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Levels of Fine Particulate Matter Bound Trace Metals in Air of Glass Industrial Area; Firozabad

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ABSTRACT: The present study deals with sequential extraction of fine particulate matter ($PM_{2.5}$) bound trace metals in an industrial area of Firozabad, India. During the study period, daily $PM_{2.5}$ concentration ranged between 73.49 $\mu g/m^3$ and 113.26 $\mu g/m^3$ with poor air quality index of 196.37. In the present study, Ca recorded the highest while Co had the lowest concentration among all analysed metals. Mn, Ni, Pb, Co, and Cu had high bioavailability (34.80%-65.80%) than other elements. Cd, Pb, and Cu were found to be highly enriched (EF> 289-6516) by varied anthropogenic activities. Hazard Quotient (HQ) for Ni, Mn, and Cr and Excess Lifetime Cancer Risk (ELCR) of $Cr^{(VI)}$ and Ni exceeded the respective safer limit (HQ>1 and ELCR$\geq 10^{-6}$), thus implying serious risk to the receptors. All the metals had the highest concentration in less mobile and residual fraction except for Ni and Co, which inferred greater risk due to their high toxicity. Overall, the results present exposure and risk assessment of metal associated particles; that provides in-depth knowledge of the risk factors through inhalation exposure pathway of particles associated with industrial environment.

Keywords: Air quality index, bioavailability index, fine particulate, sequential extraction, health risk.

INTRODUCTION

The mixture of solid particles and liquid droplets, suspended in the air is called particulate matter (PM) or particle pollution (Tiwari et al., 2020). These particles occur in many sizes and shapes. In the human respiratory tract, the extent of PM deposition is depends on the size of the particles such as coarse inhalable particles ($PM_{10-2.5}$) collected in the upper respiratory tract while fine particles ($PM_{2.5}$) travel deeper into the lungs (Sah et al., 2017).

Physical and chemical characteristics of particles, including the content of toxic substances, and solubility in biological fluids affects the potential health (Hu et al., 2012; Li et al., 2013). The chemical composition of PM includes various trace elements, water-soluble ions, organic compounds (Rohra et al., 2018a; Pipal et al., 2014). Many metals, which are considered to be important airborne toxicants such as Nickel (Ni), Chromium (Cr), Lead (Pb), and Manganese (Mn) and are widely present in PM (Mohanraj et al., 2004; Loxham et al., 2013). International Agency for Research on Cancer (IARC) classified the toxic metals into 2 groups, Group I consisted of Cd and its compounds, Ni compounds, As and its inorganic compounds. Carcinogenic elements, inorganic Pb compounds are considered as Group 2A, and group 2B consisted of Co and its compounds (Sah et al., 2017). The toxic elements such as Cr,

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Ni, Pb, K, Cu, Zn and Al are emitted from the anthropogenic activities (Rohra et al., 2018b; Izhar et al., 2016).

Both oxidation state of Cr is being toxic to animals as well as human and plants (Rohra et al., 2018a; Sah et al., 2017). It is important to know about the distributions of chemical forms of toxic elements besides their concentration, to assess the potential toxicities of trace elements, because the bioavailability of trace elements depends on the strength of their bonds, their characteristic surfaces, on the properties of solutions in contact with PM (Fernández et al., 2000). According to the International Union for Pure and Applied Chemistry (IUPAC) the fractionation is the process of classifying an analyte or group of analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties (Templeton et al., 2000). The study of Jan et al., (2018) deals with the assessment of sequential extraction of PM bound trace metals and the potential health risks associated with them in Pune of India. Sah et al., (2017) investigated the bioavailability and human health risks of toxic metals (Pb, Ni, Cr, As, Cd, and Co) in fine PM ($PM_{2.5}$) in Agra (India).

Firozabad is a densely populated industrial area consisting of 400 glass units that falls within the Taj Trapezium Zone (TTZ) (Kashif, 2016). Varshney and Agarwal, (2014) studied that 31.94% of total males and 23.51% of the total of females have complained for respiratory problems in Firozabad, India. In previous years no studies have been reported on sequential extraction, contamination, and health risk assessment of PM in glass industrially area (Firozabad district). The aim of the present study is to assess the chemical speciation and toxicity of metal bound PM in an industrial area, therefore the main objectives are (a) to assess the mass concentration of $PM_{2.5}$, (b) to analyse the elements concentration in collected $PM_{2.5}$ samples, (c) to assess metal exposure by sequential extraction procedure for the elucidation of chemical forms and the quantitative estimation of a specific element (d) to assess the bioavailability and mobility of metals in environmental physicochemical system and lastly (e) to infer the quantitative health risk posed by the toxic metals through inhalation by human.

MATERIAL AND METHODS

Sampling was carried out in Firozabad city in May 2018. It is located in Western Uttar Pradesh of North Central India (27º09ʹN, 78º24ʹE). It is spread in 21.35 km^3 with a population of 601970 (Ahmad & Bano, 2015). Sampling was done on the terrace of a home building, located in the centre of the city and surrounded by nearby glass industries and main bus stand and was approximately 500m away from National Highway (NH-2) (Figure 1).

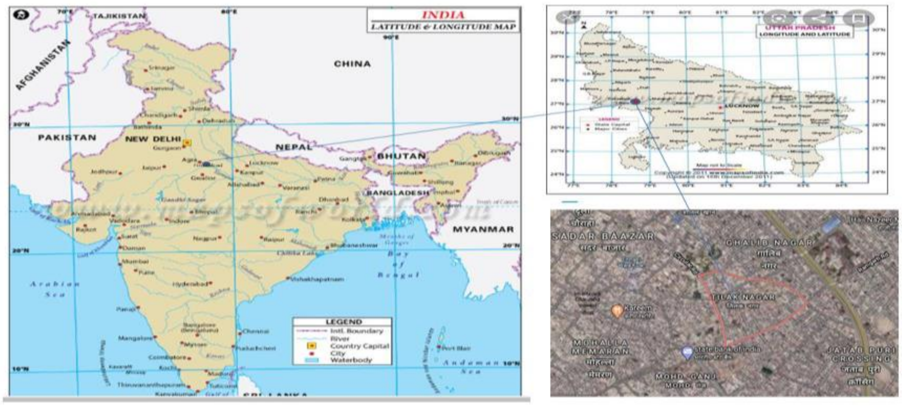

Fig. 1. A map of sampling site at Firozabad industrial area

Table 1. Meteorological parameters observed during the sampling event*

High Temp	42 °C	Precipitation	17.0 mm	Wind	3 km/h
Low Temp	27 °C	Humidity	37%	Pressure	1001 mbar
Mean Temp	35 °C	Dew Point	17 °C	Visibility	km

*https://www.timeanddate.com/weather/india/firozabad

The meteorological parameters during the sampling period were depicted in Table 1.

$PM_{2.5}$ samples were collected with the help of Fine Particulate Sampler (Envirotech APM 550) on PTFE filter paper (2µm pore size and 47 mm diameter). The sampling was done for 8h/day at a flow rate 16.67 L/min. Filter papers were weighed thrice before and after sampling for accuracy by using 4- digit Contech Analytical Microbalance (CAS-44). After the sampling, desiccator was used to equilibrate the samples at 20-30ºC and relative humidity of 30-40% for 24-48 hours. Filter cassettes were used to carry weighed filter papers to the sampling site. These filters were transformed to filter holders and carried on to site location. After sampling, the exposed filter papers were then wrapped with aluminium foil and taken back to the laboratory and placed in desiccators for 24 hours for further post weighing. Field blank filter were collected to reduce gravimetric bias due to filter handling during and after sampling. After weighing, samples were stored in the refrigerator at 4^0C to prevent the evaporation of volatile compounds.

Fractionation Procedure was used to partitioning the heavy metals into 4 different fractions F1, F2, F3, and F4 (Tessier et al., 1979).

In F1 fraction 15 ml Milli- Q water was added to the polypropylene tubes containing the small strips of filter paper, then shaking for 3 hour followed by centrifugation (15 minutes, 4000 rpm). The supernatant was decanted from the residue. In the F2 fraction, 10ml of hydroxylamine hydrochloride ($NH_2OH.HCl$) solution (0.25M) (at pH 2.0) was added to the residue obtained from the F1 fraction and shaken for 5 hours followed by centrifugation (15 minutes at 4000 rpm) than decanted. After the addition of 15ml of hydrogen peroxide (H_2O_2) (30%) into the residue left from F2 fraction was kept at water bath at the concentrate temperature of 95ºC until near dryness, then added 15ml Ammonium Acetate (CH_3COONH_4) (2.5M) and agitated at room temperature at 95ºC than centrifuged (15 min) and collected in polypropylene bottles (F3 fraction). In F4 fraction 10ml of HNO_3, HCl and $HClO_4$ (6:2:5) were added to the residue obtained after extraction of F3 and digested in microwave oven followed by evaporation on a hot plate. The final volume was diluted to 30 ml. After extraction, samples in all 4 fractions (F1, F2, F3, and F4) were placed in a refrigerator at 4 ºC until analysis. The metals (Ca, Al, Cd, Cr, Cu, Co, Fe, Mn, Ni, Mg, Zn and Pb,) were quantified by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; iCAP 6300, Thermo Scientific) equipped with a multiplier collector.

During the monitoring period the sampler was cleaned time to time to make it free from contamination. Flow rate of Sampler (Envirotech APM 550) was checked per day. The Contech Analytical weighing Balance (CAS-44) was calibrated before weighing the samples. Teflon tap coated tweezers were used to handle the filters. Filters were wrapped in tissue paper and aluminium foil. The method detection limits (MDL) for Cr, Cd, Pb, Ni, As and Co, were 1.89, 2.17, 3.19, 2.68, 1.63 and 2.33 ng/m^3, respectively.

“Air Quality Index” (AQI) may be defined as a single term used for reporting the air quality with respect to its effects on the human health (CPCB, 2015).

$$I_p = \frac{I\,high - I\,low}{Bp\,High - Bp\,Low}(Cp - Bp\,Low) + I\,Low \qquad (1)$$

where, I_p= AQI value for the pollutant ($PM_{2.5}$); C_p = Absolute concentration of Pollutant; BP_{high}=Break Point Value that is ≥ C_p;BP_{Low}= Break Point Value that is ≤ C_p; I_{High}= the AQI value corresponding to BP_{High}; I_{Low}= the AQI value corresponding to BP_{Low}. The index range AQI is categorized into 4 categories such as 0-100 (Good to Moderate AQ), 101-200 (Unhealthy AQ), 201-400 (Very Unhealthy AQ), AQI> 400 (Hazardous AQ) (CPCB, 2015).

The potential mobility and bioavailability of metal are assessed through the percent contributions of F1 and F2 to the total metal concentration further referred to as a bioavailability index (BIs) (Sah et al., 2017).

$$BI = \frac{F1 + F2}{Total\ concentration} \times 100 \tag{2}$$

The obtained higher BIs value of metals is considered to be physiologically active and may pose more health risks to the living being than the metals with lower BIs. In our study, on the basis of BI values metals were divided into 2 categories, less bioavailablity, when BI <30%, and high bioavailability when BI >30% (Sah et al., 2017).

Enrichment Factor (EF) is a common approach in estimating the anthropogenic impact in an air samples with that of a selected reference element that is entirely crustal in origin. The EF can be calculated by equation 3.

$$EF = \left(C_x / C_{ref}\right)_{sample} / \left(C_x / C_{ref}\right)_{crust} \tag{3}$$

where, Cx is the concentration of metal in the air and Cref is the concentration of reference element in the crust respectively. Fe was considered as the reference element in each fraction in the present study and their concentrations in the upper continental crust were taken from Wedepohl (1995) (Rohra et al., 2018a). In general, classification of metals follows; EF < 10, EF 10–100 and EF > 100 for less, moderately and highly enriched elements in most of the studies (Rohra et al., 2018a).

The Individual Contamination Factor (ICF) (equation 4) may be defined as the single number used to calculate the contamination of metals in the environment with respect to its retention time. It is given by means of ICF and Global Contamination Factor (GCF) (Jan et al., 2018). ICF can be divided into 4 categories, ICF> 1 (low contamination), 1≤ ICF≤ 3 (moderate contamination), 3≤ ICF ≤ 6 (high contamination), ICF>6 (very high contamination) (Jan et al., 2018).

$$ICF = \frac{C_{nonresistant}}{C_{resistant}} = \frac{C\left(F1 + F2 + F3\right)}{CF4} \tag{4}$$

where, $C_{resistant}$ is the concentration of metal in F4 fraction (residual fraction) which is not available for plants and humans. $C_{nonresistant}$ stands for the metals concentration in the water soluble, mobile, and less mobile fractions (the first 3 fractions), which become available to the human body and or plants, on changing the pH. The sum of the ICFs of all the elements in a sample shows the GCF (equation 5).

$$GCF = \sum ICF \tag{5}$$

A model developed by United State Environmental Protection Agency (USEPA) for the risk assessment was used in the present study to calculate the exposure concentration of metal to human through inhalation. Risk characterization for a receptor exposed via inhalation pathway at last involved the estimation of the Hazard Quotient (HQ) and Excess Lifetime Cancer Risk (ELCR) for non-carcinogenic and carcinogenic risk respectively. HQ is defined as the ratio of exposure to an appropriate reference dose. "Excess lifetime cancer risk" (ELCR) is additional risk that someone might have of getting cancer if that person is exposed to cancer-causing materials for a longer time (Rohra et al., 2018a). The mathematical expressions described in Figure 2 were used to calculate Carcinogenic and Non-Carcinogenic health risk (USEPA, 2009).

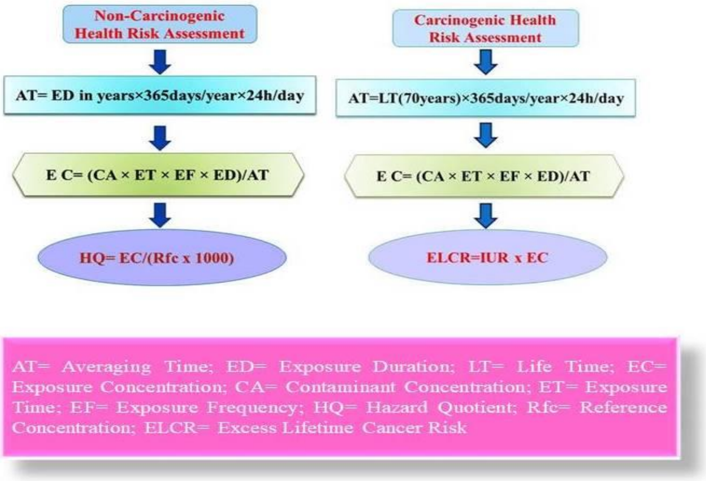

Fig. 2. Overall methodology of Health Risk Assessment Calculation*
***USEPA (2009)**
Exposure factors for this model are depicted in Table 2 (USEPA, 2011; Rohra et al., 2018a).

Table 2. Exposure Factors for USEPA Health Risk Assessment Models*

Factors	Definition	Unit	Values of Exposure Concentration	
			Child	Adult
EC	Exposure Concentration	$\mu g/m^3$	-	-
CA	Contaminant Concentration	$\mu g/m^3$	-	-
ET	Exposure Time	h/day	24	24
EF	Exposure Frequency	Day/Year	350	350
ED	Exposure Duration	Year	6	20
AT	Average Time	Days	365 x ED	x ED

*(Rohra et al., 2018a)

The Chronic Reference concentration and Inhalation Unit Risk is denoted by RfC (mg/m^3) and IUR (µg/m^3). When HQ≤ 1 indicates no adverse health effects and HQ> 1 indicates likely adverse health effects (USEPA, 1993). When HQ values are <1, there is no obvious risk to the population but if these values exceed 1, there may be a concern for potential non carcinogenic effects. For adult and children overall calculated value of ELCR of **Cr$^{(VI)}$** and **Ni is ≥ 10^{-6}** that proposed higher carcinogenic risk. It is to be noted that the total both Cr$^{(VI)}$ and Cr$^{(III)}$ concentration exist in the air with ratio (1:6) (Rohra et al., 2018a). According to the Hieu and Lee (2010) the carcinogenic health risk from Cr$^{(VI)}$ was calculated as 1/7th of the total Cr concentration.

RESULTS AND DISCUSSION

During the sampling period PM$_{2.5}$ concentration ranged from 73.49µg/m^3 to 113.26µg/m^3. The average mass concentration of PM$_{2.5}$ was found to be 88.97±15.34 µg/m^3. The value exceeded 1.48 times the 24 hour standard limit of PM$_{2.5}$(60µg/m^3) set by the Indian National Ambient Air Quality Standard, as prescribed by the Central Pollution Control Board (CPCB) (NAAQS, 2009) and 3.5 times higher than the WHO 24 hour PM$_{2.5}$ guide*lin*es (25µg/m^3) (WHO, 2005).

It was concluded that for all the number of days air quality remains hazardous except the 3rd day (Figure 3).

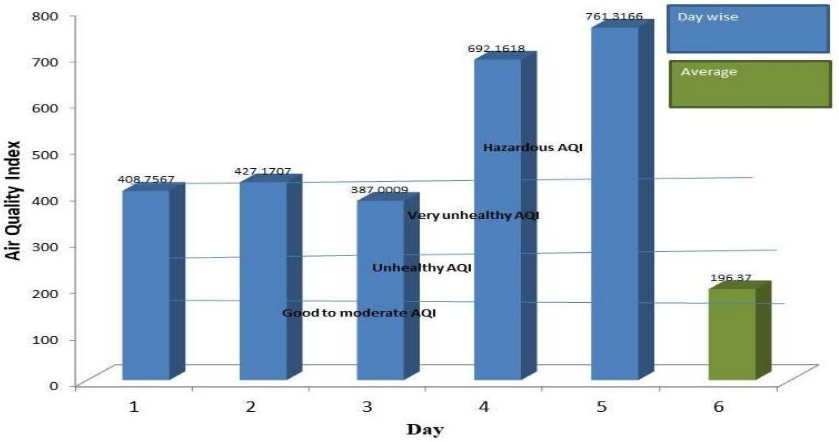

Fig. 3. Air Quality Index (AQI) of $PM_{2.5}$

For the average $PM_{2.5}$ concentration, the AQI value (196.37) too exceeded the hazardous limit (101-200). These results thereby infer that the Firozabad city is highly affected by $PM_{2.5}$ pollution due to vast number of anthropogenic activities including industrial emissions carried out in this area (Ahmad & Bano, 2015).

On the basis of the obtained overall concentration, elements were grouped into 2 categories; Group I and Group II. Group I consisted of elements (Ca, Mg, Fe) having concentration in range 0.82-17.84µg/m^3 while the remaining ones having concentration ranged as 0.005-0.093µg/m^3 were termed as group Group II elements. Overall, in our study the Ca concentration was the highest while Co had the lowest concentration among all the analysed metals.

Soluble and exchangeable fraction (F1) shows that the metals are adsorbed on particle surfaces, and they are mobile and easily extracted in aqueous solutions (Chaudhary & Banerjee, 2007). The relative distribution of metals in the soluble fraction followed the order: Co (42.18%)>Pb (19.07%)> Cu (18.39%)>Ca (5.92%)> Mg (5.03%)>Al (4.90%)>Mn (3.51%)> Fe (2.93%)>Cr (2.83%)> Ni (1.93%)> Cd (1.04%)> Zn (0.11%) as shown in Figure 4. Feng et al., (2009) reportedthe sequential extraction of $PM_{2.5}$ in Guangzhou, South China, and it was concluded that more than 40% Cd and 30% Ni was water-soluble.

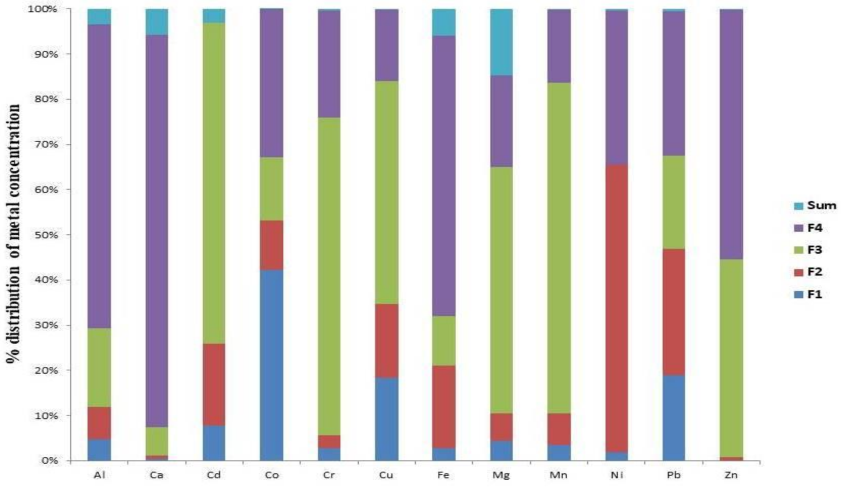

Fig. 4. Percentage distribution of metals in the different fractions

Carbonates, oxides and reducible fraction (F2) retained almost equal proportions of Al, Ca and Co (7-10%) and lower proportions of Cu, Cr, Mg, Mn (2.8-16.5%). This fraction also consisted of higher proportions of Cd, Fe, Pb and Ni, Zn (18.8-63.9%). In the reducible fraction, metals can become more mobile and can be released into the environment (Bhattacharyya et al., 2014). Cd (26.4%), As (39.9%), Cr (14.4%), Pb (50.7%) and Ni (17.8%) in fine particulate matter ($PM_{2.5}$) was reported by Li et al., (2015) in Nanjing, China.

Trace metals bound to various forms of organic matter are extracted in *Organic-matter bound, oxidizable and sulfidic metalic fraction (F3).* (Sah et al., 2017).Ca is retained maximum in this fraction (75.61%) followed by Cr, Mg, Mn, Zn, and Cu (7.09%). More than 40% of Ni and more than 30% of Co, Cr associated with F3 fraction in $PM_{2.5}$ reported by Feng et al., (2009) in Guangzhou, China.

Metals in this fraction are stable and are categorized as a *residual fraction (F4)* (Feng et al., 2009). Maximum concentration of Al (69.59%), Fe (66.08%), Zn (55.41%), Ni (34.19%), Pb (32.12%), and Co (32.81%) were found in this fraction with relatively lower proportions of Cr (23.82%), Mg (23.82%), Mn (16.15%), Cu (15.71%) and Ca(10.46%) (Figure 4). Feng et al., (2009) observed that Cr (>50%) was the dominant metal in the residual fraction while varying amounts of As (5.8%), Cd (30.7%), $Cr^{(VI)}$ (33.0%), Ni (9.6%) and Pb (10.0%) in $PM_{2.5}$was observed by Li et al., (2015).

On the basis of mass concentrations, the metals in environmentally highly mobile fraction (F1) in the $PM_{2.5}$ samples decreased in following order: Co>Pb>Cu>Ca>Mg> Al>Mn>Fe>Cr>Ni> Cd>Zn as shown in Table 3.

With regard to the mobile proportions of metals (Fraction 2), a decrease in the order: Ni>Pb>Fe>Cu>Co>Cd>Al>Mg>Mn>Cr> Cd>Zn was observed. For the less mobile Fraction (F3), the metals decrease in the order: Ca>Mn>Cr>Mg>Cu>Zn>Pb>Al>Co >Fe> Cd. While the metals in the immobile Fraction (4) decrease in the order: Al>Fe> Zn>Ni>Co>Pb>Mg>Cr>Mn>Cu>Ca. The fraction wise mass concentrations of the metals observed at the present site are compared with other sites is depicted in the Table 4.

On comparison, it was found that the metal concentration obtained in the present study on an average exceeded those of the previous study (Sah et al. 2019) conducted in the Agra region; that might be attributed to the ‘*industrial impact’*. On global comparison, the values obtained were found to be lower than those obtained in studies conducted in Pune (Jan et al. 2018) and Indonesia (Betha et al. 2013).

From the results, it is clear that Mn, Ni, Pb, Co, and Cu had high bioavailability given in range (34.8%-65.8%), while the remaining elements demonstrated low bioavailability (0.82%-22.35%) depicted in the Figure 5.

Table 3. Absolute concentration (μg/m^3) of metals in different fractions

METALS	F1	F2	F3	F4	F1+F2+F3+F4
Al	0.1322	0.1984	0.4894	1.8762	2.6962
Ca	3.1268	4.2262	39.9322	5.5254	52.8104
Cd	0.0032	0.0076	0.0296	ND	0.0404
Co	0.0162	0.0042	0.0054	0.0126	0.0384
Cr	0.0070	0.0070	0.1740	0.0588	0.2468
Cu	0.0398	0.0356	0.1070	0.0340	0.2164
Fe	0.1380	0.9128	0.5426	3.1042	4.6976
Mg	0.6494	0.9278	8.2550	3.0752	12.9074
Mn	0.0074	0.0146	0.1544	0.0340	0.2104
Ni	0.0060	0.1980	ND	0.1060	0.3100
Pb	0.0722	0.1058	0.0790	0.1216	0.3786
Zn	0.0002	0.0012	0.0744	0.0942	0.1700

Where- ND: Not detected

Table 4. Comparison of the metals concentration (µg/m^3) in the air of Firozabad with the other cities in India, or other cities around the globe

S.No.	References/ Area of study	Fractions	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1.	Present study Firozabad, India	F1	0.0032	0.0162	0.0070	0.0398	0.1380	0.0074	0.0060	0.0722	0.0002
		F2	0.0076	0.0042	0.0070	0.0356	0.9128	0.0146	0.1980	0.1058	0.0012
		F3	0.0296	0.0054	0.1740	0.1070	0.5426	0.1544	ND	0.0790	0.0744
		F4	ND	0.0126	0.0588	0.0340	3.1042	0.0340	0.1060	0.1216	0.0942
		F1+F2+F3+F4	0.0404	0.0384	0.2648	0.2164	4.6976	0.2104	0.3100	0.3786	0.1700
2.	Sah et al. 2019 Agra, India	F1	0.0140	ND	0.0017	0.030	0.080	0.024	0.027	0.032	0.156
		F2	0.0010	ND	0.0020	0.061	0.647	0.022	0.045	0.039	0.012
		F3	0.0110	ND	0.003	0.030	0.152	0.045	0.025	0.029	0.135
		F4	0.0260	ND	0.011	0.092	1.099	0.053	0.025	0.039	0.227
		F1+F2+F3+F4	0.054	ND	0.019	0.215	1.98	0.146	0.123	0.139	0.646
3.	Jan et al. 2018 Pune, India	F1	0.033	0.067	0.055	0.040	0.060	0.034	0.051	0.055	0.107
		F2	0.026	0.082	0.064	0.025	0.097	0.049	0.026	0.102	0.087
		F3	0.018	0.051	0.113	0.106	0.675	0.052	0.163	0.037	0.195
		F4	0.021	0.066	0.0870	0.017	1.368	0.090	0.390	0.091	0.148
		F1+F2+F3+F4	0.099	0.265	0.319	0.240	2.200	0.225	0.630	0.285	0.538
4.	Li et al. 2015 Nanjing, China	F1	0.002	ND	0.007	0.023	0.080	0.031	0.005	0.043	0.292
		F2	0.001	ND	0.003	0.015	0.168	0.021	0.002	0.091	0.099
		F3	0.0003	ND	0.007	0.018	0.303	0.013	0.005	0.043	0.046
		F4	0.001	ND	0.006	0.006	0.069	0.010	0.002	0.023	0.032
		F1+F2+F3+F4	0.004	ND	0.023	0.062	0.62	0.075	0.014	0.20	0.469
5.	Betha et al. 2013 Kalimantan, Indonesia	F1	0.039	0.039	0.243	0.400	2.305	0.091	0.249	0.033	0.398
		F2	0.007	0.026	0.689	0.497	5.780	0.465	0.614	0.080	0.572
		F3	0.046	0.066	0.233	0.213	2.102	0.129	1.420	0.017	0.115
		F4	0.013	0.107	0.169	1.355	3.378	0.141	0.819	0.331	0.704
		F1+F2+F3+F4	0.105	0.238	1.334	2.465	13.565	0.826	3.102	0.461	1.789

Where- ND: Not detected

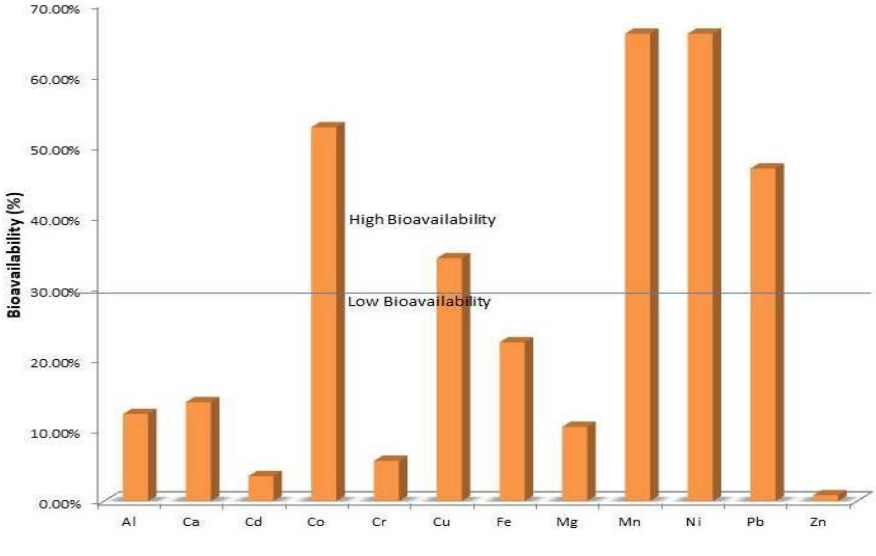

Fig. 5. Bioavailability of different metals in PM$_{2.5}$

A comparison between the metal concentrations and the limits imposed by the NAAQS (2009), European Commission (EC, 2000) and the World Health Organization (WHO, 2007) is presented in the Figure 6.

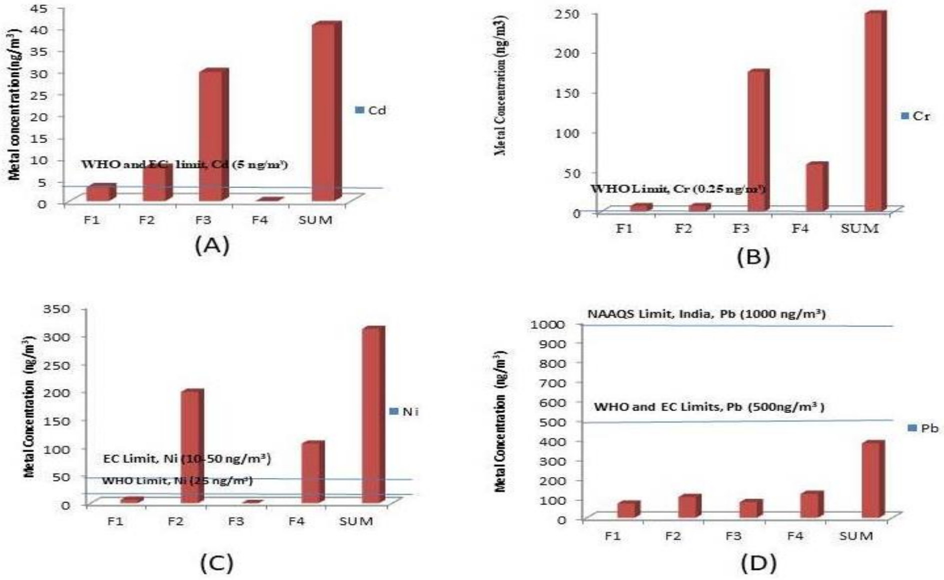

Fig. 6. Metal Concentration (μg/m^3) in different fractions

[The blue line shows the NAAQ Standard set by National Ambient Air Quality Standard in India (NAAQS, 2009), European commission (2000), and WHO limit (WHO 2007)]

The Pb concentration in the 4 chemical forms as well as in the sum of the 4 fractions was below the NAAQS, EC and WHO guideline value. The concentration of Cd was below the EC and WHO guideline value in F1 and F4 fraction only Ni concentration exceeded the EC and WHO guideline value in F2 and F4 and in the sum of the fractions only. The concentration of Cr in F3 and F4 fractions was found higher as compare to WHO respective standards. The results of this comparison show that the levels of these metals are lower than the benchmark limits in the bioavailable fractions (F1 and F2) except for Cd and Ni. Hence it may be inferred that although concentrations of metals are higher, associated health risks are meagre as the concentrations in the bioavailable fractions are comparatively low.

As can be seen from Figure 7, the most enriched elements are Cd (6516.16), Pb (374.24), and Cu (289.21) (mean values). These high EF values indicate that the source of accumulation of Cd Pb, and Cu originates from anthropogenicity and is mainly from the traffic emissions and coal combustion (Tokalioglu et al., 2003), although industrial sources can also cause an effective accumulation for Cd and Pb (Wang et al., 2010).

After calculating the ICF of all metals in $PM_{2.5}$, it was found that the value of ICF for Al, Cd, Fe, and Zn was low (0.02-0.80) while in case of Co, Ni, Pb, the contamination was moderate (1.92-2.11). The contamination was considerable for the Cu, Cr, Mg, Mn (3.19-5.36) while the contamination factor value of Ca was found to be very high (8.55). From the results, it was inferred that the metals with high, moderate and considered ICF (Ca, Co, Ni, Pb, Cu, Cr, Mg, Mn) indicate the high environmental mobility and lower retention time of the metals and these metals pose more risk to the local environment (Figure 8). The GCF for all considered metal was 33.11. Sah et al. (2019) showed that Cd, Cu, Mn, Zn and Pb had high environmental mobility and lower retention time due to the higher value of ICF of these metals in their study.

The Exposure Concentration (EC) of a pollutant via an inhalation as exposure pathway was estimated (table 5).

Overall, the total value of HQ for all the metals in all fractions was obtained as 27.61 (Table 6). For Ni, Mn, and Cr was HQ>1 while for Al, the HQ value was below the benchmark limit. This infers that Ni posed a maximum non-carcinogenic risk while Al in presently obtained concentration doesn't pose any non-carcinogenic risk through inhalation. Following trend of non- carcinogenic risk for metals in varied fractionating stages was obtained as: Ni>Mn>Cr>Al (F1), Ni>Mn> Cr>Al (F2), Mn>Cr>Al>Ni (F3), Ni>Mn> Cr>Al (F4). This trend infers that Ni posed highest non- carcinogenic risk in F2 fraction that is the bio-available form of Ni posed 13 times higher risk (Non-Carcinogenic health risk) than safer limit while Mn and Cr as a potentially effective fraction (F3) didn't pose substantial non-carcinogenic risk.

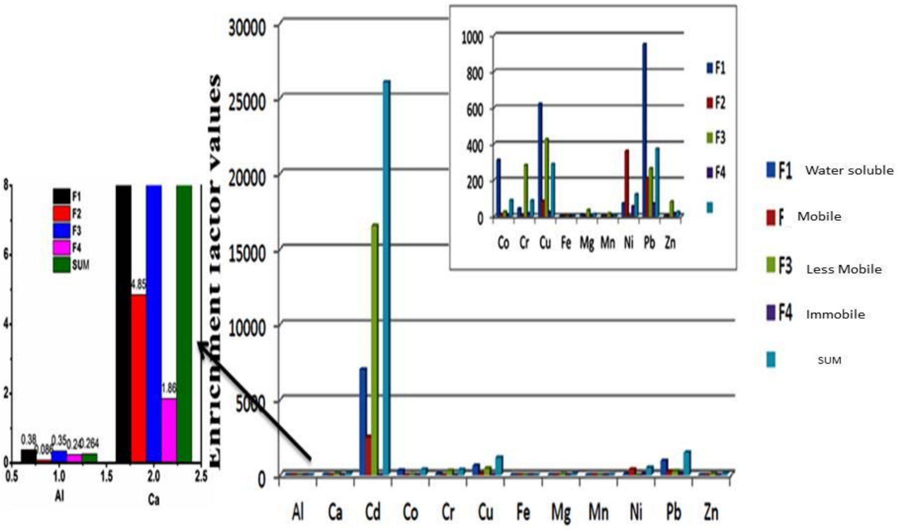

Fig. 7. EF of the metals in four different fractions

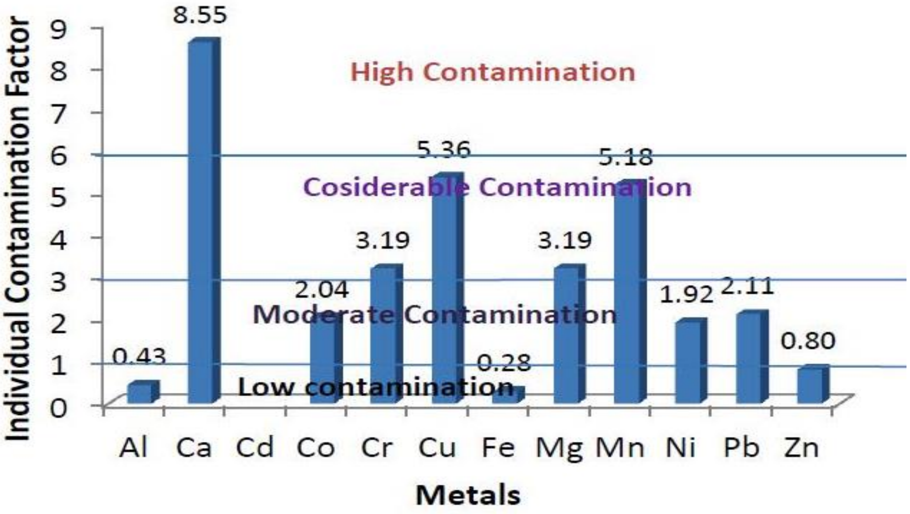

Fig. 8. ICF of metals

Table 5. Exposure Concentration (μg/m^3) [For (A) Non carcinogenic health risk and (B) Carcinogenic health risk] of metals in four different fractions

(A)

Elements	Exposure Concentration				
	Adult				
	F1	F2	F3	F4	SUM (F1+F2+F3+F4)
Al	0.120	0.190	0.460	1.790	2.570
Cr	0.006	0.006	0.166	0.055	0.230
Mn	0.007	0.014	0.148	0.032	0.200
Ni	0.005	0.189	ND	0.101	0.290

ND: Not detected

(B)

Metals	Exposure Concentration									
	F1		F2		F3		F4		SUM (F1+F2+F3+F4)	
	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Cr(VI)	0.0002	0.00008	0.0002	0.00008	0.0065	0.0019	0.0020	0.00067	0.0090	0.0028
Ni	0.0016	0.0004	0.0540	0.0160	ND	ND	0.0290	0.0087	0.0840	0.0250
Pb	0.0190	0.0050	0.0280	0.0080	0.0210	0.0060	0.0330	0.0090	0.1030	0.0310

ND: Not detected

Table 6. HQ or Non- Carcinogenic health risk (via inhalation) of total and fractional concentration of metals

Elements	Rfc Values*	HQ				
		Adult				
		F1	F2	F3	F4	TOTAL (F1+F2+F3+F4)
Al	5.0E-3	0.02	0.038	0.09	0.35	0.51
Cr	1.0E-4	0.06	0.06	1.66	0.56	2.36
Mn	5.0E-5	0.14	0.28	2.96	0.65	4.03
Ni	1.4E-5	0.36	13.56	ND	7.26	20.71
Total		0.58	13.93	4.71	8.82	27.61

ND: Not detected *Rohra et al., 2018a

Table 7. ELCR or Carcinogenic health risk of total and fractional concentration of metals Where- ND: Not detected *(USEPA, 2011; Rohra et al., 2018a)

Metals	IUR Values*	F1		F2		F3		F4		SUM (F1+F2+F3+F4)	
		Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
$Cr^{(VI)}$	8.40e-02	2.30×10^{-5}	6.90×10^{-6}	2.30×10^{-5}	6.90×10^{-6}	5.50×10^{-4}	1.60×10^{-4}	1.80×10^{-4}	5.60×10^{-5}	8.05×10^{-4}	2.40×10^{-4}
Ni	2.40e-04	3.94×10^{-7}	1.18×10^{-7}	1.30×10^{-5}	3.90×10^{-6}	ND	ND	6.90×10^{-6}	2.09×10^{-6}	2.03×10^{-5}	6.11×10^{-6}
Pb	1.20e-05	2.30×10^{-7}	7.10×10^{-8}	3.48×10^{-7}	1.04×10^{-7}	2.60×10^{-7}	7.20×10^{-8}	4.00×10^{-7}	1.20×10^{-7}	1.20×10^{-7}	3.70×10^{-7}
Total		2.3×10^{-5}	6.10×10^{-6}	3.60×10^{-5}	1.00×10^{-5}	5.50×10^{-4}	1.60×10^{-4}	1.80×10^{-4}	5.80×10^{-5}	8.20×10^{-4}	2.40×10^{-4}

The overall ELCR value for the complete study was found to be 8.2 x 10^{-4} for adult and for children 2.4 x 10^{-4} (Table 7). The value exceeded the benchmark limit of 1x10^{-6} as prescribed by USEPA (2009).

This shows that 820 adults and 240 children out of 1 million are likely to develop carcinogenic effects if exposed to such concentration. For both adult and children ELCR of $Cr^{(VI)}$ and Ni exceeded the safer limits for carcinogenic risk while Pb in present concentration does not imply any cancerous risk. The highest risk of $Cr^{(VI)}$ was obtained in F3 fraction when bound to organic matter. The results further display higher risk posed to adults than children through inhalation of particulate laden air bounded to toxic $Cr^{(VI)}$ and Ni (Table 7).

CONCLUSIONS

This study depicts the exposure of fine PM concentration and associated heavy metals in $PM_{2.5}$ in an industrial area of Firozabad. The $PM_{2.5}$ concentration obtained was 88.97±15.34 $\mu g/m^3$ that was1.48-3.55 times higher than the safer limit prescribed by the government monitoring agencies (WHO and NAAQS). Among the analyzed metals Ca had the highest concentration in all fractions (F1,F2, F3, and F4 fractions). Zn had the minimum concentration in the highly mobile fraction (F1) and a less mobile fraction (F2) while Co reported the least concentration in F3 and F4 fraction. Mn, Ni, Pb, and Co showed high bioavailability (34.80%-65.80%) and considered to be physiologically active and may pose more risks to humans than the metals with lower BIs (Fe, Al, Ca, Co, Cr, Zn, Mg). For adults overall calculated value of HQ for Ni, Cr, and Mn is >1 that proposed higher non- carcinogenic risks. For adult and children overall calculated value of ELCR of $Cr^{(VI)}$ and Ni is $\geq \mathbf{10^{-6}}$ that proposed higher carcinogenic risk while ELCR of Pb was under benchmark limits as prescribed by USEPA. Overall the study showed that health risk due to exposure to $PM_{2.5}$ through inhalation is not negligible to residents. As the chemical composition of PM determines the degree of toxicity, the calculated results highlight that $Cr^{(VI)}$ exhibited the higher carcinogenic and Ni exhibited the highest non carcinogenic risk. These results imply that, more attention should be paid to the environmental quality to reduce the health risks to children and adults residing in the vicinity of the present industrial site.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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