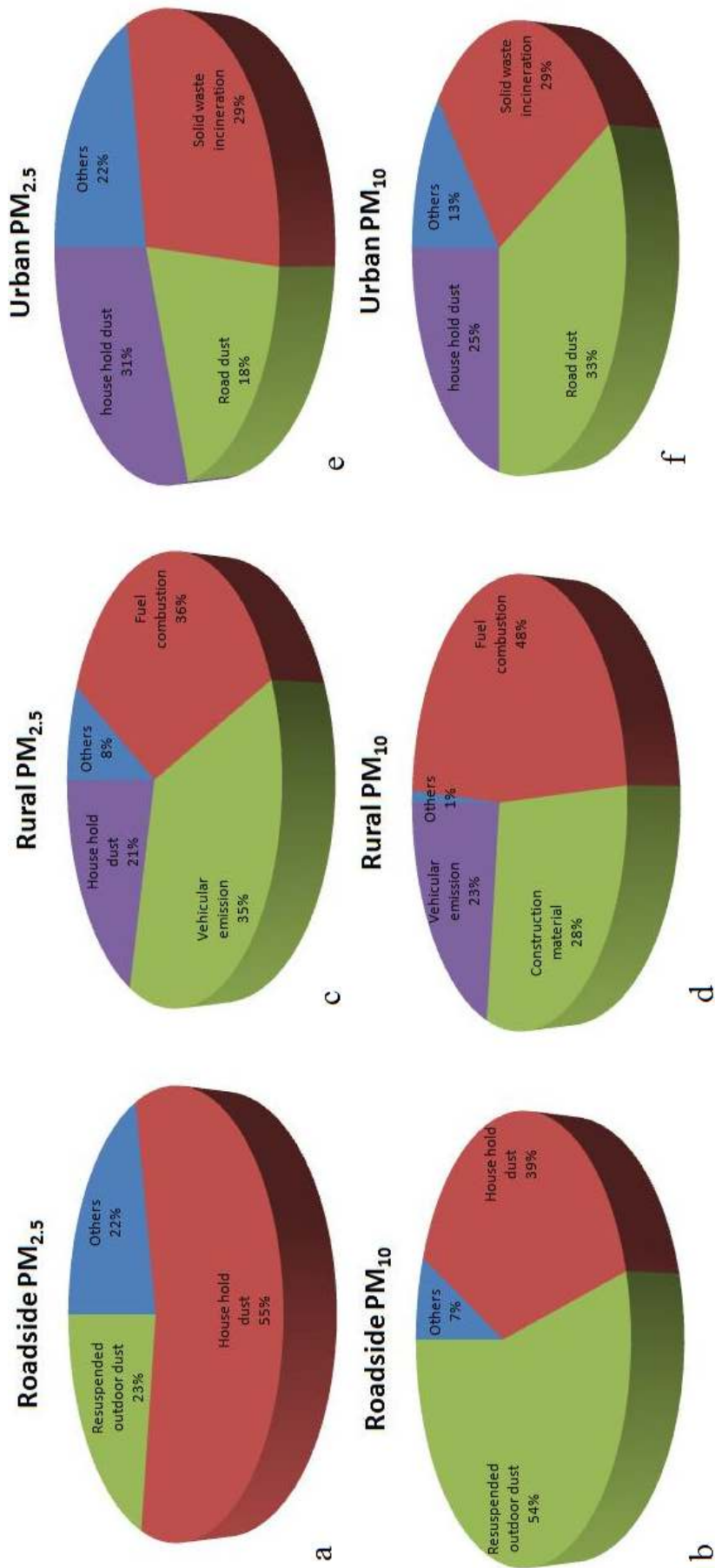


Fig. 4. Pie diagrams showing source distribution of particle constituent at three sites in PM<sub>10</sub> and PM<sub>2.5</sub>.

emitted from domestic heating (Ward and Noonm, 2007), while Mn and Pb can be attributed to smoking and cooking (Lai and Chen, 2007; Ghio *et al.*, 2008). Dust from house carry chemicals included in paints (Booher, 1988). Factor two is represented by Fe and Zn with 22.7% variance and was attributed to penetration from outdoors. Zn is emitted from abrasion of tires (Kulshrestha *et al.*, 2009a, Massey *et al.*, 2012b) while Fe can be emitted from resuspended road dust. In PM<sub>10</sub> at roadside two sources were identified explaining 93% of source contribution (Fig. 4(b)). PM<sub>10</sub> concentration, Fe, Mn and Zn comprised first factor with 54% variance and is attributed to outdoor dust seeped indoor. Factor two represents Pb, Cu, Ni and Cr with 39% variance and is attributed to household dust emitted by walls, cleaning, cooking other human activities.

#### Rural Site

Rural houses in Villages are basically made of mud, grasses and bamboos, with very less traffic; roads are made up of mud with lots of greenery around. In winters where fields are covered with crops, in the summers they are barren and dry. Construction is one of the most flourishing industries on this site. As the people living here are either farmers or laborers engaged in construction or any other temporary activities, they belong to low income group. At this site cooking is done on either chullas made of mud or oil stoves. Fuel used for such cooking is either wood, coal or kerosene. At this site electric power is not continuous and therefore at night people generally use oil lamps for lightening purposes. Three factors were identified in PM<sub>2.5</sub> which explains 92.5% of sources (Fig. 4(c)). Factor one comprise PM concentration Ni and Cr with 36% variance and is attributed to fuel combustion (Kulshrestha *et al.*, 2009a; Massey *et al.*, 2013). Factor two is comprised of Pb and Zn with 35% variance and is attributed to vehicular activity which are used for agricultural and construction purposes (Park and Dam, 2010). Factor three comprises Fe and Cu with 21% variance and is attributed to house dust. In PM<sub>10</sub>, three factors were determined (Fig. 4(d)) which explains 99% of the sources. Factor one comprises Fe, Pb, Ni and Cr with 48% variance and is attributed to coal and other fuel combustion. Factor two comprises Fe, Cu and Cr with 28% variance and is attributed to construction material seeped inside the house. Factor three is comprised of Pb and PM concentration with 23% variance and is attributed to vehicular emission.

#### Urban Site

There are usually modern types of houses, having parking garages inside or beneath the houses. The houses were well planned and evenly distributed having good ventilation condition and also have greenery around this site. Outside the house there are markets for daily needs, food shops, restaurants and other activities like automobile repairing, Xerox shops. Waste dumping and incineration activities can be seen in small piles at these sites also. Three factors were determined in PM<sub>2.5</sub> at urban site which explains 78% of sources (Fig. 4(e)). Fe, Mn, Ni and Cr represent factor 1 with 29% variance which is attributed to solid waste

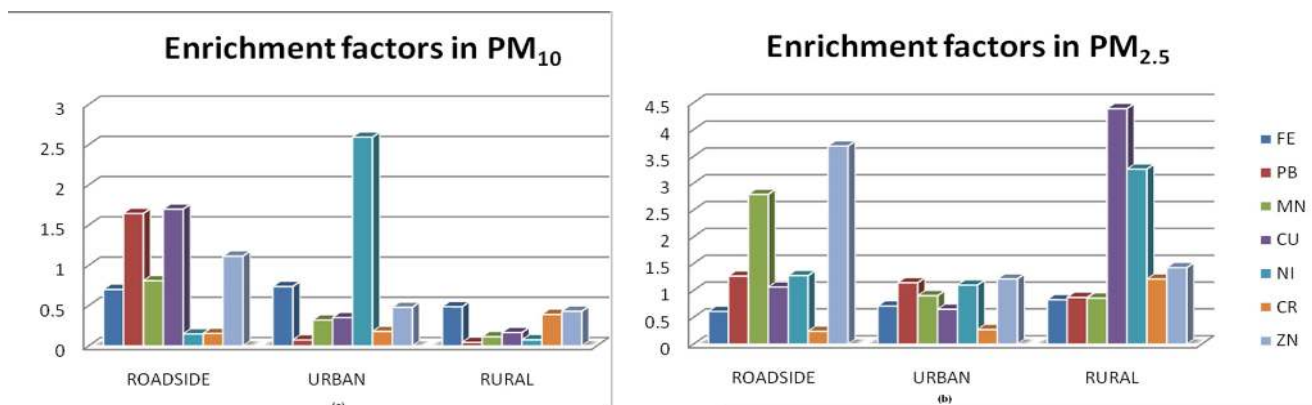
incineration activities (Cao *et al.*, 2008, Massey *et al.*, 2012b). Factor two is represented by PM concentration, Cu and Cr with 18% variance and is attributed to road dust. Factor three is comprised of Zn and Pb with 30.9% variance and are attributed to household dust. Pb is emitted from paint on the walls (Jonathan and John 2003). Three factors were determined in PM<sub>10</sub> which explains 86.7% of sources (Fig. 4(f)). PM concentration and Cu represent first factor with 32.6% variance and is attributed to road dust. Factor two is represented by Fe, Mn and Cr with 29% variance and is attributed to solid waste incineration (Yoo *et al.*, 2003). Factor three is represented by Pb and Ni with 25% variance and is attributed to household dust. The interpretation obtained from the PCA analysis is well justified by intercorrelation of metals.

#### Enrichment from Outdoors

Indoor aerosols may originate from outdoor air. A comparison between the atmospheric aerosol elements, when they are found to be higher than expected level in their natural forms according to their proportions in the background aerosol (outdoors), is of utmost importance. This comparison enables us to decide whether these elements are emitted indoors or originated from outdoors. This can be done by calculating enrichment ratios for the various elements in aerosol relative to the outdoors, usually normalized to an element considered as being the most unambiguous indicator of source material (Rahn, 1976). Here the PM concentration is taken as reference assuming all PM in the air to be of outdoor origin to determine enrichment factors in metals indoors. The enrichment factors can be calculated as:

$$EF_{\text{INDOOR}} = \{X_{\text{INDOOR}}/PM_{\text{INDOOR}}\} / \{X_{\text{OUTDOOR}}/PM_{\text{OUTDOOR}}\} \quad (1)$$

where X is the concentration of the element whose enrichment ratio is to be determined. Elements with enrichment factors close to unity are likely to have the outdoor air as the main source and are considered “non-enriched”. Elements with enrichment factors significantly greater than unity are called “enriched” and probably have another major source besides the outdoor air. Fig. 5 shows the enrichment factors of analyzing metals in PM<sub>10</sub> and PM<sub>2.5</sub> respectively at three sites. At roadside, Pb, Cu and Zn with enrichment factors (EF) 1.60, 1.70 and 1.12 respectively were enriched in PM<sub>10</sub>, while in PM<sub>2.5</sub> Pb, Mn, Cu, Ni and Zn (EF = 1.27, 2.79, 1.06, 1.28, 3.69 respectively) are enriched and may have some other sources indoors. At urban site only Ni (EF = 2.59) was found to be enriched in PM<sub>10</sub> while in PM<sub>2.5</sub> Pb, Ni and Zn (1.14, 1.10, 1.12, 1.21 respectively) are found to have enrichment factor greater than one and therefore have some sources indoors which are well discussed above. At the rural site no metal in PM<sub>10</sub> showed EF greater than one which means that all metals analyzed in coarse mode particles indoors have penetrated from outdoors. In PM<sub>2.5</sub> Cu, Ni, Cr and Zn (EF = 4.39, 3.26, 1.21, 1.43 respectively) showed enrichment greater than one. Which means that indoor sources of these metals contribute to fine sizes while outdoor sources to coarse mode.



**Fig. 5.** Enrichment factors of metals with respect to outdoors (taking PM concentration as the reference) at three sampling locations.

Pb was found to be enriched at the roadside and urban site which may be due to wall dust indoors at these sites which contains paint. Colored pigments adopted in paints include iron oxides, manganese dioxide, lead antimonate, chromium oxide, cadmium selenide, antimony oxide and lead, zinc and barium chromates. Lead is also employed as a drier or corrosion inhibitor in “lead-free” paints (Booher, 1988). At the rural site Pb in both size particulate are emitted from outdoor sources. It is because in India, rural homes use slaked lime ( $\text{CaCO}_3$ ) to color homes, in place of paints and distemper. Ni and Zn are found to have additional sources indoors at all sites. This might be due to the use of cosmetics, household utensils and burning cigarettes. High levels of Zn indoors compared to outdoors have also been reported by Feng and Barratt (1993). Madany *et al.* (1994) reported Cr concentration to be associated with Ni and Zn suggesting a common source for these metals indoors. Cr was found to have additional sources at rural site and that too in  $\text{PM}_{2.5}$ , which might be due to burning kerosene for food cooking and lightening house purpose, which emits Cr. At other two sites Cr is emitted from outdoor sources. Fe at all sites and sizes was found to have EF less than one and therefore is emitted from outdoor sources only.

## CONCLUSION

The study concluded that the quality of the air was found to be relatively better at urban site as the site was away from major vehicular pollution and has greenery around whereas the roadside, and rural areas were much affected from the vehicular traffic and biomass burning. At all the three location iron was found to be dominating element followed by Zinc, Lead and Chromium. As a fact, contaminated household dust might represent a significant route of exposure for humans to these toxic metals. Results obtained from Correlation and Principal component analysis indicated vehicular, resuspension and waste incineration were the most common sources of particulate matter and their associated metal ions at outdoor points whereas in indoors they are generated due to the fuel combustion which happens during cooking, frying and the other sources were smoking and house dust. The reported dominated metals were found

to be enriched in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  both size particles. Pb, Ni, Mn and Cu were found to be enriched indicating their indoor sources at all the three studied locations. Thus the outcomes of the study are of practical importance in identifying sources and processes that control levels of fine particulate matter in a respirable size range which determines human susceptibility to pollution processes. Further more studies are required to establish major sources of some metals within the house and bioavailability of these metals specially in the case of women and young children.

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