



## Seasonal Variations and Sources of Heavy Metals in Free Fall Dust in an Industrial City of Western India

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Received: April 24, 2014; Accepted in Revised Form: June 11, 2014

**Abstract:** This study investigates seasonal variations in average concentrations of metals in free fall dust samples (350) collected at various sampling sites situated in five different zones of an industrial city Kota, India. Average concentrations of heavy metals (Cu, Cd, Zn and Pb) were higher in winter and lower in summer and reverse trend was observed for crustal metals (Fe, Ca and Mg). Overall, the order of average concentrations of heavy metals were Zn > Pb > Cu > Cd in both seasons. Seasonal differences in metal concentrations were due to differences in wind direction, wind strength, temperature, relative humidity and anthropogenic activities at sampling sites. Enrichment factor and positive correlation between anthropogenic metal species such as Cu and Cd; Cu and Zn; Cu and Pb; Cd and Zn; Cd and Pb; Zn and Pb in both seasons indicate that their origin source is common i.e. coal combustion at thermal power station.

**Key words:** Free fall dust • Heavy metals • Wind direction • Enrichment coefficients • Thermal power station • Correlation coefficients

### INTRODUCTION

Urbanization is a process which involves economic and industrial development and consequently population growth. This in turn leads to higher energy production and consumption, resulting in problems related to air pollution. As reported in previous studies [1,2], air pollution is a major problem in urban areas due to emissions from transportation and the interaction of air pollutants originating from a variety of sources and may have a significant effect on the environment. Emissions from the urban atmosphere which originate from anthropogenic activities such as the use of motor vehicles, open burning, coal burning and industrial emissions [3-5], are the major sources of air pollution in Kota city [6]. Nevertheless, airborne particles in the atmosphere have serious environmental impacts on climate [7, 8], biogeochemical cycling in ecosystems [9, 10], outside visibility [11] and health of living organisms [12, 13].

Over the last few decades, intensive monitoring programs of heavy metals in atmospheric precipitations have been carried out worldwide, which are mainly focused on the chemical characteristics, deposition fluxes and long-term temporal trends [14- 18]. According to these studies, the loadings and sources of heavy metals in precipitation have great spatial variability over different locations, which is mainly caused by different meteorological conditions (prevailing wind directions and type, frequency and amount of precipitation) and the emission patterns of pollutants (emission sources, distance from emission sources and the sampling sites). Therefore, more in-depth studies, especially on the regional level, of trace metal pollution in the air are necessarily important for the assessment of impacts of heavy metals on ecosystems [19, 20]. Very few studies have reported the heavy metal load and health implications of particulate matter in Indian cities despite many cities being densely populated and polluted [21].

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City Kota has a Kota Super Thermal Power Station (KSTPS), a major coal based thermal power plant, where huge amount i.e. approximate 3000 metric tonne per day of fly ash (homogeneous mixture of several metal oxides viz.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{CuO}$ ,  $\text{CdO}$ ,  $\text{MnO}_2$ ,  $\text{NiO}_2$ ,  $\text{ZnO}$ ,  $\text{PbO}$  etc.) is produced and released in the atmosphere. Several small and large scale industries including DCM Shriram Consolidated Limited (DSCL), Multimetals Limited, Samtel Glass Limited, Chambal Fertilizers and Chemicals Limited (CFCL), Shriram Fertilizers and Metal India, ShriramRayons and a number of Kota stone cutting polishing units further enhance the heavy metal burden of the city environment. Research studies related to atmospheric pollution in Kota city are scanty and mostly been restricted in the form of internal reports. Therefore, the present study was conducted, with the main objectives being: (1) to determine the composition of free fall atmospheric dust in terms of crustal (Fe, Ca and Mg) and anthropogenic (Cu, Cd, Zn and Pb) metals at various sampling sites located in five different zones covering entire Kota city area; (2) to identify possible sources of heavy metals associated with free fall atmospheric dust using enrichment factor and Pearson correlation coefficient; (3) to study the effect of climate on the concentration levels of heavy metals as a function of sampling sites, distance from KSTPS, seasons and meteorological parameters such as temperature, relative humidity, wind speed and wind direction. The study has indicated the influence of coal based thermal power plant and industrialization of the rapidly growing city on the concentration levels of heavy metals in free fall atmospheric dust.

**Background of the Study Area:** Kota is one of the major industrial cities of Rajasthan States in India. It is situated  $25^{\circ}11\text{ N}$  and  $75^{\circ}51\text{ E}$  on the eastern bank of river Chambal in the southern part of Rajasthan with an elevation of 271 meters (889 feet) above the sea level on the south-east of Aravali ranges. According to the 2011 census Kota district has a population of 19,50,491 residents. The total geographical area of the district is 5,21,133 hectares as per land. Kota has a semi arid climate with temperature varying from minimum of  $6^{\circ}\text{C}$  in winter (January) to maximum  $47^{\circ}\text{C}$  in summer (June) and an average annual rainfall about 885.6 mm. The monsoon season follows with comparatively lower temperatures, but higher humidity and frequent, torrential downpours. The study of wind roses makes it possible to conclude that the predominate

wind directions in the city during this study were north-east in winter (25.74%) and summer (15.31%). Many large and small scale industries are present due to availability of river water and power. Kota district is a power production centre of the country where coal based KSTPS is situated. A popular cost effective building stone i.e. Kota stone is being excavated, cut to various sizes and polished in more than 200 units generating huge amount of slurry waste containing mainly  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{SiO}_2$ .

## MATERIALS AND METHODS

**Sampling Sites:** The sampling sites for atmospheric precipitation were chosen with the help of cartographic charts, field job and GPS (Global Positioning System). The choice of the sampling sites followed some criteria laid by ASTM D 5111 Standards [22]. These criteria were: I) distance from point source (approximately a radius of 12 km from KSTPS); ii) predominant wind direction; iii) the distance from obstacles that could interfere in sampling (twice the height of obstacles); and iv) logistics (security, access, electric power supply). The entire city area was divided into five zones (Figure 1). The location of the zones with respect to the point source KSTPS of emissions and possible source of heavy metal emission in them are presented in Table 1.

**Sample Collection and Analysis:** In total, 350 free fall dust samples ( $n = 1\text{ zone} \times 10\text{ samples} \times 7\text{ months} = 70\text{ samples}$ , so  $n = 5\text{ zones} \times 10\text{ sample} \times 7\text{ months} = 350\text{ samples}$ ) were collected monthly in both summer (March, April and October) and winter (January, February, November and December) seasons during 2011-2012 at five zones (10 sample per month). The sample size was estimated using the statistic formula,  $n = (Z \cdot \text{SD} / e)^2$ , where Z is standard score, SD is standard deviation and e is half of the width of a 95% confidence interval on the mean [23]. The calculated number of samples was 346. Dust samples falling freely due to gravity were collected in all zones at a height of 6 m above the ground surface on plastic trays of  $1\text{ m}^2$  area. All free fall dust samples collected, here, represent only dry fall out, as there was no rain during the sampling period. After sampling, dry depositions were scraped off the trays and these trays were washed with milli-Q water to recover stuck particles. The water was evaporated slowly at  $50^{\circ}\text{C}$  and the residue was mixed and homogenized with the scraped samples [24]. Then samples were digested for the analysis.



were inserted during the analytical measurement to detect contamination and drift. The elemental concentrations of the blanks were < 1 % of the mean analyte concentration for all metals and the precision (RSD) of the control standards and replicates were generally lower than 5%. The recovery rates for the metals in the standard material ranged from 96 to 99%. Detection limits were: 0.02 ppm for Fe; 0.005 ppm for Zn; 0.01 ppm for Cu; 0.002 ppm for Cd; 0.0005 ppm for Mg; 0.05 ppm for Pb; 0.06 ppm for Ca.

The results were summarized into a multi-elemental database using MS – Excel 2007. Analysis of variance (ANOVA) on all experimental data was performed with SPSS version 16 software.

## RESULT AND DISCUSSION

### Seasonal Variations of Heavy Metals Concentration:

The average concentrations of all the analyzed metals (Fe, Ca, Mg, Cu, Cd, Zn and Pb) of environmental concern in free fall dust collected at various sampling sites of five different zones in winter and summer seasons are given in Table 2. Average concentrations of Cd, Zn and Pb in all the studied zones are found to exceed WHO standard limits which might be due to coal combustion activity at point source KSTPS. We observe variations in the elemental concentration as a function of sampling sites, distance from sources of emissions and the wind velocity (speed and direction).

Among all the studied zones, zone 1 was found to have highest average concentrations of heavy metals i.e. Cu, Cd, Zn and Pb in both seasons due to presence of coal based thermal power plant there while zone 5, which is a

residential area, with least number of anthropogenic sources is found to have lowest concentrations of all the measured metal species in both seasons. North-east direction (21.01%) of wind blow from KSTPS encourages the worrying level of heavy metals in the study region present in fly ash. The relative abundances of these heavy metals in free fall dust samples follow the order Zn > Pb > Cu > Cd in all zones. Despite the use of lead free petrol, high concentration of Pb could be due to Pb particles in street dust accumulated from earlier vehicular exhaust for a long time due to its high residence time in environment [27].

Seasonal variation of the average concentrations of all the analysed metals were generally consistent from site to site; but were different depending on the metal species. In all the zones, concentrations of crustal metal species viz. Ca, Mg and Fe were lower in winter and higher in summer while heavy metal species viz. Cu, Cd, Zn and Pb concentrations were higher in winter and lower in summer. The difference in concentration levels between the two seasons i.e. winter and summer can be explained by difference in meteorological conditions. During the sampling period in winter, Kota city had witnessed low average temperature (19.7 °C), high relative humidity (42.29%) and low wind speed (2 Km/h) leading to high levels of anthropogenic metal species in ambient air while summers had high average temperature (29.0 °C), low relative humidity (22.05%) and high average wind speed (4 Km/h) causing decreased concentrations of anthropogenic metal species (Table 3). The high wind strength during summer is responsible for deflation or entrainment and transport of crustal metals as coarse

Table 2: Average concentrations (ppm) of analyzed metals in five zones in winter and summer seasons of Kota city in 350 free fall dust samples

Metal	WHO-2004 (ppm)	Season	Average concentrations of metals in ppm				
			Zone 1(n=70)	Zone 2(n=70)	Zone 3(n=70)	Zone 4(n=70)	Zone 5(n=70)
Mg	30	Winter	11.6412	11.1502	12.5099	12.9228	13.5926
		Summer	12.8683	12.4835	14.0077	14.5591	15.2426
Ca	75	Winter	1238.38	1199.15	1452.10	1717.48	1866.11
		Summer	1627.14	1584.44	1885.23	2138.11	2320.64
Fe	0.3	Winter	68.1247	66.4600	73.6781	75.8754	78.1915
		Summer	77.4418	76.4287	81.9803	83.2715	87.1370
Cu	2.0	Winter	0.9959	0.7698	0.8422	0.7430	0.6618
		Summer	0.8961	0.5556	0.6942	0.5415	0.4501
Cd	0.003	Winter	0.1691	0.1093	0.1277	0.1039	0.0801
		Summer	0.0741	0.0552	0.0598	0.0523	0.0459
Zn	3.0	Winter	5.7631	4.5043	4.9548	4.3678	3.8493
		Summer	5.0828	3.7207	4.0352	3.4837	3.1151
Pb	0.01	Winter	3.2195	2.1639	2.6018	2.8155	1.2996
		Summer	2.5212	1.6974	1.8840	2.1298	1.0686

\*n = No. Of samples

Table 3: meteorological conditions at the sampling zones during sampling periods

Meteorological parameter	Winter	Summer
Temperature (°C)	19.7 ± 3.7	29.0 ± 2.6
Humidity (RH) (%)	42.29 ± 5.4	22.05 ± 9.7
Wind speed (km/h)	2.0 ± 0.8	4.0 ± 1.0
Rain fall (mm)	9.0	0.0

Table 4: Correlation coefficients between concentrations values of analyzed metals in free fall dust in Kota city (\*significant at 5% level)

Metal	Mg	Ca	Fe	Cu	Cd	Zn	Pb
Mg	1.000	0.496*	0.665*	-0.273	-0.150	-0.353	-0.346
Ca	0.563*	1.000	0.519*	-0.233	-0.370	-0.359	-0.385
Fe	0.483*	0.584*	1.000	-0.258	-0.146	-0.230	-0.398
Cu	-0.209	-0.236	-0.251	1.000	0.153	0.285*	0.259*
Cd	-0.399	-0.316	-0.288	0.442*	1.000	0.501*	0.369*
Zn	-0.278	-0.246	-0.270	0.300*	0.506*	1.000	0.542*
Pb	-0.333	-0.258	-0.395	0.472*	0.493*	0.596*	1.000

\* Winter, n=200 and \*Summer, n=150

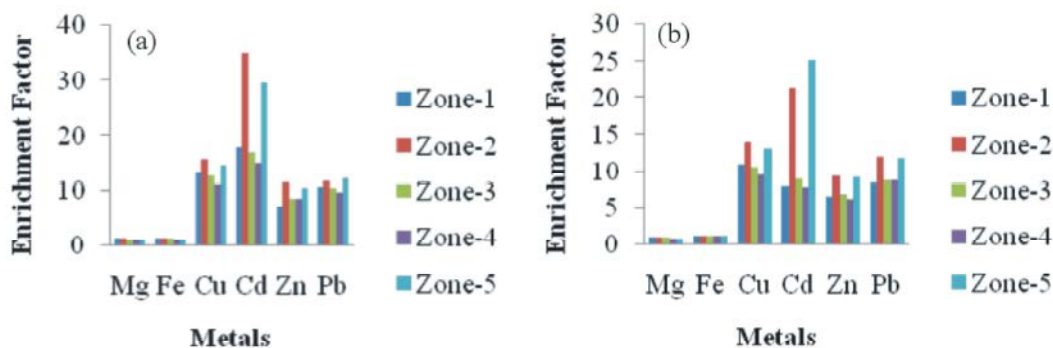


Fig. 2: Enrichment factors of metals in free fall dust at each zone in Kota city in (a) winter and (b) summer seasons

particles are influenced by gravity [28] whereas wind strength available to transport these metals drops significantly in the winter. Secondly, the stable and cold conditions during winter months favour the prolonged life of ambient particles in the atmosphere leading to elevated levels of heavy metals in free fall particulate matter.

The results obtained in the present study are in accordance with earlier studies done in India [29 - 30] and other countries [31 - 32].

In winter and summer periods, the Pearson correlation coefficient ( $r$ ) was calculated from the elemental concentration in order to predict the possibility of a common source (Table 4). Significant positive correlations found between Mg and Ca; Mg and Fe; Ca and Fe indicate that these metals have a common source, possibly natural soil. Similarly, significant positive correlation found between Cu and Cd; Cu and Zn; Cu and Pb; Cd and Zn; Cd and Pb; Zn and Pb in both seasons suggest their common origin i.e. point source KSTPS mainly beside other industrial activities.

Enrichment Factor: Calculation of enrichment factor (EF) helps to determine whether a certain element has an

additional or anthropogenic source other than its major or natural source. Calcium (Ca) has been used as a reference element for an EF evaluation, assuming that the contribution from its anthropogenic sources to the atmosphere is negligible [33], this study used the EF calculation formula as follows:

$$EF = \frac{(X/C)_{\text{precipitation}}}{(X/C)_{\text{reference material}}}$$

Where  $x$  is the concentration of the ion of interest and  $c$  is the concentration of the reference ion.

If the EF value approaches unity, then crustal sources are predominant while an  $EF > 5$  indicates that a large fraction of the element can be attributed to non-crustal or anthropogenic sources [34]. Figure 2 shows the seasonal mean enrichment factors (EFs), based on average seasonal metal concentration of heavy metals identified in free fall dust collected from the five zones. EF values for Cd were the highest, followed by Cu, Pb and Zn and their EFs were much higher than 5. This indicates that the collected dust samples were extremely contaminated by

anthropogenic sources. Seasonal EF values of Cu, Cd, Zn and Pb metal species showed similar trends in both the seasons. The higher EF values of metals (Cu, Cd, Zn and Pb) during winter season than summer may be attributed to transport of fly ash from coal combustion activity from point source KSTPS and stable and cold meteorological conditions.

### CONCLUSION

It is concluded that the concentrations of all anthropogenic metal species (Cu, Cd, Zn and Pb) were highest in zone 1, which is located within 2 Km radii from point source KSTPS while lowest in zone 5, mainly a residential area, located far away from thermal power plant and having comparatively low traffic load in both winter and summer seasons. Concentrations of anthropogenic metal species are found higher in winter and lower in summer while reverse trend is observed for crustal metal species. The high enrichment coefficients and positive correlations showed that heavy metals viz. Cu, Cd, Zn and Pb have similar origin source in the city and particularly can be related to point source coal based thermal power plant besides other industrial activities and traffic load.

In view of the warning level of heavy metals in the city environment there is an urgent need to maintain the receptive capacity of the atmosphere by adopting proper abatement procedures by industrial and mining sector for maintaining the healthy environment to breathe.

### ACKNOWLEDGEMENTS

The authors are thankful to A. Mukhopadhyay and DST, New Delhi for instrumental support provided through DST – FIST project sanctioned to Govt. College, Kota and University Grants Commission, New Delhi for Minor Research Project sanctioned to Manju Meena for this work.

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