Real-time monitoring of black carbon aerosols in the glaciated valley of northwestern Indian Himalaya

Aerosols play an important role in climate change processes. Among the various aerosols, black carbon (BC) has been recognized as the second most important anthropogenic agent for climate change and the primary tracer for adverse health effects caused by air pollution[1,2]. The increasing concentration of BC in the atmosphere has now become a matter of serious concern, especially in the high Himalayan glaciated region that has the most vulnerable ecosystem with pristine environment, rich biodiversity and pollution-free ambient air quality. However, due to unsustainable developmental activities, pollution in the form of aerosols, particularly BC generated from local, regional and global sources accumulates over the Himalayan region and alters atmospheric conditions that consequently have an adverse impact on natural and socio-economic resources, including human health. Aerosols at regional scale are also said to be responsible for deflected Himalayan rainfall and snow precipitation pattern, local ecosystem and natural weather cycles. The monitoring of BC aerosols in the high Himalaya remains a challenging task due to harsh climatic conditions with inaccessible terrain. The high Himalayan region encompasses various important natural resources such as glaciers, snow, alpine flora and fauna, etc. that are essential for various ecosystem services, including recharging the Himalayan rivers and freshwater springs. Besides ecosystem services, the high Himalayan region also provides sustainable livelihood to millions of its inhabitants as well as the downstream population. Therefore, any change in atmospheric composition of the high Himalayan region due to BC and other aerosols is bound to influence the natural resources and their associated contribution in ecological services and socio-economic activities of large populations.

In spite of serious environmental and ecosystem implications of BC, real-time data for most of the high Himalayan region are not available due to inhospitable working conditions. Therefore, considering the vital role of BC aerosols, it was felt important to monitor them at priority level. With the view to conduct long-term monitoring of BC aerosols in the high Himalayan region, especially in snow-bound and glaciated areas, two all-weather BC monitoring stations were established in the Gangotri Glacier Valley in Chirbasa at an altitude of 3600 m amsl and in Bhojbasa at an altitude of 3800 m amsl (Figure 1). Since Chirbasa station is located close to the treeline ecotone and Bhojbasa is close to the snowline, both stations represent ecologically sensitive zones in the area (Figure 2). A portable aethalometer (AE-33-7) permanently installed 3 m above the ground surface on an iron tower at the observation site is being used to monitor BC concentration. A solar power system (Tata) with 600 Wp (0.8 kW) capacity solar panel and 12 V 100 Ah tubular gel batteries was used to provide continuous power supply to the aethalometer for round-the-clock data recording. Special insulation boxes were used to provide suitable operating temperature to the mounted aethalometer and protect underground batteries from power discharge due to extreme low temperature ranging from –37°C to –34°C in December and January[3]. The aethalometer is based on 'dual spot' technology and analyses carbon at seven different wavelengths between 370 and 950 nm UV and IR and has a BC measurement range 0.01–100 μg/m^3. The measurement frequency of the aethalometer was programmed 1 minute with flow rate of 5 lpm, as the study area is a pristine locality away from human settlements.

Although the observation site was established to record long-term seasonal behaviour with annual variation in BC aerosols, available 12 months' data recorded from January to December 2016 at Chirbasa station were adequate to show current status during winter and summer season, including tourist and non-tourist seasons. The detailed monthly variation depicted in Figure 3 shows that maximum BC concentration was 1899 ng/m^3 biomass burning with 1180 ng/m^3 BC during May and minimum concentration of 168 ng/m^3 biomass burning and 123 ng/m^3 BC in August. Field studies revealed that both natural as well as anthropogenic factors contribute to BC aerosols in the Gangotri Valley (Figure 4). The tourist season from April to June showed remarkable increase in BC aerosols concentration

Figure 1. Black carbon (BC) monitoring station at Chirbasa.

Figure 2. Ecotone vegetation opposite to the BC monitoring station at Chirbasa.

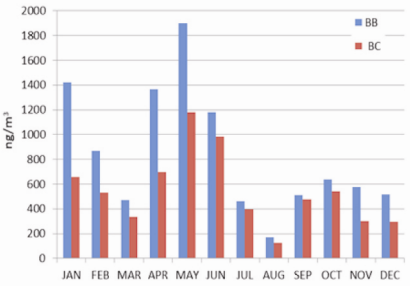

Figure 3. Monthly variation of BC concentration at Chirbasa.

Figure 4. Glaciated Gangotri Valley: aethalometer (foreground), Bhagirathi peaks (background).

due to anthropogenic activities. More than 87,736 tourists/pilgrims visited the Gangotri Temple within 14 days after the beginning of the tourist season in May 2016 (ref. 4). The direct and indirect activities related to tourism are the potential contributors of BC aerosols. It has been reported that winds blowing from down valley to uphill can easily transport BC to the monitoring station from Gangotri Temple vicinity[5]. Moreover, summer tourist season witnesses local forest fires that are active contributors of biomass burning component of BC aerosols. It is evident from the observed data that occasionally, forest fire incidences independently enhanced BC concentration even during the non-tourist season of January and February. The second highest BC aerosols concentration was reported during September and October, which are also autumn tourist months and contribute significant aerosols to the surrounding atmosphere. The lowest BC concentration was recorded during August followed by December. It is observed that due to the absence of tourist activities and forest fire incidences during these months, BC concentration in the atmosphere remains at the lowest level. Moreover, natural phenomena such as rain wash of the pollutants – aerosols from atmosphere during rainy season before August and snow precipitation during winter season, especially in December are considered important for low BC concentration during these months.

The foremost local sources of organic BC aerosols observed during field study are forest fires, domestic and commercial fuelwood burning and seasonal burning of unused agricultural and forest biomass. Hence, biomass burning (BB) is reported higher in comparison to BC throughout the year. Forest fires and unused agriculture burning contribute significantly to BB during summer season, especially during May–June, while sources for elemental BC include exhaust from automobiles and electricity generators that use fossil fuel, viz. petrol, diesel and liquefied petroleum gas (LPG). Excessive use of kerosene and LPG stoves during tourist season is also considered to be a significant source of BC pollution. Besides these local sources, considerable amount of BC travels along with wind currents from Asian cities and other parts of the world and accumulates over the Himalayan region due to low pressure gradient. The annual BC average at Chirbasa is 0.691 $\mu g/m^3$, which is far below in comparison to the nearest stations, viz. Nainital (1.40 $\mu g/m^3$) and Kullu (4.60 $\mu g/m^3$) in the northwestern Himalayan region[2]. The stations under comparison are located quite close to human settlements and, hence, show anthropogenic impact on BC concentration. The low BC concentration during non-tourist and non-forest fire season is considered relevant to such a pristine area and other similar localities in the Himalayan region. However, the high BC concentration during summer season, especially May and June, is likely to affect the sensitive ecosystem along with its resources, eco-biological processes and their overall dependents including local inhabitants, visitors and those residing in the lower catchment areas. The reported BC concentration in ambient air at the observation site is far below from the respirable pollutants limit, i.e. 60 $\mu g/m^3$ set by the Indian National Ambient Air Quality Standard and World Health Organization (WHO), i.e. 25 μg/cubic meter (ref. 6). These limits for ambient air quality are standardized for urban areas with a focus on human health, and not for the sensitive Himalayan ecosystem that has high vulnerability towards atmospheric changes. In the high Himalayan region, even a change of 1°C in temperature may result in significant decrease in snow cover area along with habitat loss of important flora and fauna. A decrease in snow cover area near the snowline and an increase in forest area near the treeline have already been reported in the area as well as in the Himalayan region[7–9]. This change in snow cover area is evident from gradual upward movement of climate markers, i.e. snowline and treeline in their spatial existence and can be attributed to climate change driven by atmospheric factors. The observed higher concentration of BC during summer season is bound to accelerate atmospheric warming that adversely affects the ecosystem and associated resources in the sensitive and ecologically fragile Himalayan region. Hence, the prevailing atmospheric conditions are crucial for the Himalayan ecosystem as well as the health of inhabitants of the area[10,11].

Further, BC aerosols when coupled with plant allergens in the surrounding air, produce bio-aerosols that further increase the particulate matter (PM) and deteriorate the air quality of the terrain. Air mixed with bio-aerosols consequently exhibits harmful effects on human health such as allergy, respiratory ailments, carcinogenic symptoms and various other health complications. Apart from adverse effects in the remote Himalayan region, air pollution due to BC aerosols, has already become a silent killer in some urban areas; hence, it is now recognized as a major critical global risk factor for diseases. According to the State of Global Air Report 2017, exposure to PM 2.5 was ranked the fifth highest risk factor for death, responsible for 4.2 million deaths from heart disease and stroke, lung cancer, chronic lung disease and other respiratory diseases[12]. During 2012, China reported the highest, i.e. one million deaths due to PM 2.5 and PM 10 air pollution. India reported 621,138 deaths, nearly 10% of the global toll associated with outdoor and indoor air pollution. The air quality in the National Capital Region Delhi has become the worst among world megacities, as concentration of fine particulate matter (PM 2.5) was reported almost four times above daily acceptable levels, on average, for the one week period from 22 to 28 September 2016. For long-term exposure, these 24-h levels are nearly 11 times more than the standards prescribed by WHO[13]. BC and other PM produced in Indian cities also reach the Himalayan region along with monsoon and wind currents, and adversely affect the atmospheric air composition and associated resources.

In order to mitigate the implications of increasing BC concentration and associated air pollution in the high Himalaya and other areas, its origin from anthropogenic as well as natural sources needs to be reduced by providing sustainable and eco-friendly arrangements for activities that are responsible for aerosols generation. Moreover, public awareness through proper education, social interaction and training on potential implication of BC will play a significant role in mitigating aerosol pollution and conserving natural resources with ambient air quality in the Himalaya and adjoining regions.

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Effectiveness of amino acids for carbon storage and utilization applications

Carbon dioxide (CO_2), the primary greenhouse gas, can have a major impact on global warming, if present in the earth's atmosphere beyond permissible limits. In fact, the accumulative emissions of CO_2 gas in the atmosphere are progressively increasing causing the global temperature rise by 1.5°C to 2°C (ref. 1). On the other hand, CO_2 also can form clathrate hydrates under some favourable thermodynamic conditions.

The gas hydrates (clathrate hydrates) are non-stoichiometric inclusion compounds of guest (gas) and host (cages formed from hydrogen-bonded water molecules) motifs. The gas hydrates of CO_2 molecules crystallize into a space group (Pm3n) with unit cell composition of $6L•2S•46H_2O$, where L (large) and S (small) are the cages capable of hosting guest molecules with $5^{12}6^2$ and 5^{12} faces respectively. Thus, ideally one mole of water (host) can store up to 0.174 moles of gas (guest) in the form of hydrates. In other words, the gravimetric capacity of CO_2 in hydrates is 425 mg/g. However, because of the molecular size of CO_2, it can be populated only in the large cages. Thus, the gravimetric capacity is reduced to 319 mg/g (0.130 mol/mol). On the other hand, the cage occupancy values for CO_2 gas molecules for $5^{12}6^2$ and 5^{12} cages are predicted as 0.9614 and 0.5011 respectively, using CSMGem model and thus the storage capacity is reduced to 0.147 mol (or 359 mg/g). In any case, these numbers are attractive in the perspective of carbon capture, storage and utilization (CCS&U) applications. However, the bottlenecks are slower and inefficient hydrate conversions. The common methods for increasing clathrate formation kinetics, e.g. use of high pressure (driving force), vigorous mechanical mixing, surfactants, or micron-sized ground/sieved ice particles, can be adopted in the laboratory environment. However, these may be less cost-effective and impractical in real gas-storage applications. The conversion process is quite inefficient and time-consuming in a typical batch-type reactor without an agitator and therefore, special types of reactors and/or the addition of some kinetic promoters or surfactants to the hydrate-forming (gas + water) system are often currently being used; such experiments are still at laboratory-scale.

Recently, aqueous solutions with amino acids have been demonstrated as superior thermodynamic inhibitors for both methane and CO_2 hydrates. The amino acids are attractive because of their ability to mix with water through hydrogen bonding; also, they are non-toxic and eco-friendly nature. There are 20 different essential amino acids in nature that are found in proteins. On the basis of propensity of the side chain to interact with polar solvents like water, they are classified as hydrophobic, polar or charged. In a series of papers by different researchers, it has been proved experimentally that the use of aqueous solution consisting of amino acids helps in decreasing the CO_2 hydrate formation rate, and that thermodynamic inhibition is more at higher amino acid concentration[2]. Most of these experiments were conducted under stirred conditions to form CO_2 hydrates[2]. The inhibition effect has been correlated with hydrophobicity, length and constituents of the side chain, and concentration in aqueous water. But there is no thorough agreement among various experiments conducted by different groups and thus the underlined mechanism is more obscure. On the other hand, Cai *et al.*[3] reported that some amino acids like L-methionine, L-norvaline and L-norleucine have a large CO_2 gas storage potential in the form of hydrates and with faster gas uptake, even under non-stirred configuration. Thus, some amino acids could be a useful material for CCS&U applications. The present study aims at assessing the CO_2 gas storage capacity in four different amino acids, mostly found in proteins, namely L-valine (l-val), L-phenylalanine (l-phe), L-cystein (l-cys) and L-methionine (l-met) in isochroic and non-stirred conditions. The chosen amino acids have significant variations in parameters such as hydrophobicity, length and type of the side chains.

Figure 1 describes the experimental procedure adopted and is self-explanatory. The experimental procedure and data analysis are similar to our earlier studies[4,5]. Briefly, the solution was introduced in