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Carbonaceous Content Analysis of PM₁₀ Aerosols at Residential Suburb of Delhi, India

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Abstract

Estimation of PM₁₀ carbonaceous components like organic carbon(OC) and elemental carbon (EC) were carried out over Delhi, the capital city of India during winter and summer 2017. For OC/EC content analysis, PM₁₀ samples were analysed by Thermo/Optical carbon analyser. Black carbon (BC), a form of elemental carbon has also been measured using AE-51aethelometer and showed a distinctive diurnal and seasonal variation. As per the study, mass concentration of PM₁₀, OC, EC. BC. Total carbonaceous aerosol (TCA) and Organic matter (OM) were maximum during winter and minimum during summer. Strong positive correlation between OC and EC (r=0.72), and significant average value of OC/EC indicate similar sources of emission like biomass burning and vehicular emission. The average concentration of OC and EC during summer and winter were 7.09+2.12, $12.71+12.01 \mu g/m^3$ and 47.08+17.53, 22.38+7.49 µg/m³ respectively. Diurnal variation of BC reports higher values during morning and evening hours, which possibly could be the result of variation in mixing layer height and traffic rush hours. Variation of carbonaceous aerosol with Aerosol Optical Depth (AOD) and meterology has also been analysed.

Introduction

In developing countries like India, there has been a lot of work on emission inventories of Total Suspended Particles (TSP), PM_{10} and $PM_{2.5}$.Particulate matter has been studied thoroughly in recent years due to its potential health effects and role in disturbing the atmospheric basics. Ambient air quality, chemistry of atmosphere, Earth's radiation budget, visibility and climate are significantly affected by the atmospheric aerosols (Sharma *et al*, 2014). Ambient aerosols are the mixture of inorganic and organic pollutants, mineral dust, sea salts and soil dust. Carbonaceous aerosols play an important

role in altering the Earth's energy budget and have negative health effects, therefore need to be studied for their changing concentration profile every day. When it comes to urban carbonaceous matter, EC and OC are one of the major constituents (Yu and Yu., 2009). Smoke particles comprises approximately 60% OC and 5-10%EC (Sharma et al., 2014). EC, an important component of fine aerosols, absorbs harmful VOCs, which in turn has adverse effects on human health (Dachs and Eisenrich, 2000). EC (or BC), produced due to incomplete combustion affects the earth's energy balance due to its light absorption capacity, on the contrary OC is emitted during combustion, formed by secondary condensation process in the atmosphere and oxidation process of Hydrocarbons (Kim et al., 2003). OC/EC ratio assessment is important, as it provides an insight into the source approximation and impact analysis of aerosols on radiative forcing (Novakov et al., 2005). BC and EC differ in terms of measurement techniques, former is measured with optical technique, whereas latter mass calculation is based on thermal oxidation and reduction. Now, a days EC is used as a substitute in the monitoring of diesel particulate matter (NIOSH, 1996). Longterm changes in the biomass burning, vehicular emission and industrial emission shall impact the percentage source contribution of carbonaceous aerosols (Christoforou et al., 2000). Indo Gangetic Basin (IGB) comprises aerosols of different types (Srivastava et al., 2012a) and they are responsible for considerable radiative forcing over this region (Srivastava et al., 2012b). Vehicular pollution, open burning of biomass, fire crackers, pollution from small and large-scale industries and burning of crops in nearby states are the major sources of pollution in Delhi

The present work report emission of PM_{10} , OC, EC and BC in Delhi during 2017 and is focused to study their seasonal, temporal and diurnal variation. This study also examines the role of meterology and highlights the possible potential emission sources.

Method

Study Area

Delhi, capital city of India, located in northern part is stretched in the north from $28^{0}24'17''$ to $28^{0}53'00''$ and in the east from $76^{0}50'24''$ to $77^{0}20'37$ and covers a geographical area of 1483 sq. km (CPCB, 2016). Delhi experiences sub-tropical climate has influenced in the north by Himalayas and in the west by Thar Desert (Tiwari *et al.*, 2013a). Measurement for BC, OC and EC were made at Arjun nagar, Pitampura, Janakpuri and Sirifort in Delhi (Table 1, Figure 1), which are heavily populated, traffic dominated residential areas. Air mass flow in Delhi during Winters is from northeast to northwest and in summers from southeast to southwest (Goyal and Sidharta., 2002). Pollution scenario turns out to be nastiest during winters due to fog and during summers due to dust storm (Tiwari *et al.*, 2013b). Thus, monitoring has been carried out during winter and summer 2017.

Location	Land-Use Type	Lat/Long		
Arjun Nagar	Residential Area	28.3920 [°] N, 77.1741 [°] E		
Pitampura	Residential Area	28.4208 [°] N, 77.0807 [°] E		
Janakpuri	Residential Area	28.3714 [°] N, 77.0509 [°] E		
Sirifort	Residential Area	28.3315 [°] N, 77.1307 [°] E		

Table 1: Land-use type and Geo-coordinates of sampling locations in Delhi



Figure 1: Location Map

Sampling Technique

Samples for PM_{10} aerosols were collected by Respirable Dust sampler (Model: Envirotech APM 460 BL) at 3m height above ground on PalltissuQuartz filter Paper for 24hrs a day for two days, at each location of Delhi during winter (January) and summer (June), 2017. Collection of particulate matter was carried out on prebaked and dessicated filters. Ambient air was passed through the filter paper of size 8"*10 " at a flow rate of 1000 mlpm for 24 hrs a day. Filter paper was changed every 8 hr during the sampling period for the better analysis. In order to determine the mass of PM_{10} , Palltissuquartz filter papers were weighed pre and post sampling. PM_{10} mass concentration was calculated on the basis of the difference between intial and final weight of filters, which is then divided by the total volume of air passed through it.

OC/EC Analysis

PM₁₀ filter papers are then analysed with Thermal/Optical Carbon Analyser (DRI Model 2001) using IMPROVE_A, Interagency monitoring of Protected Visual Environment (Total optical Reflectance) Method (DRI SOP 2-216.1, revised Nov, 2005). Measurement of OC and EC by Thermal/Optical Carbon Analyzer is based on the principle of preferential oxidation of carbon compounds at different temperatures (Table

2). Organic compounds are volatilized from the sample punch in non-oxidizing helium (He) atmosphere, whereas elemental carbon gets combusted in the presence of an oxidizer like heated MnO_2 (Manganese dioxide). These carbon compounds are first oxidised to CO_2 in the presence of MnO_2 , which is then reduced to methane (CH₄) by passing through the methanator under the presence of hydrogen enriched nickel catalyst and is then quantified with flame ionisation detector (FID). The optical laser reflectance and transmittance are continuously monitored within the instrument to avoid the underestimation of charring OC into EC.

Table 2: Temperature profile of carbonaceous aerosols.

OC_1	Ambient Temp- 140
OC_2	140-280 °C
OC_3	280-480 °C
OC_4	480-580 °C
EC_1	580 °C
EC_2	580 to 740 °C
EC ₃	740 to 840 °C

Black Carbon (BC) estimation

Black Carbon has been monitored by AE51 Micro aethalometer at a wavelength of 880nm for 8 hrs (1000-1800hrs) a day. Aethelometer has been operated at a temporal resolution of 5 min and flow rate of 100mlpm. BC mass concentration is measured by measuring the rate change in absorption of transmitted light due to continuous deposition of aerosol on Teflon coated glass fiber filter. Aerosol Optical Depth for the study period has been taken from MODIS Terra at 550 nm. Meteorological data has been acquired from Central Pollution Control Board (CPCB) by using Continuous Ambient Air Quality Monitoring System (CAAQMS).

Results and Discussion

 PM_{10} average mass concentration of 335.66±48.45 and 216.25±57.47 µg/m³ were reported during winter and summer, respectively, which is higher than the prescribed annual limit of 100µg/m³in India as per the National ambient air quality standard, 2009. PM_{10} mean values range from 207– 546µg/m³ during winter and 138.33 - 300.66µg/m³ during summer. During 2010, Sharma *et al.*, 2014b, reported average PM_{10} mass concentration around 213.1±14.9µg/m³ during winter season, which is approximately 1.57 times lower than the present concentration in 2017. Higher PM_{10} concentration during winter season possibly could be the cumulative result of lower mixing height, low temperature, burning activities, vehicular pollution and precipitation absenteeism. The increase in particulate matter concentration may be attributed to increase in urbanization, construction activities and vehicular density.

Organic carbon and Elemental Carbon

PM₁₀ samples were analyzed for OC/EC by Carbon analyzer. Seasonal varation of OC and EC showed the maximum mass concentration during winter and minimum during summer. OC concentration varied from 22.33-114.67 µg/m³ with an average of $47.08+17.53 \mu \text{g/m}^3$ during winter. Extremely high concentration of OC i.e. 114.67 $\mu \text{g/m}^3$ has been recorded at Janakpuri which could possibly be the result of high traffic density, burning in and around nearby areas or some extreme event during that period. Lower mass concentration of OC/EC was reported during summer. OC mean value ranges from 3.55-10.61 μ g/m³, with an average of 7.09 μ g/m³, while for EC it varied from 0.78-38.80 μ g/m³, with an average mass concentration of 22.38 μ g/m³. During summer, high EC mass concentration has been recorded at most of the locations, which outweighed OC concentration, this could possibly be the result of large vehicular emission and less burning activities in that area during study period. Total carbonaceous aerosol (TCA) constitutes around 12.76% of PM₁₀ mass, while it accounted for 20.56% during winters. OC and EC found to have a positive linear relationship with PM_{10} . Table 3 shows the concentration profile of OC and EC in PM₁₀ at different locations of Delhi during winter and summer season.

Summer										
			OC/				% OC of	% EC of	OC + EC %	
	OC	EC	EC	PM_{10}	TCA	OM	PM_{10}	PM_{10}	of PM ₁₀	
Pitampura	8.40	15.69	0.54	200.16	29.12	13.43	4.19	7.83	12.03	
Arjun Nagar	4.46	28.38	0.16	145.91	35.51	7.14	3.05	19.45	22.50	
Janakpuri	9.17	1.78	5.17	271.58	16.45	14.67	3.37	0.65	4.03	
Sirifort	6.34	5.01	1.27	247.33	15.15	10.14	2.56	2.02	4.58	
Winter										
Pitampura	44.33	24.17	1.83	376.16	95.10	70.93	11.68	6.50	18.19	
Arjun Nagar	44.67	17.67	2.53	329.83	89.13	71.47	13.48	5.30	18.78	
Janakpuri	70.83	32.17	2.20	367.16	145.50	113.33	19.29	8.69	27.98	
Sirifort	28.50	15.50	1.84	269.50	61.10	45.60	10.57	5.75	16.32	

Table 3: Monthly mean concentration of OC,EC, TCA, OC/EC, PM_{10} , BC and OM at Delhi during 2017

OC- Organic Carbon $(\mu g/m^3)$

EC- Elemental Carbon ($\mu g/m^3$)

TCA (Total Carbonaceous Aerosol) (μ g/m³)= 1.6*OC+EC

OM (Organic Matter) ($\mu g/m^3$)= 1.6*OC

OC/EC ratio

Higher OC/EC ratio (given in table 3) was reported during winter as compared to summer. A significant correlation (r= 0.72) was observed between OC and EC, which implies similar source of emission like vehicular emission (Salma et al.,2004)

contributing to ambient carbonaceous particles. On the other hand, a minor correlation, between the two specifies the secondary aerosol formation because of the atmospheric photochemical reaction (Sharma *et al.*, 2014). As per Ram and Sarin, 2010 study, lower OC/EC ratio indicates fossil fuel emission as the major source, whereas higher ratio is the result of biomass burning. Higher OC/EC (5.17) ratio indicates secondary aerosol formation (Hussain *et al.*, 2007, Tiwari *et al.*, 2013c). An OC/EC ratio for the urban location falls in the range of 2.0-3.0 (Turpin and Huntzicker, 1995). As per the present study, most of the ratios are analogous to those observed at urban sites.

Seasonal and Temporal analysis of OC and EC

As expected mean mass concentration of OC during winter was higher than summer at every location of Delhi (Figure 2). Janakpuri being traffic dominated and located nearby the industrial areas reported higher OC during study period. EC concentration was highest in Arjun nagar followed by Pitampura, Sirifort and Janakpuri during summer, 2017.



Figure 2: Scatter plot of OC and EC over Delhi during 2017.

BC variation

Average BC mass concentration values showed the same spatial and temporal variation (Figure 3) as elemental carbon. Black carbon interchangeably used as Elemental carbon differs in their mass concentration due to the difference in measurement techniques.BC is that carbonaceous aerosol which absorbs light, whereas EC absorbs light in visible region and is graphitic carbon (Andreae and Galencser, 2006).

Diurnal variation of Black carbon during the study period is shown in figure4. As expected, BC showed higher concentration during morning (10-12hr) and evening (17-18 hr.), owing to rush hour traffic and lower mixing height.

AOD is the measure of extinction of light beam by the aerosols in the atmosphere. AOD in the present study has been acquired from MODIS Terra. BC exhibits a significant correlation with AOD. In this work, correlation of AOD with respect to OC/EC when plotted (Figure 5), clearly indicate that strong correlation exist between the two. With increase in OC/EC mean mass concentration, a decrease has been noted in AOD which may be because of the absorption of light beam by the carbonaceous aerosols.



Figure 3(a, b): Pareto chart representing the percentage constitution of BC at different locations of Delhi during 2017.



Figure4: Diurnal variation of BC during 2017

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Figure5: Variation of AOD with OC and EC during January 2017

Meteorological impact on BC

During the study period, impact of wind speed (WS) and relative humidity (RH) on BC has been observed through correlation analysis As per the result (Figure 7) significant positive correlation exist between BC and RH, which implies that when the atmosphere is laden with moisture, it traps the BC particles resulting in high BC concentration. A negative correlation was observed between BC and WS. Higher wind speed leads to dispersal of pollutants, which in turn reduces the mass concentration of pollutant at a location.



Figure 7(a, b): Correlation between BC and Meteorological parameters (wind speed and relative humidity)

Carbonaceous aerosols like BC, EC and OC are the major constituents in atmosphere and plays an important role in climate change by altering the radiation balance. As per the result, Delhi is laden with PM_{10} mass concentration, which is more than the annual prescribed limit of NAAQS (National Ambient Air Quality Standard). OC, EC and BC mass concentration are reported to be higher during winter season as compared to summer. OC/EC ratio indicates the common source of emission, while at some location higher ratios also indicate the formation of secondary aerosol. Diurnal variation of BC clearly indicates the high carbonaceous concentration during peak rush hours in morning and evening. AOD varies inversely with carbonaceous aerosols. With the increase in mass concentration of OC and EC, AOD decreases due to the absorption of transmitted light by the aerosols. Meteorological parameters like WS and RH affect the pollutant mass concentration. With the increase in RH in the atmosphere, concentration of carbonaceous aerosols increases, whereas high WS facilitates the dispersal of pollutants. In cities, due to urbanization and industrialization no of vehicles, population and anthropogenic activities are increasing continuosly, which in turn is deteriorating the environment by polluting it. There is a need to keep a check on the pollutants level and mitigate their effect by controlling them.

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Abbreviation

AOD- Aerosol Optical Depth; BC- Black Carbon; OC- Orgaic Carbon; EC-Elemental Carbon; MODIS-Moderate Resolution Imaging Spectroradiometer

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