Chemical Characterization of Fine Atmospheric Particles of Water-Soluble Ions and Carbonaceous Species in a Tropical Urban Atmosphere over the Eastern Indo-Gangetic Plain

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ABSTRACT

Ambient fine aerosols and their sources were evaluated in an eastern Indian megacity, Kolkata (KOL), from September 2010 to August 2011. A submicron aerosol sampler (SAS) with two stage stacked filter units (SFU) was devised for simultaneous but discrete collection of water-soluble inorganic ions (WSII) and carbonaceous aerosols (CA; elemental carbon (EC) and organic carbon (OC)). Characteristics of the WSII and CA were identified using ion chromatography and an OC-EC analyzer, respectively, adopting the Interagency Monitoring of PROtected Visual Environments (IMPROVE-A) protocol. The mean annual concentrations of the WSII showed a predominance of cations (anions), consisting of Ca2+, Mg2+, and Na+(Cl–, NO3–, and SO42–), with secondary aerosols (NH4+, NO3–, and SO42–) and Ca2+ each constituting 25% and 30%, respectively, of the total WSII (TWSII). The highest mean monthly concentration of SO42– and NO3– was observed during the winter month of February and the summer months of March and May, respectively. A pronounced peak in the monthly mean for the non-sea salt-K+(nss-K+) concentration was noticed during October and April, implying the strong influence of biomass burning emissions during these months. Among the sea salt (SS), anthropogenic (AN), and dust (DT) sources of the TWSII, a predominant contribution from DT in August and from AN in November, April, and May was inferred. The mean annual concentration of OC was three times higher than that of EC, with 43% of it being secondary OC. Whereas the major sources of OC were inferred to be paved dust, coal combustion, and biomass burning, those of EC were industrial and motor-vehicle non-exhaust emissions, coal combustion, and motor vehicle exhaust.

Keywords: Water-soluble inorganic ions; Carbonaceous aerosols; OC-EC ratio; Source apportionment.

INTRODUCTION

Increasing concentration of anthropogenic aerosols in recent years has been inferred to perturb the earth system exerting detrimental effects on climate, visibility, and human health (IPCC, 2013). A large uncertainty is reported in the radiative forcing exerted due to aerosols (Lee et al., 2016). The chemical composition of aerosols has an important role in determining their relative efficiency to absorb and scatter the solar radiation. Also, the amount of water-soluble aerosol species in the atmosphere would impact the development of cloud condensation nuclei and thereby contribute to the quantity, lifetime, and brightness of clouds (Eichel et al., 1996; Lohmann and Feichter, 2005; Rosenfeld et al., 2008). Fine aerosol particles (aerodynamic diameter ≤ 2.5 µm) accumulate in the atmosphere due to the least efficient particle removal mechanisms for them, and hence have a considerably longer atmospheric residence time than coarser or ultrafine aerosol particles (Jaenicke, 1984). These particles thus play a vital role in degrading air quality, reducing visibility, causing adverse health effects and climate change. The chemical composition of fine aerosols, their physical and optical properties, and therefore their interaction with solar radiation and impact on Earth’s radiation balance tends to be different from the coarser particles (aerodynamic diameter ≥ 2.5 µm) (Pandolfo et al., 2011; Seinfeld and Pandis, 2012). It is therefore necessary to examine the atmospheric abundance and properties of fine aerosols segregating them from the coarser particles. In general, the chemical composition of atmospheric aerosols contains water-soluble inorganic species, organic carbon (OC), elemental carbon (EC) and metals (Poschl,
Knowledge of aerosol chemical composition can provide essential information about sources and processes that can affect the aerosol concentration at a particular place (Perrino et al., 2009; Zhang et al., 2017). Though the atmospheric abundance of aerosol constituents is known in general, the chemical composition would exhibit temporal and spatial heterogeneity owing to the short residence time of aerosol species, influence from source- and region-specific emission sources and meteorological effects. This heterogeneity therefore leads to uncertainty in the prediction of aerosol-induced climatic impacts, and therefore necessitates examining temporal features of aerosol chemical species, and that distinctly for fine and coarse aerosol particles on a regional to local scale.

In the recent past, campaigns and individual measurements over the Indian mainland provided insights on the chemical composition of aerosols (e.g., over southern India: Hedge et al., 2007; George et al., 2008; Aswini et al., 2018; northern India: Ram et al., 2010a; Rai et al., 2016; Rajput et al., 2018; western India: Rastogi et al., 2014; Gawhane et al., 2017; eastern India: Chatterjee et al., 2012; Das et al., 2015; high altitude location: Chatterjee et al., 2010; Ram et al., 2010; Satsangi et al., 2014). The above measurements were mostly limited to characterization of water-soluble inorganic ions (WSII) or carbonaceous aerosols (CA). There is a lack of information from the available studies on simultaneous analysis of both WSII and carbonaceous aerosols (CA) (discretely sampled for a better characterization) influencing the air mass characteristics over the region.

In the present study, we examine the fine aerosol (aerodynamic diameter ≤ 1.6 µm) chemical constituents of WSII and CA over a tropical urban atmosphere (urb-atm) in the lower Indo-Gangetic Plain (IGP) in eastern India during the daytime. Sampling is done using a devised submicron aerosol sampler (SAS) with the two-stage stacked filter units (SFU) for the simultaneous but discrete sampling of WSII and CA. Discrete sampling using separate substrates is done for a better characterization of WSII and CA (Solomon et al., 1989; Berg et al., 1993; Vecchi et al., 2009). The chemical sampling is carried out during daytime hours (10:00–16:00 IST) to evaluate the relative abundance of daytime fine aerosol chemical composition in the urb-atm. The daytime mean aerosol concentration exhibits a low hourly variability and corresponds to the well-mixed layer of atmosphere (Verma et al., 2013; Pani and Verma, 2014). The daytime analysis of aerosol chemical characteristics thus aids in linking the change in the temporal feature (e.g., the trend of monthly mean values) of the measured tracer aerosol species concentration in the atmosphere primarily to the impact of emission sources (Verma et al., 2017). Also, this analysis leads to accounting for aerosol species which would be interacting with the incoming solar radiation and influencing the aerosol optical depth in the eastern Indian urb-atm.

The primary focus of the present study is on the fine aerosol-chemistry through the investigation of the temporal variation of the water-soluble inorganic species, organic and elemental carbonaceous species, along with the partitioning of the aerosols into natural and anthropogenic aerosols. This study also intends to determine the probable sources of aerosol and their monthly variation over a tropical megacity, KOL, where air pollution is already a severe concern. This urb-atm in eastern India (KOL) is also typical as it evinces a strong outflow of aerosol pollutants from the IGP (Kumar and Verma, 2016).

**METHODS**

Sampling of ambient fine aerosol particles was carried out over a tropical eastern India urb-atm in the lower IGP, at KOL (Fig. 1(a)). Measurements were carried out at the Indian Institute of Technology (IIT), Kharagpur, Extension Centre (22.57°N, 88.42°E) situated at the outskirts of Kolkata city, on the rooftop of a building 12 m above the ground level from September 2010 to August 2011. Kolkata, a metropolitan city, is the third most populous city in India with rapid urbanization and confronts severe pollution (Census of India, 2011, Verma et al., 2013). The Sundarbans delta is located approximately 150 km to the south of the city. Several industries including those manufacturing chemicals, plywood, rubber products, metals and electrical equipment manufacturing industries are located in and around KOL. The monthly mean of temperature (temp), relative humidity (RH), wind speed (WS), and the rainfall (RF) at the study site is presented in Fig. 1(b). The post-monsoon months of October–December and winter months of January–February are accompanied with a moderately low to the lowest monthly mean of temp, WS, RF and moderately high to the lowest RH. The pre-monsoon months of March to May consist of the highest monthly mean of temp and WS, the lowest to moderately high RF and RH. The southwest monsoon months of June to September consist of the highest monthly mean of temp, RH, RF and a moderately high WS. The surface wind direction at the study site as obtained from the wind rose diagram (figure not shown) indicates surface wind being mostly from the north and northwest during post-monsoon months and from the northeast during winter months indicating the influence of air masses mostly from the continental origin. The surface winds during pre-monsoon and monsoon months are found to be mostly from the south and southwest, indicating the influence of marine air mass on aerosols measured in these months. In order to know the possible influence of air mass pathways (e.g., through oceanic or continental regions) on aerosols measured at the study site, seven-day (7-d) back trajectory is calculated using NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) (Draxler and Hess, 1998) for the days of measurement. Back trajectories integrate back in time the path of travel of an air parcel arriving at a receptor location at a given time. The 7-d back trajectory calculations are performed taking into account the residence time of aerosols of the order of a week in the lower atmosphere (Jaenicke, 1981). Further, cluster analysis (Ward, 1963; Sinha et al., 2012; Kumar and Verma, 2016) of back trajectories is done to find out the major pathways (Fig. 1(a)). This analysis led to identifying six pathways of air mass at the...
study site, as follows: (i) Path A (IO/AS/SI/ECI), those which originate from Indian Ocean (IO) and traverse over Arabian Sea (AS), South India (SI) and east coast of India (ECI); (ii) Path B (BoB), those which originate and traverse over the Bay of Bengal (BoB); (iii) Path C (IGP), back trajectories which originate in the IGP; (iv) Path D (AFWA/WA/NWI/CNI), those which originate from Africa (AFWA) and pass through west Asia (WA), northwest India (NWI), central India (CNI) and IGP; (v) Path E (NEI), back trajectories originating from northeast India (NEI); (vi) Path F (IO/BoB), those which originate in the IO and spend relatively longer time over BoB. Analysis of back trajectory clusters indicated a relatively higher frequency of air mass at the study site from Path B and Path C (about 30% each) than the rest of the paths (4–15%) (Fig. 1(a)).

**Description of Submicron Aerosol Sampler**

An SAS was indigenously designed and fabricated at the workshop of IIT, Kharagpur, using the considerations of Norwegian Institute for Air Research (NILU) protocol (Gabriel et al., 2002; Mayol-Bracero et al., 2002). The framework of SAS consisted of two SFUs in parallel (Fig. 2(a)) with a common inlet of 20 mm connected to a pick-off tube of 1.8 cm and a suction pump. The air sucked using a suction pump passes via the common inlet, bifurcates to parallel conduit consisting of four perforated stainless steel filter holders each sandwiched between two polyethylene rings of diameter 34 mm. Nuclepore filter paper (47 mm, 8.0 µm) was placed on the first stage of both the SFU to collect the coarser fraction (see later). While a quartz filter (Pallflex Tissuquartz 2500 QAT-UP) was placed on the one side, a PTFE membrane filter of pore size 2.0 µm was placed on the other side of the SFU’s second stage. The quartz filter and PTFE filters were used for the collection of respectively the carbonaceous and WSII species. Discrete sampling using separate substrates is helpful for a better characterization of WSII and CA; e.g., PTFE for WSII (Solomon et al., 1989; Berg et al., 1993; Vecchi et al., 2009) and quartz for CA through thermal carbon analysis (Chow et al., 1993, 2007, 2011). A study examining a simultaneous but discrete measurement of both WSII and CA has been carried out over the Indian oceanic region during the Indian Ocean Experiment (Gabriel et al., 2002; Mayol-Bracero et al., 2002). The quartz filter was pre-fired at 850°C for 12 hours before use to remove organic impurities (Mayol-Bracero et al., 2002). Quartz filters are highly durable for thermal methods, which involve high temperatures, desorption. The main advantages of using PTFE filters are these being (i) highly durable, (ii) chemically inert with fewer impurities, (iii) absorbs less moisture and endure a wide range of weather conditions (Vecchi et al., 2009; Chakraborty and Gupta, 2010).
**Operational Details of SAS**

The designed SAS with SFU consists of integrated flow meters (CM-flow meter) (Fig. 2(a)). The integrated flow meter measures the flow rate with an accuracy of ±5% and a precision of 2 to 5% (http://www.cmflowmeters.in/home/). The flow rate is recorded on both the SFUs at regular intervals of 15-minutes. The flow meter is factory calibrated (http://www.cmflowmeters.in/home/) maintaining an interval of 6 months between the calibrations. The flow meter is calibrated with National Standard to comply with SI traceability, and a calibration certificate is provided by the manufacturer as per National Accreditation Board for Testing and Calibration Laboratories (NABL), New Delhi, India, guidelines.

The SAS was designed to maintain a flow rate of 25 L min⁻¹ to achieve a face velocity of 47 cm s⁻¹. Resultant face velocity for the given flow rate is calculated using the following formula:

\[ v = \frac{Q}{A} \]  

(1)

where \( v \) is the filter face velocity in m s⁻¹; \( Q \) is the volumetric flow rate in m³ s⁻¹ and \( A \) is the filter exposed area in m² (McDow and Huntzicker, 1990). As mentioned earlier, during operation, a Nuclepore pre-filter (polycarbonate membrane; nominal pore size: 8.0 µm; Corning Costar) was placed in the first stage of each SFU to collect the coarser aerosol fraction. At the calculated face velocity of 47 cm s⁻¹ corresponding to the designed flow rate of 25 L min⁻¹ of the devised SAS, the Nuclepore filter would entrap particles of cut-off diameter 1.3 µm (refer to Fig. S1, adopted from John et al. (1983). However, during the study period over the tropical urban environment, the average face velocity obtained was 28 cm s⁻¹. Also, the devised SAS is designed to transmit particles at 50% efficiency, with a “cut-off size” of 6.8–9.6 µm, and at 90% efficiency, with a cut-off size of 2.6–3.7 µm (Blomquist et al., 2001). Hence, the coarse fraction collected on Nuclepore filter would consist of particles larger than 1.6 µm (cut-off size) (calculated for an average face velocity of 28 cm s⁻¹) and smaller than 10 µm (50% cut-off size of the sampler transmission) aerodynamic diameter. Based on the above, the cut-off size for particle collected on PTFE which is chemically characterized in the present study is 1.6 µm (referred as fine particle in the present study). The analysis of WSII species and CA were carried out using ion chromatography (IC) and OC/EC analyzer, respectively (discussed in subsequent sections). The handling of filters (both PTFE and quartz) and their quality assurance were maintained following the considerations of NILU protocol (https://www.nilu.no/projects/ccc/manual/index.html).

The sample collection was done weekly with at least one sample collected during the middle of each week of a month, amounting to a total of about seventy samples during the period between September 2010 to August 2011. The number of samples used in chemical analysis for the present study were sixty-one. These for each month is as follows: September: 5; October: 5; November: 8; December: 6; January: 5; February: 4; March: 7; April: 6; May: 6; July: 6; August: 3. Aerosol embedded filter papers were stored in containers and refrigerated at 4°C until chemical analysis of the respective filters (Chatterjee et al., 2012). The PTFE was subjected to gravimetric analysis to estimate the total mass of aerosol species embedded on the filter. The sum of the chemical determinations consisting of WSII, particulate organic matter (POM), and EC was compared with the mass amount determined on PTFE to estimate the unanalyzed aerosol mass (refer to the section “Characteristics of Organic and Elemental Carbonaceous Aerosol Fractions”).

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**Fig. 2.** (a) Submicron aerosol sampler (SAS) with stacked filter unit (SFU). SEM images of (b–c) PTFE filter and (d–e) Nuclepore filter.
The present study is mainly focused on evaluating the fine aerosol-chemistry over the eastern Indian urb-atm at KOL using for the first time the devised SAS with SFU. The devised SAS with SFU was used for discrete sampling using separate substrates for a better characterization of WSII and CA. In this study, we aimed to only determine the OC-EC for the sample on quartz filter. We have not carried out the gravimetric analysis of quartz filters or the chemical determination of aerosol species (other than OC-EC) on it.

**Determination of Inorganic Ions Using Ion Chromatography**

Fine aerosols impregnated on the PTFE Teflon filter are analyzed chemically for the apportionment of chemical species as described in Gabriel et al. (2002). The watersoluble ion species collected on PTFE Teflon filters are first wetted with 0.5 ml of methanol, and 39.5 ml Milli-Q water solution (resistivity greater than 18 milliohm), WSII from the filter are extracted into the solution by using ultra-sonicator for 30 minutes of treatment, the necessary time for the complete recovery (78–98%). The solution containing extracted ions are then analyzed by Metrohm 761 Compact IC for inorganic anions and cations. An electrolyte solution 3.2 mmol L⁻¹ Na₂CO₃ and 1.0 mmol Na₃HCO₃ at a flow rate of 0.7 mL min⁻¹ was used as an eluent for anion analysis. For the cation analysis, an electrolyte solution of 4 mmol L⁻¹ of tartaric acid and 0.75 mmol L⁻¹ of PDCA (Pyridine-2, 6-dicarboxylic acid) at a flow rate of 1 mL min⁻¹ was used as an eluent. The instrumental detection limit of the measured water soluble ionic species is between 0.01 and 0.08 µg m⁻³. An instrumental detection limit of the measured water soluble ionic species is between 0.01 and 0.08 µg m⁻³. An analytical precision between 2% and 6% was obtained.

The WSII species measured using IC were as follows: sulfate (SO₄²⁻), nitrate (NO₃⁻), fluoride (F⁻), chloride (Cl⁻), phosphate (PO₄³⁻), potassium (K⁺), sodium (Na⁺), calcium (Ca²⁺), magnesium (Mg²⁺) and ammonium (NH₄⁺). The measured Na⁺ is considered as the reference species to estimate the sea-salt fraction (e.g., Granat, 1972). The non-sea salt components of potassium, nss-K⁺ (Hitchcock et al., 1980); sulfate, nss-SO₄²⁻ (Millero and Sohn, 1992); calcium, nss-Ca²⁺ (Morales et al., 1998); magnesium, nss-Mg²⁺ (Virkkula et al., 2006); and chloride, nss-Cl⁻ (Holland et al., 1984), are calculated as follows by considering sodium as a reference species (Keene et al., 1986):

\[
\begin{align*}
nss-K^+ &= K^+_{\text{measured}} + Na^+ \times 0.037 \\
nss-SO_4^{2-} &= SO_4^{2-}_{\text{measured}} - Na^+ \times 0.2516 \\
nss-Ca^{2+} &= Ca^{2+}_{\text{measured}} - Na^+ \times 0.0373 \\
nss-Mg^{2+} &= Mg^{2+}_{\text{measured}} - Na^+ \times 0.12 \\
nss-Cl^- &= Cl^-_{\text{measured}} - Na^+ \times 1.174
\end{align*}
\]

Furthermore, we have classified and analyzed the sources of aerosols using individual WSII species such as sea-salt (SS) aerosols (Na⁺, sea-salt components of Cl⁻, Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻), anthropogenic (AN) aerosols (NH₄⁺, nss-K⁺, F⁻, NO₃⁻, PO₄³⁻, nss-Cl⁻ and nss-SO₄²⁻), and dust (DT) aerosols (nss-Ca²⁺ and nss-Mg²⁺).

**Examination of Filters under Scanning Electron Microscope**

Visualization and qualitative analysis of aerosol particles impregnated on the Nuclepore and PTFE filters of SFU were analyzed using ZEISS EVO 60 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDS) at the central research facility (CRF), IIT, Kharagpur. The magnification of SEM varied from about 1000 to 10,000 times with an accelerating voltage of 20 kV and the working distance of 7 mm. This working condition enables to visualize aerosols from a few nanometers to a hundred nanometers. A portion of the Nuclepore and PTFE filter are cut and examined under SEM, and the images obtained are presented in the Figs. 2(b)–2(e). The images of the PTFE filter (Figs. 2(b)–2(c)) show clusters and individual aerosol particles entrapped on the filter, and size analysis reveals the presence of discrete particles less than 1 µm. Two types of particle shape were mainly distinguished from the SEM analysis of the PTFE filter: (i) spherical and (ii) irregular. As inferred from available studies (e.g., Buseck and Posfai, 1999; Satsangi et al., 2014), the atmospheric particles of natural origin (e.g., soil dust or minerals) have, in general, irregular shapes, and those of anthropogenic origin (e.g., from combustion processes) have a variable morphology. The anthropogenic particles are suggested occurring as individual particle as well as in aggregated form (Satsangi et al., 2014). These particles with spherical shape are inferred being the result of the secondary reactions; irregular particles in the fine range result from coagulation processes (Breed et al., 2002; Satsangi et al., 2014; Li and Shao, 2009). Images of Nuclepore filter paper (Figs. 2(d)–2(e)) evince the presence of larger particles in the range of 2 to 8 µm. Thus, the presence of fine aerosol particles (mostly submicronic) on the second stage of the filter unit as evinced from the results of SEM analysis, corroborates our inference on cut-off size of particles (1.6 µm) as discussed in the section “Operational Details of SAS,” and which are chemically characterized in the present study.

**Probable Source of Water-soluble Inorganic Ion Species**

The sources of WSII may be natural or anthropogenic; the primary sources of WSII documented from the available information are given as follows. (1) Marine sources: Salts are predominantly formed by sodium and chloride, with a smaller portion made up of sulfate, calcium, magnesium and potassium. Sodium is considered as the main tracer for the particulate matter in marine salt since chlorine gets depleted due to gas phase reactions in atmosphere (White, 2008). Anthropogenic sources of chloride include coal combustion, biomass burning, and waste incineration (Knipping et al., 2003). (2) Crustal sources: The dominant components are aluminum, iron, calcium and potassium, which are generally from crustal origin (Alomary and Belhadj, 2007). Phosphates in the atmosphere are also from the crustal source through incorporation from sedimentary
Determination of Carbonaceous Aerosols Using IMPROVE-A Protocol

Carbonaceous aerosol embedded on the quartz filter was analyzed using thermal/optical reflectance (TOR) using the IMPROVE-A in a DRI Model 2001A Thermal/Optical Carbon Analyzer (Desert Research Institute, USA) at CSIR-National Physical Laboratory (CSIR-NPL), New Delhi. OC/EC carbon analyzer works on the principle of preferential oxidation of OC and EC at different temperatures, first in the presence of pure helium at four temperatures (140, 280, 480 and 580°C) and second in the presence of 98% helium and 2% oxygen at three temperatures (580, 740 and 840°C). In a non-oxidizing helium atmosphere, OC must be volatilized while EC should be combusted in the presence of an oxidizer from the same deposit. The introduction of oxygen into helium atmosphere and evolution of carbon (pyrolyzed OC (OP)) between the process and the return of reflectance to its initial value is defined as the OC/EC split. With the step by step up-gradation of temperature as mentioned above (corresponding to pure helium and helium along with oxygen), eight carbon fractions are released which corresponds to OC_1, OC_2, OC_3, OC_4, EC_1, EC_2, EC_3 and pyrolyzed carbon fraction OP from different carbon sources (Chow et al., 2004). Abundance of carbon from each of these eight carbon fractions will vary with different sources (Ellis and Novakov, 1982; Ho et al., 2003; Patil et al., 2013). EC1 was found to be abundant in biomass burning and OC1 in coal combustion. OC3 and OC4 are reported to be emitted from paved road dust which is associated with motor vehicle emissions such as brake and tire wear, and oil drips (Ho et al., 2003; Patil et al., 2013). EC1 was found enriched in industrial and motor-vehicle emissions sample, EC2 and EC3 were chiefly identified from coal combustion and motor vehicle exhaust (Cao et al., 2005).

Furthermore, amount of primary organic carbon (POC) and secondary organic carbon (SOC) are determined in this study using EC tracer method (Castro et al., 1999). The minimum OC/EC value observed during the study period is considered as OC/EC_{min} (i.e., 1.91), and is used for the calculation of SOC in the atmospheric aerosols for the region of interest. Following equations are used for the estimation of POC and SOC:

\[
[\text{POC}] = \left[ \frac{\text{OC}}{\text{EC}_{\text{min}}} \right] \times \text{EC} + c \quad (7)
\]

\[
[\text{SOC}] = [\text{OC}] - [\text{POC}] \times \text{EC} \quad (8)
\]

where POC is primary OC and SOC is secondary OC and c is a parameter to account for noncombustible sources contributing to POC and OC concentration and is assumed negligible in the present study.

The accuracy of DRI carbon analyzer for TOR for Total Carbon (TC), determined by analyzing a known amount of carbon, is 2–6% (Rau, 1986). Accuracy of the OC/EC split is 5–10%. This accuracy is also influenced by the filter loading and source type. Most of the uncertainty for low concentration samples is from the standard deviation of the field blanks or backup filters. The precision of the instrument for TC, OC, EC and OC/EC is 4, 6, 4 and 3%, respectively (DRI, 2000). The minimum detection limit (MDL) of the DRI carbon analyzers (based on individual quartz-fiber filters and defined as 3 times the standard deviation (3σ) of their measured results) is obtained as 0.81 µg cm^{-2} for OC and 0.19 µg cm^{-2} for EC (DRI, 2000).

The reported concentrations of the measured carbonaceous aerosols (OC and EC) in the present study have been corrected for their respective blank concentrations in the filters. Filter blank values in the present study were 0.31 µg cm^{-2} for OC and 0.06 µg cm^{-2} for EC, respectively.

RESULTS AND DISCUSSION

Chemical Composition of Fine Aerosol

The monthly mean concentrations of the total WSII (T_{WSII}: sum of analyzed WSII species) are shown in Fig. 3(a). The monthly mean of T_{WSII} is estimated as 45–86 µg m^{-3} with an annual mean of 65 ± 13 µg m^{-3}. In general, monthly mean of T_{WSII} concentrations during October, November, January, and April–May months are found exceeding their respective annual mean value at the study site. These concentrations are twice the lowest mean concentration observed during August. The lowest monthly mean concentration of T_{WSII} in the southwest monsoon
month of August is expected due to wet scavenging of aerosols with the rainfall (Fig. 1(b)) High monthly mean value during post-monsoon and winter months is expected due to build-up of atmospheric aerosol load after the monsoon season from anthropogenic activities (refer to “Methods”). The surface wind direction at the study site also indicates the influence of air masses mostly from the continental origin during post-monsoon and winter months. Analysis of back trajectories for the days of measurement also indicates their high frequency to originate in the IGP (Fig. 1(a)). High concentration of aerosols during post-monsoon and winter months is also attributed to a strong emission flux contribution potential from the IGP towards eastern India (Kumar and Verma, 2016). The monthly mean of TWSII is also found to be high during pre-monsoon months corresponding to summer season, attributed to an increased influence from biomass burning activities prevalent over the Indian region (Venkataraman et al., 2006; Sahu et al., 2015). Additionally, a high concentration of WSII during summer season is also attributed to an increase in secondary aerosol formation associated with the meteorological conditions of high temperature and RH prevailing during summer season (Fig. 1(b)). Such meteorological conditions have been inferred being favorable to photochemical oxidation mechanisms (Sharma et al., 2007; Chatterjee et al., 2010, 2012). Analysis of WSII aerosol species is further carried out to get insights into their relative chemical composition distribution and the likely sources influencing atmospheric aerosols.

The monthly mean concentrations and their fractional distribution (%) of the WSII species are presented in Figs. 3(b)–3(u). It is seen that species such as Ca2+, CI−, Mg2+, NO3−, Na+ and SO42− contributes more to TWSII than NH4+, K+, PO43− and F−. Annual mean concentrations of WSII show Na+ as one of the abundant species next to Ca2+ and Mg2+. Monthly mean concentration of sodium is specifically higher during months of October, November, January, and April than that of the annual mean (Fig. 3(b)), indicating the increased contribution from marine aerosols in these months. The relative fractional distribution of sodium is as high as 16% in October. The marine air mass influence to aerosols at KOL is corroborated by analysis of back trajectory (Fig. 1(a)) for the study site, which indicates the pathway of the trajectory over the AS and the BoB, and specifically during days of measurement (dashed black lines in Fig. 1(a) shown for October and November). Also, the surface winds during summer month are found to be mostly from the south and southwest, indicating the influence of marine air-mass on aerosols measured in these months (refer to “Methods”).

The annual mean concentration of anions shows Cl− as one of the abundant anions followed by NO3− and SO42−. The monthly mean concentration of Cl− is seen exhibiting a low variability about the annual mean suggesting the lack of predominating influence of any season specific sources (e.g., biomass burning) of chloride in the urb-atm at KOL. The monthly mean trend of Cl− is found to exhibit a notable dissimilarity with sodium indicating their likely origin from different sources. Calcium (tracer for dust) is higher in concentrations than the other species throughout the study period with nss-Ca2+ accounting for 99% of the total Ca2+. A peak is spotted in Ca2+ during August, which is twice the monthly mean concentration observed during the other months. A low variability noticed in monthly mean values of calcium concentration during the study period implies the absence of seasonality. The relative fraction of calcium is the highest in August (67%), compared to 22–34% in the other months. It is remarkable to note that the monthly mean temporal trend of magnesium is akin with calcium throughout the period except July and August. A good association (R2 = 0.72) of magnesium is marked with calcium, which suggests their source to be similar (i.e., crustal) except during July and August. The pattern of concentration of magnesium during the monsoon month of July and August suggest its source in urb-atm being, besides crustal, likely also from urban and industrial. The monthly mean of the fractional contribution of Mg2+ is the highest during August (26%) followed by that during July (17%) with its contribution being relatively low (10–14%) during other months. Annual mean of nss-Mg2+ accounts for 93% of the total Mg2+. A higher concentration of calcium and magnesium among analyzed aerosol constituents as found at the study site has also been reported at few other locations over India (e.g., Kanpur and Raipur) (Balakrishna and Pervez, 2009; Srivastava et al., 2009; Chakraborty and Gupta, 2010). Potassium is generally considered to be the biomass burning marker (Andreae, 1983). Prominent peaks of nss-K+, a biomass burning tracer, is identified during October and April. These peaks corroborate with the information on biomass burning occurrences of crop waste burning and forest biomass as reported in earlier studies (Venkataraman et al., 2006; Sahu et al., 2015). Enhanced concentration of nss-K+ reported in the present study is also consistent with the peak in fire counts obtained from ATSR World Fire Atlas (WFA) (http://due.esrin.esa.int/wfa/) over Indian region. The concentration of nss-K+ accounts to 94% of the total K+, indicating the relative dominance of non-marine sources of K+ at Kolkata. Also, a weak correlation is obtained between Na+ and K+ (R2 = 0.26) suggesting their primary sources to be different. Concentrations of F− and PO43− are relatively low with their maximum observed during November and July. Monthly mean fractional contribution of phosphate (4–8%) is higher than fluoride (1–2%) with high values during November and July. We recall a relatively higher value of TWSII during specific months (October, November, January, and April–May as mentioned before) than that during December and February. The WSII species analysis indicates a relatively higher concentration of Na+, NH4+, K+, and PO4 during these specific months than that during December and February, attributed to a higher influence of marine and biomass burning sources.

Analysis of secondary WSII aerosols (NH4+, NO3−, and SO42−) indicate the annual mean fractional contribution comprising 25% of the TWSII. NH4+ is formed by secondary chemical reactions when gaseous NH3 reacts with gaseous HNO3 or H2SO4 to produce NH4NO3 or (NH4)2SO4 (Appel et al., 1981). Production of NH4NO3 depends on ammonium
Fig. 3. (a) Monthly mean concentration of TWSII. (b–u) Monthly mean concentration (Columns 1, 3) and relative mass fractions (Columns 2, 4) to the respective species concentration of WSII. The relative fraction is estimated as e.g., (Monthly mean conc. of WSII species (i.e., Na\(^+\))/(Monthly mean conc. of TWSII (refer to Fig. 3(a) of TWSII)) \times 100. The annual mean concentration of individual WSII species is marked as solid black line and its respective value is given in µg m\(^{-3}\). Missing data of some of the aerosol species in the bar-plots is due to their significantly low value (below the instrument detection limit, refer to the section “Determination of Inorganic Ions Using Ion Chromatography”) in samples analyzed.
rich conditions which enhances the formation of NH₄NO₃ whereas NH₄⁺-deficit conditions will favor (NH₄)₂SO₄.

The trend of the monthly mean concentration of NH₄⁺ is found to peak during January and September months with the monthly mean values during these months being higher than the annual mean. The peaks observed in NH₄⁺ during January and September are attributed to the combined influence of the various sources of NH₄⁺ (refer to the section “Probable Source of Water-soluble inorganic ion Species”). It is to be noted that unlike NH₄⁺, the nss-K⁺, a biomass burning tracer, is observed peaking during October and April, attributed to season specific biomass burning. A molar ratio \([\text{NH}_4^-]/[\text{SO}_4^{2-}]\) greater/less than 2 is used to identify the conditions of NH₄⁺ as rich/deficit (Alves et al., 2007; Sudheer et al., 2014). Estimated molar ratios show NH₄⁺-rich conditions during January and September and NH₄⁺-deficit condition during other months.

The monthly mean concentration of SO₄²⁻ is found to be the highest (lowest) in February (September) and its fractional contribution to TWSII is 7–18%. The annual mean concentration of SO₄²⁻ is observed being 2 times the annual mean concentration. The fractional contribution of NO₃⁻ is 6–24% with this being the highest during May. While the peak in the monthly mean concentration of SO₄²⁻ is observed during November–February (winter), this of NO₃⁻ is during March and May (summer). High NO₃⁻ levels in summer could be formed by OH⁻ radical produced by enhanced photochemical reaction favored by high relative humidity with NO₂ leading to HNO₃ which in turn form particulate NO₃⁻ (Hertel et al., 2012). Nevertheless, under high-temperature conditions, the NO₃⁻ tends to be volatile, and transforms to HNO₃ (Matsumoto and Tanaka, 1996). Thus, the HNO₃ formed could react with either calcium carbonate or magnesium chloride to produce particulate calcium nitrate and magnesium nitrate for the evolution of nitrate (Poulain et al., 2011). Nitrate can also exist in the form of NH₄NO₃, which is generated by neutralization reaction of HNO₃ with NH₃ and can occur efficiently only under ammonium rich conditions. However, NH₄NO₃ volatilizes under high temperature; hence, the available nitrate manifested during summer in this study might have existed as calcium nitrate and/or magnesium nitrate. It is remarkable to notice the annual mean concentrations of NO₃⁻ being slightly higher than SO₄²⁻ at the study site; this result also concurs with that reported at Kanpur (Chakraborty and Gupta, 2010). The mass ratio of NO₃⁻ to SO₄²⁻ greater/less than 1 has been used to identify the relative predominating influence of respectively mobile or stationary sources to atmospheric aerosols (Arimoto et al., 1996). The monthly mean ratio of NO₃⁻ to SO₄²⁻ is between 0.56 and 4.72 with an annual mean value of 1.6 ± 1.2. This ratio is ≥1 during the entire study period except September and February, when it is ≤1. The pattern of this ratio at the study site thus indicates a predominant influence of mobile sources compared to the stationary sources to atmospheric aerosol throughout the study period except during September and February.

It is found that the monthly mean of secondary WSII aerosols (SA; sum of NO₃⁻, SO₄²⁻, and NH₄⁺) and primary WSII aerosols (PA; sum of Na⁺, K⁺, Ca²⁺, Mg²⁺, F⁻, Cl⁻, and PO₄³⁻), are 19–38% and 62–81% of the respective monthly mean of TWSII except that for August. The chemical analysis of WSII in August showed the concentration values of SA species and most of PA species (except Ca²⁺, Mg²⁺, Na⁺) to be notably low (below the instrument detectable limit), possibly due to the washout of atmospheric pollutants. This indicates the presence of dust and SS as prominent aerosol species in the urb-atm at KOL during the monsoon season. The presence of SS is attributed to marine air mass influence (refer to “Methods”) due to the onset of monsoon season. The presence of dust during monsoon season is also corroborated by available studies (e.g., Vinod et al., 2014).

A comparison of the fine WSII at KOL (November to September averaged) in the present study with the measurement at two other urban locations in northern India over the IGP, e.g., Kanpur (KNP; November 11 to January 12) and New Delhi (NDL; November 9 to March 10) is presented in the Table 1. Among the analyzed WSII, the chemical composition shows predominance of SO₄²⁻, and that followed by Cl⁻, NO₃⁻, and NH₄⁺ at NDL, compared to that of NO₃⁻ and followed by SO₄²⁻, Ca²⁺, and NH₄⁺ at KNP. Unlike at KNP and NDL, there is a predominance of Ca²⁺ followed by Cl⁻, Na⁺, and NH₄⁺ among analyzed WSII at KOL. It is further seen that winter mean concentration of sulfate and nitrate values at NDL and KNP is 2–4 times higher than that at KOL. However, sulfate values are slightly higher than nitrate values at both NDL and KOL but is vice-versa at KNP. A similar feature showing the prevalence of dust as exhibited from chemical analysis in the present study has also been inferred based on AERONET observations at Kolkata (Priyadharshini et al., 2018). These observations also indicated the aerosol type in the eastern Indian urban atmosphere being a mixture of urban/open burning with mixed desert dust. The source of desert dust to the study area is mainly due to long-range transport from the semi-arid regions of India or west Asia (Kumar and Verma, 2016; Priyadharshini et al., 2018).

The mean ion ratio (the ratio of the sum of anions (\(\Sigma^-\)) to the sum of the cations (\(\Sigma^+\))) for the entire study period is estimated as 0.83. It is expected that the missing charges are mainly associated with the possible missing anions in measurements like bicarbonate (HCO₃⁻), weak organic acids (HCOO⁻, CH₃COO⁻, C₂H₃O₂⁻). As mentioned earlier, this study also did not include measurement of insoluble inorganic components (fly ash and mineral dust). A value close to unity (0.7) was also reported by Roy et al. (2016) for a study site at KOL.

**Sea Salt, Anthropogenic and Dust Aerosols**

We examine the relative distribution of sea-salt (SS), anthropogenic (AN) and dust (DT) components of WSII at KOL. The monthly mean concentration of SS (sum of Na⁺, sea-salt components of Cl⁻, Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻), AN (sum of NH₄⁺, nss-K⁺, nss-Cl⁻, F⁻, NO₃⁻, PO₄³⁻, and nss-SO₄²⁻), and DT (sum of nss-Ca²⁺ and nss-Mg²⁺) is shown.
in Fig. 4(a). The relative percent contribution of SS, AN, DT to $T_{WSII}$ is also presented in Fig. 4(b). The trend of monthly mean concentration of SS exhibits the highest value in October and followed by that in November and January. The back trajectory analysis at surface layers (10, 100 and 500 m) indicate the air masses having traversed over the Bay of Bengal before reaching the receptor site (Fig. 1(a), also see dashed lines specifically for sampling days in October–November), thereby corroborating the feature of the monthly mean trend of SS. The trend of monthly mean anthropogenic aerosols concentration is observed having the highest value in the months of November, April, and May. These observed peaks are inferred being associated with the increase in K$^+$ and NO$_3^-$ which therefore leads to a higher anthropogenic aerosol during these months than the other months. The monthly mean of dust concentrations at the study site (excluding for August) do not exhibit notable variation; the dust concentration for August is observed typically higher than other months. The relative percent distributions of monthly mean of SS, AN, and DT is in general observed as 7–35, 26–52, and 30–45%, except that of August which has exceedingly high concentration of DT. This relative contribution of AN is predominant among analyzed SS, AN, and DT for most of the period except for October, December and February. For the month of October, the relative fractional contribution of SS and DT are equivalent to each other, whereas, for the month of December and February the relative contribution of DT is found predominant. The overall mean for the entire study period indicates equivalent values of AN and DT (about 26 µg m$^{-3}$ each and relative distribution of 40% each) at the study site over eastern Indian urb-atm.

### Characteristics of Organic and Elemental Carbonaceous Aerosol Fractions

The monthly mean concentration of OC and EC for the study period is presented in Fig. 5(a). Monthly mean concentration of OC and EC during the period of study are 19–34 and 4–11 µg m$^{-3}$ with the annual mean of OC (24 ± 5 µg m$^{-3}$) being 3 times the EC (7 ± 2 µg m$^{-3}$). The trend of the monthly mean of OC peaks during September to November. The highest monthly mean of EC is observed during September with the lowest being in April–May. The possible sources of EC-OC during the study period are presented later.

Total estimated aerosol mass (Fig. 5 (b)) analyzed in the present study is calculated by summing the individual species measured (i.e., EC, POM (OC × 1.6), and the water-soluble ions) and does not include insoluble inorganic components (fly ash and mineral dust). A conversion factor of 1.6 is used to convert OC to particulate organic matter (POM) (Chatterjee et al., 2012; Ram et al., 2016). However, this conversion is not precisely known and has been reported ranging from 1.2 to 2.6 (Turpin and Lim, 2001). This uncertainty in the conversion could lead to errors in the determination of OM and, therefore, the total estimated aerosol mass. The monthly mean of total estimated aerosol mass during September to July (excluding August due to absence of OC-EC data) is 97–141 µg m$^{-3}$ with their
Fig. 4. (a) Temporal trend of monthly mean concentration of SS, AN and DT aerosols along with T_{WSII} at KOL. Shaded regions along with line plot indicate the standard deviation. (b) Relative fractional distribution (%), e.g., (Monthly mean conc. of DT)/Monthly mean conc. of T_{WSII}), of the monthly mean of SS, AN, DT aerosols at KOL.

Fig. 5. (a) Trend of monthly mean concentration of OC (denoted in bars) and EC (denoted as circles). (b) The relative fractional distribution of monthly mean of WSII, POM and EC. The monthly mean of total estimated concentration is also shown at the top of each bar. (c) Monthly mean of OC to EC ratio (denoted as bars) and of nss-K^+ concentration (denoted as inverted triangles).

Annual mean being 132 µg m⁻³. Among the analyzed aerosol components (WSII, POM, EC), the relative fraction (Fig. 5(b)) of WSII is the highest throughout, except during September, and is about 2–3 times of POM (27–38%), with the lowest being that of EC (4–10%). During the month of September, an increase in POM and EC concentration and a decrease in WSII concentration is noticed, with the relative fraction of POM and WSII being equivalent to each other (45% each). The noted feature in the month of September is attributed to the combined impact of biomass burning, coal combustion, and vehicular emissions (based on analysis of OC-EC thermograms; refer to Fig. 6, discussed later), in conjunction with the washout of atmospheric pollutants during the monsoon month.
Based on the estimated aerosol mass chemically characterized (discussed above) and the total aerosol mass of PM$_{1.6}$ from the gravimetric analysis of PTFE (48–151 µg m$^{-3}$), the unanalyzed fraction is estimated. The unanalyzed fraction during the period of study is estimated as 5–25% with a higher value for September–October (10–15%) and the highest for December (25%). The unanalyzed fraction is attributed to unanalyzed insoluble inorganic components (fly ash and mineral dust). This fraction may also be due to PM-bound and PM-adsorbed water on PTFE (Perrino et al., 2013).

The estimated monthly mean of SOC (POC) values using EC tracer method (refer to the Section “Determination of Carbonaceous Aerosols Using IMPROVE-A Protocol”) is about 23–61% (39–77%) of the respective monthly mean total OC. The annual mean of these values is 43% (57%) of that of total OC. While the highest value for SOC is observed during the month of May and the lowest during February, it is vice-versa for POC. The highest SOC production during May is attributed to the prevalent meteorological conditions. A relatively high value of temperature and relative humidity during May (Fig. 1(b)) is inferred being favorable to enhance the photochemical process (Chatterjee et al., 2012). In contrast of that during May, a relatively low temperature and relative humidity during February (Fig. 1(b)) might have led to the lower production of SOC.

The ratio of OC to EC is further analyzed (Fig. 5(c)) to qualitatively evaluate the potential emission sources and the possible mechanism of SOC formation through gas-to-particle conversion. The monthly mean of nss-K$^+$ is also presented in Fig. 5(c). The calculated monthly mean of OC to EC ratio during the study period is 2–5 with an annual mean value of 3 (also mentioned before). A ratio higher than 2 is inferred as being the presence of secondary organic aerosols (Chow et al., 1996). Peak in this ratio is observed during October–November and then during March–July. The trend of the monthly mean of nss-K$^+$ indicates the highest peak during October and April with moderate peak during November, January, May, and September. The peaked values of OC-EC ratio is concordant to nss-K$^+$ during most of the period, thereby indicating a predominant influence of biomass combustion sources to OC measured in eastern Indian urb-atm. A previous study conducted over a residential-cum-commercial site in Kolkata during 2006 by Chatterjee et al. (2012) reported annual mean concentrations of OC, EC, and OC to EC ratio as 12 ± 6, 6 ± 3 and 2.0 ± 0.4 µg m$^{-3}$. Comparison of the present study with Chatterjee et al. (2012) indicates an increase of 2 times in OC and 1.5 times in OC to EC ratio with only a slight increase in EC for the present study.

Studies conducted on carbonaceous aerosols over the last decade on different temporal scales (monthly/annual mean) in various regions of India reported OC to EC ratio in the range of 2–8.4 (Venkataraman et al., 2002; Rengarajan et al., 2007; Ram et al., 2008; Rastogi and Sarin, 2009; Ram and Sarin, 2010; Ram et al., 2012; Tiwari et al., 2013; Safai et al., 2014; Panda et al., 2016; Singh et al., 2016). A ratio of 6–8 is reported over northwestern India (viz., Ahmedabad, Mount Abu) and northern India (viz., Allahabad, Hisar) whereas a ratio less than 3 (Mumbai) is detected over western India and eastern India (viz., Bhubaneswar). Annual mean of the ratio of OC to EC obtained in the present study is 1.5 to 2 times higher than the ratios reported in Chatterjee et al. (2012) and Panda et al. (2016) over eastern India while this ratio is 2 times lower than the ratio reported over northern, northwestern and western India (Rengarajan et al., 2007; Ram et al., 2008; Rastogi and Sarin, 2009; Ram and Sarin, 2010; Tiwari et al., 2013; Safai et al., 2014, Pipal et al., 2016). Inferences referred from the above studies showing a high OC to EC ratio is attributed to the predominance of biomass burning over the specific regions (Rengarajan et al., 2007; Ram et al., 2008; Rastogi and Sarin, 2009; Ram and Sarin, 2010; Rastogi et al., 2015).

We also analyze the ratio of the aerosol species, i.e., EC/OC, nss-K$/EC$, $SO_4^{2-} /EC$, in order to qualitatively know the possible emission sources to measured aerosols. The value of these ratios is shown in the Table 1. These ratios are shown as a range of the monthly mean for the entire period of study. The value of these ratios used in available studies to suggest the possible impact of emission sources is also shown in Table 1. The ratio EC/OC from the present study is in general found to be low (< 0.4) throughout the study period and indicates the predominant signature of biomass burning sources influencing the atmospheric aerosols. The high value of ratio K$/EC$ (i.e., > 0.2) also indicates the similar signature as the above. However, the ratio $SO_4^{2-} /EC$, which is near to 1 throughout the study period, indicates signature of urban influence. The chemical characterization of fine aerosol particles suggests the signatures of mixed influence of urban, open burning, and dust impacting atmospheric aerosols over eastern Indian urban atmosphere. A mixed influence of emission sources to ambient aerosols over eastern Indian urban atmosphere has also been suggested in a recent study based on a hybrid source-receptor analysis through application of fuzzy c-means clustering to back-trajectory data combined with emission flux and residence time weighted aerosols analysis (Kumar and Verma, 2016). The quantitative evaluation of the impact of emission sources to aerosol species needs to be further done through simulating emissions in a chemical transport model in conjunction with that through Positive Matrix Factorization (PMF) applied to the measured concentration.

The OC and EC fractions (refer to “Determination of Carbonaceous Aerosols Using IMPROVE-A Protocol”) obtained from thermograms of OC-EC are presented respectively in Figs. 6(a)–(d) and Figs. 6(e)–6(g). The monthly mean of OC$_1$ is observed peaking during months of March to September, also concordant with the peaks in nss-K$^+$ and OC to EC ratio (Fig. 5(c)) (discussed previously) thereby manifesting the influence of biomass burning during these months. The monthly mean of OC$_3$ is found high during the months of April to May followed by July to September and October to November, indicative of possibly enhanced contribution to OC from coal combustion activities in industrial sector. The concentration of components OC$_3$
and OC$_4$ is observed to be high during months of October, November, February, March, July, and September, indicative of possibly enhanced contribution to OC from paved dust associated with motor vehicle emissions. Analysis of the relative contribution (%) of annual mean of OC fractions (i.e., OC$_1$, OC$_2$, OC$_3$, OC$_4$) to that of the total carbon (TC) indicates a larger fractional contribution from OC$_3$ and OC$_4$ (41%) than that from OC$_2$ (27%) and OC$_1$ (2%). This analysis, therefore, indicates the predominant influence of re-suspended paved dust followed by coal combustion and biomass burning sources at the study site.

Amongst the three EC components (EC$_1$, EC$_2$, EC$_3$), the monthly mean of EC$_1$ (indicative of influence from industrial and motor-vehicle emissions) is typically high.

**Fig. 6.** Temporal trend of monthly mean concentration of thermally derived OC fractions and EC fractions. (a–d) OC$_1$–OC$_4$. (e–g) EC$_1$–EC$_3$. 

(a) OC$_1$. (b) OC$_2$. (c) OC$_3$. (d) OC$_4$. (e) EC$_1$. (f) EC$_2$. (g) EC$_3$. 

Months

Oct Nov Dec Jan Feb Mar Apr May Jul Sep

OC$_1$, OC$_2$, OC$_3$, OC$_4$, EC$_1$, EC$_2$, EC$_3$. 

October, November, December, January, February, March, April, May, June, July, and September.
CONCLUSIONS

In the present study, fine particulate matter (≤ 1.6 µm) in a tropical urban atmosphere (above Kolkata (KOL), on the lower Indo-Gangetic Plain in eastern India) was sampled during the daytime and chemically characterized to evaluate the relative abundance, temporal variation, and probable sources of the ambient aerosol species. A submicron aerosol particle sampler (SAS) with double two stage stacked filter units (SFU) was devised for a simultaneous but discrete collection of water-soluble inorganic ions (WSII) and carbonaceous aerosols (CA; elemental carbon (EC) and organic carbon (OC)).

The most abundant WSII species throughout the period of study were Ca$^{2+}$, Mg$^{2+}$, and Na$^+$ among the cations and Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ among the anions. The mean monthly concentrations of these cations and anions constituted 41–57% and 28–46%, respectively, of the total WSII ($T_{WSII}$). The secondary WSII aerosols (NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$) contributed 25% of the $T_{WSII}$, which was almost equal to the portion from Ca$^{2+}$ (30%).

Whereas the mean monthly concentration of SO$_4^{2-}$ peaked during winter (February), that of NO$_3^-$ peaked during summer (March and May). The concentration of NO$_3^-$ was 2–3 times higher than that of SO$_4^{2-}$ in summer, unlike during the other months, when the concentrations were nearly identical.

The trend of the monthly mean of nss-K$^+$ exhibited pronounced peaks in October and April, suggesting the predominant influence of biomass burning emissions at the study site during these months. Of the sea-salt (SS), anthropogenic (AN), and dust (DT) components of the $T_{WSII}$, DT was predominant during August, AN during November, April, and May, and SS during October, November, and January. The fractional contribution of AN was predominant among these three components for most of the study period.

The mean monthly concentration of OC exhibited a larger variability than that of EC, and the mean annual concentration of the former—43% of which was formed by secondary OC—was 3 times that of the latter. The monthly mean of the OC to EC ratio displayed temporal peaks concurrent with those of nss-K$^+$. The contribution to the monthly mean (September–July) from the WSII, POM, and EC was 45–69%, 27–45%, and 4–10%, respectively, of the total estimated aerosol mass concentration of these components. WSII’s contribution peaked during April and May, whereas POM and EC’s contributions peaked during September. The information derived from our measurements indicated high SO$_4^{2-}$/EC and nss-K$^+$/EC ratios in conjunction with low EC/OC ratios throughout the experimental period at the study site. Based on the analysis of the OC-EC thermograms, the main source of OC was probably paved road dust, followed by coal combustion and biomass burning, whereas the main sources of EC were probably industrial and non-exhaust motor vehicle emissions, followed by coal combustion and motor vehicle exhaust.

The chemical profile of these fine aerosol particles suggests the mixed influence of urban, open burning, and dust aerosols in the urban atmosphere of eastern India. Further analysis via positive matrix factorization (PMF) to quantify the sources affecting the chemical composition of this atmosphere (above Kolkata) is in progress and will be presented in a future study. The current study provides information on the relative abundance of fine aerosol species, which are responsible for the extinction of incoming solar radiation and an increase in aerosol optical depth. This data will be used in an aerosol optical property and radiative transfer model to estimate species-specific effects in the eastern Indian urban atmosphere.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaur.org.

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