PROSPECTIVE HEALTH RISK OF EXPOSURE TO FINE PARTICULATE MATTER AND ITS ELEMENTAL COMPOSITION IN SHOE INDUSTRIES IN AGRA

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Abstract —

The present study shows the current scenario of the prospective health risk of exposure to fine particulate matter and its composition at industry level. The indoor and outdoor sampling of fine particulate matter was conducted in residential site (Industry-1) and road site (Industry-2) shoe industry in Agra city. The average concentration of PM sizes accounted in indoor during sampling duration were 30.11μg/m^3±10.29μg/m^3 for $PM_{1.0}$, 47.79 μg/m^3±45.49μg/m^3 for $PM_{2.5}$ and 90.15μg/m^3±33.61 μg/m^3 for PM_{10} at industry-1, and 7.66 μg/m^3±1.86 μg/m^3 for $PM_{1.0}$, 22.24 μg/m^3±3.69 μg/m^3 for $PM_{2.5}$ and 60.89 μg/m^3±49.06 μg/m^3 for PM_{10} at industry-2. The concentration of the three components of PM ($PM_{1.0}$, $PM_{2.5}$, PM_{10}) was found to be highest in industry-1 in comparison to industry-2. The full-day variation of fine particulate matter concentration and indoor meteorological parameters were also monitored. The average mass concentrations of various fraction of PM ($PM_{1.0}$, $PM_{2.5}$, PM_{10}) were collected at indoor and outdoor environment in two leather (shoe) small scale industries by APM 550. After acid digestion, quantification of 16 major metals Cu, Ba, Cd, Cr, Fe, Mn, Ni, Pb, Al, K, Ca, Na, Mg, As, Co and Zn was done using ICP-AES (Inductive Couple Plasma-Atomic Emission Spectroscopy) and AAS (Atomic Absorption spectroscopy).

***Keywords**:* Air pollution, Indoor air quality (IAQ), Fine particulate matter, heavy metals, correlation analysis, Occupational Exposure Levels.

I. INTRODUCTION

The air we breathe is a mixture of gases, solid and liquid substances. Air pollution occurs when the air contains substances in such quantities that could harm the comfort or health of humans and animals, or could damage plants and material [1,2]. Industries and auto exhausts are responsible for rising discomfort, increasing airborne diseases and deterioration of an artistic and cultural heritage in urban and industrial area [3]. The fine particles in ambient air have been reported to be associated with many health problems [4]. The fractions smaller than 2.5 μm ($PM_{2.5}$) are getting more and more attention worldwide, which can result in the prolonged exposure, promoting or aggravating health problems [5]. Because the $PM_{2.5}$ has a long residential time of several days to weeks in atmosphere, it can travel hundreds to thousands of kilometers. Previous studies indicated that smaller particles of $PM_{2.5}$ are water soluble and hygroscopic, and make them bio-available [6,7]. On the other hand, the $PM_{2.5}$ has high concentrations of toxic trace metals, such as chromium (Cr), cadmium (Cd), manganese (Mn), nickel (Ni), lead (Pb), arsenic (As), zinc (Zn), etc [8]. Those toxic heavy metals incorporated with $PM_{2.5}$ may enter the body through inhalation and have been suggested as causative agents associated with adverse respiratory health effects.

II. EXPERIMETAL

Agra, the city of Taj Mahal, (27.18˚N, 78.02˚E) is located in north central part of Indian state of Uttar Pradesh located on banks of the river Yamuna[9] (Fig.1) The area of Agra district is 4,041 sq. km. with a population of 4,418,797 (male 54% and female 46%) [10].Literacy rate of Agra district is 71.58% [11].

A. Industrial Layout

Agra has 7200 small Industrial Units, which are spread all over the district (Table-I). **The leather industry is among the most traditional and original industry of Agra**.

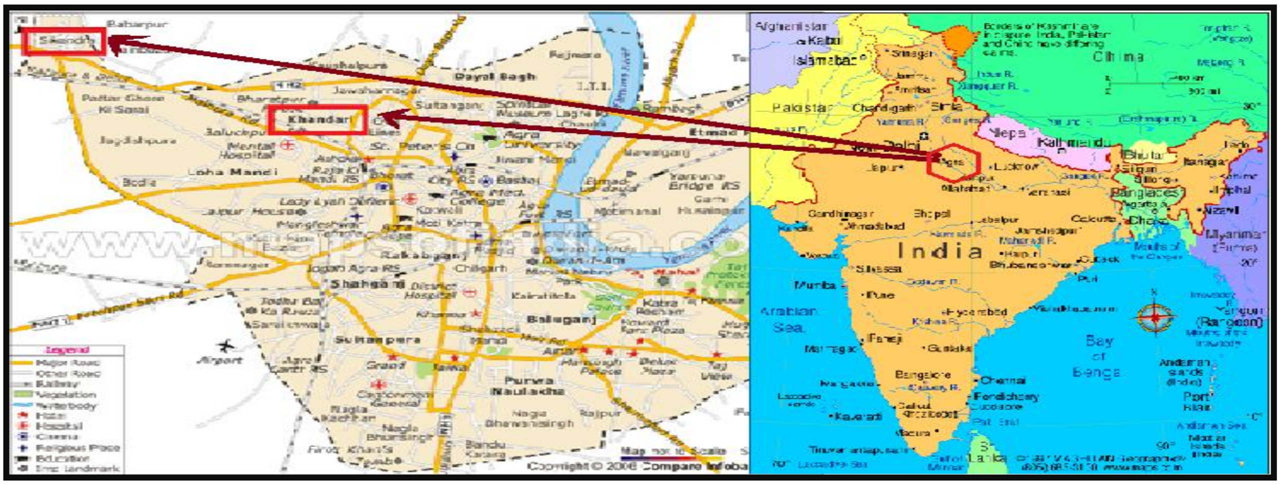

Fig.1: Site Map of Agra

Table 1: Number and types of Industries in Agra

S.No	Kind of SSI Units	Number of SSI units till 2006	Increased Units in 2006-2007	Increased Units in 2007-2008	Increased Units in 2008-2009	Increased Units in 2009-2010	Total No of SSI Units in 2010
1.	Non–Metallic Mineral Products	341	-	-	-	-	341
2.	Metal Products	166	10	28	1	-	205
3.	Machinery & Part Except Electrical	253	-	51	36	24	364
4.	Electrical Machinery & Apparatus	63	-	8	-	-	71
5	Repairing & Servicing Industry	1719	183	-	210	195	2306
6.	Chemical & Chemical	113	1	5	3	5	127
7.	Rubber & Plastic	194	2	43	5	6	250
8.	**Leather Products**	**263**	**54**	**174**	**174**	**163**	**828**
9.	Paper Product & Printing	63	4	22	4	2	95
10.	Beverage and Tobacco products[12]	04	-	-	-	-	04

B. Number of Footwear Units in Agra

Agra is the hub of shoe industry. There are about 60 organized footwear units, 3000 tiny manufacturing units and about 30,000 households' artisans units. Above 1.5 lakh pair of shoes is manufactured per day in Agra by the cottage, small scale and medium scale footwear unit (Table-II).

C. Sample Collection

Indoor and outdoor samples of fine particles from shoe industry were collected using airborne particulate matter sampler (APM 550, Envirotech, New Delhi, India) on 47 mm diameter polytetrafluoroethylene (PTFE) filter papers. APM 550 runs at a constant flow rate of 16.6 l/minute. The instrument was generally positioned in manufacturing units where occupants of the industry spend most of their time. Inlet head was positioned as close as possible to head height, which is the breathing zone for the occupants. The air exchange rate was measured on sampling site by using (YES-206) indoor air quality monitor from (Young Environment Systems, Inc., Canada). GRIMM 31-channel portable aerosol spectrometer model no.1.109 was used for monitoring the indoor mass concentration of $PM_{2.5}$ at a flow rate of 1.2 L min^{-1} ±5% constant with controller for continuous measurement during the sampling period. The obtained mean mass concentration from the GRIMM-1.109 PAS was regularly compared with a medium volume APM 550, filter-based sampler.

Table 2: Location of major sites for shoe industry present in Agra

S. No.	Name of the Major Area	Name of Mohallas
1.	Sadar Bhalti	DoliKar, Ghatia Mannu Bhanja, Nala Mantola, Teelanandram and Mantola
2.	Nai ki Mandi	Khattara Nail, Chota Galivpura, Haveli-Ka-Berka, Choti Adoye.
3.	Shahganj	Prakash Nagar, Prem Nagar, Rui Ki Mandi, Bharakambha, Bhogipura, Prithwinath & Namak Ki Mandi
4.	Lohamandi	Jagdishpura, Gadi Badoria, Madiyakatra
5.	Taliya	Nala Kajipara, Kotwali Basti, Chakkipat
6.	Agra Cononment	Nandpura, Nayi Basti, Pakkisarar
7.	Collectorate	Sunderpara, Idgah
8.	Agra Mathura Road (Bye-Pass)	**Khandari**, Sheetla Road, **Sikandra**, Artoni [12].

D. Chemical Analysis

9 ml of hydrochloric acid (HCl 37%) and 3 ml of nitrate (HNO_3 65%) were mixed together and then poured into a Teflon cup. Samples were then heated to 50 °C on a hot plate for 2 h. Samples after digestion on the hotplate were then filtered. After filtration, the sample solution was added to 0.2% HNO_3 to produce a 100 ml solution. The samples were maintained at 4°C in a refrigerator and analysis was conducted using inductively coupled plasma - atomic emission spectrometer (ICP-AES, Perkin Elmer Optima 2100 Plasma Emission Spectrometer) analysis. Concentrations of Cu, Ba, Cd, Cr, Fe, Mn, Ni, Pb, Al, K, Ca, Na, Mg, As, Co and Zn were determined.

III. RESULTS AND DISCUSSIONS

A. Meteorological Parameters

Meteorological conditions which shown in Table-III play a predominant factor governing the concentration variation of particulate matter [13].

Table 3: Average metrological parameters measured during sampling

	Indoor			Outdoor			
Parameter Measured	**CO_2 (ppm)**	**Ventilation Rate (lps)**	**Temp. (˚C)**	**CO_2 (ppm)**	**Temp. (˚C)**	**R.H. (%)**	**Wind speed (m/s)**
Mean	642.40	22.03	36.71	497.33	37.49	58.6	4.0
Median	620.27	22.16	37.70	491.21	37.32	56.3	4.1
Minimum	556.78	15.53	36.28	487.15	36.67	45.6	1.6
Maximum	772.30	28.28	37.10	519.75	38.7	79.7	6.6
Skewness	1.33	-0.13	-0.01	1.83	0.53	1.12	-0.18
Stdev	91.64	5.27	0.44	15.15	0.98	11.23	1.79

Skewness=3(Mean-Median)/Standard deviation

Table-IV Shows the PM concentrations are inversely proportional to the wind speed (PM concentration increases with decrease in wind speed). The wind speed and the turbulence in the ambient atmosphere mainly determine the air borne PM residence time at the ground surface and the rate of formation of secondary PM. Increase in the percentage of humidity increases the PM level. As the relative humidity increases. Therefore, the humidity affects the concentrations of coarse and fine particle at the study region [14].

Table-4 Correlation Matrix between $PM_{2.5}$, WS (m/s), Relative Humidity (%) and Temperature

	$PM_{2.5}$	WS (m/s)	% RH	Temp.˚C
$PM_{2.5}$	1			
WS (m/s)	-0.9213	1		
% RH	0.8473	-0.8030	1	
Temp.˚C	0.1428	0.2438	-0.0489	1

B. Mass Concentration of Particulate Matter

Sampling of PM_{10}, $PM_{2.5}$, and $PM_{1.0}$ was done with GRIMM Aerosol Spectrometer (GRIMM 1.109), with a flow rate (2L/min) from 9 June 2014 to 19 June 2014 at Industry-1 which is situated at Galana Road, Sikandra, Agra and Industry-2 which is situated at Transport Nagar, Agra. Monitoring was done in inside and outside of the industries. Measurements were done during working hours (8 am to 6 pm). The average mass concentrations of various fraction of PM ($PM_{1.0}$, $PM_{2.5}$, PM_{10}) were collected at indoor environment in two leather (shoe) small scale industries. Table-3 presents the average, median, standard deviation, maximum and minimum concentration along with skewness for particles $PM_{1.0}$, $PM_{2.5}$, and PM_{10}, in inside the leather industry at industry-1 and industry-2 during sampling.

Table 5: Statistical summary of the particulate matter trends at indoor environment in leather (shoe) industries

Industry-1						
Pollutant	**Average**	**Max.**	**Median**	**Min.**	**Skew**	**SD**
PM-1.0	30.11	64.2	28.4	15	1.04	10.29
PM-2.5	47.79	187	32.1	6.4	1.24	45.49
PM-10	90.15	227.3	89.4	31.7	0.99	33.61
Industry-2						
Pollutant	**Average**	**Max.**	**Median**	**Min.**	**Skew**	**SD**
PM-1.0	7.66	12.3	8.15	4.6	0.0037	1.86
PM-2.5	22.24	38.6	22.3	14.4	1.21	3.69
PM-10	60.89	419.5	51.2	33.2	2.45	49.06

The average concentration of PM sizes accounted in indoor during sampling duration were 30.11μg/m³±10.29μg/m³ for $PM_{1.0}$, 47.79 μg/m³±45.49μg/m³ for $PM_{2.5}$ and 90.15μg/m³±33.61 μg/m³ for PM_{10} at industry-1, and 7.66 μg/m³±1.86 μg/m³ for $PM_{1.0}$, 22.24 μg/m³±3.69 μg/m³ for $PM_{2.5}$ and 60.89 μg/m³±49.06 μg/m³ for PM_{10} at industry-2.

The concentration of all the three components of PM ($PM_{1.0}$, $PM_{2.5}$, PM_{10}) was found to be highest in industry-1 in comparison to industry-2 (Fig.2). In industry-1 regular cutting, casting, adhesive, stitching, pressing and packing was seen more due to more number of workers in comparison to the industry-2. Moreover, to view the shape of distribution, skewness was calculated. This showed that the mean concentrations of PM was positively skewed i.e. the data is distributed to the right of the median, at both the industries. Skewness was higher in industry-2 (0.003, 1.21 and 2.45 for $PM_{1.0}$, $PM_{2.5}$ and PM_{10}).

Such positive skewness depicts that there are some higher values that are not offset by corresponding lower values in the data distribution, that tend to make the mean greater than the median. Thus by using the relationship between the mean and median, the extent up to which the data distribution is skewed can be measured. It is called as the Pearsonian coefficient of skewness. It ranges between -3 to +3 and skewness zero means a normal frequency curve or perfectly symmetrical distribution [15].

Furthermore, to compare mean concentration at both industries, paired sample T Test was applied. This showed that p-value for $PM_{1.0}$, $PM_{2.5}$ and PM_{10} at industry-1 was ≤ 0.06 which signifies 94% significant difference in their mean values. Similarly p-value for $PM_{1.0}$, $PM_{2.5}$ and PM_{10} at industry-2 was ≤ 0.13 which signifies 87% significant difference in their mean values. The above results indicate that the particulate size decreasing with a significant difference in their mean values. Thus, we can say that PM concentrations are found higher surrounded by so many residential houses and somewhat decline with the distance from polluted areas i.e. road areas. The higher values of PM at industry-1 which had more workers strength and more activity as compare to industry-2, which is situated at road side and surrounded by so many commercial shops and attributed to road dust, diesel/petrol vehicular emissions, as the major sources of pollution. Nearby commercial activities was also one of the reasons, which pollutes outdoor air.

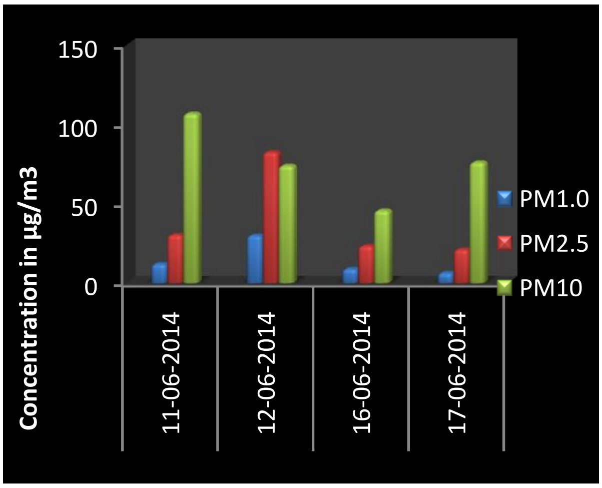

Fig.2: Concentration of PM inside at two leather (shoe) small scale industries

C. Air Quality Standard

In India, indoor environment air quality standards have not been recommended yet, therefore the concentration of PM_{10} and $PM_{2.5}$ were compared with WHO, 2010 standards (Table-VI) and NAAQS for two different leather industries. Standards for $PM_{1.0}$ have not been proposed by any of the agencies till now.

Table-6: Comparison of Particulate Matter Concentration with WHO and NAAQS Standards

Parameters	WHO Standards[16]	NAAQS Standards[17]	Present Study	Comments (permissible limits)
PM_{10}	20 µg/m³ (Annual) 50 µg/m³(24 hrs)	60 µg/m³ (Annual) 100 µg/m³ (24 hrs)	90.15 µg/m³ (Ind.-1)	Above from WHO and Lower from NAAQS
			60.89 µg/m³ (Ind.-2)	Above from WHO and Lower from NAAQS
$PM_{2.5}$	10 µg/m³ (Annual) 25 µg/m³ (24 hrs)	40 µg/m³ (Annual) 60 µg/m³ (24 hrs)	47.79 µg/m³ (Ind.-1)	Above from WHO and Lower from NAAQS
			22.24 µg/m³ (Ind.-2)	Lower from Both WHO and NAAQS

The mean of the PM_{10} is 1.8 and 1.2 times higher than the standards of WHO in industry-1 and industry-2 it is 0.9 and 0.6 times lower than the standards of NAAQS, while the concentration of $PM_{2.5}$ is 1.9 times higher than WHO standard in industry-1 and 0.8 times lower than WHO standard in industry-2 whereas it is 0.79 times and 0.37 times lower than the standards of NAAQS. This result is probably due to the activities of buffing, pasting, cutting and shaving in leather industries. PM_{10} and $PM_{2.5}$ concentration may produce some potential health effect on workers who are exposed.

High level of exposure are associated with chronic respiratory and cardiovascular health effects including a decline in lung function, an increase in blood plasma viscosity, a reduction of heart rate variability and multiple signs of inflammation. Research studies suggest that exposure to PM may be linked to brain damage by chronic inflammatory processes as well [18]. The present study clearly suggest that the inhalable particulate matter released from leather industries are not simply inert dust, but also contain mineral dust with a high content of potential toxic elements such as Fe, Cu, Zn. Cr, Co, Cd and Pb [19].

D. Time Series Data

During the study period, time series data of PM concentration was also taken, which showed higher concentration during the morning hours in all the two industries because of more activities performed by high strength of workers. Also in the morning office hour's, large numbers of vehicle pass on the road adjacent to these industries and changing the shift of workers at that time. In industry-1 (Fig.3) the average concentration of PM in morning hours was higher than afternoon and evening hours.

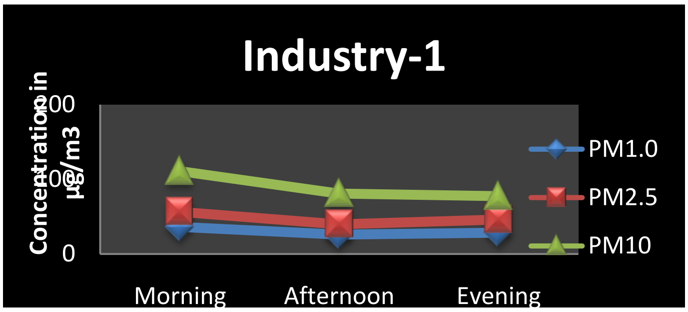

Fig.3: Time series data show in industry-1

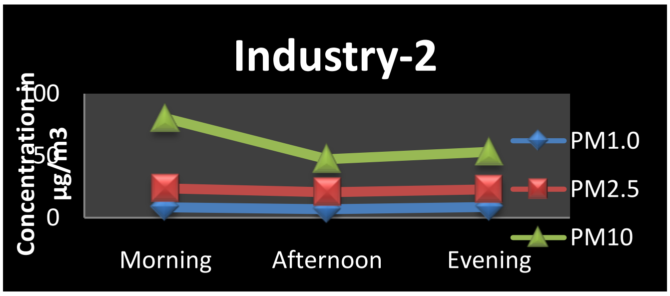

Fig.4: Time series data show in industry-2

The maximum concentration of PM was found at the morning hours. In industry-2 (Fig.4) the average concentration of PM in morning hours was higher than afternoon and evening hour, due to maximum activities at this time. This included changing the shift of workers as well as cutting, casting, stitching, pressing and packing activity performed.

E. Elemental Concentration of the $Pm_{2.5}$ Fraction

The eight samples were collected from two leather (shoe) industries. Analysis of Sixteen heavy metals Cu, Ba, Cd, Cr, Fe, Mn, Ni, Pb, Al, K, Ca, Na, Mg, As and Zn was done on ICP-AES (Table-VII and VIII). Higher mean was obtained for Fe and Zn from industry-1 outdoor and indoor (187.085 µg/l and 6.723 µg/l) and (5.145 µg/l and 102.485 µg/l) and Industry-2 outdoor and indoor (276.909

µg/l and 29.071µg/l) and (6.003 µg/l and 180.123 µg/l) respectively.

Table-7: Statistical analysis of heavy metal concentration of indoor and outdoor PM in leather industry-1 (µg/l or ppb)

Industry-1								
	Outdoor				Indoor			
	Mean	Max	Min	SD	Mean	Max	Min	SD
Cu	0.987	1.256	0.712	0.372	0.956	1.025	0.887	0.093
Zn	6.723	10.567	3.012	5.345	5.145	6.181	4.099	1.473
Fe	187.902	314.489	59.697	180.167	102.485	144.232	60.77	58.994
Pb	0.562	0.665	0.459	0.145	0.542	0.602	0.482	0.084
Cd	0.512	0.672	0.351	0.226	0.165	0.221	0.112	0.078
Co	0.023	0.033	0.009	0.016	0.019	0.024	0.0143	0.006
Al	8.264	8.712	7.821	6.298	9.087	9.082	9.087	ND
Ba	0.342	0.364	0.325	0.027	1.225	1.703	0.748	0.675
Cr	0.112	0.223	ND	0.156	ND	ND	ND	ND
Ni	0.489	0.542	0.425	0.081	0.458	0.501	0.415	0.068
Mn	0.176	0.342	ND	0.245	ND	ND	ND	ND
K	0.006	0.007	0.006	0.006	0.007	0.009	0.006	0.002
Ca	0.132	0.167	0.099	0.046	0.127	0.137	0.117	0.013
Na	0.143	0.198	0.095	0.067	0.124	0.132	0.115	0.012
Mg	0.023	0.024	0.016	0.006	0.023	0.028	0.019	0.007
As	0.091	0.096	0.095	0.002	0.094	0.097	0.083	0.009

Table-8: Statistical analysis of heavy metal concentration of indoor and outdoor PM in leather industry-2 (µg/l or ppb)

Industry-2								
	Outdoor				Indoor			
	Mean	Max	Min	SD	Mean	Max	Min	SD
Cu	1.707	2.148	1.266	0.623	2.001	2.003	1.002	0.281
Zn	29.071	53.77	4.372	34.923	6.003	7.003	5.001	1.875
Fe	276.987	521.39	32.428	345.745	180.123	278.023	82.009	138.568
Pb	1.257	1.902	0.612	0.912	1.023	1.034	1.023	0.162
Cd	0.115	0.221	ND	0.156	ND	ND	ND	0.173
Co	0.023	0.028	0.019	0.006	ND	ND	ND	0.003
Al	11.105	12.33	9.887	1.732	6.987	7.056	6.034	0.311
Ba	0.666	1.088	0.244	0.596	1.125	1.045	1.349	0.357
Cr	ND	ND	ND	ND	ND	ND	ND	ND
Ni	0.815	0.991	0.632	0.255	1.326	1.067	1.006	0.007
Mn	0.904	1.809	ND	1.279	ND	ND	ND	0.071
K	0.004	0.0065	0.003	0.002	ND	ND	ND	0.003
Ca	0.085	0.114	0.056	0.041	ND	ND	ND	0.042
Na	0.856	0.117	0.053	0.045	ND	ND	ND	0.023
Mg	0.0123	0.018	0.005	0.009	ND	ND	ND	0.005
As	0.109	0.123	0.097	0.017	ND	ND	ND	0.064

The percentage contribution of Fe, Cu was higher in outdoor environment of industry-1 whereas Ba, Fe and Cu were higher in indoor environment of industry-1. Fe, Pb, Ba and Ni were higher in outdoor environment of industry-2, while Fe, Zn, Cu Pb and Al were higher in indoor environment of industry-2, due to unauthorized coal burning, domestic fuel burning and very fine particulate matter travelling from industries [20]. According to Sharma et al., (2004)[21] vehicles in major cities of India are estimated to account for 70% of respective total pollution load and some additional toxic air pollutants emitted by motor vehicles comprise cadmium, chromium and lead.

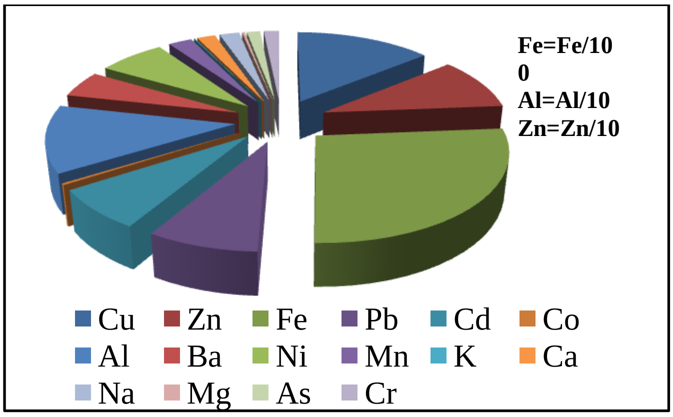

Fig.5A: Contribution of each element in industry-1 (outdoor)

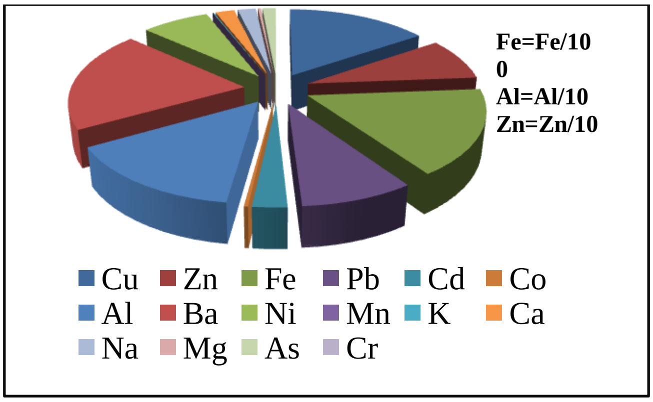

Fig.5B: Contribution of each element in industry-1 (indoor)

The percentage contribution of these elements in $PM_{2.5}$ followed the trend Fe>Cu>Al>Zn>Pb>Cd=Ni>Ba>Mn=Na=Ca=Cr>As>Mg=Co=K (Fig. 5A) at outdoor and Ba>Fe>Al=Cu>Pb>Zn>Ni>Cd>Ca=Na>As>Mg=Co=K=Mn=Cr (Fig. 5B) at indoor in industry-1.

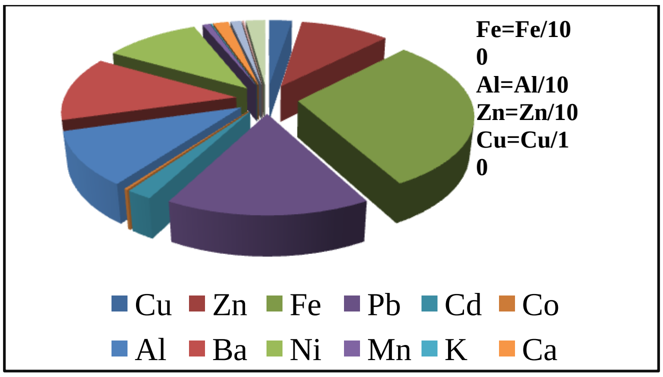

Fig.5C: Contribution of each element in industry-2 (outdoor)

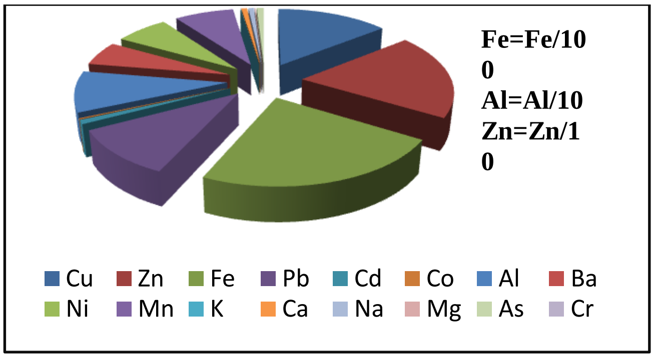

Fig.5D: Contribution of each element in industry-2 (indoor)

The percentage contribution of these elements in $PM_{2.5}$ followed the trend Fe>Pb>Ba>Ni>Al=Zn>Cu>Ca=As=Cd>Na=Mn>Co=Mg=K=Cr (Fig. 5C) at outdoor and Fe>Zn>Cu>Pb>Al>Mn>Ni>Ba>Ca=As=Na=Cd>Co=Mg=K=Cr (Fig. 5D) at indoor in industry-2.

F. Correlation Matrix

By evaluating the bivariate Pearson correlation coefficient for all the elements present in $PM_{2.5}$ collected in shoe industry A and B, Table-IX indicates indoor and outdoor inter elemental association. The values R≥0.5 show the stronger correlation. Cu is strongly correlated with Zn (r=0.74), Fe (r=0.79), Pb (r=0.99), Ni (r=0.98), Mn (r=0.72), As (r=0.76); the sources of copper are road dust, vehicular exhaust and biomass burning [24, 29]. Zn is strongly correlated with Fe (r=0.87), Pb (r=0.83), Co (r=0.78), Al (r=0.80), Ni (0.87), and Mn (r=0.99); sources of zinc are vehicle exhaust, road dust, fossil fuel combustion and biomass burning [22, 25, 26]. Fe is positively correlated with Pb (r=0.84), Ni (r=0.87), and Mn (r=0.90); Fe indicates soil origin and road resuspension in correlation with Pb outdoor traffic polluted resuspended road dust enters indoors at few industry. The symptoms chest pain, shortness of breath, upper respiratory problems also gives an indication of asthma among workers [30]. Pb is strongly correlated with Ni (r=1), Mn (r=0.80), and As (r=0.65); the sources of lead vehicle exhaust, biomass burning, fossil fuels combustion and road [23, 27, 28]. Ni is strongly correlated with Mn (r=0.84) and As (r=0.61); sources of nickel are fossils fuel combustion, biomass burning, road dust and vehicle exhaust [27, 28]. Cd is strongly correlated with Ca (r=0.70), Cr (r=0.99), Na (r=0.81), Mg (r=0.70), and $PM_{2.5}$ (r=0.8); vehicular emissions, and industrial emission, automobile lubricants activities are the possible sources of cadmium in ambient air [22].

Table-9: Correlation Matrix of Heavy Metals at indoor and outdoor in leather industries

	Cu	Zn	Fe	Pb	Cd	Co	Al	Ba	Cr	Ni	Mn	K	Ca	Na	Mg	As	PM2.5
Cu	**1**																
Zn	**0.73**	**1**															
Fe	**0.79**	**0.87**	**1**														
Pb	**0.98**	**0.82**	**0.84**	**1**													
Cd	-0.64	-0.36	-0.11	-0.62	**1**												
Co	0.18	**0.78**	0.65	0.31	0.21	**1**											
Al	0.22	**0.81**	0.47	0.36	-0.16	**0.89**	**1**										
Ba	-0.15	-0.21	-0.61	-0.16	-0.66	-0.39	0.04	**1**									
Cr	-0.54	-0.28	0.01	-0.52	**0.99**	0.24	-0.15	-0.74	**1**								
Ni	**0.97**	**0.86**	**0.87**	**0.99**	-0.57	0.38	0.41	-0.21	-0.47	**1**							
Mn	**0.71**	**0.99**	**0.91**	**0.79**	-0.26	**0.82**	**0.79**	-0.31	-0.17	**0.83**	**1**						
K	-0.81	-0.94	-0.98	-0.86	0.22	-0.71	-0.61	0.47	0.12	-0.93	-0.96	**1**					
Ca	-0.98	-0.81	-0.77	-0.99	**0.71**	-0.27	-0.37	0.04	**0.61**	-0.98	-0.77	**0.82**	**1**				
Na	-0.89	-0.39	-0.43	-0.82	**0.81**	0.25	0.11	-0.15	**0.73**	-0.78	-0.32	0.44	**0.85**	**1**			
Mg	-0.98	-0.63	-0.69	-0.95	**0.69**	-0.03	-0.11	0.07	**0.61**	-0.93	-0.58	**0.78**	**0.96**	**0.94**	**1**		
As	**0.75**	0.12	0.39	**0.65**	-0.47	-0.43	-0.46	-0.15	-0.39	**0.65**	0.09	-0.31	-0.62	-0.88	-0.82	**1**	
PM2.5	-0.08	-0.07	0.36	-0.09	**0.79**	0.19	-0.26	-0.95	**0.86**	-0.06	0.03	-0.19	0.23	0.35	0.13	0.09	**1**

Bold value in parenthesis indicates correlation is significant at the 0.05 level (2-tailed).

Table-10: Comparison of present study element levels with other indoor concentration of industrial areas worldwide

Site	$PM_{2.5}$/TSP	Cr μg/m³	Cu μg/m³	Fe μg/m³	Pb μg/m³	Zn μg/m³	Cd μg/m³	Al μg/m³	Ni μg/m³	References
Agra, U.P.	$PM_{2.5}$	0.03 μg/l	1.29 μg/l	186.7 μg/l	0.83 μg/l	11.7 μg/l	0.23 μg/l	8.71 μg/l	0.59 μg/l	Present study
Wah Cantt, Pakistan	TSP	0.068	1.11	1.70	0.27	3.49	-	-	-	Nazir et al., (2011)[36]
Colombo, South Brazil	$PM_{2.5}$	-	0.0	0.308	-	-	2.30	3.30	0.17	Godoi et al., (2008)[37]
Guangzhou, China	$PM_{2.5}$	0.007	0.036	0.414	0.185	0.407	-	-	-	Hong et al., (2007)[38]
Mexico City, Mexico	$PM_{2.5}$	0.033	0.97	0.644	0.039	0.365	-	-	-	Ahumada et al., (2007)[39]
Minneapoli-st. Paul, USA	$PM_{2.5}$	0.001	0.004	0.063	0.003	0.010	-	-	-	Adegate et al., (2007)[40]
Hangfors, Sweeden	$PM_{2.5}$	-	0.001	0.027	0.004	0.025	-	-	-	Molnar et al., (2005)[41]
Goteborg, Sweeden	$PM_{2.5}$	-	0.009	0.039	0.003	0.017	-	-	-	Molnar et al., (2006)[42]
Sohar industrial State, Oman	TSP	0.004	0.005	-	0.030	2.060	-	-	-	Abdul-wahabe et al., (2004)[43]
southeast china	$PM_{2.5}$	1152 ng/m³	126 ng/m³		392 ng/m³	924 ng/m³			7.2 ng/m³	Deng et al., (2006) [44]

Co is strongly correlated with Al (r=0.90) and Mn (r=0.83); a strong correlation is seen in between Al and Mn (r=0.80); the main contributor of aluminium is the motor-vehicle emission. About 13% of atmospheric aluminium is attributed to anthropogenic emissions [20]. Cr is strongly correlated with Ca (r=0.61), Na (r=0.74), Mg (r=0.60) and $PM_{2.5}$ (r=0.86). The sources of chromium are road dust, dyes and pigments, for greatly increasing resistance and durability of metals and chrome plating, leather tanning, and wood preserving. Manufacturing, disposal of products or chemicals containing chromium, or fossil fuel burning release chromium to the air, vehicular emission and metal processing also contribute for emission in atmosphere [23]. K is strongly correlated with Ca (r=0.83) and Mg (r=0.70); K also has many sources, such as biomass burning, coal/charcoal burning, soil dust, and even traffic exhaust emissions in small amounts [31, 32],Na is strongly correlated with Mg (r=0.95); Mg is positively correlated with Cr (r=0.60). Along these probabilities, metal processes like polishing was seen in leather industry. Mn and Pb are also associated with Zn (r=0.99 and 0.82) indoors, which may due to the emissions of paints, varnishes usage, in leather industry, along with polluted road dust [33]. The high correlations between heavy metals in air may reflect the fact that these heavy metals had similar pollution levels and similar pollution sources such as shaving, buffing and anthropogenic activities [34, 35].

G. Comparison of Present Studies with Other Studies

The comparison of average values of the elements in study was done with various studies done in the indoor and outdoor of industrial areas located in other part of world. It is evident that the metal (Fe, Zn and Al) concentration of $PM_{2.5}$ in our study is higher than other studies in the world as shown in Table-X.

H. Assessment of Occupational Exposure Levels

In order to have some idea of the possible effect of the adverse IAQ on the workers health in leather industry, a relationship between the past health records and present increase in symptoms were investigated by analyzing the 35 questionnaire, as shown in Table-XI. Shoe workers were exposed to perilous condition for 80 to 90 hour/week without proper personal protective equipments.

On the basis of questionnaire survey Fig.6 was plotted to show the percentage of symptoms that were commonly found in the workers exposed to the shoe (shaving and buffing) dust in these two leather industries.

These symptoms were found higher in industry-1 shoe workers than that at industry-2 shoe workers. drinking habits were found 0.5 times higher in industry-1 shoe workers and 0.3 times higher smoking habits in industry-2 shoe workers. Though workers have to go outside the industry for smoking. Because smoking was prohibited in shoe industry. Above health symptoms can be associated with industry-1 and industry-2 shoe workers. This is mainly because workers working in small scale industry did not wear any protective equipment due to negligence or not being aware of the benefits of the protective equipment. Thus there is need to differentiate types of particulate matter and their controlling measures

Table:11 Symptom of workers in the leather (shoe) industry based on questionnaire survey

Symptoms	**(N=35)**	
	Industry 1	**Industry 2**
Difficulty in breathing	25	34
Dry Throat	20	18
Back pain	18	16
Dizziness	7	8
Itching	5	7
Sneezing	10	15
High stress	20	19
Eye irritation	10	25
Headache	20	20
Drowsiness	18	17
Cold and flu	17	18
Allergies	7	9
Heart disease	17	18
Liver problem	17	18
Smoking (outside industry)	20	26
Blood Pressure	17	17
Drinking	34	25

I. CONCLUSIONS

In this study, Prospective Health Risk of Exposure to Fine Particulate Matter and its Elemental Composition was found in Shoe Industries in Agra. Aaverage concentration of PM sizes accounted in indoor during sampling duration were **30.11μg/m^3±10.29μg/m^3** for **$PM_{1.0}$**, **47.79μg/m^3±45.49 μg/m^3** for **$PM_{2.5}$** and **90.15μg/m^3±33.61 μg/m^3** for **PM_{10}** at **industry-1**, and **7.66 μg/m^3±1.86 μg/m^3** for **$PM_{1.0}$**, **22.24 μg/m^3±3.69 μg/m^3** for **$PM_{2.5}$** and **60.89 μg/m^3±49.06 μg/m^3** for **PM_{10}** at **industry-2.** The mean of the **PM_{10}** is **4.5** and **3.04** times higher than the standards of **WHO** in **industry-1 and industry-2**. While the concentration of **$PM_{2.5}$ is 4.78 and 2.24** times higher than WHO standard in **industry-1**

and industry-2. As this is a short term study and due to the scarcity of such a kind of work, more study is needed to support this database and examine the range and various health effects linked with these indoor and outdoor air pollutants.

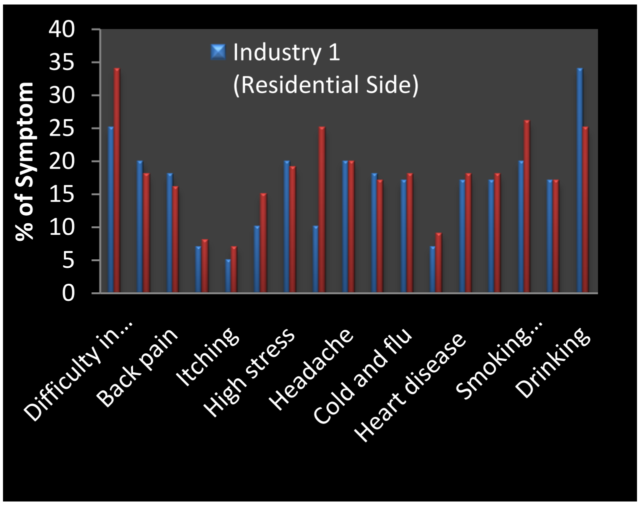

Fig.6: Survey Analysis on the basis of Health Effects

RECOMMENDATIONS

The workers working in small scale or medium scale industries do not wear proper protective equipment. This is either due to workers being uneducated or due to non-caring attitude. Some solutions can be provided to industries which could help them reduce the amount of respiratory particulate matter. Exhaust ventilation should be used, Direct skin contact should be prevented by gloves, wearing respiratory protection during cleanup is very essential, and Education awareness programs for workers should be instituted about hazard of exposure to leather particulate matter.

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