

# Chemical Characterization of Ambient Pm<sub>10</sub> Aerosol in a Steel City, Rourkela, India

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## **Abstract**

A comprehensive study for ambient particulate air pollution was carried out between January 2011 and December 2011 in a steel city, Rourkela to investigate the  $PM_{10}$  aerosol mass concentration and its major metallic and anionic characterization. The 8 hourly average concentration of  $PM_{10}$  varied from  $80.88\mu g/m^3$  to  $225.93\mu g/m^3$ . Major heavy metals obtained are iron (102.14 ng/ $m^3$ ), aluminium (50.53 ng/ $m^3$ ) and zinc (41.90 ng/ $m^3$ ), while sulphate (1920 ng/ $m^3$ ) dominates the anionic species. Both heavy metals and anions followed the same seasonal trend as  $PM_{10}$  showing a lower concentration during summer and monsoon and higher values during winter and spring. These seasonal variations can be explained by the nature of sources, climatic characteristics of the city and anthropogenic activities near monitoring sites. Spearman rank correlation study was performed between  $PM_{10}$  and its major chemical constituents. Ambient particulate iron of the steel city has obtained inverse spearman rank correlation with Ni, Zn, Cu and Al.

**Keywords:** Aerosol, PM<sub>10</sub>, heavy metals, anions, steel city.

## Introduction

Chronic exposure to air pollutants is a worldwide problem<sup>1</sup>. Air pollution especially those in south and southeast Asia has been of considerable interest from both scientific and regulatory perspectives because of its impact on global atmospheric chemistry, climate change<sup>2,3</sup>, rapid population growth and urbanization<sup>4</sup>. Atmospheric aerosol is termed as tiny liquid or solid particulate matter suspended in the air. Aerosols have received increasing attention due to the roles that they play in environmental processes<sup>2,5</sup>. Atmospheric aerosols play both direct and indirect roles in various atmospheric phenomena<sup>6</sup>. The direct effect includes absorption or scattering of solar irradiance by aerosols while indirect influence modifies the cloud microphysical properties<sup>7</sup>. The scattering type of aerosols incorporating inorganic and organic materials increase the atmospheric albedo resulting decrease in atmospheric irradiance to the earth surface causing cooling effect<sup>8</sup>. The interaction of these aerosols with soil might bring about changes in physical as well as chemical nature of top layer of soil as well as reduce the Air Pollution Tolerance Index (APTI) of plants<sup>9,10</sup>. Aerosols are unique among air contaminants because of their potential complexity in terms of both chemical composition and physical properties<sup>11</sup>.

Particulate matter with aerodynamic diameters less than or equal to 10  $\mu m$  (PM $_{10}$ ) have been found to be associated with health problems such as increased in daily mortality and asthma  $^{12,13}.$  Moreover, atmospheric electric conductivity is reduced in an aerosol polluted atmosphere as compared to that in a clean atmosphere  $^{14}.$  Several studies have examined the composition and sources of PM $_{10}$  aerosols  $^{15,16}.$  Some of the main constituents

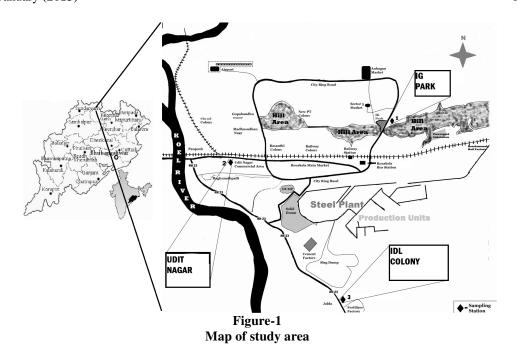
of aerosols that can hazardous to health are found to be heavy metals like mercury, lead, nickel etc. Beside industries, other causatives of heavy metals pollution are found to be wastes that are generated by different sections such as e-waste, solid waste in urban areas<sup>17,18</sup>. Researches on aerosols have attained equal importance in recent years due to its impact on the climate and environment.

The  $PM_{10}$  sampling was carried out at three sites in steel city, Rourkela between January 2011 to December 2011 inorder to study the respirable fraction, seasonal effects and their correlation on chemical composition of the aerosols. An effort was made to estimate the aerosol chemical characteristics.

The widespread concern of ambient particulate air pollution led the present study to focus on characterization of atmospheric trace metals and soluble ions in aerosols over the Indian steel city. Also, the investigation of aerosol chemistry in the steel city of India to date is limited for  $PM_{10}$ , more investigation is needed to understand the chemical composition of aerosol.

# Methodology

**Study Area:** A steel city, Rourkela (22°12' N, 84°54' E) of mean sea level about 219 m is selected as a study area in the present research work. It is located in Sundargarh district of the State of Odisha, India at the heart of a rich mineral belt and surrounded by a range of hills and encircled by rivers. As per 2011 census report of India, population of Rourkela is 6,89,298. It has a tropical climate having average annual rainfall between 160 and 200 mm.



Three monitoring sites have been selected for the present ambient air quality study as shown in figure 1.

**Aerosol Sampling:** Environmental monitoring and assessment has become an important part of environmental impact statement in satisfying the requirements of national environmental policy act. Variations in ambient air quality data are caused by changes in the pollutant emission rate, and meteorological and topographical conditions of the place. Mass concentration of aerosol is a measure of air quality and aerosol source strength at a particular location. The radioactive and other environmental impacts of aerosol strongly depend on their chemical composition, apart from their size distribution<sup>19</sup>. Its evaluation is the fundamental requirement towards assessment of the nature and extent of air quality variables. The PM<sub>10</sub> is being monitored in the present study during January 2011 to December 2011 at Rourkela with the help of a respirable dust sampler (NETEL, NPM-HVS/R) on the quartz microfiber filter paper.

Chemical Analysis: The  $PM_{10}$  concentrations were measured gravimetrically by weighing the particulate mass deposited on the quartz microfiber filters and calculating the total volume of air sampled. Filter papers were stored in envelope and kept in desiccator containing dry silica gel for 24 h before and after the sample collection<sup>20,21</sup>. The amount of air sampled through the weighted filter paper is recorded and the filters are placed in appropriately labelled envelope and transported along with blank filter to the laboratory for analysis. Field and laboratory blank filter samples were routinely analysed for  $PM_{10}$  to evaluate analytical bias and precision<sup>20</sup>.

After gravimetric analysis, a known portion of the exposed quartz microfiber filters were digested in HNO<sub>3</sub> (nitric acid) and

used for trace metal analysis<sup>22</sup>. After digestion a colourless solution was obtained that was evaporated to dryness. Reagent blank was also prepared by using unexposed filter following the same procedure. Cool filtrate was made to a known volume using freshly prepared distilled water and is analyzed for metal constituents using Atomic Absorption Spectrophotometer (Perkin Elmer, AA200) for copper (Cu), chromium (Cr), zinc (Zn), lead (Pb), potassium (K), magnesium (Mg), nickel (Ni), and iron (Fe). During sample analysis, standard solution was repeatedly aspirated to ensure that the calibration was within the limits of control chart. An intensive quality control program was implemented to maintain the accuracy and precision throughout the study. This study also includes the analysis of F and SO<sub>4</sub><sup>2</sup>. The concentration of F was measured by using the Thermo Scientific Orion 9409BN Half-Cell Fluoride and Orion 9609BNWP combination fluoride electrodes, whereas the concentration of SO<sub>4</sub><sup>2</sup> was determined by adding barium chloride to the solution upon which it gives a thick white precipitate of barium sulphate which can be measured spectrophotometrically. Blank samples were also prepared from the unexposed filter papers in the same procedure as that of exposed filter samples and analysed for the anionic species.

**Data Analysis:** Correlation analysis helps in detecting unseen relationships between different parameters in the data. These statistical techniques are now being used in wide verity of applications, even in the detection of earthquakes<sup>23</sup>. Statistical analysis was carried out on PM<sub>10</sub> and its characterized metallic and anionic species. In this study, the Spearman rank correlation analysis has been performed between measured aerosol and its metallic and anionic species to investigate the relationships between them. The Spearman rank correlation coefficient (r) measures the relationship between two variables, the extent to

which one variable increases as the other also increases, regardless of the numerical size of the increase.

## **Results and Discussion**

The population growth in India with increasing urbanization and industrialization, the aerosol mass concentration over the Indian sub-continent is found to increase<sup>24</sup>. The knowledge of aerosol loading is important as it can change the weather and climatic patterns. In order to understand the aerosol loading, continuous monitoring for longer duration is required. There is a scarcity of literature expressing aerosol characterization in Indian steel city data. The statistical summary of metallic and anionic mass concentration of PM<sub>10</sub> is tabulated and presented in table 1 for the study period. The 8-hrly average values of PM<sub>10</sub> are in the range of 80.88 µg/m<sup>3</sup> to 225.93 µg/m<sup>3</sup> during January 2011 to December 2011. The occurrence and prevalence of heavy metallic and anionic contamination have been increased by anthropogenic activities. In addition to industrial emissions, large vehicular traffic also contributed to the high level of PM<sub>10</sub> aerosol.

Variation of Trace Metallic and Anionic Composition: The observed levels of PM<sub>10</sub> aerosol patterns reflect the seasonal variations in their emissions. The fine particles are mainly secondary aerosols largely emitted through the reaction of atmospheric gas, whereas most of the coarse particles are directly emitted into the atmosphere. In order to study the similarities and differences in chemical composition of aerosol, histograms representing the mass fractions of various anionic and metallic constituents in the aerosol samples are presented in figures 2 and 3. Significant amount of metals like Fe (102.14) ng/m<sup>3</sup>), Cr (30.86 ng/m<sup>3</sup>), Zn (41.90 ng/m<sup>3</sup>), K (30.94 ng/m<sup>3</sup>), Mg (31.08 ng/m<sup>3</sup>) and Al (50.53 ng/m<sup>3</sup>) have been measured in the one year duration of study. Comparatively higher iron concentration may be due to the influence of nearby iron and steel industry. The Zn and Pb are mostly trace elements from fossil fuels. Copper may have industrial as well as crustal source.

Since the major sources of sulphate are fossil fuel burning and industrial activities, comparatively higher mass fraction of  ${\rm SO_4}^{2^{12}}$  indicate the anthropogenic influence in the study area. The study area may be characterized by moderated anthropogenic activities and also it is proximity to a steel plant. Mass concentration of fluoride in air could be due to crustal origin or from nearby industrial sources like fertilizer plants and coal operations. More measurements are required to assess the contribution of individual sources.

The results of spearman rank correlation study (table 2) shows that iron has inverse spearman rank correlation with Ni (-0.320), Zn (-0.103), Cu (-0.093) and Al (-0.030). Fluoride has inverse correlation with Cr (-0.013), Zn (-0.023), K (-0.069), Pb (-0.158), Mg (-0.081), Si (-0.019) and Al (-0.083). The Si has inverse correlation with Zn (-0.190), Pb (-0.058) and Mg (-0.154). Sources of Zn and Pb in ambient aerosol are non-ferrous metal production, iron and steel manufacturing, and coal and wood combustion. Untill a decade ago, one of the major sources of atmospheric Pb was vehicular emission but the ban on leaded petrol decreases its atmospheric abundance<sup>25</sup>.

Seasonal Variations of PM<sub>10</sub> aerosol and its chemical constituents: The large diversity in aerosol sources can cause significant variation in their chemical composition. To study the seasonal variation of aerosol mass, the observed data for the entire period are grouped according to the different seasons. The climate of Rourkela reflects its summer of the year (April to June) which is associated with strong winds, low humidity that can substantially reduce the level of ambient pollutants. In contrast, the monsoon of the year (July to September) is associated with low wind speeds and medium to heavy precipitation, reduces the air pollution potential of Rourkela. The winter (October to December) and spring (January to March) of the year is associated with low wind speeds and negligible rainfall resulting in increase of the air pollution level of Rourkela.

 $Table - 1 \\ Statistical summary of the metallic and anionic species of PM_{10}$ 

Concentration (ng/m³)	Mean (ng/m³)	Minimum (ng/m³)	Maximum (ng/m³)	SD	Range	
Fe	102.14	67.01	198.19	30.38	131.17	
Ni	17.44	11.06	35.21	5.28	24.15	
Cr	30.86	19.96	60.87	9.24	40.92	
Zn	41.90	27.29	81.98	12.48	54.69	
K	30.94	19.87	60.11	9.19	40.24	
Cu	0.10	0.00	1.16	0.40	2.12	
Pb	1.22	0.29	2.87	0.50	2.58	
Mg	31.08	19.97	60.14	9.24	40.18	
Si	0.74	0.13	2.03	0.35	1.90	
Al	50.53	33.11	98.34	15.05	65.23	
F	1.73	0.78	3.70	0.59	2.92	
$SO_4^{-2}$	1920.0	1260.0	3750.0	570.0	2490.0	

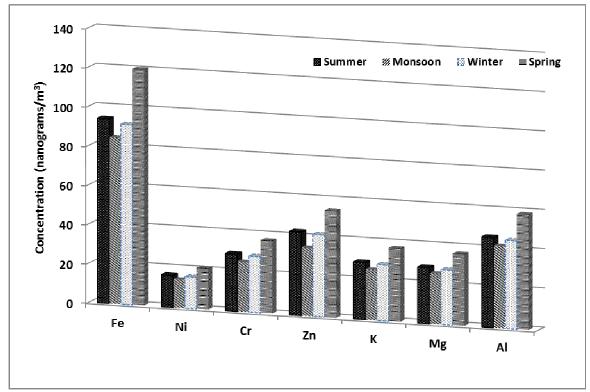


Figure-2 Seasonal variations of heavy metals

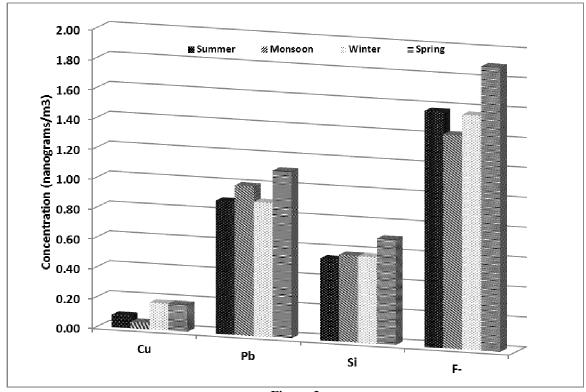


Figure-3
Seasonal variations of selected heavy metals and anion

Table-2
Correlation matrix with Spearman coefficient and p values (gray-shaded) anions and trace element data. Significant correlation in bold (i.e. p< 0.05)

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	$PM_{10}$	Fe	Ni	Cr	Zn	K	Cu	Pb	Mg	Si	Al	F	SO <sub>4</sub> <sup>-2</sup>
PM <sub>10</sub>		0.085	0.085	0.093	-0.065	-0.004	0.073	-0.184	0.082	0.112	-0.283	0.125	0.044
Fe	0.482		-0.320	0.131	-0.103	0.124	-0.093	0.057	0.013	0.115	-0.030	0.267	0.142
Ni	0.483	0.007		0.029	-0.015	0.000	-0.262	-0.213	-0.161	0.011	0.095	0.098	-0.063
Cr	0.444	0.281	0.809		0.007	0.213	0.019	0.089	-0.006	0.005	-0.105	-0.014	-0.123
Zn	0.594	0.394	0.902	0.954		-0.102	0.086	0.104	0.067	-0.190	-0.015	-0.023	0.012
K	0.975	0.305	0.997	0.077	0.400		-0.020	-0.024	0.216	0.017	0.156	-0.069	-0.008
Cu	0.547	0.445	0.028	0.873	0.480	0.870		-0.081	0.007	0.008	-0.017	0.253	-0.004
Pb	0.128	0.640	0.077	0.466	0.392	0.842	0.507		-0.157	-0.058	0.247	-0.158	-0.058
Mg	0.501	0.918	0.184	0.957	0.581	0.072	0.953	0.193		-0.154	-0.168	-0.081	-0.251
Si	0.358	0.345	0.931	0.967	0.116	0.892	0.949	0.631	0.203		-0.256	-0.019	0.188
Al	0.018	0.805	0.433	0.389	0.903	0.198	0.887	0.040	0.164	0.032		-0.083	-0.125
F	0.301	0.026	0.419	0.910	0.848	0.570	0.035	0.191	0.504	0.876	0.497		0.191
SO <sub>4</sub> -2	0.720	0.239	0.606	0.311	0.925	0.948	0.971	0.636	0.036	0.119	0.302	0.114	

The seasonal variations of aerosol mass averaged over different seasons are shown in figures 2 and 3. Mineral dust is one of the contributors of the aerosol composition during all seasons. From the one year measured aerosol data at Rourkela, we can predict that monsoon does affect the atmospheric turbidity with a decrease in aerosol concentration due to wet scavenging and increase in mostly post-monsoon period. Precipitation in monsoon results in washout of  $PM_{10}$  aerosol making atmosphere comparatively clean from dust particles. During the rainy season, particulate matter concentration diminished while much reduction in metal concentration is not very transparent. This suggests that metals are not precipitated and washed by the rain in a big proportion because most of them are in the finer fraction of respirable size and stay in the atmosphere inspite of the precipitation.

Highest level of particulate concentration has been observed during spring with an average value  $156.75~\mu g/m^3$ . Next higher concentration of  $PM_{10}$  aerosol is being observed during winter (129.55  $\mu g/m^3$ ) then summer (122.01  $\mu g/m^3$ ) and minimum during monsoon (102.71  $\mu g/m^3$ ). Lower concentration in summer may be due to wind turbulence that blows away the aerosol from the city. Particulate pollutants are also released from motor vehicles. Humidity plays an important role in modifying the aerosol characteristics such as mean density and size  $^{26}$ . The aerosol concentration is higher in spring and winter, while quite less in monsoon.

Monsoon Pb is slightly higher than the summer as shown in figure 3. During summer, turbulence of wind causes resuspension of road dust and soil dust. Presently, lead in road dust and nearby soil dust is reduced drastically due to use of

unleaded petrol. Hence, it may lead to slightly lower in summer Pb than monsoon.

In this context it is to be emphasized that winter and spring season characterized by calm wind conditions, moderate temperature and scanty rainfall. The major natural sources will be less active during winter and spring seasons. Similarly the wet removal of aerosols also is less efficient during winter and spring. Under the influence of moderately high wind and convective mixing during summer, mineral dust derived from the disturbed soils is lifted in the atmosphere. Scanty rainfall in the winter and spring seasons and consequent longer detention time of aerosols increase the atmospheric concentrations of  $PM_{10}$  and its metallic and anionic mass concentrations. On the other hand, rainfall during monsoon causes washout of the suspended particles resulting in lower aerosol mass<sup>27</sup>.

### Conclusion

The objective of measurements for the aerosol mass and its chemical characterization were to study the variations of the aerosol. This study has investigated the major metallic and anionic species of the  $PM_{10}$  aerosols in steel city, Rourkela, India. The metallic and anionic compositions of the measured aerosol showed pronounced variation. The seasonal variation of the chemical composition in  $PM_{10}$  aerosols can be explained by the nature of sources, the climatic characteristics of Rourkela and the anthropogenic activities near the monitoring sites.

The  $PM_{10}$  exposure has been associated with a variety of adverse health effects. Quantifying the relative source contribution of  $PM_{10}$  is important as it provides policymakers

critical information needed to formulate successful pollution reduction programs. The measured metallic and anionic components in the  $PM_{10}$  aerosols could be attributed to crustal and anthropogenic activities. There is a need for better understanding of aerosol distribution and require source apportionment to have an idea of the various sources and their contribution.

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