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Elemental composition and source apportionment of particulate matter over Sub-urban Chennai

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Abstract: This study is on the characterization of airborne particulate matter of size up to 10microns (PM10) over sub-urban Chennai (Latitude: 12.81N, Longitude: 80.03 E) during January, February and March 2014. High Volume Sampler is used for measuring the PM10 in which PM10 is collected by the inlet of the instrument and deposits on the glass fiber filter. The filter paper with a size 1cm² is made and is subjected to Scanning Electron Microscopic (SEM) and Energy Dispersive Spectroscopic (EDAX) analysis to identify the shape, size and the elements of PM 10. Further, principal component analysis has been carried out for the percentage contributions of elements of PM 10 to identify the sources. HYSPLIT Back trajectories of 1hr to 7 days have been plotted to understand the short and long range transport mechanism of PM10.

From the SEM analysis, it is clear that the PM shows wide range of different shapes and dimensional distribution. Some of the particles have size range of 0.1 -5 µ while the most of them in this group are of 2-3 µ size. EDAX analysis disclosed the presence of elements such as Potassium (K), Barium (Ba), Calcium (Ca), Aluminium (Al), Carbon(C), Sodium (Na), Silicon (Si) in many samples, whereas elements like Iron (Fe), Zinc (Zn), Magnesium (Mg), Copper (Cu), Indium (In), Ruthenium (Ru), Mercury (Hg) in some of the samples. Sodium (Na) is mainly due to the contribution of sea salt that is transported by the wind to the study location. Potassium (K), Calcium (Ca), Silicon (Si), Barium (Ba), Aluminium(Al) are contributed by the earth crust mostly. Carbon can be either Organic or Inorganic. Organic Carbon is mostly from open burning whereas inorganic carbon is obtained from the incomplete combustion of matter (e.g.: vehicular transmission). The 7 – day and 1 – hour back trajectories of PM10 revealed the nature of continental aerosols and emissions from local areas.

Keywords: Elemental composition and source apportionment of particulate matter over Sub-urban Chennai.

Introduction

Particulate Matter (PM) is one of the most important pollutants monitored for the air quality assessment and in particular, the PM in the range of nano size is highly hazardous to human life[1]. Ambient Particulate Matter in nano order causes the oxidative stress and make them highly reactive leading to skin ageing etc. This

pollutant deals with a wide range of sources either anthropogenic or natural. The morphology and the elements present in PM10 is of great importance in order to understand the air quality as well as their effects in changing the earth radiation by means of scattering and absorption characteristics.

To identify the possible sources and pathways of Particulate Matter, HYSPLIT back trajectory analysis is of immense help[2]. This Particulate matter may be originated from local industries or from distant land areas or from the ocean. These features can be clearly seen when the back trajectories arrive in the site are made for 1 hour to 7 days time interval.

The smallest particles in PM10 reach the deepest parts of the human respiratory organs (Lungs) and directly interact with the blood. Due to the different possible formation pathways (photo chemical reaction ins in atmosphere, nucleation, condensation, coagulation and cloud processes), the Particulate Matter shows a wide range of different shapes and dimensional distribution. All these information could be of great interest due to the need of understanding how the pollution from Particulate Matter takes place in a specific area. The size and shapes of Particulate Matter can be examined through Scanning Electron Microscope (SEM) Imaging. Also the concentration of elements present over the sample of Particulate Matter can be studied by using Energy Dispersive Spectroscopy (EDS). These methods are widely used and the results reported are highly reliable when the analysis is done for many numbers of samples[3].

So, in the present work, we have studied the trajectories of PM 10 measured from High Volume Sampler (Respirable Dust Sampler supplied by Envirotech Pvt, Chennai) for the months January, February and March 2014 .The main focus aimed to understand the morphology and elemental analysis of PM10 by subjecting the samples t o SEM/EDAX Analysis.

Experimental Setup and Methodology

High Volume Sampler

A High Volume Sampler (PM10) draws a known volume of ambient air at a constant flow rate through a size selective inlet and a filter. Particles in the PM10 size range are then collected on the filter during the specified 24-hour sampling period. Each sample filter is weighed before and after sampling to determine the net weight (mass) gain of the collected PM10 sample. The total volume of air sampled is determined from the measured volumetric flow rate and the sampling time. More details on High Volume Sampler cab be found from www.envirotechindia.com.

The High Volume Sampler has been operated at SRM university (12.83N; 80.03E) located in the sub urban Chennai region. Particles with aerodynamic diameter less than 10 micrometers (PM10) were collected on glass fibre filter papers during the alternate days of the study period January to March 2014. The concentration of PM10 in the ambient air is computed as the total mass of collected particles in the PM10 size range divided by the volume of air sampled. High Volume Sampler draws ambient air at the rate of 1m³/minute. The total air mass concentration deposited on filter can be obtained from the weight difference of coated and uncoated papers. Figure.1 depicts the glass fibre filter paper before and after deposition of PM10.

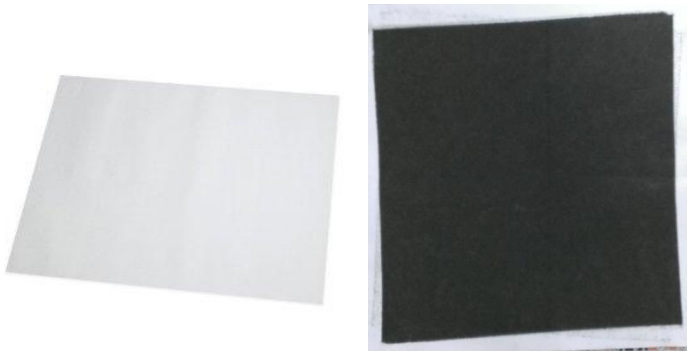


Figure 1. Glass fibre filter paper before deposition and after deposition

Scanning Electron Microscope (SEM)

The SEM operates by scanning an energetic, finely focused electron beam over an individual feature or a field of features. This primary electron beam interacts with the specimen producing a variety of secondary signals that can be monitored with appropriate detectors. These signals can be collected in synchronization with the position of the scanned electron beam to generate high-resolution images providing detailed spatial and composition information. More details on SEM can be found in[4]1.

In the present study, we have subjected the glass fibre filter papers with air mass obtained from the High Volume Sampler to SEM and the morphology is studied. Filter papers with 24 hr and 12 hr (day and night separately) were also subjected to SEM analysis.

Energy Dispersive Spectroscopy (EDAX) analysis

EDAX analysis is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied.

The Edax analsyis of the test samples were carried out for the study period to understand the basic elements present in the ambient air. The common and uncommon elements traced from the analysis are tabulated and discussed.

Results and Discussion

The mean Air Mass Concentration for the months January, February and March are 196 µg/m³, 170 µg/m³ and 167 µg/m³ respectively. January and February are the months of Winter season, the average Air Mass Concentration for the winter season is obtained as 188 µg/m³.It is higher than the March month's Air Mass Concentration (represents the summer season)[5]. The reason for changes in Air Mass Concentration during winter and summer season is mainly due to horizontal transport of winds and temperature variations. As the temperature during the winter season is less compared to summer season, dense air prevails in this winter season at the ground level. In the summer season due to the high thermals more dispersion of Particulate Matter takes place there, low air mass concentration is witnessed.

As we know the Air Mass Concentration over a study area is a combination of local wind generated due to convection and transport of wind from other sites to the study area due to the horizontal transport of wind. In order to study the possible sources and the pathways for the PM(10) over the study location, HYSPLIT Back Trajectory Analysis (source and details:www.arl.noaa.gov) has been performed. These Back trajectory Analysis enable us to understand mainly the sources of PM 10 coming from either land or ocean which is of more important to have an idea for the seasonal variation of PM 10.

In present work, we have carried out back trajectories using HYSPLIT Back Trajectory Analysis for the periods 1hr, 3hr, 6hr, 12hr, 24hr and 7days.

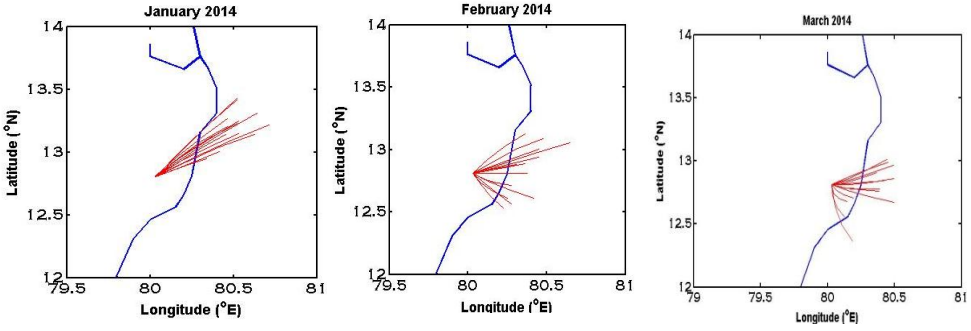


Figure 2 (a, b & c). 3 hours back trajectories for January, February & March 2014

Figure 2(a, b & c) shows the back trajectories arriving the study location during the 3hour period. It is understood from the figure that all the trajectories are originated from Bay of Bengal and reached the test site.

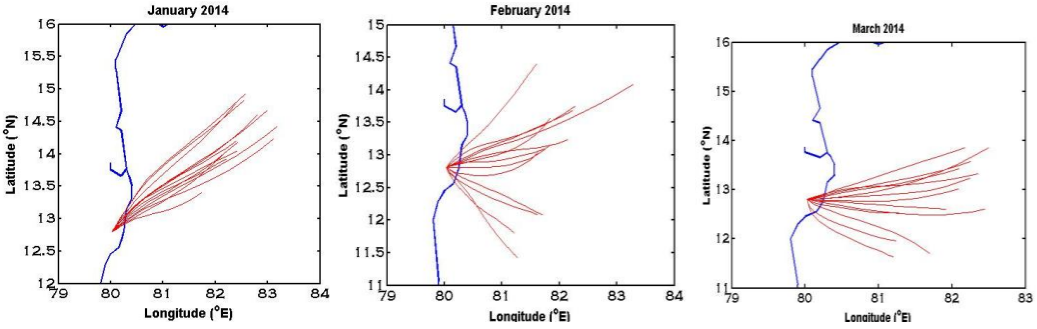


Figure 3. (a, b & c). 12 hours back trajectories for January, February & March 2014

Similarly Figure 3(a, b & c) shows the back trajectories for the 12hr period. We could not find any difference in pathways during study period from 3hr to 12hr trajectories. It can be interpreted that some of the sea salt aerosols may reach the test site due to the study areas proximity to the sea. Also these sea winds may carry some of the natural/anthropogenic aerosols from the land during their way to the test site.

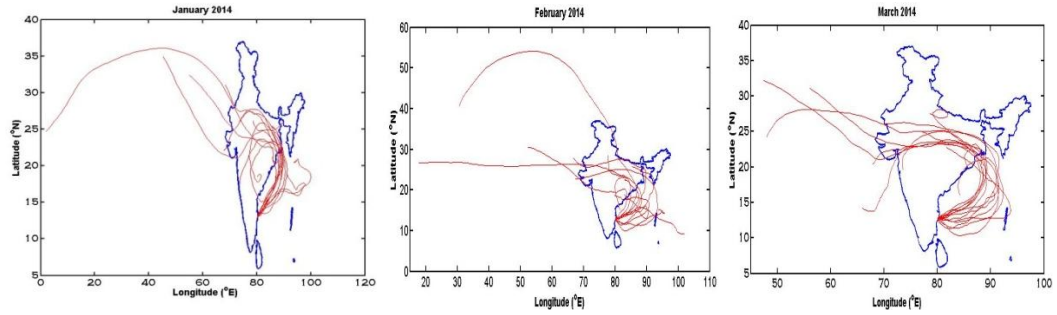


Figure 4 (a. b & c). 7 day - back trajectories for January, February & March 2014

To understand long range transport of PM 10, we carried out 7- days Back Trajectory Analysis for the study period which is shown in the Figure 4(a, b & c). It is conspicuous that trajectories are mainly from the land of Northwestern part of India. These trajectories started from north western India and took the path of Bay of Bengal and finally reached the test site. To confirm the pathway of trajectories we have compared the trajectories with the wind direction data which was collected from Indian Meteorological Department (IMD) Chennai.

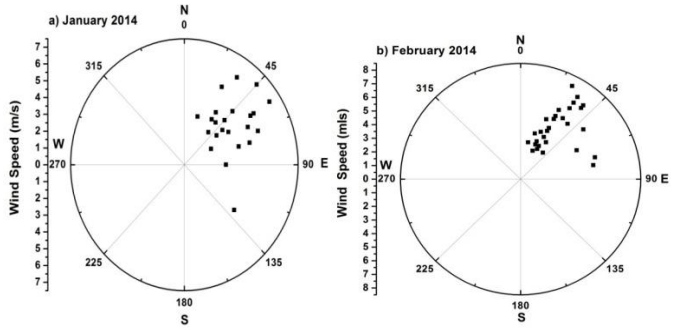


Figure 5 (a&b): Wind Speed and Wind Direction for January and February 2014

The figure 5(a&b) shows the polar diagram of wind speed along with wind direction. The wind speed in the February month is found to be high than January and the direction in both the months are north easterlies. This direction of wind for 2 months is analogous to the pathway shown in the figures 2(a, b, &c).

SEM Imaging and EDAX analysis

To know the morphological properties of Particulate Matter SEM imaging of the sample has been done. The sample has been cut into size of 1cm² and subjected for imaging. The SEM images have been obtained for different resolutions such as 100µ, 50µ, 30µ, 30µ, 10µ, 5µ. The specifications for SEM imaging were maintained uniformly with a magnification of 1600x to 16000x, accelerating voltage of 20KV and with a frame rate of 30ms.

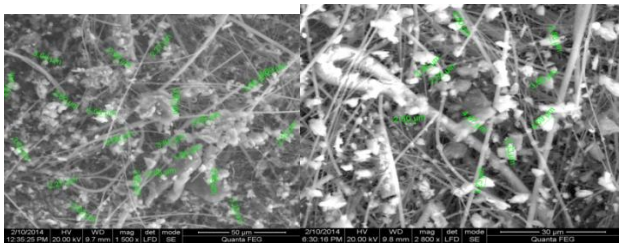


Figure 6 (a &b). SEM image of the sample 7/2/14(24hour) & 9-2-2014(12hour)

The fibers appeared in the samples are from the empty filter paper. From the SEM images obtained, it is clear that the size of the particles deposited on the surface of filter paper is in between the range of 0.1 -5 µ (Fig.6). And most number of particles are in the size range of 2-3 µ. Hence this type of studies are important. Because as the size of the Particulate Matter reduce, higher the chance of human beings inhaling it and it can cause lots of respiratory diseases. Hence the size range study has been done throughout the study time.

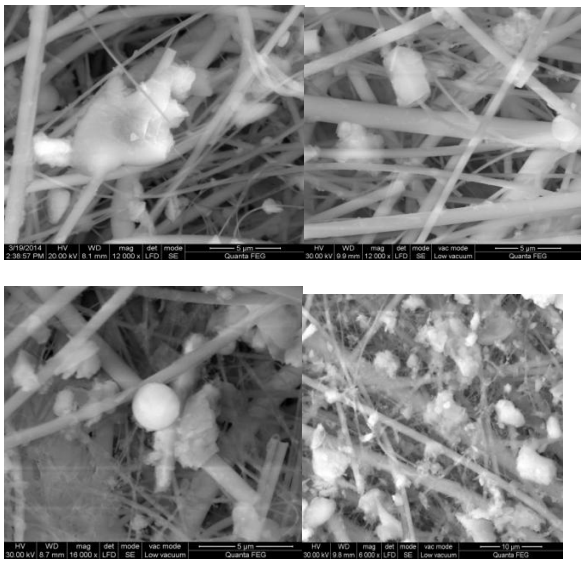
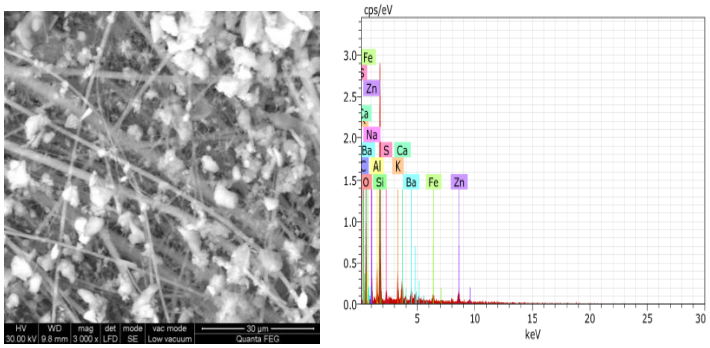


Figure 7 (a, b, c & d). Different shaped particles obtained from the SEM imaging

Lot of particles with non-uniform shape is seen in SEM images (Fig.7). Also spherical shaped, tubular shape, elongated particles are seen in the images. Particles with fractal shape are also seen. Cluster of particles can also be seen in the SEM images. SEM imaging also have been carried out for 12H and 24H samples, to know whether sample time has any influence on it. It can be seen that as the deposition time increases, number of particles that get deposited is getting high and some of the particles get merged over the other.



Spectrum: training

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	41.00	44.60	54.82	9.11
Si	14	K-series	18.62	20.26	14.18	0.95
C	6	K-series	10.85	11.80	19.32	5.36
Ba	56	L-series	4.26	4.63	0.66	0.25
Na	11	K-series	3.83	4.17	3.57	0.45
Al	13	K-series	3.13	3.41	2.48	0.27
K	19	K-series	3.11	3.39	1.70	0.20
Ca	20	K-series	2.77	3.02	1.48	0.19
Zn	30	K-series	2.57	2.80	0.84	0.19
S	16	K-series	0.89	0.97	0.59	0.11
Fe	26	K-series	0.88	0.96	0.34	0.10
		Total:	91.93	100.00	100.00	

Figure 8. SEM image and EDS analysis of a 12 hour sample (10-4-2014)

Energy Dispersive Spectroscopy (EDAX) analysis gives the number of elements present in the samples and also their percentage of contribution to the Particulate Matter. Four EDAX analysis has been done for each SEM image of 1cm² sized sample, to know whether any high variation of elements present is there in different places of the sample. EDAX analysis for the sample is shown in the Fig.8 for the date :10.04.2014.

The study of EDAX analysis for 15 samples were taken during the study period. It resulted the existence of some common and uncommon elements and information is tabulated in Table 1.

Table 1(a & b): common and uncommon elements present in the 12hr and 24 hr samples

12 hour	Common elements	Uncommon elements
19-3-2014(day)	K, Ba, Ca, Al, C, Na, O, Si	Zn
19-3 to 20-3-2014(night)	K, Ba, Ca, Al, C, Na, O, Si	Hg
9-2-2014(night)	K, Ba, Ca, Al, C, Na, O, Si	Fe, Ru, S
28-3-2014(day)	K, Ba, Ca, Al, C, Na, O, Si	S, In
28-3-2014(night)	K, Ba, Ca, Al, C, Na, O, Si	Zn
3-4-2014(day)	K, Ba, Ca, Al, C, Na, O, Si	Cu, In, Zn
3-4-2014(night)	K, Ba, Ca, Al, C, Na, O, Si	Cu, Zn, S
10-4-2014(day)	K, Ba, Ca, Al, C, Na, O, Si	Fe, Zn, S, Cl
10-4-2014(night)	K, Ba, Ca, Al, C, Na, O, Si	In, Cu, Zn, S

24 hour	Common elements	Uncommon elements
7-2-2014	K, Ba, Ca, Al, C, Na, O, Si	Fe, Ru
13-3-2014	K,Ba,Ca,Al,C,Na,O, Si	Zn, S
16-3-2014	K, Ba, Ca, Al, C, Na, O, Si	Zn, S
25-3-2014	K, Ba, Ca, Al, C, Na, O, Si	Fe, Zn
1-4-2014	K, Ba, Ca, Al, C, Na, O, Si	Zn, S
12-4-2014	K, Ba, Ca, Al, C, Na, O, Si	Mg, Cu, S, In, Zn

From the EDAX analysis it has been observed that elements like Potassium (K), Barium (Ba), Calcium (Ca), Aluminium (Al), Carbon(C), Sodium (Na), Oxygen (O), Silicon (Si) are present in many samples. Whereas elements like Iron (Fe), Zinc (Zn), Magnesium (Mg), Copper (Cu), Indium (In), Ruthenium (Ru), Mercury (Hg) are also obtained from some of the samples. Sodium (Na) is mainly due to the contribution of sea salt aerosols. Potassium (K), Calcium (Ca), Silicon (Si), Barium (Ba), Aluminium(Al) are contributed by the earth crust mostly. Carbon can be either Organic or Inorganic. Organic Carbon is where inorganic carbon is obtained from the incomplete combustion of matter (e.g.: vehicular transmission).

Air Quality Index (AQI)

With the measured amounts of PM10, the authors have estimated the air quality during the study period over the test location. Please note that this AQI cam also be estimated by using the inputs of ozone concentration, PM2.5, Carbon Monoxide (ppm) and Sulpher Dioxide (ppm). By using the low and high values of PM10 obtained over a month, AQI has been calculated and the values are 122.2, 109.9 and 106.9 for January, February and March months respectively. The values indicate that the air quality over the study area is unhealthy for sensitive groups. The formula for calculating AQI and the classification of air quality based on PM10 can be found in Report of United States Environmental Protection Agency on Air Quality Index.

Conclusions

The study mainly focuses in obtaining Air Mass Concentration over Sub Urban Chennai (12.81 N & 80.03 E) and in studying the characteristics of PM 10.The results of the study region are given below.

- The Air Mass Concentration of PM 10 is high during winter than in summer.
- The HYSPLIT Back Trajectories for 1- day and 7 days are from the Bay of Bengal and Northwestern part of India respectively.
- The SEM analysis witnessed the air particles are mainly in the size range 2-5µ.
- The Air Quality Index obtained from PM 10 value study location is in the range of 100-150 which indicates that the atmosphere in study region is Unhealthy for sensitive groups.

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