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High rise in carbonaceous aerosols under very low anthropogenic emissions over eastern Himalaya, India: Impact of lockdown for COVID-19 outbreak

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ABSTRACT
The present study has been conducted to investigate the relative changes of carbonaceous aerosols (CA) over a high altitude Himalayan atmosphere with and without (very low) anthropogenic emissions. Measurements of atmospheric organic (OC) and elemental carbon (EC) were conducted during the lockdown period (April 2020) due to global COVID 19 outbreak and compared with the normal period (April 2019). The interesting, unexpected and surprising observation is that OC, EC and the total CA (TCA) during the lockdown (OC: 12.1 ± 5.5 μg m⁻³; EC: 2.2 ± 1.1 μg m⁻³; TCA: 21.5 ± 10 μg m⁻³) were higher than the normal period (OC: 7.04 ± 2.2 μg m⁻³; EC: 1.9 ± 0.7 μg m⁻³; TCA: 13.2 ± 4.1 μg m⁻³). The higher values for OC/EC ratio too was observed during the lockdown (5.7 ± 0.9) compared to the normal period (4.2 ± 1.1). Much higher surface O₃ during the lockdown (due to very low NO) could better promote the formation of secondary OC (SOC) through the photochemical oxidation of biogenic volatile organic compounds (BVOCs) emitted from Himalayan coniferous forest cover. SOC during the lockdown (7.6 ± 3.5 μg m⁻³) was double of that in normal period (3.8 ± 1.4 μg m⁻³). Regression analysis between SOC and O₃ showed that with the same amount of increase in O₃, the SOC formation increased to a larger extent when anthropogenic emissions were very low and biogenic emissions dominate (lockdown) compared to when anthropogenic emissions were high (normal). Concentration weighted trajectory (CWT) analysis showed that the anthropogenic activities over Nepal and forest fire over north-east India were the major long-distant sources of the CA over Darjeeling during the normal period. On the other hand, during lockdown, the major source regions of CA over Darjeeling were regional/local. The findings of the study indicate the immense importance of Himalayan biosphere as a major source of organic carbon.

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1. Introduction

Carbonaceous components are the major components of the fine mode aerosols in the atmosphere having significant importance because of their roles in climate change, perturbation in the Earth’s radiative balance and visibility degradation (Lim and Turpin, 2002; Hansen et al., 2005). Carbonaceous aerosols poses adverse health effect with various physiological disorders related to asthma, bronchitis, cancer and heart disease (McClurian, 1996; Garza et al., 2008; Mauderly and Chow, 2008). The carbonaceous aerosols are consisting of elemental carbon (EC) and organic carbon (OC). EC is emitted into the atmosphere from the incomplete combustion processes whereas OC is composed of various organic species including the water soluble organic compounds and form a complex mixture with different physical and chemical properties. OC can be directly emitted into atmosphere from different primary sources like vehicular emissions (Zhao et al., 2007; He et al., 2008; Xie et al., 2017) biomass burning (Zhang et al., 2008; Xu et al., 2018), plant debris (Li et al., 2018), fungal spore etc. (Jiang et al., 2017). However there are some secondary sources too. Volatile and semi-volatile compounds get photochemically oxidized in the presence of OH radical, NOx and O3 and form secondary organic aerosols enhancing the atmospheric loading of total organic carbonaceous aerosols (Haque et al., 2016). Both the primary and secondary organic compounds (POC and SOC) significantly control the physio-chemical properties of aerosol particles (Kanakidou et al., 2005). The coating of water soluble organics (which are secondary in nature) on the hydrophobic carbonaceous aerosols make them partially soluble and hydrophilic which in turn allow them to act as cloud condensation nuclei (CCN). Therefore organic carbon bears the potential to affect the microphysical properties of clouds too (Rosenfeld, 2008). EC (and black carbon, BC) on the other hand can absorb solar radiation and contribute to global warming significantly (Andreae and Gelencsér, 2006; Jacobson, 2001; Ramanathan and Carmichael, 2008). Elevated absorbing carbonaceous aerosols concentrations can accelerate the melting rate of the glaciers. In addition to these direct effects, incorporation of absorbing carbonaceous aerosols inside the cloud drops can change the cloud lifetime (Jacobson, 2006; Mikhailov et al., 2006) affecting the precipitation pattern over a region. Venkataraman et al. (2005) estimated the emission budget of absorbing carbonaceous aerosols from India. It was 0.41 Tg per year with the main sources of fossil fuel burning (25%), open burning (42%) and biofuel burning (33%). The fine mode carbonaceous aerosols can also be transported from long distant source regions due to their high atmospheric lifetime (7–10 days in the absence of precipitation). The densely populated Indo Gangetic Plain (IGP) is one of the major source regions of carbonaceous aerosols in India as well as south Asia (Nair et al., 2007; Ramanathan and Ramana, 2005; Ram and Sarin, 2011).

The number of studies conducted on carbonaceous aerosols is many in India covering urban (Ram and Sarin, 2011; Tiwari et al., 2013), rural (Begam et al., 2017), remote (Singla et al., 2019) as well as high altitude atmospheres (Ram et al., 2008; Sarkar et al. 2014, 2015) but very few over eastern Himalaya in India. The atmospheric carbonaceous aerosols 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 bio-diversity. Our earlier studies on gaseous and particulate carbonaceous compounds over eastern Himalaya (Sarkar et al., 2014, 2015, and 2019) have shown significant contributions from regional/long-range transport in addition to the local anthropogenic and natural (biogenic) sources. However the quantitative determination of local and long-range transport contribution through mathematical modeling involves huge uncertainties and complexities. Therefore carbonaceous aerosols in absence of local anthropogenic sources could help us understanding the impact of both local and transported sources.

The Coronavirus disease 2019 (COVID 19) emerged in China in late 2019, unfolded as a global outbreak and World Health Organization (WHO) declared it as pandemic. The Govt of India called a complete lockdown in the entire country from March 25, 2020 that ran till May 31, 2020. However this lockdown period has given us a unique opportunity to understand the relative changes in carbonaceous aerosols with and without (or very low) anthropogenic emissions.

The present study has been conducted on carbonaceous aerosols (OC and EC) over a high altitude station, Darjeeling (27.01° N, 88.15° E, 2200 m asl) at eastern Himalaya, India. Measurements were conducted during the lockdown period (April 2020) and compared with the normal period (April 2019). The study is focused on the investigation of the relative changes in the atmospheric loading of carbonaceous aerosols with (normal period) and without anthropogenic emissions (lockdown period). The dataset generated from the study would help us better understand the role of natural emissions on carbonaceous aerosols and fine tune the existing regional climate model.

2. Study area, sampling schedule and synoptic meteorology

The study was carried out over Darjeeling (27.1° N and 88.15° E, 2000 m asl) situated in Eastern Himalaya. Fig. 1 shows the geographical position of the study area and the sampling location. Darjeeling is situated ~ 70 km from the nearest point of Indo Gangetic Plain (IGP) and ~20 km from the Nepal border. The apex region of Darjeeling is encircled by the Indo–Nepal border with an elevation of roughly 3800 m asl while the southern part is mostly covered with marshy low lying area with an average altitude of 200–300 m asl. The Hill area of Darjeeling is located within the lesser and Sub Himalayan belts of the Eastern Himalaya. The area is bounded by the Sikkim Himalaya in the north, the Bhutan Himalaya in the east and Nepal Himalaya in the west.

The southern foothill is separated by a highly dissipated platform of terrace deposits extending along the east west. 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.

The nearest road with significant vehicular activity is about 200 m away from the study site. Several major and minor tea gardens are situated within the ~10 km radius of the town. The township is 32 km away from another important commercial hub Kurseong (26.88° N, 88.27° E, and 1482 m asl) and 64 km away from a foothill city called Siliguri (26.72° N, 88.39° E and 122 m asl). The sampling site is located at an elevation of 200 m from the main town and covered with dense vegetation. The vegetation or biosphere cover is mainly consisting of typical high altitude Himalayan coniferous forest of the type Japanese cedar (Cryptomeria japonica). Briefly, Darjeeling represents a typical Himalayan urban atmosphere. More details about the study site can be found in our earlier papers (Sarkar et al., 2019; Roy et al., 2019).

Aerosol sampling was conducted at the rooftop of Bose Institute building at a height of ~15 m from the ground where all the samplers are co-located. Government of India called a complete lockdown in the country from March 25, 2020, ran through April and ended on May 31, 2020. During the lockdown period all the activities related to governmental and private sectors were shutdown. However some emergency services were open. Over Darjeeling, no anthropogenic activities were observed during this lockdown period. However some heavy duty vehicles were allowed only during nights for carrying essential commodities for people suffering from lockdown. Such night-time plying of heavy duty vehicles in Darjeeling are not usually seen under normal periods. However, domestic cooking could be considered as the only anthropogenic sources during the lockdown period. We made observations of carbonaceous aerosols (OC and EC) and other parameters during April 2020 and therefore this month is referred to as lockdown period.

We have compared the data with April 2019 (normal period) when all the anthropogenic activities and sources were present. The total numbers of sampling days during normal and lockdown periods were 20 and 17 respectively.

Darjeeling falls in the humid subtropical climate zone in India. The
diurnal variations of the micro-meteorological parameters during normal and lockdown periods are shown in Fig. 2. The mean temperatures were almost equal during normal (12.5 ± 1.2 °C) and lockdown period (11.8 ± 1.2 °C) with the maximum recorded during 1300–1400 h. The mean wind speeds were found to be exactly equal (≈0.3 ms⁻¹) during both the periods with the strongest in afternoon. The nights in both the periods were highly humid (>90%), however the day-time humidity were >80% too. The solar radiative fluxes reached 500 Wm⁻² in the afternoon during both the periods. We performed two-tailed t-test with the meteorological parameters individually for normal and lockdown periods. The meteorological parameters did not show any significant differences (p > 0.05). Therefore the meteorological impact on the aerosol loading in the atmosphere could be normalized for two different periods.

3. Methods

3.1. Measurement of OC and EC

Organic and Elemental Carbon were analyzed using a semi-continuous OC-EC Carbon Aerosol Analyzer (Sunset Laboratory Inc, USA, model 4) based on NIOSH 5040 method (Bauer et al., 2009). Measurements were carried out at 30-min cycles collecting air samples through a PM₁₀.₅ cycle inlet. Previously mounted quartz filter paper punches containing the samples undergoes a step by step temperature ramp increase up to 850 °C in the oven filled with Helium. Then the furnace is cooled down to 550 °C and heated up again to 870 °C with O₂/He mixture. The carbon fragments are desorbed in a MnO₂ oven and reduced to CO₂ gas which is then detected by NDIR spectroscopy. The split between EC and OC fractions are determined by monitoring the loaded filters continuously using a laser light transmission at 660 nm. Any charring of OC results to the increase in the initially recorded laser absorbance. During the switching of He to He/O₂ environment, all EC is oxidized and the absorbance is reduced to background level. After reviewing the overlay at the second phase oxidation ramp when the absorbance equals to the initial absorbance is called split. Prior to the split point, any EC detected and charred is then subtracted from the calculated EC area. The laser light being transmitted through the quartz filter also provides the optical EC measurements as a function of absorbance in the sp² bonds of graphitic carbon (Brown et al., 2019). Here we have used the mean value of thermally and optically measured EC and OC for better precision of results. The OC/EC analyzer was calibrated using known amount of methane gas introduced into the oven and measuring its response. Standardization was performed using standard sucrose solution. The details of calibration/standardization are given in the supplementary information.

3.2. Measurement of ozone

Continuous monitoring of ozone gas was done with the Thermo Environmental Model 49i UV absorption instrument which had been calibrated in regular intervals. The instrument operates on the principle that ozone absorbs UV light at a wavelength of 254 nm. While ambient air is sampled by one of the cells an ozone scrubber is used to remove O₃ from the air sample going to the other cell. The degree to which the UV light is absorbed in both cells is directly related to the ozone concentration as described by the Beer-Lambert Law. The precision of the measurement is ±1 ppb.

3.3. Measurement of NO and NO₂ (NOx)

The continuous measurement of NO–NO₂-NOx was done by a NOx analyzer manufactured by Thermo Fisher Scientific (Model 42i) based on the Chemiluminescence method. Nitric oxide (NO) and ozone (O₃) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. The ambient air is drawn into the Model 42i through a bulkhead, and flows through a capillary, followed by the mode solenoid valve. The solenoid valve routes the sample either straight to the reaction chamber (NO mode) or through the NO₂-to NO converter and then to the reaction chamber (NO₂ mode). A flow sensor to the reaction chamber measures the sample flow. Dry air enters in the dry air bulkhead, passes through a flow switch, and then through a silent discharge ozonator. The ozonator produces the ozone needed for the chemiluminescent reaction. At the reaction chamber, the ozone reacts with the NO in the sample to produce excited NO₂ molecules. A photomultiplier tube (PMT) detects the luminescence generated during this reaction. The NO and NOx concentrations calculated in the NO and NOx modes and the difference between the concentrations is used to calculate the NO₂ concentration. The precision of the measurement is ±0.4 ppb.

3.4. Measurement of CO

The continuous measurement of CO was done by a CO analyzer manufactured by Thermo Fisher Scientific (Model 48i) based on the absorbance of infra-red radiation by CO at a wavelength of 4.6 μm. An
Internally stored calibration curve is used to transform the basic nonlinear analyzer signal to a linear output up to a concentration range of 10000 ppm and above. The sample bulkhead is used to draw the sample which is then allowed to flow through an optical bench. An infrared radiation is then chopped and passed through a gas filter which alternates between CO and N\textsubscript{2}. The radiation is then passed through an interference filter with a narrow band pass and gets absorbed by the sample gas as it enters the optical bench. It falls on an infrared detector as it gets out of the optical bench. A measurement beam is produced by the N\textsubscript{2} side of the filter wheel which is transparent to the infrared radiation. CO absorbs the measurement beam in the cell. The two gas filters modulate the chopped detector signal with amplitude related to the cell CO concentration. The detection limit is 0.04 ppm and the precision of measurement is ±0.1 ppm.

3.5. Measurement of meteorological parameters

Monitoring of different meteorological parameters (with the Interval of 1 min) using an automated weather station was done throughout the entire sampling period. The weather station was co-located with the aerosol monitoring instruments. Monitoring of the meteorological parameters was done using different sensors like temperature and relative humidity (Model No. HMP45C-L, Campbell Scientific, USA) wind speed (Anemometer: Model No. 05103, Young) and total incoming solar radiation (Pyranometer: Model No. SP Lite2, Kipp and Zonen).

3.6. Concentration weighted trajectory (CWT) analysis

The significant potent source regions of Black Carbon aerosols over Darjeeling were investigated by using the Concentration Weighted Trajectory (CWT) model (Wang et al., 2014). CWT is a method where species concentration at the receptor site is assigned to the corresponding air mass back trajectory. In this study, 5-day air-mass back trajectories, culminating at 500m agl (model derived height) over the sampling location had been taken for all the sampling days using the HYSPLIT-4 model developed by NOAA, USA (Draxler et al., 2016). Then, the expected source regions were divided into an array of \( i \) by \( j \) grid cells and the Concentration Weighted Trajectory for the \( ij \)th grid cell was calculated as follows:

\[
C_{ij} = \frac{1}{\sum_{l=1}^{M} \sum_{l'=1}^{M} C_l \tau_{ijl}}
\]

Where, \( C_{ij} \) is the average weighted concentration in the \( ij \)th grid cell, \( C_l \) is the species concentration at the receptor site on arrival of trajectory \( l \), \( M \) is the total number of trajectories, and \( \tau_{ijl} \) is the total number of trajectory endpoints in the \( ij \)th grid cell associated with the \( C_l \) sample. In order to eliminate the grid cells containing few trajectory endpoints, the CWT method also employs an arbitrary weight function. The CWT values are presented with a color scale over the domain, where red color signifies high potent source region while blue color represents low potent source region.

3.7. Active fire data

We have used MODIS collection 6 data (a combined product from Terra and Aqua, MCD14ML from Fire Information for Resource Management System, FIRMS) in order to obtain the active fire spots over India during the sampling periods. MODIS Collection 6 provides best available active fire products with high efficiency of detecting small fires, improved cloud masking and expanded sunlight rejection. Data with confidence level ≥80% were taken and plotted using open source GIS software MeteoInfo. More information can be found in MODIS Collection 6 Active Fire Product User’s Guide Revision B.

3.8. Uncertainties of the measurement

Multiple instruments have been used in the study and therefore the gross error associated with the entire methodology is difficult to estimate. The uncertainties associated with each instrument have been reduced by calibration conducted on regular basis and the quality control of the data. Standard three-sigma elimination of data outliers has implied. The precision for NOx analyzer (±0.4 ppb), ozone analyzer (±1 ppb) and EC-OC analyzer (<±6%) have been calculated and the precision values are lower compared to the calculated errors in the dataset. The calibration of the instruments was done once in a fortnight.
4. Results and discussion

4.1. Total and differential carbonaceous aerosols during normal and lockdown period

The OC, EC, total carbonaceous aerosol (TCA), OC/EC ratio and the SOC during the normal and lockdown events have been shown in Fig. 3. TCA was calculated by the sum of EC and the organic matter (OM) where OM was calculated multiplying OC by 1.6 (for urban atmosphere) (Cao et al., 2003; Rengarajan et al., 2007). Though the anthropogenic activities during the lockdown event were very low, the differential and the total carbonaceous aerosols were higher than the normal event. The average OC and TCA concentrations during the lockdown event (OC: 4.8–22.4 μg m⁻³; TCA: 8.6–41 μg m⁻³) was ~70% higher than the normal event (OC: 3.8–12.1 μg m⁻³; TCA: 7.4–22.2 μg m⁻³). However, EC shows slightly higher loading in lockdown event (0.9–4.9 μg m⁻³ in lockdown and 0.9–3.7 μg m⁻³ in normal event). During the normal event, the OC/EC ratio ranged from 2.8 to 7.5 with an average of 4.2 ± 1.1 whereas it ranged from 3.6 to 7.2 with an average of 5.7 ± 0.9. The OC/EC ratio is often used to characterize and separate out the emission sources. Normally, higher ratio indicates the dominance of biomass burning emissions whereas the lower ratio indicates the dominance of fossil fuel emissions (Ram et al., 2008; Saarikoski et al., 2008). The ratios of 0.7 and 1.1 were reported for the dominance of fossil fuel mainly the vehicular emissions whereas the ratios of 6.6–9.0 were reported for wood/biomass burning (Saarikoski et al., 2008; Watson et al., 2001; Sandradewi et al., 2008). Watson et al. (2001) also reported the ratio value of 2.7 for the coal combustion. The ratio also differentiates between the primary and secondary sources of carbonaceous aerosols. Higher ratio value (>2.0) indicates the formation of secondary organic aerosols (Pani et al., 2017). The mean ratio value (>2.0) observed in the present study strongly indicates the formation of SOC. The photochemical oxidation of several volatile organic compounds under high solar radiative flux and temperature in the month of April could also enhance the SOC. Earlier we reported higher photo-decomposition of VOCs and carbonyl compounds to form SOC during the entire premonsoon season (March–May) over Darjeeling (Sarkar et al., 2014).

However, the high tourist related activities mainly the vehicular emissions were the major local anthropogenic source both for OC and EC during the normal event. SOC is calculated using EC-tracer method followed by Castro et al. (1999) where minimum ratio of OC to EC is applied. Since EC is directly emitted as a product of organic matter combustion, it is used as a tracer for primary OC (POC) co-emitted from these sources. Briefly, total OC can be defined as the sum of primary and secondary organic carbon.

\[
\text{SOC} = \text{OC}_{\text{total}} - \cdot \text{POC}
\]

\[
\text{POC} = \text{EC} \times \left(\text{OC}/\text{EC}\right)_{\text{pr}}
\]

\(\text{OC}/\text{EC}_{\text{pr}}\) is the estimated primary carbon ratio, the lowest OC to EC ratio observed in the entire dataset. They were 1.62 for the normal period and 2.02 for the lockdown period.

The SOC ranged between 2.6 and 13.3 μg m⁻³ with an average of 7.6 ± 3.5 μg m⁻³ during the lockdown which is exactly double of that in normal event (3.8 ± 1.4 μg m⁻³) ranging between 1.7 and 7.5 μg m⁻³. The higher OC/EC ratio as well as SOC concentrations during the lockdown event has been explained while discussing the diurnal features and identification of source regions through CWT analysis.

4.2. Diurnal variations of carbonaceous aerosols

The diurnal variations of OC, EC and SOC during the normal and lockdown period are shown in Fig. 4.

4.2.1. Organic carbon

During the normal event, OC shows prominent peaks at 1100 h and 1900 h with ~10 μg m⁻³. These morning and evening peaks are well expected and could be associated with the rush-hour anthropogenic activities. After the morning peak, OC shows gradual decrease followed by almost constant values (7.3–7.7 μg m⁻³) during the entire afternoon and till the evening peak. During afternoon, the higher temperature and solar insolation could favor the radiative heating of the mountain surface that in turn favors the transport of OC from the plain land foothill regions driven by the up-slope thermal valley wind. This valley wind transport could compensate the fall in aerosols concentration due to the subdued anthropogenic activities during afternoon. Valley wind transport of aerosols has also been reported by our earlier study (Sarkar et al., 2015) over Darjeeling. The afternoon OC concentrations were ~70% higher than the night-time concentrations. After the evening peak the concentrations were found to gradually fall till the late night and remained almost constant (~5 μg m⁻³) till the early morning. After the sunrise (~0600 h), OC concentrations were sharply built-up from early morning which could be due to the fumigation effect bringing aerosols from the nocturnal residual layer after breaking the night-time inversion layer (Stull, 1989).

During the lockdown period, OC shows no prominent diurnal variation. However a gradual increase in OC was observed from night till late morning (from ~8 to ~10 μg m⁻³) followed by sharp rise and a broad peak during afternoon when OC remained almost constant at ~16 μg m⁻³. The higher OC during afternoon could not be associated with the up-slope valley wind transport as anthropogenic emissions over the low and plain land regions were also absent (or very low) during lockdown. Rather, photochemical production of secondary organic carbon under higher temperature and intense radiation during afternoon could enhance the OC concentration. This has been explained in detail in the following section. However, OC falls sharply from the evening till late night. The most interesting observation is that OC during lockdown shows higher values during all the hours of the day than the normal period.

4.2.2. Elemental carbon

The diurnal feature of EC was found to be similar to that of OC during
normal period with prominent morning and evening peaks. However the morning peak was found to be broader in nature during 0900–1100 h (~3 μg m⁻³). OC during 0900–1000 h shows almost equal loading, ~8.5 μg m⁻³ and then peaked up at 1100 h to ~10 μg m⁻³. The morning rush hour activities as well as tourist activities were predominant during the period of 0900–1100 h. In addition, the increase in temperature and solar radiative flux could also enhance OC loading through secondary formation. These two factors, anthropogenic primary emissions as well as secondary formation could be prominent at 1100 h showing sharp peak for OC but not for EC as the later could be due only to anthropogenic primary emissions. The afternoon EC was almost constant (~2.5 μg m⁻³) and higher than the night-time values (1–1.5 μg m⁻³). The afternoon EC could also be associated with the up-slope valley wind transport and the sharp rise in EC from early morning till the morning peak could be associated with the fumigation effect as observed in case of OC. On the other hand, during the lockdown period, EC shows a unimodal hourly distribution with the peak at 0700 h (~3 μg m⁻³). EC shows gradual build-up from night till the morning peak followed by a gradual decrease till night. During lockdown, EC shows higher concentrations at night (till early morning) and lower concentrations during rest of the time of the day compared to normal period. The anthropogenic activities and hence EC emissions during the entire night in normal period could be ignored. On the other hand, heavy duty vehicles carrying the necessary commodities (for the people in Darjeeling district suffering from lockdown) were allowed only during night. This additional night-time EC sources during lockdown could enhance the night-time EC concentrations (Lockdown: 2.3 μg m⁻³, Normal: 1.5 μg m⁻³). Moreover, EC particles emitted into the atmosphere at night over the plain land foothill regions could also get uplifted to the higher altitudes due to the breaking of nocturnal residual layer after the sunrise enhancing early morning concentrations. However during rest of the hours of the day (morning till night) in lockdown period, EC was much less than the normal period.

4.2.2.3. Secondary organic carbon

The diurnal features of SOC during normal and lockdown period were different and similar to the respective diurnal features of OC. During normal period, SOC showed little variation during night and morning and peaks at 1100 h (5.7 μg m⁻³) and 1900 h (5.5 μg m⁻³). During afternoon (1300–1700 h), SOC showed little variation (3.2–4.2 μg m⁻³) till the evening peak. The fall in SOC during afternoon could be due to the subdued anthropogenic activities; however, the transport of VOCs through valley winds and their subsequent oxidation could be the reason for significant SOC loading during afternoon. During lockdown, little variation of SOC was observed during night (~4.6–6.0 μg m⁻³), sharp rise from morning till afternoon with the peak during 1400–1500 h (~12 μg m⁻³) and sharp fall till late evening. The high SOC during afternoon could be well associated with the photochemical oxidation of VOCs under higher temperature and intense solar radiation. However the significant loading of SOC during night-time in both the periods could be associated with the aqueous phase oxidation and production of secondary aerosols under high relative humidity (RH) conditions (>80%). Saffari et al. (2016) reported that under high liquid water content, the dissolution of the hydrophilic primary carbonaceous compounds in the aqueous phase is facilitated by RH of >70% in an urban atmosphere in USA. The very high night-time RH (>90%) over Darjeeling could support the above fact. Because of high tourist influx in the month of April, the biomass burning in relatively colder nights and the domestic heating in the resorts, hotels etc as well as emissions from the cooking in the restaurants could also be the additional factors for the night-time loading of SOC during the normal period. But the higher night-time SOC during lockdown is difficult to explain. The night-time emissions of primary OC (from heavy duty vehicles) could also undergo aqueous phase oxidation under very high rather near-saturation conditions to form SOC. However the exceptionally high SOC during afternoon in lockdown period could be explained as follows.

4.2.3. Influence of biogenic VOCs. The VOCs over Darjeeling could be consisting of anthropogenic (AVOC) and biogenic VOC (BVOC). During the lockdown period, the anthropogenic VOC emissions could be considered as very low as no sources were present other than the domestic cooking. However, biogenic VOCs (BVOCs) could play a major role. The high altitude Himalayan coniferous biosphere cover surrounding the study site could be a major source of such BVOCs. Coniferous forest is a good emitter of monoterpenes (Wiedinmyer et al., 2006; Chen et al., 2018). April is the month for vigorous coniferous forest growth over eastern Himalaya under relatively higher temperature and intense solar radiation. Our earlier study (Chatterjee et al., 2018) has
shown very high evapo-transpiration and emissions of H₂O vapor from the coniferous forest near the present sampling site in the month of April. Such high evapo-transpiration could also facilitate the emissions of several BVOCs into the atmosphere. The BVOCs easily get photo-oxidized catalyzed by O₂ to form SOC (Haque et al., 2016; Alves and Pio, 2005). We observed higher O₃ during the lockdown period (∼44 ppb) compared to the normal period (∼31 ppb). The diurnal variations of O₃, NO and NO₂ during normal and lockdown periods have been shown in Fig. 5a, b and c respectively. It shows that the daytime O₃ concentrations were ∼50 ppb and crossed 50 ppb at 1400 h during lockdown while it was ∼30–35 ppb during the normal period. Now the question is why the O₃ concentrations during lockdown were higher than normal period? The formation of tropospheric O₃ is controlled by VOCs and NOX. Under low NOX conditions, O₃ formation gets promoted and VOCs have little control on it. Under low VOC conditions, NOX (NO) helps in depleting O₃ through the following reactions (Finlayson-Pitts and Pitts, 1999):

\[
\text{NO}_2 + \text{hv} (<420 \text{ nm}) = \text{NO} + \text{O}_2 (^1\text{P})
\]

\[
\text{O}_2 (^1\text{P}) + \text{O}_2 = \text{O}_3
\]

\[
\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2
\]

Therefore NO₂ is the major precursor for O₃ and when NO₂ is low, NO becomes low too, leading to less depletion or higher accumulation of O₃ in the atmosphere. Again, NOX can also scavenge atmospheric OH radical through OH + NO₂ = HONO₂ reaction. Therefore when NOX is low, the availability of OH radicals increases and they react with VOCs to form O₃. During the normal period, VOCs (anthropogenic + biogenic) could be expected to be higher because of normal anthropogenic activities. The diurnal variations of NO and NO₂ during normal period show clear morning and evening peaks in normal period. The daytime concentrations of NO and NO₂ during normal period were 4.9 ± 0.6 ppb and 9.2 ± 0.8 ppb respectively. The high NO₂ and VOCs could produce O₃ under higher solar insolation but the high NO could also deplete O₃ significantly during this normal period. During lockdown, the anthropogenic VOCs (AVOCs) could be expected to be limited. The night-time emissions of anthropogenic VOCs from heavy-duty diesel vehicles could be transported to the plain land regions through the night-time down-slope mountain winds. But the emissions of anthropogenic VOCs from the domestic cooking and heating could not be ruled out during lockdown. Considering CO as the marker of anthropogenic emissions, we made correlation analysis between SOC and CO (taking hourly data) and shown in Fig. 6a and b. We observed very poor correlation during lockdown \((R^2 = 0.02)\) and strong correlation during normal period \((R^2 = 0.65)\). This suggests very little contribution of anthropogenic activities to the formation of SOC during lockdown whereas the anthropogenic activities dominated during normal period. However BVOCs could be considered to be same as in normal period. NO and NO₂ showed no prominent diurnal variations and with very low daytime concentrations \((\text{NO}: 0.8 \pm 0.15 \text{ ppb}; \text{NO}_2: 3.9 \pm 0.4 \text{ ppb})\) compared to the normal period. NO during lockdown was remarkably (∼6 times) lower than the normal period. Under this low NOX conditions, the O₃ formed (BVOCs + low NO₂ + intense solar radiation) could get accumulated more than the normal period because the O₃ depletions species NO was also low. Such high O₃ (and hence OH radicals) could promote the photo-oxidation of BVOCs to form SOC. Globally, most of the SOC formation is due to the ozone induced oxidation of monoterpenes like α-pinene, β-pinene and limonene (Watne et al., 2017). Recently Wu et al. (2020) have shown that 70% of SOC is formed from the BVOCs in China.

We have made linear regression analysis between SOC and O₃ concentrations (taking hourly data) during normal and lockdown events and shown in Fig. 6c and d. It was observed that during the normal events, the regression was very poor \((R^2 = 0.003)\) whereas that in lockdown events was very strong \((R^2 = 0.7)\). The slope during the lockdown event was also higher (0.41) than the normal event (0.014). This indicates that when the biogenic emissions dominate, the little increase in O₃ could enhance SOC to a larger extent compared to when anthropogenic emissions dominate. Therefore O₃ and the biogenic VOCs play a major role in governing the formation of the secondary organic compounds over eastern Himalaya under limited anthropogenic activities. The possible SOC formation mechanisms during the normal and lockdown period are shown as a schematic diagram (Fig. 7). 4.3. Identification of source regions through CWT analysis

The CWT analyses for EC, OC and SOC have been shown in Fig. 8 for the normal and lockdown events. The black dots on the map represent the active fire spots retrieved from MODIS related to open burning/forest fire. During the normal event, the air mass trajectories were found
to be originated and arrived mainly from Nepal, Bhutan and three north-eastern states of India; Sikkim, western parts of Assam and Meghalaya. Few trajectories were also observed arriving from some parts of central and eastern IGP as well as regional transport (north-eastern parts of West Bengal). The regions associated with the maximum concentrations (hotspots) of EC, OC and SOC were regional, Assam, parts of Meghalaya and central parts of Nepal.

The fire spots in these north-eastern states are due to the forest fire, the air masses arrived from. According to Forest Survey of India (FSI), the total number of forest fire spots over the entire north-east India was 10210 during November 2018–June 2019. These are attributed to the slash-and-burn cultivation or commonly called Jhum Cultivation. The hotspots in Nepal could be attributed to the high pollution episode in the month of April for local New Year celebration commonly called Bisket Jatra. Islam et al. (2019) reported 3–4 times increase in fine mode aerosols, OC, EC as well as VOCs over Nepal because of the pollution episode in this festive occasion. Our earlier study showed IGP and Nepal to be the major source regions for BC (Sarkar et al., 2019) during pre-monsoon. Therefore biomass burning over north-east India and the urban anthropogenic activities over Nepal could well contribute to the carbonaceous aerosols over eastern Himalaya. During lockdown, higher OC and EC were associated with the regional/local sources and Sikkim followed by the contribution from central parts of IGP. Few air masses originating and passing over fire spots over Madhya Pradesh (central India) associated with the deciduous forest fire. No air masses were observed from Nepal and the north-east Indian states with forest fire. For SOC, the hotspots were the regional or local sources for higher values (>4.0). The contribution from local/regional sources for higher SOC further strengthens and supports the biogenic sources (Himalayan coniferous forest cover) of secondary organic compounds as discussed earlier. However this is surprising to see the significant numbers of fire spots at IGP, central India and the north-eastern states even in the lockdown period.

5. Implication of the study

The high loading of secondary organic carbon in absence of anthropogenic emissions (but from the biogenic sources) demands an in-detailed study on the water soluble organic compounds in the high altitude atmosphere of eastern Himalaya. These secondary organic aerosols could have the potential serving as cloud condensation nuclei and therefore modify the microphysical characteristics of the clouds, especially the low-level clouds. This in turn could affect the cloud lifetime and cloud albedo and hence the cloud radiative forcing. Therefore the role of biogenic sources could be taken in to account with utmost importance while working with cloud/atmospheric radiative or regional climate model. The major and the most important finding of the study was that when NOx is limited, O3 becomes high and this in turn enhances the SOC where biogenic VOC emissions are significant. Therefore, control of vehicular emissions (major source of NOx) in turn increases the organic carbonaceous aerosols to a large extent over eastern Himalaya and this should bring the attention of the policy makers.

6. Summary and conclusion

The present study was an attempt to investigate the relative changes of carbonaceous aerosols over a high altitude urban atmosphere in eastern Himalaya in the presence (April 2019) and absence (April 2020 during lockdown due to COVID 19 outbreak) of the anthropogenic
emissions. The major findings and the outcome of the study are summarized below:

The major source of NO/NO₂, the vehicular emissions, was absent or very much limited during the lockdown period. The daytime NO concentration was remarkably lower than the normal period with anthropogenic influences. Such sharp fall in NO in turn enhanced the O₃ concentrations that promoted the photochemical oxidation of BVOCs emitted from the Himalayan coniferous forest cover producing high amount of SOC. Such high amount of SOC increased organic carbonaceous aerosols (hence total carbonaceous aerosols) by ~70% compared to the normal period. It was observed that with the same amount of increase in O₃, SOC formation was ~40 times higher during the lockdown period in the absence of anthropogenic emissions. While the anthropogenic activities over Nepal and the forest fire at the north-east Indian states were the major long-distance source regions for carbonaceous aerosols during the normal period, the regional and local sources, mostly the biogenic emissions from coniferous forest covers dominated during the lockdown period as revealed from concentration weighted trajectory analysis.

The study indicates the immense importance and the vital role of the Himalayan coniferous forest cover as the source of biogenic aerosols that play important role as good as anthropogenic sources. The dataset generated from the study would help us quantify the biogenic contributions to the carbonaceous aerosols and develop or modify the existing regional climate model.

CRedit authorship contribution statement

Abhijit Chatterjee: Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Supervision. Sauryadeep Mukherjee: Formal analysis, Methodology. Monami Dutta: Formal analysis, Figures. Abhinandan Ghosh: Formal analysis, Figures. Sanjay K. Ghosh: Formal analysis, Writing - review & editing. Arindam Roy: Formal analysis, Writing - review & editing, Figures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.atmosenv.2020.117947.

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Fig. 8. Concentration weighted trajectory (CWT) analysis of EC, OC and SOC during normal (upper panel) and lockdown (lower panel) period.
