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Organic and inorganic markers and stable C-, N-isotopic compositions of tropical coastal aerosols from megacity Mumbai: sources of organic aerosols and atmospheric processing

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Abstract. To better understand the sources of PM_{10} samples in Mumbai, India, aerosol chemical composition, i.e., total carbon (TC), organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), and inorganic ions were studied together with specific markers such as methanesulfonate (MSA), oxalic acid (C_2), azelaic acid (C_9), and levoglucosan. The results revealed that biofuel/biomass burning and fossil fuel combustion are the major sources of the Mumbai aerosols. Nitrogen-isotopic ($\delta^{15}N$) composition of aerosol total nitrogen, which ranged from 18.1 to 25.4 ‰, also suggests that biofuel/biomass burning is a predominate source in both the summer and winter seasons. Aerosol mass concentrations of major species increased 3–4 times in winter compared to summer, indicating enhanced emission from these sources in the winter season. Photochemical production tracers, C_2 diacid and $nssSO_4^{2-}$, do not show diurnal changes. Concentrations of C_2 diacid and WSOC show a strong correlation ($r^2 = 0.95$). In addition, WSOC to OC (or TC) ratios remain almost constant for daytime (0.37 ± 0.06 (0.28 ± 0.04)) and nighttime (0.38 ± 0.07 (0.28 ± 0.06)), suggesting that mixing of fresh secondary organic aerosols is not significant and the Mumbai aerosols are photochemically well processed. Concentrations of MSA and C_9 diacid present a positive correlation ($r^2 = 0.75$), indicating a marine influence on Mumbai aerosols in addition to local/regional influence. Backward air mass trajectory analyses further suggested that the Mumbai aerosols are largely influenced by long-range continental and regional transport. Stable C-isotopic ratios ($\delta^{13}C$) of TC ranged from -27.0 to -25.4 ‰, with slightly lower average (-26.5 ± 0.3 ‰) in summer than in winter (-25.9 ± 0.3 ‰). Positive correlation between WSOC / TC ratios and $\delta^{13}C$ values suggested that the relative increment in ^{13}C of wintertime TC may be caused by prolonged photochemical processing of organic aerosols in this season. This study suggests that in winter, the tropical aerosols are more aged due to longer residence time in the atmosphere than in summer aerosols. However, these conclusions are based on the analysis of a limited number of samples ($n = 25$) and more information on this topic may be needed from other similar coastal sites in future.

1 Introduction

About half of the world's population resides in the Indian subcontinent (South Asia) and China (East Asia), and these two areas are recognized as potentially important source regions for anthropogenic aerosols on a global scale (Lelieveld et al., 2001; Menon et al., 2002; Yamaji et al., 2004). The chemical characterization of aerosol particles in these regions is especially important to better understand their sources, transport, and transformation, which are needed for regional models to predict aerosol distributions and effects, monsoon activity, and air quality (Adhikary et al., 2007).

In South Asia, extensive aerosol characterization studies have been performed during the Indian Ocean Experiment (INDOEX) in 1999 (Clarke et al., 2002; Lelieveld et al., 2001; Mitra, 2001; Ramanathan et al., 2001). This

experiment was designed to investigate the significance of long-range transport of continental aerosols over the remote Indian Ocean and to characterize their physical, optical, and chemical properties. One of the major outcomes of the IN-DOEX campaign was the discovery of significant loading of pollutants over the Indian Ocean. This ocean, including the Arabian Sea and Bay of Bengal, is inferred as the receptor region of the outflows from South and Southeast Asia. The major sources of carbonaceous aerosols identified over the region are biofuels/biomass burning and fossil fuel combustion. Such receptor regions can further act as a source of aged aerosols for the coastal and sub-coastal regions (Aggarwal and Kawamura 2008, 2009; Mochida et al., 2003; Takami et al., 2007). The aging factor largely controls the aerosol properties and their effects (Quinn et al., 2005; 2006; Shilling et al., 2007).

In aerosol research, identification of sources and understanding of atmospheric processing of water-soluble organics including secondary organic aerosols (SOAs) are important issues. There are several recent review studies (Carlton et al., 2009; Hallquist et al., 2009; Ervens et al., 2011), that include model, laboratory, and field observations describing the possible atmospheric pathways of SOA formation. There are two major mechanisms that efficiently lead to SOA formation: (i) the condensation of low-volatility and semivolatile gas compounds on preexisting particles (Mochida et al., 2008; Herner et al., 2006; Robinson et al., 2007; Heald et al., 2010), and (ii) the formation of low-volatility compounds in the aqueous phase (Ervens et al., 2004; Sorooshian et al., 2007; Warneck, 2003). During their lifetime in the atmosphere, particles can get processed, and thus aerosol characteristics are observed to be altered significantly with time (Zhang et al., 2007). These changes are not limited to the modification of chemical properties, but also physical properties including color and hygroscopicity are impacted (Laskin et al., 2010). Therefore, such atmospheric processing (aging) leads to a bias in constraining the aerosol climate effects.

To reduce the uncertainties in evaluating the modeling results of aerosol effects, it is important to incorporate changes in particle characteristics with time. Zhang et al. (2007) reported the real-time chemical composition of aerosol particles at different sites on the globe using aerosol mass spectrometry (AMS). This study suggested that the significant changes in composition of aerosol particles may occur due to long-range atmospheric transport and the subsequent aging. This study revealed that aerosol chemical composition is region and location specific. Therefore, region-specific and wide-range data of aerosol chemical composition are needed for better constraining model input (Adhikary et al., 2007).

In this study we determined the chemical composition of tropical aerosols from the megacity Mumbai, which is located on the west coast of the Indian Peninsula. Here we present the results on the chemical composition of PM_{10} collected at a background urban site in Mumbai in two different seasons – summer (June 2006) and winter (February 2007).

Mass concentrations for aerosol total carbon (TC), elemental carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC), and inorganic major ions together with marker compounds and stable C-, N-isotope ratios are presented and discussed in the context of aerosol sources and atmospheric aging in two different seasons. This paper discusses the possible seasonal differences in the lifetime of aerosols in the atmosphere.

2 Experimental

2.1 Sampling site and aerosol sampling

Mumbai, formerly called Bombay (location: 19° 05′ N, 72° 50′ E – area about 600 km²), is the second most populous city in the word (population: about 14 million). Along with the neighboring areas, including Mumbai Suburban, Thane, Navi Mumbai and Raigad, it is one of the most populated urban areas in the world (population: about 18 million). The Mumbai metropolitan region lies on the west coast of India, facing the Arabian Sea. It is an important source region for urban aerosols. However, chemical composition of aerosol particles in Mumbai has scarcely been studied and thus aerosol sources are not properly understood.

We conducted sampling of particulate matter of $\leq 10\,\mu m$ in diameter (PM_{10}) during 2006 and 2007 on precombusted (at 450 °C at least for 6 h) quartz filters (25×20 cm) using a high-volume air sampler ($\sim 1.2\,m^3\,min^{-1}$) on the rooftop ($\sim 12\,m$ a.g.l.) of the building of the Centre for Environmental Science and Engineering at the Indian Institute of Technology Bombay (IITB) campus, Mumbai. The detailed site description is given in Venkataraman et al. (2002). Briefly, it is a background urban site, about 10 km inland from the coast. The site is unlikely affected by proximate transportation and industrial sources, with the nearest traffic roadway about 1 km to the east and industrial cluster about 3 km to the southeast. Samples were collected during daytime (06:00–18:00 h, local time) and nighttime (18:00–06:00 h) in late summer (8–14 June 2006; $n = 14$) and late winter (13–18 February 2007; $n = 10$). A blank sample was also collected on February 18, 2007. The filter samples were placed in a clean glass jar (precombusted) individually with a Teflon-lined screw cap, and stored at –20 °C prior to analysis.

2.2 Chemical analyses

Organic carbon (OC), elemental carbon (EC), total carbon (TC), total nitrogen (TN), inorganic ions, water-soluble organic carbon (WSOC), and individual water-soluble compounds (i.e., dicarboxylic acids and sugars) together with stable C- and N- isotopes were determined in the samples.

OC and EC were determined by a thermal optical method. Typically, a 1.4 cm diameter punch of the filter was placed in a quartz tube inside the chamber of the Semi-Continuous Carbon Analyzer (Sunset Laboratory Inc., Model 4L). We

Table 1. Major aerosol constituents (μg m^{-3}) in the Mumbai aerosol samples (PM$_{10}$).

	Summer (8–14 June 2006)			Winter (13–17 February 2007)		
	Min.	Max.	Avg. $\pm$ SD	Min.	Max.	Avg. $\pm$ SD
Total carbon (TC)	4.2	9.3	6.0 $\pm$ 1.7	16	32	22 $\pm$ 4.7
Organic carbon (OC)	3.3	6.1	4.5 $\pm$ 0.91	12	23	15 $\pm$ 3.3
Elemental carbon (EC)	0.70	3.7	1.5 $\pm$ 0.88	4.5	8.9	6.4 $\pm$ 1.5
Water-soluble organic carbon (WSOC)	1.2	2.7	1.7 $\pm$ 0.43	3.5	9.5	6.0 $\pm$ 2.0
Total inorganic ions (T_IN)	4.1	7.2	5.1 $\pm$ 0.84	10	26	15 $\pm$ 5.0
Aerosol mass (AM)	11	19	14 $\pm$ 2.6	37	68	46 $\pm$ 10

AM = [T_IN + (OC $\times$ 1.6) + EC]
(Last digit of the data given in the table is rounded off)

followed the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal protocol for the analysis, and assumed that carbonate carbon in the sample is negligible (this issue is discussed in details in Section 3.5) (Agarwal et al., 2010). The analytical errors (reproducibility) were estimated to be within 9 % by the analyses of different punch cuts ($n = 3$) of the same filter samples.

For the measurement of inorganic ions, a 1.4 cm diameter disk of a filter sample was extracted with Milli-Q water (>18 MΩ cm, 7.0 ml) in a plastic bottle using an ultrasonic bath for 30 min. The water extracts were filtered using a membrane disc filter (Millex-GV, Millipore, 0.22 μm). The major ions (i.e., SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Na^+) were determined using a Metrohm-761 ion chromatograph (IC) coupled with an autosampler (Agarwal et al., 2010). The analytical errors (repeatability) were estimated to be 4 % based on the duplicate analysis. The different punch cuts ($n = 3$) of the same filter show up to $\sim$5 % variations in the concentration of major ions (i.e., SO_4^{2-} and NH_4^+).

For the determination of water-soluble organic carbon (WSOC), a 2.0 cm disk of the filter sample was extracted with Milli-Q water (7.0 ml) in a glass bottle using an ultrasonic bath for 30 min. Particles in the extracts were removed using a disc filter. A 2 M HCl solution (0.1 ml) was added to 5 ml of water extracts. After purging for 10 min with ultra pure air (80 ml min^{-1}), 100 μl of solution were injected into a TOC analyzer (Shimadzu TOC-5000A) (Agarwal et al., 2010). An analytical error (repeatability) was estimated to be within 6 % by the duplicate analyses.

Water-soluble dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls in the aerosol filter samples were determined by the methods described elsewhere (Kawamura, 1993; Kawamura and Ikushima, 1993). Briefly, a part of the filter ($\sim$6 cm^2) was cut off and extracted with Milli-Q water (12–15 ml) using an ultrasonic bath (3 $\times$ 10 min). Organic acids and carbonyls in the extracts were derivatized with 14 % BF$_3$ in n-butanol to esters and acetals, respectively. The derivatives were determined using a capillary gas chromatograph (GC) (HP 6890 GC) with a flame ionization detector (FID). Recoveries of diacids in the analytical procedure were $\sim$80 % for oxalic acid and better than 80 % for other species.

The analytical errors (repeatability) in the determination of diacids were within 6 % for major diacids based on duplicate analysis. In this paper we use only C$_2$ and C$_9$ diacid concentrations to discuss the aerosol sources. Full data sets will be published elsewhere.

Sugars were extracted from another aliquot of the filter with a dichloromethane and methanol mixture (2:1), derivatized with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) (containing 1 % trimethylsilyl chloride) and pyridine as a catalyst, and determined using a GC/mass spectrometry (GC/MS) (HP 6890 GC, 5973 MSD) (Fu et al., 2008; Agarwal et al., 2010). Recoveries of all sugar compounds determined during the analytical procedure were >90 %, while the analytical errors (repeatability) were within 10 % based on duplicate analysis. In this paper we only use the data of levoglucosan to discuss the aerosol sources.

TC and TN content in aerosol samples and their stable isotopic ratios were determined using an elemental analyzer (EA) (Carlo Erba, NA 1500) and an isotope ratio mass spectrometer (irMS) (Finnigan MAT Delta Plus) connected in series, respectively (Kawamura et al. 2004; Narukawa et al., 1999). A filter cut, typically of 1.4 cm diameter of a sample, was packed in a tin cup and loaded on an autosampler for the analyses. The analytical errors (repeatability) for TC and TN measurements by the duplicate analyses were estimated to be within 4 %, whereas for their stable isotopic ratios within 0.4 ‰.

Concentrations (μg m^{-3} or ng m^{-3}) of OC, EC, TN, TC, inorganic ions, WSOC, and individual compounds are reported here after the corrections for the field blank.

3 Results and discussion

3.1 Chemical composition and aerosol mass

Mass concentrations of major constituents in both summer and winter aerosols are summarized in Table 1. Aerosol mass is estimated as a sum of identified major component masses, i.e., [$\sum$(inorganic ions) + (OC $\times$ 1.6) + EC], where 1.6 is

Table 2. Selected marker species (ng m^{-3}) and their ratios (%) to different aerosol components determined in the Mumbai aerosol samples (PM$_{10}$).

	Summer (8–14 June 2006)			Winter (13–17 February 2007)		
	Min.	Max.	Avg. ± SD	Min.	Max.	Avg. ± SD
nssSO$_4^{2-}$	1900	2700	2200 ± 190	5000	16000	8900 ± 3300
nssK$^+$	1	100	30 ± 30	440	1230	670 ± 230
nssCa^{2+}	80	650	230 ± 160	260	1670	750 ± 460
MSA$^-$	218	354	260 ± 42	164	390	275 ± 74
C$_2$ diacid	57	131	85 ± 21	163	594	326 ± 151
C$_9$ diacid	23	68	37 ± 14	29	72	47 ± 17
Levoglucosan	29	196	69 ± 46	251	715	462 ± 146
nssSO$_4^{2-}$ / T_IN	35	52	44 ± 5	49	69	57 ± 5
nssSO$_4^{2-}$ / AM	12	20	16 ± 2	12	24	18 ± 4
EC / TC	15	40	24 ± 7	27	35	32 ± 2
EC / AM	5	22	11 ± 4	11	16	14 ± 2
nssK$^+$ / T_IN	0	2.2	0.5 ± 0.7	2.7	5.7	4.5 ± 1.1
nssK$^+$ / AM	0	0.9	0.2 ± 0.3	1.1	2.0	1.4 ± 0.3
Levoglucosan-C / WSOC	0.9	4.7	1.8 ± 1.0	1.3	6.7	3.8 ± 1.7
Levoglucosan-C / OC	0.3	1.6	0.7 ± 0.4	0.7	2.0	1.4 ± 0.4
C$_2$-C / WSOC	0.8	1.9	1.4 ± 0.3	1.1	1.8	1.4 ± 0.2

a conversion factor to estimate organic matter (OM) mass from OC mass (hereafter, aerosol mass concentration should be regarded as estimated aerosol mass (AM) concentration). A conversion factor of more than 1.4 is suggested for urban aerosols or rural aerosols far from the urban centers (Zhang et al., 2005; Pang et al., 2006; Aiken et al., 2008). The Mumbai metropolitan region is a major source for urban aerosols. Therefore, apart from local emission sources at the sampling site, the air quality is also likely influenced by the regional emissions (Lelieveld et al., 2001; Venkataraman et al. 2002). We adopted 1.6 as a factor to convert OC to OM (e.g., Aggarwal and Kawamura, 2009).

It is also important to briefly mention the meteorological conditions during the sampling period, especially temperature and humidity recorded at the site. Figure 1 shows higher temperature and humidity in summer (averaged: 31 ± 2 °C and 77 ± 12 %, respectively) than in winter (averaged: 25 ± 3 °C and 37 ± 5 %, respectively) at the site. According to climatological table given in the website of the Indian Meteorological Department, the average temperature of Mumbai in summer (April–June) and winter (December–February) is 29.2 and 24.5 °C, respectively. This suggests that weather conditions at the time of sampling were representative of summer and winter seasons.

Concentrations of carbonaceous constituents (i.e., EC, OC, WSOC), total inorganic ions (T_IN) and AM were ∼3–4 times higher in winter than in summer. This is possibly due to (i) enhanced continental/regional anthropogenic activities in winter and (ii) pronounced oxidative exhaustion of particles and wet removal of particles in summer because of the high temperature and humidity in the tropics. These points will be discussed in the following sections.

The sample-to-sample variability in aerosol mass and its major constituents are shown in Fig. 2. This figure shows higher average mass loadings of total aerosol and individual aerosol constituents in winter than in summer. In both seasons, OM is the dominant fraction in aerosol mass (Fig. 2a). OM in summer and winter comprised 52 ± 3 and 54 ± 5 % of aerosol mass, respectively. In contrast, total inorganic ion (and the other counterpart, i.e., EC) fraction accounted for 38 ± 5 and 33 ± 6 % (and 11 ± 4 and 14 ± 2 %) of aerosol mass in both seasons, respectively. In general, this indicates that although concentration of bulk constituents is higher in winter, their contribution to aerosol mass does not vary considerably between two seasons – a point to be discussed in the following sections.

Among inorganic constituents, sulfate is the dominant ion in both summer and winter with a concentration range of 2.1–2.8 and 5.1–16 µg m^{-3}, respectively, contributing to 47 ± 4 and 58 ± 5 % of the total inorganic ion mass, respectively. This possibly suggests an enhanced contribution of anthropogenic emission in winter. However, like other bulk components (i.e., OM, EC and T_IN), SO$_4^{2-}$ contribution to AM remained almost constant at levels of 18 ± 3 % in summer and 19 ± 5 % in winter.

3.2 Contribution of local versus regional/continental emission

Because of the geographical location of the sampling site, the Mumbai aerosols are likely influenced by regional emissions as well as long-range transport from the continent across the Arabian Sea. An air mass 5-day backward-trajectory analysis was performed for each sample using HYSPLIT4 model. The backward trajectories are plotted in Fig. 3, which shows
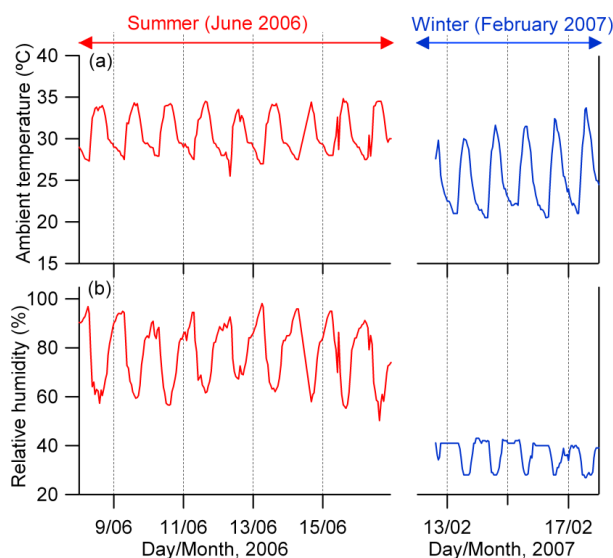
Fig. 1. Temperature and humidity recorded at the site during the campaign.

Fig. 2. Temporal variations of aerosol mass loading with the **(a)** major component concentrations (where, OM = OC ×1.6), **(b)** composition of carbonaceous mass, and **(c)** inorganic ion composition.

that air masses encountered at Mumbai during sampling period in both seasons were transported from far continental sites across the Arabian Sea. In winter the air masses originate from subcontinental sites northwest of Mumbai, while summer air masses are transported from the subcontinent in the southwest, and traveled longer distances over the Arabian Sea before arriving at Mumbai. It is also important to note that winter air masses were transported over the neighboring suburban areas, thus they could have more chances to mix with regional air masses influenced by anthropogenic emissions.

Concentrations of some marker species determined in the Mumbai samples are shown in Table 2. To better understand the influences of local emissions, we plotted non-sea-salt sulfate (nssSO_4^{2-}) and oxalic acid (C_2 diacid) concentrations for daytime and nighttime samples in Fig. 4a and b, respectively. Both of the species are largely formed through photochemical reactions from their precursors and thus can be used as photochemical production tracers (Charlson et al., 1987; Takami at al., 2007; Aggarwal and Kawamura, 2008; Kawamura and Yasui, 2005). Therefore, a diurnal change in their concentrations with maximum values during daytime and minimum values during nighttime can be expected if the aerosols are freshly emitted from local sources. However, as shown in Fig. 4a and b, nssSO_4^{2-} and C_2 diacid concentrations do not follow the diurnal pattern, i.e., they do not always show higher values during daytime. Interestingly, they exhibit a very good correlation ($r^2 = 0.91$) to each other. These results suggest that the Mumbai aerosols were not strongly affected by local photochemical processes, but they were already well processed in the atmosphere before arriving at the sampling site.
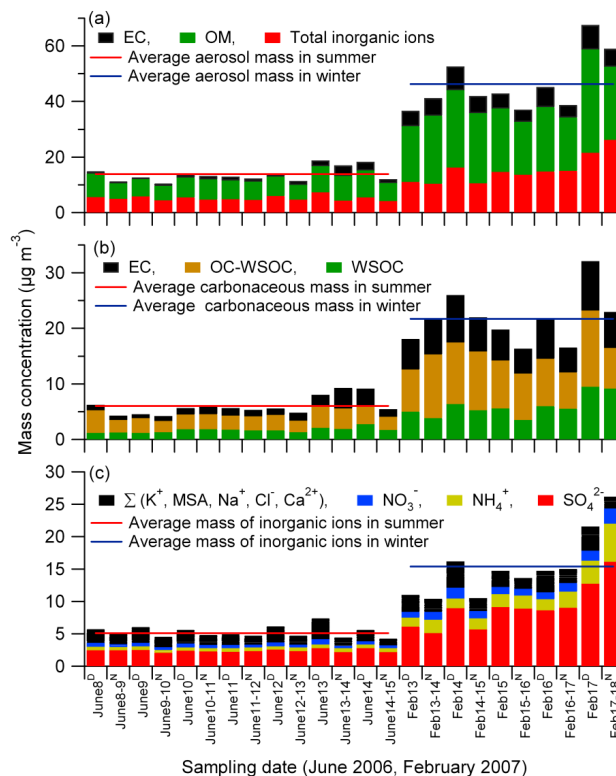
We also compared WSOC/OC (and WSOC/TC) ratios for daytime and nighttime samples. Contributions of WSOC to OC (and to TC) in daytime and nighttime samples were 36 (28) and 38 % (28 %) in summer, and 39 (27) and 38 % (27 %) in winter. This similarity again indicates that influences of local emissions and local secondary production of WSOC were not significant. Instead, regional influence may be more pronounced.

As seen in Fig. 4c, methanesulfonate (MSA) and azelaic acid (C_9 diacid) concentrations show clear diurnal changes. These species are largely produced through photochemical oxidation of marine-derived precursors. MSA is the photooxidation product of dimethylsulfide (DMS) (Charlson et al., 1987), whereas C_9 is produced through heterogeneous oxidation of unsaturated fatty acids, which are derived from marine phytoplankton (Kawamura and Gagosian, 1987). As shown in Fig. 5, C_9 diacid and MSA correlate well ($r^2 = 0.75$), indicating that the Mumbai aerosols are influenced by marine air masses coming from the surrounding and open ocean. These results together with the information obtained from air mass backward-trajectory analyses suggest that the Mumbai aerosols are already aged and more influenced by the long-range transport of continental/regional emissions than the local emissions.
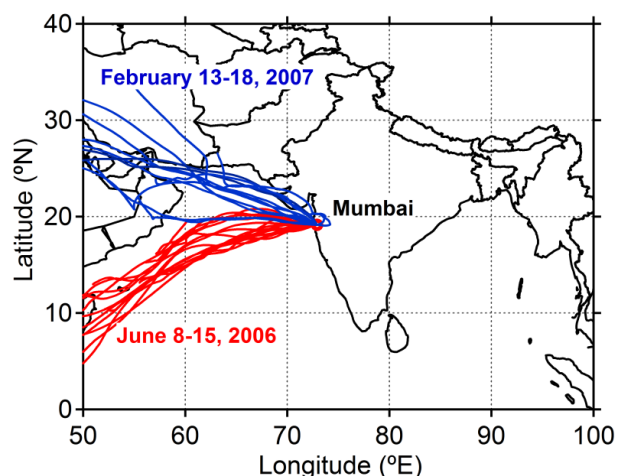
Fig. 3. Five-day backward trajectories obtained for each of the samples. The analysis was performed using the HYSPLIT4 model (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, Maryland, United States). These trajectories were calculated for air masses starting from the sampling site (with sampling ending time) at 1000 m height using the model vertical velocity and reanalysis data. The flow pattern was updated every 6 h.
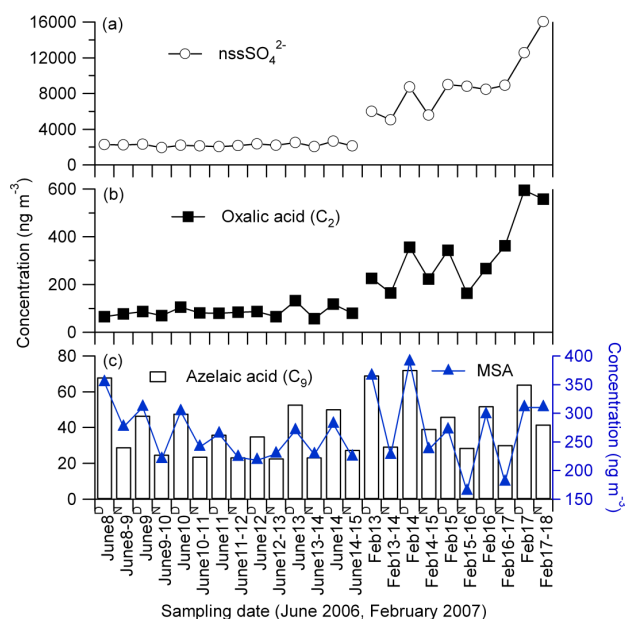

Fig. 4. Temporal variation in concentration of photochemical production tracers: (a) $nssSO_4^{2-}$, (b) oxalic acid, and (c) marine source tracers, i.e., azelaic acid and methanesulfonate.
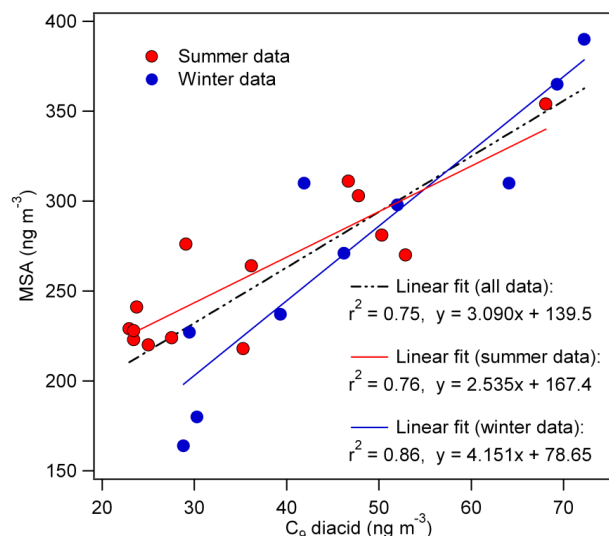

Fig. 5. Correlations between marine source tracers: methanesulfonate (MSA) and azelaic acid (C_9 diacid) (r^2 is based on the complete data set).

3.3 Seasonal variation in chemical markers: implication for source identification

To better understand the aerosol sources in two different seasons, we use several marker species, such as $nssSO_4^{2-}$ for mixed anthropogenic activities (especially from fossil fuel burning), $nssK^+$ and levoglucosan for wood/biofuel burning, and EC for mixed combustion activities. Their contribution to total aerosol mass (AM), total inorganic mass (T_IN) or carbonaceous mass (i.e., TC) can suggest a dominant source in a particular season. In Table 2 we summarized the individual concentration of these markers as well as their ratios with major aerosol components. As discussed above, both $nssSO_4^{2-}$ and EC are the major fractions of Mumbai AM (Table 2). Their fractions of total aerosol mass do not vary significantly in summer and in winter, suggesting that in general the different source contribution of Mumbai aerosols in both the seasons may not be very diverse. However, $nssSO_4^{2-}$ / T_IN and EC / TC ratios are higher in winter than in summer, suggesting a slightly enhanced contribution from anthropogenic sources in the winter season. Being consistent with this, wood/biofuel burning tracers such as $nssK^+$ and levoglucosan (Simoneit et al., 1999; 2004) also give higher ratios with T_IN or AM, and WSOC or OC in winter than in summer. This indicates that an enhanced contribution of such sources is possible in winter (possibly from regional transport).

The higher mass loading of aerosol bulk components (i.e., OC, EC and T_IN) may be associated with enhanced source emissions in wintertime. To see the effect of planetary boundary layer (PBL) height on the seasonal variations of aerosol mass loading, we have computed PBL heights for
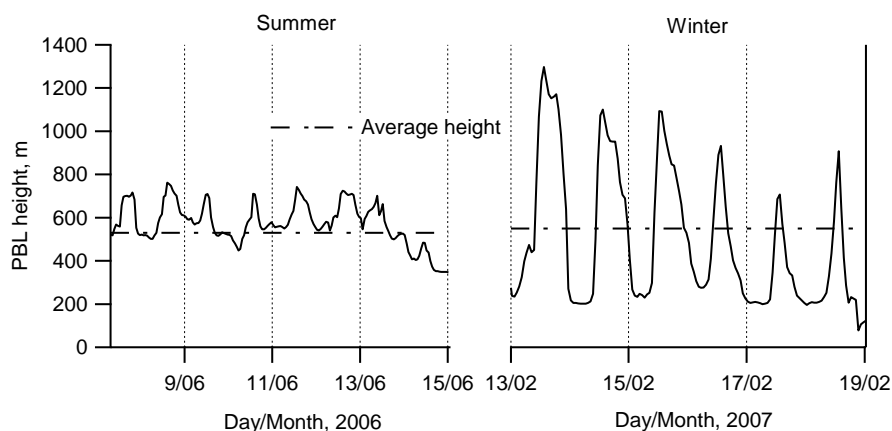
Fig. 6. Planetary boundary layer (PBL) heights for the sampling periods in Mumbai, which are computed using "weather research and forecasting reference" software (WRF of Mesoscale and Microscale Meteorology Division, National Center for Atmospheric Research, Boulder).
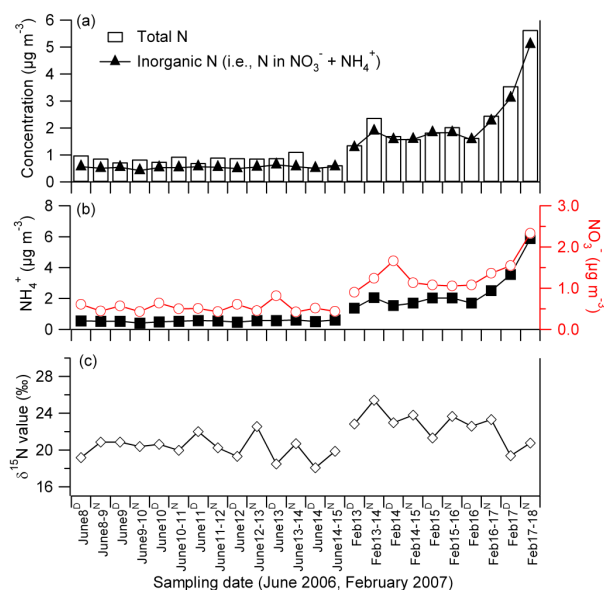

Fig. 7. Temporal variations in concentrations of **(a)** total nitrogen (TN) and inorganic nitrogen, **(b)** NH_4^+ and NO_3^-, and **(c)** $\delta^{15}N$ values of TN.

the sampling periods in Mumbai using "weather research and forecasting reference" software (WRF of Mesoscale and Microscale Meteorology Division, National Center for Atmospheric Research, Boulder), and data are shown in Fig. 6. In the winter season, a large variation in PBL heights for daytime and nighttime can be seen compared to that of the summer season. However, a clear response of aerosol concentration (which is based on 12 h sampling time, Fig. 2) to the PBL height (nighttime high and daytime low) is not observed. Further, not much difference was observed in average

PBL heights between winter (548 m) and summer (532 m) seasons.

Although the ratios discussed above became higher in the winter season, C_2-C / WSOC ratios rather stayed constant in summer (1.4 ± 0.3 %) and winter (1.4 ± 0.2 %). The C_2 and WSOC are mainly derived from biofuel/biomass burning and fossil fuel combustion and from photochemical aging in aerosols (e.g., Agarwal et al., 2010). This similarity of the ratios in both seasons suggest that, although the source emissions may be enhanced in winter, the sources remain mostly similar in both the seasons for the Mumbai aerosols.

3.4 Total nitrogen content and nitrogen isotopic composition ($\delta^{15}N$): sources versus atmospheric processing

Total nitrogen (TN), inorganic nitrogen (i.e., N associated with NH_4^+ and NO_3^-), and NH_4^+ and NO_3^- concentrations along with $\delta^{15}N$ of TN are shown in Fig. 7. Concentrations of TN and inorganic nitrogen in summer are 0.83 ± 0.15 and $0.53 \pm 0.15\,\mu g\,m^{-3}$, respectively. They are 3–4 times higher in winter (i.e., 2.4 ± 1.3 and $2.2 \pm 1.1\,\mu g\,m^{-3}$) than in summer. This also suggests that most of the TN is the composite of inorganic nitrogen. On average, about 66 % and 91 % of TN are inorganic nitrogen in summer and winter, respectively. The higher contribution of inorganic nitrogen to TN in winter is possibly associated with increased contribution of biofuel/biomass burning to the Mumbai aerosols in this season. On the other hand, also a possible reason could be the elevated temperature in summer, which would result in evaporation of inorganic nitrogen, and loss to the gas phase.

Average concentrations of NH_4^+ and NO_3^- in the Mumbai aerosols are 0.54 ± 0.05 and $0.53 \pm 0.11\,\mu g\,m^{-3}$ in summer, and 2.4 ± 1.4 and $1.3 \pm 0.42\,\mu g\,m^{-3}$ in winter, respectively. NO_3^- shows a clear diurnal trend, especially in summer with

daytime maxima and nighttime minima (Fig. 7b). Because vehicular emissions are one of the potential sources for particulate NO_3^- in the atmosphere, this result suggests a possible local influence on summer aerosols. However, NO_3^- contents are relatively low as compared to sulfate (see Fig. 2c), which does not show such a diurnal trend (see Fig. 4a).

The stable N-isotope ratio is measured as the ratio of the heavier isotope to the lighter isotope, $^{15}N / ^{14}N$, and reported as δ value in parts per 1000 or per mil (‰) relative to delta value of atmospheric N_2. N-isotope ratios ($\delta^{15}N$) of aerosol particles provide important information on primary and secondary nitrogen sources (Widory, 2007; Kundu et al., 2010; Pavuluri et al., 2010; Agnihotri et al., 2011).

In the Mumbai aerosols, nitrogen isotopic ($\delta^{15}N$) values of TN ranged from 18.1 to 25.4‰ (21.3 ± 1.8‰) with lower values (20.2±1.2‰) in summer and higher values (22.8 ± 1.4‰) in winter. The Student's t test (two-tailed, pooled equal variance) suggests that this seasonal difference in $\delta^{15}N$ values is statistically significant at the 95% confidence level ($p = 0.000272$). The high values in winter may be mainly associated with (i) changes in source contribution, and also (ii) longer processing time of aerosols (because of less photochemical activities). For the aerosols from Chennai, which is located on the southeast coast of India, Pavuluri et al. (2010) found that animal excreta and biofuel/biomass burning are two major sources for aerosol N. They found an isotopic enrichment of ^{15}N in aerosol N, which they interpreted as atmospheric processing of aerosols (i.e., gas-to-particle conversion of NH_3 and subsequent exchange reaction between NH_3 and NH_4^+).

The Mumbai winter aerosols are affected by the enhanced contribution of biofuel/biomass burning. The observed changes in $\delta^{15}N$ values in the Mumbai aerosols can be interpreted as the changes in sources contribution. Widory (2007) reported $\delta^{15}N$ data sets for different aerosols (PM_{10}) from Paris (France). The aerosols derived from fossil fuel combustion sources showed the following $\delta^{15}N$ values: diesel (4.6 ± 0.8‰), natural gas (7.7 ± 5.9‰), fuel oil (−7.5±8.3‰), coal (−5.3‰), and unleaded gasoline (avg. 4.6‰) ranging from −16 to 16‰. For the aerosols generated from waste incineration, they reported the values of 5.5 to 8.0‰. Similarly, Turekian et al. (1998) reported $\delta^{15}N$ values for laboratory-generated aerosols from the burning of C3 (2.0 to 19.5‰) and C4 (9.8 to 22.7‰) plant material. Because biofuel (in particular cow dung cake) for cooking energy is very common in South Asia (Venkataraman et al., 2005; Stone et al., 2010), it is also important to note that $\delta^{15}N$ values for cow dung cake (unburned) is reported to be 13.4 to 15.5‰ (Pavuluri et al., 2010). These comparisons suggest that $\delta^{15}N$ values of the Mumbai aerosols are higher than those reported for the important fossil fuel burning aerosols, whereas they are close to $\delta^{15}N$ values reported for C3 and C4 plant material burning aerosols and unburned cow dung
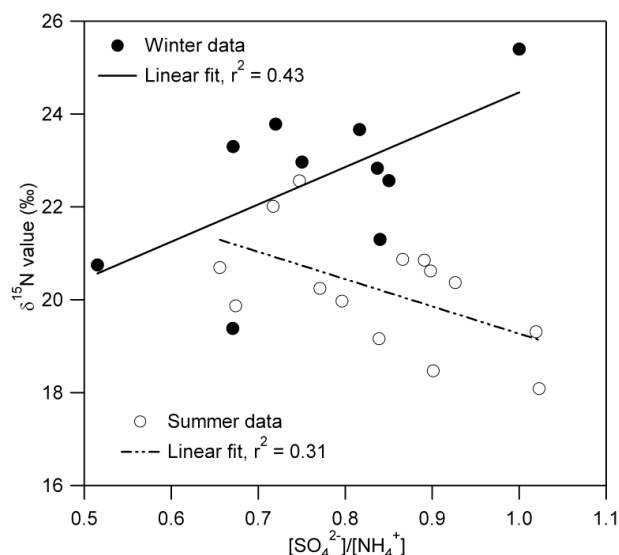

Fig. 8. Relation between $\delta^{15}N$ values of TN and molar ratios of SO_4^{2-} to NH_4^+ in summer and winter aerosols (r^2 is based on the complete data for respective season).

cake material. This again supports that the biofuel/biomass burning is the dominant source for the Mumbai aerosols.

To better understand the influence of atmospheric processing in the enrichment of ^{15}N in aerosol N, we plot $\delta^{15}N$ values of aerosol TN against molar ratios of SO_4^{2-} to NH_4^+ (Fig. 8). The $[SO_4^{2-}] / [NH_4^+]$ ratio can be used as an indicator for atmospheric processing of aerosols (Pavuluri et al., 2010). Interestingly, between the two sets of values we observed a negative correlation ($r^2 = 0.31$) in summer and a positive correlation ($r^2 = 0.43$) in winter. These correlations suggest that higher $\delta^{15}N$ values in winter are related to atmospheric processing of aerosol N. Pavuluri et al. (2010) also reported the similar results for Chennai aerosols, where the correlation for late winter was 0.27, but a good correlation did not exist for summer aerosols (i.e., $r^2 = 0.04$). Also, in their study the $[SO_4^{2-}] / [NH_4^+]$ ratios were very similar to those obtained in this study, i.e., for late winter and summer these ratios were 0.7 and 0.6, respectively.

As suggested in Pavuluri et al. (2010) and references therein, our results also support that enrichment of ^{15}N in aerosol N is largely due to the exchange reaction between $NH_3 \Leftrightarrow NH_4^+$, and also between $HNO_3 \Leftrightarrow NO_3^-$, which are more favorable in winter conditions (less evaporation, i.e., lower temperature). If these equilibrium (i.e., $NH_3 \Leftrightarrow NH_4^+$ and $HNO_3 \Leftrightarrow NO_3^-$) are shifted towards the particle phase, particulate nitrogen gets more enriched in ^{15}N because N that evaporates from particles is likely more enriched in the lighter isotope (^{14}N). Although NO_3^- concentrations showed a clear diurnal trend in summer (see Fig. 7b), such a trend was not observed in winter. This result suggests that aerosol
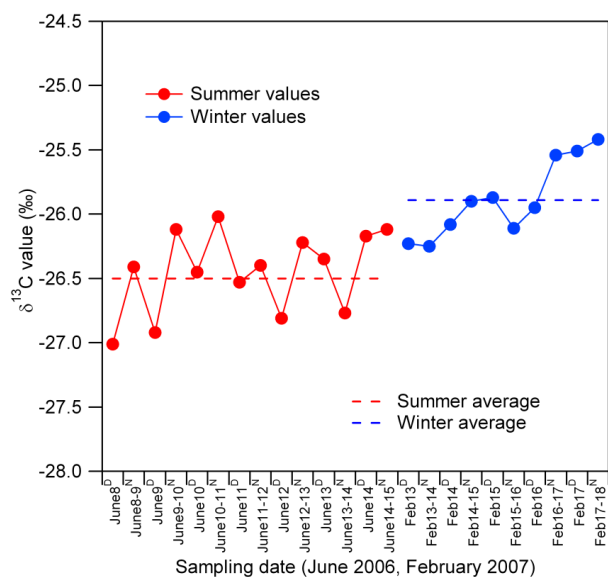
Fig. 9. Temporal variations in $\delta^{13}C$ values of TC.

nitrogen in Mumbai is more processed in winter than in summer.

3.5 Stable carbon isotopic compositions ($\delta^{13}C$) of total carbon: implication for seasonal difference in aerosol lifetime

Stable carbon isotopic composition of aerosol particles has been used as a tracer to evaluate the contribution of different sources and source regions of organic aerosols for more than two decades (Cachier et al., 1986). Recently, the compound-specific stable carbon isotopic composition of dicarboxylic acids was used as a tracer for photochemical aging of organic aerosols (Kawamura and Watanabe, 2004; Aggarwal and Kawamura, 2008; Pavuluri and Kawamura, 2012). More recently, the enrichment of ^{13}C in organic carbon was ascribed to photochemical aging of atmospheric aerosols (Wang et al., 2010). In other words, $\delta^{13}C$ values (a measure of the ratio of stable isotopes $^{13}C:{}^{12}C$, given in parts per thousand (per mil, ‰)) of aerosol TC was reported to be increased (i.e., become less negative) with aerosol photochemical aging. During the atmospheric oxidation process by the reaction with OH radical, organic compounds break down to release CO_2/CO, whose isotopic composition is enriched with the lighter isotope (^{12}C). Meanwhile, the remaining organic matter of aerosol particle gets enriched in the heavier isotope (^{13}C). Thus, the enrichment of ^{13}C in aerosol TC can largely be attributed to aerosol photochemical processing, although initial ^{13}C values of the carbonaceous aerosols depend on their sources.

For the Mumbai aerosols, $\delta^{13}C$ values of aerosol TC ranged from –27.0 to –25.4 ‰. These values are lower than

those reported in Agnihotri et al. (2011) for the Goa aerosols (Goa – located ∼600 km south of Mumbai), i.e., –24.5 to –25.2 ‰. Figure 9 shows sample-to-sample variability in $\delta^{13}C$ values, while these values are increased from summer (average: -26.5 ± 0.3 ‰) to winter (-25.9 ± 0.3 ‰). Recently, Narukawa et al. (2008) reported similar $\delta^{13}C$ values (-25.7 ± 0.7 ‰) of TC for arctic aerosols in winter, which were strongly influenced by the anthropogenic air masses transported from the midlatitudes. Narukawa et al. (1999) also reported the $\delta^{13}C$ values of TC (∼27.5 to ∼26.0 ‰) of aerosols collected in Singapore during a large-scale forest fire (C3 plants) that occurred in Indonesia (Southeast Asia) in October–November 1997. However, these values in aerosols collected after the forest fire (relatively aged aerosols) were slightly increased (∼–26.2 to –25.5 ‰). Martinelli et al. (2002) determined average $\delta^{13}C$ values of –25.8 ± 0.5 ‰ (range: –26.9 to –24.9 ‰) for fine aerosol particles ($PM_{2.0}$) from the rainforest of the Amazon Basin, Brazil, in May–August 2000 (i.e., mostly biogenic secondary aerosols).

In a study in Vancouver, $\delta^{13}C$ of tunnel aerosols (relatively fresh aerosols) is reported to be ∼–27.3 ‰ for OC and EC fraction with no significant differences (Huang et al., 2006). Kawamura et al. (2004) reported $\delta^{13}C$ values of aerosol TC for particles collected over a period of 1 yr (2001–2002) at Gosan site in Jeju Island, South Korea. They found $\delta^{13}C$ values between ∼–23 to –25 ‰ (other than spring samples, which show slightly higher values due to possible Asian dust contribution) for anthropogenic aged aerosols largely transported from China.

All these examples discussed above revealed that $\delta^{13}C$ values of TC in the Mumbai aerosols are consistent with the values obtained for aerosols from the mixed anthropogenic activities and the specific sources such as fossil fuel and biomass burning. It is also important to note that the values from these sources became higher (less negative) when the aerosols were relatively aged (i.e., photochemically more processed). For the Mumbai aerosols, to better understand the factors responsible for the relative increment in ^{13}C of aerosol TC in the winter season (i.e., source versus atmospheric processing), we study the correlations between the concentration ratios of different marker species to TC and $\delta^{13}C$ values of aerosol TC.

Kawamura et al. (2004) found higher $\delta^{13}C$ values of TC in Gosan site aerosol samples collected during dust events, whose $nssCa^{2+}$ (a chemical tracer for dust, i.e., carbonate carbon in this discussion) concentration was higher (3–13 μg m^{-3}). In our samples, $nssCa^{2+}$ concentrations were comparatively low (average 0.45 μg m^{-3}; see Table 2 for summer and winter concentrations). In addition, low values of $nssCa^{2+}$ / AM and $nssCa^{2+}$ / TC ratios are determined in the samples (average: 0.016 ± 0.008 and 0.035 ± 0.018, respectively). Further, in order to examine the possibilities of the relative increment of ^{13}C in aerosol C due to carbonate carbon, we examined correlations between $nssCa^{2+}$ / TC
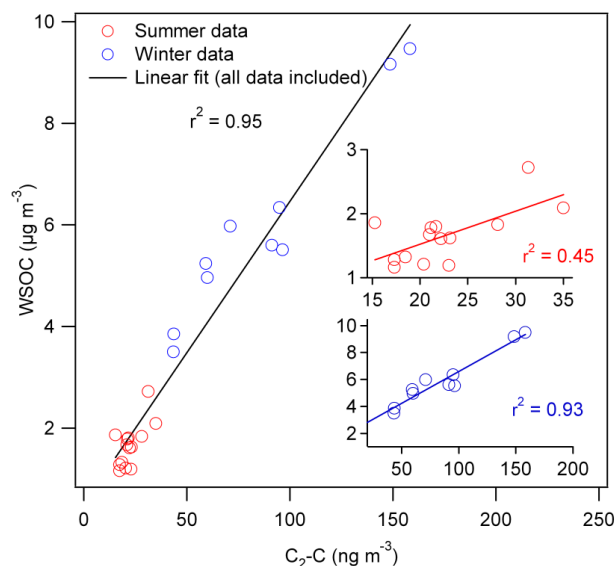
Fig. 10. Relation between WSOC and oxalic acid (C_2 diacid) concentrations determined in the Mumbai aerosols in summer and winter (inset figures represent the relation for summer and winter data separately).

ratios and $\delta^{13}C$ values (the results are not shown as a figure). However, we do not find any significant correlations, suggesting that dust derived carbonate carbon was not present in a concentration level that can considerably affect the $\delta^{13}C$ ratios.

Lower molecular weight diacids are likely produced in the atmosphere by photochemical oxidation of the precursor species, which includes higher molecular weight diacids. Oxalic acid (C_2 diacid) is the smallest diacid and considered as an end product of such photochemical processes in this compound class. Therefore, it has been used to trace the photochemical processes in several studies (e.g., Agarwal et al., 2010). A large fraction of WSOC in aerosols is generally secondary if aerosols are not from nearby specific sources, e.g., biomass burning, soil resuspension aerosols, etc. Thus the plot between WSOC and oxalic acid carbon (C_2-C) concentrations can suggest the degree of secondary nature (formed photochemically) of WSOC.

In the Mumbai aerosol samples, WSOC ($\mu g\,m^{-3}$) shows an excellent correlation ($r^2 = 0.95$) with C_2-C ($ng\,m^{-3}$) (Fig. 10). This suggests that WSOC fraction is largely secondary in the Mumbai aerosols. The r^2 value in Fig. 10 for winter aerosol samples (0.93) is twice as high as that of summer samples (0.45). Concentrations of WSOC and C_2 diacid also increased by a factor of 3–4 in winter (see Table 2). This further suggests the possibilities of (i) increased source emissions in winter, (ii) enhanced evolution of oxidized organics (Kessler et al., 2010; Jimenez et al., 2009) in summer in tropics (i.e., fast conversion of particulate oxidized matter, POM to gaseous form, e.g., CO_2) is as efficient as wet

deposition as a removal process (Molina et al., 2004 and references therein), or in other words, enrichment of oxidized organics in winter due to slow evolution rate (i.e., slow conversion of POM to CO_2 and volatile organic products), and (iii) higher wet deposition rates in summer due to higher RH (Fig. 1).

The lifetime of organic aerosols has been estimated previously to be 4–5 days, assuming wet removal to be the dominant sink (Molina et al., 2004 and reference therein). In a laboratory study, under the conditions similar to real ambient, volatilization lifetime of organic particles (alkane aerosols, 10–200 nm in size) has been estimated to be ~6 days (Molina et al., 2004). This suggests that volatilization may not be a major sink, like wet removal, but it might be an important removal pathway for organic aerosols (Molina et al., 2004; Petters et al., 2006).

Because the relation between C_2 and WSOC implies that WSOC in Mumbai aerosols is largely secondary in nature, WSOC to TC ratios can be an indicator for photochemical aging of organic aerosols. In order to further understand the nature of organic aerosols (source versus atmospheric aging), we plotted WSOC / TC ratios against $\delta^{13}C$ values in Fig. 11. We found a positive correlation between WSOC / TC ratios and $\delta^{13}C$ of TC in Mumbai aerosols. The regression fit for summer samples shows a moderate correlation ($r^2 = 0.42$), whereas correlation for winter samples is much stronger ($r^2 = 0.70$). This finding suggests that (i) increments in $\delta^{13}C$ of aerosol C, especially in winter, may be caused by longer processing time of organic aerosols in tropics, and thus (ii) aging of tropical aerosols is more prolonged in winter than in summer.

In general, organic aerosol (OA) sinks can be represented by two major terms, i.e., d[OA]/dt = −(wet removal) − (chemical loss). The "wet removal" term is larger for summer than in winter because RH(summer) >RH(winter). This implies that particles stay longer in the atmosphere in winter than in summer, which in turn exposes them for longer to the oxidants to be photochemically processed. The "chemical loss" term can be expressed as "[OH]·time". Since OH is lower in winter than in summer (i.e., lower solar radiation and less photochemical activity) but the exposure time is longer, the chemical loss terms for winter and summer might be similar over the total lifetime of OA.

However, in view of all data discussed here, a possible explanation for prolonged aging of OA in tropics in the winter season is the longer OA lifetime due to a less efficient wet removal rate that makes chemical losses, i.e., volatilization due to photochemical processes, relatively more important (note that similar meteorological conditions exist in summer in several nontropical regions). During the summer season, when humidity is higher in the tropics, wet removal likely dominates OA loss, and thus due to limited particle lifetime, volatilization by chemical processes might not be a major
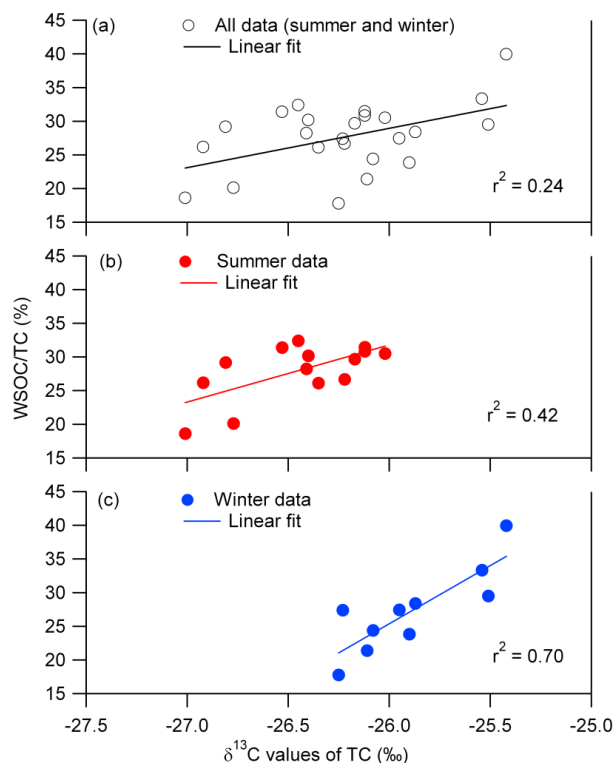
Fig. 11. Relation between WSOC/TC ratios and $\delta^{13}C$ values of TC in **(a)** both seasons, **(b)** the summer season, and **(c)** the winter season.

removal process of organics – in agreement with prior studies (Molina et al., 2004; Petters et al., 2006).

In Fig. 9, the day–night trend of $\delta^{13}C$ values in summer (generally lower in days and higher in consecutive nights) also supports the above conclusion that during daytime (high temperature and humidity) due to shorter particle lifetime, chemical processes are relatively less important. Because of the low wet removal and chemical processing rates of organic aerosols in winter, they possibly sustain for a longer period in the atmosphere. Thus, this study suggests that the atmospheric lifetime of tropical urban aerosols could be longer in winter than in summer. However, in this study we have analyzed a limited number of samples ($n = 25$). Additional observations are needed from similar coastal locations to support the results of this study in future.

4 Summary and conclusions

PM_{10} samples were collected in two different seasons (summer and winter) at a background urban site in Mumbai, a city on the west coast of India. Extensive chemical analyses at bulk and molecular level together with stable C and N isotopic composition were conducted for the first time for the Mumbai aerosols. Aerosol mass loading including mass con-

centration of individual components, i.e., OC, EC, WSOC, and T_IN, was found to increase by a factor of 3–4 from summer to winter. Concentrations of some marker species such as $nssSO_4^{2-}$, $nssK^+$, levoglucosan, and oxalic acid (C_2 diacid) are also several times higher in winter than in summer, suggesting an enhanced contribution of anthropogenic source emissions in the winter season. Potential sources identified for Mumbai aerosols are biofuel/biomass burning and fossil fuel combustion in both seasons. Photochemical production tracers, i.e., $nssSO_4^{2-}$ and C_2 diacid, do not show any diurnal trend. C_2 diacid and WSOC concentrations present a strong relation ($r^2 = 0.95$). In addition, WSOC to OC or TC ratios for daytime and nighttime remain almost unchanged, suggesting that the Mumbai aerosols were not seriously affected by local photochemical processes and they were already well processed in the atmosphere before reaching the site. Further, MSA and C_9 diacid show a good correlation ($r^2 = 0.75$), indicating the influence of marine air mass. Backward air mass trajectory analyses also suggested that Mumbai aerosols were significantly influenced by long-range atmospheric transport over the Arabian Sea and, in addition, by regional transport, especially in winter.

$\delta^{15}N$ values of TN in the Mumbai aerosols (ranged 18.1 to 25.4 ‰) supported that the most abundant source in both seasons is biofuel/biomass burning. $\delta^{13}C$ values of TC ranged from -27.0 to -25.4 ‰ with lower average value (-26.5 ± 0.3 ‰) in summer and higher values (-25.9 ± 0.3 ‰) in winter. However, plots between WSOC / TC ratios and $\delta^{13}C$ values suggest that the relative increment in ^{13}C of aerosol C in the winter season is caused by prolonged photochemical processing of organic aerosols in wintertime.

Our results suggest that (i) the abundant source for the Mumbai aerosols is biofuel/biomass burning, (ii) in a coastal city like Mumbai, aerosols are significantly influenced by long-range continental and regional transport (i.e., aerosols are aged). This is similar to the Chennai aerosols characteristics (Chennai is the other megacity on the southeast coast of India, Pavuluri et al., 2011), and (iii) aerosol aging in the tropics is possibly more prolonged in winter than in summer. The latter two factors can significantly increase the oxidized organic matter in aerosols. Therefore, these factors should be taken into account in regional models to reduce the uncertainty in the prediction of aerosol effects as well as in secondary organic aerosol distributions. This study also revealed that organic aerosol aging pathways may be different in the summer and winter seasons. In summer the evolution would be rather faster, while in winter it is slower (because of less photochemical activities). Hence, the bulk C-isotopic fractionation is more pronounced in winter than in summer.

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