Water-soluble organic compounds (WSOCs) in PM$_{2.5}$ and PM$_{10}$ at a subtropical site of India

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ABSTRACT

PM$_{2.5}$ and PM$_{10}$ samples collected at a suburban site of northeastern part of India have been analysed for particle mass, total carbon (TC), water-soluble total carbon (WSTC), water-soluble organic carbon (WSOC), water-soluble inorganic carbon (WSIC), organic acids (formic, acetic, proponoic and oxalic acids) along with inorganic ions (NO$_3^-$, SO$_4^{2-}$ and NH$_4^-$). Most of the PM$_{10}$ consists of PM$_{2.5}$ in the present site (ratio 54–74%). WSTC content in PM$_{2.5}$ and PM$_{10}$ corresponds to 21% and 16%, respectively, of their total particle masses. Thermo gravimetric analysis showed the presence of humic-like substances (16–22%) in particulate samples. Domestic heating and stagnant atmospheric conditions enhanced the levels of these carbonaceous compounds in PM$_{2.5}$ and PM$_{10}$ in winter. Qualitative estimation of various functional groups by Fourier transform infrared (FTIR) analysis indicates the presence of carboxylic, hydroxyl, aliphatic and aromatic hydrocarbons, amines and sulphurous compounds in these aerosols. Absolute principal component analysis applied on the aerosol data resolves four factors. These factors are associated with carbonaceous aerosols released from combustion of coal and wood, secondary inorganic and organic aerosols and water-soluble inorganic fraction.

1. Introduction

Atmospheric inhalable (PM$_{2.5}$) and respirable (PM$_{10}$) particles have been found to play an important role in human health problem, especially respiratory diseases, visibility reduction and climate change (Kanakidou et al., 2005). Emissions of the particles specially less than 2.5 μm are of greater concern since they are small enough to penetrate into the lungs, where they may exacerbate conditions such as bronchitis and asthma (Seaton et al., 1995; Nicolai, 2002). The morphology, size, chemical composition of particles and capacity to carry potentially toxic substances (such as organic substances or metallic compounds) adsorbed on the particle surfaces play a crucial role in adverse effect on health and environment (Senlin et al., 2008).

Carbonaceous aerosols are a dominant component of fine particles contributing up to 10–70% of their total mass with concentration ranging from a few pg m^{-3} to hundreds ng m^{-3} and are comprised of myriad of individual species with vastly different chemical and thermodynamic properties (Tsapakis et al., 2002). These aerosol originating from anthropogenic sources like fossil fuel (coal, diesel and gasoline) combustion from mobile and stationary sources, biomass burning and wood are known to contain high amount of carcinogenic polycyclic aromatic hydrocarbons as well as light absorbing carbon compounds (black carbon), which significantly influence the aerosol radiative forcing and the atmospheric photochemistry. They consist of elemental carbon (EC) and a complex mixture of numerous organic compounds. EC is derived from combustion processes while organic carbon (OC) is produced by both primary and secondary sources (Yu et al., 2004). Water-soluble organic carbon (WSOC) also contributes significantly to carbonaceous aerosol and may potentially act as cloud condensation nuclei (Wang et al., 2005). It contribute significantly to aerosol total carbon (TC, up to 30%) and organic mass (more than 50%) (Kiss et al., 2002; Mader et al., 2004).

In situ reactions of unsaturated organic compound present in the atmosphere are also one of the major sources of secondary organic aerosol (SOA, Tsapakis et al., 2002). Beside their major contribution to total mass of fine particles, organic particles are the least studied and analysed fraction of aerosol due to complexity of organic mixture. Only about 10–20% of the organic PM$_{2.5}$ and PM$_{10}$ mass is typically identified at the molecular level (Saxena and Hildeman, 1996). Molecular level characterization of selected tracers is extremely

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valuable for source apportionment. However, chemically relevant information about the entire mass of organic fine particulate matter is needed to understand the effects of atmospheric aerosol on visibility, climate and health (Kanakidou et al., 2005).

In India, particle pollution has increasingly become a severe problem due to fast industrialization and urbanization in the past two decades Major cities of India are highly polluted by particles (CPCB, 2007). However, data on aerosol composition in India are limited, since only few studies on PM$_{2.5}$ and PM$_{10}$ were conducted (Kumar et al., 2001; Guazzotti et al., 2003; Sharma and Maloo, 2005; Chowdhury et al., 2007; Rengarajan et al., 2007; Sharma et al., 2007; Kothai et al., 2008; Khare and Baruah, 2008, 2009; Badarinath, et al., 2009; Chakraborty and Gupta, 2009; Fu et al., 2009, 2010; Pavuluri et al., 2010; Rastogi and Sarin, 2009). Most of these studies report characterization of inorganic fraction of aerosol (Kumar et al., 2001; Sharma and Maloo, 2005; Sharma et al., 2007), which is influenced by vehicular and industrial pollution. Most of these reports concentrated on the temporal and spatial variability in trace elements particle concentrations; very few studies investigated the organic compounds in such particles (Sharma and Maloo, 2005; Khare and Baruah, 2008, 2009). This work represents the first simultaneous measurements of PM$_{2.5}$ and PM$_{10}$ samples from the suburban site of India in heating (winter) and non-heating season (summer) where the major sources of these particles are coal-based industries, wood burning and road dust resuspension. Here, winter is called heating season due to maximum usages of wood and biomass for heating purposes. Seasonal variation of both particle sizes with their TC, WSOC is reported. Thermo gravimetric (TG) analysis was applied to investigate the refractory properties—in terms of weight loss evaluation of WSTC from PM$_{2.5}$ and PM$_{10}$.

2. Experimental method

2.1. Sampling site

The sampling site is located at southwest of the Jorhat city (25°49' and 27°17' north latitude and 93°18' and 95°26' east longitude) of northeastern part of India (See Fig. S1). The site is surrounded by a variety of deciduous trees, agricultural fields and residential colonies. Highway is about 1 km away from the site. Traffic density on highway was 1.4×10^4 vehicles per day during the period of study. Coke ovens of various capacities (50–100 kg d^{-1} capacity) are situated near the sampling site. The site is surrounded by several tea gardens using coal for tea drying and brick kilns using coal for firing. One refinery is situated at the south of the sampling site (45 km away, arial distance). One airport is situated 2 km away from the sampling site. The frequency of airplanes arrival and departure is very less (2 and 3 flights in a day). Hence, contribution by aviation is negligible as a source of OC.

2.2. Meteorological parameters

The climate of Jorhat is humid subtropical. The weather is under the influence of the Asian monsoon system, which is characterized by a marked change of temperature, humidity and rainfall during winter and summer periods. In Jorhat, the year can be divided into cold and rainy/summer seasons. The southwest monsoon in the region begins from the middle of June. The area experiences a very high average annual rainfall of about 2200 mm per year and a bulk of precipitation occurs in the months of April–October. Winter conditions prevail during the months of November–February. December and January are the coldest months in a year with minimum rainfall. In the rainy season, temperature varies between 25°C and 36°C, whereas in winter, temperature ranges from 4°C to 12°C. The average humidity ranges from 87% to 91% during the wet months. Summer and rainy seasons cannot be separated as intermittent rainfall occurs during summer.

2.3. Sample collection

Samples ($N = 60$) were collected during 24 h on a pre-fired (≥ 2 h at 600°C), pre-conditioned (48 h) in air and pre-weighted quartz fibre filters using PM$_{2.5}$ and PM$_{10}$ from January 2007 to December 2008. Sample collections took place every sixth day with a flow rate (1 m^3 h^{-1}) using fine particulate samplers (APM-550, Envirotech India and Model PEM-ADS 2.5/10, M/S Poll tech Inst. India) at 3 m above the ground level. Sampling months were November, December, January and February in winter, while May, June, July and August in summer. The procedure for preparation of the blank filters consists of 2-h pre-heating at 550°C, 48-h equilibration of the filters in an air-conditioned weighing room at 20°C and 40% relative humidity, triple weighing by means of analytical balance. After particle collection, the filters are reconditioned for another 48 h in desiccators containing CaCO$_3$ in the air-conditioned room and subsequently analysed for total mass.

After re-weighing, the exposed filters were stored in a freezer to limit losses of volatile components (Hueglin et al., 2005). Proper care was taken in handling of quartz fibre filters to avoid the mass loss.

For weighing operation, Sartorius balance is used. Fully automatic adjustment (calibration and linearization) using internal weight is performed every morning. The quality control measures were adopted by using 0.1 g certified weight before and after weighing operations. The readout data are monitored by means of a control chart for individuals (ASTM, 1991).

Quartz fibre filters can adsorb volatile organic compounds (VOCs) causing positive artefacts for particulate OC. On the other hand, semi-VOCs in aerosols may partially evaporate during sampling and even during the conditioning step in a chamber for mass measurements resulting in negative artefacts (Wang et al., 2005).

The available data do not allow us to evaluate the magnitude of these artefacts. However, some studies suggest that quartz fibre filters may cause larger positive artefacts that the negative one (Madar et al., 2003).

Colocative sampling of $PM_{2.5}$ samplers had been conducted before the field study. Two samplers were run simultaneously for instrumental comparison in order to determine the uncertainty of measurements. The deviations of mass concentration of the samplers were within 10% (Lonati et al., 2005).

2.4. Extraction of $PM_{2.5}$ and PM_{10} water and organic

2.4.1. WSOC. The WSOC samples were extracted by shaking half of each filter with ultra pure water (50 ml). The final slurry obtained was filtered though a membrane filter of 0.22 μm pore size. Filter blanks were also treated in a similar manner. To obtain sufficient mass for the TG analyses, the aqueous extracts were batch together (group of three samples) according to similar ambient condition. Samples were preserved at 4°C for further analysis.

2.4.2. Dichloromethane extract of particulate samples. The dried filter paper containing the particulate air sample was put in an extraction thimble made of filter paper Whatman # 1 in a Soxhlet extractor. Samples were extracted in methylene chloride at the rate of 4 cycles per h for 16 h under protection from light. The extract was concentrated upto 1 ml in rotatory vacuum evaporator under reduced pressure. (Bhargava et al., 2004).

Filter and field blank were also extracted in same manner.

2.5. Carbon, hydrogen and nitrogen (CHN) analysis

TC, WSTC and WSOC contents of the particles were determined by using CHN elemental analyser (Tru Spec, Leco) with a high sensitive catalyst named N-catalyst. The mass range and precision of instrument is 0.002–100% and <1% (Relative Standard deviation, RSD), respectively. The non-purgeable organic carbon (NPOC) method determined WSOC, which measures the non-volatile OC present in the sample. Inorganic carbon (carbonate, hydrogen carbonate and dissolved carbon dioxide) was eliminated in the NPOC method by acidifying the sample with 1% hydrochloric acid (Feng et al., 2006; Saarikoski et al., 2007). Filter and field blanks were also analysed in the same manner.

The calibration of Carbon analysis was done by certified standards supplied by Leco. RMS error of the calibration curve was 0.011. RSD (5) for replicates was 0.0013 (0.003%). The uncertainty of the WSOC method was estimated to be 11%. In addition, one-third of the samples were randomly selected and their water extracts were analysed for carbonate carbon. Soluble carbonate concentrations in all the samples analysed were found to be very low (concentrations were similar to those of field blanks). Low pH (<5.6) of water extract of $PM_{2.5}$ and PM_{10} also indicate the same. Total water-soluble inorganic carbon (WSIC) was obtained by subtracting WSOC from WSTC.

2.6. Fourier transform infrared (FTIR) analysis

Dichlormethane extract of particulate samples were analysed for the functional group and bond information of FTIR spectroscopy. An aliquot of the extract (100 μl) was spiked on ZnSe disk (on IR transparent substrate), the solvent was evaporated under the hood and each sample was analysed in FTIR spectrometer (Perkin–Elmer system 2000, model 640B; wavelength 400–4000 cm^{-1}, with an accuracy of ± 0.3). The spectra for 124 scans were recorded at a resolution of 2 cm^{-1}. Software facilities were used for baseline corrections of spectra. Field blanks were prepared and analysed in a similar manner and the resulting spectra were subtracted from the spectra of samples.

2.7. Thermo gravimetric analyses (TGA)

TGA of WSOC were performed using Leco TGA-07 connected to a computer through interface. For each WSOC, a 3 mg aliquot was placed in a crucible and heated upto 750 °C under air (20 ml min^{-1} flow) under programmed temperature control. The temperature program used includes three steps of heating at 10 °C min^{-1}, with a hold time at the final temperature of each step: 60 min at 60 °C, 60 min at 100 °C and 30 min at 750 °C. (Duarte and Duarte, 2008). Precession, balance accuracy and stability of the instrument are 0.02% (RSD), 2% and 2%, respectively.

2.8. High performance liquid chromatographic (HPLC) and UV-Vis analyses

Formic acid, acetic acid, oxalic acid and pyruvic acids were analysed using HPLC (waters) with UV-Vis detector (Waters 486) at a flow rate of 0.5 ml min^{-1}. Calibration curves were using salts of these acids. Precession of the method was <1% (RSD). Nitrogen dioxide (NO_2) (Jacob and Hochheiser, 1958), NH_4^+ (Weatherburn, 1967), NO_3^- and SO_4^{2-} (APHA, 1992) were analysed spectrophotometrically.

Filter and field blanks were also analysed in a similar manner. The sample results were corrected by the average of the blank concentration.

3. Results and discussion

3.1. $PM_{2.5}$, PM_{10} and their organic and inorganic constituents

The concentrations of $PM_{2.5}$, PM_{10} mass and their carbonaceous constituents are given in Table 1. The daily average of $PM_{2.5}$, PM_{10} in the study area exceeds the national ambient air quality annual standard of India, that is, 45 μg m^{-3} and 100 μg m^{-3}, respectively. $PM_{2.5}$ and PM_{10} show linear regression with each other (Fig. 1). $PM_{2.5}/PM_{10}$ ratios were 0.67 and 0.62 in winter and summer, respectively, with an average of 0.66. The average contribution of TC to $PM_{2.5}$ and PM_{10} were 80% and 56%, respectively. The ratios of TC in $PM_{2.5}$/TC in PM_{10} ranged

Table 1. Mean PM$_{2.5}$ and PM$_{10}$ mass, TC, WSOC, WSTC, WSOM and WSIC (and associated standard deviations) at a suburban site of India during winter and summer (in μg m^{-3})

Season		PM$_{10}$				
		PM$_{10}$	TC	WSOC	WSTC	WSIC
Summer	Mean	207.9	137.0	26.0	37.5	7.8
	SD	39	32	5	9	2
Winter	Mean	222.9	142.8	29.2	37.4	8.2
	SD	47	33	7	7	2
		PM$_{2.5}$				
Summer	Mean	132.1	101.0	21.83	28.29	6.4
	SD	18	15	4	4	1
Winter	Mean	143.5	110.4	22.94	30.26	7.3
	SD	23	18	4	4	1

between 0.71 and 0.96. Average percentages of WSTC were 21% and 16% of the PM$_{2.5}$ and PM$_{10}$ masses. The ratio of WSOC in PM$_{2.5}$/total WSOC in PM$_{10}$ ranged between 0.69 and 0.97. The WSOC/TC ratios ranged from 20% to 75% and 21% to 77% in PM$_{2.5}$ and PM$_{10}$. WSOC/TC ratios in PM$_{2.5}$ at the present site are slightly higher than reported for urban locations of China (14–57%) (Mader et al., 2004; Yang et al., 2005). It indicates that these aerosols are enriched with carbonaceous fraction, and finer portion of aerosol has more carbon content. WSIC contributes only up to 4% to total mass of PM$_{2.5}$ and PM$_{10}$. The average ratio of WSIC of PM$_{2.5}$ to PM$_{10}$ was 0.64.

Some of the components like organic acids, SO$_4$, NO$_3$ and CO$_3$ were analysed in WSOC of PM$_{2.5}$ and PM$_{10}$, whereas the remaining organic constituents of aerosols were only identified

by FTIR and is discussed in Section 3.2. Table 2 shows the concentration of organic acids in PM$_{2.5}$, pH, inorganic acids, NH$_4$ in PM$_{2.5}$ and PM$_{10}$. The pH of water-soluble extract of PM$_{10}$ is lower than that of PM$_{2.5}$. Acidity of particulate matter is due to HCO$_3^-$, NO$_3^-$ and SO$_4^{2-}$. Here, high concentrations of NO$_3^-$ and SO$_4^{2-}$ in PM$_{10}$ and negligible carbonate ions indicate that these ions are responsible for lower pH in PM$_{10}$. Concentrations of proponoic acid were higher than other organic acids, while that of oxalic acid was very low. Formic and proponoic acids show higher concentrations in winter while magnitude of acetic acid was similar in both the seasons.

No correlation was observed between WSOC and TC of PM$_{2.5}$ and PM$_{10}$, which is due to small contributions of WSOC to TC ($r^2 = 0.43$) (see Table S1). A good correlation between WSTC and WSOC in PM$_{2.5}$ has been observed in both the seasons (Table S1). Similar slopes of regression were found between summer and winter, implying similar emission sources contributing to the WSOC fraction of fine particles. However, WSTC and WSOC of PM$_{10}$ shown good correlation in winter only months. Their slopes of regression in winter and summer were dissimilar, indicating contribution of different sources or processes to their levels in PM$_{10}$. In winter, fresh emissions of solid fuel burning are major contributor to WSOC. Oxygenated functional groups are introduced during the formation of SOA via exposure of gaseous precursors and aerosols to oxidants (Temesi et al., 2003; Szidat et al., 2004). While in summer photochemical oxidation and regional scale SOA formation contribute to WSOC concentration in aerosols (Viana et al., 2007). Insignificant correlation between WSOC and WSIC indicates they have either different sources or different formation processes in aerosols. Seasonal differences in PM$_{2.5}$, PM$_{10}$, TC, WSTC, WSOC and WSIC concentrations were tested by one-way analysis of
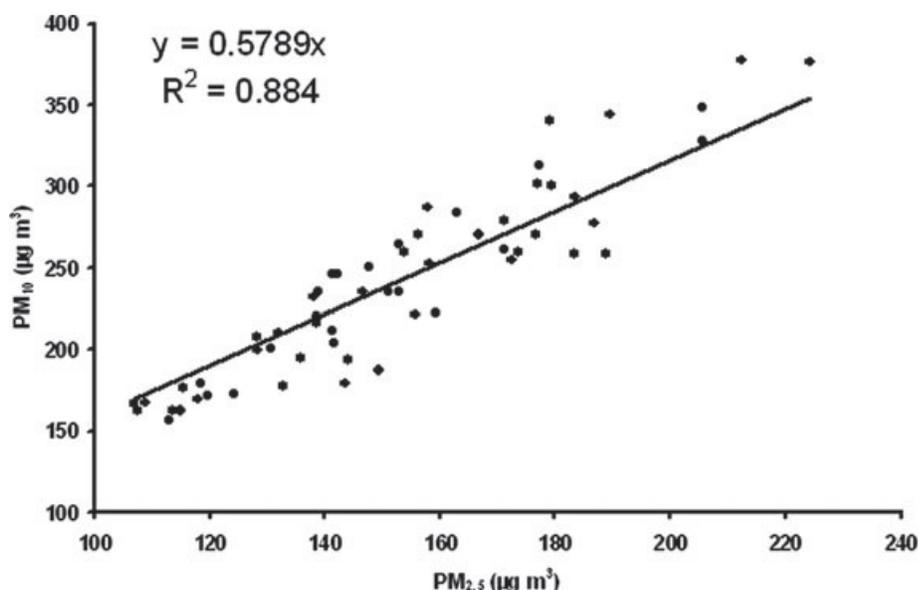

Fig. 1. Relationship between PM$_{2.5}$ and PM$_{10}$ in a suburban site of India.

Table 2. Concentrations of NO$_2$, formate (FA), acetate (AA), oxalic acid (OA), proponoic acid (PA), NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, pH with F/A ratios in PM$_{2.5}$ (in μg m^{-3})

	NO$_2$[a]	FA	AA	OA	PA	F/A	NO$_3$		SO$_4$		NH$_4$		pH	
							PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$
Summer														
Mean	6.33	0.11	0.25	0.01	0.60	1.13	3.87	5.32	4.67	9.72	2.32	5.02	5.45	4.25
SD	0.97	0.10	0.22	0.02	0.25	1.11	0.73	0.82	2.22	3.99	0.6	0.7	0.27	0.29
Winter														
Mean	9.53	0.33	0.24	0.00	1.81	1.93	4.87	6.19	5.74	11.09	2.42	5.69	4.75	4.21
SD	2.68	0.43	0.28	0.00	3.33	1.10	0.48	1.01	3.84	4.62	0.5	0.5	0.66	0.32

[a]Nitrogen dioxide.

variance (ANOVA) method, using the statistical software package SPSS v 10.0 (see Table S2). Significant ($p < 0.05$) seasonal variability in concentration of PM$_{2.5}$, PM$_{10}$, TC, WSTC, WSOC was found with higher concentrations in winter. Wood burning, coal combustion and vehicular emissions are the dominant sources of the organic aerosols in the present area. The elevated levels of PM$_{2.5}$ and PM$_{10}$ in winter are due to usages of wood for domestic heating in colder months. Higher levels of TC in PM$_{2.5}$ and PM$_{10}$ in winter month are consistent with this fact. In addition, stagnant atmospheric conditions in winter may also decrease the dispersion of pollutants (Khare et al., 1998). High mixing height in summer may also decrease pollution concentration (Feng et al., 2006). Furthermore, gas/particle partitioning is also temperature dependent. The difference in ambient temperatures (from 25 °C to 36 °C in summer and from 4°C to 12°C in winter), high wind speed and precipitation in summer months and low level temperature inversion in winter should also be the other reasons for this seasonal variation (Cao et al., 2004).

3.2. Organic functionalities

Organic absorption due to aliphatic hydrocarbons, carbonyls and organo sulphur compounds are identified using FTIR (Fig. 2). All spectra are characterized by strong OH functionalities (alcohols, phenols and carboxylic acids) as evidenced by a large broad peak centre at 3350–3450 cm^{-1} coupled with band at 1600–1640 cm^{-1}. Generally, in spectra of particle samples, aerosol water (OH) has a contribution in absorbance range 1620–1650 cm^{-1}. However, these are organic extracts. Thus, this absorbance could represent organic –OH and/or could be produced by the stretching of carbonyls. Organonitrates also absorb in this region ($\sim$1630 cm^{-1}), their presence was supported by the simultaneous occurrence of two sharp peaks at 1280 cm^{-1} and 861 cm^{-1}. It is reported that emissions from cooking and biomass burning are major sources of amide in indoor and outdoor environments (Simoneit et al., 2003, Reff et al., 2005). Higher intensities in this range during heating season (winter) are consistent with this fact. Both smog-chamber and ambient aerosol experiments also show that aromatic VOCs, isoprene and monoterpene oxidation products oligomerize readily in the particle phase under both acidic and non-acidic conditions, forming constituents like organosulphates and organonitrates (Limbeck et al., 2003; Claeys et al., 2004; Ervens et al., 2005; Romero and Oehme, 2005; Reemtsma et al., 2006; Surratt et al., 2007; Dron et al., 2008; Reinnig et al., 2008; Lukács et al., 2009), which may explain a large part of the till now unidentified fraction of SOA.

Doublets observed near 3100–2800 cm^{-1} are due to CH stretching bands. CH$_3$ groups near 2960 cm^{-1} and 2870 cm^{-1} and the CH$_2$ bands are at 2930 cm^{-1} and 2850 cm^{-1}. Doublet observed near 2855–2859 cm^{-1} due to CH stretching mode
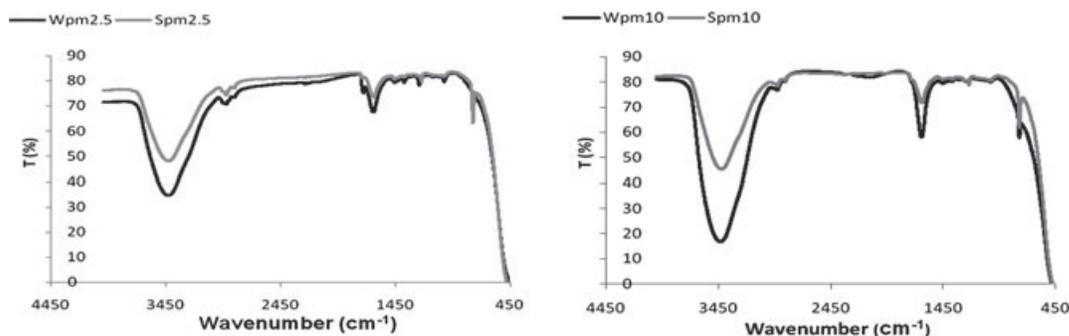
Fig. 2. FTIR spectra of PM$_{2.5}$ and PM$_{10}$ (W PM$_{2.5}$: PM$_{2.5}$ in winter, S PM$_{2.5}$: PM$_{2.5}$ in summer, W PM$_{10}$: PM$_{10}$ in winter, S PM$_{10}$: PM$_{10}$ in summer).

of the aldehydes group appears as the Fermi doublet. Peak intensity of CH$_2$ group is found higher than CH$_3$ groups in all the spectra. It indicates the presence of low solubility aliphatic hydrocarbons. Organic compounds containing the C=O group show very strong IR absorption in the range 1850–1650 cm^{-1}. The actual position of peak within this range is characteristics of the type of compounds. However, a single carbonyl peak in the region 1750–1700 cm^{-1} could indicate presence of ester, aldehyde and ketone (including cyclo ketones) (Guo and Bustin, 1998). Peak observed between 1590 and 1580 cm^{-1} is attributed to NH$_2$ deformation of primary alkyl amides. Anti-symmetric deformation of the HCH angles of CH$_3$ group and bending of methylene (–CH$_2$–) group give rise to very strong IR absorption in the 1470–1440 cm^{-1} region.

The symmetric and asymmetric stretching of SO$_3$ present in sulphonic acid (a class of organic compounds containing the functional group (RSO$_2$OH) occur at 1369–1290 cm^{-1} and 1170–1120 cm^{-1}, respectively. Two strong bands near to 1379 cm^{-1} and 1121 cm^{-1} are due to alkyl and aryl sulphonic acids and sulphonates, respectively.

The peaks observed near 1071–1087 cm^{-1} are due to the stretching vibration of the S=O group in sulphoxides. A very weak peak is observed near 660 cm^{-1} is due to C–S and S–S bonds.

Peaks at 1285–1288 cm^{-1} and 1021–1039 cm^{-1} are representative of aromatic C–H bonds. This is consistent with the presence of aromatic hydrocarbons. A small, less sharp peak at 3060 cm^{-1} also associated with aromatic hydrocarbons is also detected in all extracts. A distinct spectral feature of all spectra is the occurrence of three sharp peaks at 900–700 cm^{-1}, representative of polyaromatic hydrocarbons. These bands are assigned to aromatic structures with isolated aromatic hydrogen (870 cm^{-1}), two adjacent hydrogen per ring (815 cm^{-1}) and four adjacent

aromatic hydrogen (750 cm^{-1}). The number of adjacent hydrogen per ring provides an estimate of degree of hydrogen in the aromatic rings. The band observed near 872, 771 and 745 cm^{-1} attributed to the presence of di- and tri-substituted aromatic rings and/or aromatic structures with 1–2 rings in particulate matter.

In this paper, we reported only qualitative analysis of different organic functional groups not quantitative analysis. However, relative intensities of a particular band may provide useful information regarding their seasonal variability. Bands belongs to hydrocarbons (2930 and 2850 cm^{-1}), hydroxyl (3350–3450 cm^{-1}), amide ($\sim$ 1630 cm^{-1}) and carboxylic groups have high peak intensities in winter seasons suggesting more emissions of these compounds in winter season.

3.3. TG analysis of WSOC and kinetic study

Typical TG curves and the first derivative of TG (DTG, differential thermograph) of PM$_{2.5}$ and PM$_{10}$ are shown in the Supporting Information (Fig. S2). The thermogram can be divided into four regions according to mass degradation of various types of carbon compounds. The vaporization of water/WSIC and WSIC/volatile OC may occur in the temperature regions 0–180 °C and 180–280 °C, respectively. While temperature region 300–350 °C corresponds to mass degradation of oxygenated, saturated and unsaturated organic compounds, region 380–560 °C belongs to mass degradation of polycyclic, and polyaromatic compounds (Peuravuori et al., 1999; Kucerik et al., 2004). The comparison of percentage of mass loss at different temperature ranges with percentage of WSTC, WSOC, WSIC in PM$_{2.5}$ and PM$_{10}$ is shown in Fig. 3. The highest percentage of mass loss in the 400–740 °C range is observed for the sample collected during winter season, which is consistent with high percentage of WSTC and WSOC content in aerosols. On
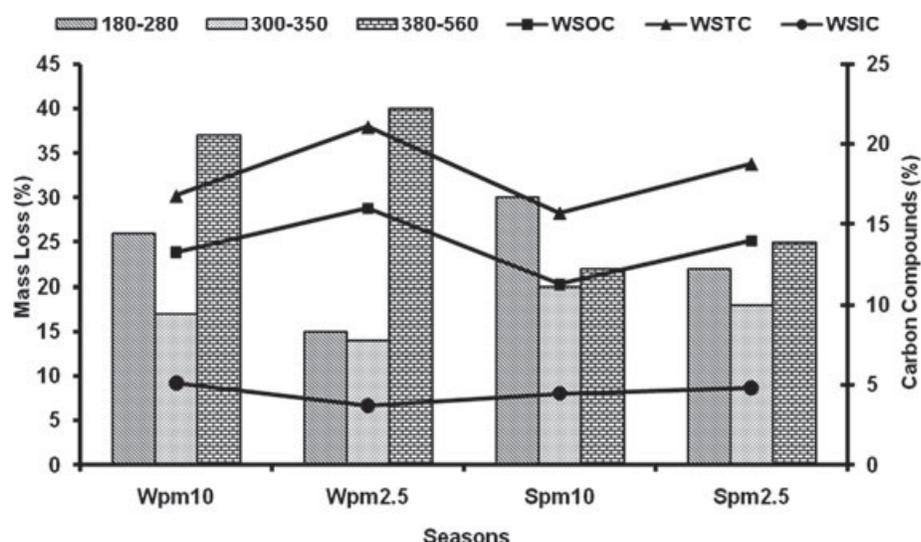

Fig. 3. Comparison of mass losses (%) of WSTC at different temperature ranges, concentrations of WSOC, WSTC and WSIC of PM$_{2.5}$ and PM$_{10}$ during winter and summer.

Table 3. Correlation matrix between PM$_{2.5}$ mass, their organic and inorganic components

	PM$_{2.5}$	TC	WSOC	WSTC	WSIC	NO$_2$	FA	AA	OA	PA	NO$_3$	SO4	NH4	pH
PM$_{2.5}$	1.00													
TC	0.87	1.00												
WSOC	0.65	0.07	1.00											
WSTC	0.68	0.64	0.95	1.00										
WSIC	0.40	0.18	0.34	0.62	1.00									
NO$_2$	0.04	0.10	−0.06	−0.07	−0.06	1.00								
FA	−0.26	−0.18	0.61	−0.37	−0.35	0.42	1.00							
AA	0.04	−0.08	0.74	0.09	0.07	−0.11	−0.33	1.00						
OA	−0.27	−0.21	−0.20	−0.16	0.02	−0.15	−0.27	0.40	1.00					
PA	0.01	0.04	0.04	−0.09	−0.27	−0.13	0.18	0.05	−0.15	1.00				
NO$_3$	0.37	0.25	0.52	0.41	0.42	0.01	−0.50	−0.05	−0.25	−0.03	1.00			
	−0.22	−0.33	−0.39	−0.37	−0.11	−0.16	0.63	0.72	−0.01	−0.16	−0.13	1.00		
NH$_4$	0.03	0.22	0.29	0.34	0.06	0.43	0.53	0.44	0.05	0.26	0.62	0.43	1.00	
pH	−0.21	−0.13	0.08	0.04	−0.06	0.04	0.30	0.13	0.23	0.16	−0.43	−0.65	0.44	1.00

$P = 0.001$.

Table 4. Apparent activation energies, Ea (kJ mol^{-1}), for the thermal degradation of aerosol WSOC calculated using the pseudo first-order method at 10 °C min^{-1}

Temperature	PM$_{2.5}$		PM$_{10}$	
	Summer	Winter	Summer	Winter
50–170	52	54	51	51
180–280	98	100	100	100.8
300–350	107	101	106	102
380–560	116	164	114	160
600–750	77	126	124	130

the other hand, below 400 °C, the highest percentages of mass loss are observed for PM$_{2.5}$ and PM$_{10}$ WSOC collected during summer.

In this study, pseudo first-order method was applied to estimate the apparent activation energies for the different multistep degradation stages (Hatakeyama and Quinn, 1994) (see Fig. S2). Activation energies will provide thermal stability of WSTC in different season. Calculated activation energies for fine regions are given in Table 4. Particularly notable variations in activation energies are in the region IV and V. In these regions, relatively higher activation energies were observed in winter, suggesting increased coal and wood burning in the winter season generate more thermally stable compounds. Higher TC and WSOC content in winter could explain the existence of a fast rate of degradation with simultaneous increase in the activation energies in thermal regions IV and V (Fig. 3).

Peak observed in region 300–800 °C could be due to mass loss of humic-like substances. TGA curves of standard humic acids also show strong peak in this region (Duarte et al., 2007). Strong peaks at 3350–3450 cm^{-1} and 1620–1650 cm^{-1} belonging to carboxylic and hydroxyl groups show the presence of

humic acid. It is reported that fine particles are composed of atmospheric humic matter, which gives 30–35% of water-soluble organic fraction. In our study, all samples exhibit peaks of thermal degradation in the temperature range between 310 °C and 375 °C with a mass loss of 16–22% (Fig. 3) suggesting the more formation of humic-like substance in summer season. These humic-like substances could be regarded as secondary aerosol particles, which formed from precursor compounds (Temesi et al., 2003), which is consistent with higher percentage of mass loss during winter.

3.4. Source apportionment

Source profiling is done by using absolute principal component analysis (APCA) models requiring relatively little quantitative knowledge of sources and emission profiles, models requiring relatively little quantitative knowledge of sources and emission profiles, even though they do require initial qualitative knowledge of the sources present in the study area (Chan and Mozurkewich, 2007). APCA is an effective tool to identify independent factors using the eigenvector decomposition of a matrix of pair wise correlations among compound concentrations (Miller et al., 2002).

Prior to APCA, correlation analysis was done for the preliminary assessments of sources. Results of correlation and APCA are shown in Table 3 and Fig. 4, respectively. We chose the results with a minimum eigenvalue larger than 1. The first component (factor 1) is loaded with TC, WSOC and particulate matter, and it contributes 34% of the total variance. This factor represents combustion sources enriched with carbonaceous aerosols. Presence of sulphate in this factor indicates that coal is the major source. Since, coals used in industrial purposes have high sulphur content (Khare and Baruah, 2010) and produce large amount of SO$_2$ and sulphate. The major source of these
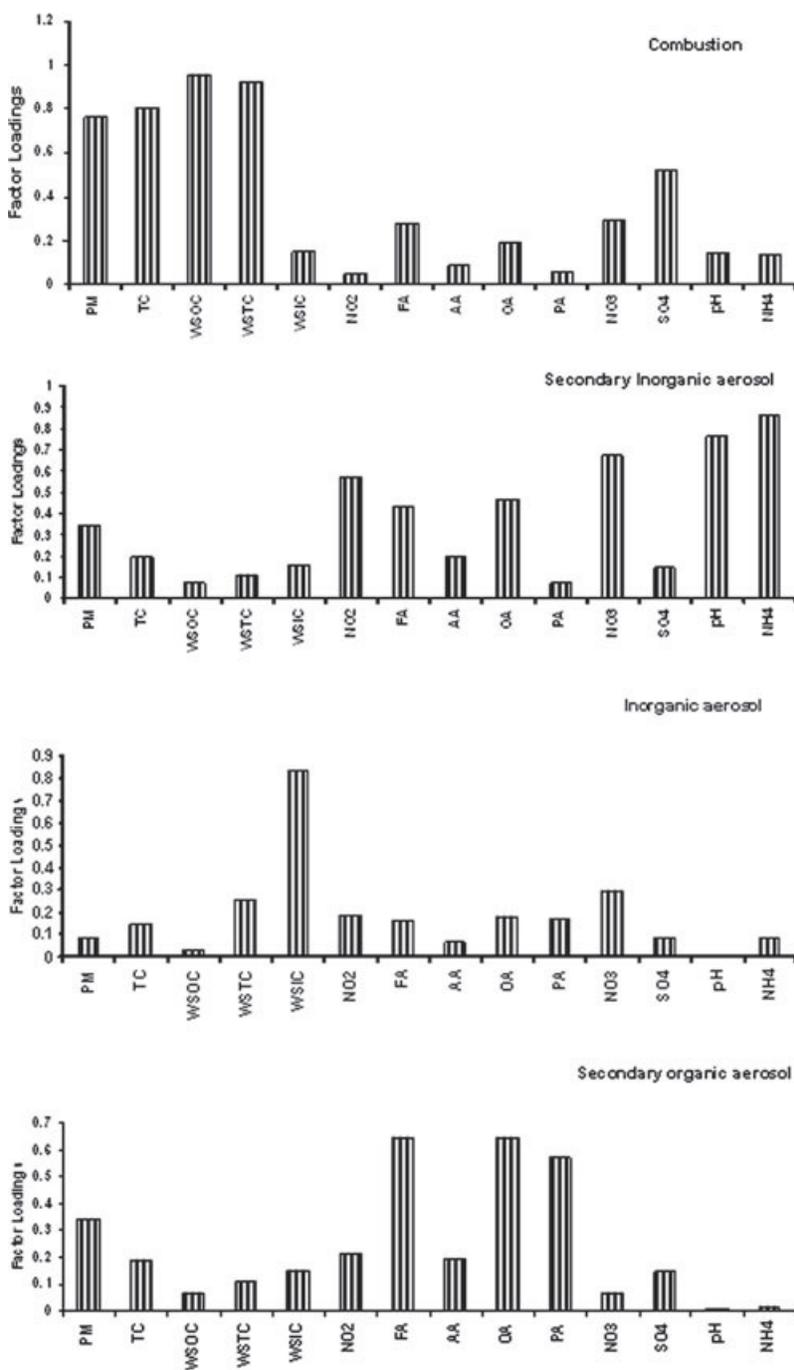
Fig. 4. Factor loadings of organic and inorganic components of aerosols along with nitrogen dioxide (NO$_2$).

carbonaceous aerosols is coal used for industrial (coke oven, tea garden) purposes. Wood burning is another major source of carbonaceous aerosols during winter months. Factor 2 contains NO$_2$, NO$_3$, pH and NH$_4$. The second source component (total variance 19.60%) was assigned to secondary inorganic aerosols. Presence of NO$_2$ and NO$_3$ in this factor indicates production of HNO$_3$ by photo-oxidation of NO$_2$ (Zhuang et al., 1999). Presence of ammonium in this faction is due to formation of its nitrate. Organic acids characterized the third component, which

contributes 14% of the total variance. The compounds primarily originate from incomplete combustion of fossil fuels mainly by automobiles and aircraft and secondarily from photochemical reactions of anthropogenic hydrocarbons and other precursors in the atmosphere (Chebbi and Carlier, 1996; Kawamura et al., 2000).

Secondary formation processes may also produce significant fraction of WSOC via exposure of gaseous precursors and aerosols to oxidants. The fourth components have relevant loads

of WSIC (total variance 7.0%) and reflect presence of inorganic carbon. Generally, the main constituents of WSIC are carbonate and hydrogen carbonate, which are formed by crustal species and emission of industries (Wang et al., 2002).

4. Conclusions

The distribution of particle mass, TC, water-soluble total carbon (WSTC), WSOC, WSIC and organic acids (formic, acetic, proponoic and oxalic acids) along with inorganic ions (NO_3^-, SO_4^{2-}, NH_4^-) in $PM_{2.5}$ and PM_{10} was investigated at a suburban, tropical site of India.

Qualitative analysis of FTIR indicates the presence of hydroxyl, aliphatic, aromatic and amine functionalities. Intensities of peaks that belong to these functionalities were relatively higher intensities in the winter seasons in both the size fractions ($PM_{2.5}$ and PM_{10}). Presence of humic-like substances was also observed (16–22%) in these aerosols. The seasonal pattern showed that in winter the concentrations of carbonaceous aerosols and their organic constituents were higher, probably due to increased in anthropogenic emissions and stagnant climatic conditions. APCA applied on particulate data enabled to identify and apportion the major sources types; solid fuel burning, secondary inorganic and organic aerosol formation and water-soluble inorganic carbonaceous components. The study will provide preliminary data on these carbonaceous aerosols. However, detailed quantitative analysis of organic and inorganic constituents of aerosols will also be required to get a clear picture of source profiling.

5. Acknowledgment

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Supporting Information

Additional supporting information may be found in the online version of this article:

Table S1. Relationship of WSOC with TC, WSTC and WSIC concentration in PM_{10} and $PM_{2.5}$ samples during winter and summer (y = WSOC, x = TC/WSTC/WSIC)

Table S2. One-way ANOVA for mass, TC, WSOC, WSTC, WSOM and WSIC of $PM_{2.5}$ and PM_{10}

Fig. S1. Map of sampling site.

Fig. S2. DTG curves of WSTC of $PM_{2.5}$ and PM_{10} in winter and summer.

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