Atmospheric Concentration of Trace Metals in PM_{2.5} and Their Bioavailability in Different Areas of Gwalior Region

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Abstract :

The contemporary study aims to explore the concentration of particulate matter (PM), sources and their inherent health risk of exposure in different urban and rural areas of Gwalior, India. In the month of June and July in 2017, with the help of fine particulate sampler, the fine particles $(PM_{2.5})$ were collected on polytetrafluoroethylene (PTFE) filter paper. The average mass concentration of $PM_{2.5}$ was $63.02\pm27.71\mu g/m^3$ (urban) and $73.07\pm32.17 \mu g/m^3$ (rural). The metal concentration of $PM_{2.5}$ was characterized using atomic absorption spectroscopy (AAS). Results publicised that mostly the toxic metals were primarilypresent in bioavailable fractions. The estimated bioavailable fractions of chromium and lead were 86.62 $\mu g/m^3$ and 28.96 $\mu g/m^3$ respectively shows the incremental cancer risk, indicating the potential impact on residents of urban and rural areas.

Keywords: *PM*_{2.5}, *AAS*, *toxic metals*, *incremental cancer risk*, *Bioavailable*

I. INTRODUCTION

In spite of the elevating concerns over the last decades regarding evaluation of metal exposure from ambient particulate matter (APM) or dust via inhalation is inherently complex and lacks consequences on many levels. PM or Particulate matter present in the air is considered mainly as fine suspended particles which are mainly heterogeneous in nature with respect to their size and chemical compositions. As a result of which mostly PM particles are classified depending upon their diameter firstly into (PM_{10}) where these particles are also referred as coarse particles having particle size ranging between 10 to 2.5 µm, secondly into (PM 2.5) also referred as fine particles having a diameter size of 2.5 to 0.1 μ m and thirdly into (PM_{0.1}) called as Ultrafine particles consisting of a diameter upto 0.1 µm [1]. Perilous toxicological effects on organisms are mainly due to these particle sizes [2,3] where (PM_{2.5}) or fine particulate matter is considered as the

most outrageous of all due to the characteristic they possess which allow them to reside in the atmosphere for a longer period of time and their capability to breach through the alveolus make them even more fatal [4,5]. Toxicological and epidemiological studies carried out have proved that trace metals present in particulate matter are responsible for causing carcinogenic effects [6,7] and their toxic effects are also in association with the water solubility of metals in size segregated atmospheric particles [8,9]. For instance Chen and Lippmann [10] showed that Nickel (Ni), Zinc (Zn), Vanadium (Vn) and Lead (Pb) are some elements which results into acute cardiac functional changes. Particulate matter consisting toxic heavy metals possess different fractions that unveil different bioavailability and their possible health impacts on human beings. Adamson et al.[11] and Sun et al. [12] revealed that observed pulmonary toxicity from water soluble fraction of toxic metals present in airborne PM were correlated positively. Past studies of Heal et al. [13] showed that the bioavailable form, is the dominant fraction of PM_{2.5} bound heavy metals in the urban atmospheres of developed countries where the major source of PM are automobile emission. During our routine day to day activities, millions of particles are inhaled by us during respiration and they reaches to our lungs which are emanated from different sources i.e. industries, home and environmental settings. Usually in urban areas heavy metals bound with PM originate from various mixed sources and different aging processes, which also affects their distribution and form in different PM size fractions, which ultimately governs their bioavailability and respiratory deposition rate. Nevertheless various toxicological studies have stipulated that transition metals solubility play a major role in bioavailability of PM and also in chronic and adverse health effects rather than total metals. Wide range variations have been reported in studies carried out on solubility of transition metals due to variations in their sources and processes. Vousta and Samara [14] in their study elucidated that the breathing is the major path for the entry of airborne particulate matter in the humans which was explained on the basis of bioavailabilty of trace metals. The study carried out over here in Gwalior (considered as one of the populous city in India) highlights chemical speciation of trace metals which are linked to PM_{2.5.} In past two decades most of the studies carried out in India are mainly on total concentration of metals and their sources [15,16]. Pervez and Pandey [17] in 1994 reported toxic metals in kidneys and gallstone sections of workers of a steel plant but little is known on the bioavailability of PM_{2.5}-bound metals [18]. Due to intensification in air pollution and numerous PM sources in the studied area, the compositions of PM₂₅ and chemical speciation of PM2.5-bound trace metals may be different from those of the other urban and rural areas. The primary aim of the carried out study was to evaluate the bioavailability and the PM_{2.5} bound trace metals concentration with respect to their related health effects on residents and commuters of Gwalior city. Incremental lifetime cancer risks were evaluated for specific trace metals depending on the basis of literature data. The study provided important evidences on the baseline data of toxic metals and their potential health risks to the residents due to inhalation of PM_{2.5} in Gwalior urban and rural areas. This study has been done in Gwalior, India during the month of June and July. 2017.

II. METHODS AND MATERIALS

A. Site Description

Gwalior (26.22°N and 78.18°E) on of the most populated city in India is situated in the central part of India (Fig 1). The city being a boon of having historical background like, the mighty Gwalior Fort, Jai Vilas Palace which is presently converted to museum and the glorious Sun temple catches a lot of tourist attraction in this city. By the cessation of 20th century the city turned into a million plus agglomeration and now it's a one of the major metropolitan city of central India. The city circumferences a total of 4560 sq. km area having a density of 450/Km². The city packs in a total population of 2,032,036 according to the Directorate of Census Operation in MP. 2011 [19]. From the total population 1,273,792 people resides in urban areas while 758,244 in the rural part. A study conducted in 2016 revealed that the city pose highest level of air pollution in India and ranks second in the world, which is primarily due to the burning of garbage and fossil fuels, ultimately making the air hazardous to breathe [20]. The city is well linked to other parts of Madhya Pradesh and India by National Highways i.e. NH-3 and NH-75 and witnesses very high loads of traffic.



Fig1: Site Map of Gwalior

B. Sample collection

In the present study, Fine particulate medium-volume air sampler APM 550 Envirotech was used for sampling outside the houses in porch area where the fine particles were collected on a PTFE filter paper. The sampler was set on a flow rate of 16.6 L min⁻¹. Three houses were selected from rural and urban areas particularly and a total of 24 samples were collected from outdoor, four from each house. Daily flow rate calculations (gas meter reading/ time reading) were being made to make sure that the fluctuations in flow rate are within the range. It has a portable Wins-Anderson impactor for the sampling of PM_{2.5}. Sampling was done for the month of June and July at urban and rural areas.

C. Gravimetric analysis and storage

Prior to initial weighing, 47mm PTFE filter papers were stored in a dessicator for 24-h and then weighed by using four digit balance (Shimadzu UniBloc ATX224) with sensitivity of \pm 0.2 mg. After sampling filters were again re-weighed for gravimetric analysis. For plummeting the probability of contamination filter papers were handled only with tweezers layered with Teflon tape. Blank filters from field were aslo collected to diminish the gravimetric bias due to filter handling during and after sampling. Gravimetrically, the mass concentration of fine particles was calculated by subtracting the initial average mass of the blank filter from the difference in mass of the filter paper of post and pre weighed dividing by air volume passed in m³[18].

D. Extraction and chemical analysis

All apparatus and glassware used for extraction and storage were pre washed by soaking them in 2% HNO₃ and then followed by rinsing them with deionized water again followed by double distilled water for number of times. For extraction of metals a

two stage method was employed, where at first ammonium acetate extraction method was carried out to determine soluble elements and secondly acid extraction method for non-soluble elements.

Filter, digestion, extraction and multi-element determination

Firstly, for the determination of soluble portion the filter paper was digested using 0.01 M ammonium acetate (AA) solution at pH 7 to simulate neutral lung environment and then 10 ml solution with filter paper was transferred to 15-ml polypropylene centrifuge tubes. Further the tubes were sealed and immersed in the shaking water bath for 2 h at 37°C (1 h shaking followed by 1 h still). At room temperature extractions were cooled followed bv centrifugationand then separated by filtration. The residue of the same filter was then digested ultrasonically for 6 days by using the solution of HF-HNO₃ in the ratio of 3:1 in a hot water bath at 60°C with two 30-min ultrasonic intervals. Multi-elemental analysis was performed using atomic absorption spectroscopy (AAS) for the digested samples [18].

E. Statistical analysis

For calculating various statistical functions i.e. mean, median, skewness and Pearson correlation coefficient, SPSS software version 17.0 was employed.The metal concentration was calculated by the method given by United States Environmental Protection Agency [21].Bioavailability Index (BI) was also calculated using the relation given below:

Bioavailability Index (%) = $\frac{Cs}{Ct} * 100$

Where, C_s and C_t are the soluble and total concentrations, respectively

III. RESULTS AND DISCUSSION

A. Particulate Concentration:

Sampling was carried out during the month of May 2017 to June 2017 where a total of 24 samples from each site were collected from urban and rural area. As shown in Table I it represents statistical parameters like mean, median, standard deviation, skewness followed by maximum concentration and minimum concentration of PM2.5 at urban and rural environments. Throughout the study duration it was found that mean concentration with standard deviation at urban and rural environments were $\mu g/m^3$ $73.07 \pm 32.17 \mu g/m^3$ 63.02±27.71 and respectively. On comparison it was found that PM_{2.5} concentrations exceeded 1.57 times in the urban site and 1.8 times at the rural when compared with standards implemented by National Ambient Air Quality Standards (NAAQS) [22] as specified by Central Pollution Control Board (CPCB) of India (40 $\mu g/m^3$ annual average for PM_{2.5}). Also looking further into it when the obtained results were compared with World Health Organization (WHO) air quality guidelines [23](25 μ g/m³ 24 h average for PM_{2.5}), values were found to be 1.57 times higher in urban and 1.8 times higher in rural areas. PM_{2.5} concentration was found to be elevated at rural sampling sites which may be attributed to resuspension of road and soil dust from construction activities and dust emission from stone crusher plant as some of our sites were near roadside locations. Throughout the study period large significant variations in PM2.5 concentration with positive skewness of 0.34 and 0.94 at urban and rural sites respectively was pragmatic. The deviation in concentration of PM throughout the study is due to varying anthropogenic sources and meteorological conditions.

Table I Explorative Statistical Parameters of Concentrations for $PM_{2.5}$ in Urban and Rural Homes

Paramet ers	PM _{2.5} urban (μg/m ³)	PM _{2.5} rural (μg/m ³)	Tem p. °C	Relativ e humidi ty (%)	Wind speed (km/h r)
M± S.D.	63.02±27.	73.07±32.	34±6	56±11.	4.5±0.
	71	17	.2	03	8
Md	59.13	60.16	32	57	4
Skew	0.34	0.94	-0.31	-0.2	2.5
Max	118.93	141.92	45	100	6
Min	15.40	29.39	25	18	4

M: Mean; Md: Median S.D.: Standard Deviation; Skew: Skewness; Max: Maximum; Min: Minimum

B. Concentration of metals:

The concentration of non-soluble metals in $PM_{2.5}$ is illustratedin fig 2. The concentration of all metals was higher in urban sites except for Cu and Na which were higher at rural sites. The major sources of copper concentration in atmospheric particulate matter were mainly from mining activities and industries. Schroeder et al. [24] in his study elucidated that copper present in $PM_{2.5}$ is expected to instigate from wind-blown soil and dust. The other causes of Cu in the ambient air are fungicides, emission from metal working factories and electroplating materials[25]. In both the sites, Fe was the most abundant element in $PM_{2.5}$. At urban site, Fe accounts for 4.39µg/m³ followed by Cr (3.23 µg/m³),

soluble

C. Correlation Analysis:

Correlation analysis is a statistical technique which

was performed to determine the relationship between

different metals in PM2.5. Table II and III shows the

correlation coefficient matrix for soluble and non-

soluble metals in PM_{2.5}. On applying correlation

analysis, from the results significantly different

correlation trend in non-soluble fraction as well as in

Mn (0.45 μ g/m³), Zn (0.08 μ g/m³) and Cu (0.01 μ g/m³) while at rural sites Fe was 1.56 μ g/m³ followed by Cr (1.35 μ g/m³), Mn (0.42 μ g/m³), Cu (0.02 μ g/m³) and Zn (0.01 μ g/m³). The highest value of Fe was probably due to industrial activities and it may originate from soil dusts, poorly managed transport, crusher plants around the sites and building construction. Mostly, heavy metals are toxic and it is a big concern to health. The most abundant species at both sampling sites indicates that there arefusionof sources i.e. natural and anthropogenic, since Fe is predominantly crustal element, while Zn and Cu are chiefly anthropogenic elements[26].



Fig2: Concentration of non-soluble metals in PM_{2.5}

	Cu	Mn	Fe	В	Zn	Pb	Cr	Li	Na	K	PM2.5
Cu	1.00										
Mn	-0.30	1.00									
Fe	0.12	0.16	1.00								
В	-0.58	-0.11	0.13	1.00							
Zn	0.52*	0.14	0.50*	-0.37	1.00						
Pb	0.58*	-0.23	-0.01	-0.35	0.33	1.00					
Cr	0.30	-0.27	0.08	0.09	0.22	0.57*	1.00				
Li	0.17	0.05	0.15	-0.32	0.18	0.14	0.29	1.00			
Na	0.00	0.51*	0.07	0.04	-0.13	-0.08	0.11	0.11	1.00		
K	-0.26	-0.05	-0.27	0.03	-0.17	-0.25	-0.53	-0.34	-0.44	1.00	
PM2.5	0.31	-0.23	0.03	-0.28	0.14	0.26	0.22	0.24	-0.01	0.06	1.00

Table II Correlation Coefficient Matrix for Elements in Soluble Fraction

*Correlation is significant at the 0.01level (two-tailed)

Table III: Correlation Coefficient Matrix for Elements in Non-Soluble Fraction

	Си	Mn	Fe	В	Zn	Pb	Cr	Li	Na	K	PM2.5
Cu	1.00										
Mn	0.13	1.00									
Fe	0.09	-0.01	1.00								
В	-0.05	0.32	-0.11	1.00							

Zn	-0.08	0.02	-0.07	0.53*	1.00						
Pb	-0.06	0.24	-0.03	0.27	0.18	1.00					
Cr	-0.36	0.59*	-0.05	0.59*	0.51*	0.50*	1.00				
Li	-0.01	-0.27	0.21	-0.36	0.17	-0.24	-0.17	1.00			
Na	0.16	-0.14	-0.56	0.00	0.10	-0.07	-0.22	0.05	1.00		
К	-0.19	-0.06	0.32	0.50*	0.50*	0.11	0.30	0.07	-0.22	1.00	
PM2.5	0.19	0.31	-0.25	0.10	0.16	0.36	0.26	-0.12	0.45	-0.28	1.00

*Correlation is significant at the 0.01level (two-tailed)

fraction (p<0.01) was concluded. There was moderate correlation between Cu and Pb and Cu and Zn in soluble fraction as they were originated from the similar sources i.e. the exhaust emitted from the automobiles powered by regular gasoline and road traffic[27]. Cr and Pb shows positive correlation in both soluble and non-soluble fraction i.e. 0.57 and 0.50 respectively whose probable sources are peeling paint and renovations resulting in dusts or fumes from paints[28]. In non-soluble fraction Cr and Mn, Cr and Zn and Cr and B shows positive correlation indicating to similar sources.

D. Bioavailability of metals in $PM_{2.5}$

Investigations carried out by [9] states that only the soluble fraction part of heavy metals play a crucial role on the health due to its bioavailability. The meaning of solubility states that it mainly depends upon the speciation process, and a few literature approaches have used this by comparing water and acid extracted metals[9,29]. EPA defines bioavailability as the degree to which soluble concentration of metals which is engross or adsorb across the biological membranes of organisms. In the existing study it was determined that the total metal concentration in PM_{2.5} was 80.35 μ g/m³ in which the bioavailable fraction which simulates the neutral lung environment at pH 7 is 8.5%. Figure3 shows metal bioavailability in PM2.5, Cu has the highest bioavailability index (BI) i.e. 77.78% followed by Cr (56.75%), Zn (52.91%), B (33.59%), Pb (13.51%) and Fe (4.27%). Cu and Cr are the most toxic metals in the present study. Their greater BI values indicate that they are more hazardous to human health once inhaled to lung system. In meanwhile, Rohra et.al [30], also estimated bioavailable index for five metals respectively and found that Lead (Pb) showed highest BI of (0.21), followed by Zinc (Zn) which showed (0.19) and calcium (Ca) by (0.10) while metals like Magnesium (Mg) and Potassium (K) were found to

be lower than near around 0.06 and 0.03 respectively in PM_{2.5.} A Study carried out by Niu et al. [31] showed that 'ammonium acetate' extraction for bioaccessible fractions in urban PM in Ottawa and presented that 16-29% bioavailable Pb was found, while on the contrary Heal et al. [13] stated 35% Pb bioavailability in his study. Environment protection agency (EPA) characterised Cu as a group D carcinogen as it contributes to bioavailability in the study [32].Prieditisand Adamson present [33], elucidated the exposure of soluble Cu which is the main cause of pulmonary injury and inflammation. At urban site, fine dust and vehicular exhausts in the ambient air from different sources causes more hazard to the exposed persons as it can be inhaled more deeply into the lung, thereby evading the mucocilliary escalator. Irritation of vital organs headaches, nausea, dizziness and diarrhoea are some impacts which are caused due to long term exposure of Cu dust. Chromium is abundant in nature. There are rare valid data on Cr bioavailability in the atmospheric air [34]. Chromium is introduced in the atmosphere primarily due to the combustion of coal and oil, mainly because of diesel fed vehicles, incinerations [35]. Bioavailable metal fraction of few heavy metals are sensitive to the exposed inhabitants. Chromium gaseous in nature is rarely found in the environment [36] because of its boiling point. Serious health distresses can be created due to the bioavailable form of soluble chromium rather than insoluble form. Gaseous chromium is rarely encountered in the environment [36] due to its boiling point. The bioavailable form of chromium i.e. soluble form may produce serious health effects than insoluble forms. Zinc and its compounds were released in the atmosphere from different sources and toxic if considered taken up through inhalation[37].As stated in Reports on Carcinogen [38], lead (Pb) is considered to be carcinogenic and its interaction with dissimilar enzymes present in the bodycauses toxicity.



Fig3: Bioavailability of elements in $PM_{2.5}$

E. Risk assessment of PM_{2.5}

Metal bound PM_{2.5}in the ambient air can easily breach deep down into human lung tissues on inhalation via breathing. Accumulation of some heavy metals is carcinogenic and causes serious health risks on inhalation[39]. Fig 4 shows the frequently arising symptoms of different health effects. The consequences revealed that these problems were mainly dominant near the trafficjunction sites due to windblown dust and soil. Principallyfine particles have toxic metals which are directly linked to human health. The effect of heavy metals depends on the concentration, toxicity and duration of exposure. IARC has classified five transition metals-As, Cd, Cr (VI), Be and Ni as carcinogens in any form on inhalation [40]. According to USEPA classification of carcinogens, cadmium is considered as carcinogenic in the B1 category for humans while Cr (VI) is classified as group A which indicates that it is a known human carcinogen by the inhalation route of exposure. Lead is considered as a probable human carcinogen in group B2, but human evidence is inadequate and its unit risk is currently being amended by the USEPA. In the present study, Cr and Pb were selected for determining the incremental cancer risk from the PM_{2 5}-bound metals. The incremental lifetime cancer risk of metals can be calculated by multiplying the concentration of pollutant with its inhalation unit risk.Table IV illustrates the cancer risk of Cr and Pb in the soluble and total concentration and found that the estimated cancer risk of Cd and Pb was altered from total to bioavailable because of their high BI value (i.e., 0.8 for Cr and 0.2 for Pb). In order to associate the risks to a one-in-a million standard the excess cancer risk of these heavy metals was multiplied by 10^{-6} . From this calculation, it was assumed that the bioavailable form is mostly associated with environmental and health risk problems instead of total metal content. Thus, the result from the present studyshows that occupant's easily obtain serious health problem on exposure to toxic trace metals in ambient air. Thus, in future researches for assessing the toxicological effects of metals in PM2.5 should become a routine analysis in ambient pollution studies. On comparing the PM_{2.5} concentration and other heavy metals of present sitewith other locations worldwide given in the literature, it is evident that the concentration of Fe and Mn in our study is found to be higher than other studies and explains in tableV. The most probable reasons for these metals were may be attributed soil dust, crusher plant and industries. The combined effect of meterological conditions and emissionsfrom anthropogenicsources such as vehicular exhaust, waste incineration, coal and biomass and biofuel combustion and resuspended soil dust are the main contributor of PM2 5in Agradue to these reasons the concentration of PM_{2.5} was higher in Agra than Gwalior[18,41]

Table IV: Incremental Lifetime Cancer Risk of Cr and Pb in PM2.5

Element	Concentration (µg/m ³)	Inhalation Unit Risk (µg/m ³) ⁻¹	Incremental Lifetime Cancer Risk (µg/m ³) ⁻¹
Cr (soluble)	72.18	1.2*10 ⁻²	86.62
Cr (total)	127.17	1.2*10 ⁻²	152.60
Pb (soluble)	16.09	1.8*10 ⁻³	28.96
Pb (total)	119.06	1.8*10 ⁻³	214.31



Fig4Survey analysis on the basis of health effects

Table V: Comparison of PM_{2.5} and Other Metals at Present Site with Other Cities Worldwide

Locatio n	PM _{2.5} (μg/ m ³)	Ρb (μg/ m ³)	Fe (μg/ m ³)	Cu (µg/ m ³)	Mn (μg/ m ³)	Referen ces
Gwalio r, India	63.02	-2.69	4.39	0.01	0.45	Present study
Agra, India	86.35	0.04	4.10	0.04	0.15	Varshne y et al. 2016 [18]
Florida, USA	12.7	0.005	0.08	0.002	0.002	Olson et al. 2008 [42]
Barcelo na, Spain	34.5	0.1	0.000 3	0.01	0.05	Querol et al. 2001 [43]
Helsink i, Finland	11.8	0.006	0.1	0.003	0.003	Pakkane n et al. 2001 [44]
Hong Kong, China	29	-	0.1	0.01	0.005	Hagler et al. 2007 [45]
Italy	13	0.013	0.261	0.013	0.007	Ragosta et al. 2008 [46]

IV. CONCLUSION

Trace metal concentration and their bioavailability have been discussed in the present study. The study showed that concentration of $PM_{2.5}$ in different urban

and rural areas of Gwalior, India were much higher than the NAAQS and WHO standards (24-h). Higher concentration at these sites seemed to be mostly due to local traffic and anthropogenic activities. Metal concentration in PM2.5 was higher at urban areas except for Cu and Na which were higher at rural areas. Correlation technique was performed to know the similar sources responsible for fine particles (PM_{2.5}) emissions in the ambient environment. The major sources which contributed metal emission in the ambient air are emission from industrial and crusher plants, windblown dust, emission from diesel exhaust and outdoor anthropogenic activities. This study concluded that the percentage bioavailability of metals in PM₂ 5 followed the trend: Cu > Cr > Zn > B> Pb > Fe > Mn. This is suggested that the most toxic metals associated in PM_{2.5} were mainly bioavailable. Lead and chromium are reasonably anticipated to be human carcinogen. Therefore, the probable cancer causing metals on the basis of inhalation are Pb and Cd and the non-carcinogenic metals are Cu, Fe, Mn, B and Zn. Risk assessment related to particulate pollutant was evaluated on the basis of metal concentration. From these calculation, it seems that bioavailable form of trace metals in airborne PM_{2.5} should be used in order to more perfectlyevaluate environmental and health risks instead of total metal content. This study indicated that air particle pollution may possess serious health problems, to the inhabitantsof this populated city. Further studies should lay down exposure parameters which could contemplate local human activities mode to give more authentic risk assessment outcomes.

ACKNOWLEDGEMENT

Authors are thankful to School of Studies in Chemistry, Jiwaji University, Gwalior and for providing all necessary facilities required for this work.

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Table 1 Explorative statistical parameters of concentrations for PM_{2.5} in urban and rural homes

PARAMETERS	PM _{2.5} URBAN (µg/m ³)	$\frac{PM_{2.5}}{(\mu g/m^3)} RURAL$	Temp. °C	Relative Humidity (%)	Wind Speed (Km/hr)
M± S.D.	63.02±27.71	73.07±32.17	34±6.2	56±11.03	4.5±0.8
Md	59.13	60.16	32	57	4
Skew	0.34	0.94	-0.31	-0.2	2.5
Max	118.93	141.92	45	100	6
Min	15.40	29.39	25	18	4

M: Mean; Md: Median S.D.: Standard Deviation; Skew: Skewness; Max: Maximum; Min: Minimum