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Seasonal variations of water-soluble organic carbon

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Seasonal variations of water-soluble organic carbon, dicarboxylic acids, ketoacids, and α -dicarbonyls in the central Himalayan aerosols

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Aerosol samples were collected from a high elevation mountain site (Nainital, India; 1958 m a.s.l.) in the central Himalayas, which provide 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 significantly reduced during summer. Molecular distributions of diacids demonstrated that oxalic (C_2) acid was the most abundant species followed by C_4 and C_3 diacids. The average concentrations of total diacids ($433 \pm 108 \text{ ng m}^{-3}$), ketoacids ($48 \pm 23 \text{ ng m}^{-3}$), and α -dicarbonyls ($9 \pm 4 \text{ ng m}^{-3}$) were similar to those from Asian cities such as Tokyo, Beijing and Hong Kong. During summer season 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 in atmospheric aerosols. Based on molecular distributions and air mass backward trajectories, we report that dicarboxylic acids and related compounds in Himalayan aerosols are influenced by the anthropogenic activities from 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. As of now, Indian Ocean Experiment (INDOEX) was the ever conducted major campaign over the oceanic region, which could reveal enormous pollution transport pathways (Satheesh and Ramanathan, 2000; Lelieveld et al., 2001). Remote areas

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of the world were once thought to be less influenced by the atmospheric perturbation, hence they 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). Himalayan Mountain is located at a remote area of the Asian continent. During the last two decades, chemical studies of aerosol and snow in the Himalayan region have become 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, 2000, 2002). The influence of anthropogenic pollutants over the Himalayan region is being debated in recent years (Gautam et al., 2010). Wake et al. (1994) studied the aerosol samples collected from the southern slopes of the Himalayas to northern margin of the Tibetan Plateau and reported high concentrations of organic compounds. They revealed that the remote mountainous region and, to some extent, the middle-upper troposphere are also polluted by human activities.

Studies of organic aerosols at molecular level are limited because of their complexity and thus difficulties in the 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 the hygroscopic property, diacids play an important role in the global radiative balance (Saxena et al., 1995; Facchini et al., 1999; Kerminen, 2001). Distributions and concentrations of these organic acids in aerosols are important to understand photochemical reactions, long-range atmospheric transport and the hygroscopic properties of organic aerosols. These species are directly emitted to the atmosphere from natural and anthropogenic sources or secondarily produced by atmospheric chemical reactions (Kawamura and Kaplan, 1987;

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Schauer et al., 1999; Simoneit et al., 2005). The large spatial heterogeneity in the distribution of atmospheric aerosols demands region-specific studies. There is scarcity of the data of chemical composition at molecular level, in particular on organic aerosols over Asian region. On an average, over the entire Indian subcontinent, chemical mass balance studies based on ISRO-GBP campaign (Indian Space Research Organization-Geosphere Biosphere Programme) estimated the particulate organic matter contribution of about 20–30 % from the total aerosol mass load (George et al., 2008).

Over south Asia, Indo-Gangetic plain is considered as a densely populated region, and thus as a potentially strong source region of anthropogenic aerosols (Tripathi et al., 2005; Ram et al., 2010). Northern part of these highly populated and industrialized areas is one of chains of Himalaya Mountains. 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 Kumaon region) and about 2 km far from Nainital city (population ~0.5 million). The site is devoid of any major local pollution sources nearby and is generally free from the snow coverage during most of the time. North and northeast side of the study area are characterized by sharply peaking topography of Himalayan mountain ranges, whereas south-western side plains with very low elevation (<500 m a.s.l.) are densely populated with land merging into the Ganga basin.

To better understand the atmospheric chemistry of organic aerosols in the Himalayan range, we collected aerosol samples at Nainital at foothills of central Himalayas and performed the measurements of organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC), dicarboxylic acids and related compounds. Here, we report molecular distributions of several anthropogenic 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 climatology of this part of the Asian continent is mainly controlled by air masses originated 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 ranges play a key role in the regional climatology. It also blocks the midlatitudinal westerlies and splits the jet that moves to the north and the south of the plateau. During winter months, western disturbances (synoptic scale low pressure weather systems) occur frequently over the northwestern part of India. This cold air mass originates over the Mediterranean Sea and Atlantic Ocean and brings high moisture and snow fall over the high altitudinal locations.

A common method for the identification of the origin and the pathway of air masses is to calculate backward trajectories. Figure 1 gives the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Trajectory (HYSPPLIT) model (24 h interval; FNL Meteorological Data Draxler and Rolph, 2010; Rolph, 2010) seven days backward trajectories illustrating typical air-mass flow from different parts of the Indian subcontinent to the study area (Nainital) at three different reaching 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 first week of March air masses remain westerly/southwesterly. The trajectory patterns change again from southwesterly to westerly/northwesterly during mid June. Such shifts in wind pattern are observed every year.

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

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of meteorological parameters. The mean wind speed recorded was $<4 \text{ m s}^{-1}$ during winter months, whereas during summer months it almost doubled. The diurnal and seasonal variation for temperature and relative humidity are shown in Fig. 2. Temperature and relative humidity remain low during winter period and significantly increase during summer months. 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 building (20 m a.g.l.) 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 day (09:00 a.m. to 06:00 p.m.) and nighttime (07:00 p.m. to 08:00 a.m.), whereas during summer period the sampler was operated for less duration; day (10:00 a.m. to 01:00 p.m.) and night (08:00 to 11:00 p.m.). Filters were changed twice a day representing daytime and nighttime samples. All samples were collected with fortnight intervals. The flow rate of the sampler was set at 400 l min^{-1} . Field blanks were collected through 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-weighted using a microbalance (Model AT 20 of Mettler with a sensitivity of $\pm 2 \mu\text{g}$) and preserved $\sim -4^\circ\text{C}$ 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

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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 under 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-VSCH) 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 $\mu\text{gC m}^{-3}$.

OC and EC in the samples were measured using a semi-continuous OC/EC analyzer (Sunset Laboratory Inc., Portland, OR, USA) following the Interagency Monitoring of Protected Visual Environments (IMPROVE-B) thermal protocol. A filter disk (area 1.5 cm^2) of the sample was placed in a quartz boat which was placed inside the thermal desorption chamber of the analyzer. OC concentrations were determined in helium atmosphere at ~ 120 , 250, 450 and 550 $^{\circ}\text{C}$. Subsequently, oxygen (2 %) was introduced and EC concentrations were determined at temperatures from ~ 550 to 900 $^{\circ}\text{C}$. The pyrolytic conversion of OC to EC was monitored and corrected by using He-Ne laser. Sucrose standard used for calibration check at 4 different concentrations (20, 40, 60 and 80 μgC) show good agreement with true values. The detection limits of these measurements were 1 $\mu\text{g m}^{-3}$ for OC and 0.2 $\mu\text{g m}^{-3}$ for EC.

Samples were analyzed for diacids, ketoacids, and 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 in to pieces and extracted with ultra pure Milli-Q water (10 ml \times 3) under ultrasonication for about 10 min. After filtration with quartz wool, the extracts were combined in a 50 ml flask and concentrated to almost dryness using a rotary evaporator under vacuum. The extracts were then derivatized 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 derivatized fractions were analyzed using a capillary gas chromatography (GC; HP 6890). Peak identification was performed by GC retention times of authentic standards and confirmed by mass spectral examination using a GC-mass spectrometry (GC-MS) system.

We spiked the free diacids on a precombusted quartz fiber filters in order to evaluate the recovery. They were extracted and analysed 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

Aerosol total suspended particulate matter (TSPM) concentrations during winter period were on average $81 \pm 19 \mu\text{g m}^{-3}$ and $59 \pm 21 \mu\text{g m}^{-3}$ for day and night, respectively. During summer the concentrations were moderately higher; $92 \pm 30 \mu\text{g m}^{-3}$ and $70 \pm 16 \mu\text{g m}^{-3}$ for day and night, respectively. On an average, nighttime mass concentrations were marginally lower than daytime averages by $\sim 30\%$. This day- and night-time difference as well as seasonal variations in aerosol mass loading seems to have close association with atmospheric boundary layer dynamics followed by long-range transport. Generally, during winter period the solar insolation over the region becomes less, therefore the temperature drops to minimum especially during night. The atmospheric boundary layer (stable/nocturnal boundary layer) stay far below the

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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 and the day advances. The resulting convective motions become stronger at the valley region, initiating the up-lifting 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 decreases, thereby capping inversion breaks and pollutants from the valley region (including Indo Gangetic plains) get readily transported to higher levels. During summer this feature is more often observed as reported by Sagar et al. (2004), but for a long duration. Further, Dumka et al. (2010) have observed that, the upslope winds resulting from the radiative heating of mountain surface along valley winds during afternoon hours may transport aerosol particles from adjacent plains to the sampling site, whereas the down slope due to the radiative cooling of the mountain surface at night make 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 carbon components (OC, EC and WSOC) generally correlate well each other, showing minima during winter and maxima during summer (~2 times). As compared to day averages, nighttime concentrations were significantly lower except for EC during winter. The observed concentrations of OC (6.2 and 16.5 $\mu\text{g m}^{-3}$ for winter and summer, respectively) as well as EC (1.4 and 4.3 $\mu\text{g m}^{-3}$ for winter and summer, respectively) over Nainital were much lower than the annual average concentrations observed in Beijing (22.4 and 7.88 $\mu\text{g m}^{-3}$ for OC and EC, respectively) (Favez et al., 2008). Conversely, OC and EC concentrations in Nainital were higher than those observed in other megacities in developed countries such as Belgium (4.12 $\mu\text{g m}^{-3}$ OC and 1.80 $\mu\text{g m}^{-3}$ EC) and Italy (5.91 $\mu\text{g m}^{-3}$ OC and 1.44 $\mu\text{g m}^{-3}$ EC) (Viana et al., 2007) and in Paris by Favez et al. (2008) (OC 5.9 $\mu\text{g m}^{-3}$ and EC 1.7 $\mu\text{g m}^{-3}$).

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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. Therefore, higher OC/EC ratios indicate an influence from biomass-burning sources (as well as biogenic sources), while lower ratios are attributed 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 and 4.03 ± 1.27 , for day and night, respectively, whereas during summertime the ratios were slightly lower (3.77 ± 1.32 and 4.43 ± 1.37 for day and night, respectively). As compared to vehicular exhausts, the emissions from residential coal burning for house heating contain more organic pollutants which 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 array 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 high ratios for biomass burning release from the 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 the values of 7.3 and 1.1 for these two sources, respectively. On the contrary, aerosols generated from burning different plant fuels were characterized by Hopkins et al. (2007), suggested that changes in the biomass mode can also result in dissimilar OC/EC ratios. Because the biomass burning is quite common over the northwestern part of India, the regional air quality will considerably change during winter due to the regular practice of crop harvesting and a common exercise of wood fuel/coal burning for domestic use throughout the year. In a campaign mode measurements conducted by Engling et al. (2011), from the top of a mountain site (1960 m a.s.l.) over a remote part of the Tibetan Plateau

(Yunnan Province) unveiled a substantial regional build-up of carbonaceous particles with higher OC/EC ratios (4.3 ± 2.1) during summer, accompanied by fire activities and transport of pollution from the nearby regions of Southeast Asia and the northern part of the Indian Peninsula.

5 The dominant fraction of aerosol carbon is derived from smoldering as organics whose significant fraction is found to be water-soluble can 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
10 WSOC to the total carbon in our samples are 59 and 32% for winter and summer, respectively, with negligible differences between day and night ($\sim 5\%$). 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 WIOC which contributes considerably to OC. Water-insoluble organic carbon (WIOC) is defined as $WIOC = OC - WSOC$. The correlation scatter plots for WIOC with EC for winter and summer seasons are shown in Fig. 3a and b, respectively. The significant correlation obtained for WIOC and EC (except for winter night samples) can be explained by that WIOC has various origins, with traffic/industry and fossil fuel primary emissions being the predominant sources. Consequently, lower OC/TSPM
15 weight ratios were observed (0.09 ± 0.02 and 0.21 ± 0.15 for winter and summer, respectively), indicating a significant contribution from other inorganic constituents to bulk aerosols. At high altitudinal locations over northwestern part of India, Mount Abu (Rastogi and Sarin, 2009) and remote site over Tibetan Plateau, Yunnan Province (Engling et al., 2011), similar OC/TSPM weight ratios (0.09 and 0.16, respectively) were reported due to entrainment of mineral dust. Organic matter (OM), was calculated by
20 multiplying OC with 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 $2.85 \mu\text{g m}^{-3}$).

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Primary OC (POC) and secondary OC (SOC) were estimated using the EC tracer method; $POC = EC \times (OC/EC)_{\min}$ and $SOC = OC - POC$. Here, $(OC/EC)_{\min}$ is the minimum ratio of OC/EC for all the samples in every season (Yu et al., 2009). EC is one of the good tracers of primary combustion generated carbonaceous aerosols. In our samples POC concentrations were $2.8 \pm 1.1 \mu\text{g m}^{-3}$ and $9.5 \pm 5.9 \mu\text{g m}^{-3}$ for winter and summer seasons, respectively. Similarly, SOC concentrations were $3.3 \pm 1.3 \mu\text{g m}^{-3}$ and $7.7 \pm 3.2 \mu\text{g m}^{-3}$ for winter and summer seasons, respectively. The observed higher SOC/POC ratios (1.2) during summer period than winter period (1.1) 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.

Scatter plots of WSOC and SOC are given in Fig. 4. WSOC and SOC are highly correlated ($R^2 \geq 0.62$), except for summer season nighttime samples. The slopes with 95 % confidence intervals of the correlation were noticeably different. In contrast, WSOC was weakly correlated with POC ($R^2 \leq 0.40$) for both seasons. These results indicate that SOC and WSOC are very similar in their chemical characteristics. It is of interest to note that the average WSOC/SOC weight ratios were less than unity for most of the samples. This 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).

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 – 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. 5. Oxalic acid (C_2) concentrations are also given in parentheses. It is quite clear from the figure 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. Although this nighttime high was not observed during summer season, their average concentrations were slightly lower than the daytime concentrations.

The relative abundance (%) of the individual diacids in total straight-chain diacids (C_2 – C_{12}) is shown in Fig. 6. 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 most abundant diacid species (83 and 78 % for day and nighttime, respectively) followed by succinic (C_4 ; 3.6 and 4.7 %) and malonic (C_3 ; 3.2 and 4.5 %), being consistent with the findings in 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. Methylglyoxal was generally less abundant than glyoxal (Table 1). Similarly, for 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 annual mean of $433 \pm 108 \text{ ng m}^{-3}$. These values are comparable to those from Chennai (southwestern metro city in India; 227–1030 ng m^{-3} , ave. 612 ng m^{-3}) and those from Tokyo (90–1360 ng m^{-3} average 480 ng m^{-3}) (Kawamura and Ikushima 1993), Hong Kong (224–1381 ng m^{-3} average 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

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slightly higher than those reported in Sapporo ($106\text{--}787\text{ ng m}^{-3}$ average 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 $\sim 80\%$ higher than nighttime concentrations for the both seasons over Nainital.

During photochemical production of diacids, contributions of diacids-carbon (diacid-C) to aerosol total carbon (TC) increase in urban atmosphere (Kawamura and Yasui, 2005). In the Nainital aerosols the contributions during wintertime varied from 1.7 and 1.8% for day and night, respectively, whereas during summertime the contributions were almost 2 fold less (0.84 and 0.75% for day and night, respectively). The diurnal differences were minimum and opposite between the seasons. The annual average diacid-C/TC ratio (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 a megacity Chennai, southwest coast of India, similar annual average value (1.58%) was obtained by Pavuluri et al. (2010), but higher ratios were found during summer period. On the other hand, the studies conducted over remote marine regions like the tropical to western North Pacific (8.5%) 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). Therefore, the observed lower diacid-C/TC ratios in this study clearly indicate that, Nainital aerosols are significantly contributed by increased emission of hydrophobic carbonaceous aerosols emitted from different combustion sources, which are photochemically less aged.

The diacid-C/OC ratios are also 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 (summer: 0.41%; winter: 0.51%) (Wang et al., 2006b), but comparable to that from biomass burning (daytime: 1.7%; nighttime: 1.4%) (Kundu et al., 2010), indicating that the Nainital aerosols are influenced by both

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fossil fuel combustion and biomass burning especially during winter period.

Figure 7 shows the temporal variations of total suspended particulate matter (TSPM) along with mass fraction of total diacids, total ketoacids, and total α -dicarbonyls in TSPM for aerosol samples over the study area. The contribution of total diacids to TSPM was marginally higher (by $\sim 20\%$) in winter than summer. Day and night differences were least for summer season ($< 5\%$).

During winter the total ketocarboxylic acid concentrations were $39 \pm 12 \text{ ng m}^{-3}$ and $35 \pm 14 \text{ ng m}^{-3}$ in day and night, respectively, whereas during summer the concentrations were almost twice higher ($72 \pm 46 \text{ ng m}^{-3}$ in day and $47 \pm 18 \text{ ng m}^{-3}$ in night). Interestingly, for cold winter season, the day and nighttime differences were small ($\sim 10\%$), but for hot summer period the daytime high concentrations of several ketocarboxylic acid species were much prominent ($\sim 50\%$). 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 they are likely to be subjected to evaporation from the particles to gas phase when ambient temperature increases. However, this process seems not to affect seriously on the net production because their concentrations in aerosols rather increase in daytime. Similarly, the mass ratios of total ketoacid to TSPM were significantly higher during summer (Fig. 7c) than winter. Concentrations of α -dicarbonyls (glyoxal and methylglyoxal) also showed a maximum concentration during summer period (Table 1). Similarly, the mass ratios of total α -dicarbonyls to TSPM were remarkably higher for summer period (almost 3 times). This summertime high concentrations seem to be associated with the increased solar radiation. Similarly, the daytime concentrations were slightly higher (by $\sim 10\%$) than nighttime concentrations for both the seasons.

Oxalic acid (C_2) is the most abundant diacids species reported in the literature (e.g. 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., 2006a), because this smallest diacid is the final product of the photochemical chain oxidations of aromatic hydrocarbons,

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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 winter period, oxalic acid concentrations were $393 \pm 78 \text{ ng m}^{-3}$ and $313 \pm 88 \text{ ng m}^{-3}$ for day and night, respectively. In contrast, during summertime C_2 concentrations became $\sim 60\%$ lower than winter for 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. Aerosol characterization studies over the Indo Gangetic Plains (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 premonsoon season (April, May and June).

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 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 medium as the atmospheric liquid phase. However, Willey et al. (2000) showed that iron(III) occurred predominantly as complex with oxalate in continental summer rain, whereas in continental winter rain iron-oxalate and ferrous hydroxide were almost equal in concentration. The formation photolysis processes of the iron-oxalate complexes are therefore considered to be an efficient pathway for the destruction of oxalic acid during summer period. Ho et al. (2007) have observed significantly lower oxalic acid concentrations for 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) have been reported during summer season (Chinnam et al., 2006 and references therein).

3.4 Sources and formation pathways of dicarboxylic acids and related compounds

Oxalic acid (C_2) is generally formed by the oxidations of longer-chain diacids. Therefore, ratio of C_2 /total dicarboxylic acids can be used to assess the aging process of organic aerosols. 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 the seasons. Considerable temporal variations are also observed. The C_2 /total diacid ratios show higher values in winter ($\sim 0.8 \pm 0.04$) than summer ($\sim 0.5 \pm 0.01$), indicating that the winter aerosols were more aged (Fig. 8). As the anthropogenic aerosols that are emitted from the industrial regions of Indo Gangetic Plain areas can travel to the north and reach the sampling site by the northerly wind (comparatively lower temperature and weaker wind speed) during winter period, aging of these aerosols might occur all through the transport and thereby significantly contribute to the higher C_2 /total diacid ratios. In contrast, this trend is opposite during summer. Because the temperature over the region increase and high wind favors quick transport of pollutants, more fresh aerosols are transported over the sampling site. In summer, the production of this diacid may also relate to aqueous production from biogenic precursors (isoprene, unsaturated fatty acids and oxygenated volatile organic compounds).

For the oxalic acid production, aqueous phase chemistry in aerosol/cloud/fog droplets plays a major role (Warneck, 2003). Since solar radiation was reduced and the relative humidity was considerably high on several occasions during 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 process. Biogenic and anthropogenic VOCs can react with oxidants to produce glyoxal (Gly) and methylglyoxal (MeGly) in 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.

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Hydrated MeGly can be further oxidized to pyruvic acid, acetic acid and hydrated glyoxylic acid, which will eventually be converted to oxalic acid. However, hydrated Gly can also be oxidized to ωC_2 , and ultimately to oxalic acid (Lim et al., 2005). Overall very good correlations ($R \geq 0.8$) were observed between C_2 with ωC_2 , pyruvic acid, glyoxal and methylglyoxal especially during winter period, supporting the above interpretation. Figure 9 gives the correlation between C_2 with ωC_2 for both the seasons. It is found that comparatively more C_2 is produced in nighttime summer aerosols, as the concentrations of ωC_2 become lower in nighttime than daytime. But, during winter period an opposite trend was observed (Fig. 9a).

High correlation coefficients obtained among C_2 – C_5 diacids during summer period suggest that they are either primarily emitted (or fast secondarily produced) together with a dominant fraction as oxalic acid (i.e. direct production; vehicular emissions, wood combustion, meat cooking operations) or strongly connected to each other in the chain reaction transforming glutaric acid into oxalic acid. During summertime, the successive oxidation reactions of C_5 into shorter chain diacids are more effective (Ervens et al., 2004). Due to decrease of its major sources, the aqueous phase concentrations of OH may get reduced during winter period. Stable meteorological conditions developed in the winter over the source sites may significantly reduce the vertical mixing of air masses.

Malonic to succinic acid ratios 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 (0.25–0.44, average 0.35) are lower in vehicular exhaust than in atmospheric aerosol (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. 10a. During winter period C_3/C_4 ratios were 0.88 and 0.95 for day and night, respectively, being similar to summer

samples (0.85 and 0.90 for day and night, respectively). It is quite clear from the figure that on most of the samples the mass ratios are less than or equal to unity.

The C_3/C_4 ratio has been reported to be 0.3–0.5 from direct vehicular emissions (Kawamura and Kaplan, 1987). Relatively low C_3/C_4 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 et al., 1996; 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 ratios larger than unity 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.

There are two types of atmospheric reactions forming oxalic, malonic and succinic acids (Kawamura et al., 1996). 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). However, because unsaturated fatty acids originating from domestic cooking as well as terrestrial higher plants are common over the continental regions that are transported from Indogangetic basin, oxidation of unsaturated fatty acids is also possible over the continent. In this route, succinic acid is the precursor of malonic acid and oxalic acid. Therefore, the observed good correlation of succinic and malonic acids with oxalic acid ($R = 0.91$ and 0.92 , respectively) only for summer samples in this study indicates the potential source from the oxidation of unsaturated fatty acids.

The other possible pathway is the oxidation of aromatic hydrocarbons such as benzene and toluene, which occur predominantly in the urban atmosphere (Kawamura and Ikushima, 1993). In this route, glyoxal and glyoxylic acid are intermediates in the

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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. Warneck (2003) reported that acetylene and ethane can react with OH radicals to form glyoxal, which is further oxidized to oxalic acid under favorable atmospheric conditions.

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. Phthalic acid concentrations during wintertime were $12 \pm 2.8 \text{ ng m}^{-3}$ and $13 \pm 5.6 \text{ ng m}^{-3}$ for day and night, respectively. During summertime, its concentrations become 7 times higher than those in winter (Table 1; $88 \pm 55 \text{ ng m}^{-3}$ and $75 \pm 54 \text{ ng m}^{-3}$ for day and night, respectively). Interestingly, nighttime concentrations were marginally higher than daytime concentrations during 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 hydrocarbons, 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 variation C_6/C_9 and Ph/C_9 ratios are shown in Fig. 9a and b, 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 (0.52 and 0.75 winter and summer, respectively) and Tokyo (0.70 one year average ratio) aerosols, suggesting that adipic (C_6) acid is mostly derived from biomass burning especially during 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 infers that the contribution of phthalic (Ph) acid from other anthropogenic sources

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is more significant than that from biomass burning. In supportive of this, Ph to total diacids ratios were several times higher in all the summer samples than winter samples (Fig. 11c).

Further, phthalic/adipic (Ph/C_6) ratios are greater than unity throughout the observation (Fig. 10c), 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 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, Chennai, India and several Chinese mega cities (Table 2). These comparisons suggest the higher emission contributions from diesel combustion in the aerosols over Nainital.

It is observed that generally, trans configuration (fumaric – F) is more abundant than cis configuration (maleic acid – M) as also 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 result in fumaric acid in the atmosphere during a long range transport. The temporal variations of M/F ratios over Nainital are shown in Fig. 10b. 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 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 (average 2.8) at a pasture site in Rondônia, Brazil during an intensive biomass burning period. With the above discussion it is confirmed 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 a contrary is observed in nighttime samples for both the seasons.

The temporal variations of malic acid ($h\text{C}_4$)/ C_4 ratios are shown in Fig. 10d. Kawamura and Ikushima (1993) conjectured, based on the field observation over the urban

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atmosphere, that hC_4 can be photochemically generated from succinic acid (C_4) via hydroxylation reaction. 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 2 fold higher hC_4/C_4 ratios were observed during summer season for another megacity Chinnai, India (Pavuluri et al., 2010).

3.5 Relation between short chain dicarboxylic acids and WSOC

Primary emission from biomass burning as well as bio-fuel plume particles are reported to have large portion 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 . Similar molecular distribution was observed for the aerosols from Indonesian forest fires (Narukawa et al., 1999) and European aerosols (Legrand et al., 2007). Figure 12a shows a strong positive correlation for $\sum(C_2+C_3+C_4)$ (i.e. short chain diacids) with WSOC only for winter period, suggesting a significant contribution from biomass burning sources. However, a poor correlation was observed for summer period (Fig. 12b).

3.6 Principal component analysis for selected species

Several types of mathematical models were used in the aerosol chemical composition source apportionment studies. 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 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)

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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 winter period the first factor comprises 50% of the total variance with high loadings of C₂ with ketocarboxylic acids (@C₂ and Pyr) and α-dicarbonyls. Here, C₃, C₄ and other long chain diacids form a separate component, indicating their different origin. In contrast, during summer months, the first component shows maximum loading for C₂ along with C₃ to C₆ diacids with lesser contribution from ketocarboxylic acids. This clearly shows the presence of different source and pathways for oxalic acid formation for winter and summer seasons over the region. Phthalic and C₉ were associated in second component for both the seasons with significantly higher loading during summer season. Terephthalic acid formed a separate third component for both the seasons. Maleic acid is produced by ring opening of the aromatic hydrocarbons such as toluene and benzene (Kawamura and Sakaguchi, 1999), which was associated with fumaric and phthalic acids during winter, but was alienated during summer season. Both phthalic and maleic acids are reported to be high in polluted environment (Mochida et al., 2003). Glyoxal and t-Ph were recognized together during winter period, 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) while 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).

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 (C₂) acid was

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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 at the regional and global scales. Winter samples had significantly higher C_2 /total diacid ratios as compared to summer samples, indicating more fresh aerosols during summer due to the atmospheric transport with 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. The observed higher ratios for C_6/C_9 and Ph/ C_9 indicate that other anthropogenic sources were more important than biomass burning. The observed phthalic/adipic ratios are greater than unity, indicating the potential sources from diesel fuel vehicles (5 fold higher during summer) 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 inversion layer and also increased photochemical production during transport process of the organic pollutants from source regions of Indo-Gangetic Basin. This study suggests that the pollutants emitted from far distant sources can significantly affect the regional air quality and, therefore, contribute to the aerosol's effects applicable to climate change.

For the winter months the observation site remains above the boundary layer and represents a free tropospheric site (Hegde et al., 2008). Therefore, the observed concentrations of different organic compounds may represent the regional free tropospheric concentrations of several pollutants. On an average, for summer season, higher concentrations of several anthropogenic compounds were observed compared to winter period. Conversely, the boundary layer height increases during summer

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months and the observation site will be well within the boundary layer. Thus, the pollutants of northwestern Indian origin are readily transported towards the central Himalayas due to high wind, elevated temperature, and supplementary convection. Much higher concentrations of phthalic acid along with several other anthropogenic organic compounds were recorded in summer than winter. Summertime decline of oxalic acid may be associated with photochemical decomposition and dust transport over the region, which needs further investigation on trace metals such as iron that may involve with the decomposition process of oxalic acid.

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References

- Aggarwal, S. G. and Kawamura, K.: Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.*, 113, D14301, doi:10.1029/2007JD009365, 2008.
- Andreae, M. O., Atlas, E., Cachier, H., Cofer III, W. R., Harris, G. W., Helas, G., Koppmann, R., Lacaux, J.-P., and Ward, D. E.: Trace gas and aerosol emissions from savanna fires, in: *Biomass Burning and Global Change*, edited by: Levine, J. S., MIT Press, Cambridge, Mass, 278–295, 1996.
- Cao, J. J., Wu, F., Chow, J. C., Lee, S. C., Li, Y., Chen, S. W., An, Z. S., Fung, K. K., Watson, J. G., Zhu, C. S., and Liu, S. X.: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China, *Atmos. Chem. Phys.*, 5, 3127–3137, doi:10.5194/acp-5-3127-2005, 2005.
- Chinnam, N., Dey, S., Tripathi, S. N., and Sharma, M.: Dust events in Kanpur, northern India: Chemical evidence for source and implications to radiative forcing, *Geophys. Res. Lett.*, 33, L08803, doi:10.1029/2005GL025278, 2006.

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- 10 Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY Website (<http://ready.arl.noaa.gov/HYSPLIT.php>), NOAA Air Resour. Lab., Silver Spring, Md, 2010.
- 15 Dumka, U. C., Krishna Moorthy, K., Kumar, R., Hegde, P., Sagar, R., Pant, P., Singh, N., and Babu, S. S.: Characteristics of aerosol black carbon mass concentration over a high altitude location in the Central Himalayas from multi-year measurements, *Atmos. Res.*, 96, 510–521, doi:10.1016/j.atmosres.2009.12.010, 2011.
- 20 Engling, G., Zhang, Y. N., Chan, C. Y., Sang, X. F., Lin, M., Ho, K. F., Li, Y. S., Lin, C. Y., and Lee, J. J.: Characterization and sources of aerosol particles over the southeastern Tibetan Plateau during the Southeast Asia biomass-burning season, *Tellus B*, 63, 117–128. doi:10.1111/j.1600-0889.2010.00512.x, 2011.
- 25 Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.*, 109, D15205, doi:10.1029/2003JD004387, 2004.
- 30 Facchini, M. C., Mircea, M., Fuzzi, S., and Charlson, R. J.: Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, 401, 257–259, 1999.
- Favez, O., Cachier, H., Sciare, J., Alfaro, S. C., El-Araby, T. M., Harhash, M. A., and Abdelwahab M. M.: Seasonality of major aerosol species and their transformations in Cairo megacity, *Atmos. Environ.*, 42, 1503–1516, 2008.
- Gao, S., Hegg, D. A., Hobbs, P. V., Kirchstetter, T. W., Magi, B. I., and Sadilek, M.: Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution, and distribution, *J. Geophys. Res.*, 108, 8491, doi:10.1029/2002JD002324, 2003.
- Gautam, R., Hsu, N. C., and Lau, K. M.: Premonsoon aerosol characterization and radiative effects over the Indo-Gangetic Plains: Implications for regional climate warming, *J. Geophys. Res.*, 115, D17208, doi:10.1029/2010JD013819, 2010.
- George, S. K., Nair, P. R., Parameswaran, K., Jacob, S., and Abraham, A.: Seasonal trends in chemical composition of aerosols at a tropical coastal site of India, *J. Geophys. Res.*, 113, D16209, doi:10.1029/2007JD009507, 2008.
- Hegde, P., Pant, P., Naja, M., Dumka, U. C., and Sagar, R.: South Asian dust episode in

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June 2006: Aerosol observations in the central Himalayas, *Geophys. Res. Lett.*, 34, L23802, doi:10.1029/2007GL030692, 2007.

Hegde, P., Pant, P., and Kumar, Y. B.: An integrated analysis of lidar observations in association with optical properties of aerosols from a high altitude location in central Himalayas, *Atmos. Sci. Lett.*, 10, 48–57, 2008.

Ho, K. F., Lee, S. C., Cao, J. J., Kawamura, K., Watanabe, T., Cheng, Y., and Chow, J. C.: Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong, *Atmos. Environ.*, 40, 3030–3040, 2006.

Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. J.: Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.*, 112, D22S27, doi:10.1029/2006JD008011, 2007.

Ho, K. F., Lee, S. C., Ho, S. S. H., Kawamura, K., Tachibana, E., Cheng, Y., and Zhu, T.: Dicarboxylic Acids, Ketocarboxylic acids, α -dicarbonyls, Fatty Acids and Benzoic Acid in urban aerosols collected during 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006), *J. Geophys. Res.*, 115, D19312, doi:1029/2009JD013304, 2010.

Hopkins, R. J., Lewis, K., Desyaterik, Y., Wang, Z., Tivanski, A. V., Arnott, W. P., Laskin, A., and Gilles, M. K.: Correlations between optical, chemical, and physical properties of biomass burn aerosols, *Geophys. Res. Lett.*, 34, L18806, doi:10.1029/2007GL030502, 2007.

Jung, J., Tsatsral, B., Kim, Y. J., and Kawamura, K.: Organic and inorganic aerosol compositions in Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: Dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls, *J. Geophys. Res.*, 115, D22203, doi:10.1029/2010JD014339, 2010.

Kawamura, K.: Identification of C_2 - C_{10} ω -oxocarboxylic acids, pyruvic acid and C_2 - C_3 α -dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC-MS, *Anal. Chem.*, 65, 3505–3511, 1993.

Kawamura, K. and Gagosian, R. B.: Implications of ω -oxocarboxylic acids in the remote marine atmosphere for photooxidation of unsaturated fatty acids, *Nature*, 325, 330–332, 1987.

Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, 27, 2227–2235, 1993.

Kawamura, K. and Kaplan, I. R.: Motor exhaust emission as a primary source of dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, 21, 105–110, 1987.

Kawamura, K. and Pavuluri, C. M.: New directions: Need for better understanding of plastic waste burning as inferred from high abundance of terephthalic acid in South Asian aerosols,

Seasonal variations of water-soluble organic carbon

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Atmos. Environ., 44, 5320–5321, 2010.

Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropic, *J. Geophys. Res.*, 104, 3501–3509, 1999.

5 Kawamura, K. and Yasui, O.: Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, 39, 1945–1960, 2005.

10 Kawamura, K., Umemoto, N., Mochida, M., Bertram, T., Howell, S., and Huebert, B. J.: Water-soluble dicarboxylic acids in the tropospheric aerosols collected over East Asia and western North Pacific by ACE-Asia C-130 aircraft, *J. Geophys. Res.*, 108, 8639, doi:10.1029/2002JD003256, 2003.

15 Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., and Lee, M.: Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble Dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in: *Geochemical Investigation in Earth and Space Science: A Tribute to Issac R. Kaplan*, edited by: Hill, R. J., Leventhal, J., Aizenshtat, Z., Baedeker, M. J., Claypool, G., Eganhouse, R., Goldhaber, M., and Peters, K., *Spec. Publ. Geochem. Soc.*, 9, 243–265, 2004.

20 Kerminen, V. M.: Relative roles of secondary sulfate and organics in atmospheric cloud condensation nuclei production, *J. Geophys. Res.*, 106, 17321–17333, 2001.

Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers, *Atmos. Chem. Phys.*, 10, 2209–2225, doi:10.5194/acp-10-2209-2010, 2010.

25 Lee X., Qin, D., Jiang, G., Duan, K., and Zhou, H.: Atmospheric pollution of a remote area of Tianshan Mountain: Ice core record, *J. Geophys. Res.*, 108, 4406, doi:10.1029/2002JD002181, 2003.

30 Lelieveld, J., Crutzen, P. J., Ramanathan, V., Andreae, M. O., Brenninkmeijer, C. A. M., Campos, T., Cass, G. R., Dickerson, R. R., Fischer, H., de Gouw, J. A., Hansel, A., Jefferson, A., Kley, D., de Laat, A. T. J., Lal, S., Lawrence, M. G., Lobert, J. M., Mayol-Bracero, O. L., Mitra, A. P., Novakov, T., Oltmans, S. J., Prather, K. A., Reiner, T., Rodhe, H., Scheeren, H. A., Sikka, D., and Williams, J.: The Indian Ocean Experiment: widespread air pollution from South and Southeast Asia, *Science*, 291, 1031–1036, 2001.

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- Legrand, M., Preunkert, S., Oliveira, T., Pio, C. A., Hammer, S., Gelencse'r, A., Kasper-Giebl, A., and Laj, P.: Origin of C2-C5 dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect, *J. Geophys. Res.*, 112, D23S07, doi:10.1029/2006JD008019, 2007.
- 5 Lim, H.-J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.*, 39, 4441–4446, 2005.
- Malinowski, E. R.: Factor analysis in chemistry, (2nd edn.), Wiley-Interscience, ISBN 0-471-53009-3, *J. Chemometr.*, 5, 545 pp., doi:10.1002/cem.1180050607, 1991.
- Mayewski, P. A., Lyons, W. B., and Ahmad, N.: Chemical Composition of a High Altitude Fresh
10 Snowfall in the Ladakh Himalayas, *Geophys. Res. Lett.* 10, 105–108, 1983.
- Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass burning aerosols over Amazonia, 2, Apportionment of the chemical composition and importance of the polyacidic fraction, *J. Geophys. Res.*, 107, 8091, doi:10.1029/2001JD000522, 2002.
- 15 Miyazaki, Y., Aggarwal, S. G., Singh, K., Gupta, P. K., and Kawamura, K.: Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation processes, *J. Geophys. Res.*, 114, D19206, doi:10.1029/2009JD011790, 2009.
- Mochida, M., Kawabata, A., Kawamura, K., Hatsushika, H., and Yamazaki, K.: Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North
20 Pacific, *J. Geophys. Res.*, 108, 4193, doi:10.1029/2002JD002355, 2003.
- Moorthy, K. K., Babu, S. S., Satheesh, S. K., Srinivasan, J., and Dutt, C. B. S.: Dust absorption over the “Great Indian Desert” inferred using ground-based and satellite remote sensing, *J. Geophys. Res.*, 112, D09206, doi:10.1029/2006JD007690, 2007.
- 25 Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, 26, 3101–3104, 1999.
- Olmez, I., Beal, J. W., and Villaume, J. F.: A new approach to understanding multiple-source groundwater contamination: factor analysis and chemical mass balances, *Water Res.*, 28, 1095–1101, 1994.
- 30 Pant, P., Hegde, P., Dumka, U. C., Sagar, R., Satheesh, S. K., Moorthy, K. K., Saha, A., and Srivastava, M. K.: Aerosol characteristics at a high-altitude location in central Himalayas: Optical properties and radiative forcing, *J. Geophys. Res.*, 111, D17206,

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doi:10.1029/2005JD006768, 2006.

Pavuluri, C. M., Kawamura, K., and Swaminathan, T.: water-soluble organic carbon, dicarboxylic acids, ketoacids, and α -dicarbonyls in the tropical Indian aerosols, *J. Geophys. Res.*, 115, D11302, doi:10.1029/2009JD012661, 2010.

5 Ram, K., Sarin, M. M., and Tripathi, S. N.: A 1 year record of carbonaceous aerosols from an urban site in the Indo-Gangetic Plain: Characterization, sources, and temporal variability, *J. Geophys. Res.*, 115, D24313, doi:10.1029/2010JD014188, 2010.

Rastogi, N. and Sarin, M. M.: Quantitative chemical composition and characteristics of aerosols over western India: One-year record of temporal variability, *Atmos. Environ.*, 43, 3481–3488, 2009.

10 Rolph, G. D.: Real-time Environmental Applications and Display system (READY) Website (<http://ready.arl.noaa.gov>), NOAA Air Resour. Lab., Silver Spring, Md., 2010.

Ruellan, S. and Cachier, H., Characterisation of fresh particulate vehicular exhausts near a Paris high flow road, *Atmos. Environ.*, 35, 453–468, 2001.

15 SPSS, Manual: Advanced Statistics Manual SPSS/PC+V 3.0; SPSS Inc., 444 North Michigan Avenue, Chicago IL 60611, 1988.

Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.-M., and Hillamo, R.: Sources of organic carbon in fine particulate matter in northern European urban air, *Atmos. Chem. Phys.*, 8, 6281–6295, doi:10.5194/acp-8-6281-2008, 2008.

20 Sagar, R., Kumar, B., Dumka, U. C., Moorthy, K. K., and Pant, P.: Characteristics of aerosol spectral optical depths over Manora Peak: A high altitude station in the central Himalayas, *J. Geophys. Res.*, 109, D06207, doi:10.1029/2003JD003954, 2004.

Sandradewi, J., Prévôt, A. S. H., Szidat, S., Perron, N., Rami Alfarra, M., Lanz, V. A., Weingartner, E., and Baltensperger, U.: Using aerosol light absorption measurements for the quantitative determination of wood burning and Traffic emission contributions to particulate matter, *Environ. Sci. Technol.*, 42, 3316–3323, 2008.

25 Satheesh, S. K. and Ramanathan, V.: Large differences in tropical aerosol forcing at the top of the atmosphere and Earth's surface, *Nature*, 405, 60–63, 2000.

Saxena, P. and Hildemann, L. M.: Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57–109, 1996.

30 Saxena, P., Hildemann, L., McMurry, P., and Seinfeld, J.: Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, 100, 18755–18770, 1995.

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Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit B. R. T.: Measurement of emissions from air pollution sources: 1. C₁ through C₂₉ organic compounds from meat charbroiling, *Environ. Sci. Technol.*, 33, 1566–1577, 1999.

5 Sempere, R. and Kawamura, K.: Trans-hemispheric contribution of C₂-C₁₀ α , ω -dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global Biogeochem. Cy.*, 17, 1069, doi:10.1029/2002GB001980, 2003.

Shrestha, A. B., Wake, C. P., and Dibb, J. E.: Chemical composition of aerosol and snow in the high Himalaya during the summer monsoon season, *Atmos. Environ.*, 31, 2815–2826, 1997.

10 Shrestha, A. B., Wake, C. P., Dibb, J. E., Wayewski, P. A., Whitlow, S. I., Carmichael, G. R., and Ferm, M.: Seasonal Variations in Aerosol Concentrations and Compositions in the Nepal Himalaya, *Atmos. Environ.*, 34, 3349–3363, 2000.

Shrestha, A. B., Wake, C. P., Dibb, J. E., and Whitlow, S. I.: Aerosol and precipitation chemistry at a remote Himalayan site in Nepal, *Aerosol Sci. Technol.*, 36, 441–456, 2002.

15 Simoneit, B. R. T., Medeiros, P. M., and Didyk, B. M.: Combustion products of plastics as indicators for refuse burning in the atmosphere, *Environ. Sci. Technol.*, 39, 6961–6970, doi:10.1021/es050767x, 2005.

Tripathi, S. N., Dey, S., Tare, V., Satheesh, S. K., Lal, S., and Venkataramani, S.: Enhanced layer of black carbon in a north Indian industrial city, *Geophys. Res. Lett.*, 32, L12802, doi:10.1029/2005GL022564, 2005.

20 Turpin, B. J. and Lim, H. J.: Species contributions to PM_{2.5} mass concentrations: revisiting common assumptions for estimating organic mass, *Aerosol Sci. Technol.*, 35, 602–610, 2001.

25 Viana, M., Maenhaut, W., ten Brink, H. M., Chi, X., Weijers, E., Querol, X., Alastuey, A., Mikuska, P., and Vecera, Z.: Comparative analysis of organic and elemental carbon concentrations in carbonaceous aerosols in three European cities, *Atmos. Environ.*, 41, 5972–5983, 2007.

Volkamer, R., Platt, U., and Wirtz, K.: Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkylradical pathway from benzene, toluene, and p-xylene, *J. Phys. Chem. A*, 105, 7865–7874, doi:10.1021/jp010152w, 2001.

30 Wake, C. P., Dibb, J. E., Mayewski, P. A., Zhongqin, L., and Zichu, X.: The Chemical Composition of Aerosols over the Eastern Himalayas and Tibetan Plateau during Low Dust Periods,

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Atmos. Environ., 28, 695–704, 1994.

Wang, G., Liu, N. C., and Wang, L.: Identification of dicarboxylic acids and aldehydes of PM₁₀ and PM_{2.5} aerosols in Nanjing, China, Atmos. Environ., 36, 1941–1950, 2002.

Wang, H., Kawamura, K., and Yamazaki, K.: Water soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and western Pacific Ocean, J. Atmos. Chem., 53, 43–61, 2006a.

Wang, H., Kawamura, K., Ho, K. F., and Lee, S. C.: Low molecular weight dicarboxylic acids, ketoacids and dicarbonyls in the fine particles from a roadway tunnel: significant secondary production from the precursors in vehicular emissions, Environ. Sci. Technol., 40, 6255–6260, 2006b.

Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, Atmos. Environ., 37, 2423–2427, 2003.

Willey, J. D., Kieber, R. J., Williams, K. H., Crozier, J. S., Skrabal, S. A., and Avery Jr., G. B.: Temporal Variability of Iron Speciation in Coastal Rainwater, J. Atmos. Chem., 37, 185–205, 2000.

Yao, X., Fang, M., and Chan, C. K.: Size distributions and formation of dicarboxylic acids in atmospheric particles, Atmos. Environ., 36, 2099–2107, 2002.

Yao, X., Fang, M., Chan, C. K., Ho, K. F., and Lee, S. C.: Characterization of dicarboxylic acids in PM_{2.5} in Hong Kong, Atmos. Environ., 38, 963–970, 2004.

Yu, X.-Y., Cary, R. A., and Laulainen, N. S.: Primary and secondary organic carbon downwind of Mexico City, Atmos. Chem. Phys., 9, 6793–6814, doi:10.5194/acp-9-6793-2009, 2009.

Table 1. Concentrations (ng m^{-3}) of dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls and concentrations ($\mu\text{g m}^{-3}$) of EC (elemental carbon), OC (organic carbon), TC (total carbon) and WSOC (water soluble organic carbon) over Nainital, India.

| Compounds | Winter | | | | Summer | | | |
|-----------------------------------|-------------|---------------|---------------|---------------|--------------|---------------|----------------|---------------|
| | Day (N = 9) | | Night (N = 9) | | Day (N = 11) | | Night (N = 10) | |
| | Range | Ave. \pm SD | Range | Ave. \pm SD | Range | Ave. \pm SD | Range | Ave. \pm SD |
| Dicarboxylic acids | | | | | | | | |
| Oxalic (C_2) | 285–492 | 393 \pm 78 | 213–474 | 313 \pm 88 | 138–425 | 242 \pm 90 | 106–389 | 189 \pm 92 |
| Malonic (C_3) | 7.9–22 | 15 \pm 4.3 | 5.8–36 | 18 \pm 10 | 16–77 | 34 \pm 17 | 13–52 | 26 \pm 15 |
| Succinic (C_4) | 9.5–21 | 17 \pm 3.9 | 8.1–40 | 19 \pm 11 | 19–86 | 40 \pm 19 | 15–53 | 29 \pm 14 |
| Glutaric (C_5) | 2.3–5.5 | 3.9 \pm 1.0 | 2.2–6.4 | 3.8 \pm 1.7 | 5.0–16.5 | 8.9 \pm 3.4 | 3.9–9.8 | 6.0 \pm 2.2 |
| Adipic (C_6) | 2.7–8.2 | 4.5 \pm 1.6 | 1.9–17 | 6.4 \pm 5.5 | 5.2–17.3 | 9.6 \pm 3.5 | 3.5–7.8 | 6.0 \pm 1.5 |
| Pimelic (C_7) | 0.7–2.5 | 1.6 \pm 0.5 | 0.4–2.1 | 1.3 \pm 0.6 | 0.5–7.2 | 3.5 \pm 2.4 | 0.6–5.6 | 2.3 \pm 1.5 |
| Suberic (C_8) | 0.2–0.5 | 0.3 \pm 0.1 | 0.1–0.6 | 0.3 \pm 0.2 | 0.2–2.3 | 0.9 \pm 0.6 | 0.3–3.4 | 0.8 \pm 0.9 |
| Azelaic (C_9) | 2.9–5.5 | 4.3 \pm 0.8 | 2.3–6.1 | 3.8 \pm 1.3 | 3.4–35 | 17 \pm 11 | 3.8–27 | 14 \pm 8.2 |
| Sebacic (C_{10}) | 0.5–0.9 | 0.6 \pm 0.1 | 0.3–0.8 | 0.5 \pm 0.2 | 0.2–3.6 | 1.5 \pm 1 | 0.3–4.6 | 2.2 \pm 1.5 |
| Undecanedioic (C_{11}) | 0.6–2.5 | 1.2 \pm 0.7 | 0.4–3.0 | 1.3 \pm 0.8 | 0.2–5.1 | 1.9 \pm 1.6 | 0.4–4.6 | 1.6 \pm 1.5 |
| Dodecanedioic (C_{12}) | 0.1–0.8 | 0.3 \pm 0.2 | 0.1–0.4 | 0.2 \pm 0.1 | 0.1–2.1 | 0.9 \pm 0.6 | 0.2–1.9 | 1.1 \pm 0.7 |
| Methylmalonic ($i\text{C}_4$) | 0.3–1.4 | 0.5 \pm 0.4 | 0.1–1.1 | 0.5 \pm 0.3 | 0.5–7.4 | 2 \pm 2 | 0.1–2.1 | 1.2 \pm 0.6 |
| Methylsuccinic ($i\text{C}_5$) | 0.7–2.8 | 1.8 \pm 0.6 | 0.8–5.6 | 2.2 \pm 1.7 | 2.0–8.5 | 3.6 \pm 2.2 | 1.1–5.9 | 2.8 \pm 1.7 |
| Methylglutaric ($i\text{C}_6$) | 0.2–0.7 | 0.4 \pm 0.2 | 0.1–0.8 | 0.4 \pm 0.2 | 0.2–4.5 | 1.5 \pm 1.2 | 0.7–4.1 | 1.4 \pm 1.0 |
| Maleic (M) | 0.04–1.3 | 0.7 \pm 0.4 | 0.4–5.7 | 1.6 \pm 1.6 | 1.0–7.2 | 4.0 \pm 1.8 | 0.2–3.9 | 2.7 \pm 1.0 |
| Fumaric (F) | 0.6–0.9 | 0.8 \pm 0.1 | 0.6–1.8 | 1.0 \pm 0.4 | 1.0–6.4 | 4.0 \pm 1.5 | 1.0–11 | 3.5 \pm 3.2 |
| Methylmaleic (mM) | 0.4–0.9 | 0.7 \pm 0.2 | 0.3–3.9 | 1.3 \pm 1.1 | 0.7–4.4 | 2.3 \pm 1.4 | 0.8–14 | 3.2 \pm 3.9 |
| Phthalic (Ph) | 8.9–17 | 12 \pm 2.8 | 5.8–23 | 13 \pm 5.6 | 26–182 | 88 \pm 55 | 21–159 | 75 \pm 54 |
| Isophthalic (i-Ph) | 1.3–2.8 | 1.7 \pm 0.5 | 0.2–3.0 | 1.6 \pm 0.9 | 1.3–5.5 | 3.4 \pm 1.6 | 0.4–5.6 | 3.1 \pm 1.7 |
| Terephthalic (t-Ph) | 1.2–9.8 | 4.8 \pm 3.3 | 2.7–8.2 | 4.8 \pm 1.8 | 0.7–8.8 | 3.4 \pm 2.3 | 1.9–11 | 4.2 \pm 2.7 |
| Malic ($h\text{C}_4$) | 0.02–0.3 | 0.1 \pm 0.1 | 0.1–0.4 | 0.1 \pm 0.1 | 0.1–4.8 | 0.8 \pm 1.4 | 0.1–0.6 | 0.2 \pm 0.2 |
| Oxomalonic ($k\text{C}_3$) | 2.7–8.7 | 5.4 \pm 2.3 | 2.5–8.2 | 5.0 \pm 1.8 | 1.4–7.8 | 4.6 \pm 1.9 | 1.6–7.2 | 3.5 \pm 1.7 |
| 4-Oxopimelic ($k\text{C}_7$) | 0.3–2.8 | 1.6 \pm 0.8 | 0.8–2.7 | 1.4 \pm 0.6 | 0.8–4.8 | 2.1 \pm 1.3 | 0.6–4.0 | 1.8 \pm 1.1 |
| Subtotal | 361–591 | 473 \pm 86 | 283–569 | 400 \pm 108 | 303–729 | 480 \pm 132 | 233–592 | 380 \pm 107 |

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Table 1. Continued.

| Compounds | Winter | | | | Summer | | | |
|---------------------------------------|---------------------|-----------|-----------------------|-----------|----------------------|-----------|------------------------|-----------|
| | Day (<i>N</i> = 9) | | Night (<i>N</i> = 9) | | Day (<i>N</i> = 11) | | Night (<i>N</i> = 10) | |
| | Range | Ave. ± SD | Range | Ave. ± SD | Range | Ave. ± SD | Range | Ave. ± SD |
| Ketocarboxylic acids | | | | | | | | |
| Glyoxalic (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 | 0.7–15.4 | 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 (mGly) | 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 ($\mu\text{gC m}^{-3}$) | 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 ($\mu\text{gC m}^{-3}$) | 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 ($\mu\text{gC m}^{-3}$) | 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 ($\mu\text{gC m}^{-3}$) | 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 |

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Table 2. Weight ratios of selected diacids compared 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).

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Table 3. Results of principal component analysis of the selected dicarboxylic acids and related compounds.

| Compounds | Winter | | | Summer | | |
|------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | Component 1 | Component 2 | Component 3 | Component 1 | Component 2 | Component 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 (t-Ph) | | | 0.84 | | | 0.73 |
| Glyoxalic (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 (mGly) | 0.74 | | | | 0.42 | |
| Total variance (%) | 50 | 18 | 7 | 36 | 23 | 10 |

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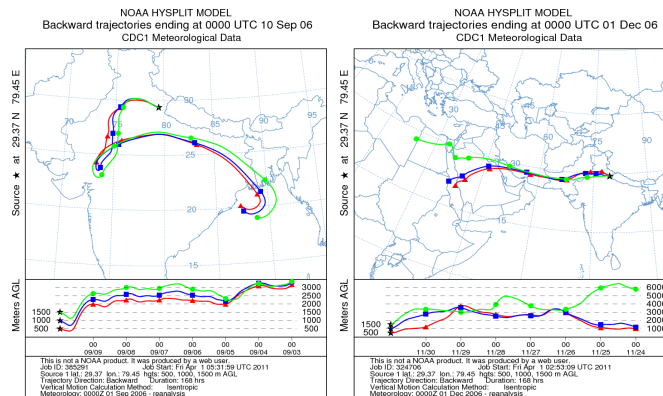
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Winter 2006



Summer 2007

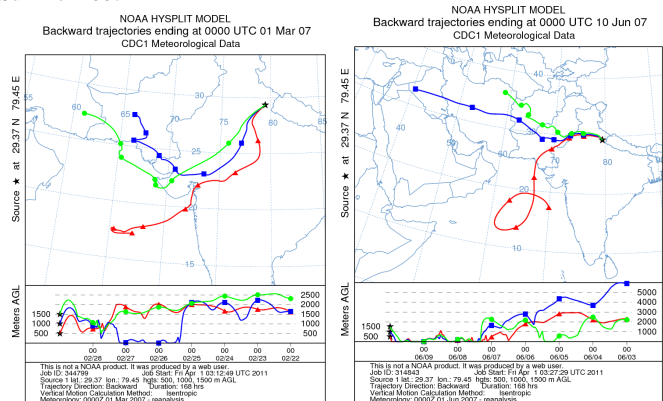


Fig. 1. Air mass backward trajectory cluster during the study period reaching Nainital (star symbol) to illustrate the long-range transport.

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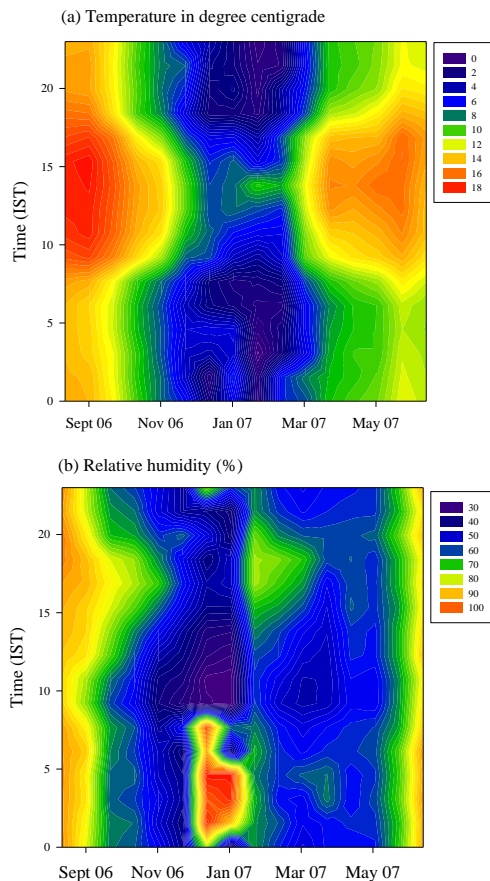


Fig. 2. Monthly mean diurnal and seasonal variation of **(a)** ambient air temperature (in degree centigrade) and **(b)** relative humidity (%) measured over the observational site during the study period.

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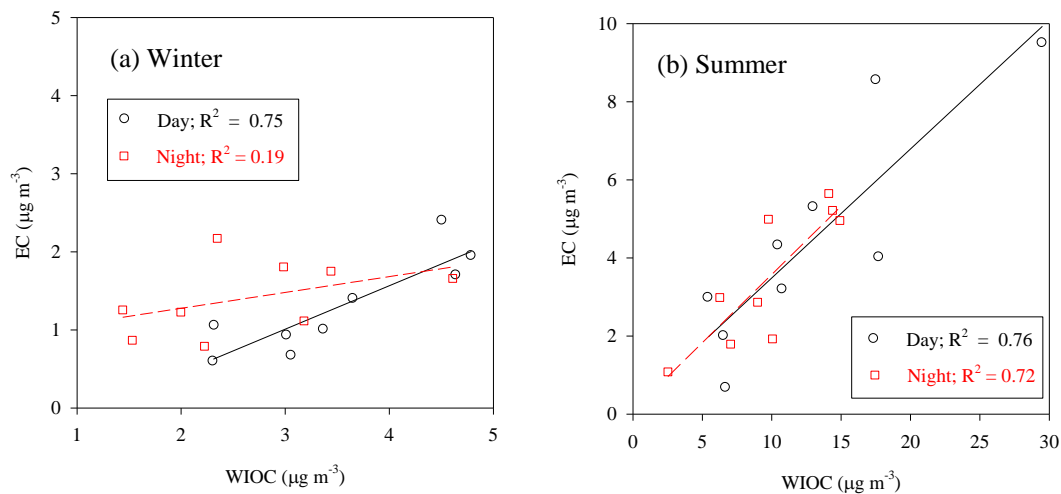
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Fig. 3. Scatter plots between water insoluble organic carbon (WIOC) and elemental carbon (EC) during (a) winter and (b) summer seasons showing a linear relation.

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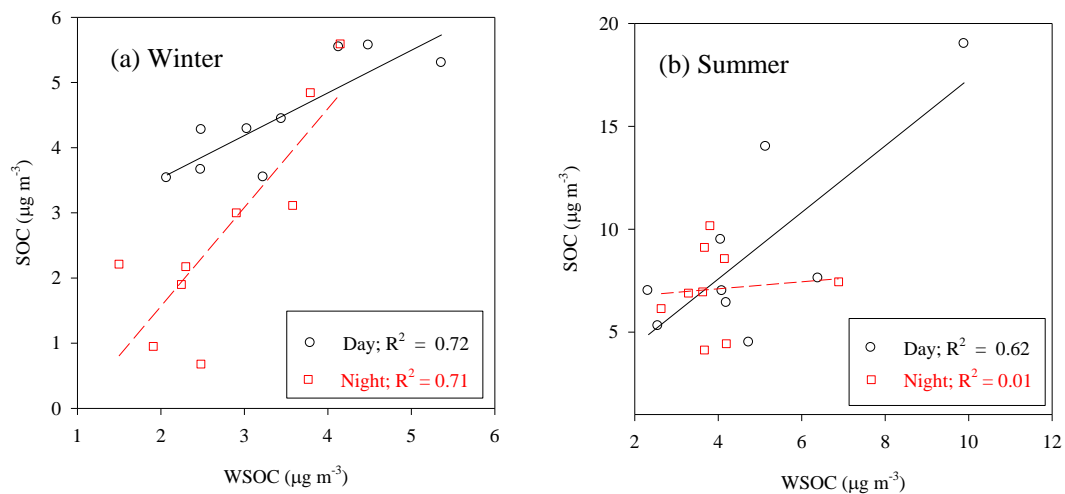
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Fig. 4. Scatter plots between water soluble organic carbon (WSOC) and secondary organic carbon (SOC) during **(a)** winter and **(b)** summer seasons showing a linear relation.

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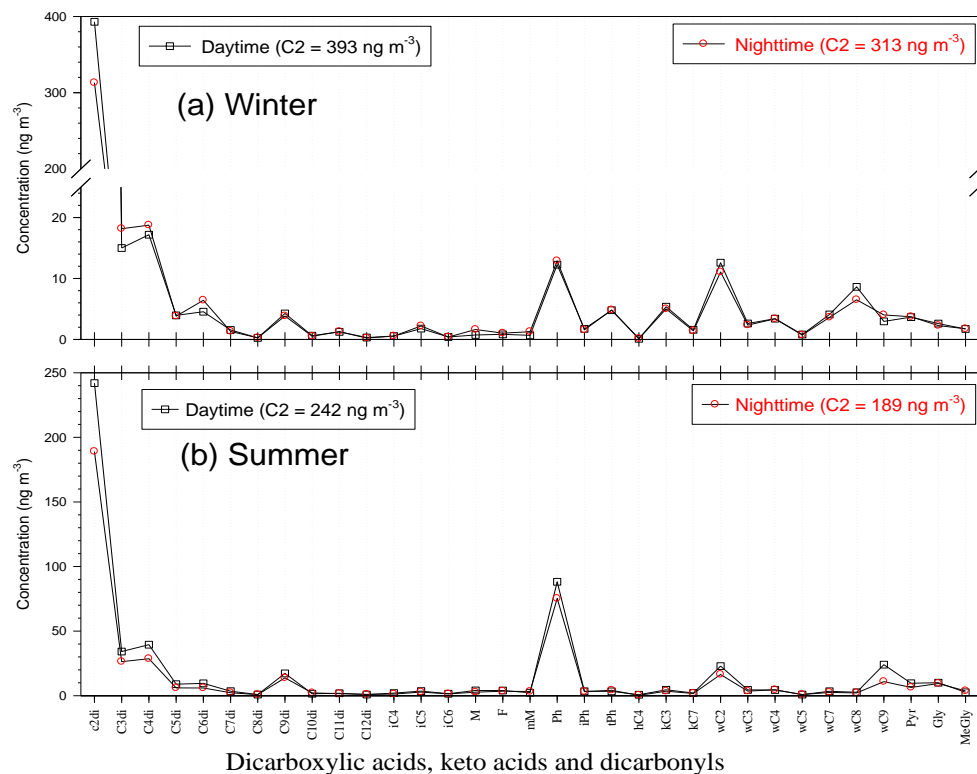


Fig. 5. Average molecular distributions of dicarboxylic acids (diacids), ketocarboxylic acids (ketoacids), and α -dicarbonyls in aerosol samples collected at Nainital, India. See Table 1 for abbreviations.

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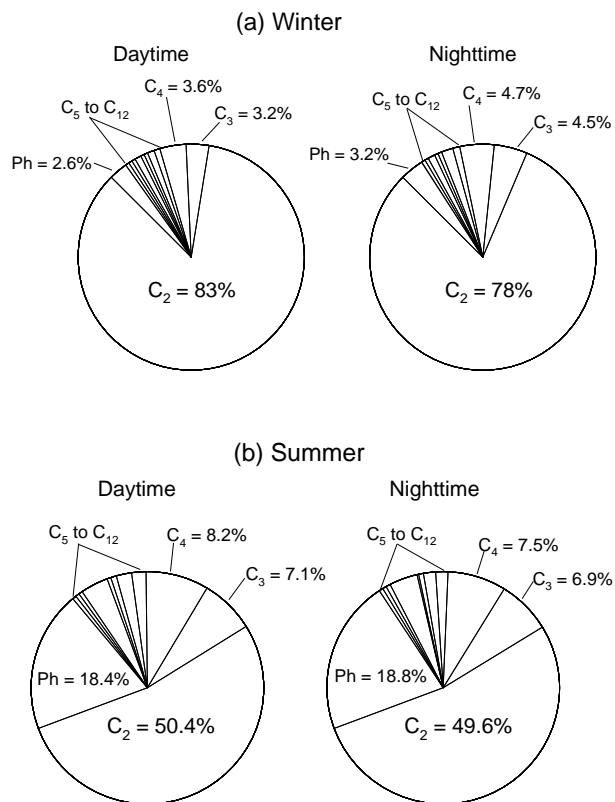


Fig. 6. Pie diagrams of relative abundances (%) of individual diacids in total straight-chain diacids (C₂–C₁₂) aerosols collected during **(a)** winter and **(b)** summer seasons in Nainital, India.

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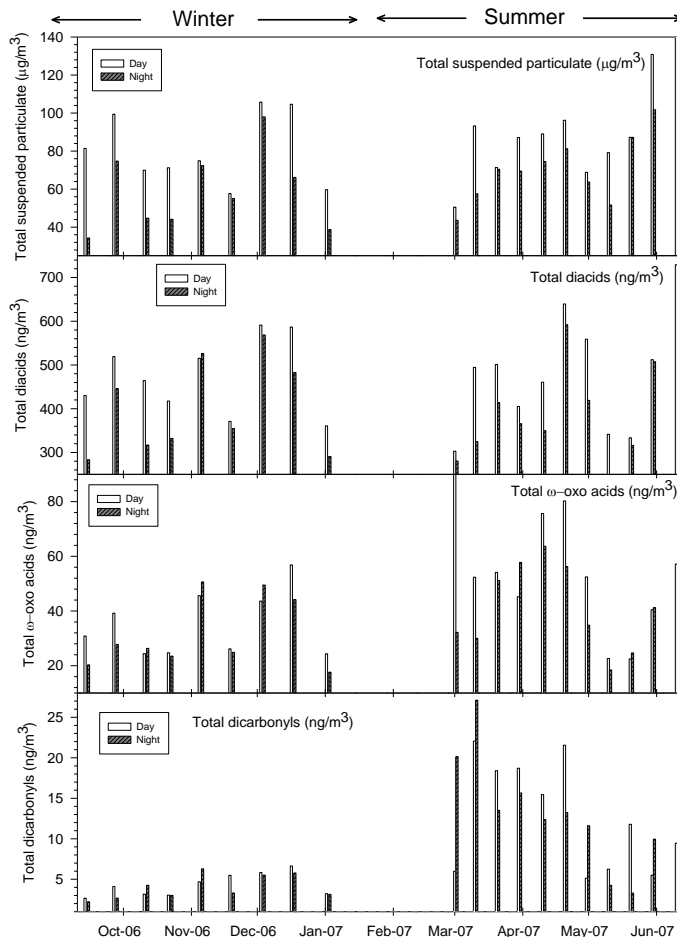


Fig. 7. Temporal variations in total suspended particulate matter (TSPM) along with mass fraction of total diacids, total ketoacids, and total α -dicarbonyls in TSPM for aerosol samples collected at Nainital, India.

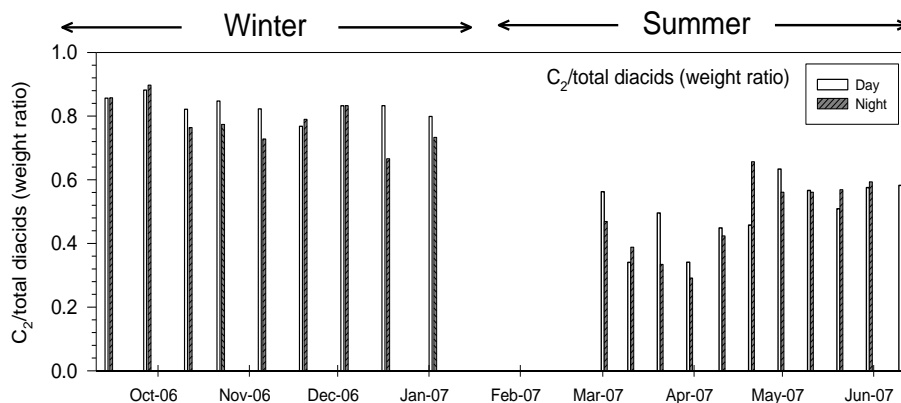
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Fig. 8. Temporal variations of C_2 /total diacid concentration ratios in aerosol samples collected at Nainital, India.

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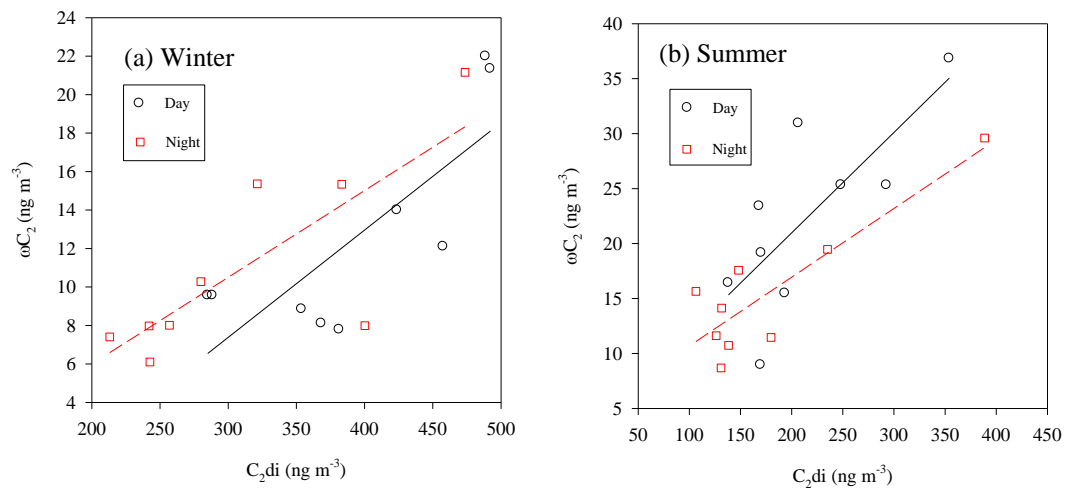
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Fig. 9. Scatter plots between oxalic (C_2) and glyoxylic (ωC_2) acids during **(a)** winter and **(b)** summer seasons showing a linear relation.

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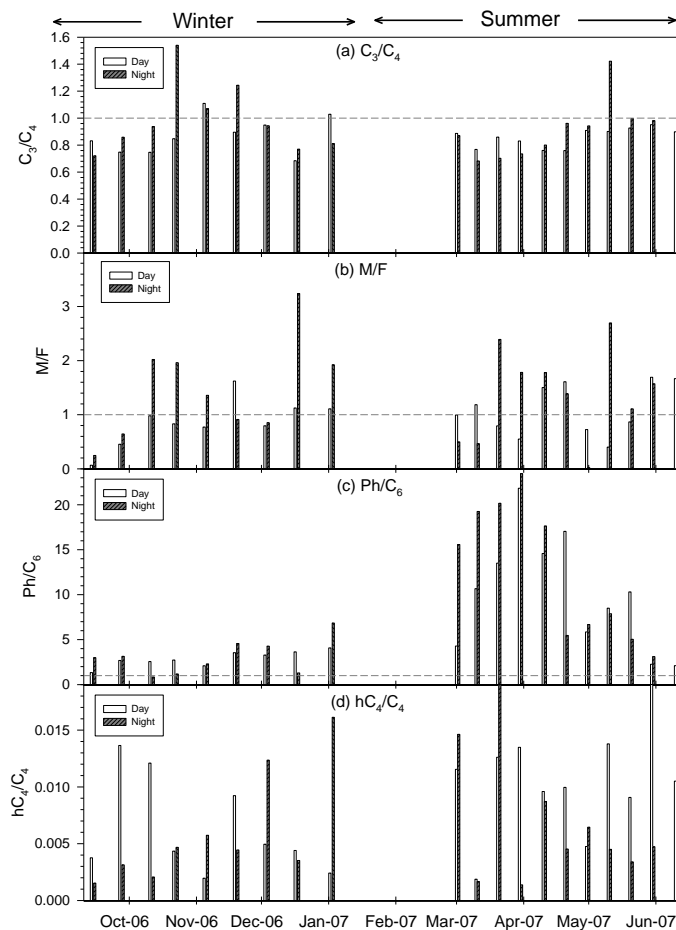


Fig. 10. Temporal variations in concentration (weight) ratios of **(a)** C_3/C_4 , **(b)** M/F, **(c)** Ph/ C_6 and **(d)** hC_4/C_4 in the aerosol samples collected at Nainital, India.

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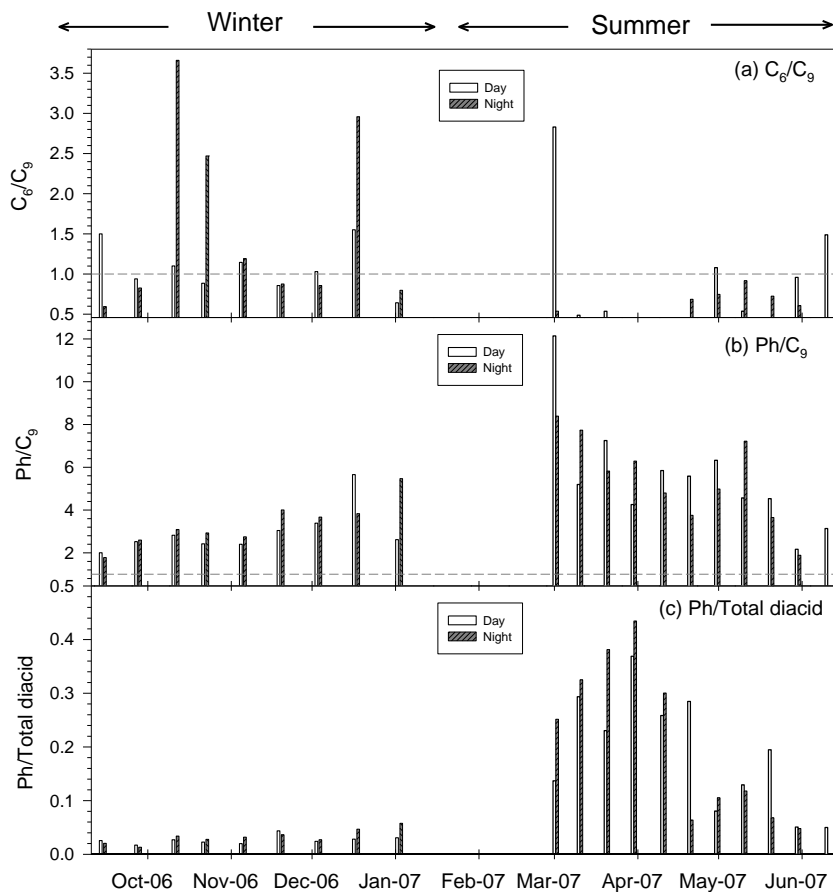


Fig. 11. Temporal variations of **(a)** C_6/C_9 concentration (weight) ratios, **(b)** Ph/C_9 concentration ratios, and **(c)** $Ph/Total\ diacid$ concentration ratios in the aerosol samples collected at Nainital, India.

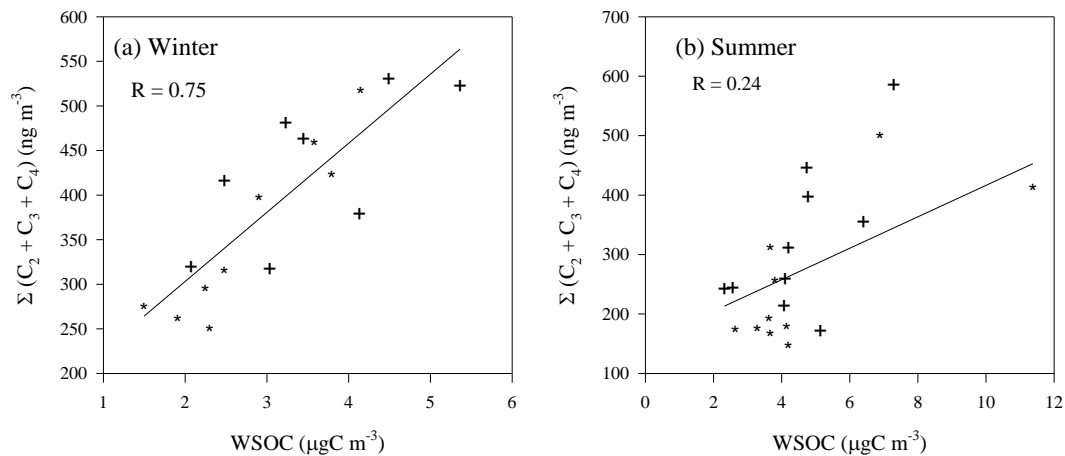
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Fig. 12. Relation between water-soluble organic carbon (WSOC) and total C₂–C₄ diacids concentrations during **(a)** winter and **(b)** summer seasons. Day and night samples are represented by star and plus symbols, respectively.

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