Heavy Metals in PM$_{10}$ Aerosols Over an Urban Industrial City

Pallavi Pradeep Khobragade, Ajay Vikram Ahirwar

Abstract: PM$_{10}$ aerosols were monitored and analyzed for heavy metal concentration at Raipur city Chhattisgarh, India for possible source identification of pollutants. Sampling of PM$_{10}$ aerosols was carried out by using respirable dust sampler during the year 2016. Daily PM$_{10}$ average concentrations varied between 122.033 and 197.854 µg/m$^3$, 91.350 and 133.950 µg/m$^3$ and 112.770 and 480.170 µg/m$^3$ in summer, monsoon and winter respectively. Chemical analysis of PM$_{10}$ samples was carried out for heavy metal determination. Heavy metal (Fe, Mn, Ni and Pb) were analyzed with the help of atomic absorption spectroscopy (AAS) and found in the range of 2.713-36.862, 0.131-9.129, 0.880-4.195 and 0.015-0.321 µg/m$^3$ for Fe, Mn, Pb and Ni respectively. PM$_{10}$ concentrations shows distinct seasonal variation being twice in winter season than in summer; winter (mean: 241.820 ± 33.912 µg/m$^3$) > summer (mean: 159.512 ± 14.360 µg/m$^3$) > monsoon (mean: 107.480 ± 9.213 µg/m$^3$). The concentration of heavy metal was different in all the seasons depending on their sources. Identification of possible sources was done by principal component analysis (PCA) illustrating industrial activities, soil (crustal) dust and biomass burning as the major sources in the region. The back trajectory analysis of the air masses depicts that the local anthropogenic activities affect the concentration of pollutants at the source. Correlation analysis between the heavy metal concentrations agreed the results obtained by PCA. The work helped in observing the seasonal trend of particulate matter concentrations and in identification of major sources of air pollution in the city.

Keywords: PM$_{10}$, Heavy metals, atomic absorption spectroscopy (AAS), principal component analysis (PCA), Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT)

I. INTRODUCTION

In the recent past aerosols received special attention due to its effect on climate change and health. Among them fine particulate matter (PM$_{2.5}$ and PM$_{10}$) played an important role in affecting human health (Soleimani et al., 2018). Heavy metals and other trace elements emitted from various natural and man-made activities are found in aerosol. PM contains heavy metals which are associated with cancer risks (Park et al., 2008). Atmospheric aerosol was responsible for 7 million deaths worldwide (WHO 2014). Increase in concentration of heavy metals is mainly due to industrialization, urbanization and enhanced vehicular activities. Steel and Iron industry can emit high amount of Fe, Zn, Mn, Pb and Cd (Amadio et al., 2013).

Fe can be associated with respiratory and heart diseases like asthma after two days of contact (Sofowote et al., 2019). Mn is relevant to anthropogenic activities including coarse dust in soil, coal, fly ash and construction dust (Pant et al., 2016). Pb affects brain and bones creating fluctuations in mineral density affecting fetal growth and brain development (Hossain et al., 2018). Bioaccumulation of Ni in human body might lead to potential health effect even at low exposure level (Feng et al., 2019).

Several studies have been carried out in India related to chemical characterization (Karar et al., 2006; Kothai et al., 2011; Chakraborty et al., 2010; Perrino et al., 2011). However, less number of studies was found for this region.

Raipur is an industrial and agricultural area. Any climate change may affect the economy of Chhattisgarh. Hence proper air pollution mitigating policies, industrial development and air pollution load studies must be carried out to identify the sources and taking proper actions by making policies. In the current study, inter-seasonal aerosol variation and analysis of heavy metals has been done along with possible source identification by using principal component analysis (PCA) and finding correlation co-efficient which will help in identification of the major sources.

II. MATERIALS AND METHOD

A. Study area

The roof top of National Institute of Technology (NIT) Raipur campus has been selected for running the PM$_{10}$ sampler which is located in Chhattisgarh, India at 303.36 m a.m.s.l. Raipur is the capital of state and is surrounded by regions where major industrial activities are being carried out. It is one of the largest cities of the state having a population of around 1.7588 million and is situated in north eastern part of India (Longitude 81º 36´34ʺ and latitude 21º 14´31ʺ). The campus is situated on one of the busiest road networks connecting the area Tatibandh to other interior regions in the city. In the campus area a mixed pattern of pollutants can be observed due to the location of Bhilai steel plant and surrounding industrial clusters within 30 km periphery. The respirable dust sampler was run during the year 2016 during which samples were collected for twice or thrice in a month excluding the monsoon season in June and July.

B. Sampling Methodology

PM$_{10}$ was collected using a respirable dust sampler, Envirotech instruments Pvt. Ltd., New Delhi, India on 8” x 10” Whatman glass fibre.
filters. Before and after sampling, filter papers were put up in dessicators for 24 hours. The blank filter papers were weighed before the analysis. The sampler was run by placing the filter paper and the total volume of air sampled is known. Particulate concentrations were gravimetrically weighed. After collecting PM$_{10}$ samples, assessment of heavy metals Fe, Mn, Ni and Pb concentration has been done by digesting the filter papers by acid digestion method. One tenth of the paper as cut in a strip and digested by adding hydrochloric acid and heating the solution on hot plate (USEPA 3050B). Continuous heating and refluxing was carried out to completely extract the metals from the filter paper followed by preparing stock solutions(1000 ppm) and diluting them for metal concentration detection by atomic absorption spectroscopy (USEPA 1999) for quantitative determination of elements using absorption of optical radiation by free atoms in the gaseous state. Quality control and quality assurance practices were followed strictly during the entire analysis.

### III. RESULTS AND DISCUSSION

#### A. PM$_{10}$ average and max-min concentration

During the study period, maximum PM$_{10}$ mass concentration was observed on 10th November 2016 (480.17 µg/m$^3$) during which the temperature was very low (19.5°C) at a very low wind speed (4.5 km/s) which causes the people to use wood burning at their homes on a higher level to stay warm. Majority of pollutants at low altitudes are generated by local anthropogenic activities. PM$_{10}$ concentration followed by another peak during the Diwali festival due to burning of fire crackers (391.00 µg/m$^3$). PM$_{10}$ concentration was higher during winter season (mean: 241.82 ± 33.912 µg/m$^3$) followed by summer (mean: 159.512 ± 14.360 µg/m$^3$) and monsoon (mean: 107.480 ± 9.213 µg/m$^3$). The seasonal behaviour may be due to meteorological conditions, anthropogenic activities, biomass burning during winter (Ganguly et al., 2019; Deshmukh et al., 2012) and local festivals. PM$_{10}$ mass concentration was continually higher during winter season during which the average temperature on sampling days was minimum (23°C ± 5°C) as compared to summer (34°C ± 5°C) and monsoon season (27°C ± 3°C). Lowest average PM$_{10}$ mass concentration was found during monsoon season (107.480 ± 9.123 µg/m$^3$) on sampling days due to washing away of pollutants with rains during wet deposition process (Ganguly et al., 2019). Table I shows the seasonal average PM$_{10}$ concentration during the year. The mixing height during winter is low and is inversely proportional to ambient concentrations (Nagar et al., 2019). Low mixing heights during winter allowed remaining the pollutant in the atmosphere for a longer duration (Anand et al., 2019). The wind rose diagrams for all the three seasons are given in Fig.2. showing the dominant wind directions and wind speeds during the three seasons.

#### B. Heavy metal analysis

The seasonal variations of heavy metals during the year 2016 are shown in Table II. The concentration of Ni was almost same in all the seasons which being negligible throughout the year in the city. From Table II it is observed that concentration of Mn: 2.464 ± 3.125, Ni: 0.598 ± 0.118and Pb: 1.825 ± 0.964 is at peak during winter days while Fe: 13.702 ± 9.114 having maximum concentration during summer. This may be due soil resuspension caused by higher wind speed during summer days leading Fe content from earth’s crust (Talbi et al., 2018). The average concentration of Fe: 19.82 ±9.225 µg/m$^3$ is highest in the month of April during which temperature in the city is at peak followed in August as 15.94±8.724 µg/m$^3$. During April month the concentration of Ni:0.045±0.079 has also been observed which was below detection limit throughout the year along with peak in the winter month of November 0.194±0.171 µg/m$^3$. The peak values of Fe:36.862, Mn:9.129 and Pb:4.195 µg/m$^3$ were observed on 15th January 2016 during the winter month when temperature is lowest followed by low wind speed.

#### C. Back-trajectory analysis

To study the influence of the dust transport on samples of high concentrations during the year, Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to calculate the air masses backward trajectories (Fig. 1) using the meteorological data of NOAA air resources laboratory(website: https://ready.arl.noaa.gov/hypub-bin/trajtype.pl). In this model 120 hours backward trajectories were calculated for 100 m, 500m and 10000 m above ground level ending at 12:00 UTC. The trajectories study implies that majority of pollutants at low altitudes are generated by anthropogenic activities during local festivals. At low altitudes PM$_{10}$ mass concentration was found highest on 10th November 2016 (480.17 µg/m$^3$) after the Diwali festival during which continuous firecrackers are burnt for around 5 days in overall India. The back trajectories depict the influence of wind direction from North and South implying influence of local burnings after the festival. Another peak in PM$_{10}$ concentration is observed on 30th October 2016 (391.00 µg/m$^3$) on the night of Diwali festival celebrated in the entire region. Perrino et al., 2011 reported the PM$_{10}$ concentration during Diwali and Holi as 767 µg/m$^3$ and 620 µg/m$^3$ in Delhi, India.

### Table II: Seasonal average concentrations (µg/m$^3$) of heavy metals (Mean + SD) in PM$_{10}$

<table>
<thead>
<tr>
<th>Season</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>13.702 ± 9.114</td>
<td>1.003 ± 1.161</td>
<td>0.023 ± 0.056</td>
<td>1.028 ± 0.181</td>
</tr>
<tr>
<td>Monsoon</td>
<td>11.534 ± 7.316</td>
<td>0.779 ± 0.554</td>
<td>0 ± 0.000</td>
<td>1.268 ± 0.109</td>
</tr>
</tbody>
</table>

Table- I: Seasonal average PM$_{10}$ concentrations (µg/m$^3$)
NOAA HYSPLIT MODEL
Forward trajectories starting at 0600 UTC 29 Oct 16
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1000 UTC 11 Nov 16
GDAS Meteorological Data

Fig. 1 Back trajectory analysis using HYSPLIT model

Fig. 2 Wind Rose diagrams for (a) Summer, (b) Monsoon and (c) Winter

Winter

\[ 11.04 \pm 9.509 \]
\[ 2.464 \pm 3.125 \]
\[ 0.598 \pm 0.118 \]
\[ 1.825 \pm 0.964 \]
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D Principal component analysis

PCA was used to identify the pollution sources for heavy metals observed at a receptor site. Variables with factor loadings more than 0.5 were considered for identification of pollution sources (Talbi et al., 2018). From Table IV, it can be observed that Factor 1 was extracted depicting 58% of the total variance. Significant principal component is selected on the basis of Kaiser criteria with eigen value greater than 1. PC1 representing Mn and Pb indicating the main source as industrial activities like steel manufacturing industries, soil and crustal dust (Soleimani et al., 2018). Mn and Pb also originate from anthropogenic activities like vehicle exhaust and non-exhaust emissions, coal mining activities (Mansha et al., 2012, Pant et al., 2016). Wearing of vehicular tyres, oil and coal burning is another cause of Pb emission. PC2 showed negative correlation and hence further components are not considered.

E Correlation

The inter-relationship between elements in Table V helps to provide information on heavy metals sources and pathways. Correlations between metals agreed the results obtained by PCA as well as from literature. Fe, Mn and Pb are derived from vehicle exhaust and non-exhaust emissions (Mansha et al., 2012). Fe is also a predominant source from soil dust (Pant et al., 2016, Begum et al., 2019), tire and brake wear and motor vehicles (Begum et al., 2019). Mn and Pb is relevant to anthropogenic activities including coarse dust in soil, coal, traffic, fly ash and construction dust (Pant et al., 2016). Industrial emissions and waste incineration is another source of Pb. In India, Pb is not considered as an exhaust emission due to the use of unleaded petrol/fuel. It exhibits its presence due to road traffic (Radulescu et al., 2017). The impact of Pb is observed more is dry season (Chakraborty et al., 2016). Industrial emissions and waste incineration is another source of Pb. In India, Pb is not considered as an exhaust emission due to the use of unleaded petrol/fuel. It exhibits its presence due to road traffic (Radulescu et al., 2017). The impact of Pb is observed more is dry season (Chakraborty et al., 2016).

Table- III: PM$_{10}$ and Heavy metal concentrations in other cities

<table>
<thead>
<tr>
<th>City (Country)</th>
<th>Study period</th>
<th>PM$_{10}$ (µg/m$^3$)</th>
<th>Fe (µg/m$^3$)</th>
<th>Mn (µg/m$^3$)</th>
<th>Ni (µg/m$^3$)</th>
<th>Pb (µg/m$^3$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raipur (India)</td>
<td>January 2016 to November 2016</td>
<td>192.71</td>
<td>11.894 ± 8.684</td>
<td>1.725 ± 2.429</td>
<td>0.0349 ± 0.091</td>
<td>1.491 ± 0.781</td>
<td>This study</td>
</tr>
<tr>
<td>Raipur (India)</td>
<td>Winter 2006-2013</td>
<td>584.39</td>
<td>27.5±15.9</td>
<td>1.2±0.6</td>
<td>-</td>
<td>-</td>
<td>Jaiswal et al., (2019)</td>
</tr>
<tr>
<td>Kolkata (India)</td>
<td>Winter 2013-2014</td>
<td>445±210</td>
<td>11.242±1.5705</td>
<td>0.249±0.27</td>
<td>0.048±0.029</td>
<td>0.349±0.384</td>
<td>Das et al., (2015)</td>
</tr>
<tr>
<td>Kanpur (India)</td>
<td>October 2002-February 2003</td>
<td>Urban-27 7.335</td>
<td>0.30-6.17</td>
<td>-</td>
<td>0.0047-0.0270</td>
<td>0.007-0.1030</td>
<td>Sharma et al., (2005)</td>
</tr>
<tr>
<td>Varanasi (India)</td>
<td>July 2014 to May 2017</td>
<td>244.8±13.58</td>
<td>1.105±0.85</td>
<td>0.0251±0.0185</td>
<td>0.0043±0.0017</td>
<td>0.03±0.0165</td>
<td>Kothai et al., (2011)</td>
</tr>
<tr>
<td>Delhi (India)</td>
<td>December 2008-December 2009</td>
<td>-</td>
<td>9.7±4.133</td>
<td>0.287±0.1</td>
<td>0.317±0.2</td>
<td>0.38±0.23</td>
<td>Khillare et al., (2012)</td>
</tr>
<tr>
<td>Agra (India)</td>
<td>May 2006 to March 2008</td>
<td>Urban-15 4.2; Rural 148.4</td>
<td>Urban-2.9±5.8; Rural-3.2±12.16</td>
<td>Urban-0.9±0; Rural-0.9±0.54</td>
<td>Urban-0.2±0; Rural-2.04</td>
<td>Urban-1.1±1.21; Rural-2.2±11.44</td>
<td>Kulshrestha et al., (2009)</td>
</tr>
</tbody>
</table>
IV. COMPARISON WITH OTHER STUDIES

The mean PM$_{10}$ concentration during the study period at Raipur is compared with the concentration at the same location 270.5 µg/m$^3$ [Deshmukh et al., 2013]; 162.69 ± 71.74 µg/m$^3$ [Ahirwar et al., 2017] and found comparable with the present study; other locations- Shimla (Ganguly et al., 2019) exhibit different pattern- higher concentration in summer may be due to tourist attraction and enhanced vehicular movement during summer season; winter: 56.465±15.43, summer: 62.137±19.91, monsoon: 39.675±29.3 µg/m$^3$. Also forest fires in the area during the summer season is another cause of this altered pattern [Ganguly et al., 2019], Delhi [Perinno et al., 2019]: 767 µg/m$^3$ in 2008 and 620 µg/m$^3$ in 2009 during Diwali, Delhi [Guttikunda et al., 2013]- 208±4.67 µg/m$^3$, Delhi [Balachandran et al., 2000]-658.45 µg/m$^3$, Varanasi [Mukherjee et al., 2018]- 244.8±135.8 µg/m$^3$, Coimbatore [Manju et al., 2018]- 65.5-98.6 µg/m$^3$ and found comparable with the current study. Several other locations in India and other countries like Agra, Hong Kong, Spain, Algiers were found to have sufficiently lower concentrations as compared to the current study. Among heavy metals, concentrations of Fe were found higher than concentrations of Mn, Pb and Ni. Fe and Mn are identified as tracer elements for iron and steel industries (Dai et al., 2015) as their concentrations were found higher near the influence of steel plant activities (Amodio et al., 2013). The average concentration of Mn is comparable with previous studies carried out in the area (Jaiswal et al., 2019). Ambient PM$_{10}$ and heavy metal concentrations at other locations are given in Table III.

<table>
<thead>
<tr>
<th>Location</th>
<th>April 2011</th>
<th>Max-553 ± 101 Min- 410 ± 95 Avg-480</th>
<th>8.63 ± 0.27</th>
<th>0.19 ± 0.00</th>
<th>0.54 ± 0.03</th>
<th>2.20 ± 0.18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peshawar (Northern Pakistan)</td>
<td>October 2004 to September 2005</td>
<td>81.3±37.7</td>
<td>1.8±0.78</td>
<td>0.050±0.030</td>
<td>0.0066±0.067</td>
<td>0.069±0.067</td>
</tr>
<tr>
<td>Hong Kong (China)</td>
<td>January 2009</td>
<td>23.123</td>
<td>-</td>
<td>0.00538</td>
<td>0.001363</td>
<td>0.003513</td>
</tr>
<tr>
<td>Navarra(Spain)</td>
<td>June &amp; December 2014</td>
<td>207.63 ± 7.82 - SW monsoon and 138.32 ± 4.67 -NE monsoon</td>
<td>0.58135±0.1694</td>
<td>0.0151±0.003</td>
<td>0.0033±0.001</td>
<td>0.2297±0.005</td>
</tr>
<tr>
<td>Cheras(Malaysia)</td>
<td>January 2014-March 2014</td>
<td>60.01</td>
<td>5.21417±1.09219</td>
<td>3.80472±3.95582</td>
<td>-</td>
<td>0.11917±0.08388</td>
</tr>
<tr>
<td>Dhaka(Bangladesh)</td>
<td>January 2015-March 2015</td>
<td>60.01</td>
<td>5.21417±1.09219</td>
<td>3.80472±3.95582</td>
<td>-</td>
<td>0.11917±0.08388</td>
</tr>
<tr>
<td>Algiers (Mediterranean coast)</td>
<td>January 2015-March 2015</td>
<td>60.01</td>
<td>5.21417±1.09219</td>
<td>3.80472±3.95582</td>
<td>-</td>
<td>0.11917±0.08388</td>
</tr>
</tbody>
</table>

Table- IV: Principal component analysis

<table>
<thead>
<tr>
<th>Variable</th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (µg/m$^3$)</td>
<td>0.51</td>
<td>0.138</td>
<td>0.849</td>
</tr>
<tr>
<td>Manganese (µg/m$^3$)</td>
<td>0.609</td>
<td>0.031</td>
<td>-0.377</td>
</tr>
<tr>
<td>Nickel (µg/m$^3$)</td>
<td>0.006</td>
<td>-0.98</td>
<td>0.154</td>
</tr>
<tr>
<td>Lead (µg/m$^3$)</td>
<td>0.607</td>
<td>-0.137</td>
<td>-0.336</td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>2.3193</td>
<td>1.0289</td>
<td>0.5547</td>
</tr>
<tr>
<td>Total variance (%)</td>
<td>58</td>
<td>25.7</td>
<td>13.9</td>
</tr>
<tr>
<td>Cumulative (%)</td>
<td>58</td>
<td>83.7</td>
<td>97.6</td>
</tr>
</tbody>
</table>

Table- V: Correlation co-efficient matrix of heavy metals in PM$_{10}$

<table>
<thead>
<tr>
<th>Variables</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.568</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>-0.063</td>
<td>-0.042</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.559</td>
<td>0.871</td>
<td>0.109</td>
<td>1</td>
</tr>
</tbody>
</table>

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V. CONCLUSION

PM$_{10}$ aerosol was monitored during the year 2016 in Raipur city. The overall air quality in the city is found to be more contaminated in winter season. Particulate matter concentrations are found to be exceeding in the region as per global guidelines giving an alarming signal in the deteriorating quality of air. Significant seasonal variation in PM$_{10}$ concentration was observed; higher during winter time as compared to summer time due to lower wind speed and low mixing heights. Local festivals in winter accompany sudden increase in particulate concentration with meteorological conditions favourable for higher pollutant concentration. Lower concentration of PM$_{10}$ during monsoon period confirmed negative correlation (r=-0.03) between PM$_{10}$ and rainfall. PM$_{10}$ exhibit positive correlation with temperature (r=0.11) and negative correlation with wind speed and humidity (r=-0.286). Heavy metal analysis revealed maximum average concentration of Fe (11.895± 17.39 µg/m$^3$) in the local air which may be due to the major industrial zones situated around the city followed by Mn (1.730±4.430 µg/m$^3$) and Pb (1.49±1.816 µg/m$^3$).Multivariate analysis and correlation analysis accompanied in identifying industrial sources, soil and crustal dust, vehicle and non-exhaust emissions as the major sources of pollution in the region. The study brings into focus the pollution levels due to anthropogenic activities, thus proper actions may be taken to reduce the pollutant concentration by adopting pollution reducing methods and bringing awareness among public.

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