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RESEARCH ARTICLE

SEM-EDX analysis of size segregated particulate matter in Allahabad located in north India

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Abstract

Aerosol samples of size ranges PM $_{<1}$, PM $_{1\text{-}2.5}$, PM $_{2.5\text{-}10}$, and PM $_{\geq 10}$ were collected from urban and rural area of Allahabad. The average mass concentration of PM $_{<1}$ was 85.87 ± 37.45 µg/m^3, PM $_{1\text{-}2.5}$ 51.14 ± 9.48 µg/m^3, PM $_{2.5\text{-}10}$ 44.25± 15.35 µg/m^3 and PM $_{\geq 10}$ was 46.22± 17.03 µg/m^3 at urban site while at rural site it was found PM $_{<1}$ 65.51 ± 20.24, µg/m^3 PM $_{1\text{-}2.5}$ 50.91 ± 9.45, µg/m^3, PM $_{2.5\text{-}10}$ 48.7 ± 6.25 µg/m^3 and PM $_{\geq 10}$ 25.08 ± 14.60 µg/m^3. Scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX) was used to understand the differences in morphology, elemental composition of particulate matters viz. PM $_{<1}$, PM $_{1\text{-}2.5}$, PM $_{2.5\text{-}10}$ and PM $_{\geq 10}$ respectively. The SEM micrograph, size segregated aerosol was different at the two sites. It was observed that SEM-EDX is a useful method to identify the source of emission of particulate matter. The results revealed concentration of pollution is site specific but largely because of industry, vehicular activities, crustal dust and soil.

Introduction

Solid or liquid particules or both dispersed in gaseous medium, found in air are termed as aerosol [Reist, 1933; Vincent, 1989]. Atmospheric aerosol consists of particle of both natural and anthropogenic origins. It is now well established that the element from natural sources are generally found in the coarse particle whereas element emitted from anthropogenic activities are associated with fine particles (Seinfeld, 1986).The importance of atmospheric aerosols is because of their impact on human health (Dockery, *et at.*, 1993), ability to scatter light, thereby affecting visibility, and their role in global climate change (Seinfeld, 1986). Most importantly, the particle size distribution of aerosols is vital for an accurate and reliable assessment of their impact on human health (Fernandez, *et al.*, 2001). This is due to the degree of respiratory penetration retention, which is a direct function of the aerodynamic diameter of these particles. It has been found that particles >30 µm in aerodynamic diameter have a low probability of entering the nasal passage of humans. Particles with diameter >5 µm are usually filtered in the nose. Particles with <1-2 µm diameter predominantly get deposited in the alveolar region of the lung during normal breathing (Mccornac, 1971). The size distribution of particles and its associated metals, which are important from the viewpoint of identification of the source of pollution and their adverse impact on human health [Espinoza, *et al.*, 2001; Haywood, *et al.*, 1997). In addition, particles size characteristic of aerosol also affect cloud physics [Muller, *et al.*, 1999; Haywood, and Ramaswamy, 1998). In the past, several investigations have been carried out on the measurements of size distribution of aerosol and associated elemental concentration in urban areas (Kushwaha, *et al.*, 2012; Infante, and Acosta, 1991; Spengler, and Thurston, 1983; Zoller, *et al.*, 1974). Size distribution of atmospheric particles where heavy metals are associated, plays a very important role not only due to their toxicity when inhaled, but also because they control the extent to which metals may be dispersed via atmospheric transportation. The elevated metal concentration can pose serious risk to human health. Therefore, the determination of metal levels is usually limited to estimating the concentration of a number of metals in TSP, although these measurements can give some indication of the general pollution level in an area (Fernandez, *et al.*, 2000). Earlier studies have indicated that the rate of

respiratory diseases is considerably higher in urban rather than rural areas. The number of deaths from asthma, bronchitis and emphysema are significantly related to the concentration of fine respirable particles in the ambient air (Gomzi, 1999). Children with asthma residing in the inner city compose an interesting group as their ambient exposures to PM can be representative of influences that stem from local, city- wide or regional sources. The children can also be significantly influenced by their indoor environment and PM that infiltrates indoor from the ambient environment. There has been considerable research which implicates PM in asthma exacerbation with end point such as decreased lung function and increased visit to the emergency room (Srivastava, and Jain, 2009). In India very few comprehensive studies using SEM-EDX have been conducted, except two studies in which Srivastava and Jain (Srivastava, and Jain, 2007a) used SEM for the morphological analysis of pollutants inside an indoor and outdoor environment of Delhi. Other studies were done by Pipal (Pipal, et al., 2011). In the present study an application of elemental composition, morphology and particle density of aerosols determined by SEM-EDX techniques have been used, with respect to different sizes of particulate matter.

Material and Methods

2.1 Study area

The district of Allahabad is located in the south of Uttar Pradesh and lies between $24^0 47^/$ N and $25^0 47^/$ N latitude and $81^0\ 9^/$ E and $82^0 21^/$ E longitude. The maximum length from east to west being 117 km and breadth from north to south about 101 km, the entire area of the city is about 7254 sq/km. Allahabad enjoys different seasons. The average temperature during winter that extends from November to January is 15.28^0C and 8.7^0C respectively. Summer season extends from mid June to September where temperature shows a variation from 40.5^0C to 33.2^0C. Sampling for size segregated particulate matters was carried out from December 2011 to February 2012 at urban site which is directly affected by traffic emissions and other anthropogenic activities owing to the sites proximity to residential area and a prominent education hub. Rural site is situated approximately 30 km away from main city. Being at the outskirts of the city, the site is surrounded by open fields and agricultural farms. Therefore, the use of cow dung cakes as fuel has to be factored in the study.

2.2 sampling and analysis

Sampling was done for PM $_{<1}$, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$ and PM $_{\geq 10}$ on the roof of buildings at urban and rural site in Allahabad. The sampling sites showed in Fig.1. Size segregated aerosol samples were collected with Dekati PM Sampler, which runs at a constant flow of 30 LPM for 24 hrs. It has a portable Anderson impactor for the sampling of PM $_{<1}$, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$ and PM $_{\geq 10}$. The particles were deposited on 25 mm diameter GF/A glass filter paper for $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$ and PM $_{\geq 10}$ whereas PM $_{<1}$ were deposited on 47 mm diameter GF/A glass filter paper. Filter paper were weighed twice before and after sampling using four digits balance (Sartorius model - GD 603) with sensitivity of ± 0.1 mg. Before weighing the samples were equilibrated in desiccators at 20-30 ◦C and relative humidity of 30-40% was maintained in humidity controlled room for 24 hrs. Particulate matter mass was determined gravimetrically by subtracting the initial average mass of the blank filter from the final average of the sampled filter dividing by air volume passed through sampler. The characterization of particles in PM $_{<1}$, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$ and PM $_{\geq 10}$ were performed using scanning electron microscopy (SEM, Zeiss EVO 40) coupled with energy dispersive X-ray (EDX- pan analytical) for determination of morphology and chemical composition of particulate matter. SEM is a method for high resolution surface imaging. It uses an electron beam for surface imaging; its advantages over light microscopy are more magnification and much larger depth of field.

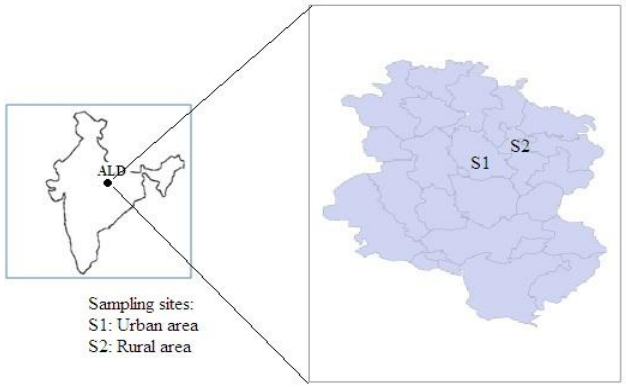


Fig.1 sampling site (not to scale)

Result and Discussion

3.1 Particulate mass concentrations

The average concentrations of size segregated particulate matter at rural and urban site are shown in Fig. 2 and 3. The average mass concentration of PM $_{<1}$ was 85.87 ± 37.45 µg m^{-3}, PM $_1$ 51.14 ± 9.48 µg/m^3, $PM_{2.5}$ 44.25± 15.35 µg m^{-3} and PM_{10} was

46.22± 17.03 µg m $^{-3}$ at urban site while at rural site was found $PM_{<1}$ 65.51 ± 20.24, µg m $^{-3}$ PM_1 50.91 ± 9.45, µg m $^{-3}$, $PM_{2.5}$ 48.7 ± 6.25 µg m $^{-3}$ and PM_{10} 25.08 ± 14.60 µg m $^{-3}$ respectively. Higher concentration of particulate matter at urban site is due to vehicular activities, crustal dust and crustal re-suspension of road dust. At rural site, burning of coal from brick kiln, wood, and cow dung cake as fuels and other anthropogenic activities are main sources of air pollution. Total concentration of particulate matter at rural site is 190.22 µg m $^{-3}$ and at urban site is 227.49 µg m $^{-3}$. Concentration of particulate matter exceeded the government norm (CBCB, 2009).

3.2 SEM – EDX Particulate matter analysis

3.2.1 PM $_{<1}$ at rural site

Fig. 4a and 4b show the scanning electron micrographs and EDX spectrum of aerosols in the rural area of Allahabad in the size range of PM $_{<1}$, and they represent spherical, irregular, fine rod-like as well as crystalline shapes. This is because rural area has relatively lower sources of pollution than that of urban ones. Fig. 4b shows the elemental composition of particles in which Ca, Fe, Zn and Ti rich particles are dominant. Both these figures show the differences between the particle density, morphology as well as elemental composition.

3.2.2. PM $_{<1}$ at urban site

Fig. 5a and 5b show SEM micrograph images of the particles in the size range $PM_{<1}$ in the urban area and it is obvious that these particles show irregular, spherical, fine-rod like and crystalline shapes. The elemental composition of these particles indicates that K, Ca and Zn rich particles were dominant. The other dominated elements were Ti, Al, Si, O. This could be inferred as the fly ash origin. These particles can be related to originate from construction activity, regional transport from the urban zones as well as agricultural vegetative burning and natural dust (Ramos, *et al.,* 2009).

3.2.3. PM $_{1\text{-}2.5}$ at rural site

From the above fig. 6a and 6b it is clear that, there is not much difference between elemental composition and morphology concerned. This is because of lower vehicular activities and almost industry- free ambient which in turn result in rounded shaped particles as well as deposited particles due to human activities (Ostro, *et al.,* 2001). The dominating elements here were Fe, Ca, K and Cl.

3.2.4. PM $_{1\text{-}2.5}$ at urban site

Fig 7a and 7b show the SEM micrographs of PM_1 at the urban roadside and the Fig 4b shows the EDS spectrum of the elemental composition. It can be concluded that the particles are of spherical, cluster and flaky shapes. Apart from the dominating elements viz. Fe, Ca, K and Cl rich particles, Na, Mg, Al and Si rich particles are also present in the size ranges which follow an irregular trend. This trend represents the presence of soot particles (Pipal, *et al.,* 2011).

3.2.5. PM $_{2.5\text{-}10}$ at rural site

Fig 8a and 8b show the SEM micrograph at the rural site for PM $_{2.5}$. This graph indicates that the particles are of flaky, cluster and irregular shapes, whereas the Fig 5b shows O rich particles are more dominated followed by Tl, Zn, Mg, Fe, K and Ca. In this micrograph Na, Zn and Si almost follow the same trend. The smoothly spherical size particles originate from fly ash (Xie, *et al.,* 2005).

3.2.6. PM $_{2.5\text{-}10}$ at urban site

Fig 9a and 9b show the SEM micrograph spectrum of aerosols in the size range PM $_{2.5}$ at the urban area. From the SEM images of the particles it is obvious that the particles of the size 2.5 show irregular, spherical and cluster shapes. Fig b shows the dominating particles K, Rh, Tl, Fe and Ca. O, Mg, Al and Si follow similar trend. All of these SEM images inferred Ca as the most dominated particle among others, which could be considered as the form of calcium carbonate related to the calcite phase, $CaCO_3$ (Ostro, *et al.,* 2001).

3.2.7. PM $_{\geq 10}$ at rural site

Fig 10a and 10b is the SEM micrographs of the PM10 at the rural area thus indicate mainly the fine rod-like crystalline shapes, spherical as well as irregular shapes. O, Ti, Zn, Fe, Ca, K and Si were more dominated followed by the Na, Mg and Al. Si is associated with Al, Na, Mg, O and Ca. This illustrated the presence of feldspar and clay minerals (Shao, *et al.,* 2007b). Al and Si might be the form of aluminosilicates which in turn might include kaolinite, illite and feldspar (Ostro, *et al.,* 2001).

3.2.8. PM $_{\geq 10}$ at urban site

Fig 11a and 11b show the SEM micrograph of PM_{10} at the urban site. The presence of particles reveals the dominance of vehicular rush in comparison to rural ones. It is clear from Table 1that the concentration of oxygen is maximum at all observations. As far as metals are concerned, Si is maximum (4.00) at the rural site for the particulate matter size PM $_{<1}$ followed by Na (1.46) and Al (0.96) respectively. Rh (0.00) and Pb (0.00) showed minimum contribution. This comparison represents the solid as well as the vapour phase aerosols in the oxygenated form. In both the rural and urban sites the other sources could be a vehicular as well as anthropogenic activity which covers Pb, Si, Al, K and Ca. Fig 11 shows the SEM micrograph of PM10 at the urban site. The presence of particles reveal the dominance of vehicular rush in comparison to rural ones. Fig11 b shows the comparison of elemental composition, where Ti, K, Ca and Pb dominated. Na reveals the

presence of crustal dust (Srivastava, and Jain, 2007a). The particles O, Na, Si, Mg and K follow the same trend. Pb came from gasoline.

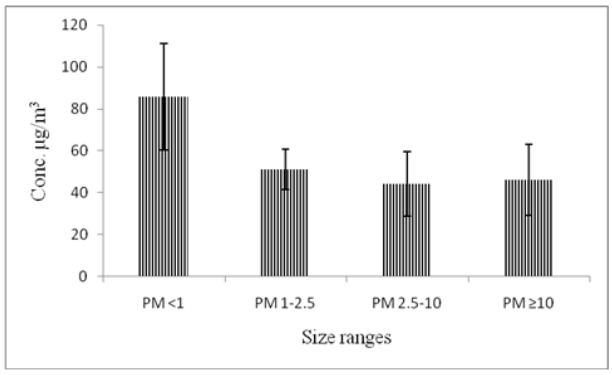


Fig.2 average concentration of size segregated particulate matter at urban site.

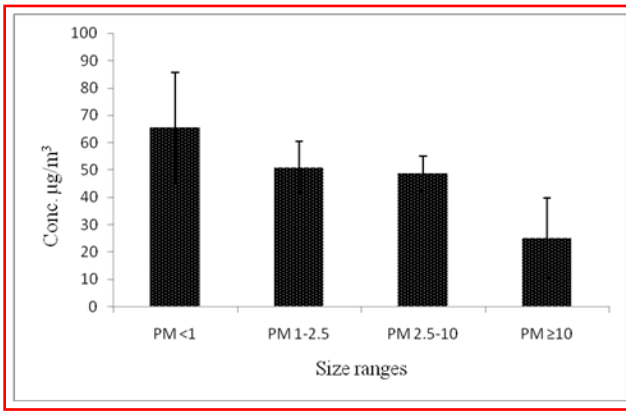
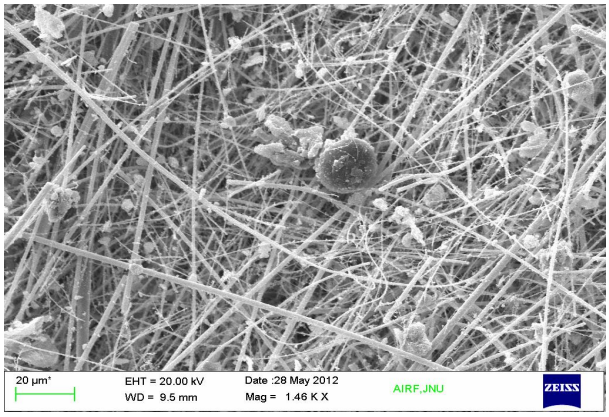
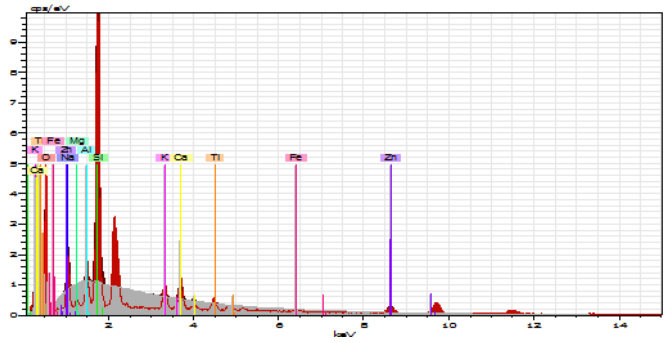


Fig. 3 average concentration of size segregated particulate matter at rural area

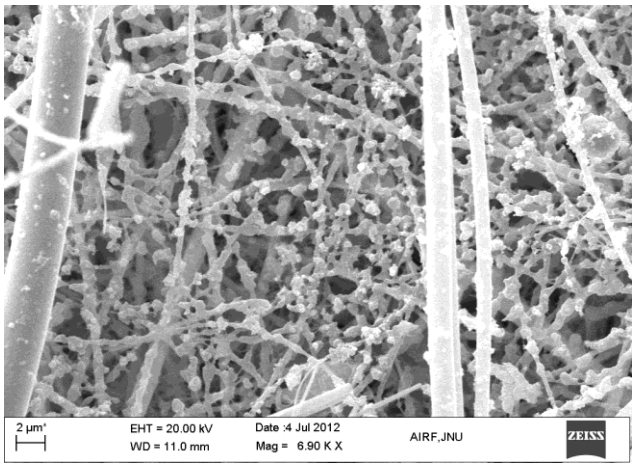


4 (a)



4 (b)

Fig. 4 scanning electron micrograph and EDX-spectra of aerosols in size ranges PM <1 µm at rural site.



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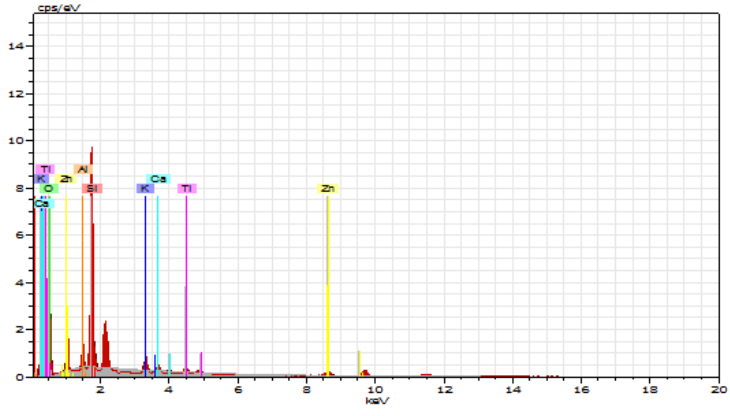
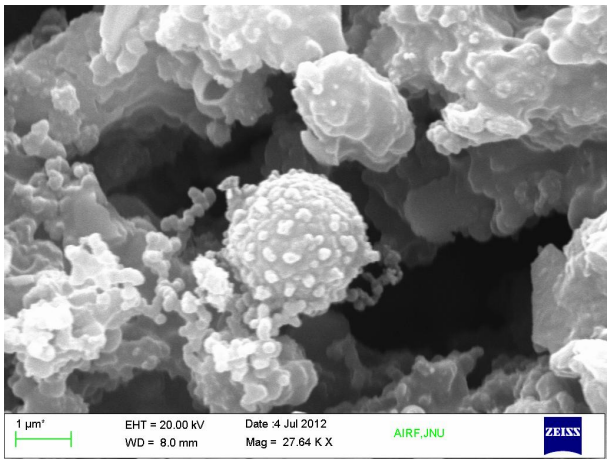
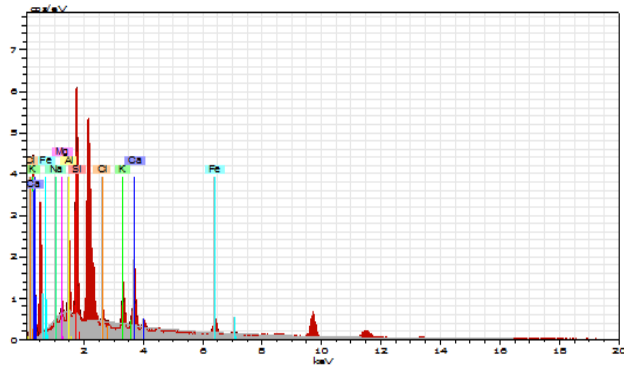


5 (b)

Fig.5 scanning electron micrograph and EDX-spectra of aerosols in size ranges PM <1 µm at urban site.

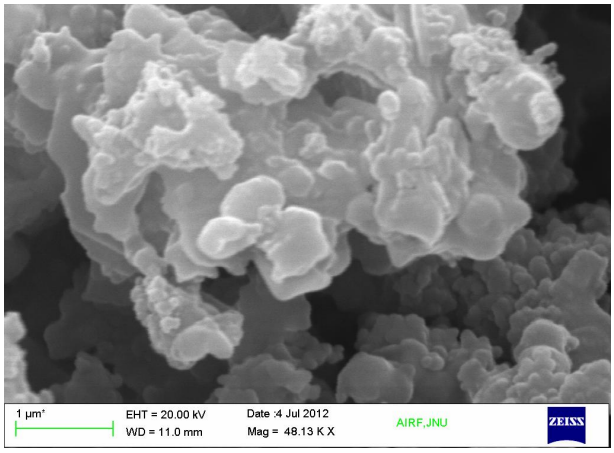


6 (a)



6 (b)

Fig. 6 scanning electron micrograph and EDX-spectra of aerosols in size ranges 1-2.5 µm at rural site.



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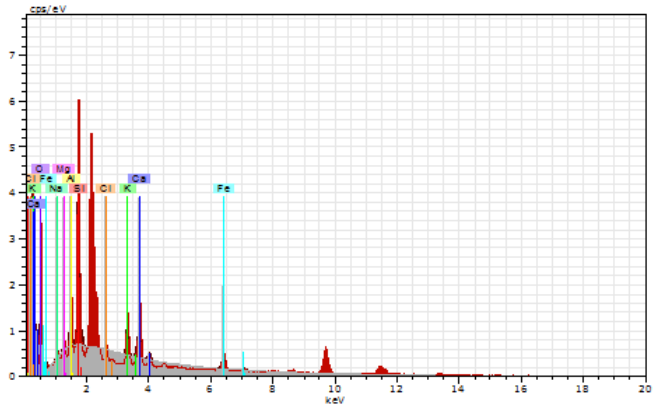
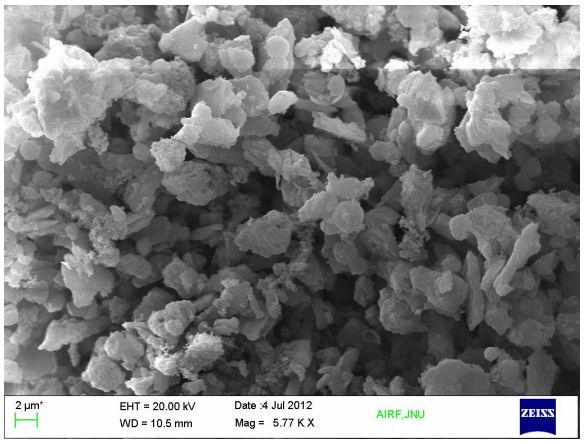
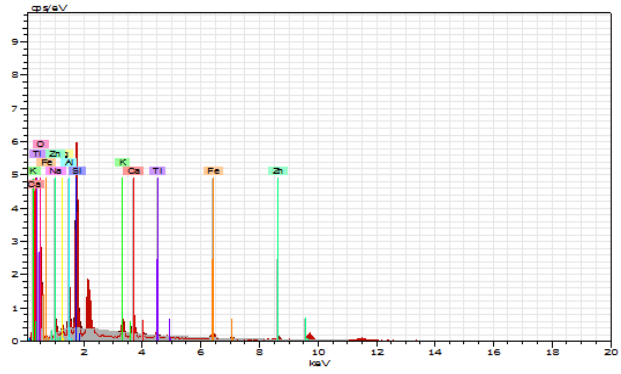


7 (b)

Fig. 7 scanning electron micrograph and EDX-spectra of aerosols in size ranges 1-2.5 µm at urban site.

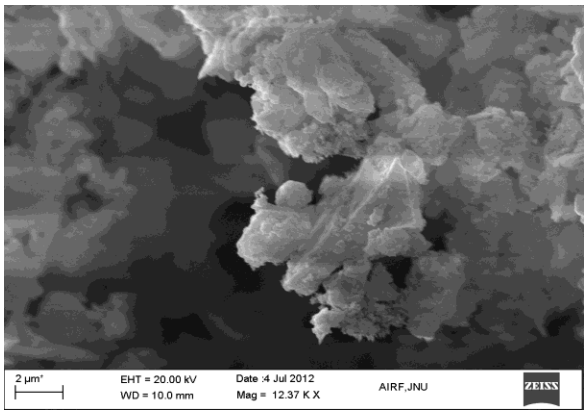


8 (a)



8 (b)

Fig. 8 scanning electron micrograph and EDX-spectra of aerosols in size ranges 2.5-10 µm at rural site.



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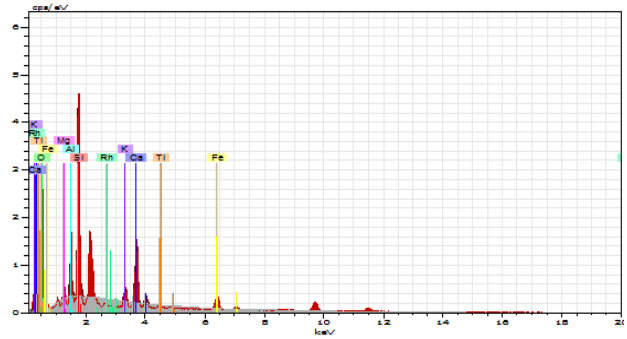
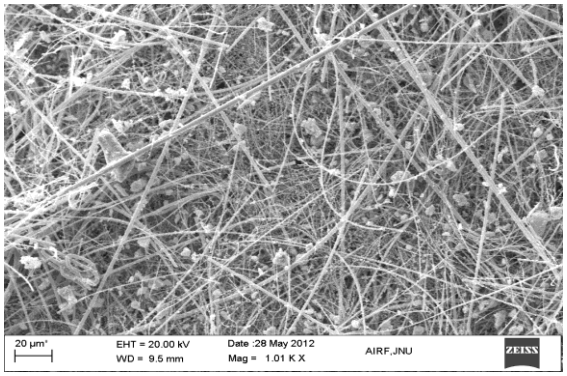
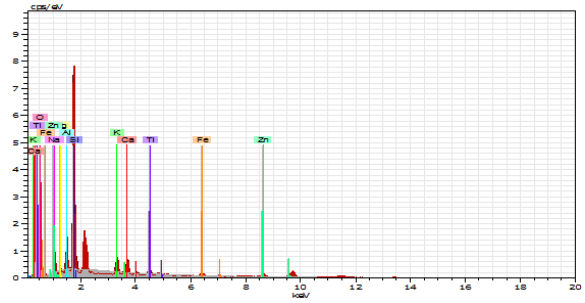


9 (b)

Fig. 9 scanning electron micrograph and EDX-spectra of aerosols in size ranges 2.5-10 µm at urban site.

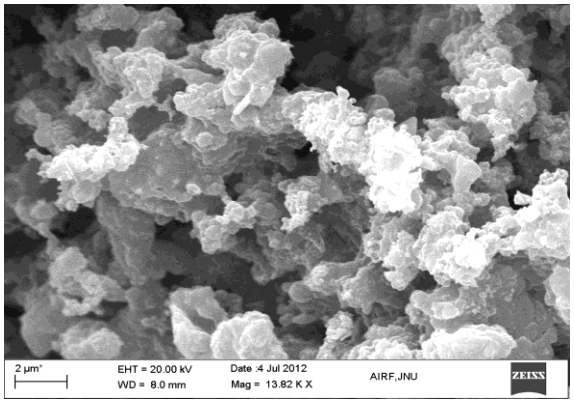


10 (a)

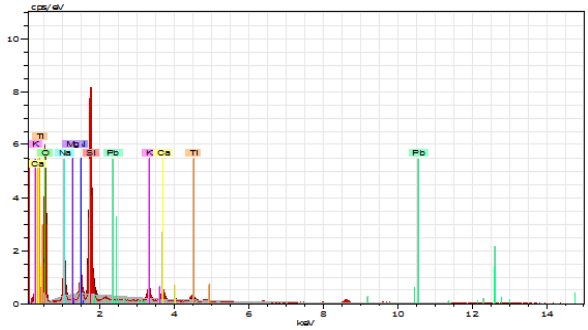


10 (b)

Fig. 10 scanning electron micrograph and EDX- spectra of aerosols in size ranges ≥ 10 µm at rural site.



11 (a)



11 (b)

Fig. 11 scanning electron micrograph and EDX-spectra of aerosols in size ranges ≥10 µm at urban site.

Conclusion

The SEM-EDX technique was used to characterize the size segregated particulate matters at Urban and Rural sites respectively. The SEM micrographs inferred that the particulate matter of urban site was different in shapes, sizes and morphology from rural site. EDX spectra of size segregated particulate matter showed the elemental composition of individual particles and indicated two main groups viz. O and Si rich particles on the basis of their percentage contribution in all four sizes of particles i.e., $PM_{<1}$, PM_1, $PM_{2.5}$ and PM_{10} µm $^{-3}$. Anthropogenic activities have an important role irrespective of the size range of particles. SEM-EDX technique was used in this study which provided valuable information on the morphology and elemental composition of the collected samples.

Rural	C	O	Na	Mg	Al	Si	K	Ca	Mg	Fe	Zn	Ti	Cl
$PM_{<1}$		94.64	1.46		0.51	4.00	0.25	0.11			.039	0.10	
$PM_{1-2.5}$		93.97			0.39	3.40	0.22	0.11			0.37	0.08	
$PM_{2.5-10}$		92.30	1.26	0.05	0.82	4.15	0.32	0.33		0.17	0.47	0.12	
$PM_{\geq 10}$	40.52	58.38		0.08	0.09	0.77	0.10	0.02	0.00	0.03		0.00	0.01
Error	10.2	0.4	0.2		0.1	0.3	0.0	0.0			0.1	0.0	0.0
Urban													
$PM_{<1}$		95.29	0.54	0.07	0.68	2.45	0.19	0.33	0.07	0.21	0.22	0.02	
$PM_{1-2.5}$		96.31	0.06		0.96	1.91	0.23	0.43			0.10	0.00	
$PM_{2.5-10}$		95.45		0.21	0.83	2.08	0.16	0.83		0.44		0.00	
$PM_{\geq 10}$		97.08	0.11		0.50	1.28	0.24	0.39	0.15	0.23			0.01
Error		0.4	0.1	0.0	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 1 Percent wise contribution of resulted elements with respect to their atomic weight

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