Atmospheric Environment 92 (2014) 493–500

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Characterization of carbonaceous aerosols over the urban tropical location and a new approach to evaluate their climatic importance

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HIGHLIGHTS

- Similar variation of OC and EC in all seasons.
- Both SOC and POC almost equally contributed to form OC.
- Dominance of POC and EC in post-monsoon and winter.
- A new term Effective carbon ratio in place of conventional OC/EC.

ARTICLE INFO

Article history:
Received 8 November 2013
Received in revised form
25 April 2014
Accepted 28 April 2014
Available online 29 April 2014

Keywords:
Organic and elemental carbon
OC/EC ratio
Primary and secondary organic carbon
Effective carbon ratio

ABSTRACT

Increasing emissions from fossil-fuel, biomass burning, land use changes and industrial growth have led to rapid increase in the atmospheric concentrations of carbonaceous species over many cities in India. The present paper deals with the results obtained from year long (2012–13) observations conducted at a tropical urban location, Pune in southwestern India on Organic and Elemental Carbon as well as Black Carbon; using the Sunset OCEC Analyzer and Aethalometer, respectively. The average mass concentrations of OC and EC were in the order of winter > post-monsoon > summer > monsoon. Mean annual OC/EC ratio was found to be 2.4 ± 1.1 during the study period, suggesting the presence of secondary organic carbon (SOC). Estimated SOC was found to form 47% of OC mass concentration. OC and EC were also significantly well correlated ($r = 0.95$, $p < 0.0001$) to each other, indicating towards common combustion sources. The primary organic carbon (POC) dominated over SOC and EC in post-monsoon and winter seasons indicating impact of anthropogenic burning activity, enhanced by prevailing meteorological conditions as well as that of long range transport. Mean annual POC + EC/TC ratio was 0.69 indicating that more than 2/3 of TC is formed from combustion sources. Thermally derived EC and optically derived BC correlated very well ($r = 0.98$, $p < 0.0001$). A new concept e.g. Effective carbon ratio (ECR) is suggested to better assess the scattering/absorptive nature and probable source identification of carbonaceous aerosols in place of conventional OC/EC ratio.

1. Introduction

A substantial contribution (about 20–50%) to the total suspended particulates (TSP) in the ambient atmosphere over urban regions comes from carbonaceous aerosols (Sillanpaa et al., 2005; Kanakidou et al., 2005). They are mainly composed of organic carbon (OC) that forms a major component contributing up to 90% and elemental carbon (EC) that shows relatively low contribution of ≤10% (Ram et al., 2008). The primary organic carbon (POC) and EC are emitted directly from fossil fuel combustion and biomass burning. The secondary organic carbon (SOC) is formed by oxidation of volatile organic reactive species in the atmosphere. Both, OC and EC have different optical and chemical properties and thereby show different impacts on the atmosphere. OC generally scatters the solar radiation while EC acts as an efficient absorber (Ackerman et al., 2000). OC comprises a large variety of organic compounds (aliphatic, aromatic compounds and acids). It is reported that some of the OC compounds act as cloud condensation nuclei (CCN) and thereby show indirect climatic effects by affecting the cloud microphysical properties and precipitation mechanism (Kulmala et al., 1996). The major source of EC to the atmosphere is incomplete combustion during vehicular exhausts and that through biomass/biofuel burning during domestic/agricultural activity. Although, EC is a minor component of carbonaceous aerosols and

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http://dx.doi.org/10.1016/j.atmosenv.2014.04.055
1352-2310/

its contribution to the overall aerosol load is generally small; it plays an important role in radiative forcing as a potential absorbing species in the atmosphere (Ramanathan et al., 2005; Bond et al., 2013; IPCC, 2013). Concentrations of OC and EC in the atmosphere and their ratios (OC/EC) are the important parameters for the assessment of direct/indirect effects of carbonaceous aerosols on the radiative forcing. Recently, the carbonaceous aerosols from South Asian region have been highlighted especially, regarding the regional air quality and also their impact on global climate system. Therefore, observations on physical as well as chemical characteristics of carbonaceous species are very important. Very few studies have been reported from the Indian region on the characteristics of both OC and EC aerosols (Rengarajan et al., 2007; Ram et al., 2008; Ram and Sarin, 2010, 2011; Satsangi et al., 2012; Tiwari et al., 2013). In this paper, observations on OC and EC aerosols over a tropical urban location, Pune are reported for a period of one year, April 2012–March 2013.

2. Sampling location and methodology

Pune (18°32′N, 73°51′E, 559 m mean sea level altitude) is eighth biggest metropolis in India and an important city in terms of industrial growth, vehicular population and rapid urbanization. Pune is also one of the premier industrial centers of India. It is one of India's most important automotive hubs, with some domestic and international auto manufacturing giants. In addition to this, a large number of engineering, electronic and electrical industries are located around this city. The industrial township of Pimpri Chinchwad, about 10 km to the north of Pune, has over 4000 manufacturing units. Population of the Pune city is more than 5 millions as per 2011 census. Along with Bangalore, Pune boasts of having maximum density of two-wheelers in the country with about 1.6 million two wheelers out of 2.0 plus million total vehicles plying on the road. The classification of seasons at Pune has been decided from the prevailing changes in general meteorology over the region e.g. March–May as summer, June–September as monsoon, October–November as post-monsoon and December–February as winter season. The weather at Pune during summer season is very hot with day time maximum temperature reaching around 40 °C. During monsoon westerly/southwesterly winds, rich in marine air masses from the Indian Ocean and Arabian Sea, prevail over this region. Pune receives almost 80% of the annual rainfall in monsoon season. During the post-monsoon and winter seasons, winds change direction from westerly to easterly, covering landmass lying to the north-east/east of the sampling location. In addition, during this period, low temperatures (minimum $\leq$ 8 °C) and less wind speeds are responsible for surface inversions, especially during night and early morning hours. Sampling was carried out on the terrace of the Indian Institute of Tropical Meteorology (IITM) building at about 12 m above the ground at Pashan which is located about 10 km from the center of Pune city.

Continuous observations on OC and EC aerosols were carried out using a Semi-continuous OCEC Analyzer of Sunset Laboratory, USA (Model 4G). The concentrations of OC and EC were analyzed using NIOSH (National Institute for Occupational Safety and Health) protocol based on thermal optical transmittance (TOT) (Birch and Cary, 1996). Aerosols under 2.5 μm size were only sampled using an inlet fitted with $PM_{2.5}$ cut off cyclone. Also, the sample was passed through parallel plate organic denuder to reduce the effects of vapor phase organic adsorption to the cleaned quarts filter. The analysis was performed in two stages: an aliquot of sample filter (1.5 cm^2) was stepwise heated in a furnace up to 820 °C in a non-oxidizing atmosphere (100% He); furnace is then cooled to 550 °C and then the filter was again stepwise heated to 870 °C in an oxidizing atmosphere (98% He and 2% O_2). During each temperature step, evolved carbon is oxidized to CO_2 and then reduced to methane and was detected by a non dispersive infra red detector (NDIR). A calibration was performed at the end of each analysis by introducing a known amount of methane gas into the oven and measuring its constant response. A diode photo detector continuously monitored the transmittance of light from a laser diode through the sample filter during the volatilization and combustion process. The correction for pyrolytic conversion of OC to EC is accomplished by monitoring the transmittance and comparing with the initial value before start of the pyrolysis which is termed as EC/OC split line. The carbon evolved before this line is quantified as OC and that evolved after this line but before methane calibration peak is quantified as EC. Standardization of the instrument was carried out by using sucrose solution (3.2 μg/μl). For quality control, the analyzer was calibrated every month by using a blank punch of pre-heated quartz fiber filter and standard sucrose solutions. Excluding some losses due to technical interruptions, about 7500 samples were collected during the period of one year using an hourly sampling cycle.

Observations on black carbon (BC) were simultaneously carried out using an Aethalometer (AE-42, Magee Sci. Inc., USA) at the same site at 5 min time interval and 3 LPM flow rate. Details on this technique and related uncertainties are discussed elsewhere (Safai et al., 2013).

3. Results and discussion

3.1. Temporal variations of OC and EC

As seen from Fig. 1a, both OC and EC showed similar variation for all the months from April 2012 to March 2013. On an annual average basis, OC was about 2.5 times more than EC and its contribution to total carbon (TC) was about 68%. However, there was seasonal difference in the concentrations of both OC and EC and subsequently that of TC (Fig. 1b). Both OC and EC showed

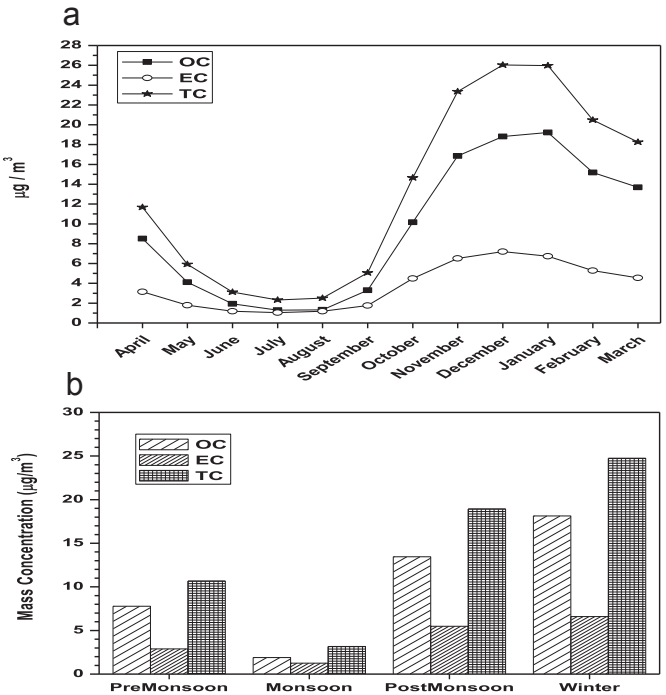

Fig. 1. a: Monthly variation of OC, EC and TC during April 2012–March 2013 at Pune. b: Seasonal variation of OC, EC and TC during April 2012–March 2013 at Pune.