

Wintertime Variation in Carbonaceous Components of PM₁₀ in the High Altitudes of Himalayas [†]

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Abstract: Carbonaceous aerosols play a significant role in the Earth's atmospheric system by affecting the visibility, hydrological cycle, climate, radiative forcing and human health. The present study analyses the PM₁₀ samples collected at three distinct urban locations (Mohal-Kullu, Nainital and Darjeeling) over the Himalayan region of India during winter 2019. The mass concentration of PM₁₀ were recorded as $51 \pm 16 \mu\text{g m}^{-3}$, $38 \pm 9 \mu\text{g m}^{-3}$ and $52 \pm 18 \mu\text{g m}^{-3}$ for Mohal-Kullu, Nainital and Darjeeling, respectively. Organic carbon (OC) dominated over elemental carbon (EC) and was found to be 50.2%, 42.8 and 47% of total carbon (TC) at Mohal-Kullu, Nainital and Darjeeling, respectively. The respective mass concentrations of carbonaceous species were higher at Mohal-Kullu (OC: 11.1 ± 5.3 , EC: 4.2 ± 1.9 , WSOC: $5.3 \pm 1.3 \mu\text{g m}^{-3}$ and TCA: $22.1 \pm 10.4 \mu\text{g m}^{-3}$) followed by Darjeeling (OC: 5.4 ± 2.0 , EC: 2.7 ± 1.0 , WSOC: $3.9 \pm 1.3 \mu\text{g m}^{-3}$ and TCA: $22.1 \pm 10.4 \mu\text{g m}^{-3}$) and Nainital (OC: 2.9 ± 1.0 , EC: 1.3 ± 0.6 , WSOC: $2.1 \pm 0.6 \mu\text{g m}^{-3}$ and TCA: $6.7 \pm 2.4 \mu\text{g m}^{-3}$). The OC/EC and WSOC/OC ratio at Mohal-Kullu (2.6 ± 0.3 , 0.6 ± 0.2), Nainital (2.0 ± 0.4 , 0.7 ± 0.2) and Darjeeling (2.3 ± 0.5 , 0.7 ± 0.2), respectively, indicates the dominance of fossil fuel combustion (coal and vehicular exhaust), with signified additional contribution from secondary organic carbon (SOC).

Keywords: carbonaceous aerosols; water soluble organic carbon; secondary organic carbon; trajectories

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1. Introduction

Atmospheric aerosols have been well known as a major pollutant worldwide due to their complex composition, effects on visibility, heat balance of the earth [1,2]. A high loading of aerosol poses severe implications to human health, global climate change and the Earth's radiation budget [3,4]. Carbonaceous aerosols (CAs) are the key component of particulate matter (PM) constituting 20–70% of coarse particulate matter [4]. Carbonaceous components of PM are classified as organic carbon (OC), and elemental carbon (EC) in terms of their optical and physical properties [4,5]. OC is emitted from combustion or indirectly from heterogeneous oxidation of volatile organic compounds (VOCs), OC have

wide variety of organic compounds originating from various sources, and is further classified as primary organic carbon (POC) and secondary organic carbon (SOC) in terms of their formation. EC is emitted primarily from incomplete combustion of Biomass (BB) and fossil fuel combustion (FFC) [6–8]. As the CAs play crucial role in atmospheric chemistry, earth's radiation budget, human health and air quality of the region, it becomes very important to measure the concentrations of carbonaceous particles to understand their transport, sources and deposition.

The Himalayan region is regarded pristine and vulnerable to environmental change due to regional and global change [6]. There has been few research on carbonaceous particles, their sources, movement, and climatic effects [7–13]. Recent studies on CAs, sources identification and transport processes [7–13] fill this gap to some extent.

The present study estimates the concentration of CAs at different locations (Mohal-Kullu, Nainital and Darjeeling) of the Himalayan region of India during winter season (January–February 2019). We chose the winter season for the study because of increased BB and CC activity for heating purposes, as well as steady and stagnant air conditions that can lead to large concentrations of CAs. Using ratios, we identify the origins and their contribution to CAs across different study locations.

2. Methodology

2.1. Observation Sites

We conducted the study over different sites of the Himalayan region of India i.e., Mohal-Kullu, Nainital, and Darjeeling.

Mohal-Kullu: G. B. Pant's National Research Institute of Himalayan Environment and Sustainable Development, Mohal-Kullu (31.9° N, 77.11° E, and 1154 m a.s.l.) is located in the western Himalayan region. The study site have sub-temperate environment and receives heavy rain during the winter period.

Nainital: Aryabhata Research Institute of Observational Sciences (ARIES), Nainital is located on Manora hill (29.39° N, 79.45° E, 1959 m a.s.l.) in the central Himalayan region.

Darjeeling: Bose Institute, Darjeeling (27.01° N, 88.15° E, 2200 m a.s.l.) is located in the eastern Himalayas. The study site is geographically adjacent to the IGP region (a global hotspot for heavy aerosol loadings) [10]. A detailed description of the sampling location is discussed in previous studies [7–10,15,16].

2.2. Sample Collection and Analysis

PM₁₀ samples were collected during winter season (January–February 2019) twice every week for 24h using respirable dust sampler with a flow rate of 1.2 m³ min⁻¹ on pre-baked (550 °C for 5 h) Pall flex Tissuequartz filters (20 × 25 cm²) at three urban locations of Mohal-Kullu, Nainital and Darjeeling.

Measurement of carbonaceous species (OC, EC) in PM₁₀ samples collected over the study locations were carried out using OC/EC analyzer. This instrument is working on thermal-optical approach. WSOC in PM₁₀ samples were quantified using TOC analyzer (Model: TOC L_{CPH/CPN}, Shimadzu) which works on the principle of catalytic-oxidation combustion at high temperatures of 680 °C. WD-XRF (wave length dispersive X-Ray fluorescence) spectrometer was used for the quantification of elements in PM₁₀ ranging from Barium to Uranium. Details of OC/EC, TOC analyzer and WD-XRF are available in reference therein [9–12].

3. Result and Discussions

3.1. Mass Concentration of PM₁₀ and Carbonaceous Components

In the present study, the average PM₁₀ concentration at Mohal-Kullu, Nainital and Darjeeling were 51 ± 16 μg m⁻³, 38 ± 9 μg m⁻³ and 52 ± 18 μg m⁻³, respectively.

The findings acquired for study sites are comparable to previously reported PM₁₀ aerosol mass and carbonaceous components at different sites of India (Table 1). In the

present study, high concentrations of OC (Darjeeling: $5.36 \pm 1.74 \mu\text{g m}^{-3}$; Nainital: $2.85 \pm 0.75 \mu\text{g m}^{-3}$; Mohal-Kullu: $10.49 \pm 4.56 \mu\text{g m}^{-3}$), EC (Darjeeling: $2.67 \pm 0.87 \mu\text{g m}^{-3}$; Nainital: $1.30 \pm 0.46 \mu\text{g m}^{-3}$; Mohal-Kullu: $4.06 \pm 1.99 \mu\text{g m}^{-3}$), WSOC (Darjeeling: $3.93 \pm 1.17 \mu\text{g m}^{-3}$; Nainital: $2.04 \pm 0.54 \mu\text{g m}^{-3}$; Mohal-Kullu: $5.23 \pm 1.35 \mu\text{g m}^{-3}$) were observed (Figure 1a) High concentrations of carbonaceous components might be due to the Increased contribution from wood burning for household heating, open biomass burning, stable atmospheric conditions leading in pollution deposition within the lower atmosphere [4,6]. The observed OC and EC concentrations are in good accord with other reported studies (Table 1). SOC and POC were quantified in this study using the EC tracer method [5].

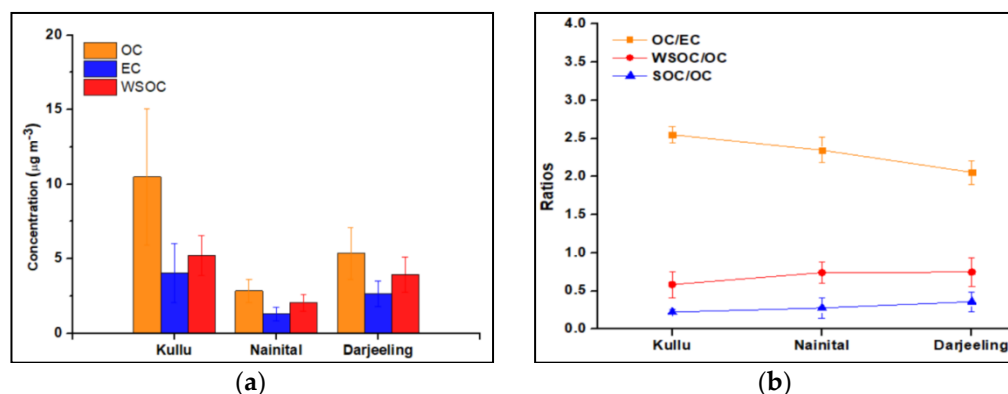


Figure 1. (a) Mass concentration of carbonaceous components of PM₁₀ (b) diagnostic ratios of carbonaceous components at different study sites of the IHR.

Table 1. Comparison of carbonaceous components and their mass ratios over high altitude locations in India.

Sampling Site	Altitude (m asl)	Time Period	PM ₁₀ (μg m ⁻³)	OC (μg m ⁻³)	EC (μg m ⁻³)	WSOC (μg m ⁻³)	OC/EC	WSOC/OC	References
Mohal, Kullu (31.9° N, 77.11° E)	1154	Jan–Feb 2019	51 ± 16	10.4 ± 4.5	4.0 ± 1.9	5.2 ± 1.3	2.6 ± 0.3	0.55 ± 0.23	Present study
Nainital (29.39° N, 79.45° E)	1959	Jan–Feb 2019	38 ± 9	2.8 ± 0.7	1.3 ± 0.4	2.0 ± 0.5	2.3 ± 0.5	0.74 ± 0.15	Present study
Darjeeling (27.01° N, 88.15° E)	2200	Jan–Feb 2019	52 ± 18	5.3 ± 1.7	2.6 ± 0.8	3.9 ± 1.1	2.0 ± 0.3	0.74 ± 0.22	Present study
Pohara (32.2° N, 76.2° E)	750	Jan–Apr 2015	52 ± 19	6.8 ± 2.3	4.8 ± 2.0	-	1.5 ± 0.4	-	Kaushal et al., 2018
Dharamshala (32.2° N, 76.3° E)	1350	Feb–Apr 2015	39 ± 23	5.0 ± 3.0	2.5 ± 0.6	-	2.0 ± 1.0	-	Kaushal et al., 2018
Manora Peak (29.39° N, 79.45° E)	1950	Feb–Mar 2005	138 ± 78	11.6 ± 5.9	1.8 ± 0.8	-	6.6 ± 0.3	-	Ram et al., 2008
Palampur (32.1° N, 76.5° E)	1300	Mar 2013	47 ± 7	6.7 ± 2.2	1.6 ± 0.9	-	4.3	-	Sharma et al., 2014
Kullu (32.2° N, 76.3° E)	1154	Mar 2013	34 ± 1	4.8 ± 1.6	1.9 ± 0.7	-	2.9	-	Sharma et al., 2014
Manora Peak (29.39° N, 79.45° E)	1950	2014–2017	32.1 ± 2.7	8.1 ± 6.0	2.4 ± 1.5	-	-	-	Srivastava and Naja, 2021

At Mohal-Kullu, Nainital and Darjeeling, an average POC concentration was observed at $8.24 \pm 3.73 \mu\text{g m}^{-3}$, $2.13 \pm 0.93 \mu\text{g m}^{-3}$ and $3.41 \pm 1.27 \mu\text{g m}^{-3}$, respectively, during the study period (Table 1). The SOC concentration was observed as $2.90 \pm 1.97 \mu\text{g m}^{-3}$, $0.75 \pm 0.36 \mu\text{g m}^{-3}$ and $1.99 \pm 1.10 \mu\text{g m}^{-3}$ at Mohal-Kullu, Nainital and Darjeeling, respectively.

3.2. Diagnostic Ratios and Scatter Plots

Diagnostic ratios of OC/EC, WSOC/OC are important for the identification of CAs emission sources and secondary organic aerosols (SOA) formation and their removal rates, ageing of atmospheric aerosols [18–20]. Figure 1b shows the OC with EC and WSOC with OC ratio at Mohal- Kullu (2.6 ± 0.3 , 0.6 ± 0.2), Nainital (2.3 ± 0.4 , 0.7 ± 0.1) and Darjeeling (2.06 ± 0.37 , 0.7 ± 0.2), respectively, which indicates the frequent practices of biomass burning during the season and formation of SOC and due to transported carbonaceous species (Figure 2) from the nearby IGP region [9–22]. The acquired ratios of OC with EC and WSOC with OC were in good agreements with earlier reported studies [11–22].

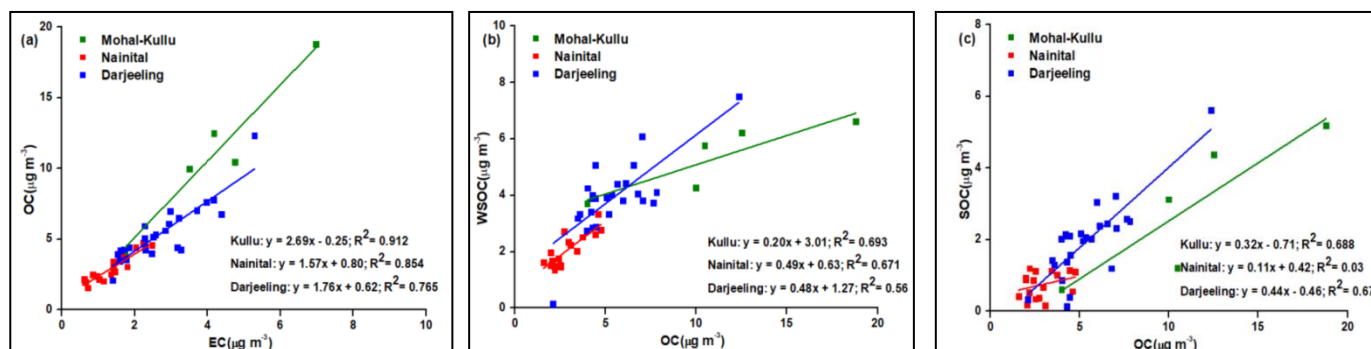


Figure 2. Scatter plots of carbonaceous components of PM₁₀ (a) OC with EC (b) WSOC with OC (c) SOC with OC at different sites of the IHR.

OC and EC exhibited significant correlation throughout the study period (Darjeeling: $R^2 = 0.765$; Nainital: $R^2 = 0.854$; Mohal-Kullu: $R^2 = 0.912$) (Figure 2a) indicating similar sources of CAs (fossil-fuel combustion (FFC), BB) and emission potential of sources [4,20,22]. Throughout the study, significant correlation of WSOC with OC (Figure 2b) was observed over study sites (Mohal-Kullu: $R^2 = 0.693$; Darjeeling: $R^2 = 0.583$; Nainital: $R^2 = 0.671$) which might be due to water soluble SOA formation [6,11,20,22]. Over the study regions, influx of pollutants from IGP region and local sources could be the major contributing sources of carbonaceous species (Figure 3).

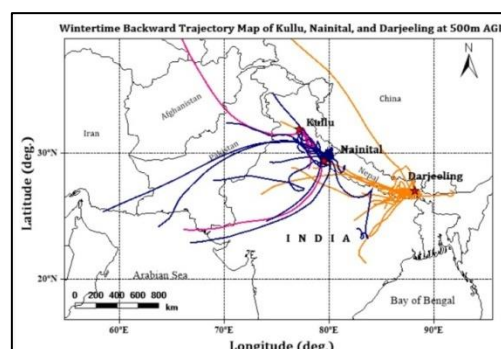


Figure 3. Wintertime air-mass backward trajectories of study sites at 500m AGL.

4. Conclusions

CAs associated with PM₁₀ has been studied during the winter season at different sites of the IHR i.e., Mohal-Kullu, Nainital and Darjeeling. The mean concentration of PM₁₀ was $51 \pm 16 \mu\text{g m}^{-3}$, $38 \pm 9 \mu\text{g m}^{-3}$ and $52 \pm 18 \mu\text{g m}^{-3}$ at Mohal-Kullu, Nainital and Darjeeling, respectively. The major results of the study are summarised below:

- In the present study, the winter concentrations of OC (Darjeeling: $5.36 \pm 1.74 \mu\text{g m}^{-3}$; Nainital: $2.85 \pm 0.75 \mu\text{g m}^{-3}$; Mohal-Kullu: $10.49 \pm 4.56 \mu\text{g m}^{-3}$), EC (Darjeeling: $2.67 \pm 0.87 \mu\text{g m}^{-3}$; Nainital: $1.30 \pm 0.46 \mu\text{g m}^{-3}$; Mohal-Kullu: $4.06 \pm 1.99 \mu\text{g m}^{-3}$), WSOC (Darjeeling: $3.93 \pm 1.17 \mu\text{g m}^{-3}$; Nainital: $2.04 \pm 0.54 \mu\text{g m}^{-3}$; Mohal-Kullu: 5.23 ± 1.35

$\mu\text{g m}^{-3}$) were observed which might be due to the enhanced contribution from wood burning for household purposes, open biomass burning, stable atmospheric conditions.

- Overall, the diagnostic ratios of OC with EC and WSOC with OC and SOC with OC, showed their positive association with carbonaceous components and major influence of BB as a source of carbonaceous species over the IHR. Linear regression analysis was performed among carbon components OC, EC, WSOC and SOC for more information on sources of CAs. OC and EC exhibited significant correlation throughout the study period which is attributed to common nature of their sources.
- Long range transported aerosols from IGP and surrounding areas contribute to carbonaceous species along with local emissions.

Author Contributions: Conceptualization by N.C. and S.K.S.; data collection and analysis were performed by N.C.; P.S.; S.M.; M.D.; J.C.K.; R.L.; A.C.; S.G.; M.N.; T.K.M. and S.K.S.; the first draft was written by N.C. and S.K.S. data interpretation was carried out by N.C., S.M., M.D., J.C.K., A.C., M.N., T.K.M. and S.K.S. All authors have read and agreed to the published version of the manuscript.

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