ARTICLE IN PRESS

Atmospheric Pollution Research xxx (xxxx) xxx–xxx

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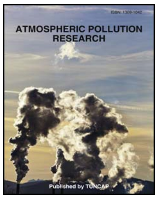
Contents lists available at ScienceDirect

Atmospheric Pollution Research

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



Study of temporal variability and mass closure of $PM_{2.5}$ and its chemical constituents during weak south-west monsoon

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ARTICLE INFO

Keywords:
Mineral aerosols
Chemical composition
Indo-Gangetic plain
SW-Monsoon
Aerosol aging
$PM_{2.5}$

ABSTRACT

Ambient $PM_{2.5}$ (n = 42) samples have been collected during a weak South-west (SW) monsoon (July–September, 2015) from central part of the Indo-Gangetic Plain (IGP; at Kanpur). Organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), water-soluble inorganic species (WSIS) and metals have been measured in this study. Air-mass back trajectory (AMBT) analysis reveals atmospheric transport from three major pathways indicated as Type-1 (n = 24; traversing through western region), Type-2 (n = 8; traversing eastern region) and Type-3 (n = 10; terrestrial air-masses). Total carbonaceous aerosols (TCA), mineral dust (MD) and WSIS in Type-1 air-mass contributed 18.7 ± 8%, 40.3 ± 14.5% and 35.2 ± 13.4%, respectively to the $PM_{2.5}$ mass. TCA, MD and WSIS mass fractions constituted 27.1 ± 13.2%, 29.1 ± 7.9% and 34.9 ± 10.7% in Type-2 air-mass and 25.2 ± 14.1%, 34.6 ± 14% and 33.3 ± 9.8% in Type-3 air-mass, respectively. Mineral dust percentage fraction and composition (based on Fe/Al ratio) suggests significant differences between Type-1 and Type-2 air-masses. Based on statistical two-tailed *t*-test, the mineral dust composition of Type-1 versus Type-3 and Type-2 versus Type-3 air-masses look near similar. However, average mass ratios of OC/EC (6.2–6.4), WSOC/OC ($\approx$0.50; exception being difference in Type-2 versus Type-3) and K^{+}_{BB}/OC (0.05–0.07; K^{+}_{BB}: biomass burning derived potassium) look near similar in $PM_{2.5}$ associated with all the three air-masses; indicating carbonaceous aerosols from well-mixed sources with dominant contribution from biomass burning emission. A significant abundance of organic aerosols and mineral dust in presence of high moisture content and their mixing over IGP has implications to perturbation in regional scale radiative forcing.

1. Introduction

Indo-Gangetic Plain (IGP) stretches from northern to eastern part in India and has a unique topography: Himalayan range in its north and Deccan plateau in the south. Seasonal and annual practices of large-scale biomass burning emission and fossil-fuel combustion in conjunction with mineral dust largely influence the variability in chemical composition and optical properties of atmospheric aerosols over the IGP (Reddy and Venkataraman, 2002; Ramanathan and Ramana, 2005; Nair et al., 2007; Dey et al., 2012; Rajput et al., 2014a; Rai et al., 2016). Biomass burning and secondary aerosol formation are the major sources of organic aerosols over northern India with large seasonal variation (Ram et al., 2010; Kaul et al., 2011; Rajput et al., 2014a; Rai et al., 2016; Singh and Gupta, 2016). Furthermore, the crustal dust also plays a crucial role in influencing the atmospheric composition, chemistry and radiative forcing besides acting as cloud condensation nuclei (CCN) (Usher et al., 2003). Previous studies have suggested that over this region there is a significant contribution of mineral dust which is transported from western region including dust from Thar Desert (Dey et al., 2004; Chakraborty and Gupta, 2010; Ghosh et al., 2014). Long-range transport of mineral dust over the region is very conspicuous during summer months resulting into high variability in aerosol chemical composition and optical properties. Thus, assessing seasonal composition of particulate matter is of utmost importance for identification of emission sources and health risk evaluation (Voutsa et al., 2002; Pipal et al., 2014; Singh and Gupta, 2016).

Indian summer monsoon, during the months from June–September, is usually marked with more than 80% of the total annual rainfall over the region. During this period, South-westerly wind system favors the transport of air-masses from oceanic region (Bay of Bengal or Arabian Sea) to the Indian sub-continent (Goswami and Mohan, 2001; Wang and LinHo, 2002). Particles concentration is generally low due to high convective mixing and frequent wet precipitation events during this period. However in 2015, less rainfall events have been recorded due to El-Niño and positive phase of PDO (Pacific Decadal Oscillations). These phenomena have caused a weak Summer Monsoon (also refered to as

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

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https://doi.org/10.1016/j.apr.2018.02.008
Received 28 September 2017; Received in revised form 16 February 2018; Accepted 17 February 2018

Please cite this article as: Rajeev, P., Atmospheric Pollution Research (2018), https://doi.org/10.1016/j.apr.2018.02.008

SW-monsoon) which facilitated us to assess the aerosol composition during this period. A priori information of these phenomena, based on long-term meteorological records, has motivated us to carry out a study focussing on composition of fine aerosols ($PM_{2.5}$) under expected high content of mineral dust resulting due to high wind speed and low moisture content in top soil layer owing to less precipitation during the weak monsoon (Zhang et al., 1997; Krishnamurthy and Krishnamurthy, 2014; Rajeev et al., 2016).

In this study, chemical composition and characteristics of fine aerosols ($PM_{2.5}$) have been assessed from central IGP during SW-monsoon. Our study provides hitherto unknown data set on chemical composition of $PM_{2.5}$ and highlights the significance of interaction of organic aerosols and mineral dust over this region. To understand the sources and chemical characteristics of $PM_{2.5}$ and interactions among various chemical constituents, organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), metals (Fe, Al, Ca and Mg) and water-soluble inorganic species (WSIS) have been measured. These chemical constituents of $PM_{2.5}$ and their characteristic ratios have been studied in detail by categorizing and segregating the dataset on the basis of distinct air-mass back trajectories (AMBTs).

2. Methodology

2.1. Site description and ambient meteorology

$PM_{2.5}$ (particulate matter with aerodynamic diameter ≤ 2.5 μm) sampling was carried out at Kanpur (26.30 °N; 80.14 °E, 142 m above mean sea level), situated in the states of Uttar Pradesh (central part of IGP). Samples have been collected on the roof-top of Centre for Environmental Science and Engineering (CESE) building in the premises of Indian Institute of Technology Kanpur. This region experiences extreme weather conditions with very hot and dry summer (April–May; temperature as high as 48 °C) and cold winters (December–February; temperature < 5 °C). Generally, IGP receives an annual rainfall of 800–1000 mm, of which over 90% of the wet-precipitation occurs during the SW-monsoon (June–September). In 2015, this region received only 375 mm of annual wet precipitation, of which only 45% occurred during SW-monsoon season due to El-Ni*ń*o and PDO phenomena. Ambient temperature and relative humidity recorded during sampling period exhibited variability from 22.1 to 37.4 °C and 53–97%, respectively. The south-westerly winds (~8 m/s) were prevalent during the study period (July–;September 2015; SW-monsoon) (Fig. 1).

2.2. Aerosol sampling and chemical analyses

$PM_{2.5}$ samples (n = 42) were collected for 8 h (from 08:00 a.m. to 04:00 p.m.) onto pre-combusted quartz fiber filters (Whatman™: 20.3 × 25.4 sq. cm) by filtering ~480 m^3 of ambient air using a high volume sampler (calibrated flow-rate: 0.97 m^3/min) from 15th July, 2015 − 30th September, 2015 (Kumar and Gupta, 2015). The collected samples were stored in deep freezer at −19 °C until further chemical analysis. Mass concentrations of $PM_{2.5}$ have been measured gravimetrically after equilibrating filters at 25 ± 2 °C temperature and 40 ± 5% RH for 8–10 h. A portion (1/4th) of each aerosol sample (pre-soaked) was extracted with 60 mL of Milli-Q water (resistivity: 18.2 MΩ cm) in pre-cleaned Teflon vials utilizing the sonication technique (Rajeev et al., 2016). Subsequently, each extract was filtered through a 0.22 μm filter in polypropylene vial. These filtered extracts have been used to measure water-soluble ionic species (WSIS) and water-soluble organic carbon (WSOC). The quantification of WSIS (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) has been achieved on a dual channel ion-chromatograph (Metrohm, Swiss) equipped with an anion column (Metrosep: A Supp 5-250/4.0) and a cation column (Metrosep: C 4-250/4.0). The dipicolinic acid (0.7 mM) has been used as an eluent for cation separation whereas a mixture of Na_2CO_3 (3.2 mM) and $NaHCO_3$ (1.0 mM) was used as an eluent for anion separation. The calibration standards and individual samples were passed through a 100 μL loop (Rajeev et al., 2016; Rajput et al., 2016b). The measurement of HCO_3^- has been performed independently in all samples by titration with a 5 mM HCl solution using Methyl orange solution (Thomas Baker) as a pH indicator. Quantification of WSOC in aqueous extracts was carried out on a total organic carbon analyzer (TOC Shimadzu) using a non-dispersive infrared detection (NDIR) technique. Linear calibrations for TC and IC were achieved ($R^2 > 0.999$) on a TOC analyzer with standard solutions of potassium hydrogen phthalate (KHP) and sodium carbonate-bicarbonate mixture ($Na_2CO_3 + NaHCO_3$), respectively.

For metal analysis, aerosol samples were treated with high purity HF (0.5 mL), HNO_3 (2 mL) and H_2O_2 (0.5 mL) along with 5 mL Milli-Q water in Teflon vials and digested at 150 °C (Rajput and Gupta, 2016). After ensuring complete digestion, samples were evaporated at 100 °C till near dryness. Subsequently, 1 mL of 8N HNO_3 was added and the final solution was made to 31 mL with Milli-Q water. Using ICP-OES (Inductively Coupled Plasma-Atomic Emission Spectrometry; Thermo Scientific; iCAP 6300), metals (Fe, Al, Ca and Mg) concentrations have been measured (Rajput et al., 2016a). The OC and EC concentrations were determined on a Sunset Lab EC-OC analyzer using thermo-optical transmittance protocol (NIOSH: National Institute for Occupational Safety and Health) (Rajput et al., 2017). Analytical accuracy in the measurement of total carbon (TC = OC + EC), was achieved by analyzing known amounts of potassium hydrogen phthalate (KHP). Analytical uncertainty of less than 7% has been estimated through replicate analyses of the samples (n = 6) for each measured species. Quality control of the data has been assessed routinely by analyzing signal-to-noise ratio from filter analysis-to-procedural blanks (S/N > 10).

3. Results and discussion

3.1. Temporal variability of $PM_{2.5}$ and major constituents

In this study, $PM_{2.5}$ concentration varied from 15.9 to 119.6 (42.2 ± 22.4) μg/m^3. Due to inefficient wet scavenging of atmospheric particles during SW-monsoon in 2015 (due to El-Ni*ń*o and positive phase of PDO: Pacific Decadal Oscillation), $PM_{2.5}$ concentration during the study period is quite comparable to that reported in a previous study from this region (37.6 μg/m^3) during pre-monsoon season (Ghosh et al., 2014). The concentrations (minimum, maximum, average and standard deviation) of measured chemical species during SW-monsoon are provided in supplementary material (Table S1). Overall, $PM_{2.5}$ concentration constitutes of 36.8% mineral dust (MD), 34.7% water soluble inorganic species (WSIS), 21.8% total carbonaceous aerosols (TCA) and 6.7% unidentified matter (UM). This unidentified matter mainly represents the moisture present in ambient aerosols. The OC, EC and WSOC varied from 0.7 to 11.9 (4.7 ± 2.4) μg/m^3, 0.1–1.8 (0.7 ± 0.4) μg/m^3 and 0.4–5.6 (2.3 ± 1.1) μg/m^3, respectively. High correlation of OC with EC ($R^2 = 0.9$) in this study plausibly indicates that they are mainly produced from the anthropogenic combustion sources. Besides this, 49% of the total OC is water-soluble (WSOC/OC ratio = 0.49 ± 0.05). The WSIS contribute 35% (WSIS/$PM_{2.5}$ = 0.35 ± 0.12) in the total $PM_{2.5}$ mass followed by 21.8% contribution of total carbonaceous species (TCA; TCA = OM + EC, where OM = 1.6*OC) (Turpin and Lim, 2001; Rajput and Sarin, 2014).

The temporal variability of $PM_{2.5}$ and its constituent fractions i.e. OC/$PM_{2.5}$, EC/$PM_{2.5}$, ΣWSIS/$PM_{2.5}$ and MD/$PM_{2.5}$ are shown in Fig. 2. $PM_{2.5}$ concentration showed a decrease on the sampling days having wet precipitation (Fig. 2a). Furthermore, there was an increase in $PM_{2.5}$ loading after mid of August due to less amount of rainfall received at the site. Mineral dust has been estimated using Al as a proxy (Al = 8% of upper continental mineral dust) (McLennan, 2001). The percentage contribution of mineral dust to $PM_{2.5}$ [~37%; MD/$PM_{2.5}$ = 0.37 ± 0.14 (0.16 − 0.78)] was predominant among all species, which can be attributed to relatively high wind speed (~8 m/s)