Measurement of respirable dust concentration and assessment of health risk due to metals around an opencast coal mine of Talcher, Odisha

Debi Prasad Tripathy and Tushar Ranjan Dash

Department of Mining Engineering, National Institute of Technology Rourkela, Odisha, India

Atmospheric pollution due to particulate matter in opencast coal mining area is a very important environmental problem and is fetching the attention of researchers worldwide since few decades. The particulate matter not only affects human but also have tremendous effects on nearby flora and fauna by degrading the ecological environment in many ways. High mechanization in mining operations leads to add heavy load of dust to the surrounding area. The adverse effects of dust depend on the quantity as well as the characteristics of the dust and the exposure dose. Taking the importance of the dust pollution in mines, a coal mine area of Talcher coalfield, was selected, which is one of the oldest coalfields of India and a very limited work has been carried out in that area on the regards of assessment of health risk due to metals on the local population. Monitoring of respirable dust (PM_{10} & $PM_{2.5}$) were performed at eight monitoring stations around a high mechanised opencast coal mine for three seasons *i.e.*, post monsoon, winter, and summer in the year 2015 as per the standard criteria of Central Pollution Control Board (CPCB), India. The seasonal variation of dust concentration was found in the order of winter > summer > post monsoon. Ten trace metals were analysed from the dust samples. Statistical analysis, such as, univariate (correlation study) and multi-variate analysis were carried out including principal component analysis (PCA) for source identification and respective contribution to particulate matter. Finally, the health risk in terms of hazards quotient (*HQ*) and hazards index (*HI*) were calculated for both children and adults for the three exposure path ways (Inhalation, ingestion and dermal exposure). The carcinogenic effects due to the presence of trace metals in the PM_{10} were evaluated for both children and adults in terms of excess cancer risk (*ECR*). The combined carcinogenic effects of all the trace metals also calculated (*ECR_{Total}*). The *HQ* values for Cr and Cd were found above the safe limit in that area for both children and adults. Likewise the ECR values for Cr and Cd also were at a very risk level for both the age group. However the risk related to other metals were found well within the safe limit. The *HI* and *ECR_{Total}* values were found above the safe limit which indicates the combined effect of trace metals on the children and adult were at and very high risk level in the study area.

Keywords: PM_{10}, $PM_{2.5}$, heavy metals, correlation analysis, PCA, health risk

1. Introduction

In opencast mining areas air pollution due to particulate matter (PM) is a serious problem and also is considered as a dominating air pollutant (Ghose and Majee, 2001). All types of mining activities are more or less responsible for the generation of PM. Different mining activities like drilling, blasting, loading, unloading and transportation (coal and overburden material) etc. generates huge quantities of PM, which affect the surrounding environment as well as the human health (Chaulya, 2004). Coal is considered as the cheapest source of energy and fulfil most part of the energy demand of the world (Franco and Diaz, 2009). The increase in the use of electricity enhances the demand of the coal production, which leads to implementation of high mechanization mining method techniques. High mechanized operation of coal extraction produces huge quantity of PM and create air pollution problem directly or indirectly (Baldauf et al., 2001). The health of the mine workers and the nearby residences depends on the dispersion pattern of PM in air. The dispersion and transportation of PM to the surrounding environment depend on the concentration, size, shape, and nature of particles along with the meteorological parameters of the area (Vesovic et al., 2001). Finer particles can be suspended in air for a longer time and transported to long distances as compared to coarse particles. The hazardous nature of the PM goes up with the reduction in the particle size. Finer particles can go directly to the deeper part of the lungs during inhalation and affects respiratory system. Taking the seriousness of the respirable PM towards the human health, it is essential to measure the concentration. The most important emissions during coal mining and coal burning are PM (PM_{10} and $PM_{2.5}$) and its content such as inorganic heavy metals and polycyclic aromatic hydrocarbons associated with PM (Gunawardana et al., 2011; Tsai and Cheng, 2004). Different organic and inorganic compounds are present in the PM. The trace metals present in the PM are emitted from various natural and anthropogenic sources such as crustal materials, road dust, motor vehicles, coal and oil combustion, incineration and other industrial activities (Arditsoglou and Samara, 2010; Shah and Shaheen, 2010).

Apart from the health effects, the PM also affects the surrounding environment, reduces visibility and also affects the flora and fauna (NIOSH, 2005). Several epidemiological studies proved a strong correlation between the exposure of PM concentration and increased mortality (Lin and Lee, 2007; Namdeo and Bell, 2005). The toxic heavy metals associated with respirable PM can cause lung and cardiopulmonary injuries, cardiovascular problems, damaged to various organs, and premature mortality in humans (Callen et al., 2009; Megas et al., 2007; Shaheen et al., 2005). Among the trace metals, Arsenic (As) is a human carcinogen and can cause respiratory tract disorders, skin ailments, cardiovascular and nervous system problem (USEPA 1984). Lead (Pb) and Cadmium (Cd) interference with normal kidney function leads to kidney disorder (USEPA, 1990). Chro-

mium (Cr) causes lung cancer like diseases and Cr (VI) is a human carcinogen. Several studies were performed on the effects of PM and associated heavy metals on the cardiovascular and respiratory system (Kloog, 2016; Yu and Chien, 2016). Limited studies were performed in India on the evaluation of health risk due to the presence of trace metals in PM (Jai Prakash et al. 2018; Samiksha et al., 2017; Jena and Singh, 2017; Izhar et al., 2016). Further the chemical compounds present in the PM differ in the concentration at different locations depending on the sources of contribution and meteorological factors. So it becomes essential to study the health risk due to metals especially in coal mining areas, where a lot of sources contribute the pollutants (Shah and Shaheen, 2010).

The use of measured trace elements concentration in source identification is very common practice. But the evaluation of health risk due to the presence of trace metals in PM for the people residing near a coal mining area is very limited. So in this study, an attempt has been made to measure the PM (PM_{10} and $PM_{2.5}$) concentrations around a highly mechanised coal mine and study the seasonal variations. Source apportionment study was carried out using statistical techniques like Principal Component Analysis (PCA) and correlation analysis. Finally the health risk was calculated for both children and adults residing near the mining area due to the presence of trace metals in the respirable PM.

2. Study area

In this study a highly mechanized opencast coal mine was selected in an area, which was one of the critically polluted area of the state Odisha, India.The mine is located in the city of Talcher and the mine is lies within latitude 20° 57′ 39″ and 20° 58′ 18″ (N) and longitude 85° 09′ 33″ and 85°12′ 12″ (E). The elevation of the study area is 85 to 120 m above the sea level. The mean annual precipitation was recorded as 1277 mm and most of which occurs during rainy season. Total mining area of the studied mine was 1410.01 ha. (CMPDI Report, 2013). Talcher is one of the oldest industrial clusters located in the central part of Odisha state of India. This location is about 120 km from the state capital Bhubaneswar and 160 km from the Bay of Bengal. With two national highways and well-connected railway lines, now the area become an industrial destination of the country. The core zone of the mine covers partly and /or fully the land from seven villages. Other coal projects situated in the buffer zone of the studied mine are Balaram opencast project (OCP), Ananta OCP, Bharatpur OCP, Bhubaneswari OCP, Jagannath OCP etc. Other than the coal mines several industries also situated in and around the buffer zone of the mine and those are Talcher Thermal Power Station (TTPS/NTPC), Talcher heavy water plant at FCI, coal washery at Balanda. The buffer zone of the studied mine also contain eight reserve forests. The map of the study area with sampling stations is shown in Fig. 1.

3. Methodology

3.1. Respirable dust measurement

Both PM_{10} and $PM_{2.5}$ samples were collected from eight sampling stations during three seasons *i.e.*, post monsoon (October and November), winter (December to February), and summer (March to June) of the year 2015–16. The sampling was carried out for 24 hourly basis. The PM_{10} and $PM_{2.5}$ samples were collected weekly twice from each stations. Total 72 samples from PM_{10} and $PM_{2.5}$ were collected for the three seasons from each sampling stations. The ambient air quality monitoring was done as per the siting criteria provided by IS: 5182 Part XIV, 2000. The sampling stations were selected in order to cover up the total mining area including mining as well as residential area around the mine. The measured concentration of PM_{10} and $PM_{2.5}$ at different sampling locations
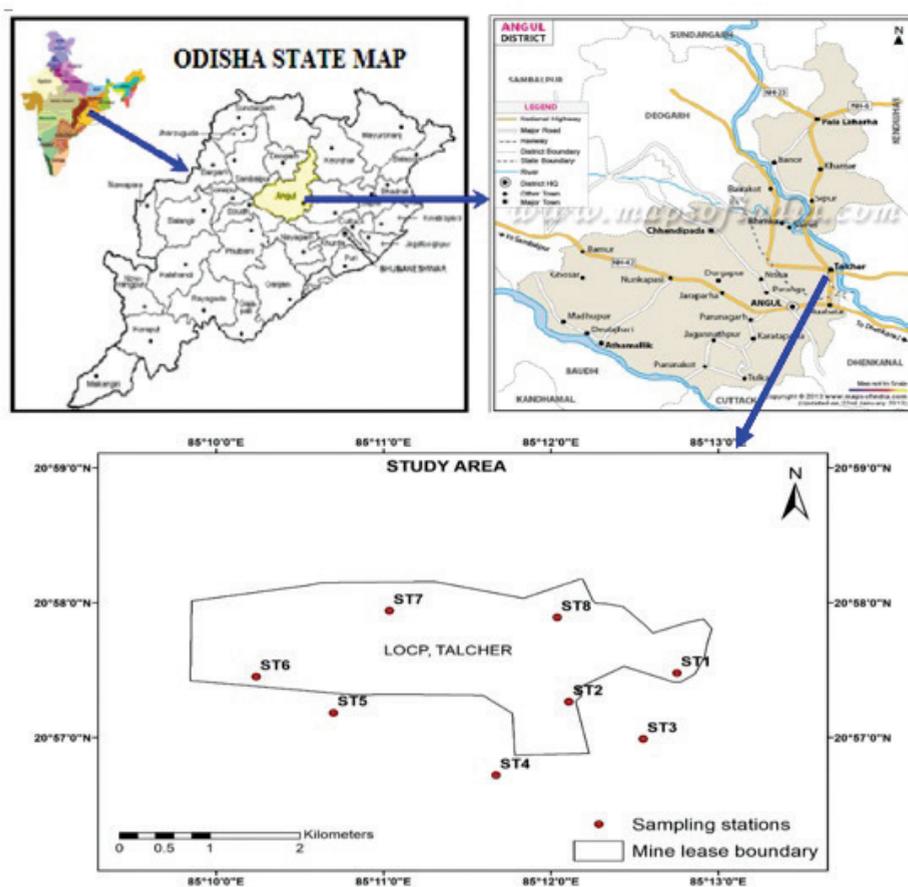
Figure 1. Map of the study area and sampling stations.

were compared with the National Ambient Air Quality Standards (NAAQS, 2009) (Tab. 1). PM_{10} samples were collected using respirable dust samplers (Envirotech APM 460 NL) with flow rate of 1.1 m^3/min on EPM2000 filters (8″ × 10″). The basic mechanism of respirable dust sampler is based on the cyclonic separation of particles by the action of centrifugal force. The PM_{10} fraction separated by the centrifugal force deposited on the EPM2000 grade glass fibre filter paper.

Table 1. NAAQS, 2009 for annual respirable particulate matter (CPCB, 2011).

Sl. No.	Pollutants	Concentration in ambient air	Methods of measurement
1	Particulate matter (size less than 10 µm) or PM_{10}, µg/m^3	100	Gravimetric
2	Particulate matter (size less than 2.5 µm) or $PM_{2.5}$, µg/m^3	60	
3	Lead (Pb), µg/m^3	0.5	AAS/ICP method after sampling on EPM 2000 or equivalent filter paper
4	Arsenic (As), ng/m^3	06	
5	Nickel (Ni), ng/m^3	20	

Table 2. Monitoring locations in details with major activities.

Station Code	Geographic Location		Mean Sea Level (MSL), in m	Dominating Activity
	North (N)	East (E)		
ST1	20057′28.80″	85012′45.1″	96	Vehicular movement, coal transportation road, railway siding 500m
ST2	20057′16.00″	85012′06.4″	112	Mining activity, coal transportation road, haul road, exposed dump, exposed dump surface, weigh bridge, coal burning, CHP
ST3	20056′59.50″	85012′33.0″	104	Residential activity, normal vehicular movement, domestic coal burning
ST4	20056′45.30″	85011′40.3″	110	Main road towards Dera, coal and non-coal transportation road, residential activity, domestic coal burning
ST5	20057′11.10″	85010′42.0″	131	Exposed dump, CHP, Bypass road to Dera, mining activity 500m away
ST6	20057′27.20″	85010′14.3″	131	Vehicle maintenance workshop, exposed mining pit. OB pit, residential area 100m.
ST7	20057′56.50″	85011′02.0″	123	Rehabilitee village having very low population, mining activity, normal transportation, domestic coal burning.
ST8	20057′53.05″	85012′02.2″	101	Railway siding area, coal stock yard, OB exposed, residential area, domestic coal burning etc.

Similarly $PM_{2.5}$ samples were collected using fine particulate samplers (Envirotech APM 550) with flow rate of 16.7 lpm on a 47 mm diameter PTFE filter. The filters were conditioned in a desiccator for 24 hours before and after sampling. The differences in the weight of the filters before and after sampling were used to calculate PM_{10} and $PM_{2.5}$ concentrations. The monitoring was performed in accordance with the IS: 5182 Part XXIII, (BIS 2006). The sampling was done at stations with geographic locations and characteristics are shown in Tab. 2.

3.2. Analysis for trace metals from the PM_{10}

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) (Katz, 1977). By using the same digestion method and chemicals a blank sample was prepared. The chemical reagents and standards used for the calibration of the instrument were of AR grade. The trace metal amounts in the samples were calculated by subtracting the blank value for the respective metal. The detection limit of various trace metals were Fe – 0.032 $\mu g/m^3$, Pb – 0.063 $\mu g/m^3$, Ni – 0.6 ng/m^3, Cu – 0.02 $\mu g/m^3$, Cd – 0.006 $\mu g/m^3$, Cr – 0.032 $\mu g/m^3$, Hg – 0.38 ng/m^3, As – 0.44 ng/m^3, and Se – 0.5 ng/m^3. The absorbance of both standard metal solution and digested sample of respective metal were compared to find the metal concentration. The digested samples were directly introduced into the flame of the instrument. Seven elements *i.e.*, Cu, Pb, Cd, Cr, Zn, Ni, and Se were directly analysed in the AAS. Hg and As were analysed by VG-AAS (Vapour Generation Atomic Absorption Spectrometer). Vapour generation is a technique performed by an additional attachment connected with AAS for the detection of trace elements like Hg and As. Iron was analysed by titration method. The concentration of the object element ($\mu g/mL$) was obtained from the calibration plot. The concentration of an element in the atmosphere is obtained from the following relation (eq. 1):

$$C(\frac{\mu g}{m^3}) = \frac{Concentration\ of\ the\ element\ in\ the\ digested\ sample\ (\mu g\ /\ mL)}{Volume\ of\ air\ sampled\ in\ m^3}$$

$$\times \frac{Total\ volume\ of\ sample\ (mL)}{Percent\ of\ filter\ area\ used\ for\ analysis} \tag{1}$$

3.3. Data analysis techniques

Obtained data were processed for statistical analysis includg univariate and multivariate methods. Basic statistical parameters such as standard deviation, mean, median, and range were computed along with correlation analysis among the different parameters (Pandit et al., 2011) using IBM SPSS version 20.

3.4. Evaluation of health risk associated with trace metals

Human health risk was assessed on the basis of observed mean concentrations of particulate-bound trace elements and it depends on specific locations and its exposure route, *i.e.*, ingestion, dermal, and inhalation (Du et al., 2013; Jai Prakash et al., 2018; Jai Prakash et al., 2018; Du et al., 2013). This study used the equations developed by USEPA to evaluate the exposure of humans to atmospheric particle bound trace elements. Mainly there are three main exposure paths through which the atmospheric elements can enter to the human body and these are ingestion, dermal absorption and inhalation through mouth and nose (Li et al., 2015). The exposure due to these paths was separately calculated by three different equations and these are given below (USEPA, 2009; USEPA, 2004a; USEPA, 1989). After the calculation of the exposure doses for the different elements and for all the pathways in exposure, the risk were calculated for both non- carcinogenic health risk and excess cancerous risk. The exposure dose for the three exposure routes were calculated by using the following equations (eqs. 2–4)

$$ED_{ing} = \frac{C \times IR_{ing} \times CF \times EF \times ED}{BW \times AT} \tag{2}$$

$$ED_{der} = \frac{C \times SA \times AF \times EVF \times DAF \times EF \times ED \times CF}{BW \times AT} \tag{3}$$

$$ED_{inh} = \frac{C \times IR_{inh} \times CF \times EF \times ED}{BW \times AT} \tag{4}$$

where:
ED_{ing} = Exposure dose due to ingestion pathway
ED_{der} = Exposure dose due to dermal contact
ED_{inh} = Exposure dose due to inhalation pathway
C = Concentration of metal in ambient air
R_{ing} = Ingestion rate
R_{inh} = Inhalation rate
ED = Exposure duration
EF = Exposure frequency
BW = Body weight
SA = Skin surface area
AF = Adherence factor soil to skin
EVF = Event frequency
DAF = Dermal absorption fraction
AT = Average time
ET   = Exposure time
CF   = Conversion factor

3.4.1. Non-carcinogenic risk

For the calculation of non-carcinogenic risk, hazard quotient (*HQ*) and hazard index (*HI*) were calculated for the trace elements for all the three exposure rotes *i.e.*, ingestion, dermal contact, and inhalation. *HQ* via ingestion (*HQ_{ing}*), inhalation (*HQ_{inh}*) and dermal (*HQ_{der}*) contact were calculated by equations bellow (eqs. 5–7).

$$HQ_{ing} = \frac{ED_{ing}}{RfD} \tag{5}$$

$$HQ_{inh} = \frac{ED_{inh}}{RfC} \tag{6}$$

$$HQ_{der} = \frac{ED_{der}}{RfD \times GIAF} \tag{7}$$

were:

RfD   = Oral reference dose (mg/kg/day),
RfC   = Inhalation reference concentrations (mg/m^3/day)
GIAF = Gastrointestinal absorption factor.

The values of *RfD*, *RfC* and *GIAF* were adopted from US EPA, 2015. If *HQ* < 1, there is no adverse effects on health and if *HQ* > 1, there is likely adverse health effects due to exposure (USEPA, 1989). To avoid the underestimate of hazard potential of one element at a time with the simultaneous exposures to multiple elements hazards index is calculated by taking the sum of all the *HQ*s vales of all the metals. *HI* was calculated as given in eq. 8 following the method earlier used by researchers (Zheng et al., 2010). The *HI* < 1 indicates no risk from non-carcinogens, while *HI* > 1 indicates significant non carcinogenic risk.

$$HI = \sum_{i=1}^{n} HQ_1 + HQ_2 + \ldots + HQ_i \tag{8}$$

where:

HQ_1 = HQ for 1st metal, let say Cr,
HQ_2 = HQ for 2nd metal, let say Cd, likewise
HQ_i = HQ for i[th] metal

3.4.2. Excess cancer risk

Excess cancer risk (ECR) is the probability of developing cancer over the lifetime period of exposure to carcinogenic metals. The ECR were calculated for each of the analysed carcinogenic metals, and the combined effects were calculated in terms of *ECR_{Total}*. The ECR can be expressed as follows (eq. 9) (USEPA, 2011):

$$ECR = \frac{C \times ET \times EF \times ED \times IUR}{AT} \qquad (9)$$

where:

C = Concentration of metal in ambient air
ET = Exposure time
EF = Exposure frequency
ED = Exposure duration
IUR = Inhalation unit risk of element
AT = Average time

The value of IUR (μg/m^3)$^{-1}$ of the element, obtained from the USEPA database, Integrated Risk Information System (IRIS) (https://www.epa.gov/iris). The details of the values of all the parameters used in equation and calculations are given in the supplementary material. The range of excess cancer risk has been recommended by the USEPA (2015) for public health. The acceptable value for carcinogenic risk falls between 10^{-6} to 10^{-4}, above which there will be potential carcinogenic health risk. In the present study, the excess cancer risk was calculated for Cr, Ni, Pb, Zn, Cd and As out of 10 trace elements which are well-known

Table 3. Factors for exposure dose calculation.

Factors	Definition	Units	Value		Source
			Children	Adult	
C	Concentration of the metal in Ambient air	mg/kg for ingestion and dermal exposure, and μg/m^3 for inhalation exposure	Children	Adult	
$Ring$	Ingestion rate	mg/day	60	30	US EPA (2007)
$Rinh$	Inhalation rate	m^3/day	10	20	US EPA (2011)
EF	Exposure Frequency	day/year	350	350	US EPA (2016b)
ED	ExposureDuration	year	6	24	US EPA (2011)
BW	Body Weight	kg	15	70	US EPA (2013)
SA	Skin surface Area Parameter	cm^2	2800	5700	US EPA (2004b)
AF	Adherence Factor soil to Skin	mg/cm^2/event	0.2	0.07	US EPA (2004b)
EVF	Event Frequency	event/day	1	1	US EPA (2004b)
DAF	Dermal absorption fraction		0.001	0.001	US EPA (2004a)
AT	Average time	days/year	365*ED	365*ED	US EPA (2004b)
ET	Exposure Time	hours/day	24	24	US EPA (2016b)
$CF(ED_{ing/der})$	Conversion Factor	kg/mg	10^{-6}	10^{-6}	US EPA (2004b)
$CF(EDinh)$	Conversion Factor	μg/m^3	10^{-3}	10^{-3}	US EPA (2004b)

Table 4. RfC ($\mu g/m^3/day$), RfD ($\mu g/m^3/day$), GIABS and IUR (($\mu g/m^3$)$^{-1}$) values for different trace elements.

Trace elements	As	Cd	Cr	Se	Cu	Ni	Pb	Zn	Hg
RfD	3.00E-04	1.00-03	3.00E-03	5E-3	4.00E-02	2.00E-02	3.50E-03	3.00E-01	1.6E-4
RfC	3.00E-04	1.00E-03	2.86E-05	2.0E-2	4.02E-02	3.52E-03	3.52E-03	3.01E-01	3.0E-4
GIABS	1	0.025	0.013	1	1	0.04	1	1	
IUR	0.0043	0.0018	0.012*	–	–	0.00024	–	0.000012	

(US EPA, 2016)/CALEPA
* Cr(VI)
RfD = Oral reference dose
RfC = Inhalation reference dose
GIABS = Gastrointestinal absorption factor, *IUR*=Inhalation unit risk

carcinogens and whose *IUR* values are given in IRIS, 1995. Different factors for exposure calculation is tabulated in Tab. 3, whereas the reference doses for metals are tabulated in Tab. 4.

4. Results and discussion

4.1. Particulate matter

The statistical distribution of the particulate matter (PM_{10} & $PM_{2.5}$) are presented in Table 5. The distributions of PM_{10} and $PM_{2.5}$ along different locations in three different seasons are plotted in Figs. 2 and 3 respectively. From these figures, the seasonal variation in particulate concentrations is quite evident. The concentrations of PM_{10} and $PM_{2.5}$ were observed highest during the winter season, followed by summer then post monsoon. Similar findings were also obtained by Dubey et al. (2012), Pandey et al. (2014), Jena and Singh (2017) around mining areas in Jharia Coalfield. Higher concentration of PM during winter is attributed to the prevalence of anti-cyclonic conditions, characterized by calm or light winds and limited mixing depth due to a stable or inversion of atmospheric lapse rate (Chaulya, 2004). The average PM_{10} concentration of all the three seasons at all the sampling stations was observed as 338.43 µg/m^3, which was about 5.64 times above the NAAQS, 2009. Similarly, the average $PM_{2.5}$ concentration of all the three seasons at all the sampling stations was observed as 103.50 µg/m^3, which was about 2.59 times above the NAAQS, 2009. The annual mean concentration of PM_{10} at different location shows that ST4 was experienced higher concentration of PM_{10} (483.94 µg/m^3) followed by ST2 (420.22 µg/m^3), ST6 (380.85 µg/m^3), ST8 (369.92 µg/m^3), ST5 (333.35), ST7 (267.27 µg/m^3), ST1 (229.69 µg/m^3) and least at ST3 (221.20 µg/m^3). Similarly, the highest mean concentration of $PM_{2.5}$ was observed at ST4 (123.84 µg/m^3), followed by ST8 (107.86 µg/m^3), ST6 (107.55 µg/m^3),
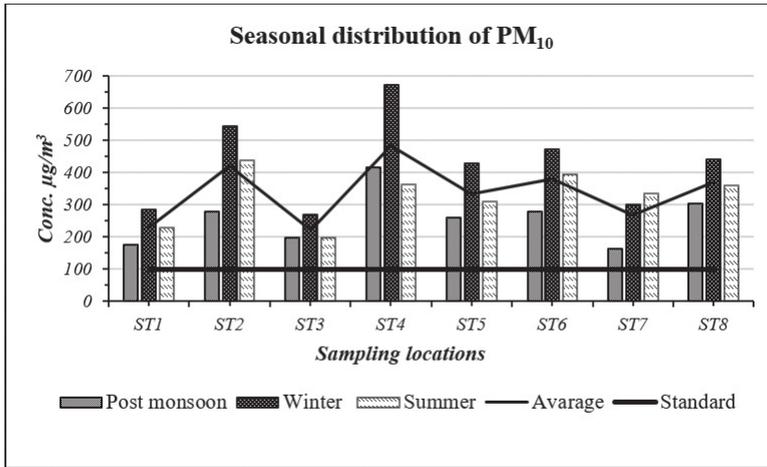
Figure 2. Distribution of PM_{10} in different seasons.
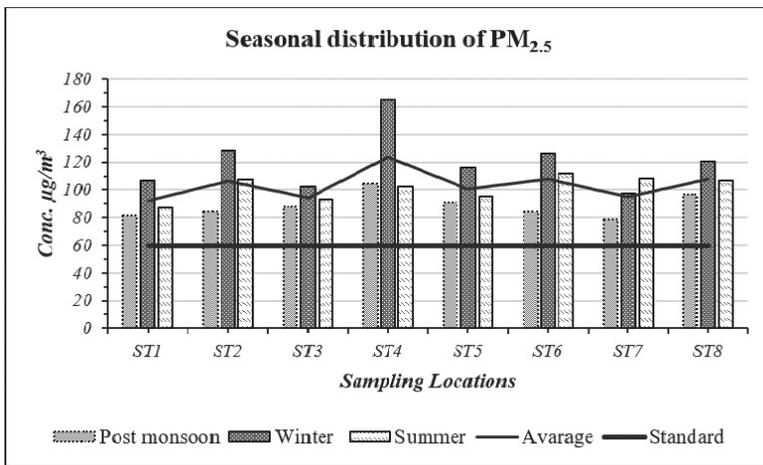
Figure 3. Distribution of $PM_{2.5}$ in different seasons.

ST2 (106.65 µg/m³), ST5 (100.74 µg/m³), ST7 (94.89 µg/m³), ST3 (94.47 µg/m³), and least at ST 1 (92.00 µg/m³). For all three observed seasons, the average particulate concentration was found highest in ST4. The highest concentrations of PM at ST4 were due to the continuous impact of mining activities in nearby locations as well as due to vehicular emissions from mining and non-mining transportation (Dubey et al., 2012; Huertas et al., 2012). All the stations were showing the average particulate concentrations above the standard value as prescribed in NAAQS 2009 (National Ambient Air Quality Standard, 2009). The maximum value of PM_{10} was

Table 5. Statistical distribution of PM_{10} and $PM_{2.5}$ in the study area in ($\mu g/m^3$).

6,5	Particulate	Maximum	Minimum	SD	Arithmetic mean	Geometric mean	Median	Ratio $PM_{2.5}/PM_{10}$
ST1	PM_{10}	582.91	94.07	133.23	232.36	204.67	180.17	0.40
	$PM_{2.5}$	173.84	38.85	37.51	92.52	85.11	94.02	
ST2	PM_{10}	960.23	149.16	199.22	425.51	385.59	372.14	0.25
	$PM_{2.5}$	199.12	27.07	46.39	107.28	97.60	95.32	
ST3	PM_{10}	421.71	99.69	92.44	220.51	202.44	193.21	0.43
	$PM_{2.5}$	208.84	36.17	42.14	94.73	85.95	88.52	
ST4	PM_{10}	1092.93	97.40	241.22	484.37	425.17	403.30	0.26
	$PM_{2.5}$	276.66	38.46	53.27	124.29	114.14	118.16	
ST5	PM_{10}	630.23	121.16	139.90	334.81	306.68	309.66	0.30
	$PM_{2.5}$	209.69	42.37	34.19	100.64	95.52	97.85	
ST6	PM_{10}	787.64	200.90	152.15	393.68	369.08	351.88	0.28
	$PM_{2.5}$	223.43	58.37	41.66	110.34	103.78	101.32	
ST7	PM_{10}	572.12	117.10	118.03	279.56	256.42	261.85	0.35
	$PM_{2.5}$	196.25	67.45	26.10	96.87	94.22	88.33	
ST8	PM_{10}	685.84	170.66	126.50	374.89	354.44	330.56	0.29
	$PM_{2.5}$	165.29	69.42	24.24	108.71	106.18	104.63	

found at ST 4 (1092.93 $\mu g/m^3$). The ratios of $PM_{2.5}$ and PM_{10} ($PM_{2.5}/PM_{10}$) calculated at all monitoring stations illustrate significant contribution of $PM_{2.5}$ to the total PM_{10} concentrations (Tab. 5). Mining operations generally contribute more fraction of large sized dust particles along with fine particles in very less fraction. High $PM_{2.5}$ to PM_{10} ratio represents significance influence of vehicular emissions (especially, tail pipe emissions), while low ratio depicts the influence of fugitive emission as well as resuspension of settled dusts. The lowest value of $PM_{2.5}$ and PM_{10} ratio in ST2 and ST4 suggested that the PM constitute more fraction of coarse particulate as compared to rest of the stations. ST2 and ST4 were more exposed to mining and transportation activity and thus having more coarse particles from crustal generation. ST5, ST6, and ST8 had slightly higher ratios, whereas ST1, ST3 and ST7 were higher $PM_{2.5}$ and PM_{10} ratio indicated more fraction of finer particles in the PM mass.

4.2. Trace elements

The average concentration of trace elements in all the three seasons at all the sampling stations was observed highest for Cd (3.465 $\mu g/m^3$) followed by Fe (2.26 $\mu g/m^3$), Zn (0.857 $\mu g/m^3$), Cr (0.748 $\mu g/m^3$), Pb (0.07 $\mu g/m^3$), Cu (0.03 $\mu g/m^3$), Ni (0.015 $\mu g/m^3$), As (0.004 $\mu g/m^3$), Se (0.0013 $\mu g/m^3$) and Hg (0.0012 $\mu g/m^3$). The decreasing elemental concentration trend of the study area was Cd>Fe>Zn>Cr>Pb>Cu>Ni>As>Se>Hg. The concentration of Fe was highest in summer and the values

ranged from 3.82 µg/m³ to 1.37 µg/m³ (Post monsoon). Similarly the average value of Cu ranged from 0.037 µg/m³ in summer to 0.029 µg/m³ in post monsoon, Pb 0.09 µg/m³ (summer) to 0.04 µg/m³ (Post monsoon), Cd 6.92 µg/m³ (winter) to 3.45 µg/m³ (post monsoon), Cr 1.54 µg/m³ (winter) to 0.67 µg/m³ (post monsoon), Zn 1.02 µg/m³ (Post monsoon) to 1.00 µg/m³ (winter). Hg 0.0016 µg/m³ (winter) to 0.0012 µg/m³ (post monsoon), Ni 0.018 µg/m³ (post monsoon) to 0.015 µg/m³ (winter), As 0.0069 µg/m³ (winter) to 0.0035 µg/m³ (post monsoon) and Se 0.0019 µg/m³ (winter) to 0.0011 µg/m³ (winter). The value of Pb in the area was minimum at ST7 in post monsoon season (0.032 µg/m³) and maximum found at ST4 in winter season (0.149 µg/m³). In all the stations the observed vales were well within the standard of NAAQS 2009 (0.5 µg/m³). The low concentration of Pb even along the transportation routes may be due to use of unleaded fuels. Ni concentrations were observed higher than the NAAQS (0.02 µg/m³) at ST1 in post monsoon (0.0211 µg/m³), ST2 in winter (0.0217 µg/m³) and summer (0.027 µg/m³), ST5 in post monsoon (0.0318 µg/m³) and summer (0.0199 µg/m³), ST7 in summer (0.446 µg/m³). The Ni concentration in ST5 in summer (0.0199 µg/m³) and ST8 in post monsoon (0.0199 µg/m³) just touched the limit of NAAQS and all other locations were well within the range. The increased concentrations of Ni in this area indicates the influence of transportation activities. The average concentration of As was from 0.0004 µg/m³ at ST1 & ST8 in summer season to 0.0152 µg/m³ at
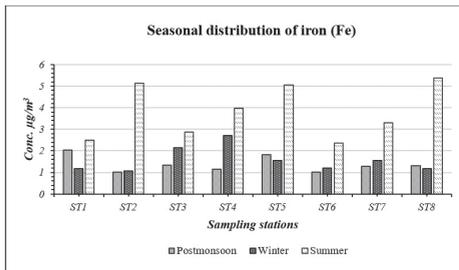
Figure 4.1. Seasonal distribution of iron.
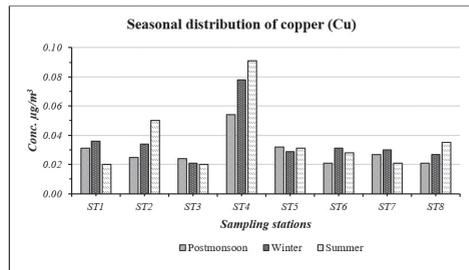
Figure 4.2. Seasonal distribution of copper.
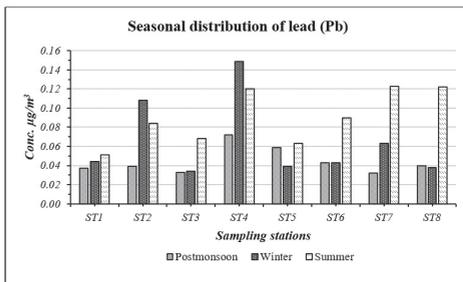
Figure 4.3. Seasonal distribution of lead.
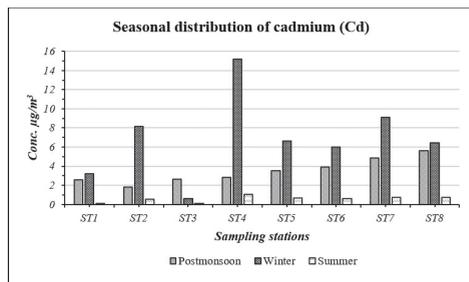
Figure 4.4. Seasonal distribution of cadmium.
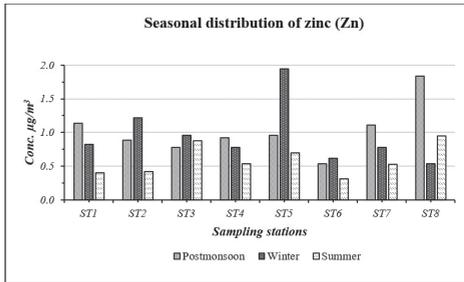
Figure 4.5. Seasonal distribution of zinc.
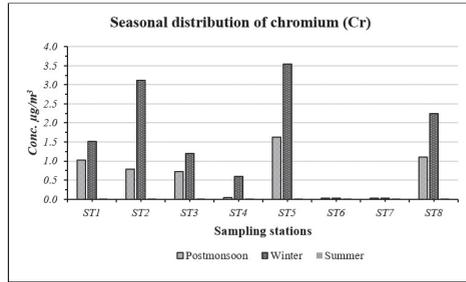
Figure 4.6. Seasonal distribution of chromium.
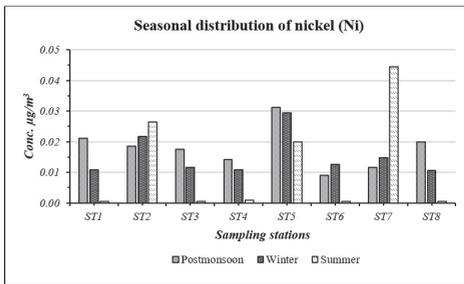
Figure 4.7. Seasonal distribution of nickel.
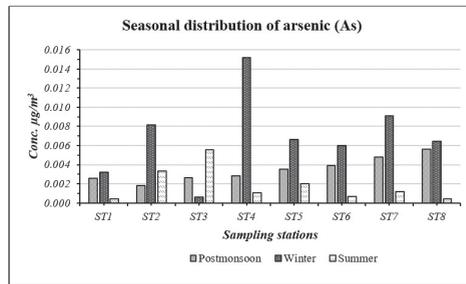
Figure 4.8. Seasonal distribution of arsenic.
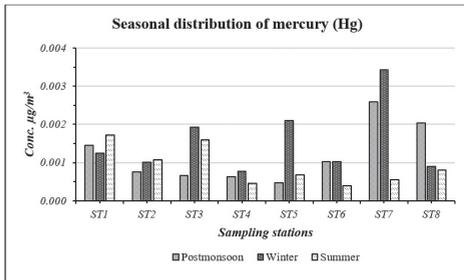
Figure 4.9. Seasonal distribution of mercury.
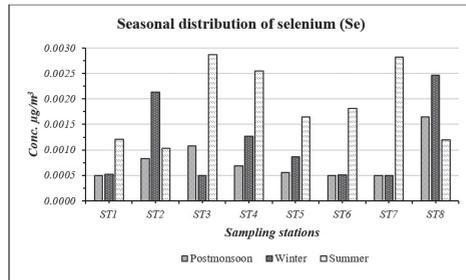
Figure 4.10. Seasonal distribution of selenium.

ST4 in winter season. In the study area the values of As was minimum at ST1 in summer (0.0004 µg/m³) and maximum at ST4 in winter (0.0152 µg/m³).The value of As were found far above the standard limit (0.0060 µg/m³) at ST2 (0.0082 µg/m³), ST4 (0.0152 µg/m³), ST5 (0.0067 µg/m³), ST6 (0.0060 µg/m³), ST7 (0.0090 µg/m³) and ST8 (0.0064 µg/m³). All other stations were within the standard limit. As is originated from automobile emissions, industrial emissions (Karar et al., 2006) and coal burning (Xie et al., 2006; Zhang et al., 2009). 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 ST7 and ST1 showed higher Hg content as compared with all the stations. Figures 4.1.–4.10. presented below are showing the variation of trace metals in different stations in different seasons.

4.3. Principal component analysis

PCA is one of the best method used for source apportionment study of metals in terms of quantitative information (Tsai and Cheng, 2004). The main application of the factor analysis is to reduce the number of variables. Hence PCA can be useful as a data reduction method. Varimax Rotated Factor Matrix method, based on the orthogonal rotation criterion was used in the PCA analysis in this study, which maximizes the variance of the squared metals in the column of a factor matrix (IBM SPSS 20.0) (Winner and Cass, 2001). This method focuses on cleaning up the factors. It produces factors that have high correlations with one smaller set of variables and little or no correlation with another set of variables. The average concentration for every trace elements in all the three seasons at all the sampling stations were taken for PCA study. Four components (principal components) having eigen values > 1 were extracted. Table

Table 6. Principal component analysis of PM and trace metals.

Factors	Component			
	PC1	PC2	PC3	PC4
PM_{10}	0.759	0.079	0.594	0.021
$PM_{2.5}$	0.748	−0.034	0.620	0.210
Fe	0.385	0.859	0.118	0.256
Cu	0.827	−0.067	0.414	0.011
Pb	0.911	−0.080	0.227	0.277
Cd	0.956	0.008	0.001	0.054
Cr	−0.284	0.916	0.202	−0.124
Zn	−0.100	0.932	−0.174	0.225
Hg	−0.243	−0.054	−0.953	0.051
Ni	0.197	0.628	−0.525	−0.470
As	0.973	0.083	−0.025	0.170
Se	0.350	0.227	−0.018	0.883
Total	4.970	2.919	2.229	1.288
% Variance	41.413	24.327	18.577	10.735
% Cumulative Variance	41.413	65.740	84.317	95.052

Extraction Method: – Principal Component,
Rotation Method: – Varimax with Kaiser Normalization

6 represents the Principal Component (PC) loadings for the different factors during the study period. PC1 with variance 41.41% shows higher loading of Cu, Pb, Cd and As which indicates close association of these elements with particulate matter. Cd and Pb are associated with mining and allied activities (Chen et al., 2015). Apart from mining activity Cd is also associated with the resuspension of road dust (Sternbeck et al., 2002). In addition to mining activity, Pb and Cd is also related to vehicular emission (Kulshrestha et al., 2009; Querol et al., 2007). Cu is mainly related to coal combustion (Zhang et al., 2014). Arsenic is associated with vehicular emission. PC2 is represented by Fe, Cr, Zn and Ni with variance 24.33%. Cr is mainly generated by coal combustion (Pandey et al., 2014; Zhang et al., 2014). Fe and Zn is from crustal origin. Fe is crustal in origin and associated with road dust or dust from OB dumps (Chakraborty and Gupta, 2009; Ragosta et al., 2002). The origin of Ni is from vehicular emission (Chen et al., 2015; Hafner et al., 2004). PC3 is represented by Hg with variance 18.58%. The negative sign of Hg indicate the negative correlation of Hg with other parameters. PC4 is represented by Se with variance 10.74%. The scree plot and component plot in rotated space for the PCA analysis is shown in Figs. 5 and 6, respectively. The scree plot shows that out of the all twelve components, four components are having eigen value greater than 1. These four components explain 95.05% of the variation in the data. The scree plot shows that the eigenvalues start to form a straight line after the fourth principal component and so these four components are adequate amount of variation explained in the data to explain the component analysis.
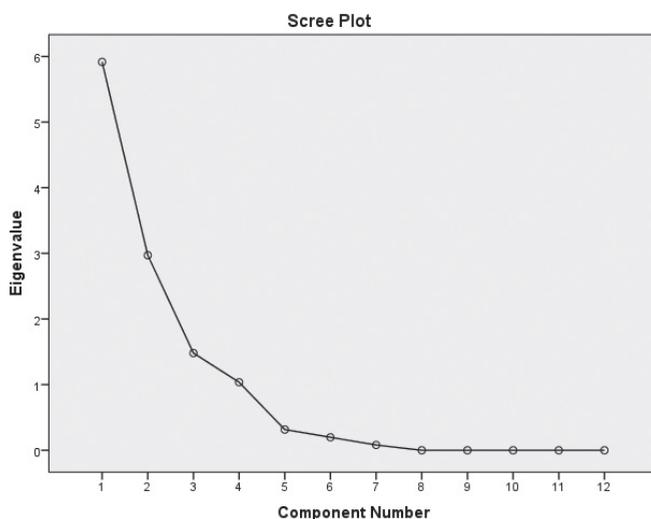
Figure 5. Screen plot for PCA analysis.
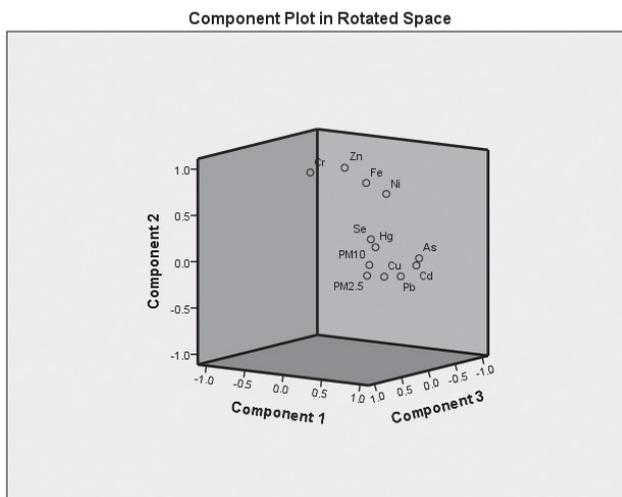
Figure 6. Component plot in rotated space.

4.4. Correlation analysis

Pearson's correlation analysis was performed to examine the correlation between all the trace metals and PM under consideration in terms of their concentrations. Correlation study was performed to identify the respective sources of generation of PM_{10} and trace metals. It is evident that elements that are strongly correlated indicate some common sources (Basha et al., 2014; Shah and Shaheen, 2010). The average concentration of all the twelve measured parameters (PM_{10}, $PM_{2.5}$ and ten trace metals) of all the three seasons of each monitoring stations were taken for correlation analysis. PM PM_{10} was significantly correlated with $PM_{2.5}$ (r=0.950) at level 0.01, Cu (r=0.788), Pb (r=0.826), Cd (r=0.739) and As (r=0.731) at level 0.05. Likewise PM2.5 also shown same level of co-relation with the metals as PM10. Very strong correlation was observed between Cu-Cd (r=0.767), Pb-Cd (r=0.840) and Pb-Cu (r=0.881). Fe, Cr were observed correlated well with each other (Fe-Cr; r =0.655). Fe and Cr are lithophile *i.e.*, concentrated more in earth's crust (White, 2013; Nordbeg et al., 2005), hence these elements are likely to be contributed from windblown dust (Basha et al., 2014). Significant correlation were also observed between Zn-Cr (r=0.801) and Zn-Fe (0.819). Strong correlation were found between As-Cu(r=0.771), As-Pb (r=0.916) and As-Cd (r=0.925) whereas significant co-relation were also observed between As-Fe (r=0.487), Ar-Se (r=0.519), Se-Fe (r=0.522) and Se-Pb (r=0.562). These metals are generally anthropogenic by origin, therefore activities like metal corrosion (Cu, Zn, Cd) (Basha et al., 2014), vehicular emission, coal burning (As, Cr, Pb) (Zhang et

Table 7. Correlation matrix of different parameters of the study area for the three seasons.

	PM10	PM2.5	Fe	Cu	Pb	Cd	Cr	Zn	Hg	Ni	As	Se
PM_{10}	1	.950**	.390	.788*	.826*	.739*	−.008	−.122	−.761*	−.085	.731*	.330
$PM_{2.5}$		1	.379	.851**	.867**	.748*	−.152	−.157	−.766*	−.300	.749*	.427
Fe			1	.372	.376	.389	.655	.819*	−.232	.399	.487	.522
Cu				1	.881**	.767*	−.212	−.199	−.555	−.158	.771*	.228
Pb					1	.840**	−.301	−.174	−.414	−.097	.916**	.562
Cd						1	−.280	−.027	−.213	.116	.925**	.349
Cr							1	.801*	−.165	.482	−.241	.009
Zn								1	−.162	.504	0.019	.339
Hg									1	.364	−.230	−.053
Ni										1	.195	−.139
As											1	.519
Se												1

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

al., 2009) were the responsible contributing sources. Zn is emitted utterly from vehicular sources like, wear and tear of vulcanized tyres, and oil combustion (Shah and Shaheen, 2012; Kulshrestha et al., 2009; Thorpe and Harrison, 2008; Karar et al., 2006; Khillare et al., 2004). 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 were developed and shown in Tab. 7 for clear indication of relations between data points.

4.5. Health risk assessment

4.5.1. Non carcinogenic health risk of trace elements via ingestion exposure and dermal exposure

The exposure of atmospheric particulates via ingestion may be through the food, drinks and hand to mouth or object to mouth transfer of particles (Hu et al., 2012). Therefore, the ingestion exposure to PM was calculated. Similarly the *HQ* ad *HI* vales for dermal exposure was also calculated. The *HI* value of different location for both children and adults due to ingestion is plotted in Fig. 7 and due to dermal exposure is plotted in Fig. 8. It is quite evident from the results that the non-carcinogenic risk due to ingestion and dermal exposure were well within the safe limit for all the people groups in all the locations. The details of the calculated results for ingestion are given in Tab. 8 and for dermal exposure are given in Tab. 9.

Table 8. Calculated values of HQ and HI for different locations due to ingestion.

			Cr	Cu	Cd	Ni	Pb	Zn	As	Se	HI
ST1	HQ	Children	1.10E-02	2.78E-06	7.44E-03	2.08E-06	4.82E-05	1.01E-05	2.65E-05	5.69E-07	1.86E-02
		Adult	1.18E-03	2.98E-07	7.97E-04	2.23E-07	5.17E-06	1.08E-06	2.84E-06	6.10E-08	1.99E-03
ST2	HQ	Children	1.69E-02	3.48E-06	1.35E-02	4.27E-06	8.44E-05	1.08E-05	5.67E-05	1.02E-06	3.05E-02
		Adult	1.81E-03	3.73E-07	1.44E-03	4.57E-07	9.04E-06	1.16E-06	6.08E-06	1.09E-07	3.27E-03
ST3	HQ	Children	8.71E-03	2.08E-06	4.25E-03	1.90E-06	4.93E-05	1.12E-05	3.75E-05	1.14E-06	1.31E-02
		Adult	9.33E-04	2.23E-07	4.55E-04	2.04E-07	5.28E-06	1.20E-06	4.02E-06	1.22E-07	1.40E-03
ST4	HQ	Children	2.88E-03	7.13E-06	2.44E-02	1.66E-06	1.25E-04	9.55E-06	8.12E-05	1.15E-06	2.75E-02
		Adult	3.09E-04	7.64E-07	2.61E-03	1.78E-07	1.33E-05	1.02E-06	8.70E-06	1.23E-07	2.94E-03
ST5	HQ	Children	2.22E-02	2.94E-06	1.38E-02	5.15E-06	5.88E-05	1.53E-05	5.18E-05	7.85E-07	3.62E-02
		Adult	2.38E-03	3.15E-07	1.48E-03	5.51E-07	6.30E-06	1.64E-06	5.55E-06	8.41E-08	3.87E-03
ST6	HQ	Children	4.09E-04	2.56E-06	1.34E-02	1.42E-06	6.43E-05	6.26E-06	4.52E-05	7.21E-07	1.39E-02
		Adult	4.38E-05	2.74E-07	1.44E-03	1.52E-07	6.89E-06	6.71E-07	4.84E-06	7.73E-08	1.49E-03
ST7	HQ	Children	4.09E-04	2.49E-06	1.87E-02	4.53E-06	7.96E-05	1.03E-05	6.44E-05	9.79E-07	1.93E-02
		Adult	4.38E-05	2.67E-07	2.01E-03	4.86E-07	8.53E-06	1.11E-06	6.89E-06	1.05E-07	2.07E-03
ST8	HQ	Children	1.44E-02	2.65E-06	1.63E-02	1.99E-06	7.31E-05	1.42E-05	5.32E-05	1.36E-06	3.09E-02
		Adult	1.54E-03	2.84E-07	1.75E-03	2.14E-07	7.83E-06	1.52E-06	5.70E-06	1.46E-07	3.31E-03

Table 9. Calculated values of HQ and HI for different locations due to dermal exposure.

			Cr	Cu	Cd	Ni	Pb	Zn	As	Se	HI
ST1	HQ	Children	7.93E-03	2.60E-08	2.78E-03	4.86E-07	4.50E-07	9.39E-08	2.47E-07	5.31E-09	1.07E-02
		Adult	1.21E-02	3.96E-08	4.24E-03	7.41E-07	6.87E-07	1.43E-07	3.77E-07	8.11E-09	1.63E-02
ST2	HQ	Children	1.21E-02	3.25E-08	5.03E-03	9.96E-07	7.88E-07	1.01E-07	5.29E-07	9.53E-09	1.72E-02
		Adult	1.85E-02	4.96E-08	7.68E-03	1.52E-06	1.20E-06	1.54E-07	8.08E-07	1.45E-08	2.62E-02
ST3	HQ	Children	6.25E-03	1.94E-08	1.59E-03	4.44E-07	4.60E-07	1.04E-07	3.50E-07	1.06E-08	7.84E-03
		Adult	9.55E-03	2.96E-08	2.42E-03	6.78E-07	7.03E-07	1.59E-07	5.35E-07	1.62E-08	1.20E-02
ST4	HQ	Children	2.07E-03	6.65E-08	9.10E-03	3.87E-07	1.16E-06	8.91E-08	7.58E-07	1.07E-08	1.12E-02
		Adult	3.16E-03	1.02E-07	1.39E-02	5.91E-07	1.78E-06	1.36E-07	1.16E-06	1.64E-08	1.71E-02
ST5	HQ	Children	1.59E-02	2.74E-08	5.17E-03	1.20E-06	5.49E-07	1.43E-07	4.83E-07	7.33E-09	2.11E-02
		Adult	2.43E-02	4.19E-08	7.89E-03	1.83E-06	8.38E-07	2.19E-07	7.38E-07	1.12E-08	3.22E-02
ST6	HQ	Children	2.94E-04	2.39E-08	5.01E-03	3.32E-07	6.00E-07	5.85E-08	4.22E-07	6.73E-09	5.30E-03
		Adult	4.48E-04	3.64E-08	7.65E-03	5.07E-07	9.16E-07	8.93E-08	6.44E-07	1.03E-08	8.10E-03
ST7	HQ	Children	2.94E-04	2.33E-08	7.00E-03	1.06E-06	7.43E-07	9.63E-08	6.01E-07	9.14E-09	7.29E-03
		Adult	4.48E-04	3.55E-08	1.07E-02	1.62E-06	1.13E-06	1.47E-07	9.17E-07	1.40E-08	1.11E-02
ST8	HQ	Children	1.04E-02	2.48E-08	6.10E-03	4.65E-07	6.82E-07	1.32E-07	4.97E-07	1.27E-08	1.64E-02
		Adult	1.58E-02	3.78E-08	9.31E-03	7.10E-07	1.04E-06	2.02E-07	7.59E-07	1.94E-08	2.51E-02

Table 10. Calculated values of HQ and HI for different locations due to inhalation.

			Cr	Cu	Cd	Ni	Pb	Zn	As	Hg	HI
ST1	HQ	Children	1.93E+01	4.61E-04	1.24E+00	1.97E-03	7.99E-03	1.67E-03	4.41E-03	3.14E-03	2.06E+01
		Adult	8.27E+00	1.98E-04	5.31E-01	8.44E-04	3.42E-03	7.16E-04	1.89E-03	1.35E-03	8.81E+00
ST2	HQ	Children	2.96E+01	5.78E-04	2.25E+00	4.04E-03	1.40E-02	1.79E-03	9.45E-03	2.02E-03	3.18E+01
		Adult	1.27E+01	2.48E-04	9.62E-01	1.73E-03	5.99E-03	7.68E-04	4.05E-03	8.68E-04	1.36E+01
ST3	HQ	Children	1.52E+01	3.45E-04	7.08E-01	1.80E-03	8.17E-03	1.85E-03	6.26E-03	2.98E-03	1.60E+01
		Adult	6.52E+00	1.48E-04	3.03E-01	7.73E-04	3.50E-03	7.95E-04	2.68E-03	1.28E-03	6.84E+00
ST4	HQ	Children	5.04E+00	1.18E-03	4.06E+00	1.57E-03	2.06E-02	1.59E-03	1.35E-02	1.31E-03	9.14E+00
		Adult	2.16E+00	5.07E-04	1.74E+00	6.73E-04	8.85E-03	6.80E-04	5.80E-03	5.63E-04	3.92E+00
ST5	HQ	Children	3.88E+01	4.88E-04	2.31E+00	4.87E-03	9.75E-03	2.55E-03	8.63E-03	2.32E-03	4.11E+01
		Adult	1.66E+01	2.09E-04	9.89E-01	2.09E-03	4.18E-03	1.09E-03	3.70E-03	9.92E-04	1.76E+01
ST6	HQ	Children	7.15E-01	4.24E-04	2.24E+00	1.35E-03	1.07E-02	1.04E-03	7.53E-03	1.73E-03	2.97E+00
		Adult	3.07E-01	1.82E-04	9.58E-01	5.78E-04	4.57E-03	4.46E-04	3.23E-03	7.40E-04	1.27E+00
ST7	HQ	Children	7.15E-01	4.13E-04	3.12E+00	4.29E-03	1.32E-02	1.71E-03	1.07E-02	4.67E-03	3.87E+00
		Adult	3.07E-01	1.77E-04	1.34E+00	1.84E-03	5.66E-03	7.34E-04	4.60E-03	2.00E-03	1.66E+00
ST8	HQ	Children	2.52E+01	4.40E-04	2.72E+00	1.89E-03	1.21E-02	2.36E-03	8.87E-03	2.66E-03	2.80E+01
		Adult	1.08E+01	1.89E-04	1.17E+00	8.09E-04	5.19E-03	1.01E-03	3.80E-03	1.14E-03	1.20E+01

4.5.2. Non carcinogenic health risk of trace elements
via inhalation exposure

Inhalation exposure is typically the principle way of direct exposure to atmospheric particulate bound trace elements (USEPA, 1989). *HQ* of 8 out of 10 trace elements (Cr, Ni, Pb, Zn, Cd, As, Hg and Cu) for inhalation pathway for both adults and children were calculated and given in Tab. 10. The *HQ* and *HI* values for Fe and Se could not been calculated in this study as their threshold values (RfD and RfC) for different exposure routes are not listed by US EPA. Table 10 represents that the *HQ* values for Cr are higher than the safe limit (=1) in in all the locations except ST6 and ST7 for both children and adults showing it might pose non-carcinogenic risk. Similarly the *HQ* value of Cd in ST1 (1.24), ST2 (1.25), ST5 (2.31) and ST6 (2.24) were higher than the limit for children and the values were within the limit for adult. In ST4 (4.06 children, 1.74 adult),
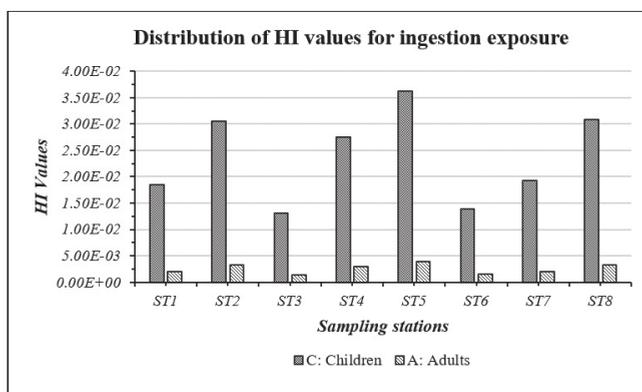
Figure 7. *HI* values due to ingestion route at different locations.
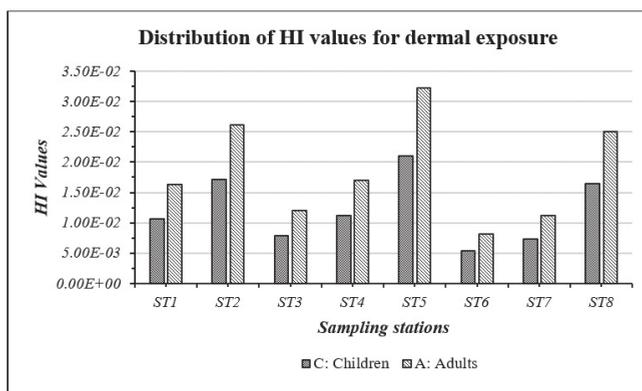
Figure 8. *HI* values due to dermal route at different locations.
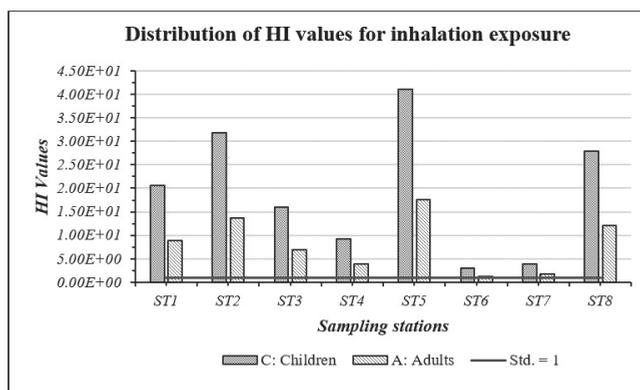
Figure 9. *HI* values due to inhalation route at different locations.

ST7 (3.12 children, 1.33 adult) and ST8 (2.72 children, 1.17 adult), both for adult and children the values were far above the limit indicating no- carcinogenic health risk due to Cadmium in those locations. Besides the two metals the *HQ* for all other considered metals the values were in acceptable range. However the combine effect of all the metals *i.e.*, the *HI* values cannot be ignored as for all the locations and for both children and adult the values were above the limit (=1) showing a deep consideration of health risk due to metal pollution. The *HI* values for both children and adult in all the sampling locations were shown in Fig. 9.

4.5.3. Carcinogenic health risk assessment

To estimate the carcinogenic risks of the particulate bound trace metals six trace element (Cr(VI), Ni, Pb, Zn, Cd, and As) from the total ten measured metals were taken into consideration by taking the carcinogenicity (IARC: International Agency for Research on Cancer) of the metals. As, Ni, Cd and Cr (VI) compounds are classified under class 1 carcinogen while Pb compounds class 2A carcinogen elements (IARC, 2013). The concentration ratio of Cr (VI) to Cr (III) is about 1:6. So, for the calculation of carcinogenic health risk due to Cr (VI), the concentration of Cr (VI) was taken as 1/7 of the total concentration of PM bound chromium (Massey et al., 2013; USEPA, 2004b). Due to unavailability of reference values of carcinogenic risk through dermal exposure and ingestion pathway, the carcinogenic risk assessment only through inhalation pathway were considered. The estimated *ECR* of PM bound carcinogenic elements for all the locations are presented in Tab. 11.

The observed *ECR* values for Cr exceeds the acceptable limit for both children and adult in ST1, ST2 ST5 and ST8. In ST3 the *ECR* value of Cr for children (0.0001) was within the limit and for adult exceeded the safe limit (0.0004). In ST4 the children were safe from the carcinogenicity effects of Cr having ECR value 0.00003 where the adults were at risk 0.00013. In ST6 and ST7 both the

Table 11. Calculated values of ECR and ECR$_{Total}$ for different locations.

	Age group	Cr	Ni	Pb	Zn	Cd	As	ECR$_{Total}$
ST1 ECR	Children	1.2E–04	2.1E–07	4.3E–08	7.8E–07	2.9E–04	7.3E–07	4.10E–04
	Adult	4.9E–04	1.2E–07	1.7E–07	3.1E–06	1.1E–03	2.9E–06	1.64E–03
ST2 ECR	Children	1.9E–04	4.4E–07	7.6E–08	8.3E–07	5.2E–04	1.6E–06	7.09E–04
	Adult	7.5E–04	2.5E–07	3.0E–07	3.3E–06	2.1E–03	6.3E–06	2.83E–03
ST3 ECR	Children	9.6E–05	2.0E–07	4.4E–08	8.6E–07	1.6E–04	1.0E–06	2.62E–04
	Adult	3.8E–04	1.1E–07	1.8E–07	3.4E–06	6.6E–04	4.2E–06	1.05E–03
ST4 ECR	Children	3.2E–05	1.7E–07	1.1E–07	7.4E–07	9.4E–04	2.2E–06	9.75E–04
	Adult	1.3E–04	9.7E–08	4.5E–07	2.9E–06	3.8E–03	9.0E–06	3.90E–03
ST5 ECR	Children	2.4E–04	5.3E–07	5.3E–08	1.2E–06	5.3E–04	1.4E–06	7.82E–04
	Adult	9.8E–04	3.0E–07	2.1E–07	4.7E–06	2.1E–03	5.7E–06	3.12E–03
ST6 ECR	Children	4.5E–06	1.5E–07	5.8E–08	4.8E–07	5.2E–04	1.2E–06	5.24E–04
	Adult	1.8E–05	8.4E–08	2.3E–07	1.9E–06	2.1E–03	5.0E–06	2.10E–03
ST7 ECR	Children	4.5E–06	4.7E–07	7.2E–08	8.0E–07	7.2E–04	1.8E–06	7.30E–04
	Adult	1.8E–05	2.7E–07	2.9E–07	3.2E–06	2.9E–03	7.1E–06	2.92E–03
ST8 ECR	Children	1.6E–04	2.1E–07	6.6E–08	1.1E–06	6.3E–04	1.5E–06	7.92E–04
	Adult	6.4E–04	1.2E–07	2.6E–07	4.4E–06	2.5E–03	5.9E–06	3.17E–03

groups were safe in the term of carcinogenicity effects of Cr. The *ECR* value of Cd for the both group of people in all the locations were above the safe limit showing the carcinogenic effect due to Cr pollution in that area. Except Cr and Cd the *ECR* value of all other metals were found well within the safe limit. The combined
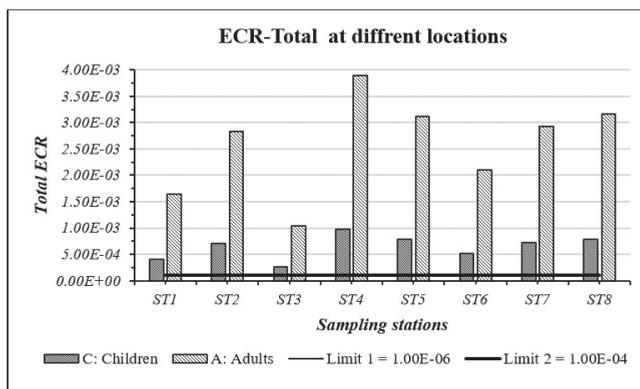
Figure 10. ECR total values due to inhalation route at different locations.

carcinogenic effect of all the metals were calculated by taking the summation of the *ECR* values of each metal under consideration. The sum of all the *ECR* values termed as ECR_{Total} and the same were calculated for all the locations of the study area. The results reviled that the *ECR* values in all the locations were far above the safe limit (10^{-6} to 10^{-4}) for both children and adult prescribed by USEPA, indicating very high risk of cancer in the study area. The ECR_{Total} for both children and adults in all the locations were plotted in Fig. 10.

5. 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} and $PM_{2.5}$) confirms about the highest concentration of particulate matter in winter season followed by summer and post monsoon. The concentrations of particulate matter were 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. Factor analysis (PCA) suggested the dominance of Cd, Cu, As, and Pb 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. PCA also suggested the abundance of Fe, Zn, Cr, and Ni in the study area represented by PC2, Hg show its abundance by representing in the PC3 and Se as PC4. The correlation analysis supports the relationship between different parameters in the study area. The calculated *HQ* value for Cr and Cd were found above safe limit in most of the location of the study area for both children and adults. The inhalation route was found as the major route of trace metal exposure for human being as compared to ingestion and dermal route. Furthermore very significant health effects were observed due to combine effects of metals in the study area. The potential carcinogenic risk via inhalation route observed for each elements and the risk due to Cr (VI) and Cd were found above the safe limit, where all others were in the safe limit. The ECR_{Total} values at all the locations were far above the safe limit. The health risk assessment study on the nearby resident of the coal mine suggested high intensification of both carcinogenic and non-carcinogenic risk from the PM bound trace metals although found in very low concentration.

References

Arditsoglou, A. and Samara, C. (2005): Levels of total suspended particulate matter and major trace elements in Kosovo: A source identification and apportionment study, *Chemosphere,* **59**, 669–678, DOI: 10.1016/j.chemosphere.2004.10.056.

Baldauf, R. W., Lane, D. D. and Marote, G. A. (2001): Ambient air quality monitoring network design for assessing human health impacts from exposures to airborne contaminants, *Environ. Monit. Assess., 66*, 63–76. DOI: 10.1023/A:1026428214799.

Basha, A. M., Yasovardhan, N., Satyanarayana, S. V., Reddy, G. V. S. and Kumar, A. V. (2014): Baseline survey of trace metals in ambient PM10 at Tummalapalle uranium mining site*, Atmos. Pollut. Res.*, **5**, 591–600, DOI: 10.5094/APR.2014.068.

BIS (Bureau of Indian Standards) (2000): Methods for measurement of air pollution: Guidelines for planning the sampling of atmosphere (second revision) IS 5182 (Part 14) (New Delhi).

Callen, M. S., de la Cruz, M. T., Lopez, J. M., Navarro, M .V. and Mastral, A. M. (2009): Comparison of receptor models for source apportionment of the PM10 in Zaragoza (Spain), *Chemosphere, 76*, 1120–1129, DOI: 10.1016/j.chemosphere.2009.04.015.

Chakraborty, A. and Gupta, T. (2009): Chemical characterization of submicron aerosol in Kanpur Region: A source apportionment study*, Int. J. Civ. Env. Eng., 1*(2), 87–90.

Chaulya, S. K. (2004): Assessment and management of air quality for an open-cast coal mining area, *J. Environ. Manage.*, **70**(9), 1–14., DOI: 10.1016/j.jenvman.2003.09.018.

Chaulya, S. K. (2004): Spatial and temporal variations of SPM, RPM, SO2 and NOX concentrations in an opencast coal mining area, *J. Environ. Monitor.*, **6**, 134–142, DOI: 10.1039/b309372g.

Chen, Y. C., Hsu, C. Y., Lin, S. L., Chang-Chien, G. P., Chen, M. J., Fang, G. C. and Chiang, H. C. (2015): Characteristics of concentrations and metal compositions for PM2.5 and PM2.5–10 in Yunlin County, Taiwan during air quality deterioration*, Aerosol. Air. Qual. Res.*, **15**, 2571–2583, DOI: 10.4209/aaqr.2015.04.0261.

Du, Y., Gao, B., Zhou, H., Ju, X., Hao, H. and Yin, S. (2013): Health risk assessment of heavy metals in road dusts in urban parks of Beijing, *China Procedia Environ. Sci.*, **18**, 299–309, DOI: 10.1016/j.proenv.2013.04.039.

Dubey, B., Pal, A. K., and Singh, G. (2012): Trace metal composition of airborne particulate matter in the coal mining and none mining areas of Dhanbad Region, Jharkhand, India*, Atmos. Pollut. Res.*, **3**, 238–246, DOI: 10.5094/APR.2012.026.

Franco, A. and Diaz, A. R. (2009): The future challenges for "clean coal technologies" joining efficiency increase and pollutant emission control, *Energy*, **34**, 348–354, DOI: 10.1016/j.energy.2008.09.012.

Ghose, M. K. and Majee, S. R. (2001): Air pollution caused by opencast mining and its abatement measures in India, *J. Environ. Manage., 63*, 193–202, DOI: 10.1006/jema.2001.0434.

Gunawardana, C., Goonetilleke, A., Egodawatta, P., Dawes, L. and Kokot, S. (2011): Source characterization of road dust based on chemical and mineralogical composition. *Chemosphere*, **87**, 163–170, DOI: 10.1016/j.chemosphere.2011.12.012.

Hafner, H. R., Wheeler, N. J. and Roberts, P. T. (2004): Analysis of air toxics monitoring data work plan, prepared for lake Michigan air directors consortium, Des Plaines, IL, by Sonoma Technology, Inc., Petaluma, CA, STI-903555-2442-WP2, 41.

Hu, X., Zhang, Y., Ding, Z., Wang, T., Lian, H., Sun, Y. and Wu, J. (2012): Bio-accessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing, China, *Atmos. Environ., 57*, 146–152, DOI: 10.1016/j.atmosenv.2012.04.056.

Huertas, J. I, Huertas, M. E., Izquierdo, S. and Gonzalez, E. D. (2012): Air quality impact assessment of multiple open pit coal mines in Northern Colombia*, J. Environ. Manage.,* 93, 121–129, DOI: 10.1016/j.jenvman.2011.08.007.

IARC (2013): Outdoor air pollution a leading environmental cause of cancer deaths. IRIS (Integrated Risk Assessment System), Vol. 1995. United States Environmental Protection Agency, available at www.epa.gov/IRIS/.

IRIS (Integrated Risk Assessment System) (1995): United States Environmental Protection Agency, available at www.epa.gov/IRIS/.

Izhar, S., Goel, A., Chakraborty, A. and Gupta, T. (2016): Annual trends in occurrence of submicron particles in ambient air and health risk posed by particle bound metals, *Chemosphere*, **146**, 582–590, DOI: 10.1016/j.chemosphere.2015.12.039.

Jai Prakash, Lohia, T., Mandariya, A. K., Habib, G., Gupta T. and Gupta, S. K. (2018): Chemical characterization and quantitative assessment of source-specific health risk of trace metals in PM1.0 at a road site of Delhi, India, *Environ. Sci. Pollut. R.,* **25**, 8747–8764, DOI: 10.1007/s11356-017-1174-9.

Jena, S. and Singh, G. (2017): Human health risk assessment of airborne trace elements in Dhanbad, India, *Atmos. Pollut. Res.*, **8**, 490–502, DOI: 10.1016/j.apr.2016.12.003.

Karar, K., Gupta, A. K., Kumar, A., and Biswas, A. K. (2006): Characterization and identification of the sources of chromium, zinc, lead, cadmium, nickel, manganese and iron in PM10 particulates at the two sites of Kolkata, India, *Environ. Monit. Assess.*, **120**, 347–360, DOI: 10.1007/s10661-005-9067-7.

Katz, M. (1977): *Standard methods for air sampling and analysis.* 2nd edition, APHA, Press Inc. Spring Field, VA.

Khillare, P. S., Balachandran, S. and Meena, B. R. (2004): Spatial and temporal variation of heavy metals in atmospheric aerosol of Delhi*, Environ. Monit. Assess.*, **90**, 1–21, DOI: 10.1023/B:EMAS.0000003555.36394.17.

Kloog, I. (2016): Fine particulate matter (PM2.5) association with peripheral artery disease admissions in northeastern United States, *Int. J. Environ. Health Res.*, **26**, 572–577, DOI: 10.1080/09603123.2016.1217315.

Kulshrestha, A., Satsangi, P. G., Masih, J. and Taneja, A. (2009): Metal concentration of PM2.5 and PM10 particles and seasonal variations in urban and rural environment of Agra, India*, Sci. Total Environ.*, **407**, 6196–6204, DOI: 10.1016/j.scitotenv.2009.08.050.

Li, H., Wang, J., Wang, Q. G., Qian, X., Qian, Y., Yang, M., Li, F., Lu, H. and Wang, C. (2015): Chemical fractionation of arsenic and heavy metals in fine particle matter and its implications for risk assessment: a case study in Nanjing*, China Atmos. Environ*, **103**, 339–346, DOI: 10.1016/j.atmosenv.2014.12.065.

Lin, J. and Lee, L. C. (2004): Characterization of the concentration and distribution of urban submicron (PM1) aerosol particles*, Atmos. Environ.*, **38**, 469–475, DOI: 10.1016/j.atmosenv.2003.09.056.

Magas, O. K., Gunter, J. T. and Regens, J. L. (2007): Ambient air pollution and daily paediatric hospitalizations for asthma, *Environ. Sci. Pollut. R.*, **14**, 19–23, DOI: 10.1065/espr2006.08.333.

Massey, D. D., Kulshrestha, A. and Taneja, A. (2013): Particulate matter concentrations and their related metal toxicity in rural residential environment of semi-arid region of India. *Atmos. Environ.*, **67**, 278–286, DOI: 10.1016/j.atmosenv.2012.11.002.

NAAQS, (2009): *National ambient air quality standard.* India, prescribed by Central Pollution Control Board. Available at http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php.

Namdeo, A. and Bell, M. C. (2005): Characteristics and health implications of fine and coarse particulates at roadside, urban background and rural sites in UK, *Environ. Int.*, **31**, 565–573, DOI: 10.1016/j.envint.2004.09.026.

NIOSH (2005): National Institute for Occupational Safety and Health, Significant Dust Dispersion Models for Mining Operations IC 9478, USA.

Nordberg, G. F., Fowler, B. A., Nordberg, M. and Friberg, L. (2005): *Handbook on the toxicology of metals.* 3rd edition. European Environmental Agency.

Odisha State Pollution Control Board (2016): *Implementation Status and Action Plan in Critically Polluted Areas, 2016.* Available at http://www.ospcboard.org/ckeditor/CKFiles/25-Jun-2016ActionPlan_Implementation_Status_Angul%20Talcher_Mar2016.compressed.pdf. Last Assessed on 2nd March 2017

Pandey, B., Agrawal, M. and Singh, S. (2014): Assessment of air pollution around coal mining area: Emphasizing on spatial distributions, seasonal variations and heavy metals, using cluster and principal component analysis, *Atmos. Pollut. Res.*, **5**, 79–86, DOI: 10.5094/APR.2014.010.

Pandit, G. G., Sahu, S. K. and Puranik, V. D. (2011): Distribution and source apportionment of atmospheric non-methane hydrocarbons in Mumbai, India, *Atmos. Pollut. Res.*, **2**, 231–236, DOI: 10.5094/APR.2011.029.

Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J., de la Campa, A. S., Artinano, B., Salvador, P., Dos Santos, S. G., Fernandez-Patier, R., Moreno-Grau, S., Negral, L., Minguillon, M. C., Monfort, E., Gil, J. I., Inza, A., Ortega, L. A., Santamaria, J. M. and Zabalza, J. (2007): Source origin of trace elements in PM from regional background, urban and industrial sites of Spain, *Atmos. Environ.*, **41**, 7219–7231, DOI: 10.1016/j.atmosenv.2007.05.022.

Ragosta, M., Caggiano, R., D'Emilio, M. and Macchiato, M. (2002): Source origin and parameters influencing levels of heavy metals in TSP, in an industrial background area of Southern Italy, *Atmos. Environ.*, **36**, 3071–3087, DOI: 10.1016/S1352-2310(02)00264-9.

Samiksha, S., Raman, R. S., Nirmalkar, J., Kumar, S. and Sirvaiya, R. (2017): PM10 and PM2.5 chemical source profiles with optical attenuation and health risk indicators of paved and unpaved road dust in Bhopal, India, *Environ. Pollut.*, **222**, 477–485, DOI: 10.1016/j.envpol.2016.11.067.

Shah, M. H., Shaheen, N. and Nazir, R. (2012): Assessment of the trace elements level in urban atmospheric particulate matter and source apportionment in Islamabad. Pakistan, *Atmos. Pollut. Res.*, **3**, 39–45, DOI: 10.5094/APR.2012.003.

Shah, M. H. and Shaheen, N. (2010): Seasonal behaviours in elemental composition of atmospheric aerosols collected in Islamabad, Pakistan, *Atmos. Res.*, **95**, 210–223, DOI: 10.1016/j.atmosres.2009.10.001.

Shaheen, N., Shah, M. H., Khalique, A. and Jaffar, M. (2005): Metal levels in airborne particulate matter in urban Islamabad, Pakistan, *B. Environ. Contam. Tox.*, **75**, 739–746, DOI: 10.1007/s00128-005-0813-x.

Sternbeck, J., Sjjodin, A. and Andreasson, K. (2002): Metal emissions from road traffic and the influence of resuspension-results from two tunnel studies, *Atmos. Environ.*, **36**, 4735–4744, DOI: 10.1016/S1352-2310(02)00561-7.

Thorpe, A. and Harrison, R. M. (2008): Sources and properties of non-exhaust particulate matter from road traffic: A review, *Sci. Total Environ.*, **400**, 270–282, DOI: 10.1016/j.scitotenv.2008.06.007.

Tsai, Y. I. and Cheng, M. T. (2004): Characterization of chemical species in atmospheric aerosols in a metropolitan basin, *Chemosphere*, **54**, 1171–1181, DOI: 10.1016/j.chemosphere.2003.09.021.

US EPA (1984): Health Assessment Document for Arsenic. Office of Health and Environmental Assessment. Environmental Criteria and Assessment Office, Research Triangle Park, NC. EPA 600/8-32-021F.

US EPA (1989): Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part a). Available at http://www.epa.gov/oswer/riskassessment/ragsa/.

US EPA (Environmental Protection Agency) (1990): Air Quality Criteria for Lead: Supplement to the 1986 Addendum. Environmental Criteria and Assessment Office, Research Triangle Park, NC. EPA-600/8e89/049F.

US EPA (2004a): Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment). Office of Superfund Remediation and Technology Innovation, Washington, D.C. Available at http://www.epa.gov/oswer/riskassessment/ragse/index.htm.

US EPA (2004b): Region 9, Preliminary Remediation Goals, Air Water Calculations.

US EPA (2009): Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual. Part F: Supplemental Guidance for Inhalation Risk Assessment. Available at http://www.epa.gov/oswer/riskassessment/ragsf/index.htm.

USEPA (2015): User's guide/technical background document for US EPA region 9's RSL (Regional Screening Levels) tables. Available at http://www.epa.gov/region9/superfund/prg/.

USEPA (2011): Risk assessment guidance for superfund. In: *Human health evaluation manual; part E, supplemental guidance for dermal risk assessment; part F, supplemental guidance for inhalation risk assessment, I,* edited by Part, A.

Vesovic, V., Auziere, A., Calviac, G. and Dauriat, A. (2001): Modelling of the dispersion and deposi-
tion of coarse particulate matter under neutral atmospheric conditions, *Atmos. Environ.*, **35**,
S99–S105, DOI: 10.1016/S1352-2310(00)00534-3.

White, W. M. (2013): Trace Elements in Igneous Process, in: *Geochemistry* (1st). John Wiley and Sons
Ltd, UK.

Winner, D. A. and Cass, G. R. (2001): Modelling the long-term frequency distribution of regional
ozone concentrations using synthetic meteorology, *Environmental Science Technology*, **35**, 3718–
3726, DOI: 10.1021/es001714c.

Xie, R., Seip, H. M., Wibetoe, G., Nori, S. and McLeod, C. W. (2006): Heavy coal combustion as the
dominant source of particulate pollution in Taiyuan, China, corroborated by high concentrations
of arsenic and selenium in PM10, *Sci. Total Environ.*, **370**, 409–415, DOI: 10.1016/j.scito-
tenv.2006.07.004.

Yu, H-L. and Chien, L-C. (2016): Short-term population-based non-linear concentration response
associations between fine particulate matter and respiratory diseases in Taipei (Taiwan): a spa-
tiotemporal analysis, *J. Expo. Sci. Environ. Epidemiology,* **26**, 197–206, DOI: 10.1038/jes.2015.21.

Zhang, Q., Shen, Z., Cao, J., Ho, K., Zhang, R., Bie, Z., Chang, H. and Liu, S. (2014): Chemical profiles
of urban fugitive dust over Xi'an in the south margin of the Loess Plateau, China, *Atmos. Pollut.
Res.*, **5**, 421–430, DOI: 10.5094/APR.2014.049.

Zhang, Y., Wang, X., Chen, H., Yang, X., Chen, J., and Allen, J. O. (2009): Source apportionment of
lead-containing aerosol particles in Shanghai using single particle mass spectrometry, *Chemo-
sphere*, **74**, 501–507, DOI: 10.1016/j.chemosphere.2008.10.004.

Zheng, N., Liu, J., Wang, Q and Liang, Z. (2010): Science of the total environment health risk as-
sessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China,
Sci. Total Environ., **408**, 726–733, DOI: 10.1016/j.scitotenv.2009.10.075.

SAŽETAK

Mjerenje koncentracije respiratorne prašine i procjena zdravstvenog rizika od teških metala u području otvorenog rudnika ugljena tvrtke Talcher, Odisha

Debi Prasad Tripathy i Tushar Ranjan Dash

Atmosfersko onečišćenje uzrokovano lebdećim česticama u blizini površinskog rud-
nika ugljena vrlo je važan ekološki problem i privlači pozornost istraživača diljem svijeta
već nekoliko desetljeća. Lebdeće čestice ne utječu samo na ljude, već imaju i ogromne
učinke na obližnju floru i faunu, degradirajući okoliš na mnogo načina. Visoka meha-
nizacija u rudarstvu dovodi do velikog opterećenja okoliša prašinom. Štetni učinci prašine
ovise o njenoj količini, svojstvima i izloženosti. S obzirom na važnost onečišćenja prašinom
u rudnicima, odabran je jedan od najstarijih indijskih rudnika ugljena (Talcher), čiji su
utjecaji na lokalno stanovništvo zdravstveni rizik zbog prisutnih teških metala do sada
bili slabo istraženi. Respirabilna prašina (PM_{10} i $PM_{2.5}$) praćena je prema standardnim
kriterijima indijskog Središnjeg odbora za kontrolu zagađenja (CPCB) na osam mjernih
postaja oko visoko-mehaniziranog otvorenog rudnika ugljena tijekom tri sezone: poslije
monsuna, te tijekom zime i ljeta 2015. godine. Utvrđene su sezonske varijacije koncen-
tracije prašine: zima > ljeto > monsun. U uzorcima prašine analizirano je deset metala u
tragovima. Provedena je univarijatna (korelacijska) i višestruka statistička analiza,
uključujući analizu glavnih komponenti (PCA) za identifikaciju izvora i procjenu
odgovarajućih doprinosa onečišćujućoj tvari. Zdravstveni rizik je procijenjen pomoću koe-

ficijenta opasnosti (*HQ*) i indeksa opasnosti (*HI*) te je za djecu i za odrasle izračunat zasebno za tri načina izlaganja (inhalacija, gutanje i izloženost kože). Kancerogeni učinci zbog prisutnosti metala u tragovima u PM_{10} procijenjeni su i za djecu i za odrasle pomoću prekomjernog rizika od raka (*ECR*). Kombinirani kancerogeni učinci svih metala u tragovima također su izračunati (*ECR_{Total}*). Vrijednosti *HQ* za Cr i Cd u promatranom području bile su iznad praga sigurnosti i za djecu i za odrasle. Isto tako, vrijednosti *ECR* za Cr i Cd bile su za obje dobne skupine iznad praga. Međutim, rizik povezan s drugim metalima bio je ispod praga. Vrijednosti *HI* i *ECR_{Total}* bile su iznad praga što ukazuje na kombinirani učinak metala u tragovima na djecu i odrasle u istraživanom području te na vrlo visoku razinu rizika.

Ključne riječi: PM_{10}, $PM_{2.5}$, teški metali, korelacijska analiza, PCA, zdravstveni rizik

Corresponding author's address: Debi Prasad Tripathy, Department of Mining Engineering, National Institute of Technology Rourkela, 769008 Odisha, India; tel: +91 661 2462 608; e-mail: debi_tripathy@yahoo.co.in