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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 from Mumbai, India, aerosol chemical compositions, 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 (δ^{15}N) composition of aerosol total nitrogen, which ranged from 18.1 to 25.4 ‰, also suggest that biofuel/biomass burning is the dominant source in both summer and winter seasons. Aerosol mass concentrations of major species increased 3–4 times in winter compared to summer, indicating an enhanced emission from these sources in 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 day- (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 rather 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 (δ^{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 δ^{13}C values suggested that the 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 the summer aerosols.

1 Introduction

About half of the world's population resides in Indian subcontinent (South Asia) and China (East Asia), and these two areas are recognized as potentially important source regions for anthropogenic aerosols on 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 that are needed for regional models to predict aerosol distributions and effects, monsoon activity and air quality (Adhikary et al., 2007).

In South Asia, aerosol study has been extensively performed during 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. As the major outcomes, the significant loadings of pollutants were observed over Indian Ocean. This ocean, including 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 subcoastal regions (Aggarwal and Kawamura, 2008, 2009; Mochida et al., 2003; Takami et al., 2007). The aging factor largely controls the aerosol properties and thus its 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 are important issues (Zhang et al., 2005, 2007; Hallquist et al., 2009). Lack of information on these issues in the topics leads to significant biases in the predicted results on the distributions of organic aerosols and their effects. There are few laboratory- and field-studies describing the possible atmospheric pathways of the secondary aerosol formation, which include (i) gas-to-particle conversion (Kulmala et al., 2004; Zhang et al., 2011), (ii) uptake of gaseous species onto pre-existing particles (Mochida et al., 2008; Herner et al., 2006), (iii) chemical modifications on particle surfaces or within the particle (aqueous phase) (Aggarwal and Kawamura, 2009; Ervens et al., 2004; Sorooshian et al., 2007; Warneck, 2003), and (iv) evaporation of particle species and further condensation under chemical equilibrium conditions (Robinson et al., 2007; Heald et al., 2010). As far as particle remains in the atmosphere, these processing can be continued, and thus aerosol characteristics are observed to be altered significantly with the time (Zhang et al., 2007). These changes do not only limit to the modification of their chemical properties but also influence their physical characteristics including the color and hygroscopicity (Laskin et al., 2010). Therefore, such atmospheric processing (aging) leads to a significant 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. Not much information are available on these topics. Zhang et al. (2007) reported the real-time chemical composition of aerosol particles at different sites on the globe using the same technique of 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 the modeling results (Adhikary et al., 2007).

In this study, we determined for the first time an extensive chemical composition in the tropical aerosols from megacity Mumbai, which is located in 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), inorganic major ions together with marker compounds and stable C-, N-isotopic 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 and 72°50′ E, area about 600 km^2), 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). Mumbai metropolitan region lies on the west coast of India, facing to the Arabian Sea. It is an important source region for urban aerosols. However, chemical composition of the aerosol particles in Mumbai has scarcely been studied and thus sources are not properly understood.

Keeping this gap in mind, we conducted sampling of particulate matter of $\leq 10\,\mu$m in diameter (PM$_{10}$) during 2006 and 2007 on pre-combusted (at 450 °C at least for 6 h) quartz filters (25 × 20 cm) using a high-volume air sampler ($\sim 1.2\,\mathrm{m^3\,min^{-1}}$) on the rooftop (~ 12 m above the ground level) of the building of the Center 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. However, Venkataraman et al. (2002) suspect that resuspension of soil dust due to sweeping activities and open burning of waste materials (including leaves and garden-waste) could be the intermittent local sources throughout Mumbai. Samples were collected on a daytime (06:00–18:00 LT) and nighttime (18:00–06:00 LT) basis during late summer (8–14 June 2006; $n = 14$) and late winter (13–18 February 2007; $n = 10$). A blank sample was also collected on 18 February 2007. The filter samples were placed in a clean glass jar (pre-combusted) 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 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 followed the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal protocol for the analysis, and assumed that carbonate carbon in the sample is negligible (Agarwal et al., 2010).

For the measurement of inorganic ions, a 1.4 cm diameter disc 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 auto-sampler (Agarwal et al., 2010).

For the determination of water-soluble organic carbon (WSOC), a 2.0 cm disc 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 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).

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 (~ 6 cm^2) was cut off, and extracted with Milli-Q water (12–15 ml) using an ultrasonic bath (3 × 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). 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). 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 elemental analyzer (EA) (Carlo Erba, NA 1500) and 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 auto-sampler for the analyses.

Concentrations ($\mu g\,m^{-3}$ 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.

2.3 Air mass backward trajectories

To characterize the air masses encountered at Mumbai during the campaign, the backward trajectory analysis was performed for each sample using HYSPLIT4 model (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, Maryland, United States). 5-day backward trajectories were calculated. These trajectories were obtained 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.

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. $[\sum(\text{inorganic ions}) + (\text{OC} \times 1.6) + \text{EC}]$, where 1.6 is 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). Because Mumbai metropolitan region is a major source for urban aerosols, apart from local emission sources at the sampling site, the air-quality is likely influenced by the regional emissions also (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: $31 \pm 2\,^{\circ}\text{C}$ and $77 \pm 12\,\%$, respectively) than in winter (averaged: $25 \pm 3\,^{\circ}\text{C}$ and $37 \pm 5\,\%$, respectively) at the site.

Aerosol mass concentrations and individual bulk constituent loadings were observed to be higher in winter than in summer in Mumbai. Concentration 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, (ii) pronounced oxidative exhaustion of particles and wet precipitation of particles in summer because of the high temperature and humidity in the tropics, and (iii) accumulation of the particles due to the lowered height of the planetary boundary layer in winter. 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 aerosol and other components 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 ions (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 the seasons, respectively. In general, this indicates that although concentration of bulk constituents is higher in winter, their contribution to aerosol mass do 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 concentration range of 2.1–2.8 and 5.1–16 $\mu g\, m^{-3}$, 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 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. The air mass backward trajectories are plotted in Fig. 3, which shows that air masses encountered at Mumbai during sampling period in both the seasons were transported from far continental sites across the Arabian Sea. In winter, the air mass source regions locate on the sub-continental 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 to Mumbai. It is also important to note that winter air masses were traveled over the neighboring suburban areas, thus they could have more chances to mix with regional air masses influenced from 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 day- and nighttime samples in Fig. 4a, b, respectively. Both of the species are largely formed through photochemical reactions from their precursors and thus can be used as the photochemical production tracers (Charlson et al., 1987; Takami et al., 2007; Aggarwal and Kawamura, 2008; Kawamura and Yasui, 2005). Therefore, a diurnal change in their concentrations with daytime high and nighttime low can be expected, if the aerosols are freshly emitted from local sources. However, as shown in Fig. 4a, b, nssSO_4^{2-} and C_2 diacid concentrations do not follow the diurnal pattern, i.e. they do not always show higher values in daytime. Interestingly, they exhibit a very good correlation ($r^2 = 0.91$) each other. These results suggest that the Mumbai aerosols were not seriously affected by local photochemical processes, rather they were already well processed in the atmosphere before arriving to the sampling site.

We also compared WSOC/OC (and WSOC/TC) ratios for day- and nighttime samples. Contributions of WSOC to OC (and to TC) in day- and nighttime samples were 36 (28) and 38 % (28 %) in summer, and 39 (27) and 38 % (27 %) in winter, respectively. This similarity again indicates that influences of local emissions and local secondary productions 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, both species give a good correlation ($r^2 = 0.75$), indicating that the Mumbai aerosols are influenced by marine air masses coming from 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.

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 aerosol major components. As discussed above, both nssSO_4^{2-} and EC are the major fractions of Mumbai AM. Their fractions in 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 winter season. Being consistent with this, wood/biofuel burning tracers such as nssK^+ and levoglucosan (Simoneit et al., 1999, 2004) also give higher ratios against 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.

The higher mass loading of aerosol bulk components (i.e. OC, EC and T_IN) may be associated with enhanced source emissions in wintertime. Further, lowering of the planetary boundary layer height, which is generally expected in winter season, may contribute to the higher mass loading in this season. Although the ratios discussed above become higher in 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). These similarity of the ratios in both the seasons suggest that, although the source emissions may be enhanced in winter, the sources are likely similar in both the seasons for the Mumbai aerosols.

3.4 Total nitrogen contents and nitrogen isotopic compositions (δ^{15}N): sources versus atmospheric processing

Nitrogen isotopic ratios (δ^{15}N) of aerosol particles provide important information on primary sources and possibly on the secondary nitrogen (Widory, 2007; Kundu et al., 2010; Pavuluri et al., 2010). Total nitrogen (TN), inorganic nitrogen (i.e. N associated with NH_4^+ and NO_3^-), and NH_4^+ and NO_3^- concentrations along with δ^{15}N of TN are shown in Fig. 6. Concentrations of TN and inorganic nitrogen in summer are 0.83±0.15 and 0.53 ± 0.15 µg m^{-3}, respectively. They became ∼3–4 folds higher in winter (i.e. 2.4 ± 1.3 and 2.2 ± 1.1 µg m^{-3}). 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.

Average concentrations of NH_4^+ and NO_3^- in the Mumbai aerosols are 0.54 ± 0.05 and 0.53±0.11 µg m^{-3} in summer, and 2.4±1.4 and 1.3±0.42 µg m^{-3} in winter, respectively. NO_3^- shows a clear diurnal trend especially in summer with daytime maxima and nighttime minima (Fig. 6b). 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).

In the Mumbai aerosols, nitrogen isotopic (δ^{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 high values in winter may be mainly associated with (i) changes in source contribution, and/or (ii) enhanced atmospheric processing of aerosols. 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 by 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 δ^{15}N values in the Mumbai aerosols can be interpreted by the changes in sources contribution. Widory (2007) reported δ^{15}N data sets for different aerosols (PM_{10}) from Paris (France). The aerosols derived from fossil fuel combustion sources showed δ^{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 (av. 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 δ^{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 δ^{15}N values for cow dung cake (un-burnt) is reported to be 13.4 to 15.5 ‰ (Pavuluri et al., 2010). These comparisons suggest that δ^{15}N values of the Mumbai aerosols are higher than those reported for the important fossil fuel burning aerosols, whereas close to δ^{15}N values reported for C3 and C4 plant material burning aerosols and un-burnt cow dung cake material. This again supports that the biofuel/biomass burning is 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 δ^{15}N values of aerosol TN against molar ratios of SO_4^{2-} to NH_4^+ (Fig. 7). $[SO_4^{2-}]/[NH_4^+]$ ratio can be used as an indicator for atmospheric processing of aerosols (Pavuluri et al., 2010). Interestingly, between the two values we observed a negative correlation ($r^2 = 0.31$) in summer and a positive correlation ($r^2 = 0.43$) in winter. These correlations at least suggest that higher δ^{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 reference 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 (especially in tropics). As long as this equilibrium (dynamic) exists in the atmosphere (i.e. $NH_3 \Leftrightarrow NH_4^+$ and $HNO_3 \Leftrightarrow NO_3^-$), particulate nitrogen gets more enriched in ^{15}N, because vapor phase N (i.e. NH_3 or HNO_3), which is evolved from particles, is likely enriched with lighter isotope (^{14}N). Although NO_3^- concentrations showed a clear diurnal trend in summer (see Fig. 6b), such as trend was not observed in winter. This result suggests that aerosol 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 is 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 C is ascribed due to photochemical aging of atmospheric aerosols (Wang et al., 2010). 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 lighter isotope (^{12}C). Meanwhile, the remaining substrate (i.e. organic matter of aerosol particle) is become enriched with heavier isotope (^{13}C). Thus the enrichment of ^{13}C in aerosol TC can largely be attributable to aerosol photochemical processing, although initial ^{13}C values of the carbonaceous aerosols depend on their sources.

For the Mumbai aerosols, δ^{13}C values of aerosol TC ranged from −27.0 to −25.4 ‰. Figure 8 shows sample-to-sample variability in δ^{13}C values, where these values are increased from summer (average: −26.5 ± 0.3 ‰) to winter (−25.9 ± 0.3 ‰). Recently, Narukawa et al. (2008) reported similar δ^{13}C values (−25.7 ± 0.7 ‰) of TC for the Arctic aerosols in winter, those were strongly influenced by the anthropogenic air masses transported from the midlatitudes. Narukawa et al. (1999) also reported the δ^{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) became relatively higher (∼ −26.2 to −25.5 ‰). Martinelli et al. (2002) determined average δ^{13}C values of −25.8±0.5 ‰ (range: −26.9 to −24.9 ‰) for fine aerosol particles ($PM_{2.0}$) from the rain forest of Amazon basin, Brazil in May–August 2000 (i.e. mostly biogenic secondary aerosols).

In a study at Vancouver, δ^{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 δ^{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 δ^{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 δ^{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 when the aerosols were relatively aged (i.e. photochemically more processed). For the Mumbai aerosols, to better understand the factors responsible for the increment in ^{13}C of aerosol TC in winter season (i.e. source versus atmospheric processing), we study the correlations between the concentration ratios of different marker species to TC and δ^{13}C values of aerosol TC.

Kawamura et al. (2004) found higher δ^{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). As stated in Sect. 2.1, resuspension of soil dust due to sweeping activities is an intermittent local source throughout Mumbai, thus carbonate carbon may exist in the samples. In order to examine the possibilities of the increment of ^{13}C in aerosol C due to carbonate carbon, we examined relations between nssCa^{2+}/TC ratios and δ^{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 which can considerably affect the δ^{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. Among diacid compound class, oxalic acid (C_2 diacid) is the smallest diacid and hence is considered as the end product of such destruction processes in this compound class. Therefore, it has been used to trace the secondary processes in several studies (e.g. Agarwal et al., 2010).

In the Mumbai aerosol samples, concentrations of WSOC (µg m^{-3}) show an excellent correlation (r^2 = 0.95) with oxalic acid carbon (C_2-C) concentrations (Fig. 9). This relation suggests that WSOC fraction is largely processed in the atmosphere in the Mumbai aerosols; in other words, organic aerosols in Mumbai are significantly aged. The r^2 value in Fig. 9 for winter aerosol samples (0.93) is twice higher than that of summer samples (0.45). Concentrations of WSOC and C_2 diacid also increased by 3–4 folds 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), and (iii) enrichment of oxidized organics in winter due to slow evolution rate (i.e. slow conversion of POM to CO_2 and other gaseous products).

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. 10. We found a positive correlation between WSOC/TC ratios and $\delta^{13}C$ of TC in Mumbai aerosols. Regression fit for summer samples shows a moderate relation ($r^2 = 0.42$), whereas correlation for winter samples is much stronger ($r^2 = 0.70$). This finding suggests that (i) increment in ^{13}C of aerosol C, especially in winter may be caused by enhanced photochemical processing of organic aerosols in tropics, and thus (ii) aging of tropical aerosols is more prolonged in winter than in summer.

In view of all data discussed here, a possible explanation for prolonged aging of organic aerosol in tropics in winter season is that the condensation, growth and subsequent oxidation of organic aerosols is more pronounced than their evolution to the final end-product (gas phase) in winter because of the lower solar radiation, temperature, humidity and increased level of precursor species (here it is important to note that similar meteorological conditions are existed in summer in several non-tropical regions). During summer season, when solar radiation, temperature and humidity are intensified in tropics and in addition, concentration of precursor species becomes lower, the condensation, growth and subsequent atmospheric aging of organic aerosols are overwhelmed by their volatilization, degradation to the final end-product (gas phase). Because of the low evolution rate 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.

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 at 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 concentration of individual components, i.e. OC, EC, WSOC, 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 winter season. Potential sources identified for Mumbai aerosols are biofuel/biomass burning and fossil fuel combustion in both the seasons. Photochemical production tracers, $nssSO_4^{2-}$ and C_2 diacid do not show 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 day- 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 to 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 abundant source in both the 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. These values and their plots against $nssSO_4^{2-}$/TC, levoglucosan-C/TC and EC/TC also supported the major sources identified for the Mumbai aerosols. However, plots between WSOC/TC ratios and $\delta^{13}C$

values suggest that the increment in ^{13}C of aerosol C in 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 coastal city like Mumbai, aerosols are significantly influenced by long-range continental and regional transport (i.e. aerosol are aged). This is similar to the Chennai aerosols characteristics (Chennai is the other mega city at southeast coast of India, Pavuluri et al., 2011), and (iii) aerosol aging in tropics possibly more prolonged in winter than in summer. The later two factors can significantly increase the oxidized organic matter in aerosols. Therefore, these factors should be taken into account in the regional model 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 evolution pathways may be different in summer and winter seasons. In summer, the evolution would be rather faster, while in winter, it is slower and possibly occurred in several steps. Hence the bulk C-isotopic fractionation is more pronounced in winter than in summer.

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Table 1. Aerosol major constituents (µg m^{-3}) 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
Total carbon (TC)	4.2	9.3	6.0 ± 1.7	16	32	22 ± 4.7
Organic carbon (OC)	3.3	6.1	4.5 ± 0.91	12	23	15 ± 3.3
Elemental carbon (EC)	0.70	3.7	1.5 ± 0.88	4.5	8.9	6.4 ± 1.5
Water-soluble organic carbon (WSOC)	1.2	2.7	1.7 ± 0.434	3.5	9.5	6.0 ± 2.0
Total inorganic ions (T_IN)	4.1	7.2	5.1 ± 0.84	10	26	15 ± 5.0
Aerosol mass (AM)	11	19	14 ± 2.6	37	68	46 ± 10

AM = [T_IN + (OC × 1.6) + EC]

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Table 2. Some 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	16 000	8900 ± 3300
$nssK^+$	1	100	30 ± 30	440	1230	670 ± 230
$nssCa^+$	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	44.5 ± 1.1
$nssK^+$/AM	0	0.9	40.2 ± 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

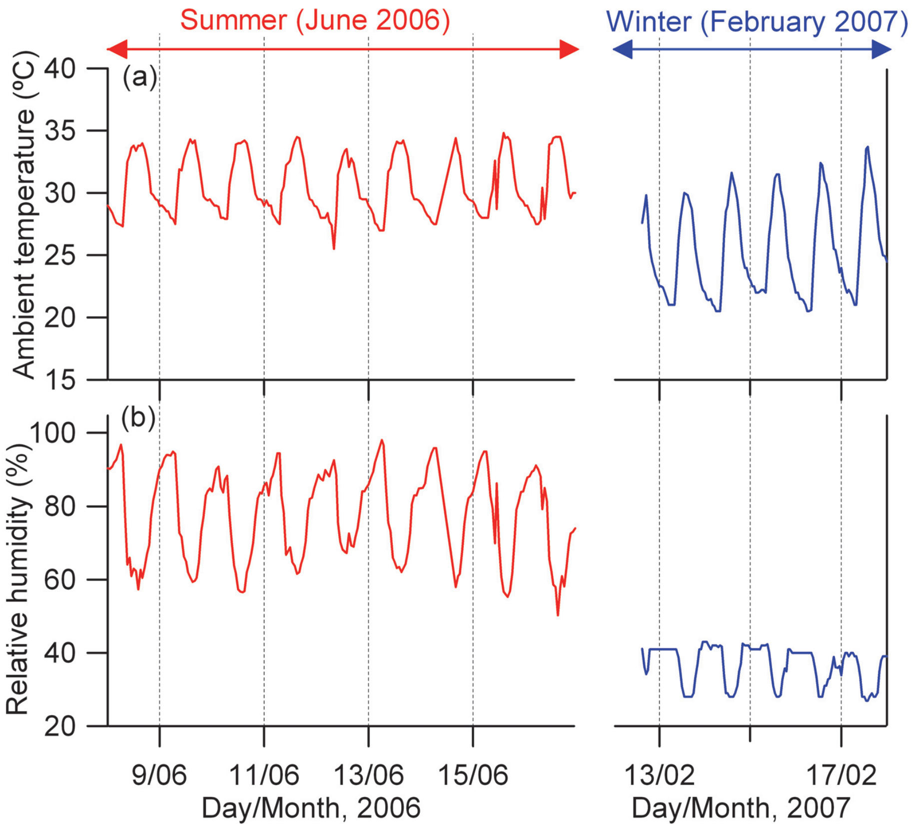

Fig. 1. Temperature and humidity recorded at the site during the campaign.

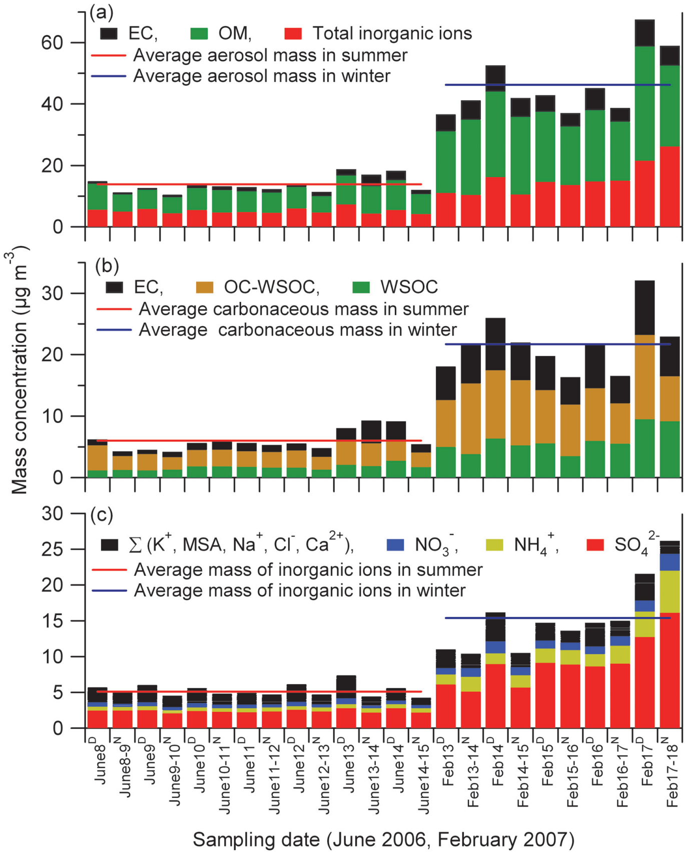

Fig. 2. Temporal variations of aerosol mass loading with the **(a)** major component concentrations (where, OM = OC × 1.6), **(b)** composition of carbonaceous mass, **(c)** inorganic ion composition.

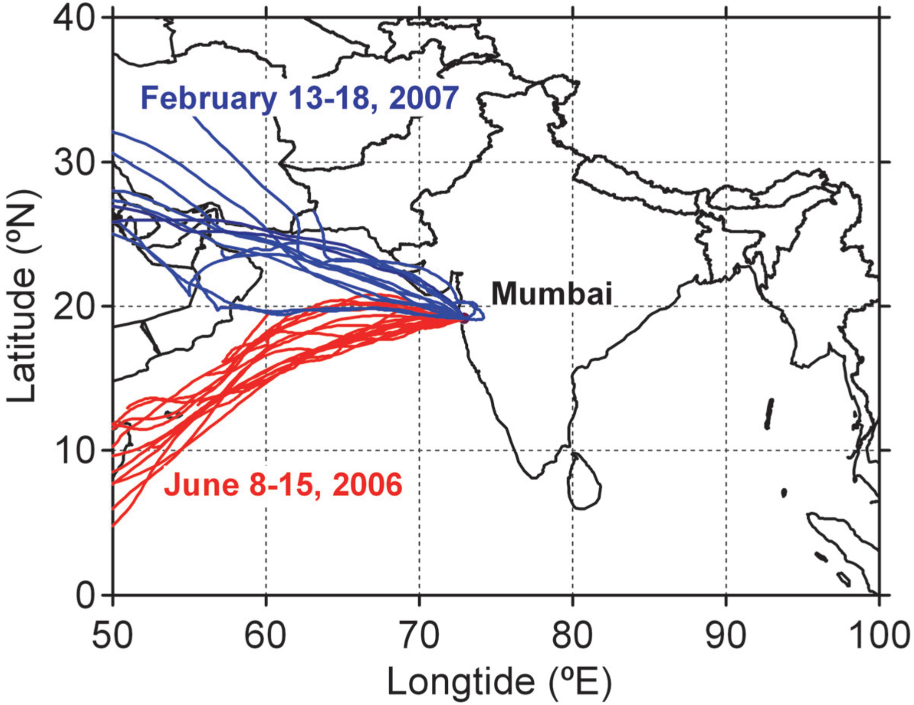

Fig. 3. Five-day backward trajectories obtained for each of the sample. The analysis was performed using the HYSPLIT4 model (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, Maryland, United States). These trajectories were calculated for air masses starting 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.

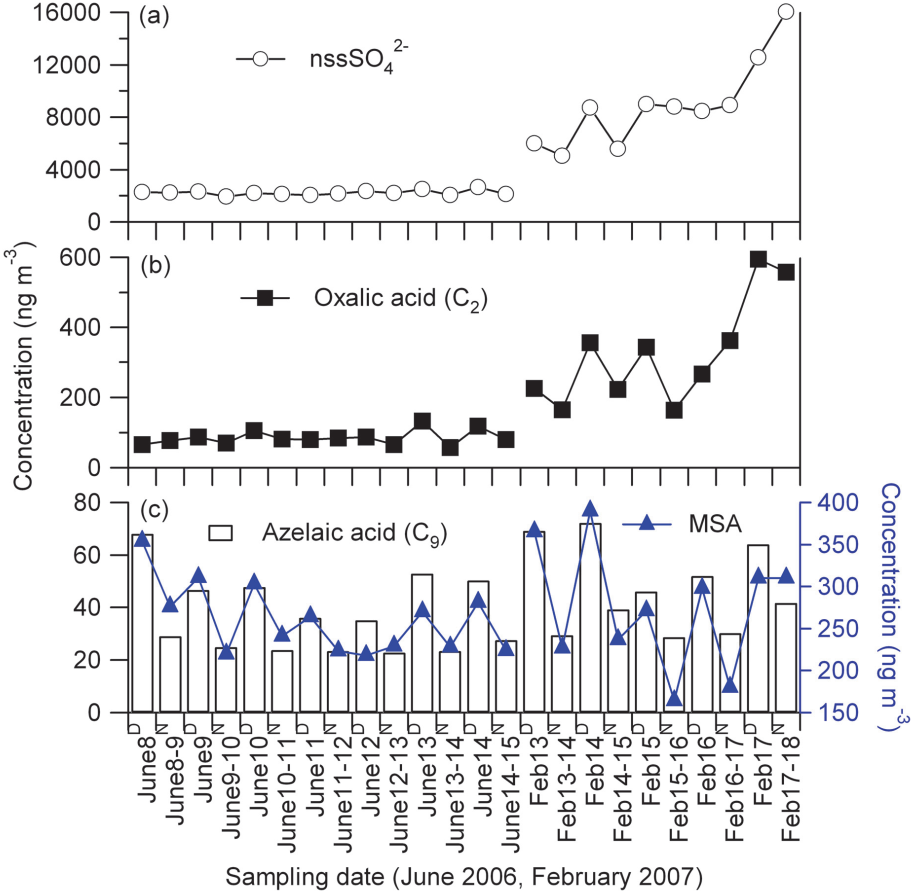

Fig. 4. Temporal variation in concentration of photochemical production tracers: **(a)** nssSO$_4^{2-}$, **(b)** oxalic acid, and **(c)** marine source tracers, i.e. azelaic acid and methanesulfonate.

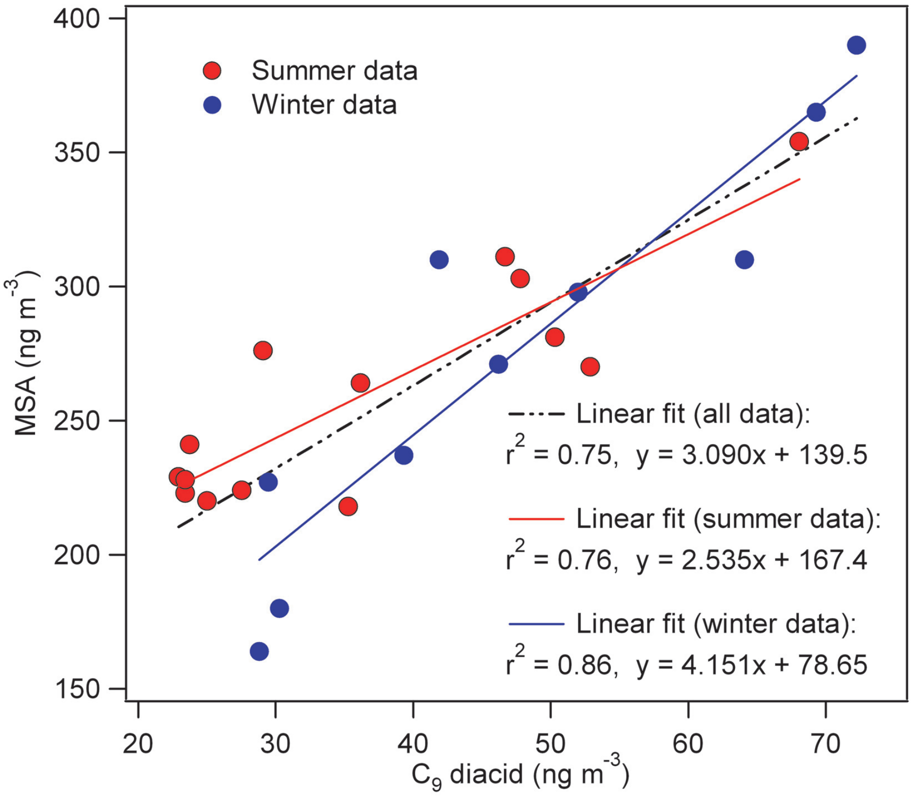

Fig. 5. Correlations between marine source tracers: methanesulfonate (MSA) and azelaic acid (C_9 diacid).

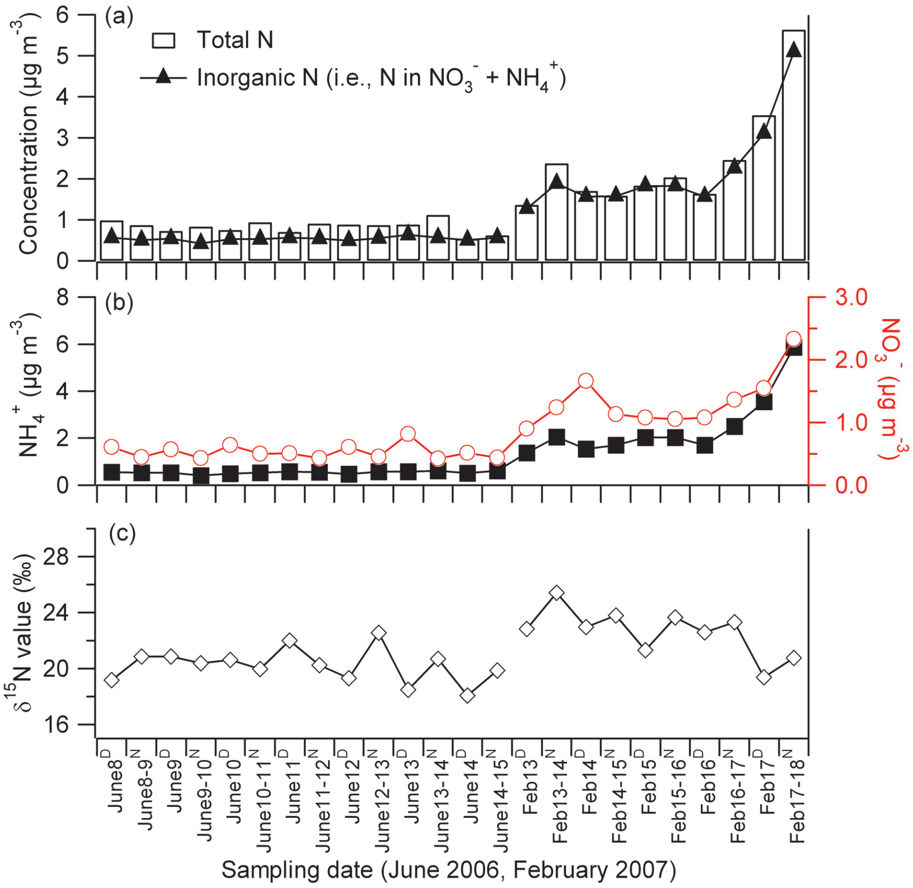

Fig. 6. Temporal variations in concentrations of **(a)** total nitrogen (TN) and inorganic nitrogen, **(b)** NH_4^+ and NO_3^-, and **(c)** $\delta^{15}N$ values of TN.

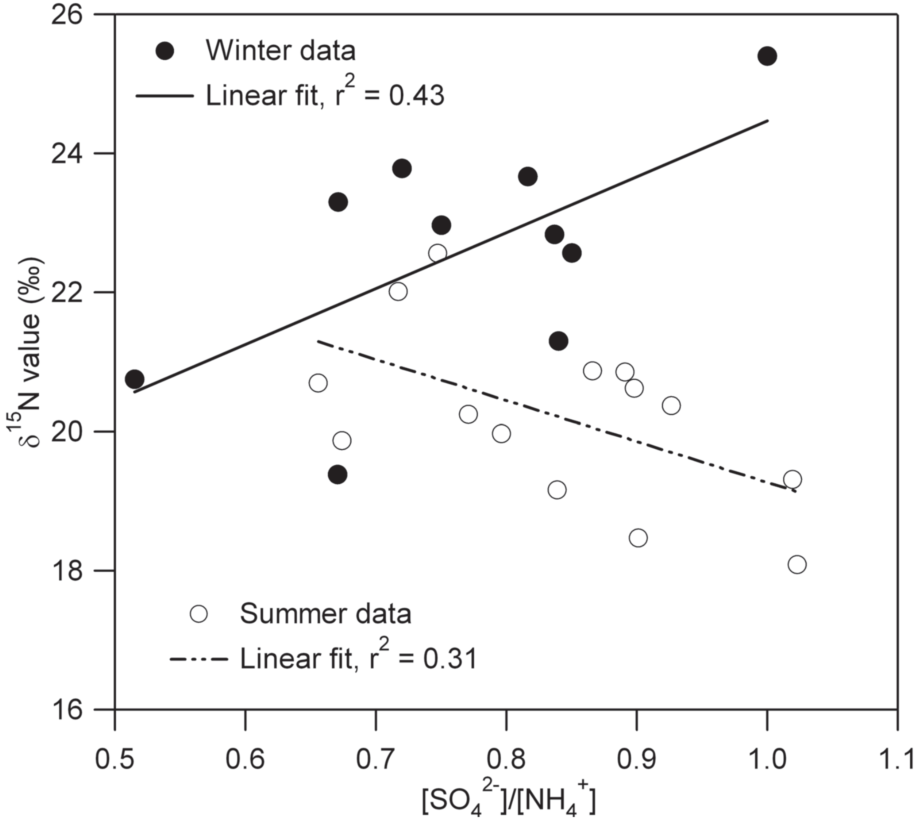

Fig. 7. Relation between δ^{15}N values of TN and molar ratios of SO_4^{2-} to NH_4^+ in summer and winter aerosols.

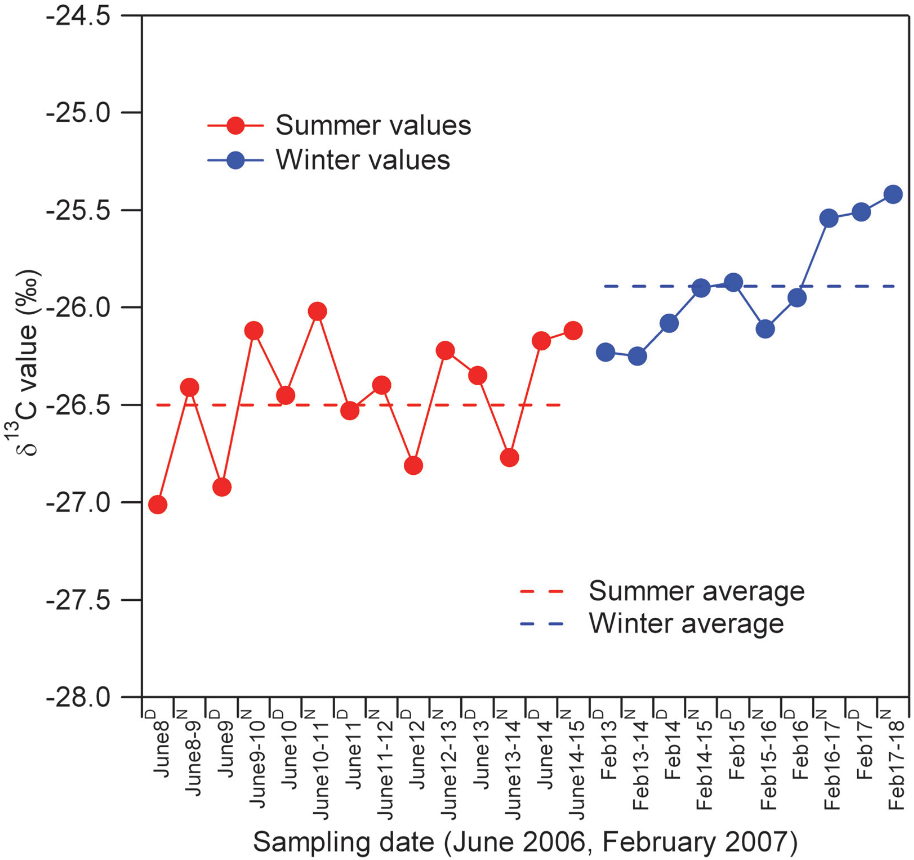

Fig. 8. Temporal variations in δ^{13}C values of TC.

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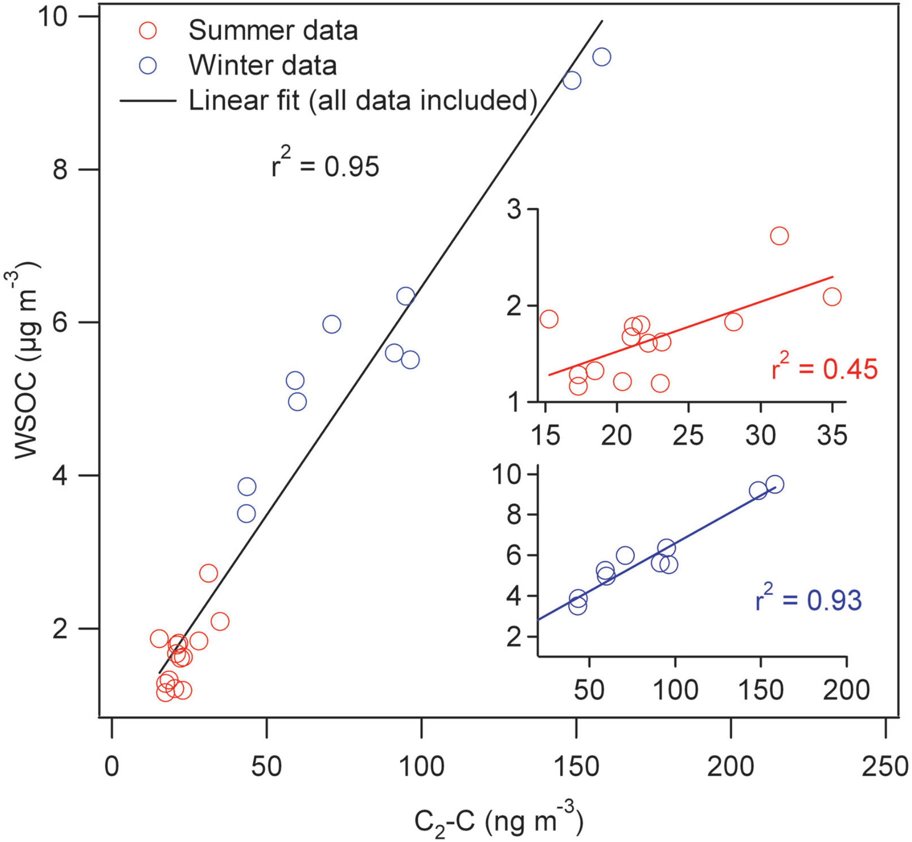

Fig. 9. Relation between WSOC and oxalic acid (C_2 diacid) concentrations determined in the Mumbai aerosols in summer and winter aerosols (inset figures represent the relation for summer and winter data separately).

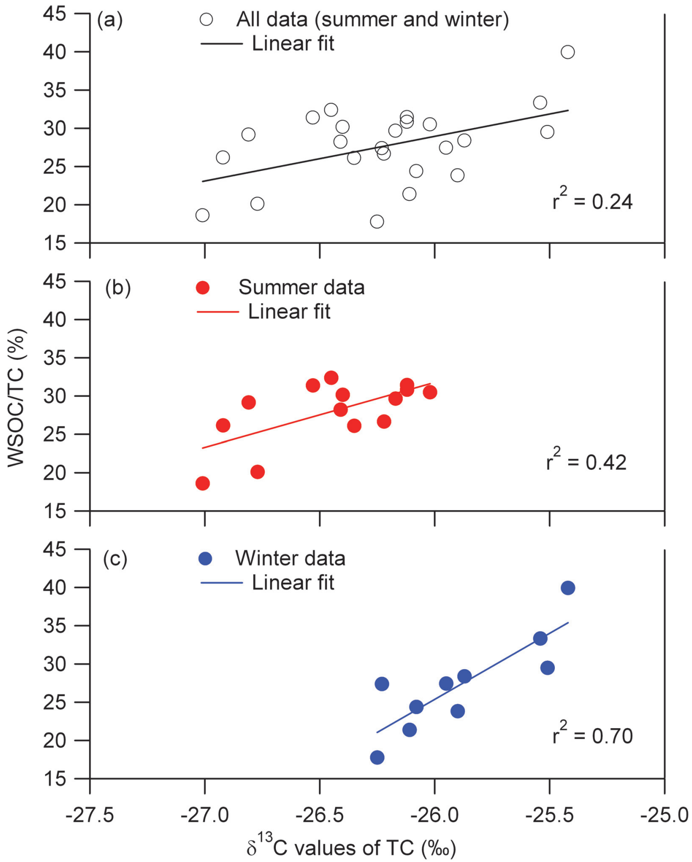

Fig. 10. Relation between WSOC/TC ratios and δ^{13}C values of TC in **(a)** both seasons, **(b)** summer season, and **(c)** winter season.