



Particulate Associated Trace Metals and Their Cancer Risk Assessment on Commuter Pathways of a Coal Mine City.

Ashok Kumar Dubey^{*1}, Gurdeep Singh¹, Joshy George², Sridevi Jena¹

¹Department of Environmental Science and Engineering, Indian School of Mines, Dhanbad, India.

²Environment Management Division, Central Institute of Mining & Fuel Research, Digwadih, Dhanbad, India

ABSTRACT

Particulate samples were collected and analyzed for their toxic metal contents in winter seasons from four prominent commuter routes in Dhanbad, India. Suspended particulate matter and PM₁₀ concentration during sampling period were 325/276, 327/263, 320/261 and 146/96 µg/m³ for routes 1, 2, 3, and 4 respectively. The enrichment factor indicated anthropogenic inputs of metals with a maximum enrichment for Cd. Principle component analysis for all four routes revealed mixed sources such as mining activities, vehicular emission and coal burning as the prominent sources of metals in particulates in all four routes however route 3 among all showed maximum polluted. The results of the investigation of element composition of particulates, enrichment factor, cancer risk assessment and identification of sources can help to understand and manage the effects of particulates on health and air quality along the prominent road network.

Keywords: Suspended particulate matter; PM₁₀; Enrichment factor; Auto-Rickshaw's, Cancer risk.

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INTRODUCTION

Countries like India, industrial development and urbanization have always walked casually with environment safety norms, which results several environmental problems. With ever increasing population in cities and migration from rural to urban areas increasing pressure on transportation activities to meet the demand of a public which increasing tremendous number in vehicles, Dhanbad the third largest city of Jharkhand state are not untouched with this. Pollution generated from mining activities, industrial and vehicular all together are destructing air quality of the city. Few studies conducted by researcher in the city demonstrated that local atmosphere was highly affected by particulate generated from mining, industries and vehicular activities moreover the particulate associated metals are also major concern for human health to this area [1] The current pollution status of the city is very high which make it to stand among most polluted areas of the India.

The present study was carry out to assess, the current status of the atmospheric trace metal burden in the urban atmosphere along the prominent four road network being used for public transport, and then to examine health risk for commuter in different silt of the day. The metals Pb, Ni, Cr, Fe, Cd, Cu, Zn and Mn were identified in the study. Principal Component Analysis (PCA) and enrichment factor were employed to trace the origin [2]. It was expected that this study would help to give a baseline data to help determine the health related pollution status of the local atmosphere on the road of the city.

STUDY AREA

Dhanbad is a coal city located in Jharkhand state of India. It lies between 23°37'3"N and 24°4' N latitude and 86°6'30"E and 86°50'E longitude with 202 m average elevation from sea level. This area comes under Chota Nagpur plateau which experience tropical climate and is characterized by pre monsoon and cold winter. Mining and associated activities has always been a cause of pollution to this area and from last few decades vehicular population has been increased dramatically which disturbing air quality from hazardous to even more verse. In the present study samples were collected along the four prominent public transport routes to assess the metal concentration, source identification and their health risk thorough inhalatory exposure. The specifications of routes are given below.

| Route Number | Route | Distance(Km) |
|--------------|-----------------------------|--------------|
| 1 | Sindri-Jharia | 15 |
| 2 | Jharia-Railway Station | 7 |
| 3 | Railway Station-Steel Gate | 5 |
| 4 | Damodar Bridge-Cahndankyari | 12 |

SAMPLING AND ANALYSIS

Suspended particulate matter (SPM) were collected by High Volume Sampler APM 415 with a flow rate of 1.1-1.7 m³/min, and respirable particulate matter (PM₁₀) were collected by Respirable Dust Sampler APM 460 BL with flow rate 0.9-1.4 m³/min. Whatman GF/A glass-fibre filters (size 800-1000 mm) were used for SPM collection whereas EPM 2000 filters were used for PM₁₀. Sampler was mounted on tata magic (four wheeler vehicles) and powered by 3KVA generator. The sampling was carried out during winter (3 November 2015 to 25 January 2016). Air samples were collected 12 h in three 4 h sifs corresponding to morning (8-12h), afternoon (12-4h) and evening (4-8h). The sample were collected twice on same filter to meet the requirement of 8 h sampling in each sift. Meteorological data collected from the meteorological station on the roof of the CIMFR building with respect to temperature, humidity, wind velocity and direction. Total 24 samples were taken by each sampler. Filter used for sampling purpose were pre cleaned by baking at 550° C for 10 hour. Before and after sampling the filters were kept in desiccator for 24 h.

For metal analysis, filters cut into four equal parts; one was transferred into the Teflon vessel containing HNO₃ and HCl mixture (3:1), and digested at 200°C for 20 min in a microwave digester (Milestone, Italy) after that 10 ml of MilliQ water was added and the resulting mixture was filtered through Whatman 42 filter paper, and the solution was transferred to a 25ml volumetric flask and diluted to the mark. All reagents were of analytical grade (Merck). The metals of the digested solution were analyzed by an ICP-OES (ICAP 6300Duo, Thermo). Commercially available ICP multi-element standard solutions (Merck) were used for development of calibration curves. All the glassware and plastic vessels were treated by dilute (1:1) nitric acid for 24 h and then rinsed with MilliQ water before use. Quality control measures included use of laboratory reagent blanks. After every tenth sample during analysis, the calibration standards were analyzed to check the analysis accuracy.

Enrichment Factor

The calculation of enrichment factors require metals concentration in atmospheric air with particular reference metal provided that should be crustal origin and not to influence by the anthropogenic activity [3]. There are several metals which have been used as a reference for enrichment factors such as Fe, K, Na, Mg, Al and Mn. Here in the study Fe selected as a reference metal which showed best correlation with other selected trace metals. The calculation of enrichment factor has been done by using the following equation [4]

$$EF_{\text{crust}} = (C_i/C_{\text{Fe}})_{\text{sample}} / (C_i/C_{\text{Fe}})_{\text{crust}} \dots \dots \dots (1)$$

Where C_i is the concentration of the element considered in the studied samples or the continental crust and C_{Fe} is the concentration of the reference element (Fe) in the studied samples or the continental crust.

Statistical Analysis

Obtained data from the analysis were used for the statistical interpretation including varimax rotation factor matrix method was used to conduct PCA. The statistical analyses were performed by using IBM SPSS Statistics 16 software.

Excess cancer risk

The excess cancer risk for particulate associated metals to the area represents unit risk that has been given to particular metals and their corresponding concentration in ambient air. It can be calculated by the simple formula [5]

$$\text{Excess cancer risk inhalation} = \text{ambient concentration of pollutant } (\mu\text{g}/\text{m}^3) \times \text{unit risk } (\mu\text{g}/\text{m}^3)^{-1}$$

RESULTS AND DISCUSSION

Particulates and Metals Concentrations

From the Table 1 average PM₁₀ concentration was 276 µg/m³ for route 1 which was followed by 263, 261 and 96 for route 2, route 3 and route 4 respectively while their associated average metal concentration was 1.963 µg/m³ for route 3 which followed by route 2, route 1 and route 4 for the concentrations 1.476, 1420 and .569 µg/m³ respectively. for the average winter SPM concentration, highest value observed for route 2 with 327 µg/m³ and followed by the 325, 320 and 146 µg/m³ for route1, route 3 and route 4

respectively whereas SPM associated average metals was recorded $2.21 \mu\text{g}/\text{m}^3$ for route 2 and followed by route 3, route 1 and route 4 for the concentration 2.014, 1.61 and $0.786 \mu\text{g}/\text{m}^3$ respectively. In the figure 2 SPM and PM_{10} associated metals shows how their concentration varies in different shift of the day for all sampling routes.

From the figure 2 it may observe that percentage contribution of PM_{10} associated metal increases for route 1, route 2 and route 4 while drop has been observed for route 3. From the observation of metal percentage distribution among four routes it has been observed that maximum percentage of particulate (PM_{10} and SPM) fall for the route 3 and followed by route 2, route 1 and route 4.

Figure 3 shows the percentage increase of particulates and their associated metal concentration. From the result it is illustrated that highest difference was observed in afternoon shift of the route 4 for PM_{10} associated metals which was followed by on same route for SPM bound metals in morning shift. Few values showed negative percentage growth such as SPM and their associated metals in afternoon shift of the route 1, PM_{10} bound metals in afternoon shift of the route 2, PM_{10} in afternoon of the route 3 and SPM in afternoon shift of the route 4.

Table 1: Average concentration of particulate on sampling routes

| $(\mu\text{g}/\text{m}^3)$ | | PM_{10} | SPM |
|----------------------------|-----------|------------------|-----|
| Route 1 | Morning | 223 | 289 |
| | Afternoon | 210 | 258 |
| | Evening | 394 | 428 |
| | Average | 276 | 325 |
| Route 2 | Morning | 227 | 295 |
| | Afternoon | 205 | 284 |
| | Evening | 358 | 401 |
| | Average | 263 | 327 |
| Route 3 | Morning | 202 | 274 |
| | Afternoon | 189 | 245 |
| | Evening | 392 | 441 |
| | Average | 261 | 320 |
| Route 4 | Morning | 74 | 145 |
| | Afternoon | 57 | 110 |
| | Evening | 157 | 184 |
| | Average | 96 | 146 |

Table 2: Excess cancer risks of PM_{10} bound carcinogenic metals

| Seasons | Routes | Metals | Concentration $\mu\text{g}/\text{m}^3$ | IUR | |
|---------|--------|--------|--|-----------------------------------|----------------------------|
| | | | | $(\mu\text{g}/\text{m}^3)\cdot 1$ | $\text{ECR}\times 10^{-6}$ |
| Winter | 1 | Ni | 0.600 | 2.4×10^{-4} | 143.9 |
| | | Cd | 0.922 | 1.8×10^{-3} | 1660 |
| | | Cr | 0.864 | 1.2×10^{-2} | 10371 |
| | 2 | Ni | 0.390 | 2.4×10^{-4} | 94 |
| | | Cd | 1.018 | 1.8×10^{-3} | 1832 |
| | | Cr | 1.012 | 1.2×10^{-2} | 12148 |
| | 3 | Ni | 1.747 | 2.4×10^{-4} | 419.38 |
| | | Cd | 1.932 | 1.8×10^{-3} | 3477 |
| | | Cr | 1.663 | 1.2×10^{-2} | 19956 |
| | 4 | Ni | 0.458 | 2.4×10^{-4} | 110 |
| | | Cd | 0.929 | 1.8×10^{-3} | 1672 |
| | | Cr | 0.472 | 1.2×10^{-2} | 5664 |

IUR* Inhalation unit risk

Enrichment Factor

Figure 4 showed the mean enrichment factors based on average metal concentration of heavy metals measured in PM_{10} and SPM collected from the four busiest routes. The higher EF values suggest a several point and non-point sources for Cd, Pb, Cu, Zn, Mn, Ni and Cr as all these metals are components of industries such as coal washery, coke oven plant and large number of vehicular activities. Mn is the crustal origin while Pb also comes from both coal mine and vehicular activities [6]. The enrichment factor was higher for all PM_{10} and SPM associated metals during sampling period. The enrichment value may be the cause of stable meteorological condition which decreases mixing height of the atmosphere. Zn comes in atmosphere through disperse road dust, exhausts, break wear, tire and fuel [7]. The prominent source

of Cd, Ni and Cr are oil combustion or exhausts from vehicles [8] while Cu has been linked to re-suspended dust and brake emission [9].

Table 3: Factor loading of metals in summer and winter

| Winter | Route 1 | | | Route 2 | | | Route 3 | | | Route 4 | | |
|---------------|---------------|--------------|---------------|--------------|--------------|--------------|---------------|--------------|--------------|--------------|--------------|--------------|
| | F 1 | F2 | F3 | F 1 | F2 | F3 | F 1 | F2 | F3 | F 1 | F2 | F3 |
| Pb | -0.156 | 0.962 | 0.222 | 0.631 | 0.755 | -0.044 | 0.639 | 0.356 | -0.482 | 0.694 | 0.052 | -0.141 |
| Ni | -0.09 | 0.984 | 0.114 | 0.85 | 0.384 | -0.343 | -0.06 | 0.975 | -0.024 | 0.38 | 0.824 | 0.17 |
| Cr | -0.829 | 0.063 | -0.2 | 0.947 | 0.016 | 0.148 | 0.733 | 0.489 | 0.454 | 0.43 | -0.34 | -0.72 |
| Fe | 0.924 | 0.049 | 0.299 | 0.052 | 0.959 | 0.185 | 0.022 | 0.86 | -0.281 | 0.885 | 0.325 | 0.057 |
| Cd | 0.911 | -0.328 | -0.152 | 0.839 | 0.328 | 0.147 | 0.657 | -0.115 | 0.409 | 0.149 | 0.045 | 0.977 |
| Cu | 0.151 | 0.415 | 0.753 | 0.369 | 0.9 | -0.178 | 0.939 | 0.01 | 0.199 | 0.132 | 0.751 | -0.616 |
| Zn | -0.244 | -0.097 | -0.933 | 0.746 | 0.412 | -0.508 | 0.115 | -0.188 | 0.937 | -0.411 | 0.764 | 0.371 |
| Mn | 0.767 | -0.05 | 0.474 | 0.061 | 0.08 | 0.982 | -0.957 | 0.146 | 0.21 | -0.884 | 0.142 | 0.002 |
| Eigen value | 3.614 | 2.764 | 0.768 | 4.959 | 1.44 | 1.204 | 3.326 | 2.35 | 1.29 | 2.784 | 2.283 | 1.635 |
| % of Variance | 45.174 | 34.547 | 9.605 | 61.993 | 18.001 | 15.047 | 41.579 | 29.373 | 16.119 | 34.796 | 28.535 | 20.436 |
| Cumulative % | 45.174 | 79.721 | 89.326 | 61.993 | 79.995 | 95.041 | 41.579 | 70.952 | 87.071 | 34.796 | 63.331 | 83.767 |

Cancer risk of carcinogenic metals

Table 2 shows the ECR of PM₁₀ bound metals for all sampling routes. The average metals value of Cd, Cr and Ni were taken for identification of ECR. The highest value was observed for Cr in route 3 with 19956 followed by 12148, 10371 and 5664 for route 2, route 1 and route 4 respectively. From the results it has been observed that ECR value correlated with the concentration of metals. In some cases lower concentration showed higher ECR value, this difference is because of the higher inhalation unit risk of Ni with $2.4 \times 10^{-4} (\mu\text{g}/\text{m}^3)^{-1}$ which followed by 1.8×10^{-3} and $1.2 \times 10^{-2} (\mu\text{g}/\text{m}^3)^{-1}$ of Cd and Cr respectively.

Principal Component Analysis

PCA was performed by the Varimax Rotated Factor Matrix method, based on the orthogonal rotation criterion that maximizes the variance of the squared metals in the column of a factor matrix. It produces factors that have high correlations with one smaller set of variables and little or no correlation with another set of variables. Table 3 presents the Principal Component (PC) loadings for the metal data of the study period with corresponding eigenvalues and variances. The data for SPM were interpreted on the basis of three factors. Three PCs with eigenvalues greater than 1.0 were extracted with significant value of 10% in respect to maximum value. For the route 1, the cumulative variances were 45.17 and 34.54 for F1 and F2 where Cr, Fe and Cd showed close association in factor 1 while Pb and Ni were observed in F2. In route 2 Cr and Cd showed close relation while Fe and Mn sole metals found in F2 and F3. In the study area, routes showed the loadings of Pb, Cd and Cr. These trace metals are well known to be associated with the industrial and automobile emissions [10] Cd and Cr have significant contributions from crude-oil combustion in the industries and vehicular emissions. One of the most important sources of cadmium, chromium and lead in the urban environment is road traffic as suggested by various researchers [11]. High loadings of Pb and Ni are due to emissions from vehicular exhaust [12, 13] After analysis of results it can be concluded that in the study area, source contribution is mainly due to coal mining, earth crust, vehicular emissions, dust through unpaved road and industrial activities.

CONCLUSION

In the present study the average concentration of SPM/PM₁₀ for winter were 325/276, 327/263, 320/261 and 146/96 $\mu\text{g}/\text{m}^3$ for routes 1, 2, 3, and 4 respectively. The observed SPM/PM₁₀ associated total average metals (Pb, Ni, Cr, Fe, Cd, Cu, Zn and Mn) concentration were 1.61/1.42, 2.21/1.47, 2.01/1.81, 0.786/0.569 $\mu\text{g}/\text{m}^3$ found. These finding indicated that air quality along these four routes are severely affected. The particulates and their associated metals were found in reasonable concentration to the study period. Enrichment factor indicated the loading of all studied metals where Cd showed maximum enrichment. Carcinogenic metals (Cd, Ni and Cr) were selected for cancer risk assessment where risk factor where higher for route 3 and 4. Source identification of SPM associated metals were conducted for all four routes where metals loading from the results indicate three possible sources namely coal mining activities, traffic pollution and coal/biomass burning. These findings indicated that the air pollution caused by particulates generated from local sources which affecting air quality along the traffic road network. The study and its generated data will help to understanding and managing the effects on health of commuter who travel through these routes daily.

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