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Seasonal variations of water-soluble organic carbon, dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls in Central Himalayan aerosols

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Abstract. Aerosol samples were collected from a high elevation mountain site (Nainital, India; 1958 m a.s.l.) in the central Himalayas, a location that provides an isolated platform above the planetary boundary layer to better understand the composition of the remote continental troposphere. The samples were analyzed for water-soluble dicarboxylic acids (C_2-C_{12}) and related compounds (ketocarboxylic acids and α-dicarbonyls), as well as organic carbon, elemental carbon and water soluble organic carbon. The contributions of total dicarboxylic acids to total aerosol carbon during wintertime were 1.7 % and 1.8 %, for day and night, respectively whereas they were significantly smaller during summer. Molecular distributions of diacids revealed that oxalic (C_2) acid was the most abundant species followed by succinic (C_4) and malonic (C_3) acids. The average concentrations of total diacids (433 ± 108 ng m^{-3}), ketoacids (48 ± 23 ng m^{-3}), and α-dicarbonyls (9 ± 4 ng m^{-3}) were similar to those from large Asian cities such as Tokyo, Beijing and Hong Kong. During summer most of the organic species were several times more abundant than in winter. Phthalic acid, which originates from oxidation of polycyclic aromatic hydrocarbons such as naphthalene, was found to be 7 times higher in summer than winter. This feature has not been reported before in atmospheric aerosols. Based on molecular distributions and air mass backward trajectories, we conclude that dicarboxylic acids and related compounds in Himalayan aerosols are derived from anthropogenic activities in the highly populated Indo-Gangetic plain areas.

1 Introduction

Understanding the physical and chemical properties of background aerosols is important in order to determine the source regions, elucidate the mechanism of long-range transport of anthropogenic pollutants and validate both regional and global atmospheric models. The Indian Ocean Experiment (INDOEX) was an international, multiplatform field campaign to assess the climatic and chemical influence of anthropogenic aerosols toward the Indian Ocean (Satheesh and Ramanathan, 2000). From the INDOEX campaign it was established that, during winter, this region would be covered by anthropogenic aerosols carrying sulphate, nitrate, organics, soot and fly ash via long-range transport of air pollution from South and Southeast Asia (Lelieveld et al., 2001). Remote areas of the world were once thought to be less influenced by human atmospheric perturbation, and hence they could provide an opportunity to evaluate the natural background levels of chemical species as well as the effect of anthropogenic pollutants on global atmospheric chemistry (Lee et al., 2003).

The Himalayan Mountain range is located in a remote area of the Asian continent. During the last three decades, chemical studies of aerosols and snow in the Himalayan region have become of great interest in order to evaluate the impact of anthropogenic pollution over the high elevation mountain regions. Several studies have been reported from the northern slope of the Himalayas (Mayewski et al., 1983; Wake et al., 1994; Shrestha et al., 1997; Shrestha et al., 2000; Shrestha et al., 2002) and also from lower elevations in middle Himalayan region (Shrestha et al., 2010). Wake et al. (1994)

studied aerosol samples collected from the southern slopes of the Himalayas to the northern margin of the Tibetan Plateau and reported high concentrations of organic compounds. The influence of anthropogenic pollutants over the Himalayan region originating from Indian subcontinent has been debated in recent years (Gautam et al., 2010). Recently, Decesari et al. (2010) reported the orographic transport of carbonaceous and sulphate aerosols upslope the Himalayas, showing that valley wind circulation brings anthropogenic aerosols into the Asian upper troposphere (>5000 m a.s.l.). Similar observations for black carbon (BC) aerosols were made by Marinoni et al. (2010) over the Nepal Climate Observatory-Pyramid, a permanent high-altitude research station located in the Khumbu valley (5079 m a.s.l.) below Mt. Everest. All these studies revealed that the remote mountainous region and, to some extent, the middle-upper troposphere are polluted by human activities.

Studies of organic aerosols at the molecular level are limited because of their complexity and thus difficulties in their measurements. Previous studies, however, demonstrated that water-soluble organic compounds account for a significant fraction (28–77 %) of organic aerosol mass (Saxena et al., 1995; Kawamura et al., 2003). Among the water-soluble organic compounds, low molecular weight dicarboxylic acids with a predominance of oxalic acid have been found as an important fraction of organic aerosols in the continental and marine atmosphere (Kawamura and Ikushima 1993; Kawamura and Sakaguchi 1999; Kawamura et al., 2004). Due to their hygroscopic property, diacids play an important role in the global radiative balance (Saxena et al., 1995; Facchini et al., 1999; Kerminen, 2001). These species are directly emitted to the atmosphere from natural and anthropogenic sources or secondarily produced by atmospheric chemical reactions (Kawamura and Kaplan, 1987; Schauer et al., 1999; Simoneit et al., 2005). However, data about diacids are limited in remote South Asia including the Himalayan region. On average, over the entire Indian subcontinent, chemical mass balance studies based on the ISRO-GBP campaign (Indian Space Research Organization - Geosphere Biosphere Programme) have estimated the particulate organic matter contribution to be about 20–30 % of the total aerosol mass load (George et al., 2008).

Over south Asia, the Indo-Gangetic plain is recognized as an especially densely populated region and thus as a potentially strong source region of anthropogenic aerosols (Tripathi et al., 2005; Ram et al., 2010). The Himalaya Mountain range exists over the northern part of these highly populated and industrialized areas. Due to its high elevation, the Himalayan range acts as a boundary limiting the northern extent of the Indian summer monsoon, and therefore observations at a high altitude location, Nainital (29.4° N; 79.5° E, 1958 m a.s.l.), would provide information about emissions over the Indian subcontinent. Our observation site is located at the highest mountain top (over the Kumaon region) and about 2 km from Nainital City (population ˜0.5 million). The site is devoid of any major local pollution sources and is generally free from snow coverage during most of the time. The north and northeast sides of study area are characterized by sharply peaking topography of the Himalayan Mountain range, whereas on the south-western side plains with very low elevation (<500 m a.s.l.) merge into the densely populated Ganga basin.

To better understand the atmospheric chemistry of organic aerosols in the Himalayan range, we collected aerosol samples at Nainital at the foothills of the central Himalayas and performed measurements of organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC), dicarboxylic acids and related compounds. Here, we report molecular distributions of water-soluble organic compounds that would provide unique information about their sources and formation pathways. Multiple sources of organic aerosols are also discussed based on air mass backward trajectories and regional meteorology.
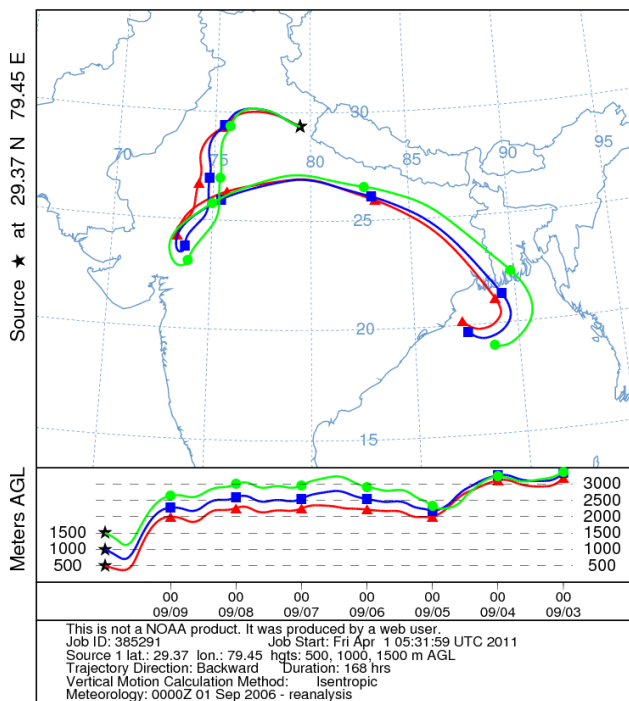
2   Experimental

2.1   Meteorology

The climate of this part of the Asian continent is mainly controlled by air masses originating from the Arctic (western disturbances), continental air masses from central Asia, and maritime air masses from the Pacific and Indian Oceans (Indian summer monsoon). The Himalayan Mountain range plays a key role in the regional climate. It blocks the midlatitudinal westerlies and splits the westerly jet into north and the south pathways over the Tibetan Plateau. During winter months, western disturbances (synoptic scale low pressure weather systems) frequently occur over the northwestern part of India. These cold air masses originate over the Mediterranean Sea and Atlantic Ocean and bring high moisture and snowfall over the high altitude locations.
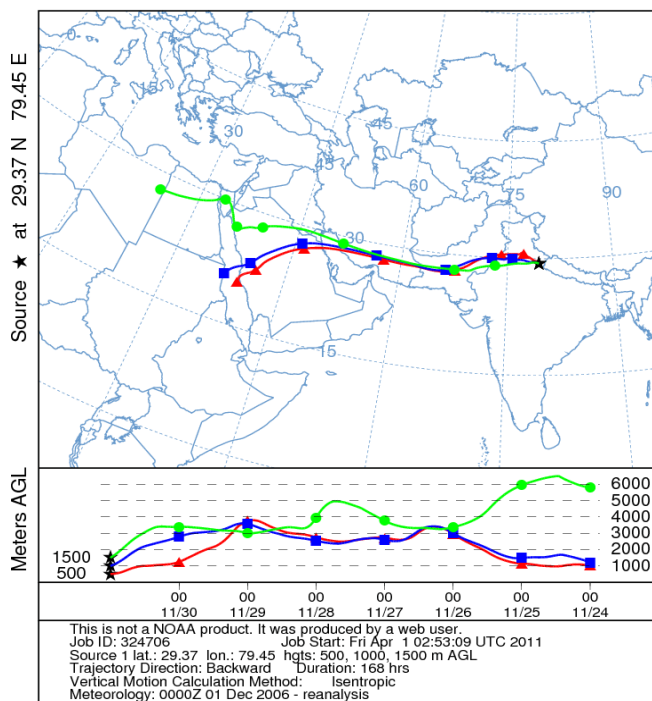
A common method for the identification of the origin and the pathway of air masses is to calculate backward trajectories. Fig. 1 gives the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Trajectory (HYSPLIT) model (24 h interval; FNL Meteorological Data: Draxler and Rolph, 2010; Rolph, 2010) seven day backward trajectories illustrating typical air-mass flows from different parts of the Indian subcontinent to the study area (Nainital) at three different heights (500 m, 1000 m and 1500 m above ground level). It is important to note that air masses at this site do not arrive from the north and northeastern sector in any season because of high mountains in that direction. From the air mass trajectories it is clear that during mid September the winds circulate mostly over the Northern Indian region and change gradually to westerly by early December, while during the first week of March air masses remain westerly/southwesterly. The trajectory patterns change

Winter 2006

NOAA HYSPLIT MODEL
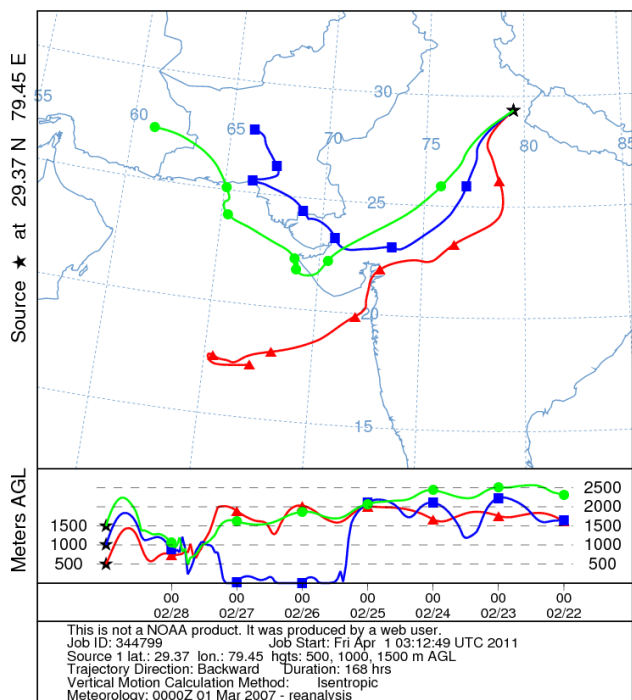Backward trajectories ending at 0000 UTC 10 Sep 06
CDC1 Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 01 Dec 06
CDC1 Meteorological Data

This is not a NOAA product. It was produced by a web user.
Job ID: 385291   Job Start: Fri Apr 1 05:31:59 UTC 2011
Source 1 lat.: 29.37 lon.: 79.45 hgts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward   Duration: 168 hrs
Vertical Motion Calculation Method: Isentropic
Meteorology: 0000Z 01 Sep 2006 - reanalysis

This is not a NOAA product. It was produced by a web user.
Job ID: 324706   Job Start: Fri Apr 1 02:53:09 UTC 2011
Source 1 lat.: 29.37 lon.: 79.45 hgts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward   Duration: 168 hrs
Vertical Motion Calculation Method: Isentropic
Meteorology: 0000Z 01 Dec 2006 - reanalysis

Summer 2007

NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 01 Mar 07
CDC1 Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 10 Jun 07
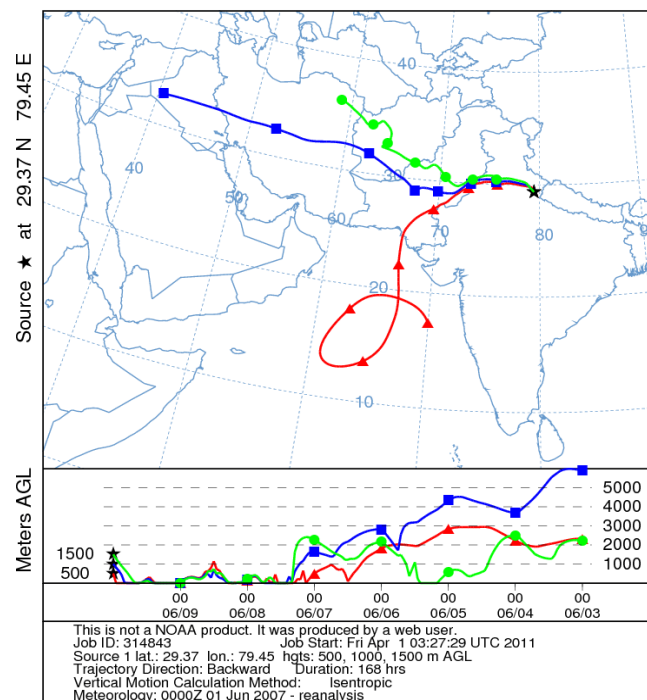CDC1 Meteorological Data

This is not a NOAA product. It was produced by a web user.
Job ID: 344799   Job Start: Fri Apr 1 03:12:49 UTC 2011
Source 1 lat.: 29.37 lon.: 79.45 hgts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward   Duration: 168 hrs
Vertical Motion Calculation Method: Isentropic
Meteorology: 0000Z 01 Mar 2007 - reanalysis

This is not a NOAA product. It was produced by a web user.
Job ID: 314843   Job Start: Fri Apr 1 03:27:29 UTC 2011
Source 1 lat.: 29.37 lon.: 79.45 hgts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward   Duration: 168 hrs
Vertical Motion Calculation Method: Isentropic
Meteorology: 0000Z 01 Jun 2007 - reanalysis

Fig. 1. Air mass backward trajectory cluster during the study period reaching Nainital (star symbol) to illustrate the long-range transport.
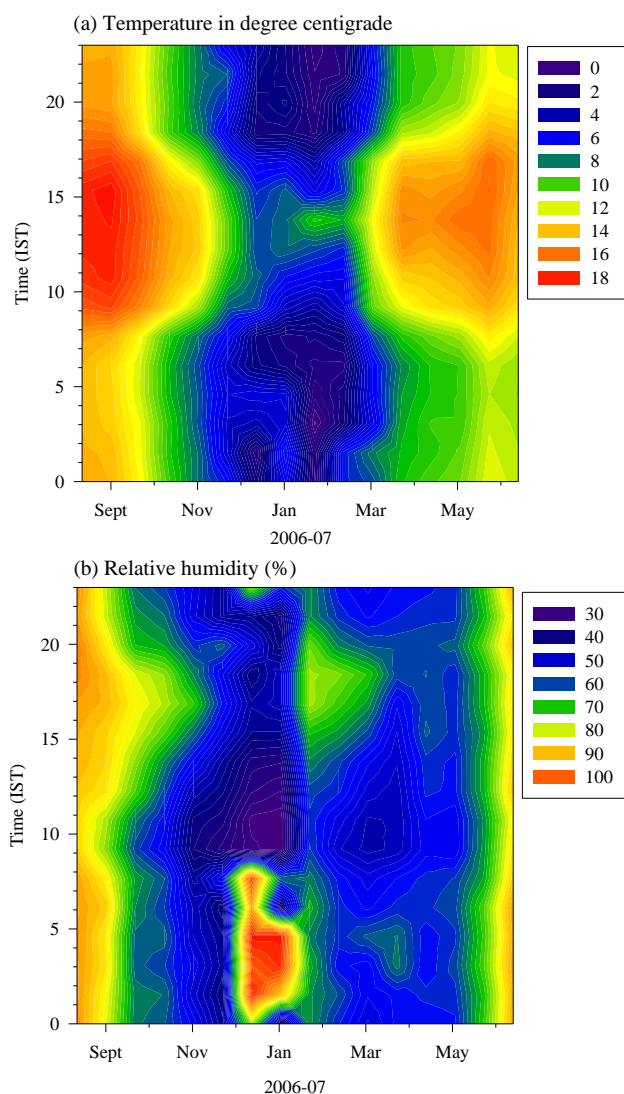
Fig. 2. Monthly mean diurnal and seasonal variation of **(a)** ambient air temperature (in degree centigrade) and **(b)** relative humidity (%) measured over the observational site during the study period.

again from southwesterly to westerly/northwesterly during mid June. Such shifts in wind pattern are observed every year.

A similar trend of change in wind direction was also noticed from surface observation by an automated weather station (AWS). Standard meteorological sensors (AWS; Dynalab, India; Campbell Scientific Inc., Canada) were used for observations of meteorological parameters. The daily mean diurnal and seasonal variation for temperature and relative humidity are shown in Fig. 2a and b, respectively. By the end of September temperature gradually started to decrease from maximum of 16 °C to minimum of 0 °C by December and January. With beginning of summer months, temperatures raised to a daytime maximum of 18 °C. Significant diurnal variation in temperature is noticed. Higher temperatures are recorded during afternoon hours and are more promi-

nent during summer months. Contemporaneous with temperature, relative humidity also shows a seasonal trend. As the monsoon rains withdraw (during September), the relative humidity gradually decreases down to 40 %. December months retain moderate to high relative humidity (50 % to 90 %). March, April and May months are relatively dry (<50 %). The mean wind speed recorded was <4 m s^{-1} during winter months, whereas during summer months it almost doubled (figure not shown). The topography around the observation site and the general meteorology prevailing during different seasons has been discussed in detail by Sagar et al. (2004) and Pant et al. (2006).

2.2 Aerosol sampling

Aerosol samples were collected from single-stage high volume sampler (Model GH2000 of Graseby Anderson, USA) using quartz fiber filters (Whatman QMA4) of 9 cm in diameter. Sampling was carried out on the terrace of a building (20 m above ground level) from September 2006 to January 2007 and March to June 2007 (hereafter referred as winter and summer seasons, respectively). During winter season, the samples were collected for daytime (9 a.m. to 6 p.m., $N = 9$) and nighttime (7 p.m. to 8 a.m., $N = 9$), whereas during summer the sampling hours were shorter; daytime (10 a.m. to 1 p.m., $N = 11$) and nighttime (8 p.m. to 11 p.m., $N = 10$). Two filters were collected in a day representing daytime and nighttime samples. During winter season, sampling frequency was 15 days, whereas during summer period the samples were collected more often; (~10 days). The flow rate of the sampler was set at 400 L min^{-1}. Field blanks were collected by putting another set of filters in the sampler for the same duration without operating the sampler. Before sampling, filter papers were pre-heated at 400 °C in an electric furnace using aluminum foil. The filters were tare-weighed using a microbalance (Mettler Model AT 20 with a sensitivity of ±2 µg) and preserved ~−4 °C in a freezer until further chemical analysis.

2.3 Chemical analysis

Concentrations of total suspended particulate matter (TSPM) in air were calculated gravimetrically on the basis of volume of air sampled and the weight of the aerosol particles. The filter papers were conditioned in a desiccator for about 48 h before and after sampling. To measure water-soluble organic carbon (WSOC), 1.4 cm in diameter filter disc was extracted with organic-free Milli-Q water using ultrasonication for 15 min. The water extracts were subsequently passed through a syringe filter (Millex-GV, 0.22 µm, Millipore), and WSOC was measured using a total organic carbon (TOC) analyzer (Shimadzu, TOC–V$_{CSH}$) equipped with a catalytic oxidation column/nondispersive infrared detector (Aggarwal and Kawamura, 2008). The sample was measured three times and the average value was used in this study. Before the sample

analysis, external calibration was performed using potassium hydrogen phthalate. The analytical error of the measurement was 15 % with a detection limit of $0.1 \, \mu g \, C \, m^{-3}$.

OC and EC in the samples were measured using a OC/EC analyzer (Sunset Laboratory Inc., Portland, OR, USA) following the Interagency Monitoring of Protected Visual Environments (IMPROVE-B) thermal protocol (Agarwal et al., 2010). A filter punch (area $1.5 \, cm^2$) of the sample was placed in a quartz tube which was placed inside the thermal desorption chamber of the analyzer. OC concentrations were determined in helium atmosphere at ~120, 250, 450 and 550 °C. Subsequently, oxygen (2 %) was introduced and EC concentrations were determined at temperatures from ~550 to 900 °C. The pyrolytic conversion of OC to EC was monitored and corrected by using a He-Ne laser. The calibration of the instrument was performed using a known amount of sucrose at 4 different concentrations (20, 40, 60 and 80 μgC). The detection limits of OC and EC, which are defined as three times the standard deviation of field blanks, were 0.26 and $0.01 \, \mu gCm^{-3}$, respectively. Conversely, these values are lower than the detection limit of $0.5 \, \mu gCm^{-3}$ provided by the manufacturer.

Samples were analyzed for diacids, ketoacids, and α-dicarbonyls using a method reported previously (Kawamura and Ikushima, 1993; Kawamura, 1993) with a pH adjustment of the water extracts to pH= 8.5–9.0 with 0.1 M KOH. Briefly, a part of the quartz-filter was cut into pieces and extracted with ultrapure Milli-Q water (10 mL ×3) using ultrasonication for about 10 min. After filtration with quartz wool, the filtrate was transferred to a 50 ml flask and concentrated to almost dryness using a rotary evaporator under vacuum. The extracts were then converted to dibutyl esters and/or dibutoxy acetals with 14 % BF_3/n-butanol at 100 °C. The butyl esters and acetals were extracted with n-hexane. The derivatised fractions were analyzed using a capillary HP 6890 gas chromatograph (GC). Peak identification was performed by GC retention times of authentic standards and confirmed by mass spectral examination using a GC-mass spectrometer (GC-MS) system.

We spiked free diacid standards on precombusted quartz fiber filters in order to evaluate the recovery. They were extracted and analyzed the same as real samples. The recoveries of authentic standards were 92 % for oxalic acid and greater than 95 % for malonic, succinic, and adipic acids. With pH adjustment, the recovery of oxalic acid was improved. The variations due to analytical errors for duplicate analysis of the filter sample were within 10 % for all the measured major species. Field and laboratory blanks showed minute peaks for oxalic, phthalic, and glyoxylic acids. Nevertheless, their amounts were less than 2 % of the actual samples. Concentrations of all diacids and related compounds reported here are corrected for field blanks, but not for recoveries.

3 Results and discussion
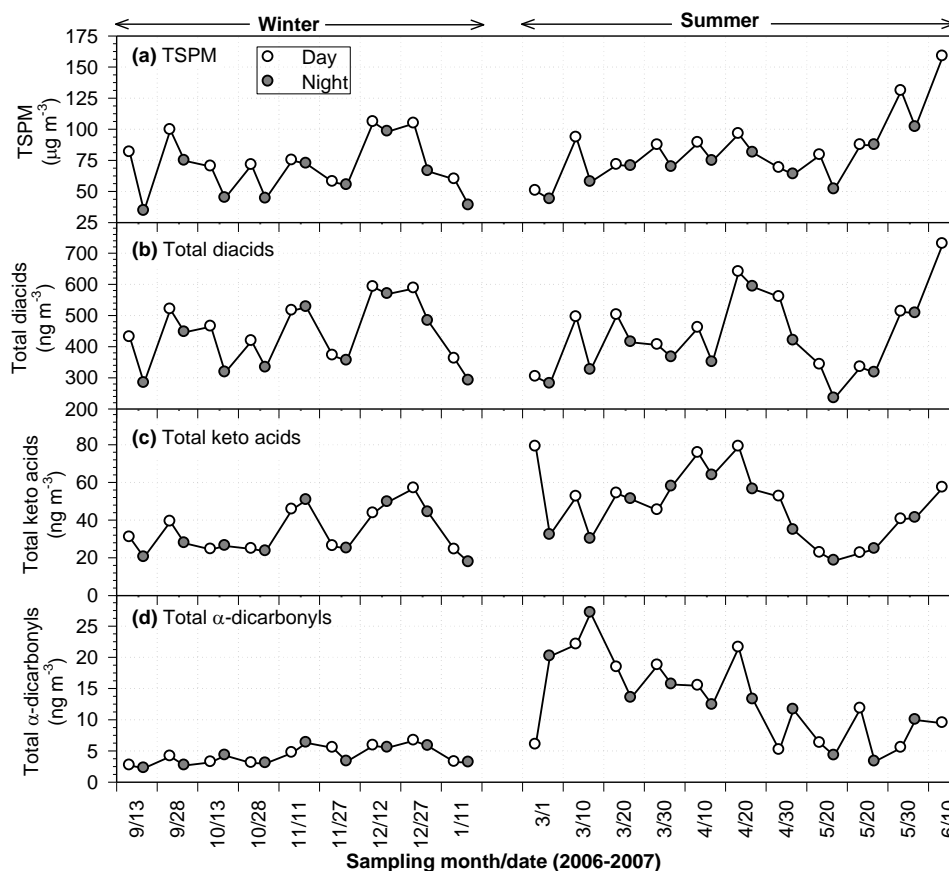
3.1 Total suspended particulate matter

Figure 3 shows the temporal variations of total suspended particulate matter (TSPM) along with the concentrations of total diacids, total ketoacids, and total α-dicarbonyls in the aerosol samples over the study area. Concentrations of TSPM during winter period were on average 81 ± 19 μg m^{-3} and $59\pm21 \, \mu g \, m^{-3}$ for day and night, respectively. During summer the concentrations were moderately higher; $92\pm30 \, \mu g \, m^{-3}$ in daytime and $70\pm16 \, \mu g \, m^{-3}$ in nighttime. On average, nighttime mass concentrations were marginally lower than daytime concentrations by ~30 %. This day- and night-time difference as well as seasonal variations in aerosol mass loading seem to be closely associated with the vertical movement of atmospheric boundary layer followed by long-range transport. Generally, during winter periods the solar insolation over the region weakens, therefore the temperature drops to minimum especially during night. The atmospheric boundary layer (stable/nocturnal boundary layer) stays far below the observation site and thus the air over the location may represent the free tropospheric features. After sunrise, thermal structure starts to develop as the land warms. The resulting convective motions become stronger at the valley region, initiating the uplifting of the inversion layer formed by low level ground-based capping along with the vertical transport of pollutants. As the day advances, the boundary layer height increases, thereby capping inversion breaks, and pollutants from the valley region (including Indo Gangetic plains) are readily transported to higher levels. During summer this feature is often observed as reported by Sagar et al. (2004), but for a longer duration. Further, Dumka et al. (2010) have observed that, the upslope winds resulting from the radiative heating of mountain surfaces along valley winds during afternoon hours may transport aerosol particles from adjacent plains to the sampling site, whereas the down slope winds due to the radiative cooling of the mountain surfaces at night create the opposite effect.

3.2 OC, EC, WSOC and WIOC

The concentrations of EC, OC, TC (total carbon) and WSOC mass concentrations in Nainital aerosol samples are given in Table 1. Overall, three carbonaceous components (OC, EC and WSOC) generally correlate well each other, showing minima during winter and maxima during summer (~2 times larger). As compared to daytime averages, nighttime concentrations were significantly lower except for EC during winter. The observed concentrations of OC ($6.2 \, \mu g \, m^{-3}$ and $16.5 \, \mu g \, m^{-3}$ for winter and summer, respectively) as well as EC ($1.4 \, \mu g \, m^{-3}$ and $4.3 \, \mu g \, m^{-3}$ for winter and summer, respectively) over Nainital were much lower than the annual average concentrations observed in Beijing ($22.4 \, \mu g \, m^{-3}$ for OC and $7.88 \, \mu g \, m^{-3}$ for EC) (Favez et al., 2008). Conversely,

Table 1. Concentrations (ng m^{-3}) of dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls and concentrations (µg m^{-3}) of elemental carbon (EC), organic carbon (OC), total carbon (TC) and water soluble organic carbon (WSOC) in Himalayan aerosols over Nainital, India.

| | Winter | | | | Summer | | | |
| | Day ($N = 9$) | | Night ($N = 9$) | | Day ($N = 11$) | | Night ($N = 10$) | |
Compounds	Range	Ave.±SD	Range	Ave.±SD	Range	Ave.±SD	Range	Ave.±SD
				Dicarboxylic acids				
Oxalic (C$_2$)	285–492	393±78	213–474	313±88	138–425	242±90	106–389	189±92
Malonic (C$_3$)	7.9–22	15±4.3	5.8–36	18±10	16–77	34±17	13–52	26±15
Succinic (C$_4$)	9.5–21	17±3.9	8.1–40	19±11	19–86	40±19	15–53	29±14
Glutaric (C$_5$)	2.3–5.5	3.9±1.0	2.2–6.4	3.8±1.7	5.0–16.5	8.9±3.4	3.9–9.8	6.0±2.2
Adipic (C$_6$)	2.7–8.2	4.5±1.6	1.9–17	6.4±5.5	5.2–17.3	9.6±3.5	3.5–7.8	6.0±1.5
Pimelic (C$_7$)	0.7–2.5	1.6±0.5	0.4–2.1	1.3±0.6	0.5–7.2	3.5±2.4	0.6–5.6	2.3±1.5
Suberic (C$_8$)	0.2–0.5	0.3±0.1	0.1–0.6	0.3±0.2	0.2–2.3	0.9±0.6	0.3–3.4	0.8±0.9
Azelaic (C$_9$)	2.9–5.5	4.3±0.8	2.3–6.1	3.8±1.3	3.4–35	17±11	3.8–27	14±8.2
Sebacic (C$_{10}$)	0.5–0.9	0.6±0.1	0.3–0.8	0.5±0.2	0.2–3.6	1.5±1	0.3–4.6	2.2±1.5
Undecanedioic (C$_{11}$)	0.6–2.5	1.2±0.7	0.4–3.0	1.3±0.8	0.2–5.1	1.9±1.6	0.4–4.6	1.6±1.5
Dodecanedioic (C$_{12}$)	0.1–0.8	0.3±0.2	0.1–0.4	0.2±0.1	0.1–2.1	0.9±0.6	0.2–1.9	1.1±0.7
Methylmalonic (iC$_4$)	0.3–1.4	0.5±0.4	0.1–1.1	0.5±0.3	0.5–7.4	2.0±2.0	0.1–2.1	1.2±0.6
Methylsuccinic (iC$_5$)	0.7–2.8	1.8±0.6	0.8–5.6	2.2±1.7	2.0–8.5	3.6±2.2	1.1–5.9	2.8±1.7
Methylglutaric (iC$_6$)	0.2–0.7	0.4±0.2	0.1–0.8	0.4±0.2	0.2–4.5	1.5±1.2	0.7–4.1	1.4±1.0
Maleic (M)	0.04–1.3	0.7±0.4	0.4–5.7	1.6±1.6	1.0–7.2	4.0±1.8	0.2–3.9	2.7±1.0
Fumaric (F)	0.6–0.9	0.8±0.1	0.6–1.8	1.0±0.4	1.0–6.4	4.0±1.5	1.0–11	3.5±3.2
Methylmaleic (mM)	0.4–0.9	0.7±0.2	0.3–3.9	1.3±1.1	0.7–4.4	2.3±1.4	0.8–14	3.2±3.9
Phthalic (Ph)	8.9–17	12±2.8	5.8–23	13±5.6	26–182	88±55	21–159	75±54
Isophthalic (iPh)	1.3–2.8	1.7±0.5	0.2–3.0	1.6±0.9	1.3–5.5	3.4±1.6	0.4–5.6	3.1±1.7
Terephthalic (tPh)	1.2–9.8	4.8±3.3	2.7–8.2	4.8±1.8	0.7–8.8	3.4±2.3	1.9–11	4.2±2.7
Malic (hC$_4$)	0.02–0.3	0.1±0.1	0.1–0.4	0.1±0.1	0.1–4.8	0.8±1.4	0.1–0.6	0.2±0.2
Oxomalonic (kC$_3$)	2.7–8.7	5.4±2.3	2.5–8.2	5.0±1.8	1.4–7.8	4.6±1.9	1.6–7.2	3.5±1.7
4-Oxopimelic (kC$_7$)	0.3–2.8	1.6±0.8	0.8–2.7	1.4±0.6	0.8–4.8	2.1±1.3	0.6–4.0	1.8±1.1
Subtotal	361–591	473±86	283–569	400±108	303–729	480±132	233–592	380±107
				Ketocarboxylic acids				
Glyoxylic (ωC$_2$)	7.8–22	13±5.5	6.1–21	11±5.1	8.9–37	23±8.1	8.7–30	16±6.8
3-Oxopropanoic (ωC$_3$)	1.6–4.4	2.6±1.0	1.3–4.3	2.3±1.1	2.1–8.6	4.5±1.8	1.8–7.2	3.6±1.7
4-Oxobutanoic (ωC$_4$)	1.7–6.5	3.4±1.6	1.5–7.4	3.4±2.0	0.2–7.8	4.4±2.7	0.3–7.8	4.6±2.0
5-Oxopentanoic (ωC$_5$)	0.4–1.3	0.8±0.3	0.4–1.4	0.7±0.3	0.1–1.8	0.9±0.6	0.2–1.6	0.9±0.4
7-Oxoheptanoic (ωC$_7$)	2.3–7.5	4.1±1.6	2.2–7.2	3.6±1.6	1.8–6.5	3.4±1.5	1.5–4.4	2.5±1.0
8-Oxooctanoic (ωC$_8$)	4.3–15	8.6±4.3	3.4–13	6.5±3.2	0.1–5.0	2.6±1.9	0.1–4.1	2.1±1.3
9-Oxononanoic (ωC$_9$)	0.5–8.6	2.9±2.3	0.8–9.9	4.0±2.9	0.7–154	24±45	0.4–33	11±13
Pyruvic (Pyr)	2.9–5.1	3.7±0.8	2.1–6.9	3.7±1.7	2.9–15	9.6±4.0	1.4–10	6.4±2.9
Subtotal	28–62	39±12	20–57	35±14	26–195	72±46	22–73	47±18
				α-Dicarbonyls				
Glyoxal (Gly)	1.5–4.1	2.6±1.0	1.3–3.8	2.3±1.0	4.2–21	10±5.5	1.6–23	9.4±6.6
Methylglyoxal (MeGly)	0.9–2.9	1.7±0.6	1.0–2.9	1.7±0.7	0.2–8.0	2.7±2.7	0.3–5.8	3.7±1.7
Subtotal	2.7–6.6	4.3±1.4	2.2–6.3	4.0±1.5	5.1–22	13±6.7	3.3–27	13±7.0
EC (µgC m^{-3})	0.6–2.4	1.3±0.6	0.8–2.2	1.4±0.5	0.7–11	4.6±2.8	1.1–8.0	3.9±2.2
OC (µgC m^{-3})	4.8–9.9	6.9±1.9	3.3–8.8	5.4±1.8	7.5–35	17±8.7	6.2–31	16±6.8
TC (µgC m^{-3})	5.4–12	8.2±2.5	4.5–10	6.8±2.1	11–46	22±11	7.3–39	19±8.8
WSOC (µgC m^{-3})	2.1–5.4	3.4±1.1	1.5–4.1	2.8±0.9	2.3–10	5.0±2.2	2.6–11	4.7±2.6

Fig. 3. Temporal variations in total suspended particulate matter (TSPM) along with mass fraction of total diacids, total ketoacids, and total α-dicarbonyls in TSPM for aerosol samples collected at Nainital, India.

OC and EC concentrations in Nainital were higher than those observed in other megacities in developed countries such as Belgium ($4.12\,\mu g\,m^{-3}$ OC and $1.80\,\mu g\,m^{-3}$ EC) and Italy ($5.91\,\mu g\,m^{-3}$ OC and $1.44\,\mu g\,m^{-3}$ EC) (Viana et al., 2007) and in Paris ($5.9\,\mu g\,m^{-3}$ OC and $1.7\,\mu g\,m^{-3}$ EC) (Favez et al., 2008).

EC is a product of incomplete combustion of residential coal, motor vehicle fuel, and biomass. OC originates from primary anthropogenic sources and also from formation (secondary OC) by chemical reactions in the atmosphere. Higher OC/EC ratios indicate an influence from biomass-burning sources (as well as biogenic sources), whereas lower ratios are attributable to fossil-fuel combustion. OC levels were considerably higher than EC for all our samples. During wintertime the OC/EC ratios were 5.86 ± 1.46 for day and 4.03 ± 1.27 for night, whereas during summertime the ratios were slightly lower (3.77 ± 1.32 and 4.43 ± 1.37). As compared to vehicular exhausts, the emissions from residential coal burning for house heating contain more organic pollutants that result in higher OC/EC ratios during winter (Cao et al., 2005). Over rural areas of northwestern India, biomass burning is quite common for house heating and cooking,

which apparently releases more organic pollutants compared to fossil fuel emissions.

The OC/EC ratios obtained in this study (annual range 1.91 to 8.29) cover the range known for the vehicular exhaust and biomass burning emissions reported by Saarikoski et al. (2008) for northern European urban environment in Helsinki, Finland. Recently, Sandradewi et al. (2008) observed relatively lower OC/EC ratios for vehicular emission from road traffic and higher ratios for biomass burning release from measurements made at a small village over the steep Alpine valley of Roveredo, Switzerland. Saarikoski et al. (2008) observed an OC/EC ratio of 6.6 for biomass burning and 0.71 for vehicular emissions, whereas Sandradewi et al. (2008) found values of 7.3 and 1.1 for these two sources, respectively. Hopkins et al. (2007) studied the particles emitted during combustion of several plant fuels at different temperatures and suggested that flaming conditions produce more EC and less OC while smoldering fires result in higher OC content. Regional air quality over the northwestern part of India during winter season is considerably influenced by the annual practice of crop harvesting. However, wood/coal burning for domestic use continues throughout the year (Ram et al., 2010). Based on an extensive campaign at the top of
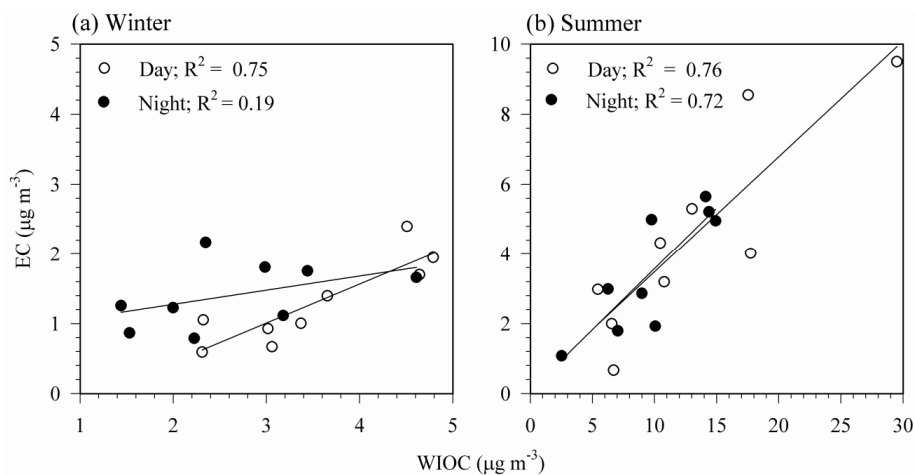
Fig. 4. Scatter plots between water insoluble organic carbon (WIOC) and elemental carbon (EC) during **(a)** winter and **(b)** summer seasons showing a linear relation.

a mountain site (1960 m a.s.l.) over a remote part of the Tibetan Plateau (Yunnan Province), Engling et al. (2011) reported higher OC/EC ratios (4.3±2.1) during spring (April and May). This experiment also revealed a substantial regional build-up of carbonaceous particles accompanied by fire activities and transport of pollutants from nearby regions of Southeast Asia and the northern part of the Indian Peninsula.

The major part of aerosol carbon is derived from smoldering in the form of water-soluble organics and it can also act as cloud condensation nuclei (CCN) (Andreae et al., 1996). Carbonaceous aerosols derived from fossil fuel combustion may be relatively less water-soluble (WSOC; 7 to 19 %) due to less oxygenated organics as reported by Ruellan and Cachier (2001). The contributions of WSOC to the total carbon in our samples are 59 % in winter and 32 % in summer, with negligible differences between day and night (~5 %). The determination of both water-soluble and insoluble organic carbon can provide additional information regarding the carbon sources. The main component of OC in TSPM samples was found to be water-insoluble organic carbon (WIOC), which contributes considerably to OC and is defined as OC-WSOC. The correlation scatter plots for WIOC with EC for winter and summer seasons are shown in Fig. 4a and b, respectively. A good correlation between WIOC and EC was apparent (except for winter night samples), indicating the influence of fossil fuel combustion over the study region. Further, lower OC/TSPM weight ratios were observed (0.09±0.02 in winter and 0.21±0.15 in summer), indicating a significant contribution from other inorganic constituents to bulk aerosols. At high altitude locations over northwestern part of India, Mount Abu (Rastogi and Sarin, 2009) and a remote site over Tibetan Plateau, Yunnan Province (Engling et al., 2011), similar OC/TSPM weight ratios (0.09 and 0.16, respectively) were reported. Organic matter (OM),

was calculated by multiplying OC by a factor of 1.6 (Turpin and Lim, 2001). OM accounted for less than 15 % of TSPM in winter and more than 35 % of the particle mass in summer. Compared to OM, EC is minor component, contributing for less than 6 % of the particle mass (EC annual average 2.85 µg m^{-3}).

Primary OC (POC) is produced both from natural (primary biogenic particles) as well as anthropogenic sources. Anthropogenic POC can be directly emitted in particulate form by emission sources like vehicular exhaust, fuel combustion and cooking. In contrast, secondary OC (SOC) is formed through gas/particle partitioning of semi-volatile reaction products involving reactive organic gases (Blando and Turpin, 2000). Due to a lack of direct analytical chemical method, separating primary and secondary organic aerosol and enormous complexity of organic aerosols have limited researchers to estimating POC and SOC using EC tracer methods (Lim and Turpin, 2002). EC is one of the good tracers of primary combustion-generated carbonaceous aerosols (Yu et al., 2009). The limitation of the EC tracer method is to assume a representative ratio of primary OC/EC for a given area because EC and POC typically have the same source (Miyazaki et al., 2006). By this method, POC and SOC were estimated using the following equations,

$$[POC] = [OC/EC]_{min} \times [EC] + c \qquad (1)$$

$$[SOC] = [OC]_{meas} - [POC] \qquad (2)$$

in which $[OC/EC]_{min}$ is the minimum ratio of OC/EC for all the samples in every season, c is the parameter to account for non-combustion sources contributing to POC, and $[OC]_{meas}$ is the measured OC concentration. In Eq. (1) we used the $[OC/EC]_{min}$ values of 2.15 µg m^{-3} and 1.91 µg m^{-3} for winter and summer seasons, respectively. If we postulate that the POC contribution from non-combustion sources (e.g., primary biogenic sources) is negligible, $[OC/EC]_{min}$
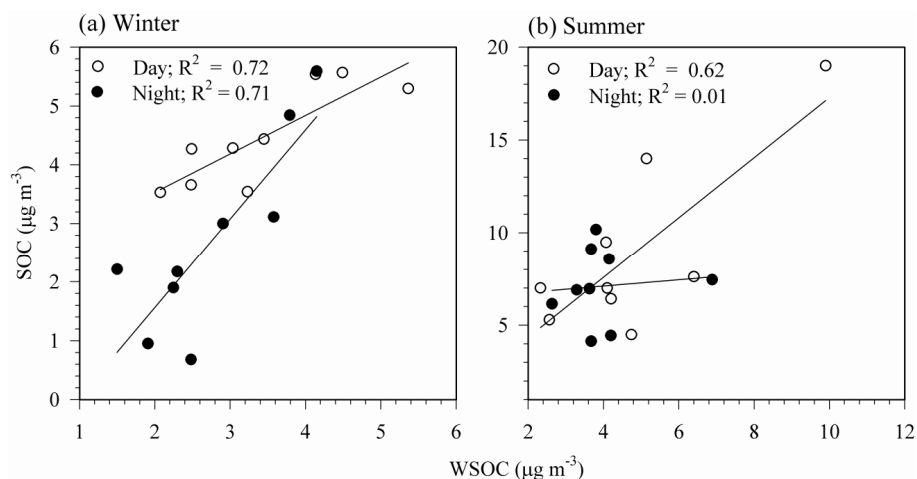
Fig. 5. Scatter plots between water-soluble organic carbon (WSOC) and secondary organic carbon (SOC) during **(a)** winter and **(b)** summer seasons showing a linear relation.

value used here seems to be reasonable because the OC/EC ratio depends upon the type of biomass as well as burn rate (Stone et al., 2010). In our samples POC concentrations were $2.8\pm1.1\,\mu g\,m^{-3}$ in winter and $9.5\pm5.9\,\mu g\,m^{-3}$ in summer. Similarly, SOC concentrations were $3.3\pm1.3\,\mu g\,m^{-3}$ in winter and $7.7\pm3.2\,\mu g\,m^{-3}$ in summer. The observed higher SOC/POC ratios (1.2) during winter than summer (0.8) suggest an enhanced photochemical production of organics under favorable meteorological conditions with a possible development of inversion layer and also increased photochemical production of SOC during the transport of organic pollutants from the source regions of Indo-Gangetic Basin.

In order to evaluate the possible uncertainties associated with the assumption of [OC/EC]$_{min}$ values representative for primary combustion-generated carbonaceous aerosols, the following exercise has been performed. For the estimate of SOC, instead of the minimum value of the OC/EC ratio, we considered the lowest 10 % of OC/EC values from each season. Lim et al. (2002) have shown that lowest 10 % of OC/EC ratios are likely contributed by primary carbonaceous aerosols. The SOC values calculated using the lowest 10 % of OC/EC ratios are always lower than those estimated using the minimum OC/EC ratio by definition. The uncertainty for the average SOC was 28 % and 39 % for winter and summer, respectively. The observed uncertainties in the present study are comparable to the reported values in the literature for Tokyo (28 %) (Miyazaki et al., 2006) and Chennai (22 %) (Pavuluri et al., 2010).

Scatter plots of WSOC and SOC are given in Fig. 5. WSOC and SOC are highly correlated ($R^2 \geq 0.62$), except for summer nighttime samples. The slopes with 95 % confidence intervals of the correlation were noticeably different. In contrast, WSOC is weakly correlated with POC ($R^2 \leq 0.40$) for both seasons. The high concentrations of SOC and WSOC/OC ratios (av. 0.41 ± 0.14; $n = 38$) as well as good

correlations between SOC and WSOC suggest that the secondary production of organic aerosols during long-range atmospheric transport is significant over the study region. It is of interest to note that the average WSOC/SOC weight ratios were less than unity for most of the samples (av. 0.92 ± 0.82; $n = 38$). This finding may suggest that not all the SOC compounds were necessarily water-soluble; some SOC compounds are considered to have large carbon-hydrogen functional groups, leading to an enhanced insolubility (Saxena and Hildemann, 1996). Similar findings to our observations have been reported by Pavuluri et al. (2010) for the tropical coastal city of Chennai, India.

3.3 Molecular characteristics of dicarboxylic acids and related compounds

Various chemical species were identified in the aerosol samples from Nainital including saturated dicarboxylic acids (normal chain; C_2 to C_{12} and branched chain; iC_4 to iC_6), unsaturated aliphatic diacids (maleic, fumaric, and methylmaleic), aromatic diacids (phthalic, isophthalic, and terephthalic), diacids with additional functional group, i.e., malic (hydroxysuccinic), ketomalonic, and 4-ketopimelic acids, together with ω-ketoacids (C_2 to C_9 except for C_6), α-ketoacid (pyruvic), and α-dicarbonyls (glyoxal and methylglyoxal). Concentrations of organic species are given in Table 1 along with EC, OC, TC and WSOC mass concentrations. Average molecular distributions of diacids, ketoacids, and α-dicarbonyls in aerosol samples are shown in Fig. 6. It is quite clear that during winter season, nighttime average concentrations of C_3, C_4, C_6, iC_5, M, Ph and ωC_9 were significantly higher than the averaged daytime concentrations (Fig. 6). This nighttime high was not observed during summer season when average concentrations were slightly lower than the daytime concentrations.
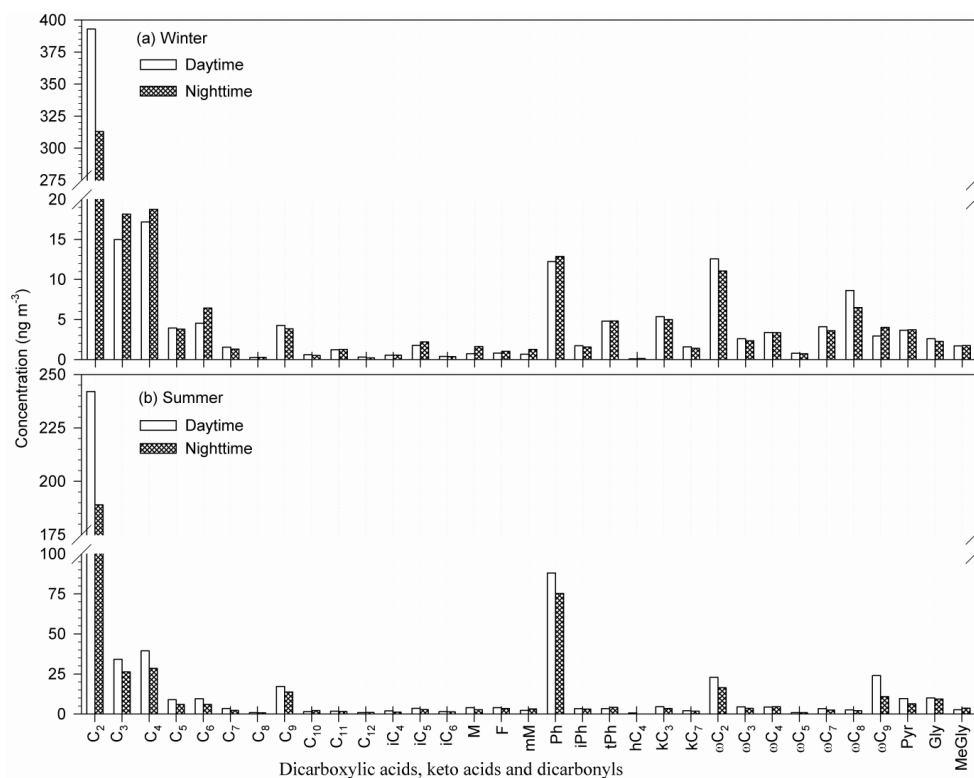
Fig. 6. Average molecular distributions of dicarboxylic acids (diacids), ketocarboxylic acids (ketoacids), and α-dicarbonyls in aerosol samples collected at Nainital, India. See Table 1 for abbreviations.

The relative abundances (%) of the individual diacids in total straight-chain diacids are shown as pie diagrams in Fig. 7. The abundances of compounds did not show any inversed relation with an increase in carbon chain length, which is generally observed for normal dicarboxylic acids (Ho et al., 2010; Pavuluri et al., 2010 and references therein). During winter, oxalic acid (C_2) was the most abundant diacid species (83 % and 78 % for day and night, respectively) followed by succinic (C_4; 3.6 % and 4.7 %) and malonic (C_3; 3.2 % and 4.5 %) acids, being consistent with the findings of previous studies (e.g., He and Kawamura, 2010). Contributions of phthalic (Ph; 2.6 % and 3.2 %), adipic (C_6; 1.0 % and 1.6 %) and azelaic (C_9; 0.9 % and 1.0 %) acids were also significant. Other dicarboxylic acids contributed less than 1 %. Among ketoacids, glyoxylic acid (ωC_2) was the most abundant, comprising ~30 % by mass. Glyoxal was generally more abundant than methylglyoxal (Table 1). This relative abundance is in contrast to urban aerosols from Tokyo, where methylglyoxal is always more abundant than glyoxal (Kawamura and Yasui, 2005). Similarly, for the summer period also, oxalic acid (C_2) was the dominant diacid (50 % and 49 % for day and night, respectively) along with succinic (C_4; 8.2 % and 7.5 %), malonic (C_3; 7.1 % and 6.9 %), phthalic (Ph; 18.4 % and 18.8 %), azelaic (C_9; 3.60 % and 3.62 %) and adipic (C_6; 1.9 % and 1.6 %) acids.

Concentrations of total diacids over Nainital varied from 295 to 620 ng m^{-3} with an annual mean of 433±108 ng m^{-3}. These values are comparable to those from Chennai (a megacity in India; 227–1030 ng m^{-3}, av. 612 ng m^{-3}) and those from Tokyo (90–1360 ng m^{-3}, av. 480 ng m^{-3}) (Kawamura and Ikushima 1993), Hong Kong (224–1381 ng m^{-3}, av. 692 ng m^{-3}) (Ho et al., 2006), and a Gosan site, Jeju Island, Korea (130–2070 ng m^{-3}, average 660 ng m^{-3}) (Kawamura et al., 2004) but slightly higher than those reported in Sapporo (106–787 ng m^{-3}, av. 406 ng m^{-3}) (Aggarwal and Kawamura, 2008). The observed total diacid concentrations were similar to those for winter and summer seasons, but daytime concentrations were ~80 % higher than nighttime concentrations for the both seasons over Nainital. The contribution of total diacids to TSPM was slightly higher (by ~20 %) in winter than summer. Day and night differences were least for both the seasons (<6 %).

The diacid-carbon/OC ratios are good tracers for pollution sources (Aggarwal et al., 2010). In Nainital aerosols the diacid-C/OC ratios during winter and summer were 2.2 % and 1.2 %, respectively. The annual average diacid-C/OC ratios (1.7±0.7) are comparable to and/or lower than those obtained at Asian megacities like New Delhi, India (1.0 %) (Miyazaki et al., 2009), and in Sapporo, Japan (4.8 %) (Aggarwal and Kawamura, 2008). Interestingly, they are several times higher than that from auto exhaust (winter: 0.51 %;

(a) Winter

Daytime

Nighttime

(b) Summer

Daytime

Nighttime
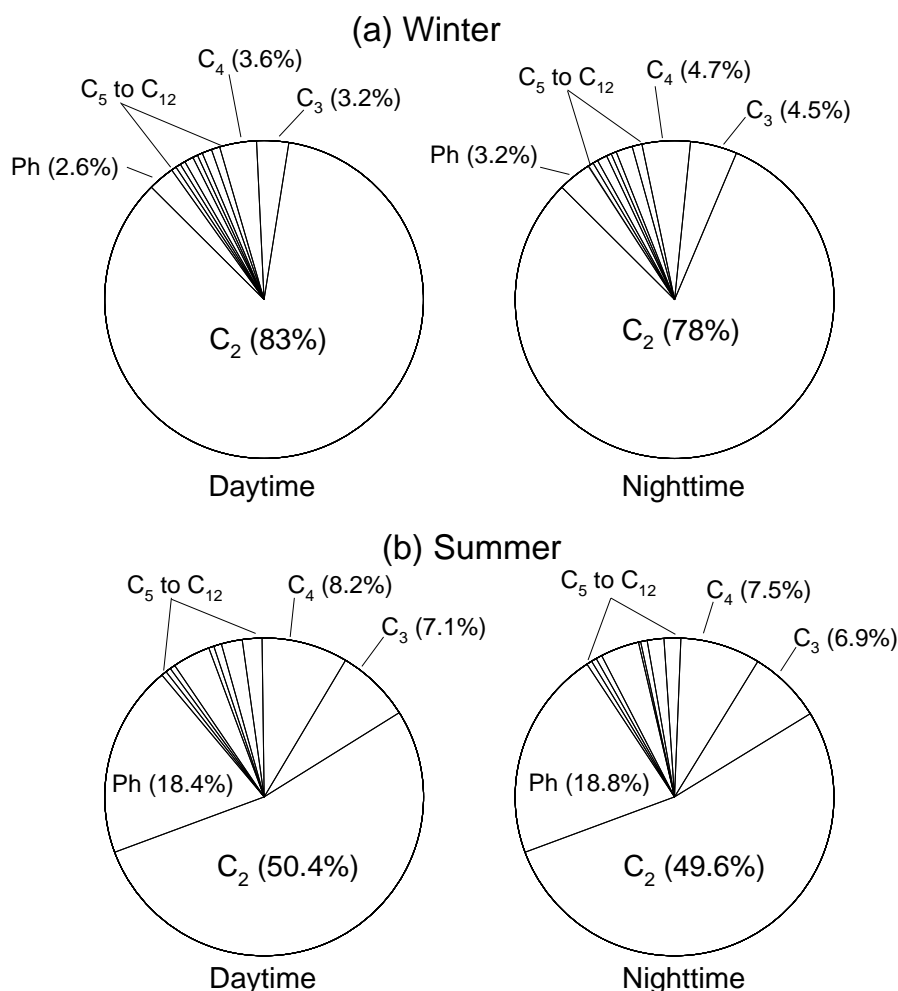
Fig. 7. Pie diagrams of relative abundances (%) of individual diacid in total straight-chain diacids in aerosols collected during **(a)** winter and **(b)** summer seasons in Nainital, India.

summer: 0.41 %) (Wang et al., 2006a), but comparable to that from biomass burning (daytime: 1.7 %; nighttime: 1.4 %) (Kundu et al., 2010), suggesting that the Nainital aerosols are largely influenced by biomass burning, especially during the winter period.

During photochemical production of diacids, contributions of diacid-carbon (diacid-C) to aerosol total carbon (TC) increase in the urban atmosphere (Kawamura and Yasui, 2005; Jung et al., 2010). In the Nainital aerosols the diacid-C/TC ratios during wintertime were 1.7 % and 1.8 % for day and night, respectively, whereas during summertime the contributions were almost halved (0.84 % for day and 0.75 % for night). The diurnal differences were minimum and opposite between the two seasons. The observed lower diacid-C/TC ratios during summer indicate not only less photochemical aging but also the enhanced contribution from hydrophobic carbonaceous aerosols from combustion sources (Aggarwal and Kawamura, 2008; Jung et al., 2010). However, many other polar organic species (e.g., carbohydrate-

like substances) also can contribute to TC and cannot be ruled out (Stone et al., 2009). The annual average diacid-C/TC ratio at Nainital (1.3 %) is slightly higher than or comparable to those obtained at Asian megacities in Tokyo (0.95 %) (Kawamura and Ikushima, 1993), capital of Mongolia – Ulaanbaatar (0.6 %) (Jung et al., 2010) and Sapporo, Japan (1.8 %) (Aggarwal and Kawamura, 2008). In megacity Chennai, southwest coast of India, a similar annual average value (1.58 %) was obtained by Pavuluri et al. (2010), but considerably higher ratios were found during the summer period. On the other hand, studies conducted over remote marine regions like the tropical to western North Pacific (8.5 %) (Kawamura and Sakaguchi, 1999) and in the western Pacific (3.2 %) (Sempéré and Kawamura, 2003) recorded several times higher diacid-C/TC ratios than Nainital due to significant photochemical processing (Kawamura and Sakaguchi, 1999).

During winter the total ketocarboxylic acid concentrations were $39\pm12\,\mathrm{ng\,m^{-3}}$ and $35\pm14\,\mathrm{ng\,m^{-3}}$ in day and

night, respectively, whereas during summer the concentrations were almost double (72 ± 46 ng m^{-3} in day and 47 ± 18 ng m^{-3} in night). Interestingly, for the cold winter season, the day and nighttime differences were small (˜10 %), but for hot summer period the daytime concentrations of several ketocarboxylic acid species were much higher (˜50 %) than nighttime. The relatively small diurnal amplitude in winter may be caused by slower production and destruction rates of the compounds (less availability of oxidants). Most of the ω-oxoacids are semi-volatile and may likely be subjected to evaporation from the particles to gas phase when the ambient temperature increases. However, this process does not seem to affect net production seriously because their concentrations in aerosols rather increase in daytime. The mass ratios of total ketoacid to TSPM were significantly higher during summer than winter. Concentrations of α-dicarbonyls (glyoxal and methylglyoxal) also showed maxima during the summer period (Table 1). Similarly, the mass ratios of total $\alpha-$dicarbonyls to TSPM were remarkably higher for summer (almost 3 times). The summertime high concentrations seem to be associated with increased solar radiation (Ho et al., 2006). The daytime concentrations were slightly higher (by ˜10 %) than nighttime concentrations for both the seasons.

Oxalic acid (C_2) is the most abundant diacid species reported in the literature (e.g., Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Gao et al., 2003). The predominance of oxalic acid in Nainital aerosols is consistent with previous studies from urban, coastal marine and remote marine aerosols (Kawamura and Sakaguchi, 1999; Wang et al., 2006b), because this smallest diacid is a final product of the photochemical chain oxidations of aromatic hydrocarbons, isoprene, ethylene, and acetylene (Ervens et al., 2004) and may also be directly contributed from fossil fuel combustion (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999). During the winter period, oxalic acid concentrations were 393 ± 78 ng m^{-3} and 313 ± 88 ng m^{-3} for day and night, respectively. In contrast, during summertime C_2 concentrations became ˜60 % lower than winter in both day and night samples. The summertime low concentrations seem to be closely associated with two different air mass pathways reaching the sampling site for individual seasons. From the air mass trajectories (Fig. 1) it is apparent that during early winter the winds circulate mostly over the densely populated Indo Gangetic Plain while during summer air masses remain westerly/southwesterly. Aerosol characterization studies over the Indo Gangetic Plain (Moorthy et al., 2007) as well as southwestern Himalayan region (Hegde et al., 2007; Gautam et al., 2010) revealed the existence of elevated dust layers during the pre-monsoon season (April, May and June).

The higher concentration of oxalic acid during winter may be associated with the contribution of isoprene to C_2 formation. Lim et al. (2005) and Myriokefalitakis et al. (2011) proposed C_2 production through isoprene oxidation in which glyoxal, methylglyoxal, pyruvic acid and glyoxylic acid are the intermediate compounds. It is important to note that oxalic acid is the ultimate diacid in the reaction scheme of oxidation of isoprene (without involving longer chain diacids). Isoprene is ubiquitous in the troposphere at a mixing ratio of about 0.1–7.0 ppb depending on season and location (von Kuhlmann et al., 2004). Measurements conducted by Padhy and Varshney (2005) over New Delhi and surrounding areas revealed significant annual average isoprene emission of 6.2 ± 3.2 µg g^{-1} leaf dry weight h^{-1} (average of six commonly grown tree species) with higher isoprene emission during September and October. Thus, formation of oxalic acid from isoprene may be enhanced during winter months in the Himalayan region.

The photochemical degradation of oxalate-iron complex and the relative depletion of oxalic acid during summer months seem to be associated with the type of air mass reaching Nainital. It has been shown that dust particles that contain alkaline and trace metals may interact with organic acids by forming organo-metal complexes (Deguillaume et al., 2005). For example, in an aerosol liquid phase, oxalic acid is an important ligand-ion for dissolving hydrated iron oxide. In the atmospheric liquid phases, the significance of this mixed complex depends on the concentrations of the potential ligands and on the value of the associated stability constant. So far there have been no measurements to determine the chemical forms of iron in complex media such as the atmospheric liquid phase. However, Willey et al. (2000) showed that iron (III) occurred predominantly as a complex with oxalate in continental summer rain, whereas in continental winter rain iron-oxalate and ferrous hydroxide were almost equal in concentration. The photolysis processes of the iron-oxalate complexes are therefore considered to be an efficient pathway for the destruction of oxalic acid during the summer period (Pavuluri and Kawamura, 2012). Ho et al. (2007) have observed significantly lower oxalic acid concentrations for the summer season as compared to winter in a study conducted over 14 Chinese cities. Over the northern part of Indian subcontinent high dust loading rich in mineral aerosols (especially iron content) has been reported during the summer season (Chinnam et al., 2006 and references therein). Kawamura et al. (2010) also reported a similar depletion of oxalic acid relative to other diacids in Arctic aerosols during the polar sunrise (spring season). They suggested that oxalic acid can be selectively decomposed under strong solar radiation in the presence of Fe. This hypothesis needs to be verified by taking into account the concentrations of Fe in aerosols in future study.
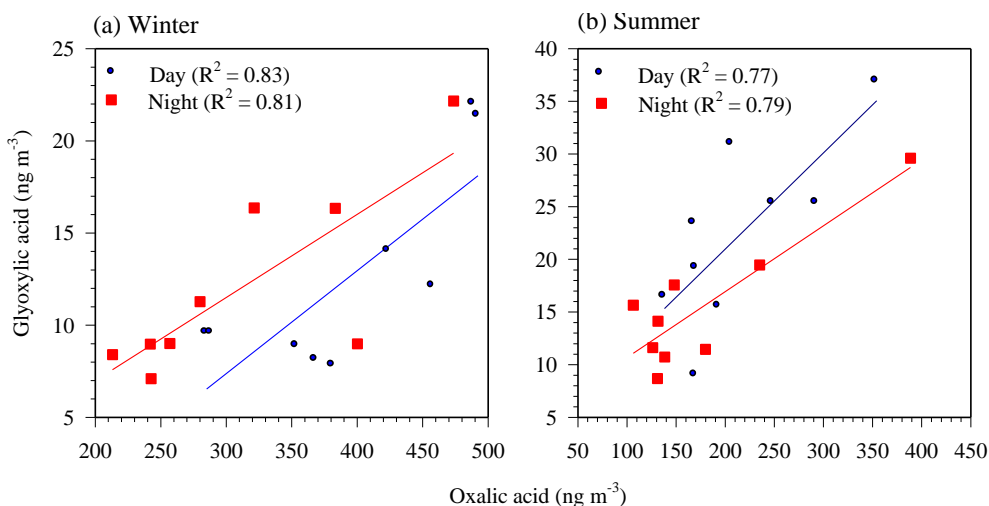
Fig. 8. Scatter plots between oxalic (C_2) and glyoxylic (ωC_2) acids during **(a)** winter and **(b)** summer seasons showing a linear relation.

## 3.4 Formation and transformation mechanisms of dicarboxylic acids

Two types of atmospheric reactions form oxalic, malonic and succinic acids (Kawamura et al., 1996a). One is the oxidation of unsaturated fatty acids, which is reported over the remote marine atmosphere such as the Pacific Ocean (Kawamura and Sakaguchi, 1999). Unsaturated fatty acids can originate from phytoplankton in the marine region and domestic cooking as well as higher plants in the continental region. In the first route, succinic acid is produced by oxidation of unsaturated acid (e.g., oleic acid; Kawamura and Sakaguchi, 1999) and then malonic and succinic acids are produced on further oxidation of succinic acid (Kawamura and Ikushima, 1993). Interestingly, we found good correlation of succinic and malonic acids with oxalic acid ($R = 0.91$ and 0.92, respectively) only for summer samples in this study, indicating a potential source from the oxidation of unsaturated fatty acids. The second possible pathway is the production from aromatic hydrocarbons such as benzene and toluene (Kawamura and Ikushima, 1993). In this route, glyoxal and glyoxylic acid are intermediates in the formation of oxalic acid but succinic and malonic acids are not produced. Good correlations were obtained for glyoxal and oxalic acid ($R = 0.61$) and glyoxylic acid and oxalic acid ($R = 0.76$) particularly during winter period, which supports this formation pathway. More detailed discussion on this formation pathway is given below.

Biogenic and anthropogenic VOCs can react with oxidants to produce glyoxal (Gly) and methylglyoxal (MeGly) in the gas phase in both daytime and nighttime. Gly and MeGly can be further hydrated in an aqueous phase to form $(OH)_2CHCH(OH)_2$ and, $CH_3COCH(OH)_2$, respectively. Hydrated MeGly can be further oxidized to pyruvic acid, acetic acid and hydrated glyoxylic acid, which will eventually be converted to oxalic acid. In contrast, hydrated Gly can be oxidized to glyoxylic acid (ωC_2), and ultimately to oxalic acid (Lim et al., 2005). In our samples, very good correlations ($R \geq 0.8$) were observed between C_2 with ωC_2, pyruvic acid, glyoxal and methylglyoxal especially during the winter period, supporting the above formation mechanism. Figure 8 gives the correlation between C_2 with ωC_2 for both seasons. We found that comparatively more C_2 is produced in nighttime summer aerosols, as the concentrations of ωC_2 become lower in nighttime than daytime. However, during the winter period an opposite trend was observed (Fig. 8a).

During summertime, the successive oxidation reactions of C_5 into shorter chain diacids are more effective (Ervens et al., 2004). In our samples, high correlation coefficients ($R \geq 0.7$) were observed among C_2–C_5 diacids only during the summer period, suggesting that they are either primarily emitted (or quickly secondarily produced) together with a dominant fraction as oxalic acid (i.e., direct production, vehicular emission, wood combustion, meat cooking operations) or strongly connected to each other in the chain reactions transforming glutaric acid into oxalic acid.

The ratio of C_2/total dicarboxylic acids can be used to assess the aging process of organic aerosols, although C_2 could be subject to photolysis under certain situation as discussed in the previous section. Typically, higher ratios are observed with the progress of aerosol aging (Kawamura and Sakaguchi, 1999). In Nainital aerosols the concentration of C_2 are significantly higher in daytime than in nighttime (for the same date). The average daytime to nighttime concentration ratio of C_2 is ~1.3 for both seasons. Considerable temporal variations are also observed. The C_2/total diacid ratios show higher values in winter (~0.8±0.04) than summer (~0.5±0.01), suggesting that the winter aerosols may be more aged (Fig. 9a). As the anthropogenic aerosols that are emitted from the industrial regions of Indo Gangetic Plain areas
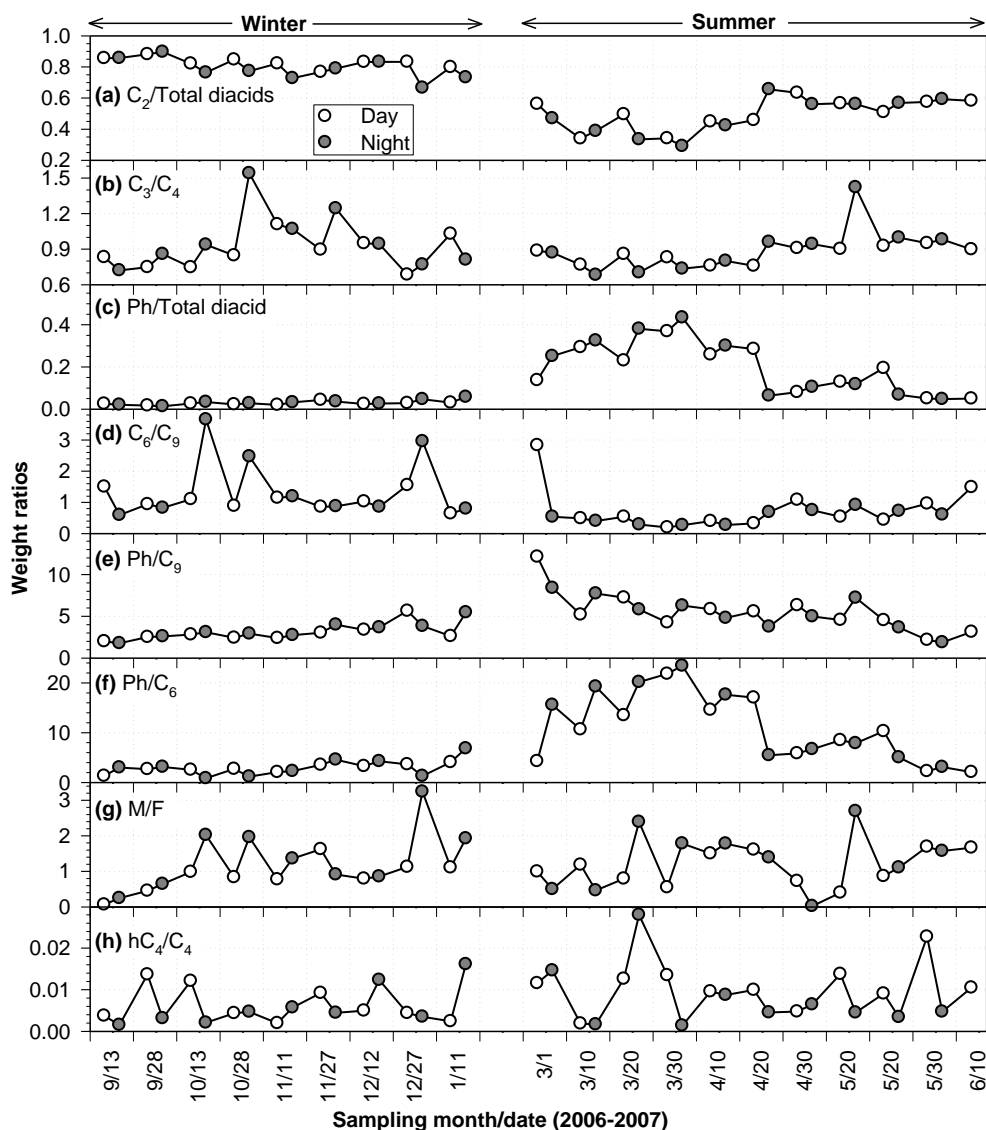
Fig. 9. Temporal variations in concentration (weight) ratios of **(a)** C_2/total diacids, **(b)** C_3/C_4, **(c)** Ph/total diacids, **(d)** C_6/C_9, **(e)** Ph/C_9, **(f)** Ph/C_6, **(g)** M/F and **(h)** hC_4/C_4 in aerosol samples collected at Nainital, India.

can travel to the north and reach the sampling site by the northerly wind (comparatively lower temperature and weaker wind speed) during the winter period, aging of these aerosols might occur during the transport and thereby significantly contribute to the higher C_2/total diacid ratios. In contrast, this trend is reversed during summer. Because the temperature over the region increase and high wind favors quick transport of pollutants, fresher aerosols are transported over the sampling site. For the oxalic acid production, aqueous phase chemistry in aerosol/cloud/fog droplets plays a major role (Warneck, 2003). Because solar radiation was reduced and relative humidity was considerably high on several occasions during the winter period (>90 % especially during western disturbances), it is possible that C_2 can be produced in aqueous phase during the cold phase of aging.

Malonic to succinic acid ratios (C_3/C_4) have been extensively used to evaluate the secondary production of dicarboxylic acids in the atmosphere (Kawamura and Ikushima 1993; Yao et al., 2004). Malonic acid (C_3) is derived from the incomplete combustion of fossil fuels or from the secondary atmospheric production. Kawamura and Ikushima (1993) reported that C_3/C_4 ratios for vehicular exhaust are lower (0.25–0.44, average 0.35) than those of atmospheric aerosols (0.56–2.9, average 1.6) because malonic acid is thermally less stable than succinic acid; the degradation of malonic acid in the combustion process is probably more significant than its production. The temporal variations of C_3/C_4 mass concentration ratios over Nainital are shown in Fig. 9b. During winter period C_3/C_4 ratios were 0.88 for day and 0.95 for night, being similar to summer samples (0.85 and 0.90).

Table 2. Weight ratios of selected diacids in Himalayan aerosols with the literature data.

Site/Type	Season	C_3/C_4	C_6/C_9	Ph/C_6	Ph/C_9
Tokyo, Japan/urban[a]	one year	1.49	0.70	0.94	0.65
Jeju Island, Korea/remote[b]	one year	1.29	1.79	1.17	2.09
Nanjing, China/urban[c]	summer	–	0.51	3.88	1.98
Nanjing, China/urban[c]	winter	–	–	–	1.00
China/14 cities average[d]	winter	0.51	0.52	5.21	2.71
China/14 cities average[d]	summer	0.77	0.75	4.48	3.37
New Delhi, India/urban[e]	winter	0.66	0.41	1.38	0.57
Chennai, India/urban[f]	winter	1.48	0.42	4.78	2.00
Chennai, India/urban[f]	summer	1.32	0.29	2.34	0.69
This study	winter	0.88	1.07	2.67	2.86
This study	summer	0.85	0.56	9.18	5.12

[a] Kawamura and Ikushima, (1993). [b] Kawamura et al. (2004).
[c] Wang et al. (2002). [d] Ho et al. (2007). [e] Miyazaki et al. (2009).
[f] Pavuluri et al. (2010).

It is quite clear from the figure that for most of the samples mass ratios are less than or equal to unity.

Relatively low C_3/C_4 diacid ratios have been found to be associated with the overwhelming contributions from vehicular exhaust to these acids in some studies, e.g., in downtown and west Los Angeles (Kawamura and Kaplan, 1987) and also in Nanjing, China (Wang et al., 2002). On the other hand, the mass ratio of C_3/C_4 in secondary atmospheric particles is much larger than unity (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Yao et al., 2002). For example, Kawamura and Ikushima (1993) reported a maximum C_3/C_4 mass ratio of 3 during the summer in Tokyo. They found that larger ratios are concurrent with elevated concentrations of oxidants and attributed the source of dicarboxylic acids to secondary atmospheric reactions. Kawamura and Sakaguchi (1999) observed the C_3/C_4 ratio of 3 in the remote marine aerosols from the Pacific Ocean, where dicarboxylic acids are expected to originate from secondary reactions.

Phthalic acid is one of the most abundant species throughout the observation. It is produced in the atmosphere by photochemical oxidation of naphthalene and its alkylated forms, which are derived from incomplete combustion of fossil fuels. The temporal variations of Ph/total diacid concentration ratios are shown in Fig. 9c. Phthalic acid concentrations during wintertime were $12\pm2.8\,\mathrm{ng\,m^{-3}}$ for day and $13\pm5.6\,\mathrm{ng\,m^{-3}}$ for night. During summertime, its concentrations become 7 times higher than those in winter (Table 1; $88\pm55\,\mathrm{ng\,m^{-3}}$ for day and $75\pm54\,\mathrm{ng\,m^{-3}}$ for night). Interestingly, nighttime concentrations were marginally higher than daytime concentrations during the winter period, whereas during summer they showed an opposite trend, indicating different origin and transformation processes of phthalic acid over the region.

Adipic (C_6) and phthalic (Ph) acids are produced by the oxidation of anthropogenic cyclohexene and aromatic hydro-carbons, whereas azelaic (C_9) acid is from biogenic unsaturated fatty acids containing a double bond at C-9 position (Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993). Therefore, C_6/C_9 and Ph/C_9 ratios can be used as markers to evaluate the source strength of anthropogenic versus biogenic precursors to dicarboxylic acids. The temporal variations of C_6/C_9 and Ph/C_9 ratios are shown in Fig. 9d and e, respectively. The mean value of the C_6/C_9 ratio (1.07 and 0.56 for winter and summer samples, respectively) in our study is considerably higher than that for urban Chinese cities (0.52 for winter) and Tokyo (0.70 one year average ratio) aerosols, suggesting that adipic (C_6) acid is mostly derived from biomass burning especially during the winter season. The mean value of the Ph/C_9 ratio in our study is comparable to that of aerosols collected from Chinese megacities (Table 2) and significantly higher than urban Tokyo (>3 times). This finding implies that the contribution of phthalic (Ph) acid from other anthropogenic sources is more significant than that from biomass burning. In support of this, Ph to total diacids ratios are several times higher in all the summer samples than winter samples (Fig. 9c).

The study conducted by Kawamura and Kaplan (1987) reported that diesel fuel vehicular exhaust shows a higher Ph/C_6 ratio (6.58) than that from gasoline fuel vehicle (2.05). In Nainital aerosols also, phthalic/adipic (Ph/C_6) ratios are greater than unity throughout the observation (Fig. 9f), suggesting that the sources from diesel fuel vehicles are more important for diacids than gasoline fuel vehicles. Interestingly, Ph/C_6 ratios were ~10 times higher on several occasions for summer samples, indicating the higher contribution from mobile sources than stationary sources. Similarly, higher Ph/C_6 ratios (1.17 to 5.21) were observed for urban areas like New Delhi and Chennai, India and several Chinese megacities (Table 2). These comparisons suggest that emissions from diesel fuel combustion contribute more to the aerosols over Nainital.

Table 3. Results of principal component analyses on the selected dicarboxylic acids and related compounds in Himalayan aerosols.

Compounds	Winter			Summer		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Oxalic (C_2)	0.78			0.90		
Malonic (C_3)		0.69		0.92		
Succinic (C_4)		0.78		0.96		
Glutaric (C_5)	0.58	0.72		0.94		
Adipic (C_6)		0.82		0.76		
Azelaic (C_9)		0.67			0.83	
Maleic (M)		0.93		0.63		
Fumaric (F)		0.74				
Phthalic (Ph)		0.67	0.60		0.87	
Terephthalic (tPh)			0.84			0.73
Glyoxylic (ωC_2)	0.80		0.55	0.84		
Pyruvic (Pyr)	0.79			0.49	0.73	
Glyoxal (Gly)	0.64		0.68		0.79	
Methylglyoxal (MeGly)	0.74				0.42	
Total variance (%)	50	18	7	36	23	10

The trans configuration (fumaric (F)) is often more abundant than cis configuration (maleic acid (M)), as reported for the remote marine atmosphere (Kawamura and Sakaguchi, 1999). Photochemical oxidation of aromatic hydrocarbons such as benzene and toluene predominantly produce maleic acid, which can be further isomerized to fumaric acid in the atmosphere during long-range transport. The temporal variations of M/F ratios over Nainital are shown in Fig. 9g. During wintertime the M/F ratios were 0.86±0.45 and 1.46±0.92 for day and night, respectively, whereas during summertime the ratios were higher (1.00±0.44 and 2.56±1.94 for day and night, respectively). This difference is in contrast to the urban aerosols (0.8–3.9, average 1.5) (Kawamura and Ikushima, 1993) and marine aerosols (0.06–1.3, average 0.26; Kawamura and Sakaguchi, 1999). Kundu et al. (2010) observed that M/F ratios in all day and night samples ranged from 0.3 to 5.6 (av. 2.8) at a pasture site in Rondonia, Brazil, during an intensive biomass-burning period. With the above discussion it is suggested that the isomerization of maleic (M) to fumaric (F) acid is suppressed under hazy conditions caused by biomass burning, in which sunlight is minimum during winter period whereas the opposite is observed in nighttime samples for both seasons.

The temporal variations of malic acid (hC_4)/C_4 ratios are shown in Fig. 9h. Kawamura and Ikushima (1993) conjectured, based on the field observation in the urban atmosphere, that hC_4 can be photochemically generated from succinic acid (C_4) via hydroxylation. The hC_4/C_4 ratios have shown higher values in summer, supporting this hypothesis. The average hC_4/C_4 ratio (1.4) in summer was found to be 3 times higher than the winter season, being consistent with the observation in urban Tokyo (Kawamura and Ikushima, 1993). Similarly, almost doubled hC_4/C_4 ratios were ob-

served during summer season for another megacity Chennai, India (Pavuluri et al., 2010).

3.5 Relation between short chain dicarboxylic acids and WSOC

Emissions from biomass burning as well as bio-fuel plume particles are reported to have large proportion of water-soluble organic species (Mayol-Bracero et al., 2002). Dicarboxylic acids in our samples show the predominance of C_2 followed by C_4 and C_3. A similar molecular distribution was observed for aerosols from Indonesian forest fires (Narukawa et al., 1999) and European aerosols (Legrand et al., 2007). Figure 10a shows a strong positive correlation between $\sum(C_2+C_3+C_4)$ (i.e., short chain diacids) and WSOC only for the winter period, suggesting a significant contribution from secondary biogenic sources. However, a poor correlation was observed for the summer period (Fig. 10b). This contrast indicates that WSOC and their precursors have different sources than short chain diacids during the summer period (Miyazaki et al., 2009). The observed high concentrations of several anthropogenic molecular markers (e.g., phthalic acid) only during summer season indicate the influence of anthropogenic sources on the increase in WSOC but not for short chain diacids.

3.6 Principal component analysis for selected species

Several types of mathematical models were used in the studies of aerosol chemical composition source apportionment. Factor analysis is a multivariate model for reducing matrices of data to their lowest dimensionality by the use of orthogonal factor space and transformations that yield predictions and/or recognizable factors (Malinowski, 1991). Factor
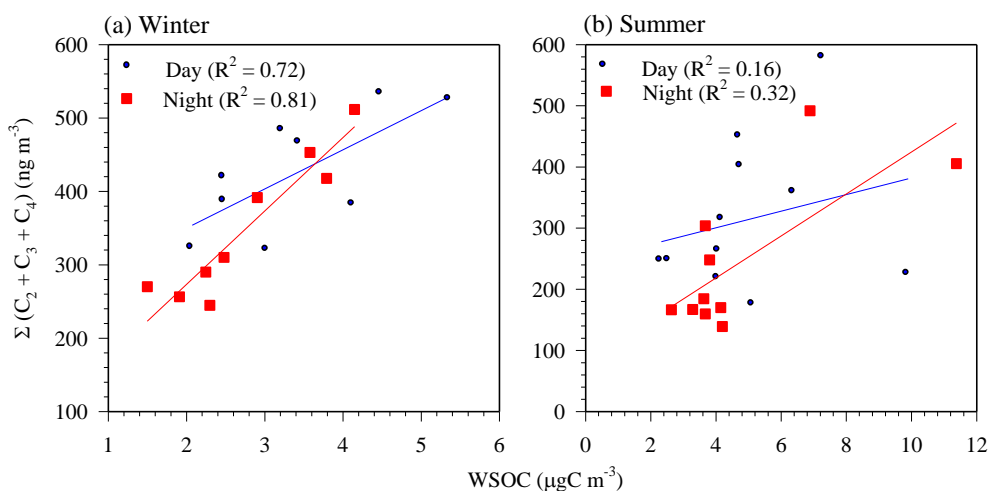
Fig. 10. Relation between water-soluble organic carbon (WSOC) and total C_2-C_4 diacid concentrations during **(a)** winter and **(b)** summer seasons.

analysis identifies groups of elements whose concentrations fluctuate together from one sample to another and separates these elements into "factors". Ideally, each extracted factor represents a source affecting the samples (Olmez et al., 1994; Kawamura and Sakaguchi, 1999). In the present study, factor analysis was applied to aerosol chemical composition data on 14 variables (Table 1) for all samples (both the seasons) by using statistical package SPSS version 12 (SPSS, 1988). The factor-loading matrix after "varimax" rotation is shown in Table 3. Here, "varimax" represents an orthogonal rotation criterion which maximizes the variance of the squared elements in the columns of a factor matrix. Weighting factors with an absolute value less than 0.5 were not listed in Table 3.

During the winter period the first factor comprises 50 % of the total variance with high loadings of C_2, ketocarboxylic acids (ωC_2 and Pyr) and α-dicarbonyls. The observed high correlation between these compounds suggests the formation of C_2 from the oxidation of isoprene (Lim et al., 2005). In contrast, C_3 to C_9, maleic, fumaric and Ph are associated with factor'2, indicating they are derived from anthropogenic sources. Maleic acid is produced via ring opening of aromatic hydrocarbons such as toluene and benzene (Kawamura and Sakaguchi, 1999). Both phthalic and maleic acids are reported to be high in polluted environments (Mochida et al., 2003). In factor 3, glyoxal and tPh were recognized together, suggesting an important emission from field burning of municipal wastes. Terephthalic acid is extensively produced during the burning of the municipal solid wastes and/or plastic polymers (Simoneit et al., 2005; Kawamura and Pavuluri, 2010) whereas glyoxal is produced during photo-oxidation of p-xylene as it is one of the important raw materials for terephthalic acid dimethyl ester (Volkamer et al., 2001).

In contrast, during summer, the first factor shows maximum loading of C_2 along with C_3 to C_6 diacids with lesser

contributions from ketocarboxylic acids (Table 3). This factor is associated with anthropogenic emissions followed by photochemical production. The observed high correlations indicate the production of C_2 from photochemical degradation of longer chain diacids (Kawamura et al., 1996b; Legrand et al., 2007). Phthalic acid and C_9 were associated in second factor. This factor seems to originate from anthropogenic and biogenic sources. Pyr, Gly and MeGly also show strong correlations with this factor because their production might be enhanced by the photo-oxidation of acetylene, ethylene and isoprene contributed from anthropogenic and/or marine emissions (Warneck, 2003) and terrestrial higher plant emissions (Guenther et al., 2006). For the third factor tPh acid is strongly loaded, suggesting the contribution of anthropogenic emissions from burning of municipal solid wastes and/or plastic polymers.

4 Summary and conclusions

This study reports, for the first time, the molecular distributions of diacids, ketoacids and α-dicarbonyls in the aerosols from the central Himalayas. Oxalic (C_2) acid was the most abundant among these species, followed by succinic (C_4), malonic (C_3) and azelaic (C_9) acids. Higher concentrations of phthalic (Ph) acid were found in summer than winter. Higher loadings of total dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls were found to correlate with higher OC/EC ratios as compared to remote areas of the world, indicating that biomass burning is a very important source for dicarboxylic acids and related compounds in this region. Winter samples had significantly higher C_2/total diacid ratios than summer samples, indicating more fresh aerosols during summer due to atmospheric transport under favorable meteorological conditions. Glyoxal and glyoxylic acid

are intermediates in the formation of oxalic acid for winter months. In contrast, during summer months, succinic acid can be decomposed to malonic acid and then to oxalic acid following the oxidative degradation of biogenic unsaturated fatty acids. Similar factors (variables) were obtained from the results of principal component analysis.

Higher C_6/C_9 ratios were observed for the winter season whereas Ph/C_9 ratios were higher during the summer season, indicating that other anthropogenic sources were more important than biomass burning in the latter season. Higher phthalic/adipic acid (Ph/C_6) ratios were observed during summer than winter, indicating greater potential sources from diesel fuel vehicles than gasoline vehicles. The higher SOC/POC ratios during winter suggest an enhanced photo-oxidation of organics under favorable meteorological conditions with a possible development of an inversion layer and also increased photochemical production during transport of organic pollutants from source regions in the Indo-Gangetic Basin. This study suggests that the pollutants emitted from far distant sources can significantly affect the regional air quality of the Himalayas and, therefore, contribute to the effects of aerosols on climate change.

For the winter months the observation site remains above the boundary layer and represents a free tropospheric site (Hegde et al., 2009). Therefore, the observed concentrations of different organic compounds may represent the regional free tropospheric concentrations of several pollutants. On average, for the summer season, higher concentrations of several anthropogenic compounds were observed than in the winter period. Conversely, the boundary layer height increases during summer months and the observation site will be well within the boundary layer. The pollutants of northwestern Indian origin are readily transported towards the central Himalayas due to high winds, elevated temperature, and supplementary convection. Much higher concentrations of phthalic acid along with several other anthropogenic organic compounds were recorded in summer than winter. A summertime decline of oxalic acid may be associated with photochemical decomposition and dust transport over the region, a process that deserves further investigation on the trace metals such as iron that may be involved with the decomposition of oxalic acid.

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