How the Atmosphere over Eastern Himalaya, India is Polluted with Carbonyl Compounds? Temporal Variability and Identification of Sources

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ABSTRACT

A study was conducted on atmospheric carbonyl compounds for the first time over a Himalayan atmosphere in India. Samples were collected from a high altitude hill station, Darjeeling (27.01°N, 88.15°E, 2200 masl) during June 2012 to May 2013. Temporal variation, meteorological influence, source apportionment and ozone formation potential etc were studied for acetaldehyde, formaldehyde, acetone, butanaldehyde, propan aldehyde, benzaldehyde, crotonaldehyde, valeraldehyde, isovaleraldehyde, hexanaldehyde, p-tolualdehyde and o-tolualdehyde. High concentration of Acetone (81.6 ± 63.5 µg m–3) was observed which could be due to the higher photochemical production from its precursor volatile organic compounds emitted from tea plants and tea processing units. The concentration of acetaldehyde (20.7 ± 47.6 µg m–3) and formaldehyde (11.6 ± 16.3 µg m –3) were found to be comparable with metro cities of India and world. The average annual concentration of total carbonyl compounds was 174.2 ± 184.6 µg m–3 with maximum during postmonsoon (456.9 ± 199.5 µg m–3) and minimum during winter season (72.2 ± 42.9 µg m–3). Meteorological parameters like temperature and surface reaching solar radiative flux played the major roles for the seasonal variation of the carbonyl concentration over the hill station. The average ratio of formaldehyde to acetaldehyde over Darjeeling was found to be 1.64 ± 1.43 well representing a typical urban atmosphere at this part of Himalaya. Positive matrix factorization model showed that the biogenic emissions from tea plants and vehicular emissions were the major sources of carbonyl compounds over the hill station.

Keywords: Himalaya; Carbonyl compound; Principal component analysis; Darjeeling.

INTRODUCTION

Atmospheric carbonyl compounds (CCs) are oxygenated volatile organic compounds, receiving worldwide attention (Andreini et al., 2000; Bakeas et al., 2003; Cavalcante et al., 2006; Pal et al., 2008; Uchiyama et al., 2012; Ho et al., 2013) since the last few decades. They are ubiquitous and are responsible for the degradation of poor air quality through the formation of tropospheric ozone and peroxy acetyl nitrate which in turn forms photochemical smog. They also adversely affect human health including carcinogenesis upon acute or chronic exposure (Jacob, 2000).

Exposure to atmospheric aldehydes and ketones cause serious health effects. The World Health Organisation (WHO) classified some CCs as toxic air pollutants (TAPs), such as formaldehyde and acetaldehyde for their adverse health effects and carcinogenic consequences on human beings (WHO, 1987; CEPA, 1993). CCs have drastic environmental effect too as they are responsible for the formation of atmospheric free radicals through photo oxidation during day time (Jacob, 2000) contributing a major part of the photochemical smog (Possanzini et al., 1996; Atkinson, 2000; Solberg et al., 2001; Possanzini et al., 2003). These compounds initiate the peroxy-acetyl nitrate or PAN formation which is responsible for photochemical smog. The presence of CCs in the atmosphere is thus of great concern in respect of their adverse effects on human health and environment.

Many studies have been performed to identify their sources and it was found that anthropogenic emissions (Kean et al., 2001; Kim et al., 2008) and biogenic emissions (Seco et al., 2007; Guo et al., 2009) are the major sources
of carbonyl compounds. Anthropogenic sources like vehicular emissions, industrial emission, solvent evaporation (Friedrich and Obermeier, 1999), biomass burning (Cruzen et al., 1985; Tanner et al., 1996) etc. produce significant amount of CCs in the atmosphere. CCs may also form from the directly emitted volatile organic compounds by secondary photochemical transformation (Possanzini et al., 1996; Lary and Shallcross, 2000; Christensen et al., 2000; Bakeas et al., 2003; Obermeyer et al., 2009).

Most of the CCs have a lifetime of several hours with respect to photolysis and OH photo-oxidation reactions (Seinfeld and Pandis, 1998; Macdonald et al., 2001) during daytime because acetone has much higher lifetime than methyl ethyl ketone. Night time reactions with ozone and nitrate radical act as the major sink of CCs (Slemr and Junkermann, 1996; Finlayson-Pitts and Pitts, 2000). CCs are also lost from the atmosphere through dry and wet deposition (Finlayson-Pitts and Pitts, 2000).

Several studies were performed on CCs across the world (Moussa et al., 2006; Ohura et al., 2006; Kim et al., 2008; Duan et al., 2012), but very few studies have been made so far in India. Studies were made over metropolitan cities like Kolkata (Dutta et al., 2009; Majumdar et al., 2014), Mumbai (Majumdar and Srivastava, 2012) and Agra (Khare, 1997) in India to determine the ambient concentration of few CCs and their emissions from waste dumping sites. As far as Himalaya is concerned, a case study was performed on atmospheric CCs in Bhutan (Wangchuk et al., 2015). Earlier we have reported high ambient level of black carbon aerosols (Sarkar et al., 2015), volatile organic compounds (Sarkar et al., 2014), submicron aerosols (Adak et al., 2014), anthropogenic aerosols (Chatterjee et al., 2010, 2012; Roy et al., 2016) over Darjeeling at eastern Himalaya. This prompted us to make a year-long study on other major part of carbonaceous pollutants like carbonyl compounds over this part of Himalaya where the loading of atmospheric pollutants are of major concern due to increased anthropogenic activities related to tourists and rapid pace of urbanization and socio-economic development.

The present study is focused on the investigation of the ambient concentrations and temporal variations of carbonyl compounds, identification of the sources of the carbonyl compounds and the impact of carbonyl compounds on the tropospheric ozone formation over Darjeeling, a high altitude hill station at eastern part of Himalaya in India.

DESCRIPTION OF THE STUDY AREA AND SYNOPTIC METEOROLOGY

The study was carried out at Darjeeling (27°01′N, 88°15′E, 2200 m asl), a well known tourist destination and a hill station over eastern Himalaya in India with the population of ~100,000 people. The geographical position of the sampling site and adjacent regions are shown in a map in Fig. 1. The densely populated Indo-Gangetic Plain (IGP) is located ~50 km south of Darjeeling. The main town centre is located ~200 m below the sampling site and ~250 m below the ridge top. The area in and around the main town centre is populated mainly by several hotels and resorts, offices, schools and colleges, bus and car stands, shopping malls, and hence is the main source of anthropogenic CCs. The road with high vehicular density is the National Highway (NH155) which starts from a plain land city called Siliguri (~2000 m below and south of Darjeeling) and ends at Darjeeling. Darjeeling Himalayan Railway (a world heritage site) is a narrow gauge railway runs by both coal and diesel along the national highway. The Darjeeling railway station and the railway workshop are situated in the main town centre. The measurement was carried out at a height of ~10 m above ground in the campus of Bose Institute. The road adjacent to the campus starts from the main town centre and ends at a tourist spot which is ~300 m west of our campus with minimum traffic density. There are several tea gardens and tea processing units/plants in and around the sampling site and a total of ~90 tea gardens covering 17500 hectares of land present in Darjeeling. About 9 millions kilogram of tea is produced per year by these tea gardens engaging more than 50% of the people of Darjeeling.

Table 1 summarizes the seasonal average of surface meteorological parameters during the entire sampling days. The study period was segregated into four seasons; winter (December–February), premonsoon (March–May), monsoon (June–September) and postmonsoon (October–November). The annual average temperature was 11.3 ± 4.4°C with the maximum during monsoon (15.9°C) followed by premonsoon (12.6°C), postmonsoon (11.2°C) and winter (5.3°C). The average temperature during monsoon was ~3 times higher than winter. Darjeeling had a typical humid atmosphere with an annual average humidity of 86.1 ± 5.0%. Wind speed was highest in premonsoon (1.3 ± 0.1 m s⁻¹) while the average wind speed during monsoon, monsoon and winter was similar (~0.7 m s⁻¹). The surface reaching solar radiation flux was also highest during premonsoon season (280 ± 104.9 w m⁻²) and clear sky conditions were observed mostly during this season (10 out of 12 sampling Days). The minimum solar radiation flux was recorded during winter season (177.1 ± 91.6 w m⁻²). The total rainfall for the entire sampling days was recorded as 493.7 mm. However, ~67% rain occurred during monsoon (329.8 mm) season only.

METHODOLOGY

Sampling Protocol and Analytical Procedure

The USEPA TO-11A (USEPA, 1996, 1999) method was followed for sampling and analysis of carbonyls due to its simplicity and good reproducibility. Analysis was done in the laboratory of CSIR (Council of Scientific and Industrial Research, Govt of India)-National Environmental Engineering Research Institute, Kolkata Zonal Laboratory.

Air samples were collected from June 2012 to May 2013 on day (7:00 am–7:00 pm) and night (7:00 pm–7:00 am) basis at every 8 day interval. One weekly sampling was not done during February and March 2013 respectively due to some technical and logistic issues. The sampling and analysis of CCs were done following the method used by Sirju and Shepson (1995), Lee et al. (2001) and Pang et al. (2001).
Table 1. Seasonal variation of the meteorological parameters during the study period.

<table>
<thead>
<tr>
<th></th>
<th>Monsoon</th>
<th>Postmonsoon</th>
<th>Winter</th>
<th>Premonsoon</th>
<th>Annual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>15.9 ± 1.1</td>
<td>11.2 ± 2.6</td>
<td>5.3 ± 1.8</td>
<td>12.6 ± 1.9</td>
<td>11.3 ± 4.4</td>
</tr>
<tr>
<td>RH (%)</td>
<td>93.3 ± 6.2</td>
<td>84.5 ± 9.1</td>
<td>82.0 ± 12.8</td>
<td>84.7 ± 12.9</td>
<td>86.1 ± 5.0</td>
</tr>
<tr>
<td>SR (W m⁻²)</td>
<td>201.0 ± 95.0</td>
<td>224.0 ± 97.2</td>
<td>177.1 ± 91.6</td>
<td>280.0 ± 104.9</td>
<td>220.6 ± 44.0</td>
</tr>
<tr>
<td>WS (m s⁻¹)</td>
<td>0.8 ± 0.1</td>
<td>0.7 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>1.3 ± 0.1</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>Total Rain (mm)</td>
<td>329.8</td>
<td>0.1</td>
<td>37.7</td>
<td>126.1</td>
<td>493.7</td>
</tr>
</tbody>
</table>

Fig. 1. The geographical location of the study area over Darjeeling.

Table 1. Seasonal variation of the meteorological parameters during the study period.
Briefly, air samples were collected by drawing air with a sampling pump (Envirotech, India) through DNPH-coated cartridges with built in ozone scrubber (BPE-DNPH cartridge sigma- Aldrich 54728-U SUPELCO). The sample collection time was 12 h; the flow rate was ~100 mL min⁻¹ (sample volume ~7.2 L). The cartridges were sealed and well wrapped in aluminium foil and stored in refrigerator at 4°C immediately after sampling until further analysis. A total of eighty six samples were collected during the entire sampling event. One laboratory blank and one field blank were included during sampling and analysis of carbonyl compounds.

2,4-Dinitrophenylhydrazone derivatives were eluted using formaldehyde free HPLC grade acetonitrile. 2–3 mL of acetonitrile was used to elute the derivatives and stored in the vial in a refrigerator for analysis. The 2,4-dinitrophenylhydrazone derivatives were analyzed using a Dionex HPLC. A five point calibration curve was used to calibrate the HPLC using a standard calibration mixture of 15 carbonyl species procured from Supelco, USA. 10 µL sample was injected into a reversed-phase C18 (RP-HPLC) column (Supelco make, C18 columns and guard column) and the derivatives were separated using gradient elution programme. A UV detector operating at 360 nm was used to quantify the derivatives. A mixture of acetonitrile and tetrahydrofuran (10% THF in water) were used as a solvent for the gradient elution programme with the flow rate of 0.3 mL min⁻¹.

Quality Assurance and Quality Control

To ensure the quality of air sampling method we have performed the breakthrough experiment and the cartridge collection efficiency were also determined. For this experiment two DNPH cartridges were connected in series and air sampling was done with the same flow rate and same duration mentioned earlier. Formaldehyde was chosen as the reference carbonyl for this experiment. Breakthrough was assumed to be occurred when the concentration of formaldehyde in the second cartridge of the series exceeded 10% of the first cartridge concentration. The breakthrough volume was 10 liter of air and ~99% of the CCs were found to be collected in the first cartridge when the sampling volume was under the breakthrough volume. The US-EPA method of detection limit development (https://www3.epa.gov/ttn/amtic/files/2009conference/swift.pdf) was followed for finding the method detection limit (MDL). The MDL was calculated as 3 times of the standard deviation of seven replicate measurements of known standard solution of each carbonyl species. The MDL values of each CC are given in Table 2. The precision of determination was calculated similarly by repeated analysis of a known standard solution and the precision was found to vary within ± 5% for each CC concentration.

RESULTS AND DISCUSSION

General Characteristics of the Carbonyl Compounds and Comparison with Other Studies

The annual average concentrations, standard deviations, maximum and minimum of individual and total CCs are given in Table 2. The average annual concentration of total CCs was 174.2 ± 184.6 µg m⁻³. Acetone had the maximum abundance with the annual average concentration of 81.6 ± 63.5 µg m⁻³ ranging between as low as 12.7 µg m⁻³ and as high as 391.1 µg m⁻³ contributing 47% to the total annual CCs concentration. Acetaldehyde had the second highest annual average concentration of 20.7 ± 47.6 µg m⁻³ ranging from 1.1 to 315.1 µg m⁻³ followed by crotonaldehyde, butanaldehyde, formaldehyde and others. The percentage contributions of all the CCs are shown in Fig. 2. Acetaldehyde contributed 12% whereas each of formaldehyde, butanaldehyde and crotonaldehyde contributed 7% to the total annual CCs concentrations.

The most important observation in this study is the very high concentration of acetone which was found to be 4 and 6 times higher than formaldehyde and acetaldehyde respectively. This high concentration of acetone could be explained by the contribution of variety of sources like vehicular emission (Dong et al., 2014), biomass burning (Lewis et al., 2013), solvent evaporation (Feng et al., 2005; Pang and Lee, 2010), biogenic emissions (Singh et al., 1994; Janson and Serves, 2001) as well as secondary photochemical

| Table 2. Minimum, maximum and average concentrations of measured carbonyl compounds. Concentrations are given in µg m⁻³. |
| Annual average | SD | Max | Min | MDL |
| Formaldehyde | 11.6 | 16.3 | 91.0 | 2.1 | 0.221 |
| Acetaldehyde | 20.7 | 47.6 | 315.1 | 1.1 | 0.139 |
| Acetone | 81.6 | 63.5 | 391.1 | 12.7 | 0.080 |
| Propanaldehyde | 2.9 | 5.4 | 24.3 | BDL | 0.133 |
| Butanaldehyde | 12.2 | 27.1 | 123.9 | BDL | 0.083 |
| Crotonaldehyde | 13.1 | 29.3 | 151.2 | 0.8 | 0.126 |
| Benzaldehyde | 9.3 | 26.6 | 152.3 | BDL | 0.134 |
| Isovaleraldehyde | 5.7 | 12.4 | 63.4 | BDL | 0.187 |
| Valeraldehyde | 8.0 | 15.0 | 85.0 | BDL | 0.219 |
| o-Tolualdehyde | 1.0 | 3.6 | 25.9 | BDL | 0.074 |
| p-Tolualdehyde | 2.7 | 8.3 | 34.7 | BDL | 0.247 |
| Hexanaldehyde | 5.5 | 11.6 | 62.6 | BDL | 0.214 |
| Total | 174.2 | 184.6 | 795.5 | 22.4 |
Fig. 2. Contributions of individual carbonyls to the total carbonyl compounds concentration.

productions (Singh and Hanst, 1981; Chatfield et al., 1987; Singh et al., 1994, 1995; Reissell et al., 1999; Orlando et al., 2000) in the atmosphere of Darjeeling. Moreover, acetone has longer lifetime (~15 Days) compared to other carbonyl compounds (few hours). Thus, it could also be transported from long-distance source regions like densely populated Indo-Gangetic Plane (IGP), sustain in the atmosphere for a longer period of time and enhance the ambient level of acetone concentration over the hill station. However, an important factor behind the high level of acetone over Darjeeling could be the biogenic emission of its precursors followed by atmospheric degradation.

Darjeeling is world famous for the production of flavoured tea. Phytofluene is a carotenoid pigment mainly found in the tea leaves (Premachandra et al., 1977; Ho et al., 2015) undergoes epoxidation and photo-oxidation and produce a volatile organic compound called geranyl acetone ((5E)-6,10-dimethylundeca-5,9-dien-2-one) which is an important aroma of black, green and oolong tea (Ho et al., 2015). Geranyl acetone having very short life time of less than 1 hour (Fruekilde et al., 1998) could further get degraded and ozonolysed to form acetone. The reaction pathway of the production of acetone from phytofluene is given in Fig. 3.

The population of tea leaves depends on the pruning and skiffing of tea plants. Pruning and skiffing helps the tea plants to provide stimulus for vegetative growth, to correct past defects in bush architecture, to reduce the incidence of pests and diseases and to regulate the crop. Winter is the pruning time of tea plants over Darjeeling resulting the decrease in the population of tea leaves. New leaves began to grow during the premonsoon season whereas heavy rainfall during monsoon helps the tea plants to grow quickly and their growth continues until the postmonsoon season before the next pruning time. Acetone concentration over Darjeeling follows this seasonal growth cycle of the tea plants showing maximum concentration in postmonsoon followed by monsoon, premonsoon and winter.

The ambient level of formaldehyde, acetaldehyde and acetone over Darjeeling have been compared with other studies and shown in Table 3. These three carbonyl compounds are the common amongst the carbonyls measured by most of the studies made earlier. The highest level of acetone over Darjeeling than other stations across the globe could be easily explained in terms of the biogenic emissions as discussed above. It is observed from Table 3 that the concentrations of formaldehyde and acetaldehyde were much higher than the study made at Bhutan at eastern Himalaya. Formaldehyde shows ~5 times and acetaldehyde shows ~20 times higher loading in the atmosphere of Darjeeling compared to Bhutan. The concentration of formaldehyde over Darjeeling was 2–5 times higher than some of the urban cities like Shimizu (Japan), Beirut (Lebanon), Niteroi (Brazil) and ~10 times higher than that in Agra (India). But, formaldehyde over Darjeeling shows much lower concentration than that in Kolkata, a metro city located at Indo-Gangetic Plain in eastern India. The ambient level of acetaldehyde over Darjeeling was found to be higher than most of the cities in India and abroad. Earlier, we observed higher concentrations of carbonaceous aerosols and VOCs (BTEX: Benzene, Toluene, Ethylbenzene, Xylene) over Darjeeling from various anthropogenic activities and their concentrations were comparable and higher than some of the metro-cities in India (Sarkar et al., 2014, 2015). The sources of carbonaceous aerosols and BTEX are similar to that of acetaldehyde over Darjeeling.

**Seasonal Variation of the Carbonyl Compounds**

The seasonal variation of total CCs is shown in Fig. 4 and the seasonal average concentrations of individual CCs are given in Table 4. Maximum concentration for total CCs
Fig. 3. Formation pathway of acetone from phytofluene via geranylacetone.

was observed during the postmonsoon season (456.9 ± 199.5 µg m⁻³) followed by monsoon (167.5 ± 142.2 µg m⁻³), winter (72.2 ± 42.9 µg m⁻³) and premonsoon (73.5 ± 38.2 µg m⁻³). The CCs concentrations during premonsoon and winter were found to be almost equal. The average CCs concentration during postmonsoon was ~2.5 times higher than monsoon and ~6 times higher than winter and premonsoon. The seasonal variations of most of the CCs were similar to that of total CCs except crotonaldehyde. Crotonaldehyde had the maximum concentration during monsoon season (23.6 ± 42.6 µg m⁻³).

Due to the massive tourist influx, Darjeeling experiences huge emissions of carbonaceous pollutants from various anthropogenic activities like vehicular emission and fossil fuel burning during premonsoon and postmonsoon which are the peak tourist seasons in this high altitude station. Black carbon aerosols during premonsoon and VOCs during postmonsoon were also observed to be higher in our previous studies (Sarkar et al., 2014, 2015). Anthropogenic activities like vehicular emission and biomass burning have been reported as the significant sources of CCs in various studies all over the world (Possanzini et al., 1996; Kean et al., 2001; Ho et al., 2002a, b; Wang et al., 2010; Chen et al., 2014). In addition to that significant emission flux of many CCs has been observed from the waste dumping sites (Majumdar et al., 2014). The human, animal and other domestic wastes are treated unscientifically over this hill station. Thus one would expect high concentration of CCs during both these seasons. Instead, we observed very low concentration of CCs during premonsoon compared to postmonsoon season (Table 4).

The phenomena can be explained by the effect of meteorological influence on the concentration of the carbonyl species. To better understand the effect of meteorological parameters we have made correlation analysis between CCs and micro-meteorological parameters over different seasons and shown in Table 5. It is observed that ambient temperature and surface reaching solar radiation could play different roles on the CCs concentration during different seasons. The incoming solar radiation flux during premonsoon season (280.0 ± 104.9 W m⁻²) was much higher than any other seasons. Average temperature during premonsoon was also higher than postmonsoon and winter season (Table 1). The higher temperature and intense solar radiation favour the photolysis of the carbonyl species (Atkinson, 1990; Anderson et al., 1996; Christensen et al., 2000). On the other hand ambient temperature and solar radiation during postmonsoon were comparatively lower and thus could help in building up the CCs over the hill station.

The second highest concentration of total CCs was found during monsoon (Table 4). The ambient temperature might play the major role in increasing the concentration of CCs in this season. The ambient temperature during monsoon was significantly higher than other seasons (Table 1). Thus fuel and solvent evaporation could be responsible for enhancing the CCs concentration over the study area as reported by the other studies too (Lee et al., 2001; Chen et al., 2014). Crotonaldehyde had the second highest concentration (23.6 ± 42.6 µg m⁻³) after acetone during monsoon. Crotonaldehyde is used in industrial sectors like industrial organic chemicals
Table 3. Comparison of formaldehyde, acetaldehyde and acetone concentrations over Darjeeling with other stations.

<table>
<thead>
<tr>
<th>Study area</th>
<th>Darjeeling, India</th>
<th>Kunglung, Bhutan</th>
<th>Agra, India</th>
<th>Kolkata, India</th>
<th>Shimizu, Japan</th>
<th>Beirut, Lebanon</th>
<th>Ansan, South Korea</th>
<th>Nan-Chie and Kaohsiung, Taiwan</th>
<th>Beijing, China</th>
<th>Shanghai, China</th>
<th>Hyytiälä, Finland</th>
<th>Rome, Italy</th>
<th>Sao Paulo, Brazil</th>
<th>Niterói, Brazil</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nature of the study area</strong></td>
<td>Hill station</td>
<td>Himalayan</td>
<td>Rural</td>
<td>Urban</td>
<td>Industrial harbor</td>
<td>Industrial complex</td>
<td>Urban</td>
<td>Urban</td>
<td>Forest</td>
<td>Urban</td>
<td>Urban</td>
<td>Urban</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Formaldehyde</strong></td>
<td>11.6</td>
<td>2.4</td>
<td>1.7</td>
<td>19.8</td>
<td>2.8</td>
<td>4.6</td>
<td>24.1</td>
<td>18.3</td>
<td>35.7</td>
<td>19.4</td>
<td>0.5</td>
<td>21.0</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td><strong>Acetaldehyde</strong></td>
<td>20.7</td>
<td>1.2</td>
<td>-</td>
<td>13.7</td>
<td>2.3</td>
<td>2.1</td>
<td>36.6</td>
<td>14.9</td>
<td>15.7</td>
<td>15.9</td>
<td>0.4</td>
<td>17.0</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td><strong>Acetone</strong></td>
<td>81.6</td>
<td>7.7</td>
<td>-</td>
<td>19.8</td>
<td>2.8</td>
<td>4.6</td>
<td>24.1</td>
<td>18.3</td>
<td>35.7</td>
<td>19.4</td>
<td>0.5</td>
<td>21.0</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>

**Reference**
- Wangchuk et al., 2015
- Khare et al., 1997
- Dutta et al., 2009
- Ohura et al., 2006
- Moussa et al., 2006
- Kim et al., 2010
- Wang et al., 2010
- Duan et al., 2012
- Huang et al., 2008
- Hell’En et al., 2004
- Possanzini et al., 1996
- Montero et al., 2001
- Ochs et al., 2011

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**Day/Night Ratios of Carbonyl Compounds**

The day/night concentration ratio for total and most of the CCs was > 1 in all the seasons as shown in Fig. 5. The higher anthropogenic emissions and the photochemistry of VOCs during the day could significantly enhance the day time concentrations of CCs during postmonsoon and winter. The day/night concentration ratio for total CCs was > 1 in all the seasons (Atkinson, 1999). The NOx radicals could also act as a sink and decrease the concentration of CCs during nighttime. But acetaldehyde and butanaldehyde were found to have slightly higher concentration during nighttime (Atkinson, 1999). The ambient temperature during nighttime is much lower than the daytime temperature. The lower ambient temperature during nighttime could act as a source to increase the nighttime concentration of CCs. The boundary layer height during nighttime is much lower than the daytime boundary layer height. Hence, the local generation of CCs is much more significant during nighttime. 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Fig. 4. Seasonal variation of total carbonyl compounds shown in box-whisker plot. (Lower, middle and upper boundary of the box correspond to 25, median and 75 percentile; lower and upper whiskers correspond to minimum and maximum and square in the box correspond to mean).

Table 4. Average concentrations of individual carbonyl compounds during different seasons.

<table>
<thead>
<tr>
<th></th>
<th>Monsoon ± SD</th>
<th>Postmonsoon ± SD</th>
<th>Winter ± SD</th>
<th>Premonsoon ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>9.1 ± 9.8</td>
<td>32.5 ± 26.4</td>
<td>26.8 ± 84.3</td>
<td>23.0 ± 7.1</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>13.3 ± 26.4</td>
<td>79.2 ± 48.3</td>
<td>22.2 ± 7.1</td>
<td>20.0 ± 3.8</td>
</tr>
<tr>
<td>Acetone</td>
<td>90.8 ± 64.4</td>
<td>138.4 ± 78.1</td>
<td>57.6 ± 41.5</td>
<td>51.9 ± 33.7</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0.9 ± 0.6</td>
<td>10.2 ± 9.2</td>
<td>0.7 ± 4.2</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>Butanaldehyde</td>
<td>4.9 ± 4.7</td>
<td>56.1 ± 40.2</td>
<td>3.0 ± 5.4</td>
<td>0.7 ± 0.8</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>23.6 ± 42.6</td>
<td>22.0 ± 33.2</td>
<td>4.6 ± 5.4</td>
<td>2.2 ± 1.0</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>10.2 ± 18.3</td>
<td>31.8 ± 51.7</td>
<td>2.0 ± 0.5</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>iso-Valeraldehyde</td>
<td>2.4 ± 4.2</td>
<td>24.3 ± 19.8</td>
<td>0.9 ± 0.8</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>6.4 ± 6.0</td>
<td>28.8 ± 25.1</td>
<td>4.2 ± 1.0</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>o-Tolualdehyde</td>
<td>3.4 ± 0.9</td>
<td>6.4 ± 7.6</td>
<td>0.4 ± 0.4</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>p-Tolualdehyde</td>
<td>2.9 ± 4.5</td>
<td>22.8 ± 18.3</td>
<td>0.3 ± 0.5</td>
<td>0.1 ± 0.1</td>
</tr>
</tbody>
</table>

Incoming solar radiation measurement sensor (Pyranometer: Model No. SP Lite2, Kipp and Zonen) and rain gauge (TE525 tipping bucket rain gauge). The data was recorded at an interval of 1 min. We have used the meteorological data of those days when the carbonyl sampling was done.

In order to evaluate the effect of meteorology on the atmospheric loading of CCs over Darjeeling we have made correlation analysis between each CCs concentration with meteorological parameters like temperature, wind speed, wind direction, total rainfall and solar radiation. But except temperature and solar radiation we did not find any significant correlation between carbonyls and other meteorological parameters. The correlation coefficients (R) for temperature and solar radiation are given in Table 5 where values higher than 0.5 are given in bold numbers.

Surface reaching solar radiation is the most important meteorological parameter that governs the photochemistry of oxygenated and non-oxygenated volatile organic compounds in the lower troposphere. UV radiation ($\lambda < 320$ nm) photochemically decomposes ozone to produce OH radical.

\[
O_3 + \text{hv} (\leq 320 \text{ nm}) \rightarrow O^*(\text{I}D) + O_2 \quad (1)
\]

\[
O^*(\text{I}D) + M \rightarrow O^*(\text{I}P) + M \text{ (where M is O}_2 \text{ or N}_2 \text{)} \quad (2)
\]

\[
O^*(\text{I}D) + H_2O \rightarrow 2OH^\cdot \text{ (radical)} \quad (3)
\]

The OH radical then reacts with different VOCs to produce carbonyl compounds by the following equations (Koppmann, 2008).

\[
\text{CH}_4 + \text{OH}^\cdot \xrightarrow{\text{O}_2,\text{NO}} \text{HCHO} \text{ (Formaldehyde)} + \text{H}_2\text{O} + \text{NO}_2 \quad (4)
\]

\[
\text{C}_2\text{H}_6 + \text{OH}^\cdot \xrightarrow{\text{O}_2,\text{NO}} \text{CH}_3\text{CHO} \text{ (Acetaldehyde)} + \text{H}_2\text{O} + \text{NO}_2 \quad (5)
\]
Table 5. Correlation coefficients (R) of carbonyl compounds with temperature and solar radiation during different seasons.

<table>
<thead>
<tr>
<th>Season</th>
<th>Formaldehyde</th>
<th>Acetaldehyde</th>
<th>Acetone</th>
<th>Acetaldehyde</th>
<th>Acetone</th>
<th>Acetone</th>
<th>Acetone</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monsoon Day</td>
<td>Night Temp</td>
<td>Postmonsoon</td>
<td>Winter Day</td>
<td>Night Temp</td>
<td>Postmonsoon</td>
<td>Night Temp</td>
<td>Total</td>
</tr>
<tr>
<td>Temp</td>
<td>-0.20</td>
<td>-0.20</td>
<td>0.36</td>
<td>0.09</td>
<td>-0.24</td>
<td>0.10</td>
<td>0.16</td>
<td>-0.08</td>
</tr>
<tr>
<td>SR</td>
<td>-0.05</td>
<td>0.08</td>
<td>-0.12</td>
<td>-0.37</td>
<td>0.17</td>
<td>-0.39</td>
<td>-0.48</td>
<td>-0.56</td>
</tr>
<tr>
<td>Temperature</td>
<td>-0.01</td>
<td>0.32</td>
<td>-0.21</td>
<td>-0.04</td>
<td>0.04</td>
<td>-0.40</td>
<td>-0.39</td>
<td>-0.56</td>
</tr>
<tr>
<td>Total</td>
<td>0.10</td>
<td>0.10</td>
<td>0.16</td>
<td>0.04</td>
<td>0.04</td>
<td>-0.03</td>
<td>-0.03</td>
<td>-0.03</td>
</tr>
<tr>
<td>Percentage</td>
<td>0.10</td>
<td>0.10</td>
<td>0.16</td>
<td>0.04</td>
<td>0.04</td>
<td>-0.03</td>
<td>-0.03</td>
<td>-0.03</td>
</tr>
<tr>
<td>Correlation</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Negative</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>R</td>
<td>0.09</td>
<td>0.08</td>
<td>0.16</td>
<td>0.04</td>
<td>0.04</td>
<td>-0.03</td>
<td>-0.03</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

Hence surface reaching solar radiation is a major factor for secondary production of CCs in the atmosphere. Again, photolysis of CCs by surface reaching solar radiation is also the main sink of the atmospheric CCs (Koppmann, 2008). The following equations show the photolysis pathway of formaldehyde, acetaldehyde and acetone in the atmosphere.

\[
\begin{align*}
\text{HCHO} + \text{hv} & \rightarrow \text{H} + \text{HCO}^* \rightarrow \text{H}_2 + \text{CO} \\
\text{CH}_3\text{CHO} + \text{hv} & \rightarrow \text{CH}_3^* + \text{HCO}^* \rightarrow \text{CH}_4 + \text{CO} \rightarrow \text{CH}_3\text{CO}^* + \text{H} \\
\text{CH}_3\text{COCH}_3 + \text{hv} & \rightarrow \text{CH}_3^* + \text{CH}_3\text{CO}^* \rightarrow 2\text{CH}_2^* + \text{CO}
\end{align*}
\]

We observed good/moderate negative correlations between surface reaching solar radiation flux and concentration of all CCs during premonsoon season suggesting photochemical degradation of CCs under higher surface reaching radiation. But we did not observe such negative correlations during other seasons. Thus it could be said that the CCs during postmonsoon, winter and monsoon are not photochemically degraded over Darjeeling. However we observed good positive correlations between surface reaching solar radiation flux and concentration of formaldehyde and acetaldehyde. We observed higher methane concentration during postmonsoon over the same sampling site and in the same year (Ganesan et al., 2013) and thus it could suggest the photochemical formation of formaldehyde from methane through the reactions 1–4 stated above. The measurement of ethane was beyond our scope and thus the photochemical formation mechanism of acetaldehyde remain unexplained. However in detail studies are needed to establish the photochemical formation/degradation of carbonyls.

Good positive correlations between ambient temperature and CCs were observed during postmonsoon. It was reported in few studies that increasing temperature increases the emission of formaldehyde and acetaldehyde from wood and building materials (Parthsarathy et al., 2011; Suzuki et al., 2014). Thus temperature also played positive role to building up the CC concentration over the hill station during postmonsoon season.

However, we did not observe any significant correlations between CCs and meteorological parameters during monsoon season.

**Formaldehyde to Acetaldehyde Ratio (C1/C2)**

The concentration ratio of formaldehyde to acetaldehyde (C1/C2) can be used to define the nature of the study area. Over the urban areas, the ratio varies between 1–2 (Feng et al., 2005; Cerón et al., 2007; Huang et al., 2008; Dutta et al., 2009; de M. Ochs et al., 2011), whereas over the rural areas the ratio becomes much higher, ~10 (Shepson et al., 1991; Possanzini et al., 1996). The probable reason for different C1/C2 ratios is the different sources of formaldehyde and acetaldehyde over different areas. Formaldehyde and acetaldehyde both have similar anthropogenic sources over urban areas like combustion of fossil fuel. But over rural areas, formaldehyde has significant biogenic source (Possanzini et al., 1996) whereas acetaldehyde does not.
Fig. 5. Day/Night ratio of carbonyl compounds during different seasons.

Hence over the urban areas the ratio varies between 1–2 when formaldehyde and acetaldehyde both have similar anthropogenic sources whereas the ratio increases significantly when rural biogenic sources play major role in production of formaldehyde and not acetaldehyde.

In the present study the annual average C1/C2 ratio value over Darjeeling was 1.64 ± 1.43 and comparable with that over an Indian mega city Kolkata (Day time: 1.32–1.59, night time: 1.44–1.89, Dutta et al., 2009). Thus Darjeeling represents a typical urban atmosphere over this part of Himalaya. The ratio values for different seasons are given in Table 6. The ratio was found to be maximum during premonsoon followed by winter, monsoon and postmonsoon. The higher C1/C2 ratio could be explained by the higher photochemical activities during the premonsoon season. The higher reaction rate constant of acetaldehyde (1.5 × 10^{11} cm^3 molecule^{-1} s^{-1}) than formaldehyde (0.9 × 10^{11} cm^3 molecule^{-1} s^{-1}) with respect to OH radical reaction (Atkinson and Arey, 2003) could be responsible for more photochemical loss of acetaldehyde during premonsoon and hence the ratio increased in this season. On the other hand, acetaldehyde generated from vehicular emissions could not get photochemically degraded during postmonsoon as the solar radiation flux was much lower in this season and hence the ratio value decreased to 0.7.

In addition to vehicular emission and secondary photochemical production biomass burning is a common practice by the local people in winter producing more formaldehyde than acetaldehyde (Holzinger et al., 1999; Akagi et al., 2011) in the atmosphere which actually elevated C1/C2 ratio during the winter season. Thus, in winter, direct emission of formaldehyde from biomass burning dominates over the meteorological control like solar radiation fluxes.

**Acetaldehyde to Propanaldehyde Ratio (C2/C3)**

The ratios of acetaldehyde to propanaldehyde (C2/C3) on annual and seasonal scale are given in Table 6. C2/C3 ratio is often used to determine whether the carbonyls have any anthropogenic sources (Ho et al., 2002b) as propanaldehyde is mainly considered to be anthropogenic origin (Anderson et al., 1996). This ratio is found to be higher in rural atmosphere than the urban atmospheres (Feng et al., 2005). Maximum value for C2/C3 ratio was observed during postmonsoon followed by monsoon, winter and premonsoon. The annual average C2/C3 ratio in the present study was 8.8 ± 11.8 which was higher than the study made over Kolkata (5.05, Dutta et al., 2009). However the minimum ratio value in premonsoon over Darjeeling (even lower than annual average ratio over Kolkata) indicates the major anthropogenic activities during this season.

**Source Apportionment Using Positive Matrix Factorization Model (PMF)**

PMF (version 5.0) was used to apportion the sources of carbonyl compounds over Darjeeling. Positive Matrix Factorization has been extensively used to identify the sources of pollutants in many studies in recent years (e.g., Jorquera and Rappengluck, 2004; Latella et al., 2005; Xie
and Berkowitz, 2006; Brown et al., 2007; Song et al., 2007; Yuan et al., 2009). This source apportionment model does not require any prior knowledge on the exact emission profiles of the individual pollutants but source contributions can be determined based on observations at the receptor site. In brief, a parameter Q is calculated by the model which is the measure of the goodness of the fit parameters. Q (true) is calculated including all data points where Q (robust) is calculated excluding data points not fit by the model. The difference between Q (true) and Q (robust) is the measure of the impact of data points with high scaled residuals whereas high uncertainties result in similar Q values. Q (robust) is used to choose the optimal run from the multiple runs. If the number of sources is estimated properly, Q (robust) will have little variability between the runs and thus we get stable Q. The variability of Q (robust) is the indication of the variability of initial base run results. More details about the PMF model can be found in several other studies (Paatero and Tapper, 1994; Paatero, 1997; Reff et al., 2007).

Six factors were resolved from the analysis. The percentage contribution of each factor and the percentage contribution of each CC in all the factors are shown in Fig. 6. Factor 1: The first factor was loaded mainly with acetone (92%) and the contributions of other CCs were almost negligible in this factor. We have already discussed in the previous section about the formation of acetone from its precursor VOC emitted from the tea plants. Thus this factor could be attributed to the biogenic emission from tea gardens. The contribution of this factor was maximum (43%) amongst all the other sources.

Factor 2: The contribution of factor 2 was 16%. Maximum loading of butanaldehyde and hexanaldehyde were present in this factor. A significant amount of acetone was also present in this factor. Several studies have identified the presence of these CCs in diesel exhaust emissions (Grosjean et al., 2001; Kean et al., 2001; Jacobet et al., 2008; Dong et al., 2014). High number of heavy duty trucks and 4 wheelers driven by diesel engines are the major transports over Darjeeling. Thus diesel driven vehicular emission could be a significant source of CCs over the study area. Factor 2 could be attributed to the diesel exhaust emissions.

Factor 3: This factor had the third highest (15%) contribution among the sources identified by PMF. Crotonaldehyde and acetone were the major CCs of this factor. Both crotonaldehyde and acetone are generated from industrial sources (Graedel et al., 1986; Grosjean 1990; Salgado, 2008). Many industries like paint manufacturing and petrochemical refinery uses acetone as the chemical solvent (Battig and Grandjean, 1964; Feng et al., 2005). Though these types of industries are not present over the hill station but these CCs could be transported (due to their higher atmospheric lifetime) to the study region from the polluted foot hill regions and other IGP regions which is the main industrial region in India. Thus factor 3 could be attributed to the industrial source.

Factor 4: This factor has similar contribution (15%) like factor 2 containing formaldehyde, acetaldehyde and hexanaldehyde mostly. Formaldehyde, acetaldehyde and hexanaldehyde have the common primary source of gasoline driven vehicular emission (Corrêa et al., 2003; Jacobson, 2007; Tunsaringkarn et al., 2012). In addition to the vehicular emission, formaldehyde and acetaldehyde could also be produced from secondary photochemical production from other primary VOCs. Thus it is not possible to assign factor 4 to a single particular source rather we have assigned factor 4 as gasoline exhaust/secondary production.

Factor 5: Contribution of Factor 5 was much less (8%) compared to the other factors. Iso-valeraldehyde and valeraldehyde are the major CCs present in this factor. These compounds are emitted during the processing/fermentation (oxidation) of tea leaves, the intermediate step for the preparation of black tea and oolong tea (Runeckles and Tso, 2013; Panda, 2016). There are many tea processing industries present over Darjeeling. Thus factor 5 could be attributed to the tea processing industries.

Factor 6: Propanaldehyde is the main contributing CC in this factor along with hexanaldehyde and acetone. This factor contributes only 3% to the total CC concentration. Propanaldehyde, hexanaldehyde and acetone together could be emitted from the waste dumping areas as reported by many other studies (US DHHS, 1993; Eitzer, 1995; Jay and Stieglitz, 1995, Majumdar et al., 2014). It has been discussed in the previous sections that the sewage system is very poor and the waste disposal system is very unscientific over Darjeeling. Thus factor 6 could be attributed to the human waste disposal.

Table 6. The average formaldehyde/acetaldehyde (C1/C2) and acetaldehyde/propanaldehyde (C2/C3) ratios during different season.

<table>
<thead>
<tr>
<th>Season</th>
<th>C1/C2 Mean ± SD</th>
<th>C2/C3 Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monsoon</td>
<td>1.10 ± 1.16</td>
<td>10.00 ± 10.51</td>
</tr>
<tr>
<td>Premonsoon</td>
<td>0.70 ± 0.77</td>
<td>6.52 ± 9.17</td>
</tr>
<tr>
<td>Winter</td>
<td>1.84 ± 1.02</td>
<td>3.77 ± 2.38</td>
</tr>
<tr>
<td>Premonsoon</td>
<td>2.52 ± 1.75</td>
<td>8.76 ± 11.78</td>
</tr>
<tr>
<td>Annual</td>
<td>1.64 ± 1.43</td>
<td>15.71 ± 20.83</td>
</tr>
</tbody>
</table>

Photochemical Reactivity and Ozone Formation Potential of Carbonyls

CCs react with OH radical to produce tropospheric ozone depending on the availability of NO, and non-methane VOC (NMVOC) concentrations (Carter, 1994). The propene-equivalent concentration (prop-equiv) (Chameides et al., 1992; So and Wang, 2004) and the maximum incremental reactivity (MIR) (Carter, 1994) scale were introduced to
estimate the reactivity of each CC towards OH radical reaction and to calculate the contribution of each CC for the photochemical production of tropospheric O$_3$. The propane equivalent concentration of a carbonyl compound is given by

$$\text{prop-equiv}(j) = \text{conc}(j) \times \frac{k_{OH}(j)}{k_{OH}(C_3H_6)}$$

(9)

where prop-equiv $(j)$ is the propane equivalent concentration of $j^{th}$ carbonyl species expressed in $\mu g \ m^{-3}$, conc $(j)$ is the concentration of $j^{th}$ carbonyl species expressed in $\mu g \ m^{-3}$, $k_{OH}(j)$ is the rate constant of $j^{th}$ carbonyl species with respect to OH radical reaction. The individual rate constant values are taken from Atkinson and Arey (2003). $k_{OH}(C_3H_6)$ is the OH rate constant of propane.

The reaction with the OH radical is the primary step for the oxidation of CCs, thus prop-equiv concentration is an indicator of the relative contribution made by each CC to the total flux of VOCs being oxidized in the area. The prop-equiv concentration of each carbonyl species are summarized in Table 7.

The significance of prop-equiv $(j)$ of $j^{th}$ carbonyl species lies in the measure of the concentration of CC$(j)$ on an OH-reactivity based scale normalized to the reactivity of propene. The total prop-equiv concentration for all the CCs measured varied over a wide range from 368 $\mu g \ m^{-3}$ during winter to 6252 $\mu g \ m^{-3}$ during postmonsoon season. The mean annual average prop-equiv concentration was 1945 $\mu g \ m^{-3}$. Crotonaldehyde had the maximum annual prop-equiv concentration of 578.5 $\mu g \ m^{-3}$ accounting for ~30% of total concentration followed by acetaldehyde (15%) and butanaldehyde (14%). It could be noted that though acetone had the maximum concentration in all the seasons but due to very low reactivity toward OH radical, acetone had the least prop-equiv concentration of 12.7 $\mu g \ m^{-3}$. This accounted for only <1% to the total concentration.
Table 7. The propane equivalent concentration of total and individual CCs during different seasons.

<table>
<thead>
<tr>
<th></th>
<th>$10^{12} \times K_{OH}$</th>
<th>Annual</th>
<th>Monsoon</th>
<th>Postmonsoon</th>
<th>Winter</th>
<th>Premonsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>9.37</td>
<td>89.6</td>
<td>78.2</td>
<td>279.2</td>
<td>30.1</td>
<td>61.4</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>15.00</td>
<td>285.0</td>
<td>183.6</td>
<td>1090.2</td>
<td>29.8</td>
<td>68.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.17</td>
<td>31.3</td>
<td>14.2</td>
<td>122.6</td>
<td>9.0</td>
<td>8.1</td>
</tr>
<tr>
<td>Propanaldehyde</td>
<td>20.00</td>
<td>527.7</td>
<td>17.1</td>
<td>187.1</td>
<td>12.9</td>
<td>36.2</td>
</tr>
<tr>
<td>Butanaldehyde</td>
<td>24.00</td>
<td>267.9</td>
<td>108.4</td>
<td>1226.1</td>
<td>8.9</td>
<td>11.1</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>48.00</td>
<td>578.5</td>
<td>1039.0</td>
<td>970.8</td>
<td>204.6</td>
<td>95.0</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>12.00</td>
<td>102.5</td>
<td>112.2</td>
<td>351.1</td>
<td>1.9</td>
<td>5.9</td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>27.00</td>
<td>141.4</td>
<td>59.0</td>
<td>602.8</td>
<td>23.0</td>
<td>23.8</td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>28.00</td>
<td>204.4</td>
<td>165.2</td>
<td>740.8</td>
<td>35.7</td>
<td>26.1</td>
</tr>
<tr>
<td>o-Tolualdehyde</td>
<td>18.00</td>
<td>16.1</td>
<td>5.4</td>
<td>70.7</td>
<td>1.2</td>
<td>4.0</td>
</tr>
<tr>
<td>p-Tolualdehyde</td>
<td>13.00</td>
<td>32.5</td>
<td>40.7</td>
<td>75.8</td>
<td>4.7</td>
<td>15.9</td>
</tr>
<tr>
<td>Hexanaldehyde</td>
<td>30.00</td>
<td>151.3</td>
<td>79.4</td>
<td>627.3</td>
<td>9.4</td>
<td>30.2</td>
</tr>
<tr>
<td>Total</td>
<td>1953.4</td>
<td>1902.4</td>
<td>6353.4</td>
<td>368.4</td>
<td>368.4</td>
<td>391.1</td>
</tr>
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</table>

O$_3$ formation potential (OFP) of CCs can be calculated as the product of the MIR coefficient of a CC and the concentration of that CC. The maximum incremental reactivity (MIR) of a carbonyl is operationally defined as the change in maximum ozone production by a small increase in emissions of that carbonyl species. MIR coefficient is dimensionless and can be defined as gram of O$_3$ produced per gram of carbonyl species. MIR coefficients for CCs were taken from Carter (2007). OFP was thus calculated as follows:

$$O_3 \text{ formation potential (j)} = \text{Concentration (j)} \times \text{MIR coefficient (j)}$$ (10)

Table 8 represents the OFP values of each CC in $\mu$g m$^{-3}$. The total annual average OFP was found to be 558 $\mu$g m$^{-3}$ and this high value of OFP indicates that carbonyl compounds could play significant role in tropospheric ozone formation over Darjeeling. The OFP varied from 127 $\mu$g m$^{-3}$ during premonsoon to 1770 $\mu$g m$^{-3}$ during postmonsoon season suggesting more secondary tropospheric ozone formation through the oxidation of volatile organic compounds during postmonsoon. Acetaldehyde had the maximum OFP followed by crotonaldehyde and formaldehyde. Acetaldehyde contributed 23.5% of total ozone formation followed by crotonaldehyde (21.5%) and formaldehyde (19.3%). Rest of the carbonyls contributed ~35% to the total tropospheric ozone formation. Hence, we observed that acetaldehyde and crotonaldehyde had higher propane equivalent concentration as well as higher OFP indicating that they are the most potential carbonyl compounds to form tropospheric ozone over Darjeeling.

CONCLUSIONS

The first ever year-long study on atmospheric carbonyl compounds over Indian Himalaya was conducted where samples were collected from a high altitude station, Darjeeling (27.01°N, 88.15°E, 2200 masl). The major findings of the study are as follows:

- Major carbonyl compounds like formaldehyde and acetaldehyde over Darjeeling were found to be comparable and higher than some of the metro cities in India and other parts of the world. Carbonyl compound concentrations over Darjeeling were also higher than Bhutan, a high altitude state at eastern Himalaya.
- Acetone over Darjeeling had the maximum abundance and its concentration was much higher compared to other carbonyls. It was even higher than that over other parts of the world. In addition to various anthropogenic sources, biogenic emissions of volatile organic compounds from tea plants followed by their photochemical transformation also played significant role in building up such high acetone in the atmosphere of Darjeeling.
- Carbonyl compounds showed distinct seasonal variation with the maximum concentrations during postmonsoon followed by monsoon, rainy–premonsoon. Surface reaching solar radiation played major role in photochemical production/degradation of carbonyl compounds over Darjeeling. In spite of higher vehicular activities, photochemical degradation due to higher solar radiation flux reduced the atmospheric loading of carbonyl compounds during premonsoon. On the other hand, low solar radiation along with higher vehicular activities helped in accumulating carbonyl compounds during postmonsoon.
- Most of the carbonyl compounds showed higher concentrations during day time except acetone and butanaldehyde during winter and postmonsoon. Biomass/wood burning by the local habitants of Darjeeling during colder nights could enhance the night time concentrations of acetone and butanaldehyde.
- Formaldehyde to acetaldehyde (C1/C2) concentration ratio over Darjeeling represents Darjeeling as a typical urban station at eastern part of Himalaya. Acetaldehyde to propanaldehyde (C2/C3) ratio showed higher anthropogenic activities during premonsoon.
- Higher propane equivalent concentration and ozone formation potential suggests that more tropospheric ozone could be produced through the oxidation of volatile organic compounds during postmonsoon and acetaldehyde and crotonaldehyde were the potential carbonyl compounds to form tropospheric ozone.
- Six major sources of carbonyl compounds were identified by PMF model analysis. Biogenic emissions from tea
Table 8. Maximum incremental reactivity and ozone formation potential of individual carbonyl species.

<table>
<thead>
<tr>
<th>Carbonyl Compound</th>
<th>MIR</th>
<th>Annual</th>
<th>Monsoon</th>
<th>Postmonsoon</th>
<th>Winter</th>
<th>Premonsoon</th>
</tr>
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<tr>
<td>Formaldehyde</td>
<td>9.24</td>
<td>107.5</td>
<td>84.1</td>
<td>300.1</td>
<td>32.3</td>
<td>66.0</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>6.34</td>
<td>131.3</td>
<td>84.6</td>
<td>502.3</td>
<td>13.7</td>
<td>31.5</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.35</td>
<td>28.6</td>
<td>31.8</td>
<td>48.5</td>
<td>20.2</td>
<td>18.2</td>
</tr>
<tr>
<td>Propanaldehyde</td>
<td>6.83</td>
<td>19.6</td>
<td>6.4</td>
<td>69.6</td>
<td>4.8</td>
<td>13.5</td>
</tr>
<tr>
<td>Butanaldehyde</td>
<td>5.75</td>
<td>70.0</td>
<td>28.3</td>
<td>322.8</td>
<td>1.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>9.14</td>
<td>120.1</td>
<td>215.6</td>
<td>201.5</td>
<td>42.5</td>
<td>19.7</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>–0.67</td>
<td>–6.2</td>
<td>–6.8</td>
<td>–21.3</td>
<td>–0.1</td>
<td>–0.4</td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>4.79</td>
<td>27.3</td>
<td>11.4</td>
<td>116.6</td>
<td>4.4</td>
<td>4.6</td>
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<tr>
<td>Valeraldehyde</td>
<td>4.89</td>
<td>38.9</td>
<td>31.4</td>
<td>141.0</td>
<td>6.8</td>
<td>5.0</td>
</tr>
<tr>
<td>α-Tolualdehyde</td>
<td>–0.54</td>
<td>–0.5</td>
<td>–0.2</td>
<td>–2.3</td>
<td>0.0</td>
<td>–0.1</td>
</tr>
<tr>
<td>p-Tolualdehyde</td>
<td>–0.54</td>
<td>–1.5</td>
<td>–1.8</td>
<td>–3.4</td>
<td>–0.2</td>
<td>–0.7</td>
</tr>
<tr>
<td>Hexanaldehyde</td>
<td>4.18</td>
<td>23.0</td>
<td>12.1</td>
<td>95.3</td>
<td>1.4</td>
<td>4.6</td>
</tr>
<tr>
<td>Total</td>
<td>558.0</td>
<td>496.8</td>
<td>1770.5</td>
<td>127.4</td>
<td>166.1</td>
<td></td>
</tr>
</tbody>
</table>

The high atmospheric loading of carbonyl compounds over Darjeeling is of a serious concern from the point of view of human health and sensitive ecosystem over this part of Indian Himalaya. Thus it is imperative to control vehicular pollution, solvent usage, adopt proper and scientific waste management system etc which are the major causes of carbonyls and other gaseous and particulate carbonaceous pollutants as well over Darjeeling.

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