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Stable carbon and nitrogen isotopic composition of fine mode aerosols (PM_{2.5}) over the Bay of Bengal: impact of continental sources

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ABSTRACT

This study reports on stable carbon ($\delta^{13}\text{C}_{\text{TC}}$) and nitrogen ($\delta^{15}\text{N}_{\text{TN}}$) isotopic composition of total carbon and nitrogen (TC and TN) in the fine mode aerosols (PM_{2.5}; $N = 31$) collected over the Bay of Bengal (BoB). The samples represent two distinct wind regimes during the cruise (27 December 2008–28 January 2009); one from the Indo-Gangetic Plain (referred as IGP-outflow) and another from Southeast Asia (SEA-outflow). The PM_{2.5} samples from the IGP-outflow show higher $\delta^{13}\text{C}_{\text{TC}}$ (-25.0 to -22.8 ‰; -23.8 ± 0.6 ‰) than those from the SEA-outflow (-27.4 to -24.7 ‰; -25.3 ± 0.9 ‰). Similarly, $\delta^{15}\text{N}_{\text{TN}}$ varied from $+11.8$ to $+30.6$ ‰ ($+20.4 \pm 5.4$ ‰) and $+10.4$ to $+31.7$ ‰ ($+19.4 \pm 6.1$ ‰) for IGP- and SEA-outflows, respectively. Based on the literature data, MODIS-derived fire hotspots and back trajectories, we infer that higher $\delta^{13}\text{C}_{\text{TC}}$ in the IGP-outflow is predominantly associated with fossil fuel and biofuel combustion. In contrast, contribution of primary organic aerosols from the combustion of C₃ plants or secondary organic aerosol (SOA) formation from biomass/biofuel-burning emissions (BBEs) can explain the lower $\delta^{13}\text{C}_{\text{TC}}$ values in the SEA-outflow. This inference is based on the significant linear correlations among $\delta^{13}\text{C}_{\text{TC}}$, water-soluble organic carbon and non-sea-salt potassium (nss-K⁺, a proxy for BBEs) in the SEA-outflow. A significant linear relationship of $\delta^{15}\text{N}$ with NH₄⁺ and equivalent mass ratio of NH₄⁺/SO₄²⁻ is evident in both the continental outflows. Since NH₄⁺ abundance dominates the TN over the BoB (>90 %), atmospheric processes affecting its concentration in fine mode aerosols can explain the observed large variability of $\delta^{15}\text{N}_{\text{TN}}$.

Keywords: stable C- and N-isotopes, Bay of Bengal, aerosols, biomass burning, fossil-fuel combustion, South Asia, South-east Asia, Indo-Gangetic Plain

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1. Introduction

The rapidly growing human activities and significant increase in emissions of airborne pollutants from South Asia are of considerable interest owing to their impact on regional climate (Ramanathan et al., 2001a; Lawrence and Lelieveld, 2010). In this context, organic aerosols are considered to be one of the important components of

atmospheric particulate matter for their crucial role in regional radiative forcing through direct and indirect effects (Kanakidou et al., 2005; Jimenez et al., 2009). Several studies have attempted to characterize the sources, transport and transformation pathways of organic aerosols over South Asia (Jayaraman et al., 1998; Novakov et al., 2000; Lelieveld et al., 2001; Ramanathan et al., 2001b; Mayol-Bracero et al., 2002a; Rengarajan et al., 2007; Lawrence and Lelieveld, 2010; Ram et al., 2010; Rajput et al., 2011; Srinivas and Sarin, 2013a, 2014). Jimenez et al. (2009) demonstrated that the identified fraction of atmospheric organic aerosols is no more than 20–30 % of total organic matter. These observations emphasize our ability to assess the impact of organic aerosols on climate forcing,

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mainly due to limited observations. Therefore, the chemical characterization of various organics and their sources from different geographical locations could provide a better means to reassess their realistic aerosol radiative forcing (Jacobson, 2012).

Recent studies on stable isotopic composition of bulk carbon and nitrogen ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of airborne particulate matter have demonstrated their usefulness to apportion the sources and formation pathways of organic aerosols (Kawamura et al., 2004; Aggarwal and Kawamura, 2008; Narukawa et al., 2008; Pavuluri et al., 2011; Aggarwal et al., 2013; Kirillova et al., 2013). Previous studies have used $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of bulk particulate matter to assess the contribution of biomass/biofuel-burning sources (Martinelli et al., 2002; Kundu et al., 2006; Ometto et al., 2006; Widory, 2007; Aggarwal and Kawamura, 2008; Agnihotri et al., 2011; Aggarwal et al., 2013; Mkombe et al., 2014). Although the stable isotopic composition of OA produced from various sources are significantly different, several processes can affect their $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, viz., ageing of air masses, condensation/evaporation of volatile organic compounds (VOCs) on/from a pre-existing particles, oxidation or chemical reactions of primary organic aerosols (POA) by O_3 or NO_x (Kirillova et al., 2013 and references therein).

However, studies from South Asia are limited in assessing the stable C- and N-isotopic composition of ambient aerosols (Agnihotri et al., 2011; Pavuluri et al., 2011; Hegde and Kawamura, 2012; Aggarwal et al., 2013). Based on the physicochemical properties of aerosols, earlier studies have demonstrated the continental impact from South and Southeast Asia over the northern Indian Ocean (NIO) (Lelieveld et al., 2001; Ramanathan et al., 2001b; Mayol-Bracero et al., 2002a). Furthermore, the predominant continental influence on the eastern part of the NIO [the Bay of Bengal (BoB)] has been emphasized by subsequent studies compared to that over the Arabian Sea, western side of the NIO (Kumar et al., 2008; Kedia et al., 2010; Sarin et al., 2010; Srinivas et al., 2011a; Srinivas and Sarin, 2012, 2013a). These studies have further suggested that the strength of the continental sources decreases from winter (December–February) to spring–intermonsoon (March–April) (Srinivas et al., 2011b; Srinivas and Sarin, 2013b, 2014).

A recent study by Agnihotri et al. (2011) has assessed stable C- and N-isotopic composition of marine aerosols from the BoB and Arabian Sea during spring to intermonsoon (March–May 2006). However, no single study deals with the assessment of $\delta^{13}\text{C}$ of bulk carbon and $\delta^{15}\text{N}$ of total nitrogen in marine aerosols from the BoB during the wintertime when marine atmospheric boundary layer (MABL) is influenced by continental air masses from South and Southeast Asia. Here, we have studied the stable isotopic composition of total carbon and nitrogen

(TC and TN) of fine mode aerosols ($\text{PM}_{2.5}$) collected from the BoB during winter season. We have also made a comparison of our results from the Bay region with those from the nearby continental sites as well as other oceanic regions. The overall objective of this study is to understand the measured stable C- and N-isotopic composition of aerosol-TC and TN, respectively, in terms of their source contribution as well as changes in composition (if any) during atmospheric transport to the oceanic region (BoB) located downwind of pollution sources.

2. Methodology

2.1. Cruise track and prevailing meteorology

Aerosol samples ($\text{PM}_{2.5}$) were collected during a cruise (SK-254) conducted in the BoB as part of Indian national programme on integrated campaign of aerosols, trace gases and radiation budget (ICARB) during 27 December 2008–28 January 2009. During the study period, prevailing winds were mostly north-easterly/westerly. The shallow boundary layer along with the relatively weak winds brings continental air masses to the MABL during the wintertime (December–February). We obtained the meteorological parameters on board (viz., relative humidity, ambient temperature, wind speed and wind direction) every hour, which were averaged for daily means. The daily average of relative humidity, ambient temperature and wind speed during the cruise varied from 49.1 to 79.8 %, 22.3 to 26.8 °C and 1.2 to 6.3 m s^{-1} , respectively (Kumar et al., 2010). Further details on wind regimes and meteorological conditions are described in our earlier publications (Kumar et al., 2010; Srinivas et al., 2011b).

2.2. Aerosol sampling and measurement of chemical constituents

In this study, we used a total number of 31 $\text{PM}_{2.5}$ samples that were collected using a high volume air sampler (HVS, Thermo-Anderson Tech., flow rate: 1.13 $\text{m}^3 \text{minute}^{-1}$) on board *ORV Sagar Kanya*. The sampler was placed on the upper deck in front of the ship's navigation room in order to avoid the contamination from the ship's smoke stack and was operated when the wind direction is from the bow and ship cruising at a speed of more than 10 knots h^{-1} . The sampler was calibrated before and after the cruise, and the variation in the flow rate was within 3 %. On average, the samples were collected for a period of ~ 20 h, and the volume of filtered air ranged between 1300 and 1400 m^3 . All $\text{PM}_{2.5}$ samples were collected on pre-combusted (at 450 °C, for 3–4 h) quartz filters (PALLFLEX[®]™, 2500 QAT-UP). After collection, aerosol filters were wrapped in

aluminium foils, sealed in zip-lock bags and stored in deep freezer at $-19\text{ }^{\circ}\text{C}$ until the chemical analyses.

In $\text{PM}_{2.5}$, water-soluble inorganic ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-}) were determined with Dionex-500 ion chromatograph equipped with suppressed conductivity detector (Srinivas et al., 2011b). Similarly, carbonaceous components (EC/OC) were measured on Sunset EC/OC analyser using NIOSH-5040 method (Srinivas and Sarin, 2013a), whereas water-soluble organic carbon (WSOC) was measured using Shimadzu TOC-5000 analyser (Srinivas and Sarin, 2013a). A part of the chemical composition data (K^+ , NO_3^- , NH_4^+ , SO_4^{2-} , EC, OC and WSOC) from earlier publications have been used here to support the inferences related to stable C- and N-isotopic composition of $\text{PM}_{2.5}$ over the BoB. For more details, see our earlier publications (Rengarajan et al., 2007; Kumar et al., 2010; Srinivas and Sarin, 2014).

To determine the blank levels, one quarter of the filter aliquot (ca. $\sim 100\text{ cm}^2$) was extracted with 50 ml of Milli-Q water (specific resistivity $\sim 18.2\text{ M}\Omega\text{-cm}$) like samples and the extracts were measured for water-soluble inorganic constituents. Except for Na^+ , K^+ and Cl^- , no signals were detected on ion chromatogram. The detection limits, as defined by three times of standard deviation of the concentrations of procedural filter blanks ($N=8$) normalized to average filtered volume of air for the $\text{PM}_{2.5}$ ($\sim 1400\text{ m}^3$), were 30 ng m^{-3} for Na^+ , 18 ng m^{-3} for K^+ and 24 ng m^{-3} for Cl^- . We have corrected the K^+ and SO_4^{2-} concentrations in $\text{PM}_{2.5}$ for the sea-salt contribution to derive the non-sea-salt (nss) K^+ and SO_4^{2-} , respectively, using measured Na^+ in aerosols (Keene et al., 1986). All $\text{PM}_{2.5}$ samples were analysed to assess the mass concentrations of total carbon and nitrogen (TC and TN) along with their stable isotopic composition ($\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{15}\text{N}_{\text{TN}}$) using an elemental analyser (EA) and EA/isotope ratio mass spectrometer as reported in Kawamura et al. (2004) and Kundu et al. (2010).

2.3. Stable C- and N-isotopic composition

For this study, stable isotopic composition of $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ were determined using an EA interfaced online to an isotope ratio mass spectrometer (EA/irMS, model: Carlo Erba NA 1500 EA + Finnigan MAT Delta Plus), and the protocol described in Kawamura et al. (2004). Briefly, the filter aliquot (ca. 2.0 cm in diameter) of aerosol sample was sealed in a tin cup, which is pre-cleaned with acetone to remove organic contaminants and dried prior to use, and introduced into EA where it is oxidized in the combustion column packed with copper oxide (CuO) filings at a temperature of $1020\text{ }^{\circ}\text{C}$. The evolved gases (CO_2 and NO_x) were subsequently introduced into a reduction column, where NO_x is converted to molecular N_2 and

thereby separated by a gas chromatograph equipped within EA. To measure stable isotopic composition of evolved CO_2 and N_2 , an interface (ConFlo II) is used to transfer the gases from EA to irMS. The measured isotopic composition of aerosol-TC and TN was expressed as $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ relative to Pee Dee Belemnite carbon standard and atmospheric N_2 , respectively, using the following equations:

$$\delta^{13}\text{C}_{\text{TC}} = \left(\frac{(13\text{C}/12\text{C})_{\text{sample}}}{(13\text{C}/12\text{C})_{\text{std}}} - 1 \right) \times 1000$$

$$\delta^{15}\text{N}_{\text{TN}} = \left(\frac{(15\text{N}/14\text{N})_{\text{sample}}}{(15\text{N}/14\text{N})_{\text{std}}} - 1 \right) \times 1000$$

2.4. Quality assurance

Prior to the measurements of $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{15}\text{N}_{\text{TN}}$, instrumental blanks are checked with pre-cleaned tin cups ($N=3$) and a five-point calibration, having standard amount between 0.2 and 0.6 mg of acetanilide (Thermo Scientific) with known stable carbon and nitrogen isotopic composition as $-27.26\text{ }_{\text{‰}}$ (Cao et al., 2016) and $+11.88\text{ }_{\text{‰}}$ (Kundu et al., 2010), respectively. Filter (lab + field) blanks were also analysed and the analytical signal of samples was suitably corrected for blanks using isotopic mass balance equations described in Turekian et al. (2003). The overall analytical uncertainties in the measurement of $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ were $0.15\text{ }_{\text{‰}}$ and $0.25\text{ }_{\text{‰}}$, respectively, as ascertained by repeat analyses of acetanilide and samples, being consistent with those reported in Kawamura et al. (2004). The uncertainties associated with each measurement were propagated and discussed when comparing the significant differences between the Indo-Gangetic Plain (IGP)- and Southeast Asia (SEA)-outflows (Supplementary Table 1).

In this study, TC concentrations (OC + EC) were measured in $\text{PM}_{2.5}$ soon after their collection on Sunset EC-OC analyser using NIOSH protocol (Rengarajan et al., 2007). These measurements show consistency with total carbon content obtained from the EA-irMS. This comparison clearly demonstrates that artefacts, if any, related to shelf storage of aerosol filters have not caused any error in the isotopic measurements. Similarly, the closure of mass concentration of water-soluble inorganic nitrogen (mainly as $\text{NH}_4^+\text{-N}$; $>90\text{ }_{\%}$) in the TN (Fig. 2) further establishing the consistency between previous measurements (Srinivas et al., 2011b) and this study. This observation clearly demonstrates the lack of artefacts related to the storage of aerosol filters.

3. Results and discussion

3.1. Temporal variability

During a winter cruise, the $PM_{2.5}$ collected over the N-BoB is influenced by the continental outflow from the IGP-outflow (27 December 2008 to 10 January 2009, Fig. 1), whereas those sampled over the S-BoB has influence from SEA-outflow (11–28 January 2009; Fig. 1). This is inferred based on the origin of 7-d isentropic air mass back trajectories (AMBTs) for the sampling days, computed using hybrid single particle Lagrangian-integrated trajectory model, HYSPLIT-4 (Draxler et al., 1999). The impact of IGP- and SEA-outflows on the chemical composition of aerosols over the BoB is a conspicuous seasonal meteorological phenomenon, occurring in winter and spring, documented through large-scale field campaigns (INDOEX and ICARB-I & II) using various optical and chemical properties of aerosols (Kumar et al., 2010; Lawrence and Lelieveld, 2010; Srinivas et al., 2011b).

Organic aerosols in winter over the IGP are mostly emitted from the fossil fuel combustion sources (FF-comb) and biomass/biofuel-burning emissions (BBEs) (wood/crop-residue combustion) (Sudheer and Sarin, 2008; Rajput et al., 2011; Srinivas and Sarin, 2014; Rastogi et al., 2015). However, with the exception of a few studies emphasizing the contribution of organic aerosols from the forest fires

over South-east Asia (Narukawa et al., 1999; Streets et al., 2003; Srinivas and Sarin, 2013a), no such detailed information exists in the literature about other pollution sources. To understand the influence of different pollution sources to atmospheric organic aerosols sampled over the BoB (this study), we have superimposed the locations of coal-fired thermal power plants in the IGP (see blue pins in Fig. 1) and MODIS-derived fire count data (red dots in Fig. 1) from South and Southeast Asia on the back trajectory cluster information (Fig. 1).

From Fig. 1, it is implicit that the SEA-outflow has a contribution from intense forest fires occurring over Indonesia, Thailand, Vietnam and Myanmar. However, no such influence from BBEs was observed in the IGP-outflow during winter. On the other hand, the IGP-outflow has a contribution of organic aerosols from coal-fired thermal power plants in the IGP [also referred as ‘coal belt of India’ (Prasad et al., 2006; Nair et al., 2007)]. Besides this, the residential biofuel (wood) combustion emissions (particularly significant in winter) also contribute to organic aerosols in the IGP-outflow (Gustafsson et al., 2009; Ram and Sarin, 2012). Therefore, we try to infer the relative significance of various sources and compositional changes in the continental outflows (consisting of emissions from coal-fired power plants, vehicular traffic and biomass burning) by comparing the observed $\delta^{13}C_{TC}$ over the BoB with

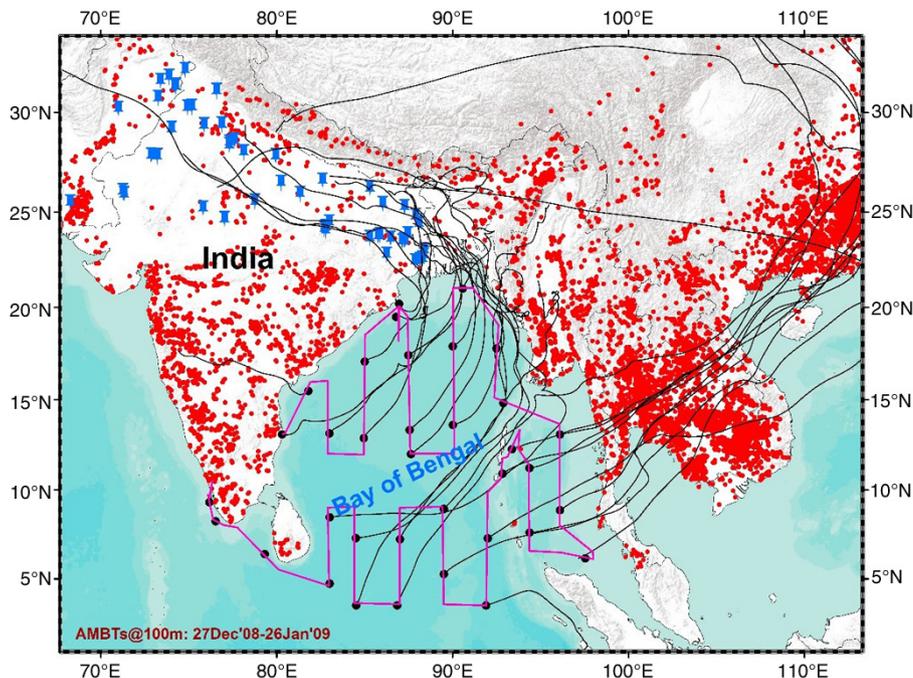


Fig. 1. Seven-day isentropic air mass back trajectories (AMBTs) computed using hybrid single particle Lagrangian-integrated trajectory model, HYSPLIT-4 (Draxler et al., 1999) for the sampling days (27 December 2008 to 26 January 2009) along the cruise track in the Bay of Bengal. Blue pins and red dots over the Indo-Gangetic Plain represent the locations of coal-fired power plants and MODIS-derived fire spots, respectively.

Table 1. Statistical description of mass concentrations (in $\mu\text{g m}^{-3}$) of chemical constituents and stable carbon and nitrogen isotopic compositions ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) in $\text{PM}_{2.5}$ collected over the Bay of Bengal during January 2009

Parameter	IGP-outflow ($N = 15$)	SEA-outflow ($N = 16$)	t -Score, df, p -value
$^a\text{PM}_{2.5}$	13.2–76.7 (38.0 ± 20.2)	2.0–35.3 (22.3 ± 9.9)	2.8, 29, <0.05
TN	0.6–8.8 (3.7 ± 2.5)	0.2–3.0 (1.4 ± 0.8)	3.7, 29, <0.05
TC	3.6–15.4 (8.1 ± 4.3)	1.1–6.5 (3.8 ± 1.8)	3.4, 29, <0.05
TC/TN	1.3–9.4 (3.0 ± 2.1)	1.9–5.4 (2.9 ± 0.8)	0.1, 29, >0.05
$\delta^{13}\text{C}_{\text{TC}}$ (‰)	–25.0 to –22.8 (-23.8 ± 0.6)	–26.9 to –24.2 (-25.3 ± 0.9)	7.3, 29, >0.05
$\delta^{15}\text{N}_{\text{TN}}$ (‰)	+11.8 to +30.6 (20.4 ± 5.4)	+10.4 to +31.7 (19.4 ± 6.1)	0.5, 29, <0.05
^aOC	1.6–11.6 (5.9 ± 3.7)	0.2–5.3 (2.6 ± 1.9)	3.0, 27, <0.05
^aEC	0.8–5.0 (2.0 ± 1.3)	0.2–1.8 (1.2 ± 0.4)	2.4, 29, <0.05
WSOC	1.5–8.3 (4.4 ± 2.4)	0.5–4.1 (2.3 ± 1.4)	2.9, 29, <0.05
WIOC	0.0–4.5 (1.6 ± 1.4)	0.0–1.8 (0.6 ± 0.5)	2.6, 29, <0.05
$^a\text{NH}_4^+$	0.4–10.1 (4.4 ± 3.0)	0.3–4.1 (2.1 ± 1.2)	2.7, 29, <0.05
$^a\text{nss-SO}_4^{2-}$	1.6–28.5 (11.8 ± 7.8)	1.3–12.1 (7.0 ± 3.1)	2.3, 29, <0.05
$(\text{NH}_4^+/\text{nss-SO}_4^{2-})_{\text{equivalent}}$	0.62–1.12 (0.92 ± 0.15)	0.60–0.93 (0.78 ± 0.11)	3.2, 29, <0.05
$\text{nss-K}^+/\text{EC}$	0.19–0.51 (0.29 ± 0.09)	0.23–0.52 (0.39 ± 0.09)	3.0, 29, <0.05
$\text{nss-SO}_4^{2-}/\text{EC}$	1.3–14.5 (6.2 ± 3.6)	2.7–10.3 (6.2 ± 2.2)	0.01, 29, >0.05

^aSupporting parameters were obtained from Kumar et al. (2010).

source-specific signatures and regression analysis between isotopic composition and other chemical tracers measured in the MABL.

TC and TN in $\text{PM}_{2.5}$ exhibit strong latitudinal variability with relatively high concentrations in the IGP-outflow (close to the continent) compared to those in the SEA-outflow (open ocean samples; Table 1). Similar north (high in the IGP-outflow) to south (low in the SEA-outflow) concentration gradient is also noteworthy for other chemical species in the $\text{PM}_{2.5}$ (e.g. OC, EC, WSOC and NH_4^+ ; Supplementary Fig. 1). The $\delta^{13}\text{C}_{\text{TC}}$ has shown pronounced spatial variability over the BoB (Fig. 3) with significantly higher $\delta^{13}\text{C}_{\text{TC}}$ (t -score: 5.5, $\text{df} = 29$; $p < 0.001$) in the IGP-outflow (–25.0 to –22.8 ‰; average -23.8 ± 0.6 ‰) than SEA-outflow (–26.9 to –24.2 ‰; average -25.3 ± 0.9 ‰). This discrepancy is due to varying contributions of aerosol-TC from FF-comb and BBEs over the North and South BoB, respectively. However, no significant differences were observed for $\delta^{15}\text{N}_{\text{TN}}$ (t -score: 0.5, $\text{df} = 29$, $p > 0.05$) in both the outflows (IGP: $+20.4 \pm 5.4$ ‰ and SEA: $+19.4 \pm 6.1$ ‰; Fig. 3).

In comparison to $\delta^{13}\text{C}_{\text{TC}}$, $\delta^{15}\text{N}_{\text{TN}}$ show large variability in both outflows (IGP: +11.8 to +31.6 ‰; SEA: +10.4 to +31.7 ‰; Table 1). The wide spread combustion of biofuels and agricultural crop residue from South and Southeast Asia is a major source of aerosol-TN over the BoB during winter and spring seasons (Srinivas et al., 2011b). In this regard, Turekian et al. (1998) documented that unlike $\delta^{13}\text{C}_{\text{TC}}$, $\delta^{15}\text{N}_{\text{TN}}$ in particles emitted from the combustion of C_3 and C_4 vegetation overlap within spread of the data. However, their study suggested that changes in combustion temperature during BBEs lead to large varia-

bility in the stable N-isotopic composition of aerosols. This is partly due to accessibility of various nitrogenous pools in the source plant at different temperatures during biomass combustion (Turekian et al., 1998). Therefore, observed large variability in the $\delta^{15}\text{N}_{\text{TN}}$ over the BoB is attributed to variations in the combustion temperature during BBEs in the continental outflows (i.e. wood burning in the IGP or forest fires in the SEA).

Although wood-burning emissions usually involved with low-temperature combustion processes than forest fires (i.e. high-temperature combustion), however, we observe no significant differences (t -score: 0.5, $\text{df} = 29$, $p > 0.05$) in the mean $\delta^{15}\text{N}_{\text{TN}}$ between both the outflows (IGP: $+20.4 \pm 5.4$ ‰ and SEA: $+19.4 \pm 6.1$ ‰; Fig. 3). This feature indicates that $\delta^{15}\text{N}_{\text{TN}}$ over the BoB in winter season is mostly governed by the atmospheric processes affecting aerosol-TN concentrations during long-range transport rather than contribution from different sources (i.e., $\delta^{15}\text{N}_{\text{TN}}$ is ‘process dependent’ over the BoB). From Fig. 2, it is obvious that the concentrations of water-soluble inorganic nitrogen species (NH_4^+ and NO_3^-) in the MABL account for more than 90 % of the TN mass. Therefore, processes affecting the relative abundances of NH_4^+ and NO_3^- in aerosol-TN might control the $\delta^{15}\text{N}_{\text{TN}}$ (Section 3.3 for a more detailed discussion).

The sudden change (t -score: 5.5, $\text{df} = 29$; $p < 0.001$) in wind regimes from the IGP- to SEA-outflow was characterized by distinct $\delta^{13}\text{C}_{\text{TC}}$ over the BoB (-23.8 ± 0.6 ‰ and -25.3 ± 0.9 ‰, respectively). This observation indicates that stable C-isotopic composition of aerosols over the BoB is ‘source dependent’. A significant linear relationship is noteworthy between TN and $\delta^{15}\text{N}_{\text{TN}}$ in both the IGP- and SEA-outflows (Fig. 4a). However, such a

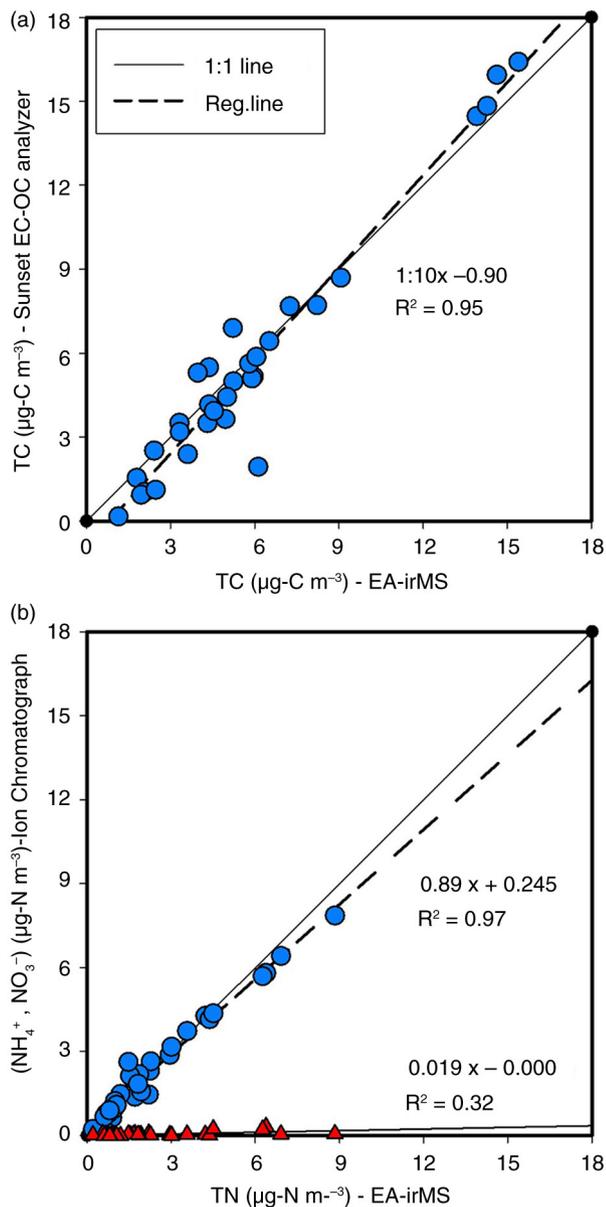


Fig. 2. (a) Comparison of mass concentrations of total carbon (TC) measured by elemental analyser coupled to isotope ratio mass spectrometer (EA-irMS) versus estimated TC concentration based on the atmospheric abundances of elemental and organic carbon (as EC + OC, measured on Sunset Carbon Analyzer), and (b) correlation plot between total nitrogen (TN) measured by EA-irMS and water-soluble inorganic nitrogen (i.e. NO_3^- and NH_4^+) in $\text{PM}_{2.5}$ samples collected over the Bay of Bengal during January 2009 cruise.

significant linear relationship between TC and $\delta^{13}\text{C}_{\text{TC}}$ is observed only in the SEA-outflow but not in the IGP-outflow (Fig. 4b). This could be due to variability in the sources of aerosol-TN and TC in the IGP-outflow (wood burning and FF-comb, respectively) than those in the SEA-

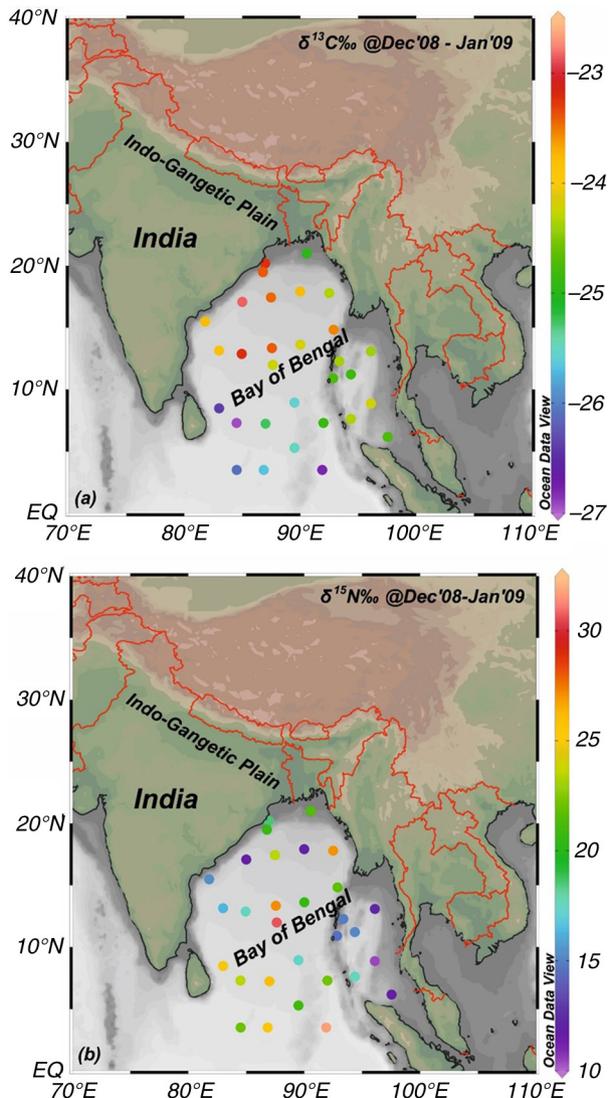


Fig. 3. Spatial distributions of (a) stable carbon ($\delta^{13}\text{C}_{\text{TC}}$) and (b) nitrogen ($\delta^{15}\text{N}_{\text{TN}}$) isotopic composition of fine mode ($\text{PM}_{2.5}$) aerosols collected from the marine atmospheric boundary layer of the Bay of Bengal during a winter cruise (27 December 2008 to 28 January 2009).

outflow (forest fires). Thus, a significant depletion of ^{13}C in TC for the SEA-outflow compared with that for the IGP-outflow, perhaps, indicates a source-specific contribution from BBEs in Southeast Asia during the cruise.

Overall, ^{13}C enrichment and depletion of TC in the IGP- and SEA-outflows, respectively, can be explained based on the differences in the source contribution of carbonaceous species and their transport history to the BoB. A noteworthy feature of the data is evident from a change in the TC concentration in the IGP-outflow with no variability in $\delta^{13}\text{C}_{\text{TC}}$ (Fig. 4b). This feature suggests that dominant

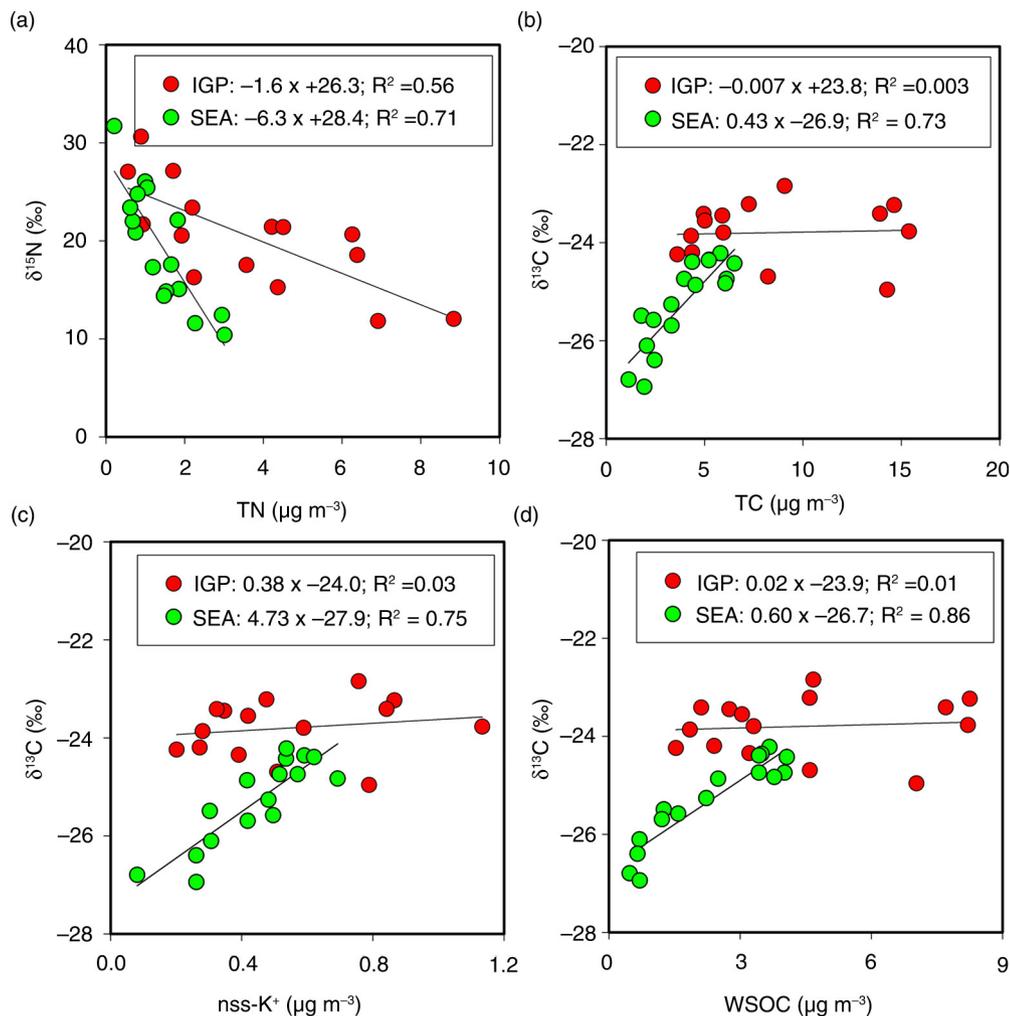


Fig. 4. Correlation plots for (a) TN versus $\delta^{15}\text{N}_{\text{TN}}$, (b) TC versus $\delta^{13}\text{C}_{\text{TC}}$, (c) nss- K^+ versus $\delta^{13}\text{C}_{\text{TC}}$ and (d) WSOC versus $\delta^{13}\text{C}_{\text{TC}}$ for fine mode aerosols collected over the Bay of Bengal during a winter cruise (27 December 2008 to 28 January 2009).

contribution of aerosol-TC in the IGP-outflow is derived from point sources in the IGP. Based on the analyses of various aerosol properties (e.g. AOD, Angstrom exponent), derived from Multiangle Imaging Spectroradiometer (MISR) level 3 remote sensing data, Prasad et al. (2006) have documented that emissions from coal-fired power plant in the IGP is a dominant source of absorbing organic aerosols and other airborne particulate matters in winter season. Furthermore, there exists a notable declining trend in the emission of organic aerosols from the biofuel (wood) combustion and an ongoing rise in coal combustion based on the comparison of energy consumption between 1990 and 2000 (Prasad et al., 2006). Therefore, we attribute coal-fired power plant emissions in the IGP is a major source of organic aerosols sampled over the N-BoB (i.e. in the IGP-outflow).

The forest fires, occurring over Southeast Asia during the cruise in the BoB (January 2009), contribute to large-

scale emissions of POA as well as VOCs. Thus, the observed depletion in ^{13}C of TC in the SEA-outflow (Fig. 3b) can be explained in terms of contribution of POA from C_3 vegetation burning and/or from the secondary organic aerosol (SOA) formation through the photochemical oxidation of VOCs. Similar to our study, lower values of $\delta^{13}\text{C}_{\text{TC}}$ (-26.6 to -23.2 ‰, average -25.0 ‰) were observed for the wheat residue-burning aerosols sampled over Mt. Tai in East Asia (Fu et al., 2012). Furthermore, Fu et al. (2012) documented a non-linear (exponential) relationship between $\delta^{13}\text{C}_{\text{TC}}$ and levoglucosan (a tracer of BBEs), suggesting that an increased contribution of BBEs causes a significant depletion of ^{13}C in aerosols ($\delta^{13}\text{C}$: -26 to -27 ‰) (Fu et al., 2012). Narukawa et al. (1999) also reported a conspicuous decrease in $\delta^{13}\text{C}_{\text{TC}}$ from -25.5 to -27.5 ‰ for the fine mode aerosols sampled from the Indonesian forest fires, in response to an increased contribution of organics from C_3 vegetation. Also, the

fractionation of stable carbon isotopes during the combustion of C_3 plants is not significant (~ 0.5 ‰ enrichment between unburned plant and aerosols (Turekian et al., 1998).

Based on the above arguments, the lower $\delta^{13}C_{TC}$ in the SEA-outflow can be attributed to contribution of organic aerosols from the combustion of C_3 plants. However, SOAs produced from the photooxidation of biogenic VOCs could also contribute to lower the $\delta^{13}C_{TC}$ (Kirillova et al., 2013). A recent laboratory photooxidation/smog chamber experiment of toluene (a VOC emitted from motor vehicles) has demonstrated formation of SOA, whose $\delta^{13}C$ values were ~ 6 ‰ lower than that of the parent toluene (Irei et al., 2006, 2011). Furthermore, $\delta^{13}C$ fractionation between gas and aerosol phases is found to be small during photooxidation (Irei et al., 2006, 2011). Similarly, the laboratory photooxidation on gaseous isoprene and ozone system results in the formation of less volatile methacrolein and methyl vinyl ketone (i.e. known gaseous isoprene oxidation products), whose $\delta^{13}C$ values are depleted by more than 3.6 and 4.5 ‰, respectively (Iannone et al., 2010). These observations, thus, support the argument that photooxidation of anthropogenic/biogenic VOCs results in not only more oxidized semi-volatile organics for which isotopic fractionation effects are found to be minimal (Irei, 2008) but also lowers the $\delta^{13}C$ values than those of precursor fuel/vegetation.

These semi-VOCs subsequently partition to SOAs and, hence, can explain their lower $\delta^{13}C$ signatures. In this regard, lower $\delta^{13}C$ values in the SEA-outflow can, therefore, be attributed to the contribution of SOAs derived from atmospheric oxidation of VOCs emitted from the BBEs in Southeast Asia. We have also observed a significant linear relationship of $\delta^{13}C_{TC}$ with $nss-K^+$ ($R^2=0.58$, $p<0.05$) and WSOC ($R^2=0.60$, $p<0.05$) in the SEA-outflow (Fig. 4c and d) but not in the IGP-outflow ($\delta^{13}C_{TC}$ vs. WSOC: $R^2=0.01$; $p>0.05$ and $\delta^{13}C_{TC}$ vs. $nss-K^+$: $R^2=0.03$; $p>0.05$). In the literature, the occurrence of $nss-K^+$ in the fine mode aerosols and linear relationship with WSOC are used to assess the contribution of carbonaceous aerosols from the BBEs (Andreae, 1983; Andreae and Merlet, 2001; Paris et al., 2010; Pachon et al., 2014; Srinivas and Sarin, 2014). Therefore, a lack of significant linear relationship between $nss-K^+$ and $\delta^{13}C_{TC}$ in the IGP-outflow sampled over the BoB (Fig. 4c), which is consistent with that of TC and $\delta^{13}C_{TC}$ (Fig. 4b), indicate the role of other sources of organic aerosols over the IGP (e.g. coal-fired power plants or vehicular emissions) than BBEs. Based on the literature, SOAs contribute significantly to atmospheric WSOC (Graham et al., 2002; Mayol-Bracero et al., 2002b; Sciare et al., 2008; Ram and Sarin, 2010; Hegde and Kawamura, 2012; Rajput et al., 2014; Srinivas and Sarin, 2014). In this regard, the BBE-derived POA and/or SOA causes ^{13}C

depletion of TC in the SEA-outflow, which can also be supported by the strong correlations of $\delta^{13}C$ with $nss-K^+$ and WSOC (Fig. 4c and d).

The impact of BBEs over FF-comb sources over the BoB can also be inferred based on the relative increase in mass ratio of $nss-K^+$ to EC (Table 1) as the latter contains negligible potassium content (Novakov et al., 2000; Mayol-Bracero et al., 2002b). Furthermore, higher $nss-K^+/EC$ ratios in the SEA-outflow (0.39 ± 0.09) compared with those in the IGP-outflow (0.29 ± 0.09) suggest the dominance of BBEs in the former samples. A significant linear relationship is noteworthy between $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in the SEA-outflow (slope = -5.5 ; $R^2=0.63$; $p<0.05$; Supplementary Fig. 3); however, no such correlation is observed for the IGP-outflow (slope = -3.5 ; $R^2=0.15$; $p=0.15$; Supplementary Fig. 3). The observed weak (or no) and strong correlation of $\delta^{13}C_{TC}$ with $\delta^{15}N_{TN}$ for the IGP- and SEA-outflows, respectively, could be due to variable contribution of TC and TN from FF-comb and BBEs over the BoB. Furthermore, moderate linear correlation is found between $nss-SO_4^{2-}$ and EC for the IGP-outflow samples ($R^2=0.57$; $p<0.05$), which indicates an impact of FF-combustion sources over the north BoB. However, rather weak linear correlation was observed for SEA-outflow between $nss-SO_4^{2-}$ and EC ($R^2=0.26$; $p=0.03$). This observation emphasizes a significant contribution of TC from FF-comb sources in the IGP over the BoB during the study period.

3.2. Relative contribution of fossil fuel versus biomass/biofuel-burning source

The $\delta^{13}C_{TC}$ in $PM_{2.5}$ over the BoB during a winter cruise can be explained based on two end-member mixing between FF-comb and BBEs. Since the IGP is a densely populated and industrialized region of India with intense ongoing anthropogenic activities (viz., coal-fired power plants, vehicular emissions, wood/post-harvest crop-residue burning), it is not logical to assume that biogenic emissions mainly contribute to aerosol-TC in the IGP-outflow. The dominant contribution of aerosol-TC in the SEA-outflow samples is from forest fires occurring in Southeast Asia (as inferred from MODIS satellite-derived fire count data; Supplementary Fig. 3).

Organic compounds, derived from phytoplankton debris and zooplankton excreta in the sea surface microlayer, are coated on sea-salt particles, contributing to marine aerosols collected over the BoB. Therefore, marine phytoplankton-derived organic aerosols have an average $\delta^{13}C$ value of ca. -22 ‰ (Miyazaki et al., 2011). However, the BoB is not a productive oceanic basin and is perennially influenced by fresh water influx from the Ganga–Brahmaputra and other

peninsular rivers. Moreover, the persistence of weak NE-monsoonal winds ($< 3 \text{ m second}^{-1}$) are not likely to trigger sea-to-air transfer of organics from the surface waters of the BoB during the continental outflow. Therefore, contribution from marine organic matter is unlikely due to prevailing winds during the study period. This is further supported by the relative contribution of sea-salts and hence particulate organic matter from the ocean surface by bubble bursting to ambient aerosols over the BoB is no more than 5 % (Srinivas and Sarin, 2014). Therefore, we believe that a two end-member mixing model is a reasonable first-order pseudo-approximation to assess the relative contribution of aerosol-TC from BBEs and FF-comb over the BoB.

The rationale for the contribution from these two sources is further supported by the observed $\text{nss-K}^+/\text{EC}$ and $\text{nss-SO}_4^{2-}/\text{EC}$ ratios in $\text{PM}_{2.5}$ over the BoB (for additional information, see Section 3.1). Higher $\text{nss-K}^+/\text{EC}$ ratios in the SEA-outflow than those in the IGP-outflow samples indicate a dominance of BBEs over the South BoB (Table 1) (Srinivas and Sarin, 2014). The $\text{nss-SO}_4^{2-}/\text{EC}$ ratio, a proxy for fossil fuel combustion with higher values documented for coal-fired power plants (~ 6) (Ramana et al., 2010), showed somewhat consistency between the IGP- and SEA-outflows (Srinivas and Sarin, 2014) (Table 1), indicating a contribution from point sources in the IGP (e.g. coal-fired power plants). Also, the 7-d AMBTs for the $\text{PM}_{2.5}$ samples collected over the north BoB have the source origin from the IGP (Fig. 1), which intercept the receptor sites dominated by carbonaceous aerosols (and hence TC) derived from coal-fired power plants (see *blue pins* in Fig. 1).

Widory (2006) and Mori et al. (1999) have documented that $\delta^{13}\text{C}$ of aerosols from coal combustion as $-23.6 \pm 0.7 \text{ ‰}$ (-22.9 to -24.9 ‰) and $-23.4 \pm 1.2 \text{ ‰}$, respectively, with almost zero fractionation (or slightly negative). On the other hand, combustion-derived particles from liquid fossil fuels (e.g. unleaded/leaded gasoline; $\delta^{13}\text{C}$: -26.4 to -28.0 ‰) are depleted in ^{13}C relative to those originated from solid fuel (coal: -24 to -21 ‰) (Widory, 2006) but are enriched with ^{13}C relative to gaseous fuels (-40 to -28 ‰) (Huang et al., 2006; Widory, 2006; López-Veneroni, 2009; Agnihotri et al., 2011; Kawashima and Haneishi, 2012). A comparison of $\delta^{13}\text{C}_{\text{TC}}$ ($-23.8 \pm 0.6 \text{ ‰}$) over the north BoB with those representative of various fossil fuels as mentioned above (coal, diesel, gasoline, etc.) suggest a dominant contribution from coal-fired power plant emissions in the IGP (Fig. 5).

Although we have observed a decrease in the number (intensity) of fire counts (derived from MODIS data) over the IGP than those over SEA, the contribution of wood-burning emissions to aerosol-TC (Gustafsson et al., 2009; Ram and Sarin, 2012) cannot be ruled out in the IGP-outflow sampled over the BoB. In this context, laboratory and natural field burning chars from C_3 grasses and trees (wood and leaves) are enriched and/or depleted in ^{13}C (e.g. $\delta^{13}\text{C}$ for Eucalyptus wood: -27.2 ‰ ; Sphagnum: -26.0 ‰ ; C_3 grasses: -28.2 to -32.4 ‰ ; Eucalyptus leaf: -28.2 ‰) compared with plant materials (Krull et al., 2003). On a similar note, based on the laboratory-based combustion, Agnihotri et al. (2011) documented that aerosols from typical BBEs in India exhibit a very narrow range of $\delta^{13}\text{C}$ ($-27.9 \pm 1.1 \text{ ‰}$). However, the observed $\delta^{13}\text{C}_{\text{TC}}$ in the

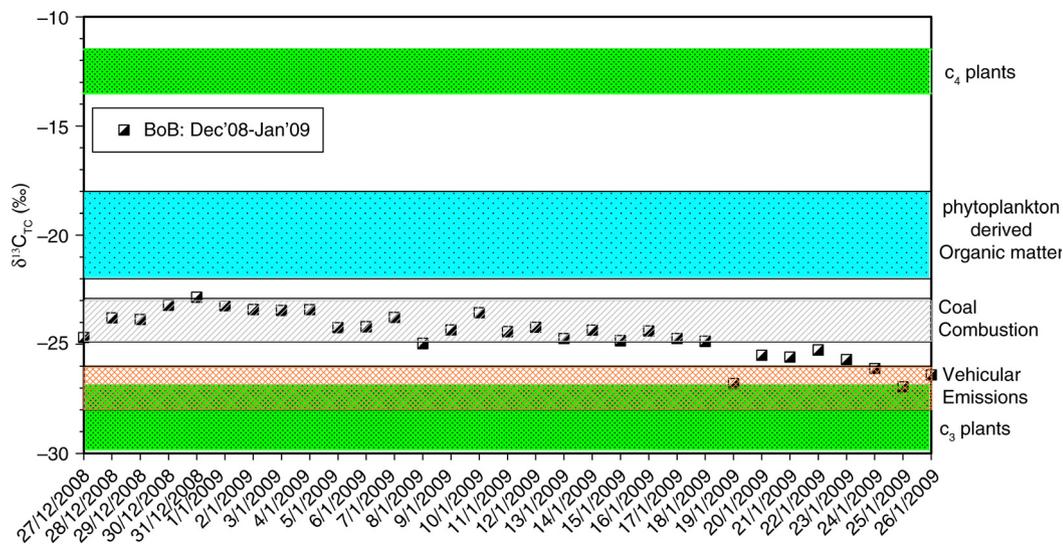


Fig. 5. Comparison of $\delta^{13}\text{C}$ of aerosol-TC over the BoB during a winter cruise (January 2009) with literature values of various sources such as combustion/emissions from C_3 , C_4 and marine phytoplankton (Turekian et al., 1998; Cao et al., 2013), coal combustion (Mori et al., 1999; Widory, 2006) and vehicular emissions (Widory, 2006; Cao et al., 2013).

IGP-outflow (-23.8 ± 0.6 ‰) is consistent with that of coal-derived emissions compared with other sources (i.e. gasoline combustion and wood-burning emissions; Fig. 5). Therefore, we have used coal-burning emissions as one end-member ($\delta^{13}\text{C}_{\text{TC}}$: -23 ‰; Widory, 2006) for explaining the observed stable carbon isotopic signatures of TC in the continental outflow sampled over the BoB during winter. We can further support the significance of coal-fired power plants as a potential source of organic aerosols in the IGP-outflow sampled over the BoB as follows.

As mentioned earlier, FF-comb (coal combustion and vehicular emissions: VEs) and BBEs (wood/crop-residue) in the IGP contribute to organic aerosols over the BoB during the winter period (Rengarajan et al., 2007; Sudheer and Sarin, 2008; Kumar et al., 2010; Srinivas and Sarin, 2013, 2014). In such cases, the $\delta^{13}\text{C}_{\text{TC}}$ of $\text{PM}_{2.5}$ over the BoB can be expressed as a product of individual fractions of TC from each of these three respective sources times their stable C-isotopic composition as below

$$\delta^{13}\text{C}_{\text{TC-sample}} = f_{\text{coal-comb-TC}} * \delta^{13}\text{C}_{\text{TC-coal}} + f_{\text{VEs-TC}} * \delta^{13}\text{C}_{\text{TC-VEs}} + f_{\text{BBEs-TC}} * \delta^{13}\text{C}_{\text{TC-BBEs}} \quad (1)$$

Based on the ^{14}C -analysis of EC, Gustafsson et al. (2009) documented near equal contribution of wood-burning emissions and fossil fuel combustion sources to Atmospheric Brown Clouds over South Asia. Therefore, we have assumed 50 % contribution from biofuels (Gustafsson et al. 2009), 30 % from coal-fired thermal power plants and 20 % from vehicular emissions (Prasad et al., 2006) to atmospheric organic aerosols in the IGP-outflow. Agnihotri et al. (2011) documented that source-specific $\delta^{13}\text{C}_{\text{TC}}$ of various biofuels and crop-residue combustion-derived aerosols from South Asia centred on -27.9 ± 1.1 ‰. Similarly, a source-specific $\delta^{13}\text{C}_{\text{TC}}$ of -23.6 ± 0.7 ‰ from coal combustion-derived particles has been documented by Widory (2006). Also, the $\delta^{13}\text{C}_{\text{TC}}$ of particles generated from diesel combustion emissions span from -28 to -26 ‰ (Widory, 2006).

Using the respective source contributions and their corresponding $\delta^{13}\text{C}_{\text{TC}}$ in eq. (1), we have estimated $\delta^{13}\text{C}$ of organic aerosols collected in the IGP-outflow to be -26 to -27 ‰. Based on the narrow spread of $\delta^{13}\text{C}_{\text{TC}}$ in the IGP-outflow (-23.8 ± 0.6 ‰), we estimated $\delta^{13}\text{C}_{\text{TC}}$ from the contribution of above-mentioned three major sources in the IGP. However, it may be argued that atmospheric oxidation, and hence, enrichment in ^{13}C could be compensated by SOA formation (with overall ^{13}C depletion) during transport. Therefore, the observed overlap of $\delta^{13}\text{C}_{\text{TC}}$ over the N-BoB with coal-fired power plant emissions in the IGP emphasizes the source significance in the IGP-outflow.

However, further studies on seasonal variability of the IGP-outflow are needed along with the $\delta^{13}\text{C}_{\text{TC}}$.

The $\delta^{13}\text{C}_{\text{TC}}$ in the SEA-outflow (-26.9 to -24.2 ‰) overlap with those derived from both vehicular emissions and forest fires (Fig. 5). However, the SEA-outflow samples are collected over the pelagic (deep) waters (i.e. away from the coast and unlike samples from the IGP-outflow, where vehicular emissions could contribute) and, therefore, not likely to have contribution from vehicular emissions. Furthermore, AMBTs originating from Southeast Asia have a significant contribution from forest fires, inferred from the MODIS fire count data (Supplementary Fig. 2). Therefore, we have considered BBEs as another end-member to account for the variability in $\delta^{13}\text{C}_{\text{TC}}$ in the SEA-outflow.

Aerosol-TC in the SEA-outflow (-25.3 ± 0.9 ‰) is significantly depleted in ^{13}C than that derived from C_4 plants (-17 to -9 ‰; average -13 ‰), being somewhat consistent with those originated from C_3 vegetation burning (-32 to -20 ‰; average -28 ‰) (Smith and Epstein, 1971). In a previous study, Turekian et al. (1998) suggested that particles from C_3 plant burning emissions showed a slight enrichment in ^{13}C in aerosol-TC (or higher in $\delta^{13}\text{C}$ by only 0.5 ‰ or less) than host plant, while C_4 plants resulted in a depletion of ^{13}C (or lower in $\delta^{13}\text{C}$ by 3.5 ‰) (Turekian et al., 1998). According to Turekian et al. (1998), the increased relative proportion of refractory components (e.g. lipids; ^{13}C depleted than bulk plant) over labile carbon pools (^{13}C enrichment) in aerosols during C_4 plant combustion causes ^{13}C depletion of TC; however, no such effects were observed for C_3 plant combustion-derived aerosols. A similar result has been reported for the smoke and ash that are derived from the combustion of C_3 plants which show negligible (or no) fractionation (Krull et al., 2003; Das et al., 2010).

Taken together of all these findings, we have assumed -23 and -28 ‰ to be the representative end-member $\delta^{13}\text{C}$ signatures for FF-comb source and BBEs, respectively, based on the two end-member mixing model, which is described as follows:

$$\delta^{13}\text{C}_{\text{sample}} = f_{\text{FF-comb}} * [\delta^{13}\text{C}]_{\text{FF-comb}} + f_{\text{BBEs}} * [\delta^{13}\text{C}]_{\text{BBEs}} \quad (2)$$

$$f_{\text{FF-comb}} + f_{\text{BBEs}} = 1 \quad (3)$$

FF-comb (%)

$$= \frac{[(\delta^{13}\text{C})_{\text{sample}} - (\delta^{13}\text{C})_{\text{BBEs}}]}{[(\delta^{13}\text{C})_{\text{FF-comb}} - (\delta^{13}\text{C})_{\text{BBEs}}]} \times 100 \quad (4)$$

Here, $f_{\text{FF-comb}}$ and f_{BBEs} refer to the fractional contribution of TC from fossil fuel combustion and biomass-burning emission sources, respectively. The end-member $\delta^{13}\text{C}$ for FF-comb and BBEs are -23.0 and -28.0 ‰, respectively. Using eq. (4), we estimated the contribution of

fossil fuel combustion to both the IGP- and SEA-outflows. In this study, the estimated contribution of FF-comb source to $\delta^{13}\text{C}_{\text{TC}}$ varied from 61 to 100 % (average 84 ± 12 %) for the IGP-outflow samples and 12 to 66 % (average 44 ± 18 %) for the SEA-outflow samples.

3.3. Elevated $\delta^{15}\text{N}$ of TN: transformation of gaseous NH_3 to particulate NH_4^+

In both the IGP- and SEA-outflows, the water-soluble inorganic nitrogen (i.e. NH_4^+ -N accounting for 81–100 %) dominates the total soluble nitrogen (Srinivas et al., 2011b). Further, a moderate-to-strong linear correlation of $\delta^{15}\text{N}_{\text{TN}}$ with NH_4^+ and equivalent mass ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ is observed in both continental outflows (Fig. 6). Since NH_4^+ dominates aerosol-TN over the BoB (i.e. >90 %; $R^2 = 0.95$; Fig. 2), atmospheric processes affecting the concentration of particulate NH_4^+ in fine mode aerosols might explain the observed $\delta^{15}\text{N}_{\text{TN}}$. The particulate NH_4^+ concentration in the MABL, however, is influenced by the atmospheric reactions of gaseous NH_3 with acidic species (e.g. H_2SO_4 , HNO_3) to form NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . Furthermore, NH_4NO_3 is formed mostly under ammonia-rich conditions (i.e. for which NH_4^+ to SO_4^{2-} equivalent mass ratio is greater than unity) because the reaction between ammonia and sulphate is preferable. However, NH_4NO_3 is thermodynamically not stable and, therefore, often dissociated into precursor chemical constituents during atmospheric transport, which also affects the ambient NH_4^+ concentration. As a result, NO_3^- mainly exists in coarse mode due to the reaction with mineral dust and sea-salt (Jickells, 2006). All these processes/reactions could influence $\delta^{15}\text{N}_{\text{TN}}$ in ambient aerosols. It is implicit from Fig. 6 that linear relationship of NH_4^+ concentration

and the equivalent mass ratios of NH_4^+ to SO_4^{2-} with $\delta^{15}\text{N}_{\text{TN}}$ can explain the observed enrichment of ^{15}N in the $\text{PM}_{2.5}$ sampled over the BoB.

The mean equivalent mass ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ in the samples from IGP- and SEA-outflow corresponds to 0.92 ± 0.15 and 0.77 ± 0.12 , respectively, suggesting an ammonia-deficit (poor) condition. Moreover, the observed ambient temperature during the cruise averages around 26.7 °C (IGP-outflow: 24.4 – 27.4 °C; SEA-outflow: 25.9 – 29.0 °C) and high nss- SO_4^{2-} concentrations facilitate the dissociation of NH_4NO_3 . Interestingly, Srinivas et al. (2011b) have documented the predominant occurrence of NO_3^- in coarse mode and NH_4^+ in fine mode aerosols during the January 2009 cruise. This implies that particulate NH_4^+ in the MABL mainly occur due to the formation of more stable NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$. In this regard, we observed a very strong correlation between NH_4^+ and SO_4^{2-} (Srinivas et al., 2011b), suggesting the formation $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 over the BoB during the study period. Therefore, we believe that atmospheric transformation of gaseous NH_3 to particulate NH_4^+ might be responsible for the observed large variability in $\delta^{15}\text{N}$ of TN over the BoB.

Similar to our study, Pavuluri et al. (2010) reported an elevated $\delta^{15}\text{N}$ of TN and its significant positive linear correlation with sulphate to ammonium molar ratio (or negative correlation with that of $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio) for the urban coastal aerosols from Chennai, India, during the late winter (January). Further, they observed a positive relationship between ambient temperature and $\delta^{15}\text{N}$; in particular, higher $\delta^{15}\text{N}$ are noteworthy for those sampling days with temperatures >20 °C (Pavuluri et al., 2010). The ambient temperature range over the BoB in this study is higher than that documented in Pavuluri et al. (2010).

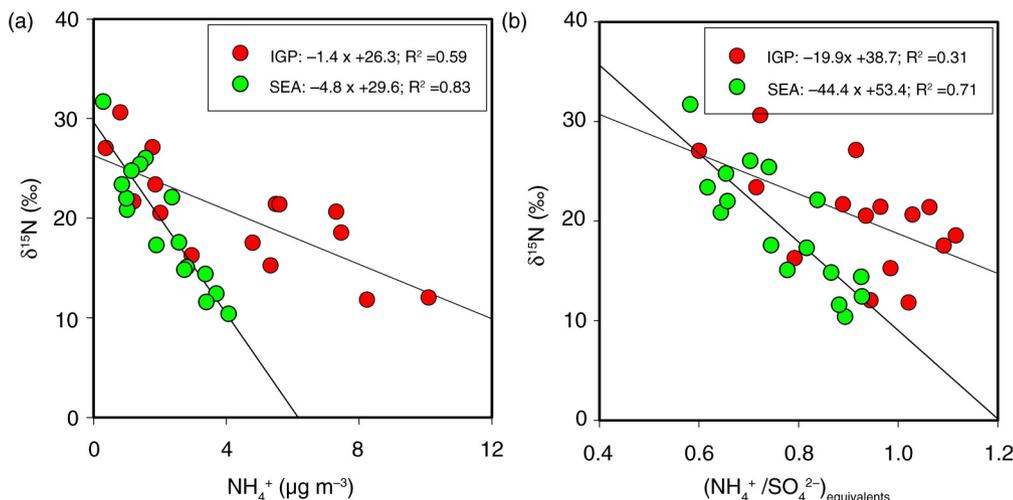


Fig. 6. Linear regression analysis between (a) concentration of NH_4^+ and $\delta^{15}\text{N}$, and (b) equivalent mass ratio of NH_4^+ to SO_4^{2-} and $\delta^{15}\text{N}$ in $\text{PM}_{2.5}$ collected over the Bay of Bengal during a winter cruise (January 2009).

During a laboratory experiment, an exposure of gaseous NH_3 to aerosol filters loaded with sulphuric acid results in the formation of $(\text{NH}_4)_2\text{SO}_4$ (i.e. ascertained through stoichiometric equilibrium between NH_4^+ and SO_4^{2-}), which is enriched in ^{15}N with isotope enrichment factor of +33 ‰ (Heaton et al., 1997). Combining all the above arguments, we believe that gas to particle formation of NH_3 to particulate NH_4^+ in the MABL can explain the enrichment of ^{15}N in the $\text{PM}_{2.5}$ sampled over the BoB during winter.

The mean value of $\delta^{15}\text{N}_{\text{TN}}$ in the IGP-outflow sampled over the BoB during a winter cruise (this study) is higher than those obtained during a spring–intermonsoon cruise [$+10.6 \pm 2.7$ ‰ (Agnihotri et al., 2011)]. Although the continental outflow from the IGP persists during spring intermonsoon, the observed depletion of ^{15}N could be explained based on the decrease in source strength/variability. The weakening of the IGP-outflow during spring–intermonsoon, compared with winter months (Table 1), is inferred by a decrease in the atmospheric concentrations of NH_4^+ ($0.01\text{--}2.3 \mu\text{g m}^{-3}$; $0.9 \pm 0.6 \mu\text{g m}^{-3}$) and nss-SO_4^{2-} ($2.5\text{--}10.3 \mu\text{g m}^{-3}$; $10.3 \pm 2.5 \mu\text{g m}^{-3}$), and equivalent mass ratios of NH_4^+ to nss-SO_4^{2-} ($0.01\text{--}0.66$; average 0.41 ± 0.20) over the BoB. Therefore, we believe that the observed decrease in particulate NH_4^+ in the marine aerosols during spring intermonsoon might indicate the non-availability of gaseous NH_3 to form NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ aerosols and, thus, explain the observed lower $\delta^{15}\text{N}_{\text{TN}}$.

Similar to our study, higher $\delta^{15}\text{N}$ values (+13.4 to +22.1 ‰) have been reported for fine mode aerosols sampled over Tanzania during dry season, which is attributed to a significant ^{15}N enrichment by isotopic exchange reaction of N between gaseous NH_3 and aerosol NH_4^+ during atmospheric transport (Mkoma et al., 2014). Similarly, Pavuluri et al. (2010) have also reported similar $\delta^{15}\text{N}$ values in PM_{10} aerosols, ranging from +18.0 to +27.8 ‰ and +18.6 to +25.7 ‰ in day and night samples, respectively, collected during winter from a coastal site in India (Chennai). Therefore, observed variability in $\delta^{15}\text{N}_{\text{TN}}$ for the IGP-outflow samples (+11.8 to +30.6 ‰) can be attributed to pronounced continental impact of anthropogenic sources (reflected from their higher ambient abundances of NH_4^+ and NO_3^- over the north BoB) to TN and also the exchange reactions between gaseous NH_3 and particulate NH_4^+ during transport. It is important to emphasize that $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ showed a good correlation for the SEA-outflow (influenced by BBes; see Fig. 1), but not in the IGP-outflow. Similar to this study, Agnihotri et al. (2011) have documented a strong correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ over the BoB during spring–intermonsoon cruise, which is also influenced by the BBes. In a previous study, Turekian et al. (1998) documented that various stages of biomass combustion resulted in a large

spread in stable nitrogen isotopic signatures of aerosol-TN. Therefore, variability in $\delta^{15}\text{N}_{\text{TN}}$ in the SEA-outflow (+10.4 to +30.7 ‰; average $+19.4 \pm 6.1$ ‰) can be explained by the highly variable temperature conditions that prevail during the forest fires in Southeast Asia.

3.4. Comparison with studies from the Northern Indian Ocean

The stable isotopic composition of TC and TN from this study (January 2009) was compared with those from earlier cruises conducted in the NIO (Agnihotri et al., 2011) and other sampling sites from South Asia. A significant difference in the $\delta^{13}\text{C}_{\text{TC}}$ is noteworthy during the cruises conducted in the BoB in January 2009 (Table 2) and March–April 2006 [range: -26.6 to -24.1 ‰; average -25.6 ± 0.6 ‰ for TSP samples (Agnihotri et al., 2011)]. Although $\delta^{13}\text{C}$ of TC for both cruises refers to different size fractions of aerosols, it is relevant to state that during long-range transport the mass size distribution of atmospheric particulates changes from coarse to fine mode due to the settling of coarser particles (Duce et al., 1991). This is most relevant for our sampling from the MABL of the BoB and the chemical composition mostly comprised dominant fine particles (Srinivas et al., 2011b). Although source strength of carbonaceous aerosols in the IGP-outflow is varied in between the cruises (i.e. higher abundances in winter than spring–intermonsoon) over the BoB, their sources remain the same, as inferred from the diagnostic mass ratios of chemical composition of aerosols (Sarin et al., 2010; Srinivas and Sarin, 2012).

The $\delta^{13}\text{C}_{\text{TC}}$ in the IGP-outflow from a winter cruise (January 2009) in the BoB (this study) is significantly higher than that obtained during spring–intermonsoon (Agnihotri et al., 2011) (Table 2). However, $\delta^{13}\text{C}_{\text{TC}}$ in the SEA-outflow sampled over the BoB in winter (11–28 January, 2009) is somewhat similar with that from spring–intermonsoon cruise (Agnihotri et al., 2011). The observed differences in $\delta^{13}\text{C}_{\text{TC}}$ during the two cruises could be related to temporal shift in the source contributions (anthropogenic aerosols accounting for more than 80 % in winter vis-à-vis near equal contribution of dust and anthropogenic species during spring–intermonsoon, March–April 2006) (Srinivas and Sarin, 2012). Analysis of MODIS fire images (Supplementary Fig. 3) clearly showed hotspots over the IGP during spring–intermonsoon (March–April 2006) and Southeast Asia during winter (January 2009; Fig. 1). Therefore, ^{13}C depleted values of TC in the IGP-outflow samples in spring–intermonsoon and the SEA-outflow samples in winter can be explained by a significant contribution of carbonaceous species from BBes. The impact of BBes in the IGP-outflow sampled over the BoB during spring–

Table 2. Comparison of stable carbon and nitrogen isotopic compositions of aerosols from this study with those documented in the literature over South Asia

Region	Season	Sample type	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	Reference
Bay of Bengal	Winter (IGP-outflow)	PM _{2.5}	-23.8 ± 0.6	20.4 ± 5.4	This study
Bay of Bengal	Winter (SEA-outflow)	PM _{2.5}	-25.8 ± 0.9	19.4 ± 6.1	This study
Bay of Bengal	Spring–intermonsoon	TSP	-25.6 ± 0.6	10.6 ± 2.7	Agnihotri et al. (2011)
Arabian Sea	Spring–intermonsoon	TSP	-26.5 ± 0.8	1.4 ± 3.2	Agnihotri et al. (2011)
Mumbai	Summer	TSP	-26.5 ± 0.3	20.2 ± 1.2	Aggarwal et al. (2013)
Mumbai	Winter	TSP	-25.9 ± 0.3	22.8 ± 1.4	Aggarwal et al. (2013)
Chennai	Summer and winter	PM ₁₀	-25.0 ± 0.6	–	Pavuluri et al. (2011)
Chennai	Winter (day)	PM ₁₀	–	25.5 ± 2.4	Pavuluri et al. (2010)
Chennai	Winter (night)	PM ₁₀	–	23.0 ± 2.3	Pavuluri et al. (2010)
Chennai	Summer (day)	PM ₁₀	–	22.2 ± 4.3	Pavuluri et al. (2010)
Chennai	Summer (night)	PM ₁₀	–	24.3 ± 3.6	Pavuluri et al. (2010)
Africa	Summer	PM ₁₀	-25.9 ± 0.3	13.7 ± 2.2	Mkoma et al. (2014)

intermonsoon and the SEA-outflow during a winter cruise was also reflected through consistent nss-K⁺/EC ratios (0.35 ± 0.11 and 0.39 ± 0.09 , respectively).

We have also observed consistency in the $\delta^{13}\text{C}_{\text{TC}}$ from this study with those documented for wintertime aerosols (-25.9 ± 0.3 ‰) (Aggarwal et al., 2013) from Mumbai (a continental site in India). The biofuel/biomass burning is a dominant source of TC over Mumbai (Venkataraman et al., 2002, 2005) and also over the IGP during winter (Rengarajan et al., 2007; Ram and Sarin, 2012; Rajput et al., 2014; Srinivas and Sarin, 2014). Therefore, the overlapping $\delta^{13}\text{C}_{\text{TC}}$ in the SEA-outflow samples in winter with those of the IGP-outflow samples from the BoB during spring–intermonsoon and of continental aerosols from Mumbai might correspond to biofuel/biomass-burning emissions.

4. Conclusions

This study reports the stable C- and N-isotopic composition of wintertime aerosols (PM_{2.5}) over the BoB. During the study period (December 2008–January 2009), the MABL is influenced by the continental outflow from the IGP- and SEA-outflows, respectively, as inferred from the 7-d AMBTs over the BoB. The $\delta^{13}\text{C}_{\text{TC}}$ in the IGP-outflow (-23.8 ± 0.6 ‰) is distinctly different than that in the SEA-outflow (-25.3 ± 0.9 ‰). A significant linear relationship of $\delta^{13}\text{C}_{\text{TC}}$ with TC, nss-K⁺ and WSOC is noteworthy in the SEA-outflow but not in the IGP-outflow, which indicates the impact of BBEs in the former samples (which is also supported by the MODIS fire count data). However, no such influence from BBEs was observed for the IGP-outflow. Besides, the temporal variability of $\delta^{13}\text{C}_{\text{TC}}$ in the IGP-outflow is rather small unlike TC concentration and overlaps with those derived from coal combustion sources (-23.6 ± 0.7 ‰) in the IGP. The observed ¹³C-depletion of aerosol-TC in the SEA-outflow

is attributed to the contribution of POA directly emitted from the BBEs or due to SOAs formed by the oxidation of BVOCs from the forest fires. We observe no significant differences in the $\delta^{15}\text{N}_{\text{TN}}$ between IGP- and SEA-outflows. Moreover, mass concentration of NH₄⁺ dominates the aerosol-TN over the BoB, showing significant linear relationship with $\delta^{15}\text{N}_{\text{TN}}$. Thus, we infer that $\delta^{15}\text{N}_{\text{TN}}$ in aerosols over the BoB during winter is governed by the atmospheric processes affecting the concentrations of aerosol water-soluble inorganic nitrogen species (e.g. NH₄⁺, NO₃⁻) during transport.

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