Carbonaceous aerosols in Indian Himalayan atmosphere: seasonal abundance, altitudinal variation and source analysis

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Abstract

The present study reports carbonaceous aerosol concentrations determined in total suspended particles (TSP) from three mountainous sites viz. Devasthal Peak, Manora Peak and Bhimtal and one low-land Tarai urban site at Pantnagar in Kumaon region of Uttarakhand, western Himalaya. The concentrations of organic carbon (OC) and elemental carbon (EC) were estimated following IMPROVE_thermal optical reflectance protocol. Results showed that TSP and OC/EC concentrations varied significantly and decreased with increasing altitudes in two seasons. Seasonal/(diurnal) analysis indicated TSP and OC/EC concentrations at mountainous sites exhibited higher values in summer/(day-time), respectively while tarai site had higher values in winter/(night-time). Higher summer/(day-time) values at mountainous sites could be associated with local emissions along with vertical movement of atmospheric boundary layer resulting uplift of air pollutants due to convective motions generated in valley region. OC and EC were noted to be strongly correlated (correlation coefficient > 0.8) indicated similar emissions source and atmospheric processes. The ratios of OC/EC were observed in the range of 2.4 to 9.3, 2.1 to 8.6, 1.9 to 4.3 and 1.8 to 3.2 for Devasthal, Manora peak, Bhimtal and Pantnagar, respectively, suggested mixed sources of biomass burning, coal combustion and vehicular emissions. The large variations in OC/EC ratios at studied sites suggested presence of secondary organic carbon (SOC). Mountainous sites experienced higher % SOC contributions (41 – 45%) to total OC in winter than low-land tarai urban site could be due favourable conditions for condensation of photo-oxidation products of organic species and biogenic VOCs emissions.

Introduction

Carbonaceous aerosols (CA) are ubiquitous in nature, constitute significant fractions of atmospheric particulates and account for approximately 20–50% of particle mass concentration [1]. It comprises thousands of species which have wide range of thermal, physico-chemical and optical characteristics [2]. They play key roles in atmospheric chemistry [3], visibility reduction [4] health hazards [5, 6], ecosystem processes [7] and global climatic effects [8]. The absorption/scattering phenomenon of CA influences the radiative balance and energy budget of the atmosphere [2].

Huge amounts of CA are released into the atmosphere during biomass burning, for example, forest fires, agricultural residues burning and bio-fuel combustion) [9]. Besides this, industrial sector, power generation, residential and transportation activities are important contributors for emissions of CA [10]. The particle size, concentrations and chemical composition of atmosphere decide the impacts of CA on the environment. The scientific understanding of CA is the key for better interpretation of links between the aerosols, climate and environment.

CA is majorly categorized into two components as organic carbon (OC) and elemental carbon (EC), with respect to their chemical properties and play important role in atmospheric behaviour [11, 12]. OC consists of diverse range of organic species (hydrocarbons, oxygenated, acids etc.) originating from primary sources as anthropogenic combustion while secondary formation process occurs via

atmospheric chemical reactions [13, 14]. The chemical reactions of volatile organic compounds (VOCs) with either hydroxyl (OH) radicals and ozone (O_3) or nitrate (NO_3) radicals, decides the OC formation [15]. OC has wide range of differential physico-chemical properties such as molecular weights, oxidation levels and gas to particle partitioning [16]. It changes the radiative budget by light absorption/scattering effects and acts as cloud condensation nuclei [10, 17]. OC may also have detrimental effects (carcinogens and mutagens) on human health due to presence of toxic substances [3].

Elemental Carbon (EC), also known as black carbon, is mainly derived from incomplete combustion of fossil fuel and biomass burning [18] as well as from the vapor phase as a condensation product. It is a mixture of graphite like particles to larger soot and chars [19]. The increased catalytic properties due to occurrence of various adsorption sites on EC surface, it influences the important chemical reactions of sulfur dioxide (SO_2), nitrogen oxides (NOx), ozone (O_3) and other gaseous compounds in the atmosphere [5, 20]. EC has warming characteristics on climate and ranks second after CO_2 as an important component of global warming in terms of direct forcing [10, 21]. It is considered as the main triggers for the reduction in atmospheric visibility [22].

The carbonaceous characterization of aerosols has been already underlined by many research works, most of which have been performed in urban [23, 24], rural [25, 26], industrial [27, 28], agricultural [29] and coastal [30, 31] regions across the world. Despite significant environmental impact of carbonaceous particles, information on their concentration in different environments over the globe, their spatial and temporal variability and on their sources is still limited, particularly in the high altitude regions. Moreover, due to rapid urbanization, transportation and tourism activities the levels of CA in the regions of higher altitudes may be consistently rising. The amounts and composition of atmospheric particles may vary largely at different altitudes of mountainous region depending upon the emission sources and meteorological conditions. Very few researches are available at the higher altitudes concerning the carbonaceous aerosols across the world [32–35]. The study concerning seasonal variations and source attributions of carbonaceous aerosols in Indian Himalayas is particularly very sparse [36–39].

It is thus imperative to examine the sources and load of carbonaceous materials in particulate matters at remote and urbanized locations of mountainous region during different seasons and compare it with the low land (*Tarai*) region. This is precisely what has been focussed in the present study. In this study we examine variations of carbonaceous particles (OC and EC) of TSP in ambient atmosphere at four sampling sites, Devasthal (DS), Manora Peak (MP), Bhimtal (BT) and Pantnagar (PN) during two seasons in Kumaon region, located at different altitudes in the western Himalayas. The main objectives of present study are: (a) to highlight seasonal and day-/night-time variations of TSP and OC/EC concentrations at varying altitudes and tarai regions of western Himalayas; (b) investigation of meteorological dependence of TSP and OC/EC concentrations; (c) source characterization and (d) estimation of primary OC and secondary OC using EC tracer method.

Materials And Methods

Study area

Total suspended particulates (TSP) sampling campaign was conducted at four sampling locations [Devasthal Peak (DS), Manora Peak (MP), Bhimtal (BT) and Pantnagar (PN)] in the Kumaon region of Uttarakhand, western Himalaya. The geographical locations of the sampling sites are shown in **Fig. 1.** The sampling site, DS mountain peak (~60 km away from Nainital city) is geographically located at 29.36 °N 79.68 °E and at an altitude of 2450 m asl of Shivalik ranges, central Himalayas. It is a remote area, inhabited by only a few villages in the radius of 3 - 5 km, far away from any urban settlements while connected via state roads to major places of the region [40]. It is managed by an astronomical institute, Aryabhatta Research Institute of Observational Sciences (ARIES), Nainital.

MP (29.35 °N 79.45 °E; 1940 m asl), sampling site is located in central Himalayas surrounded by sharply peaking mountains on three sides and open to valley below the mountain peaks. It is ~ 3km away from Nainital city and having population of about 0.9 million. It is considered as free tropospheric site due to higher elevation. There is no major pollution source nearby, while some small scale industries are present in the valley towns (Haldwani and Rudrapur, more than 30 km far away downhill at an altitude of < 500 m from asl). Third site, BT (29.35 °N 79.53 °E) is small town/hill station situated at an altitude of 1413 m asl in the Nainital district of lower Himalayan region. It has recently faced with increase in construction activities, deforestation and pollution levels due to anthropogenic activities especially from tourism in the last two decades. The climate of BT is pleasant where monthly temperatures varied in the range of 15 °C to 29 °C and 4 °C to 18 °C during summer and winter seasons, respectively.

PN (29.01 °N 79.47 °E; 224 m asl) lies in the "*Tarai*" belt, low-land region of Himalayan Shivalik range. The study was performed in G. B. Pant University of Agriculture and Technology, Pantnagar, approximately 16 km far from Rudrapur city where medium to large scale industries of automobiles, textiles and sugar mills are present. The climate of PN is characterized by sub-tropical and sub-humid with maximum temperature reached up to 42ºC during summer and minimum temperature lied between 1- 4ºC during winter.

Sampling

Intensive TSP sampling campaign was carried out at four sampling sites using High Volume Air Sampler (Envirotech APM 430, India) operated at a flow rate of 1.1 ± 0.1 m^3/minute. The air samples of TSP were collected continuously for five days at each site for twelve hours intervals of day-time (07:00 to 19:00 hrs) and night-time (19:00 to 07:00 hrs) periods during two seasons (winter and summer). Twelve hours TSP samples were collected on quartz filters (PALLFLEX^{TM}; 2500 QAT-UP, size: 20.0 cm, 25.4 cm). Before sampling, quartz filters were pre-combusted at a temperature of 900 °C in a muffle furnace to remove any residual carbon or impurities. After sampling, all the samples were kept in zip lock plastic bags followed by stored in the deep freezer at -20°C until analysis. TSP mass loadings (µg) were deduced from gravimetric measurements done before and after sampling using weighing machine (AD - 50 B, ADAIR DUTT Instruments Pvt. Ltd) and corresponding concentrations (µg/m^3) were evaluated by dividing mass

loadings to sampled air volume. Flow rate and duration of sampling period were used to estimate the volume of air sampled. Quartz filters were equilibrated in desiccator for 24 hrs at constant temperature (23 - 25°C) and relative humidity (40 - 45%) for 4 -5 hrs. Field blank filters were also taken into account in order to subtract the positive artifacts due to absorption of organic chemicals on filters during and/or after sampling. The estimated sample results were corrected by the mean values of observed blank concentration. The precision of the weighing process was < 10 μg for the blank filters and < 20 μg for the filter samples. All necessary precautions were strictly considered during handling of quartz filters to avoid any possibility of contamination.

Chemical analysis

The OC and EC concentrations in TSP were determined using OC/EC carbon analyser (DRI model 2001; Atmoslytic Inc., Calabasas, CA) following IMPROVE_A thermal/optical reflectance (TOR) protocol [41,42]. A circular cut of 0.5 cm^2 from TSP sampled filter was placed on quartz tube inside the thermal desorption chamber of the analyser. The analytical procedure consists of two stages of stepwise heating. Four OC fractions were volatilized at 140°C (OC_1), 280°C (OC_2), 480°C (OC_3) and 580°C (OC_4) in non-oxidizing [He] atmosphere during first stage of heating. However, Three EC fractions were oxidised at 580°C (EC_1), 740°C (EC_2) and 840°C (EC_3) and pyrolyzed carbon fraction (OP) are released in 2% O_2 and 98% He atmosphere during the second stage of analysis. Based on IMPROVE_TOR protocol, OC is operationally defined as sum of four OC fractions plus OP and EC is defined as sum of three EC fractions minus OP [41]. The OC/EC analyser is auto-calibrated everyday using known concentrations of CH_4 before and after sample analysis. Replicate analysis was also carried out for every ten samples run where difference estimated was smaller than 5% for the total carbon (TC, OC + EC) and 10% each for OC and EC. Detection limits for OC and EC were calculated as 0.25 μg/m³ and 0.04 μg/m³, respectively. OC and EC concentrations were also estimated in blank filters and average blank concentrations have been used to get correction in the sample results.

HYSPLIT back trajectory analysis

The occurrence of any pollutant in a region is mainly decided by either surrounding local sources or could be long range transport from distant sources. At mountainous (DS, MP and BT) and tarai (PN) sites of present study, local agriculture and domestic burning along with vehicular emissions during tourism activity are known for the local sources. In order to investigate the potential origin of distant sources and their transportation pathway (air-mass back trajectories) of carbonaceous aerosols, Hybrid Single-Particle Lagrangian Integrated Trajectory or HYSPLIT model from Air Resources Lab of National Oceanic and Atmospheric Administration (NOAA) have been used. **Fig. 2 (a–d)** illustrates the five day air mass backward trajectory for two seasons at four sampling sites during observation period. It shows the air-mass flows from different parts of the Indian subcontinent to the mountainous and tarai sites at three different heights (500 m, 1000 m and 1500 m above ground level). Back trajectories showed that most of the air mass arrives from west and north–west during winter seasons. During summer, larger air mass travel from northeast/ Indo-Gangetic plain and fewer from west at Devasthal and Manora peak. In

contrast, relatively shorter trajectories at Bhimtal and Pantnagar suggested dominance of local sources along with distant transport during summer.

Results And Discussion

Variation of TSP

The 12-hour ambient distribution (mean, maximum, minimum, 25 and 75% percentiles) of TSP for four sampling sites DS, MP, BT and PN at different altitudes of Kumaon region, western Himalaya are shown in **Fig. 3(a)**. During the study period, the mass concentrations of TSP were observed in the range of 41.5 to 90.6 μg/m³, 55.4 to 115.6 μg/m³, 58.7 to 147.4 μg/m³ and 131.9 to 309.3 μg/m³ at DS, MP, BT and PN, respectively. Significant higher TSP concentration was observed at PN (low-land Tarai urban region) as compared to that at the higher altitudes of DS (remote area) and hilly towns of MP and BT.

The observed TSP showed decreasing trends with increasing altitudes during winter and summer seasons, which is on the expected lines**.** According to the results, mean TSP concentrations were noted to be higher during summer in contrast to winter at all sampling sites except PN (**Table 1**). Mean TSP increased by 38.4%, 21.4% and 21.9% for DS, MP and BT, respectively during summer as compared to winters. On the other hand PN showed a decrease by 19.6% during summer as compared to winter season. Main reason for this behaviour is the fact that PN is a normal tarai (low lying plain) region where human activities remain normal during the two seasons hence the effect of increased boundary layer during summer leads to a dilution of the TSP concentration. The other three sites DS, MP and BT are the hill stations which shows enhanced human activities due to increased tourist activities and there is not much change in the boundary layer height, leading to higher TSP concentration during summer. In addition to this, TSP concentrations at each site during both day and night-time during observation period are shown in **Fig. 3(b)**. Day-time concentrations at mountainous sampling sites, DS, MP and BT were approximately 1.4, 1.3 and 1.2 times higher than night-time while at PN, night-time concentrations were 1.2 times higher than day-time. The variation in day- and night-time TSP concentration is also explained due to the tourist activities at hill station during day and the decrease in boundary layer height during night at PN.

The synergistic effects of variations in emission rates and seasonal meteorological conditions could be associated with seasonal and day-/night-time variability of TSP. Seasonal and day-/night-time variations of TSP at higher altitudes of DS, MP and BT in mountainous region could be attributed to vertical movement of atmospheric boundary layer and long-range transport [43]. The occurrence of convective motions in the valley regions results into the uplifting of the inversion layers along with vertical transport of the pollutants [44]. In the context of PN, lower mixing height and stable condition in atmosphere restrict the dilution and vertical diffusion increased TSP levels during winter [45]. Higher particulate concentrations during summer/pre-monsoon period are also reported in high mountainous regions of Manora peak [37,43], Mount Abu [37], Kangra [38] and Kullu and Manali [36] in Indian Himalayas.

However, PN exhibited higher TSP values during winter similar to the observed results of urban areas in previous studies [5,46].

Abundance of carbonaceous species

The statistics of seasonal averaged concentrations of OC, EC, OC/EC ratio and percentage contributions of carbonaceous components at four sampling sites of Kumaon region, western Himalaya are summarized in **Table 1.** OC and EC distributions during whole observation period are presented in **Fig. 4.** The average OC concentrations during winter/(summer) are found to be 5.9/(10.6), 10.4/(14.6), 12.9/(18.7) and 35.3/(23.1) μg/m³, while average EC were 1.5/(3.0), 2.8/(4.4), 3.6/(5.4) and 15.6/(8.8) μg/m³ for DS, MP, BT and PN, respectively. Similar to TSP, the OC and EC abundance were decreasing with increasing altitudes during both seasons (**Fig. 5**). Except for the plain station PN, the slope of decrease with altitudes is more or less similar for TSP, OC and EC indication same source of origin for all the three. Also the slopes in winter and summer also remains nearly the same. Some previous studies have also shown similar results of decreasing concentrations with increasing altitudes in the mountainous region [39,47]**. Fig. 6** illustrates the day- and night-time variations of OC/EC concentrations at the four sampling sites. Day-time concentrations of OC and EC were slightly higher (~ 1.1 to 1.2 times) as compared to night-time for mountainous sites (BT, MP and DS). However, at PN, higher concentrations occurred in night-time than during day-time which is mainly associated with a lower mixing height and calm atmospheric condition. Similar higher concentrations are generally noticed during night-time (than day-time) in urban areas [48,49].

Seasonal, day-night and site differences in TSP and OC/EC concentrations were checked by one-way analysis of variance (ANOVA) using SPSS statistical software and results of the analysis are documented in **Table 2**. Significant seasonal difference ($p < 0.05$) in TSP and OC/EC concentrations were observed for four sampling sites. Along with local emissions, vertical movement of atmospheric boundary layer and long-range transport of air parcels enhanced the concentrations during summer at sampling sites of higher altitudes (DS, MP and BT). This is in agreement with the explanation suggested by [50] and [43] which states that the differences in day- and night-time temperatures result in the development of thermal structure, followed by strong convective motion in the valley uplifting the inversion layers along with the vertical transport of pollutants from the valley region.

However, PN (Tarai urban region) exhibited higher values OC/EC for winter season because of the lower mixing depth and increased local sources from heating and burning [51]. Crop residue burning near agricultural field and fires in Himalayan foothills region could be the main reasons for enhanced OC/EC concentrations in PN [52,53]. No significant difference ($p > 0.05$) was observed between day- and night-time variations of TSP and OC/EC concentrations at all four sampling sites. ANOVA results of site to site variations showed significant differences ($p < 0.05$) of TSP and OC/EC among sampling sites of mountainous and tarai region.

The average OC/EC concentrations at mountainous sites of the present study are compared with the carbonaceous estimates of neighbouring mountainous sites of India and other parts of the world (**Table**

3). The data indicated that OC/EC concentrations were lower than those at Lhasa, China [34] and while comparable with those in Kangra [38], Manora Peak [37], Srinagar [39], Nagarkot [32] and Daihai [54]. In contrast, OC/EC concentrations were considerably much higher than remote or rural mountainous sites of Muztagh Ata [35], Tennessee valley [33] and Langtang, Nepal [32].

Meteorological dependence on measured concentrations of TSP, OC and EC

The distribution of TSP and associated carbonaceous species are influenced by prevailing meteorological conditions of the atmosphere. Therefore, correlation analysis has been carried out to examine the role of meteorology on the measured concentrations at four sampling sites during observation period and are presented in **Table 4.** The data for meteorological parameters like planetary boundary layer (PBL), solar radiation (SR), ambient temperature (T), wind speed (WS) and relative humidity (RH) are retrieved from ERA–5 reanalysis dataset, developed by the ECMWF (https://cds.climate.copernicus.eu/cdsapp#!/home). As shown in table, positive correlations of TSP and carbonaceous species were observed with PBL, SR and T at three sites of mountainous region while PN (tarai urban region) showed anti-correlation with the same parameters.

The two mountainous sites of higher altitudes (DS and MP) showed moderate to stronger correlations of TSP, OC and EC with PBL (r = 0.58 – 0.91), SR (r = 0.58 – 0.91) and T (r = 0.66 – 0.85). Other mountainous site BT exhibited relatively lower positive correlations of measured concentrations with PBL, SR and T. It indicated that TSP and carbonaceous species have elevated concentrations during summer season due to increased PBL, vertical transport of pollutants from valley regions along with long range transport. In addition to this, higher altitude sites (DS and MP) showed weak to moderate positive correlations of carbonaceous species with WS (r = 0.36 – 0.74).

PN showed negative correlations of carbonaceous aerosols with PBL, SR and T which suggested increase/(decrease) in the measured concentrations during winter/(summer). Negative correlation of TSP and associated carbons with WS suggested dispersal of pollutants. No significant correlations were noted for carbonaceous aerosols with relative humidity at DS and BT while positive and negative correlations at MP and PN, respectively.

Source characterization of OC and EC

Relationship between OC versus EC

EC mainly originates from combustion processes, considered as tracer of primary OC and in general, correlation analyses between OC versus EC provide an indication for source characterization of carbonaceous fractions in TSP [5,55]**.** Regression plot between the OC and EC concentrations for the four sampling sites are presented in **Fig. 7.** Significant correlations at the 0.01 confidence interval between OC versus EC have been observed for four sampling sites. Results showed significant Pearson correlation coefficients (r) of OC versus EC at DS, MP, BT and PN, which were 0.88, 0.82, 0.81 and 0.93, respectively. It indicated that carbonaceous aerosols were controlled by similar processes of source emissions and

transport pathway. Two sites (DS and PN) exhibited relatively higher fitting degree (R^2) between OC and EC suggesting the dominance of similar sources while lower fitting degree at MP and BT indicated a relatively lesser similarity of emission sources. Atmospheric processes at sampling sites may also influence the local sources and transport pathways [19].

OC/EC ratios

The empirical mass ratio of OC and EC (OC/EC) can be used as diagnostic indicator for estimating the emissions sources and transformation characteristics of carbonaceous fractions in aerosol. It is largely influenced by combustion process and efficiency, fuel characteristics, secondary organic aerosol formation and rates of degradation [49,56]. For source characterization, OC/EC ratios for various emission sources are reported in several studies as for biomass burning (3.8 – 13.2), coal combustion (2.5 – 10.5) and vehicular exhaust of diesel and gasoline (1.0 – 4.2) [22,57,58]. The estimated OC/EC ratios in TSP for four sampling sites during two seasons are also presented in **Table 1**.

The observed OC/EC ratios ranged from 2.4 to 9.3, 2.2 to 8.6, 1.9 to 4.3 and 2.0 to 2.5, respectively, during winter and 2.6 to 4.2, 2.1 to 4.2, 2.5 to 4.0 and 1.8 to 3.2, respectively during summer for DS, MP, BT and PN. The variability in OC/EC ratios are noted to be very low at the four sampling sites in both seasons where DS and MP exhibited largest coefficient of variations approximately equal to 0.4 during winter season. The estimated OC/EC ratios for DS and MP indicated the mixed sources of biomass burning, coal combustion and vehicle exhaust. Moderately higher mean OC/EC values at DS (4.5) and MP (4.3) during winter than summer might be attributed to increased coal combustions for heating, increase in volatile precursors emissions and low mixing height [46]. It can be also be due to the relatively lower effects of automobiles and industries which tend to enhance EC emissions compared to OC. The observed OC/EC ratios are in good agreement with reported values at other higher altitude areas of mountainous region where EC emissions are relatively in lower concentrations [59–62]. Lower OC/EC ratios in BT and PN are associated with larger proportionate carbon emissions from fresh motor vehicular and industrial emissions from nearby areas along with the mixing of carbonaceous particles from long range transport [46,63]. Although, it is very difficult to draw any conclusion for source estimation of the carbonaceous fractions in aerosols due to the influence of many factors on OC/EC ratios.

Estimation of Primary and Secondary Organic Carbon

Organic Carbon consists of primary OC (POC) and secondary OC (SOC) where direct estimation of these parameters in carbonaceous aerosols is very difficult [64]. However, a numbers of indirect methodologies have been considered for SOC estimations in the aerosol [46,65–67]. SOC are believed to form in the atmosphere if OC/EC ratio > 2.0 [23]. Large variations of OC/EC ratios at the studied sites suggested occurrence of SOC fractions in total estimated OC. The EC tracer method based on minimum OC/EC ratio proposed by Castro et al. (1999) was used for the segregation and estimation of POC and SOC[67]. Minimum OC/EC value of carbonaceous samples are expected to contain exclusively POC and effect of SOC can be omitted. The empirical formula for the estimation of POC is as follows

$POC = (OC/EC)_{min} \times EC$

$SOC = (OC)_{Total} - POC$

where $(OC/EC)_{min}$ describes the minimum value of OC/EC ratio estimated during specific season at particular site. The variations in emission strength of OC and EC for different sources along with meteorological conditions of the region resulted into the variability of minimum OC/EC ratios. Therefore, $(OC/EC)_{min}$ was estimated for each sampling site during each season for present study.

Average concentrations of estimated POC, SOC and percentage contributions of SOC to total OC at four sampling sites during two seasons are given in **Table 5.** The average concentrations of SOC and its percentage contribution were estimated to be 2.4 μg/m³ (40.7%), 4.3 μg/m³ (42.4%), 6.1 μg/m³ (45.4%) and 7.1 μg/m³ (20.1%) in winter season and 3.2 μg/m³ (28.1%), 5.4 μg/m³ (35.4%), 5.0 μg/m³ (26.7%) and 7.3 μg/m³ (32.7%) in summer season at DS, MP, BT and PN, respectively. The estimated results suggested that SOC was an important component of OC and TSP mass. Higher SOC contributions during the winter seasons at three sites of mountainous region could be due to the occurrence of favourable conditions for condensation of photo-oxidation products of organic species, biogenic VOCs emissions and long range transport of organic pollutants enhanced SOC formations [64]. The higher SOC contributions to OC in winter at the mountainous sites of the present study were consistent with the estimations of previous studies [43,51,68].

As compared to mountainous sites, the PN (Tarai-urban) experienced approximately similar levels of SOC concentrations in both seasons with higher % SOC contribution to total OC during summer than winter. Several studies have reported the higher % SOC during summer could be associated with higher temperatures and intense solar radiation which enhances photochemical activity and SOC formation [5,24].

Conclusions

This study represents first quantitative estimates for carbonaceous species of TSP at three higher altitude stations (Devasthal, Manora Peak and Bhimtal) and one Tarai (Pantnagar) site of western Himalaya region. The paper mainly focuses on seasonal variations of carbonaceous species, correlations with meteorological parameters, source attributions and SOC formation. TSP mass and OC/EC concentrations showed significant reduction with the increasing altitudes during two season with different amplitudes. The average TSP/(OC)/(EC) concentrations for respective sites of DS, MP, BT and PN were as 60.5/(8.4)/(2.3) μg/m³, 81.7/(12.5)/(3.6) μg/m³, 99.4/(15.8)/(4.5) μg/m³ and 202/(29.2)/(12.2) μg/m³. Significant positive correlations were observed for TSP and OC/EC concentrations with PBL, Temperature and solar radiation at mountainous sites while PN showed anti-correlation with these parameters. At the mountainous sites, TSP, OC and EC showed nearly similar slope of decrease with increasing altitudes and the slopes in winter and summer also remains nearly the same.

The relationship between OC and EC at four sampling sites showed significant association with high correlation coefficient ($r > 0.8$) indicated dominance of similar processes of source emissions and transport pathway. The OC/EC ratios were generally higher at mountainous sites as compared to tarai region. The ratios, at DS (2.4 to 9.3), MP (2.1 to 8.6), BT (1.9 to 4.3) and PN (1.8 to 3.2) indicated combines influence of biomass burning, coal combustion, vehicular exhaust and long range transport. SOC were investigated using minimum OC/EC ratios and it suggested higher % SOC/OC contributions at mountainous sites as for DS (34.4%), MP (38.8%) and BT (36.1%) while lower at PN (26.4%) during whole observation period. More comprehensive and long-term quantitative along with modelling approach pertaining to carbonaceous particles for different particulate fractions are needed to insight better understanding of chemical characterization, source attributions, formation and transport pathway at varying altitudes of Himalayan region.

Declarations

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Availability of data and materials

All data generated or analyzed during this study are included within the article.

Competing interests

The authors declare they have no competing interests.

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Authors' contributions

All authors read and approved the manuscript.

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Tables

Table 1 Statistical 12-hour mass concentrations of TSP, OC and EC ($\mu g/m^3$) at four sampling sites during two seasons

	TSP (μg/m³)	OC (μg/m³)	EC (μg/m³)	TC (μg/m³)	OC/EC	% OC of TSP	% EC of TSP
	Winter						
DS	50.7 ± 6.9	5.9 ± 1.3	1.5 ± 0.6	7.4 ± 1.7	4.5	11.8	3.0
MP	73.8 ± 11.2	10.4 ± 2.6	2.8 ± 1.2	13.1 ± 3.5	4.3	14.1	3.7
BT	89.7 ± 24.6	12.9 ± 4.4	3.6 ± 1.0	16.5 ± 5.1	3.6	14.3	4.1
PN	224 ± 49.8	35.3 ± 4.0	15.6 ± 2.2	50.9 ± 6.0	2.3	16.7	7.4
	Summer						
DS	70.2 ±15.8	10.9 ± 2.0	3.0 ± 0.6	13.9 ± 2.4	3.7	15.9	4.4
MP	89.6 ±18.1	14.6 ± 3.5	4.4 ± 0.9	19.0 ± 4.2	3.3	17.1	5.2
BT	109 ± 18.4	18.7 ± 3.4	5.4 ± 1.3	24.0 ± 4.6	3.5	17.2	4.9
PN	180 ± 36.9	23.1 ± 4.5	8.8 ± 3.0	32.0 ± 7.1	2.8	13.3	5.1

Table 2 One-way ANOVA of seasonal and day/-night time variability in TSP, OC and EC concentrations at studied sites

		TSP		OC		EC	
Sampling sites	Comparison criteria	F-test	p value	F-test	p value	F-test	p value
DS	Between Seasons	12.8	0.00	43.5	0.00	36.6	0.00
	Between Day and Night	14.7	0.00	0.9	0.34	1.4	0.25
MP	Between Seasons	5.5	0.03	9.4	0.01	12.9	0.00
	Between Day and Night	18.4	0.00	2.3	0.15	1.4	0.25
BT	Between Seasons	4.1	0.06	10.6	0.00	11.5	0.00
	Between Day and Night	7.2	0.01	0.9	0.37	0.9	0.35
PN	Between Seasons	4.9	0.04	41.1	0.00	32.8	0.00
	Between Day and Night	2.2	0.15	2.0	0.17	1.2	0.29
Averaged all sites	Between sites	21.6	0.00	17.7	0.00	16.2	0.00

Table 3 Comparison of observed OC/EC concentrations in present study with higher altitudes of other mountains across globe including India

Location name	Altitude (m asl)	Mean OC (μg/m³)	Mean EC (μg/m³)	Sample types	Reference
Muztagh Ata	7509	0.48	0.055	TSP	Cao et al (2009)
Langtang, Nepal	3920	2.0	0.38	$PM_{2.5}$	Carrico et al. (2003)
Lhasa, China	3363	35	6	PM_{10}	Zhang et al. (2008)
Nagarkot, Nepal	2150	2.0 - 14	0.5 – 1.5	$PM_{2.5}$	Carrico et al. (2003)
Manora Peak, India	1950	8.7	1.1	TSP	Ram et al. (2008)
Daihai, Inner Mangolia	1221	12.4 – 34.7	2.0 – 4.6	TSP	Han et al. (2008)
Kangra, India	600	13.5	5.1	PM_{10}	Kumar and Attri (2016)
Srinagar, India	560	15.3	5.2	$PM_{2.5}$	Sandeep et al. (2019)
Tannessee valley	550	3.3	0.55	$PM_{2.5}$	Tanner et al. (2005)
Devasthal, India	2450	8.3	2.3	TSP	Present study
Manora Peak, India	1950	12.5	3.6	TSP	Present study
Bhimtal, India	1413	15.8	4.5	TSP	Present study

Table 4 Pearson correlation coefficients for TSP and OC/EC concentrations with prevailing meteorological conditions at studied sites

Sites	Species	PBL	SR	T	WS	RH
	TSP	0.91**	0.91**	0.78**	0.08	-0.38
DS	OC	0.70**	0.59**	0.84**	0.36	-0.05
	EC	0.75**	0.64**	0.85**	0.45*	-0.16
	TSP	0.67**	0.74**	0.66**	0.05	-0.51*
MP	OC	0.72**	0.71**	0.74**	0.66**	-0.76**
	EC	0.58**	0.58**	0.72**	0.74**	-0.67**
	TSP	0.46*	0.51*	0.48*	-0.23	-0.24
BT	OC	0.41	0.53*	0.63**	-0.18	0.03
	EC	0.37	0.50*	0.60**	-0.24	0.15
	TSP	-0.44	-0.54*	-0.51*	-0.14	0.56*
PN	OC	-0.30	-0.56*	-0.61**	-0.54*	0.46*
	EC	-0.36	-0.57**	-0.62**	-0.49*	0.50*

$^{*}p < 0.05$, $^{**}p < 0.01$ (correlation coefficient and significance test). PBL: Planetary boundary layer,

SR: Solar radiation, Temp: Temperature, WS: Wind Speed, RH: Relative humidity

Table 5 Estimates of POC, SOC and %SOC/OC at studied sites during two seasons using minimum OC/EC ratio method

Sampling sites	Winter			Summer		
	POC	SOC	%SOC/OC	POC	SOC	%SOC/OC
DS	3.5	2.4	40.7	7.7	3.2	28.1
MP	6.1	4.3	42.4	9.2	5.4	35.4
BT	6.7	6.1	45.4	13.6	5.0	26.7
PN	28.2	7.1	20.1	15.8	7.3	32.7

POC: Primary Organic Carbon, SOC: Secondary Organic Carbon

Figures

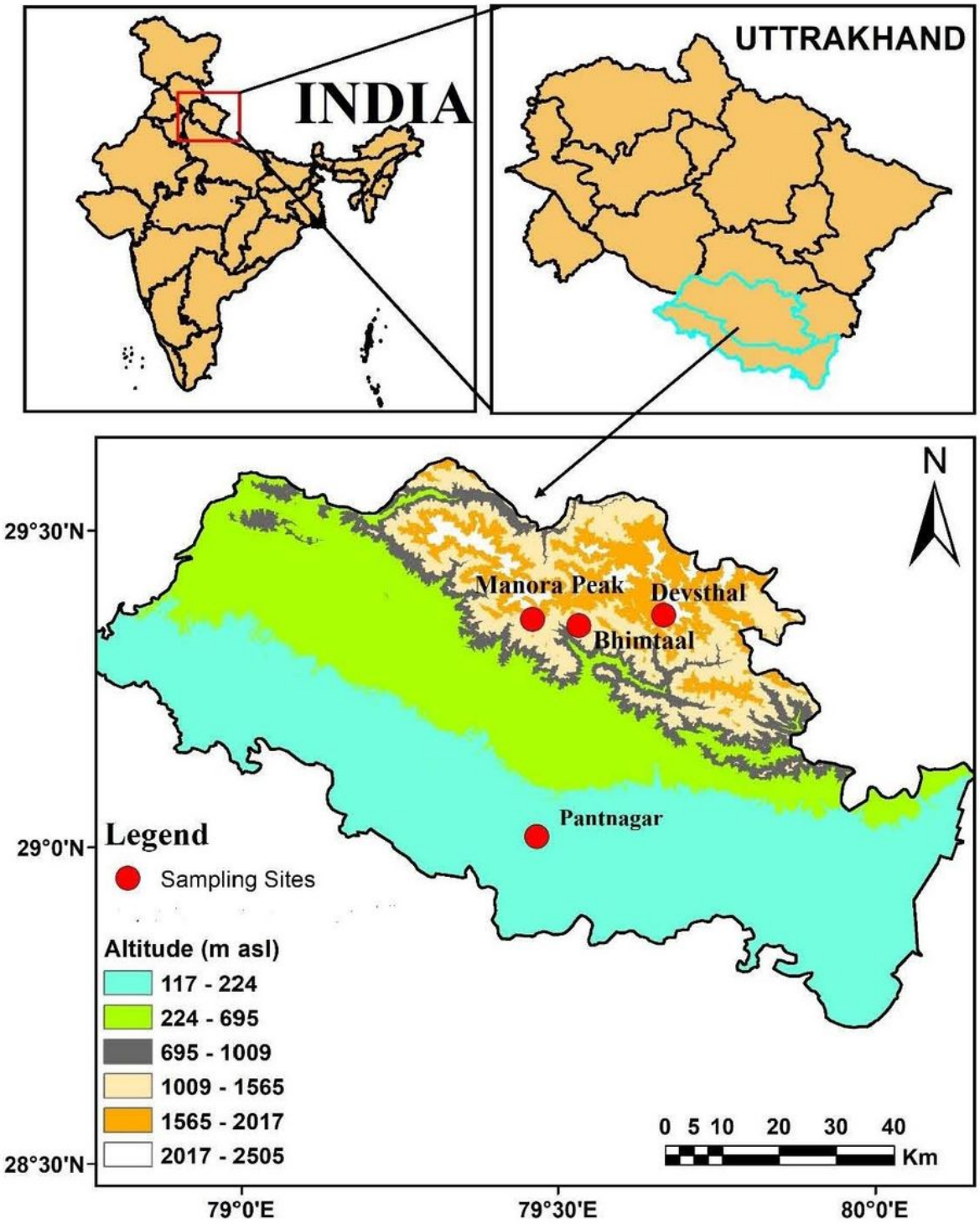

Figure 1

Terrain elevation and geographical locations of sampling sites in Kumoan region, Western Himalaya

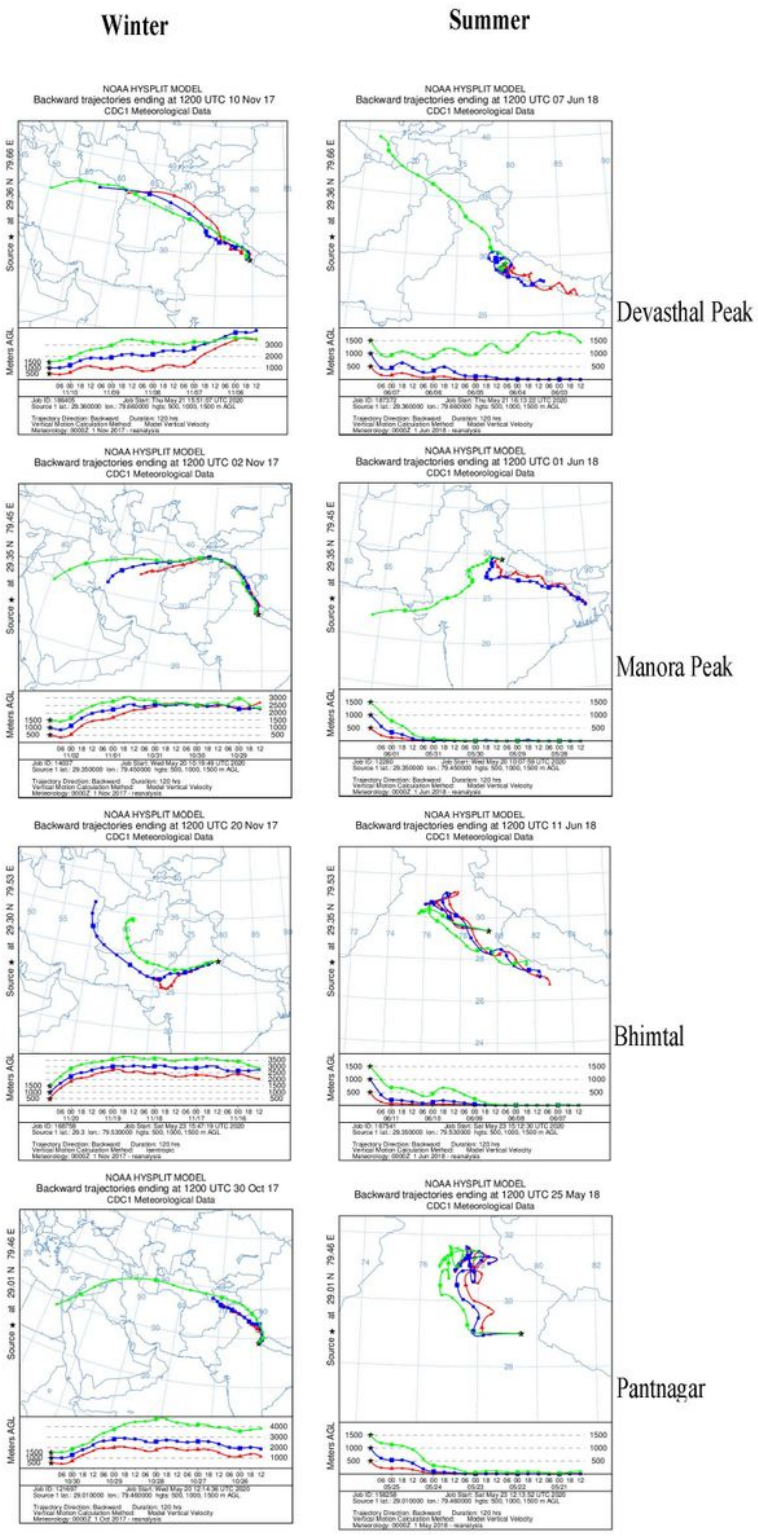

Figure 2

120-h backward air mass trajectories at four sampling sites during winter and summer seasons

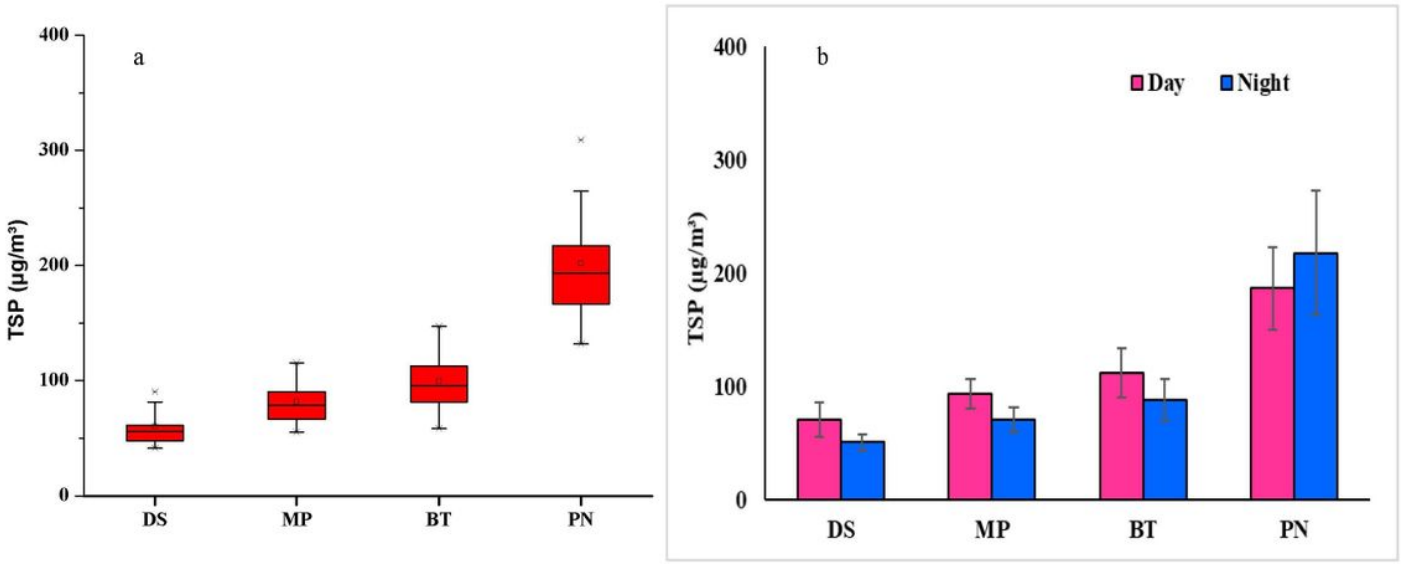

Figure 3

Distribution of TSP (μg/m³) at four sites during (a) whole observation period and (b) day-/night-time

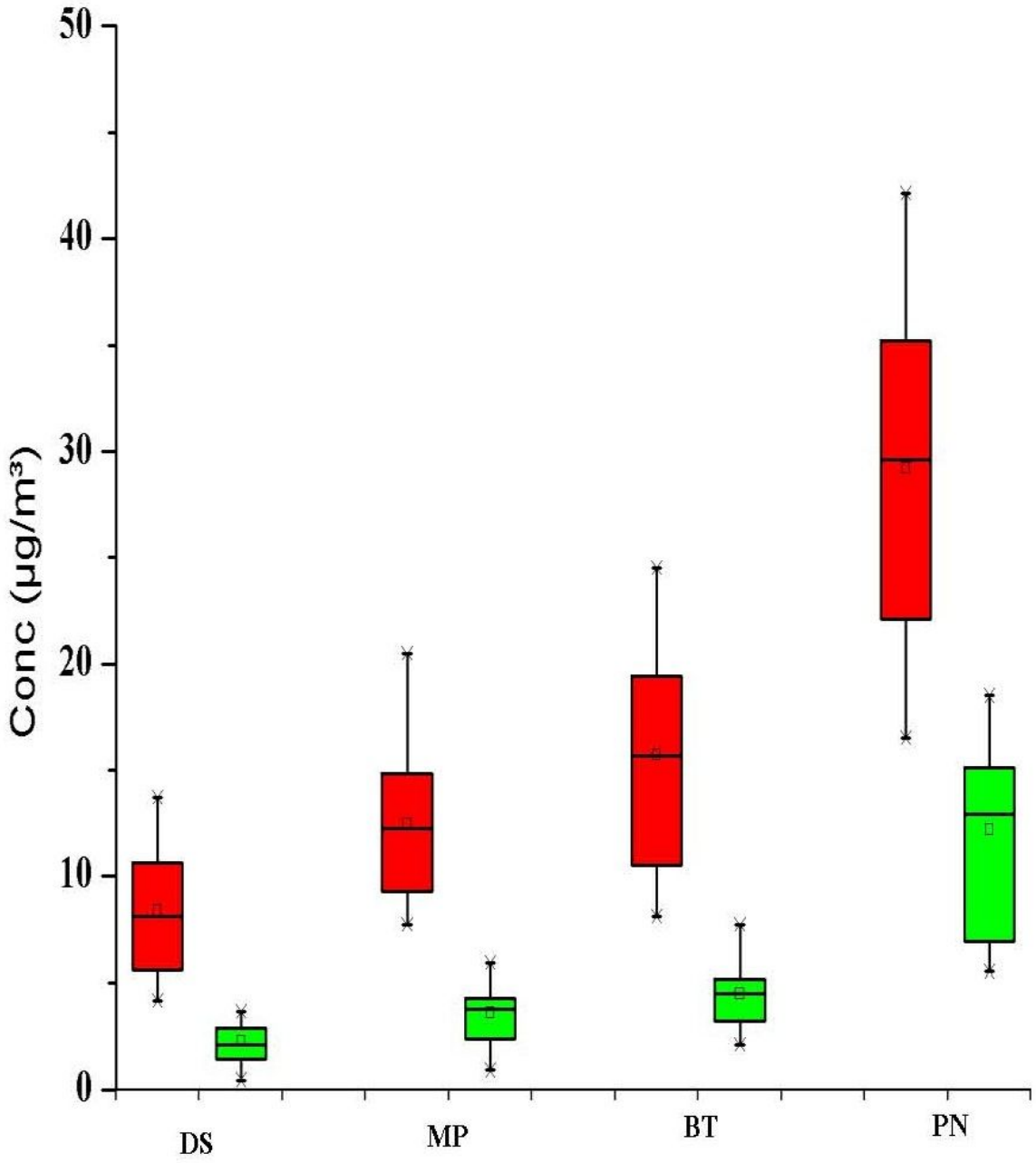

Figure 4

Box whisker plots of OC (red) and EC (green) concentrations (µg/m³) at four sampling sites

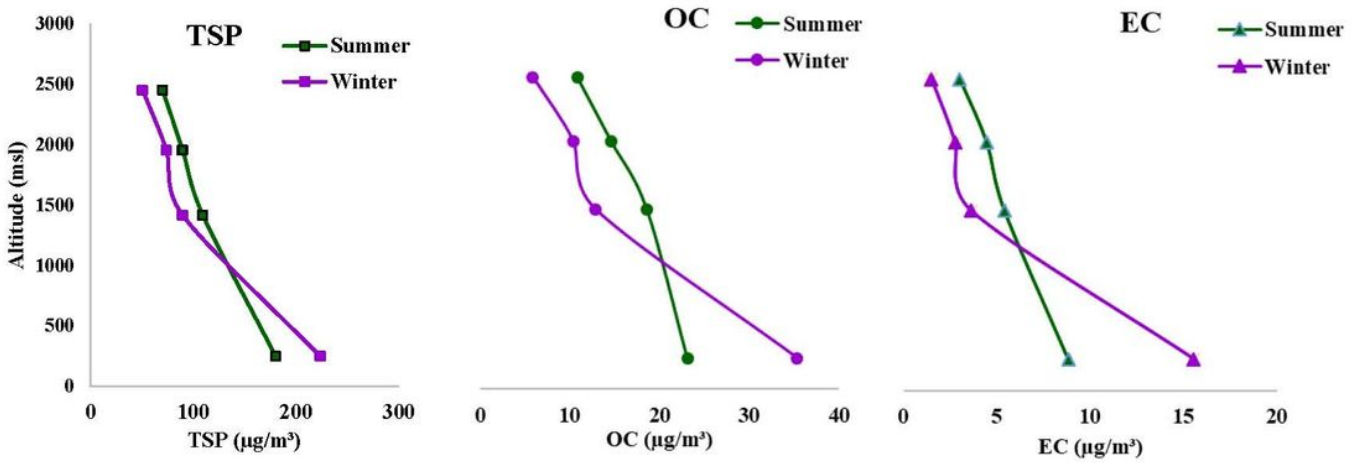

Figure 5

Altitudinal variation of mean TSP and OC/EC concentrations during two seasons

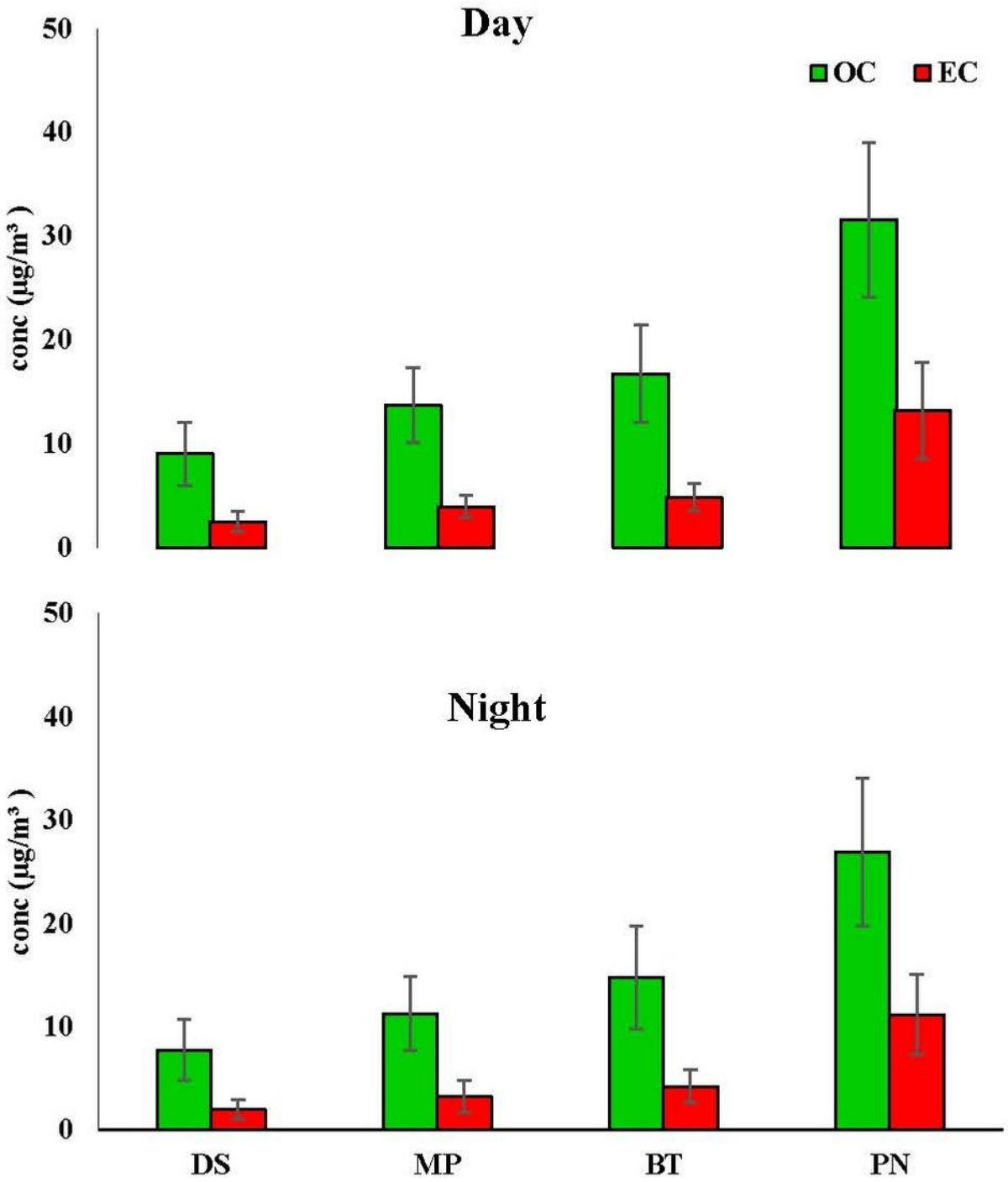

Figure 6

Day and night-time variations of OC/EC concentrations at studied sites during whole observation period

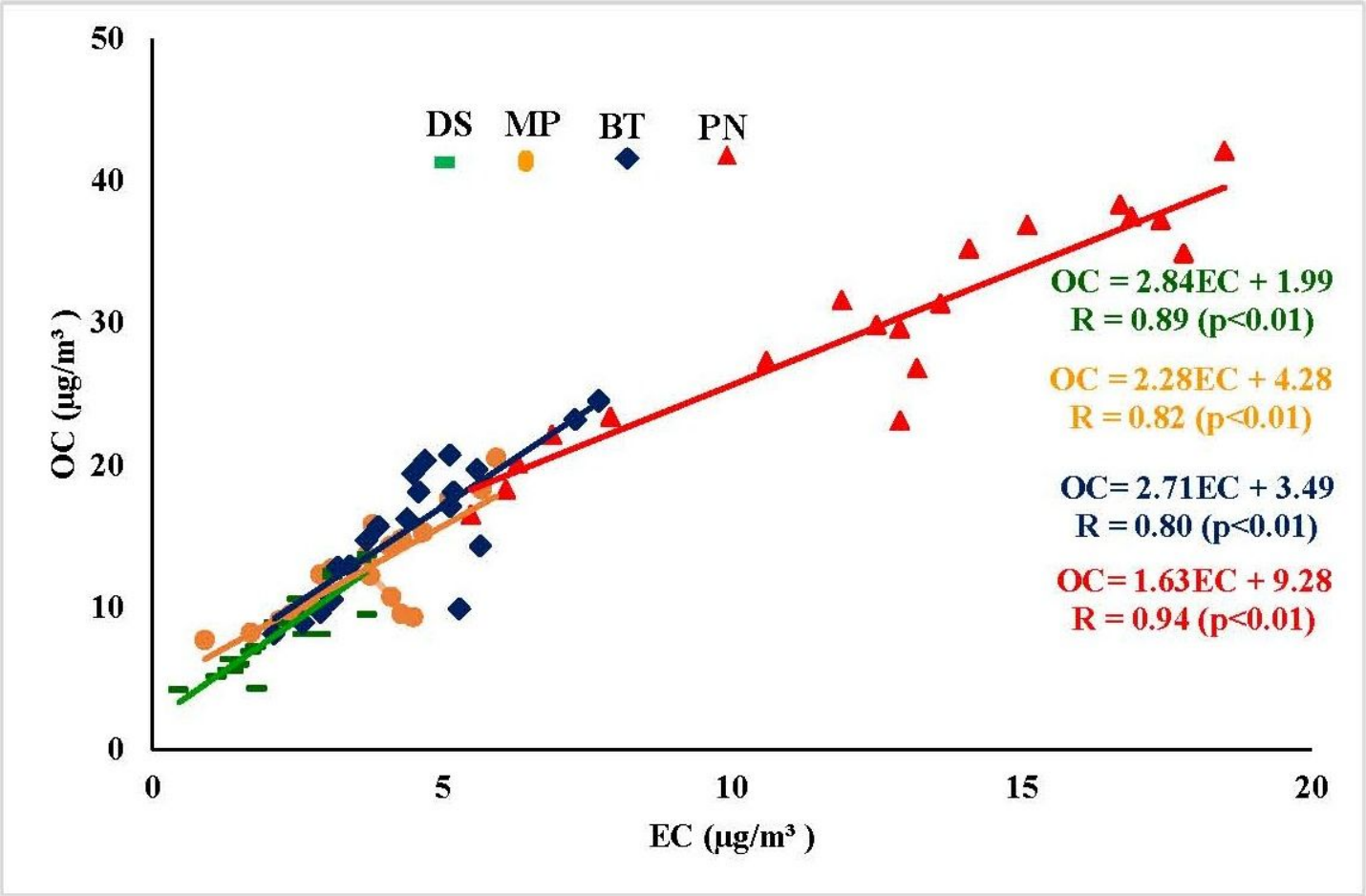

Figure 7

Correlations between OC and EC at four sampling sites during observation period