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# Tracing the Relative Significance of Primary versus Secondary Organic Aerosols from Biomass Burning Plumes over Coastal Ocean Using Sugar Compounds and Stable Carbon Isotopes

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Supporting Information

ABSTRACT: Biomass burning (BB), a pivotal source of both primary and secondary organic aerosols (POA and SOA, respectively), affects the regional and global climate. We have used stable carbon isotopic composition ( $\delta^{13}C_{TC}$ ) of total carbon (TC) and BB tracers (anhydrosugars, sugars, and sugar alcohols) to elucidate the relative significance of POA and SOA over the Bay of Bengal, influenced by the long-range transport from the Indo-Gangetic Plain (IGP-outflow) and Southeast Asia (SEA-outflow) during a winter cruise. The molecular distributions of anhydrosugars (levoglucosan, Lev; galactosan, Gal; mannosan, Man) are different between IGP- (Lev > Gal > Man) and SEA-outflows (Lev > Man > Gal). The positive linear/nonlinear relationships of  $\delta^{13}C_{TC}$  with total sugar-C, K<sup>+</sup>,



water-soluble organic carbon (WSOC), and TC in BBOA from the SEA-outflow are in sharp contrast to those from Mt. Tai, China and Rondônia, Brazil in summer; mainly because of the prevailing differences in ambient photochemical processing. The Keeling plots ( $\delta^{13}C_{TC}$  versus 1/TC, 1/WSOC, and 1/Lev) in the SEA-outflow revealed a mixing of "<sup>13</sup>C-enriched POA" and <sup>13</sup>C-depleted "fresh-SOA" of BB origin. Because the sugar compounds are mostly water-soluble and become bioavailable in the surface waters, we estimate the air-to-sea depositions of sugar-C and WSOC over the Bay of Bengal to contribute to no more than 0.1% and 13%, respectively, of their supply via peninsular rivers.

KEYWORDS: anhydrosugars, sugars, sugar alcohols, Bay of Bengal, stable carbon isotopes, organic aerosols, biomass burning, oxalic acid

# INTRODUCTION

Organic aerosols (OAs), emitted from the natural and anthropogenic sources (wood/crop-residue burning and fossil-fuel combustion), account for a major fraction (20-90%) of airborne fine particulate matter, affecting the regional air quality and climate.<sup>1</sup> Biomass burning (BB) emits a wide range of primary organic aerosols (POAs) and gaseous-phase volatile organic compounds (VOCs).<sup>2</sup> The VOCs undergo rapid and complex photochemical reactions, resulting in the formation of secondary organic aerosols (SOAs).<sup>3,4</sup> Besides, some POAs are semivolatile in nature and, thus, evaporate to contribute to gas-phase abundances of labile VOCs during long-range transport.<sup>5</sup> These labile VOCs further undergo photochemical processing in the atmosphere to form further SOAs.<sup>6,7</sup> Both field and laboratory simulations based on community multiscale air quality models have shown that VOCs emitted from the canopies interact with anthropogenic pollutants such as  $O_{3}$ ,  $OH^*$ , and  $NO_x$  to produce additional SOAs.<sup>8-10</sup> Furthermore, these VOCs are more easily dispersed during downwind transport (i.e., away from the

source) under favorable meteorological conditions than POAs. Consequently, the POA fraction dominates the BB-derived organic aerosols (BBOAs) within the source emissions<sup>3</sup> and the SOA component increases significantly during transport.<sup>11,12</sup> Some BBOAs are highly water-soluble in nature and, hence, exert a considerable influence on hygroscopicity of ambient aerosols, affecting cloud formation and cloud albedo.<sup>13</sup>

Despite numerous efforts in recent years to understand the relative significance of POA versus SOA,<sup>14,15</sup> our knowledge regarding the chemical and physical evolution of BBOA is still limited.4,15 Most of this understanding comes from controlled biomass combustion experiments reported in the litera-

Special Issue: New Advances in Organic Aerosol Chemistry

Received: May 15, 2019 Revised: June 27, 2019 Accepted: July 8, 2019 Published: July 8, 2019

ture.<sup>16,17</sup> Open burning of crop residues, wood, and dung cakes, together with forest fires in the tropics, in particular from the Asian continent, geographically span over vast regions, affecting regional climate.<sup>18</sup> Therefore, limited observations on BBOAs from field-based studies in South Asia warrant further investigation.<sup>19</sup> Probing the evolution of BBOAs over continental sites is somewhat complicated by the inadvertent mixing of source emissions and processing effects. Therefore, oceanic regions located downwind of pollution sources (e.g., the Bay of Bengal) are ideal for studying the aging of BBOAs.

The Bay of Bengal, a low nutrient and chlorophyll region, receives a large influx of freshwater and suspended sediments from Ganga, Brahmaputra, and other peninsular rivers.<sup>20</sup> The Bay of Bengal is also under the influence of long-range atmospheric transport of pollutants from the Indo-Gangetic Plain and Southeast Asia during the winter period.<sup>20</sup> This study attempts to verify the prevailing characteristics in the composition of BBOAs from the continental outflows through specific organic molecular markers. We examined here three classes of primary sugar compounds (i.e., anhydrosugars, sugars, and sugar alcohols) in the PM<sub>2.5</sub> sampled over the Bay of Bengal during a winter cruise (SK-254; ORV Sagar Kanya). This study aims to investigate the relative significance of POA versus SOA from biomass burning emissions by using the relative abundances and diagnostic mass ratios of primary sugar compounds (this study) along with other chemical composition and stable carbon isotopic signatures of total carbon (TC).<sup>20,21</sup>

## MATERIALS AND METHODS

We have collected fine mode particulate matter ( $PM_{2.5}$ ; N =31) over the Bay of Bengal using precombusted tissuguartz filters (ca. 8 in.  $\times$  10 in.; PALLFLEX) and a high-volume air sampler (Thermo-Andersson Inc.; flow rate, 1.13 m<sup>3</sup> min<sup>-1</sup>) during the SK-254 cruise (Dec. 27, 2008-Jan. 26, 2009). For more details on the sampling and other chemical composition data, reference is made to our earlier publications.<sup>20,22</sup> We also compared our results from the Bay of Bengal with the BBOAs sampled through the total suspended particulate matter (TSP) over Mt. Tai, North China Plain<sup>23</sup> and PM<sub>2.5</sub> from Rondônia, Brazil<sup>24</sup> to better understand the geographical variability of factors affecting their stable carbon isotopic composition of TC. The high-volume TSP samples (Kimoto AS-810) were collected on precombusted tissuguartz filter (ca. 8 in.  $\times$  10 in.; PALLFLEX) over the summit of Mt. Tai, situated in Shandong province in the North China Plain, influenced by wheat-crop-residue burning emissions (i.e., May 30-Jun. 30, 2006).<sup>23</sup> Likewise, the PM<sub>2.5</sub> samples were collected as part of the international collaborative effort of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia-smoke, aerosols, clouds, rainfall, and climate (LBA-SMOCC) campaign using a dichotomous virtual impactor from a pasture site (i.e., at the Fazenda Nossa Senhora Aparecida), located in the southwestern province in Rondonia (Brazil), influenced by the intense forest fires in the Amazon basin during the dry season (Sep. 16-26, 2002).<sup>24</sup>

On the basis of the moderate resolution imaging spectroradiometer (MODIS) fire count data and 7 day isentropic backward air mass trajectories, we have classified the  $PM_{2.5}$  samples collected over the Bay of Bengal into two categories, those originating from (i) the Indo-Gangetic Plain as IGP-outflow (Dec. 27, 2008–Jan. 10, 2009) and (ii)

Southeast Asia as SEA-outflow (Jan. 11–26, 2009). Accordingly, we attribute the variability in the chemical composition (i.e., sugar compounds, water-soluble inorganic ions, carbonaceous aerosol components, trace metals, dicarboxylic acids, and bulk stable carbon isotopic composition) to their respective source contribution in the continental outflows to the Bay of Bengal.<sup>20</sup>

Briefly, a portion of the aerosol sample was extracted with a dichloromethane and methanol mixture (2:1) by ultrasonic agitation (10 mL  $\times$  3 times). This solvent extract was passed through a Pasteur pipet containing glass wool to remove the suspended particles and filter fibers. The solvent extracts were preconcentrated under vacuum using a rotary evaporator to  $\sim$ 200  $\mu$ L and transferred into a 1.5 mL glass vial, later subjected to nitrogen purging to near dryness. To this vial, we added 50  $\mu$ L of silvlation reagent containing a mixture of N,Obis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% TMCS (trimethylchlorosilane) and 10  $\mu$ L of pyridine and heated at 70 °C for 3 h. After derivatization, 140 µL of C13 nalkane (1.43 ng  $\mu L^{-1}$ ) was added to the glass vial as an internal standard prior to the measurement on a gas chromatograph-mass spectrometrmeter (GC-MS) equipped with a split/splitless injector and fused silica capillary column (DB-5MS; 0.22 mm  $\times$  25 m; film thickness, 0.52  $\mu$ m). We assessed the mass concentrations of anhydrosugars by comparing the peak area of analyte relative to those of authentic standards (Sigma-Aldrich) using the analytical protocol described in earlier publications.<sup>23</sup> The recovery tests were assessed by spiking the known amounts of authentic standards on blank filters and processing them in a fashion similar to that of a sample, while levoglucosan was better than 85%, which also is used as a surrogate standard for mannosan and galactosan. The recoveries of individual anhydrosugars, sugars, and sugar alcohols were found to be 80-90%.

We have obtained the bulk stable carbon isotopic composition of total carbon  $(\delta^{13}C_{TC})^{21}$  and other molecular markers (e.g., oxalic acid)<sup>20</sup> data to substantiate the arguments on the relative significance of BB-derived POAs and SOAs over the Bay of Bengal. The  $\delta^{13}C_{TC}$ , which is an abundance ratio of  $^{13}$ C to  $^{12}$ C in samples relative to that of standard (i.e., Pee Dee Belemnite carbonate carbon), in PM<sub>2.5</sub> was analyzed using an elemental analyzer interfaced to an isotope ratio mass spectrometer (EA/irMS, Carlo Erba NA 1500 EA Finnegan MAT Delta Plus).<sup>21</sup> The external calibration was performed using acetanilide with a known  $\delta^{13}C_{TC}$  (-27.26%) according to Bikkina et al.<sup>21</sup>

$$\delta^{13}C_{TC}/\% = ([({}^{13}C/{}^{12}C)_{sample}/({}^{13}C/{}^{12}C)_{Pee Dee Belemnite}] - 1) \times 1000$$
(1)

Likewise, the aqueous extract of PM<sub>2.5</sub> was derivatized using 14% BF<sub>3</sub> in *n*-butanol (i.e., after adjusting the pH to ~8.5–9 with 0.05 M KOH) on a hot plate at 100 °C for about an hour. The dibutyl ester derivative of oxalic acid was back-extracted in *n*-hexane and injected to a gas chromatograph (GC), equipped with flame ionization detector (FID) and split/splitless injector.<sup>20</sup> We have provided elsewhere the data with the information on the measurements and quality assurance of  $\delta^{13}C_{TC}$  and oxalic acid.<sup>31</sup> We also used the chemical composition data (non-sea-salt K<sup>+</sup>; water-soluble organic carbon, WSOC; elemental carbon, EC; and TC) from our previous studies to substantiate the arguments related to source contributions/aging effects.<sup>20,21</sup>



**Figure 1.** Spatial variability in the mass concentrations of measured anhydrosugars (a–c), sugars (d–h), and sugar alcohols (i–l) along with the total load from the respective sugar class (m–o) in  $PM_{2.5}$  collected onboard *ORV Sagar Kanya* during the winter cruise (SK-254, Dec. 27, 2008–Jan. 26, 2009) in the Bay of Bengal. The dots represent the midpoint of sampling tracks used for the  $PM_{2.5}$  collection in the Bay of Bengal. The spatial contours were generated using the interpolation-based gridding technique of Ocean Data View software.<sup>82</sup>

# RESULTS AND DISCUSSION

Mass Concentrations. BB significantly contributes to the atmospheric abundances of primary saccharides in PM2.5.25,26 In addition, vegetation detritus, resuspended dust, airborne pollen, and fungal spores also contribute to these primary sugars and sugar alcohols in ambient aerosols.<sup>27,28</sup> We detected here three anhydrosugars (levoglucosan, Lev; galactosan, Gal; and mannosan, Man), five sugars (glucose, fructose, sucrose, xylose, and trehalose), and four sugar alcohols (arabitol, mannitol, erythritol, and inositol) in PM<sub>25</sub> sampled over the Bay of Bengal. Of these, anhydrosugars originate mostly from the pyrolysis of cellulose/hemicellulose during BB.<sup>29,30</sup> Xylose is a tracer for wood burning emissions.<sup>27</sup> Glucose and fructose are abundant in terrestrial vegetation and can be emitted from the BB through direct volatilization and/or formed by the hydrolysis of other polysaccharides under acidic conditions,<sup>31,32</sup> while airborne pollen contains high concentrations of sucrose, whereas fungal spores are rich in arabitol and mannitol.<sup>33,34</sup> Likewise, trehalose is a proxy for the soil organic carbon associated with fungal metabolism.<sup>27</sup> BB also contributes to high levels of erythritol and inositol.<sup>25,31</sup> Therefore, all of these tracer compounds provide useful information about the variations in the type of BBOA between IGP- and SEA-outflows.

We examined the spatial variability of mass concentrations of primary sugar compounds over the Bay of Bengal (Figure 1) to understand the heterogeneity in the composition of BBOA between IGP- and SEA-outflows. Similar spatial trends of levoglucosan and mannosan (Figure 1a,b) suggest their ubiquitous BB signatures in both outflows, while galactosan showed a strong N–S gradient (i.e., high to low) from IGPto SEA-outflow (Figure 1c). Galactosan is a tracer for the recent fire activity (or fresh BB)<sup>24,35</sup> and usually abundant in crop-residue burning emissions.<sup>36</sup> Postharvest agricultural crop-residue burning is an important source of organic aerosols over the Indo-Gangetic Plain during early winter<sup>20</sup> and, hence, contributes to high concentrations of galactosan along with the other two anhydrosugars in the IGP-outflow.

Glucose, fructose, sucrose, and xylose exhibited somewhat similar spatial variability (Figure 1d-f) over the Bay of Bengal, particularly high concentrations in the coastal sampling tracks near Southeast Asia. These observations further advocate a greater emission strength of these primary sugar compounds from forest fires in the SEA-outflow. A lack of such spatial variability for the remaining sugar/sugar alcohols over the Bay of Bengal (Figure 1g-l) emphasizes their different source emissions other than BBOA and common transport history. The spatial variability is in particular significant, assessed on the basis of an unpaired two-tailed *t*-test (Table 1), only for the atmospheric loadings of galactosan, xylose, and trehalose. Of these, both galactosan and trehalose showed higher concentrations in the IGPoutflow and decreased by a factor of 4.8 and 2.9, respectively, in the SEA-outflow. In contrast, we also observed a factor of 2 increase in the average concentration of xylose from IGP- to SEA-outflow. Comparable levels of other sugar compounds in both of the continental outflows (Table 1) indicate their ubiquitous signatures and near equal source strength of BB between IGP- and SEA-outflows. The total mass concentrations of anhydrosugars, sugars, and sugar alcohols also resemble their individual class of compounds (Figure 1m-o), highlighting their variable sources and emission strength in both continental outflows.

Molecular Distributions: Relative Abundances of POA over SOA. The relative abundances of the three anhydrosugars in the total mass concentrations also exhibited significant spatial variability over the Bay of Bengal (Figure Table 1. Statistical Summary of Concentrations (ng m<sup>-3</sup>), Mass Ratios, and Relative Abundances of Saccharides in  $PM_{2.5}$ Sampled from the Indo-Gangetic Plain (IGP-) and Southeast Asian (SEA-) Outflows over the Bay of Bengal during SK-254 cruise (Dec. 27, 2008–Jan. 26, 2009) Based on the Unpaired Two-Tailed *t*-Test (at 95% Confidence Interval)<sup>*a*,*b*</sup>

		IGP-outflow		SEA-outflow		
saccharide type	compd name	min-max	av, median	min—max	av, median	<i>t</i> -score, <i>p</i> -value, df
anhydrosugars	levoglucosan	0.85-17.3	5.4, 2.7	0.11-31.7	6.18, 5.12	0.28, >0.05, 29
	galactosan	0.11-3.96	1.15, 0.78	0.004-1.23	0.24, 0.21	3.17, <0.05, 28
	mannosan	0.06-1.16	0.36, 0.25	0.01-1.24	0.31, 0.26	0.44, >0.05, 28
	$\Sigma$ anhydrosugars	1.1-224	6.93, 3.66	0.13-34.2	6.7, 5.4	0.07, >0.05, 29
	Σanhydrosugars (%)	19.2-64.5	46.6, 47.3	17.6-74.5	42.9, 41.9	0.64, >0.05, 29
	Lev/Man	8.67-25.1	14.7, 13.9	3.3-27.6	15.5, 15.9	0.22, >0.05, 28
	Lev/Gal	2.6-12.8	5.5, 4.6	1.9-82.6	26.6, 23.3	3, <0.05, 28
	Lev/(Man+Gal)	1.98-8.48	4.0, 3.5	1.5-20.7	9.1, 9.5	2.84, <0.05, 28
	Man/Gal	0.21-0.58	0.35, 0.32	0.26-3.1	1.6, 1.4	4.51, <0.05, 28
	Lev/nss-K <sup>+</sup>	0.003-0.02	0.01, 0.005	0.004-0.04	0.011, 0.01	0.7, >0.05, 29
	Lev-C/WSOC (%)	0.02-0.09	0.05, 0.03	0.01-0.23	0.070, 0.06	1.24, >0.05, 29
	Lev-C/OC (%)	0.02-0.07	0.04, 0.02	0.004-0.19	0.055, 0.04	1.36, >0.05, 29
	Σanhydrosugar-C/WSOC (%)	0.03-0.12	0.06, 0.04	0.008-0.23	0.078, 0.06	0.91, >0.05, 29
	Σanhydrosugar-C/OC (%)	0.03-0.09	0.04, 0.03	0.005-0.19	0.061, 0.05	1.05, >0.05, 29
sugars	glucose	1.12-4.35	2.14, 1.66	0.17-5.73	2.37, 2.50	0.39, >0.05, 29
	fructose	0.38-2.18	0.86, 0.65	0.02-2.06	0.81, 0.86	0.21, >0.05, 29
	sucrose	0.25-1.08	0.51, 0.47	0.03-1.30	0.53, 0.44	0.13, >0.05, 29
	xylose	0.07-0.56	0.23, 0.17	0.03-1.43	0.51, 0.49	2.27, <0.05, 24
	trehalose	0.14-1.16	0.40, 0.30	0.03-0.58	0.14, 0.10	3.21, <0.05, 28
	Σsugars	2.1-8.7	4.14, 3.40	0.23-9.4	4.2, 4.2	0.08, >0.05, 29
	$\Sigma$ Sugars(%)	24.6-55.2	39.1, 40.1	17.9-73.2	47.5, 47.5	1.74, >0.05, 29
	$\Sigma$ sugar-C/WSOC(%)	0.03-0.10	0.04, 0.04	0.020-0.11	0.06, 0.06	1.53, >0.05, 29
	$\Sigma$ sugar-C/OC(%)	0.02-0.08	0.04, 0.03	0.01-0.09	0.05, 0.05	1.46, >0.05, 29
sugar alcohols	arabitol	0.08-0.96	0.39, 0.26	0.02-0.99	0.29, 0.23	0.96, >0.05, 27
	mannitol	0.07-1.04	0.34, 0.15	0.01-0.98	0.19, 0.13	1.41, >0.05, 27
	erythritol	0.16-2.34	0.67, 0.40	0.03-1.42	0.39, 0.38	1.55, >0.05, 28
	inositol	0.07-0.80	0.28, 0.16	0.005-0.66	0.27, 0.30	0.09, >0.05, 26
	Σsugar alcohols	0.7-4.4	1.68, 1.04	0.09-3.5	1.1, 1.1	1.5, >0.05, 28
	Σsugar alcohols (%)	7.8-25.7	14.3, 12.4	6.3-16.5	10.0, 10.2	2.86, <0.05, 28
	Σsugar alcohol-C/WSOC (%)	0.01-0.05	0.016, 0.014	0.005-0.02	0.01, 0.01	1.02, >0.05, 28
	Σsugar alcohol-C/OC (%)	0.005-0.03	0.013, 0.011	0.003-0.02	0.01, 0.01	0.79, >0.05, 28
	$\Sigma$ saccharides-C/WSOC (%)	0.08-0.19	0.12, 0.10	0.035-0.35	0.15, 0.13	1.01, >0.05, 29
	$\Sigma$ saccharides-C/OC (%)	0.05-0.14	0.092, 0.083	0.02-0.27	0.12, 0.11	1.12, >0.05, 29

<sup>*a*</sup>Here av = average, df = degrees of freedom; Lev-C = Levoglucosan carbon content; and  $\Sigma$ saccharides-C = sum of concentrations of anhydrosugars, sugars, and sugar alcohols. <sup>*b*</sup>Bold highlights indicate the significant differences between IGP- and SEA-outflows.

2a). Levoglucosan is the most abundant anhydrosugar followed by galactosan in the IGP-outflow and mannonsan in most of the SEA-outflow (11 out of 15  $PM_{2.5}$ ) samples. We included three PM2.5 samples from the northern Bay of Bengal into the SEA-outflow due to their remarkable similarity in the relative abundance of mannosan over galactosan and a sudden shift in the origin air mass back-trajectories (i.e., at 500 and 1000 m) from the Indo-Gangetic Plain to Southeast Asia. Overall, there is a change in molecular distribution of anhydrosugars (Figure 2a) from the IGP-outflow (Lev  $\gg$  $Gal \ge Man$ ) to SEA-outflow (Lev  $\gg$  Man  $\ge$  Gal). Smoke particles from the open burning of crop residues have a higher abundance of galactosan over mannosan.<sup>36,37</sup> This source is active in the Indo-Gangetic Plain and, hence, contributes to the IGP-outflow. Similar to the distribution in SEA-outflow, aerosols sampled from the forest fires in Thailand, Southeast Asia,<sup>38</sup> and Amazon basin<sup>24</sup> also show the dominance of mannosan over galactosan.

Anhydrosugars, sugars, and sugar alcohols are mostly emitted as POA. We can assess the overall relative significance of POAs and SOAs over the Bay of Bengal on the basis of the mass ratio of the total primary sugar-C to that of a major SOA-tracer compound (e.g., oxalic acid<sup>20</sup>). The sugar-C/ oxalic acid-C ratio is rather low in the IGP-outflow (Figure 2b), suggesting the predominance of SOAs because of the distal influence of BB emissions in the Northwest Indo-Gangetic Plain (Punjab and Haryana). In contrast, we observed an increase of sugar-C/oxalic acid-C ratios in the SEA-outflow (Figure 2b) because of the proximity and influence of forest fires in Southeast Asia.

We compared the fractional relative abundances of three anhydrosugars over the Bay of Bengal with those reported over the East China Sea,<sup>39</sup> a round-the-world cruise,<sup>40</sup> remote ocean islands in the North Pacific (i.e., Okinawa<sup>41</sup> and Chichijima<sup>27</sup>), the Canadian high Arctic,<sup>42</sup> the Eastern Mediterranean Sea,<sup>43</sup> and the Atlantic Ocean<sup>44</sup> (Figure 3a). This comparison has unveiled the geographical differences in the source strength of BB. There exists a large spread in the fractional relative abundance of levoglucosan for the marine basins in the North Pacific (East China Sea, Okinawa, and Chichijima) influenced by the East Asian outflow compared to the Bay of Bengal (i.e., influenced by South/Southeast Asian



**Figure 2.** Spatial variability of percentage fractional relative abundances of (a) anhydrosugars, sugars, and sugar alcohols and (b) total sugar-C (i.e., anhydrosugars + sugars + sugar alcohols) and oxalic acid-C in  $PM_{2.5}$  collected over the Bay of Bengal (BoB). Panel a also includes 7 day isentropic air mass back-trajectories from hybrid single particle Lagrangian integrated trajectory (HYSPLIT) model ("blue" indicates from the IGP-outflow and "black" indicates SEA-outflow) and the moderate resolution imaging spectroradiometer (MODIS) derived fire count data for South and Southeast Asia.



**Figure 3.** Comparison of relative abundances of (a) anhydrosugars, (b) all three sugar compound classes (anhydrosugars, sugars, and sugar alcohols) sampled over the Bay of Bengal (number of samples, N = 12 for the IGP-outflow and N = 19 for the SEA-outflow) during the winter cruise with those reported in the literature. For comparison, we included data sets from East China Sea (N = 51),<sup>39</sup> a round-the-world cruise (N = 13),<sup>40</sup> Alert-Canadian-Arctic (N = 16),<sup>42</sup> Okinawa (average value),<sup>41</sup> Chichijima (N = 43),<sup>27</sup> East Mediterranean Sea (average value),<sup>43</sup> and Atlantic Ocean (N = 5).<sup>44</sup>

outflow), East Mediterranean Sea, and the Canadian Arctic (Figure 3a). This observation highlights that later marine basins are more susceptible to the influence of BB. Likewise, we compared the fractional abundances of total anhydrosugars, sugars, and sugar alcohols in their total mass concentration over the Bay of Bengal with other coastal and remote oceans (Figure 3b). We observe a sharp contrast in the predominance of anhydrosugars (40–100%) and sugars (0–60%) over the Bay of Bengal compared to other oceanic regions (Figure 3b), where we found higher fractional abundances of sugars (>50–100%) and sugar alcohols (0–80%). This comparison also corroborates the strong influence

of BB emissions over the Bay of Bengal compared to other oceanic basins.

**Diagnostic Mass Ratios: Probable Sources.** Linear relationships among the primary sugar compounds provide their common source emissions and/or long-range atmospheric transport over a receptor site. Strong correlations of some sugars (i.e., glucose, fructose, and xylose) and sugar alcohols (erythritol and inositol) with anhydrosugars in the IGP-outflow indicate their origin from crop-residue/wood burning emissions in the Indo-Gangetic Plain. Likewise, moderate to strong correlations (r > 0.6) of glucose, fructose erythritol, and inositol with levoglucosan and mannosan in the



Figure 4. (a) Comparison of Lev/Man and  $Lev/nss-K^+$  ratios in PM<sub>2.5</sub> with biomass burning source profiles. Pane b is the geochemical budget of atmospheric dry-deposition of carbonaceous species and total sugar-C to the Bay of Bengal and comparison with other external inputs (e.g., riverine supply).

SEA-outflow suggest forest fires in Southeast Asia as their common source. The mass concentrations of trehalose correlated well with arabitol and mannitol in the IGP-outflow, representing their origin from airborne fungal spores associated with fine alluvium from the Indo-Gangetic Plain. In contrast, arabitol strongly correlated with trehalose but not with the mannitol, possibly due to contribution from different types of fungal spores in the SEA-outflow.

Among these statistical correlations, the linear relationship of levoglucosan with mannosan and galactosan (Man + Gal), non-sea-salt K<sup>+</sup>, WSOC, and TC (Supporting Information Figure S1) is, in particular, useful for characterizing the type of BBOA (softwood, hardwood, rice straw, and grasses). Here, the apparent variability in the regression slopes and differences in diagnostic mass ratios of sugar compounds (Table 1) would then reflect the source strength and compositional similarities/differences of BBOA in the respective continental outflows. Overall, much steeper slopes of Lev with these other BB tracers in the SEA-outflow (Figure S1) show a stronger impact from the forest fires in Southeast Asia. We found no significant differences in the Lev/Man ratios (t-score = 0.22; p-value > 0.05; df = 28) between IGP-outflow (14.7  $\pm$ 5.3) and SEA-outflow (15.2  $\pm$  8.5). Furthermore, these Lev/ Man ratios are comparable to those originating from burning of hardwood  $(10-100^{45,46})$  and crop residues  $(10-100^{45,47})$ but higher than those of softwood  $(2.5-10^{45,46})$ . Lev/Gal ratios are different for the burning of wood  $(\sim 10-50)^4$ versus that of leaves  $(\sim 1)$ .<sup>47,48</sup> Therefore, high Lev/Gal ratios over the Bay of Bengal (IGP-outflow: 5.5  $\pm$  3.5 and SEAoutflow: 26  $\pm$  24) are comparable to those of wood-burning emissions. Lev/(Man + Gal) ratios in the SEA-outflow (8.95  $\pm$  6.12) are also higher than that in the IGP-outflow (3.9  $\pm$ 2.1) but similar to those reported for Amazonian forest fires (night, ~17; day, ~19).<sup>24</sup> Likewise, Lev/(Man + Gal) ratios in the IGP-outflow are consistent with the crop-residue/wood burning emissions sampled over urban Delhi in the IGP during winter ( $\sim 4.5 \pm 3.8$ ).<sup>49</sup>

The Lev/K<sup>+</sup> ratios in the crop-residue burning (i.e., <1) are distinctly different from those emitted from woody biomass (hardwood, 1–100; softwood, 10–1000).<sup>45</sup> In the case of wood, different phases of BB (i.e., smoldering versus flaming) could cause distinct mass ratios of Lev/nss-K<sup>+</sup> but similar contributions of levoglucosan carbon content to WSOC and

TC (i.e., Lev-C/WSOC and Lev-C/TC<sup>50,51</sup>). This is because K<sup>+</sup> emissions are high in the flaming phase of wood burning<sup>52,53</sup> and anhydrosugars are largely emitted in both flaming and smoldering phase.<sup>51,54</sup> Therefore, Lev/nss-K<sup>+</sup> ratios in the IGP-outflow are consistent with crop-residue burning emissions (i.e., <1), whereas those in the SEA-outflow suggest a likely contribution from the flaming phase of forest fires in Southeast Asia. Such typical low mass ratios of Lev/nss-K<sup>+</sup> are a characteristic signature of the flaming phase of forest fires (Savanna, 0.03; Amazon, 0.23<sup>56</sup>) than smoldering phase (wood,  $1-4^{45,46}$ ).

Because the Lev/Man and Lev/K<sup>+</sup> ratios vary with BB types, hence, their cross-plot is useful for the source apportionment of BBOA over the Bay of Bengal (Figure 4a). This approach has unveiled that both crop-residue and hardwood burning emissions are the major sources of BBOA in the IGP- and SEA-outflows. We also observed rather low values of Lev/nss-K<sup>+</sup> (0.001–0.01) and Lev/Man (1–10) for some SEA-outflow samples, which could be due to the burning of leaves from the forest fires.<sup>47</sup> Overall, the spatial variability of diagnostic mass ratios (i.e., Lev/Man, Lev/Gal, Lev/(Man + Gal), Lev/nss-K<sup>+</sup>, nss-K<sup>+</sup>/EC, and Man/Gal) and the relative abundances of sugar compounds in their total mass concentration highlights the variable BB source emissions in the continental outflows to the Bay of Bengal (Figure S2).

Previous studies have estimated the contribution of BBderived OC using the ambient levels of Lev times the sourcespecific mass ratio of OC/Lev (i.e., averaged across different BB-fuel types).<sup>46,57</sup> These estimates are uncertain because of the semivolatile nature<sup>58</sup> and ability to undergo photochemical oxidation of this tracer compound during transport.<sup>35,59</sup> Therefore, we observed low mass ratios of Lev-C/ OC over the Bay of Bengal (Table 1), perhaps owing to the oxidative loss of this marker and increased formation of OC contributed from SOAs during transport. Unfortunately, we could not analyze the PM2.5 samples for the radiocarbon isotopic composition ( $\Delta^{14}$ C) of TC, an unambiguous tracer for assessing the biomass versus fossil fraction, because of the higher carbon demands for the measurement ( $\sim$ 50–150 µg of C)<sup>60</sup> and observed low carbon loadings over the Bay of Bengal. Unlike  $\Delta^{14}$ C, the estimates of BB-derived OC based on  $\delta^{13}C_{TC}$  are somewhat troubled by the choice of end

members ( $\delta^{13}C_{bior}$  –28% $_{ei}$ ; and  $\delta^{13}C_{fossilr}$  –23% $_{ei}$ ) and the oxidation of OC during atmospheric transport (i.e., affecting the  $\delta^{13}C_{TC}$ ). Both these factors introduce a considerable uncertainty in our earlier source apportionment.<sup>21</sup> Recently, the  $\Delta^{14}C_{TC}$  from the IGP- and SEA-outflows have unveiled a larger share of biomass component (70–90%).<sup>60,61</sup> Therefore, we assumed that organic aerosols in the SEA-outflow have minor contributions from sources other than forest fires in Southeast Asia.

We used positive matrix factorization,<sup>62</sup> a powerful statistical tool (https://www.epa.gov/air-research/positivematrix-factorization-model-environmental-data-analyses), to apportion the probable sources of measured saccharides in  $PM_{2.5}$  over the Bay of Bengal. In this analysis, observed mass concentration (X) of saccharides  $(j \approx 1, 2, 3, ..., m)$  in aerosol samples  $(i \approx 1, 2, 3, ..., n)$  could be expressed as a linear combination of possible source profiles  $(g_{ik})$  times the source contributions  $(f_{ki})$ .

$$X_{ij} = \sum_{k=1}^{p} (g_{ik}f_{kj}) + e_{ij}; \quad \text{here, } e_{ij} = \text{fit residuals}$$
(2)

Positive matrix factorization input requires the concentrations of measured saccharides  $(x_{ij})$  and their associated analytical uncertainties  $(u_{ij})$ . Using these input parameters, the PC-based algorithm solves the source profiles and their contributions by minimizing the objective function  $(Q_{true} \text{ or } Q)$ , which is the sum of squared residuals normalized to their uncertainties.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{X_{ij} - \sum_{k=1}^{p} (g_{ik} f_{kj})}{u_{ij}} \right]^{2}$$
(3)

The analytical uncertainties for measured saccharides in positive matrix factorization analysis are  $\sim$ 15%. On the basis of the literature knowledge, we infer five factors (sources) contributing to measured saccharides (Figure S3).

Factor 1 has high loadings of trehalose (36%), arabitol (37%), and mannitol (44%). This observation implies a significant contribution of airborne fungal spores and the soil carbon associated with fungal metabolism to PM<sub>2.5</sub>. Factor 2 showed low loadings for levoglucosan (18%), glucose (18%), and fructose (10%), whereas high loadings for galactosan (89%), mannosan (40%), trehalose (46%), erythritol (44%), arabitol (22%), mannitol (27%), and inositol (24%). Higher loading of galactosan and mannosan with other saccharides in this factor 2 corresponds to contributions from crop-residue burning and associated resuspension of dust transported over the Bay of Bengal. Factor 3 has rather high loading of xylose (96%), which could be due to contribution from wood burning. Xylose is a monosaccharide present in wood and, thereby, traditionally referred to as wood sugar.<sup>27</sup> Wood burning emissions over the IGP contribute significantly to atmospheric OA. Therefore, factor 3 indicates source emissions from "wood burning". Factor 4 has higher loadings of glucose, fructose, and sucrose compared to other measured saccharides. Sucrose is an excellent tracer for airborne pollen but is also emitted significantly from BB.27 Airborne pollen grains vary in sizes between 1.2 and 12  $\mu$ m.<sup>34</sup> Therefore, we could interpret the factor 3 as an airborne pollen contribution to  $PM_{2.5}$  over the Bay of Bengal.

Factor 5 has high loadings of levoglucosan (64%) along with mannosan (44%), glucose (32%), fructose (38%), arabitol (39%), mannitol (20%), erythritol (22%), and inositol

(44%) in factor 5, indicating their origin from "forest fires". Galactosan decomposes at high temperatures of flames during forest fires in Southeast Asia compared to low-temperature burning of wood/crop residue over the Indo-Gangetic Plain (Figure 2a). Accordingly, high loadings of galactosan in factor 2 (i.e., 89%) compared to the near absence in factor 5 suggest their different BB source type. Aeolian input of saccharides significantly contributes to their bioavailable organic carbon in the surface seawater. It is, therefore, important to assess how much of the saccharide-C along with other carbonaceous species delivers through atmospheric deposition vis-à-vis that of fluvial supply to the Bay of Bengal.

**Dry-deposition Flux of Sugars.** The Bay of Bengal receives a lower amount of rainfall during continental outflow (December–April) and, therefore, only dry-deposition is the major removal pathway by which airborne sugar compounds, OC, and EC enter into the surface waters. We estimated the dry-deposition fluxes ( $f_{dry}$ ) of total sugar-C, OC, and EC (aka "Black Carbon" or BC) to the Bay of Bengal by using their mass concentrations in PM<sub>2.5</sub> times the dry-deposition velocity ( $V_d$ ).

$$f_{\rm dry-sugar-C} \approx [{\rm sugar-C}]_{\rm aero} V_{\rm d}$$
 (4)

$$f_{\rm dry-OC} \approx [OC]_{\rm aero} V_{\rm d}$$
 (5)

$$f_{\rm dry-BC} \approx [EC]_{\rm aero} V_{\rm d}$$
 (6)

The dry-deposition velocity is difficult to constrain, which depends on several factors including wind stress, surface roughness, and prevailing meteorology. Therefore, it is a common practice to model the  $V_{\rm d}$  and use the best estimates while assessing the  $f_{dry}$ .<sup>63</sup> The Group of Experts on Scientific Aspects of Marine Pollution (GESAMP) have recently reemphasized the use of previously suggested  $V_d$  of Duce et al.<sup>64</sup> for assessing the  $f_{dry}$  to the world's oceans. Because of the measured saccharides, OC, and EC being in fine mode aerosols  $(PM_{2.5})$  over the Bay of Bengal, we assumed 0.001 m  $s^{-1}$  as the  $V_d$  for this study for estimating the dry-deposition fluxes to the surface ocean. The  $f_{dry-sugar-C'}$ ,  $f_{dry-OC'}$  and  $f_{dry-BC}$  varied from 0.05 to 1.7  $\mu$ g of C m<sup>-2</sup> day<sup>-1</sup>, from 0.02 to 1 mg of C m<sup>-2</sup> day<sup>-1</sup>, and from 0.01 to 0.43 mg of C m<sup>-2</sup> day<sup>-1</sup> respectively. It is worthwhile to mention here that continental outflow lasts only 4-5 months during dry northeast-monsoon period ( $\sim$ 150 days) and the entire marine basin is under the influence of South/Southeast Asian outflow.<sup>20</sup> Because of the seasonal reversal of winds from ocean to land during the southwest monsoon, a period with an increase in the number of precipitation amounts and less influence from the continents, the effect of wet-deposition of these sugar compounds on the surface waters of the Bay of Bengal may not be significant.

We have extrapolated the daily estimates of dry-deposition fluxes to annual scale and also for the entire area of the Bay of Bengal (ca. 2.2 million km<sup>2</sup>) to calculate to annual inputs of total sugar-C, OC, EC, and WSOC (aka dissolved organic carbon, DOC). Therefore, the Bay of Bengal receives ~0.015-0.57 Gg of C year<sup>-1</sup> as saccharides, 28-331 Gg of C year<sup>-1</sup> as OC, 4.6-142 Gg of C year<sup>-1</sup> as EC, and 14-235 Gg of C year<sup>-1</sup> as WSOC (i.e., comparable to DOC from river/seawater) through the atmospheric input. It is important to note that these estimates carry some uncertainty due to the inherent errors in the assumed  $V_d$ , which may vary by a factor of 2–3. We have further compared these dry-deposition fluxes with other external inputs such as fluvial supply (i.e., through rivers) to the Bay of Bengal (Figure 4b). The annual delivery of riverine fluxes of total dissolved sugar compounds<sup>65</sup> and organic carbon<sup>66</sup> to the Bay of Bengal is ~430 and ~1820 Gg of C year<sup>-1</sup>, respectively. Therefore, upper estimates of atmospheric input of sugar-C and WSOC contribute to no more than ~0.12% and ~13% of their riverine supply to the Bay of Bengal, respectively.

Geographical/Seasonal Variability of the Relationship between  $\delta^{13}C_{TC}$  and BB Tracers. The relationship of  $\delta^{13}C_{TC}$  with BB tracers (e.g., anhydrosugars and nss-K<sup>+</sup>) can provide insights into processes affecting BBOAs. We observed positive nonlinear trends of  $\delta^{13}C_{TC}$  with total sugar-C mass and nss-K<sup>+21</sup> in the SEA-outflow (Figure 5a, left panel), suggesting POAs from the forest fires in Southeast Asia might control  $\delta^{13}C_{TC}$  over the Bay of Bengal during winter. BB significantly contributes to organic aerosols, most of which are water-soluble.<sup>27</sup> Accordingly, both WSOC and TC also correlated well with the  $\delta^{13}C_{TC}$  in SEA-outflow<sup>21</sup> (Figure 5). However, these trends in the SEA-outflow are contrary to those of the BBOA data sets from the North China Plain<sup>2</sup> and Rondônia (Brazil).<sup>24</sup> While the Bay of Bengal samples are from the winter season, the other two BBOAs collected over the North China Plain and Rondônia (Brazil) are from summer months. Therefore, these opposite trends (i.e., SEAoutflow in winter and the North China Plain and Rondônia in summer) perhaps reflect the seasonal differences in the  $\delta^{13}C_{TC}$ of BBOAs. It is important to understand what type of OA dominates and what process could affect the stable carbon isotopic composition before interpreting the observed seasonal patterns in the relationships between organic/inorganic chemical tracers and  $\delta^{13}C_{TC}$ .

The  $\delta^{13}C_{TC}$  of BBOA (i.e., POA or SOA) over a receptor site depends on the contributions from source types and transformations occurring in the atmosphere. For instance, if BB-derived POA with higher abundance is oxidized via the cleavage of C-C bond resulting in loss of a small carbon skeleton or moiety to gas phase, the remaining POA in the particulate phase then would have a lower abundance and be enriched in <sup>13</sup>C.<sup>67</sup>. Alternatively, if BB- and/or anthropogenicderived VOCs are oxidized in the atmosphere, this process would deplete in <sup>13</sup>C for the newly formed SOA because of the kinetic isotope effect (KIE).<sup>68-72</sup> This means lighter carbon (<sup>12</sup>C) containing isotopologues of VOCs preferentially react to form labile VOCs (i.e., <sup>13</sup>C-depleted).<sup>68-70</sup> However, condensation of labile VOCs to form SOA only involves a phase change (i.e., gas  $\rightarrow$  particle) and would not affect their  $\delta^{13}C^{67}$  due to their larger molecular masses than that of water vapor and, hence, can have negligible equilibrium isotopic fractionation effects.<sup>68,73</sup> Therefore, the  $\delta^{13}$ C of the freshly produced and less aged SOA is depleted in <sup>13</sup>C compared to the precursor VOC pool.74 These SOAs when subjected to further ambient photochemical processing increase their  $\delta^{13}$ C. This effect is more pronounced during summer due to a relative increase in atmospheric abundance of oxidants. Therefore, by contrasting linear/nonlinear trends of  $\delta^{13}C_{TC}$ with BB tracers between this study (Bay of Bengal) and others (Mt. Tai and Rondônia, Brazil), the differences in the photochemical processing are likely because of organic aerosols.

The coastal ocean aerosols of the SEA-outflow had more influence from forest fires in Southeast Asia. Higher relative

abundances of Lev-C/OC (0.09  $\pm$  0.04%) in these samples coincide with higher  $\delta^{13}\mathrm{C}_{\mathrm{TC}}$  (-24.5  $\pm$  0.4‰) in the SEA-outflow (Figure S4). This agreement could be consistent with source-specific stable carbon isotopic composition of BBOA from Southeast Asia ( $\delta^{13}\mathrm{C}_{\mathrm{TC-SEA}}$ ) or the result of their oxidation during long-range transport. The  $\delta^{13}\mathrm{C}_{\mathrm{TC-SEA}}$  from the vicinity of forest fires in Thailand (-26.0  $\pm$  1.2‰)^{38} and Vietnam (-26.0  $\pm$  0.44)^{25} are lower, assessed on the basis of the Monte Carlo error propagation method,<sup>75</sup> than those found for the SEA-outflow samples collected over coastal ocean (t-score = 3.7; df = 49; p < 0.05;  $\Delta\delta^{13}\mathrm{C}_{\mathrm{TC}} \approx \delta^{13}\mathrm{C}_{\mathrm{TC-SEA}} - \delta^{13}\mathrm{C}_{\mathrm{TC-SEA}} \approx +1.5 \pm 1.3‰)$ . We, thus, rule out the possibility that BBOAs from Southeast Asia (i.e., dominated by C<sub>3</sub> vegetation) carry their source-specific  $\delta^{13}\mathrm{C}_{\mathrm{TC}}$  signature to the SEA-outflow.

The  $\delta^{13}C_{TC-SEA}$  in BBOA over Southeast Asia is higher<sup>46,51</sup> than that of their C<sub>3</sub> plant leaves ( $\delta^{13}C_{\text{plant-SEA}}$ , -28.6  $\pm$  1.05%°).<sup>76</sup>. Their difference in  $\delta^{13}C_{TC}$  is not statistically significant ( $\Delta\delta^{13}C \approx \delta^{13}C_{TC-SEA} - \delta^{13}C_{\text{plant-SEA}} \approx + 2.6 \pm$  1.1%°; *t*-score, 0.25; df = 52; p > 0.05) but is somewhat larger than those of BBOA generated in a chamber (i.e., +0.5%°).<sup>77</sup> Turekian et al.<sup>77</sup> collected all particles from the C<sub>3</sub> plant combustion on a filter substrate and examined for isotopic discrimination between biomass source material and aerosol-TC. In contrast, BB in a natural atmosphere (e.g., here in Southeast Asia) resembles a distillation process and the emitted substances are easily dispersed by the prevailing meteorology. Therefore, the  $\delta^{13}C_{TC}$  in ambient aerosols collected downwind of the forest fires in Southeast Asia depends on what fraction of organic compounds in the BB (i.e., labile or less labile) have contributed to TC.

Loss of volatiles (CO, CO<sub>2</sub>, and non-methane hydrocarbons, etc.) during the initial phase of BB at <180 °C causes <sup>13</sup>C enrichment of residual unburnt plant material.<sup>71</sup> Subsequent pyrolysis of cellulose and hemicellulose (i.e., together account for >80% biomass) as well as lignin compounds at >300 °C results in the formation of sugars and other volatile products,<sup>29</sup> which are enriched in <sup>13</sup>C rather than that in the bulk plant. Sang et al.<sup>78</sup> observed a significant enrichment of <sup>13</sup>C of levoglucosan than holocellulose (i.e., cellulose + hemicellulose) of plant biomass. There exists a subtle but measurable difference in the  $\delta^{13}$ C signatures between plant biomass and the various constituent carbon pools. More labile fractions (e.g., sugars, cellulose, and hemicellulose) are somewhat enriched in <sup>13</sup>C, and the less labile components (e.g., lipids and lignins) are depleted in <sup>13</sup>C than bulk plant biomass.<sup>79</sup> Therefore, higher  $\delta^{13}C_{TC}$  with changing sugar-C content for the SEA-outflow samples collected near Southeast Asia ( $\sim -24.5 \pm 0.4\%$ ) could be explained by higher contribution from labile components of plant biomass to OA (i.e., mostly as POAs) during forest fires.

The difference in  $\delta^{13}C_{TC}$  between BBOA from the forest fires and plant biomass in Southeast Asia (i.e., based on Montecarlo error propagation) is even larger for the SEA-outflow samples collected along coastal cruise tracks ( $\Delta\delta^{13}C \approx \delta^{13}C_{TC-SEA-outflow} - \delta^{13}C_{plant} \approx +4.1 \pm 1.1\%$ ). The  $\Delta\delta^{13}C$  ( $\delta^{13}C_{TC-SEA-outflow} - \delta^{13}C_{plant}$ ) estimated here is more than those actually predicted to arise from the labile components (cellulose, starch, and sugars are enriched in <sup>13</sup>C by 1.29‰, 2.02‰, and 1.71‰, respectively<sup>80</sup>) of plant biomass. Nevertheless, oxidation of these BB-derived POAs during transport from Southeast Asia to the Bay of Bengal significantly affects the  $\delta^{13}C_{TC}$  (i.e., <sup>13</sup>C enrichment) and,



Figure 5. Scatter plots of  $\delta^{13}C_{TC}$  with levoglucosan (Lev), water-soluble potassium (K<sup>+</sup>), and water-soluble organic carbon (WSOC) and total carbon (TC) in biomass burning influenced aerosols collected over (a) the Bay of Bengal, Southeast Asian (SEA)-outflow, (b) Mt. Tai, North China Plain (N = 89),<sup>23</sup> and (c) Rondônia, Brazil (N = 11).<sup>24</sup> The concentration of water-soluble K<sup>+</sup> over the Bay of Bengal is corrected for the contribution from sea salts. In the bottom left panel, the encircled data with high TC concentration is the PM<sub>2.5</sub> collected very near to both the Indo-Gangetic Plain and Southeast Asia.

hence, explains the observed higher  $\delta^{13}C_{TC}$  values for the SEA-outflow samples collected along the coastal cruise track. Some SEA-outflow samples are more depleted in  $^{13}C(-26.9\%)$  to -25.3%) than the remaining samples, which also coincide with the lower abundance of total sugar-C, nss-

K<sup>+</sup>, WSOC, and TC. Additionally, these SEA-outflow samples also have lower ratios of sugar-C to oxalic acid-C (0.01–0.05; Figure 2b). Taking together all of these observations, we attribute that lower  $\delta^{13}C_{TC}$  in the SEA-outflow is mainly due to a larger share of SOA over POA and vice versa.



**Figure 6.** Linear regression analysis between the stable carbon isotopic composition of total carbon  $(\delta^{13}C_{TC})$  and reciprocal mass concentrations of (a) total carbon (TC), (b) water-soluble organic carbon (WSOC), and (c) levoglucosan (Lev). The logarithmic relationship of  $\delta^{13}C_{TC}$  with (d) levoglucosan carbon content in TC (*Lev-C*/TC (%)), (e) levoglucosan carbon content in WSOC (*Lev-C*/WSOC (%)), and (f) levoglucosan to *nonsea-salt-K*<sup>+</sup> (*Lev*/nss-K<sup>+</sup>) in PM<sub>2,5</sub> sampled over the Bay of Bengal during the impact of forest fires in Southeast Asia.

In BBOAs collected over Mt. Tai in summer, Fu et al.<sup>23</sup> have observed an exponential decrease of  $\delta^{13}C_{TC}$  (~-22% to -26%) with an increase in the concentrations of Lev (~88-1210 ng m<sup>-3</sup>). Higher  $\delta^{13}C_{TC}$  values in their samples correspond with higher loadings of biogenic SOA tracers.<sup>23</sup> This result contradicts the theoretical considerations of stable carbon isotopic fractionations based on the photochemical oxidation experiments of biogenic/BB-derived VOCs, which corroborate the argument that freshly emitted VOCs and nascent SOA are, in general, depleted in <sup>13</sup>C.<sup>69,71,74</sup> Thus, we would expect a lower  $\delta^{13}C_{TC}$  if the SOA component dominates TC mass. This is the case for the SEA-outflow samples collected over the Bay of Bengal during the winter cruise (Figure 2b), where lower  $\delta^{13}C_{TC}$  corresponds to lower concentrations of saccharide-C, nss-K<sup>+</sup>, WSOC, and TC; altogether this represents a less aged or fresh SOA (Figure 5a). It is plausible that there could be a higher photochemical activity (or oxidation) of biogenic SOA over Mt. Tai in summer compared to those sampled over the Bay of Bengal in winter. Thus, higher  $\delta^{13}C_{TC}$  (i.e.,  $^{13}C$ -enriched) values with the lower atmospheric abundances of Lev, K<sup>+</sup>, WSOC, and TC over Mt. Tai (Figure 5b; middle panels) suggest the aged nature of SOAs. A similar feature is noticeable for the OAs (Figure 5c; right-side panels) sampled from the Amazonian forest fires in summer.<sup>24</sup> Coincidently, the  $\delta^{13}C_{TC}$  in summertime aerosols sampled from Indonesian forest fires is negatively correlated with TC;<sup>81</sup> hence, higher  $\delta^{13}C_{TC}$  values with concomitant lower concentrations of saccharide-C, nss-K<sup>+</sup>, WSOC, and TC over Mt. Tai, the North China Plain, and Rondônia, Brazil point to their aged SOA character. Overall, the relationship between BB tracers and bulk  $\delta^{13}C_{TC}$  in wintertime BBOAs are governed by the extent of POA contribution and their aged character during transport, whereas photochemical aging of SOAs and their relative abundances in summer mostly dictate the bulk  $\delta^{13}C_{TC}$ .

Processes Affecting Stable Carbon Isotopic Composition of TC. The Keeling plots (Figure 6a-c), depicting reciprocal TC concentrations versus  $\delta^{13}C_{TC}$  (i.e., a binary mixing curve) are in particular useful for understanding the possible sources/processes affecting the composition of organic aerosols in the atmosphere.  $\delta^{13}C_{TC}$  (i.e., on the ordinate) has exhibited a negative linear relationship with reciprocal mass concentrations of TC, WSOC and Lev (i.e., on the abscissa) for the SEA-outflow. However, such relationships were absent in the IGP-outflow (Figure S5). This observation is consistent with air mass trajectories and MODIS fire count data, which showed a strong impact from the forest fires in Southeast Asia on PM2.5 sampled over the Bay of Bengal than those from the crop-residue/wood burning emission in the IGP-outflow. Therefore, TC in the SEAoutflow is a combination of contributions from both directly emitted BBOAs and background organic aerosols (BGOAs) from the forest fires in Southeast Asia (see eq 7)).

$$\Gamma C \approx BBOA + BGOA$$
 (7)

$$[TC]\delta^{13}C_{TC} \approx [BBOA]\delta^{13}C_{BBOA} + [BGOA]\delta^{13}C_{BGOA}$$
(8)

$$\delta^{13}C_{TC} \approx \frac{1}{[TC]} (\delta^{13}C_{BGOA} - \delta^{13}C_{BBOA}) [BGOA] + \delta^{13}C_{BBOA}$$
(9)

The intercepts on the ordinate in Figure 6a–c converge to a similar number (~-24‰), which corresponds to the source-specific  $\delta^{13}$ C signature of BBOAs in the SEA-outflow ( $\delta^{13}C_{BBOA}$ ). Because Lev is a pyrolysis product of <sup>13</sup>C-enriched cellulose/hemicellulose (i.e., by up to +4‰ than bulk biomass,  $-28‰^{80}$ ), the intercept value ( $\delta^{13}C_{BBOA}$ ) from the linear relationship of  $\delta^{13}C_{TC}$  with 1/Lev (Figure 6c) is similar to those with 1/TC and 1/WSOC (Figure 6a,b), which overall suggests a larger share of BBOA from the labile

carbon pool. Therefore,  $\delta^{13}C_{TC}$  in the SEA-outflow depends on the proportions of labile versus refractory components of BB products in Southeast Asia. Additionally, we used Lev-C/ TC (%), Lev-C/WSOC (%), and Lev/nss-K<sup>+</sup> in the SEAoutflow as a surrogate proxy for assessing the relative contribution of POAs in total BBOAs. Coincidentally, we observed a similar positive nonlinear trend of Lev-C/TC (%), Lev-C/WSOC (%), and Lev/nss-K<sup>+</sup> with  $\delta^{13}C_{TC}$  in the SEAoutflow (Figure 6d–f). Here, an increase in Lev-C/TC, Lev-C/WSOC, and Lev/nss-K<sup>+</sup> with rather a small variability and higher  $\delta^{13}C_{TC}$  values advocates for a predominance of POAs for the coastal ocean aerosols in the SEA-outflow. In contrast, a decrease in these diagnostic mass ratios corresponds to lower  $\delta^{13}C_{TC}$  for the open ocean aerosols in the SEA-outflow, implying a greater proportion of SOAs ( $\delta^{13}C_{BGOA}$ ).

In general, oxidation of POA during transport often results in enrichment of <sup>13</sup>C. If the forest fires in Southeast Asia contributed to POA in the SEA-outflow, then we would expect significant enrichment of <sup>13</sup>C for the samples collected over the remote ocean compared to those over coastal ocean. In contrast, we witnessed lower  $\delta^{13}C_{TC}$  for the remote ocean aerosols than coastal ocean aerosols of the SEA-outflow. This implies that BB-derived POA in Southeast Asia is not a factor governing the lower  $\delta^{13}C_{TC}$  values in the SEA-outflow sampled over the open ocean waters of the Bay of Bengal. Alternatively, SOA formation from the VOCs could cause depletion in <sup>13</sup>C.<sup>68,74</sup> As a result, BGOAs (i.e., mostly as SOA) from either IGP- and/or SEA-outflow could be responsible for the observed lower  $\delta^{13}C$  in these remote ocean aerosols collected over the Bay of Bengal.

We have here two possible scenarios: (i) BGOA from the IGP-outflow are mixed with BBOAs in the SEA-outflow, and (ii) a relative increase in the contribution of BGOA occurs compared to BBOA within the SEA-outflow. According to scenario i, TC from the forest fires in Southeast Asia is BBOA and all other organic aerosols from the IGP-outflow are BGOA, which includes both contributions from POA and SOA. Of these two fractions (i.e., primary versus secondary) in the IGP-outflow, only the SOA formation causes <sup>13</sup>C depletion of organic aerosols. Therefore, the mixing of this secondary component in the BGOA from the IGP-outflow could explain lower  $\delta^{13}C_{TC}$  (i.e., <sup>13</sup>C-depleted) values of the SEA-outflow. Because of the long distance from the source emissions in the IGP to distal locations sampled over the southern Bay of Bengal, oxidation of fresh-SOA in the BGOA during transport further results in <sup>13</sup>C enrichment of TC than those observed in the IGP-outflow (-24.7%) to -22.8%). Thus, the contribution of BGOA from the IGP-outflow could not explain the lower  $\delta^{13}C_{TC}$  in the remote ocean aerosols from the SEA-outflow  $(-26.0 \pm 0.6\%)$ .

SOA formed via the oxidation of BB-VOCs are more abundant over the Bay of Bengal compared to those over source emissions. Although POA fraction dominates the BBOAs within the forest fires in Southeast Asia, however, the proportion of SOAs (i.e., condensation of oxidized and BB-derived labile VOCs) in BBOA increases in the SEA-outflow during transport. Therefore, the observed linear relationship between  $\delta^{13}C_{TC}$  and 1/TC in the SEA-outflow would simply suggest mixing of BB-derived POAs with BGOAs (i.e., BB-SOA). According to scenario ii, if fresh-SOA is formed by the oxidation of VOCs emitted from the forest fires in Southeast Asia, it should contribute to BGOA that would lead to lower  $\delta^{13}C_{TC}$  in the SEA-outflow. In such a case, we should have

more contribution from SOAs over POAs in the BBOAs sampled in the SEA-outflow. Coincidently, the mass ratio of total sugar-C to oxalic acid-C (i.e., the surrogate ratio of the POAs to SOAs; range, 0.01–0.05) decreased from coastal to remote ocean aerosols in the SEA-outflow (Figure 2b). We also observed lower mass concentrations of Lev (0.09–0.21 ng m<sup>-3</sup>) and concomitant rather low  $\delta^{13}C_{TC}$  (–26.1% to –27.0%) in the four SEA-outflow samples. The  $\delta^{13}C_{TC}$  in these four PM<sub>2.5</sub> samples, perhaps representing the significant contribution from SOA, is lower than other IGP-/SEA-outflow samples (–25.7 to –22.8%). Therefore, lower  $\delta^{13}C_{TC}$  in the SEA-outflow samples could be explained by the contribution of SOA formed by the oxidation of VOCs emitted from the forest fires in Southeast Asia.

#### CONCLUSIONS

We measured the mass concentrations of anhydrosugars, sugars, and sugar alcohols in marine aerosols over the Bay of Bengal during the winter period. The diagnostic mass ratios of sugar compounds with other chemical tracers revealed the sources of organic aerosols as crop-residue/wood burning emissions in the continental outflows sampled from the Indo-Gangetic Plain and forest fires in Southeast Asia. The molecular distributions of anhydrosugars also clearly showed differences between continental outflows sampled and, therefore, could be an ideal choice when examining the various types of BB. We found that there exists a considerable geographic variability in the relationship of bulk  $\delta^{13}C_{TC}$  with total sugar-C, water-soluble K<sup>+</sup>, and WSOC and TC for the different biomass burning influenced aerosols (Bay of Bengal, winter; Mt. Tai and North China Plain, summer; Rondonia, Brazil, summer). This could be due to differences in the relative contributions of BB-derived POAs and SOAs together with their extent of photochemical aging. We also demonstrate that application of the Keeling plots (i.e.,  $\delta^{13}C_{TC}$  versus 1/TC, 1/WSOC, and 1/Lev) provide sourcespecific  $\delta^{13}$ C values in the continental outflows and, therefore, are useful when discussing the possible sources and their processing effects of BBOA.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspace-chem.9b00140.

Figures including (i) scatter plot of levoglucosan with other anhydrosugars and chemical tracers, (ii) spatial variability of diagnostic mass ratios of sugars, (iii) source profiles resolved by positive matrix factorization method, (iv) spatial variability of relative abundances of levoglucosan in OC and  $\delta^{13}C_{TC}$ , and (v) Keeling plots for the IGP outflow (PDF)

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## **Author Contributions**

S.B. wrote the manuscript. S.B. and M.M.H. performed the analysis of anhydrosugars and other chemical composition data under the guidance of K.K./M.S. M.S. and S.B. were involved in the cruise planning and aerosol collection. All authors are actively involved in the entire discussion of the manuscript.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

M.S. acknowledges partial financial support from the ISRO-GBP for the aerosol collection and analysis of supporting chemical measurements. S.B. and K.K. are thankful for the financial support from the Japan Society for the Promotion of Science (JSPS) through Grant-in-Aid No. 24221001.

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