# PROJECT COMPLETION REPORT

# CHARACTERIZATION OF FINE PARTICULATES IN INDOOR MICROENVIRONMENT

**UGC FILE NO.43- 209/ 2014 (SR) (MRP-MAJOR-CHEM- 2013- 25775) dated: 23/Jul/2015**

**BY**

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- Project Report: **FINAL**

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- Title of the Research Project: **CHARACTERIZATION OF FINE PARTICULATES IN INDOOR MICROENVIRONMENT**

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- **BRIEF OBJECTIVES OF THE PROJECT**:
  - To provide quantitative information on the mass concentration of fine particulate in typical microenvironments (domestic homes classified on the basis of location & income) with analyzed temporal variability and size distribution providing overview of their formation, chemical composition, morphology and bioavailability.

- Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary tables and figures.

## EXPERIMENTAL SET-UP:

*SITE DESCRIPTION*

Agra, the city of inimitable Taj Mahal, is situated in Uttar Pradesh, the North Central part of India (27°10'N, 78°20'E), approximately 200 km of south of New Delhi. The climate of Agra is continental subtropical type, with hot summers during months of April to June with temperature reaching up to 50$^{o}$C and prevalence of hot dry winds. The monsoonal period is from July to September having about 67 cm (27 inches) of rainfall annually, and the temperature drops to 26–37$^{o}$C with occasional rains. Relative humidity in summers range between 18-48% that rises upto 70-90% in monsoons. Agra City has about 1,585,704 total population, and the population density is about 1084 persons/km$^2$ (http://www.census2011.co.in/census/city/115-agra.html; accessed on 25.06.17). The city generally experiences high atmospheric pollution load in which 60% is mainly due to vehicular pollution (Massey et al., 2012). Four major national highways NH–2, 3, 11 and 93 are passing all the way through the city serving serious traffic. Besides, the refinery located in Mathura region that is situated 35 kms towards the north, and glass manufacturing industry 40kms away, located in Firozabad district bounded on the east of the Agra city contributes to its pollution levels.The metrological parameters were taken from the CPCB (Central Pollution Control Board) website for Agra region for the whole sampling duration and are given in Table 1.

**Table 1**: Meteorological parameters during the study period

| **Season type** | **Month** | **AmbientTemp ($^{o}$C)** | | | **Humidity (%)** | | | **Wind Speed (m/s)** | | | **Wind direction** | **Rainfall (mm)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Avg* | *Min* | *Max* | *Avg* | *Min* | *Max* | *Avg* | *Min* | *Max* | *Avg* | *Max* |
| Winter | Jan | 14.8 | 5.8 | 27.5 | 74.3 | 27.7 | 100 | 1.6 | 0 | 9.8 | 294(NW) | ---- |
| Winter | Feb | 20.1 | 10.0 | 30.9 | 56.4 | 14.9 | 93.7 | 2.0 | 0 | 10.4 | 5(N) | ----- |
| | Mar | 25.3 | 13.2 | 41.0 | 44.5 | 9.9 | 94.5 | 2.0 | 0 | 14.1 | 316(NW) | 18.7 |
| Summer | Apr | 32.9 | 22.0 | 43.1 | 24.7 | 9.1 | 64.8 | 2.2 | 0 | 15.2 | 273(SW) | ---- |
| Summer | May | 34.3 | 22.9 | 44.2 | 36.6 | 12.5 | 91.8 | 2.2 | 0 | 17.4 | 232(SW) | 6.8 |
| Summer | Jun | 33.3 | 24.3 | 45.1 | 53.2 | 17.1 | 95.8 | 2.3 | 0 | 15.3 | 116(SE) | 11.1 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Monsoon | Jul | 30.9 | 25.8 | 39.2 | 72.9 | 37.5 | 96.3 | 2.1 | 0 | 11.1 | 130(SE) | 33.2 |
| Monsoon | Aug | 29.7 | 25.2 | 38.1 | 78.2 | 41.8 | 97.8 | 2.2 | 0 | 12.8 | 242(SW) | 18.7 |
| Monsoon | Sep | 30.8 | 23.4 | 40.5 | 66.9 | 31.6 | 97.3 | 1.9 | 0 | 12.9 | 190(S) | 29.9 |
| Post-monsoon | Oct | 30.1 | 19.6 | 40.2 | 44.4 | 13.9 | 79.9 | 1.4 | 0 | 9.8 | 354(N) | 0.0 |
| Post monsoon | Nov | 21.2 | --- | ---- | 60.9 | --- | ---- | 1.2 | --- | ---- | 249.46 | 0.0 |
| Winter | Dec | 12.6 | ---- | ---- | 54.1 | --- | --- | 1.4 | ---- | --- | 274.55 | 0.0 |

- *Selection of sampling sites:*

The city of Agra can be considered as representative of different conditions viz. main citified, backcountry, roadway, inner-city, industrial and tourist centre.Therefore, to assess the city complete pollution status, homes in three different areas were chosen for residential sampling (1) urban site (2) rural site (3) roadside sites.

Roadside sites

Three homes were selected adjacent to road or traffic intersection. The homes in the roadside microenvironment were adjacent to a road in the posh area of the city experiencing heavy to moderate traffic in the morning and evening hours. These houses were multi-storied unlike urban houses and were modern type and newly built with moderate greenery in the surrounding areas.

| Sampling site | Home age (yrs) | Home height (m) | Living area ($m^2$) | Indoor furnishing | No. of occupants | Ventilation | Outdoor environment |
|---|---|---|---|---|---|---|---|
| House 1 Mughal Road | 8 | 5.79 | 22.12 | Chips/marble flooring, painted walls | 6 | Air conditioning | Commercial and residential area with high traffic flow, 20 meters from busy road |
| House 2. Delhi Gate | 12 | 3.28 | 31.21 | Chips flooring with painted walls | 5 | Natural/ air coolers/ AC | 50 meters near busy road, very high traffic flow throughout day, less greenery |
| House 3. New Agra/ Bhagwan Talkies | 6 | 4.5 | 34.7 | Marble flooring, wallpaper | 3 | Central AC | No greenery, very high traffic flow, roadside colony |

Rural sites

Indoor and outdoor sampling was carried out in houses of three different villages that were about 20 kms away from the main city. These houses were cemented (unfurnished) with greenery and agricultural land on the surroundings They experience very less traffic, with muddy roads and lots of greenery around.

| Sampling site | Home age | Home height | Living area ($m^2$) | Indoor furnishing | No. of occupants | Ventilation | Outdoor environment |
|---|---|---|---|---|---|---|---|
| House 1. Shiv colony, Iradatnagar | 10 | 2.32 | 16.12 | Cemented flooring, house made of bricks | 8 | Small opening in the wall, usually door open | Muddy road, lots of greenery |
| House 2. Sadoopura | 16 | 4.86 | 21.3 | House made of stones and bricks | 6 | Door open during most of the time/ Natural ventilation | Less traffic with greener surroundings |
| House 3. Ekta colony, Iradatnagar | 19 | 2.57 | 27.7 | House made of stones and bricks | 5 | Poor ventilation/ small doors and windows | Irrigation filed outside with lots of greenery and no traffic flow except gensets for irrigation |

Urban sites

Different colonies were selected in Agra city to represent the urban area. The three homes selected houses in the urban microenvironment were old; closely build in a narrow street with houses at both the side of the street due to lack of space. The houses were congested to each other which is believed to be due to lack of proper planning.

| Sampling site | Home age | Home height | Living area ($m^2$) | Indoor furnishing | No. of occupants | Ventilation | Outdoor environment |
|---|---|---|---|---|---|---|---|
| House 1 Kamla Nagar | 18 | 3.42 | 20.75 | Chips flooring, painted walls | 6 | Natural/air coolers | Medium traffic with less greenery |
| House 2. Dayalbagh | 26 | 2.76 | 19.63 | Marble flooring, painted walls | 8 | Natural / exhaust fan | Unplanned colony with very less greenery, away from road |
| House 3. Karamyogi | 32 | 5.56 | 16.42 | Tile flooring with painted walls | 5 | Natural/ AC | Shoe factory outside, 1600 meters away from main road, greenery in verandah of homes, low traffic flow |

Low, Middle and High- Income Groups

The urban homes that were selected were classified into three different types based upon the income limits which were then termed as low-, middle- and high-income houses. Low income groups (LIG) were defined as those where income earning was <5k INR per month while Middle Income Groups (MIG) were those whose income limits laid between 5k-60K INR per month. For High Income Groups (HIG), the family income was around 70k or more per month. These houses consist of educated residents involved in service or business. Their homes were equipped with amenities like microwave, induction, refrigerators, washing machines, air conditioners etc. The LIG completely lacked these amenities and usage of wood/cow dung burning as a medium of heating was occasional in winters in these categorized homes. These houses mainly consisted of skilled labors and housemaid workers and were thus uneducated. Their houses were improperly planned with no separate kitchen. The homes of the MIG laid in mediocre category with less usage of modern appliances like microwave, induction, air conditioners. The detailed information is provided in Table 2.

**Table 2**: Demographic characteristics of different urban socio-economic homes

| Characteristics | LIG | MIG | HIG |
|---|---|---|---|
| Home Age (years) | 20-25 | 38-43 | 16-21 |
| Home height (metre) | 2.98-3.10 | 3.26- 4.15 | 5.12-5.98 |
| Living room area ($m^2$) | 18.90- 14.13 | < 22.14 | 22.45-24.16 |
| Home type | *Pucca* (brick & cement) | *Pucca*(brick & cement) | *Pucca*(brick & cement) |
| Home furnishing | Cemented flooring, cemented walls | Tile flooring with painted walls | Marble flooring with wallpapers/ painted walls |
| Kitchen separate | Yes/ No | Yes | Yes |
| Occupancy (no. of members) | 6 | 3 | 5 |
| Cooking medium | Chulha, mud stoves, LPG | LPG | LPG, microwave, induction |
| Ventilation | Natural | Natural, air coolers | Air conditioners, air coolers |
| Prominent characteristic | Smoking prevalent, Incense burning with candles, No exhaust in kitchen | Kitchen with exhaust, incense burning | Pet in house, incense burning, Kitchen with exhaust fan |
| Awareness of Indoor Air Pollution | ignorant | Slightly aware | slightly aware |
| Use of generators | No | No | Yes |
| Outdoor environment | Farms located outside. Biomass burning occasional | | Near to roadside area |

- ***Sampling of size segregated PM***

Filter samples were collected using Leland Legacy Pump (SKC Inc. 84 PA USA) in combination with Sioutas Cascade Impactors that collected particles in the following aerodynamic particle diameter ranges: 2.5-10µm; 1.0-2.5µm; 0.5-1.0µm; 0.25-0.5µm and <0.25 µm. (Misra et al., 2002). The collection substrates were 37 mm PTFE filters (Whatmann; pore size: 2.0 µm) for the <0.25µm (back up stage) and 25 mm PTFE filters (Whatman; pore size 0.5 µm) for the remaining stages.The pump flow rate was set at 9L/min and the calibration was performed using a DryCal DC-2 calibrator (Bios International Corporation, NJ USA).In accordance to the particle loading tests, the impactor can collect up to 0.7 and 3.16 mg of coarse and fine particles respectively with no loss in collection efficiency of PM up to 10 µm in atmosphere (Singh et al., 2003; Sioutas, 2004). In our study, particles were defined as coarse mode particles (2.5-10µm), quasi- accumulation mode particles (q-Acc) (0.25-2.5µm) and quasi -ultrafine particles (q-UF) (<0.25µm). q-UF and q-Acc are terms used to denote particles <0.25 µm and 0.25-2.5 µm, respectively, to elucidate their detachment from the conventionally defined ultrafine PM (<0.1 µm) and accumulation PM (0.1-2.5 µm). Notably, the term $PM_{10}$ used in the manuscript refers to sum of all stages while $PM_{2.5}$ refers to sum of last four stages (Fig. 1(a))

In our study, the sampling device was placed on a tripod stand at an average inhalation height of a person i.e. 1.6 meter in the living area of the home where cooking and other daily activities were common (Fig. 1(b)) and alsowhere people spend substantial time when indoors (Massey et al., 2012); while for outdoors positioning of instrument was done at porch of the house. The equipment was placed in a compact manner indoors while the inlet head was positioned closely to the head height. Sampling was conducted for 18-20 hours for two consecutive days each in indoor and outdoor from morning to evening period. A total of 270 samples (90 per season) from 9 houses were collected from both indoor and outdoorresidential locations over a period of April 2016 to January 2018 (summer, monsoon and winter) from roadside, urban and rural locations. Sampling instrument was alternatively positioned inside and outside sampling homes due to lack of multiple samplers.

For assessing the diurnal/temporal variation, Grimm 31-channel Portable Aerosol Spectrophotometer (model no. 1.109) was selected to cover the variation of particulate levels in relation with activities performed in the indoor environment. It monitored indoor PM mass concentration of at flow rate of 1.2L/min ± 5% constant with controller for continuous

measurement during the sampling period. It collected particles by a vertical 5 cm long vertical sampling head. The real time measurement was based on the principal of scattering of light at $90^{o}$in 32 sized channels from 0.22 to 32 mm with each unit NIST certified. It was placed in a compact manner and its inlet head was positioned as close as possible to inhalation height of the person. The instrument was run for 3 consecutive hours each in morning, afternoon and evening time and was set to average data per min to explore the clear picture of diurnal trend in respect to activity pattern of PM concentration levels.

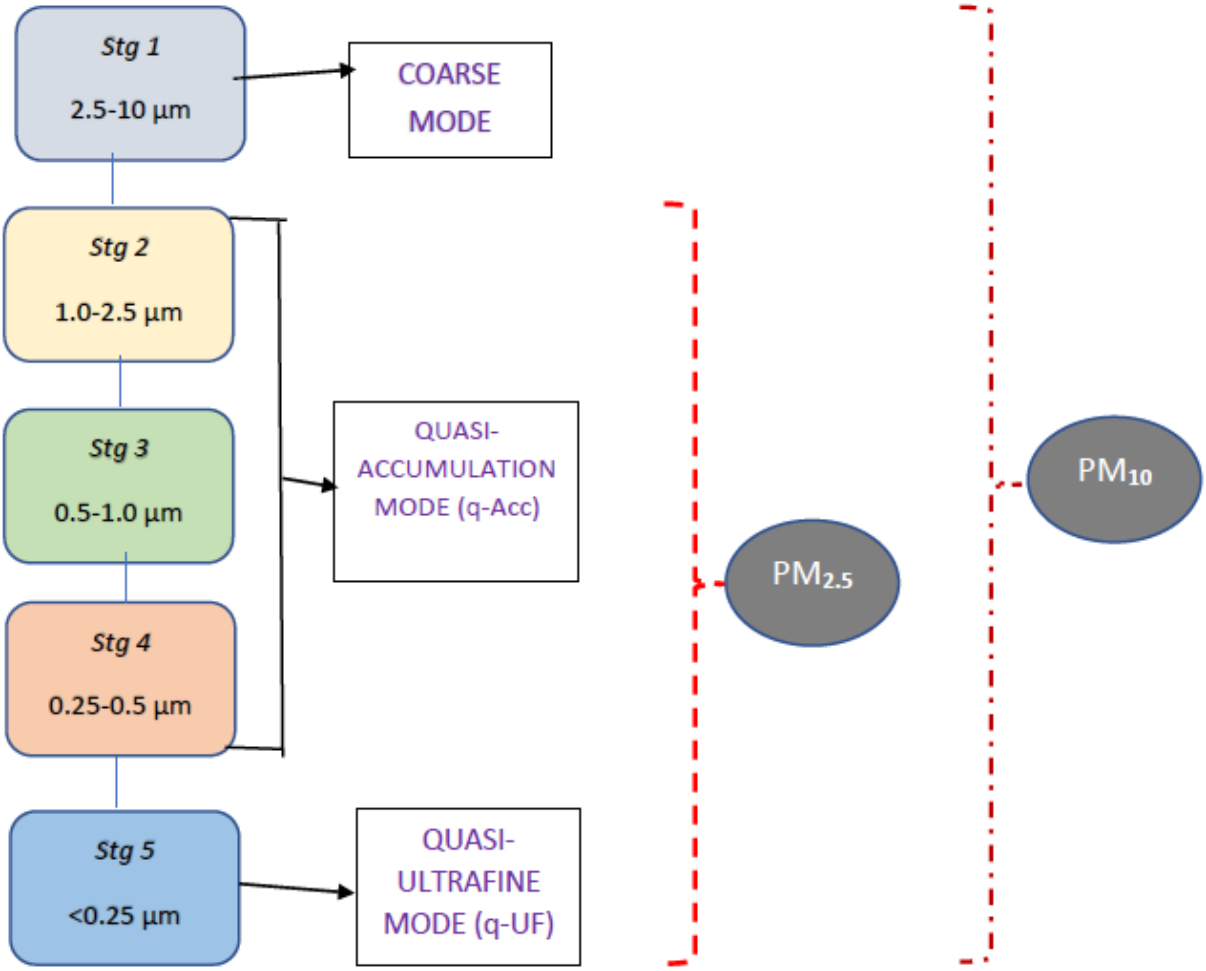



**Fig. 1(a):** Description of SKC cascade impactor and its collection stages

**Fig. 1(b):** Experimental setup of cascade impactor at sampling sites

- ***Gravimetric analysis and storage***

To maintain the quality control in the work all the glassware used for extraction and storage were cleaned by soaking in 2% $HNO_3$ overnight in follow up with rinsing it with de-ionized water several times. The filter paper was cut into two equal halves. One part was used for determining the total concentration (through acid digestion) and the remaining was employed for estimating the soluble fraction (through ammonium acetate) of the same metal. A twostep procedure was involved in which in the first step filters were extracted by digesting in a 6-8 ml analytical grade (Merck) $HNO_3$ and keeping them on a hot plate at 40-60$^o$ C for 90 minutes. The solution was

subsequently diluted to 50 ml with distilled deionized water and then stored in polypropylene bottles (initially dipped in 2% $HNO_3$) until analysis (Massey et al., 2013). This gave us the total concentration of the metals.For soluble content in the metal was extracted using 0.01M ammonium acetate buffered at pH 7 to simulate the neutral lung environment. The remaining filter paper was inserted a 15 mL polypropylene centrifuge tubes containing 10 mL of ammonium acetate solution. After that the tube was sealed and submerged in shaking water bath at 37$^{o}$C for 1 hour and was then kept still (with no shaking) in the same conditions. After cooling of the extractants at room temperature, it was centrifuged at 3500 rpm for 20 minutes and then separated and stored for elemental determination (Varshney et al., 2015)

**Inductive coupled Plasma- Optical Emission Spectroscopy (ICP-OES**) was employed for multi-element analysis of digested samples (for operating conditions refer Table 3). The information regarding the minimum detection limit and the accuracy of the elements is provided in Table 4.

ICP-OES set up

**Table 3**: Operating/ experimental conditions for sample introduction system in ICP-OES

| | |
|---|---|
| Argon out put pressure | 80-120 psig |
| Nitrogen output pressure | 40-120 psig |
| Shear gas supply (compressed air) | 80-120psig |
| RF frequency | 40 MHz |
| RF-power (W) | 1500 |
| Plasma observation height (mm, above the load coil) | 2.0 |
| Plasma gas flow rate (L $min^{-1}$) | 15 |
| Auxiliary argon flow | 1.0-1.5 |
| Nebulizer argon flow(L $min^{-1}$) | 0.4-0.5 |
| Sample flow (mL $min^{-1}$) | 3.0 |
| Purge gas flow rate (L $min^{-1}$) | 1.4 |
| Shear gas flow rate (L $min^{-1}$) | 25 |
| Equilibrium time | 15 sec |
| Drain removal rate (mL $min^{-1}$) | 5660 |

- **Quality control/ Quality assurance**

Special attention was given to quality assurance and quality control during sampling and analysis procedures. Tweezers coated with Teflon tape were made in use for handling filters to reduce any chances of contamination. Periodic cleaning of the sampler was done to make the sampler dust free so that the dust on the sampler may not be counted with the concentration of sample. Moreover, daily flow rate calculations (volume of air passed shown in meter reading/ timer reading) was made to ensure that the fluctuation in flow rate was within the range.

At least 10% of samples were spiked with a known amount of metallic species for determination of their recovery efficiencies. The recovery test results for elements were as follows: Al 90.1%, Ba 89.9%, Ca 93.1%, Cd 91%, Co 95.3%, Cu 95.2%, Fe 102.0%, K 93.8%, Mg 96.1%, Mn 100.1%, Pb 93.9% and Zn 100.1%. The range of recovery efficiencies varied from 89.9 to 102%. The analysis of the same standard solution was repeated 10 times. The reproducibility test

providing the relative standard deviations of the elements is expressed as precision of the element at a concentration. The metal concentrations in air samples were calculated following the method given by USEPA (1999).

**Table 4:** QA/ QC details of element analysis by ICP-OES

| | Al | Ba | Ca | Cu | Fe | K | Mg | Mn | Pb | Co | Zn | Cd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Detection limit (mg/L) | 0.02 | 0.0005 | 0.0005 | 0.005 | 0.005 | 0.10 | 0.0005 | 0.001 | 0.05 | 0.005 | 0.005 | 0.005 |
| Accuracy (%) | 4.1 | 5.5 | 3.62 | 4.93 | 3.72 | 5.1 | 3.24 | 4.5 | 4.17 | 1.5 | 2.17 | 4.2 |
| Precision (%)at 0.2 mg/ml | 1.1 | 1.4 | 1.2 | 0.72 | 0.5 | 1.8 | 1.3 | 0.91 | 1.66 | 1.2 | 1.19 | 1.13 |

**FE-SEM/ EDX Analysis**

The characterization of q-Acc i.e. $PM_{1.0-0.5}$, $PM_{0.5-0.25}$and q-UF particles i.e. $PM_{<0.25}$ samples were performed using field emission scanning microscopy (FESEM, Hitachi-PU,SU8010) coupled with energy dispersive spectrometer (EDX, BRUKERS XFLASH 6130)for determination of morphology (sizes and shapes) and chemical composition of airborne particles. Field emission scanning electron microscopy (FESEM) provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field. Compared with convention scanning electron microscopy (SEM), field emission SEM (FESEM) produces clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nanometers – three to six times better. It has high ability to examine smaller-area contamination spots at electron accelerating voltages compatible EDS. Approximately, one-fourth of PTFE filter was cut and coated with gold. Samples were examined by field emission scanning electron microscopy (FESEM, Hitachi, SU-8020) coupled with energy-dispersive X-ray (EDX, Oxford X-MaxN Model). 0.5 cm of the dry and loaded glass fiber filter samples were cut and coated with a thin film of platinum (Pt) to make the samples electrically conductive for SEMEDX analysis. Samples were placed in the corner of SEM-EDX chamber and two images of each sample were taken at a magnification of X5000 and X20000. After which, EDX spectra of individual particles were obtained after scanning an electron beam with an accelerating voltage of 20 kV, a beam current of 10 μA and a Si (Li) detector 15 mm away from the samples which

are to be analyzed. Peaks were identified and the quantifying function of the computer programme was used to determine the peak intensities, which were converted to percentage weight.

FESEM, Hitachi-PU,SU8010

## DETAILED ANALYSIS OF RESULTS INDICATING CONTRIBUTION MADE TOWARDS INCREASING STATE OF KNOWLEDGE:

### 1. $PM_{10}$ and $PM_{2.5}$annual mass concentration

During the study period, annual average $PM_{10}$& $PM_{2.5}$ concentrations were 287.16±22.43 and 196.51±12.58 and 256.41±64.35 and 223.51±66.16 μg/$m^3$ for indoors and outdoors respectively. On comparison of our annual average (overall) particulate concentrations with NAAQS prescribed by CPCB, $PM_{10}$ exceeded 4-5 times higher in indoors as well as outdoors while $PM_{2.5}$ concentration exceeded the benchmark limits by 4-5 times in indoors and 5-6 times in outdoors. We also compared our data with WHO standards and found that our results exceeded 13-15 times in indoor and 14-15 times in outdoors whereas for $PM_{2.5}$, results exceeded 18-20 times indoors and 18-25 times outdoors. This indicates high particulate pollution in residential areas of the world heritage city 'Agra'.

To assess the '*location'* effect, the averageconcentrations of particulatesseparately in indoors and outdoors ofhomes located in urban, rural and roadside sites in $PM_{10}$ and $PM_{2.5}$ were further calculated. At urban site, $PM_{10}$ and $PM_{2.5}$ concentrations were 312.76±79.41 $\mu gm^{-3}$ and 200.39±47.42 $\mu gm^{-3}$ and 287.15±49.32 $\mu gm^{-3}$and 191.16±61.47 $\mu gm^{-3}$for indoors and outdoors respectively. At rural site, $PM_{10}$ and $PM_{2.5}$ concentrations were 270.95±51.47 $\mu gm^{-3}$and 206.7±47.13 $\mu gm^{-3}$and 299.62±37.16 $\mu gm^{-3}$ and 179.76±26.54 $\mu gm^{-3}$ for indoors and outdoors respectively. At roadside sites, $PM_{10}$ and $PM_{2.5}$ concentrations were 277.78±34.71 $\mu gm^{-3}$ and 182.44±62.53 $\mu gm^{-3}$ and 299.62±97.85 $\mu gm^{-3}$ and 179.76±76.52 $\mu gm^{-3}$ respectively.

The trends of particulate mass concentration were obtained as follows:

| Particulate Size | Indoor Trend | Outdoor trend |
|---|---|---|
| PM10 | Urban>Roadside>Rural | Roadside>Rural>Urban |
| PM2.5 | Rural>Urban>Roadside | Roadside>Urban>Rural |

This indicates that air quality at residential sites of Agra city is extensively affected by PM pollution in indoor environment of urban and rural houses while roadside houses (that were newly built with proper infrastructure) have relatively better air quality. For outdoors, heavy vehicular traffic flow especially at roadside sites with resuspension of road and soil dust contributed to increase in PM pollution. Higher fine particulate pollution ($PM_{2.5}$) in indoors of rural homes can be attributed to activities like smoking and biomass cooking prevalent in such homes. The indoor concentrations were in general higher than outdoor concentrations except for urban areas where indoor and outdoor concentrations were variable. For homes in roadside areas, outdoor concentrations exceeded that of indoors.

## 2. Size segregated trend of PM

The partitioning of $PM_{10}$within each of the size mode particulate (coarse, quasi-accumulation, quasi-ultrafine) obtained by deployment of Cascade impactor is discussed herewith. The percentage of $PM_{10}$ for indoor and outdoor in each of particle fractions (2.5-10μm, 1.0-2.5μm, 0.5-1.0μm, 0.25-0.5μm, 0.25μm) is shown in Fig2(a)

Observation elucidate that fine particles (<2.5 μm) were found to dominate $PM_{10}$ concentration (64-76% indoors and 62-80% outdoors) leaving a difference of 23-35% and 18-37% for coarse mode PM in indoors and outdoors respectively. Moreover, the percentage contribution of q-Acc and q-UF stages in indoor and outdoor $PM_{2.5}$(Fig. 2(b)) suggest that fraction of q-UF particles represent a significant portion of fine particulate mass in indoor (29-32%) and outdoors (24-35%).

Thus, these results allow concluding that residents of Agra city in northern India have high concentration of fine particles with substantial contribution from q-UF particles in their residences whereby 75-80% of human time is spent.

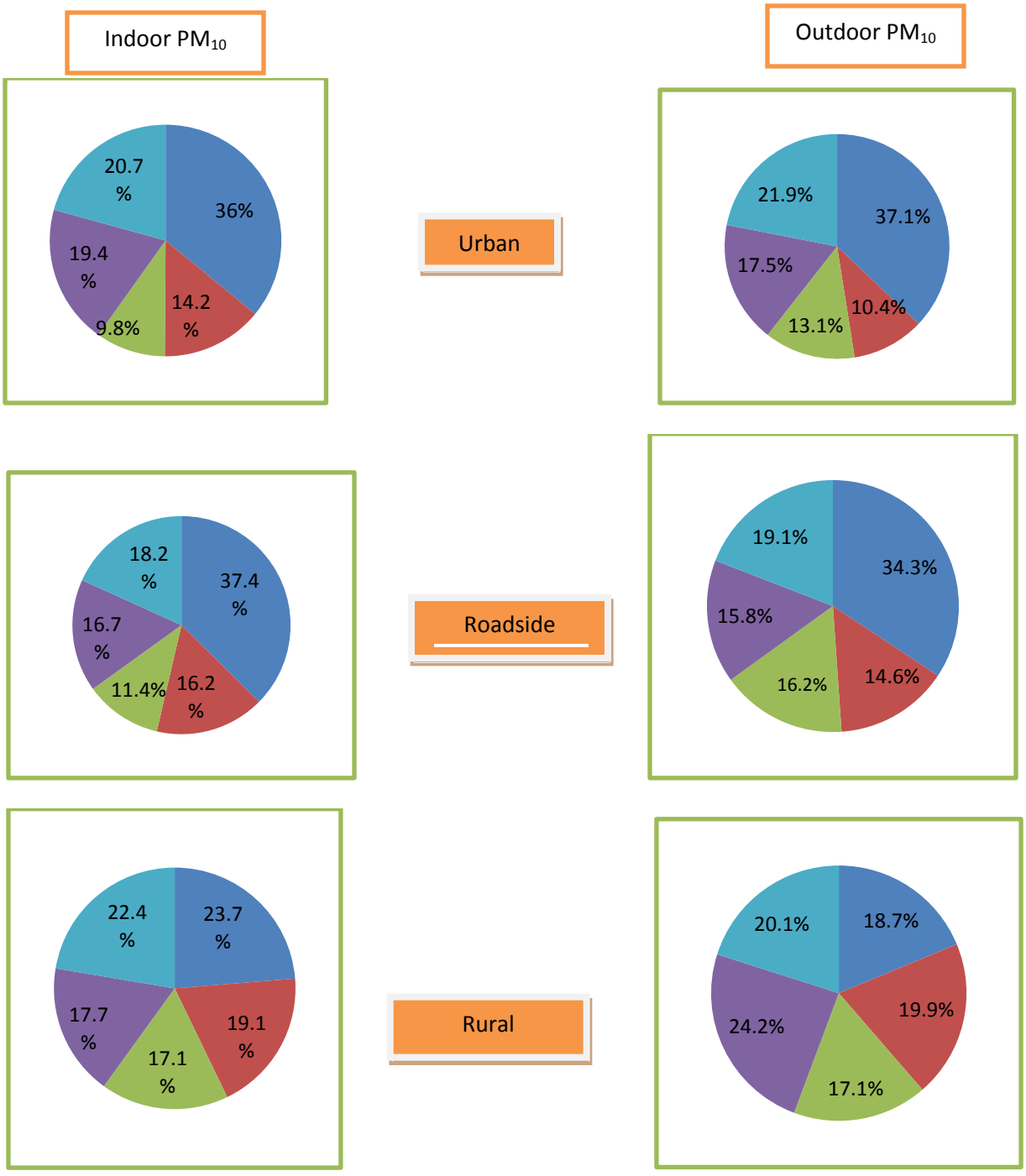



**Fig. 2(a):** Percentage of contribution of varied size fractions in $PM_{10}$

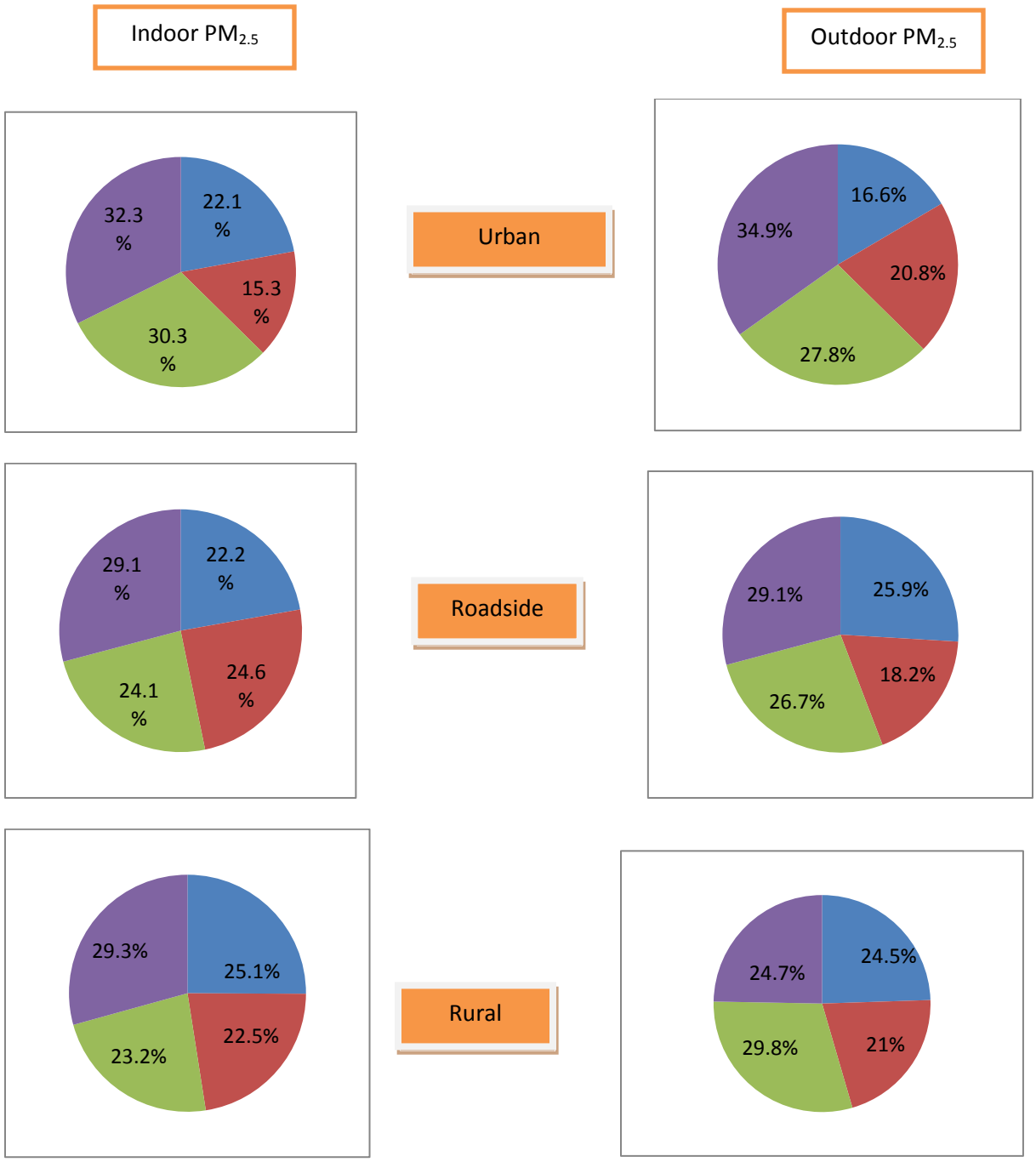



Fig. **2(b):**Percentage of contribution of varied size fractions in $PM_{2.5}$

## 3. Particulate inter-correlations and seasonal variation

To further gain insight into the scenario of size segregated PM, inter-correlations between different particulate stages were assessed (throughout the sampling tenure) through application of $R^2$(coefficient of determination), Pearson correlation (r). These results were validated through application of 1-ANOVA test (Table 5)

**Table 5:**Interrelationship (Coefficient of determination; $R^2$) between different PM fractions (Annual average & seasonal variation)

| | Annual | Summer | Monsoon | Winter |
|---|---|---|---|---|
| Coarse & fine | 0.205 (p=0.0019) | 0.262 | 0.130 | 0.486 |
| q-Acc& coarse | 0.155 (p=0.0009) | 0.115 | 0.230 | 0.769 |
| Coarse & q-UF | 0.268 (p=0.0199) | 0.679 | 0.0004 | 0.480 |
| q-Acc& q-UF | 0.672 (p=0.111) | 0.026 | 0.276 | 0.706 |

Results evidenced a low linear relationship between coarse and fine particles ($R^2$= 0.205) attributed to different mechanism cited for origin, behavior and removal mechanism of particles in atmosphere. Similarly, inter-fine particulate relationships within $PM_{2.5}$ size modes were further assessed. Comparatively, greater correlation found between q-Acc and q-UF mode described their inter-formation within modes as accumulation mode is anticipated to be formed via coagulation of small particles of UF/nuclei mode. These results have been supported through application of 1-ANOVA test which indicated significant difference between coarse and fine (p=0.0019) and coarse and q-Acc mode particles (p=0.0009).

Seasonal trend indicated better inter particulate mode correlation in winters due to high suspension of particles within atmosphere influenced by stable atmospheric conditions. Whereas monsoons recorded lowest linear relation between coarse and fine PM attributing to removal of coarse particulates during wet precipitation by gravitational settlement.

The seasonal variation of size segregated PM in indoor and outdoor air is shown in form of box-whisker plots in Fig 3.

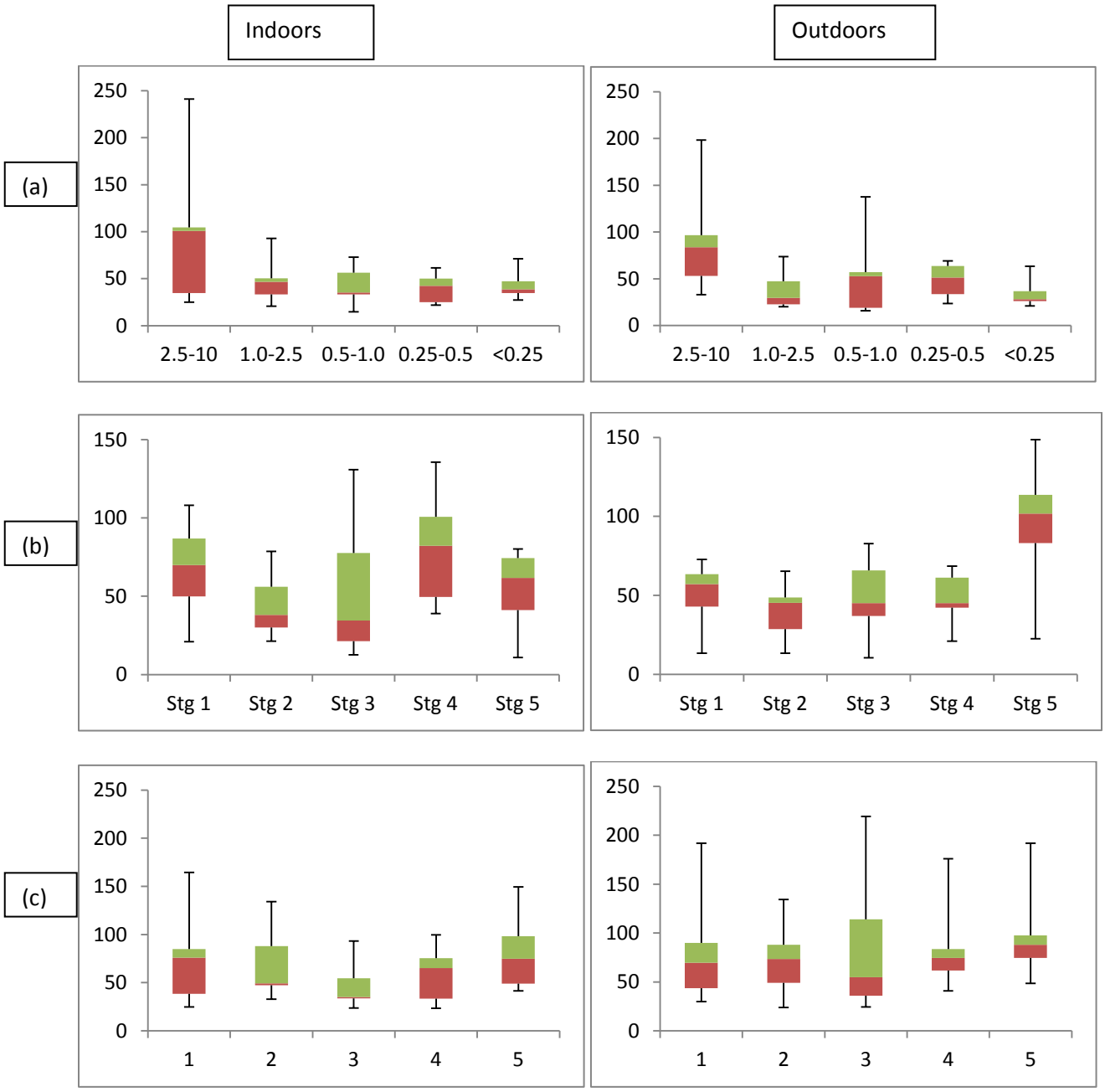



**Fig.3:**Box-whisker plots of size segregated indoor and outdoor PM mass concentrations in

(a) summers(b) monsoons and (c) winters

The middle line corresponds to median concentration while the upper and lower lines refers to 25$^{th}$ and 75$^{th}$ percentile values. Upper and lower bars correspond to the maximum and minimum values

The plots indicate that coarse mode particles contribute a high percentage to total aerosol content during summer months while during winters and monsoons, accumulation and quasi-ultrafine range seem to dominate. Increase levels of $PM_{2.5-10}$ in summer result from increased re-suspension of coarse particles due to drier summertime ambient conditions. Variability (as shown by height of box) for coarse and q-UF particle fractions is comparatively less pronounced in outdoor concentration than indoors while for accumulation ranged particles, reverse holds good. This may be attributed to due to variability in homes that contribute primarily to indoor coarse and ultrafine particles.Moreover, as per seasonal variation, variability in concentrations for coarse and q-UF particles is higher in summers and winters respectively unlike q-Acc that shows higher variability in concentration during monsoons. This parameter points towards heterogeneity of sources contributing to individual particle size mode concentrations.q-Acc ranged particles in residential microenvironments exhibited non-symmetric variations in their minimum, maximum, $25^{th}$ percentile, $75^{th}$ percentile and median values unlike coarse and q-UF stage particles which showed relatively symmetric distribution, henceforth pointing towards consistently varying concentrations of coarse and q-UF particles.

To investigate the effect of seasonality on indoor and ambient PM varied size fractions, winter to summer ratios and winter to monsoon ratios for each of the size fractions in PM were calculated and are shown in Table 6.

**Table 6:** Seasonal ratios of PM size segregated particles in indoor and outdoor air

| | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.25-0.5 | PM<0.25 |
|---|---|---|---|---|---|
| Winter/ summer | | | | | |
| Ind | 1.64 | 1.23 | 1.25 | 1.41 | 1.55 |
| Out | 1.27 | 1.77 | 1.72 | 1.78 | 1.99 |
| Winter/monsoon | | | | | |
| Ind | 2.75 | 1.50 | 1.28 | 1.92 | 1.85 |
| Out | 3.80 | 2.61 | 2.37 | 2.41 | 2.26 |

On comparing the winter/summer ratio for different PM size fractions, it was observed that coarse mode ($PM_{2.5-10}$) in indoors and q-UF mode ($PM_{<0.25}$) in outdoors exhibited the highest ratio. This means higher sources of coarse particles exist in indoors due to high human activity and also less abundance of UF particles is evidenced in summers.

Similarly, comparing winter to monsoon ratio across PM fractions infers very low abundance of coarse particles in monsoons in ambient air which is pretty obvious due to the wash out effect of coarse particles in monsoons. Comparatively less ratio in indoor atmosphere rules out the possibility of infiltration of coarse mode particles and point towards influence of an indoor coarse particles source.

## 4. Socio-economic *'ladder'* effect with day-night variability

For urban homes, the annual average $PM_{2.5}$ concentration in LIG were 25-32% higher than MIG and 37-39% higher in HIG. This may be attributed to poor constructed/cemented homes in LIG. Other than that, factors like use of wood and cow dung especially during winters for heating purpose, frequent smoking, dusting and alsothe use of kerosene lamps occasionally for lightening purpose played an important role in elevation of $PM_{2.5}$ concentration. Furthermore, it was observed that the fine PM for LIG stood extrinsically high while for MIG and HIG were roughly comparable (8-11% variation). The MIG had much better construction than LIG and used better modes like LPG, microwave etc for cooking purpose. Whereas population residing in HIG used more efficient cooking hobs like electric chimneys, microwave, vacuum cleaners etc that tend to decrease in PM concentration.

Diurnal variability (day-night variation) was investigated by examining differences in average minute concentration across the day (Fig. 4). As observed, indoor PM2.5 concentration differed significantly ($p<0.05$) between hours of the day. In general, the average concentration of $PM_{2.5}$ was78.62% higher in morning (7.00-11.00) and evening periods (5.00-8.00) than during noon hours (1.00-4.00). This is obvious as the noon hours were times with little or no activities.LIG recorded highest concentration in evening hours while MIG and HIG recorded maximal concentrations in morning hours. This discrepancy in temporal variability can be linked to variation in indoor activities with time. In general, houses of LIG that we selected consisted mostly of household maids and workers. In our sampling, it was usually observed that these people leave their homes early in morning and perform their household chores like cleaning, dusting, washing utensils etc. during evening hours. Moreover, during these hours, numbers of people in the homes were the greatest, including people returning from work.

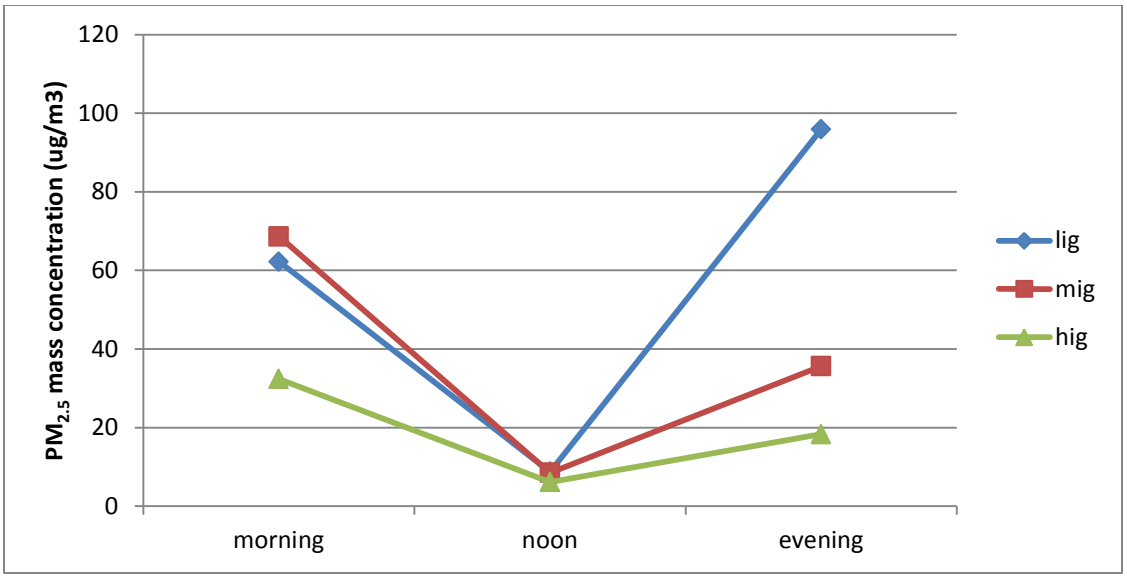



**Fig. 4:** Diurnal Variation of fine particulate concentration at three socio-economic homes (lig=low income groups, mig=middle income groups, hig= high income groups).

## 5. Element concentration and seasonal variability

In total, 14 elements were analyzed in both indoor and outdoor PM. In all, elements were divided into two categories based upon their concentration. Among the metals in the indoor environment, Group I (major) elements consisted of Ca, Fe, Al, Mg, K while Group II (minor) elements were Zn, Co, Ba, Cd, Cu, Mn, Cr, Pb, Ni. It is to be noted that, Ba, Co, Cd were not quantified or were below detection limits in summers. Table 7 represents the average metal concentrations in indoor and outdoor particulates in each of the size fractionated modes of PM for (a)summers, (b)monsoons and (c)winters. The last column of the table indicates fine to coarse ratio of the metals. As seen during summers, all the elements including PM (except Al, Pb) depicted their association with coarser fraction that further indicates the dominance of coarse particulate attributed to wind-blown dust during long range transport during summers. The result for Pb indicates their derivation from anthropogenic source like paints in indoor environment and also a constituent of traffic exhaust that may have infiltrated indoors through opening of windows frequent during summers. The result of Al, which is usually a crustal element goes unexpected; that suggests its multi-sourced contribution from both anthropogenic and natural emissions.

For monsoons, the F/C ratio was homogeneous across all metals and were >1 or ~1 indicating negligible contribution from coarse particulate size. During winters, the F/C ratio showed a mixed pattern and were heterogeneous across metals indicating the association of some metals (K, Ni, Mn, Pb, Zn) with coarser fraction while others (Ca, Cd, Cu, Mg) showed their association with finer fraction indicating their derivation from anthropogenic sources. It is to be noted that Al displayed multi-sourced contribution from both natural and anthropogenic sources for both indoors and outdoors. The highest F/C ratio was exhibited by Ba in ambient atmosphere which is generally anticipated to source from brake wears and industrial processes in fine particles.

**Table 7 (a):** Average metal concentrations ($\mu g/m^3$) in PM size fractions during summers

| ***INDOORS*** | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.25-0.5 | PM,0.25 | PM2.5 | F/C |
| Al | 0.893 | 1.843 | 1.0274 | 1.526 | 4.592 | 2.247 | 2.515 |
| Ca | 3.024 | 2.204 | 1.128 | 0.982 | 0.723 | 1.260 | 0.416 |
| Ni | 0.018 | 0.026 | 0.014 | 0.004 | 0.010 | 0.014 | 0.734 |
| Cr | 0.147 | 0.040 | 0.016 | 0.013 | 0.005 | 0.018 | 0.124 |
| Cu | 0.373 | 0.215 | 0.182 | 0.032 | 0.059 | 0.122 | 0.327 |
| Fe | 2.996 | 1.958 | 0.758 | 1.585 | 0.507 | 1.202 | 0.402 |
| K | 1.773 | 2.559 | 1.112 | 1.087 | 0.863 | 1.405 | 0.793 |
| Mg | 2.014 | 1.586 | 0.832 | 2.701 | 1.286 | 1.601 | 0.795 |
| Mn | 0.253 | 0.254 | 0.098 | 0.060 | 0.520 | 0.233 | 0.919 |
| Pb | 0.616 | 0.579 | 0.775 | 1.441 | 4.680 | 1.869 | 3.032 |
| Zn | 0.780 | 0.673 | 0.755 | 0.495 | 0.389 | 0.578 | 0.741 |
| PM | 84.113 | 44.933 | 37.856 | 48.506 | 52.583 | 45.970 | 0.547 |
| ***OUTDOORS*** | | | | | | | |
| | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.25-0.5 | PM<0.25 | PM2.5 | F/C |
| Al | 0.411 | 2.376 | 0.294 | 0.584 | 2.688 | 1.486 | 3.612 |
| Ca | 6.854 | 4.059 | 1.956 | 2.339 | 1.648 | 2.500 | 0.365 |
| Ni | 0.027 | 0.031 | 0.0141 | 0.027 | 0.007 | 0.020 | 0.740 |
| Cu | 0.015 | 0.029 | 0.013 | 0.015 | 0.166 | 0.056 | 3.760 |
| Fe | 1.642 | 0.943 | 0.690 | 0.902 | 0.609 | 0.786 | 0.479 |
| K | 3.498 | 2.459 | 1.416 | 1.098 | 1.086 | 1.514 | 0.433 |
| Mg | 2.496 | 1.955 | 0.825 | 1.988 | 1.059 | 1.457 | 0.584 |
| Mn | 0.350 | 0.270 | 0.052 | 0.023 | 0.520 | 0.216 | 0.618 |
| Pb | 0.667 | 3.552 | 0.743 | 0.448 | 2.525 | 1.817 | 2.723 |
| Zn | 1.273 | 1.174 | 0.897 | 1.151 | 0.333 | 0.889 | 0.698 |
| PM | 106.260 | 40.167 | 35.973 | 49.430 | 46.430 | 42.998 | 0.405 |

**Table 7(b):** Average metal concentrations in PM size fractions during monsoons

| ***INDOORS*** | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.25-0.5 | PM>0.25 | PM2.5 | F/C |
| Al | 0.912 | 0.906 | 0.916 | 0.990 | 1.057 | 0.967 | 1.061 |
| Ba | 0.006 | 0.008 | 0.006 | 0.011 | 0.009 | 0.009 | 1.352 |
| Ca | 1.224 | 1.330 | 1.756 | 1.696 | 1.543 | 1.582 | 1.292 |
| Cd | 0.001 | 0.001 | 0.002 | 0.002 | 0.002 | 0.002 | 1.660 |
| Co | 0.003 | 0.003 | 0.004 | 0.003 | 0.007 | 0.004 | 1.582 |
| Cu | 0.064 | 0.064 | 0.062 | 0.064 | 0.065 | 0.064 | 0.999 |
| Fe | 0.343 | 0.373 | 0.451 | 0.381 | 0.380 | 0.396 | 1.154 |
| K | 0.154 | 0.155 | 0.179 | 0.183 | 0.294 | 0.203 | 1.317 |
| Mg | 0.539 | 0.582 | 0.612 | 0.822 | 0.731 | 0.687 | 1.274 |
| Mn | 0.029 | 0.027 | 0.028 | 0.030 | 0.029 | 0.028 | 0.979 |
| Pb | 0.0404 | 0.045 | 0.060 | 0.036 | 0.033 | 0.043 | 1.068 |
| Zn | 0.030 | 0.056 | 0.056 | 0.041 | 0.088 | 0.061 | 2.032 |
| PM conc | 67.465 | 44.031 | 51.560 | 79.999 | 96.393 | 67.996 | 1.008 |
| ***OUTDOORS*** | | | | | | | |
| | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.25-0.5 | PM>0.25 | PM2.5 | F/C |
| Al | 1.277 | 1.462 | 1.439 | 1.423 | 1.632 | 1.489 | 1.166 |
| Ba | 0.009 | 0.014 | 0.016 | 0.022 | 0.021 | 0.018 | 1.856 |
| Ca | 2.612 | 2.944 | 2.750 | 3.034 | 2.985 | 2.928 | 1.121 |
| Cd | 0.001 | 0.002 | 0.002 | 0.002 | 0.003 | 0.00 | 1.438 |
| Co | 0.003 | 0.003 | 0.004 | 0.006 | 0.006 | 0.005 | 1.871 |
| Cu | 0.012 | 0.016 | 0.011 | 0.016 | 0.021 | 0.016 | 1.287 |
| Fe | 0.953 | 1.244 | 0.822 | 1.147 | 0.898 | 1.028 | 1.079 |
| K | 0.113 | 0.118 | 0.168 | 0.145 | 0.203 | 0.159 | 1.403 |
| Mg | 1.383 | 1.465 | 1.757 | 1.378 | 1.329 | 1.483 | 1.072 |
| Mn | 0.038 | 0.038 | 0.034 | 0.034 | 0.037 | 0.035 | 0.932 |
| Pb | 0.083 | 0.073 | 0.106 | 0.065 | 0.083 | 0.082 | 0.987 |
| Zn | 0.021 | 0.022 | 0.019 | 0.023 | 0.055 | 0.030 | 1.411 |
| PM conc | 51.758 | 40.488 | 49.151 | 47.202 | 54.125 | 47.742 | 0.922 |

**Table 7(c):** Average metal concentrations in PM size fractions during winters

| ***INDOORS*** | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.25-0.5 | PM>0.25 | PM2.5 | F/C |
| Al | 1.508 | 1.332 | 1.321 | 1.837 | 1.134 | 1.406 | 0.932 |
| Ba | 0.041 | 0.036 | 0.036 | 0.029 | 0.046 | 0.037 | 0.914 |
| Ca | 2.815 | 1.782 | 2.355 | 2.507 | 2.453 | 2.274 | 0.808 |
| Cd | 0.011 | 0.015 | 0.012 | 0.007 | 0.011 | 0.011 | 1.059 |
| Co | 0.037 | 0.031 | 0.032 | 0.060 | 0.042 | 0.041 | 1.114 |
| Cr | 0.110 | 0.130 | 0.067 | 0.140 | 0.104 | 0.110 | 1.001 |
| Cu | 0.024 | 0.036 | 0.079 | 0.056 | 0.054 | 0.056 | 2.433 |
| Fe | 0.727 | 0.854 | 0.820 | 0.794 | 0.691 | 0.790 | 1.086 |
| K | 0.919 | 1.049 | 0.666 | 0.542 | 0.773 | 0.758 | 0.824 |
| Mg | 0.534 | 0.471 | 0.688 | 0.621 | 1.099 | 0.720 | 1.348 |
| Mn | 0.255 | 0.286 | 0.179 | 0.205 | 0.122 | 0.198 | 0.776 |
| Ni | 0.052 | 0.018 | 0.063 | 0.080 | 0.086 | 0.0618 | 1.187 |
| Pb | 0.160 | 0.117 | 0.104 | 0.109 | 0.134 | 0.116 | 0.727 |
| Zn | 0.900 | 0.775 | 0.716 | 0.675 | 0.486 | 0.663 | 0.736 |
| PM | 137.790 | 55.087 | 47.180 | 68.483 | 81.670 | 63.105 | 0.458 |
| ***OUTDOORS*** | | | | | | | |
| | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.25-0.5 | PM>0.25 | PM2.5 | F/C |
| Al | 1.845 | 1.909 | 1.625 | 1.813 | 1.616 | 1.741 | 0.942 |
| Ba | 0.027 | 0.558 | 0.287 | 0.034 | 0.177 | 0.264 | 9.682 |
| Ca | 1.083 | 1.901 | 1.346 | 1.830 | 1.131 | 1.552 | 1.433 |
| Cd | 0.008 | 0.009 | 0.014 | 0.012 | 0.016 | 0.013 | 1.573 |
| Co | 0.032 | 0.015 | 0.034 | 0.028 | 0.047 | 0.031 | 0.976 |
| Cr | 0.181 | 0.149 | 0.138 | 0.082 | 0.109 | 0.120 | 0.662 |
| Cu | 0.052 | 0.095 | 0.076 | 0.066 | 0.076 | 0.078 | 1.488 |
| Fe | 0.898 | 1.303 | 1.091 | 0.833 | 0.882 | 1.027 | 1.144 |
| K | 0.608 | 0.819 | 0.964 | 0.880 | 0.700 | 0.841 | 1.383 |
| Mg | 0.767 | 0.824 | 0.652 | 1.689 | 0.973 | 1.034 | 1.349 |
| Mn | 0.140 | 0.371 | 0.197 | 0.176 | 0.178 | 0.230 | 1.649 |
| Ni | 0.033 | 0.047 | 0.034 | 0.032 | 0.056 | 0.042 | 1.277 |
| Pb | 0.120 | 0.097 | 0.119 | 0.137 | 0.128 | 0.120 | 1.002 |
| Zn | 1.430 | 2.597 | 1.519 | 1.922 | 1.440 | 1.869 | 1.307 |
| PM | 134.820 | 70.933 | 61.933 | 88.081 | 92.267 | 78.304 | 0.581 |

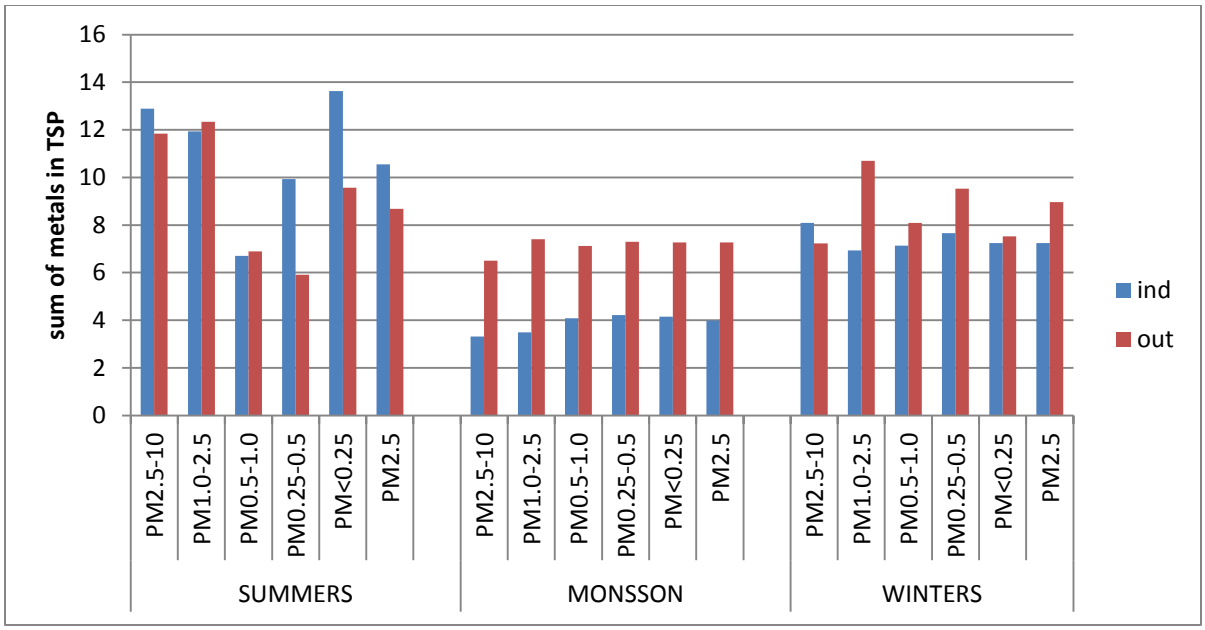



**Fig 5:** Sum of metals (µg/m$^3$) in indoor and outdoor size fractionated PM samples

We also investigated the sum of total metal concentration in indoor and outdoor TSP (Fig. 5). During summer, the sum of average concentrations of all analyzed elements in TSP was 55.08 and 59.59µg/m$^3$ in indoor and outdoor environment respectively. During monsoons, the sum was 19.25 and 35.59 µg/m$^3$ while for winters, the sum was 37.06 and 43.08µg/m$^3$in indoor and outdoor environment respectively. In general, the highest concentration of elements usually occurs during winters (Padoan et al., 2016); whereas in our study highest concentration of metals in TSP was found in summers. According to Kadi (2014), high temperature during summers result in increase in energy consumption used in air conditioners unlike winters and monsoons whereby heating is not required due to mild temperatures. Similarly, high consumption of fossil fuels could be a reason explaining higher elemental concentration during summers that might also be shared by active surface winds and dust storms prevalent during summer season.

High contribution of metals was seen in fine particulate samples than coarse particulate except in indoor samples winters whereby metals contributed maximally to coarse PM.

Going a step further, our study investigated metal contribution with respect to each of the particle size in size segregated fine PM. As seen from Fig. 5, $PM_{1.0\text{-}2.5}$ contained highest metal mass loadings in ambient atmosphere. Whereas for indoors, heterogeneous variation w.r.t particle size

fraction was noted (q-UF in summers, q-Acc in monsoons and coarse in winters) that indicates strong indoor sources with consistently varying metal concentrations.

## 6. **Spatial distribution of metal concentration**:

By the comparison of element concentration in urban, roadside and rural areas, spatial distribution characteristics of most of the single element concentrations were also found. Overall, the annualaverage mass concentration of Group I (major) elements in urban, rural and RS areas was 28.63, 22.06, 22.26 μg/$m^3$ for indoor samples and 24.42, 29.85, 18.43 μg/$m^3$ for outdoor TSP samples. Concerning the minor elements (Group II elements), the mass concentration in urban, rural, RS residential sites were 55.80, 13.50, 58.90 μg/m3 for indoors and 90.70, 10.94 and 16.20 μg/$m^3$ for outdoor samples respectively.

By comparison, following annual spatial trends were obtained:

| | | |
|---|---|---|
| Major elements | Ind | Urban >RS >~ rural |
| | Out | Rural > urban >RS |
| Minor elements | Ind | RS >~ Urban > Rural |
| | Out | Rural > urban > RS |

## 7. Size segregated metal distribution pattern with seasonal variation:

The density function relating to the size distribution pattern of PMand bounded elements is presented as lognormal distributions (Table8) after method described by Tare et al (2006) and were plotted usingORIGIN 6.0 software. The distributions were evaluated as being unimodal. (single peak) or bimodal ("U shaped" distribution) by observing if thesize distribution is characterized by one or two maximum values. Fig. 6 represents the size distribution of PM and associated elemental concentration in (a) summer (b) monsoon and (c) winter seasons. The concentrations have been represented as average of all the three sites.Applying the lognormal distribution criteria, subsequent patterns were identified for metal concentrations (Table9) for both indoor and outdoor air samples in each of the three seasons.

**Table 8:** Effective cut off diameter (ecd) of each stage of sampler

| Stage | Size range (µm) | 50% ecd | d $\log_e D_p$ [a] |
|---|---|---|---|
| 1 | 2.5-10 | 2.5 | 1.386 |
| 2 | 2.5-1.0 | 1.0 | 0.916 |
| 3 | 1.0-0.5 | 0.5 | 0.693 |
| 4 | 0.5-0.25 | 0.25 | 0.693 |
| 5 | <0.25 | 0.01[b] | 0.916 |

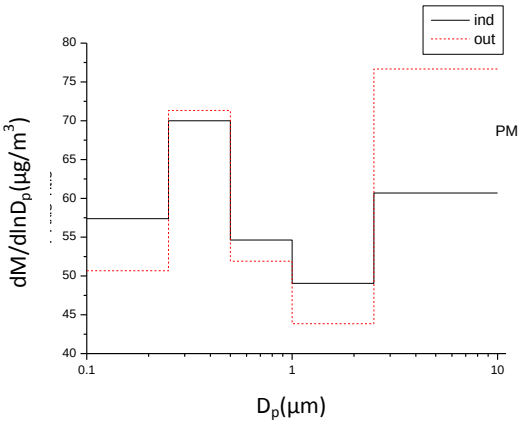
[a]d $\log_e D_p = \log_e D_{pn}$-1 – $\log_e D_{pn}$; $D_{pn}$ is the value of 50% ecd of stage n

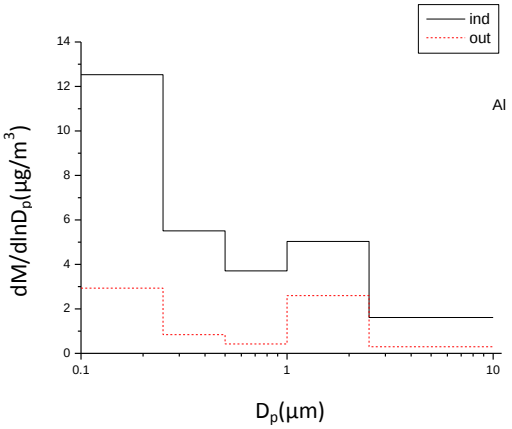
**Table 9:** Seasonal distribution pattern obtained for PM and bounded elemental in indoor and outdoor air

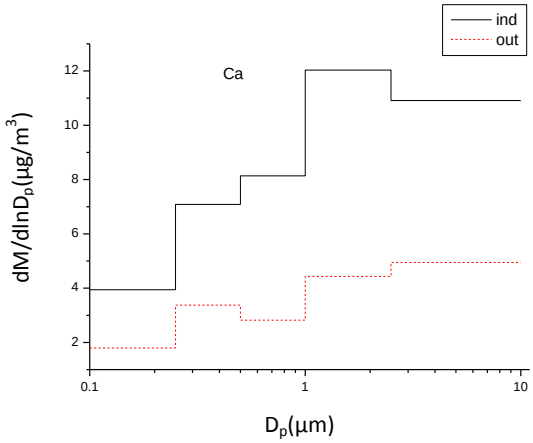
| | **Summer** | | **Monsoon** | | **Winter** | |
|---|---|---|---|---|---|---|
| Element | *Indoor* | *Outdoor* | *Indoor* | *Outdoor* | *Indoor* | *Outdoor* |
| **PM** | **2A3C** | **2CA3** | **1A3** | **1A2** | **2CA3** | **2A3C** |
| Al | 1U | 2UA3 | 1A3 | 1A2 | 1A3 | 1A3 |
| Ba | ---- | ----- | 1A3 | 1A3 | 2A2U | 2A2U |
| Ca | 1A1 | 1C | 1A2 | 1A3 | 1A3 | 2A3A1 |
| Cd | ---- | ----- | 2UA2 | 2UA2 | 2A2U | 1A2 |
| Co | --- | ----- | 2UA2 | 1A3 | 1A3 | 3UA2C |
| Cr | 1C | ---- | --- | ---- | 2A3A1 | 1A2 |
| Cu | 3CA2U | 1U | 1A3 | 1A3 | 1A2 | 1A2 |
| Fe | 2A3C | 1U | 1A2 | 2A1A3 | 1A2 | 1A2 |
| K | 1A1 | 1A2 | 1U | 2A2U | 1A1 | 1A3 |
| Mg | 2A3A1 | 1U | 1A3 | 1A2 | 1UA2 | 1A3 |
| Mn | 2UA1 | 2UA1 | 1A3 | 1A2 | 2A3A1 | 1A1 |
| Ni | 1A1 | 2A1A3 | --- | ----- | 2A2C | 2UA1 |
| Pb | 1U | 2A1U | 1A2 | 1A2 | 1A2 | 1A3 |
| Zn | 1A2 | 1A2 | 2UA2 | 1U | 1A2 | 2A1A3 |

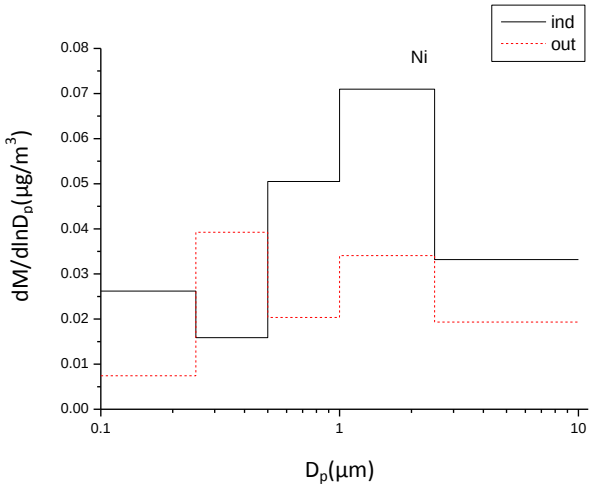
1 and 2 corresponds to unimodal and bimodal distributions respectively

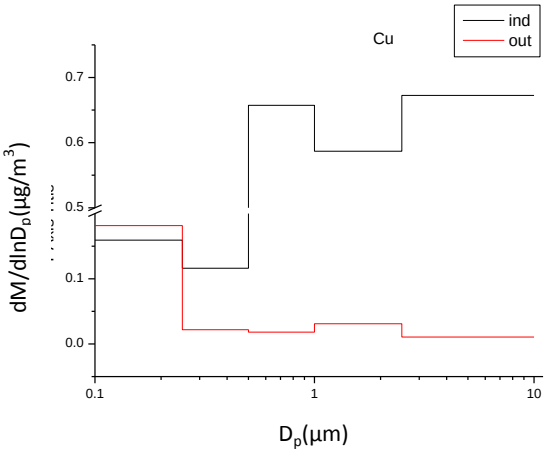
Patterns: C refers to peak in coarse range, U refers to peak in ultrafine range; A1, A2, A3 refers to peak in accumulation range 2.5-1.0, 1.0-0.5, 0.5-0.25 µm. Blank refers to non- detectable concentrations.

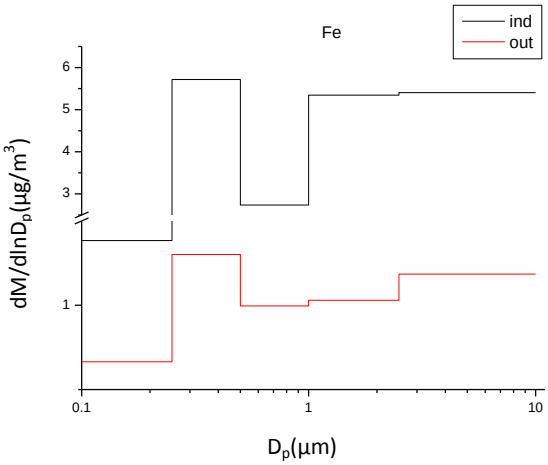

ind
out
PM
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Al
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Ca
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Ni
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Cu
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Fe
dM/dlnDp(μg/m3)
Dp(μm)

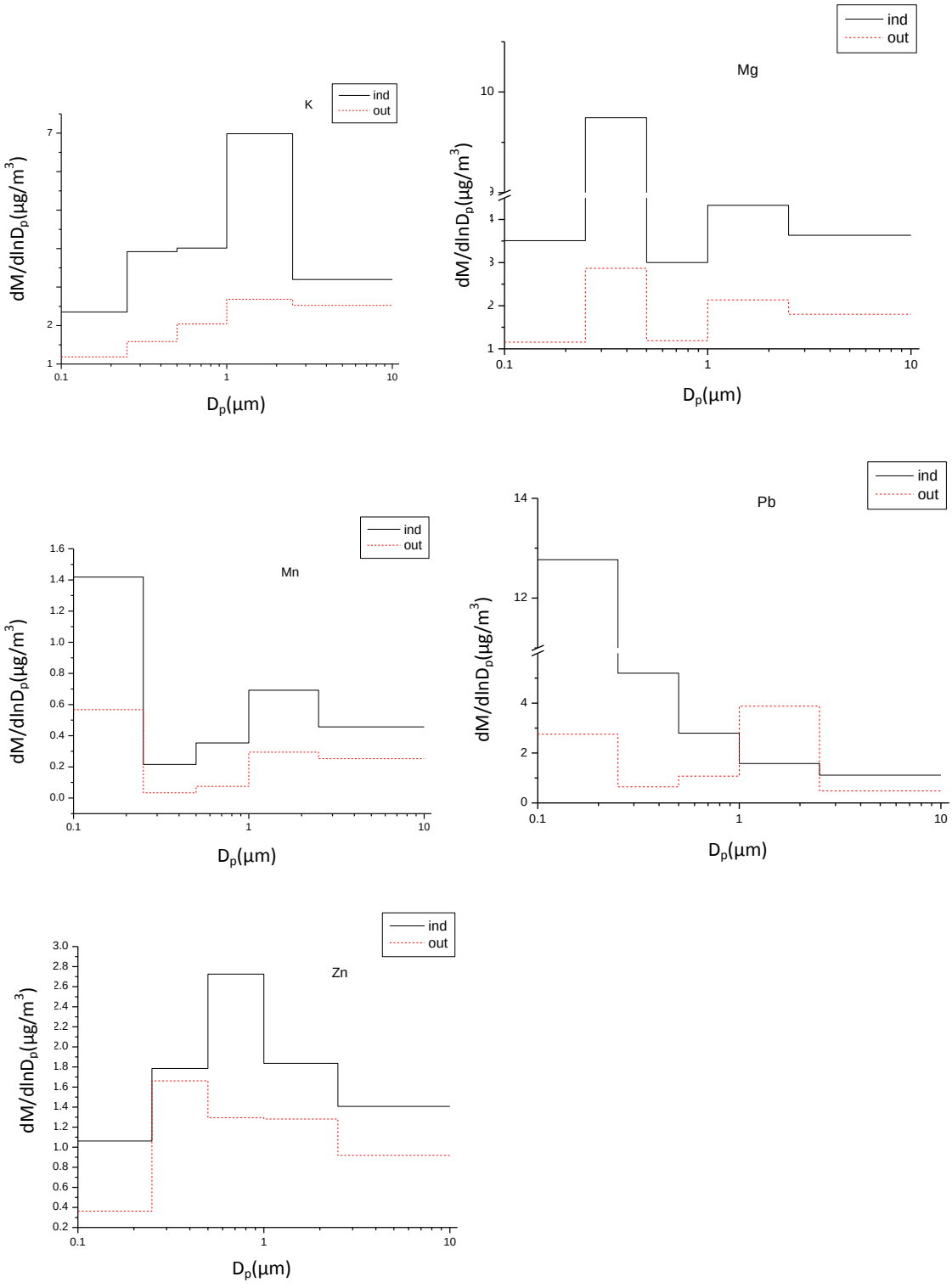
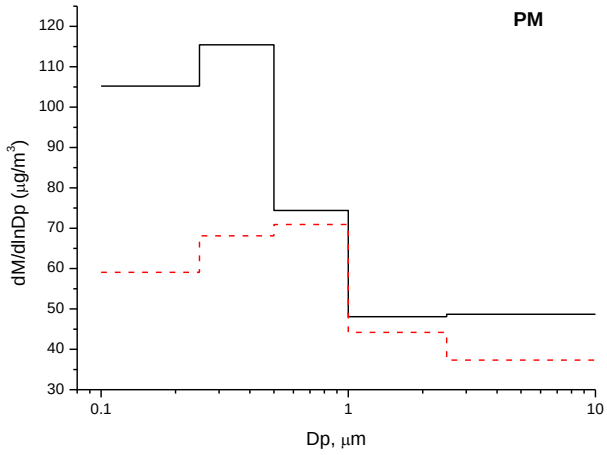
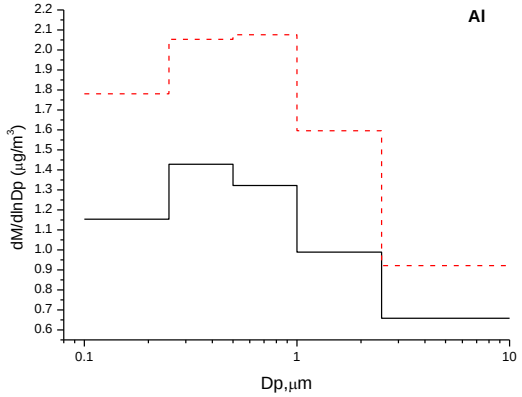
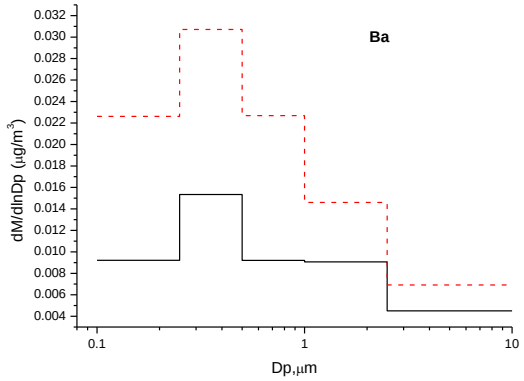
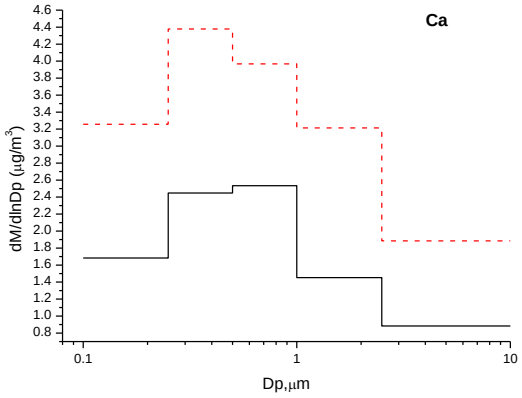


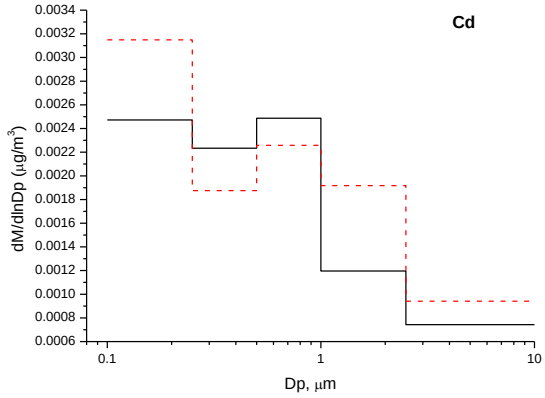

**Fig 6 (a):**Size distribution of PM and associated elements (mean concentrations) in indoor (solid line) and outdoor air (dotted line) samples of residential environment in summers

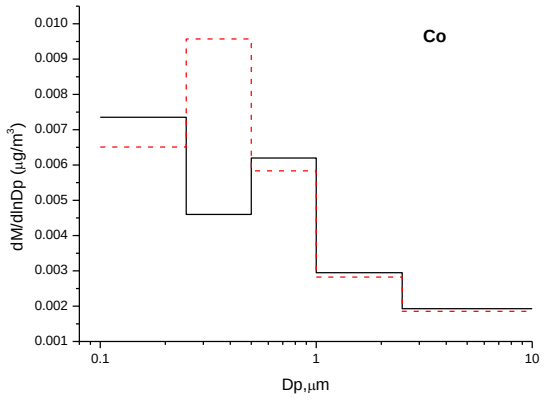

PM
dM/dlnDp (μg/m3)
Dp, μm

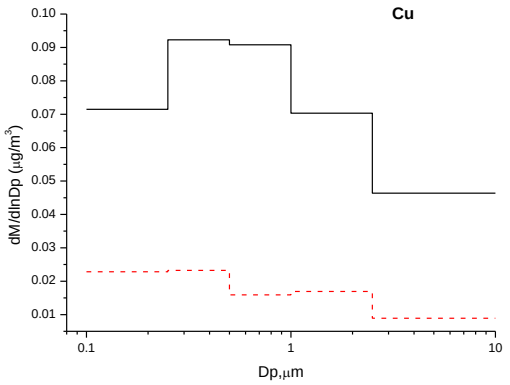

Al
dM/dlnDp (μg/m3)
Dp,μm

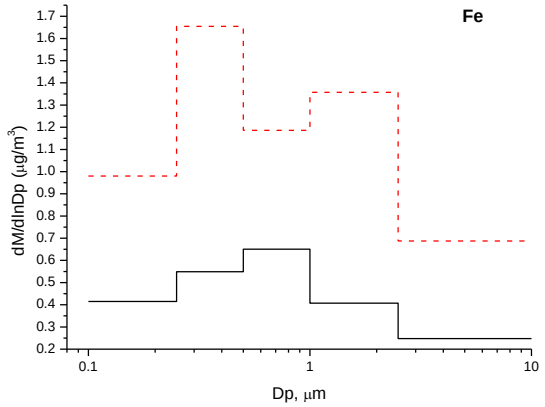

Ba
dM/dlnDp (μg/m3)
Dp,μm

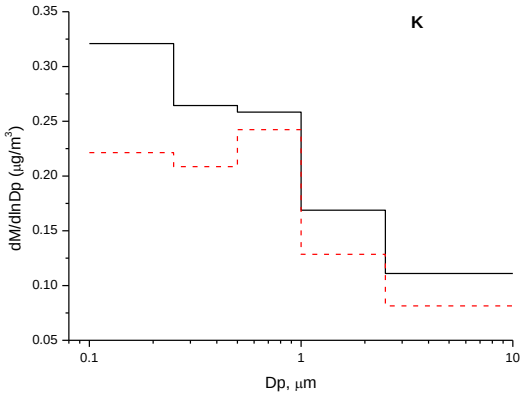

Ca
dM/dlnDp (μg/m3)
Dp,μm

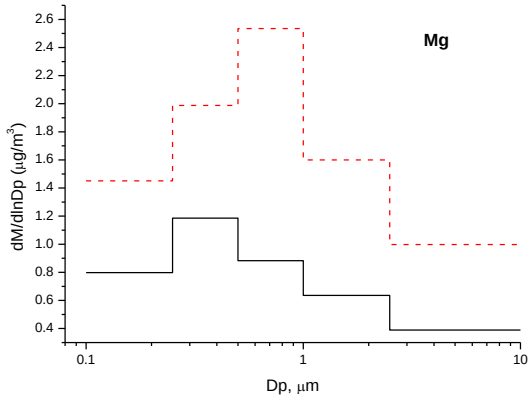

Cd
dM/dlnDp (μg/m3)
Dp, μm

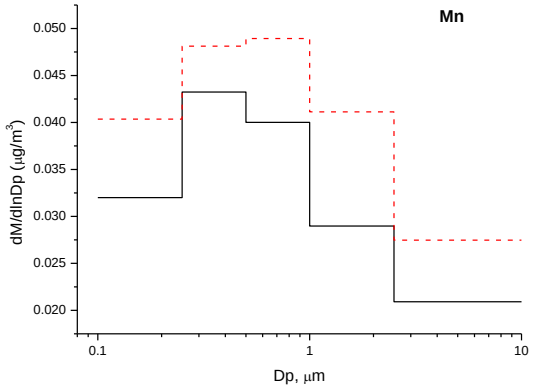

Co
dM/dlnDp (μg/m3)
Dp,μm


Cu
dM/dlnDp (μg/m3)
Dp,μm


Fe
dM/dlnDp (μg/m3)
Dp, μm


K
dM/dlnDp (μg/m3)
Dp, μm


Mg
dM/dlnDp (μg/m3)
Dp, μm


Mn
dM/dlnDp (μg/m3)
Dp, μm

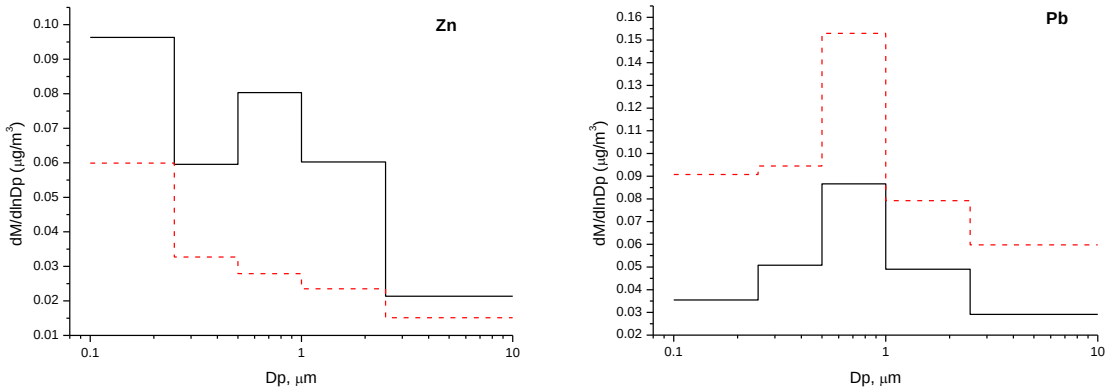
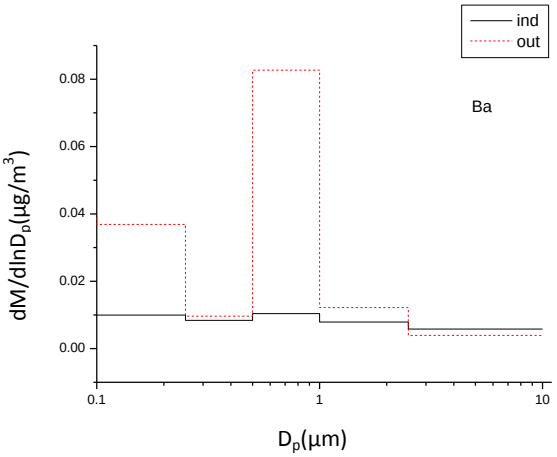
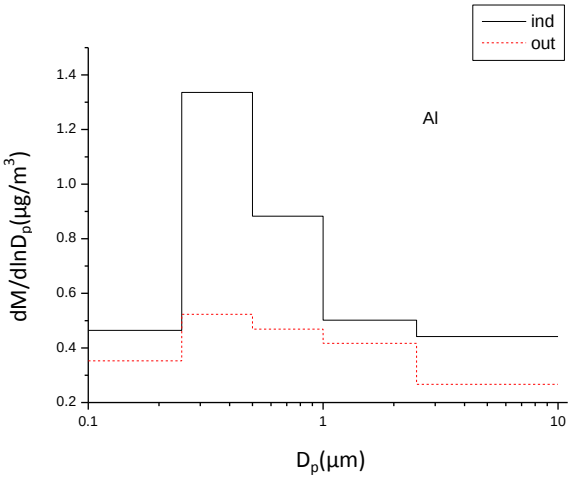
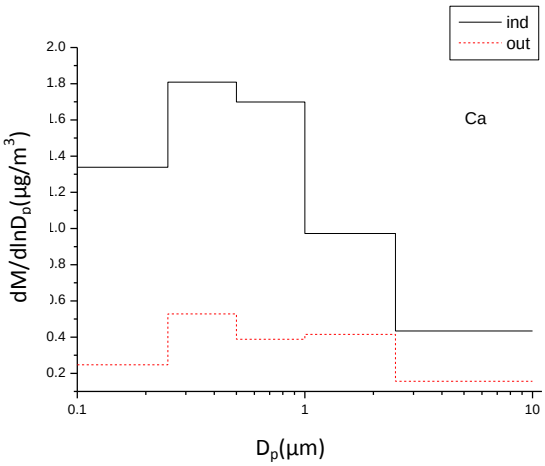
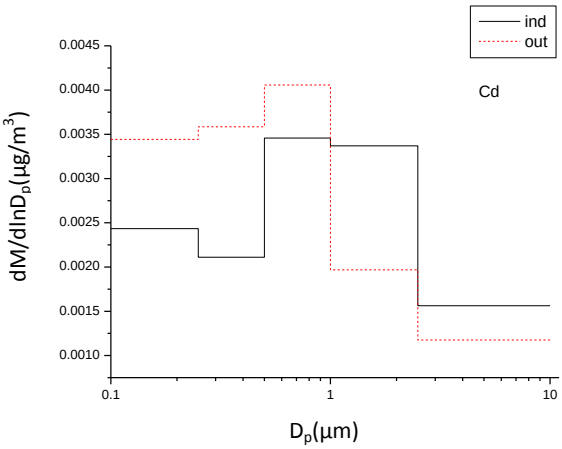


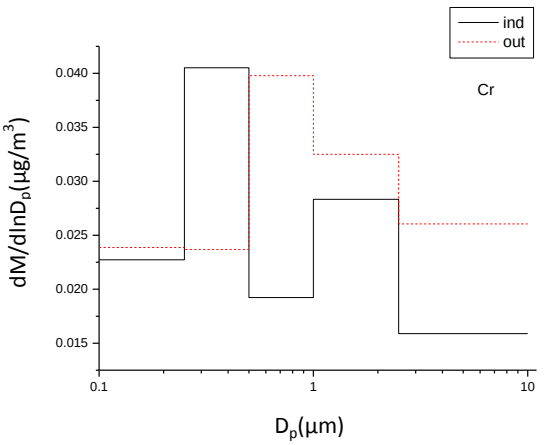

**Fig. 6 (b):** Size distribution of PM and associated elements (mean concentrations) in indoor (solid line) and outdoor air (dotted line) samples of residential environment in monsoons

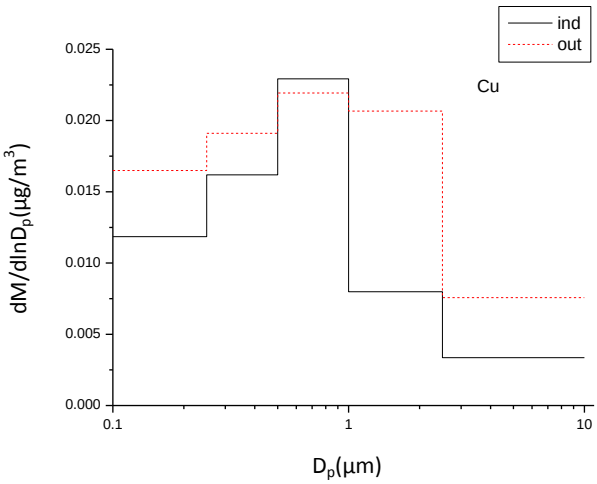

ind
out
Ba
dM/dlnDp(μg/m3)
0.08
0.06
0.04
0.02
0.00
0.1
1
10
Dp(μm)

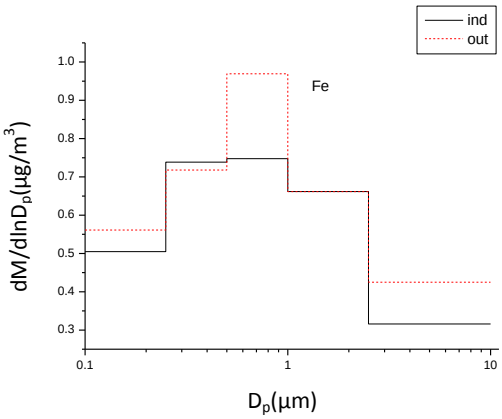

ind
out
Al
dM/dlnDp(μg/m3)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
1
10
Dp(μm)

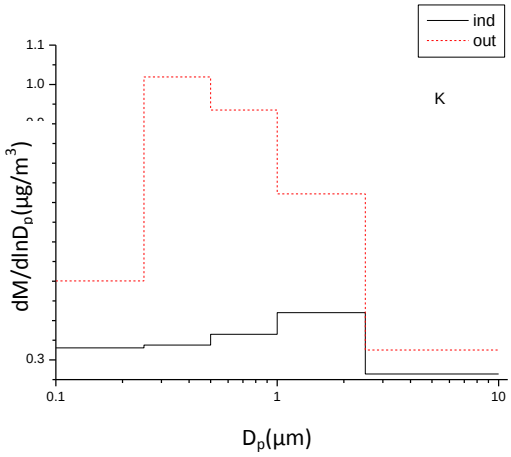

ind
out
Ca
dM/dlnDp(μg/m3)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
1
10
Dp(μm)

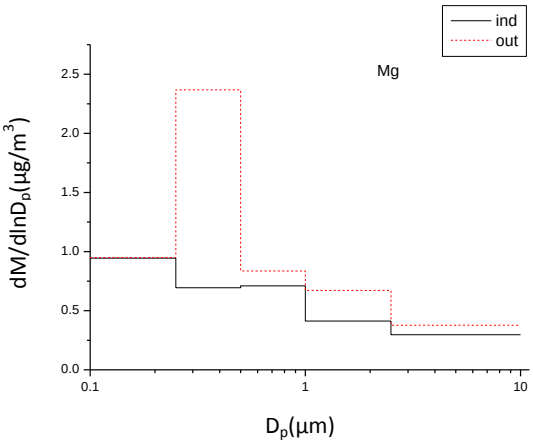

ind
out
Cd
dM/dlnDp(μg/m3)
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.1
1
10
Dp(μm)

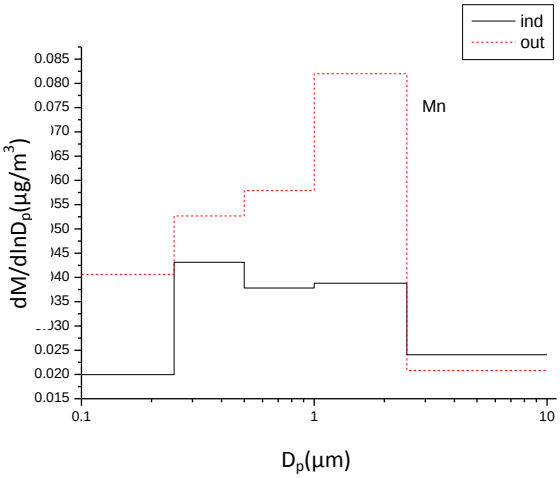

ind
out
Cr
dM/dlnDp(μg/m3)
0.040
0.035
0.030
0.025
0.020
0.015
0.1
1
10
Dp(μm)

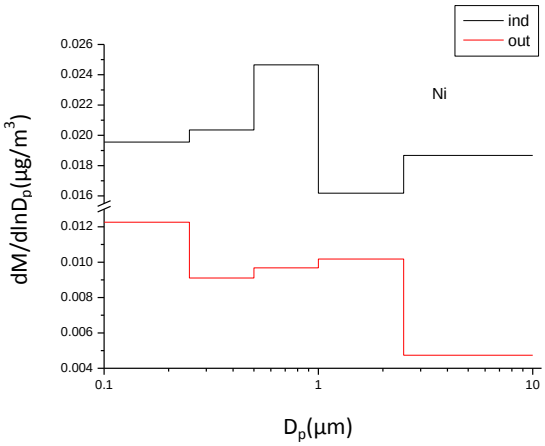

ind
out
Cu
dM/dlnDp(μg/m3)
0.025
0.020
0.015
0.010
0.005
0.000
0.1
1
10
Dp(μm)

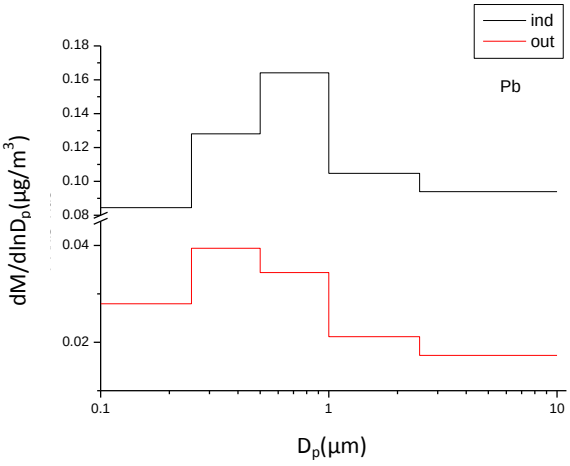

ind
out
Fe
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
K
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Mg
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Mn
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Ni
dM/dlnDp(μg/m3)
Dp(μm)


ind
out
Pb
dM/dlnDp(μg/m3)
Dp(μm)

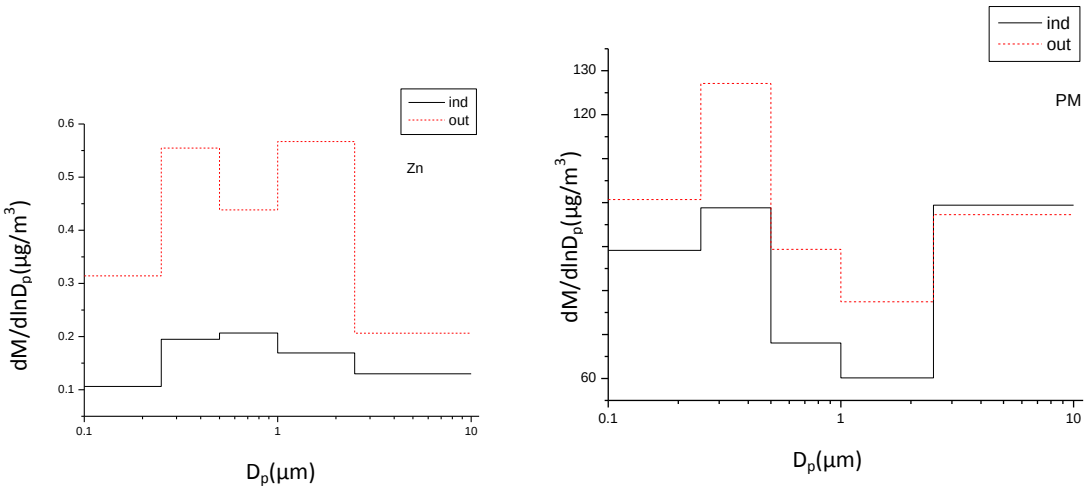



**Fig 6(c):**Size distribution of PM and associated elements (mean concentrations) in indoor (solid line) and outdoor air (dotted line) samples of residential environment in winters

The mass size distribution of PM in both indoor and outdoor air of residentialhomes for the monsoon period is single modal. The maximumof the density function occurs in q-Acc mode between 0.5 and0.25 µmand 1.0–0.5 µmfor indoor and outdoor air respectively. The occurrenceof monomodal peak in 1.0–0.5 µm in outdoors is indicative ofthe droplet mode; usually observed during high levels of relative humidity while for summers and winters a bimodal partitioning pattern is figured. For summers and winters, a secondary peak in coarse mode is identified that relates to natural emission from re-suspended soil dust. Literature has signified increase in PM concentration over coarse particle ranges during dry weather conditions. This is coincident with our study result where coarse particles concentration was found to be enhanced during winter and summer season. Dry atmospheric conditions produce more suspended particulate from surface of roads and soils.

The size distribution of elements was different as regard the 3 seasonal groups and 2 indoor-outdoor conditions. The prominent characteristics of elements distribution are highlighted as follows:

- A modal shift in accumulation particles towards larger size for Ca is noticeable from winters to monsoon to summers. Similarly, presence of primary peak in coarse mode for Fe suggests dominance of coarse mode particles for these mineral elements that suggests influence of indoor sources like resuspension of dust in indoor environment.
- The unanticipated association of Cr in dominant with coarser fraction may be linked to literature that suggests its multi-sourced relation with bimodal contribution from both anthropogenic and natural emissions including soil dust, re-suspension and second aerosol aggregation especially during summers.
- Ca and K evidenced presence of larger size accumulation mode (PM2.5-1.0) in summers whereas smaller diameter mode prevailed in monsoon and winters (PM1.0-0.25)
- The bimodal distribution of Cd. The bimodal distribution of Cd with respect to particle size 0.5–1.0 μm and <0.25 links its supposed association to accumulation of particles related to emission from local sources. Moreover, similar modal pattern for indoors and outdoors in monsoons suggest infiltration of particles as one of the indoor source. For winters, loss of q-UF particles during infiltration from outdoors to indoors by Brownian diffusion is further noticeable in winters.
- The change in trimodal distribution pattern to unimodality observed for Co points towards loss of coarse and UF particles during infiltration process for which techniques like gravitational settlement and Brownian diffusion are most efficiently known for such particles respectively.
- Bimodal distribution of Mn in summers (indoors) and winters (indoors) suggest that Mn is associated with emissions from traffic, waste burning and is moreover dominated by coarse dust sources too.
- Occurrence of Ni in q-UF range in ambient atmosphere of winters can be linked to its existence as a tracer for emissionsin oil combustions.
- Presence of Fe in coarse range in summers unlike accumulation range in winters and monsoons direct towards wind-blown dust generally observed during summers. Road dust of which crustal dust is a key component, consists of primarily coarse sized particles generally shows temporal variations.

- Except Mn, Pb and Cu, the outdoor distribution pattern of elements followed that for indoors. This suggests a better exchange of air from indoors to outdoors during summers that may be attributed to opening of windows and ventilation conditions during summers.

## 8. Spatial variability of elemental size distribution: Influence of traffic emissions

Toinvestigate the effect of traffic emissions on elemental mass size distribution, modal distributions were assessed for Roadside homes and those for those away from road traffic environment (averaged of urban and rural homes). These distributions have only been assessed for outdoor ambient conditions to eliminate the effect of infiltration. The modal distribution patterns for elements have been presented in Table 10.

**Table 10:**Elemental size distribution patterns identified in homes with high (roadside homes) and low traffic (urban-rural homes) emissions in outdoor air of residential homes

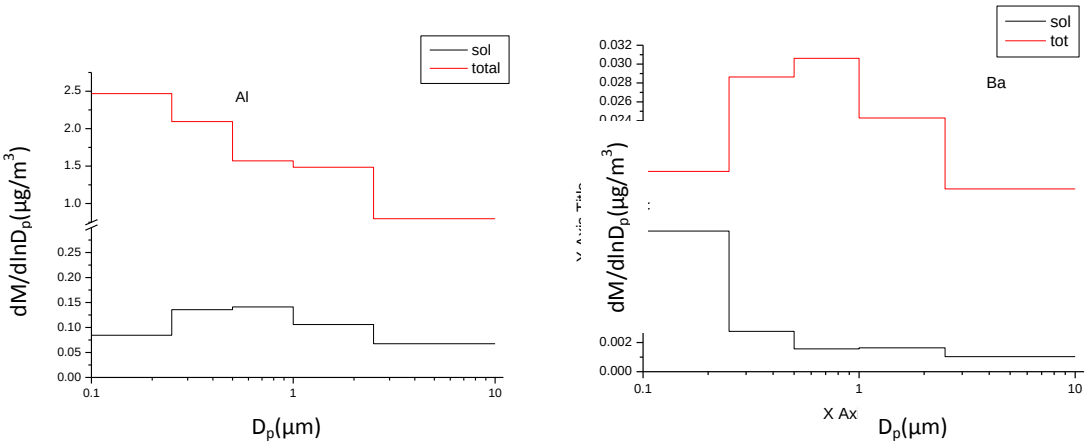
| Element | RS | Urban-Rural (average) |
|---|---|---|
| Al | 1A2 | 2A1A3 |
| Ba | 2A1U | 1U |
| Ca | 2A1A3 | 2A1A3 |
| Cd | 2A2U | 1A3 |
| Cr | 2CU | 1A2 |
| Cu | 1A2 | 2A3A1 |
| Fe | 2A1A3 | 1A2 |
| K | 1A2 | 1A2 |
| Mg | 1A3 | 1A3 |
| Mn | 1U | 2A1A3 |
| Ni | 1U | 2A2U |
| Pb | 1A3 | 1A2 |
| Zn | 2A2U | 2A1A3 |

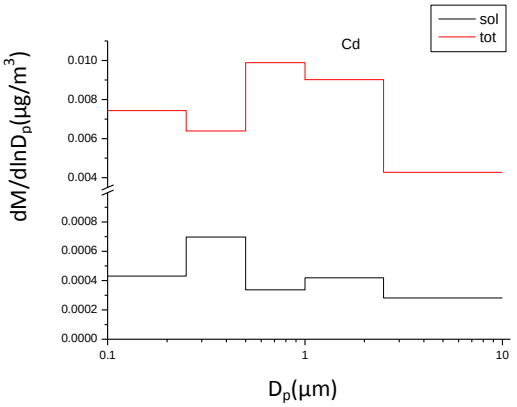
When spatial variability in homes located in high (roadside homes) and low traffic areas of the city were compared, it was found that elements found in ambient air influenced by high traffic emissions showed a marked shift towards finer size fractions. For Ba, Ni, Mn and Zn (tracer of

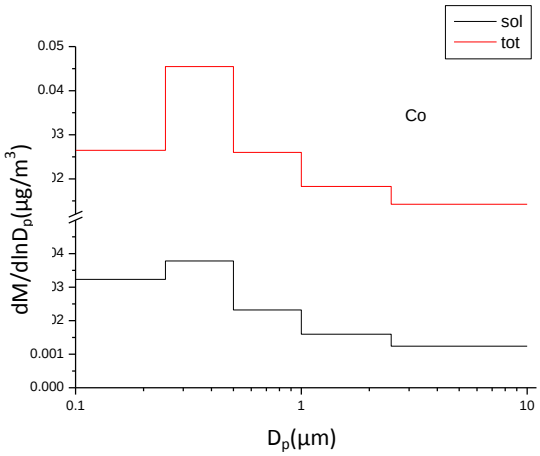
vehicular emission in ultrafine range) decrease in accumulation mass followed by modal peak in ultrafine range was noticeable This can generally be attributed to the influence of fresh vehicular emissions on increased fraction of ultrafine particles. Pb that is generally regarded as a tracer of vehicular emission(Rohra et al., 2018) showed a modal shift towards finer accumulation range ($PM_{0.5-0.25}$). For elements such as Cr (that showed of primary peak in coarse range) and Cu (that showed a shift to unimodality with primary peak in larger size fraction) contributions from sources other than traffic emissions may explain the variance considered at this site. Moreover, dominance of accumulation mode other than ultrafine size range in roadside homes of present study could be attributed to mechanism and atmospheric ageing of fresh vehicular emissions(composed of ultrafine particles) leading to coagulation with subsequent increase in particle size.

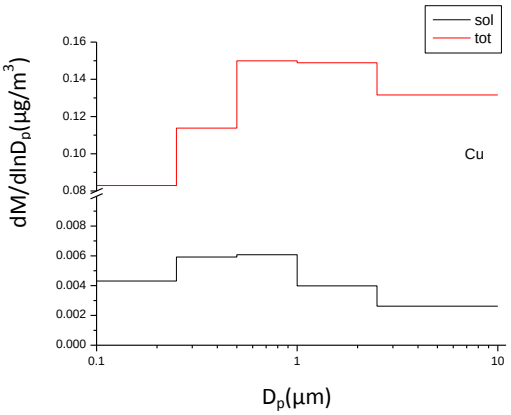
## 9. Impact of solubility on size distribution pattern

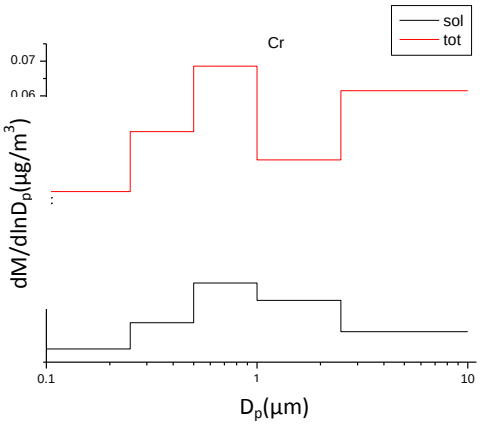
Figure7 displays the normalized size distribution of total and soluble (bioavailable) annual average indoor concentrations of some elements. Figures suggest that the distribution pattern of bioavailable concentrations did not necessarily coincide with those of total elemental concentration. The bioavailable concentration of elements especially toxic metals (Ba, Zn, Co, Cu, Cr, Pb except Cd) exhibited a modal shift towards smaller particle sizes when compared to total concentration size distribution pattern. These results imply that higher risk from finer particle size due to bioavailable fractions being easily accessible to human body.

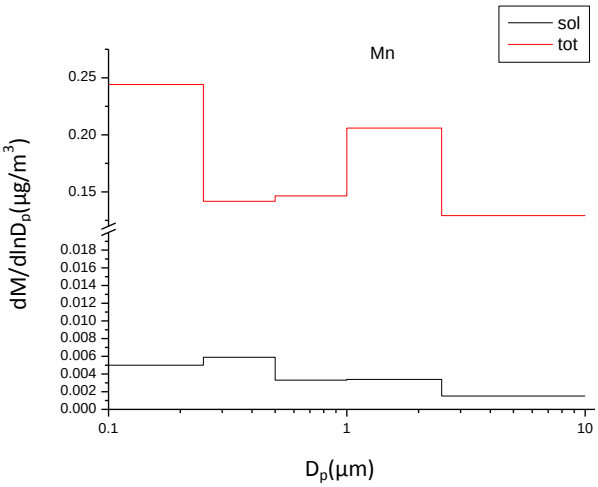


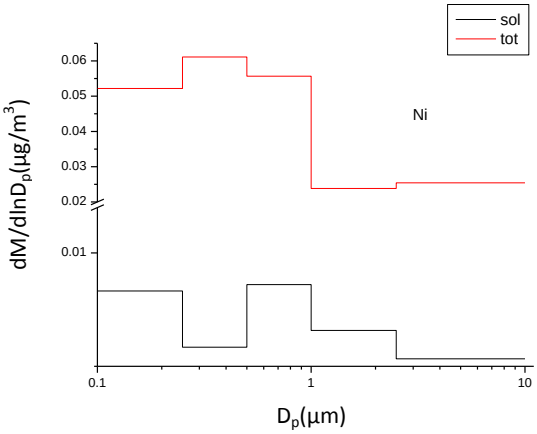

Cd
sol
tot
dM/dlnDp(µg/m3)
Dp(µm)


Co
sol
tot
dM/dlnDp(µg/m3)
Dp(µm)


Cu
sol
tot
dM/dlnDp(µg/m3)
Dp(µm)


Cr
sol
tot
dM/dlnDp(µg/m3)
Dp(µm)


Mn
sol
tot
dM/dlnDp(µg/m3)
Dp(µm)


Ni
sol
tot
dM/dlnDp(µg/m3)
Dp(µm)

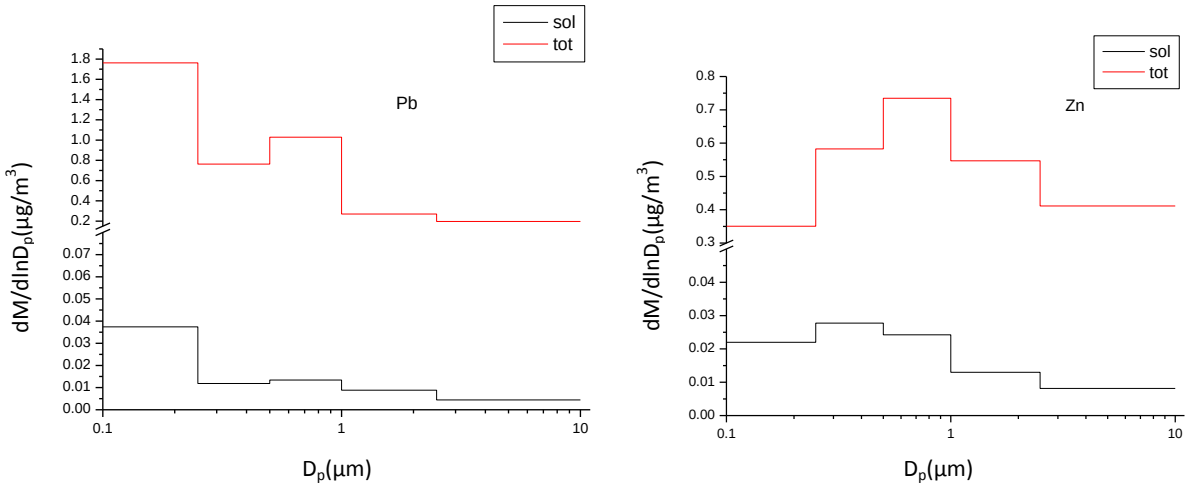



**Fig.7:** Lognormal distribution graphs of total and soluble (bioavailable) concentrations

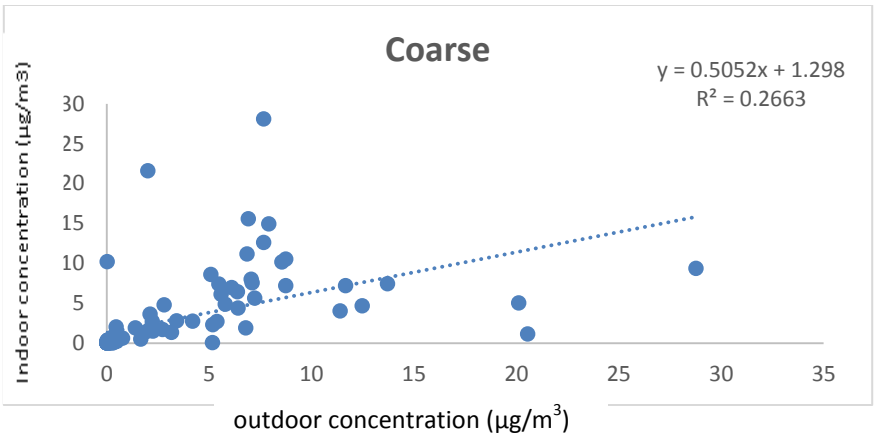
## 10. Indoor-outdoor Regression Analysis:

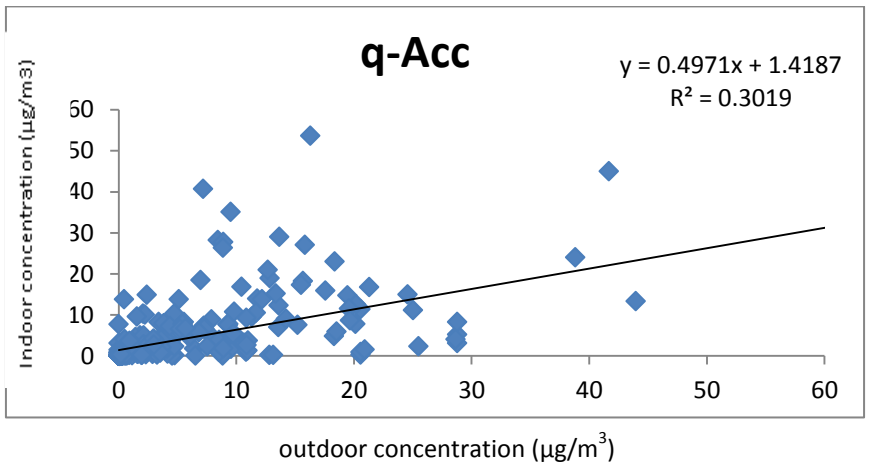
To evaluate the effect of outdoor PM bounded metal concentration on indoor concentration, a regression analysis method has been adopted and implemented in the study. The model proposed after Sangiorgi et al. (2013) is adopted in which indoor concentration is treated as dependent variable and is a function of outdoor concentration (independent variable). Linear regression analysis corresponding to following equation was applied

$$Cin = Finf.\ Cout + Cig$$

The slope of the regression line corresponds to the fraction of outdoor generated PM penetrating into the indoor environment (F*inf*) while the intercept is a measure of contribution of indoor sources (C*ig*). The $R^2$ value obtained from linear regression plots is used as an indicator to which a PM species measured indoors is attributed to infiltration from outdoors.

Seasonal-average indoor-outdoor regression of varied particle sizes has been explored and the plots are indicated in Fig8.



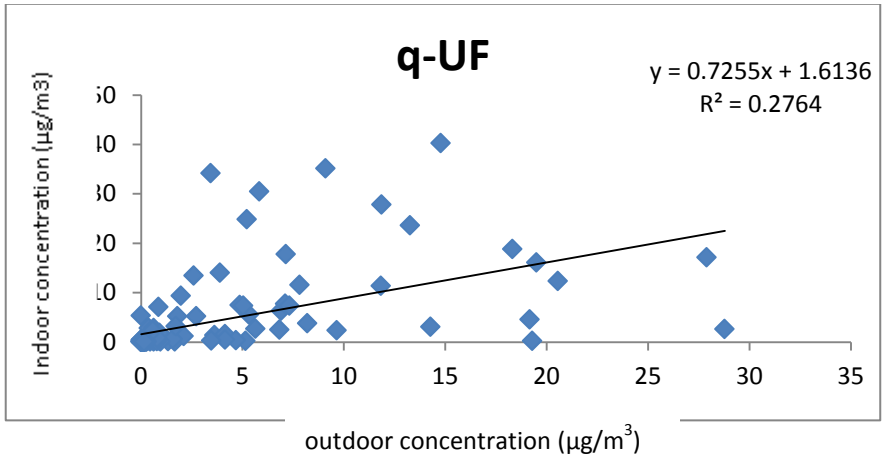
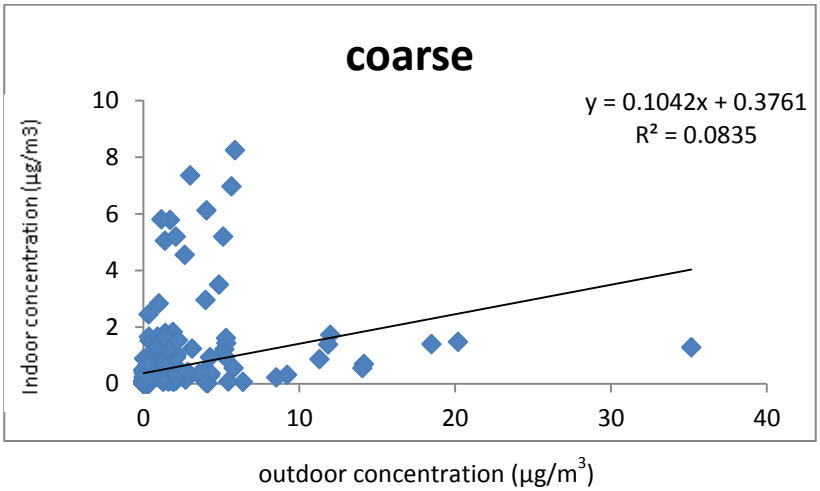
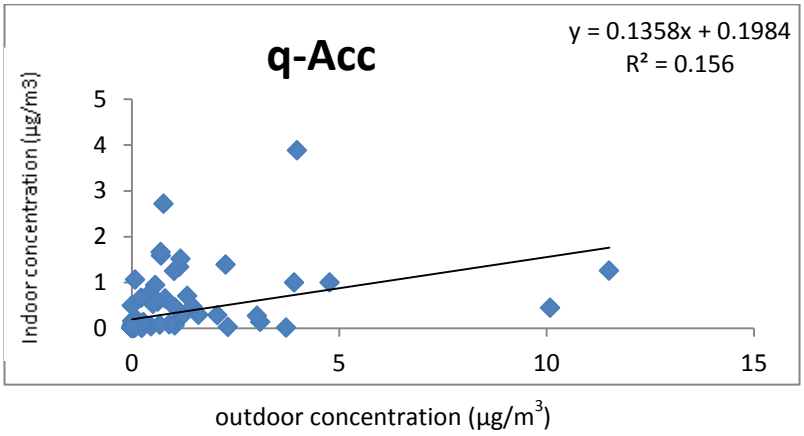




**Fig. 8(a)** Indoor-outdoor regression plots for winters



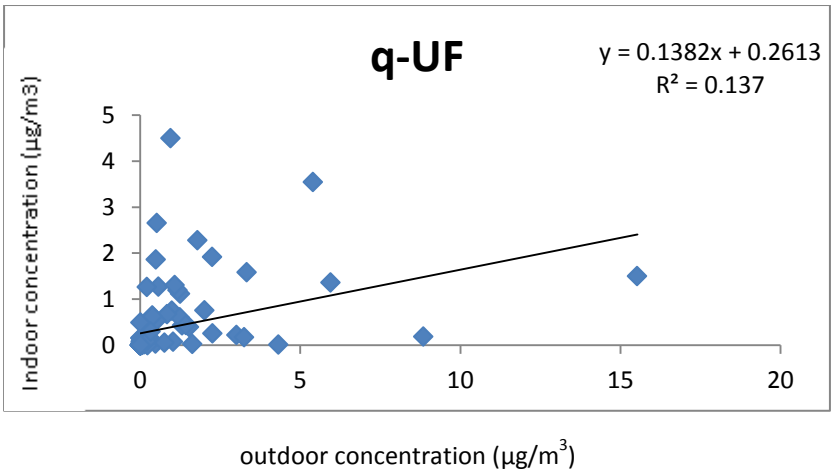
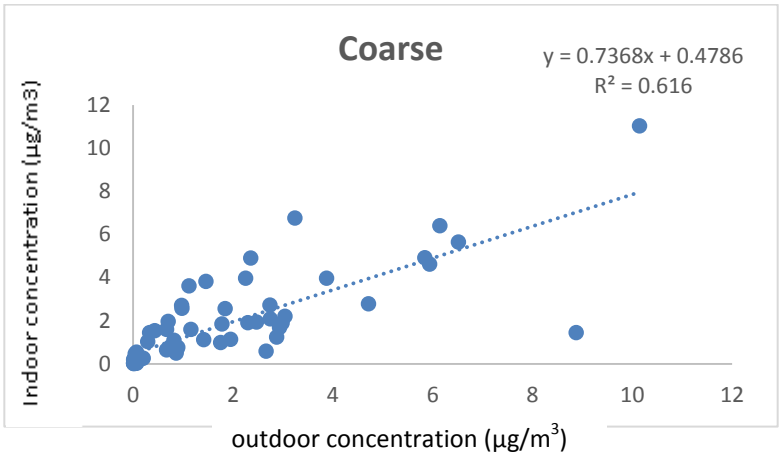
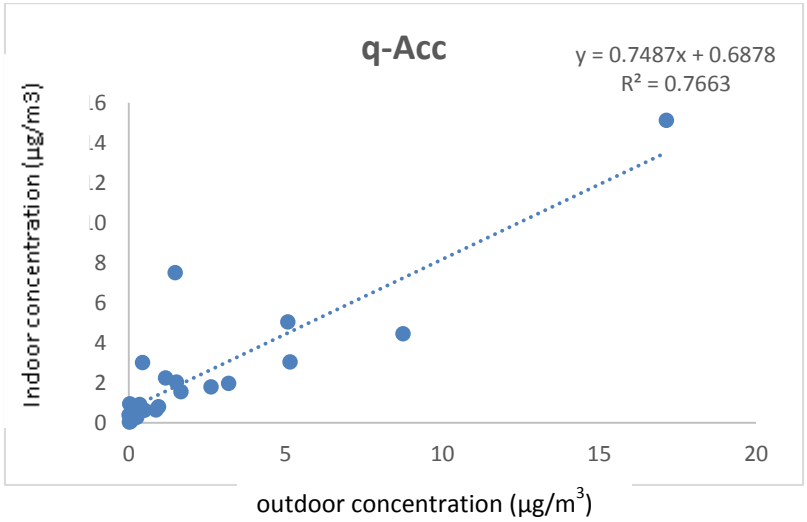




**Fig. 8(b)** Indoor-outdoor regression plots for monsoons



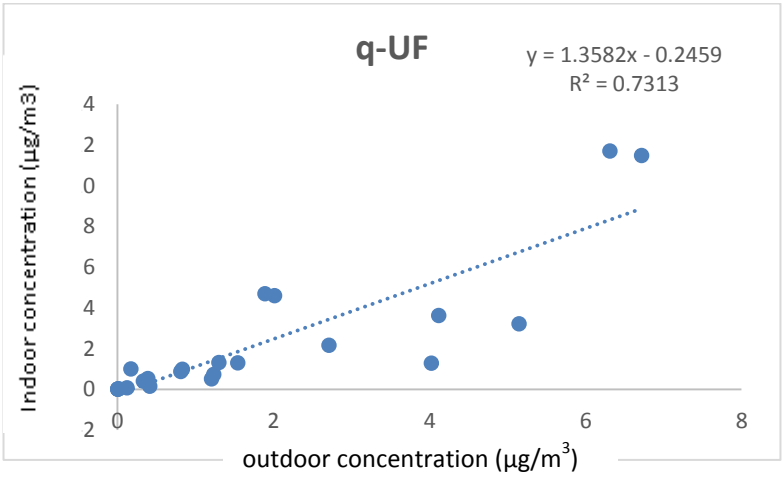




**Fig. 8(c)** Indoor-outdoor regression plots for summers

Results suggest that elements in q-UF and q-Acc range presented comparatively higher correlation slopes (F*inf*) than larger sized particles (coarse mode). This further reflects that a significant fraction of elemental indoor concentrations in q-Acc and q-UF modes can be attributed to outdoors.During monsoons, flat slopes obtained for coarse mode particles elucidate high deposition velocities and low penetration efficiency. $R^2$value (coefficient of determination) of the plots further indicates the contribution of outdoor concentration in explaining variations for indoor concentrations. As observed, the $R^2$ value for coarse particles remain to be lowest during monsoons (0.0835) and winters (0.2663) thereby suggesting that there may be significant contributions of indoor sources to the metals (Cig= 0.38 for monsoons and Cig=1.298 for winters) (Chen and Zhao, 2011).This might also be related to the wash out of coarse particles from outdoor atmosphere during monsoons. Summers presented comparatively better correlation for all the three particle size modes. Literature has associated higher indoor-outdoor correlation attributes to high frequency of open windows in summers (Kearny et al., 2014, Massey et al., 2012)even though window opening was also observed during day time in winters in the current study. According to MacNeill et al. (2012), absolute temperature difference in summers brought by the usage of air conditioning (in roadside and few of the urban homes) is expected to increase infiltration through creation of pressure differential that increase air exchange through doorways and window slits.

Moreover, high wind speed usually occurring during dust events in summers also contributes to high infiltration of particles (especially q-UF) in indoors.Although ultrafine particle loss through Brownian diffusion during infiltration process is known to occur, yet in our study ultrafine particles reported higher infiltration capacity whereas accumulation mode particles showed a good correlation.

In our present work, we also attempted to identify infiltration effect and indoor-outdoor correlation with reference to spatial variability. In our study, surprisingly, roadside homes recorded poor correlation ($R^2$= 0.169) and lowest infiltration factor (Finf= 0.325). This can be attributed to construction parameter(building tightness) with more mechanical (use of air conditioning)than natural (window opening) ventilation that may have resulted in a verylow penetration of the ambient PM, for all sizes. Older homes as of urban sites were associated with high $F_{inf}$(1.039) and a good correlation ($R^2$= 0.355) which may likely be due to deterioration of building structure with time enhancing high frequency of air (pollutant) exchange (Kearny et al.

2014). For rural homes ($F_{inf}$= 0.442; $R^2$= 0.411) other factors like size of window openings affected by window type contribute to the unexplained variability of indoor-outdoor correlation.

## 11.Bioavailability Index

The annual average total concentration of all elements in $PM_{2.5}$ was 7.28 µg/$m^3$ in which soluble fraction accounted to 1.97 µg/$m^3$limiting itself to 27.07%. For coarse fraction ($PM_{2.5-10}$), the value bounded to 14.53%. This shows the impact of smaller size particulate in simulated lung environment. This is in concurrent with studies that have shown that fine particles contain more mobile and bio accessible fractions (Caneparti et al., 2014, Jiang et al., 2015).

A closer look at the size segregated trend of BI of metals (annual average) has been depicted in Fig9.

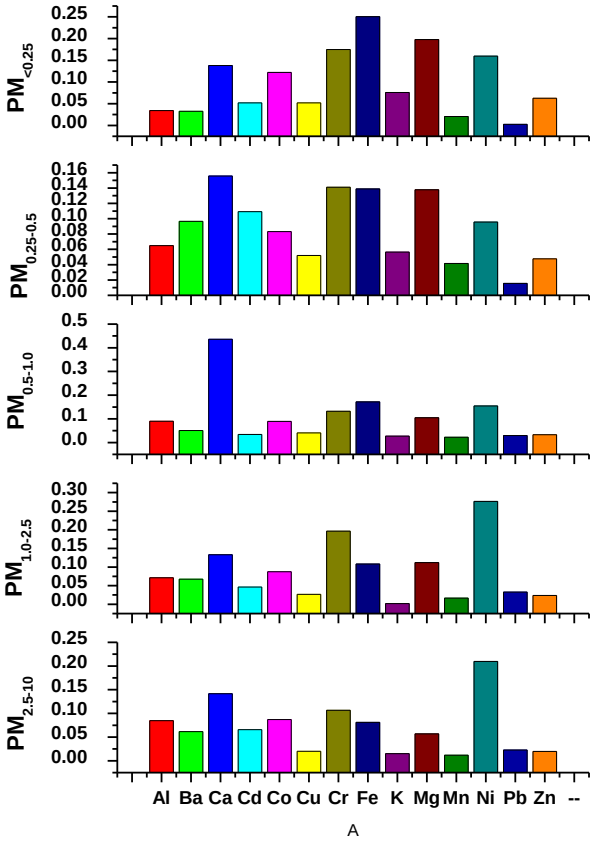



**Fig.9:** Annual average BI (bioavailability index) of metals in varied PM size fractions

From Fig. 9., it can be observed that all the metalsin finer size particulate had higher BI; generally attributed to rise in particle surface area to volume ratio with decrease in diameter; in turn inferring higher chance of getting adsorbed into the body. Metals such as Zn, Mg, K, Fe revealed highest BI in ultrafine size whereas for the remaining metals, highest BI was revealed in$PM_{2.5\text{-}0.25}$. These results show that metals in UF and accumulation stage were more bioavailable than coarse stage.

Apart from size-dependency, bioavailability is known to exhibit elemental variability. Metals showed the following trend for BI:

Ca> Ni> Fe> Cr> Mg> Co> Al> Ba> Cd> Cu> Zn>K> Mn>Pb.This elemental trend for BI was similar in both $PM_{10}$ and $PM_{2.5}$ except the fact that Cr showed comparatively higher BI than Fe in $PM_{10}$ than $PM_{2.5}$.

Overall, the result indicates that in indoor fine particulate ($PM_{2.5}$), 68.6% of Ni,64.4% of Cr,38.2% of Co, 24.8% of Ba, 24.2% of Cd, 17.1% of Cu, 10.1% of Mn and 8.1% of Pbcontributes to bioavailability by inhalation. From this observation, it can be inferred that Ni, Cr, Co, Ba etc. though regarded as minor elements, exhibited higher bioavailable fractions; that again becomes a concern of utmost attention.

The BI demonstrated a mixed elemental variation between summers and winters; although monsoons reported lower values of most of the elements (Fig. 10). During summer, the sum of BI of all analysed elements in coarse and fine PM was 1.561 and 1.475. These values were nearly comparable to winters with total BI amounting to 1.464 and 1.508 in coarse and fine PM respectively; although opposite trend was seen in summers with coarse PM reporting high BI than fine PM. However, monsoons recorded lowest BI in both coarse and fine PM.

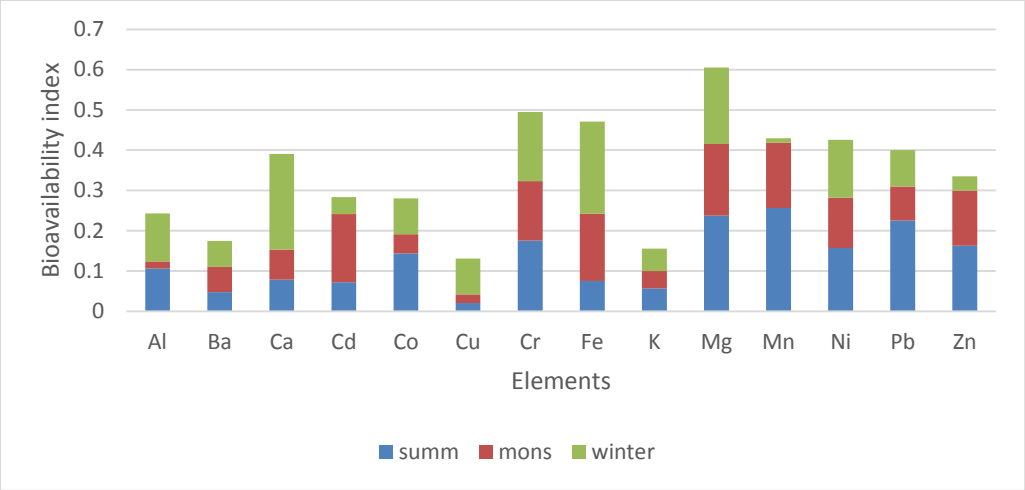



**Fig10.** Seasonal average of BI (bioavailability index) of elements in PM

Thus, according to the seasonal average fraction of soluble concentration in total elemental concentration (also refereed as BI), monsoons season can be comparatively considered safer with lower shares of critical elements w.r.t toxicity and bioavailability of metals than other seasons. Toxic elements such as Co, Cr, Mn, Ni, Pb, Zn showed higher fraction of bioavailable concentration in summers indicating their ease of availability to human body.Generally, it can be concluded that although winter is a season with high particle mass concentration, it has at the same time lower shares of critical elements with respect to bioavailability of metals than summers. This broadly infers that during annual course, times with low PM mass concentration (summers in our study) are not necessarily the periods safe for human health and thus negative health implications from distinct metals can also occur during summer. Overall, these results suggest complexity of different emission sources and formation mechanism of these elements during course of year.

## 12.Health Risk Analysis

Risk quantification (a four-step process) for each receptor (children and adult) residing in homes by metal-bound particle among the four singular sampler stages ($PM_{>2.5}$, $PM_{2.5-1.0}$, $PM_{1.0-0.5,}$ $PM_{0.5-0.25,}$ $PM_{<0.25}$)was performed using a four-step methodology as prescribed by USEPA (2009).At the first place, Al, Ba, Cd, Co, Cr, Mn, Ni were identified as toxic elements inducing non-carcinogenic effects and Cd, Co, Cr (VI), Ni, Pb were identified as carcinogenic elements. The total Cr concentration was used in this study (Taner et al, 2013). It is to be noted that both Cr

(VI) (Group A human carcinogen) and Cr (III) (Group D human carcinogen) exists in air with ratio of 1:6. Thus the risk of Cr (VI) was calculated as $1/7^{th}$ of the total Cr concentration.

The chronic exposure concentration in the next step was calculated using the following formula (USEPA, 2009)

$$EC = (CA \times ET \times EF \times ED) / AT \qquad (1)$$

where: EC ($\mu g/m^3$ ) = exposure concentration (defined as time weighted average concentration based upon exposure scenario); CA ($\mu g/m^3$ ) = contaminant concentration in air; ET= exposure time(period over which a person is likely to be exposed over the course of a typical day) which in our study was 24 hours/day; EF (days/year) = exposure frequency (defined as the number of exposure events in an exposure duration) which was taken as 350 days/year; ED (years) = exposure duration (period over which a person is exposed during lifetime) which was taken as 20 years and 6 years for adult resident and child respectively; AT = averaging time (period over which exposure is averaged) that equals to ED in years x 365 days/year x 24 hours/day for non-carcinogens and LT (lifetime of 70 years) x 365 days/year x 24 hours/day) for carcinogens. All the above default values were applied keeping in mind the residential criteria as mentioned in USEPA (2014).

Risk characterization for a receptor exposed via inhalation pathway at last involved the estimation of the Hazard Quotient (HQ) (Eq. 2) and Excess Lifetime Cancer Risk (ELCR) (Eq. 3) for non-carcinogenic and carcinogenic risk respectively. (Taner et al., 2013)

$$HQ = EC / (\text{Toxicity Value} \times 1000\ \mu g/mg) \qquad (2)$$

$$ELCR = IUR \times EC \qquad (3)$$

The toxicity value refers to Chronic Reference concentration (RfC) (mg $m^{-3}$) and IUR ($\mu g/m^3$) = Inhalation Unit Risk. In accordance with Environmental Protection Agency (EPA), RfC is defined as an estimate of a continuous inhalation exposure to human population that is likely to be without appreciable risk of deleterious effects during a lifetime whereas IUR is defined as the upper bound excess lifetime cancer risk estimated to result from continuous exposure to a 1 $\mu g/m^3$ agent in air (USEPA, 2009).The values for RfC and IUR for different metals were taken from the databases provided by EPA's Integration Risk Information Systems. (https://rais.ornl.gov/tutorials/toxvals.html).

The annual non-carcinogenic risk (HQ)posed by all the metals in overall PM10was 10.50 while the value of carcinogenic risk (ELCR) was 2.17E-04 and 5.50E-05. This means that 217 adults

and 55 children out of 1 million are likely to develop carcinogenic effects in the sampled residences annually.

Table 11 and 12 depicts non-carcinogenic and carcinogenic risk respectively posed by different metals in size fractionated particulates.In our study it was noted that the overall non-carcinogenic and cancerous risk was posed by metals in different size ranges. As seen, the highest value of HQ is posed by metals in q-UF particles while carcinogenic risk (ELCR) is posed maximally by metals in coarse particles range. Overall the trend of HQ and ELCR is as follows: $PM_{<0.25>}$ $PM_{0.5-0.25}$>$PM_{2.5-10}$>$PM_{1.0-2.5}$>$PM_{0.5-1.0}$and $PM_{2.5-10}$>$PM_{0.5-1.0}$>$PM_{0.5-0.25}$>$PM_{1.0-2.5}$>$PM_{<0.25}$respectively.

These resultsemphasize the importance of the smaller sized ultrafine particles as an utmost cause of concern attributed to their high non-carcinogenic toxicityand also that the impact of coarse particles should not be excluded owing to their capability of causing additional carcinogenic risk when deposited in upper parts of respiratory tract.

In view of independent elemental hazard, highest non-carcinogenic risk was posed by Co followed by Mn and Ni while for elements s.a. Al, Ba, Cd, Cr the HQ was found to be below the benchmark limits (HQ>1). Thus, it is evident that Cr posed least non-carcinogenic risk; but in view of cancerous risk, Cr displayed highest value of ELCR(Cr(VI); Group A human carcinogen) among all metals; much higher than the acceptable benchmark level (1* 10−6) (USEPA, 2009) for both adults and children. This is followed by Co>Cd>Ni>Pb.The study takes inaccount the refinery dustform of Ni (Group A carcinogen) existence among other forms as it contains nickel subsulfate, nickel oxide and metallic nickel while Cd and Pb are known to be probable human carcinogen (BI category for Cd and B2 category for Pb) regarding their inadequate existence. In the present study, surprisingly all the metals exerted carcinogenic risk with exclusion of Pb (except q-UF range) and Ni in children.

Thus, considerable HQ and ELCR results obtained in the present study suggest receptors to be greatly prone to health risk factor posed by particlebound respective elements in their indoor environments over the annual course of year which are in concomitant with substantial health effects.

**Table 11:** Non-carcinogenic risk (HQ) posed by metal-bound size fractionated PM in both adults and children

| **Metal** | **PM2.5-10** | **PM1.0-2.5** | **PM0.5-1.0** | **PM0.5-0.25** | **PM<0.25** |
|---|---|---|---|---|---|
| Al | 0.21 | 0.26 | 0.21 | 0.28 | 0.43 |
| Ba | 0.05 | 0.04 | 0.04 | 0.04 | 0.05 |
| Cd | 0.57 | 0.79 | 0.66 | 0.42 | 0.65 |
| Co | 3.16 | 2.68 | 2.88 | 5.03 | 3.88 |
| Cr | 0.82 | 0.37 | 0.46 | 0.33 | 0.29 |
| Mn | 3.44 | 3.62 | 1.95 | 1.88 | 4.29 |
| Ni | 2.41 | 1.49 | 2.64 | 2.90 | 3.28 |
| **∑(NC)** | **10.65** | **9.25** | **8.83** | **10.89** | **12.87** |

**Table 12:** Carcinogenic risk (ELCR) posed by metal-bound size fractionated PM in

(a) Adults

| Metal | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.5-0.25 | PM<0.25 |
|---|---|---|---|---|---|
| Cd | 2.92E-06 | 4.08E-06 | 3.38E-06 | 2.18E-06 | 3.36E-06 |
| Co | 4.87E-05 | 4.13E-05 | 4.44E-05 | 7.77E-05 | 5.98-05 |
| Cr(VI) | 2.80E-04 | 1.26E-04 | 1.56E-04 | 1.13E-04 | 9.78E-05 |
| Ni | 2.32E-06 | 1.43E-06 | 2.54E-06 | 2.79E-06 | 3.14E-06 |
| Pb | 8.95E-07 | 8.13E-07 | 1.03E-06 | 1.74E-06 | 5.31E-06 |
| **∑($ELCR_A$)** | **3.35E-04** | **1.73E-04** | **2.08E-04** | **1.98E-04** | **1.69E-04** |

**(b)** Children

| Metal | PM2.5-10 | PM1.0-2.5 | PM0.5-1.0 | PM0.5-0.25 | PM<0.25 |
|---|---|---|---|---|---|
| Cd | 8.77E-07 | 1.22E-06 | 1.01E-06 | 6.55E-07 | 1.01E-06 |
| Co | 1.46E-05 | 1.24E-05 | 1.33E-05 | 2.33E-05 | 1.79E-05 |
| Cr(VI) | 8.41E-05 | 3.76E-05 | 4.69E-05 | 3.40E-05 | 2.93E-05 |
| Ni | 6.95E-07 | 4.30E-07 | 7.61E-07 | 8.36E-07 | 9.43E-07 |
| Pb | 2.69E-07 | 2.44E-07 | 3.09E-07 | 5.21E-07 | 1.59E-06 |
| **∑($ELCR_A$)** | **1.01E-04** | **5.19E-05** | **6.23E-05** | **5.93E-05** | **5.08E-05** |

Recently attempts have been made to assess the ELCR of bioavailable forms of the metal in addition to computation for its totalconcentration. The change in cancer risk when evaluated from total to soluble fraction of the metal has found to vary in inverseproportion with BI of that particular metal (Rohra et al., 2018a; Varshney et al., 2015). As an example, ELCR of total and soluble Cr(VI) sizesegregated concentration has been accounted with respect to BI value of metal as obtained in different size fractions of PM (depictedin Table 13).

As clearly visualized for Cr, for high BI value (e.g. in $PM_{1.0\text{-}2.5}$), the estimated cancer risk slightly changed from total tobioavailable while in contrast (i.e. for the small BI value observed in $PM_{2.5–1.0}$), the change was significant. In other words, lower carcinogenic risk values (5-9 times) were reported from water-soluble than total concentration of metals in PM.

Apparently, these results indicate that bioavailable forms rather than total contents of trace metals in PM should be considered in abetter way to assess the health and environmental risk likewise.

**Table 13:** Bioavailability index (BI) and associated ELCR in varied particulate size fractions of Cr concentration

| | **$PM_{2.5\text{-}10}$** | **$PM_{1.0\text{-}2.5}$** | **$PM_{0.5\text{-}1.0}$** | **$PM_{0.25\text{-}0.5}$** | **$PM_{<0.25}$** |
|---|---|---|---|---|---|
| **BI value** | 0.11 | 0.19 | 0.13 | 0.14 | 0.17 |
| ***Adults*** | | | | | |
| ELCR (total) | 0.280 | 0.125 | 0.156 | 0.113 | 0.098 |
| ELCR(soluble) | 0.029 | 0.025 | 0.021 | 0.016 | 0.017 |
| ***Children*** | | | | | |
| ELCR(total) | 0.084 | 0.038 | 0.047 | 0.034 | 0.029 |
| ELCR(soluble) | 0.009 | 0.007 | 0.006 | 0.005 | 0.001 |

ELCR= (Excess Lifetime Cancer Risk) is mentioned in $10^{-7}$

## 13. SOURCE IDENTIFICATION

### *Enrichment factor calculation*

Enrichment factors (EF) depicts the notch of enrichment of the metals in an air sample with that of a selected reference element that is entirely crustal in origin. Rahn (1976) introduced its concept in hand with the establishment of the extent of the abundance of a particular metal in air whose roots tend to be crustal in origin. The following formula is widely used for its calculation

$$EF = (Cx/Cref)_{sample} / (Cx/Cref)_{crust}$$

Here *Cx* and *Cref* are indicative to the concentration of metal and reference element in air and crust respectively. There is no fixed directive of the choice of reference element, rather depends upon the analyst. In the present study Al was chosen as the reference element as it has low spatial variability and stable chemical properties and also because soil is considered to be major source of Al in aerosol. Their concentrations in the upper continental crust were derived from Wedepohl (1995).

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 (Khillare and Sarkar, 2012; Rahn, 1976). Considerable variations are occasionally noticeable in line with the discrepancy related to crustal composition from one site to another and yet due to fractionating probability during formation of soil derived aerosols (Lakhani et al, 2008).

The values of EFs have been calculated separately by season and sampling site, with the aim of concluding a hypothesis about their spatial and temporal trends. Results are shown in Table 14 and Fig.11.

**Table 14:**Enrichment factors of elements with respect to earth's crustal composition

| Metal | Rural | Urban | Roadside |
|---|---|---|---|
| Ba | 1.18 | 4.69 | 2.50 |
| Ca | 4.81 | 7.47 | 2.30 |
| Cd | 4731.97 | 5126.25 | 6039.26 |
| Co | 102.95 | 116.89 | 87.08 |
| Cr | --- | 264.49 | 200.19 |
| Cu | 186.63 | 164.56 | 234.25 |
| Fe | 0.93 | 1.59 | 6.15 |
| K | 1.02 | 1.15 | 0.75 |
| Mg | 3.50 | 4.73 | 3.70 |
| Mn | 4.53 | 38.07 | 11.28 |
| Ni | --- | 171.82 | 136.77 |
| Pb | 295.27 | 251.73 | 340.97 |
| Zn | 65.96 | 1332.70 | 810.59 |

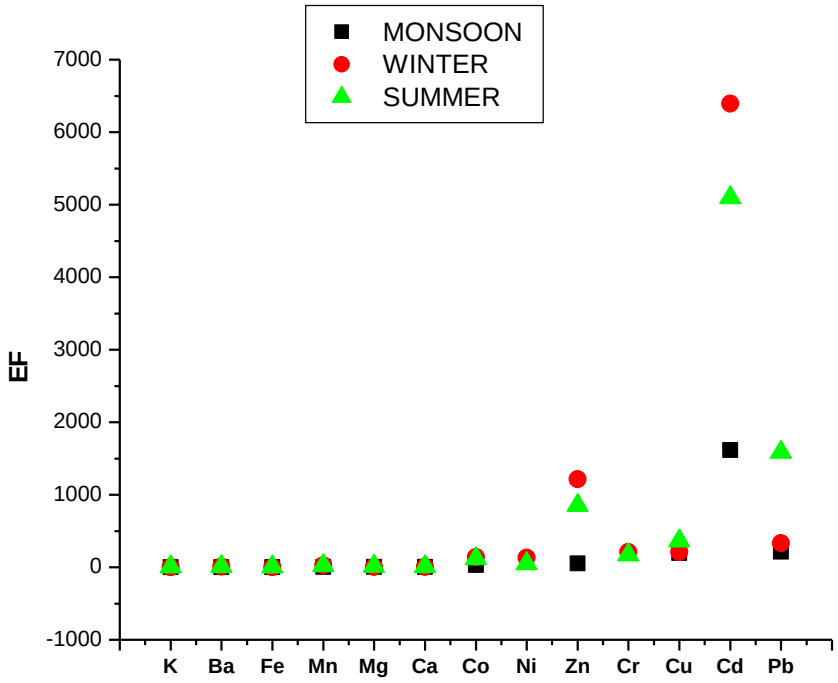



**Fig. 11:**Seasonal average of Enrichment factors (EF) of metals

Metals viz. Ca, Fe, K, Mg and surprisingly Ba had their EF values closer to unity(non-enriched) indicating natural contribution to be predominantwhile Cd, Cu, Ni andPb having EF>100 were thus termed 'highly enriched' having their roots originated from entirely anthropogenic factors. In general, metals showed higher enrichment at urban site while comparatively lower enrichment at rural site indicating predominance of soil crust sources at rural site.

Most of the metals in cold season were lower than in warm season probably due to presence of dust storms. Similar to the metal concentration patterns, the average EFs of most of the metals computed for summer and winter were higher than those calculated for monsoons. This demonstrates once again that wash out effect in monsoons determines a general removal of metals in airborne particulate matter.In our study, high TSP loadings in summers explained due to high consumption of fossil fuels shared by active winds and prevailing natural dust storms (SW direction prevailing winds) seems to overpower the usual effect of lower air turnover in cold periods that in general leads to accumulation of metals in atmosphere.

## 14.Morphological analysis

In view of understanding the sources of pollutants in indoor environment, electron micrographs (Fig. 12) of aerosols in three different size ranges in each of the urban microenvironment separated by income i.e. LIG, MIG, HIG are provided in each size range at all the three locations for summer season. The micrographs have been presented both in bulk and zoomed in view to understand the morphology. The EDX micrographs is provided besides the micrographs in Fig, 11 whereas the complied EDX data is shown in Table 16. Here, it is important to mention that the occurrence of large concentration of carbon and especially fluorine particles in all the samples may be attributed to matrix effect and coming from PTFE filter paper (Ikezawa et al., 2011).

*14.1Size range 1.0-0.5 μm (quasi-accumulation particles)*

From SEM micrograph, it can be inferred that in the size range 1.0-0.5 μm, there were noted differences between the particle morphology, density and elemental composition in LIG from that of MIG and HIG. At LIG, the particles are very dense with almost invisibility of filter paper and dominance of particles that are floccule in shape with cloud like aggregates. From EDX spectra, it is seen that F, C and O- rich particles dominate over other elements. Apart from that, Si, Mg, Ca, and slight amount of Al, Fe and K particles are also present in this size range in LIG that followed the trend O>C>F>Ca>Mg>Si>Al>Fe>K. This confirms the presence of soot particles. The sole cooking medium of LIG was biomass burning on *chullah* and mud stoves. This may be regarded as the reason of high concentration of F along with soot particles observed in the spectra. Moreover, the presence of K (regarded as a marker of biomass combustion) though in low percentage confirms biomass combustion as the dominant source. The absence of S in soot particles specifies that no gas to particle conversion has taken place that in usual occurs through transport. Considerable concentration of Mg along with Si and Al in indoor environment of MIG and HIG shows cosmetics and talc as one of the possible indoor sources of submicron particles. Al-Si-O linkage along with elements like Ca and Mg identifies the presence of aluminosilicates. Moreover, fewerconcentrations of crustal elements like Al, Mg over other elements confirms that in LIG most particles are primarily of anthropogenic origin. The existence of Ca and Mg may indicate quantities of calcium magnesium carbonates which are generally attributed to use of fertilizers and vegetative burning. As the areas of LIG had farms in

close proximity, the above sources seem to be well fitted into this criterion mainly accredited to infiltration from outdoor environment.

At MIG and HIG, the case seems to be somewhat different. The particles seem to be flaky with bar shaped particles also visible. The particles were loosely packed with fibers of filter paper also visible in hand unlike soot particles that had almost covered up in LIG. The trend of elements as revealed by EDX spectra was O>Si>C>Al>Fe>F>Ca>K>Mg>S and F>C>O>Si>Al>Ca>Mg of MIG and HIG respectively. High content of Si and O indicate the presence of aluminosilicates. Pipal et al (2011) identified two kinds of aluminosilicates based up on their Mg, Fe, Si, Al content. In our study, the minerals in HIG were of Felsic type while in MIG, contribution of mafic type aluminisilicates though in low amount also can also be witnessed. The puff shaped soot particles were present in HIG unlike chain like aggregates in MIG. Mineral particles are evidenced more in MIG in comparison to HIG which can also be confirmed through EDS spectra details. Slight decrease in C content and very low decrease in F content in MIG as compared to other categorized home point towards low usage of coal combustion practice. It is generally observed that as we proceed up the ladder, people living did not use solid fuel for cooking and heating, instead use better means of cooking including LPG and electric cooking, so C and F were not the only major elements in the MIG (18.12%) unlike LIG (81.35%). The residents of HIG made use of diesel generators in case of power failures that may have attributed to rise in the percentage of F and C in HIG (81.35%) (Webber, 2009).

14.2. *Size range 0.5-0.25µm (quasi-accumulation particles*)

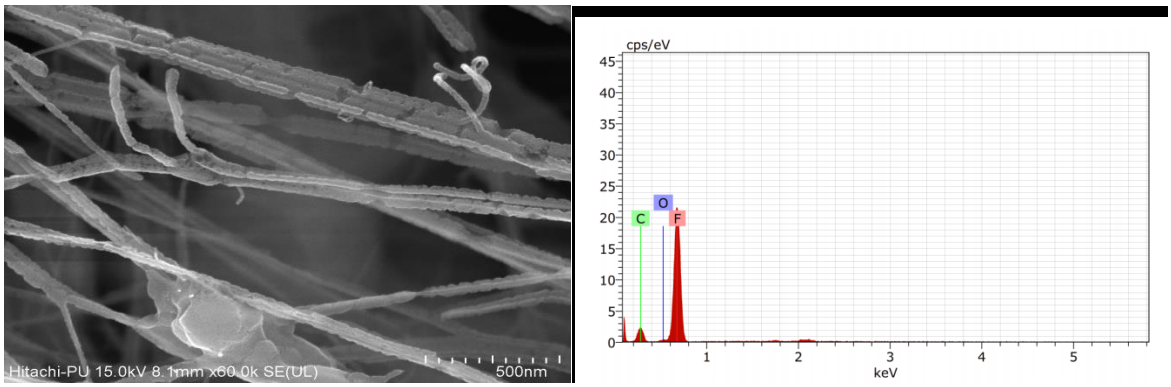
The particles in this size range exhibited regular shapes indicating their secondary reaction origin unlike geological origin in larger size range which can be inferred by their irregular shape (Shi et al., 2003). Another difference which is to be noted is that for LIG, the proportion of soot is greater in this stage while elements including Fe, K, Mg having crustal origin seems to be absent in this stage unlike bigger sized (1.0-0.5µm) particulates. Trace amounts of Si, Al and O present may point towards aluminosilicates specifically felsic type. The SEM micrograph reveals cloud like soot particles to occupy all over the spectral micrograph.

The EDX spectra revealed the trend O>C>Si>F>S>Al>Fe>K>Ca>Mg>Na and O>C>Si>Al>K>S>Fe>Ca>Na>Mg>Cl for MIG and HIG respectively. As seen, the spectra reveal high concentration of oxygen (unlike in LIG indicating solid and vapor phase aerosols in oxygenated form (Kushwaha et al. 2013). The combination of sulfur, potassium with oxygen and

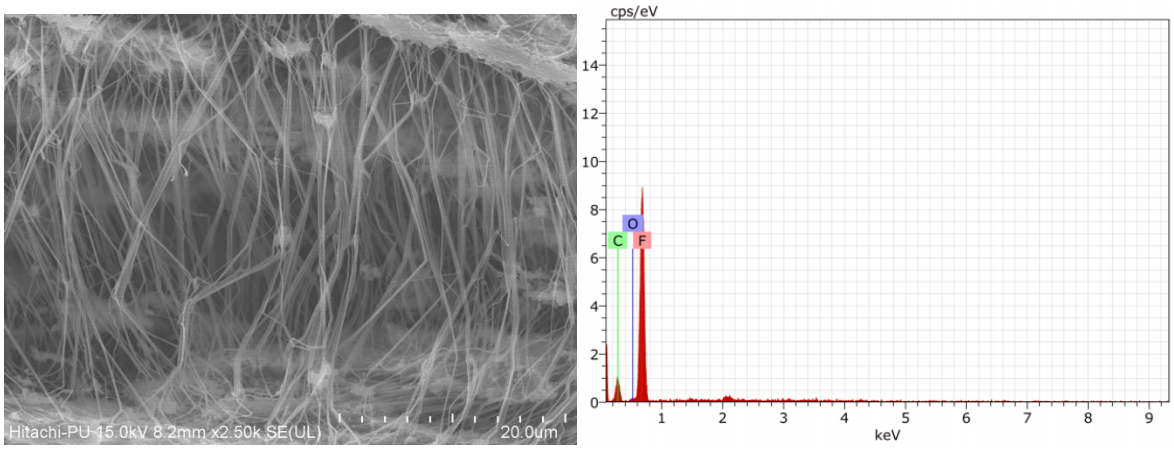
carbon may indicate presence of tar balls. For HIG, the particles are less densely packed with respect to MIG. The absence of Fluorine was highly noticeable. The edged defined particles may point towards sodium chloride crystals. The grouping of elements viz. S, O, Cl, Na indicate regular mineral particles (Lu et al., 2012). This combination of elements was absent in 1.0-0.5micron range where presence of Si, Al, K, Na, Ca indicated mineral particles of geological origin. Lu et al (2011) proposed that minerals with regular micro shape, fly ash and soot aggregated are found primarily in 0.5-0.25 μm particulates.

14.3. *Size range <0.25μm (quasi-ultrafine particles)*

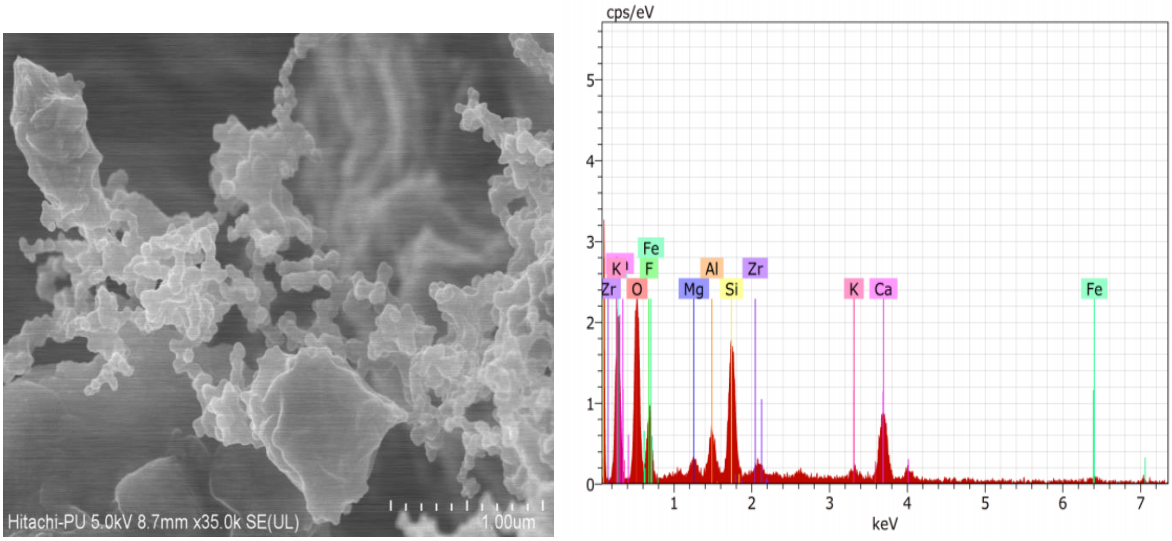
This range clearly demonstrated the clear dominance of soot particles in accord with literature (Srivastava and Jain, 2003). From spectral micrographs and EDX details, it is clear that in this particular size range, F is maximum followed by carbon at all the three sites pointing towards the presence of soot. The trend of elements was found to be F>C>Ca>Mg in LIG while F>C>Cl> Mg>S and F>C>O>>Si>S>K>Mg in MIG and HIG respectively. The fact that can be noticeable in this size range is that as we move down the range of particulates i.e. towards the smaller size, the oxygen percentage tends to decrease with complete absence in spectra of LIG. Thus, indicates the absence of oxygenated aerosol particles in lower size bins of PM. This indicates anthropogenic activity as the main source in this size range. Moreover, the absence of elements like Al, Si, Fe, K in the q-UF range suggests no contribution from crustal sources to this size range.



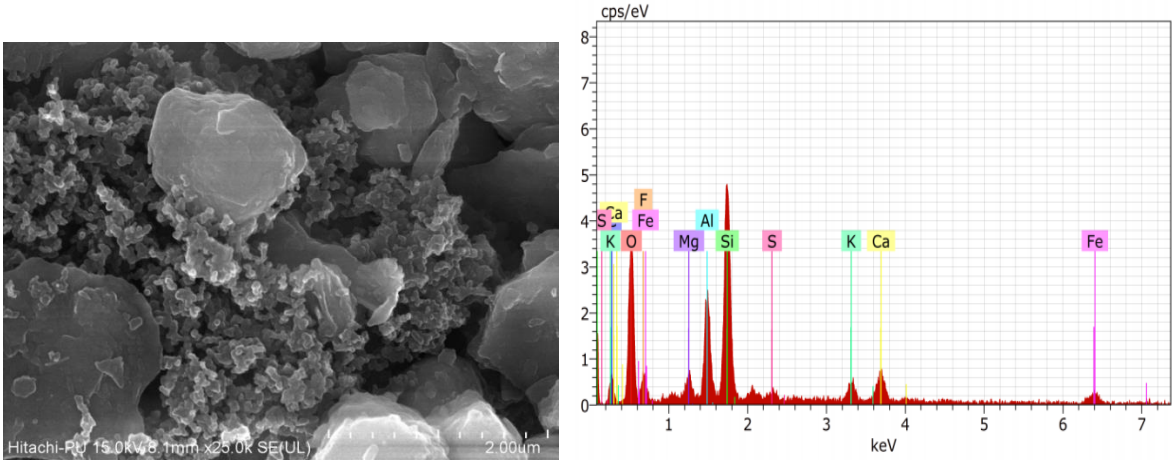

**Blank ($PM_{1.0-0.25}$)**



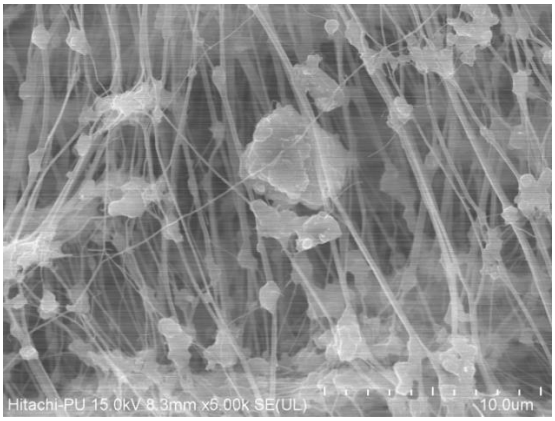

**Blank ($PM_{<0.25}$)**

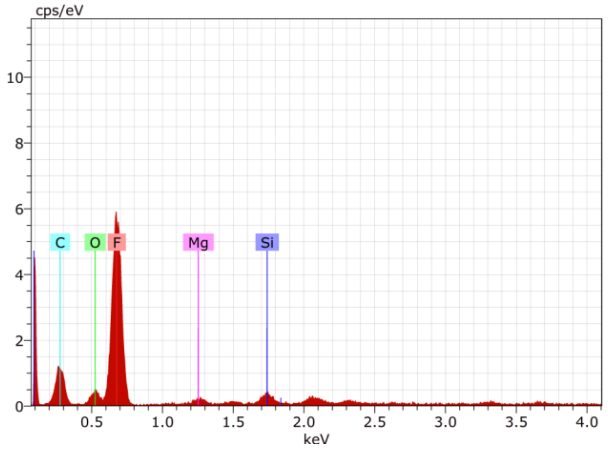



**$PM_{1.0-0.5}$; LIG**

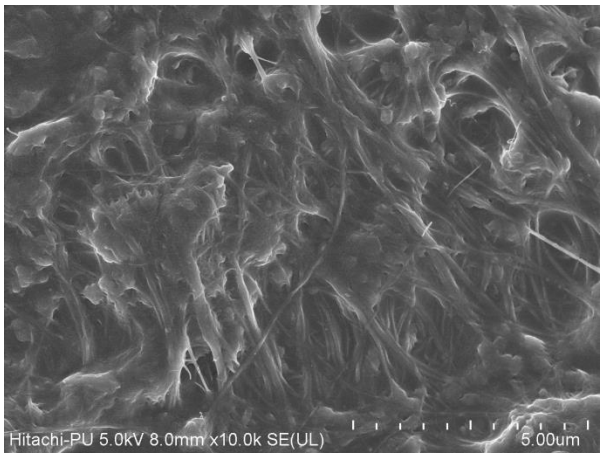


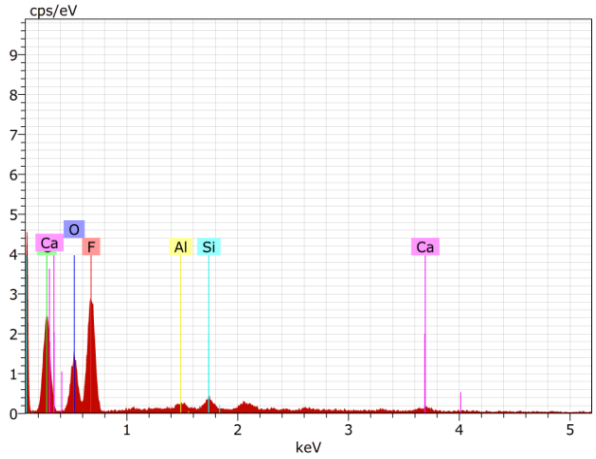

**$PM_{1.-0.5}$; MIG**



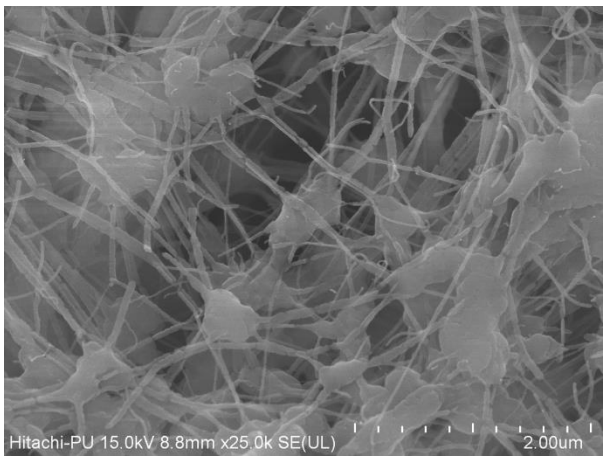



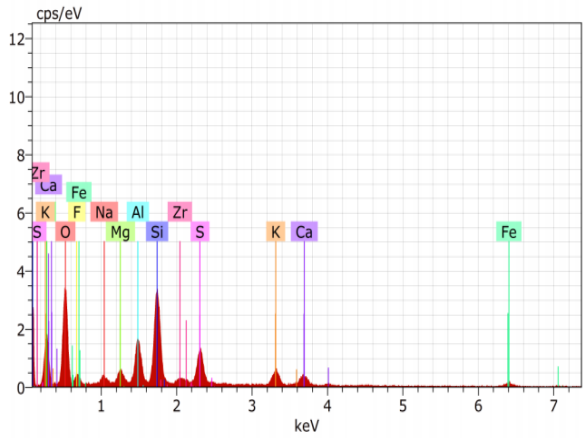

**$PM_{1.0\text{-}0.5}$; HIG**



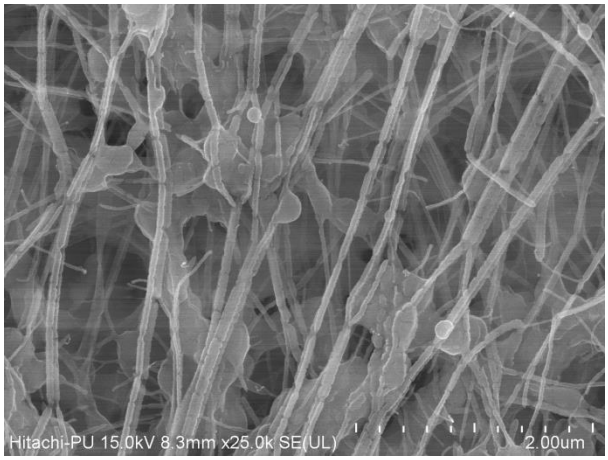



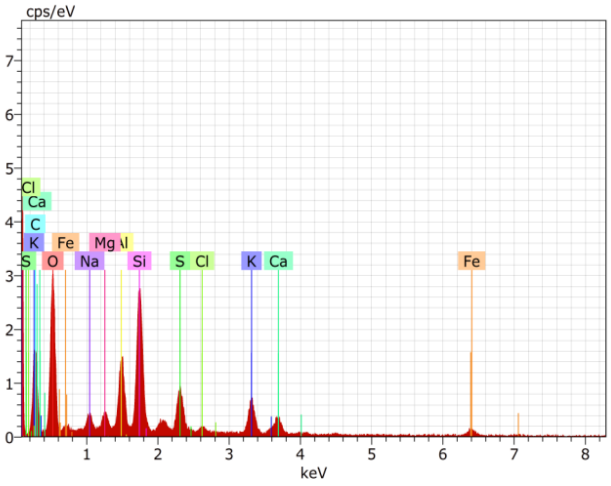

**$PM_{0.5\text{-}0.25}$; LIG**



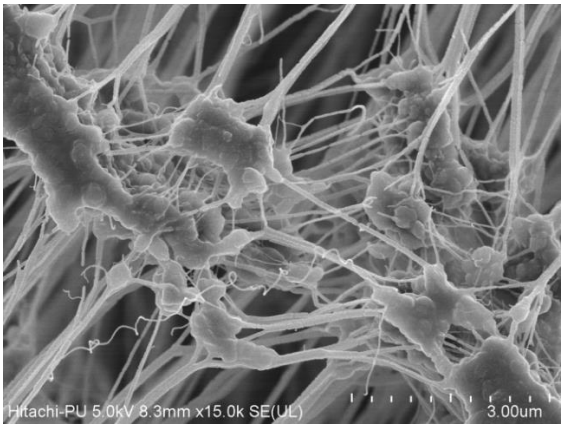



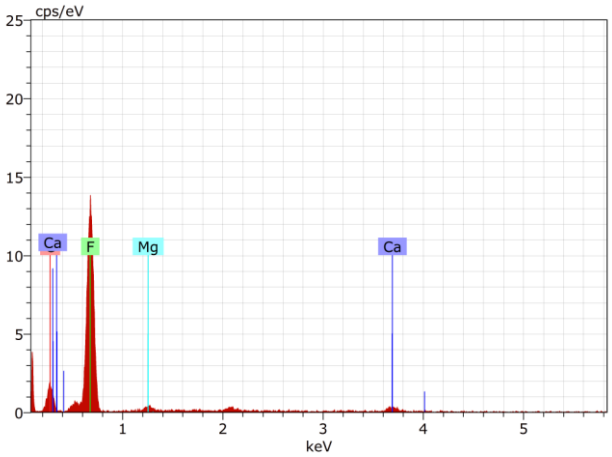

**$PM_{0.5\text{-}0.25}$; MIG**



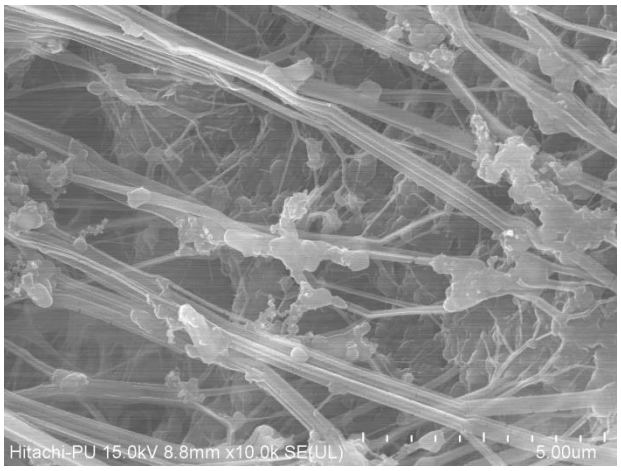



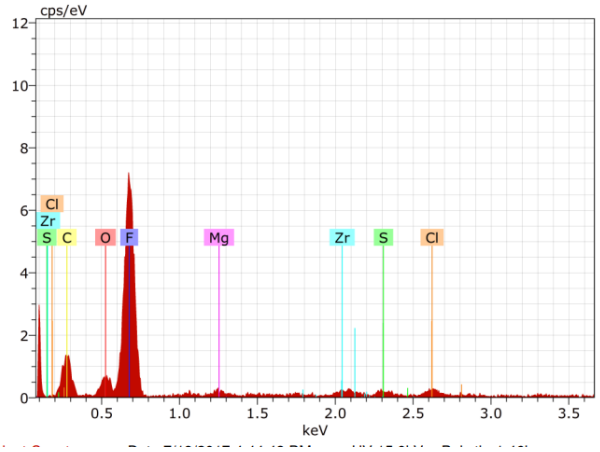

**$PM_{0.5-0.25}$; HIG**



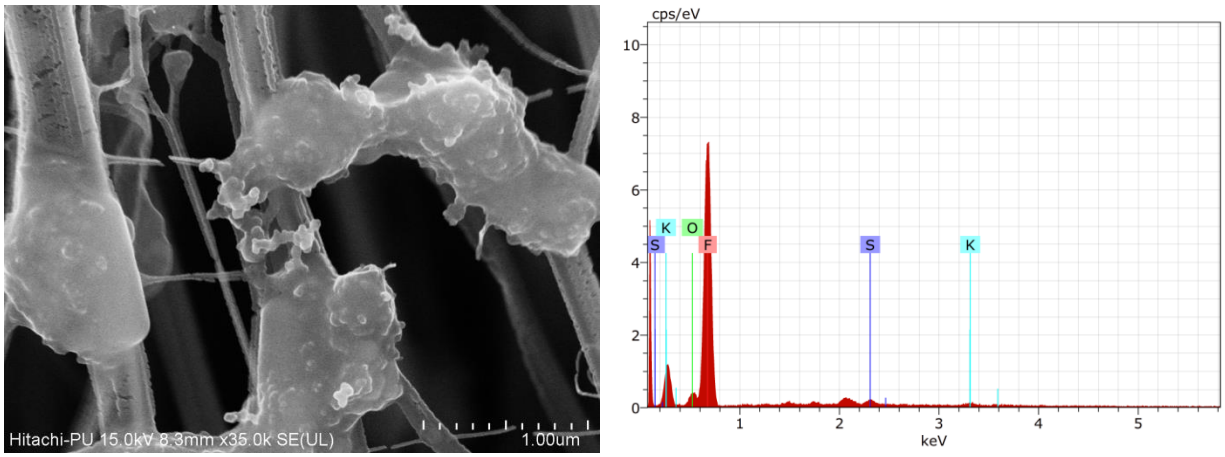




**$PM_{<0.25}$; LIG**




**$PM_{<0.25}$; MIG**




**$PM_{<0.25}$; HIG**

**Fig. 12:** FE-SEM micrographs with EDX spectra of varied particle size fractions in different urban indoor microenvironments. (LIG=low income group; MIG= middle income group; HIG=high income group)

**Table 15:** Percentage contribution (wt%) of each element in EDX spectra

| Site | PM size (μm) | F | C | O | Si | Al | Ca | Mg | S | K | Fe | Na | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *LIG* | 1.0-0.5 | 14.3 | 28.7 | 41.5 | 9.2 | 2.9 | 11.6 | 1.1 | - | 0.9 | 2.5 | - | - |
| | 0.5-0.25 | 54.6 | 36.3 | 43.4 | 2.3 | 1.3 | 2.0- | - | - | - | - | - | - |
| | <0.25 | 83.9 | 22.6 | - | - | - | 3.0 | 1.8 | - | - | - | - | - |
| *MIG* | 1.0-0.5 | 6.8 | 11.4 | 41.3 | 19.5 | 8.3 | 5.9 | 1.7 | 0.5 | 2.7 | 7.7 | - | - |
| | 0.5-0.25 | 11.3 | 27.0 | 37.4 | 12.12 | 5.4 | 3.0 | 1.5 | 11.0 | 3.5 | 3.7 | 1.2 | - |
| | <0.25 | 73.7 | 25.6 | 7.7 | - | - | - | 0.9 | 0.9 | - | - | - | 1.8 |
| *HIG* | 1.0-0.5 | 62.9 | 18.5 | 10.9 | 4.8 | 1.9 | 1.6 | 0.5 | | | | | |
| | 0.5-0.25 | - | 26.1 | 45.0 | 13.3 | 6.4 | 3.5 | 1.5 | 4.9 | 5.4 | 4.6 | 2.0 | 0.6 |
| | <0.25 | 76.7 | 25.0 | 4.8 | 1.6 | - | - | 0.6 | 1.0 | - | - | - | |

Blank refers to not detectable metal wt%.

## 15. CONCLUSION SUMMARISING THE ACHIEVEMENTS AND IMPORTANCE OF WORK DONE

The present study addresses the issue of indoor air quality for particulate concentrations of coarse, fine, and quasi-ultrafine PM with trace metal concentrations (Al, Ca, Ni, Cr, Cu, Fe, K, Mg, Mn, Pb, Zn) from different microenvironments of north central part of India (Agra) between April 2016 to February 2018. The three different microenvironments chosen were nine homes from urban, rural and roadside sites. Sampling was undergone in indoors and outdoors to monitor PM concentration in different sizes i.e. PM2.5-10, PM1.0-2.5, PM0.5-1.0, PM0.25-0.5, PM<0.25. Inter-size PM correlation, indoor-outdoor regression, size segregated distribution pattern analysis was used for the interpretation of data.

During the study period, annual average $PM_{10}$& $PM_{2.5}$ concentrations were 287.16±22.43 and 196.51±12.58 and 256.41±64.35 and 223.51±66.16 $\mu g/m^3$ for indoors and outdoors respectively. On comparison results were approximately 4-6 times higher than NAAQS (CPCB) and 13-15 times higher than WHO standards. This indicate that air quality at residential sites of Agra city is extensively affected by PM pollution in indoor environment of urban and rural homes while roadside homes (newly built with proper infrastructure) had better indoor PM quality. For outdoors, trend obtained was roadside>urban>rural. Seasonal variation indicated trend: winters >summers> monsoons. Fine particles were known to dominate (62-80%) of PM10 concentration in which q-UF particles occupied a significant portion (24-35%) of fine PM mass. Low linear relationship obtained between coarse and fine particles was attributed to their different origin, behavior and removal mechanism; while greater correlation between q-Acc & q-UF mode describe their inter-formation. Higher inter-mode correlation in winters and low in monsoons can be traced to factors *s.a.* stable atmospheric conditions and efficient gravitational settlement pertaining in winters and monsoons respectively. Higher contribution of coarse mode to TSP during summers was observed; whereas for winters and monsoons, q-Acc and q-UF range seemed to dominate. As per analyzing the aggregate relation between pollution-income, LIG of urban homes recorded 25-32% higher fine PM concentration than MIG and HIG. Temporal variation revealed that morning (7.00-11.00) and evening hours (5.00-8.00) recorded 78.6% higher $PM_{2.5}$ concentration than noon hours (1.00-4.00). Identifying the metal concentration, Ca, Fe, Al, Mg, K were termed as Group I elements (major) and Zn, Co, Ba, Cd, Cu, Mn, Cr, Pb, Ni

were classified as Group II (minor) elements. Interestingly, the sum of total metal concentration was observed higher in summers than winters unlike PM concentration that recorded higher concentration in winters. In view of size-segregated trend $PM_{1.0-0.5}$ recorded highest metal mass loading in ambient air whereas for indoors, heterogeneous variation w.r.t. particle size fraction was noted indicating strong indoor sources with consistently varying concentration. Differential distribution pattern of PM indicated a uni-modality with preference to q-Acc mode ($PM_{0.5-0.25}$ in indoor & $PM_{1.0-0.5}$ in outdoor). For summers and winters, bimodal pattern with secondary peak in coarse mode was identified. Elements s.a. Ba, Ni, Mn, Zn found in ambient air of roadside homes displayed a marked shift towards finer size with modal peak in q-UF range generally attributed to influence of fresh vehicular emissions on ultrafine particles. Indoor-outdoor regression results suggest higher infiltration capacity of q-UF and q-Acc ranged particles than larger size particles elucidating high deposition and low penetration efficiency for coarse particles. Summers presented comparatively better correlation between indoor and outdoor levels attributed to high frequency of window opening. Poor correlation ($R^2$=0.169) and low $F_{inf}$ (=0.325) recorded for roadside homes was attributed to their high building tightness with more mechanical than natural ventilation. Investigation of SEM-EDX data. In view of elemental bioavailability, Ni recorded highest BI (22.4%) followed by Mg (19.4%). Particle size effect on elemental bioavailability was assessed whereby metals in q-UF and q-Acc were more bioavailable (27.1%) than coarser range (14.53%). The bio-available concentration of toxic metals (s.a. Cu, Cr, Pb, Zn) exhibited a modal shift towards smaller particle size fraction; attributed to rise in particle SA/vol ratio with decrease in diameter. According to seasonal trend of BI, monsoon season can be considered comparatively safer with low shares of critical elements w.r.t bio-availability whereas highest BI of toxic metals obtained during summers. Overall, results suggest complexity of different emission sources and formation mechanism of these elements during course of year that poses a challenge for the control of pollution caused by these elements.

The comprehensive assessment of indoor PM in urban, rural and roadside homes with different particle size fraction including accumulation and ultrafine modes and their relationship to different outdoor sources with analysed toxicity of total and bioavailable metal concentration in human body would significantly contribute to the present understanding of people exposure in homes (that were previously considered to be safe) to the society. The obtained information

through measurements can be a leading step to work for consistency between emission standards and to develop a better understanding of particle size, source and related toxicity. Moreover, in view of void indoor standards in Indian context, such robust study can surely aid the regulatory agencies and policy makers for implementation of guidelines and environmental strategies vital for establishing cost effective pollution control policy. The outcomes of this study may offer opportunity in development of improved particle monitoring programme in residential areas and may aid too in establishing relatively small international elemental modality dataset that could be incorporated in the exposure and risk assessment of atmospheric particles. More studies are needed to strengthen this database and investigate the range of pollutant levels in both indoor and outdoor air. Moreover, these studies should also emphasize on the work that relates to the control of indoor particulate pollution.

## 16. STRATEGIES TO REDUCE EXPOSURE

As people spend more time indoors, the need for research for interventions that reduce exposure rises tremendously. It would be exceptionally valuable to establish monitoring networks that provide cross sectional and longitudinal information about the state of pollutants in representative buildings throughout the state. Many developing countries don't have monitoring of fine and ultrafine particles and also no national standards especially for indoors. Thus, efforts paved to obtain data in different microenvironments will help policy makers to design interventions. Apart from that, SOPs (Standard operating Procedures) should be designed in a way to determine chemical composition of particulate matter of all sizes especially in ultrafine range which may be utilised by the national and international pollution control boards.

Besides, the monitoring of exposure of PM in indoor spaces, research relating to better understanding of the relationship between human health and indoor environment are particularly required for all class of population to develop exposure atlas for regions. Such information would vastly enhance our knowledge and understanding of the chemicals that we inhale.

17. B**ENEFITS ACCRUED:**

***Publications:***

Six publications (five research papers and one book chapter) have been produced out of this project that are (Offprints attached)

- Himanshi Rohra, Rahul Tiwari, Puja Khare & Ajay Taneja, Indoor-Outdoor Association of particulate matter and bounded elemental composition within coarse, quasi-accumulation and quasi-ultrafine ranges in residential areas of northern India, *Science of the Total Environment*, 631-632: 1383-97 (**2018**) [**IF=5.1**]
- Himanshi Rohra, Rahul Tiwari, Neha Khandelwal & Ajay Taneja, Mass distribution and health risk assessment of size segregated articulate in different microenvironments of Agra, India- A case study, *Urban Climate*, 24: 139-152 (**2018**) [**IF=1.3**]
- Himanshi Rohra& Ajay Taneja, Indoor Air Quality scenario in India- An outline of household fuel combustion, *Atmospheric Environment*, 129: 243-255 (**2016**) [**IF-3.841**]
- Rahat Parveen. Renuka Saini & Ajay Taneja, Chemical characterization and health risk assessment of soil and airborne particulates metals and metalloids in populated semiarid region, Agra, India, *Environ Geochem Health*, DOI 10.1007/s10653-016-9822-4 (**2016**) [**IF-2.079**]
- Poorti Varsheny, Renuka Saini & Ajay Taneja, Trace element concentration in fine particulate matter (PM2.5) and their bioavailability in different microenvironments in Agra, India: a case study, *Environ Geochem Health*, 38: 593-605 (**2016**) [**IF-2.079**]
- Atar S. Pipal, Himanshi Rohra, Ajay Taneja & P.G. Satsangi, Particulate matter and its consequences in ambient air: The current scenario, Advances in Environmental Research, Vol 50. Edited by Justin A. Daniels. ISBN 978-1-63485-477-1, *Nova Science Publishers*, New York, 1-27 (**2016**)

***Presentations in workshops & conferences:***

- Environmental Air Determinants Importance of Including Indoor Settings in National Conference on Environmental Pollution Burden and Strategies for control 27-28 March 2018 in Isabella Thoburn(IT) college, Lucknow (**Key Note address**)
- **'**Socio-economic& location effect on fine particulate in residential homes of Agra, India' in International Conference of the Public Health Foundation of India and Pacific Basin Consortium on Environmental Health & Sustainable Development, 14-16$^{th}$ November 2017, New Delhi (**Poster Presentation**)
- 'Mass Segregation of Particulate Matter and Heavy Metals between Coarse and Accumulation Range in Diverse Indoor Microenvironments of Agra, India' in 5$^{th}$ International conference of ICC in Bali, Indonesia,7-9 June,2017 (**Oral Presentation**)

- Air Pollution studies in Agra and Challenges Ahead in Indo-US workshop on Combating Air Pollution in North India organized by IIT Delhi and RTI International USA 25-26 May, 2016 in Hotel Vivanta-Taj, Lucknow. (**Oral Presentation**)
- Indoor air pollution case studies in National Seminar on Environmental Protection and Sustainable Development Issues and Challenges(EPSDIC) 22-23 September 2016 in Sir C R Reddy Autonomous College ELURU, Andhra Pradesh **(Invited Talk**)

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