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Characterization of carbonaceous aerosols in fine and coarse particles at Agra, India

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Abstract

A continuous measurement of organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ and PM_{10} was carried out at Agra situated in North central region of India. $PM_{2.5}$ and PM_{10} samples were collected from Jan to Dec 2012 and were analyzed for OC and EC using thermal optical transmittance (TOT) protocol. The results showed that the mass concentrations of $PM_{2.5}$ and PM_{10} ranged from 25.6 to 164.6µg/m^3 and 45.5 to 490µg/m^3 respectively. Both OC and EC exhibited a clear seasonal pattern with highest concentration observed in winter followed by summer and monsoon which may be due to the combined effect of changes in emission rates and different meteorology in various seasons. TCA accounted for an averaged 51.3% of $PM_{2.5}$ mass and 40.4% of PM_{10} mass. This indicates that the carbonaceous fraction nearly accounted for more than one third of PM_{10} mass and about half of $PM_{2.5}$ mass which shows that fine particles are enriched with carbonaceous species. The annual average OC/EC ratio was found to be 6.6 ± 2.8 and 6.9 ± 3.6 for $PM_{2.5}$ and PM_{10} respectively. This ratio is similar to the ratio reported for biomass burning emissions. The SOC concentrations were found to be higher during winter season in both $PM_{2.5}$ and PM_{10}. During winter season, SEM/EDX analysis revealed the dominance of carbonaceous particles whose origin is mainly anthropogenic in nature.

Keywords: Organic carbon, Elemental carbon, $PM_{2.5}$ and PM_{10}.

Introduction

The airborne solid and liquid particles in the nanometer to micrometer size range influence the energy balance of the Earth, the hydrological cycle, atmospheric circulation and the abundance of greenhouse and reactive trace gases. Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. According to surface and volume distributions there are two distinct groups of particles contributing to atmospheric aerosols; Particles with diameter greater than 2.5 µm are identified as coarse particles (PM_{10}). Particles of diameter less than or equal to 2.5 µm are called as fine particles ($PM_{2.5}$). Coarse particles (PM_{10}) which are in the "inhalable" size range can settle in the bronchi and lungs and cause health problems. On the other hand, fine particles ($PM_{2.5}$) tend to penetrate into the gas-exchange regions of the lung and cause or enhance respiratory, cardiovascular, infectious and premature death. Over the last two decades a large number of epidemiological studies have observed associations between ambient particle concentrations and excesses in daily mortality and morbidity. These findings have underlined the importance of ambient particles and the need for monitoring fine ($PM_{2.5}$) and coarse (PM_{10}) particles. Carbonaceous aerosols are significant subgroup of atmospheric aerosols which can be broadly classified into two fractions: organic carbon (OC) and elemental carbon (EC, also called as black carbon or soot). Elemental carbon is emitted into the atmosphere as a by-product of combustion processes such as vegetation burning, industrial effluents and motor vehicle exhausts. On the other hand, OC which can be directly emitted from sources (primary OC, POC) or produced from atmospheric reactions involving gaseous organic precursors (secondary OC, SOC).

Several studies on the chemical composition, sources and formation mechanism of fine as well as coarse particles have been carried out in a large variety of environments worldwide. In India also, there are few studies in Indo - Gangetic plain which focuses on the field measurements of carbonaceous aerosols in TSP[1-9], PM_{10},[10,11] and $PM_{2.5}$[12,13] but the detailed information regarding the chemical composition, concentration, sources and formation mechanism of fine as well as coarse particles is still limited in India. Therefore, the present study will be useful in determining the concentration levels, sources and their effects at Agra.

Material and methods

Description of sampling site: Agra is the home to the world famous heritage monument Taj Mahal. Being surrounded by the Thar Desert of Rajasthan, the site has calcareous soil with excess of soil content. The year is divisible into summer (March–June), monsoon (July–September) and winter (October – February) seasons. The aerosol sources at the sampling site includes both local as well as long range transport sources from Mathura refinery, Firozabad glass industries and brick kiln factories which are situated nearby Agra.

Collection of samples and quality control: Collection of aerosol samples was carried out on the roof of Science Faculty building in Dayalbagh Institute campus. All $PM_{2.5}$ and PM_{10} samples were collected using Fine Particulate Sampler (Envirotech APM 550) operated at a constant flow rate of 16.6 $Lmin^{-1}$ on pre-weighed 47 mm quartz fibre filters (Pallflex, Tissuquartz). Sampling was done for 24 h with frequency of once a week from Jan to Dec 2012. Filter papers were weighed thrice before and after sampling using four digit balances (Mettler, Toledo).

Analysis of carbonaceous aerosol samples and quality control: The analysis of samples for organic and elemental carbon was carried out by using NIOSH 5040 method based on TOT (Thermal Optical Transmittance) as described in Birch M.E. et al.[14] and Pachauri T. et al.[15].

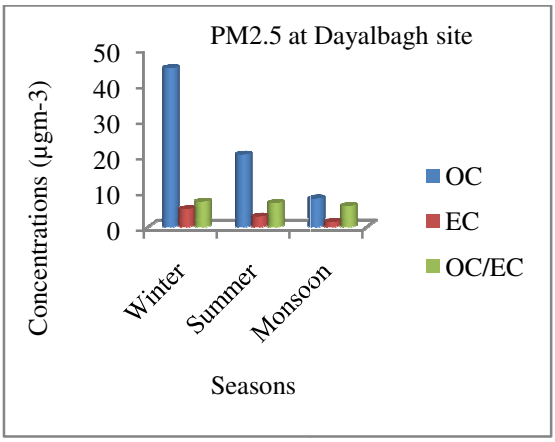
SEM-EDX Analysis: Aerosol samples were analyzed by SEM - EDX at National Institute of Oceanography, Goa. The SEM – EDX analysis was carried out with the help of computer controlled field emission scanning electron microscope SEM (JSM – 5800 LV) equipped with an energy dispersive X – ray system (Oxford 6841).

Results and discussion

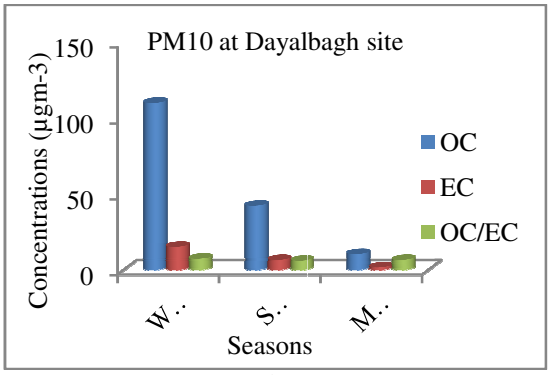
Concentration levels of $PM_{2.5}$ and PM_{10}: At Dayalbagh site, the mass concentrations of $PM_{2.5}$ and PM_{10} ranged from 25.6 to 164.6 $\mu g/m^3$ and 45.5 to 340 $\mu g/m^3$ respectively. The annual average concentration was found to be 80.7 ± 41.5 $\mu g/m^3$ and 210.7 ± 113 $\mu g/m^3$ for $PM_{2.5}$ and PM_{10}. The results indicated that the fine particles ($PM_{2.5}$) contribute about 38% of total PM_{10} mass. The average daily concentration of PM during the measurement period exceeded the 24 hour National Ambient Air Quality Standard[16] of India which are 60 and 100 $\mu g/m^3$ for $PM_{2.5}$ and PM_{10}, respectively. The combined impact of climatic conditions and anthropogenic emissions were found to be responsible for higher level of particulate matter at this site.

The seasonal average concentrations of $PM_{2.5}$ showed that during winter season, $PM_{2.5}$ mass concentration was 1.7 and 2.8 times higher than in summer and monsoon seasons. The seasonal average concentrations of PM_{10} was 198.9 ± 59.6 $\mu g/m^3$ in summer, 328.5 ± 60.9 $\mu g/m^3$ in winter and 82 ± 27.9 $\mu g/m^3$ in monsoon season respectively. The increased biomass, coal and fossil fuel combustion in addition to meteorological conditions play significant role to elevated concentrations during winter season. On the other hand, washout effect during monsoon season leads to low concentrations of particulate matter.

Concentration of carbonaceous species in $PM_{2.5}$ and PM_{10}: At Dayalbagh, the annual average concentrations of OC and EC were found to be 23.8 ± 15.9 $\mu g/m^3$ and 3.5 ± 1.7 $\mu g/m^3$ in $PM_{2.5}$ while in PM_{10} it was found to be 75.2 ± 62.5 $\mu g/m^3$ and 11.1 ± 9.5 $\mu g/m^3$. A distinct seasonal variation of OC and EC in both $PM_{2.5}$ and PM_{10} was observed with the highest concentration in winter followed by summer and monsoon (Figure-1). During winter, summer and monsoon seasons, the average concentrations of OC in $PM_{2.5}$ was 35.1 ± 18.1, 21.3 ± 6.1 and 9.0 ± 2.2 $\mu g/m^3$ respectively. During winter season the OC mass concentration was about 1.8 and 4.4 times higher than summer and monsoon seasons, respectively.



(a)



(b)

Figure-1: Seasonal variation of carbonaceous aerosols in $PM_{2.5}$ and PM_{10} aerosols at Agra.

Contribution of carbonaceous species to $PM_{2.5}$ and PM_{10} mass: Total carbonaceous aerosol was calculated by the sum of EC and organic matter (OM) which was estimated by multiplying the amount of OC by 1.6 (TCA = 1.6*OC + EC). During winter, summer and monsoon seasons, the average concentration of TCA was 63.7, 35.2 and 15.1 $\mu g/m^3$ in $PM_{2.5}$ while 191.5, 74.5 and 18.3 $\mu g/m^3$ in PM_{10}. However, the annual concentration of TCA was found to be 41.1 and 95.9 $\mu g/m^3$ in $PM_{2.5}$ and PM_{10} respectively. During winter season, $PM_{2.5}/PM_{10}$ mass ratio was highest accounting for about 41.8% due to increased emission sources. TCA accounted for an averaged 51.3% of $PM_{2.5}$ mass and 40.4% of PM_{10} mass. This indicates that the carbonaceous fraction nearly accounted for more than one third of PM_{10} mass and about half of $PM_{2.5}$ mass which shows that fine particles are enriched with carbonaceous species.

Relationship between OC and EC: To interpret the emission and transformation characteristics of carbonaceous aerosol, the mass ratio OC to EC (OC/EC) can be used. The ratio of OC/EC ranged from 4.3 to 9.8, 3.2 to 14.5 and 2.4 to 8.5 respectively in $PM_{2.5}$ and 4.1 to 7.1, 4.6 to 12.3 and 2.7 to 9.7 respectively in PM_{10} for summer, winter and monsoon. During winter months, the highest OC/EC ratio could be attributed to several reasons namely: increased residential combustion of coal and wood contribute more to OC than EC, resulting in increased emission of volatile organic precursors, the stagnant and dry meteorological conditions resulted in more SOA formation in wintertime, more semi – volatile organic compounds condensed into aerosol in lower temperature. The annual average OC/EC ratio was found to be 6.6 ± 2.8 and 6.9 ± 3.6 for $PM_{2.5}$ and PM_{10} respectively. The ratio is similar to that reported in the literature for combined emissions from coal, kitchen and biomass burning. Most of samples have high value for OC/EC ratio i.e. 2 which shows the dominance of OC derived from various burning sources (coal, biomass and biofuel) and secondary aerosol formation.

Estimation of secondary organic carbon (SOC): The concentration of SOC was estimated from primary carbonaceous compounds and TOC (total organic carbon) using following equation:

SOC = TOC – POC; POC = EC × (OC/EC) min

Where: (OC/EC) min is the value of the lowest OC/EC ratio. Since the ratios of OC/EC is usually affected by many factors such as types of emission sources, temporal and spatial variation, ambient temperature etc. Therefore, the measurements of POC and SOC are semi-quantitative[17]. During summer, monsoon and winter seasons, the observed values of (OC/EC) min were 4.6, 2.2 and 3.2 for $PM_{2.5}$ while 4.1, 2.7 and 4.6 for PM_{10}, respectively.

The annual average concentration of SOC in $PM_{2.5}$ and PM_{10} samples were 10.8 ± 8.8 and 22 ± 19.5 µg/m^3. The seasonal average concentration of SOC in $PM_{2.5}$ samples were 21.5, 5.2 and 4.2 µg/m^3 while in PM_{10} it was found to be 39.6, 15.2 and 6.6 µg/m^3 in winter, summer and monsoon respectively. The results indicated that the SOC concentration in $PM_{2.5}$ samples was 4 times while in PM_{10} it was around 2.6 times higher in winter than during summer. High SOC concentration may be attributed to combined effect of anthropogenically emitted VOCs (namely benzene, toluene and xylene, BTX) from combustion sources as well as naturally emitted terpenes (as the site is surrounded by deciduous trees which emit terpenes). These emitted VOCs were assumed to act as source for secondary aerosol formation.

SEM/EDX characterization of $PM_{2.5}$ samples: Analysis of individual particles collected from Dayalbagh site was differentiated into two types of particles: soot aggregates and minerogenic (mineral dust) particles. Soot particles were clearly characterized by chain like and "fluffy" appearance while minerogenic particles were of irregular shape (Figure-2). Soot particles were strongly enriched with carbon (> 98% relative contribution by weight) while minerogenic particles were a complex mixture of carbon rich particle containing varying amount of soil related components like Na, K, Mg, Ca and Al.

Conclusion

$PM_{2.5}$ and PM_{10} samples were investigated for their abundance and seasonal characteristics at Agra, India. Samplig was carried out from Jan–Dec 2012. The carbonaceous samples show higher concentration during winter followed by summer and monsoon season respectively. The combined effect of changes in emission rates and different meteorological conditions are responsible for the fluctuations in concentrations in different seasons. The annual average OC/EC ratio in $PM_{2.5}$ and PM_{10} samples is similar to that reported in the literature for combined emissions from coal, kitchen and biomass burning.

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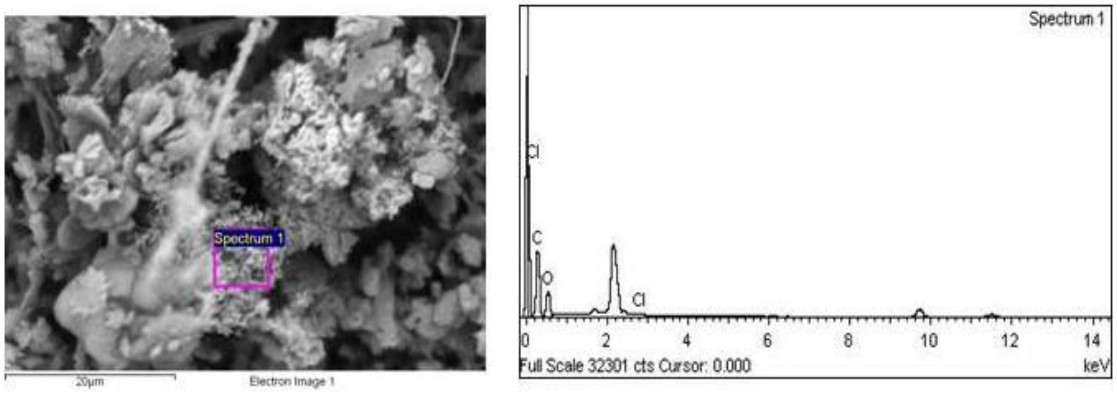

Figure-2: A single soot particle with characterized by chain like and "fluffy" appearance.

References

1. Rengarajan R., Sarin M.M. and Sudheer A.K. (2007). Carbonaceous and inorganic species in atmospheric aerosols during wintertime over urban and high-altitude sites in North India. *Journal of Geophysical Research,* 112, D21, 307. doi:10.1029/2006JD008150.

2. Sudheer A.K. and Sarin M.M. (2008). Carbonaceous aerosols in MABL of Bay of Bengal: Influence of continental outflow. *Atmospheric Environment*, 42(18), 4089-4100.

3. Ram K. and Sarin M.M. (2010). Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over Northern India. *Journal of Aerosol Science*, 41(1), 88-98.

4. Satsangi A, Pachauri T., Singla V., Lakhani A. and Maharaj Kumari K. (2012). Organic and Elemental Carbon Aerosols at a Suburban site. *Atmospheric Research*, 113, 13-21.

5. Satsangi A., Pachauri T., Singla V., Lakhani A. and Kumari Maharaj K. (2010). Carbonaceous aerosols at a suburban site in Indo–Gangetic plain. *Indian Journal of Radio and Space Physics,* 39, 218-222.

6. Pachauri T., Satsangi A., Singla V., Lakhani A. and Kumari K.M. (2013). Characteristics and Sources of Carbonaceous aerosols in $PM_{2.5}$ during wintertime in Agra, India. *Aerosol and Air Quality Research*, 13(3), 977- 991.

7. Pachauri T., Singla V., Satsangi A., Lakhani A. and Kumari K.M. (2012). Number and mass of ultrafine, fine and coarse atmospheric particles during different seasons at Agra, India. *Journal of Research in Ecology,* 1, 001-009.

8. Pachauri T., Singla V., Satsangi A., Lakhani A. and Kumari K.M. (2013). SEM–EDX Characterization of Individual Coarse Particles in Agra, India. *Aerosol and Air Quality Research,* 13(2), 523-536.

9. Pachauri T., Singla V., Satsangi A., Lakhani A. and Kumari K.M. (2013). Characterization of Carbonaceous aerosols with special reference to episodic events at Agra, India. *Atmospheric Research*, 128, 98-110.

10. Venkataraman C., Reddy C.K., Josson S. and Reddy M.S. (2002). Aerosol size and chemical characteristics at Mumbai, India, during the INDOEX-IFP (1999). *Atmospheric Environment*, 36(12), 1979-1991.

11. Ram K. and Sarin M.M. (2011). Day–night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo – Gangetic Plain: Implications to secondary aerosol formation. *Atmospheric Environment*, 45(2), 460-468. doi: 10.1016/j.atmosenv.2010.09.055.

12. Ram K., Sarin M.M. and Tripathi S.N. (2010). A 1 year record of carbonaceous aerosols from an urban site in the Indo-Gangetic Plain: characterization, sources and temporal variability. *Journal of Geophysical Research,* 115, D24, 313, doi: 10.1029/2010JD014188.

13. Rengarajan R., Sudheer A.K. and Sarin M.M. (2011). Wintertime $PM_{2.5}$ and PM_{10} carbonaceous and inorganic constituents from urban site in western India. *Atmospheric Research,* 102(4), 420-431.

14. Birch M.E. and Cary R.A. (1996). Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust: methodology and exposure issues. *The Analyst,* 25(3), 121-241.

15. Pachauri T., Saraswat R.K., Singla V., Lakhani A. and Kumari Maharaj K. (2013). Characterization of Organic and Elemental carbon in $PM_{2.5}$ aerosols at Agra, India. *Research Journal of Recent Sciences*, 2(ISC- 2012), 1-6.

16. NAAQS (2009). The gazette of India, ministry of environmental and forests notification. National Ambient Air Quality Standards 16.

17. Castro L.M., Pio C.A., Harrison R.M. and Smith D.J.T. (1999). Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. *Atmospheric Environment,* 33(17), 2771-2781.