Physico-Chemical Characteristics of Airborne Particulate Matter in and around a Mechanised Opencast Coal Mine – A Case Study

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Air pollution is a major risk to health in many developed and developing countries of the world. Most of the pulmonary diseases related to air polltuin are generally directly or indirectly related to the respirable particulate matter (PM_{10}). Further the health impacts depends on the physical and chemical characteristic of the particulate matter. Mining industries produces huge amount of dust by drilling, blasting, transportation, loading, unloading and mine fires. Now-a-days in India, coal mining is mainly done by opencast methods rather than underground, which generates huge quantities of respirable dust. This paper focuses on the physico-chemical characterisation of particulate matter (PM_{10} and $PM_{2.5}$) in and around mechanized opencast coal mines of Talcher coalfields (Mahanadi Coalfield Limited), Odisha, India. The study was carried out for a period of one year from March 2015 to February 2016. The monitoring of particulate concentration reveals that the concentration of both PM_{10} and $PM_{2.5}$ levels were far above the standard limit of NAAQS, 2009. The trace metal study by atomic absorption spectrophotometer (AAS) indicated the presence of Fe, Cu, Cr, Zn, Ni, Cd, Pb, As, Se and Hg in the samples. For the qualitative analysis, techniques like Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM) and XRD were used. Source apportionment study of particulate matter was also carried out based on the characterization. Statistical analysis such as correlation analysis and Principle Component Analysis (PCA) was also carried out. Different studies on the particulate matter suggested that monitoring stations near the mining area were mainly affected by the emission from opencast coal mining and its associated activities.

Key words: - Respirable dust, AAS, FTIR, XRD, SEM-EDX

1.0 Introduction

From past few decades, the concern about air pollution exclusively with reference to particulate matter (PM) is receiving importance worldwide [1]. Large-scale mechanized opencast coal mining generates vast quantity of airborne dust which may cause safety and health hazards due to poor visibility, failure of equipment, multiplied maintenance cost, and lowering of labor productivity [2]. It has also been reported that coal mining particulates are respirable in nature and hazardous to human health [3]. Long-term exposure to increased PM concentrations might result in a marked reduction in life expectancy due to increase of cardio-pulmonary disease and lung cancer [4,5]. However, limited studies are available on physico-chemical composition of PM_{10} that is responsible for adverse health effects. The sources of PM emission in opencast coal mines include blasting and drilling operations, transportation of coal and overburden on haul roads, coal handling plant operation, loading and transport of overburden and coal by shovel-dumper combination, crushing, conveying, and handling of overburden by draglines, and vehicular emission from unpaved roads [6]. In addition to the above mentioned sources, coal mine fire has been found to be one of the major sources of PM emission [7]. Along with the gaseous pollutants, a huge amount of PM is also emitted from the mine fire areas. The increased PM level in air in mine fire locality is the prime concern of the inhabitants residing at close proximity to the mine fire area. The particles of concern to human health are the respirable particles (also referred to as PM_{10}, particulate matter having equivalent diameter less

than 10 μm) that can enter human lungs through the respiratory system and therefore potentially be the cause of respiratory diseases [8,9]. The paper presents the findings of a study on physicochemical characterization of dust arround a highly mechanised opencast coal mine of Talcher coal fields, Odisha , India.

2.0 Material and methods

2.1 Study area

The Talcher Coalfield is one of the most important coalfields in India operating under Mahanadi Coal Fields Limited (MCL), a subsidiary of Coal India Limited (CIL), located in Talcher, basically from Angul district of Odisha state. The study area is positioned between latitude 20^{o} 57' 39" and 20^{o} 58' 18" (N) and longitude 85^{o}09' 33" and 85^{o}12' 12" (E). The elevation above mean sea level is 85 to 120 m. The area experiences a sub-tropical warm temperature. The mean annual precipitation is 1277mm out of which 70% occur during rainy season. The mean temperature varies from 6.7^{o}C to 45.5^{o}C. The industrial activities in this area picked up in sixties, eighties and during first decade of this century. This area has grown steadily and now is a prominent industrial hub of the country. The core zone of the mine covers partly and /or fully the land from 7 villages. The buffer zone of study area also contains eight reserve forests. The map of the study area with sampling location is shown in Figure 1.

Fig. 1 Map of the study Area

2.2 Sampling Methods

Particulate sampling was carried out at four stations from April 2015 to March 2016 in three distinct seasons, i.e., winter (December–March), summer (April–June), and post-monsoon (October–November). Monitoring stations were selected as per the siting criteria IS: 5182 Part XIV with special consideration of meteorological data and sources of pollution, apart from security, accessibility, and availability of electricity. Air quality monitoring has been carried out following standard methodologies and protocols as per Central Pollution Control Board (CPCB)/National Ambient Air Quality Standard (NAAQS), India norms [10].

2.3 Morphology and chemical composition

Physical characterization of dust samples was performed using electron scanning microscopy (SEM, JEOL Model JSM-6390LV, Japan) for determination of morphology of airborne particles. Filter paper was cut into pieces of 1x1 cm and coated with platinum to prepare the samples for SEM analysis. Techniques like X-ray diffraction (XRD) patterns, atomic absorption spectroscopy (AAS) and Fourier transform infrared (FTIR) spectroscopy were also used for the further analysis of dust samples. XRD patterns of dust samples were taken at room

temperature in a wide range of Bragg angle 2θ (10°≤2θ≤90°) with scanning speed of 1° per minute using Rigaku X-Ray difractometer. The operating condition involved the use of CuKα radiation at 34 kV, 24 mA, and Ni filter [11]. After the gravimetric analysis for PM_{10}, the EPM2000 filters were digested in nitric acid and the concentration of heavy metals were analysed by using Atomic Absorption Spectrophotometer (AAS- Model ThemoFisher iCE 3300). Samples were directly introduced into the frame for all other elements except Hg, As and Fe. Hg and As was done by VG-AAS and Fe by titration method. The concentration of the object element (µg/mL) was obtained from the calibration plot. Fourier transform infrared (FTIR) spectroscopy technique was adapted for identification and characterization of inorganic and organic compounds.

3.0 Results and discussion

3.1 Dust concentration

PM_{10} and $PM_{2.5}$ concentrations during study period are summarized in Figure 2 and Figure 3 respectively. Arithmetic average concentration of PM_{10} was found to be 413.98 µg m^{-3}, for the whole study period. The average level of PM_{10} was lowest during post monsoon, i.e., 319.92 µg m^{-3}. PM_{10} level during winter was highest, i.e., 533.13 µg m^{-3}, while the values during summer season lies in between winters and post monsoon (388.90 µg m^{-3}) . The concentrations of PM_{10} in the study area during three distinct seasons, i.e., summer, winter, and post-monsoon, were respectively 3.9, 5.3, and 3.2 times higher than NAAQS (100 µg m^{-3}) (CPCB 2009) guidelines of India. Similarly the average concentration of $PM_{2.5}$ was found 111.47 µg m^{-3} for the study period. The average concentration of $PM_{2.5}$ also was following the same trend of PM_{10} and highest in winter with concentration of 134.99 µg m^{-3}, lowest in postmonsoon of 92.45 µg m^{-3} and in between in summer the value was 106.96 µg m^{-3}. During summer and winter season the particles remain airborne through nonlinear processes for days to weeks. The elevated concentration of particulate during winter can also be attributed to low temperature and low wind speed, which cause the lower mixing height and poor dispersion conditions. During summer season, particulate concentration is lower than during winter due to enhanced dispersion caused by vertical mixing of air under unstable atmospheric conditions [7].

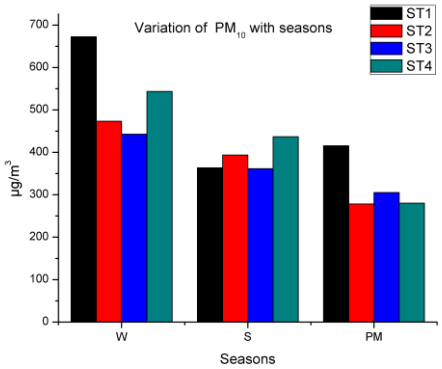

Fig. 2 Variation of PM_{10} with seasons

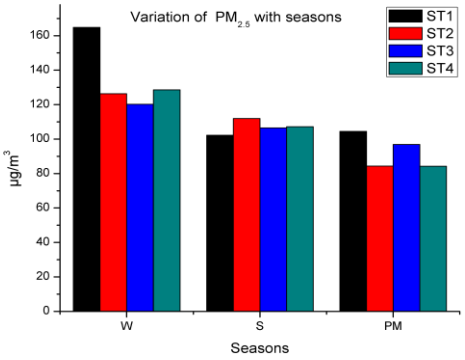

Fig. 3 Variation of $PM_{2.5}$ with seasons

3.2 Characterization of Particulate Matter

3.2.1 Trace Metal Analysis

Elemental analysis of dust samples reveals the presence of trace metals such as Fe, Cr, Cd, Cu, Pb, Zn, Ni, Hg, Se, and As. The variations of individual elemental concentration of dust samples are shown in Figures 4(a & b). The highest mean concentration was found for Cd (6.25 µg/m^3) followed by Fe (2.29µg/m^3), Cr (1.32 µg/m^3), Zn (0.80µg/m^3), Pb (0.08 µg/m^3),

Cu (0.04 µg/m^3), Ni (14.25 ng/m^3), Se (1.44 ng/m^3), Hg (1.40ng/m^3) and As (0.53 ng/m^3). The decreasing elemental concentration trend was Cd>Fe>Cr>Zn>Pb>Cu>Ni>Se>Hg>As for the study area. The range of average Pb concentrations were detected between 0.06 µg/m^3 to 0.12 µg/m^3 at all monitoring stations during this study period, which was below the NAAQS limit of 0.5 µg/m^3. The low concentration of Pb even along the transportation routes may be due to use of unleaded fuels. The range of average Ni concentrations were observed between 8.65 ng/m^3 (ST1) to 22.25 ng/m^3 (ST4). Ni concentrations were observed higher than the NAAQS (20 ng/m^3) at ST4 where all other monitoring stations were within the standard range. The increased concentrations of Ni in this area indicates the influence of transportation activities. The average concentration of As was from 0.04ng/m^3 at ST3 to 1.15ng/m^3 at ST4. As is originated from automobile emissions, industrial emissions [12] and coal burning [13]. Even though Hg is not listed in NAAQS, the analysis value of dust samples of all the stations are showing some amount of Hg in all the season. The dust of ST1 showed higher Hg content (3.04ng/m^3)as compared with all the stations. Figures 4 (a-b) presented below are showing the trace metal concentration of different sampling locations.

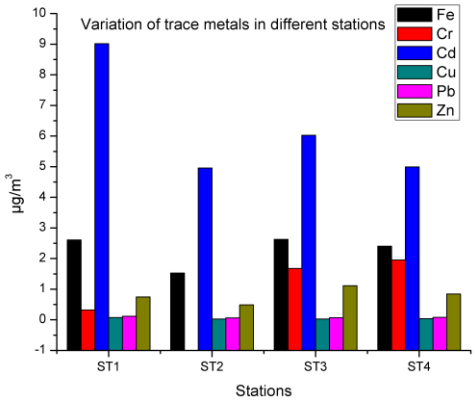

Fig. 4 (a)

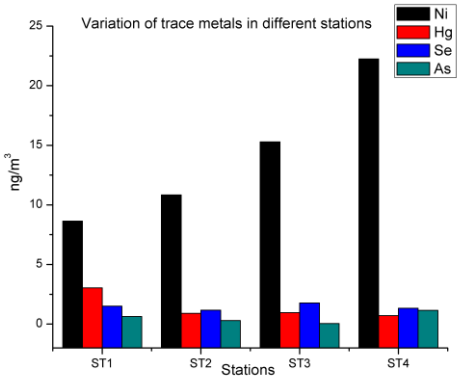

Fig. 4(b)

Figure 4 Variation of trace metals concentration

3.2.2 FTIR Analysis of Dust

Spectral analysis Representative FTIR spectra of dust sample is shown in Figure 5. Specific organic molecules could not be confirmed; however, organic functional groups were assigned. Dominant peaks of the frequency levels 1020, 1430–1455, 2360–2336, and 3448 cm^{-1} were observed in the samples. This frequency data are reflecting the presence of S–O, CO_2, SO_2, C≡C, and SiO–H bond stretch. SiO-H stretch, methyl, inorganic sulphate, silica and inorganic phosphate etc. are also present in the dust samples.

3.2.3 XRD analysis of Dust

Samples from each monitoring stations in all three seasons were analyzed through X-ray diffraction technique. X-ray diffractrogram pattern is shown in Figure 6. The presence of quartz, copper arsenide, cadmium, mercury etc. were reflected by the X-ray diffractogram pattern of the study area. The XRD study also confirms the presence of minerals like Aluminum Oxide, Lead oxide, etc. in the dust.

3.2.4 SEM-EDX Analysis

Physical characteristics of dust plays a vital role to identify the source. Microscopic analysis of PM was made by SEM during different seasons (Figure 7(a & b)). The shape of dust particles varies from compact and rounded to thin flakes, fibers, and angular as well as aggregates[14]. Irregular shape of the particle with adhered smaller particles on the surface with size indicates

vehicular source[15]. The most abundant group found in this size is association of Fe,Ni,Si, Al and Mg with minor amount of K, and Na indicating the probable sources of coal burning [16]. Mineral particles have irregular shapes, and they are mainly derived from natural sources such as soil dust, resuspension of dust from road, and some other anthropogenic activities such as mining and vehicles [17].

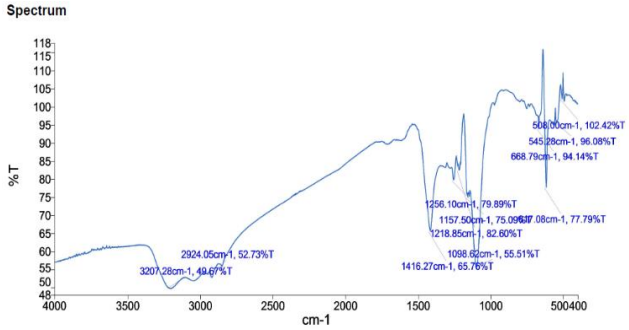

Fig. 5 FTIR spectra of dust sample

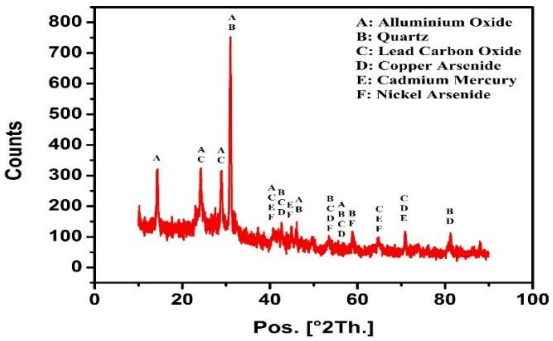

Fig. 6 X-ray diffractrogram pattern of dust sample

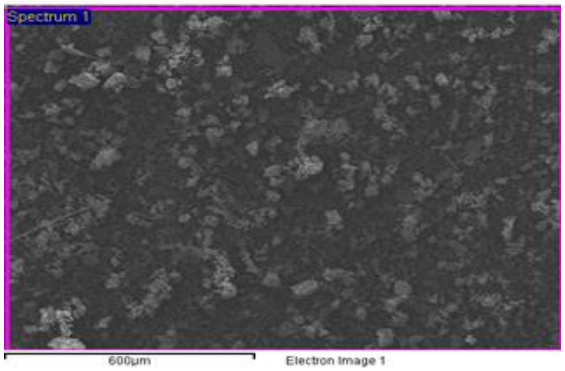

Fig. 7(a)

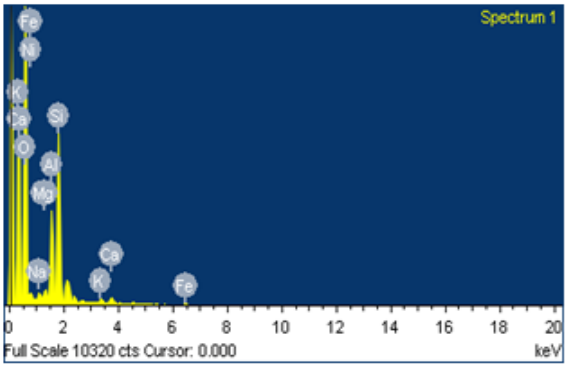

Fig. 7(b)

Figure 7 SEM-EDX images of dust sample

4.0 Data Analysis

4.1 Pearson's correlation analysis

Pearson's correlation analysis was performed to investigate the correlation between all the trace elements and particulate matter under consideration in terms of its concentrations. Because, it is apparent that elements that are strongly correlated indicate some common sources [18]. The average data of the study period was used for correlation analysis. Particulate matter (PM_{10}) was significantly correlated with Cu (r = 0.965), Pb (r =0.964) at level 0.05. Similarly $PM_{2.5}$ was significantly correlated with Cd(r=0.975), Cu (r=0.971) and Hg (r=0.999) at level 0.05. Very strong correlation was observed between Pb-Cu (r=0.989), Hg-Cd (r=0.977) and Hg-Cu (r= 0.962). Significant correlation were also observed between Zn-Cr (r=0.582) and Zn-Fe (0.825). The metals are generally contributed by anthropogenic activities such as vehicular emission and metal corrosion (Cu, Zn, Cd) [19], coal burning (As, Cr, Pb) [20]. Zn is emitted utterly from vehicular sources like, wear and tear of vulcanized tyres, and oil combustion [21]. Hence, the most prominent sources of trace elements in the study area were resuspension of road dust due to vehicular emission and coal burning. Correlation matrix was developed and is shown in Table 1 for clear indication of relations between data points.

Table 1 Correlation matrix of particulate and trace metals

	PM_{10}	$PM_{2.5}$	Fe	Cr	Cd	Cu	Pb	Zn	Ni	Hg	Se	As
PM_{10}	1	.881	.407	-.816	.806	**.965***	**.964***	-.181	-.301	.864	-.052	.549

$PM_{2.5}$		1	.399	-.995	**.975***	**.971***	.937	-.121	-.660	**.999****	.181	.088
Fe			1	-.566	.552	.467	.583	.825	.226	.391	.816	.156
Cr				1	-.996	-.948	-.935	.582	.930	-.998*	-.027	.113
Cd					1	.932	.918	.090	-.620	**.977***	.396	-.025
Cu						1	**.989***	-.097	-.476	**.962***	.123	.317
Pb							1	.029	-.357	.925	.207	.374
Zn								1	.439	-.119	.907	-.164
Ni									1	-.682	.019	.534
Hg										1	.193	.053
Se											1	-.427
As												1

** Correlation is significant at the 0.01 level
*Correlation is significant at the 0.05 level

4.2 Principle component analysis

Principle component analysis best explains the quantitative information of these metals and their corresponding sources [22]. The principal application of factor analysis is to reduce the number of variables. Therefore, factor analysis can be applied as a data reduction method. PCA was performed by the Varimax Rotated Factor Matrix method (IBM SPSS 20.0) [23]. In the study area, two components (principal components) having eigen values > 1 were extracted accounting about 67.24% of the cumulative variance in the entire data set. Table 2 represents the principal component (PC) loadings for the different factors during the study period. PC1 with variance 67.24% shows higher loading of Cd, Cu, Pb and Hg which indicates close association of these elements with PM. Cd and Pb are associated with mining and allied activities [20]. Apart from mining activity Cd is also associated with the resuspension of road dust [24]. In addition to mining activity, Pb and Cd is also related to vehicular emission [25]. Cu is mainly related to coal combustion [26]. PC2 is represented by Fe and Se with variance 32.76% and Zn is from crustal origin. Fe and As are also significant elements in PC2. Fe is crustal in origin and associated with road dust or dust from OB dumps [27].

Table 2: Extracted principal components of different variables

Factors	Component	
	PC1	PC2
PM_{10}	**.884**	-.468
$PM_{2.5}$	**1.000**	.032
Fe	.456	**.890**
Cr	-.992	-.128
Cd	**.976**	.216
Cu	**.981**	-.194
Pb	**.972**	-.233
Zn	-.682	**.732**
Ni	-.875	-.484
Hg	**.998**	.065
Se	-.101	**.995**
As	.016	-1.000
Total	8.069	3.931
% Variance	67.24	32.76

% Cumulative Variance	67.24	100.000

5.0 Concluding remarks

The result obtained by the monitoring of particulate matter suggested that the study area is highly loaded with particulate pollution from mining and non-mining sources. The seasonal variations of particulate matter (PM_{10} & $PM_{2.5}$) confirm about the highest concentration of particulate matter in winter season followed by summer and then post monsoon. The concentration of particulate matter is above the standard level all over the year as prescribed by NAAQS, 2009. After analysis of results, it can be concluded that in the study area, source contribution is mainly due to earth crust i.e., mining and associated mining activities, vehicular emissions and road dust through unpaved roads. The characterization of trace metal sources in the study area is quite challenging due to a large number of source contributions to the study area. The trace metal analysis suggests the presence of Fe, Cr,Cd,Cu,Pd, Zn etc. in the dust sample. Some traces of harmful trace metals such as Hg, As and Se were also found in the sample. Similarly the XRD, FTIR and SEM study of the sample gave a clear picture about the presence of different functional groups, minerals and elements in the dust samples. It also helps for source identification study. Factor analysis (PCA) suggested the dominance of Cd, Cu, Pb and Hg in dust of the study area and represented as PC1. These were mainly contributed by vehicular emission from transportation of coal, running of mine machineries and coal burning in the study area. The correlation analysis supports the relationship between different parameters in the study area.

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