Seasonal Variation and Sources of Carbonaceous Species and Elements in PM_{2.5} and PM₁₀ Over the Eastern Himalaya

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Seasonal variation and sources of carbonaceous species and elements in PM_{2.5} and PM₁₀ over the eastern Himalaya

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Abstract

The study represents the seasonal characteristics (carbonaceous aerosols and elements) and contribution of prominent sources PM_{2.5} and PM₁₀ in the high altitude of the eastern Himalaya (Darjeeling) during August 2018-July 2019. Carbonaceous aerosols [organic carbon (OC), elemental carbon (EC) and water soluble organic carbon (WSOC)] and elements (Al, Fe, Ti, Cu, Zn, Mn, Cr, Ni, Mo, Cl, P, S, K, Zr, Pb, Na, Mg, Ca, and B) in PM_{2.5} and PM₁₀ were analyzed to estimate their possible sources. The annual average concentration of PM_{2.5} and PM₁₀ were computed as 37±12 µg m⁻³ and 58±18 µg m⁻³, respectively. In the present case, total carbonaceous species in PM_{2.5} and PM₁₀ were accounted for 20.6% of PM_{2.5} and 18.6% of PM₁₀, respectively. Whereas, trace elements in PM_{2.5} and PM₁₀ were estimated as 15% of PM_{2.5} and 12% of PM₁₀, respectively. Monthly and seasonal variations in concentrations of carbonaceous aerosols and elements in PM_{2.5} and PM₁₀ were also observed during the observational period. The positive relationship between OC & EC and OC & WSOC of PM_{2.5} and PM₁₀ during all the seasons (except monsoon in case of PM₁₀) indicate their common sources. The enrichment factors (EFs) and significant positive correlation of Al with other crustal elements (Fe, Ca, Mg and Ti) of fine and coarse mode aerosols indicates the influence of mineral dust at the Darjeeling. Principal component analysis (PCA) resolved the four common sources (biomass burning + fossil fuel combustion (BB+FFC), crustal/soil dust, vehicular emissions (VE) and industrial emissions (IE)) of PM_{2.5} and PM₁₀ in Darjeeling.

Keywords: PM_{2.5}, PM₁₀, OC, EC, WSOC, Elements, PCA

1. Introduction

The urban agglomeration of hilly region of India is under serious threat various forms of anthropogenic activities and pollutants (Gajananda et al. 2005; Sharma et al. 2020a;b). Due to rapid urbanization, industrialization, increasing vehicular traffic due to increased tourism-related activities, increase in energy demands (for lighting, cooking and heating etc.) have resulted in contamination/deterioration of ambient air quality, vegetation and climate of the hilly region (Chatterjee et al. 2010; Rai et al. 2020a). From last few decades the fine and coarse mode of aerosol/particulate matter (PM) has been altered the atmospheric particle chemistry, Earth's climate system (radiative balance), and human health (Pant and Harrison 2012; Bond et al. 2013). Therefore, quantification and identification of chemical species and sources of aerosol is essential to explore the appropriate mitigation option to improve the ambient air quality, human health and climate (Ramana et al. 2010; Cao et al. 2006; Bond et al. 2013; Pope et al. 2009; Ramgolam et al. 2009; Sharma et al. 2018 a; b; Rai et al., 2020b).

Carbonaceous aerosols (CAs) are the major fractions (OC, and EC) of PM_{2.5} and PM₁₀ in the atmosphere and have significant role in the Earth's radiative balance, visibility degradation, alteration of atmospheric chemistry (Lim and Turpin 2002; Hansen et al. 2005; Bond et al. 2013; Pope et al. 2009). Various toxic gases (CO, CO₂, SO_x, NH₃, and NO_x, etc.), organics and hydrocarbons (like, VOCs: volatile organic compounds; PAHs: polycyclic aromatic hydrocarbons) are produced during the combustion process/emissions of CAs and therefore affect the respiratory/cardiovascular system of the human (Lighty et al. 2000; Pope et al. 2009). Both primary and secondary organic aerosols significantly control of physico-chemical properties of particles/aerosols (Kanakidou et al. 2005) and influenced the formation cloud condensation nuclei (CCN), whereas EC absorb solar radiation and contribute for radiative change (Bond et al., 2013).

PM consists of organics (OC, EC, and other components), mineral/crustal/soil dust, metals, non-metals, inorganic pollutants as well as sea salts and relative exuberance of these components are highly variable both spatially and temporally (Ram et al. 2011; Jain et al. 2017). Generally, the elements linked with the PM are non-volatile in nature and remain unaffected even though they go for regional as well as long-range transportation (Morawska and Zhang, 2002). Some of the transition/toxic metals (like Fe, Cu, Mn, Zn, Ni, Cr, As, Pb, Hg) which are coming from the various sources into the ambient air have acute toxic and mutagenic effects on human health, when inhaled at higher concentrations. Elements like Fe, Al, Si, Ca and Ti are also available in the fine and coarse mode PM is originated from mineral dust/crustal dust (Sharma et al. 2014a). Soluble K in PM mostly originated

from biomass burning, however, it is also attributed to dust in PM (Viana et al. 2008), whereas Cl originated from sea salt is also considered from coal burning in aerosols (Pant and Harrison 2012).

Several studies conducted in past on carbonaceous aerosols, inorganic aerosols and elements in particulate matter and their potential sources in urban (Ram and Sarin, 2011; Mandal et al. 2014; Sharma et al. 2016; Gupta et al. 2018; Shivani et al. 2019; Jain et al. 2020a,b), rural, remote (Begam et al. 2017) as well as high altitude atmosphere (Ram et al. 2008; Kumar and Attri, 2016; Sarkar et al. 2017; Kaushal et al. 2018) but very limited study (Sharma et al. 2020b) has been conducted in the eastern Himalayan region of India. Considering the importance of atmospheric carbonaceous species and elements in PM_{2.5} and PM₁₀ and from their perspective on climate change, the present study has been carried out at Darjeeling (the eastern Himalaya). In this paper, we report the carbonaceous components (OC, EC, and WSOC) and elements (Al, Fe, Ti, Cu, Zn, Mn, Cr, Ni, Mo, Cl, P, S, K, Zr, Pb, Na, Mg, Ca, and B) of PM_{2.5} and PM₁₀ over the eastern Himalaya (Darjeeling) during August 2018 – July 2019. Principal component analysis (PCA) and HYSPLIT trajectory were applied to resolve the potential sources and source region, respectively of PM_{2.5} and PM₁₀ at Darjeeling.

2. Materials and methods

2.1 Description of study site

The study was carried out in the campus of Bose Institute, Darjeeling (27.01 °N and 88.15°E; 2200 m asl) situated in the Eastern Himalaya (Fig. 1). The hilly districts of Darjeeling are situated within the lower and sub-Himalayan ranges of the eastern Himalaya. Darjeeling is surrounded by Sikkim Himalayas, Bhutan Himalaya and Nepal Himalaya from the north, east and west sides, respectively (Chatterjee et al. 2021). The study area is considered as a semi-urban and is under the influence of biomass burning, vehicle emissions, agriculture and tourism activities (Adak et al. 2014). The climate of Darjeeling is subtropical and temperate with wet summer/pre-monsoon and monsoonal rains (June-September). The annual average maximum temperature was estimated to be 12.2 °C (in summer: March-May) whereas the average minimum temperature was estimated as 3.4 °C (in winter: January-February) with monthly mean temperatures ranging from 5.8 to 17.2 °C. The monthly average meteorology (ambient temperature, relative humidity (RH), wind speed and wind directions) during the study period are depicted in Fig. S1 (see the supplementary information). The detail information on topography, weather, township and influences of local pollution sources at the study site is described in Chatterjee et al. (2021).

2.2 Sample collection and analysis

PM_{2.5} ($n = 94$) and PM₁₀ ($n = 102$) samples were collected simultaneously on pre-combusted (at 550 °C) Pallflex tissue quartz filters (47mm for PM_{2.5} and 20×25 cm² for PM₁₀) using Fine Particle Sampler (flow rate: 1m³ h⁻¹ ± 2 %) and Respirable Particle Sampler (flow rate: 1.2 m³ min⁻¹ ± 2 %), respectively for 24h from August 2018-July 2019 (PM_{2.5} sampling was not carried out in July 2019). The particle sampler was placed on the rooftop of the Bose Institute at the height of 15m above the ground level. The gravimetric mass (in µg) of PM_{2.5} and PM₁₀ was computed by the difference between the initial and final weight using a calibrated weighing balance (M/s. Sartorius, resolution: ± 10 µg) of the filter. The concentrations of PM_{2.5} and PM₁₀ (in µg m⁻³) were further computed by dividing the PM mass to the total volume of air passed during the sampling period (24h). Before chemical analysis the samples were stored at -20°C.

The concentrations of OC and EC in PM_{2.5} and PM₁₀ samples were estimated by OC/EC Carbon analyzer (Model: DRI 2001A; Make: Atmoslytic Inc., Calabasas, CA, USA) using IMPROVE-A Protocol (Chow et al. 2004). OC/EC carbon analyzer is working on the preferential oxidation of OC and EC at different temperatures plateaus (140, 280, 480 and 580°C; for OC1, OC2, OC3 and OC4, respectively) in pure helium and three temperature plateaus (580, 740 and 840°C for EC1, EC2 and EC3, respectively) in 98 % helium and 2 % oxygen (Chow et al. 2004). A proper punch of ~0.536 cm² area of the filter was cut and analyzed in triplicate along with field blank filters. The standard calibration for peak area verification was performed daily using 5% CH₄+balance helium gas (before and after sample analysis). Calibration of the OC/EC analyzer was performed by 4.8% of CO₂ + balance He gas along with known amounts of KHP (potassium hydrogen phthalate) and sucrose solution (Sharma et al. 2020b). In the present case, repeatability error of OC and EC analysis were estimated as 3-7% ($n=3$). Total carbonaceous aerosols (TCA) of PM_{2.5} and PM₁₀ are computed as (1.6×OC)+EC (Rengarajan et al. 2007; Srinivas and Sarin 2014).

A known punch size of PM_{2.5} (~3.46 cm²) and PM₁₀ (~7.07 cm²) filters were cut into four halves and was soaked in 20 ml of de-ionized water (18.2 MΩ-cm) and ultrasonicated three times for 10 min each. The 10ml filtered extract was transferred into a pre-cleaned glass vial and analyzed for WSOC and WIOC using a TOC analyzer operating on catalytically-aided combustion oxidation (Model: Shimadzu TOC-L CPH/CPN, Japan). Field blank filters were also analyzed using the same analytical procedure and subtracted from the respective PM_{2.5} and PM₁₀

samples to obtain the analytical results (WSOC and WIOC = OC–WSOC)). Calibration of the instrument was performed before analysis of the samples using standard solution of five different concentrations. 3-10% of repeatability errors were estimated in WSOC analysis ($n=3$). The detail, analytical procedures is described in Rai et al. (2020a).

Wavelength Dispersive X-ray Fluorescence Spectrometer (WD-XRF) was used to analyzed the concentrations of Al, Fe, Ti, Cu, Zn, Mn, Cr, Ni, Mo, Cl, P, S, K, Zr, Pb, Na, Mg, Ca, and B in PM_{2.5} and PM₁₀ (with repeatability errors 5-10%). The samples were analyzed in triplicate and for major and trace elements. The detail, analytical procedures is available in Jain et al. (2020a;b).

2.3 Primary organic carbon (POC) and secondary organic carbon (SOC)

The concentrations of POC in PM_{2.5} and PM₁₀ samples are estimated using minimum OC/EC ratio for the each season (winter, summer, monsoon and post-monsoon). Both OC and EC in ambient aerosols are considered to be originated from combustion sources and EC is a good marker for POC (Castro et al. 1999). POC are computed using the following equation,

$$POC = [OC/EC]_{min} \times [EC] + c \quad (1)$$

where, c is the contribution from non-combustion sources which is negligible in the present case. SOC is estimated as the difference of OC and POC (SOC= OC–POC).

2.4 Enrichment Factors (EFs)

Crustal EFs refers the origin of the elements (either anthropogenic or natural) and their abundance in the ambient particulates (Amato et al., 2016). The EFs of the elements present in PM_{2.5} and PM₁₀ samples are computed (Taylor and McLennan, 1995) as:

$$EF = \frac{El_{sample}/X_{sample}}{El_{crust}/X_{sample}} \quad (2)$$

where,

El_{sample} = element (El) mass concentration

X_{sample} = reference element (X) mass concentration

El_{crust} = element (El) concentration in upper continental crust

X_{crust} = reference element (X) concentration in upper continental crust

Aluminium (Al) is used as the reference element in this study, which is also supported by the previous studies (Sharma et al. 2014a; 2020b).

2.5 Principal component analysis (PCA)

In this study, PCA was applied on chemical constituents of PM_{2.5} and PM₁₀ to identify the potential sources contributing to fine and coarse fractions aerosols. It uses orthogonal decomposition to identify individual groups of components which are then tied to variables by loading factors (Viana et al. 2008). The total variability of the data sets is shared between these components, whereas the maximum is shared by the first component (Belize et al. 2013). In PCA, the chemical data are transformed into a dimensionless standardized form:

$$Z_{ij} = \frac{C_{ij} - \overline{C_j}}{\sigma_j} \quad (2)$$

where $i = 1, \dots, n$ samples; $j=1, \dots, m$ elements; C_{ij} is the concentration of element j in sample i ; and $\overline{C_j}$ and σ_j are the arithmetic mean concentration and the standard deviation for element j , respectively. The PCA model is expressed as:

$$Z_{ij} = \sum_{k=1}^p g_{ik} h_{kj} \quad (3)$$

Where $k = 1, \dots, p$ sources, and g_{ik} and h_{kj} are the factor loadings and the factor scores, respectively. This equation is solved by Eigenvector decomposition (Song et al. 2006).

3. Results and discussion

3.1. Seasonal variations of chemical species of PM_{2.5} and PM₁₀

3.1.1. Seasonal variability of PM_{2.5} and PM₁₀

The annual average PM_{2.5} and PM₁₀ concentrations were estimated as $37 \pm 12 \mu\text{g m}^{-3}$ (range: $16\text{--}77 \mu\text{g m}^{-3}$) and $56 \pm 18 \mu\text{g m}^{-3}$ (range: $21\text{--}116 \mu\text{g m}^{-3}$), respectively (Table 1). The maximum monthly average mass concentration of PM_{2.5} was recorded in October ($58 \mu\text{g m}^{-3}$) and the minimum monthly average concentration of PM_{2.5} was observed in January ($27 \mu\text{g m}^{-3}$). Whereas, monthly average maxima of PM₁₀ was observed in March ($73 \mu\text{g m}^{-3}$) and monthly average minima in the month of January ($43 \mu\text{g m}^{-3}$). The monthly average and temporal variations in PM_{2.5} and PM₁₀ concentrations are shown in Figs.S2-S3 (see the supplementary information). The highest seasonal average concentration of both PM_{2.5} ($41 \pm 14 \mu\text{g m}^{-3}$) and PM₁₀ ($64 \pm 20 \mu\text{g m}^{-3}$) were found during summer and minimum seasonal average mass concentration of both PM_{2.5} ($31 \pm 9 \mu\text{g m}^{-3}$) and PM₁₀ ($51 \pm 17 \mu\text{g m}^{-3}$) were recorded during

winter. In post-monsoon, the mass concentrations of PM_{2.5} (40±11 µg m⁻³) and PM₁₀ (55±17 µg m⁻³) were recorded higher than the winter and monsoon (Table 1). In the present case, non-significant seasonal variation in mass concentrations of both PM_{2.5} and PM₁₀ was recorded at Darjeeling (except winter). Sharma et al. (2014b) reported the similar concentration of PM_{2.5} (at Kullu: 34±2 µg m⁻³; at Shimla: 32±3 µg m⁻³) at the north-western Himalayan region during winter 2013, whereas Kaushal et al. (2018) recorded the 52±18 µg m⁻³ of PM₁₀ concentration at Pohara of north-western Himalaya (Himachal Pradesh) during winter 2015. Sharma et al. (2020a) reported the PM₁₀ concentration as 54±12 µg m⁻³ and 39±10 µg m⁻³ during post-monsoon and winter, respectively at Nainital a central Himalaya. Sharma et al. (2020b) also reported the PM₁₀ concentration as 48±16 µg m⁻³ during winter in Darjeeling. The monthly variation in mass concentration of PM_{2.5} and PM₁₀ in relation ambient temperature, RH, wind direction and wind speed is depicted in Figs.S1-S2 (see the supplementary information). It has been observed that the prevailing meteorology of the sampling site influenced the seasonal variation in mass concentrations of PM_{2.5} and PM₁₀ at Darjeeling. However, the higher concentration of pollutants during the summer season at Darjeeling might be due to more influence of tourism activities (Gajananda et al. 2005; Chatterjee et al. 2021) as well as long-range transportation of pollutants at sampling site of the Darjeeling (Rai et al. 2020a).

3.1.2. Variation of OC, EC and WSOC in PM_{2.5} and PM₁₀

Temporal variations in OC, EC and WSOC concentrations of PM_{2.5} and PM₁₀ during study period are shown in Fig.S3 (b-d) (see the supplementary information). The annual average concentrations of OC, EC, WSOC and WIOC of PM_{2.5} were 3.46±1.59 µg m⁻³, 1.93±0.93 µg m⁻³, 1.88±1.05 µg m⁻³ and 1.69±0.85 µg m⁻³, respectively. Whereas the annual average of OC, EC, WSOC and WIOC in PM₁₀ were 5.06±2.03 µg m⁻³, 2.34±1.18 µg m⁻³, 3.55±1.75 µg m⁻³ and 1.51±0.92 µg m⁻³, respectively. Figure 2 shows the monthly average of OC, EC and WSOC in PM_{2.5} and PM₁₀ during study period in Darjeeling. Highest monthly average OC in PM_{2.5} (4.76 µg m⁻³) and PM₁₀ (6.30 µg m⁻³) was found in November (post-monsoon), whereas monthly average minima of OC in PM_{2.5} (2.03 µg m⁻³) and PM₁₀ (3.31 µg m⁻³) was found in August (monsoon) and May (summer), respectively. Similar monthly average maxima and minima of EC (in PM_{2.5} and PM₁₀) was recorded in March and August, respectively (Fig. 2). Highest monthly average WSOC concentration in both PM_{2.5} (2.77 µg m⁻³) and PM₁₀ (5.51 µg m⁻³) was recorded in November (post-monsoon) might be due to the influence of stubble burning in northern states of India (Punjab, Haryana and western Uttar Pradesh of IGP). Figure 3 shows the seasonal average OC, EC, WSOC, WIOC, POC, SOC and TCA

concentrations of PM_{2.5} and PM₁₀ during winter, summer, monsoon and post-monsoon seasons in Darjeeling. Highest seasonal average OC concentration of PM_{2.5} ($4.07 \pm 1.55 \mu\text{g m}^{-3}$) and PM₁₀ ($5.69 \pm 2.09 \mu\text{g m}^{-3}$) was recorded in post-monsoon season and minimum seasonal average concentration of OC in PM_{2.5} ($2.21 \pm 0.86 \mu\text{g m}^{-3}$) and PM₁₀ ($3.62 \pm 0.86 \mu\text{g m}^{-3}$) was recorded during monsoon (Table 1). Similarly, seasonal average maxima and minima of EC in PM_{2.5} and PM₁₀ were recorded in summer and monsoon seasons, respectively. Average WSOC in both PM_{2.5} ($2.17 \pm 0.98 \mu\text{g m}^{-3}$) and PM₁₀ ($4.44 \pm 1.55 \mu\text{g m}^{-3}$) were found highest during post-monsoon season and minimum in monsoon season (Fig. 3).

The annual average concentration of TCA contributes 20.6% of PM_{2.5} ($7.6 \pm 3.4 \mu\text{g m}^{-3}$) and 18.6% of PM₁₀ ($10.4 \pm 4.3 \mu\text{g m}^{-3}$). The highest TCA in PM_{2.5} and PM₁₀ were recorded in winter (22.7% of PM_{2.5} and 22.4% of PM₁₀) season followed by post-monsoon (21.7% of PM_{2.5} and 20.3% of PM₁₀), summer (21.6% of PM_{2.5} and 17.6% of PM₁₀) and monsoon (12.5% of PM_{2.5} and 13.4% of PM₁₀) seasons. The annual average concentration of POC in PM_{2.5} was recorded to be $2.35 \pm 1.06 \mu\text{g m}^{-3}$ (66% of OC), and SOC was $1.19 \pm 0.57 \mu\text{g m}^{-3}$ (34% of OC). Similarly, the annual average POC concentration in PM₁₀ was recorded as $3.18 \pm 1.13 \mu\text{g m}^{-3}$ (63% of OC), whereas, SOC was recorded as $2.05 \pm 0.98 \mu\text{g m}^{-3}$ (37% of OC). In PM_{2.5} the seasonal contribution of POC and SOC were ranging from 55-77% and 33-45% of OC, respectively, whereas in PM₁₀ the seasonal contribution of POC and SOC were ranging from 51-73% and 37-49% of OC, respectively. Sen et al. (2018) reported the similar OC ($7.7 \pm 0.7 \mu\text{g m}^{-3}$) and EC ($3.7 \pm 0.6 \mu\text{g m}^{-3}$) concentrations in PM₁₀ at Darjeeling and high OC ($10.3 \pm 5.6 \mu\text{g m}^{-3}$) and EC ($5.4 \pm 2.9 \mu\text{g m}^{-3}$) values in PM₁₀ at Kullu-Mohal (north-western Himalayas) during winter. Whereas, Rai et al. (2020a) observed the low OC ($3.7 \pm 1.3 \mu\text{g m}^{-3}$) and EC ($1.3 \pm 0.6 \mu\text{g m}^{-3}$) in PM₁₀ at Darjeeling. Sharma et al. (2020a) also found the similar OC and EC concentrations in PM₁₀ over Nainital (central Himalayas) during post-monsoon (OC: $4.7 \pm 1.1 \mu\text{g m}^{-3}$ and EC: $1.1 \pm 0.5 \mu\text{g m}^{-3}$) and winter (OC: $3.2 \pm 1.1 \mu\text{g m}^{-3}$ and EC: $1.4 \pm 0.6 \mu\text{g m}^{-3}$) seasons.

Figure 2 shows the monthly average OC/EC and WSOC/OC ratios of PM_{2.5} and PM₁₀ at Darjeeling, whereas seasonal relationship between OC and EC, WSOC and OC of PM_{2.5} and PM₁₀ are depicted in Figs. S4-S5 (see the supplementary information). The seasonal average OC/EC of PM_{2.5} was 1.87 (range: 1.40 - 2.81), 1.92 (range: 1.22 - 2.82), 1.85 (range: 1.30 - 2.57) and 1.94 (range: 1.05 - 2.87) during winter, summer, monsoon and post-monsoon, respectively. The seasonal average WSOC/OC ratio of PM_{2.5} was computed as 0.50, 0.52, 0.53 and 0.54 during winter, summer, monsoon and post-monsoon, respectively. Similarly, the seasonal average OC/EC of PM₁₀ was 2.04, 1.74, 3.37 and 3.01 during winter, summer, monsoon and post-monsoon, respectively, whereas, the seasonal

average WSOC/OC of PM₁₀ was 0.71, 0.61, 0.65 and 0.79 during winter, summer, monsoon and post-monsoon, respectively. Hegde et al. (2016) also observed a similar (0.51±0.06 for TSP) WSOC/OC value in Nainital during winter. Due to poor solubility of organics emitted from the combustion of liquid fossil fuels the WSOC/OC values for vehicular emissions are low as compared to biomass burning. In this study, significant positive correlation between OC vs. EC (for PM_{2.5}: $R^2 = 0.88, 0.86, 0.63$ and 0.80 at $p < 0.05$; for PM₁₀: $R^2 = 0.77, 0.85, 0.09$ and 0.74 at $p < 0.05$ during winter, summer, monsoon and post-monsoon seasons, respectively) of PM_{2.5} and PM₁₀ has been observed during all the seasons (except monsoon season for PM₁₀) (Figs. S4-S5; in supplementary information), which is indicative of their common sources (Rengarajan et al. 2007; Ram and Sarin 2011). The scatter plots between WSOC and OC (for PM_{2.5}: $R^2 = 0.63, 0.73, 0.62$ and 0.83 ; and for PM₁₀: $R^2 = 0.69, 0.91, 0.17$ and 0.87 during winter, summer, monsoon and post-monsoon seasons, respectively) of PM_{2.5} and PM₁₀ (except monsoon season for PM₁₀) shows significant positive correlation suggesting that both OC and EC are obtained from the same primary emission source or by similar secondary processes (Figs. S4-S5; in supplementary information). The non-significant positive correlation of K (a tracer of biomass) with Ca, Mg, WSOC of PM_{2.5} and significant positive correlation of K with Ca, Mg, WSOC of PM₁₀ during all the seasons (except post-monsoon season for PM_{2.5}) demonstrate the abundance of soil/road dust contributed by soluble organic sources to PM_{2.5} and PM₁₀ at study site (Tables: S1-S8; in supplementary information). I may also be considered that the soil suspension, fuel combustion (Urban et al. 2012), and formation of secondary water soluble organic aerosols (Lim et al. 2010) might be the some other sources of WSOC in the sampling site of Darjeeling.

3.1.3. Major and trace elements in PM_{2.5} and PM₁₀

During the sampling 17 common elements (Al, Fe, Ti, Cu, Zn, Mn, Cr, Ni, Mo, Cl, P, S, K, Zr, Pb, Na, Mg, Ca, and B) were extracted in PM_{2.5} and PM₁₀ (Cu and Pb in PM₁₀ but traced in few PM_{2.5} samples also) using X-RF technique of sampling site (Table 1). In PM_{2.5} samples, Na has observed highest annual average concentration ($1.014 \pm 0.392 \mu\text{g m}^{-3}$) followed by Ca ($0.918 \pm 0.813 \mu\text{g m}^{-3}$), S ($0.667 \pm 0.404 \mu\text{g m}^{-3}$), Fe ($0.502 \pm 0.195 \mu\text{g m}^{-3}$), K ($0.388 \pm 0.224 \mu\text{g m}^{-3}$), and so on with higher loading in summer season (Table 1). Whereas in case of PM₁₀, S has recorded highest annual average concentration ($1.260 \pm 0.744 \mu\text{g m}^{-3}$) followed by Ca ($0.985 \pm 0.299 \mu\text{g m}^{-3}$), Al ($0.922 \pm 0.446 \mu\text{g m}^{-3}$), K ($0.650 \pm 0.376 \mu\text{g m}^{-3}$), Fe ($0.635 \pm 0.266 \mu\text{g m}^{-3}$), Na ($0.607 \pm 0.396 \mu\text{g m}^{-3}$), and so on. The annual average concentrations of elements in PM_{2.5} and PM₁₀ are $5.71 \pm 3.67 \mu\text{g m}^{-3}$ (accounted for 15% of

PM_{2.5}) and $6.44 \pm 3.58 \mu\text{g m}^{-3}$ (accounted for 12% of PM₁₀), respectively. The monthly average concentrations of elements of PM_{2.5} and PM₁₀ are shown in Fig. S6 (see the supplementary information). Higher average concentrations of elements are recorded during summer (21% of PM_{2.5} and 12% of PM₁₀) followed by winter (16.5% of PM_{2.5} and 11.7 of PM₁₀), post-monsoon (11.6% of PM_{2.5} and 11% of PM₁₀) and monsoon (9% of PM_{2.5} and 13% of PM₁₀) seasons (Fig. 4). During winter 2013 land campaign, Sharma et al. (2014b) found the Na, Mg, Ca, Al, P, S, Si, Cl, K, Ti, Sr, Zr, Pb, Sb, Ag, Cs, Hg, Mn, Fe and Zn in PM_{2.5} (which had accounted for ~27% of PM_{2.5}) over the north-western Himalaya. Sharma et al. (2020a) also reported the elements contribution to PM₁₀ as 16% and 13% during post-monsoon and winter seasons, respectively at central Himalaya (Nainital). The similar contribution of elements to the PM₁₀ over the Himalayan region and other high altitude regions are discussed in our earlier publication (Sharma et al. 2020b).

Figure 5 represents the seasonal enrichment factors (EFs) of the elements (Al, Fe, Ti, Cu, Zn, Mn, Cr, Ni, Mo, Cl, P, S, K, Zr, Pb, Na, Mg, Ca, and B) available in PM_{2.5} and PM₁₀ samples. Al, Fe, Ti, K, Mg, and Ca in both PM_{2.5} and PM₁₀ have recorded low EFs (< 5) for all the seasons, which indicate that, elements mostly arrived from crustal/soil sources. The element like Cu, Zn, Ni, Pb, Cr, Mo and B have higher EFs (>10) in both PM_{2.5} and PM₁₀ and therefore are likely of anthropogenic origin. The higher the EF of Cr, Ni, Pb and Zn of PM were also attributed to industrial emission (IE) sources. Generally Cu, Mn, Zn, Ni, Cd, Fe, Mo, S and Cr use as a marker for IE in India (Shridhar et al. 2010).

The annual and seasonal statistical summary of elements recorded in PM_{2.5} and PM₁₀ samples is tabulated in Table 1. The possible sources of trace metals present in a fine and coarse fraction of particulates can be primarily crustal/mineral dust. In this study, Al, is significantly positive correlated with Fe, Ca, Mg and Ti (as well as with PM₁₀) and the average Fe/Al ratio is 0.69 (winter: 0.76; summer: 0.74; monsoon: 0.45 and post-monsoon: 0.79), which indicates the dominant source of mineral dust. Similarly, Ca/Al ratio (1.07) indicates that PM over the eastern Himalayan region is rich in Ca mineral as compared to average continental crust. Similar results were also observed in case of elements extracted in PM_{2.5} over the eastern Himalaya. Sarin et al. (1979) had reported that the Fe/Al ratio in north Indian plains ranged from 0.55 to 0.63. Kumar and Sarin (2009) reported Fe/Al ratio as 0.59 for PM_{2.5-10} at a remote high altitude sampling site (Manora Peak) of western India. McLennan, (2001) recorded the average Ca/Al ratio as 1.07 in PM₁₀ whereas, the corresponding ratio in the upper continental crust is 0.38. Sharma et al. (2020a) also reported Ca/Al ratio as 1.52 and 1.19 in PM₁₀ during post-monsoon and winter seasons, respectively at central

Himalayas (Nainital), whereas Kumar and Sarin (2009) had recorded the Ca/Al ratio as 0.73 in PM_{2.5} and 1.74 in PM₁₀ at Manora Peak, a high altitude site of the western India. The significant positive correlation of Al with Fe, Ca, Mg and Ti of coarse and fine (except few in PM_{2.5}) fractions of PM during all the seasons are also indicated the abundance of mineral dust at the sampling site of Darjeeling (Table S1-S8; in supplementary information).

3.2. Possible sources and source regions

3.2.1 Possible sources of PM_{2.5} and PM₁₀

PCA has been performed with chemical species of 20PM_{2.5} and 22PM₁₀ (OC, EC, WSOC, Na, Ca, Mg, Al, Fe, Ti, K, Cl, P, S, Cr, Ni, Cu, Zn, Mn, Mo, Zr, Pb and B) to identify the factor loading to PM_{2.5} and PM₁₀. The factor profiles (a yearlong data) of the possible sources of PM_{2.5} and PM₁₀ extracted by PCA are summarized in Table 2. On the basis of the factor loading PCA resolved the four common sources [biomass burning + fossil fuel combustion (BB+FFC), crustal/soil dust (SD), vehicular emissions (VE) and industrial emissions (IE)] of PM_{2.5} and PM₁₀ at Darjeeling.

Factor 1: The first factor of PM_{2.5} represents the BB+FFC, characterized (38.3% of the variance) by highly loaded with OC, EC, WSOC, K, Cl and S. K⁺ and Levoglucosan are considered BB (cow dung, crop residue, fuel wood, and wildfires, etc.) marker, whereas presence of Cl in the factor reveals the wood and coal burning (Pant and Harrison, 2012). WSOC/OC and OC/EC mass ratios also evidence the BB+FFC as a one of the sources of PM_{2.5} at the observational site of Darjeeling (Sharma et al. 2020b; Chatterjee et al. 2021). The first factor of PM₁₀ represented by high loading (36.7% of the variance) of crustal elements like, Al, Ti, Fe, Ca, Mg, K and Na which inferred the source as crustal/soil/road dust (Begam et al. 2011; Sharma et al. 2014a; Jain et al. 2020b). The abundance of these elements at the study site as crustal origin is also confirmed by EFs (Fig. 5) as well as positive correlations of Al with Ca, Mg and Ti (Table S1-S8).

Factor 2: This factor of PM_{2.5} was resolved as crustal/soil dust by high loading of Al, Ti, Fe, Ca, Mg, K and Na (17.6% of the variance of factor loading) (Table 2). The EFs of these elements are also suggesting the crustal origin the elements at sampling site (Fig. 5) as well as the positive correlations of Al with Ca, Mg and Ti. Whereas second factor of PM₁₀ represented by BB+FFC with high loadings of OC, EC, WSOC, K, Cl and S (Begam et al. 2011; Pant and Harrison 2012). WSOC/OC and OC/EC ratios are also suggesting the influence of BB+FFC as a source of PM₁₀ at Darjeeling (Sharma et al. 2020b; Chatterjee et al. 2021).

Factor 3: The third factor of both PM_{2.5} and PM₁₀ constitutes the vehicular emissions (VE) with the dominant presence of EC, OC, Zn, Mn, Zr and B, indicates the emission derived from road side vehicles (Pant and Harrison, 2012; Jain et al. 2020b). Since, EC and OC are majorily emitted from the combustion sources, so these components are considered as important tracers for VE globally (Yin et al. 2010; Begam et al. 2011). Zn and Mn are used as marker of brake and tire wear, two stroke engine emissions (Zn as fuel additive), heavy duty diesel truck emission (Mn as fuel additive) (Kothai et al. 2008; Sharma et al. 2014a). VE is inferred to be one of the major sources of aerosols (Sharma et al. 2020b) at in urban sites of Himalayan region may due to the great influence of tourism activities (Gajananda et al. 2005; Chatterjee et al. 2021).

Factor 4: The fourth source of both PM_{2.5} and PM₁₀ is characterized as industrial emissions (IE) considering to the higher loading of Cu, Zn, Ni, Cr and Mo in aerosol samples (Table 2). These metals (Cu, Zn, Ni, Cr and Mo) might be originated from the small to medial scale industries, metal processing industries and industrial effluents (Gupta et al. 2007; Jain et al. 2019). Sharma et al. (2020b) also reported the solid waste + IE a source of PM₁₀ in Darjeeling with these marker elements.

3.2.2 Air mass backward trajectory

To investigate the transport pathway of fine (PM_{2.5}) and coarse fractions (PM₁₀) of aerosols at the observational site of Darjeeling, 5-days air-mass back trajectory was computed using the HYSPLIT model (Draxeler and Ralph, 2003) at an altitude of 100m, 500 m and 100m AGL for all the sampling day (Fig.6). In the present case, air parcels approaching to sampling site of Darjeeling is mainly from Bhutan, Nepal, China, Arunachal Pradesh, IGP (Punjab, Haryana, Uttar Pradesh, Bihar and West Bengal) and surrounding regions during all the seasons. During monsoon season, air mass also approaching to sampling site from Bay of Bengal. Chatterjee et al. (2021) reported the similar air parcels towards the Darjeeling during summer and winter season (Sharma et al. 2020b).

4. Conclusions

In this study seasonal variation in carbonaceous aerosols and elements in fine and coarse fractions of aerosol (PM_{2.5} and PM₁₀) were estimated to explore the prominent sources of PM_{2.5} and PM₁₀ in the high altitude of eastern Himalaya during August 2018 - July 2019. The average PM_{2.5} and PM₁₀ concentrations were recorded as 37±12 µg m⁻³ and 58±18 µg m⁻³, respectively during the study. The annual total carbonaceous aerosols in PM_{2.5} and PM₁₀ were

accounted for 20.6% of PM_{2.5} and 18.6% of PM₁₀, respectively (along with season variation). The concentrations of elements present in PM_{2.5} and PM₁₀ were accounted for 15% and 12%, respectively. During all the seasons, significant positive linear relationship between OC and EC; and OC and WSOC (as well as OC/EC and WSOC/OC) indicate the common sources (BB+FFC) of both PM_{2.5} and PM₁₀. EFs analysis the elements present in PM indicates the abundance of mineral dust at the eastern Himalaya. PCA resolved the four common sources [(BB+FFC), crustal/SD, (VE) and (IE)] of PM_{2.5} and PM₁₀ at Darjeeling. 5 days HYSPLIT back trajectory air parcels indicate that the pollutants approaching to Darjeeling are mainly from Bhutan, Nepal, China, Arunachal Pradesh and IGP region (Punjab, Haryana, Uttar Pradesh, Bihar and West Bengal) during all the seasons as well as the Bay of Bengal (mainly in monsoon season).

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Data availability: The datasets developed during the current study are available from the corresponding author on reasonable request.

Compliance with ethical standards

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Fig. 1 Map of the observational site (Source: Google maps).

Fig. 2: Monthly average concentrations of OC, EC and WSOC and their mass ratios of PM_{2.5} and PM₁₀ at Darjeeling.

Fig. 3: Average concentrations of carbonaceous species of PM_{2.5} and PM₁₀ during winter, summer, monsoon and post-monsoon seasons at Darjeeling.

Fig. 4: Average concentrations of major and trace elements in PM_{2.5} and PM₁₀ during winter, summer, monsoon and post-monsoon seasons at Darjeeling.

Fig. 5: Enrichment factor of trace elements of $PM_{2.5}$ and PM_{10} during winter, summer, monsoon and post-monsoon seasons at Darjeeling.

Fig. 6: Five day air mass backward trajectory at sampling site at (a) 100m, (b) 500m, and (c) 1000 m AGL during winter, summer (pre-monsoon), monsoon and post-monsoon seasons.

Table 1. Annual average and seasonal concentrations of PM_{2.5} and PM₁₀ and their chemical species ($\mu\text{g m}^{-3}$) in Darjeeling.

Species	Annual		Winter		Summer		Monsoon		Post monsoon	
	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀
PM	37±12	56±18	31±9	51±17	41±14	64±20	38±8	52±11	40±11.4	55±17
OC	3.56±1.59	5.06±2.03	3.29±1.37	5.43±2.02	4.04±1.67	5.18±2.14	2.21±0.86	3.62±0.87	4.07±1.55	5.69±2.09
EC	1.93±0.93	2.34±1.18	1.80±0.81	2.72±1.01	2.23±0.92	3.01±1.15	1.21±0.43	1.25±0.38	2.19±1.06	2.05±1.02
WSOC	1.88±1.05	3.55±1.75	1.66±0.95	3.80±1.28	2.15±1.19	3.43±2.19	1.14±0.51	2.31±0.77	2.17±0.98	4.44±1.55
WIOC	1.69±0.85	1.51±0.92	1.63±0.85	1.63±1.21	1.94±0.91	1.75±0.68	1.07±0.55	1.31±0.90	1.86±0.78	1.25±0.85
POC	2.35±1.06	3.18±1.31	2.52±1.13	3.56±1.31	2.68±1.10	3.82±1.46	1.57±0.56	1.87±1.31	2.30±1.12	3.07±1.52
SOC	1.19±0.57	2.05±0.98	0.77±0.51	1.87±1.08	1.48±0.76	1.37±0.98	0.64±0.54	1.75±0.91	1.74±0.74	2.62±1.11
TCA	7.63±3.43	10.43±4.25	7.06±2.97	11.41±4.14	8.89±3.54	11.29±4.51	4.74±1.73	6.94±1.55	8.65±3.47	11.15±4.25
Na	1.014±0.392	0.607±0.395	0.801±0.247	0.525±0.343	1.351±0.437	0.776±0.484	0.780±0.272	0.573±0.389	1.002±0.243	0.501±0.239
Mg	0.209±0.075	0.244±0.108	0.172±0.044	0.237±0.066	0.279±0.073	0.191±0.160	0.168±0.052	0.103±0.080	0.195±0.062	0.123±0.041
Ca	0.918±0.813	0.985±0.299	0.716±0.504	0.972±0.178	2.097±0.706	1.051±0.442	0.249±0.213	0.871±0.232	0.229±0.213	1.007±0.182
Cl	0.250±0.147	0.223±0.140	0.221±0.127	0.274±0.126	0.291±0.149	0.171±0.054	0.170±0.050	0.206±0.092	0.283±0.180	0.244±0.118
P	0.078±0.037	0.077±0.034	0.054±0.029	0.212±0.179	0.105±0.026	0.033±0.024	0.081±0.034	0.032±0.013	0.070±0.039	0.033±0.009
S	0.667±0.404	1.260±0.744	0.675±0.382	1.277±0.768	0.956±0.370	1.680±0.744	0.223±0.181	0.771±0.495	0.620±0.284	1.098±0.629
K	0.388±0.224	0.650±0.376	0.360±0.110	0.699±0.295	0.608±0.226	0.774±0.435	0.174±0.050	0.353±0.242	0.307±0.171	0.681±0.346
Al	0.261±0.164	0.922±0.446	0.203±0.104	0.860±0.291	0.454±0.143	0.943±0.661	0.143±0.065	1.061±0.386	0.179±0.068	0.845±0.215
Fe	0.502±0.195	0.635±0.266	0.423±0.141	0.652±0.189	0.737±0.153	0.694±0.381	0.390±0.087	0.482±0.188	0.391±0.067	0.663±0.142
Ti	0.035±0.015	0.057±0.022	0.031±0.009	0.061±0.017	0.047±0.013	0.058±0.031	0.024±0.008	0.049±0.016	0.032±0.018	0.056±0.013
Cr	0.291±0.143	0.122±0.114	0.299±0.102	0.146±0.125	0.372±0.199	0.093±0.014	0.254±0.081	0.132±0.032	0.215±0.074	0.122±0.114
Ni	0.092±0.025	0.084±0.008	0.072±0.012	0.044±0.008	0.110±0.027	0.045±0.006	0.094±0.014	0.049±0.007	0.090±0.021	0.043±0.011
Cu	-	0.028±0.014	-	0.032±0.008	-	0.029±0.005	-	0.034±0.026	-	0.018±0.004
Zn	0.079±0.032	0.092±0.033	0.069±0.035	0.088±0.032	0.088±0.035	0.081±0.027	0.072±0.016	0.097±0.038	0.084±0.031	0.105±0.034
Mn	0.033±0.012	0.048±0.018	0.037±0.010	0.055±0.013	0.037±0.010	0.053±0.016	0.033±0.012	0.036±0.015	0.031±0.015	0.044±0.021
Mo	0.245±0.169	0.060±0.013	0.318±0.236	0.063±0.010	0.337±0.224	0.058±0.013	0.144±0.034	0.061±0.014	0.133±0.028	0.058±0.015
Zr	0.107±0.094	0.061±0.013	0.117±0.099	0.041±0.009	0.102±0.039	0.042±0.012	0.132±0.112	0.038±0.016	0.086±0.026	0.033±0.011
Pb	-	0.076±0.064	-	0.084±0.010	-	0.072±0.069	-	0.069±0.059	-	0.079±0.067
B	0.533±0.389	0.376±0.220	0.455±0.179	0.302±0.174	0.575±0.324	0.510±0.262	0.321±0.096	0.343±0.203	0.702±0.472	0.307±0.132

± Standard deviation (at 1 σ)

Table 2. PCA factor loading of PM_{2.5} and PM₁₀ samples in Darjeeling, India.

Species	PM _{2.5}				PM ₁₀			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
OC	0.942	0.159	0.482	0.013	0.262	0.912	0.416	0.046
WSOC	0.872	0.095	0.029	-	0.197	0.856	0.174	0.092
EC	0.563	0.138	0.743	0.126	0.182	0.846	0.586	0.186
Na	0.139	0.735	0.031	-	0.851	0.063	0.162	0.142
Mg	0.056	0.832	0.048	0.061	0.909	0.188	0.083	0.098
Ca	0.035	0.877	0.229	0.233	0.935	0.196	0.049	-
Al	0.219	0.898	0.198	0.191	0.860	0.126	0.074	0.368
Fe	0.132	0.852	0.031	0.282	0.882	0.294	-	0.064
Ti	0.383	0.497	0.052	-	0.866	0.257	0.067	0.032
K	0.608	0.588	0.316	0.097	0.628	0.696	0.010	0.055
Cl	0.636	0.137	-	0.394	0.072	0.853	0.389	0.095
P	0.075	0.594	0.160	0.283	0.107	-	0.964	0.068
S	0.574	0.348	0.237	0.361	0.468	0.623	-	0.274
Cr	0.061	0.138	0.235	0.760	0.065	-	0.468	0.674
Ni	-	0.029	0.740	0.396	0.185	-	0.235	0.704
Cu	-	-	-	-	0.109	-	0.425	0.838
Zn	0.281	0.102	0.754	0.467	0.216	0.013	0.530	0.619
Mn	-	0.120	0.436	0.701	0.197	0.056	0.140	0.364
Mo	0.101	0.087	0.891	0.069	-	-	0.037	0.876
Zr	-	-	0.266	0.701	-	-	0.010	0.246
Pb	-	-	-	-	-	0.063	0.273	0.273
B	0.106	-	0.730	0.016	0.523	0.152	0.428	0.428
% Variance	38.5	17.6	11.6	8.7	36.7	16.2	12.4	10.8
Cumulative variance (%)	38.3	55.9	67.5	76.2	36.7	52.9	65.3	76.1
Sources	BB+FFC	Crustal/SD	VE	IE	Crustal/SD	BB+FFC	VE	IE

Extraction method: principal component analysis; rotation method: Varimax with Kaiser Normalization; Eigenvalue >1.00; factor loading ≥ 0.40 .

BB: biomass burning; FFC: fossil fuel combustion; SD: soil dust; VE: vehicular emissions; IE: industrial emission.

Figures

Figure 1

Map of the observational site (Source: Google maps).

Figure 2

Monthly average concentrations of OC, EC and WSOC and their mass ratios of PM_{2.5} and PM₁₀ at Darjeeling.

Figure 3

Average concentrations of carbonaceous species of PM_{2.5} and PM₁₀ during winter, summer, monsoon and post-monsoon seasons at Darjeeling.

Figure 4

Average concentrations of major and trace elements in PM_{2.5} and PM₁₀ during winter, summer, monsoon and post-monsoon seasons at Darjeeling

Figure 5

Enrichment factor of trace elements of PM_{2.5} and PM₁₀ during winter, summer, monsoon and post-monsoon seasons at Darjeeling.

Figure 6

Five day air mass backward trajectory at sampling site at (a) 100m, (b) 500m, and (c) 1000 m AGL during winter, summer (pre-monsoon), monsoon and post-monsoon seasons.

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