RESEARCH ARTICLE

Seasonal variation and sources of carbonaceous species and elements in PM$_{2.5}$ and PM$_{10}$ over the eastern Himalaya

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Abstract
The study represents the seasonal characteristics (carbonaceous aerosols and elements) and the contribution of prominent sources of PM$_{2.5}$ and PM$_{10}$ 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 PM$_{10}$ were analyzed to estimate their possible sources. The annual concentrations of PM$_{2.5}$ and PM$_{10}$ 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 PM$_{10}$ were accounted for 20.6% of PM$_{2.5}$ and 18.6% of PM$_{10}$, respectively, whereas trace elements in PM$_{2.5}$ and PM$_{10}$ were estimated to be 15% of PM$_{2.5}$ and 12% of PM$_{10}$, respectively. Monthly and seasonal variations in mass concentrations of carbonaceous aerosols and elements in PM$_{2.5}$ and PM$_{10}$ were also observed during the observational period. In PM$_{2.5}$, the annual concentrations of POC and SOC were 2.35 ± 1.06 μg m$^{-3}$ (66% of OC) and 1.19 ±0.57 μg m$^{-3}$ (34% of OC), respectively, whereas annual average POC and SOC concentrations in PM$_{10}$ were 3.18 ± 1.13 μg m$^{-3}$ (63% of OC) and 2.05±0.98 μg m$^{-3}$ (37% of OC), respectively. The seasonal contribution of POC and SOC were ranging from 55 to 77% and 33 to 45% of OC in PM$_{2.5}$, respectively, whereas in PM$_{10}$, the seasonal contributions of POC and SOC were ranging from 51 to 73% and 37 to 49% of OC, respectively. The positive relationship between OC & EC and OC & WSOC of PM2.5 and PM10 during all the seasons (except monsoon in case of PM10) indicates 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 indicate the influence of mineral dust at 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 PM$_{10}$ in Darjeeling.

Keywords PM$_{2.5}$ · PM$_{10}$ · Organic carbon · Elemental carbon · Water soluble organic carbon · Major and trace elements

Introduction
The urban agglomeration of the hilly region of India is under serious threat from the influence of various forms of anthropogenic activities and pollutants (Gajananda et al. 2005; Sharma et al. 2020a, 2020b). Rapid urbanization, industrialization, and increasing vehicular traffic have increased the energy demands (for lighting, cooking and heating, etc.) that resulted in contamination/deterioration of ambient air quality, vegetation, and climate of the hilly region (Chatterjee et al. 2010; Rai et al. 2020a). From the last few decades, the fine and coarse mode of aerosols/particulate matter (PM) has 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 the aerosols are 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. 2017, 2018a, 2018b; Rai et al. 2020b).

Carbonaceous aerosols (CAs) are the major fractions of PM$_{2.5}$ and PM$_{10}$ in the atmosphere and have a significant role in the Earth’s radiative balance, visibility degradation, and alteration of atmospheric chemistry (Lim and Turpin 2002; Hansen et al. 2005; Bond et al. 2013; Pope et al. 2009). Various toxic gases (CO, CO$_2$, SO$_x$, NH$_3$, 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 of cloud condensation nuclei (CCN), whereas EC absorbs solar radiation and contributes to 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 that are highly variable both spatially and temporally (Ram and Sarin 2011; Jain et al. 2017; Sharma et al. 2015, 2017). Generally, the elements linked with the PM are non-volatile 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 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).

Sen et al. (2018) reported the average concentrations of OC and EC in PM$_{10}$ as 7.7 $\mu$g m$^{-3}$ and 3.7 $\mu$g m$^{-3}$, respectively, at Darrjeeling (eastern Himalaya) whereas average concentrations of OC and EC in PM$_{10}$ as 10.3 $\mu$g m$^{-3}$ and 5.4 $\mu$g m$^{-3}$, respectively, at Kullu (north-western Himalaya) during a campaign in 2014. The higher concentrations of OC (13.5 $\mu$g m$^{-3}$) and EC (5.1 $\mu$g m$^{-3}$) in PM$_{10}$ at the sampling site of Kangra (northern Himalaya) were recorded by Kumar and Attri. (2016). Sharma et al. (2020a) recorded the average concentrations of OC and EC as 3.66 $\mu$g m$^{-3}$ and 1.29 $\mu$g m$^{-3}$ at Nainital (central Himalaya) during 2018–2019. Several studies are conducted in the past on carbonaceous aerosols, inorganic aerosols, and elements in PM 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, 2020b), 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 limited study (Sharma et al. 2020b) has been conducted in the eastern Himalayan region of India (Table 1). The atmospheric carbonaceous species and elements in PM bear immense importance from the perspective of climate change and biogeochemical cycles as far as eastern Himalaya is concerned because of its close proximity to the glaciers and rich biodiversity. Therefore the seasonal changes in mass loading and possible sources of carbonaceous aerosols as well as elements in fine and coarse mode PM over the eastern Himalayan region are essential. Considering the importance of atmospheric carbonaceous species and elements in PM$_{2.5}$ and PM$_{10}$ and from their perspective on climate change, the present study has been carried out at Darjeeling (over 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 PM$_{10}$ over the eastern Himalaya (Darjeeling) during August 2018–July 2019. Principal component analysis (PCA) was also applied to resolve the potential sources of PM$_{2.5}$ and PM$_{10}$ at Darjeeling.

Materials and methods

Description of study site

The study was carried out on 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 semi-urban and is under the influence of biomass burning, vehicle emissions, agriculture, and tourism activities (Adak et al. 2014). The main township of Darjeeling has numerous hotels and resorts, restaurants, residential complex, commercial and public transport stands, and markets with high density of vehicles on roads (Chatterjee et al. 2021). 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 detailed information on topography,
| Locations | Altitude | PM | OC | EC | WSOC | Ca | Mg | Al | Fe | Ti | Cr | Ni | Cu | Zn | Mo | B | Mn | Pb | References |
|-----------|----------|----|----|----|------|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|---------|
| Darjeeling | 2200 m | PM$_{2.5}$ | 3.56 | 1.93 | 1.88 | 0.92 | 0.21 | 0.26 | 0.50 | 0.035 | 0.29 | 0.09 | - | 0.079 | 0.245 | 0.53 | - | - | Present study |
| Darjeeling | 2200 m | PM$_{10}$ | 5.06 | 2.34 | 3.55 | 0.99 | 0.24 | 0.92 | 0.64 | 0.057 | 0.12 | 0.08 | 0.03 | 0.092 | 0.060 | 0.38 | - | - | Present study |
| Darjeeling | 2200 m | PM$_{10}$ | 5.39 | 2.60 | 3.87 | 0.81 | 0.18 | 0.76 | 0.61 | 0.062 | 0.14 | 0.05 | 0.02 | 0.086 | 0.063 | 0.24 | - | - | Sharma et al. (2020b) |
| Nainital | 1958 m | PM$_{10}$ | 3.66 | 1.29 | 2.28 | 1.07 | 0.18 | 0.79 | 0.85 | 0.061 | 0.14 | 0.04 | 0.02 | 0.110 | 0.041 | 0.26 | 0.04 | 0.056 | Sharma et al. (2020a) |
| Nainital | 1958 m | PM$_{10}$ | 8.1 | 2.4 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | Srivastava and Naja (2021) |
| Palampur | 1300 m | PM$_{2.5}$ | 6.73 | 1.64 | - | 3.79 | 0.76 | 1.47 | 0.44 | 0.008 | - | - | - | 0.029 | - | - | - | 0.004 | Sharma et al. 2014a |
| Kullu | 1154 m | PM$_{2.5}$ | 4.80 | 1.90 | - | 2.11 | 0.39 | 1.64 | 0.45 | 0.013 | - | - | - | 0.023 | - | - | - | 0.003 | Sharma et al. 2014b |
| Shimla | 2206 m | PM$_{2.5}$ | 3.81 | 1.75 | - | 1.40 | 0.93 | 2.04 | 0.60 | 0.083 | - | - | - | 0.137 | - | - | - | 0.003 | Sharma et al. 2014a |
| Solan | 1303 m | PM$_{2.5}$ | 5.64 | 2.03 | - | 2.38 | 0.63 | 1.34 | 0.43 | 0.072 | - | - | - | 0.105 | - | - | - | 0.004 | Sharma et al. 2014b |
| Nahan | 907 m | PM$_{2.5}$ | 7.62 | 3.50 | - | 1.84 | 0.56 | 1.13 | 0.28 | 0.043 | - | - | - | 0.072 | - | - | - | 0.003 | Sharma et al. 2014a |
| Kullu | 1154 m | PM$_{10}$ | 10.3 | 5.4 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | Sen et al. (2018) |
| Pohara | 750 m | PM$_{10}$ | 6.8 | 4.8 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | Kaushal et al. (2018) |
| Kangra | 1250 m | PM$_{10}$ | 13.5 | 5.1 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | Kumar and Attri (2016) |
| Dharamshala | 1350 m | PM$_{10}$ | 5.0 | 2.5 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | Kaushal et al. (2018) |
| Bhagwanpur | 450 m | PM$_{2.5}$ | - | - | - | 10.64 | 5.19 | 4.19 | 1.59 | - | 0.48 | 0.38 | 0.35 | 2.69 | - | - | 0.76 | 0.07 | Panwar et al. (2020) |
| Dehradun | 457 m | PM$_{10}$ | - | - | - | 0.93 | - | 1.72 | - | 0.96 | 0.15 | 0.13 | 0.35 | - | - | 0.12 | 0.16 | Soni et al. (2020) |
Sample collection and analysis

PM$_{2.5}$ ($n = 94$) and PM$_{10}$ ($n = 102$) samples were collected simultaneously on pre-combusted (at 550 °C) Pallflex tissue quartz filters (47mm for PM$_{2.5}$ and 20×25 cm$^2$ for PM$_{10}$) using fine particle sampler (flow rate: 1 m$^3$ h$^{-1}$ ± 2 %) and respirable particle sampler (flow rate:1.2 m$^3$ min$^{-1}$ ± 2 %), respectively, for 24h from August 2018–July 2019 (PM$_{2.5}$ sampling was not carried out in July 2019 due to some technical issue). The particle sampler was placed on the rooftop of the Bose Institute at the height of 15m above the ground level (AGL). The gravimetric mass (in μg) of PM$_{2.5}$ and PM$_{10}$ 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 PM$_{10}$ (in μg m$^{-3}$) were further computed by dividing the PM mass by 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 PM$_{10}$ 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 cm$^2$ 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% CH$_4$ + balance helium gas (before and after sample analysis). Calibration of the OC/EC analyzer was performed by 4.8% of CO$_2$ + balance He gas. Calibration of the OC/EC carbon analyzer was performed daily using 5% CH$_4$ + balance helium gas (Chow et al. 2004). A proper punch of ~0.536 cm$^2$ 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% CH$_4$ + balance helium gas (before and after sample analysis). Calibration of the OC/EC analyzer was performed by 4.8% of CO$_2$ + 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 PM$_{10}$ are computed as (1.6 × OC) + EC (Rengarajan et al. 2007; Srinivas and Sarin 2014).

A known punch size of PM$_{2.5}$ (3.5 cm$^2$) and PM$_{10}$ (7.1 cm$^2$) filters was 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 PM$_{10}$ samples to obtain the analytical results (WSOC and WIOC = OC−WSOC). Calibration of the instrument was performed before analysis of the samples using a standard solution of five different concentrations. Three to ten percent of repeatability errors were estimated in WSOC analysis ($n=3$). The detailed analytical procedures are described in Rai et al. (2020a).

Wavelength dispersive X-ray fluorescence spectrometer (WD-XRF) was used to analyze 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 PM$_{10}$ (with repeatability errors:5–10%). The analysis of major and trace elements was carried out by a non-destructive method of quantitative elemental analysis using wavelength dispersive X-ray fluorescence spectrometer (ZSX Primus, Rigaku, Japan). Measurement of elements were taken under standard reference conditions (vacuum condition, 36°C temperature and 2.4 kW tube rating). The parameter method was employed in the quantitative analysis given in ZSX software package of WD-XRF. The instrument WD-XRF was calibrated periodically using micro-matter thin-film standards (Watson et al. 1999). The samples were analyzed in triplicate for major and trace elements. The detailed analytical procedures are available in Jain et al. 2020a, 2020b).

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

The concentrations of POC in PM$_{2.5}$ and PM$_{10}$ 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; Rengarajan et al. 2007; Rastogi and Sarin 2009). POC are computed using the following equation:

$$POC = [OC/EC]_{\text{max}} \times [EC] + c$$  

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

**Enrichment factors (EFs)**

Crustal EFs refer to the origin of the elements (either anthropogenic or natural) and their abundance in the ambient particles (Amato et al. 2016). The EFs of the elements present in PM$_{2.5}$ and PM$_{10}$ samples are computed (Taylor and McLennan 1995) as:

$$EF = \frac{E_{\text{sample}}}{E_{\text{crust}}} \times \frac{X_{\text{sample}}}{X_{\text{crust}}}$$

where:

- $E_{\text{sample}}$: element (El) mass concentration
- $X_{\text{sample}}$: reference element (X) mass concentration
- $E_{\text{crust}}$: element (El) concentration in upper continental crust
- $X_{\text{crust}}$: reference element (X) concentration in upper continental crust

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

**Principal component analysis (PCA)**

In this study, PCA was applied on chemical constituents of PM$_{2.5}$ and PM$_{10}$ to identify the potential sources contributing to fine (PM$_{2.5}$) and coarse fraction (PM$_{10}$) of 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 datasets is shared between these components, whereas the maximum is shared by the first component (Belis et al. 2013). In PCA, the chemical data are transformed into a dimensionless standardized form:
PM\(_{10}\) was observed in March (73 \(\pm\) 9 \(\mu g\) m\(^{-3}\)) and January (27 \(\mu g\) m\(^{-3}\)) which might be due to the influence of stubble burning in northern states of India (Punjab, Haryana, and western Uttar Pradesh) to the Darjeeling. The higher concentrations of PM\(_{2.5}\) and PM\(_{10}\) during colder months could be attributed to the prevailing meteorological conditions, i.e., low temperature, stable atmosphere (cool air causes inversions that stagnate the air and trap the pollutant close to ground), and low wind speed (Chatterjee et al. 2010; Gopalswami 2016). Sharma et al. (2014b) reported the similar concentration of PM\(_{2.5}\) (at Kullu: 34\(\pm\)2 \(\mu g\) m\(^{-3}\); at Shimla: 32\(\pm\)3 \(\mu g\) m\(^{-3}\)) at the north-western Himalayan region during winter 2013, whereas Kaushal et al. (2018) recorded the 52\(\pm\)18 \(\mu g\) m\(^{-3}\) of PM\(_{10}\) concentration at Pohara of north-western Himalaya (Himachal Pradesh) during winter 2015. Sharma et al. (2020a) reported the PM\(_{10}\) concentration as 54\(\pm\)12 \(\mu g\) m\(^{-3}\) and 39\(\pm\)10 \(\mu g\) m\(^{-3}\) during the post-monsoon and winter, respectively, at Nainital, a central Himalayan region. Sharma et al. (2020b) also reported the PM\(_{10}\) concentration as 48 \(\pm\)16 \(\mu g\) m\(^{-3}\) during winter in Darjeeling. The monthly variation in mass concentrations of PM\(_{2.5}\) and PM\(_{10}\) in relation with 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 PM\(_{10}\) 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 the sampling site of Darjeeling (Rai et al. 2020a).

### Results and discussion

#### Seasonal variations of chemical species of PM\(_{2.5}\) and PM\(_{10}\)

##### Seasonal variability of PM\(_{2.5}\) and PM\(_{10}\)

The annual average of PM\(_{2.5}\) and PM\(_{10}\) concentrations were estimated as 37\(\pm\)12 \(\mu g\) m\(^{-3}\) (range: 16\(\quad\)77 \(\mu g\) m\(^{-3}\)) and 56 \(\pm\)18 \(\mu g\) m\(^{-3}\) (range: 21\(\quad\)116 \(\mu g\) m\(^{-3}\)), respectively (Table 2). The maximum monthly average mass concentration of PM\(_{2.5}\) was recorded in October (58 \(\mu g\) m\(^{-3}\)) and the minimum monthly average concentration of PM\(_{2.5}\) was observed in January (27 \(\mu g\) m\(^{-3}\)), whereas monthly average maxima of PM\(_{10}\) was observed in March (73 \(\mu g\) m\(^{-3}\)) and monthly average minima in January (43 \(\mu g\) m\(^{-3}\)). The monthly average and temporal variations in PM\(_{2.5}\) and PM\(_{10}\) concentrations are shown in Figs.S2-S3 (see the supplementary information). The highest seasonal average concentrations of both PM\(_{2.5}\) (41\(\pm\)14 \(\mu g\) m\(^{-3}\)) and PM\(_{10}\) (64\(\pm\)20 \(\mu g\) m\(^{-3}\)) were found during summer, and minimum seasonal average mass concentrations of both PM\(_{2.5}\) (31\(\pm\)9 \(\mu g\) m\(^{-3}\)) and PM\(_{10}\) (51\(\pm\)17 \(\mu g\) m\(^{-3}\)) were recorded during winter. In post-monsoon, the concentrations of PM\(_{2.5}\) (40\(\pm\)11 \(\mu g\) m\(^{-3}\)) and PM\(_{10}\) (55\(\pm\)17 \(\mu g\) m\(^{-3}\)) were recorded higher than the winter and monsoon (Table 2). In the present case, non-significant seasonal variation in mass concentrations of both PM\(_{2.5}\) and PM\(_{10}\) was recorded at Darjeeling (except winter). In the present study, bimodal monthly peaks of aerosols (PM\(_{2.5}\) and PM\(_{10}\)) loading were observed during the sampling period. The higher vehicular activities due to high influx of tourists in Darjeeling could be the reason behind the higher loading of aerosols mass concentration in summer months, whereas the higher aerosols mass loading during post-monsoon months may be due to long-range transportation of pollutants (from crop residue/stubble burning) from the north-western states of Indo Gangetic Plain (IGP) of India (Punjab, Haryana, and Uttar Pradesh) to the Darjeeling. The higher

\[
Z_{ij} = \frac{C_{ij} - \bar{C}_j}{\sigma_j}
\]

where \(i = 1, \ldots, n\) samples; \(j = 1, \ldots, m\) elements; \(C_{ij}\) is the concentration of element \(j\) in sample \(i\); and \(\bar{C}_j\) and \(\sigma_j\) are the arithmetic mean concentration and the standard deviation for element \(j\), respectively. The PCA model is expressed as:

\[
Z_{ij} = \sum_{k=1}^{p} g_{ik} h_{kj}
\]

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

#### Variation of OC, EC, and WSOC in PM\(_{2.5}\) and PM\(_{10}\)

Temporal variations in OC, EC, and WSOC concentrations of PM\(_{2.5}\) and PM\(_{10}\) during the 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\(\pm\)1.59 \(\mu g\) m\(^{-3}\), 1.93\(\pm\)0.93 \(\mu g\) m\(^{-3}\), 1.88\(\pm\)1.05 \(\mu g\) m\(^{-3}\), and 1.69\(\pm\)0.85 \(\mu g\) m\(^{-3}\), respectively, whereas the annual average of OC, EC, WSOC, and WIOC in PM\(_{10}\) were 5.06 \(\pm\)2.03 \(\mu g\) m\(^{-3}\), 2.34\(\pm\)1.18 \(\mu g\) m\(^{-3}\), 3.55\(\pm\)1.75 \(\mu g\) m\(^{-3}\), and 1.51 \(\pm\)0.92 \(\mu g\) m\(^{-3}\), respectively. Figure 2 shows the monthly average of OC, EC, and WSOC in PM\(_{2.5}\) and PM\(_{10}\) during the study period in Darjeeling. The highest monthly average OC in PM\(_{2.5}\) (4.76 \(\mu g\) m\(^{-3}\)) and PM\(_{10}\) (6.30 \(\mu g\) m\(^{-3}\)) was found in November (post-monsoon), whereas monthly average minima of OC in PM\(_{2.5}\) (2.03 \(\mu g\) m\(^{-3}\)) and PM\(_{10}\) (3.31 \(\mu g\) m\(^{-3}\)) was found in August (monsoon) and May (summer), respectively. Similar monthly average maxima and minima of EC (in PM\(_{2.5}\) and PM\(_{10}\)) were recorded in March and August, respectively (Fig. 2). The highest monthly average WSOC concentration in both PM\(_{2.5}\) (2.77 \(\mu g\) m\(^{-3}\)) and PM\(_{10}\) (5.51 \(\mu g\) m\(^{-3}\)) was recorded in November (post-monsoon) which 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,
| Species | Annual | Winter | Summer | Monsoon | Post-monsoon |
|---------|--------|--------|--------|---------|-------------|
| PM      | 37±12  | 56±18  | 41±14  | 38±8    | 40±11.4     |
| OC      | 3.56±1.59 | 5.06±2.03 | 4.04±1.67 | 2.21±0.86 | 4.07±1.55   |
| EC      | 1.93±0.93 | 2.34±1.18 | 2.23±0.92 | 1.21±0.43 | 2.19±1.06   |
| WSOC    | 1.88±1.05 | 3.55±1.75 | 2.15±1.19 | 1.14±0.51 | 2.17±0.98   |
| WIOC    | 1.69±0.85 | 1.51±0.92 | 1.94±0.91 | 1.07±0.55 | 1.86±0.78   |
| POC     | 2.35±1.06 | 3.18±1.31 | 2.68±1.10 | 1.57±0.56 | 2.30±1.12   |
| SOC     | 1.19±0.57 | 2.05±0.98 | 1.48±0.76 | 0.64±0.54 | 1.74±0.74   |
| TCA     | 7.63±3.43 | 10.43±4.25 | 8.89±3.54 | 4.74±1.73 | 8.65±3.47   |
| Na      | 0.607±0.395 | 1.01±0.392 | 0.776±0.484 | 0.573±0.389 | 0.501±0.239 |
| Mg      | 0.209±0.075 | 0.24±0.108 | 0.279±0.073 | 0.168±0.052 | 0.195±0.062 |
| Ca      | 0.918±0.813 | 0.985±0.299 | 2.097±0.706 | 0.249±0.213 | 0.229±0.213 |
| Cl      | 0.250±0.147 | 0.22±0.127 | 0.291±0.149 | 0.170±0.050 | 0.283±0.180 |
| P       | 0.078±0.037 | 0.077±0.034 | 0.105±0.026 | 0.081±0.034 | 0.070±0.039 |
| S       | 0.667±0.404 | 1.260±0.744 | 0.956±0.370 | 0.223±0.181 | 0.620±0.284 |
| K       | 0.388±0.224 | 0.650±0.376 | 0.608±0.226 | 0.174±0.050 | 0.307±0.171 |
| Al      | 0.261±0.164 | 0.922±0.446 | 0.454±0.143 | 0.143±0.065 | 0.179±0.068 |
| Fe      | 0.502±0.195 | 0.635±0.266 | 0.737±0.153 | 0.390±0.087 | 0.391±0.067 |
| Ti      | 0.035±0.015 | 0.057±0.022 | 0.047±0.013 | 0.024±0.008 | 0.032±0.018 |
| Cr      | 0.291±0.143 | 0.122±0.114 | 0.372±0.199 | 0.254±0.081 | 0.215±0.074 |
| Ni      | 0.092±0.025 | 0.084±0.008 | 0.110±0.027 | 0.094±0.014 | 0.090±0.021 |
| 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 | 0.088±0.032 | 0.087±0.027 | 0.084±0.031 |
| Mn      | 0.033±0.012 | 0.048±0.018 | 0.037±0.010 | 0.033±0.012 | 0.031±0.015 |
| Mo      | 0.245±0.169 | 0.060±0.013 | 0.337±0.224 | 0.144±0.034 | 0.133±0.028 |
| Zr      | 0.107±0.094 | 0.061±0.013 | 0.102±0.039 | 0.132±0.112 | 0.086±0.026 |
| 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 | 0.321±0.096 | 0.702±0.472 |

± Standard deviation (at 1σ)
WIOC, POC, SOC, and TCA concentrations of PM$_{2.5}$ and PM$_{10}$ during winter, summer, monsoon, and post-monsoon seasons in Darjeeling. The highest seasonal average OC concentration of PM$_{2.5}$ (4.07±1.55 $\mu$g m$^{-3}$) and PM$_{10}$ (5.69±2.09 $\mu$g m$^{-3}$) was recorded in post-monsoon season, and minimum seasonal average concentration of OC in PM$_{2.5}$ (2.21±0.86 $\mu$g m$^{-3}$) and PM$_{10}$ (3.62±0.86 $\mu$g m$^{-3}$) was recorded during monsoon (Table 2). Similarly, seasonal average maxima and minima of EC in PM$_{2.5}$ and PM$_{10}$ were recorded in summer and monsoon seasons, respectively. Average WSOC concentration in both PM$_{2.5}$ (2.17±0.98 $\mu$g m$^{-3}$) and PM$_{10}$ (4.44±1.55 $\mu$g m$^{-3}$) were found highest during the post-monsoon season and minimum in monsoon season (Fig. 3). During the year-long sampling of PM$_{2.5}$ and PM$_{10}$, the bimodal peaks in mass concentrations of OC, EC, and WSOC were recorded in summer months (March) and post-monsoon months (November). The higher vehicular activities due to high influx of tourists, coal burning, and biogenic VOCs emissions from the vigorous coniferous forest under relatively higher temperature and intense solar radiation in summer could be the major source of carbonaceous aerosols in Darjeeling (Chatterjee et al. 2010, 2021), whereas the long-range transportation of pollutants (from crop residue burning) from the north-western states of IGP, India (Punjab, Haryana, and Uttar Pradesh) could be the major source of carbonaceous aerosols in Darjeeling (including local sources: coal and wood burning during colder months) during post-monsoon months (Chatterjee et al. 2010; Ghosh et al. 2021). The massive coal and biomass burning (domestic, industrial, and Darjeeling Himalayan railways) throughout the year also enhanced the concentrations of carbonaceous species in PM$_{2.5}$ and PM$_{10}$ over Darjeeling (Ghosh et al. 2021). A comparison of mass concentrations of OC, EC, WSOC and elements in PM$_{2.5}$ and PM$_{10}$ over the various locations of Himalayan region of India is summarized in Table 1.

The annual average concentration of TCA contributes 20.6% of PM$_{2.5}$ (7.6±3.4 $\mu$g m$^{-3}$) and 18.6% of PM$_{10}$ (10.4

Fig. 2 Monthly average concentrations of OC, EC, and WSOC and their mass ratios (of PM$_{2.5}$ and PM$_{10}$) at Darjeeling
±4.3 μg m$^{-3}$). The highest TCA in PM$_{2.5}$ and PM$_{10}$ was recorded in winter (22.7% of PM$_{2.5}$ and 22.4% of PM$_{10}$) season followed by post-monsoon (21.7% of PM$_{2.5}$ and 20.3% of PM$_{10}$), summer (21.6% of PM$_{2.5}$ and 17.6% of PM$_{10}$), and monsoon (12.5% of PM$_{2.5}$ and 13.4% of PM$_{10}$) seasons. The annual average concentration of POC in PM$_{2.5}$ was recorded to be 2.35 ± 1.06 μg m$^{-3}$ (66% of OC), and SOC was 1.19±0.57 μg m$^{-3}$ (34% of OC). Similarly, the annual average POC concentration in PM$_{10}$ was recorded as 3.18 ± 1.13 μg m$^{-3}$ (63% of OC), whereas SOC was recorded as 2.05±0.98 μg m$^{-3}$ (37% of OC). In PM$_{2.5}$, the seasonal contributions of POC and SOC were ranging from 55 to 77% and 33 to 45% of OC, respectively, whereas in PM$_{10}$, the seasonal contributions of POC and SOC were ranging from 51 to 73% and 37 to 49% of OC, respectively. Sen et al. (2018) reported similar OC (7.7±0.7 μg m$^{-3}$) and EC (3.7±0.6 μg m$^{-3}$) concentrations in PM$_{10}$ at Darjeeling and high OC (10.3±5.6 μg m$^{-3}$) and EC (5.4±2.9 μg m$^{-3}$) values in PM$_{10}$ at Kullu-Mohal (north-western Himalayas) during winter, whereas Rai et al. (2020a) observed low OC (3.7±1.3 μg m$^{-3}$) and EC (1.3±0.6 μg m$^{-3}$) concentrations in PM$_{10}$ at Darjeeling. Sharma et al. (2020a) also found similar OC and EC concentrations in PM$_{10}$ over Nainital (central Himalayas) during post-monsoon (OC: 4.7±1.1 μg m$^{-3}$ and EC: 1.1±0.5 μg m$^{-3}$) and winter (OC: 3.2±1.1 μg m$^{-3}$ and EC: 1.4±0.6 μg m$^{-3}$) seasons.

Figure 2 shows the monthly average OC/EC and WSOC/OC ratios of PM$_{2.5}$ and PM$_{10}$ at Darjeeling, whereas the seasonal relationship between OC and EC and WSOC and OC of PM$_{2.5}$ and PM$_{10}$ is depicted in Figs. S4-S5 (see the supplementary information). The seasonal average OC/EC ratio 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 ratio of PM$_{10}$ was 2.04, 1.74, 3.37, and 3.01 during winter, summer, monsoon, and post-monsoon, respectively, whereas the seasonal average WSOC/OC ratio of PM$_{10}$ 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 the 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 and EC (for PM$_{2.5}$: $R^2 = 0.88$, 0.86, 0.63, and 0.80 at $p < 0.05$; for PM$_{10}$: $R^2 = 0.77$, 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 PM$_{10}$ has been observed during all the seasons (except monsoon season for
PM$_{10}$) (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 PM$_{10}$: $R^2 = 0.69, 0.91, 0.17$, and 0.87 during winter, summer, monsoon, and post-monsoon seasons, respectively) of PM$_{2.5}$ and PM$_{10}$ (except monsoon season for PM$_{10}$) show 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, and WSOC of PM$_{2.5}$ and significant positive correlation of K with Ca, Mg, WSOC of PM$_{10}$ 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 PM$_{10}$ at the study site (Tables: S1-S8; in supplementary information). It may also be considered that the soil suspension, fuel combustion (Urban et al. 2012; Ghosh et al. 2021), and formation of secondary water soluble organic aerosols (Lim et al. 2010) might be some other sources of WSOC in the sampling site of Darjeeling.

**Major and trace elements in PM$_{2.5}$ and PM$_{10}$**

During the sampling, 19 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 both PM$_{2.5}$ and PM$_{10}$ (Cu and Pb obtained in PM$_{10}$ but traced in few PM$_{2.5}$ samples also) using XRF technique (Table 2). In PM$_{2.5}$ samples, Ca was observed highest annual average concentration ($0.918 \pm 0.813 \mu g \cdot m^{-3}$) followed by S ($0.667 \pm 0.404 \mu g \cdot m^{-3}$), Na ($0.607 \pm 0.395 \mu g \cdot m^{-3}$), Fe ($0.502 \pm 0.195 \mu g \cdot m^{-3}$), K ($0.388 \pm 0.224 \mu g \cdot m^{-3}$), and so on, with higher loading in summer season (Table 2), whereas, in case of PM$_{10}$, S has recorded highest annual average concentrations ($1.260 \pm 0.744 \mu g \cdot m^{-3}$) followed by Na ($1.014 \pm 0.392 \mu g \cdot m^{-3}$), Ca ($0.985 \pm 0.299 \mu g \cdot m^{-3}$), Al ($0.922 \pm 0.446 \mu g \cdot m^{-3}$), K ($0.650 \pm 0.376 \mu g \cdot m^{-3}$), Fe ($0.635 \pm 0.266 \mu g \cdot m^{-3}$), and so on. The annual average concentrations of elements in PM$_{2.5}$ and PM$_{10}$ are $5.71 \pm 3.67 \mu g \cdot m^{-3}$ (accounted for 15% of PM$_{2.5}$) and $6.44 \pm 3.58 \mu g \cdot m^{-3}$ (accounted for 12% of PM$_{10}$), respectively. The monthly average concentrations of the elements of PM$_{2.5}$ and PM$_{10}$ 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 PM$_{10}$) followed by winter (16.5% of PM$_{2.5}$ and 11.7% of PM$_{10}$), post-monsoon (11.6% of PM$_{2.5}$ and 11% of PM$_{10}$), and monsoon (9% of PM$_{2.5}$ and 13% of PM$_{10}$) seasons (Fig. 4). During winter 2013 land campaign, Sharma et al. (2014b) found 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 contribution of the elements to PM$_{10}$ as 16% and 13% during post-monsoon and winter seasons, respectively, at central Himalaya (Nainital). The similar contribution of elements to the PM$_{10}$ over the Himalayan region and other high altitude hill stations is discussed in our earlier publication (Sharma et al. 2020b). It is observed that the concentrations of sodium and chloride are several times higher than all other hill stations indicating the strong influence of sea salt aerosols over Darjeeling (due to long-range transportation of sea salts from Bay of Bengal and Arabian sea). In addition to strong influence of sea salt aerosols, massive coal and biomass burning (domestic, industrial and Darjeeling Himalayan railways) throughout the year enhanced the concentrations of non-sea salt chloride in PM$_{2.5}$ and PM$_{10}$ over Darjeeling (Chatterjee et al. 2010).

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 PM$_{10}$ samples. Al, Fe, Ti, K, Mg, and Ca in both PM$_{2.5}$ and PM$_{10}$ have recorded low EFs (< 5) for all the seasons, which indicates that elements mostly arrived from crustal/soil sources. The elements like Cu, Zn, Ni, Pb, Cr, Mo, and B have higher EFs (>10) in both PM$_{2.5}$ and PM$_{10}$ and therefore are likely of anthropogenic origin. The higher EF of Cr, Ni, Pb, and Zn of PM was also attributed to industrial emission (IE) sources. Generally, Cu, Mn, Zn, Ni, Cd, Fe, Mo, S, and Cr were used as a marker for IE in India (Shridhar et al. 2010). EF value of Na was observed >5 in all the seasons accrediting the intrusion of sea salt (Na$^+$) over the region (Chatterjee et al. 2010).

The annual and seasonal statistical summary of elements recorded in PM$_{2.5}$ and PM$_{10}$ samples is tabulated in Table 2. The possible sources of trace metals present in fine and coarse fraction of PM can be primarily of crustal/mineral dust. In this study, Al is significantly positive correlated with Fe, Ca, Mg, and Ti (as well as with PM$_{10}$), 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 the 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 a Fe/Al ratio of 0.59 for PM$_{2.5-10}$ at the remote high altitude sampling site (Manora Peak) of western India. McLennan (2001) recorded the average Ca/Al ratio of 1.07 in PM$_{10}$, 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 PM$_{10}$ 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 PM$_{10}$ at Manora Peak, a high altitude site of 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 also indicated the abundance of mineral dust at the sampling site of Darjeeling (Table S1-S8; in supplementary information).
PCA has been performed with chemical species of 20 PM$_{2.5}$ and 22 PM$_{10}$ (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 PM$_{10}$. The factor profiles (year-long data) of the possible sources of PM$_{2.5}$ and PM$_{10}$ extracted by PCA are summarized in Table 3. Based on 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 PM$_{10}$ 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 Levoglucosan are considered to be BB (cow dung, crop residue, fuelwood, wildfires, etc.) marker, whereas the presence of Cl reveals the wood and coal burning (Pant and Harrison 2012). WSOC/OC and OC/EC ratios also evidence the BB + FFC as one of the sources of PM$_{2.5}$ at the observational site of Darjeeling (Sharma et al. 2020b; Chatterjee et al. 2021). Coal and biomass burning in domestic, industrial, and Darjeeling Himalayan railways throughout the year are the major source of BB + FFC in Darjeeling (Chatterjee et al. 2010; Rai et al. 2020a). The first factor of PM$_{10}$ is represented by high loading (36.7% of the variance) of crustal elements (like, Al, Ti, Fe, Ca, Mg, K and Na) which inferred as the abundance of crustal/soil/road dust (Begum et al. 2011; Sharma et al. 2014a; Jain et al. 2020b). The abundance of these elements at the study site as the crustal origin is also confirmed by EFs (Fig. 5) as well as positive correlation of Al with Ca, Mg, and Ti (Table S1-S8). The loading of dust particulates enriched with Ca, Mg, Al, Ti and Fe in Himalayan region is mostly due to long-range transport of dust particulates originated from the western part of India (Chatterjee et al. 2010).

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 3). The EFs of these

| 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      | 0.143     | 0.736     | 0.043    | -        | 0.843     | 0.059     | 0.163    | 0.149    |
| 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    | -         | -         | 0.030    | 0.426    |
| 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; 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
elements are also suggesting the crustal origin of the elements at the sampling site (Fig. 5) as well as the positive correlation of Al with Ca, Mg, and Ti, whereas the second factor of PM$_{10}$ is represented by BB + FFC with high loadings of OC, EC, WSOC, K, Cl, and S (Begum 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 PM$_{10}$ at Darjeeling (Sharma et al. 2020b; Chatterjee et al. 2021). The stable carbon isotopic study of PM also reveals the abundance of BB and FFC in Darjeeling and its surrounding areas (Sen et al. 2018; Sharma et al. 2015, 2017).

Factor 3: The third factor of both PM$_{2.5}$ and PM$_{10}$ constitutes the vehicular emissions (VE) with the dominant presence of EC, OC, Zn, Mn, Zr, and B indicating that the emissions were derived from road side vehicles (Pant and Harrison 2012; Jain et al. 2020b). Since EC and OC are majorly emitted from the combustion sources, so these components are considered as important tracers for VE globally (Yin et al. 2010; Begum et al. 2011). Zn and Mn are used as a marker of brake and tire wear, two stroke engine emissions (Zn as a fuel additive), and heavy duty diesel truck emissions (Mn as a 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 an urban site of the Himalayan region that might be due to the great influence of tourism activities as well as Darjeeling Himalayan Railways (Gajananda et al. 2005; Chatterjee et al. 2021).

Factor 4: The fourth source of both PM$_{2.5}$ and PM$_{10}$ is characterized as industrial emissions (IE) considering to the higher loading of Cu, Zn, Ni, Cr, and Mo in PM samples (Table 3). These metals (Cu, Zn, Ni, Cr, and Mo) might be originated from the small to medium scale industries, metal processing industries, and industrial effluents (Gupta et al. 2007; Jain et al. 2017). Sharma et al. (2020b) also reported the solid waste + IE as a source of PM$_{10}$ in Darjeeling with these marker elements.

**Conclusions**

In this study, seasonal variation in carbonaceous aerosols and elements in fine and coarse fractions of aerosols (PM$_{2.5}$ and PM$_{10}$) is estimated to explore the prominent sources of PM$_{2.5}$ and PM$_{10}$ in the high altitude hill station of eastern Himalaya during August 2018–July 2019. The average PM$_{2.5}$ and PM$_{10}$ concentrations were recorded as $37\pm12$ g m$^{-3}$ and $58\pm18$ g m$^{-3}$, respectively, during the study. The annual CAs in PM$_{2.5}$ and PM$_{10}$ were accounted for 20.6% of PM$_{2.5}$ and 18.6% of PM$_{10}$, respectively (along with season variation). The concentrations of elements present in PM$_{2.5}$ and PM$_{10}$ were accounted for 15% and 12%, respectively. During all the seasons, significant positive linear relationship between OC & EC and OC & WSOC (as well as OC/EC and WSOC/OC) indicate the common sources (BB + FFC) of both PM$_{2.5}$ and PM$_{10}$. The annual concentrations of POC and SOC in PM$_{2.5}$ were $2.35 \pm 1.06$ g m$^{-3}$ (66% of OC) and $1.19 \pm 0.57$ g m$^{-3}$ (34% of OC), respectively, whereas the annual concentrations of POC and SOC in PM$_{10}$ were $3.18 \pm 1.13$ g m$^{-3}$ and $2.05 \pm 0.98$ g m$^{-3}$, respectively. EFs analysis of the elements present in PM indicates the abundance of mineral dust in the eastern Himalayas. PCA resolved the four common sources [(BB + FFC), crustal/SD, (VE), and (IE)] of PM$_{2.5}$ and PM$_{10}$ at Darjeeling.

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

**Declarations**

**Ethical approval** Not applicable.

**Consent to participate** Not applicable.

**Consent to publish** Not applicable.

**Competing interests** The authors declare no competing interests.

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